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Supplementary Material

A Visible Light Photoredox Catalysed Radical Pictet-Spengler Reaction

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Contents

1. General Information

All reagents were purchased from commercial suppliers and used without further purification. Proton NMR (^{1}H NMR) and carbon NMR (^{13}C NMR) were recorded on Bruker 400 Ultrashield (400 MHz) and Ascend 400 (400 MHz). Chemical shifts (δ) are quoted in parts per million (ppm). Multiplicities are abbreviated as s, singlet; d, doublet; dd, doublet of doublets; t, triplet; q, quarter; m, mulitplet; b, broad. Coupling constants (*J*) are reported in Hertz (Hz). Analytical thin layer chromatography (TLC) was carried out using aluminium-backed Merck Kieselgel KG60 F254 silica plates and visualised by exposure to UV light (254 nm). Flash chromatography was performed on Grace Davidson Davisil LC60A 40-63 micron silica gel. Yields refer to isolated yields, unless otherwise stated. After purification product purity was determined to be >95% by ^{1}H NMR spectroscopy.

Mass spectrometric analyses were performed on a Thermo Scientific Q Exactive mass spectrometer fitted with a HESI-II ion source. Positive ion electrospray mass spectra were recorded in an appropriate mass range set for **140,000** mass resolution. Positive ion EI mass spectra were run on a Thermo Scientific DFS mass spectrometer using an ionisation energy of 70 eV. Accurate mass measurements were obtained with a resolution of 5000-10000 using PFK (perfluorokerosene) as the reference compound.

Photocatalytic reactions were performed in a custom made LED photoreactor as shown in Figure X. The photoreactor comprised of two plates of blue LEDs (7 × 1 W @ 447 nm, www.luzeonstar.com) with PC cooling fans and heat sinks for temperature control.

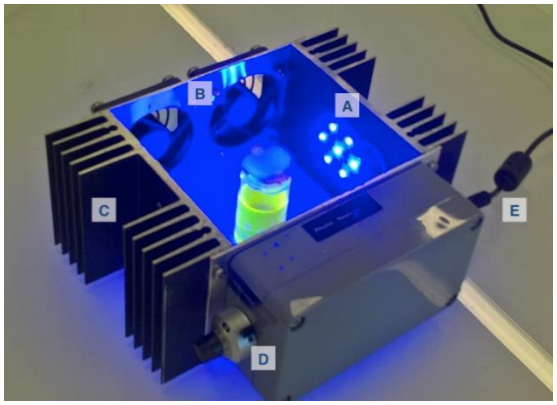
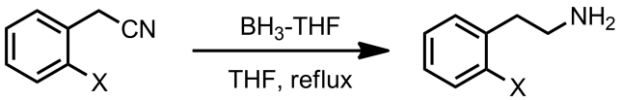


Figure S1. Custom-built LED photoreactor; a) blue LED assembly; b) PC cooling fans; c) heat sinks; d) intensity control; e) 12 V power supply.

2. Experimental Procedures

Synthesis of Phenylethylamines

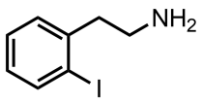


28: X = I
29: X = F

30: X = I
31: X = F

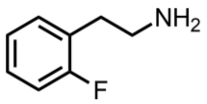
General Procedure

A solution of BH_3 in THF (1 M, 50.2 ml, 2.4 equiv.) was added dropwise, at 0 °C, to a solution of phenylacetonitrile (5.00 g, 1.0 equiv.) in anhydrous THF (25 ml). The reaction mixture was heated at 65 °C under inert atmosphere overnight. After cooling to r.t., the reaction mixture was diluted with methanol and concentrated under reduced pressure. The residue was dissolved in 6 M aqueous HCl solution and heated at reflux for 1 h. After cooling to r.t., the reaction was washed with diethyl ether (3×) and the combined aqueous layers were basified to pH 12 with 6 M aqueous NaOH solution. The mixture was extracted with CH_2Cl_2 (3×), washed with brine, and dried ($MgSO_4$). The solvent was removed under reduced pressure to give the desired product, which was used without further purification.



2-Iodophenylethanamine (30): obtained as an orange oil (4.14 g, 81% yield) **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 7.87 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.33-7.29 (m, 2H), 7.26- 7.24 (m, 2H), 6.95 (td, *J* = 15.1, 1.9, 1H), 3.00-2.97 (m, 2H), 2.93-2.89 (m, 2H), 1.29 (br s, 2H) **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 142.5, 139.7, 130.0, 128.4, 128.2, 100.9, 44.8, 42.5

Data match that reported in the literature.[1]

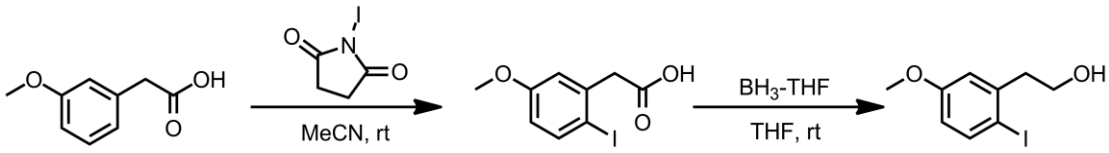


2-Fluorophenylethanamine (31): obtained as a pale yellow oil (2.83 g, 92% yield) **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 7.21-7.16 (m, 2H), 7.08-6.99 (m, 2H), 2.95 (t, *J* = 7.1 Hz, 2H), 2.78 (t, *J* = 6.9 Hz, 2H), 1.13 (br s, 2H) **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 162.6 (d, J_{C-F} = 244.7 Hz), 131.2 (d, J_{C-F} = 5.1 Hz), 128.0 (d, J_{C-F} = 7.9 Hz), 126.9 (d, J_{C-F} = 15.9 Hz), 124.1 (d, J_{C-F} = 3.4 Hz), 115.5 (d, J_{C-F} = 22.3 Hz), 42.5, 33.7

HRMS (ESI) *m/z* calc. for $C_8H_{11}NF$ $[M+H]^+$ 140.0870, found 140.0870

Synthesis of 2-Iodophenylethanol Intermediates

2-Iodo-5-methoxyphenylethanol[2]



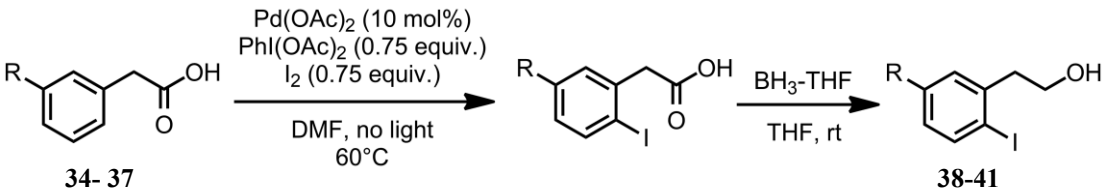
32 **33**

A solution of 3-methoxyphenylacetic acid (3.00 g, 18.05 mmol, 1.00 equiv.) and *N*-iodosuccinimide (4.26 g, 18.96 mmol, 1.05 equiv.) in MeCN (24 ml) was stirred at room temperature overnight, whilst being protected from light. The reaction mixture was extracted with Et_2O (3×), washed with saturated aqueous NaS_2O_3 solution and brine, and dried ($MgSO_4$). The solvent was removed under reduced pressure to give 2-iodo-5-methoxyphenylacetic acid as an off-white solid, which was used without further purification.

A solution of BH_3 in THF (1 M, 2.00 equiv.) was added dropwise, at 0 °C, to a solution of 5-methoxy-2-iodophenylacetic acid (1.00 equiv.) in anhydrous THF. The mixture was heated at reflux under inert atmosphere overnight. The reaction was allowed to cool to room temperature, diluted with water and extracted with Et_2O (3×). The combined organic extracts were washed with brine and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by flash chromatography on silica, eluting with 15-20% EtOAc/*n*-pentane to give 5-methoxy-2-iodophenyl ethanol.

2-(2-Iodo-5-methoxyphenyl)ethanol (33): obtained as a pale yellow oil (1.78 g, 95%) **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 7.69 (d, *J* = 8.7 Hz, 1H), 6.84 (d, *J* = 3.0 Hz, 1H), 6.55 (dd, *J* = 8.7, 3.0 Hz, 1H), 3.68 (t, *J* = 6.3 Hz, 2H), 3.78 (s, 3H), 2.99 (t, *J* = 6.7 Hz, 2H) **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 160.1, 142.2, 140.2, 116.6, 114.4, 89.3, 62.4, 55.5, 43.9

2-Iodophenylethanol Intermediates with Electron Poor Substituents[3]



34- 37 **38-41**

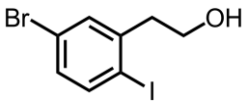
General Procedure

A solution of phenylacetic acid (1.00 g, 1.00 equiv.), $Pd(OAc)_2$ (0.10 equiv.), $PhI(OAc)_2$ (0.75 equiv.), and I_2 (0.75 equiv.) in anhydrous DMF was stirred at 60 °C for 24 h. After cooling to room temperature, the reaction mixture was filtered through a plug of Celite with Et_2O. The filtrate was washed with saturated aqueous $Na_2S_2O_3$ solution, extracted with Et_2O (3×) and the combined organic extracts were washed with

brine and dried over $MgSO_4$. The solvent was removed under reduced pressure to gives 2-iodophenylacetic acid, which was used without further purification.

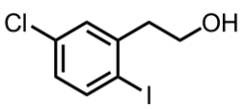
A solution of BH_3 in THF (1 M, 2.00 equiv.) was added dropwise, at 0 °C, to a solution of 2-iodophenylacetic acid (1.00 equiv.) in anhydrous THF. The mixture was heated at reflux under inert atmosphere overnight. The reaction was allowed to cool to room temperature, diluted with water and extracted with Et_2O (3×). The combined organic extracts were washed with brine and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by flash chromatography, eluting with 15-20% EtOAc/*n*-pentane to give the desired product.

Characterisation Data



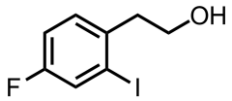
2-(5-Bromo-2-iodophenyl)ethanol (38): obtained as a white solid (1.15g, 48% yield)
^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.69 (d, *J* = 8.4 Hz, 1H), 7.42 (d, *J* = 2.4 Hz, 1H), 7.08 (dd, *J* = 8.4, 2.4 Hz, 1H), 3.88 (q, *J* = 6.3 Hz, 2H), 3.00 (t, *J* = 6.6 Hz, 2H)
^{13}C NMR ($CDCl_3$, 100 MHz): δ = 143.5, 140.9, 133.2, 131.6, 122.7, 98.8, 62.1, 43.6

Data match that reported in the literature.[4]

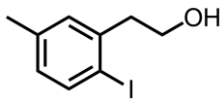


2-(5-Chloro-2-iodophenyl)ethanol (39): obtained as a white solid (0.66 g, 32% yield).
^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.74 (d, *J* = 8.4 Hz, 1H), 7.25 (d, *J* = 1.0 Hz, 1H) overlapping with $CDCl_3$, 6.93 (dd, *J* = 8.6, 2.5 Hz, 1H), 3.87 (m, 2H), 2.99 (t, *J* = 6.6

Hz, 2H). **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 143.2, 140.6, 134.7, 130.4, 128.6, 97.9, 62.1, 43.6. HRMS (EI) *m/z* calc. for C_8H_8ClIO 281.9308, found 281.9301

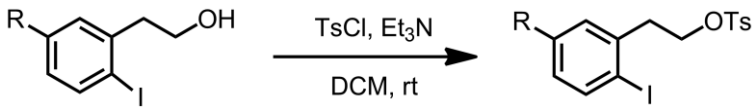


2-(4-Fluoro-2-iodophenyl)ethanol (40): obtained a s a colourless solid (182.5 mg, 22 %). **^{1}H NMR (400 MHz, CDCl3):** δ = 7.55 (dd, *J* = 2.6, 8.1 Hz, 1H), 7.22 (dd, *J* = 6.0, 8.5 Hz, 1H), 7.02 (dt, *J* = 2.6, 8.3 Hz, 1H), 3.83 (t, *J* = 6.7 Hz, 2H), 2.98 (t, *J* = 6.7 Hz, 2H) **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 160.8 (d, $J_{C\text{-}F}$ = 250.0 Hz), 137.1 (d, $J_{C\text{-}F}$ = 3.3 Hz), 130.8 (d, $J_{C\text{-}F}$ = 8.0 Hz), 126.5 (d, $J_{C\text{-}F}$ = 23.4 Hz), 115.4 (d, $J_{C\text{-}F}$ = 20.5 Hz), 99.7 (d, $J_{C\text{-}F}$ = 8.1 Hz), 62.3 (s), 42.8 (s).



2-(2-Iodo-5-methylphenyl)ethanol (41): obtained as a white solid (199.9 mg, 68 %). **^{1}H NMR (400 MHz, CDCl3): δ** = 7.69 (d, *J* = 8.0 Hz, 1H), 7.08 (d, *J* = 2.2 Hz, 1H), 6.75 (dd, *J* = 2.1, 7.9 Hz, 1H), 3.84 (q, *J* = 6.5 Hz, 2H), 2.97 (t, *J* = 6.8 Hz, 2H), 2.29 (s, 3H). **^{13}C NMR ($CDCl_3$, 100 MHz): δ** = 141.0, 139.6, 138.6, 131.6, 129.7, 96.9, 62.4, 43.8, 21.0

Synthesis of 2-Iodophenethyl 4-Methylbenzenesulfonate Intermediates[5]

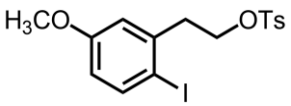


33, 38-41 **42-46**

General Procedure

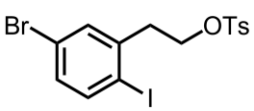
p-Toluenesulfonyl chloride (1.6 equiv.) was added to a solution of 2-iodophenyl ethanol (1.0 equiv.) and triethylamine (3.7 equiv.) in anhydrous CH_2Cl_2 at 0 °C. Ice bath was removed, and the reaction mixture was stirred at room temperature overnight. It was diluted with CH_2Cl_2, washed with 2 M aqueous HCl solution, followed by saturated aqueous $NaHCO_3$ solution and brine, and dried ($MgSO_4$). The solvent was removed under reduced pressure and the residue was purified by flash chromatography, on silica, eluting with 5-10% EtOAc/*n*-pentane to give the desired 2-iodophenethyl 4-methylbenzenesulfonate.

Characterisation Data



2-Iodo-5-methoxyphenethyl 4-methylbenzenesulfonate (42): obtained as a colourless oil (1.23 g, 49% yield) **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 7.71-7.67 (m, 2H), 7.59 (d, *J* = 8.7 Hz, 1H), 7.28-7.26 (m, 2H) overlapping with $CDCl_3$, 6.73 (d, *J* = 3.0 Hz, 1H), 6.53 (dd, *J* = 8.7, 3.0 Hz, 1H), 4.23-4.19 (m, 2H), 3.75 (s, 3H), 3.04 (t, *J* = 7.0 Hz, 2H), 2.43 (s, 3H) **^{13}C NMR ($CDCl_3$, 100 MHz):** δ =160.1, 144.8, 140.1, 139.9, 133.0, 130.0, 127.9, 116.6, 115.1, 88.7, 69.0, 55.5, 40.2, 21.8

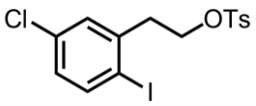
HRMS (ESI) *m/z* calc. for $C_{16}H_{18}O_4IS$ $[M+H]^+$ 432.9965, found 432.9959



5-Bromo-2-iodophenethyl 4-methylbenzenesulfonate (43): obtained as a white solid (1.35g, 87% yield) **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 7.70 (d, *J* = 8.3 Hz, 2H), 7.58 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.3 Hz, 2H), 7.25 (d, *J* = 2.4 Hz, 1H), 7.04 (dd, *J* = 8.4,

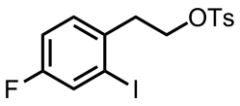
2.4 Hz, 1H), 4.24 (t, *J* = 6.7 Hz, 2H), 3.04 (t, *J* = 6.7 Hz, 2H), 2.43 (s, 3H) **^{13}C NMR (CDCl$_3$, 100 MHz):** δ = 144.9, 141.2, 140.9, 133.4, 132.8, 131.9, 129.9, 127.9, 122.7, 98.3, 68.5, 39.8, 21.8

HRMS (EI) *m/z* calc. for $C_{15}H_{14}O_3BrIS$ 479.886, found 479.8895

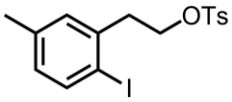


5-Chloro-2-iodophenethyl 4-methylbenzenesulfonate (44): obtained as a pale yellow solid (0.77g, 76% yield) **^{1}H NMR (CDCl$_3$, 400 MHz):** δ = 7.70-7.68 (m, 2H), 7.64 (d, *J* = 8.4 Hz, 1H), 7.29 (m, 2H), 7.11 (d, *J* = 2.5 Hz, 1H), 6.91 (dd, *J* = 8.4, 2.5 Hz, 1H), 4.24 (t, *J* = 6.7 Hz, 2H), 3.05 (t, *J* = 6.7 Hz, 2H), 2.43 (s, 3H) **^{13}C NMR (CDCl$_3$, 100 MHz):** δ = 144.9, 140.9, 140.6, 134.8, 132.8, 130.6, 130.0, 129.0, 127.9, 97.3, 68.5, 39.9, 21.8

HRMS (EI) *m/z* calc. for $C_{15}H_{14}O_3ClIS$ 435.9397, found 435.9388

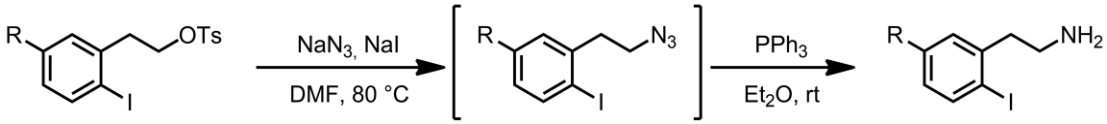


4-Fluoro-2-iodophenethyl 4-methylbenzenesulfonate (45): solid (402.4 mg, 92%). **^{1}H NMR (400 MHz, CDCl$_3$):** δ = 7.62 - 7.71 (m, 2H), 7.40 - 7.46 (m, 1H), 7.23 - 7.30 (m, 2H), 7.13 (dd, J = 5.9, 8.4 Hz, 1H), 6.96 (dt, *J* = 2.6, 8.3 Hz, 1H), 4.19 (t, *J* = 6.8 Hz, 2H), 3.04 (t, *J* = 6.7 Hz, 2H), 2.43 (s, 3H). **^{13}C NMR (CDCl$_3$, 100 MHz):** δ = 161.01 (d, J_{C-F} = 251.0 Hz), 144.87 (s), 134.88 (d, J_{C-F} = 3.3 Hz), 132.72 (s), 131.26 (d, J_{C-F} = 8.0 Hz), 129.88 (s), 127.89 (s), 126.40 (d, J_{C-F} = 23.6 Hz), 115.52 (d, J_{C-F} = 21.0 Hz), 99.23 (d, J_{C-F} = 7.8 Hz), 68.89 (s), 62.27 (s), 42.73 (s), 39.03 (s), 21.72 (s).



2-Iodo-5-methylphenethyl 4-methylbenzenesulfonate (46): solid (459.2 mg, 90%). **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.65 – 7.72 (m, 2H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.23 – 7.31 (m, 2H), 6.97 (d, *J* =2.2 Hz, 1H), 6.66 -6.78 (m, 1H), 4.20 (t, 2H), 3.02 (t, 2H), 2.39 – 2,45 (br s, 3H), 2.24 (br s, 3H). **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 144.9, 139.5, 138.7, 131.7, 130.0, 128.0, 96.3, 69.3, 40.0, 21.9, 21.1.

Synthesis of 2-Iodophenylethanamines[4, 6]



42-46 **47-51**

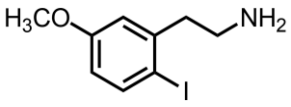
General Procedure

Sodium azide (2.0 equiv.) and sodium iodide (0.5 equiv.) were added to a solution of 2-iodophenylethylsulfonate (1.0 equiv.) in DMF at room temperature, under inert atmosphere. The mixture was heated at 80 °C overnight. The reaction was allowed to cool to room temperature and quenched with water. The mixture was extracted with Et_2O (3×), washed with brine and dried over $MgSO_4$. The in-situ azide was used in the next step without further purification.

A solution of azide (1.0 equiv.) and PPh_3 (1.5 equiv.) in Et_2O was stirred at 0 °C for 3 h. Water was added to the reaction mixture. The reaction was allowed to warm to room temperature and stirred overnight. It was then acidified with 1 M aqueous HCl solution and washed with Et_2O (3×). The aqueous layers were basified with 1 M aqueous NaOH

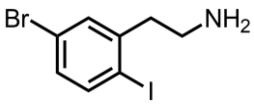
solution, extracted with Et_2O (3×), washed with brine and dried over $MgSO_4$. The solvent was evaporated under reduced pressure to give 5-substituted-2-iodophenylethylamines.

Characterisation Data



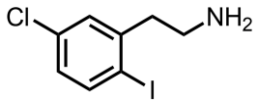
2-(2-Iodo-5-methoxyphenyl)ethanamine (47): obtained as a yellow oil (1.09 g, 69% yield) **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 7.69 (d, *J* = 8.7 Hz, 1H), 6.80 (d, *J* = 3.0 Hz, 1H), 6.53 (dd, *J* = 8.8, 3.0 Hz, 1H), 3.77 (s, 3H), 2.97-2.93 (m, 2H), 2.85-2.82 (m, 2H), 1.29 (br s, 2H) **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 160.1, 143.6, 140.1, 116.2, 114.1, 89.4, 55.5, 45.0, 42.5

HRMS (ESI) *m/z* calc. for $C_9H_{13}ONI$ $[M+H]^+$ 278.0036, found 278.0034

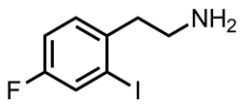


2-(5-Bromo-2-iodophenyl)ethanamine (48): obtained as a white solid (0.57 g, 68% yield) **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 7.67 (d, *J* = 8.4 Hz, 1H), 7.36 (d, *J* = 2.4 Hz, 1H), 7.05 (dd, *J* = 8.4, 2.4 Hz, 1H), 2.97-2.93 (m, 2H), 2.85-2.82 (m, 2H), 1.16 (br s, 2H) **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 144.7, 140.9, 132.8, 131.3, 122.7, 98.8, 44.6, 42.2

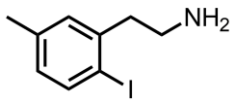
HRMS (ESI) *m/z* calc. for $C_8H_{10}NBrI$ $[M+H]^+$ 325.9036, found 325.9030



2-(5-Chloro-2-iodophenyl)ethanamine (49): obtained as a white solid (0.28 g, 65% yield) **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 7.74 (d, *J* = 8.4 Hz, 1H), 7.21 (d, *J* = 2.5 Hz, 1H), 6.92 (dd, *J* = 8.4, 2.6 Hz, 1H), 2.97-2.93 (m, 2H), 2.85-2.82 (m, 2H), 1.26 (br s, 2H) **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 144.4, 140.6, 134.6, 129.9, 128.4, 97.9, 44.7, 42.3

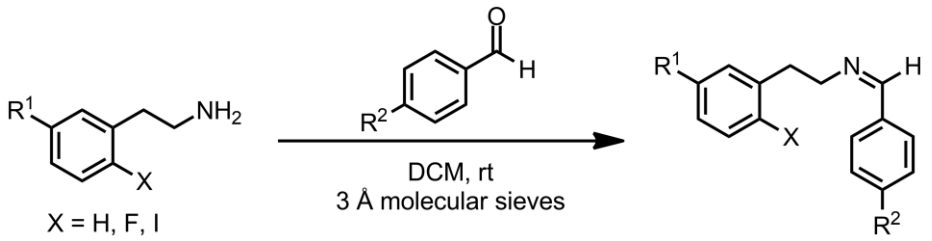


2-(4-Fluoro-2-iodophenyl)ethanamine (50): colourless oil (80.6 mg, 56 %) **^{1}H NMR (400 MHz, CDCl3):** δ = 7.52 (dd, *J* = 2.6, 8.1 Hz, 1H), 7.14 (dd, *J* = 6.0, 8.5 Hz, 1H), 6.98 (dt, *J* = 2.6, 8.3 Hz, 1H), 2.77-2.94 (m, 4H). **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 160.6 (d, $J_{C\text{-}F}$ = 249.7 Hz), 138.3 (d, $J_{C\text{-}F}$ = 3.2 Hz), 130.3 (d, $J_{C\text{-}F}$= 7.9 Hz), 126.3 (d, $J_{C\text{-}F}$ = 23.3 Hz), 115.3 (d, $J_{C\text{-}F}$ = 20.6 Hz), 99.7 (d, $J_{C\text{-}F}$ = 7.9 Hz), 43.7 (s), 42.4 (s).



2-(2-Iodo-5-methylphenyl)ethanamine (51): colourless oil (141.2 mg, 74 %) **^{1}H NMR (400 MHz, CDCl3):** δ = 7.67 (d, *J* = 8.0 Hz, 1 H), 7.03 (d, *J* = 2.0 Hz, 1 H), 6.73 (dd, *J* = 1.9, 7.9 Hz, 1 H), 2.98 - 2.89 (m, 2 H), 2.87 - 2.78 (m, 2 H), 2.28 (s, 3 H). **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 142.3, 139.7, 138.7, 131.1, 129.5, 97.0, 44.5, 42.6, 21.2.

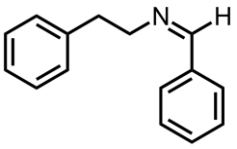
General Procedure for the Preparation of Aldimines



5, 25, 26, 52- 64

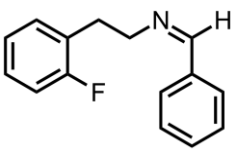
A solution of 2-iodophenylethamine (1.0 equiv.) and benzaldehyde (1.05 equiv.) in CH_2Cl_2 was stirred at room temperature overnight. The reaction was filtered through a plug of Celite with CH_2Cl_2. The solvent was then removed under reduced pressure and the residue was dried under vacuum to remove traces of benzaldehyde. The aldimines were used without further purification.

Characterisation Data



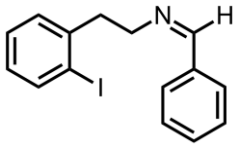
***N*-Phenethyl-1-phenylmethanimine (25)**: obtained as a yellow solid (0.68 g, 79% yield) **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 8.17 (s, 1H), 7.71-7.69 (m, 2H), 7.42-7.40 (m, 3H), 7.30-7.27 (m, 2H), 7.25-7.18 (m, 3H), 3.89 (td, *J* = 7.4, 1.2 Hz, 2H), 3.04 (t, *J* = 7.5 Hz, 2H) **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 161.6, 140.1, 136.3, 130.7, 129.2, 128.7, 128.5, 128.2, 126.2, 63.3, 37.6.

Data match that reported in the literature.[7]



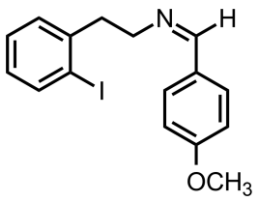
***N*-(2-Fluorophenethyl)-1-phenylmethanimine (26)**: obtained as a brown oil (0.36 g, 87% yield) **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 8.19 (s, 1H), 7.71-7.69 (m, 2H), 7.42-7.39 (m, 3H), 7.25-7.16 (m, 2H), 7.07-7.00 (m, 2H), 3.88 (td, *J* = 7.4, 1.2 Hz, 2H), 3.08 (t, *J* = 7.4 Hz, 2H) **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 162.6 (d, $J_{C\text{-}F}$ = 244.9 Hz), 161.7, 136.3, 131.6 (d, $J_{C\text{-}F}$ = 4.8 Hz), 130.7, 128.7, 128.2, 128.1 (d, $J_{C\text{-}F}$ = 8.0 Hz), 126.9 (d, $J_{C\text{-}F}$ = 15.9 Hz), 124.0 (d, $J_{C\text{-}F}$ = 3.3 Hz), 115.4 (d, $J_{C\text{-}F}$ = 22.2 Hz), 61.6, 30.9

HRMS (ESI) *m/z* calc. for $C_{15}H_{15}NF$ $[M+H]^+$ 228.1183, found 228.1179



***N*-(2-Iodophenethyl)-1-phenylmethanimine (5)**: obtained as a yellow oil (0.62 g, 91% yield) **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 8.20 (s, 1H), 7.84 (d, *J* = 7.8 Hz, 1H), 7.73-7.70 (m, 2H), 7.43-7.39 (m, 3H), 7.25-7.24 (m, 2H), 6.91-6.87 (m, 1H), 3.87 (td, *J* = 7.6, 1.2 Hz, 2H), 3.16 (t, *J* = 7.5 Hz, 2H) **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 161.9, 142.6, 139.6, 136.3, 130.8, 130.6, 128.7, 128.4, 128.2, 100.9, 61.2, 42.2

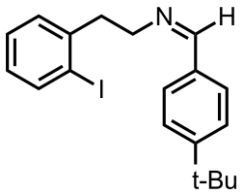
HRMS (ESI) *m/z* calc. for $C_{15}H_{15}NI$ $[M+H]^+$ 336.0244, found 336.0239



***N*-(2-Iodophenethyl)-1-(4-methoxyphenyl)methanimine (52)**: obtained as an orange solid (0.27 g, 74% yield) **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 8.11 (s, 1H), 7.83 (d, *J* = 7.6 Hz, 1H), 7.69 (d, *J* = 8.7 Hz, 2H), 7.25-7.24 (m, 2H) overlapping with $CDCl_3$, 6.94-6.87 (d, *J* = 8.8 Hz, 2H) overlapping with 6.90 (m, 1H), 3.85 (s, 3H) overlapping with

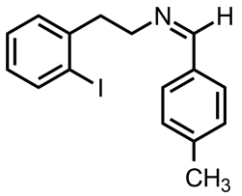
3.84-3.80 (m, 2H), 3.15 (t, J = 7.4 Hz, 2H) **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 161.8, 161.3, 142.6, 139.6, 130.6, 129.9, 129.1, 128.4, 128.2, 114.1, 100.9, 61.2, 55.5, 42.3

HRMS (ESI) *m/z* calc. for $C_{16}H_{17}ONI$ $[M+H]^+$ 366.0349, found 366.0346



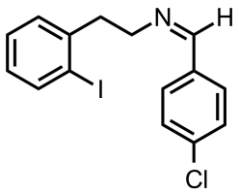
1-(4-(*tert*-Butyl)phenyl)-*N*-(2-iodophenethyl)methanimine (53): 4-*tert*-butyl benzaldehyde (2.05 equiv.), obtained as a pale yellow solid (0.43 g, 90% yield) **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 8.18 (s, 1H), 7.84 (d, J = 7.8 Hz, 1H), 7.66-7.63 (m, 2H), 7.44-7.41 (m, 2H), 7.25-7.24 (m, 2H) overlapping with $CDCl_3$, 6.90-6.87 (m, 1H), 3.84 (td, J = 7.5, 1.2 Hz, 2H), 3.14 (t, J = 7.5 Hz, 2H), 1.33 (s, 9H) **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 161.7, 154.1, 142.6, 139.6, 133.6, 130.6, 128.3, 128.1, 128.0, 125.7, 100.9, 61.5, 42.3, 35.0, 31.4

HRMS (ESI) *m/z* calc. for $C_{19}H_{23}NI$ $[M+H]^+$ 392.0870, found 432.9966



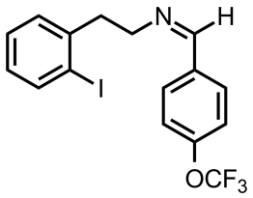
***N*-(2-Iodophenethyl)-1-(*p*-tolyl)methanimine (54)**: obtained as an off white solid (0.30 g, 82% yield) **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 8.16 (s, 1H), 7.83 (d, J = 7.7 Hz, 1H), 7.61 (d, J = 8.1 Hz, 2H), 7.25-7.20 (m, 4H), 6.91-6.86 (m, 1H), 3.84 (td, J = 7.1, 1.2 Hz, 2H), 3.15 (t, J = 7.4 Hz, 2H), 2.38 (s, 3H) **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 161.8, 142.7, 141.0, 139.6, 133.7, 130.6, 129.4, 128.3, 128.2, 128.2, 100.9, 61.4, 42.3, 21.6

HRMS (ESI) *m/z* calc. for $C_{16}H_{17}NI$ $[M+H]^+$ 350.0400, found 350.0394



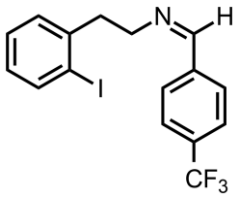
1-(4-chlorophenyl)-*N*-(2-iodophenethyl)methanimine (55): 4-chlrobenzaldehyde (1.15 equiv.), obtained as a dark yellow solid (0.32 g, 76% yield) **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 8.15 (s, 1H), 7.84 (d, *J* = 7.8 Hz, 1H), 7.66-7.63 (m, 2H), 7.39-7.37 (m, 2H), 7.25-7.22 (m, 2H) overlapping with $CDCl_3$, 6.91-6.87 (m, 1H), 3.86 (td, *J* = 7.4, 1.2 Hz, 2H), 3.15 (t, *J* = 7.4 Hz, 2H) **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 160.5, 142.5, 139.6, 136.7, 134.7, 130.6, 129.4, 129.0, 128.4, 128.2, 100.9, 61.4, 42.1

HRMS (ESI) *m/z* calc. for $C_{15}H_{14}NClI$ $[M+H]^+$ 369.9854, found 369.9852



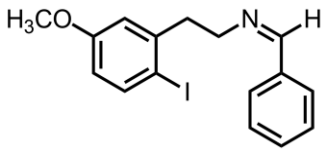
***N*-(2-iodophenethyl)-1-(4-(trifluoromethoxy)phenyl)methanimine (56)**: 4-(trifluoromethoxy)-benzaldehyde (2.05 equiv.), obtained as a yellow solid (0.38 g, 86% yield) **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 8.18 (s, 1H), 7.84 (d, *J* = 8.3 Hz, 1H), 7.76-7.73 (m, 2H), 7.25-7.24 (m, 4H) overlapping with $CDCl_3$, 6.92-6.88 (m, 1H), 3.87 (td, *J* = 7.4, 1.1 Hz, 2H), 3.15 (t, *J* = 7.4 Hz, 2H) **^{13}C NMR ($CDCl_3$, 100 MHz):** δ =160.1, 150.9, 142.4, 139.7, 134.8, 130.6, 129.7, 128.4 (d, J_{C-F} = 12.6 Hz), 121.8 (q, J_{C-F} = 258.2 Hz), 121.0, 100.9, 61.4, 42.1.

