Supporting Information for

Synthesis of Selectively 4-Substituted 9,9´-Spirobifluorenes and Modulation of Their Photo-physical Properties.

Reinhard P. Kaiser, Jiří Mosinger, Ivana Císařová, and Martin Kotora

Contents

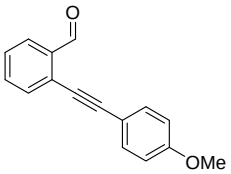
I General

All reagents were commercially available and obtained from Sigma-Aldrich, Acros Organics, and Strem Chemicals companies. Solvents were purified and dried by distillation: tetrahydrofuran (THF) and toluene from sodium/benzophenone, dichloromethane from calcium hydride. Other solvents and all reagents were used without further purification. All reactions were performed under argon atmosphere unless otherwise noted. Chromatography was performed on Merck Silica gel 60 and aluminum oxide from Sigma-Aldrich. Thin layer chromatography was performed on Merck silica gel 60 F_{254} coated aluminum sheets. The ^{1}H NMR and ^{13}CNMR spectra were recorded on a Bruker AVANCE III Spectrometer (^{1}H at 600 or 400 MHz and ^{13}C at 150 or 100 MHz) as solutions in $CDCl_3$, chemical shifts are given in δ-scale (^{1}H NMR spectra were referenced to residual peak of $CDCl_3$ at δ 7.26, ^{13}C NMR spectra to $CDCl_3$ at δ 77.00), coupling constants *J* are given in Hz. The IR spectra were recorded on a Bruker IFS 55 spectrometer in KBr tablets and are reported in wave numbers (cm^{-1}). The MS spectra were recorded on a VG-Analytical ZAB-SEQ device. All melting points are uncorrected and were determined on a Kofler apparatus.

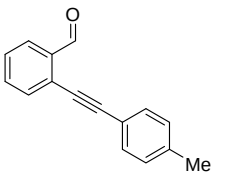
II Synthesis of starting material

A: General procedure for Sonogashira reaction[1] (preparation of S). 2-Bromobenzaldehyde (230 μL, 2.0 mmol), $PdCl_2(PPh_3)_2$ (69 mg, 0.1 mmol, 5 mol%) and CuI (38 mg, 0.2 mmol, 10 mol%) were dissolved in a Schlenk flask with reflux condensor in triethylamine (7 mL) and THF (7 mL), afterwards alkyne compound (*p*-tolylacetylene, 305 μL, 2.4 mmol) was added and the reaction was stirred 3 h under reflux. The reaction mixture was cooled down, filtered off with celite/silica and washed with diethyl ether. The organic fraction was concentrated on vacuum evaporator. Column chromatography of the residue on silica gel (hexanes/EtOAc) provided products.

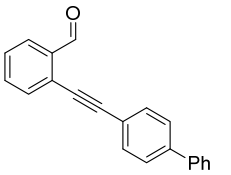
2-((4-Methoxyphenyl)ethynyl)benzaldehyde (Sa). With 4-ethynylanisole (311 μL, 2.4 mmol) following the general procedure A. Column chromatography (10/1 hexanes/EtOAc) yielded 450 mg (96%) of the title compound as yellow oil: ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.65 (d, *J* = 0.8 Hz, 1H), 7.93 (ddd, *J* = 7.8, 1.3, 0.5 Hz, 1H), 7.61 (ddd, *J* = 7.8, 1.3, 0.5 Hz, 1H), 7.57 (dt, *J* = 7.3, 1.4 Hz, 1H), 7.51 (m, 2H), 7.43 (m, 1H), 6.91 (m, 2H), 3.85 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 191.9, 160.2, 135.7, 133.8, 133.2, 133.0, 128.2, 127.4, 127.2, 114.4, 114.2, 96.6, 83.8, 55.4. The spectral data were in accordance with previously published results.[2]



2-(*p*-Tolylethynyl)benzaldehyde (Sb). With *p*-tolylacetylene (305 μL, 2.4 mmol) following the general procedure A. Column chromatography (10/1 hexanes/EtOAc) yielded 392 mg (89%) of the title compound as pale yellow solid: ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.66 (d, *J* = 0.8 Hz, 1H), 7.95 (ddd, *J* = 7.8, 1.4, 0.5 Hz, 1H), 7.63 (ddd, *J* = 7.8, 1.3, 0.5 Hz, 1H), 7.58 (dt, *J* = 7.4, 1.4 Hz, 1H), 7.47 (m, 2H), 7.44 (m, 1H), 7.19 (m, 2H), 2.39 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 191.8, 139.4, 135.7, 133.7, 133.1, 131.6, 129.3, 128.4, 127.17, 127.15, 119.2, 96.6, 84.3, 21.6. The spectral data were in accordance with previously published results.[3]



2-([1,1'-Biphenyl]-4-ylethynyl)benzaldehyde (Sc). With 4-ethynylbiphenyl (428 mg, 2.4 mmol) following the general procedure A. Column chromatography (10/1 hexanes/EtOAc) yielded 520 mg (92%) of the title compound as a light yellow solid: ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.68 (d, *J* = 0.8 Hz, 1H), 7.96 (dd, *J* = 7.8, 1.0 Hz, 1H), 7.59-7.86 (m, 8H), 7.47 (m, 3H), 7.38 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 191.7, 141.8, 140.1, 135.8, 133.8, 133.2, 132.1, 128.9, 128.6, 127.8, 127.3, 127.2, 127.1, 126.9, 121.2, 96.3, 85.6. The spectral data were in accordance with previously published results.[4]



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[1] D. Peña, D. Pérez, E. Guitián, L. Castedo; *Eur. J. Org. Chem.* **2003**, 1238-1243.
[2] S. Bhunia, K. Wang, R. Liu; *Angew. Chem. Int. Ed.* **2008**, *41*, 5063-5066.
[3] M. Alfonsi, M. Dell´Acqua, D. Facoetti, A. Arcadi, G. Abbiati, E. Rossi; *Eur. J. Org. Chem.* **2009**, 2852-2862.
[4] Z. Chai, Z. Xie, X. Liu, G. Zhao, J. Wang; *J. Org. Chem.* **2008**, *73*, 2947-2950.

2-(Phenylethynyl)benzaldehyde (Sd). With phenylacetylene (260 μL, 2.4 mmol) following the general procedure A. Column chromatography (5/1 hexanes/EtOAc) yielded 399 mg (96%) of the title compound as a yellow oil: ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.66 (d, *J* = 0.8 Hz, 1H), 7.95 (ddd, *J* = 7.8, 1.4, 0.6 Hz, 1H), 7.65 (ddd, *J* = 7.8, 1.3, 0.6 Hz, 1H), 7.59 (dt, *J* = 7.4, 1.4 Hz, 1H), 7.56-7.58 (m, 2H), 7.44-7.47 (m, 1H), 7.38-7.40 (m, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 191.7, 135.8, 133.8, 133.2, 131.7, 129.1, 128.6, 128.5, 127.2, 126.9, 122.3, 96.3, 84.9. The spectral data were in accordance with previously published results.[3]

2-((4-Chlorophenyl)ethynyl)benzaldehyde (Se). With 1-chloro-4-ethynylbenzene (238 mg, 2.4 mmol) following the general procedure A. Column chromatography (10/1 hexanes/EtOAc) yielded 431 mg (90%) of the title compound as a colorless oil: ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.62 (d, *J* = 0.8 Hz, 1H), 7.95 (ddd, *J* = 7.8, 1.4, 0.6 Hz, 1H), 7.64 (ddd, *J* = 7.8, 1.3, 0.6 Hz, 1H), 7.60 (dt, *J* = 7.3, 1.4 Hz, 1H), 7.46-7.51 (m, 3H), 7.36-7.38 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 191.5, 133.8, 133.2, 132.9, 128.9, 128.8, 127.5, 126.4, 120.8, 95.1, 85.9. The spectral data were in accordance with previously published results.[5]

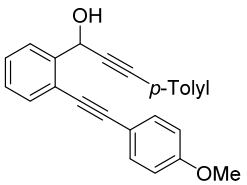
2-((4-(Trifluoromethyl)phenyl)ethynyl)benzaldehyde (Sf). With 1-ethynyltrifluortoluene (392 μL, 2.4 mmol) following the general procedure A. Column chromatography (5/1 hexanes/EtOAc) yielded 442 mg (80%) of the title compound as a light brown solid: ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.62 (d, *J* = 0.8 Hz, 1H), 7.97 (ddd, *J* = 7.8, 1.4, 0.5 Hz, 1H), 7.64-7.68 (m, 5H), 7.59 (dt, *J* = 7.4, 1.4 Hz, 1H), 7.50 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 191.2, 136.0, 133.8, 133.4, 131.9, 130.8 (q, $^2J_{C\text{-}F}$ = 32.8 Hz), 129.2, 127.6, 126.1, 125.8, 125.4 (q, $^3J_{C\text{-}F}$ = 3.8 Hz), 121.1-126.5 (q, $^1J_{C\text{-}F}$ = 272.3 Hz), 94.5, 87.2. The spectral data were in accordance with previously published results.[5]

4-((2-Formylphenyl)ethynyl)benzonitrile (Sg). With 4-ethynylbenzonitrile (305 mg, 2.4 mmol) following the general procedure A. Column chromatography (10/1 hexanes/EtOAc) yielded 392 mg (84%) of the title compound as a light yellow solid: ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.59 (d, *J* = 0.8 Hz, 1H), 7.97 (ddd, *J* = 7.8, 1.3, 0.5 Hz, 1H), 7.65-7.69 (m, 5H), 7.63 (dt, *J* = 7.3, 1.4 Hz, 1H), 7.53 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 191.0, 136.0, 133.9, 133.5, 132.19, 132.16, 129.5, 127.9, 127.2, 125.3, 118.3, 112.3, 94.1, 89.1. The spectral data were in accordance with previously published results.[6]

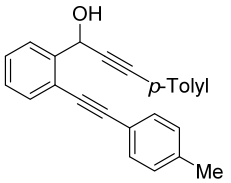
[5] J. Chen, B. Liu, Y. Chen. Q. He, C. Yang; *RSC Adv.* **2014**, *4*, 11168-11175.
[6] N. Patil, A. Mutyala, P. Lakshmi, P. Raju, B. Sridhar; *Eur. J. Org. Chem* **2010**, 1999-2007.

B: General procedure for alkynylation reaction[1] (preparation of 1). *n*-BuLi 1.6M (1.8 mL, 2.7 mmol) was added dropwise to a solution of 1-ethynyl-4-*p*-toluene (340 µL, 2.7 mmol) in anhydrous THF (15 mL), at -78 °C. After 30 min of stirring, starting material **S** (1.78 mmol) in THF (5 mL) was added and the reaction mixture was stirred for 5 min at -78 °C, afterwards it was allowed to warm up to ambient temperature and the reaction was stirred 4 h. Then NH_4Cl aq was used to quench the reaction mixture, it was extracted with diethyl ether (3 x 15 mL), the combined organic fractions were washed with a saturated solution of $NaHCO_3$, the organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. Column chromatography of the residue on silica gel (hexanes/EtOAc) provided products.

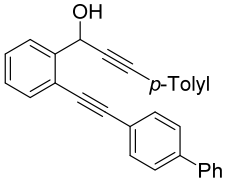
1-(2-((4-Methoxyphenyl)ethynyl)phenyl)-3-(*p*-tolyl)prop-2-yn-1-ol (1a). With **Sa** (450 mg, 1.9 mmol) following the general procedure. following the general procedure B. Column chromatography (5/1 hexanes/EtOAc) yielded 560 mg (84%) of the title compound as pale yellow oil: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.55 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.51 (m, 2H), 7.39 (dt, *J* = 7.6, 1.3 Hz, 1H), 7.35 (m, 2H), 7.33 (dt, *J* = 7.6, 1.4 Hz, 1H), 7.10 (d, *J* = 7.9 Hz, 2H), 6.88 (m, 2H), 6.15 (d, *J* = 5.9 Hz, 1H), 3.83 (s, 3H), 2.84 (d, *J* = 5.9 Hz, 1H), 2.34 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.9, 142.1, 138.6, 133.1, 132.3, 131.6, 129.0, 128.5, 128.2, 126.8, 121.8, 119.4, 114.9, 114.1, 95.1, 87.6, 86.6, 85.4, 63.9, 55.3, 21.5. The spectral data were in accordance with previously published results.[7]



3-(*p*-Tolyl)-1-(2-(*p*-tolylethynyl)phenyl)prop-2-yn-1-ol (1b). With **Sb** (392 mg, 1.78 mmol) following the general procedure B. Column chromatography (5/1 hexanes/EtOAc) yielded 545 mg (91%) of the title compound as pale yellow oil: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.57 (dd, *J* = 7.6, 1.0 Hz, 1H), 7.46 (d, *J* = 8.1 Hz, 2H), 7.40 (dt, *J* = 7.6, 1.4 Hz, 1H), 7.35 (d, *J* = 8.1 Hz, 2H), 7.33 (dt, *J* = 7.5, 1.1 Hz, 1H), 7.16 (d, *J* = 7.8 Hz, 2H), 7.10 (d, *J* = 7.8 Hz, 2H), 6.15 (d, *J* = 5.9 Hz, 1H), 2.77 (d, *J* = 5.9 Hz, 1H), 2.38 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 142.3, 138.8, 138.6, 132.4, 131.7, 131.5, 129.2, 129.0, 128.7, 128.2, 126.8, 121.7, 119.7, 119.4, 95.3, 87.6, 86.7, 86.0, 63.9, 21.53, 21.46. The spectral data were in accordance with previously published results. [8]



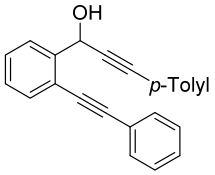
1-(2-([1,1'-Biphenyl]-4-yl-ethynyl)phenyl)-3-(*p*-tolyl)prop-2-yn-1-ol (1c). With **Sc** (540 mg, 1.8 mmol) following the general procedure. Column chromatography (5/1 hexanes/EtOAc) yielded 650 mg (90%) of the title compound as a light yellow oil: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.80 (ddd, *J* = 7.8, 0.9, 0.4 Hz, 1H), 7.60-7.66 (m, 7H), 7.47 (m, 2H), 7.42 (dt, *J* = 7.6, 1.3 Hz, 1H), 7.34-7.40 (m, 4H), 7.10 (d, *J* = 7.9 Hz, 2H), 6.18 (d, *J* = 5.9 Hz, 1H), 2.78 (d, *J* = 5.9 Hz, 1H), 2.34 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 142.4, 141.3, 140.2, 138.6,



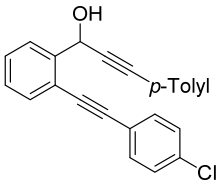
[7] L. Wang, H. Zhu, L. Lu, F. Yang, X. Liu, Y. Liang; *Org.Lett.* **2012**, *14*, 1990-1993.
[8] J. Lian, R. Liu; *Chem. Comm.* **2007**, 1337-1339.

132.5, 132.0, 131.7, 129.0, 128.9, 128.9, 128.3, 127.7, 127.1, 127.0, 126.8, 121.7, 121.5, 119.4, 95.0, 87.6, 87.3, 86.7, 63.9, 21.5; IR (KBr) ν_{max} 3548, 3342, 3060, 3028, 2947, 2920, 2866, 2211, 1595, 1512, 1494, 1446, 1404, 1374, 1275, 1224, 1183, 1108, 1027, 1009, 967, 842, 815, 764, 698 cm^{-1}; HRMS (*m/z*) for $C_{30}H_{22}ONa$ (M + Na) calcd: 421.15629 found: 421.15630; R_f(2/1 hexanes/EtOAc) = 0.43 (silica gel plate).

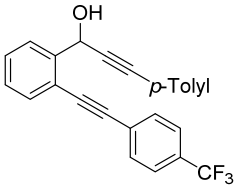
1-(2-(Phenylethynyl)phenyl)-3-(*p*-tolyl)prop-2-yn-1-ol (1d). With **Sd** (396 mg, 1.95 mmol) following the general procedure B. Column chromatography (5/1 hexanes/EtOAc) yielded 590 mg (93%) of the title compound as pale yellow oil: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.80 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.57-7.60 (m, 3H), 7.42 (dt, *J* = 7.6, 1.4 Hz, 1H), 7.33-7.37 (m, 6H), 7.10 (d, *J* = 7.8 Hz, 2H), 6.16 (d, *J* = 5.9 Hz, 1H), 2.76 (d, *J* = 5.9 Hz, 1H), 2.34 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 142.4, 138.6, 132.5, 131.64, 131.58, 129.0, 128.9, 128.6, 128.4, 128.3, 126.8, 122.8, 121.5, 119.4, 95.0, 87.5, 86.7, 86.6, 63.8, 21.5. The spectral data were in accordance with previously published results.[9]



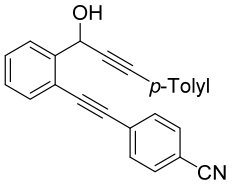
1-(2-((4-Chlorophenyl)ethynyl)phenyl)-3-(*p*-tolyl)prop-2-yn-1-ol (1e). With **Se** (434 mg, 1.8 mmol) following the general procedure B. Column chromatography (5/1 hexanes/EtOAc) yielded 570 mg (89%) of the title compound as colorless solid: mp (decomp) 126-131 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.56 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.48 (m, 2H), 7.42 (dt, *J* = 7.7, 1.3 Hz, 1H), 7.32-7.36 (m, 5H), 7.10 (d, *J* = 7.8 Hz, 2H), 6.12 (s, 1H), 2.67 (s, 1H), 2.34 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 142.4, 138.7, 134.6, 132.8, 132.5, 131.6, 129.1, 129.0, 128.8, 128.3, 126.8, 121.3, 121.2, 119.3, 93.8, 87.6, 87.5, 86.8, 63.8, 21.5; IR (KBr) ν_{max} 3276, 3189, 3066, 3034, 2989, 2914, 2864, 2851, 2217, 1568, 1512, 1488, 1470, 1392, 1284, 1219, 1186, 1090, 1027, 1015, 970, 830, 818, 749 cm^{-1}; HRMS (*m/z*) for $C_{24}H_{17}OClNa$ (M + Na) calcd: 379.08601, found: 379.08618; R_f (2/1 hexanes/EtOAc) = 0.45 (silica gel plate).



3-(*p*-Tolyl)-1-(2-((4-(trifluoromethyl)phenyl)ethynyl)phenyl)prop-2-yn-1-ol (1f). With **Sf** (442 mg, 1.6 mmol) following the general procedure B. Column chromatography (5/1 hexanes/EtOAc) yielded 564 mg (90%) of the title compound as colorless solid: mp (decomp) 133-138 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.81 (dd, *J* = 7.8, 1.1 Hz, 1H), 7.66 (d, *J* = 8.1 Hz, 2H), 7.60 (m, 3H), 7.45 (dt, *J* = 7.6, 1.3 Hz, 1H), 7.36 (dt, *J* = 7.6, 1.2 Hz, 1H), 7.33 (d, *J* = 8.1 Hz, 2H), 7.10 (d, *J* = 7.9 Hz, 2H), 6.13 (d, *J* = 5.9 Hz, 1H), 2.63 (d, *J* = 5.9 Hz, 1H), 2.34 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 142.6, 138.8, 132.7, 131.8, 131.6, 130.2 (q, $^2J_{C\text{-}F}$ = 32.7 Hz), 129.5, 129.0, 128.4, 126.8, 126.7, 125.3 (q, $^3J_{C\text{-}F}$ = 3.8 Hz), 121.2-126.7 (q, $^1J_{C\text{-}F}$ = 272.3 Hz), 120.8, 119.3, 93.4, 89.0, 87.5, 86.8, 63.7, 21.5; IR (KBr) ν_{max} 3273, 3180, 3066, 3028, 2992, 2926, 2875, 2223, 1610, 1509, 1476, 1404, 1332, 1165, 1108, 1066, 1030, 967, 842, 815, 749 cm^{-1}; HRMS (*m/z*) for $C_{25}H_{18}OF_3$ (M + H) calcd: 391.13043, found: 391.13058; R_f(2/1 hexanes/EtOAc) = 0.47 (silica gel plate).

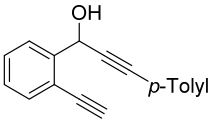


4-((2-(1-Hydroxy-3-(*p*-tolyl)prop-2-yn-1-yl)phenyl)ethynyl)benzonitrile (1g). With **Sg**

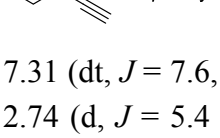


(392 mg, 1.7 mmol) following the general procedure B. Column chromatography (5/1 hexanes/EtOAc) yielded 556 mg (94%) of the title compound as light brown solid: mp (decomp) 151-156 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.81 (dd, *J* = 7.8, 0.6 Hz, 1H), 7.63 (s, 4H), 7.58 (dd, *J* = 7.6, 0.9 Hz, 1H), 7.46 (dt, *J* = 7.6, 1.3 Hz, 1H), 7.37 (dt, *J* = 7.6, 1.2 Hz, 1H), 7.32 (m, 2H), 7.10 (d, *J* = 7.9 Hz, 2H), 6.10 (d, *J* = 5.1 Hz, 1H), 2.62 (d, *J* = 5.1 Hz, 1H), 2.34 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 142.7, 138.9, 132.7, 132.1, 132.0, 131.6, 129.8, 129.1, 128.4, 127.8, 126.9, 120.5, 119.2, 118.4, 111.8, 93.1, 91.0, 87.4, 86.9, 63.6, 21.5; IR (KBr) ν_{max} 3279, 3324, 3192, 3060, 3028, 2992, 2914, 2881, 2857, 2226, 1598, 1504, 1473, 1455, 1407, 1290, 1183, 1120, 1105, 1027, 973, 839, 818, 752 cm^{-1}; HRMS (*m/z*) for $C_{25}H_{17}NO$ (M^+) calcd: 347.1310, found: 347.1311; R_f (2/1 hexanes/EtOAc) = 0.38 (silica gel plate).

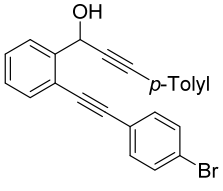
1-(2-Ethynylphenyl)-3-(*p*-tolyl)prop-2-yn-1-ol (5a). With 2-ethynylbenzaldehyde (650 mg, 5.0 mmol) following the general procedure B. Column chromatography (5/1 hexanes/EtOAc) yielded 1.19 g (96%) of the title compound as light brown oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.54 (dd, *J* = 7.7, 1.2 Hz, 1H), 7.43 (dt, *J* = 7.6, 1.4 Hz, 1H), 7.36 (m, 2H), 7.31 (dt, *J* = 7.6, 1.3 Hz, 1H), 7.11 (d, *J* = 7.9 Hz, 2H), 6.12 (d, *J* = 5.4 Hz, 1H), 3.41 (s, 1H), 2.74 (d, *J* = 5.4 Hz, 1H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.9, 138.7, 133.2, 131.6, 129.4, 129.0, 128.3, 126.9, 120.4, 119.3, 87.3, 86.8, 82.7, 81.0, 63.5, 21.5; IR (KBr) ν_{max} 3536, 3291, 3063, 3031, 2914, 2863, 2226, 1509, 1476, 1443, 1383, 1266, 1207, 1180, 1096, 1021, 967, 821, 761 cm^{-1}; HRMS (*m/z*) for $C_{18}H_{14}ONa$ (M + Na) calcd: 269.09369, found: 269.09360; R_f (2/1 hexanes/EtOAc) = 0.43 (silica gel plate).



Preparation of 1-(2-Ethynylphenyl)hex-2-yn-1-ol (5b). With 2-ethynylbenzaldehyde (1.3 g, 10.0 mmol) and 1-pentyne (1.5 mL, 15 mmol) following the general procedure B. Column chromatography (5/1 hexanes/EtOAc) yielded 1.8 g (91%) of the title compound as light brown oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (dd, *J* = 7.8, 1.0 Hz, 1H), 7.50 (dd, *J* = 7.6, 1.1 Hz, 1H), 7.40 (dt, *J* = 7.6, 1.3 Hz, 1H), 7.29 (dt, *J* = 7.6, 1.3 Hz, 1H), 5.88 (s, 1H), 3.37 (s, 1H), 2.49 (d, *J* = 4.5 Hz, 1H), 2.25 (dt, *J* = 7.1, 2.0 Hz, 2H), 1.56 (m, 2H), 0.99 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.5, 133.1, 129.4, 128.1, 126.7, 120.3, 87.7, 82.5, 81.1, 79.2, 63.1, 22.0, 20.8, 13.5; IR (KBr) ν_{max} 3545, 3288, 3069, 3028, 2962, 2932, 2905, 2869, 2836, 2283, 2223, 1482, 1452, 1383, 1335, 1275, 1201, 1132, 1036, 991, 758 cm^{-1}; HRMS (*m/z*) for $C_{14}H_{14}O$ (M^+) calcd: 198.1045, found: 198.1044; R_f (5/1 hexanes/EtOAc) = 0.25 (silica gel plate).

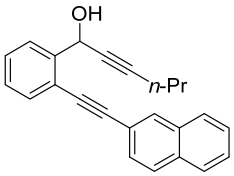


1-(2-((4-Bromophenyl)ethynyl)phenyl)-3-(*p*-tolyl)prop-2-yn-1-ol (1h). 5a (736 mg, 4.6 mmol), 1-bromo-4-iodobenzene (1.1 g, 3.6 mmol), $PdCl_2(PPh_3)_2$ (104 mg, 0.15 mmol, 5 mol%) and CuI (57 mg, 0.3 mmol, 10 mol%) were dissolved in a flask in diisopropylamine (30 mL) and the reaction was stirred 16 h at 50 °C. The reaction mixture was cooled down, filtered off with celite/silica

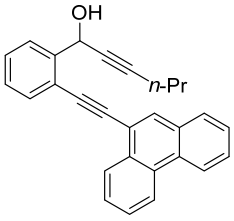


and washed with diethyl ether. The organic fraction was concentrated on vacuum evaporator. Column chromatography of the residue on silica gel (2/1 hexanes/EtOAc) yielded 1.15 g (95%) of the title compound as brown solid: mp (decomp) 127-132 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.56 (dd, *J* = 7.5, 1.1 Hz, 1H), 7.47-7.50 (m, 2H), 7.40-7.44 (m, 3H), 7.32-7.36 (m, 3H), 7.09 (d, *J* = 7.9 Hz, 2H), 6.12 (d, *J* = 4.9 Hz, 1H), 2.74 (d, *J* = 4.9 Hz, 1H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.4, 138.7, 133.0, 132.5, 131.7, 131.6, 129.1, 129.0, 128.3, 126.8, 122.9, 121.8, 121.1, 119.3, 93.9, 87.8, 87.5, 86.7, 63.7, 21.5; IR (KBr) ν_{max} 3548, 3342, 3060, 3022, 2914, 2863 2223, 1506, 1488, 1446, 1389, 1314, 1269, 1189, 1099, 1069, 1024, 1012, 961, 821, 758, 525 cm^{-1}; HRMS (*m/z*) for $C_{24}H_{17}OBrNa$ (M + Na) calcd: 423.03550, found: 423.03553; R_f (2/1 hexanes/EtOAc) = 0.46 (silica gel plate).

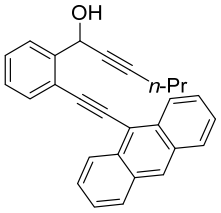
1-(2-(Naphthalen-2-ylethynyl)phenyl)hex-2-yn-1-ol (8a). With **5b** and 2-bromonaphthalene (397 mg, 2.0 mmol) following the general procedure A. Column chromatography (3/1 hexanes/EtOAc) yielded 434 mg (57%) of the title compound as a light brown oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.82 (m, 3H), 7.75 (dd, *J* = 7.8, 0.9 Hz, 1H), 7.59 (m, 2H), 7.50 (m, 2H), 7.41 (dt, *J* = 7.5, 1.4 Hz, 1H), 7.34 (dt, *J* = 7.6, 1.3 Hz, 1H), 6.02 (s, 1H), 2.64 (s, 1H), 2.27 (dt, *J* = 7.1, 2.0 Hz, 2H), 1.56 (m, 2H), 0.99 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.9, 135.2 133.0, 132.4, 131.5, 128.9, 128.2, 128.12, 128.08, 127.80, 127.78, 126.8, 126.7, 126.6, 121.4, 120.2, 95.20, 87.56, 87.01, 79.49, 63.5, 22.0, 20.9, 13.5; IR (KBr) ν_{max} 3368, 3055, 2962, 2929, 2869, 2220, 1601, 1503, 1482, 1467, 1434, 1272, 1183, 1135, 1096, 1030, 997, 955, 896, 857, 815, 749, cm^{-1}; HRMS (*m/z*) for $C_{24}H_{20}O$ (M^+) calcd: 324.1514 found: 324.1515; R_f (2/1 hexanes/EtOAc) = 0.44 (silica gel plate).



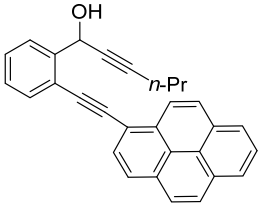
1-(2-(Phenanthren-9-ylethynyl)phenyl)hex-2-yn-1-ol (8b). With **5b** and 2-bromo-phenanthrene (40 mg, 0.2 mmol) following the general procedure A. Column chromatography (2/1 hexanes/EtOAc) yielded 53 mg (71%) of the title compound as a light brown oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (dd, *J* = 5.9, 3.6 Hz, 1H), 8.67 (d, *J* = 8.3 Hz, 1H), 8.60 (m, 1H), 8.12 (s, 1H), 7.88 (d, *J* = 7.8 Hz, 1H), 7.81 (d, *J* = 7.7 Hz, 1H), 7.67-7.74 (m, 4H), 7.62 (t, *J* = 7.5 Hz, 1H), 7.45 (t, *J* = 7.5 Hz, 1H), 7.38 (t, *J* = 7.5 Hz, 1H), 6.12 (s, 1H), 2.64 (s, 1H), 2.28 (t, *J* = 7.1 Hz, 2H), 1.58 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.9, 132.7, 132.2, 131.2, 131.0, 130.4, 130.1, 129.0, 128.6, 128.2, 127.6, 127.2, 127.1, 127.01, 126.97, 126.6, 122.8, 122.6, 121.5, 119.4, 93.2, 91.1, 87.7, 79.6, 63.5, 22.0, 20.9, 13.5; IR (KBr) ν_{max} 3545, 3354, 3058, 2962, 2932, 2902, 2869, 2833, 2280, 2214, 1598, 1479, 1449, 1377, 1278, 1245, 1180, 1126, 1096, 1039, 1000, 955, 893, 755, 722 cm^{-1}; HRMS (*m/z*) for $C_{28}H_{22}ONa$ (M + Na) calcd: 397.15629 found: 397.15631; R_f (2/1 hexanes/EtOAc) = 0.42 (silica gel plate).



1-(2-(Anthracen-9-ylethynyl)phenyl)hex-2-yn-1-ol (8c). With **5b** and 2-bromonaphthalene (257 mg, 1.0 mmol) following the general procedure A. Column chromatography (5/1 hexanes/EtOAc) yielded 153 mg (41%) of the title compound as a light brown oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (dd, *J* = 8.7, 0.9 Hz, 2H), 8.45 (s, 1H), 8.01 (d, *J* = 8.5 Hz, 2H), 7.86 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.81 (dd, *J* = 7.5, 1.3 Hz, 1H), 7.62 (m, 2H), 7.52 (m, 2H), 7.47 (dt, *J* = 7.5, 1.5 Hz, 1H), 7.43 (dt, *J* = 7.5, 1.6 Hz, 1H), 6.21 (s, 1H), 2.64 (s, 1H), 2.27 (dt, *J* = 7.1, 2.1 Hz, 2H), 1.54 (m, 2H), 0.95 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.6, 132.8, 132.7, 131.1, 129.0, 128.7, 128.2, 128.1, 126.8, 126.7, 126.5, 125.7, 121.8, 97.9, 91.7, 87.8, 79.8, 63.5, 22.0, 20.9, 13.5; IR (KBr) ν_{max} 3304, 3053, 2962, 2932, 2902, 2870, 2224, 2187, 1621, 1597, 1483, 1436, 1412, 1362, 1259, 1183, 1096, 1034, 1013, 999, 888, 845, 756, 739, 693 cm^{-1}; HRMS (*m/z*) for $C_{28}H_{22}ONa$ (M + Na) calcd: 397.25629 found: 397.25602; R_f(2/1 hexanes/EtOAc) = 0.41 (silica gel plate).



1-(2-(Pyren-2-ylethynyl)phenyl)hex-2-yn-1-ol (8d). With **5b** and 2-bromopyrene (281 mg, 1.0 mmol) following the general procedure A. Column chromatography (5/1 hexanes/EtOAc) yielded 246 mg (62%) of the title compound as a light brown oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (d, *J* = 9.1 Hz, 1H), 8.16-8.22 (m, 4H), 8.00-8.12 (m, 4H), 7.83 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.74 (dd, *J* = 7.5, 1.3 Hz, 1H), 7.46 (dt, *J* = 7.5, 1.5 Hz, 1H), 7.40 (dt, *J* = 7.5, 1.5 Hz, 1H), 6.19 (s, 1H), 2.73 (s, 1H), 2.30 (dt, *J* = 7.1, 2.1 Hz, 2H), 1.57 (m, 2H), 0.99 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.8, 132.6, 131.9, 131.4, 131.2, 131.0, 129.7, 128.9, 128.5, 128.2, 128.2, 127.2, 126.6, 126.2, 125.7, 125.6, 125.4, 124.5, 124.4, 124.2, 121.7, 117.4, 94.1, 92.3, 87.7, 79.7, 63.6, 22.0, 20.9, 13.5; IR (KBr) ν_{max} 3545, 3291, 3044, 2961, 2932, 2902, 2871, 2206, 1927, 1600, 1508, 1486, 1448, 1435, 1379, 1275, 1242, 1184, 1133, 1033, 998, 848, 757, 717 cm^{-1}; HRMS (*m/z*) for $C_{30}H_{22}ONa$ (M + Na) calcd: 421.15629 found: 421.15618; R_f(2/1 hexanes/EtOAc) = 0.40 (silica gel plate).

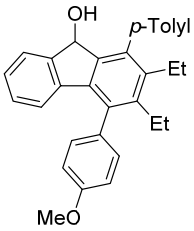


III Synthesis 9,9'-spirobifluorenes 4

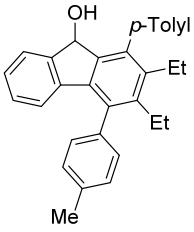
III-1 Cyclotrimerization reaction

C: General procedure for cyclotrimerization with Wilkinson's catalyst $RhCl(PPh_3)_3$.[9] (Preparation of 2). A dry microwave vial was charged with starting diynol (0.5 mmol), 3-hexyne (115 µL, 1.0 mmol) and dissolved under argon atmosphere in THF (15 mL). After addition of Wilkinson's catalyst (23 mg, 0.015 mmol, 3 mol%) and the additive Ag_2CO_3 (14 mg, 0.05 mmol, 10 mol%) the reaction mixture was sealed and heated up to 180°C for 1.5 h in a microwave reactor. The reaction mixture was cooled down to room temperature and the solvent was evaporated under reduced pressure. Column chromatography of the residue on silica gel yielded products.

2,3-Diethyl-4-(4-methoxyphenyl)-1-(*p*-tolyl)-9*H*-fluoren-9-ol (2a). With **1a** (176 mg, 0.5 mmol) following the general procedure C. Column chromatography (5/1 hexanes/EtOAc) yielded 103 mg (47%) of the title compound as a brown oil: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 (m, 1H), 7.25-7.36 (m, 6H), 7.10 (dt, *J* = 7.4, 1.0 Hz, 1H), 7.06-7.08 (m, 2H), 6.97 (dt, *J* = 7.4, 0.7 Hz, 1H), 6.07 (d, *J* = 7.8 Hz, 1H), 5.45 (d, *J* = 4.7 Hz, 1H), 3.94 (s, 3H), 2.60-2.66 (m, 1H), 2.55 (q, *J* = 7.5 Hz, 2H), 2.50-2.53 (m, 1H), 2.46 (s, 3H), 1.69 (d, *J* = 4.7 Hz, 1H), 1.03 (t, *J* = 7.5 Hz, 3H), 1.02 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 158.8, 145.2, 142.0, 141.5, 140.7, 139.9, 138.9, 137.0, 136.30, 136.27, 136.1, 132.5, 130.47, 130.45, 129.8, 129.6, 129.0, 128.6, 128.4, 126.7, 124.6, 122.6, 114.2, 114.1, 73.9, 55.3, 22.83, 22.81, 21.3, 15.9, 15.8; IR (KBr) ν_{max} 3566, 3452, 3069, 3040, 3022, 2968, 2929, 2869, 2839, 1607, 1571, 1515, 1467, 1428, 1374, 1284, 1245, 1177, 1105, 1033, 854, 824, 764, 746 cm^{-1}; HRMS (*m/z*) for $C_{31}H_{30}O_2Na$ (M + Na) calcd: 457.21380, found: 457.21381; R_f (5/1 hexanes/EtOAc) = 0.36 (silica gel plate).

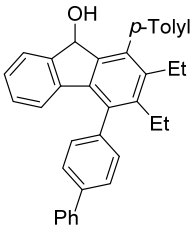


2,3-Diethyl-1,4-di-*p*-tolyl-9*H*-fluoren-9-ol (2b). With **1b** (168 mg, 0.5 mmol) following the general procedure C. Column chromatography (5/1 hexanes/EtOAc) yielded 133 mg (64%) of the title compound as a light brown viscous oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.4, Hz, 1H), 7.30-7.36 (m, 6H), 7.23-7.27 (m, 2H), 7.10 (dt, *J* = 7.4, 1.0 Hz, 1H), 6.95 (dt, *J* = 7.6, 0.7 Hz, 1H), 6.02 (d, *J* = 7.8 Hz, 1H), 5.44 (d, *J* = 4.7 Hz, 1H), 2.60-2.66 (m, 1H), 2.55 (q, *J* = 7.5 Hz, 2H), 2.50-2.53 (m, 1H), 2.51 (s, 3H), 2.47 (s, 3H), 1.68 (d, *J* = 4.7 Hz, 1H), 1.03 (t, *J* = 7.5 Hz, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 145.1, 141.7, 141.5, 140.7, 139.9, 138.9, 137.2, 137.0, 136.8, 136.7, 136.3, 135.8, 129.8, 129.7, 129.5, 129.4, 129.3, 129.2, 129.0, 128.7, 128.3, 126.6, 124.6, 122.6, 73.9, 22.84, 22.79, 21.4, 21.3, 15.9, 15.8; IR (KBr) ν_{max} 3425, 3058, 3019, 2968, 2926, 2890, 2869, 1598, 1556, 1470, 1437, 1374, 1290, 1195, 1177, 1072, 1024, 734, 758, 701 cm^{-1}; HRMS (*m/z*) for $C_{31}H_{30}ONa$ (M + Na) calcd: 441.21889, found: 441.21893; R_f(5/1 hexanes/EtOAc) = 0.46 (silica gel plate).

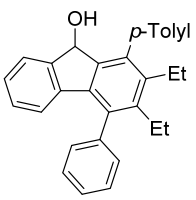


[9] M. Taylor, T. Swager; *Org. Lett.* **2007**, 3695-3697.

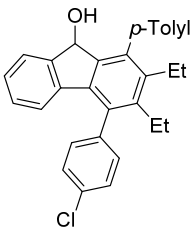
4-([1,1'-Biphenyl]-4-yl)-2,3-diethyl-1-(*p*-tolyl)-9*H*-fluoren-9-ol (2c). With **1c** (199.1 mg, 0.5 mmol) following the general procedure C. Column chromatography (5/1 hexanes/EtOAc) yielded 115 mg (48%) of the title compound as a viscous brown oil: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78-7.82 (m, 4H), 7.52 (m, 2H), 7.40-7.47 (m, 4H), 7.32-7.38 (m, 4H), 7.11 (dt, *J* = 7.4, 1.0 Hz, 1H), 6.94 (dt, *J* = 7.4, 0.8 Hz, 1H), 6.11 (d, *J* = 7.9 Hz, 1H), 5.47 (d, *J* = 4.7 Hz, 1H), 2.63-2.69 (m, 1H), 2.60 (q, *J* = 7.5 Hz, 2H), 2.51-2.57 (m, 1H), 2.48 (s, 3H), 1.71 (d, *J* = 4.7 Hz, 1H), 1.07 (t, *J* = 7.5 Hz, 3H), 1.05 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 145.2, 141.7, 141.6, 140.7, 140.5, 140.0, 139.9, 139.4, 139.1, 137.1, 136.24, 136.23, 135.7, 129.93, 129.90, 129.8, 129.6, 129.1, 128.9, 128.6, 128.4, 127.4, 127.33, 127.27, 127.0, 126.74, 124.67, 122.5, 73.9, 22.9, 22.8, 21.3, 15.9 (2xCH_3); IR (KBr) ν_{max} 3566, 3440, 3049, 3028, 2968, 2926, 2866, 1598, 1515, 1488, 1473, 1449, 1431, 1371, 1311, 1290, 1251, 1180, 1141, 1102, 1066, 1021, 1012, 857, 839, 824, 767, 746, 698 cm^{-1}; HRMS (*m/z*) for $C_{36}H_{32}ONa$ (M + Na) calcd: 503.23454, found: 503.23464; R_f (5/1 hexanes/EtOAc) = 0.42 (silica gel plate).



2,3-Diethyl-4-phenyl-1-(*p*-tolyl)-9*H*-fluoren-9-ol (2d). With **1d** (161 mg, 0.5 mmol) following the general procedure C. Column chromatography (5/1 hexanes/EtOAc) yielded 122 mg (61%) of the title compound as a light brown solid: mp (decomp) 70-75 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.48-7.57 (m, 3H), 7.30-7.41 (m, 7H), 7.09 (dt, *J* = 7.4, 1.0 Hz, 1H), 6.92 (dt, *J* = 7.4, 0.7 Hz, 1H), 5.93 (d, *J* = 7.9 Hz, 1H), 5.44 (d, *J* = 4.7 Hz, 1H), 2.60-2.66 (m, 1H), 2.55 (q, *J* = 7.5 Hz, 2H), 2.50-2.53 (m, 1H), 2.47 (s, 3H), 1.68 (d, *J* = 4.7 Hz, 1H), 1.03 (t, *J* = 7.5 Hz, 3H), 1.02 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 145.2, 141.6, 141.5, 140.6, 140.3, 140.0, 139.0, 137.1, 136.6, 136.2, 135.7, 129.8, 129.6, 129.5, 129.4, 129.1, 128.8, 128.7, 128.6, 128.4, 127.3, 126.7, 124.6, 122.5, 73.9, 22.9, 22.8, 21.3, 15.9, 15.8; IR (KBr) ν_{max} 3572, 3443, 3078, 3049, 3022, 2968, 2932, 2866, 1598, 1515, 1470, 1446, 1431, 1371, 1308, 1242, 1180, 1141, 1099, 1069, 1036, 1021, 997, 830, 797, 743, 764, 707 cm^{-1}; HRMS (*m/z*) for $C_{30}H_{28}ONa$ (M + Na) calcd: 427.20324, found: 427.20329; R_f (5/1 hexanes/EtOAc) = 0.44 (silica gel plate).

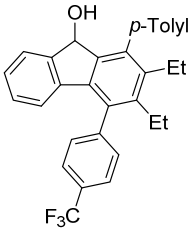


4-(4-Chlorophenyl)-2,3-diethyl-1-(*p*-tolyl)-9*H*-fluoren-9-ol (2e). With **1e** (178 mg, 0.5 mmol) following the general procedure C. Column chromatography (5/1 hexanes/EtOAc) yielded 97 mg (44%) of the title compound as a viscous brown oil: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.51-7.53 (m, 2H), 7.41 (m, 1H), 7.28-7.35 (m, 6H), 7.12 (dt, *J* = 7.4, 1.0 Hz, 1H), 6.98 (dt, *J* = 7.4, 0.7 Hz, 1H), 6.05 (d, *J* = 7.8 Hz, 1H), 5.44 (d, *J* = 4.6 Hz, 1H), 2.59-2.65 (m, 1H), 2.53 (q, *J* = 7.5 Hz, 2H), 2.47-2.53 (m, 1H), 2.46 (s, 3H), 1.68 (d, *J* = 4.7 Hz, 1H), 1.02 (t, *J* = 7.5 Hz, 3H), 1.01 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 145.2, 141.8, 141.5, 140.3, 140.1, 139.4, 138.8, 137.2, 136.1, 135.6, 135.2, 133.3, 131.0, 130.9, 129.8, 129.6, 129.10, 129.09, 129.0, 128.6, 128.5, 126.9, 124.8, 122.3, 73.8, 22.81, 22.77, 21.3, 15.9, 15.7; IR (KBr) ν_{max} 3563, 3437, 3066, 3049, 3022, 2962, 2929, 2866, 1607, 1565,

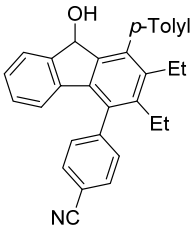


1518, 1491, 1470, 1461, 1425, 1392, 1371, 1248, 1204, 1183, 1141, 1087, 1069, 1018, 997, 857, 821, 803, 761, 749, 516 cm^{-1}; HRMS (*m/z*) for $C_{30}H_{27}OClNa$ (M + Na) calcd: 461.16426, found: 461.16433; R_f(5/1 hexanes/EtOAc) = 0.43 (silica gel plate).

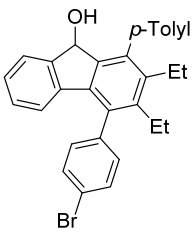
2,3-Diethyl-1-(*p*-tolyl)-4-(4-(trifluoromethyl)phenyl)-9*H*-fluoren-9-ol (2f). With **1f** (195 mg, 0.5 mmol) following the general procedure C. Column chromatography (5/1 hexanes/EtOAc) yielded 115 mg (49%) of the title compound as a viscous brown oil: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.82 (m, 2H), 7.50-7.54 (m, 2H), 7.41 (m, 1H), 7.29-7.36 (m, 4H), 7.12 (dt, *J* = 7.4, 1.0 Hz, 1H), 6.95 (dt, *J* = 7.6, 1.1 Hz, 1H), 5.89 (d, *J* = 7.8 Hz, 1H), 5.45 (d, *J* = 4.6 Hz, 1H), 2.60-2.66 (m, 1H), 2.51 (q, *J* = 7.5 Hz, 2H), 2.47-2.54 (m, 1H), 2.47 (s, 3H), 1.70 (d, *J* = 4.6 Hz, 1H), 1.03 (t, *J* = 7.4 Hz, 3H), 1.01 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 145.2, 144.3, 141.9, 141.2, 140.2, 140.1, 139.6, 137.2, 136.0, 135.4, 135.0, 130.04, 130.01, 129.9, 129.8 (q, $^2J_{C\text{-}F}$ = 32.4 Hz), 129.53, 129.1, 128.6, 128.5, 127.0, 125.8 (q, $^3J_{C\text{-}F}$ = 3.8 Hz), 124.9, 121.6-127.0 (q, $^1J_{C\text{-}F}$ = 272.1 Hz), 122.1, 73.8, 22.8, 22.7, 21.3, 15.8, 15.7; IR (KBr) ν_{max} 3566, 3428, 3075, 3046, 3016, 2968, 2932, 2872, 1616, 1565, 1509, 1464, 1404, 1374, 1323, 1245, 1171, 1132, 1102, 1069, 1021, 866, 827, 767 cm^{-1}; HRMS (*m/z*) for $C_{31}H_{27}OF_3Na$ (M + Na) calcd: 495.19062, found: 495.19065; R_f (5/1 hexanes/EtOAc) = 0.41 (silica gel plate).



4-(2,3-Diethyl-9-hydroxy-1-(*p*-tolyl)-9*H*-fluoren-4-yl)benzonitrile (2g). With **1g** (178 mg, 0.5 mmol) following the general procedure C. Column chromatography (5/1 hexanes/EtOAc) yielded 65 mg (30%) of the title compound as a light brown solid: mp (decomp) 227-232 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.85 (m, 2H), 7.50-7.54 (m, 2H), 7.42 (m, 1H), 7.33-7.36 (m, 3H), 7.29 (m, 1H), 7.13 (dt, *J* = 7.4, 1.0 Hz, 1H), 6.97 (dt, *J* = 7.5, 0.8 Hz, 1H), 5.88 (d, *J* = 7.8 Hz, 1H), 5.44 (d, *J* = 4.6 Hz, 1H), 2.59-2.65 (m, 1H), 2.47-2.53 (m, 3H), 2.47 (s, 3H), 1.70 (d, *J* = 4.6 Hz, 1H), 1.02 (t, *J* = 7.5 Hz, 3H), 1.00 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 145.7, 145.2, 142.0, 140.8, 140.3, 139.9, 139.8, 137.3, 135.8, 135.2, 134.5, 132.7, 132.6, 130.63, 130.59, 129.9, 129.5, 129.2, 128.53, 128.50, 127.1, 125.0, 121.9, 118.9, 111.5, 73.7, 22.9, 22.7, 21.3, 15.8, 15.7; IR (KBr) ν_{max} 3476, 3090, 3075, 3049, 3028, 2971, 2926, 2866, 2235, 1607, 1515, 1473, 1428, 1395, 1371, 1308, 1263, 1192, 1144, 1099, 1069, 1033, , 860, 818, 761, 740, 567 cm^{-1}; HRMS (*m/z*) for $C_{31}H_{27}NO$ (M^+) calcd: 429.2093, found: 429.2095; R_f(5/1 hexanes/EtOAc) = 0.31 (silica gel plate).

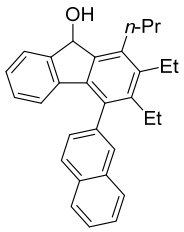


4-(4-Bromophenyl)-2,3-diethyl-1-(*p*-tolyl)-9*H*-fluoren-9-ol (2h). With **1h** (100 mg, 0.25 mmol) following the general procedure C. Column chromatography (5/1 hexanes/EtOAc) yielded 61 mg (51%) of the title compound as a brown solid: mp (decomp) 147-152 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (m, 2H), 7.41 (m, 1H), 7.33 (m, 3H), 7.24-7.30 (m, 3H), 7.13 (dt, *J* = 7.4, 1.0 Hz, 1H), 6.99 (dt, *J* = 7.5, 0.8 Hz, 1H), 6.05 (d, *J* = 7.8 Hz, 1H), 5.44 (bs, 1H), 2.58-2.67 (m, 1H), 2.52 (q, *J* = 7.5 Hz, 2H), 2.48-2.53 (m, 1H), 2.47 (s, 3H), 1.69 (bs, 1H), 1.02 (t, *J* = 7.5 Hz, 3H), 1.01 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$)

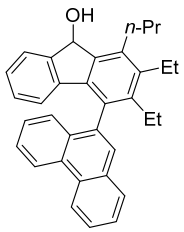


δ 145.2, 141.8, 141.4, 140.2, 140.1, 139.4, 139.3, 137.1, 136.1, 135.5, 135.2, 132.02, 131.96, 131.32, 131.29, 129.8, 129.6, 129.1, 128.6, 128.5, 126.9, 124.8, 122.3, 121.5, 73.8, 22.81, 22.75, 21.3, 15.84, 15.75; IR (KBr) ν_{max} 3563, 3047, 3025, 2962, 2929, 2869, 1601, 1512, 1488, 1467, 1431, 1392, 1371, 1263, 1183, 1099, 1069, 1012, 821, 764, 522 cm^{-1}; HRMS (*m/z*) for $C_{30}H_{27}OBrNa$ (M + Na) calcd: 505.11375, found: 505.11368; R_f (5/1 hexanes/EtOAc) = 0.42 (silica gel plate).

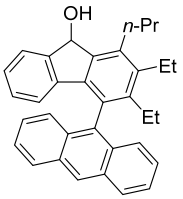
2,3-Diethyl-4-(naphthalen-2-yl)-1-propyl-9*H*-fluoren-9-ol (9a). With **8a** (162 mg, 0.5 mmol) following the general procedure C. Column chromatography (5/1 hexanes/EtOAc) yielded 91 mg (45%) of the title compound as a light brown solid: mp (decomp) 93-98 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (m, 2H), 7.86 (m, 1H), 7.79 (d, *J* = 8.9 Hz, 1H), 7.53-7.60 (m, 3H), 7.45 (ddd, *J* = 13.1, 8.3, 1.6 Hz, 1H), 7.09 (dt, *J* = 7.4, 0.9 Hz, 1H), 6.81 (dt, *J* = 7.7, 0.9 Hz, 1H), 5.86 (d, *J* = 7.8 Hz, 1H), 5.67 (s, 1H), 3.15 (m, 1H), 2.86 (m, 1H), 2.82 (dq, *J* = 7.5, 2.2 Hz, 2H), 2.46-2.63 (m, 2H), 1.77 (m, 2H), 1.73 (s, 1H), 1.29 (t, *J* = 7.5 Hz, 3H), 1.17 (t, *J* = 7.3 Hz, 3H), 0.99 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.0, 142.1, 141.1, 140.6, 140.5, 140.4, 139.1, 139.0, 138.0, 135.9, 135.0, 133.6, 132.5, 128.6, 128.3, 128.19, 128.16, 128.15, 128.13, 128.08, 128.0, 127.9, 126.7, 126.1, 125.9, 124.48, 124.47, 122.5, 74.6, 31.9, 31.8, 25.02, 24.96, 22.90, 22.88, 21.8, 16.0, 15.9, 15.1; IR (KBr) ν_{max} 3386, 3052, 2965, 2932, 2866, 1604, 1565, 1470, 1434, 1371, 1302, 1189, 1102, 1069, 1021, 964, 863, 806, 761, 752, cm^{-1}; HRMS (*m/z*) for $C_{30}H_{30}O$ (M^+) calcd: 406.2297, found: 406.2295; R_f (5/1 hexanes/EtOAc) = 0.45 (silica gel plate).



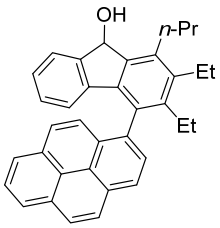
2,3-Diethyl-4-(phenanthren-9-yl)-1-propyl-9*H*-fluoren-9-ol (9b). With **8b** (94 mg, 0.25 mmol) following the general procedure C. Column chromatography (5/1 hexanes/EtOAc) yielded 67 mg (59%) of the title compound as a light brown solid: mp (decomp) 109-114 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.83 (m, 2H), 7.88 (m, 1H), 7.71-7.77 (m, 2H), 7.63-7.68 (m, 2H), 7.37-7.60 (m, 3H), 7.02 (m, 1H), 6.65 (dt, *J* = 7.8, 0.9 Hz, 1H), 5.83 (dd, *J* = 7.8, 2.5 Hz, 1H), 5.70 (d, *J* = 9.8 Hz, 1H), 3.11-3-31 (m, 1H), 2.91 (m, 1H), 2.83 (m, 2H), 2.55 (m, 1H), 2.27 (m, 1H), 1.79 (m, 2H), 1.73 (d, *J* = 9.9 Hz, 1H), 1.31 (dt, *J* = 7.3, 1.0 Hz, 3H), 1.19 (dt, *J* = 7.2, 2.2 Hz, 3H), 0.93 (dt, *J* = 7.4, 1.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.0, 142.86, 142.83, 141.4, 140.8, 140.24, 140.22, 139.29, 139.20, 136.54, 136.52, 136.51, 136.47, 132.58, 132.56, 131.8, 131.74, 131.73, 130.5, 130.20, 130.18, 128.79, 128.77, 128.68, 128.65, 127.8, 127.7, 126.9, 126.75, 126.73, 126.66, 126.63, 126.56, 126.53, 124.38, 124.35, 122.9, 122.7, 122.5, 122.4, 74.65, 74.62, 32.11, 31.61, 25.21, 24.91, 23.3, 21.84, 21.81, 16.23, 16.20, 16.17, 16.12, 15.13; IR (KBr) ν_{max} 3321, 3072, 2959, 2932, 2866, 1607, 1494, 1464, 1452, 1374, 1251, 1195, 1099, 1060, 1009, 908, 812, 770, 755, 725 cm^{-1}; HRMS (*m/z*) for $C_{34}H_{32}ONa$ (M + Na) calcd: 479.23454, found: 479.23450; R_f (5/1 hexanes/EtOAc) = 0.38 (silica gel plate).



4-(Anthracen-9-yl)-2,3-diethyl-1-propyl-9*H*-fluoren-9-ol (9c). With **8c** (94 mg, 0.25 mmol) following the general procedure C. Column chromatography (5/1 hexanes/EtOAc) yielded 55 mg (48%) of the title compound as a light brown solid: mp (decomp) 104-109 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (s, 1H), 8.08 (dd, *J* = 8.5, 3.9 Hz, 2H), 7.61 (dd, *J* = 8.8, 0.9 Hz, 1H), 7.41–7.50 (m, 4H), 7.22-7.28 (m 2H), 6.93 (dt, *J* = 7.4, 1.0 Hz, 1H), 6.47 (dt, *J* = 7.6, 0.8 Hz, 1H), 5.73 (d, *J* = 8.4 Hz, 1H), 4.91 (d, *J* = 7.8 Hz, 1H), 3.24 (m, 1H), 2.96 (m, 1H), 2.85 (q, *J* = 7.6 Hz, 2H), 2.24 (q, *J* = 7.5 Hz, 2H), 1.86 (m, 2H), 1.78 (d, *J* = 9.2 Hz, 1H), 1.33 (t, *J* = 7.4 Hz, 3H), 1.21 (t, *J* = 7.3 Hz, 3H), 0.66 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.9, 143.3, 141.7, 141.1, 140.1, 139.4, 137.1, 134.9, 131.6, 130.7, 130.5, 130.4, 128.6, 128.4, 126.64, 126.59, 126.5, 126.4, 125.6, 125.4, 125.3, 124.3, 121.8, 74.7, 31.9, 25.1, 23.5, 21.8, 16.2, 15.5, 15.1; IR (KBr) ν_{max} 3549, 3261, 2961, 2930, 2870, 2205, 1947, 1818, 1605, 1519, 1465, 1441, 1408, 1375, 1230, 1190, 1101, 1059, 1012, 973, 884, 845, 762, 738 cm^{-1}; HRMS (*m/z*) for $C_{34}H_{32}ONa$ (M + Na) calcd: 479.23454, found: 479.23448; R_f (5/1 hexanes/EtOAc) = 0.39 (silica gel plate).



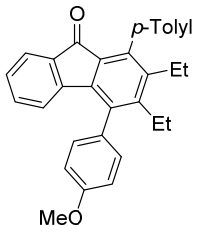
2,3-Diethyl-1-propyl-4-(pyren-2-yl)-9*H*-fluoren-9-ol (9d). With **8d** (100 mg, 0.25 mmol) following the general procedure C. Column chromatography (5/1 hexanes/EtOAc) yielded 64 mg (54%) of the title compound as a light brown solid: mp (decomp) 98-103 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (dd, *J* = 7.8, 4.7 Hz, 1H), 8.24 (m, 1H), 8.13-8.20 (m, 3H), 8.02 (dt, *J* = 7.6, 2.6 Hz, 1H), 7.94-8.00 (dd, *J* = 17.0, 7.8 Hz, 1H), 7.90 (dd, *J* = 9.2, 6.1 Hz, 1H), 7.64-7.78 (dd, *J* = 46.1, 9.2 Hz, 1H), 7.50 (d, *J* = 7.4 Hz, 1H), 6.98 (m, 1H), 6.53 (dt, *J* = 7.6, 0.5 Hz, 1H), 5.75 (dd, *J* = 9.7, 4.5 Hz, 1H), 5.21 (d, *J* = 7.8 Hz, 1H), 3.17-3.32 (m, 1H), 2.94 (m, 1H), 2.86 (m, 2H), 2.48 (m, 1H), 2.31 (m, 1H), 1.88 (m, 2H), 1.77 (d, *J* = 10.4 Hz, 1H), 1.34 (dt, *J* = 7.3, 1.2 Hz, 3H), 1.26 (dt, *J* = 7.2, 1.6 Hz, 3H), 0.86 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.97, 145.94, 142.85, 142.82, 141.35, 140.77, 140.76, 140.39, 139.33, 139.29, 136.67, 136.63, 135.63, 135.57, 133.18, 133.16, 131.38, 131.37, 131.22, 131.21, 130.75, 130.74, 129.62, 129.55, 128.60, 128.58, 127.97, 127.80, 127.61, 127.57, 127.46, 127.41, 126.55, 126.53, 126.02, 125.40, 125.28, 125.07, 125.05, 125.04, 124.95, 124.92, 124.38, 124.37, 122.15, 122.11, 74.69, 74.66, 32.05, 31.80, 25.16, 25.00, 23.2, 21.9, 16.19, 16.17, 15.77, 15.75, 15.16, 15.15; IR (KBr) ν_{max} 3545, 3349, 3043, 2961, 2930, 2869, 1697, 1602, 1464, 1374, 1306, 1191, 1178, 1099, 1057, 1022, 944, 847, 760, 743 cm^{-1}; HRMS (*m/z*) for $C_{36}H_{32}ONa$ (M + Na) calcd: 503.23454, found: 503.23448; R_f(5/1 hexanes/EtOAc) = 0.34 (silica gel plate).



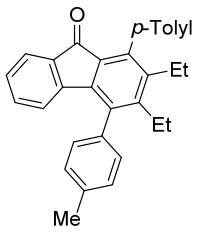
III-2 Oxidation

D: General procedure for Oxidation reaction with PCC (preparation of 3). To a solution of pyridinium chlorochromate (PCC, 64 mg, 0.3 mmol) and celite (64 mg) in anhydrous DCM (10 mL) the starting fluorenol (0.2 mmol) was added and the mixture was stirred for 3 h at rt. Afterwards the residue was filtered through a celite/silica gel plug. Column chromatography of the residue on silica gel yielded products.

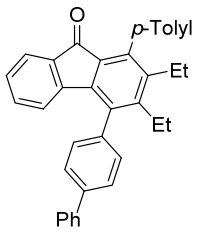
2,3-Diethyl-4-(4-methoxyphenyl)-1-(*p*-tolyl)-9*H*-fluoren-9-one (3a). With **2a** (87 mg, 0.26 mmol) following the general procedure D. Column chromatography (10/1 hexanes/EtOAc) yielded 69 mg (80%) of the title compound as a bright yellow solid: mp (decomp) 231-236 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 (m, 1H), 7.28 (m, 4H), 7.16 (m, 2H), 7.08 (m, 2H), 7.05 (m, 2H), 5.92 (m, 1H), 3.95 (s, 3H), 2.55 (q, *J* = 7.5 Hz, 2H), 2.53 (q, *J* = 7.5 Hz, 2H), 2.47 (s, 3H), 1.03 (t, *J* = 7.5 Hz, 3H), 0.99 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 193.3, 159.1, 148.4, 144.1, 142.3, 141.0, 140.6, 136.9, 136.6, 135.0, 134.9, 133.8, 131.4, 130.3, 129.1, 128.7, 128.5, 127.9, 123.4, 122.6, 114.3, 55.3, 23.4, 22.4, 21.4, 15.6, 15.4; IR (KBr) ν_{max} 3022, 3001, 2962, 2932, 2893, 2869, 2836, 1712, 1613, 1586, 1562, 1512, 1461, 1422, 1302, 1284, 1242, 1192, 1186, 1066, 1030, 842, 824, 779 cm^{-1}; HRMS (*m/z*) for $C_{31}H_{28}O_2$ (M^+) calcd: 432.2089, found: 432.2091; R_f (5/1 hexanes/EtOAc) = 0.39 (silica gel plate).



