Supporting Information for

Palladium-Catalyzed Highly Efficient Synthesis of Tetracenes and Pentacenes

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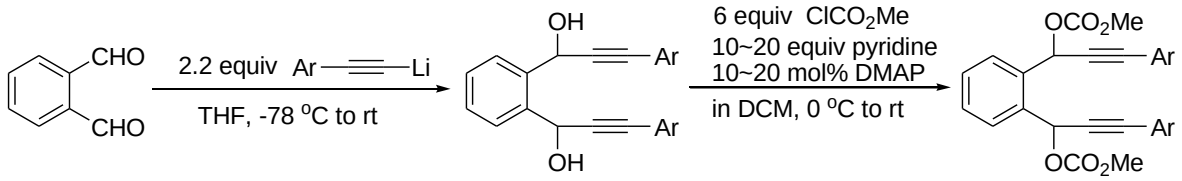
Contents:

Experimental section

General Methods. All reactions were carried out under argon. THF was distilled from sodium and benzophenone. Unless noted, all commercial reagents were used without further purification. $Pd(PPh_3)_4$ was purchased from J&KCHEMICA Chemical Company. ^1H NMR spectra was recorded at 300 or 400 MHz, ^{13}C NMR spectra was recorded at 75.4 or 100.6 MHz, in $CDCl_3$ (containing 0.03% TMS) solutions. ^1H NMR spectra was recorded with tetramethylsilane (δ= 0.00 ppm) as internal reference; ^{13}C NMR spectra was recorded with $CDCl_3$ (δ = 77.00 ppm) as internal reference. High-resolution mass spectra was obtained by using Waters Micromass GCT, Bruker Daltonics, Inc. APEXIII 7.0 TESLA FTMS and IonSpec 4.7 Tesla FTMS mass spectrometer. Single crystal X-ray diffraction data was collected on Bruker APEX-II CCD diffractometer at 133(2) K with graphite-monochromated Mo-Kα radiation (λ=0.71073 Å).

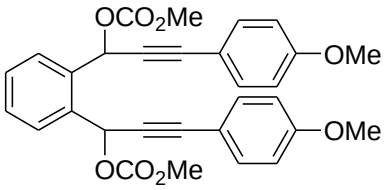
Synthesis of 1,7-diyn-3,6-bis(propargyl carbonate)s.



1a, Ar = Ph

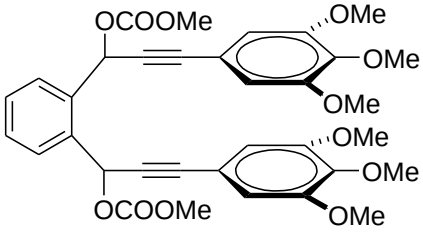
Typical procedure for the synthesis of 11,1'-(1,2-phenylene)bis(3-phenylprop-2-yne-1,1-diyl) dimethyl dicarbonate (1a). To a solution of ethynylbenzene (13.2 mL, 120.0 mmol) in THF (120.0 mL) was added n-BuLi (44.0 mL, 110.0 mmol, 2.5 M) at –78 °C. After stirring at the same temperature for 0.5 h, dry-ice/ acetone bath was withdrawed, then after ca. 10-15 min, phthalaldehyde (6.71 g, 50.0 mmol) was added. The resulting solution was stirred at room temperature for 1.5 h. Then the mixture was quenched with saturated ammonium chloride solution. The reaction mixture was extracted with ethyl acetate, and dried over anhydrous Na_2SO_4. The solvent was evaporated and the residue was purified by chromatography on silica gel (eluent: petroleum ether: acetone = 3:1) to afford 1,1'-(1,2-phenylene)bis(3-phenylprop-2-yn-1-ol) as a sticky yellow oil.

To a solution of above alcohol (1.7 g, 5.0 mmol) in DCM (30 mL) were added pyridine (4.0 mL, 50.0 mmol) and DMAP (61.0 mg, 0.50 mmol) at 0 °C. After stirring for several minutes, methyl chloroformate (2.35 mL, 30.0 mmol) was added. The resulting solution was warmed up to room temperature and stirred for 2 h. Then the mixture was quenched with saturated ammonium chloride solution. The reaction mixture was extracted with ethyl acetate or DCM and dried over anhydrous Na_2SO_4. The solvent was evaporated and the residue was purified by chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 5:1) to afford compound (**1a**) as a mixture of two diastereomers with a ratio of 1.05 : 1 (2.27 g, 100% isolated yield) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) two isomers: δ 7.81-7.75 (m), 7.46-7.41 (m), 7.31-7.25 (m), 6.98 (s, 1H), 6.95 (s, 1H), 3.79 (s, 3H), 3.72 (s, 3H). ^{13}C NMR (100.6 MHz, $CDCl_3$) two isomers: δ 154.55, 154.52, 134.76, 134.59, 131.93, 131.89, 129.72, 129.65, 129.43, 128.87, 128.85, 128.79, 128.15, 128.11, 121.82, 88.64, 88.21, 84.76, 84.68, 67.54, 67.16, 55.03, 55.00. HRMS (ESI) calcd for $C_{28}H_{22}O_6Na$ $[M+Na]^+$: 477.1314, found 477.1326.



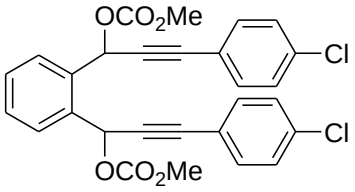
1b

1,1'-(1,2-Phenylene)bis(3-(4-methoxyphenyl)prop-2-yne-1,1-diyl) dimethyl dicarbonate (1b). Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate =2:1) afforded the title product as a mixture of two diastereomers with a ratio of 1 : 1 in 82% isolated yield over two steps as a light yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) two isomers: δ 7.80-7.74 (m), 7.45-7.43 (m), 7.40-7.34 (m), 6.96 (s, 1H), 6.93 (s, 1H), 6.80-6.76 (m, 4H), 3.78 (s, 6H), 3.77 (s, 3H), 3.74 (s, 3H). ^{13}C NMR (100.6 MHz, $CDCl_3$) two isomers: δ 159.98, 159.94, 154.58, 154.55, 134.91, 134.73, 133.49, 133.45, 129.62, 129.52, 129.37, 128.76, 113.93, 113.92, 113.77, 113.71, 88.68, 88.25, 83.50, 83.46, 67.71, 67.30, 55.21, 55.20, 55.00, 54.97. HRMS (ESI) calcd for $C_{30}H_{26}O_8Na$ $[M+Na]^+$: 537.1525, found 537.1512.



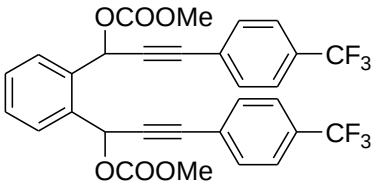
1c

1,1'-(1,2-Phenylene)bis(3-(3,4,5-trimethoxyphenyl)prop-2-yne-1,1-diyl) dimethyl dicarbonate (1c). Column chromatography on silica gel (eluent: petroleum ether: acetone = 3:1) afforded the title product as a mixture of two diastereomers with a ratio of 1.5 : 1 in 82% isolated yield over two steps as a brown solid. ^{1}H NMR (400 MHz, $CDCl_3$) two isomers: δ 7.80-7.75 (m), 7.48-7.45 (m), 6.99 (s, minor isomer), 6.95 (s, major isomer), 6.69 (s, minor isomer), 6.68 (s, major isomer), 3.83 (s), 3.81 (s), 3,79 (s), 3.78 (s), 3.74 (s). ^{13}C NMR (100.6 MHz, $CDCl_3$) two isomers: δ 154.51, 154.48, 152.87, 152.83, 139.14, 134.64, 134.52, 129.70, 129.65, 129.16, 128.89, 116.66, 109.07, 109.06, 88.60, 88.15, 83.71, 83.66, 67.41, 67.19, 60.82, 56.02, 56.00, 55.06, 55.00. HRMS (ESI) calcd for $C_{34}H_{34}O_{12}Na$ $[M+Na]^+$: 657.1948, found 657.1957 .



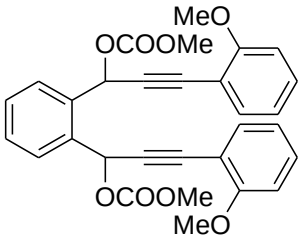
1d

1,1'-(1,2-Phenylene)bis(3-(4-chlorophenyl)prop-2-yne-1,1-diyl) dimethyl dicarbonate (1d). Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 4:1) afforded the title product as a mixture of two diastereomers with a ratio of 1.3 : 1 in 83% isolated yield over two steps as a light yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) two isomers: δ 7.77-7.72 (m), 7.47-7.44 (m), 7.35-7.32 (m), 7.26-7.22(m), 6.94 (s, major isomer), 6.92 (s, minor isomer), 3.80 (s, major isomer), 3.74 (s, minor isomer). ^{13}C NMR (100.6 MHz, $CDCl_3$) two isomers: δ 154.53, 154.49, 135.06, 135.01, 134.57, 134.42, 133.14, 133.12, 129.86, 129.76, 129.41, 128.85, 128.57, 128.52, 120.26, 120.25, 87.50, 87.04, 85.70, 85.65, 67.40, 67.06, 55.15, 55.10. HRMS (ESI) calcd for $C_{28}H_{20}Cl_2O_6Na$ $[M+Na]^+$: 545.0535, found 545.0548.



1e

1,1'-(1,2-Phenylene)bis(3-(4-(trifluoromethyl)phenyl)prop-2-yne-1,1-diyl) dimethyl dicarbonate (1e). Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 5:1) afforded the title product as a mixture of two diastereomers with a ratio of 1.9 : 1 in 91% isolated yield over two steps as a brown solid. ^{1}H NMR (400 MHz, $CDCl_3$) two isomers: δ 7.80-7.74 (m), 7.52-7.47 (m), 6.99 (s, minor isomer), 6.97 (s, major isomer), 3.82 (s, minor isomer), 3.74 (s, major isomer). ^{13}C NMR (100.6 MHz, $CDCl_3$) two isomers: δ 154.52, 154.48, 134.41, 134.26, 132.13, 132.08, 130.60 (q, $^{2}J_{C\text{-}F}$ = 32.6 Hz), 130.63 (q, $^{2}J_{C\text{-}F}$ = 32.9 Hz), 129.99, 129.90, 129.43, 128.94, 125.52, 125.50, 125.16, 125.06 (q, $^{3}J_{C\text{-}F}$ = 4.3 Hz), 125.05, 123.68 (q, $^{1}J_{C\text{-}F}$ = 270.3 Hz), 87.14, 87.06, 86.98, 86.66, 67.24, 66.95, 55.19, 55.12. HRMS (ESI) calcd for $C_{30}H_{20}F_6O_6Na$ $[M+Na]^+$: 613.1062, found 613.1069.



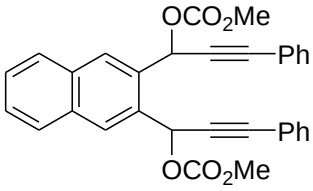
1f

1,1'-(1,2-Phenylene)bis(3-(2-methoxyphenyl)prop-2-yne-1,1-diyl) dimethyl dicarbonate (1f). Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 3:1) afforded the title product as a mixture of two diastereomers with a ratio of 1.8 : 1 in 84% isolated yield over two steps as a light yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) two isomers: δ 7.90-7.87 (m), 7.43-7.36 (m), 7.25-7.20 (m), 7.07 (s, minor isomer), 7.00 (s, major isomer), 6.84-6.76 (m, 4H), 3.78 (s), 3.75 (s), 3.74 (s), 3.70 (s). ^{13}C NMR (100.6 MHz, $CDCl_3$) two isomers: δ 160.36, 160.22, 154.36, 154.32, 134.71, 134.35, 133.46, 130.24, 130.19, 129.73, 129.44, 129.37, 128.85, 119.94, 119.91, 110.80, 110.73, 110.36, 88.49, 88.42, 85.01, 84.77, 67.77, 66.97, 55.39, 55.37, 54.72, 54.71. HRMS (ESI) calcd for $C_{30}H_{26}O_8Na$ $[M+Na]^+$: 537.1525, found 537.1499.

1g

1,1'-(1,2-Phenylene)bis(3-phenylprop-2-yne-1,1-diyl) di-*tert*-butyl dicarbonate (1g). To a solution of 1,1'-(1,2-phenylene)bis(3-phenylprop-2-yn-1-ol) (3.38 g, 10.0 mmol) in DCM (50 mL) were added triethylamine (8.34 mL, 60.0 mmol) and DMAP (244 mg, 2 mmol) at 0 °C. After stirring for several minutes, di-*tert*-butyl dicarbonate (8.7 g, 40 mmol) was added. The resulting solution was warmed up to room temperature and stirred for 2 h. Then the mixture was quenched with saturated ammonium chloride solution. The reaction mixture was extracted with ethyl acetate and dried over anhydrous Na_2SO_4. The solvent was evaporated and the residue was purified by chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 3:1) to afford the title product (**1g**) as a mixture of two diastereomers with a ratio of 1.4:1 in 97% isolated yield over two steps as a light yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) two isomers: δ 7.82-7.80 (m), 7.77-7.74 (m), 7.44-7.40 (m, 6H), 7.28-7.21 (m, 6H), 6.96 (s, minor isomer), 6.94 (s, major isomer), 1.47 (s, minor isomer), 1.45 (s, major isomer). ^{13}C NMR (100.6 MHz, $CDCl_3$) two isomers: δ 152.12, 135.00, 134.82, 131.82, 129.41, 129.25,

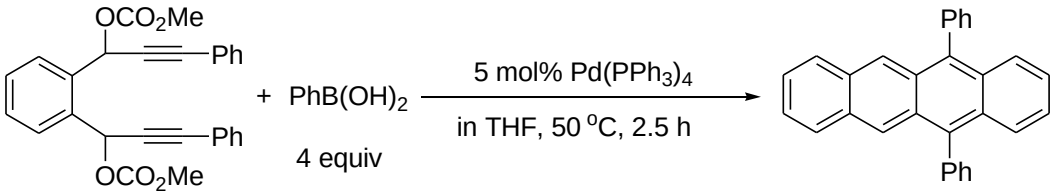
129.07, 128.61, 128.57, 128.36, 128.06, 128.01, 122.03, 122.02, 88.00, 87.55, 85.38, 85.29, 82.88, 82.85, 66.11, 65.81, 27.64, 27.60. HRMS (ESI) calcd for $C_{34}H_{34}O_6Na$ $[M+Na]^+$: 561.2253, found 561.2253.



3

Dimethyl 1,1'-(naphthalene-2,3-diyl)bis(3-phenylprop-2-yne-1,1-diyl) dicarbonate (3). Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 3:1) afforded the title product as a mixture of two isomers with a ratio of 1.5 : 1 in 86% isolated yield over two steps (from naphthalene-2,3-dicarbaldehyde[1]) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) two isomers: δ 8.29 (s, minor isomer), 8.26 (s, major isomer), 7.90-7.88 (m), 7.54-7.43 (m), 7.30-7.24 (m), 7.13 (s, minor isomer), 7.10 (s, major isomer), 3.80 (s, minor isomer), 3.72 (s, major isomer). ^{13}C NMR (100.6 MHz, $CDCl_3$) two isomers: δ 154.60, 154.55, 133.15, 131.92, 131.88, 129.64, 128.98, 128.85, 128.78, 128.16, 128.10, 128.04, 128.01, 127.33, 127.25, 121.80, 88.80, 88.34, 84.86, 84.75, 67.95, 67.59, 55.06, 55.01. HRMS (ESI) calcd for $C_{32}H_{24}O_6Na$ $[M+Na]^+$: 527.1471, found 527.1481.

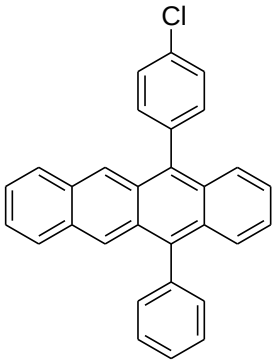
Typical procedure for the synthesis of 5,12-diphenyltetracene 2a.



1a **2a**

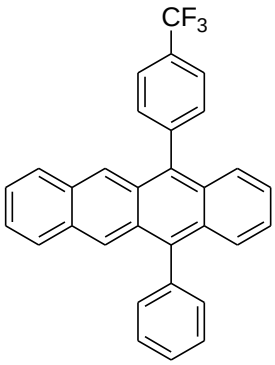
To a solution of 1,1'-(1,2-phenylene)bis(3-phenylprop-2-yne-1,1-diyl) dimethyl dicarbonate (**1a**) (91.0 mg, 0.2 mmol) and phenylboronic acid (97.5 mg, 0.8 mmol) in THF (5 mL) was added $Pd(PPh_3)_4$ (12.0 mg, 0.01 mmol). After stirring for 2.5 h at 50 °C, the solvent was evaporated under the reduced pressure and the residue was purified by chromatography on silica gel (eluent: n-pentane) to afford the title product 5,12-diphenyltetracene (**2a**) in 90% isolated yield (68.5 mg) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (s, 2H), 7.77 (dd, J = 6.6, 3.6 Hz, 4H), 7.69-7.54 (m, 12H), 7.28-7.22 (m, 4H). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 139.28, 137.01, 131.50, 130.92, 129.29, 129.06, 128.51, 128.38, 127.56, 126.96,

125.69, 125.16, 124.73. The spectroscopic data are in agreement with that previously reported.[2]



2b

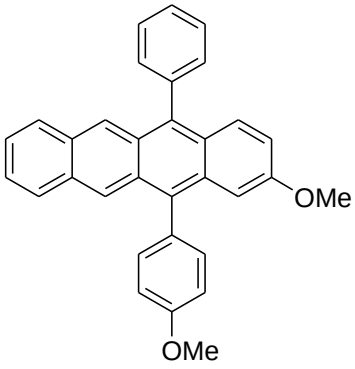
5-(4-Chlorophenyl)-12-phenyltetracene (2b). Column chromatography on silica gel (eluent: n-pentane) afforded the title product in 94% isolated yield as a yellow solid. M.p. 181-183 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (s, 1H), 8.26 (s, 1H), 7.77-7.75 (m, 2H), 7.68-7.59 (m, 7H), 7.53 (d, *J* = 6.0 Hz, 2H), 7.47 (d, *J* = 8.0 Hz, 2H), 7.29-7.20 (m, 4H). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 139.11, 137.73, 137.47, 135.40, 133.65, 132.88, 131.44, 131.07, 130.95, 129.30, 129.23, 129.00, 128.93, 128.86, 128.54, 128.40, 128.29, 127.65, 127.08, 126.54, 125.86, 125.39, 125.27, 125.25, 125.04, 124.77. HRMS (EI) calcd for $C_{30}H_{19}Cl$:414.1175, found 414.1176.



2c

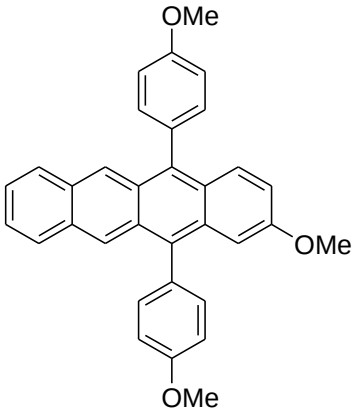
5-Phenyl-12-(4-(trifluoromethyl)phenyl)tetracene (2c). Column chromatography on silica gel (eluent: n-pentane) afforded the title product in 77% isolated yield as a yellow solid. M.p. 181-182 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (s, 1H), 8.18 (s, 1H), 7.92 (d, *J* = 8.0 Hz, 2H), 7.79-7.76 (m, 2H), 7.70-7.52 (m, 9H), 7.30-7.23 (m, 4H).^{13}C NMR (100.6 MHz, $CDCl_3$) δ 143.37 (q, $^{5}J_{C\text{-}F}$ = 1.1 Hz), 139.02, 137.84, 135.01, 131.96, 131.41, 131.18, 130.99, 129.90 (q, $^{2}J_{C\text{-}F}$ = 32.9 Hz), 129.20, 129.17, 128.96, 128.71, 128.57, 128.41, 128.26 127.71, 127.16,

126.31, 125.98, 125.58 (q, $^{3}J_{C\text{-}F}$ = 3.8 Hz), 125.51, 125.35, 125.27, 125.00, 124.43 (q, $^{1}J_{C\text{-}F}$ = 272.2 Hz), 124.81. HRMS (EI) calcd for $C_{31}H_{19}F_3$:448.1439, found 448.1435.



2d

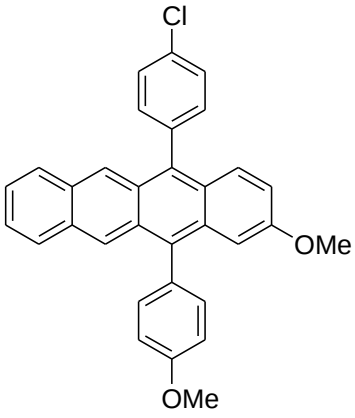
2-Methoxy-12-(4-methoxyphenyl)-5-phenyltetracene (2d). Column chromatography on silica gel (eluent: n-pentane to petroleum ether: ethyl acetate =5:1) afforded the title product in 90% isolated yield as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (s, 2H), 7.81-7.75 (m, 2H), 7.62 – 7.57 (m, 4H), 7.53-7.51 (m, 2H), 7.45 (d, *J* = 8.4 Hz, 2H), 7.27-7.24 (m, 2H), 7.18 (d, *J* = 8.4 Hz, 2H), 6.95 (dd, *J* = 9.8, 2.6 Hz, 1H), 6.86 (d, *J* = 2.4 Hz, 1H), 3.97 (s, 3H), 3.70 (s, 3H).^{13}C NMR (100.6 MHz, $CDCl_3$) δ 158.88, 156.28, 139.29, 137.03, 134.14, 132.44, 131.66, 131.42, 131.03, 130.55, 130.32, 129.90, 128.83, 128.46, 128.37, 128.27, 128.16, 127.53, 126.46, 125.82, 125.10, 124.84, 124.68, 120.34, 114.10, 101.81, 55.32, 54.97. HRMS (EI) calcd for $C_{32}H_{24}O_2$:440.1776, found 440.1779.



