Supplementary Information

Phenanthrenes/Dihydrophenanthrenes: The Selectivity Controlled by Different Benzynes and Allenes

Liangliang Yao, Bo Fang, Qiong Hu, Yu Lei, Li Bao and Yimin Hu*

School of Chemistry and Materials Science, Anhui Normal University,

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

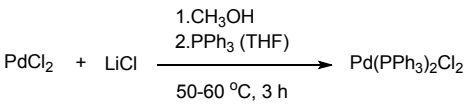
Contents

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 TCI Chemicals. All solvents and materials were pre-dried, redistilled or recrystallized before use. ^{1}H NMR (400 MHz, 500 MHz) and ^{13}C NMR (100 MHz, 125 MHz) spectra were recorded on a Bruker Avance 400 or 500 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 77.2 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 **4a, 4k** and **5j** 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.

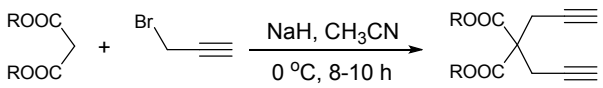
(1) General procedure for preparation of tetraynes 1:[1]

Preparation of catalyst $Pd(PPh_3)_2Cl_2$



3.54 g $PdCl_2$ and 4 g LiCl were mixed in a 500 mL three-necked flask with 150-200 mL methanol as solvent, magnetically stirred and heated in oil bath at 50-60 °C. After the solid was dissolved, 25 mL of THF (removed water with sodium wire) containing 13.1 g PPh_3 were added in the above three-necked flask, and the color of the solution changed from brown to yellow, reflux reaction for 3 hours. After reaction solution cooled, filtered and washed with anhydrous ethanol, yellow solid $Pd(PPh_3)_2Cl_2$ catalyst was obtained finally.

Preparation of diyne substrates

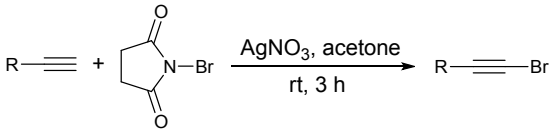


R = Me, Et, ^{i}Pr

10 g NaH (60%) and 200-300 mL acetonitrile were added in 500 mL three-necked flask with magnetic stirring. 100 mmol malonate and 30 g 3-bromopropyne (98%) were added in the above 500 mL three-

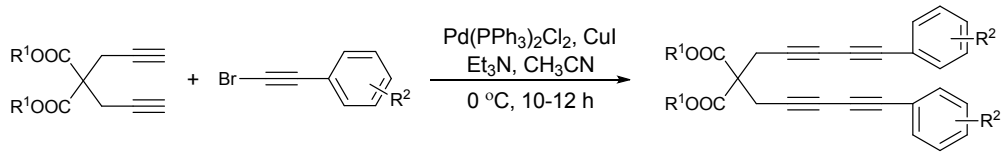
necked flask dropwise in turn by separatory funnel, magnetically stirred for 8-10 h under ice-water bath. The organic phase was extracted with ethyl acetate and dried with anhydrous $MgSO_4$. The solvent was evaporated in vacuo and diyne substrates as white solid were obtained finally.

Preparation of brominated alkynes



10.68 g 1-bromopyrrolidine-2,5-dione (NBS), 0.43 g $AgNO_3$, and 50 mmol phenylacetylene or substituted phenylacetylene or alkyl alkyne were added in 250 mL three-necked flask in turn, 100 mL acetone as a solvent, magnetically stirred at room temperature for 3 h. The organic phase was extracted with *n*-hexane and dried with anhydrous $MgSO_4$. The solvent was evaporated in vacuo and brominated alkynes compound as brown solid were obtained finally.

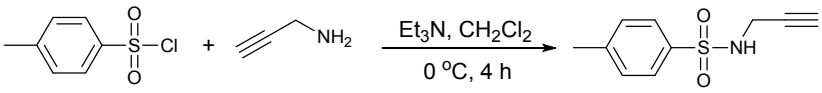
*Preparation of tetrayne substrate***s**



R^1 = Me, Et, ^{i}Pr
R^2 = H, *p*-Me, *m*-Me, *p*-Et, *p*-Cl, *p*-F

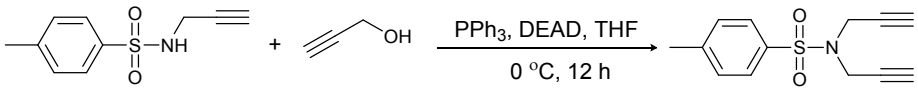
0.3 g $Pd(PPh_3)_2Cl_2$, 0.25 g CuI and 20 mmol diyne substrate were added in 500 mL three-necked flask, protected with anhydrous anaerobic conditions under argon. After 0.5 h, 200-300 mL acetonitrile, 8.08 g Et_3N and 50 mmol brominated aryl alkyne were added in turn, magnetically stirred for 10-12 h under ice-water bath. The organic phase was extracted with ethyl acetate and dried with anhydrous $MgSO_4$. It was separated by column chromatography on silica gel to obtain tetrayne substrate as yellow solid finally.

Preparation of tetrayne substrate



50 mmol *p*-toluenesulfonyl, 50 mmol propargylamine chloride and 200 mL CH_2Cl_2 were added in 500 mL three-necked flask. After 0.5 h, 50 mmol Et_3N was added, magnetically stirred under ice-water bath for 4 h. The solvent was evaporated in vacuo to obtain the product as yellow solid finally.

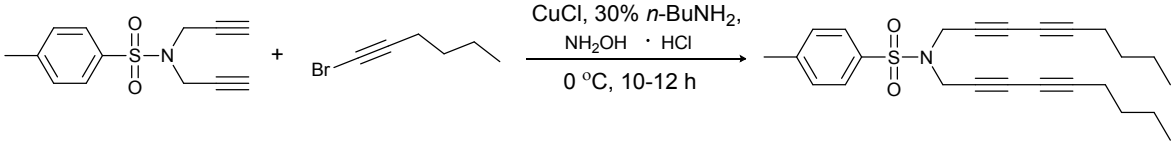
Preparation of 4-methyl-N, N-di (prop-2-yn-1-yl) benzenesulfonamide



50 mmol 4-methyl-*N*-(prop-2-yn-1-yl) benzenesulfonamide, 55 mmol PPh_3, 200 mL tetrahydrofuran (THF) as solvent were added in 500 mL three-necked flask, protected with anhydrous anaerobic conditions under argon. After 0.5 h, 55 mmol propargyl alcohol and 50 mmol diethyl azodicarboxylate (DEAD) were added dropwise by constant pressure funnel in turn, magnetically stirred under ice-water

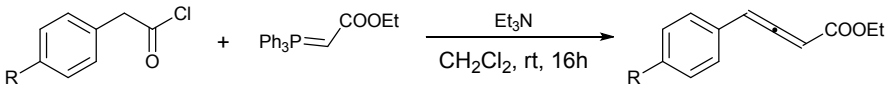
bath, reaction for 12 hours. The organic phase was extracted with ethyl acetate and dried with anhydrous $MgSO_4$. It was separated by column chromatography on silica gel to obtain the product as yellow solid finally.

Preparation of 4-methyl-N, N-di (nona-2,4-diyn-1-yl) benzenesulfonamide



0.35 g CuCl, 0.14 g NH_2OH•HCl and 10 mmol 4-methyl-*N*, *N*-di (prop-2-yn-1-yl) benzenesulfonamide were added in 500 mL three-necked flask, protected with anhydrous anaerobic conditions under argon. After 0.5 h, 45 mL 30% *n*-$BuNH_2$ aqueous solution (13.5 g *n*-$BuNH_2$ + 32 mL water) and 30 mmol 1-bromide hexyne (freshly prepared) was added dropwise by the constant pressure funnel in turn, 100-150 mL CH_2Cl_2 as solvent, magnetically stirred under ice-water bath, reaction for 10-12 h. The organic phase was extracted with ethyl acetate and dried with anhydrous $MgSO_4$. It was separated by column chromatography on silica gel to obtain the product as yellow oil finally.

(2) General procedure for preparation of allenes 3:[2]



R = H, F, OMe, naphthyl

Et_3N (63 mmol, 1.1 equiv) was added to a stirred solution of (carbethoxymethylene)triphenylphosphorane (57.5 mmol, 1 equiv) in CH_2Cl_2 (200 mL). After stirring for 10 min, the required acyl chloride (57.5 mmol, 1 equiv) was added dropwise over 30 min at room temperature. After stirring overnight, the resulting mixture was poured unto a Büchner funnel packed with silica gel and was washed with CH_2Cl_2 several times. The combined filtrate was carefully concentrated and the resulting crude oil was purified by flash column chromatography (EtOAc: petroleum ether = 1: 20) to provide the 4-substituted 2,3-butadienoates.

(3) General procedure for preparation of dihydrophenanthrenes 4:

Tetraynes (1.0 mmol), substituted allenes (1.1 equiv), are mixed in an oven-dried Schlenk tube (50 mL) equipped with a magnetic stir bar and heated in a 100–105 °C oil bath in 2 ml toluene for 8 hours under air. Then the reaction mixture was cooled to room temperature, quenched with saturated NaCl, and extracted with ethyl acetate (3 × 10 mL). The combined organic extracts were dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (ethyl acetate/petroleum ether = 1/60) to afford products 4.

(4) General procedure for preparation of phenanthrenes 5:

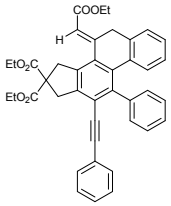
Classical method-derived benzyne precursors (1.0 mmol), substituted allenes (1.1 equiv), CsF (3.0 equiv), are mixed in an oven-dried Schlenk tube (50 mL) equipped with a magnetic stir bar and heated in a 60–65 ^{o}C oil bath in 2 ml acetonitrile for 12 hours under air. Then the reaction mixture was cooled to room temperature, quenched with saturated NaCl, and extracted with ethyl acetate (3 × 10 mL). The combined organic extracts, were dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (ethyl acetate/petroleum ether = 1/40) to afford products **5**.

References:

1. (*a*) J. Chen, V. Palani and T. R. Hoye, *J. Am. Chem. Soc.*, 2016, **138**, 4318−4321; (*b*) N.-K. Lee, S. Y. Yun, P. Mamidipalli, R. M. Salzman, D. Lee, T. Zhou and Y. Xia, *J. Am. Chem. Soc.*, 2014, **136**, 4363−4368; (*c*) B. Liu, C. Mao, Q. Hu, L. Yao and Y. Hu, *Org. Chem. Front.*, 2019, 6, 2788−2791; (*d*) X. Zheng, B. Liu, F. Yang, Q. Hu, L. Yao, Y. Hu, *Org. Lett.*, 2020, **22**, 956–959.

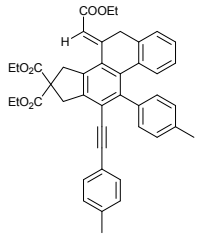
2. S. Castellano, H. D. G. Fiji, S. S. Kinderman, M. Watanabe, P. de Leon, F. Tamanoi and O. Kwon, *J. Am. Chem. Soc.*, 2007, **129**, 5843−5845.

2. Characterization Data for the New Compounds



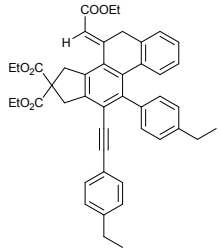
(*E*)-diethyl 7-(2-ethoxy-2-oxoethylidene)-11-phenyl-12-(phenylethynyl)-15,17-dihydro-6*H*-cyclopenta[*a*]phenanthrene-16,16(7*H*)-dicarboxylate (4a)

White solid; (499 mg, 80 % yield); m. p. 190-191 ℃; TLC (petroleum ether/EtOAc = 10:1): R_f = 0.35. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.40-7.37 (m, 3H), 7.36-7.31 (m, 3H), 7.28-7.27 (m, 2H), 7.25-7.19 (m, 3H), 7.02 (dt, J = 7.5, 1.5 Hz, 1H), 6.77-6.71 (m, 2H), 5.96 (s, 1H), 4.30-4.22 (m, 8H), 3.87 (s, 2H), 3.84 (s, 2H), 1.35-1.29 (m, 9H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 171.6, 166.5, 154.1, 143.4, 141.3, 140.9, 135.8, 134.3, 133.6, 133.4, 131.6, 131.0, 129.9, 128.4, 128.3, 128.2, 127.7, 127.4, 127.2, 125.8, 123.4, 122.2, 117.8, 98.2, 87.5, 62.2, 60.4, 60.0, 41.8, 41.2, 34.3, 14.5, 14.2. **FT-IR** (KBr): v = 2946, 1729, 1629, 1489, 1300, 1152, 881, 787, 756, 695 cm^{-1}. **HRMS** (APCI-TOF): *m/z* calcd for $C_{41}H_{36}O_6$ $[M+H]^+$ 625.2585, found 625.2588.



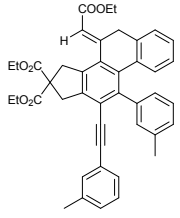
(*E*)-diethyl 7-(2-ethoxy-2-oxoethylidene)-11-(*p*-tolyl)-12-(*p*-tolylethynyl)-15,17-dihydro-6*H*-cyclopenta[*a*]phenanthrene-16,16(7*H*)-dicarboxylate (4b)

White solid; (541 mg, 83 % yield); m. p. 169-170 ℃; TLC (petroleum ether/EtOAc = 10:1): R_f = 0.35. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.25 (d, J = 7.5 Hz, 1H), 7.21-7.16 (m, 4H), 7.12-7.07 (m, 4H), 7.03-7.00 (m, 1H), 6.78-6.75 (m, 2H), 5.94 (s, 1H), 4.29-4.21 (m, 8H), 3.85 (s, 2H), 3.83 (s, 2H), 2.41 (s, 3H), 2.33 (s, 3H), 1.34-1.28 (m, 9H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 171.7,166.6, 154.2, 143.2, 141.2, 138.6, 137.8, 136.9, 135.8, 135.6, 134.0, 133.8, 133.4, 131.5, 130.8, 130.0, 129.1, 128.9, 127.6, 127.0, 125.8, 122.5, 120.4, 117.6, 98.4, 87.1, 62.1, 60.3, 60.0, 41.8, 41.2, 34.3, 21.7, 21.5, 14.5, 14.2. **FT-IR** (KBr): v = 2915, 1731, 1629, 1446, 1305, 1149, 873, 815, 749 cm^{-1}. **HRMS** (APCI-TOF): *m/z* calcd for $C_{43}H_{40}O_6$ $[M+H]^+$ 653.2898, found 653.2894.



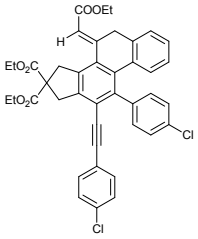
(*E*)-diethyl 7-(2-ethoxy-2-oxoethylidene)-11-(4-ethylphenyl)-12-((4-ethylphenyl)ethynyl)-15,17-dihydro-6*H*-cyclopenta[*a*]phenanthrene-16,16(7*H*)-dicarboxylate (4c)

White solid; (592 mg, 87 % yield); m. p. 139-140 ℃; TLC (petroleum ether/EtOAc = 10:1): R_f = 0.37. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.25 (d, J = 7.5 Hz, 1H), 7.23-7.18 (m, 4H), 7.12-7.07 (m, 4H), 7.03-7.00 (m, 1H), 6.77-6.74 (m, 2H), 5.95 (s, 1H), 4.29-4.21 (m, 8H), 3.85 (s, 2H), 3.83 (s, 2H), 2.71 (q, J = 7.5 Hz, 2H), 2.62 (q, J = 7.5 Hz, 2H), 1.34-1.28 (m, 12H), 1.21 (t, J = 7.5 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 171.7, 166.6, 154.3, 144.9, 143.4, 143.1, 141.4, 138.1, 135.8, 135.6, 134.0, 133.8, 133.4, 131.6, 130.9, 130.0, 127.9, 127.7, 127.6, 127.0, 125.8, 122.6, 120.7, 117.6, 98.5, 87.2, 62.1, 60.3, 60.0, 41.8, 41.2, 34.3, 29.0, 28.9, 16.1, 15.5, 14.5, 14.2. **FT-IR** (KBr): v = 2936, 1731, 1632, 1507, 1305, 1165, 883, 848, 790, 749.cm^{-1}. **HRMS** (APCI-TOF): *m/z* calcd for $C_{45}H_{44}O_6$ $[M+H]^+$ 681.3211, found 681.3207.



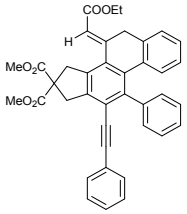
(*E*)-diethyl 7-(2-ethoxy-2-oxoethylidene)-11-(*m*-tolyl)-12-(*m*-tolylethynyl)-15,17-dihydro-6*H*-cyclopenta[*a*]phenanthrene-16,16(7*H*)-dicarboxylate (4d)

White solid; (535 mg, 82 % yield); m. p. 153-154 ℃; TLC (petroleum ether/EtOAc = 10:1): R_f = 0.33. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.24-7.23 (m, 2H), 7.18-7.14 (m, 3H), 7.10-7.06 (m, 2H), 7.04-7.00 (m, 3H), 6.77-6.76 (m, 2H), 5.95 (s, 1H), 4.30-4.21 (m, 8H), 3.86-3.85 (m, 2H), 3.84-3.83 (m, 2H), 2.35 (s, 3H), 2.31 (s, 3H), 1.35-1.29 (m, 9H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 171.6, 166.6, 154.2, 143.2, 141.4, 140.7, 138.0, 137.6, 135.7, 135.6, 134.1, 133.7, 133.3, 132.2, 131.6, 130.0, 129.3, 128.6, 128.2, 128.1, 128.0, 127.6, 127.1, 125.8, 123.2, 122.2, 117.6, 98.4, 87.3, 62.2, 60.4, 60.0, 41.8, 41.2, 34.3, 21.7, 21.4, 14.5, 14.2. **FT-IR** (KBr): v = 2946, 1733, 1629, 1486, 1303, 1160, 881, 784, 746, 687 cm^{-1}. **HRMS** (APCI-TOF): *m/z* calcd for $C_{43}H_{40}O_6$ $[M+H]^+$ 653.2898, found 653.2901.



(*E*)-diethyl 11-(4-chlorophenyl)-12-((4-chlorophenyl)ethynyl)-7-(2-ethoxy-2-oxoethylidene)-15,17-dihydro-6*H*-cyclopenta[*a*]phenanthrene-16,16(7*H*)-dicarboxylate (4e)

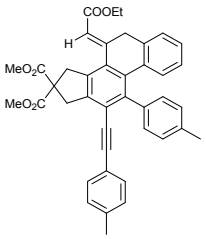
White solid; (491 mg, 71 % yield); m. p. 190-191 ℃; TLC (petroleum ether/EtOAc = 10:1): R_f = 0.30. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.35 (d, J = 8.0 Hz, 2H), 7.28-7.25 (m, 5H), 7.13 (d, J = 8.5 Hz, 2H), 7.05 (t, J = 7.5 Hz, 1H), 6.81 (t, J = 7.5 Hz, 1H), 6.69 (d, J = 8.0 Hz, 1H), 5.95 (s, 1H), 4.29-4.21 (m, 8H), 3.83 (s, 4H), 1.34-1.29 (m, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 171.5, 166.4, 153.6, 143.5, 139.8, 139.3, 136.3, 135.9, 134.7, 134.6, 133.5, 133.4, 133.2, 132.7, 132.4, 129.9, 128.9, 128.5, 127.9, 127.4, 126.0, 121.7, 121.6, 118.0, 97.3, 88.1, 62.2, 60.5, 60.0, 41.7, 41.2, 34.2, 14.2. **FT-IR** (KBr): v = 2954, 1733, 1638, 1491, 1244, 1160, 1092, 1015, 830, 748 cm^{-1}. **HRMS** (APCI-TOF): *m/z* calcd for $C_{41}H_{34}Cl_2O_6$ $[M+H]^+$ 693.1805, found 693.1799.



(*E*)-dimethyl 7-(2-ethoxy-2-oxoethylidene)-11-phenyl-12-(phenylethynyl)-15,17-dihydro-6*H*-cyclopenta[*a*]phenanthrene-16,16(7*H*)-dicarboxylate (4f)

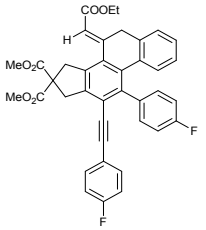
White solid; (465 mg, 78 % yield); m. p. 206-207 ℃; TLC (petroleum ether/EtOAc = 10:1): R_f = 0.20. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.38-7.36 (m, 3H), 7.33-7.27 (m, 3H), 7.25-7.15 (m, 4H), 7.02 (t, J = 7.0 Hz, 1H), 6.77-6.68 (m, 3H), 5.95 (s, 1H), 4.30 (s, 2H), 4.23 (q, J = 7.0 Hz, 2H), 3.89 (s, 2H), 3.86 (s, 2H),

3.82 (s, 6H), 1.34 (t, J = 7.0 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 172.1, 166.5, 154.0, 143.1, 141.3, 140.8, 135.8, 135.7, 134.2, 133.6, 133.5, 131.6, 131.0 129.9, 128.5, 128.4, 128.3, 128.2, 127.7, 127.4, 127.2, 125.8, 123.3, 122.2, 117.8, 98.3, 87.4, 60.4, 59.9, 53.4, 41.9, 41.3, 34.3, 14.5. **FT-IR** (KBr): v = 2955, 1736, 1636, 1436, 1270, 1160, 756, 689 cm^{-1}. **HRMS** (APCI-TOF): *m/z* calcd for $C_{39}H_{32}O_6$ $[M+H]^+$ 597.2272, found 597.2270.



(*E*)-dimethyl 7-(2-ethoxy-2-oxoethylidene)-11-(*p*-tolyl)-12-(*p*-tolylethynyl)-15,17-dihydro-6*H*-cyclopenta[*a*]phenanthrene-16,16(7*H*)-dicarboxylate (4g)

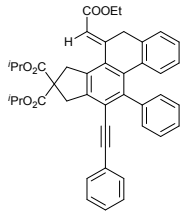
White solid; (499 mg, 82 % yield); m. p. 182-183 ℃; TLC (petroleum ether/EtOAc = 10:1): R_f = 0.23. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.24 (s, 1H),7.21-7.16 (m, 4H), 7.13-7.07 (m, 4H), 7.04-7.00 (m, 1H), 6.79-6.74 (m, 2H), 5.93 (s, 1H), 4.29 (s, 2H), 4.23 (q, J = 7.0 Hz, 2H), 3.87 (s, 2H), 3.84 (s, 2H), 3.81 (s, 6H), 2.41 (s, 3H), 2.34 (s, 3H), 1.33 (t, J = 7.5 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 172.1, 166.5, 154.2, 143.0, 141.2, 138.7, 137.7, 136.9, 135.7, 135.4, 134.0, 133.8, 133.5, 131.5, 130.8, 130.0, 129.1, 128.9, 127.6, 127.1, 125.8, 122.5, 120.4, 117.6, 98.5, 87.0, 60.4, 59.8, 53.4, 41.9, 41.3, 34.3, 21.7, 21.5, 14.5. **FT-IR** (KBr): v = 2951, 1737, 1629, 1512, 1308, 1162, 1040, 874, 817, 749 cm^{-1}. **HRMS** (APCI-TOF): *m/z* calcd for $C_{41}H_{36}O_6$ $[M+H]^+$ 625.2585, found 625.2581.



(*E*)-dimethyl 7-(2-ethoxy-2-oxoethylidene)-11-(4-fluorophenyl)-12-((4-fluorophenyl)ethynyl)-15,17-dihydro-6*H*-cyclopenta[*a*]phenanthrene-16,16(7*H*)-dicarboxylate (4h)

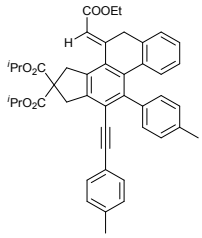
White solid; (430 mg, 68 % yield); m. p. 166-167 ℃; TLC (petroleum ether/EtOAc = 10:1): R_f = 0.16. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.30-7.27 (m, 3H), 7.22-7.19 (m, 2H), 7.09-7.03 (m, 3H), 6.99 (t, J = 9.0 Hz, 2H), 6.81-6.78 (m, 1H), 6.68-6.67 (m, 1H), 5.94 (s, 1H), 4.29 (s, 2H), 4.23 (q, J = 7.0 Hz, 2H), 3.86 (s, 2H), 3.85 (s, 2H), 3.82 (s, 6H), 1.33 (t, J = 7.0 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 172.0, 166.4, 163.6 (d, $J_{C\text{-}F}$ = 50 Hz), 161.6 (d, $J_{C\text{-}F}$ = 46.3 Hz), 153.7, 143.2, 140.0, 136.7, 135.9, 135.8, 134.4, 133.7, 133.5, 133.4, 133.3, 132.7 (d, $J_{C\text{-}F}$ = 7.5 Hz), 129.8, 127.8, 127.4, 125.9, 122.0, 119.2, 117.9, 115.8 (d, $J_{C\text{-}F}$ = 22.5 Hz), 115.3 (d, $J_{C\text{-}F}$ = 21.3 Hz), 97.4, 89.4, 86.9, 60.5, 59.8, 53.4, 41.9, 41.3, 34.2, 14.5. **FT-IR**

(KBr): v = 2956, 1736, 1600, 1508, 1230, 1157, 837, 753 cm^{-1}. **HRMS** (APCI-TOF): *m/z* calcd for $C_{39}H_{30}F_2O_6$ $[M+H]^+$ 633.2083, found 633.2078.



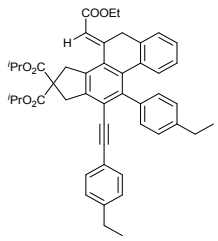
(*E*)-diisopropyl 7-(2-ethoxy-2-oxoethylidene)-11-phenyl-12-(phenylethynyl)-15,17-dihydro-6*H*-cyclopenta[*a*]phenanthrene-16,16(7*H*)-dicarboxylate (4i)

White solid; (522 mg, 80 % yield); m. p. 120-121 ℃; TLC (petroleum ether/EtOAc = 10:1), R_f = 0.44. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.39-7.35 (m, 3H), 7.33-7.31 (m, 2H), 7.27-7.26 (m, 2H), 7.25-7.23 (m, 2H), 7.20-7.18 (m, 2H), 7.01 (dt, J = 7.0, 1.5 Hz, 1H), 6.76-6.71 (m, 2H), 5.97 (s, 1H), 5.12-5.07 (m, 2H), 4.29 (s, 2H), 4.23 (q, J = 7.0 Hz, 2H), 3.83 (s, 2H), 3.80 (s, 2H), 1.33 (t, J = 7.0 Hz, 3H), 1.29 (d, J = 2.0 Hz, 6H), 1.28 (d, J = 2.5 Hz, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 171.2, 166.5, 154.1, 143.5, 141.3, 140.9, 135.9, 135.8, 134.3, 133.7, 133.4, 131.6, 131.0, 130.0, 128.4, 128.3, 128.2, 127.7, 127.4, 127.1, 125.8, 123.5, 122.2, 117.7, 98.1, 87.5, 69.7, 60.3, 60.1, 41.7, 41.2, 34.3, 21.7, 14.5. **FT-IR** (KBr): v = 2926, 1729, 1637, 1440, 1374, 1198, 1068, 912, 754, 690 cm^{-1}. **HRMS** (APCI-TOF): *m/z* calcd for $C_{43}H_{40}O_6$ $[M+H]^+$ 653.2898, found 653.2892.



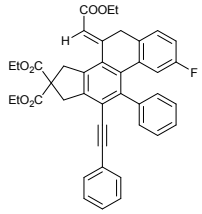
(*E*)-diisopropyl 7-(2-ethoxy-2-oxoethylidene)-11-(*p*-tolyl)-12-(*p*-tolylethynyl)-15,17-dihydro-6*H*-cyclopenta[*a*]phenanthrene-16,16(7*H*)-dicarboxylate (4j)

White solid; (564 mg, 83 % yield); m. p. 163-164 ℃; TLC (petroleum ether/EtOAc = 10:1): R_f = 0.44. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.24 (d, J = 7.5 Hz, 1H), 7.21-7.15 (m, 4H), 7.12-7.06 (m, 4H), 7.03-6.7.00 (m, 1H), 6.78-6.75 (m, 2H), 5.95 (s, 1H), 5.12-5.07 (m, 2H), 4.28 (s, 2H), 4.22 (q, J = 7.0 Hz, 2H), 3.81 (s, 2H), 3.79 (s, 2H), 2.40 (s, 3H), 2.33 (s, 3H), 1.32 (t, J = 7.0 Hz, 3H), 1.28 (d, J = 2.5 Hz, 6H), 1.27 (d, J = 2.5 Hz, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 171.2, 166.6, 154.3, 143.4, 141.1, 138.6, 137.8, 136.9, 135.8, 135.7, 134.1, 133.8, 133.3, 131.5, 130.8, 130.0, 129.1, 128.9, 127.6, 127.0, 125.8, 122.5, 120.5, 117.6, 98.3, 87.1, 69.6, 60.3, 60.1, 41.7, 41.2, 34.3, 21.7, 21.6, 21.5, 14.5. **FT-IR** (KBr): v = 2926, 1731, 1632, 1509, 1384, 1160, 1040, 817, 751 cm^{-1}. **HRMS** (APCI-TOF): *m/z* calcd for $C_{45}H_{44}O_6$ $[M+H]^+$ 681.3211, found 681.3208.



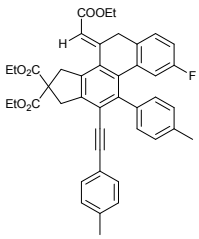
(*E*)-diisopropyl 7-(2-ethoxy-2-oxoethylidene)-11-(4-ethylphenyl)-12-((4-ethylphenyl)ethynyl)-15,17-dihydro-6*H*-cyclopenta[*a*]phenanthrene-16,16(7*H*)-dicarboxylate (4k)

White solid; (602 mg, 85 % yield); m. p. 141-142 ℃; TLC (petroleum ether/EtOAc = 10:1), R_f = 0.47. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.25-7.18 (m, 5H), 7.11-7.06 (m, 4H), 7.03-7.00 (m, 1H), 6.77-6.74 (m, 2H), 5.95 (s, 1H), 5.12-5.07 (m, 2H), 4.29 (s, 2H), 4.22 (q, J = 7.0 Hz, 2H), 3.82 (s, 2H), 3.79 (s, 2H), 2.71 (q, J = 7.5 Hz, 2H), 2.62 (q, J = 7.5 Hz, 2H), 1.34-1.29 (m, 6H), 1.28 (d, J = 2.5 Hz, 6H), 1.27 (d, J = 3.0 Hz, 6H), 1.21 (t, J = 7.5 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 171.2, 166.6, 154.3, 144.9, 143.4, 143.2, 141.3, 138.2, 135.8, 135.7, 134.0, 133.8, 133.3, 131.6, 130.9, 130.0, 127.9, 127.7, 127.6, 127.0, 125.7, 122.5, 120.7, 117.6, 98.4, 87.2, 69.6, 60.3, 60.1, 41.7, 41.2, 34.3, 29.0, 28.9, 21.7, 16.1, 15.5, 14.5. **FT-IR** (KBr): v = 2931, 1726, 1637, 1456, 1371, 1193, 983, 907, 830, 749 cm^{-1}. **HRMS** (APCI-TOF): *m/z* calcd for $C_{47}H_{48}O_6$ $[M+H]^+$ 709.3524, found 709.3521.



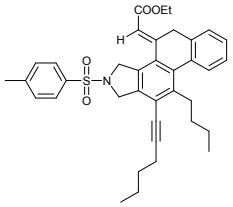
(*E*)-diethyl 7-(2-ethoxy-2-oxoethylidene)-2-fluoro-11-phenyl-12-(phenylethynyl)-15,17-dihydro-6*H*-cyclopenta[*a*]phenanthrene-16,16(7*H*)-dicarboxylate (4l)

White solid; (539 mg, 84 % yield); m. p. 138-139 ℃; TLC (petroleum ether/EtOAc = 10:1): R_f = 0.23. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.42-7.40 (m, 3H), 7.32-7.27 (m, 5H), 7.25-7.18 (m, 3H), 6.73 (td, J = 8.0, 2.5 Hz, 1H), 6.39 (dd, J = 11.5, 3.0 Hz, 1H), 5.96 (s, 1H), 4.29-4.22 (m, 8H), 3.87 (s, 2H), 3.84 (s, 2H), 1.34 (t, J = 7.0 Hz, 3H), 1.30 (t, J = 7.0 Hz, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 171.6, 166.4, 161.0 (d, $J_{C\text{-}F}$ = 240 Hz), 153.6, 143.9, 141.5, 140.2, 136.0, 135.4 (d, $J_{C\text{-}F}$ = 2.5 Hz), 134.1, 132.5, 131.6, 131.4, 130.8, 128.7 (d, $J_{C\text{-}F}$ = 7.5 Hz), 128.6, 128.4 (d, $J_{C\text{-}F}$ = 6.3 Hz), 127.8, 123.2, 122.3, 117.9, 116.7 (d, $J_{C\text{-}F}$ = 25 Hz), 113.9 (d, $J_{C\text{-}F}$ = 22.5 Hz), 98.5, 87.2, 62.2, 60.5, 60.0, 41.8, 41.2, 33.4, 14.5, 14.2. **FT-IR** (KBr): v = 2925, 1733, 1637, 1490, 1245, 1158, 757, 690 cm^{-1}. **HRMS** (APCI-TOF): *m/z* calcd for $C_{41}H_{35}FO_6$ $[M+H]^+$ 643.2490, found 643.2489.