HRMS (ESI) *m/z* calc. for $C_{16}H_{14}ONF_3I$ $[M+H]^+$ 420.0067, found 420.0069



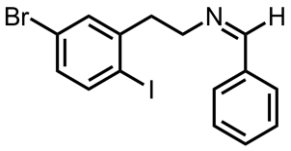
***N*-(2-Iodophenethyl)-1-(4-(trifluoromethyl)phenyl)methanimine (57)**: 4-(trifluoromethyl)-benzaldehyde (2.05 equiv.), obtained as a pale yellow oil (0.40 g, 94% yield) **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 8.22 (s, 1H), 7.84-7.81 (m, 3H), 7.67 (d, *J* = 8.2 Hz, 2H), 7.25-7.24 (m, 2H), 6.92-6.88 (m, 1H), 3.90 (td, *J* = 7.3, 1.2 Hz, 2H), 3.17 (t, *J* = 7.4 Hz, 2H) **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 160.4, 142.3, 139.7, 139.4, 132.4 (q, J_{C-F} = 32.6 Hz), 130.6, 128.4, 128.3 (q, J_{C-F} = 8.8 Hz), 125.7 (q, J_{C-F} = 3.8 Hz), 125.4 (q, J_{C-F} = 272.4 Hz), 100.9, 61.4, 42.0

HRMS (ESI) *m/z* calc. for $C_{16}H_{14}NF_3I$ $[M+H]^+$ 404.0118, found 404.0119



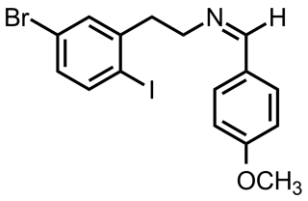
***N*-(2-Iodo-5-methoxyphenethyl)-1-phenylmethanimine (58)**: obtained as a yellow solid (0.14 g, 70% yield) **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 8.20 (s, 1H), 7.73-7.70 (m, 2H), 7.69 (d, *J* = 8.7 Hz, 1H), 7.43-7.39 (m, 3H), 6.83 (d, *J* = 3.0 Hz, 1H), 6.53 (dd, *J* = 8.7, 3.0 Hz, 1H), 3.86 (td, *J* = 7.4, 1.2 Hz, 2H), 3.71 (s, 3H), 3.12 (t, *J* = 7.4 Hz, 2H) **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 161.9, 159.9, 143.6, 139.9, 136.3, 130.8, 128.7, 128.2, 116.3, 114.5, 89.3, 61.4, 55.4, 42.3

HRMS (ESI) *m/z* calc. for $C_{16}H_{17}ONI$ $[M+H]^+$ 366.0349, found 366.0348



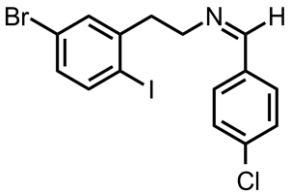
***N*-(5-Bromo-2-iodophenethyl)-1-phenylmethanimine (59)**: obtained as a yellow solid (0.16 g, 82% yield) **^{1}H NMR (CDCl$_3$, 400 MHz):** δ = 8.23 (s, 1H), 7.73-7.71 (m-2H), 7.67 (d, *J* = 3.2 Hz, 1H), 7.43-7.41 (m, 4H), 7.05 (dd, *J* = 8.4, 2.4 Hz, 1H), 3.85 (td, *J* = 7.2, 1.2 Hz, 2H), 3.11 (t, *J* = 7.4 Hz, 2H) **^{13}C NMR (CDCl$_3$, 100 MHz):** δ = 162.1, 144.8, 140.8, 136.2, 133.4, 131.3, 130.9, 128.7, 128.3, 122.6, 98.8, 61.1, 42.1

HRMS (ESI) *m/z* calc. for $C_{15}H_{14}NBrI$ $[M+H]^+$ 413.9349, found 413.9348



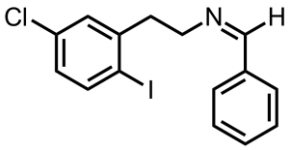
***N*-(5-Bromo-2-iodophenethyl)-1-(4-methoxyphenyl)methanimine (60)**: obtained as a yellow solid (0.16 g, 80% yield) **^{1}H NMR (CDCl$_3$, 400 MHz):** δ = 8.16 (s, 1H), 7.67-7.65 (m, 3H), 7.41 (d, *J* = 2.4 Hz, 1H), 7.04 (dd, *J* = 8.5, 2.4 Hz, 1H), 6.94-6.92 (m, 2H), 3.85 (s, 3H), 3.80 (td, *J* = 7.4, 1.0 Hz, 2H), 3.10 (t, *J* = 7.4 Hz, 2H) **^{13}C NMR (CDCl$_3$, 100 MHz):** δ = 161.8, 161.4, 145.0, 140.8, 133.3, 131.2, 129.8, 129.1, 122.5, 114.1, 98.8, 61.0, 55.5, 42.2

HRMS (ESI) *m/z* calc. for $C_{16}H_{16}ONBrI$ $[M+H]^+$ 443.9454, found 443.9456



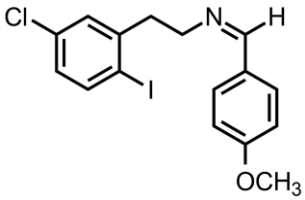
***N*-(5-Bromo-2-iodophenethyl)-1-(4-chlorophenyl)methanimine (61)**: obtained as an off white solid (0.18 g, 86% yield) **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 8.17 (s, 1H), 7.67-7.64 (m, 3H), 7.40-7.38 (m, 3H), 7.05 (dd, *J* = 8.4, 2.4 Hz, 1H), 3.84 (td, *J* = 7.3, 1.3 Hz, 2H), 3.11 (t, *J* = 7.3 Hz, 2H) **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 160.7, 144.7, 140.8, 136.8, 134.6, 133.4, 131.3, 129.5, 129.0, 122.6, 98.8, 61.0, 41.9

HRMS (ESI) *m/z* calc. for $C_{15}H_{13}NBrClI$ $[M+H]^+$ 447.8959, found 447.8962



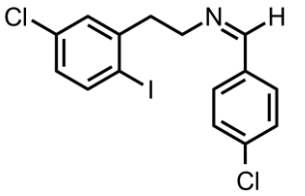
***N*-(5-Chloro-2-iodophenethyl)-1-phenylmethanimine (62)**: obtained as an off-white solid (0.16 g, 81% yield) **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 8.24 (s, 1H), 7.74-7.71 (m, 3H), 7.43-7.40 (m, 3H), 7.27 (d, *J* = 2.6 Hz, 1H) overlapping with $CDCl_3$, 6.92 (dd, *J* = 8.5, 2.5 Hz, 1H), 3.85 (td, *J* = 7.4, 1.2 Hz, 2H), 3.12 (t, *J* = 7.4 Hz, 2H) **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 162.1, 144.5, 140.5, 136.1, 134.5, 130.9, 130.5, 128.7, 128.4, 128.3, 97.9, 61.1, 42.1

HRMS (ESI) *m/z* calc. for $C_{15}H_{14}NClI$ $[M+H]^+$ 369.9854, found 369.9851



***N*-(5-Chloro-2-iodophenethyl)-1-(4-methoxyphenyl)methanimine (63)**: obtained as a pale yellow solid (0.17 g, 86% yield) **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 8.16 (s, 1H), 7.73 (d, *J* = 8.4 Hz, 1H), 7.67-7.65 (m, 2H), 7.26 (m, 1H) overlapping with $CDCl_3$, 6.94-6.88 (m, 3H), 3.85 (s, 3H), 3.81 (td, *J* = 7.4, 1.2 Hz, 2H), 3.10 (t, *J* = 7.4 Hz, 2H) **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 161.8, 161.3, 144.6, 140.5, 134.5, 130.4, 129.8, 129.1, 128.3, 114.1, 97.9, 61.0, 55.5, 42.3

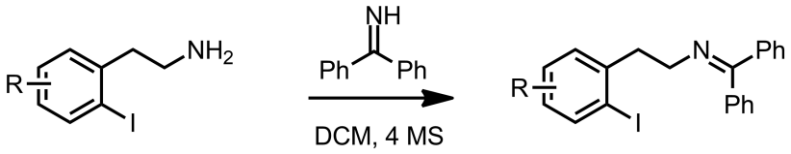
HRMS (ESI) *m/z* calc. for $C_{16}H_{16}ONClI$ $[M+H]^+$ 399.9960, found 399.9958



***N*-(5-Chloro-2-iodophenethyl)-1-(4-chlorophenyl)methanimine (64)**: obtained as a white solid (0.12 g, 87% yield) **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 8.18 (s, 1H), 7.74 (d, *J* = 8.4 Hz, 1H), 7.66-7.64 (m, 2H), 7.40-7.38 (m, 2H), 7.25 (d, *J* = 2.5 Hz, 1H), 6.92 (dd, *J* = 8.4, 2.6 Hz, 1H), 3.85 (td, *J* = 7.3, 1.2 Hz, 2H), 3.11 (t, *J* = 7.3 Hz, 2H) **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 160.7, 144.4, 140.5, 136.8, 134.6, 134.5, 130.5, 129.5, 129.0, 128.4, 97.9, 61.0, 42.0

HRMS (ESI) *m/z* calc. for $C_{15}H_{13}NCl_2I$ $[M+H]^+$ 403.9464, found 403.9464

General Procedure for the Preparation of Ketimines

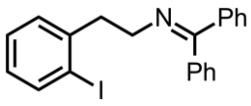


47-51 **65- 69**

General Procedure:

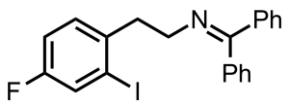
Benzophenone imine (558 mg, 3.1 mmol) was added to a solution of 2-(2-iodophenyl)ethylamine (760 mg, 3.1 mmol) in dichloromethane (5.5 mL). 3A molecular sieves (760 mg) were added to the solution, and it was stirred at room temperature overnight. The mixture was filtered through a pad of Celite with dichloromethane and concentrated under reduced pressure. The crude reaction mixture was purified under reduced pressure using bulb-to-bulb distillation under reduced pressure.

Characterisation Data

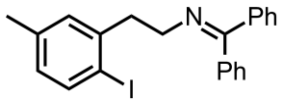


N-(Diphenylmethylene)-2-(2-iodophenyl)ethanamine (65) : brown oil (1.6 g, 63 %). **^{1}H NMR (400 MHz, CDCl3):** δ = 7.69 - 7.80 (m, 1H), 7.53 - 7.65 (m, 2H), 7.27 - 7.53 (m, 6H), 7.17 - 7.24 (m, 2H), 6.93 - 7.01 (m, 2H), 6.81 - 6.90 (m, 1H), 3.66 (t, *J* = 7.24 Hz, 2H), 3.13 (t, *J* = 7.24 Hz, 2H). **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 168.9, 142.8, 139.8, 139.4, 136.7, 130.6, 129.9, 128.5, 128.4, 128.4, 128.3, 128.1, 128.1, 127.9, 127.7, 100.9, 53.6, 42.1.

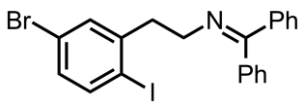
HRMS (ESI) *m/z* calc. for $C_{21}H_{18}IN$ $[M+H]^+$ 412.0517, found 412.0544.



***N*-(Diphenylmethylene)-2-(4-fluoro-2-iodophenyl)ethanamine (66):** (71.9 mg, 72%) **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 7.53 - 7.74 (m, 2H), 7.30 - 7.52 (m, 9H), 7.17 (dd, J = 5.97, 8.51 Hz, 1H), 6.92 - 7.01 (m, 1H), 3.64 (t, J = 7.14 Hz, 2H), 3.10 (t, J = 7.04 Hz, 2H). **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 178.44 (s), 169.02 (s), 160.54 (d, J_{C-F} = 249.5 Hz), 139.74 (s), 138.82 (d, J_{C-F} = 3.3 Hz), 136.69 (s), 130.96 (d, J_{C-F} = 7.8 Hz), 130.08 (s), 128.84 (s), 128.57 (s), 128.45 (s), 128.41 (s), 128.15 (s), 127.76 (s), 127.34 (s), 127.25 (s), 126.02 (d, J_{C-F} = 23.5 Hz), 115.10 (d, J_{C-F} = 20.6 Hz), 99.73 (d, J_{C-F} = 7.9 Hz), 53.59 (s), 41.15 (s).

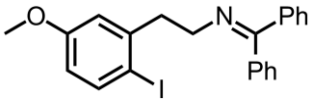


N-(Diphenylmethylene)-2-(2-iodo-5-methylphenyl)ethanamine (67): (71.3 mg, 70 %). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 7.33 - 7.63 (m, 11H), 7.04 (d, *J* = 2.15 Hz, 1H), 6.69 (dd, *J* = 2.15, 8.02 Hz, 1H), 3.66 (t, *J* = 7.24 Hz, 2H), 3.09 (t, *J* = 7.24 Hz, 2H), 2.23 (s, 3H). **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 178.0, 168.4, 142.1, 139.4, 138.6, 137.5, 136.3, 131.1, 129.5, 128.5, 128.4, 128.0, 128.0, 127.8, 127.6, 127.4, 126.8, 96.4, 53.3, 41.6, 20.5.



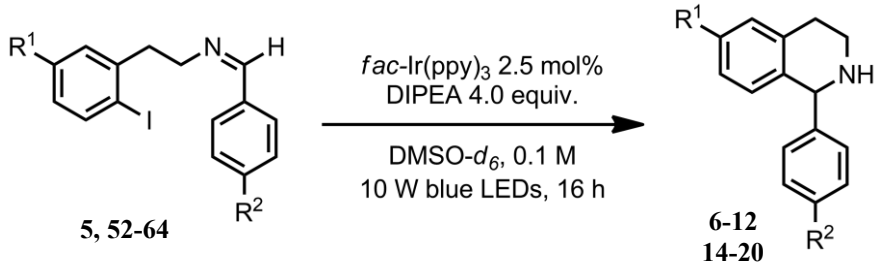
2-(5-Bromo-2-iodophenyl)-N-(diphenylmethylene)ethanamine (68): (47.9 mg, 72 %) **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 7.55 - 7.72 (m, 11H), 6.96 - 7.04 (m, 3H), 3.65

(t, J = 7.14 Hz, 2H), 3.09 (t, J = 7.14 Hz, 2H). **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 177.9, 144.7, 139.3, 139.6, 132.7, 130.2, 129.6, 127.6, 121.2, 98.2, 52.1, 41.5. **HRMS** (ESI) *m/z* calc. for $C_{21}H_{17}BrIN$ $[M+H]^+$ 489.9679, found 489.9651



***N*-(Diphenylmethylene)-2-(2-iodo-5-methoxyphenyl)ethanamine (69):** (66 %) **^{1}H NMR ($CDCl_3$, 400 MHz**): δ = 7.58 - 7.64 (m, 2H), 7.29 - 7.49 (m, 9H), 6.92 - 6.99 (m, 1H), 6.79 (d, J = 3.13 Hz, 1H), 6.48 (dd, J = 2.93, 8.61 Hz, 1H), 3.68 - 3.75 (m, 3H), 3.61 - 3.67 (m, 2H), 3.04 - 3.12 (m, 2H). **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 168.7, 159.6, 143.7, 139.6, 139.5, 136.5, 129.8, 128.3, 127.9, 127.6, 116.2, 114.0, 89.3, 55.1, 53.4, 42.1 **HRMS** (ESI) *m/z* calc. for $C_{22}H_{20}INO$ $[M+H]^+$ 442.0623, found 442.0662.

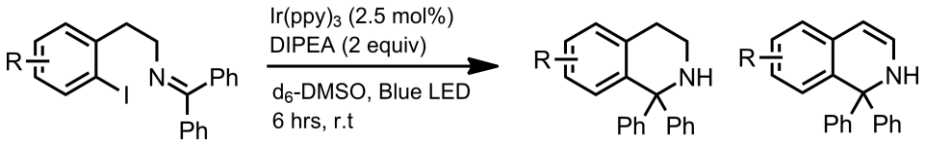
Photoredox Cyclisation



General Procedure for the Cyclisation of Aldimines

A solution of the aldimine (67 mg, 0.2 mmol), *fac*-Ir(ppy)$_3$ (3.3 mg, 5.0×10^{-3} mmol), DIPEA (0.8 mmol, 140 μL), in DMSO (2.00 mL) was freeze-pump-thaw degassed under inert atmosphere. The reaction was stirred at room temperature under irradiation with 10 W blue LED light for 16 h. Internal standard (sulfolene, 23.6 mg, 0.2 mmol) was added and analysed by ^{1}H NMR spectroscopy.

General Procedure for the Cyclisation of Ketimines



65- 69 **13, 21-24**

A solution of ketimine (0.2 mmol), *fac*-Ir(ppy)$_3$ (3.3 mg, 5.0 × 10^{-3} mmol), DIPEA (0.4 mmol, 70 μL), in DMSO (2.0 mL) was freeze-pump-thaw degassed under inert atmosphere. The reaction was stirred at room temperature under irradiation with 10 W blue LED light for 16 h. Internal standard (sulfolene, 23.6 mg, 0.2 mmol) was added and the reaction mixture was analysed directly by ^{1}H NMR spectroscopy.

Representative ^{1}H NMR spectrum:

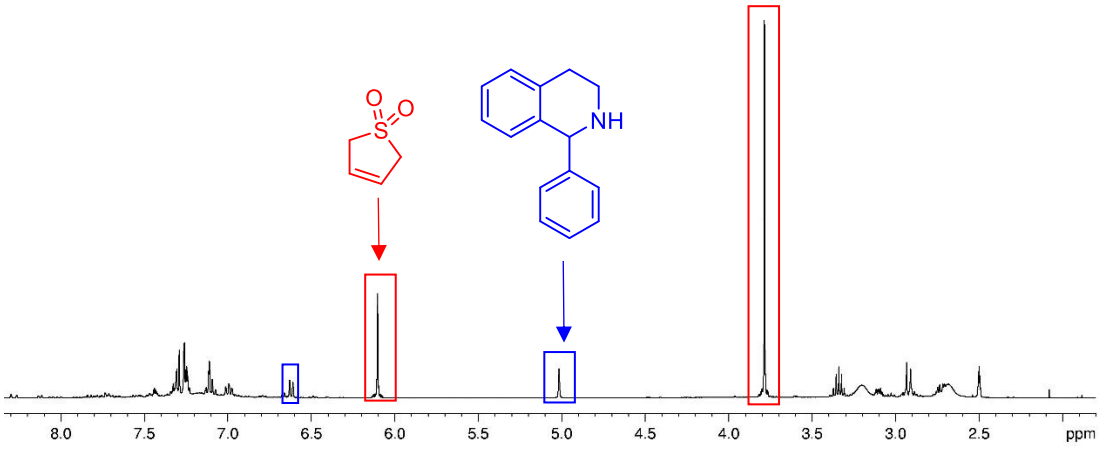
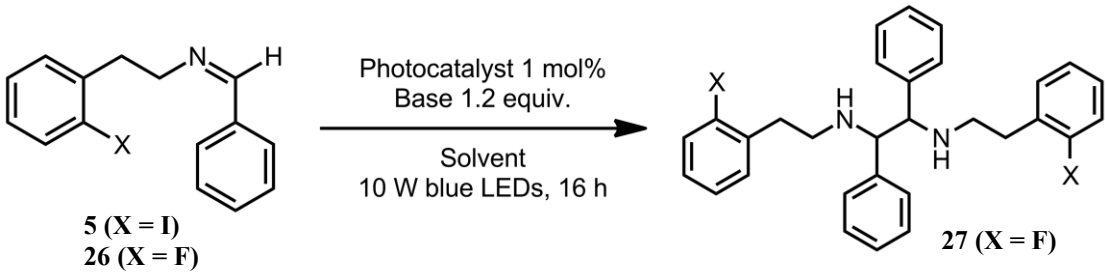


Figure S2. ^{1}H NMR spectra (DMSO-d$_6$) of reaction mixture of THIQ (blue) with sulfolene (red) as internal standard highlighting the resonances used for integration

Photoredox Dimerisation[8]



General Procedure

A solution of imine (0.2 mmol), photocatalyst (2.0×10^{-3} mmol), base (0.24 mmol), in solvent (2.00 mL) was freeze-pump-thaw degassed under inert atmosphere. The reaction was stirred at room temperature under irradiation with 10 W blue LED light for 16 h. Internal standard (sulfolene, 23.6 mg, 0.2 mmol) was added and analysed by ^{1}H NMR spectroscopy.

3. References

[1] Ren, W.; Yamane, M. *J. Org. Chem.* **2010,** *75*, 8410-8415.
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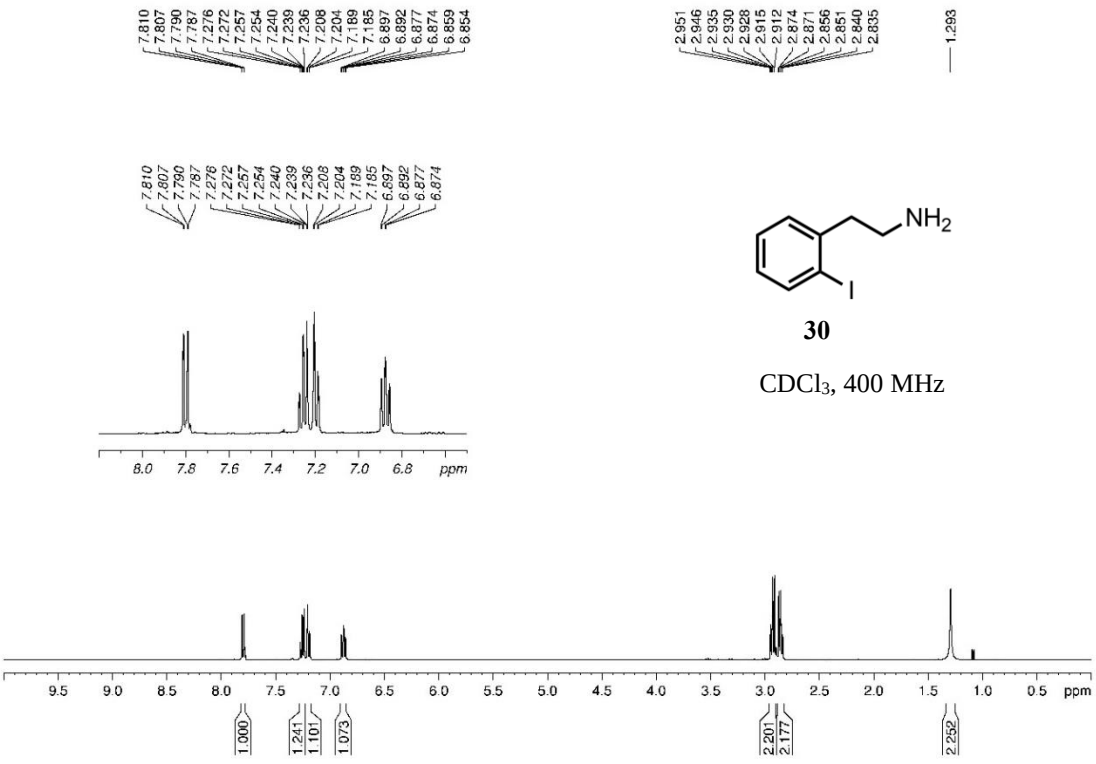
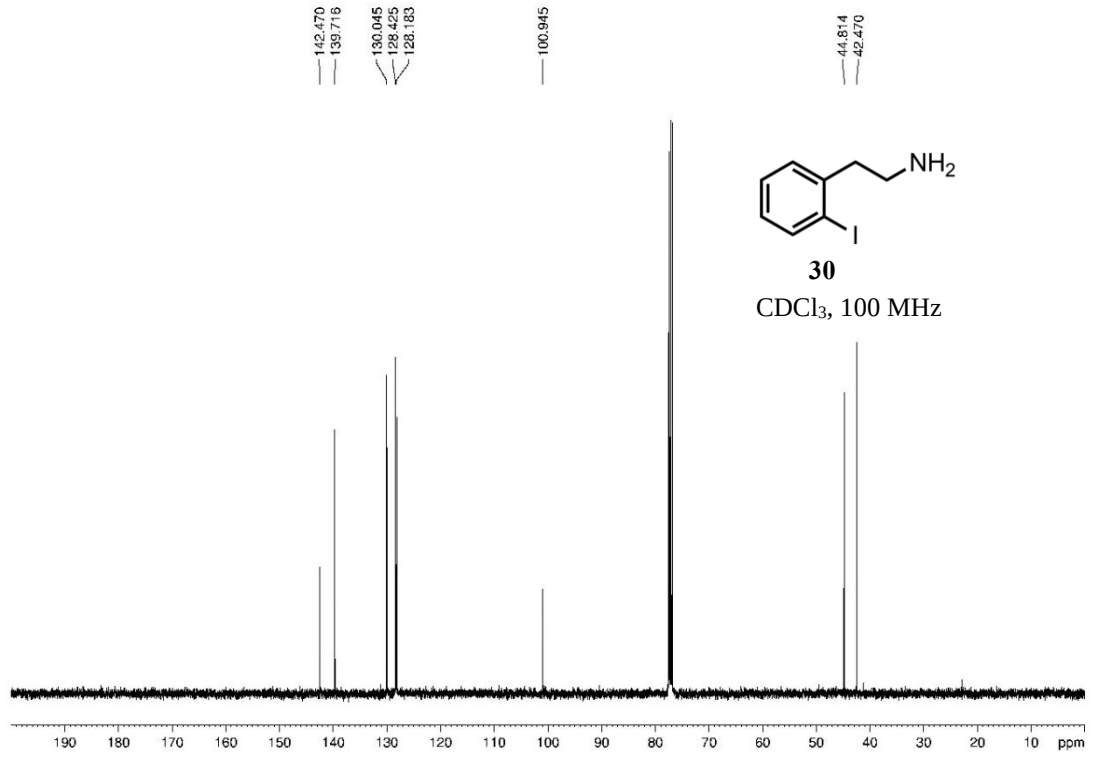
[7] Wang, C.; Chen, C.; Han, J.; Zhang, J.; Yao, Y.; Zhao, Y. *Eur. J. Org. Chem.* **2015,** *2015*, 2972-2977.
[8] Nakajima, M.; Fava, E.; Loescher, S.; Jiang, Z.; Rueping, M. *Angew. Chem. Int. Ed.* **2015,** *54*, 8828-8832.

