Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supplementary Information

Direct Methylation and Carbonylation of in Situ Generated Aryne via HDDA-Wittig Coupling

Baohua Liu, Chunyan Mao, Qiong Hu, Liangliang Yao, and Yimin Hu*

School of Chemistry and Materials Science, Anhui Normal University,

Wuhu, Anhui 241002, China E-mail: yiminhu@ahnu.edu.cn

Contents

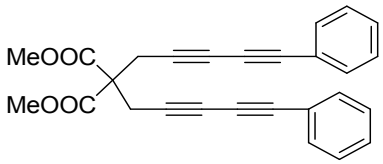
1. General experimental procedures

All the catalytic reactions were performed under an argon atmosphere using the oven-dried Schlenk flask. The chemicals were purchased from Alfa Aesar and Acros Chemicals. All solvents and materials were pre-dried, redistilled or recrystallized before use. ^{1}H NMR (300 MHz) and ^{13}C NMR (125 MHz) spectra were recorded on a Bruker Avance 300 spectrometer with $CDCl_3$ as the solvent. Chemical shifts are reported in ppm by assigning TMS resonance in the ^{1}H NMR spectra as 0.00 ppm and $CDCl_3$ resonance in the ^{13}C spectra as 77.0 ppm. All coupling constants (*J* values) were reported in Hertz (Hz). Column chromatography was performed on silica gel 300–400 mesh. Melting points were determined using a Gallenkamp melting point apparatus and are uncorrected. The FT-IR spectra were recorded from KBr pellets or thin film from $CHCl_3$ on the NaCl window in the 4000-400 cm^{-1} ranges on a Nicolet 5DX spectrometer. High-resolution mass spectra were recorded on an Agilent model G6220 mass spectrometer (APCI). X-ray Crystallography diffraction data of **3h** and **3y** were collected at room temperature with a Bruker SMART Apex CCD diffractometer with Mo-Kα radiation (λ = 0.71073 Å) with a graphite monochromator using the ω-scan mode. Data reductions and absorption corrections were performed with SAINT and SADABS software, respectively. The structure was solved by direct methods and refined on F^2 by full-matrix least squares using SHELXTL. All non-hydrogen atoms were treated anisotropically. The positions of hydrogen atoms were generated geometrically.

General procedures:

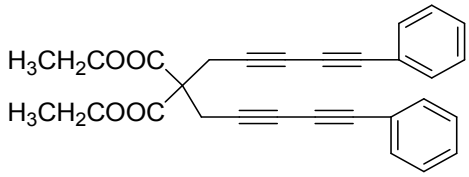
Typical experimental procedure: Tetraynes (1.0 equiv), (carbomethoxymethylene)triphenylphosphorane (1.05 equiv), Water (2.0 equiv), were added to toluene (1.5 mL), the mixture was stirred at room temperature for half an hour and then heated at 100℃ for 9 hours under argon. The reaction mixture was cooled to room temperature, and the solvent was evaporated in vacuo. The residue was purified by preparative thin-layer chromatography (TLC) on silica gel with the appropriate mixture of petroleum ether and ethyl acetate to give the fused multifunctionalized ethyl 2-methylbenzoates or *o*-tolylethanones derivatives.

2. Compound Data of Tetraynes 1



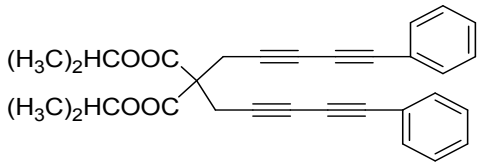
Dimethyl 2,2-bis(5-phenylpenta-2,4-diyn-1-yl)malonate

Yellow solid; 3.06 g (75% yield); m.p. 96-97℃; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.48-7.46 (d, 4H), 7.33-7.25 (m, 6H), 3.81 (s, 6H), 3.21 (s, 4H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 168.6, 132.6, 129.2, 128.4, 121.5, 77.6, 76.0, 73.7, 68.5, 56.6, 53.4, 52.9, 50.5, 24.2, 19.6 ppm; FT-IR (KBr): $\bar{\nu}$ 3462, 1744, 1491, 1300, 1207, 1069, 758, 691, 527 cm^{-1}; HRMS(APCI): *m/z* $[M+H]^+$ calcd for $C_{27}H_{20}O_4$: 409.1434; found: 409.1435.



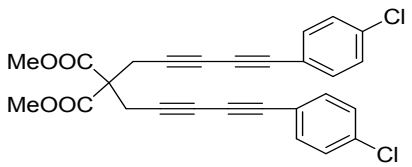
Diethyl 2,2-bis(5-phenylpenta-2,4-diyn-1-yl)malonate

Colorless solid; 3.40 g (78% yield); m.p. 62-63℃; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.39-7.35 (m, 2H), 7.25 (s, 2H), 7.07-7.03 (m, 6H), 4.30- 4.23 (q, J=6 Hz, 4H), 3.31 (s, 4H), 1.30-1.25(t, J=6 Hz, 6H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 168.2, 132.6, 129.1, 128.4, 121.5, 77.8, 75.9, 73.8, 68.4, 62.4, 56.6, 24.1, 14.0 ppm; FT-IR (KBr): $\bar{\nu}$ 3474, 1736, 1441, 1190, 1047, 758, 691, 527 cm^{-1}; HRMS (APCI): m/z $[M+H]^+$ calcd for $C_{29}H_{24}O_4$: 437.1747; found: 437.1746.



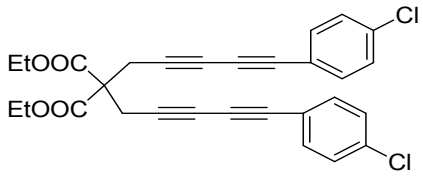
Diisopropyl 2,2-bis(5-phenylpenta-2,4-diyn-1-yl)malonate

Colorless solid, 3.71 g (80% yield); m.p. 130-131℃; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.48-7.46 (m, 4H), 7.32-7.26 (m, 6H), 5.14-5.10 (m, 2H), 3.17 (s, 4H), 1.28-1.26(d, J=6 Hz, 12H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 167.8, 132,6, 129.1, 128.4, 121.6, 78.0, 75.8, 73.9, 70.0, 68.3, 56.5, 24.0, 21.5 ppm; FT-IR (KBr): $\bar{\nu}$ 3466, 1732, 1302, 1219, 1120, 1952, 758, 689, 528 cm^{-1}; HRMS (APCI): m/z $[M+H]^+$ calcd for $C_{31}H_{28}O_4$: 465.2060; found: 465.2056.



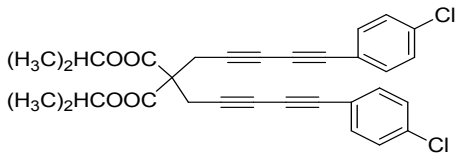
Dimethyl 2,2-bis(5-(4-chlorophenyl)penta-2,4-diyn-1-yl)malonate

Yellow solid, 3.90 g (82% yield); m.p. 123-124℃; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.41-7.38 (d, 4H), 7.30-7.27 (d, 4H), 3.81 (s, 6H), 3.20 (s, 4H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 168.5, 135.3, 133.7, 128.8, 120.0, 78.2, 74.8, 74.7, 68.3, 56.5, 53.4, 52.9, 50.4, 24.2, 19.5 ppm; FT-IR (KBr): $\bar{\nu}$ 2447, 1740, 1489, 1433, 1302, 1213, 829, 525 cm^{-1}; HRMS (APCI): m/z $[M+H]^+$ calcd for $C_{27}H_{18}Cl_2O_4$: 477.0655; found: 477.0652.



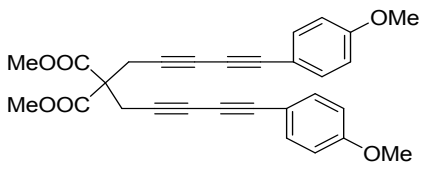
Diethyl 2,2-bis(5-(4-chlorophenyl)penta-2,4-diyn-1-yl)malonate

Yellow solid, 4.08 g (81% yield); m.p. 104-105℃; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.43-7.38 (m, 4H), 7.33-7.26 (m, 4H), 4.30-4.23 (q, J = 6 Hz, 4H), 3.19 (s, 4H), 1.31-1.26 (t, J=6 Hz, 6H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 168.1, 135.3, 133.7, 130.9, 129.3, 128.7, 120.0, 78.4, 74.6, 72.1, 68.1, 62.4, 56.4, 24.0, 23.7, 14.0 ppm; FT-IR (KBr): $\bar{\nu}$ 3474, 1736, 1641, 1489, 1285, 1188, 1011, 837, 528 cm^{-1}; HRMS (APCI): m/z $[M+H]^+$ calcd for $C_{29}H_{22}Cl_2O_4$:505.0968; found: 505.0966.



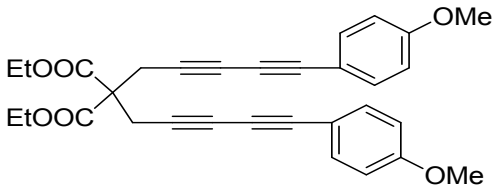
Diisopropyl 2,2-bis(5-(4-chlorophenyl)penta-2,4-diyn-1-yl)malonate

Yellow solid, 4.20 g (79% yield); m.p. 85-86℃; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.40-7.38 (m, 4H), 7.29-7.26 (m, 6H), 5.14-5.10 (m, 2H), 3.16 (s, 4H), 1.28-1.26(d, J=6Hz, 12H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 167.6, 135.2, 133.7, 128.7, 120.1, 78.6, 74.8, 74.6, 70.0, 68.1, 56.4, 24.0, 21.5 ppm; FT-IR (KBr): $\bar{\nu}$ 3449, 1736, 1489, 1290, 1205, 1105, 1012, 825, 525 cm^{-1}; HRMS (APCI): m/z $[M+H]^+$ calcd for $C_{31}H_{26}Cl_2O_4$: 534.1034; found: 534.1039.



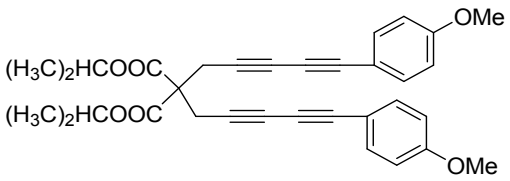
Dimethyl 2,2-bis(5-(4-methoxyphenyl)penta-2,4-diyn-1-yl)malonate

Yellow solid, 3.60 g (77% yield); m.p. 101-102℃; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.44-7.41 (d, 4H), 6.84-6.82 (d, 4H), 3.81 (s, 12H), 3.21 (s, 4H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 168.7, 160.2, 134.2, 114.1, 113.3, 77.5, 76.1, 72.6, 68.6, 56.7, 55.3, 53.4, 24.2 ppm; FT-IR (KBr): $\bar{\nu}$ 3474, 1744, 1603, 1508, 1257, 1201, 1024, 829, 532 cm^{-1}; HRMS (APCI): m/z $[M+H]^+$ calcd for $C_{29}H_{24}O_6$: 469.1646; found: 469.1645.



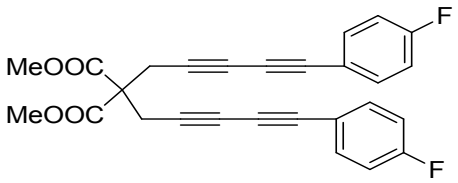
Diethyl 2,2-bis(5-(4-methoxyphenyl)penta-2,4-diyn-1-yl)malonate

Yellow solid, 3.92 g (79% yield); m.p. 69-70℃; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.43-7.40 (d, 4H), 6.84-6.81 (d, 4H), 4.30-4.23 (q, J=6 Hz, 4H), 3.81 (s, 4H), 1.31-1.27 (t, J=6 Hz, 6H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 168.3, 160.3, 134.2, 114.1, 113.5, 77.3, 76.1, 72.7, 68.6, 62.3, 56.6, 55.3, 24.1, 14.1 ppm; FT-IR (KBr): $\bar{\nu}$ 3447, 1728, 1603, 1508, 1246, 1178, 829, 532 cm^{-1}; HRMS (APCI): m/z $[M+H]^+$ calcd for $C_{31}H_{28}O_6$: 497.1959; found: 497.1953.



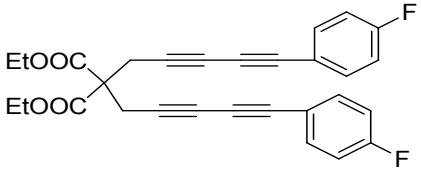
Diisopropyl 2,2-bis(5-(4-methoxyphenyl)penta-2,4-diyn-1-yl) malonate

Colorless crystal, 4.40 g (84% yield); m.p. 81-82℃; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.42-7.39 (d, 4H), 6.83-6,81 (d, 4H), 5.14-5.10 (m, 2H), 3.80 (s, 6H), 3.16 (s, 4H), 1.28-1.26 (d, J=6 Hz, 12H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 167.8, 160.2, 134.1, 114.0, 113.6, 77.4, 72.7, 69.9, 68.5, 56.6, 55.3, 24.0, 21.5 ppm; FT-IR (KBr) $\bar{\nu}$ 3447, 1734, 1600, 1508, 1292, 1254, 1211, 1101, 1028, 835, 534 cm^{-1}; HRMS (APCI): m/z $[M+H]^+$ calcd for $C_{33}H_{32}O_6$: 525.2272; found: 525.2275.



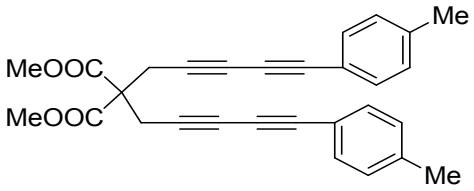
Dimethyl 2,2-bis(5-(4-fluorophenyl)penta-2,4-diyn-1-yl)malonate

Yellow solid, 3.69 g (83% yield); m.p. 116-117℃; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.52-7.47 (m, 4H), 7.07-7.01 (t, 4H), 3.84 (s, 6H), 3.24 (s, 4H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 168.6, 164.6, 161.3, 134.6, 134.5, 117.6, 117.6, 115.9, 115.6, 77.6, 74.8, 73.5, 68.3, 56.6, 53.4, 24.1 ppm; FT-IR (KBr): $\bar{\nu}$ 3447, 1738, 1508, 1289, 1211, 1151, 1069, 837, 528 cm^{-1}; HRMS (APCI): m/z $[M+H]^+$ calcd for $C_{27}H_{18}F_2O_4$: 445.1246; found: 445.1246.



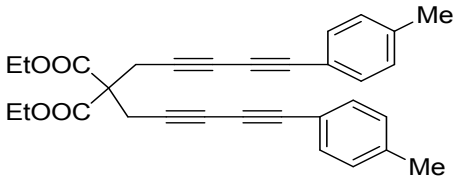
Diethyl 2,2-bis(5-(4-fluorophenyl)penta-2,4-diyn-1-yl)malonate

Yellow solid, 3.78 g (80% yield); m.p. 64-65℃; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.51-7.47 (m, 4H), 7.07-7.01 (m, 4H), 4.34-4.28 (q, J=6 Hz, 4H), 3.23 (s, 4H), 1.35-1.30 (t, J=6 Hz, 6H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 168.1, 164.7, 161.3, 134.6, 134.6, 134.5, 134.4, 116.0, 115.9, 115.7, 115.6, 77.8, 74.8, 68.2, 62.4, 56.5, 24.1, 14.0 ppm; FT-IR (KBr) $\bar{\nu}$ 3487, 1740, 1599, 1508, 1302, 1234, 1194, 1157, 831, 528 cm^{-1}; HRMS (APCI): m/z $[M+H]^+$ calcd for $C_{29}H_{22}F_2O_4$: 473.1559; found: 473.1560.



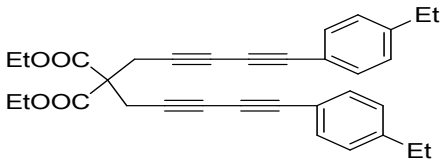
Dimethyl 2,2-bis(5-(p-tolyl)penta-2,4-diyn-1-yl)malonate

Yellow solid, 3.40 g (78% yield); m.p. 102-103℃; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.38-7.35 (d, 4H), 7.12-7.10 (d, 4H), 3.80 (s, 6H), 3.20 (s, 4H), 2.34 (s, 6H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 168.6, 139.5, 132.5, 129.1, 118.4, 77.5, 76.3, 73.2, 68.6, 56.7, 53.4, 24.2, 21.6 ppm; FT-IR (KBr): $\bar{\nu}$ 3487, 1740, 1508, 1431, 1335, 1287, 1198, 1063, 1049, 816, 529 cm^{-1}; HRMS (APCI): m/z $[M+H]^+$ calcd for $C_{29}H_{24}O_4$: 437.1747; found: 437.1752.



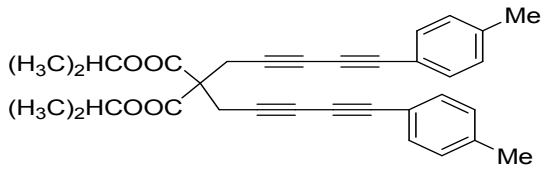
Diethyl 2,2-bis(5-(p-tolyl)penta-2,4-diyn-1-yl)malonate

Yellow solid, 3.67 g (79% yield); m.p. 88-89℃; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.38-7.35 (d, 4H), 7.12-7.10 (d, 4H), 4.30-4.24 (q, J=6 Hz, 4H), 3.19 (s, 4H), 2.35 (s, 6H), 1.31-1.27 (t, J=6 Hz, 6H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 168.2, 139.5, 132.5, 132.3, 129.2, 129.1, 118.4, 81.5, 77.5, 76.1, 73.3, 68.5, 62.3, 56.6, 24.1, 21.6, 14.0 ppm; FT-IR (KBr): $\bar{\nu}$ 3466, 1742, 1058, 1423, 1298, 1200, 1072, 808, 525 cm^{-1}; HRMS (APCI): m/z $[M+H]^+$ calcd for $C_{31}H_{28}O_4$: 465.2060; found: 465.2058.



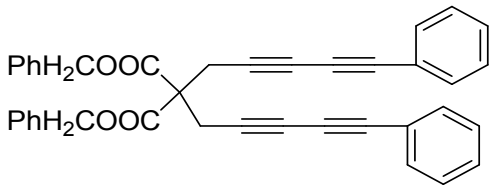
Diethyl 2,2-bis(5-(4-ethylphenyl)penta-2,4-diyn-1-yl)malonate

Yellow solid, 3.94 g (80% yield); m.p. 74-75℃; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.40-7.38 (d, 4H), 7.15-7.12 (d, 4H), 4.30-4.24 (q, J=6 Hz, 4H), 3.19 (s, 4H), 2.68-2.60 (q, J=6 Hz, 4H), 1.32-1.19 (m, 12H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 168.2, 145.7, 132.6, 127.9, 118.6, 77.4, 76.1, 73.2, 68.5, 62.4, 56.6, 28.9, 24.1, 15.2, 14.0 ppm; FT-IR (KBr): $\bar{\nu}$ 3462, 1740, 1508, 1300, 1192, 1051, 1016, 829, 538 cm^{-1}; HRMS (APCI): m/z $[M+H]^+$ calcd for $C_{33}H_{32}O_4$: 493.2373; found: 493.2374.



Diisopropyl 2,2-bis(5-(p-tolyl)penta-2,4-diyn-1-yl)malonate

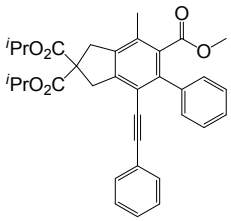
Yellow solid, 3.64 g (74% yield); m.p. 91-92℃; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.37-7.34 (m, 4H), 7.11-7.09 (m, 4H), 5.14-5.10 (m, 2H), 3.16 (s, 4H), 2.34 (s, 6H), 1.28-1.26(d, J=6 Hz, 12H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 167.8, 139.4, 132.5, 132.3, 129.2, 129.1, 118.5, 77.6, 76.0, 73.3, 69.9, 68.4, 56.5, 24.0 21.6, 21.5 ppm; FT-IR (KBr): $\bar{\nu}$ 3466, 1734, 1508, 1298, 1211, 1196, 1105, 1064, 818, 528 cm^{-1}; HRMS (APCI): m/z $[M+H]^+$ calcd for $C_{33}H_{32}O_4$: 493.2373; found: 493.2378.



Dibenzyl 2,2-bis(5-phenylpenta-2,4-diyn-1-yl)malonate

Yellow solid, 4.09 g (73% yield); m.p. 79-80℃; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.49-7.25 (m, 20H), 5.18 (s, 4H), 3.24 (s, 4H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 167.9, 134.9, 132.6, 129.1, 128.6, 128.4, 128.4, 128.2, 128.0, 121.6, 77.6, 76.0, 73.9, 68.7, 68.0, 56.9, 24.2 ppm; FT-IR (KBr): $\bar{\nu}$ 3449, 1734, 1489, 1281, 1202, 1173, 1051, 759, 694, 527 cm^{-1}; HRMS (APCI): m/z $[M+H]^+$ calcd for $C_{39}H_{28}O_4$: 561.2060; found: 561.2058.

3. Characterization Data for the New Compounds



2,2-Diisopropyl 5-methyl 4-methyl-6-phenyl-7-(phenylethynyl)-1H-indene-2,2,5(3H)- tricarboxylate (3a)

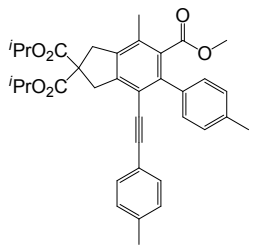
Colorless solid; (431 mg, 80% yield); m. p. 128.6℃; TLC (petroleum ether/EtOAc = 30:1): R_f = 0.50.

^{1}H NMR (300 MHz, $CDCl_3$): *δ* 7.40-7.19 (m, 10H), 5.15-5.06 (m, 2H), 3.81 (s, 2H), 3.61 (s, 2H), 3.50 (s, 3H), 2.30 (s, 3H), 1.33-1.25 (m, 12H).

^{13}C NMR (125 MHz, $CDCl_3$): *δ* 171.4, 170.1, 144.0, 141.6, 139.3, 139.1, 136.2, 133.9, 131.7, 131.2, 129.8, 128.5, 128.0, 127.8, 123.6, 117.4, 96.4, 86.9, 77.6, 77.4, 77.1, 69.8, 59.6, 52.1, 41.4, 40.3, 21.9, 17.1 ppm.

FT-IR (KBr) $\bar{\nu}$ 2978, 2924, 1745, 1732, 1714, 1490, 1446, 1373, 1271, 1255, 1234, 1192, 1161, 1105, 1039, 763, 694cm^{-1}.

HRMS (APCI): *m/z* calcd for $C_{34}H_{34}O_6$ $[M+H]^+$,539.2428, found 539.2432.



2,2-Diisopropyl 5-methyl 4-methyl-6-(p-tolyl)-7-(p-tolylethynyl)-1H-indene-2,2,5(3H)- tricarboxylate (3b)

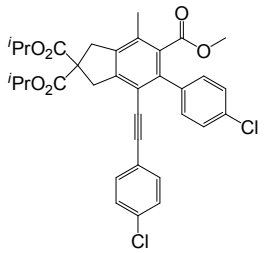
Colorless solid; (471 mg, 83% yield); m. p. 162.7℃; TLC (petroleum ether/EtOAc = 30:1): R_f = 0.52.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.29-7.05 (m, 8H), 5.12-5.04 (m, 2H), 3.78 (s, 2H), 3.58 (s, 2H), 3.52 (s, 3H), 2.39 (s, 3H), 2.32 (s, 3H), 2.27 (s, 3H) 1.28-1.26 (m, 12H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 171.4, 170.3, 143.9, 141.3, 138.8, 138.6, 137.3, 136.3, 134.0, 131.6, 130.8, 129.7, 129.3, 128.7, 120.6, 117.6, 96.5, 86.4, 77.6, 77.4, 77.1, 69.8, 59.5, 52.1, 41.4, 40.3, 21.9, 21.9, 21.7 ppm.

FT-IR (KBr) $\bar{\nu}$ 2980, 2360, 1734, 1510, 1433, 1354, 1271, 1253, 1234, 1180, 1166, 1109, 1099, 1056, 819, 528 cm^{-1}.

HRMS (APCI): *m/z* calcd for $C_{36}H_{38}O_6$ $[M+H]^+$,567.2741, found 567.2740.



2,2-Diisopropyl 5-methyl 6-(4-chlorophenyl)-7-((4-chlorophenyl)ethynyl)-4-methyl- 1H-indene-2,2,5(3H)-tricarboxylate (3c)

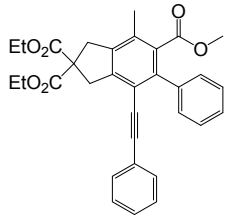
Colorless solid; (473 mg, 78% yield); m. p. 137.5℃; TLC (petroleum ether/EtOAc = 30:1): R_f = 0.47;

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.38-7.10 (m, 8H), 5.12-5.04 (m, 2H), 3.75 (s, 2H), 3.59 (s, 2H), 3.52 (s, 3H), 2.27 (s, 3H), 1.27 (d, J = 6 Hz, 12H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 170.7, 169.2, 143.6, 139.6, 139.0, 137.1, 134.1, 133.4, 132.3, 131.0, 130.7, 128.4, 127.7, 121.2, 116.4, 104.8, 95.0, 86.9, 77.1, 76.8, 76.5, 69.3, 58.9, 51.8, 40.7, 39.7, 21.3, 16.6 ppm.

FT-IR (KBr): $\bar{\nu}$ 2981,1730, 1490, 1276, 1249, 1165, 1101, 825 cm^{-1}.

HRMS (APCI): *m/z* calcd for $C_{34}H_{32}Cl_2O_6$ $[M+H]^+$,607.1649, found 607.1645.



