Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supplementary Information

C-O/C-S Difunctionalized Benzene Derivatives via Multicomponent Coupling from Tetraynes

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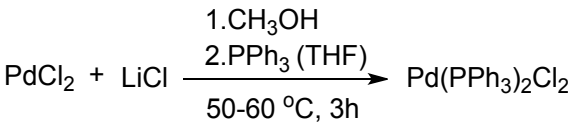
1. General experimental procedures

All the catalytic reactions were performed under an argon atmosphere using the oven-dried Schlenk flask. The chemicals were purchased from Aladdin and TCI Chemicals. All solvents and materials were pre-dried, redistilled or recrystallized before use. ^{1}H NMR (300 MHz, 500 MHz) and ^{13}C NMR (75 MHz, 125 MHz) spectra were recorded on a Bruker Avance 300 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** and **4m** 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.

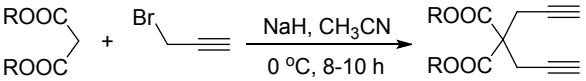
(1) General procedure for preparation of tetrayne 1:[1]

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.

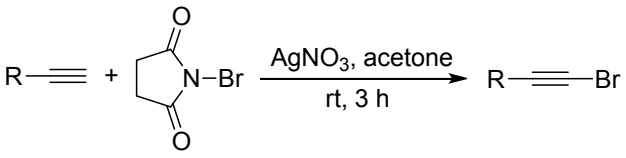
Preparation of diyne substrates



R = Me, Et, ^{i}Pr

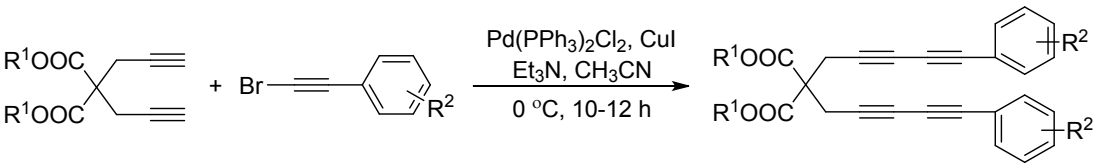
10 g NaH (60%) and 200-300 mL acetonitrile were added in 500 mL three-necked flask with magnetic stirring. 100 mmol malonate and 30 g 3-bromopropyne (98%) were added in the above 500 mL three-necked flask dropwise in turn by separatory funnel, magnetically stirred for 8-10 h under ice-water bath. The 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



21.36 g 1-bromopyrrolidine-2,5-dione (NBS), 0.85 g $AgNO_3$, and 100 mmol phenylacetylene or substituted phenylacetylene or alkyl alkyne were added in 250 mL three-necked flask in turn, 150 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.

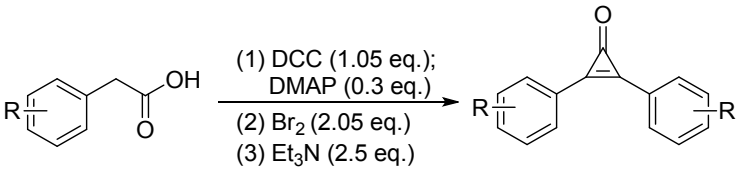
*Preparation of tetrayne substrate***s**



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

0.6 g $Pd(PPh_3)_2Cl_2$, 0.5 g CuI and 40 mmol diyne substrate were added in 500 mL three-necked flask, protected with anhydrous anaerobic conditions under argon. After 0.5 h, 250-300 mL acetonitrile, 16.16 g Et_3N and 100 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 white solid finally.

(2) General procedure for preparation of cyclopropenone 2:[2]



Substituted cyclopropenones were prepared in three steps from substituted phenylacetic acid. (1) The 1,3-diphenylpropan-2-one was prepared by adding substituted phenylacetic acid (1 equiv) to a stirring solution of DCC (1.05 equiv) and DMAP (0.3 equiv) in THF at room temperature. After 60 minutes, the reaction was filtered through Celite. The 1,3-diphenylpropan-2-one was purified by flash chromatography

on silica gel (ethyl acetate/petroleum ether = 1/60); (2) The 1,3-diphenylpropan-2-one was then dissolved in acetic acid, and a solution of bromine (2.05 equiv) in acetic acid was added dropwise. After 3 hours, the reaction was poured into water and the product (1,3-dibromo-1,3-diphenylpropan-2-one) was collected by filtration; (3) The crude product (1,3-dibromo-1,3-diphenylpropan-2-one) was air dried for several hours, then dissolved in dry dichloromethane. This solution was added to a stirring solution of triethylamine (2.5 equiv) in dichloromethane, and stirred at room temperature for 1 hour. The reaction mixture was then washed with 1 M HCl, followedby brine, dried with sodium sulfate, and concentrated under reduced pressure. The product was purified by column chromatography on silica gel (ethyl acetate/petroleum ether = 1/5).

(3) General procedure for preparation of C-O/C-S difunctionalized benzene derivative 4:

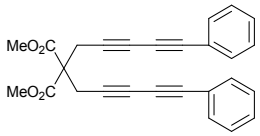
Tetraynes (0.5 mmol), cycolpropenones (1.1 equiv) and H_2O (1.0 equiv) were added to sulfoxides (2 mL), the mixture was stirred at room temperature then heated at 120 °C for 8 hours in air. Then the reaction mixture was cooled to room temperature, quenched with saturated NaCl, and extracted with ethyl 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 = 1/20) to afford C-O/C-S difunctionalized benzene derivatives.

References:

1. (*a*) J. Chen, V. Palani and T. R. Hoye, Reactions of HDDA-derived benzynes with sulfides: mechanism, modes, and three-component reactions, *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, Hydroarylation of arynes catalyzed by silver for biaryl synthesis, *J. Am. Chem. Soc.*, 2014, **136**, 4363−4368; (*c*) B. Liu, C. Mao, Q. Hu, L. Yao and Y. Hu, Direct methylation and carbonylation of *in situ* generated arynes *via* HDDA-Wittig coupling, *Org. Chem. Front.*, 2019, **6**, 2788−2791; (*d*) X. Zheng, B. Liu, F. Yang, Q. Hu, L. Yao, Y. Hu, Access to benzoxazepines and fully substituted indoles *via* HDDA coupling, *Org. Lett.*, 2020, **22**, 956–959.

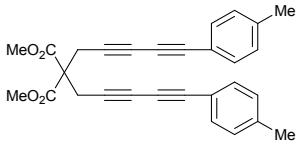
2. (*a*) X. Li, C. Han, H. Yao and A. Lin, Organocatalyzed [3 + 2] annulation of cyclopropenones and *β*-ketoesters: an approach to substituted butenolides with a quaternary center, *Org. Lett.*, 2017, **19**, 778–781; (*b*) C. M. Vanos and T. H. Lambert, Development of a catalytic platform for nucleophilic substitution: cyclopropenone-catalyzed chlorodehydration of alcohols, *Angew. Chem. Int. Ed.*, 2011, **50**, 12222–12226.

2. Characterization of Tetraynes 1



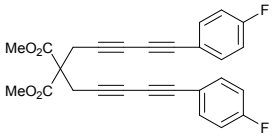
Dimethyl 2,2-bis(5-phenylpenta-2,4-diyn-1-yl)malonate (1a)

Yellow solid; 12.2 g (75 % yield); m. p. 96-97 ℃; **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.48-7.46 (m, 4H), 7.33-7.25 (m, 6H), 3.81 (s, 6H), 3.21 (s, 4H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 168.6, 132.6, 129.2, 128.4, 121.5, 77.6, 76.0, 73.7, 68.5, 56.6, 53.4, 52.9, 50.5, 24.2, 19.6 ppm; **HRMS** (APCI-TOF): *m/z* calcd for $C_{27}H_{20}O_4$ $[M+H]^+$ 409.1434, found 409.1435.



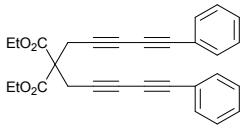
Dimethyl 2,2-bis(5-(*p*-tolyl)penta-2,4-diyn-1-yl)malonate (1b)

Yellow solid, 13.6 g (78 % yield); m. p. 102-103 ℃; **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.38-7.35 (m, 4H), 7.12-7.10 (m, 4H), 3.80 (s, 6H), 3.20 (s, 4H), 2.34 (s, 6H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 168.6, 139.5, 132.5, 129.1, 118.4, 77.5, 76.3, 73.2, 68.6, 56.7, 53.4, 24.2, 21.6 ppm; **HRMS** (APCI-TOF): *m/z* calcd for $C_{29}H_{24}O_4$ $[M+H]^+$ 437.1747, found 437.1752.



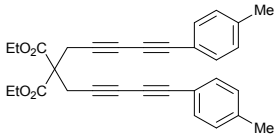
Dimethyl 2,2-bis(5-(4-fluorophenyl)penta-2,4-diyn-1-yl)malonate (1c)

Yellow solid, 14.7 g (83 % yield); m. p. 116-117 ℃; **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.52-7.47 (m, 4H)，7.07-7.01 (m, 4H), 3.84 (s, 6H), 3.24 (s, 4H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 168.6, 164.6, 161.3, 134.7 (d, $J_{C\text{-}F}$ = 7.5 Hz), 117.6 (d, $J_{C\text{-}F}$ = 7.5 Hz), 115.9 (d, $J_{C\text{-}F}$ = 22.5 Hz), 77.6 (d, $J_{C\text{-}F}$ = 7.5 Hz), 76.9 (d, $J_{C\text{-}F}$ = 37.5 Hz), 74.9, 73.6, 68.4, 56.7, 53.4, 24.2 ppm; **HRMS** (APCI-TOF): *m/z* calcd for $C_{27}H_{18}F_2O_4$ $[M+H]^+$ 445.1246, found 445.1246.



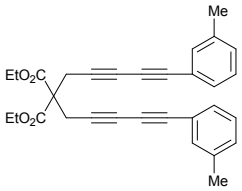
Diethyl 2,2-bis(5-phenylpenta-2,4-diyn-1-yl)malonate (1d)

White solid; 13.6 g (78 % yield); m. p. 62-63 ℃; **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.39-7.35 (m, 2H), 7.25 (s, 2H), 7.07-7.03 (m, 6H), 4.26 (q, J = 6.0 Hz, 4H), 3.31 (s, 4H), 1.28 (t, J = 6.0 Hz, 6H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 168.2, 132.6, 129.1, 128.4, 121.5, 77.8, 75.9, 73.8, 68.4, 62.4, 56.6, 24.1, 14.0 ppm; **HRMS** (APCI-TOF): *m/z* calcd for $C_{29}H_{24}O_4$ $[M+H]^+$ 437.1747, found 437.1746.



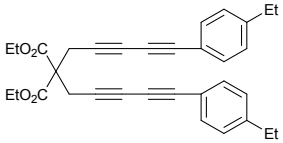
Diethyl 2,2-bis(5-(*p*-tolyl)penta-2,4-diyn-1-yl)malonate (1e)

Yellow solid, 14.7 g (79 % yield); m. p. 88-89 ℃; **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.38-7.35 (m, 4H), 7.12-7.10 (m, 4H), 4.27 (q, J = 6.0 Hz, 4H), 3.19 (s, 4H), 2.35 (s, 6H), 1.29 (t, J = 6.0 Hz, 6H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 168.2, 139.5, 132.5, 132.3, 129.2, 129.1, 118.4, 81.5, 77.5, 76.1, 73.3, 68.5, 62.3, 56.6, 24.1, 21.6, 14.0 ppm; **HRMS** (APCI-TOF): *m/z* calcd for $C_{31}H_{28}O_4$ $[M+H]^+$ 465.2060, found 465.2058.



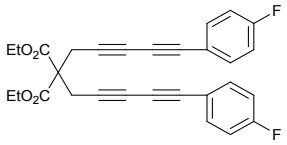
Diethyl 2,2-bis(5-(*m*-tolyl)penta-2,4-diyn-1-yl)malonate (1f)

Yellow solid, 13.9 g (75 % yield); m. p. 79-80 ℃; **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.75-7.71 (m, 2H), 7.39-7.35 (m, 2H), 7.11-7.08 (m, 4H), 4.27 (q, J = 6.0 Hz, 4H), 3.19 (s, 4H), 2.34 (s, 6H), 1.29 (t, J = 6.0 Hz, 6H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 168.2, 139.5, 132.5, 132.3, 129.2, 129.1, 118.4, 81.5, 77.6, 76.1, 73.3, 68.5, 62.3, 56.6, 24.1, 21.6, 14.1 ppm; **HRMS** (APCI-TOF): *m/z* calcd for $C_{31}H_{28}O_4$ $[M+H]^+$ 465.2060, found 465.2055.



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

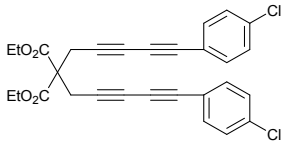
Yellow solid, 15.7 g (80 % yield); m. p. 74-75 ℃; **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.40-7.38 (m, 4H), 7.15-7.12 (m, 4H), 4.27 (q, J = 6.0 Hz, 4H), 3.19 (s, 4H), 2.64 (q, J = 6.0 Hz, 4H), 1.32-1.19 (m, 12H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 168.2, 145.7, 132.6, 127.9, 118.6, 77.4, 76.1, 73.2, 68.5, 62.4, 56.6, 28.9, 24.1, 15.2, 14.0 ppm; **HRMS** (APCI-TOF): *m/z* calcd for $C_{33}H_{32}O_4$ $[M+H]^+$ 493.2373, found 493.2374.



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

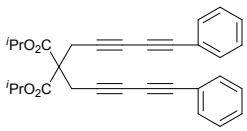
Yellow solid, 15.1 g (80 % yield); m. p. 64-65 ℃; **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.51-7.47 (m, 4H), 7.07-7.01 (m, 4H), 4.31 (q, J = 6.0 Hz, 4H), 3.23 (s, 4H), 1.33 (t, J = 6.0 Hz, 6H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 168.2, 164.7, 161.3, 134.7 (d, $J_{C\text{-}F}$ = 7.5 Hz), 134.6 (d, $J_{C\text{-}F}$ = 7.5 Hz), 116.1 (d, $J_{C\text{-}F}$ = 7.5 Hz),

115.7 (d, $J_{C\text{-}F}$ = 7.5 Hz), 77.7 (d, $J_{C\text{-}F}$ = 30.0 Hz), 76.8 (d, $J_{C\text{-}F}$ = 30.0 Hz), 74.8, 68.3, 62.4, 56.6, 24.1, 14.0 ppm; **HRMS** (APCI-TOF): *m/z* calcd for $C_{29}H_{22}F_2O_4$ $[M+H]^+$ 473.1559, found 473.1560.



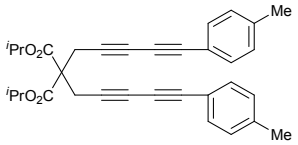
Diethyl 2,2-bis(5-(4-chlorophenyl)penta-2,4-diyn-1-yl)malonate (1i)

Yellow solid, 16.3 g (81 % yield); m. p. 104-105 ℃; **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.43-7.38 (m, 4H), 7.33-7.26 (m, 4H), 4.27 (q, J = 6.0 Hz, 4H), 3.19 (s, 4H), 1.29 (t, J = 6.0 Hz, 6H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 168.1, 135.3, 133.7, 130.9, 129.3, 128.7, 120.0, 78.4, 74.6, 72.1, 68.1, 62.4, 56.4, 24.0, 23.7, 14.0 ppm; **HRMS** (APCI-TOF): *m/z* calcd for $C_{29}H_{22}Cl_2O_4$ $[M+H]^+$ 505.0968, found 505.0966.



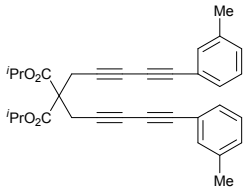
Diisopropyl 2,2-bis(5-phenylpenta-2,4-diyn-1-yl)malonate (1j)

White solid, 14.9 g (80 % yield); m. p. 130-131 ℃; **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.48-7.46 (m, 4H), 7.32-7.26 (m, 6H), 5.14-5.10 (m, 2H), 3.17 (s, 4H), 1.27 (d, J = 6.0 Hz, 12H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 167.8, 132,6, 129.1, 128.4, 121.6, 78.0, 75.8, 73.9, 70.0, 68.3, 56.5, 24.0, 21.5 ppm; **HRMS** (APCI-TOF): *m/z* calcd for $C_{31}H_{28}O_4$ $[M+H]^+$ 465.2060, found:465.2056.



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

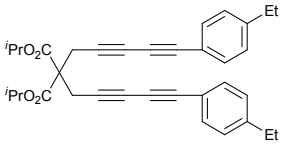
Yellow solid, 14.6 g (74 % yield); m. p. 91-92 ℃; **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.37-7.34 (m, 4H), 7.11-7.09 (m, 4H), 5.14-5.10 (m, 2H), 3.16 (s, 4H), 2.34 (s, 6H), 1.27 (d, J = 6.0 Hz, 12H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 167.8, 139.4, 132.5, 132.3, 129.2, 129.1, 118.5, 77.6, 76.0, 73.3, 69.9, 68.4, 56.5, 24.0 21.6, 21.5 ppm; **HRMS** (APCI-TOF): *m/z* calcd for $C_{33}H_{32}O_4$ $[M+H]^+$ 493.2373, found 493.2378.



Diisopropyl 2,2-bis(5-(*m*-tolyl)penta-2,4-diyn-1-yl)malonate (1l)

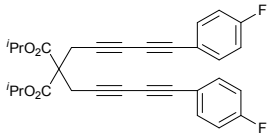
Yellow solid, 13.6 g (69 % yield); m. p. 84-85 ℃; **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.74-7.71 (m, 2H), 7.39-7.34 (m, 2H), 7.11-7.08 (m, 4H), 5.14-5.10 (m, 2H), 3.16 (s, 4H), 2.36 (s, 6H), 1.27 (d, J = 6.0 Hz, 12H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 167.8, 139.5, 132.4, 132.3, 129.2, 129.1, 118.6, 77.6, 76.0, 73.2,

69.9, 68.4, 56.5, 24.0 21.6, 21.4 ppm; **HRMS** (APCI-TOF): *m/z* calcd for $C_{33}H_{32}O_4$ $[M+H]^+$ 493.2373, found 493.2371.



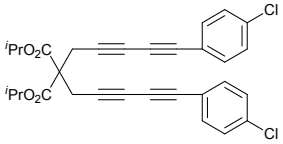
Diisopropyl 2,2-bis(5-(4-ethylphenyl)penta-2,4-diyn-1-yl)malonate (1m)

Yellow solid, 15.2 g (73 % yield); m. p. 94-95 ℃; **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.40-7.38 (m, 4H), 7.15-7.12 (m, 4H), 5.14-5.10 (m, 2H), 3.19 (s, 4H), 2.64 (q, J = 6.0 Hz, 4H) 1.32-1.19 (m, 18H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 167.4, 139.7, 132.8, 132.5, 129.2, 128.1, 118.6, 77.5, 76.2, 73.2, 69.9, 68.4, 56.6, 24.2 21.6, 21.4, 14.2 ppm; **HRMS** (APCI-TOF): *m/z* calcd for $C_{35}H_{36}O_4$ $[M+H]^+$ 521.2673, found 521.2670.



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

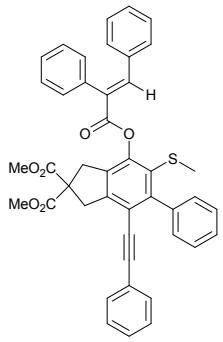
Yellow solid, 15.2 g (76 % yield); m. p. 62-63 ℃; **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.52-7.47 (m, 4H), 7.07-7.01 (m, 4H), 5.14-5.10 (m, 2H), 3.17 (s, 4H), 1.27 (d, J = 6.0 Hz, 12H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 168.6, 164.6, 161.3, 134.8 (d, $J_{C\text{-}F}$ = 7.5 Hz), 117.7 (d, $J_{C\text{-}F}$ = 7.5 Hz), 115.4 (d, $J_{C\text{-}F}$ = 22.5 Hz), 77.6 (d, $J_{C\text{-}F}$ = 7.5 Hz), 76.9 (d, $J_{C\text{-}F}$ = 37.5 Hz), 75.1, 73.6, 68.6, 56.7, 53.4, 24.4, 21.5 ppm; **HRMS** (APCI-TOF): *m/z* calcd for $C_{31}H_{26}F_2O_4$ $[M+H]^+$ 501.1816, found 501.1819.



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

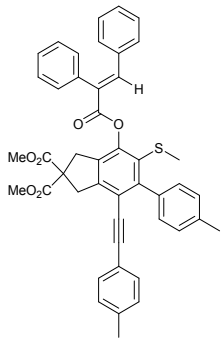
Yellow solid, 16.8 g (79 % yield); m. p. 85-86 ℃; **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.40-7.38 (m, 4H), 7.29-7.25 (m, 4H), 5.14-5.10 (m, 2H), 3.16 (s, 4H), 1.27(d, J = 6.5 Hz, 12H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 167.6, 135.2, 133.7, 128.7, 120.1, 78.6, 74.8, 74.6, 70.0, 68.1, 56.4, 24.0, 21.5 ppm; **HRMS** (APCI-TOF): *m/z* calcd for $C_{31}H_{26}Cl_2O_4$ $[M+H]^+$ 534.1034, found 534.1039.

3. Characterization Data for the New Compounds



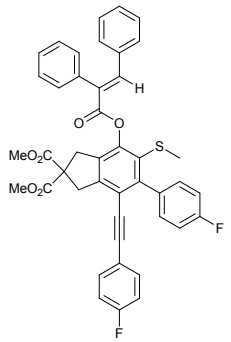
(*E*)-dimethyl 4-((2,3-diphenylacryloyl)oxy)-5-(methylthio)-6-phenyl-7-(phenylethynyl)-1*H*-indene-2,2(3*H*)-dicarboxylate (4a)

White solid; 278 mg (82 % yield); m. p. 175-176 ℃; TLC (petroleum ether/EtOAc = 8:1): R_f = 0.14; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.41-7.36 (m, 9H), 7.30-7.23 (m, 5H), 7.19-7.17 (m, 2H), 7.13-7.11 (m, 4H), 3.84 (s, 2H), 3.80 (s, 6H), 3.63 (s, 2H), 1.87 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 171.8, 165.5, 149.4, 149.0, 144.6, 142.9, 139.7, 135.6, 134.5, 132.7, 131.5, 131.1, 130.2, 130.0, 129.7, 129.0, 128.5, 128.4, 128.3, 128.2, 128.1, 127.7, 127.6, 123.2, 118.4, 96.8, 86.5, 59.6, 53.4, 41.4, 38.8, 19.2. **FT-IR** (KBr): ν = 3053, 3024, 2958, 2918, 2864, 2364, 1730, 1625, 1440, 1145 cm^{-1}; **HRMS** (APCI-TOF): *m/z* calcd for $C_{43}H_{34}O_6S$ $[M+H]^+$ 679.2149, found 679.2149.



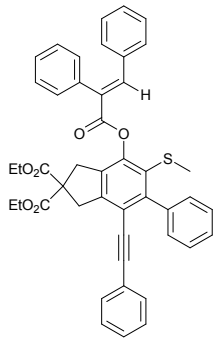
(*E*)-dimethyl 4-((2,3-diphenylacryloyl)oxy)-5-(methylthio)-6-(*p*-tolyl)-7-(*p*-tolylethynyl)-1*H*-indene-2,2(3*H*)-dicarboxylate (4b)

White solid; 265 mg (75 % yield); m. p. 190-191 ℃; TLC (petroleum ether/EtOAc = 8:1): R_f = 0.19; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.41 (s, 5H), 7.25 (s, 5H), 7.19-7.17 (m, 2H), 7.13-7.11 (m, 2H), 7.04 (s, 4H), 3.83 (s, 2H), 3.79 (s, 6H), 3.62 (s, 2H), 2.43 (s, 3H), 2.31 (s, 3H), 1.87 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 171.8, 165.5, 149.3, 148.8, 144.5, 142.8, 138.5, 137.1, 136.8, 135.6, 134.5, 132.4, 131.5, 131.4, 131.1, 130.0, 129.7, 129.1, 128.9, 128.4, 128.3, 128.2, 128.0, 120.2, 118.7, 96.9, 86.1, 59.5, 53.4, 41.4, 38.8, 21.6, 21.5, 19.3. **FT-IR** (KBr): ν = 3047, 3024, 2953, 2924, 2353, 1741, 1624, 1440, 1139, 817 cm^{-1}; **HRMS** (APCI-TOF): *m/z* calcd for $C_{45}H_{38}O_6S$ $[M+H]^+$ 707.2462, found 707.2457.



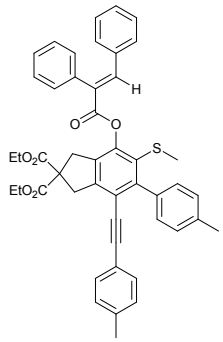
(*E*)-dimethyl 4-((2,3-diphenylacryloyl)oxy)-6-(4-fluorophenyl)-7-((4-fluorophenyl)ethynyl)-5-(methylthio)-1*H*-indene-2,2(3*H*)-dicarboxylate (4c)

White solid; 247 mg (69 % yield); m. p. 163-164 ℃; TLC (petroleum ether/EtOAc = 8:1): R_f = 0.12; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.41 (s, 5H), 7.37-7.32 (m, 2H), 7.28-7.20 (m, 3H), 7.16-7.11 (m, 6H), 6.95 (t, J = 8.4 Hz, 2H), 3.82 (s, 2H), 3.79 (s, 6H), 3.63 (s, 2H), 1.86 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 171.7, 165.5, 163.5 (d, $J_{C\text{-}F}$ = 40 Hz), 161.5 (d, $J_{C\text{-}F}$ = 36.3 Hz), 149.1, 148.1, 144.7, 143.0, 135.6, 134.4, 133.4 (d, $J_{C\text{-}F}$ = 7.5 Hz), 133.0, 131.9 (d, $J_{C\text{-}F}$ = 7.5 Hz), 131.4, 131.1, 130.0, 129.8, 129.0, 128.5, 128.3, 119.1, 118.3, 115.7 (d, $J_{C\text{-}F}$ = 21.3 Hz), 114.6 (d, $J_{C\text{-}F}$ = 21.3 Hz), 95.8, 86.0, 59.5, 53.4, 41.4, 38.8, 19.1. **FT-IR** (KBr): ν = 3059, 3030, 2953, 2924, 2358, 1730, 1625, 1435, 1143, 835 cm^{-1}; **HRMS** (APCI-TOF): *m/z* calcd for $C_{43}H_{32}F_2O_6S$ $[M+H]^+$ 715.1960, found 715.1953.



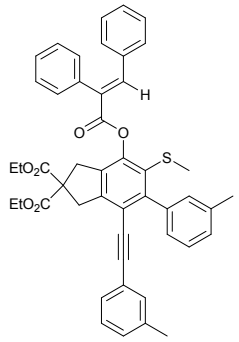
(*E*)-diethyl 4-((2,3-diphenylbut-2-enoyl)oxy)-5-(methylthio)-6-phenyl-7-(phenylethynyl)-1*H*-indene-2,2(3*H*)-dicarboxylate (4d)

White solid; 306 mg (85 % yield); m. p. 147-148 ℃; TLC (petroleum ether/EtOAc = 8:1): R_f = 0.27; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.41-7.38 (m, 10H), 7.24-7.20 (m, 6H), 7.17-7.11 (m, 4H), 4.25 (q, J = 6.9 Hz, 4H), 3.83 (s, 2H), 3.62 (s, 2H), 1.87 (s, 3H), 1.29 (t, J = 7.2 Hz, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 171.3, 165.5, 149.4, 149.0, 144.8, 142.8, 139.8, 135.7, 134.5, 132.8, 131.5, 131.1, 130.2, 130.0, 129.7, 128.9, 128.4, 128.3, 128.2, 128.0, 127.6, 127.5, 123.2, 118.4, 96.7, 86.5, 62.2, 59.7, 41.3, 38.6, 19.2, 14.2. **FT-IR** (KBr): ν = 3053, 3024, 2993, 2929, 2364, 1737, 1624, 1440, 1145, 758 cm^{-1}; **HRMS** (APCI-TOF): *m/z* calcd for $C_{45}H_{38}O_6S$ $[M+H]^+$ 707.2462, found 707.2458.



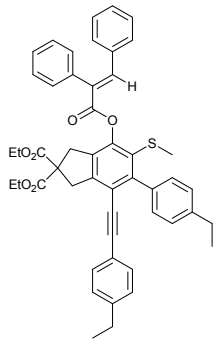
(*E*)-diethyl 4-((2,3-diphenylacryloyl)oxy)-5-(methylthio)-6-(*p*-tolyl)-7-(*p*-tolylethynyl)-1*H*-indene-2,2(3*H*)-dicarboxylate (4e)

White solid; 294 mg (80 % yield); m. p. 144-145 ℃; TLC (petroleum ether/EtOAc = 8:1): R_f = 0.29; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.40 (s, 5H), 7.24-7.17 (m, 7H), 7.13-7.11 (m, 2H), 7.04 (s, 4H), 4.25 (q, J = 6.9 Hz, 4H), 3.81 (s, 2H), 3.60 (s, 2H), 2.43 (s, 3H), 2.31 (s, 3H), 1.87 (s, 3H), 1.28 (t, J = 7.2 Hz, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 171.4, 165.5, 149.2, 148.8, 144.6, 142.7, 138.4, 137.0, 136.8, 135.7, 134.5, 132.5, 131.6, 131.4, 131.1, 130.0, 129.9, 129.6, 129.0, 128.9, 128.4, 128.3, 128.2, 127.9, 120.3, 118.6, 96.8, 86.1, 62.2, 59.6, 41.3, 38.6, 21.6, 21.5, 19.3, 14.2. **FT-IR** (KBr): v = 3059, 3030, 2987, 2924, 2364, 1735, 1618, 1512, 1143, 813 cm^{-1}; **HRMS** (APCI-TOF): *m/z* calcd for $C_{47}H_{42}O_6S$ $[M+H]^+$ 735.2775, found 735.2773.



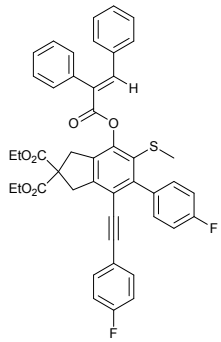
(*E*)-diethyl 4-((2,3-diphenylacryloyl)oxy)-5-(methylthio)-6-(*m*-tolyl)-7-(*m*-tolylethynyl)-1*H*-indene-2,2(3*H*)-dicarboxylate (4f)

White solid; 301 mg (82 % yield); m. p. 163-164 ℃; TLC (petroleum ether/EtOAc = 8:1): R_f = 0.33; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.40 (s, 5H), 7.32 (t, J = 7.5 Hz, 1H), 7.25-7.19 (m, 6H), 7.14-7.04 (m, 4H), 6.95-6.92 (m, 2H), 4.25 (q, J = 6.9 Hz, 4H), 3.81 (s, 2H), 3.61 (s, 2H), 2.40 (s, 3H), 2.28 (s, 3H), 1.88 (s, 3H), 1.29 (t, J = 6.9 Hz, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 171.3, 165.5, 149.5, 148.9, 144.7, 142.7, 139.7, 137.9, 137.0, 135.7, 134.5, 132.6, 132.2, 131.6, 131.1, 130.9, 130.0, 129.7, 129.2, 128.9, 128.5, 128.4, 128.2, 127.9, 127.5, 127.2, 123.1, 118.4, 96.9, 86.4, 62.2, 59.7, 41.3, 38.6, 21.7, 21.3, 19.3, 14.2. **FT-IR** (KBr): v = 3053, 3030, 2981, 2924, 2364, 1737, 1620, 1400, 1145, 792 cm^{-1}; **HRMS** (APCI-TOF): *m/z* calcd for $C_{47}H_{42}O_6S$ $[M+H]^+$ 735.2775, found 735.2770.