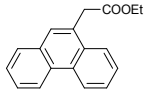
(*E*)-diethyl 7-(2-ethoxy-2-oxoethylidene)-2-fluoro-11-(*p*-tolyl)-12-(*p*-tolylethynyl)-15,17-dihydro-6*H*-cyclopenta[*a*]phenanthrene-16,16(7*H*)-dicarboxylate (4m)

White solid; (577 mg, 86 % yield); m. p. 174-175 ℃; TLC (petroleum ether/EtOAc = 10:1): R_f = 0.23. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.19-7.18 (m, 5H), 7.12-7.07 (m, 4H), 6.74-6.70 (m, 1H), 6.45-6.42 (m, 1H), 5.95 (s, 1H), 4.29-4.21 (m, 8H), 3.85 (s, 2H), 3.83 (s, 2H), 2.42 (s, 3H), 2.33 (s, 3H), 1.35-1.28 (m, 9H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 171.6, 166.5, 160.9 (d, $J_{C\text{-}F}$ = 240 Hz), 153.8, 143.7, 141.4, 138.7, 137.3 (d, $J_{C\text{-}F}$ = 26.3 Hz), 135.7, 135.6, 135.5 (d, $J_{C\text{-}F}$ = 8.8 Hz), 133.9, 132.5, 131.5, 131.3, 130.6, 129.1, 128.6 (d, $J_{C\text{-}F}$ = 7.5 Hz), 122.6, 120.3, 117.8, 116.8 (d, $J_{C\text{-}F}$ = 23.8 Hz), 113.8 (d, $J_{C\text{-}F}$ = 21.3 Hz), 98.6, 86.8, 62.2, 60.4, 60.0, 41.8, 41.2, 33.5, 21.7, 21.5, 14.5, 14.2. **FT-IR** (KBr): ν = 2924, 1733, 1635, 1510, 1244, 1161, 1096, 1046, 881, 816 cm^{-1}. **HRMS** (APCI-TOF): *m/z* calcd for $C_{43}H_{39}FO_6$ $[M+H]^+$ 671.2803, found 671.2807.



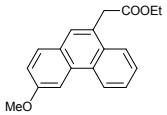
(*E*)-ethyl 2-(10-butyl-11-(hex-1-yn-1-yl)-2-tosyl-2,3-dihydro-1*H*-naphtho[2,1-*e*]isoindol-4(5*H*)-ylidene)acetate (4n)

White solid; (417 mg, 70 % yield); m. p. 196-197 ℃; TLC (petroleum ether/EtOAc = 10:1): R_f = 0.20. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.81 (d, J = 8.4 Hz, 2H), 7.38-7.24 (m, 6H), 6.47 (s, 1H), 4.94 (s, 1H), 4.70 (s, 2H), 4.67-4.55 (m, 2H), 4.12-4.04 (m, 2H), 2.70-2.61 (m, 2H), 2.48 (t, J = 7.2 Hz, 2H), 2.42 (s, 3H), 1.63-1.58 (m, 3H), 1.52-1.45 (m, 4H), 1.34 (q, J =7.2 Hz, 2H), 1.09 (t, J = 7.2 Hz, 3H), 0.97 (t, J = 7.2 Hz, 3H), 0.92 (t, J = 7.2 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 170.5, 143.9, 141.3, 139.4, 138.5, 135.6, 134.3, 134.1, 130.1, 128.8, 128.2, 127.9, 127.7, 124.7, 121.9, 119.1, 100.0, 61.3, 54.7, 54.2, 52.8, 31.8, 31.0, 29.5, 22.9, 22.1, 21.7, 19.6, 14.2, 14.0, 13.7. **FT-IR** (KBr): ν = 2925, 1734, 1636, 1457, 1385, 1162, 1098, 809, 754, 670 cm^{-1}. **HRMS** (APCI-TOF): *m/z* calcd for $C_{37}H_{41}NO_4S$ $[M+H]^+$ 596.2829, found 596.2838.



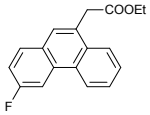
Ethyl 2-(phenanthren-9-yl)acetate (5a)

White solid; (182 mg, 69 % yield); m. p. 84-85 ℃; TLC (petroleum ether/EtOAc = 15:1): R_f = 0.39. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.73-8.72 (m, 1H), 8.65 (d, J = 8.5 Hz, 1H), 8.04-8.03 (m, 1H), 7.85-7.84 (m, 1H), 7.68 (s, 1H), 7.66-7.61 (m, 3H), 7.59-7.56 (m, 1H), 4.16 (q, J = 7.0 Hz, 2H), 4.10 (s, 2H), 1.22 (t, J = 7.0 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 171.8, 131.7, 131.3, 130.9, 130.3, 129.3, 128.9, 128.5, 127.0, 126.9, 126.8, 126.6, 124.6, 123.3, 122.6, 61.2, 40.0, 14.3. **FT-IR** (KBr): v = 2925, 1732, 1366, 1329, 1183, 1026, 895, 794, 753, 729 cm^{-1}. **HRMS** (APCI-TOF): *m/z* calcd for $C_{18}H_{16}O_2$ $[M+H]^+$ 265.1223, found 265.1231.



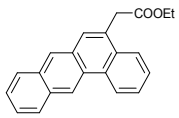
Ethyl 2-(3-methoxyphenanthren-9-yl)acetate (5b)

White solid; (171 mg, 58 % yield); m. p. 61-62 ℃; TLC (petroleum ether/EtOAc = 15:1): R_f = 0.29. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.65-8.63 (m, 1H), 8.02-8.00 (m, 2H), 7.76 (d, J = 9.0 Hz, 1H), 7.64-7.61 (m, 3H), 7.24-7.21 (m, 1H), 4.16 (q, J = 7.0 Hz, 2H), 4.06 (s, 2H), 4.00 (s, 3H), 1.22 (t, J = 7.0 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 171.9, 158.6, 131.6, 131.5, 130.3, 129.9, 128.6, 127.0, 126.8, 126.4, 126.2, 124.7, 123.3, 117.0, 104.0, 61.1, 55.6, 39.8, 14.3. **FT-IR** (KBr): v = 2961, 1728, 1368, 1327, 1177, 1030, 812, 765 cm^{-1}. **HRMS** (APCI-TOF): *m/z* calcd for $C_{19}H_{18}O_3$ $[M+H]^+$ 295.1329, found 295.1332.



Ethyl 2-(3-fluorophenanthren-9-yl)acetate (5c)

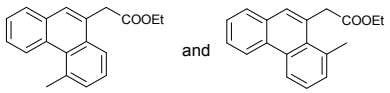
White solid; (217 mg, 77 % yield); m. p. 97-98 ℃; TLC (petroleum ether/EtOAc = 15:1): R_f = 0.35. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.57-8.55 (m, 1H), 8.24 (dd, J = 11.0, 2.5 Hz, 1H), 8.03-8.01 (m, 1H), 7.80 (dd, J = 9.0, 6.0 Hz, 1H), 7.67-7.64 (m, 3H), 7.32 (td, J = 8.5, 2.5 Hz, 1H), 4.17 (q, J = 7.0 Hz, 2H), 4.07 (s, 2H), 1.22 (t, J = 7.0 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 171.7, 161.8 (d, $J_{C\text{-}F}$ = 243.8 Hz), 131.8 (d, $J_{C\text{-}F}$ = 7.5 Hz), 131.5, 130.5 (d, $J_{C\text{-}F}$ = 8.7 Hz), 130.2 (d, $J_{C\text{-}F}$ = 5.0 Hz), 128.6, 128.4, 128.3, 127.6, 126.7, 124.7, 123.5, 115.9 (d, $J_{C\text{-}F}$ = 23.8 Hz), 107.8 (d, $J_{C\text{-}F}$ = 22.5 Hz), 61.2, 39.8, 14.3. **FT-IR** (KBr): v = 2981, 1729, 1323, 1277, 1178, 1028, 869, 774 cm^{-1}. **HRMS** (APCI-TOF): *m/z* calcd for $C_{18}H_{15}FO_2$ $[M+H]^+$ 283.1129, found 283.1124.



Ethyl 2-(tetraphen-5-yl)acetate (5d)

Light yellow liquid; (198 mg, 63 % yield); TLC (petroleum ether/EtOAc = 15:1): R_f = 0.39. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 9.10-9.08 (m, 1H), 9.02 (d, J = 8.5 Hz, 1H), 8.14-8.12 (m, 1H), 7.95 (d, J = 7.5 Hz, 1H), 7.83-7.82 (m, 1H), 7.73-7.70 (m, 2H), 7.65-7.60 (m, 3H), 7.57-7.55 (m, 1H), 4.16 (q, J = 7.5 Hz,

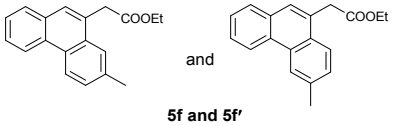
2H), 4.13 (s, 2H), 1.20 (t, J = 7.0 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 171.6, 133.6, 132.3, 130.8, 130.5, 130.1, 129.6, 128.9, 128.7, 128.6, 128.1, 127.7, 127.4, 126.6, 126.3, 125.9, 125.8, 124.3, 61.2, 39.6, 14.3. **FT-IR** (KBr): v = 2960, 1739, 1367, 1258, 1156, 1030, 888, 815, 754 cm^{-1}. **HRMS** (APCI-TOF): *m/z* calcd for $C_{22}H_{18}O_2$ $[M+H]^+$ 315.1380, found 315.1387.



5e and 5e′

Ethyl 2-(5-methylphenanthren-9-yl)acetate and Ethyl 2-(8-methylphenanthren-9-yl)acetate (5e and 5e′)

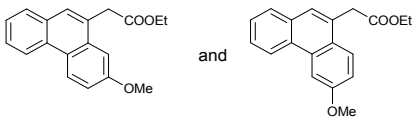
White solid; (183 mg, 66% yield); m. p. 52-53 ℃; TLC (petroleum ether/EtOAc = 15:1): R_f = 0.37. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.81-8.80 (m, 1H), 8.64-8.60 (m, 2H), 7.92-7.90 (m, 1H), 7.85-7.83 (m, 1H), 7.77-7.75 (m, 1H), 7.63 (s, 1H), 7.59-7.54 (m, 4H), 7.53-7.46 (m, 3H), 7.38-7.21 (m, 2H), 4.29-4.06 (m, 4H), 4.19-4.14 (m, 4H), 3.11-2.85 (m, 6H), 1.22 (t, J = 7.0 Hz, 3H), 1.20 (t, J = 7.0 Hz, 3H); Representative peak of minor isomer, **^{1}H NMR** (500 MHz, $CDCl_3$) of minor isomer δ 4.29 (s, 2.4H), 4.06 (s, 1.6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 172.5, 171.8, 136.1, 134.8, 133.0, 132.8, 132.4, 131.9, 131.5, 131.4, 131.3, 131.1, 130.9, 130.8, 129.6, 129.5, 128.6, 127.9, 127.6, 126.8, 126.7, 126.1, 126.0, 125.6, 123.1, 122.9, 122.1, 61.1, 61.0, 43.7, 40.6, 27.7, 25.5, 14.3. **FT-IR** (KBr): v = 2979, 1736, 1464, 1367, 1157, 1034, 890, 749 cm^{-1}. **HRMS** (APCI-TOF): *m/z* calcd for $C_{19}H_{18}O_2$ $[M+H]^+$ 279.138, found 279.1388.



5f and 5f′

Ethyl 2-(7-methylphenanthren-9-yl)acetate and Ethyl 2-(6-methylphenanthren-9-yl)acetate (5f and 5f')

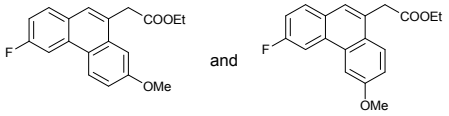
Light yellow liquid; (189 mg, 68 % yield); TLC (petroleum ether/EtOAc = 15:1): R_f = 0.25. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.62-8.60 (m, 1H), 8.57-8.55 (m, 2H), 8.47 (s, 1H), 7.91-7.89 (m, 1H), 7.79-7.78 (m, 3H), 7.61 (s, 1H), 7.59-7.55 (m, 3H), 7.54-7.49 (m, 2H), 7.44 (dq, J = 4.5, 1.5 Hz, 2H), 4.17-4.12 (m, 4H), 4.04 (s, 4H), 2.58 (s, 3H), 2.55 (s, 3H), 1.22-1.18 (m, 6H); Representative peak of minor isomer, **^{1}H NMR** (500 MHz, $CDCl_3$) of minor isomer δ 2.58 (s, 3H), 2.55 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 171.8, 171.7, 136.6, 136.2, 131.9, 131.4, 131.3, 130.9, 130.3, 130.0, 129.2, 129.1, 129.0, 128.9, 128.6, 128.5, 128.4, 128.3, 127.9, 126.7, 126.6, 126.5, 126.4, 124.4, 124.2, 123.2, 123.1, 122.6, 122.4, 61.1, 61.0, 39.9, 22.0, 21.9, 14.3. **FT-IR** (KBr): v = 2979, 1733, 1367, 1256, 1154, 1030, 890, 821, 749 cm^{-1}. **HRMS** (APCI-TOF): calcd for $C_{19}H_{18}O_2$ $[M+H]^+$ 279.1380, found 279.1381.



5g and 5g′

Ethyl 2-(7-methoxyphenanthren-9-yl)acetate and Ethyl 2-(6-methoxyphenanthren-9-yl)acetate (5g and 5g′)

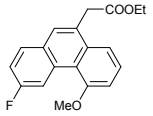
White solid; (197 mg, 67 % yield); m. p. 67-68 ℃; TLC (petroleum ether/EtOAc = 15:1): R_f = 0.27. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.59-8.58 (m, 1H), 8.55-8.51 (m, 2H), 8.07-8.06 (m, 1H), 7.96-7.94 (m, 1H), 7.81-7.79 (m, 2H), 7.65 (s, 1H), 7.58-7.54 (m, 3H), 7.53-7.48 (m, 2H), 7.41-7.40 (m, 1H), 7.28-7.22 (m, 2H), 4.15 (q, J = 7.0 Hz, 2H), 4.14 (q, J = 7.0 Hz, 2H), 4.04-4.03 (m, 4H), 3.98-3.94 (m, 6H), 1.20 (t, J = 7.0 Hz, 6H); Representative peak of minor isomer, **^{1}H NMR** (500 MHz, $CDCl_3$) of minor isomer δ 3.98 (s, 3.4H), 3.94 (s, 2.53H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 171.7, 171.6, 158.6, 158.4, 132.7, 132.4, 132.2, 130.6, 130.4, 129.8, 129.5, 129.2, 128.7, 128.5, 128.4, 126.9, 126.8, 126.6, 126.3, 126.1, 125.9, 125.8, 125.1, 124.9, 122.6, 122.1, 116.6, 116.5, 105.6, 104.8, 61.2, 61.1, 55.5, 55.4, 40.3, 40.0, 14.3, 14.2. **FT-IR** (KBr): v = 2935, 1731, 1367, 1229, 1149, 1029, 824, 748 cm^{-1}. **HRMS** (APCI-TOF): *m/z* calcd for $C_{19}H_{18}O_3$ $[M+H]^+$ 295.1329, found 295.1335.



5h and 5h′

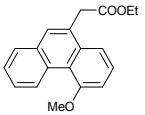
Ethyl 2-(3-fluoro-7-methoxyphenanthren-9-yl)acetate and Ethyl 2-(3-fluoro-6-methoxyphenanthren-9-yl)acetate (5h and 5h′)

White solid; (234 mg, 75 % yield); m. p. 139-140 ℃; TLC (petroleum ether/EtOAc = 15:1): R_f = 0.31. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.38-7.90 (m, 4H), 7.83-7.57 (m, 4H), 7.44-7.35 (m, 2H), 7.28-7.20 (m, 4H), 4.15 (q, J = 7.0 Hz, 4H), 3.99-3.97 (m, 4H), 3.95-3.92 (m, 6H), 1.21 (t, J = 7.5 Hz, 6H); Representative peak of minor isomer, **^{1}H NMR** (500 MHz, $CDCl_3$) of minor isomer δ 3.99 (s, 3.1H), 3.97 (s, 0.9H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 171.6, 171.5, 162.8 (d, $J_{C\text{-}F}$ = 243.8 Hz), 161.4 (d, $J_{C\text{-}F}$ = 243.8 Hz), 159.0, 158.3, 132.9, 131.8 (d, $J_{C\text{-}F}$ = 8.7 Hz), 131.7 (d, $J_{C\text{-}F}$ = 5.0 Hz), 131.1 (d, $J_{C\text{-}F}$ = 8.7 Hz), 130.4 (d, $J_{C\text{-}F}$ = 8.7 Hz), 128.8, 128.4 (d, $J_{C\text{-}F}$ = 2.5 Hz), 127.9 (d, $J_{C\text{-}F}$ = 2.5 Hz), 127.3, 126.2, 126.0, 125.9, 125.0, 124.4, 117.4, 116.6, 115.8 (d, $J_{C\text{-}F}$ = 23.7 Hz), 114.8 (d, $J_{C\text{-}F}$ = 23.7 Hz), 107.7 (d, $J_{C\text{-}F}$ = 21.2 Hz), 107.1 (d, $J_{C\text{-}F}$ = 22.5 Hz), 105.6, 104.7, 61.1, 55.5, 55.4, 40.1, 39.8, 14.3, 14.2. **FT-IR** (KBr): v = 2955, 1735, 1323, 1223, 1029, 873, 840, 808 cm^{-1}. **HRMS** (APCI-TOF): *m/z* calcd for $C_{19}H_{17}FO_3$ $[M+H]^+$ 313.1234, found 313.1225.



Ethyl 2-(3-fluoro-5-methoxyphenanthren-9-yl)acetate (5i)

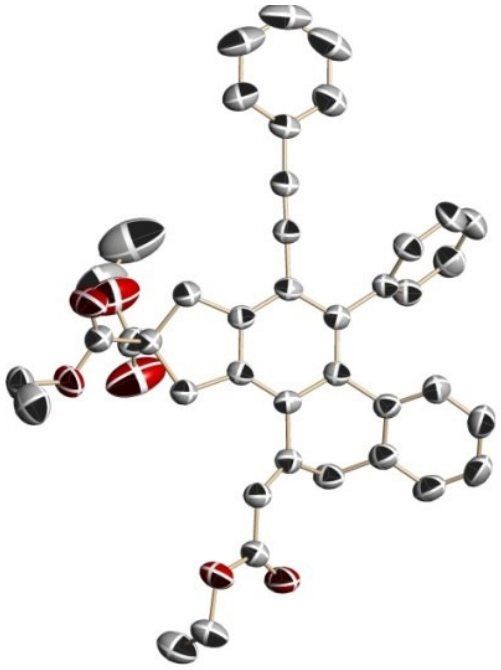
White solid; (250 mg, 80 % yield); m. p. 120-121 ℃; TLC (petroleum ether/EtOAc = 15:1): R_f = 0.32. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 9.35 (dd, J = 14.0, 2.5 Hz, 1H), 7.81 (dd, J = 8.5, 6.5 Hz, 1H), 7.67-7.64 (m, 2H), 7.60 (t, J = 8.0 Hz, 1H), 7.33 (td, J = 7.5, 2.5 Hz, 1H), 7.18 (d, J = 7.5 Hz, 1H), 4.17 (q, J = 7.0 Hz, 2H), 4.14 (s, 3H), 4.06 (s, 2H), 1.22 (t, J = 7.5 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 171.8, 162.2, 160.3, 159.4, 134.0, 131.4 (d, $J_{C\text{-}F}$ = 10.0 Hz), 129.8, 129.7, 129.0, 128.3, 127.6, 121.0, 117.2, 117.2, 115.0 (d, $J_{C\text{-}F}$ = 25.0 Hz), 114.1 (d, $J_{C\text{-}F}$ = 25.0 Hz), 108.4, 61.2, 55.9, 40.6, 14.3. **FT-IR** (KBr): v = 2972, 1731, 1339, 1177, 805, 759 cm^{-1}. **HRMS** (APCI-TOF): *m/z* calcd for $C_{19}H_{17}FO_3$ $[M+H]^+$ 313.1234, found 313.1231.



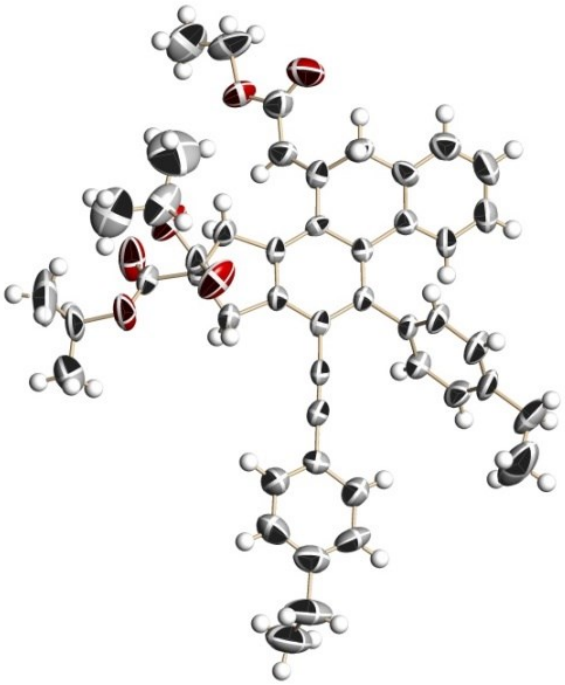
Ethyl 2-(5-methoxyphenanthren-9-yl)acetate (5j)

White solid; (209 mg, 71 % yield); m. p. 90-91 ℃; TLC (petroleum ether/EtOAc = 15:1): R_f = 0.23. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 9.64 (d, J = 8.5 Hz, 1H), 8.84 (dd, J = 8.0, 1.5 Hz, 1H), 7.69 (s, 1H), 7.67-7.65 (m, 1H), 7.63-7.60 (m, 1H), 7.59-7.55 (m, 1H), 7.19 (d, J = 8.0 Hz, 1H), 4.16 (q, J = 7.5 Hz, 2H), 4.13 (s, 3H), 4.08 (s, 2H), 1.21 (t, J = 7.5 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 171.9, 159.4, 133.8, 132.3, 130.4, 130.3, 129.0, 128.7, 128.3, 126.9, 126.6, 126.2, 121.5, 117.2, 108.7, 61.1, 55.9, 40.7, 14.3. **FT-IR** (KBr): v = 2965, 1734, 1332, 1241, 1182, 1019, 739, 715 cm^{-1}. **HRMS** (APCI-TOF): *m/z* calcd for $C_{19}H_{18}O_3$ $[M+H]^+$ 295.1329, found 295.1330.