2,3-Diethyl-1,4-di-*p*-tolyl-9*H*-fluoren-9-one (3b). With **2b** (83 mg, 0.2 mmol) following the general procedure D. Column chromatography (10/1 hexanes/EtOAc) yielded 70 mg (84%) of the title compound as a bright yellow solid: mp (decomp) 76-81 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39 (m, 1H), 7.34 (d, *J* = 7.6 Hz, 2H), 7.28 (d, *J* = 7.6 Hz, 2H), 7.25 (d, *J* = 7.9 Hz, 2H), 7.16 (d, *J* = 7.6 Hz, 2H), 7.05 (dt, *J* = 7.4, 1.2 Hz, 1H), 7.02 (dt, *J* = 7.5, 1.5 Hz, 1H), 5.87 (m, 1H), 2.55 (q, *J* = 7.5 Hz, 2H), 2.54 (q, *J* = 7.5 Hz, 2H), 2.51 (s, 3H), 2.47 (s, 3H), 1.03 (t, *J* = 7.4 Hz, 3H), 0.99 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 193.3, 148.1, 144.1, 142.3, 141.0, 140.3, 137.4, 137.3, 136.6, 136.2, 135.0, 134.9, 133.7, 129.7, 129.11, 129.08, 128.7, 128.5, 127.9, 123.3, 122.6, 23.4, 22.4, 21.4 (2xCH_3), 15.6, 15.4; IR (KBr) ν_{max} 3078, 3046, 3025, 2965, 2932, 2893, 2872, 1709, 1607, 1586, 1556, 1515, 1467, 1446, 1422, 1374, 1299, 1195, 1063, 875, 818, 779, 764, 725 cm^{-1}; HRMS (*m/z*) for $C_{31}H_{28}O$ (M + Na) calcd: 416.2140, found: 416.2142; R_f (5/1 hexanes/EtOAc) = 0.49 (silica gel plate).

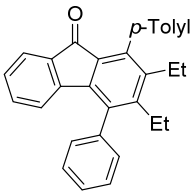


4-([1,1'-Biphenyl]-4-yl)-2,3-diethyl-1-(*p*-tolyl)-9*H*-fluoren-9-one (3c). With **2c** (96 mg, 0.2 mmol) following the general procedure D. Column chromatography (10/1 hexanes/EtOAc) yielded 78 mg (82%) of the title compound as a bright yellow solid: mp (decomp) 194-199 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.81 (m, 2H), 7.78 (m, 2H), 7.53 (m, 2H), 7.46 (m, 2H), 7.42 (m, 2H), 7.29 (m, 2H), 7.18 (m, 2H), 7.06 (dt, *J* = 7.4, 1.1 Hz, 1H), 7.02 (dt, *J* = 7.6, 1.4 Hz,

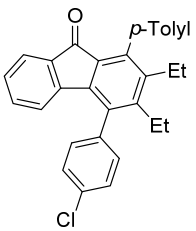


1H), 5.96 (d, *J* = 7.6 Hz, 1H), 2.59 (q, *J* = 7.5 Hz, 2H), 2.56 (q, *J* = 7.5 Hz, 2H), 2.47 (s, 3H), 1.04 (t, *J* = 7.5 Hz, 3H), 1.00 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 193.2, 147.9, 144.0, 142.4, 141.2, 140.39, 140.37, 140.3, 138.3, 136.8, 136.7, 135.0, 134.9, 133.8, 129.8, 129.2, 128.9, 128.7, 128.5, 128.0, 127.6, 127.5, 127.0, 123.4, 122.6, 23.4, 22.4, 21.4, 15.6, 15.4; IR (KBr) ν_{max} 3078, 3049, 3022, 2974, 2938, 2878, 1712, 1601, 1583, 1559, 1488, 1467, 1446, 1302, 1230, 1186, 1117, 1063, 1006, 872, 776, 752, 695 cm^{-1}; HRMS (*m/z*) for $C_{36}H_{30}O$ (M^+) calcd: 478.2297, found: 478.2296; R_f (5/1 hexanes/EtOAc) = 0.47 (silica gel plate).

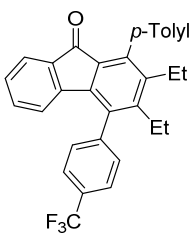
2,3-Diethyl-4-phenyl-1-(*p*-tolyl)-9*H*-fluoren-9-one (3d). With **2d** (81 mg, 0.2 mmol) following the general procedure D. Column chromatography (10/1 hexanes/EtOAc) yielded 69 mg (86%) of the title compound as a bright yellow solid: mp (decomp) 71-76 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.51-7.57 (m, 3H), 7.38-7.42 (m, 3H), 7.29 (d, *J* = 7.6 Hz, 2H), 7.17 (m, 2H), 7.05 (dt, *J* = 7.5, 1.0 Hz, 1H), 7.00 (dt, *J* = 7.6, 1.4 Hz, 1H), 5.79 (d, *J* = 7.6 Hz, 1H), 2.560 (q, *J* = 7.5 Hz, 2H), 2.559 (q, *J* = 7.5 Hz, 2H), 2.47 (s, 3H), 1.04 (t, *J* = 7.5 Hz, 3H), 1.01 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 193.2, 147.7, 144.0, 142.3, 141.1, 140.2, 139.3, 137.2, 136.6, 134.9, 134.9, 133.7, 129.3, 129.1, 129.0, 128.7, 128.5, 127.9, 127.8, 123.4, 122.5, 23.4, 22.4, 21.4, 15.6, 15.3; IR (KBr) ν_{max} 3049, 3022, 2971, 2929, 2869, 1715, 1601, 1559, 1512, 1464, 1440, 1305, 1186, 1060, 1009, 952, 866, 764, 719, 707 cm^{-1}; HRMS (*m/z*) for $C_{30}H_{26}O$ (M^+) calcd: 402.1984, found: 402.1988; R_f (5/1 hexanes/EtOAc) = 0.53 (silica gel plate).



4-(4-Chlorophenyl)-2,3-diethyl-1-(*p*-tolyl)-9*H*-fluoren-9-one (3e). With **2e** (87 mg, 0.2 mmol) following the general procedure D. Column chromatography (10/1 hexanes/EtOAc) yielded 75 mg (86%) of the title compound as a bright yellow solid: mp (decomp) 193-198 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.54 (m, 2H), 7.42 (m, 1H), 7.34 (m, 2H), 7.28 (m, 2H), 7.15 (m, 2H), 7.08 (m, 2H), 5.91 (m, 1H), 2.53 (q, *J* = 7.5 Hz, 2H), 2.52 (q, *J* = 7.5 Hz, 2H), 2.47 (s, 3H), 1.02 (t, *J* = 7.5 Hz, 3H), 0.99 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 193.0, 147.6, 143.7, 142.5, 141.4, 140.2, 137.8, 136.7, 135.7, 134.9, 134.7, 133.9, 133.8, 130.8, 129.3, 129.2, 128.7, 128.4, 128.1, 123.6, 122.4, 23.3, 22.4, 21.4, 15.6, 15.3; IR (KBr) ν_{max} 3081, 3063, 3052, 3025, 2974, 2929, 2866, 1712, 1607, 1589, 1556, 1512, 1488, 1464, 1425, 1302, 1198, 1087, 955, 872, 821, 773, 725 cm^{-1}; HRMS (*m/z*) for $C_{30}H_{26}OCl$ (M + H) calcd: 437.16667, found: 437.16665; R_f (5/1 hexanes/EtOAc) = 0.52 (silica gel plate).

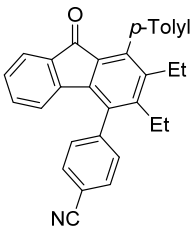


2,3-Diethyl-1-(*p*-tolyl)-4-(4-(trifluoromethyl)phenyl)-9*H*-fluoren-9-one (3f). With **2f** (95 mg, 0.2 mmol) following the general procedure D. Column chromatography (10/1 hexanes/EtOAc) yielded 57 mg (61%) of the title compound as a bright yellow solid: mp (decomp) 77-82 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.83 (d, *J* = 7.9 Hz, 2H), 7.54 (d, *J* = 7.8 Hz, 2H), 7.42 (m, 1H), 7.29 (m, 2H), 7.16 (m, 2H), 7.08 (dt, *J* = 7.5, 1.0 Hz, 1H), 7.04 (dt, *J* = 7.6, 1.4 Hz, 1H), 5.76 (m, 1H), 2.54 (q, *J* = 7.5 Hz, 2H), 2.49 (q, *J* = 7.5 Hz, 2H), 2.47 (s, 3H), 1.02

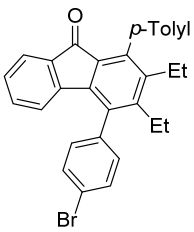


(t, J = 7.5 Hz, 3H), 1.00 (t, J = 7.5 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 192.8, 147.2, 143.5, 143.3, 142.7, 141.7, 139.9, 136.8, 135.5, 134.9, 134.6, 133.9, 130.2 (q, $^{2}J_{C\text{-}F}$ = 32.6 Hz), 129.9, 129.3, 128.8, 128.4, 128.3, 126.0 (q, $^{3}J_{C\text{-}F}$ = 3.8 Hz), 121.5-126.9 (q, $^{1}J_{C\text{-}F}$ = 272.2 Hz), 123.7, 122.2, 23.4, 22.3, 21.4, 15.5, 15.3; IR (KBr) ν_{max} 3028, 2965, 2932, 2869, 1715, 1619, 1601, 1559, 1464, 1401, 1374, 1332, 1323, 1192, 1162, 1132, 1123, 1102, 1069, 1021, 872, 857, 824, 770, 719 cm^{-1}; HRMS (*m/z*) for $C_{31}H_{26}OF_3$ (M + H) calcd: 471.19303, found: 471.19297; R_f(5/1 hexanes/EtOAc) = 0.54 (silica gel plate).

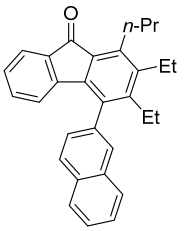
4-(2,3-Diethyl-9-oxo-1-(*p*-tolyl)-9*H*-fluoren-4-yl)benzonitrile (3g). With **2g** (65 mg, 0.15 mmol) following the general procedure D. Column chromatography (10/1 hexanes/EtOAc) yielded 47 mg (73%) of the title compound as a bright yellow solid: mp (decomp) 239-244 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.87 (m, 2H), 7.55 (m, 2H), 7.43 (m, 1H), 7.29 (d, J = 7.7 Hz, 2H), 7.14 (m, 2H), 7.10 (dt, J = 7.5, 1.0 Hz, 1H), 7.05 (dt, J = 7.6, 1.4 Hz, 1H), 5.76 (d, J = 7.6 Hz, 1H), 2.54 (q, J = 7.5 Hz, 2H), 2.48 (q, J = 7.5 Hz, 2H), 2.46 (s, 3H), 1.01 (t, J = 7.5 Hz, 3H), 0.99 (t, J = 7.5 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 192.6, 146.8, 144.6, 143.2, 142.8, 141.9, 139.7, 136.9, 135.0, 134.9, 134.4, 133.9, 132.8, 130.5, 129.3, 128.8, 128.41, 128.35, 123.8, 122.0, 118.6, 112.1, 23.4, 22.3, 21.4, 15.5, 15.2; IR (KBr) ν_{max} 3120, 3081, 3066, 3046, 3022, 2977, 2926, 2893, 2872, 2229, 1718, 1604, 1559, 1512, 1467, 1422, 1371, 1320, 1169, 1069, 1021, 949, 872, 833, 764, 716 cm^{-1}; HRMS (*m/z*) for $C_{31}H_{26}ON$ (M + H) calcd: 428.20089, found: 428.20087; R_f (5/1 hexanes/EtOAc) = 0.37 (silica gel plate).



4-(4-Bromophenyl)-2,3-diethyl-1-(*p*-tolyl)-9*H*-fluoren-9-one (3h). With **2h** (510 mg, 1.1 mmol) following the general procedure D. Column chromatography (5/1 hexanes/EtOAc) yielded 475 mg (93%) of the title compound as a bright yellow solid: mp (decomp) 78-83 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.69 (m, 2H), 7.42 (m, 1H), 7.27-7.30 (m, 4H), 7.15 (m, 2H), 7.08 (m, 2H), 5.92 (m, 1H), 2.53 (q, J = 7.5 Hz, 2H), 2.51 (q, J = 7.5 Hz, 2H), 2.46 (s, 3H), 1.02 (t, J = 7.5 Hz, 3H), 0.99 (t, J = 7.5 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 193.0, 147.6, 143.7, 142.5, 141.4, 140.1, 138.2, 136.8, 135.7, 134.9, 134.7, 133.9, 132.2, 131.1, 129.2, 128.7, 128.4, 128.2, 123.6, 122.4, 122.0, 23.3, 22.3, 21.4, 15.6, 15.3; IR (KBr) ν_{max} 3022, 2968, 2932, 2866, 1709, 1604, 1556, 1515, 1485, 1464, 1422, 1371, 1302, 1192, 1120, 1072, 1012, 949, 869, 824, 761, 719 cm^{-1}; HRMS (*m/z*) for $C_{30}H_{26}OBr$ (M + H) calcd: 481.11615, found: 481.11621; R_f(5/1 hexanes/EtOAc) = 0.51 (silica gel plate).

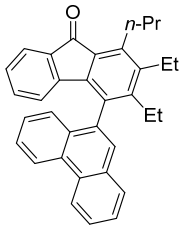


2,3-Diethyl-4-(naphthalen-2-yl)-1-propyl-9*H*-fluoren-9-one (10a). With **9a** (81 mg, 0.2 mmol) following the general procedure D. Column chromatography (5/1 hexanes/EtOAc) yielded 84 mg (91%) of the title compound as a bright yellow solid: mp (decomp) 69-74 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.00 (m, 2H), 7.87 (m, 1H), 7.81 (s, 1H), 7.56-7.61 (m, 2H), 7.53 (d, J = 7.2 Hz, 1H), 7.44 (dd, J = 8.3, 1.6 Hz, 1H), 7.04 (t, J = 7.4 Hz, 1H), 6.86 (dt, J = 7.6, 1.1 Hz, 1H), 5.71 (d, J = 7.6 Hz, 1H), 3.15 (m, 2H), 2.75 (q, J = 7.5 Hz, 2H),

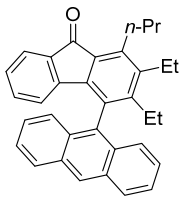


2.45-2.53 (m, 2H), 1.65 (m, 2H), 1.25 (t, J = 7.4 Hz, 3H), 1.16 (t, J = 7.2 Hz, 3H), 0.99 (t, J = 7.5 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 194.9, 147.9, 144.0, 142.9, 142.2, 140.7, 136.9, 135.7, 135.1, 133.8, 133.5, 132.7, 128.8, 128.6, 128.14, 128.10, 127.9, 127.8, 127.7, 126.4, 126.2, 123.2, 122.5, 29.7, 24.7, 23.5, 21.4, 15.7, 15.4, 14.9; IR (KBr) ν_{max} 3052, 2962, 2929, 2866, 1700, 1601, 1562, 1467, 1428, 1374, 1299, 1186, 1102, 1063, 1012, 961, 860, 806, 764, 746, 716 cm^{-1}; HRMS (*m/z*) for $C_{30}H_{28}O$ (M^+) calcd: 404.2140, found: 404.2141; R_f (5/1 hexanes/EtOAc) = 0.56 (silica gel plate).

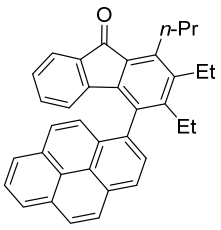
2,3-Diethyl-4-(phenanthren-9-yl)-1-propyl-9*H*-fluoren-9-one (10b). With **9b** (100 mg, 0.22 mmol) following the general procedure D. Column chromatography (5/1 hexanes/EtOAc) yielded 85 mg (86%) of the title compound as a bright yellow solid: mp (decomp) 81-86 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.82 (d, J = 8.3 Hz, 2H), 7.90 (dd, J = 7.9, 1.3 Hz, 1H), 7.77 (dt, J = 7.1, 1.4 Hz, 1H), 7.75 (s, 1H), 7.66-7.71 (m, 2H), 7.59 (dd, J = 8.2, 1.1 Hz, 1H), 7.45-7.50 (m, 2H), 6.97 (dt, J = 7.5, 0.9 Hz, 1H), 6.72 (dt, J = 7.6, 1.3 Hz, 1H), 5.71 (d, J = 7.7 Hz, 1H), 3.33 (m, 1H), 3.11 (m, 1H), 2.79 (m, 2H), 2.53 (m, 1H), 2.25 (m, 1H), 1.73 (m, 2H), 1.28 (t, J = 7.5 Hz, 3H), 1.19 (t, J = 7.2 Hz, 3H), 0.93 (t, J = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.0, 148.6, 143.6, 143.2, 142.6, 141.5, 135.4, 135.0, 133.9, 133.3, 131.6, 131.3, 130.6, 130.3, 129.2, 128.8, 127.9, 127.7, 127.1, 126.99, 126.95, 126.9, 126.3, 123.2, 123.0, 122.7, 122.5, 29.7, 24.7, 23.9, 21.5, 15.84, 15.82, 14; IR (KBr) ν_{max} 3075, 2965, 2935, 2869, 1703, 1604, 1562, 1491, 1470, 1449, 1377, 1257, 1192, 1060, 761, 746, 722 cm^{-1}; HRMS (*m/z*) for $C_{34}H_{31}O$ (M + H) calcd: 455.23694, found: 455.23707; R_f (5/1 hexanes/EtOAc) = 0.49 (silica gel plate).



4-(Anthracen-9-yl)-2,3-diethyl-1-propyl-9*H*-fluoren-9-one (10c). With **9c** (100 mg, 0.23 mmol) following the general procedure D. Column chromatography (5/1 hexanes/EtOAc) yielded 84 mg (83%) of the title compound as a bright yellow solid: mp (decomp) 75-80 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (s, 1H), 8.10 (d, J = 8.5 Hz, 2H), 7.66 (d, J = 8.8 Hz, 2H), 7.46–7.50 (m, 3H), 7.32 (m 2H), 6.89 (dt, J = 7.6, 0.6 Hz, 1H), 6.55 (dt, J = 7.6, 1.1 Hz, 1H), 4.82 (d, J = 7.7 Hz, 1H), 3.28 (m, 2H), 2.84 (q, J = 7.4 Hz, 2H), 2.25 (q, J = 7.5 Hz, 2H), 1.79 (m, 2H), 1.32 (t, J = 7.4 Hz, 3H), 1.24 (t, J = 7.3 Hz, 3H), 0.69 (t, J = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.0, 149.2, 143.34, 143.0, 142.2, 135.0, 133.8, 133.4, 131.6, 131.5, 130.3, 129.5, 128.5, 127.6, 127.2, 126.1, 126.0, 125.5, 123.0, 121.8, 29.8, 24.8, 24.0, 21.5, 15.9, 15.2, 14.9; IR (KBr) ν_{max} 3049, 2959, 2926, 2886, 1703, 1601, 1562, 1464, 1404, 1293, 1245, 1222, 1183, 1096, 1054, 1012, 973, 890, 848, 785, 761, 737, 716 cm^{-1}; HRMS (*m/z*) for $C_{34}H_{31}O$ (M + H) calcd: 455.23694, found: 455.23681; R_f (5/1 hexanes/EtOAc) = 0.50 (silica gel plate).



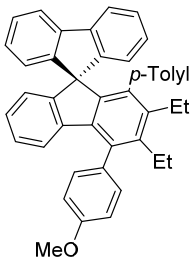
2,3-Diethyl-1-propyl-4-(pyren-2-yl)-9*H*-fluoren-9-one (10d). With **9d** (96 mg, 0.2 mmol) following the general procedure D. Column chromatography (5/1 hexanes/EtOAc) yielded 80 mg (84%) of the title compound as a bright yellow solid: mp (decomp) 87-93 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, *J* = 7.8 Hz, 1H), 8.25 (dd, *J* = 7.6, 1.0 Hz, 1H), 8.16–8.22 (m, 3H), 8.04 (t, *J* = 7.6 Hz, 1H), 7.98 (d, *J* = 3.4 Hz, 1H), 7.95 (d, *J* = 4.8 Hz, 1H), 7.75 (d, *J* = 9.2 Hz, 1H), 7.50 (m 1H), 6.93 (dt, *J* = 7.5, 0.8 Hz, 1H), 6.58 (dt, *J* = 7.6, 1.2 Hz, 1H), 5.06 (d, *J* = 7.7 Hz, 1H), 3.31 (m, 1H), 3.18 (m, 1H), 2.81 (m, 2H), 2.48 (m, 1H), 2.29 (m, 1H), 1.73 (m, 2H), 1.31 (t, *J* = 7.4 Hz, 3H), 1.29 (t, *J* = 7.2 Hz, 3H), 0.85 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.0, 148.6, 143.8, 143.2, 142.6, 141.6, 135.1, 134.3, 133.9, 133.8, 131.4, 131.2, 131.0, 129.5, 129.2, 128.0, 127.71, 127.68, 127.6, 127.5, 126.2, 125.33, 125.29, 125.1, 125.0, 124.9, 124.8, 123.2, 122.2, 29.8, 24.8, 23.8, 21.5, 15.9, 15.4, 14.9; IR (KBr) ν_{max} 3040, 2963, 2931, 2870, 1702, 1603, 1565, 1465, 1423, 1375, 1297, 1187, 1057, 1011, 952, 872, 849, 838, 761, 721 cm^{-1}; HRMS (*m/z*) for $C_{36}H_{31}O$ (M + H) calcd: 479.23694, found: 479.23680; R_f(5/1 hexanes/EtOAc) = 0.46 (silica gel plate).



III-3 9,9'-Spirobifluorenes

E: General procedure for creation of 9,9'-spirobifluorene (preparation of 4).[10] A solution of 2-bromobiphenyl (40 µL, 0.23 mmol) in anhydrous THF (3 mL) was cooled down to -78 °C and *n*-BuLi 1.6 M (140 µL, 0.23 mmol) was added dropwise. The resulted solution was stirred for 30 min, followed by the addition of fluorenone (0.15 mmol) in THF (3 mL) and stirred for 3 h first for 15 min at -78 °C, but during time it was allowed to reach ambient temperature. The reaction mixture was poured in a saturated solution of $NaHCO_3$ solution and extracted with diethyl ether (3 x 15 mL). The combined organic fractions were dried over $MgSO_4$ and concentrated under reduced pressure. The crude was purified by column chromatography on silica gel (10/1 hexanes/EtOAc) to yield desired alcohols. The alcohols were dissolved in acetic acid (10 mL) with a catalytic amount of HCl (12 mol/L) and the resulted solution stirred under reflux for 3 h. The reaction mixture was neutralized with H_2O and K_2CO_3 and extracted with diethyl ether (3 x 15 mL). Column chromatography of the residue on silica gel provided products.

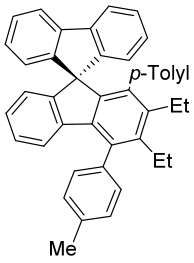
2,3-Diethyl-4-(4-methoxyphenyl)-1-(*p*-tolyl)-9,9'-spirobifluorene (4a). With **3a** (65 mg, 0.15 mmol) following the general procedure E. Column chromatography of the residue on silica gel (20/1 hexanes/EtOAc) provided 71 mg (83%) of the title compound as a colorless solid: mp (decomp) 260-265 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 (m, 2H), 7.30 (d, *J* = 7.6 Hz, 2H), 7.18 (dt, *J* = 7.4, 1.0 Hz, 2H), 7.14 (m, 2H), 7.04 (dt, *J* = 7.4, 1.0 Hz, 2H), 6.90 (dt, *J* = 7.3, 1.1 Hz, 1H), 6.84 (dt, *J* = 7.4, 1.1 Hz, 1H), 6.79 (d, *J* = 7.5 Hz, 2H), 6.40 (d, *J* = 7.4 Hz, 1H), 6.37 (d, *J* = 7.7 Hz, 2H), 6.19 (d, *J* = 7.8 Hz, 1H), 5.95 (d, *J* = 7.9 Hz, 2H), 3.98 (s, 3H), 2.59 (q, *J* = 7.4 Hz, 2H), 2.31 (q, *J* = 7.4 Hz, 2H), 2.18 (s, 3H), 1.06



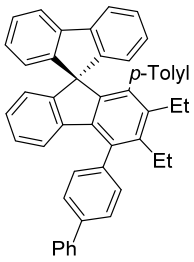
[10] Z. Jiang, H. Yao, Z. Zhang, C. Yang, Z. Liu, Y. Tao, J. Qin, D. Ma; *Org. Lett.* **2009**, *11* 2607-2610.

(t, *J* = 7.4 Hz, 3H), 0.87 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 158.8, 149.7, 149.1, 143.7, 142.01, 141.99, 140.5, 140.3, 139.3, 138.3, 135.8, 134.2, 134.1, 133.1, 130.8, 129.1, 126.9, 126.8, 126.74, 126.70, 126.5, 123.8, 123.2, 122.6, 119.4, 114.1, 65.5, 55.3, 23.1, 22.9, 21.1, 15.8, 15.7; IR (KBr) ν_{max} 3063, 3040, 3022, 2956, 2932, 2869, 2839, 1613, 1574, 1512, 1476, 1467, 1440, 1425, 1371, 1290, 1245, 1177, 1111, 1063, 1033, 824, 815, 770, 737 cm^{-1}; HRMS (*m/z*) for $C_{43}H_{37}O$ (M + H) calcd: 569.28389, found: 569.28369; R_f (20/1 hexanes/EtOAc) = 0.36 (silica gel plate).

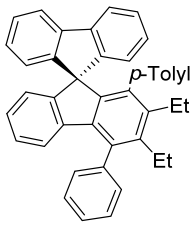
2,3-Diethyl-1,4-di-*p*-tolyl-9,9'-spirobifluorene (4b). With **3b** (62 mg, 0.15 mmol) following the general procedure E. Column chromatography of the residue on silica gel (20/1 hexanes/EtOAc) provided 61 mg (74%) of the title compound as a colorless solid: mp (decomp) 226-231 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 (s, 4H), 7.29 (d, *J* = 7.6 Hz, 2H), 7.18 (dt, *J* = 7.5, 1.0 Hz, 2H), 7.04 (dt, *J* = 7.5, 1.0 Hz, 2H), 6.88 (dt, *J* = 7.6, 1.2 Hz, 1H), 6.83 (dt, *J* = 7.4, 1.2 Hz, 1H), 6.79 (d, *J* = 7.5 Hz, 2H), 6.39 (d, *J* = 7.5 Hz, 1H), 6.37 (d, *J* = 7.7 Hz, 2H), 6.14 (d, *J* = 7.8 Hz, 1H), 5.95 (d, *J* = 7.9 Hz, 2H), 2.57 (q, *J* = 7.4 Hz, 2H), 2.55 (s, 3H), 2.30 (q, *J* = 7.4 Hz, 2H), 2.16 (s, 3H), 1.06 (t, *J* = 7.4 Hz, 3H), 0.86 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 149.7, 149.1, 143.7, 142.0, 140.3, 140.2, 139.2, 138.0, 137.7, 136.8, 136.2, 134.2, 134.0, 129.6, 129.4, 129.1, 126.9, 126.8, 126.7, 126.5, 123.8, 123.1, 122.6, 119.4, 65.5, 23.1, 22.9, 21.5, 21.1, 15.8, 15.7; IR (KBr) ν_{max} 3060, 3043, 3016, 2977, 2959, 2929, 2869, 1515, 1476, 1449, 1428, 1371, 1281, 1239, 1111, 1060, 1021, 863, 824, 755, 749, 734 cm^{-1}; HRMS (*m/z*) for $C_{43}H_{37}$ (M + H) calcd: 553.28898, found: 553.28902; R_f(20/1 hexanes/EtOAc) = 0.50 (silica gel plate).



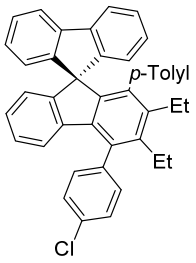
4-([1,1'-Biphenyl]-4-yl)-2,3-diethyl-1-(*p*-tolyl)-9,9'-spirobifluorene (4c). With **3c** (72 mg, 0.15 mmol) following the general procedure E. Column chromatography of the residue on silica gel (20/1 hexanes/EtOAc) provided 58 mg (63%) of the title compound as a colorless solid: mp (decomp) >270 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.86 (m, 2H), 7.83 (m, 2H), 7.60 (m, 2H), 7.54 (t, *J* = 7.5 Hz, 2H), 7.42 (m, 2H), 7.30 (d, *J* = 7.6 Hz, 2H), 7.19 (dt, *J* = 7.4, 1.0 Hz, 2H), 7.05 (dt, *J* = 7.4, 1.0 Hz, 2H), 6.87 (dt, *J* = 7., 1.4 Hz, 1H), 6.84 (dt, *J* = 7.4, 1.4 Hz, 1H), 6.81 (d, *J* = 7.4 Hz, 2H), 6.40 (m, 1H), 6.38 (d, *J* = 7.6 Hz, 2H), 6.22 (m, 1H), 5.96 (d, *J* = 7.9 Hz, 2H), 2.62 (q, *J* = 7.4 Hz, 2H), 2.32 (q, *J* = 7.4 Hz, 2H), 2.18 (s, 3H), 1.09 (t, *J* = 7.4 Hz, 3H), 0.88 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 149.7, 149.1, 143.8, 142.0, 141.8, 140.8, 140.5, 140.1, 139.9, 139.8, 139.5, 137.9, 135.8, 134.11, 134.10, 130.3, 129.1, 128.9, 127.4, 127.3, 127.1, 126.9, 126.78, 126.77, 126.73, 126.6, 123.8, 123.2, 122.6, 119.4, 65.5, 29.7, 23.1, 23.0, 21.1, 15.9, 15.7; IR (KBr) ν_{max} 3078, 3058, 3043, 3016, 2968, 2929, 2869, 1601, 1518, 1491, 1440, 1386, 1368, 1111, 1060, 1006, 848, 824, 755, 737 cm^{-1}; HRMS (*m/z*) for $C_{48}H_{39}$ (M + H) calcd: 615.30463, found: 615.30474; R_f(20/1 hexanes/EtOAc) = 0.40 (silica gel plate).



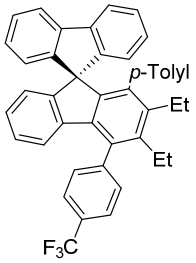
2,3-Diethyl-4-phenyl-1-(*p*-tolyl)-9,9'-spirobifluorene (4d). With **3d** (60 mg, 0.15 mmol) following the general procedure E. Column chromatography of the residue on silica gel (20/1 hexanes/EtOAc) provided 56 mg (73%) of the title compound as a colorless solid: mp (decomp) 238-243 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.60 (m, 2H), 7.54 (m, 3H), 7.30 (d, *J* = 7.6 Hz, 2H), 7.18 (dt, *J* = 7.4, 1.0 Hz, 2H), 7.04 (dt, *J* = 7.4, 1.0 Hz, 2H), 6.86 (dt, *J* = 7.4, 1.3 Hz, 1H), 6.83 (dt, *J* = 7.4, 1.4 Hz, 1H), 6.79 (d, *J* = 7.5 Hz, 2H), 6.39 (m, 1H), 6.37 (d, *J* = 7.6 Hz, 2H), 6.07 (m, 1H), 5.96 (d, *J* = 7.9 Hz, 2H), 2.58 (q, *J* = 7.4 Hz, 2H), 2.31 (q, *J* = 7.4 Hz, 2H), 2.18 (s, 3H), 1.06 (t, *J* = 7.4 Hz, 3H), 0.87 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 149.7, 149.1, 143.7, 142.0, 141.8, 140.9, 140.4, 139.9, 139.4, 137.8, 136.2, 134.13, 134.08, 129.8, 129.1, 128.8, 127.3, 126.9, 126.8, 126.72, 126.70, 126.5, 123.8, 123.2, 122.5, 119.4, 65.5, 23.0, 22.9, 21.1, 15.8, 15.7; IR (KBr) ν_{max} 3052, 3013, 2968, 2926, 2869, 1601, 1488, 1446, 1428, 1350, 1251, 1198, 1183, 1126, 1018, 860, 815, 758, 749, 701 cm^{-1};HRMS (*m/z*) for $C_{42}H_{35}$ (M + H) calcd: 539.27333, found: 539.27337; R_f (20/1 hexanes/EtOAc) = 0.44 (silica gel plate).



4-(4-Chlorophenyl)-2,3-diethyl-1-(*p*-tolyl)-9,9'-spirobifluorene (4e). With **3e** (65 mg, 0.15 mmol) following the general procedure E. Column chromatography of the residue on silica gel (20/1 hexanes/EtOAc) provided 72 mg (82%) of the title compound as a colorless solid: mp (decomp) 247-252 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.58 (m, 2H), 7.48 (m, 2H), 7.29 (d, *J* = 7.6 Hz, 2H), 7.18 (dt, *J* = 7.4, 1.0 Hz, 2H), 7.04 (dt, *J* = 7.4, 1.0 Hz, 2H), 6.92 (dt, *J* = 7.3, 1.1 Hz, 1H), 6.86 (dt, *J* = 7.4, 1.1 Hz, 1H), 6.77 (d, *J* = 7.5 Hz, 2H), 6.41 (d, *J* = 7.4 Hz, 1H), 6.37 (d, *J* = 7.7 Hz, 2H), 6.17 (d, *J* = 7.8 Hz, 1H), 5.94 (d, *J* = 7.9 Hz, 2H), 2.54 (q, *J* = 7.4 Hz, 2H), 2.30 (q, *J* = 7.4 Hz, 2H), 2.18 (s, 3H), 1.04 (t, *J* = 7.4 Hz, 3H), 0.86 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 149.8, 148.9, 143.9, 142.0, 141.5, 140.6, 140.0, 139.8, 139.3, 137.7, 134.7, 134.2, 134.0, 133.3, 131.3, 129.1, 129.0, 126.9, 126.82, 126.80, 126.78, 126.75, 123.8, 123.4, 122.3, 119.4, 65.5, 23.0, 22.9, 21.1, 15.7, 15.6; IR (KBr) ν_{max} 3060, 3040, 3016, 2971, 2965, 2929, 2866, 1598, 1512, 1494, 1476, 1443, 1368, 1281, 1223, 1090, 1060, 1015, 842, 821, 758, 740 cm^{-1}; HRMS (*m/z*) for $C_{42}H_{33}Cl$ (M + H) calcd: 573.23436, found: 573.23444; R_f(20/1 hexanes/EtOAc) = 0.57 (silica gel plate).

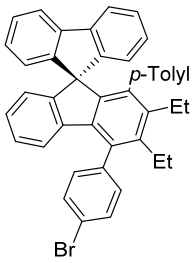


2,3-Diethyl-1-(*p*-tolyl)-4-(4-(trifluoromethyl)phenyl)-9,9'-spirobifluorene (4f). With **3f** (47 mg, 0.1 mmol) following the general procedure E. Column chromatography of the residue on silica gel (20/1 hexanes/EtOAc) provided 55 mg (90%) of the title compound as a colorless solid: mp (decomp) 202-207 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.9 Hz, 2H), 7.68 (d, *J* = 7.9 Hz, 2H), 7.30 (d, *J* = 7.6 Hz, 2H), 7.19 (dt, *J* = 7.5, 1.0 Hz, 2H), 7.05 (dt, *J* = 7.5, 1.0 Hz, 2H), 6.89 (dt, *J* = 7.4, 1.3 Hz, 1H), 6.85 (dt, *J* = 7.4, 1.5 Hz, 1H), 6.79 (d, *J* = 7.5 Hz, 2H), 6.42 (m, 1H), 6.38 (d, *J* = 7.6 Hz, 2H), 6.03 (m, 1H), 5.95 (d, *J* = 7.9 Hz, 2H), 2.53 (q, *J* = 7.4 Hz, 2H), 2.31 (q, *J* = 7.4 Hz, 2H), 2.18 (s, 3H), 1.04 (t, *J* = 7.4 Hz, 3H), 0.87 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 149.8, 148.8, 144.9, 144.1, 142.0, 141.3, 140.7, 140.0, 139.7, 137.4, 134.6, 134.2, 133.9, 126.9-133.1, (q, $^1J_{C\text{-}F}$ = 275.6

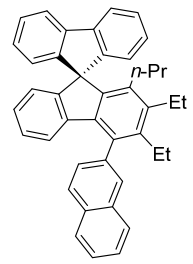


Hz), 130.36, 129.6, (q, $^{2}J_{C\text{-}F}$ = 32.6 Hz), 129.4, 129.0, 128.7, 127.9, 127.6, 127.0, 126.8, 125.7 (q, $^{3}J_{C\text{-}F}$ = 3.5 Hz), 123.8, 123.4, 122.1, 119.4, 65.5, 23.0, 22.9, 21.1, 15.71, 15.65; IR (KBr) ν_{max} 3060, 3037, 3013, 2968, 2932, 2869, 1613, 1512, 1473, 1452, 1374, 1320, 1165, 1129, 1108, 1069, 1021, 851, 758, 743, 728 cm^{-1}; HRMS (*m/z*) for $C_{43}H_{34}F_3$ (M + H) calcd: 607.26071, found: 607.26063; R_f(20/1 hexanes/EtOAc) = 0.46 (silica gel plate).

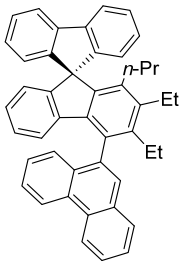
4-(4-Bromophenyl)-2,3-diethyl-1-(*p*-tolyl)-9,9'-spirobifluorene (4h). With **3h** (495 mg, 1.03 mmol) following the general procedure E. Column chromatography of the residue on silica gel (20/1 hexanes/EtOAc) provided 466 mg (74%) of the title compound as a slight yellow solid: mp (decomp) 111-116 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.74 (m, 2H), 7.42 (m, 2H), 7.30 (d, *J* = 7.5 Hz, 2H), 7.19 (dt, *J* = 7.4, 1.1 Hz, 2H), 7.05 (dt, *J* = 7.5, 1.1 Hz, 2H), 6.93 (dt, *J* = 7.4, 1.3 Hz, 1H), 6.86 (dt, *J* = 7.4, 1.2 Hz, 1H), 6.78 (d, *J* = 7.5 Hz, 2H), 6.41 (d, *J* = 7.4 Hz, 1H), 6.38 (d, *J* = 7.7 Hz, 2H), 6.19 (d, *J* = 7.8 Hz, 1H), 5.94 (d, *J* = 7.9 Hz, 2H), 2.55 (q, *J* = 7.4 Hz, 2H), 2.30 (q, *J* = 7.4 Hz, 2H), 2.18 (s, 3H), 1.05 (t, *J* = 7.4 Hz, 3H), 0.86 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 149.7, 148.9, 144.0, 142.0, 141.5, 140.6, 139.9, 139.81, 139.79, 137.6, 134.7, 134.2, 133.9, 132.0, 131.7, 129.0, 126.9, 126.84, 126.80, 126.78, 126.76, 123.8, 123.4, 122.3, 121.4, 119.40, 65.47, 23.0, 22.9, 21.1, 15.74, 15.65; IR (KBr) ν_{max} 3066, 3013, 2959, 2926, 2866, 1512, 1491, 1449, 1425, 1371, 1156, 1111, 1069, 1003, 839, 824, 758, 752, 737, 522 cm^{-1}; HRMS (*m/z*) for $C_{42}H_{34}Br$ (M + H) calcd: 617.18384, found: 617.18402; R_f(20/1 hexanes/EtOAc) = 0.53 (silica gel plate).



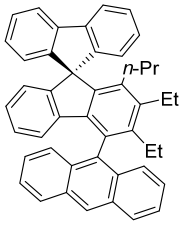
2,3-Diethyl-4-(naphthalen-2-yl)-1-propyl-9,9'-spirobifluorene (11a). With **10a** (84 mg, 0.21 mmol) following the general procedure E. Column chromatography of the residue on silica gel (20/1 hexanes/EtOAc) provided 64 mg (57%) of the title compound as a colorless solid: mp (decomp) 154-159 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.4 Hz, 1H), 8.02 (m, 1H), 7.98 (s, 1H), 7.93 (m, 1H), 7.88 (d, *J* = 7.6 Hz, 2H), 7.58-7.63 (m, 3H), 7.39 (dt, *J* = 7.5, 0.8 Hz, 2H), 7.16 (m, 2H), 6.90 (t, *J* = 7.6 Hz, 2H), 6.79 (dt, *J* = 7.4, 1.1 Hz, 1H), 6.70 (dt, *J* = 7.8, 1.2 Hz, 1H), 6.39 (d, *J* = 7.5 Hz, 1H), 5.98 (d, *J* = 7.7 Hz, 1H), 2.64 (q, *J* = 7.4 Hz, 2H), 2.60 (m, 1H), 2.52 (m, 1H), 1.81 (m, 2H), 1.15 (t, *J* = 7.4 Hz, 3H), 1.02 (t, *J* = 7.4 Hz, 3H), 0.69 (m, 2H), 0.35 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.8, 149.6, 143.2, 141.72, 141.69, 141.65, 140.8, 140.6, 138.5, 138.4, 137.8, 134.8, 133.7, 132.6, 128.6, 128.4, 128.3, 128.2, 127.9, 127.7, 127.4, 126.7, 126.4, 126.1, 125.9, 124.3, 124.2, 122.8, 122.5, 120.0, 66.0, 31.1, 23.7, 22.9, 21.7, 16.1, 15.9, 14.8; IR (KBr) ν_{max} 3055, 3019, 2974, 2959, 2950, 2929, 2869, 1604, 1506, 1470, 1446, 1392, 1374, 1281, 905, 860, 833, 806, 755, 746 cm^{-1}; HRMS (*m/z*) for $C_{42}H_{37}$ (M + H) calcd: 541.28898, found: 541.28907; R_f(20/1 hexanes/EtOAc) = 0.46 (silica gel plate).



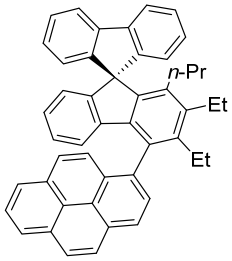
2,3-Diethyl-4-(phenanthren-9-yl)-1-propyl-9,9'-spirobifluorene (11b). With **10b** (65 mg, 0.15 mmol) following the general procedure E. Column chromatography of the residue on silica gel (20/1 hexanes/EtOAc) provided 81 mg (91%) of the title compound as a colorless solid: mp (decomp) >270°C °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.86 (dd, *J* = 8.3, 2.6 Hz, 2H), 7.96 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.91 (s, 1H), 7.88 (dd, *J* = 7.6, 0.7 Hz, 2H), 7.78 (dt, *J* = 7.0, 1.4 Hz, 1H), 7.65-7.72 (m, 3H), 7.51 (m, 1H), 7.39 (ddt, *J* = 7.5, 2.8, 1.1 Hz, 2H), 7.18 (m, 2H), 6.95 (d, *J* = 7.5 Hz, 1H), 6.83 (d, *J* = 7.5 Hz, 1H), 6.70 (dt, *J* = 7.4, 1.1 Hz, 1H), 6.53 (dt, *J* = 7.9, 1.2 Hz, 1H), 6.35 (d, *J* = 7.5 Hz, 1H), 5.97 (d, *J* = 7.8 Hz, 1H), 2.66 (q, *J* = 7.4 Hz, 2H), 2.60 (m, 1H), 2.32 (m, 1H), 1.85 (m, 2H), 1.16 (t, *J* = 7.4 Hz, 3H), 0.93 (t, *J* = 7.4 Hz, 3H), 0.73 (m, 2H), 0.36 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.8, 149.7, 149.5, 143.4, 141.7, 141.6, 141.3, 141.1, 139.1, 138.0, 137.0, 132.4, 132.1, 131.9, 130.6, 130.3, 128.9, 127.9, 127.8, 127.7, 127.5, 127.4, 127.0, 126.78, 126.76, 126.7, 126.6, 126.4, 124.4, 124.0, 122.9, 122.8, 122.7, 122.5, 120.0, 66.1, 31.2, 23.7, 23.2, 21.7, 16.23, 16.18, 14.8; IR (KBr) ν_{max} 3071, 3015, 2965, 2931, 2869, 1599, 1472, 1447, 1426, 1373, 1281, 1154, 1059, 891, 866, 757, 745, 725 cm^{-1}; HRMS (*m/z*) for $C_{46}H_{38}$ (M + H) calcd: 591.30463, found: 591.30468; R_f(20/1 hexanes/EtOAc) = 0.38 (silica gel plate).



4-(Anthracen-9-yl)-2,3-diethyl-1-propyl-9,9'-spirobifluorene (11c). With **10c** (68 mg, 0.15 mmol) following the general procedure E. Column chromatography of the residue on silica gel (20/1 hexanes/EtOAc) provided 45 mg (51%) of the title compound as a light brown solid: mp (decomp) 251-256 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (d, *J* = 8.8 Hz, 2H), 7.88 (d, *J* = 7.6 Hz, 2H), 7.74 (d, *J* = 8.7 Hz, 2H), 7.64 (m, 2H), 7.39-7.44 (m, 4H), 7.28 (m, 1H), 7.19 (dt, *J* = 7.7, 1.2 Hz, 2H), 6.87 (d, *J* = 7.5 Hz, 2H), 6.64 (dt, *J* = 7.4, 1.1 Hz, 1H), 6.40 (dt, *J* = 7.6, 1.2 Hz, 1H), 6.31 (d, *J* = 7.5 Hz, 1H), 5.10 (d, *J* = 7.9 Hz, 1H), 2.66 (q, *J* = 7.4 Hz, 2H), 2.22 (q, *J* = 7.5 Hz, 2H), 1.88 (m, 2H), 1.16 (t, *J* = 7.4 Hz, 3H), 0.78 (m, 2H), 0.64 (t, *J* = 7.5 Hz, 3H), 0.38 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.8, 149.7, 149.5, 143.4, 141.8, 141.6, 141.3, 141.1, 139.2, 138.1, 137.0, 132.4, 132.1, 132.0, 130.6, 130.3, 128.9, 127.9, 127.82, 127.76, 127.51, 127.46, 127.0, 126.81, 126.78, 126.7, 126.6, 126.4, 124.4, 124.0, 122.9, 122.8, 122.7, 122.5, 120.0, 68.1, 31.2, 23.8, 23.2, 21.7, 16.3, 16.2, 14.8; IR (KBr) ν_{max} 3064, 2963, 2871, 1525, 1468, 1446, 1372, 1345, 1262, 1241, 1155, 1055, 1027, 938, 755, 737 cm^{-1}; HRMS (*m/z*) for $C_{46}H_{39}$ (M + H) calcd: 591.30463, found: 591.30469; R_f(20/1 hexanes/EtOAc) = 0.43 (silica gel plate).

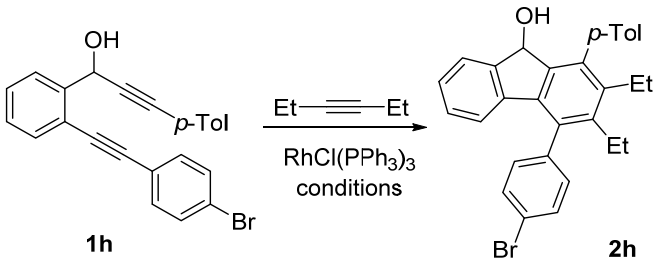


2,3-Diethyl-1-propyl-4-(pyren-2-yl)-9,9'-spirobifluorene (11d). With **10d** (72 mg, 0.15 mmol) following the general procedure E. Column chromatography of the residue on silica gel (20/1 hexanes/EtOAc) provided 54 mg (59%) of the title compound as a colorless solid: mp (decomp) 159-164 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, *J* = 7.8 Hz, 1H), 8.21-8.27 (m, 3H), 8.17 (d, *J* = 6.9 Hz, 1H), 8.13 (d, *J* = 7.8 Hz, 1H), 8.04 (t, *J* = 7.7 Hz, 1H), 7.99 (d, *J* = 9.2 Hz, 1H), 7.89 (d, *J* = 7.5 Hz, 2H), 7.83 (d, *J* = 9.2 Hz, 1H), 7.43 (t, *J* = 7.4 Hz, 1H), 7.21 (t, *J* = 7.5 Hz, 1H), 7.18 (t, *J* = 7.4 Hz, 1H), 6.96 (d,



J = 7.5 Hz, 1H), 6.90 (d, *J* = 7.4 Hz, 1H), 6.66 (t, *J* = 7.4 Hz, 1H), 6.39 (t, *J* = 7.8 Hz, 1H), 6.34 (d, *J* = 7.5 Hz, 1H), 5.32 (d, *J* = 7.7 Hz, 1H), 2.68 (q, *J* = 7.4 Hz, 2H), 2.51 (m, 1H), 2.36 (m, 1H), 1.87 (m, 2H), 1.19 (t, *J* = 7.4 Hz, 3H), 0.85 (t, *J* = 7.4 Hz, 3H), 0.78 (m, 2H), 0.38 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.7, 149.6, 149.5, 143.4, 141.8, 141.7, 141.6, 141.4, 141.1, 139.3, 138.1, 136.2, 133.0, 131.4, 131.3, 130.8, 129.9, 128.2, 127.83, 127.82, 127.76, 127.71, 127.65, 127.50, 127.46, 127.37, 126.7, 126.4, 126.0, 125.4, 125.2, 125.11, 125.07, 125.0, 124.4, 124.1, 122.7, 122.2, 120.03, 120.00, 66.1, 31.2, 23.7, 23.2, 21.8, 16.3, 15.7, 14.8; IR (KBr) ν_{max} 3039, 2963, 2929, 2870, 1601, 1584, 1470, 1446, 1424, 1374, 1282, 1242, 1177, 1154, 1056, 848, 820, 756, 740, 726 cm^{-1}; HRMS (*m/z*) for $C_{48}H_{39}$ (M + H) calcd: 615.30463, found: 615.30465; R_f(20/1 hexanes/EtOAc) = 0.37 (silica gel plate).

IV Optimization of cyclotrimerization of 1h with 3-hexyne to 2h



SI-Table 1. Variation of the catalyst load.

Entry	Solvent	cat. (mol%)	T (°C)	t (h)	Additive	rec. **1h** (%)	**2h** (%)
1	toluene	5	90	16			30
2	toluene	5	90	16	Ag_2CO_3		32
3	DMF	5	90	16			8
4	DMF	5	90	16	Ag_2CO_3		15
5	toluene	4	90	16			29
6	toluene	4	90	16	Ag_2CO_3		36
7	toluene	3	90	16		7	25
8	toluene	3	90	16	Ag_2CO_3	11	28
9	toluene	2	90	16		28	15
10	toluene	2	90	16	Ag_2CO_3	41	14
11	toluene	2	90	96		14	19
12	toluene	2	90	96	Ag_2CO_3	7.5	21
13	toluene	1	90	96		23	16
14	toluene	1	90	96	Ag_2CO_3	20	18

SI-Table 2. Variation of additives.

Entry	Solvent	cat. (mol%)	T (°C)	t (h)	Additive	rec. **1h** (%)	**2h** (%)
1	toluene	4	90	16	$AgSbF_6$		9
2	toluene	4	90	16	$AgNO_3$		37
3	toluene	4	90	16	$AgOOCCF_3$	13	21
4	toluene	4	90	16	AgOTf		0
5	toluene	4	90	16	Ag_3PO_4	16	21
6	toluene	4	90	16	$AgBF_4$		6
7	toluene	4	90	16	$AgOOCCH_3$		19
8	toluene	4	90	16	$AgClO_4$	31	7
9	toluene	4	90	16	Ag_2SO_4		31

SI-Table 3. Variation of solvent.

Entry	Solvent	cat. (mol%)	T (°C)	t (h)	Additive	rec. **1h** (%)	**2h** (%)
1	DCM	4	90	16	Ag_2CO_3	5	30
2	Et_2O	4	90	16	Ag_2CO_3	10	32
3	THF	4	90	16	Ag_2CO_3		41

SI-Table 4. Cyclotrimerization in THF in the presence of different additives.

Entry	Solvent	cat. (mol%)	T (°C)	t (h)	Additive	rec. **1h** (%)	**2h** (%)
1	THF	4	90	16	-		48
2	THF	4	90	16	$AgNO_3$	38	29
2	THF	4	90	16	AgOTf		21
4	THF	4	90	16	$AgOOCCF_3$	93	5

SI-Table 5. Effect of temperature.

Entry	Solvent	cat. (mol%)	T (°C)	t (h)[a]	Additive	rec. **1h** (%)[b]	**2h** (%)[b]
1	THF	4	50	16	Ag_2CO_3	67	15
2	THF	4	50	16	-	81	11
3	THF	4	70	16	Ag_2CO_3	29	26
4	THF	4	70	16	-	31	29
5	THF	4	80	16	Ag_2CO_3		42
6	THF	4	80	16	-		41
7	THF	4	110	16	Ag_2CO_3		35
8	THF	4	110	16	-		33
9	THF	4	150	1, MW	Ag_2CO_3	10	37
10	THF	4	150	1, MW	-	13	34
11	THF	4	150	1.5, MW	Ag_2CO_3		41
12	THF	4	150	1.5, MW	-		29
13	THF	4	180	1, MW	Ag_2CO_3		51
14	THF	4	180	1, MW	-	6	40
15	THF	4	180	2, MW	Ag_2CO_3		32
16	THF	4	180	1, MW	AgOTf		3
17	THF	4	180	1, MW	$AgSbF_6$		4
18	THF	4	180	1, MW	$AgNO_3$		32
19	THF	4	180	1, MW	Ag_2SO_4		6

[a] MW = microwave heating. [b] Isolated yields

SI-Table 6. Variation of the catalyst load and temperature.

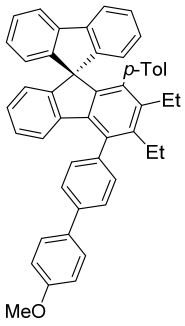
Entry	Solvent	cat. (mol%)	T (°C)	t (h)[a]	Additive	rec. **1h** (%)[b]	**2h** (%)[b]
1	THF	10	180	1, MW	Ag_2CO_3		47
2	THF	5	180	1, MW	Ag_2CO_3		43
3	THF	3	180	1, MW	Ag_2CO_3		49
4	THF	3	180	1.5, MW	Ag_2CO_3		57
5	THF	2	180	1, MW	Ag_2CO_3		32
6	THF	4	170	1, MW	Ag_2CO_3		51
7	THF	3	170	1, MW	Ag_2CO_3		37
8	THF	2	170	1, MW	Ag_2CO_3		27
9	THF	4	190	1, MW	Ag_2CO_3		43
10	THF	3	190	1, MW	Ag_2CO_3		40

[a] MW = microwave heating. [b] Isolated yields

V Synthesis compounds 6, 7, and 12

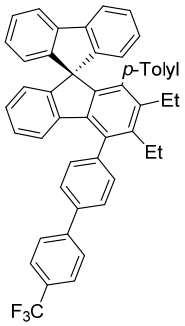
F: General procedure for Suzuki reaction (preparation of 6). Starting compound **4h** (0.1 mmol), boronic acid compound (0.12 mmol), $Pd(OAc)_2$ (1.3 mg, 5 mol%) and K_2CO_3 (17 mg, 0.12 mmol) were dissolved in a microwave vial ethanol (5 mL) and the reaction was stirred 3 h at 80 °C. The reaction mixture was cooled down, quenched with water and extracted with diethyl ether. The organic fraction was dried over Mg_2SO_4, filtered off and concentrated on vacuum evaporator. Column chromatography of the residue on silica gel (hexanes/EtOAc) provided products.

2,3-Diethyl-4-(4'-methoxy-[1,1'-biphenyl]-4-yl)-1-(*p*-tolyl)-9,9'-spirobifluorene (6a). With



4h (61 mg, 0.1 mmol) and 4-methoxyphenylboronic acid following the general procedure F. Column chromatography of the residue on silica gel (20/1 hexanes/EtOAc) provided 40 mg (62%) of the title compound as a colorless solid: mp (decomp) 138-143 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.1 Hz, 2H), 7.76 (d, *J* = 8.7 Hz, 2H), 7.58 (d, *J* = 8.1 Hz, 2H), 7.31 (d, *J* = 7.6 Hz, 2H), 7.20 (dt, *J* = 7.3, 0.7 Hz, 2H), 7.08 (d, *J* = 8.8 Hz, 2H), 7.06 (dt, *J* = 7.4, 0.8 Hz, 2H), 6.88 (dt, *J* = 7.3, 1.3 Hz, 1H), 6.82-6.85 (m, 3H), 6.39-6-43 (m, 3H), 6.25 (dd, *J* = 6.9, 1.1 Hz, 1H), 5.97 (d, *J* = 7.9 Hz, 2H), 3.92 (s, 3H), 2.63 (q, *J* = 7.4 Hz, 2H), 2.33 (q, *J* = 7.4 Hz, 2H), 2.19 (s, 3H), 1.10 (t, *J* = 7.4 Hz, 3H), 0.89 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3, 149.7, 149.1, 143.8, 142.0, 141.9, 140.5, 140.2, 139.5, 139.4, 139.3, 137.9, 135.9, 134.2, 134.1, 133.4, 130.2, 129.1, 128.1, 127.0, 126.9, 126.81, 126.76, 126.6, 123.9, 123.3, 122.6, 119.4, 114.4, 65.6, 55.5, 23.1, 23.0, 21.1, 15.9, 15.7; IR (KBr) ν_{max} 3069, 3037, 3013, 2953, 2836, 1604, 1500, 1470, 1437, 1278, 1251, 1086, 1039, 1009, 827, 809, 743 cm^{-1}; HRMS (*m/z*) for $C_{49}H_{41}O$ (M + H) calcd: 645.31519, found: 645.31521; R_f(20/1 hexanes/EtOAc) = 0.30 (silica gel plate).

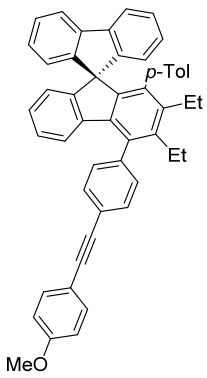
2,3-Diethyl-1-(*p*-tolyl)-4-(4'-(trifluoromethyl)-[1,1'-biphenyl]-4-yl)-9,9'-spirobifluorene



(6b). With **4h** (61 mg, 0.1 mmol) following the general procedure F. Column chromatography of the residue on silica gel (20/1 hexanes/DCM) provided 39 mg (58%) of the title compound as a colorless solid: mp (decomp) 157-162 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, J = 8.1 Hz, 2H), 7.87 (d, J = 8.2 Hz, 2H), 7.79 (d, J = 8.3 Hz, 2H), 7.65 (d, J = 8.2 Hz, 2H), 7.30 (d, J = 7.6 Hz, 2H), 7.19 (dt, J = 7.4, 0.9 Hz, 2H), 7.06 (dt, J = 7.5, 1.0 Hz, 2H), 6.87 (dt, J = 7.3, 1.6 Hz, 1H), 6.84 (dt, J = 7.4, 1.4 Hz, 1H), 6.80 (d, J = 7.6 Hz, 2H), 6.43 (m, 1H), 6.38 (d, J = 7.8 Hz, 2H), 6.22 (m, 1H), 5.96 (d, J = 7.9 Hz, 2H), 2.61 (q, J = 7.4 Hz, 2H), 2.33 (q, J = 7.4 Hz, 2H), 2.18 (s, 3H), 1.09 (t, J = 7.4 Hz, 3H), 0.88 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.8, 149.0, 144.3, 143.9, 142.0, 141.7, 141.0, 140.6, 140.0, 139.7, 138.4, 137.7, 135.4, 134.2, 134.0, 130.6, 129.8, 129.1, 127.5, 127.4, 126.8 (q, $^2J_{C\text{-}F}$ = 16.8 Hz), 125.8, (q, $^3J_{C\text{-}F}$ = 3.6 Hz), 123.2-126.5 , (q, $^1J_{C\text{-}F}$ = 160.1 Hz) 123.8, 123.3, 122.4, 119.4, 65.5, 23.1, 23.0, 21.1, 15.9, 15.7; IR (KBr) ν_{max} 3063, 3037, 3019, 2965, 2929, 2872, 1622, 1515, 1470, 1446, 1371, 1326, 1165, 1129, 1069, 1006, 836, 824,

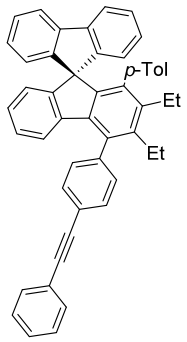
758, 746, 737 cm^{-1}; HRMS (*m/z*) for $C_{49}H_{38}F_3$ (M + H) calcd: 683.29201, found: 683.29207; R_f(20/1 hexanes/EtOAc) = 0.52 (silica gel plate).

2,3-Diethyl-4-(4-((4-methoxyphenyl)ethynyl)phenyl)-1-(*p*-tolyl)-9,9'-spirobifluorene (7a).

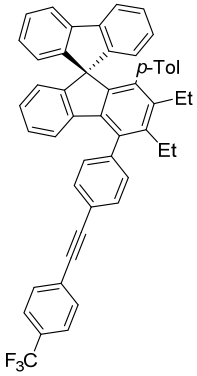


Starting compound **4h** (61 mg, 0.1 mmol), $PdCl_2(PPh_3)_2$ catalyst (8.5 mg, 5 mol%) and CuI (0.01 mmol, 10 mol%) were dissolved in a microwave vial in diisopropylamine (5 mL), afterwards 4-ethynylanisole (29 µL, 0.2 mmol) was added and the reaction was stirred at 180 °C in the microwave reactor for1 h. The reaction mixture was cooled down, filtered off with celite/silica and washed with diethyl ether. The organic fraction was concentrated on vacuum evaporator. Column chromatography of the residue on silica gel (20/1 hexanes/EtOAc) provided 36 mg (54%) of the title compound as a colorless solid: mp (decomp) 131-136 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.1 Hz, 2H), 7.56 (d, *J* = 8.7 Hz, 2H), 7.52 (d, *J* = 8.1 Hz, 2H), 7.30 (d, *J* = 7.5 Hz, 2H), 7.19 (dt, *J* = 7.4, 0.6 Hz, 2H), 7.05 (dt, *J* = 7.5, 0.6 Hz, 2H), 6.93 (d, *J* = 8.7 Hz, 2H), 6.91 (dt, *J* = 7.5, 0.9 Hz, 1H), 6.85 (dt, *J* = 7.4, 0.9 Hz, 1H), 6.79 (d, *J* = 7.5 Hz, 2H), 6.41 (d, *J* = 7.6 Hz, 1H), 6.37 (d, *J* = 7.8 Hz, 2H), 6.24 (d, *J* = 7.7 Hz, 1H), 5.95 (d, *J* = 7.9 Hz, 2H), 3.87 (s, 3H), 2.58 (q, *J* = 7.4 Hz, 2H), 2.31 (q, *J* = 7.4 Hz, 2H), 2.18 (s, 3H), 1.05 (t, *J* = 7.4 Hz, 3H), 0.87 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.7, 149.7, 149.0, 143.9, 142.0, 141.6, 140.8, 140.5, 139.9, 139.7, 137.6, 135.5, 134.2, 134.1, 133.1, 131.9, 130.0, 129.1, 127.0, 126.9, 126.81, 126.78, 126.7, 123.8, 123.3, 122.6, 122.5, 119.4, 115.4, 114.1, 89.8, 88.2, 65.5, 55.4, 23.1, 22.9, 21.1, 15.8, 15.7; IR (KBr) ν_{max} 3040, 2971, 2872, 2836, 2211, 1604, 1565, 1518, 1446, 1371, 1287, 1251, 1171, 1105, 1030, 839, 755, 743 cm^{-1}; HRMS (*m/z*) for $C_{51}H_{41}O$ (M + H) calcd: 669.31519, found: 669.31522; R_f (20/1 hexanes/EtOAc) = 0.25 (silica gel plate).