2e

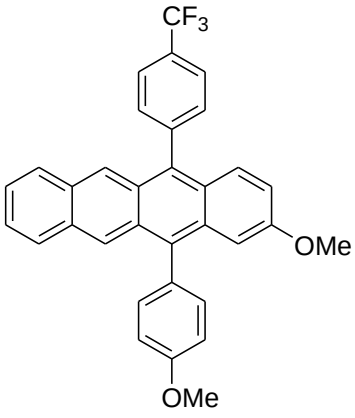
2-Methoxy-5,12-bis(4-methoxyphenyl)tetracene (2e). Column chromatography on silica gel (eluent: ethyl acetate: n-pentane = 1:6) afforded the title product in 77% isolated yield as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (s, 1H), 8.25 (s, 1H), 7.77 (d, *J* = 8.8 Hz, 2H), 7.62 (d, *J* = 9.6 Hz, 1H), 7.42 (t, *J* = 8.8 Hz, 4H), 7.26- 7.24 (m, 2H), 7.14 (t, *J* = 9.0 Hz, 4H), 6.94 (d, *J* = 9.2 Hz, 1H), 6.84 (s, 1H), 3.94 (s, 3H), 3.92 (s, 3H), 3.68 (s, 3H). ^{13}C NMR

(100.6 MHz, $CDCl_3$) δ 159.03, 158.87, 156.28, 136.85, 133.94, 132.46, 132.45, 131.71, 131.29, 131.03, 130.59, 130.30, 129.96, 128.91, 128.52, 128.40, 128.26, 126.78, 125.90, 125.07, 124.81, 124.63, 120.22, 114.09, 113.89, 101.80, 55.32, 55.29, 54.94. HRMS (EI) calcd for $C_{33}H_{26}O_3$:470.1882, found 470.1883.



2f

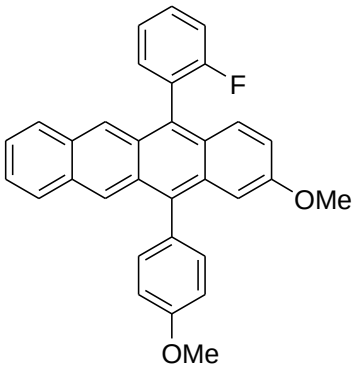
5-(4-Chlorophenyl)-2-methoxy-12-(4-methoxyphenyl)tetracene (2f). Column chromatography on silica gel (eluent: n-pentane to n-pentane: ethyl acetate = 8:1) afforded the title product in 88% isolated yield as a yellow solid. M.p. 203-204 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (s, 1H), 8.20 (s, 1H), 7.78-7.76 (m, 2H), 7.61- 7.59 (m, 2H), 7.54 (d, *J* = 9.6 Hz, 1H), 7.45-7.42 (m, 4H), 7.28-7.26 (m, 2H), 7.18-7.16 (m, 2H), 6.96 (dd, *J* = 9.6, 2.4 Hz, 1H), 6.86 (d, *J* = 2.4 Hz, 1H), 3.97 (s, 3H), 3.70 (s, 3H). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 158.97, 156.30, 137.76, 135.43, 134.59, 133.62, 132.80, 132.40, 131.52, 131.08, 130.52, 130.48, 129.86, 128.80, 128.39, 128.29, 128.03, 126.49, 125.39, 125.21, 125.02, 124.90, 120.69, 114.14, 101.94, 55.33, 54.99. HRMS (EI) calcd for $C_{32}H_{23}O_2Cl$:474.1387, found 474.1391.



2g

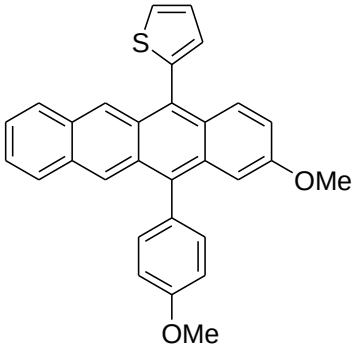
2-Methoxy-12-(4-methoxyphenyl)-5-(4-(trifluoromethyl)phenyl)tetracene (2g). Column chromatography on silica gel (eluent: n-pentane to n-pentane: ethyl acetate =10:1) afforded

the title product in 88% isolated yield as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (s, 1H), 8.13 (s, 1H), 7.91 (d, *J* = 8.0 Hz, 2H), 7.79-7.77 (m, 2H), 7.65 (d, *J* = 7.6 Hz, 2H), 7.48-7.44 (m, 3H), 7.30-7.27 (m, 2H), 7.19 (d, *J* = 2.0 Hz, 2H), 6.98 (dd, *J* = 9.6, 2.4 Hz, 1H), 6.88 (d, *J* = 2.4 Hz, 1H), 4.00 (s, 3H), 3.72 (s, 3H).^{13}C NMR (100.6 MHz, $CDCl_3$) δ 159.03, 156.33, 143.39 (q, $^{5}J_{C\text{-}F}$ = 1.2 Hz), 135.06, 134.95, 132.39, 131.89, 131.44, 131.12, 130.58, 130.51, 129.88 (q, $^{2}J_{C\text{-}F}$ = 32.5 Hz), 129.82, 128.32, 128.26, 128.16, 127.80, 126.36, 125.54 (q, $^{3}J_{C\text{-}F}$ = 3.6 Hz), 125.30, 125.15, 125.04, 124.40 (q, $^{1}J_{C\text{-}F}$ = 272.0 Hz), 120.95, 114.19, 102.02, 55.36, 55.02. HRMS (EI) calcd for $C_{33}H_{23}O_2F_3$:508.1650, found 508.1647.



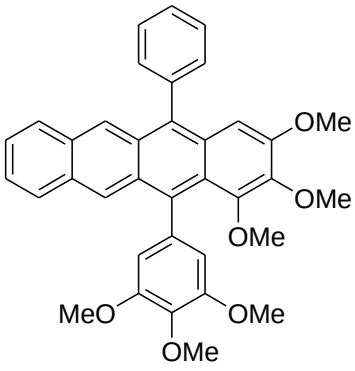
2h

5-(2-Fluorophenyl)-2-methoxy-12-(4-methoxyphenyl)tetracene (2h). Column chromatography on silica gel (eluent: ethyl acetate: petroleum ether = 1:8) afforded the title product in 90% isolated yield as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (s, 1H), 8.22 (s, 1H), 7.78-7.76 (m, 2H), 7.58-7.53 (m, 2H), 7.48-7.42 (m, 3H), 7.40-7.36 (m, 2H), 7.26-7.24 (m, 2H), 7.16 (d, *J* = 9.2 Hz, 2H), 7.00 (dd, *J* = 9.6, 2.4 Hz, 1H), 6.88 (d, *J* = 2.4 Hz, 1H), 3.93 (s, 3H), 3.69 (s, 3H). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 160.90 (d, $^{1}J_{C\text{-}F}$ = 246.5 Hz), 158.96, 156.32, 135.06, 133.61 (d, $^{3}J_{C\text{-}F}$ = 4.0 Hz), 132.48, 132.36, 131.52, 131.15, 130.63, 130.59, 130.18, 129.97 (d, $^{3}J_{C\text{-}F}$ = 7.0 Hz), 129.95, 128.35, 128.29, 128.13, 128.07, 126.90, 126.45 (d, $^{2}J_{C\text{-}F}$ = 16.9 Hz), 125.20, 125.13, 124.96, 124.90, 124.32 (d, $^{4}J_{C\text{-}F}$ = 3.2 Hz), 120.98, 116.02 (d, $^{2}J_{C\text{-}F}$ = 21.8 Hz), 114.15, 114.07, 102.09, 55.29, 54.98. HRMS (EI) calcd for $C_{32}H_{23}O_2F$: 458.1682, found 458.1686.



2i

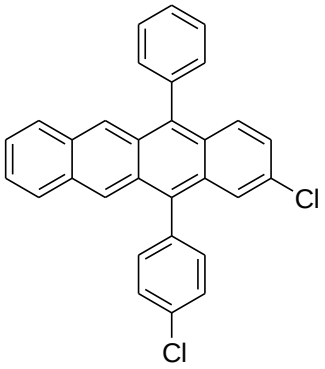
2-(2-Methoxy-12-(4-methoxyphenyl)tetracen-5-yl)thiophene (2i). Column chromatography on silica gel (eluent: petroleum ether to petroleum ether: ethyl acetate = 4:1) afforded the title product in 78% isolated yield as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (s, 1H), 8.25 (s, 1H), 7.84-7.82 (m, 1H), 7.80-7.77 (m, 2H), 7.67-7.65 (m, 1H), 7.45-7.43 (m, 2H), 7.37-7.34 (m, 1H), 7.30-7.27 (m, 3H), 7.19-7.17 (m, 2H), 7.03 (dd, *J* = 9.8, 2.4 Hz, 1H), 6.84 (d, *J* = 2.4 Hz, 1H), 3.98 (s, 3H), 3.71 (s, 3H). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 158.97, 156.34, 139.48, 135.59, 132.33, 131.44, 131.13, 130.62, 130.50, 129.80, 129.62, 129.44, 1 28.60, 128.55, 128.43, 128.38, 128.29, 127.22, 126.79, 125.50, 125.22, 124.97, 124.94, 120.94, 114.12, 101.84, 55.34, 55.02. HRMS (EI) calcd for $C_{30}H_{22}O_2S$:446.1341, found 446.1336.



2j

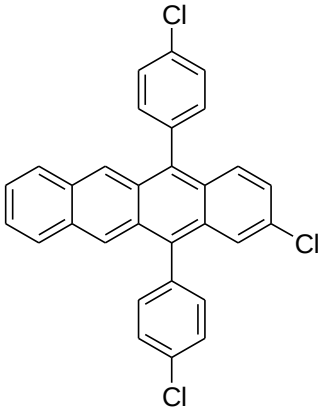
1,2,3-Trimethoxy-5-phenyl-12-(3,4,5-trimethoxyphenyl)tetracene (2j). Column chromatography on silica gel (eluent: ethyl acetate: petroleum ether = 1:3) afforded the title product in 89% isolated yield as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (s, 1H), 8.12 (s, 1H), 7.82-7.79 (m, 1H), 7.74-7.72 (m, 1H), 7.68-7.66 (m, 2H), 7.64-7.59 (m, 1H), 7.52 (d, *J* = 7.6 Hz, 2H), 7.27-7.23 (m, 2H), 6.74 (s, 2H), 6.67 (s, 1H), 4.06 (s, 3H), 3.92 (s, 3H), 3.86 (s, 6H), 3.72 (s, 3H), 3.50 (s, 3H). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 152.20, 151.84, 148.49, 142.12, 139.82, 138.48, 136.24, 134.77, 134.17, 131.14, 130.85, 130.34, 129.46, 128.88, 128.69, 128.61, 128.00, 127.84, 127.52, 126.03, 125.18, 124.71, 124.45, 122.45,

107.26, 99.64, 61.11, 60.77, 60.65, 56.04, 55.25. HRMS (MALDI/DHB) calcd for $C_{36}H_{32}O_6$: 560.2199, found 560.2190.



2k

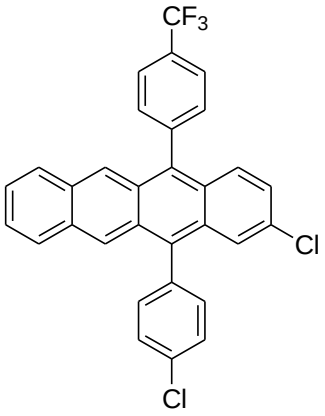
2-Chloro-12-(4-chlorophenyl)-5-phenyltetracene (2k). Column chromatography on silica gel (eluent: n-pentane) afforded the title product in 87% isolated yield as a yellow solid. M.p. 222-224 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (s, 1H), 8.23 (s, 1H), 7.80-7.76 (m, 2H), 7.67-7.59 (m, 7H), 7.51-7.44 (m, 4H), 7.32-7.29 (m, 2H), 7.14 (dd, *J* = 9.4, 2.0 Hz, 1H). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 138.56, 138.06, 137.02, 134.66, 133.96, 132.77, 131.42, 131.29, 131.20, 131.10, 129.42, 129.32, 129.07, 128.94, 128.62, 128.39, 128.26, 127.89, 127.34, 126.13, 125.99, 125.74, 125.50, 125.28, 124.53. HRMS (EI) calcd for $C_{30}H_{18}Cl_2$:448.0786, found 448.0791.



2l

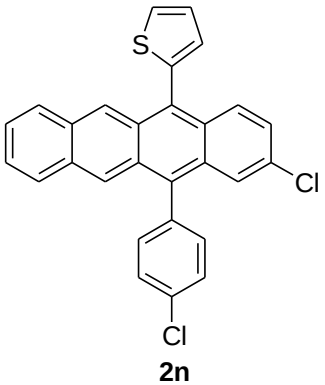
2-Chloro-5,12-bis(4-chlorophenyl)tetracene (2l). Column chromatography on silica gel (eluent: n-pentane) afforded the title product in 87% isolated yield as a yellow solid. M.p. 248-250 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (s, 1H), 8.23 (s, 1H), 7.79 (dd, *J* = 6.6, 3.2 Hz, 2H), 7.64-7.57 (m, 6H), 7.44 (s, 2H), 7.42 (s, 2H), 7.32 (dd, *J* = 6.8, 3.2 Hz, 2H), 7.17-7.14 (m, 1H). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 137.00, 136.85, 136.46, 135.12, 134.06, 134.03, 132.70, 132.67, 131.45, 131.26, 131.25, 129.36, 129.26, 129.10, 128.99, 128.81,

128.64, 128.30, 128.27, 127.35, 126.31, 125.86, 125.74, 125.71, 125.47, 124.66. HRMS (EI) calcd for $C_{30}H_{17}Cl_3$:482.0396, found 482.0395.



2m

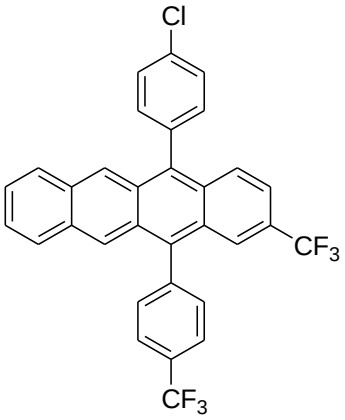
2-Chloro-12-(4-chlorophenyl)-5-(4-(trifluoromethyl)phenyl)tetracene (2m). Column chromatography on silica gel (eluent: n-pentane) afforded the title product in 86% isolated yield as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (s, 1H), 8.18 (s, 1H), 7.93 (d, *J* = 8.0 Hz, 2H), 7.82-7.79 (m, 2H), 7.66-7.61 (m, 5H), 7.52 (d, *J* = 9.6 Hz, 1H), 7.46-7.44 (m, 2H), 7.35-7.33 (m, 2H), 7.18 (dd, *J* = 9.2, 2.0 Hz, 1H). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 142.62 (q, $^5J_{C\text{-}F}$ = 1.7 Hz), 136.76, 136.05, 135.50, 134.15, 132.68, 131.77, 131.49, 131.36, 131.31, 130.24 (q, $^2J_{C\text{-}F}$ = 32.6 Hz), 129.32, 129.22, 129.15, 128.60, 128.40, 128.30, 128.28, 127.22, 126.56, 125.96, 125.87, 125.72 (q, $^3J_{C\text{-}F}$ = 3.72 Hz), 125.60, 125.47, 124.75, 124.30 (q, $^1J_{C\text{-}F}$ = 272.1 Hz). HRMS (EI) calcd for $C_{31}H_{17}F_3Cl_2$:516.0659, found 516.0654.



2n

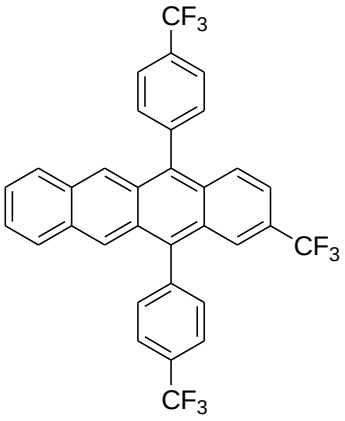
2-(2-Chloro-12-(4-chlorophenyl)tetracen-5-yl)thiophene (2n). Column chromatography on silica gel (eluent: n-pentane to petroleum ether) afforded the title product in 45% isolated yield as a yellow solid. M.p. 238-239 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (s, 1H), 8.21 (s, 1H), 7.86-7.78 (m, 3H), 7.70-7.63 (m, 3H), 7.58 (m, 1H), 7.44 (dd, *J* = 8.0, 0.8 Hz, 2H), 7.39-7.37 (m, 1H), 7.35-7.32 (m, 2H), 7.30-7.28 (m, 1H), 7.28-7.20 (m, 1H). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 138.57, 136.79, 136.07, 134.09, 132.64, 131.51, 131.39, 131.30, 130.22,

129.88, 129.77, 129.33, 129.21, 129.09, 128.82, 128.43, 128.27, 127.37, 127.18, 126.56, 125.86, 125.82, 125.76, 125.39, 124.52. HRMS (EI) calcd for $C_{28}H_{16}SCl_2$:454.0350, found 454.0352.



2o

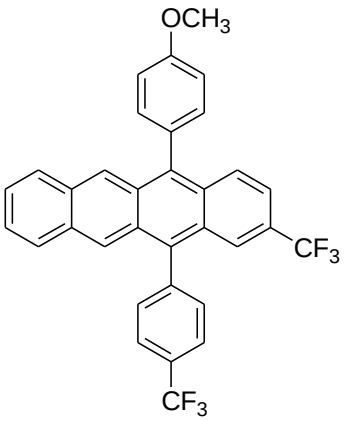
5-(4-Chlorophenyl)-2-(trifluoromethyl)-12-(4-(trifluoromethyl)phenyl)tetracene (2o). Column chromatography on silica gel (eluent: n-pentane) afforded the title product in 71% isolated yield as a yellow solid. M.p. 218-220 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (s, 1H), 8.23 (s, 1H), 7.96 (d, *J* = 8.0 Hz, 2H), 7.90 (s, 1H), 7.85-7.82 (m, 2H), 7.78 (d, *J* = 9.2 Hz, 1H), 7.68-7.64 (m, 4H), 7.48-7.45 (m, 2H), 7.40-7.35 (m, 3H). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 141.99 (q, $^{5}J_{C\text{-}F}$ = 1.1 Hz), 137.79, 136.85, 136.78, 134.24, 132.65, 131.79, 131.76, 131.60, 130.54 (q, $^{2}J_{C\text{-}F}$ = 32.6 Hz), 129.62, 129.11, 129.04, 129.03, 128.45, 128.36, 128.31, 127.25, 126.87 (q, $^{2}J_{C\text{-}F}$ = 32.0 Hz), 126.26, 126.15, 125.87 (q, $^{3}J_{C\text{-}F}$ = 3.4 Hz), 125.86, 125.79, 124.26 (q, $^{1}J_{C\text{-}F}$ = 272.6 Hz), 124.69 (q, $^{3}J_{C\text{-}F}$ = 5.4 Hz), 124.12 (q, $^{1}J_{C\text{-}F}$ = 272.6 Hz), 120.00 (q, $^{3}J_{C\text{-}F}$ = 2.8 Hz). HRMS (EI) calcd for $C_{32}H_{17}F_6Cl$:550.0923, found 550.0924.



2p

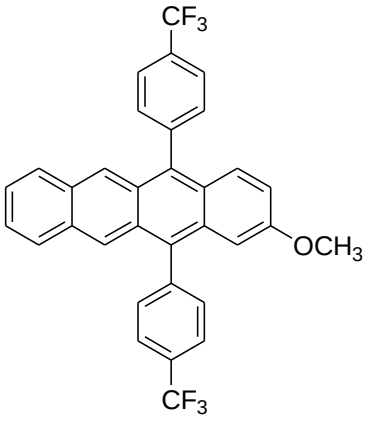
2-(Trifluoromethyl)-5,12-bis(4-(trifluoromethyl)phenyl)tetracene (2p). Column chromatography on silica gel (eluent: n-pentane to petroleum ether) afforded the title product

in 82% isolated yield as a yellow solid. M.p. 231-232 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (s, 2H), 7.97 (dd, *J* = 8.0, 4.0 Hz, 4H), 7.92 (s, 1H), 7.84 (dd, *J* = 6.4, 3.6 Hz, 2H), 7.72-7.67 (m, 5H), 7.40-7.37 (m, 3H). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 142.38 (q, $^{5}J_{C\text{-}F}$ = 0.9 Hz), 141.90 (q, $^{5}J_{C\text{-}F}$ = 0.9 Hz), 138.17, 136.44, 131.91, 131.76, 131.74, 131.65, 130.63 (q, $^{2}J_{C\text{-}F}$ = 32.7 Hz), 130.46 (q, $^{2}J_{C\text{-}F}$ = 33.0 Hz), 129.41, 129.01, 128.92, 128.39, 128.29, 128.22, 128.14, 127.22, 126.94 (q, $^{2}J_{C\text{-}F}$ = 32.2 Hz), 126.40, 126.24, 125.91 (q, $^{3}J_{C\text{-}F}$ = 3.7 Hz), 125.84 (q, $^{3}J_{C\text{-}F}$ = 3.6 Hz), 125.631, 124.78 (q, $^{3}J_{C\text{-}F}$ = 5.2 Hz), 124.08 (q, $^{1}J_{C\text{-}F}$ = 271.7 Hz), 124.28 (q, $^{1}J_{C\text{-}F}$ = 271.5 Hz), 124.26 (q, $^{1}J_{C\text{-}F}$ = 272.2 Hz), 120.25 (q, $^{3}J_{C\text{-}F}$ = 2.9 Hz). HRMS (EI) calcd for $C_{33}H_{17}F_9$:584.1187, found 584.1188.