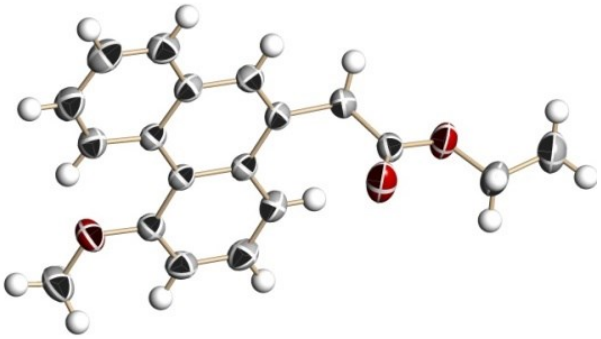
3. X-Ray Structure for 4a, 4k and 5j



4a

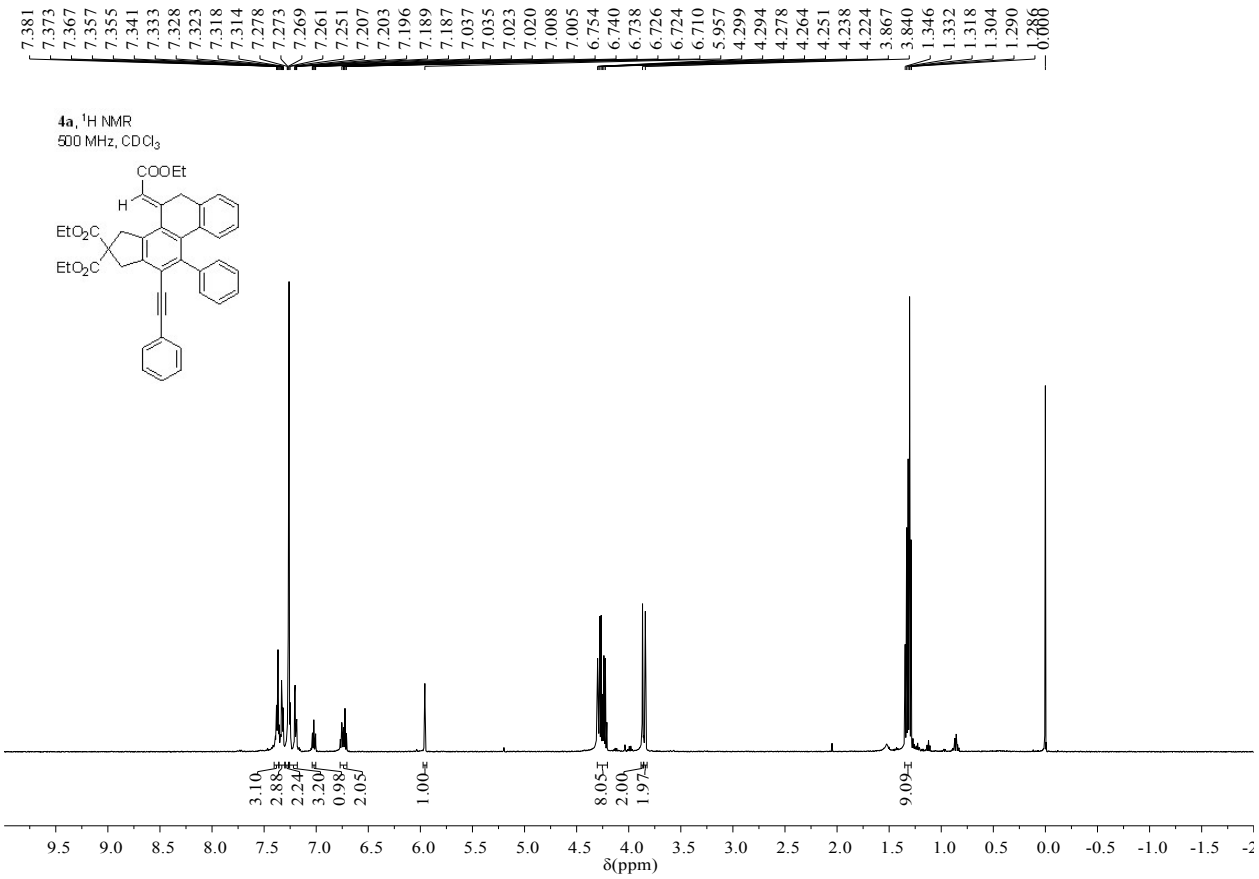


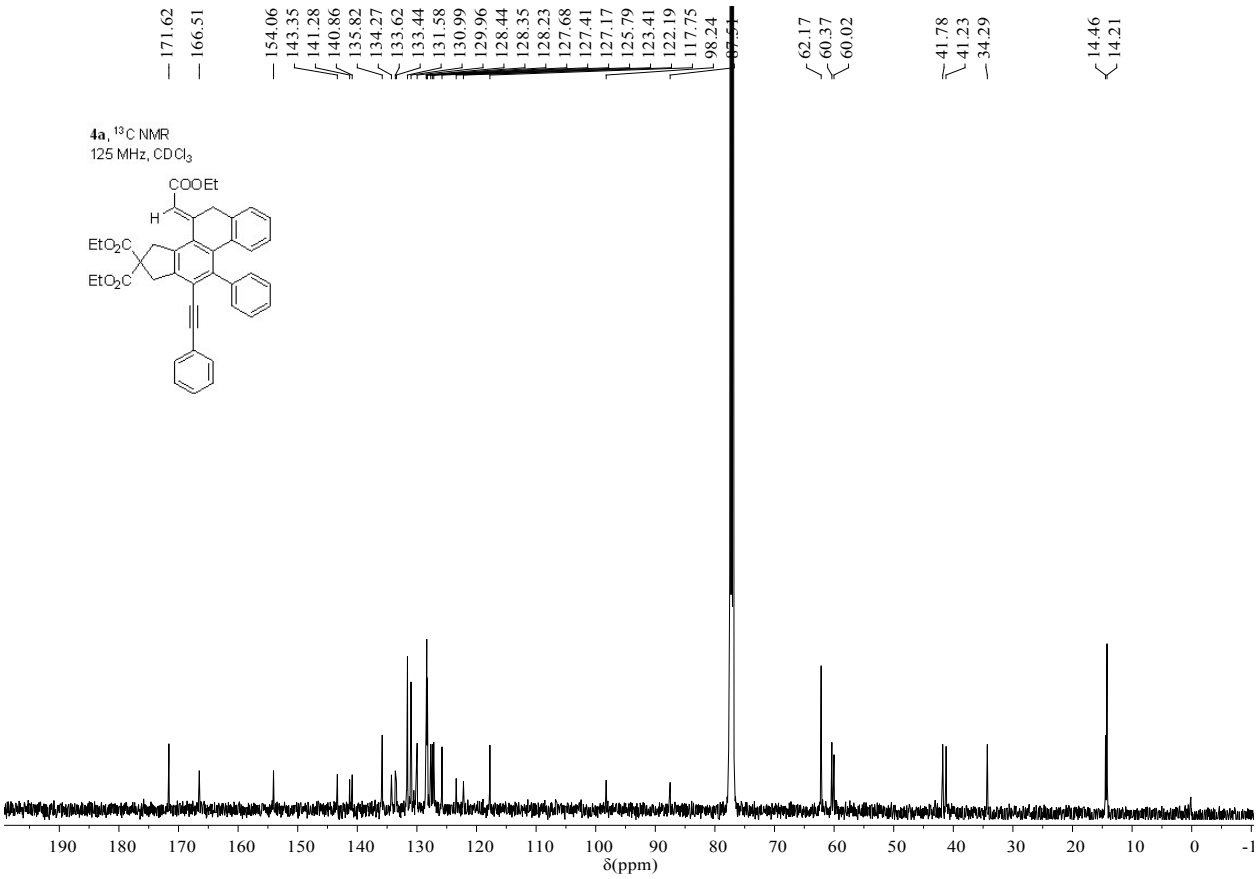
4k

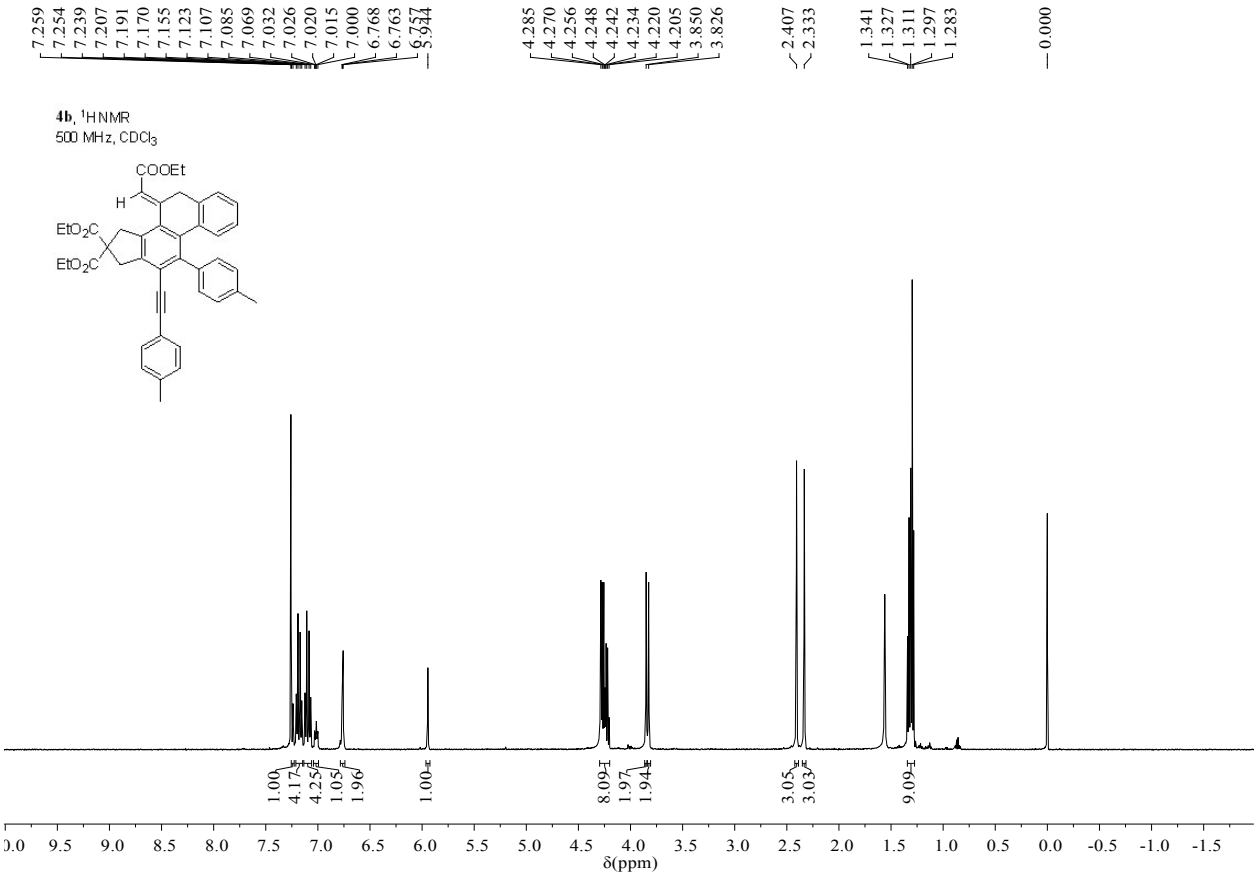


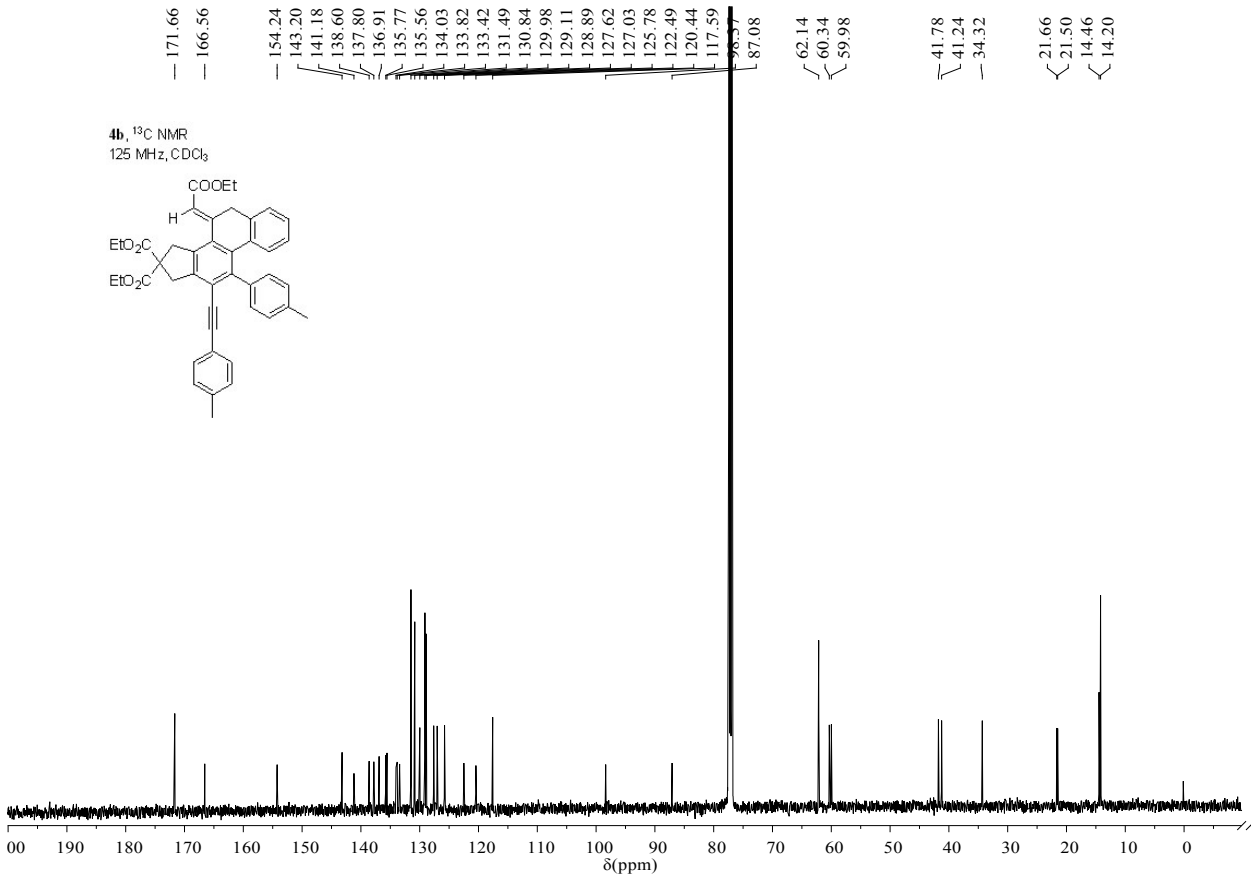
5j

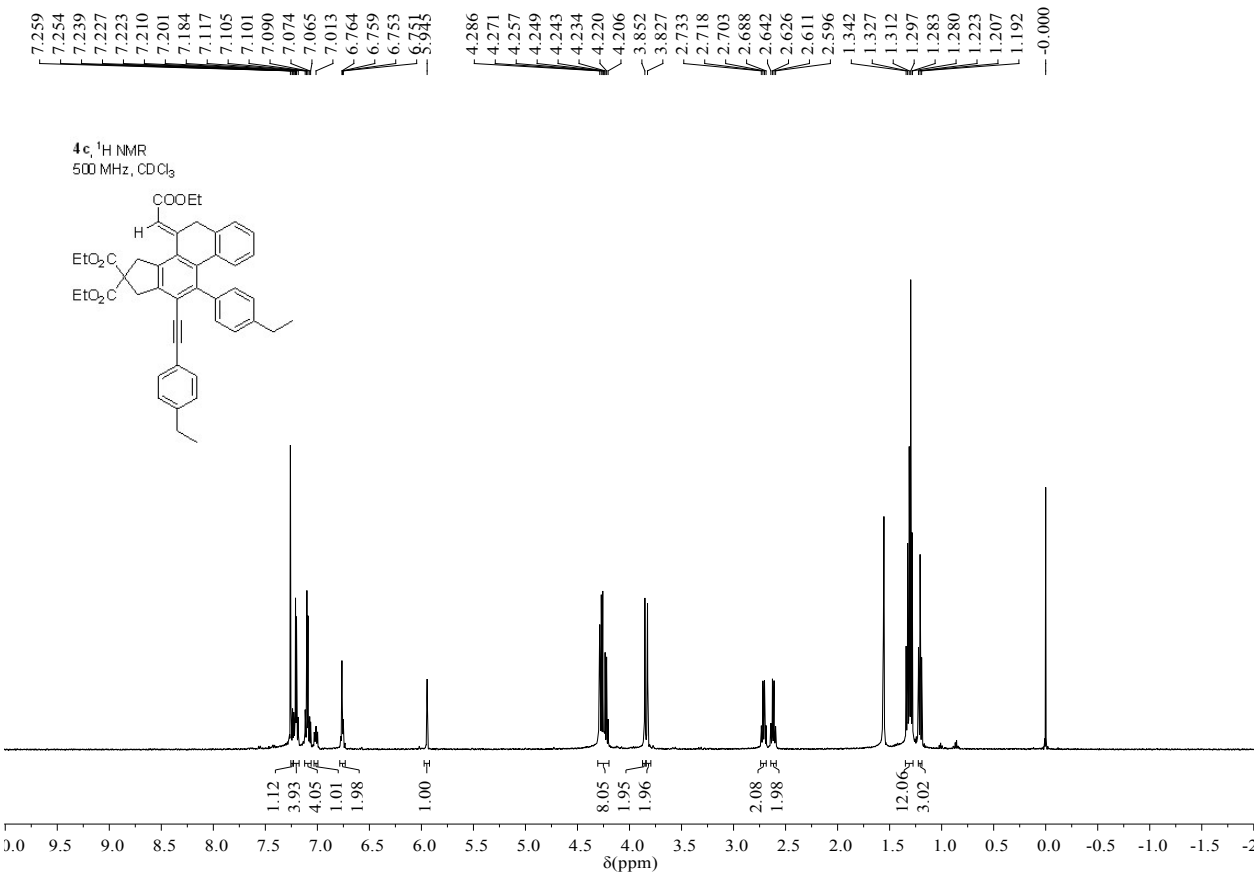
4. ^{1}H NMR & ^{13}C NMR Spectra for New Compounds

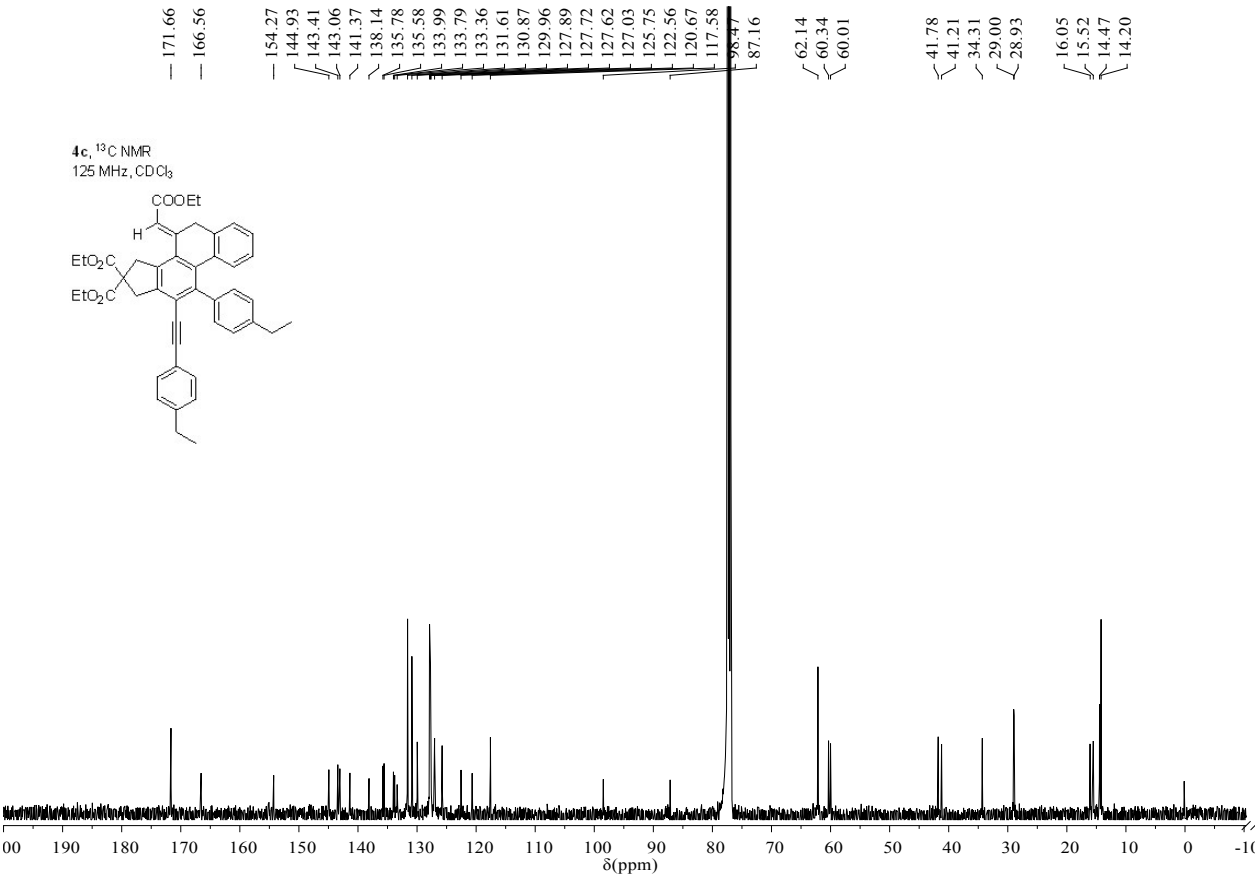


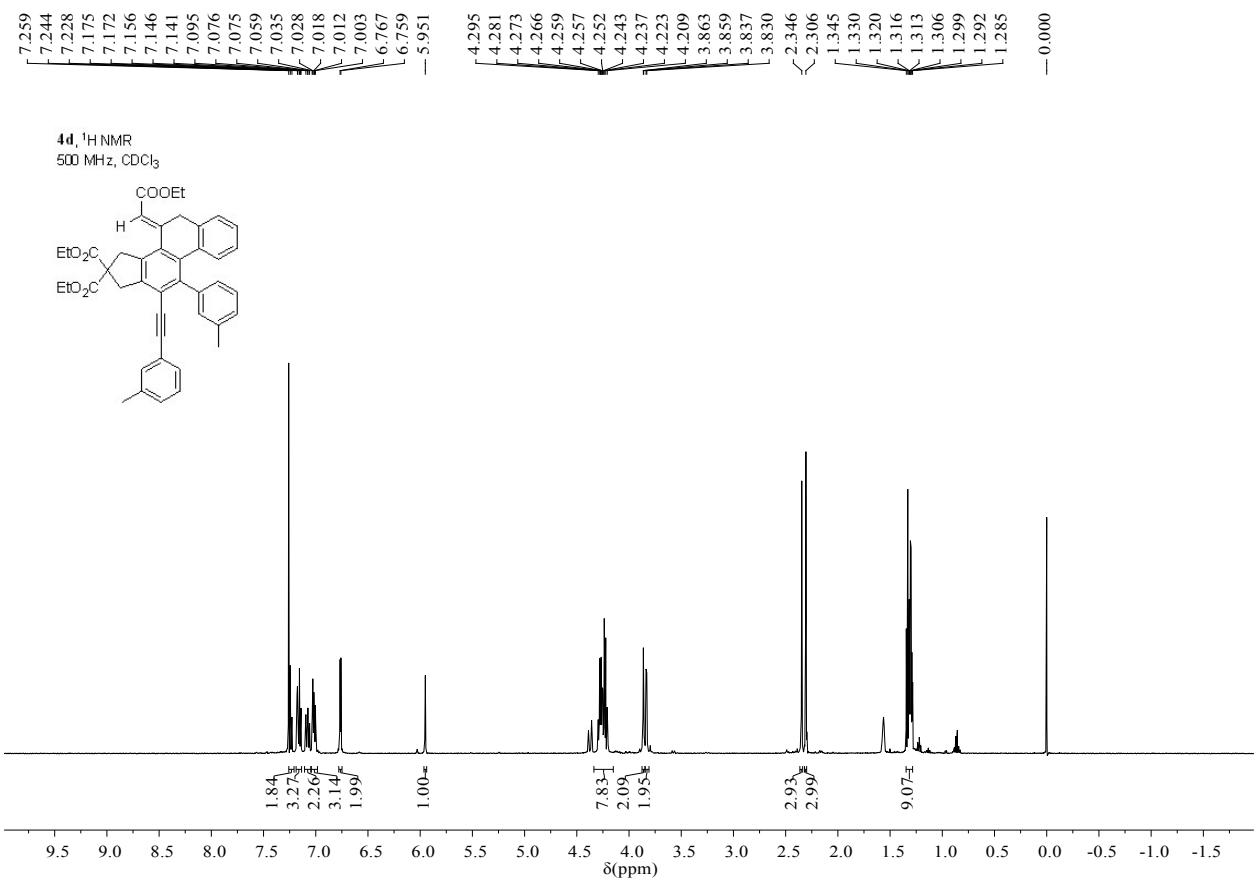


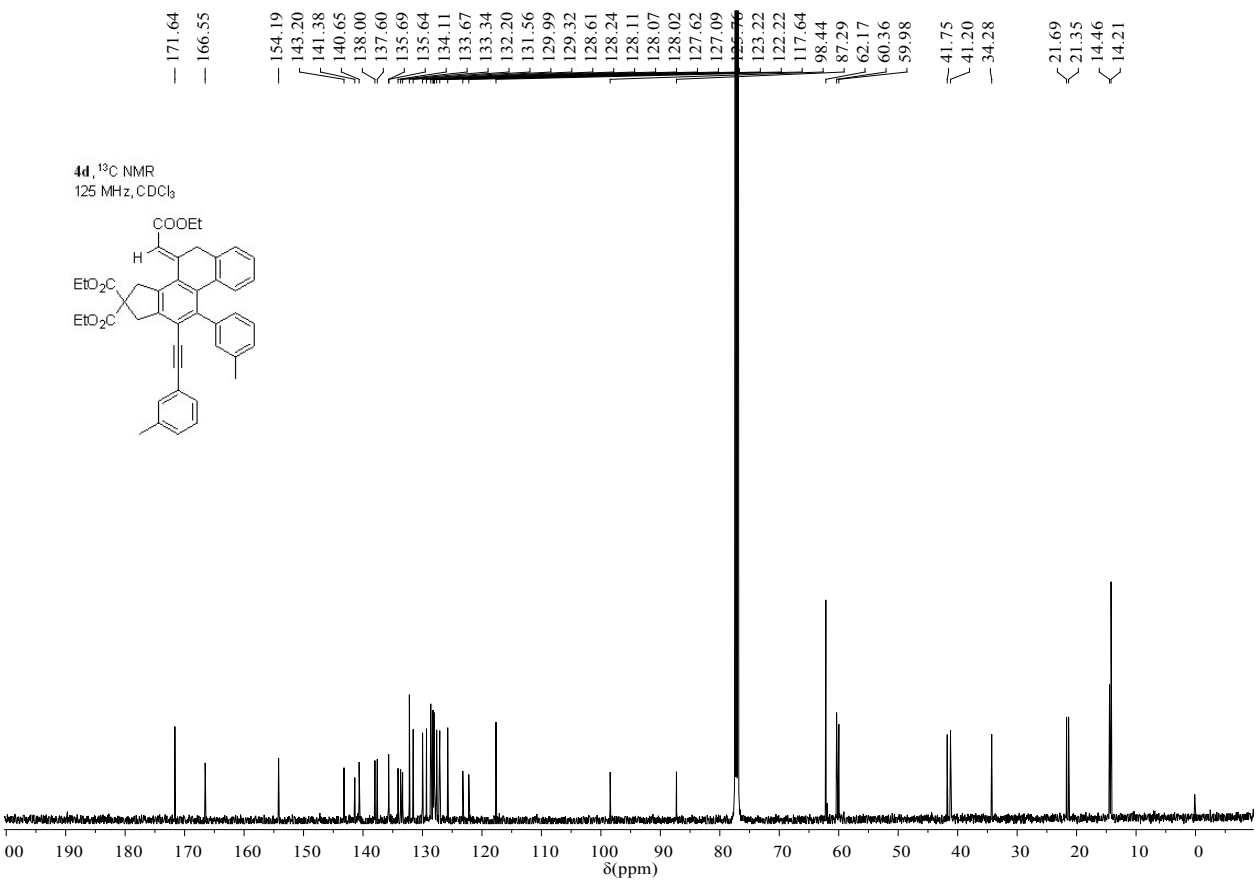

4b, ^{1}H NMR
500 MHz, $CDCl_3$
COOEt
H
EtO_2C
EtO_2C
δ(ppm)

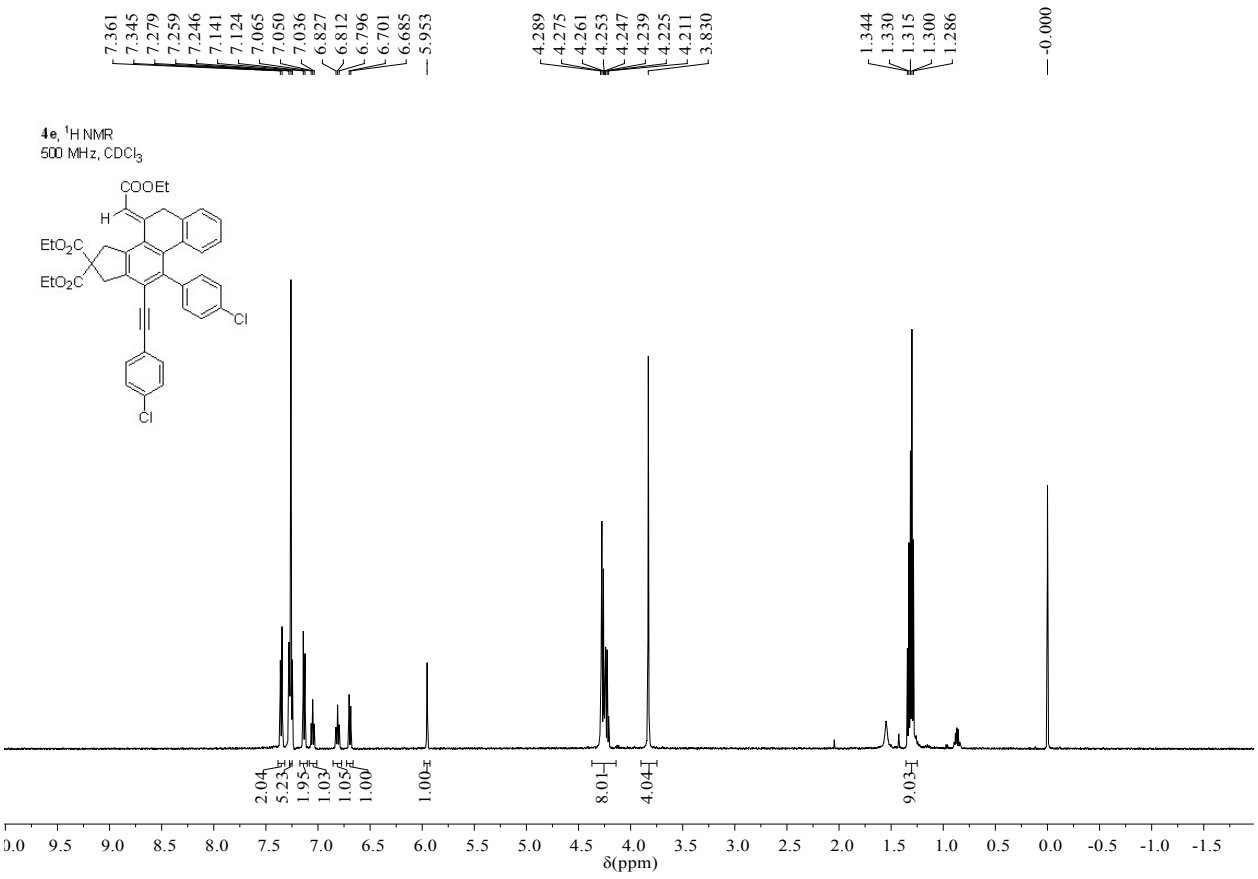

4b, ^{13}C NMR
125 MHz, $CDCl_3$
COOEt
H
EtO_2C
EtO_2C
δ(ppm)

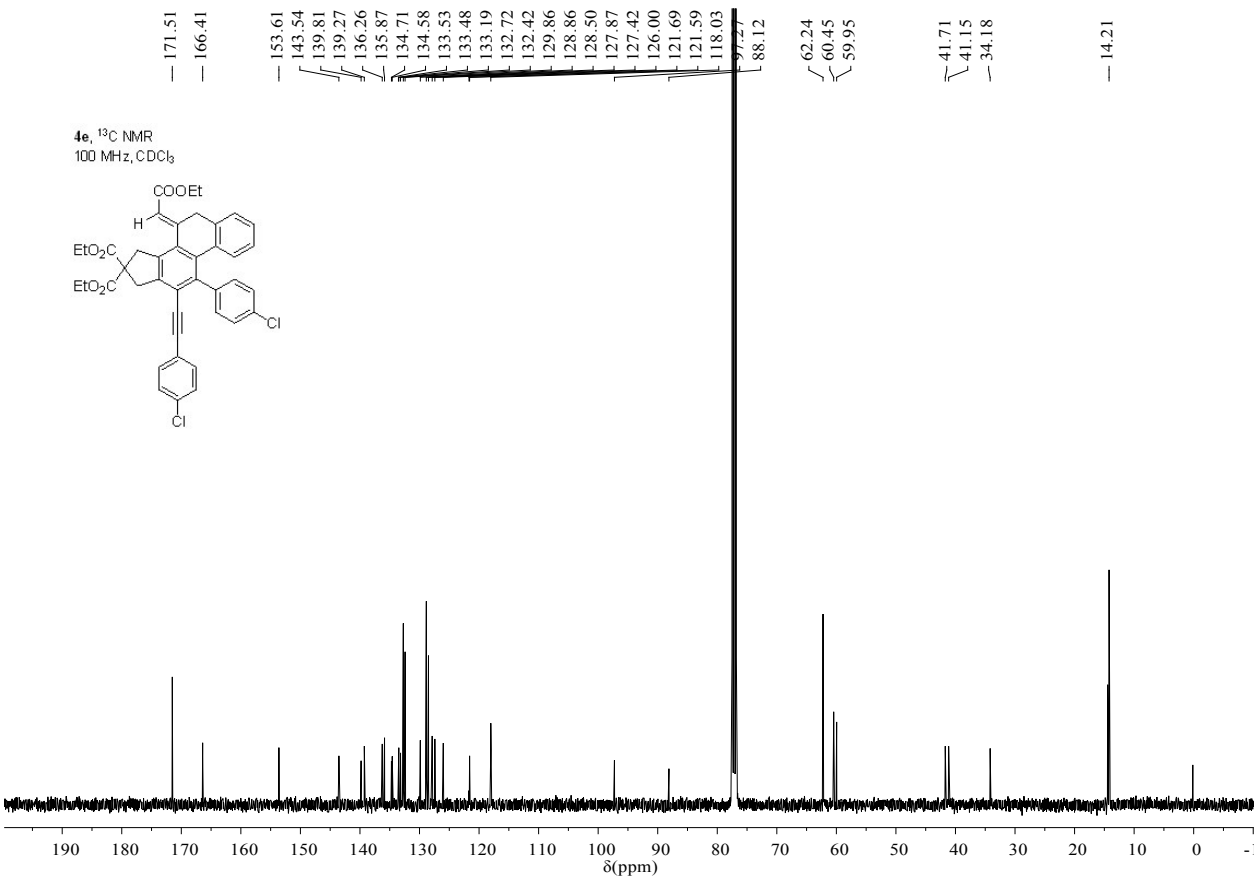

4c, 1H NMR
500 MHz, CDCl3
COOEt
H
EtO2C
EtO2C
7.259
7.254
7.239
7.227
7.223
7.210
7.201
7.184
7.117
7.105
7.101
7.090
7.074
7.065
7.013
6.764
6.759
6.753
6.751
5.945
4.286
4.271
4.257
4.249
4.243
4.234
4.220
4.206
3.852
3.827
2.733
2.718
2.703
2.688
2.642
2.626
2.611
2.596
1.342
1.327
1.312
1.297
1.283
1.280
1.223
1.207
1.192
-0.000
1.12
3.93
4.05
1.01
1.98
1.00
8.05
1.95
1.96
2.08
1.98
12.06
3.02
δ(ppm)

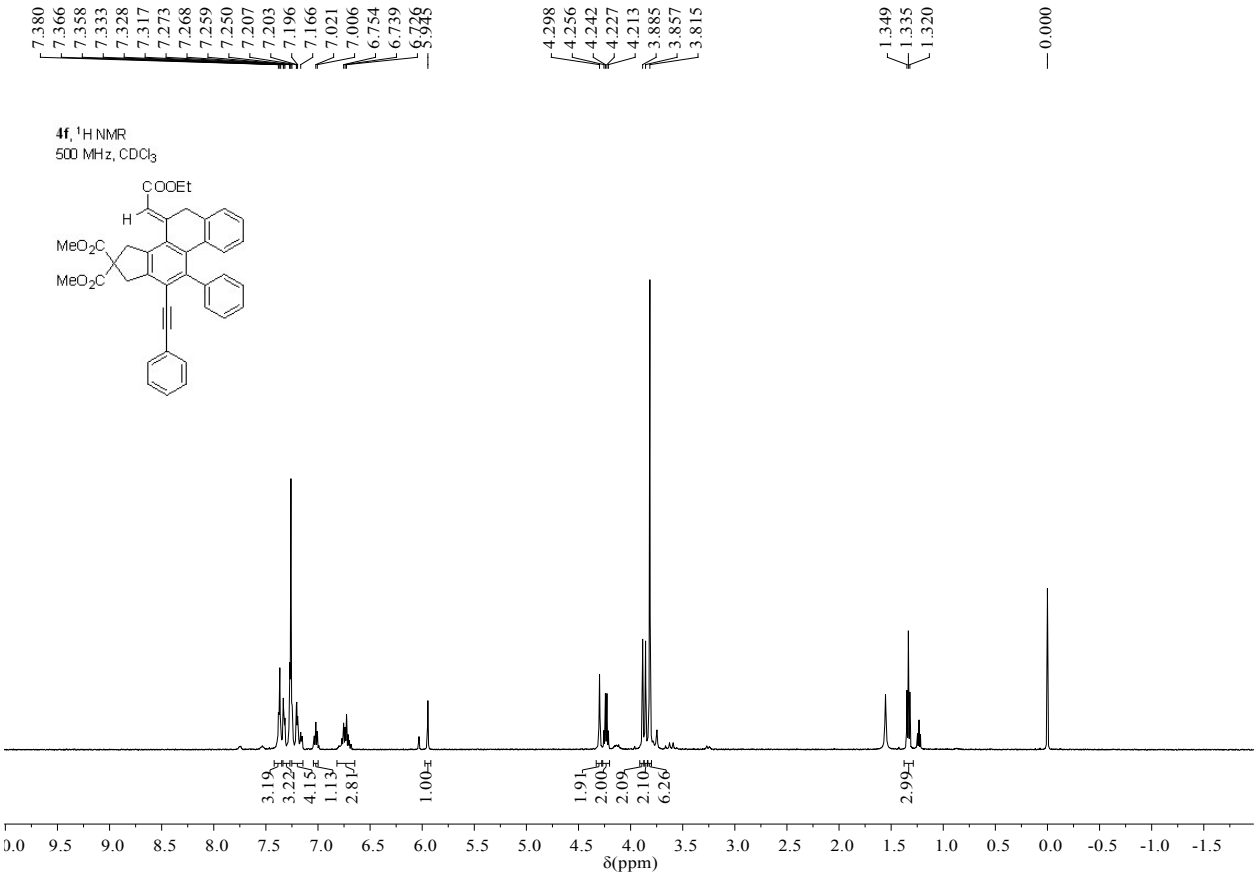

4c, 13C NMR
125 MHz, CDCl3
COOEt
H
EtO2C
EtO2C
171.66
166.56
154.27
144.93
143.41
143.06
141.37
138.14
135.78
135.58
133.99
133.79
133.36
131.61
130.87
129.96
127.89
127.72
127.62
127.03
125.75
122.56
120.67
117.58
98.47
87.16
62.14
60.34
60.01
41.78
41.21
34.31
29.00
28.93
16.05
15.52
14.47
14.20
δ(ppm)

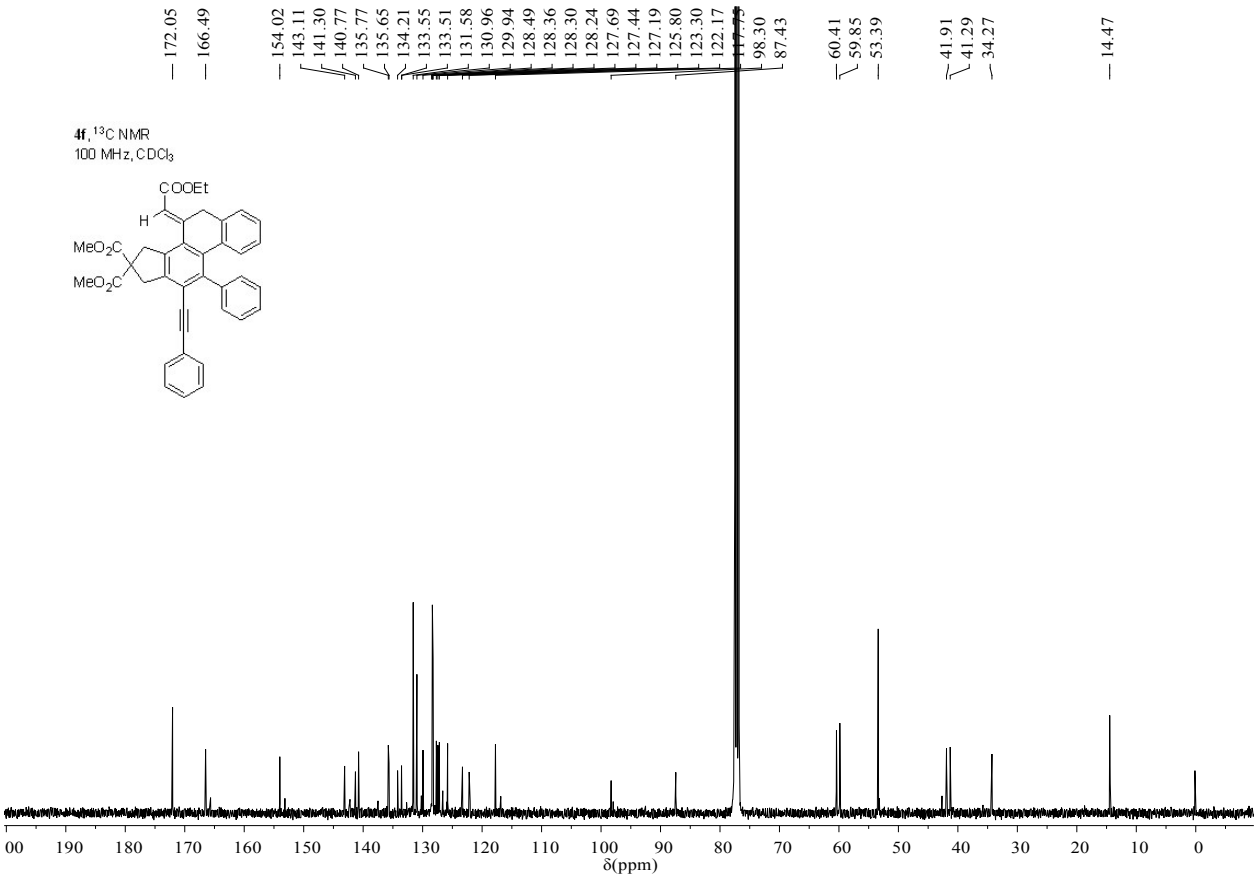

7.259
7.244
7.228
7.175
7.172
7.156
7.146
7.141
7.095
7.076
7.075
7.059
7.035
7.028
7.018
7.012
7.003
6.767
6.759
5.951
4.295
4.281
4.273
4.266
4.259
4.257
4.252
4.243
4.237
4.223
4.209
3.863
3.859
3.837
3.830
2.346
2.306
1.345
1.330
1.320
1.316
1.313
1.306
1.299
1.292
1.285
0.000
4d, 1H NMR
500 MHz, CDCl3
COOEt
H
EtO2C
EtO2C
1.84
3.27
2.26
3.14
1.99
1.00
7.83
2.09
1.95
2.93
2.99
9.07
δ(ppm)