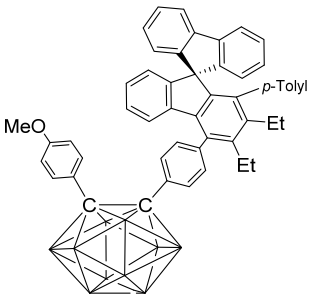
2,3-Diethyl-4-(4-(phenylethynyl)phenyl)-1-(*p*-tolyl)-9,9'-spirobifluorene (7b). Starting compound **4h** (122 mg, 0.25 mmol), PEPPSI-IPr catalyst (8.5 mg, 5 mol%) and CuI (0.01 mmol, 10 mol%) were dissolved in a microwave vial in triethylamine (2 mL) and THF (3 mL), afterwards phenylacetylene (55 µL, 0.5 mmol) was added and the reaction was stirred 3 h at 80 °C. The reaction mixture was cooled down, filtered off with celite/silica and washed with diethyl ether. The organic fraction was concentrated on vacuum evaporator. Column chromatography of the residue on silica gel (20/1 hexanes/EtOAc) provided 116 mg (72%) of the title compound as a colorless solid: mp (decomp) 167-172 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (m, 2H), 7.62 (m, 2H), 7.53 (m, 2H), 7.35-7.43 (m, 3H), 7.29 (d, *J* = 7.6 Hz, 2H), 7.18 (dt, *J* = 7.4, 1.0 Hz, 2H), 7.04 (dt, *J* = 7.4, 1.0 Hz, 2H), 6.91 (dt, *J* = 7.3, 1.1 Hz, 1H), 6.86 (dt, *J* = 7.4, 1.1 Hz, 1H), 6.79 (d, *J* = 7.5 Hz, 2H), 6.40 (d, *J* = 7.5 Hz, 1H), 6.37 (d, *J* = 7.6 Hz, 2H), 6.22 (d, *J* = 7.9 Hz, 1H), 5.94 (d, *J* = 7.9 Hz, 2H), 2.56 (q, *J* = 7.4 Hz, 2H), 2.30 (q, *J* = 7.4 Hz, 2H), 2.17 (s, 3H), 1.05 (t, *J* = 7.4 Hz, 3H), 0.86 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.7, 149.0, 143.9, 142.0, 141.6, 141.2, 140.5, 139.9, 139.7, 137.6, 135.4, 134.2, 134.0, 132.5, 132.1, 131.7, 130.0, 129.2, 129.0, 128.43, 128.36, 126.94, 126.86, 126.80, 126.77, 126.7,



123.8, 123.31, 123.27, 122.5, 122.2, 119.4, 89.8, 89.5, 29.7, 23.0, 22.9, 21.1, 15.8, 15.7; IR (KBr) ν_{max} 3060, 2969, 2931, 2870, 2251, 2230, 1596, 1515, 1487, 1446, 1373, 1281, 1238, 1179, 1158, 1068, 1019, 913, 848, 823, 755, 742, 689 cm^{-1}; HRMS (*m/z*) for $C_{50}H_{38}Na$ (M + Na) calcd: 661.28657, found: 661.28601; R_f(20/1 hexanes/EtOAc) = 0.46 (silica gel plate).

2,3-Diethyl-1-(*p*-tolyl)-4-(4-((4-(trifluoromethyl)phenyl)ethynyl)phenyl)-9,9'-spirobifluorene (7c). 

Starting compound **4h** (61 mg, 0.1 mmol), $PdCl_2(PPh_3)_2$ (3.5 mg, 5 mol%) and CuI (0.01 mmol, 10 mol%) were dissolved in a microwave vial in DMF (3 mL) and NEt_3 (2 mL), afterwards 1-ethynyl-trifluortoluene (65 µL, 0.15 mmol) was added and the reaction was stirred over night at 80 °C. The reaction mixture was cooled down, filtered off with celite/silica and washed with diethyl ether. The organic fraction was concentrated on vacuum evaporator. Column chromatography of the residue on silica gel (10/1 hexanes/DCM) provided 40 mg (57%) of the title compound as a light brown solid: mp (decomp) 151-156 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.3 Hz, 2H), 7.72 (d, *J* = 8.1 Hz, 2H), 7.66 (d, *J* = 8.2 Hz, 2H), 7.56 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 7.4 Hz, 2H), 7.19 (dt, *J* = 7.4, 1.1 Hz, 2H), 7.05 (dt, *J* = 7.5, 1.1 Hz, 2H), 6.91 (dt, *J* = 7.4, 1.3 Hz, 1H), 6.86 (dt, *J* = 7.4, 1.3 Hz, 1H), 6.79 (d, *J* = 7.4 Hz, 2H), 6.41 (m, 1H), 6.38 (d, *J* = 7.7 Hz, 2H), 6.21 (m, 1H), 5.95 (d, *J* = 7.9 Hz, 2H), 2.56 (q, *J* = 7.4 Hz, 2H), 2.31 (q, *J* = 7.4 Hz, 2H), 2.18 (s, 3H), 1.06 (t, *J* = 7.4 Hz, 3H), 0.87 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.8, 148.9, 144.0, 142.0, 141.8, 141.5, 140.6, 139.81, 139.78, 137.5, 135.3, 134.2, 134.0, 132.2, 131.9, 130.1, 129.0, 127.0 (q, $^2J_{C\text{-}F}$ = 32.6 Hz), 126.8, 125.3 (q, $^3J_{C\text{-}F}$ = 3.6 Hz), 123.8, 123.4, 122.4, 121.5, 121.3-126.8, (q, $^1J_{C\text{-}F}$ = 272.1 Hz), 119.4, 91.9, 88.4, 65.5, 23.0, 22.9, 21.1, 15.74, 15.66; IR (KBr) ν_{max} 3069, 3037, 2968, 2932, 2875, 2220, 1610, 1518, 1476, 1449, 1374, 1323, 1171, 1132, 1108, 1069, 1015, 845, 824, 758, 743 cm^{-1}; HRMS (*m/z*) for $C_{51}H_{38}F_3$ (M + H) calcd: 707.29201, found: 707.29211; R_f(20/1 hexanes/EtOAc) = 0.51 (silica gel plate).

1-[2,3-Diethyl-4-phenyl)-1-(*p*-tolyl)-9,9'-spirobifluorenyl]-2-(4-methoxyphenyl)-1,2-dicarba-*closo*-dicarborane (12). 

Starting compound **7a** (67 mg, 0.1 mmol and 6,9-$(Me_2S)_2B_{10}H_{12}$ (70 mg, 0.15 mmol) were dissolved in a microwave vial under argon atmosphere in toluene (5 mL) and the reaction was stirred at 120 °C for 16 h. The reaction mixture was cooled down, quenched with MeOH and concentrated on vacuum evaporator. Column chromatography of the residue on silica gel (2/1 hexanes/EtOAc) provided 47 mg (60%) of the title compound as a colorless solid: mp (decomp) 149-154 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.5 Hz, 2H), 7.53 (m, 2H), 7.35 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 7.4 Hz, 2H), 7.18 (dt, *J* = 7.4, 1.0 Hz, 2H), 7.02 (dt, *J* = 7.5, 1.1 Hz, 2H), 6.82 (dt, *J* = 7.5, 1.0 Hz, 1H), 6.76 (d, *J* = 9.0 Hz, 2H), 6.72 (d, *J* = 7.5 Hz, 2H), 6.66 (dt, *J* = 7.9, 1.2 Hz, 1H), 6.36-6-39 (m, 3H), 5.91 (d, *J* = 8.0 Hz, 2H), 5.69 (d, *J* = 7.8 Hz, 1H), 3.74 (s, 3H), 2.35 (q, *J* = 7.4 Hz, 2H), 2.26 (q, *J* = 7.4 Hz, 2H), 2.17 (s, 3H), 0.90 (t, *J* = 7.4 Hz, 3H), 0.83 (t, *J* = 7.4 Hz, 3H); additional: ^{1}H-^{11}B NMR (400 MHz, $CDCl_3$) 3.41 (bs, 2H), 2.70 (bs, 2H), 2.61 (bs,

4H), 2.41 (bs, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.9, 149.8, 148.8, 143.9, 143.1, 142.0, 141.2, 140.6, 139.9, 139.7, 137.1, 134.3, 134.2, 133.8, 132.3, 131.2, 130.0, 129.9, 128.9, 126.9, 126.8, 126.7, 126.6, 123.7, 123.4, 123.2, 122.0, 119.4, 113.6, 86.1, 85.6, 65.4, 55.2, 23.0, 22.7, 21.1, 15.60. 15.58; IR (KBr) ν_{max} 3219, 3063, 2966, 2932, 2870, 2592, 1607, 1514, 1462, 1447, 1374, 1301, 1260, 1184, 1075, 1032, 836, 824, 756, 744, 730 cm^{-1}; HRMS (*m/z*) for $C_{51}H_{50}OB_{10}Na$ (M + Na) calcd: 811.46844, found: 811.46871, for $C_{51}H_{50}O^{10}BB_9Na$ (M + Na) calcd: 810.47207, found: 810.47278, for $C_{51}H_{50}O^{10}B_2B_8Na$ (M + Na) calcd: 809.47571, found: 809.47651, for $C_{51}H_{50}O^{10}B_3B_7Na$ (M + Na) calcd: 808.47934, found: 808.48029; R_f (20/1 hexanes/EtOAc) = 0.27 (silica gel plate).

VI X-ray data

Crystallographic data for **4a**, **4c**, **4e**, **6a**, **7b**, **11b**, and **12** were collected on Nonius KappaCCD diffractometer equipped with Bruker APEX-II CCD detector by monochromatized MoKα radiation (λ = 0.71073 Å) at a temperature either 120 K or 150(2) K. The structures were solved by direct methods (SHELXS)[11] and refined by full matrix least squares based on F^2 (SHELXL97).11 The absorption corrections were carried on using multi-scan method. The hydrogen atoms were found on difference Fourier map and were recalculated into idealized positions. All hydrogen atoms were refined as fixed (riding model) with assigned temperature factors $H_{iso}(H) = 1.2\ U_{eq}$(pivot atom) or 1.5 U_{eq} for methyl moiety. The crystallographic data are summarized in Table SI-1.

[11] Sheldrick, G.M. *Acta Cryst*. **2008**, *A64*, 112-122.

Table S1. X-Ray crystallographic data for 9,9'-spirobifluorenes **4**.

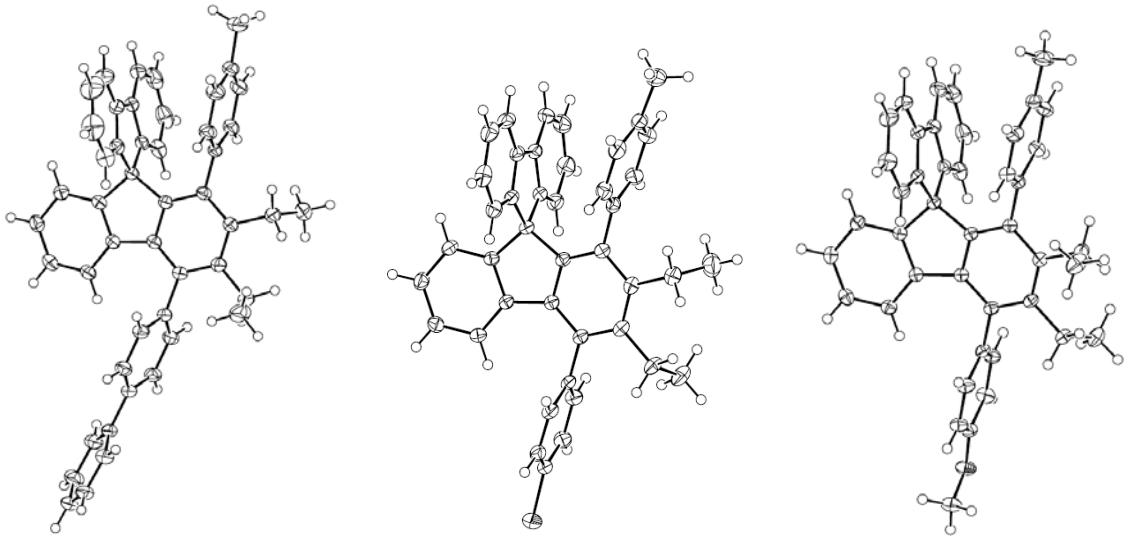
	4a (RK-174)	**4c** (RK-173)	**4e** (RK-175)
Formula	$C_{43}H_{36}O$	$C_{48}H_{38}$	$C_{42}H_{33}Cl$
M.w.	568.72	614.78	573.13
Crystal system	monoclinic	triclinic	monoclinic
Space group [No.]	$P2_1/n$ (No14)	$P1$ (No. 2)	$P2_1/n$ (No 14)
a [Å]	9.4308 (2)	8.3330 (2)	35.6573 (8)
b [Å]	17.6455 (3)	11.6908 (3)	9.6469 (2)
c [Å]	18.5101 (3)	18.3693 (4)	22.6588 (4)
a [°]		88.570 (1)	
β [°]	92.764 (1)	86.248 (1)	128.8580 (5)
γ [°]		72.826 (1)	
Z	4	2	8
V *[Å^3]*	3076.70 (10)	1706.04 (7)	6069.4 (2)
D_x [g cm^{-3}]	1.228	1.197	1.254
Crystal size [mm]	0.22×0.58×0.60	0.14×0.39×0.65	0.57×0.56×0.41
Crystal color, shape	a colorless prism	a colorless prism	a colorless prism
μ [mm^{-1}]	0.071	0.067	0.156
T_{min}, T_{max}	0.89, 0.98	0.93, 0.99	0.83, 0.94
Measured reflections	21163	18051	16117
Independent diffractions (R_{int} [a])	7059 (0.019)	7428 (0.024)	6626 (0.018)
Observed diffract. [I>2σ(I)]	5820	5525	5486
No. of parameters	401	436	391
R^b	0.041	0.0471	0.042
$wR(F^2)$ for all data	0.118	0.1366	0.111
GOF[c]	1.00	1.06	0.97
Residual electron density [e/Å^3]	0.28, -0.25	0.25, -0.22	0.61, -0.30
CCDC no.	1542107	1542108	1542109

[a] $R_{int} = \Sigma \left| F_o^2 - F_{o,mean}^2 \right| / \Sigma F_o^2$ [b] $R(F) = \Sigma \left| \left| F_o \right| - \left| F_c \right| \right| / \Sigma \left| F_o \right|$, $wR(F^2) = [\Sigma(w(F_o^2 - F_c^2)^2)/(\Sigma w(F_o^2)^2)]^{½}$. [c] GOF = $[\Sigma(w(F_o^2 - F_c^2)^2)/(N_{diffrs} - N_{params})]^{½}$

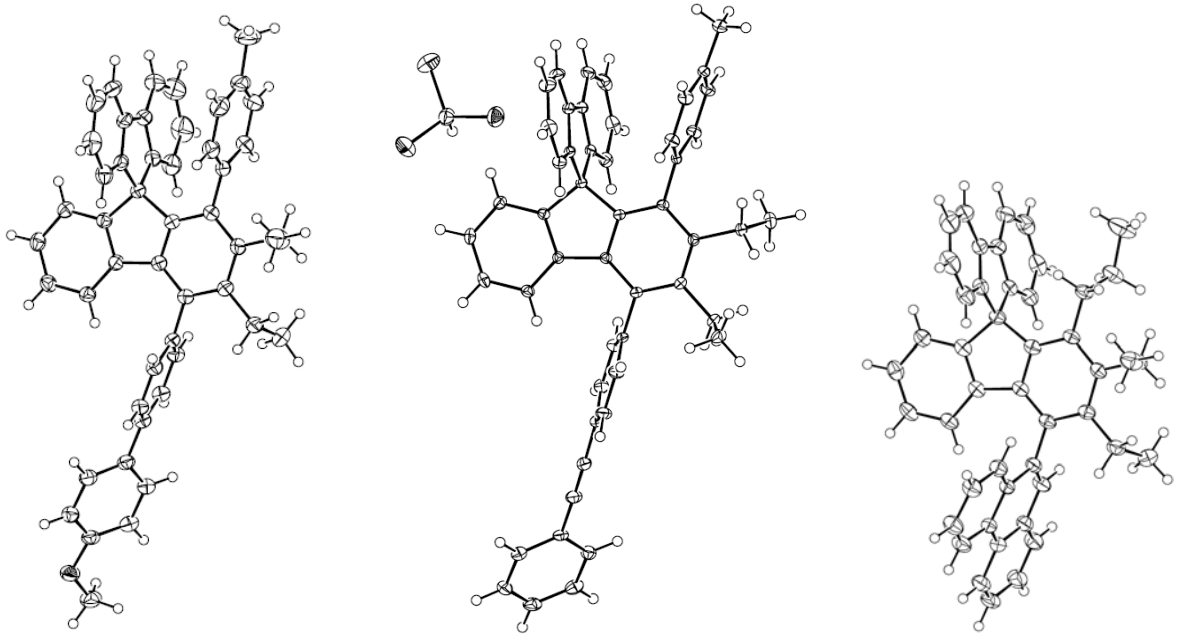
Table S2. X-Ray crystallographic data for 9,9'-spirobifluorenes **6a**, **7b**, **11b**, and **12**, .

	6a (RK-356)	**7b** (RK-308))	**11b** (RK-384)	**12** (RK-414)
Formula	$C_{49}H_{40}O$	$C_{50}H_{38}$, $CHCl_3$	$C_{46}H_{38}$	$C_{51}H_{50}B_{10}O$
M.w.	644.81	758.17	590.76	787.01
Crystal system	triclinic	triclinic	monoclinic	monoclinic
Space group [No.]	*P*1 (No 2)	*P*1 (No 2)	*P1* (21/c1)	*P*21/c
a [Å]	8.8276 (3)	9.9228(4)	16.8419(5)	16.9235(4)
b [Å]	11.6527 (3)	12.9083(6)	8.6097(2)	9.1410(2)
c [Å]	18.1740 (5)	16.2089(7)	23.3066(6)	28.7305(7)
a [°]	91.5340(10)	75.028(2)		
β [°]	90.2770(10)	85.120(2)	98.9400(10)	100.7280(10)
γ [°]	107.9720(10)	71.846(2)		
Z	2	2	4	4
V *[Å^3]*	1777.45(9)	1905.80(15)	3338.49(15)	4366.86(18)
D_x [g cm^{-3}]	1.205	1.321	1.175	1.197
Crystal size [mm]	0.24×0.16×0.15	0.15×0.17×0.27	0.22×0.13×0.04	0.35×0.20×0.12
Crystal color, shape	a colorless prism	a colorless prism	a colorless bar	a colorless plate
μ [mm^{-1}]	0.533	0.278	0.498	0.489
T_{min}, T_{max}	0.86, 0.96	0.93, 0.96	0.82, 0.98	0.85, 0.94
Measured reflections	34479	42155	25788	48496
Independent diffractions (R_{int} [a])	6986 (0.029)	8754 (0.067)	6307 (0.051)	8591 (0.034)
Observed diffract. [I>2σ(I)]	5694	7212	5047	7272
No. of parameters	455	490	418	603
R[b]	0.043	0.042	0.057	0.045
$wR(F^2)$ for all data	0.110	0.124	0.137	0.121
GOF[c]	1.04	1.05	1.057	1.03
Residual electron density [e/Å^3]	0.19, -0.21	0.43, -0.68	0.43, -0.27	0.22, -0.24
CCDC no.	1542110	1542111	1542112	1542113

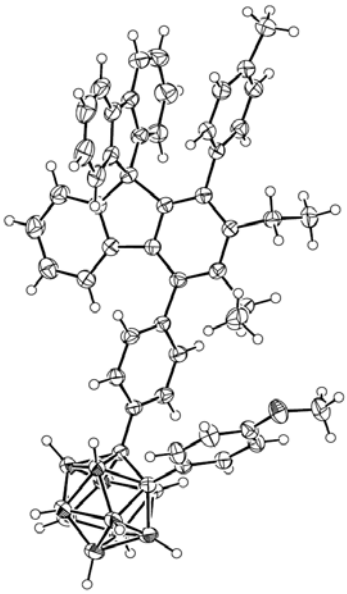
[a] $R_{int} = \Sigma \left| F_o^2 - F_{o,mean}^2 \right| / \Sigma F_o^2$ [b] $R(F) = \Sigma \left| \left| F_o \right| - \left| F_c \right| \right| / \Sigma \left| F_o \right|$, $wR(F^2) = [\Sigma(w(F_o^2 - F_c^2)^2)/(\Sigma w(F_o^2)^2)]^{½}$. [c] $GOF = [\Sigma(w(F_o^2 - F_c^2)^2)/(N_{diffrs} - N_{params})]^{½}$



SI-Figure 1. Platon plots of **4c**, **4e**, and **4a** showing displacement ellipsoids on the 50% probability level.



SI-Figure 2. Platon plots of **6a**, **7b**, and **11b** showing displacement ellipsoids on the 50% probability level.



SI-Figure 4. A Platon plot of **12** showing displacement ellipsoids on the 50% probability level.

VII UV/Vis absorption and emission spectroscopy

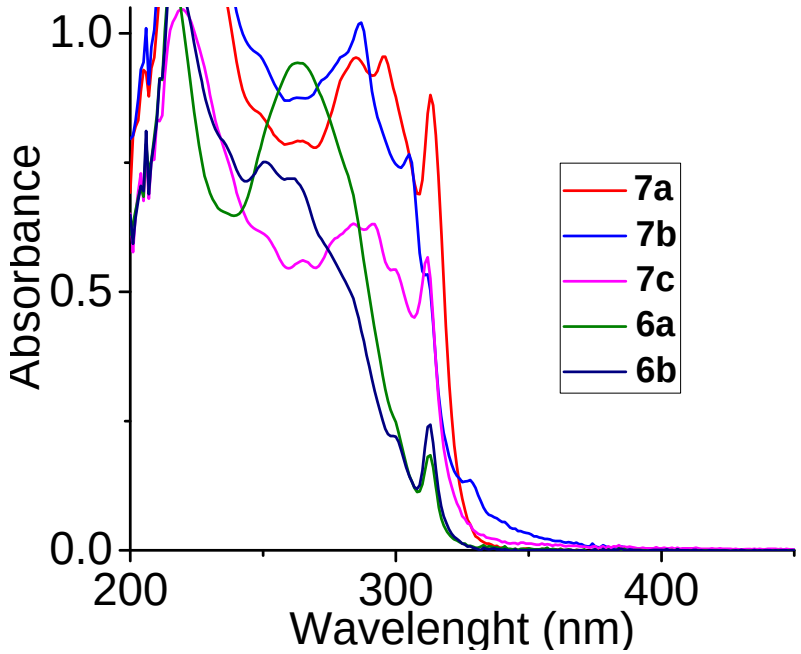
The UV/Vis absorption spectra were recorded using Unicam 340 spectrometer. Corrected steady-state emission spectra were recorded on an Aminco Bowman (AB2) spectrometer.

Quantum yields of fluorescence of a sample (Φ_s) were calculated relative to DPA (Φ_{ref} = 0.97 in cyclohexane[12]) as a reference. Φ_s was determined according to the following equation:

$$\Phi_s = \Phi_{ref} \times A_s / A_{ref} \qquad (1)$$

where A_s and A_{ref} represent integrated areas of the emission (in arbitrary units) of a sample and the reference excited to an isosbestic point, respectively (Figures SI-4-7).

Micromolar solutions of the reference (DPA) and the samples were prepared in cyclohexane. The absorption of the reference and the samples were the same at the selected excitation wavelength (A < 0.05). Quantum yields were calculated from 5 independent measuring.

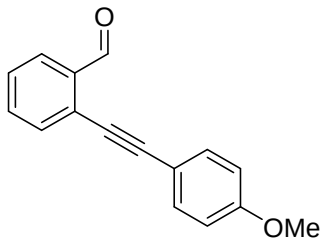


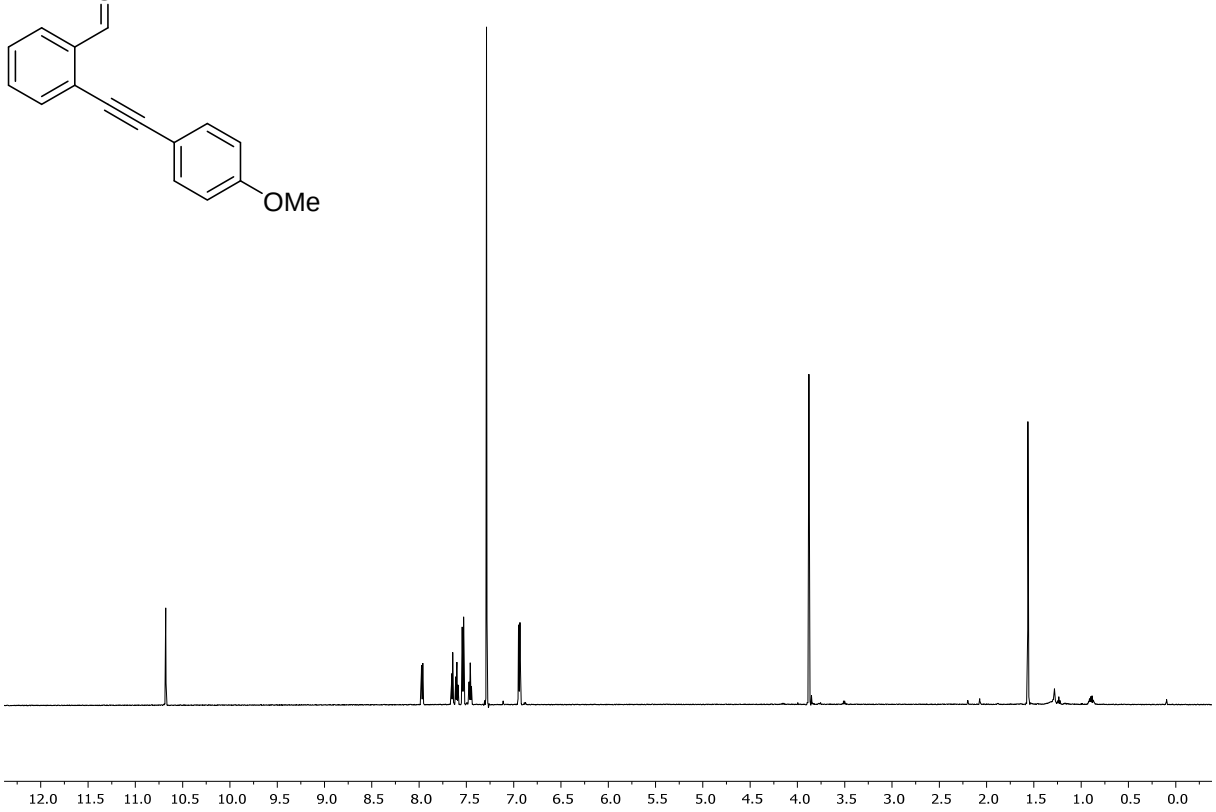
SI-Figure 5. Zoomed absorption spectra of **6** and **7**.

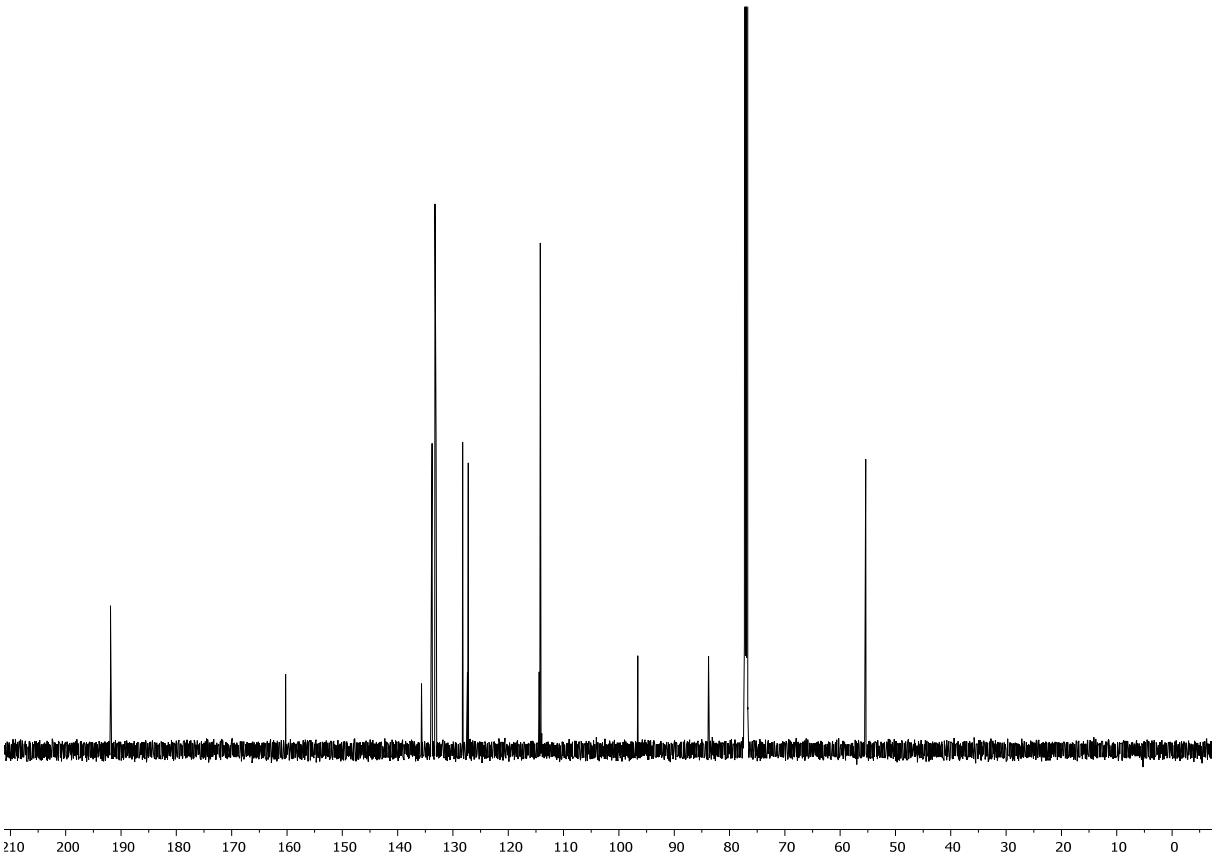
[12] A.M.Brouwer *Pure Appl.Chem.* **2011**, *83*, 2213-2228.

VIII Copies of ^{1}H and ^{13}C NMR spectra

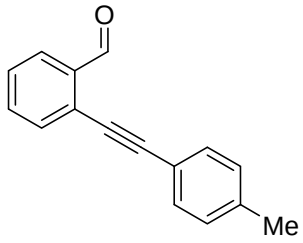
2-((4-Methoxyphenyl)ethynyl)benzaldehyde (Sa).

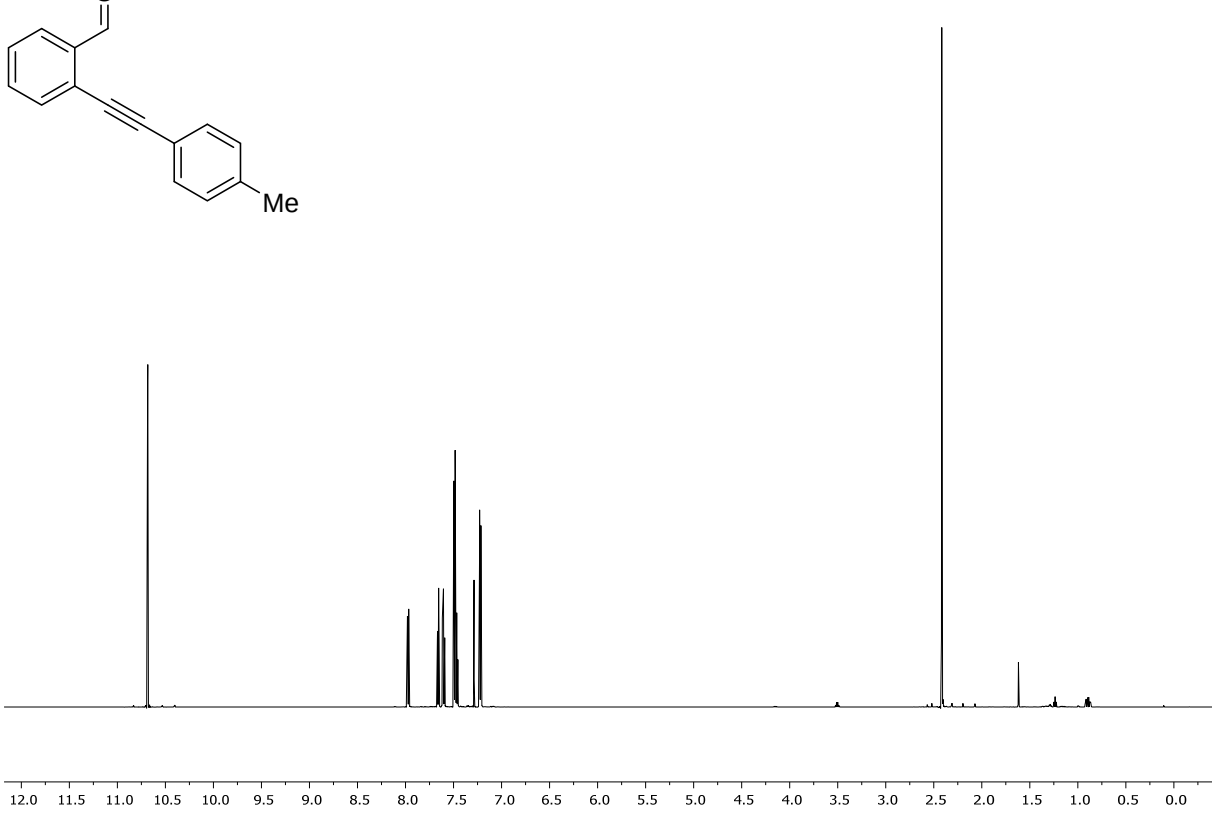


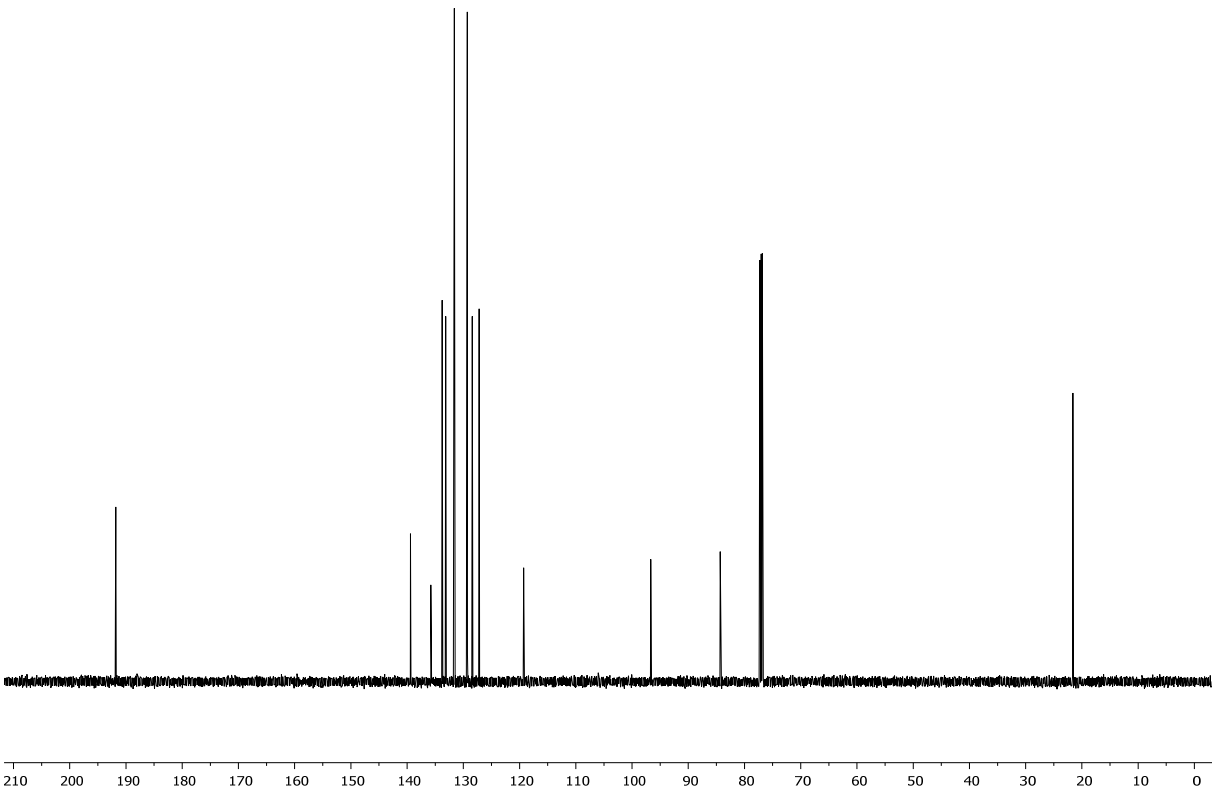




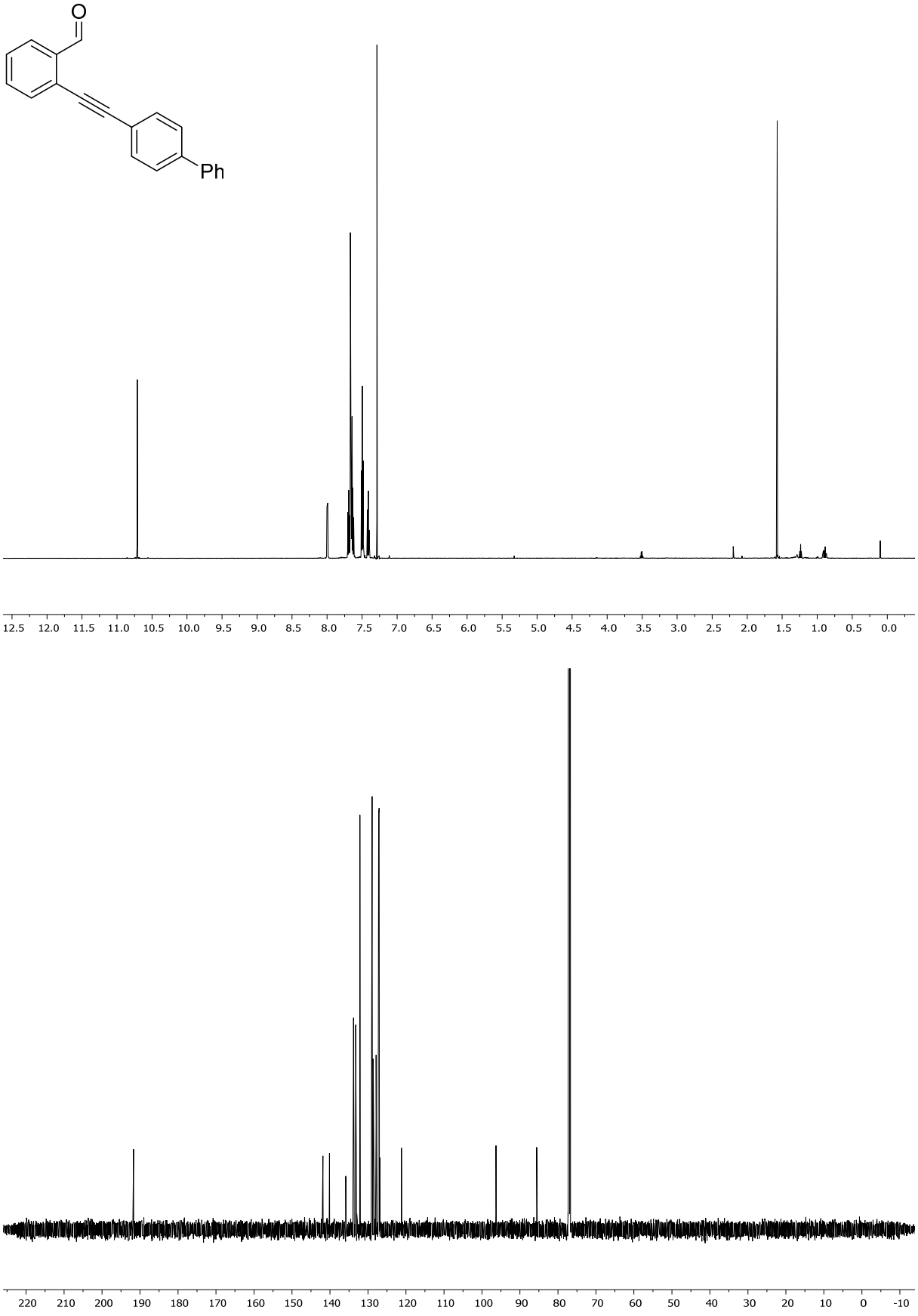
2-(*p*-Tolylethynyl)benzaldehyde (Sb).



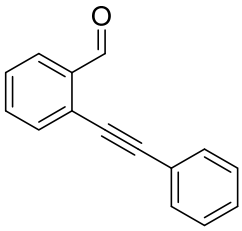


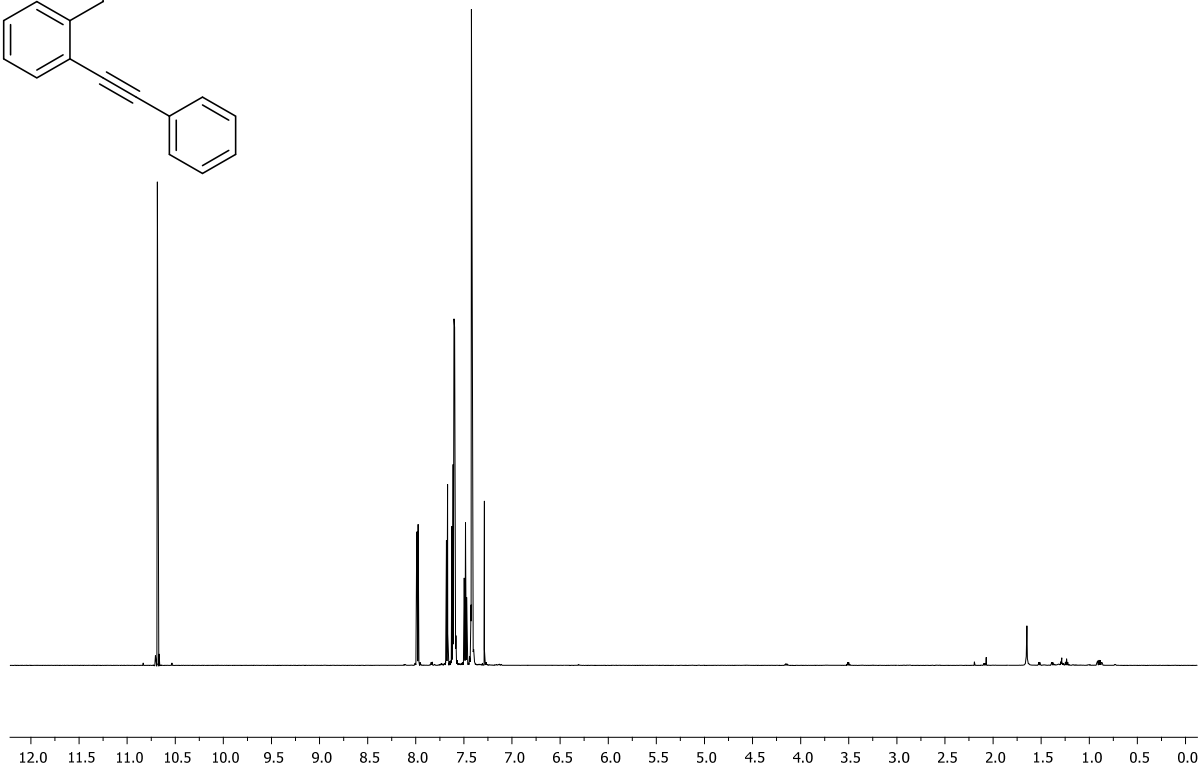


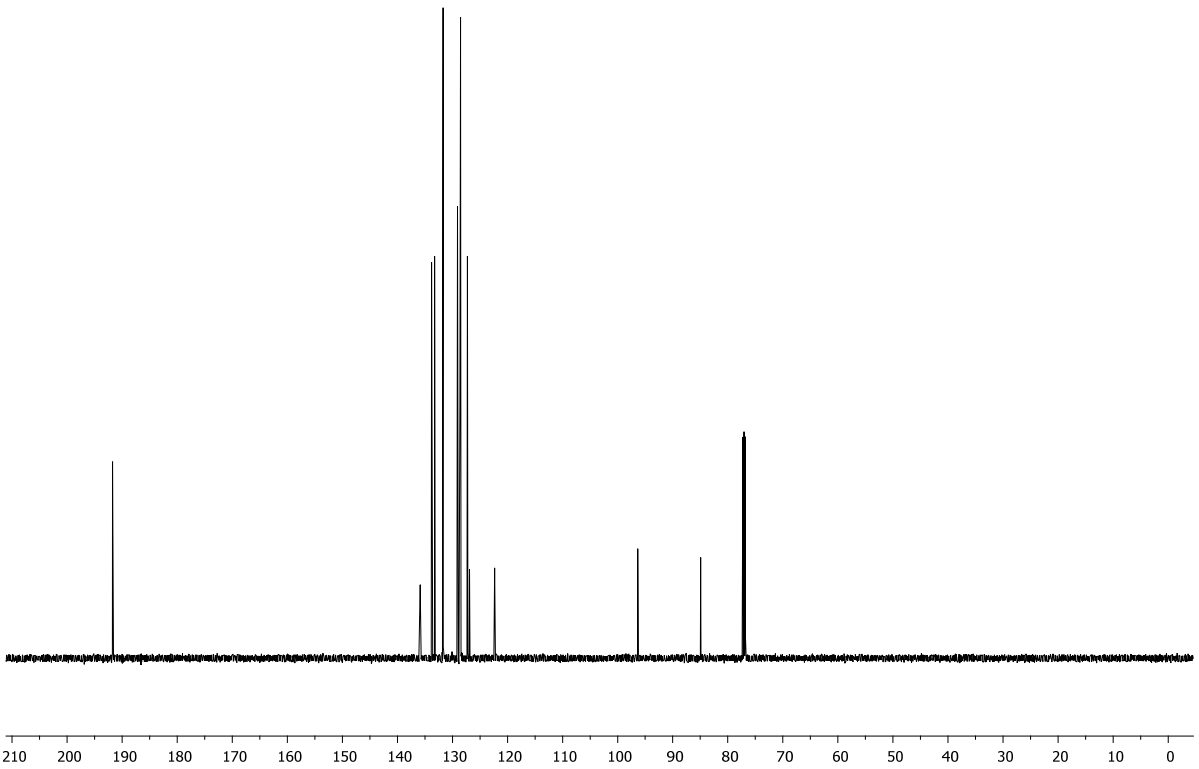
2-([1,1'-Biphenyl]-4-ylethynyl)benzaldehyde (Sc).



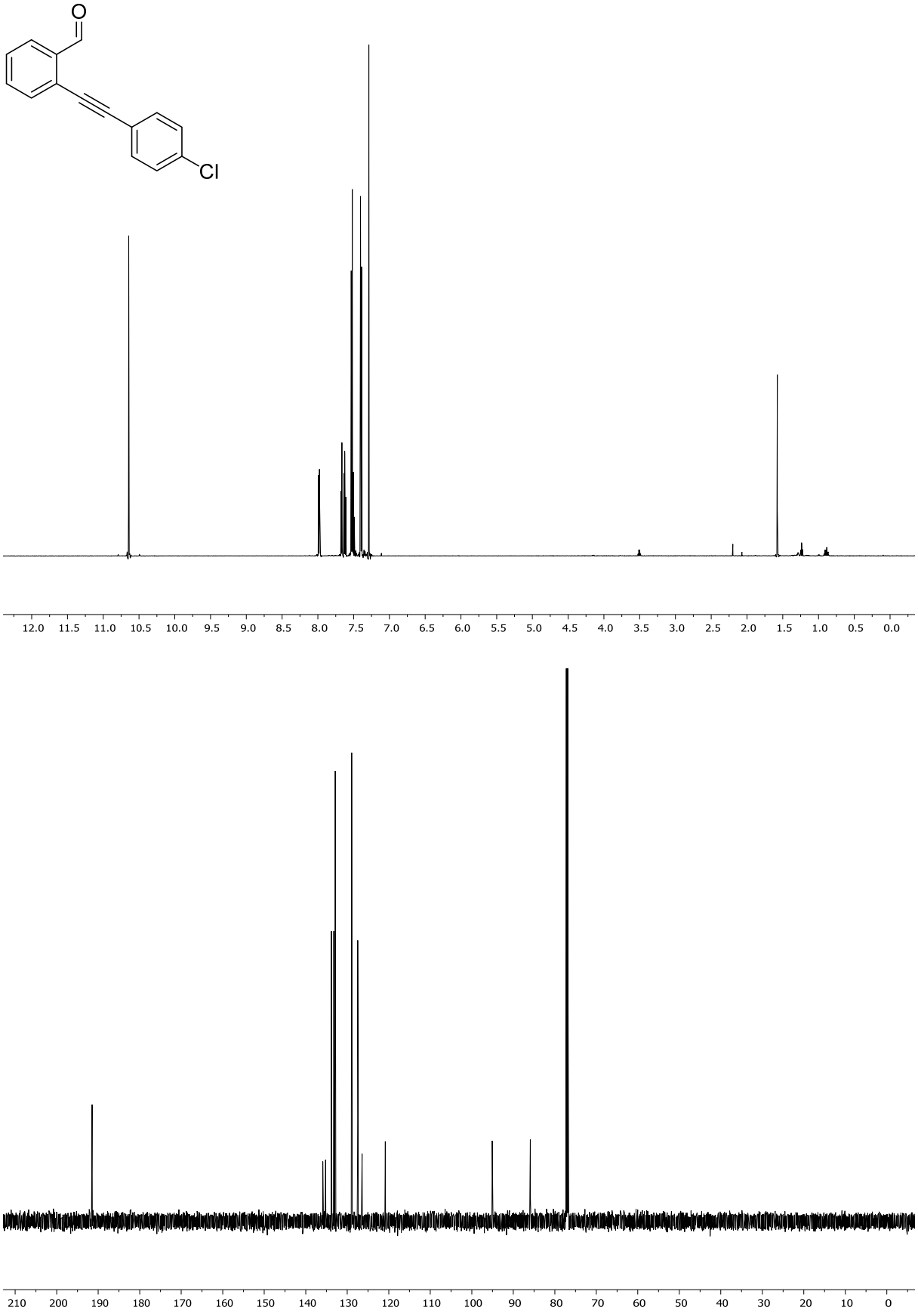
2-(Phenylethynyl)benzaldehyde (Sd).



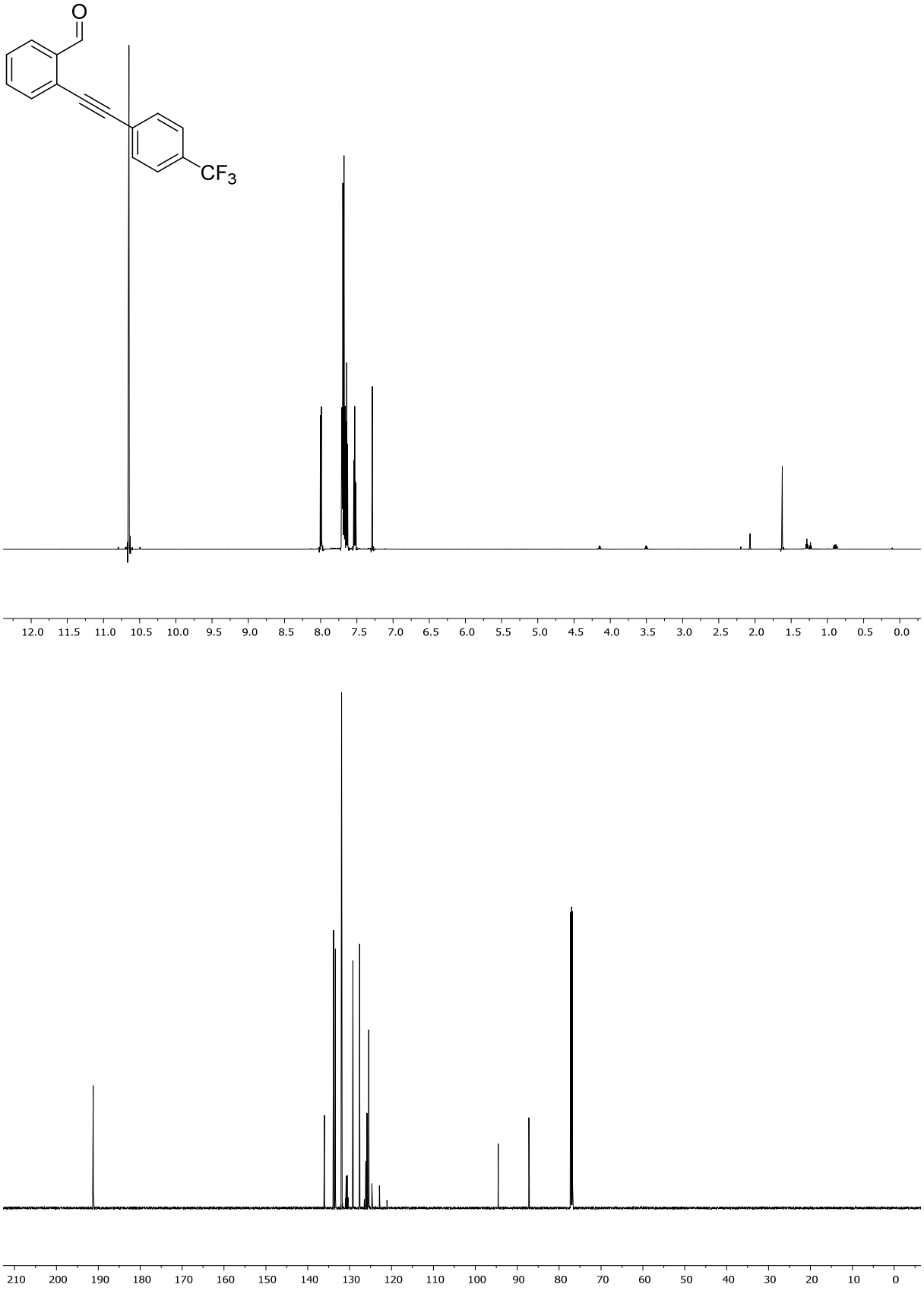




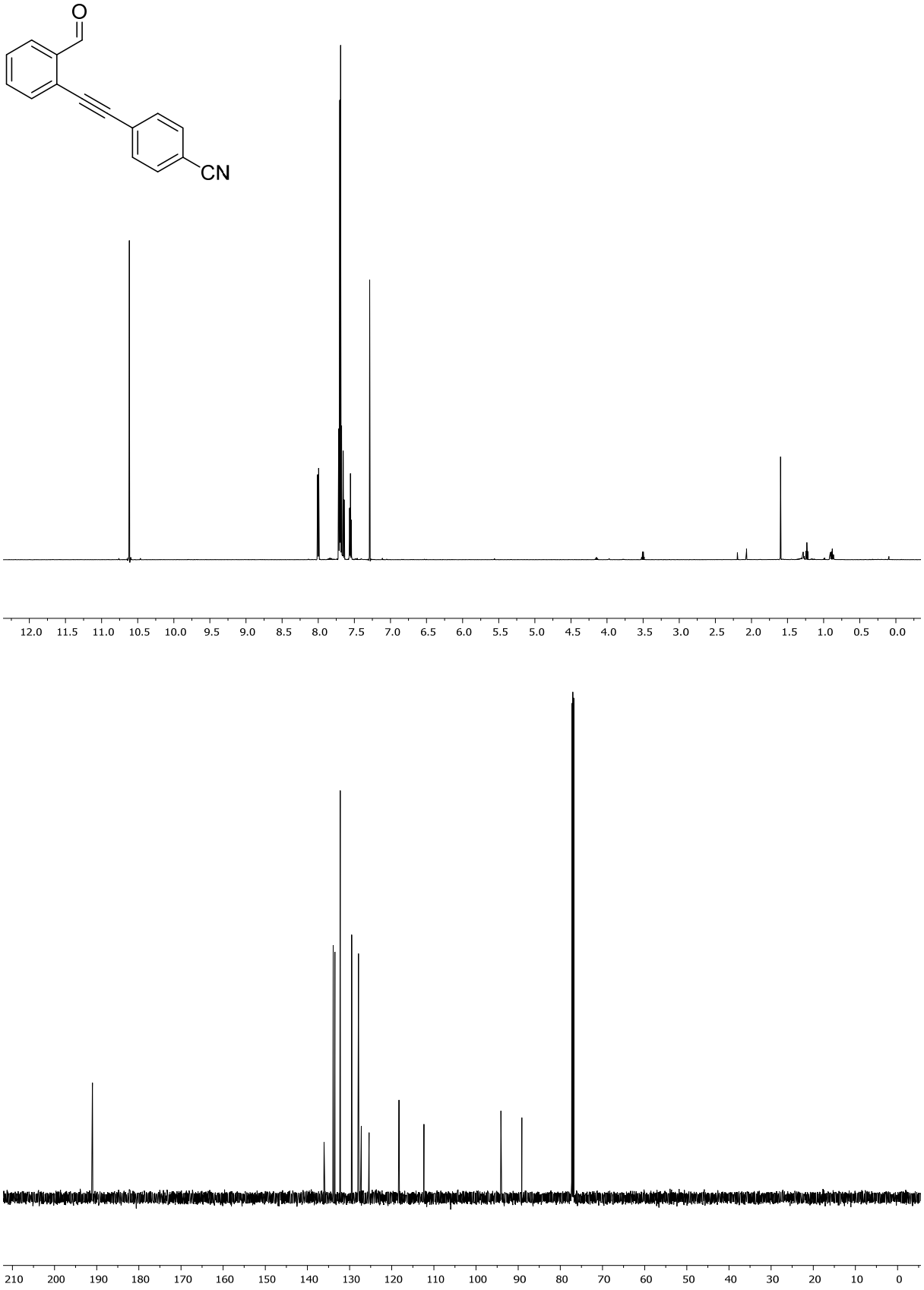
2-((4-Chlorophenyl)ethynyl)benzaldehyde (Se).



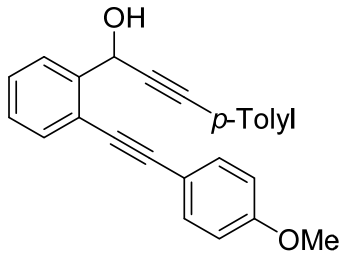
2-((4-(Trifluoromethyl)phenyl)ethynyl)benzaldehyde (Sf).

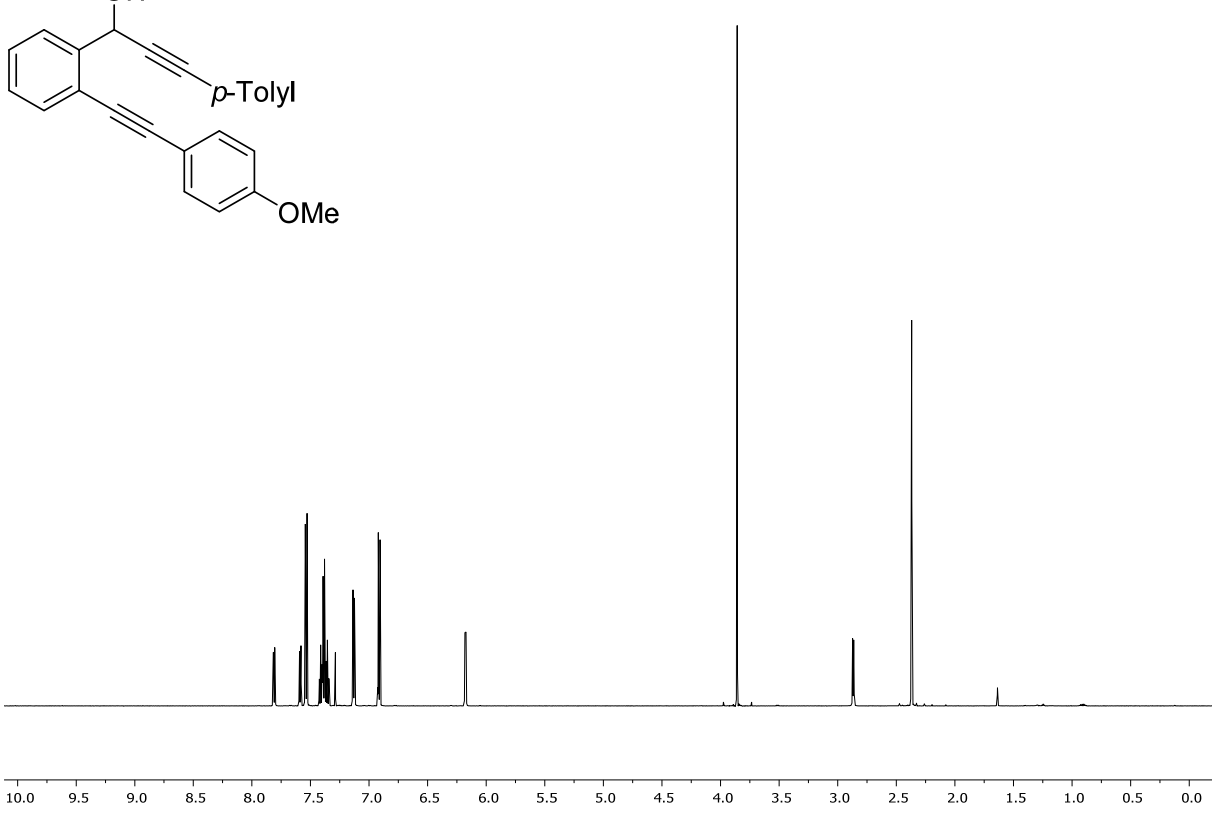


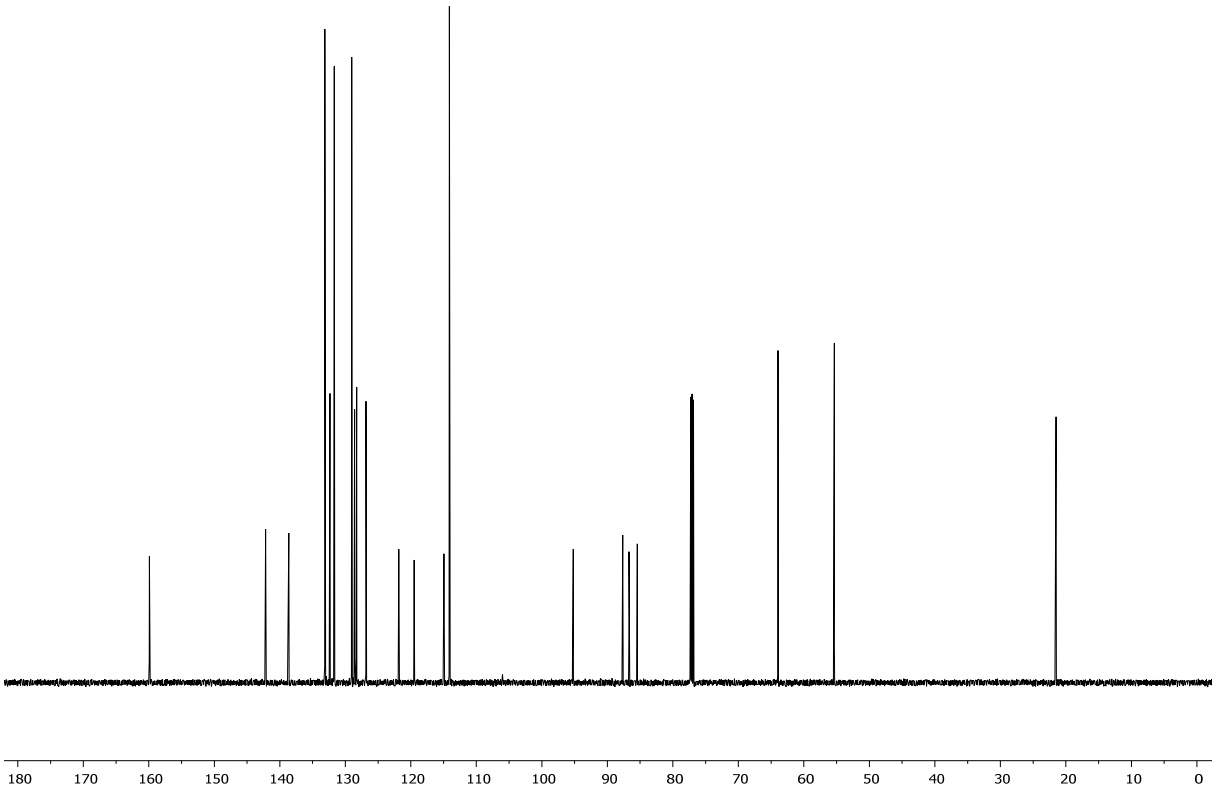
4-((2-Formylphenyl)ethynyl)benzonitrile (Sg).



