

Supplementary Material

Organometallic Complexes for Non-Linear Optics. 59. Syntheses and Optical Properties of Some Octupolar (*N*-Heterocyclic Carbene)gold Complexes

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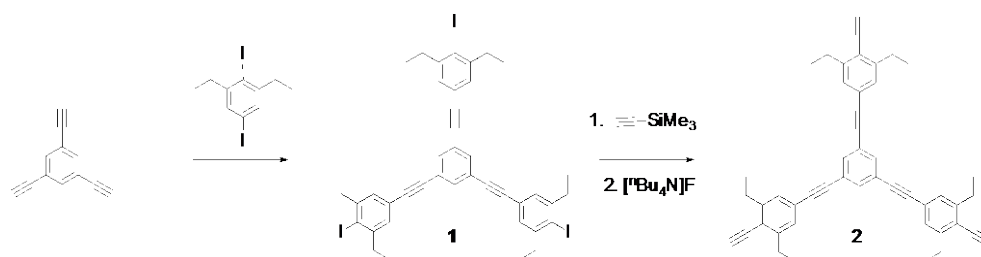
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Contents:	Page
Syntheses	2
NMR spectra	8
DFT calculations	22
References	32

Syntheses

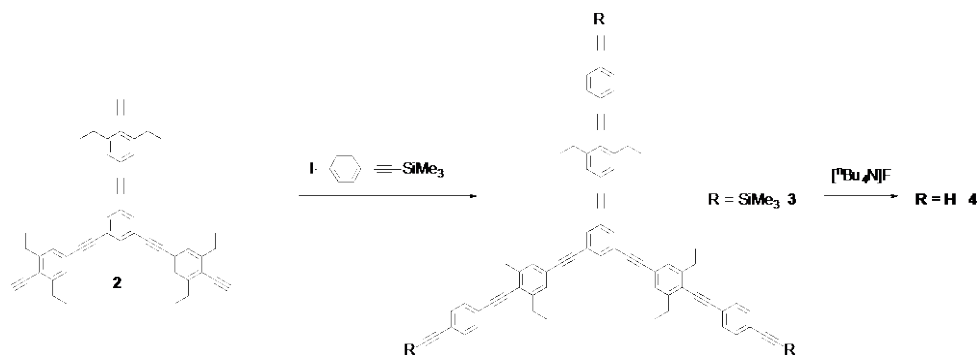


Synthesis of 1,3,5-(4-I-3,5-Et₂C₆H₂-1-C≡C)₃C₆H₃ (**1**)

1,3,5-(HC≡C)₃C₆H₃ (0.900 g, 5.99 mmol) and 2,6-Et₂-1,4-I₂C₆H₂ (7.32 g, 19.0 mmol) were dissolved in triethylamine (60 mL), and PdCl₂(PPh₃)₂ (0.250 g, 0.360 mmol) and CuI (0.090 g, 0.48 mmol) were added. The mixture was then stirred at 80 °C overnight. The reaction mixture was allowed to cool to room temperature, filtered to remove the precipitate, and the solvent was removed under reduced pressure. The resulting residue was passed through a short pad of silica using hexane as eluent. Removal of the solvent afforded the crude product, and crystallization from hexane provided 1,3,5-(4-I-3,5-Et₂C₆H₂-1-C≡C)₃C₆H₃ (**1**) as a white solid (4.260 g, 4.61 mmol, 77%). IR (CH₂Cl₂): $\nu(\text{C}\equiv\text{C})$ 2161 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 7.65 (s, 3H, CH aromatic), 7.21 (s, 6H, CH aromatic), 2.81 (q, $J = 7.5$ Hz, 12H, CH₂CH₃), 1.24 (t, $J = 7.5$ Hz, 18H, CH₂CH₃) ppm; ¹³C NMR (101 MHz, CDCl₃): δ 147.55, 134.04, 128.69, 124.01, 122.57, 108.05, 90.12, 88.22, 35.42, 14.47 ppm; HRMS (ESI): m/z calcd for C₄₂H₃₉I₃: 924.0186; found 924.0186. Anal. Calc. for C₄₂H₃₉I₃: C 54.57, H 4.25. Found: C 54.61, H 4.20%.

Synthesis of 1,3,5-((4-HC≡C)-3,5-Et₂C₆H₂-1-C≡C)₃C₆H₃ (**2**)

1,3,5-(4-I-3,5-Et₂C₆H₂-1-C≡C)₃C₆H₃ (**1**, 2.000 g, 2.16 mmol) was dissolved in NEt₃ (60 mL) and Pd(PPh₃)₄ (0.130 g, 0.11 mmol), CuI (0.030 g, 0.16 mmol) and trimethylsilylacetylene (1.20 mL, 8.57 mmol) were added in sequence under a N₂ atmosphere. After stirring at 50 °C overnight, the reaction mixture was allowed to cool to room temperature, filtered to remove the precipitate, and the solvent was removed under reduced pressure. This product proved difficult to purify by chromatography, and so was reacted on without further purification. The residue was dissolved in THF (30 mL), [tBu₄N]F (1.0 M in THF, 8 mL, 8 mmol) was added, and the mixture was stirred at ambient temperature for 15 min. After removal of the solvent, the residue was passed through a short column using hexane/CH₂Cl₂ (8:1) as eluent. Reduction in volume of the solvent afforded 1,3,5-((4-HC≡C)-3,5-Et₂C₆H₂-1-C≡C)₃C₆H₃ (**2**) as a light-yellow solid (0.810 g, 1.30 mmol, 60%). IR (CH₂Cl₂): $\nu(\text{C}\equiv\text{C})$ 2097 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 7.68 (s, 3H, CH aromatic), 7.28 (s, 6H, CH aromatic), 3.57 (s, 3H, HC≡C), 2.87 (q, $J = 7.5$ Hz, 12H, CH₂CH₃), 1.30 (t, $J = 7.5$ Hz, 18H, CH₂CH₃) ppm; ¹³C NMR (101 MHz, CDCl₃): δ 147.32, 134.10, 128.47, 124.04, 122.69, 121.17, 90.78, 88.78, 86.25, 80.24, 27.74, 14.56 ppm.

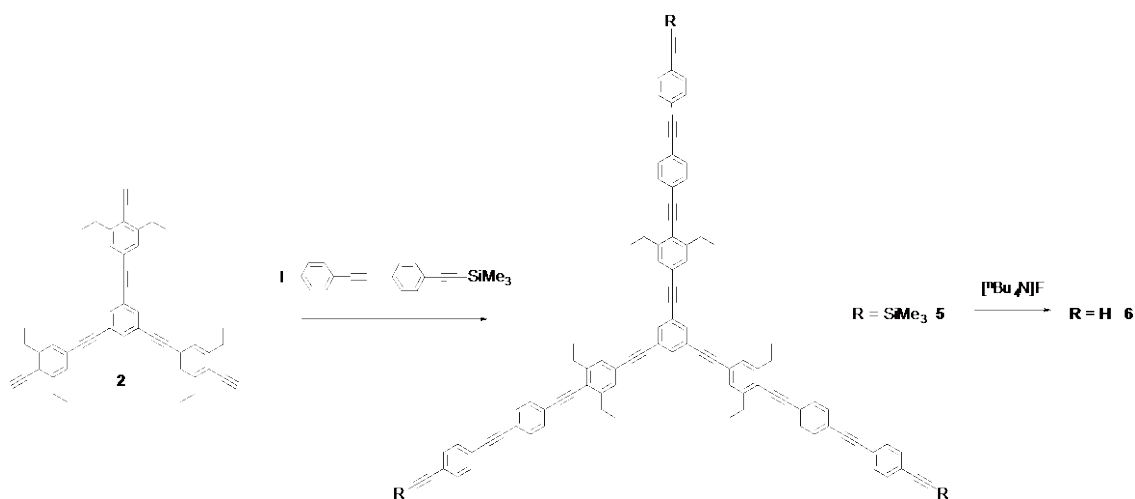


Synthesis of 1,3,5-(4-(4-Me₃SiC≡CC₆H₄-1-C≡C)-3,5-Et₂C₆H₂-1-C≡C)₃C₆H₃ (3)

1,3,5-(4-(4-Me₃SiC≡CC₆H₄-1-C≡C)₃C₆H₃ (**2**, 0.440 g, 0.710 mmol) and 4-IC₆H₄C≡CSiMe₃ (0.660 g, 2.20 mmol) were dissolved in NEt₃/THF (30 mL/30 mL), and Pd(PPh₃)₄ (25 mg, 0.022 mmol) and CuI (15 mg, 0.079 mmol) were added. The resulting solution was stirred at 80 °C overnight. The reaction mixture was allowed to cool to room temperature, filtered to remove the precipitate, and the solvent was removed under reduced pressure. The residue was passed through a short column using hexane/CH₂Cl₂ (5:1) as eluent. Reduction in volume of the solvent afforded 1,3,5-(4-(4-Me₃SiC≡CC₆H₄-1-C≡C)-3,5-Et₂C₆H₂-1-C≡C)₃C₆H₃ (**3**) as a light yellow solid (0.580 g, 0.510 mmol, 72%). IR (CH₂Cl₂): ν(C≡C) 2155 cm⁻¹; UV-vis (CH₂Cl₂): 367 [19.8], 350 [22.2], 343 [22.4]; ¹H NMR (400 MHz, CDCl₃): δ 7.67 (s, 3H, CH aromatic), 7.46 (s, 12H, CH aromatic), 7.29 (s, 6H, CH aromatic), 2.90 (q, *J* = 7.5 Hz, 12H, CH₂CH₃), 1.33 (t, *J* = 7.5 Hz, 18H, CH₂CH₃), 0.27 (s, 27H, Si(CH₃)₃) ppm; ¹³C NMR (101 MHz, CDCl₃): δ 146.69, 134.13, 132.03, 131.19, 128.64, 124.15, 123.71, 123.07, 122.56, 122.04, 104.73, 98.37, 96.43, 91.03, 88.98, 88.41, 27.98, 14.64, 0.001 ppm; HRMS (ESI): *m/z* calcd for C₈₁H₇₈Si₃: 1134.5411; found 1134.5413. Anal. Calc. for C₈₁H₇₈Si₃: C 85.66, H 6.92. Found: C 85.50, H 6.98%.

Synthesis of 1,3,5-(4-(4-HC≡CC₆H₄-1-C≡C)-3,5-Et₂C₆H₂-1-C≡C)₃C₆H₃ (4)

1,3,5-(4-(4-Me₃SiC≡CC₆H₄-1-C≡C)-2,6-Et₂C₆H₂-1-C≡C)₃C₆H₃ (**3**, 0.570 g, 0.500 mmol) was dissolved in THF (30 mL), [tBu₄N]F (1.0 M in THF, 3 mL, 3 mmol) was added, and the resulting solution was stirred at ambient temperature for 1 h. After removing the solvent, the residue was passed through a small pad of silica using hexane/CH₂Cl₂ (5:1) as eluent. Reduction in volume of the solvent afforded 1,3,5-(4-(4-HC≡CC₆H₄-1-C≡C)-3,5-Et₂C₆H₂-1-C≡C)₃C₆H₃ (**4**) as a light-yellow solid (0.430 g, 0.470 mmol, 94%). IR (CH₂Cl₂): ν(C≡C) 2106 cm⁻¹; UV-vis (CH₂Cl₂): 363 [16.5], 340 [18.9]; ¹H NMR (400 MHz, CDCl₃): δ 7.69 (s, 3H, CH aromatic), 7.51 (s, 12H, CH aromatic), 7.31 (s, 6H, CH aromatic), 3.21 (s, 3H, HC≡C), 2.93 (q, *J* = 7.5 Hz, 12H, CH₂CH₃), 1.35 (t, *J* = 7.5 Hz, 18H, CH₂CH₃) ppm; ¹³C NMR (101 MHz, CDCl₃): δ 146.66, 134.08, 132.15, 131.23, 128.59, 124.07, 122.55, 121.94, 121.90, 98.07, 90.95, 88.94, 88.42, 83.30, 79.00, 27.93, 14.59 ppm; HRMS (ESI): *m/z* calcd for C₇₂H₅₄: 918.4226; found 918.4255.



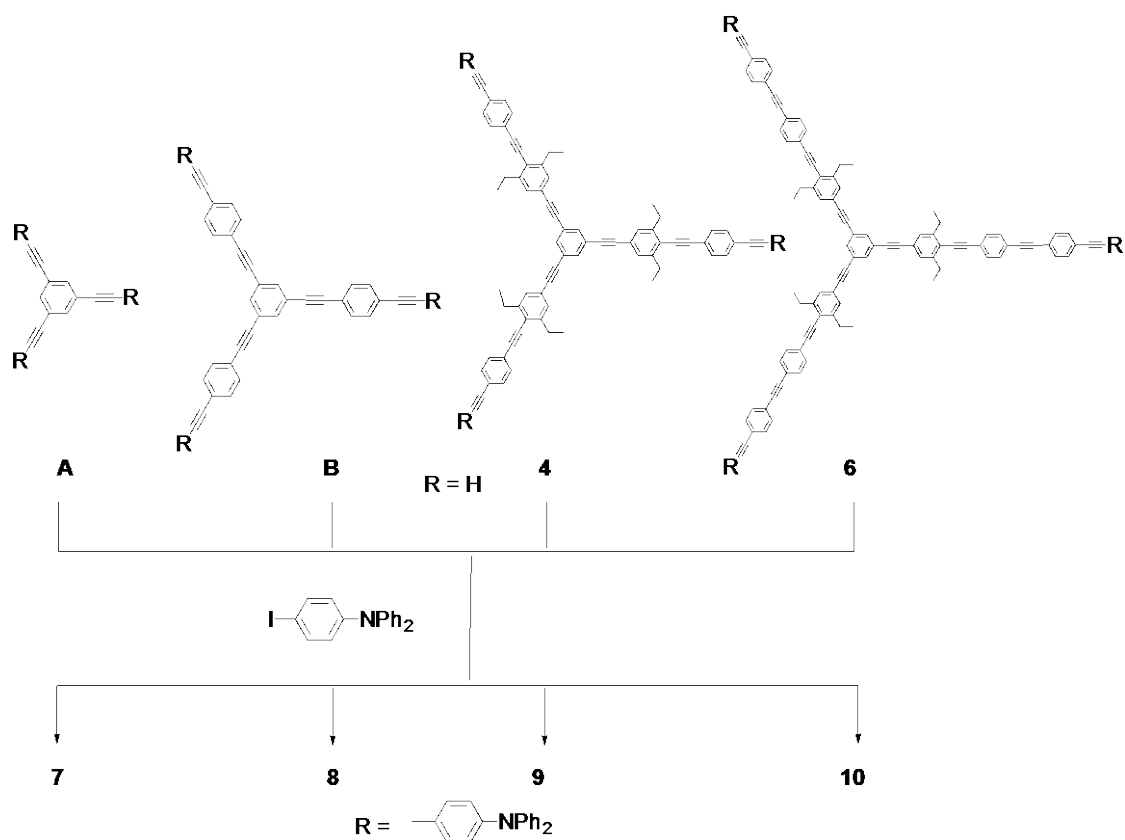
Synthesis of 1,3,5-{4-(4-Me₃SiC≡CC₆H₄-1-C≡C-4-C₆H₄-1-C≡C)-3,5-Et₂C₆H₂C≡C}₃C₆H₃ (5)

1,3,5-(4-HC≡C-3,5-Et₂C₆H₂-1-C≡C)₃C₆H₃ (**2**, 0.440 g, 0.710 mmol) and 4-Me₃SiC≡CC₆H₄-1-C≡C-4-C₆H₄-1-I (0.880 g, 2.20 mmol) were dissolved in NEt₃/THF (30 mL/30 mL), and Pd(PPh₃)₄ (25 mg, 0.022 mmol) and CuI (15 mg, 0.079 mmol) were added. The mixture was stirred at 80 °C overnight. The reaction mixture was allowed to cool to room temperature, filtered to remove the precipitate, and the solvent was then removed under reduced pressure. The residue was passed through a short column using hexane/CH₂Cl₂ (4:1) as eluent. Reduction in volume of the solvent afforded 1,3,5-{4-(4-Me₃SiC≡CC₆H₄-1-C≡C-4-C₆H₄-1-C≡C)-3,5-Et₂C₆H₂C≡C}₃C₆H₃ (**5**) as a light-yellow solid (0.660 g, 0.460 mmol, 64%). IR (CH₂Cl₂): ν(C≡C) 2159 cm⁻¹; UV-vis (CH₂Cl₂): 356 [30.5]; ¹H NMR (400 MHz, CDCl₃): δ 7.68 (s, 3H, CH aromatic), 7.52-7.44 (m, 24H, CH aromatic), 7.30 (s, 6H, CH aromatic), 2.92 (q, *J* = 7.5 Hz, 12H, CH₂CH₃), 1.34 (t, *J* = 7.5 Hz, 18H, CH₂CH₃), 0.26 (s, 27H, Si(CH₃)₃) ppm; ¹³C NMR (101 MHz, CDCl₃): δ 146.71, 134.16, 132.02, 131.70, 131.50, 131.40, 128.66, 124.15, 123.71, 123.23, 123.14, 122.94, 122.59, 122.04, 104.68, 98.42, 96.57, 91.12, 91.06, 89.03, 88.54, 28.01, 14.68, 0.01 ppm; HRMS (ESI): *m/z* calcd for C₁₀₅H₉₀Si₃: 1434.6350; found 1434.6359.