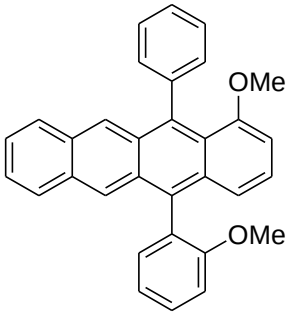
2q

5-(4-Methoxyphenyl)-2-(trifluoromethyl)-12-(4-(trifluoromethyl)phenyl)tetracene (2q). NMR analysis of the reaction crude indicated that two isomers of **2q** and **2q'** were formed in 40% and 50% NMR yields, respectively. **2q** was isolated in 17% yield as a yellow solid. M.p. 247-249 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (s, 1H), 8.21 (s, 1H), 7.96 (d, *J* = 8.0 Hz, 2H), 7.88-7.81 (m, 4H), 7.68 (d, *J* = 7.6 Hz, 2H), 7.45 (d, *J* = 8.8 Hz, 2H), 7.38-7.34 (m, 3H), 7.21 (d, *J* = 8.4 Hz, 2H), 4.01 (s, 3H). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 159.46, 142.24, 138.34, 137.11, 132.40, 131.84, 131.62, 131.57, 130.43 (q, $^{2}J_{C\text{-}F}$ = 32.6 Hz), 130.32, 130.12, 129.37, 129.16, 128.98, 128.43, 128.34, 127.36, 126.78 (q, $^{2}J_{C\text{-}F}$ = 32.1 Hz), 126.39, 126.00, 125.97, 125.83 (q, $^{3}J_{C\text{-}F}$ = 3.4 Hz), 125.77, 124.57 (q, $^{3}J_{C\text{-}F}$ = 4.8 Hz), 124.30 (q, $^{1}J_{C\text{-}F}$ = 272.3 Hz), 124.21 (q, $^{1}J_{C\text{-}F}$ = 272.4 Hz), 119.55 (q, $^{3}J_{C\text{-}F}$ = 2.6 Hz), 114.19, 55.44. HRMS (EI) calcd for $C_{33}H_{20}OF_6$:546.1418, found 546.1414.



2q'

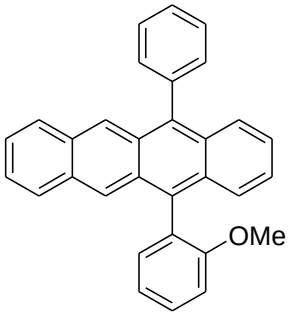
2-Methoxy-5,12-bis(4-(trifluoromethyl)phenyl)tetracene (2q'). 2q' was isolated in 31% yield as an orange red solid. M.p. 294-295 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (s, 1H), 8.10 (s, 1H), 7.96-7.91 (m, 4H), 7.79 (d, *J* = 8.4, 2H), 7.69-7.65 (m, 4H), 7.50 (d, *J* = 9.6, 1H), 7.32-7.31 (m, 2H), 7.01-6.99 (m, 1H), 6.69 (s, 1H), 3.71 (s, 3H). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 156.81, 143.56, 143.08, 136.07, 133.09, 131.83, 131.80, 131.40, 130.65, 130.07, 129.96 (q, $^{2}J_{C\text{-}F}$ = 32.6 Hz), 129.70 (q, $^{2}J_{C\text{-}F}$ = 32.8 Hz), 129.15, 128.41, 128.31, 128.18, 127.66, 126.22, 125.85 (q, $^{3}J_{C\text{-}F}$ = 3.9 Hz), 125.72, 125.62 (q, $^{3}J_{C\text{-}F}$ = 3.5 Hz), 125.50, 125.27, 124.41 (q, $^{1}J_{C\text{-}F}$ = 272.1 Hz), 124.37, 124.37 (q, $^{1}J_{C\text{-}F}$ = 271.8 Hz), 121.07, 101.30, 55.07. HRMS (EI) calcd for $C_{33}H_{20}OF_6$:546.1418, found 546.1419.



2r

1-Methoxy-5-(2-methoxyphenyl)-12-phenyltetracene (2r). Column chromatography on neutral Al_2O_3 gel (eluent: n-pentane to ethyl acetate: petroleum ether = 1:50) afforded **2r** and **2r'** in 61% and 7% isolated yields, respectively. **2r**: a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (s, 1H), 8.17 (s, 1H), 7.76-7.71 (m, 2H), 7.59-7.54 (m, 1H), 7.51-7.45 (m, 4H), 7.42-7.40 (m, 1H), 7.35 (dd, *J* = 7.2, 1.6, 1H), 7.25-7.18 (m, 5H), 7.11 (dd, *J* = 8.8, 7.6 Hz, 1H), 6.49 (d, *J* = 7.2 Hz, 1H), 3.62 (s, 3H), 3.41 (s, 3H). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 158.11, 156.99, 143.81, 135.70, 133.54, 133.00, 131.12, 131.01, 130.68, 130.30, 129.82, 129.77, 129.28, 129.15, 128.72, 128.42, 128.15, 126.93, 126.74, 125.82, 125.13, 124.82,

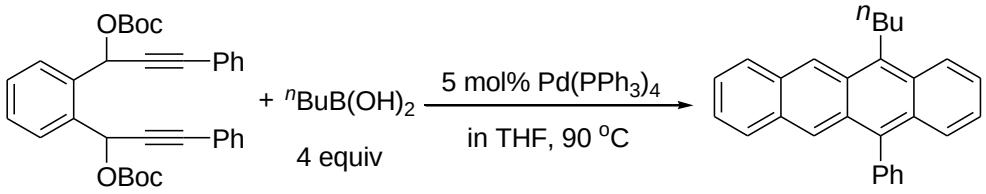
124.70, 124.42, 122.96, 120.85, 119.85, 111.39, 102.87, 55.74, 55.38. HRMS (EI) calcd for $C_{32}H_{24}O_2$:440.1776, found 440.1779.



2r'

5-(2-Methoxyphenyl)-12-phenyltetracene (2r'). 2r': a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (s, 1H), 8.26 (s, 1H), 7.80-7.76 (m, 2H), 7.69-7.54 (m, 8H), 7.40-7.37 (m, 1H), 7.28-7.22 (m, 6H), 3.65 (s, 3H). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 158.20, 139.43, 136.87, 133.83, 133.14, 131.60, 131.57, 130.95, 130.93, 129.48, 129.43, 129.41, 129.24, 129.06, 128.44, 128.40, 127.78, 127.47, 127.06, 126.91, 125.75, 125.40, 124.98, 124.94, 124.65, 124.62, 120.85, 111.40, 55.76. HRMS (EI) calcd for $C_{31}H_{22}O$:410.1671, found 410.1676.

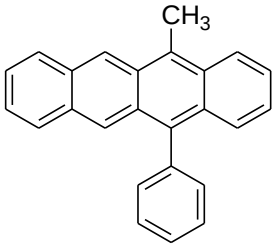
Typical procedure for the synthesis of 5-butyl-12-phenyltetracene 2s.



1g **2s**

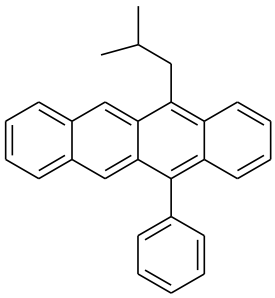
To a solution of 1,1'-(1,2-phenylene)bis(3-phenylprop-2-yne-1,1-diyl) di-*tert*-butyl dicarbonate (**1g**) (108.0 mg, 0.2 mmol) and n-butylboronic acid (82.0 mg, 0.8 mmo) in THF (5 mL) in a sealable tube was added $Pd(PPh_3)_4$ (12.0 mg, 0.01 mmol). The tube was sealed and immersed into an oil bath at 90 °C. After stirring for 3 h, the solvent was evaporated under the reduced pressure and the residue was purified by chromatography on neutral Al_2O_3 gel (eluent: ethyl acetate: n-pentane = 1:50) to afford the title product 5-butyl-12-phenyltetracene (**2s**) in 74% isolated yield (53 mg) as an orange red solid. M.p. 127-128 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.94 (s, 1H), 8.31 (d, *J* = 9.2, 1H), 8.27 (s, 1H), 8.03 (d, *J* = 8.4, 1H), 7.76 (d, *J* = 8.4, 1H), 7.65-7.56 (m, 4H), 7.48 (dd, *J* = 8.0, 1.2, 2H), 7.43-7.22 (m, 4H), 3.83 (t, *J* = 8.0, 2H), 1.98-1.94 (m, 2H), 1.74-1.68 (m, 2H), 1.10 (t, *J* = 7.2, 3H). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 139.58, 135.70, 135.37, 131.58, 131.00, 130.74, 129.50, 129.35,

128.49, 128.48, 128.42, 128.36, 128.19, 127.81, 127.39, 126.43, 125.18, 125.02, 124.81, 124.57, 124.42, 122.94, 33.61, 28.34, 23.56, 14.16. HRMS (EI) calcd for $C_{28}H_{24}$:360.1878, found 360.1880.



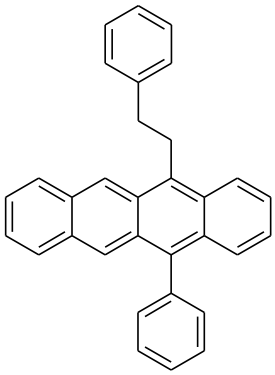
2t

5-Methyl-12-phenyltetracene (2t). Column chromatography on neutral Al_2O_3 gel (eluent: ethyl acetate: n-pentane = 1:50) afforded the title product in 59% isolated yield as an orange red solid. M.p. 178-180 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 8.93 (s, 1H), 8.33-8.30 (m, 1H), 8.26 (s, 1H), 8.01 (d, *J* = 8.4, 1H), 7.76 (d, *J* = 8.0, 1H), 7.64-7.56 (m, 4H), 7.47-7.45 (m, 2H), 7.41-7.23 (m, 4H), 3.29 (s, 3H). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 139.51, 135.60, 131.62, 130.94, 130.76, 130.08, 129.40, 129.12, 129.01, 128.88, 128.45, 128.42, 128.36, 127.68, 127.41, 126.28, 125.23, 125.05, 124.77, 124.72, 124.44, 123.23, 14.63. HRMS (EI) calcd for $C_{25}H_{18}$:318.1409, found 318.1408.



2u

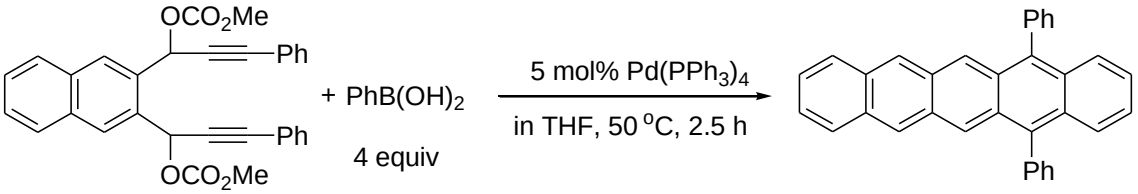
5-Isobutyl-12-phenyltetracene (2u). Column chromatography on neutral Al_2O_3 gel (eluent: ethyl acetate: n-pentane = 1:50) afforded the title product in 74% isolated yield as a yellow solid. M.p. 140-141 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 8.95 (s, 1H), 8.33 (d, *J* = 9.2, 1H), 8.26 (s, 1H), 8.01 (d, *J* = 8.4, 1H), 7.76 (d, *J* = 8.4, 1H), 7.65-7.56 (m, 4H), 7.49- 7.46 (m, 2H), 7.41-7.21 (m, 4H), 3.74 (d, *J* = 7.2, 2H), 2.45-2.35 (m, 1H), 1.12 (d, *J* = 6.4, 6H). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 139.62, 135.86, 134.50, 131.58, 130.84, 130.64, 129.46, 129.31, 129.28, 128.90, 128.54, 128.43, 128.31, 127.76, 127.39, 126.35, 125.20, 125.15, 125.04, 124.61, 124.34, 123.66, 36.81, 31.23, 23.26. HRMS (EI) calcd for $C_{28}H_{24}$:360.1878, found 360.1879.



2v

5-Phenethyl-12-phenyltetracene (2v). Column chromatography on neutral Al_2O_3 gel (eluent: ethyl acetate: n-pentane = 1:50) afforded the title product in 50% isolated yield as an orange red solid. M.p. 137-138 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 8.97 (s, 1H), 8.35 (d, *J* = 9.2 Hz, 1H), 8.29 (s, 1H), 8.03 (d, *J* = 8.8 Hz, 1H), 7.78 (d, *J* = 8.8 Hz, 1H), 7.68-7.58 (m, 4H), 7.51-7.36 (m, 8H), 7.33-7.22 (m, 3H), 4.13 (dd, *J* = 8.4 Hz, 2H), 3.25 (dd, *J* = 8.4 Hz, 2H). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 142.19, 139.45, 136.24, 133.82, 131.55, 131.19, 130.77, 129.50, 129.34, 128.67, 128.50, 128.48, 128.44, 128.37, 128.36, 128.06, 127.93, 127.46, 126.60, 126.25, 125.35, 125.18, 125.11, 124.47, 124.20, 122.65, 37.23, 30.65. HRMS (EI) calcd for $C_{32}H_{24}$: 408.1878, found 408.1875.

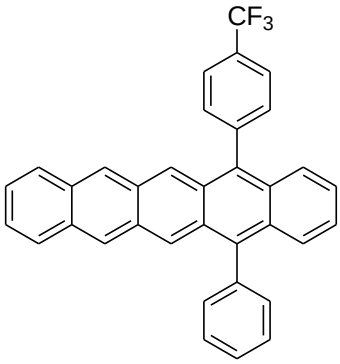
Typical procedure for the synthesis of 5,14-diphenylpentacene 4a.



3 **4a**

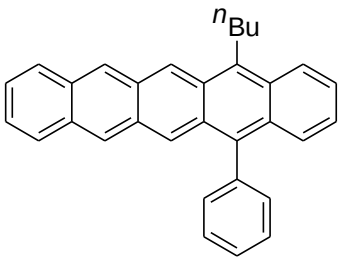
To a solution of dimethyl 1,1'-(naphthalene-2,3-diyl)bis(3-phenylprop-2-yne-1,1-diyl) dicarbonate (**3**) (100.9 mg, 0.2 mmol) and phenylboronic acid (97.5 mg, 0.8 mmol) in THF (5 mL) was added $Pd(PPh_3)_4$ (12.0 mg, 0.01 mmol). Then the Schlenk tube was sealed with parafilm. After stirring for 2.5 h at 50 ^oC, the solvent was evaporated under the reduced pressure and the residue was purified by chromatography on neutral Al_2O_3 gel (eluent: ethyl acetate: n-pentane = 1:100 to 1:50) to afford the title product 5,14-diphenylpentacene (**4a**) in 54% isolated yield (46.5 mg) as a purple solid. It is noted that pentacene derivatives should be isolated immediately after the reaction was complete due to its instability over a longer period.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (s, 2H), 8.47 (s, 2H), 7.82-7.80 (m, 2H), 7.70-7.58 (m, 12H), 7.26-7.24 (m, 2H), 7.19-7.16 (m, 2H). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 139.32, 136.91, 131.56, 131.54, 129.56, 129.28, 129.23, 128.59, 128.35, 127.64, 127.06, 126.55, 126.07, 125.05, 124.72. HRMS (EI) calcd for $C_{34}H_{22}$: 430.1722, found 430.1721.



4b

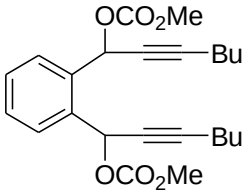
To a solution of dimethyl 1,1'-(naphthalene-2,3-diyl)bis(3-phenylprop-2-yne-1,1-diyl) dicarbonate (**3**) (100.9 mg, 0.2 mmol) and (4-(trifluoromethyl)phenyl)boronic acid (152.0 mg, 0.8 mmol) in THF (5 mL) was added $Pd(PPh_3)_4$ (12.0 mg, 0.01 mmol). Then the Schlenk tube was sealed with parafilm. After stirring for 2.5 h at 50 ^{o}C, the solvent was evaporated under the reduced pressure and the residue was purified by chromatography on neutral Al_2O_3 gel (eluent: ethyl acetate: n-pentane = 1:50) to afford the title product 5-phenyl-14-(4-(trifluoromethyl)phenyl)pentacene (**4b**) in 59% isolated yield (59 mg) as a purple solid. It is noted that pentacene derivatives should be isolated immediately after the reaction was complete due to its instability over a longer period. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (s, 1H), 8.46 (s, 2H), 8.45 (s, 1H), 7.94 (d, J = 8.4 Hz, 2H), 7.82-7.79 (m, 2H), 7.71-7.62 (m, 6H), 7.57-7.55 (m, 2H), 7.52-7.49 (m, 1H), 7.26-7.24 (m, 2H), 7.20-7.17 (m, 2H). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 143.40 (q, $^{5}J_{C\text{-}F}$ = 1.0 Hz), 139.05, 137.72, 134.88, 132.01, 131.72, 131.62, 131.46, 129.95 (q, $^{2}J_{C\text{-}F}$ = 32.4 Hz), 129.67, 129.54, 129.12, 129.10, 129.08, 128.85, 128.63, 128.32, 127.77, 127.25, 126.62, 126.45, 126.39, 125.65 (q, $^{3}J_{C\text{-}F}$ = 3.4 Hz), 125.60, 125.38, 125.28, 125.25, 125.20, 124.77, 124.45 (q, $^{1}J_{C\text{-}F}$ = 272.4 Hz). HRMS (EI) calcd for $C_{35}H_{21}F_3$: 498.1595, found 498.1598.

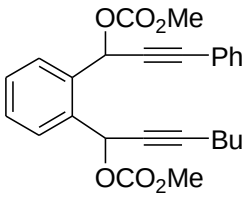


4c

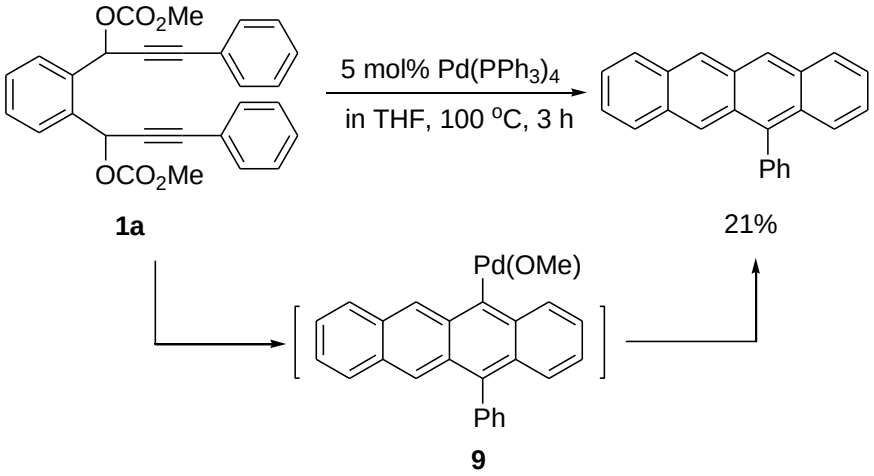
In a sealed tube, to a solution of dimethyl 1,1'-(naphthalene-2,3-diyl)bis(3-phenylprop-2-yne-1,1-diyl) dicarbonate (**3**) (100.9 mg, 0.2 mmol) and n-butylboronic acid (82.0 mg, 0.8 mmo) in THF (5 mL) was added $Pd(PPh_3)_4$ (12.0 mg, 0.01 mmol). Then the Schlenk tube was sealed with parafilm. After stirring at 90 ^oC for 2.5 h, the solvent was evaporated under the reduced pressure and the residue was purified by chromatography on neutral Al_2O_3 gel (eluent: ethyl acetate: n-pentane = 1:50) to afford the title product 5-butyl-14-phenylpentacene (**4c**) in 68% isolated yield (56 mg) as a purple solid. It is noted that pentacene derivatives should be isolated immediately after the reaction was complete due to its instability over a longer period. ^1H NMR (400 MHz, $CDCl_3$) δ 9.24 (s, 1H), 8.70 (s, 1H), 8.56 (s, 1H), 8.45 (s, 1H), 8.26 (d, *J* = 8.8 Hz, 1H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.66-7.58 (m, 4H), 7.52-7.50 (dd, *J* = 8.0, 1.6 Hz, 2H), 7.37-7.24 (m, 3H), 7.18 (dd, *J* = 8.2, 6.6 Hz, 1H), 3.88-3.83 (m, 2H), 2.04-1.98 (m, 2H), 1.78-1.72 (m, 2H), 1.13 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 139.60, 135.61, 135.24, 131.64, 131.61, 131.51, 129.70, 129.54, 129.42, 129.39, 128.50, 128.39, 128.35, 128.28, 127.91, 127.46, 126.78, 126.50, 126.49, 125.05, 124.98, 124.82, 124.70, 124.40, 123.07, 33.57, 28.46, 23.65, 14.20. HRMS (EI) calcd for $C_{32}H_{26}$: 410.2035, found 410.2037.

We carried out the reactions of the following substrates with phenylboronic acid catalyzed by 5 mol% $Pd(PPh_3)_4$ in THF, however, no desired tetracenes were obtained.





We also carried out the cyclization reaction of dicarbonate **1a** catalyzed by 5 mol% $Pd(PPh_3)_4$ in the absence of aryl boronic acids. It was found that 5-phenyltetracene was formed in 21% yield. This result may support the formation of intermediate **9**.



