Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Carbene catalyzed C(sp^3)-Cl activation of chlorinated solvent for benzyne chlorination

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I. General Information

Commercial reagents were purchased from TCI, J&K, 3A Chemicals, Accela, Macklin, energy, bide, meryer, CIL, or Adamas and used without further purification. The solvents used in the experiments were all purchased as anhydrous solvents and used directly. All reactions were carried out with oven-dried glassware. Analytical thin-layer chromatography was performed on 0.20 mm silica gel HSGF-254 plates (Huanghai, China), and visualized under 254 nm UV light. Column chromatography was performed on 200-300 mesh silica gel (General-Reagent, China).

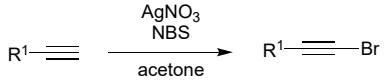
^{1}H, ^{19}F, and ^{13}C NMR spectra were recorded on a Bruker Ascend 400MHz or 600 MHz spectrometers. Chemical shifts were recorded in parts per million (ppm, δ) relative to chloroform (for ^{1}H NMR, δ = 7.26 ppm, singlet; for ^{13}C NMR, δ = 77.16 ppm, triplet). ^{1}H NMR splitting patterns are designated as singlet (s), doublet (d), triplet (t), quartet (q), dd (doublet of doublets); m (multiplets), etc. All first-order splitting patterns were assigned on the basis of the appearance of the multiplet. Splitting patterns that could not be easily interpreted are designated as multiplet (m) or broad (br).

High-resolution mass spectra of new compounds were recorded on LTQ Orbitrap Elite LC/MS (ESI or APCI) (Thermofisher). Infrared (IR) spectra were recorded on the PerkinElmer Frontier spectrometer and reported in wave numbers (cm^{-1}). Gas chromatography-mass spectrometry (GCMS) was recorded on GCMS-QP2010 SE (Shimadzu) or Agilent 5977B GC/MSD. The determination of enantiomeric excesses was performed via chiral stationary phases analysis using Waters Acquity UltraPerformance Convergence Chromatography (UPCC) (Chiral stationary phases column: Trefoil CEL2 column from Waters). Its X-ray diffraction data were collected on an Agilent Gemini Ultra diffractometer (CuKα radiation, Agilent, Oxfordshire, UK).

II. General Procedure

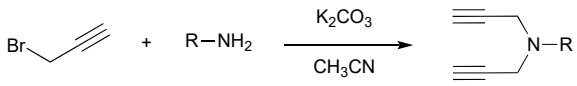
A. General Procedure of HDDA precursors synthesis

1. Synthesis of Alkyne Bromide[1]

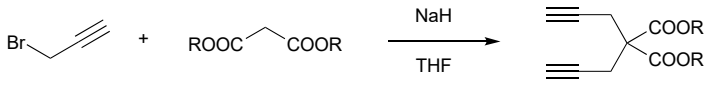


Under a nitrogen atmosphere, silver nitrate (339.7 mg, 2 mmol, 0.1 equiv.), N-bromosuccinimide (NBS, 3.92 g, 22 mmol, 1.1 equiv.) and acetone (10 mL) were added into a 100 mL round-bottom flask with magnetic stirring. Alkyne solution (20 mmol, 1.0 equiv., 1M in acetone) was added dropwise. The mixture was stirred at room temperature for further 8 h. After the reaction was completed (monitored by TLC), it was extracted with *n*-hexane, washed with brine, dried over Na_2SO_4, and concentrated by rotary evaporator to give the crude product of alkyne bromide.

2. Synthesis of Dialkyne[2]

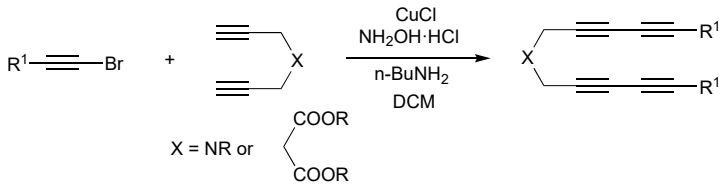


Under a nitrogen atmosphere, sulfamides (20 mmol), potassium carbonate (13.8 g, 100 mmol, 5.0 equiv.) and acetonitrile (60mL) were added into a 250 mL round-bottom flask with magnetic stirring. After stirring in dark for 30 min, propargyl bromide (5.2 mL, 60 mmol, 3.0 equiv.) was subsequently added and the mixture was stirred at room temperature overnight. After the reaction was completed (monitored by TLC), the mixture was filtered through celite, and the filtrate was concentrated by rotary evaporator to give the crude product, which was further purified by silica gel column chromatography (hexanes/ethyl acetate as eluant).



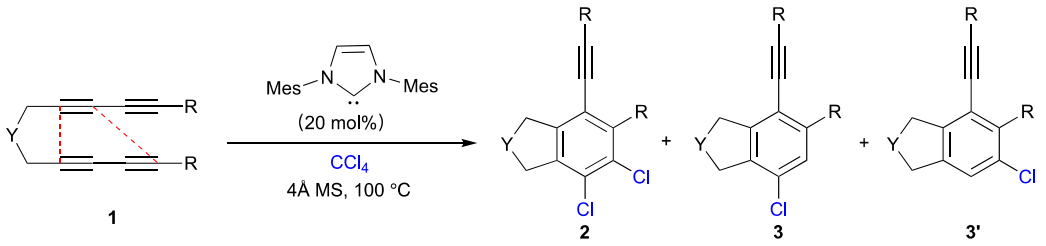
Malonate (20 mmol), sodium hydride (80 mmol, 60% mineral dispersion, 4.0 equiv.) and THF (60 mL) were added into a 250 mL round-bottomed flask with magnetic stirring in an ice-bath. After stirring at rt for 15 min, propargyl bromide (3.5 mL, 40 mmol, 2.0 equiv.) was added and the mixture was stirred overnight. After the reaction was completed (monitored by TLC), the mixture was filtered through celite, the filtrate was concentrated under reduced pressure. The crude product was purified by silica gel column chromatography.[2]

3. Cadiot–Chodkiewicz Alkyne Cross-Coupling [3]



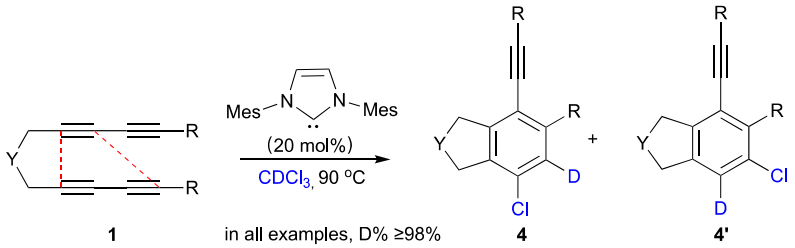
Under a nitrogen atmosphere, copper(I) chloride (99 mg, 1 mmol, 0.2 equiv.), hydroxylamine hydrochloride (382.2 mg, 5.5 mmol, 1.1 equiv.) were added into a 250 mL three-necked round-bottom flask with magnetic stirring. After cooling to -10°C,10 mL of 40% (v/v) *n*-butylamine aqueous solution was added, and the solution was stirred for about 15 min until it became colorless and transparent. Dialkyne (from procedure A-2, 5 mmol in 5 mL of DCM) was added through a pressure-equalizing dropping funnel to form some yellow powders immediately. After slowly addition of alkyne bromide (from procedure A-1, 3.0 equiv., 0.2 M in DCM) with robust stirring until the yellow powders completely dissolved, the reaction was stirred at 0 °C for further 8 h. After the reaction was completed (monitored by TLC), it was quenched by 40 mL of NH_4Cl (sat. aq.), extracted by DCM, washed with brine, dried over Na_2SO_4, and concentrated by rotary evaporator to give the crude product of tetrayne, which was purified by silica gel column chromatography and stored in 2~8 ℃ for further use.

B. General Procedure of NHC-catalyzed benzyne dichlorination with CCl_4



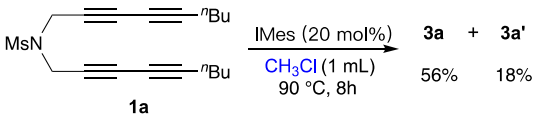
Under nitrogen atmosphere, alkyne **1** (0.2 mmol), IMes (12.2 mg, 20 mol%), 4Å MS (200 mg) and CCl_4 (2 mL) were added into a 15 mL pressure tube with magnetic stirring. The solution was stirred at 100 °C for about 4 h. After the reaction was completed (monitored by TLC), the mixture was concentrated by rotary evaporator, and the residue was purified by silica gel column chromatography (hexanes/ethyl acetate as eluant) to give product **2** (**3** and **3'** were the main byproduct).

C. General Procedure of NHC-catalyzed benzyne deuteron-chlorination with $CDCl_3$

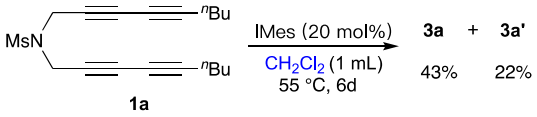


Under nitrogen atmosphere, alkyne **1** (0.2 mmol), IMes (12.2 mg, 20 mol%) and $CDCl_3$ (2 mL) were added into a 15 mL pressure tube with magnetic stirring. The solution was stirred at 90°C for 6 - 24 h. After the reaction was completed (monitored by TLC), the mixture was concentrated by rotary evaporator, and the residue was purified by silica gel column chromatography (hexanes/ethyl acetate as eluant) to give products **4** and **4'**.

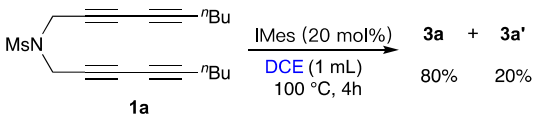
D. NHC-catalyzed benzyne chlorination with other chlorinated solvents



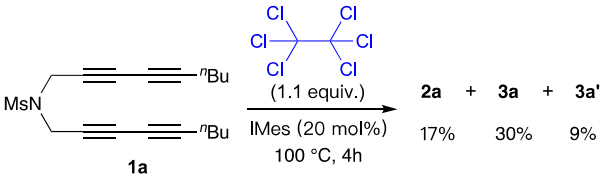
Under nitrogen atmosphere, alkyne **1a** (33.3 mg, 0.1 mmol), IMes (6.1 mg, 20 mol%), and CH_3Cl (1 mL) were added into a 15 mL pressure tube with magnetic stirring. The solution was stirred at 90 ℃ for 8 h. The mixture was concentrated by rotary evaporator, and the residue was purified by silica gel chromatography (hexanes/ethyl acetate 50:1 ~ 10:1, v/v as eluant) to give product **3a** (white solid, 20.5 mg, 56% yield) and **3a'** (white solid, 6.5 mg, 18% yield).



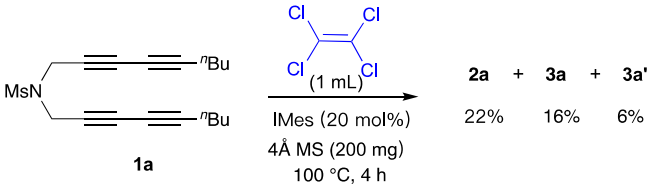
Under nitrogen atmosphere, alkyne **1a** (33.3 mg, 0.1 mmol), IMes (6.1 mg, 20 mol%) and CH_2Cl_2 (1 mL) were added into a 15 mL pressure tube with magnetic stirring. The solution was stirred at 55 ℃ for about 6 days. After the reaction was completed (monitored by TLC), the mixture was concentrated by rotary evaporator to give a crude product containing **3a** (43% yield) and **3a'** (22% yield) (yields were detected by ^1H NMR, with 1,3,5-trimethoxybenzene as an internal standard)



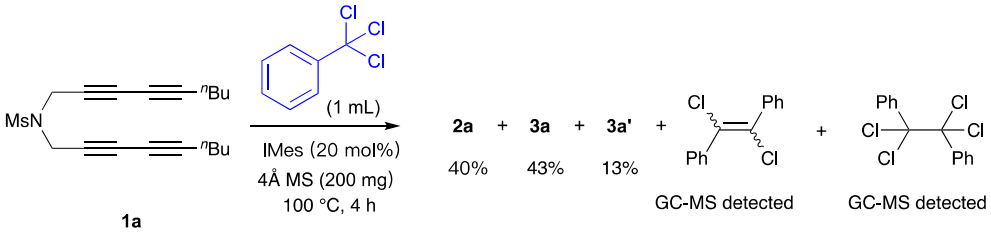
Under nitrogen atmosphere, alkyne **1a** (33.3 mg, 0.1 mmol), IMes (6.1 mg, 20 mol%) and 1,2-dichloroethane (1 mL) were added into a 15 mL pressure tube with magnetic stirring. The solution was stirred at 100 ℃ for about 4 h. After the reaction was completed (monitored by TLC), The mixture was concentrated by rotary evaporator to give a crude product containing **3a** (80% yield) and **3a'** (20% yield) (yields were detected by ^1H NMR, with 1,3,5-trimethoxybenzene as an internal standard)



Under nitrogen atmosphere, alkyne **1a** (33.3 mg, 0.1 mmol), IMes (6.1 mg, 20 mol%), and C_2Cl_6 (26 mg, 1.1 equiv.) were added into a 15 mL pressure tube with magnetic stirring. The mixture was stirred at 100 ℃ for about 4 h. After the reaction was completed (monitored by TLC), the yields of **2a** (17%), **3a** (30%) and **3a'** (9%) were detected by ^{1}H NMR, with 1,3,5-trimethoxybenzene as an internal standard.



Under nitrogen atmosphere, alkyne **1a** (33.3 mg, 0.1 mmol), IMes (6.1 mg, 20 mol%), 4Å MS (200 mg), and tetrachloroethylene (1 mL) were added into a 15 mL pressure tube with magnetic stirring. The solution was stirred at 100 ℃ for about 4 h. After the reaction was completed (monitored by TLC), the mixture was concentrated by rotary evaporator, the yields of **2a** (22%), **3a** (16%) and **3a'**(6%) were detected by ^{1}H NMR, with 1,3,5-trimethoxybenzene as an internal standard.



Under nitrogen atmosphere, alkyne **1a** (33.3 mg, 0.1 mmol), IMes (6.1 mg, 20 mol%), 4Å MS (200 mg), and benzotrichloride (1 mL) were added into a 15 mL pressure tube with magnetic stirring. The solution was stirred at 100 ℃ for about 4 h. After the reaction was completed (monitored by TLC), the mixture was detected by a GC-MS (Agilent 5977B GC/MSD) to show the solvent degradation product (Fig. S1).

Then the mixture was concentrated by rotary evaporator, and the residue was purified by silica gel column chromatography (hexanes/ethyl acetate 99:1 ~ 10:1, v/v as eluant) to give product **2a** (white solid, 17 mg, 40%), with **3a** (white solid, 16 mg, 43%) and **3a'** (white solid, 5 mg, 13%) as byproducts.

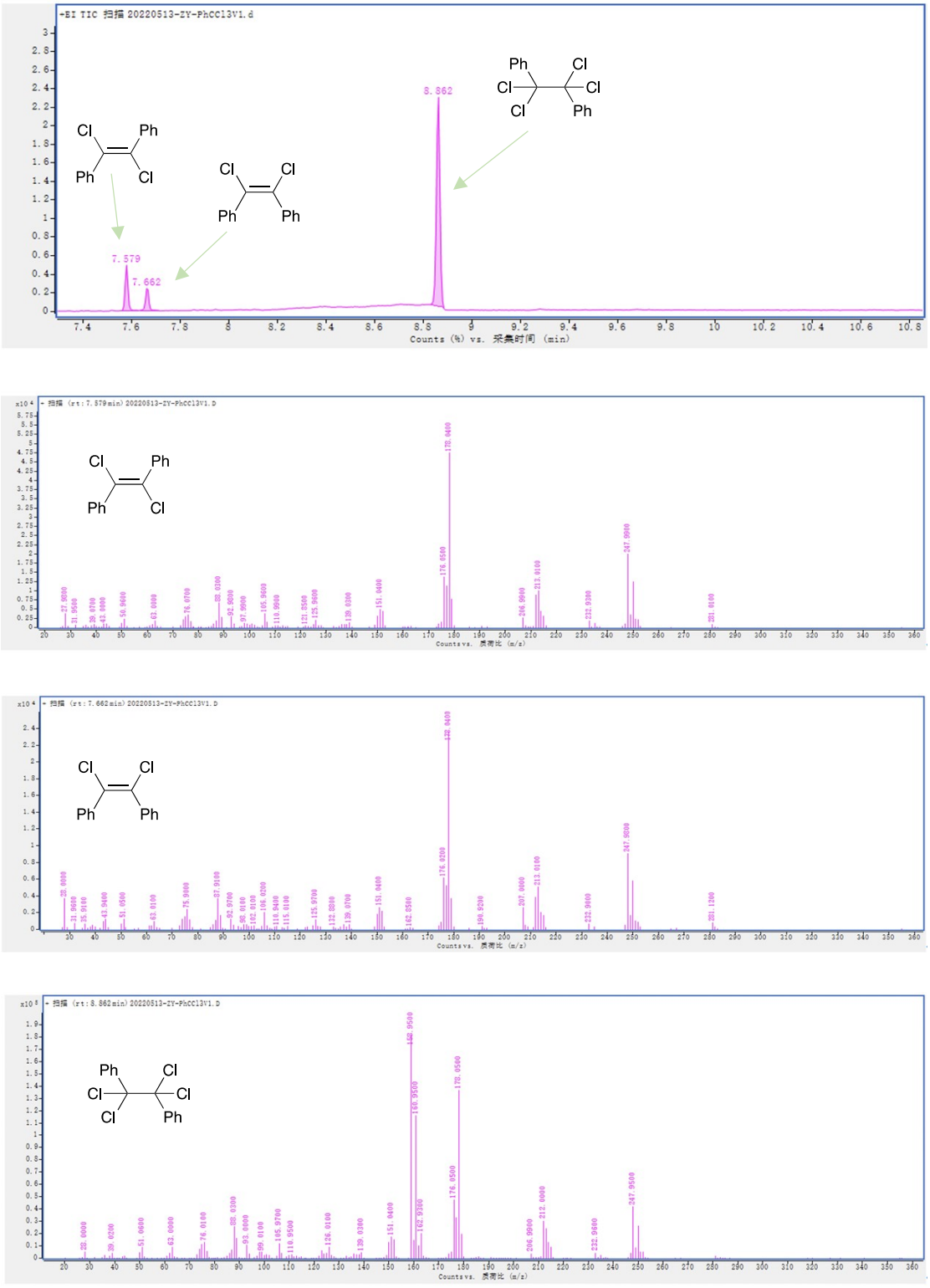
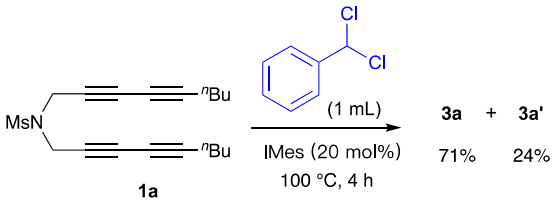


Fig. S1 Copies of chromatograms and mass spectrogram for 1,1,2,2-tetrachloro-1,2-

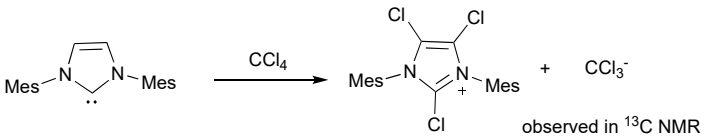
diphenylethane and 1,2-dichloro-1,2-diphenylethene determination

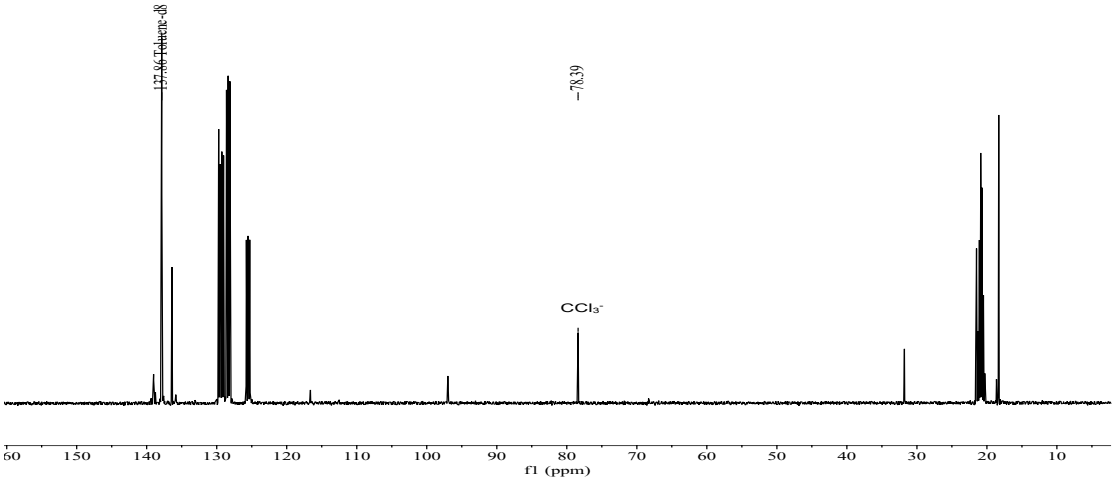


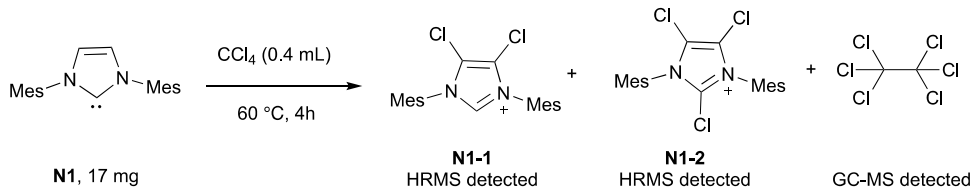
Under nitrogen atmosphere, alkyne **1a** (33.3 mg, 0.1 mmol), IMes (6.1 mg, 20 mol%), and (dichloromethyl)benzene (1 mL) were added into a 15 mL pressure tube with magnetic stirring. The solution was stirred at 100 ℃ for about 4 h. After the reaction was completed (monitored by TLC), the mixture was concentrated by rotary evaporator, and the residue was purified by silica gel chromatography (hexanes/ethyl acetate 50:1 ~ 10:1, v/v as eluant) to give product **3a** (white solid, 26 mg, 71% yield) and **3a'** (white solid, 9 mg, 24% yield).

III. mechanism study

1. in-situ ^{1}H NMR study of CCl_4 activation with IMes (*cf.* Scheme 5a)

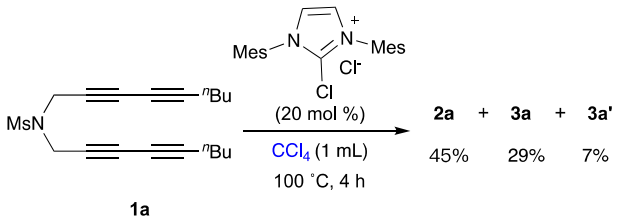






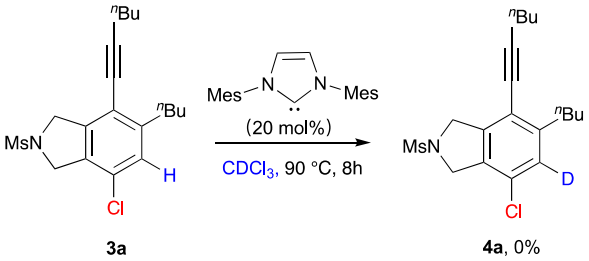
Under nitrogen atmosphere, **N1** (17 mg) and CCl_4 (0.4 mL) were added into a 15 mL pressure tube with magnetic stirring. The solution was stirred at 60 ℃ for about 4 h. After the reaction was completed, the mixture was detected by high-resolution mass spectrometry (HRMS) and chromatography-mass spectrometry (Agilent 5977B GC/MSD).