Synthesis of 1,3,5-{4-(4-HC≡CC₆H₄-1-C≡C-4-C₆H₄-1-C≡C)-3,5-Et₂C₆H₂-1-C≡C}₃C₆H₃ (6)

1,3,5-{4-(4-Me₃SiC≡CC₆H₄-1-C≡C-4-C₆H₄-1-C≡C)-3,5-Et₂C₆H₂-1-C≡C}₃C₆H₃ (**5**, 0.660 g, 0.460 mmol) was dissolved in THF (30 mL) and [nBu₄N]F (1.0 M in THF, 3 mL, 3.0 mmol) was added. The resulting solution was stirred at ambient temperature for 3 h. After removing the solvent, the residue was passed through a short pad of silica using hexane/CH₂Cl₂ (5:1) as eluent. Reduction in volume of the solvent afforded 1,3,5-{4-(4-HC≡CC₆H₄-1-C≡C-4-C₆H₄-1-C≡C)-3,5-Et₂C₆H₂-1-C≡C}₃C₆H₃ (**6**) as a light-yellow solid (0.540 g, 0.440 mmol, 96%). IR (CH₂Cl₂): ν(C≡C) 2108 cm⁻¹; UV-vis (CH₂Cl₂): 354 [25.5]; ¹H NMR (400 MHz, CDCl₃): δ 7.68 (s, 3H, CH aromatic); 7.52 (s, 12H, CH aromatic), 7.49 (s, 12H, CH aromatic), 7.30 (s, 6H, CH aromatic), 3.19 (s, 3H, HC≡C), 2.92 (q, *J* = 7.5 Hz, 12H, CH₂CH₃), 1.34 (t, *J* = 7.5 Hz, 18H, CH₂CH₃) ppm; ¹³C NMR (101 MHz, CDCl₃): δ 146.65, 134.08, 132.12, 131.65, 131.50, 131.32, 128.60, 124.09, 123.71, 123.51, 122.81, 122.53, 122.14, 121.97, 98.32, 91.10, 90.97, 90.77, 88.94, 88.50, 83.25, 79.05, 27.94, 14.59 ppm.

Preparation of aniline compounds **7 - 10**



General procedure: the octupolar alkyne (1 mmol) and 4-iodo-*N,N'*-diphenylaniline (1.450 g, 4.00 mmol) were dissolved in NEt₃/THF (30 mL/30 mL) and Pd(PPh₃)₄ (0.092 g, 0.080 mmol) and CuI (0.019 g, 0.10 mmol) were added. The resulting solution was stirred at 80 °C overnight. The reaction mixture was allowed to cool to room temperature, filtered to remove the precipitate, and the solvent was then removed under reduced pressure. The residue was passed through a short column using hexane/CH₂Cl₂ (2:1) as eluent. Reduction in volume of the solvent afforded a yellow-green solid. Compounds **7-10** decomposed slowly over a period of days, precluding elemental analysis.

*Synthesis of 1,3,5-(4-Ph₂NC₆H₄-1-C≡C)₃C₆H₃ (**7**)*

7 was prepared by the general procedure. Yield: (0.220 g, 0.250 mmol, 25%). IR (CH₂Cl₂): ν(C≡C) 2203 cm⁻¹; UV-vis (CH₂Cl₂): 370 [12.4]; ¹H NMR (400 MHz, CDCl₃): δ 7.57 (s, 3H, core CH aromatic), 7.37-7.28 (m, 18H, CH aromatic), 7.13-6.99 (m, 24H, CH aromatic); ¹³C NMR (101 MHz, CDCl₃): δ 148.21, 147.17, 133.42, 132.65, 129.43, 125.10, 124.29, 123.67, 122.16, 115.61, 90.74, 87.33; HRMS (ESI): *m/z* calcd for C₆₆H₄₅N₃: 879.3613; found: 879.3608.

*Synthesis of 1,3,5-(4-Ph₂NC₆H₄-1-C≡C-4-C₆H₄-1-C≡C)₃C₆H₃ (**8**)*

8 was prepared by the general procedure. Yield: (0.190 g, 0.160 mmol, 16%). IR (CH₂Cl₂): ν(C≡C) 2202 cm⁻¹; UV-vis (CH₂Cl₂): 382 [15.4], 307 [11.6]; ¹H NMR (400 MHz, CDCl₃): δ 7.65 (s, 3H, core CH aromatic), 7.50 (s, 12H, CH aromatic), 7.39-7.26 (m, 18H, CH aromatic), 7.13-7.00 (m, 24H, CH aromatic) ppm; ¹³C NMR (101 MHz, CDCl₃): δ 148.17, 147.13, 134.12, 132.60, 131.61, 131.42,

129.42, 125.08, 123.98, 123.66, 122.72, 122.14, 122.09, 115.64, 91.97, 90.48, 89.41, 88.35 ppm; HRMS (ESI): m/z calcd for $C_{90}H_{57}N_3$: 1179.4552; found: 1179.4590.

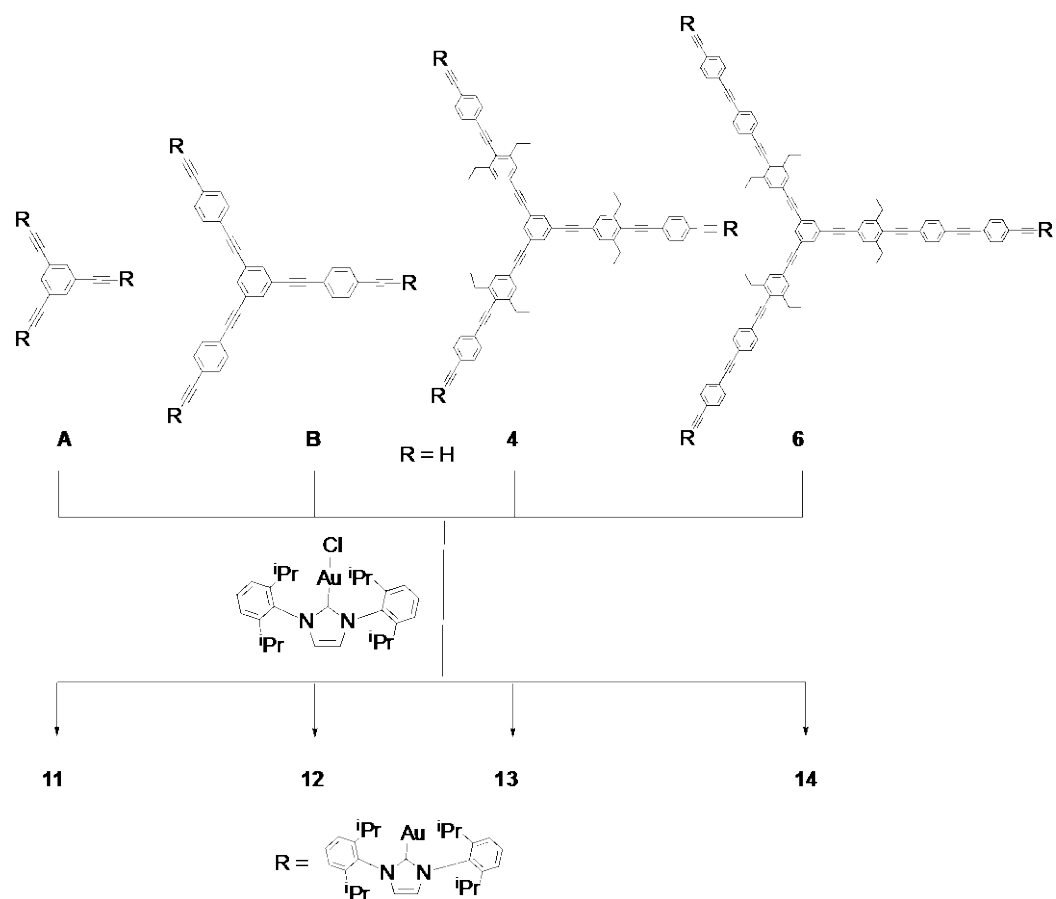
Synthesis

of

1,3,5-{4-(4- $Ph_2NC_6H_4$ -1- $C\equiv C$ -4- C_6H_4 -1- $C\equiv C$ -4- C_6H_4 -1- $C\equiv C$)-3,5- $Et_2C_6H_2$ -1- $C\equiv C$ } $_3C_6H_3$ (**10**)

10 was prepared by the general procedure. Yield: (0.310 g, 0.159 mmol, 16%). IR (CH_2Cl_2): $\nu(C\equiv C)$ 2206 cm^{-1} ; UV-vis (CH_2Cl_2): 378 [30.1]; 1H NMR (400 MHz, $CDCl_3$): δ 7.67 (s, 3H, core CH aromatic), 7.52-7.28 (m, 48H, CH aromatic), 7.15-6.98 (m, 24H, CH aromatic), 2.92 (q, $J = 7.5$ Hz, 12H, CH_2CH_3), 1.34 (t, $J = 7.5$ Hz, 18H, CH_2CH_3) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 148.14, 147.12, 146.62, 134.06, 132.58, 131.61, 131.54, 131.40, 131.32, 129.42, 128.58, 125.07, 124.07, 123.77, 123.65, 123.54, 122.97, 122.50, 122.37, 122.13, 121.99, 115.65, 98.39, 91.91, 91.22, 90.99, 90.87, 88.95, 88.41, 88.44, 27.93, 14.60 ppm; MS (MALDI) m/z calcd for $C_{150}H_{105}N_3$: 1947.83; found: 1947.77.

Preparation of NHC-Au acetylide complexes **11** - **14**



General procedure: the alkyne (1 eq., 0.100 mmol) was dissolved in THF (50 mL) and potassium *tert*-butoxide (0.138 g, 1.00 mmol) was added. The solution was then stirred at 80 °C for 0.5 h. AuCl(NHC-*i*Pr) (0.186 g, 0.300 mmol) was added, and the solution was stirred at 80 °C overnight. The reaction mixture was filtered to remove the precipitate and the solvent was removed under reduced pressure. The residue was dissolved in CH_2Cl_2 (2 mL) and the solution was slowly added dropwise to

stirring hexane (200 mL). The mixture was filtered and the white solid collected, washed with hexane, and dried.

Synthesis of 1,3,5-[(NHC-ⁱPr)Au]C≡C₃C₆H₃ (11)

The compound 1,3,5-[(NHC-ⁱPr)Au]C≡C₃C₆H₃ (**11**) has been reported previously, prepared from the Au(OH)(NHC-ⁱPr) precursor (84%).¹ In the present case, **11** was prepared by the general procedure with a similar yield to the earlier report. Yield: (0.150 g, 0.080 mmol, 80%). IR (CH₂Cl₂): ν(C≡C) 2106 cm⁻¹; UV-vis (CH₂Cl₂): 290 [7.7]; ¹H NMR (400 MHz, CDCl₃): δ 7.47 (t, *J* = 8.0 Hz, 6H, CH aromatic), 7.27 (d, *J* = 8.0 Hz, 12H, CH aromatic), 7.10 (s, 6H, CH imidazole), 6.96 (s, 3H, core CH aromatic), 2.59 (m, 12H, CH(CH₃)₂), 1.34 (d, *J* = 7.0 Hz, 36H, CH(CH₃)₂), 1.20 (d, *J* = 6.9 Hz, 36H, CH(CH₃)₂) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 191.59, 145.57, 134.31, 133.88, 130.41, 127.47, 124.63, 124.12, 122.97, 103.92, 28.78, 24.54, 24.06 ppm; HRMS (ESI): *m/z* calcd for C₉₃H₁₁₁Au₃N₆: 1903.7945 [M+H]⁺; found: 1903.7944.

Synthesis of 1,3,5-[(NHC-ⁱPr)Au]C≡C-4-C₆H₄-1-C≡C₃C₆H₃ (12)

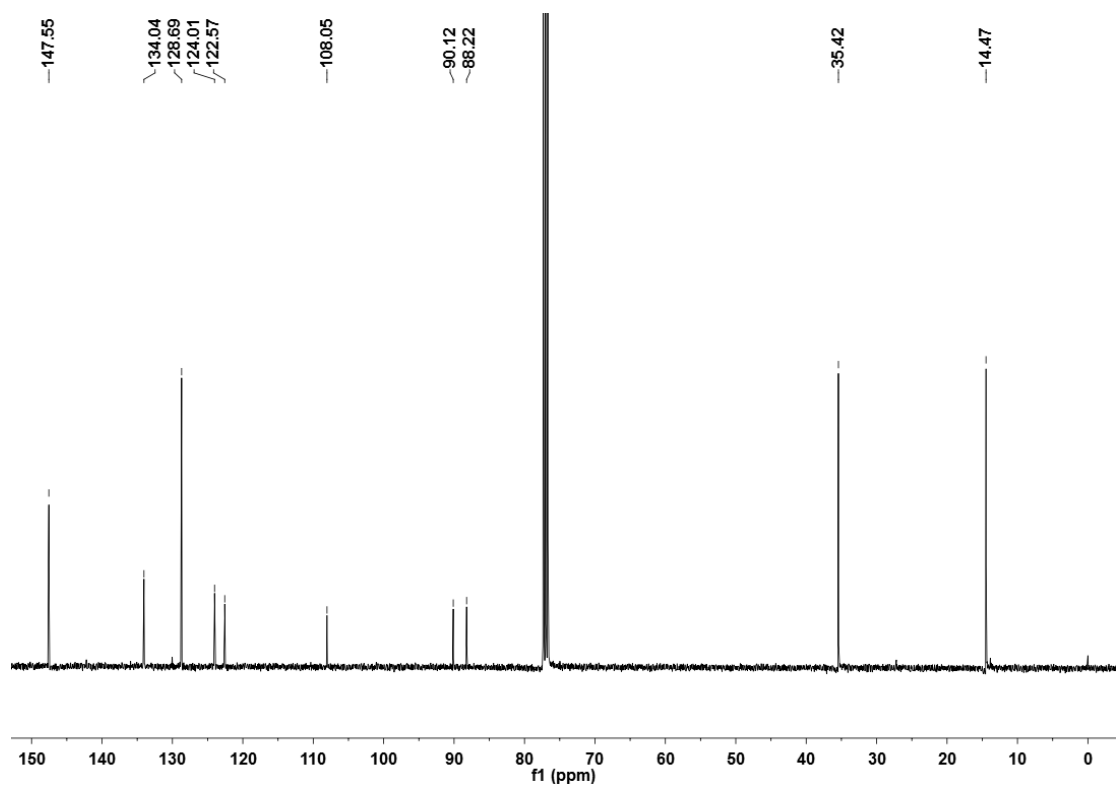
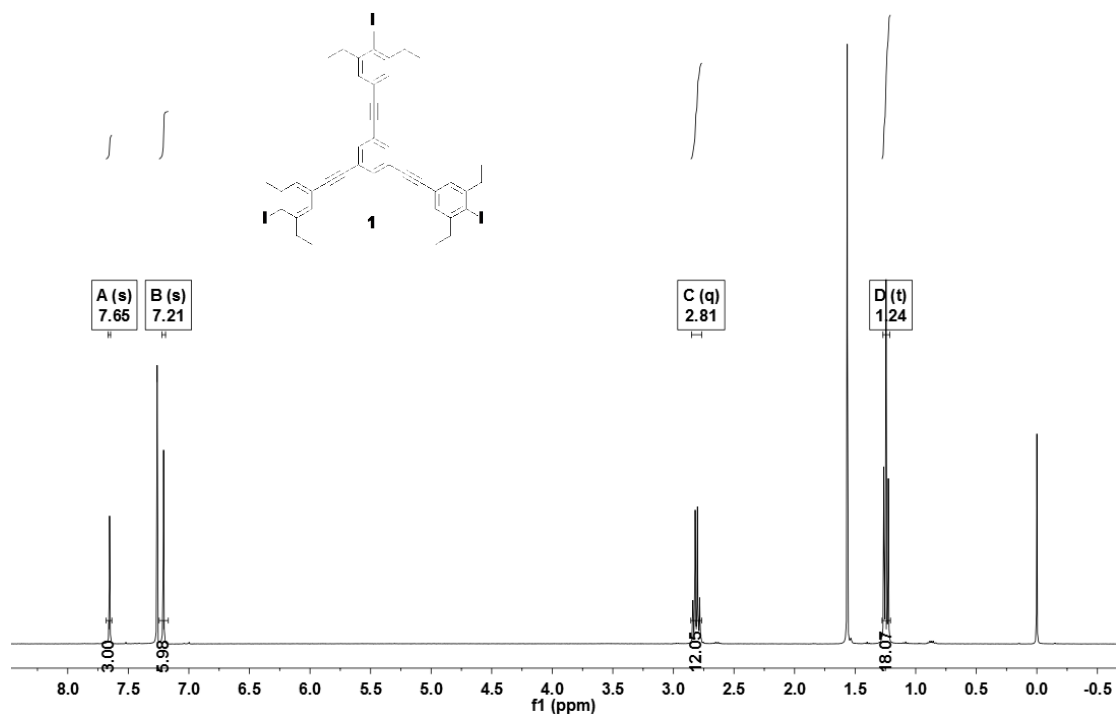
12 was prepared by the general procedure. Yield: (0.165 g, 0.075 mmol, 75%). IR (CH₂Cl₂): ν(C≡C) 2109 cm⁻¹; UV-vis (CH₂Cl₂): 346 [14.1], 325 [16.2]; ¹H NMR (400 MHz, CDCl₃): δ 7.49 (t, *J* = 8.0 Hz, 6H, CH aromatic), 7.47 (s, 3H, core CH aromatic), 7.29 (d, *J* = 8.0 Hz, 12H, CH aromatic), 7.25 (s, 12H, CH aromatic), 7.12 (s, 6H, CH imidazole), 2.60 (m, 12H, CH(CH₃)₂), 1.38 (d, *J* = 7.0 Hz, 36H, CH(CH₃)₂), 1.21 (d, *J* = 7.0 Hz, 36H, CH(CH₃)₂) ppm; ¹³C NMR (101 MHz, CDCl₃): δ 190.91, 145.62, 134.27, 133.57, 132.66, 132.18, 130.97, 130.51, 126.47, 124.18, 124.06, 123.20, 119.75, 103.59, 90.85, 88.52, 28.83, 24.61, 24.03 ppm; HRMS (ESI): *m/z* calcd for C₁₁₇H₁₂₃Au₃N₆: 2203.8884 [M+H]⁺; found: 2203.9502.