2,2-Diethyl 5-methyl 4-methyl-6-phenyl-7-(phenylethynyl)-1H-indene-2,2,5(3H)-tricarboxylate (3d)

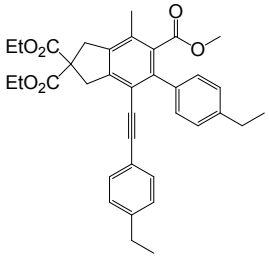
Colorless solid; (409 mg, 80% yield); m. p. 131.3℃; TLC (petroleum ether/EtOAc = 20:1): R_f = 0.45 .

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.38-7.18 (m,10H), 4.25 (q, J = 6 Hz, 4H), 3.83 (s, 2H), 3.63 (s, 2H), 3.48 (s, 3H), 2.29 (s, 3H), 1.25 (t, J = 7.5 Hz, 6H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 143.4, 141.1, 138.8, 138.6, 133.5, 131.3, 130.8, 129.4, 128.1, 127.6, 127.5, 123.1, 117.0, 96.0, 86.4, 77.2, 77.0, 76.7, 62.0, 59.1, 51.8, 41.0, 39.9, 16.8, 14.0 ppm.

FT-IR (KBr) $\bar{\nu}$ 2981, 1728, 1490, 1442, 1271, 1257, 123, 1166, 1076, 759, 692 cm^{-1}.

HRMS (APCI): *m/z* calcd for $C_{32}H_{30}O_6$ $[M+H]^+$, 511.2115, found 511.2111.



2,2-Diethyl 5-methyl 6-(4-ethylphenyl)-7-((4-ethylphenyl)ethynyl)-4-methyl-1H-in-dene-2,2,5 (3H)-tricarboxylate (3e)

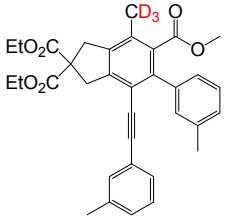
Colorless solid; (481 mg, 85% yield); m. p. 98.6℃; TLC (petroleum ether/EtOAc = 20:1): R_f = 0.50.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.31-7.06 (m, 8H), 4.26 (q, J = 7 Hz, 4H), 3.81 (s, 2H), 3.62 (s, 2H), 3.50 (s, 3H), 2.65 (ddd, J = 6Hz, 15 Hz, 27 Hz, 4H), 2.27 (s, 3H), 1.31-1.17 (m, 12H) .

^{13}C NMR (125 MHz, $CDCl_3$): δ 171.5, 169.9, 144.6, 143.3, 143.2, 141.1, 138.3, 136.1, 133.6, 131.3, 130.4, 129.3, 127.7, 127.1, 120.4, 117.3, 102.7, 102.4, 96.2, 86.0, 77.2, 77.0, 76.7, 61.9, 59.1, 51.8, 41.0, 39.9, 30.9, 28.8, 28.7, 16.7, 15.7, 15.4, 14.0 ppm.

FT-IR (KBr): $\bar{\nu}$ 2964, 1722, 1512, 1433, 1273, 1251, 1234, 1182, 1166, 1055, 833 cm^{-1}.

HRMS (APCI): *m/z* calcd for $C_{36}H_{38}O_6$[M+H]$^+$,567.2741, found 567.2742.



2,2-Diethyl 5-methyl 4-methyl-6-(m-tolyl)-7-(m-tolylethynyl)-1H-indene-2,2,5(3H)-tricarboxylate (3f)

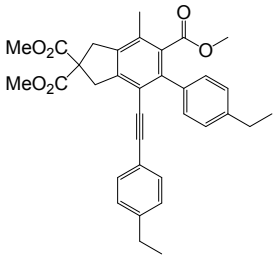
Colorless solid; (433 mg, 80% yield); m. p. 65℃; TLC (petroleum ether/EtOAc = 20:1): Rf = 0.48;

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.28-7.03 (m, 8H), 4.27-4.22 (m, 4H), 3.83 (s, 2H), 3.63 (s, 2H), 3.51 (s, 3H), 2.39 (s, 3H), 2.29 (s, 3H), 1.29 (t, J = 7.5 Hz, 6H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 171.9, 170.2, 143.8, 141.6, 139.1, 138.8, 138.2, 137.3, 134.0, 132.3, 131.0, 130.5, 129.4, 128.7, 128.6, 128.4, 127.9, 126.8, 123.4, 117.4, 113.2, 96.7, 86.7, 77.6, 77.4, 77.1, 62.3, 59.5, 52.1, 41.5, 40.4, 21.8, 21.5, 14.4 ppm.

FT-IR (KBr): $\bar{\nu}$ 2978, 2949, 2918, 1734, 1722, 1602, 1581, 1487, 1431, 1365, 1269, 1201, 1184, 1072, 858, 792, 692 cm^{-1}.

HRMS (APCI): *m/z* calcd for $C_{34}H_{31}D_3O_6$[M+H]$^+$,542.2616, found 542.2613.



Trimethyl 6-(4-ethylphenyl)-7-((4-ethylphenyl)ethynyl)-4-methyl-1H-indene-2,2,5(3H) -tricarboxylate (3g)

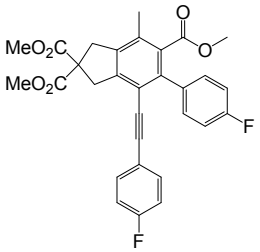
Colorless solid; (436 mg, 81% yield); m. p. 142.9℃; TLC (petroleum ether/EtOAc = 10:1): R_f= 0.26.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.31-7.10 (m, 8H), 3.83-3.77 (m, 4H), 3.64 (s, 2H), 3.51 (s, 3H), 2.72- 2.61 (m, 4H), 2.28 (s, 3H), 1.31-1.19 (m, 6H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 172.3, 170.2, 145.0, 143.8, 143.5, 141.6, 138.6, 136.5, 134.1, 131.7, 130.8, 129.8, 128.1, 127.5, 120.8, 117.8, 96.7, 86.4, 77.6, 77.4, 77.1, 59.5, 53.5, 52.2, 41.6, 40.5, 29.2, 29.1, 17.1, 16.1, 15.7 ppm.

FT-IR (KBr):$\bar{\nu}$ 2956, 1753, 1732, 1508, 1436, 1232, 1193, 1163, 1056, 837 $cm^{-1.}$.

HRMS (APCI): *m/z* calcd for $C_{34}H_{34}O_6[M+H]^+$,539.2428, found 539.2427.



Trimethyl 6-(4-fluorophenyl)-7-((4-fluorophenyl)ethynyl)-4-methyl-1H-indene- 2,2,5(3H)- tricarboxylate (3h)

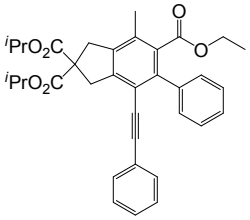
Colorless solid; (389 mg, 75% yield); m. p. 159.3℃; TLC (petroleum ether/EtOAc = 10:1): R_f= 0.19.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.37-7.16 (m, 4H), 7.12-6.94 (m, 4H), 3.80 (s, 8H), 3.64 (s, 2H), 3.52 (s, 3H), 2.27 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 172.2, 169.9, 162.8(d, 1JFC= 271Hz), 143.7, 140.3, 139.1, 135.1(d, 4JFC= 3.75 Hz), 134.2, 133.6(d, 3JFC= 8 Hz), 131.6(d, 3JFC = 8 Hz), 131.3, 119.4(d, 4JFC = 2 Hz), 117.4, 116.0(d, 2JFC= 21Hz), 115.0(d, 2JFC= 21Hz), 95.6, 86.2, 77.6, 77.4, 77.1, 59.4, 53.6, 52.3, 41.5, 40.4, 17.2 ppm.

FT-IR (KBr):$\bar{\nu}$ 2954, 1734, 1697, 1598, 1506, 1433, 1284, 1247, 1226, 1201, 1157, 530 $cm^{-1.}$

HRMS (APCI): *m/z* calcd for $C_{30}H_{24}F_2O_6$ $[M+H]^+$,519.1614, found 519.1615.



5-Ethyl 2,2-diisopropyl 4-methyl-6-phenyl-7-(phenylethynyl)-1H-indene-2,2,5(3H)-tricarboxylate (3i)

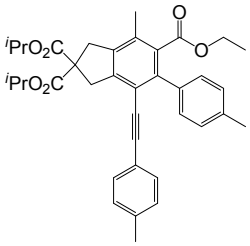
Colorless solid; (436 mg, 79% yield); m. p. 121.4℃; TLC (petroleum ether/EtOAc = 30:1), R_f= 0.51;

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.38-7.19 (m, 10H), 5.13-5.05 (m, 2H), 3.96 (dd, J =9, 15 Hz, 2H), 3.79 (s, 2H), 3.60 (s, 2H), 2.30 (s, 3H), 1.28 (d, J = 6 Hz, 12H), 0.89 (t, J = 7.5 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 171.0, 169.1, 143.4, 141.2, 139.0, 138.7, 133.7, 131.3, 130.8, 129.6, 128.1, 128.1, 127.5, 127.4, 123.3, 117.0, 95.9, 86.5, 77.2, 77.0, 76.7, 69.4, 60.9, 59.2, 41.0, 40.0, 21.5, 16.7, 13.5 ppm.

FT-IR (KBr): $\bar{\nu}$ 2986, 1718, 1523, 1245, 1143, 1123, 834, 517 cm^{-1}.

HRMS (APCI): *m/z* calcd for $C_{35}H_{36}O_6[M+H]^+$,553.2585, found 553.2579.



5-Ethyl 2,2-diisopropyl 4-methyl-6-(p-tolyl)-7-(p-tolylethynyl)-1H-indene-2,2,5(3H)- tricarboxylate (3j)

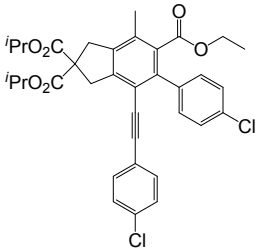
Colorless solid; (482 mg, 81% yield); m. p. 161.5℃; TLC (petroleum ether/EtOAc = 30:1): R_f = 0.51.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.28 (d, J = 9 Hz, 2H), 7.17 (d, J = 6 Hz,2H), 7.08 (dd, J = 9,15 Hz, 4H), 5.12-5.04 (m, 2H), 3.98 (dd, J = 7.5, 13.5 Hz, 2H), 3.77 (s, 2H), 3.58 (s, 2H), 2.38 (s, 3H), 2.32 (s, 3H), 2.28 (s, 3H), 1.27 (d, J = 6 Hz, 12H), 0.94 (t, J = 7.5 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 171.0, 169.3, 143.3, 141.0, 138.4, 138.2, 136.9, 136.0, 133.7, 131.2, 130.4, 129.4, 128.9, 128.2, 120.3, 117.2, 96.1, 86.0, 77.2, 77.0, 76.7, 69.3, 60.9, 59.1, 41.0, 39.9, 21.5, 21.4, 21.3, 16.7, 13.6 ppm.

FT-IR (KBr): $\bar{\nu}$ 2981, 1728, 1510, 1255, 1180, 1101, 817, 526 cm^{-1}.

HRMS (APCI): *m/z* calcd for $C_{37}H_{40}O_6$ $[M+H]^+$,581.2898, found 581.2891.



5-Ethyl 2,2-diisopropyl 6-(4-chlorophenyl)-7-((4-chlorophenyl)ethynyl)-4-methyl-1H- indene-2,2,5(3H)-tricarboxylate (3k)

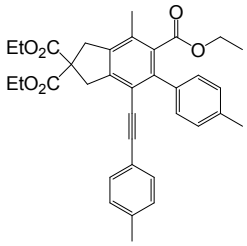
Colorless solid; (471 mg, 76% yield); m. p. 108.1℃; TLC (petroleum ether/EtOAc = 30:1), R_f = 0.45.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.34 (dd, J = 9, 15 Hz, 4H), 7.15 (d, J = 9 Hz, 2H), 7.11 (d, J = 6 Hz, 2H), 5.13-5.04 (m, 2H), 4.00 (q, J = 7 Hz, 2H), 3.76 (s, 2H), 3.59 (s, 2H), 2.29 (s, 3H), 1.28 (d, J = 6 Hz, 12H), 0.97 (t, J = 7.5 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 170.9, 168.8, 143.6, 139.8, 139.2, 137.4, 134.3, 133.6, 133.5, 132.5, 131.2, 131.0, 128.6, 127.8, 121.5, 116.8, 95.1, 92.9, 87.1, 85.4, 77.2, 77.0, 76.7, 69.5, 61.1, 59.1, 48.6, 40.9, 39.9, 29.7, 21.5, 16.7, 13.6 ppm.

FT-IR (KBr): $\bar{\nu}$ 2966, 2931, 1732, 1512, 1367, 1269, 1253, 1236, 1184, 1174, 1161, 1076, 829 cm^{-1}.

HRMS (APCI): *m/z* calcd for $C_{35}H_{34}Cl_2O_6$ $[M+H]^+$,621.1805, found 621.1800.



Triethyl 4-methyl-6-(p-tolyl)-7-(p-tolylethynyl)-1H-indene-2,2,5(3H)-tricarboxylate (3l)

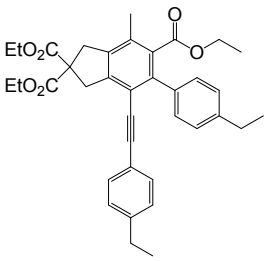
Colorless solid; (430 mg, 78% yield); m. p. 112.8℃; TLC (petroleum ether/EtOAc = 20:1): R_f = 0.48.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.23 (dd, J = 9, 30 Hz, 4H), 7.08 (dd, J = 9, 15 Hz, 4H), 4.25 (dd, J = 6, 15 Hz, 4H), 3.99 (dd, J = 6, 15 Hz, 2H), 3.81 (s, 2H), 3.61 (s, 2H), 2.38 (s, 3H), 2.32 (s, 3H), 2.28 (s, 3H), 1.29 (t, J = 7.5 Hz, 6H), 0.93 (t, J = 6 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 171.5, 169.3, 143.2, 141.0, 138.3, 138.2, 136.9, 135.9, 133.8, 131.2, 130.4, 129.4, 128.9, 128.2, 120.2, 117.3, 105.1, 96.1, 86.0, 77.2, 77.0, 76.7, 61.9, 60.9, 59.1, 41.1, 40.0, 30.9, 21.5, 21.3, 16.7, 14.0, 13.6 ppm.

FT-IR (KBr) $\bar{\nu}$ 2966, 2360, 1728, 1606, 1510, 1460, 1427, 1365, 1253,1244, 1298, 1188, 1153, 1095, 1066, 846, 549 cm^{-1}.

HRMS (APCI): *m/z* calcd for $C_{35}H_{36}O_6$[M+H]$^+$,553.2585, found 553.2582.



Triethyl 6-(4-ethylphenyl)-7-((4-ethylphenyl)ethynyl)-4-methyl-1H-indene-2,2,5(3H)- tricarboxylate (3m)

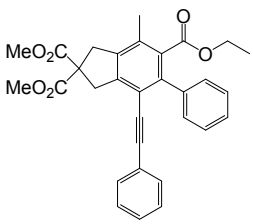
Colorless solid; (475 mg, 82% yield); m. p. 97.7℃; TLC (petroleum ether/EtOAc = 20:1): R_f = 0.51;

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.25 (dd, J = 9, 27 Hz, 4H), 7.15-7.02 (m, 4H), 4.29-4.20 (m, 4H), 4.01-3.93 (m, 2H), 3.81 (s, 2H), 3.62 (s, 2H), 2.73-2.57 (m, 4H), 2.29 (s, 3H), 1.32-1.17 (m, 12H), 0.91-0.85 (m, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 171.5, 169.3, 144.5, 143.4, 143.1, 141.2, 138.3, 136.2, 133.7, 131.3, 130.4, 129.5, 127.7, 127.0, 120.4, 117.3, 96.2, 86.1, 77.2, 77.0, 76.7, 61.9, 60.9, 59.1, 41.0, 40.0, 28.8, 28.7, 19.2, 16.7, 15.9, 15.4, 14.0, 13.5 ppm.

FT-IR (KBr): $\bar{\nu}$ 2966, 2931, 1732, 1512, 1367, 1269, 1253, 1236, 1184, 1174, 1161, 1076, 829 cm^{-1}.

HRMS (APCI): *m/z* calcd for $C_{37}H_{40}O_6$[M+H]$^+$,581.2898, found 581.2893.



5-Ethyl 2,2-dimethyl 4-methyl-6-phenyl-7-(phenylethynyl)-1H-indene-2,2,5(3H)-tricarboxylate (3n)

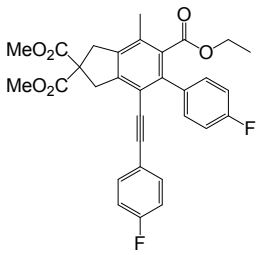
Colorless solid; (381 mg, 74% yield); m. p. 127.9℃; TLC (petroleum ether/EtOAc = 10:1): R_f = 0.20.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.39-7.20 (m, 10H), 3.97(q, J = 6 Hz, 2H), 3.84-3.65 (m, 10H), 2.31 (s, 3H), 0.89 (t, J = 6 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 171.9, 169.1, 143.2, 141.2, 138.9, 138.5, 133.8, 131.3, 130.8, 129.6, 128.2, 127.6, 127.5, 123.1, 117.1, 96.1, 86.4, 77.2, 77.0, 76.7, 60.9, 59.1, 5.2, 41.2, 40.1, 16.7, 13.5 ppm.

FT-IR (KBr): $\bar{\nu}$ 2978, 1735, 1708, 1440, 1286, 1249, 1176, 1155, 756, 700, 690 cm^{-1}.

HRMS (APCI): *m/z* calcd for $C_{31}H_{28}O_6[M+H]^+$,497.1959, found 497.1955.



5-Ethyl 2,2-dimethyl 6-(4-fluorophenyl)-7-((4-fluorophenyl)ethynyl)-4-methyl-1H-ind-ene-2,2,5 (3H)-tricarboxylate (3o)

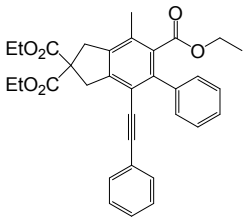
Colorless solid; (415 mg, 73% yield); m. p. 135.6℃; TLC (petroleum ether/EtOAc = 10:1): Rf = 0.18 .

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.36 (ddd, J =5.7, 8.4, 54 Hz, 4H), 7.03 (dt, J = 9, 39 Hz, 4H), 4.00 (dd, J = 9, 15 Hz, 2H), 3.80 (s, 8H), 3.64 (s, 2H), 2.29 (s, 3H), 0.96 (t, J = 7.5 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 171.8, 168.9, 163.2(d, 1JFC = 230 Hz), 161.5, 161.3, 143.2, 139.9, 138.7, 134.8(d, 4JFC = 3.75 Hz), 133.9, 133.2(d, 3JFC J = 8 Hz), 131.3(d, 3JFC = 8 Hz), 130.9,119.0(d, 4JFC= 2 Hz), 117.0, 115.6(d, 2JFC = 22 Hz), 114.6(d, 2JFC = 21Hz), 106.1, 95.2, 85.8, 77.2, 77.0, 76.7, 61.0, 59.0, 53.2, 41.1, 40.0, 16.7, 13.7 ppm.

FT-IR (KBr) $\bar{\nu}$ 2956, 1751, 1732, 1600, 1508, 1444, 1273, 1234, 1197, 1178, 1157, 1035, 844, 530 cm^{-1};

HRMS (APCI): *m/z* calcd for $C_{31}H_{26}F_2O_6$ $[M+H]^+$, 553.1770, found 553.1769.



Triethyl 4-methyl-6-phenyl-7-(phenylethynyl)-1H-indene-2,2,5(3H)-tricarboxylate (3p)

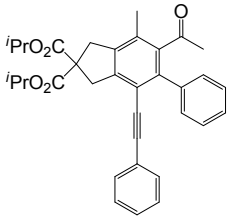
Colorless solid; (403 mg, 77% yield); m. p. 127.4℃; TLC (petroleum ether/EtOAc = 20:1): R_f = 0.45.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.38-7.18 (m,10H), 4.26 (q, J = 7 Hz,4H), 3.96 (q, J = 6 Hz, 2H), 3.83 (s, 2H), 3.63 (s, 2H), 2.30 (s, 3H), 1.30 (t, J = 6 Hz, 6H), 0.89 (t, J = 6 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 171.5, 169.1, 143.3, 141.2, 138.9, 138.6, 133.7, 131.3, 130.8, 129.6, 128.1, 127.5, 127.4, 123.2, 117.0, 96.0, 86.5, 77.2, 77.0, 76.7, 62.0, 60.9, 59.1, 41.0, 40.0, 16.7, 14.0, 13.5 ppm.

FT-IR (KBr): $\bar{\nu}$ 2981, 1728, 1442, 1273, 1255, 1236, 1180, 1159, 758, 698 cm^{-1}.

HRMS (APCI): *m/z* calcd for $C_{33}H_{32}O_6$ $[M+H]^+$,525.2272, found 525.2269.



Diisopropyl 5-acetyl-4-methyl-6-phenyl-7-(phenylethynyl)-1H-indene-2,2(3H)-dicarboxylate (3q)

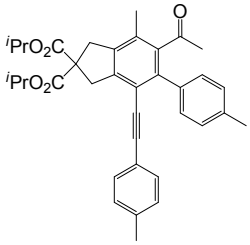
Colorless solid; (428 mg, 80 % yield); m. p. 143.5℃; TLC (petroleum ether/EtOAc = 20:1): R_f = 0.40;

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.37-7.33 (m, 2H),7.20-7.17 (m, 2H), 7.39 (dt, *J* = 9, 42 Hz, 4H), 5.14-5.05 (m, 5H), 3.77 (s, 2H), 3.59 (s, 2H), 2.20 (s, 3H), 1.90 (s, 3H), 1.28 (d, *J* = 6Hz,12H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 207.3, 171.5, 143.4, 142.0, 139.6, 139.5, 138.7, 123.6, 117.2, 96.4, 86.9, 69.8, 59.4, 41.4, 40.5, 32.5, 32.2, 22.1, 16.8 ppm.

FT-IR (KBr): $\bar{\nu}$ 2980, 1743, 1707, 1697, 1490, 1375, 1273, 1253, 1190, 1103, 761, 692 cm^{-1};

HRMS (APCI): *m/z* calcd for $C_{34}H_{34}O_5$ $[M+H]^+$ 523.2479, found 523.2482.



Diisopropyl 5-acetyl-4-methyl-6-(p-tolyl)-7-(p-tolylethynyl)-1H-indene-2,2(3H)-dicarboxylate (3r)

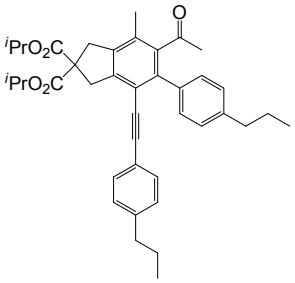
Colorless solid; (451 mg, 82 % yield); m. p. 120.7℃; TLC (petroleum ether/EtOAc = 20:1): R_f = 0.42.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.28-7.18 (m, 4H), 7.10 (q, *J* = 9Hz,4H), 5.13-5.05 (m, 2H), 3.78 (s, 2H), 3.58 (s, 2H), 2.40 (s, 3H), 2.32 (s, 3H), 2.20 (s, 3H), 1.86 (s, 3H), 1.28 (d, *J* = 6,12H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 207.2, 171.1, 142.9, 141.6, 139.1, 138.8, 138.2, 137.5, 136.3, 135.3, 131.2, 130.2, 128.9, 128.6, 125.3, 120.3, 117.0, 96.1, 86.0, 77.2, 77.0, 76.7, 69.4, 59.0, 41.04, 40.10, 32.1, 21.5, 21.5, 21.3, 16.4 ppm.

FT-IR (KBr): $\bar{\nu}$ 2980, 1722, 1693, 1510, 1452, 1425, 1375, 1354, 1278, 1271, 1246, 1195, 1107, 1058, 819 cm^{-1}.

HRMS (APCI): *m/z* calcd for $C_{36}H_{38}O_5$ $[M+H]^+$ 551.2792, found 551.2793.



Diisopropyl 5-acetyl-4-methyl-6-(4-propylphenyl)-7-((4-propylphenyl)ethynyl)-1H- indene- 2,2(3H)-dicarboxylate (3s)

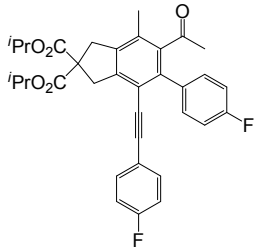
Colorless solid; (527 mg, 87% yield); m. p. 127.8℃; TLC (petroleum ether/EtOAc = 20:1): R_f = 0.46;

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.29-7.19 (m, 4H), 7.13-7.04 (m, 4H), 5.11-5.07 (m, 2H), 3.79 (s, 2H), 3.59 (s, 2H), 2.64 (t, *J* = 6Hz, 3H), 2.55 (t, *J* = 6Hz, 3H), 2.20 (s, 3H), 1.86 (s, 3H), 1.70-1.59 (m, 4H), 1.28 (d, *J* = 6Hz, 12H), 0.98-0.89 (m, 6H).

^{13}C NMR (125 MHz, $CDCl_3$): *δ* 207.1, 171.1, 143.0, 142.8, 142.2, 141.6, 139.4, 138.8, 135.7, 131.2, 130.2, 129.0, 128.3, 128.0, 120.5, 117.1, 96.2, 86.1, 77.2, 77.0, 76.7, 69.4, 59.1, 41.0, 40.1, 37.9, 37.7, 32.0, 24.5, 24.3, 21.5, 16.4, 13.7 ppm.