2. catalytic activity of N1-2Cl (*cf.* Scheme 5b)



Under nitrogen atmosphere, alkyne **1a** (33.3 mg, 0.1 mmol), 2-chloro-1,3-dimesityl-1*H*-imidazol-3-ium chloride[4] (7.5 mg, 20 mol%), and CCl_4 (1 mL) were added into a 15 mL pressure tube with magnetic stirring. The solution was stirred at 100 ℃ for about 4 h. After the reaction was completed (monitored by TLC), the mixture was concentrated by rotary evaporator, and the residue was purified by flash chromatography on silica gel (hexanes/ethyl acetate 99:1 ~ 10:1, v/v as eluant) to give product **2a** (white solid, 19 mg, 45%) (**3a** (white solid, 11 mg, 29%) and **3a'** (white solid, 2.6 mg, 7%) were the main byproducts).

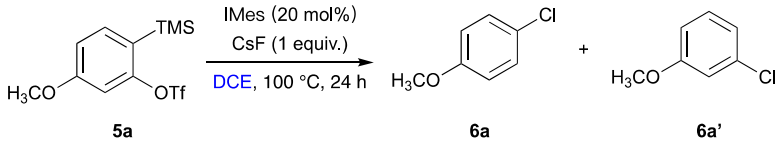
3. the possibility of NHC catalyzed phenyl D/H exchange (*cf.* Scheme 5c)



3a **4a**, 0%

Under nitrogen atmosphere, **3a** (37 mg, 0.1 mmol), IMes (6.1 mg, 20 mol%), and $CDCl_3$ (1 mL) were added into a 15 mL pressure tube with magnetic stirring. After stirring at 90 ℃ for about 8 h, the deuteration rate of 3a remained 0% as shown in ^1H NMR. The possibility of NHC catalyzed phenyl D/H exchange was excluded.

4. reaction with Kobayashi benzyne precursor (*cf.* Scheme 5d)

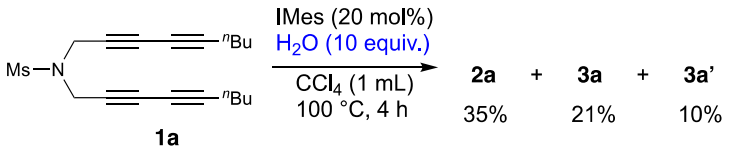


5a **6a** **6a'**

< 5% (GC-MS)

Under nitrogen atmosphere, **5a** (33 mg, 0.1 mmol), IMes (6.1 mg, 20 mol%), CsF (15.2 mg, 1 equiv.), and 1,2-dichloroethane (1 mL) added into a 15 mL pressure tube with magnetic stirring. The solution was stirred at 100 ℃ for about 24 h. Products **6a** and **6a'** were observed by GC-MS. But the yields were too low to be isolated.

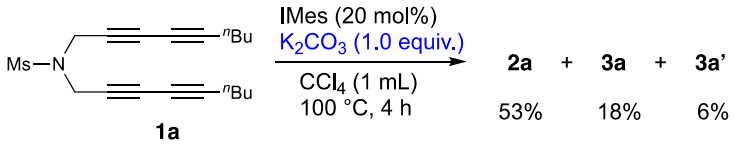
5. effect of water and base on the reaction



1a

Under nitrogen atmosphere, alkyne **1a** (33.3 mg, 0.1 mmol), IMes (6.1 mg, 20 mol%), CCl_4 (1 mL), and H_2O (18 μL, 10 equiv.) were added to a 15 mL pressure tube with magnetic stirring. The solution was stirred at 100 ℃ for 4 h. After the reaction was completed (monitored by TLC), the mixture was concentrated by rotary evaporator,

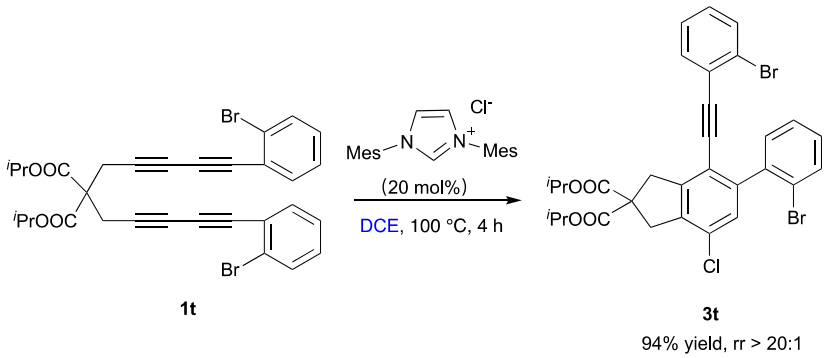
and the yields of **2a** (35%), **3a** (21%), and **3a'**(10%) were detected by ^{1}H NMR, with 1,3,5-trimethoxybenzene as an internal standard.



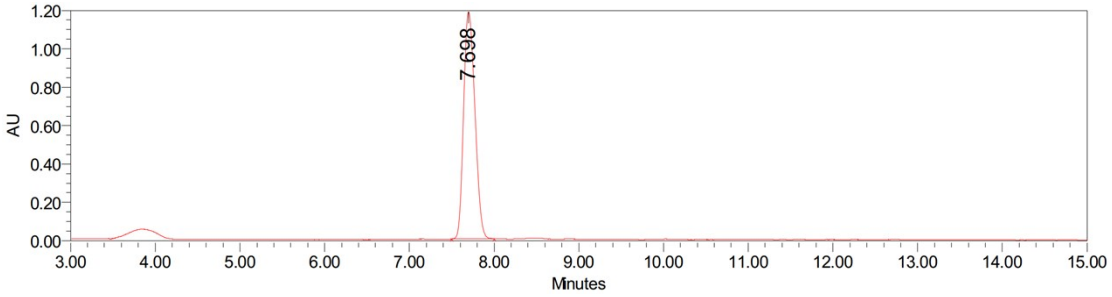
Under nitrogen atmosphere, alkyne **1a** (33.3 mg, 0.1 mmol), IMes (6.1 mg, 20 mol%, CCl_4 (1 mL), and K_2CO_3 (13.8 mg, 1.0 equiv.) were added to a 15 mL pressure tube with magnetic stirring. The solution was stirred at 100 °C for 4 h. After the reaction was completed (monitored by TLC), the mixture was concentrated by rotary evaporator, the yields of **2a** (53%), **3a** (18%), and **3a'**(6%) were detected by ^{1}H NMR, with 1,3,5-trimethoxybenzene as an internal standard.

IV. Atroposelective control with chiral NHC

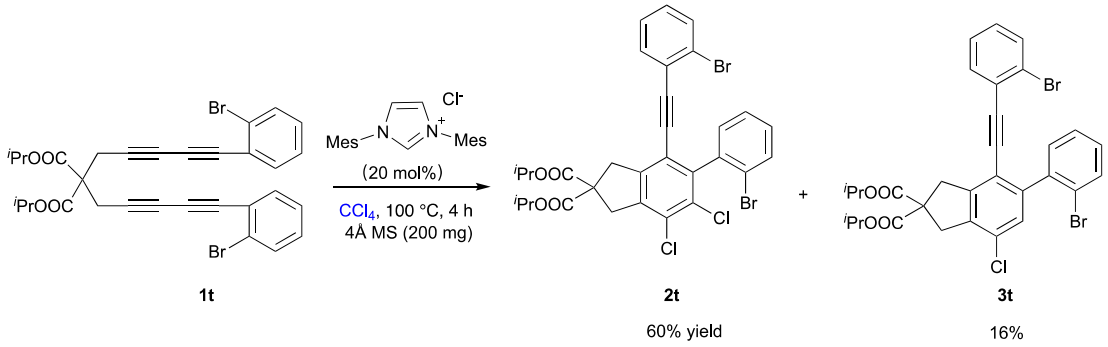
1. Synthesis of hydrochlorination product



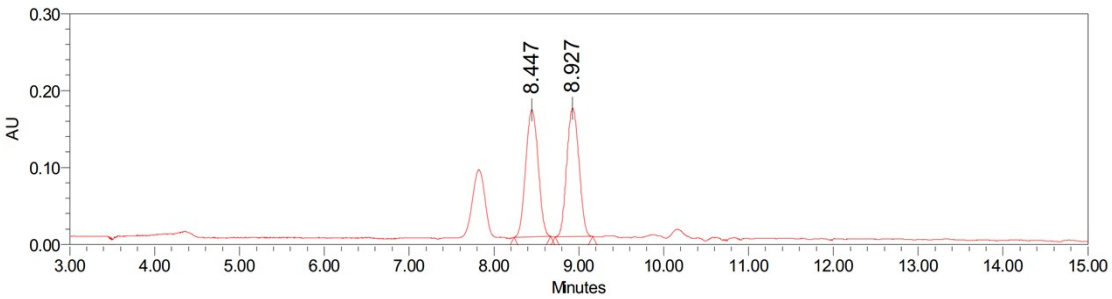
Under nitrogen atmosphere, alkyne **1t** (62 mg, 0.1 mmol), IMesCl (6.8 mg, 20 mol%), and DCE (1 mL) were added into a 15 mL pressure tube with magnetic stirring. The solution was stirred at 100 °C for about 4 h. After the reaction was completed (monitored by TLC), the mixture was concentrated by rotary evaporator, and the residue was purified by flash chromatography on silica gel (hexanes/ethyl acetate 50:1, v/v as eluant) to give product **3t** (white solid, 62 mg, 94%).



2. Synthesis of the racemic 2t



Under nitrogen atmosphere, alkyne **1t** (62 mg, 0.1 mmol), IMesCl (6.8 mg, 20 mol%), 4Å MS (200 mg), and CCl_4 (1 mL) were added into a 15 mL pressure tube with magnetic stirring. The solution was stirred at 100 °C for about 4 h. After the reaction was completed (monitored by TLC), the mixture was concentrated by rotary evaporator, and the residue was purified by silica gel chromatography (hexanes/ethyl acetate 50:1, v/v as eluant) to give a crude product containing **2t** and **3t** (with the same polarity and not isolatable by chromatography). The yields of **2t** and **3t** were measured by ^{1}H NMR as 60% and 16%, respectively.



	RT	Area	Height	% Area
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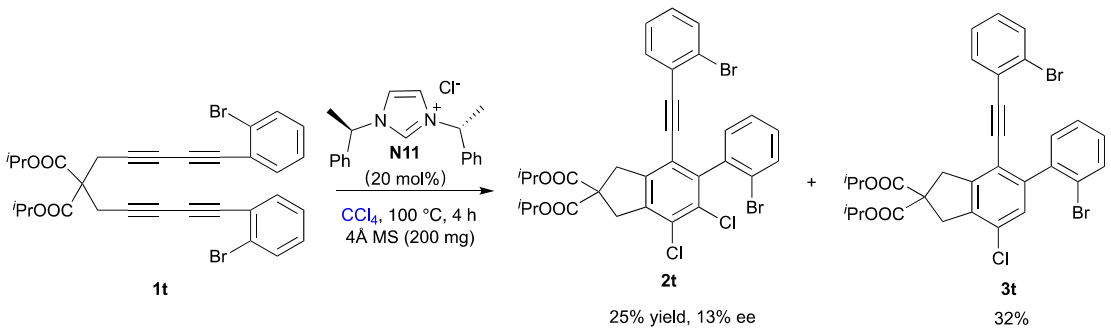
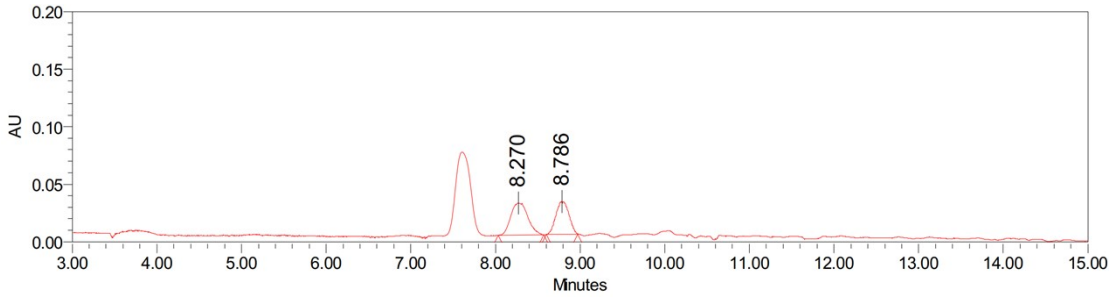
2	8.927	1657774	167139	49.55

3. Synthesis of the Chiral 2t



Under nitrogen atmosphere, alkyne **1t** (62 mg, 0.1 mmol), **N11** (6.3 mg, 20 mol%), 4Å MS (200 mg), and CCl_4 (1 mL) were added into a 15 mL pressure tube with magnetic stirring. The solution was stirred at 100 ℃ for about 4 h. After the reaction was completed (monitored by TLC), the mixture was concentrated by rotary evaporator, and the residue was purified by silica gel chromatography (hexanes/ethyl acetate 50:1, v/v as eluant) to give a crude product containing **2t** and **3t** (with the same polarity and not isolatable by chromatography). The yields of **2t** and **3t** were measured by ^{1}H NMR as 25% and 32%, respectively.



	RT	Area	Height	% Area
1	8.270	393610	27910	56.37
2	8.786	304613	28569	43.63

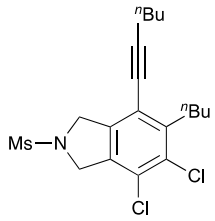
V. References cited in the SI

1. X. Chen, J. T. Merrett and P. W. H. Chan, *Org. Lett.*, 2018, ***20***, 1542-1545.
2. M. Wilking, C. Mueck-Lichtenfeld, C. G. Daniliuc and U. Hennecke, *J. Am. Chem. Soc.*, 2013, ***135***, 8133-8136.
3. H. Shen, X. Xiao, M. K. Haj, P. H. Willoughby and T. R. Hoye, *J. Am. Chem. Soc.*, 2018, ***140***, 15616-15620.

4. J. Back, J. Park, Y. Kim, H. Kang, Y. Kim, M. J. Park, K. Kim and E. Lee, *J. Am. Chem. Soc.*, 2017, ***139***, 15300-15303.

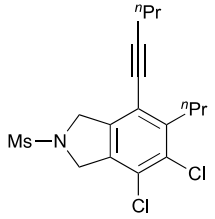
VI. Characterization of Products

5-butyl-6,7-dichloro-4-(hex-1-yn-1-yl)-2-(methylsulfonyl)isoindoline (2a)



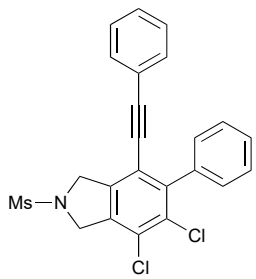
white solid; 50% yield, 40 mg; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 4.90 – 4.56 (m, 4H), 2.99 – 2.92 (m, 2H), 2.91 (s, 3H), 2.46 (t, *J* = 6.9 Hz, 2H), 1.64 – 1.57 (m, 2H), 1.56 – 1.38 (m, 6H), 0.96 (t, *J* = 7.2 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$, ppm) δ 144.6, 138.2, 133.5, 131.9, 126.9, 11.7, 100.5, 75.4, 55.1, 54.7, 35.4, 33.1, 31.1, 30.8, 23.0, 22.1, 19.4, 14.0, 13.7; **HRMS** (ESI): calcd for $C_{19}H_{25}Cl_2NO_2SNa^+$ $[M+Na]^+$ requires 424.0875, found 424.0882; **IR** (neat, cm^{-1}): 2957, 2927, 2858, 1328, 1148, 1091, 964.

4,5-dichloro-2-(methylsulfonyl)-7-(pent-1-yn-1-yl)-6-propylisoindoline (2b)



white solid; 38% yield, 28 mg; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 4.74 (s, 2H), 4.72 (s, 2H), 2.96 – 2.91 (m, 2H), 2.91 (s, 3H), 2.44 (t, *J* = 7.0 Hz, 2H), 1.89 – 1.51 (m, 4H), 1.06 (t, *J* = 7.4 Hz, 3H), 1.00 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$, ppm) δ 144.4, 138.2, 133.7, 132.0, 127.0, 118.8, 100.4, 75.6, 55.1, 54.7, 35.5, 35.3, 22.4, 22.3, 21.7, 14.3, 13.7; **HRMS** (ESI): calcd for $C_{17}H_{21}Cl_2NO_2SNa^+$ $[M+Na]^+$ requires 396.0562, found 396.0565; **IR** (neat, cm^{-1}): 2961, 2921, 1461, 1422, 1321, 1148.

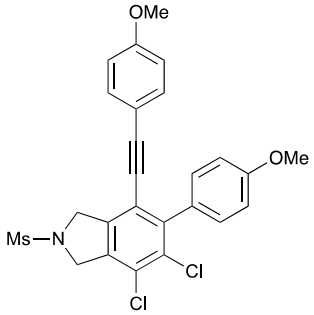
4,5-dichloro-2-(methylsulfonyl)-6-phenyl-7-(phenylethynyl)isoindoline (2c)



white solid; 45% yield, 40 mg; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 7.53 – 7.44 (m, 3H), 7.38 – 7.33 (m, 2H), 7.33 – 7.27 (m, 2H), 7.23 (d, *J* = 1.9 Hz, 1H), 7.12 (dt, *J* = 6.7, 1.6 Hz, 2H), 4.92 (s, 2H), 4.84 (s, 2H), 2.97 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$, ppm) δ 144.6, 137.9, 137.7, 135.6, 131.9, 131.7, 129.8, 129.2, 128.5, 128.5, 128.3, 127.9, 122.1, 118.5, 99.0, 84.4, 55.0, 54.8, 35.8; **HRMS** (ESI): calcd for $C_{23}H_{18}Cl_2NO_2S^+$ $[M+H]^+$ requires 442.0430, found 442.0418; **IR** (neat, cm^{-1}): 2928, 1344, 1166, 1155, 1094, 776, 754, 706, 689.

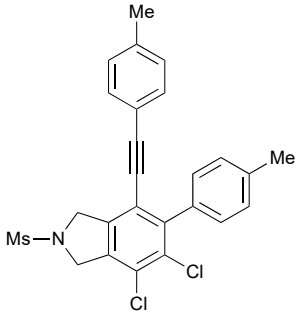
4,5-dichloro-6-(4-methoxyphenyl)-7-((4-methoxyphenyl)ethynyl)-2-

(methylsulfonyl)isoindoline (2d)



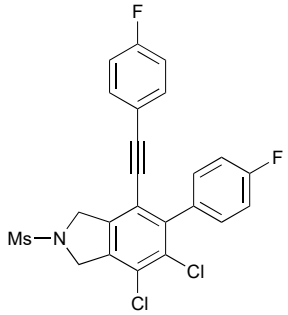
white solid; 58% yield, 58 mg; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 7.30 (d, *J* = 8.9 Hz, 2H), 7.11 (d, *J* = 8.9 Hz, 2H), 7.02 (d, *J* = 8.8 Hz, 2H), 6.79 (d, *J* = 8.9 Hz, 2H), 4.89 (s, 2H), 4.82 (s, 2H), 3.89 (s, 3H), 3.80 (s, 3H), 2.96 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$, ppm) δ 160.4, 159.7, 143.8, 137.6, 135.2, 133.2, 132.1, 131.2, 130.0, 127.4, 119.1, 114.2, 114.2, 113.6, 99.1, 83.6, 55.5, 55.1, 54.8, 35.7; **HRMS** (ESI): calcd for $C_{25}H_{22}Cl_2NO_4S^+$ $[M+H]^+$ requires 502.0641, found 502.0629; **IR** (neat, cm^{-1}): 2920, 2851, 1634, 1511, 1471, 1334, 1248, 1161, 1033, 833, 760.

4,5-dichloro-2-(methylsulfonyl)-6-(*p*-tolyl)-7-(*p*-tolylethynyl)isoindoline (2e)



white solid; 52% yield, 49 mg; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 7.32 – 7.23 (m, 4H), 7.12 – 7.00 (m, 4H), 4.90 (s, 2H), 4.83 (s, 2H), 2.97 (s, 3H), 2.45 (s, 3H), 2.33 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$, ppm) δ 144.6, 139.5, 138.3, 137.9, 135.5, 134.9, 132.1, 131.6, 129.8, 129.3, 128.9, 127.7, 119.3, 118.9, 99.3, 84.1, 55.1, 54.8, 35.9, 21.6, 21.5; **HRMS** (ESI): calcd for $C_{25}H_{22}Cl_2NO_2S^+$ $[M+H]^+$ requires 470.0743, found 470.0732; **IR** (neat, cm^{-1}): 2953, 2961, 2848, 1509, 1461, 1337, 1162, 1095, 964, 812.

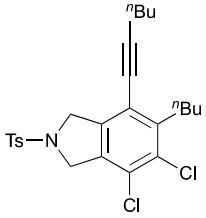
4,5-dichloro-6-(4-fluorophenyl)-7-((4-fluorophenyl)ethynyl)-2-(methylsulfonyl)isoindoline (2f)



white solid; 39% yield, 37 mg; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 7.36 – 7.31 (m, 2H), 7.20 – 7.11 (m, 4H), 6.98 (t, *J* = 8.7 Hz, 2H), 4.90 (s, 2H), 4.84 (s, 2H), 2.98 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$, ppm) δ 163.1 (d, *J* = 251.5 Hz), δ 162.8 (d, *J* = 248.0 Hz), 143.4, 138.0, 135.9, 133.6 (d, *J* = 8.5 Hz), 132.1, 131.7 (d, *J* = 8.3 Hz), 129.3, 128.1, 118.4, 118.0 (d, *J* = 3.6 Hz), 116.0 (d, *J* = 22.4 Hz), 115.4 (d, *J* = 21.6 Hz), 98.1, 84.0, 55.0, 54.7, 35.9; **^{19}F NMR** (377 MHz, $CDCl_3$) δ -108.87, -112.88; **HRMS** (APCI): calcd for

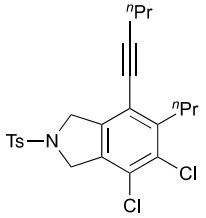
$C_{23}H_{16}Cl_2F_2NO_2S^+$ $[M+H]^+$ requires 478.0241, found 478.0236; **IR** (neat, cm^{-1}): 2952, 2920, 2848, 1600, 1507, 1345, 1155, 968, 843.

5-butyl-6,7-dichloro-4-(hex-1-yn-1-yl)-2-tosylisoindoline (2g)



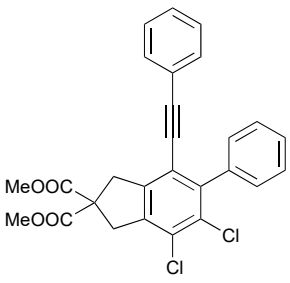
white solid; 48% yield, 46 mg; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 7.78 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 4.65 (s, 2H), 4.60 (s, 2H), 3.04 – 2.79 (m, 2H), 2.46 (t, *J* = 6.9 Hz, 2H), 2.41 (s, 3H), 1.66 – 1.55 (m, 2H), 1.55 – 1.44 (m, 4H), 1.43 – 1.32 (m, 2H), 0.95 (dt, *J* = 14.5, 7.2 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$, ppm) δ 144.3, 144.1, 138.2, 133.7, 133.6, 131.6, 130.1, 127.7, 126.7, 118.5, 100.2, 75.5, 55.1, 54.6, 33.0, 31.1, 30.8, 22.9, 22.1, 21.7, 19.4, 14.0, 13.7; **HRMS** (ESI): calcd for $C_{25}H_{29}Cl_2NO_2SNa^+$ $[M+Na]^+$ requires 500.1188, found 500.1195; **IR** (neat, cm^{-1}): 2953, 2868, 1346, 1159, 1098, 1072, 808, 669.