Synthesis of 1,3,5-[4-[(NHC-ⁱPr)Au]C≡C-4-C₆H₄-1-C≡C)-3,5-Et₂C₆H₂-1-C≡C]₃C₆H₃ (13)

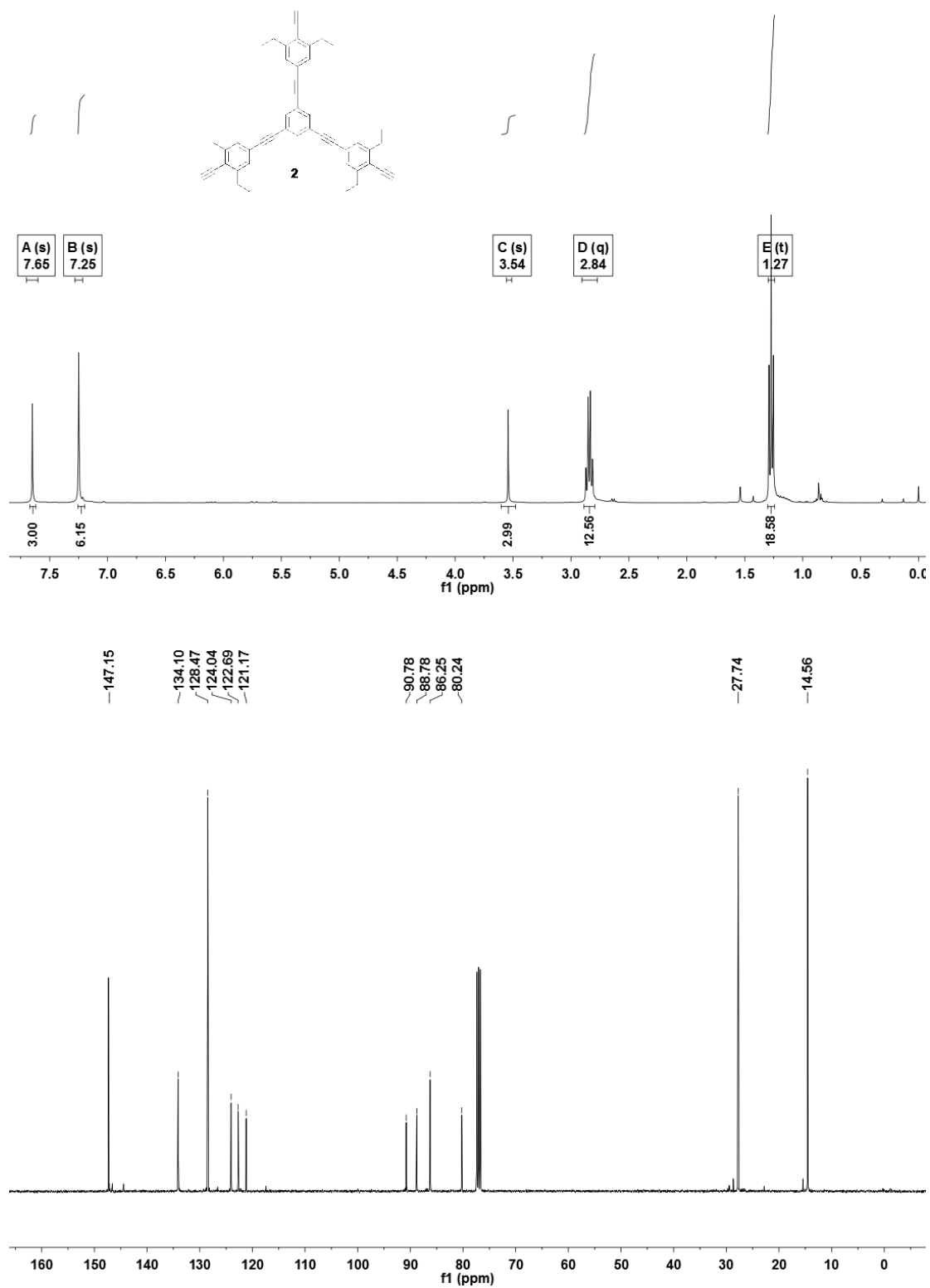
13 was prepared by the general procedure. Yield: (0.192 g, 0.072 mmol, 72%). IR (CH₂Cl₂): ν(C≡C) 2109 cm⁻¹; UV-vis (CH₂Cl₂): 362 [20.1], 348 [21.3]; ¹H NMR (400 MHz, CDCl₃): δ 7.62 (s, 3H, core CH aromatic), 7.50 (t, *J* = 8.0 Hz, 6H, CH aromatic), 7.30 (d, *J* = 8.0 Hz, 12H, CH aromatic), 7.28-7.27 (m, 12H, CH aromatic), 7.23 (s, 6H, CH aromatic), 7.13 (s, 6H, CH imidazole), 2.85 (q, *J* = 7.5 Hz, 12H, CH₂CH₃), 2.61 (m, 12H, CH(CH₃)₂), 1.39 (d, *J* = 7.0 Hz, 36H, CH(CH₃)₂), 1.28 (t, *J* = 7.5 Hz, 18H, CH₂CH₃), 1.22 (d, *J* = 7.0 Hz, 36H, CH(CH₃)₂) ppm; ¹³C NMR (101 MHz, CDCl₃): δ 190.83, 146.36, 145.63, 134.29, 133.94, 132.55, 132.25, 130.64, 130.52, 128.44, 126.26, 124.20, 124.08, 123.24, 122.49, 121.92, 120.56, 103.66, 99.33, 91.03, 88.67, 86.97, 28.84, 27.86, 24.64, 24.04, 14.54 ppm.

NMR spectra

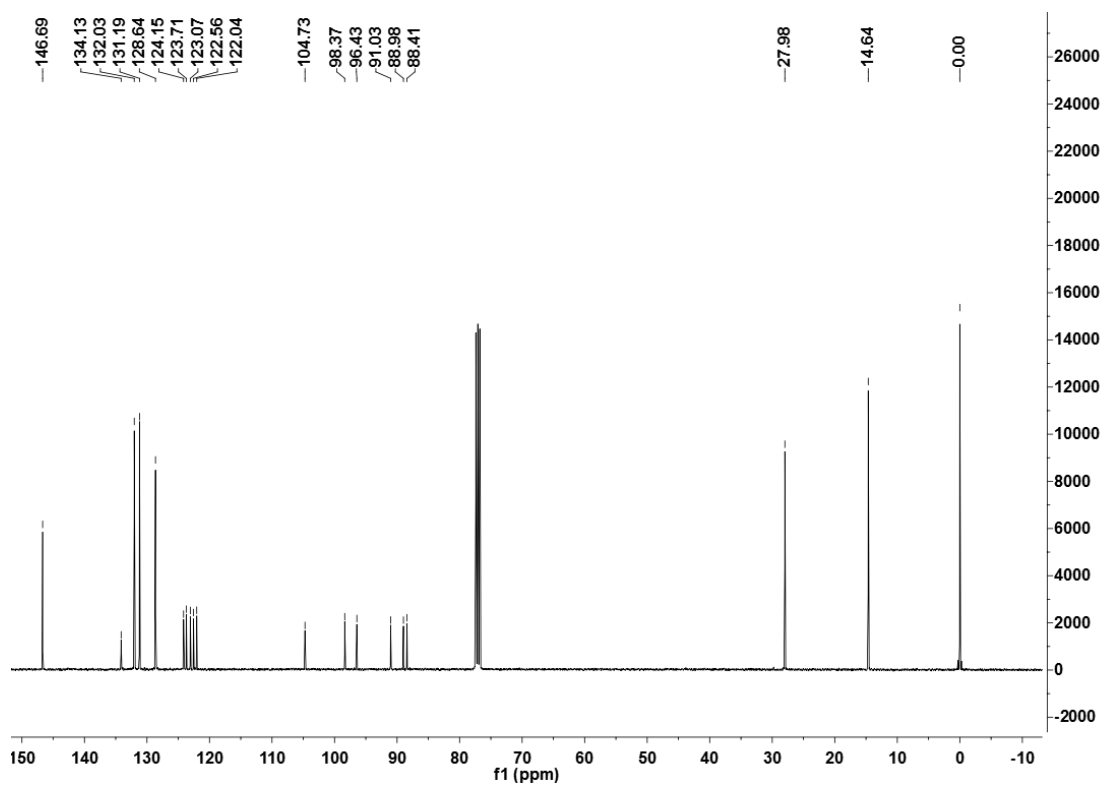
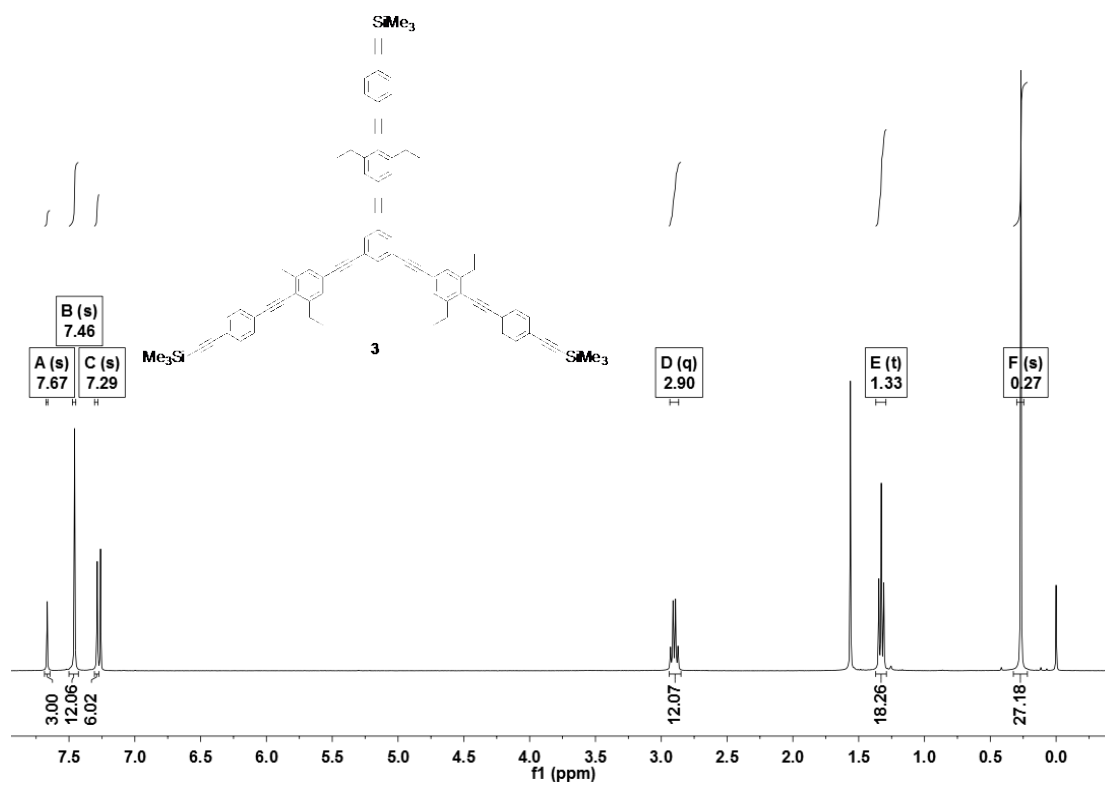
1,3,5-(4-*I*-3,5-Et₂C₆H₂-1-C≡C)₃C₆H₃ (**1**)



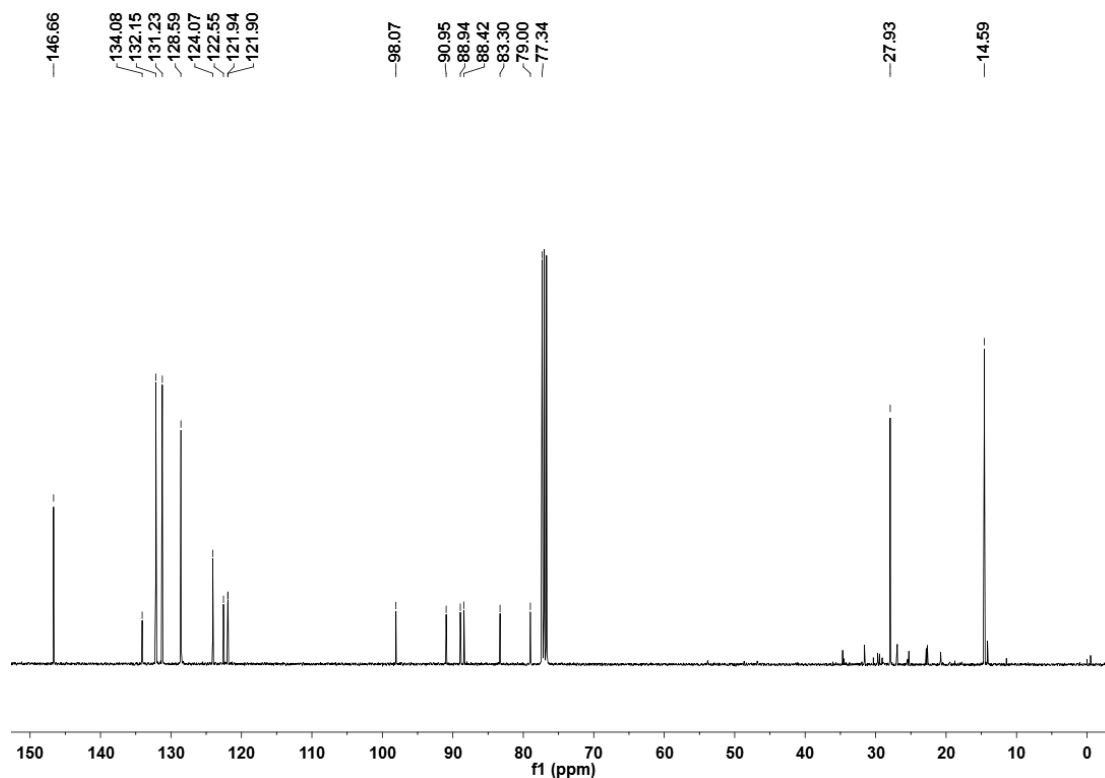
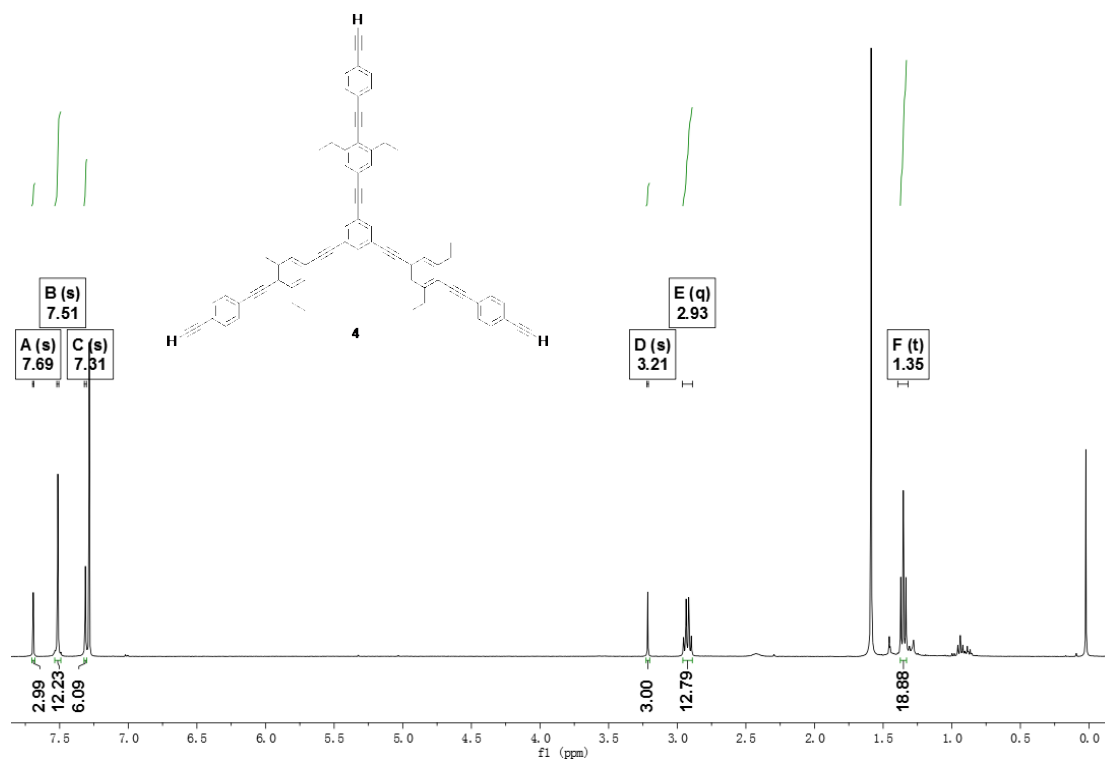
1,3,5-(4-HC≡C-3,5-Et₂C₆H₂-1-C≡C)₃C₆H₃ (2)