FT-IR (KBr): $\bar{\nu}$ 2956, 1728, 1705, 1508, 1375, 1273, 1247, 1188, 1103, 1060, 813 cm^{-1} .

HRMS (APCI): *m/z* calcd for $C_{40}H_{46}O_5$ $[M+H]^+$, 607.3418, found 607.3425.



Diisopropyl 5-acetyl-6-(4-fluorophenyl)-7-((4-fluorophenyl)ethynyl)-4-methyl-1H- indene- 2,2(3H)-dicarboxylate (3t)

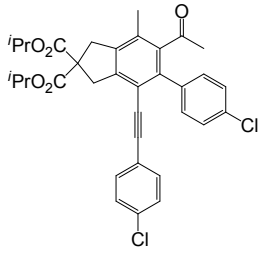
Colorless solid; (408 mg, 78% yield); m. p. 146.6℃; TLC (petroleum ether/EtOAc = 20:1): R_f = 0.37;

^{1}H NMR (300 MHz, $CDCl_3$): *δ* 7.37-7.32 (m, 2H), 7.21- 7.17 (m, 2H), 7.04 (dt, *J* =9, 42 Hz, 4H), 5.13-5.05 (m, 2H), 3.77 (s, 2H), 3.59 (s, 2H), 2.20 (s, 3H), 1.89 (s, 3H), 1.28 (d, 12H).

^{13}C NMR (125 MHz, $CDCl_3$): *δ* 207.1, 171.4, 162.8 (d, 1JFC= 246 Hz), 143.4, 142.1, 139.7, 138.3, 134.6(d, 4JFC= 3 Hz), 133.6 (d, 3JFC= 8 Hz), 132.5(d, 3JFC=8 Hz), 129.7, 119.5(d, 4JFC= 2 Hz), 117.2, 116.0 (d, 2JFC= 21 Hz), 115.4(d, *J* = 21 Hz), 95.5, 86.3, 69.9, 59.4, 41.3, 40.4, 32.5, 21.9, 16.8 ppm.

FT-IR (KBr): $\bar{\nu}$ 2981, 1728, 1699, 1598, 1506, 1273, 1247, 1228, 1101, 837 cm^{-1}.

HRMS (APCI): *m/z* calcd for $C_{34}H_{32}F_2O_5$$[M+H]^+$,559.2291, found 559.2285.



Diisopropyl 5-acetyl-6-(4-chlorophenyl)-7-((4-chlorophenyl)ethynyl)-4-methyl-1H- indene- 2,2(3H)-dicarboxylate (3u)

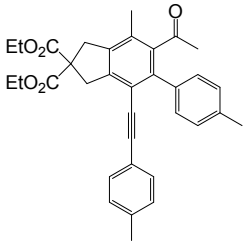
Yellow solid; (472 mg, 79% yield); m. p. 179.5℃; TLC (petroleum ether/EtOAc = 20:1): R_f= 0.38.

^{1}H NMR (300 MHz, $CDCl_3$): *δ* 7.40-7.24 (m, 8H), 7.13 (d, 2H), 5.13-5.05 (m, 2H), 3.76 (s, 2H), 3.59 (s, 2H), 2.20 (s, 3H) 1.91 (s, 3H), 1.28 (d, 12H).

^{13}C NMR (125 MHz, $CDCl_3$): *δ* 206.6, 171.0, 143.2, 141.7, 139.6, 137.8, 136.7, 134.4, 134.1, 132.5, 131.7, 129.6, 128.6, 128.2, 121.5, 116.5, 95.2, 87.1, 77.2, 77.0, 76.7, 69.5, 59.0, 40.9, 40.0, 32.3, 21.5, 16.5 ppm.

FT-IR (KBr): $\bar{\nu}$ 2988, 1731, 1698, 1489, 1276, 1243, 1099, 824 cm^{-1};

HRMS (APCI): *m/z* calcd for $C_{34}H_{32}Cl_2O_5$ $[M+H]^+$,591.1700, found 591.1694.



Diethyl 5-acetyl-4-methyl-6-(p-tolyl)-7-(p-tolylethynyl)-1H-indene-2,2(3H)-dicarboxylate (3v)

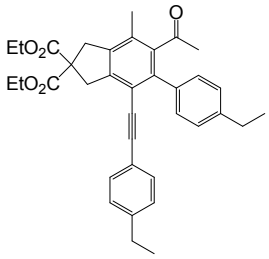
Colorless solid; (423 mg, 81% yield); m. p. 148.7℃; TLC (petroleum ether/EtOAc = 20:1): R_f = 0.36.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.29-7.19 (m, 4H), 7.15-7.04 (m, 4H), 4.30-4.20 (m, 4H), 3.82-3.58 (m, 4H), 2.40 (s, 3H), 2.36 (s, 3H), 2.33 (s, 3H), 2.20 (s, 3H),1.87 (s, 3H), 1.32-1.23 (m, 6H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 207.1, 171.6, 142.8, 141.6, 139.2, 138.7, 138.3, 137.5, 135.3, 131.2, 130.2, 129.0, 128.9, 128.6, 120.2, 117.0, 114.5, 96.1, 85.9, 77.2, 77.0, 76.7, 61.9, 59.0, 41.1, 40.1, 32.1, 21.5, 21.3, 16.4, 14.0 ppm.

FT-IR (KBr) $\bar{\nu}$ 2966, 1739, 1724, 1508, 1458, 1444, 1392, 1301, 1244, 1184, 1053, 831, 767, 702 cm^{-1}.

HRMS (APCI): *m/z* calcd for $C_{34}H_{34}O_5$[M+H]$^+$,523.2479, found 523.2475.



Diethyl 5-acetyl-6-(4-ethylphenyl)-7-((4-ethylphenyl)ethynyl)-4-methyl-1H-indene- 2,2(3H)-dicarboxylate (3w)

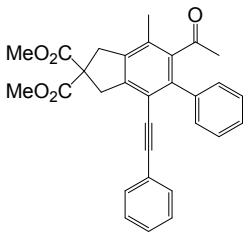
Colorless solid; (451 mg, 84% yield); m. p. 165.8℃; TLC (petroleum ether/EtOAc = 20:1): R_f = 0.38.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.29-7.20 (m, 4H), 7.13-7.05 (m, 4H), 4.24 (dd, *J* =6, 9 Hz, 4H), 3.81 (s, 2H), 3.61 (s, 2H), 2.69 (dd, *J* =9, 15 Hz, 2H), 2.60 (dd, *J* =9, 15 Hz, 2H), 2.19 (s, 3H), 1.86 (s, 3H), 1.31-1.16 (m, 12H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 207.6, 172.0, 145.0, 144.3, 143.1, 142.0, 139.7, 139.1, 135.9, 131.7, 130.7, 129.4, 128.1, 127.8, 120.8, 117.5, 86.4, 77.6, 77.4, 77.1, 62.3, 59.4, 41.5, 40.5, 29.2, 29.1, 16.9, 16.1, 15.8, 14.4 ppm.

FT-IR (KBr) $\bar{\nu}$ 2978, 1728, 1701, 1508, 1436, 1280, 1267, 1247, 1184, 1155, 1070, 817, 528 cm^{-1}.

HRMS (APCI): *m/z* calcd for $C_{36}H_{38}O_5$[M+H]$^+$,551.2792, found 551.2795.



Dimethyl 5-acetyl-4-methyl-6-phenyl-7-(phenylethynyl)-1H-indene-2,2(3H)-dicarboxylate (3x)

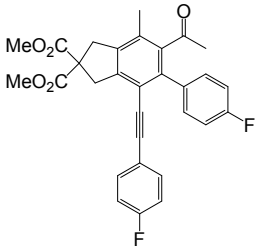
Colorless solid; (361 mg, 81% yield); TLC (petroleum ether/EtOAc = 10:1): R_f = 0.20.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.39-7.22 (m, 10H), 3.84 (s, 2H), 3.81 (s, 6H), 3.65 (s, 2H), 2.21 (s, 3H), 1.87 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 207.3, 172.3, 143.1, 142.1, 139.7, 139.2, 138.6, 131.7, 130.7, 129.7, 128.6, 128.3, 123.5, 117.3, 96.5, 86.8, 77.6, 77.4, 77.1, 59.4, 53.6, 41.6, 40.6, 32.5, 16.8 ppm.

FT-IR (KBr): $\bar{\nu}$ 2961, 1724, 1686, 1578, 1512, 1437, 1276, 1236, 1148, 845, 521 cm^{-1}.

HRMS (APCI): *m/z* calcd for $C_{30}H_{26}O_5[M+H]^+$,467.1862, found 467.1865.



Dimethyl 5-acetyl-6-(4-fluorophenyl)-7-((4-fluorophenyl)ethynyl)-4-methyl-1H-ind ene-2,2(3H)-dicarboxylate (3y)

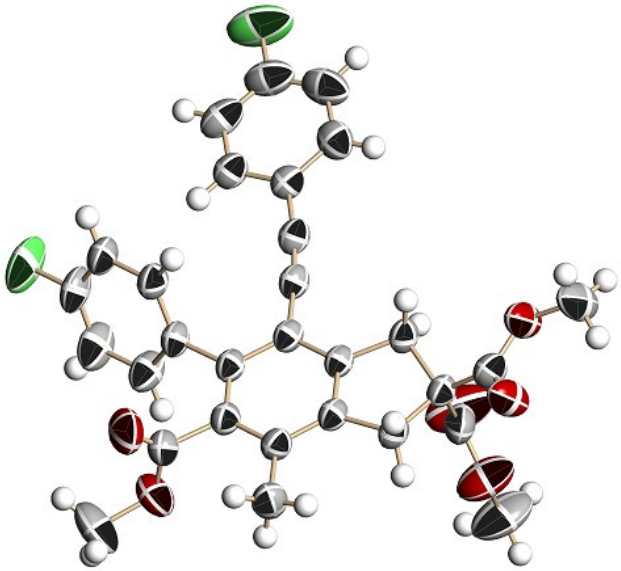
Colorless solid; (382 mg, 76% yield); m. p. 165.3℃; TLC (petroleum ether/EtOAc = 10:1): R_f = 0.15.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.37-7.32 (m, 2H), 7.22-7.17 (m, 2H), 7.11 (t, *J* = 9 Hz, 2H), 6.97 (t, *J* = 9 Hz, 2H), 3.81 (s, 8H), 3.64 (s, 2H), 2.20 (s, 3H), 1.90 (s, 3H).

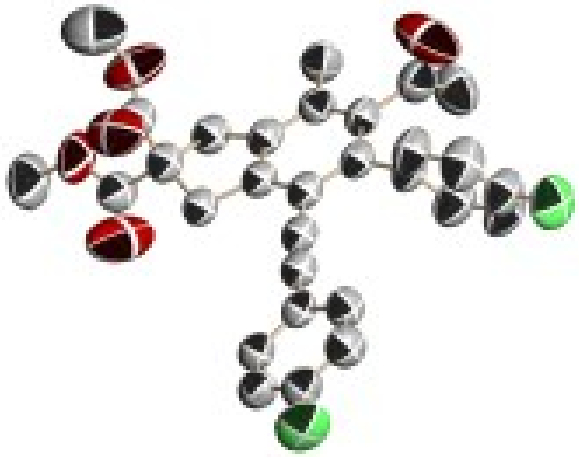
^{13}C NMR (125 MHz, $CDCl_3$): δ 206.7, 171.9, 162.5(d, 1JFC = 247 Hz), 142.7, 141.8, 139.1, 137.9, 134.1(d, 4JFC = 3 Hz), 133.2(d, 3JFC = 8 Hz), 132.1(d, 3JFC= 8 Hz), 129.4, 119.0(d, 4JFC= 3 Hz), 116.8, 115.6(d, 4JFC = 22 Hz), 115.0(d, 4JFC= 21 Hz), 95.2, 85.8, 58.9, 53.2, 41.1, 40.1, 32.1, 16.4 ppm.

FT-IR (KBr):$\bar{\nu}$ 2954, 1734, 1697, 1598, 1506, 1435, 1284, 1226, 1157, 837, 526 cm^{-1}.
HRMS (APCI): *m/z* calcd for $C_{30}H_{24}F_2O_5$ $[M+H]^+$,503.1665, found 503.1664.

4. X-Ray Structure for 3h and 3y

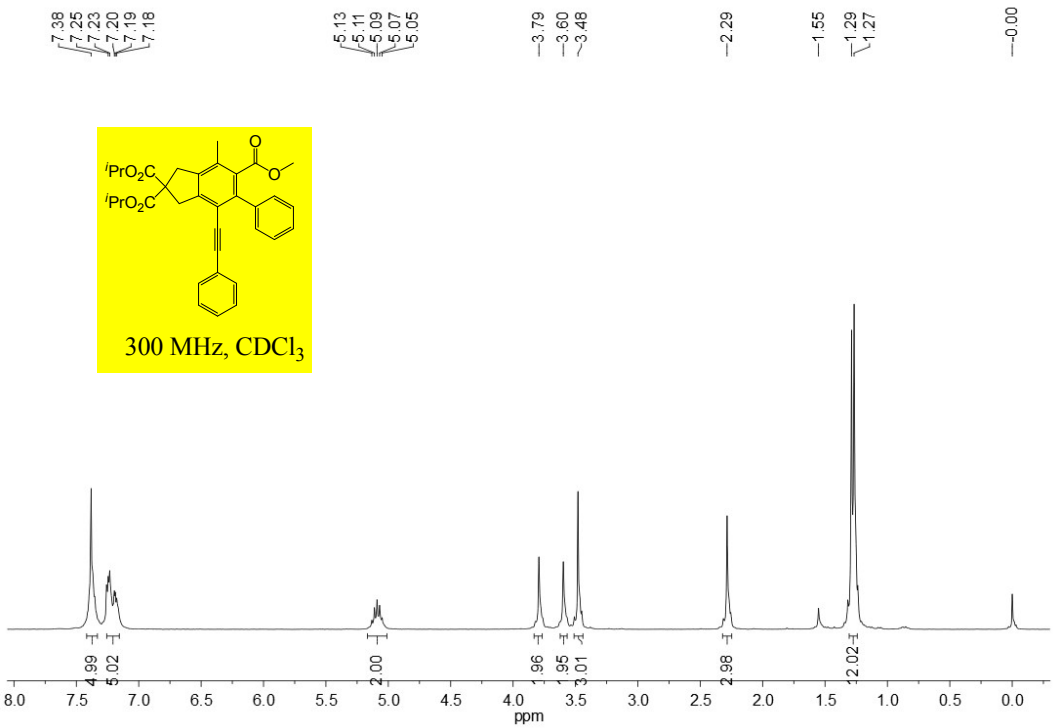


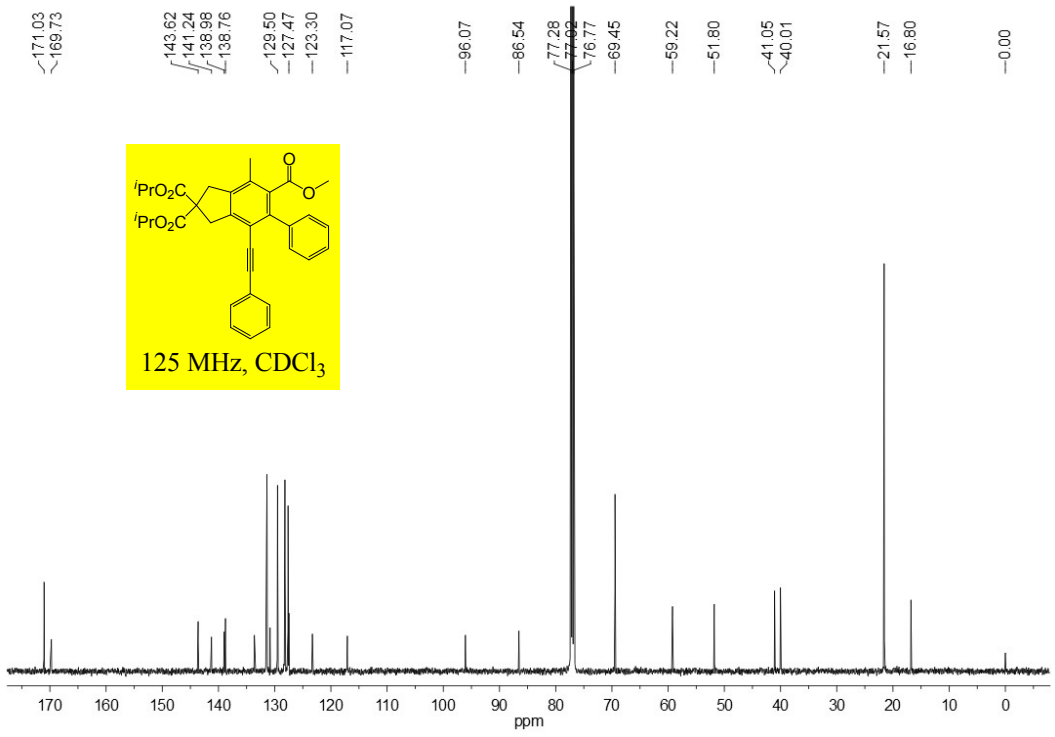
3h

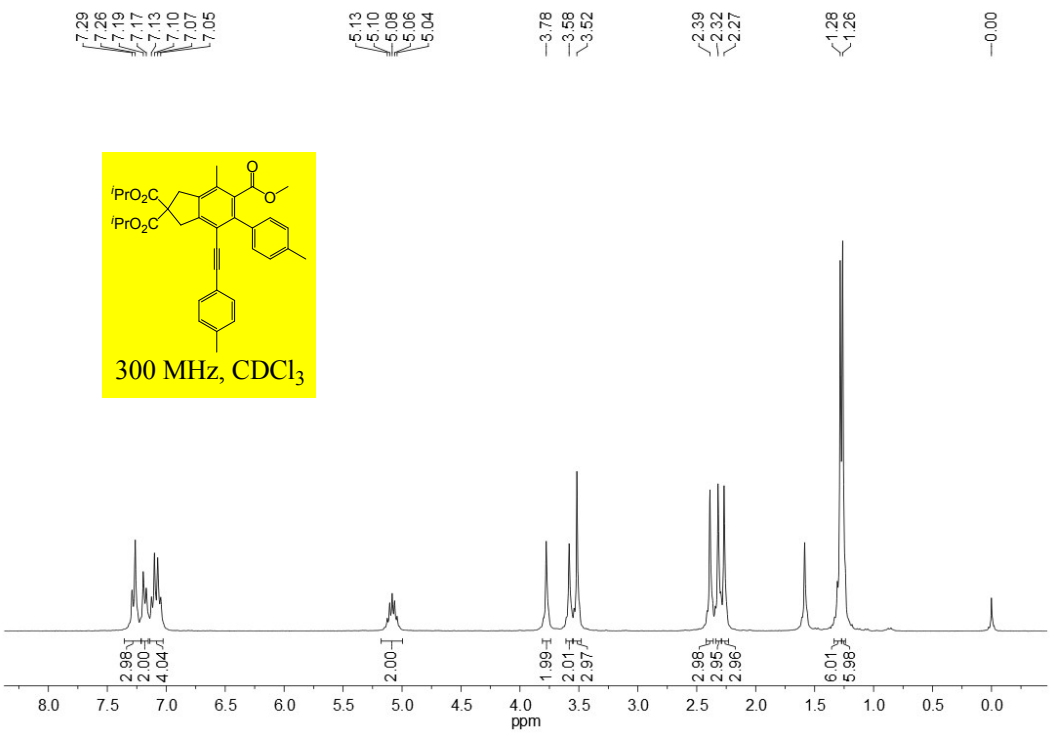


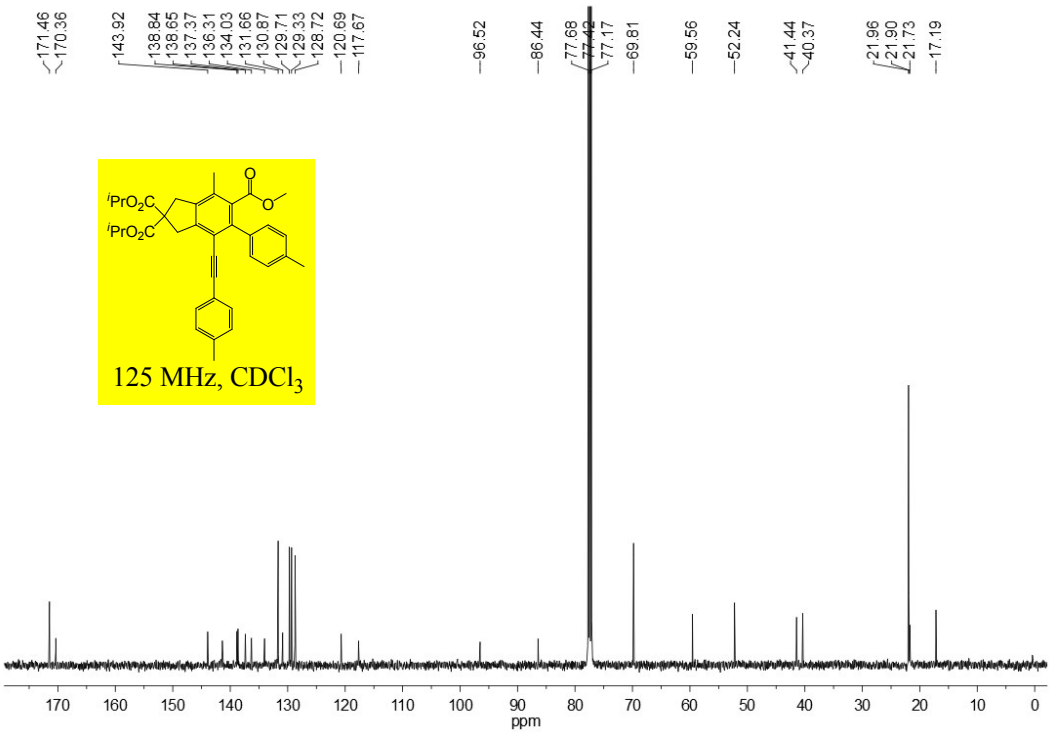
3y

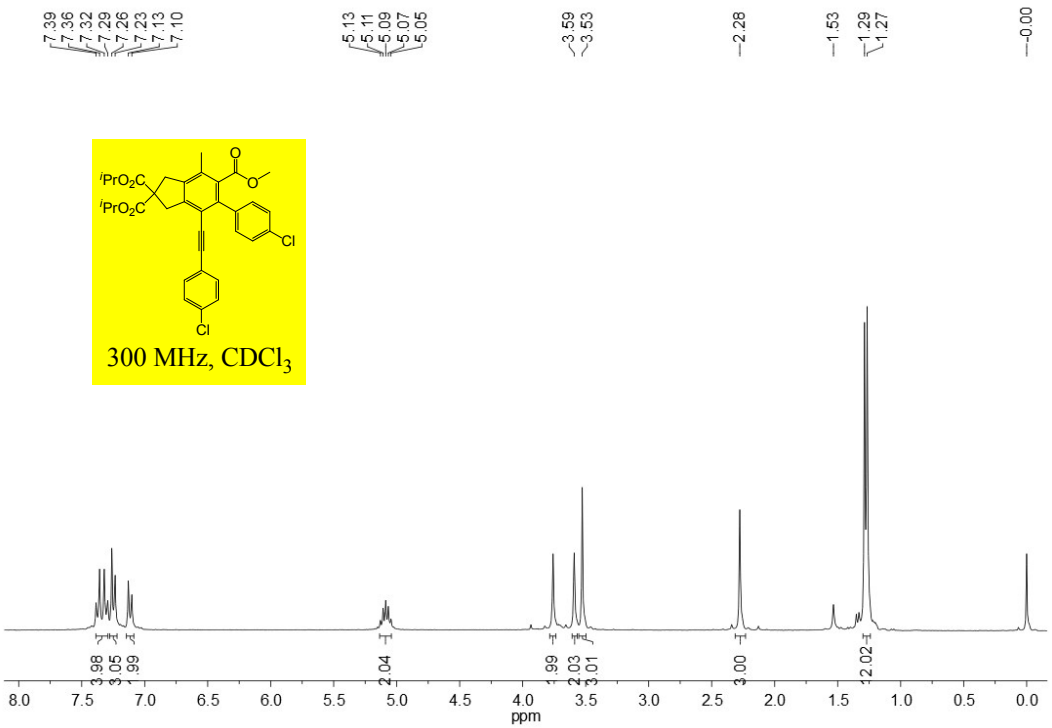
5. ^{1}H NMR & ^{13}C NMR Spectra for New Compounds