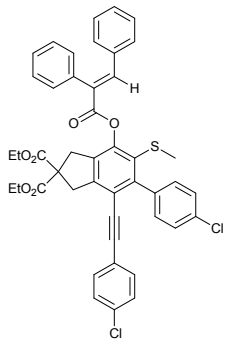
(*E*)-diethyl 4-((2,3-diphenylacryloyl)oxy)-6-(4-ethylphenyl)-7-((4-ethylphenyl)ethynyl)-5-(methylthio)-1*H*-indene-2,2(3*H*)-dicarboxylate (4g)

White solid; 317 mg (83 % yield); m. p. 131-132 ℃; TLC (petroleum ether/EtOAc = 8:1): R_f = 0.27; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.41 (s, 5H;), 7.27-7.23 (m, 5H), 7.22-7.17 (m, 2H), 7.14-7.11 (m, 2H), 7.04-7.01 (m, 4H), 4.25 (q, J = 7.2 Hz, 4H), 3.81 (s, 2H), 3.60 (s, 2H), 2.74 (q, J = 7.5 Hz, 2H), 2.60 (q, J = 7.5 Hz, 2H), 1.87 (s, 3H), 1.34-1.17 (m, 12H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 171.4, 165.5, 149.5, 148.8, 144.8, 144.5, 143.4, 142.7, 137.2, 135.7, 134.5, 132.5, 131.6, 131.5, 131.1, 130.1, 130.0, 129.6, 128.9, 128.4, 128.2, 127.9, 127.8, 127.1, 120.5, 118.8, 96.9, 86.2, 62.2, 59.7, 41.3, 38.6, 29.0, 28.9, 19.3, 15.9, 15.5, 14.2. **FT-IR** (KBr): v = 3053, 3030, 2987, 2924, 2364, 1732, 1620, 1508, 1153, 831 cm^{-1}; **HRMS** (APCI-TOF): *m/z* calcd for $C_{49}H_{46}O_6S$ $[M+H]^+$ 763.2775, found 763.2773.



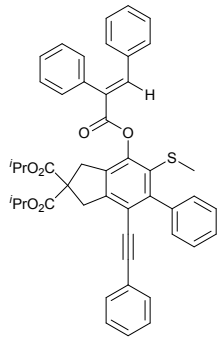
(*E*)-diethyl 4-((2,3-diphenylacryloyl)oxy)-6-(4-fluorophenyl)-7-((4-fluorophenyl)ethynyl)-5-(methylthio)-1*H*-indene-2,2(3*H*)-dicarboxylate (4h)

White solid; 267 mg (72 % yield); m. p. 133-134 ℃; TLC (petroleum ether/EtOAc = 8:1): R_f = 0.29; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.41 (s, 5H), 7.34 (dd, J = 6.0, 1.8 Hz, 2H), 7.25-7.20 (m, 3H), 7.17-7.13 (m, 3H), 7.13-7.11 (m, 3H), 6.95 (t, J = 8.4 Hz, 2H), 4.25 (q, J = 7.2 Hz, 4H), 3.80 (s, 2H), 3.61 (s, 2H), 1.86 (s, 3H), 1.29 (t, J = 7.2 Hz, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 171.3, 165.5, 163.3 (d, $J_{C\text{-}F}$ = 40 Hz), 161.5 (d, $J_{C\text{-}F}$ = 36.3 Hz), 149.2, 148.2, 144.9, 142.9, 135.7, 134.5, 133.4 (d, $J_{C\text{-}F}$ = 8.8 Hz), 133.1, 132.0 (d, $J_{C\text{-}F}$ = 8.8 Hz), 131.5, 131.1, 130.0, 129.7, 129.0, 128.5, 128.3, 119.2, 118.3, 115.7 (d, $J_{C\text{-}F}$ = 21.3 Hz), 114.6 (d, $J_{C\text{-}F}$ = 21.3 Hz), 95.8, 86.1, 62.2, 59.7, 41.3, 38.7, 19.1, 14.2. **FT-IR** (KBr): v = 3035, 2993, 2929, 2382, 2347, 1732, 1625, 1400, 1145, 817 cm^{-1}; **HRMS** (APCI-TOF): *m/z* calcd for $C_{45}H_{36}F_2O_6S$ $[M+H]^+$ 743.2273, found 743.2277.



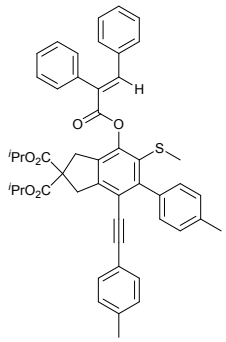
(*E*)-diethyl 5-(4-chlorophenyl)-4-((4-chlorophenyl)ethynyl)-7-((2,3-diphenylacryloyl)oxy)-6-(methylthio)-1*H*-indene-2,2(3*H*)-dicarboxylate (4i)

White solid; 271 mg (70 % yield); m. p. 138-139 ℃; TLC (petroleum ether/EtOAc = 8:1): R_f = 0.29; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.43-7.41 (m, 7H), 7.32-7.29 (m, 2H), 7.25-7.18 (m, 5H), 7.13-7.11 (m, 2H), 7.08-7.05 (m, 2H), 4.25 (q, J = 6.9 Hz, 4H), 3.79 (s, 2H), 3.61 (s, 2H), 1.86 (s, 3H), 1.29 (t, J = 7.2 Hz, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 171.2, 165.4, 149.3, 148.0, 145.1, 143.0, 138.1, 135.6, 134.6, 134.4, 133.6, 133.3, 132.7, 131.7, 131.4, 131.1, 130.0, 129.8, 129.0, 128.8, 128.5, 128.3, 128.1, 127.9, 121.5, 118.0, 95.8, 87.2, 62.3, 59.6, 41.2, 38.6, 19.2, 14.2. **FT-IR** (KBr): v = 3059, 3030, 2993, 2924, 2364, 1732, 1620, 1490, 1139, 758 cm^{-1}; **HRMS** (APCI-TOF): *m/z* calcd for $C_{45}H_{36}Cl_2O_6S$ $[M+H]^+$ 775.1682, found 775.1680.



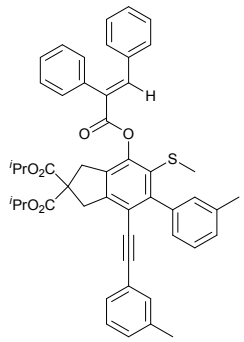
(*E*)-diisopropyl 4-((2,3-diphenylacryloyl)oxy)-5-(methylthio)-6-phenyl-7-(phenylethynyl)-1*H*-indene-2,2(3*H*)-dicarboxylate (4j)

White solid; 327 mg (89 % yield); m. p. 159-160 ℃; TLC (petroleum ether/EtOAc = 8:1): R_f = 0.35; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.42-7.41 (m, 7H), 7.38-7.36 (m, 3H), 7.25-7.24 (m, 3H), 7.22-7.17 (m, 3H), 7.14-7.11 (m, 4H), 5.13-5.04 (m, 2H), 3.78 (s, 2H), 3.58 (s, 2H), 1.86 (s, 3H), 1.27 (d, J = 6.0 Hz, 12H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 170.8, 165.5, 149.4, 149.0, 144.9, 142.7, 139.8, 135.7, 134.5, 132.8, 131.6, 131.5, 131.1, 130.2, 130.0, 129.7, 128.9, 128.4, 128.3, 128.2, 127.9, 127.6, 127.5, 123.3, 118.4, 96.6, 86.6, 69.7, 59.7, 41.2, 38.5, 21.7, 19.2. **FT-IR** (KBr): v = 3059, 3030, 2993, 2924, 2364, 1732, 1620, 1490, 1139, 758 cm^{-1}; **HRMS** (APCI-TOF): *m/z* calcd for $C_{47}H_{42}O_6S$ $[M+H]^+$ 735.2775, found 735.2770.



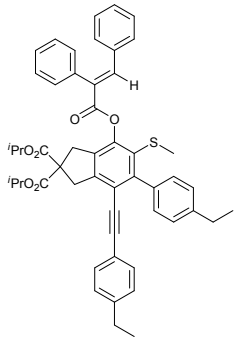
(*E*)-diisopropyl 4-((2,3-diphenylacryloyl)oxy)-5-(methylthio)-6-(*p*-tolyl)-7-(*p*-tolylethynyl)-1*H*-indene-2,2(3*H*)-dicarboxylate (4k)

White solid; 313 mg (82 % yield); m. p. 152-153 ℃; TLC (petroleum ether/EtOAc = 8:1): R_f = 0.40; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.40 (s, 5H), 7.24-7.22 (m, 5H), 7.19-7.17 (m, 2H), 7.14-7.11 (m, 2H), 7.04 (s, 4H), 5.12-5.04 (m, 2H), 3.76 (s, 2H), 3.57 (s, 2H), 2.43 (s, 3H), 2.31 (s, 3H), 1.86 (s, 3H), 1.27 (d, J = 6.3 Hz, 12H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 170.9, 165.5, 149.2, 148.8, 144.8, 142.6, 138.4, 137.0, 136.9, 135.7, 134.5, 132.6, 131.6, 131.4, 131.1, 130.1, 130.0, 129.6, 129.0, 128.9, 128.4, 128.3, 128.2, 127.8, 120.3, 118.6, 96.7, 86.1, 69.6, 59.7, 41.2, 38.5, 21.7, 21.6, 21.5, 19.3. **FT-IR** (KBr): v = 3059, 3035, 2987, 2924, 2370, 1730, 1620, 1400, 1139, 813 cm^{-1}; **HRMS** (APCI-TOF): *m/z* calcd for $C_{49}H_{46}O_6S$ $[M+H]^+$ 763.3088, found 763.3084.



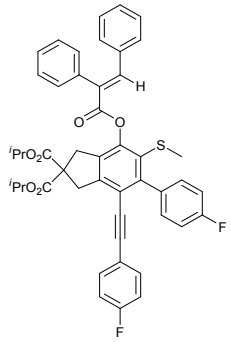
(*E*)-diisopropyl 4-((2,3-diphenylacryloyl)oxy)-5-(methylthio)-6-(*m*-tolyl)-7-(*m*-tolylethynyl)-1*H*-indene-2,2(3*H*)-dicarboxylate (4l)

White solid; 305 mg (80 % yield); m. p. 158-159 ℃; TLC (petroleum ether/EtOAc = 8:1): R_f = 0.38; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.40 (s, 5H), 7.35-7.22 (m, 4H), 7.20-7.17 (m, 3H), 7.14-7.10 (m, 3H), 7.07-7.04 (m, 1H), 6.94-6.92 (m, 2H), 5.12-5.04 (m, 2H), 3.77 (s, 2H), 3.57 (s, 2H), 2.40 (s, 3H), 2.28 (s, 3H), 1.87 (s, 3H), 1.27 (d, J = 6.3 Hz, 12H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 170.9, 165.5, 149.5, 148.9, 144.8, 142.7, 139.7, 137.9, 137.0, 135.7, 134.5, 132.7, 132.2, 131.6, 131.1, 130.9, 130.0, 129.7, 129.2, 128.9, 128.5, 128.4, 128.2, 127.8, 127.5, 127.2, 123.2, 118.4, 96.8, 86.4, 69.7, 59.7, 41.2, 38.5, 21.7, 21.3, 19.3. **FT-IR** (KBr): v = 3053, 2981, 2924, 2358, 1730, 1618, 1598, 1400, 1145, 790 cm^{-1}; **HRMS** (APCI-TOF): *m/z* calcd for $C_{49}H_{46}O_6S$ $[M+H]^+$ 763.3088, found 763.3085.



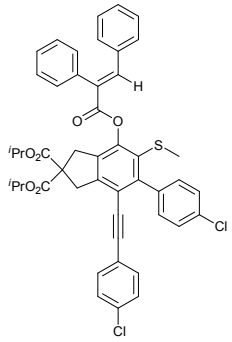
(*E*)-diisopropyl 4-((2,3-diphenylacryloyl)oxy)-6-(4-ethylphenyl)-7-((4-ethylphenyl)ethynyl)-5-(methylthio)-1*H*-indene-2,2(3*H*)-dicarboxylate (4m)

White solid; 328 mg (83 % yield); m. p. 139-140 ℃; TLC (petroleum ether/EtOAc = 8:1): R_f = 0.40; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.40 (s, 5H), 7.26-7.22 (m, 6H), 7.19-7.11 (m, 3H), 7.07-7.00 (m, 4H), 5.12-5.04 (m, 2H), 3.76 (s, 2H), 3.57 (s, 2H), 2.73 (q, J = 7.5 Hz, 2H), 2.60 (q, J = 7.8 Hz, 2H), 1.87 (s, 3H), 1.34-1.17 (m, 18H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 170.9, 165.5, 149.5, 148.8, 144.7, 144.6, 143.3, 142.6, 137.2, 135.8, 134.6, 132.6, 131.7, 131.5, 131.1, 130.2, 130.0, 129.6, 128.9, 128.4, 128.2, 127.8, 127.1, 120.6, 118.8, 96.8, 86.3, 69.6, 59.8, 41.2, 38.6, 28.9, 21.7, 19.3, 15.9, 15.5. **FT-IR** (KBr): v = 3059, 3030, 2987, 2958, 2364, 1730, 1620, 1508, 1153, 831 cm^{-1}; **HRMS** (APCI-TOF): *m/z* calcd for $C_{51}H_{50}O_6S$ $[M+H]^+$ 791.3401, found 791.3403.



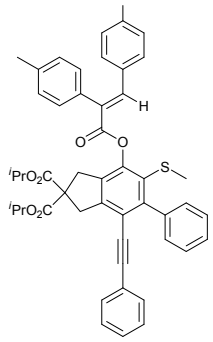
(*E*)-diisopropyl 4-((2,3-diphenylacryloyl)oxy)-6-(4-fluorophenyl)-7-((4-fluorophenyl)ethynyl)-5-(methylthio)-1*H*-indene-2,2(3*H*)-dicarboxylate (4n)

White solid; 301 mg (78 % yield); m. p. 139-140 ℃; TLC (petroleum ether/EtOAc = 8:1): R_f = 0.36; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.41 (s, 5H), 7.37-7.32 (m, 2H), 7.24-7.20 (m, 3H), 7.17-7.10 (m, 6H), 6.95 (t, J = 8.7 Hz, 2H), 5.12-5.04 (m, 2H), 3.76 (s, 2H), 3.58 (s, 2H), 1.85 (s, 3H), 1.27 (d, J = 6.0 Hz, 12H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 170.8, 165.4, 163.5 (d, $J_{C\text{-}F}$ = 38.8 Hz), 161.5 (d, $J_{C\text{-}F}$ = 35 Hz), 149.1, 148.1, 145.0, 142.8, 135.7, 134.4, 133.3 (d, $J_{C\text{-}F}$ = 7.5 Hz), 133.2, 132.0 (d, $J_{C\text{-}F}$ = 7.5 Hz), 131.5, 131.1, 130.0, 129.7, 128.9, 128.5, 128.2, 128.1, 119.2, 118.3, 115.7 (d, $J_{C\text{-}F}$ = 22.5 Hz), 114.6 (d, $J_{C\text{-}F}$ = 21.3 Hz), 95.7, 86.1, 69.7, 59.7, 41.1, 38.6, 21.7, 19.1. **FT-IR** (KBr): v = 3053, 3035, 2981, 2924, 2364, 1730, 1618, 1506, 1139, 835 cm^{-1}; **HRMS** (APCI-TOF): *m/z* calcd for $C_{47}H_{40}F_2O_6S$ $[M+H]^+$ 771.2586, found 771.2585.



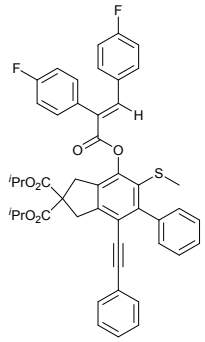
(*E*)-diisopropyl 5-(4-chlorophenyl)-4-((4-chlorophenyl)ethynyl)-7-((2,3-diphenylacryloyl)oxy)-6-(methylthio)-1*H*-indene-2,2(3*H*)-dicarboxylate (4o)

White solid; 301 mg (75 % yield); m. p. 151-152 ℃; TLC (petroleum ether/EtOAc = 8:1): R_f = 0.40; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.40 (s, 6H), 7.31-7.25 (m, 4H), 7.23-7.18 (m, 4H), 7.14-7.11 (m, 2H), 7.07-7.05 (m, 2H), 5.12-5.04 (m, 2H), 3.75 (s, 2H), 3.57 (s, 2H), 1.85 (s, 3H), 1.27 (d, J = 6.0 Hz, 12H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 170.7, 165.4, 149.3, 148.0, 145.2, 142.9, 138.1, 135.6, 134.5, 134.4, 133.5, 133.4, 132.6, 131.7, 131.4, 131.1, 129.9, 129.7, 128.9, 128.8, 128.5, 128.2, 128.0, 127.9, 121.5, 117.9, 95.7, 87.2, 69.8, 59.7, 41.1, 38.5, 21.7, 19.2. **FT-IR** (KBr): v = 3035,2987, 2935, 1726, 1624, 1490, 1400, 1149, 825, 705 cm^{-1}; **HRMS** (APCI-TOF): *m/z* calcd for $C_{47}H_{40}Cl_2O_6S$ $[M+H]^+$ 803.1995, found 803.1992.



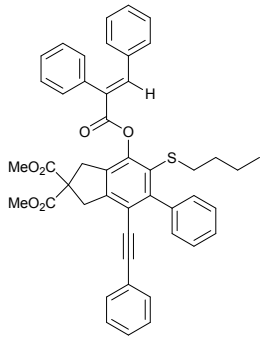
(*E*)-diisopropyl 4-((2,3-di-p-tolylacryloyl)oxy)-5-(methylthio)-6-phenyl-7-(phenylethynyl)-1*H*-indene-2,2(3*H*)-dicarboxylate (4p)

White solid; 324 mg (85 % yield); m. p. 150-151 ℃; TLC (petroleum ether/EtOAc = 8:1): R_f = 0.33; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.44-7.36 (m, 5H), 7.30-7.28 (m, 2H), 7.23-7.20 (m, 5H), 7.12-7.10 (m, 2H), 7.03 (dd, J = 8.0, 19.0 Hz, 4H), 5.10-5.05 (m, 2H), 3.77 (s, 2H), 3.57 (s, 2H), 2.39 (s, 3H), 2.29 (s, 3H), 1.88 (s, 3H), 1.27 (d, J = 6.0 Hz, 12H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 170.8, 165.8, 149.3, 149.2, 144.9, 142.5, 140.0, 139.9, 137.8, 132.9, 131.9, 131.5, 131.1, 130.6, 130.2, 129.8, 129.6, 129.2, 128.3, 128.0, 127.6, 127.5, 123.3, 118.3, 96.6, 86.7, 69.6, 59.8, 41.2, 38.6, 21.7, 21.5, 19.2. **FT-IR** (KBr): v = 3057, 3035, 2980, 2925, 1727, 1603, 1493, 1273, 1142, 751 cm^{-1}; **HRMS** (APCI-TOF): *m/z* calcd for $C_{49}H_{46}O_6S$ $[M+H]^+$ 763.2775, found 763.2780.



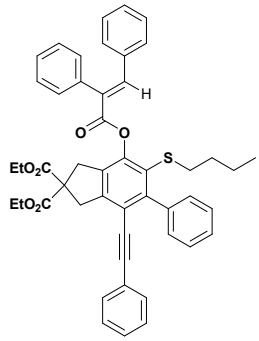
(*E*)-diisopropyl 4-((2,3-bis(4-fluorophenyl)acryloyl)oxy)-5-(methylthio)-6-phenyl-7-(phenylethynyl)-1*H*-indene-2,2(3*H*)-dicarboxylate (4q)

White solid; 285 mg (74 % yield); m. p. 141-142 ℃; TLC (petroleum ether/EtOAc = 8:1): R_f = 0.35; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.45-7.40 (m, 3H), 7.39-7.36 (m, 4H), 7.25-7.21 (m, 3H), 7.13-7.10 (m, 6H), 6.92 (t, J = 9.0 Hz, 2H), 5.11-5.06 (m, 2H), 3.78 (s, 2H), 3.56 (s, 2H), 1.86 (s, 3H), 1.27 (d, J = 2.0 Hz, 6H), 1.26 (d, J = 2.5 Hz, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 170.8, 165.2, 164.1 (d, $J_{C\text{-}F}$ = 72.5 Hz), 162.1 (d, $J_{C\text{-}F}$ = 68.8 Hz), 149.5, 148.9, 145.1, 141.8, 139.7, 133.0 (d, $J_{C\text{-}F}$ = 8.8 Hz), 132.8, 131.9 (d, $J_{C\text{-}F}$ = 8.8 Hz), 131.5, 131.4, 130.5, 130.2, 128.3, 127.8, 127.7, 127.6, 123.3, 118.6, 116.2 (d, $J_{C\text{-}F}$ = 21.3 Hz), 115.8 (d, $J_{C\text{-}F}$ = 21.3 Hz), 96.8, 86.5, 69.7, 59.8, 41.2, 38.6, 21.7, 19.2. **FT-IR** (KBr): v = 3057, 2963, 2933, 1729, 1598, 1506, 1417, 1263, 1098, 804 cm^{-1}; **HRMS** (APCI-TOF): *m/z* calcd for $C_{47}H_{40}F_2O_6S$ $[M+H]^+$ 771.2586, found 771.2583.



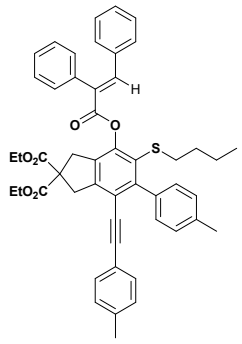
(*E*)-dimethyl 5-(butylthio)-4-((2,3-diphenylacryloyl)oxy)-6-phenyl-7-(phenylethynyl)-1*H*-indene-2,2(3*H*)-dicarboxylate (4r)

White solid; 285 mg (79 % yield); m. p. 108-109 ℃; TLC (petroleum ether/EtOAc = 8:1): R_f = 0.19; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.42-7.38 (m, 10H), 7.25-7.24 (m, 3H), 7.22-7.19 (m, 3H), 7.17-7.11 (m, 4H), 3.85 (s, 2H), 3.80 (s, 6H), 3.64 (s, 2H), 2.23 (t, J = 7.2 Hz, 2H), 1.20-1.13 (m, 2H), 1.10-1.01 (m, 2H), 0.69 (t, J = 7.2 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 171.8, 165.4, 149.7, 149.2, 144.5, 142.8, 139.8, 135.7, 134.6, 132.6, 131.5, 131.1, 130.4, 130.1, 129.7, 128.9, 128.5, 128.3, 128.2, 127.6, 127.5, 126.9, 123.3, 118.3, 96.8, 86.6, 59.6, 53.4, 41.5, 38.9, 35.4, 31.5, 21.8, 13.6. **FT-IR** (KBr): v = 3088, 3059, 3030, 2953, 2929, 2870, 2353, 1732, 1490, 758 cm^{-1}; **HRMS** (APCI-TOF): *m/z* calcd for $C_{46}H_{40}O_6S$ $[M+H]^+$ 721.2618, found 721.2620.



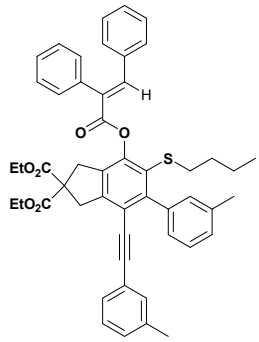
(*E*)-diethyl 5-(butylthio)-4-((2,3-diphenylacryloyl)oxy)-6-phenyl-7-(phenylethynyl)-1*H*-indene-2,2(3*H*)-dicarboxylate (4s)

White solid; 300 mg (80 % yield); m. p. 111-112 ℃; TLC (petroleum ether/EtOAc = 8:1): R_f = 0.28; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.42-7.38 (m, 10H), 7.25-7.17 (m, 6H), 7.13-7.12 (m, 4H), 4.25 (q, J = 6.9 Hz, 4H), 3.83 (s, 2H), 3.62 (s, 2H), 2.23 (t, J = 6.9 Hz, 2H), 1.29 (t, J = 7.2 Hz, 6H), 1.20-1.12 (m, 2H), 1.10-1.03 (m, 2H), 0.69 (t, J = 7.2 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 171.4, 165.3, 149.7, 149.2, 144.7, 142.7, 139.8, 135.7, 134.6, 132.7, 131.7, 131.5, 131.0, 130.4, 130.1, 129.6, 128.9, 128.4, 128.3, 128.2, 127.5, 127.4, 126.8, 123.3, 118.3, 96.7, 86.7, 62.2, 59.7, 41.3, 38.7, 35.4, 31.5, 21.8, 14.2, 13.6. **FT-IR** (KBr): v = 3088, 3053, 3024, 2987, 2870, 2358, 1726, 1620, 1490, 756 cm^{-1}; **HRMS** (APCI-TOF): *m/z* calcd for $C_{48}H_{44}O_6S$ $[M+H]^+$ 749.2931, found 749.2928.



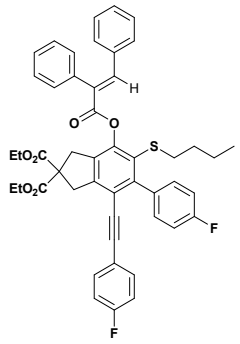
(*E*)-diethyl 5-(butylthio)-4-((2,3-diphenylacryloyl)oxy)-6-(*p*-tolyl)-7-(*p*-tolylethynyl)-1*H*-indene-2,2(3*H*)-dicarboxylate (4t)

White solid; 287 mg (74 % yield); m. p. 104-105 ℃; TLC (petroleum ether/EtOAc = 8:1): R_f = 0.30; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.40 (s, 5H), 7.25-7.22 (m, 5H), 7.19-7.17 (m, 2H), 7.13-7.11 (m, 2H), 7.04 (s, 4H), 4.24 (q, J = 6.9 Hz, 4H), 3.81 (s, 2H), 3.61 (s, 2H), 2.42 (s, 3H), 2.31 (s, 3H), 2.22 (t, J = 6.9 Hz, 2H), 1.28 (t, J = 7.2 Hz, 6H), 1.19-1.12 (m, 2H), 1.10-1.03 (m, 2H), 0.69 (t, J = 6.9 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 171.4, 165.3, 149.5, 149.0, 144.6, 142.6, 138.4, 136.9, 135.7, 134.6, 132.5, 131.7, 131.4, 131.0, 130.3, 130.1, 129.6, 129.1, 128.9, 128.4, 128.2, 126.7, 120.4, 118.6, 96.8, 86.2, 62.2, 59.7, 41.3, 38.7, 35.4, 31.5, 21.9, 21.6, 21.5, 14.2, 13.7. **FT-IR** (KBr): v = 3088, 3059, 3030, 2981, 2870, 2358, 1732, 1620, 1139, 813 cm^{-1}; **HRMS** (APCI-TOF): *m/z* calcd for $C_{50}H_{48}O_6S$ $[M+H]^+$ 777.3244, found 777.3241.



(*E*)-diethyl 5-(butylthio)-4-((2,3-diphenylacryloyl)oxy)-6-(*m*-tolyl)-7-(*m*-tolylethynyl)-1*H*-indene-2,2(3*H*)-dicarboxylate (4u)

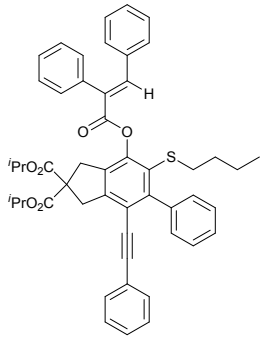
White solid; 295 mg (76 % yield); m. p. 95-96 ℃; TLC (petroleum ether/EtOAc = 8:1): R_f = 0.34; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.40 (s, 5H), 7.33-7.22 (m, 4H), 7.19-7.17 (m, 3H), 7.13-7.04 (m, 4H), 6.95-6.92 (m, 2H), 4.25 (q, J = 6.9 Hz, 4H), 3.82 (s, 2H), 3.61 (s, 2H), 2.39 (s, 3H), 2.28 (s, 3H), 2.24 (t, J = 7.2 Hz, 2H), 1.29 (t, J = 6.9 Hz, 6H), 1.20-1.13 (m, 2H), 1.11-1.04 (m, 2H), 0.70 (t, J = 7.2 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 171.4, 165.3, 149.8, 149.1, 144.6, 142.6, 139.7, 137.9, 136.9, 135.7, 134.6, 132.6, 132.2, 131.7, 131.0, 130.1, 129.6, 129.2, 128.9, 128.5, 128.4, 128.2, 128.1, 127.5, 127.4, 126.7, 123.2, 118.3, 96.9, 86.5, 62.2, 59.7, 41.3, 38.7, 35.4, 31.5, 21.8, 21.7, 21.3, 14.2, 13.7. **FT-IR** (KBr): v = 3088, 3059, 3030, 2964, 2929, 2358, 1730, 1614, 1139, 781 cm^{-1}; **HRMS** (APCI-TOF): *m/z* calcd for $C_{50}H_{48}O_6S$ $[M+H]^+$ 777.3244, found 777.3250.



(*E*)-diethyl 5-(butylthio)-4-((2,3-diphenylacryloyl)oxy)-6-(4-fluorophenyl)-7-((4-fluorophenyl)ethynyl)-1*H*-indene-2,2(3*H*)-dicarboxylate (4v)

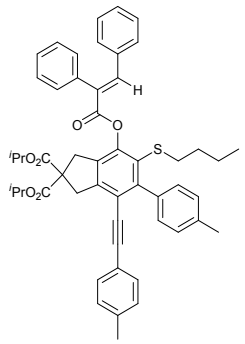
White solid; 267 mg (68 % yield); m. p. 118-119 ℃; TLC (petroleum ether/EtOAc = 8:1): R_f = 0.27; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.40 (s, 5H), 7.36-7.31 (m, 2H), 7.24-7.18 (m, 3H), 7.13-7.09 (m, 6H), 6.95 (t, J = 8.4 Hz, 2H), 4.25 (q, J = 6.9 Hz, 4H), 3.80 (s, 2H), 3.61 (s, 2H), 2.21 (t, J = 7.2 Hz, 2H), 1.29 (t, J = 7.2 Hz, 6H), 1.19-1.13 (m, 2H), 1.11-1.04 (m, 2H), 0.70 (t, J = 6.9 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 171.3, 165.3, 163.5 (d, J_{C-F} = 43.8 Hz), 161.5 (d, J_{C-F} = 38.8 Hz), 149.3, 148.4, 144.8, 142.8, 135.6, 134.5, 133.4 (d, J_{C-F} = 7.5 Hz), 133.0, 132.2 (d, J_{C-F} = 8.8 Hz), 131.5, 131.1, 130.0, 129.7, 128.9, 128.5, 128.2, 127.0, 119.2, 118.2, 115.5 (d, J_{C-F} = 22.5 Hz), 114.5 (d, J_{C-F} = 21.3 Hz), 95.7, 86.1, 62.2, 59.6, 41.3, 38.7, 35.4, 31.5, 21.8, 14.2, 13.6. **FT-IR** (KBr): v = 3059,3024,2958, 2929, 2870, 2353,

1732, 1620, 1508, 835 cm^{-1}; **HRMS** (APCI-TOF): *m/z* calcd for $C_{48}H_{42}F_2O_6S$ $[M+H]^+$ 785.2743, found 785.2746.