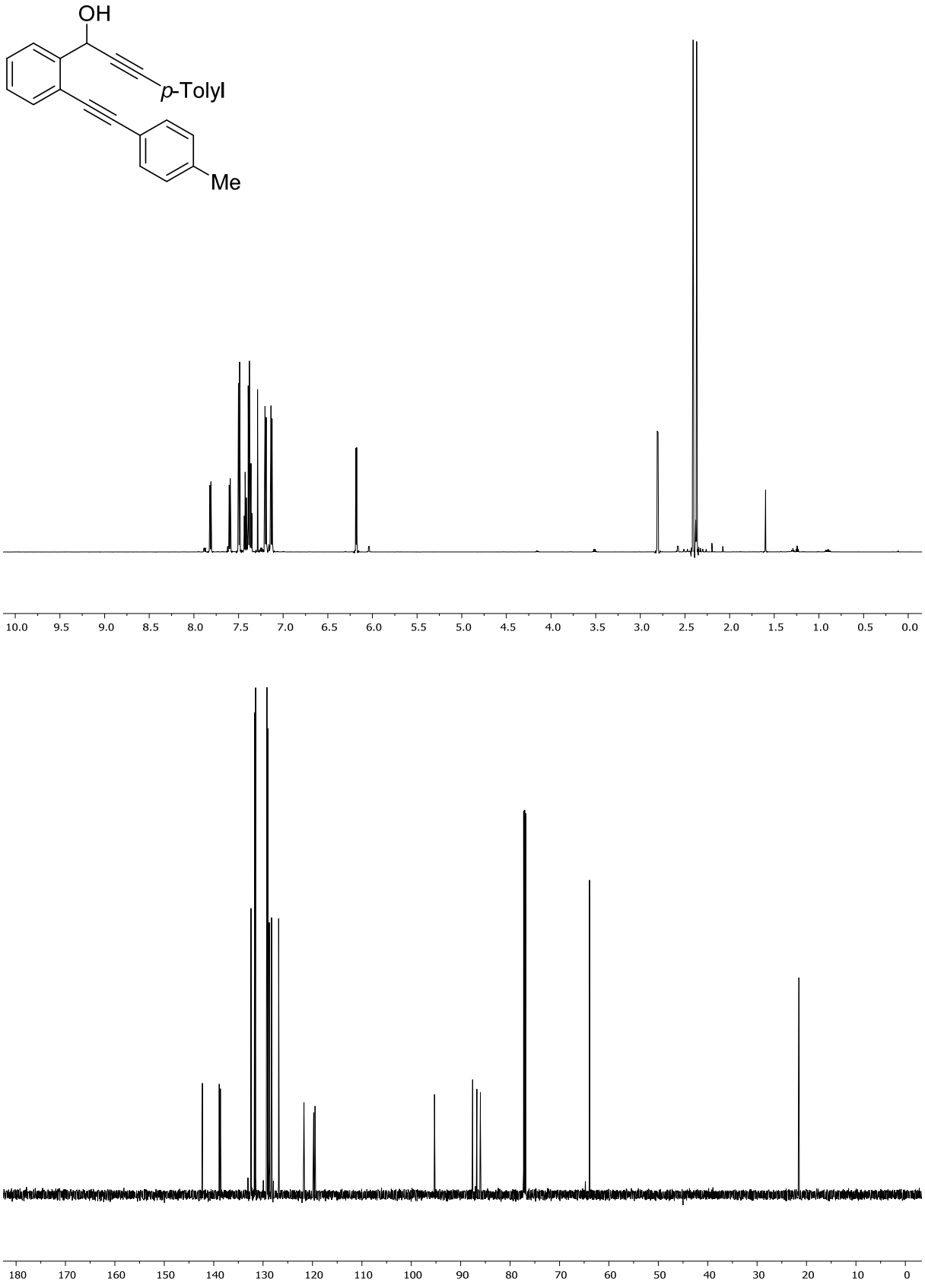
1-(2-((4-Methoxyphenyl)ethynyl)phenyl)-3-(*p*-tolyl)prop-2-yn-1-ol (1a).



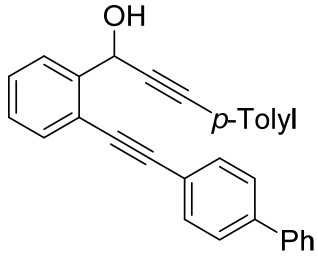


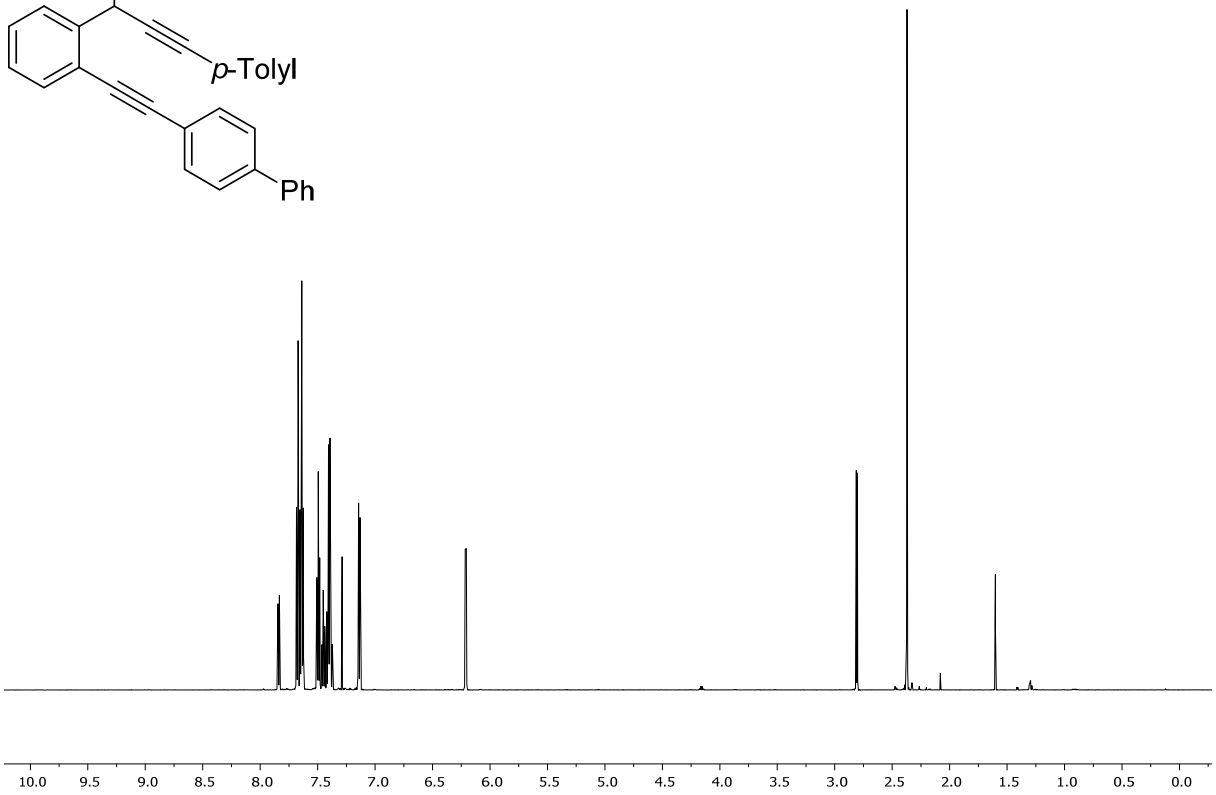


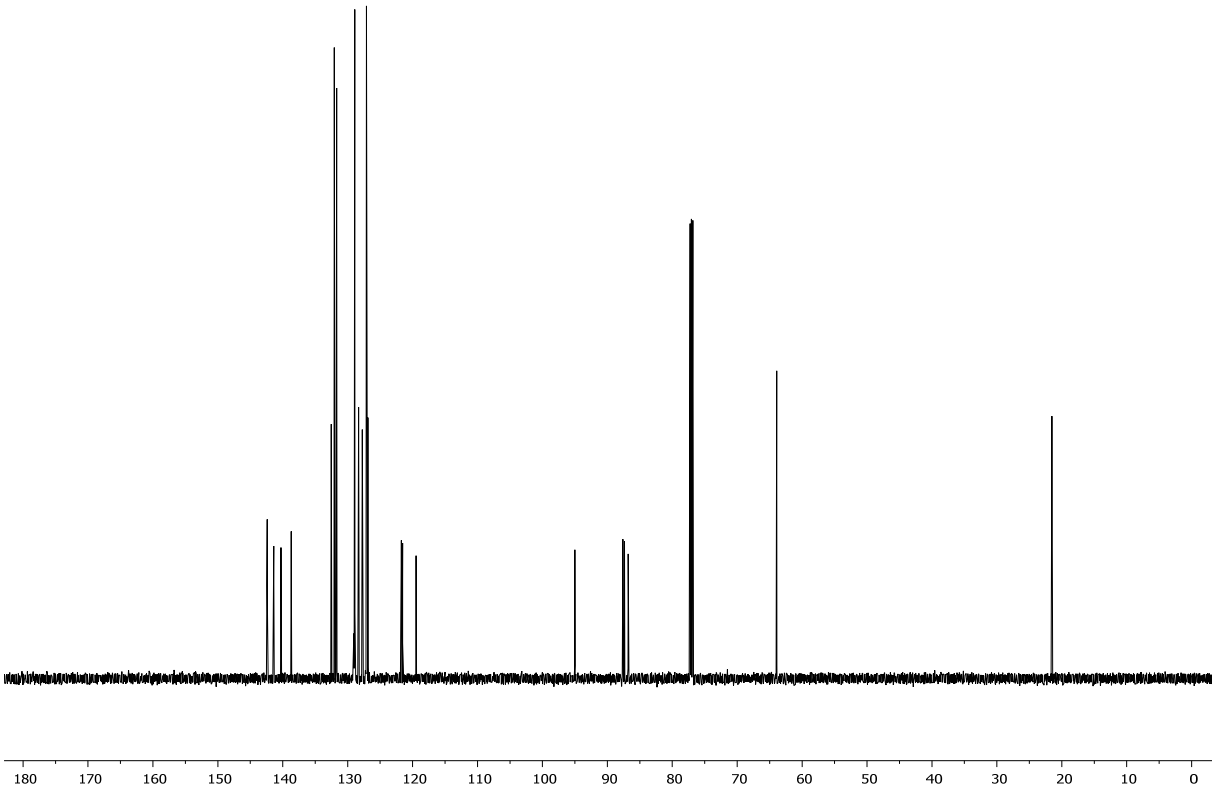
3-(*p*-Tolyl)-1-(2-(*p*-tolylethynyl)phenyl)prop-2-yn-1-ol (1b).



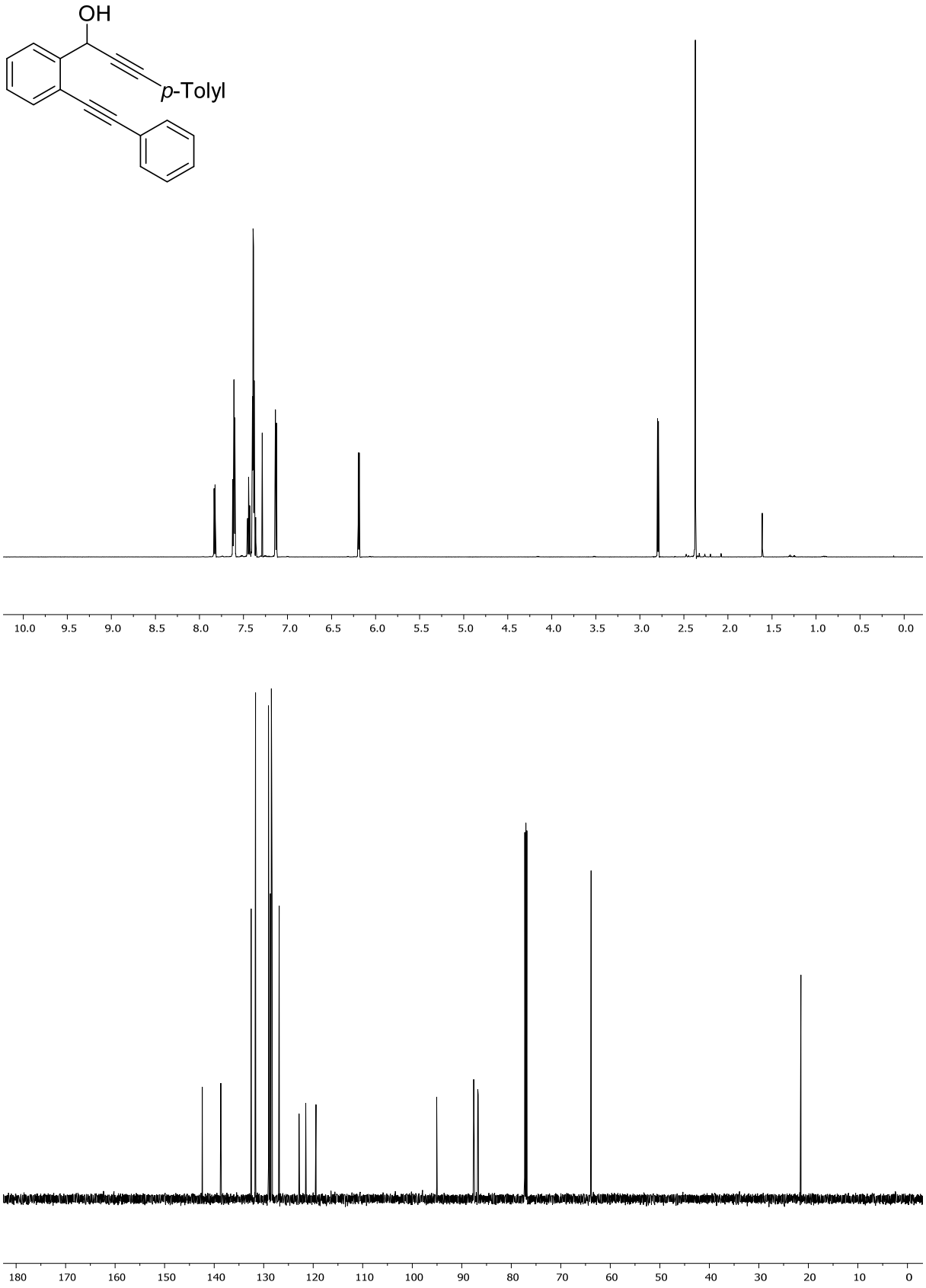
1-(2-([1,1'-Biphenyl]-4-yl-ethynyl)phenyl)-3-(*p*-tolyl)prop-2-yn-1-ol (1c).



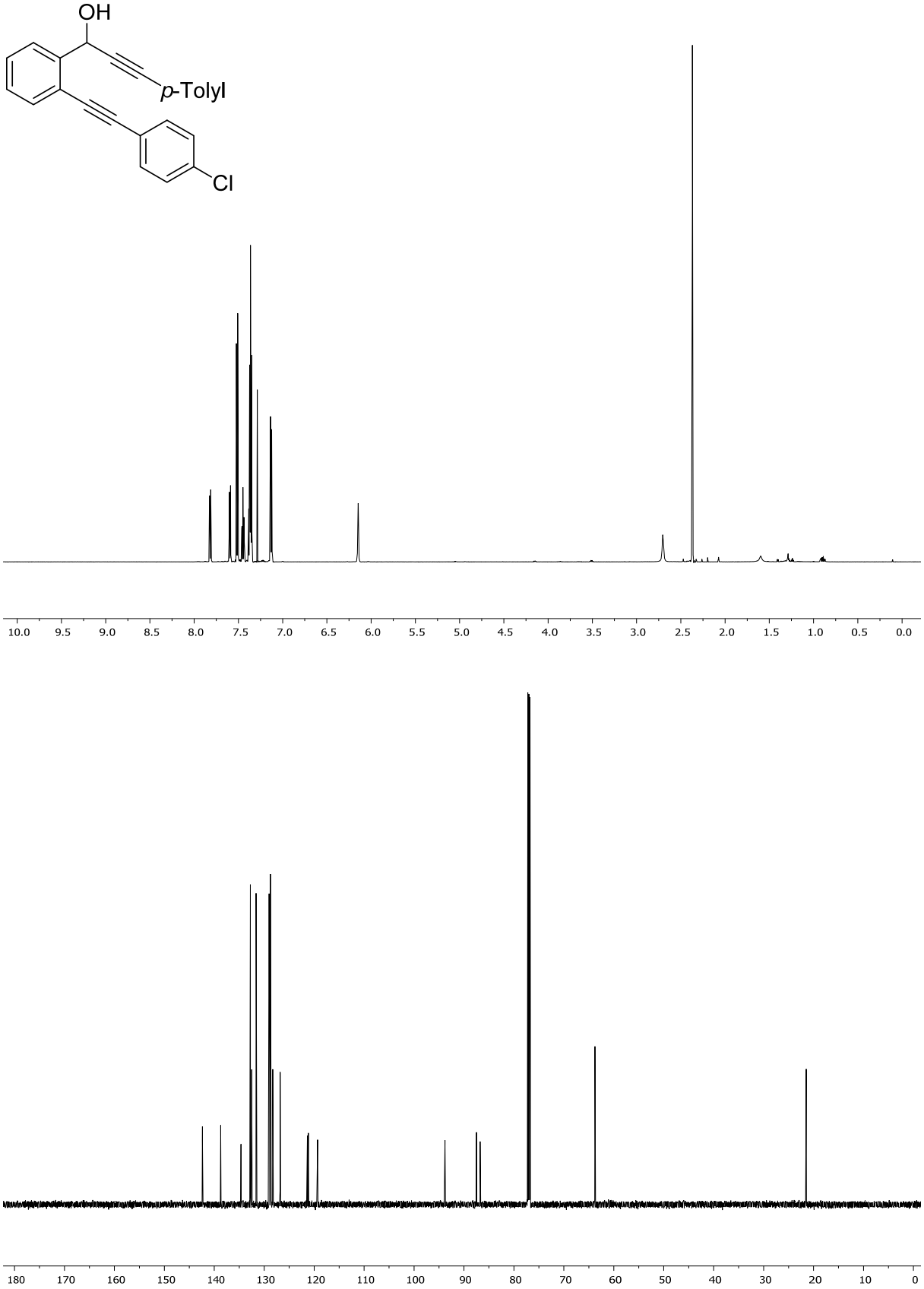




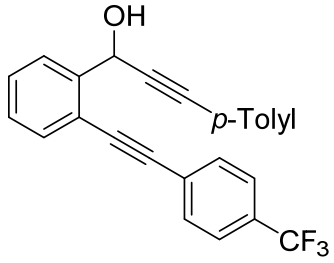
1-(2-(Phenylethynyl)phenyl)-3-(*p*-tolyl)prop-2-yn-1-ol (1d).

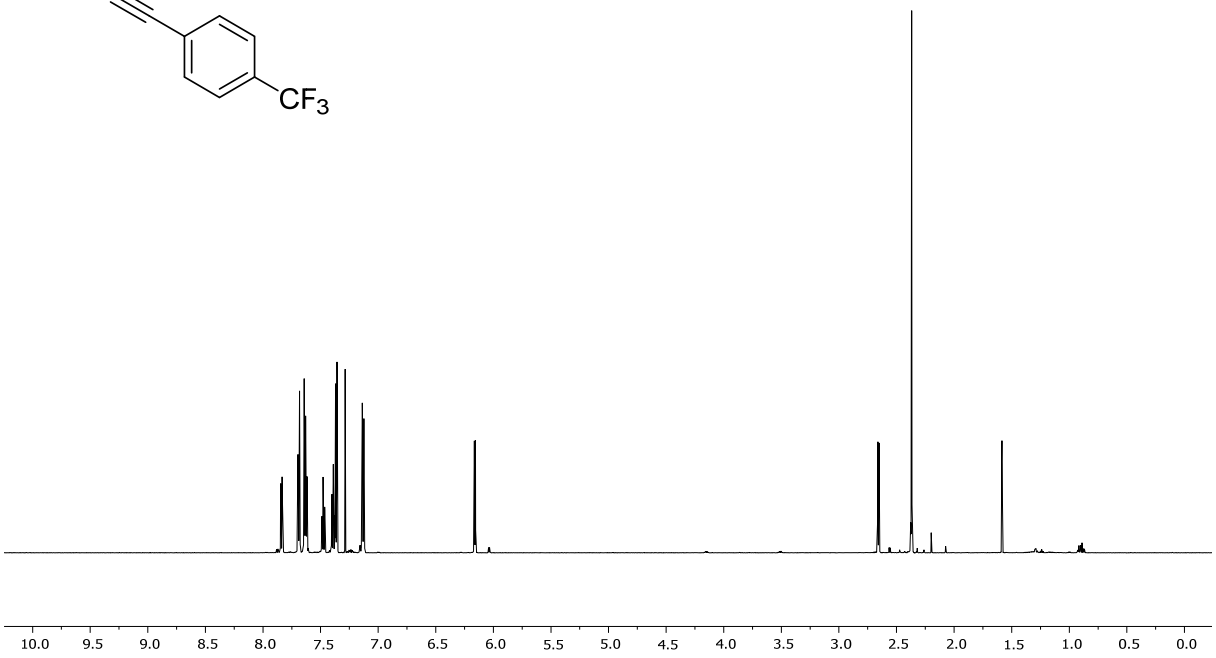


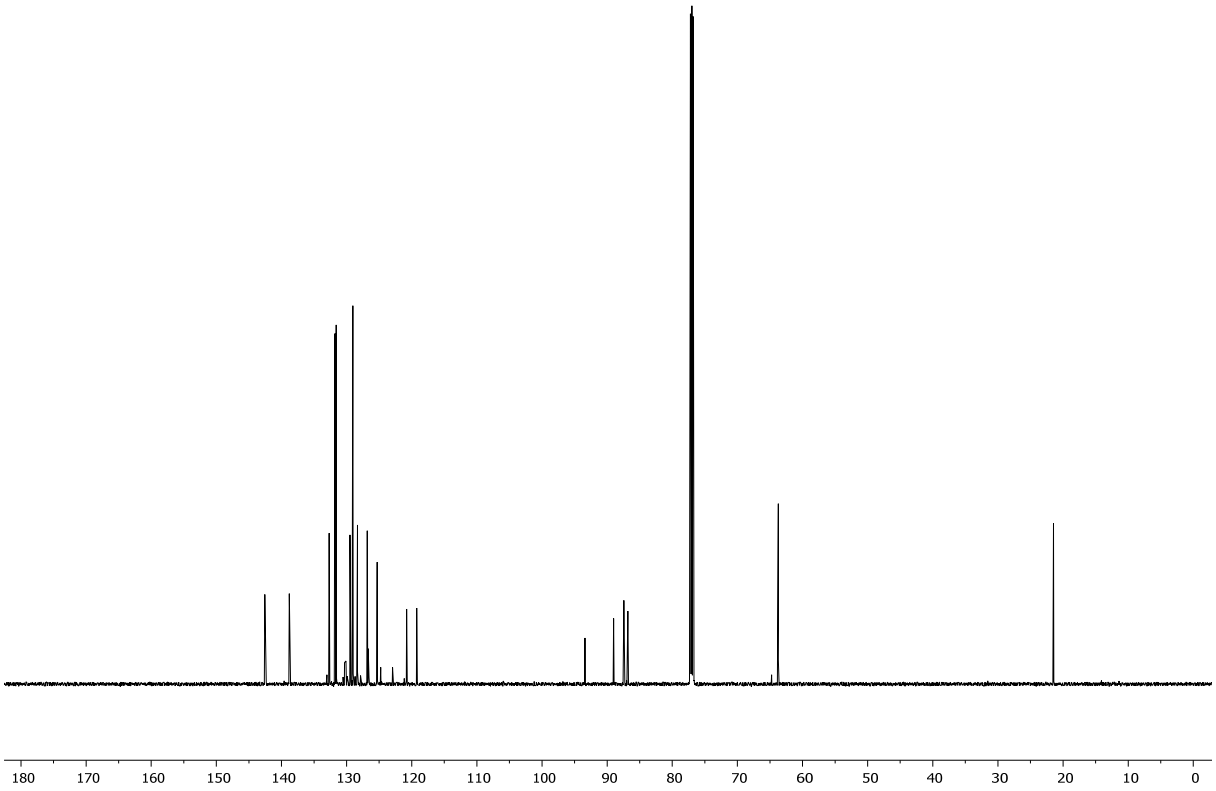
1-(2-((4-Chlorophenyl)ethynyl)phenyl)-3-(*p*-tolyl)prop-2-yn-1-ol (1e).



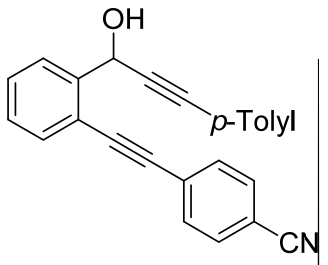
3-(*p*-Tolyl)-1-(2-((4-(trifluoromethyl)phenyl)ethynyl)phenyl)prop-2-yn-1-ol (1f).

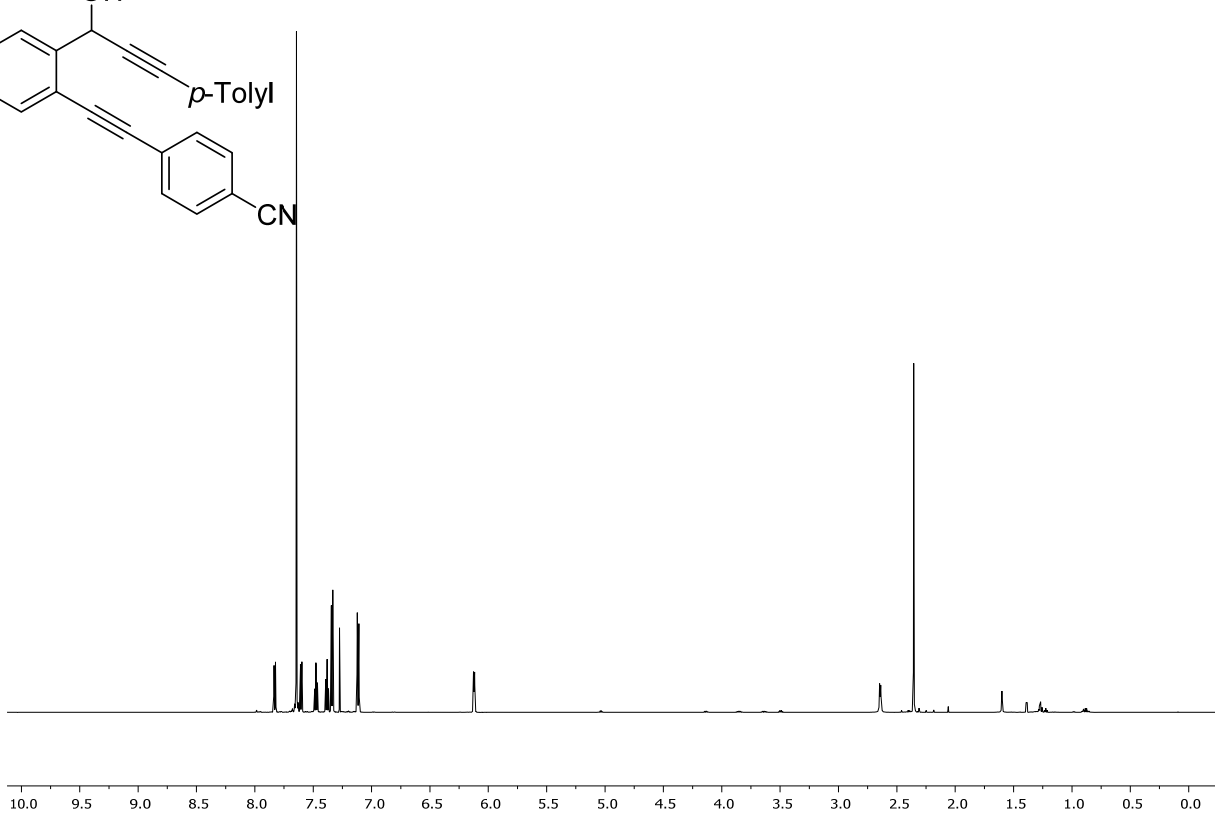


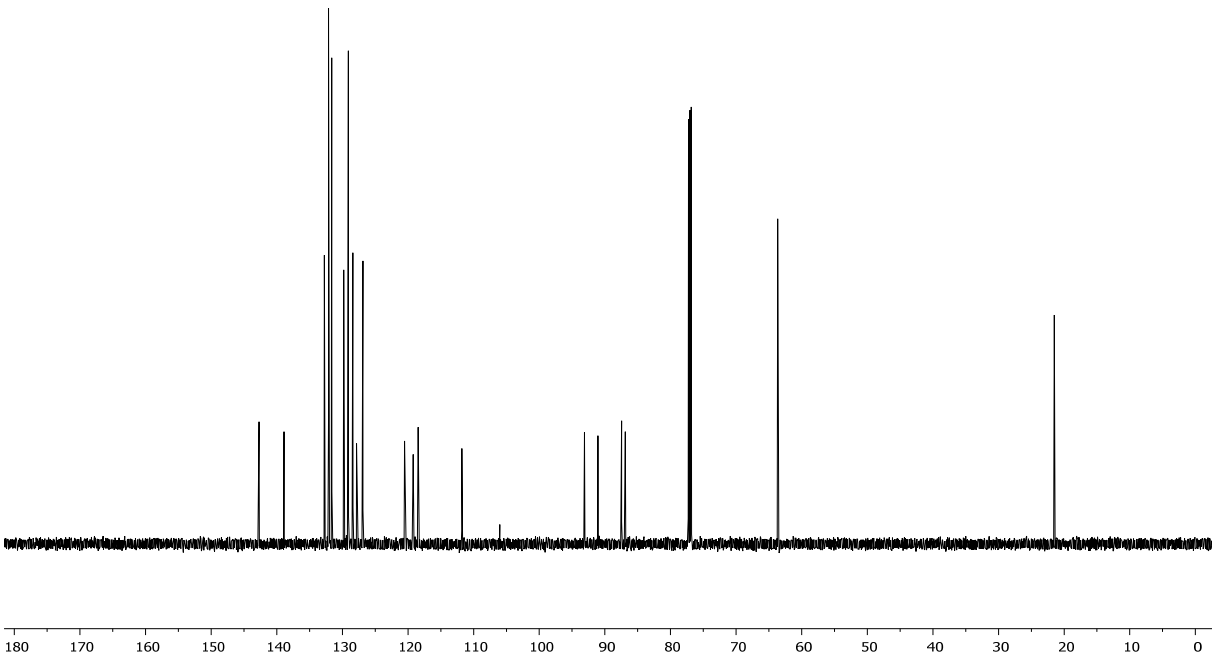




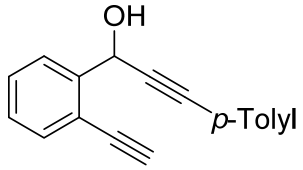
4-((2-(1-Hydroxy-3-(*p*-tolyl)prop-2-yn-1-yl)phenyl)ethynyl)benzonitrile (1g).

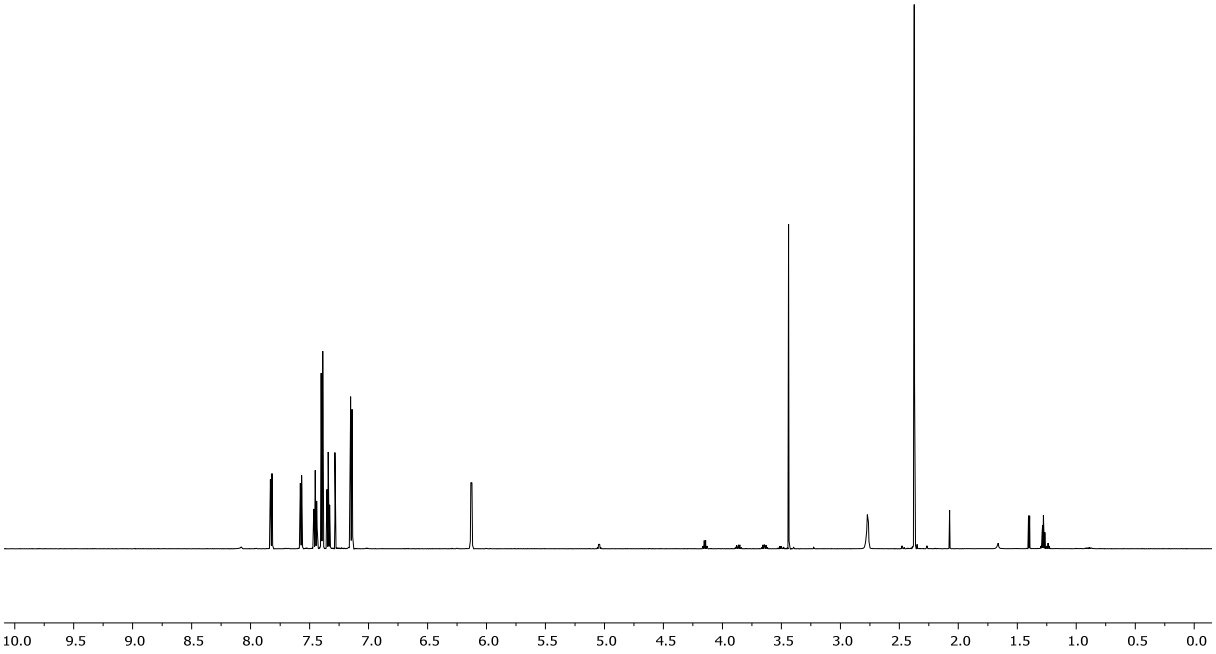


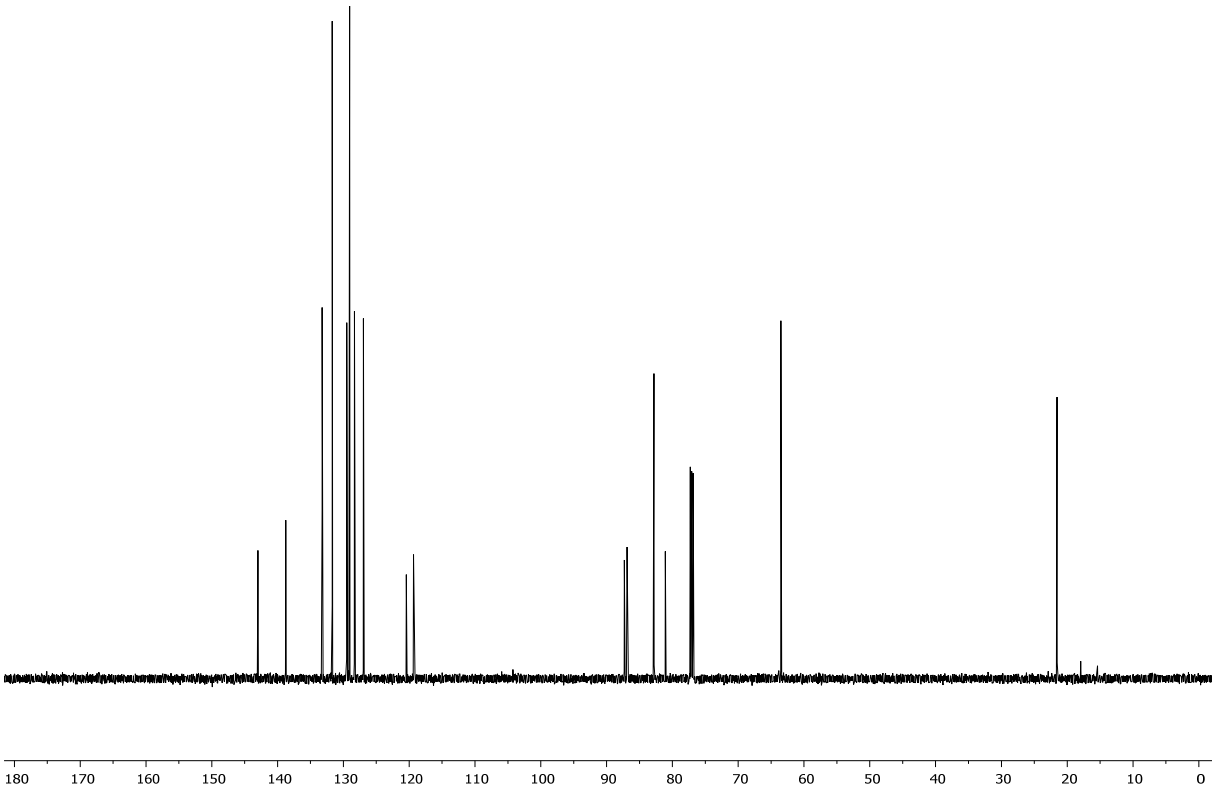




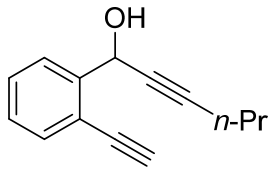
1-(2-Ethynylphenyl)-3-(*p*-tolyl)prop-2-yn-1-ol (5a).

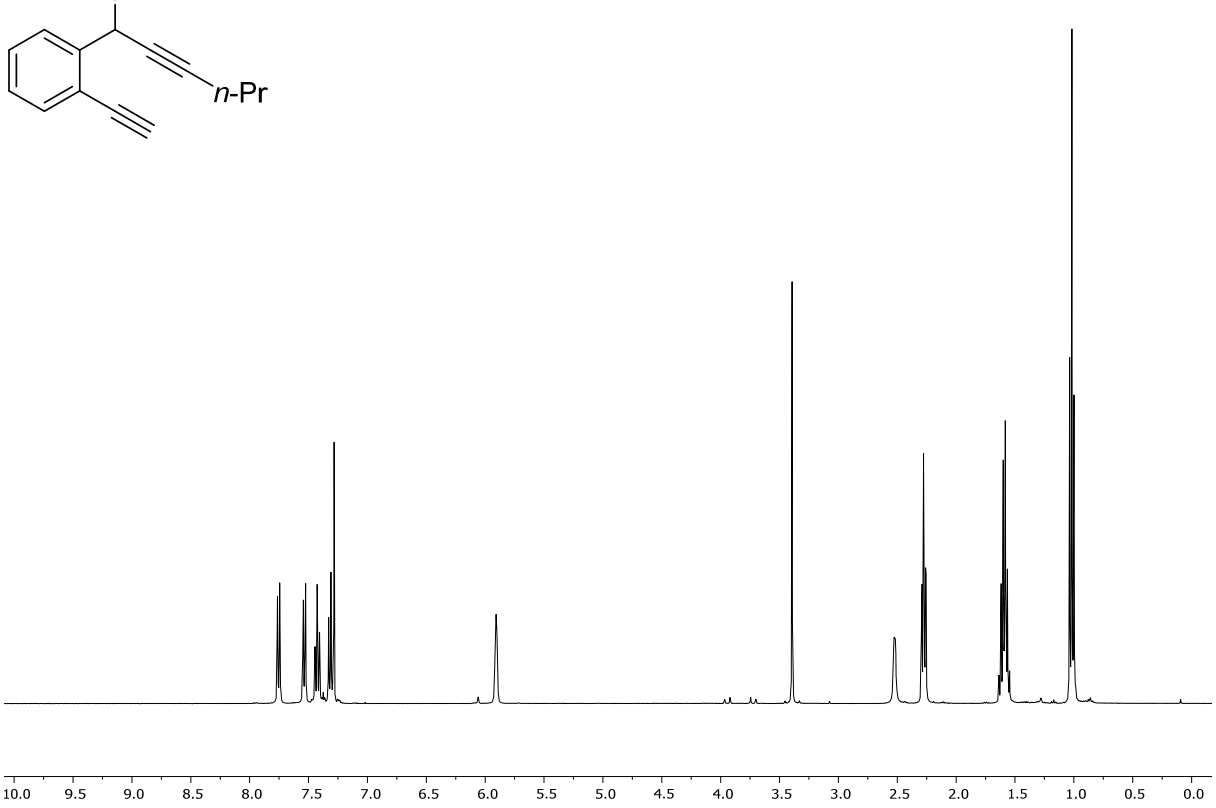


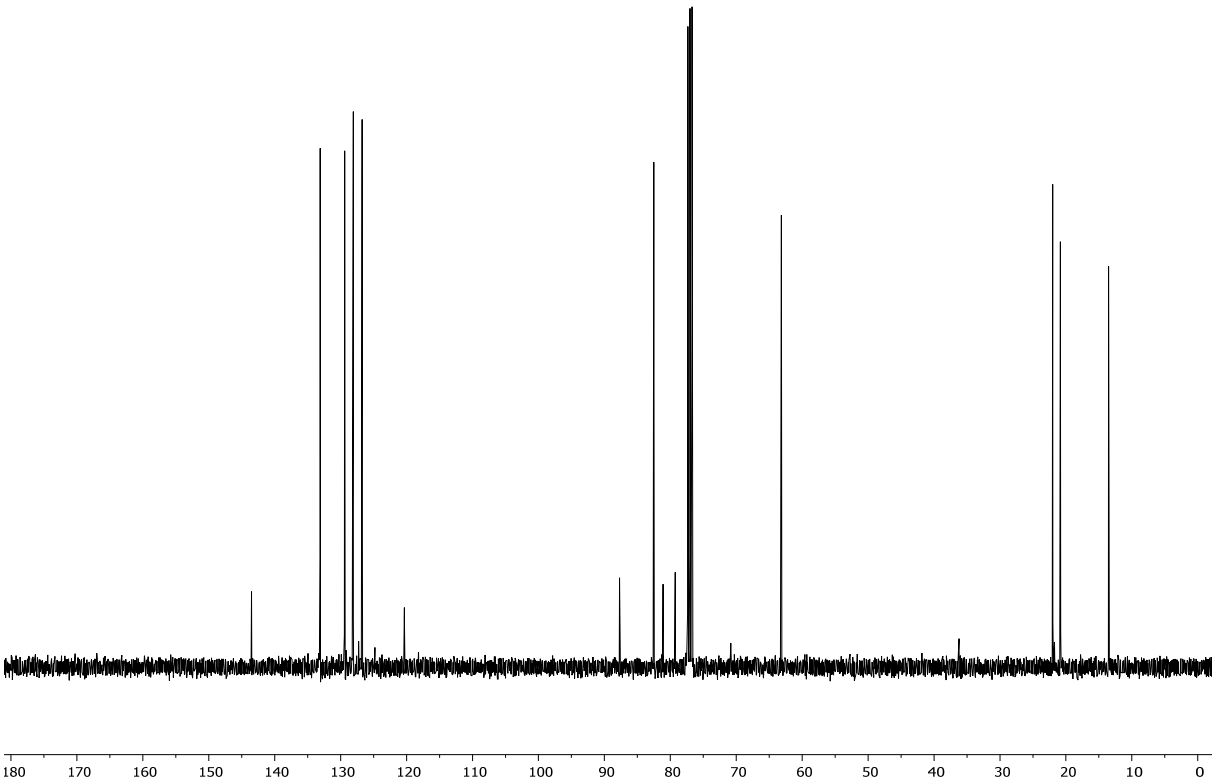




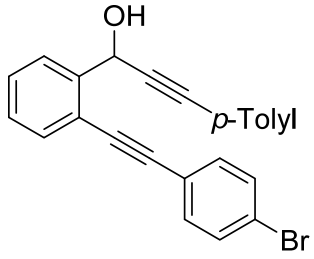
1-(2-Ethynylphenyl)hex-2-yn-1-ol (5b).

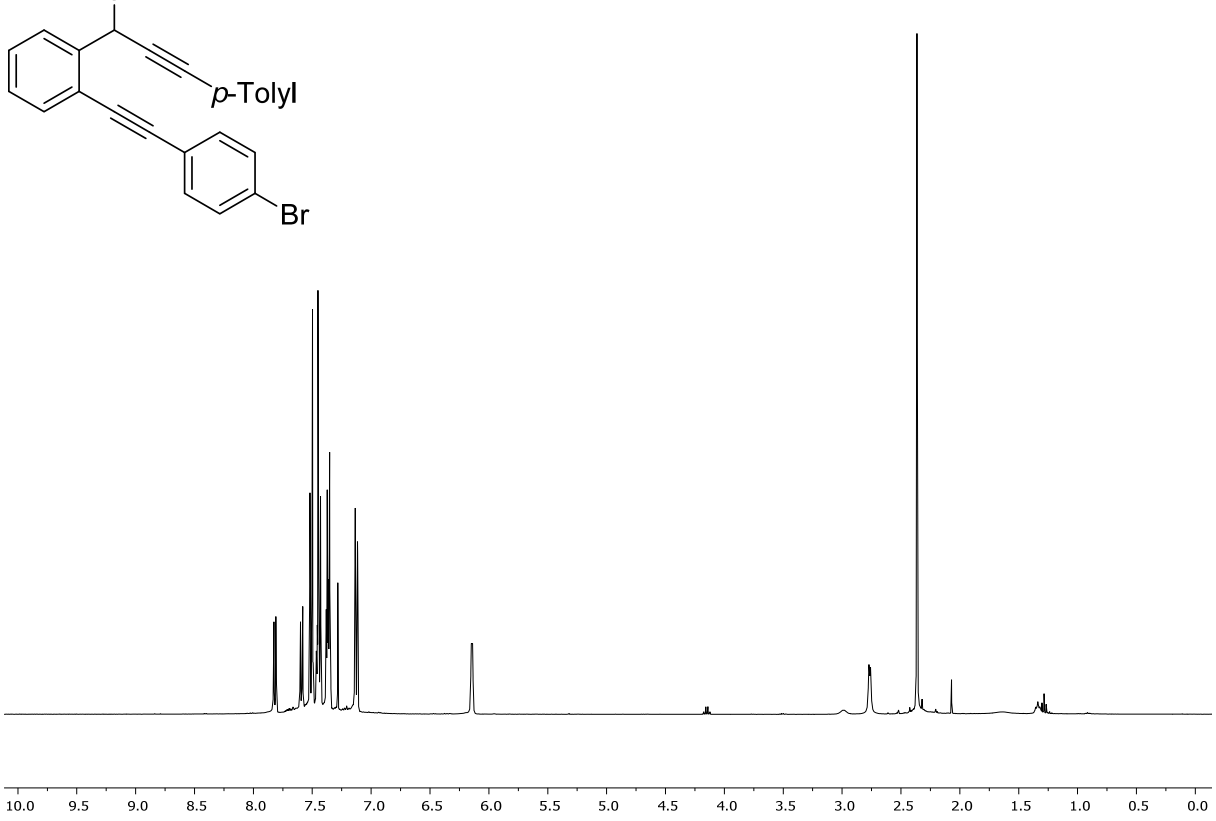


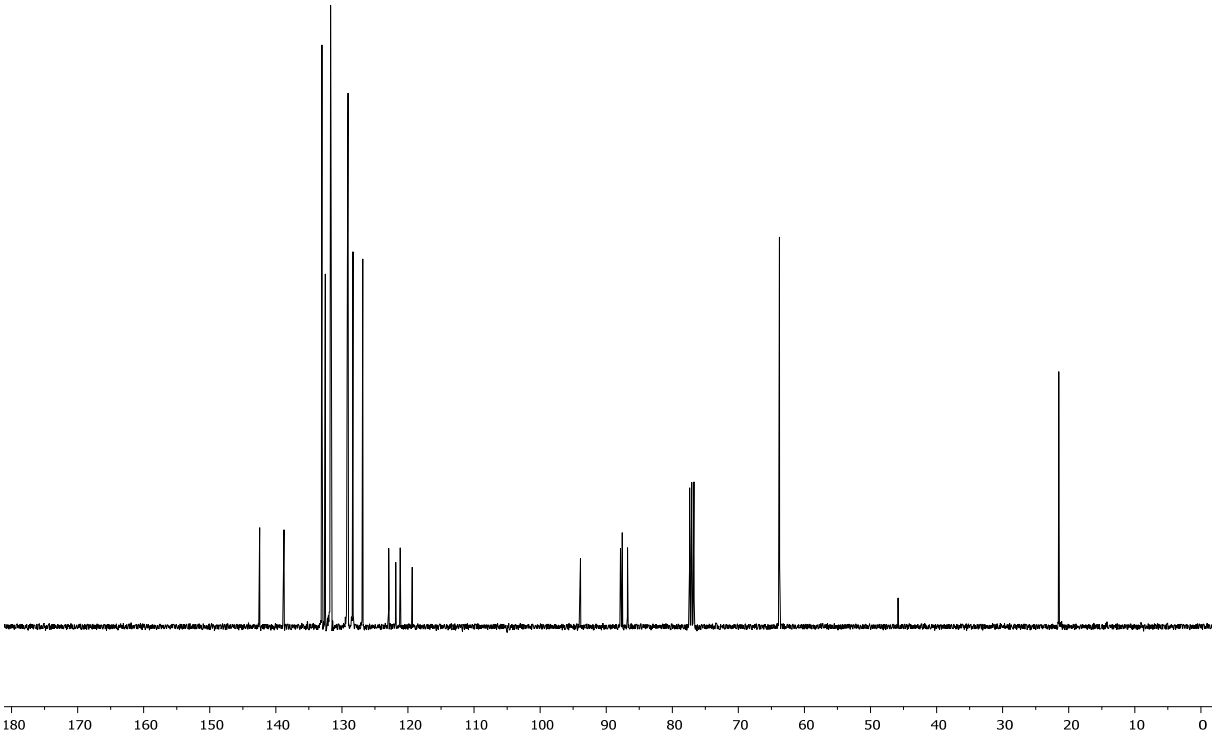




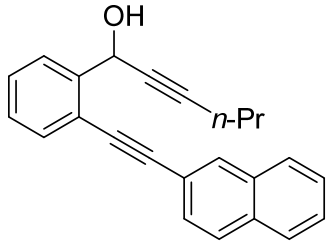
1-(2-((4-Bromophenyl)ethynyl)phenyl)-3-(*p*-tolyl)prop-2-yn-1-ol (1h).

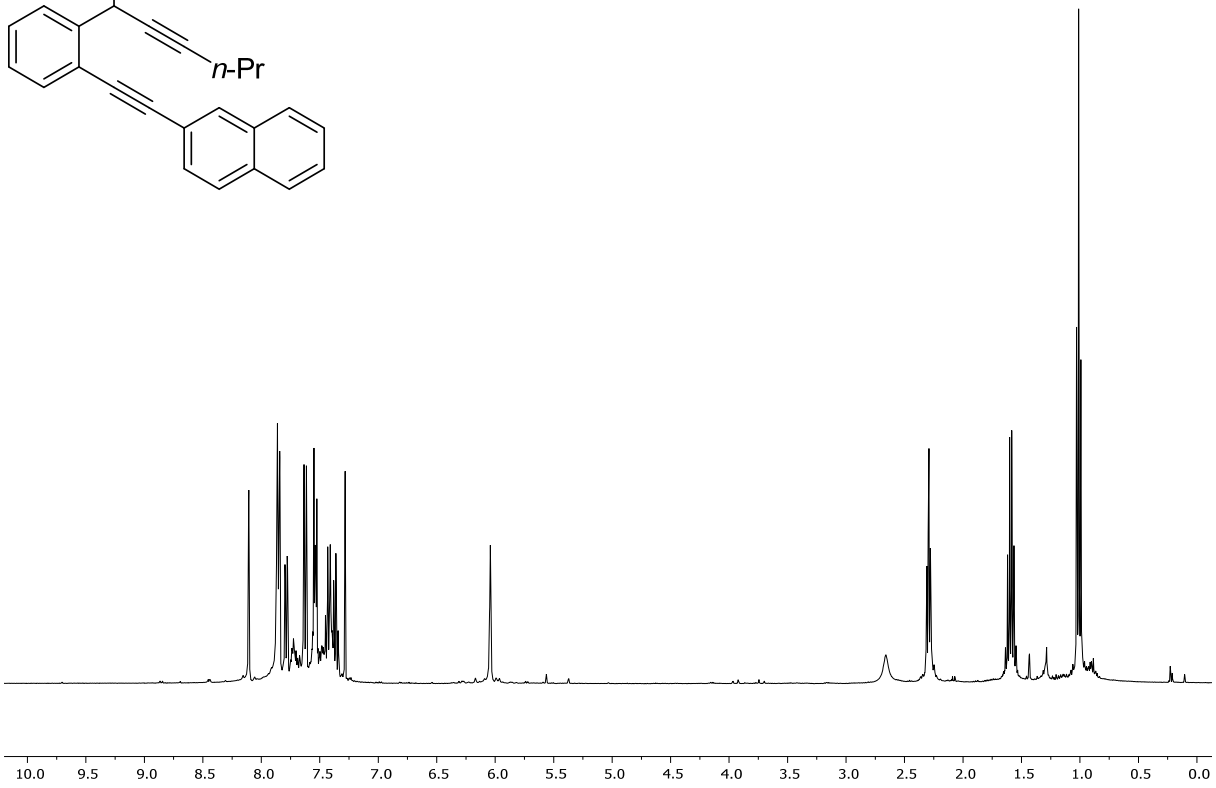


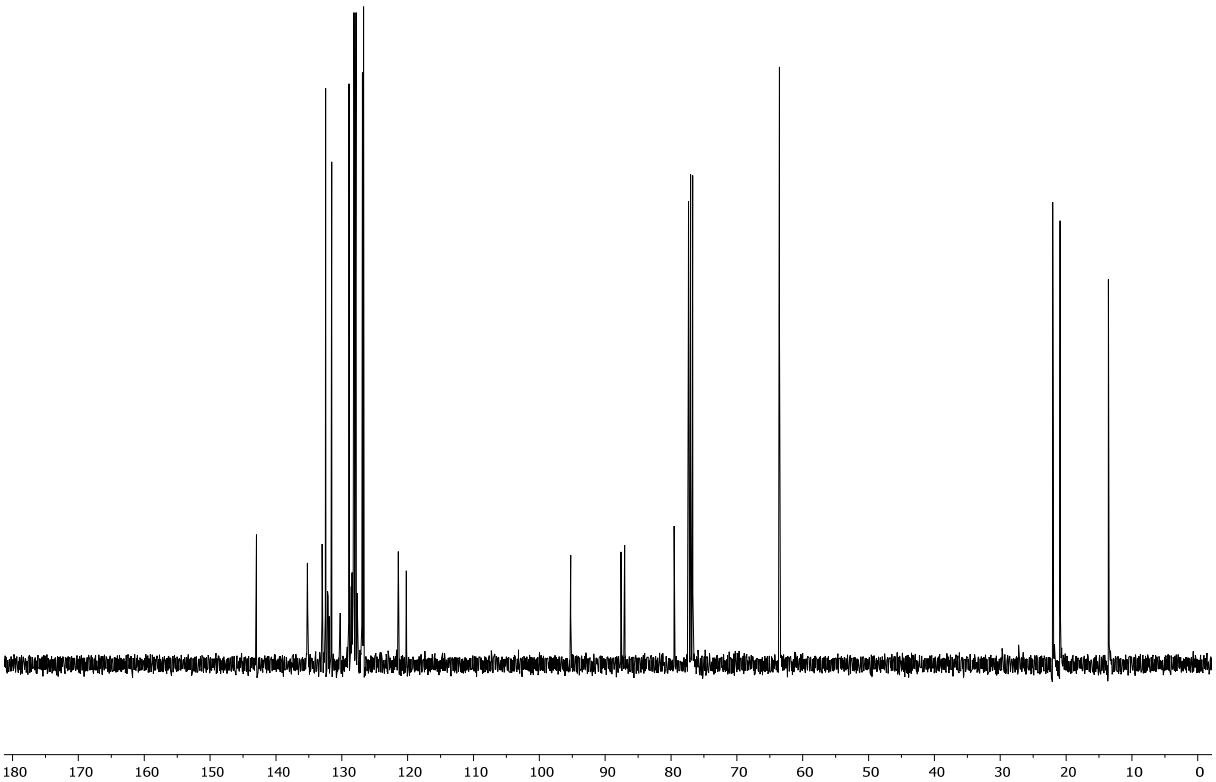




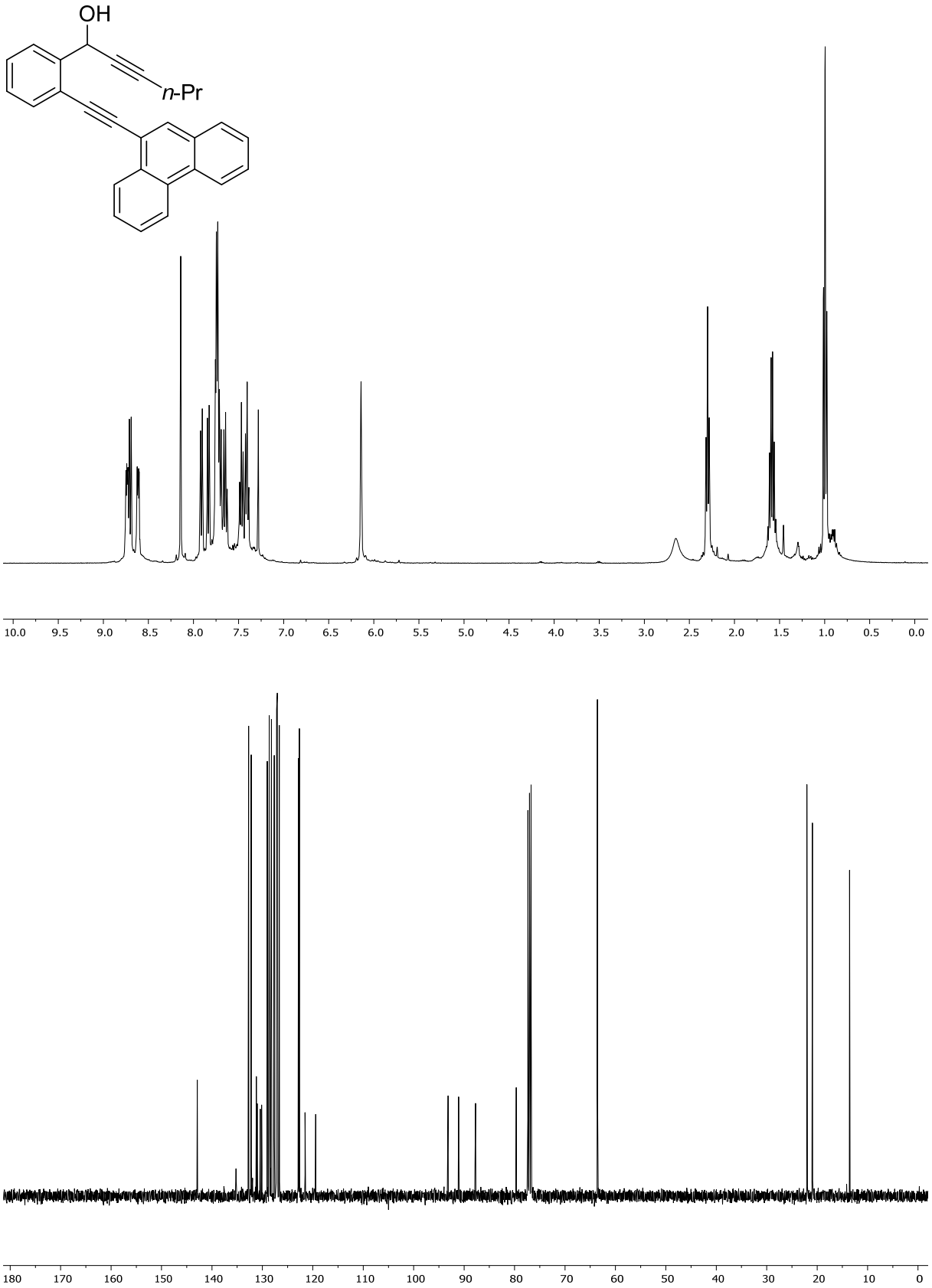
1-(2-(Naphthalen-2-ylethynyl)phenyl)hex-2-yn-1-ol (8a).



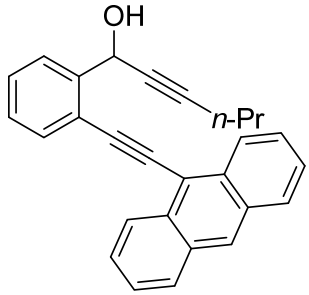


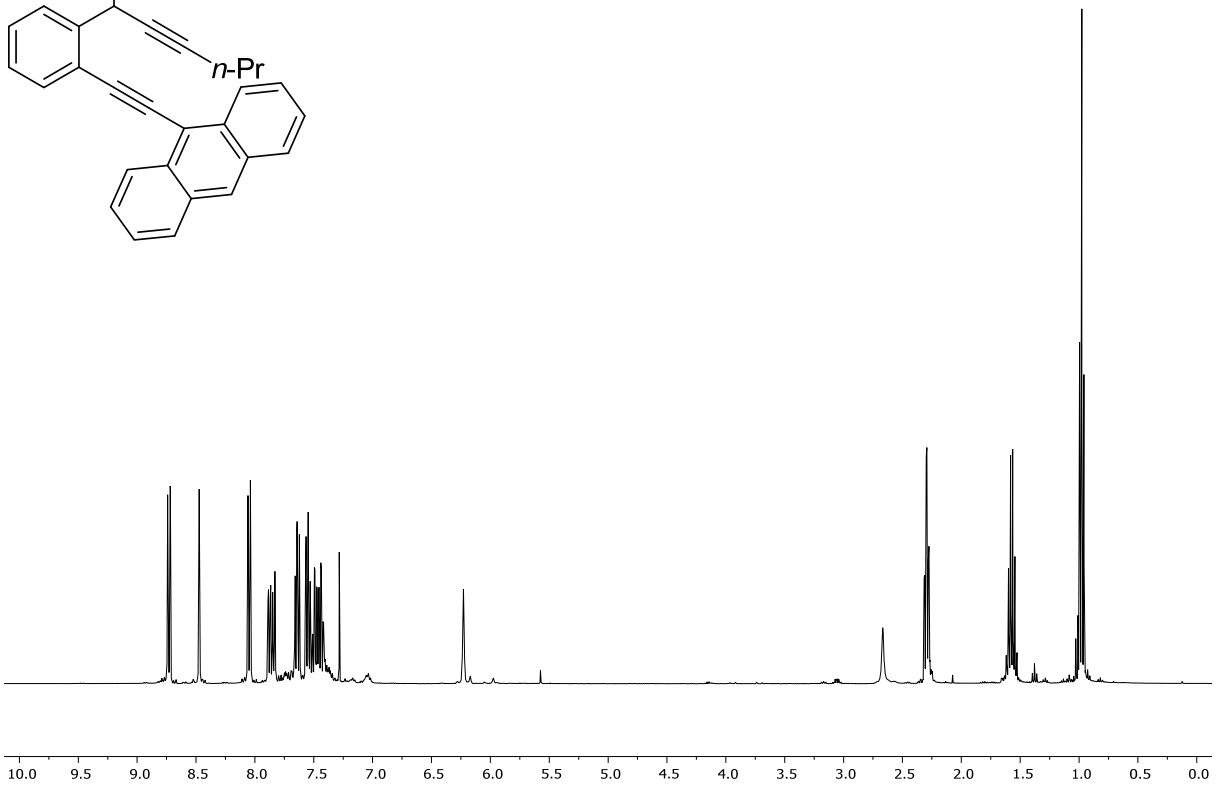


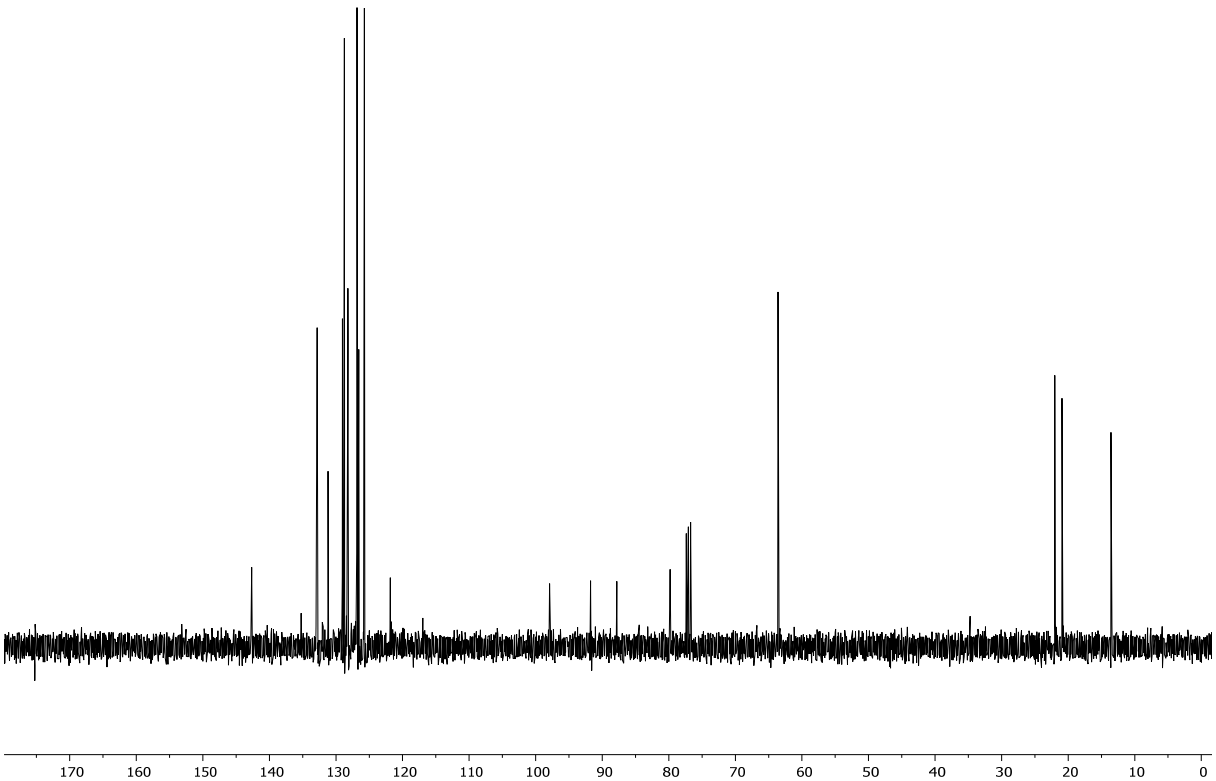
1-(2-(Phenanthren-9-ylethynyl)phenyl)hex-2-yn-1-ol (8b).