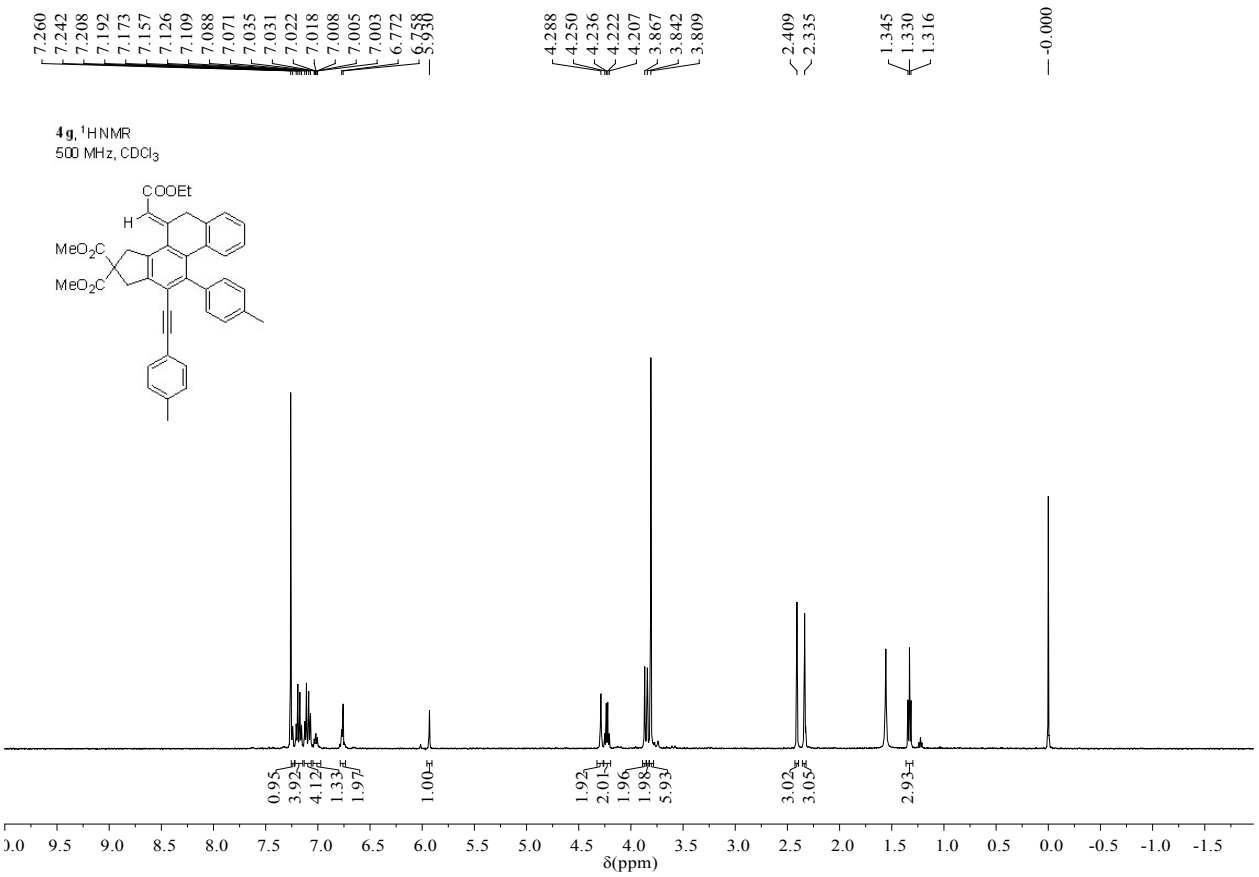

171.64
166.55
154.19
143.20
141.38
140.65
138.00
137.60
135.69
135.64
134.11
133.67
133.34
132.20
131.56
129.99
129.32
128.61
128.24
128.11
128.07
128.02
127.62
127.09
123.22
122.22
117.64
98.44
87.29
62.17
60.36
59.98
41.75
41.20
34.28
21.69
21.35
14.46
14.21
4d, 13C NMR
125 MHz, CDCl3
COOEt
H
EtO2C
EtO2C
δ(ppm)

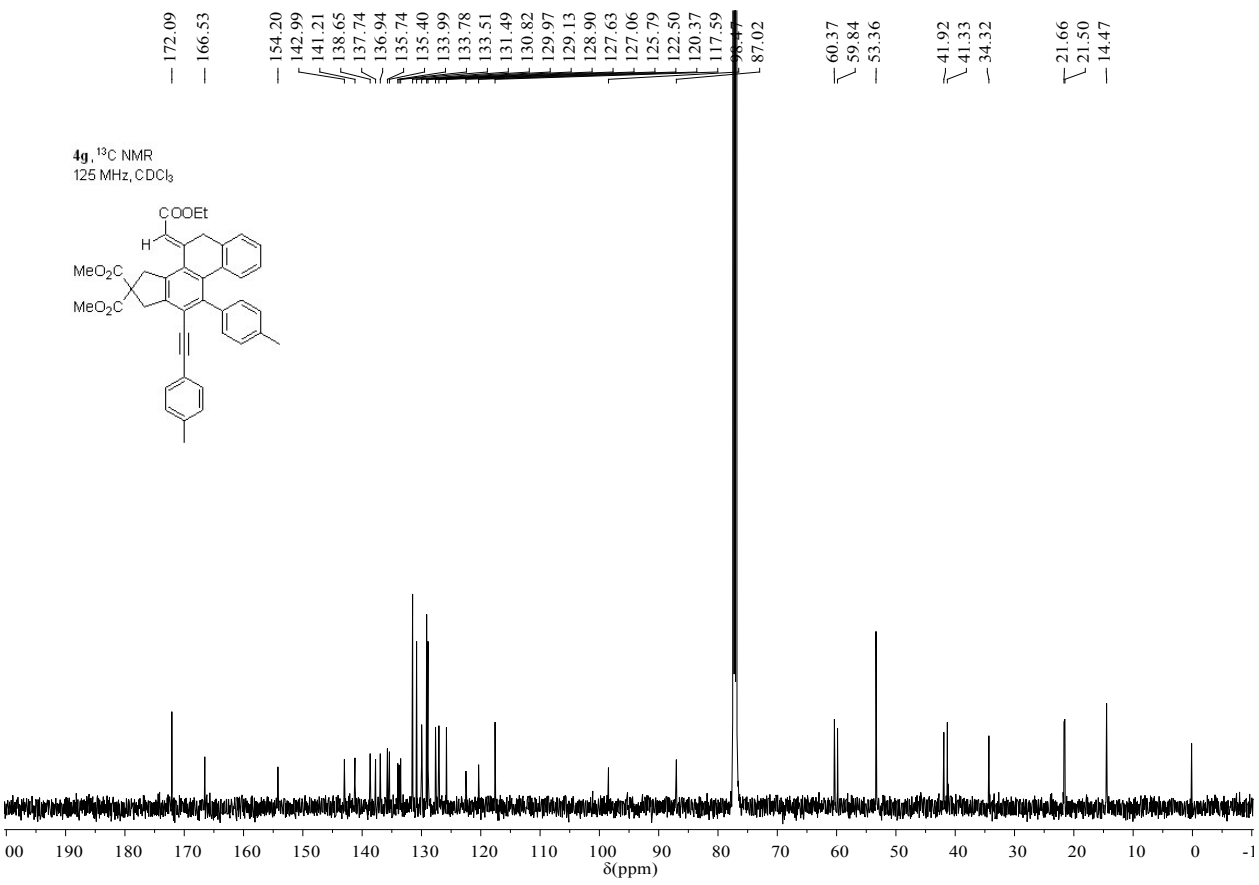

4e, 1H NMR
500 MHz, CDCl3
δ(ppm)

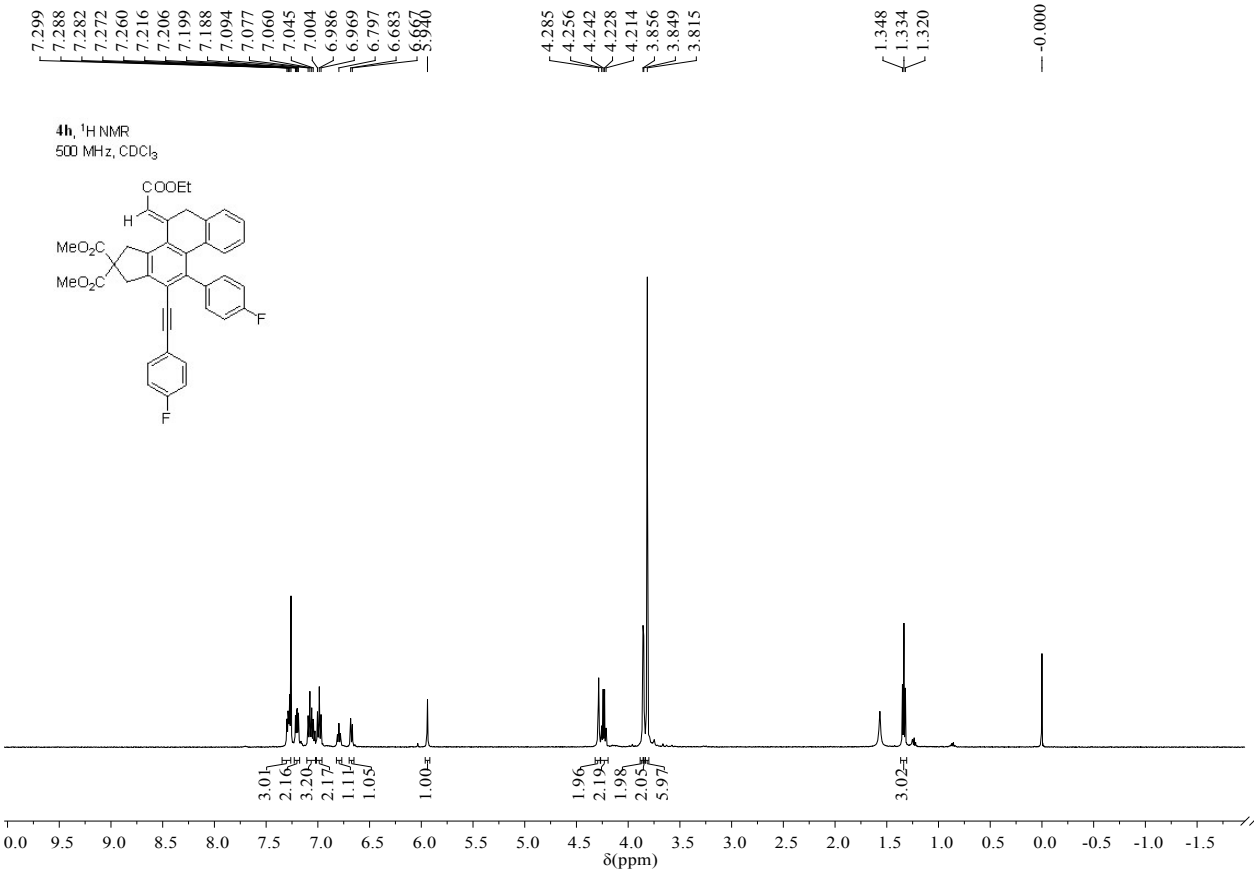

4e, 13C NMR
100 MHz, CDCl3
δ(ppm)

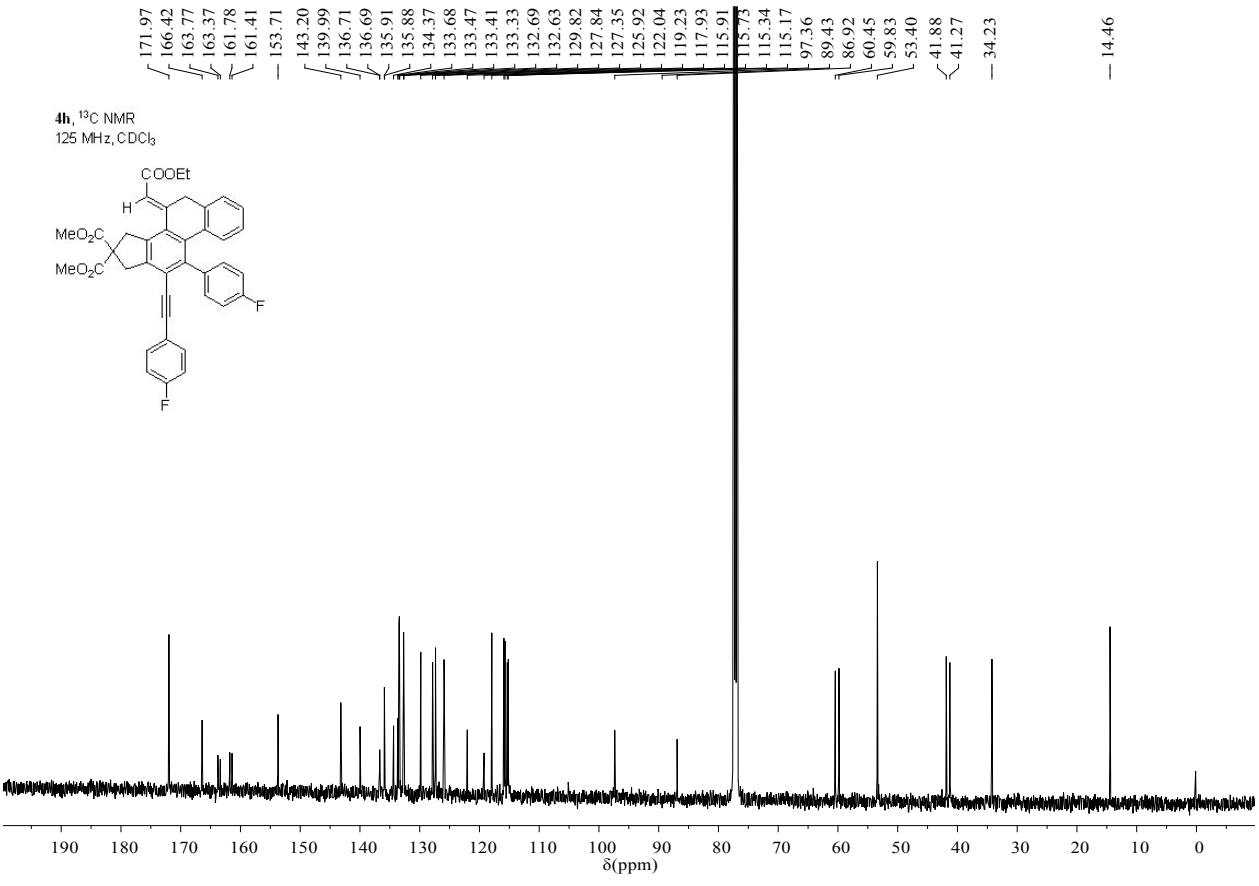

7.380
7.366
7.358
7.333
7.328
7.317
7.273
7.268
7.259
7.250
7.207
7.203
7.196
7.166
7.021
7.006
6.754
6.739
6.726
5.945
4.298
4.256
4.242
4.227
4.213
3.885
3.857
3.815
1.349
1.335
1.320
0.000
4f, 1H NMR
500 MHz, CDCl3
COOEt
H
MeO2C
MeO2C
3.19
3.22
4.15
1.13
2.81
1.00
1.91
2.00
2.09
2.10
6.26
2.99
δ(ppm)

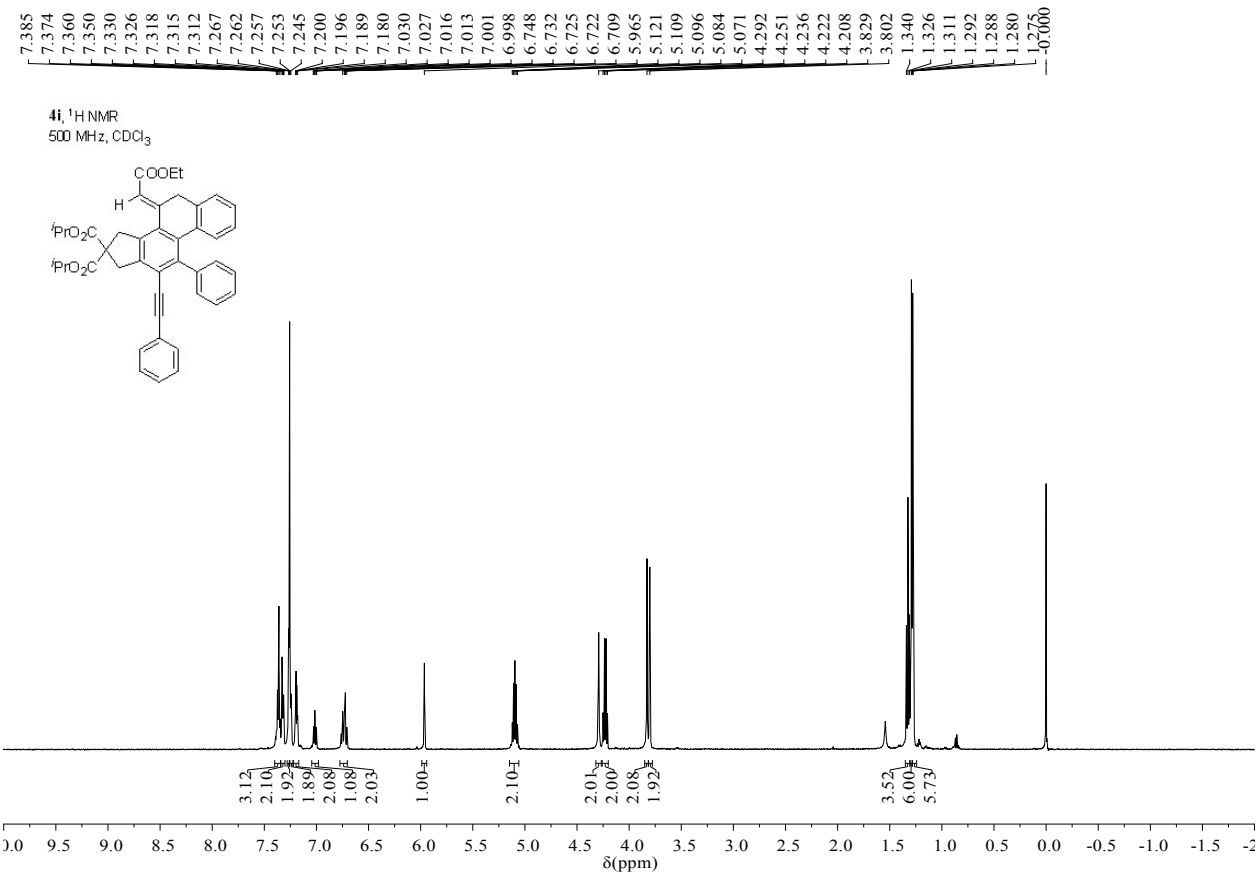

172.05
166.49
154.02
143.11
141.30
140.77
135.77
135.65
134.21
133.55
133.51
131.58
130.96
129.94
128.49
128.36
128.30
128.24
127.69
127.44
127.19
125.80
123.30
122.17
98.30
87.43
60.41
59.85
53.39
41.91
41.29
34.27
14.47
4f, 13C NMR
100 MHz, CDCl3
COOEt
H
MeO2C
MeO2C
δ(ppm)

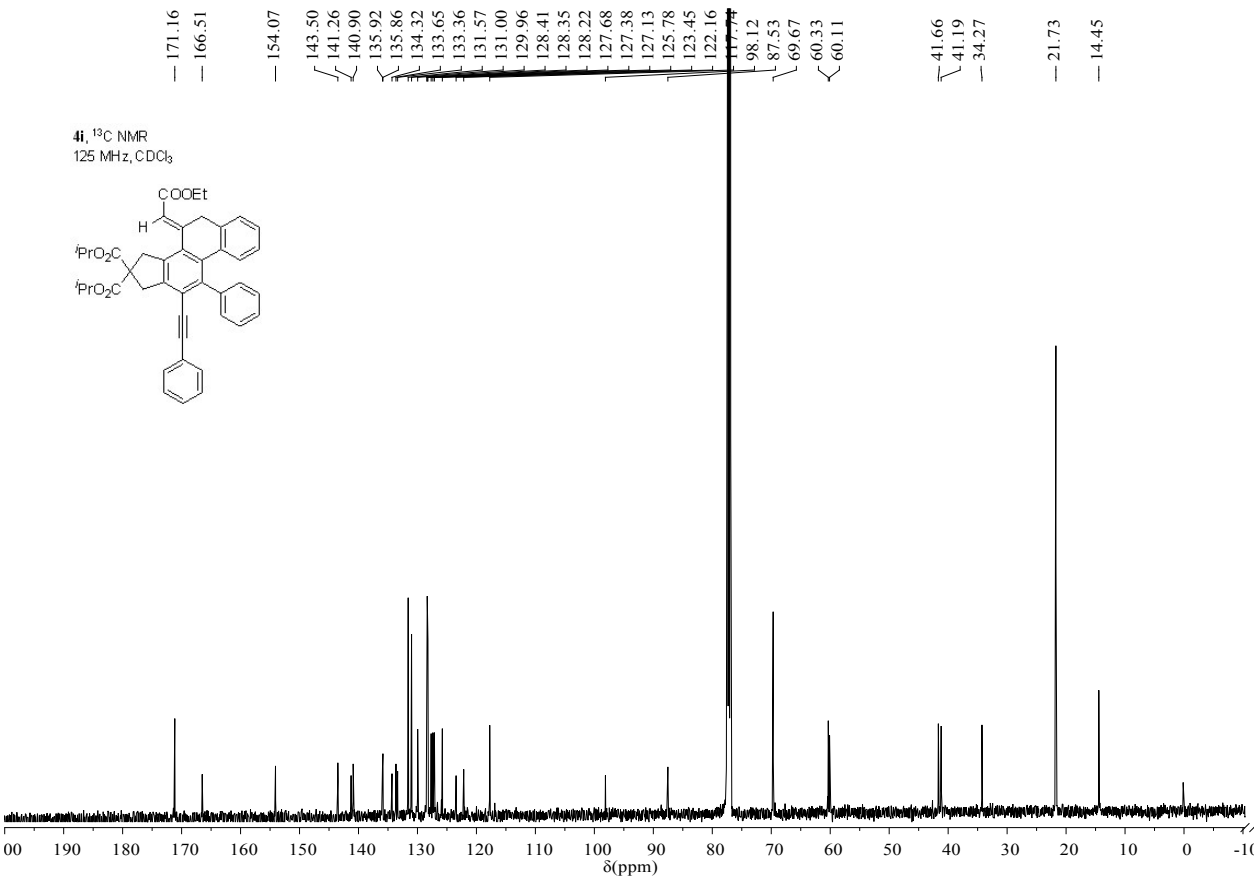

4g, 1H NMR
500 MHz, CDCl3
COOEt
H
MeO2C
MeO2C
δ(ppm)

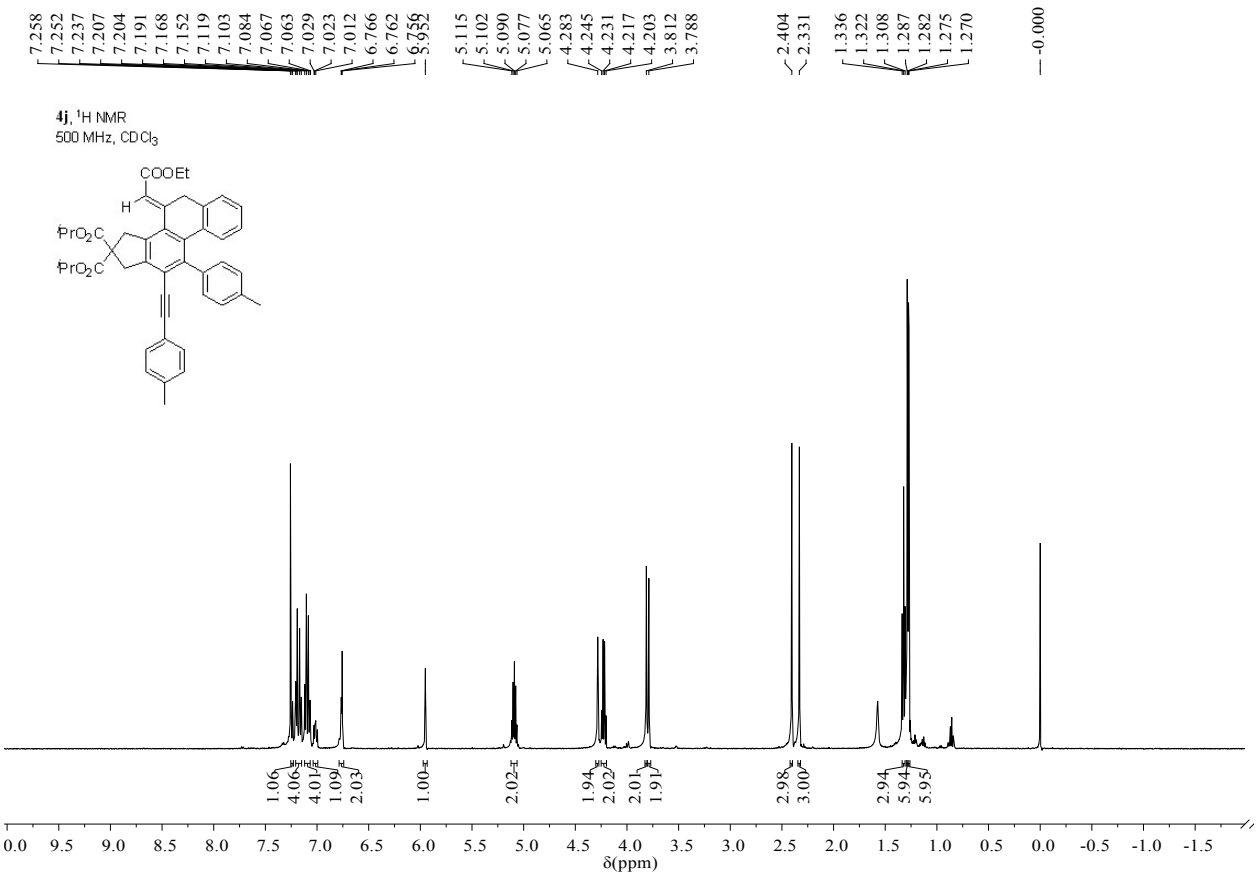

4g, 13C NMR
125 MHz, CDCl3
COOEt
H
MeO2C
MeO2C
δ(ppm)

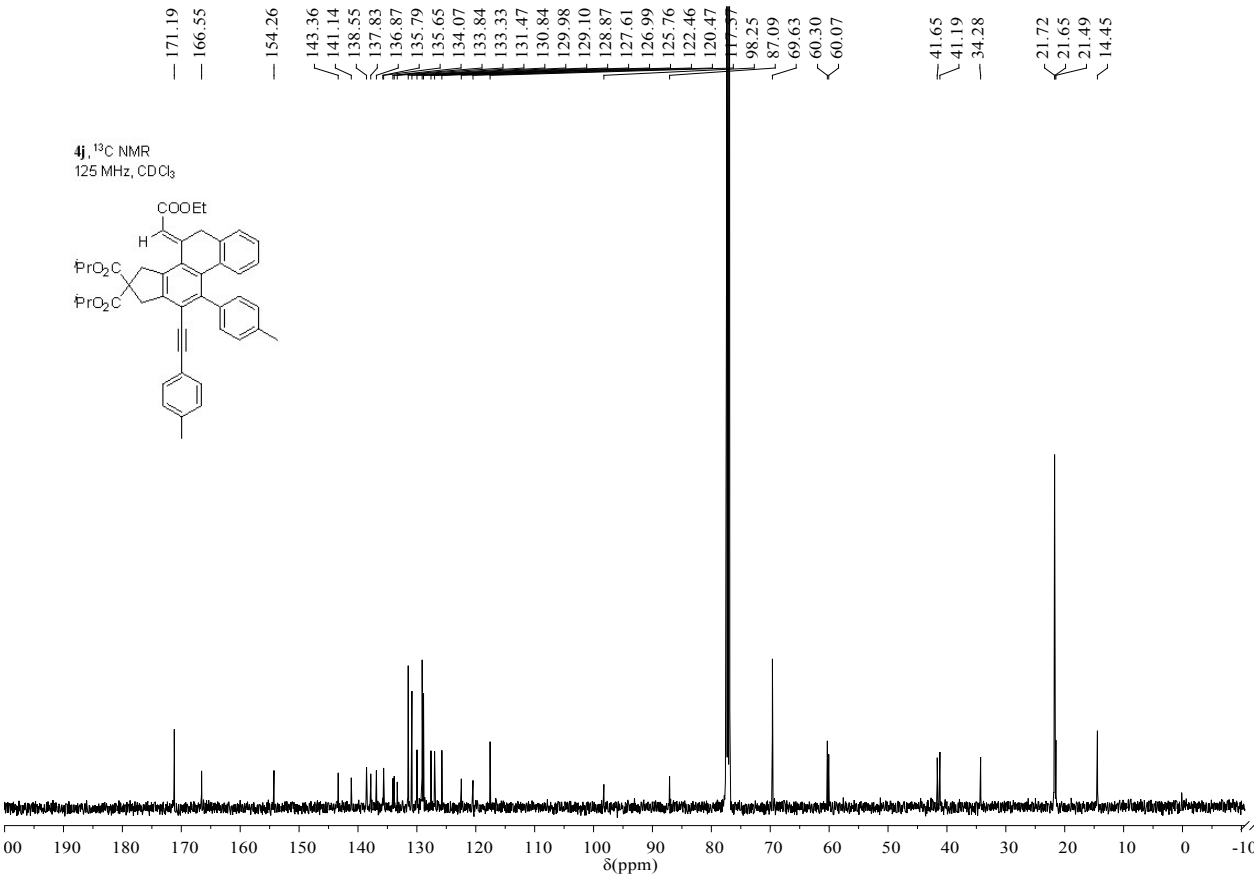

7.299
7.288
7.282
7.272
7.260
7.216
7.206
7.199
7.188
7.094
7.077
7.060
7.045
7.004
6.986
6.969
6.797
6.683
6.667
5.940
4.285
4.256
4.242
4.228
4.214
3.856
3.849
3.815
1.348
1.334
1.320
0.000
4h, 1H NMR
500 MHz, CDCl3
COOEt
H
MeO2C
MeO2C
F
F
3.01
2.16
3.20
2.17
1.11
1.05
1.00
1.96
2.19
1.98
2.05
5.97
3.02
δ(ppm)