4,5-dichloro-7-(pent-1-yn-1-yl)-6-propyl-2-tosylisoindoline (2h)



white solid; 54% yield, 48 mg; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 7.78 (d, *J* = 8.3 Hz, 2H, ppm), 7.34 (d, *J* = 8.3 Hz, 2H), 4.66 (s, 2H), 4.60 (s, 2H), 2.93 – 2.83 (m, 2H), 2.44 (t, *J* = 6.9 Hz, 2H), 2.41 (s, 3H), 1.65 (dt, *J* = 14.4, 7.2 Hz, 2H), 1.60 – 1.49 (m, 2H), 1.06 (t, *J* = 7.4 Hz, 3H), 0.96 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$, ppm) δ 144.0, 138.2, 133.8, 133.6, 131.7 130.1, 128.2, 127.7, 126.8, 118.6, 100.1, 75.6, 55.1, 54.5, 35.2, 22.3, 22.2, 21.3, 21.7, 14.3, 13.7; **HRMS** (ESI): calcd for $C_{23}H_{25}Cl_2NO_2SNa^+$ $[M+Na]^+$ requires 472.0375, found 472.0377; **IR** (neat, cm^{-1}): 2960, 2924, 2870, 1463, 1423, 1347, 1156, 1099, 672.

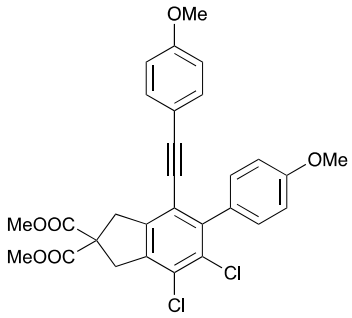
dimethyl 4,5-dichloro-6-phenyl-7-(phenylethynyl)-1,3-dihydro-2*H*-indene-2,2-dicarboxylate (2i)



white solid; 70% yield, 67 mg; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 7.50 – 7.43 (m, 3H), 7.38 – 7.33 (m, 2H), 7.25 (m, 3H), 7.15 – 7.11 (m, 2H), 3.86 (s, 2H), 3.82 (s, 6H), 3.79 (s, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$, ppm) δ 171.6, 143.5, 141.7, 139.1, 138.4, 131.6, 130.7, 129.9, 129.3, 128.7, 128.4, 128.1, 128.1, 122.7, 119.5, 97.9, 85.8, 58.9, 53.4, 41.6, 41.5; **HRMS** (ESI): calcd for

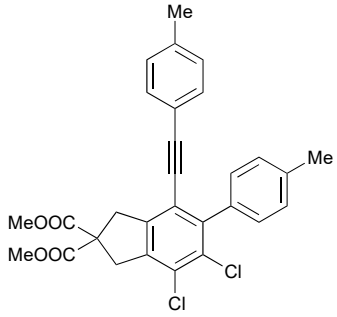
$C_{27}H_{21}Cl_2O_4^+$ $[M+H]^+$ requires 479.0811, found 479.0801; **IR** (neat, cm^{-1}): 2920, 2850, 1737, 1269, 1241.

dimethyl 4,5-dichloro-6-(4-methoxyphenyl)-7-((4-methoxyphenyl)ethynyl)-1,3-dihydro-2*H*-indene-2,2-dicarboxylate (2j)



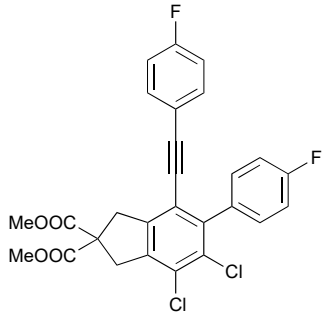
white solid; 65% yield, 70 mg; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 7.30 (d, *J* = 8.8 Hz, 2H), 7.13 (d, *J* = 8.8 Hz, 2H), 7.00 (d, *J* = 8.8 Hz, 2H), 6.78 (d, *J* = 8.8 Hz, 2H), 3.88 (s, 3H), 3.82 (s, 2H), 3.81 (s, 6H), 3.79 (s, 3H), 3.76 (s, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$, ppm) δ 171.7, 160.0, 159.3, 142.8, 141.5, 138.8, 133.1, 131.3, 130.9, 130.8, 128.8, 120.0, 114.9, 114.1, 113.4, 97.9, 84.9, 58.9, 55.4, 53.4, 41.7, 41.4; **HRMS** (ESI): calcd for $C_{29}H_{25}Cl_2O_6^+$ $[M+H]^+$ requires 539.1023, found 539.1011; **IR** (neat, cm^{-1}): 2920, 2850, 2212, 1737, 1606, 1510, 1287, 1248, 1175, 1032, 832.

dimethyl 4,5-dichloro-6-(*p*-tolyl)-7-(*p*-tolylethynyl)-1,3-dihydro-2*H*-indene-2,2-dicarboxylate (2k)



white solid; 72% yield, 73 mg; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 7.30 – 7.23 (m, 4H), 7.06 (s, 4H), 3.84 (s, 2H), 3.81 (s, 26H), 3.77 (s, 2H), 2.44 (s, 3H), 2.32 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$, ppm) δ 171.7, 143.4, 141.6, 138.9, 138.9, 137.7, 135.5, 131.5, 130.7, 129.8, 129.1, 129.0, 128.7, 119.8, 119.8, 98.0, 85.4, 58.9, 53.4, 41.7, 41.5, 21.6, 21.5; **HRMS** (ESI): calcd for $C_{29}H_{25}Cl_2O_4^+$ $[M+H]^+$ requires 507.1124, found 507.1115; **IR** (neat, cm^{-1}): 2953, 2211, 1737, 1510, 1434, 1268, 1239, 817.

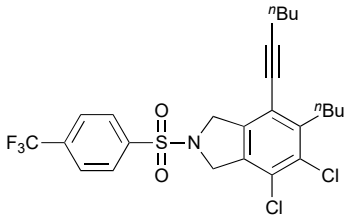
Dimethyl 4,5-dichloro-6-(4-fluorophenyl)-7-((4-fluorophenyl)ethynyl)-1,3-dihydro-2*H*-indene-2,2-dicarboxylate （2l）



white solid; 56% yield, 58 mg; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 7.36 – 7.30 (m, 2H), 7.21 – 7.10 (m, 4H), 7.00 – 6.93 (m, 2H), 3.82 (d, *J* = 1.5 Hz, 8H), 3.77 (s, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$, ppm) δ 171.6, 162.9 (d, *J* = 250.5 Hz), 162.6 (d, *J* = 247.1 Hz), 142.3, 141.8, 139.4, 134.3 (d,

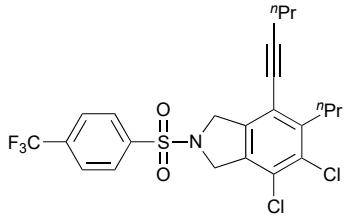
J = 3.4 Hz), 133.5 (d, *J* = 8.3 Hz), 131.8 (d, *J* = 8.2 Hz), 130.8, 129.5, 119.4, 118.7 (d, *J* = 3.5 Hz), 115.9 (d, *J* = 22.2 Hz), 115.1 (d, *J* = 21.5 Hz), 96.9, 85.3, 58.9, 53.5, 41.6, 41.4; **^{19}F NMR** (377 MHz, $CDCl_3$, ppm) δ -109.79, -113.66; **HRMS** (APCI): calcd for $C_{27}H_{19}Cl_2F_2O_4^+$ $[M+H]^+$ requires 515.0623, found 515.0621; **IR** (neat, cm^{-1}): 2920, 2850, 1737, 1508, 1238, 837.

5-butyl-6,7-dichloro-4-(hex-1-yn-1-yl)-2-((4-(trifluoromethyl)phenyl)sulfonyl)isoindoline (2m)



white solid; 54% yield, 57 mg; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 8.03 (d, *J* = 8.1 Hz, 2H), 7.82 (d, *J* = 8.1 Hz, 2H), 4.69 (s, 2H), 4.65 (s, 2H), 2.99 – 2.62 (m, 2H), 2.47 (t, *J* = 6.9 Hz, 2H), 1.66 – 1.58 (m, 2H), 1.54 – 1.44 (m, 4H), 1.39 (h, *J* = 7.5 Hz, 2H), 0.95 (dt, *J* = 14.6, 7.2 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$, ppm) δ 144.6, 140.6, 137.6, 134.9 (q, *J* = 32.9 Hz), 133.1, 131.9, 128.0, 126.8, 126.7 (q, *J* = 3.7 Hz), 123.3 (q, *J* = 272.9 Hz), 118.6, 100.5, 75.4, 55.1, 54.6, 33.1, 31.1, 30.8, 23.0, 22.1, 19.4, 14.0, 13.7; **^{19}F NMR** (377 MHz, $CDCl_3$, ppm) δ -63.15; **HRMS** (ESI): calcd for $C_{25}H_{27}Cl_2F_3NO_2S^+$ $[M+H]^+$ requires 532.1086, found 532.1079; **IR** (neat, cm^{-1}): 2957, 2930, 2861, 1348, 1325, 1161, 1128, 1108, 1063, 714, 638.

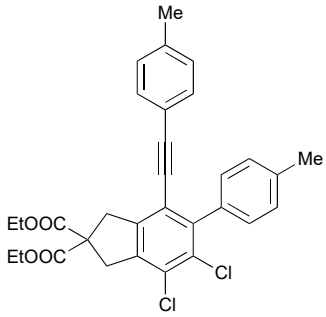
4,5-dichloro-7-(pent-1-yn-1-yl)-6-propyl-2-((4-(trifluoromethyl)phenyl)sulfonyl)isoindoline (2n)



white solid; 53% yield, 53 mg; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 8.03 (d, *J* = 8.1 Hz, 2H), 7.82 (d, *J* = 8.2 Hz, 2H), 4.69 (s, 2H), 4.65 (s, 2H), 2.92 – 2.84 (m, 2H), 2.45 (t, *J* = 7.0 Hz, 2H), 1.66 (p, *J* = 7.2 Hz, 2H), 1.61 – 1.49 (m, 2H), 1.06 (t, *J* = 7.4 Hz, 3H), 0.97 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$, ppm) δ 144.3, 140.5, 137.6, 134.8 (q, *J* = 33.1 Hz), 133.2, 131.9, 128.0, 126.8, 126.7 (q, *J* = 3.7 Hz), 123.3 (q, *J* = 273.2 Hz), 118.7, 100.3, 75.5, 55.1, 54.6, 35.2, 22.3, 22.2, 21.7, 14.3, 13.7; **^{19}F NMR** (377 MHz, $CDCl_3$, ppm) δ -63.15; **HRMS** (ESI): calcd for $C_{23}H_{23}Cl_2F_3NO_2S^+$ $[M+H]^+$ requires 504.0773, found 504.0759; **IR** (neat, cm^{-1}): 2961, 2938, 2871, 1349, 1325, 1163, 1128, 1108, 1063, 715, 638.

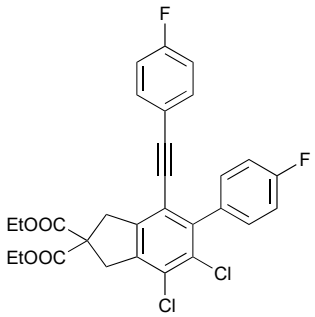
diethyl 4,5-dichloro-6-(*p*-tolyl)-7-(*p*-tolylethynyl)-1,3-dihydro-2*H*-indene-2,2-

dicarboxylate (2o)



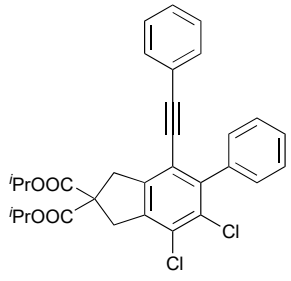
white solid; 46% yield, 49 mg; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 7.26 (d, *J* = 3.0 Hz, 4H), 7.06 (m, 4H), 4.27 (q, *J* = 7.1 Hz, 4H), 3.82 (s, 2H), 3.76 (s, 2H), 2.44 (s, 3H), 2.32 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$, ppm) δ 171.3, 143.3, 141.8, 139.0, 138.9, 137.7, 135.5, 131.5, 130.6, 129.8, 129.1, 129.0, 128.7, 119.8, 119.7, 97.9, 85.5, 62.3, 59.0, 41.5, 41.4, 21.6, 21.5, 14.2; **HRMS** (ESI): calcd for $C_{31}H_{29}Cl_2O_4^+$ $[M+H]^+$ requires 535.1437, found 535.1423; **IR** (neat, cm^{-1}): 2979, 2920, 2851, 2210, 1733, 1510, 1262, 1237, 1182, 1156, 815.

diethyl 4,5-dichloro-6-(4-fluorophenyl)-7-((4-fluorophenyl)ethynyl)-1,3-dihydro-2*H*-indene-2,2-dicarboxylate (2p)



white solid; 53% yield, 57 mg; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 7.36 – 7.29 (m, 2H), 7.21 – 7.10 (m, 4H), 7.02 – 6.92 (m, 2H), 4.27 (qd, *J* = 7.1, 1.0 Hz, 4H), 3.81 (s, 2H), 3.76 (s, 2H), 1.30 (t, *J* = 7.1 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$, ppm) δ 171.2, 162.8 (d, *J* = 250.6 Hz), 162.6 (d, *J* = 247.3 Hz), 142.3, 142.0, 139.6, 134.3 (d, *J* = 3.3 Hz), 133.5 (d, *J* = 8.4 Hz), 131.8 (d, *J* = 8.1 Hz), 130.7, 129.4, 119.4, 118.7 (d, *J* = 3.6 Hz), 115.8 (d, *J* = 22.2 Hz), 115.1 (d, *J* = 21.6 Hz), 96.8, 85.4, 62.3, 59.0, 41.5, 41.4, 14.2; **^{19}F NMR** (377 MHz, $CDCl_3$, ppm) δ -109.85, -113.70; **HRMS** (ESI): calcd for $C_{29}H_{23}Cl_2F_2O_4^+$ $[M+H]^+$ requires 543.0936, found 543.0920; **IR** (neat, cm^{-1}): 2921, 2850, 1733, 1508, 1264, 1237, 1157, 837.

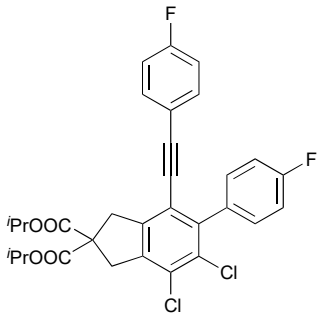
diisopropyl 4,5-dichloro-6-phenyl-7-(phenylethynyl)-1,3-dihydro-2*H*-indene-2,2-dicarboxylate (2q)



white solid; 61% yield, 70 mg; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 7.51 – 7.42 (m, 3H), 7.39 – 7.34 (m, 2H), 7.28 – 7.21 (m, 3H), 7.17 – 7.10 (m, 2H), 5.11 (hept, *J* = 6.3 Hz, 2H), 3.80 (s, 2H), 3.73 (s, 2H), 1.29 (dd, *J* = 6.3, 1.4 Hz, 12H); **^{13}C NMR** (101 MHz, $CDCl_3$, ppm) δ 170.8, 143.4, 142.0, 139.4, 138.5,

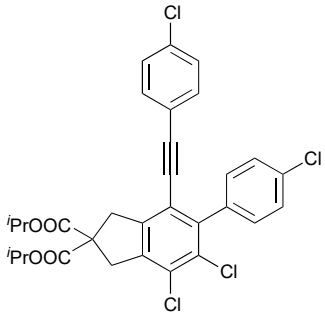
131.6, 130.5, 129.9, 129.4, 129.2, 128.6, 128.4, 128.0, 122.8, 119.45, 97.7, 85.9, 69.8, 59.0, 41.4, 41.3, 21.7; **HRMS** (ESI): calcd for $C_{31}H_{29}Cl_2O_4^+$ $[M+H]^+$ requires 535.1437, found 535.1426; **IR** (neat, cm^{-1}): 2981, 2921, 1730, 1269, 1242, 1193, 1104.

diisopropyl 4,5-dichloro-6-(4-fluorophenyl)-7-((4-fluorophenyl)ethynyl)-1,3-dihydro-2*H*-indene-2,2-dicarboxylate (2r)



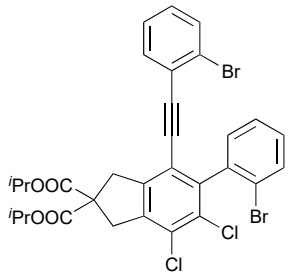
white solid; 77% yield, 88 mg; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 7.42 – 7.27 (m, 2H), 7.23 – 7.06 (m, 4H), 7.01 – 6.92 (m, 2H), 5.10 (p, *J* = 6.3 Hz, 2H), 3.77 (s, 2H), 3.72 (s, 2H), 1.29 (dd, *J* = 6.3, 1.4 Hz, 12H); **^{13}C NMR** (101 MHz, $CDCl_3$, ppm) δ 170.7, 162.8 (d, *J* = 250.5 Hz), 162.6 (d, *J* = 247.2 Hz), 142.3, 142.1, 139.7, 134.4 (d, *J* = 3.3 Hz), 133.5 (d, *J* = 8.4 Hz), 131.8 (d, *J* = 8.2 Hz), 130.7, 129.5, 119.4, 118.8 (d, *J* = 3.6 Hz), 115.8 (d, *J* = 22.2 Hz), 115.1 (d, *J* = 21.6 Hz), 96.8, 85.4, 69.9, 59.0, 41.4, 41.4, 21.7; ^{19}F NMR (377 MHz, $CDCl_3$) δ -109.93, -113.77; **HRMS** (ESI): calcd for $C_{31}H_{27}Cl_2F_2O_4^+$ $[M+H]^+$ requires 571.1249, found 571.1232; **IR** (neat, cm^{-1}): 2983, 1727, 1599, 1506, 1286, 1229, 1217, 1197, 834, 808, 527.

diisopropyl 4,5-dichloro-6-(4-chlorophenyl)-7-((4-chlorophenyl)ethynyl)-1,3-dihydro-2*H*-indene-2,2-dicarboxylate (2s)



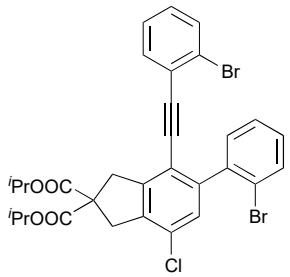
white solid; 60% yield, 72 mg; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 7.44 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 7.25 (d, *J* = 8.7 Hz, 2H), 7.07 (d, *J* = 8.4 Hz, 2H), 5.10 (hept, *J* = 6.3 Hz, 2H), 3.77 (s, 2H), 3.72 (s, 2H), 1.29 (dd, *J* = 6.3, 1.4 Hz, 12H); **^{13}C NMR** (101 MHz, $CDCl_3$, ppm) δ 170.7, 142.3, 142.1, 139.9, 136.8, 134.9, 134.2, 132.7, 131.4, 130.5, 129.7, 128.9, 128.4, 121.1, 119.0, 96.8, 86.5, 69.9, 59.0, 41.4, 41.3, 21.7; **HRMS** (ESI): calcd for $C_{31}H_{27}Cl_4O_4^+$ $[M+H]^+$ requires 603.0658, found 603.0643; **IR** (neat, cm^{-1}): 2982, 2922, 1729, 1491, 1270, 1242, 1103, 829.

diisopropyl 5-(2-bromophenyl)-4-((2-bromophenyl)ethynyl)-6,7-dichloro-1,3-dihydro-2H-indene-2,2-dicarboxylate (2t)



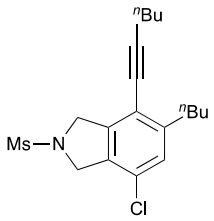
white solid; 25% yield, 17 mg; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 7.71-7.66 (m, 2H), 7.51-7.48 (m, 2H), 7.38 – 7.34 (m, 2H), 7.21 – 7.15 (m, 2H), 5.16 – 5.04 (m, *J* = 6.3 Hz, 2H), 3.88 (s, 2H), 3.75 (s, 2H), 1.28 (dd, *J* = 6.4, 3.6 Hz, 12H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.9, 170.5, 142.7, 142.4, 140.2, 139.6, 133.6, 132.8, 132.4, 131.3, 130.9, 129.8, 129.8, 129.6, 127.5, 125.2, 125.0, 123.9, 119.1, 95.9, 89.4, 69.8, 59.1, 59.0, 41.6, 41.4, 21.7; **HRMS** (ESI): calcd for $C_{31}H_{26}Br_2Cl_2O_4Na^+$ $[M+Na]^+$ requires 712.9467, found 712.9448; UPCC analysis: 13% ee (Trefoil CEL2, CO_2/CH_3OH = 70/30, 0.5 mL/min, detector: 254 nm), Rt (minor) = 8.7 min, Rt (major) = 8.2 min.

diisopropyl 5-(2-bromophenyl)-4-((2-bromophenyl)ethynyl)-7-chloro-1,3-dihydro-2H-indene-2,2-dicarboxylate (3t)



colorless oil; 94% yield, 62 mg; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.0 Hz, 1H), 7.50 (d, *J* = 7.9 Hz, 1H), 7.37 – 7.33 (m, 2H), 7.24 – 7.20 (m, 2H), 7.19 – 7.14 (m, 2H), 7.13 – 7.07 (m, 1H), 5.17 – 5.05 (m, 2H), 3.90 (s, 2H), 3.71 (s, 2H), 1.28 (dd, *J* = 6.2, 3.4 Hz, 12H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.1, 168.1, 145.2, 143.9, 140.5, 138.3, 133.5, 132.8, 132.5, 131.7, 130.2, 129.6, 129.5, 128.8, 127.2, 127.0, 125.4, 125.2, 123.6, 117.7, 95.1, 90.2, 69.7, 59.1, 41.9, 40.4, 21.7; **HRMS** (ESI): calcd for $C_{31}H_{27}Br_2ClO_4Na^+$ $[M+Na]^+$ requires 678.9857, found 678.9844; **IR** (neat, cm^{-1}): 2983, 2920, 2850, 1732, 1471, 1280, 1251, 1191, 1104.

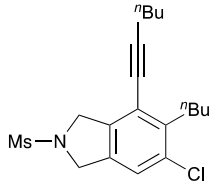
5-butyl-7-chloro-4-(hex-1-yn-1-yl)-2-(methylsulfonyl)isoindoline (3a)



white solid; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 7.10 (s, 1H), 4.75 (s, 2H), 4.70 (s, 2H), 2.90 (s, 3H), 2.75 – 2.68 (m, 2H), 2.45 (t, *J* = 7.0 Hz, 2H), 1.65 – 1.56 (m, 4H), 1.52 – 1.44 (m, 2H), 1.41 – 1.32 (m, 2H), 0.98 – 0.87 (m, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$, ppm) δ 146.8, 140.6, 131.9, 128.4, 127.6, 117.4, 100.0, 75.4, 55.2, 54.1, 35.2,

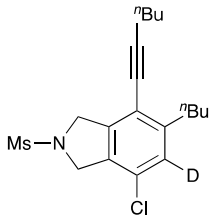
33.9, 32.8, 30.9, 22.6, 22.1, 19.4, 14.0, 13.7; **HRMS** (ESI): calcd for $C_{19}H_{27}ClNO_2S^+$ $[M+H]^+$ requires 368.1446, found 368.1451; **IR** (neat, cm^{-1}): 2956, 2930, 2872, 1462, 1323, 1147, 1092, 965, 759.

5-butyl-6-chloro-4-(hex-1-yn-1-yl)-2-(methylsulfonyl)isoindoline (3a')



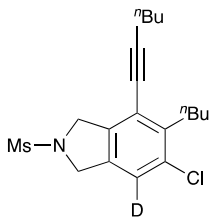
white solid; **^{1}H NMR** (400 MHz, $CDCl_3$ ppm) δ 7.15 (s, 1H), 4.66 (s, 4H), 2.93 – 2.88 (m, 2H), 2.88 (s, 3H), 2.47 (t, *J* = 6.9 Hz, 2H), 1.63 – 1.58 (m, 2H), 1.55 – 1.38 (m, 6H), 0.96 (t, *J* = 7.3 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$ ppm) δ 142.2, 137.8, 134.4, 134.0, 122.8, 120.6, 99.9, 75.9, 54.2, 54.1, 35.1, 31.9, 31.4, 30.9, 23.0, 22.1, 19.4, 14.1, 13.7; **HRMS** (ESI): calcd for $C_{19}H_{27}ClNO_2S^+$ $[M+H]^+$ requires 368.1446, found 368.1451; **IR** (neat, cm^{-1}): 2957, 2928, 2858, 1455, 1316, 1149, 966, 761.