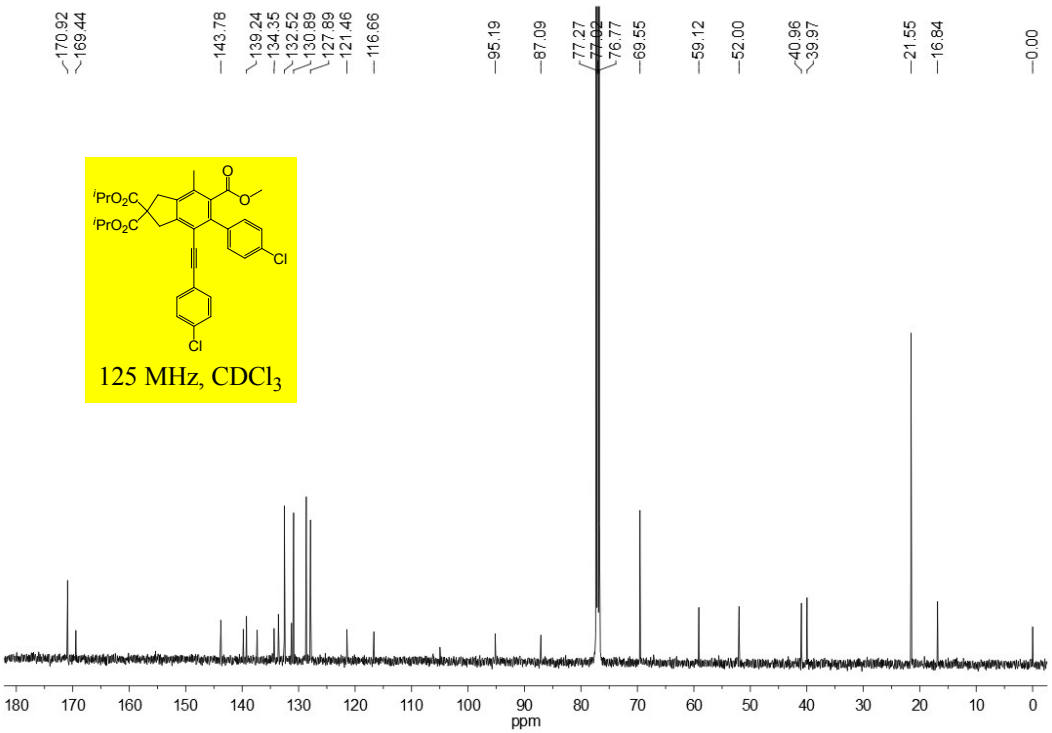


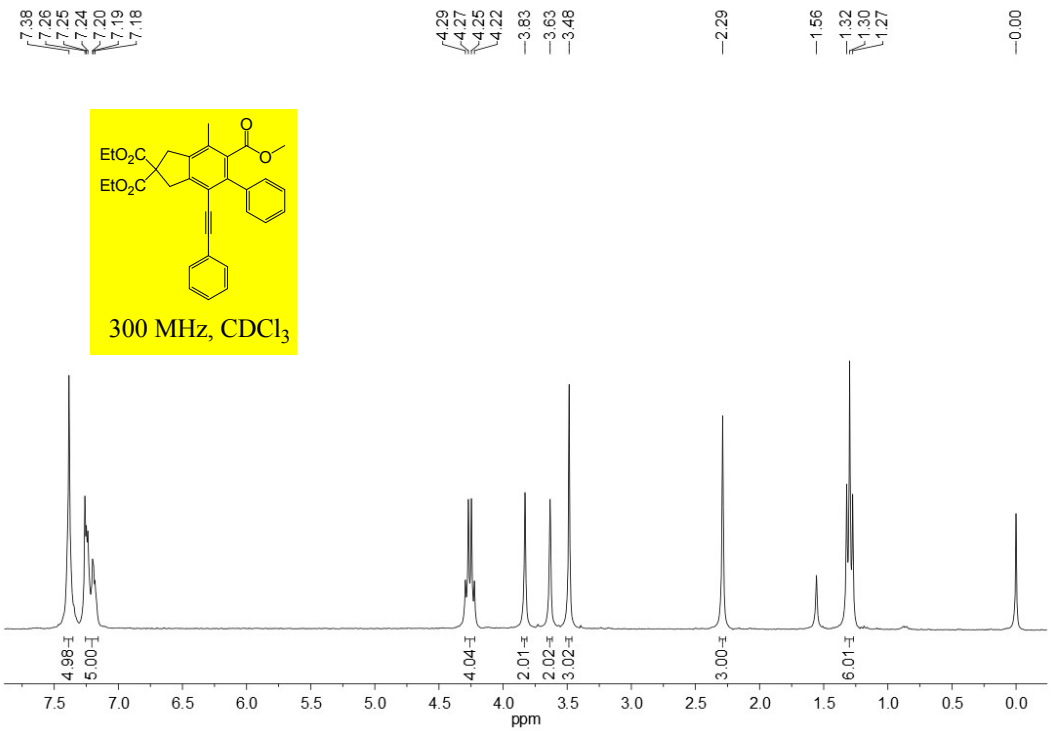


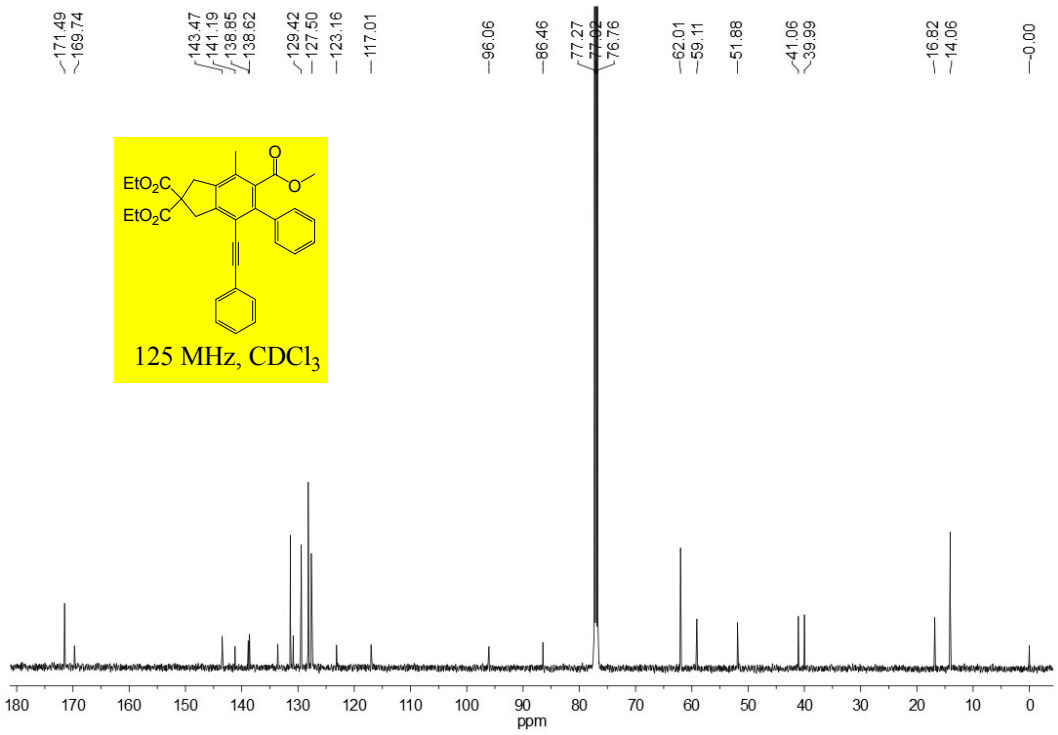

7.29
7.26
7.19
7.17
7.13
7.10
7.07
7.05
5.13
5.10
5.08
5.06
5.04
3.78
3.58
3.52
2.39
2.32
2.27
1.28
1.26
0.00
iPrO2C
iPrO2C
O
O
300 MHz, CDCl3
2.98
2.00
4.04
2.00
1.99
2.01
2.97
2.98
2.95
2.96
6.01
5.98
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

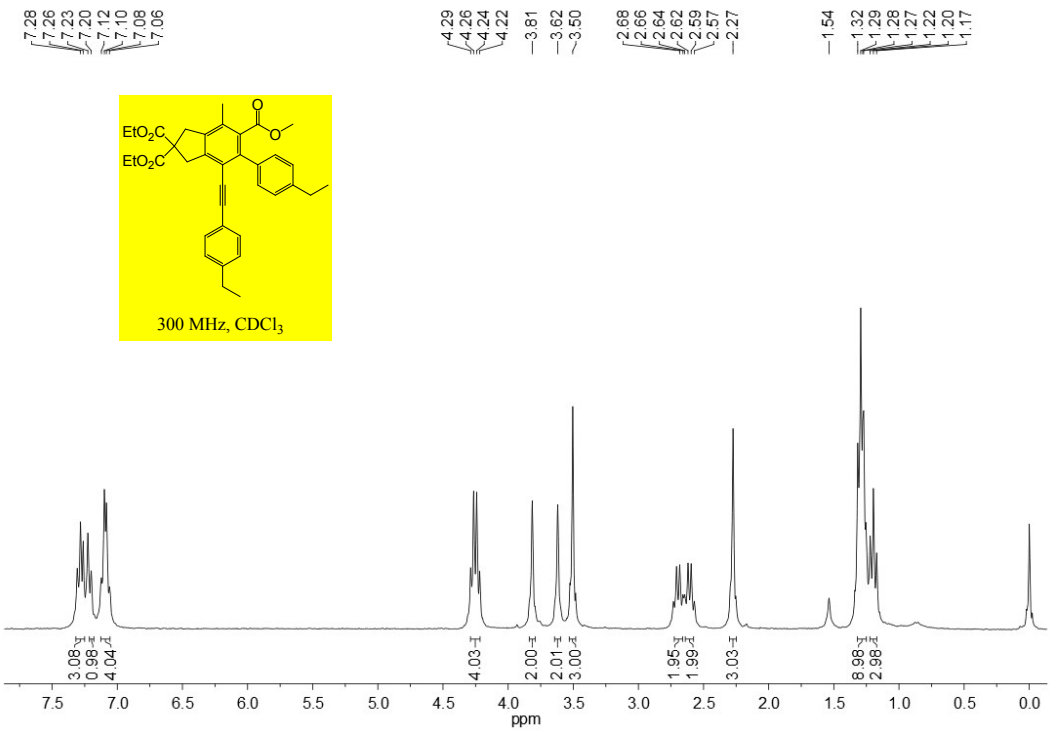

171.46
170.36
143.92
138.84
138.65
137.37
136.31
134.03
131.66
130.87
129.71
129.33
128.72
120.69
117.67
96.52
86.44
77.68
77.42
77.17
69.81
59.56
52.24
41.44
40.37
21.96
21.90
21.73
17.19
iPrO2C
iPrO2C
O
O
125 MHz, CDCl3
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

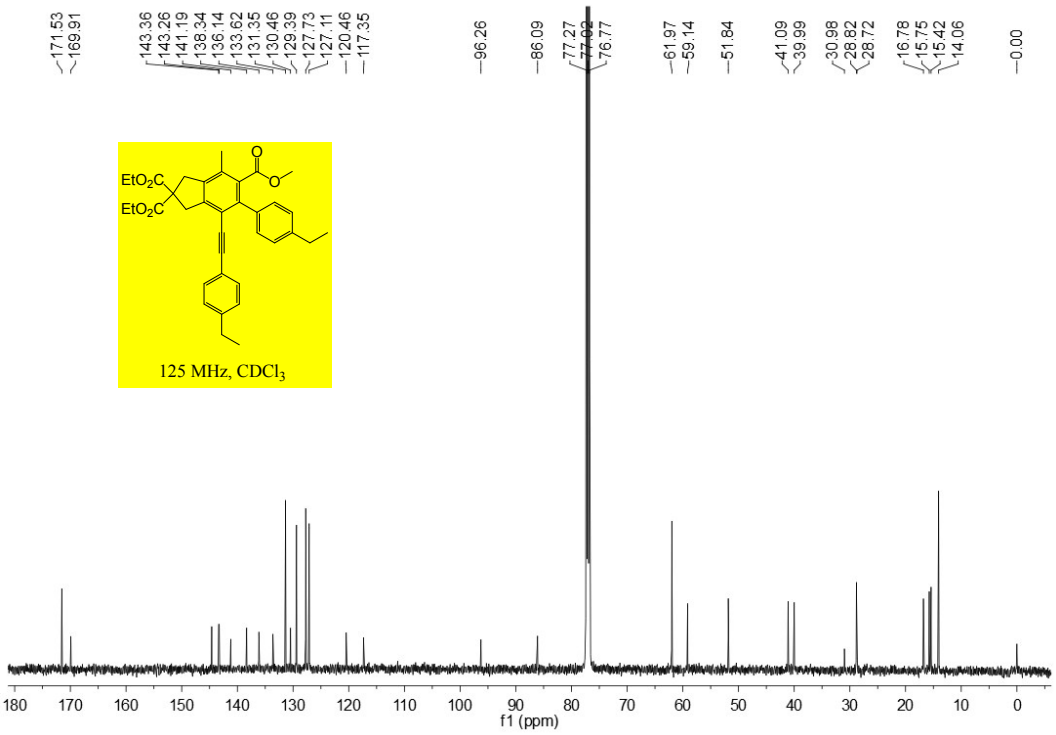

7.39
7.36
7.32
7.29
7.26
7.23
7.13
7.10
5.13
5.11
5.09
5.07
5.05
3.59
3.53
2.28
1.53
1.29
1.27
0.00
iPrO2C
iPrO2C
O
O
Cl
Cl
300 MHz, CDCl3
3.98
3.05
1.99
2.04
1.99
2.03
3.01
3.00
12.02
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

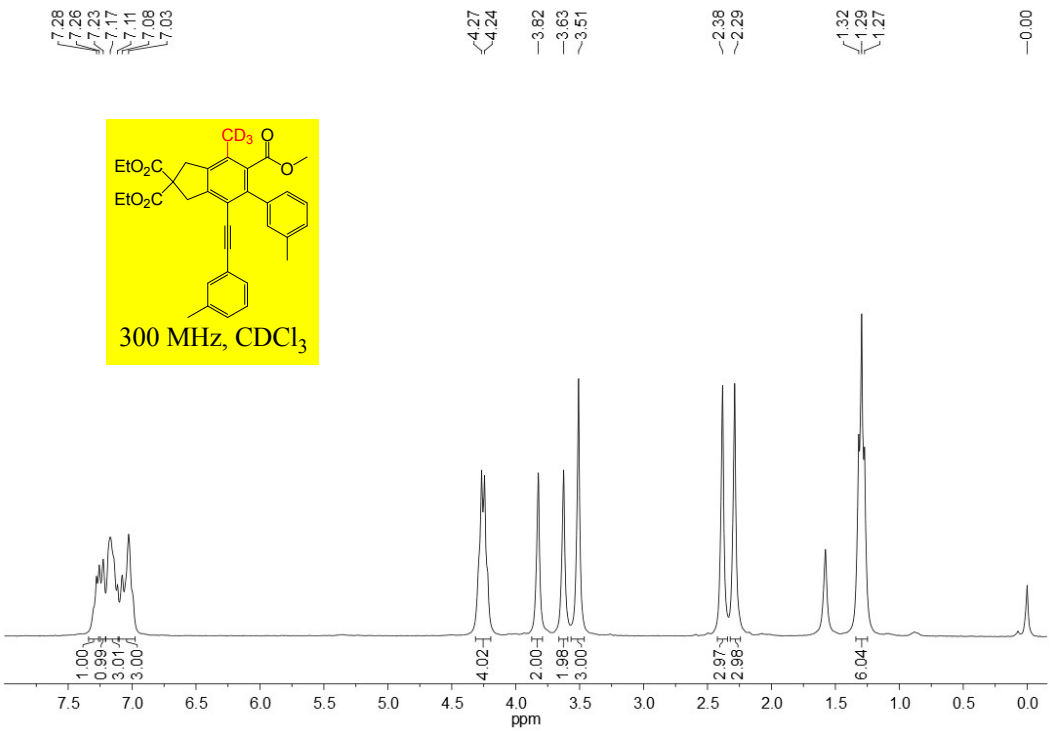

170.92
169.44
143.78
139.24
134.35
132.52
130.89
127.89
121.46
116.66
95.19
87.09
77.27
77.02
76.77
69.55
59.12
52.00
40.96
39.97
21.55
16.84
0.00
iPrO2C
iPrO2C
O
O
Cl
Cl
125 MHz, CDCl3
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

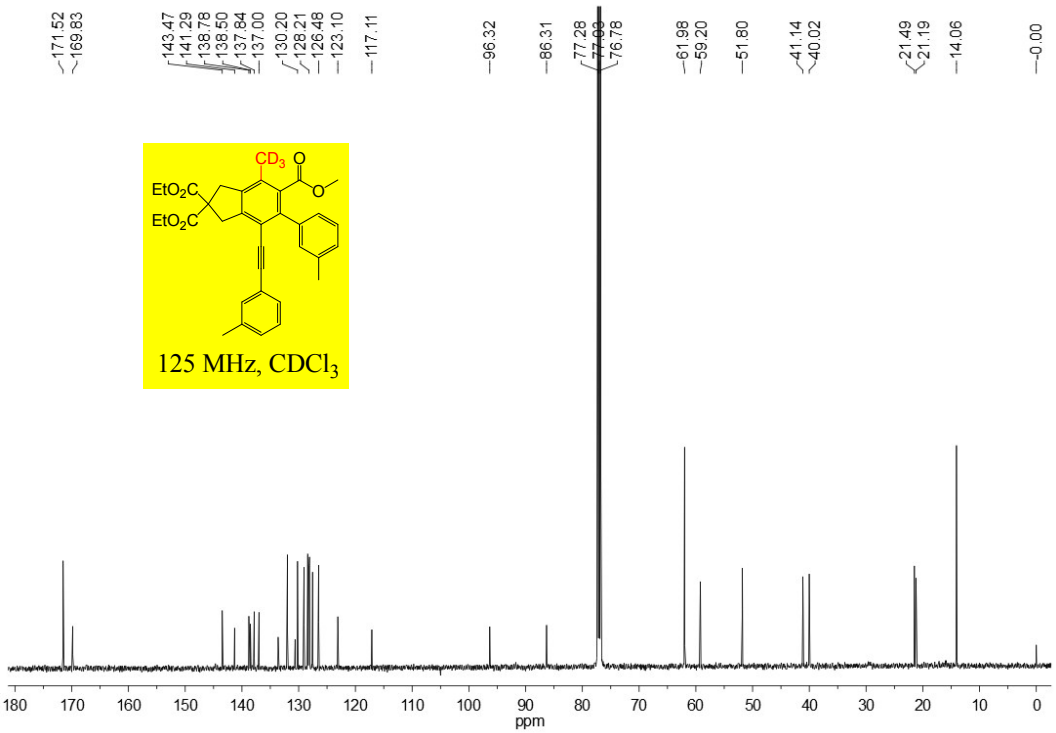

7.38
7.26
7.25
7.24
7.20
7.19
7.18
4.29
4.27
4.25
4.22
3.83
3.63
3.48
2.29
1.56
1.32
1.30
1.27
0.00
EtO2C
EtO2C
O
O
300 MHz, CDCl3
4.98
5.00
4.04
2.01
2.02
3.02
3.00
6.01
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

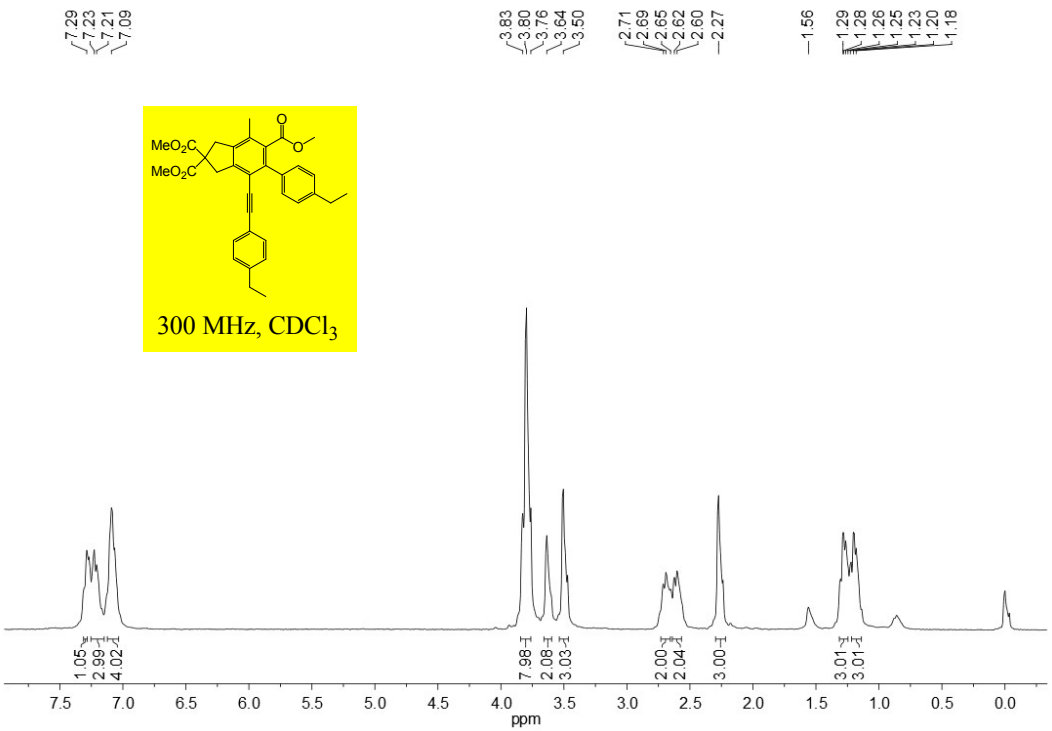

171.49
169.74
143.47
141.19
138.85
138.62
129.42
127.50
123.16
117.01
96.06
86.46
77.27
77.02
76.76
62.01
59.11
51.88
41.06
39.99
16.82
14.06
0.00
EtO2C
EtO2C
O
O
125 MHz, CDCl3
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

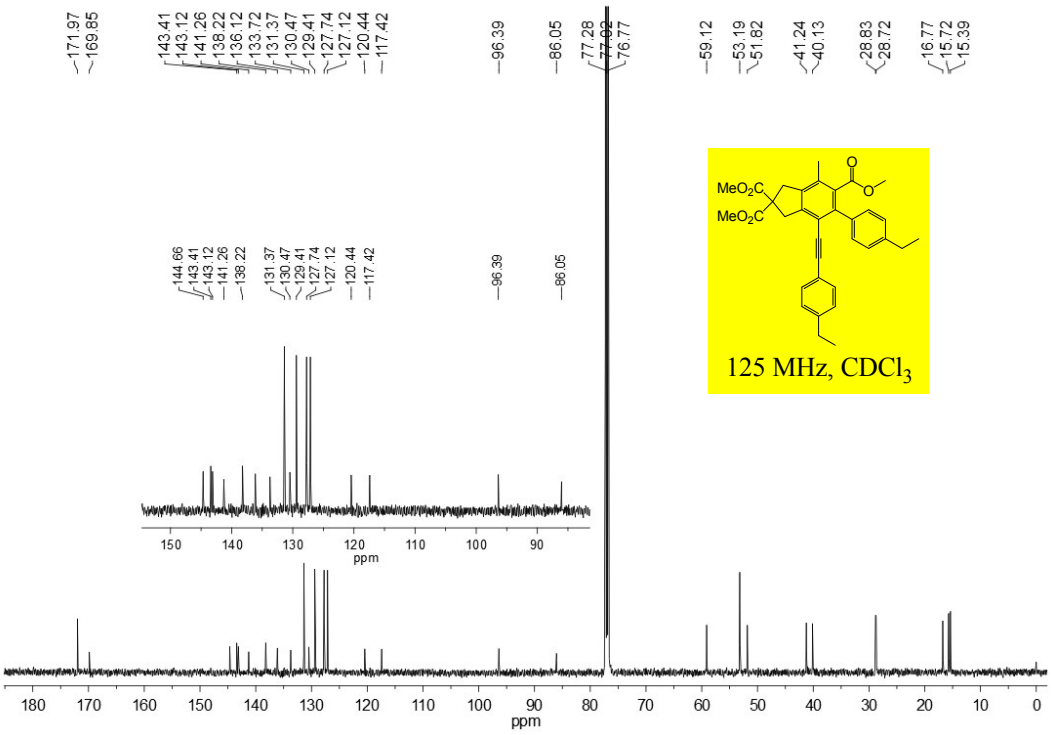

7.28
7.26
7.23
7.20
7.12
7.10
7.08
7.06
4.29
4.26
4.24
4.22
3.81
3.62
3.50
2.68
2.66
2.64
2.62
2.59
2.57
2.27
1.54
1.32
1.29
1.28
1.27
1.22
1.20
1.17
EtO2C
EtO2C
O
O
300 MHz, CDCl3
3.08
0.98
4.04
4.03
2.00
2.01
3.00
1.95
1.99
3.03
8.98
2.98
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

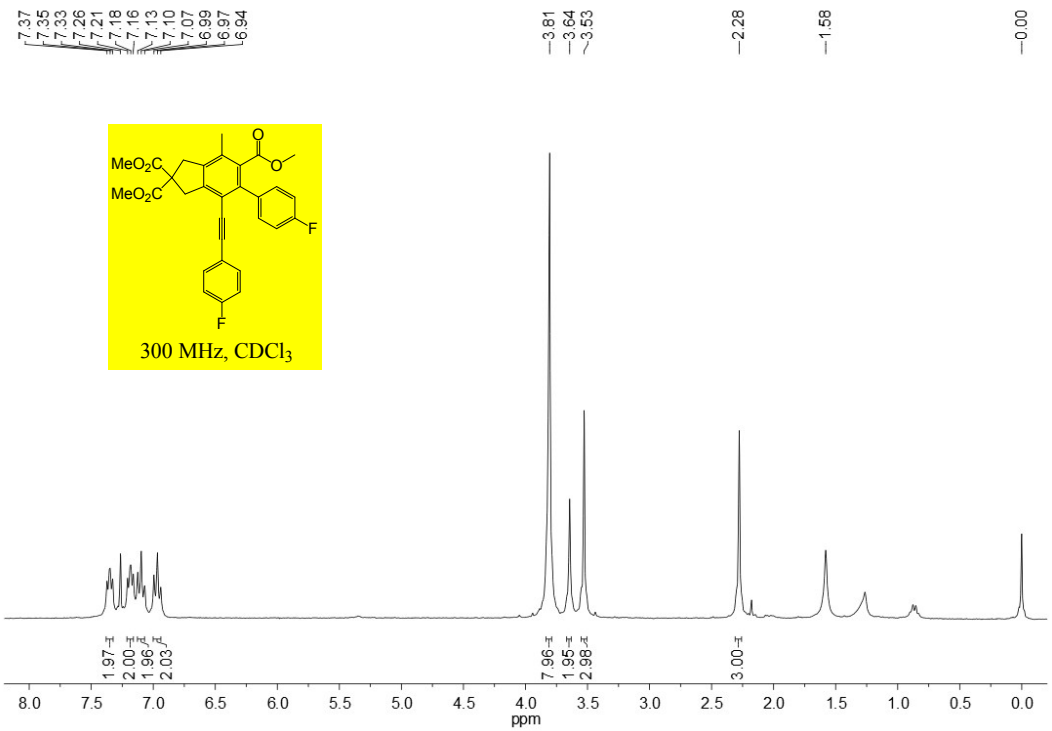

171.53
169.91
143.36
143.26
141.19
138.34
136.14
133.62
131.35
130.46
129.39
127.73
127.11
120.46
117.35
96.26
86.09
77.27
77.00
76.77
61.97
59.14
51.84
41.09
39.99
30.98
28.82
28.72
16.78
15.75
15.42
14.06
0.00
EtO2C
EtO2C
O
O
125 MHz, CDCl3
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