(*E*)-diisopropyl 5-(butylthio)-4-((2,3-diphenylacryloyl)oxy)-6-phenyl-7-(phenylethynyl)-1*H*-indene-2,2(3*H*)-dicarboxylate (4w)

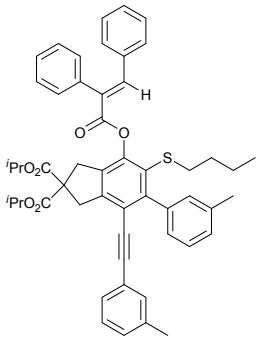
White solid; 319 mg (82 % yield); m. p. 148-149 ℃; TLC (petroleum ether/EtOAc = 8:1): R_f = 0.36; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.40-7.37 (m, 10H), 7.25-7.24 (m, 2H), 7.23-7.17 (m, 4H), 7.13-7.11 (m, 4H), 5.12-5.04 (m, 2H), 3.78 (s, 2H), 3.59 (s, 2H), 2.22 (t, *J* = 7.2 Hz, 2H), 1.27 (d, *J* = 6.0 Hz, 12H), 1.19-1.12 (m, 2H), 1.10-1.02 (m, 2H), 0.69 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 170.9, 165.3, 149.6, 149.2, 144.9, 142.6, 139.9, 135.7, 134.6, 132.8, 131.7, 131.5, 131.0, 130.4, 130.0, 129.6, 128.9, 128.4, 128.3, 128.2, 127.5, 127.4, 126.6, 123.4, 118.3, 96.6, 86.7, 69.7, 59.8, 41.2, 38.6, 35.4, 31.5, 21.8, 21.7, 13.6. **FT-IR** (KBr): *v* = 3082, 3059, 3030, 2981, 2935, 2353, 1730, 1624, 1512, 817 cm^{-1}; **HRMS** (APCI-TOF): *m/z* calcd for $C_{50}H_{48}O_6S$ $[M+H]^+$ 777.3244, found 777.3239.



(*E*)-diisopropyl 5-(butylthio)-4-((2,3-diphenylacryloyl)oxy)-6-(*p*-tolyl)-7-(*p*-tolylethynyl)-1*H*-indene-2,2(3*H*)-dicarboxylate (4x)

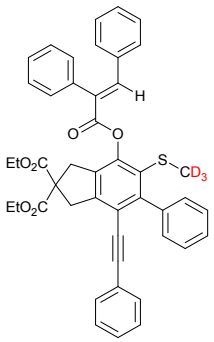
White solid; 322 mg (80 % yield); m. p. 170-171 ℃; TLC (petroleum ether/EtOAc = 8:1): R_f = 0.37; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.39 (s, 5H), 7.25-7.22 (m, 5H), 7.19-7.17 (m, 2H), 7.13-7.09 (m, 2H), 7.04 (s, 4H), 5.12-5.03 (m, 2H), 3.77 (s, 2H), 3.57 (s, 2H), 2.41 (s, 3H), 2.31 (s, 3H), 2.22 (t, *J* = 7.2 Hz, 2H), 1.26 (d, *J* = 6.3 Hz, 12H), 1.18-1.12 (m, 2H), 1.10-1.03 (m, 2H), 0.69 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 170.9, 165.3, 149.5, 149.0, 144.7, 142.5, 138.4, 136.9, 136.8, 135.7, 134.6, 131.7, 131.4, 131.0, 130.3, 130.0, 129.6, 129.0, 128.8, 128.4, 128.2, 128.1, 126.6, 120.4, 118.5, 96.7, 86.3, 69.6, 59.8, 41.2, 38.6, 35.3, 31.5, 21.9, 21.7, 21.6, 21.5, 13.7. **FT-IR** (KBr): *v* = 3088, 3059, 3030, 2981,

2929, 2358, 1730, 1624, 1512, 817 cm^{-1}; **HRMS** (APCI-TOF): *m/z* calcd for $C_{52}H_{52}O_6S$ $[M+H]^+$ 805.3557, found 805.3555.



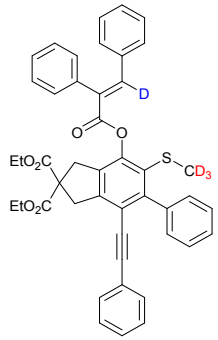
(*E*)-diisopropyl 5-(butylthio)-4-((2,3-diphenylacryloyl)oxy)-6-(*m*-tolyl)-7-(*m*-tolylethynyl)-1*H*-indene-2,2(3*H*)-dicarboxylate (4y)

White solid; 318 mg (79 % yield); m. p. 155-156 ℃; TLC (petroleum ether/EtOAc = 8:1): R_f = 0.39; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.40 (s, 5H), 7.33-7.22 (m, 3H), 7.19-7.17 (m, 4H), 7.14-7.04 (m, 4H), 6.95-6.92 (m, 2H), 5.12-5.04 (m, 2H), 3.78 (s, 2H), 3.58 (s, 2H), 2.39 (s, 3H), 2.28 (s, 3H), 2.23 (t, *J* = 7.2 Hz, 2H), 1.27 (d, *J* = 5.7 Hz, 12H), 1.20-1.12 (m, 2H), 1.10-1.03 (m, 2H), 0.70 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 170.9, 165.3, 149.7, 149.1, 144.7, 142.6, 139.7, 137.9, 136.8, 135.7, 134.5, 132.6, 132.2, 131.7, 131.1, 131.0, 130.0, 129.6, 129.1, 128.9, 128.5, 128.4, 128.2, 128.0, 127.5, 127.4, 126.5, 123.2, 118.3, 96.8, 86.5, 69.6, 59.8, 41.2, 38.6, 35.4, 31.5, 21.8, 21.7, 21.3, 13.7. **FT-IR** (KBr): *v* = 3082, 3059, 3030, 2976, 2929, 2364, 1730, 1620, 1508, 817 cm^{-1}; **HRMS** (APCI-TOF): *m/z* calcd for $C_{52}H_{52}O_6S$ $[M+H]+$ 805.3557, found 805.3560.



(*d*-4d)

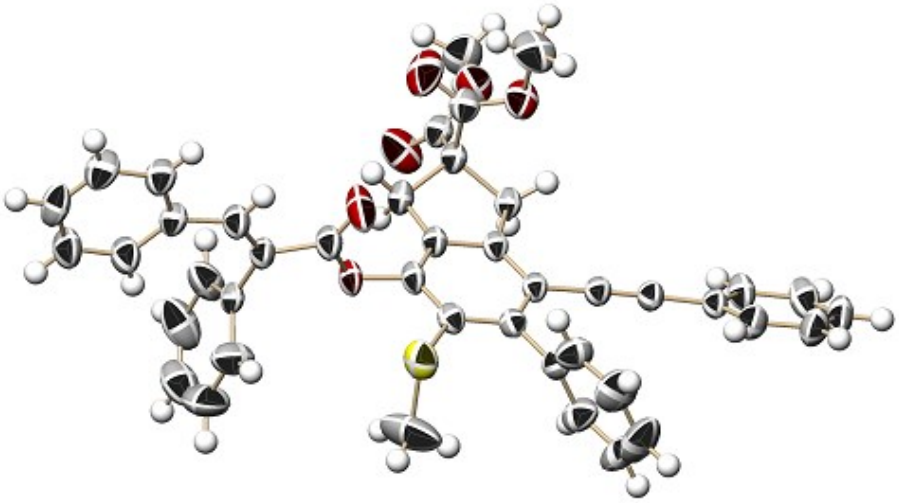
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.41-7.38 (m, 10H), 7.25-7.17 (m, 6H), 7.13-7.11 (m, 4H), 4.25 (q, *J* = 6.9 Hz, 4H), 3.82 (s, 2H), 3.62 (s, 2H), 1.29 (t, *J* = 7.2 Hz, 6H).



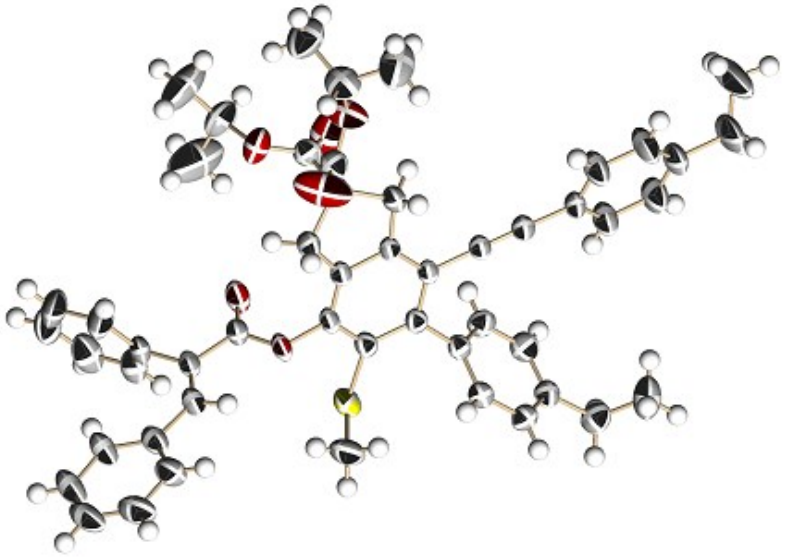
(*d*-4d′)

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41-7.38 (m, 10H), 7.24-7.18 (m, 6H), 7.14-7.12 (m, 4H), 4.25 (q, J = 7.2 Hz, 4H), 3.82 (s, 2H), 3.62 (s, 2H), 1.29 (t, J = 7.2 Hz, 6H).

4. X-Ray Structure for 4a and 4m

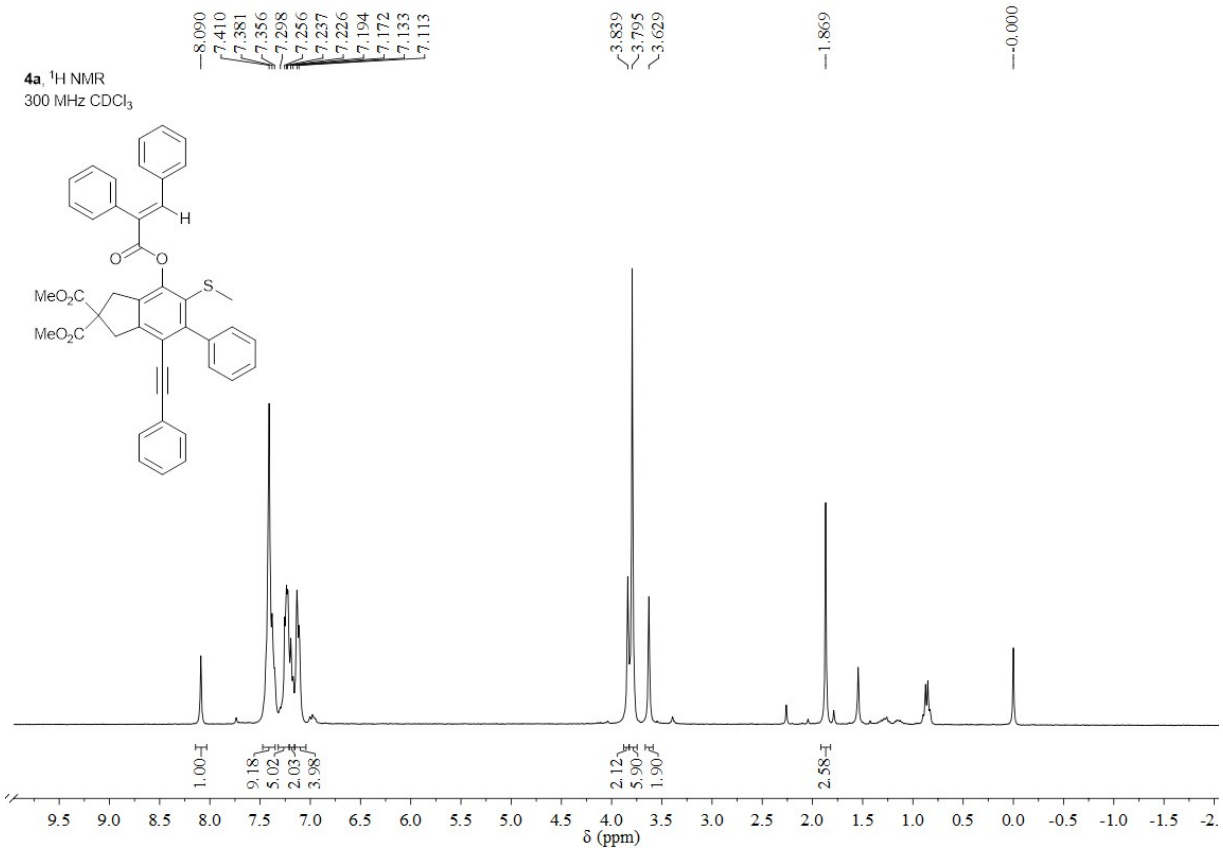


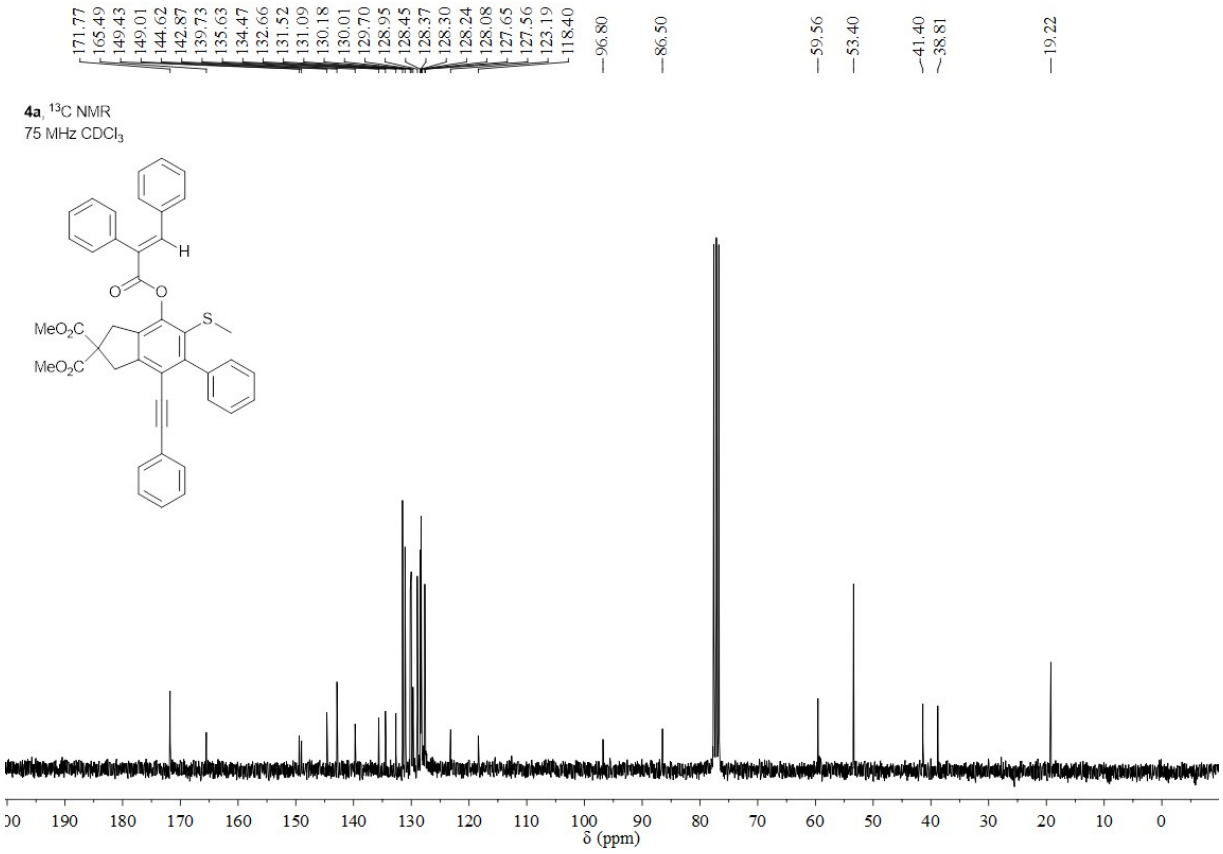
4a

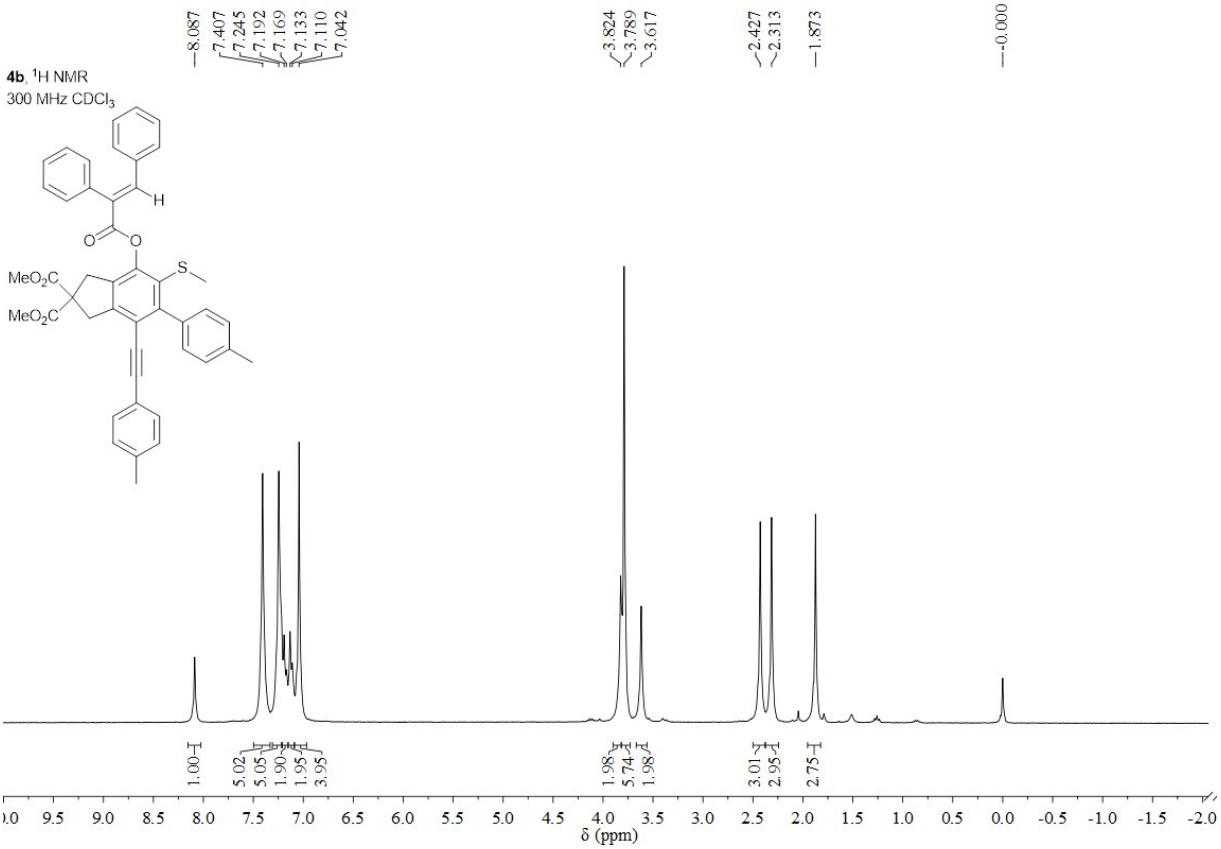


4m

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



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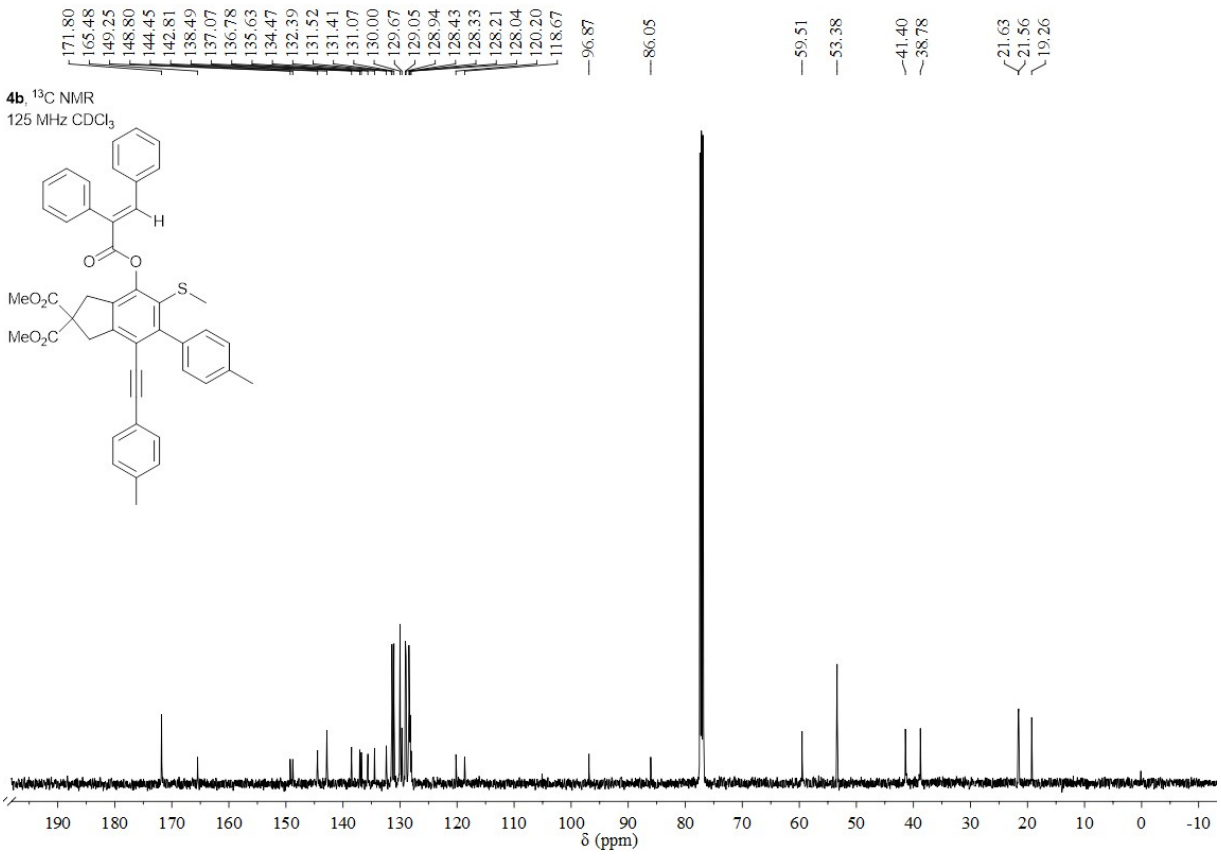
7.407
7.245
7.192
7.169
7.133
7.110
7.042
3.824
3.789
3.617
2.427
2.313
1.873
0.000
4b, 1H NMR
300 MHz CDCl3
MeO2C
MeO2C
S
O
O
H
1.00
5.02
5.05
1.90
1.95
3.95
1.98
5.74
1.98
3.01
2.95
2.75
δ (ppm)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165.48
149.25
148.80
144.45
142.81
138.49
137.07
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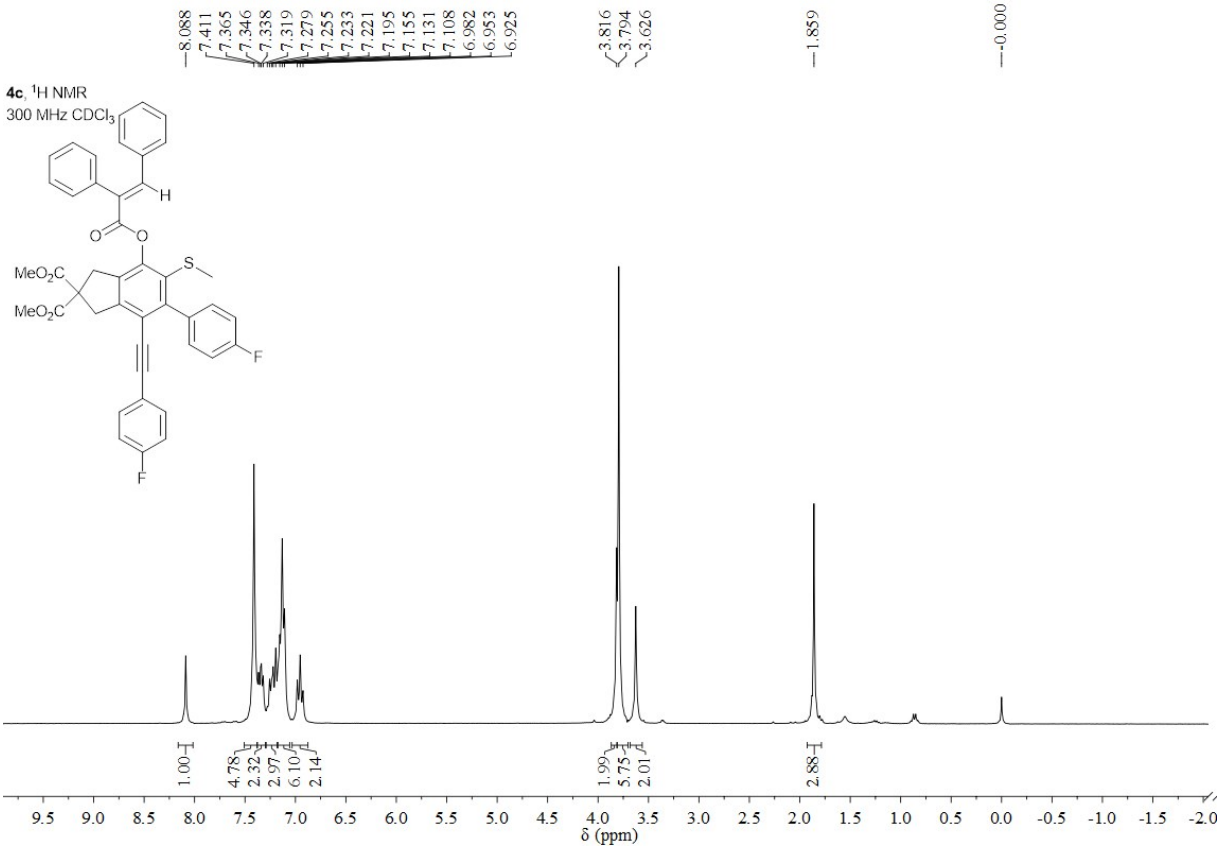
135.63
134.47
132.39
131.52
131.41
131.07
130.00
129.67
129.05
128.94
128.43
128.33
128.21
128.04
120.20
118.67
96.87
86.05
59.51
53.38
41.40
38.78
21.63
21.56
19.26
4b, 13C NMR
125 MHz CDCl3
MeO2C
MeO2C
S
O
O
H
δ (ppm)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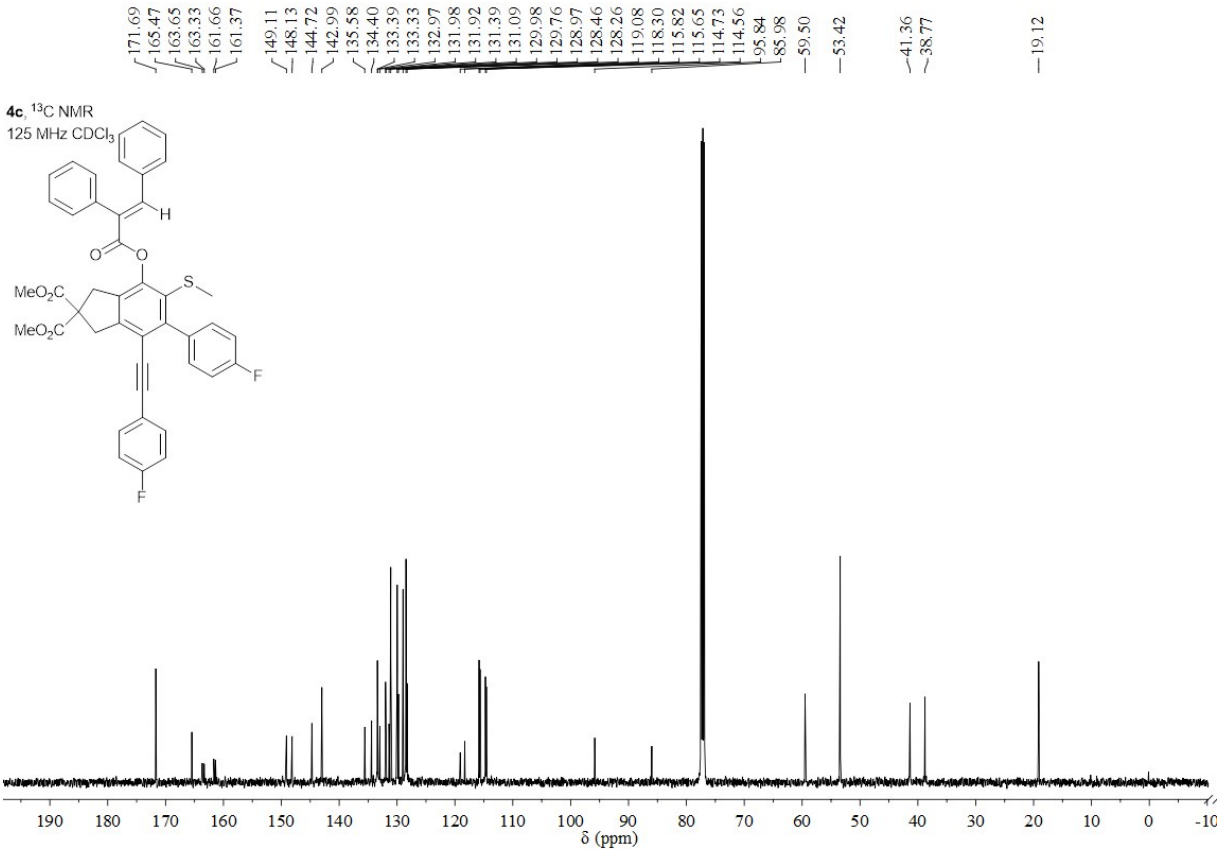
7.346
7.338
7.319
7.279
7.255
7.233
7.221
7.195
7.155
7.131
7.108
6.982
6.953
6.925
3.816
3.794
3.626
1.859
0.000
4c, 1H NMR
300 MHz CDCl3
MeO2C
MeO2C
S
F
F
1.00
4.78
2.32
2.97
6.10
2.14
1.99
5.75
2.01
2.88
δ (ppm)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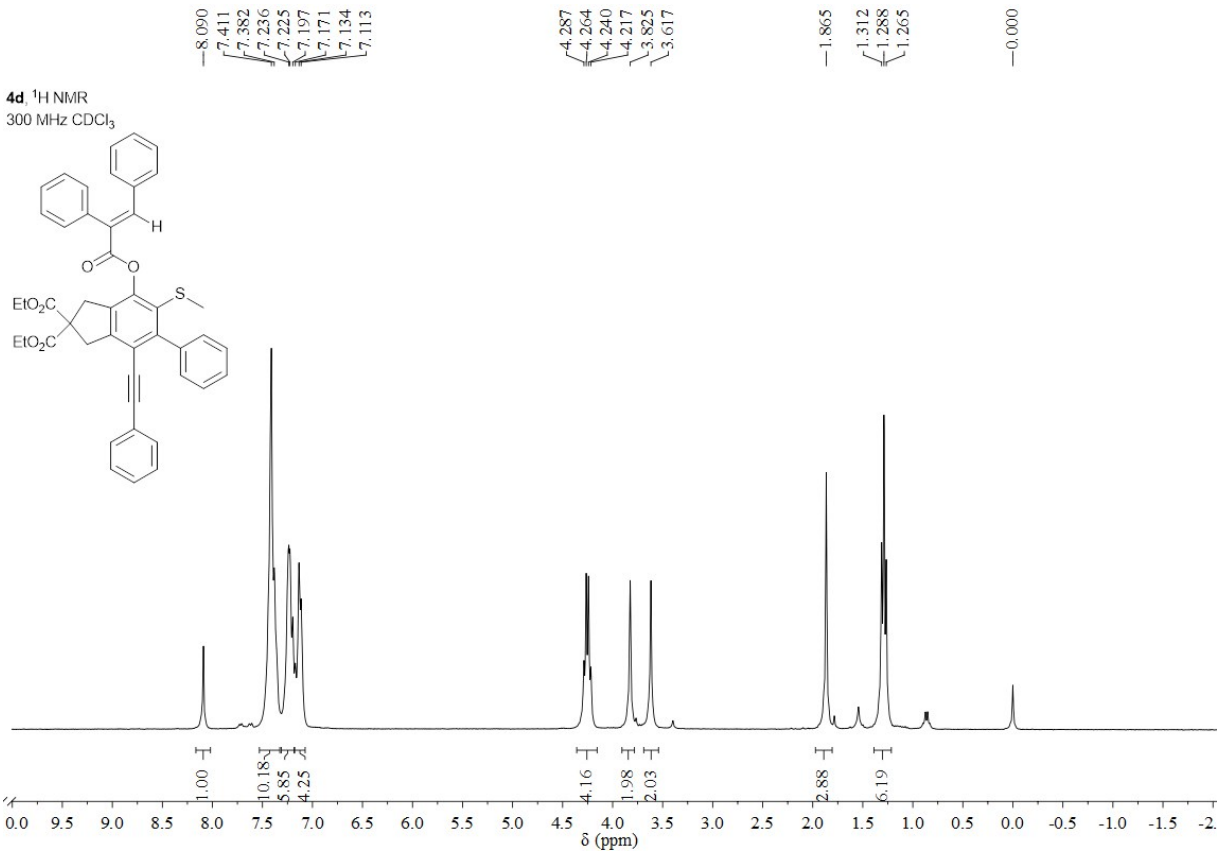
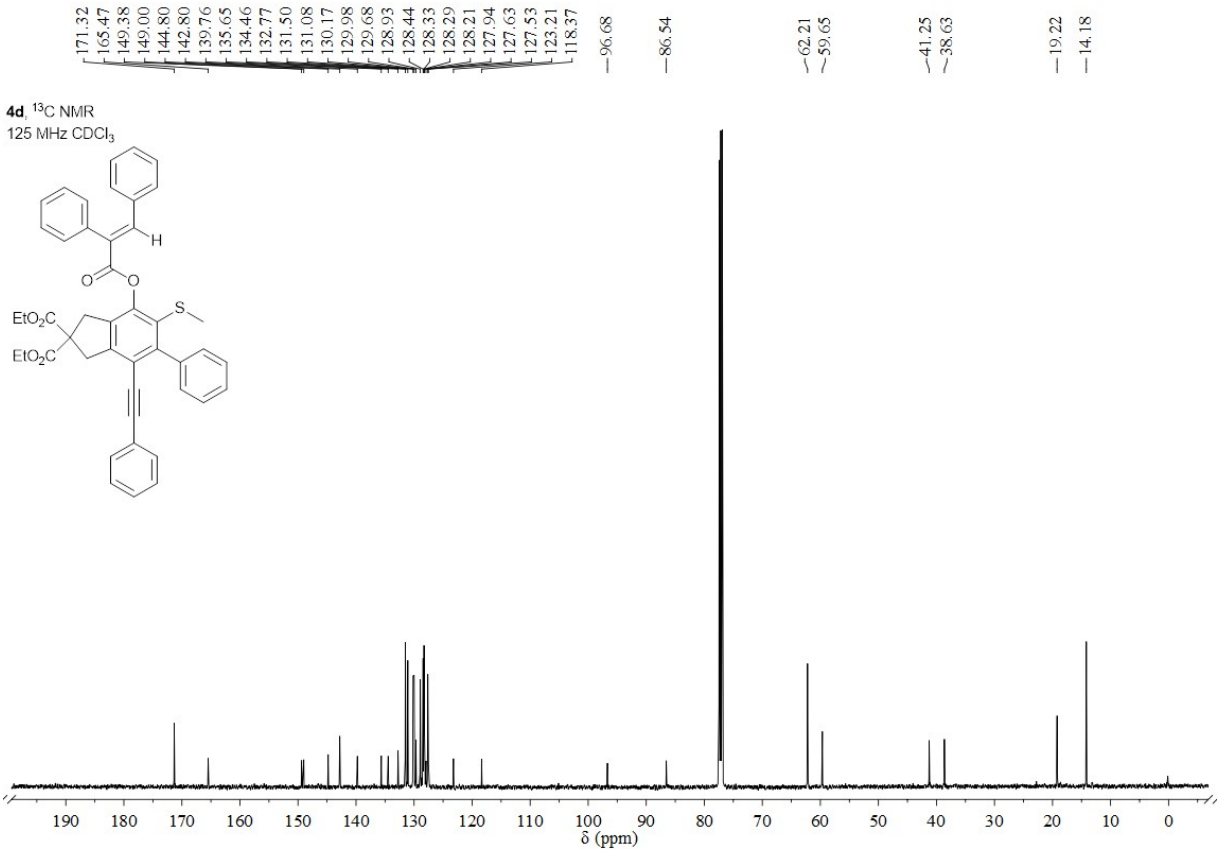
165.47
163.65
163.33
161.66
161.37
149.11
148.13
144.72
142.99
135.58
134.40
133.39
133.33
132.97
131.98
131.92
131.39
131.09
129.98
129.76
128.97
128.46
128.26
119.08
118.30
115.82
115.65
114.73
114.56
95.84
85.98
59.50
53.42
41.36
38.77
19.12
4c, 13C NMR
125 MHz CDCl3
MeO2C
MeO2C
S
F
F
δ (ppm)