5-butyl-7-chloro-4-(hex-1-yn-1-yl)-2-(methylsulfonyl)isoindoline-6-*d* (4a)



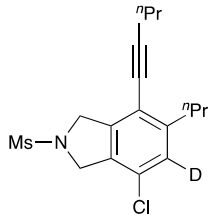
white solid; 51% yield, 38 mg, D% = 98%; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 4.74 (s, 2H), 4.69 (s, 2H), 2.89 (s, 3H), 2.80 – 2.62 (m, 2H), 2.45 (t, *J* = 6.9 Hz, 2H), 1.65 – 1.53 (m, 4H), 1.48 (ddd, *J* = 10.2, 7.7, 6.0 Hz, 2H), 1.42 – 1.31 (m, 2H), 0.94 (q, *J* = 7.2 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$, ppm) δ 146.7, 140.5, 131.9, 128.1 (t, *J* = 24.3 Hz), 127.5, 117.4, 99.9, 75.4, 55.2, 54.0, 35.2, 33.8, 32.8, 30.9, 22.6, 22.1, 19.4, 14.0, 13.7; **HRMS** (ESI): calcd for $C_{19}H_{26}DClNO_2S^+$ $[M+H]^+$ requires 369.1508, found 369.1498; **IR** (neat, cm^{-1}): 2956, 2929, 2858, 1739, 1435, 1329, 1147, 1092, 965, 824, 759, 524, 514.

5-butyl-6-chloro-4-(hex-1-yn-1-yl)-2-(methylsulfonyl)isoindoline-7-*d* (4a')



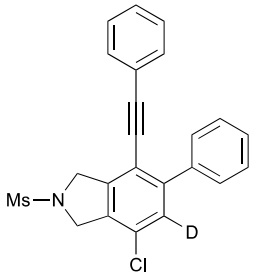
white solid; 25% yield, 18 mg, D% = 98%; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 4.66 (s, 4H), 2.91 (dd, *J* = 6.4, 3.9 Hz, 2H), 2.88 (s, 3H), 2.47 (t, *J* = 6.9 Hz, 2H), 1.66 – 1.34 (m, 4H), 1.68 – 1.36 (m, 4), 1.11 – 0.65 (m, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$, ppm) δ 142.1, 137.8, 134.3, 133.9, 122.5 (t, *J* = 25.0 Hz), 120.6, 99.9, 75.9, 54.2, 54.1, 35.1, 31.9, 31.4, 30.8, 23.0, 22.1, 19.4, 14.0, 13.7; **HRMS** (ESI): calcd for $C_{19}H_{26}DClNO_2S^+$ $[M+H]^+$ requires 369.1508, found 369.1498; **IR** (neat, cm^{-1}): 2957, 2929, 2858, 1455, 1421, 1355, 1316, 1149, 1094, 966, 760, 532, 513.

7-chloro-2-(methylsulfonyl)-4-(pent-1-yn-1-yl)-5-propylisoindoline-6-*d* (4b)



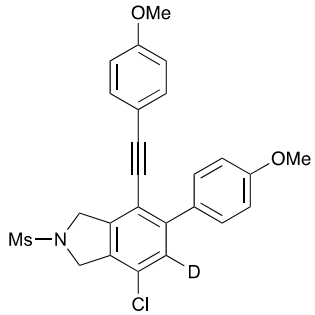
white solid; 48% yield, 33 mg, D% > 99%; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 4.76 (s, 2H), 4.70 (s, 2H), 2.90 (s, 3H), 2.82 – 2.64 (m, 2H), 2.43 (t, *J* = 7.0 Hz, 2H), 1.67 – 1.61 (m, 4H), 1.05 (t, *J* = 7.4 Hz, 3H), 0.95 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$, ppm) δ 146.5, 140.6, 131.9, 127.5, 122.8, 117.5, 99.8, 75.6, 55.2, 54.1, 36.1, 35.2, 23.8, 22.3, 21.7, 14.0, 13.7; **HRMS** (ESI): calcd for $C_{17}H_{22}DClNO_2S^+$ $[M+H]^+$ requires 341.1195, found 341.1189; **IR** (neat, cm^{-1}): 2959, 2924, 1436, 1324, 1147, 1093, 966, 825.

7-chloro-2-(methylsulfonyl)-5-phenyl-4-(phenylethynyl)isoindoline-6-d (4c)



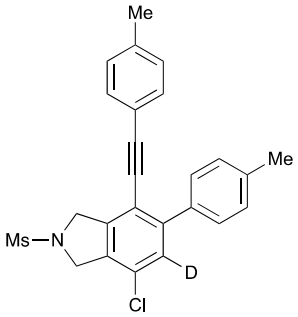
white solid; 43% yield, 35 mg, D% > 99%; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 7.67 – 7.56 (m, 2H), 7.53 – 7.40 (m, 3H), 7.32 (s, 5H), 4.96 (s, 2H), 4.83 (s, 2H), 2.97 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$, ppm) δ 145.4, 141.2, 138.6, 133.7, 131.6, 129.3, 129.0, 128.7, 128.6, 128.4, 128.4, 122.5, 115.7, 97.9, 85.0, 55.3, 54.2, 35.5. **HRMS** (ESI): calcd for $C_{23}H_{18}DClNO_2S^+$ $[M+H]^+$ requires 409.0882, found 409.0872; **IR** (neat, cm^{-1}): 2920, 2850, 1658, 1632, 1470, 1324, 1145.

7-chloro-5-(4-methoxyphenyl)-4-((4-methoxyphenyl)ethynyl)-2-(methylsulfonyl)isoindoline-6-*d* (4d)



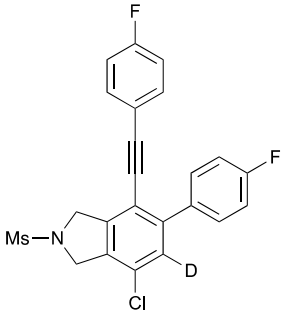
white solid; 56% yield, 52 mg, D% > 99%; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 7.58 (d, *J* = 8.8 Hz, 2H), 7.30 (d, *J* = 8.9 Hz, 2H), 7.00 (d, *J* = 8.8 Hz, 2H), 6.84 (d, *J* = 8.9 Hz, 2H), 4.93 (s, 2H), 4.81 (s, 2H), 3.88 (s, 3H), 3.82 (s, 3H), 2.96 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$, ppm) δ 160.2, 159.8, 144.7, 140.9, 133.2, 133.1, 131.1, 130.5, 128.3, 115.8, 114.7, 114.2, 113.7, 113.4, 98.0, 84.1, 55.5, 55.5, 55.3, 54.2, 35.4; **HRMS** (ESI): calcd for $C_{25}H_{22}DClNO_4S^+$ $[M+H]^+$ requires 469.1094, found 469.1083; **IR** (neat, cm^{-1}): 2923, 2853, 1606, 1511, 1459, 1248, 1158.

7-chloro-2-(methylsulfonyl)-5-(*p*-tolyl)-4-(*p*-tolylethynyl)isoindoline-6-*d* (4e)



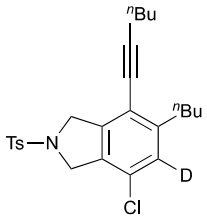
white solid; 42% yield, 37 mg, D% > 99%; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 7.54 (d, *J* = 8.2 Hz, 2H), 7.26 (t, *J* = 8.4 Hz, 4H), 7.12 (d, *J* = 7.7 Hz, 2H), 4.93 (s, 2H), 4.81 (s, 2H), 2.96 (s, 3H), 2.43 (s, 3H), 2.35 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$, ppm) δ 145.2, 141.1, 139.3, 138.3, 135.7, 133.3, 131.5, 129.3, 129.1, 129.0, 128.5, 119.6, 115.7, 98.1, 84.6, 55.3, 54.2, 35.5, 21.7, 21.4; **HRMS** (ESI): calcd for $C_{25}H_{22}DClNO_2S^+$ $[M+H]^+$ requires 437.1195, found 437.1183; **IR** (neat, cm^{-1}): 2920, 2850, 1646, 1470, 1421, 1347, 1160.

7-chloro-5-(4-fluorophenyl)-4-((4-fluorophenyl)ethynyl)-2-(methylsulfonyl)isoindoline-6-*d* (4f)



white solid; 55% yield, 49 mg, D% > 99%; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 7.58 (ddt, *J* = 7.2, 5.4, 2.0 Hz, 2H), 7.31 (dt, *J* = 5.3, 3.7 Hz, 2H), 7.16 (td, *J* = 8.6, 2.0 Hz, 2H), 7.02 (td, *J* = 8.6, 2.1 Hz, 2H), 4.93 (s, 2H), 4.82 (s, 2H), 2.97 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$, ppm) δ 163.1 (d, *J* = 251.2 Hz), 162.9 (d, *J* = 248.5 Hz), 144.3, 141.2, 134.6 (d, *J* = 3.4 Hz), 133.9, 133.6 (d, *J* = 8.2 Hz), 131.0 (d, *J* = 8.2 Hz), 128.9, 118.5 (d, *J* = 3.4 Hz), 116.0 (d, *J* = 22.3 Hz), 115.5, 115.4 (d, *J* = 21.5 Hz), 97.0, 84.5, 55.2, 54.1, 35.7; **^{19}F NMR** (377 MHz, $CDCl_3$, ppm) δ -109.26, -113.29. **HRMS** (APCI): calcd for $C_{23}H_{15}DF_2NO_2S^+$ $[M-Cl]^+$ requires 409.0933, found 409.0923; **IR** (neat, cm^{-1}): 2921, 2850, 1729, 1508, 1341, 1233, 1156, 839.

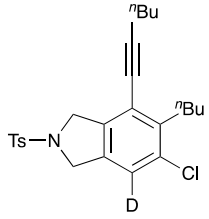
5-butyl-7-chloro-4-(hex-1-yn-1-yl)-2-tosylisoindoline-6-*d* (4g)



white solid; 45% yield, 36 mg, D% > 99%; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 7.79 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 4.67 (s, 2H), 4.59 (s, 2H), 2.73 – 2.62 (m, 2H), 2.45 (t, *J* = 6.9 Hz, 2H), 2.41 (s, 3H), 1.64 – 1.58 (m, 2H), 1.56 – 1.45 (m, 4H), 1.33 (dq, *J* = 14.0, 6.9 Hz, 2H), 0.94 (dt, *J* = 22.0, 7.3 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$, ppm) δ 146.4, 143.9, 140.5, 133.8, 131.9, 130.1, 127.7, 127.3, 117.2, 99.7, 75.4, 55.1, 53.9, 33.8, 32.8, 30.9, 22.6, 22.1, 21.7, 19.4, 14.0, 13.7; **HRMS** (ESI): calcd for $C_{25}H_{30}DClNO_2S^+$ $[M+H]^+$ requires 445.1821, found 445.1813; **IR** (neat, cm^{-1}): 2955,

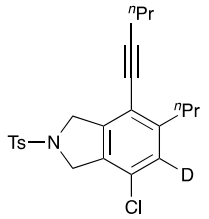
2930, 2859, 1351, 1165, 1098, 674, 546.

5-butyl-6-chloro-4-(hex-1-yn-1-yl)-2-tosylisoindoline-7-*d* (4g')



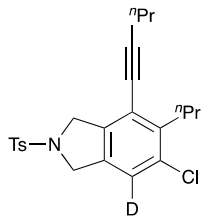
white solid; 18% yield, 16 mg, D% > 99%; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 7.76 (d, *J* = 7.9 Hz, 2H), 7.32 (d, *J* = 7.9 Hz, 2H), 4.57 (d, *J* = 6.9 Hz, 4H), 2.85 (t, *J* = 7.9 Hz, 2H), 2.47 (t, *J* = 6.9 Hz, 2H), 2.41 (s, 3H), 1.59 (q, *J* = 7.0 Hz, 2H), 1.49 (q, *J* = 7.7 Hz, 4H), 1.38 (dt, *J* = 17.5, 8.9 Hz, 2H), 0.95 (dt, *J* = 14.9, 7.2 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$, ppm) δ 143.9, 141.8, 137.8, 134.3, 133.7, 133.5, 130.0, 127.7, 120.4, 99.7, 75.9, 54.1, 54.0, 31.8, 31.3, 30.8, 23.0, 22.1, 21.7, 19.4, 14.0, 13.7; **HRMS** (ESI): calcd for $C_{25}H_{30}DClNO_2S^+$ $[M+H]^+$ requires 445.1821, found 445.1813; **IR** (neat, cm^{-1}): 2955, 2928, 2859, 1420, 1343, 1157, 1101, 669, 606, 551.

7-chloro-4-(pent-1-yn-1-yl)-5-propyl-2-tosylisoindoline-6-*d* (4h)



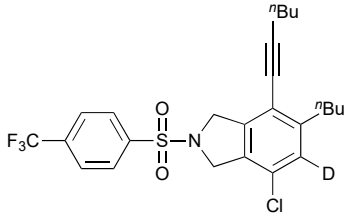
white solid; 36% yield, 30 mg, D% > 99%; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 7.79 (d, *J* = 8.3 Hz, 2H), 7.47 – 7.29 (m, 2H), 4.67 (s, 2H), 4.59 (s, 2H), 2.77 – 2.58 (m, 2H), 2.44 (d, *J* = 7.0 Hz, 2H), 2.41 (s, 3H), 1.72 – 1.50 (m, 4H), 1.05 (t, *J* = 7.4 Hz, 3H), 0.91 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$, ppm) δ 146.2, 143.9, 140.6, 133.8, 131.9, 130.0, 127.7, 127.3, 117.3, 99.6, 75.6, 55.1, 53.9, 36.1, 23.8, 22.3, 21.8, 21.67, 14.0, 13.6; **HRMS** (ESI): calcd for $C_{23}H_{26}DClNO_2S^+$ $[M+H]^+$ requires 417.1508, found 417.1500; **IR** (neat, cm^{-1}): 2960, 2931, 2870, 1462, 1435, 1351, 1309, 1163, 1097, 1065, 814, 650, 673, 588, 546.

6-chloro-4-(pent-1-yn-1-yl)-5-propyl-2-tosylisoindoline-7-*d* (4h')



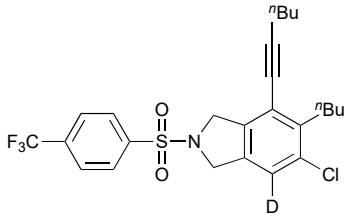
white solid; 15% yield, 12 mg, D% > 99%; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 7.78 – 7.74 (m, 2H), 7.35 – 7.30 (m, 2H), 4.57 (dd, *J* = 8.3, 2.1 Hz, 4H), 2.89 – 2.72 (m, 2H), 2.44 (t, *J* = 6.9 Hz, 2H), 2.41 (s, 3H), 1.64 (q, *J* = 7.2 Hz, 2H), 1.54 (d, *J* = 7.6 Hz, 2H), 1.06 (t, *J* = 7.4 Hz, 3H), 0.96 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$, ppm) δ 143.9, 141.6, 137.8, 134.4, 133.9, 133.7, 130.0, 127.7, 120.5, 99.6, 76.1, 54.1, 53.9, 34.0, 22.5, 22.3, 21.7, 21.7, 14.3, 13.7; **HRMS** (ESI): calcd for $C_{23}H_{26}DClNO_2S^+$ $[M+H]^+$ requires 417.1508, found 417.1500.

5-butyl-7-chloro-4-(hex-1-yn-1-yl)-2-((4-(trifluoromethyl)phenyl)sulfonyl)isoindoline-6-*d* (4i)



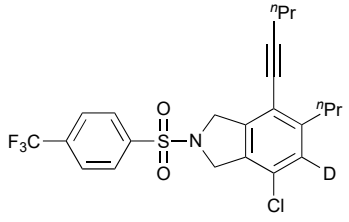
white solid, 44% yield, 44 mg, D% > 99%; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 8.03 (d, *J* = 8.1 Hz, 2H), 7.81 (d, *J* = 8.1 Hz, 2H), 4.70 (s, 2H), 4.64 (s, 2H), 2.67 (t, *J* = 7.8 Hz, 2H), 2.46 (t, *J* = 6.9 Hz, 2H), 1.64 – 1.55 (m, 2H), 1.50 (dt, *J* = 14.9, 7.5 Hz, 4H), 1.34 (dd, *J* = 8.6, 6.3 Hz, 2H), 0.97 (t, *J* = 7.3 Hz, 3H), 0.91 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$, ppm) δ 146.8, 140.7, 140.0, 134.8 (q, *J* = 33.1 Hz), 131.4, 128.0, 127.4, 126.6 (q, *J* = 3.7 Hz), 123.3 (q, *J* = 273.0 Hz), 117.3, 100.0, 75.4, 55.2, 54.0, 33.8, 32.8, 31.6, 30.9, 30.9, 30.3, 22.6, 22.1, 22.1, 19.4, 14.0, 13.7; **^{19}F NMR** (377 MHz, $CDCl_3$, ppm) δ -63.15; **HRMS** (ESI): calcd for $C_{25}H_{27}DClF_3NO_2S^+$ $[M+H]^+$ requires 499.1539, found 499.1522; **IR** (neat, cm^{-1}): 2957, 2930, 2859, 1405, 1350, 1324, 1163, 1127, 1108, 1063, 715, 613.

5-butyl-6-chloro-4-(hex-1-yn-1-yl)-2-((4-(trifluoromethyl)phenyl)sulfonyl)isoindoline-7-*d* (4i')



white solid, 22% yield, 22 mg, D% > 99%; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 8.01 (d, *J* = 8.0 Hz, 2H), 7.87 – 7.68 (m, 2H), 4.62 (s, 4H), 2.98 – 2.77 (m, 2H), 2.48 (td, *J* = 6.9, 1.8 Hz, 2H), 1.67 – 1.54 (m, 2H), 1.55 – 1.45 (m, 4H), 1.40 (p, *J* = 7.3 Hz, 2H), 0.95 (dtd, *J* = 16.3, 7.2, 1.8 Hz, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$, ppm) δ 142.2, 140.8, 137.3, 134.8 (q, *J* = 33.2 Hz), 133.9, 133.8, 128.0, 126.6 (q, *J* = 3.6 Hz), 123.3 (d, *J* = 273.3 Hz), 120.6, 100.0, 75.9, 54.2, 54.1, 31.9, 31.3, 30.8, 23.0, 22.1, 19.4, 14.0, 13.7; **^{19}F NMR** (377 MHz, $CDCl_3$, ppm) δ -63.16; **HRMS** (ESI): calcd for $C_{25}H_{27}DClF_3NO_2S^+$ $[M+H]^+$ requires 499.1539, found 499.1522; **IR** (neat, cm^{-1}): 2956, 2931, 2861, 1348, 1324, 1162, 1128, 1107, 1063.

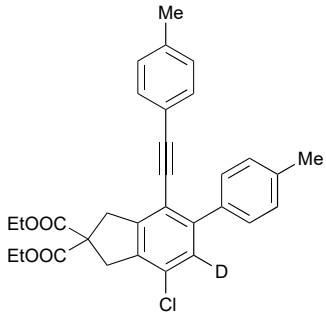
7-chloro-4-(pent-1-yn-1-yl)-5-propyl-2-((4-(trifluoromethyl)phenyl)sulfonyl)isoindoline-6-*d* (4j)



white solid; 58% yield, 55 mg, D% > 99%; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 8.03 (d, *J* = 8.1 Hz, 2H), 7.82 (d, *J* = 8.2 Hz, 2H), 4.71 (s, 2H), 4.64 (s, 2H), 2.65 (dd, *J* = 8.7,

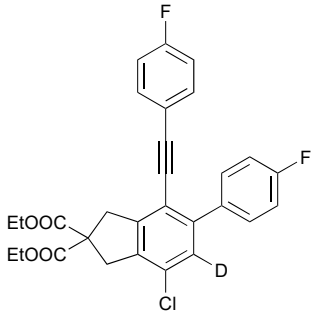
6.6 Hz, 2H), 2.44 (t, *J* = 6.9 Hz, 2H), 1.70 – 1.59 (m, 4H), 1.06 (t, *J* = 7.3 Hz, 3H), 0.92 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$, ppm) δ 146.4 140.7, 139.9, 134.6 (q, *J* = 33.0 Hz), 131.4, 127.9, 127.8, 127.3, 126.5 (q, *J* = 3.7 Hz), 123.2 (d, *J* = 272.9 Hz), 117.3, 99.7, 75.4, 55.0, 53.9, 36.0, 23.6, 22.2, 21.6, 13.8, 13.5; **^{19}F NMR** (376 MHz, $CDCl_3$, ppm) δ -63.14; **HRMS** (ESI): calcd for $C_{23}H_{23}DClF_3NO_2S^+$ $[M+H]^+$ requires 471.1226, found 471.1213; **IR** (neat, cm^{-1}): 2960, 2921, 2851, 1633, 1403, 1350, 1323, 1175, 1160, 1131, 1107, 1063, 715.

diethyl 7-chloro-5-(*p*-tolyl)-4-(*p*-tolylethynyl)-1,3-dihydro-2*H*-indene-2,2-dicarboxylate-6-*d* (4k)



white solid; 78% yield, 78 mg, D% > 99%; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 7.56 (d, *J* = 8.1 Hz, 2H), 7.33 – 7.24 (m, 4H), 7.14 (d, *J* = 8.0 Hz, 2H), 4.29 (q, *J* = 7.1 Hz, 4H), 3.90 (s, 2H), 3.76 (s, 2H), 2.44 (s, 3H), 2.37 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$, ppm) δ 171.4, 145.1, 144.1, 138.6, 137.6, 136.9, 136.5, 131.4, 129.9, 129.2, 128.8, 120.3, 116.7, 96.9, 86.0, 62.1, 59.0, 41.8, 40.3, 21.6, 21.4, 14.1; **HRMS** (ESI): calcd for $C_{31}H_{29}DClO_4^+$ $[M+H]^+$ requires 502.1890, found 502.1880; **IR** (neat, cm^{-1}): 2920, 1732, 1510, 1430, 1269, 1242, 1182, 816.