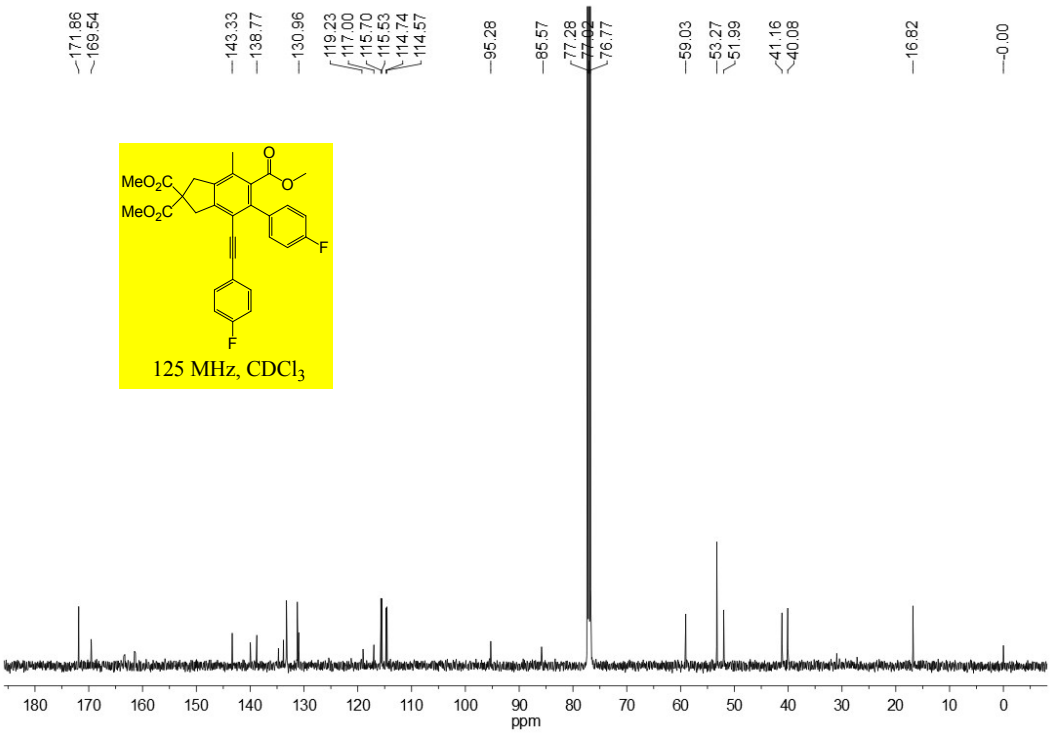

7.28
7.26
7.23
7.17
7.11
7.08
7.03
4.27
4.24
3.82
3.63
3.51
2.38
2.29
1.32
1.29
1.27
0.00
CD3
O
O
EtO2C
EtO2C
300 MHz, CDCl3
1.00
0.99
3.01
3.00
4.02
2.00
1.98
3.00
2.97
2.98
6.04
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

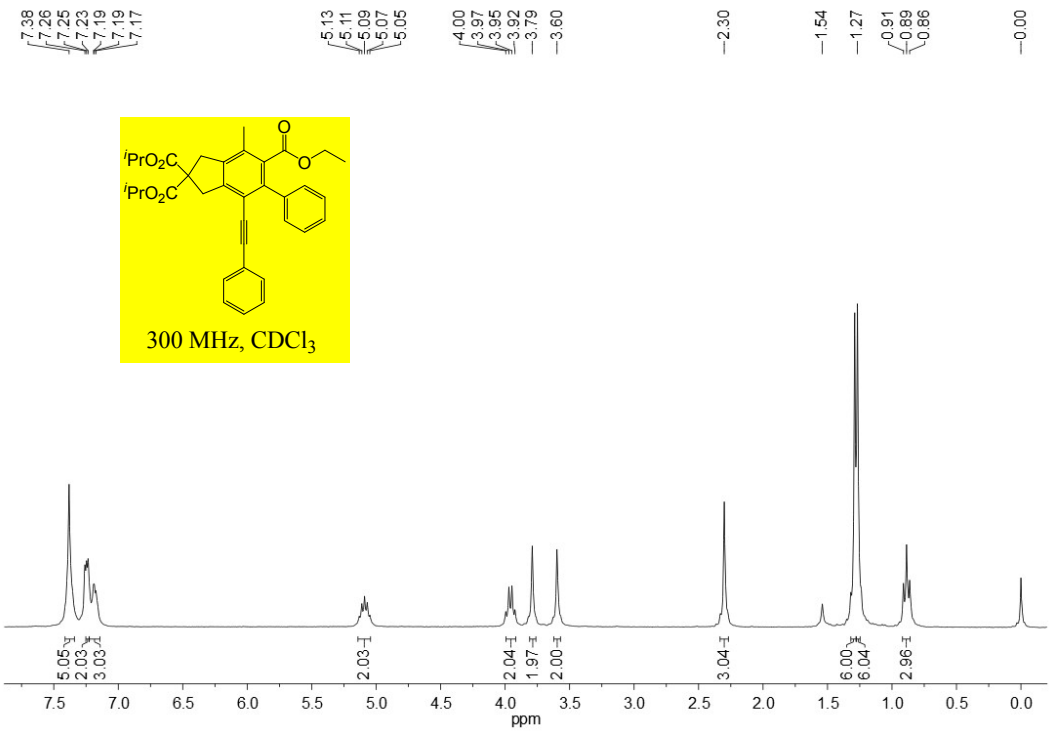

171.52
169.83
143.47
141.29
138.78
138.50
137.84
137.00
130.20
128.21
126.48
123.10
117.11
96.32
86.31
77.28
77.03
76.78
61.98
59.20
51.80
41.14
40.02
21.49
21.19
14.06
0.00
CD3
O
O
EtO2C
EtO2C
125 MHz, CDCl3
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

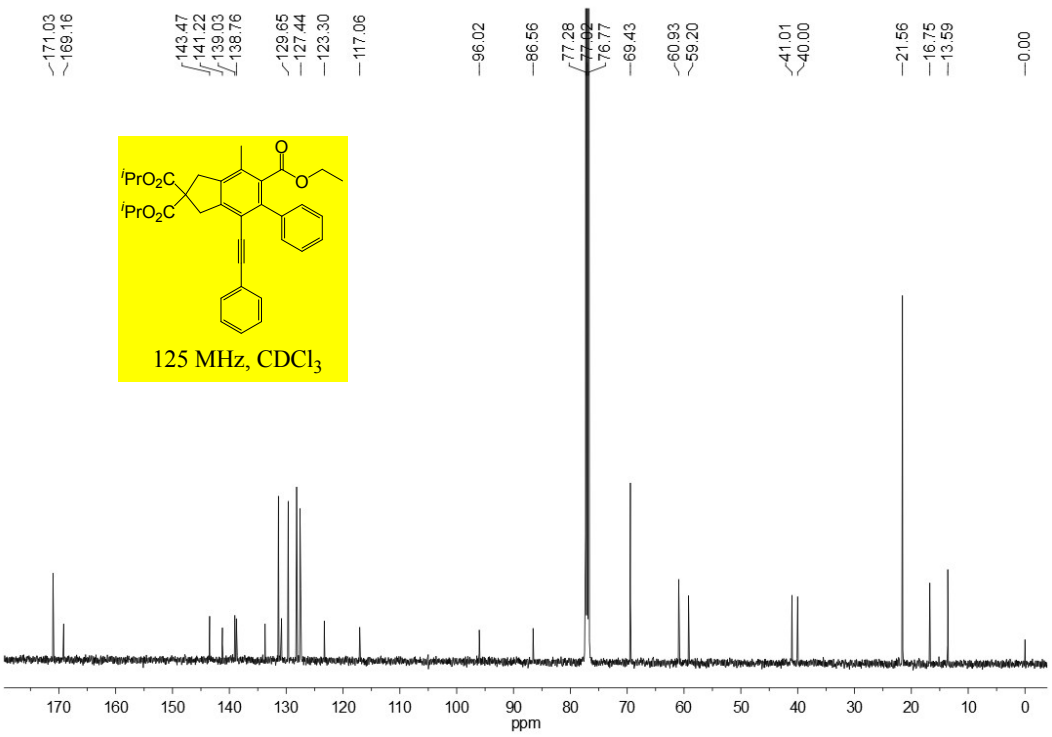

7.29
7.23
7.21
7.09
3.83
3.80
3.76
3.64
3.50
2.71
2.69
2.65
2.62
2.60
2.27
1.56
1.29
1.28
1.26
1.25
1.23
1.20
1.18
MeO2C
MeO2C
O
O
300 MHz, CDCl3
1.05
2.99
4.02
7.98
2.08
3.03
2.00
2.04
3.00
3.01
3.01
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

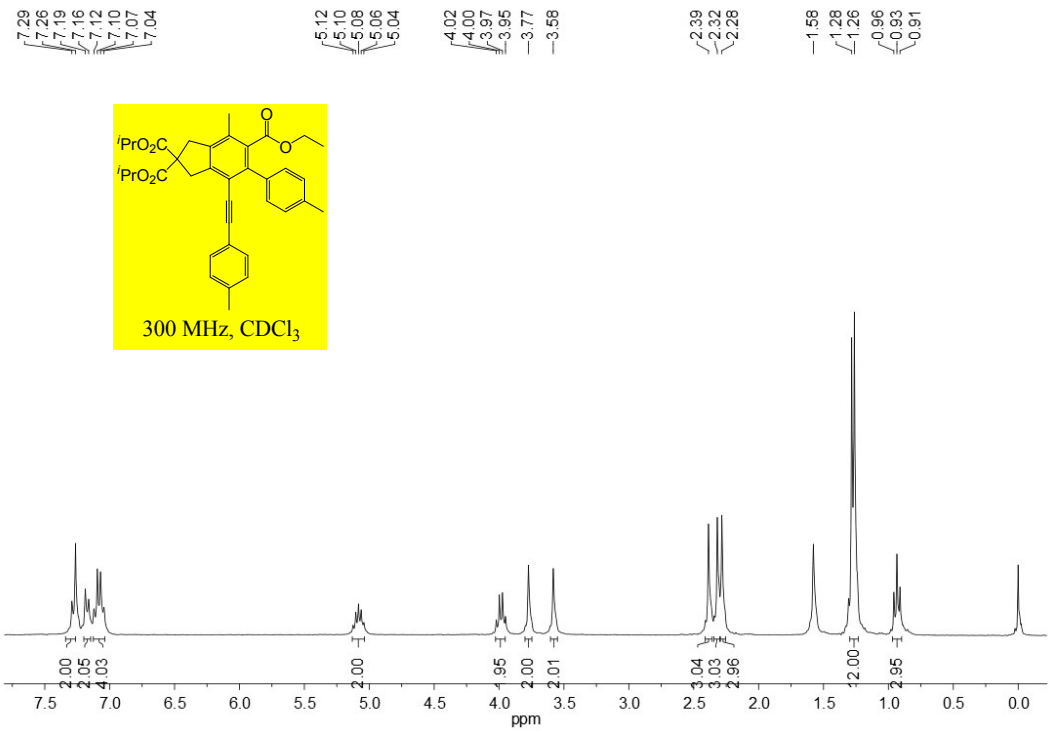

171.97
169.85
143.41
143.12
141.26
138.22
136.12
133.72
131.37
130.47
129.41
127.74
127.12
120.44
117.42
96.39
86.05
77.28
77.02
76.77
59.12
53.19
51.82
41.24
40.13
28.83
28.72
16.77
15.72
15.39
MeO2C
MeO2C
O
O
125 MHz, CDCl3
144.66
143.41
143.12
141.26
138.22
131.37
130.47
129.41
127.74
127.12
120.44
117.42
96.39
86.05
150
140
130
120
110
100
90
ppm
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

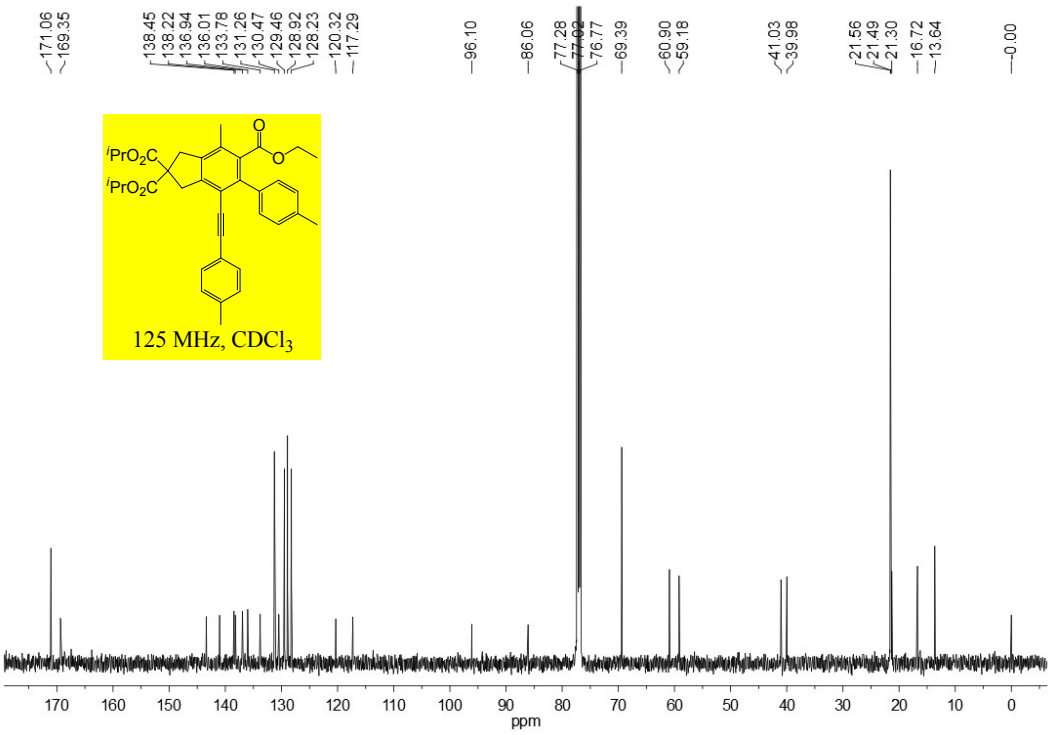

7.37
7.35
7.33
7.26
7.21
7.18
7.16
7.13
7.10
7.07
6.99
6.97
6.94
3.81
3.64
3.53
2.28
1.58
0.00
MeO2C
MeO2C
O
O
F
F
300 MHz, CDCl3
1.97
2.00
1.96
2.03
7.96
1.95
2.98
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

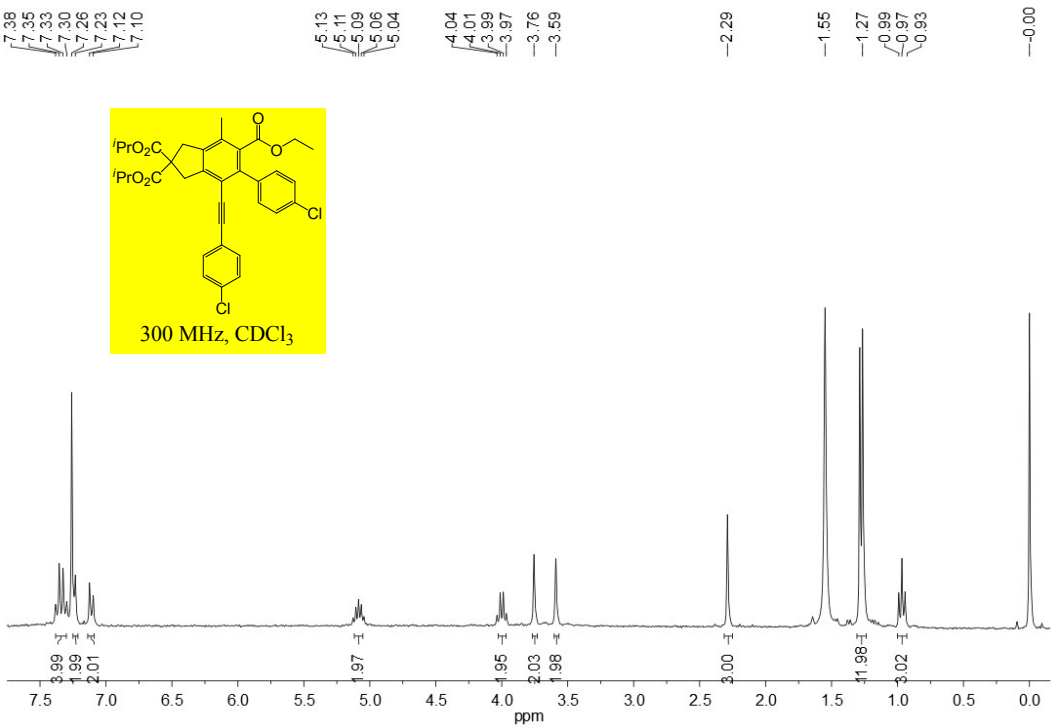

171.86
169.54
143.33
138.77
130.96
119.23
117.00
115.70
115.53
114.74
114.57
95.28
85.57
77.28
77.02
76.77
59.03
53.27
51.99
41.16
40.08
16.82
0.00
MeO2C
MeO2C
O
O
F
F
125 MHz, CDCl3
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

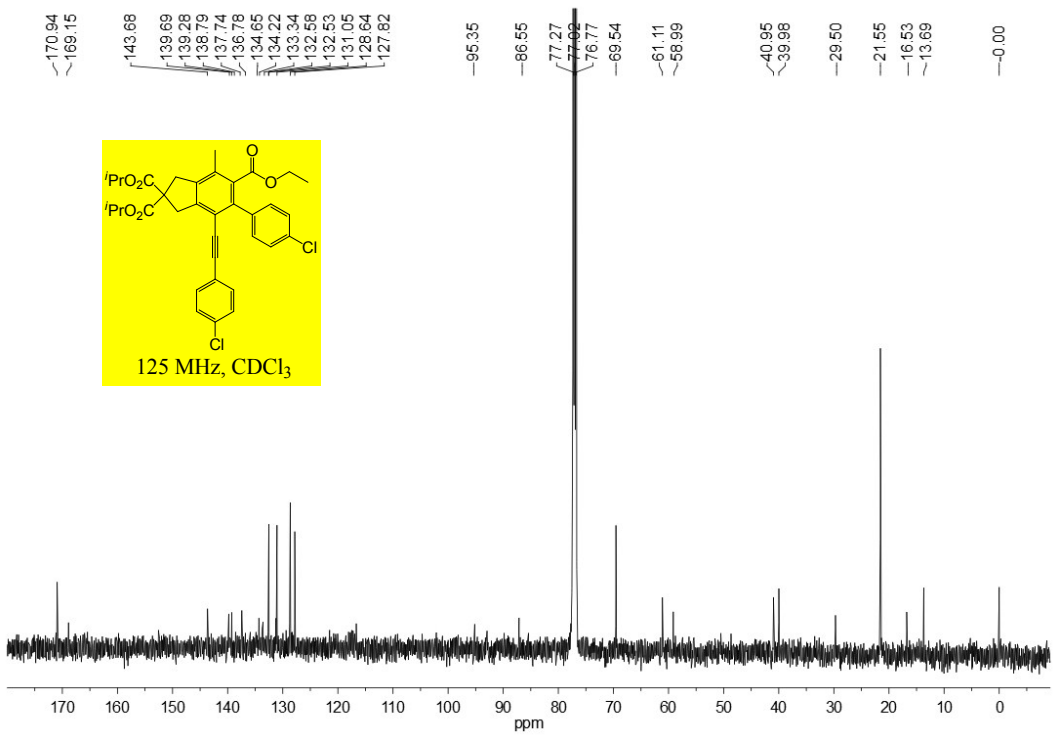

7.38
7.26
7.25
7.23
7.19
7.19
7.17
5.13
5.11
5.09
5.07
5.05
4.00
3.97
3.95
3.92
3.79
3.60
2.30
1.54
1.27
0.91
0.89
0.86
0.00
iPrO2C
iPrO2C
O
O
300 MHz, CDCl3
5.05
2.03
3.03
2.03
2.04
1.97
2.00
3.04
6.00
6.04
2.96
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

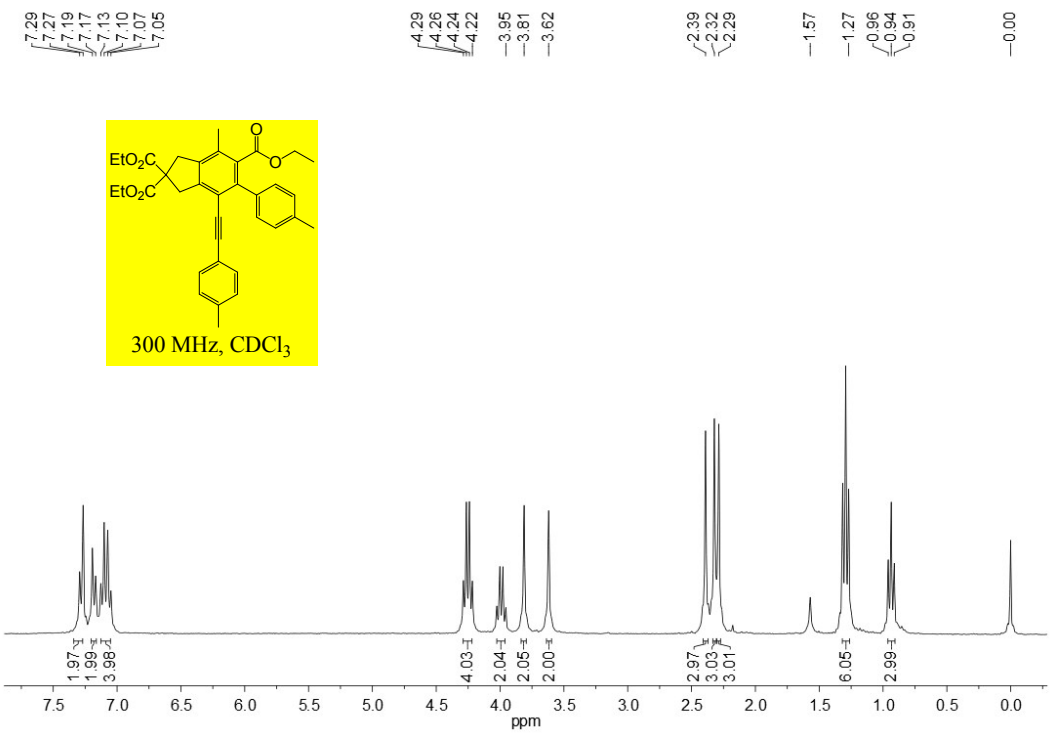

171.03
169.16
143.47
141.22
139.03
138.76
129.65
127.44
123.30
117.06
96.02
86.56
77.28
77.02
76.77
69.43
60.93
59.20
41.01
40.00
21.56
16.75
13.59
0.00
iPrO2C
iPrO2C
O
O
125 MHz, CDCl3
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

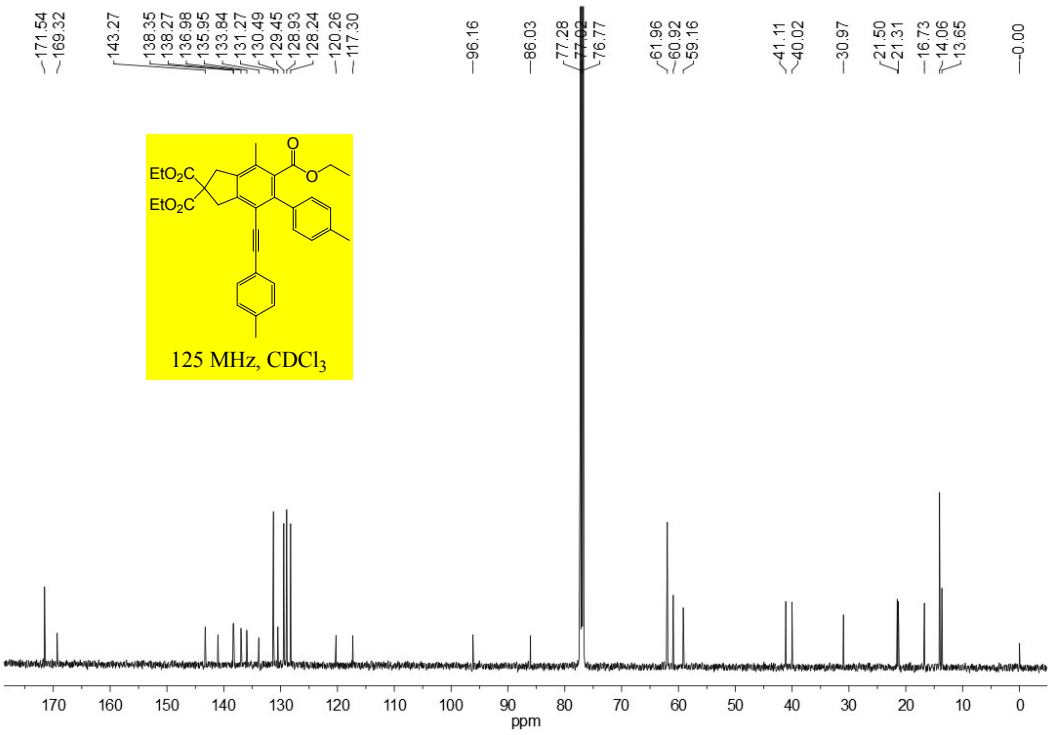

7.29
7.26
7.19
7.16
7.12
7.10
7.07
7.04
5.12
5.10
5.08
5.06
5.04
4.02
4.00
3.97
3.95
3.77
3.58
2.39
2.32
2.28
1.58
1.28
1.26
0.96
0.93
0.91
iPrO2C
iPrO2C
O
O
300 MHz, CDCl3
2.00
2.05
4.03
2.00
1.95
2.00
2.01
3.04
3.03
2.96
12.00
2.95
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