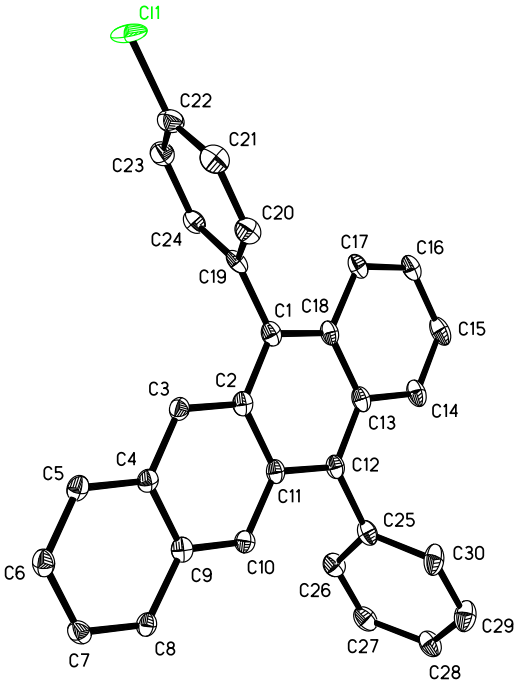
For characterization of 5-phenyltetracene: A light yellow solid. M.p. 188-190 °C (lit[3]: 190-191 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (s, 1H), 8.67 (s, 1H), 8.28 (s, 1H), 8.02 (d, *J* = 8.8 Hz, 1H), 7.97 (d, *J* = 8.4 Hz, 1H), 7.79 (d, *J* = 8.4 Hz, 1H), 7.65-7.58 (m, 4H), 7.51-7.49 (m, 2H), 7.39-7.24 (m, 4H). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 138.95, 136.88, 131.41, 131.34, 131.14, 131.12, 129.94, 129.60, 129.33, 128.73, 128.46, 127.92, 127.54, 126.82, 126.66, 126.38, 125.59, 125.29, 125.09, 124.98, 124.80. HRMS (EI) calcd for $C_{24}H_{16}$: 304.1252, found 304.1254.

References:

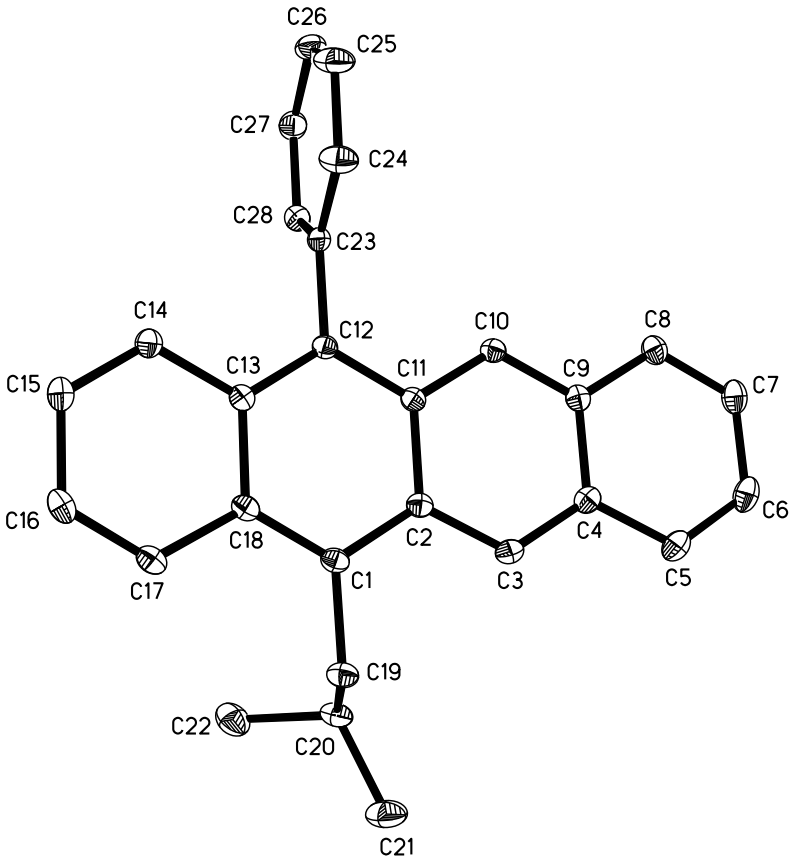
1 (a) A. Mallouli and Y. Lepage, *Synthesis*, **1980**, *9*, 689; (b) C. -H. Lin, K. -H. Lin, B. Pal and L. -D. Tsou, *Chem. Commun.* **2009**, 803.

2 O. Toshimichi, K. Akihito and S. Michinori, *Org. Lett.* **2011**, *13*, 1238.

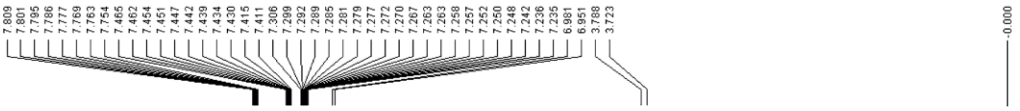
3 H. Straub and J. Hambrecht, *Synthesis*, **1975**, 425.



X-ray crystal structure of compound **2b** (Chloro atom is positional disordered)



X-ray crystal structure of compound **2u**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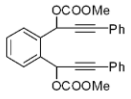
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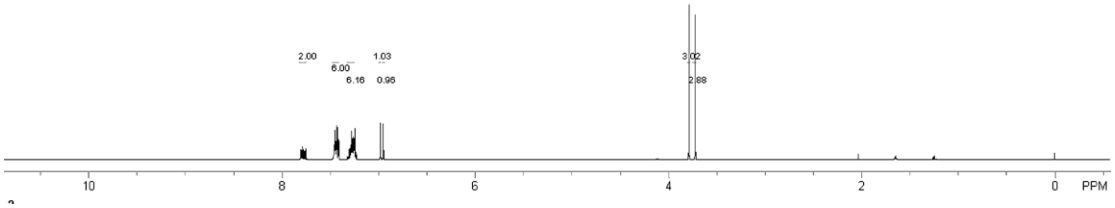
1a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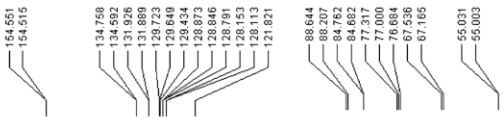
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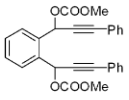
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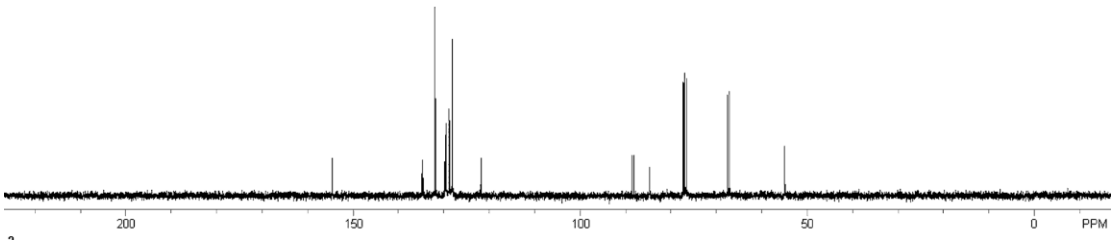
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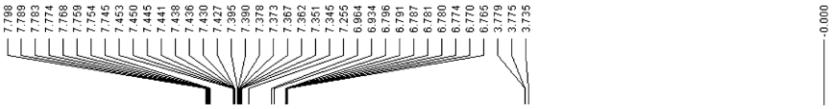
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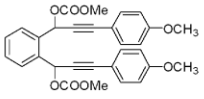
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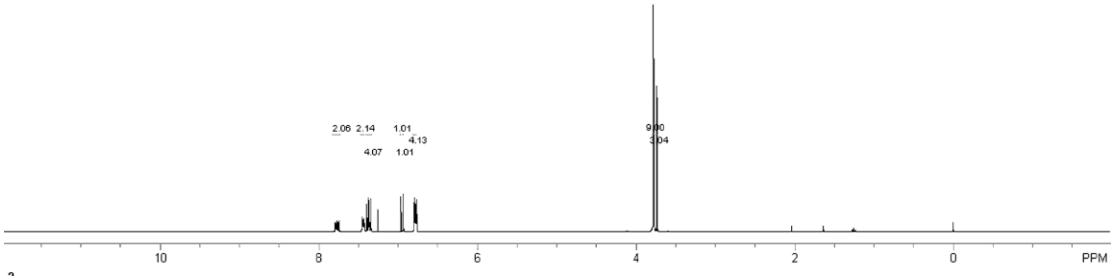
1b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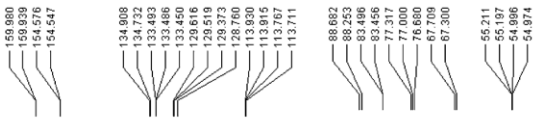
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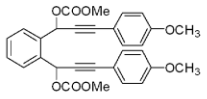
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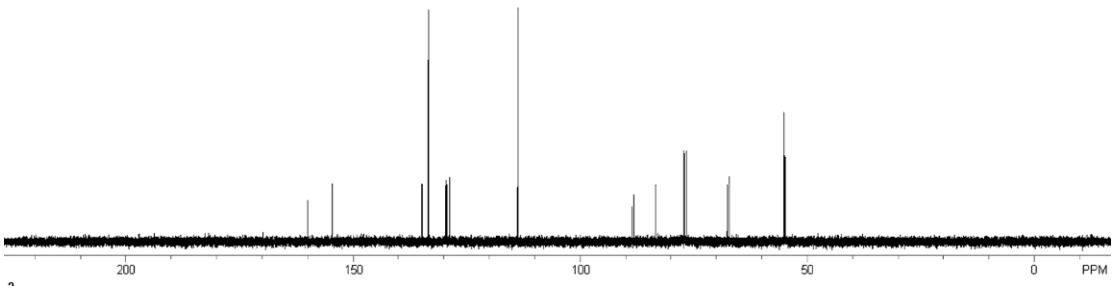
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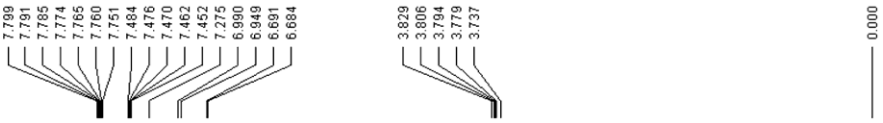
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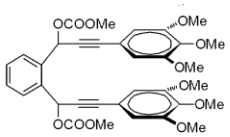
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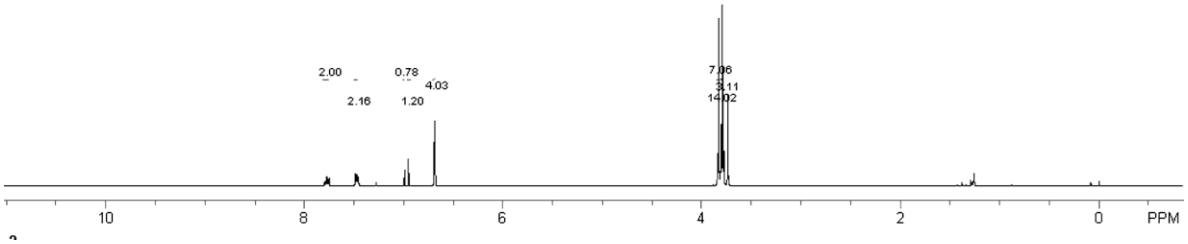
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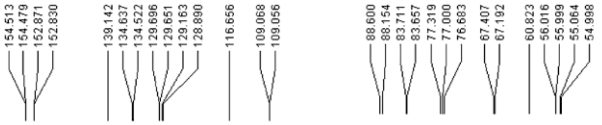
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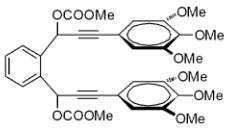
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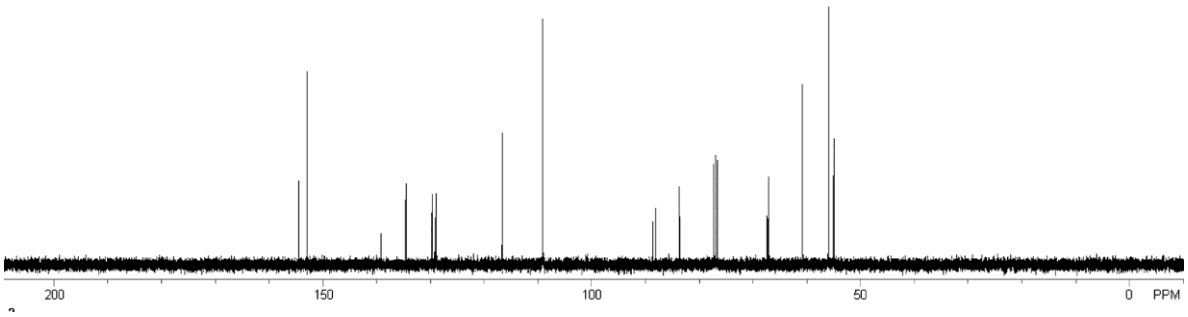
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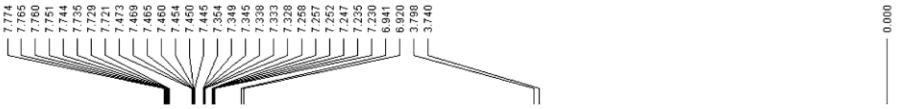
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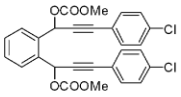
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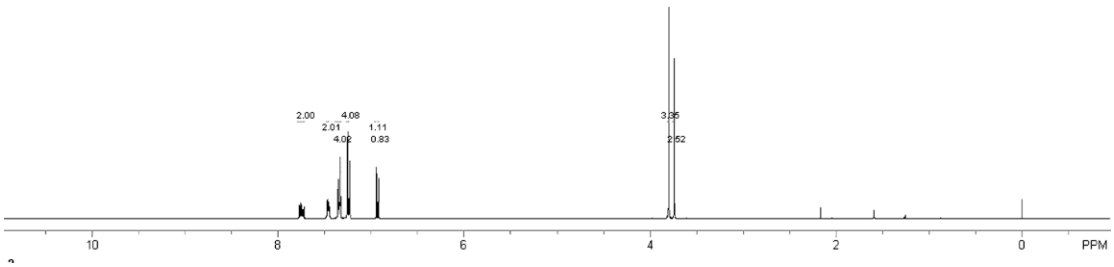
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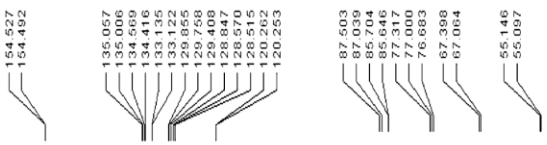
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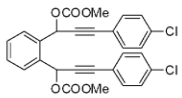
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Cl
Cl
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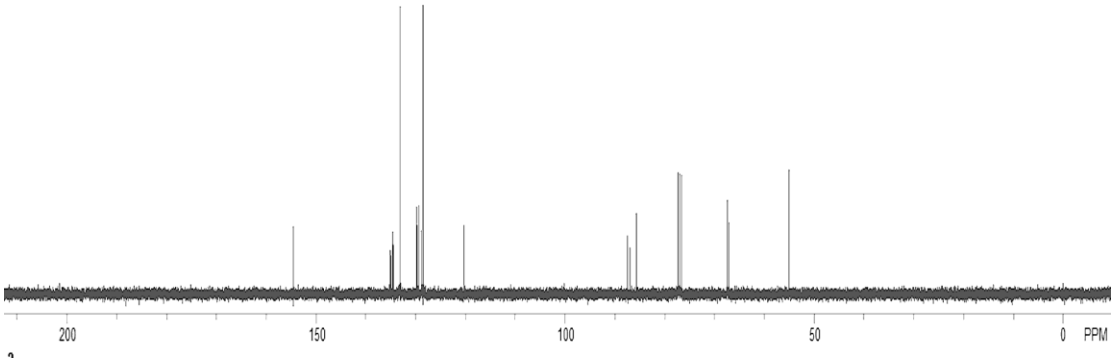
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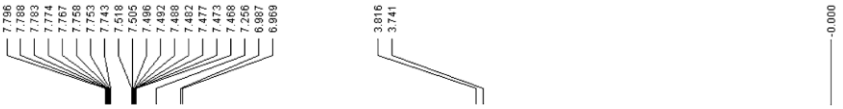
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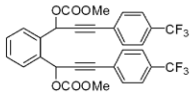
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CF3
CF3
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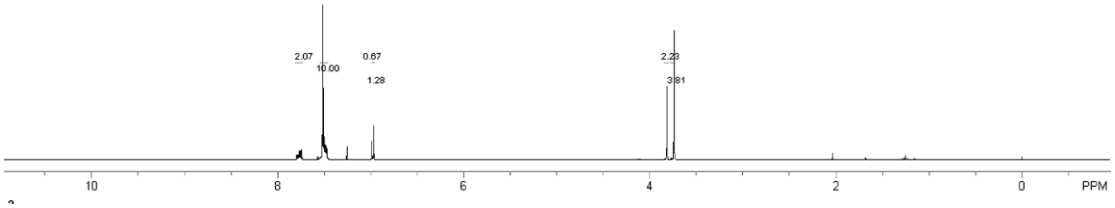
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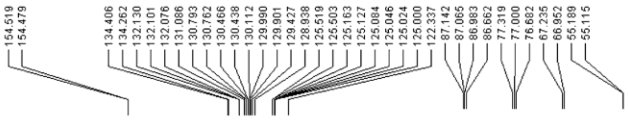
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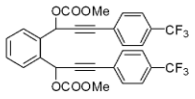
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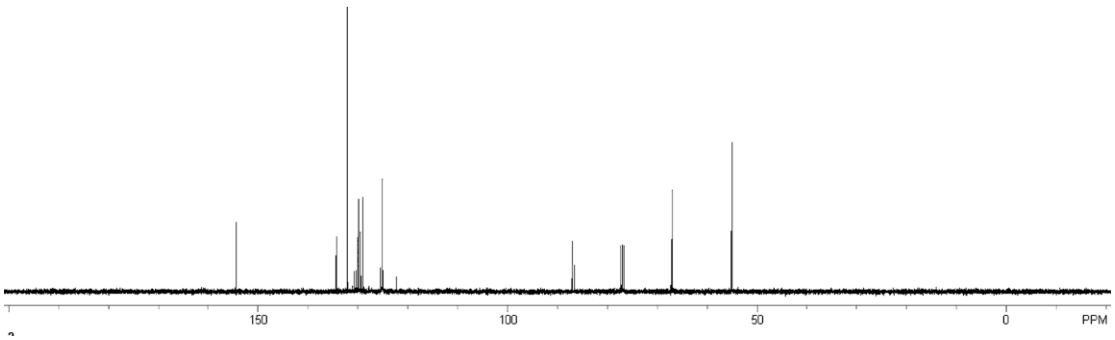
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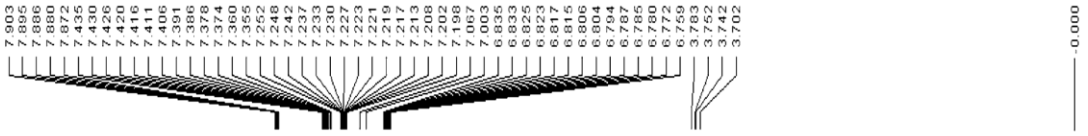
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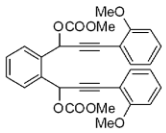
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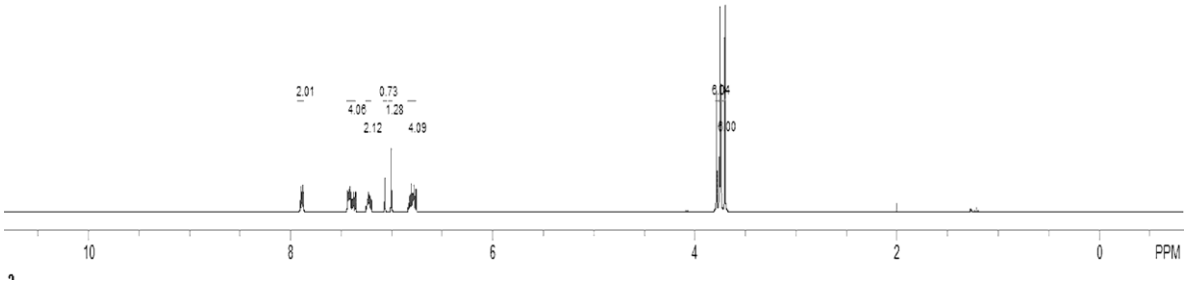
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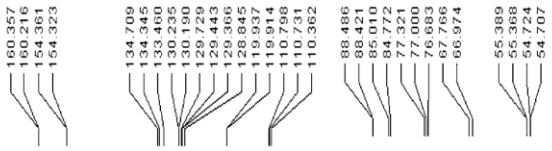
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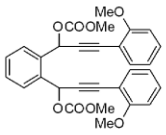
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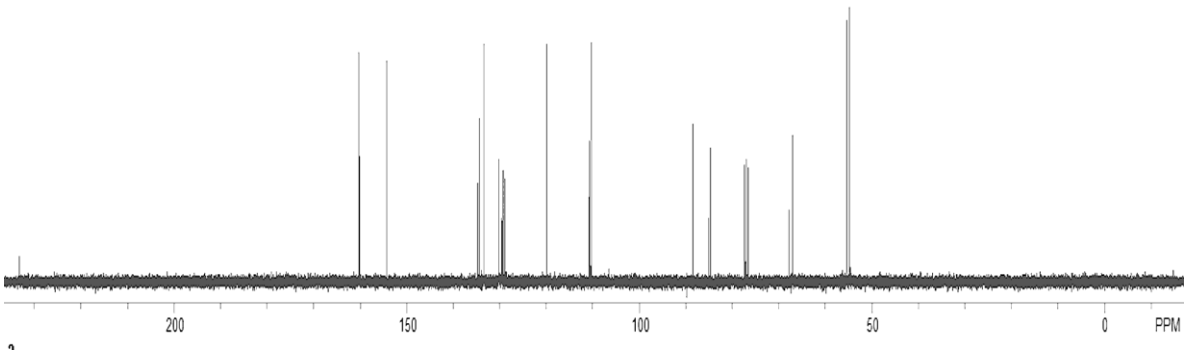
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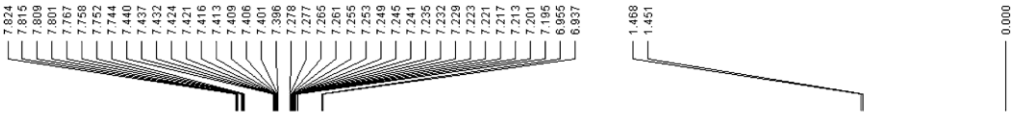
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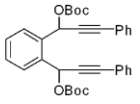
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OBoc