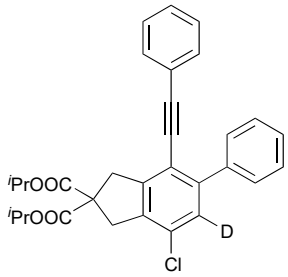
diethyl 7-chloro-5-(4-fluorophenyl)-4-((4-fluorophenyl)ethynyl)-1,3-dihydro-2*H*-indene-2,2-dicarboxylate-6-*d* (4l)



white solid; 87% yield, 89 mg, D% > 99%; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 7.61 – 7.50 (m, 2H), 7.35 – 7.29 (m, 2H), 7.13 (m, *J* = 8.7 Hz, 2H), 7.01 (m, *J* = 7.9 Hz, 2H), 4.28 (q, *J* = 7.0 Hz, 4H), 3.86 (s, 2H), 3.73 (s, 2H), 1.31 (t, *J* = 7.2 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$, ppm) δ 171.3, 162.7 (d, *J* = 250.3 Hz), 162.7 (d, *J* = 247.3 Hz), 145.2, 143.3, 137.5, 135.4 (d, *J* = 3.3 Hz), 133.4 (d, *J* = 8.3 Hz), 131.0 (d, *J* = 8.1 Hz), 130.3, 128.2 (t, *J* = 29.0 Hz), 119.2 (d, *J* = 3.5 Hz), 116.5, 115.8 (d, *J* = 22.1 Hz), 115.1 (d, *J* = 21.5 Hz), 95.7, 86.0, 62.2, 59.0, 41.7, 40.3, 14.2; **^{19}F NMR** (376 MHz, $CDCl_3$, ppm) δ -110.22, -114.21; **HRMS** (ESI): calcd for $C_{29}H_{23}DClF_2O_4^+$ $[M+H]^+$ requires 510.1389,

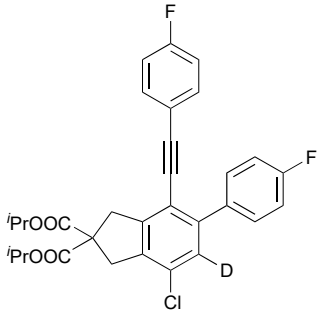
found 510.1378; **IR** (neat, cm^{-1}): 2982, 1729, 1600, 1506, 1432, 1269, 1231, 1185, 1155, 1069, 834.

diisopropyl 7-chloro-5-phenyl-4-(phenylethynyl)-1,3-dihydro-2*H*-indene-2,2-dicarboxylate-6-*d* (4m)



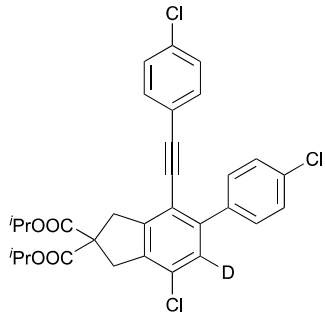
white solid; 82% yield, 82 mg, D% > 99%; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 7.64 (dd, *J* = 8.2, 1.4 Hz, 2H), 7.46 (dd, *J* = 8.2, 6.5 Hz, 2H), 7.43 – 7.39 (m, 1H), 7.38 – 7.34 (m, 2H), 7.33 – 7.28 (m, 3H), 5.12 (hept, *J* = 6.2 Hz, 2H), 3.87 (s, 2H), 3.73 (s, 2H), 1.31 (d, *J* = 6.3 Hz, 12H); **^{13}C NMR** (101 MHz, $CDCl_3$, ppm) δ 170.9, 145.3, 144.4, 139.4, 137.4, 131.5, 130.2, 129.3, 128.5, 128.4, 128.1, 127.9, 123.3, 116.7, 96.6, 86.5, 69.6, 59.1, 41.7, 40.3, 21.7; **HRMS** (ESI): calcd for $C_{31}H_{29}DClO_4^+$ $[M+H]^+$ requires 502.1890, found 502.1881; **IR** (neat, cm^{-1}): 2981, 2922, 1728, 1272, 1248, 1192, 1103, 755, 690.

diisopropyl 7-chloro-5-(4-fluorophenyl)-4-((4-fluorophenyl)ethynyl)-1,3-dihydro-2*H*-indene-2,2-dicarboxylate-6-*d* (4n)



white solid; 79% yield, 85 mg, D% > 99%; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 7.62 – 7.52 (m, 2H), 7.37 – 7.27 (m, 2H), 7.13 (t, *J* = 8.7 Hz, 2H), 7.01 (t, *J* = 8.7 Hz, 2H), 5.10 (p, *J* = 6.3 Hz, 2H), 3.81 (s, 2H), 3.69 (s, 2H), 1.29 (d, *J* = 6.3 Hz,12); **^{13}C NMR** (101 MHz, $CDCl_3$, ppm) δ 170.9, 164.0 (d, *J* = 5.9 Hz), 161.5 (d, *J* = 2.8 Hz), 145.3, 143.3, 137.6, 135.4 (d, *J* = 3.3 Hz), 133.4 (d, *J* = 8.4 Hz), 131.0 (d, *J* = 8.2 Hz), 130.3, 128.2 (t, *J* = 31.5 Hz), 119.3 (d, *J* = 3.4 Hz), 116.5, 115.8 (d, *J* = 22.2 Hz), 115.1 (d, *J* = 21.5 Hz), 95.7, 86.0, 69.7, 59.1, 41.7, 40.3, 21.7; **^{19}F NMR** (376 MHz, $CDCl_3$, ppm) δ -110.29, -114.27; **HRMS** (ESI): calcd for $C_{31}H_{27}DClF_2O_4^+$ $[M+H]^+$ requires 538.1702, found 538.1691; **IR** (neat, cm^{-1}): 2982, 2935, 1728, 1508, 1272, 1235, 1104, 837.

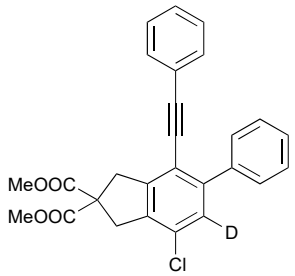
diisopropyl 7-chloro-5-(4-chlorophenyl)-4-((4-chlorophenyl)ethynyl)-1,3-dihydro-2*H*-indene-2,2-dicarboxylate-6-*d* (4o)



white solid; 75% yield, 82 mg, D% > 99%; **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 7.53 (d, *J* = 8.5 Hz, 2H), 7.41 (d, *J* =

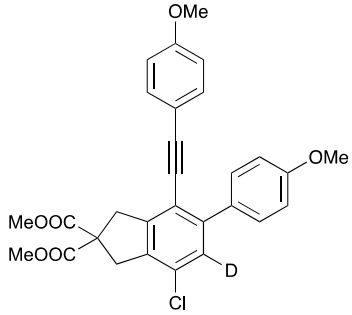
8.5 Hz, 2H), 7.32 – 7.22 (m, 4H), 5.10 (hept, J = 6.2 Hz, 2H), 3.81 (s, 2H), 3.69 (s, 2H), 1.29 (d, J = 6.3 Hz, 12H); **^{13}C NMR** (101 MHz, $CDCl_3$, ppm) δ 170.8, 145.5, 143.1, 137.9, 137.8, 134.7, 134.1, 132.7, 131.7, 130.6, 130.6, 128.9, 128.3, 121.5, 116.3, 95.7, 87.1, 69.7, 59.1, 41.7, 40.3, 21.7; **HRMS** (ESI): calcd for $C_{31}H_{27}DCl_3O_4^+$ $[M+H]^+$ requires 570.1111, found 570.1110; **IR** (neat, cm^{-1}): 2981, 2936, 1726, 1491, 1277, 1249, 1192, 1102, 1091, 1013, 828.

dimethyl 7-chloro-5-phenyl-4-(phenylethynyl)-1,3-dihydro-2*H*-indene-2,2-dicarboxylate-6-*d* (4p)



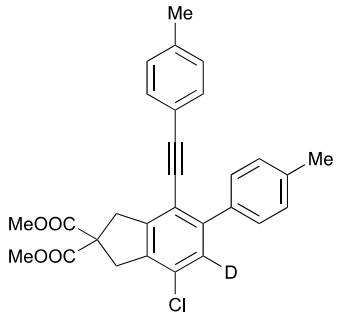
white solid; 85% yield, 76 mg, > 99% D; **^{1}H NMR** (600 MHz, $CDCl_3$, ppm) δ 7.62 (dt, J = 6.5, 1.3 Hz, 2H), 7.45 (td, J = 7.2, 1.3 Hz, 2H), 7.42 – 7.38 (m, 1H), 7.36 – 7.33 (m, 2H), 7.30 (dt, J = 4.1, 2.4 Hz, 3H), 3.90 (s, 2H), 3.82 (s, 6H), 3.75 (s, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$, ppm) δ 171.9, 145.0, 144.5, 139.3, 137.1, 132.7, 131.5, 130.2, 129.4, 128.5, 128.4, 128.1, 128.0, 123.3, 116.7, 96.8, 86.5, 59.0, 53.3, 42.0, 40.4; **HRMS** (ESI): calcd for $C_{27}H_{21}DClO_4^+$ $[M+H]^+$ requires 446.1263, found 446.1255; **IR** (neat, cm^{-1}): 2922, 2853, 1744, 1459, 1376.

dimethyl 7-chloro-5-(4-methoxyphenyl)-4-((4-methoxyphenyl)ethynyl)-1,3-dihydro-2*H*-indene-2,2-dicarboxylate-6-*d* (4q)



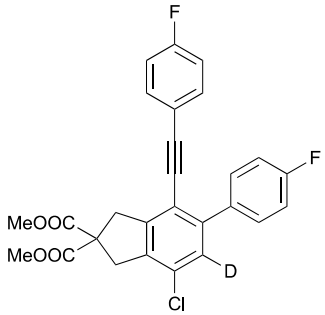
white solid; 65% yield, 66 mg, > 99% D. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 7.58 (d, J = 8.7 Hz, 2H), 7.32 (d, J = 8.8 Hz, 2H), 6.98 (d, J = 8.7 Hz, 2H), 6.84 (d, J = 8.7 Hz, 2H), 3.87 (s, 2H), 3.86 (s, 3H), 3.81 (d, J = 1.4 Hz, 9H), 3.73 (s, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$, ppm) δ 171.9, 159.8, 159.4, 144.7, 143.7, 136.5, 133.0, 131.9, 130.5, 130.5, 129.7, 128.0 (t, J = 30.8 Hz), 116.8, 115.4, 114.1, 113.5, 96.8, 85.4, 58.9, 55.4, 55.4, 53.3, 41.9, 40.3; **HRMS** (ESI): calcd for $C_{29}H_{25}DClO_6^+$ $[M+H]^+$ requires 506.1475, found 506.1460; **IR** (neat, cm^{-1}): 2954, 2838, 2206, 1734, 1605, 1509, 1432, 1286, 1244, 1175, 1033, 832.

dimethyl 7-chloro-5-(*p*-tolyl)-4-(*p*-tolylethynyl)-1,3-dihydro-2*H*-indene-2,2-dicarboxylate-6-*d* (4r)



white solid; 68% yield, 64 mg, > 99% D. **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ 7.57 (d, *J* = 8.1 Hz, 2H), 7.36 – 7.22 (m, 4H), 7.23 – 7.11 (m, 2H), 3.91 (s, 2H), 3.84 (s, 6H), 3.77 (s, 2H), 2.45 (s, 3H), 2.38 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$, ppm) δ 171.9, 144.9, 144.2, 138.7, 137.7, 136.8, 136.4, 132.6, 131.4, 129.9, 129.2, 128.8, 120.2, 116.8, 96.9, 86.0, 58.9, 53.3, 42.0, 40.4, 21.7, 21.4; **HRMS** (ESI): calcd for $C_{29}H_{24}DClO_4Na^+$ $[M+Na]^+$ requires 496.1396, found 496.1409; **IR** (neat, cm^{-1}): 2953, 2921, 1737, 1510, 1510, 1433, 1281, 1246, 817.

dimethyl 7-chloro-5-(4-fluorophenyl)-4-((4-fluorophenyl)ethynyl)-1,3-dihydro-2H-indene-2,2-dicarboxylate-6-d (4s)



white solid; 63% yield, 61 mg, > 99% D; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.60 – 7.52 (m, 2H), 7.35 – 7.29 (m, 2H), 7.17 – 7.09 (m, 2H), 7.04 – 6.97 (m, 2H), 3.87 (s, 2H), 3.81 (s, 6H), 3.74 (s, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.8, 162.8 (d, *J* = 250.3 Hz), δ 162.7 (d, *J* = 247.2 Hz), 145.0, 143.3, 137.3, 135.3 (d, *J* = 3.3 Hz), 133.4 (d, *J* = 8.4 Hz), 131.0 (d, *J* = 8.1 Hz), 130.3, 128.3 (d, *J* = 29.4 Hz), 119.1 (d, *J* = 3.5 Hz), 116.5, 115.8 (d, *J* = 22.2 Hz), 115.1 (d, *J* = 21.4 Hz), 95.8, 85.9, 58.9, 53.4, 41.9, 40.4; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -110.18, -114.17; **HRMS** (ESI): calcd for $C_{27}H_{18}DClF_2O_4Na^+$ $[M+Na]^+$ requires 504.0895, found 504.0898; **IR** (neat, cm^{-1}): 2920, 2850, 1737, 1508, 1236, 837.

VII X-Ray Crystallographic Data

The absolute configuration of product **2k** was assigned based on the crystal X-ray. A colorless rodlike crystal of **2k** was obtained by vaporization of methanol/DCM (5:1) solution of compound **2k**.

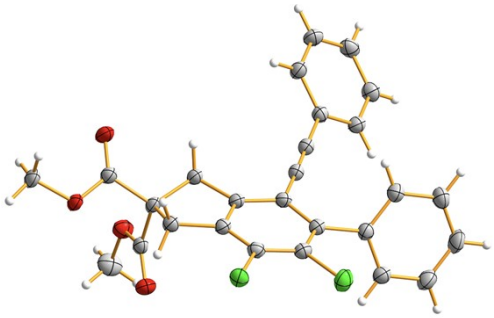


Fig. S3 The crystal structure of **2k**

Table S1 Crystal data and structure refinement

Identification code	**2k**
Empirical formula	$C_{27}H_{20}Cl_2O_4$
Formula weight	479.33
Temperature/K	99.99(10)
Crystal system	triclinic
Space group	P-1
a/Å	10.1092(3)
b/Å	10.3061(4)
c/Å	11.5747(5)
α/°	89.965(3)
β/°	75.580(3)
γ/°	78.193(3)
Volume/Å^3	1141.61(8)
Z	1
ρ_{calc}g/cm^3	1.394
μ/mm^{-1}	2.827
F(000)	496.0
Crystal size/mm^3	0.25 × 0.2 × 0.1
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.898 to 148.748
Index ranges	-12 ≤ h ≤ 11, -12 ≤ k ≤ 9, -12 ≤ l ≤ 14
Reflections collected	11410
Independent reflections	4465 [R_{int} = 0.0430, R_{sigma} = 0.0465]
Data/restraints/parameters	4465/0/300
Goodness-of-fit on F^2	1.075
Final R indexes [I>=2σ (I)]	R_1 = 0.0475, wR_2 = 0.1282
Final R indexes [all data]	R_1 = 0.0572, wR_2 = 0.1339
Largest diff. peak/hole / e Å^{-3}	0.52/-0.65

The absolute configuration of product **2n** was assigned based on the crystal X-ray. A colorless needle crystal of **2n** was obtained by vaporization of methanol/DCM (5:1) solution of compound **2n**.

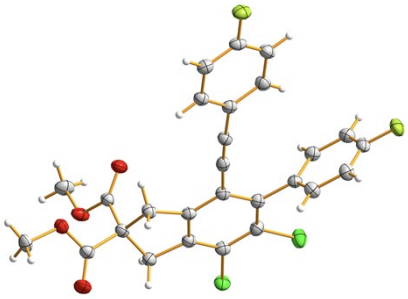


Fig. S4 The crystal structure of **2n**

Table S2 Crystal data and structure refinement

Identification code	**2n**
Empirical formula	$C_{27}H_{18}Cl_2F_2O_4$
Formula weight	515.32
Temperature/K	100.00(10)
Crystal system	triclinic
Space group	P-1
a/Å	7.9175(3)
b/Å	10.7651(4)
c/Å	14.7038(6)
α/°	71.582(3)
β/°	76.336(3)
γ/°	82.757(3)
Volume/Å^3	1153.60(8)
Z	1
ρ_{calc}g/cm^3	1.484
μ/mm^{-1}	2.970
F(000)	528.0
Crystal size/mm^3	0.3 × 0.05 × 0.02
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	6.478 to 148.674
Index ranges	-9 ≤ h ≤ 9, -11 ≤ k ≤ 13, -11 ≤ l ≤ 18
Reflections collected	10917
Independent reflections	4504 [R_{int} = 0.0368, R_{sigma} = 0.0461]
Data/restraints/parameters	4504/0/318
Goodness-of-fit on F^2	1.106
Final R indexes [I>=2σ (I)]	R_1 = 0.0448, wR_2 = 0.1127
Final R indexes [all data]	R_1 = 0.0612, wR_2 = 0.1176
Largest diff. peak/hole / e Å^{-3}	0.30/-0.57

The absolute configuration of product **2r** was assigned based on the crystal X-ray. A colorless rodlike crystal of **2r** was obtained by vaporization of methone/DCM (5:1) solution of compound **2r**.

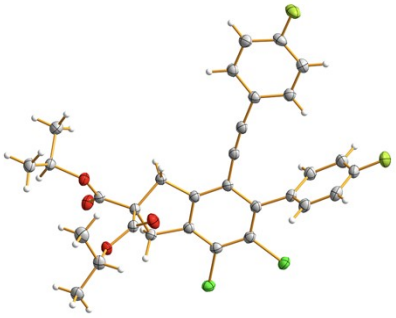


Fig. S5 The crystal structure of **2r**

Table S3 Crystal data and structure refinement

Identification code	**2r**
Empirical formula	$C_{31}H_{26}Cl_2F_2O_4$
Formula weight	571.42
Temperature/K	99.99(10)
Crystal system	triclinic
Space group	P-1
a/Å	9.4833(2)
b/Å	12.1890(2)
c/Å	13.7941(3)
α/°	68.666(2)
β/°	77.043(2)
γ/°	67.681(2)
Volume/Å^3	1367.09(5)
Z	2
ρ_{calc}g/cm^3	1.388
μ/mm^{-1}	2.560
F(000)	592.0
Crystal size/mm^3	0.2 × 0.1 × 0.06
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	6.914 to 148.738
Index ranges	-11 ≤ h ≤ 11, -14 ≤ k ≤ 15, -10 ≤ l ≤ 17
Reflections collected	14190
Independent reflections	5374 [R_{int} = 0.0349, R_{sigma} = 0.0413]
Data/restraints/parameters	5374/0/356
Goodness-of-fit on F^2	1.066
Final R indexes [I>=2σ (I)]	R_1 = 0.0377, wR_2 = 0.0991
Final R indexes [all data]	R_1 = 0.0448, wR_2 = 0.1021
Largest diff. peak/hole / e Å^{-3}	0.34/-0.35

The absolute configuration of product **4a'** was assigned based on the crystal X-ray. A colorless needle crystal of **4a'** was obtained by vaporization of ethyl acetate/DCM (10:1) solution of compound **4a'**.

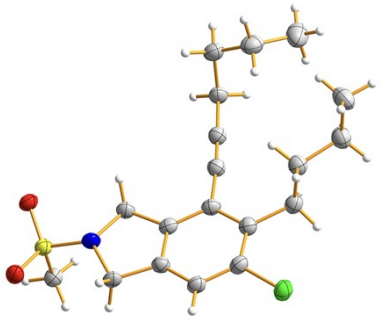
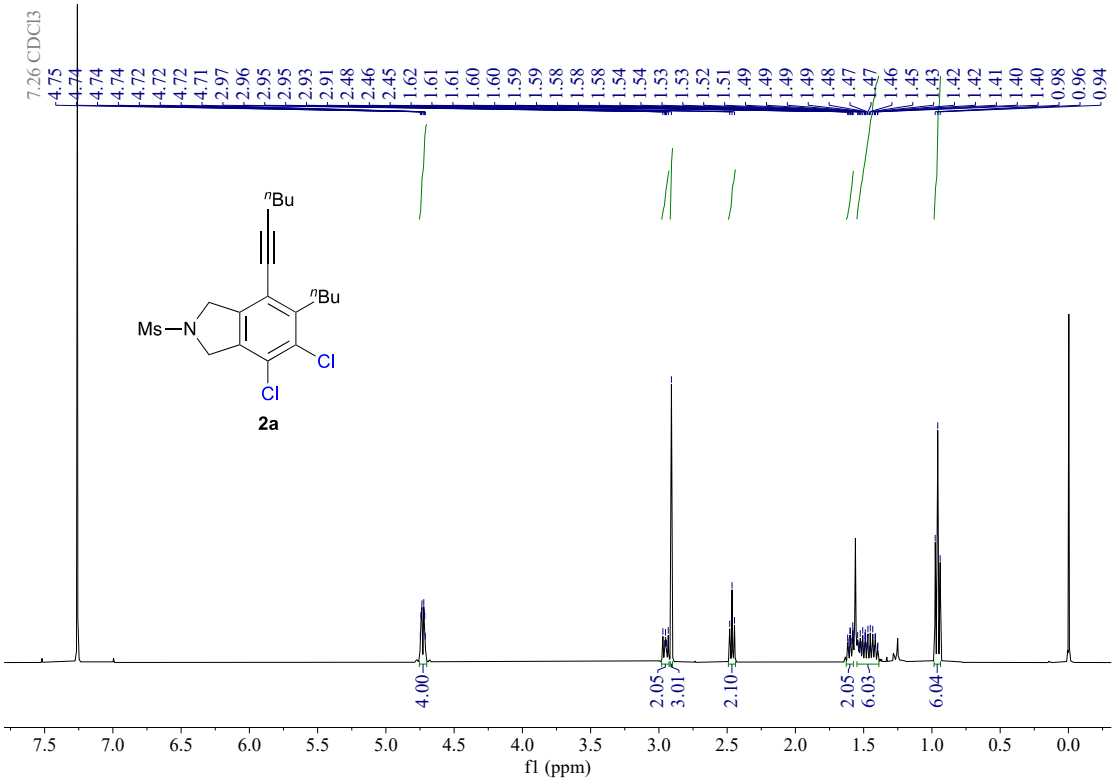


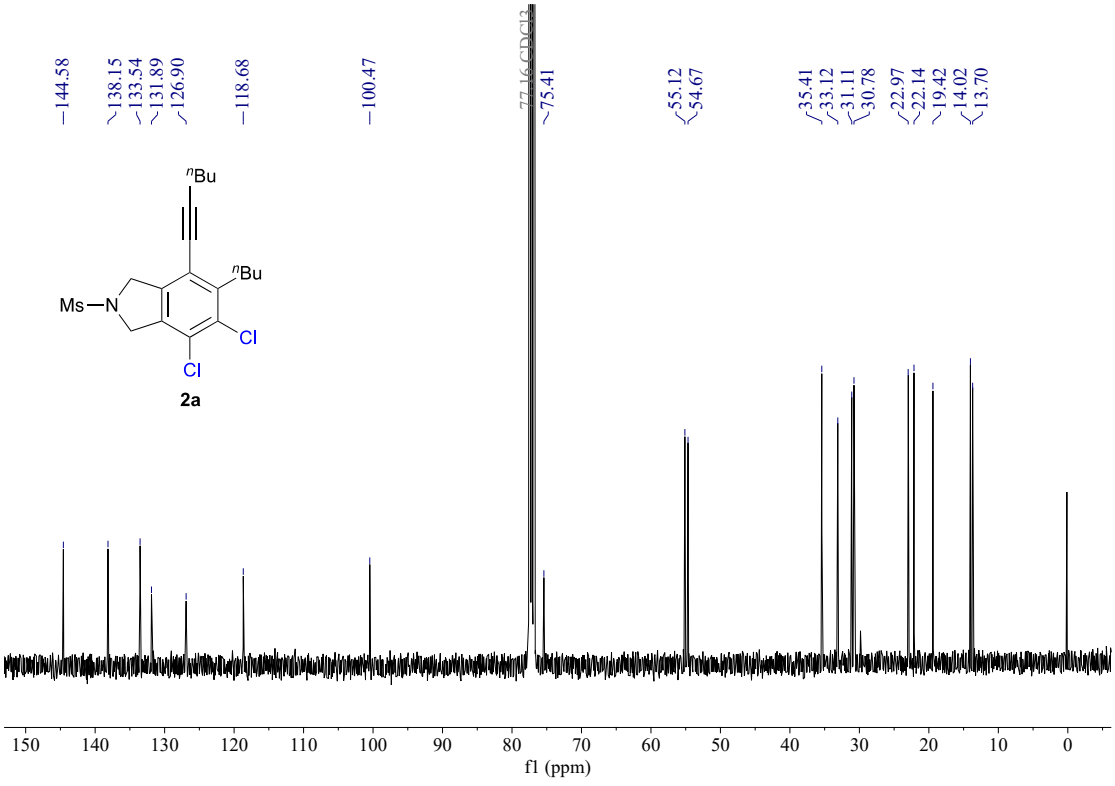
Fig. S6 The crystal structure of **4a'**