8.090
7.411
7.382
7.236
7.225
7.197
7.171
7.134
7.113
4.287
4.264
4.240
4.217
3.825
3.617
1.865
1.312
1.288
1.265
0.000
4d, 1H NMR
300 MHz CDCl3
EtO2C
EtO2C
S
O
H
1.00
10.18
5.85
4.25
4.16
1.98
2.03
2.88
6.19
δ (ppm)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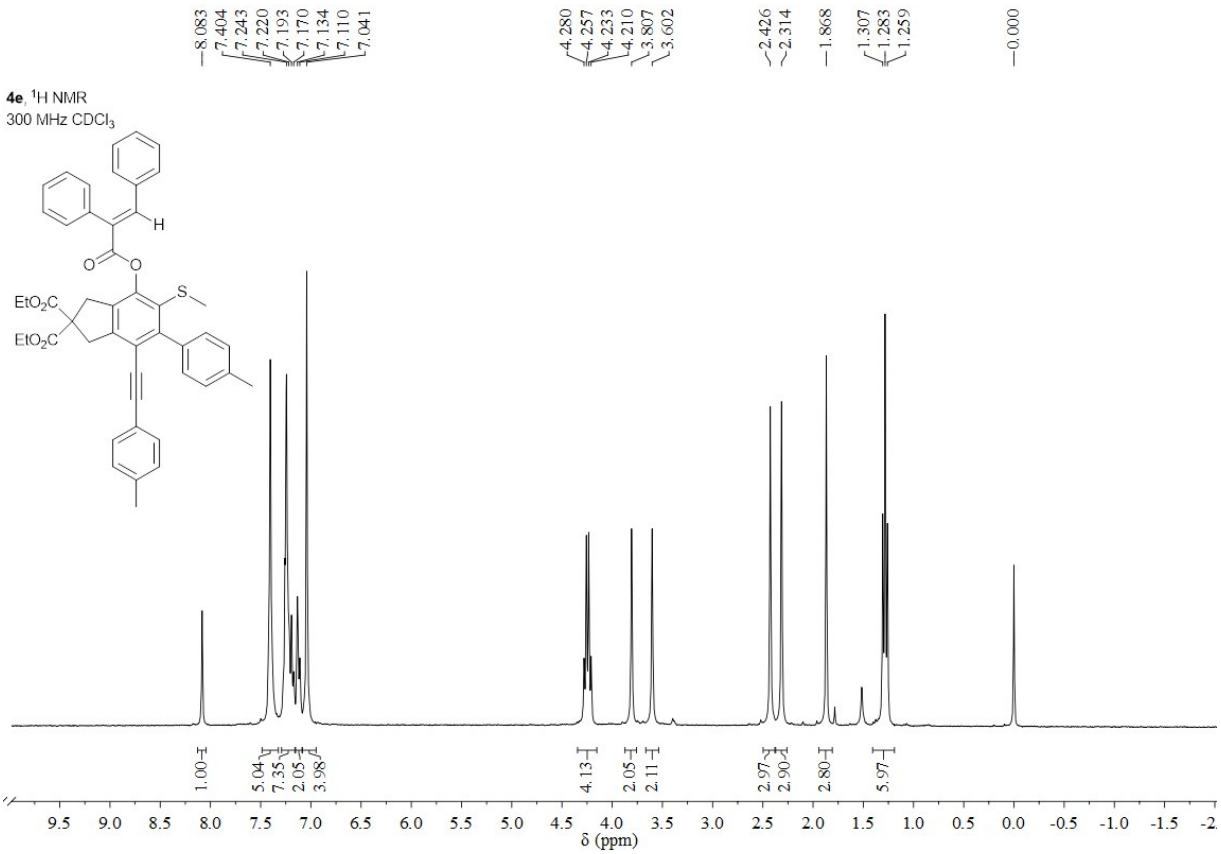
131.50
131.08
130.17
129.98
129.68
128.93
128.44
128.33
128.29
128.21
127.94
127.63
127.53
123.21
118.37
96.68
86.54
62.21
59.65
41.25
38.63
19.22
14.18
4d, 13C NMR
125 MHz CDCl3
EtO2C
EtO2C
S
O
H
δ (ppm)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4.257
4.233
4.210
3.807
3.602
2.426
2.314
1.868
1.307
1.283
1.259
0.000
4e, 1H NMR
300 MHz CDCl3
EtO2C
EtO2C
S
H
O
1.00
5.04
7.35
2.05
3.98
4.13
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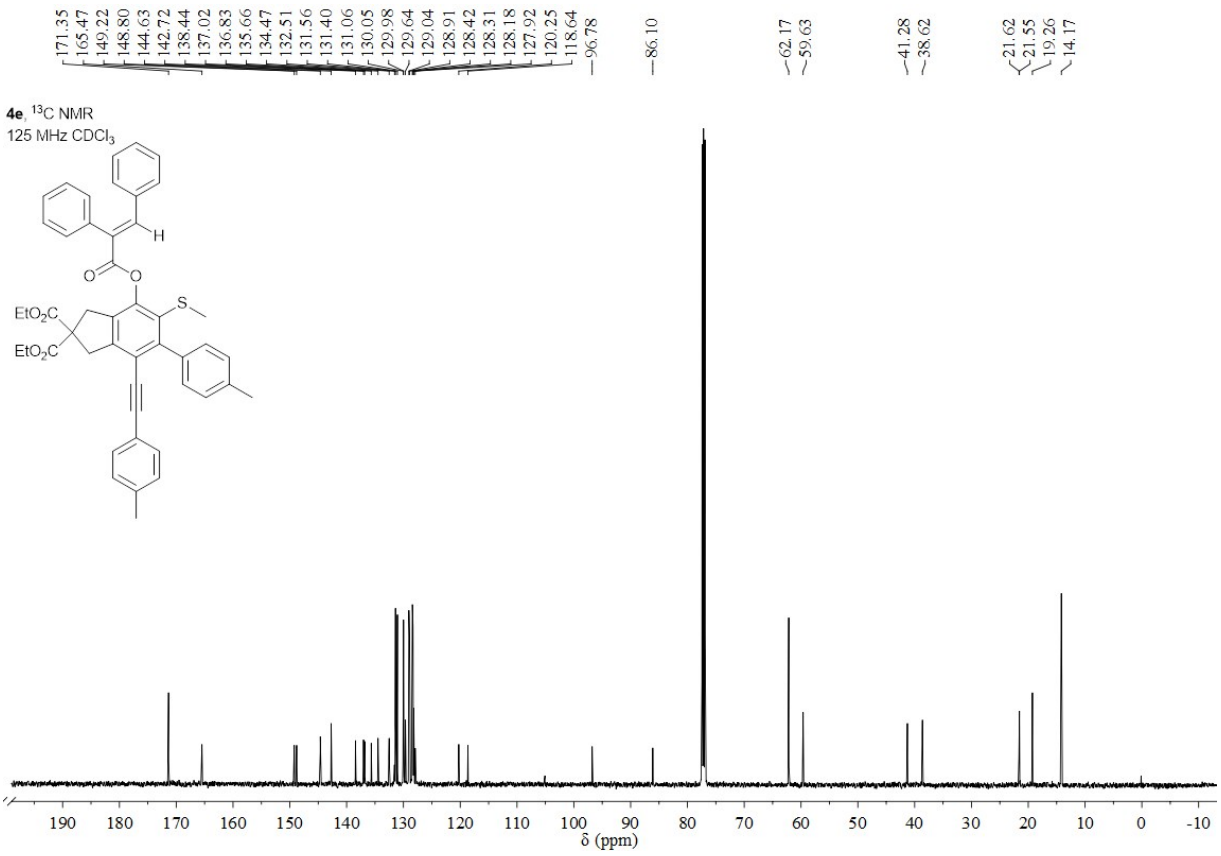
2.97
2.90
2.80
5.97
δ (ppm)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142.72
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134.47
132.51
131.56
131.40
131.06
130.05
129.98
129.64
129.04
128.91
128.42
128.31
128.18
127.92
120.25
118.64
96.78
86.10
62.17
59.63
41.28
38.62
21.62
21.55
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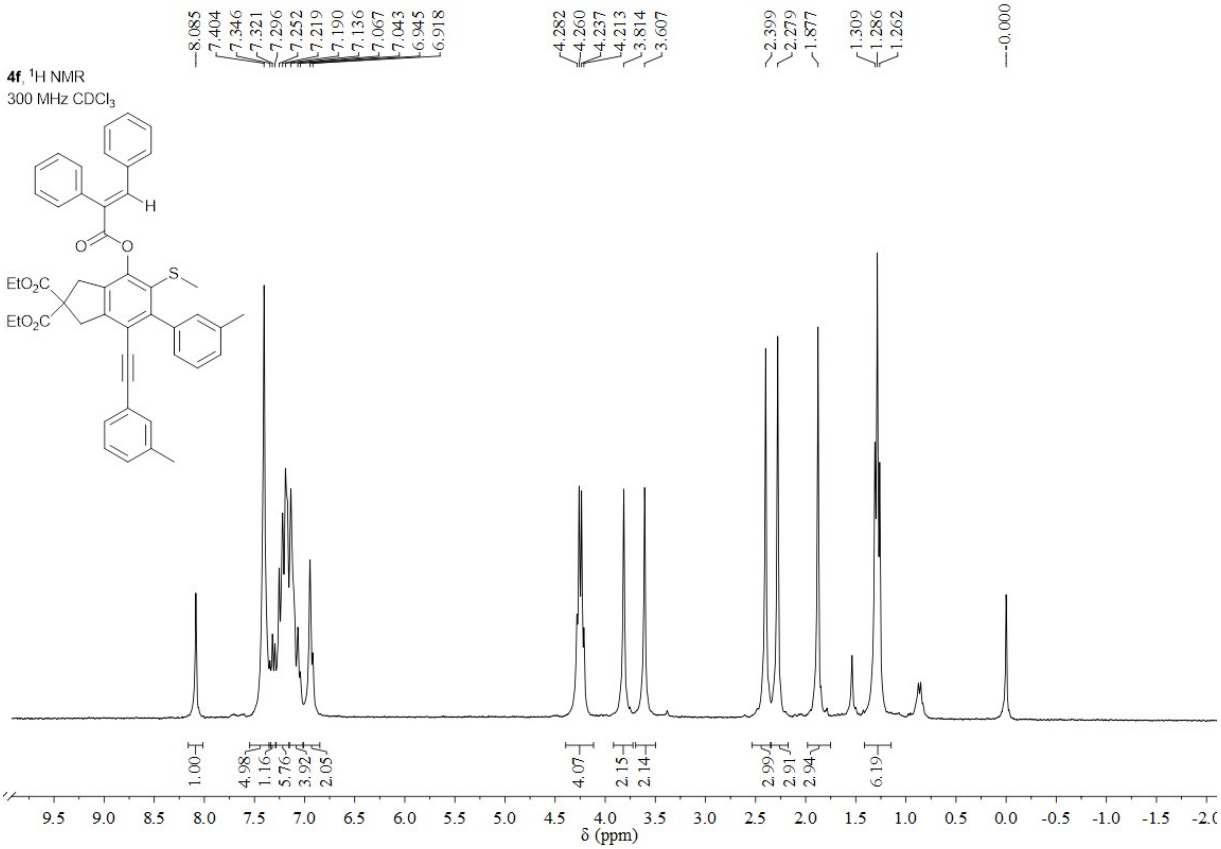
14.17
4e, 13C NMR
125 MHz CDCl3
EtO2C
EtO2C
S
H
O
δ (ppm)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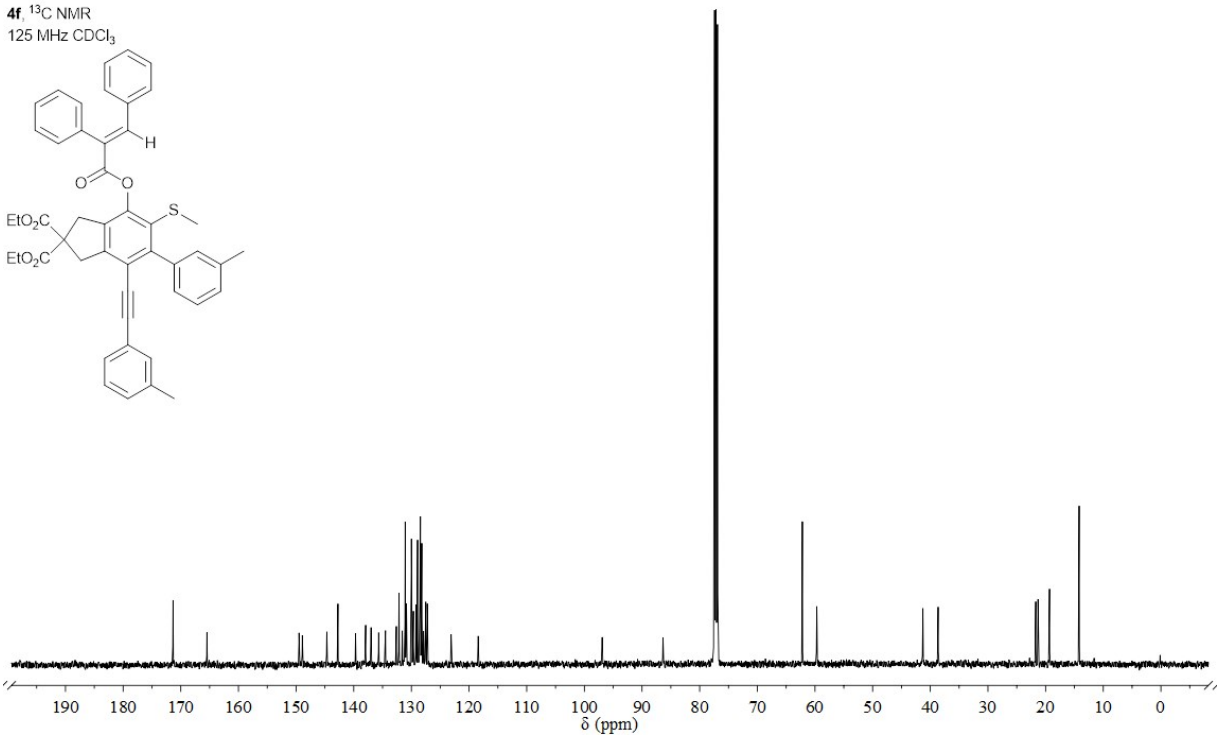
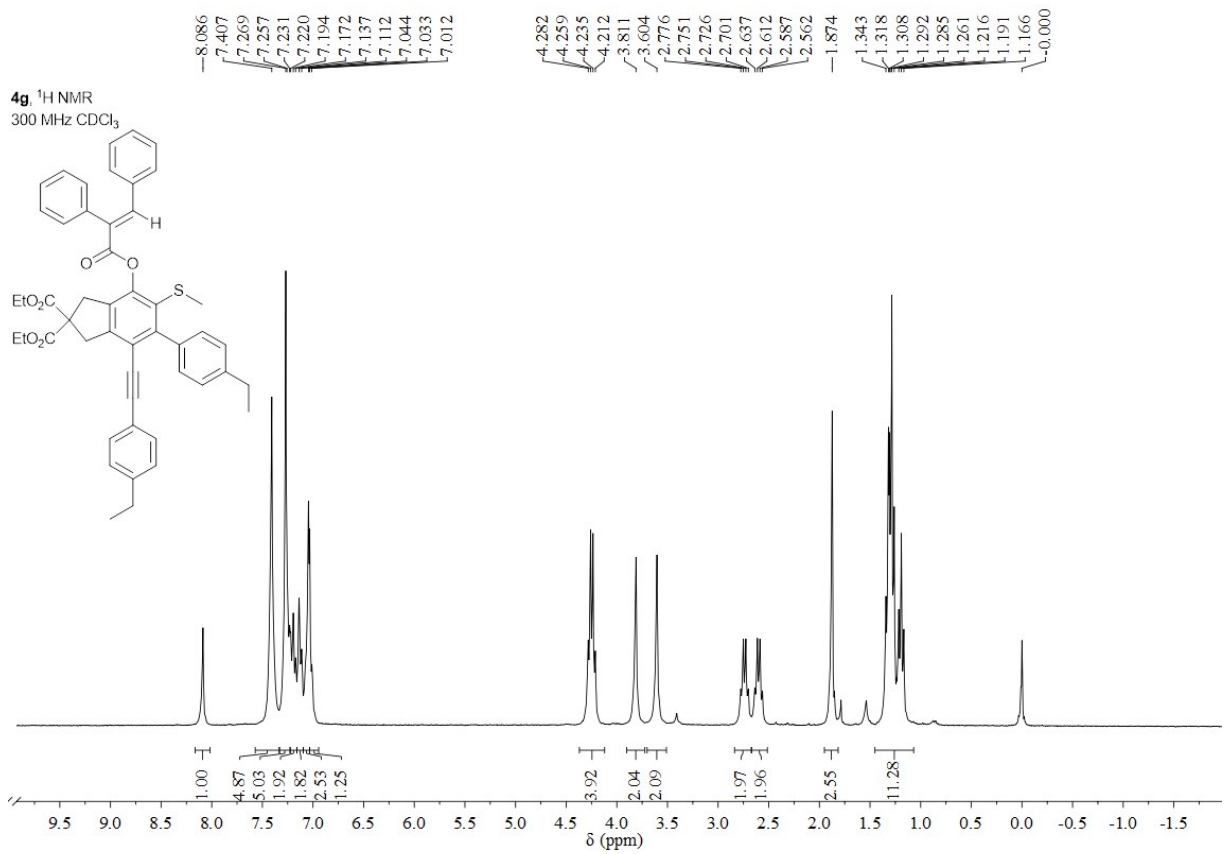
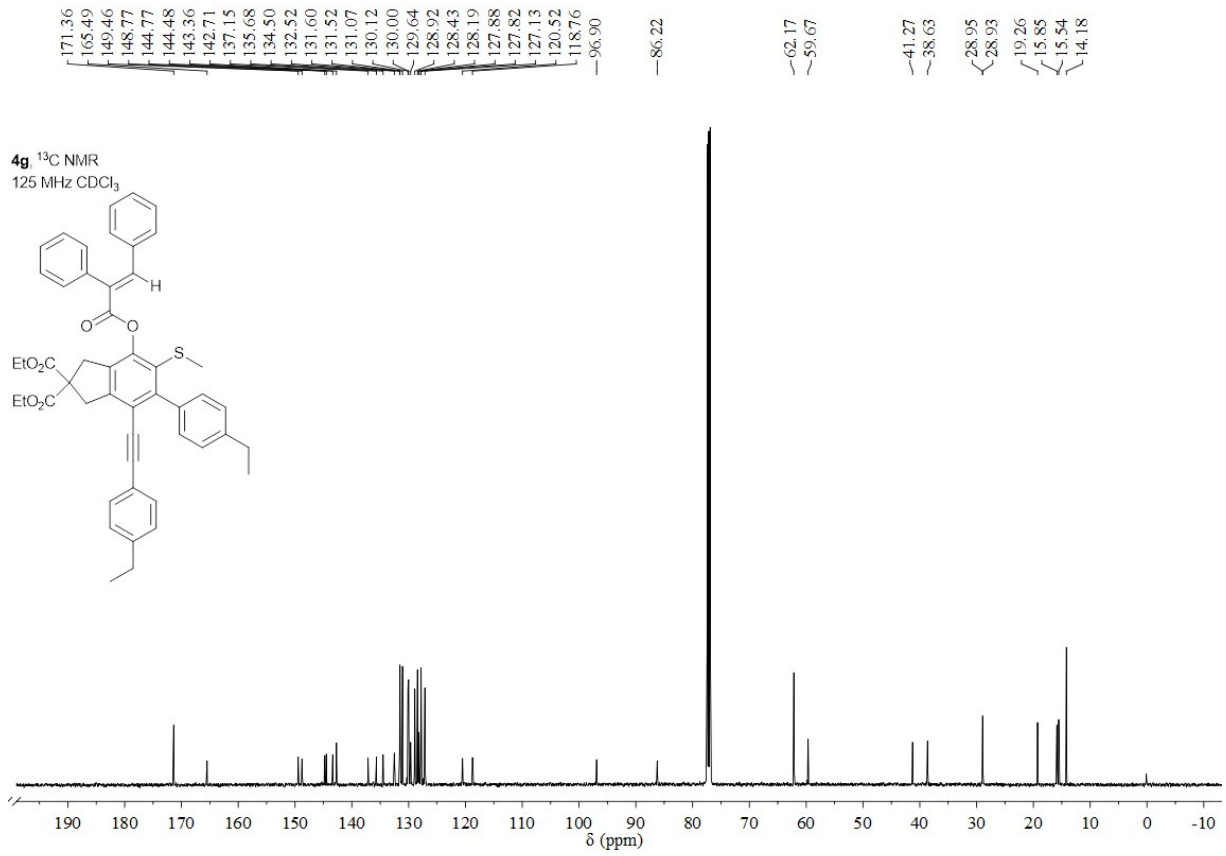
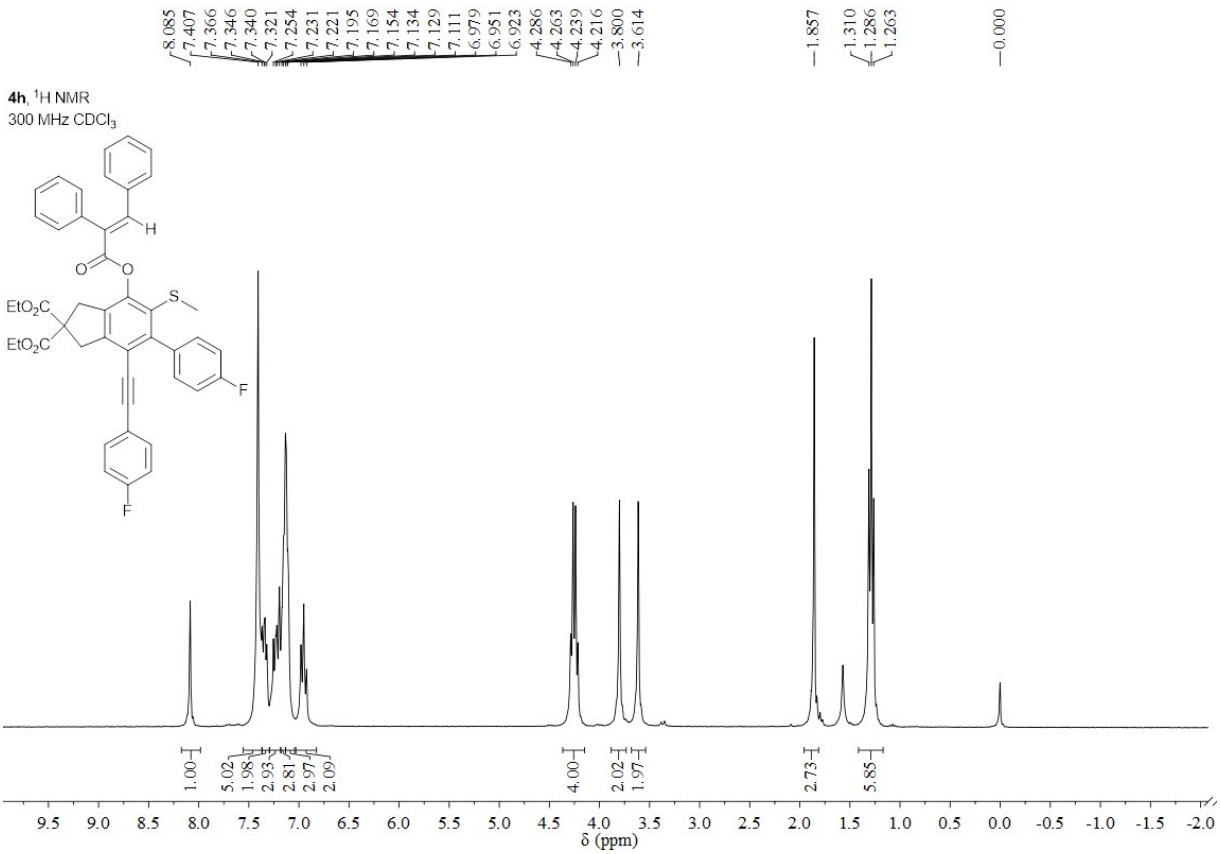
300 MHz CDCl3
δ (ppm)


4f, 13C NMR
125 MHz CDCl3
δ (ppm)


4g, 1H NMR
300 MHz CDCl3
δ (ppm)