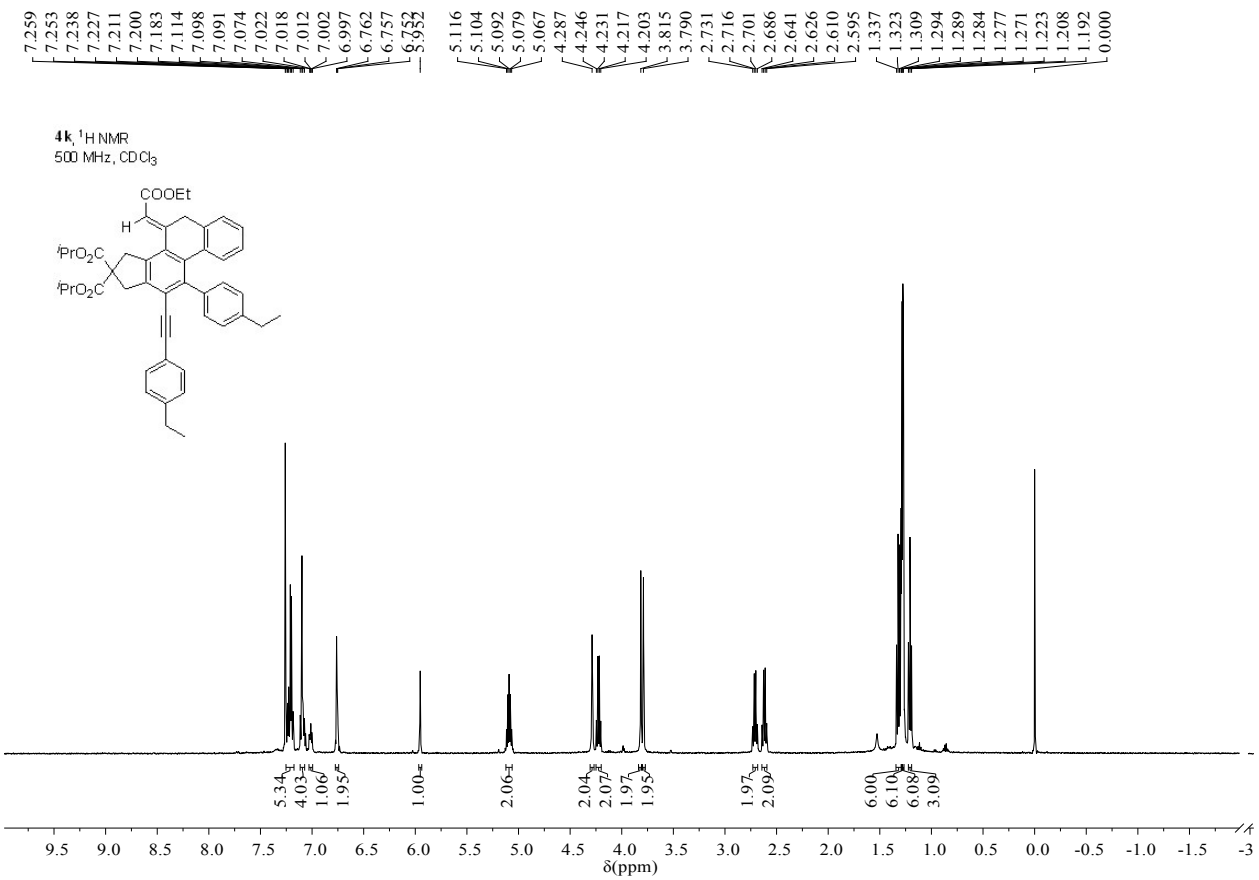

171.97
166.42
163.77
163.37
161.78
161.41
153.71
143.20
139.99
136.71
136.69
135.91
135.88
134.37
133.68
133.47
133.41
133.33
132.69
132.63
129.82
127.84
127.35
125.92
122.04
119.23
117.93
115.91
115.73
115.34
115.17
97.36
89.43
86.92
60.45
59.83
53.40
41.88
41.27
34.23
14.46
4h, 13C NMR
125 MHz, CDCl3
COOEt
H
MeO2C
MeO2C
F
F
δ(ppm)

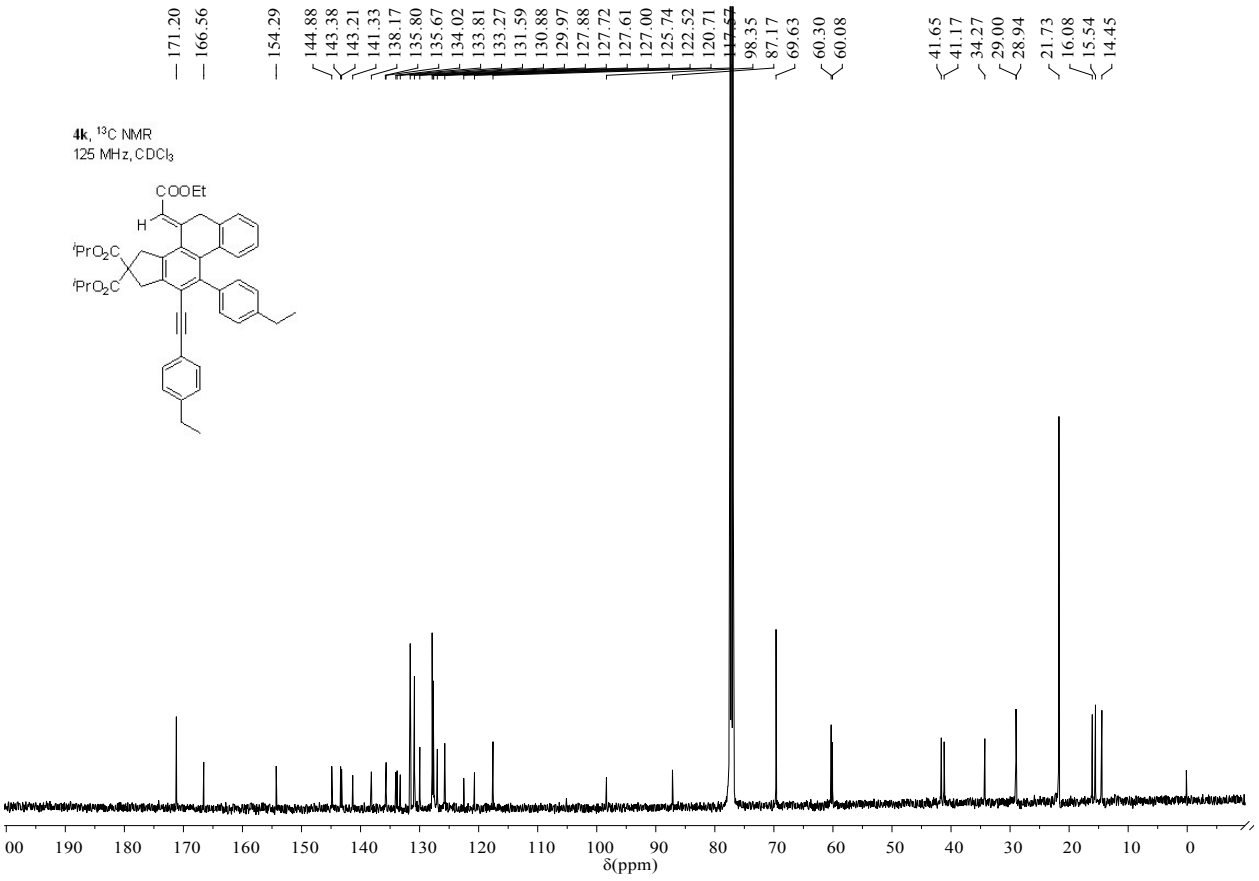

4i, ^{1}H NMR
500 MHz, CDCl$_3$
δ(ppm)

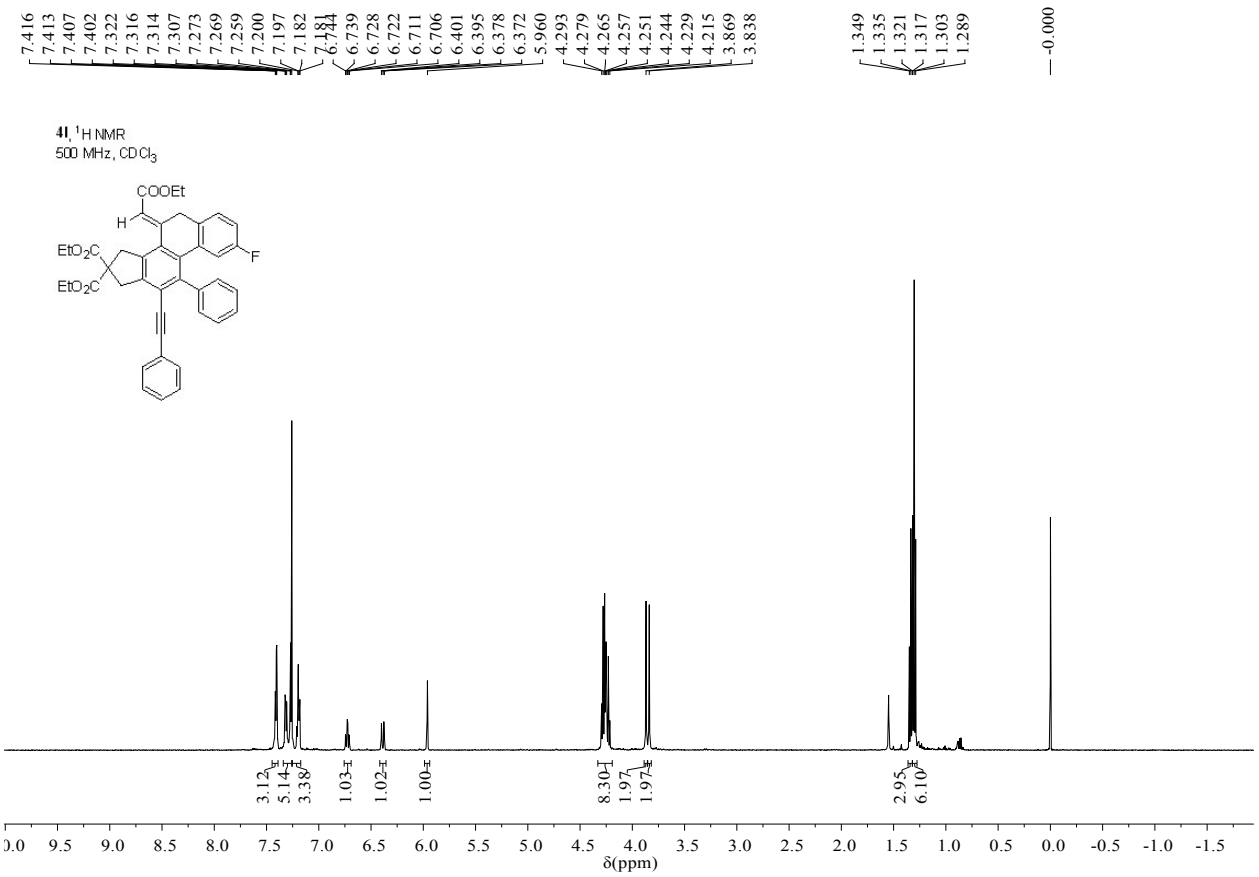

4i, ^{13}C NMR
125 MHz, CDCl$_3$
δ(ppm)

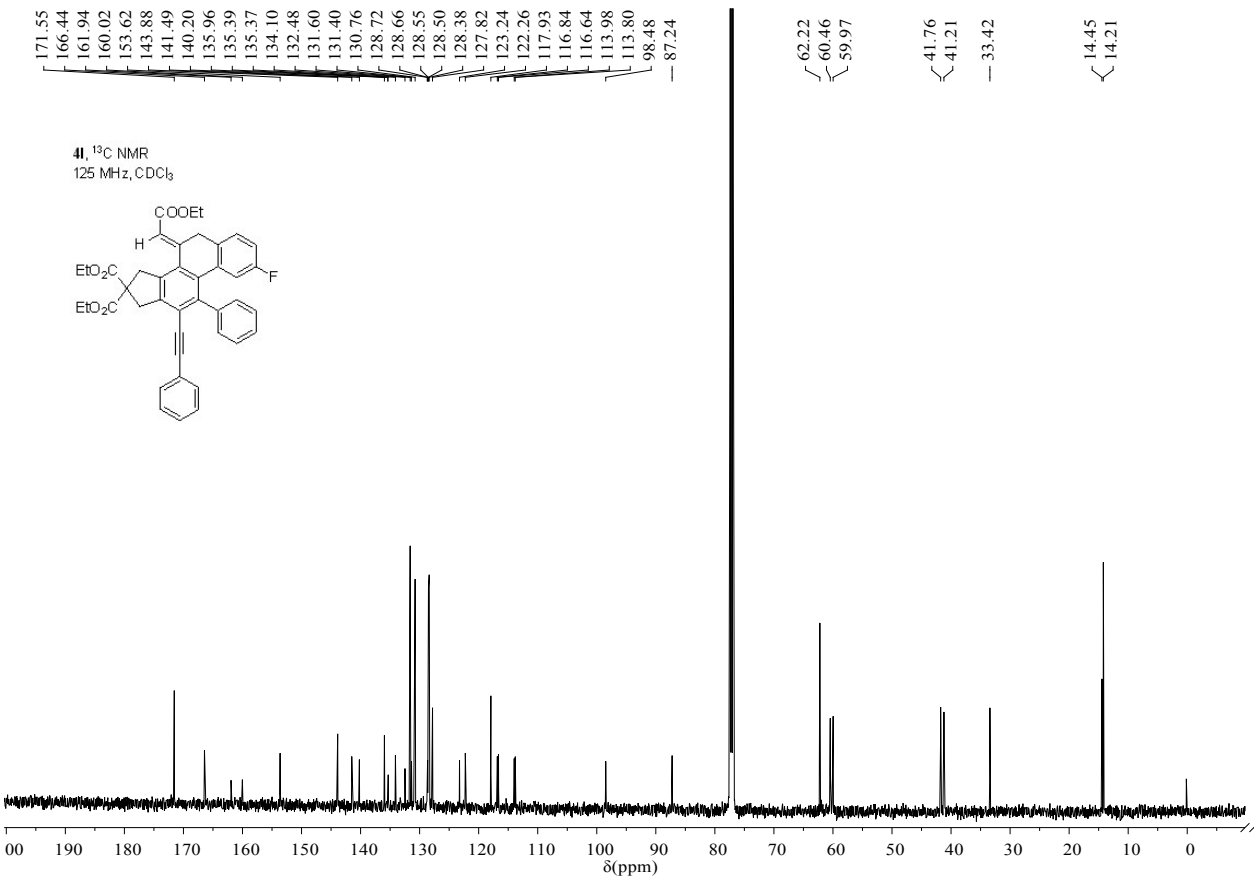

4j, 1H NMR
500 MHz, CDCl3
δ(ppm)

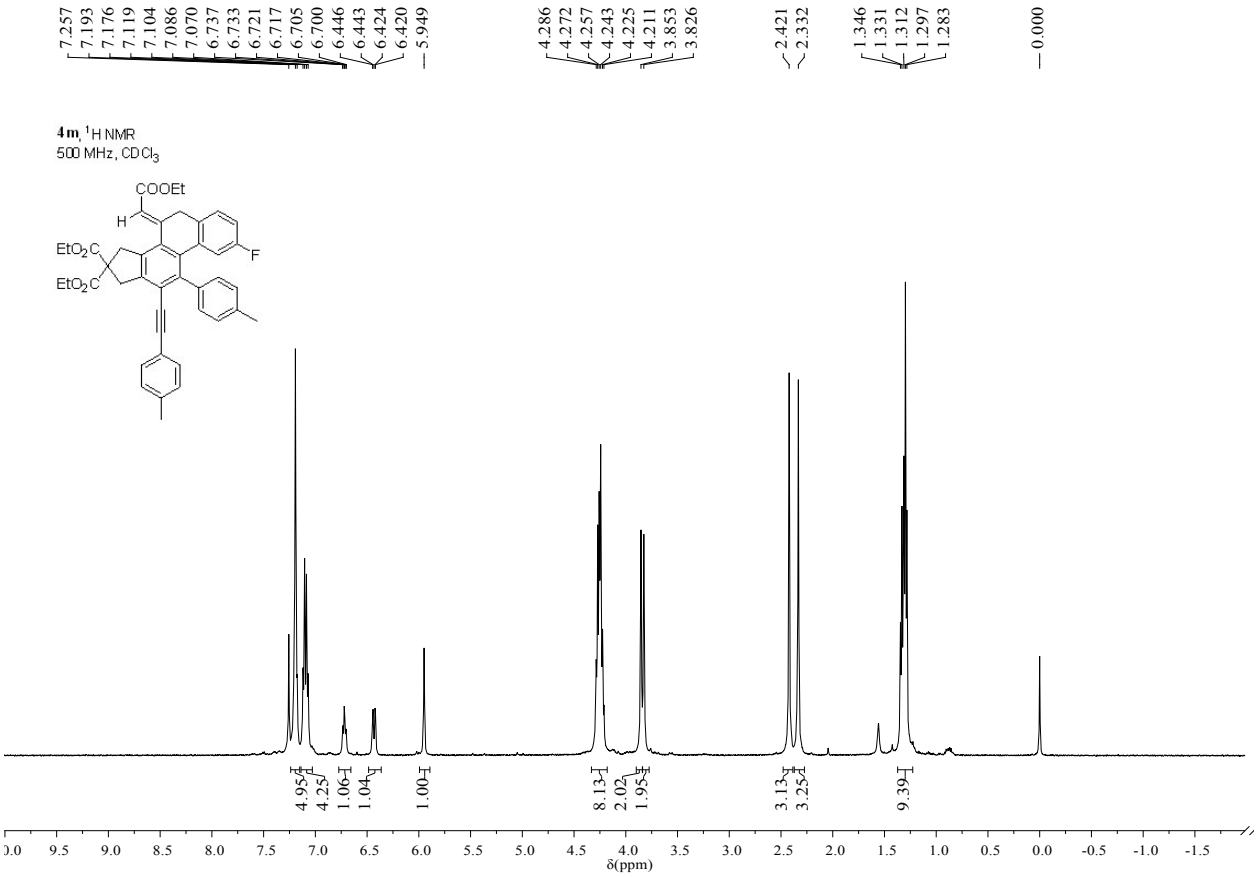

4j, 13C NMR
125 MHz, CDCl3
δ(ppm)

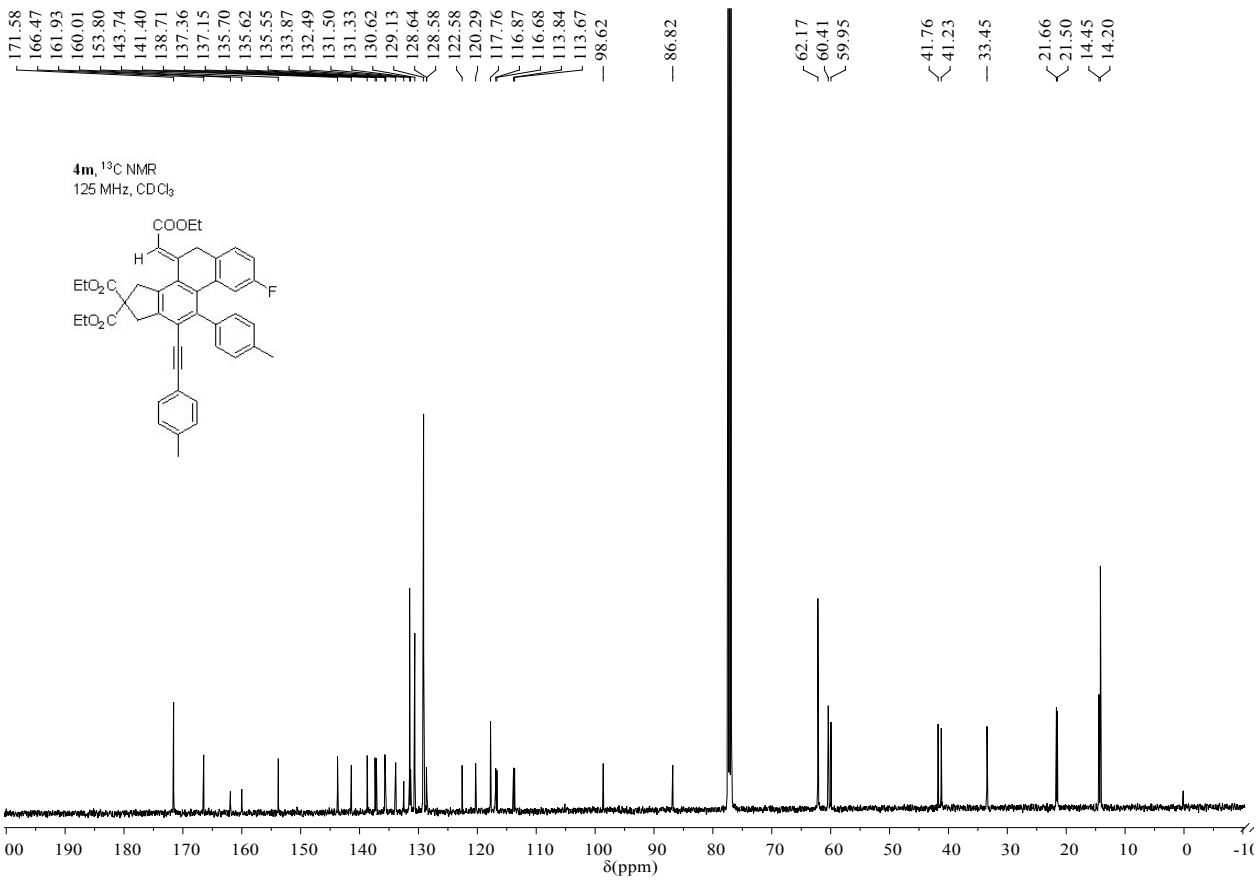

4k, 1H NMR
500 MHz, CDCl3
δ(ppm)

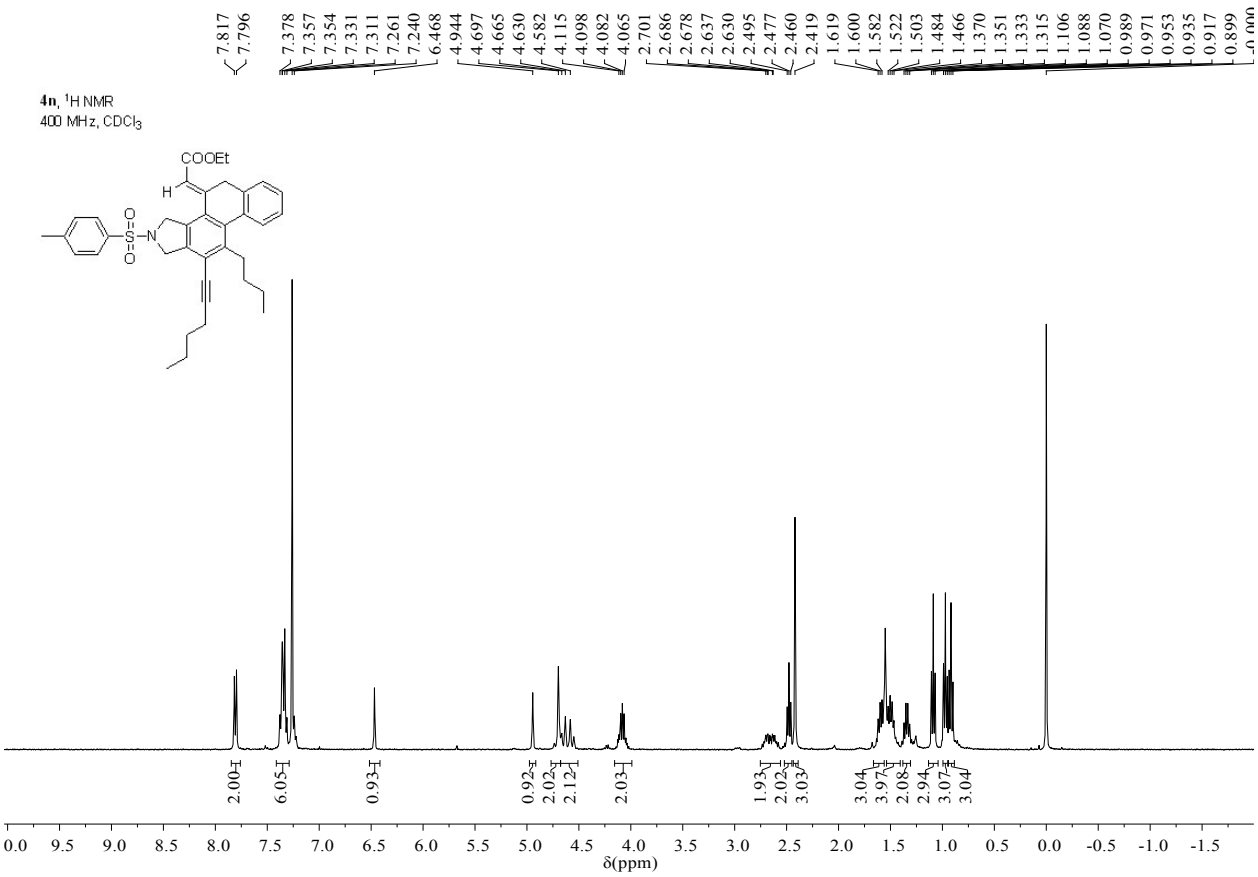

4k, 13C NMR
125 MHz, CDCl3
δ(ppm)

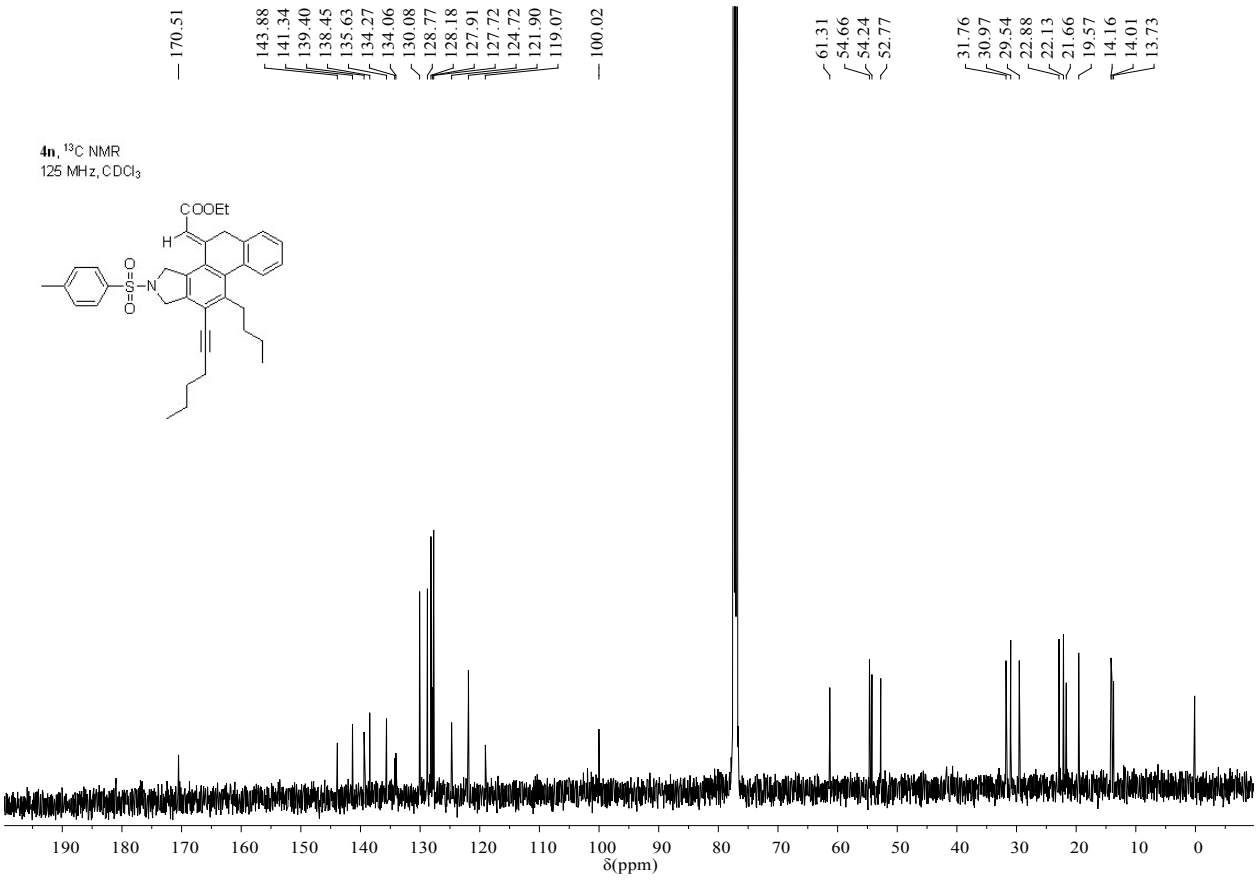

4l, ^{1}H NMR
500 MHz, $CDCl_3$
δ(ppm)

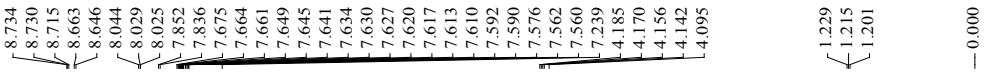

4l, ^{13}C NMR
125 MHz, $CDCl_3$
δ(ppm)


7.257
7.193
7.176
7.119
7.104
7.086
7.070
6.737
6.733
6.721
6.717
6.705
6.700
6.446
6.443
6.424
6.420
5.949
4.286
4.272
4.257
4.243
4.225
4.211
3.853
3.826
2.421
2.332
1.346
1.331
1.312
1.297
1.283
0.000
4m, 1H NMR
500 MHz, CDCl3
COOEt
H
EtO2C
EtO2C
F
4.95
4.25
1.06
1.04
1.00
8.13
2.02
1.95
3.13
3.25
9.39
δ(ppm)

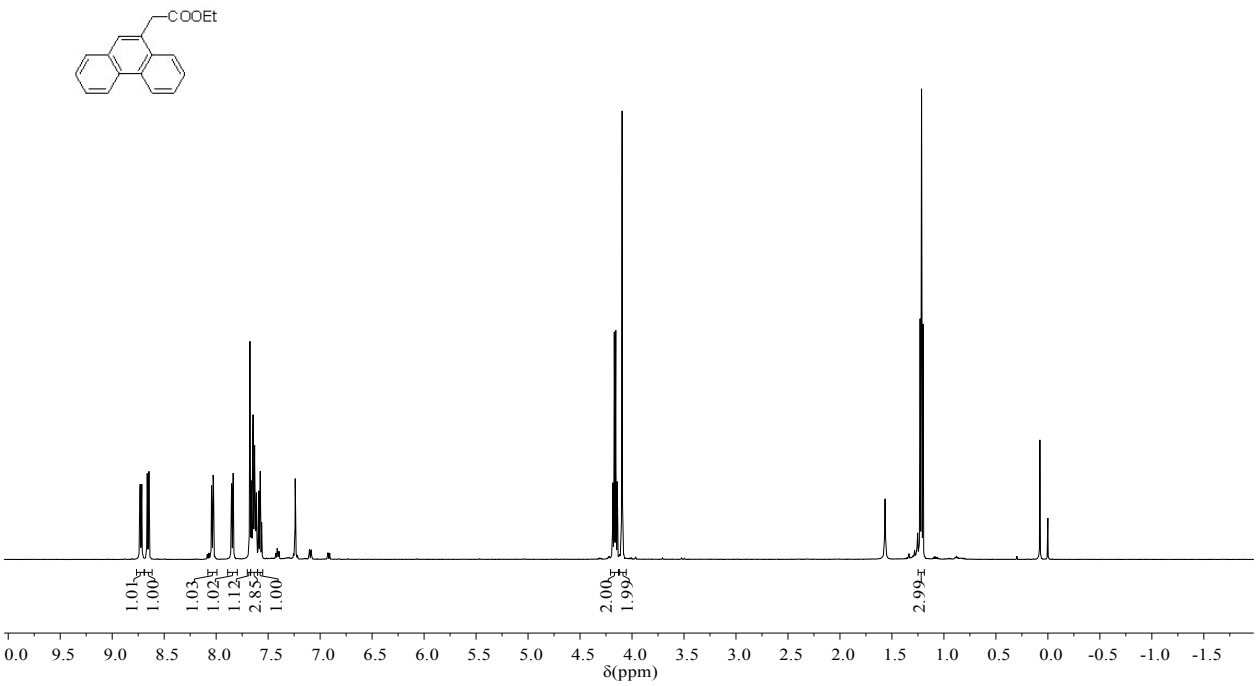

171.58
166.47
161.93
160.01
153.80
143.74
141.40
138.71
137.36
137.15
135.70
135.62
135.55
133.87
132.49
131.50
131.33
130.62
129.13
128.64
128.58
122.58
120.29
117.76
116.87
116.68
113.84
113.67
98.62
86.82
62.17
60.41
59.95
41.76
41.23
33.45
21.66
21.50
14.45
14.20
4m, 13C NMR
125 MHz, CDCl3
COOEt
H
EtO2C
EtO2C
F
δ(ppm)

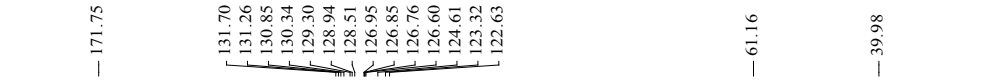

4n, 1H NMR
400 MHz, CDCl3
COOEt
H
δ(ppm)


4n, 13C NMR
125 MHz, CDCl3
COOEt
H
δ(ppm)