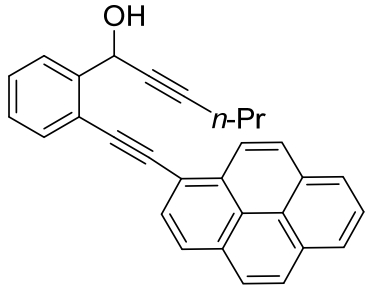
1-(2-(Anthracen-9-ylethynyl)phenyl)hex-2-yn-1-ol (8c).

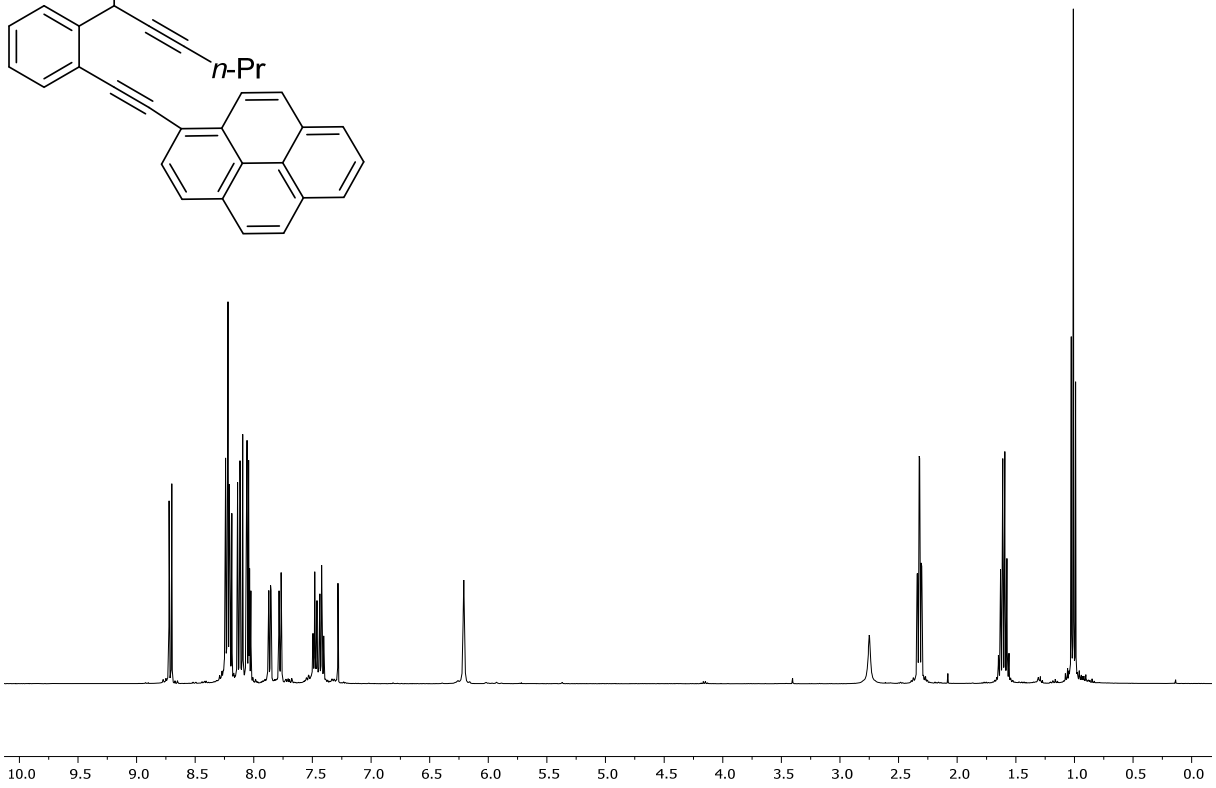


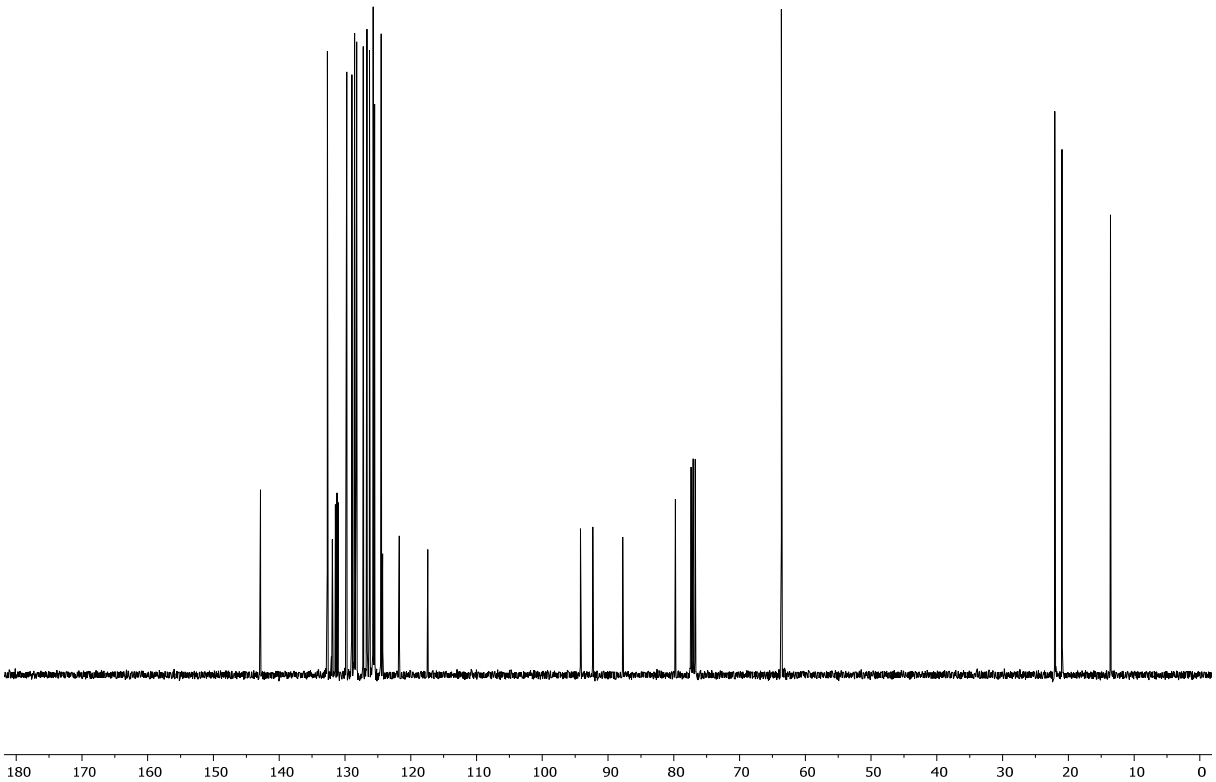




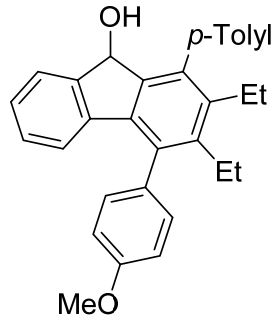
1-(2-(Pyren-2-ylethynyl)phenyl)hex-2-yn-1-ol (8d).

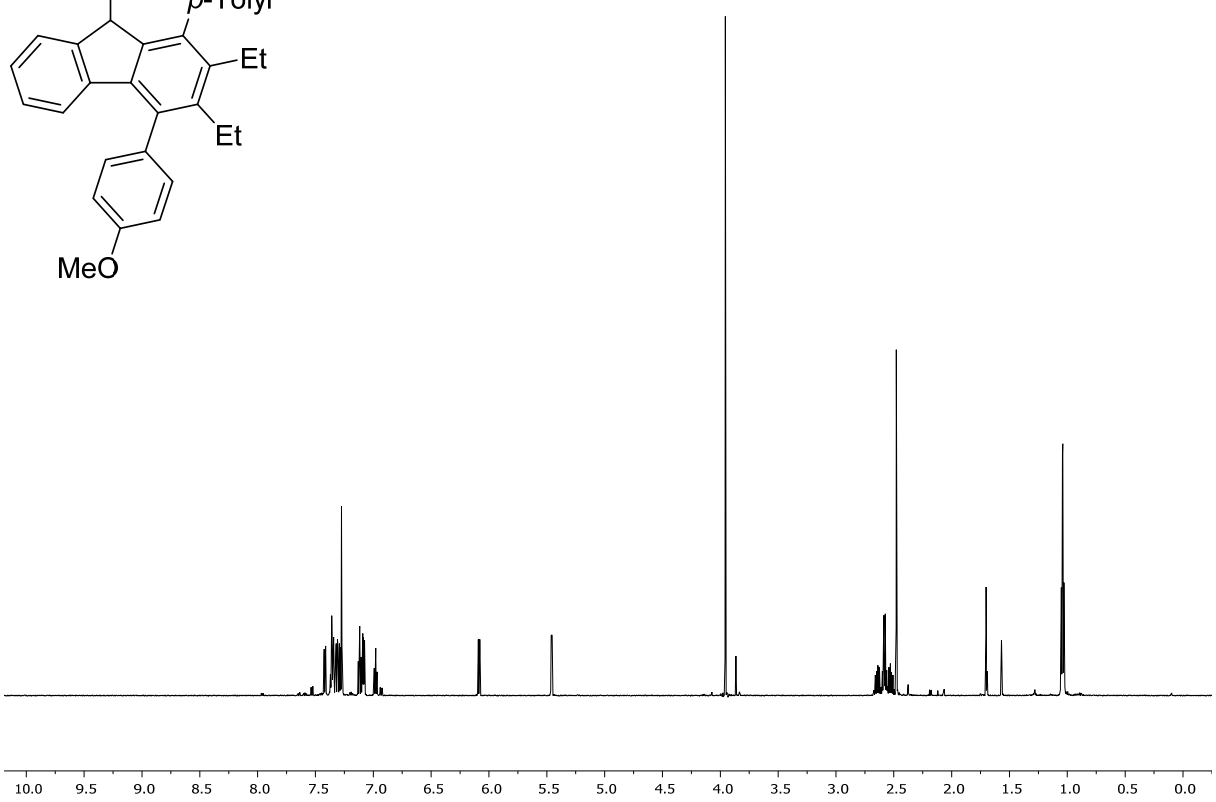


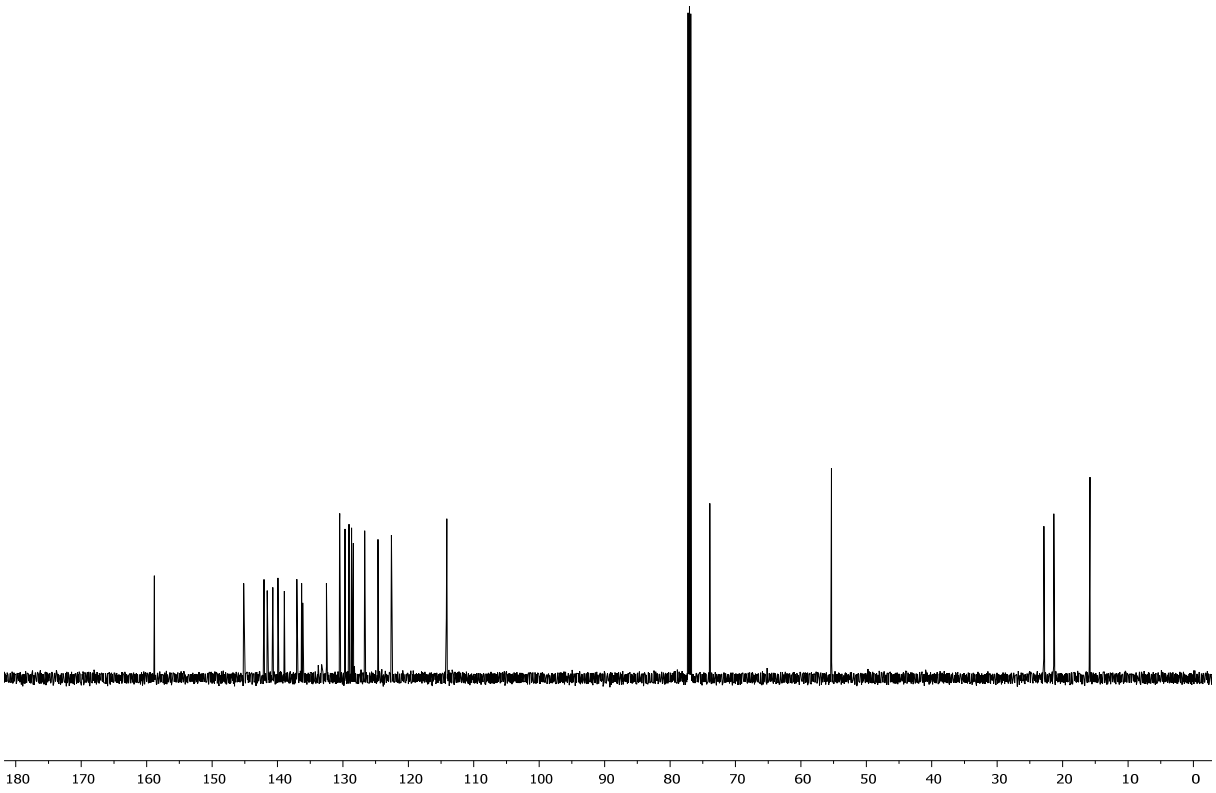




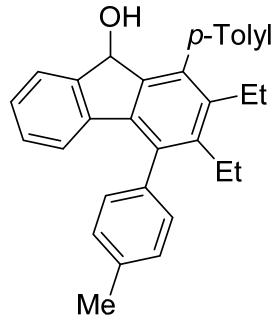
2,3-Diethyl-4-(4-methoxyphenyl)-1-(*p*-tolyl)-9*H*-fluoren-9-ol (2a).

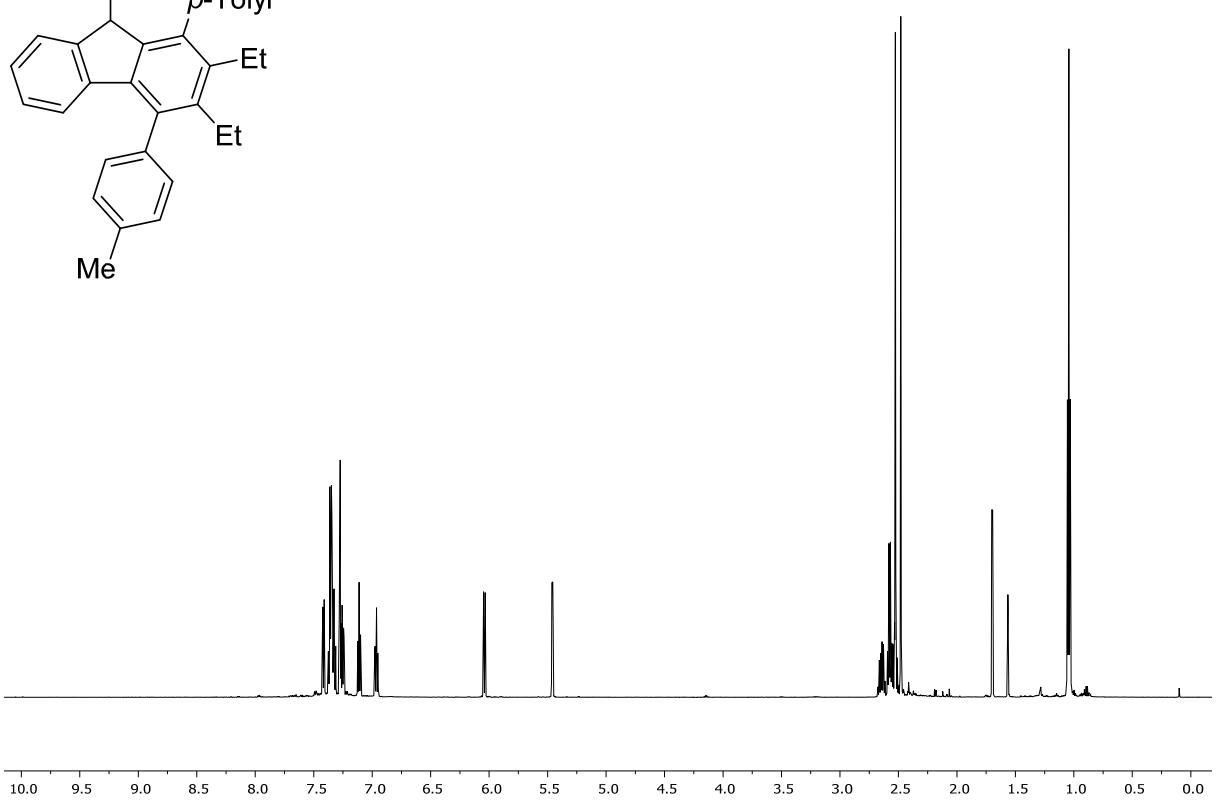


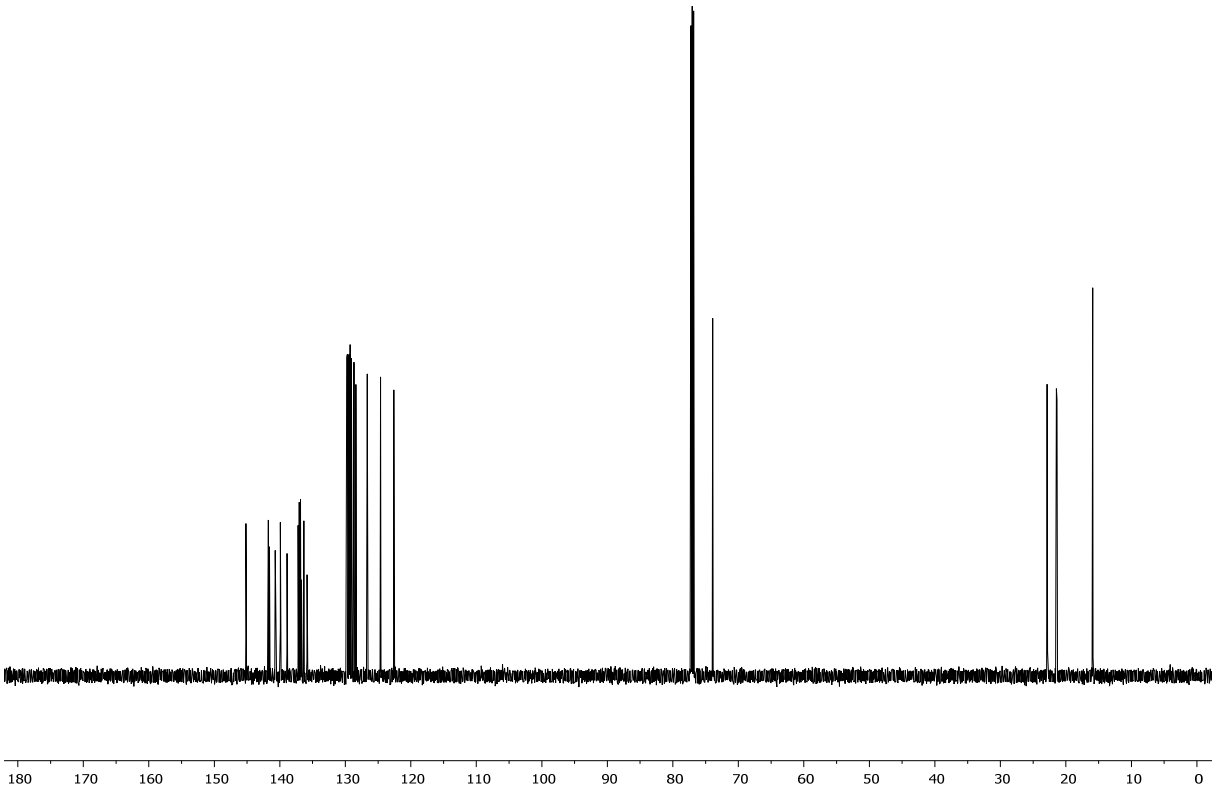




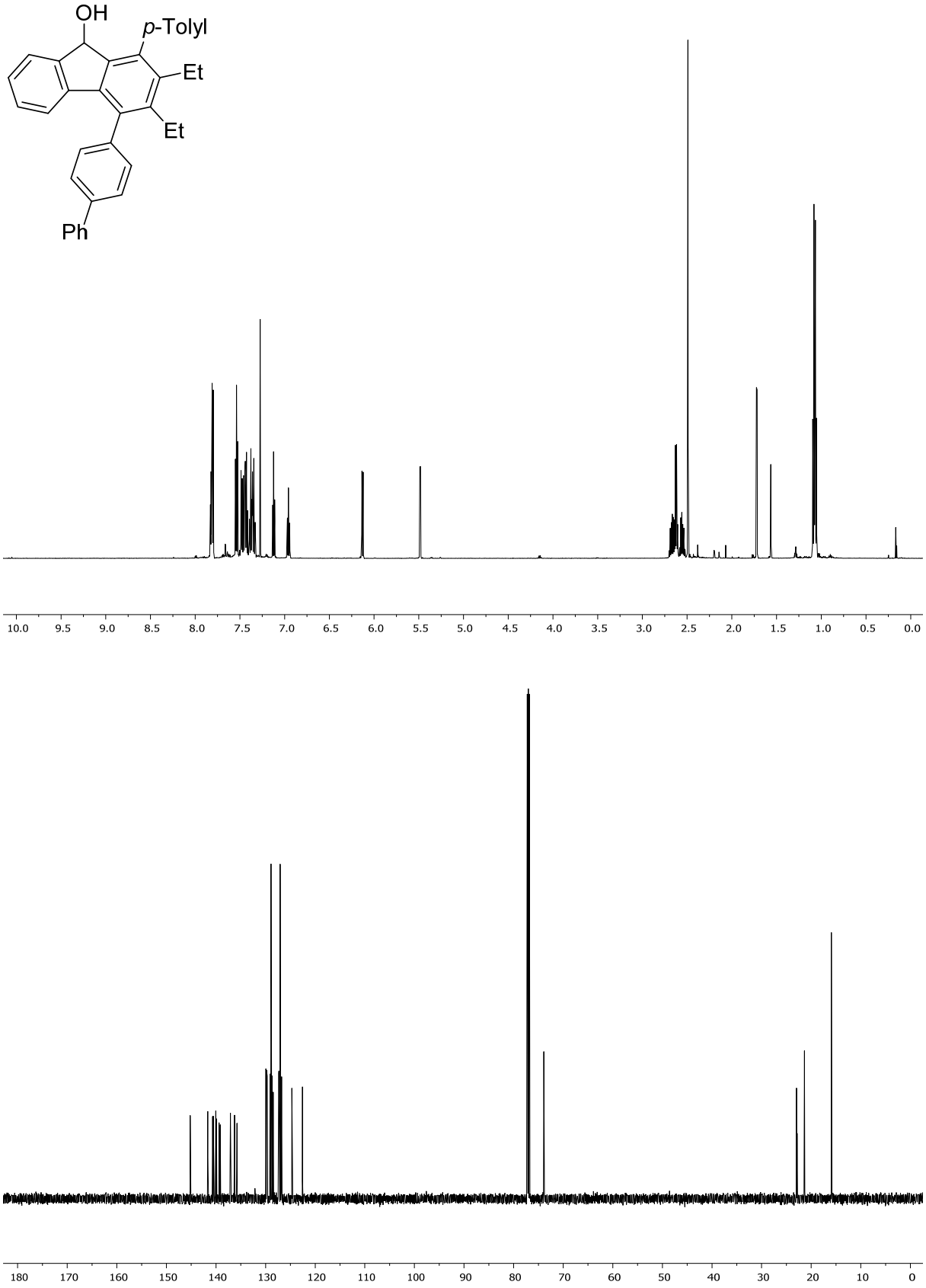
2,3-Diethyl-1,4-di-*p*-tolyl-9*H*-fluoren-9-ol (2b).



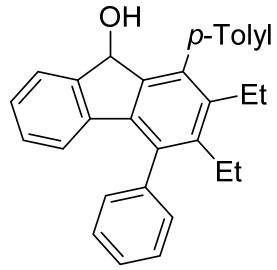


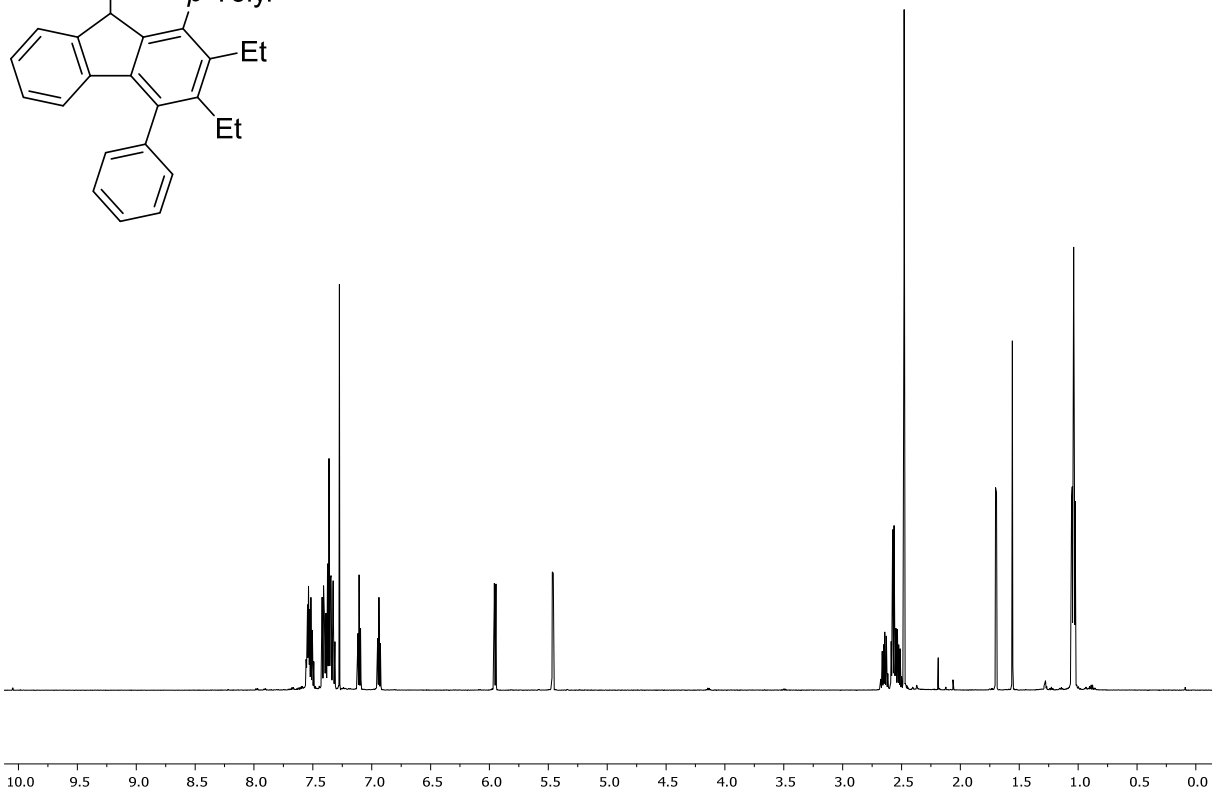


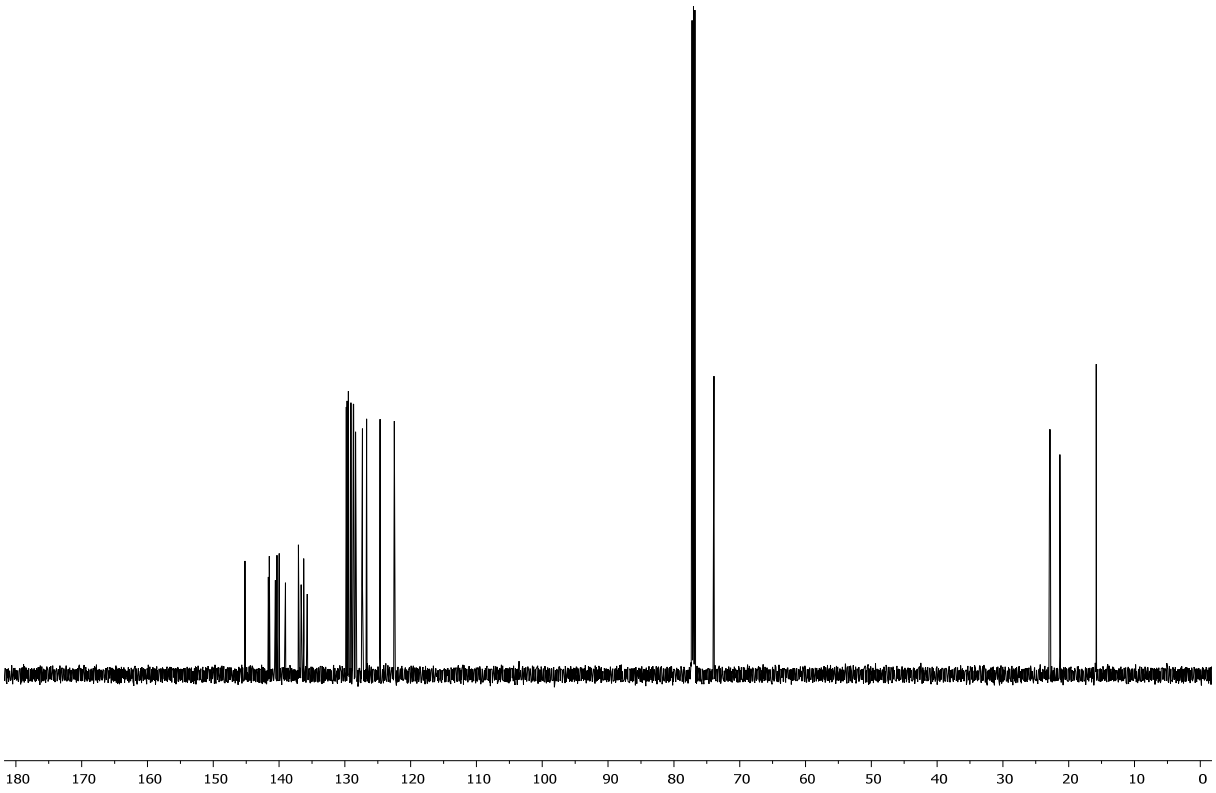
4-([1,1'-Biphenyl]-4-yl)-2,3-diethyl-1-(*p*-tolyl)-9*H*-fluoren-9-ol (2v).



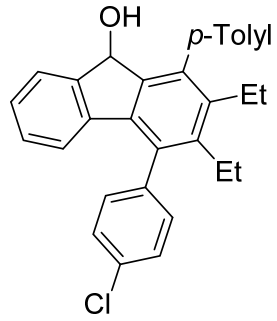
2,3-Diethyl-4-phenyl-1-(*p*-tolyl)-9*H*-fluoren-9-ol (2d).

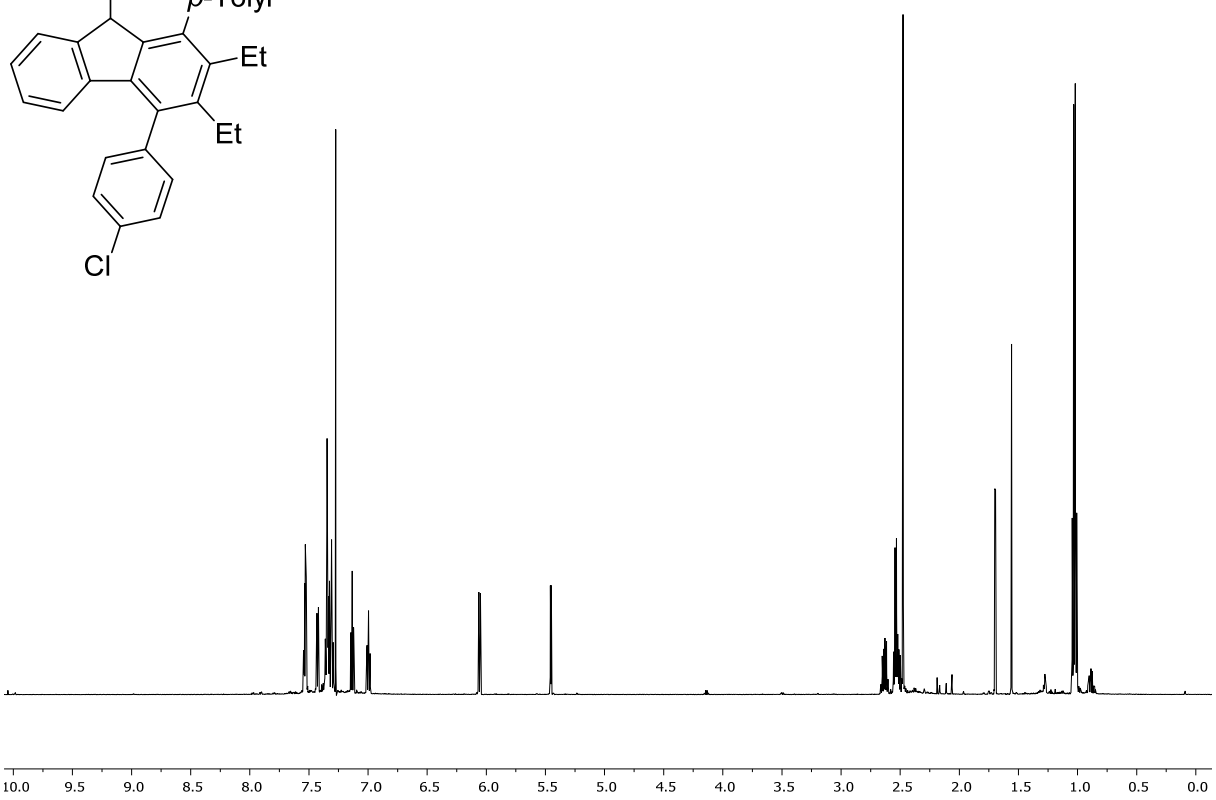


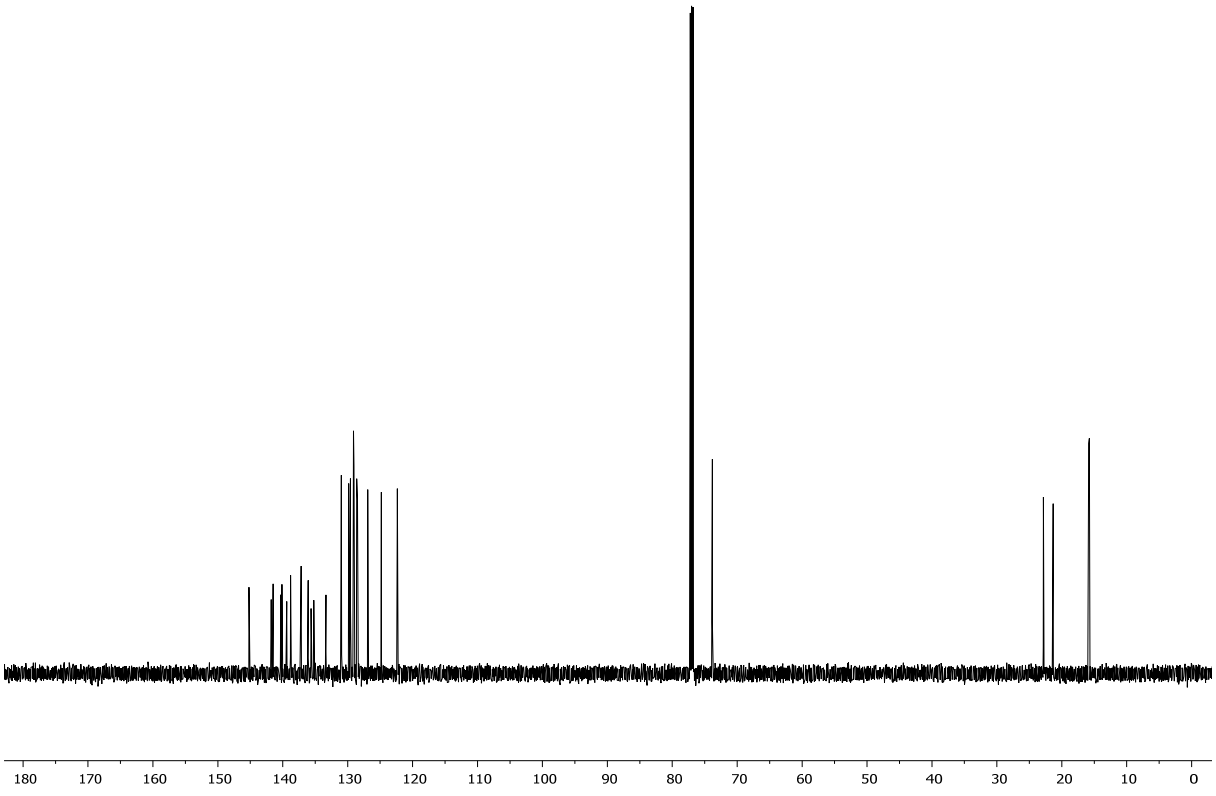




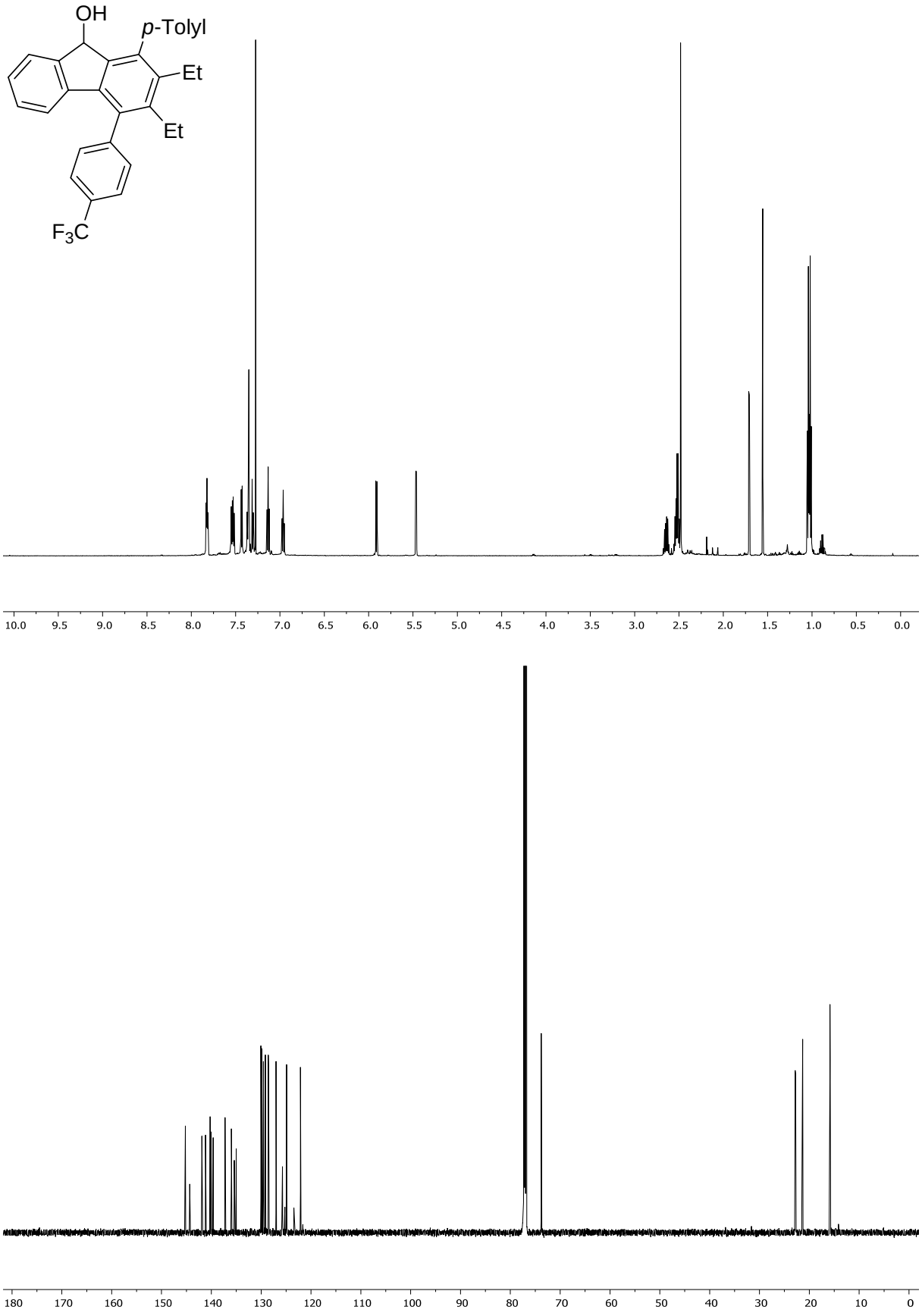
4-(4-Chlorophenyl)-2,3-diethyl-1-(*p*-tolyl)-9*H*-fluoren-9-ol (2e).



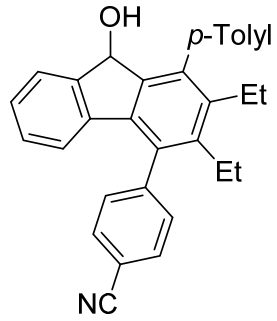


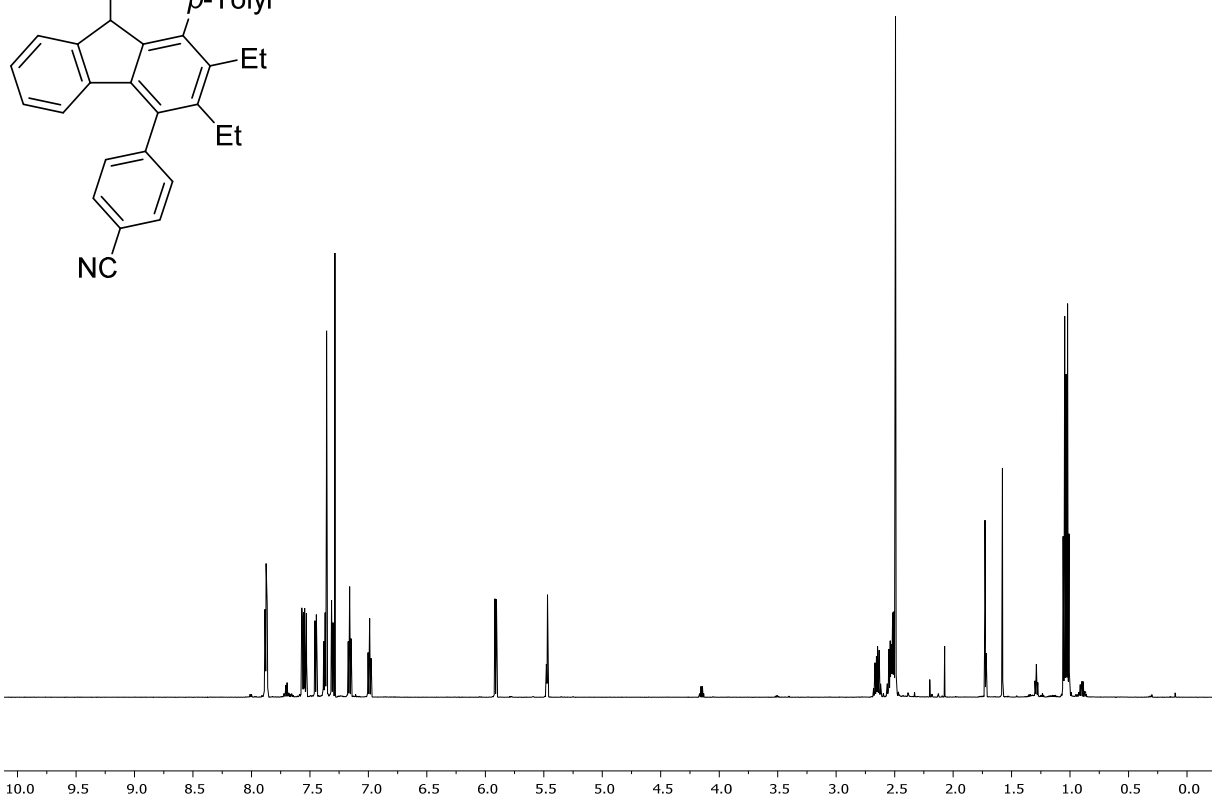


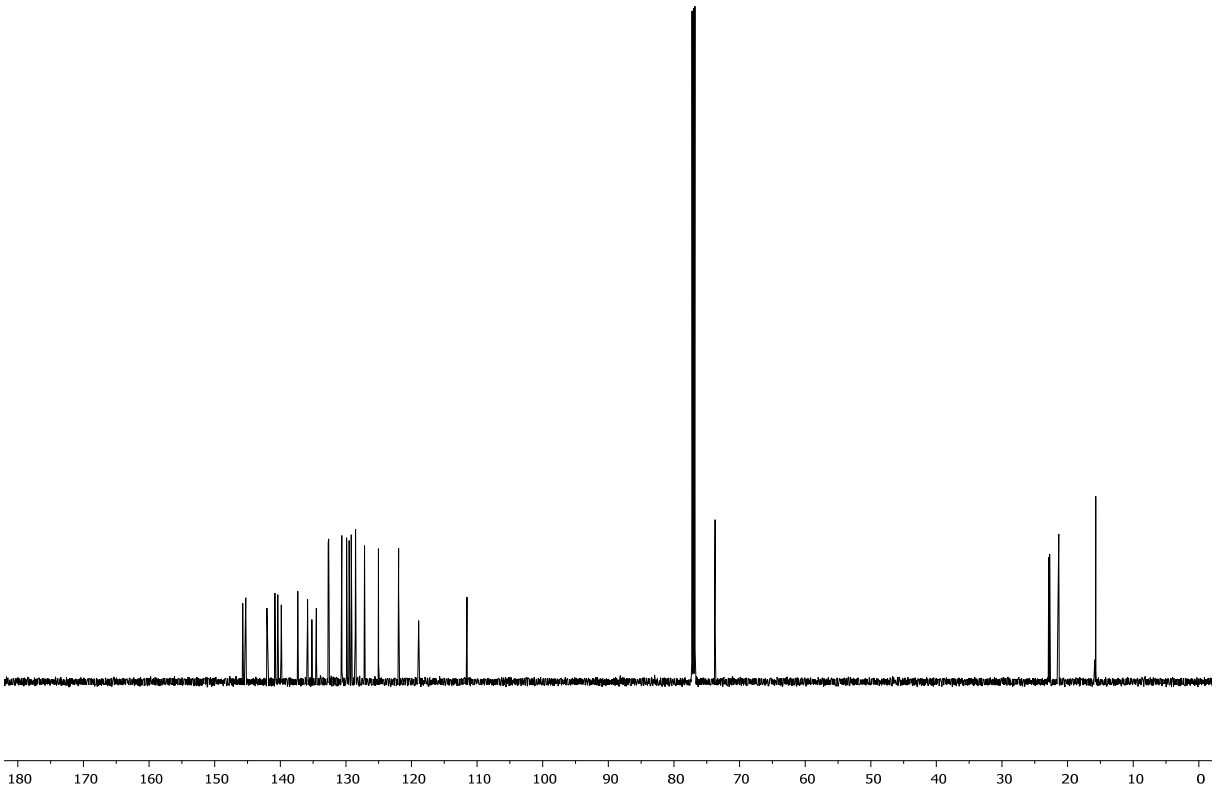
2,3-Diethyl-1-(*p*-tolyl)-4-(4-(trifluoromethyl)phenyl)-9*H*-fluoren-9-ol (2f).



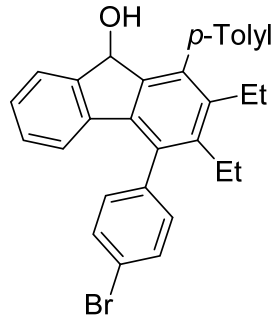
4-(2,3-Diethyl-9-hydroxy-1-(*p*-tolyl)-9*H*-fluoren-4-yl)benzonitrile (2g).

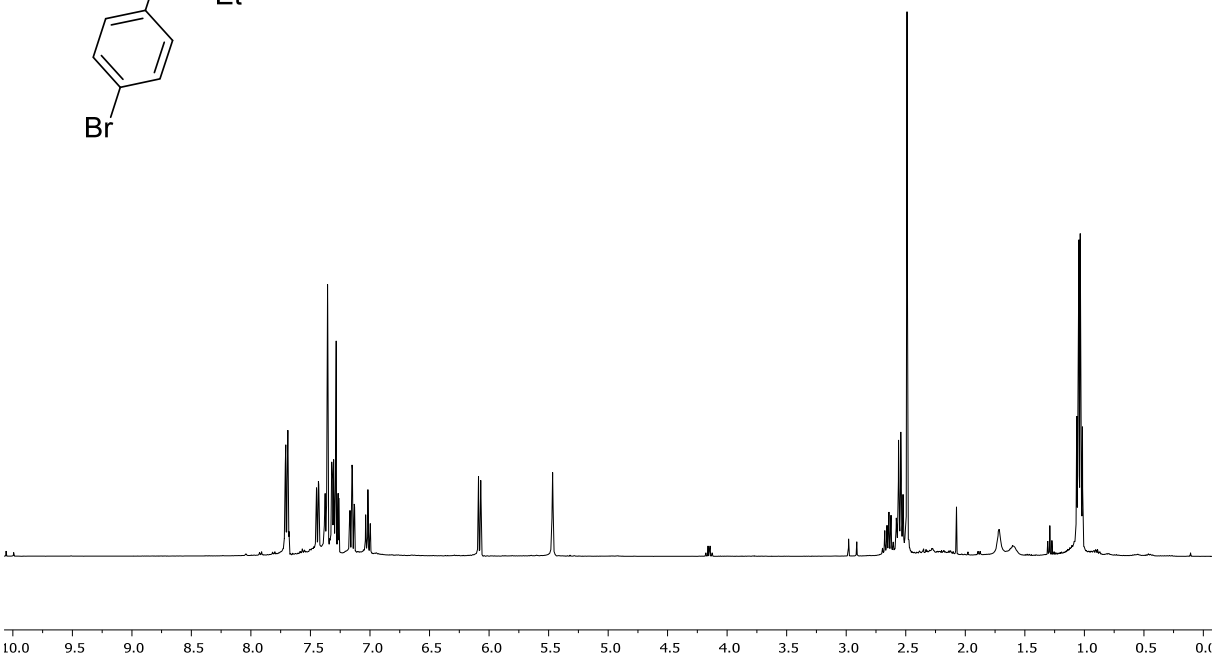


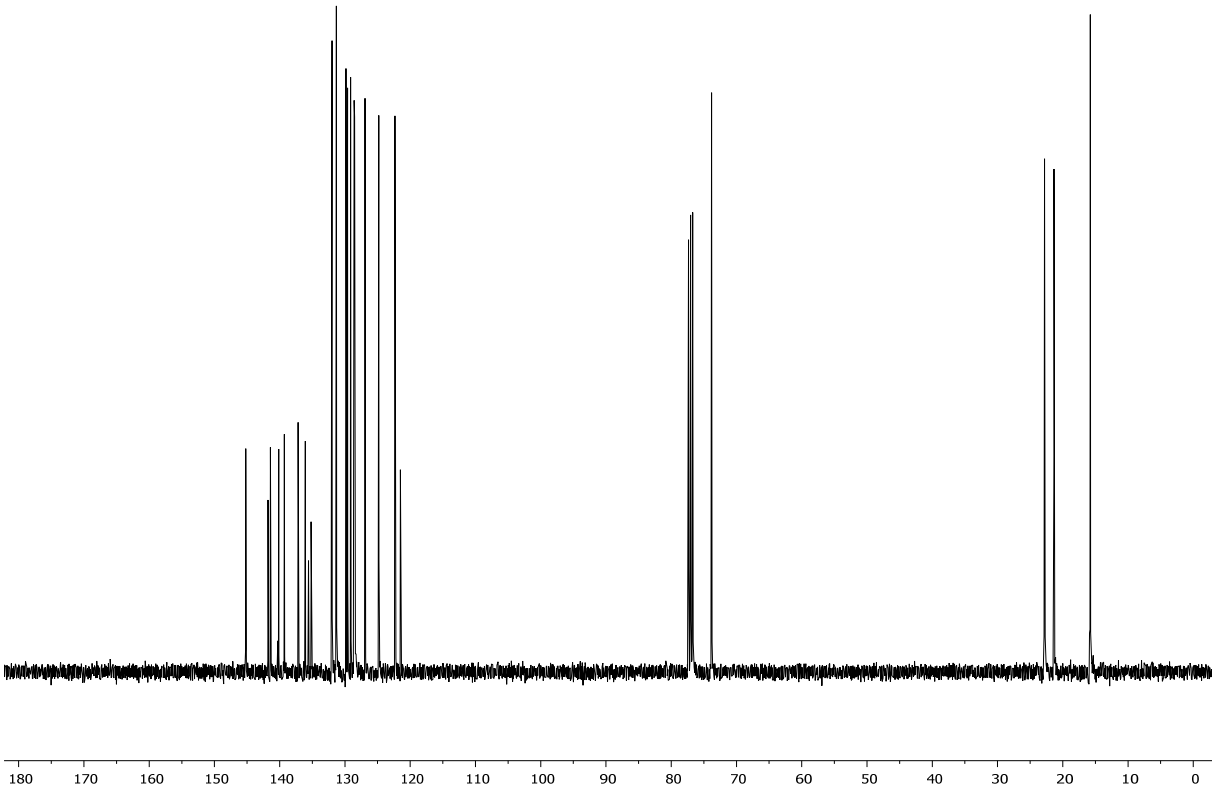




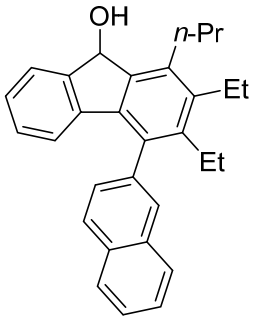
4-(4-Bromophenyl)-2,3-diethyl-1-(*p*-tolyl)-9*H*-fluoren-9-ol (2h).

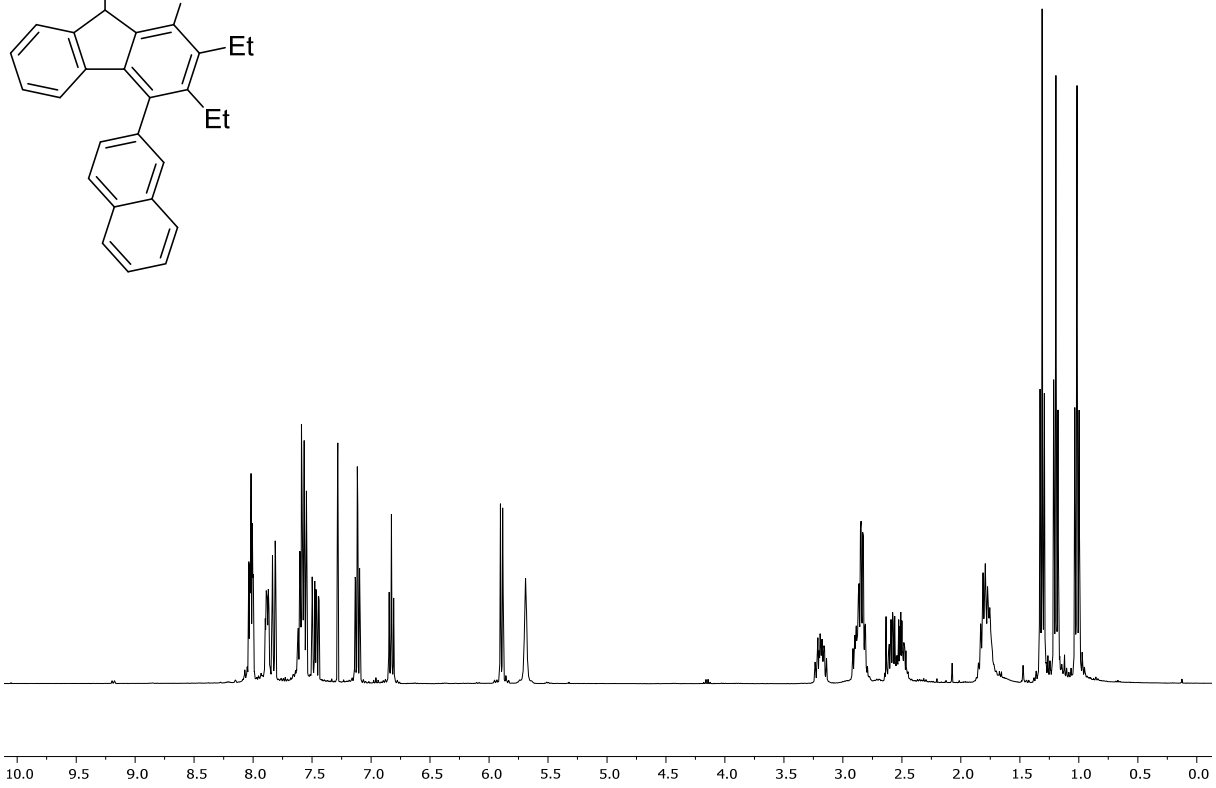


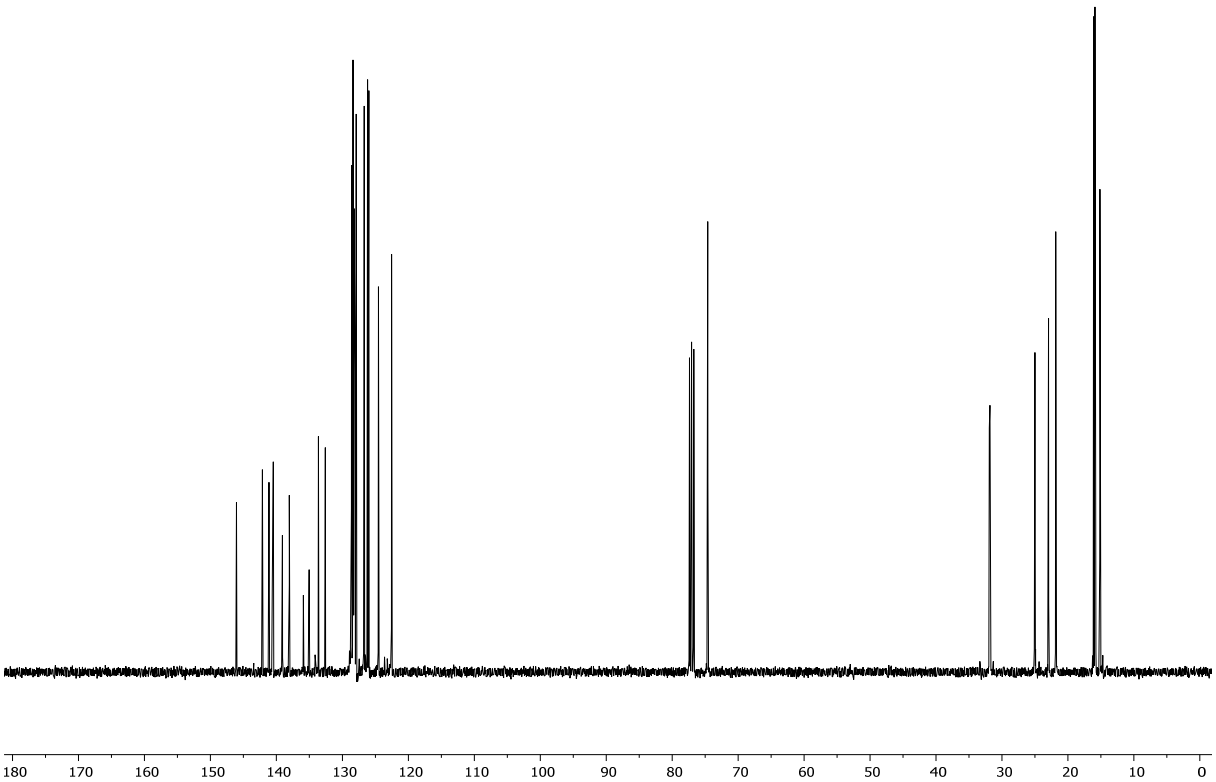




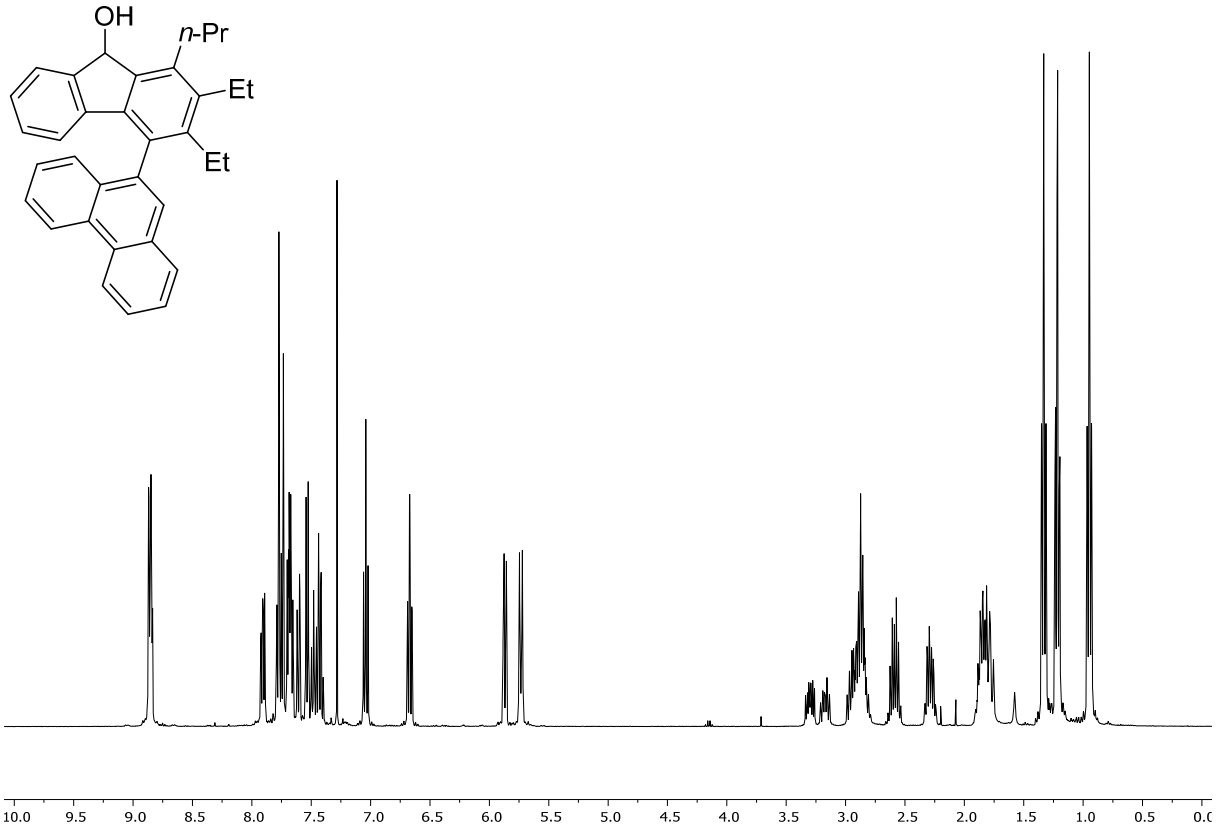
2,3-Diethyl-4-(naphthalen-2-yl)-1-propyl-9*H*-fluoren-9-ol (9a).