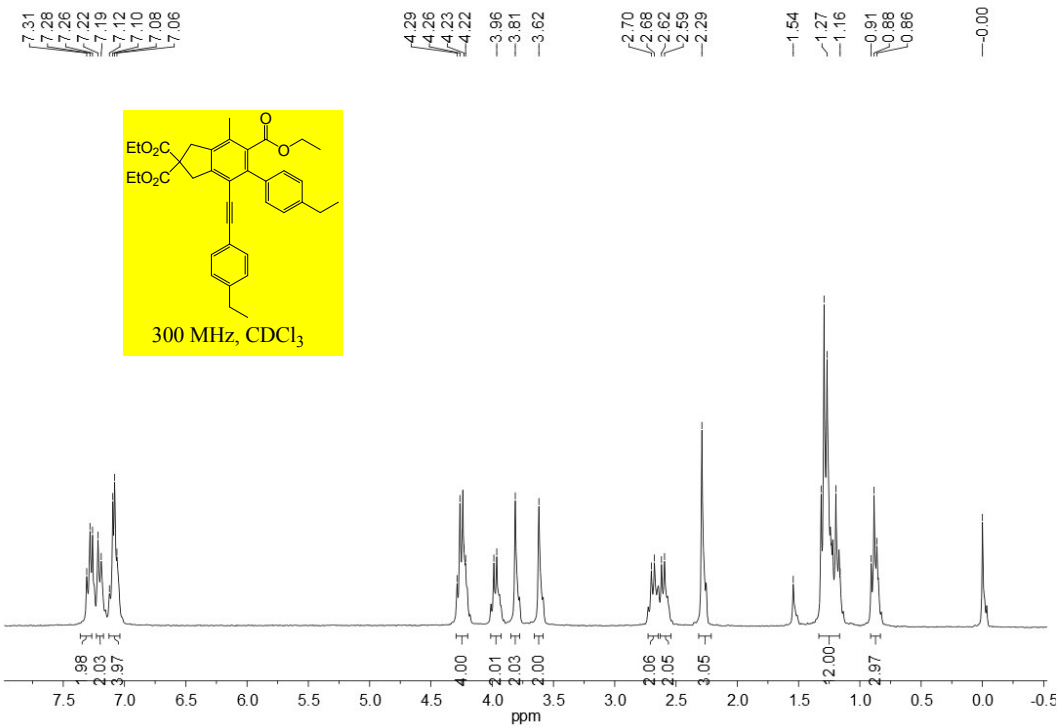

171.06
169.35
138.45
138.22
136.94
136.01
133.78
131.26
130.47
129.46
128.92
128.23
120.32
117.29
96.10
86.06
77.28
77.02
76.77
69.39
60.90
59.18
41.03
39.98
21.56
21.49
21.30
16.72
13.64
0.00
iPrO2C
iPrO2C
O
O
125 MHz, CDCl3
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

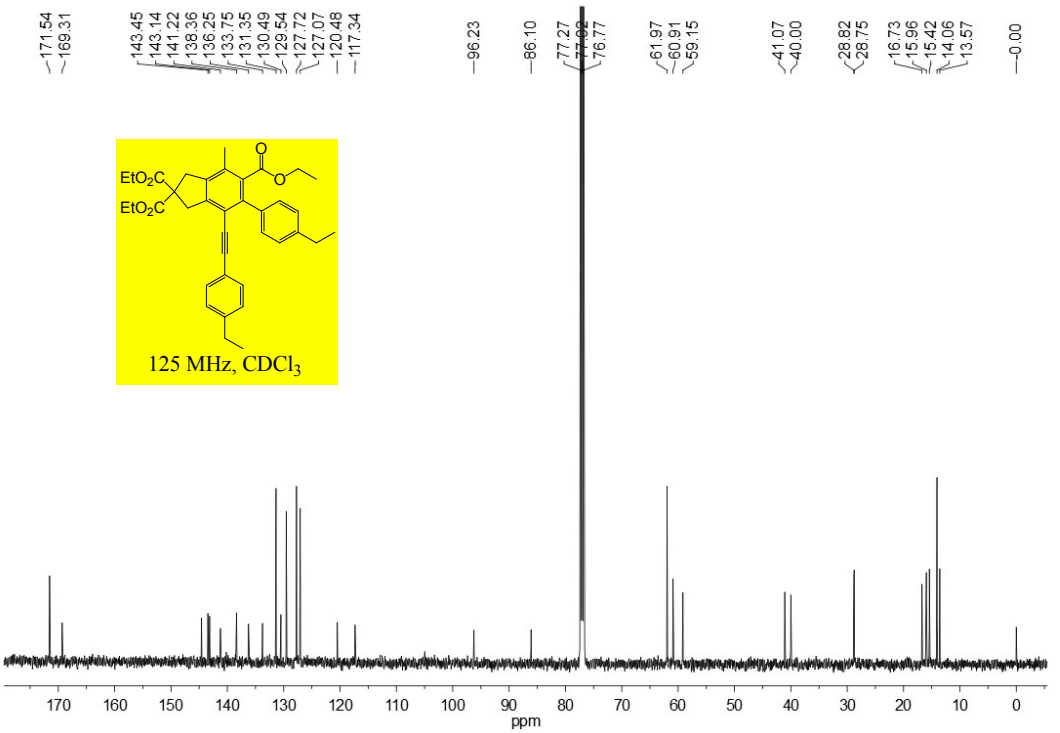

7.38
7.35
7.33
7.30
7.26
7.23
7.12
7.10
5.13
5.11
5.09
5.06
5.04
4.04
4.01
3.99
3.97
3.76
3.59
2.29
1.55
1.27
0.99
0.97
0.93
0.00
iPrO2C
iPrO2C
O
O
Cl
Cl
300 MHz, CDCl3
3.99
1.99
2.01
1.97
1.95
2.03
1.98
3.00
11.98
3.02
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

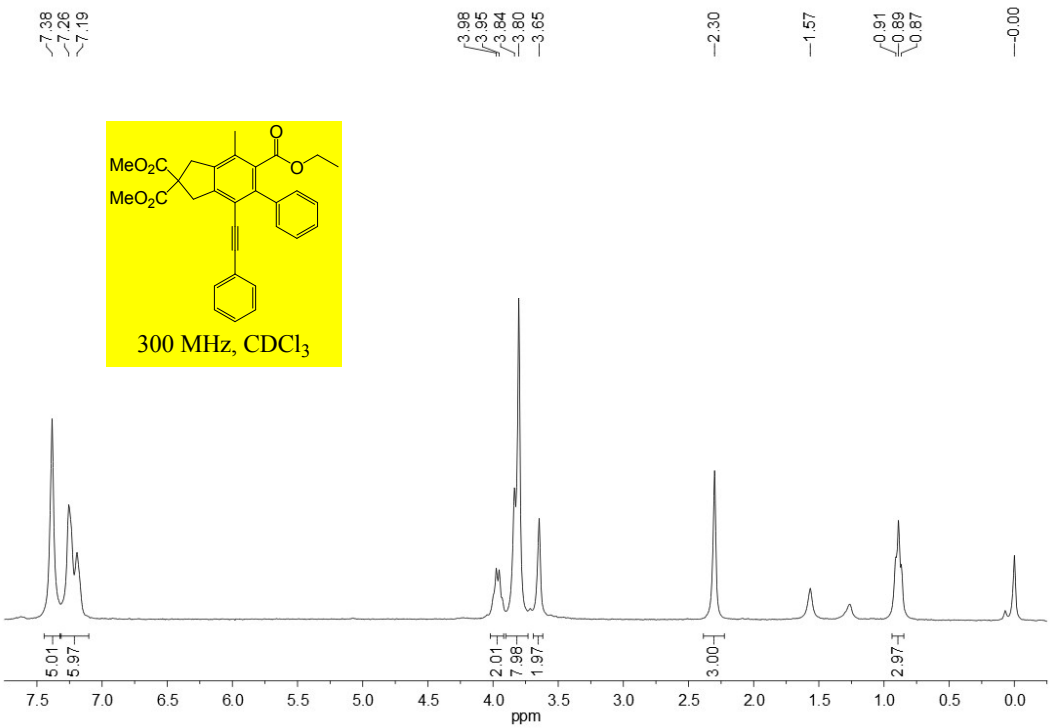

170.94
169.15
143.68
139.69
139.28
138.79
137.74
136.78
134.65
134.22
133.34
132.58
132.53
131.05
128.64
127.82
95.35
86.55
77.27
77.02
76.77
69.54
61.11
58.99
40.95
39.98
29.50
21.55
16.53
13.69
0.00
iPrO2C
iPrO2C
O
O
Cl
Cl
125 MHz, CDCl3
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

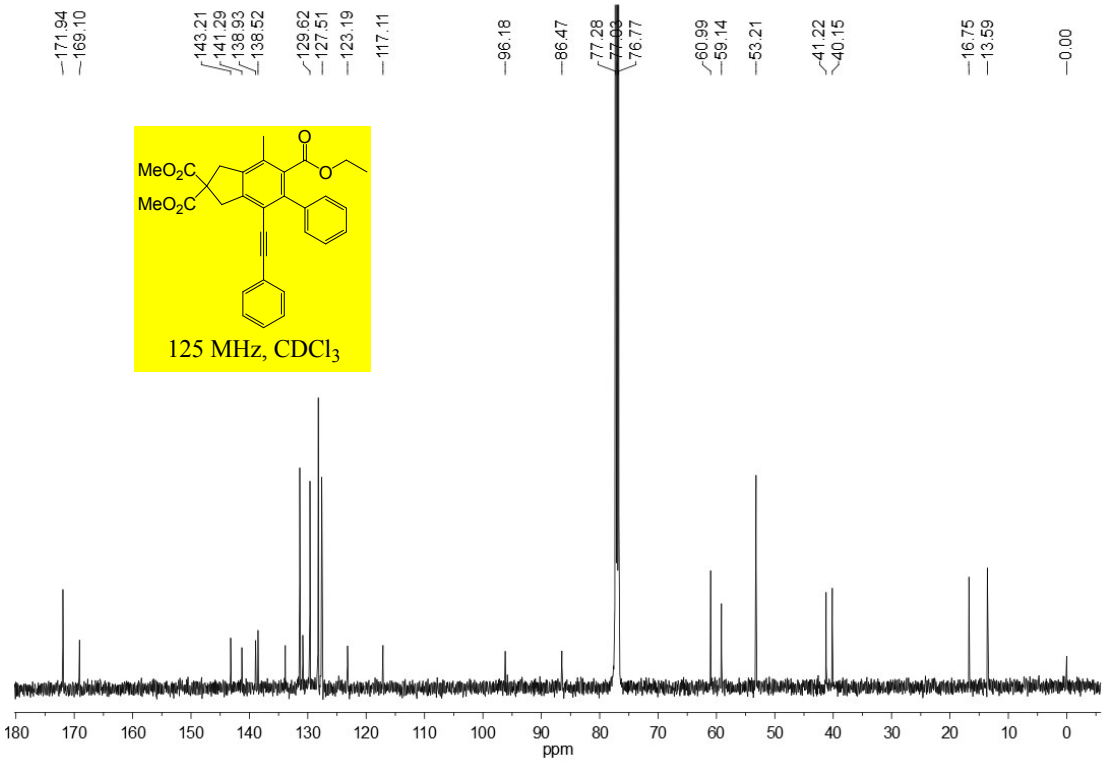

7.29
7.27
7.19
7.17
7.13
7.10
7.07
7.05
4.29
4.26
4.24
4.22
3.95
3.81
3.62
2.39
2.32
2.29
1.57
1.27
0.96
0.94
0.91
0.00
EtO2C
EtO2C
O
O
300 MHz, CDCl3
1.97
1.99
3.98
4.03
2.04
2.05
2.00
2.97
3.03
3.01
6.05
2.99
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

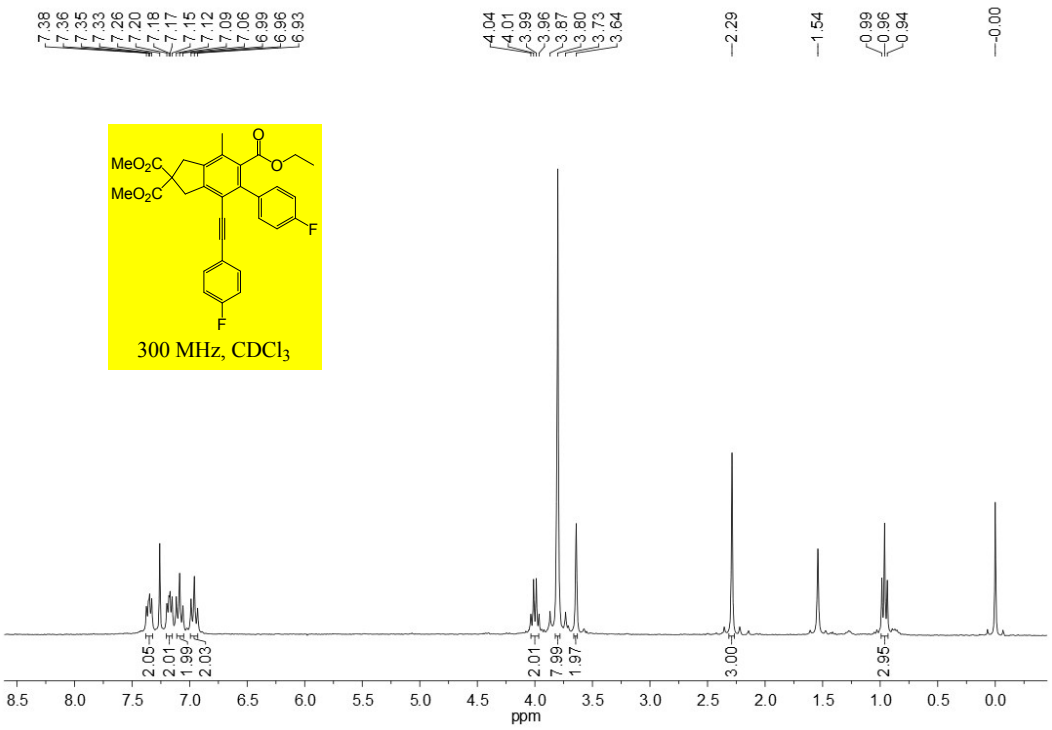

171.54
169.32
143.27
138.35
138.27
136.98
135.95
133.84
131.27
130.49
129.45
128.93
128.24
120.26
117.30
96.16
86.03
77.28
77.02
76.77
61.96
60.92
59.16
41.11
40.02
30.97
21.50
21.31
16.73
14.06
13.65
0.00
EtO2C
EtO2C
O
O
125 MHz, CDCl3
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

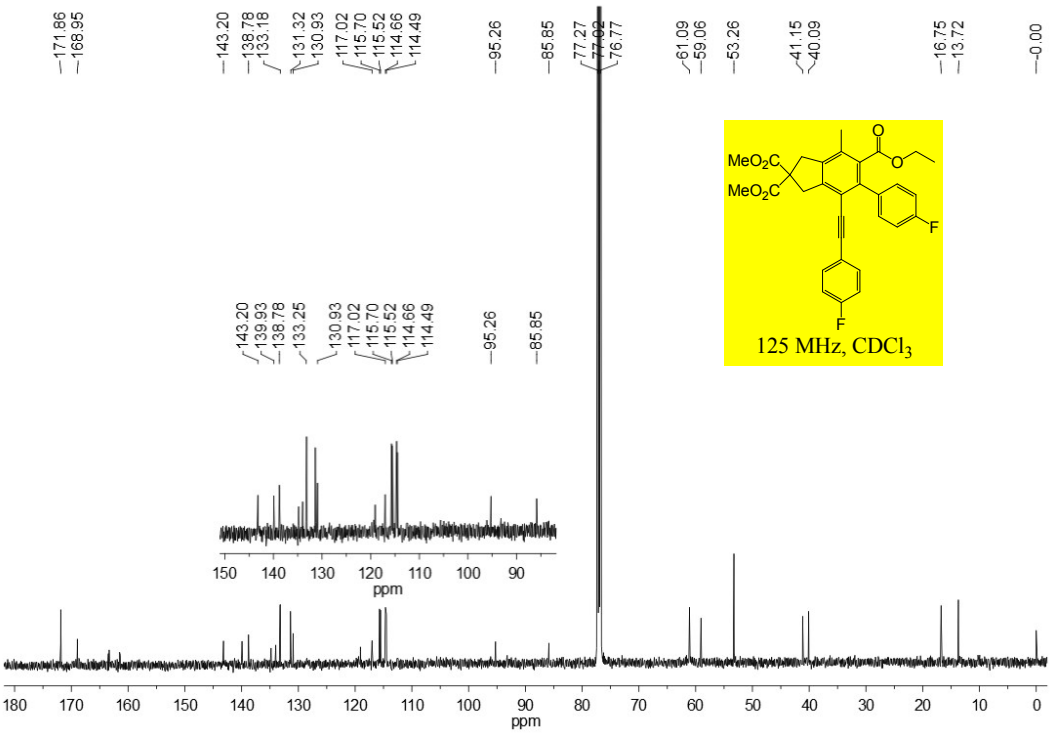

7.31
7.28
7.26
7.22
7.19
7.12
7.10
7.08
7.06
4.29
4.26
4.23
4.22
3.96
3.81
3.62
2.70
2.68
2.62
2.59
2.29
1.54
1.27
1.16
0.91
0.88
0.86
0.00
EtO2C
EtO2C
O
O
300 MHz, CDCl3
1.98
2.03
3.97
4.00
2.01
2.03
2.00
2.06
2.05
3.05
12.00
2.97
ppm

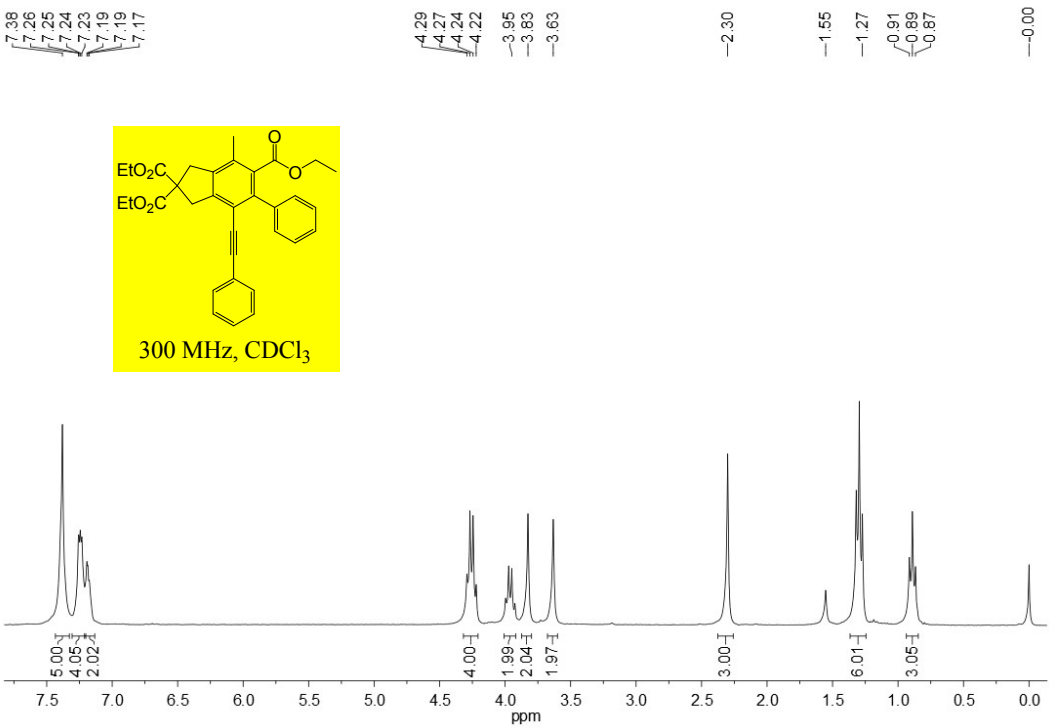

171.54
169.31
143.45
143.14
141.22
138.36
136.25
133.75
131.35
130.49
129.54
127.72
127.07
120.48
117.34
96.23
86.10
77.27
77.02
76.77
61.97
60.91
59.15
41.07
40.00
28.82
28.75
16.73
15.96
15.42
14.06
13.57
0.00
EtO2C
EtO2C
O
O
125 MHz, CDCl3
ppm

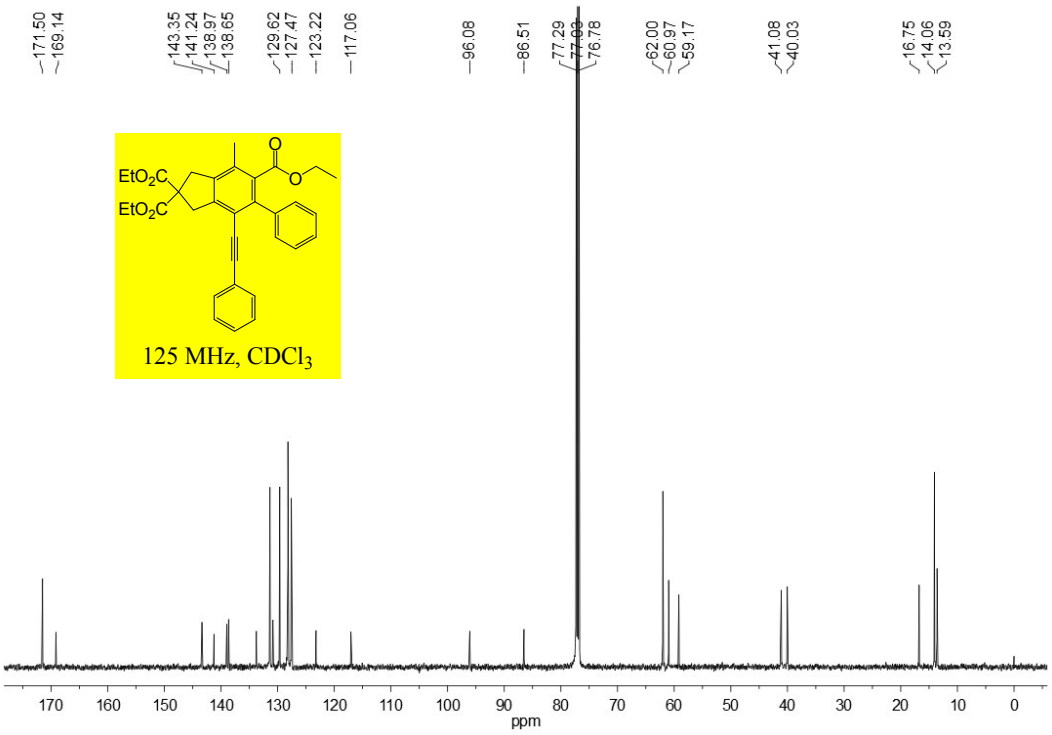

7.38
7.26
7.19
3.98
3.95
3.84
3.80
3.65
2.30
1.57
0.91
0.89
0.87
0.00
MeO2C
MeO2C
O
O
300 MHz, CDCl3
5.01
5.97
2.01
7.98
1.97
3.00
2.97
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

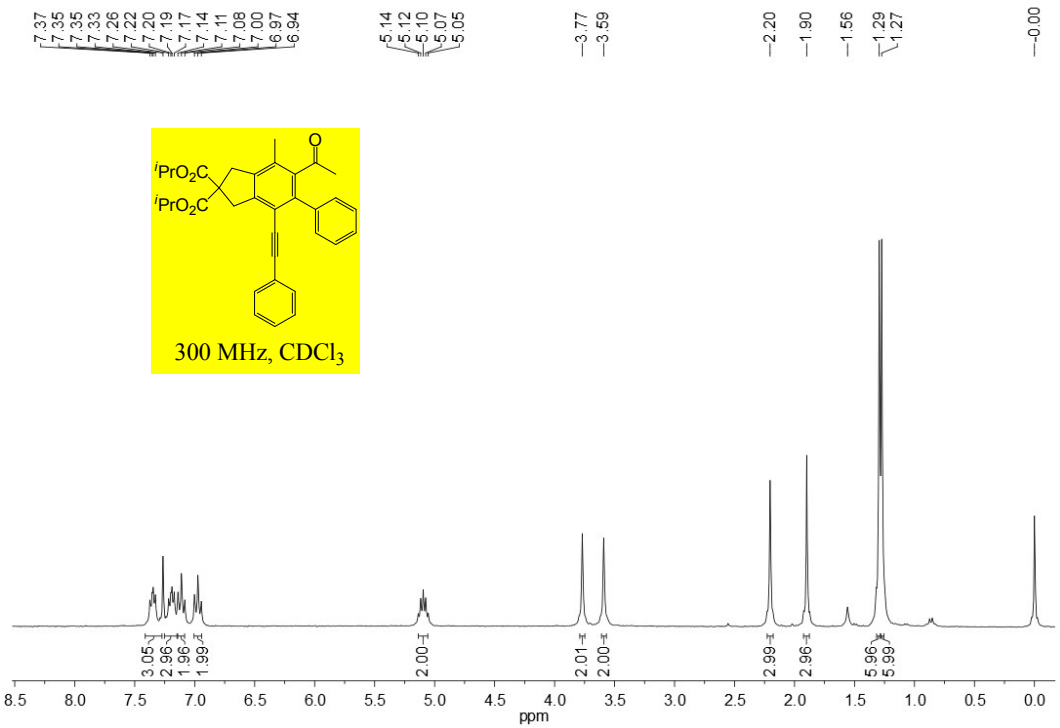

171.94
169.10
143.21
141.29
138.93
138.52
129.62
127.51
123.19
117.11
96.18
86.47
77.28
77.03
76.77
60.99
59.14
53.21
41.22
40.15
16.75
13.59
0.00
MeO2C
MeO2C
O
O
125 MHz, CDCl3
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