4. ^{1}H NMR and ^{13}C NMR spectra



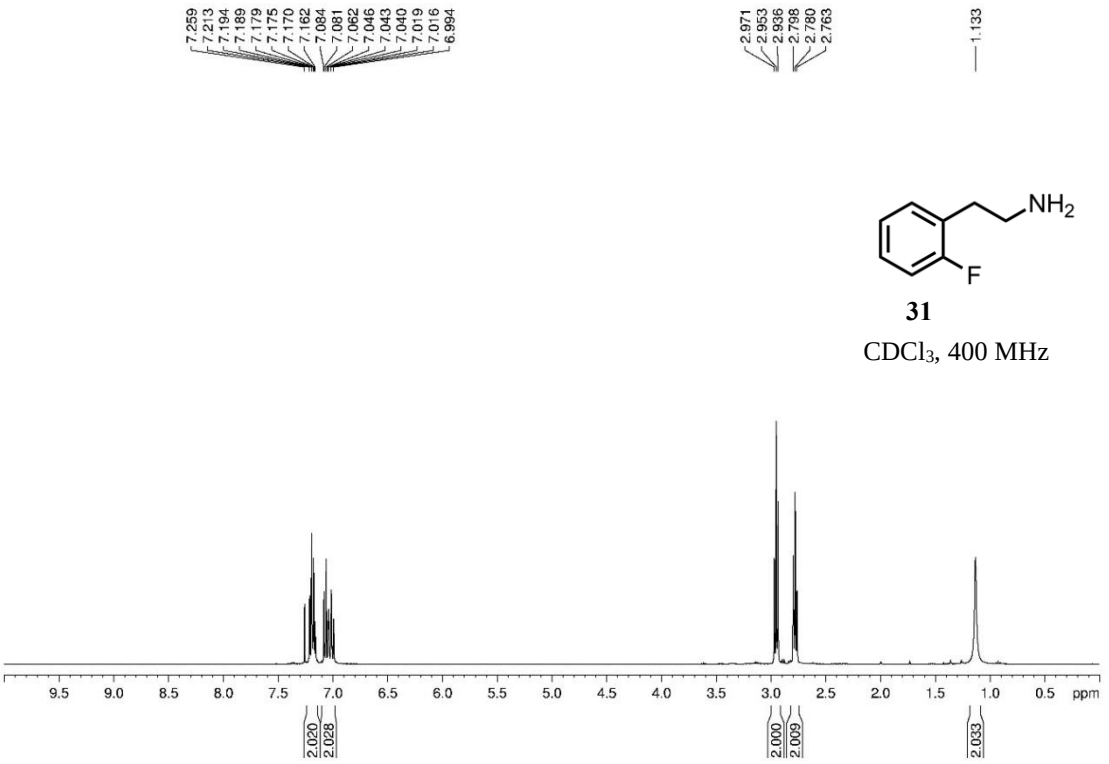
30

$CDCl_3$, 400 MHz



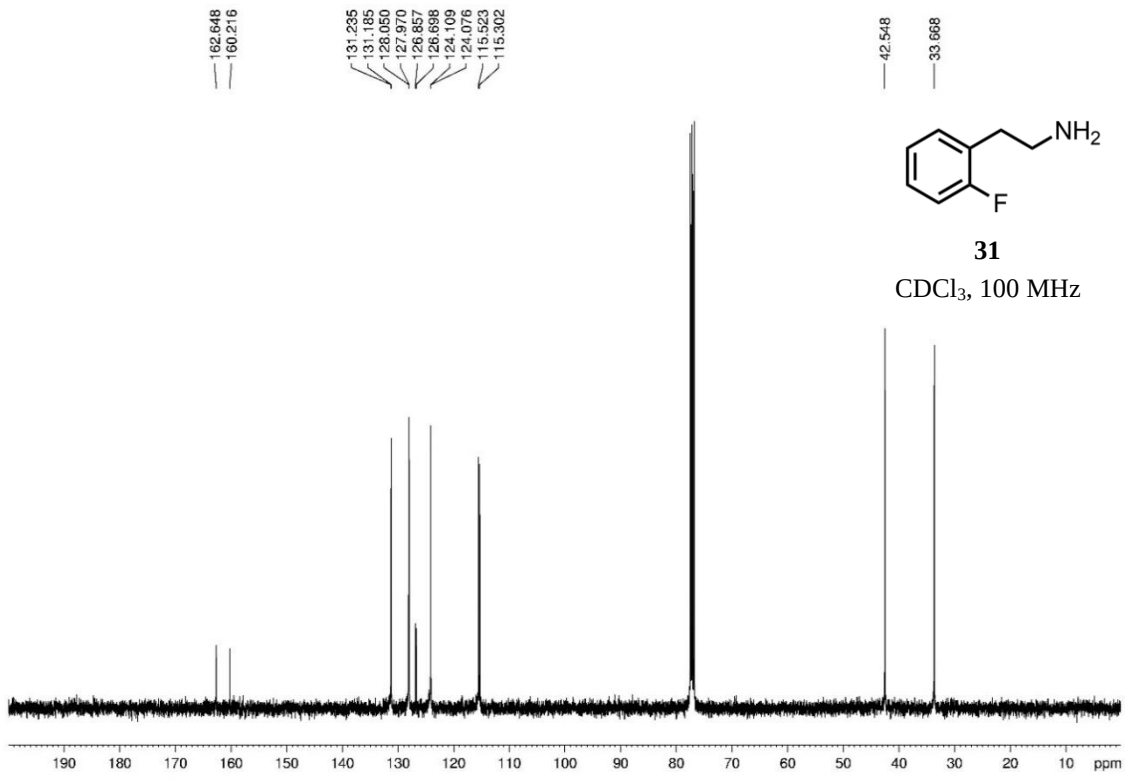
30

$CDCl_3$, 100 MHz



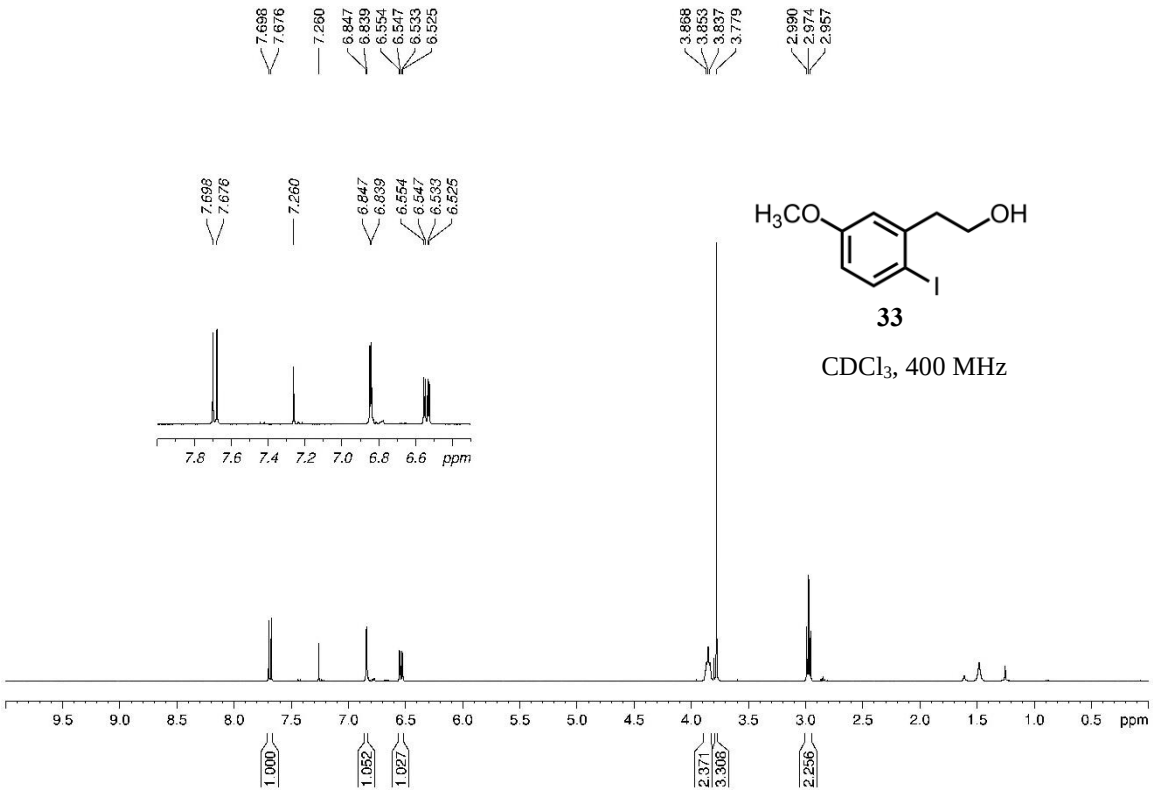
31

$CDCl_3$, 400 MHz



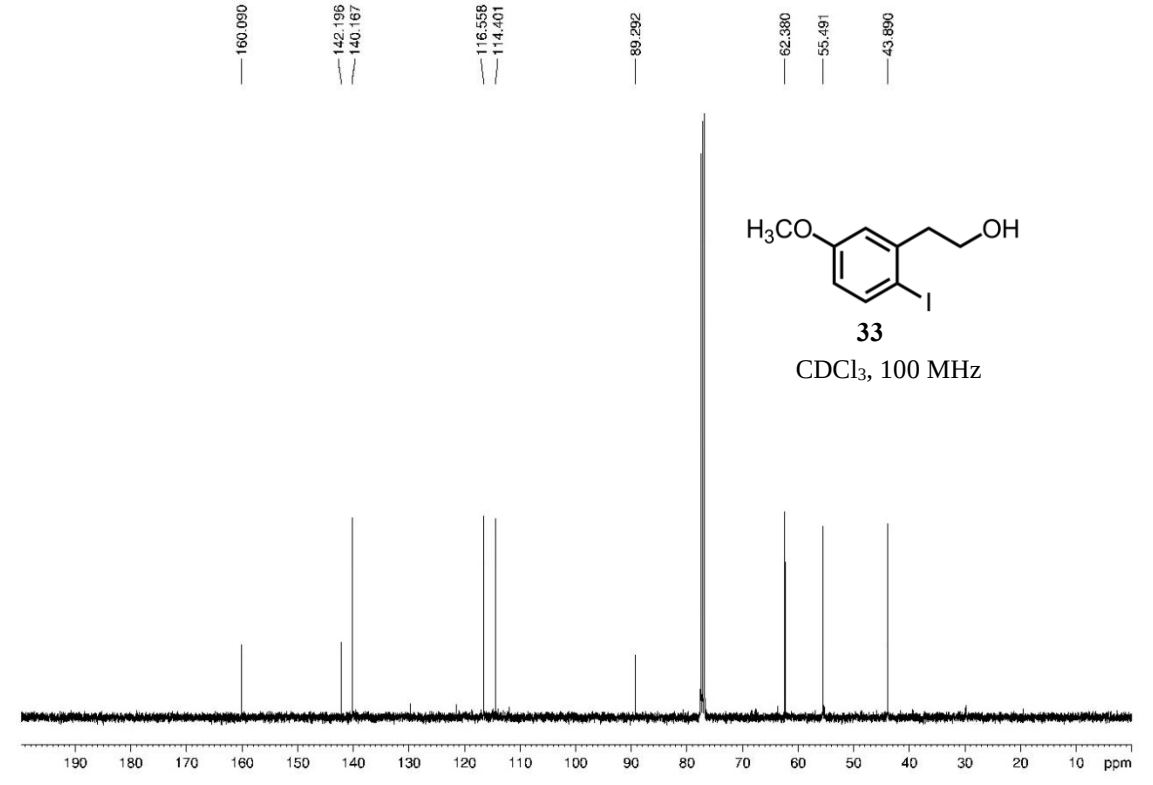
31

$CDCl_3$, 100 MHz



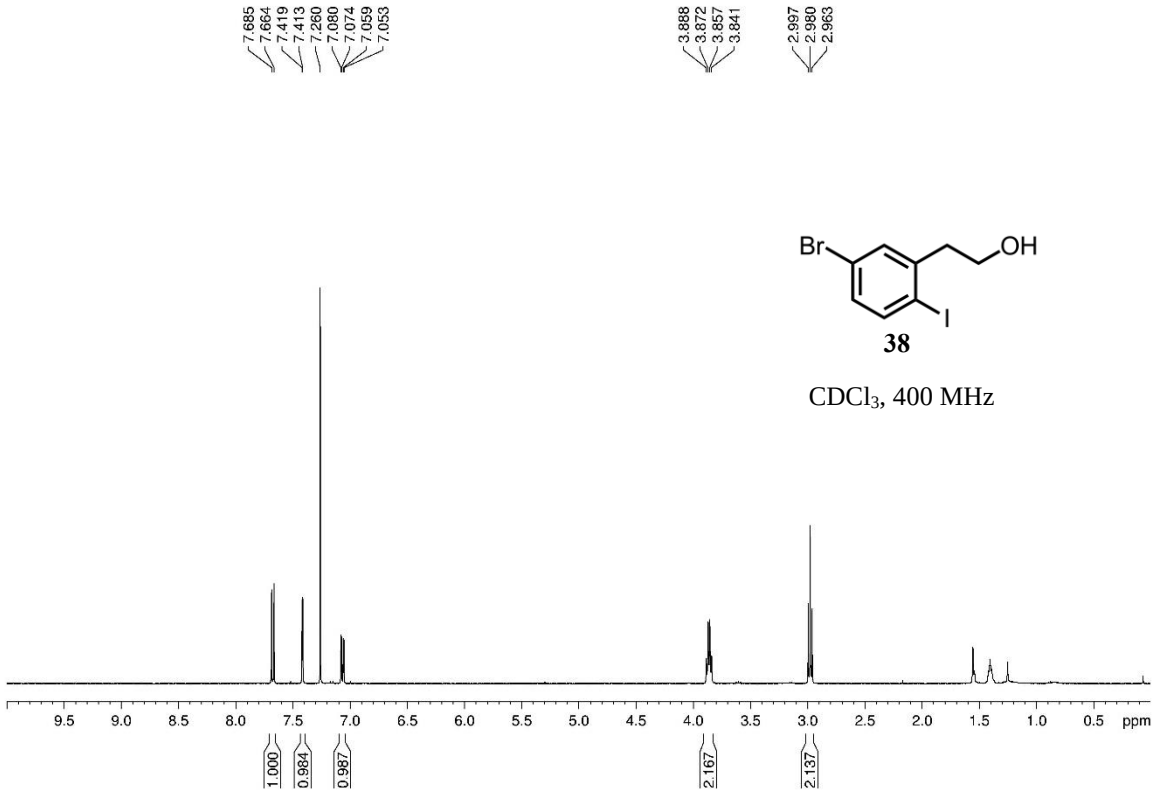
33

$CDCl_3$, 400 MHz



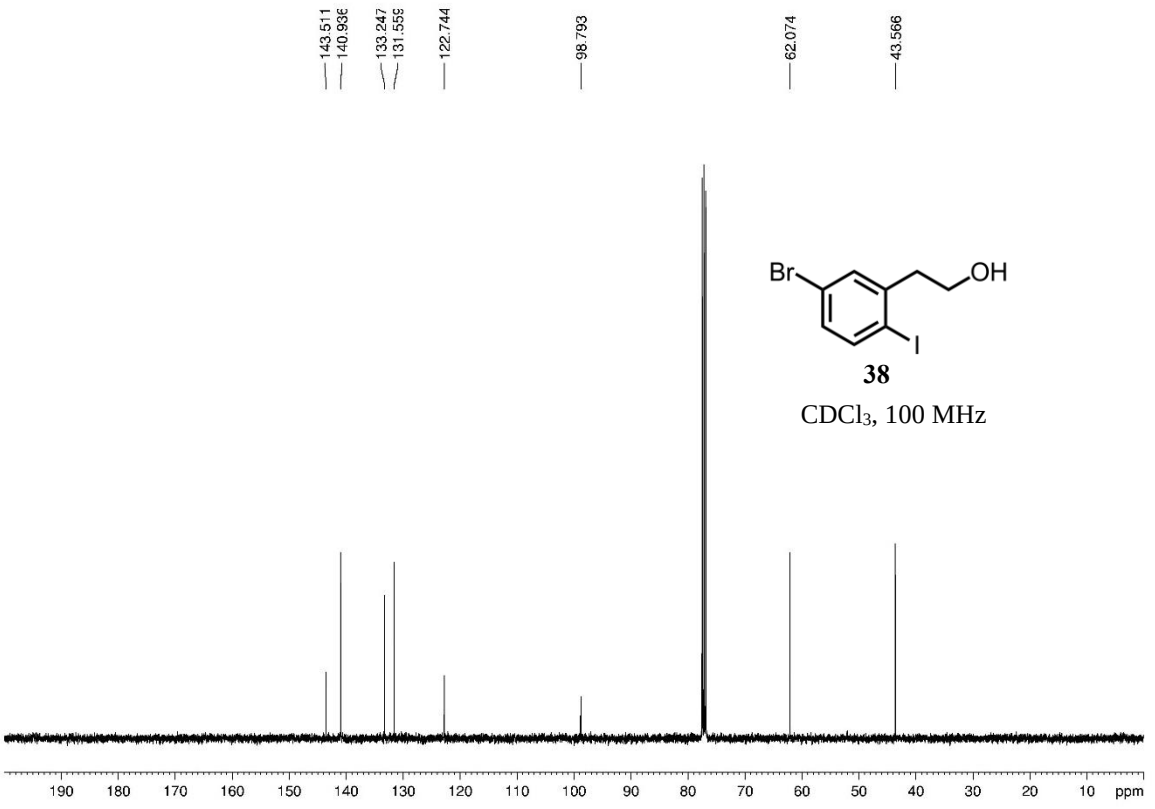
33

$CDCl_3$, 100 MHz



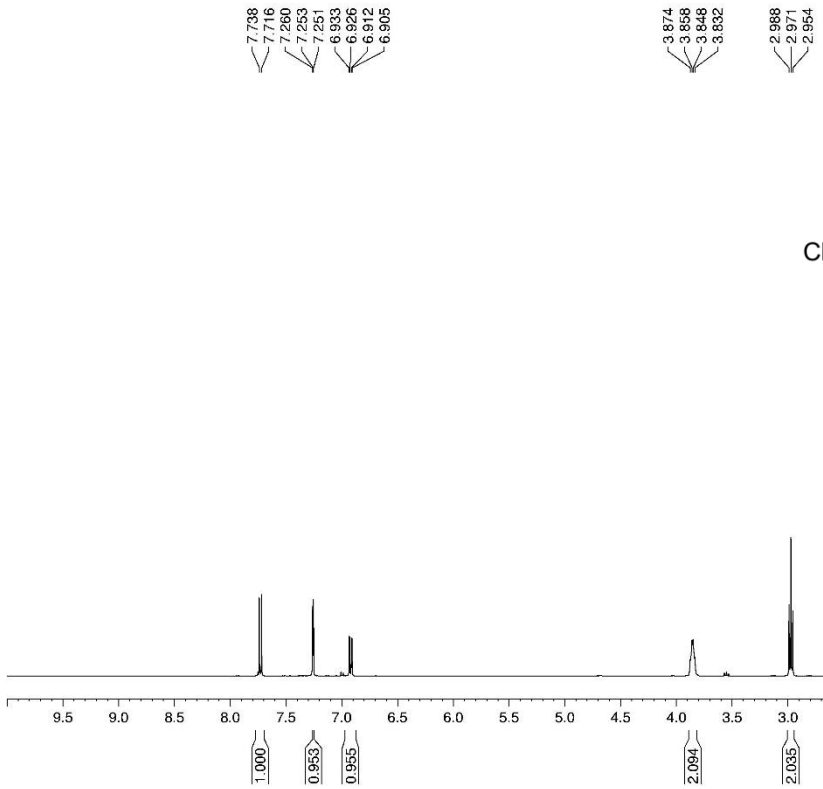
38

$CDCl_3$, 400 MHz



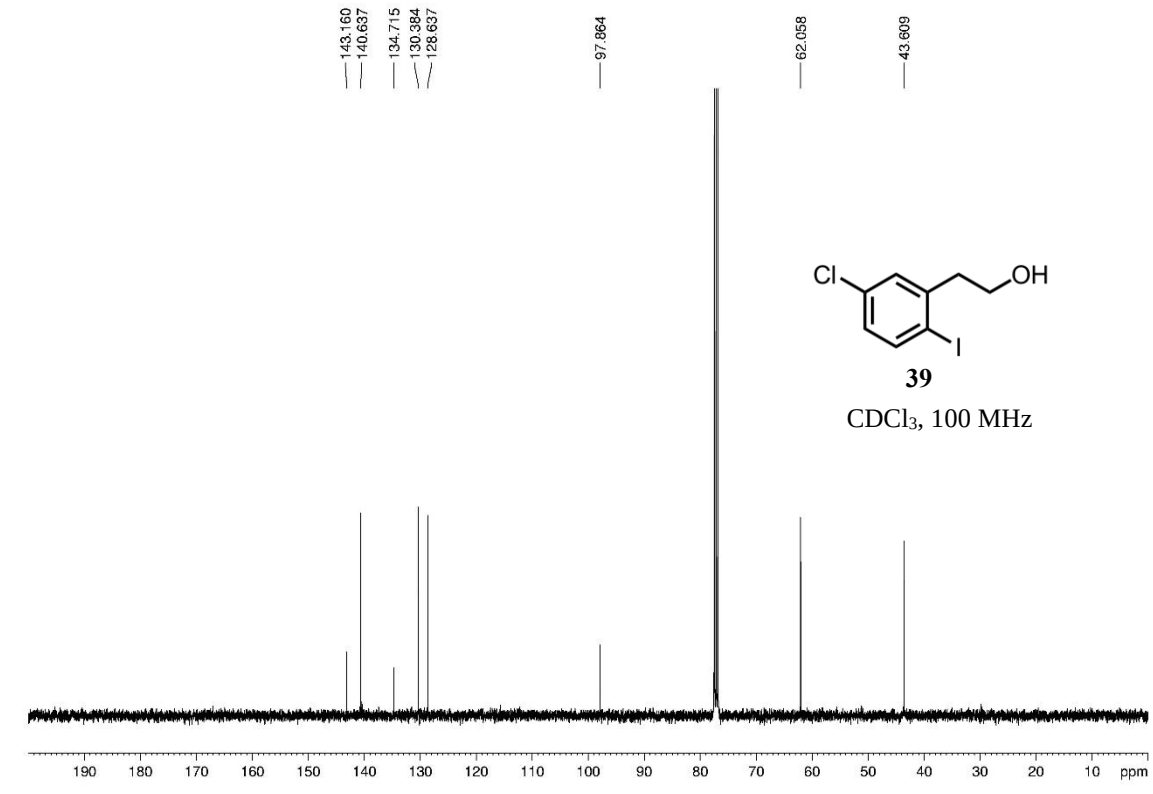
38

$CDCl_3$, 100 MHz



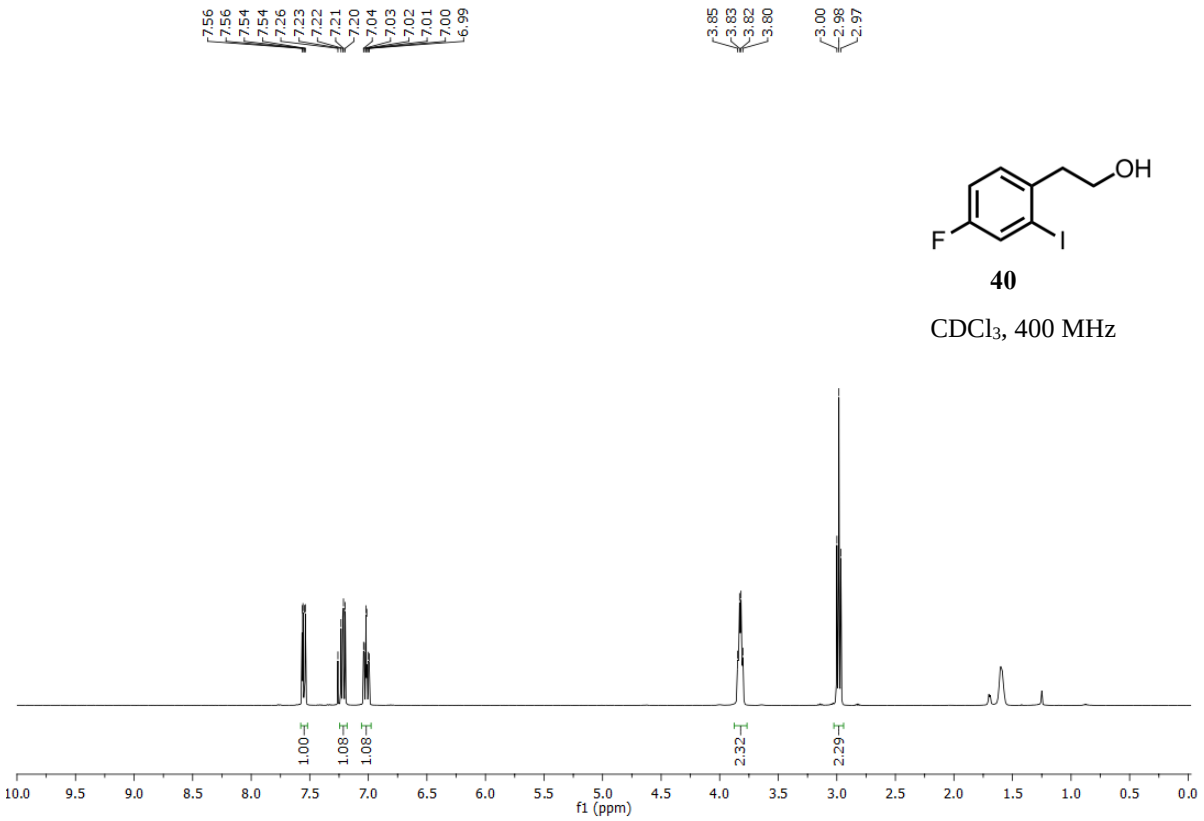
39

$CDCl_3$, 400 MHz



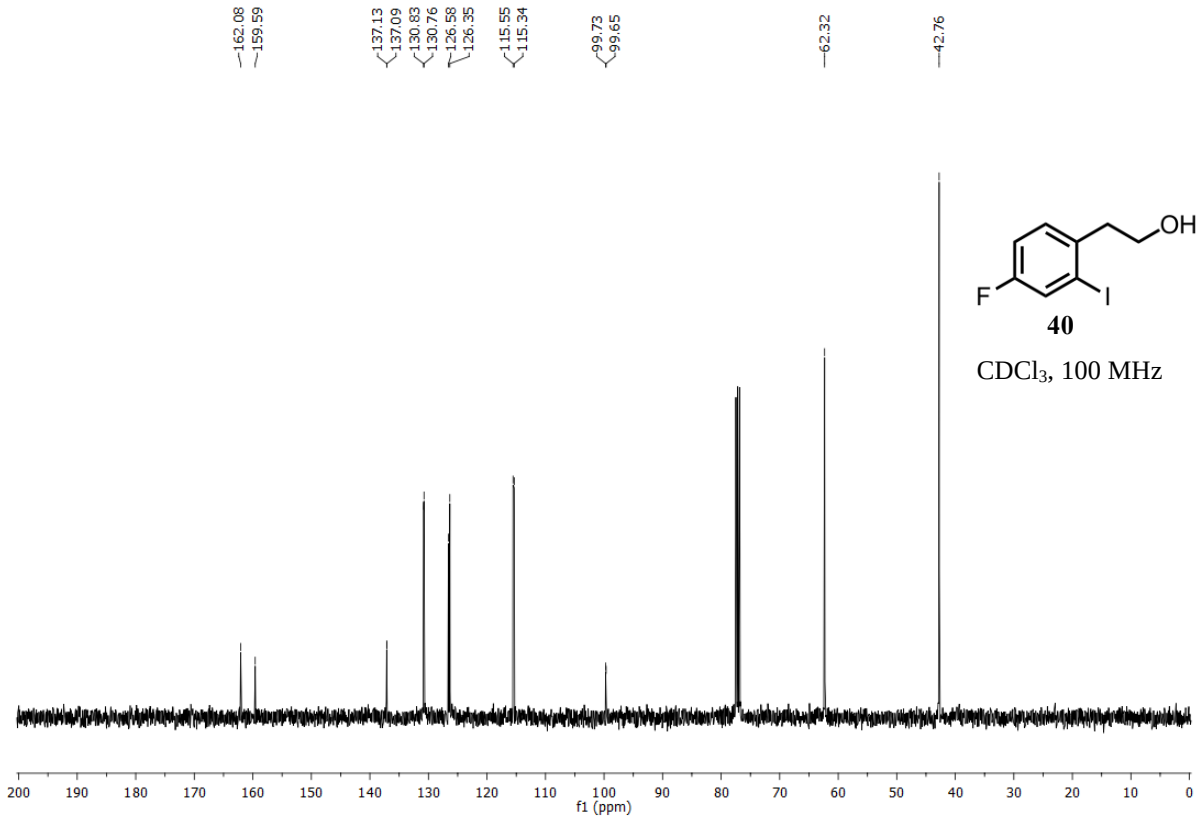
39

$CDCl_3$, 100 MHz



40

$CDCl_3$, 400 MHz



40

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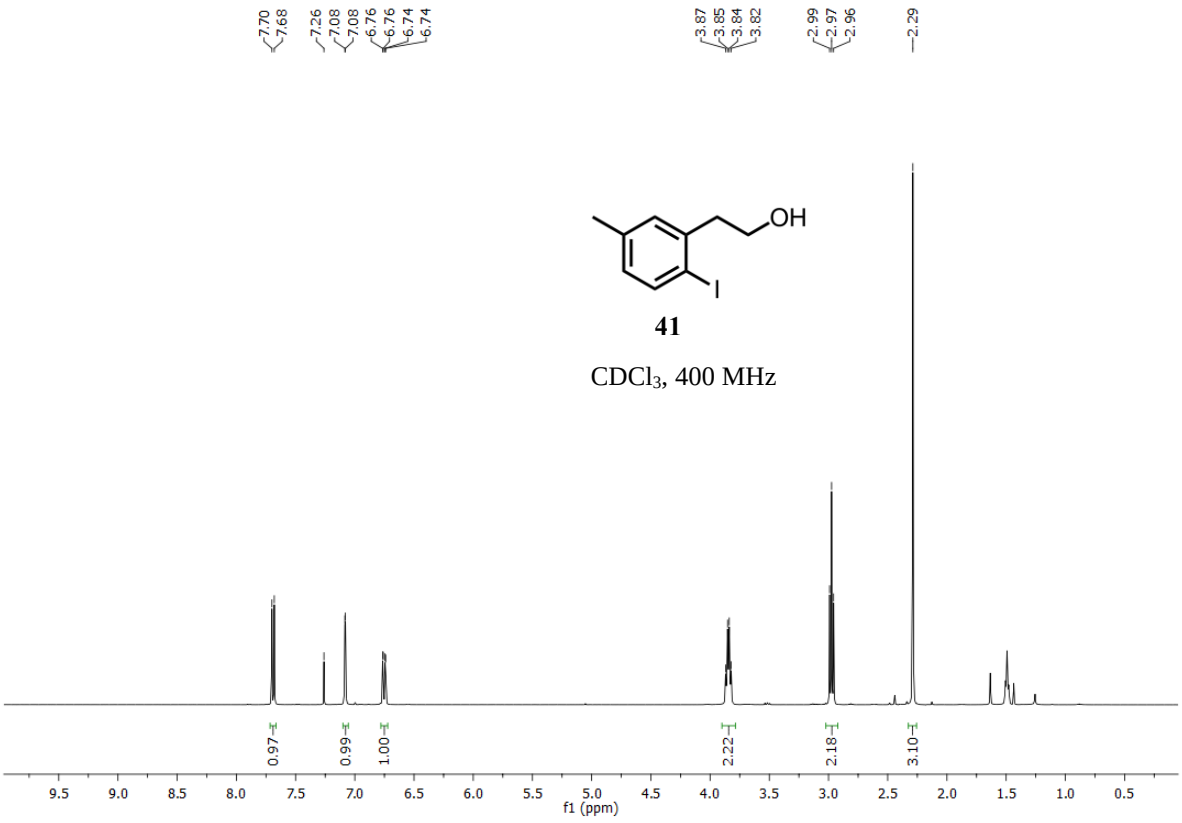
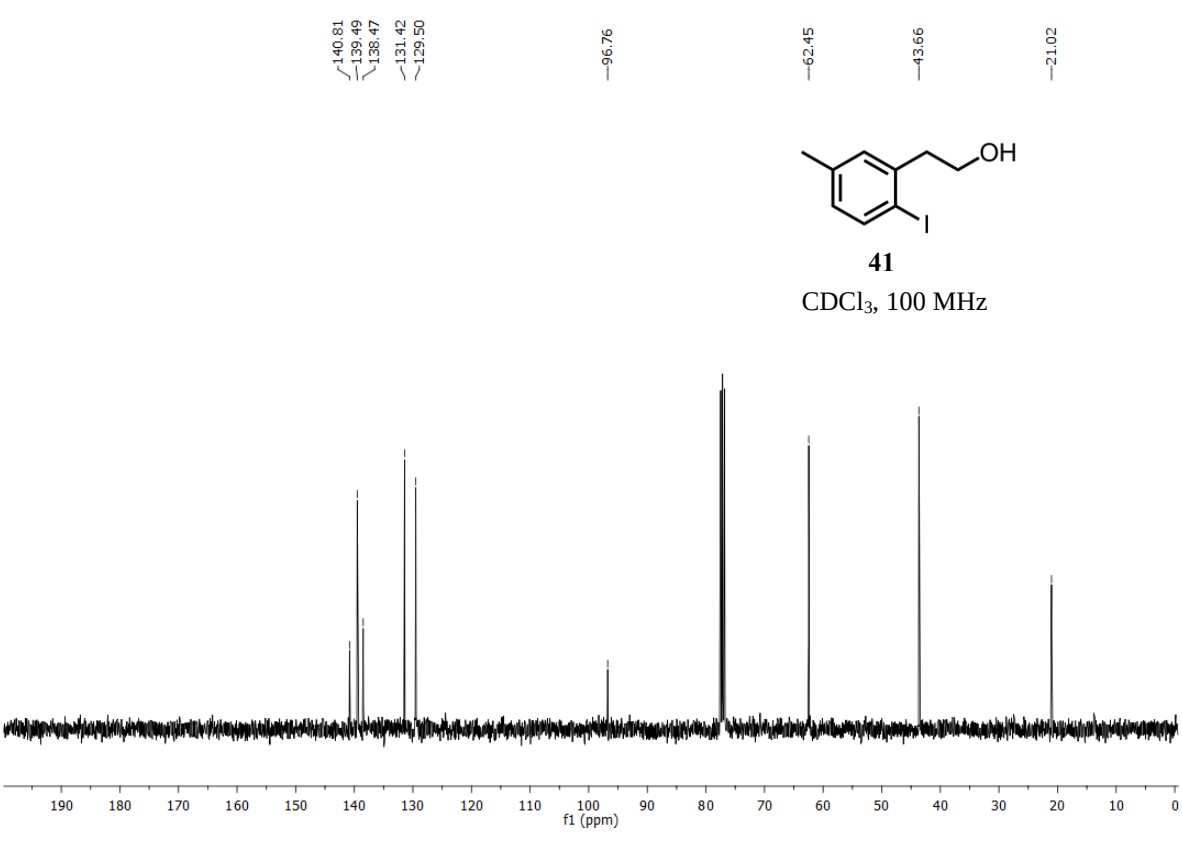