4g, 13C NMR
125 MHz CDCl3
δ (ppm)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7.231
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7.169
7.154
7.134
7.129
7.111
6.979
6.951
6.923
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4.263
4.239
4.216
3.800
3.614
1.857
1.310
1.286
1.263
0.000
4h, 1H NMR
300 MHz CDCl3
EtO2C
EtO2C
S
F
F
1.00
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2.81
2.97
2.09
4.00
2.02
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2.73
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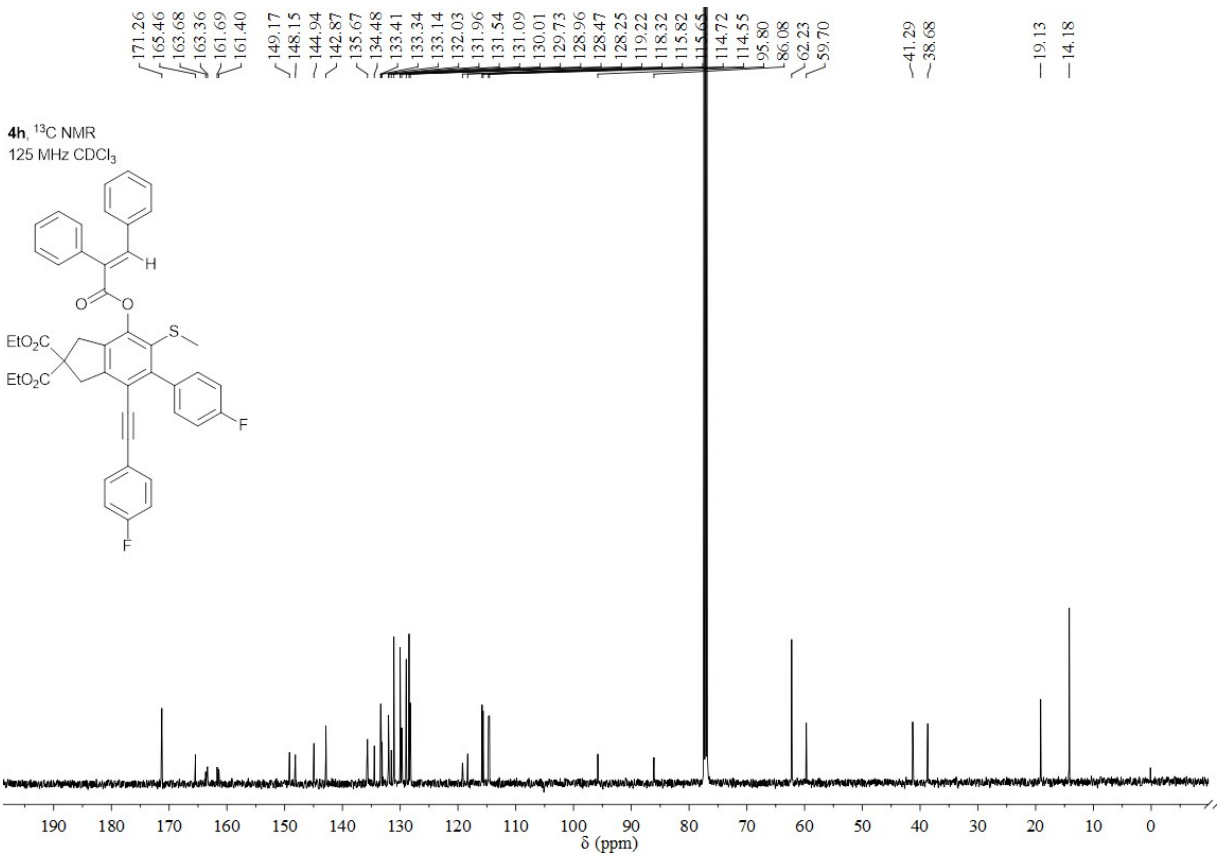
δ (ppm)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115.82
115.65
114.72
114.55
95.80
86.08
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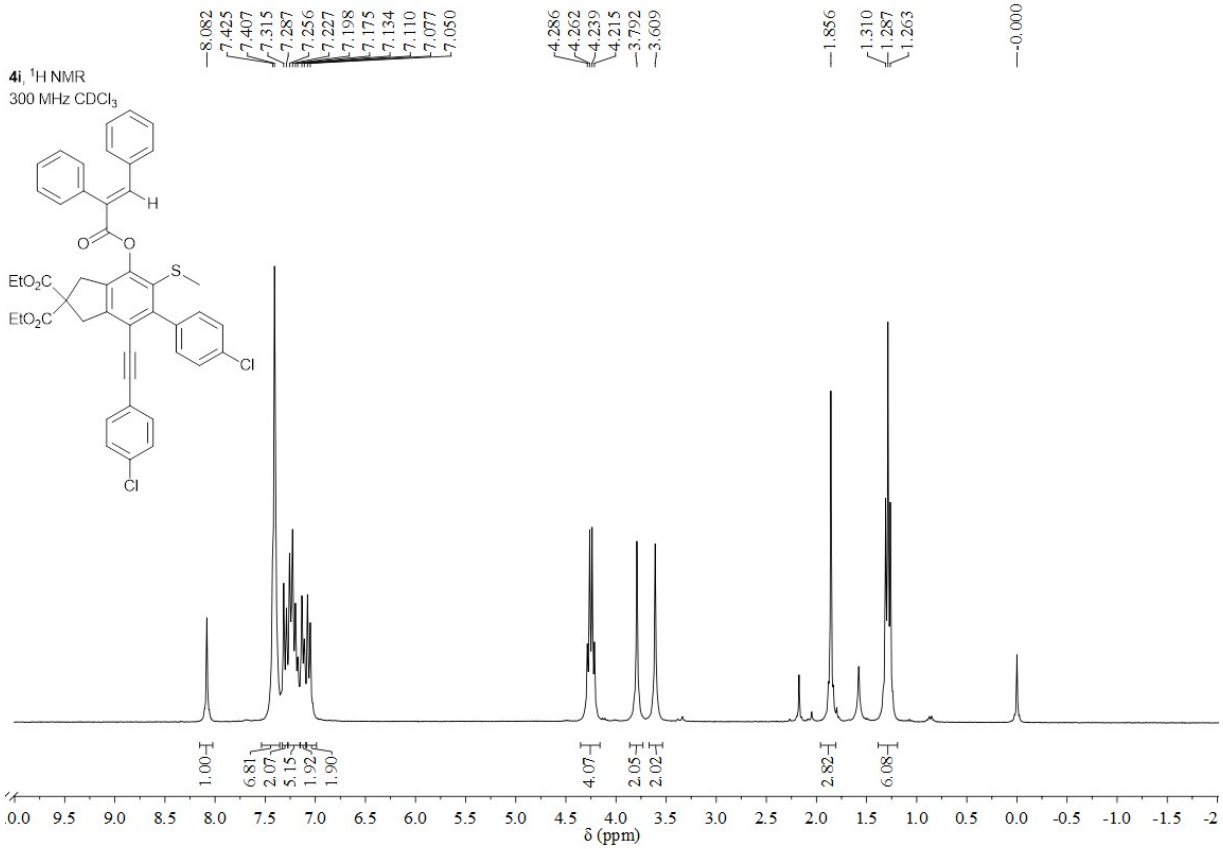
14.18
4h, 13C NMR
125 MHz CDCl3
EtO2C
EtO2C
S
F
F
δ (ppm)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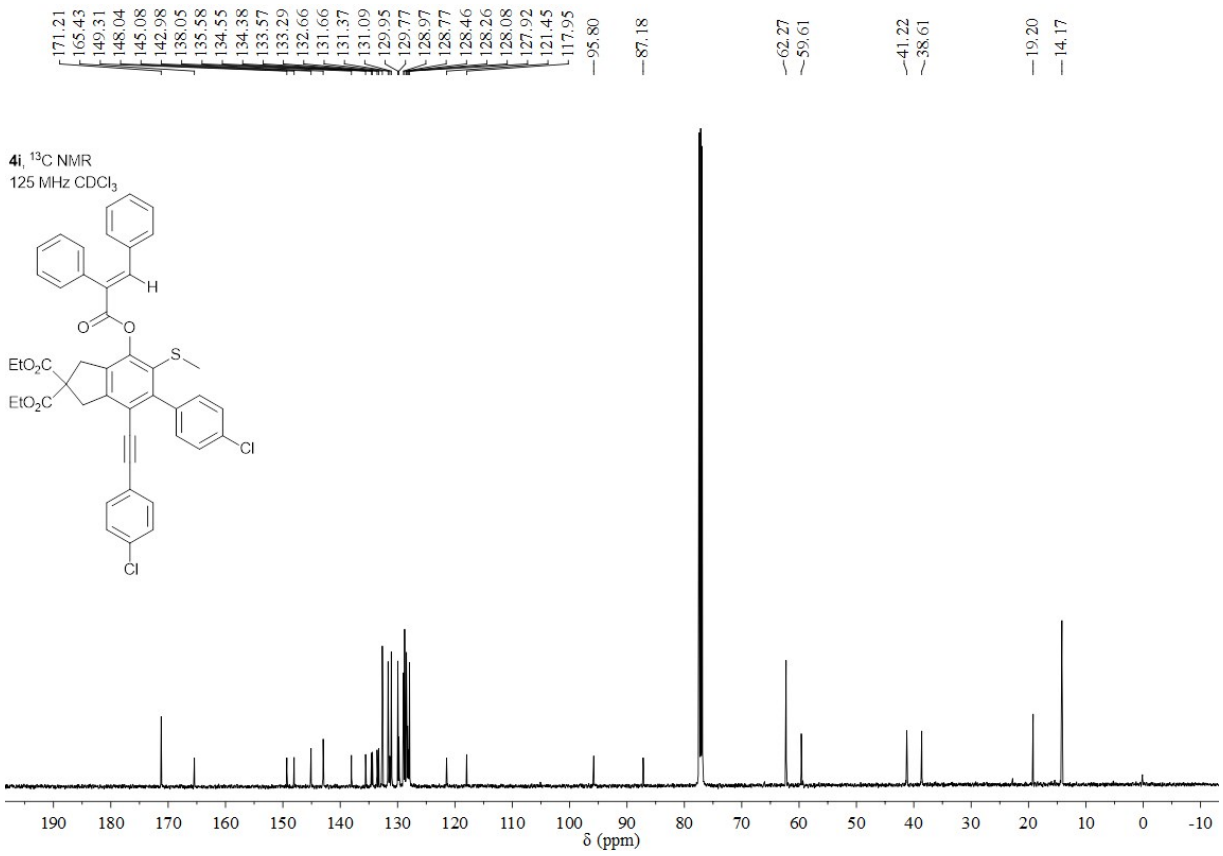
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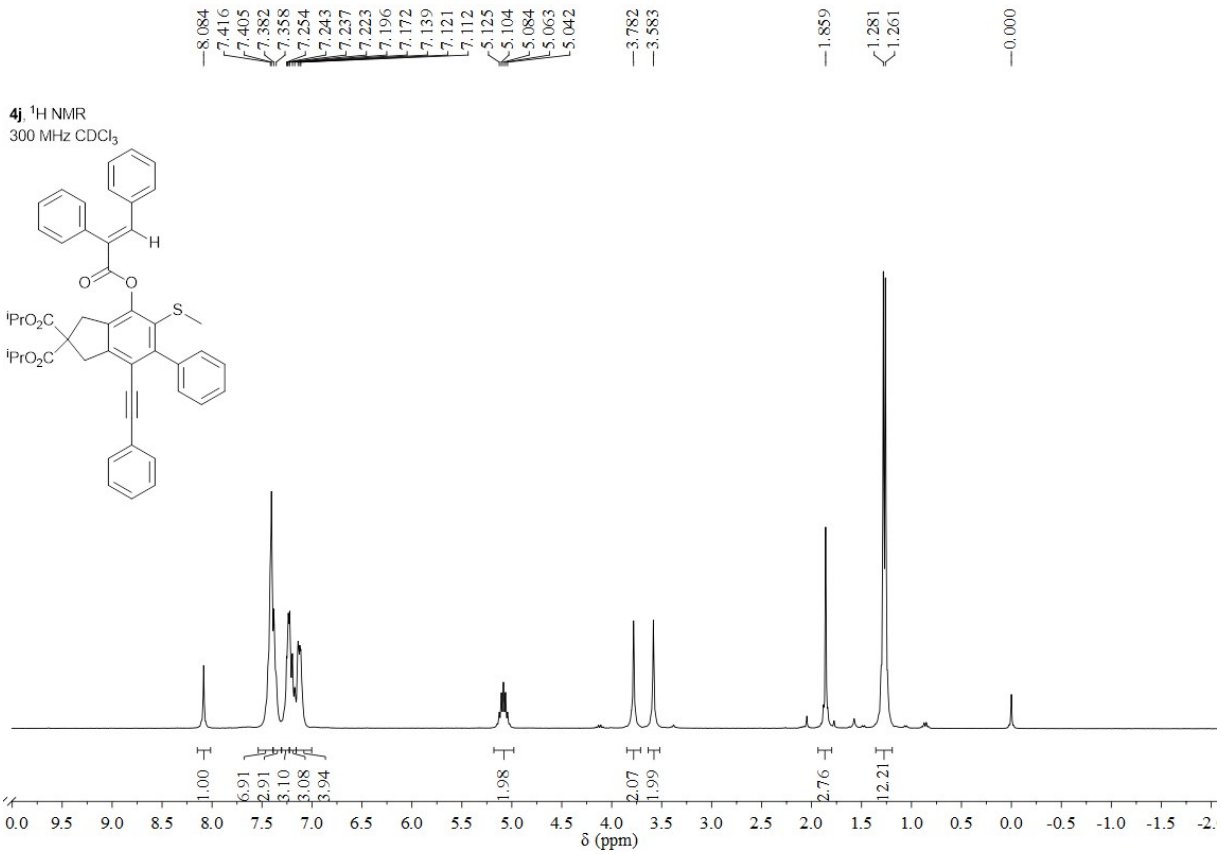
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7.112
5.125
5.104
5.084
5.063
5.042
3.782
3.583
1.859
1.281
1.261
0.000
4j, 1H NMR
300 MHz CDCl3
H
O
O
S
iPrO2C
iPrO2C
1.00
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3.10
3.08
3.94
1.98
2.07
1.99
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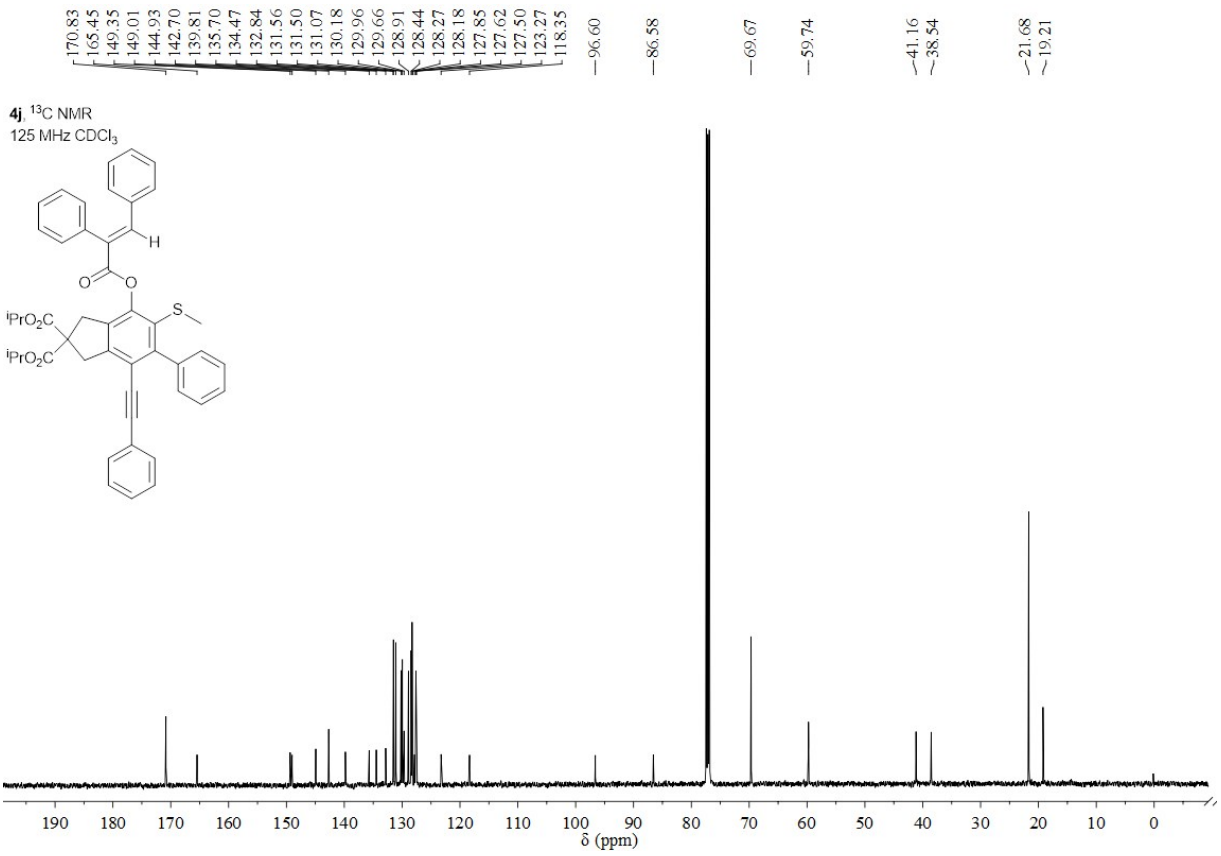
δ (ppm)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128.27
128.18
127.85
127.62
127.50
123.27
118.35
96.60
86.58
69.67
59.74
41.16
38.54
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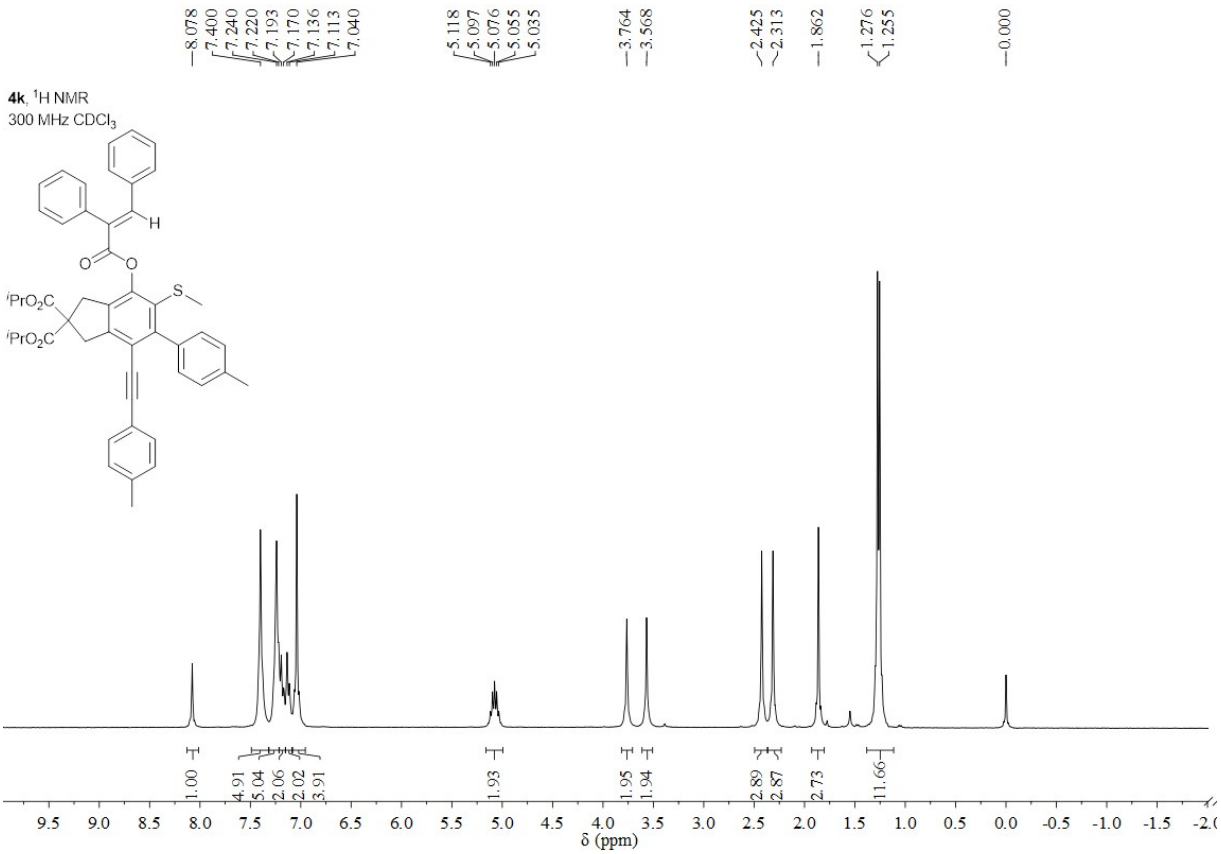
19.21
4j, 13C NMR
125 MHz CDCl3
H
O
O
S
iPrO2C
iPrO2C
δ (ppm)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7.113
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5.076
5.055
5.035
3.764
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2.313
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1.276
1.255
0.000
4k, 1H NMR
300 MHz CDCl3
1.00
4.91
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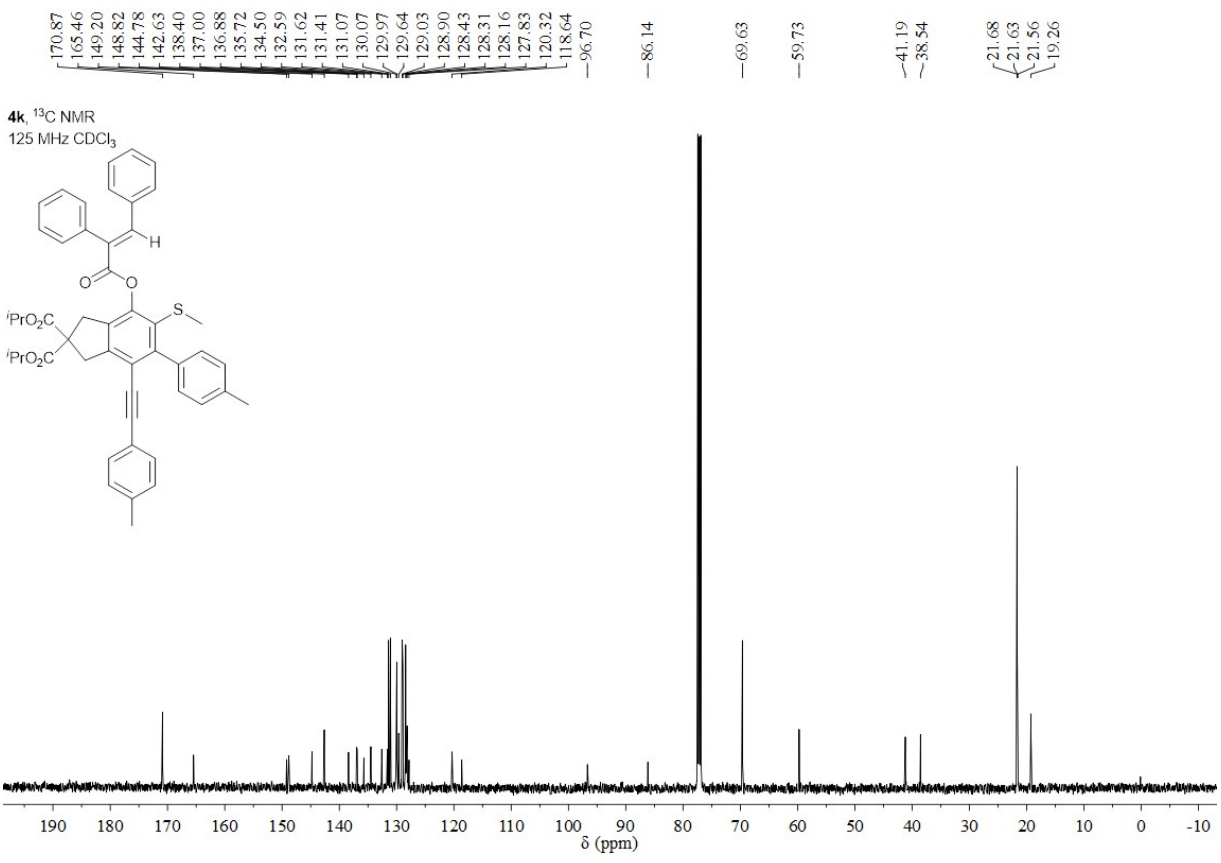
δ (ppm)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131.41
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130.07
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129.64
129.03
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118.64
96.70
86.14
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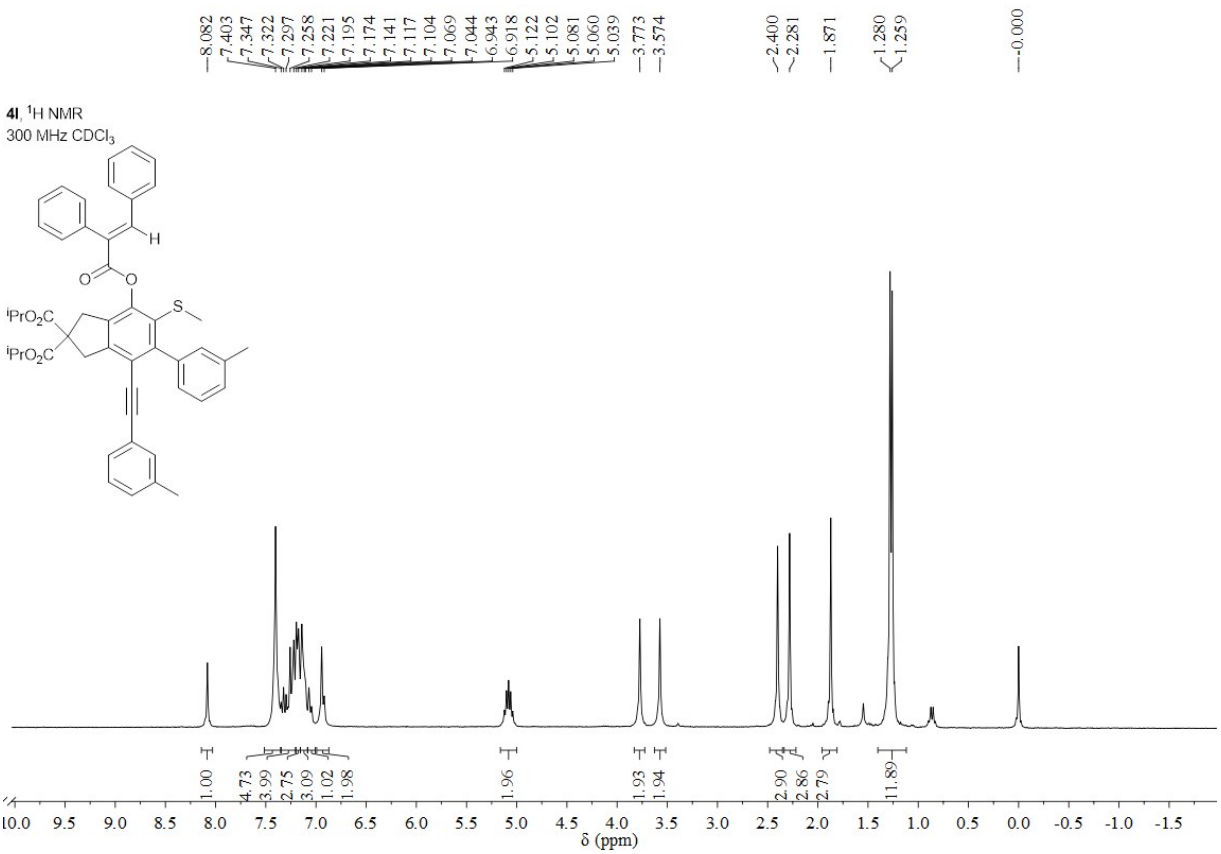
21.63
21.56
19.26
4k, 13C NMR
125 MHz CDCl3
δ (ppm)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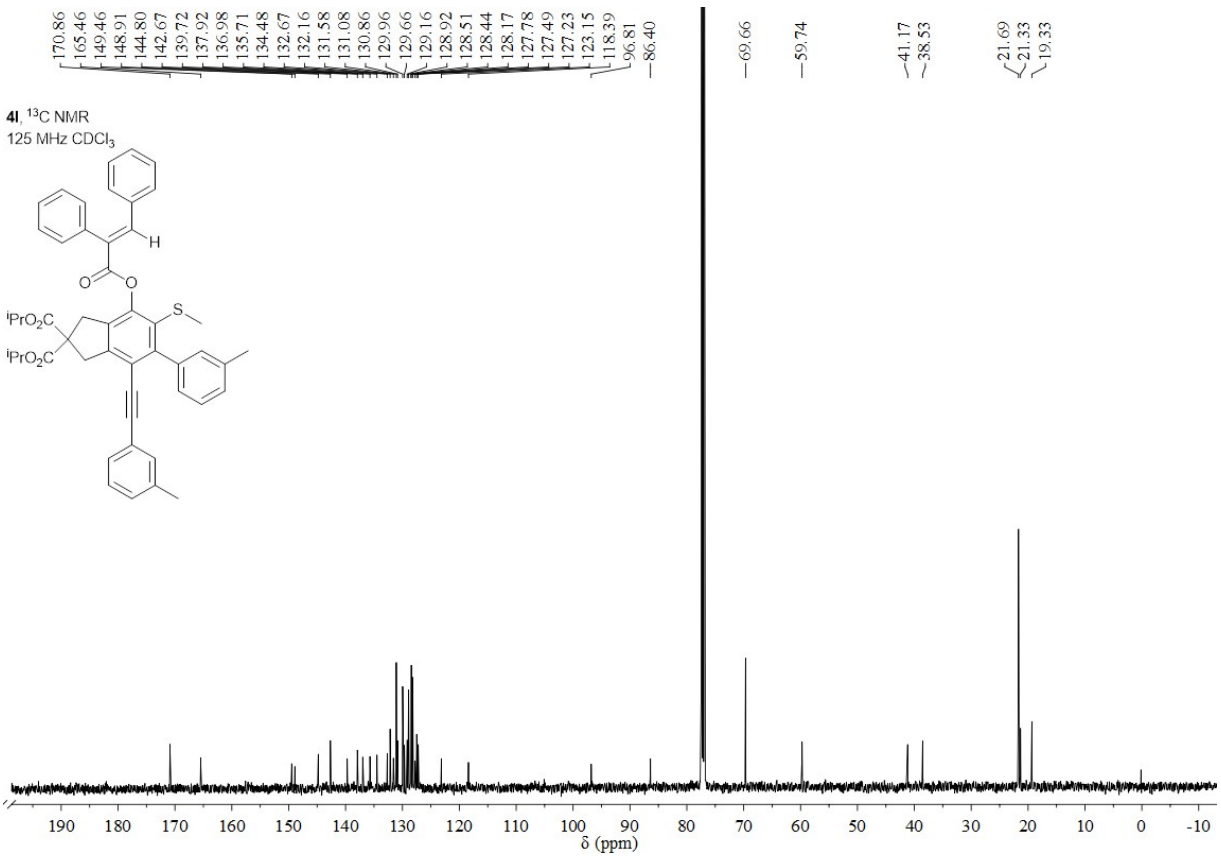
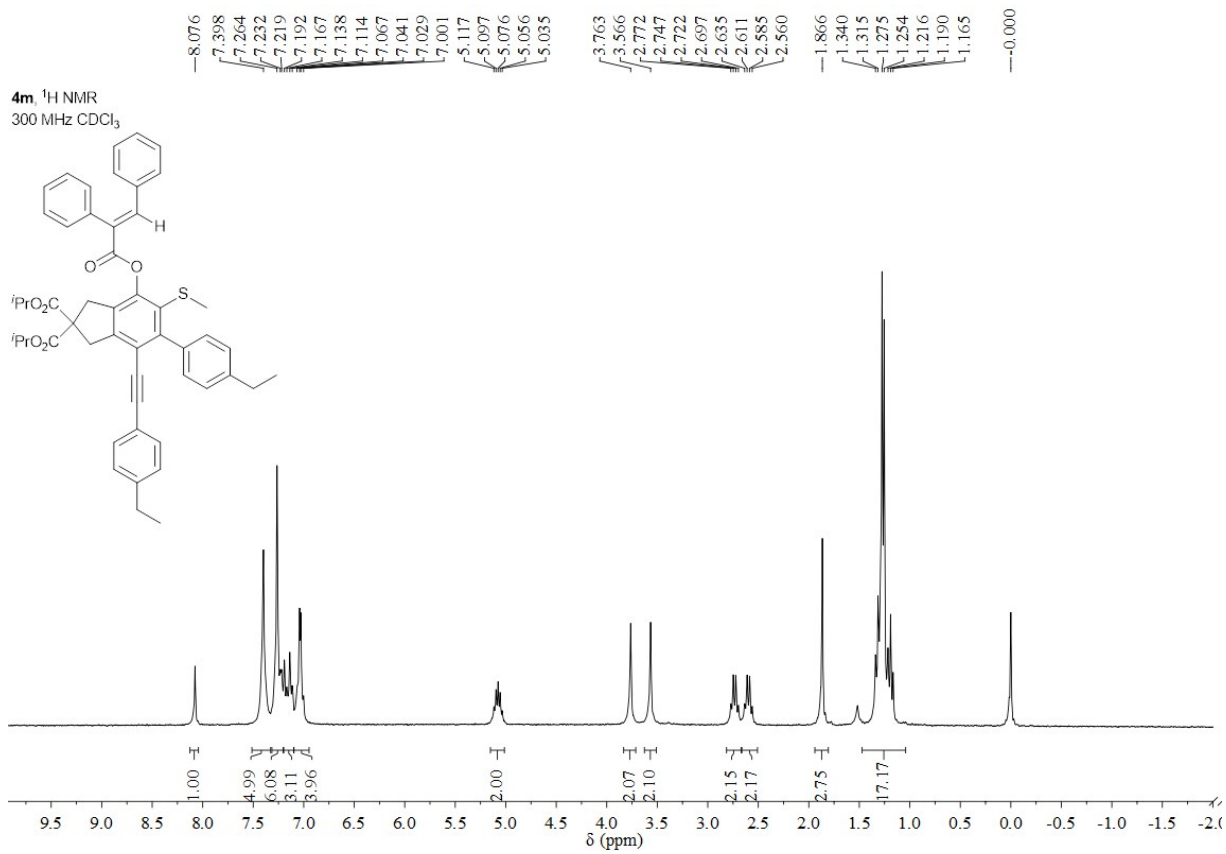
300 MHz CDCl3
δ (ppm)