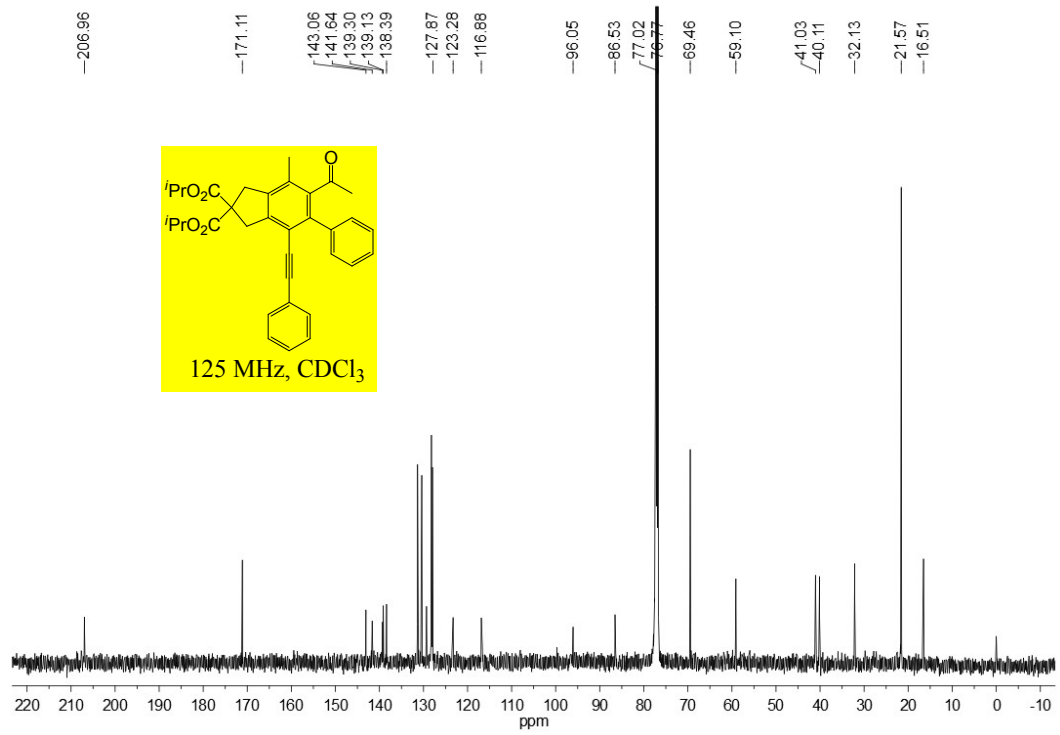

7.38
7.36
7.35
7.33
7.26
7.20
7.18
7.17
7.15
7.12
7.09
7.06
6.99
6.96
6.93
4.04
4.01
3.99
3.96
3.87
3.80
3.73
3.64
2.29
1.54
0.99
0.96
0.94
0.00
MeO2C
MeO2C
O
O
F
F
300 MHz, CDCl3
2.05
2.01
1.99
2.03
2.01
7.99
1.97
3.00
2.95
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

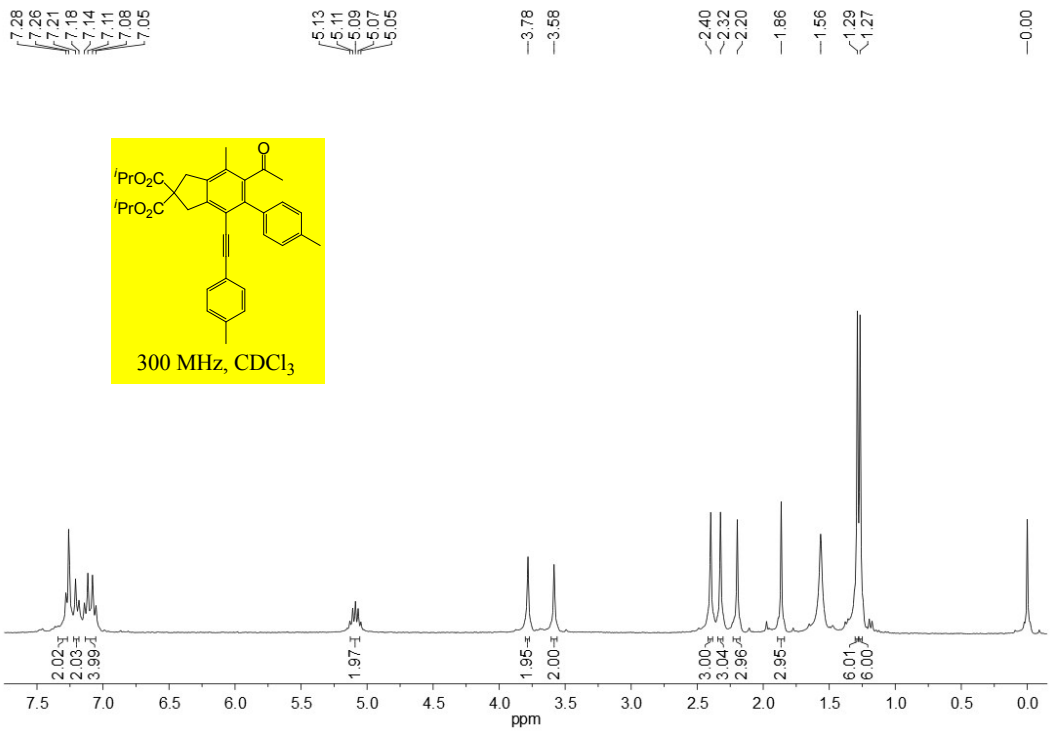

171.86
168.95
143.20
138.78
133.18
131.32
130.93
117.02
115.70
115.52
114.66
114.49
95.26
85.85
77.27
77.02
76.77
61.09
59.06
53.26
41.15
40.09
16.75
13.72
0.00
MeO2C
MeO2C
O
O
F
F
125 MHz, CDCl3
143.20
139.93
138.78
133.25
130.93
117.02
115.70
115.52
114.66
114.49
95.26
85.85
150 140 130 120 110 100 90
ppm
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

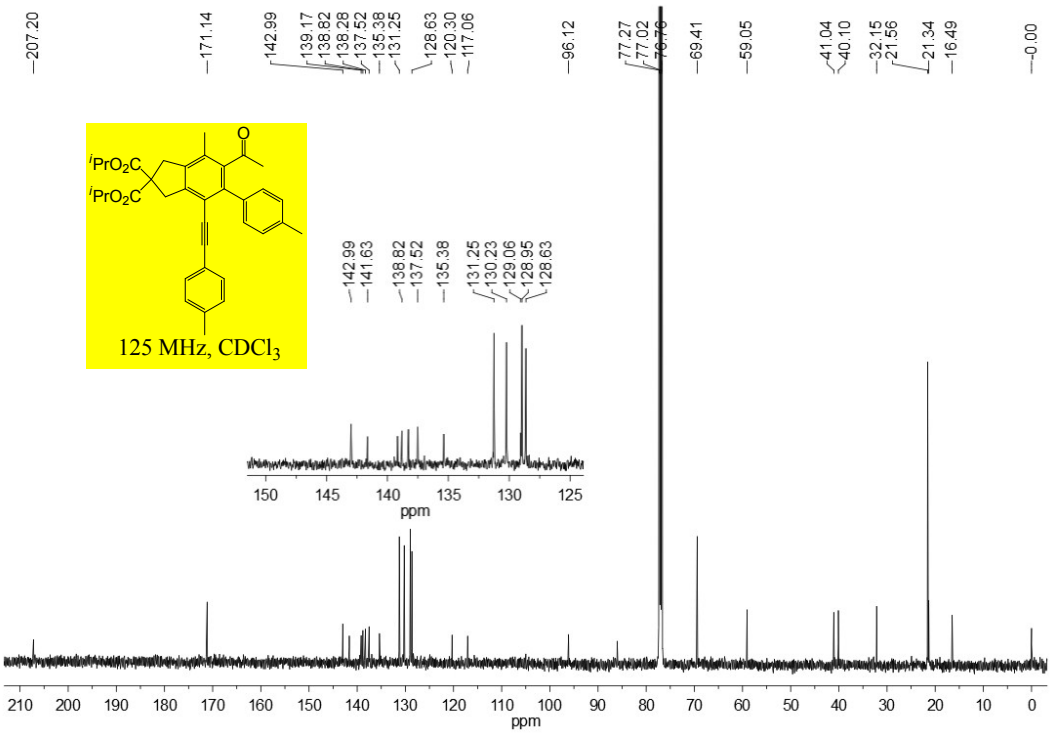

7.38
7.26
7.25
7.24
7.23
7.19
7.19
7.17
4.29
4.27
4.24
4.22
3.95
3.83
3.63
2.30
1.55
1.27
0.91
0.89
0.87
0.00
EtO2C
EtO2C
O
O
300 MHz, CDCl3
5.00
4.05
2.02
4.00
1.99
2.04
1.97
3.00
6.01
3.05
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

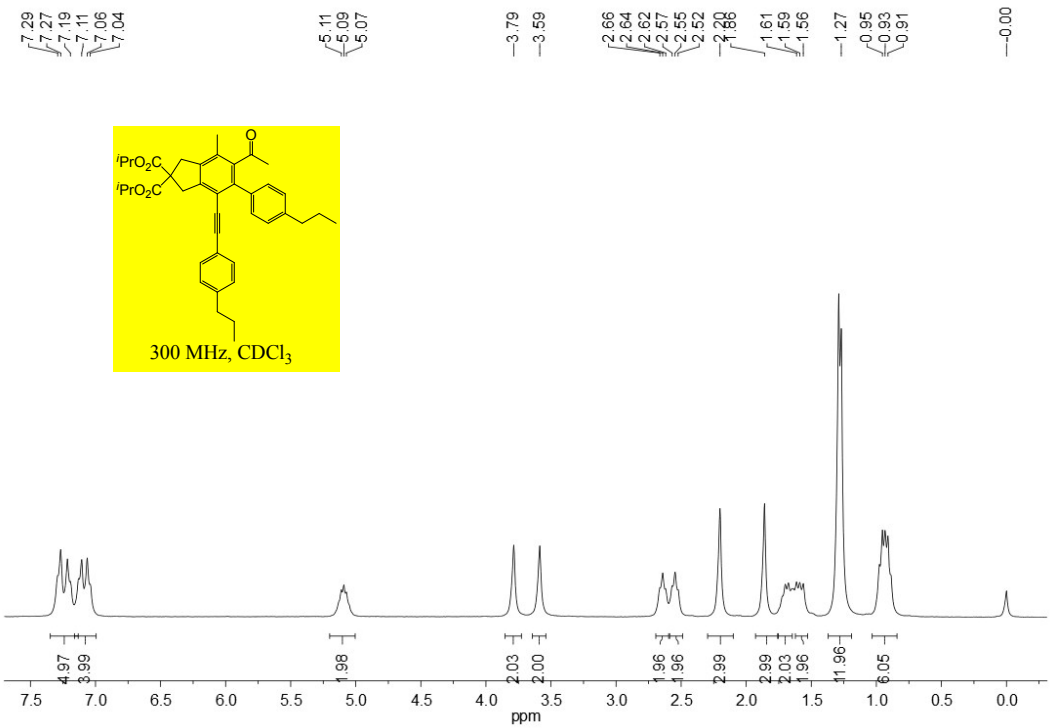

171.50
169.14
143.35
141.24
138.97
138.65
129.62
127.47
123.22
117.06
96.08
86.51
77.29
77.00
76.78
62.00
60.97
59.17
41.08
40.03
16.75
14.06
13.59
EtO2C
EtO2C
O
O
125 MHz, CDCl3
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

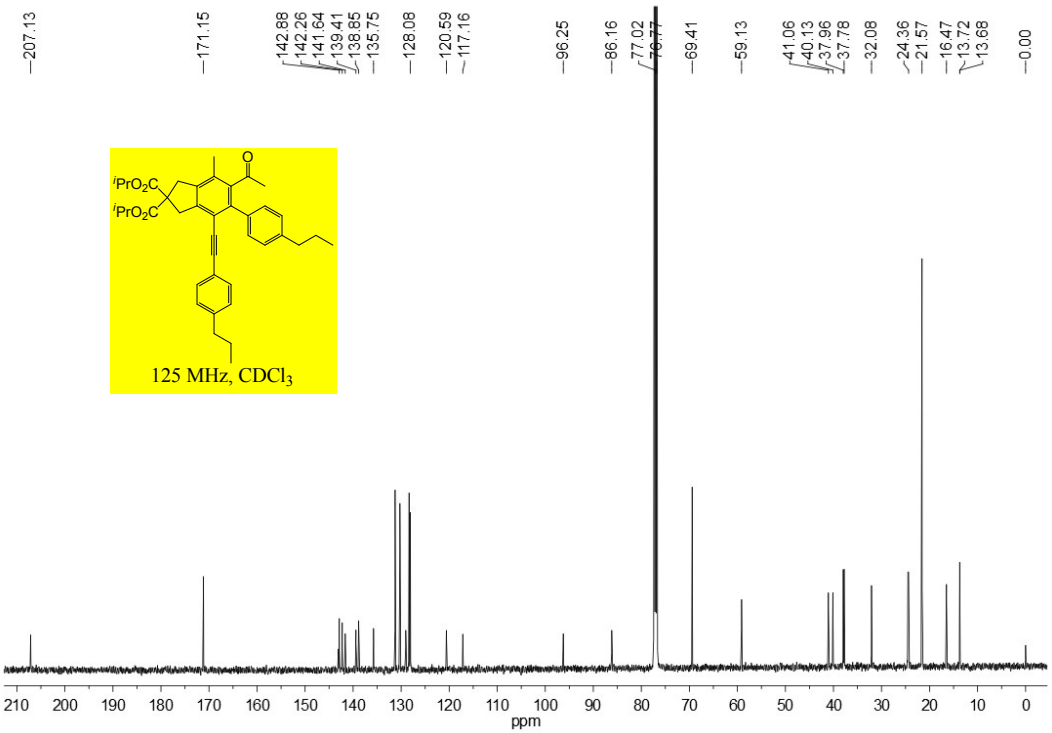

7.37
7.35
7.35
7.33
7.26
7.22
7.20
7.19
7.17
7.14
7.11
7.08
7.00
6.97
6.94
5.14
5.12
5.10
5.07
5.05
3.77
3.59
2.20
1.90
1.56
1.29
1.27
0.00
iPrO2C
iPrO2C
O
300 MHz, CDCl3
3.05
2.96
1.96
1.99
2.00
2.01
2.00
2.99
2.96
5.96
5.99
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

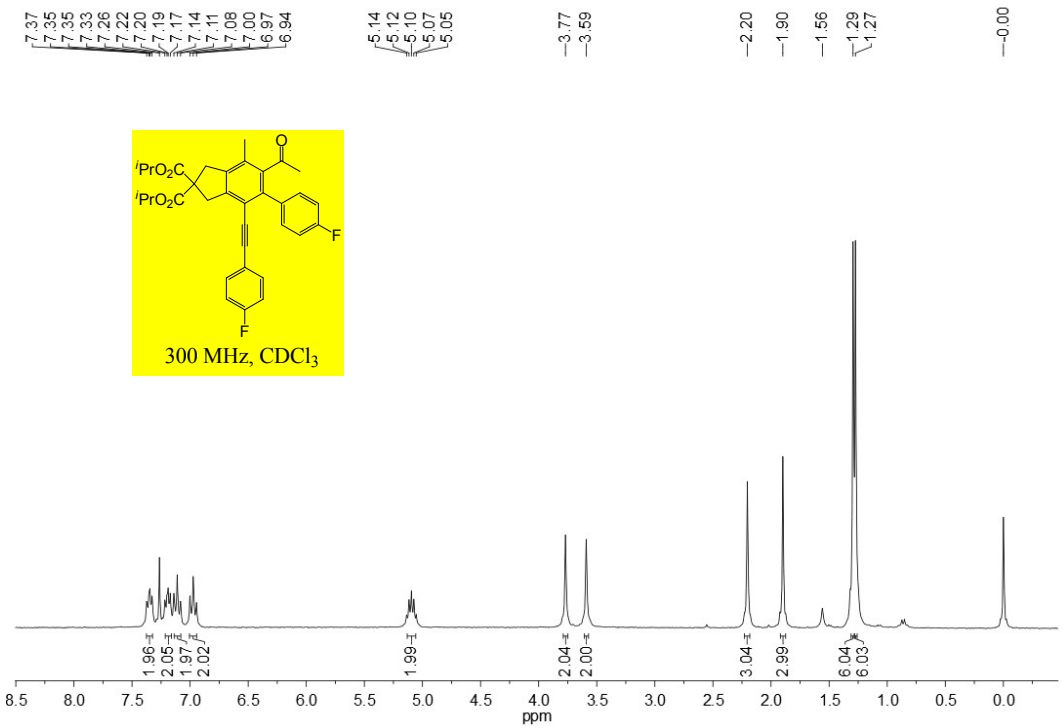

206.96
171.11
143.06
141.64
139.30
139.13
138.39
127.87
123.28
116.88
96.05
86.53
77.02
76.77
69.46
59.10
41.03
40.11
32.13
21.57
16.51
iPrO2C
iPrO2C
O
125 MHz, CDCl3
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm

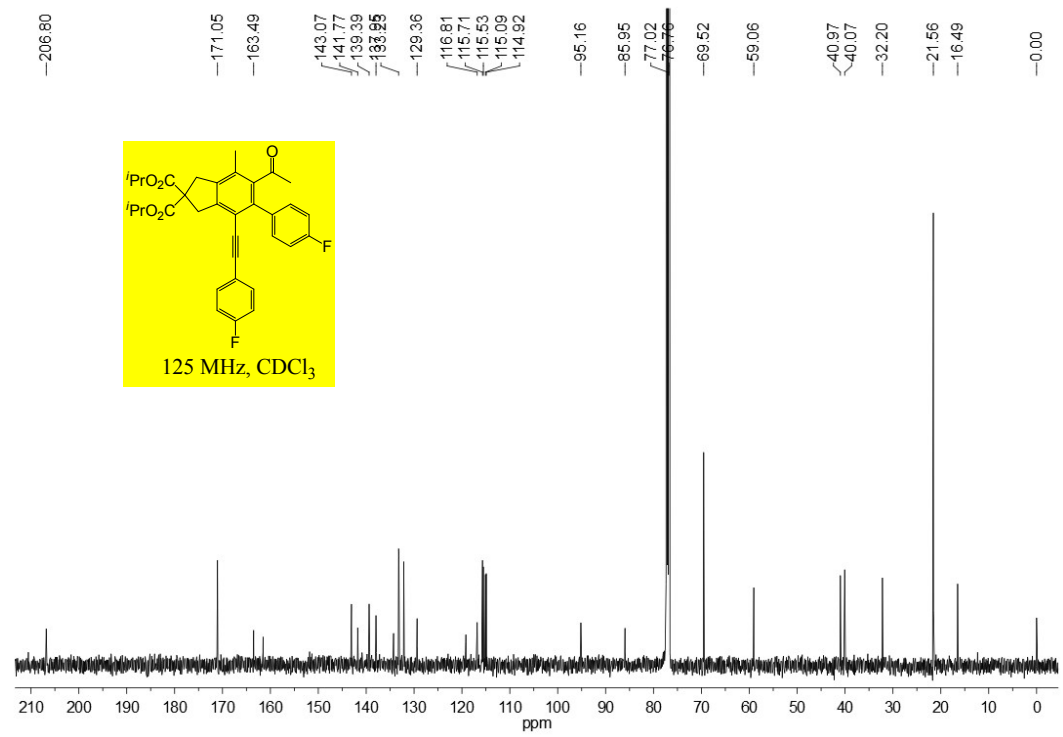

7.28
7.26
7.21
7.18
7.14
7.11
7.08
7.05
5.13
5.11
5.09
5.07
5.05
3.78
3.58
2.40
2.32
2.20
1.86
1.56
1.29
1.27
0.00
iPrO2C
iPrO2C
O
300 MHz, CDCl3
2.02
2.03
3.99
1.97
1.95
2.00
3.00
3.04
2.96
2.95
6.01
6.00
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

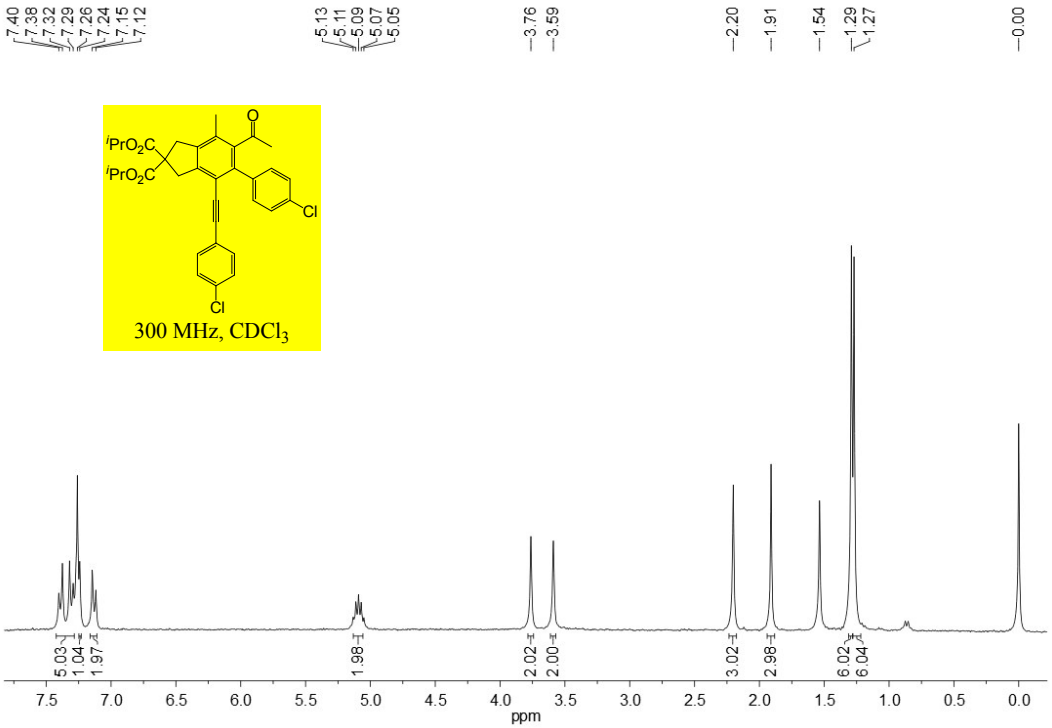

207.20
171.14
142.99
139.17
138.82
138.28
137.52
135.38
131.25
128.63
120.30
117.06
96.12
77.27
77.02
76.76
69.41
59.05
41.04
40.10
32.15
21.56
21.34
16.49
0.00
iPrO2C
iPrO2C
O
125 MHz, CDCl3
142.99
141.63
138.82
137.52
135.38
131.25
130.23
129.06
128.95
128.63
150 145 140 135 130 125
ppm
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

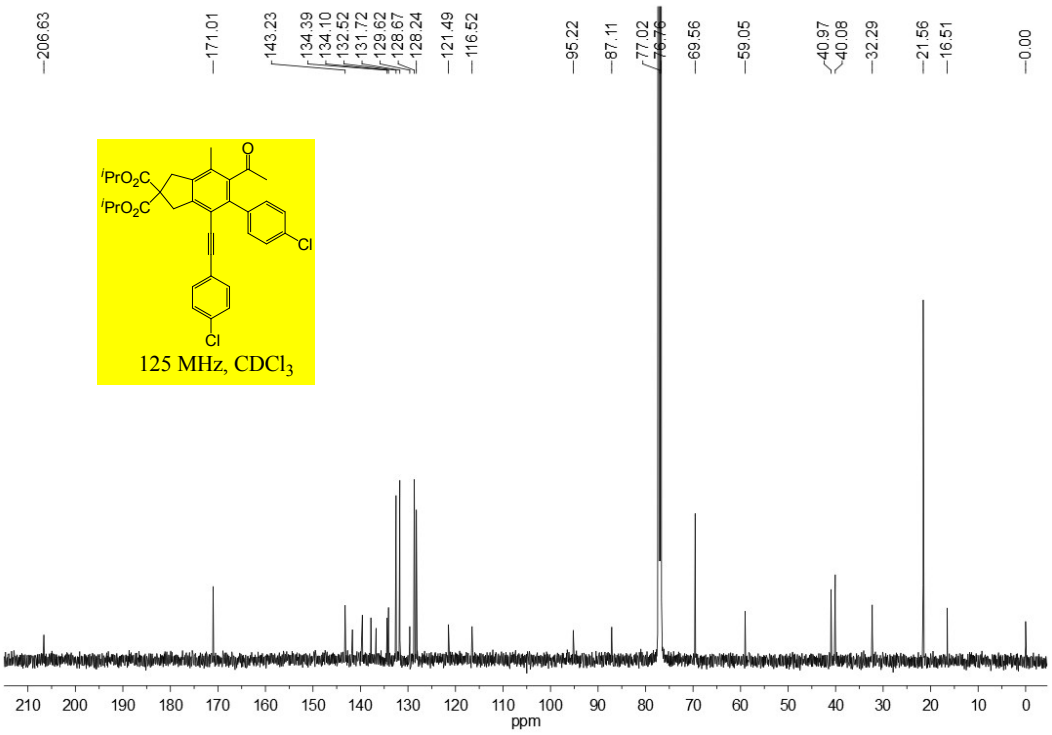

7.29
7.27
7.19
7.11
7.06
7.04
5.11
5.09
5.07
3.79
3.59
2.66
2.64
2.62
2.57
2.55
2.52
2.20
1.86
1.61
1.59
1.56
1.27
0.95
0.93
0.91
0.00
iPrO2C
iPrO2C
O
300 MHz, CDCl3
4.97
3.99
1.98
2.03
2.00
1.96
1.96
2.99
2.99
2.03
1.96
11.96
6.05
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