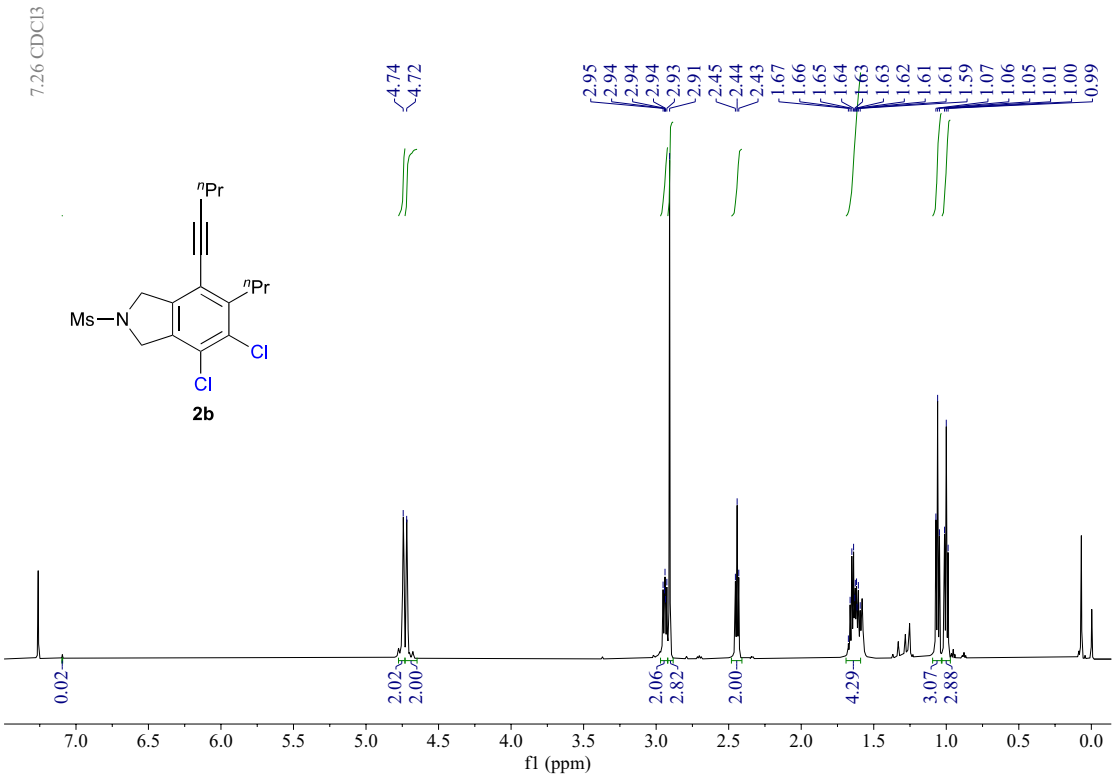
Table S4 Crystal data and structure refinement

Identification code	**4a'**
Empirical formula	$C_{38}H_{52}Cl_2N_2O_4S_2$
Formula weight	735.83
Temperature/K	100.00(10)
Crystal system	triclinic
Space group	P-1
a/Å	4.9398(3)
b/Å	10.5774(6)
c/Å	18.6718(11)
α/°	75.489(5)
β/°	84.576(5)
γ/°	84.679(5)
Volume/Å^3	937.84(10)
Z	1
ρ_{calc}g/cm^3	1.303
μ/mm^{-1}	2.925
F(000)	392.0
Crystal size/mm^3	0.1 × 0.05 × 0.03
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.658 to 148.36
Index ranges	$-3 \le h \le 6$, $-12 \le k \le 13$, $-23 \le l \le 23$
Reflections collected	8138
Independent reflections	3619 [R_{int} = 0.0450, R_{sigma} = 0.0551]
Data/restraints/parameters	3619/0/220
Goodness-of-fit on F^2	1.064
Final R indexes [I>=2σ (I)]	R_1 = 0.0728, wR_2 = 0.2103
Final R indexes [all data]	R_1 = 0.0839, wR_2 = 0.2198
Largest diff. peak/hole / e Å^{-3}	0.99/-0.73

VIII. Copies of ^{1}H NMR, ^{13}C NMR, and ^{19}F NMR spectra of products



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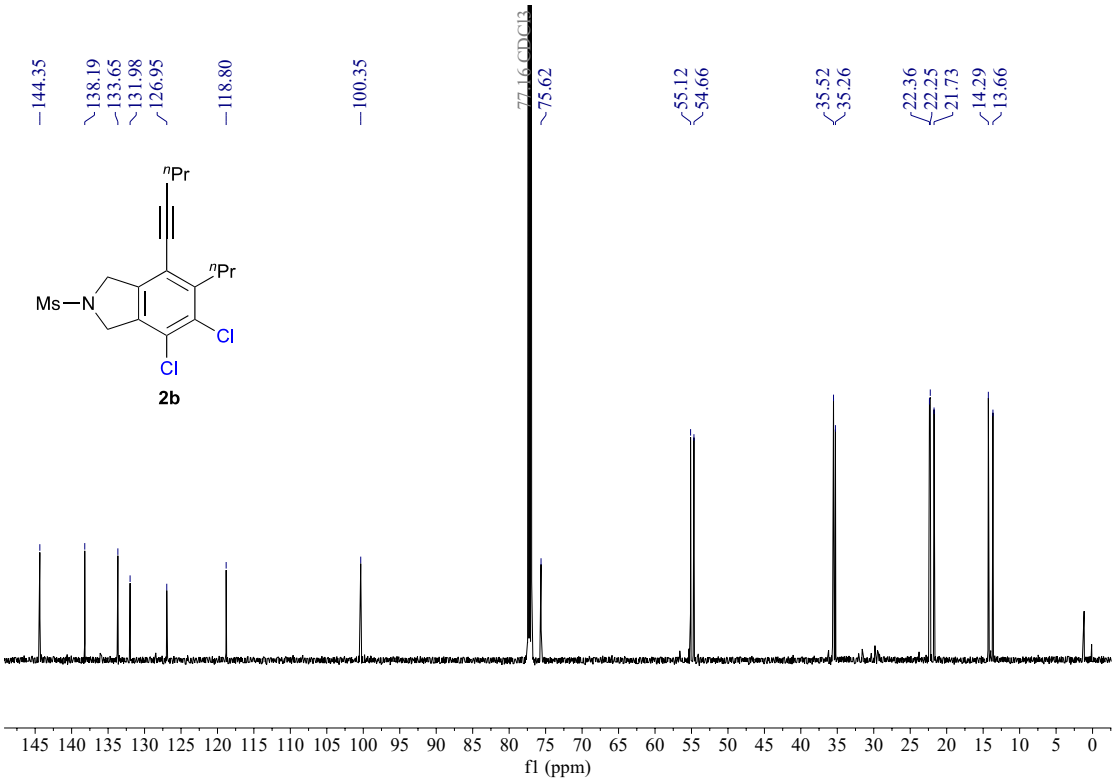
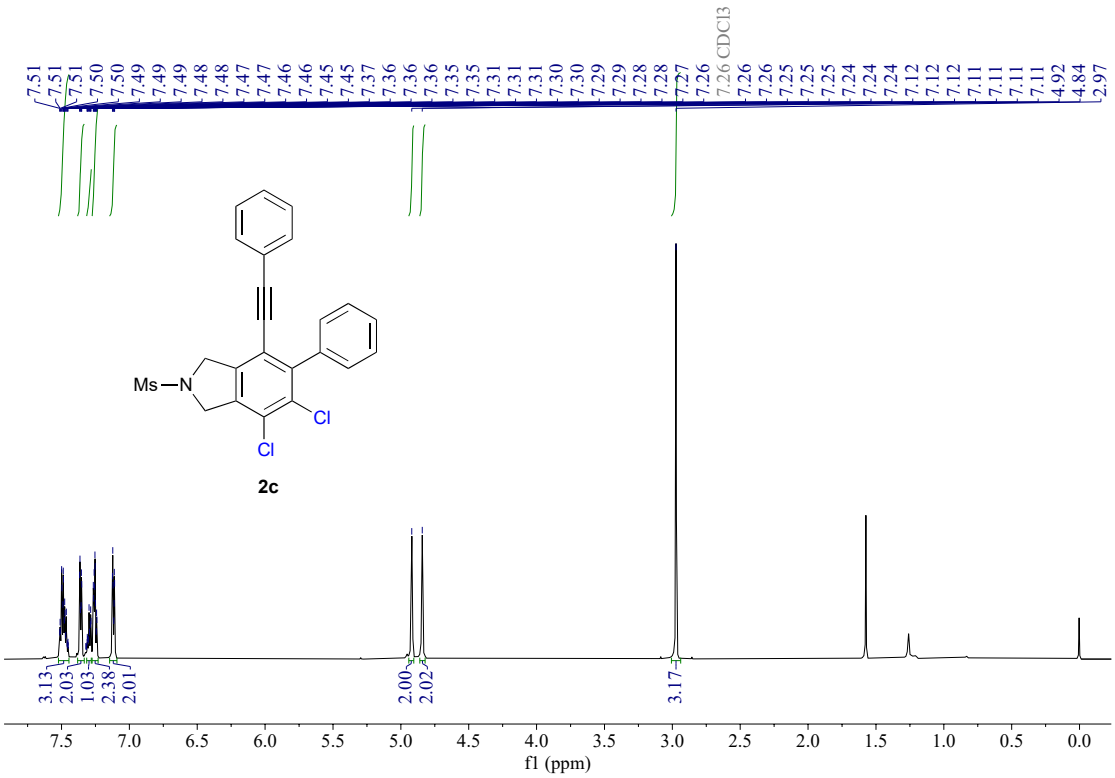
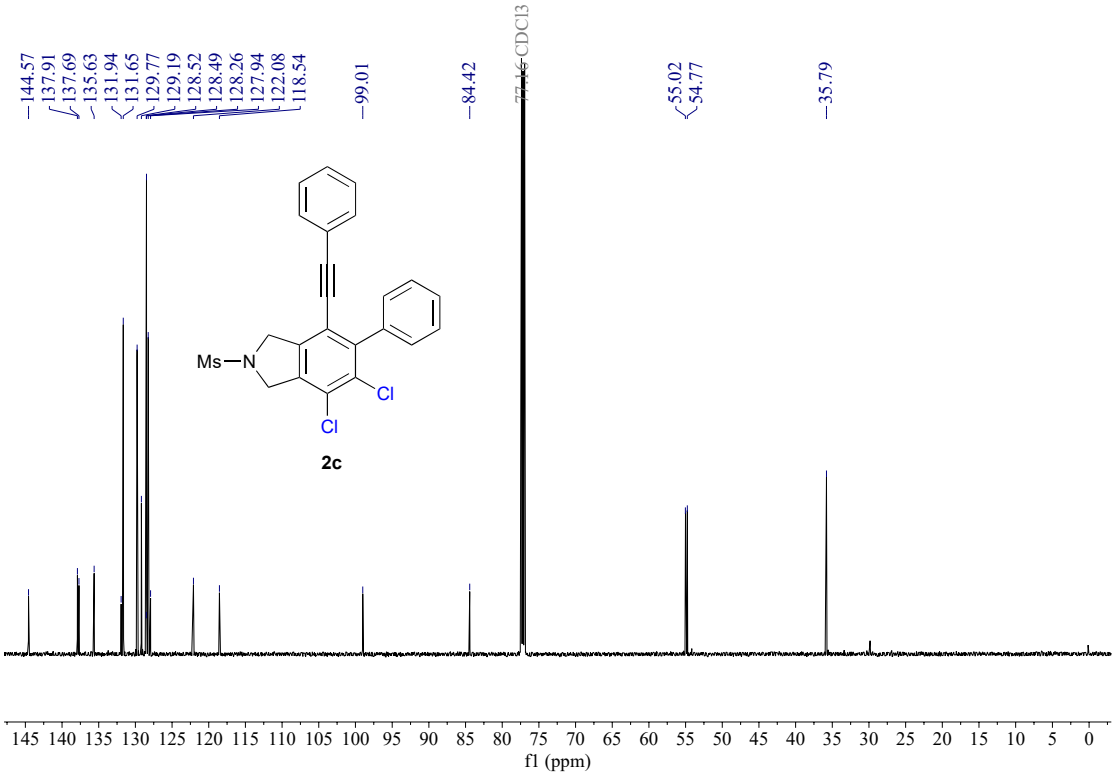
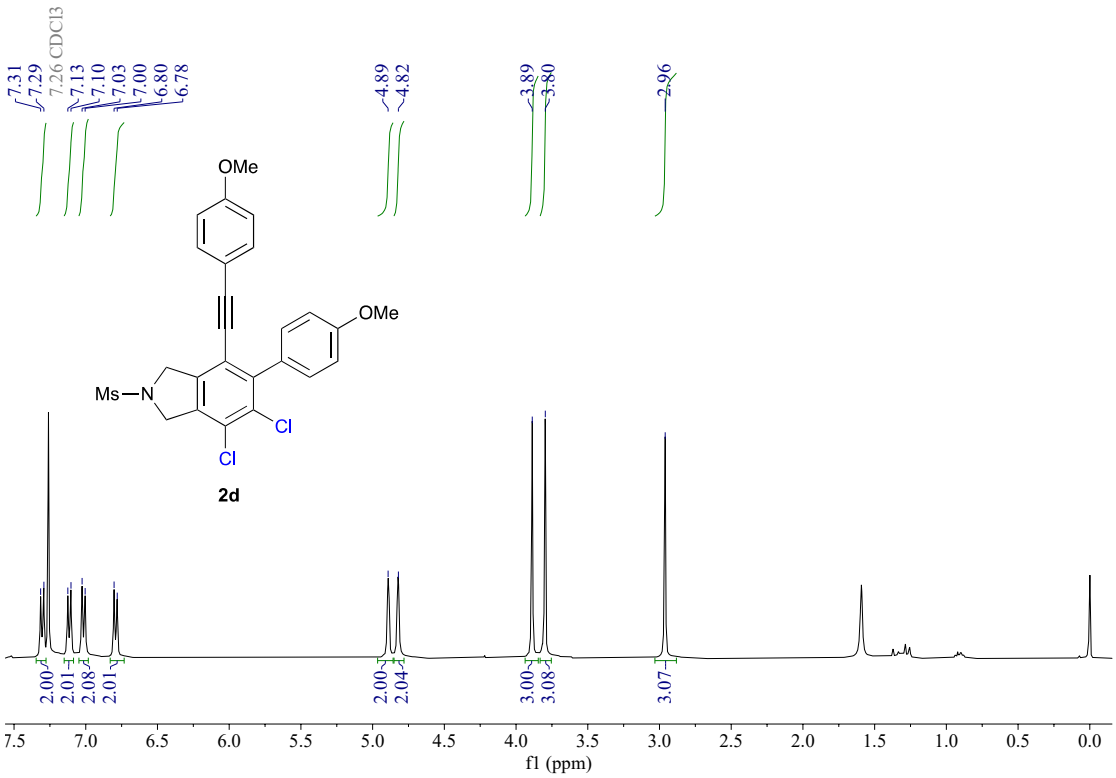
2.94
2.94
2.94
2.93
2.91
2.45
2.44
2.43
1.67
1.66
1.65
1.64
1.63
1.63
1.62
1.61
1.61
1.59
1.07
1.06
1.05
1.01
1.00
0.99
nPr
nPr
Ms—N
Cl
Cl
2b
0.02
2.02
2.00
2.06
2.82
2.00
4.29
3.07
2.88
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


144.35
138.19
133.65
131.98
126.95
118.80
100.35
77.16 CDCl3
75.62
55.12
54.66
35.52
35.26
22.36
22.25
21.73
14.29
13.66
nPr
nPr
Ms—N
Cl
Cl
2b
145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)


Ms—N
Cl
Cl
2c
f1 (ppm)