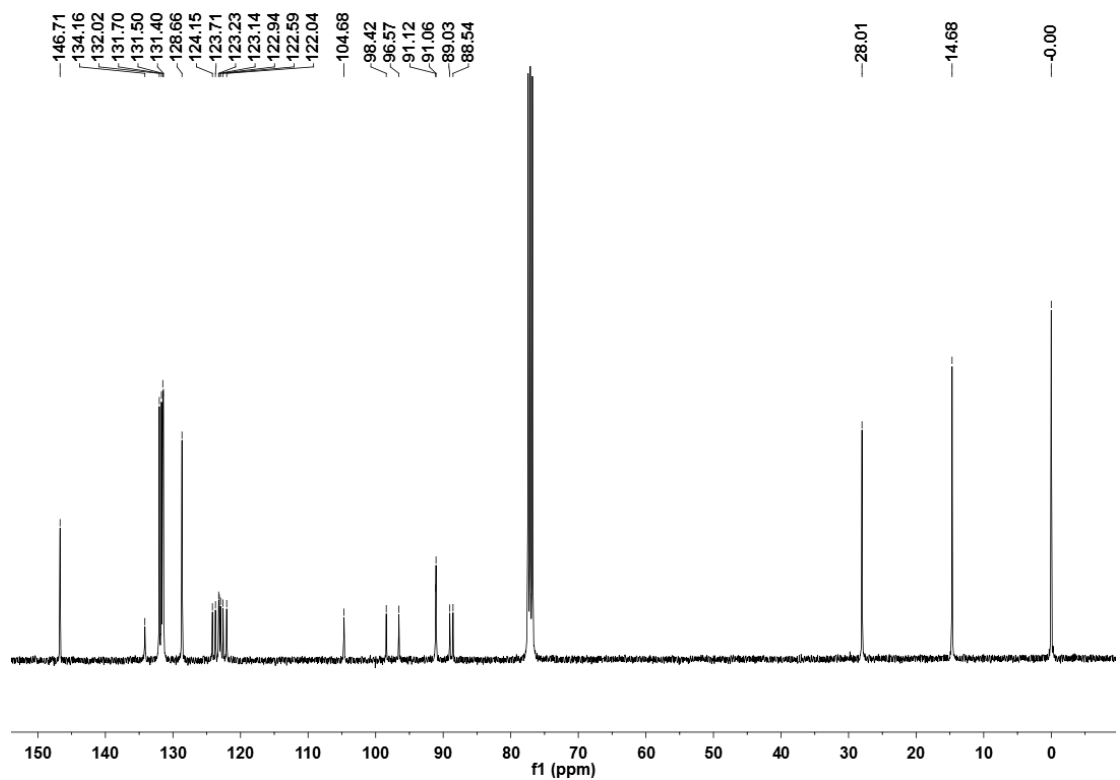
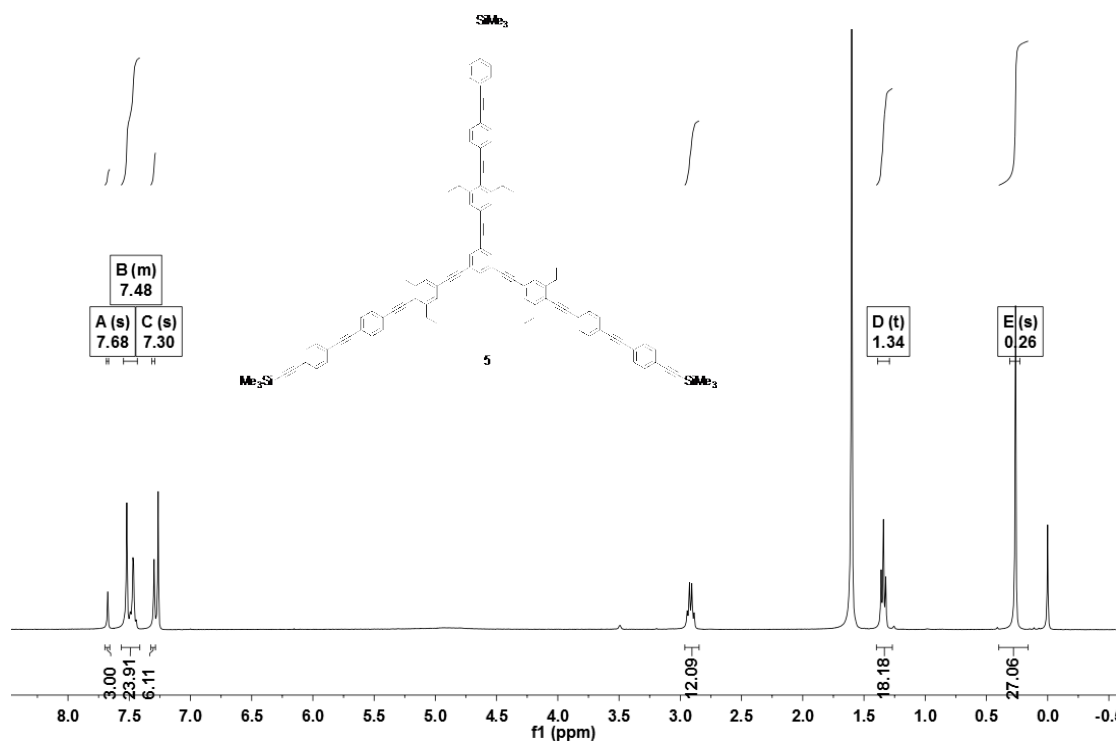
1,3,5-{4-(4-Me₃SiC≡CC₆H₄-1-C≡C)-3,5-Et₂C₆H₂-1-C≡C}₃C₆H₃ (3)



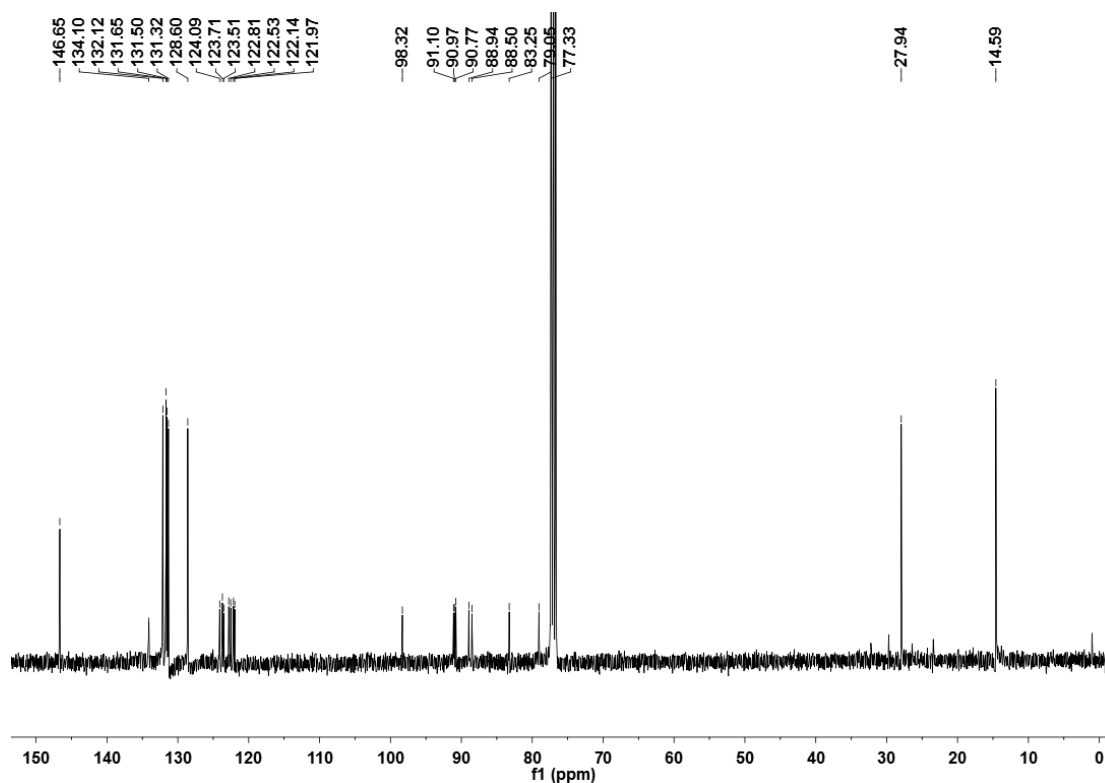
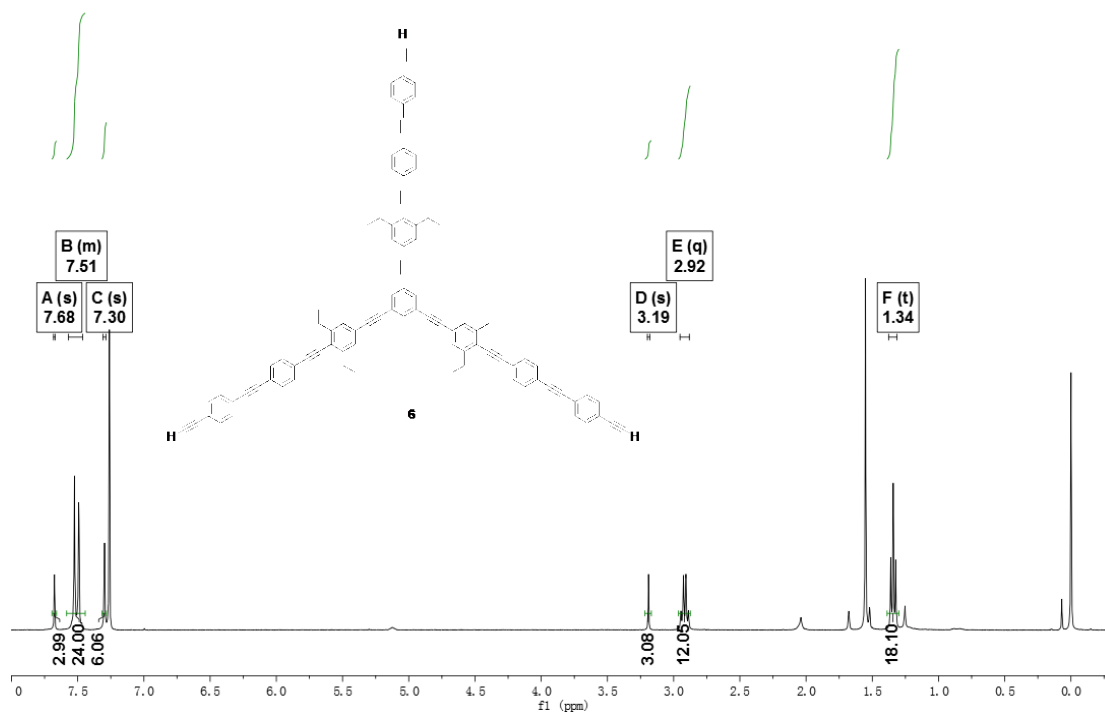
1,3,5-{4-(4-HC≡CC₆H₄-1-C≡C)-3,5-Et₂C₆H₂-1-C≡C)₃C₆H₃ (**4**)