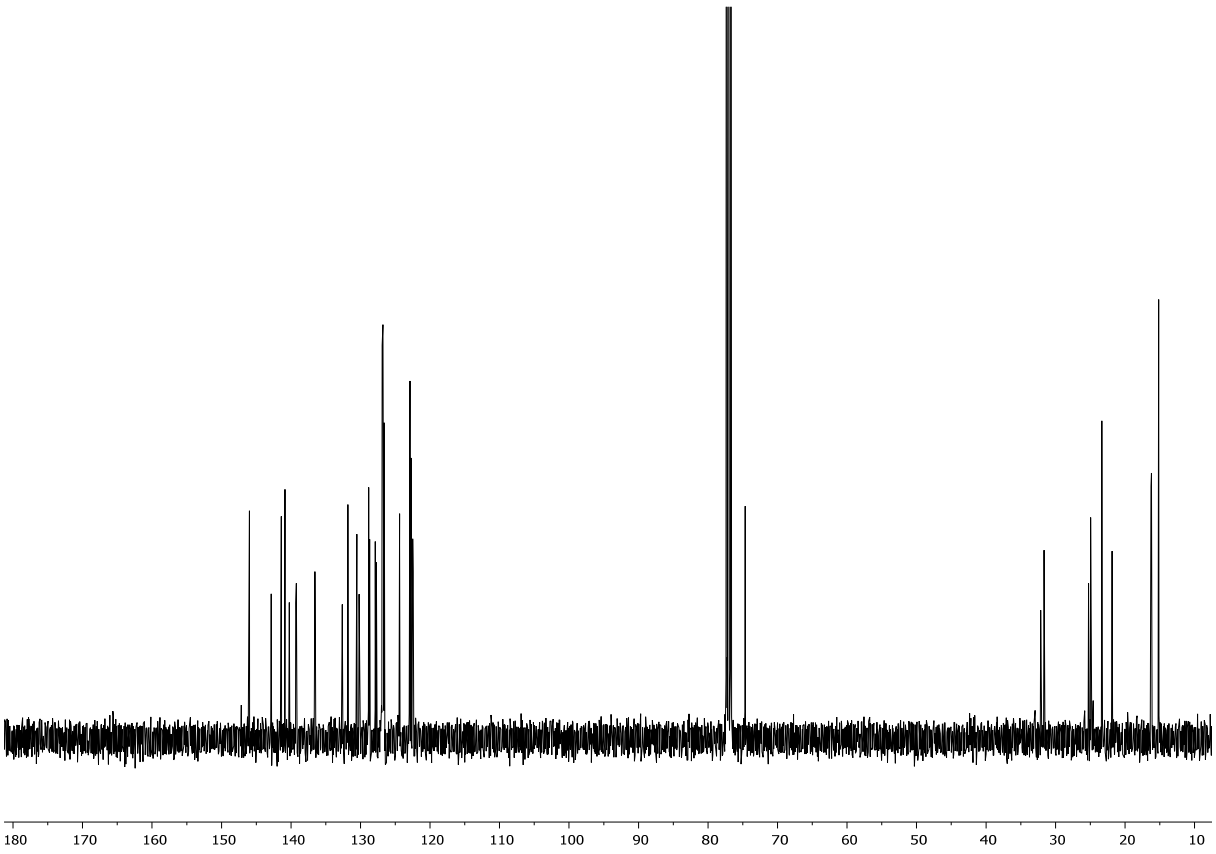




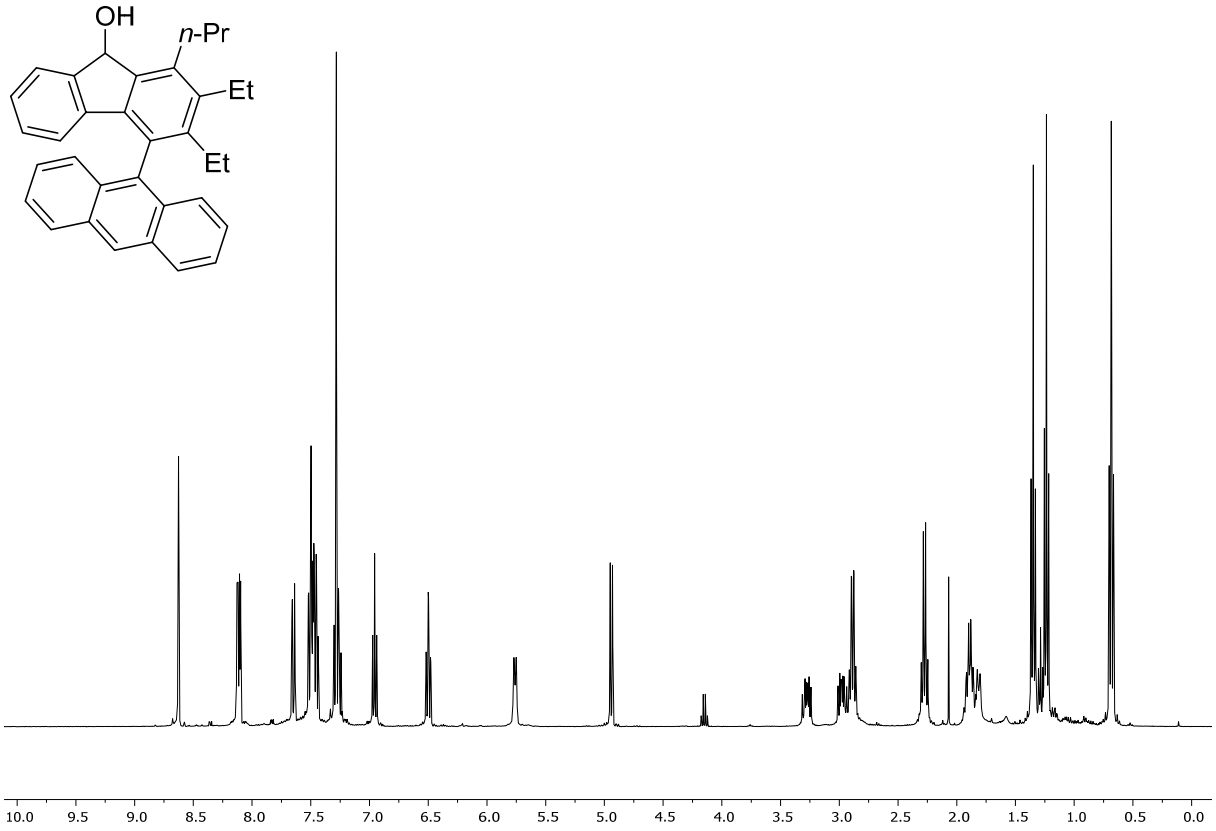


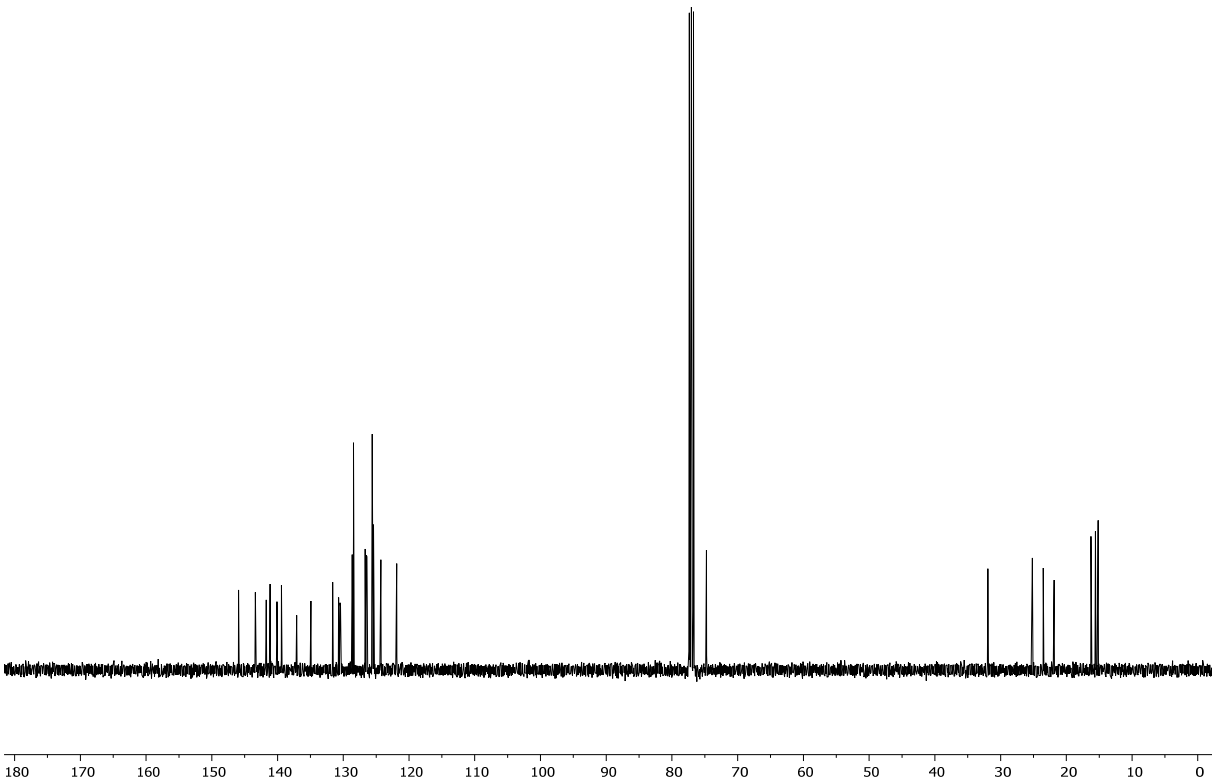
2,3-Diethyl-4-(phenanthren-9-yl)-1-propyl-9*H*-fluoren-9-ol (9b).



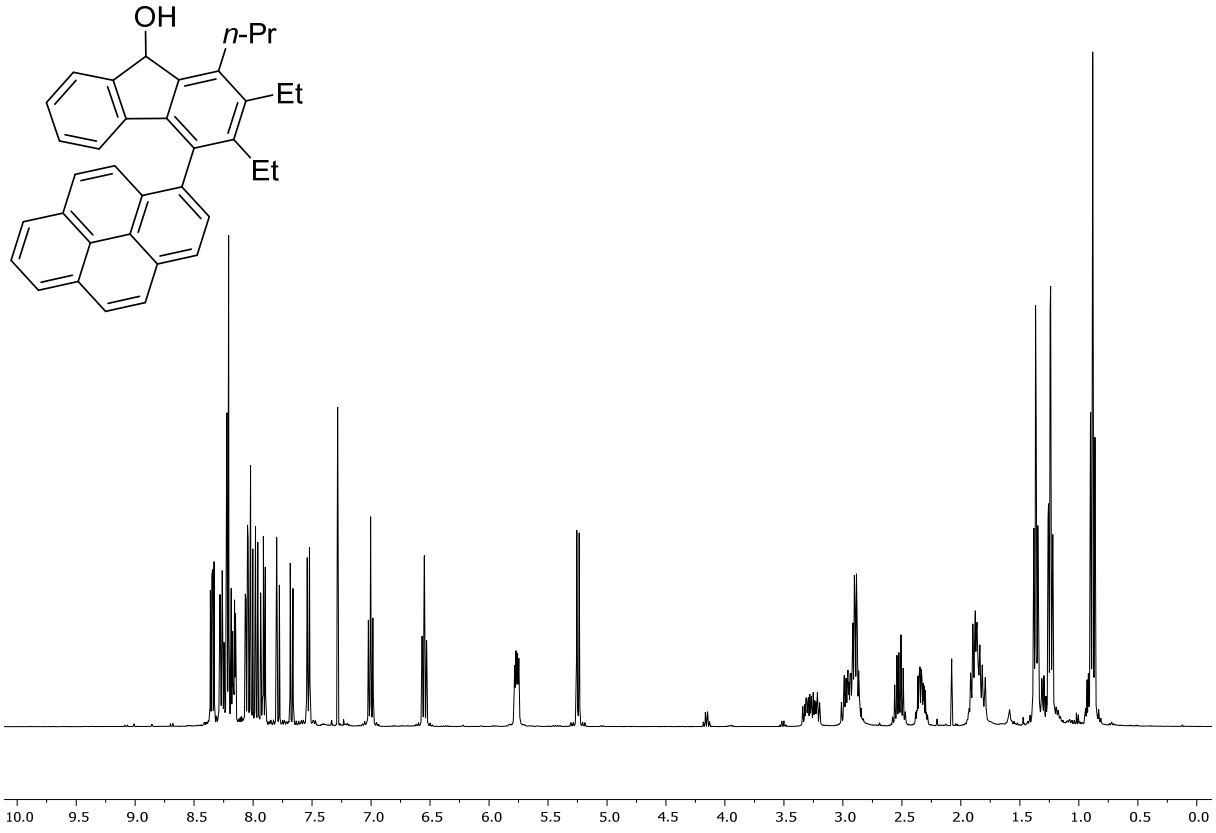


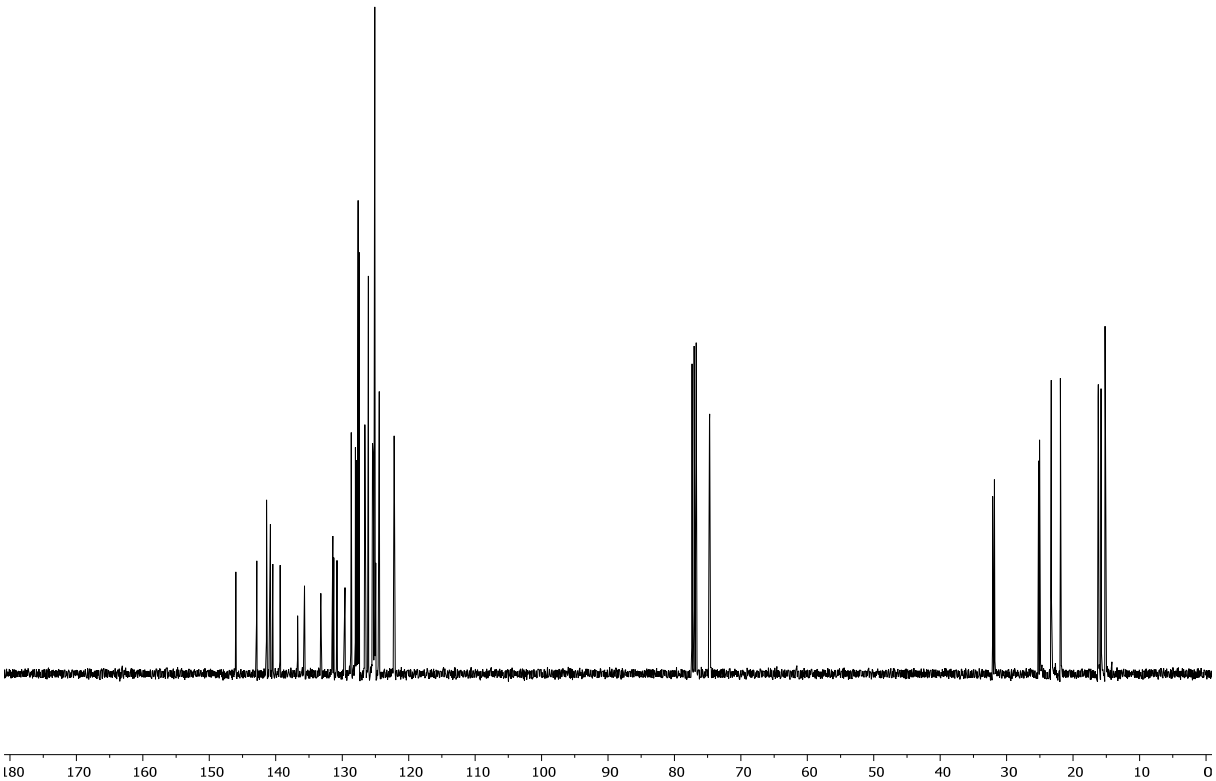
4-(Anthracen-9-yl)-2,3-diethyl-1-propyl-9*H*-fluoren-9-ol (9c).

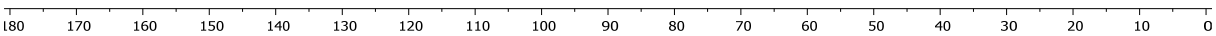




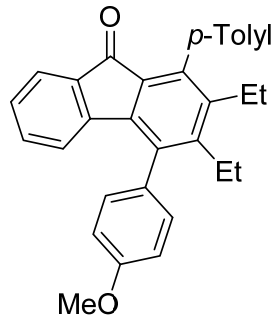
2,3-Diethyl-1-propyl-4-(pyren-2-yl)-9*H*-fluoren-9-ol (9d).

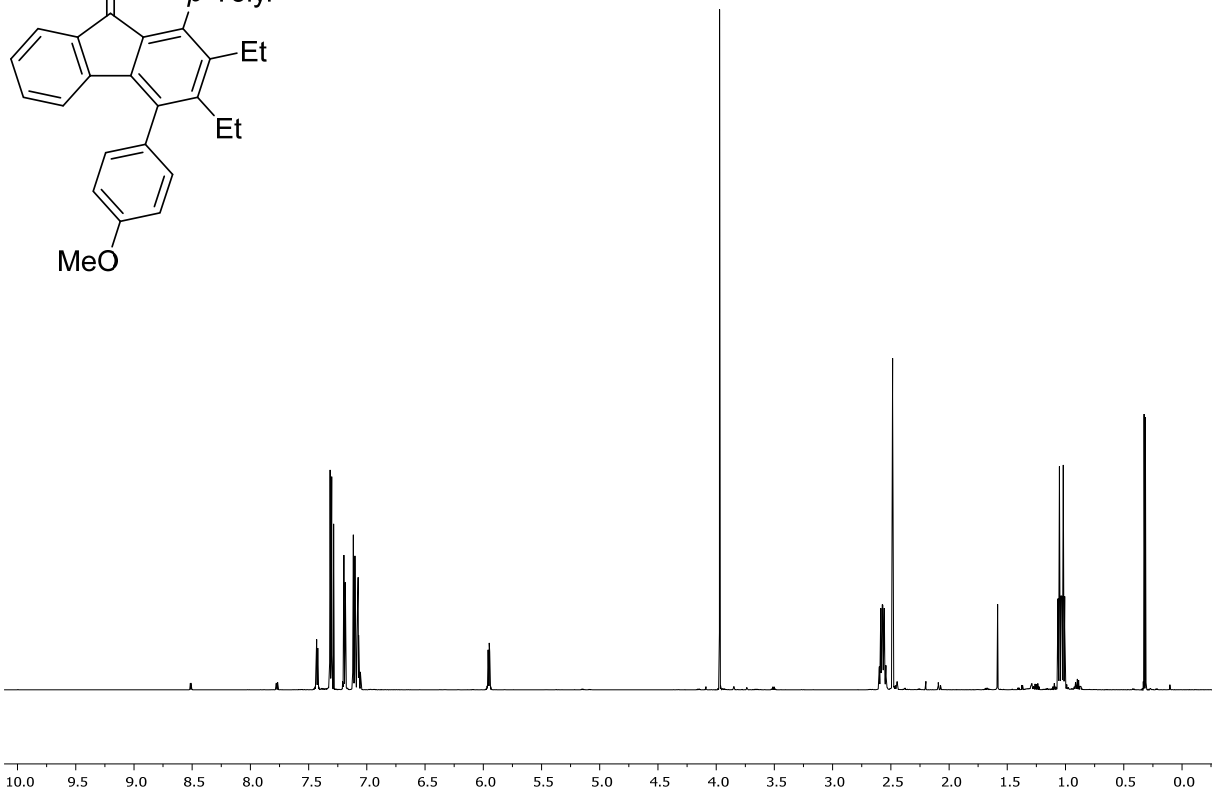


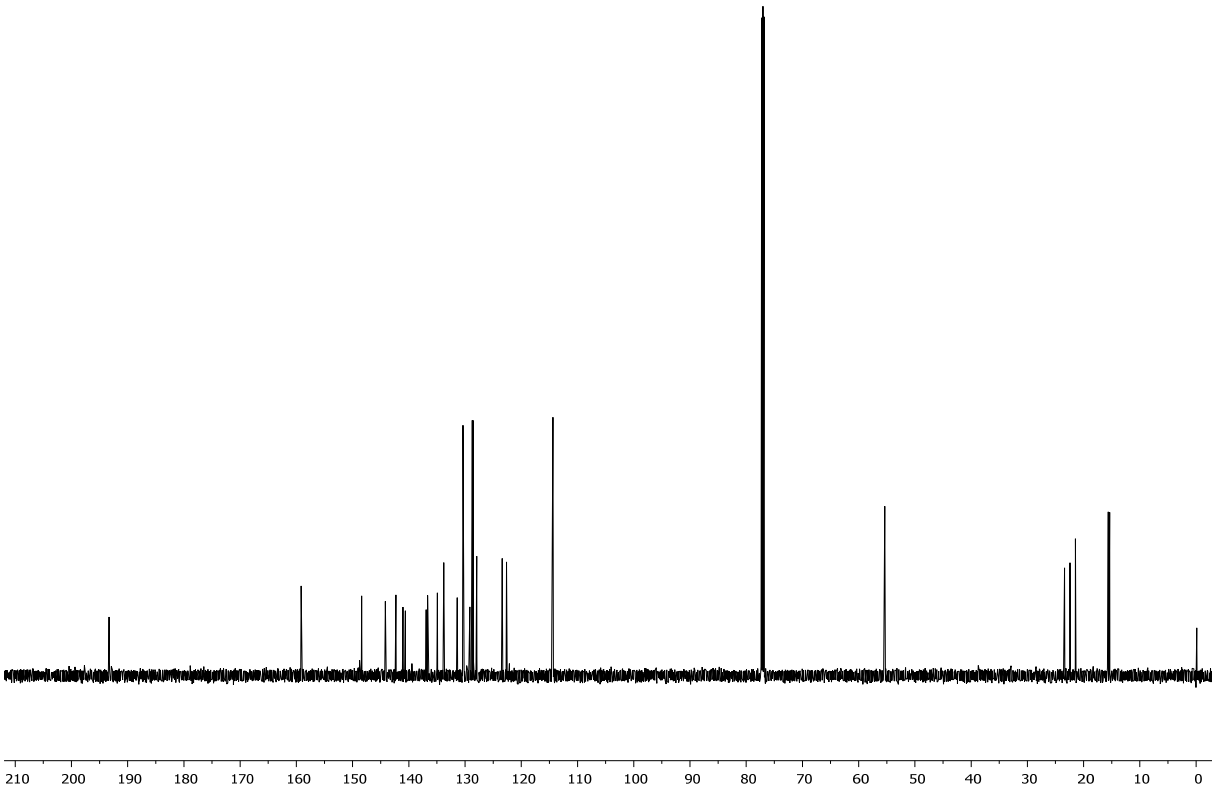




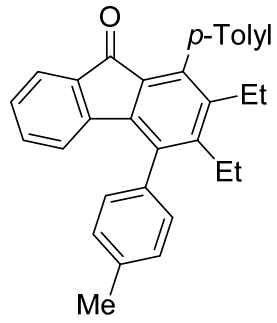
2,3-Diethyl-4-(4-methoxyphenyl)-1-(*p*-tolyl)-9*H*-fluoren-9-one (3a).

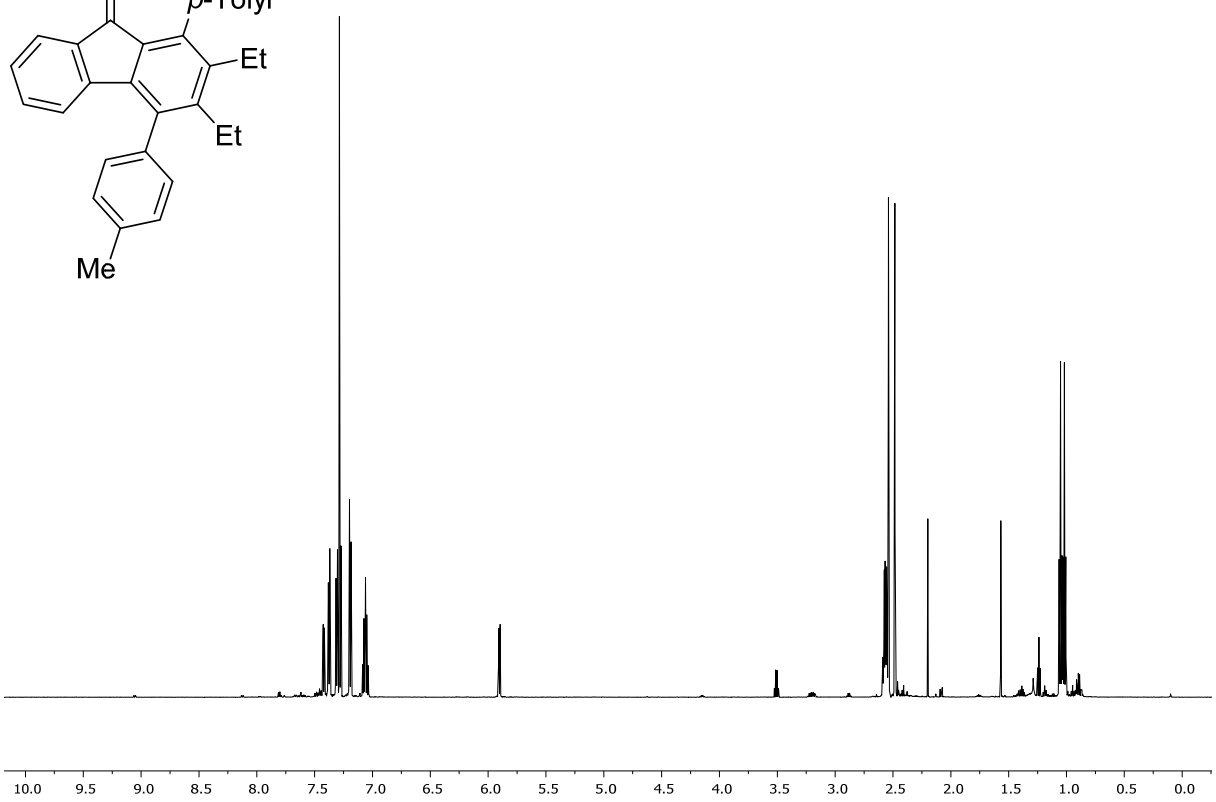


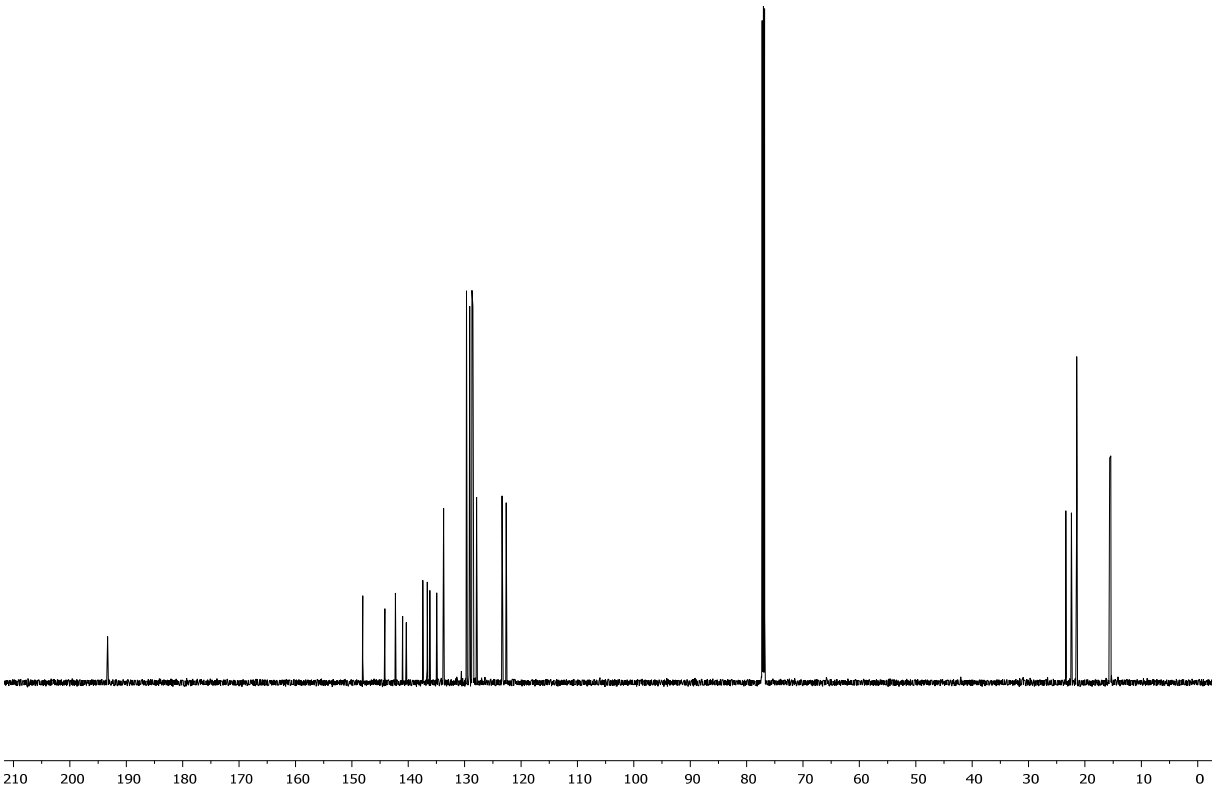




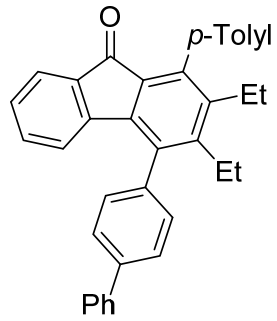
2,3-Diethyl-1,4-di-*p*-tolyl-9*H*-fluoren-9-one (3b).

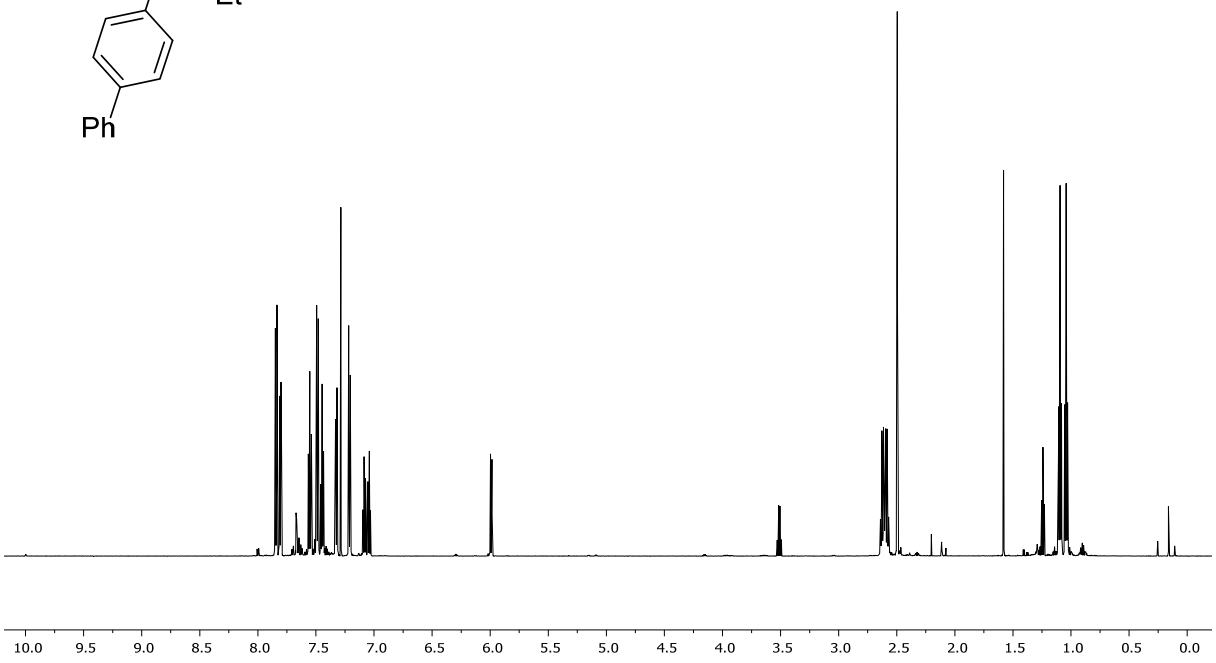


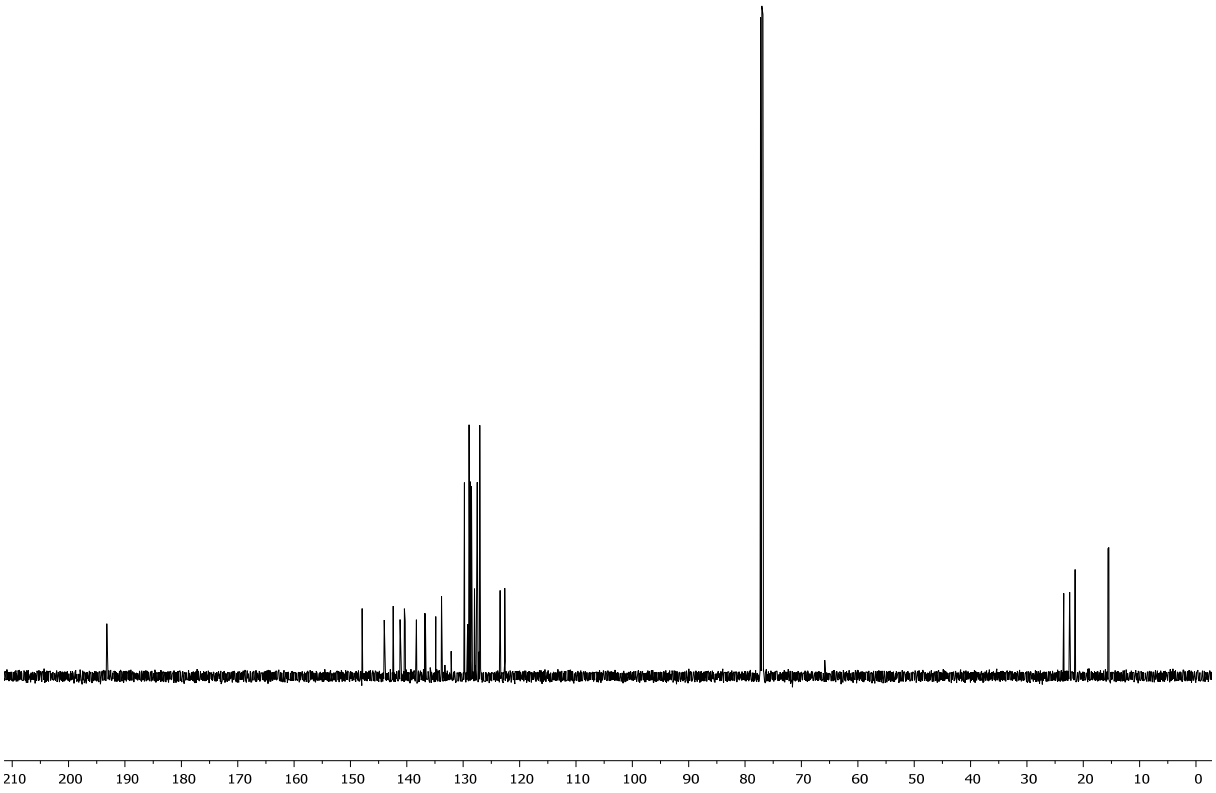




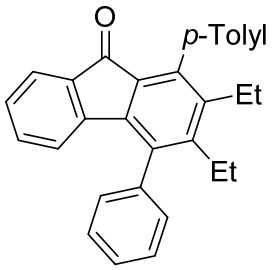
4-([1,1'-Biphenyl]-4-yl)-2,3-diethyl-1-(*p*-tolyl)-9*H*-fluoren-9-one (3c).

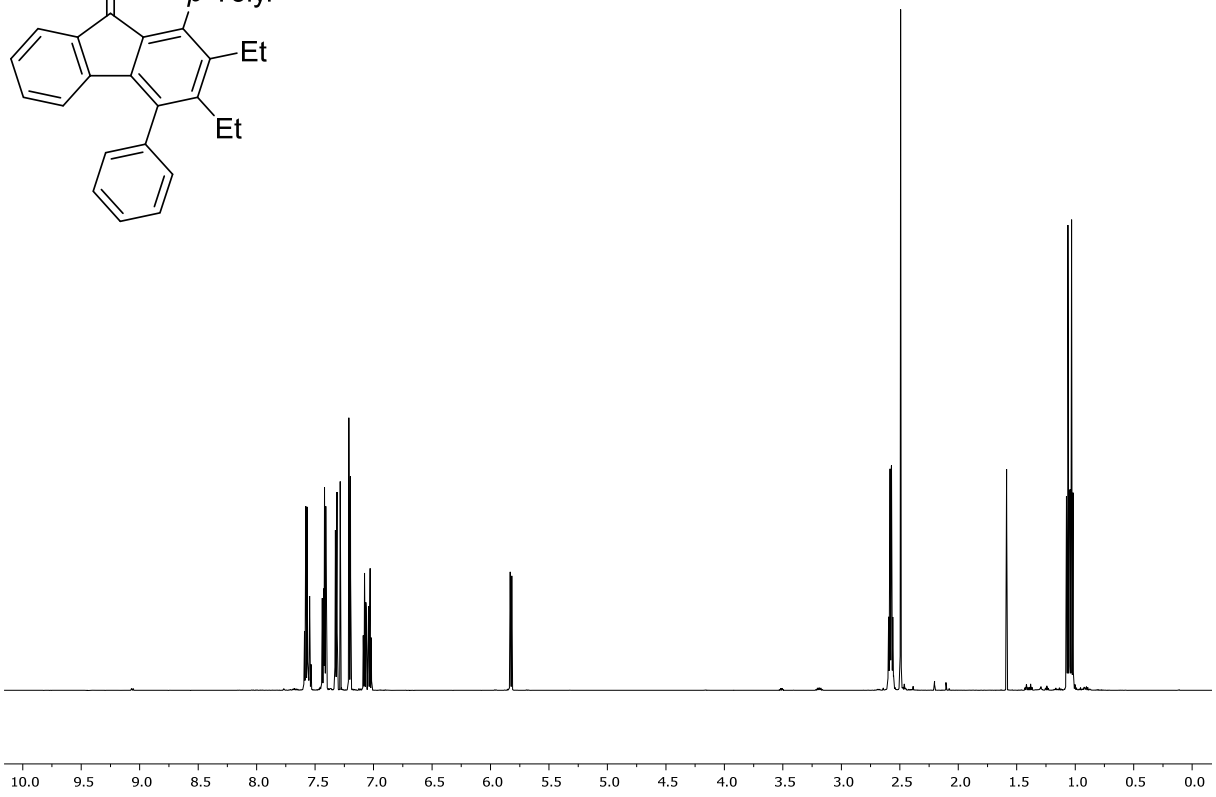


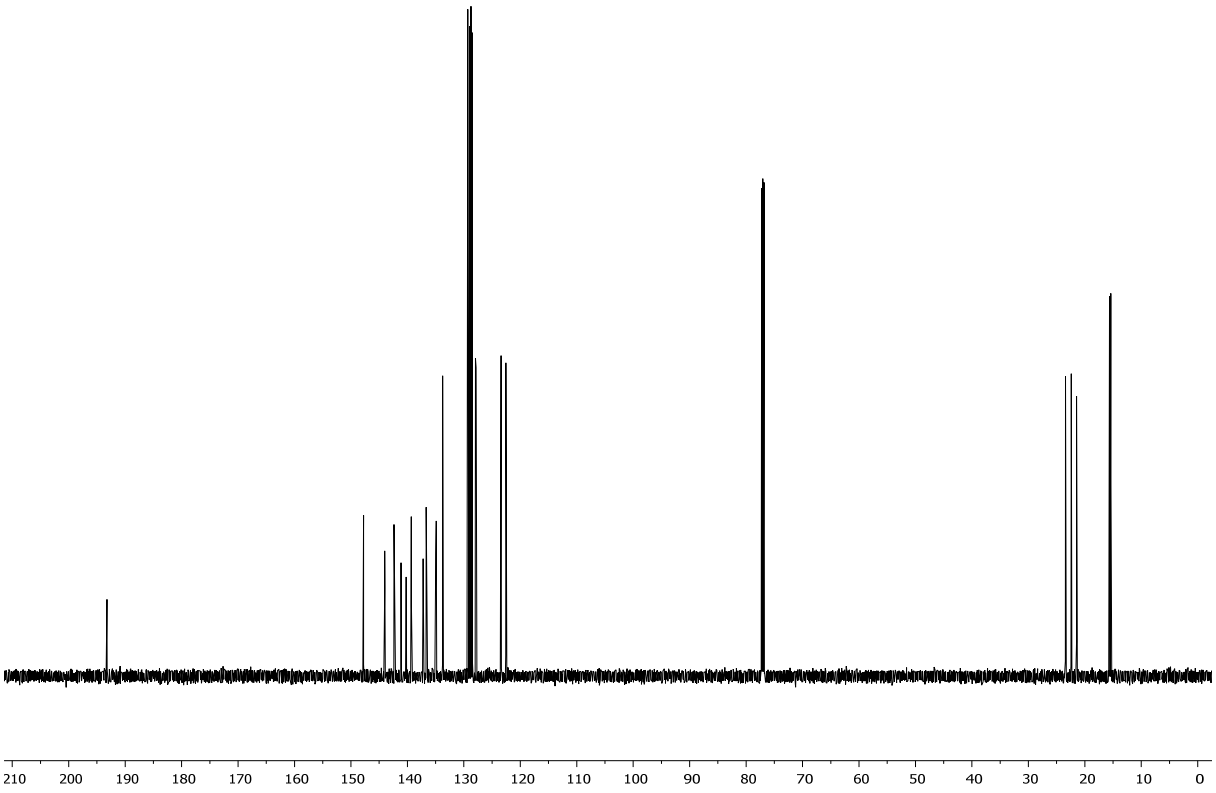




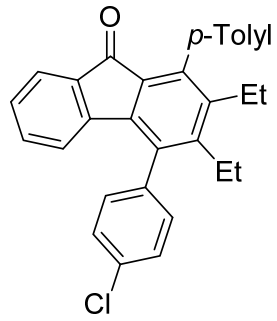
2,3-Diethyl-4-phenyl-1-(*p*-tolyl)-9*H*-fluoren-9-one (3d).

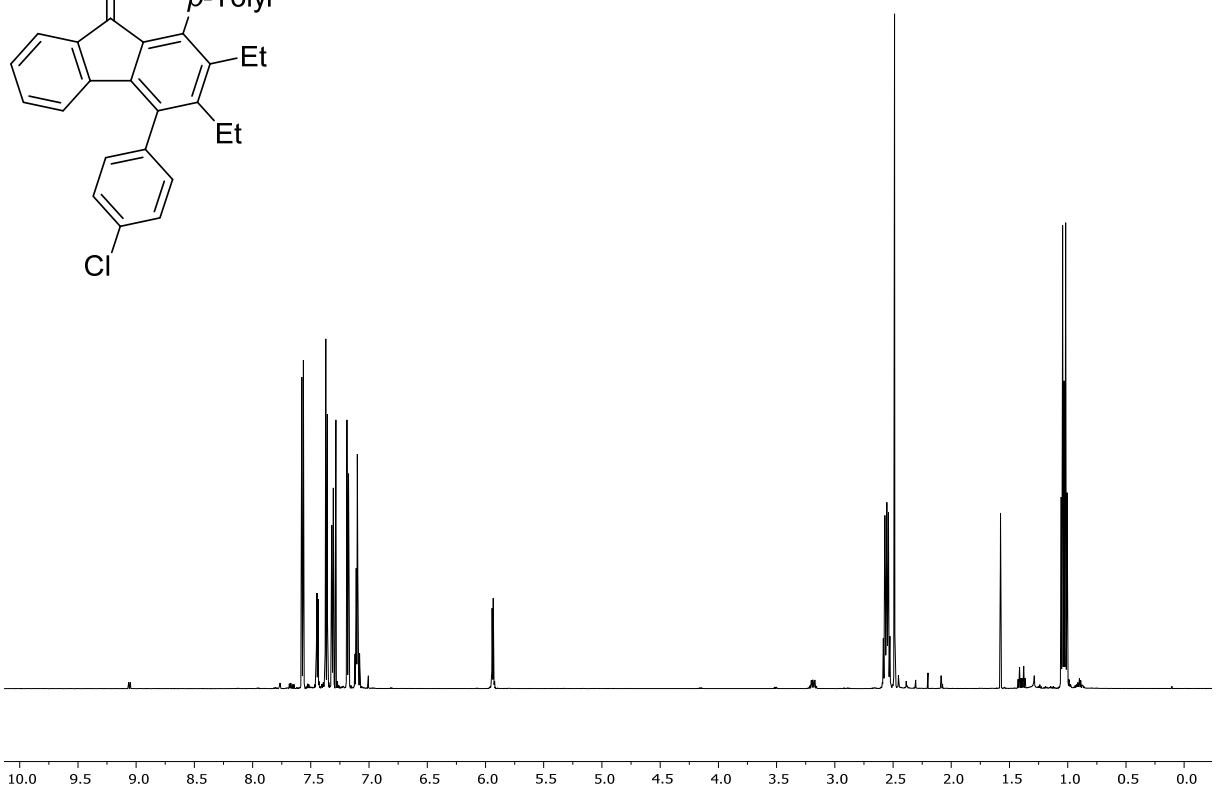


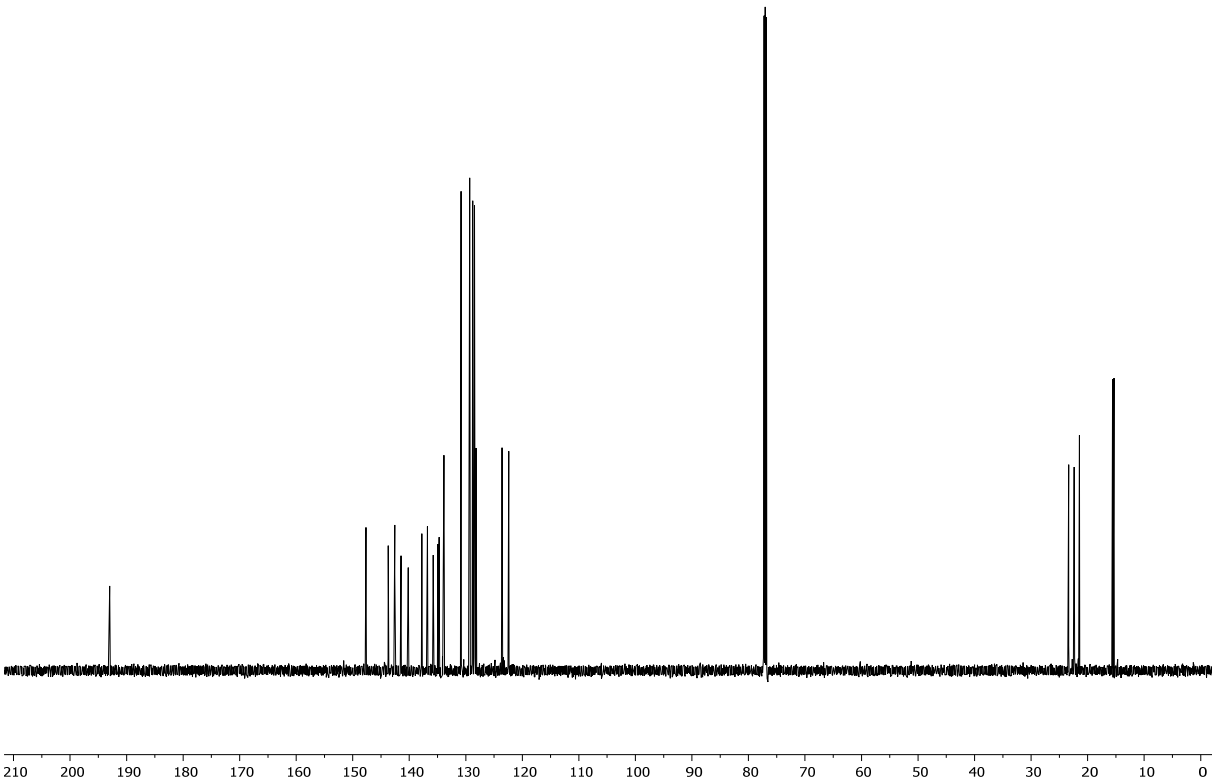




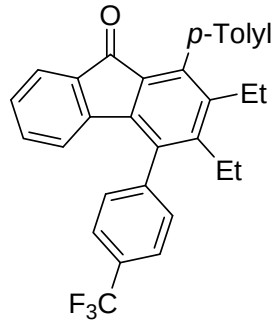
4-(4-Chlorophenyl)-2,3-diethyl-1-(*p*-tolyl)-9*H*-fluoren-9-one (3e).

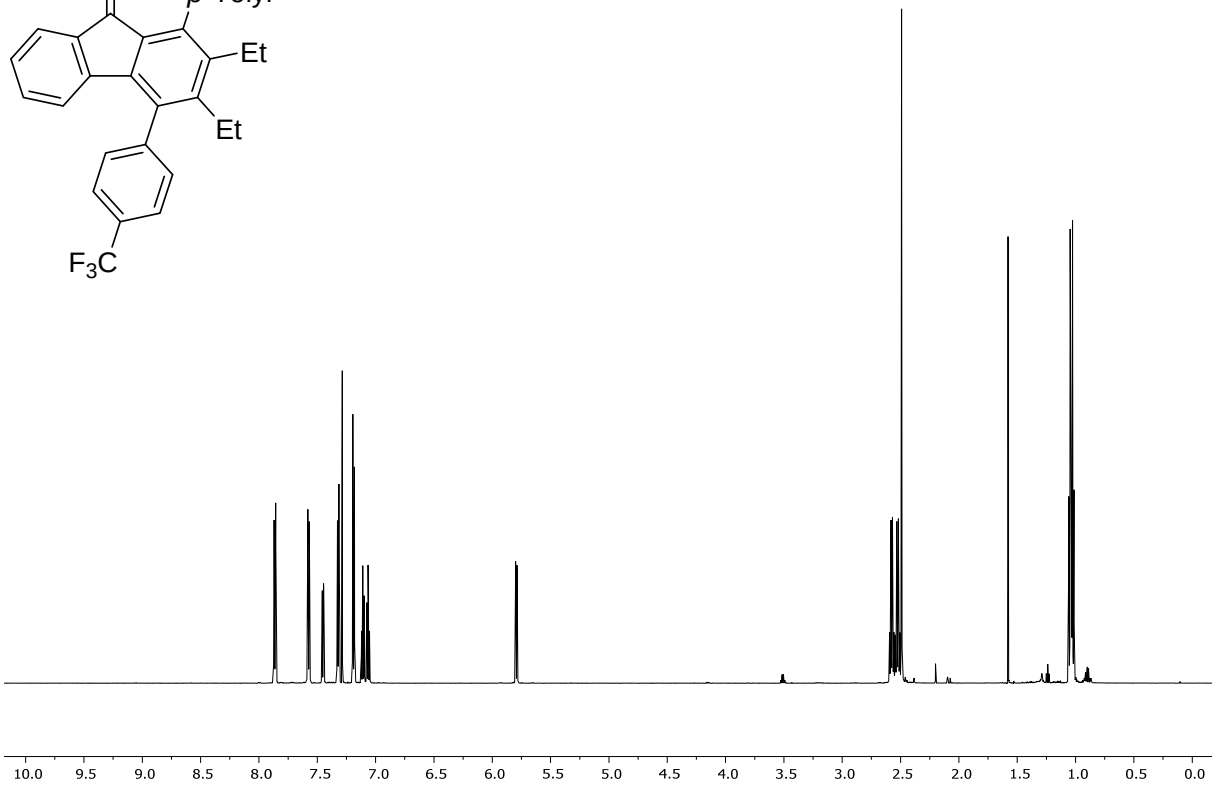


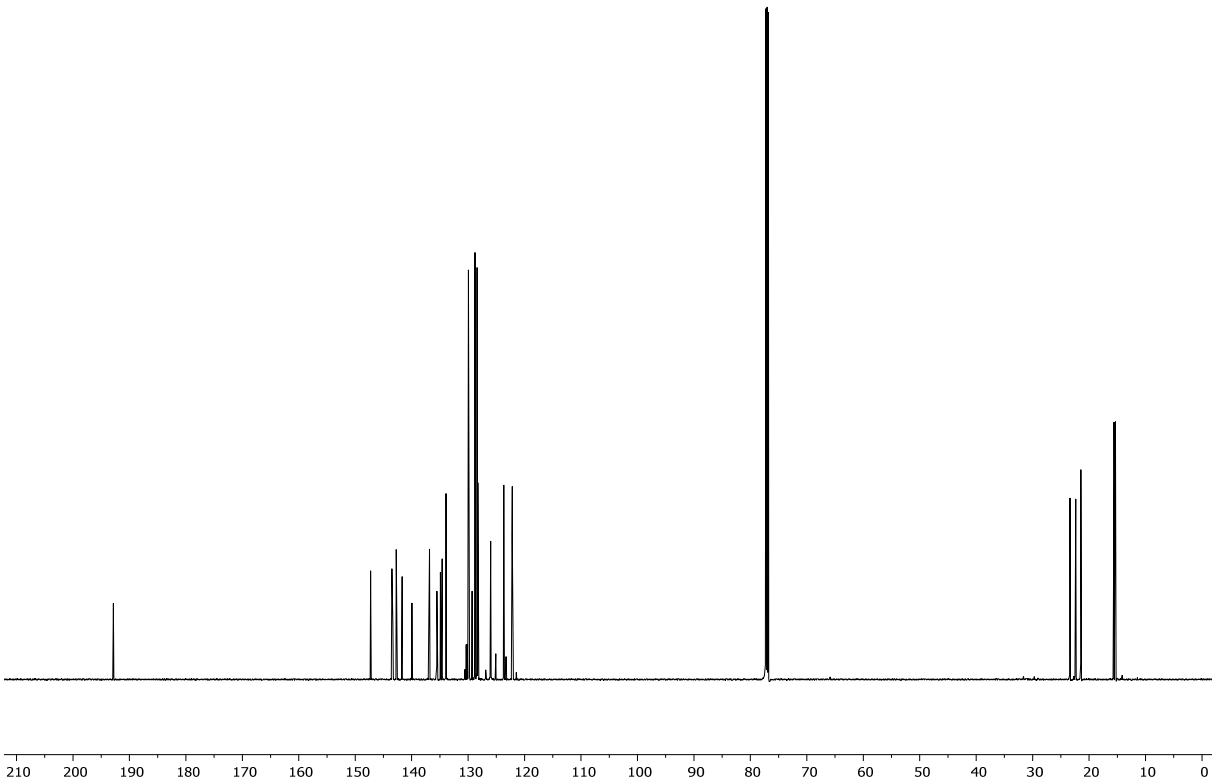




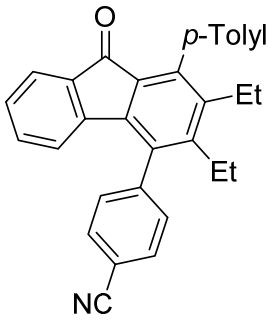
2,3-Diethyl-1-(*p*-tolyl)-4-(4-(trifluoromethyl)phenyl)-9*H*-fluoren-9-one (3f).

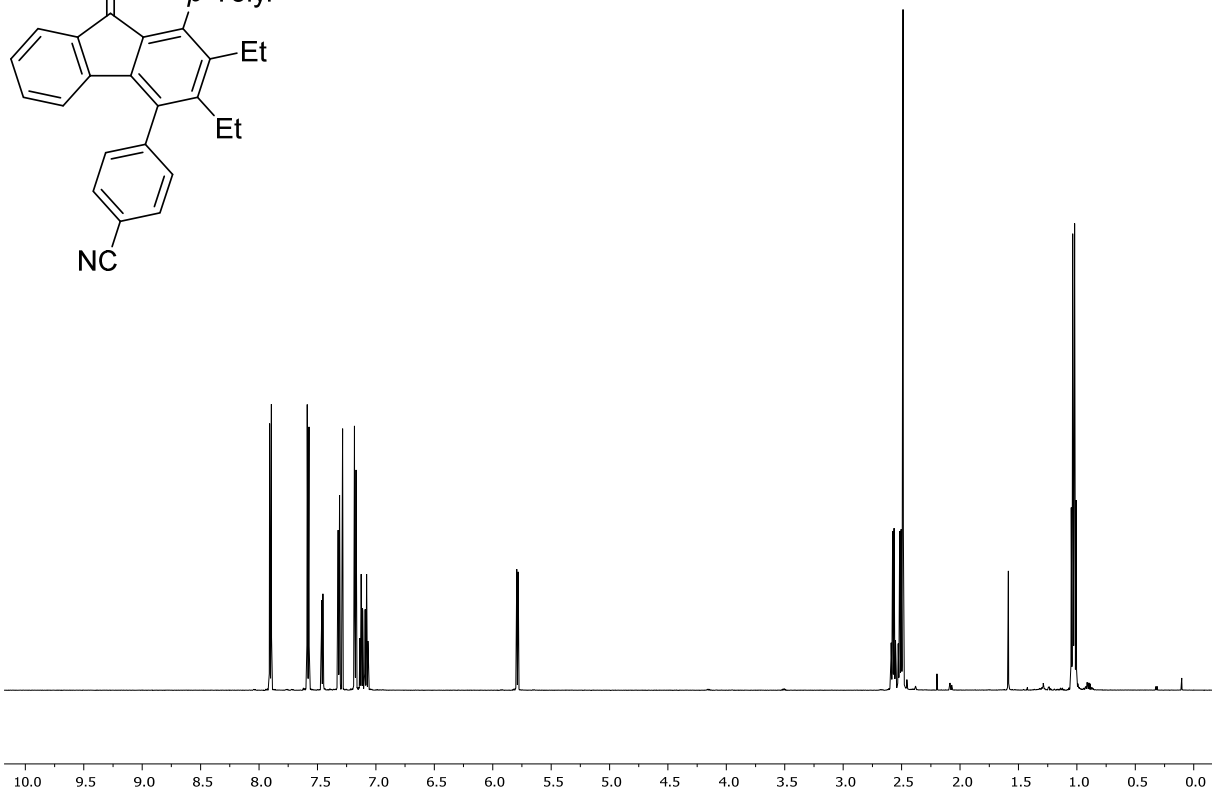


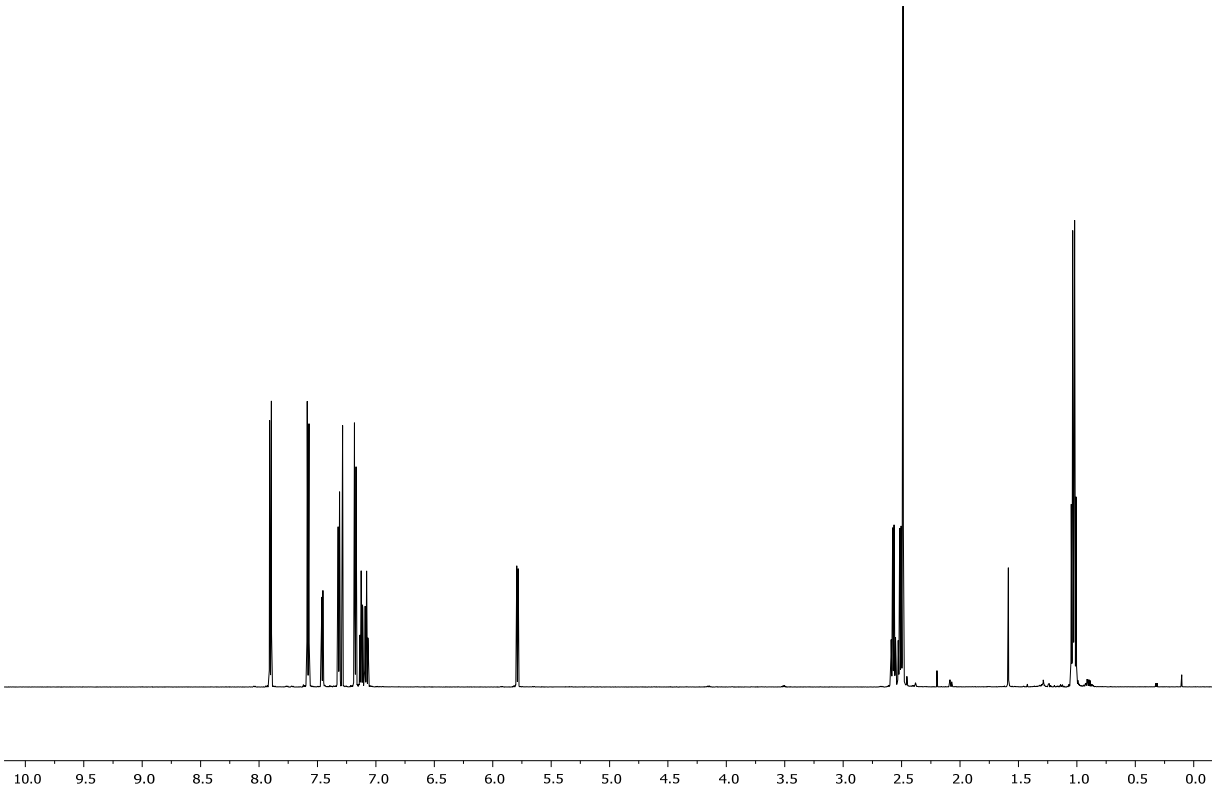




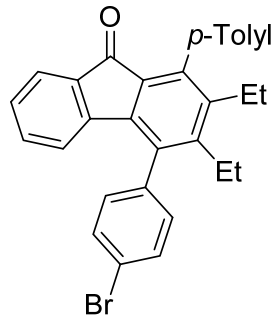
4-(2,3-Diethyl-9-oxo-1-(*p*-tolyl)-9*H*-fluoren-4-yl)benzonitrile (3g).