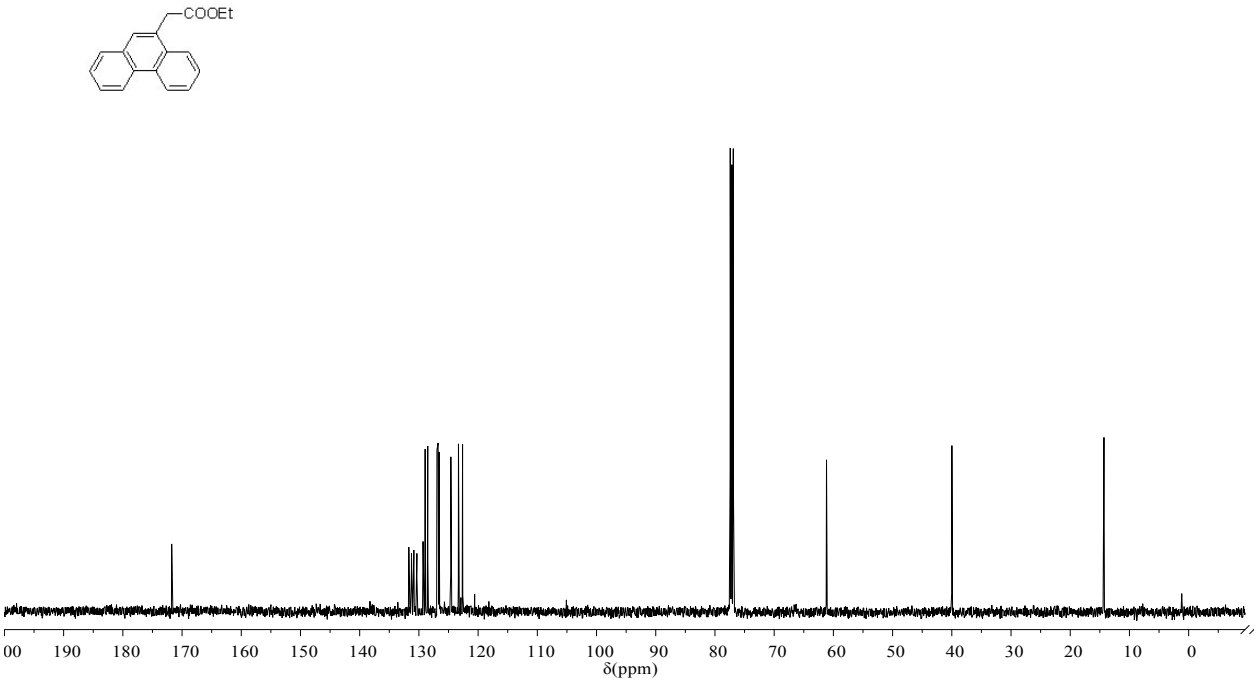


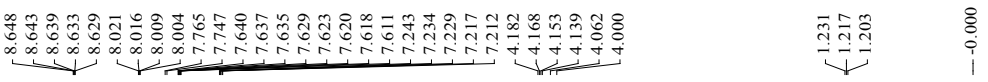
5a, ^{1}H NMR
500 MHz, $CDCl_3$



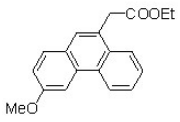


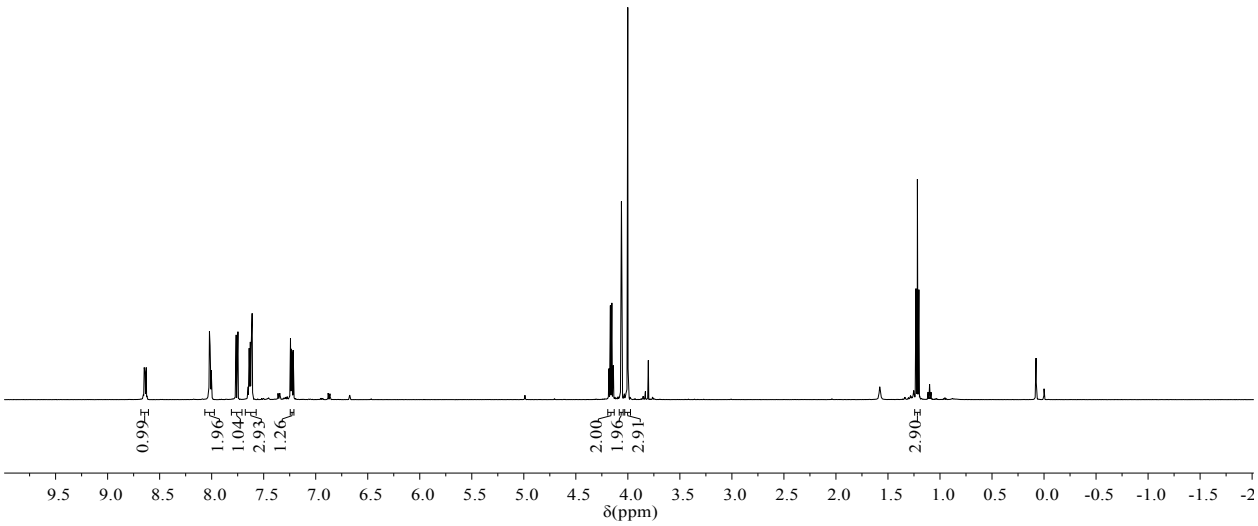
5a, ^{13}C NMR
125 MHz, $CDCl_3$



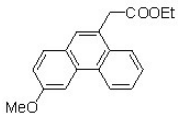


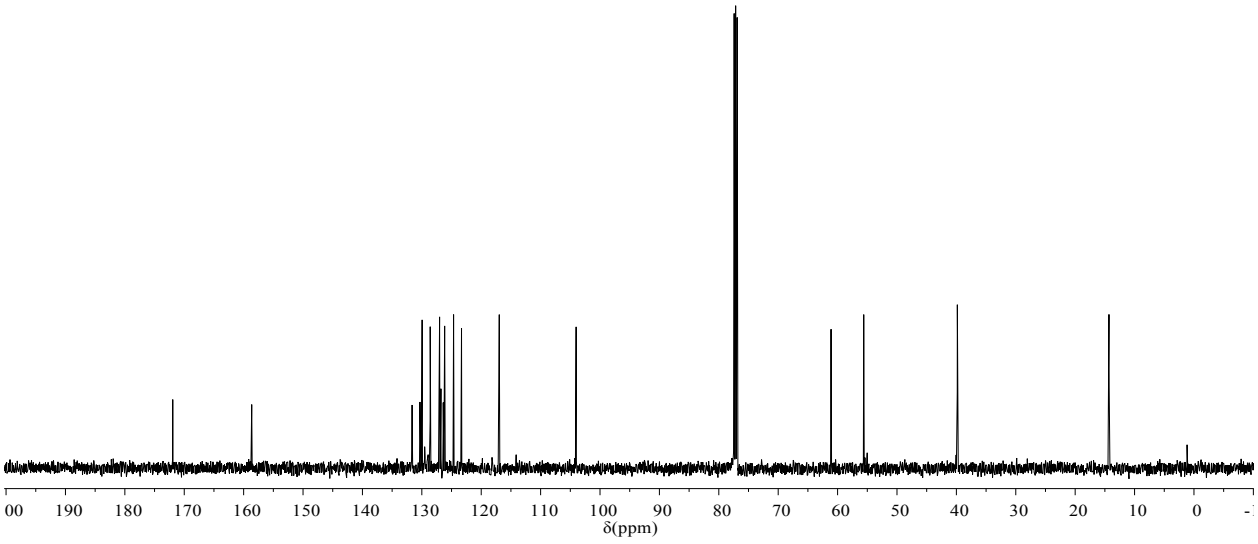
5b, ^{1}H NMR
500 MHz, $CDCl_3$

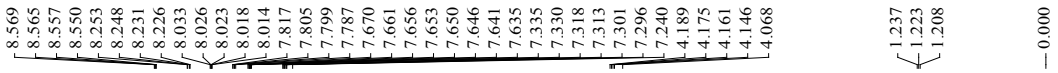




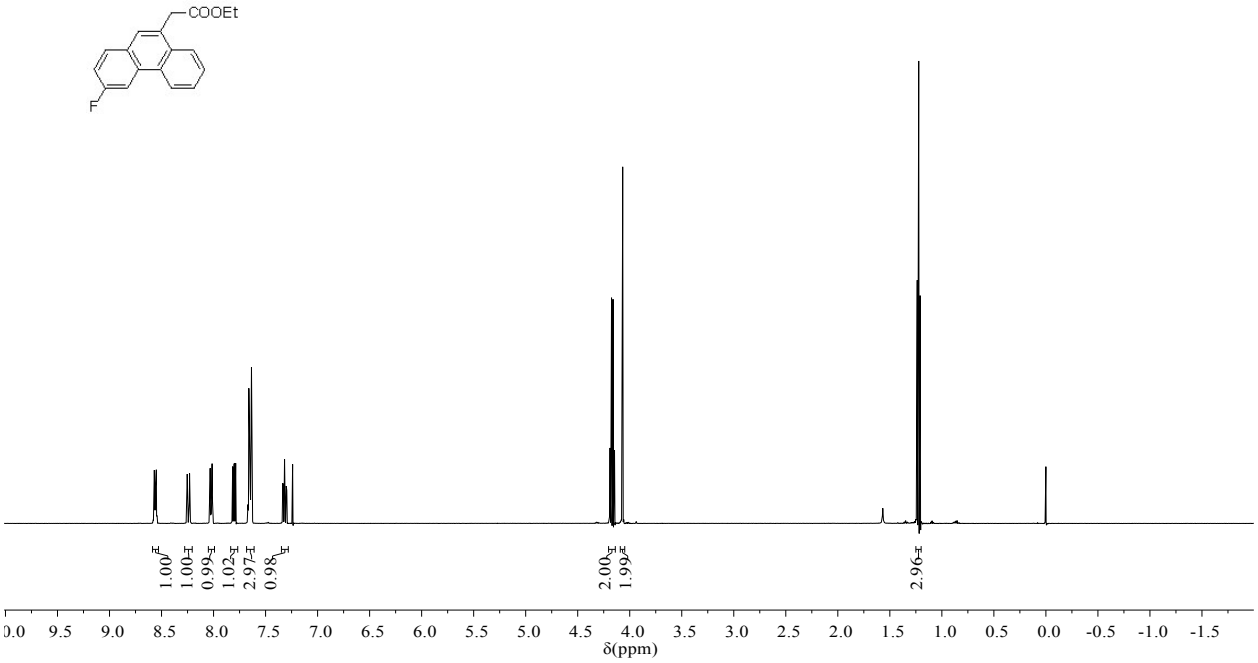
5b, ^{13}C NMR
125 MHz, $CDCl_3$

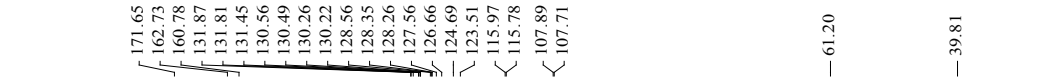




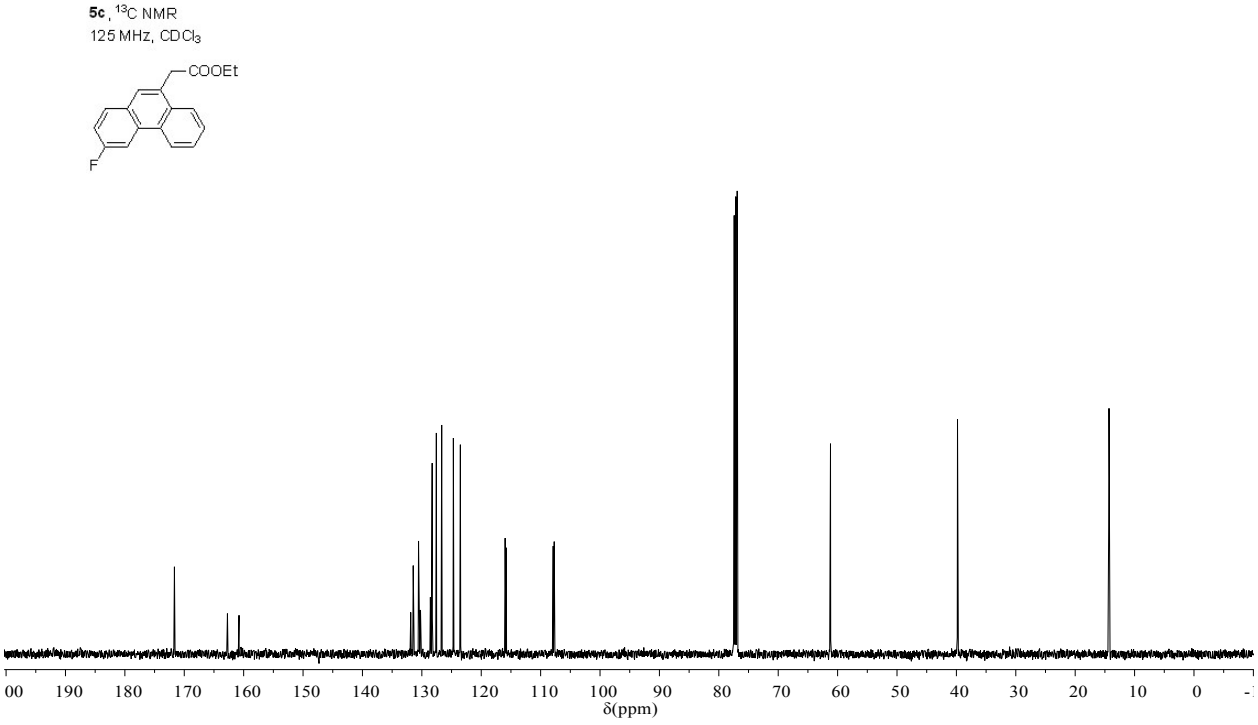


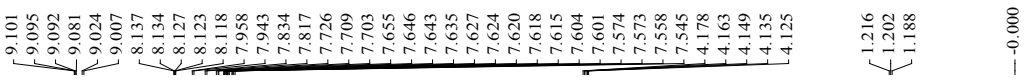
5c, ^{1}H NMR
500 MHz, $CDCl_3$



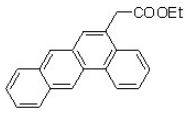


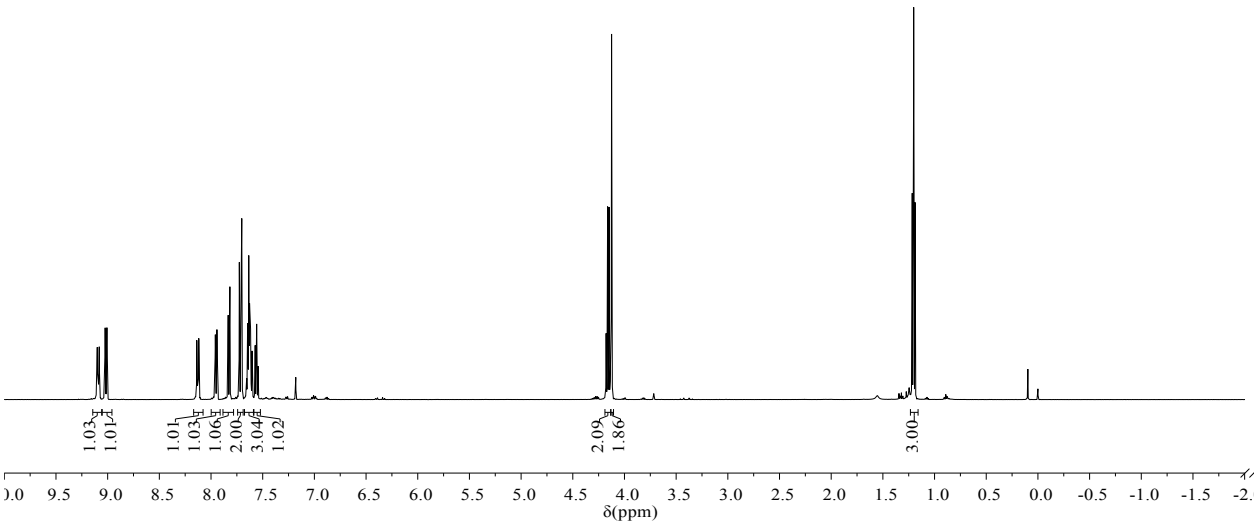
5c, ^{13}C NMR
125 MHz, $CDCl_3$



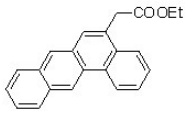


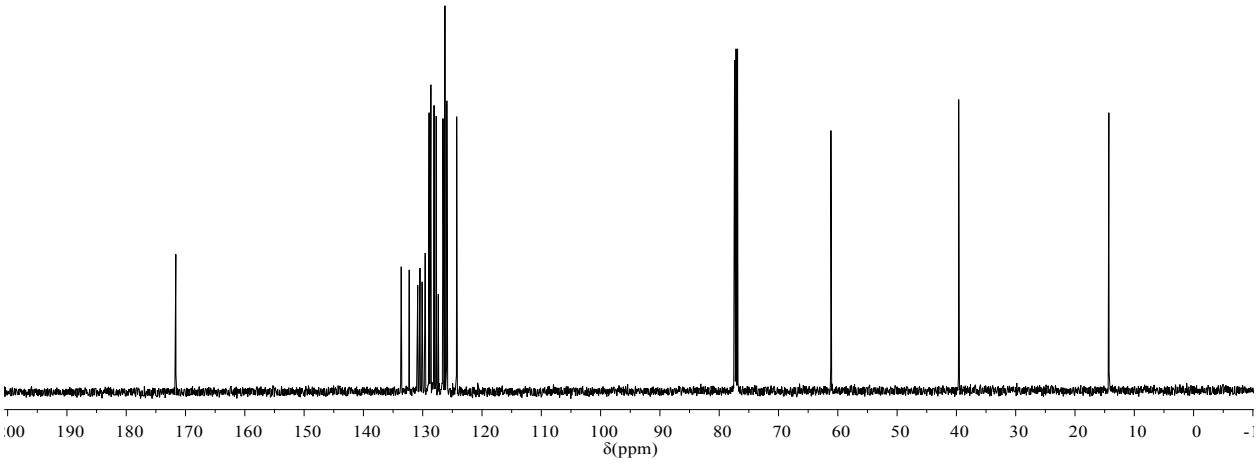
5d, ^{1}H NMR
500 MHz, $CDCl_3$

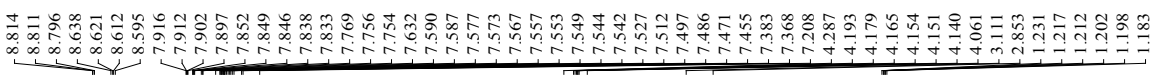


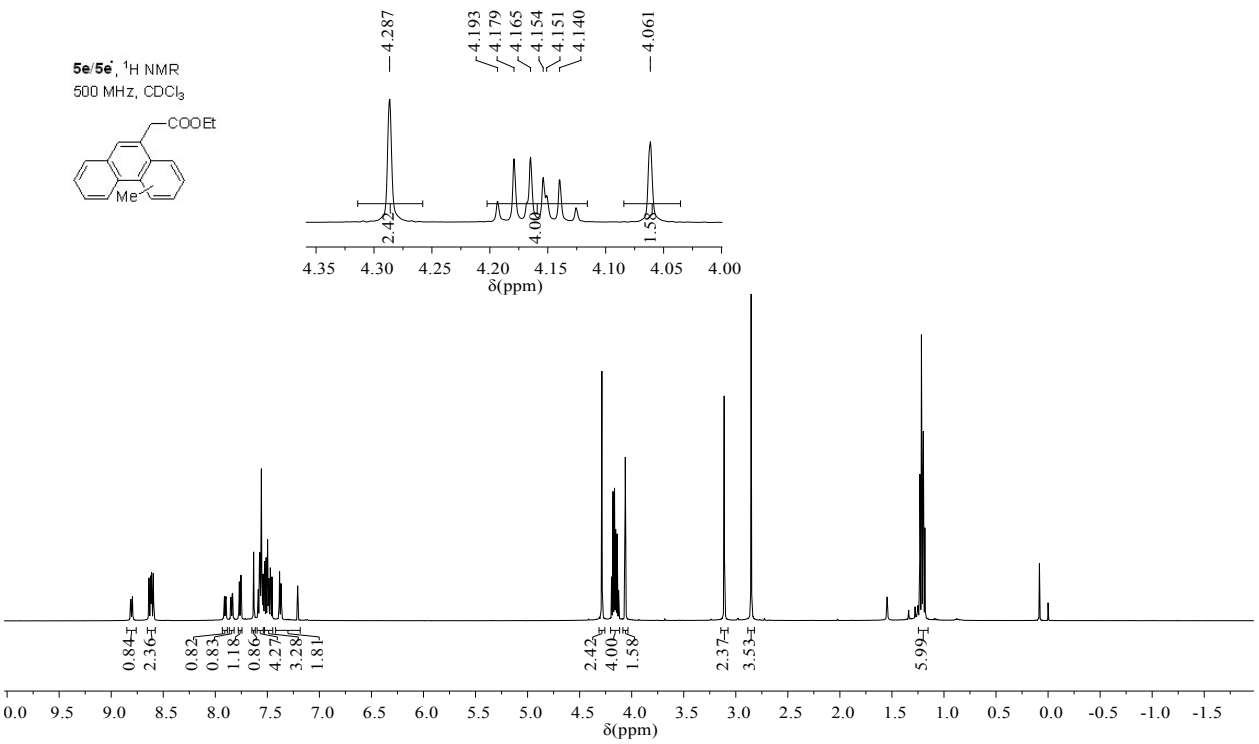


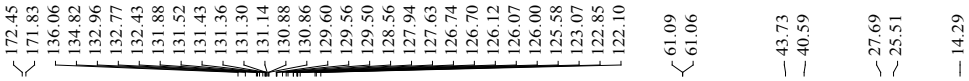
5d, ^{13}C NMR
125 MHz, $CDCl_3$

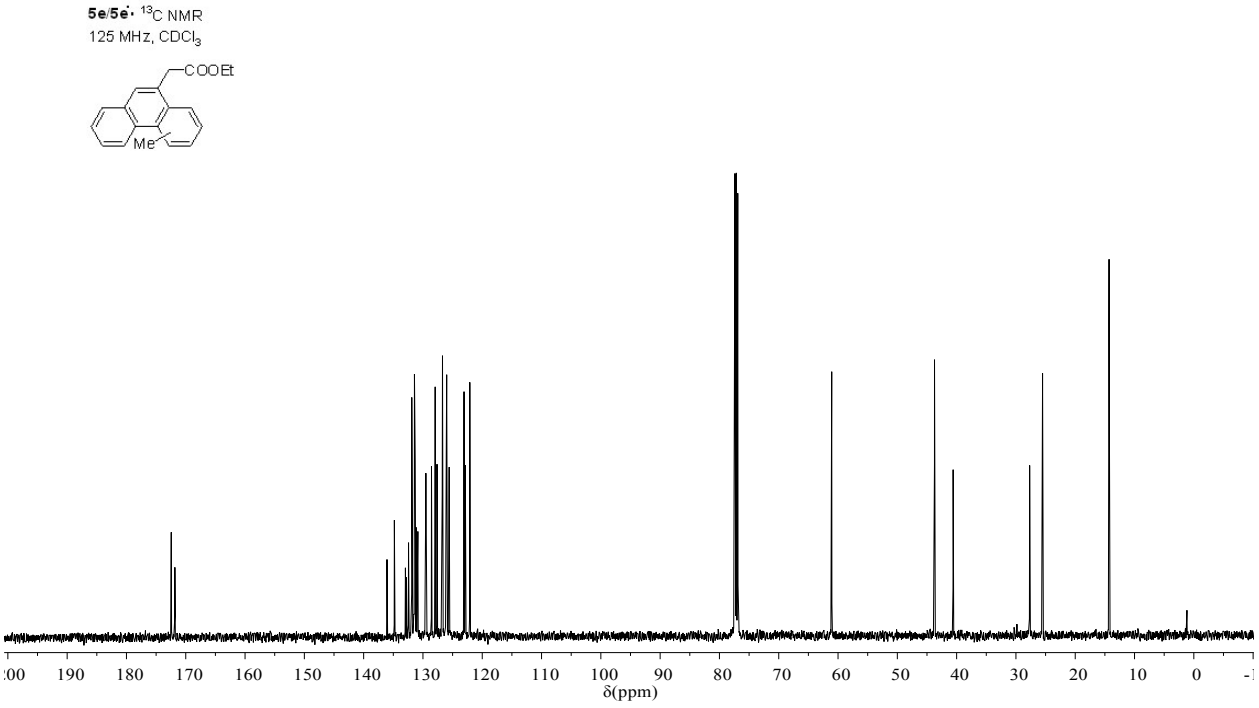




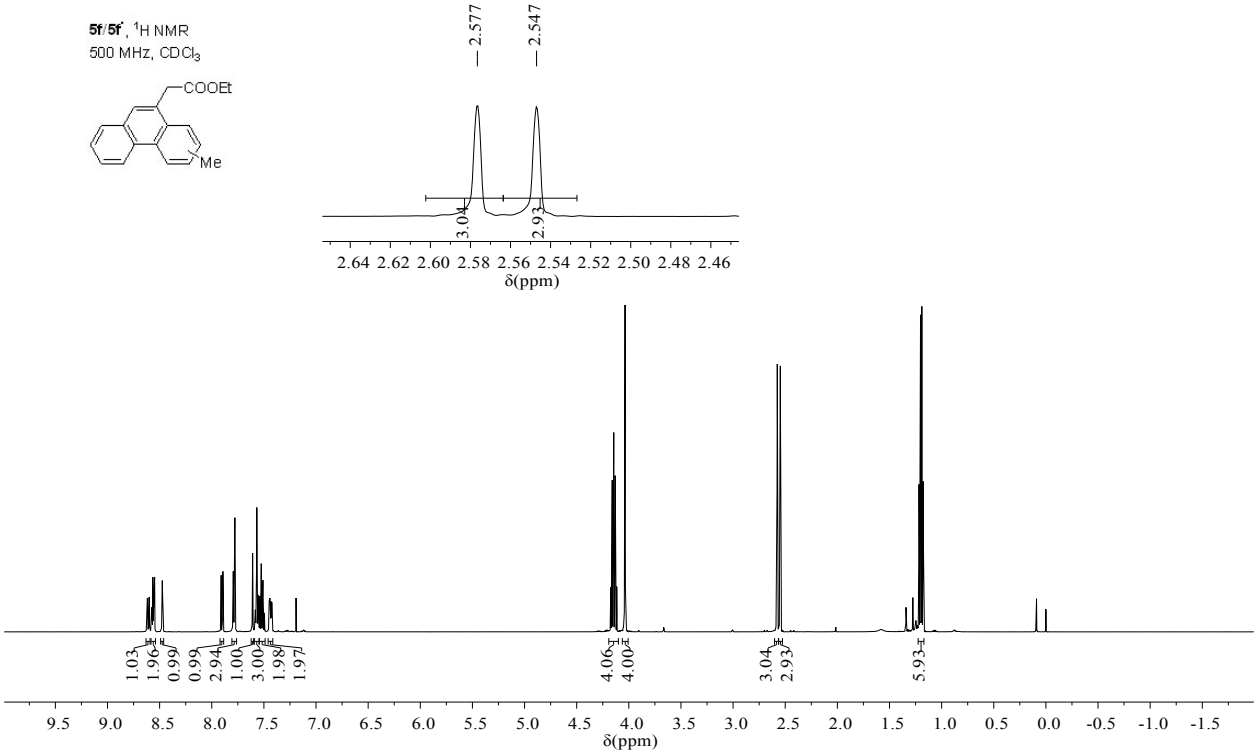

8.814
8.811
8.796
8.638
8.621
8.612
8.595
7.916
7.912
7.902
7.897
7.852
7.849
7.846
7.838
7.833
7.769
7.756
7.754
7.632
7.590
7.587
7.577
7.573
7.567
7.557
7.553
7.549
7.544
7.542
7.527
7.512
7.497
7.486
7.471
7.455
7.383
7.368
7.208
4.287
4.193
4.179
4.165
4.154
4.151
4.140
4.061
3.111
2.853
1.231
1.217
1.212
1.202
1.198
1.183

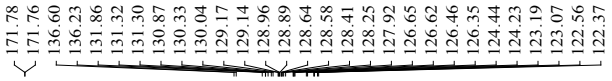

5e/5e', 1H NMR
500 MHz, CDCl3
COOEt
Me
4.287
4.193
4.179
4.165
4.154
4.151
4.140
4.061
2.42
4.00
1.58
δ(ppm)
0.84
2.36
0.82
0.83
1.18
0.86
4.27
3.28
1.81
2.42
4.00
1.58
2.37
3.53
5.99
δ(ppm)

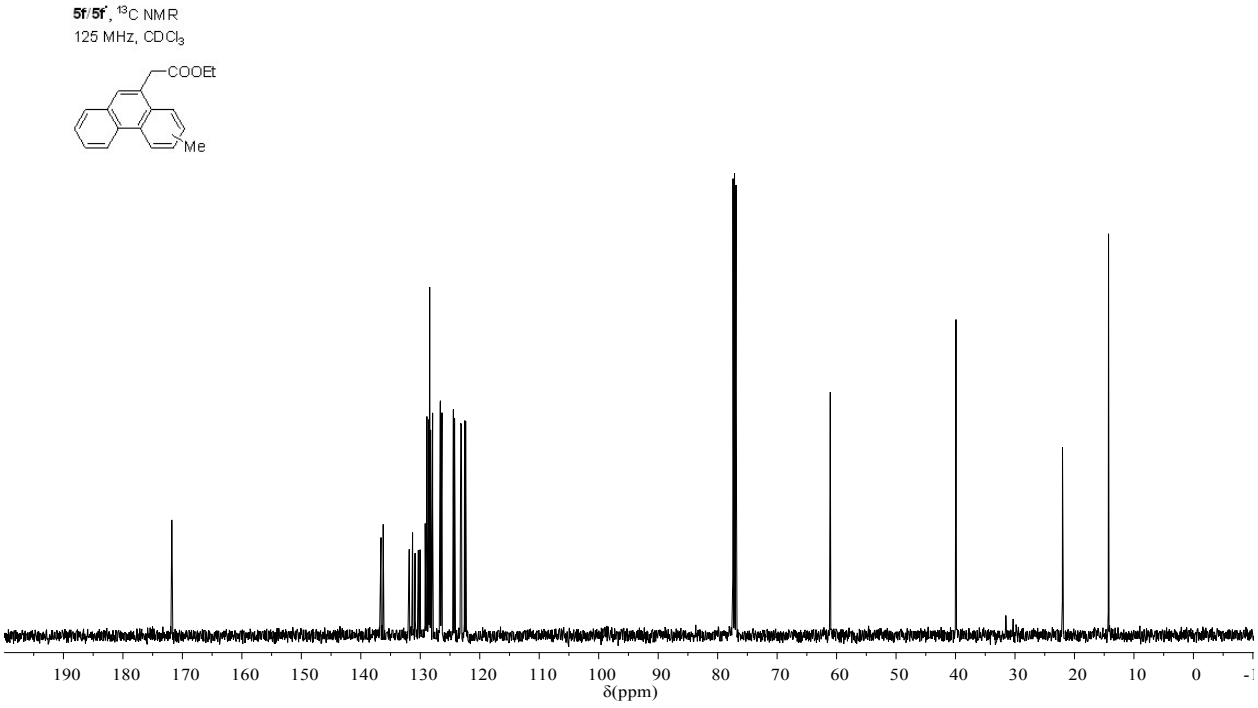

172.45
171.83
136.06
134.82
132.96
132.77
132.43
131.88
131.52
131.43
131.36
131.30
131.14
130.88
129.60
129.56
129.50
128.56
127.94
127.63
126.74
126.70
126.12
126.07
126.00
125.58
123.07
122.85
122.10
61.09
61.06
43.73
40.59
27.69
25.51
14.29

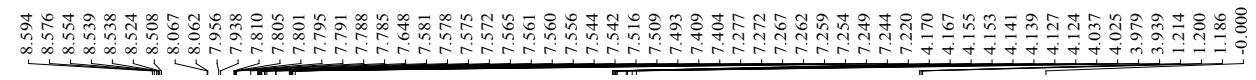

5e/5e' 13C NMR
125 MHz, CDCl3
COOEt
Me
δ(ppm)


8.602
8.601
8.573
8.565
8.558
8.557
8.548
7.910
7.893
7.794
7.781
7.778
7.608
7.587
7.585
7.582
7.579
7.574
7.568
7.563
7.557
7.554
7.552
7.549
7.541
7.538
7.525
7.523
7.511
7.509
7.496
7.493
7.450
7.447
7.441
7.438
7.433
7.430
7.425
7.422
4.174
4.159
4.145
4.130
4.116
4.036
2.577
2.547
1.216
1.204
1.202
1.190
1.188
1.175