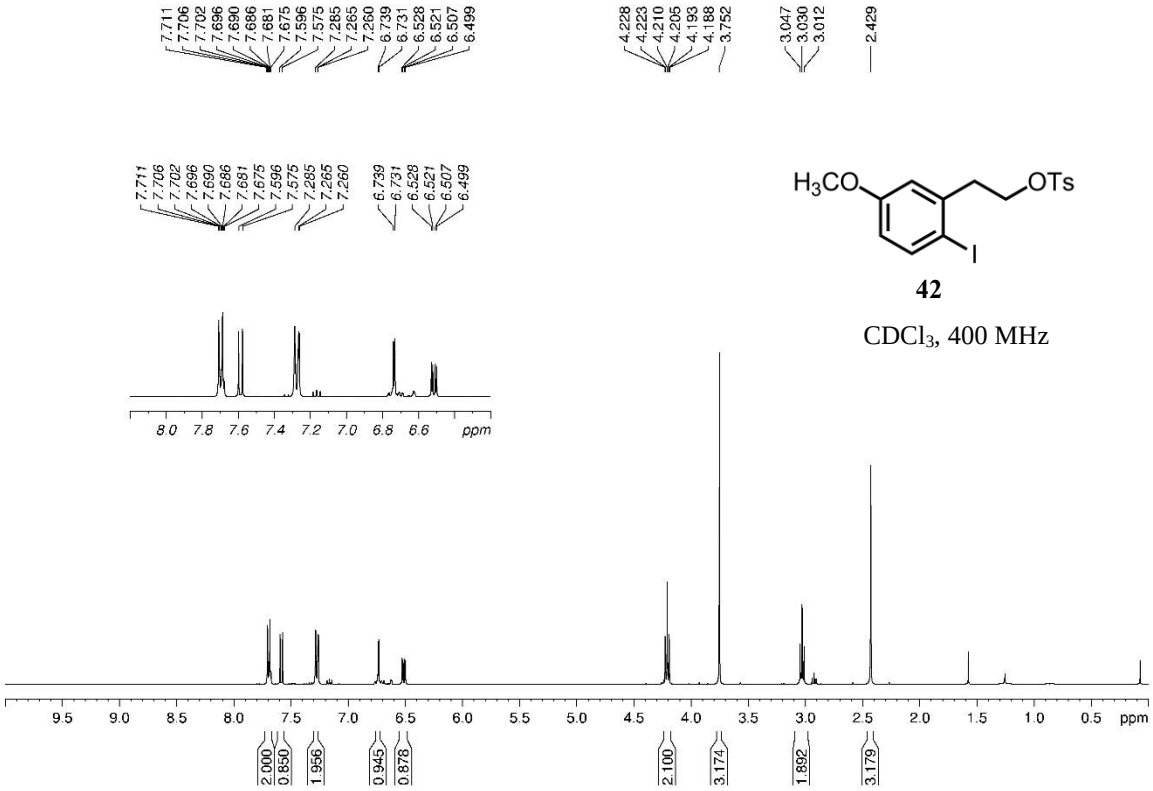
41

$CDCl_3$, 400 MHz



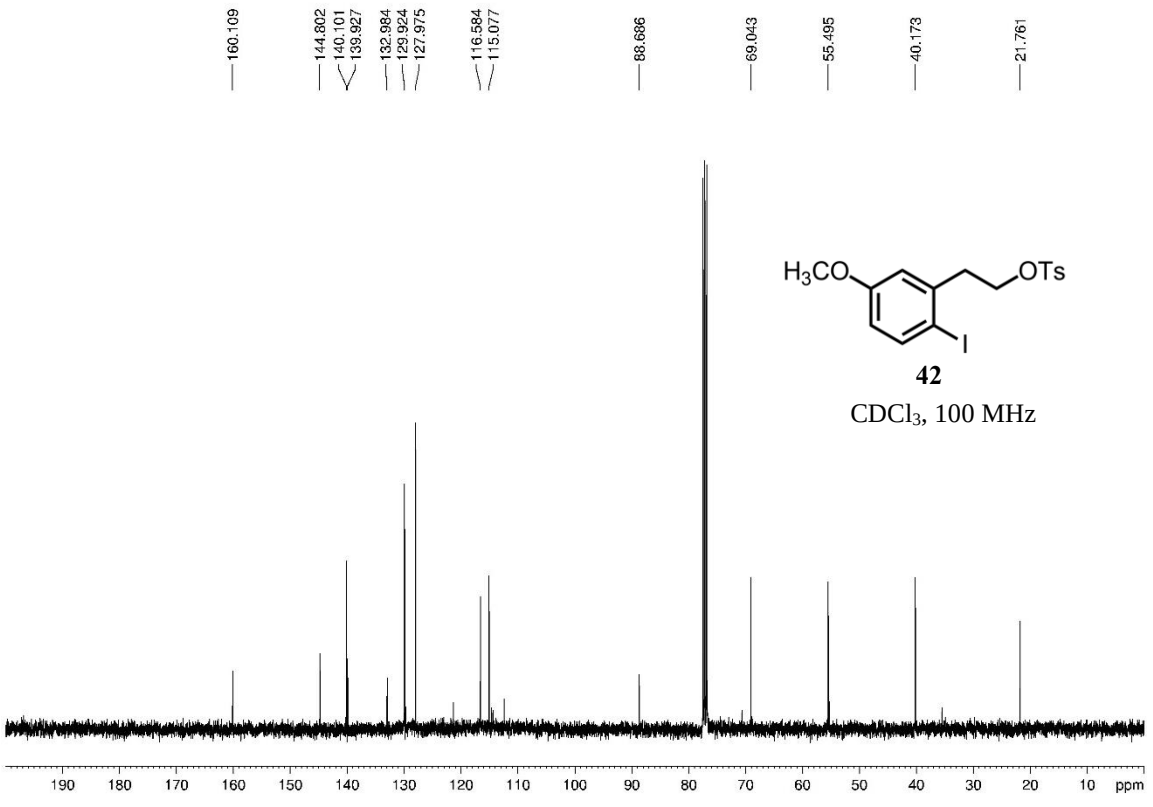
41

$CDCl_3$, 100 MHz



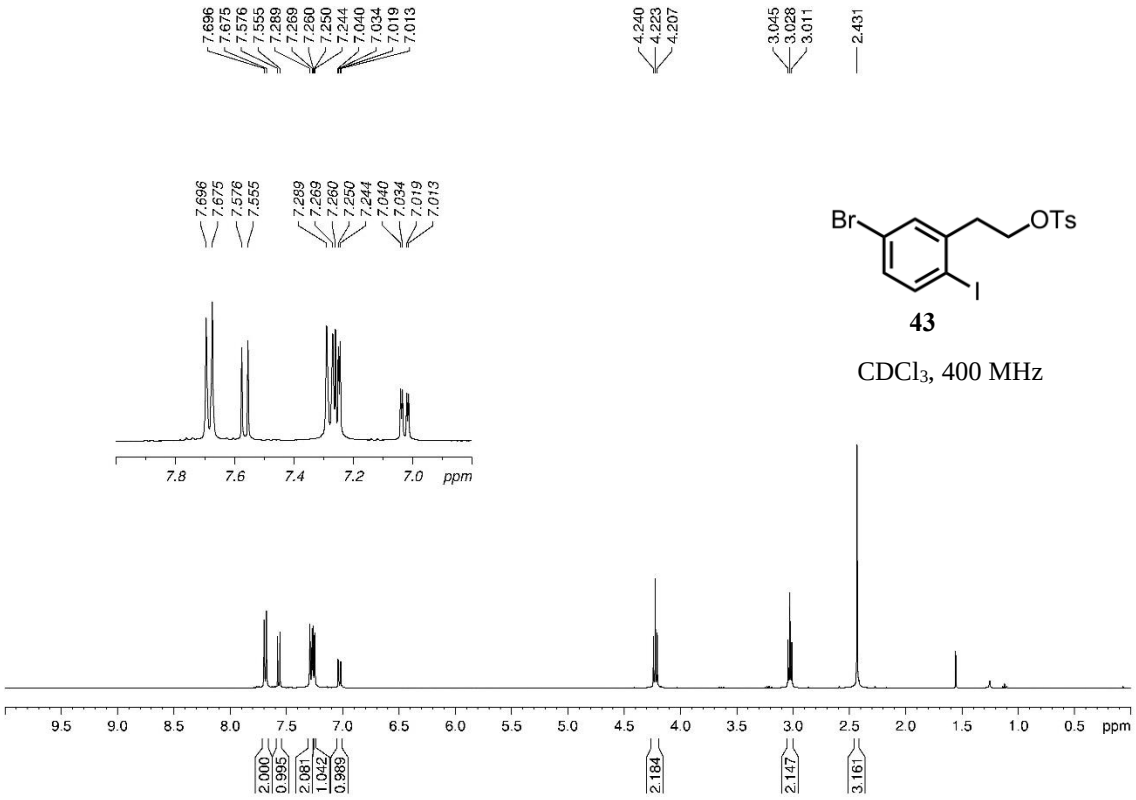
42

$CDCl_3$, 400 MHz



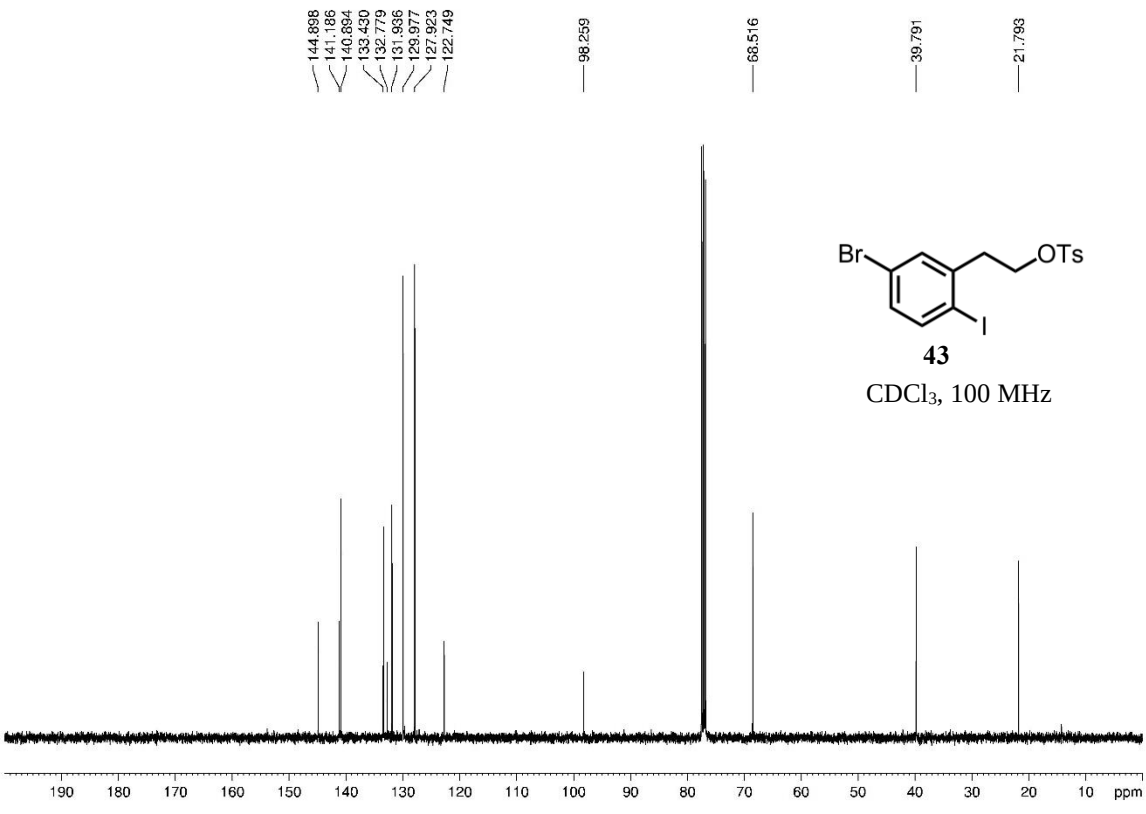
42

$CDCl_3$, 100 MHz



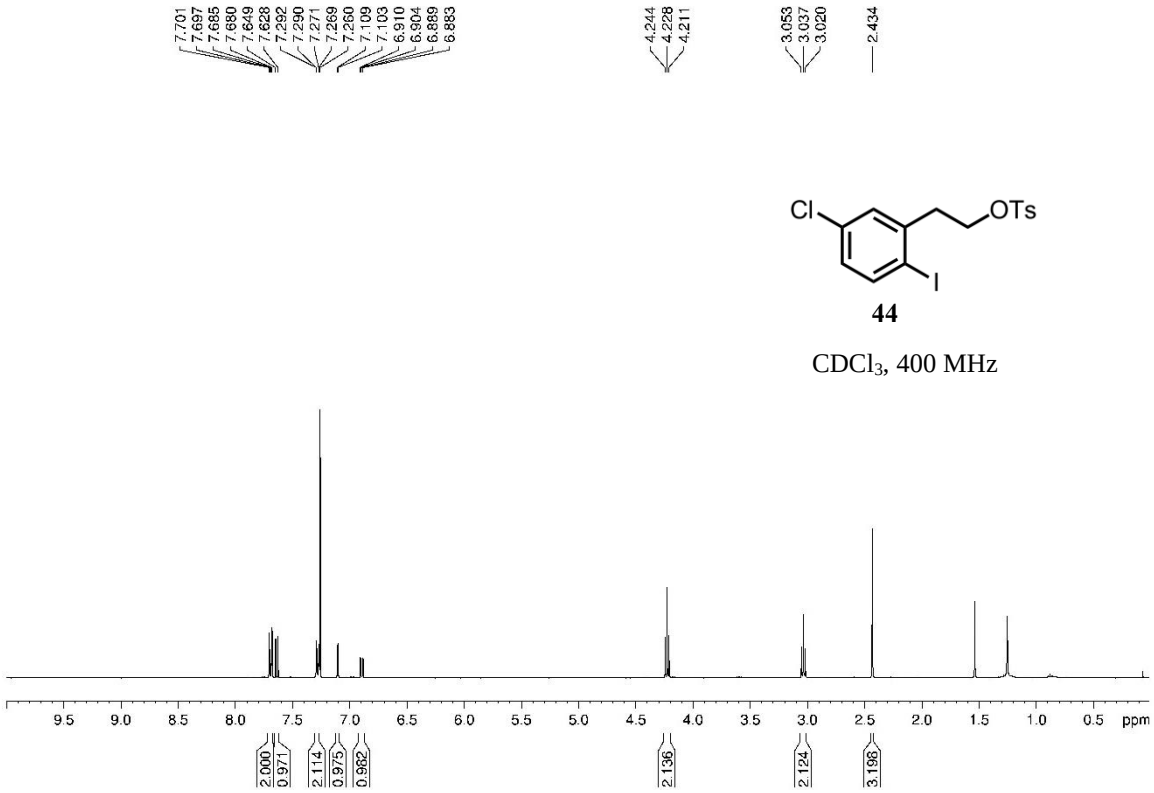
43

$CDCl_3$, 400 MHz



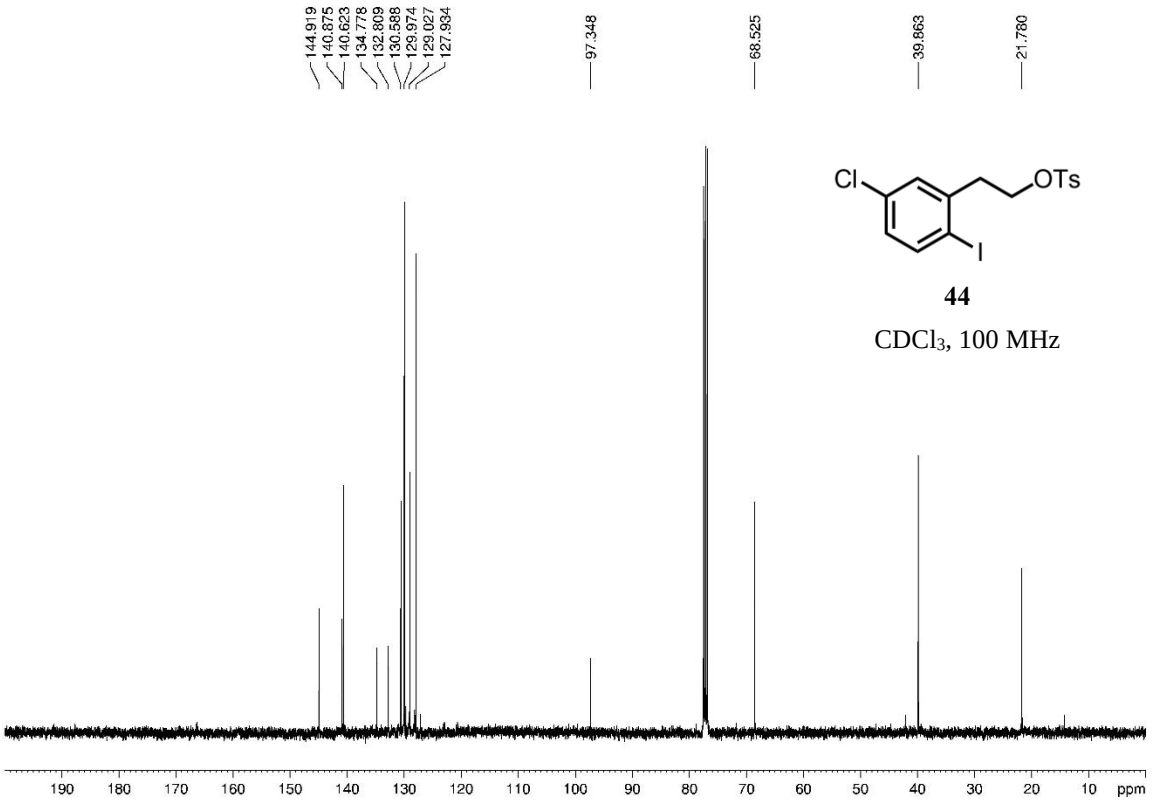
43

$CDCl_3$, 100 MHz



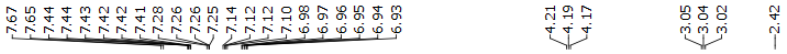
44

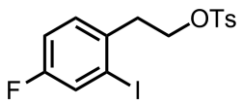
$CDCl_3$, 400 MHz



44

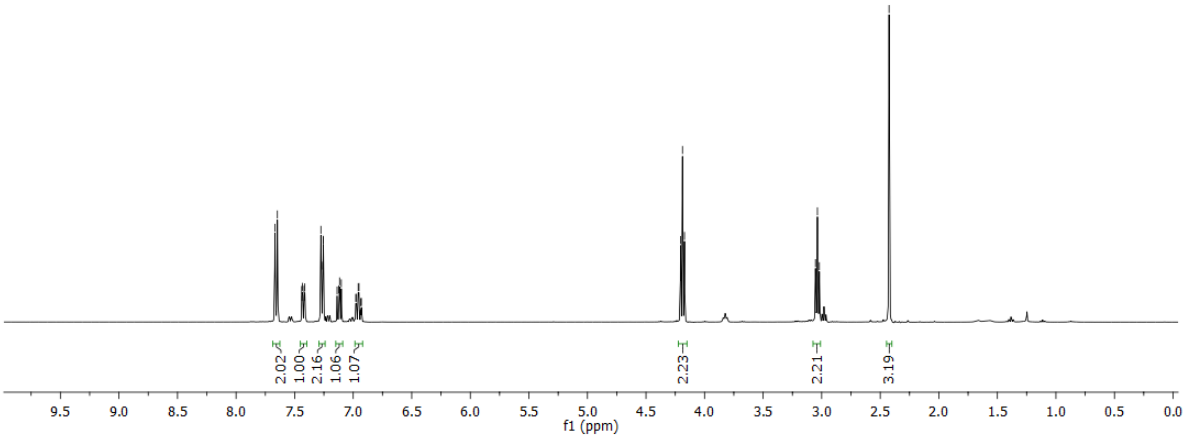
$CDCl_3$, 100 MHz

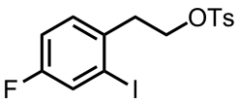




45

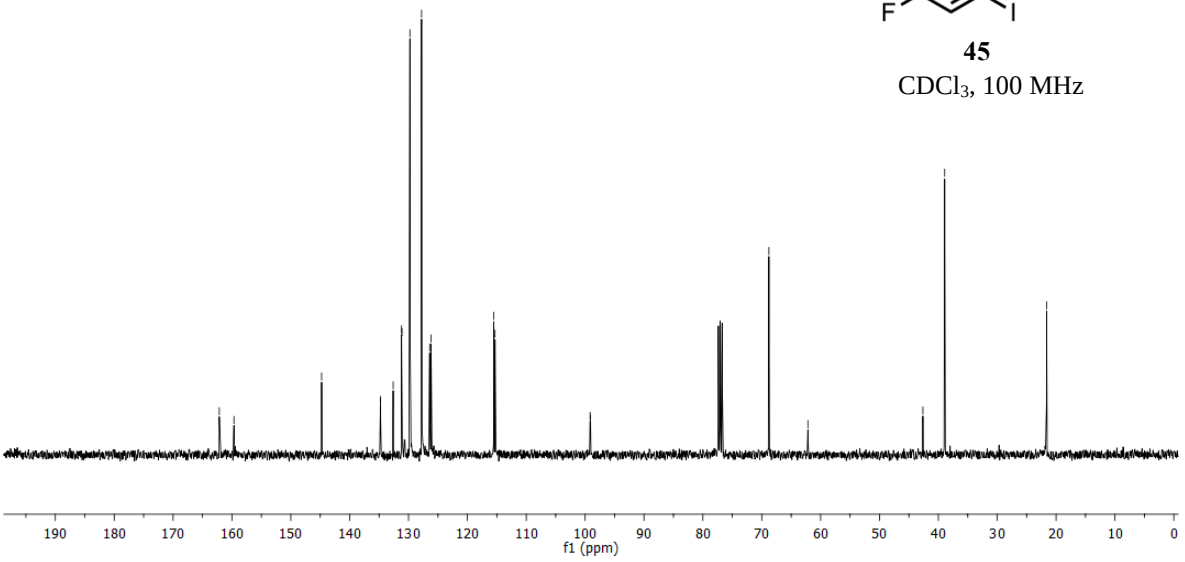
$CDCl_3$, 400 MHz

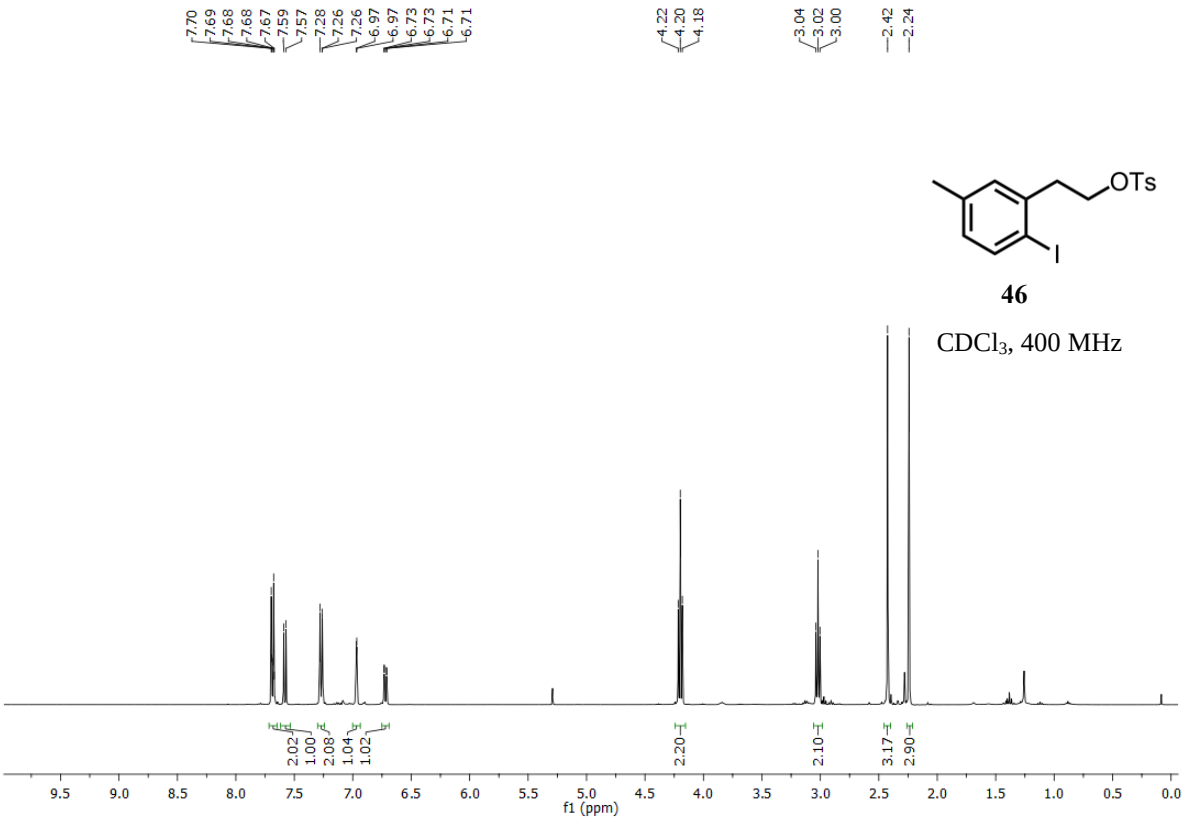




45

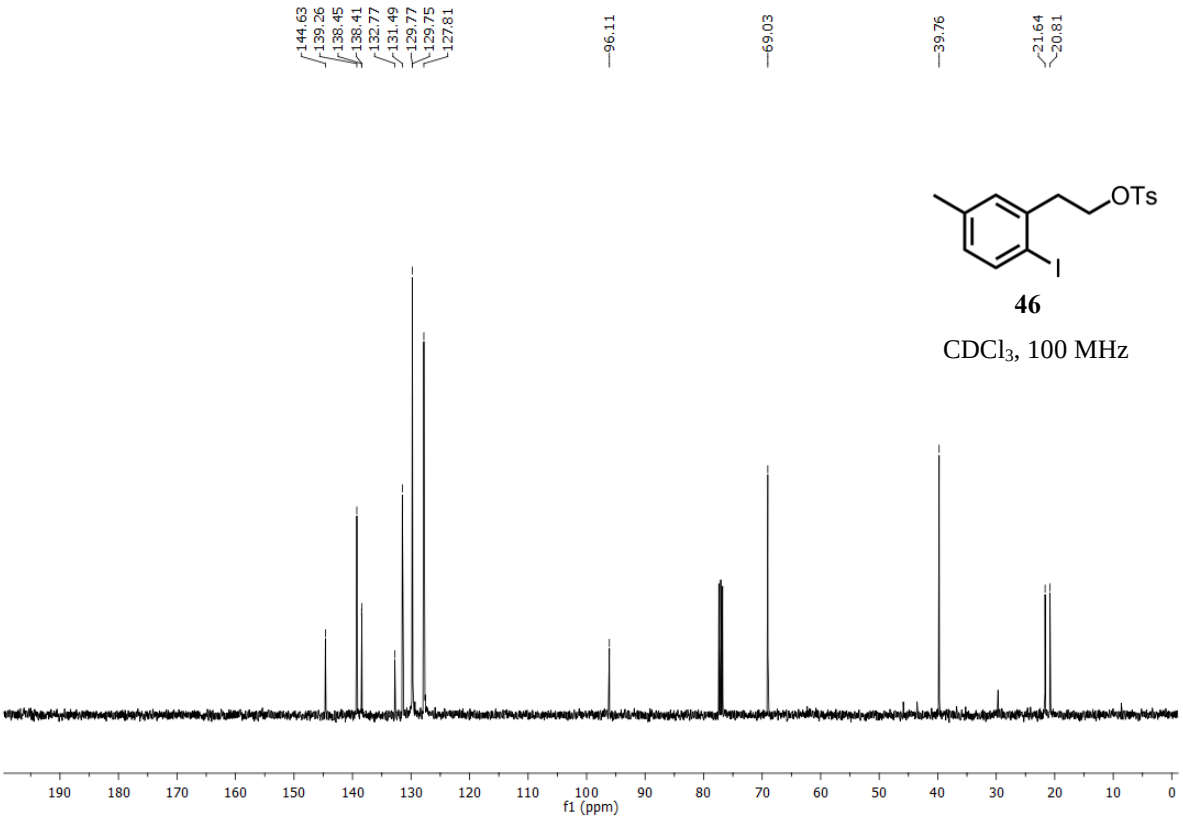
$CDCl_3$, 100 MHz





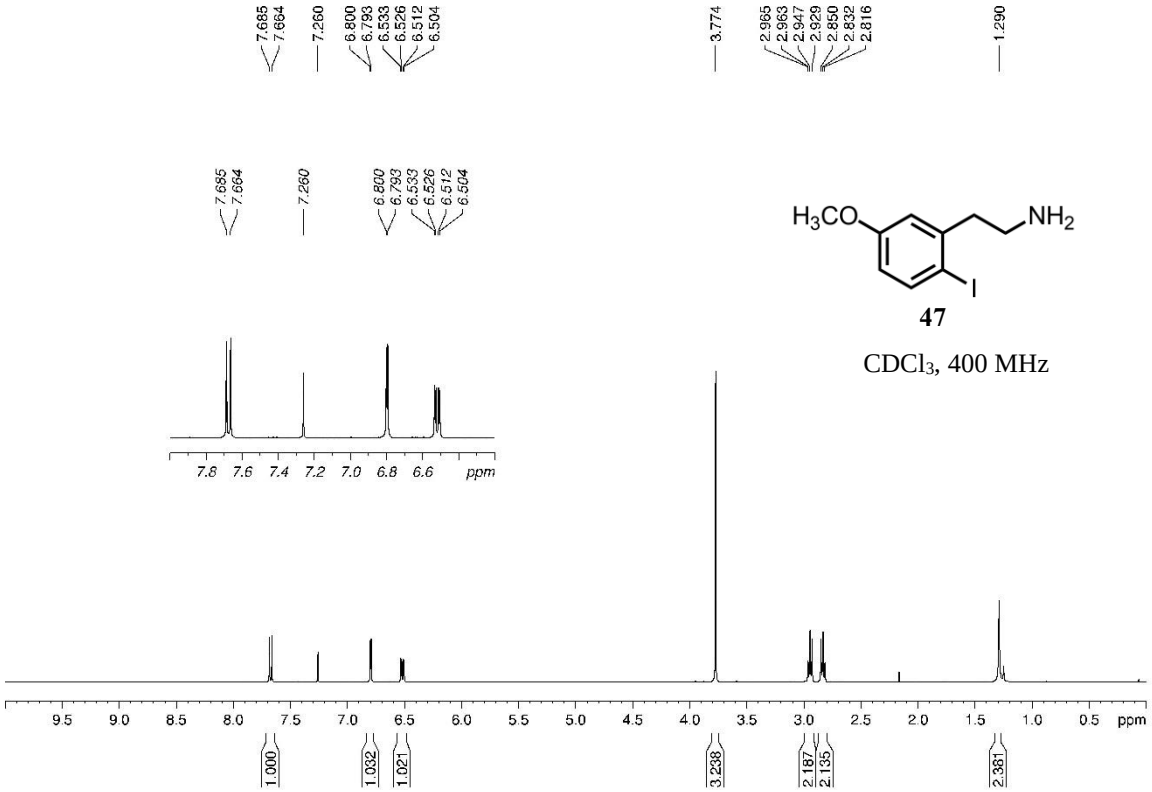
46

$CDCl_3$, 400 MHz



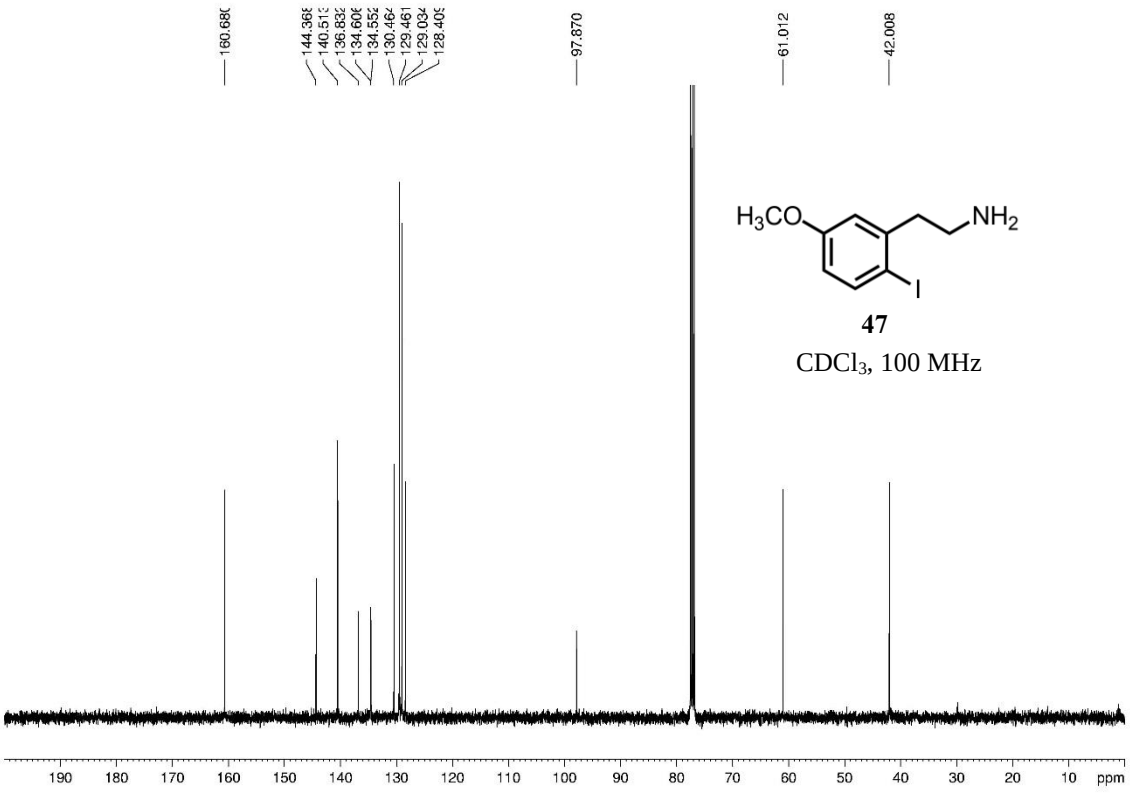
46

$CDCl_3$, 100 MHz



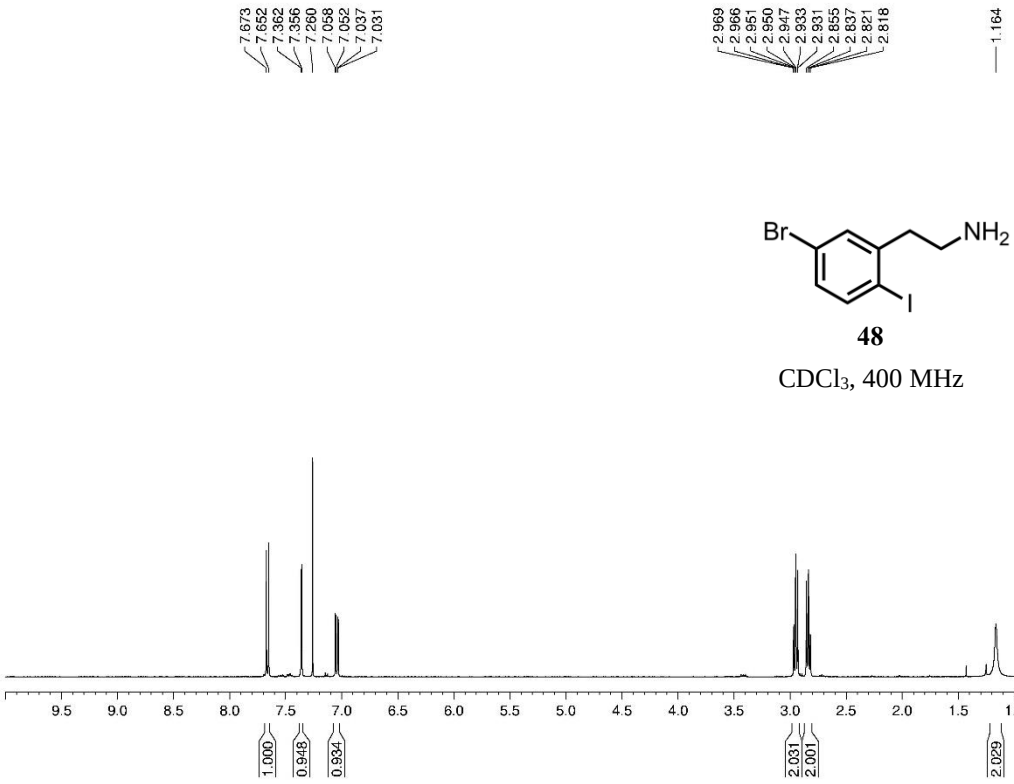
47

$CDCl_3$, 400 MHz



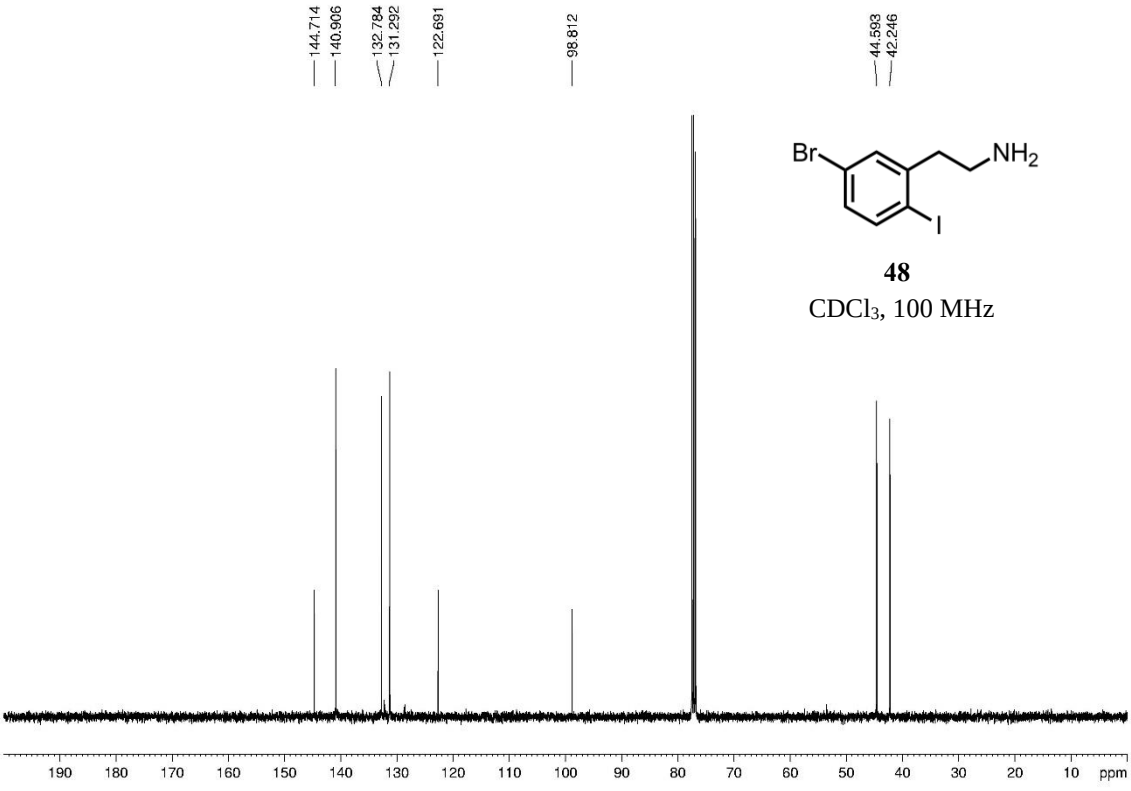
47

$CDCl_3$, 100 MHz



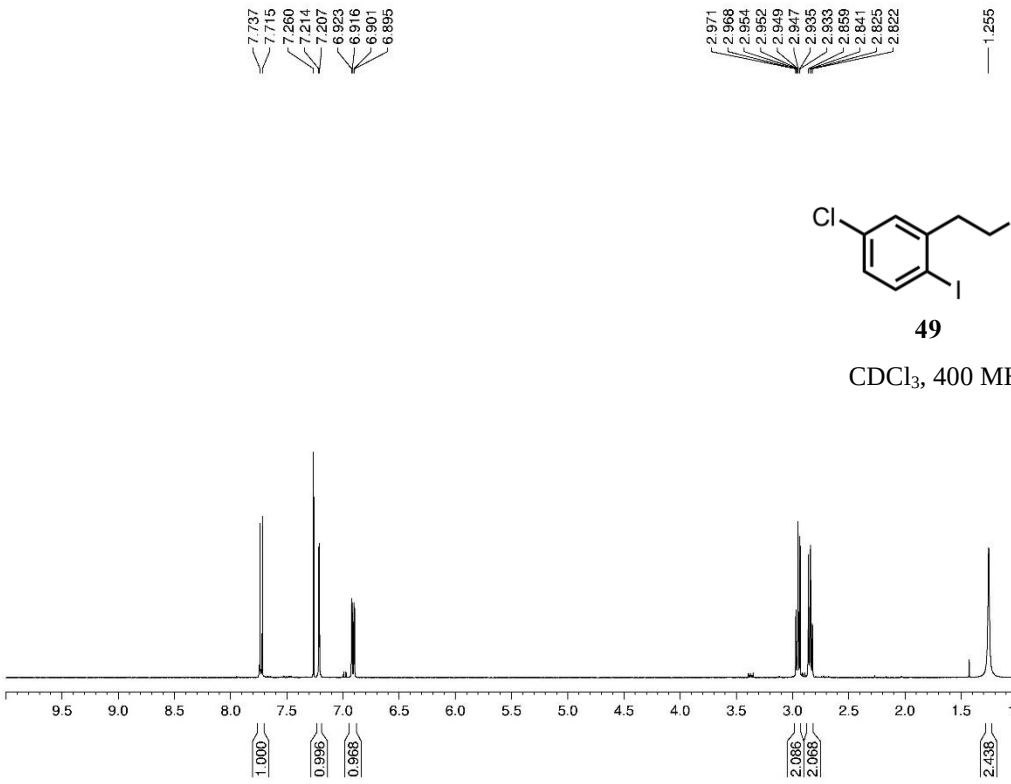
48

$CDCl_3$, 400 MHz



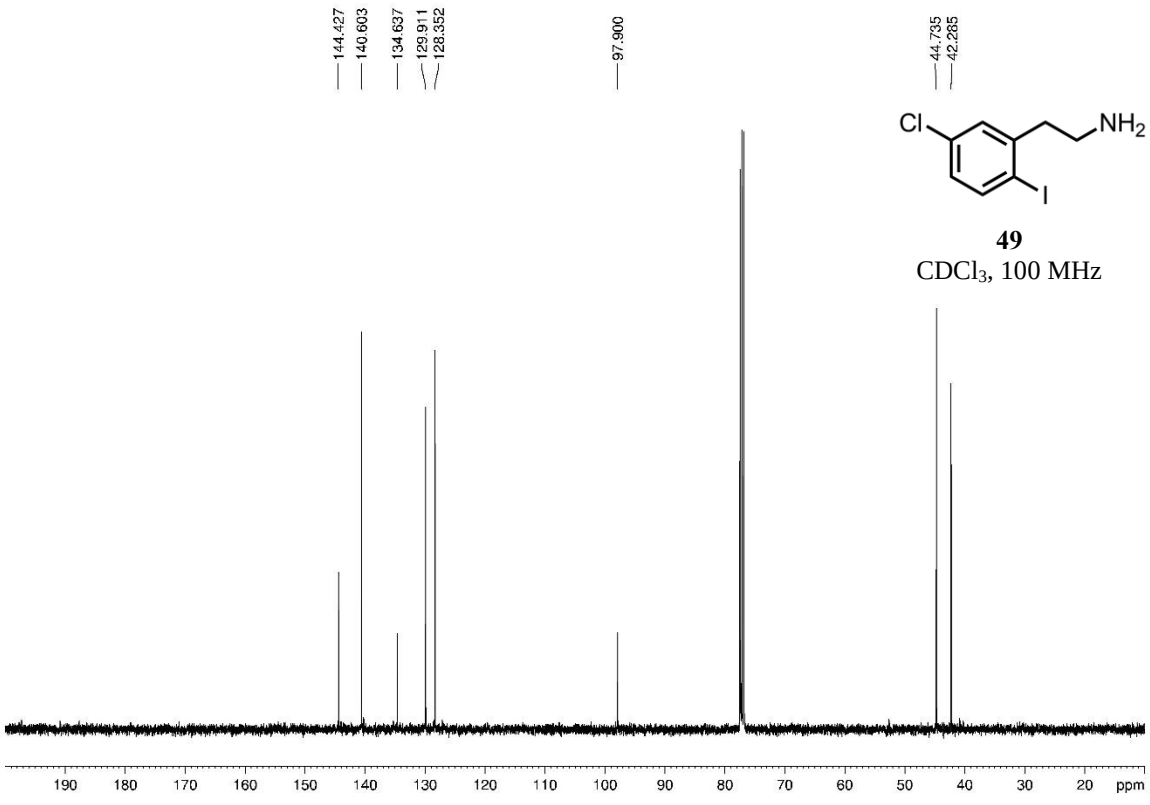
48

$CDCl_3$, 100 MHz