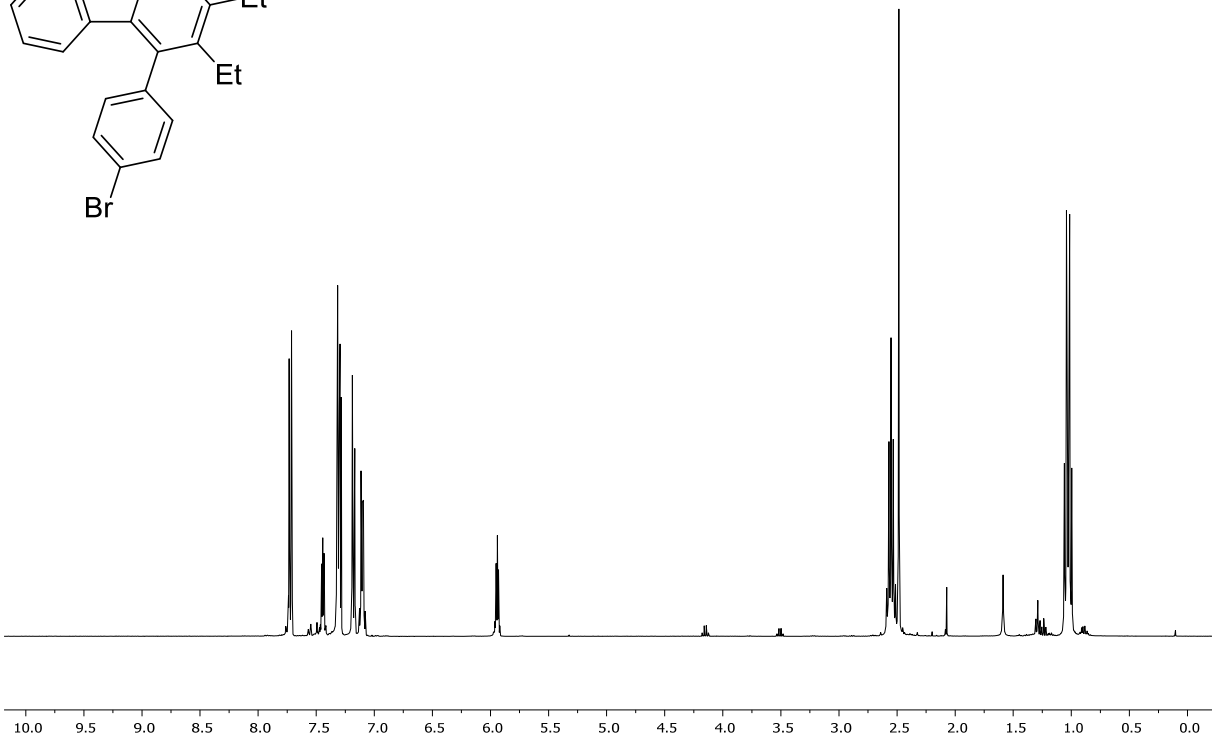


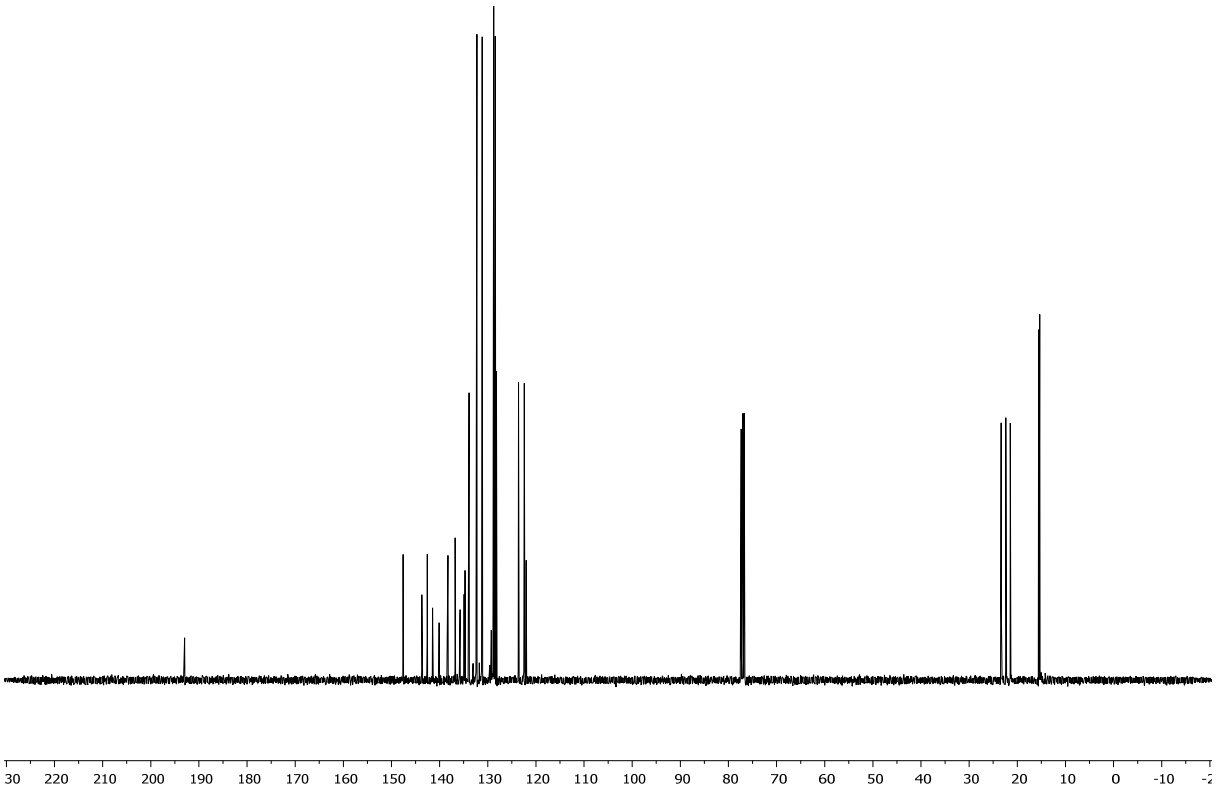




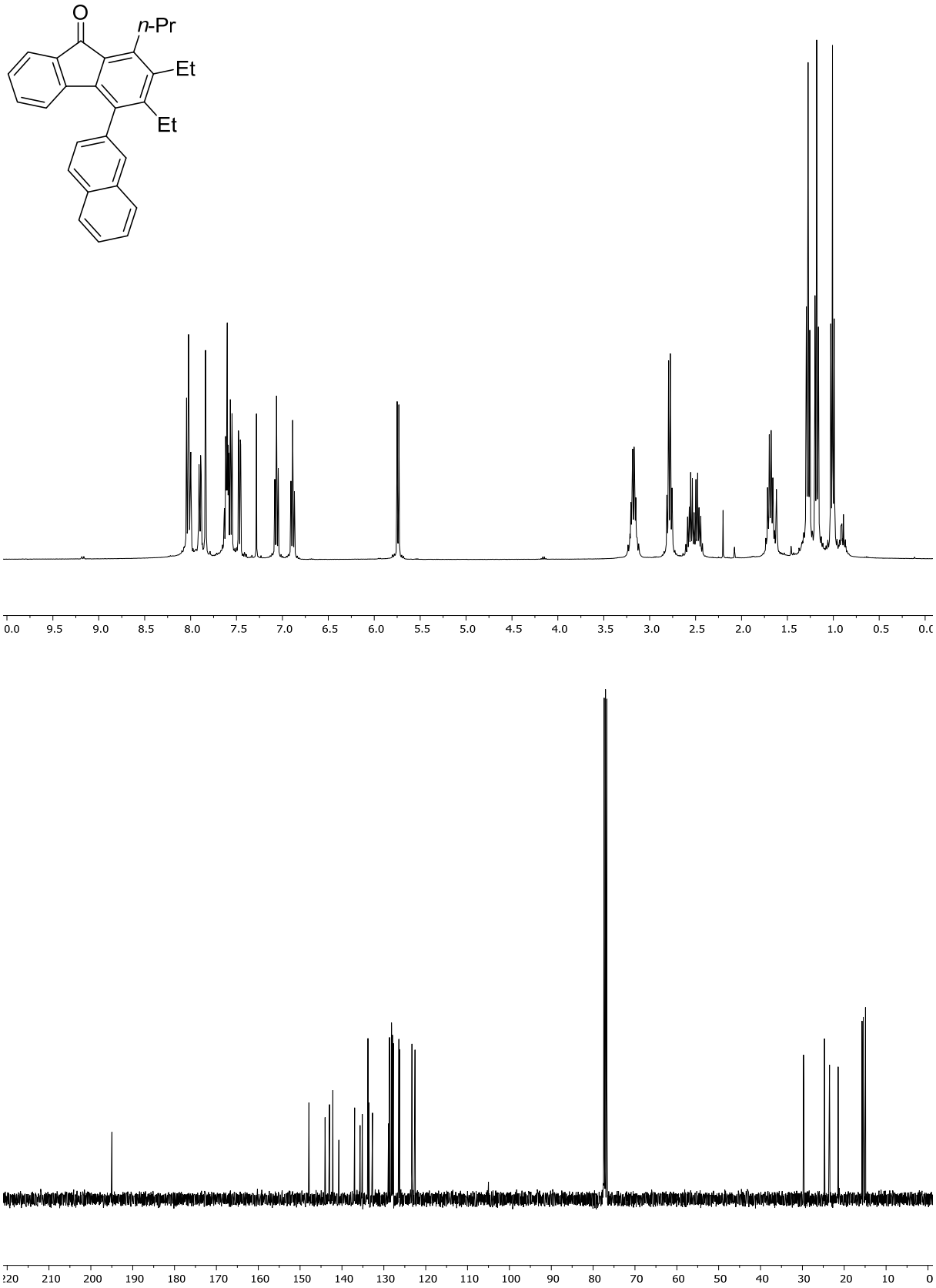
4-(4-Bromophenyl)-2,3-diethyl-1-(*p*-tolyl)-9*H*-fluoren-9-one (3h).



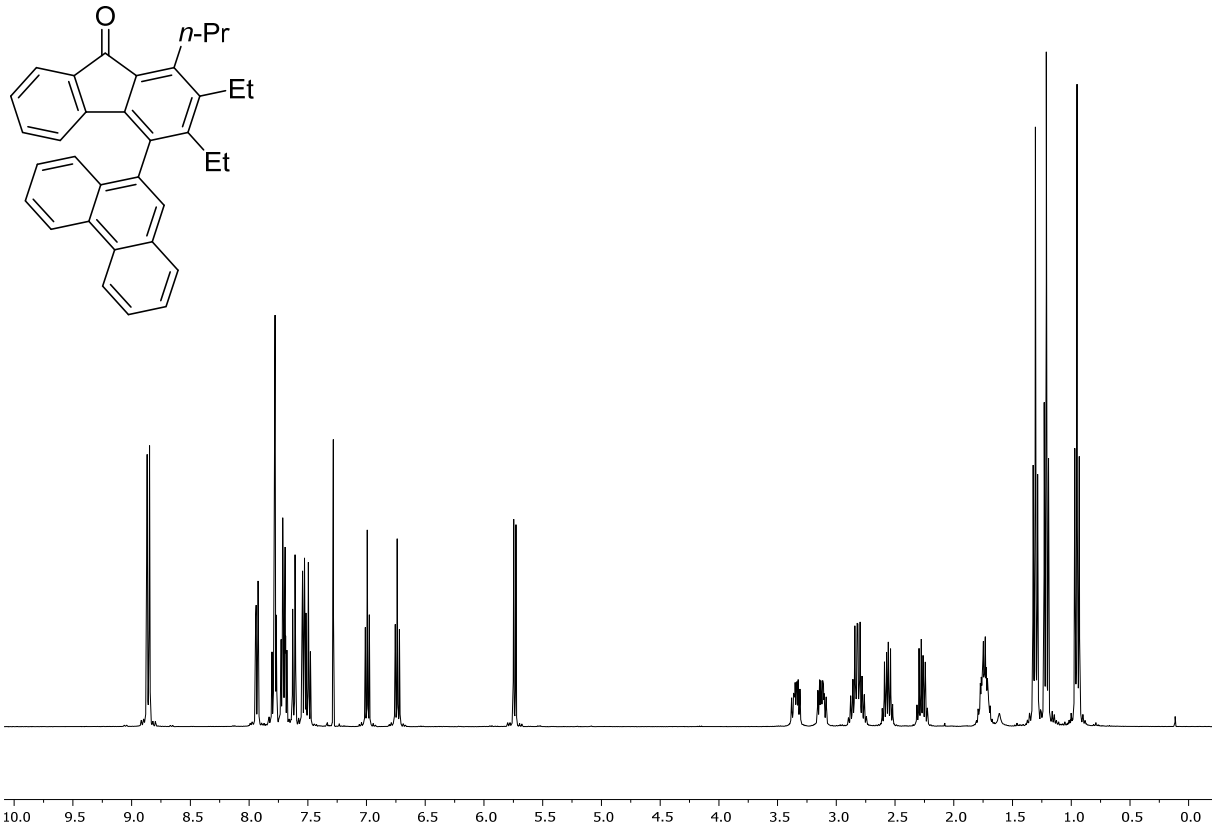


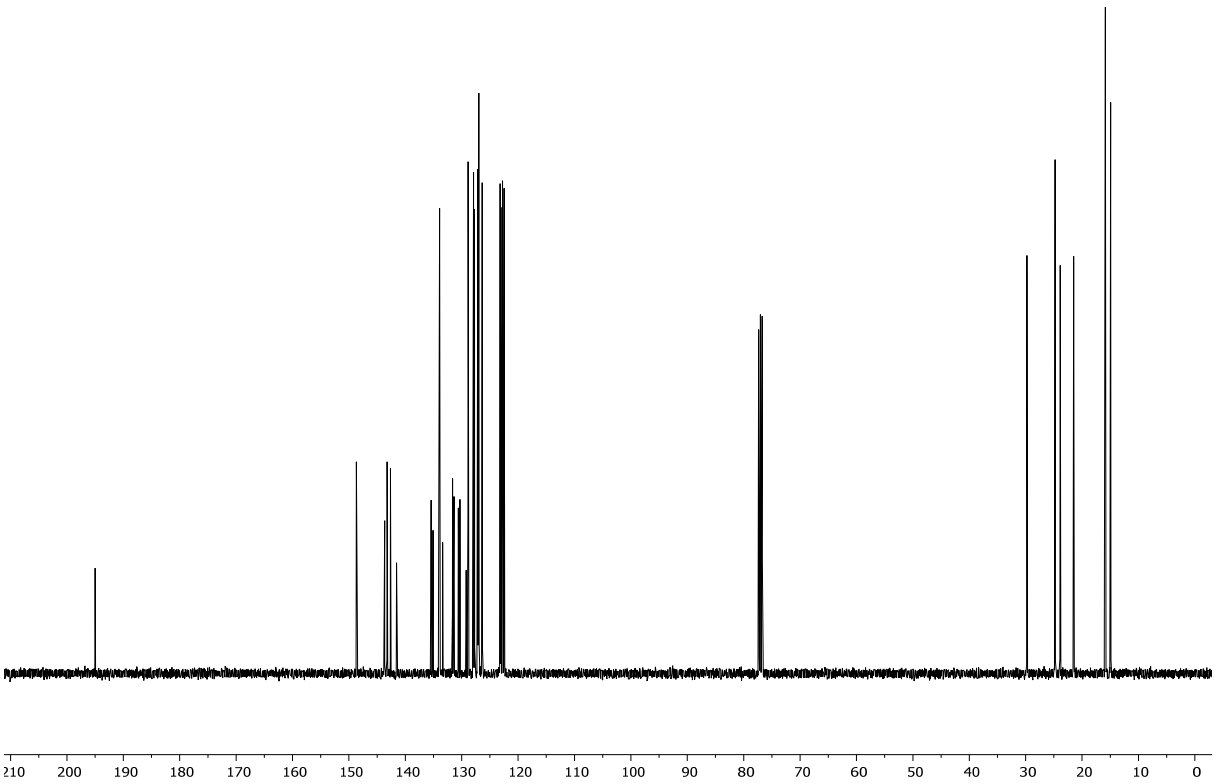


2,3-Diethyl-4-(naphthalen-2-yl)-1-propyl-9*H*-fluoren-9-one (10a).

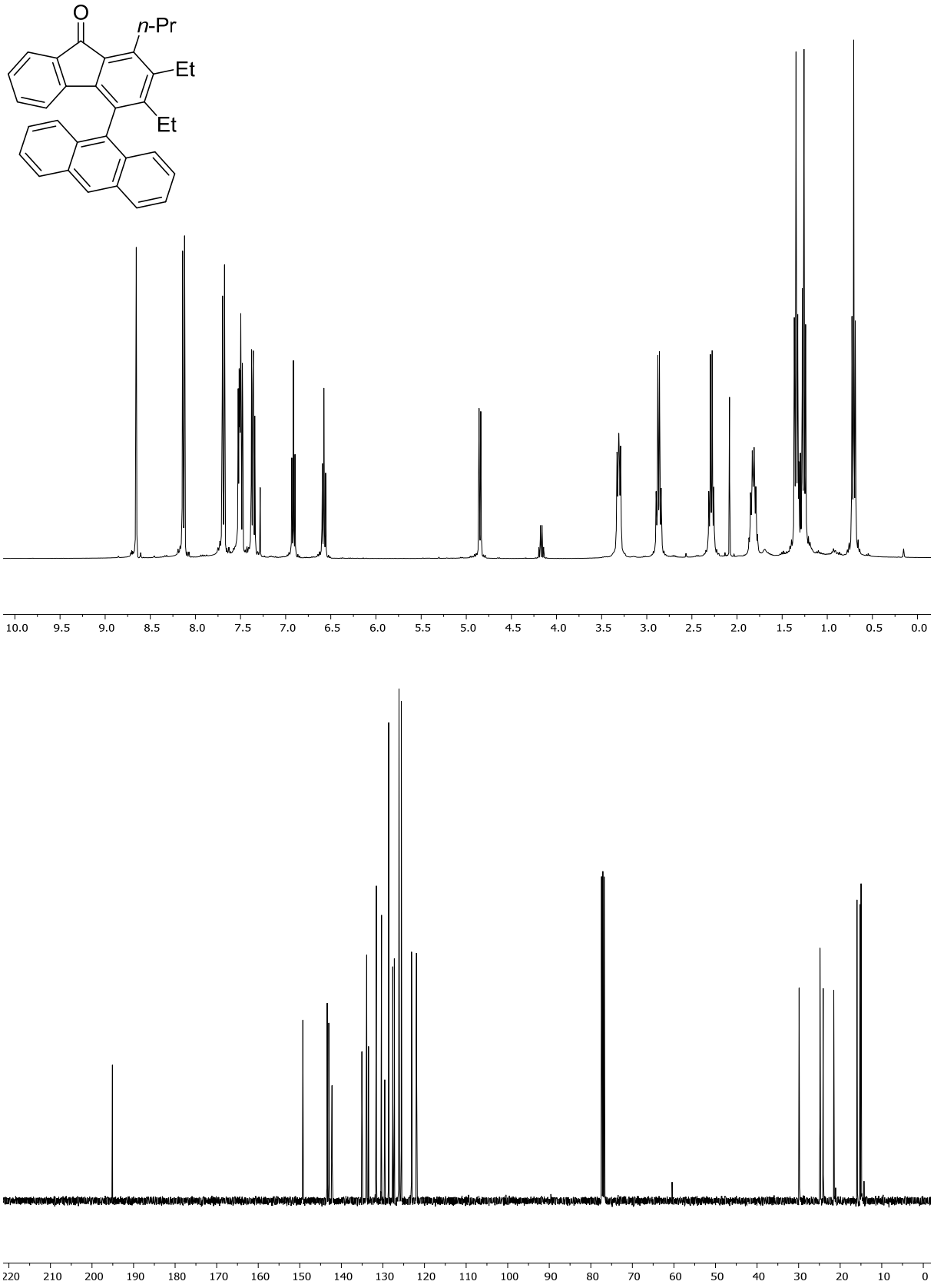


2,3-Diethyl-4-(phenanthren-9-yl)-1-propyl-9*H*-fluoren-9-one (10b).

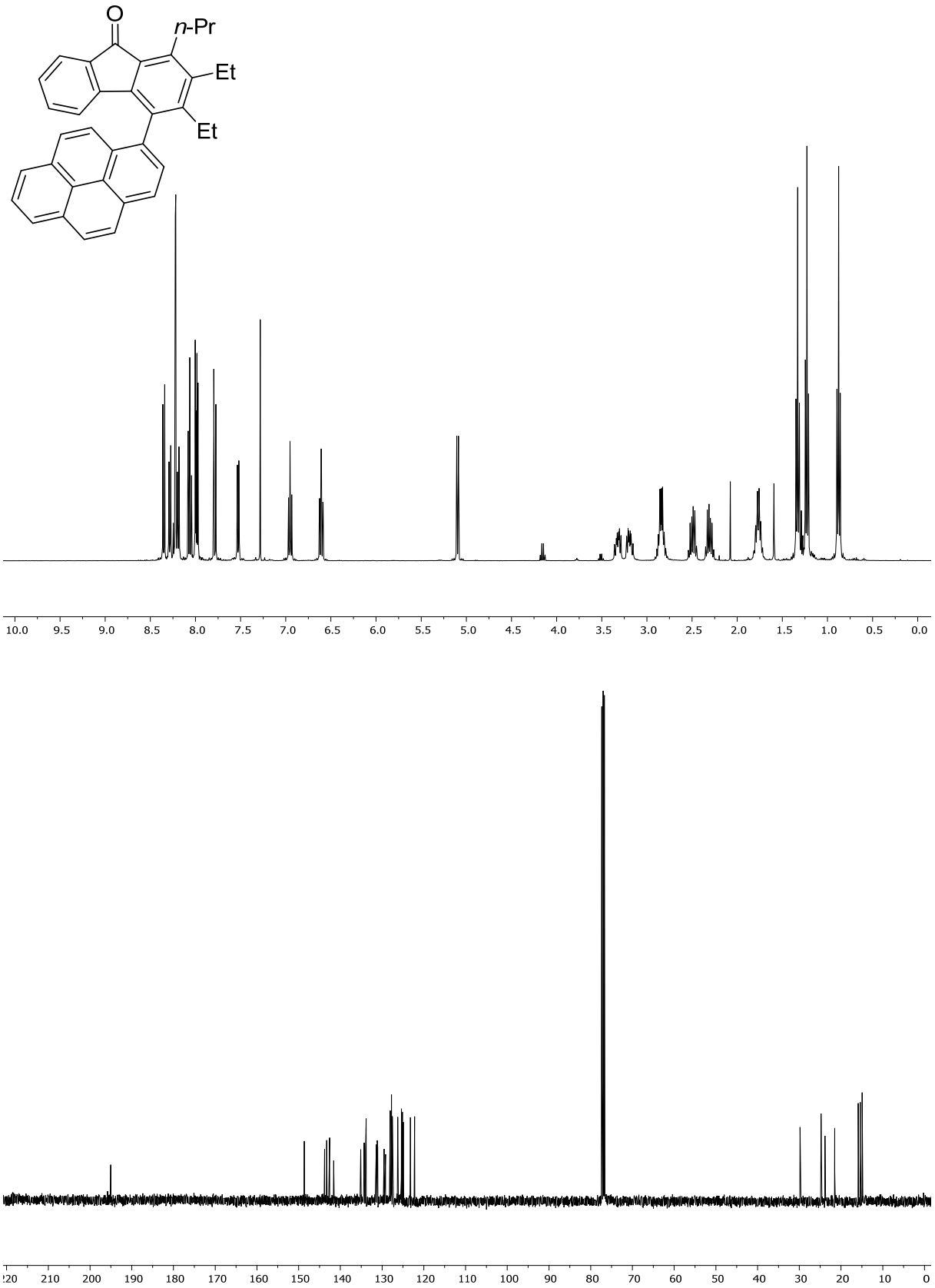




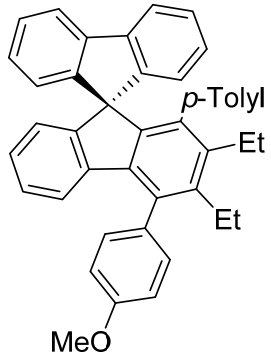
4-(Anthracen-9-yl)-2,3-diethyl-1-propyl-9*H*-fluoren-9-one (10c).

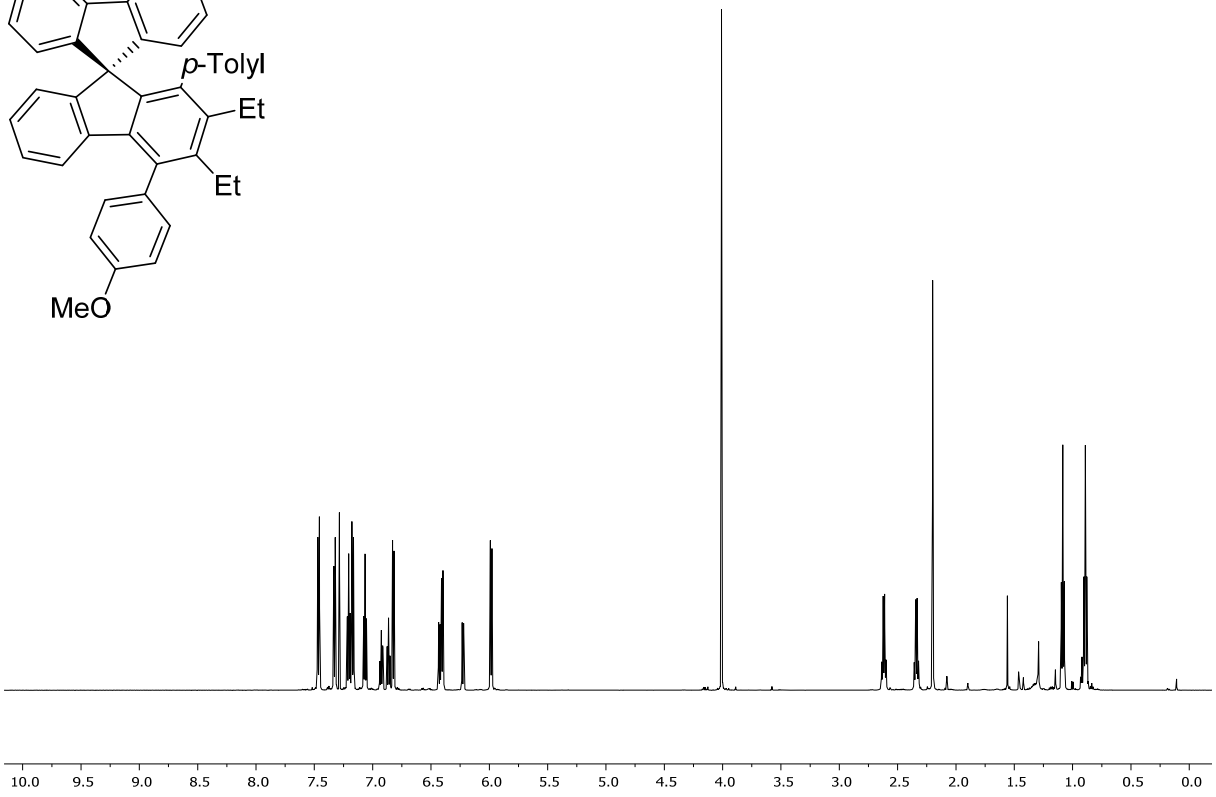


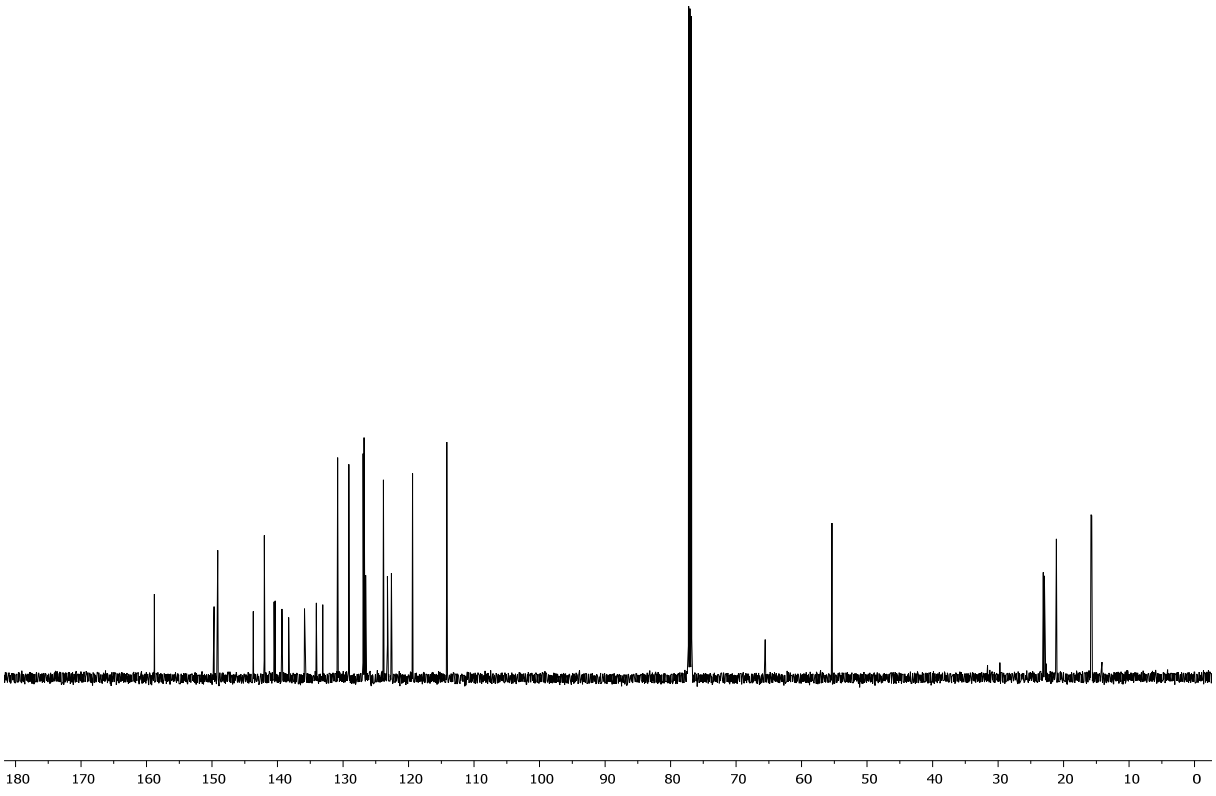
2,3-Diethyl-1-propyl-4-(pyren-2-yl)-9*H*-fluoren-9-one (10d).



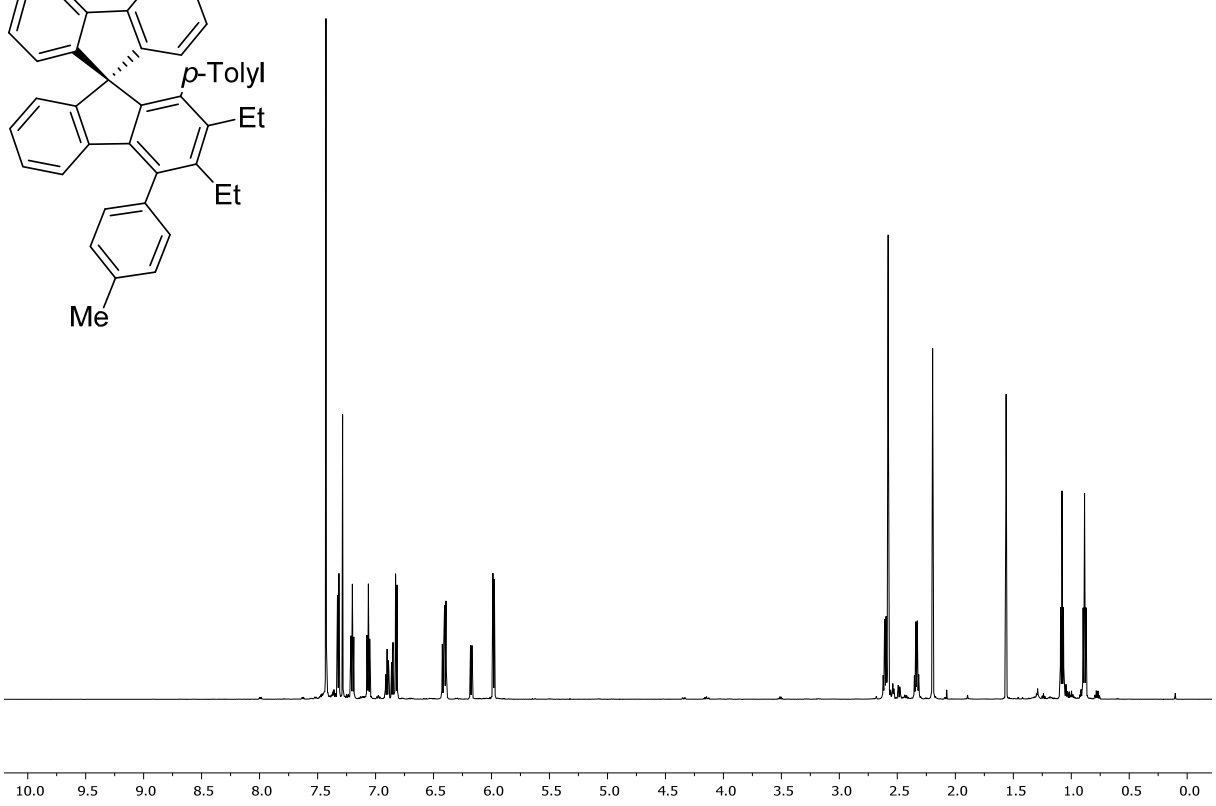
2,3-Diethyl-4-(4-methoxyphenyl)-1-(*p*-tolyl)-9,9'-spirobifluorene (4a).

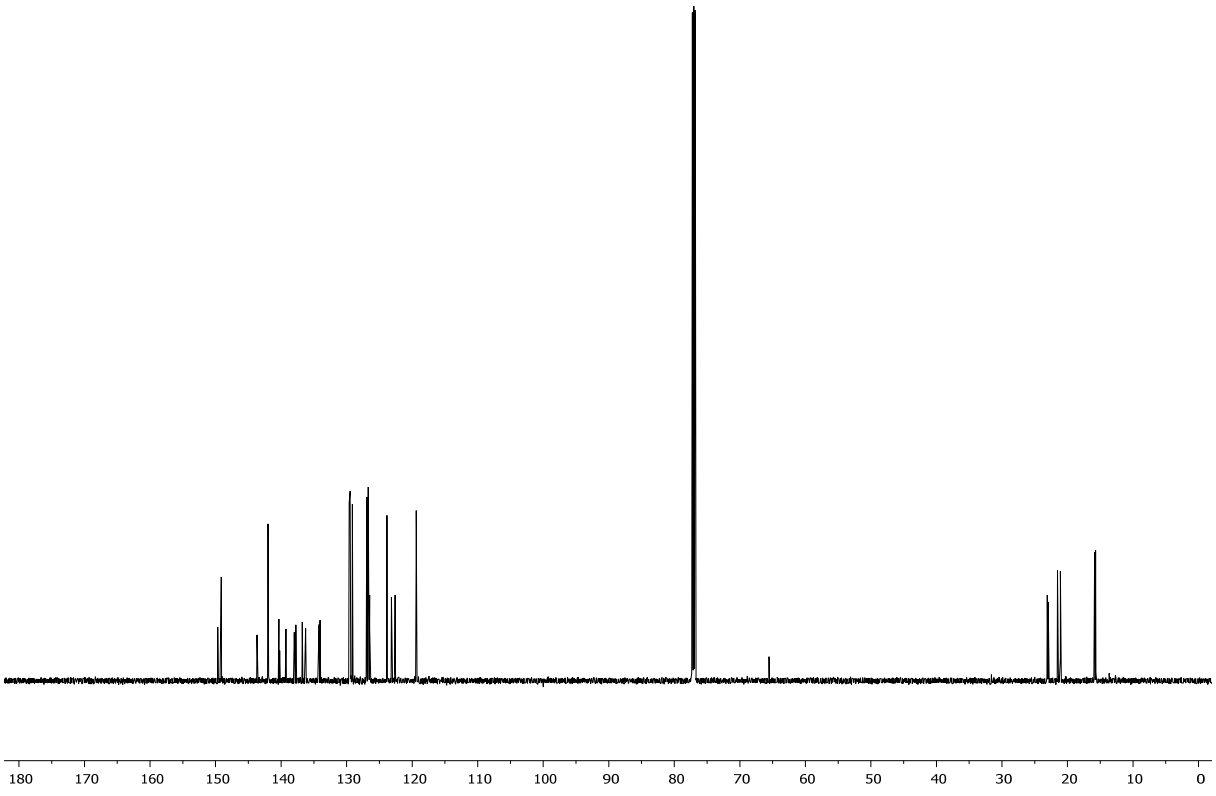




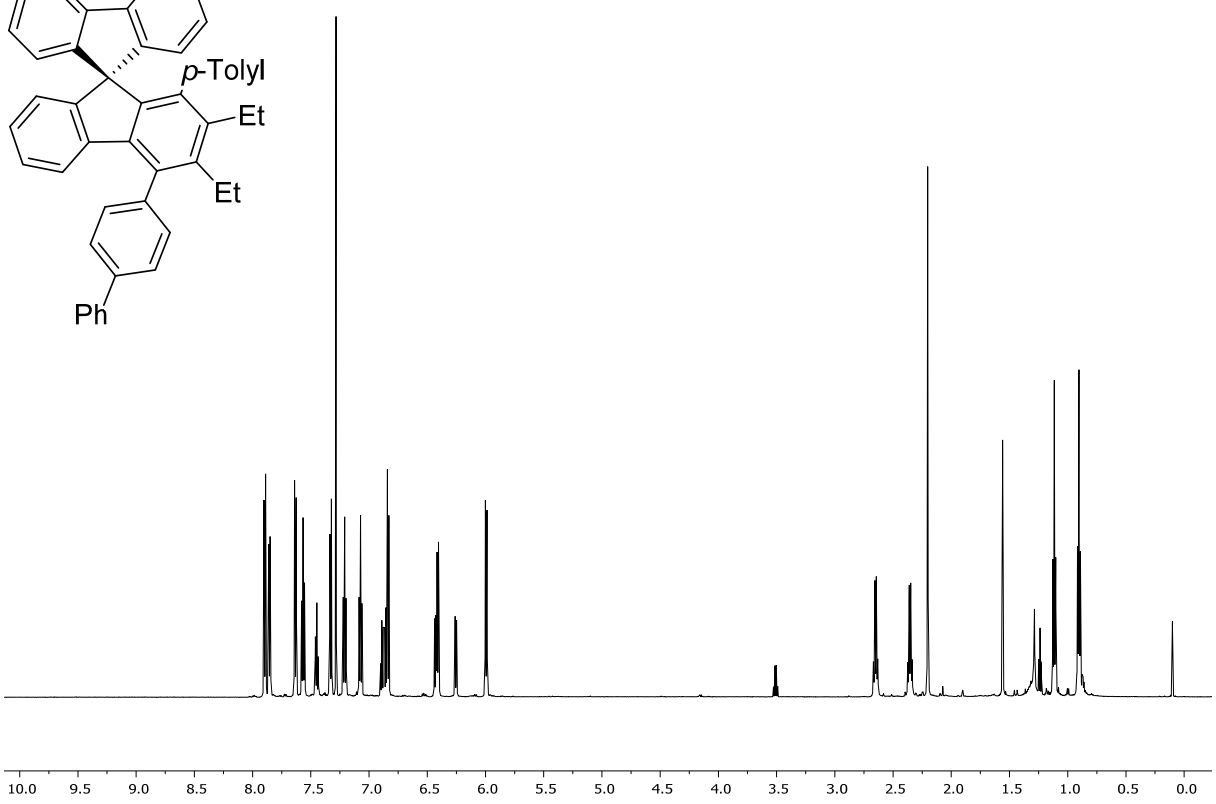


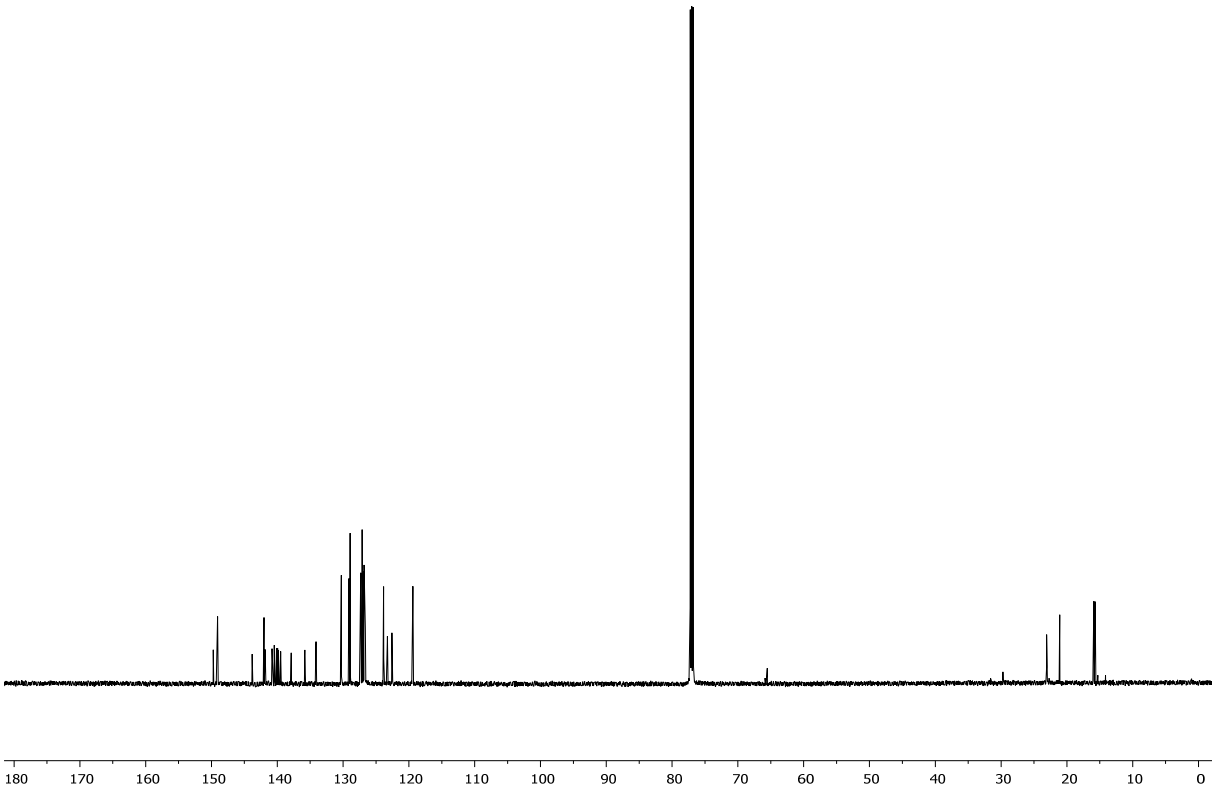
2,3-Diethyl-1,4-di-*p*-tolyl-9,9'-spirobifluorene (4b).



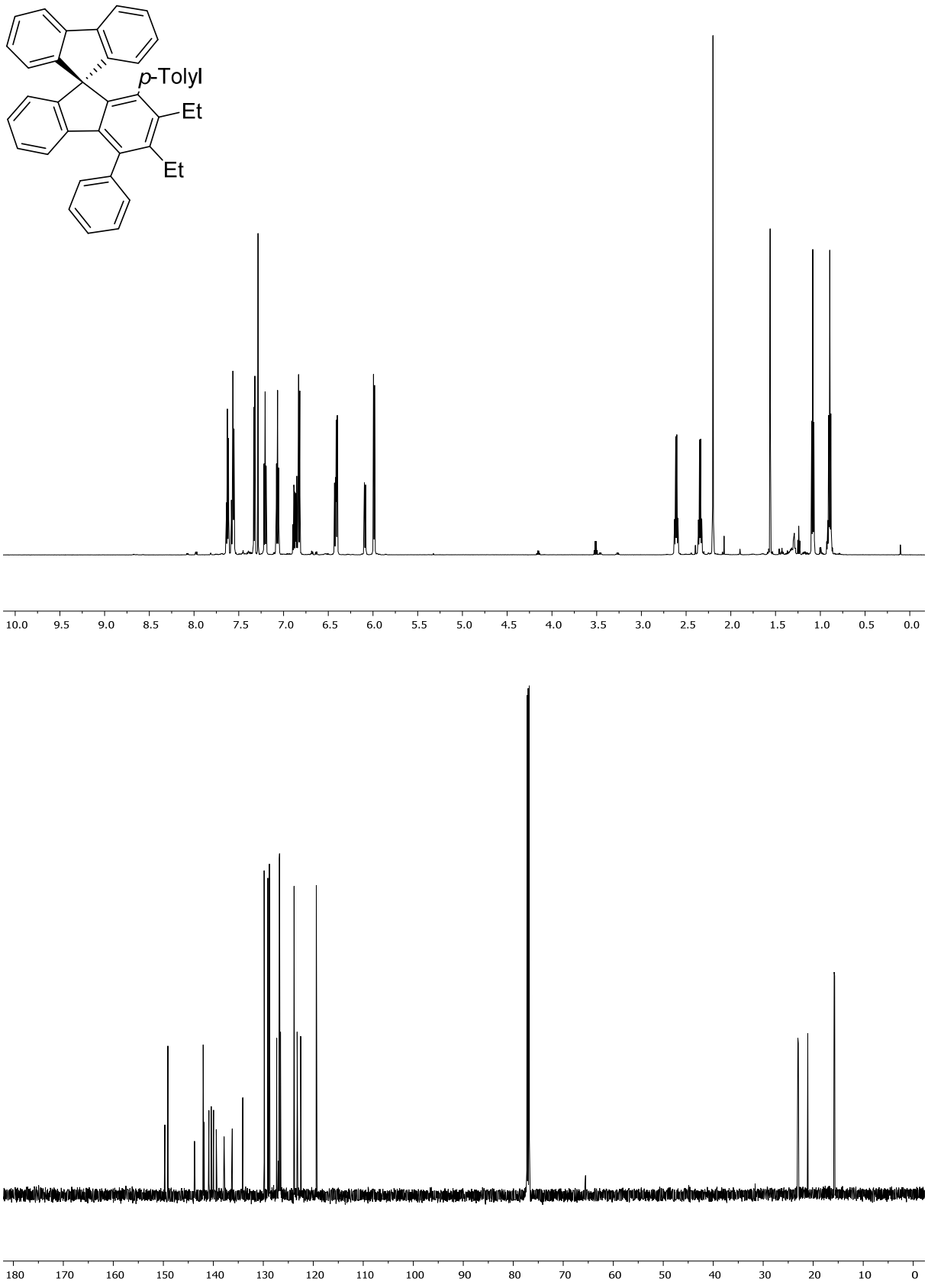


4-([1,1'-Biphenyl]-4-yl)-2,3-diethyl-1-(*p*-tolyl)-9,9'-spirobifluorene (4c).

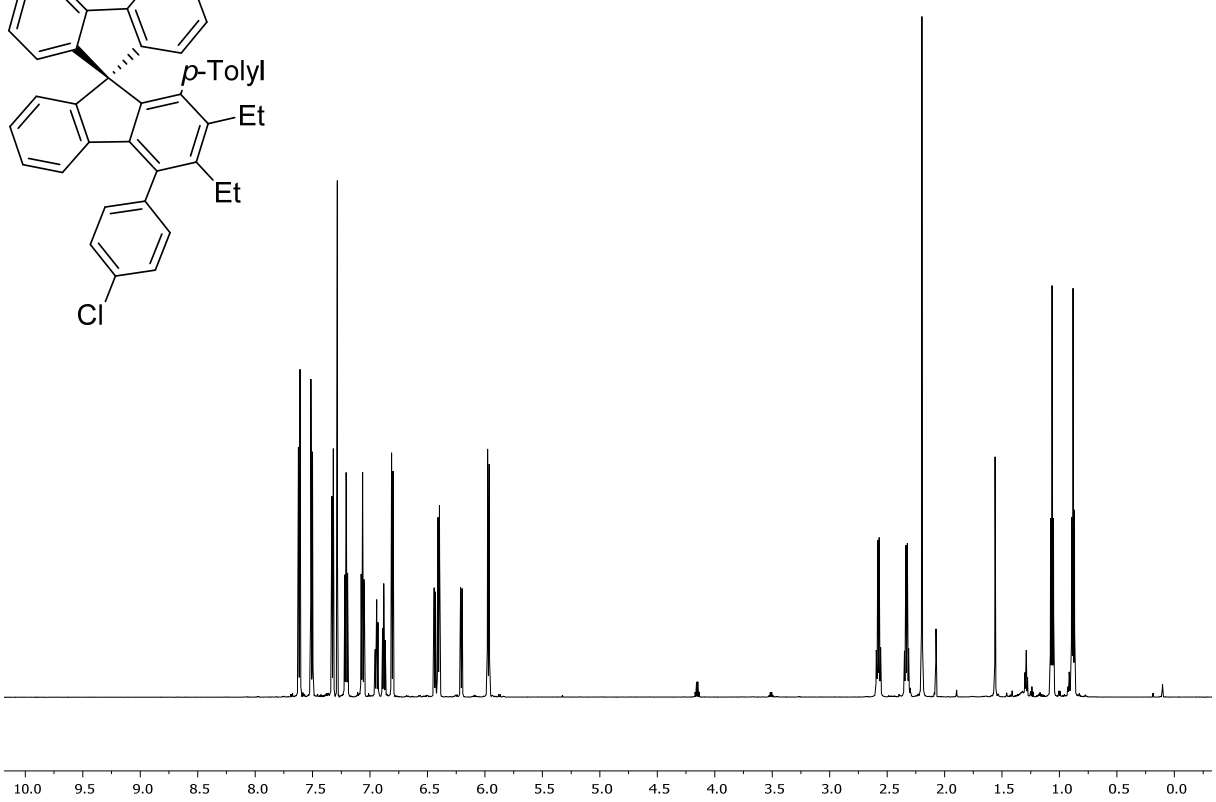


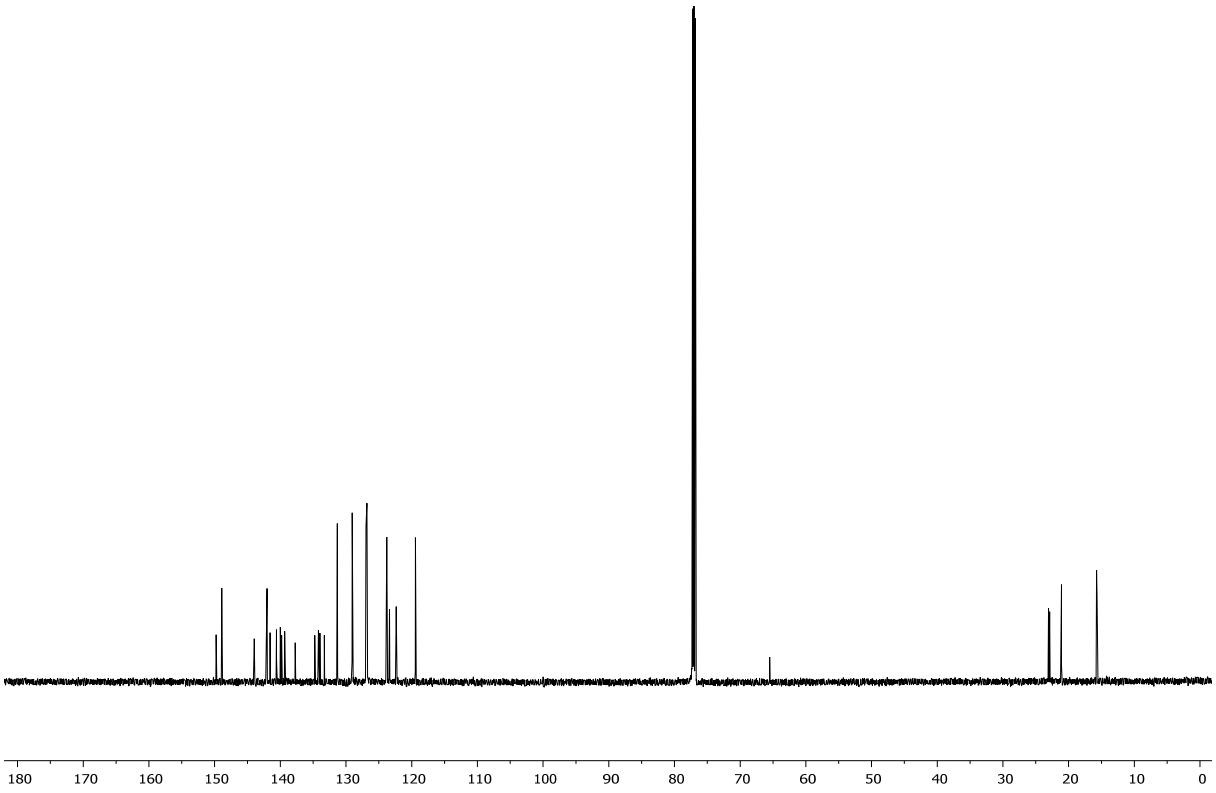


2,3-Diethyl-4-phenyl-1-(*p*-tolyl)-9,9'-spirobifluorene (4d).

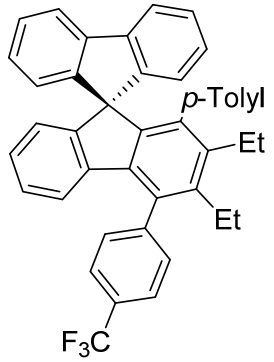


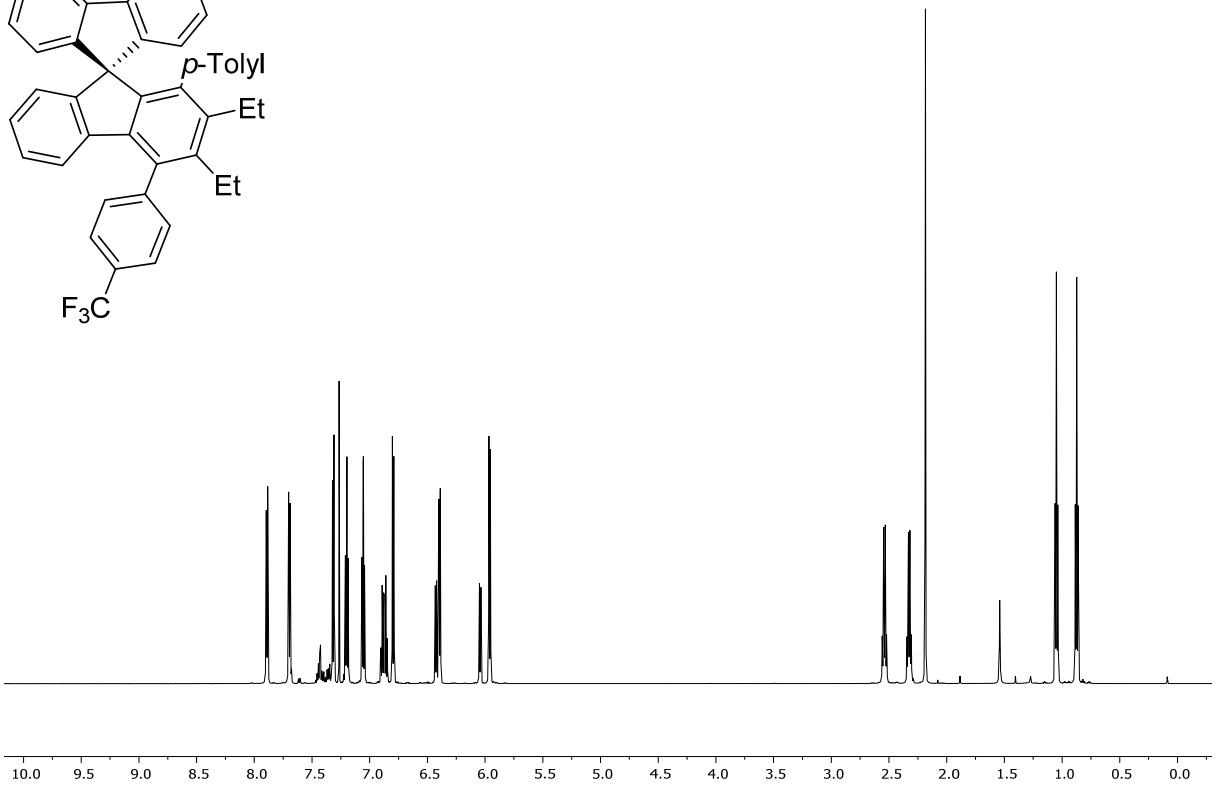
4-(4-Chlorophenyl)-2,3-diethyl-1-(*p*-tolyl)-9,9'-spirobifluorene (4e).

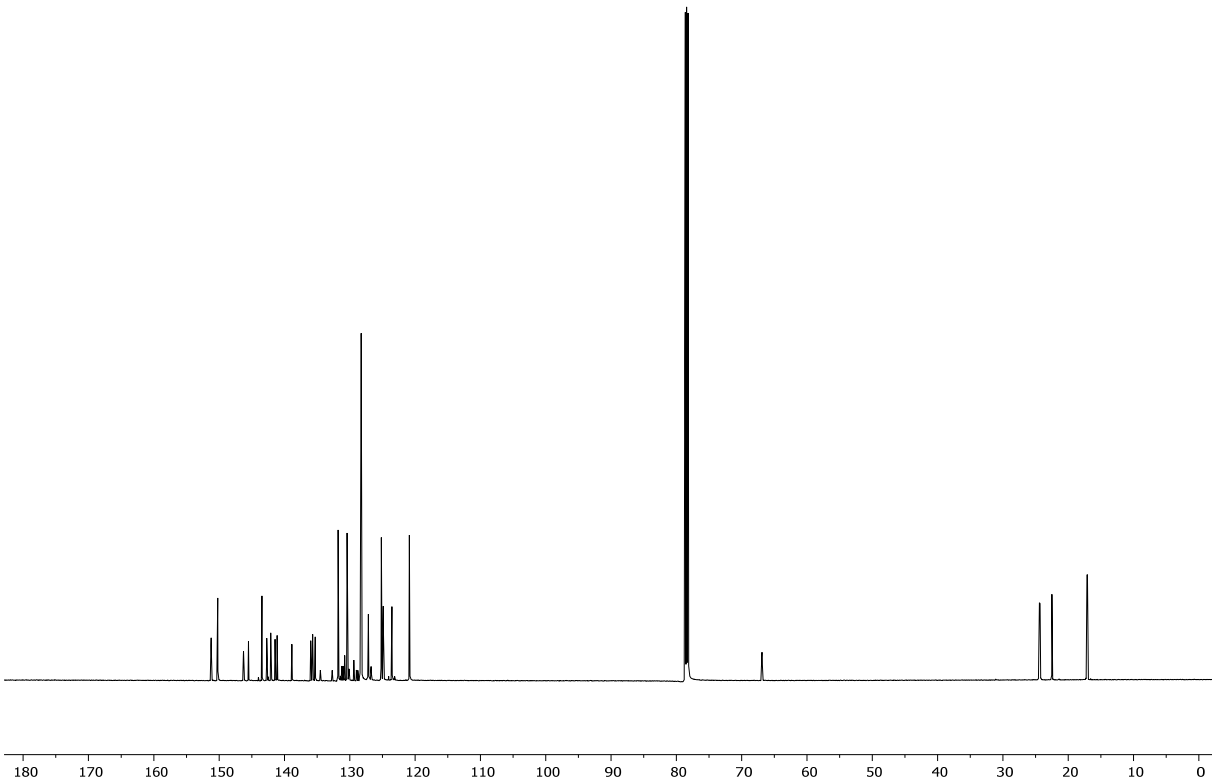




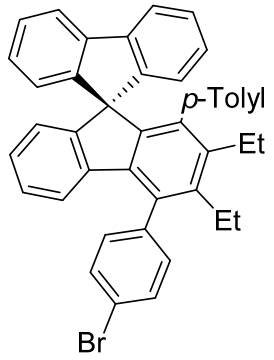
2,3-Diethyl-1-(*p*-tolyl)-4-(4-(trifluoromethyl)phenyl)-9,9'-spirobifluorene (4f).

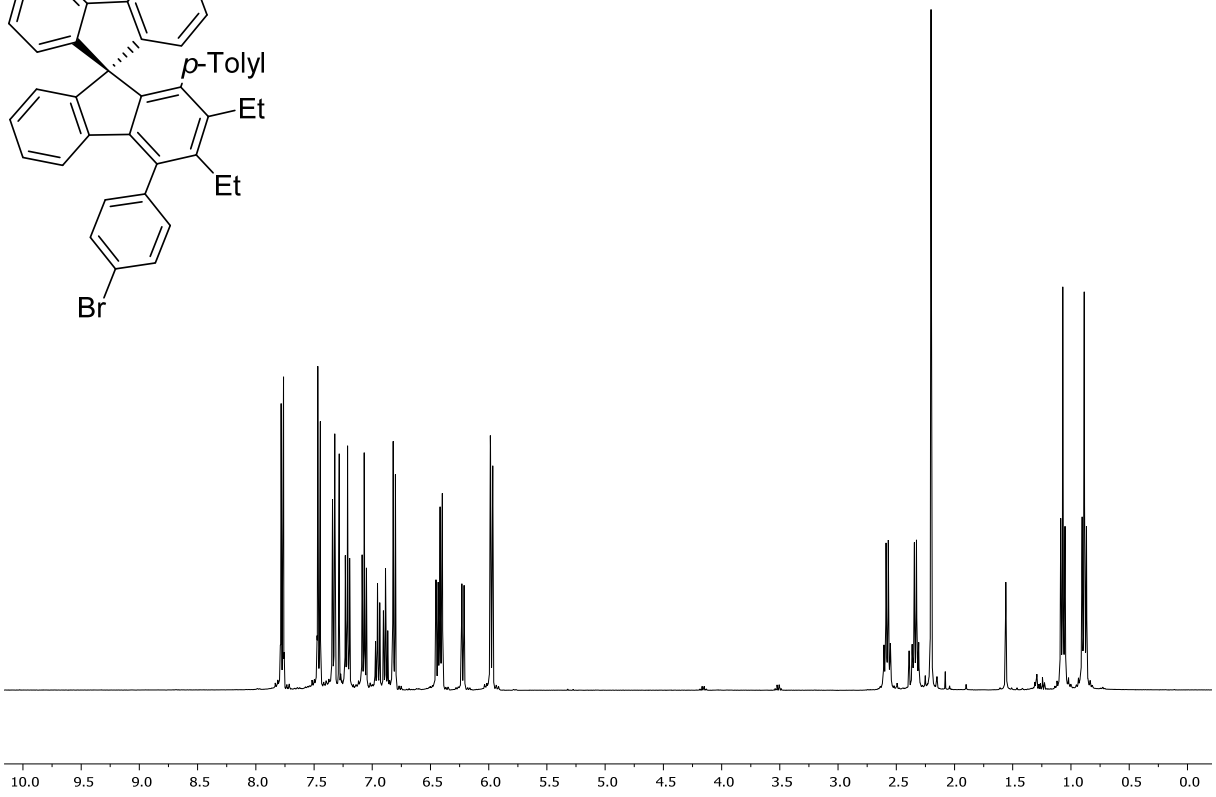


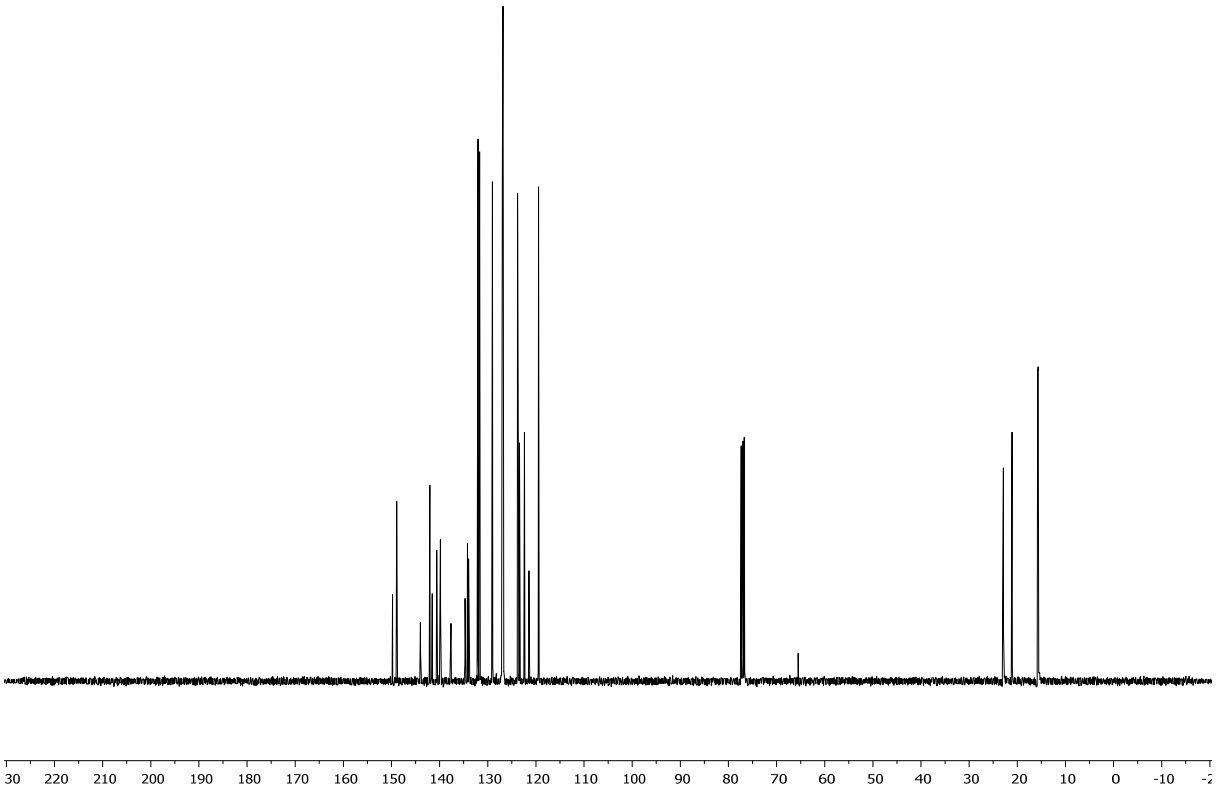




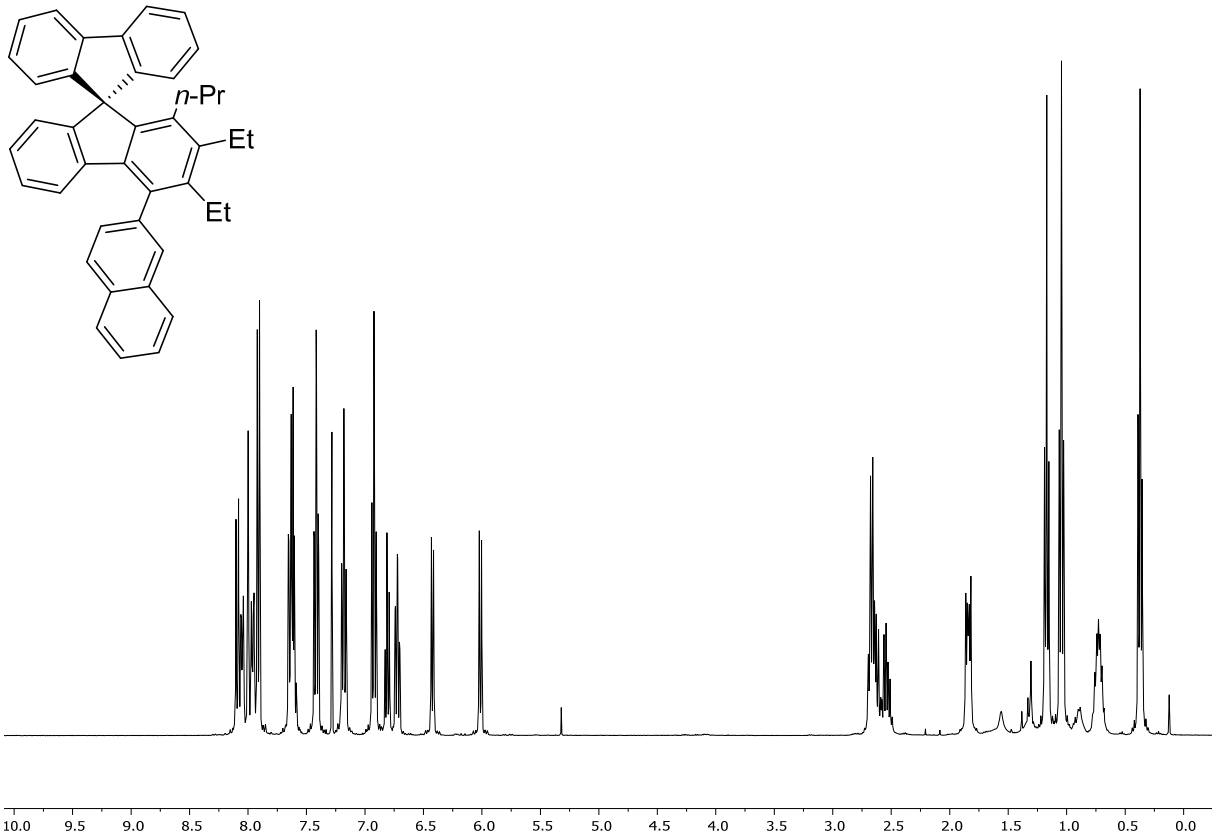
4-(4-Bromophenyl)-2,3-diethyl-1-(*p*-tolyl)-9,9'-spirobifluorene (4h).