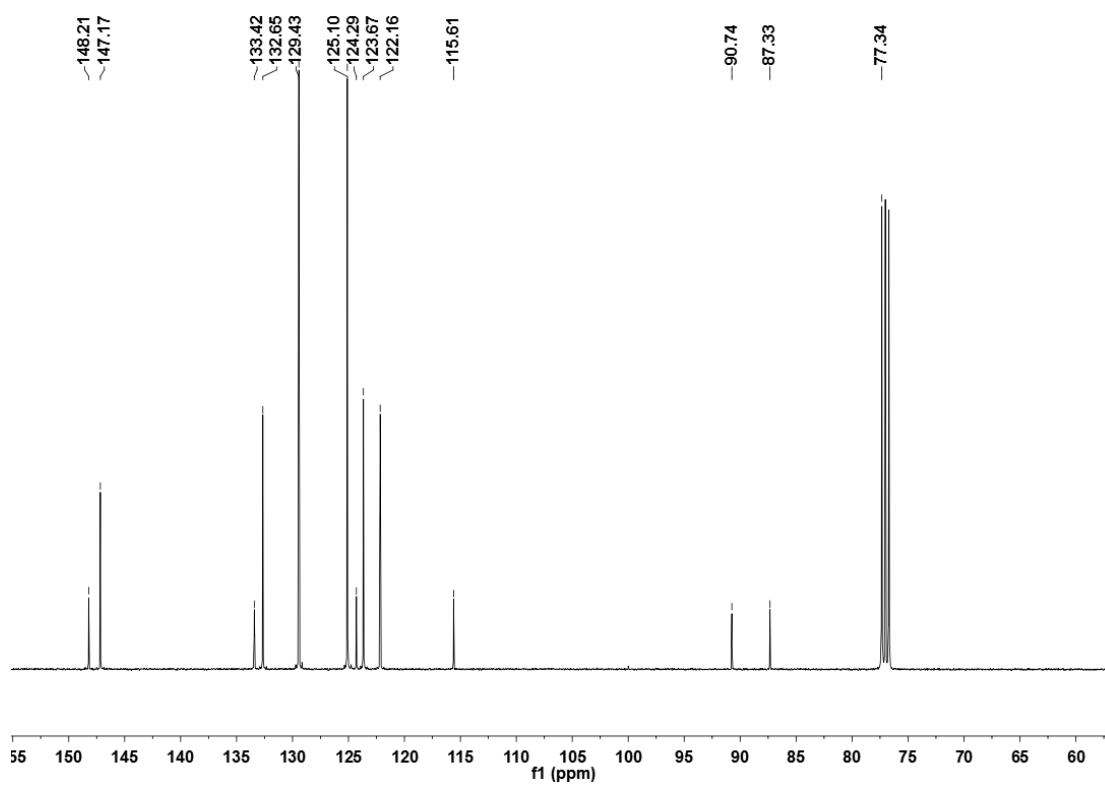
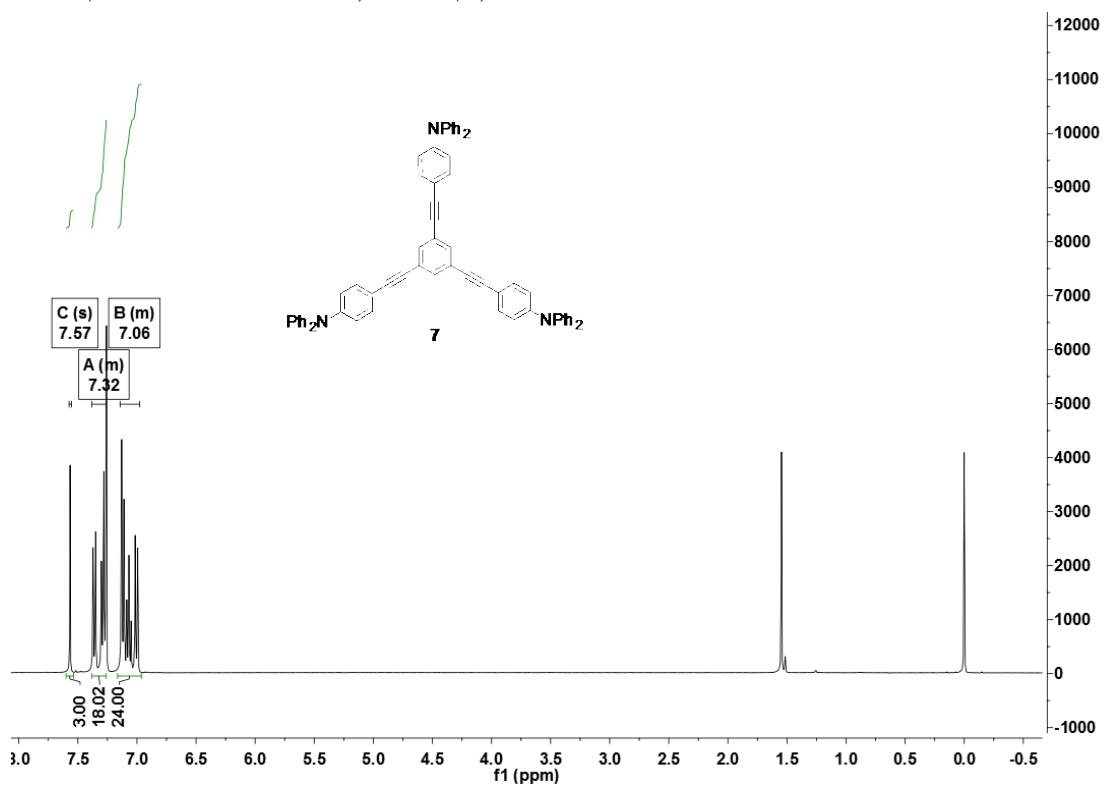
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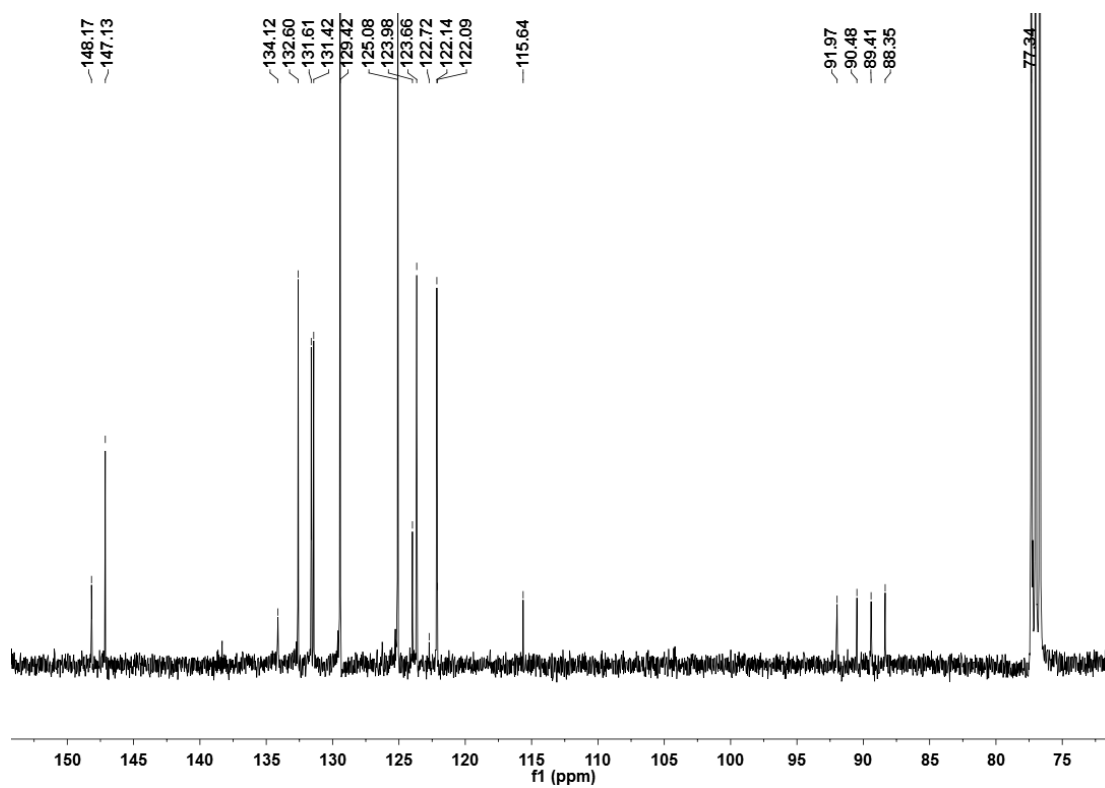
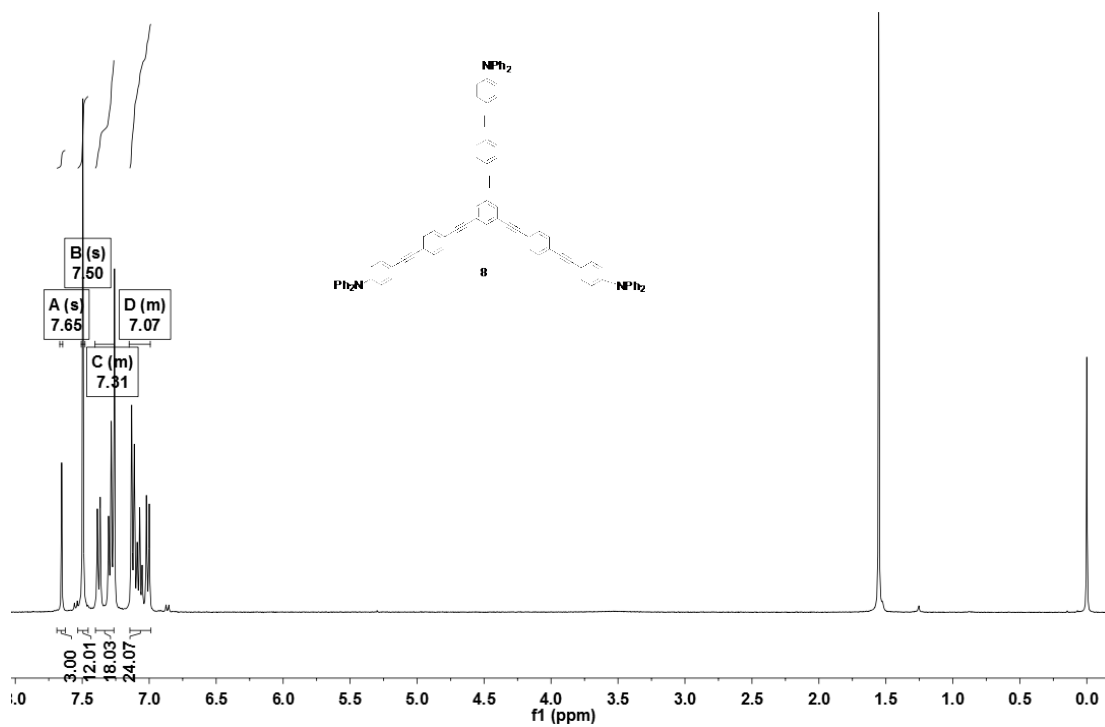
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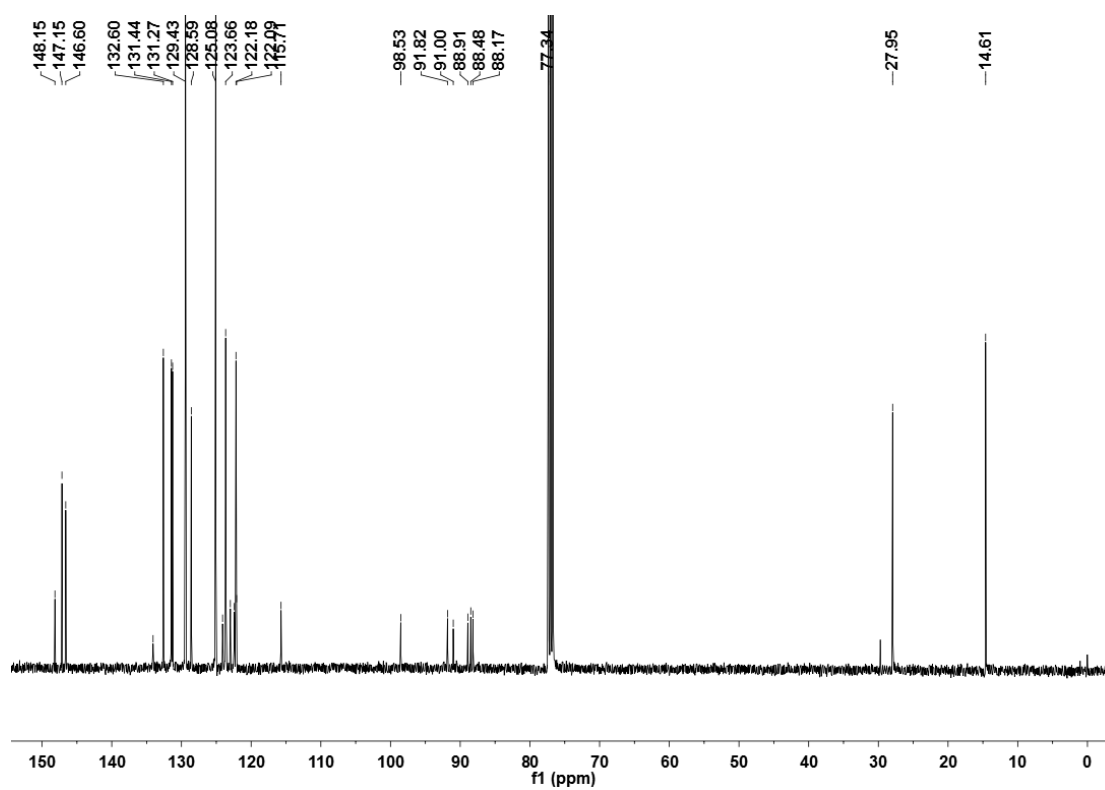
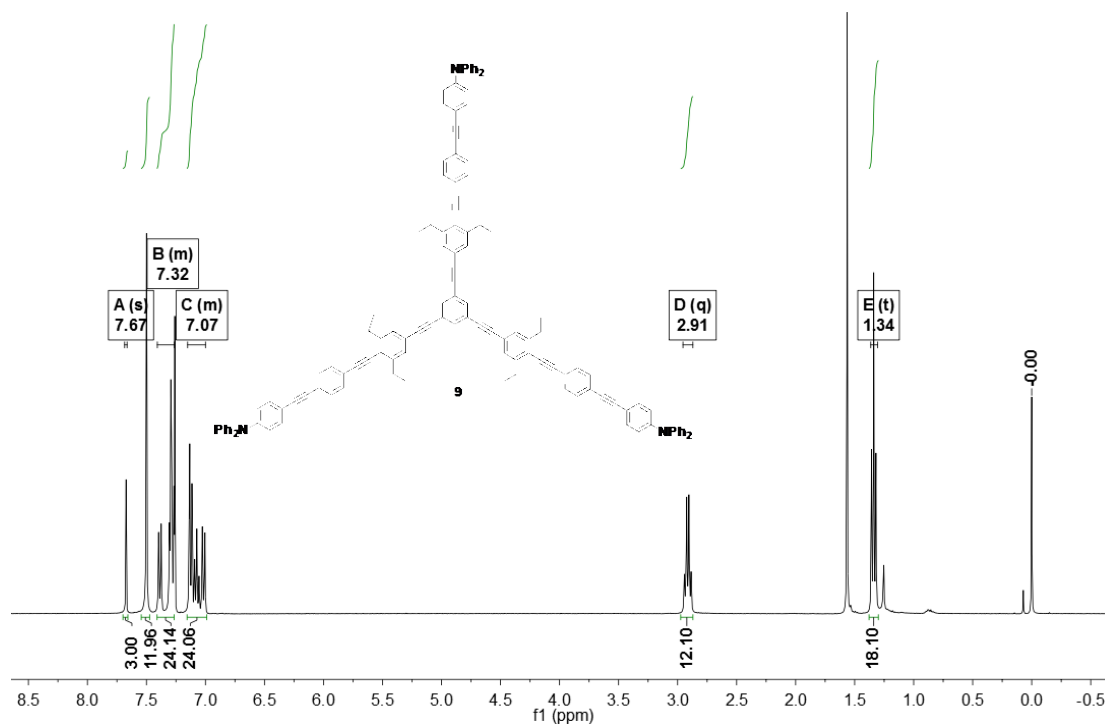
1,3,5-(4-Ph₂NC₆H₄-1-C≡C)₃C₆H₃ (7)



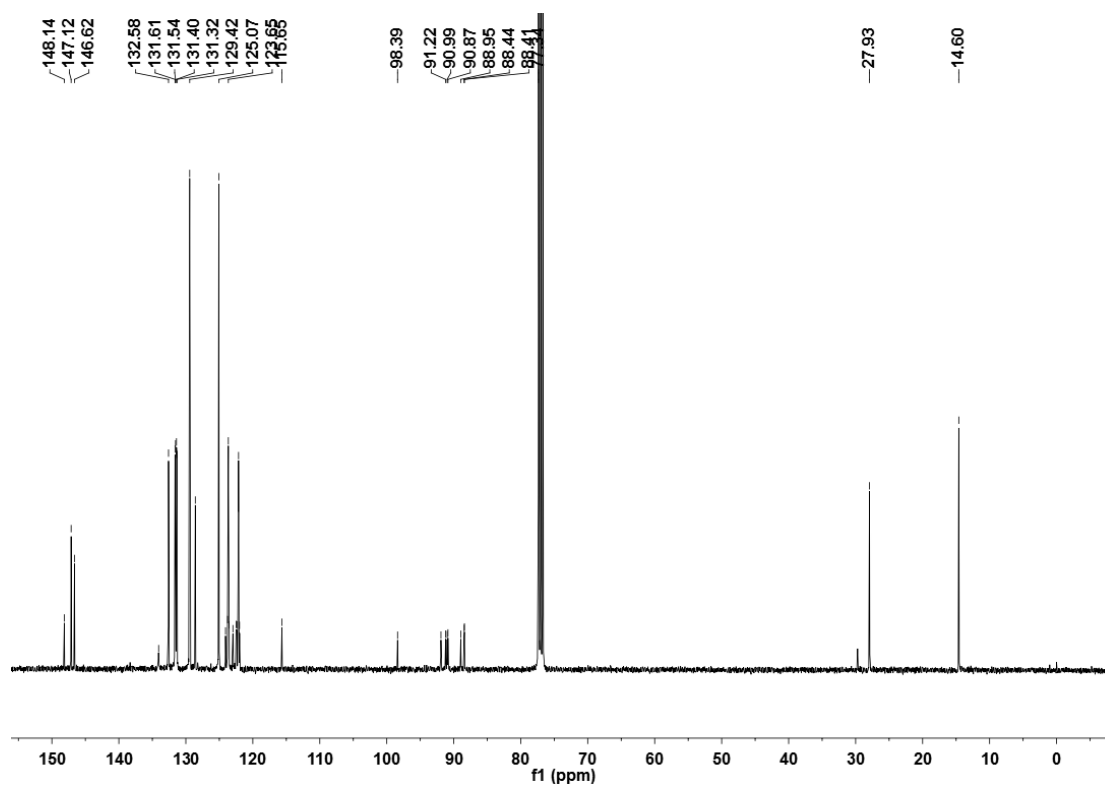
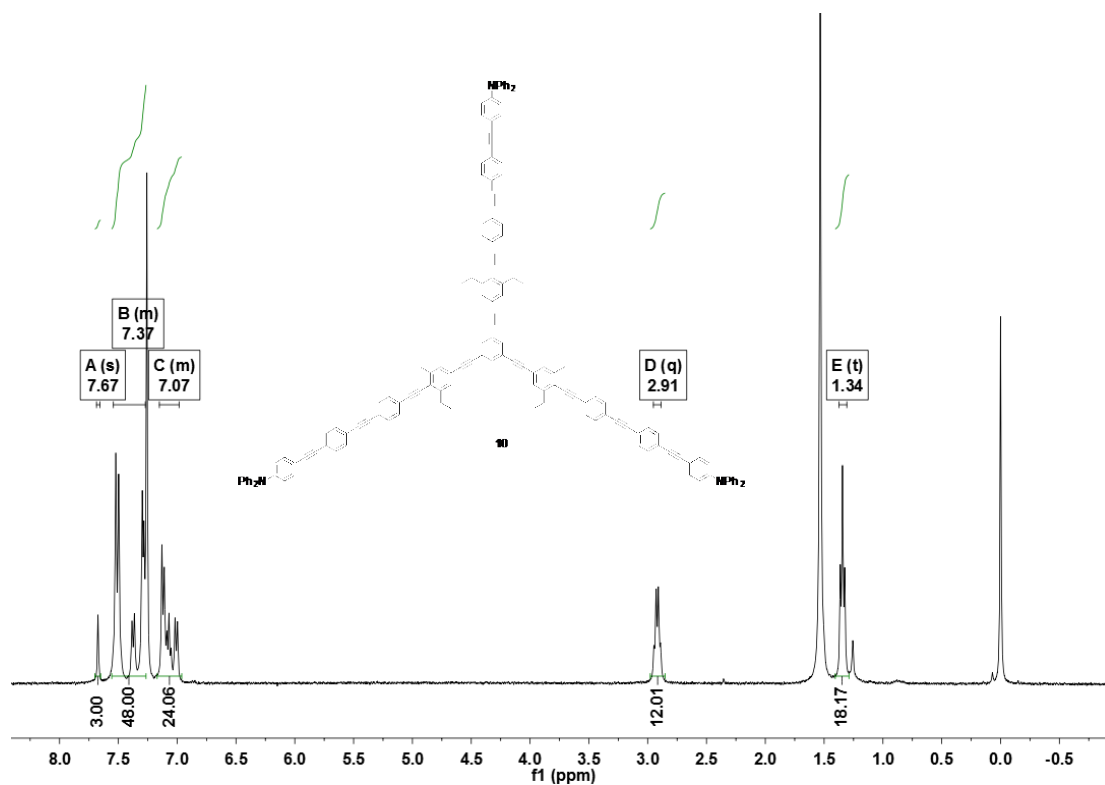
1,3,5-(4-Ph₂NC₆H₄-1-C≡C-4-C₆H₄-1-C≡C)₃C₆H₃ (8)