Ms—N
Cl
Cl
2c
f1 (ppm)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7.13
7.10
7.03
7.00
6.80
6.78
4.89
4.82
3.89
3.80
2.96
OMe
OMe
Ms—N
Cl
Cl
2d
2.00
2.01
2.08
2.01
2.00
2.04
3.00
3.08
3.07
7.5
7.0
6.5
6.0
5.5
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1.0
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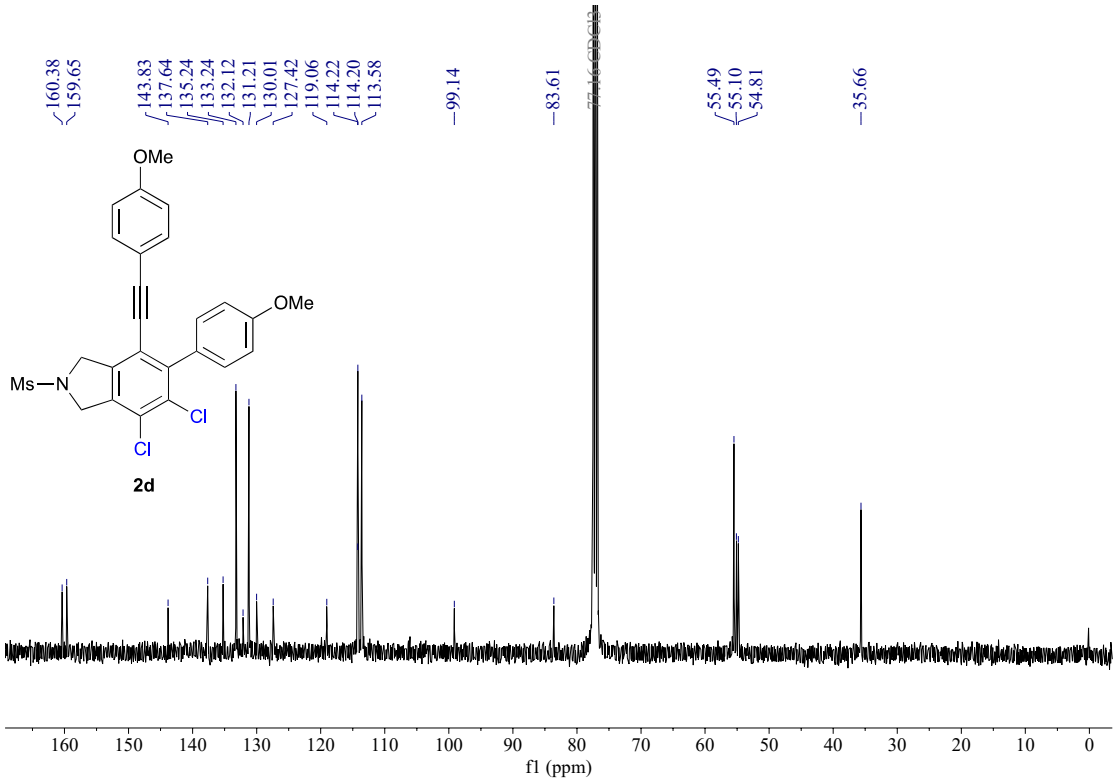
0.0
f1 (ppm)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159.65
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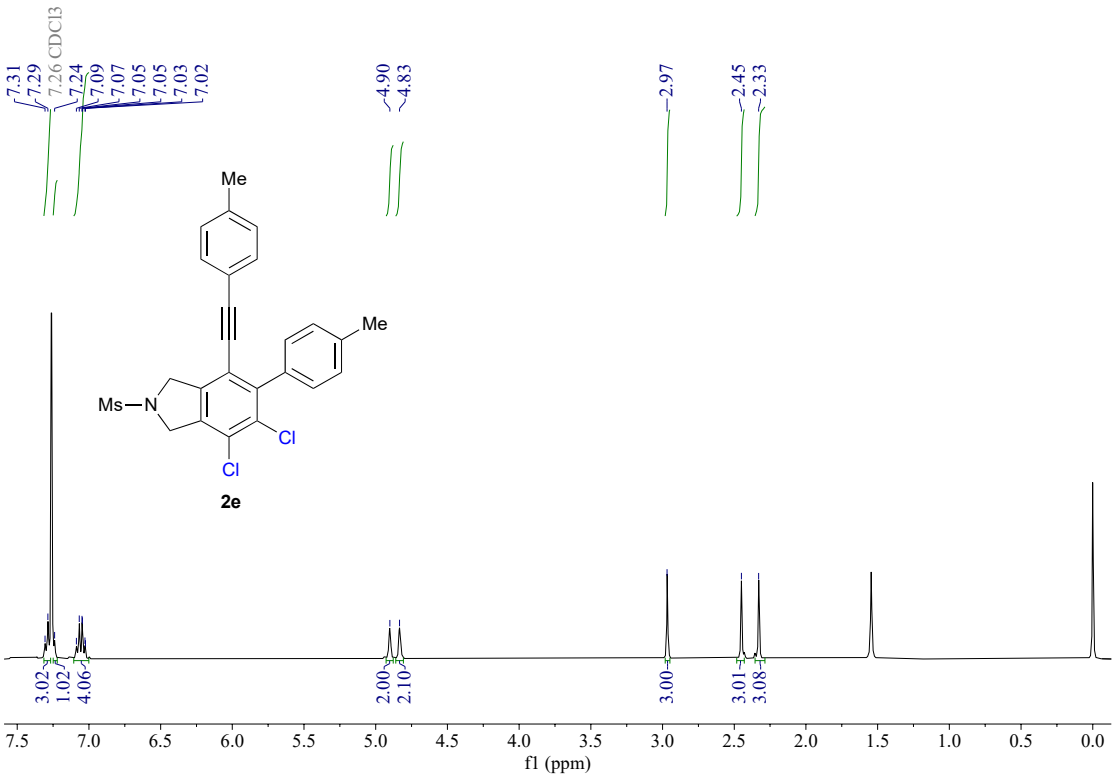
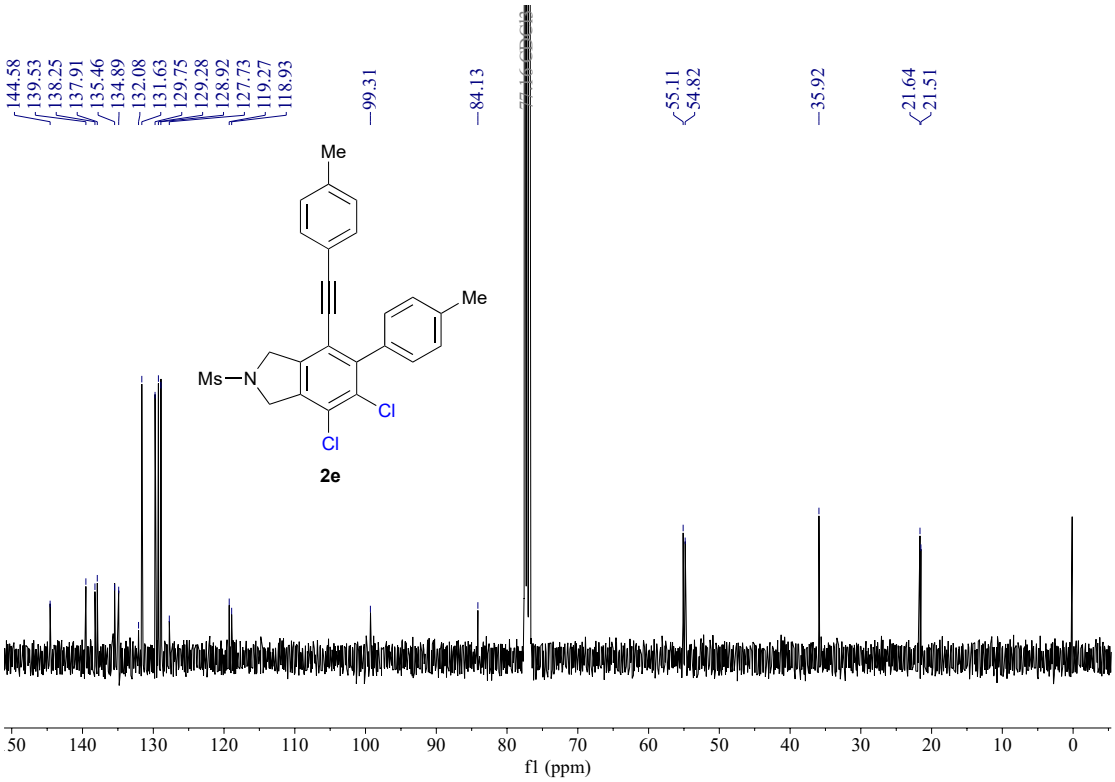
137.64
135.24
133.24
132.12
131.21
130.01
127.42
119.06
114.22
114.20
113.58
99.14
83.61
77.16 CDCl3
55.49
55.10
54.81
35.66
OMe
OMe
Ms—N
Cl
Cl
2d
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.31
7.29
7.26 CDCl3
7.24
7.09
7.07
7.05
7.05
7.03
7.02
4.90
4.83
2.97
2.45
2.33
Me
Me
Ms—N
Cl
Cl
2e
3.02
1.02
4.06
2.00
2.10
3.00
3.01
3.08
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
f1 (ppm)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132.08
131.63
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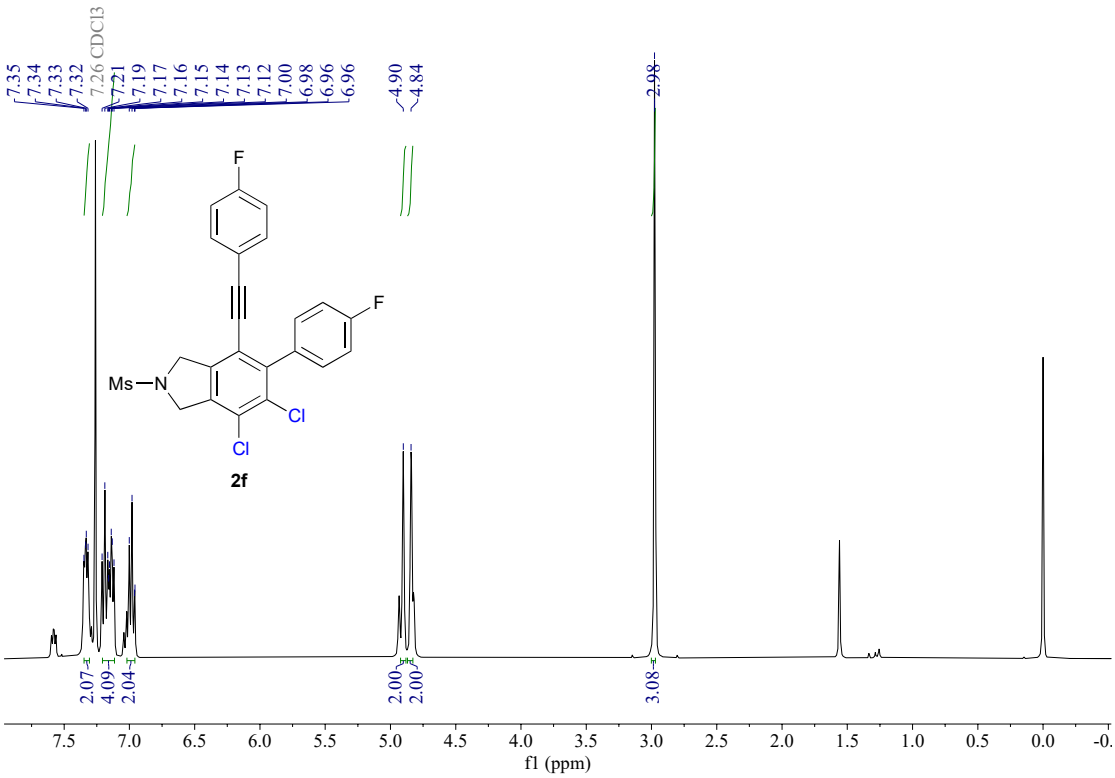
129.28
128.92
127.73
119.27
118.93
99.31
84.13
55.11
54.82
35.92
21.64
21.51
Me
Me
Ms—N
Cl
Cl
2e
50
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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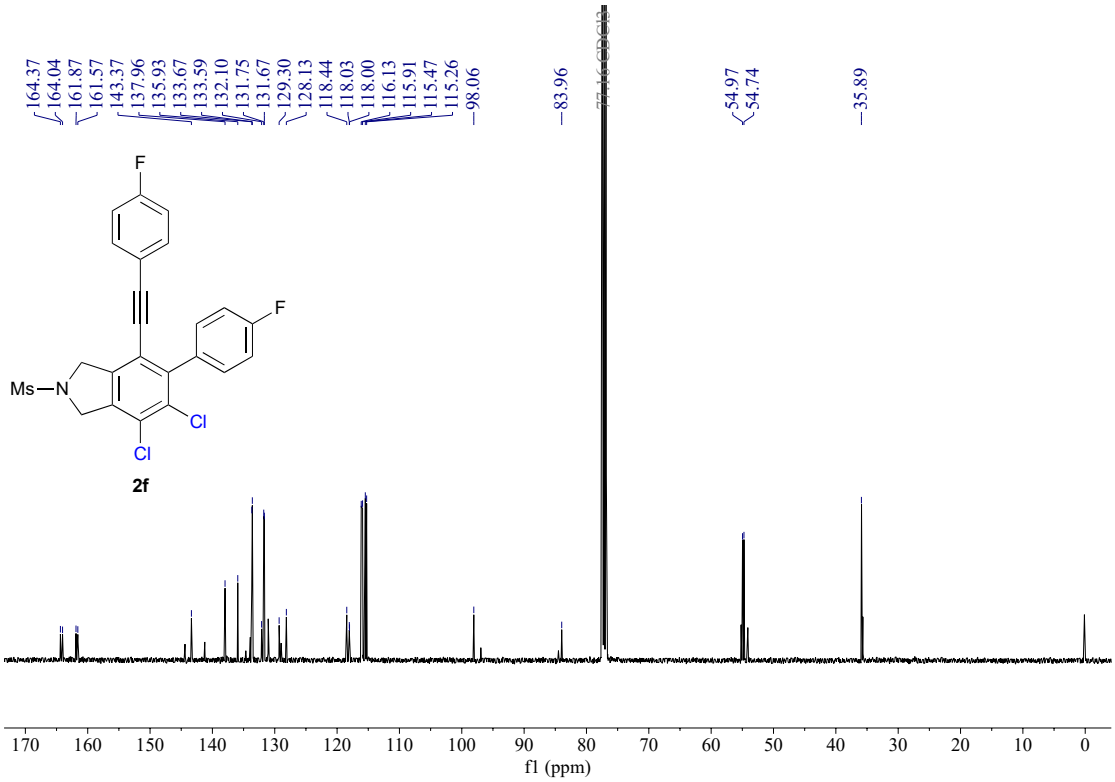
7.34
7.33
7.32
7.26 CDCl3
7.21
7.19
7.17
7.16
7.15
7.14
7.13
7.12
7.00
6.98
6.96
6.96
4.90
4.84
2.98
F
F
Ms—N
Cl
Cl
2f
2.07
4.09
2.04
2.00
2.00
3.08
f1 (ppm)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135.93
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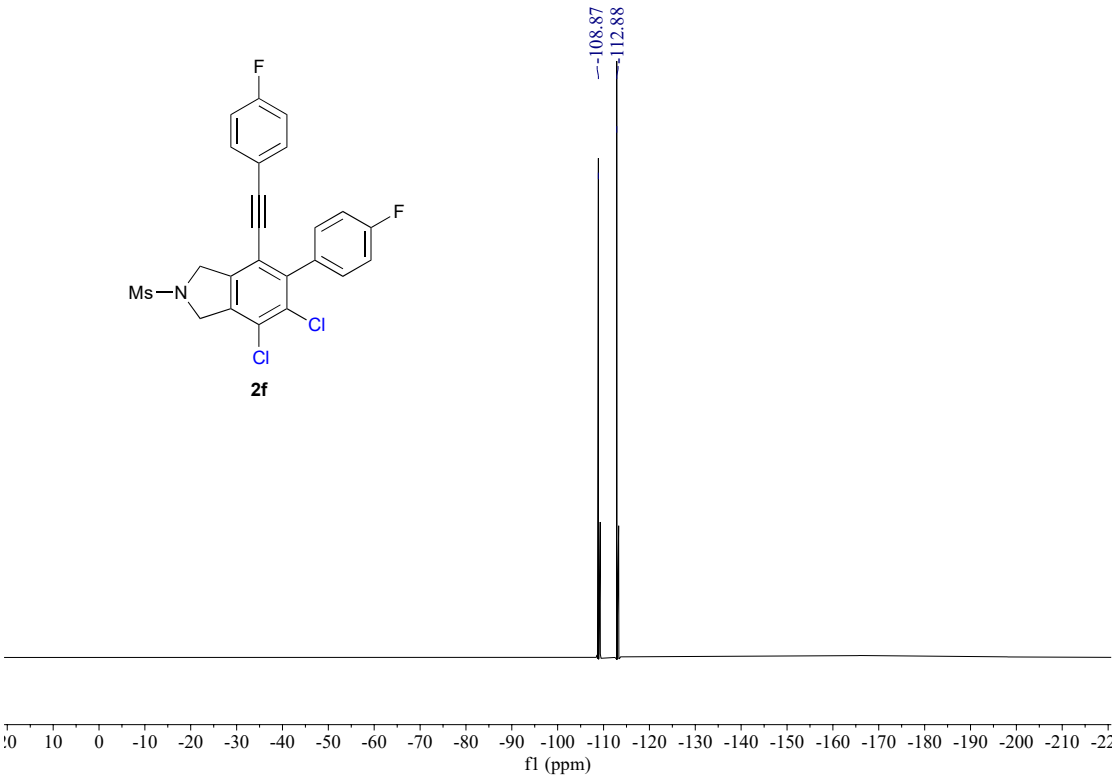
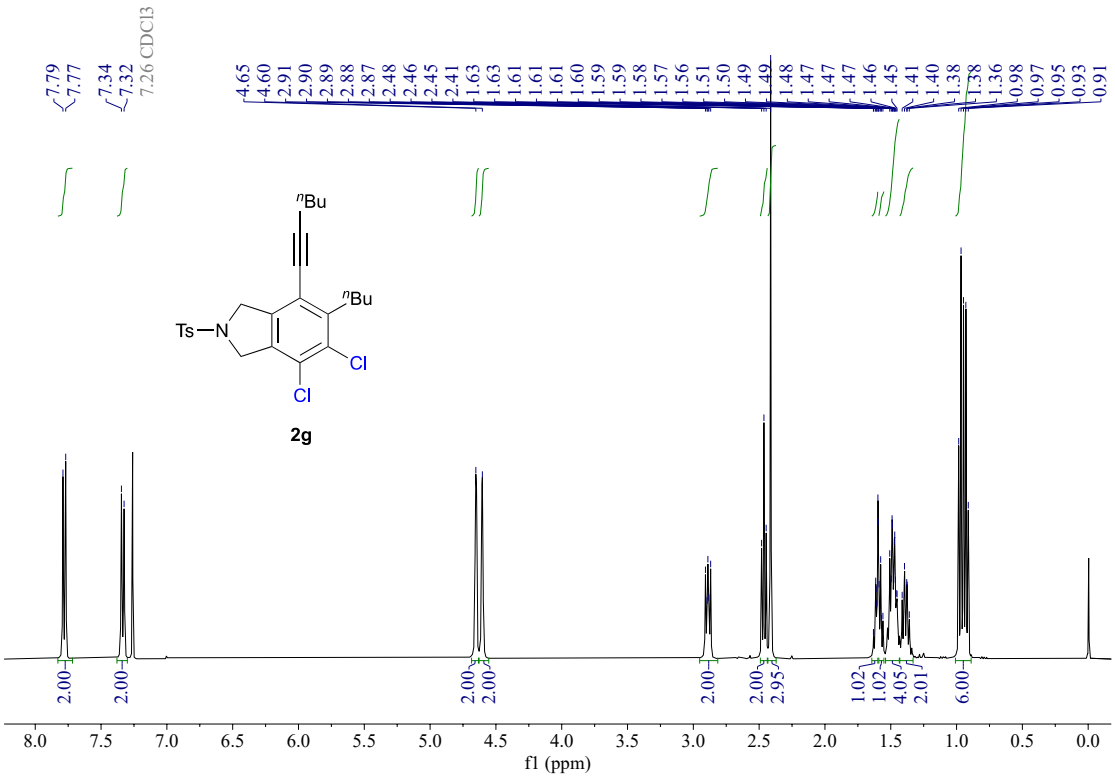
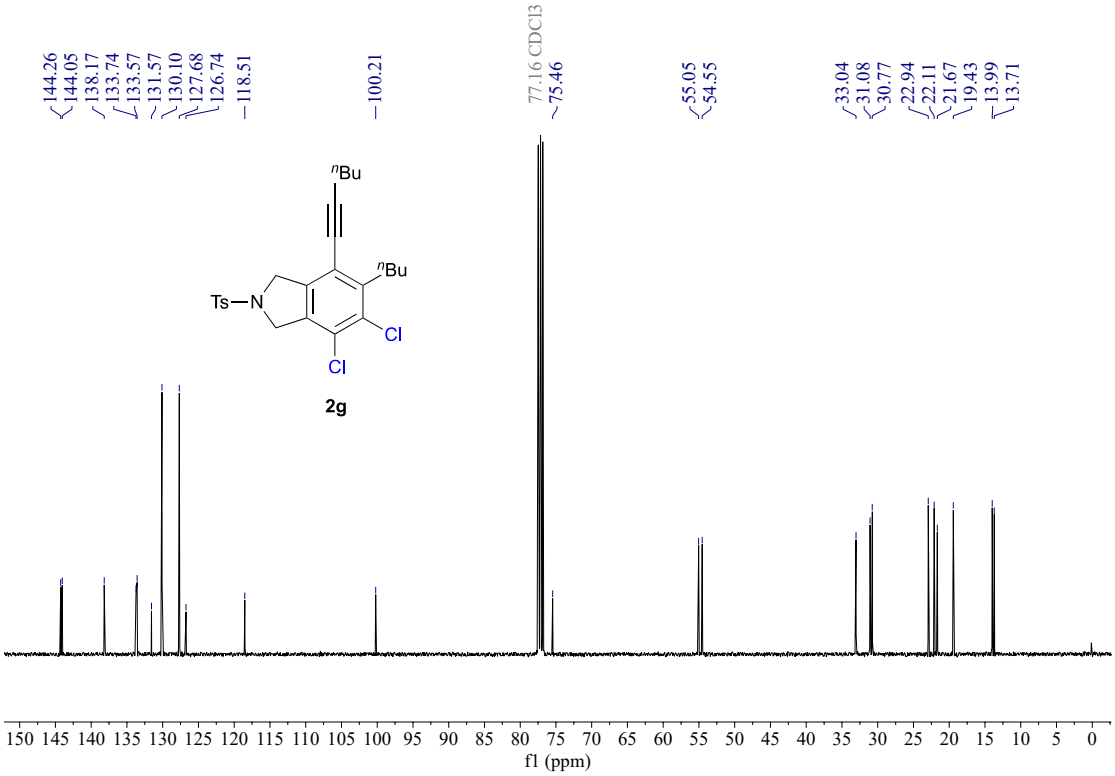
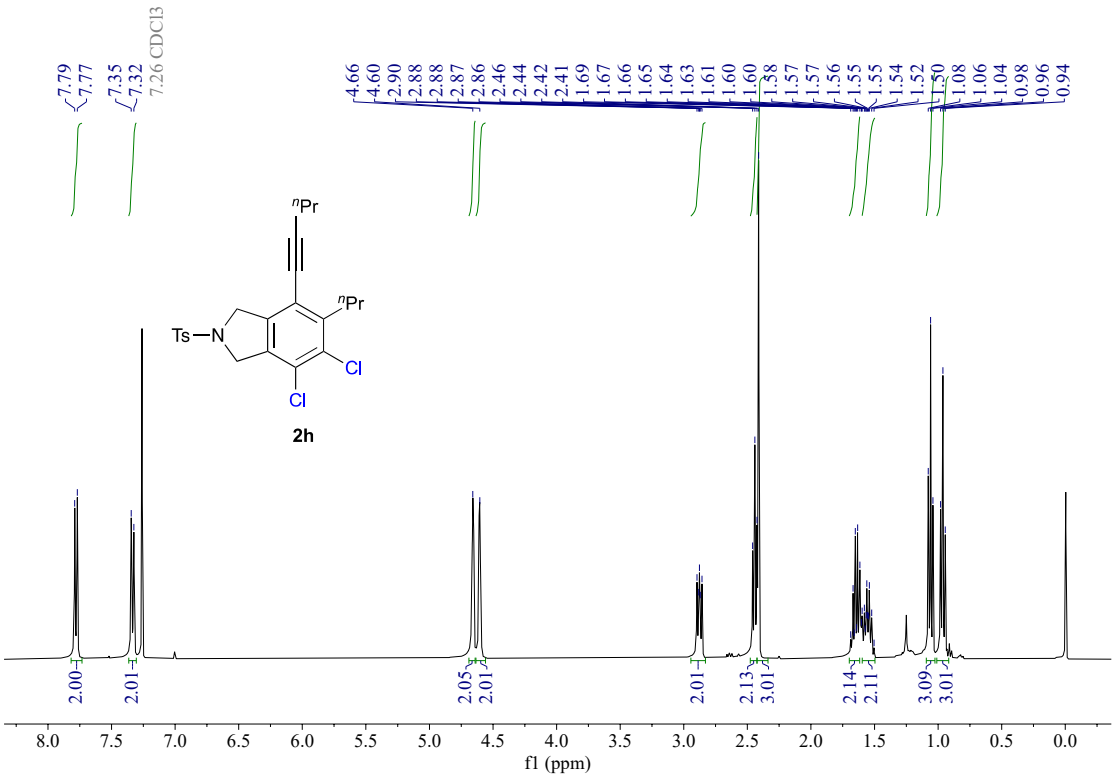
133.59
132.10
131.75
131.67
129.30
128.13
118.44
118.03
118.00
116.13
115.91
115.47
115.26
98.06
83.96
77.16 CDCl3
54.97
54.74
35.89
F
F
Ms—N
Cl
Cl
2f
f1 (ppm)

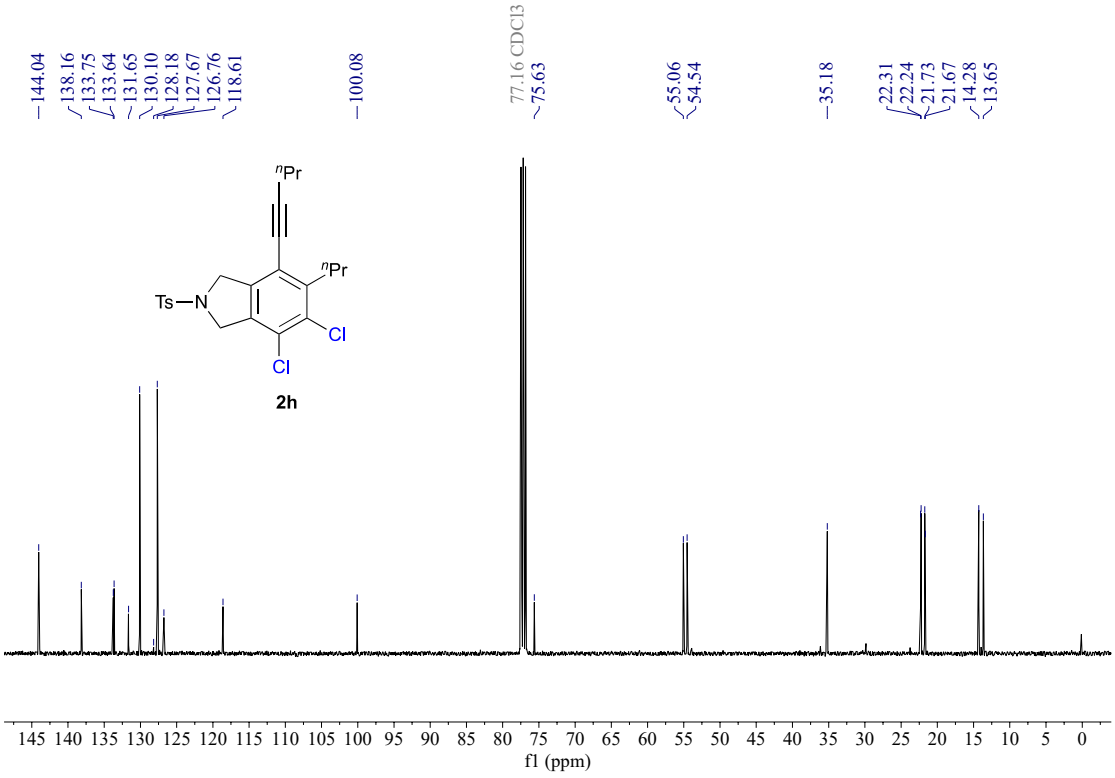

F
F
Ms—N
Cl
Cl
-108.87
-112.88
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

2f


7.79
7.77
7.34
7.32
7.26 CDCl3
4.65
4.60
2.91
2.90
2.89
2.88
2.87
2.48
2.46
2.45
2.41
1.63
1.63
1.61
1.61
1.61
1.60
1.59
1.59
1.58
1.57
1.56
1.51
1.50
1.49
1.49
1.48
1.47
1.47
1.47
1.46
1.45
1.41
1.40
1.38
1.38
1.36
0.98
0.97
0.95
0.93
0.91
nBu
nBu
Ts—N
Cl
Cl
2g
2.00
2.00
2.00
2.00
2.00
2.00
2.95
1.02
1.02
4.05
2.01
6.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


144.26
144.05
138.17
133.74
133.57
131.57
130.10
127.68
126.74
118.51
100.21
77.16 CDCl3
75.46
55.05
54.55
33.04
31.08
30.77
22.94
22.11
21.67
19.43
13.99
13.71
nBu
nBu
Ts—N
Cl
Cl
2g
150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)