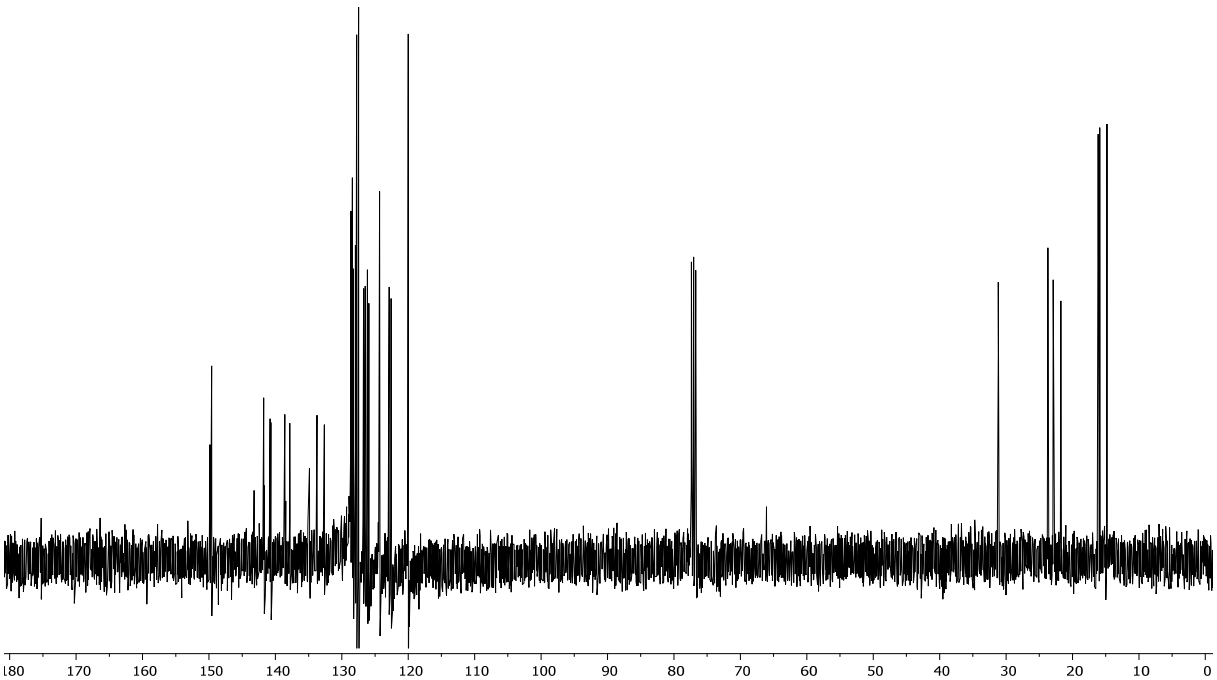




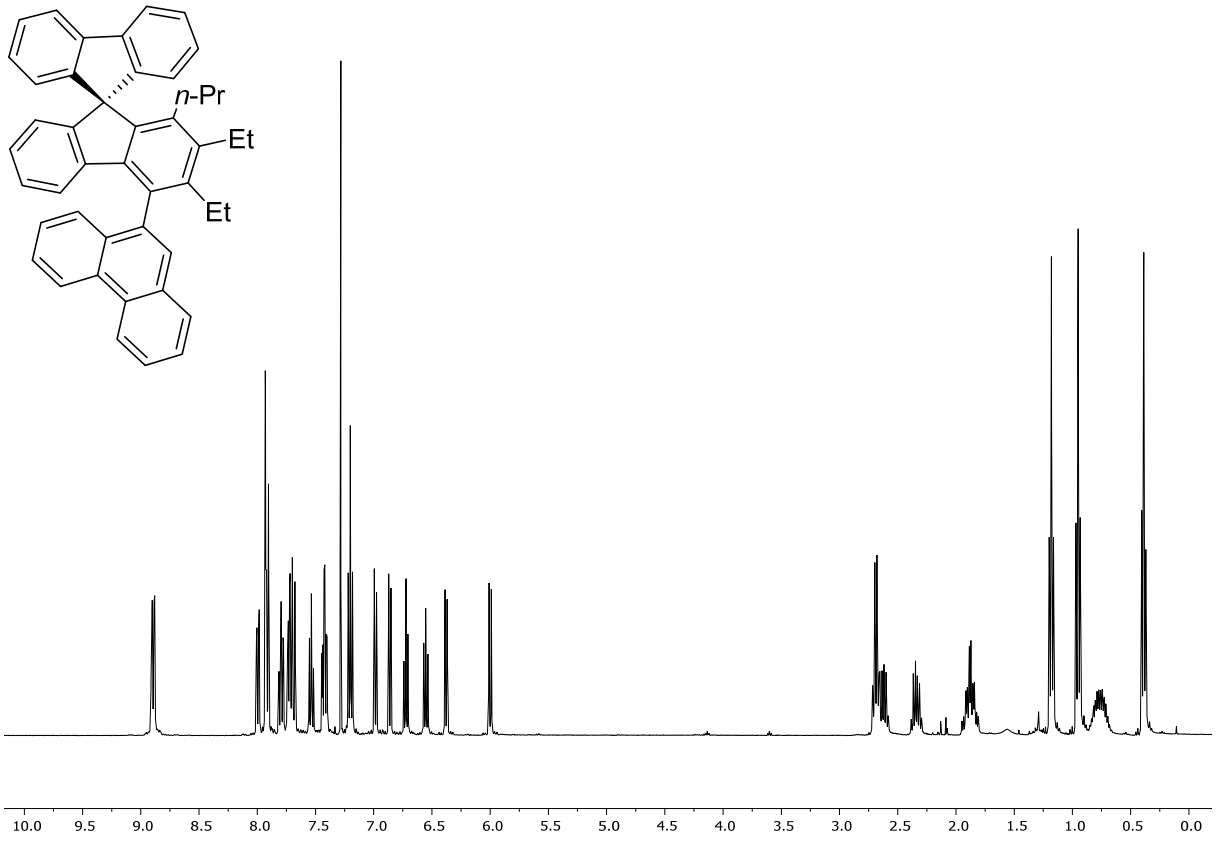


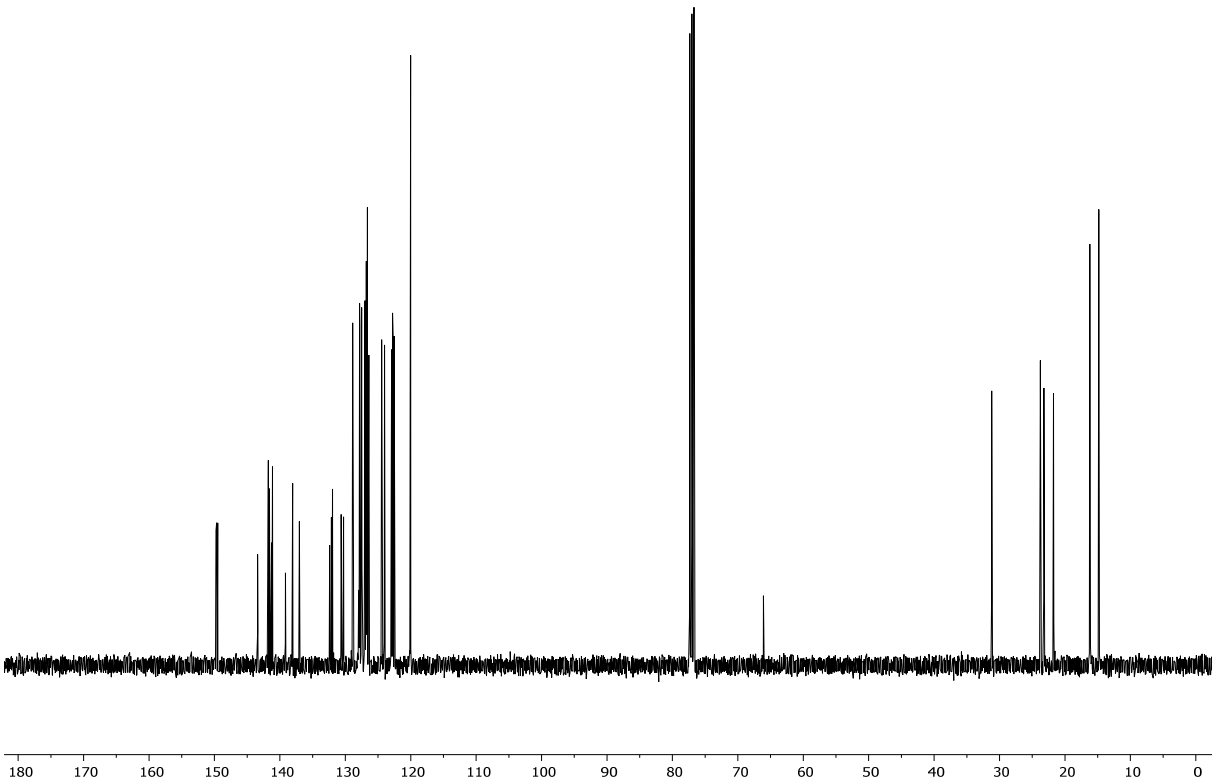
2,3-Diethyl-4-(naphthalen-2-yl)-1-propyl-9,9'-spirobifluorene (11a).



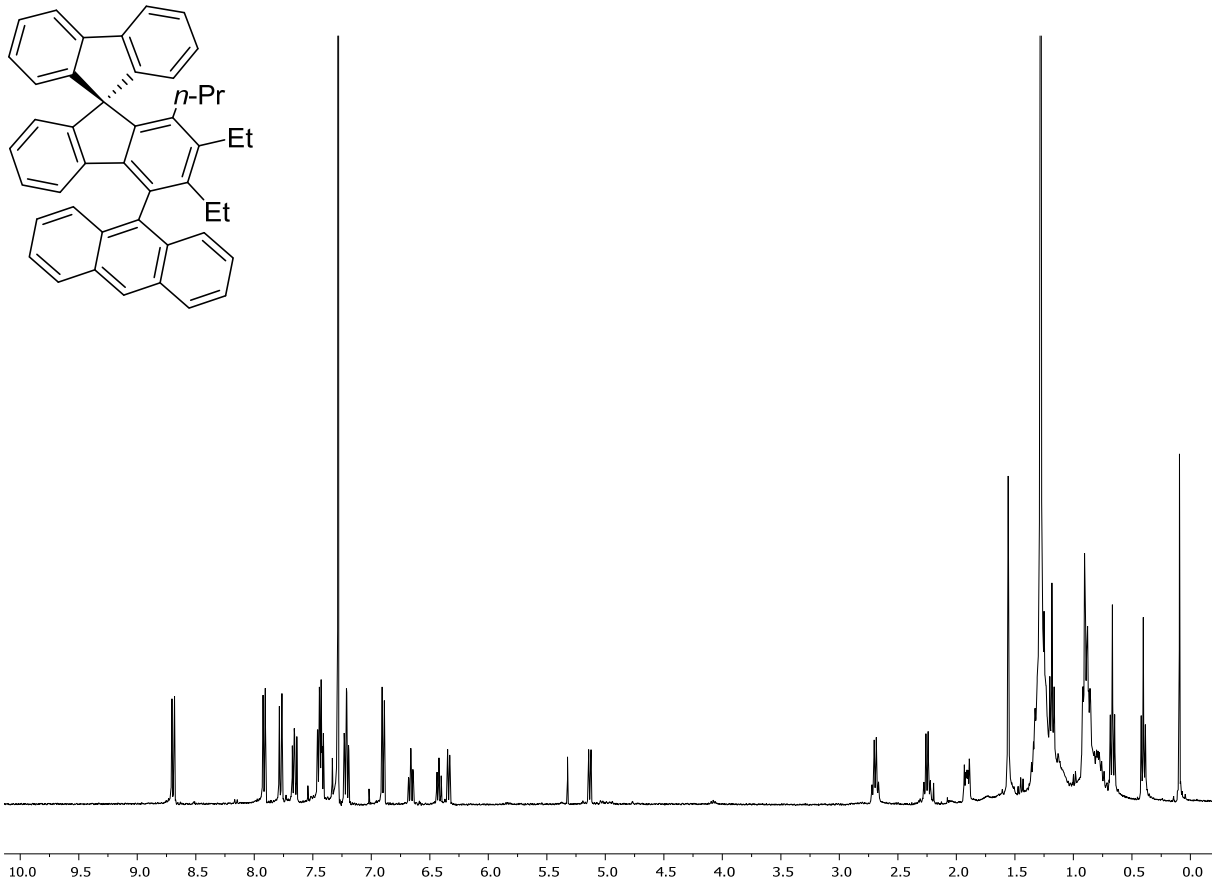


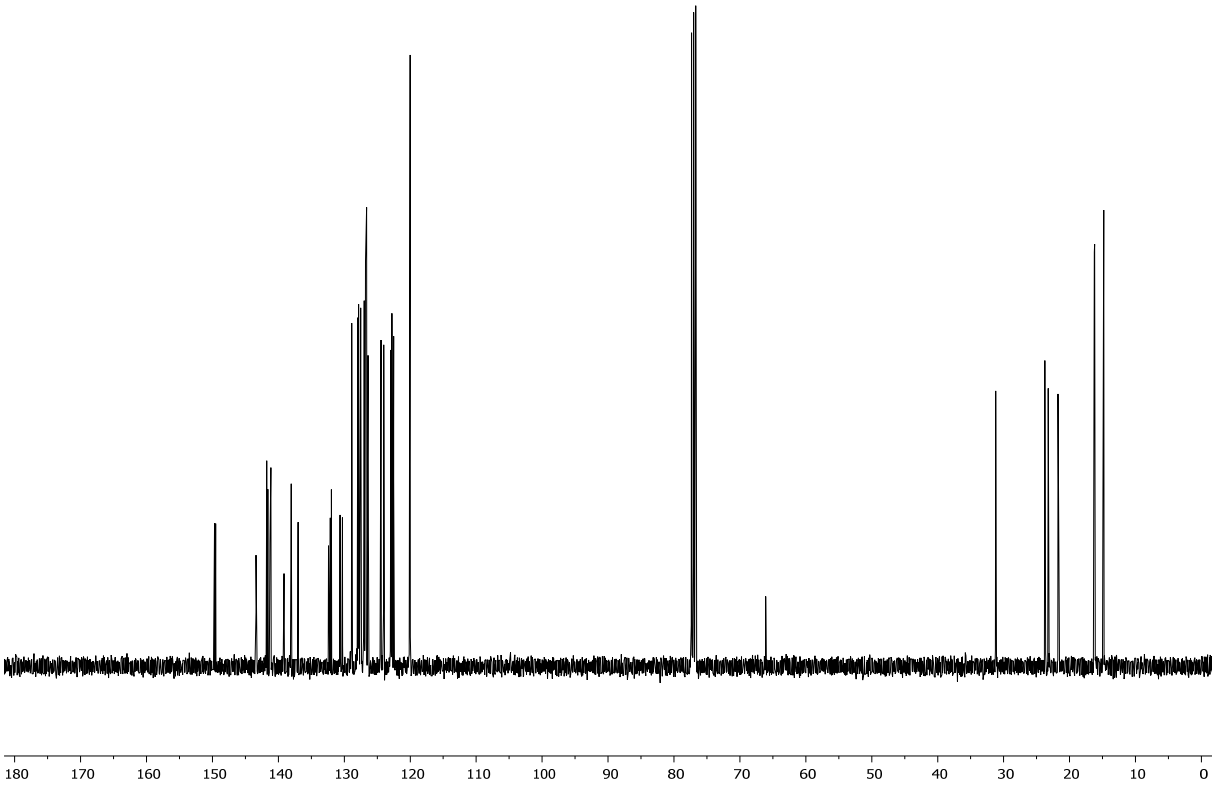
2,3-Diethyl-4-(phenanthren-9-yl)-1-propyl-9,9'-spirobifluorene (11b).



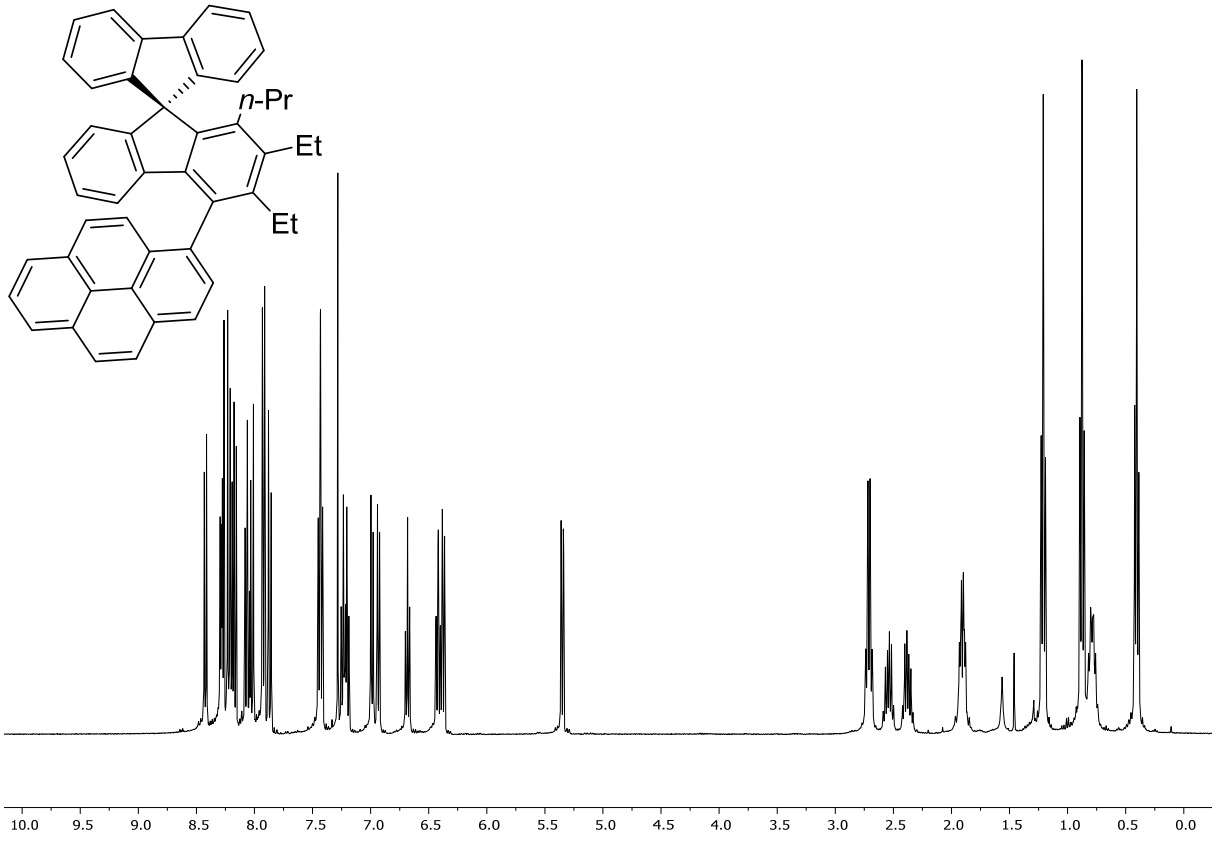


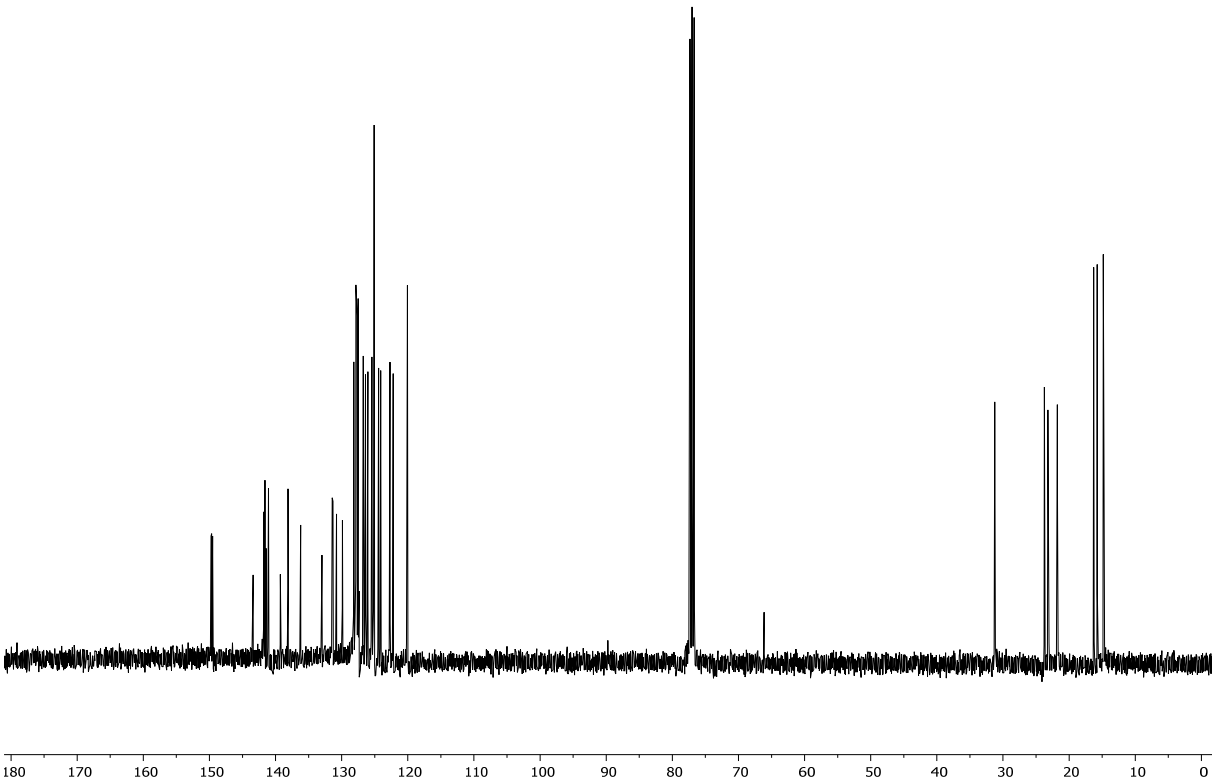
4-(Anthracen-9-yl)-2,3-diethyl-1-propyl-9,9'-spirobifluorene (11c).



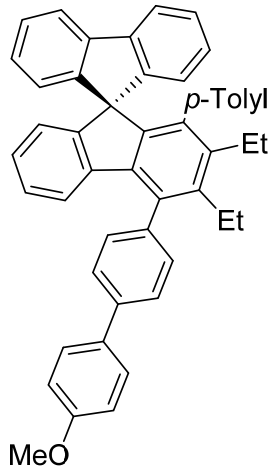


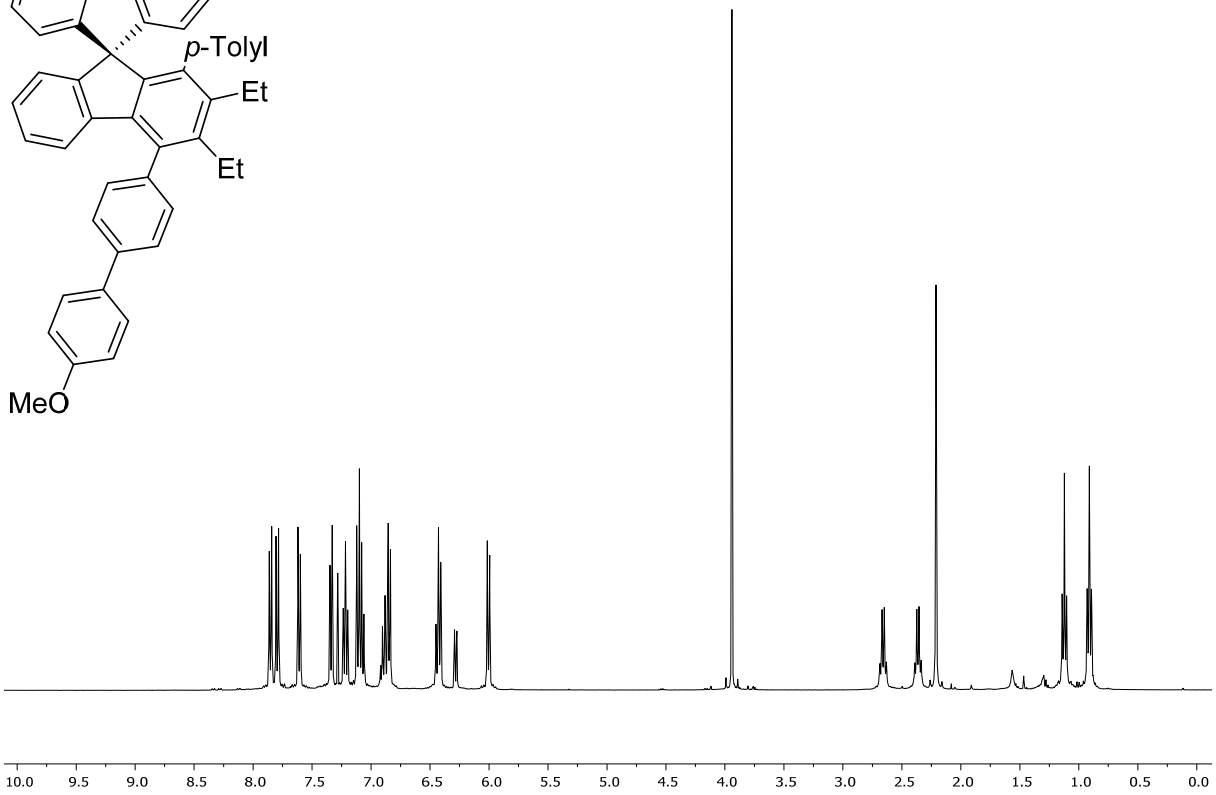
2,3-Diethyl-1-propyl-4-(pyren-2-yl)-9,9'-spirobifluorene (11d).

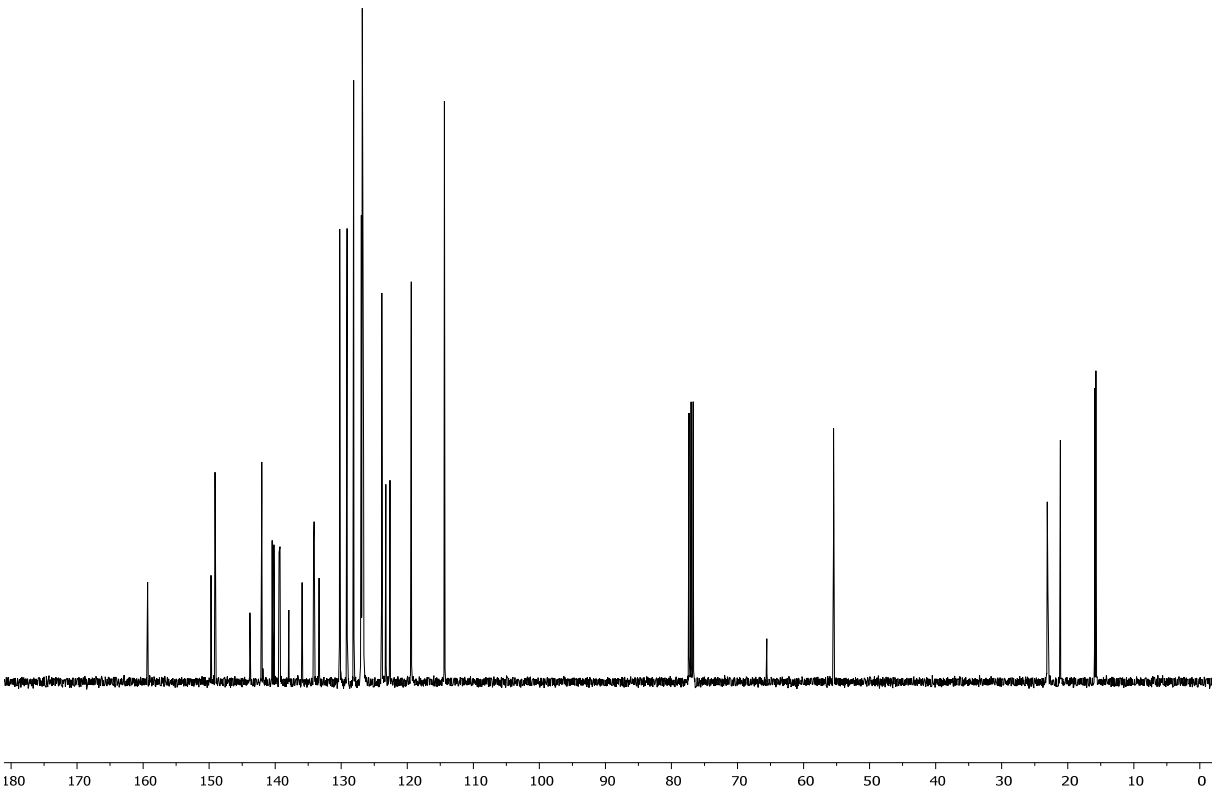




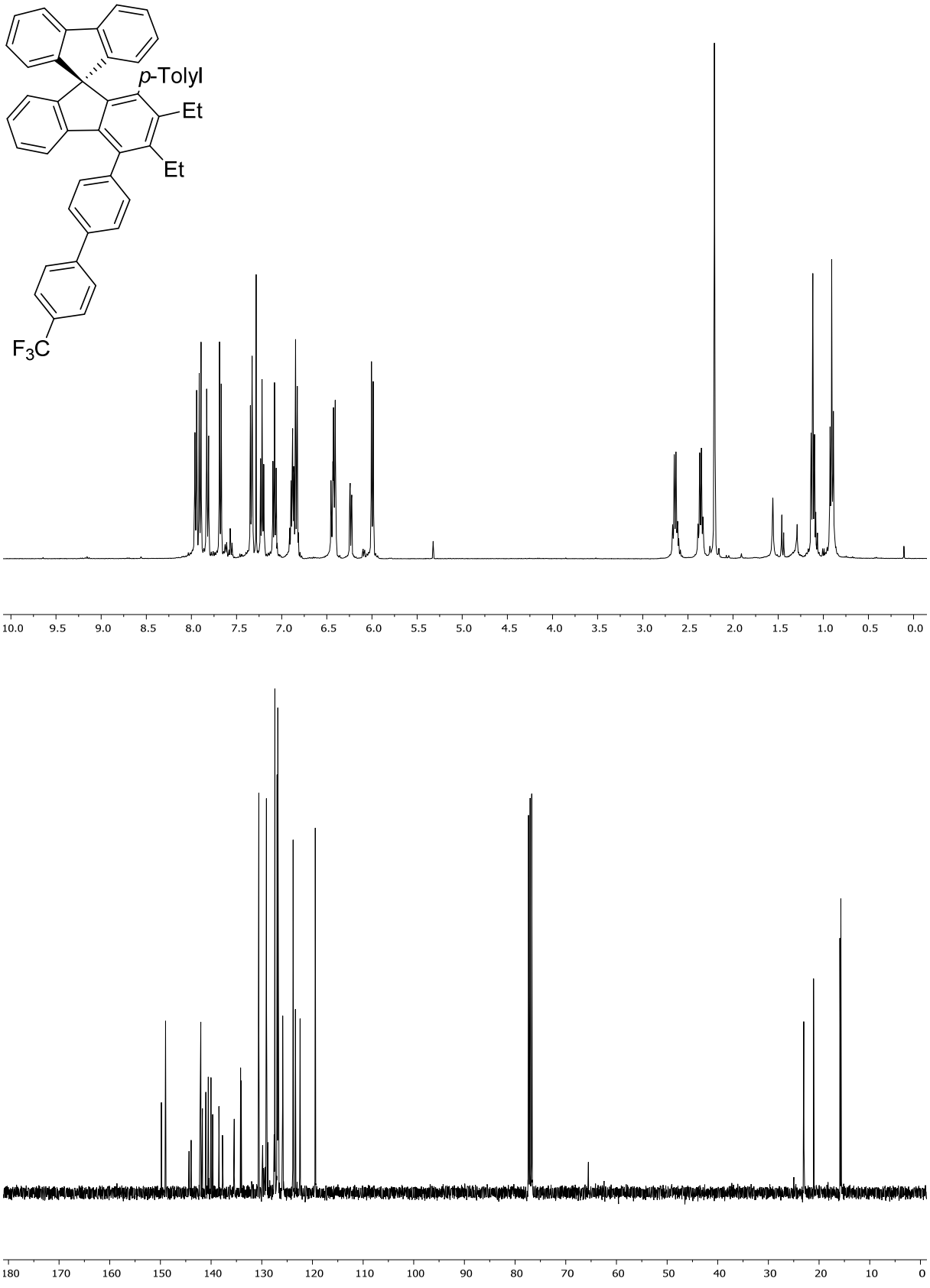
2,3-Diethyl-4-(4'-methoxy-[1,1'-biphenyl]-4-yl)-1-(*p*-tolyl)-9,9'-spirobifluorene (6a).



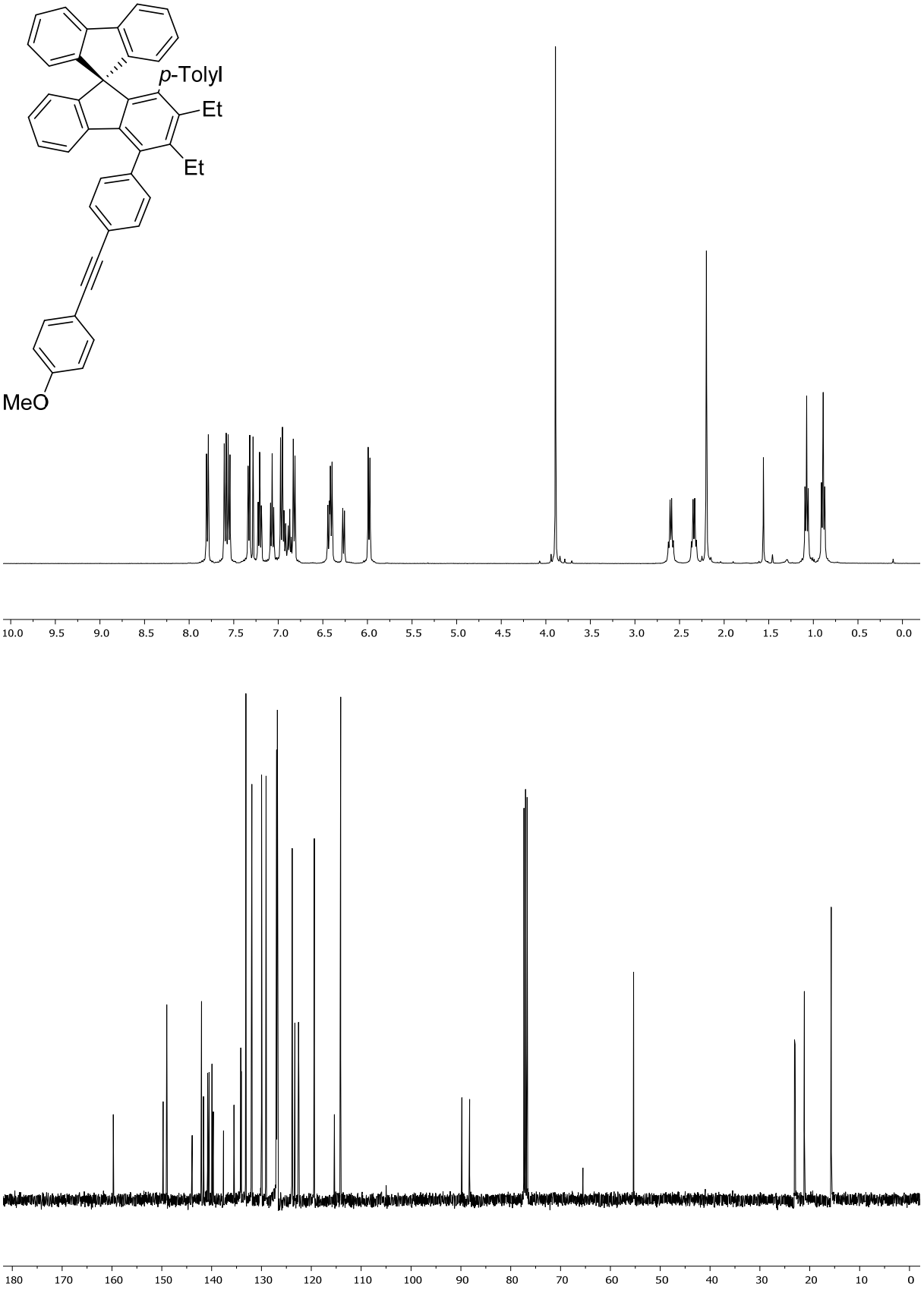




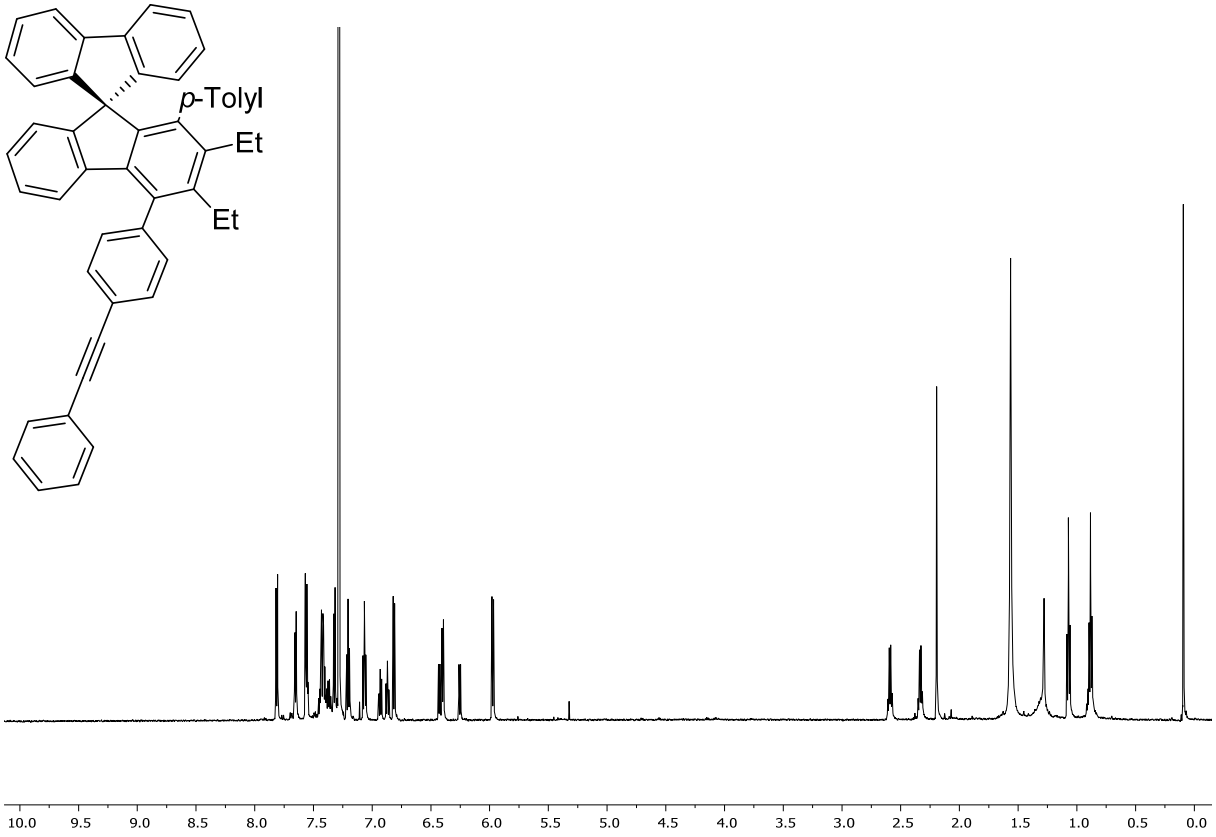
2,3-Diethyl-1-(*p*-tolyl)-4-(4'-(trifluoromethyl)-[1,1'-biphenyl]-4-yl)-9,9'-spirobifluorene (6b).

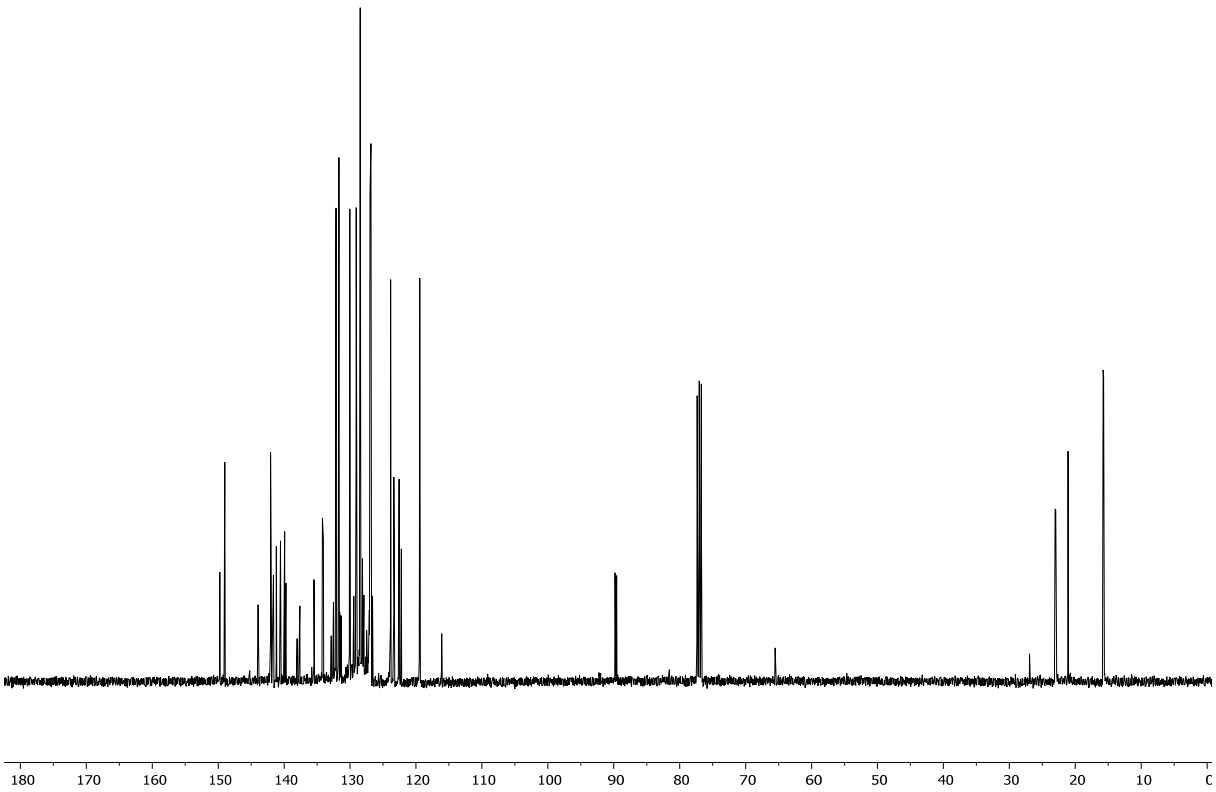


2,3-Diethyl-4-(4-((4-methoxyphenyl)ethynyl)phenyl)-1-(*p*-tolyl)-9,9'-spirobifluorene (7a).

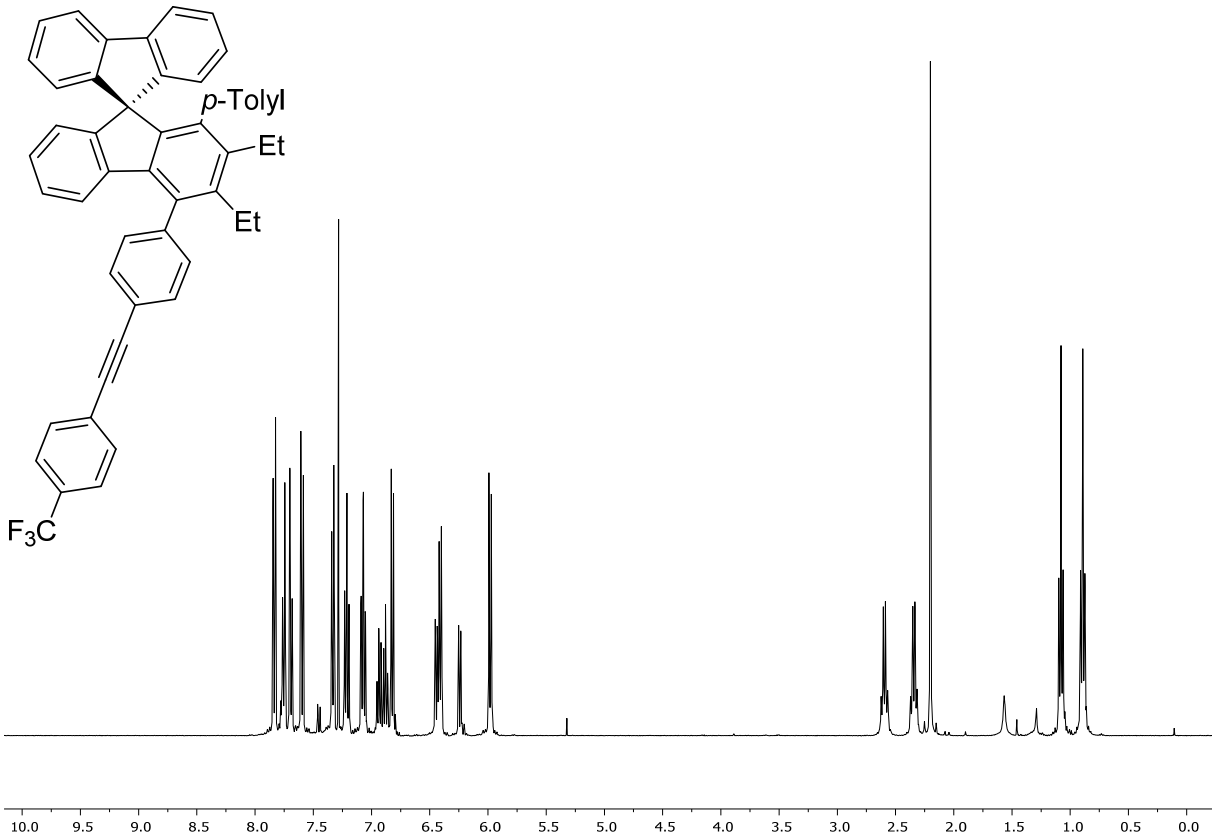


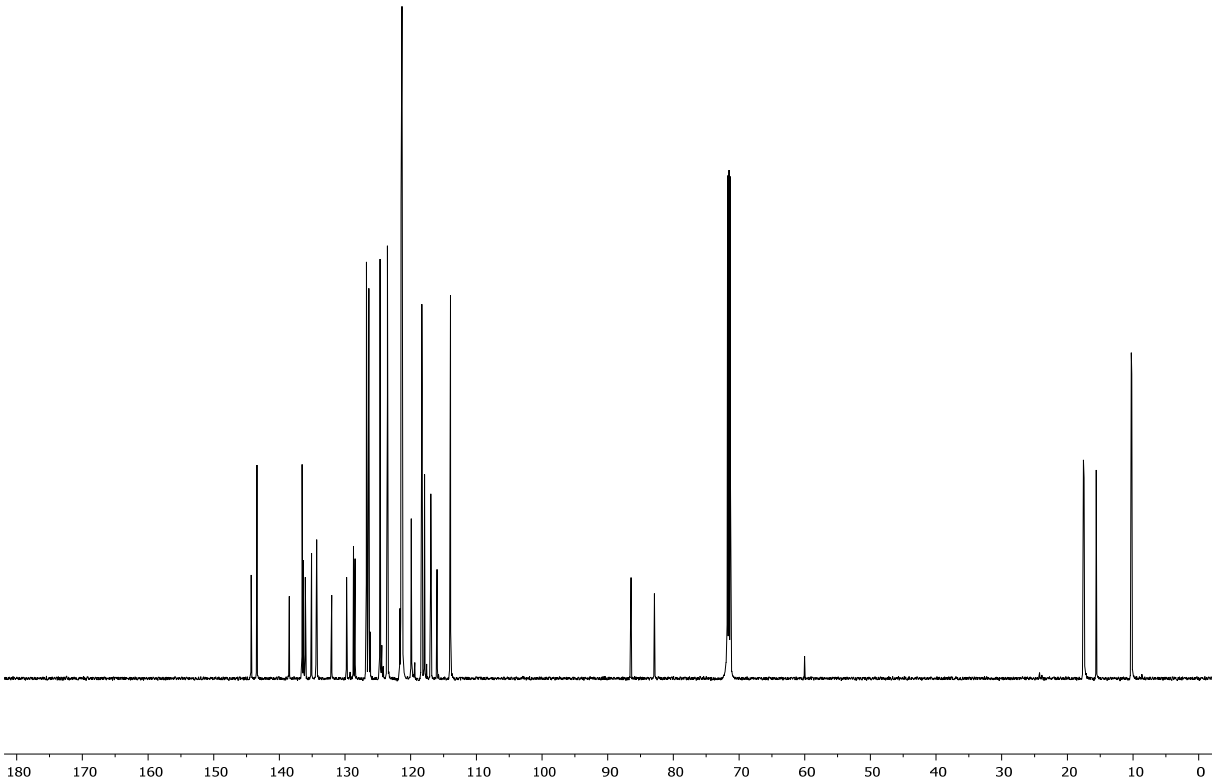
2,3-Diethyl-4-(4-(phenylethynyl)phenyl)-1-(*p*-tolyl)-9,9'-spirobifluorene (7b).



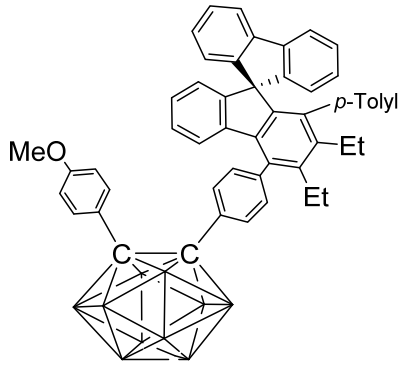


2,3-Diethyl-1-(*p*-tolyl)-4-(4-((4-(trifluoromethyl)phenyl)ethynyl)phenyl)-9,9'-spirobifluorene (7c).

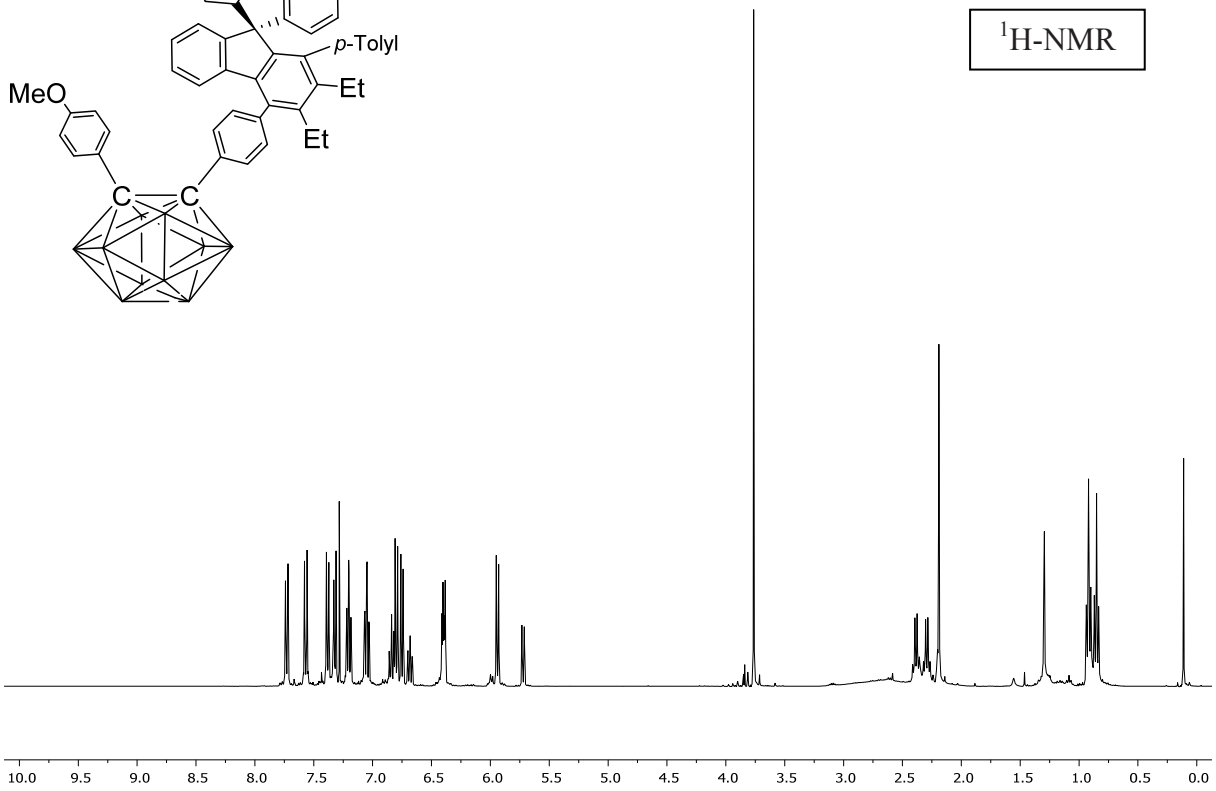




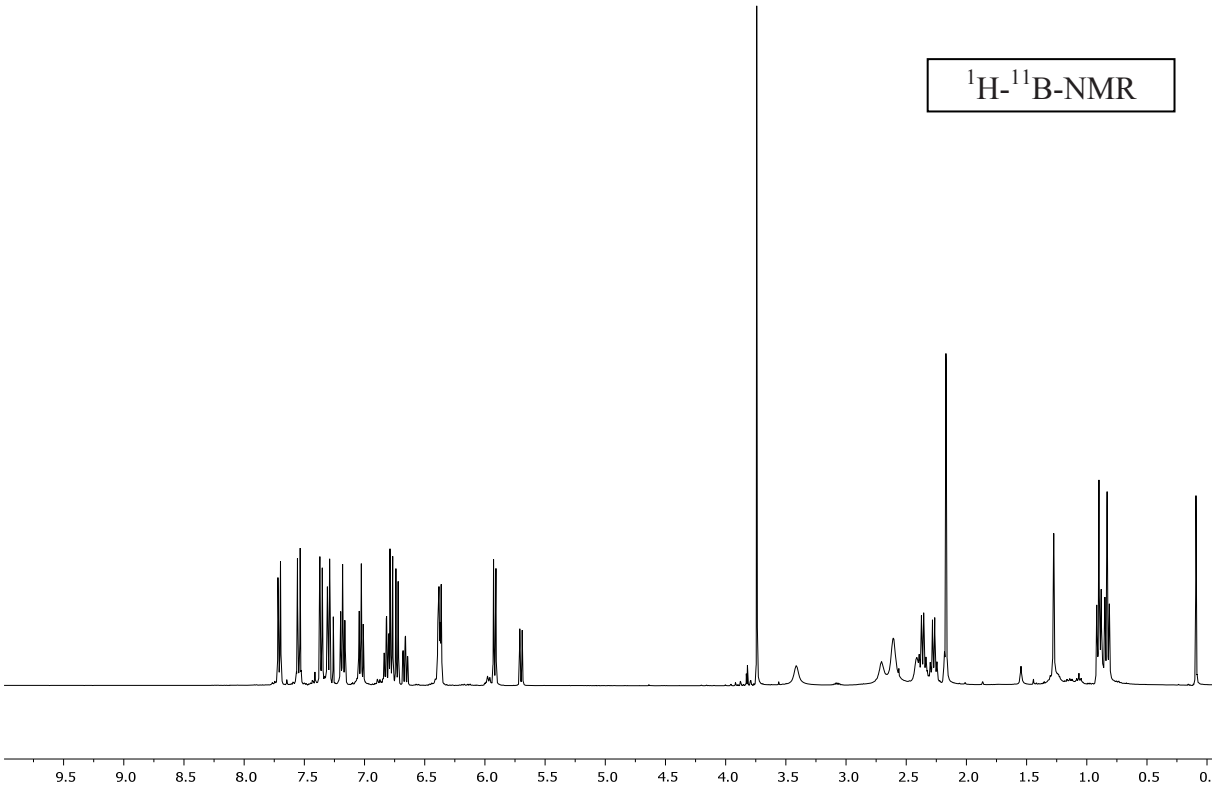
1-[2,3-Diethyl-4-phenyl)-1-(*p*-tolyl)-9,9'-spirobifluorenyl]-2-(4-methoxyphenyl)-1,2-dicarba-*closo*-dicarborane (12).



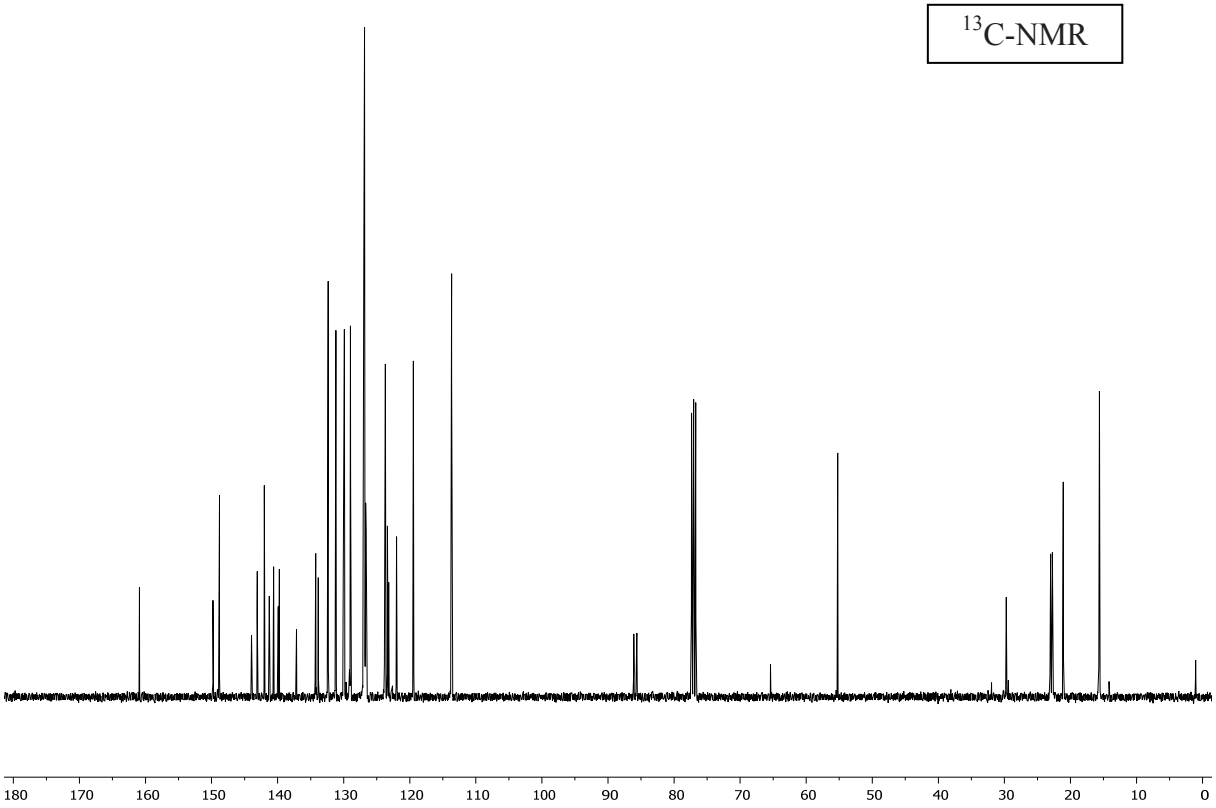
^{1}H-NMR



^{1}H-^{11}B-NMR



^{13}C-NMR



^{11}B-NMR