4l, 13C NMR
125 MHz CDCl3
δ (ppm)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7.001
5.117
5.097
5.076
5.056
5.035
3.763
3.566
2.772
2.747
2.722
2.697
2.635
2.611
2.585
2.560
1.866
1.340
1.315
1.275
1.254
1.216
1.190
1.165
0.000
4m, 1H NMR
300 MHz CDCl3
1.00
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6.08
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2.15
2.17
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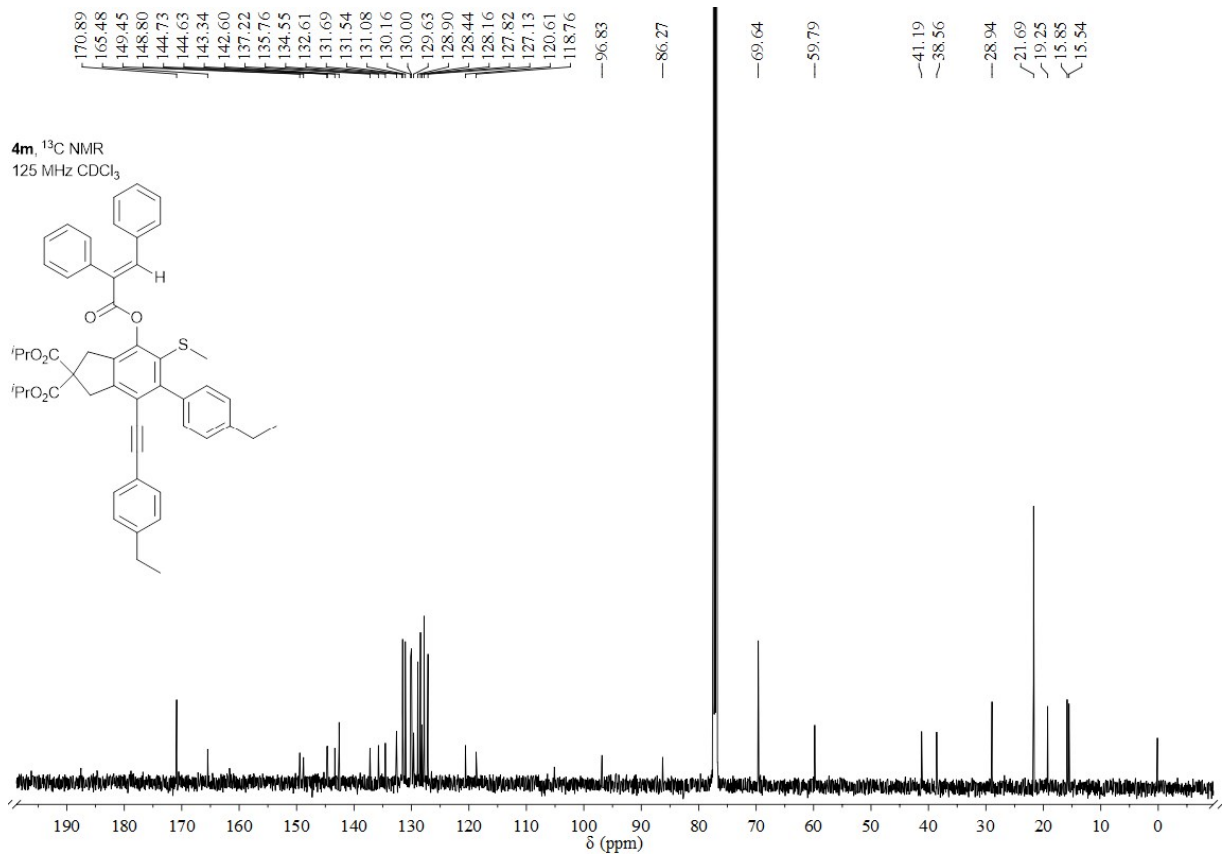
δ (ppm)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131.69
131.54
131.08
130.16
130.00
129.63
128.90
128.44
128.16
127.82
127.13
120.61
118.76
96.83
86.27
69.64
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28.94
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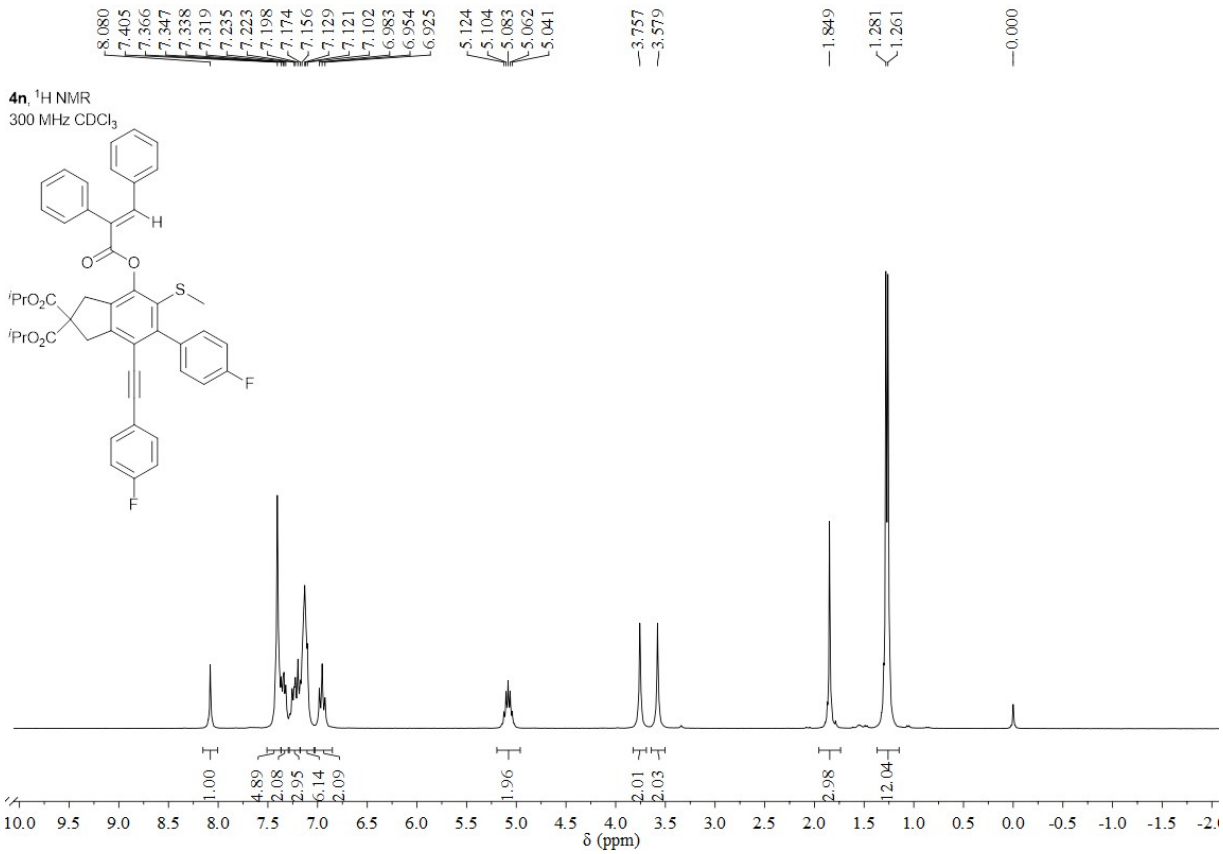
15.54
4m, 13C NMR
125 MHz CDCl3
δ (ppm)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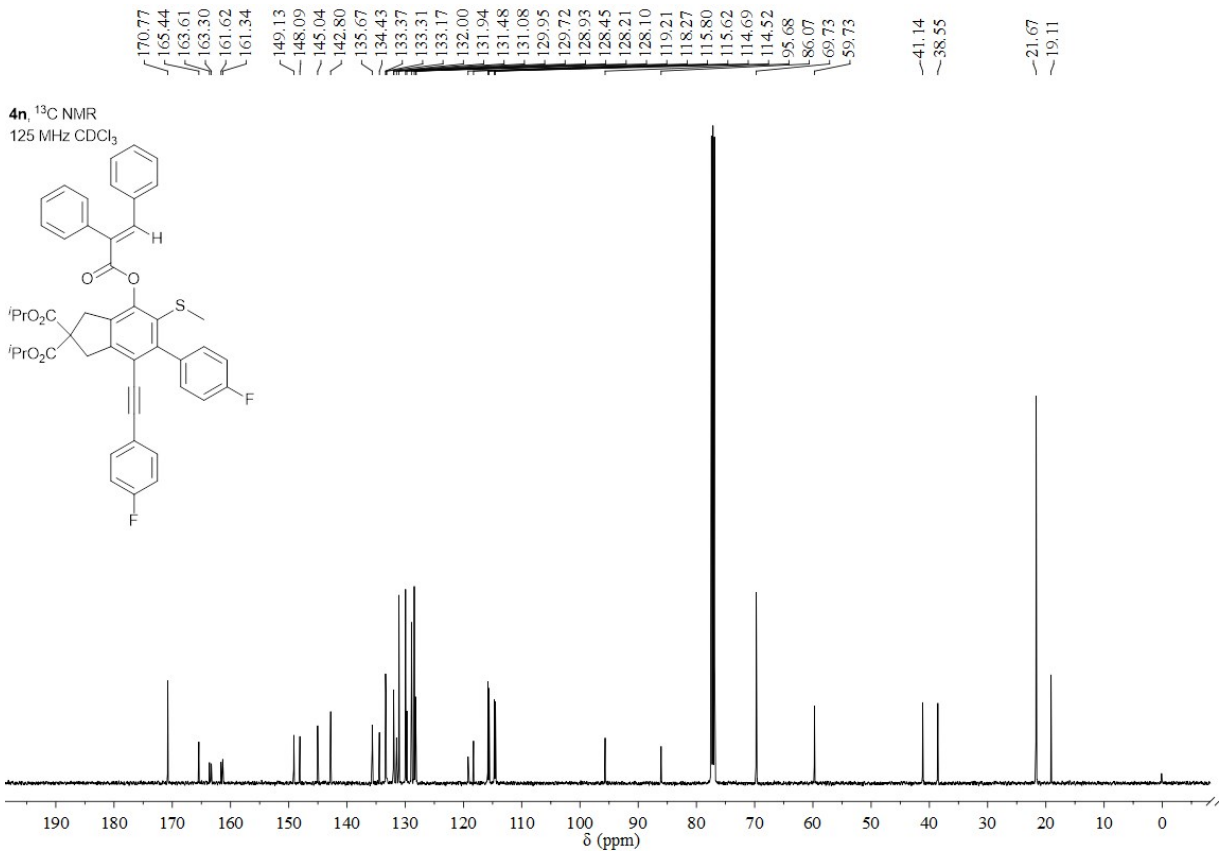
6.983
6.954
6.925
5.124
5.104
5.083
5.062
5.041
3.757
3.579
1.849
1.281
1.261
0.000
4n, 1H NMR
300 MHz CDCl3
1.00
4.89
2.08
2.95
6.14
2.09
1.96
2.01
2.03
2.98
12.04
δ (ppm)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133.17
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131.48
131.08
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128.93
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118.27
115.80
115.62
114.69
114.52
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59.73
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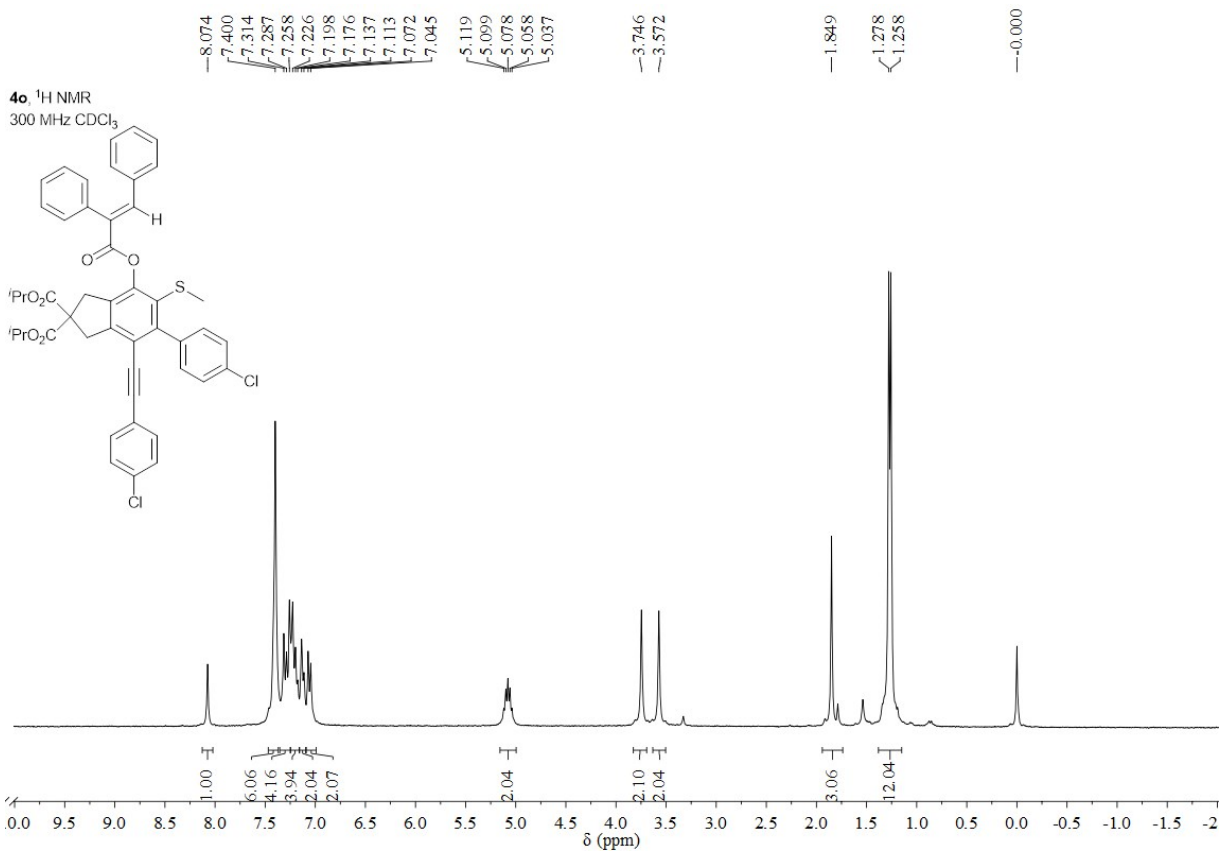
19.11
4n, 13C NMR
125 MHz CDCl3
δ (ppm)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7.113
7.072
7.045
5.119
5.099
5.078
5.058
5.037
3.746
3.572
1.849
1.278
1.258
0.000
4o, 1H NMR
300 MHz CDCl3
iPrO2C
iPrO2C
S
Cl
Cl
1.00
6.06
4.16
3.94
2.04
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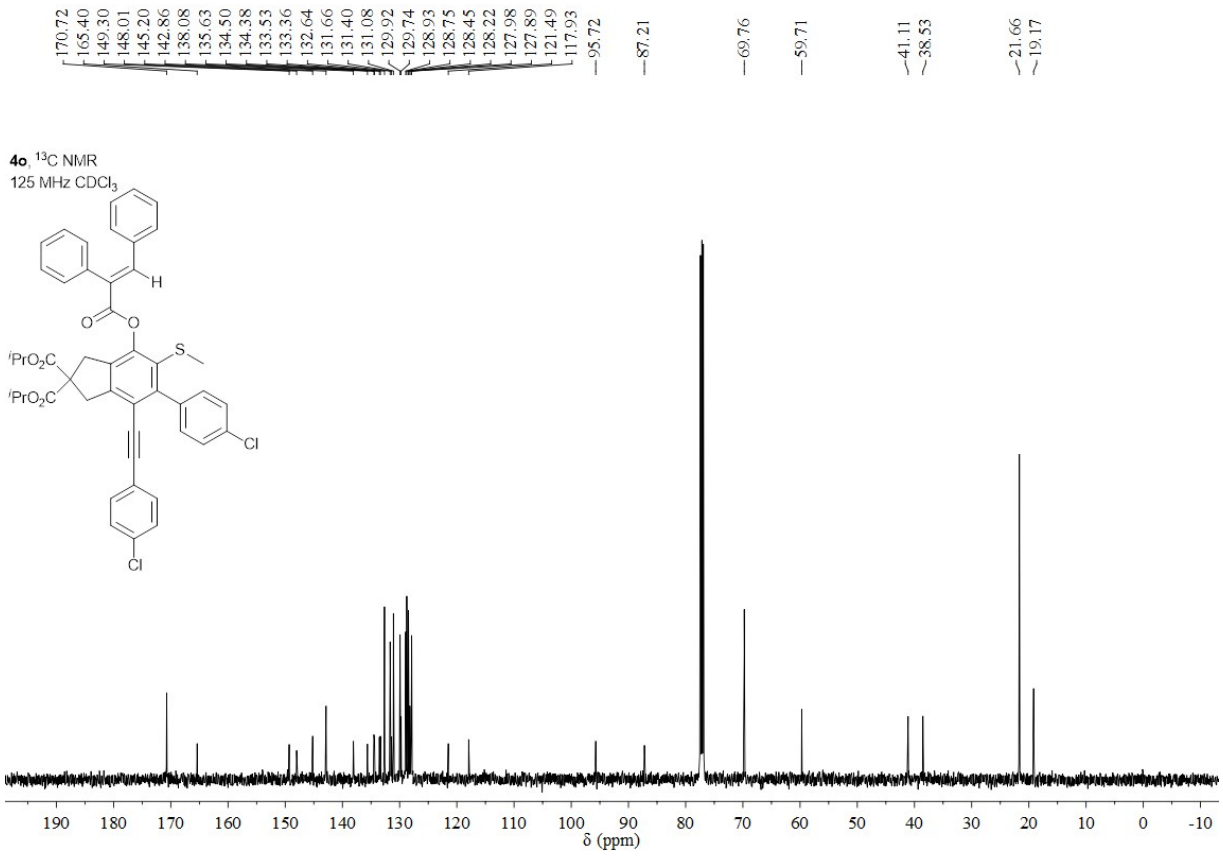
2.10
2.04
3.06
12.04
δ (ppm)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131.66
131.40
131.08
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128.93
128.75
128.45
128.22
127.98
127.89
121.49
117.93
95.72
87.21
69.76
59.71
41.11
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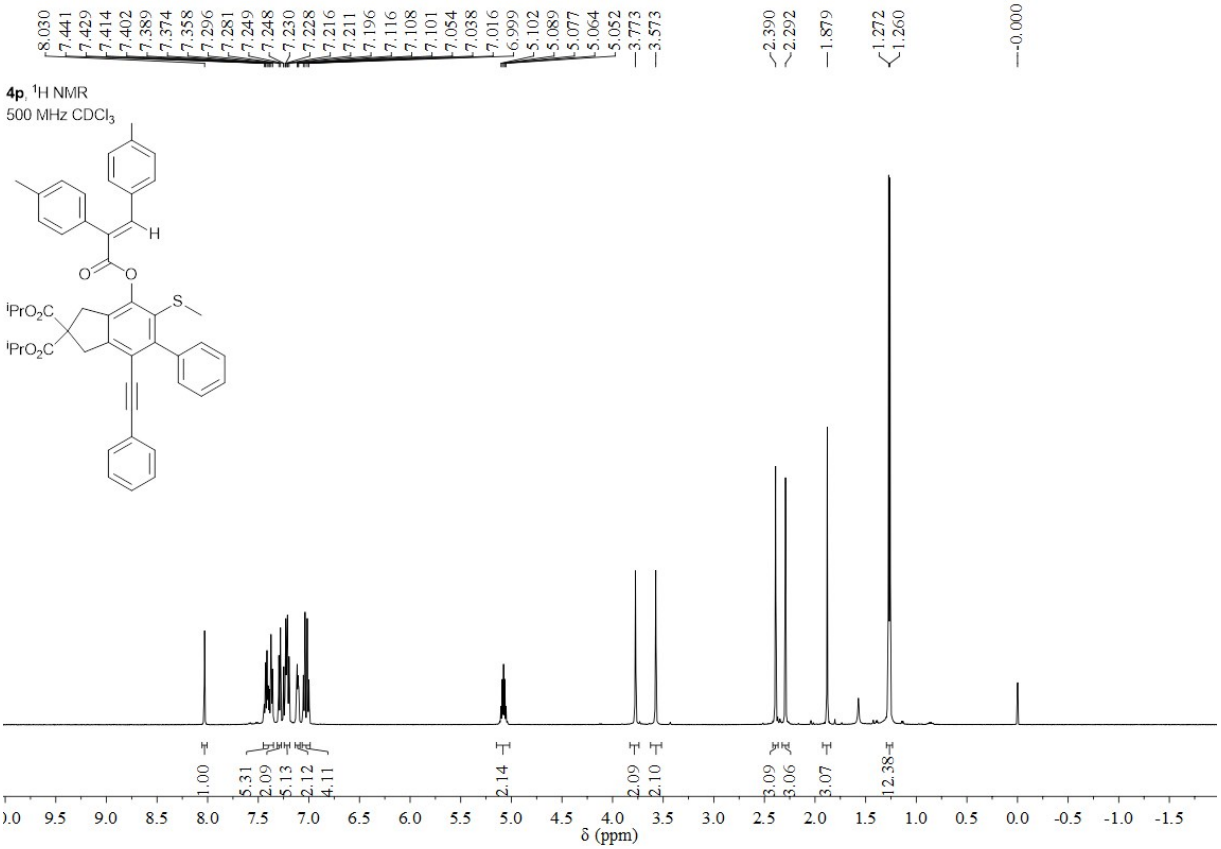
19.17
4o, 13C NMR
125 MHz CDCl3
iPrO2C
iPrO2C
S
Cl
Cl
δ (ppm)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7.230
7.228
7.216
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7.108
7.101
7.054
7.038
7.016
6.999
5.102
5.089
5.077
5.064
5.052
3.773
3.573
2.390
2.292
1.879
1.272
1.260
0.000
4p, 1H NMR
500 MHz CDCl3
1.00
5.31
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2.10
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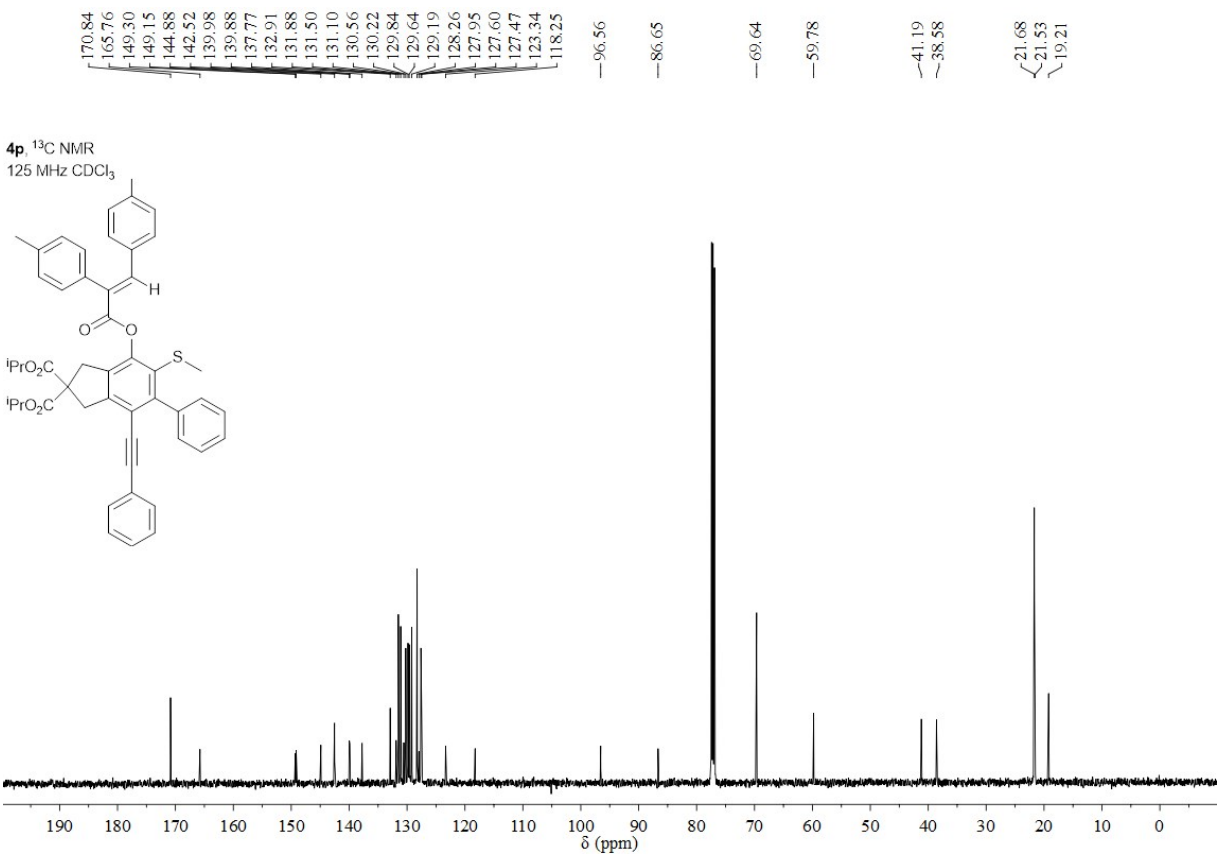
3.06
3.07
12.38
δ (ppm)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129.64
129.19
128.26
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127.47
123.34
118.25
96.56
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41.19
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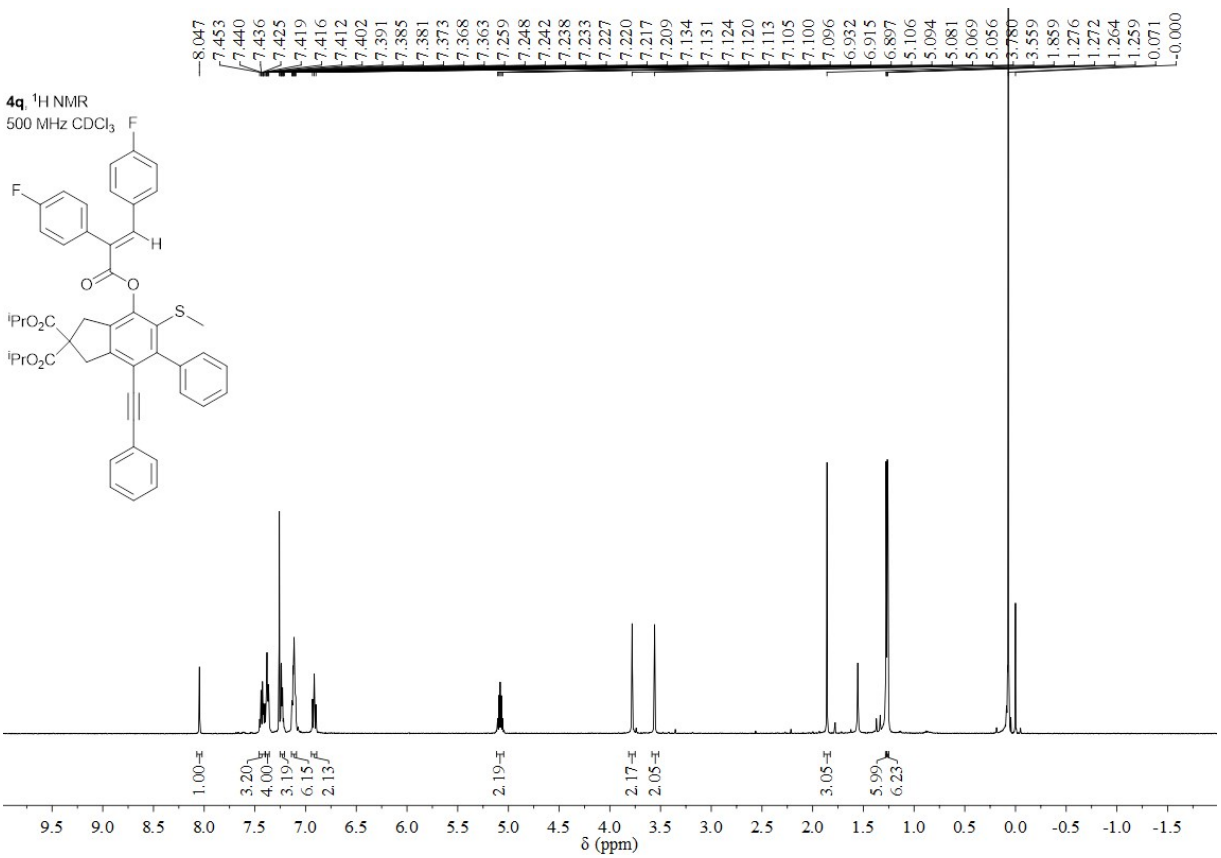
21.53
19.21
4p, 13C NMR
125 MHz CDCl3
δ (ppm)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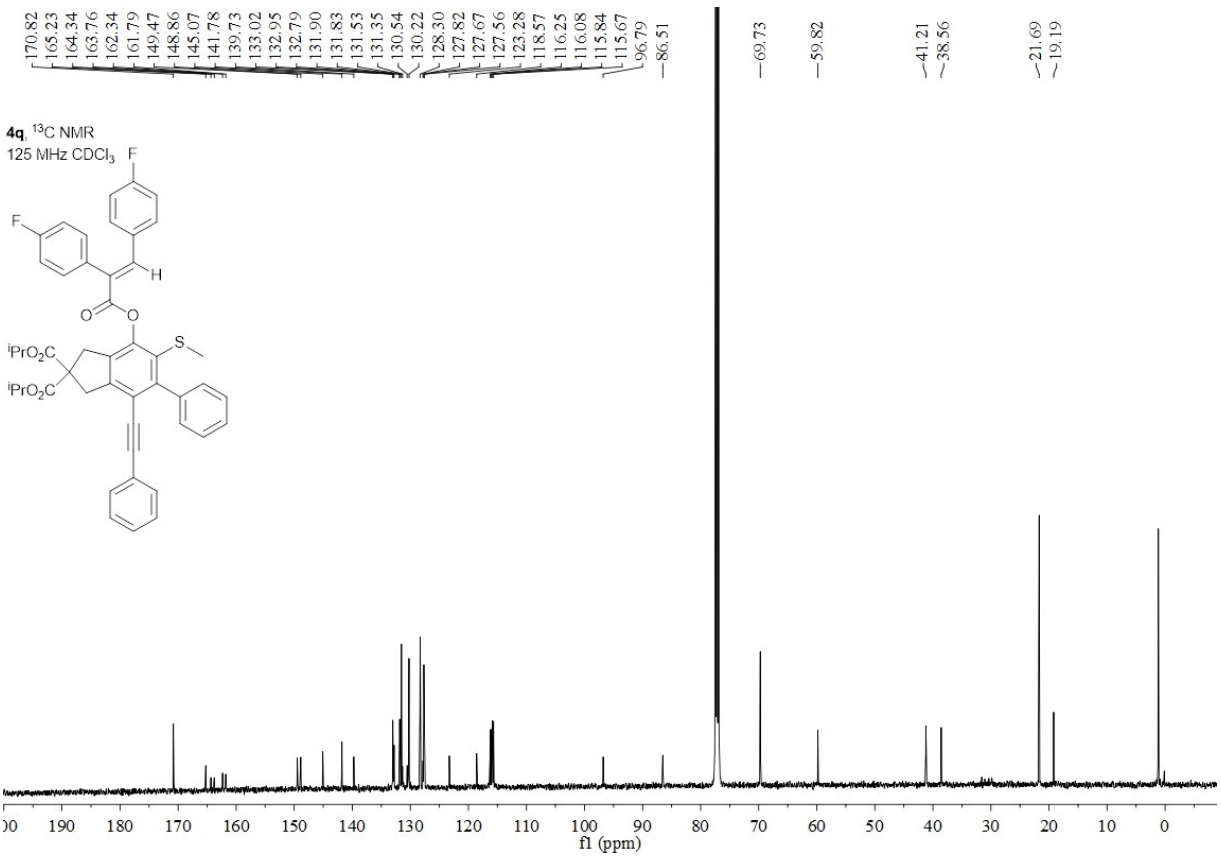
δ (ppm)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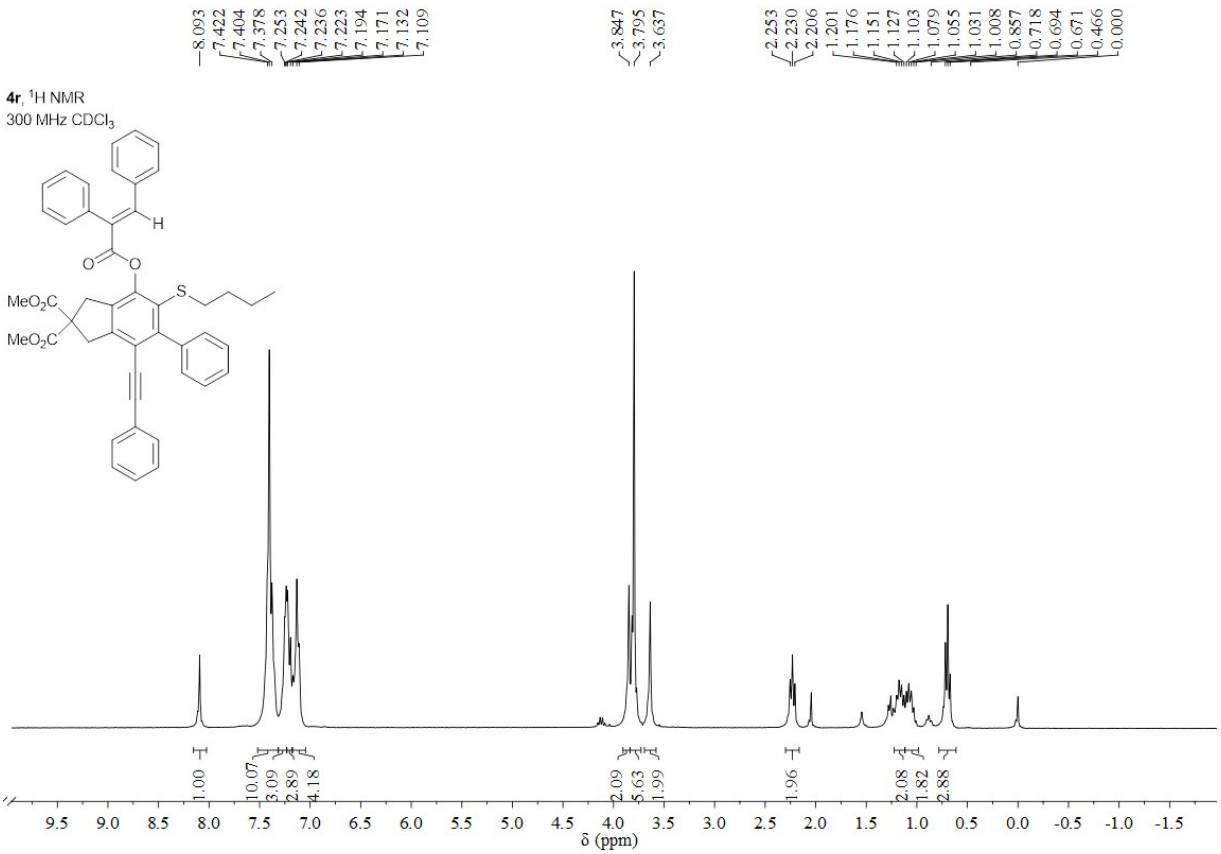
f1 (ppm)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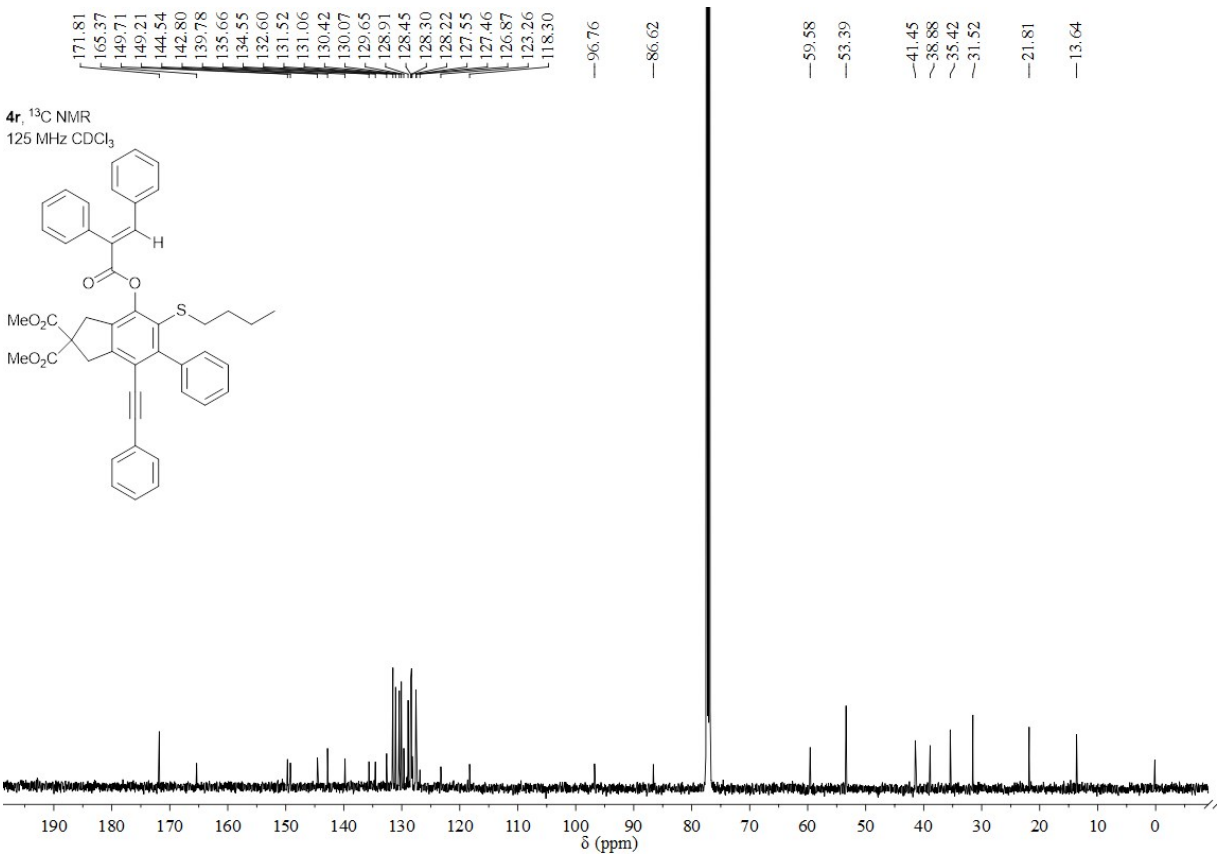
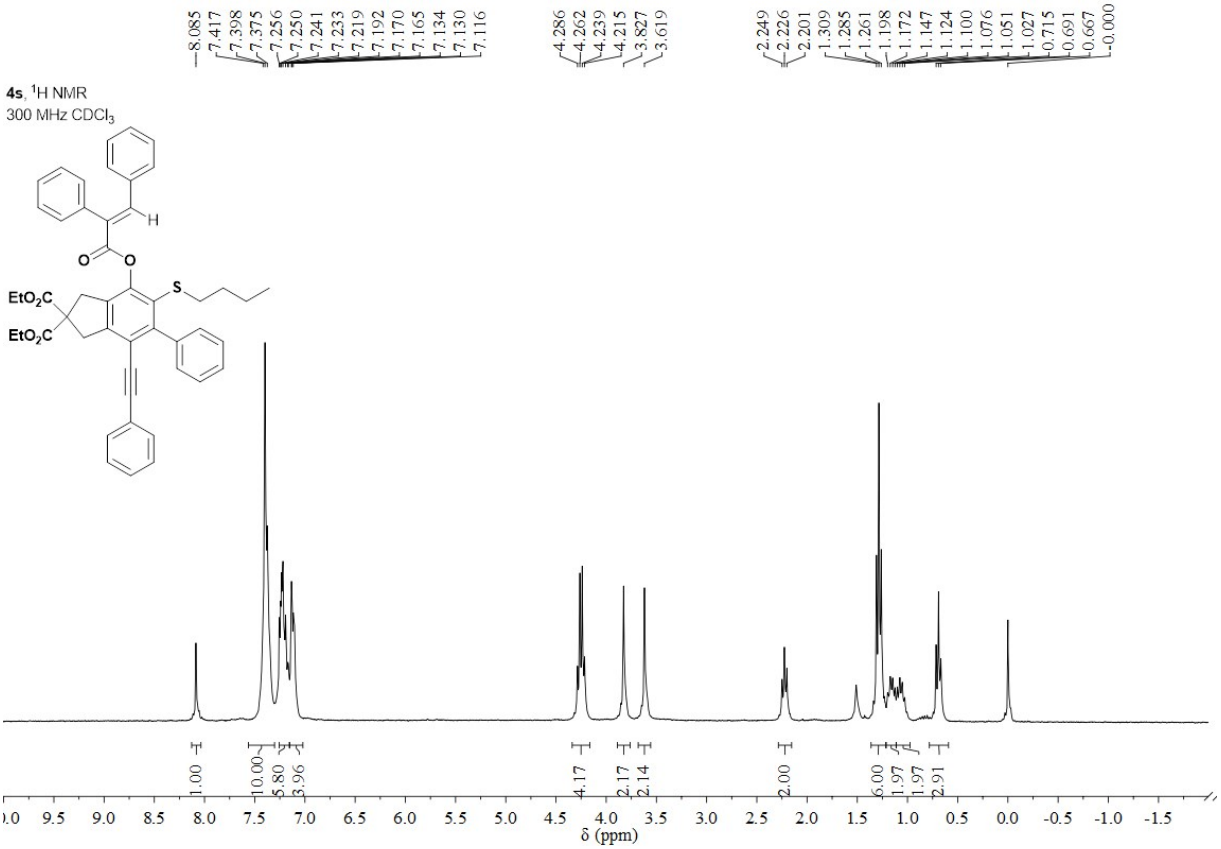
300 MHz CDCl3
δ (ppm)