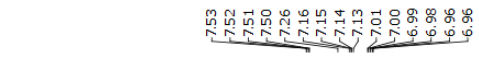
49

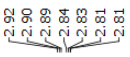
$CDCl_3$, 400 MHz

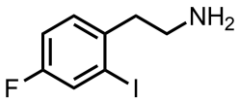


49

$CDCl_3$, 100 MHz

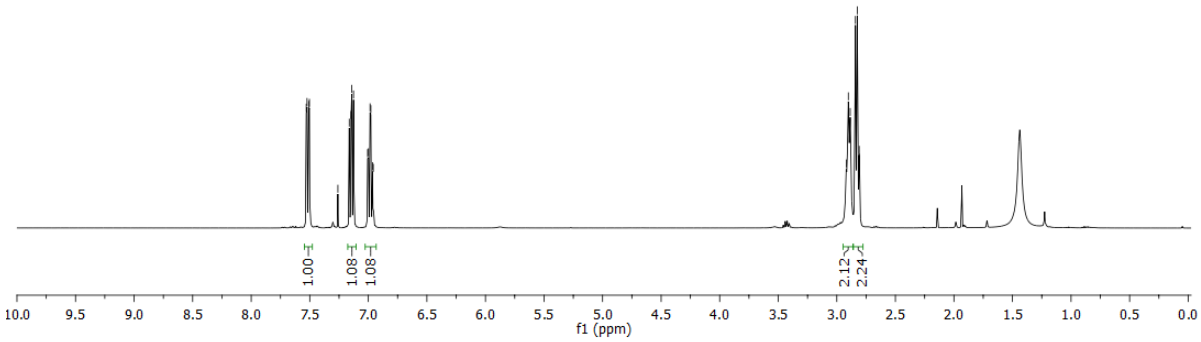


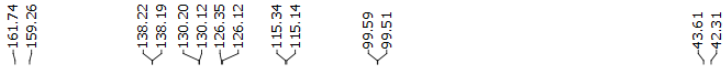


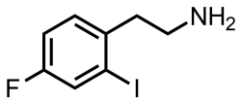


50

$CDCl_3$, 400 MHz

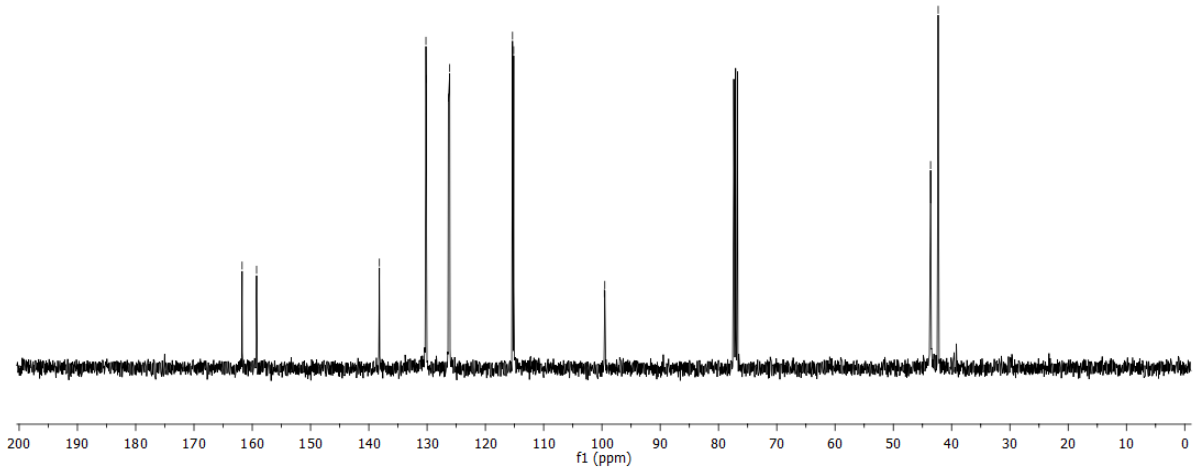


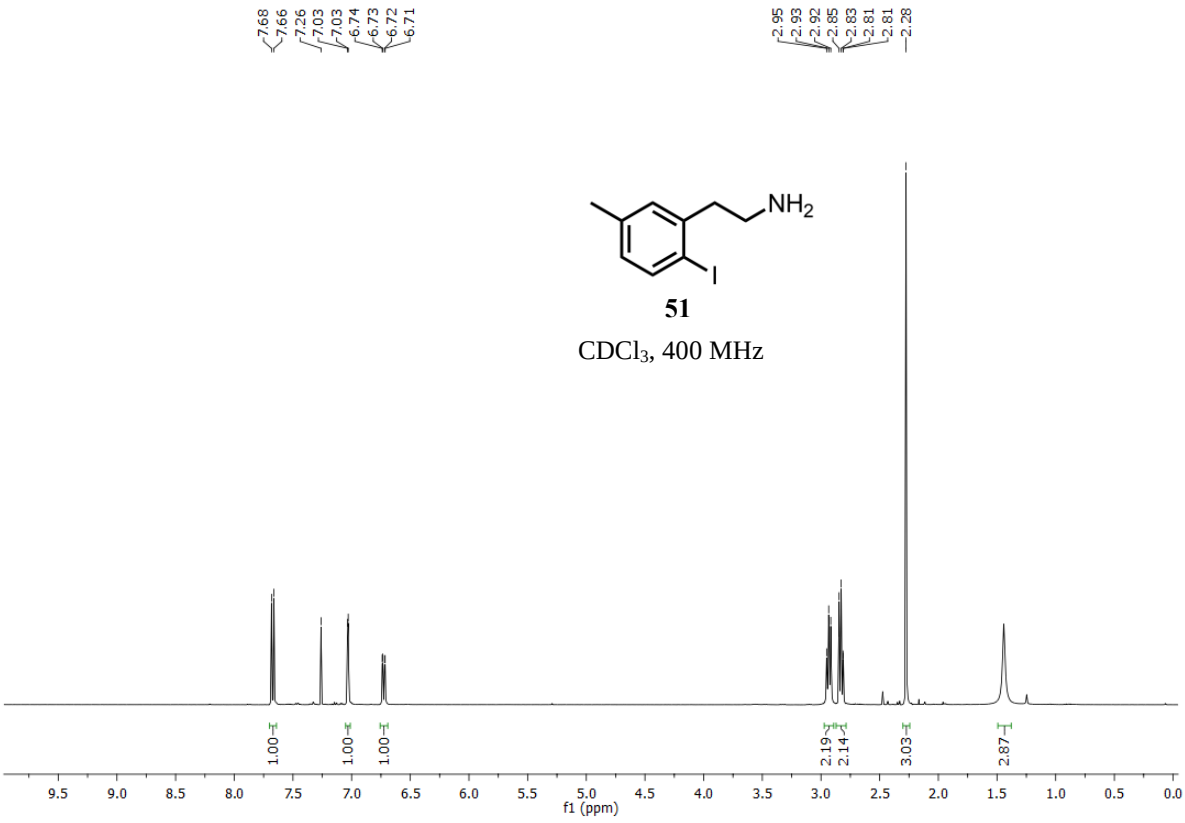




50

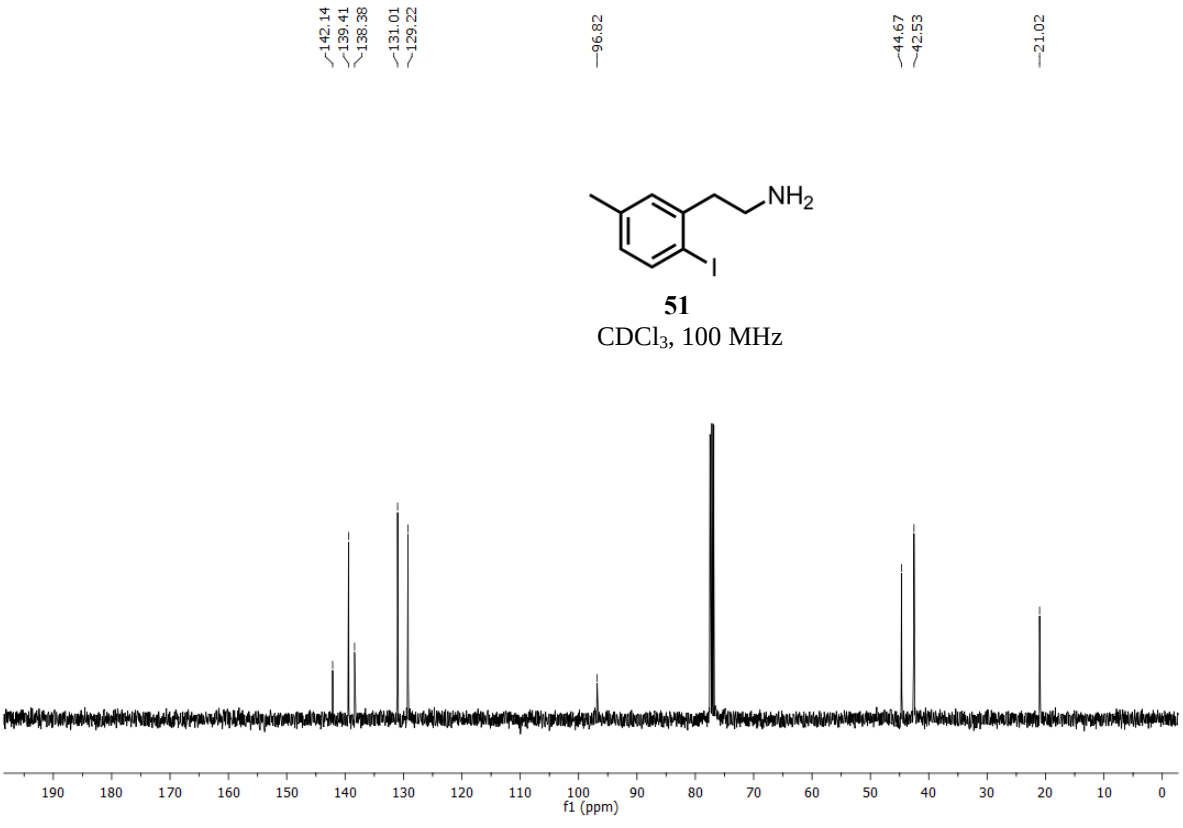
$CDCl_3$, 100 MHz





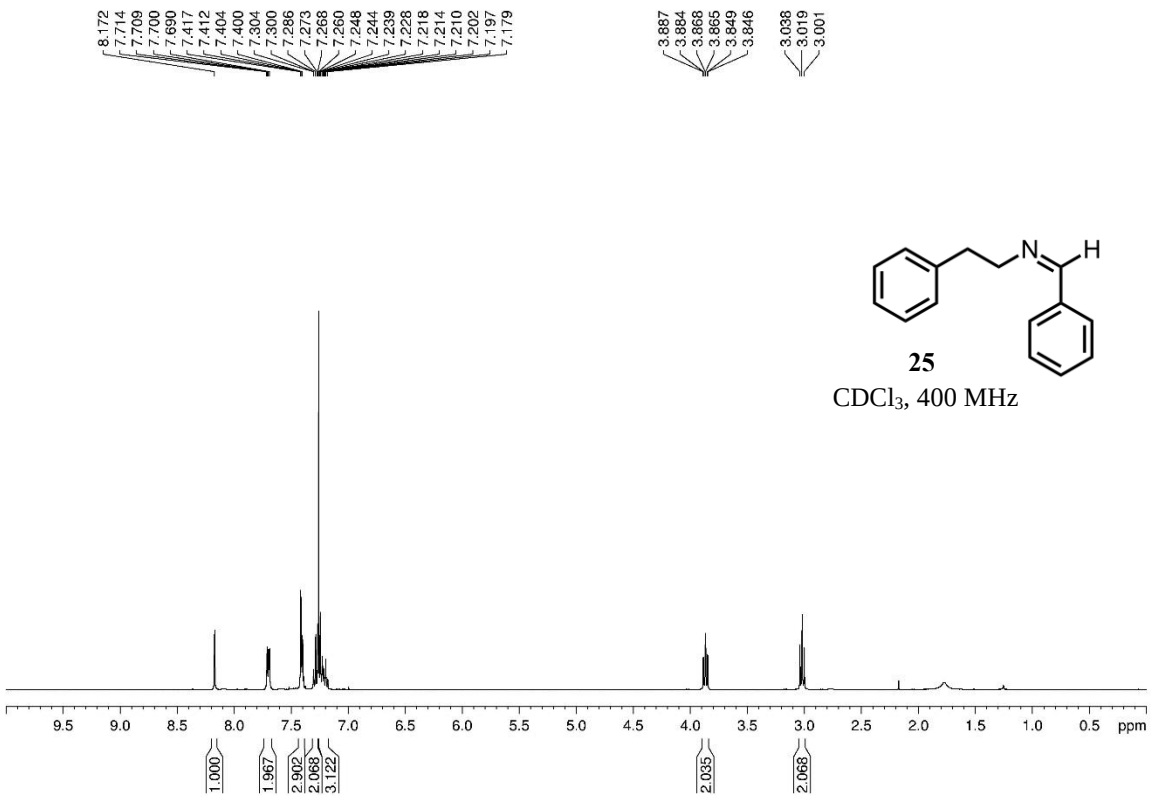
51

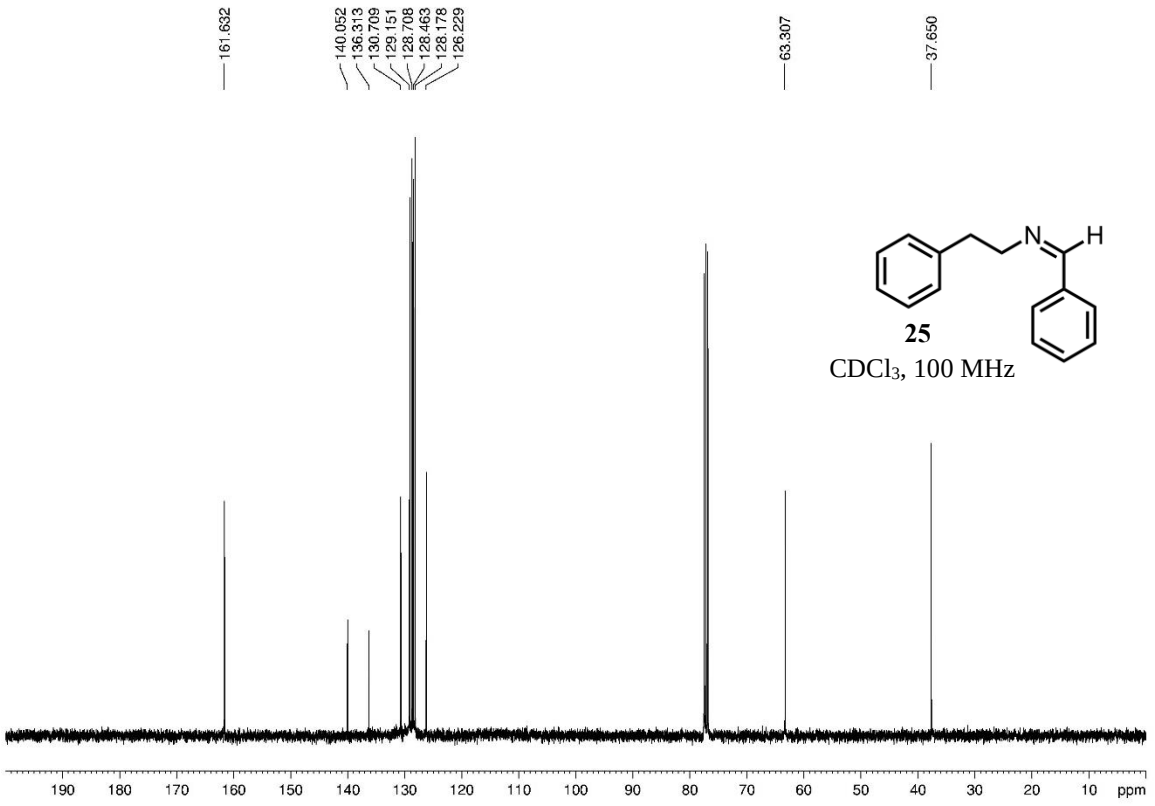
$CDCl_3$, 400 MHz

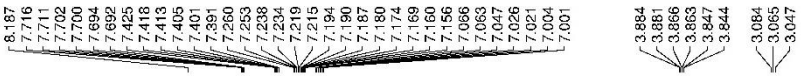


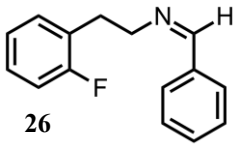
51

$CDCl_3$, 100 MHz


8.172
7.714
7.709
7.700
7.690
7.417
7.412
7.404
7.400
7.304
7.300
7.286
7.273
7.268
7.260
7.248
7.244
7.239
7.228
7.218
7.214
7.210
7.202
7.197
7.179
3.887
3.884
3.868
3.865
3.849
3.846
3.038
3.019
3.001
N
H
25
CDCl3, 400 MHz
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.000
1.967
2.902
2.068
3.122
2.035
2.068

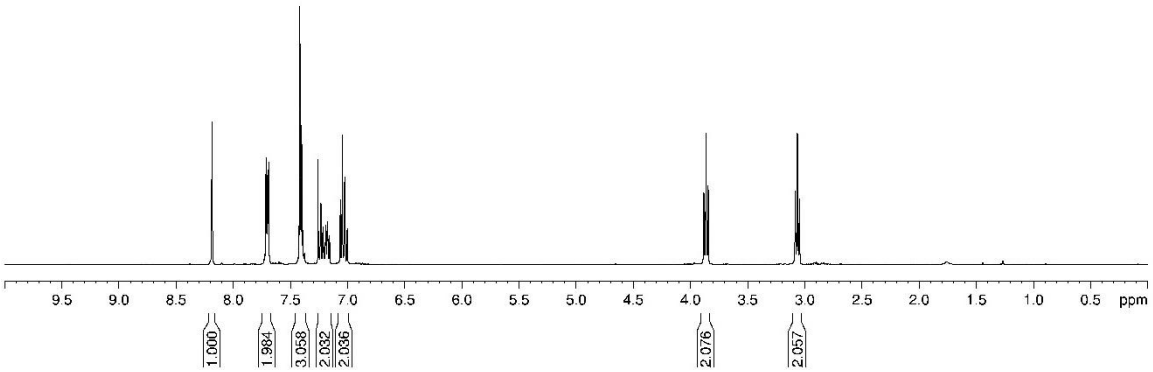

161.632
140.052
136.313
130.709
129.151
128.708
128.463
128.178
126.229
63.307
37.650
N
H
25
CDCl3, 100 MHz
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