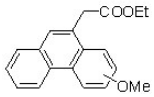

5f/5f', 1H NMR
500 MHz, CDCl3
COOEt
Me
2.577
2.547
3.04
2.93
2.64 2.62 2.60 2.58 2.56 2.54 2.52 2.50 2.48 2.46
δ(ppm)
1.03
1.96
0.99
0.99
2.94
1.00
3.00
1.98
1.97
4.06
4.00
3.04
2.93
5.93
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
δ(ppm)

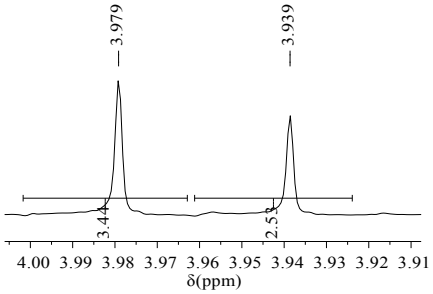

171.78
171.76
136.60
136.23
131.86
131.32
131.30
130.87
130.33
130.04
129.17
129.14
128.96
128.89
128.64
128.58
128.41
128.25
127.92
126.65
126.62
126.46
126.35
124.44
124.23
123.19
123.07
122.56
122.37
61.06
61.04
39.92
22.01
21.93
14.27

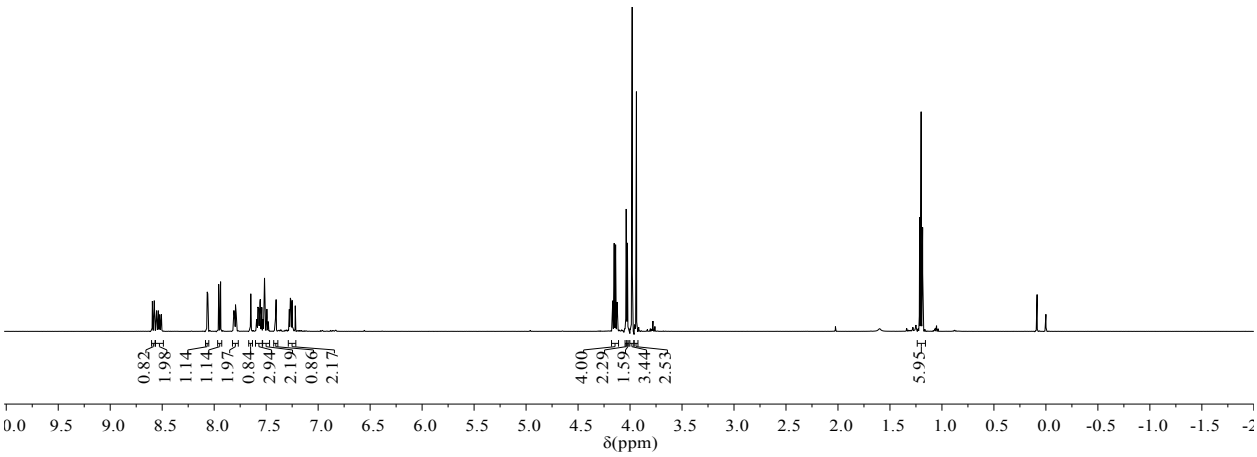

5f/5f', 13C NMR
125 MHz, CDCl3
COOEt
Me
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ(ppm)

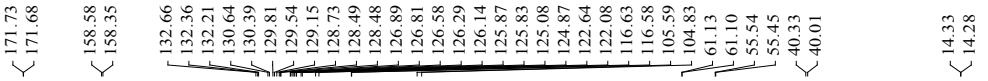


5g/**5g'**, ^{1}H NMR
500 MHz, $CDCl_3$

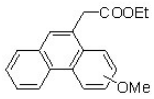


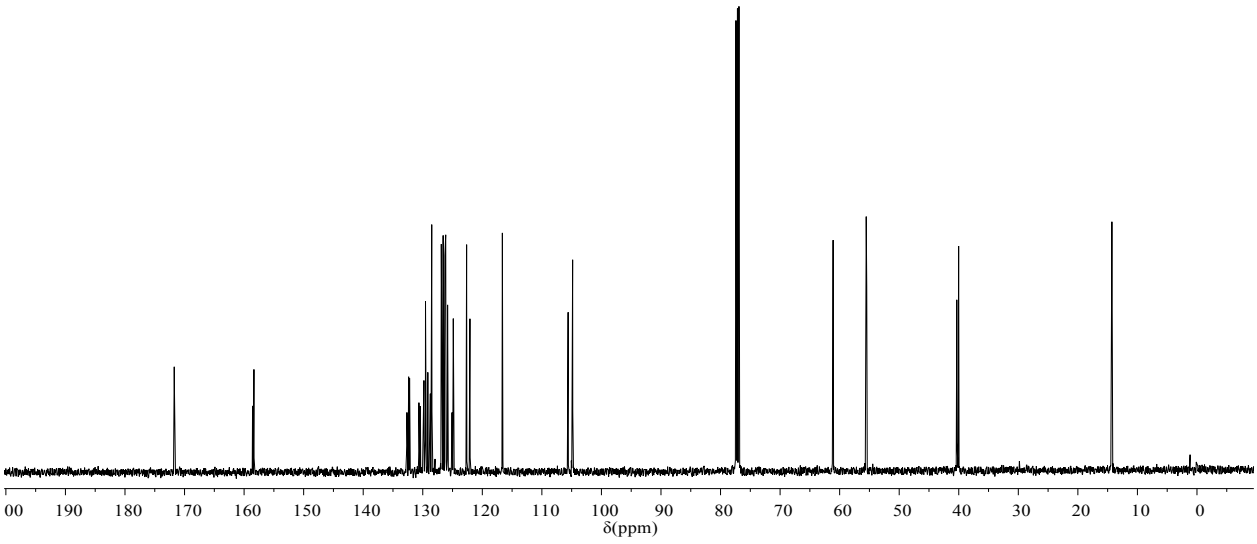


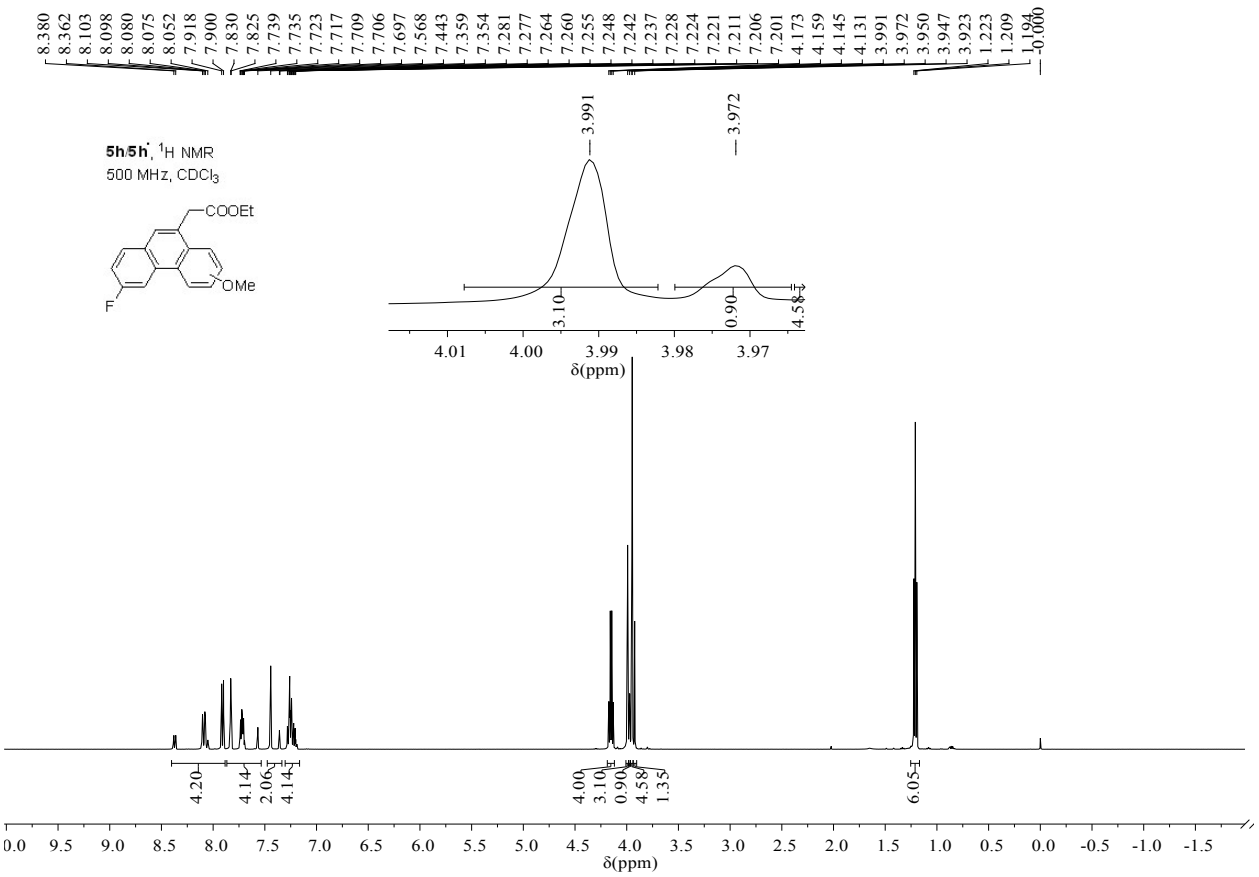


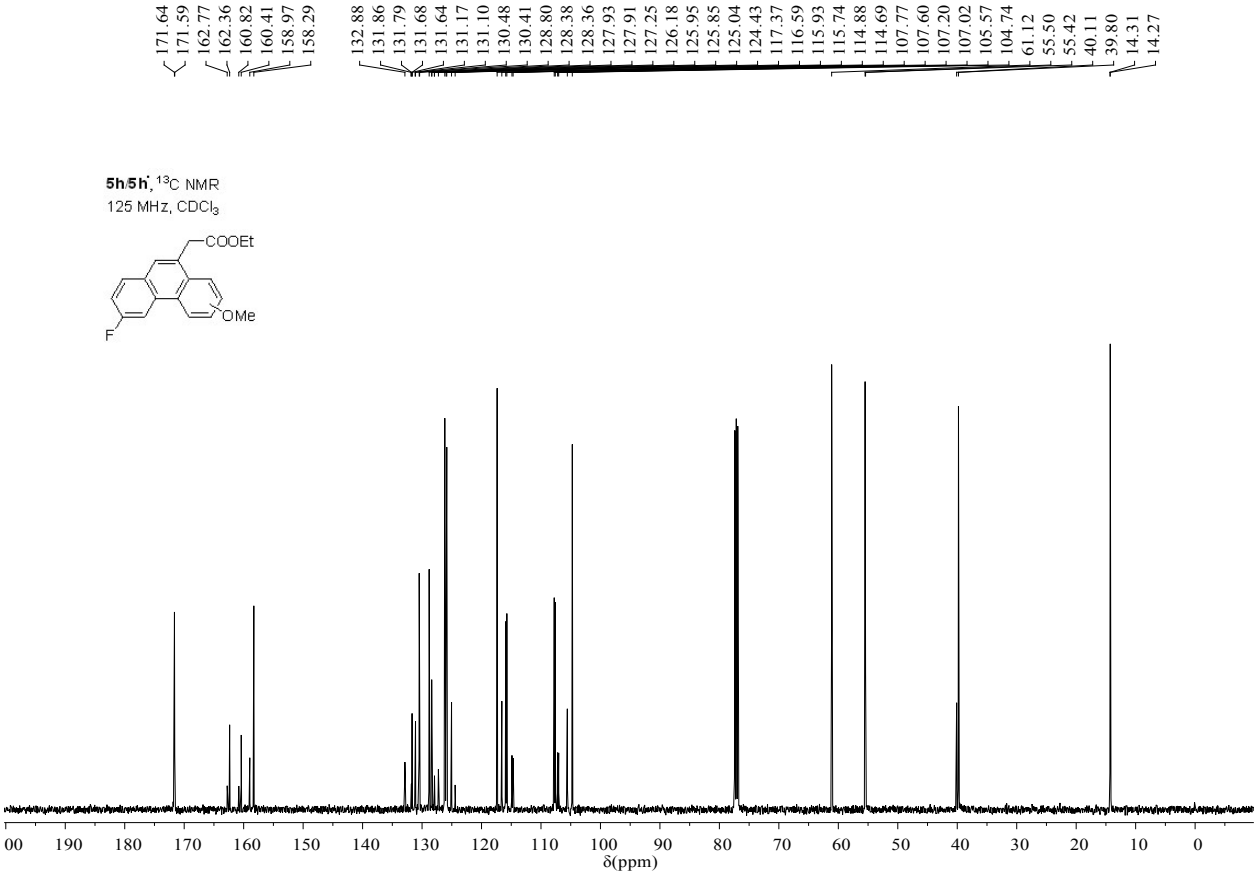


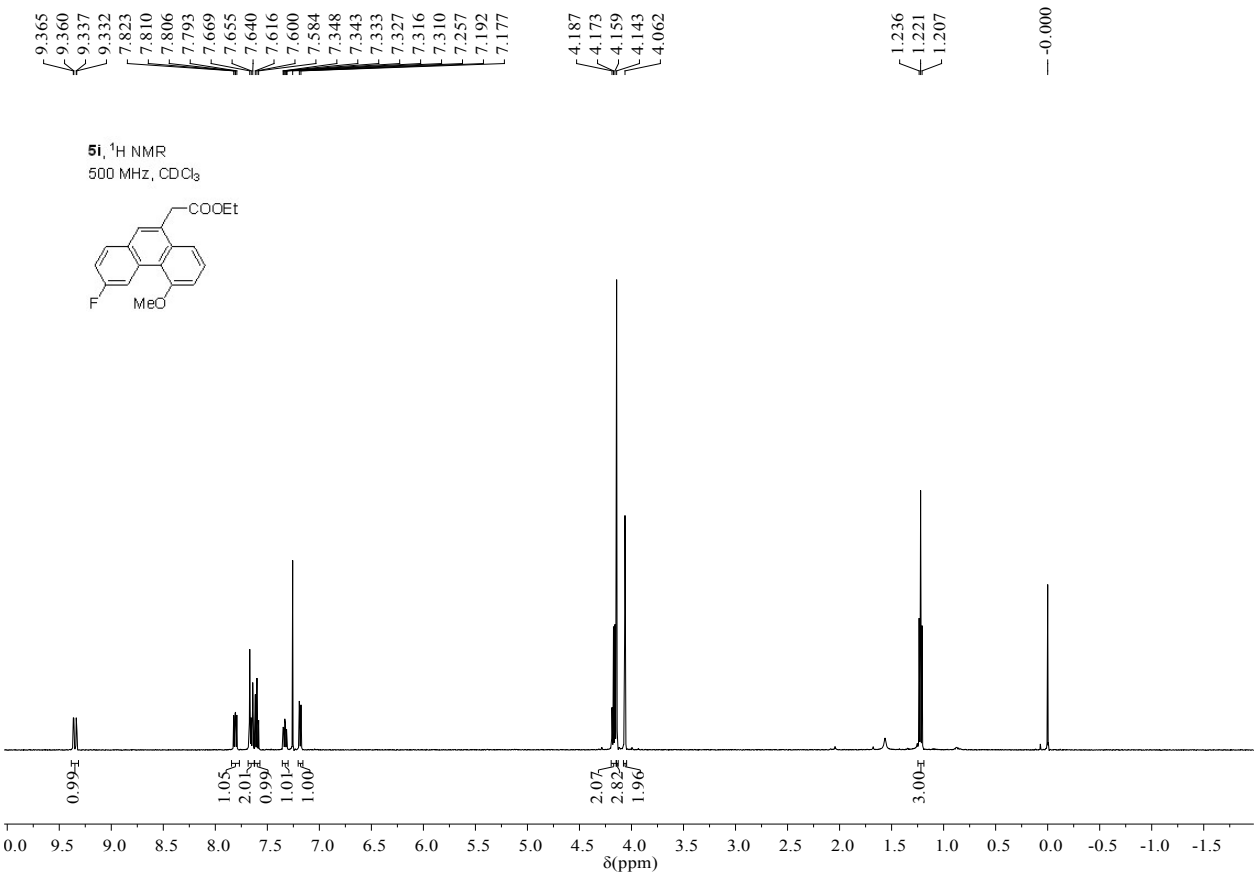
5g/**5g'**, ^{13}C NMR
125 MHz, $CDCl_3$

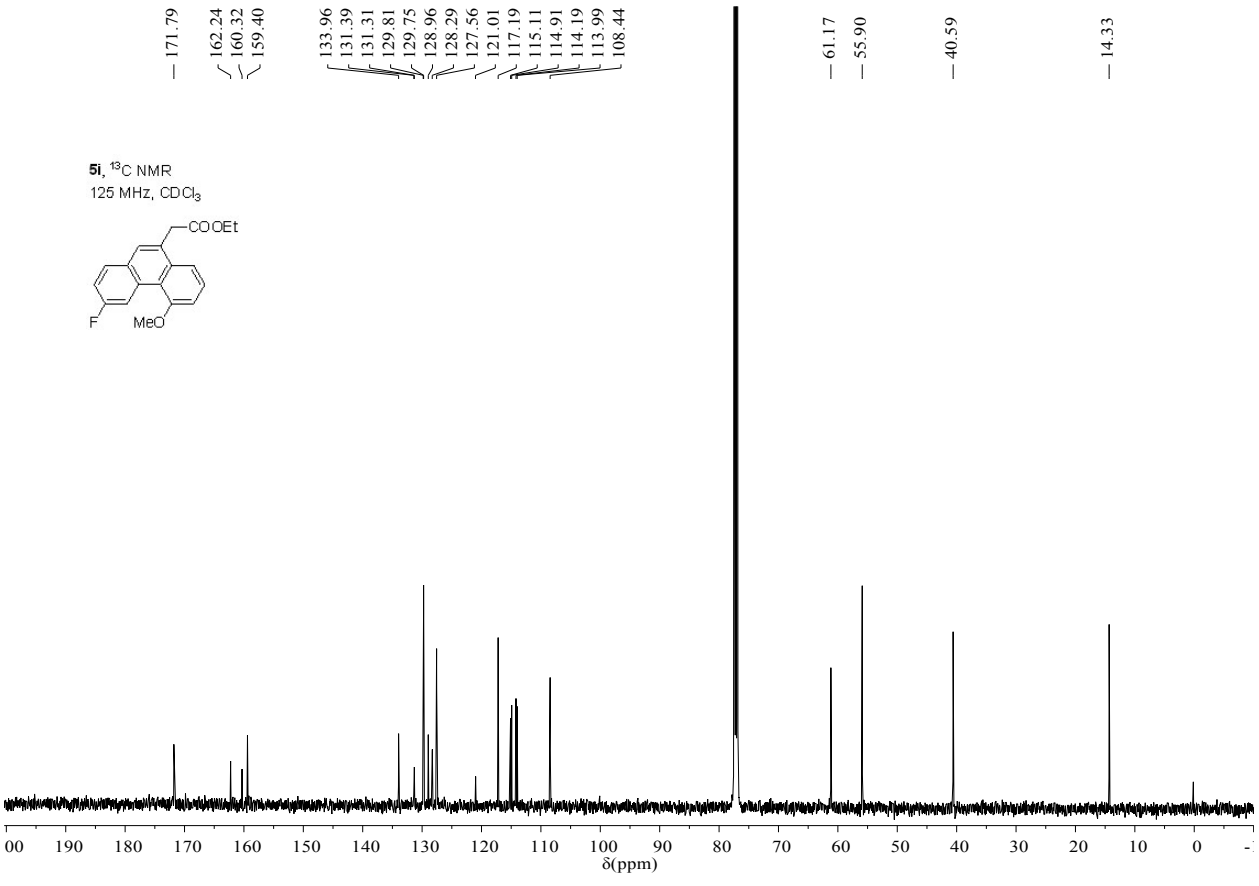


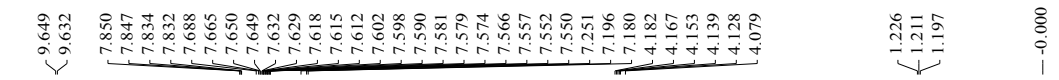



8.380
8.362
8.103
8.098
8.080
8.075
8.052
7.918
7.900
7.830
7.825
7.739
7.735
7.723
7.717
7.709
7.706
7.697
7.568
7.443
7.359
7.354
7.281
7.277
7.264
7.260
7.255
7.248
7.242
7.237
7.228
7.224
7.221
7.211
7.206
7.201
4.173
4.159
4.145
4.131
3.991
3.972
3.950
3.947
3.923
1.223
1.209
1.194
0.000
5h/5h', 1H NMR
500 MHz, CDCl3
COOEt
OMe
F
3.991
3.972
3.10
0.90
4.58
4.01
4.00
3.99
3.98
3.97
δ(ppm)
4.20
4.14
2.06
4.14
4.00
3.10
0.90
4.58
1.35
6.05
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
δ(ppm)

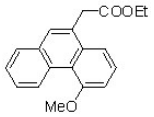

171.64
171.59
162.77
162.36
160.82
160.41
158.97
158.29
132.88
131.86
131.79
131.68
131.64
131.17
131.10
130.48
130.41
128.80
128.38
128.36
127.93
127.91
127.25
126.18
125.95
125.85
125.04
124.43
117.37
116.59
115.93
115.74
114.88
114.69
107.77
107.60
107.20
107.02
105.57
104.74
61.12
55.50
55.42
40.11
39.80
14.31
14.27
5h/5h', 13C NMR
125 MHz, CDCl3
COOEt
OMe
F
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
δ(ppm)

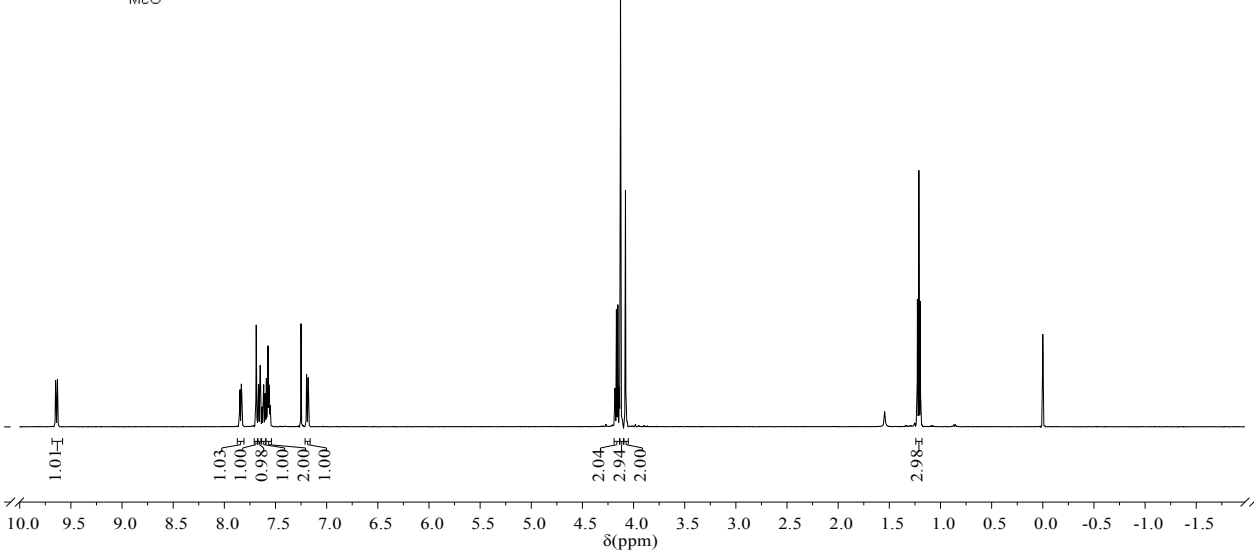

9.365
9.360
9.337
9.332
7.823
7.810
7.806
7.793
7.669
7.655
7.640
7.616
7.600
7.584
7.348
7.343
7.333
7.327
7.316
7.310
7.257
7.192
7.177
4.187
4.173
4.159
4.143
4.062
1.236
1.221
1.207
-0.000
5i, 1H NMR
500 MHz, CDCl3
COOEt
F
MeO
0.99
1.05
2.01
0.99
1.01
1.00
2.07
2.82
1.96
3.00
δ(ppm)


171.79
162.24
160.32
159.40
133.96
131.39
131.31
129.81
129.75
128.96
128.29
127.56
121.01
117.19
115.11
114.91
114.19
113.99
108.44
61.17
55.90
40.59
14.33
5i, 13C NMR
125 MHz, CDCl3
COOEt
F
MeO
δ(ppm)

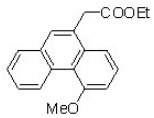


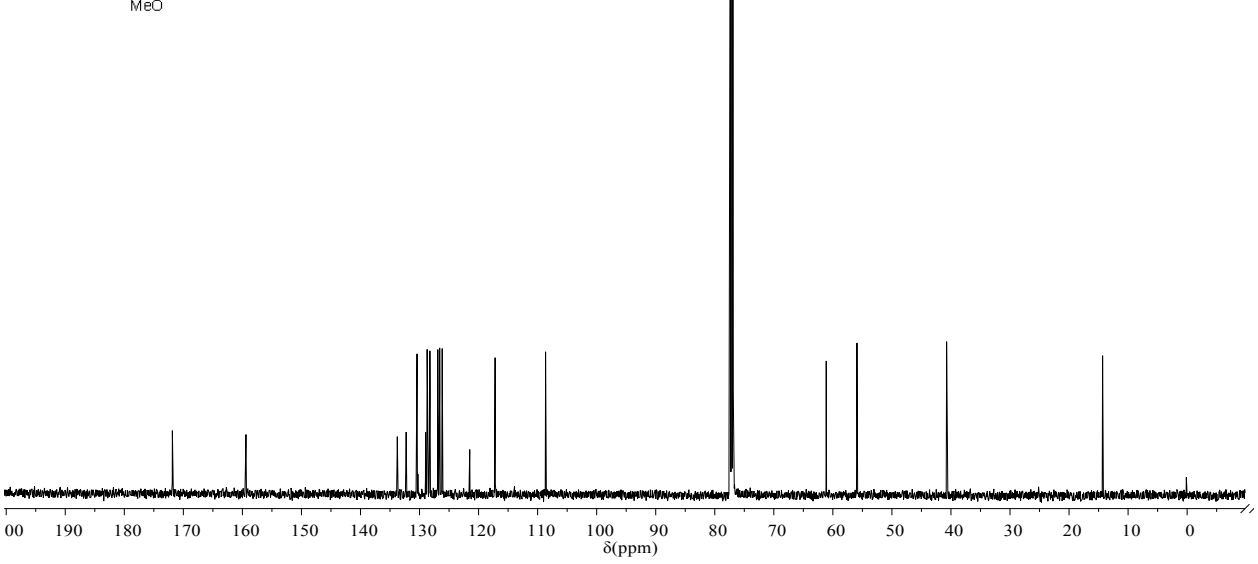
5j, ^{1}H NMR
500 MHz, $CDCl_3$





5j, ^{13}C NMR
125 MHz, $CDCl_3$





5. Computational Details

Geometry optimizations and frequency calculations were performed at B3LYP-D3(BJ)/6-31G** level,[1] D3 denoting Grimme's dispersion interaction correction method. Single-point energies were calculated at B3LYP-D3(BJ)/6-311+G(2d,p) level using the SMD model with 1,4-dioxane as solvent.[2] All calculations were performed using the Gaussian 09 package.[3]

1. (*a*) C. Lee, W. Yang and R. G. Parr, *Phys. rev. B*, 1988, **37**, 785–789; (*b*) A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648–5652; (*c*) S. Grimme, S. Ehrlich and L. Goerigk, *J. Comput. Chem.*, 2011, **32**, 1456–1465; (*d*) S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *J. Chem. Phys.*, 2010, **132**, 154104; (*e*) P. C. Hariharan and J. A. Pople, *Theoret. Chimica Acta.*, 1973, **28**, 213–222; (*f*) M. M. Francl, W. J. Pietro, W. J. Hehre, J. S. Binkley, M. S. Gordon, D. J. DeFrees and J. A. Pople, *J. Chem. Phys.*, 1982, **77**, 3654–3665.

2. (*a*) R. Krishnan, J. S. Binkley, R. Seeger and J. A. Pople, *J. Chem. Phys.*, 1980, **72**, 650–654. (*b*) A. V. Marenich, C. J. Cramer and D. G. Truhlar, *J. Phys. Chem. B*, 2009, **113**, 6378–6396.

3. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian 09, *Revision E.01*, 2009, Gaussian, Inc., Wallingford CT.