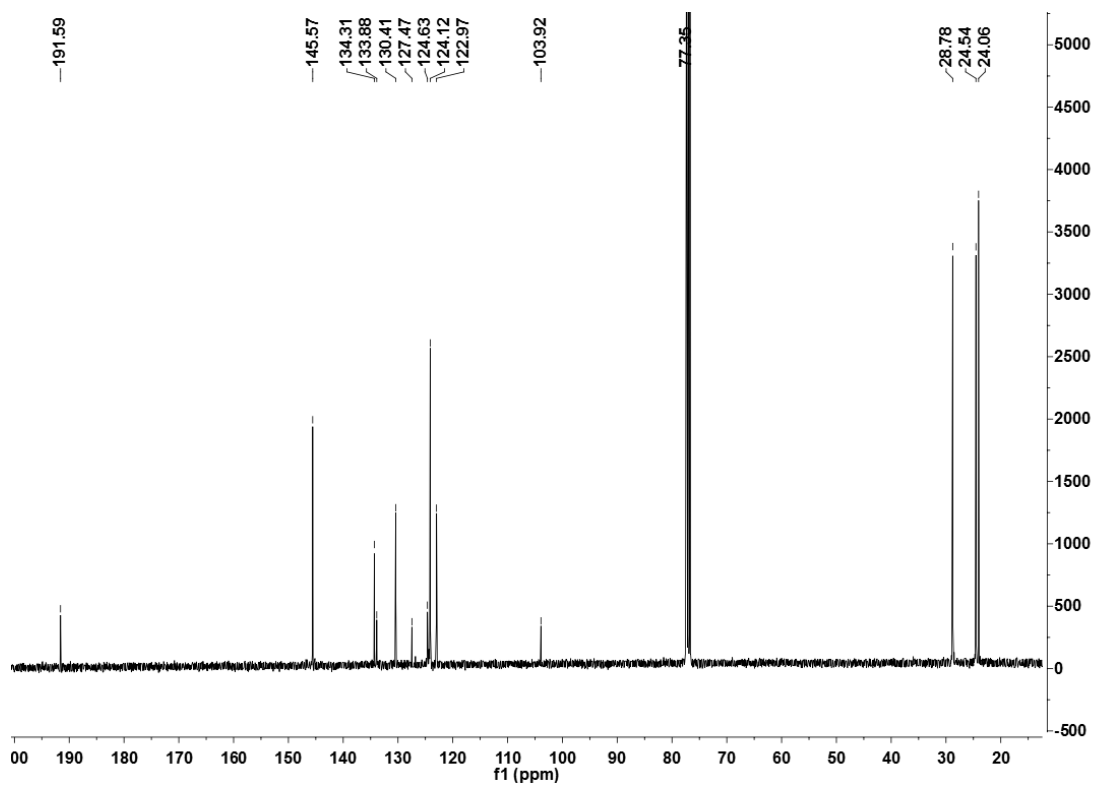
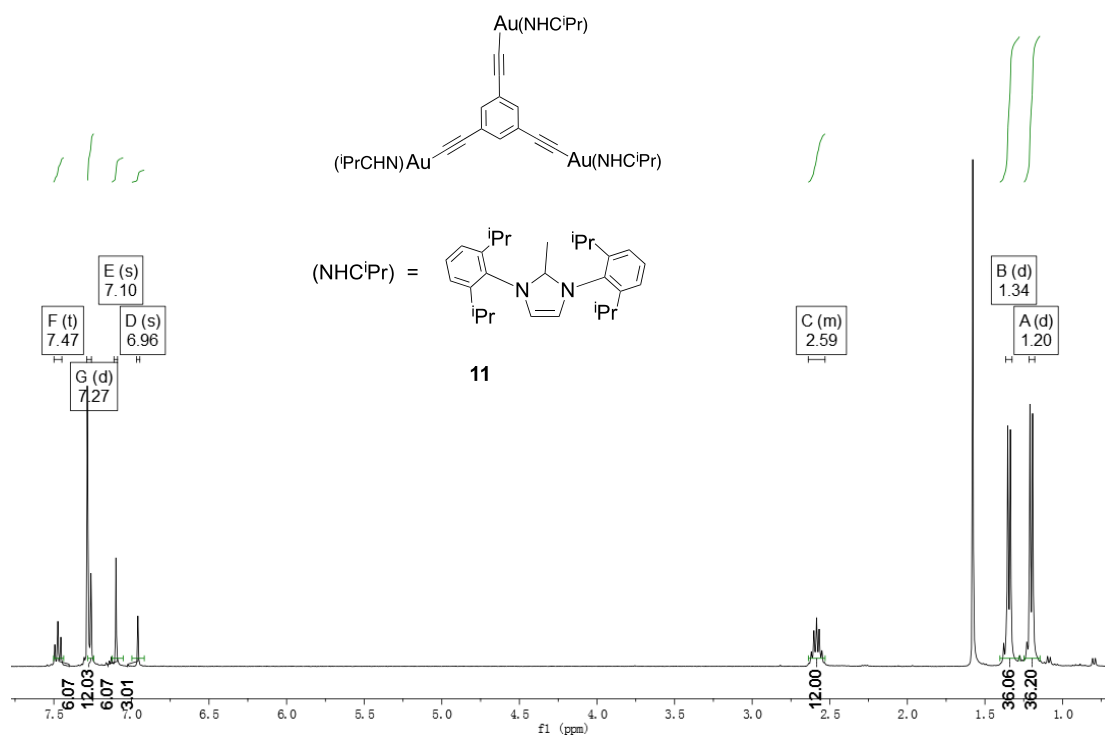
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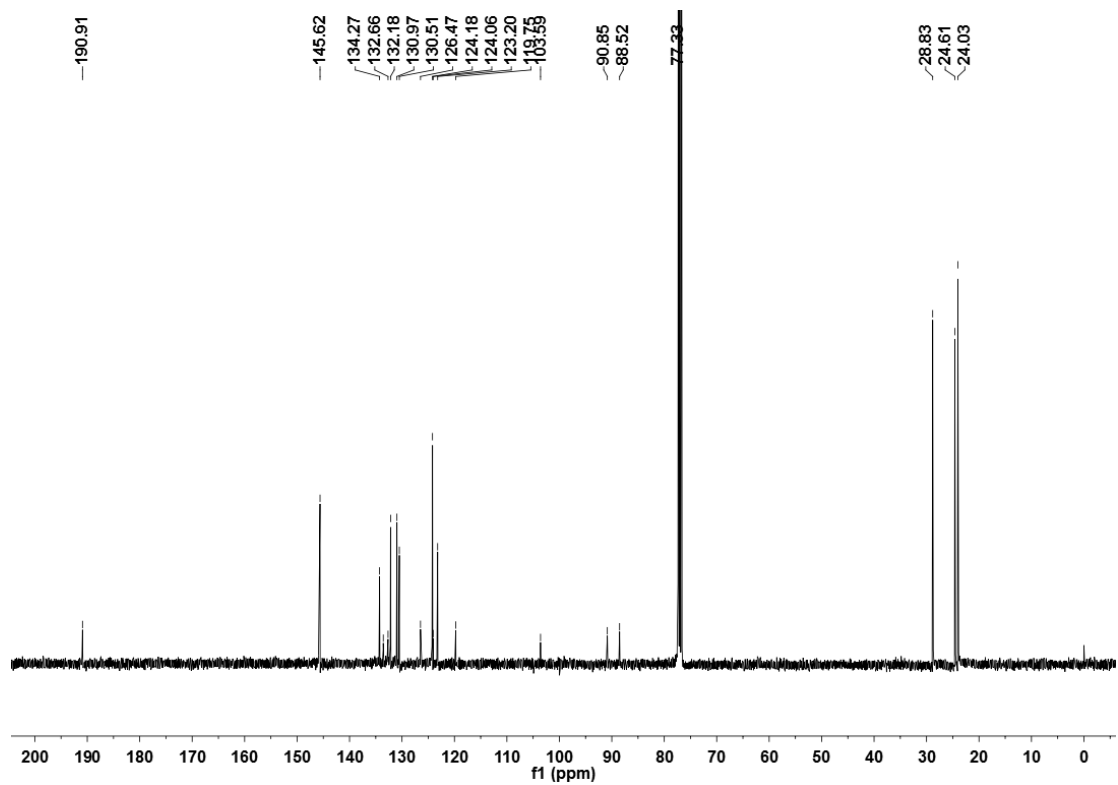
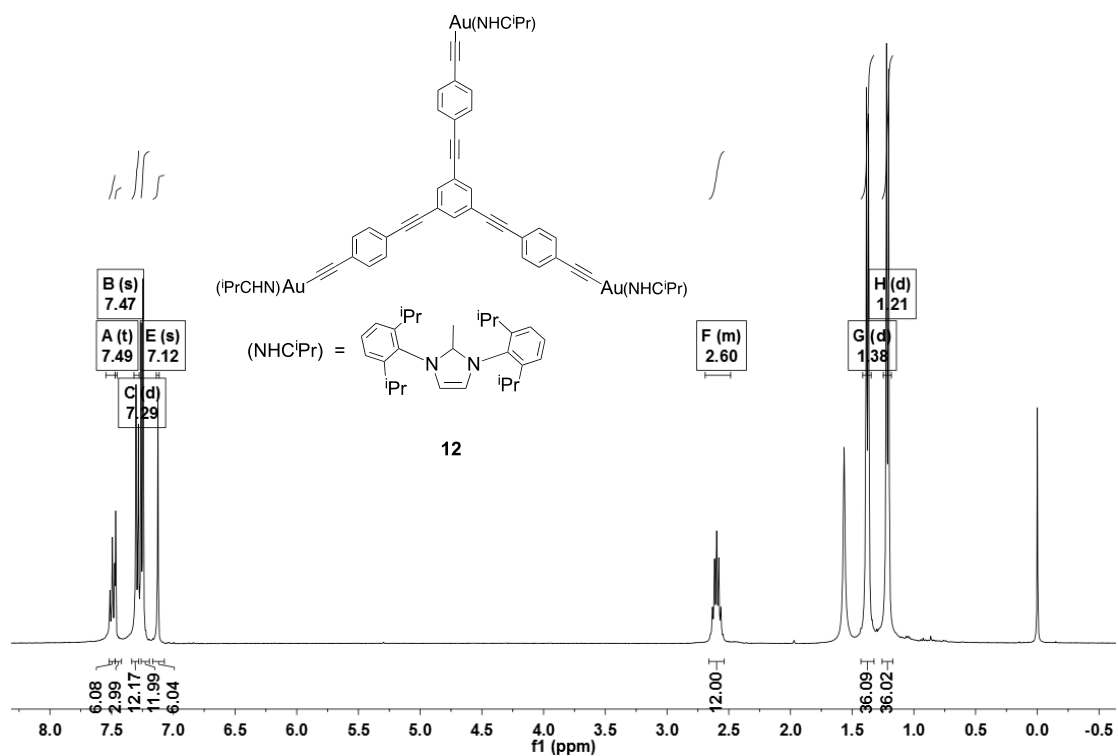
1,3,5-{4-(4-Ph₂NC₆H₄-1-C≡C-4-C₆H₄-1-C≡C-4-C₆H₄-1-C≡C)-3,5-Et₂C₆H₂-1-C≡C}₃
C₆H₃ (**10**)



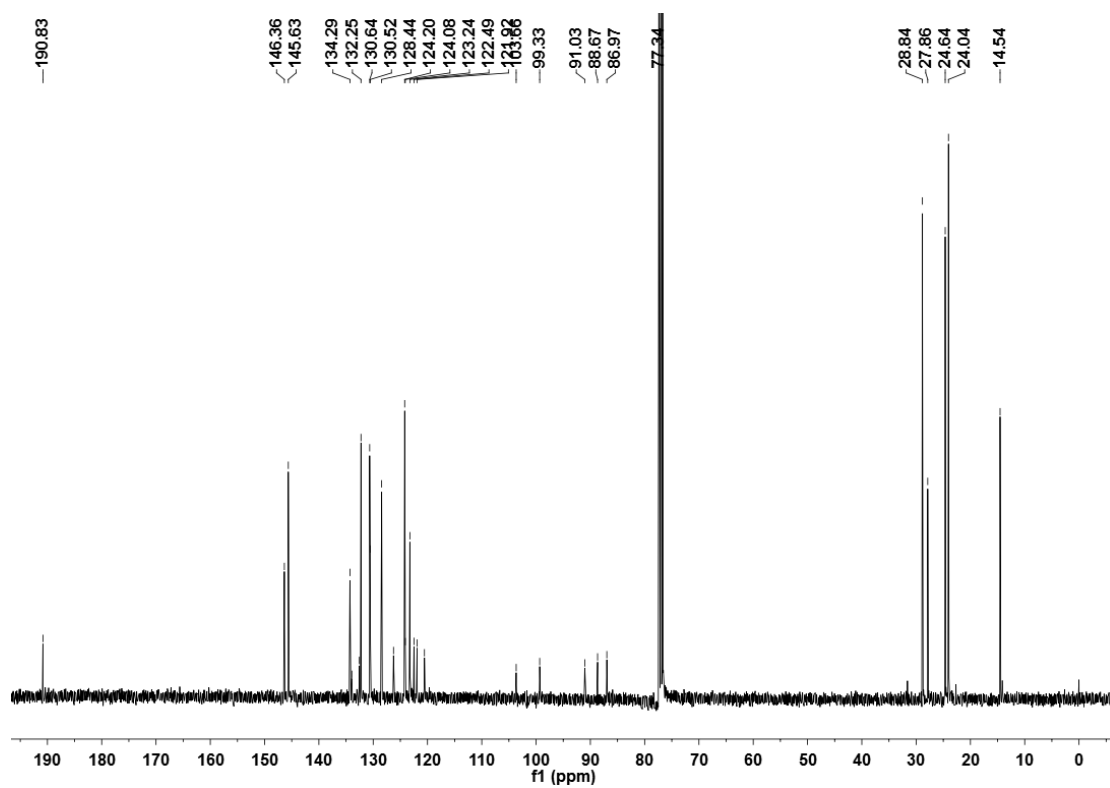
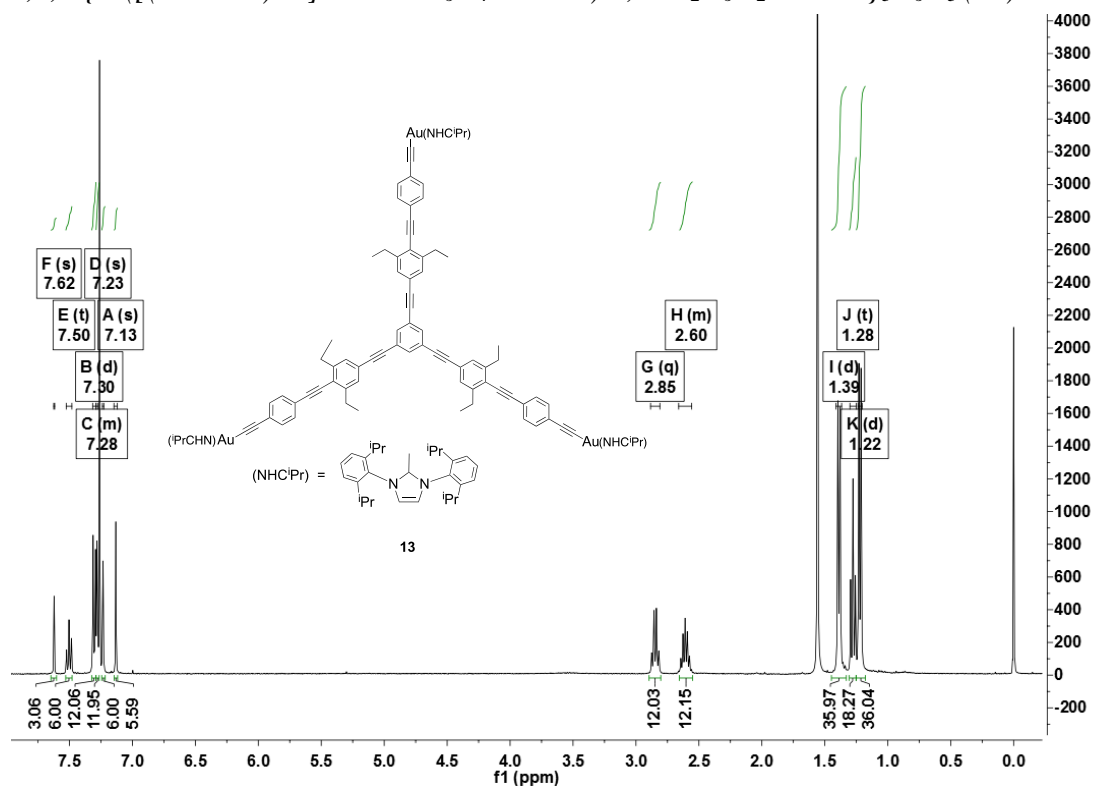
1,3,5-[[*(NHCⁱPr)Au*]*C*≡*C*]₃*C*₆*H*₃ (**11**)



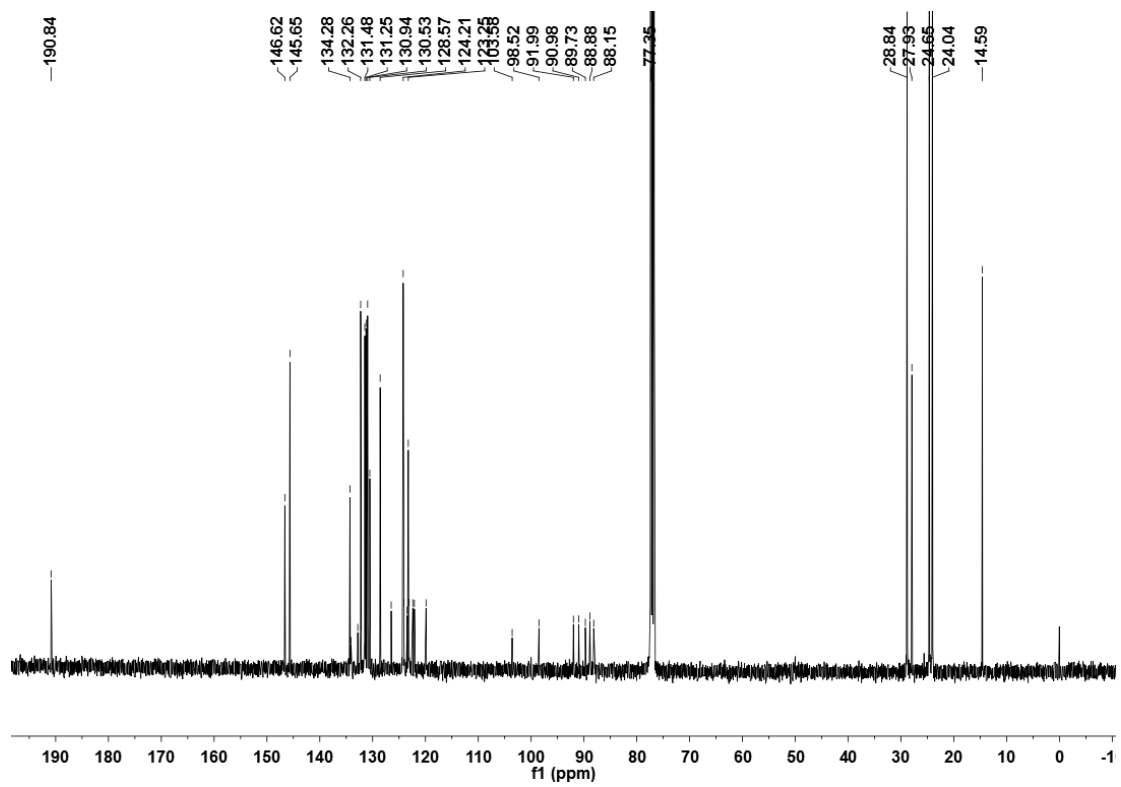
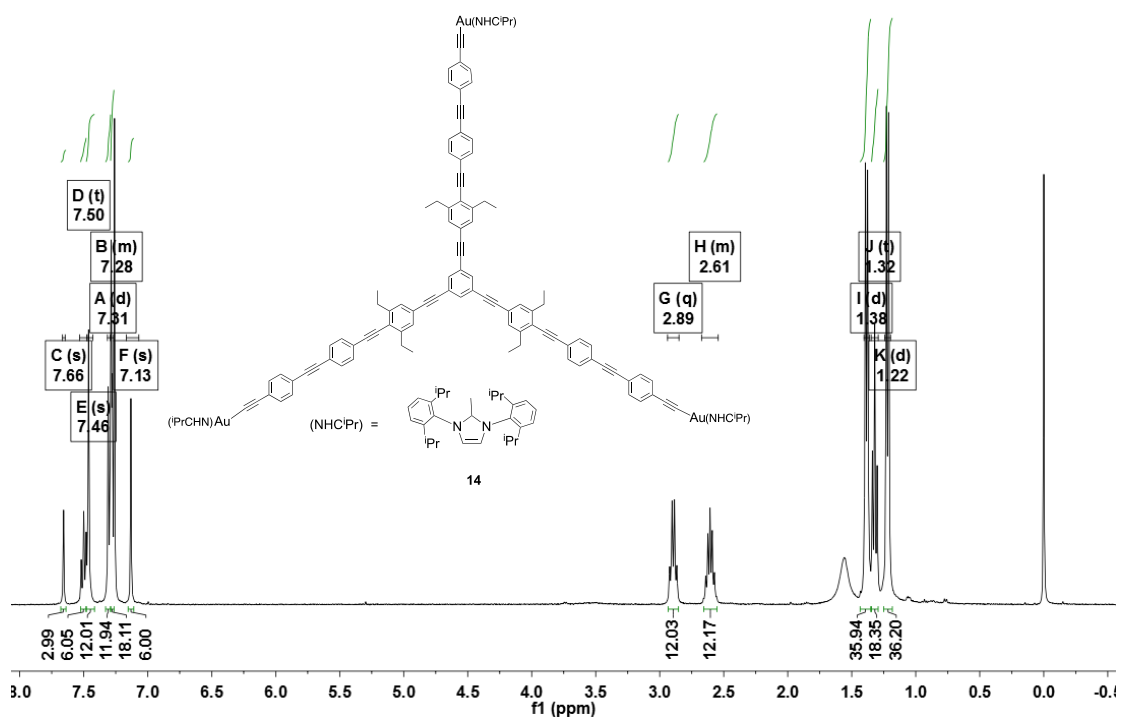
1,3,5-[[*(NHCⁱPr)Au*]C≡C-4-C₆H₄-1-C≡C]₃C₆H₃ (**12**)