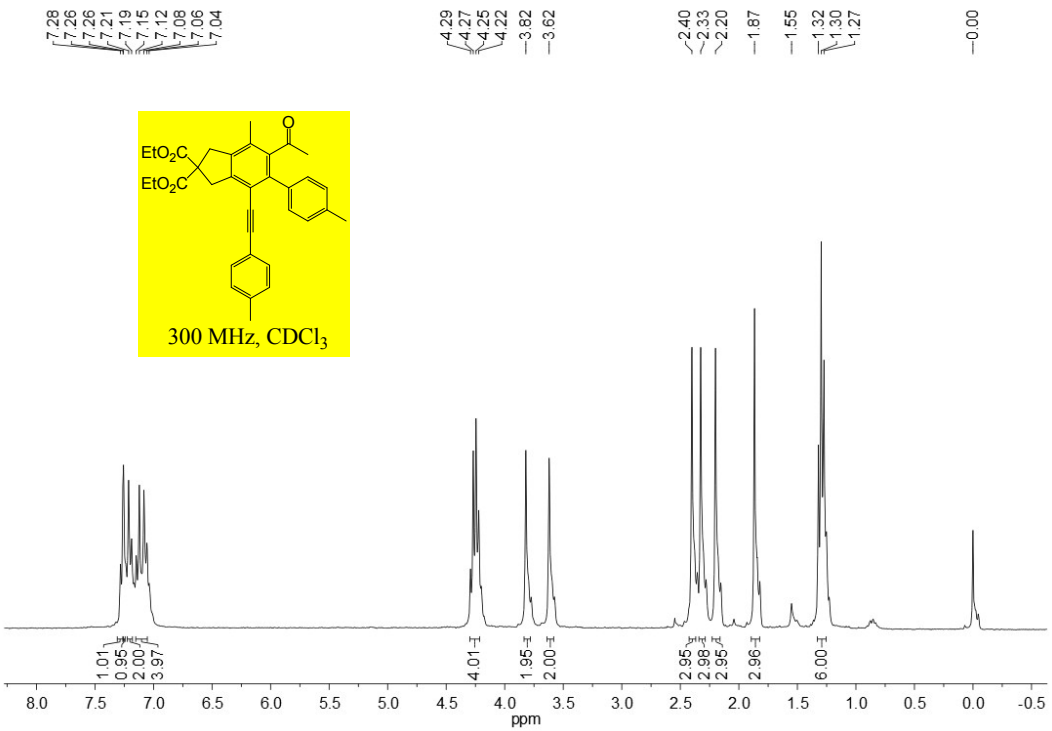

207.13
171.15
142.88
142.26
141.64
139.41
138.85
135.75
128.08
120.59
117.16
96.25
86.16
77.02
76.77
69.41
59.13
41.06
40.13
37.96
37.78
32.08
24.36
21.57
16.47
13.72
13.68
0.00
iPrO2C
iPrO2C
O
125 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

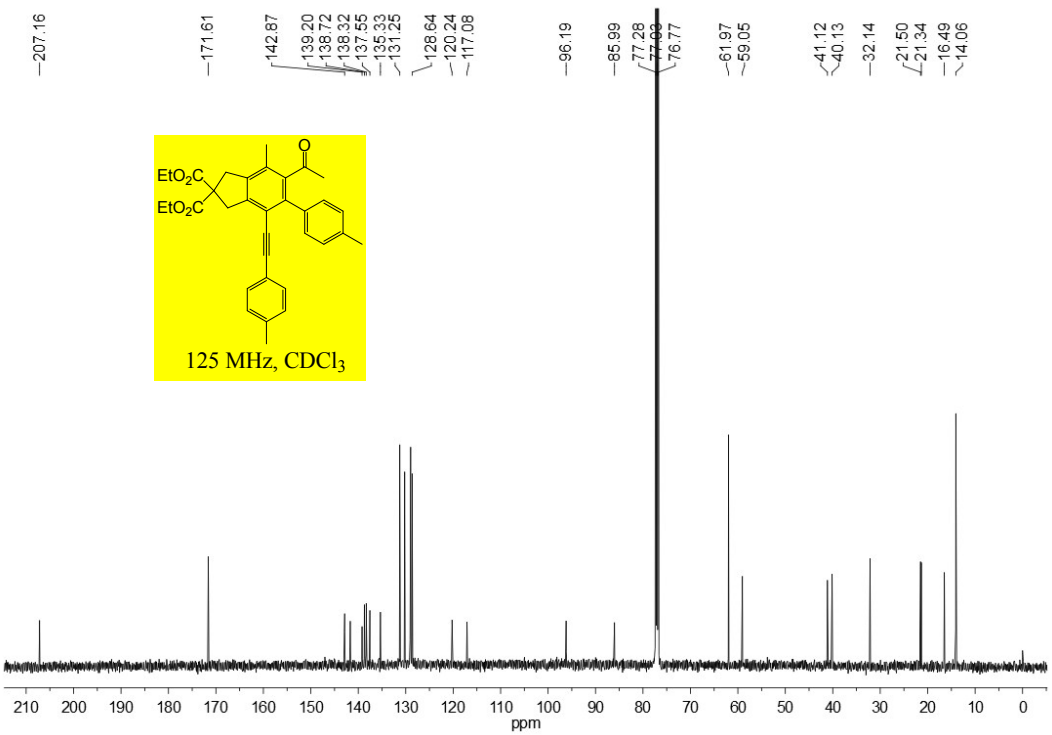

7.37
7.35
7.35
7.33
7.26
7.22
7.20
7.19
7.17
7.14
7.11
7.08
7.00
6.97
6.94
5.14
5.12
5.10
5.07
5.05
3.77
3.59
2.20
1.90
1.56
1.29
1.27
0.00
iPrO2C
iPrO2C
O
F
F
300 MHz, CDCl3
1.96
2.05
1.97
2.02
1.99
2.04
2.00
3.04
2.99
6.04
6.03
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

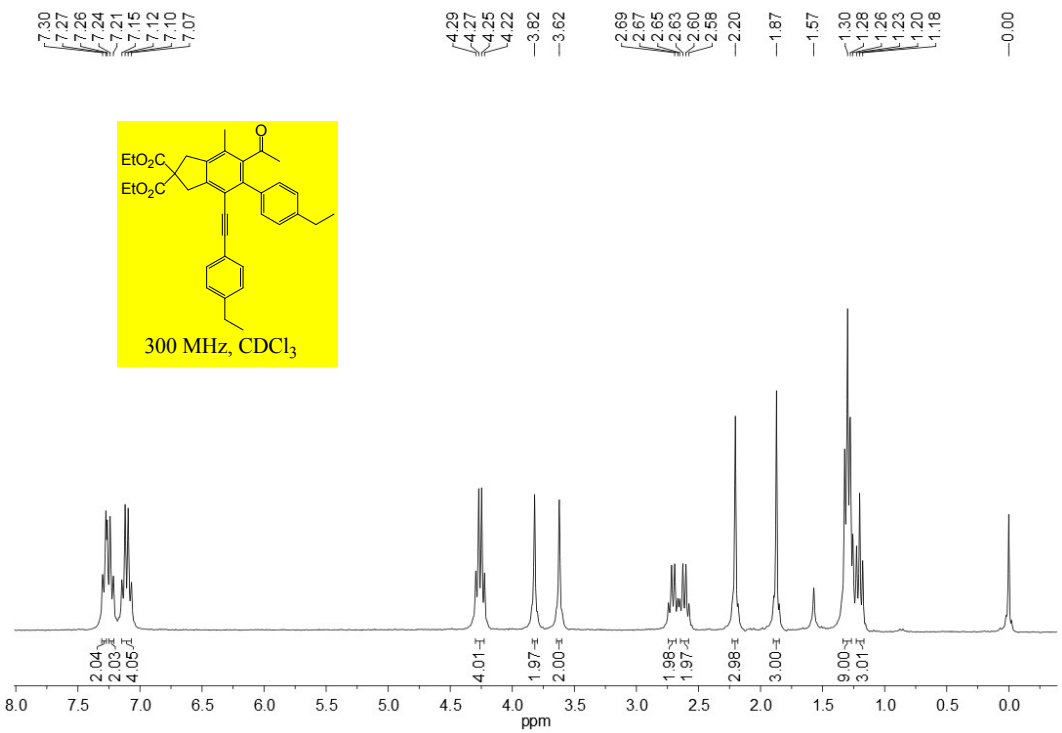

206.80
171.05
163.49
143.07
141.77
139.39
129.36
116.81
115.71
115.53
115.09
114.92
95.16
85.95
77.02
76.70
69.52
59.06
40.97
40.07
32.20
21.56
16.49
0.00
iPrO2C
iPrO2C
O
F
F
125 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

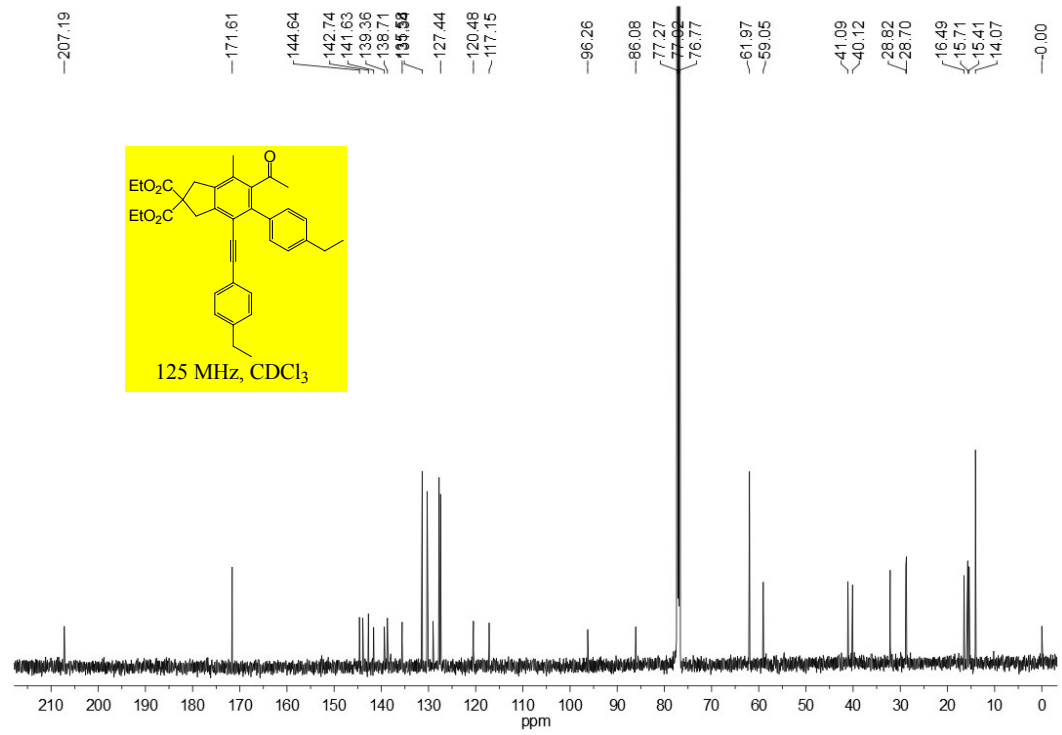

7.40
7.38
7.32
7.29
7.26
7.24
7.15
7.12
5.13
5.11
5.09
5.07
5.05
3.76
3.59
2.20
1.91
1.54
1.29
1.27
0.00
O
iPrO2C
iPrO2C
Cl
Cl
300 MHz, CDCl3
5.03
1.04
1.97
1.98
2.02
2.00
3.02
2.98
6.02
6.04
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

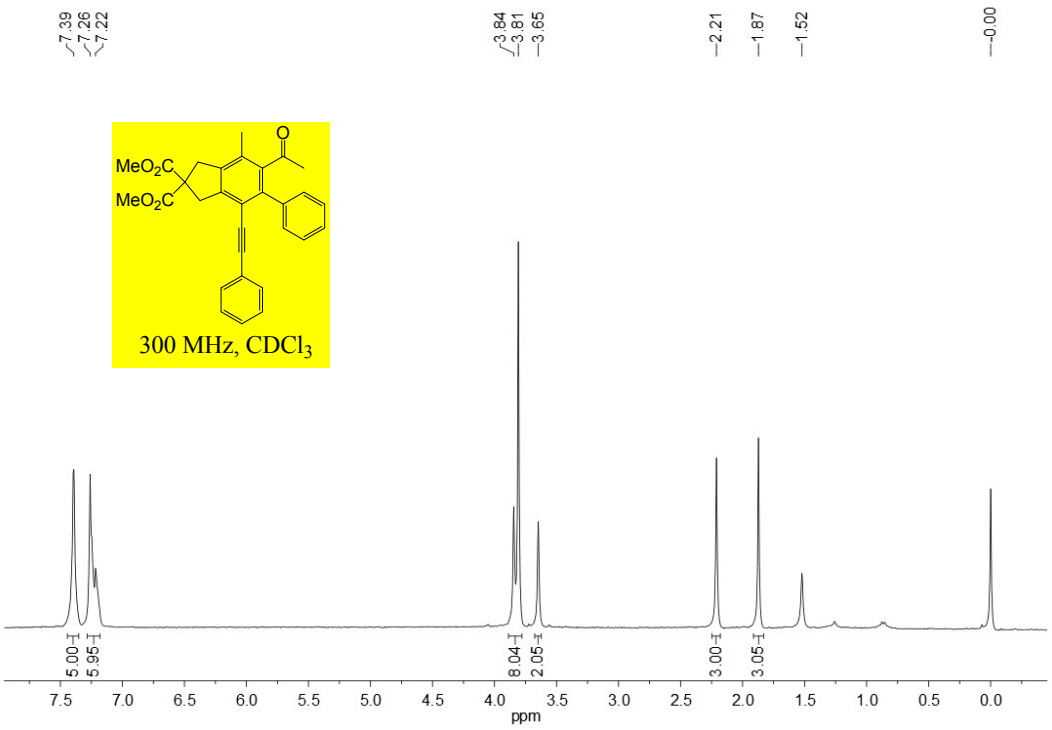

206.63
171.01
143.23
134.39
134.10
132.52
131.72
129.62
128.67
128.24
121.49
116.52
95.22
87.11
77.02
76.76
69.56
59.05
40.97
40.08
32.29
21.56
16.51
0.00
O
iPrO2C
iPrO2C
Cl
Cl
125 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

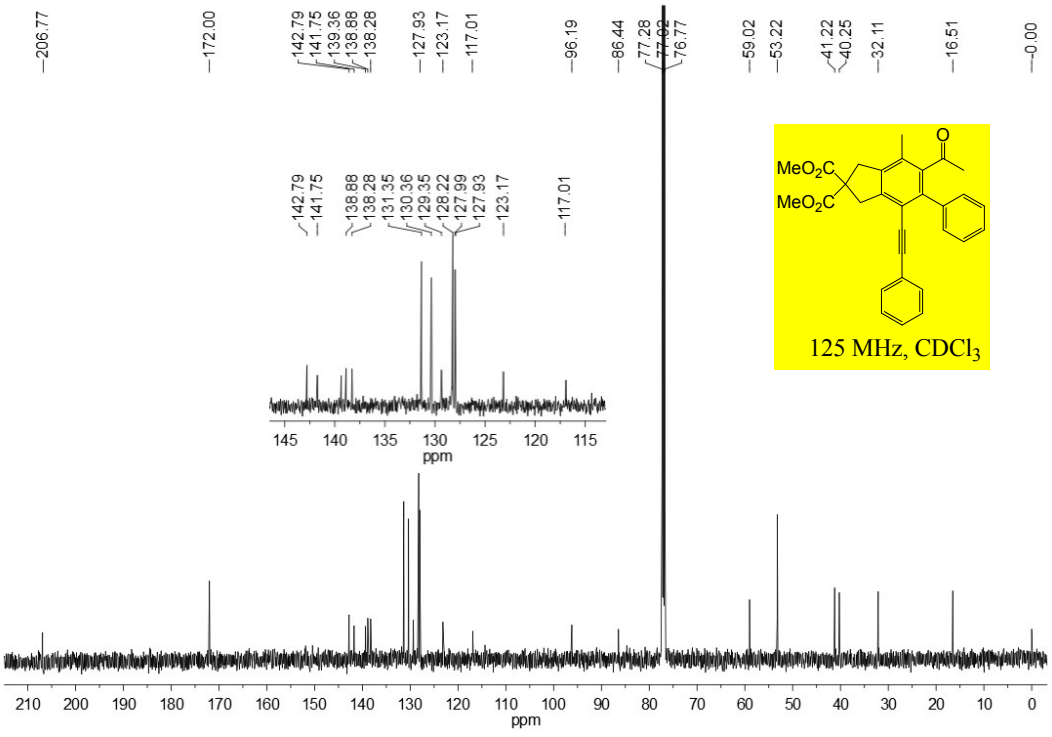

7.28
7.26
7.26
7.21
7.19
7.15
7.12
7.08
7.06
7.04
4.29
4.27
4.25
4.22
3.82
3.62
2.40
2.33
2.20
1.87
1.55
1.32
1.30
1.27
0.00
EtO2C
EtO2C
O
300 MHz, CDCl3
1.01
0.95
2.00
3.97
4.01
1.95
2.00
2.95
2.98
2.95
2.96
6.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
ppm

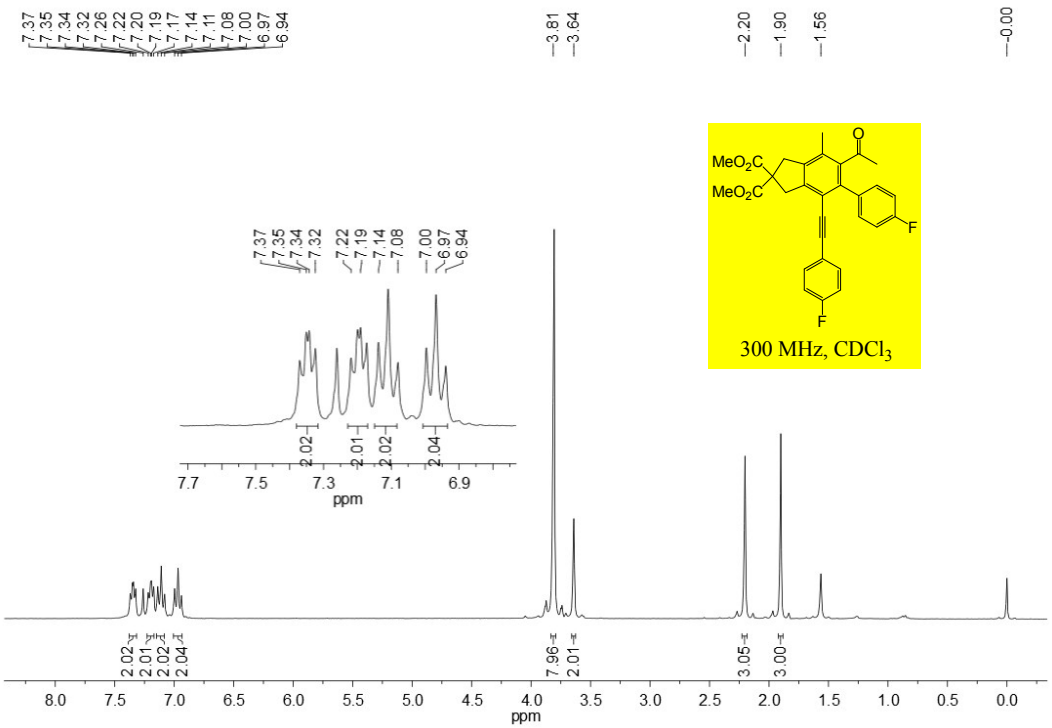

207.16
171.61
142.87
139.20
138.72
138.32
137.55
135.33
131.25
128.64
120.24
117.08
96.19
85.99
77.28
77.00
76.77
61.97
59.05
41.12
40.13
32.14
21.50
21.34
16.49
14.06
EtO2C
EtO2C
O
125 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

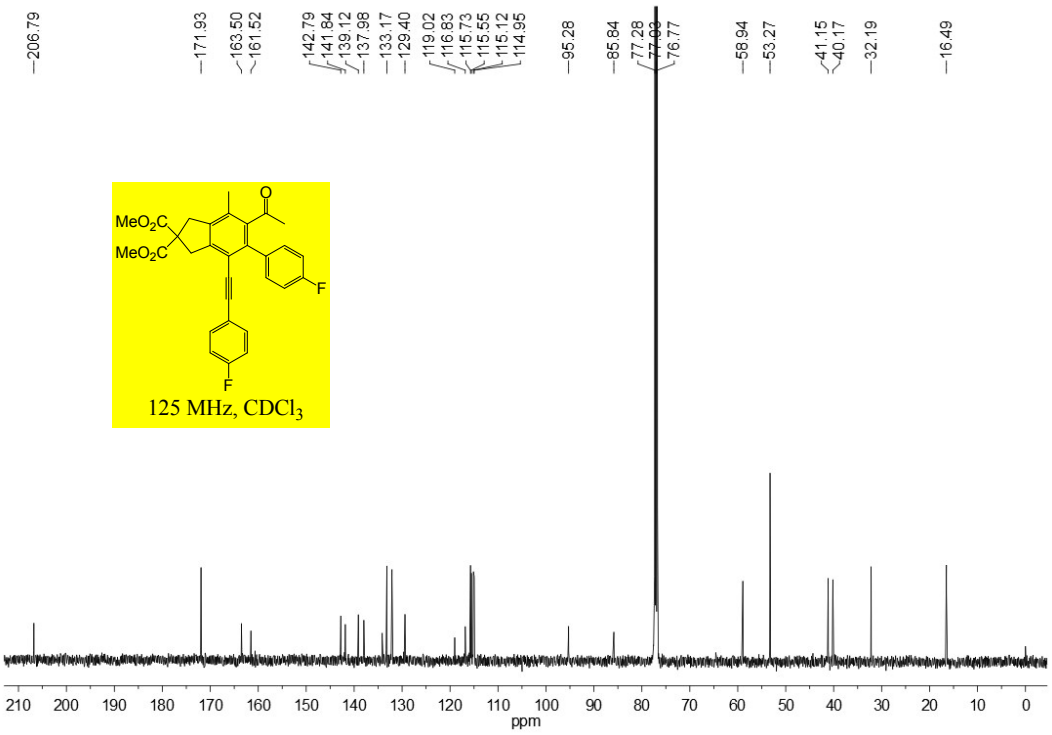

7.30
7.27
7.26
7.24
7.21
7.15
7.12
7.10
7.07
4.29
4.27
4.25
4.22
3.82
3.62
2.69
2.67
2.65
2.63
2.60
2.58
2.20
1.87
1.57
1.30
1.28
1.26
1.23
1.20
1.18
0.00
EtO2C
EtO2C
O
300 MHz, CDCl3
2.04
2.03
4.05
4.01
1.97
2.00
1.98
1.97
2.98
3.00
9.00
3.01
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm


207.19
171.61
144.64
142.74
141.63
139.36
138.71
127.44
120.48
117.15
96.26
86.08
77.27
76.77
61.97
59.05
41.09
40.12
28.82
28.70
16.49
15.71
15.41
14.07
0.00
EtO2C
EtO2C
O
125 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm


7.39
7.26
7.22
3.84
3.81
3.65
2.21
1.87
1.52
0.00
MeO2C
MeO2C
O
300 MHz, CDCl3
5.00
5.95
8.04
2.05
3.00
3.05
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm


206.77
172.00
142.79
141.75
139.36
138.88
138.28
127.93
123.17
117.01
96.19
86.44
77.28
77.02
76.77
59.02
53.22
41.22
40.25
32.11
16.51
0.00
MeO2C
MeO2C
O
125 MHz, CDCl3
145
140
135
130
125
120
115
ppm
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


7.37
7.35
7.34
7.32
7.26
7.22
7.20
7.19
7.17
7.14
7.11
7.08
7.00
6.97
6.94
3.81
3.64
2.20
1.90
1.56
0.00
MeO2C
MeO2C
O
F
F
300 MHz, CDCl3
2.02
2.01
2.02
2.04
7.96
2.01
3.05
3.00
ppm


206.79
171.93
163.50
161.52
142.79
141.84
139.12
137.98
133.17
129.40
119.02
116.83
115.73
115.55
115.12
114.95
95.28
85.84
77.28
77.03
76.77
58.94
53.27
41.15
40.17
32.19
16.49
MeO2C
MeO2C
O
F
F
125 MHz, CDCl3
ppm