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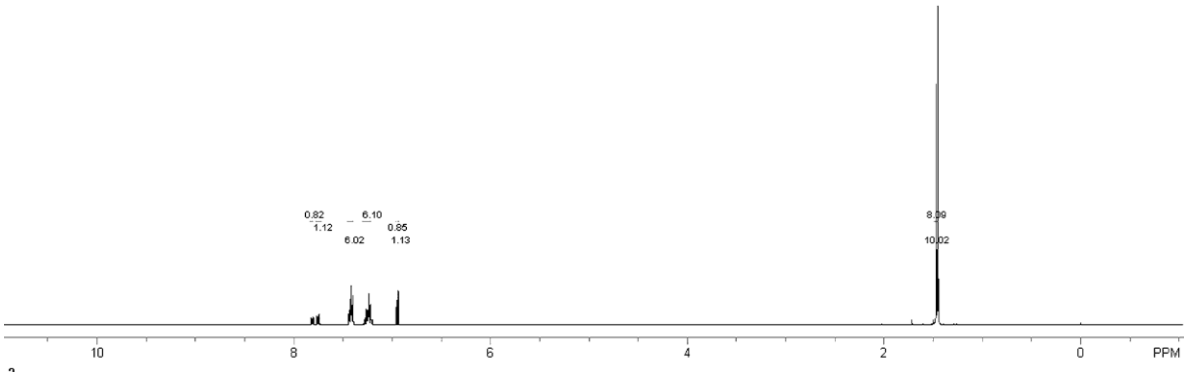
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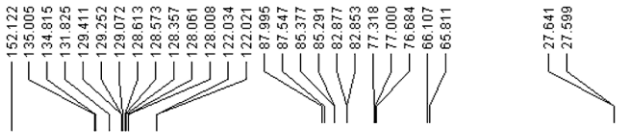
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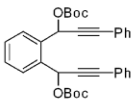
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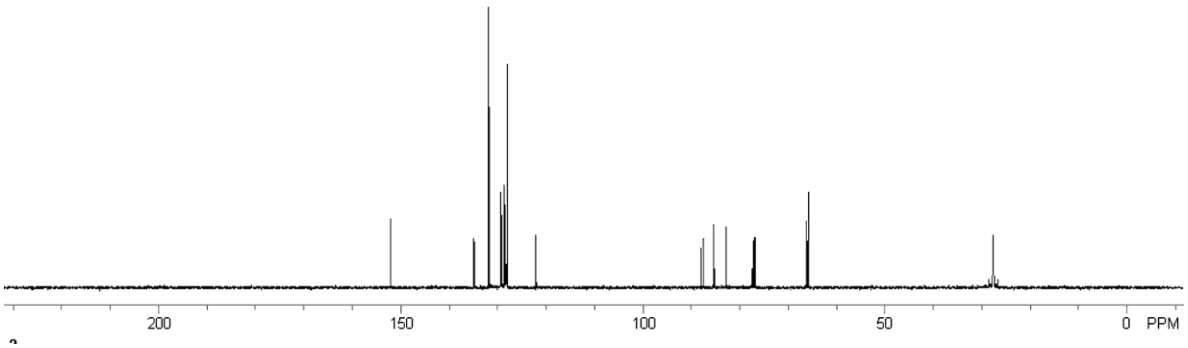
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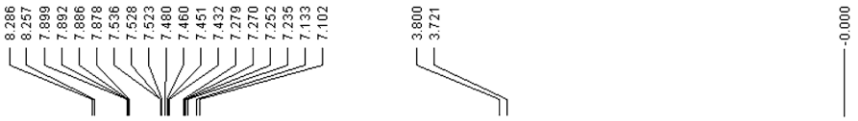
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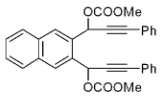
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Ph
Ph
OCOOMe

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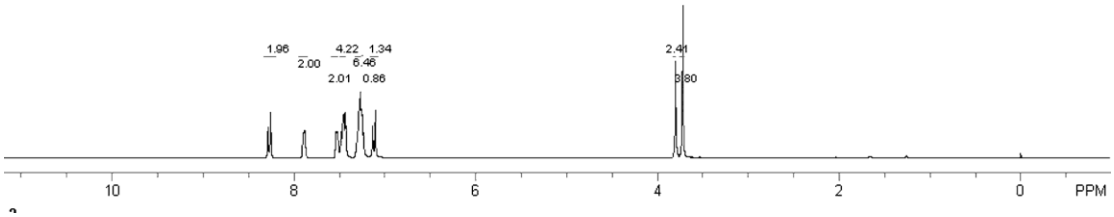
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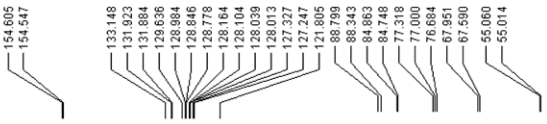
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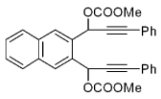
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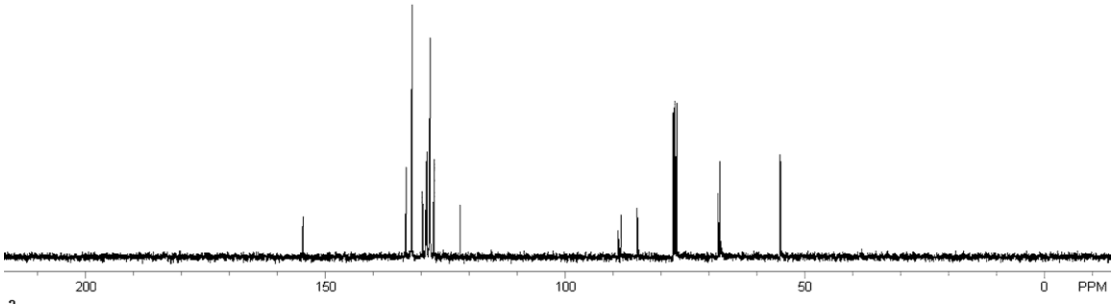
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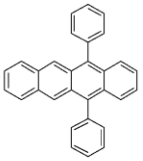

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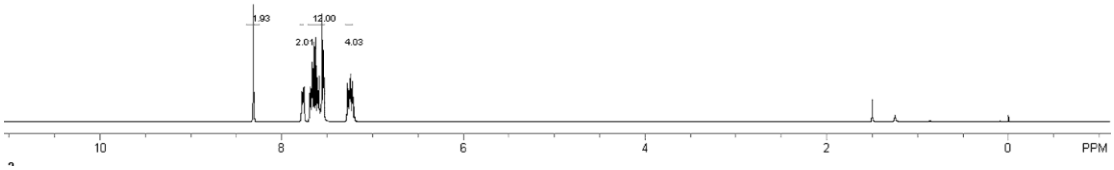
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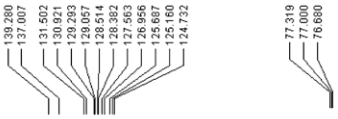
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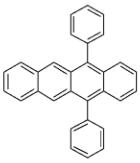
76.680



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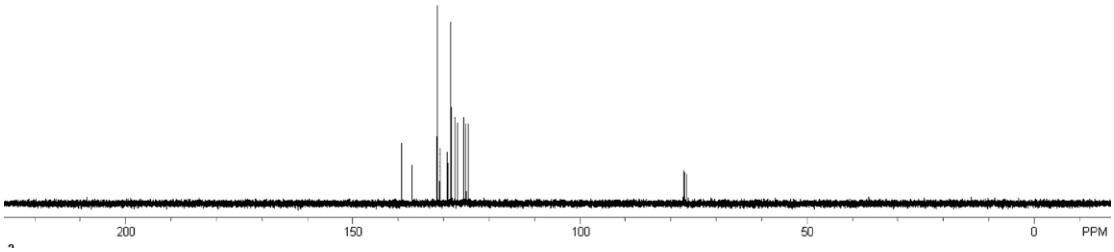
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7.610
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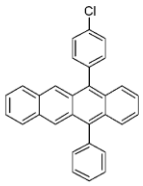
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2b