1,3,5-{4-[(NHCⁱPr)Au]C≡C-4-C₆H₄-1-C≡C}-3,5-Et₂C₆H₂-1-C≡C}C₃H₃ (**13**)



1,3,5-{4-[(NHCⁱPr)Au]C≡C-4-C₆H₄-1-C≡C-4-C₆H₄-1-C≡C}-3,5-Et₂C₆H₂-1-C≡C}₃C₆H₃ (14)



DFT calculations

We undertook density functional theory (DFT) and time-dependent (TD-DFT) calculations to rationalize the experimental optical properties. All models were constrained to either D_3 (organic compounds) or D_{3h} (organometallic complexes) symmetry. In addition, isopropyl (*i*Pr) groups of the NHC ligand in the laboratory gold complexes and ethyl substituents used as an aid to mitigate solubility issue in the laboratory compounds **9**, **10**, **13**, and **14** were replaced with hydrogens for computational expediency. We constrained the dihedral angle between the planes of a substituted phenyl and the NHC group to 90° . Initial geometries were optimized using hybrid B3LYP^{1,2} functional. For TD-DFT calculations, the hybrid PBE1PBE^{3,4} (or PBE0) functional was employed. The 6-31G(d) (for optimization) and 6-31G(d,p) (for TD-DFT studies) basis sets were employed for main group elements. Gold was modelled using the SDD⁵ basis set and associated pseudopotential. All calculations were performed using the Gaussian09⁶ program package.

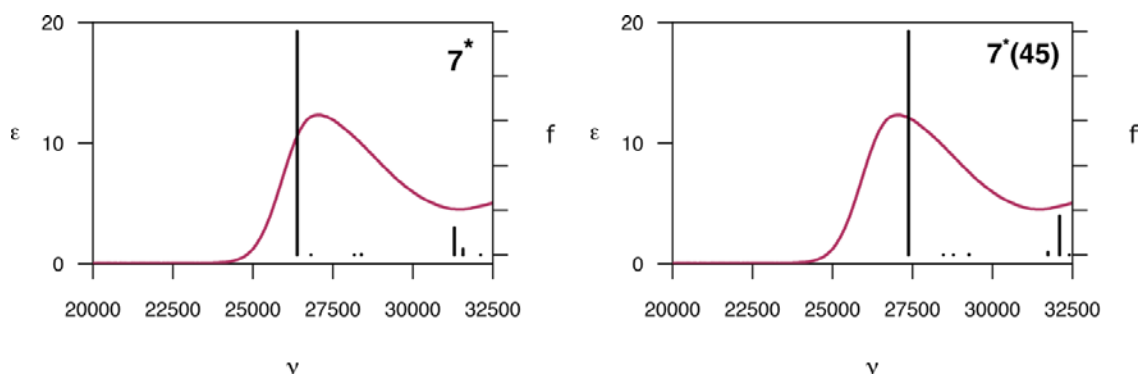


Figure S1. Calculated UV-Vis spectra of two different model conformations of **7**, namely, **7*** (all phenylene rings including core are co-planar) and **7*(45)** (dihedral angle between two planes of adjacent phenylene rings is constrained to 45°). The solid (red) lines show the experimental absorption spectra. Abbreviations: ϵ , molar extinction coefficient ($10^4 \text{ M}^{-1} \text{ cm}^{-1}$). ν , wavenumbers (cm^{-1}). f , relative oscillator strengths.

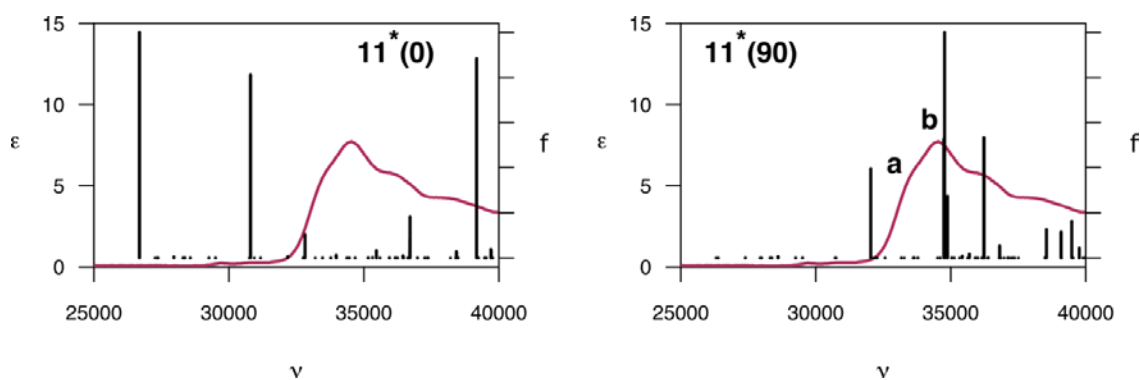
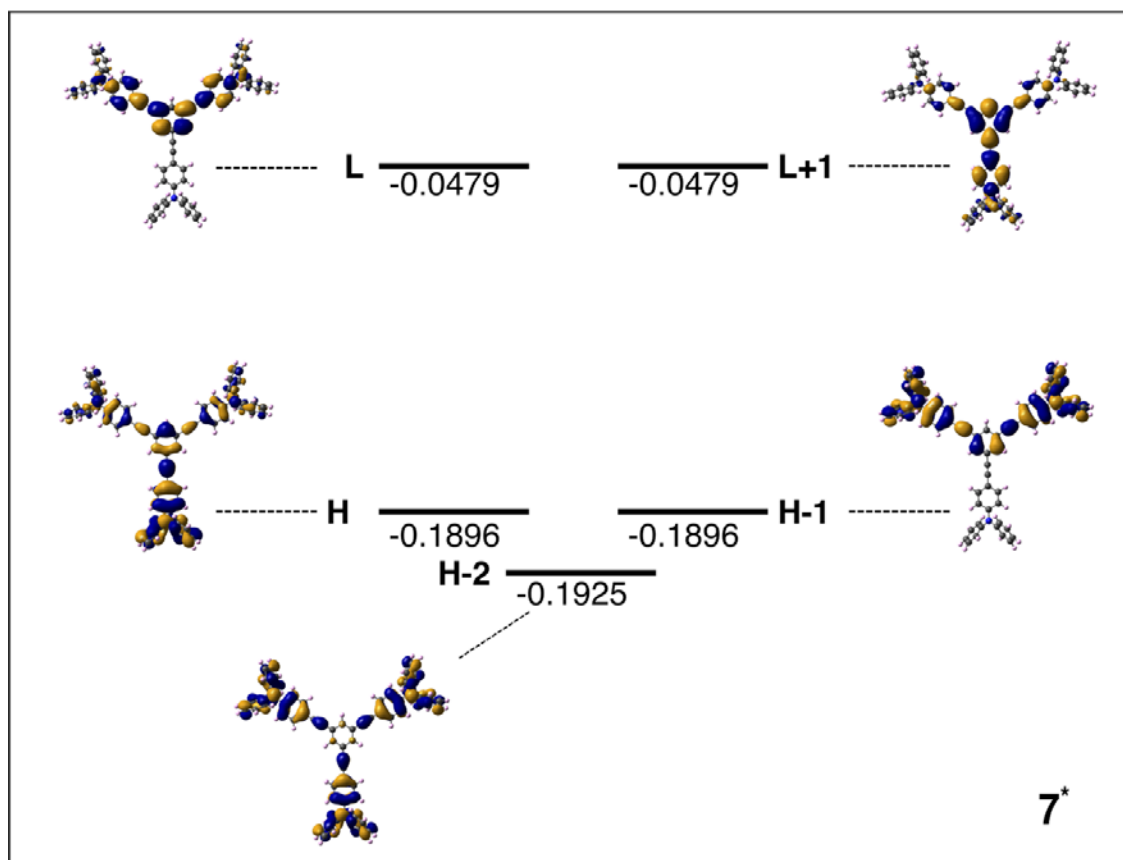
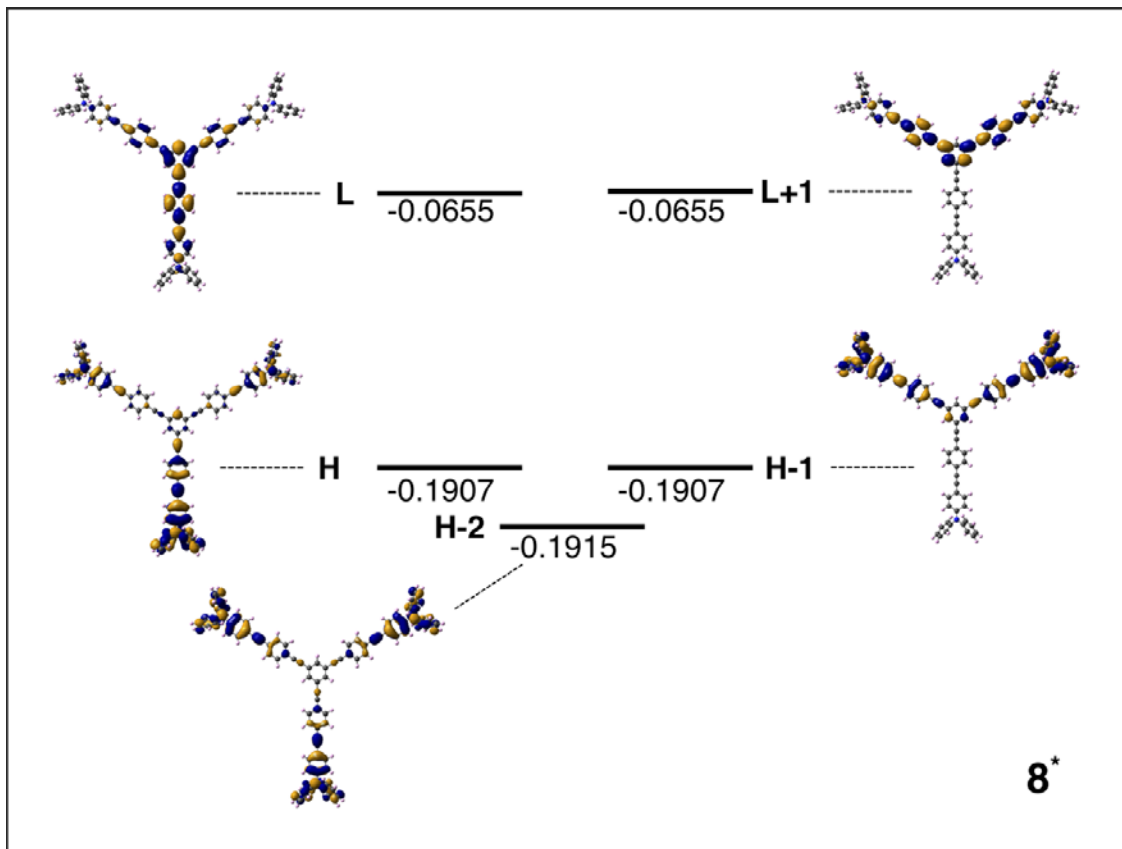


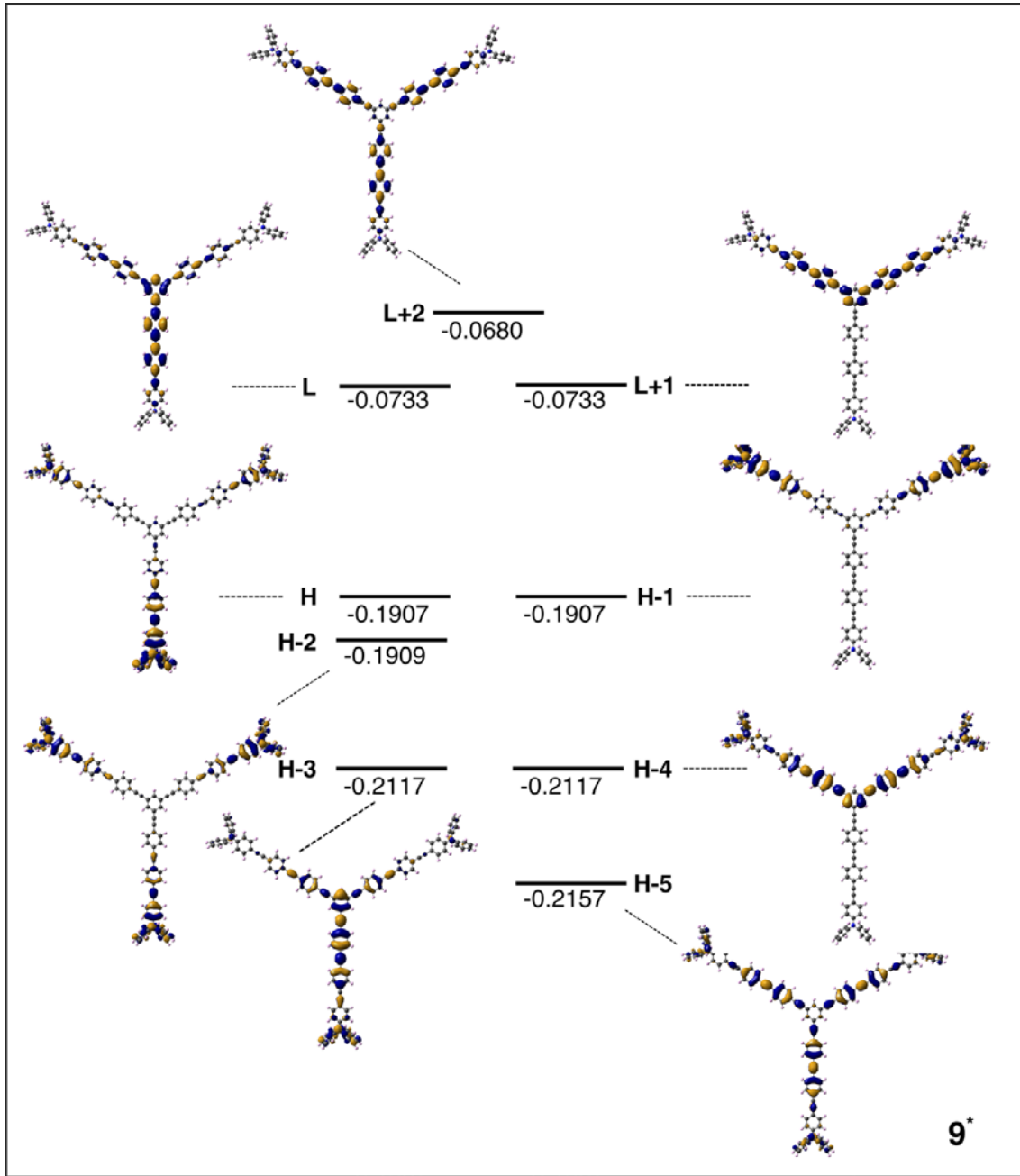
Figure S2. Comparison of calculated UV-Vis data between two different conformations of **11***, namely, **11*(0)** (core ring and all NHC groups are co-planar) and **11*(90)** (dihedral angle between the planes of the core and each NHC ring is constrained to 90°). The solid (maroon) lines show the experimental absorption spectra and the vertical sticks display the calculated oscillator strengths. Abbreviation: ϵ , molar extinction coefficients ($10^4 \text{ M}^{-1} \text{ cm}^{-1}$). ν , wavenumbers (cm^{-1}). f , relative oscillator strengths.

Figure S3. Selected frontier molecular orbital plots (0.015 e bohr^3) for 7^* to 10^* (top to bottom).

Abbreviations: H, HOMO. L, LUMO.