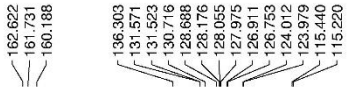


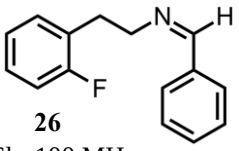


26

$CDCl_3$, 400 MHz

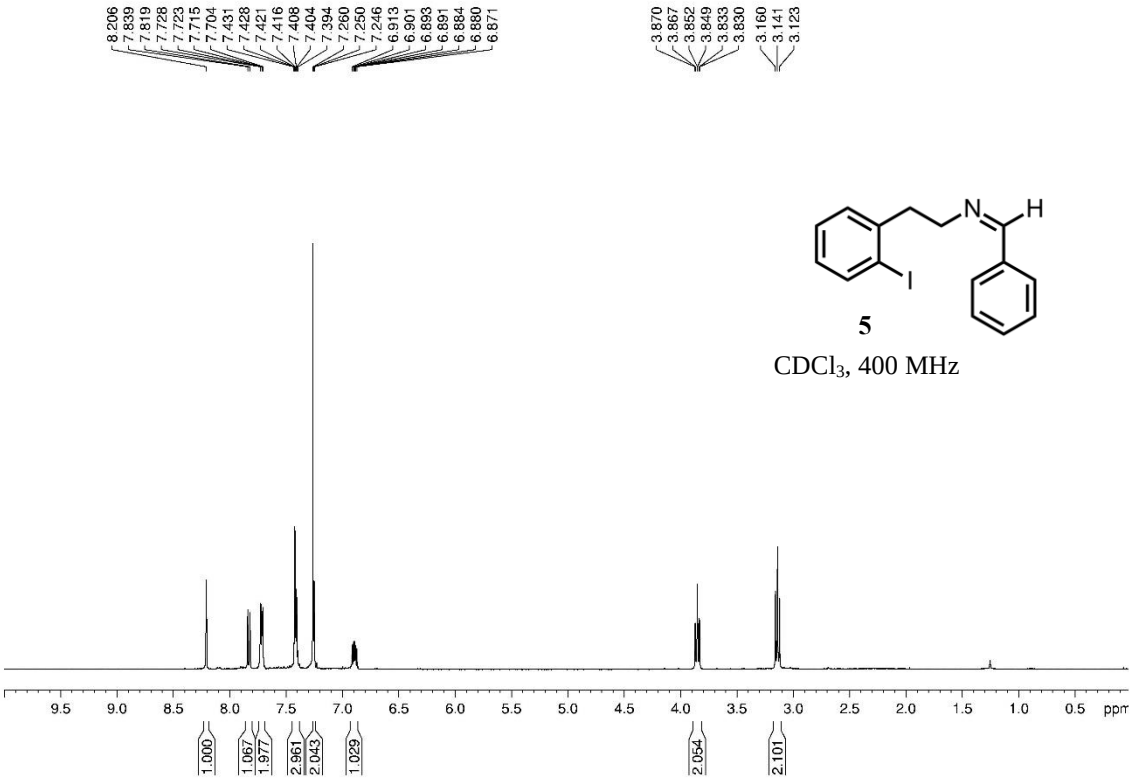


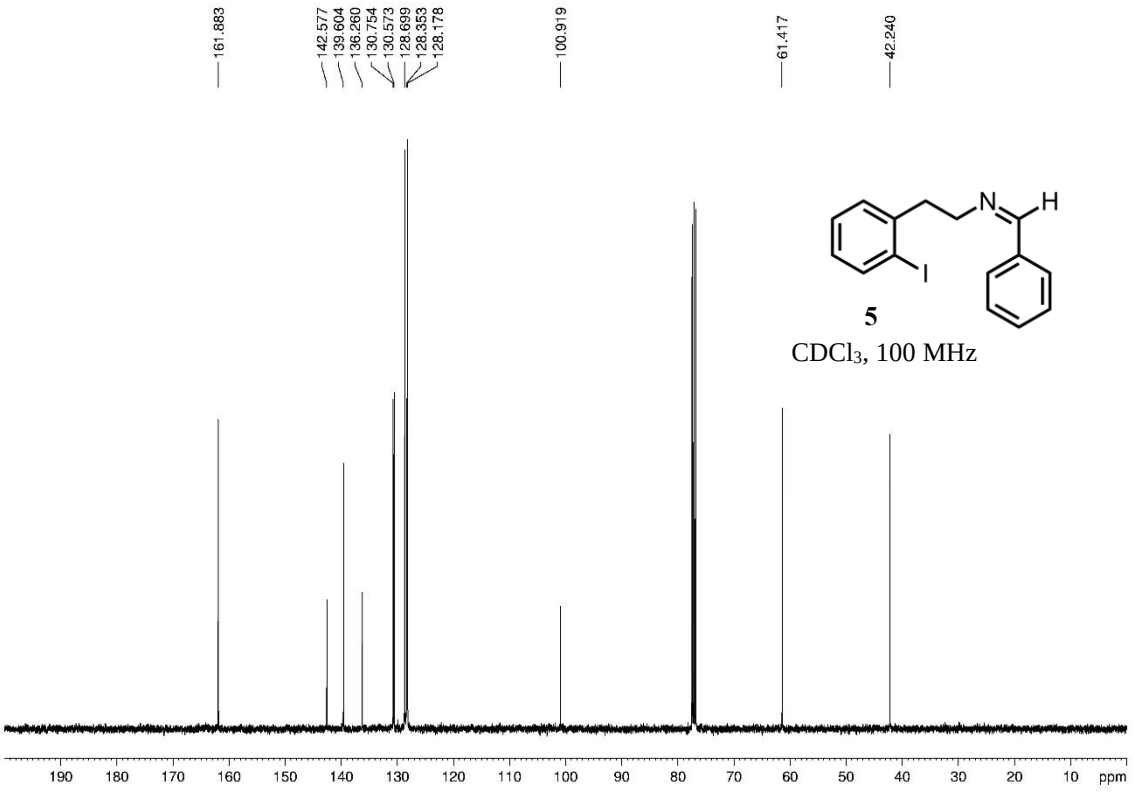


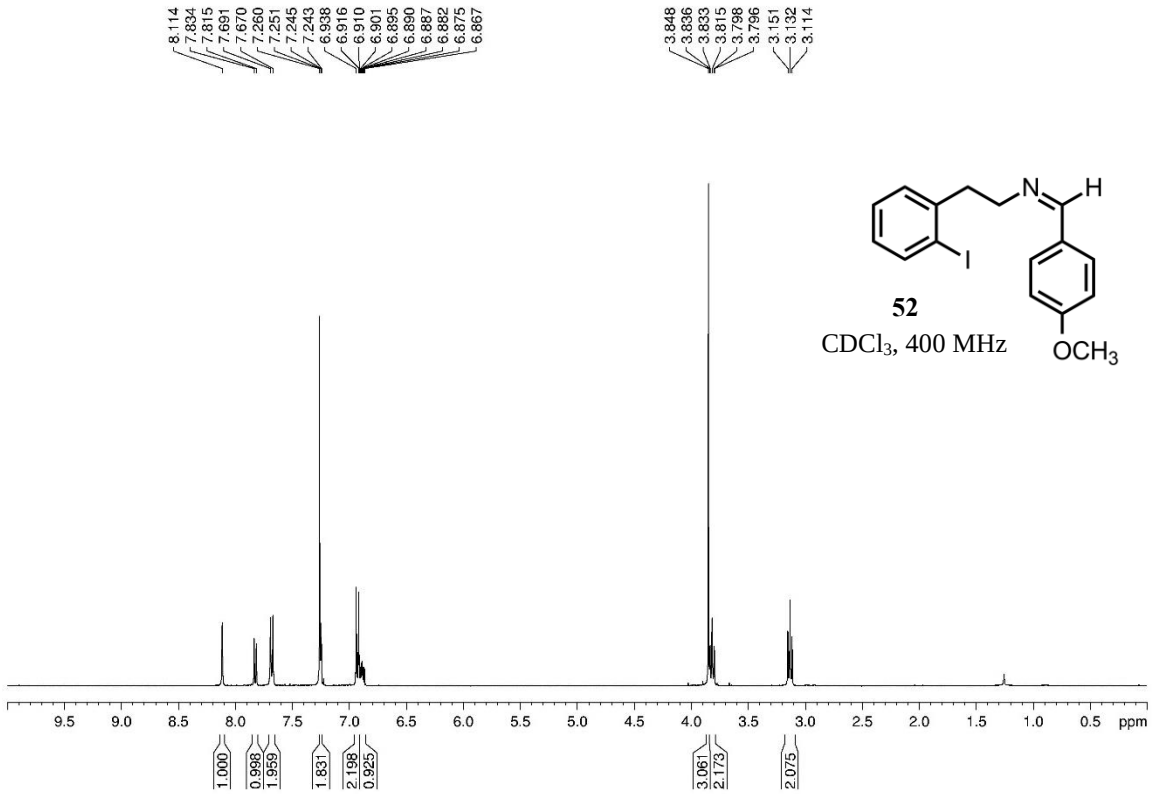


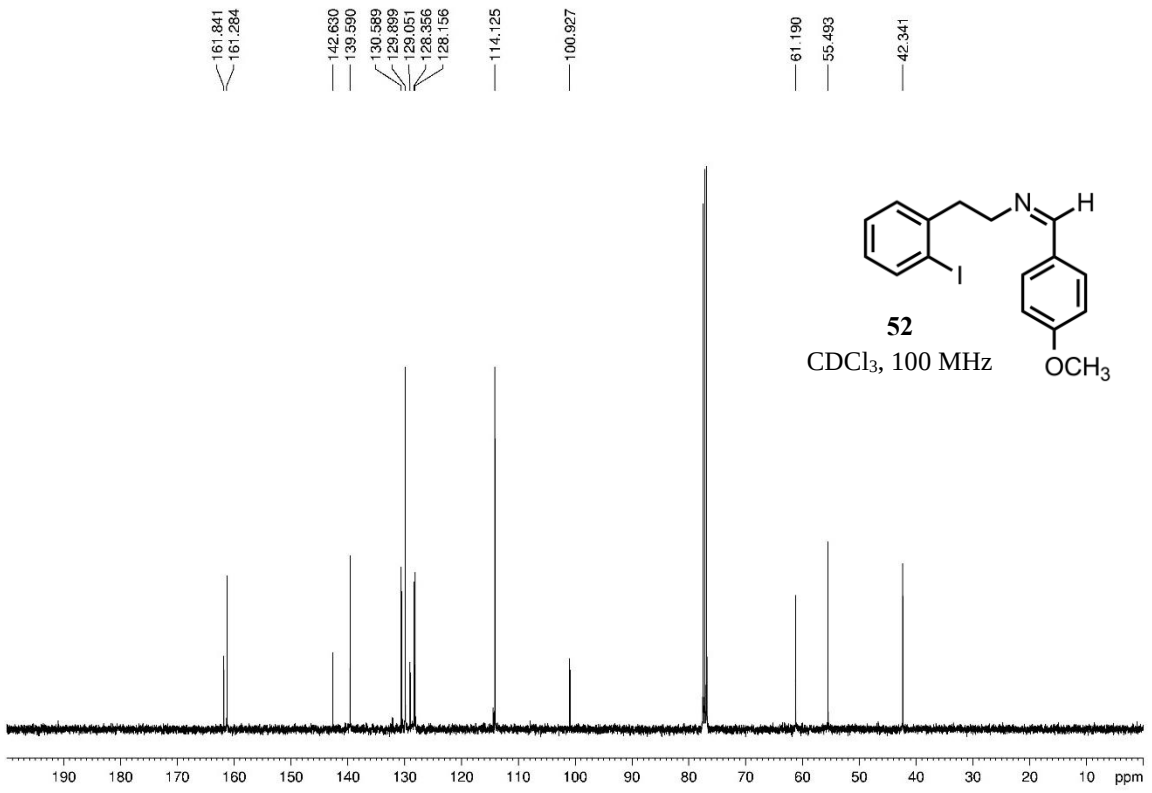
26

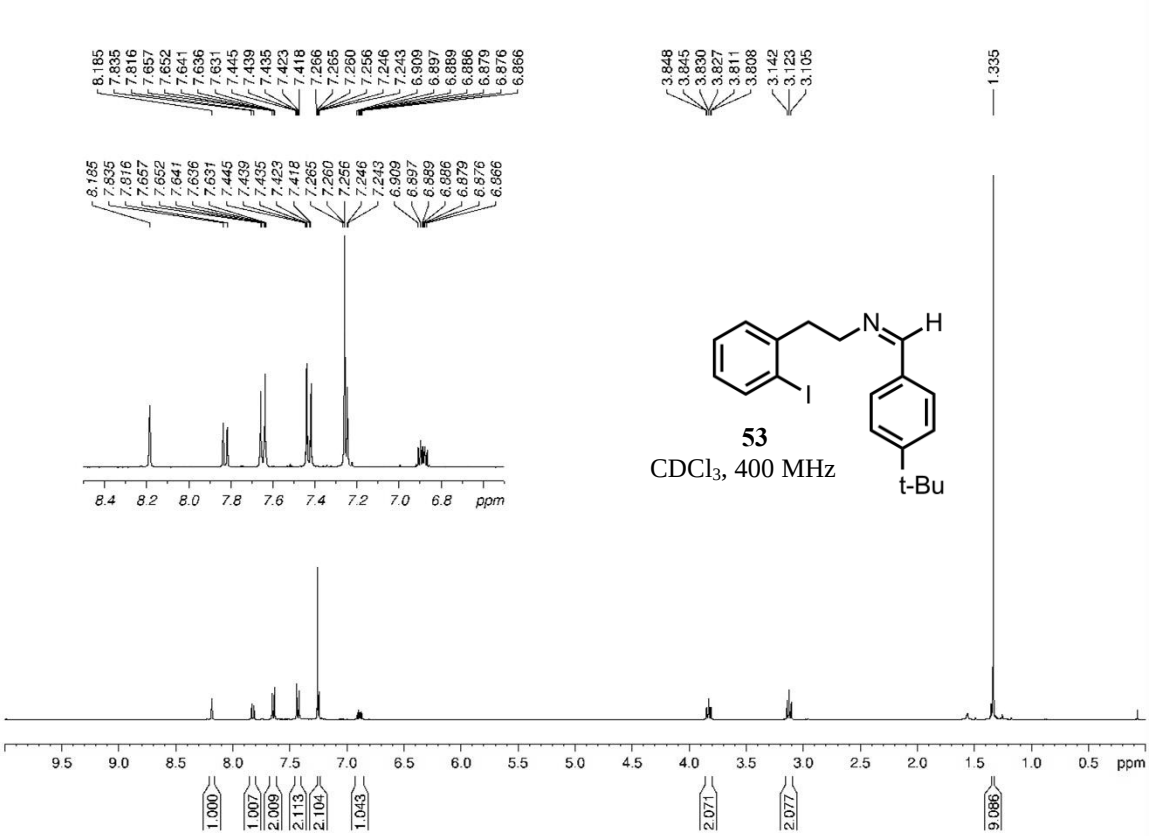
$CDCl_3$, 100 MHz

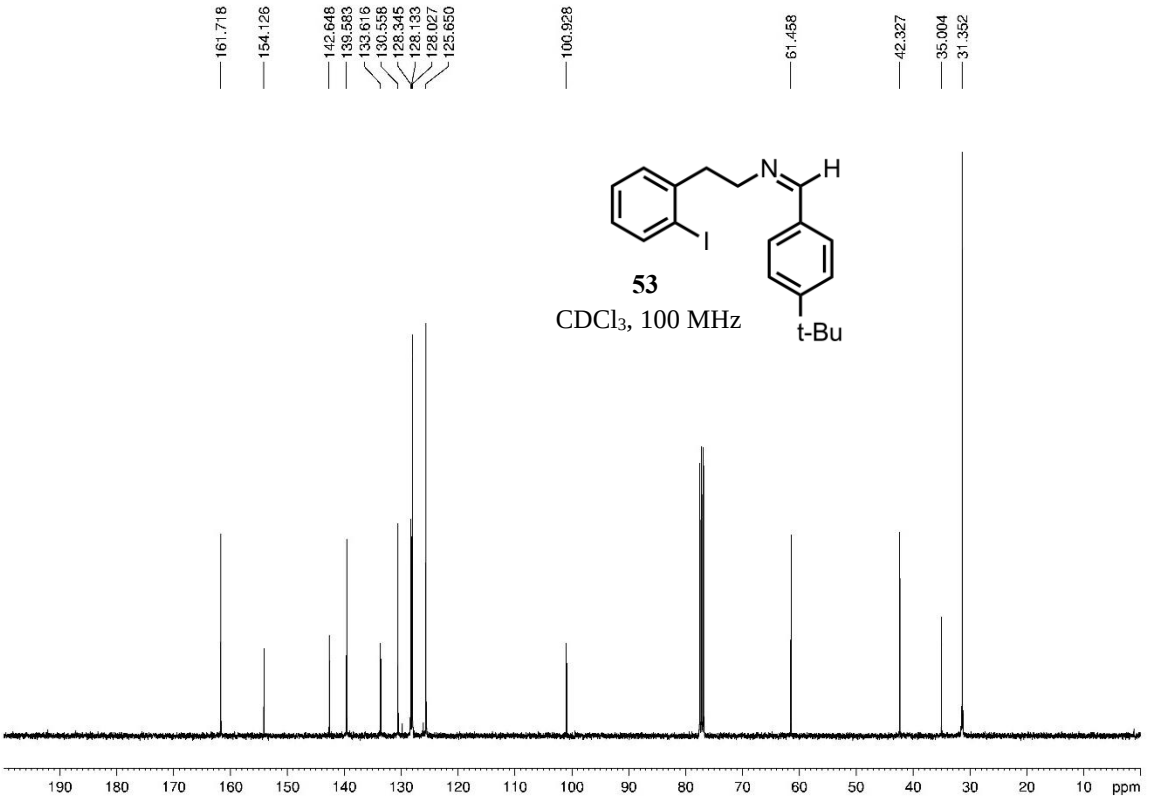

8.206
7.839
7.819
7.728
7.723
7.715
7.704
7.431
7.428
7.421
7.416
7.408
7.404
7.394
7.260
7.250
7.246
6.913
6.901
6.893
6.891
6.884
6.880
6.871
3.870
3.867
3.852
3.849
3.833
3.830
3.160
3.141
3.123
N
H
I
5
CDCl3, 400 MHz
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.000
1.067
1.977
2.961
2.043
1.029
2.054
2.101

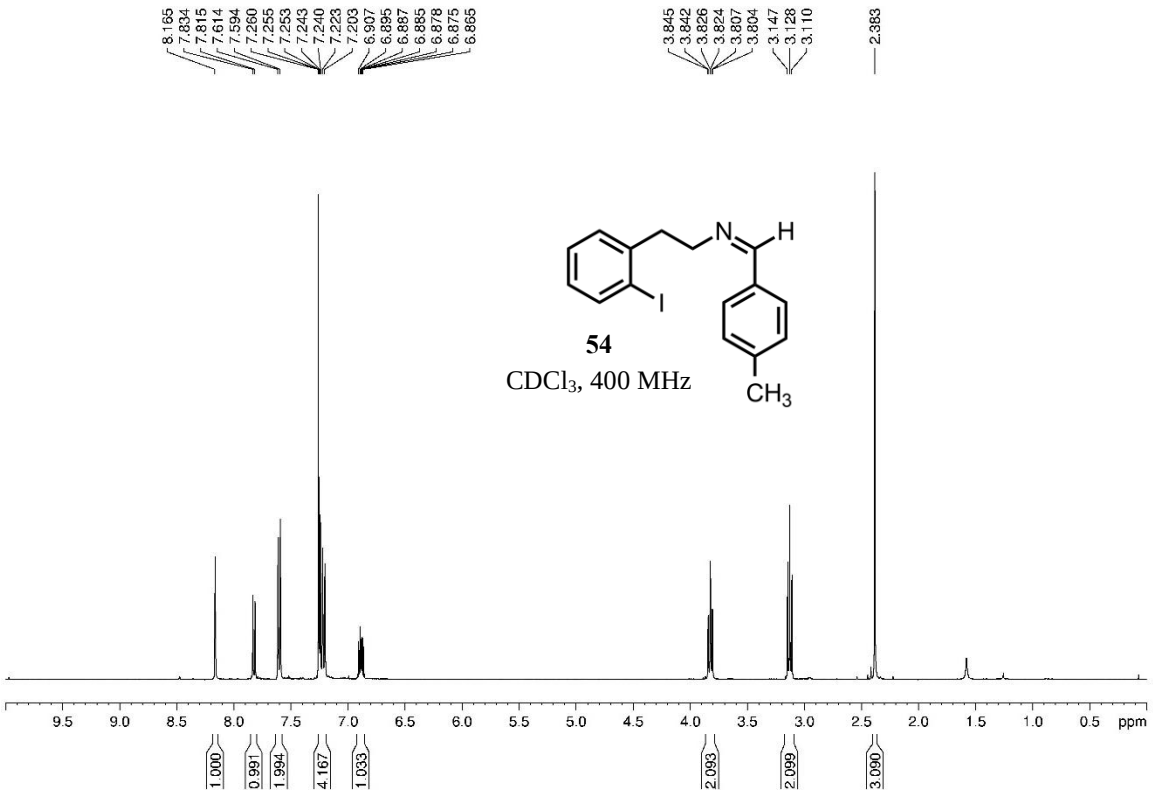

161.883
142.577
139.604
136.260
130.754
130.573
128.699
128.353
128.178
100.919
61.417
42.240
N
H
I
5
CDCl3, 100 MHz
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


8.114
7.834
7.815
7.691
7.670
7.260
7.251
7.245
7.243
6.938
6.916
6.910
6.901
6.895
6.890
6.887
6.882
6.875
6.867
3.848
3.836
3.833
3.815
3.798
3.796
3.151
3.132
3.114
N
H
I
OCH3
52
CDCl3, 400 MHz
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.000
0.998
1.959
1.831
2.198
0.925
3.061
2.173
2.075


161.841
161.284
142.630
139.590
130.589
129.899
129.051
128.356
128.156
114.125
100.927
61.190
55.493
42.341
N
H
I
OCH3
52
CDCl3, 100 MHz
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

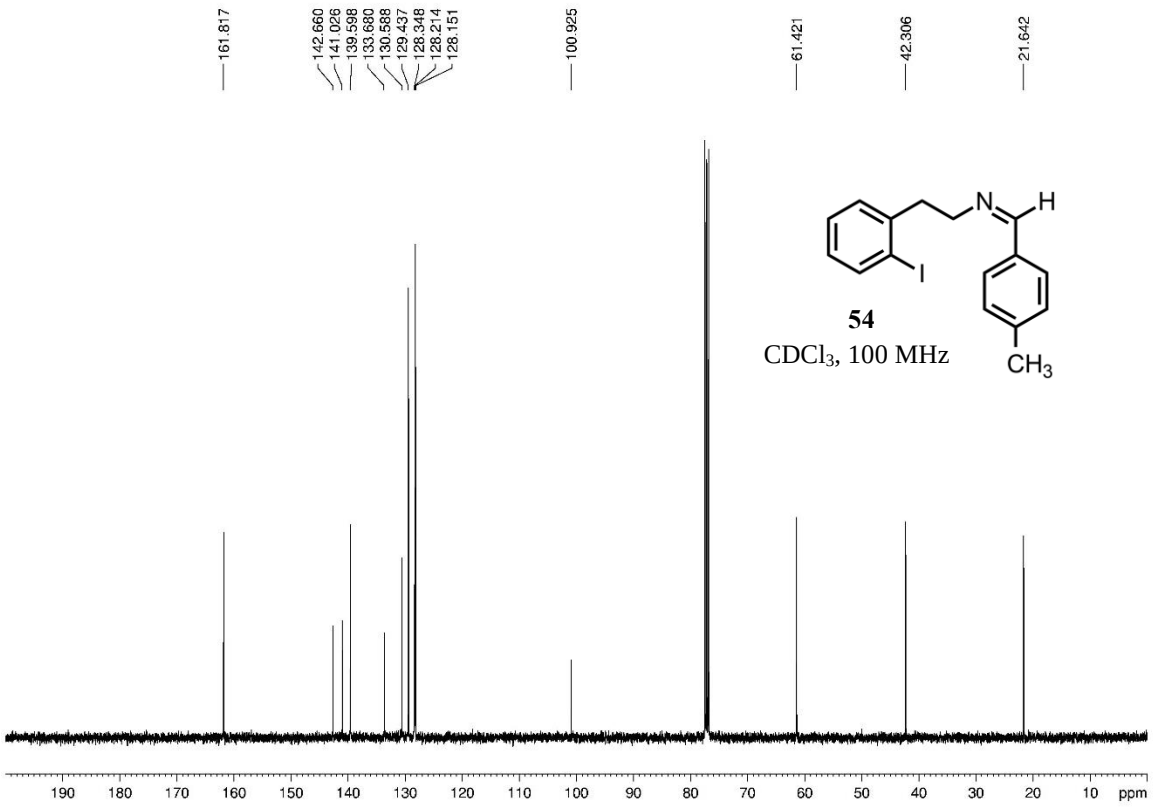

8.185
7.835
7.816
7.657
7.652
7.641
7.636
7.631
7.445
7.439
7.435
7.423
7.418
7.266
7.265
7.260
7.256
7.246
7.243
6.909
6.897
6.889
6.886
6.879
6.876
6.866
3.848
3.845
3.830
3.827
3.811
3.808
3.142
3.123
3.105
1.335
8.4 8.2 8.0 7.8 7.6 7.4 7.2 7.0 6.8 ppm
N
H
I
t-Bu
53
CDCl3, 400 MHz
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.000
1.007
2.009
2.113
2.104
1.043
2.071
2.077
9.086


161.718
154.126
142.648
139.583
133.616
130.558
128.345
128.133
128.027
125.650
100.928
61.458
42.327
35.004
31.352
N
H
I
t-Bu
53
CDCl3, 100 MHz
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm



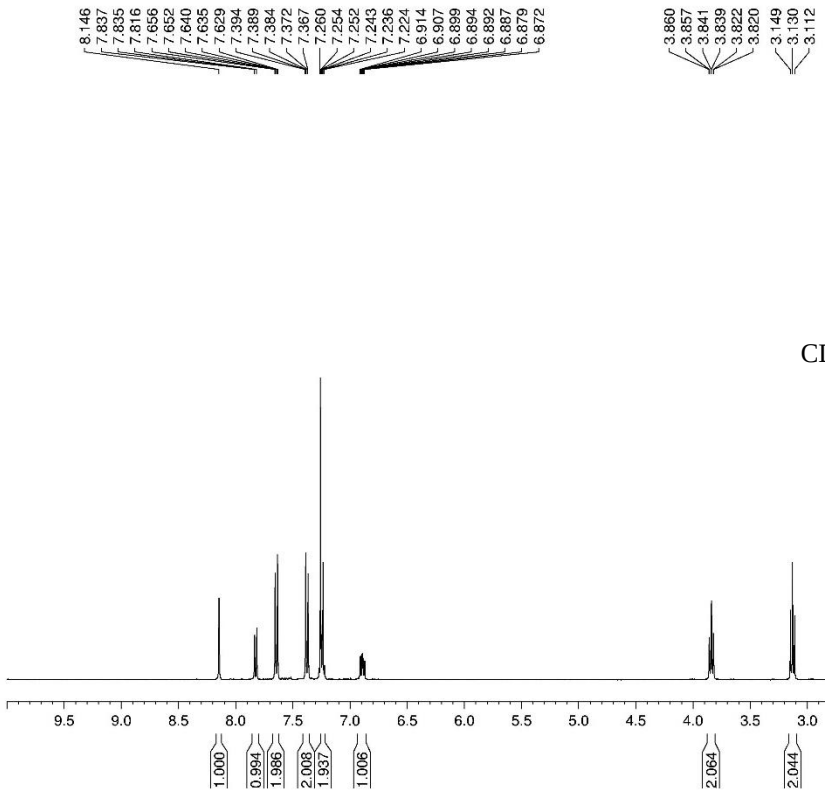
54

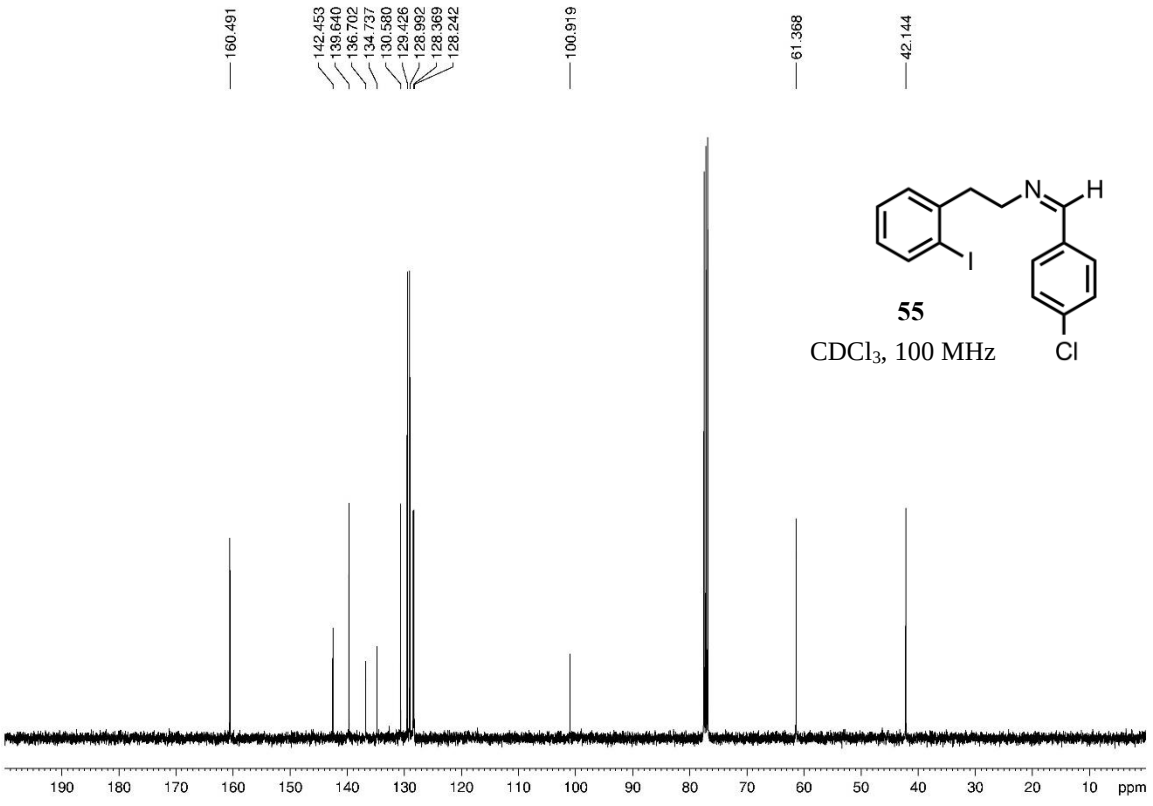
$CDCl_3$, 400 MHz

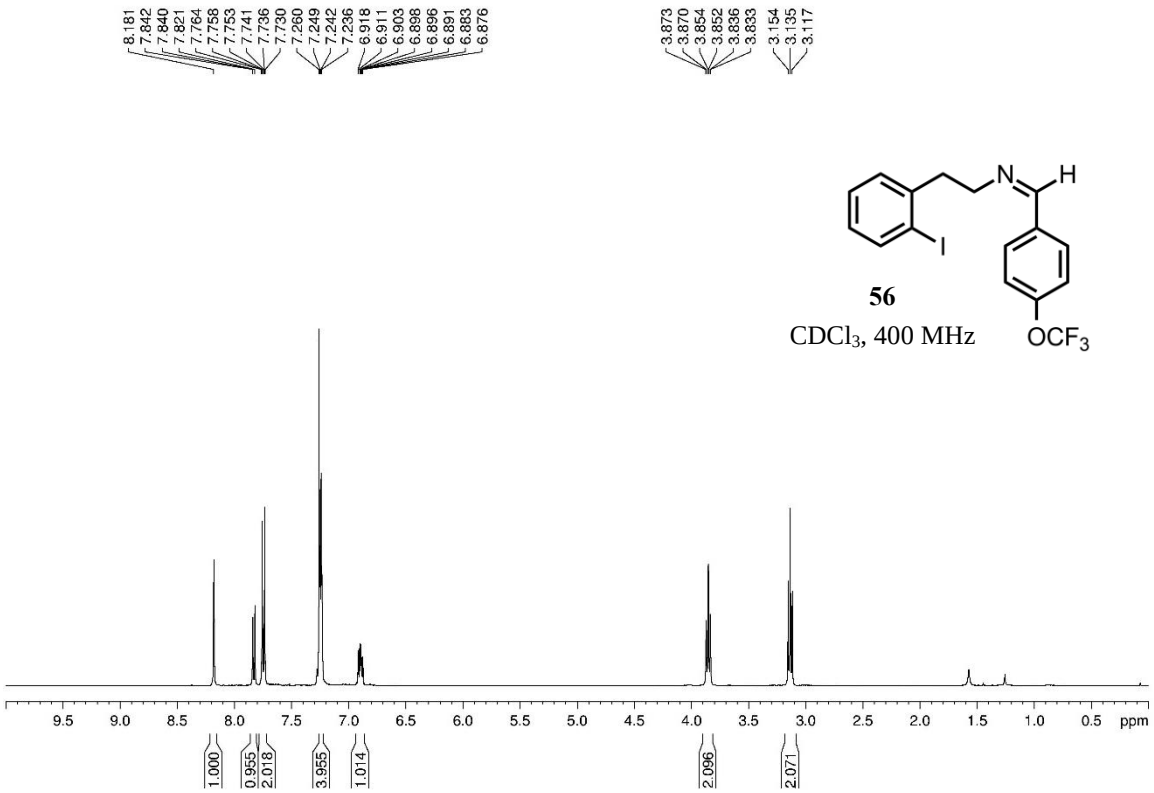


54

$CDCl_3$, 100 MHz

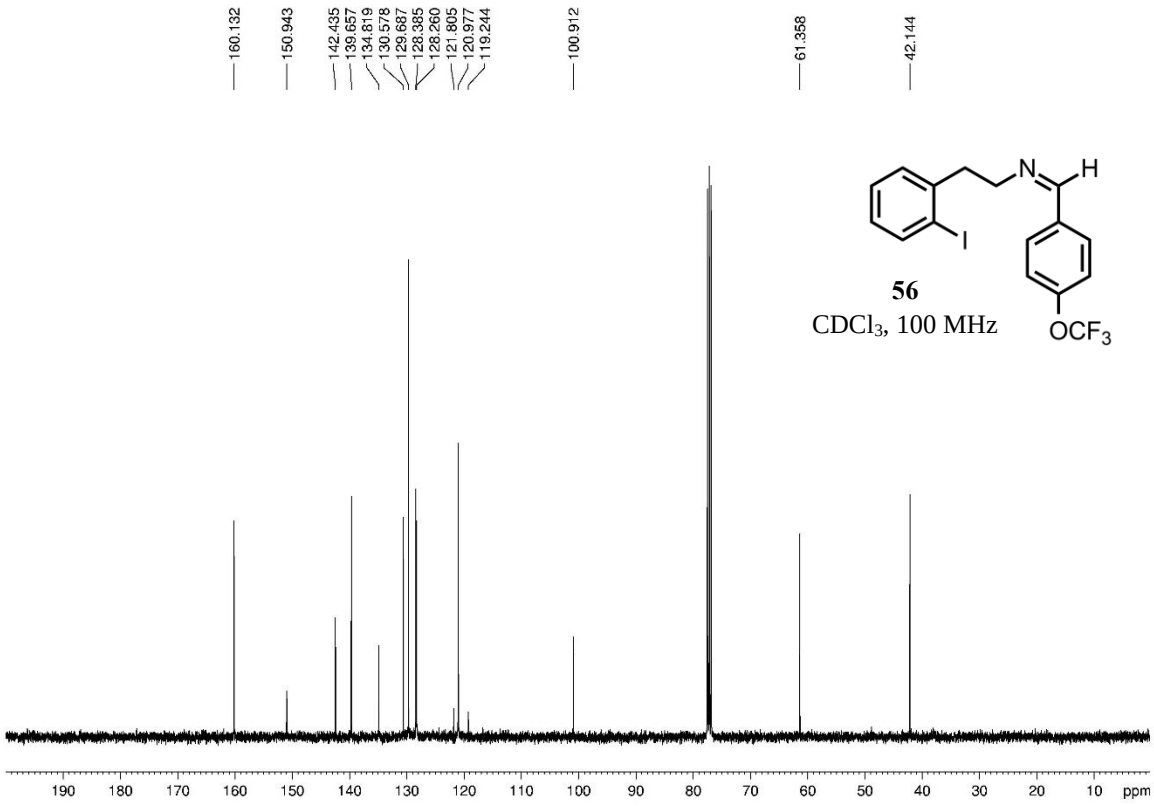

8.146
7.837
7.835
7.816
7.656
7.652
7.640
7.635
7.629
7.394
7.389
7.384
7.372
7.367
7.260
7.254
7.252
7.243
7.236
7.224
6.914
6.907
6.899
6.894
6.892
6.887
6.879
6.872
3.860
3.857
3.841
3.839
3.822
3.820
3.149
3.130
3.112
N
H
I
Cl
55
CDCl3, 400 MHz
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.000
0.994
1.986
2.008
1.937
1.006
2.064
2.044