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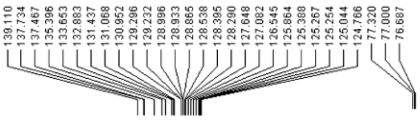
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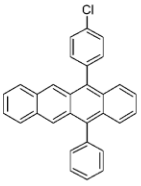
76.687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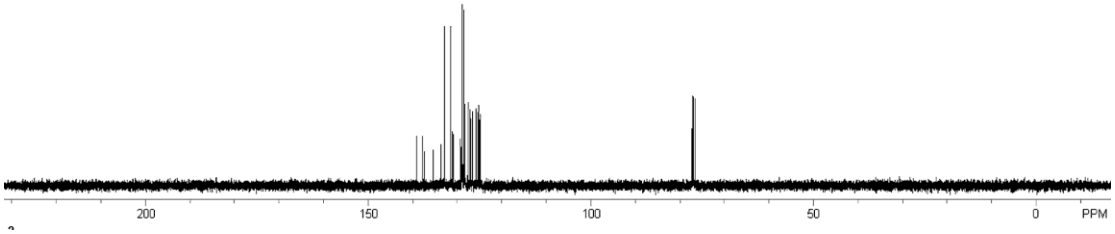
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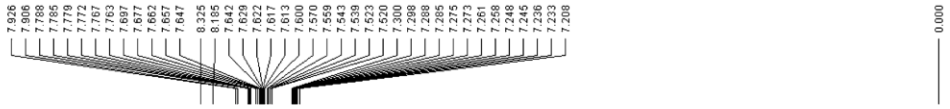
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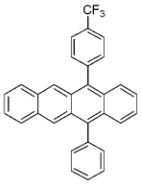
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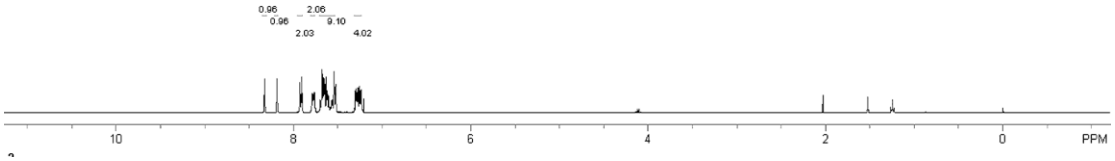
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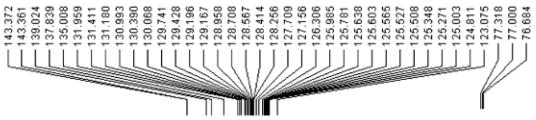
PPM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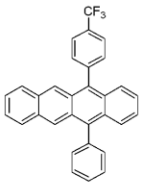
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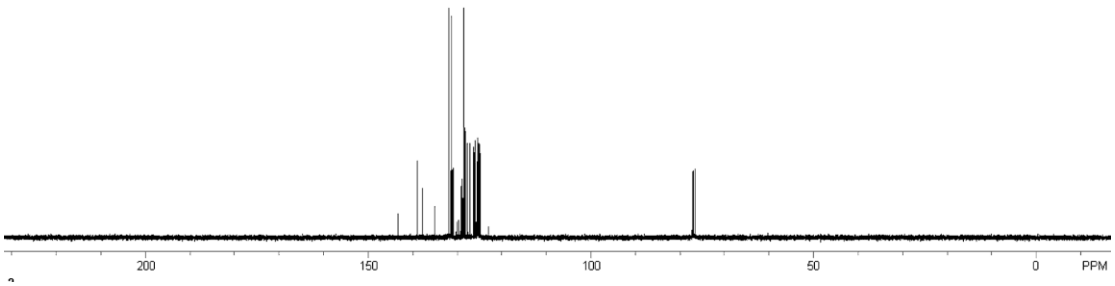
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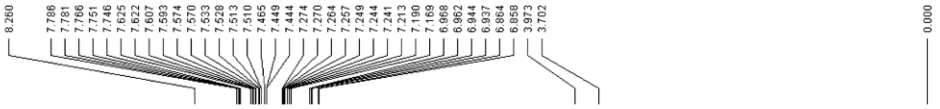
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7.449
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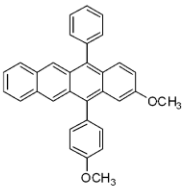
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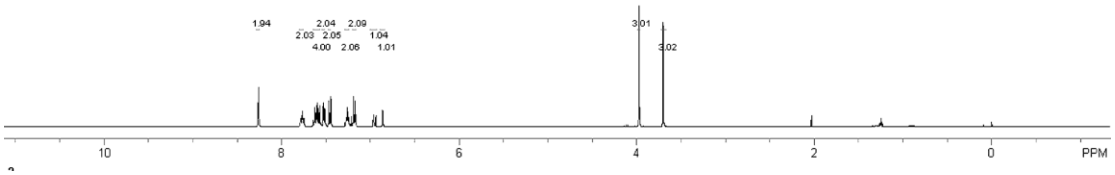
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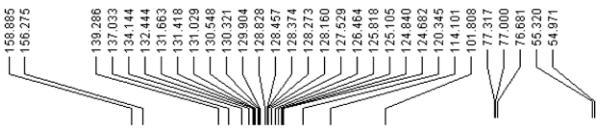
PPM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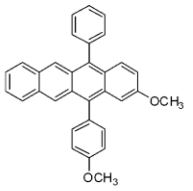
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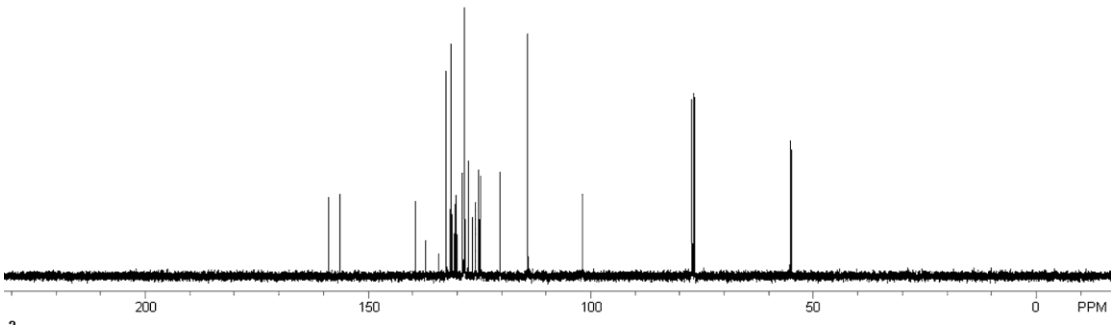
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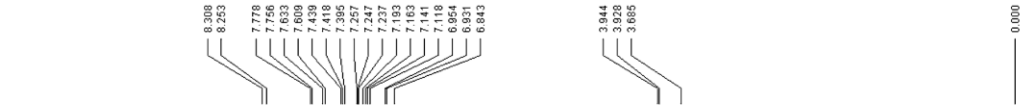
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7.418
7.395
7.257
7.247
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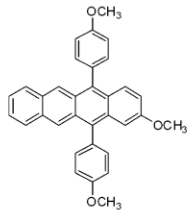
3.928
3.665
0.000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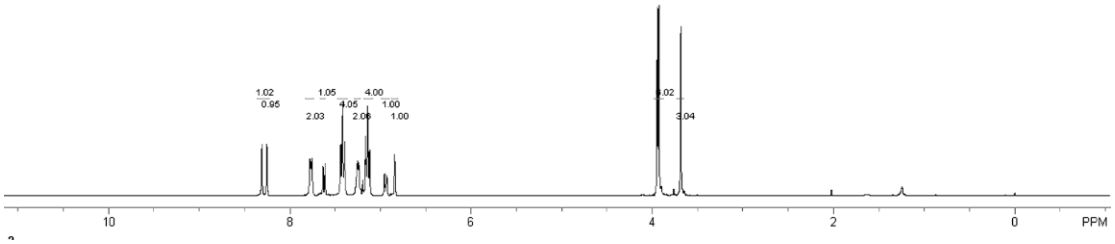
2e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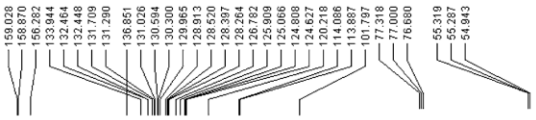
PPM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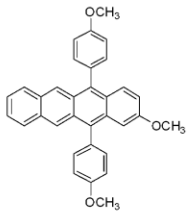
54.943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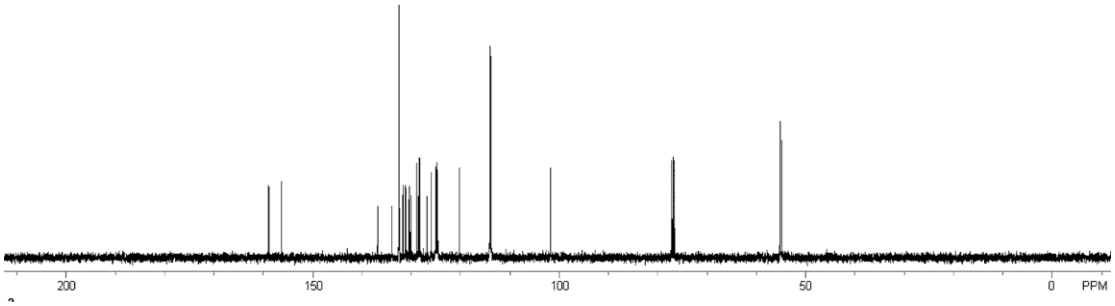
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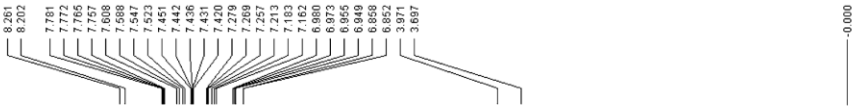
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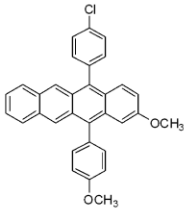
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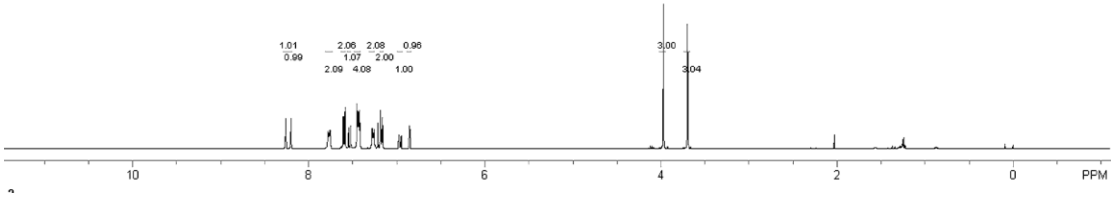
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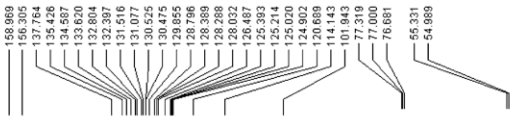
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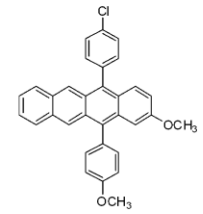
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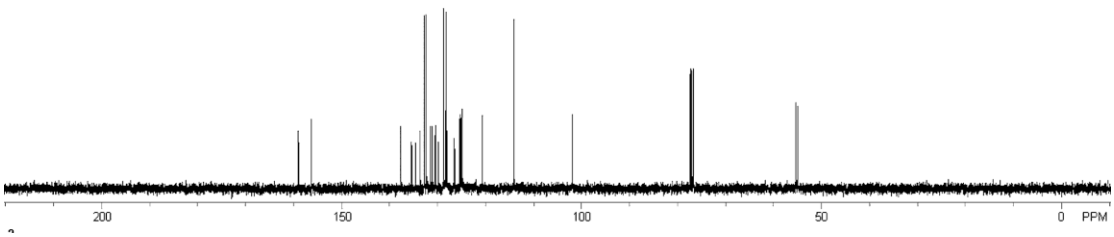
2f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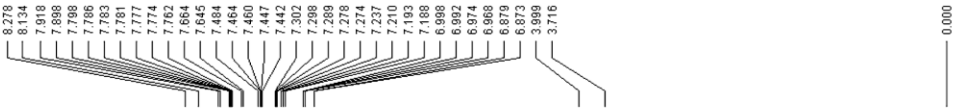
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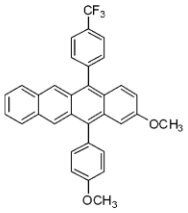
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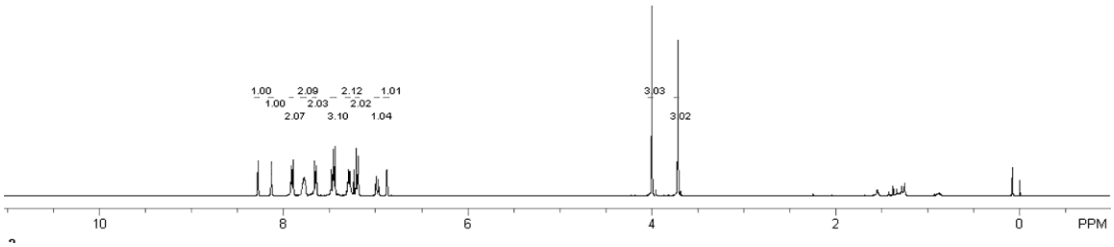
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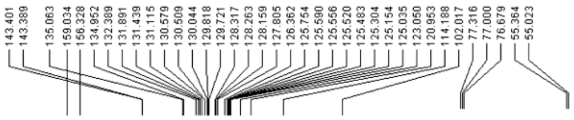
0
PPM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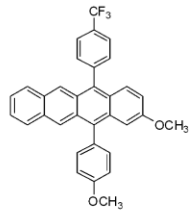
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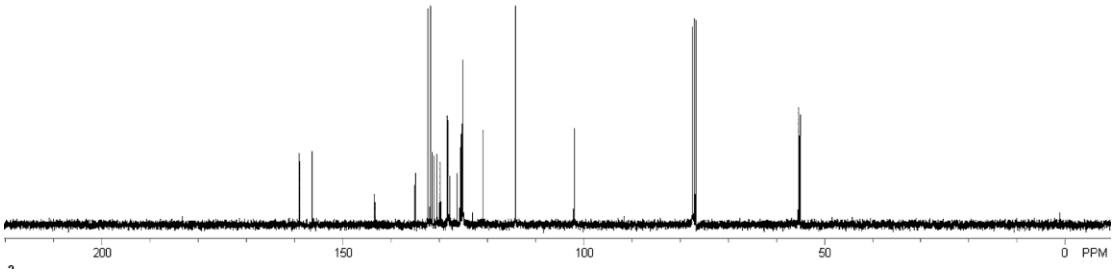
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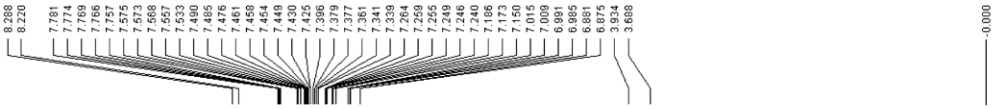
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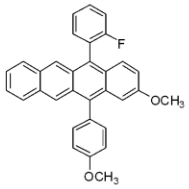
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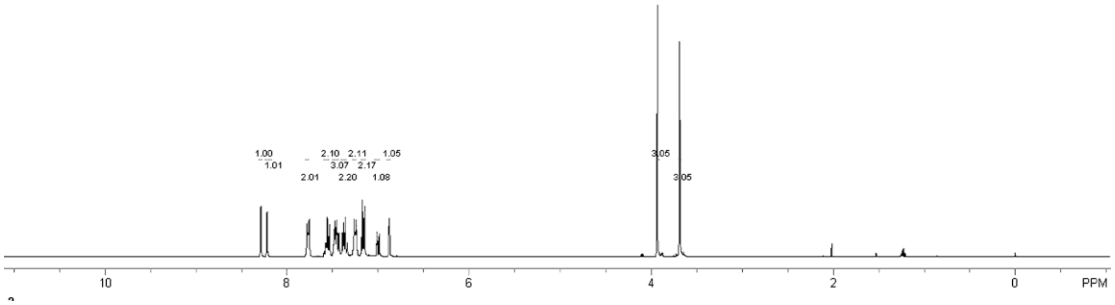
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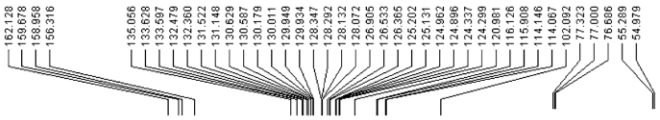
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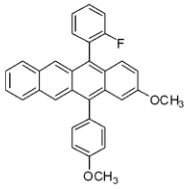
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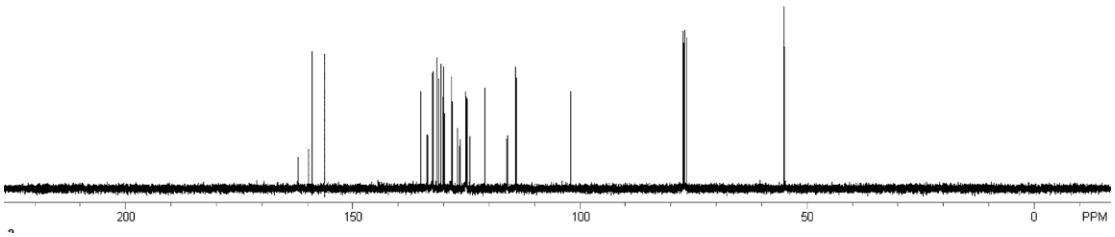
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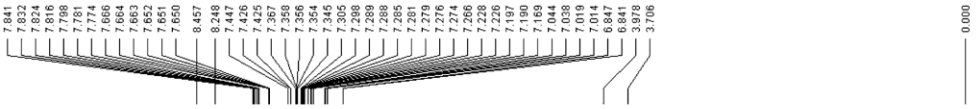
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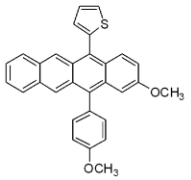
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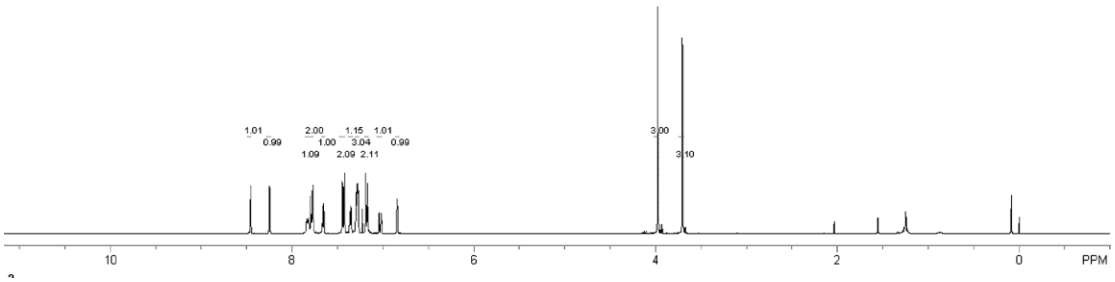
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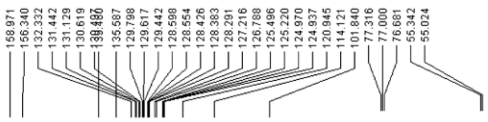
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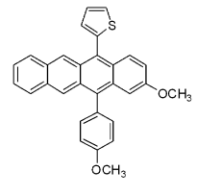
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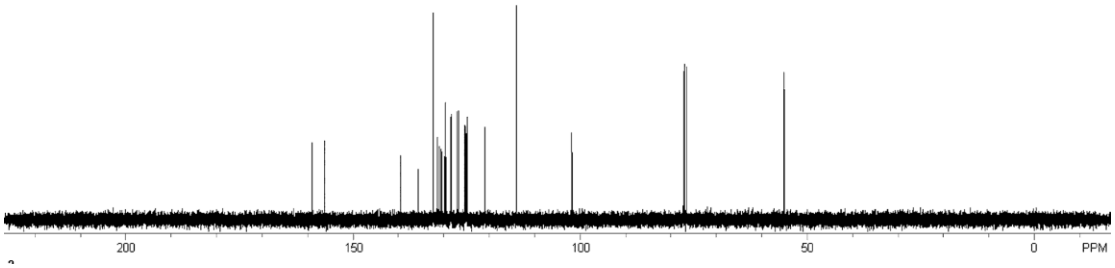
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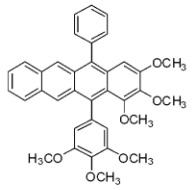
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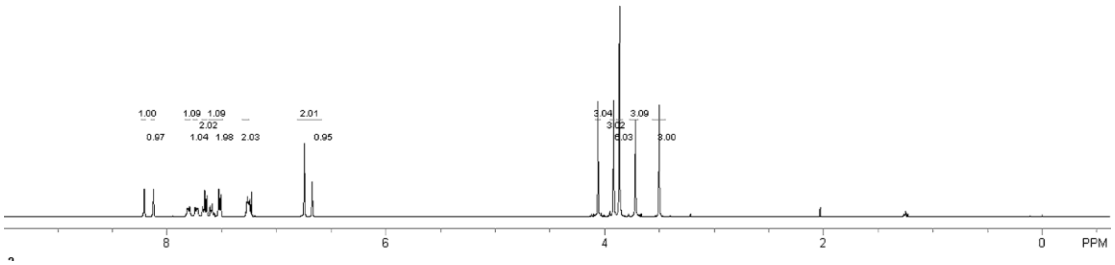
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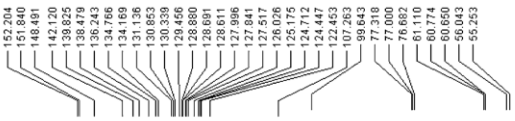
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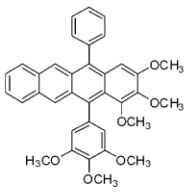
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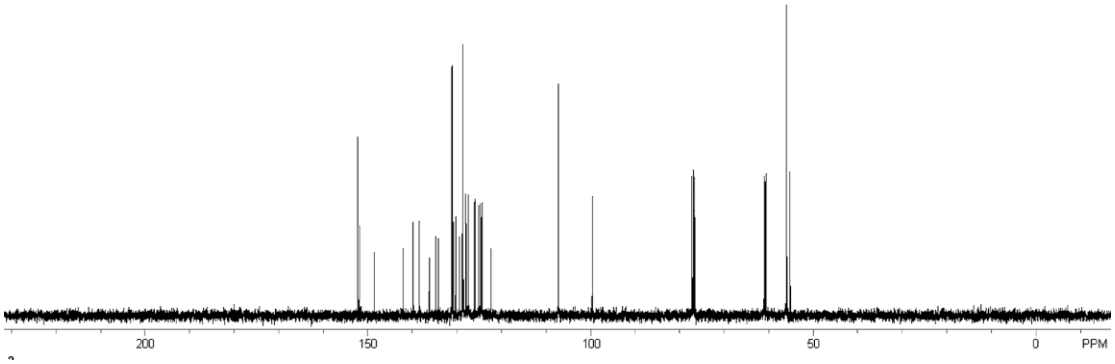
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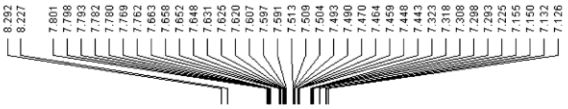
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7.509
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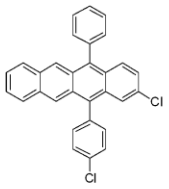
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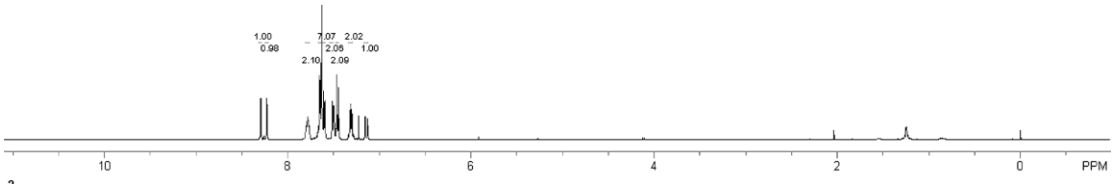
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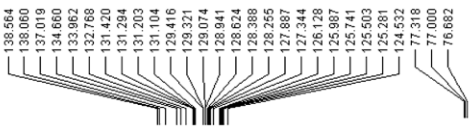
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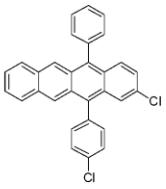
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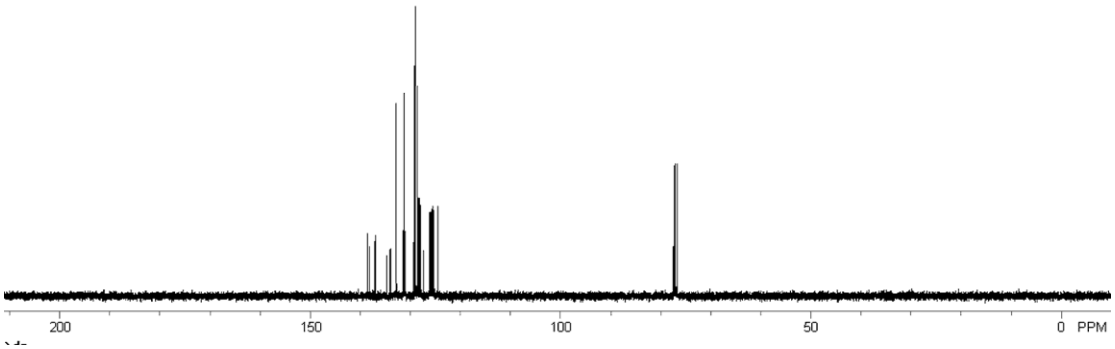
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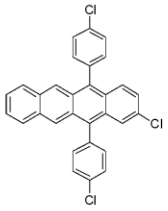
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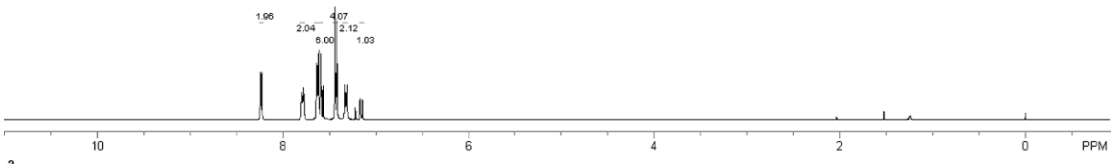