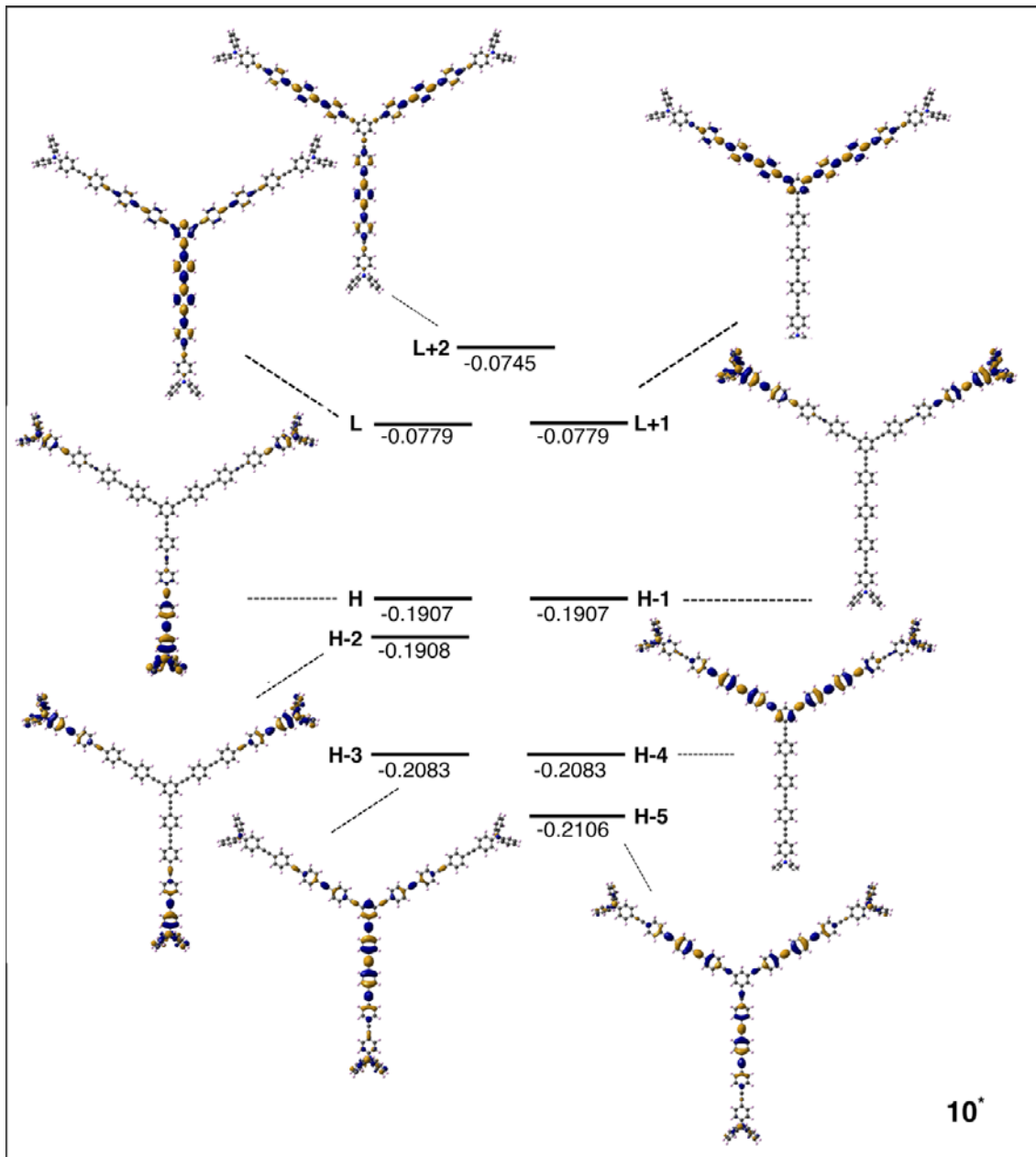
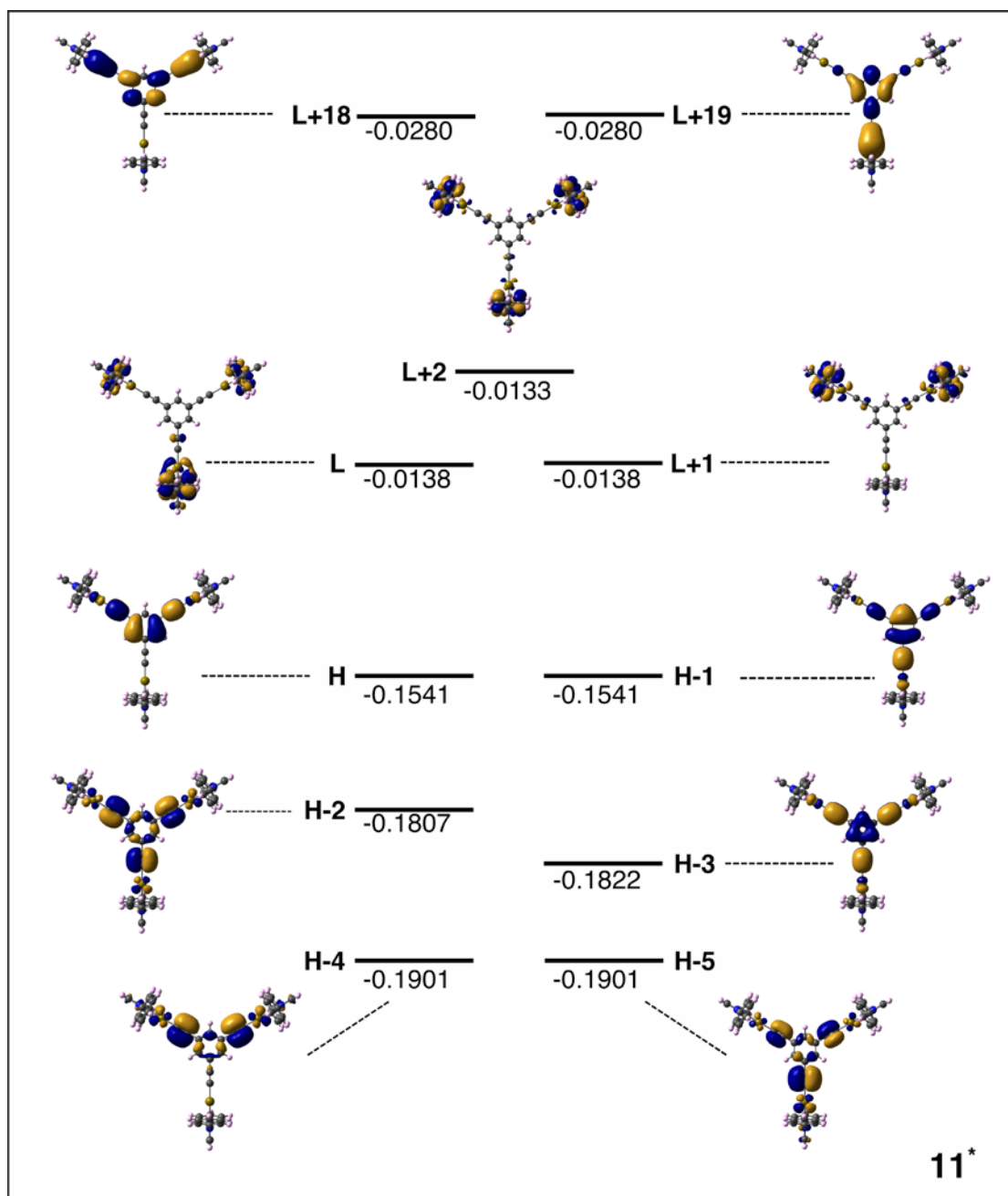
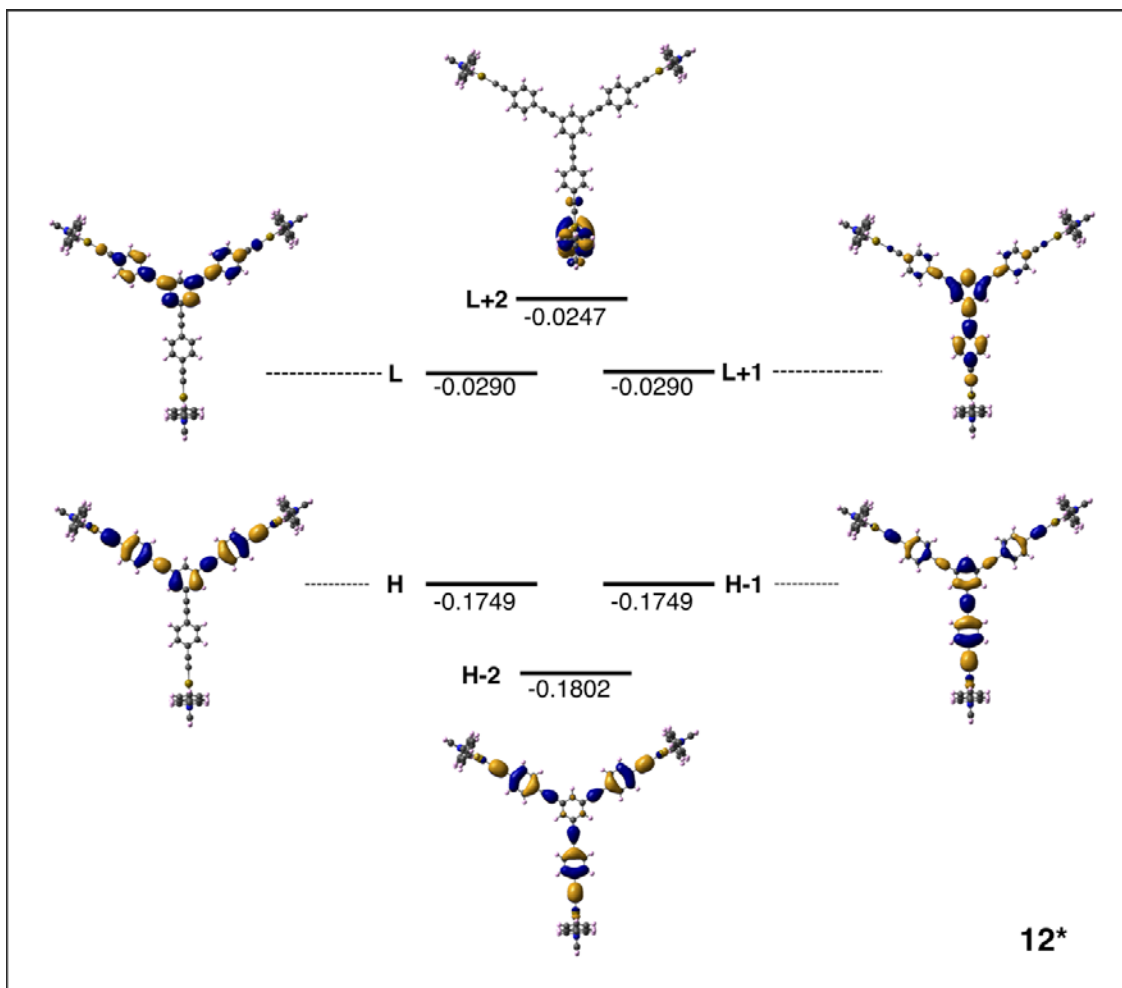
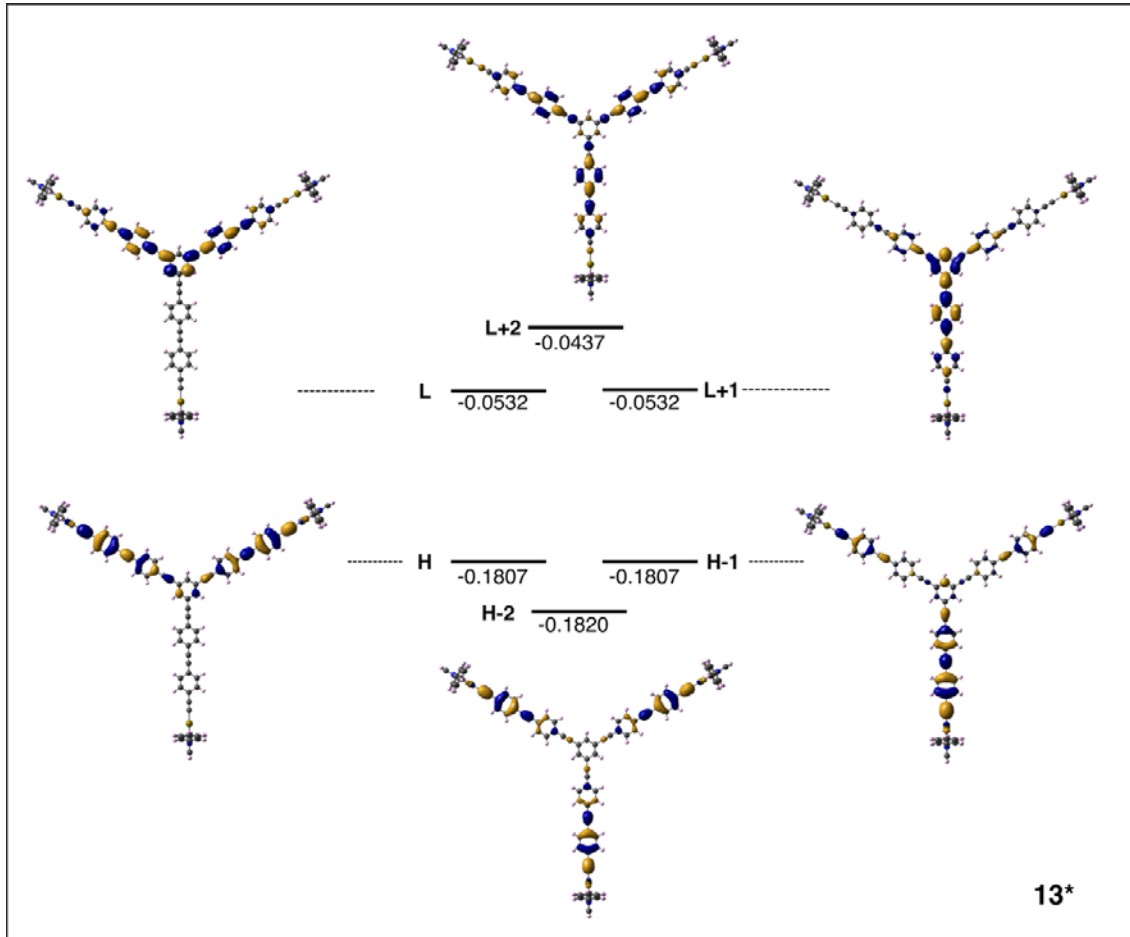
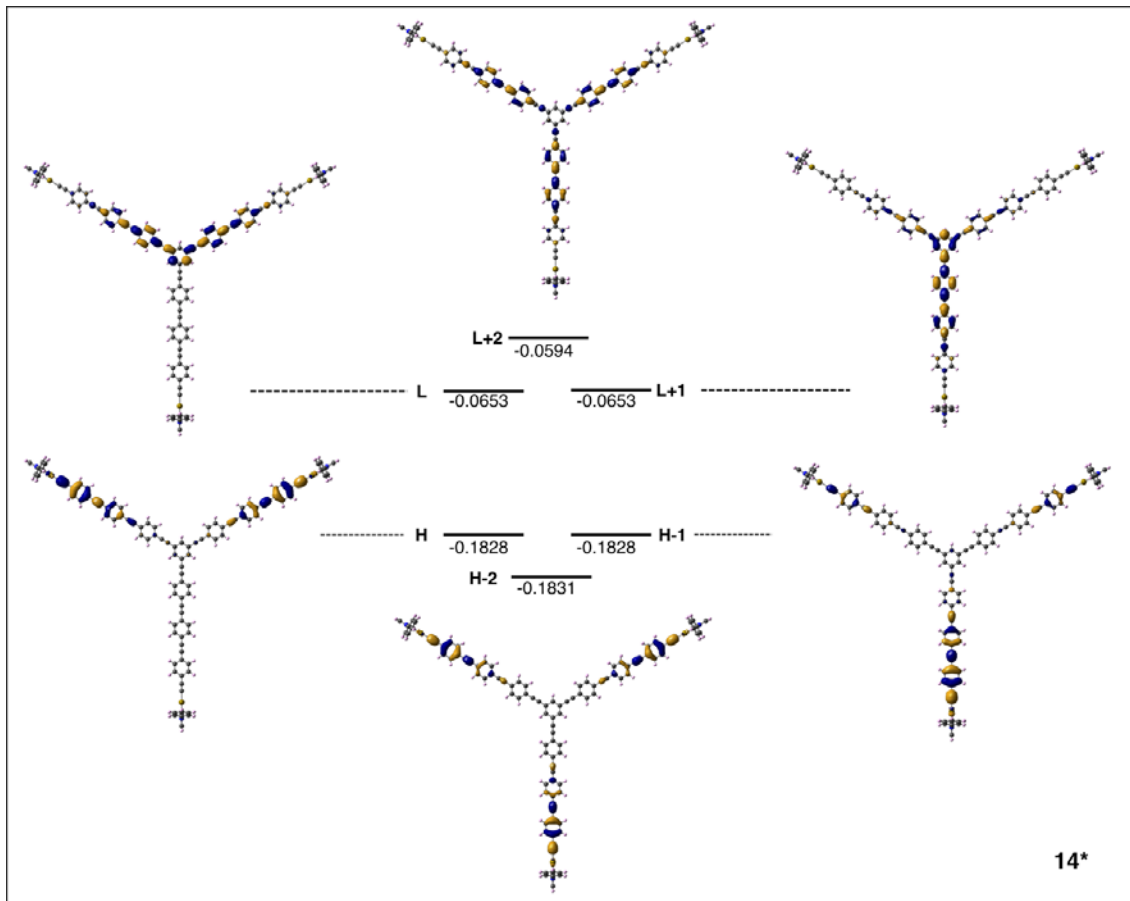


Figure S4. Selected frontier molecular orbital plots (0.02 e bohr^3) for 11^* - 14^* (top to bottom).
Abbreviations: H, HOMO. L, LUMO.









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