160.491
142.453
139.640
136.702
134.737
130.580
129.426
128.992
128.369
128.242
100.919
61.368
42.144
N
H
I
Cl
55
CDCl3, 100 MHz
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm



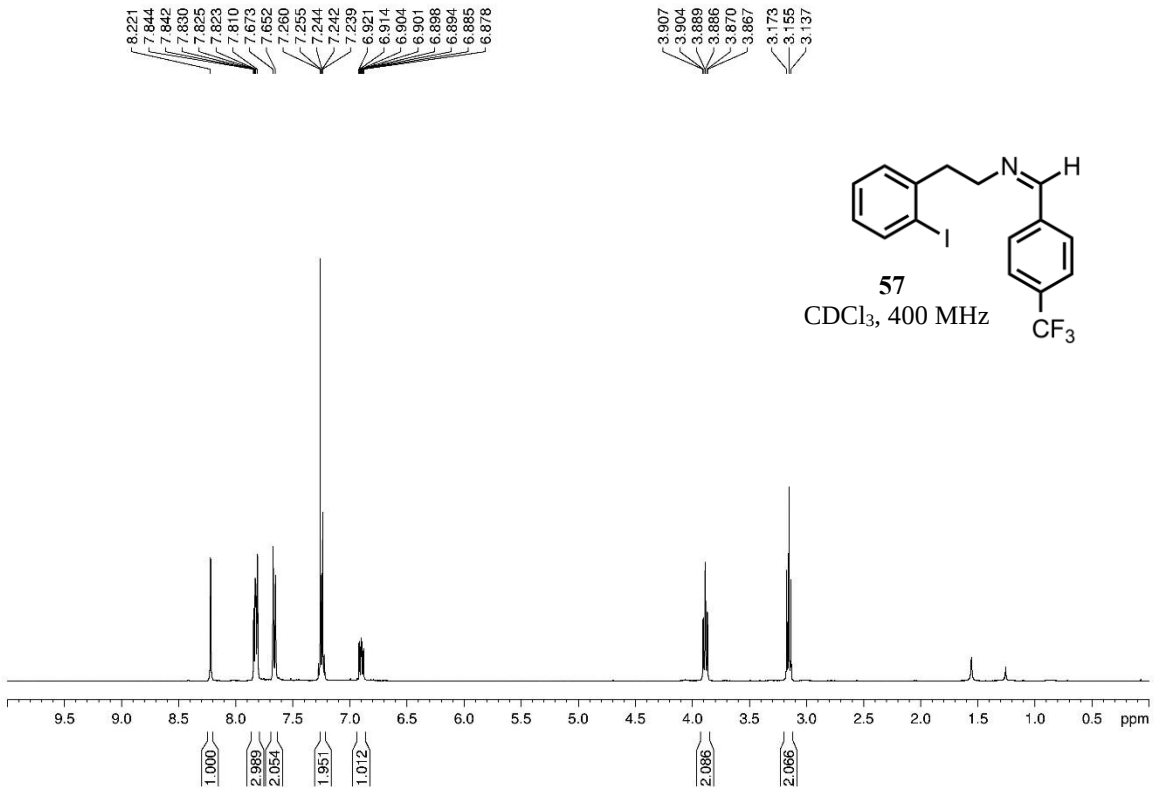
56

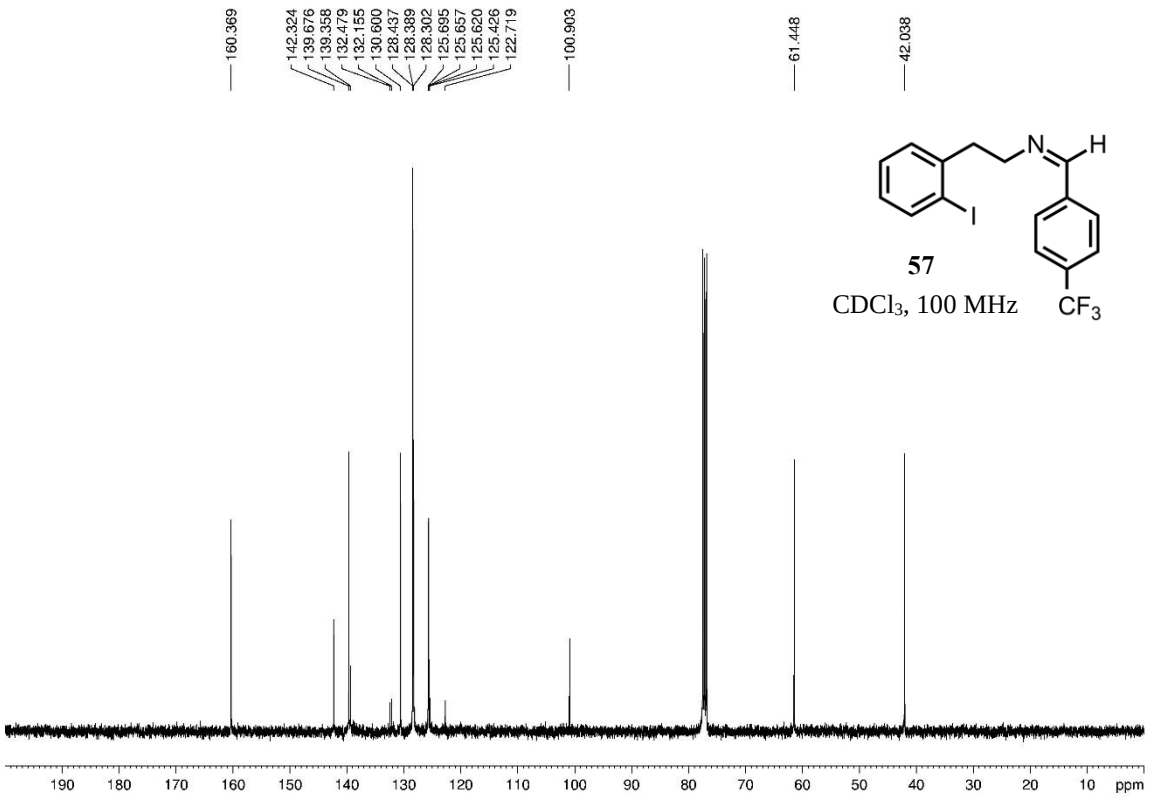
$CDCl_3$, 400 MHz

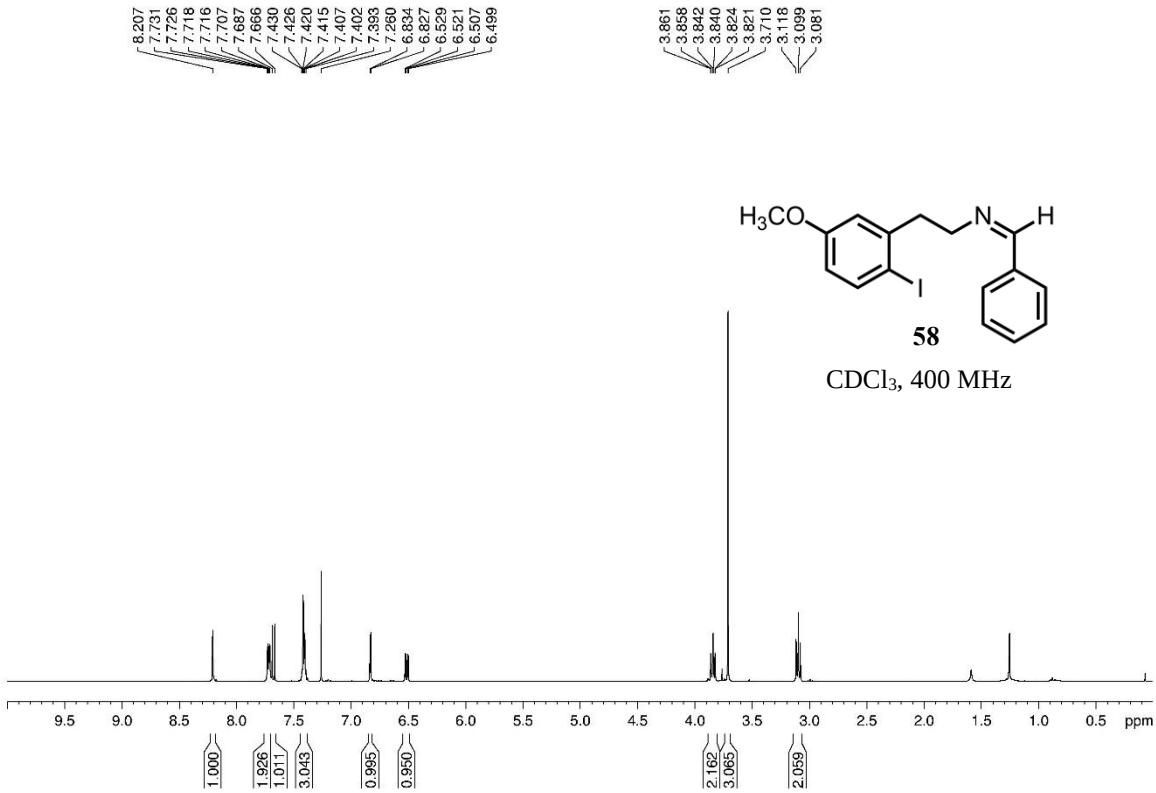


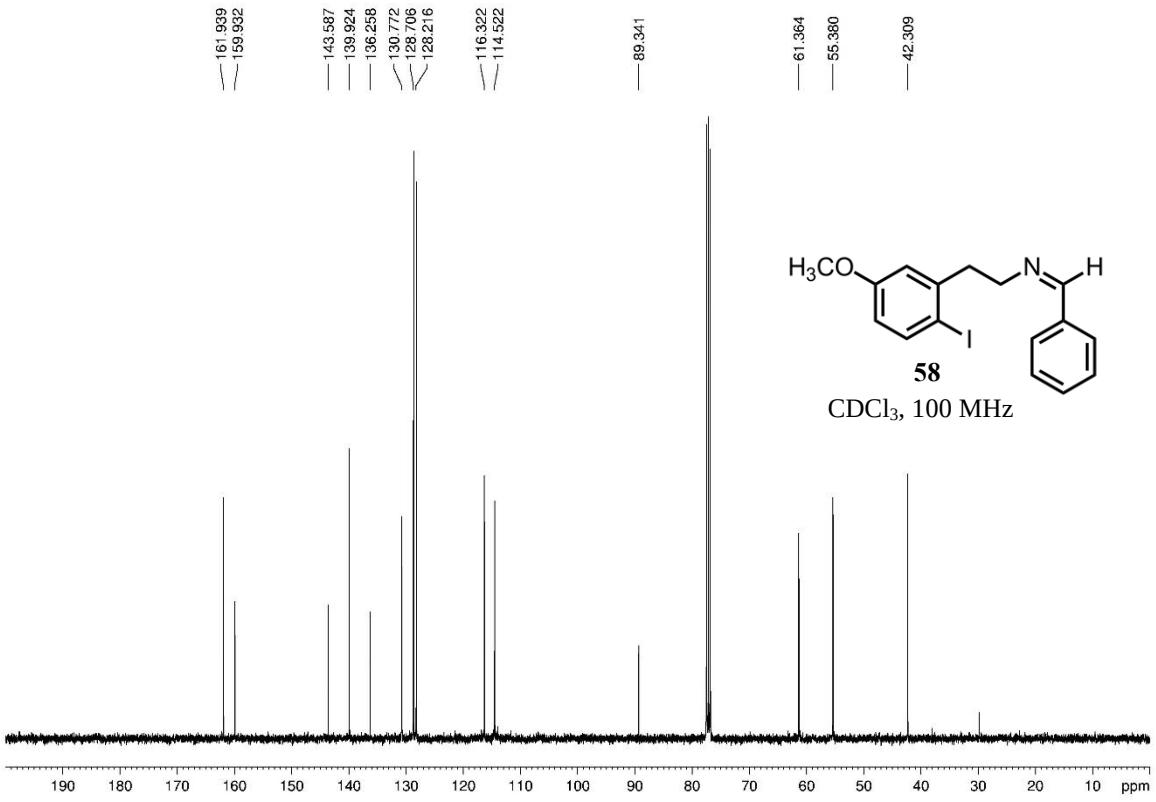
56

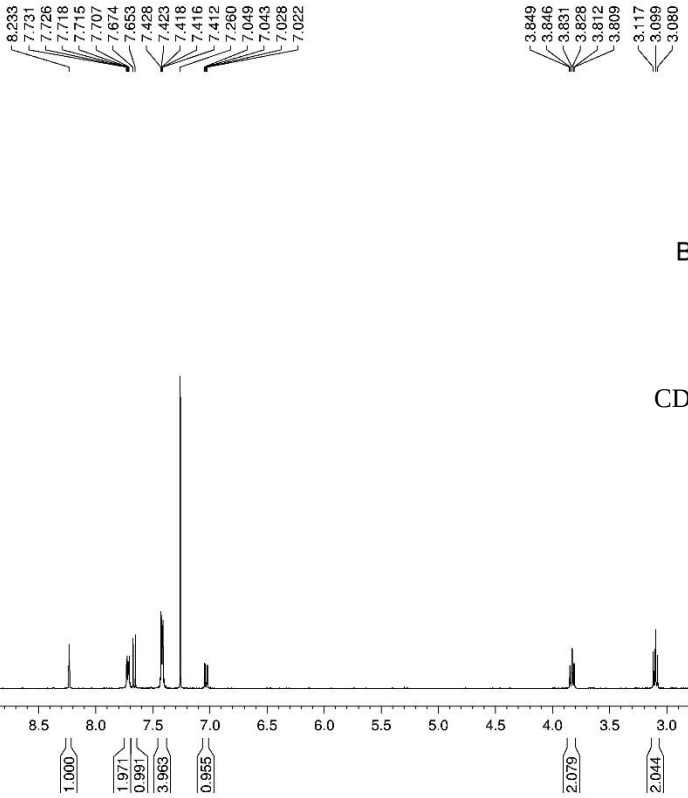
$CDCl_3$, 100 MHz

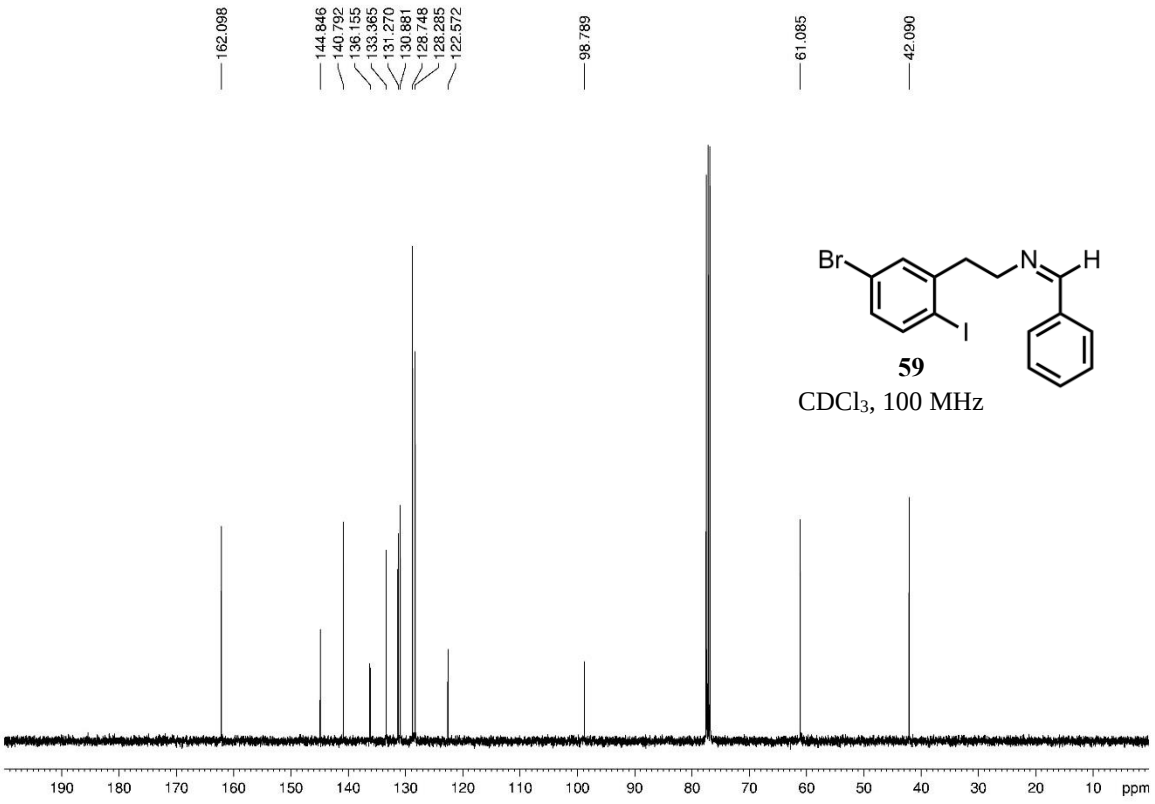

8.221
7.844
7.842
7.830
7.825
7.823
7.810
7.673
7.652
7.260
7.255
7.244
7.242
7.239
6.921
6.914
6.904
6.901
6.898
6.894
6.885
6.878
3.907
3.904
3.889
3.886
3.870
3.867
3.173
3.155
3.137
N
H
I
CF3
57
CDCl3, 400 MHz
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.000
2.989
2.054
1.951
1.012
2.086
2.066

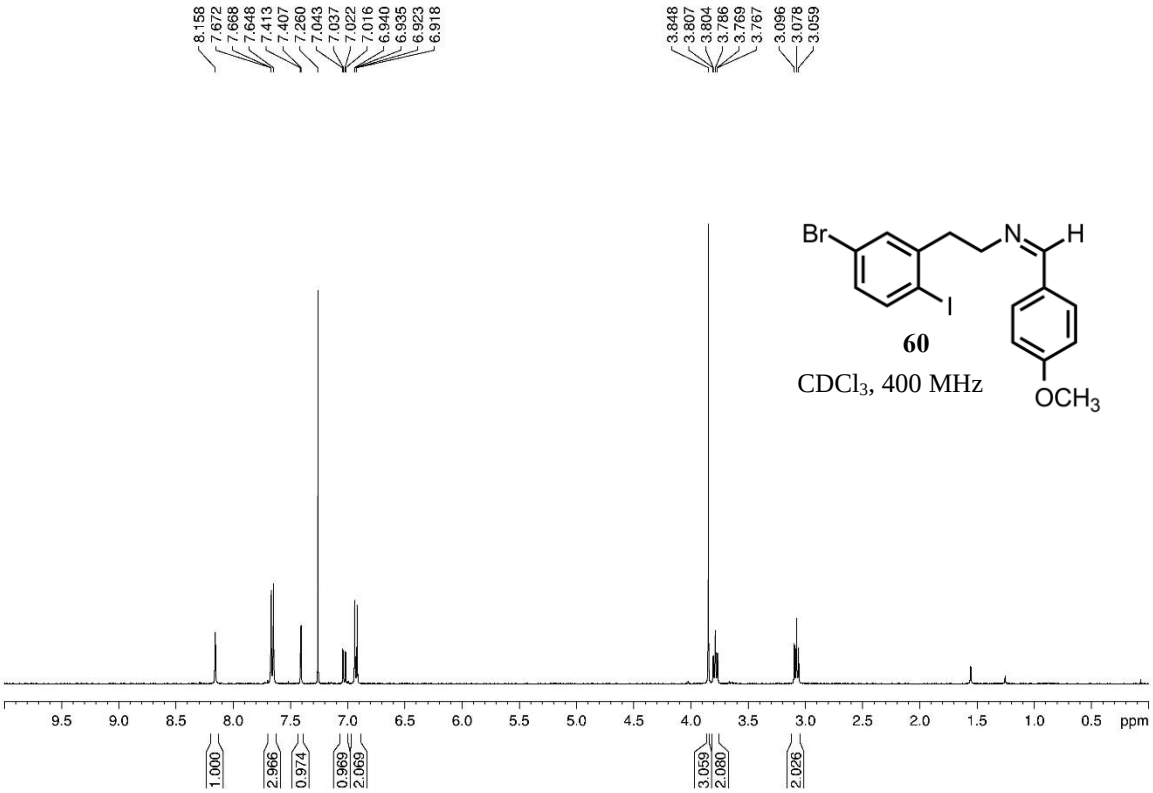

160.369
142.324
139.676
139.358
132.479
132.155
130.600
128.437
128.389
128.302
125.695
125.657
125.620
125.426
122.719
100.903
61.448
42.038
N
H
I
CF3
57
CDCl3, 100 MHz
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

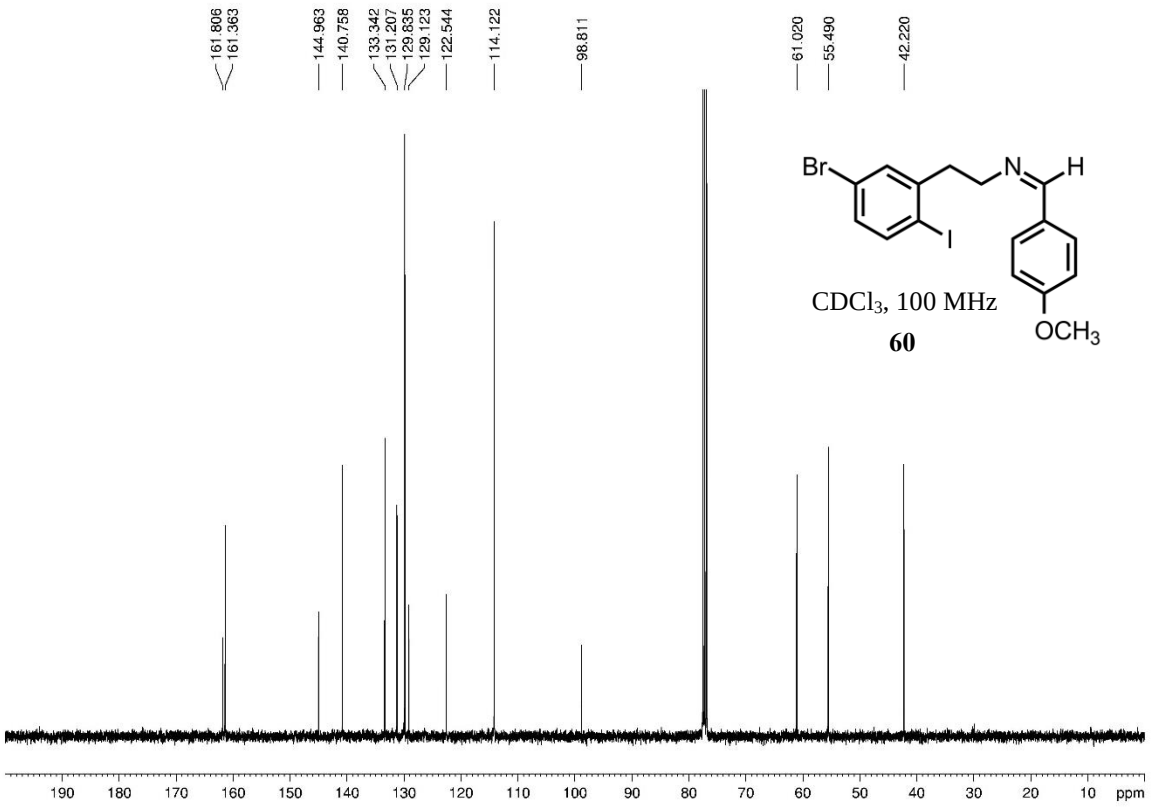

8.207
7.731
7.726
7.718
7.716
7.707
7.687
7.666
7.430
7.426
7.420
7.415
7.407
7.402
7.393
7.260
6.834
6.827
6.529
6.521
6.507
6.499
3.861
3.858
3.842
3.840
3.824
3.821
3.710
3.118
3.099
3.081
H3CO
N
H
I
58
CDCl3, 400 MHz
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.000
1.926
1.011
3.043
0.995
0.950
2.162
3.065
2.059

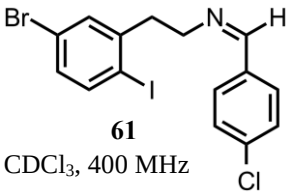

161.939
159.932
143.587
139.924
136.258
130.772
128.706
128.216
116.322
114.522
89.341
61.364
55.380
42.309
H3CO
N
H
I
58
CDCl3, 100 MHz
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


8.233
7.731
7.726
7.718
7.715
7.707
7.674
7.653
7.428
7.423
7.418
7.416
7.412
7.260
7.049
7.043
7.028
7.022
3.849
3.846
3.831
3.828
3.812
3.809
3.117
3.099
3.080
Br
N
H
I
59
CDCl3, 400 MHz
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.000
1.971
0.991
3.963
0.955
2.079
2.044


162.098
144.846
140.792
136.155
133.365
131.270
130.881
128.748
128.285
122.572
98.789
61.085
42.090
Br
N
H
I
59
CDCl3, 100 MHz
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

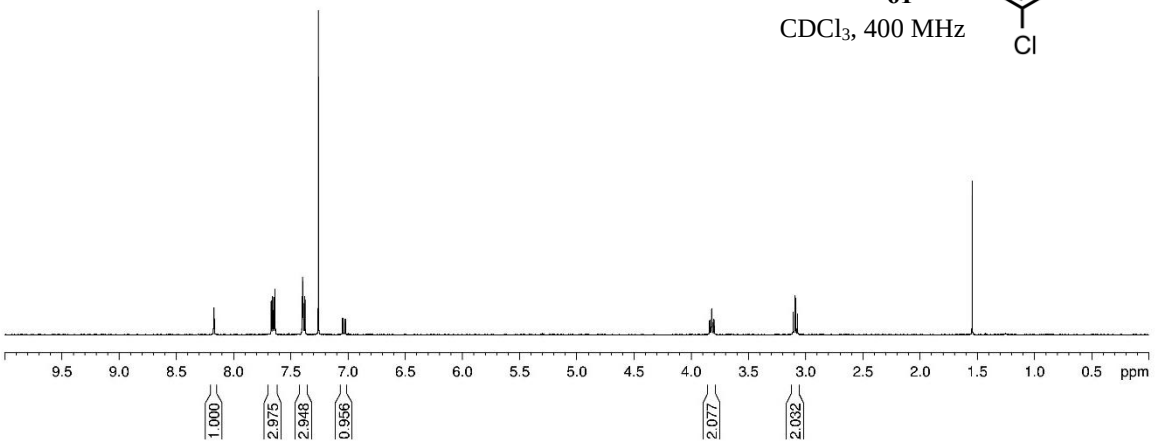

8.158
7.672
7.668
7.648
7.413
7.407
7.260
7.043
7.037
7.022
7.016
6.940
6.935
6.923
6.918
3.848
3.807
3.804
3.786
3.769
3.767
3.096
3.078
3.059
Br
N
H
I
OCH3
60
CDCl3, 400 MHz
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.000
2.966
0.974
0.969
2.069
3.059
2.080
2.026

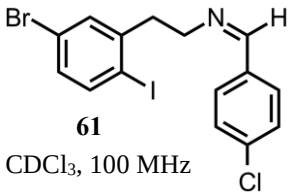

161.806
161.363
144.963
140.758
133.342
131.207
129.835
129.123
122.544
114.122
98.811
61.020
55.490
42.220
Br
N
H
I
OCH3
CDCl3, 100 MHz
60
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm