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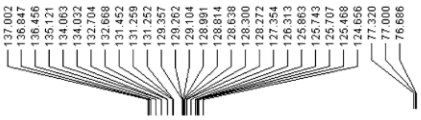
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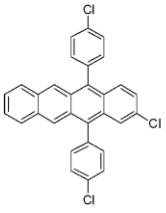
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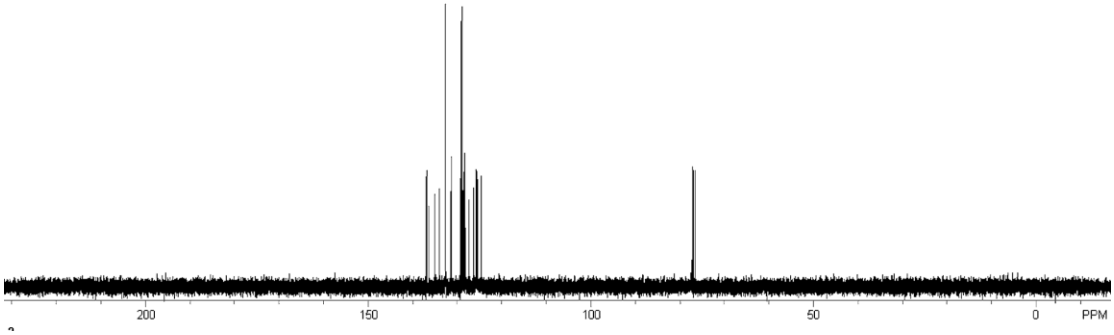
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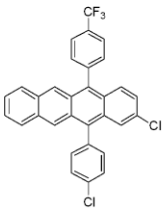
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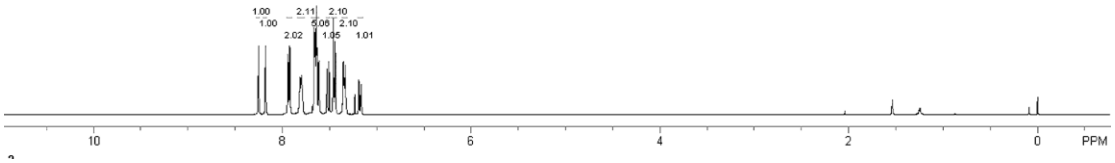
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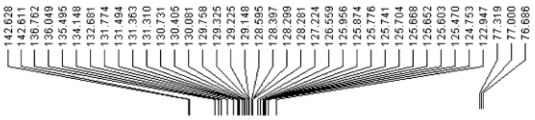
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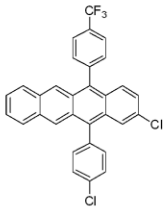
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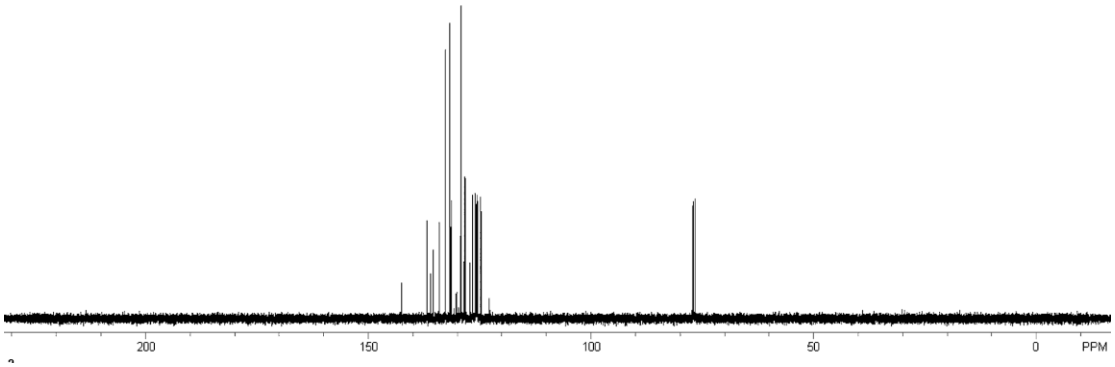
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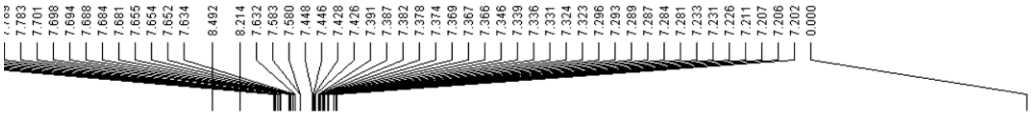
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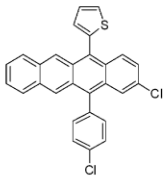
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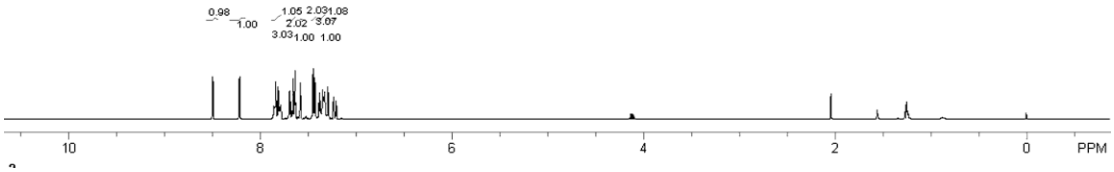
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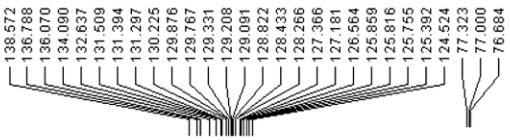
PPM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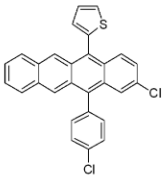
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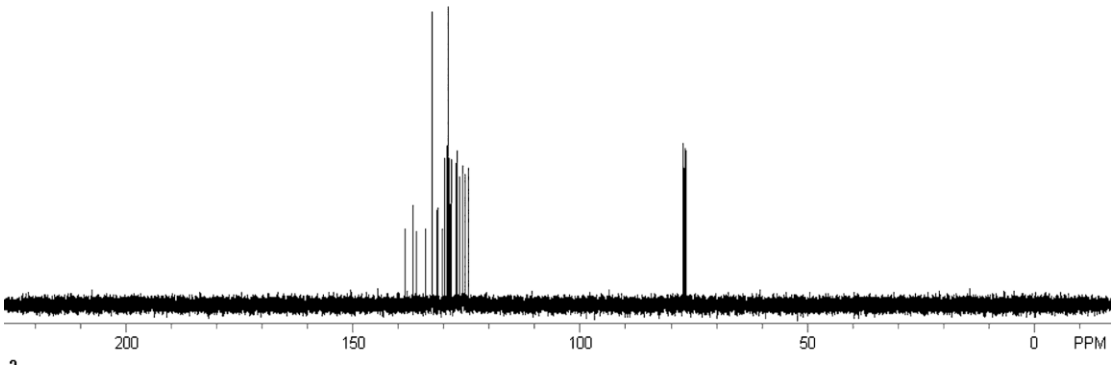
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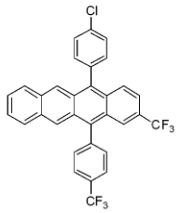
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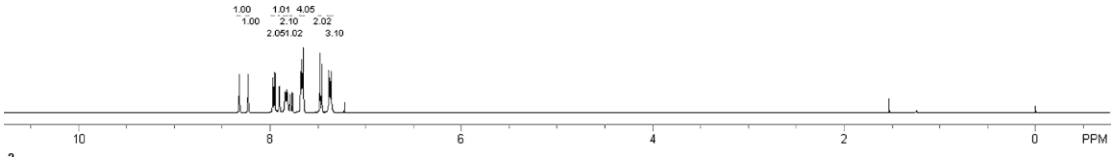
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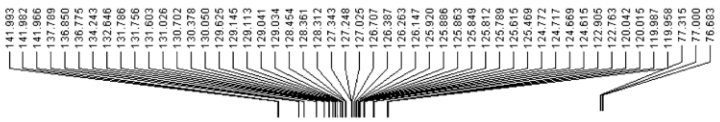
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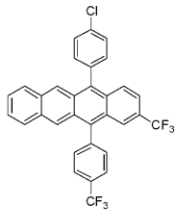
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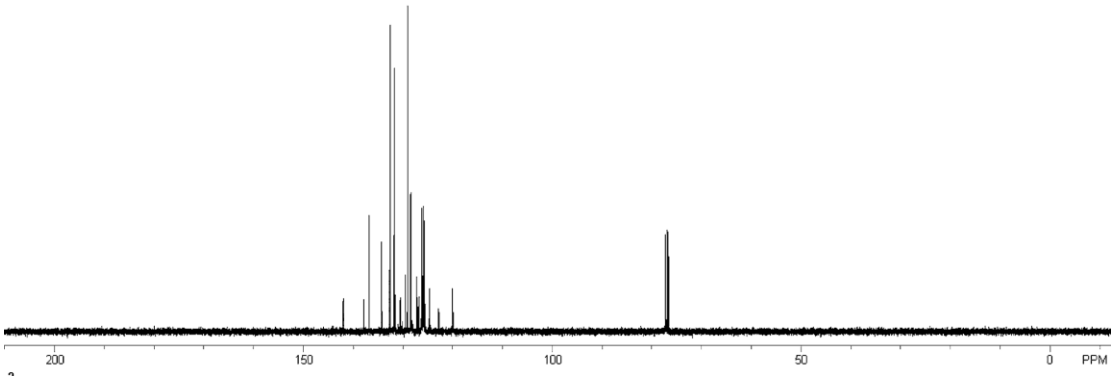
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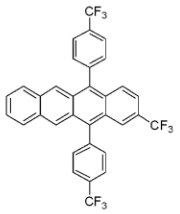
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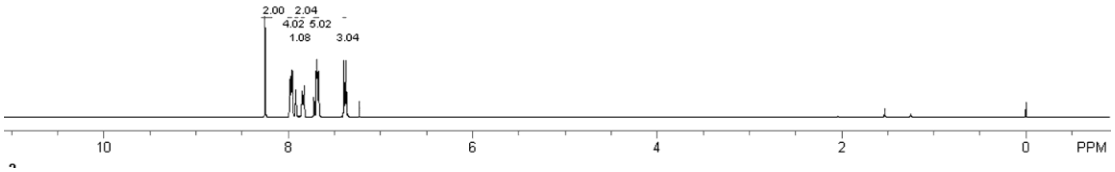
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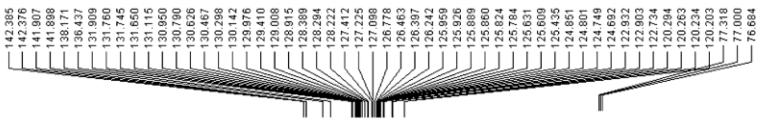
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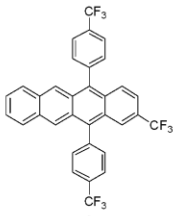
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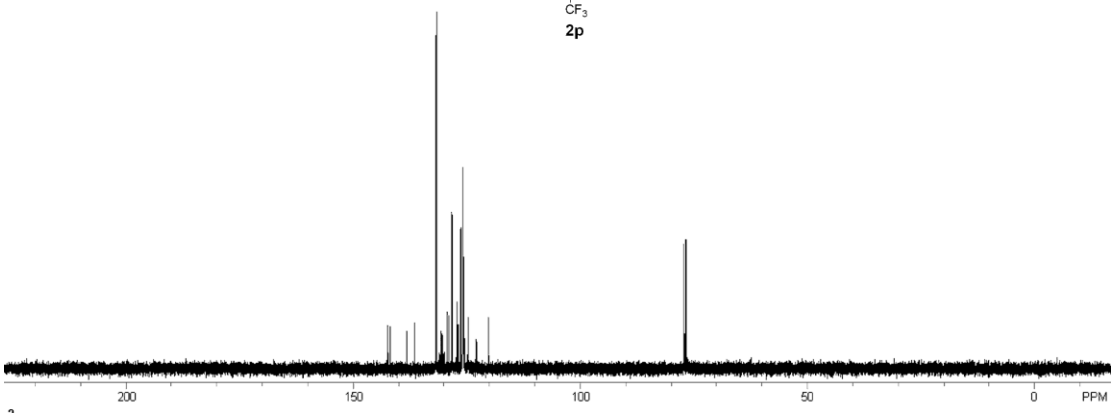
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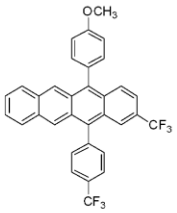
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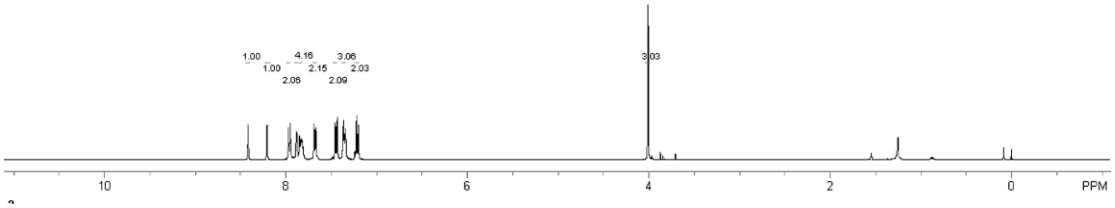
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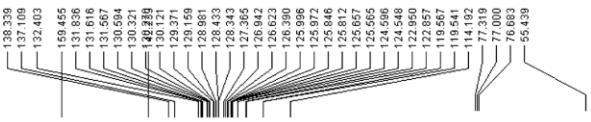
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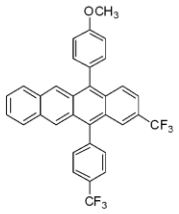
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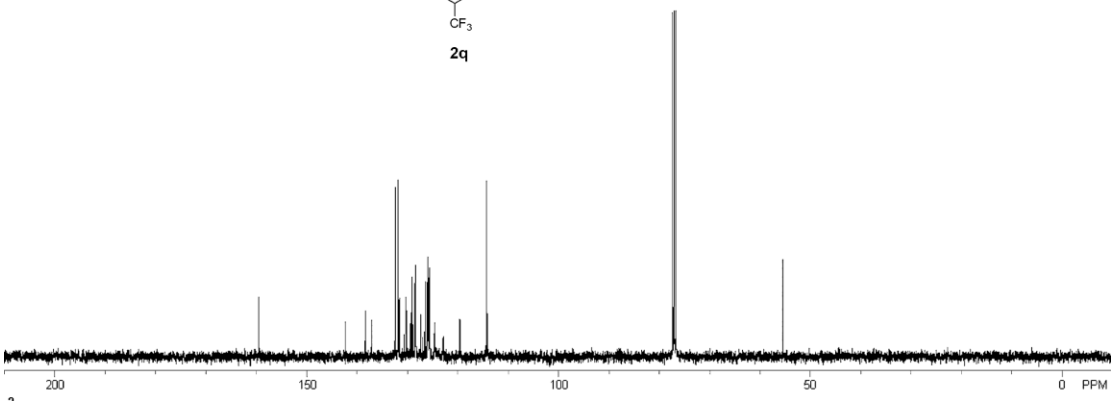
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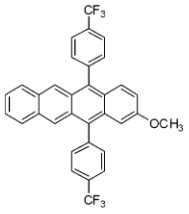
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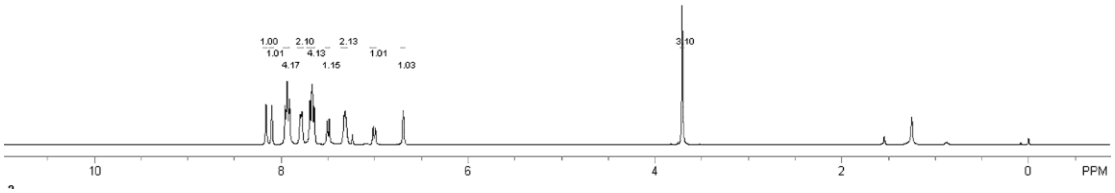
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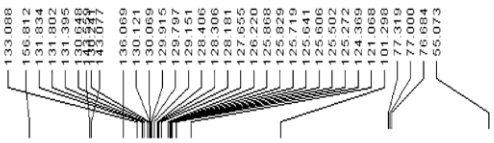
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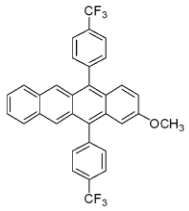
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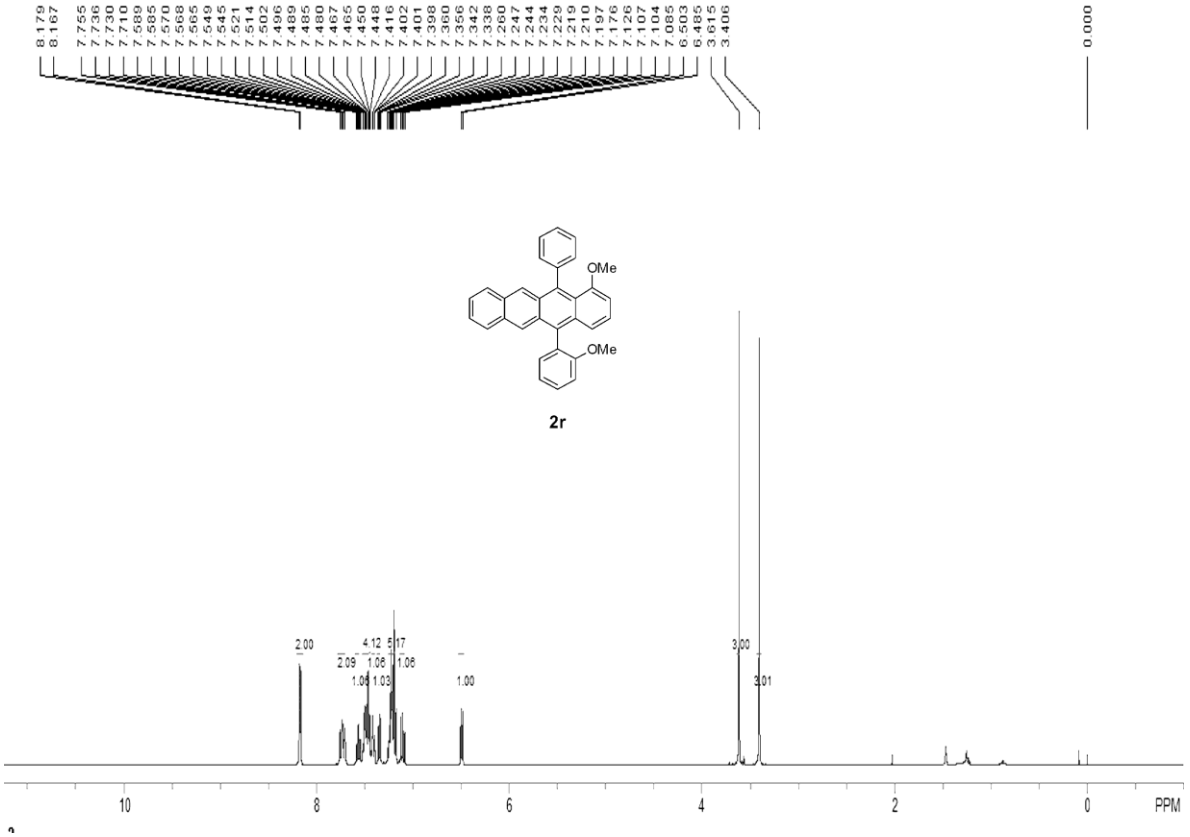
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OMe
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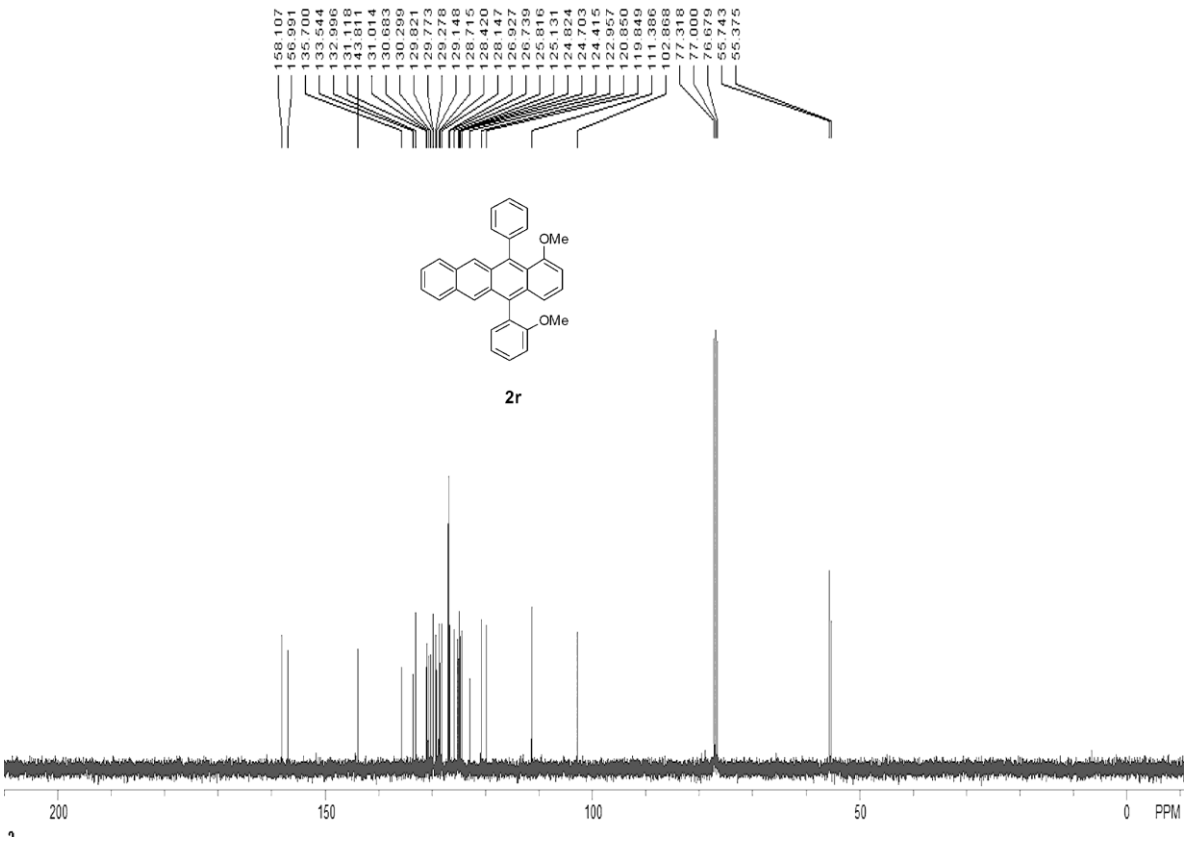
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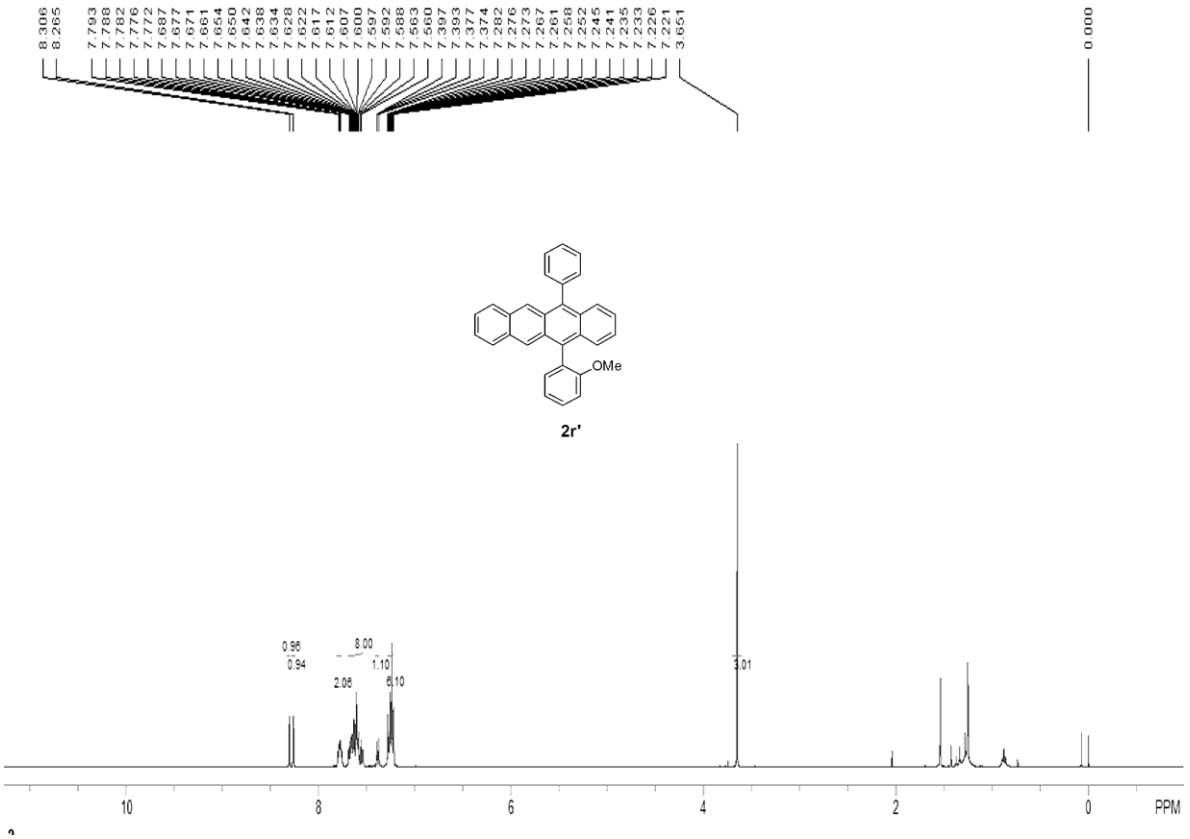
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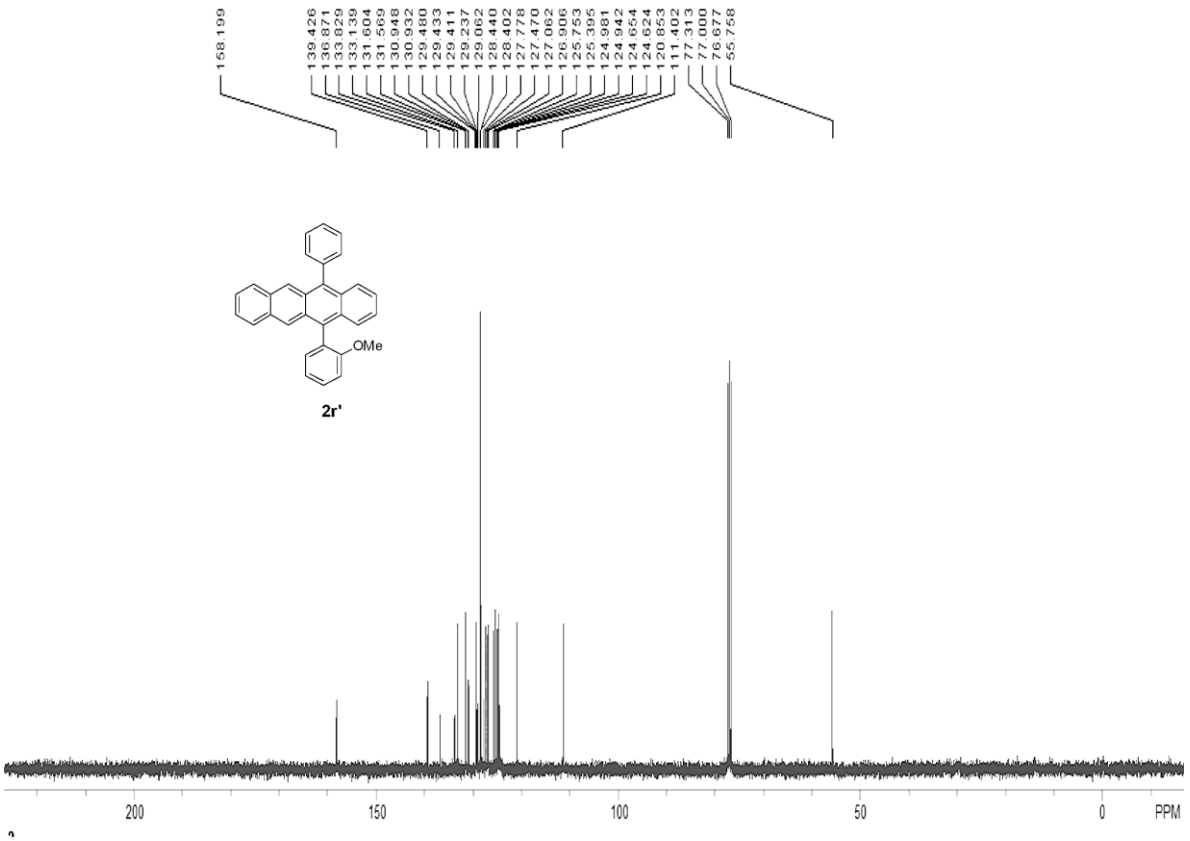
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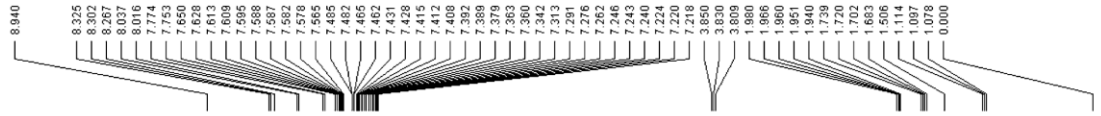
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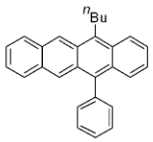
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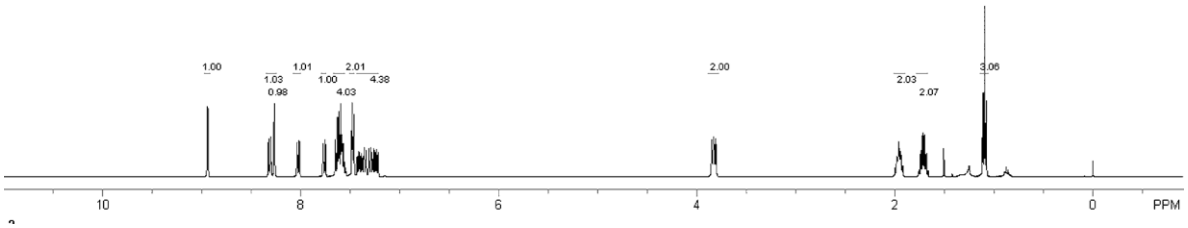
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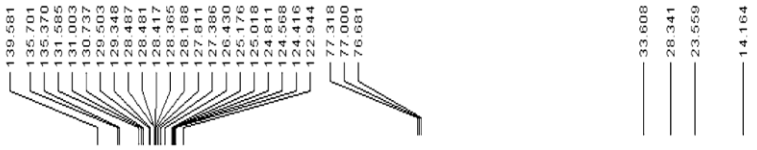
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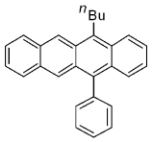
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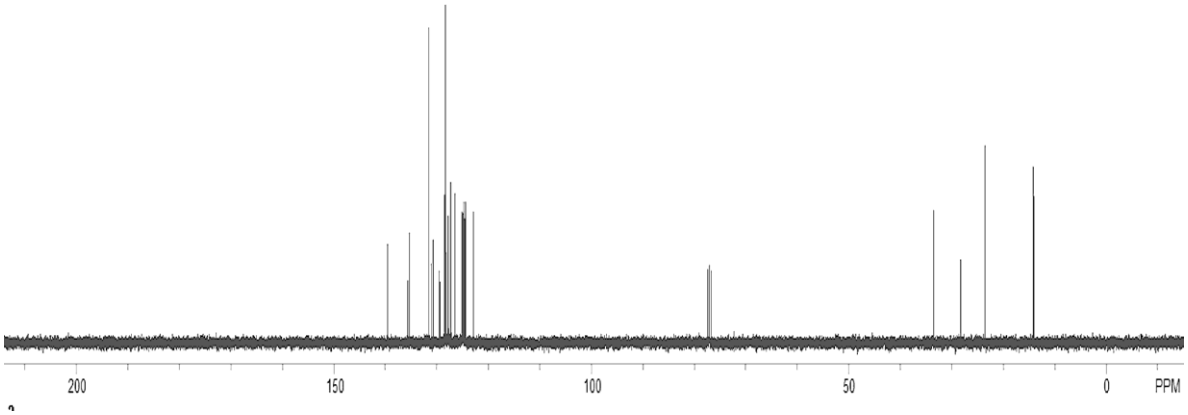
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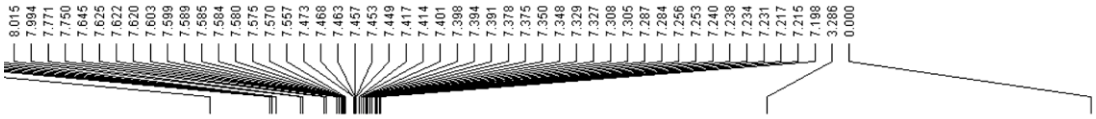
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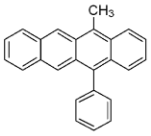
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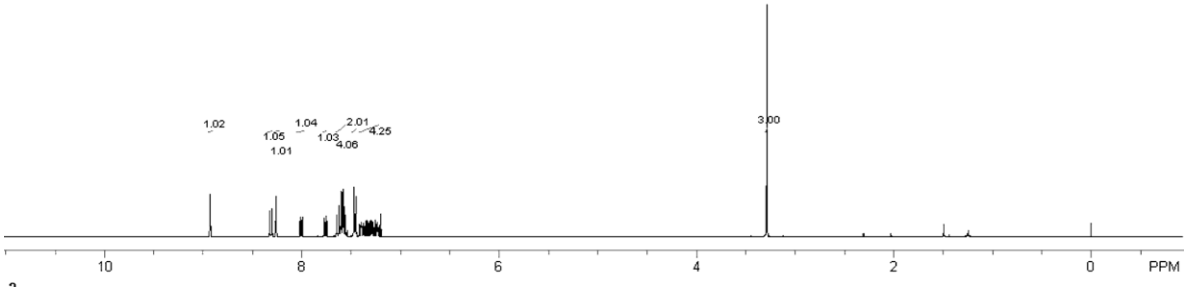
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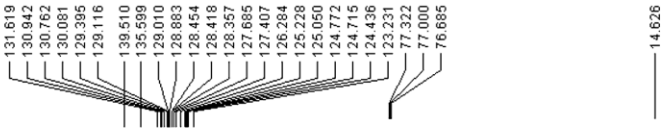
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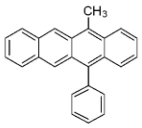
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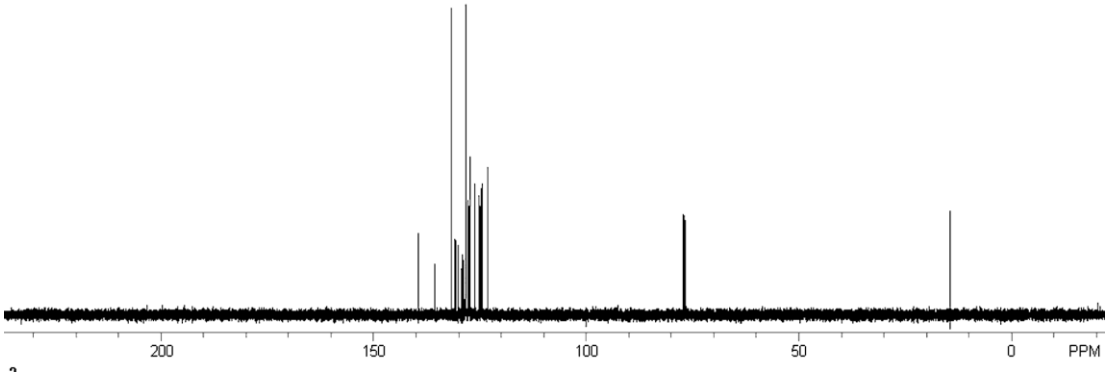
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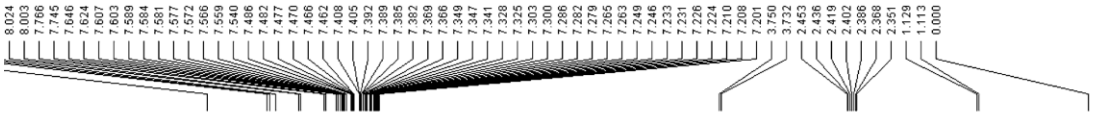
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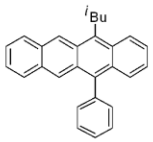
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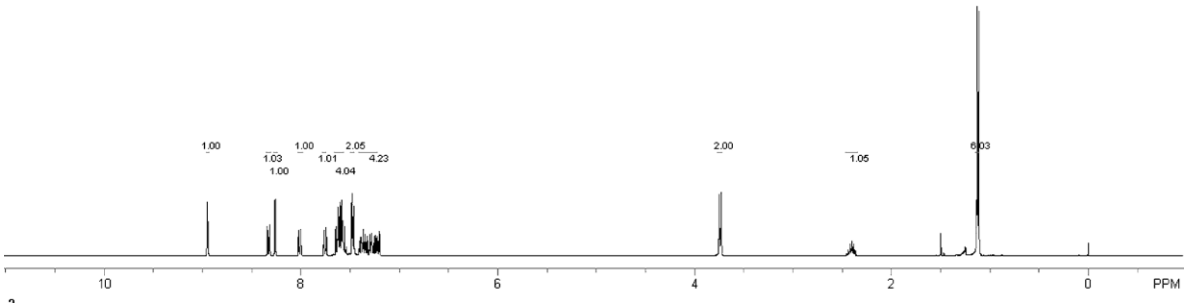
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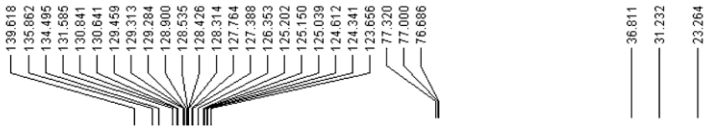
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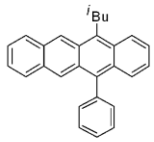
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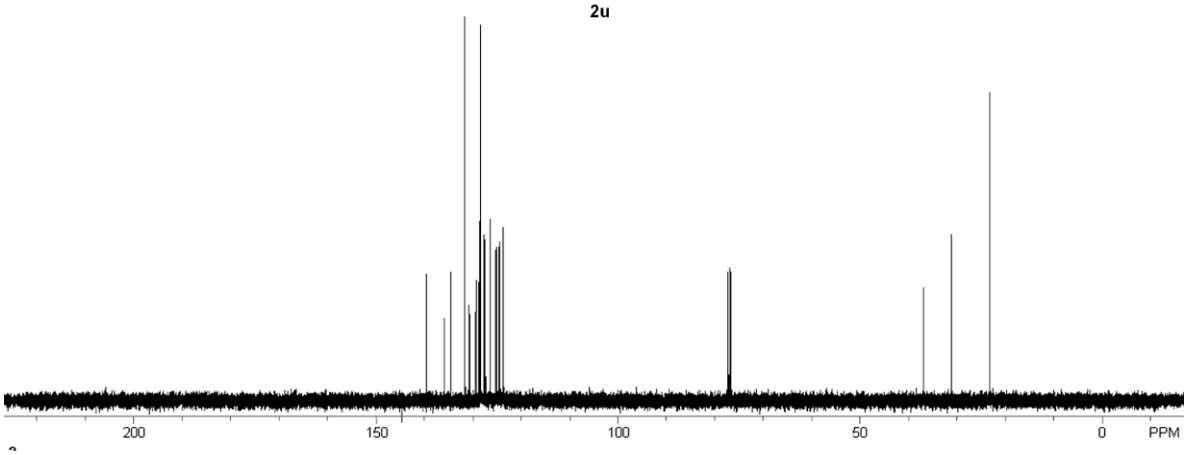
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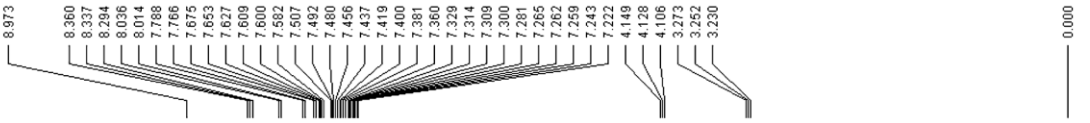
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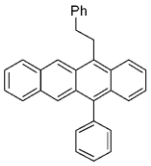
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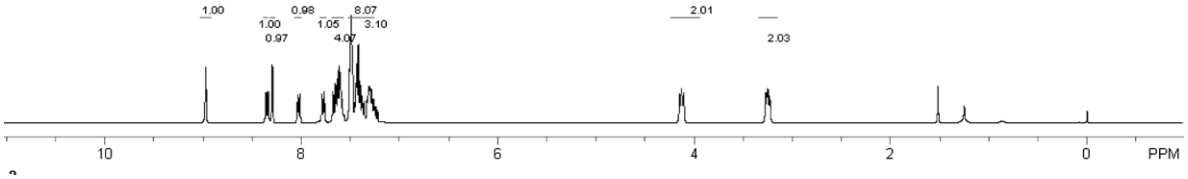
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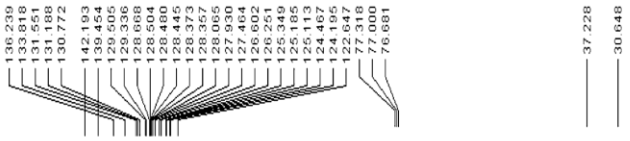
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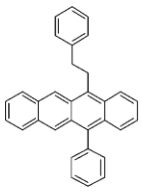