4r, 13C NMR
125 MHz CDCl3
δ (ppm)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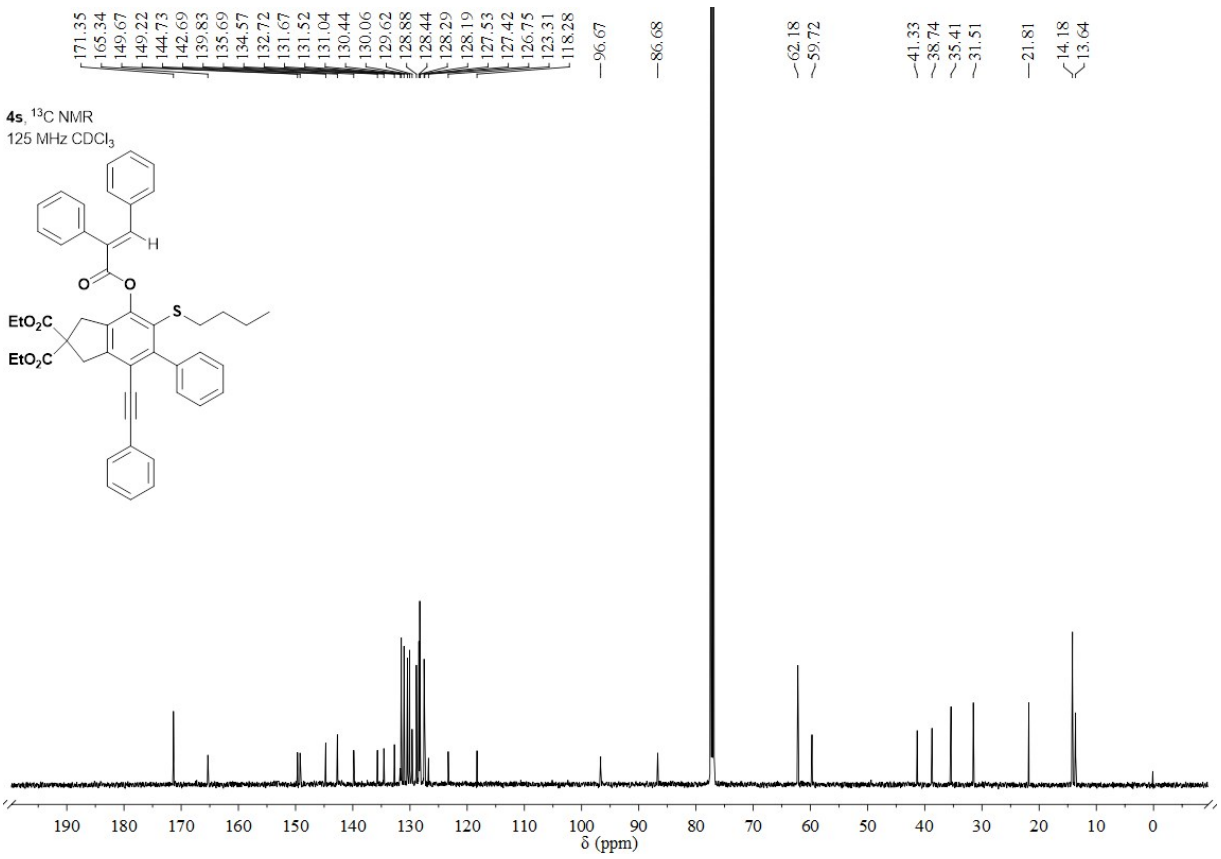
δ (ppm)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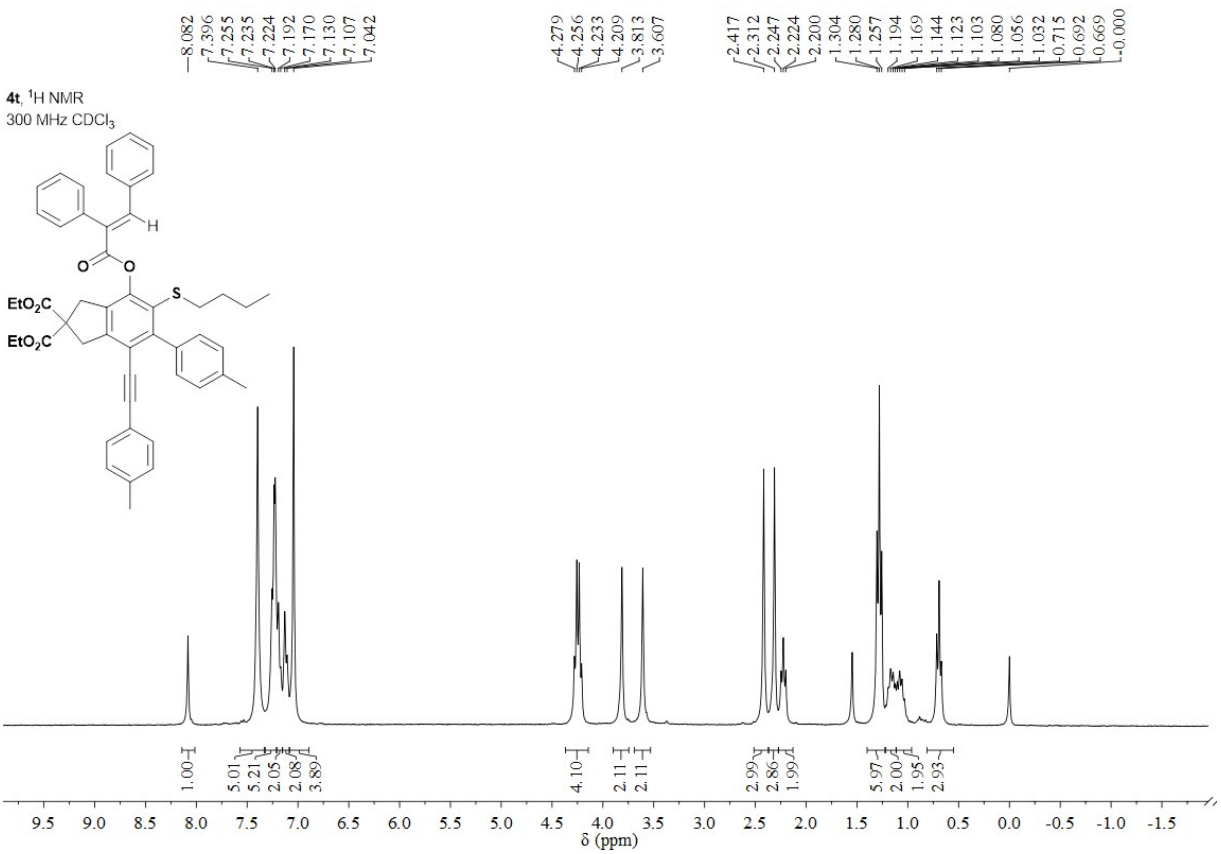
125 MHz CDCl3
δ (ppm)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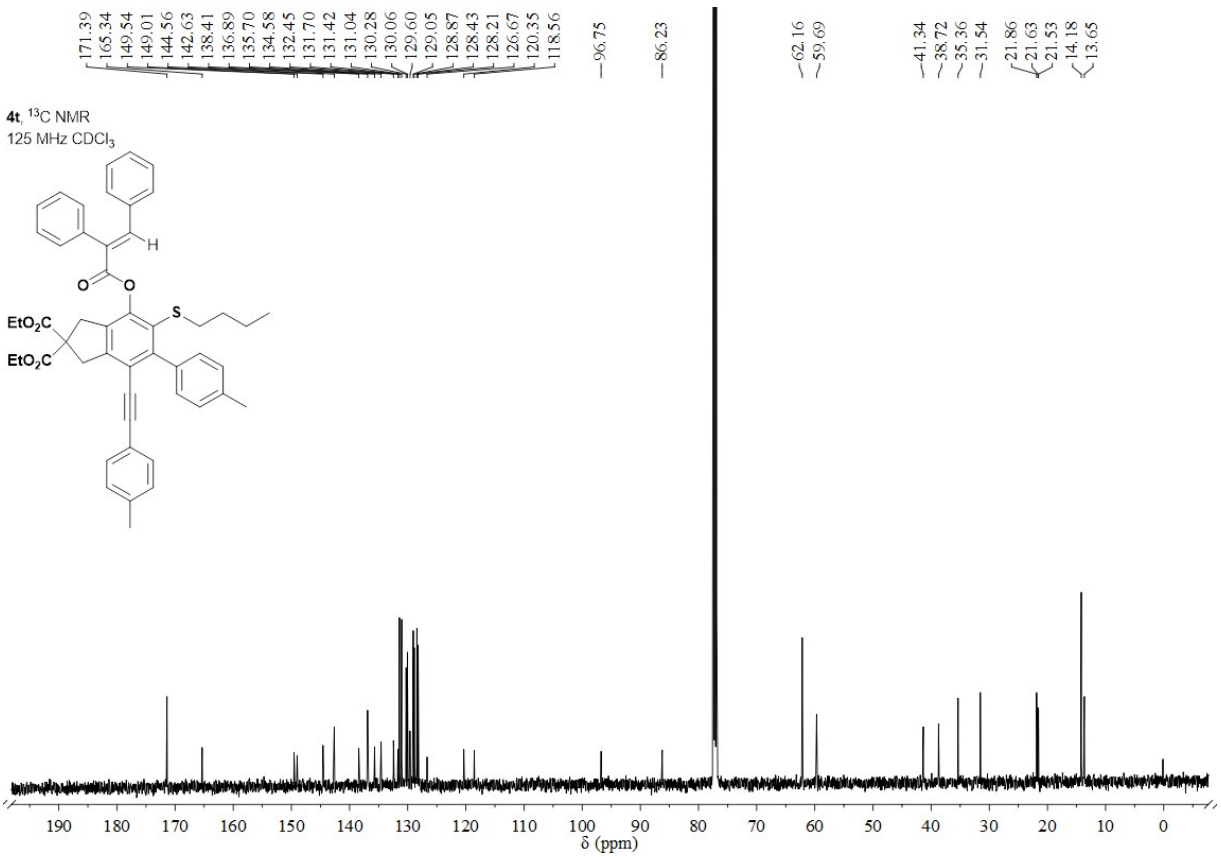
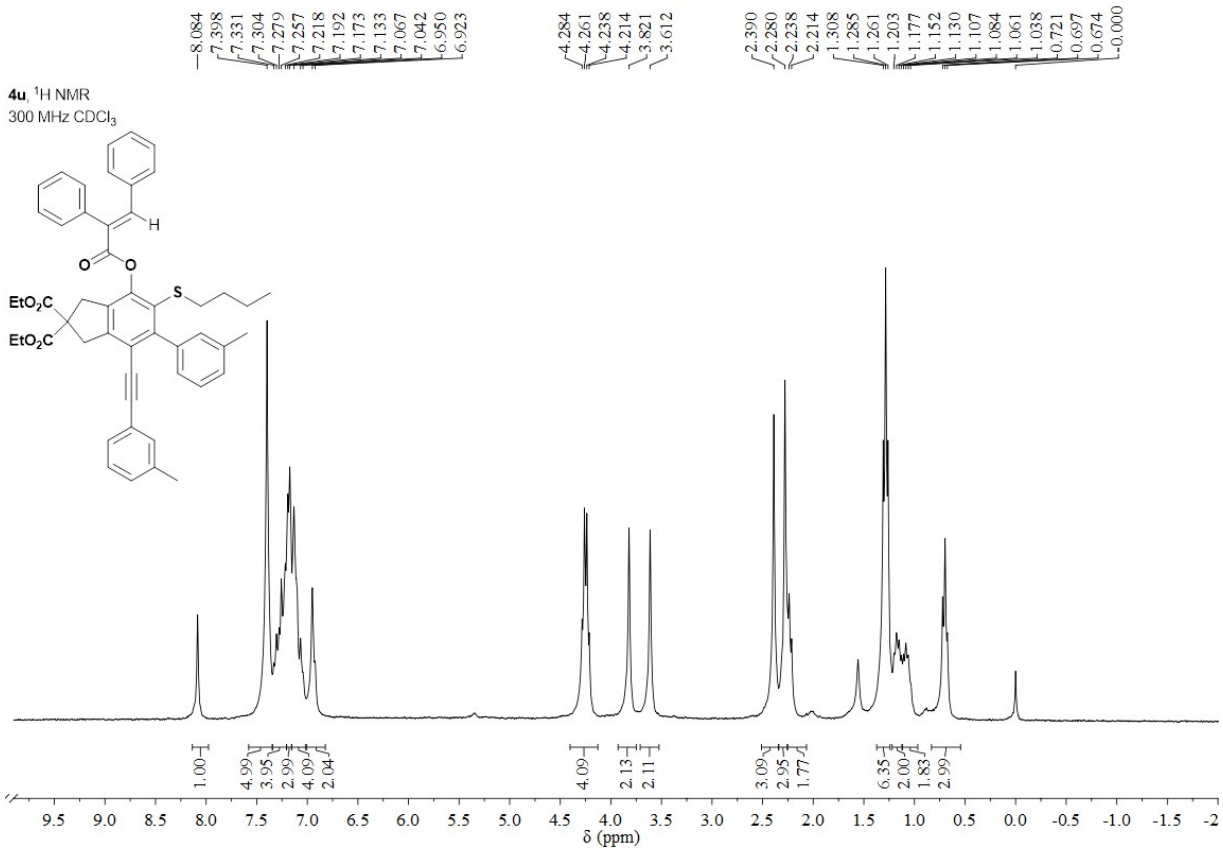