61

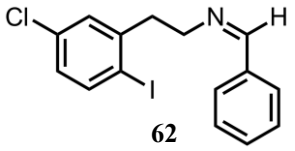
$CDCl_3$, 400 MHz





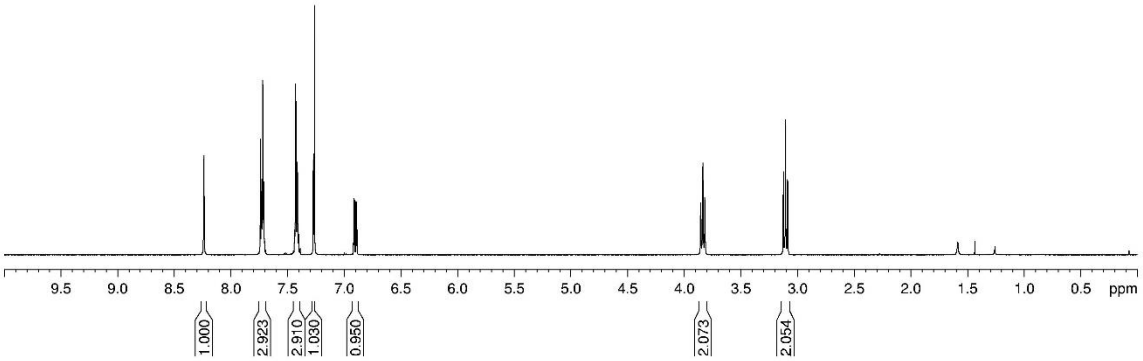
61

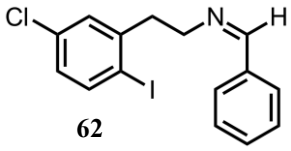
$CDCl_3$, 100 MHz



62

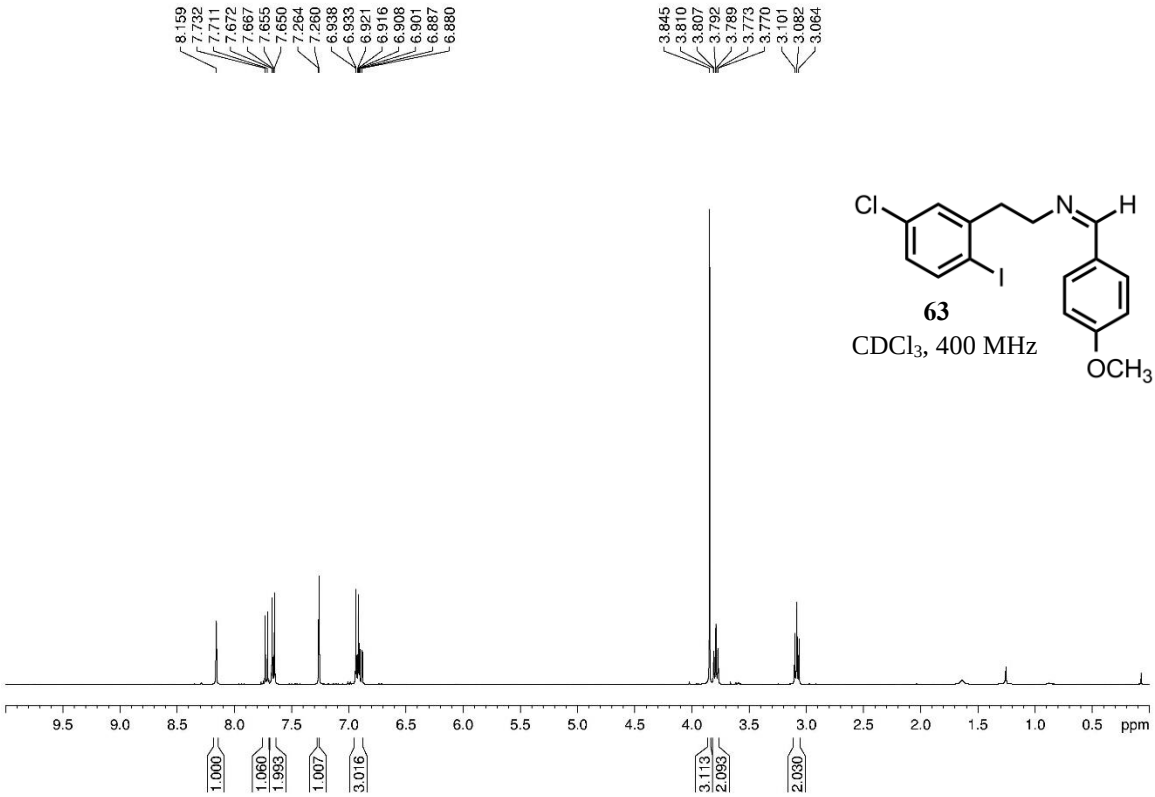
$CDCl_3$, 400 MHz

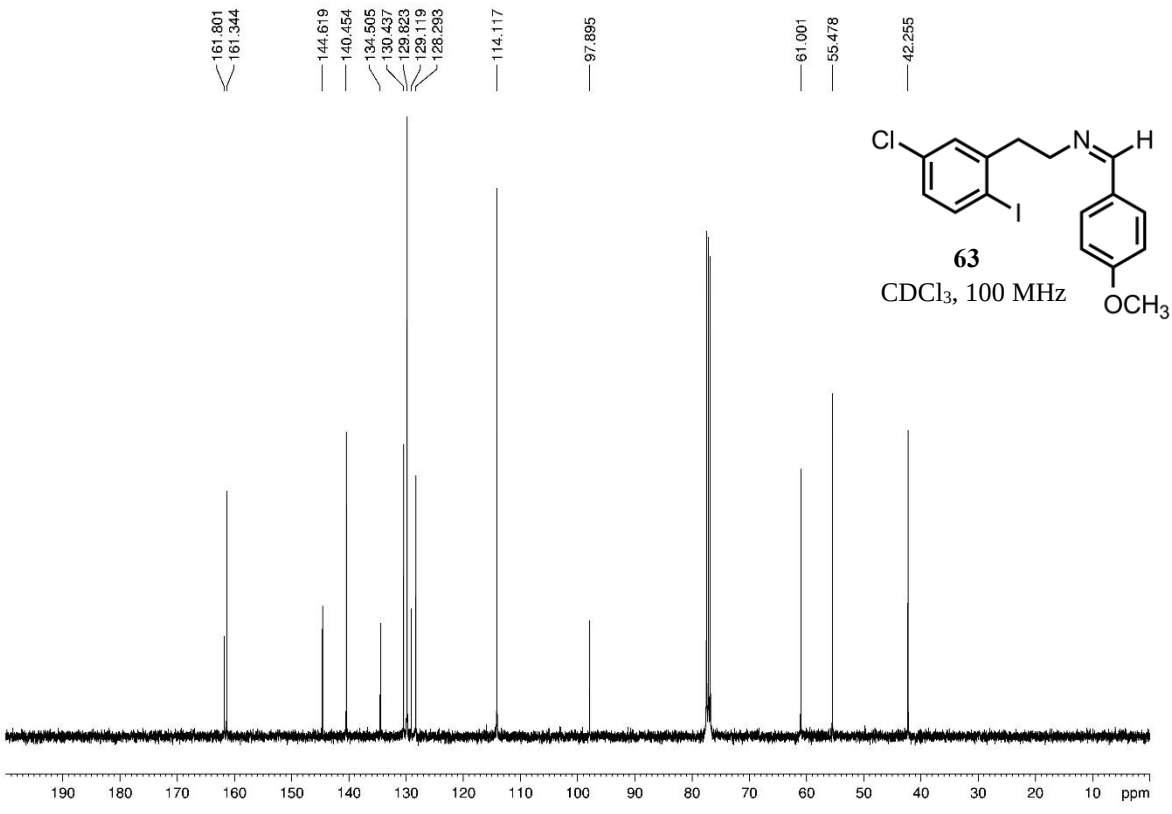


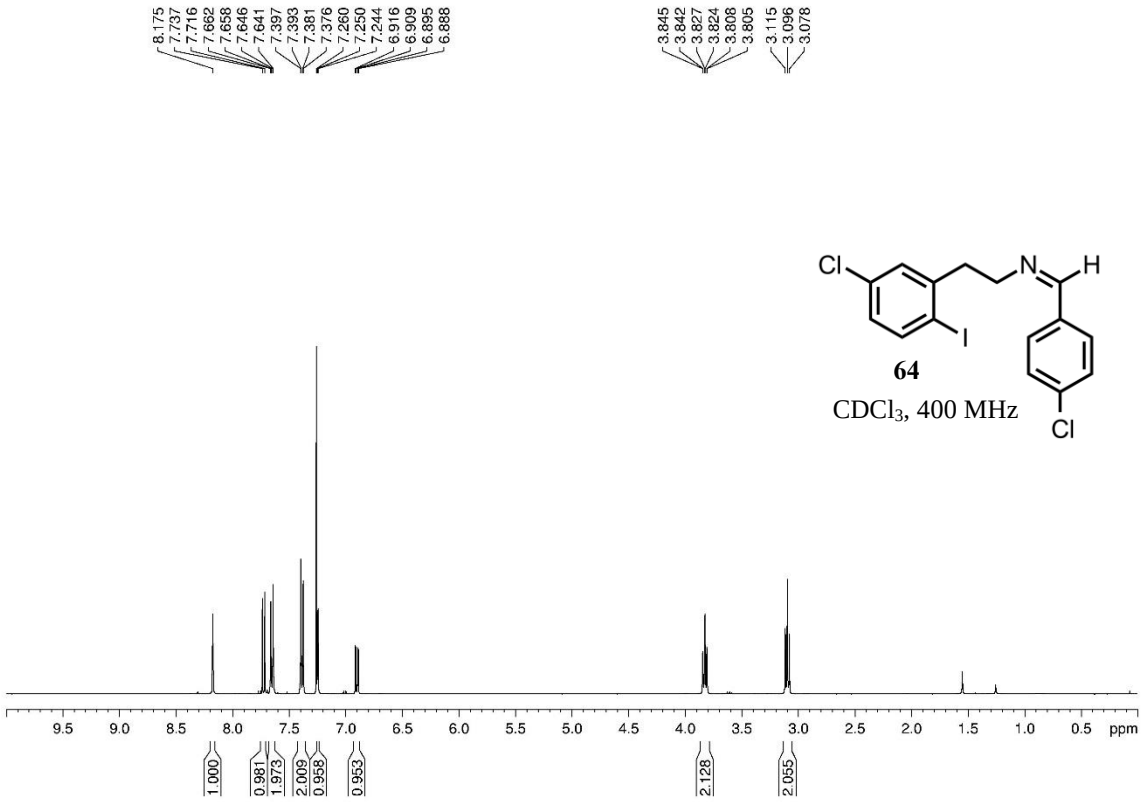


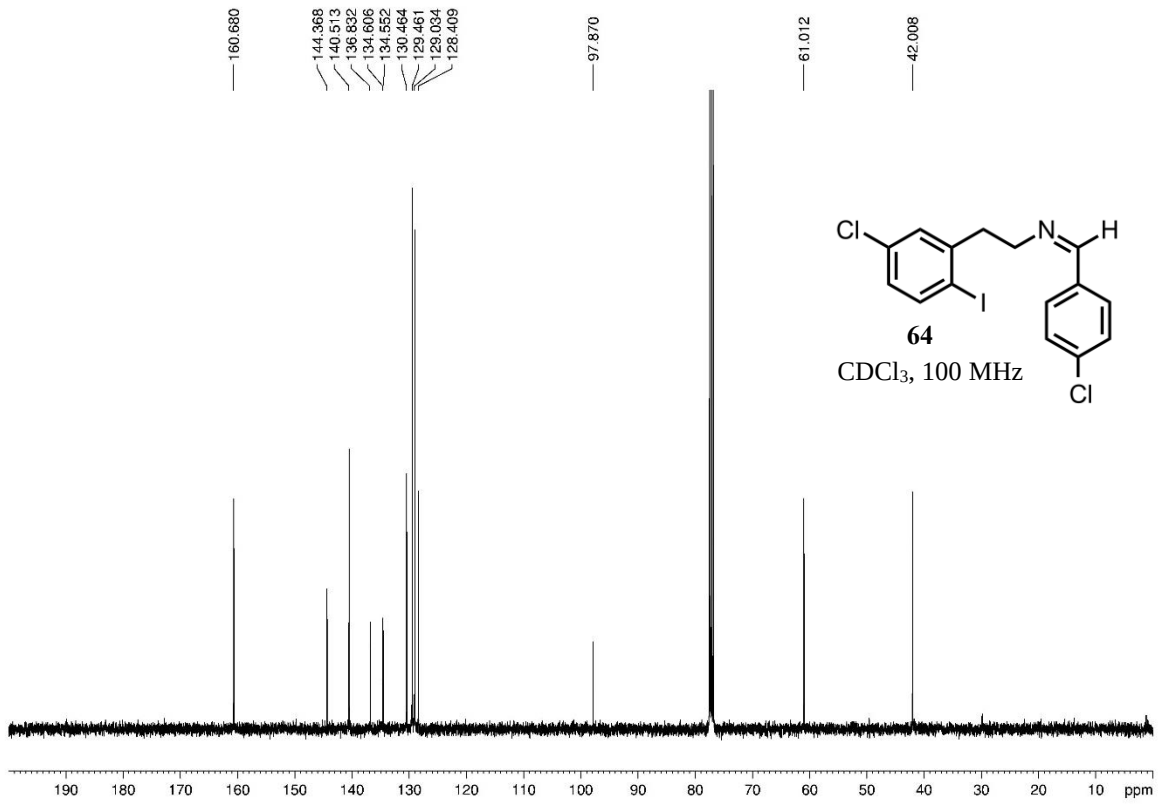
62

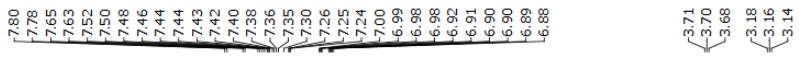
$CDCl_3$, 100 MHz

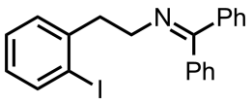

8.159
7.732
7.711
7.672
7.667
7.655
7.650
7.264
7.260
6.938
6.933
6.921
6.916
6.908
6.901
6.887
6.880
3.845
3.810
3.807
3.792
3.789
3.773
3.770
3.101
3.082
3.064
Cl
N
H
I
OCH3
63
CDCl3, 400 MHz
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.000
1.060
1.993
1.007
3.016
3.113
2.093
2.030


161.801
161.344
144.619
140.454
134.505
130.437
129.823
129.119
128.293
114.117
97.895
61.001
55.478
42.255
Cl
N
H
I
OCH3
63
CDCl3, 100 MHz
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


8.175
7.737
7.716
7.662
7.658
7.646
7.641
7.397
7.393
7.381
7.376
7.260
7.250
7.244
6.916
6.909
6.895
6.888
3.845
3.842
3.827
3.824
3.808
3.805
3.115
3.096
3.078
Cl
N
H
I
Cl
64
CDCl3, 400 MHz
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.000
0.981
1.973
2.009
0.958
0.953
2.128
2.055

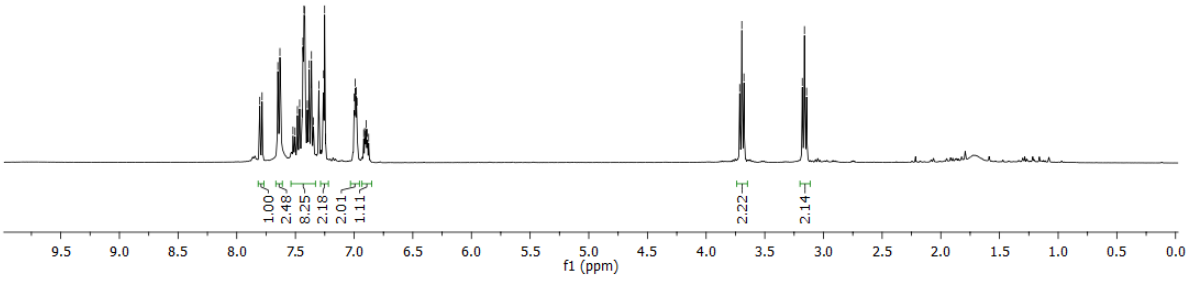

160.680
144.368
140.513
136.832
134.606
134.552
130.464
129.461
129.034
128.409
97.870
61.012
42.008
Cl
N
H
I
Cl
64
CDCl3, 100 MHz
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

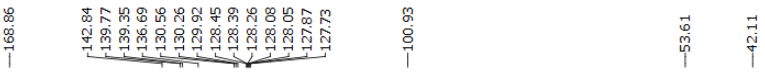


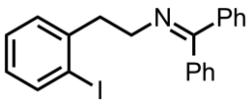


65

$CDCl_3$, 400 MHz

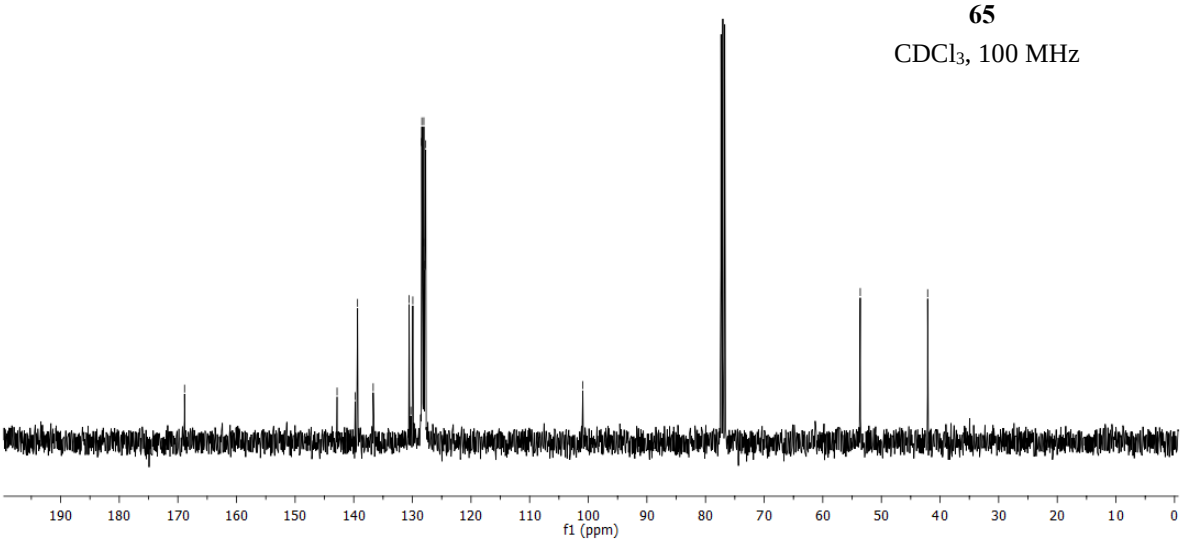


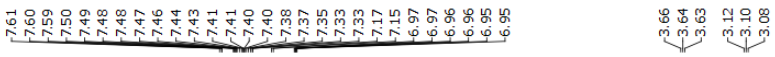


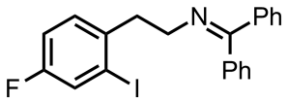


65

$CDCl_3$, 100 MHz

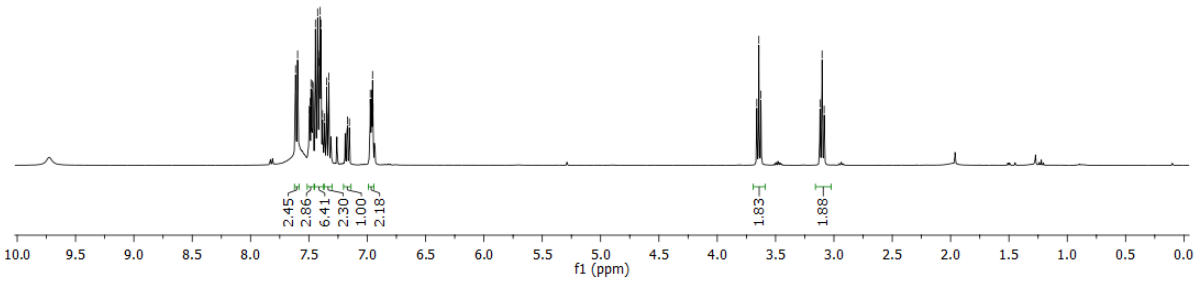


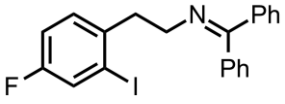




66

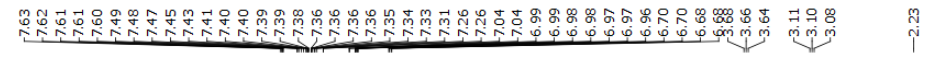
$CDCl_3$, 400 MHz

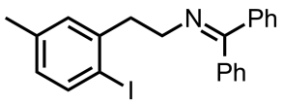




66

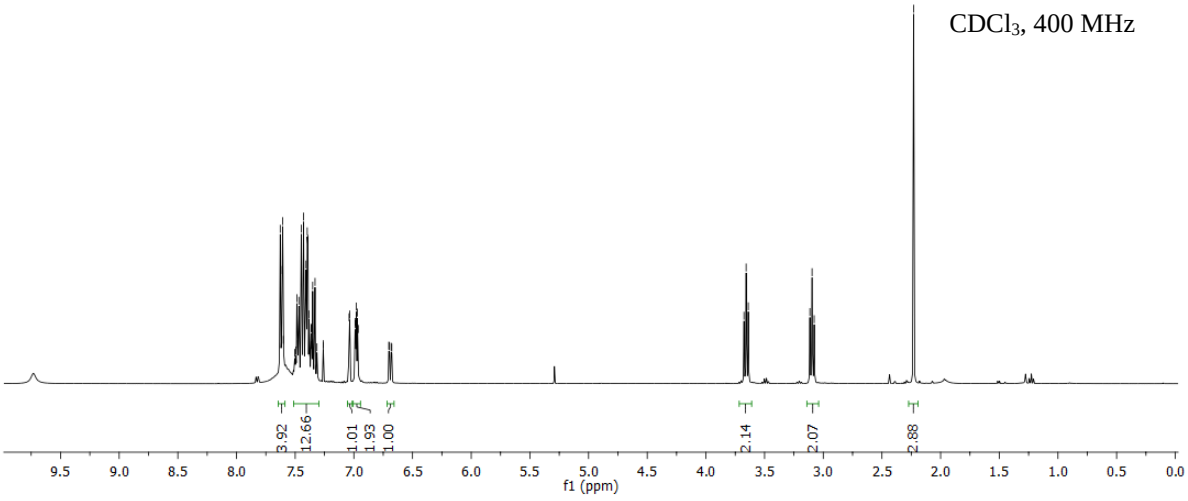
$CDCl_3$, 100 MHz

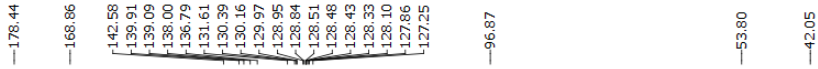


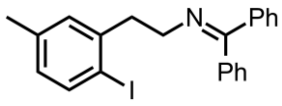


67

$CDCl_3$, 400 MHz

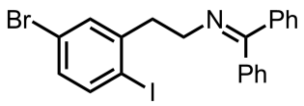






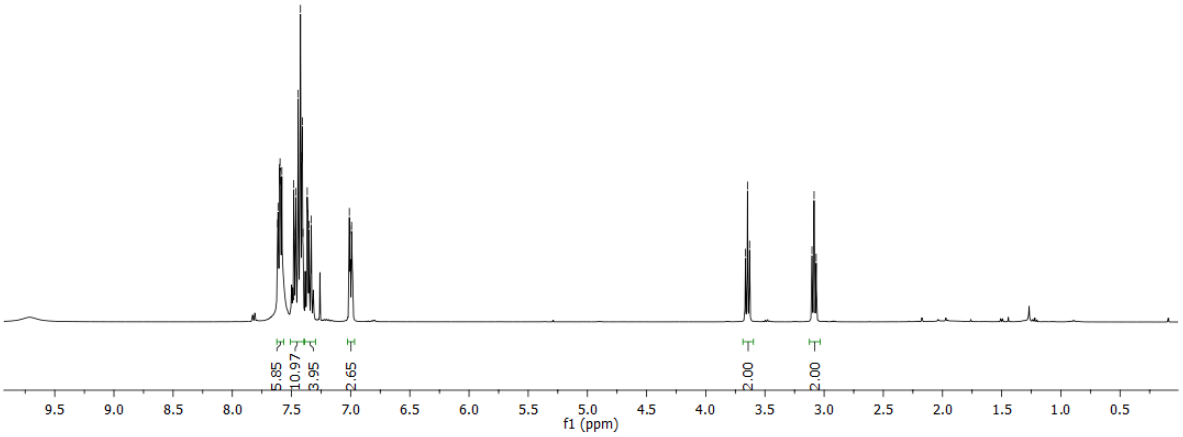
67

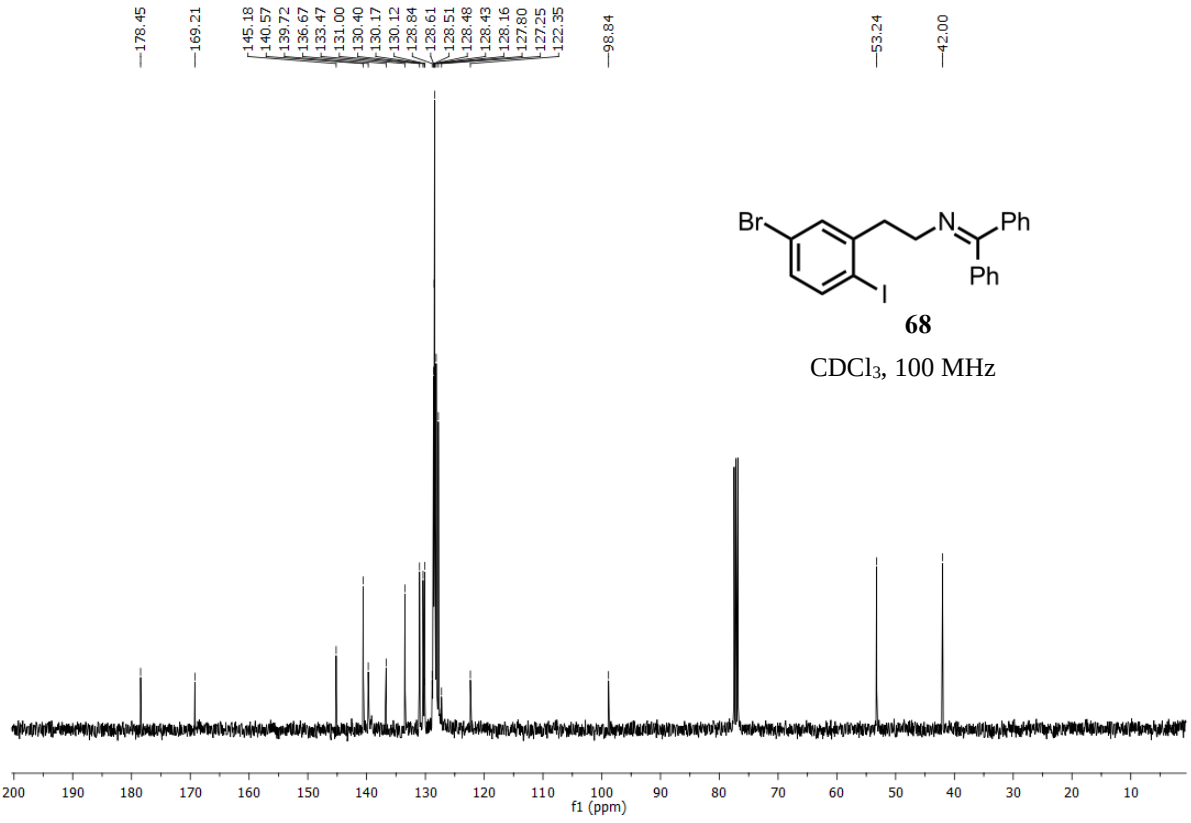
$CDCl_3$, 100 MHz



68

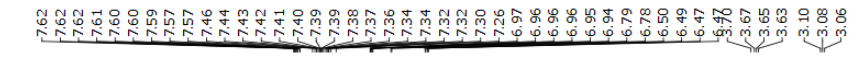
$CDCl_3$, 400 MHz

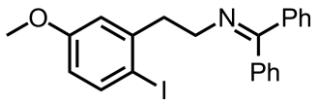




68

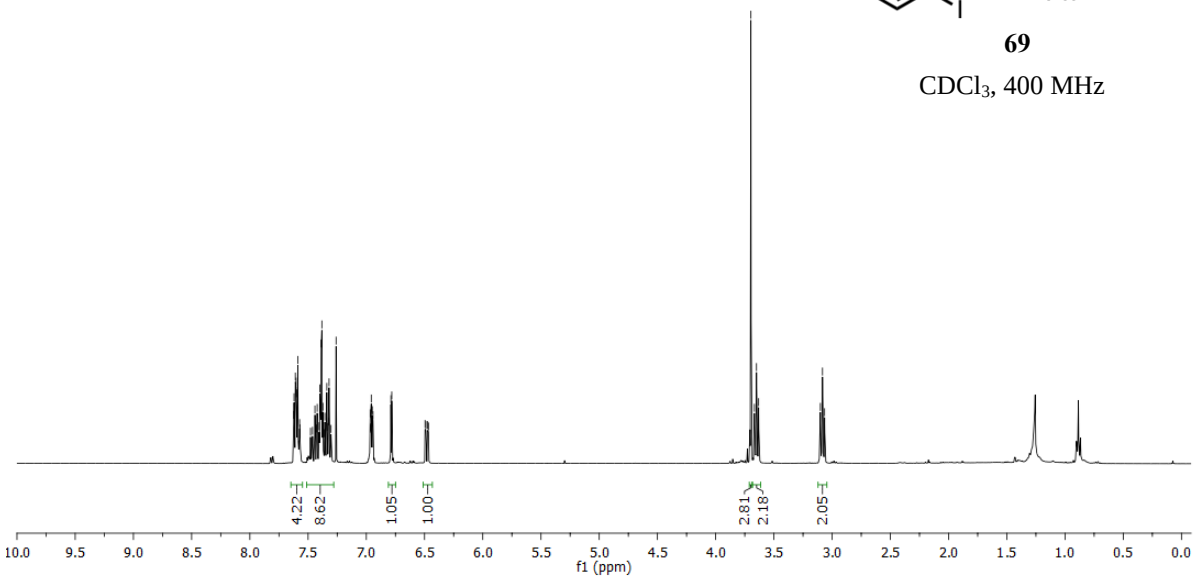
$CDCl_3$, 100 MHz

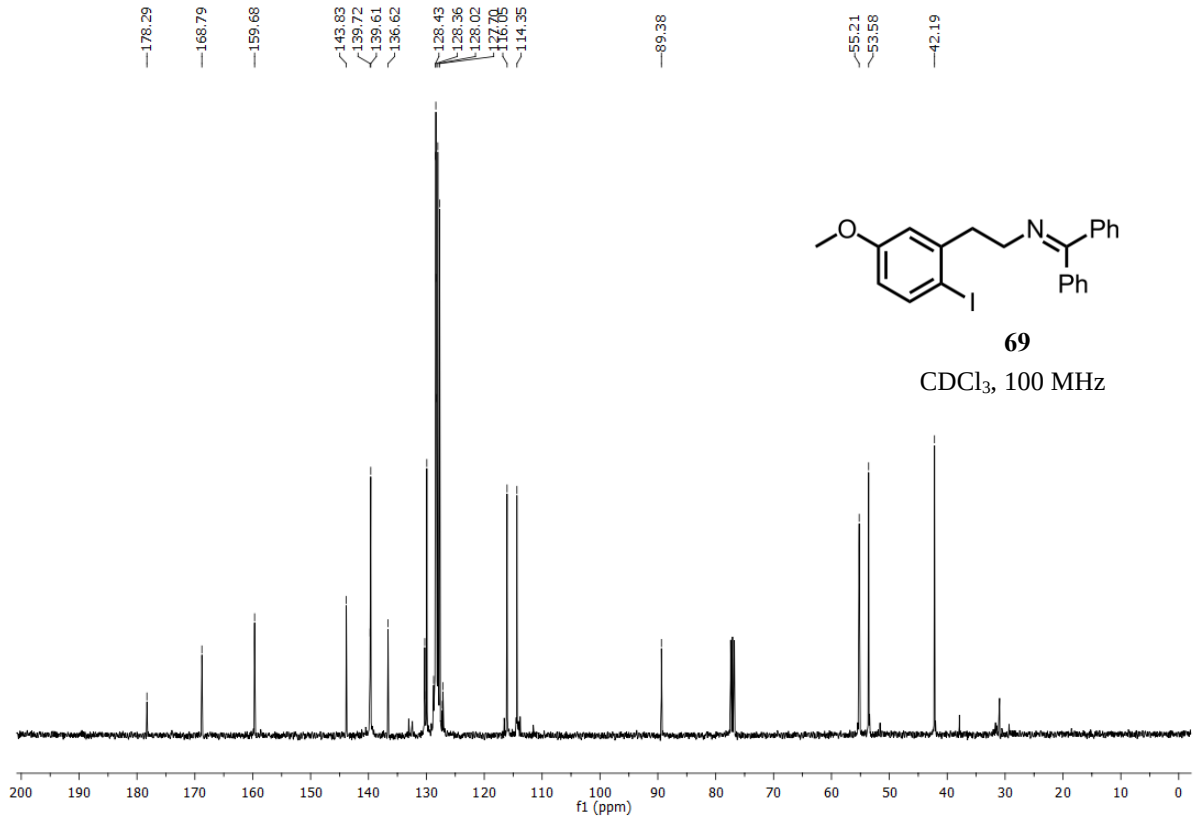




69

$CDCl_3$, 400 MHz





69

$CDCl_3$, 100 MHz