2v

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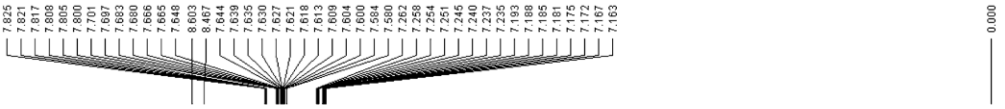
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7.613
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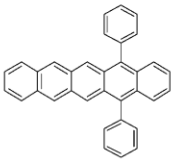

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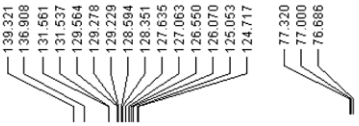
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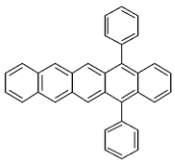

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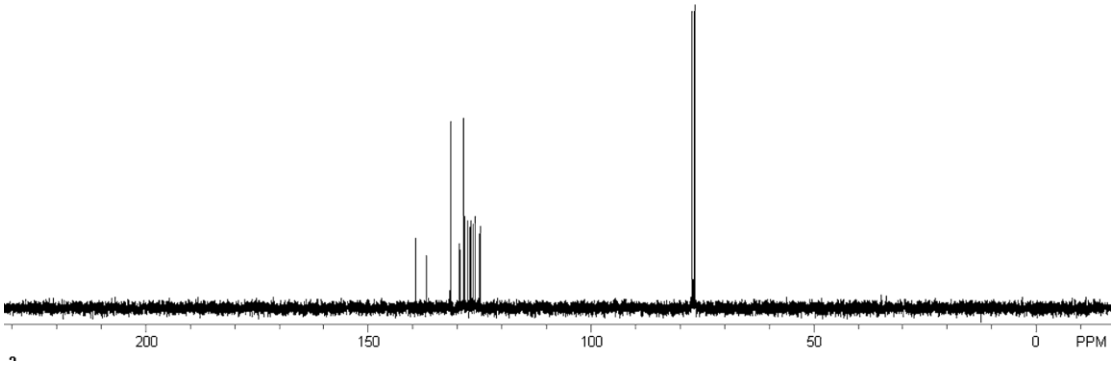
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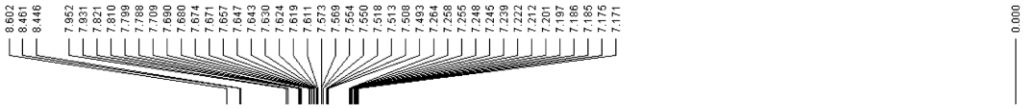
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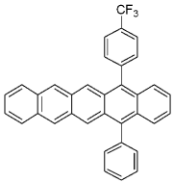
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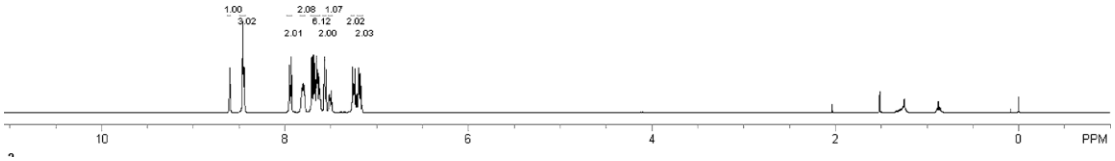
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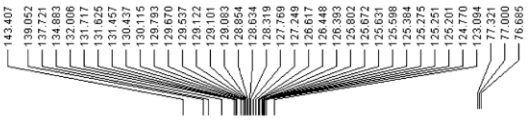
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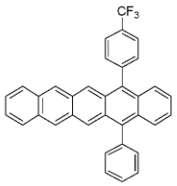
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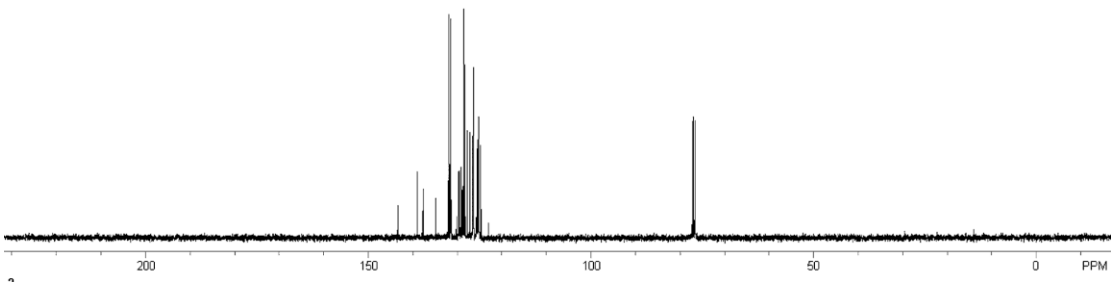
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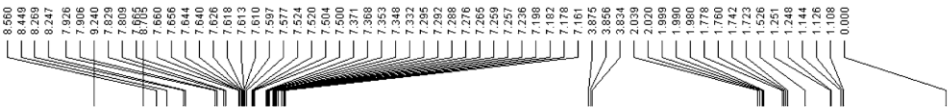
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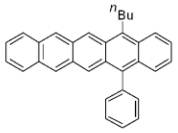
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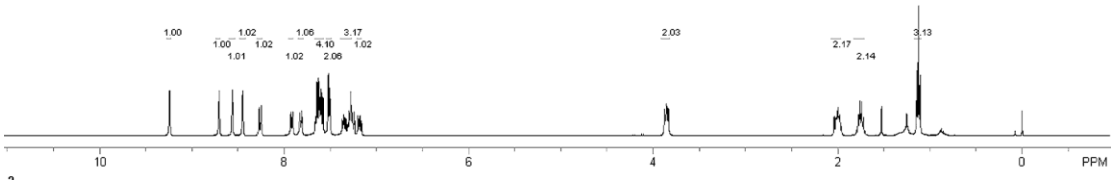
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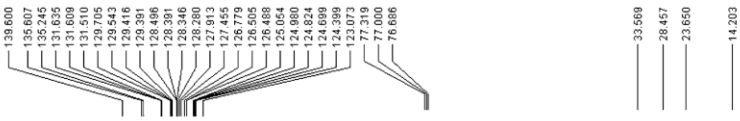
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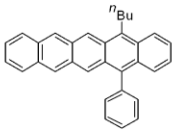
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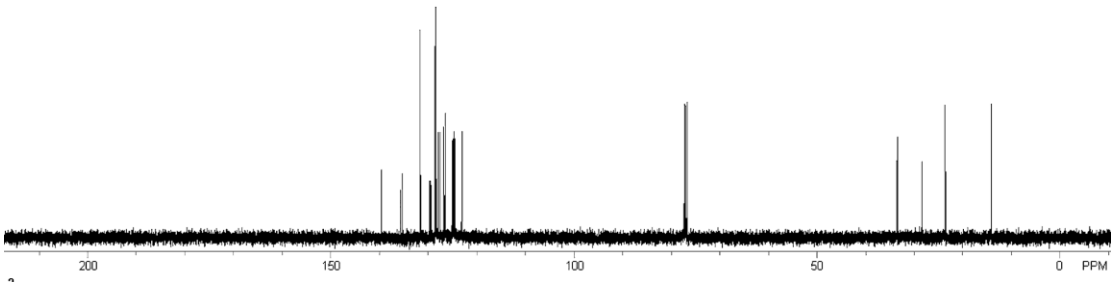
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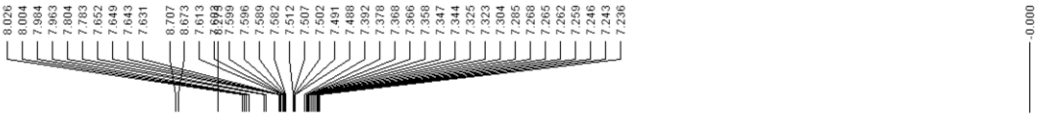
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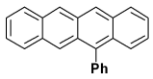
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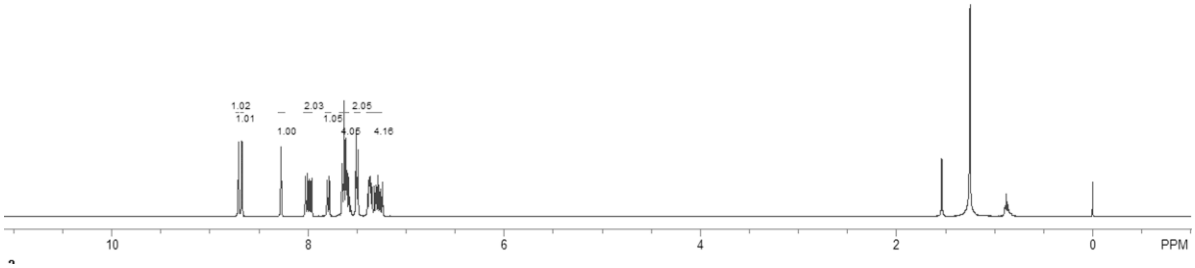
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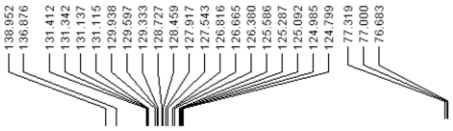
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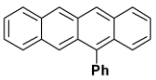
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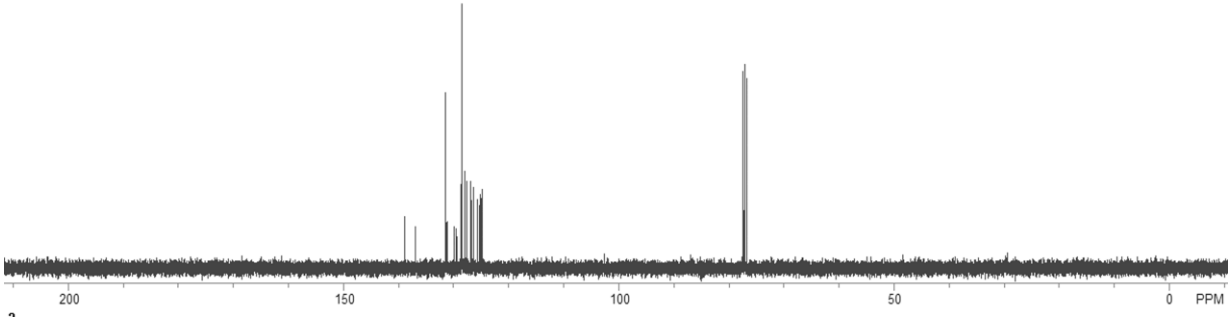
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