Calculated Energy Values

Table S1. Energies (in kcal/mol) calculated at B3LYP+D3(BJ)/6-311+G(2d,p)

Species	E_{elec} / a.u.	G_{corr} / a.u.	G / (kcal/mol)
IN1	-1420.869734	0.386256	-891367.587023
3a	-615.156093232	0.166379	-385912.195578
TS1	-2036.039048	0.576898	-1277272.853452
IN2	-2036.163991	0.590639	-1277342.633844
TS2	-2036.115008	0.581015	-1277317.936035
4a	-2036.217179	0.589587	-1277376.670319

IN3	-231.003792	0.047657	-144927.284375
TS3	-846.168865	0.234513	-530832.265156
IN4	-846.317880	0.246410	-530918.308046
TS4	-846.263709	0.241612	-530887.326111
TS5	-846.230249	0.242218	-530865.949512
F^-	-100.028418	-0.014159	-62777.717609
IN5	-946.3894731	0.243754	-593715.900200
TS6	-946.392925	0.241462	-593712.304708
IN6	-846.365432	0.248332	-530946.941523
5a	-846.386809	0.247540	-530960.852570

Cartesian Coordinates for All Species

IN1

C 1.27182300 -1.96552600 -0.80393500
C 0.47968700 -0.81007000 -0.65093500
C -0.93595500 -0.83725700 -0.56682500
C -1.66878500 -2.08298000 -0.64851800
C -0.76393200 -3.12812200 -0.77524700
C 0.48204900 -3.10000300 -0.86921100
C -1.60539100 0.39414200 -0.33508100
C -2.14128000 1.46400400 -0.11467400
C -2.83825600 2.67962500 0.13204700
C -2.15403900 3.91078200 0.16313100
C -2.85223700 5.09098800 0.40293000
C -4.23346500 5.06282200 0.61423600
C -4.91876500 3.84489300 0.58535400
C -4.23163200 2.65832500 0.34691600
C -3.13041900 -2.24184600 -0.55676100
C -3.64257800 -3.41611800 0.02354900
C -5.01566800 -3.62008800 0.12845300
C -5.90611200 -2.65757200 -0.35447000
C -5.40960100 -1.49773000 -0.95258500
C -4.03478900 -1.28935300 -1.05636400
C 2.73580800 -1.64821600 -0.87776800
C 2.79832200 -0.16391900 -0.39278800
C 1.36007900 0.41184000 -0.60491400
C 3.85651000 0.63955100 -1.14189100
C 3.12445000 -0.04372500 1.09737700
O 5.04764300 0.03250900 -1.04544500
O 2.59735200 -1.04655800 1.80423600
O 3.65142500 1.67003800 -1.74925900
O 3.73427000 0.89143300 1.57985000
C 6.18929000 0.72093200 -1.62845500
C 2.74825700 -0.97924600 3.24999500
C 6.72674600 1.77152200 -0.67640900
C 2.01739900 -2.16932700 3.82867900
H -1.08178300 3.92760700 -0.00209700
H -2.31742100 6.03548300 0.42522200
H -4.77328600 5.98587100 0.80169800
H -5.99154300 3.82003000 0.75030400
H -4.75739500 1.70934000 0.32535300
H -2.94958800 -4.16220500 0.40174800
H -5.39124100 -4.52913300 0.58834100
H -6.97728200 -2.81484500 -0.27292300
H -6.09361000 -0.75425300 -1.35071500
H -3.66525400 -0.39721200 -1.54505800
H 3.35223400 -2.30986900 -0.26750500
H 3.09268800 -1.72488300 -1.91114900
H 1.07419400 1.11447000 0.18257100
H 1.32648800 0.96397500 -1.54970800
H 6.91738800 -0.07203300 -1.80705300
H 5.88719500 1.15472000 -2.58386500
H 3.81559000 -0.99420900 3.48727400
H 2.33158700 -0.02966900 3.59634100
H 7.62678000 2.22463400 -1.10455900
H 5.98985500 2.56107000 -0.50850200
H 6.98935100 1.32393900 0.28657600
H 2.10567400 -2.15438400 4.91926200
H 0.95538000 -2.14014600 3.56739500
H 2.44339200 -3.10764500 3.46097900

3a

C 4.68222200 -0.30126300 -0.02660900
C 3.52947900 -1.06128600 -0.22379300
C 2.26653800 -0.44969800 -0.24255200
C 2.18117500 0.94129100 -0.05883200
C 3.33314500 1.69665600 0.13748300
C 4.58861500 1.07939400 0.15435000

H 5.65239900 -0.78878900 -0.01433100
H 3.60145900 -2.13596600 -0.36472200
H 1.20862600 1.42448900 -0.06914200
H 3.25371400 2.77041600 0.27879600
H 5.48523700 1.67193200 0.30826200
C 1.07218600 -1.28691900 -0.45195700
H 1.24440300 -2.35724500 -0.57054300
C -0.16529800 -0.86203600 -0.50453000
C -1.40668700 -0.43673100 -0.56051800
H -1.83367000 -0.15141300 -1.51731900
C -2.22406000 -0.34625000 0.68299400
O -1.79485600 -0.61838600 1.78914100
C -4.11171300 0.38635200 -0.70291300
H -3.57120300 1.22108500 -1.16008000
H -4.05096400 -0.48243600 -1.36585100
O -3.50517000 0.06212700 0.57491400
C -5.55245100 0.75948700 -0.42691600
H -6.04973600 1.01180100 -1.36848200
H -6.08902000 -0.07411400 0.03572100
H -5.60994600 1.62634000 0.23800600

TS1

C -0.26711500 -4.40359900 0.58786000
C -1.29716300 -3.50984900 0.24600100
C -1.59122000 -3.25362700 -1.11803000
C -0.78311000 -3.85091500 -2.10849600
C 0.25430700 -4.70070700 -1.75584400
C 0.51178100 -4.98420400 -0.40292600
H -0.07993600 -4.62451000 1.63378700
H -1.97776600 -3.15956100 1.01200900
H -0.98860500 -3.63952500 -3.15355000
H 0.86650500 -5.15421400 -2.52913900
H 1.31696800 -5.66187500 -0.13670400
C -2.64628500 -2.34674300 -1.50305400
H -2.79265100 -2.17462100 -2.56963900
C -3.34219500 -1.58911800 -0.66118700
C -4.33872000 -1.09755700 0.04514500
H -4.28618100 -0.13320600 0.53449500
C -5.60712200 -1.85994400 0.18571300
O -5.84584400 -2.95530600 -0.28931400
C -7.77790100 -1.76944400 1.14402400
H -8.24255200 -1.95842800 0.17168900
H -7.63010100 -2.73256700 1.64151400
C 0.95506600 -1.06148000 0.65123100
C -0.40190800 -1.25622600 0.52024800
C -1.29619200 -0.37170900 0.32292100
C -1.04591300 0.99194800 0.19910100
C 0.35481200 1.31144700 0.30097100
C 1.31072600 0.29394900 0.51714100
C -8.59688400 -0.81681200 1.98662800
H -9.58557300 -1.24947200 2.16816200
H -8.11721800 -0.63637100 2.95342600
H -8.72911600 0.14251400 1.47715200
O -6.48231700 -1.15421900 0.92812200
C 2.15237200 -1.93477700 0.89641700
H 2.20039600 -2.23966100 1.94776000
H 2.15047100 -2.84227900 0.29425300
C 2.80147000 0.45998600 0.65754800
H 3.23160000 1.12512000 -0.09672400
H 3.06880000 0.87595000 1.63452200
C 3.35448700 -0.99844900 0.54867500
C 3.84634600 -1.20358800 -0.88476600
C 4.54762900 -1.23449200 1.46774200
O 5.01133500 -1.11373300 -1.22233600
O 5.11688600 -0.37926100 2.11437000
O 4.87791200 -2.53219500 1.47646000
O 2.83168500 -1.42467700 -1.72509100
C 6.02386500 -2.90486000 2.28838300
H 6.89799400 -2.35793000 1.92351900
H 5.83421500 -2.59842600 3.32081600
C 6.19693700 -4.40165400 2.16231800
H 7.05594800 -4.71984100 2.76095100
H 5.30989600 -4.93032900 2.52421400
H 6.37639000 -4.68917000 1.12199000
C 3.15654700 -1.51789800 -3.13957500
H 3.75813500 -2.41784500 -3.29652200
H 3.75908600 -0.64858500 -3.41532000
C 1.84633500 -1.56829300 -3.89196000
H 1.25669400 -0.66543200 -3.70651100
H 2.04504600 -1.63831700 -4.96576700
H 1.25637900 -2.43752300 -3.58985200
C -2.08385300 2.03448900 0.02079600
C -2.02445500 2.95319700 -1.03785800
C -3.15230300 2.11564200 0.92711200
C -3.01286700 3.92648200 -1.18718400
H -1.20916900 2.89592800 -1.75092700
C -4.13998400 3.08895400 0.77804700
H -3.19225300 1.42005800 1.76010600
C -4.07260700 3.99832600 -0.27987900
H -2.95779500 4.62476200 -2.01705500
H -4.95791300 3.13976700 1.49052600
H -4.84083300 4.75659800 -0.39742000
C 0.79530100 2.66047400 0.21225600
C 1.17071900 3.81602700 0.14811100

C 1.54173800 5.18661200 0.05209300
C 2.89195700 5.57905800 0.14030200
C 0.54893400 6.17025700 -0.13589000
C 3.23599000 6.92453400 0.04236000
H 3.65687700 4.82299100 0.28418400
C 0.90496000 7.51231300 -0.23226900
H -0.49079100 5.86719900 -0.20521700
C 2.24667500 7.89405800 -0.14334500
H 4.27897800 7.21807300 0.11146600
H 0.13392900 8.26298300 -0.37666300
H 2.51995800 8.94203700 -0.21852000

IN2

C 0.80633900 -1.19114700 -0.69938600
C 0.47626900 0.15896100 -0.76568000
C -0.83062900 0.59577300 -0.51016300
C -1.86223900 -0.36847100 -0.35543300
C -1.54922000 -1.74078000 -0.44382000
C -0.19036400 -2.15082100 -0.44867600
C -1.08850800 1.98862000 -0.39773900
C -1.27773600 3.18536400 -0.28903100
C -1.57884400 4.56994800 -0.16274800
C -2.90518000 4.97911500 0.08628400
C -3.20623700 6.33247100 0.20690300
C -2.19806400 7.29282300 0.08277800
C -0.88127200 6.89413200 -0.16309900
C -0.56779500 5.54337100 -0.28550000
C -3.22742600 0.11415800 -0.00143400
C -3.81622300 -0.29968800 1.20161400
C -5.07743000 0.16681700 1.57372100
C -5.76670500 1.05674800 0.74832200
C -5.18655000 1.47914300 -0.45083500
C -3.92494100 1.01527800 -0.82081100
C 2.26693000 -1.36567300 -1.07101900
C 2.86385500 0.05543200 -0.87371200
C 1.66497000 1.01240100 -1.11186500
C 4.01664800 0.33618700 -1.83049100
C 3.44210900 0.15176200 0.54337700
O 4.48923700 1.57538000 -1.62349300
O 2.61788100 0.76061600 1.39829000
O 4.43568400 -0.43184600 -2.67132400
O 4.53140800 -0.29996200 0.83858800
C 5.66192700 1.97162500 -2.38755000
C 3.05057700 0.83114100 2.78342300
C 6.92612900 1.45585200 -1.72796000
C 1.98911400 1.59867200 3.53901400
C -2.65445900 -2.79680000 -0.54825100
C -2.14565000 -4.19983100 -0.83303600
C -0.85951900 -4.54198200 -0.59701600
C 0.11243300 -3.56667400 -0.14361400
C -3.77976500 -2.43314700 -1.50535500
C -4.56854100 -3.38315500 -2.03613400
C -4.29279900 -4.79554000 -1.82552000
C -3.11907100 -5.18220000 -1.27273500
C 1.16023900 -4.01389900 0.60353000
C 2.20280400 -3.28877300 1.35154400
O 3.35747800 -3.68700100 1.36084000
O 1.91261000 -2.17446900 2.06398800
C 0.61819100 -1.87447900 4.07455700
C 0.58726100 -1.85617400 2.55932400
H -3.68280800 4.22808500 0.18091300
H -4.22986900 6.63966100 0.39805600
H -2.43756400 8.34743600 0.17769300
H -0.09657100 7.63820400 -0.25946400
H 0.45300800 5.22843900 -0.47568700
H -3.27477100 -0.98007700 1.85187000
H -5.51756300 -0.16086200 2.51072000
H -6.74882700 1.41930900 1.03615200
H -5.71767600 2.16819600 -1.10060900
H -3.48157700 1.33864000 -1.75649800
H 2.83158700 -2.11689600 -0.52673600
H 2.33862300 -1.62914200 -2.13246300
H 1.73279700 1.92758300 -0.52409400
H 1.61911000 1.30217800 -2.16948000
H 5.62415800 3.06224600 -2.39220900
H 5.55661600 1.60300400 -3.40985200
H 3.16972700 -0.19044600 3.14985900
H 4.02231700 1.33114200 2.81860100
H 7.80020900 1.81821800 -2.27865500
H 6.94794400 0.36290100 -1.72676700
H 6.99623400 1.80991900 -0.69520700
H 2.26830000 1.66491300 4.59503000
H 1.88686600 2.61452700 3.14518000
H 1.01843900 1.09956600 3.46951100
H -3.13712000 -2.87802800 0.44328000
H -0.55466700 -5.58392500 -0.65125800
H -3.98021200 -1.39012600 -1.70148900
H -5.40957400 -3.10414100 -2.66457800
H -4.99877400 -5.53386000 -2.19361500
H -2.84148100 -6.23142800 -1.22032800
H 1.29225600 -5.09052700 0.66947600
H -0.36297100 -1.57898500 4.46133700
H 0.84665700 -2.87877300 4.44521400
H 1.36543800 -1.17906300 4.46604600

H 0.34312100 -0.86617800 2.17076800
H -0.13951800 -2.57281100 2.17952600

TS2

C 0.14106700 -4.57566800 0.23682200
C 0.93349600 -3.42683100 -0.06809600
C 2.28110700 -3.66327500 -0.65158600
C 2.65160300 -5.04428100 -0.96688400
C 1.80768900 -6.07909400 -0.70916500
C 0.55548200 -5.84662500 -0.06557300
H -0.79013600 -4.44385600 0.76460000
H 4.26664500 -2.87594100 -0.91216700
H 3.63381900 -5.20560800 -1.39838700
H 2.10305300 -7.09409000 -0.95429600
H -0.07787900 -6.68883400 0.19088200
C 3.25165400 -2.62800500 -0.63454300
H 1.39576800 -3.48629700 -1.47968000
C 2.99220700 -1.38072100 -0.04163000
C 4.00774300 -0.53345000 0.41717400
H 3.74985200 0.37520100 0.93435600
C 5.40915100 -0.77209400 0.27666300
O 5.99296600 -1.70666200 -0.28740700
C 7.55940300 0.12659300 0.79497300
H 7.86335800 0.06520600 -0.25608300
H 7.88895900 -0.79828500 1.28267500
C -0.80529100 -1.66263600 0.31339900
C 0.54821100 -2.03533200 0.14414300
C 1.55296200 -1.00295700 0.08711400
C 1.14934900 0.35792400 0.11312600
C -0.20819100 0.69294100 0.33301700
C -1.16031900 -0.33000700 0.45609900
C 8.15181100 1.34732500 1.47049000
H 9.24496700 1.30402200 1.42944300
H 7.82458800 2.26573700 0.97258700
H 7.84898600 1.39856600 2.52127200
O 6.13203500 0.23778800 0.88014100
C 2.05169700 1.49861900 -0.22538600
C 2.58487000 1.60326000 -1.51684100
C 2.31451000 2.51550000 0.70215100
C 3.38002800 2.69308500 -1.86846400
H 2.37798100 0.82192900 -2.24150300
C 3.11653500 3.60240400 0.35334100
H 1.90277200 2.44402200 1.70358000
C 3.65156000 3.69491300 -0.93364900
H 3.78687400 2.76051900 -2.87309600
H 3.32310700 4.37587700 1.08705600
H 4.27420300 4.54173100 -1.20607200
C -0.65101100 2.04352800 0.34046500
C -1.07407100 3.18402600 0.33274700
C -1.49733600 4.54183700 0.31795400
C -0.54599800 5.57206900 0.16981900
C -2.86073700 4.87329600 0.44696300
C -0.95609400 6.90175300 0.15385400
H 0.50321000 5.31450700 0.06834700
C -3.25874300 6.20697500 0.42871800
H -3.59232100 4.07974200 0.55900400
C -2.31041900 7.22329100 0.28277100
H -0.21827400 7.68997300 0.03975700
H -4.31100300 6.45490000 0.52813000
H -2.62573400 8.26199000 0.26886500
C -2.06137200 -2.51378300 0.30062800
H -2.06477200 -3.27466500 -0.47922100
H -2.21614300 -3.00596300 1.26754100
C -2.64428800 -0.15916200 0.63242800
H -2.89707900 -0.07991300 1.69431900
H -3.04580100 0.72052700 0.12924300
C -3.19834100 -1.48368800 0.04701200
C -4.50658500 -1.98273000 0.64918500
C -3.42537100 -1.33068700 -1.46557700
O -5.34007800 -2.60314400 0.01655100
O -2.92005100 -2.02484100 -2.32344500
O -4.59712100 -1.71661100 1.95538000
O -4.25173900 -0.30905100 -1.71506100
C -5.77390400 -2.23037700 2.64191900
H -6.66235800 -1.80884600 2.16420200
H -5.79874900 -3.31633500 2.51738300
C -5.65918400 -1.82432800 4.09333200
H -6.52990500 -2.19534300 4.64253900
H -4.75857400 -2.24685800 4.54877900
H -5.62637400 -0.73539900 4.19453500
C -4.56243900 -0.04829300 -3.11076700
H -3.62524700 0.11473700 -3.64988100
H -5.04934100 -0.93452500 -3.52756500
C -5.46008100 1.16764500 -3.15039800
H -5.71549800 1.39692100 -4.18944800
H -6.38774600 0.98846400 -2.59865900
H -4.95748400 2.03859600 -2.71877900

4a

C 0.05692000 -1.44503100 0.02115700
C -0.53538800 -0.20441900 0.26344200
C 0.21329200 0.97582100 0.21531500
C 1.60494200 0.90930700 -0.07931100
C 2.21099400 -0.34295800 -0.29455000

C 1.42224100 -1.53256800 -0.25737600
C -0.43951500 2.22658300 0.39253300
C -1.01362100 3.28894600 0.53797300
C -1.61105800 4.56903900 0.70789600
C -0.81196000 5.72875100 0.63618000
C -1.38850500 6.98416400 0.80413400
C -2.76058700 7.10342300 1.04341200
C -3.55850500 5.95821300 1.11489400
C -2.99318100 4.69691300 0.94898100
C 2.33269000 2.19921500 -0.24581900
C 2.84649400 2.56101800 -1.49873300
C 3.49502000 3.78323400 -1.67169200
C 3.63834000 4.66068900 -0.59446200
C 3.12745300 4.30895400 0.65725300
C 2.47434400 3.08808700 0.82884600
C -0.99722500 -2.52849900 0.04782200
C -2.31621100 -1.73769400 -0.13368300
C -2.01769300 -0.34131900 0.48567200
C -3.50955200 -2.48523700 0.44746000
C -2.61073300 -1.55520200 -1.63170300
O -4.30212700 -1.70294600 1.18709200
O -3.81630600 -0.99649900 -1.80181100
O -3.70916500 -3.66446400 0.22419100
O -1.86110800 -1.85803200 -2.53562200
C -5.54537300 -2.29141700 1.66428500
C -4.23879800 -0.74904600 -3.17163500
C -6.61215500 -2.22290800 0.58860200
C 3.66721500 -0.51097800 -0.55912700
C 4.07878100 -1.60584200 -1.35104300
C 3.03135300 -2.60220200 -1.80398600
C 2.08969200 -2.79426300 -0.64098900
C 4.65259900 0.32769600 -0.01444000
C 6.00188800 0.12853700 -0.30080400
C 6.39450200 -0.92159600 -1.13153500
C 5.43065000 -1.79323900 -1.64000000
C 1.97962000 -3.98767500 -0.03005300
C -5.64295800 -0.19207500 -3.11137400
C 1.18292900 -4.34429100 1.16927100
O 0.49190100 -5.34841800 1.18549400
O 1.20747800 -3.56995700 2.27551800
C 2.73644200 -2.82107700 3.96692500
C 2.24632400 -2.59298600 2.55187600
H 0.25250800 5.62848900 0.45015500
H -0.76666600 7.87237700 0.74831100
H -3.20621800 8.08480300 1.17345000
H -4.62436200 6.04863400 1.30050100
H -3.60828800 3.80466700 1.00308600
H 2.73617400 1.87861300 -2.33557100
H 3.88586500 4.05166300 -2.64864100
H 4.14502300 5.61152300 -0.72918400
H 3.23717600 4.98403700 1.50069300
H 2.07944900 2.81523800 1.80209600
H -0.86044200 -3.28969300 -0.71974300
H -1.01616400 -3.02717100 1.02109300
H -2.60440600 0.45957000 0.03236800
H -2.25343000 -0.35168500 1.55537800
H -5.80946800 -1.68961700 2.53528800
H -5.35037500 -3.31825200 1.97925200
H -3.53553500 -0.04663200 -3.62769200
H -4.19201600 -1.69128900 -3.72409500
H -7.55752000 -2.60373200 0.98843400
H -6.33505200 -2.83129400 -0.27626700
H -6.76655600 -1.19075100 0.26085800
H 2.47760000 -2.20844100 -2.66794600
H 3.49840500 -3.54370700 -2.09953700
H 4.36708600 1.13550200 0.64596200
H 6.74468400 0.79145700 0.13238300
H 7.44426300 -1.07838500 -1.36054000
H 5.72782900 -2.63922100 -2.25331600
H 2.47270400 -4.84535400 -0.47973400
H -5.99651300 0.01192200 -4.12665700
H -6.32708300 -0.90703600 -2.64476600
H -5.66994400 0.74223500 -2.54258300
H 3.48860900 -2.06544900 4.21630200
H 1.91515200 -2.73903200 4.68516100
H 3.19277400 -3.81057600 4.06766800
H 3.05709200 -2.69534700 1.82987000
H 1.80203100 -1.60193000 2.43937100

IN3

C -1.46474600 -0.13309900 0.00007100
C -0.62560700 -1.23678000 -0.00013100
C 0.62551700 -1.23677700 0.00007700
C 1.46485600 -0.13311800 -0.00000500
C 0.70347700 1.05722800 -0.00004200
C -0.70352000 1.05728600 -0.00000400
H -2.54884500 -0.13264600 0.00009300
H 2.54892900 -0.13259700 0.00011700
H 1.22975800 2.00834500 -0.00000800
H -1.22970000 2.00845900 -0.00000300

TS3

C 2.59743500 -1.65055100 1.59621800

C 1.48744100 -1.25500900 0.83641600
C 1.41375300 -1.57983800 -0.53867200
C 2.49328900 -2.26601500 -1.13092800
C 3.60010100 -2.62867700 -0.37574100
C 3.65571900 -2.32017900 0.99252000
H 2.62693800 -1.42093100 2.65671000
H 0.62827900 -0.81298300 1.32663900
H 2.44959600 -2.50387100 -2.18981600
H 4.42543000 -3.15409500 -0.84637600
H 4.52067000 -2.61428500 1.57909600
C 0.29713600 -1.15697900 -1.36219800
H 0.30877100 -1.46189200 -2.40889800
C -0.65082400 -0.31196200 -0.98511900
C -1.77694700 0.26458100 -0.62247400
H -1.89451100 1.34285300 -0.59734300
C -2.94872200 -0.55757600 -0.22168900
O -2.99001300 -1.77379600 -0.17875900
C -5.20542700 -0.42594700 0.50341400
H -5.52636100 -1.09247600 -0.30257400
H -4.99143700 -1.03856600 1.38423100
C 2.97672400 1.85736300 0.86567800
C 1.88578700 1.20357700 0.32782300
C 0.97604500 1.67123100 -0.41854900
C 0.92391000 2.99574100 -0.83954100
C 2.00385900 3.76341400 -0.35493500
C 2.99993700 3.21256900 0.47143800
H 3.73553500 1.42127400 1.50762300
H 0.15564500 3.43124900 -1.47176000
H 2.06860500 4.81338800 -0.62944900
H 3.81251400 3.84667900 0.81695600
C -6.23330800 0.64475400 0.79512900
H -7.17018500 0.17364500 1.10816500
H -5.89490100 1.30535500 1.59917100
H -6.43282300 1.24980400 -0.09449300
O -3.98464000 0.24277800 0.09493000

IN4

C 3.87607400 -0.73947700 -0.13235000
C 2.44811800 -0.40742600 -0.50362100
C 1.45960700 -1.45960300 -0.04911100
C 1.94463700 -2.81231400 0.11819500
C 3.27152100 -3.07542400 0.20381200
C 4.24848000 -2.00102400 0.14617500
H 4.61986400 0.04680500 -0.17900100
H -0.55969100 -1.95901400 0.32653200
H 1.20953200 -3.60143300 0.25025900
H 3.61797200 -4.09039200 0.37374000
H 5.29062000 -2.23318000 0.34462100
C 0.14646600 -1.16203400 0.13231200
C -0.37131000 0.18385400 0.06376900
C -1.71347700 0.45757400 0.01642000
H -2.05240400 1.48232300 -0.05739500
C -2.79726000 -0.52122000 0.02513400
O -2.72282500 -1.74385500 0.09280400
C -5.16740200 -0.71991000 -0.05652300
H -5.11470800 -1.40671400 -0.90741500
H -5.17580200 -1.32200000 0.85763300
C 2.89593800 2.07776700 -0.26386300
C 1.98783200 1.01284100 -0.20794600
C 0.62710700 1.28459200 0.06061400
C 0.24446700 2.61136800 0.33657900
C 1.16200100 3.65273900 0.30466700
C 2.49539300 3.38638200 -0.01218400
H 3.93458800 1.89127800 -0.50989100
H -0.78391500 2.83244100 0.59541900
H 0.83936700 4.66553200 0.52474800
H 3.22296900 4.19116100 -0.05294800
O -3.99264100 0.12071900 -0.05607300
C -6.37562600 0.18799200 -0.14197900
H -7.28871000 -0.41545300 -0.14372900
H -6.41482500 0.86911700 0.71370200
H -6.35496700 0.78319400 -1.06014500
H 2.43843300 -0.48864300 -1.61058000

TS4

C 3.89606700 -0.73588400 -0.10000100
C 2.52285500 -0.35639200 -0.00061200
C 1.50677200 -1.43006000 0.10229900
C 1.98198100 -2.81176900 0.03244100
C 3.30802500 -3.09886600 -0.06267200
C 4.27666600 -2.05190800 -0.13427700
H 4.65132600 0.03580400 -0.17546500
H -0.58794800 -1.94147100 0.10243300
H 1.23300700 -3.59583100 0.06665200
H 3.63713800 -4.13214600 -0.10046200
H 5.32874400 -2.30327900 -0.21343700
C 0.11529500 -1.12109300 0.06886300
H 1.95001500 -1.06244400 1.17601500
C -0.37950300 0.18935900 0.01325400
C -1.75552200 0.48352300 -0.03643200
H -2.09105700 1.50655400 -0.12126500
C -2.80122500 -0.48411600 0.00463200
O -2.72688400 -1.71854700 0.08821700
C -5.17404100 -0.74562700 -0.01254200

H -5.14722900 -1.34006000 0.90802700
H -5.13448600 -1.44882700 -0.85262700
C 2.94431600 2.09021700 0.00965300
C 2.02953700 1.01424400 0.01200300
C 0.62638300 1.28233400 0.00856100
C 0.22437100 2.63419800 0.01974000
C 1.13831700 3.67521800 0.00968100
C 2.51245900 3.40344000 -0.00021300
H 4.00861800 1.89135400 0.02083500
H -0.82901600 2.87848500 0.04492500
H 0.78434000 4.70143100 0.01499600
H 3.23477300 4.21333100 -0.00359100
C -6.42025900 0.11528300 -0.07430900
H -7.31332900 -0.51724100 -0.04160600
H -6.45884800 0.80839300 0.77224100
H -6.44710700 0.69985400 -0.99957500
O -4.03985300 0.13023300 -0.05803100

TS5

C -1.34840000 1.90841600 -1.42913700
C -1.16286500 0.93299500 -0.38727800
C -0.75538000 1.41482900 0.94832100
C -0.52490800 2.81686700 1.12563700
C -0.66786000 3.68764000 0.07901300
C -1.07825800 3.23066300 -1.21272300
H -1.70645400 1.56895400 -2.39646000
H 0.47762300 0.74168300 2.56888300
H -0.19951200 3.16731300 2.10103000
H -0.46721900 4.74483100 0.22588200
H -1.19267800 3.95021200 -2.01758200
C -0.25572200 0.45146500 1.82711500
C -0.22571000 -0.83618000 1.21259900
C 0.86121600 -1.09634600 0.34555700
H 0.81423600 -1.96619100 -0.30555800
C 2.24121000 -0.57642300 0.56550800
O 2.62009400 0.10345900 1.50309100
C 4.41027600 -0.48357700 -0.39752100
H 4.40430900 0.61005300 -0.36577500
H 4.86961400 -0.84688800 0.52650200
C -3.12134800 -0.58277100 -1.08605500
C -1.97765200 -0.30458900 -0.33078400
C -1.49724700 -1.26719300 0.58081100
C -2.11573700 -2.51001100 0.69873800
C -3.25795700 -2.77840700 -0.05937800
C -3.75781200 -1.81671700 -0.94371800
H -3.52106800 0.16489300 -1.76407800
H -1.71667300 -3.25306300 1.38227300
H -3.75997600 -3.73570000 0.04184200
H -4.65282800 -2.02766000 -1.52138700
O 3.03867500 -0.95430800 -0.45048500
C 5.11715900 -1.01040800 -1.62657200
H 6.15830100 -0.67345800 -1.61980300
H 5.10951000 -2.10446700 -1.64477200
H 4.64190600 -0.64169100 -2.54060000
H 0.17273100 0.02644900 -0.55203500

IN5

C -4.14454000 -0.05405300 -0.43152900
C -2.76284800 -0.13834800 -0.14288500
C -2.22064300 -1.40974600 0.20988600
C -3.08136700 -2.53600900 0.26765400
C -4.42762300 -2.42187000 -0.01665700
C -4.96412200 -1.16821100 -0.37201100
H -4.58339900 0.89857300 -0.70596400
H -0.44487700 -2.54464600 0.65926600
H -2.65551400 -3.49913500 0.53715300
H -5.07203800 -3.29506600 0.03107900
H -6.02180000 -1.07387400 -0.59912300
C -0.82254700 -1.54563400 0.45294400
C 0.06966800 -0.49637000 0.38646800
C 1.49890400 -0.73697800 0.62411100
H 1.70393500 -1.71982700 1.04916800
C 2.49636300 -0.34835200 -0.33759900
O 2.43262900 0.49629100 -1.23464700
C 4.78753400 -0.64537100 -0.93911700
H 4.98978500 0.42485700 -0.81361700
H 4.53947900 -0.80513200 -1.99490900
C -2.34042200 2.31600700 -0.43067800
C -1.86672500 1.00840200 -0.16141600
C -0.47947700 0.83479400 0.13975500
C 0.33910600 1.98583800 0.24508600
C -0.15799800 3.25095200 -0.00094200
C -1.50634300 3.41564900 -0.36582000
H -3.38420900 2.46870500 -0.67950000
H 1.36367500 1.86138800 0.56162200
H 0.49031200 4.11727800 0.09483200
H -1.90005800 4.40647600 -0.57361000
C 5.98175500 -1.48203600 -0.52320000
H 6.85379000 -1.22013000 -1.13138800
H 6.23216500 -1.30989400 0.52864300
H 5.77745700 -2.54928000 -0.65755200
O 3.68180700 -1.03087300 -0.11352100
H 2.08886200 0.28560800 1.74328400
F 2.52387600 0.98431000 2.34574100

TS6

C -4.09137000 -0.16140600 -0.48145000
C -2.71905000 -0.18082900 -0.13887300
C -2.14558000 -1.41693700 0.27929100
C -2.96114500 -2.57375800 0.34622000
C -4.29935100 -2.52342600 0.00914700
C -4.86800600 -1.30477600 -0.41080500
H -4.55551800 0.76270800 -0.80667700
H -0.34369600 -2.46103700 0.84532000
H -2.50838200 -3.50858100 0.66631700
H -4.91167000 -3.41875200 0.06473400
H -5.91921700 -1.26023500 -0.67941900
C -0.75170700 -1.48696100 0.58528100
C 0.08931300 -0.40392700 0.52392200
C 1.53808500 -0.56643200 0.82168300
H 1.74218800 -1.52445000 1.30579600
C 2.47013800 -0.35316800 -0.28460800
O 2.32396400 0.35515900 -1.27638400
C 4.69833100 -0.77173100 -1.01826000
H 4.92546400 0.29958500 -1.05392600
H 4.35454300 -1.06618100 -2.01587200
C -2.37310700 2.27301300 -0.52760600
C -1.86731600 0.99888500 -0.17180600
C -0.48898100 0.89097100 0.19288100
C 0.29366600 2.07062900 0.25934000
C -0.23599500 3.30128400 -0.07704000
C -1.57573200 3.40104800 -0.49472800
H -3.41085200 2.37642800 -0.82273600
H 1.30494600 1.99568700 0.63735700
H 0.38005500 4.19368100 -0.01095800
H -1.99206800 4.36556400 -0.77095600
C 5.90661000 -1.57916100 -0.58885100
H 6.72762800 -1.42648100 -1.29686600
H 6.24860200 -1.27353300 0.40513300
H 5.67272400 -2.64824900 -0.55969100
O 3.65464000 -1.01011100 -0.05854800
H 2.03062500 0.41332600 1.66235200
F 2.52366500 1.30446900 2.24079200

IN6

C -3.57921400 -0.94791000 -0.69855600
C -2.38435900 -0.49146900 -0.11695300
C -1.46659400 -1.43760000 0.38023100
C -1.76546400 -2.79980200 0.30883000
C -2.96247200 -3.24051300 -0.25514700
C -3.86917600 -2.30832100 -0.76429700
H -4.28247400 -0.23857200 -1.12087200
H 0.58544700 -1.75266900 0.95863900
H -1.04780600 -3.51836400 0.69522000
H -3.17947300 -4.30305800 -0.30904400
H -4.79667800 -2.63983000 -1.22112800
C -0.17338300 -0.97497600 1.00962700
H -0.35495600 -0.78032500 2.07946300
C 0.32845100 0.30901400 0.40459700
C 1.61597700 0.54573500 0.06232300
H 1.87764300 1.49108600 -0.39959400
C 2.74582100 -0.37973900 0.23055100
O 2.74748900 -1.47695000 0.77306100
C 5.06578600 -0.63589100 -0.22404700
H 5.27636900 -0.83774000 0.83070700
H 4.89537000 -1.59544800 -0.72183200
C -3.03007600 1.94187700 -0.16860600
C -2.05155900 0.94647000 -0.01792700
C -0.70903800 1.34379700 0.21280300
C -0.39606100 2.71125300 0.27591800
C -1.37834600 3.68201600 0.11266400
C -2.70188300 3.29283800 -0.10870500
H -4.06555300 1.65868900 -0.31983300
H 0.62460600 3.01241000 0.48615000
H -1.11793400 4.73376600 0.17702700
H -3.48040800 4.04109100 -0.22166100
C 6.17938600 0.14993700 -0.88130200
H 6.33750000 1.10634200 -0.37349300
H 7.10991400 -0.42398600 -0.83173100
H 5.95235400 0.34674700 -1.93353900
O 3.85992300 0.15939600 -0.31637400

5a

C 3.16441800 -1.72634200 0.20490500
C 2.04839500 -0.87582600 0.02799900
C 0.79080500 -1.47305100 -0.26601100
C 0.68855600 -2.87944300 -0.37306400
C 1.79577400 -3.68571100 -0.19486000
C 3.04262300 -3.10048200 0.09633600
H 4.13797500 -1.30679400 0.42890500
H -1.29793900 -1.15562600 -0.67730500
H -0.28152100 -3.31391200 -0.59814100
H 1.70713100 -4.76452700 -0.27876400
H 3.91615000 -3.72977400 0.23699400
C -0.36527400 -0.64804000 -0.45093900
C -0.31764800 0.71056300 -0.35378800
C -1.55264600 1.57092300 -0.55654900

H -1.42938900 2.20272800 -1.44136200
C -2.81899800 0.76576200 -0.74364000
O -3.32883200 0.50730400 -1.81687800
C -4.49514500 -0.48582800 0.38244100
H -5.30113800 0.07956900 -0.09427200
H -4.27922200 -1.35917500 -0.23985000
C 3.33673400 1.24293600 0.41480000
C 2.12369400 0.57472600 0.12953400
C 0.94505900 1.36024700 -0.06403600
C 1.04014800 2.76962800 0.02965600
C 2.24219900 3.39283700 0.30715700
C 3.40008700 2.62132300 0.50333100
H 4.24344000 0.67019000 0.56896600
H 0.15504200 3.37625800 -0.12089000
H 2.28978500 4.47542300 0.37334200
H 4.34663700 3.10548100 0.72328200
C -4.83837600 -0.87455800 1.80326800
H -5.73107800 -1.50760400 1.80260300
H -4.01924300 -1.43459000 2.26453600
H -5.04436800 0.01013300 2.41336300
O -3.30949900 0.35047100 0.43612200