4t, 13C NMR
125 MHz CDCl3
δ (ppm)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6.950
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4.284
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4.238
4.214
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3.612
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2.238
2.214
1.308
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1.203
1.177
1.152
1.130
1.107
1.084
1.061
1.038
0.721
0.697
0.674
0.000
4u, 1H NMR
300 MHz CDCl3
EtO2C
EtO2C
S
1.00
4.99
3.95
2.99
4.09
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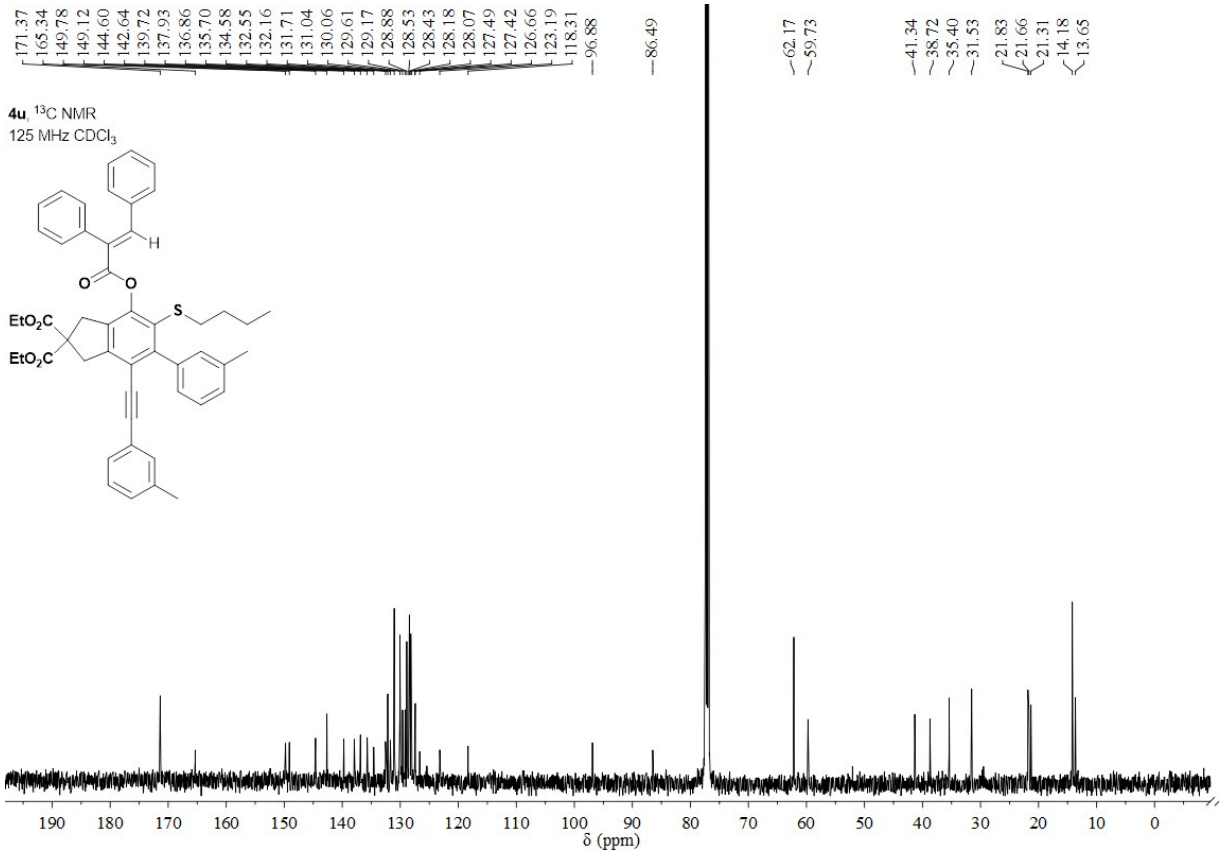
δ (ppm)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132.16
131.71
131.04
130.06
129.61
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128.18
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127.42
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123.19
118.31
96.88
86.49
62.17
59.73
41.34
38.72
35.40
31.53
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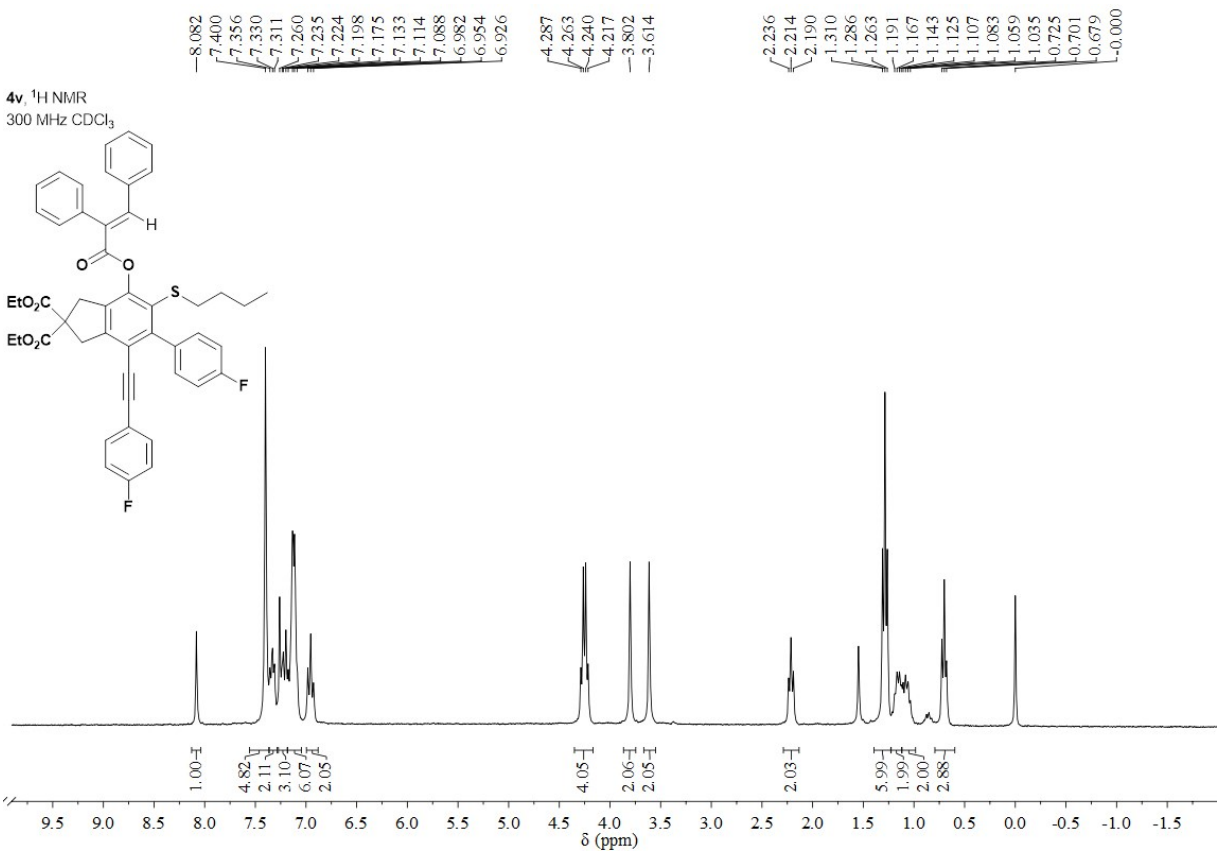
21.66
21.31
14.18
13.65
4u, 13C NMR
125 MHz CDCl3
EtO2C
EtO2C
S
δ (ppm)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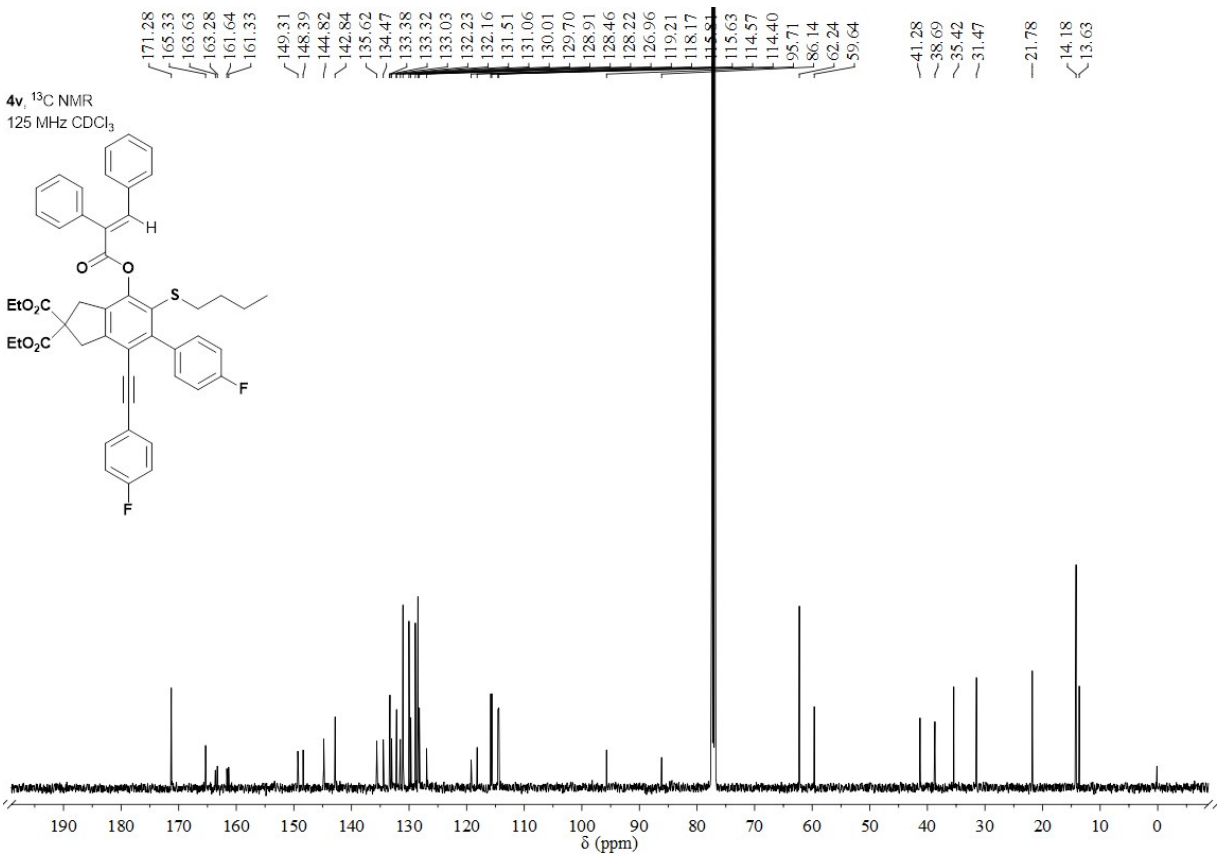
300 MHz CDCl3
δ (ppm)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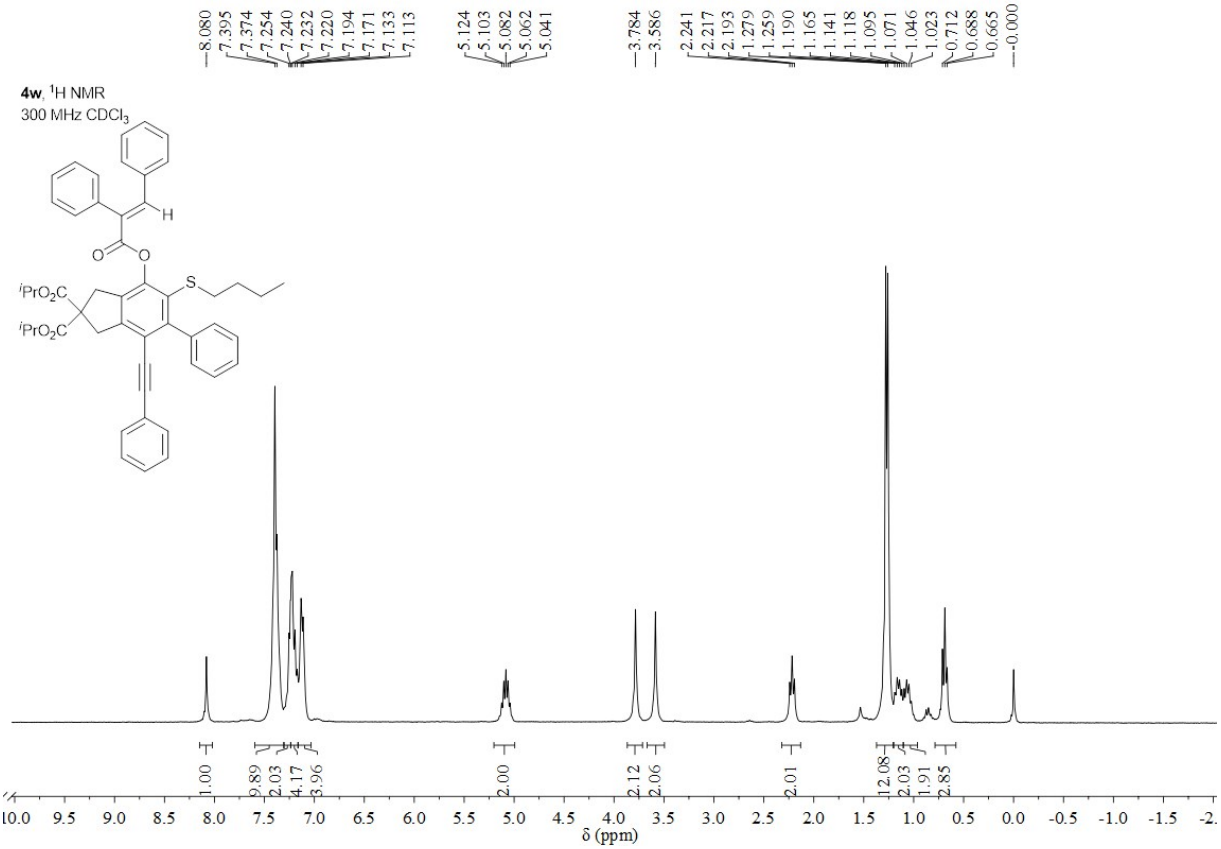
125 MHz CDCl3
δ (ppm)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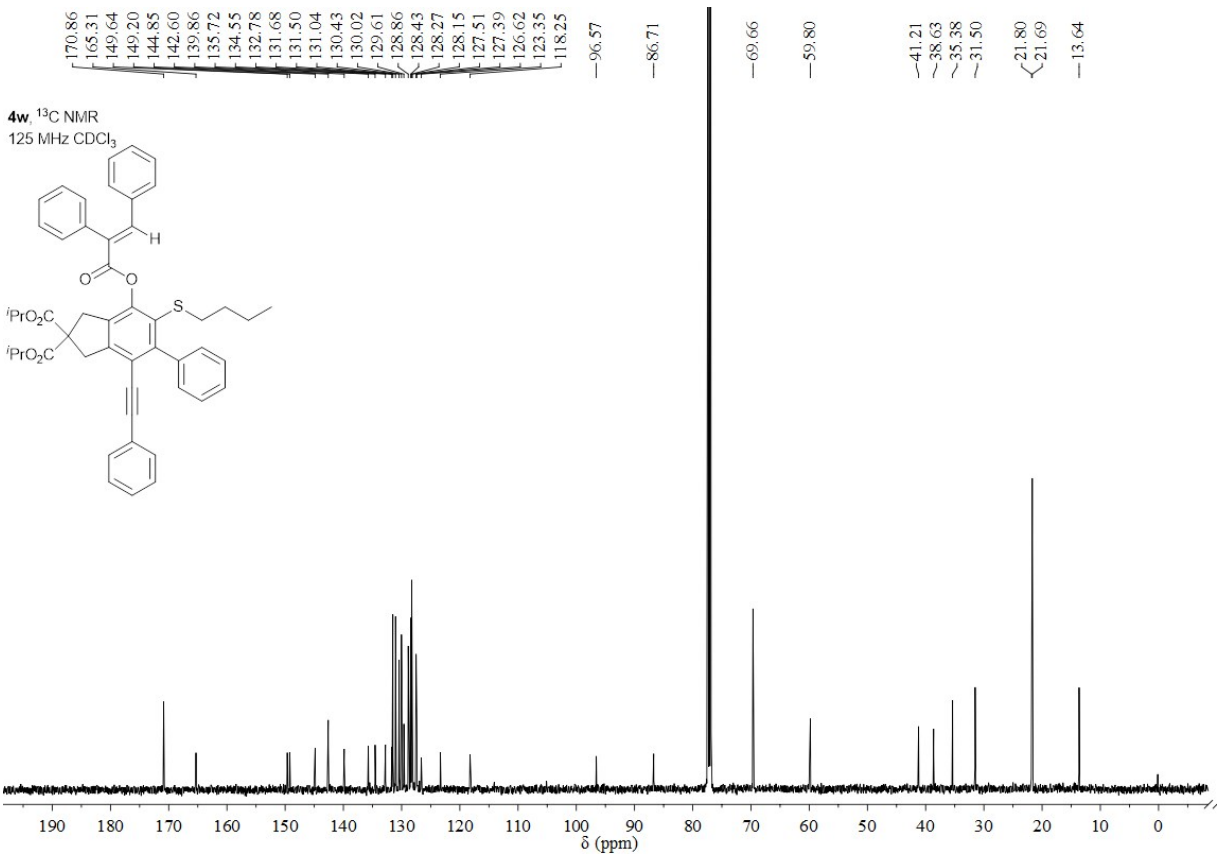
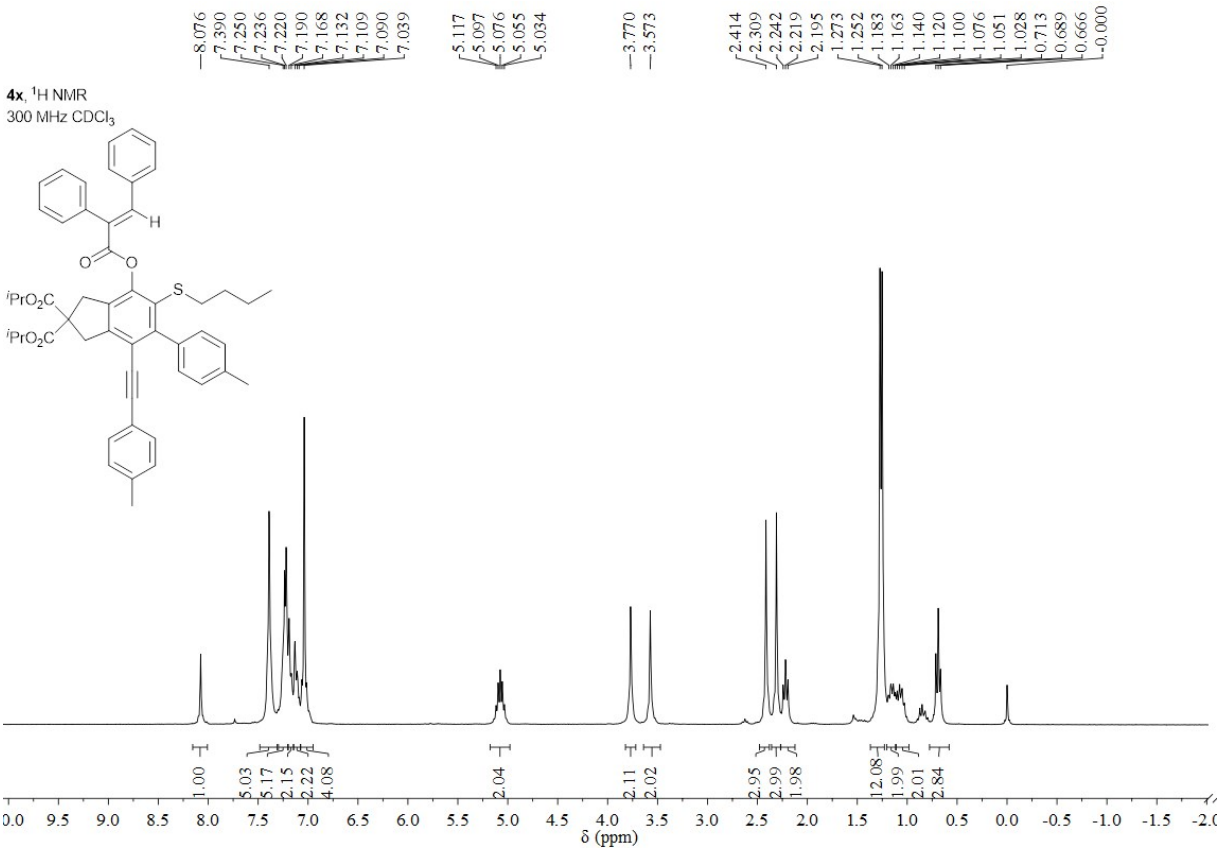
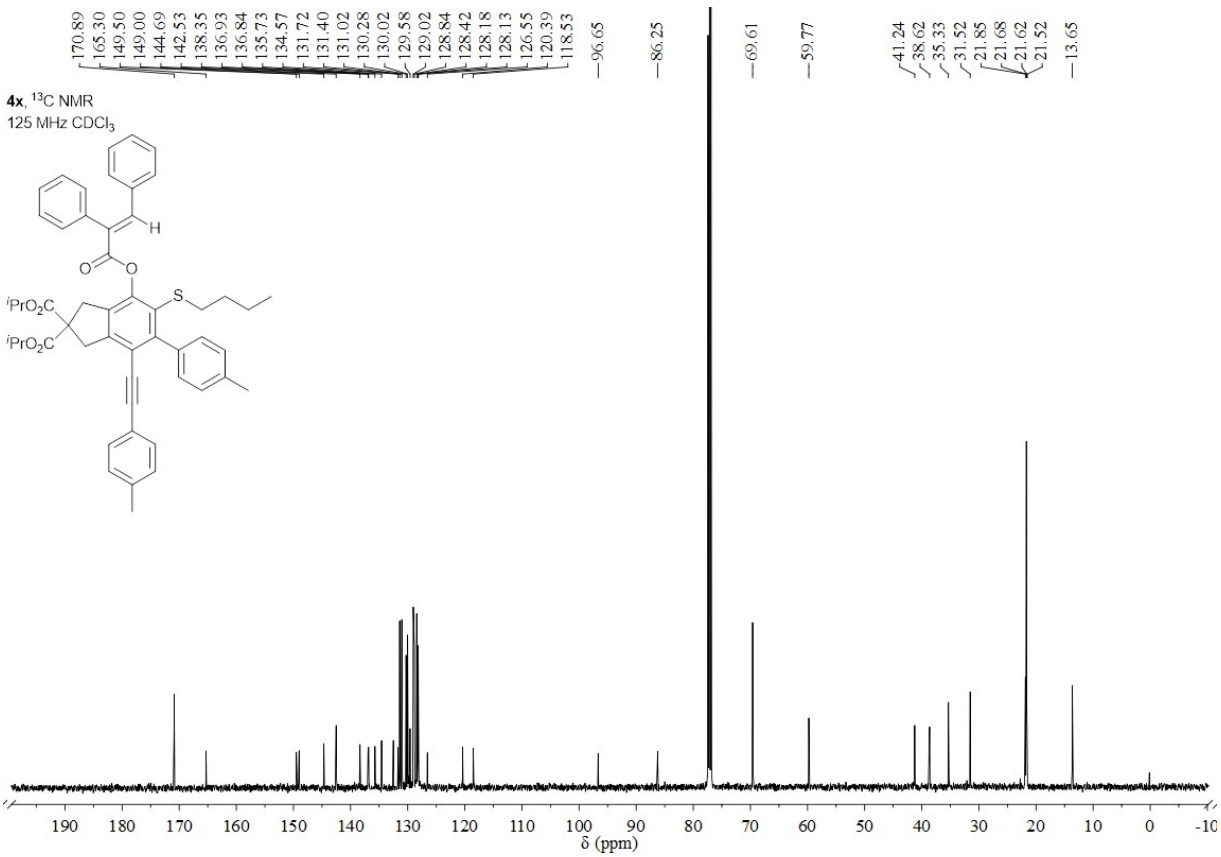
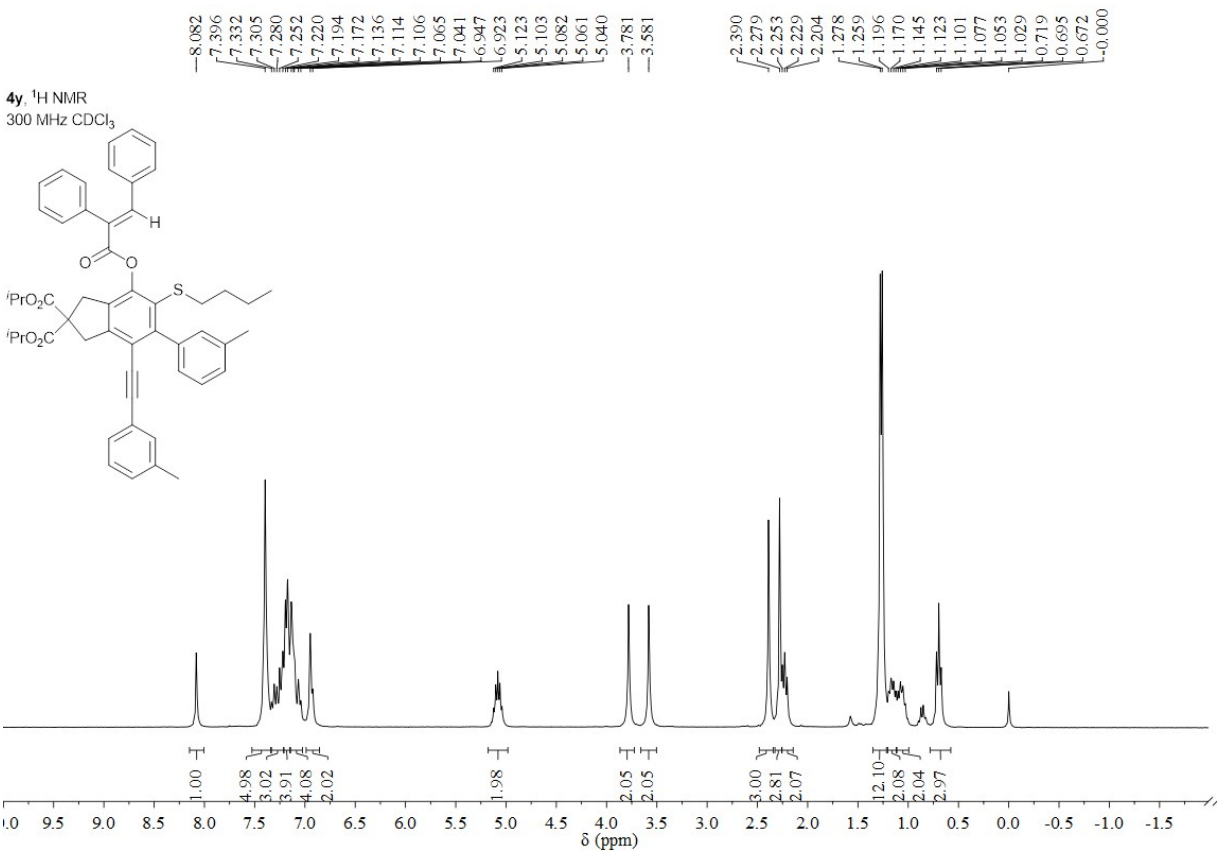
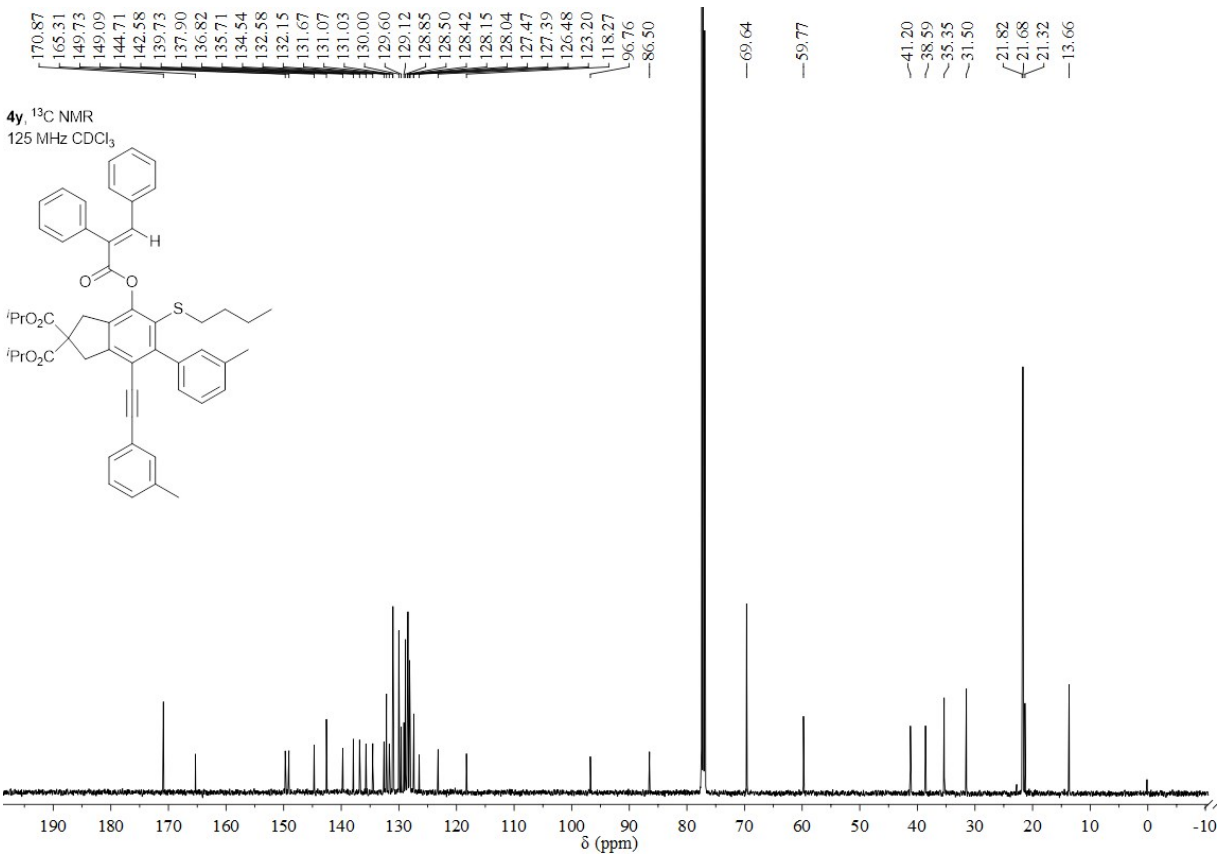
3.586
2.241
2.217
2.193
1.279
1.259
1.190
1.165
1.141
1.118
1.095
1.071
1.046
1.023
0.712
0.688
0.665
-0.000
4w, 1H NMR
300 MHz CDCl3
1.00
9.89
2.03
4.17
3.96
2.00
2.12
2.06
2.01
12.08
2.03
1.91
2.85
δ (ppm)

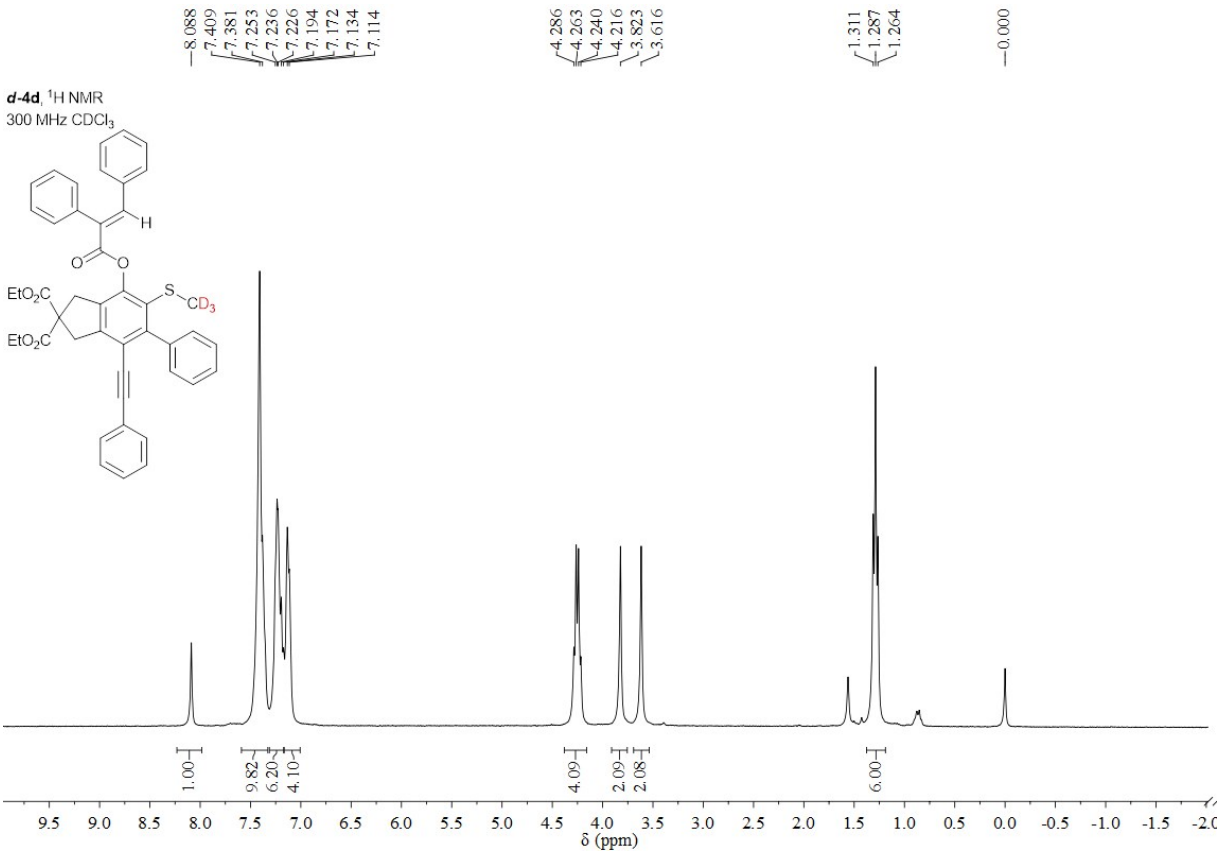

170.86
165.31
149.64
149.20
144.85
142.60
139.86
135.72
134.55
132.78
131.68
131.50
131.04
130.43
130.02
129.61
128.86
128.43
128.27
128.15
127.51
127.39
126.62
123.35
118.25
96.57
86.71
69.66
59.80
41.21
38.63
35.38
31.50
21.80
21.69
13.64
4w, 13C NMR
125 MHz CDCl3
δ (ppm)

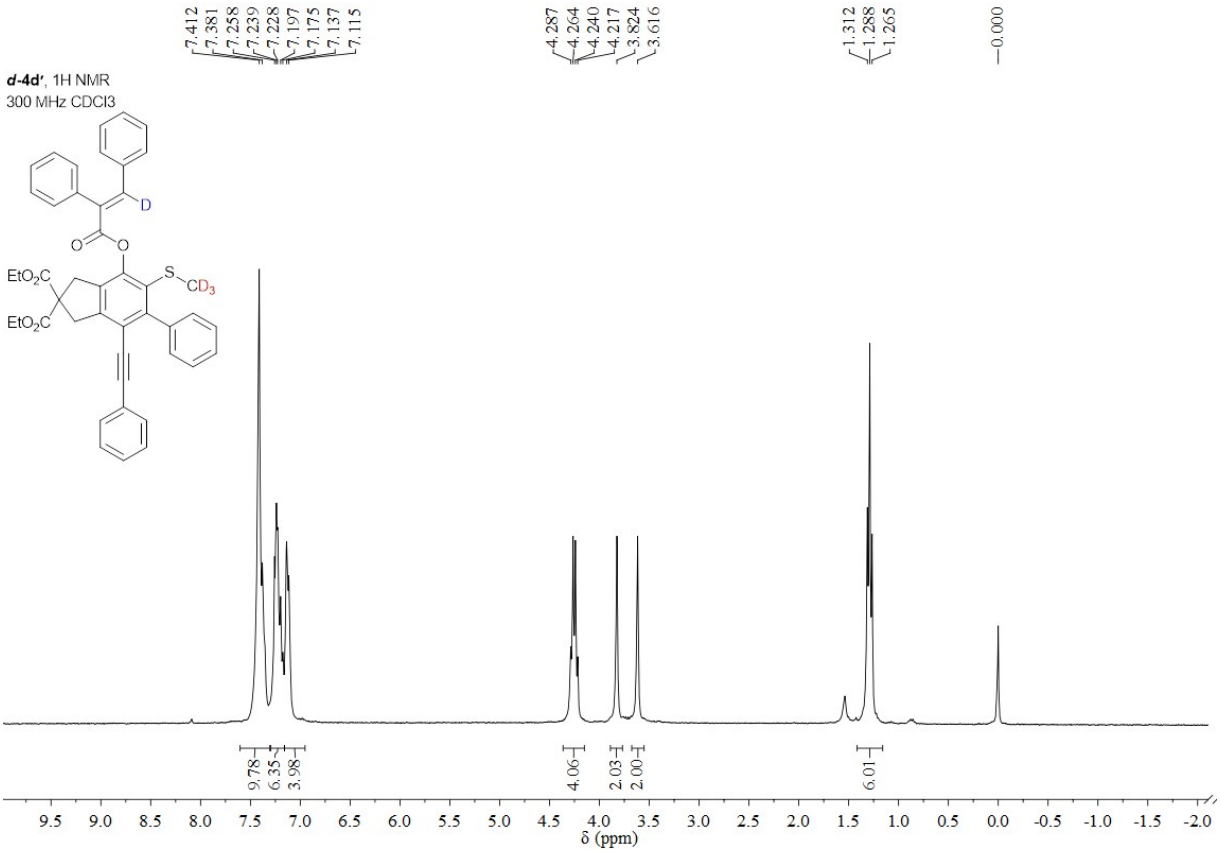

4x, 1H NMR
300 MHz CDCl3
δ (ppm)


4x, 13C NMR
125 MHz CDCl3
δ (ppm)


4y, 1H NMR
300 MHz CDCl3
δ (ppm)


4y, 13C NMR
125 MHz CDCl3
δ (ppm)


8.088
7.409
7.381
7.253
7.236
7.226
7.194
7.172
7.134
7.114
4.286
4.263
4.240
4.216
3.823
3.616
1.311
1.287
1.264
0.000
d-4d, 1H NMR
300 MHz CDCl3
H
O
O
EtO2C
EtO2C
S
CD3
1.00
9.82
6.20
4.10
4.09
2.09
2.08
6.00
δ (ppm)


7.412
7.381
7.258
7.239
7.228
7.197
7.175
7.137
7.115
4.287
4.264
4.240
4.217
3.824
3.616
1.312
1.288
1.265
0.000
d-4d', 1H NMR
300 MHz CDCl3
D
O
O
EtO2C
EtO2C
S
CD3
9.78
6.35
3.98
4.06
2.03
2.00
6.01
δ (ppm)