7.79
7.77
7.35
7.32
7.26 CDCl3
4.66
4.60
2.90
2.88
2.88
2.87
2.86
2.46
2.44
2.42
2.41
1.69
1.67
1.66
1.65
1.64
1.63
1.61
1.60
1.60
1.38
1.57
1.57
1.56
1.55
1.55
1.54
1.52
1.50
1.08
1.06
1.04
0.98
0.96
0.94
nPr
nPr
Ts—N
Cl
Cl
2h
2.00
2.01
2.05
2.01
2.01
2.13
3.01
2.14
2.11
3.09
3.01
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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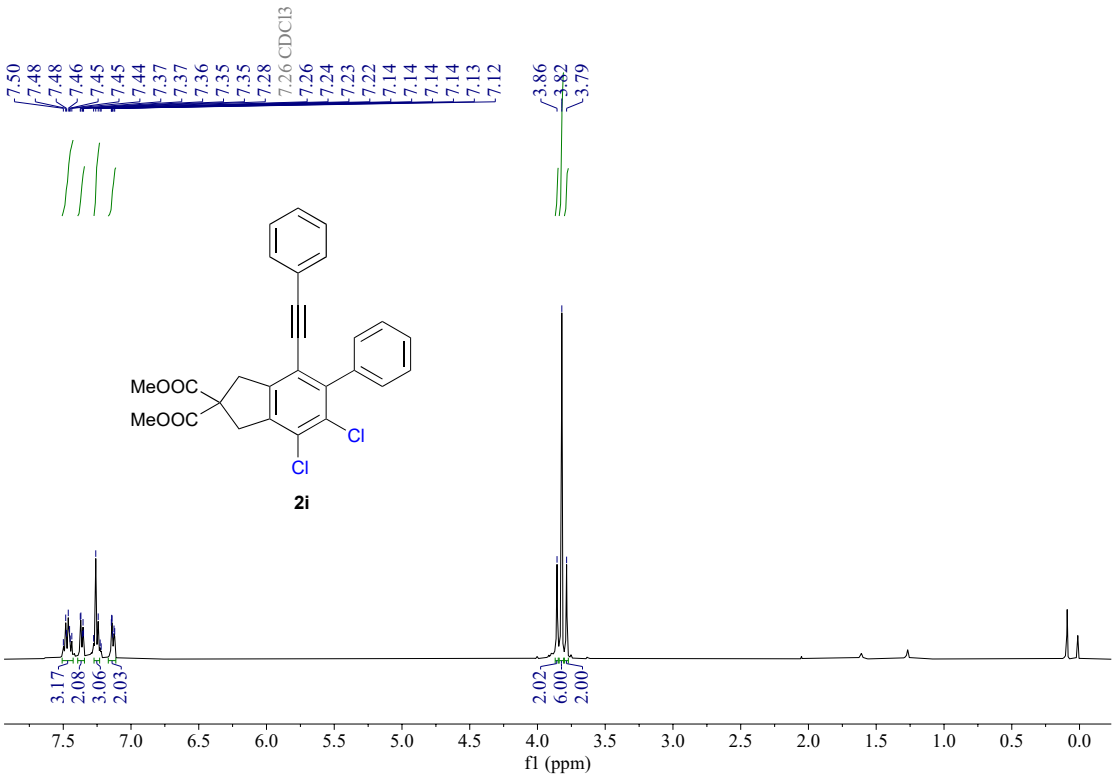
138.16
133.75
133.64
131.65
130.10
128.18
127.67
126.76
118.61
100.08
77.16 CDCl3
75.63
55.06
54.54
35.18
22.31
22.24
21.73
21.67
14.28
13.65
nPr
nPr
Ts—N
Cl
Cl
2h
145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)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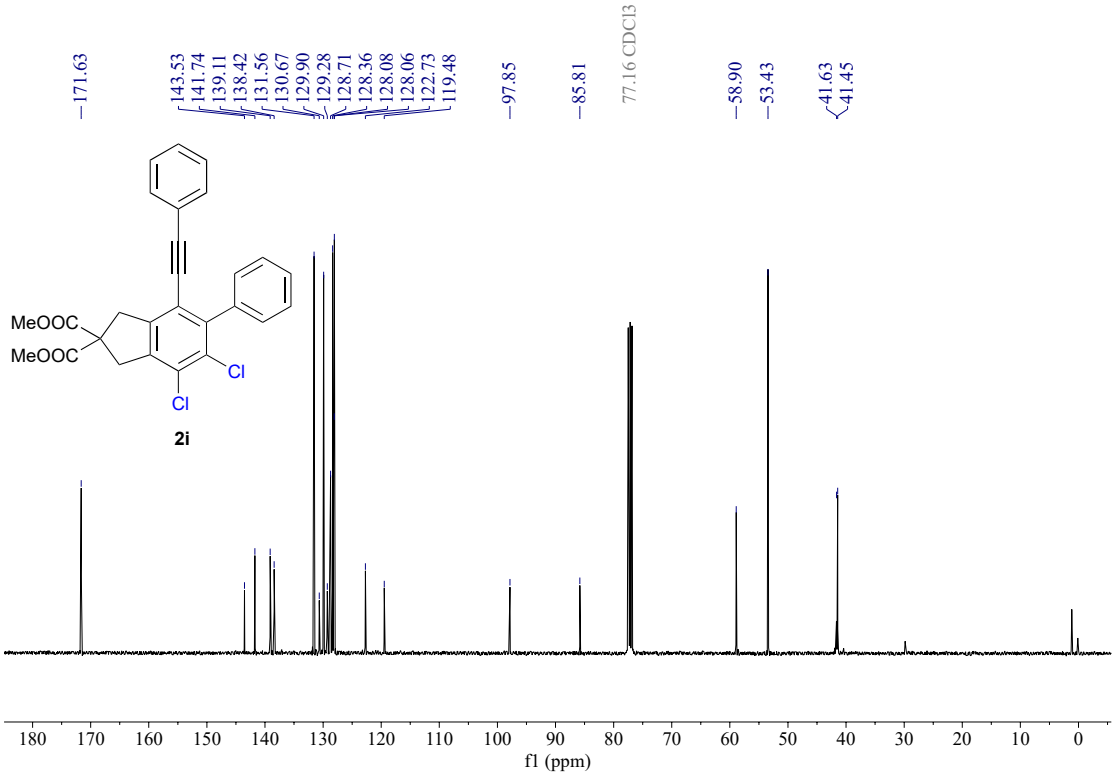
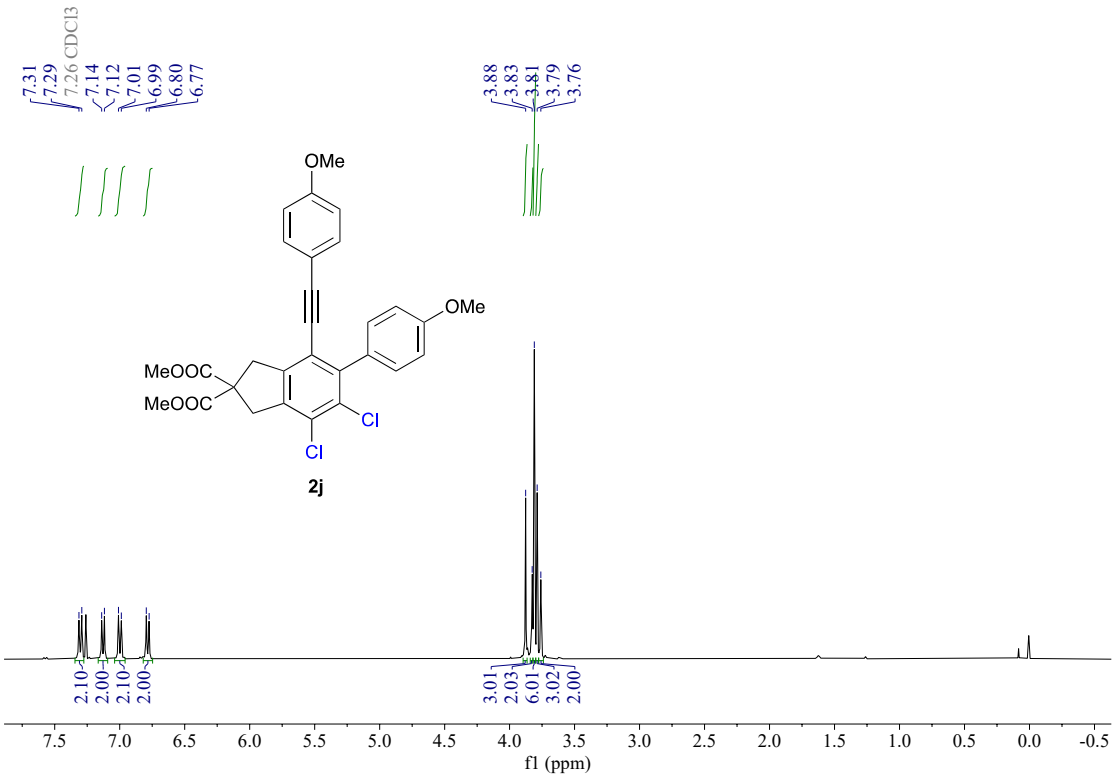
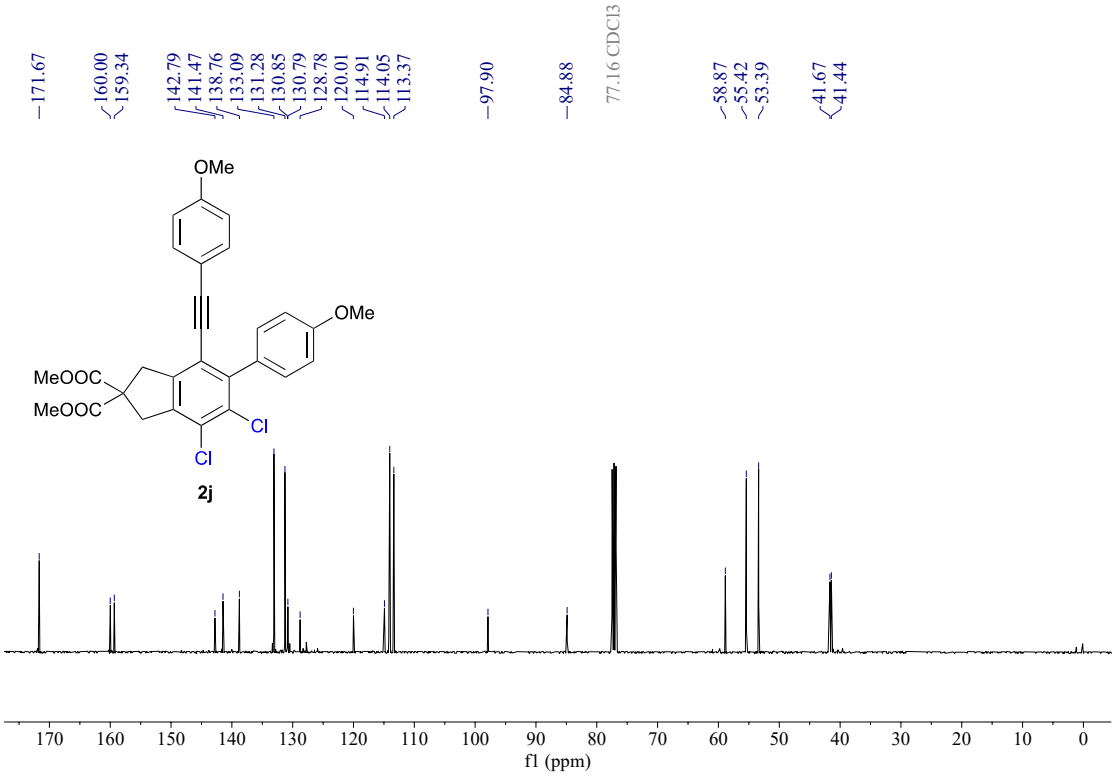
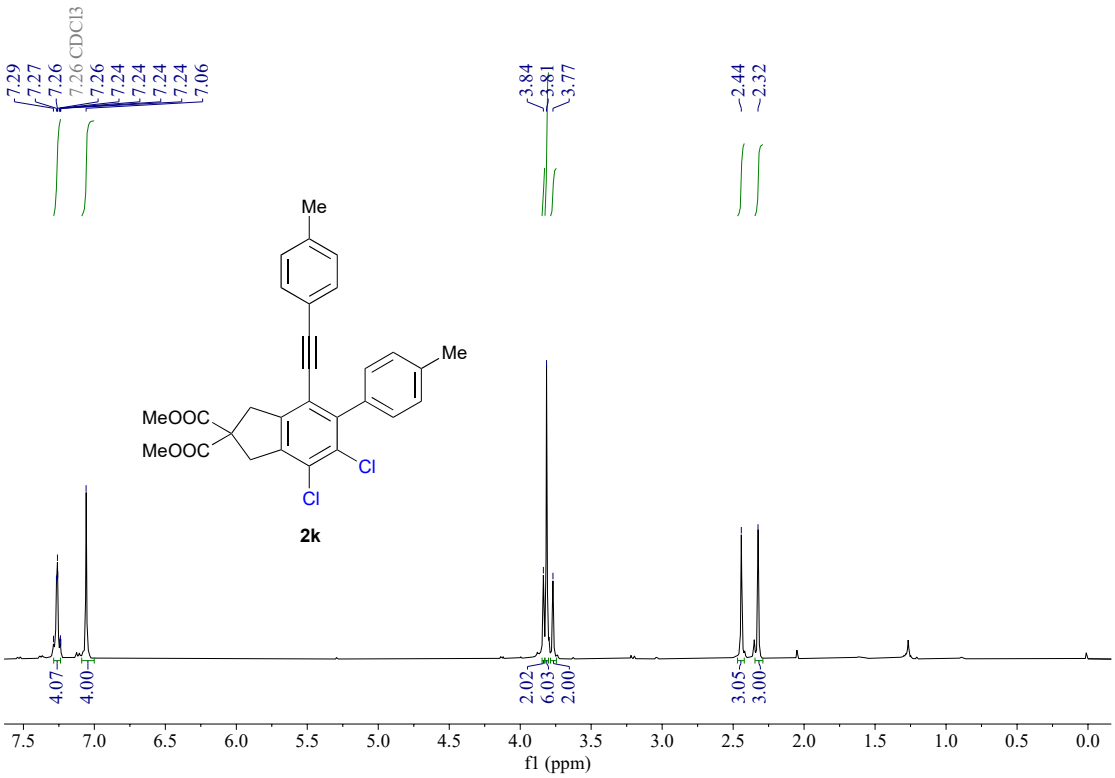
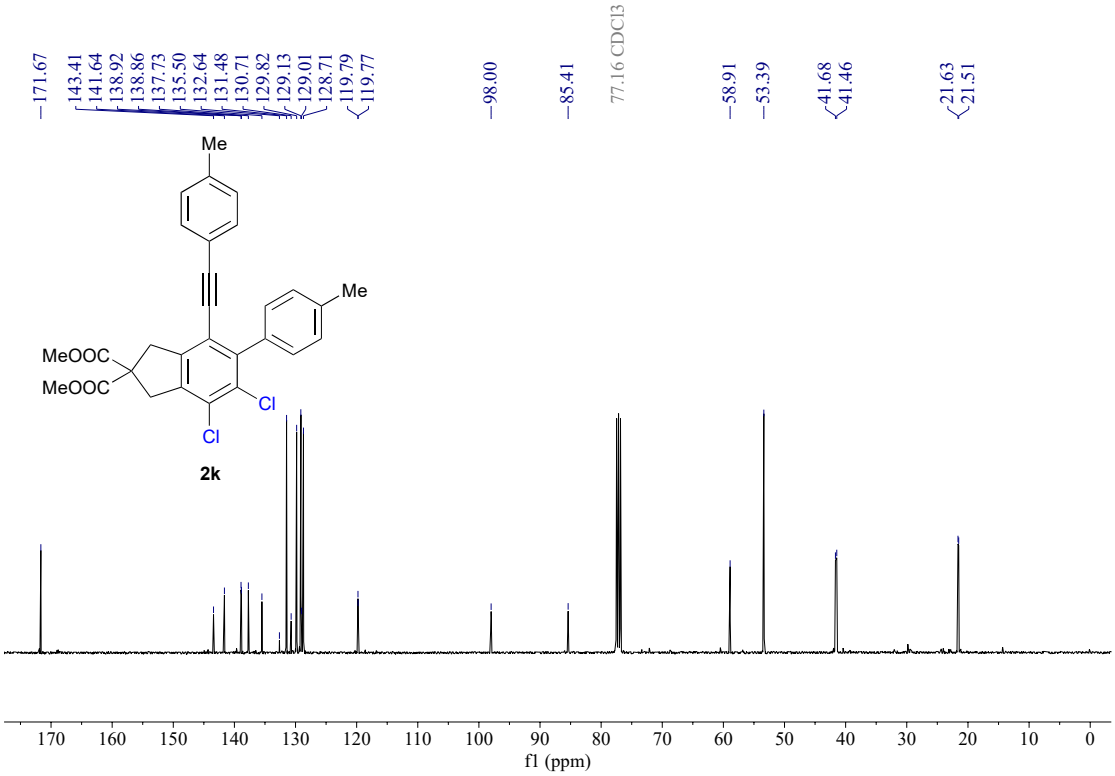
7.48
7.48
7.46
7.45
7.45
7.44
7.37
7.37
7.36
7.35
7.35
7.28
7.26 CDCl3
7.26
7.24
7.23
7.22
7.14
7.14
7.14
7.14
7.13
7.12
3.86
3.82
3.79
MeOOC
MeOOC
Cl
Cl
2i
3.17
2.08
3.06
2.03
2.02
6.00
2.00
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

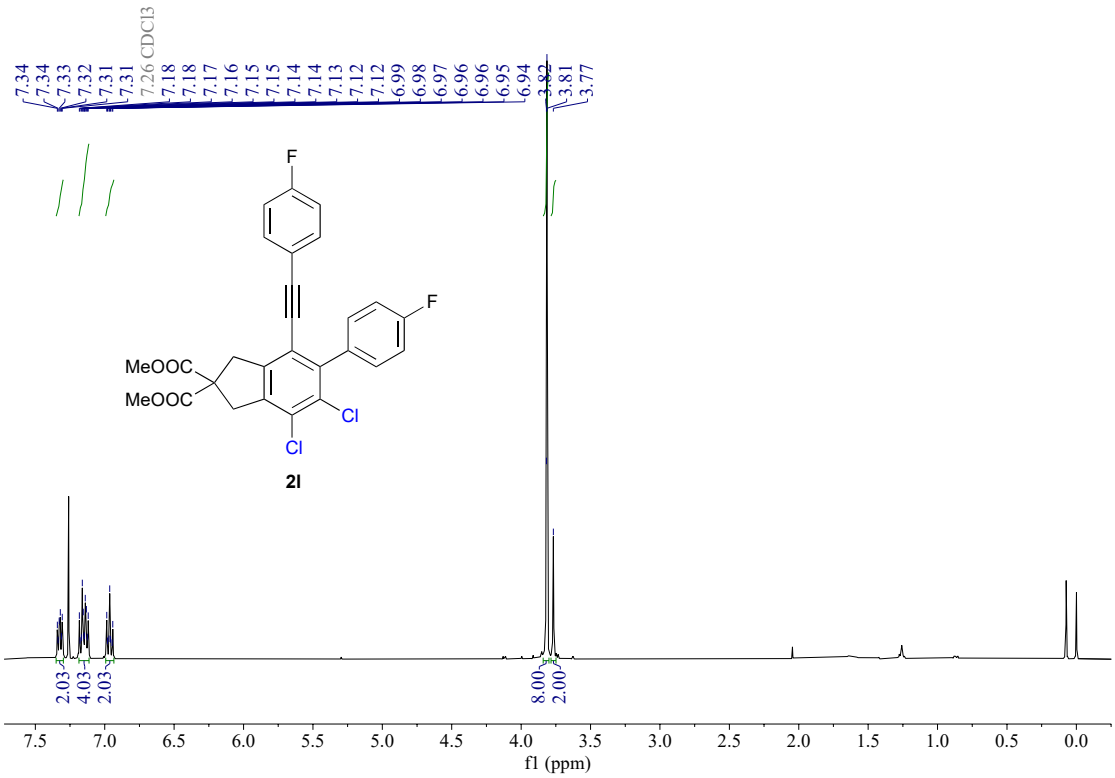

171.63
143.53
141.74
139.11
138.42
131.56
130.67
129.90
129.28
128.71
128.36
128.08
128.06
122.73
119.48
97.85
85.81
77.16 CDCl3
58.90
53.43
41.63
41.45
MeOOC
MeOOC
Cl
Cl
2i
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

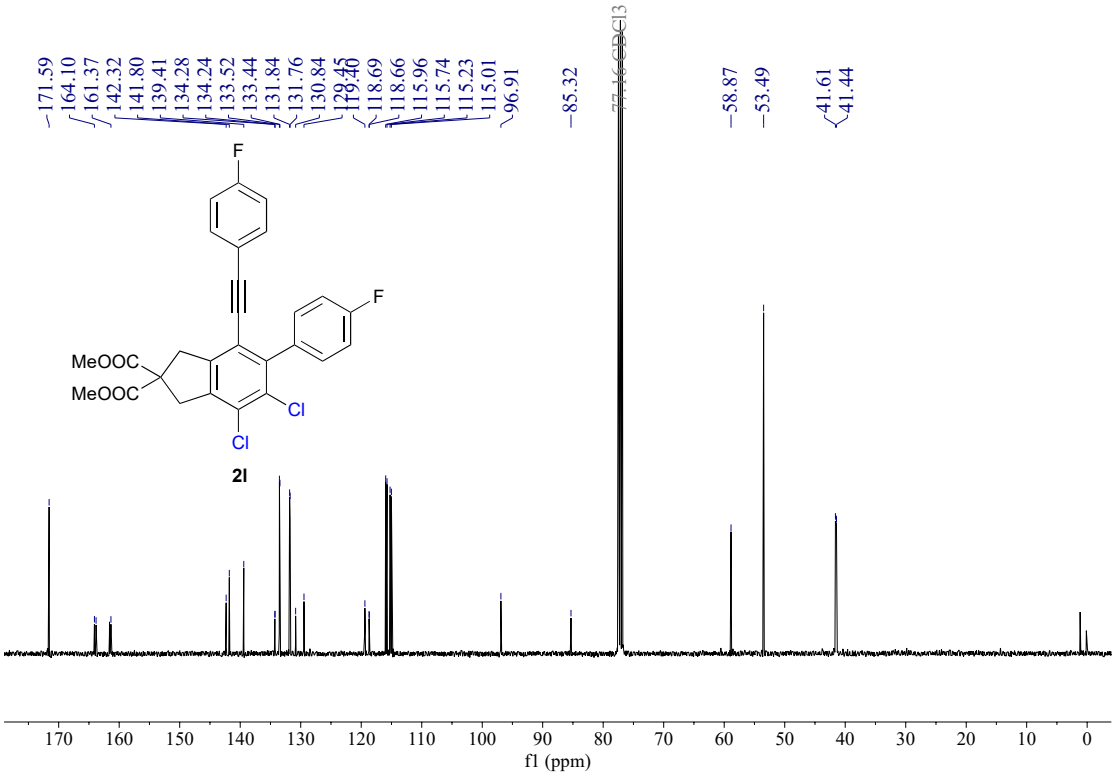

7.31
7.29
7.26 CDCl3
7.14
7.12
7.01
6.99
6.80
6.77
3.88
3.83
3.81
3.79
3.76
OMe
OMe
MeOOC
MeOOC
Cl
Cl
2j
2.10
2.00
2.10
2.00
3.01
2.03
6.01
3.02
2.00
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

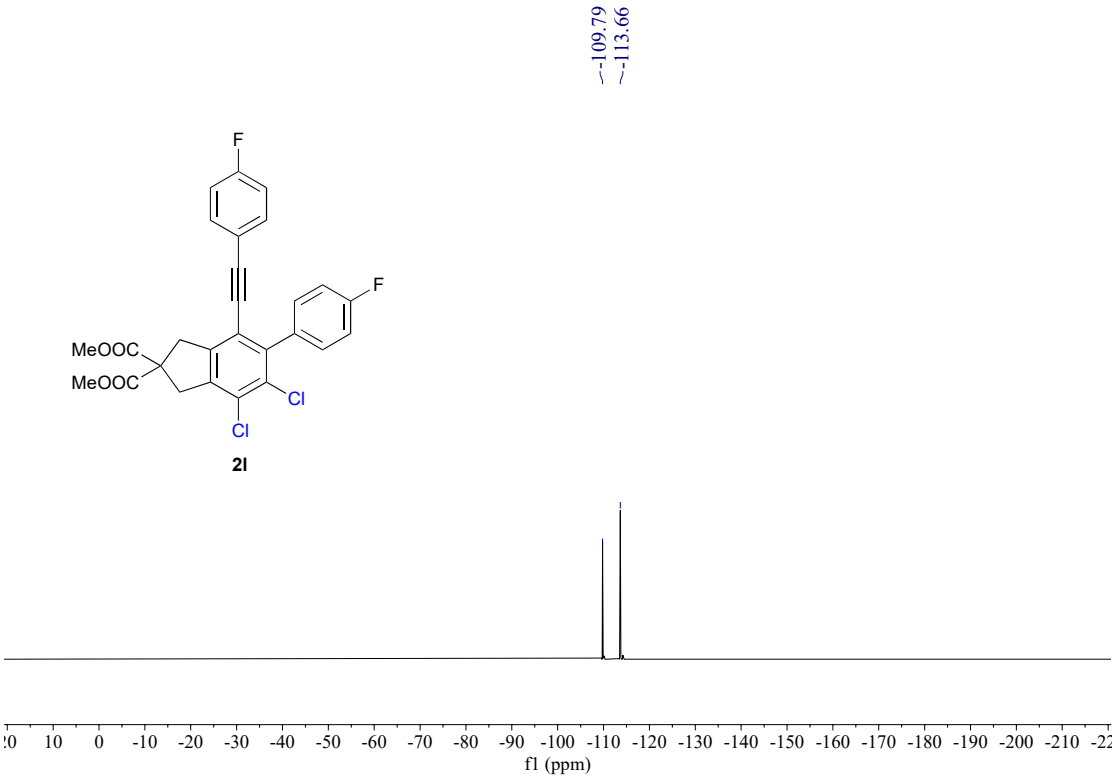

171.67
160.00
159.34
142.79
141.47
138.76
133.09
131.28
130.85
130.79
128.78
120.01
114.91
114.05
113.37
97.90
84.88
77.16 CDCl3
58.87
55.42
53.39
41.67
41.44
OMe
OMe
MeOOC
MeOOC
Cl
Cl
2j
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

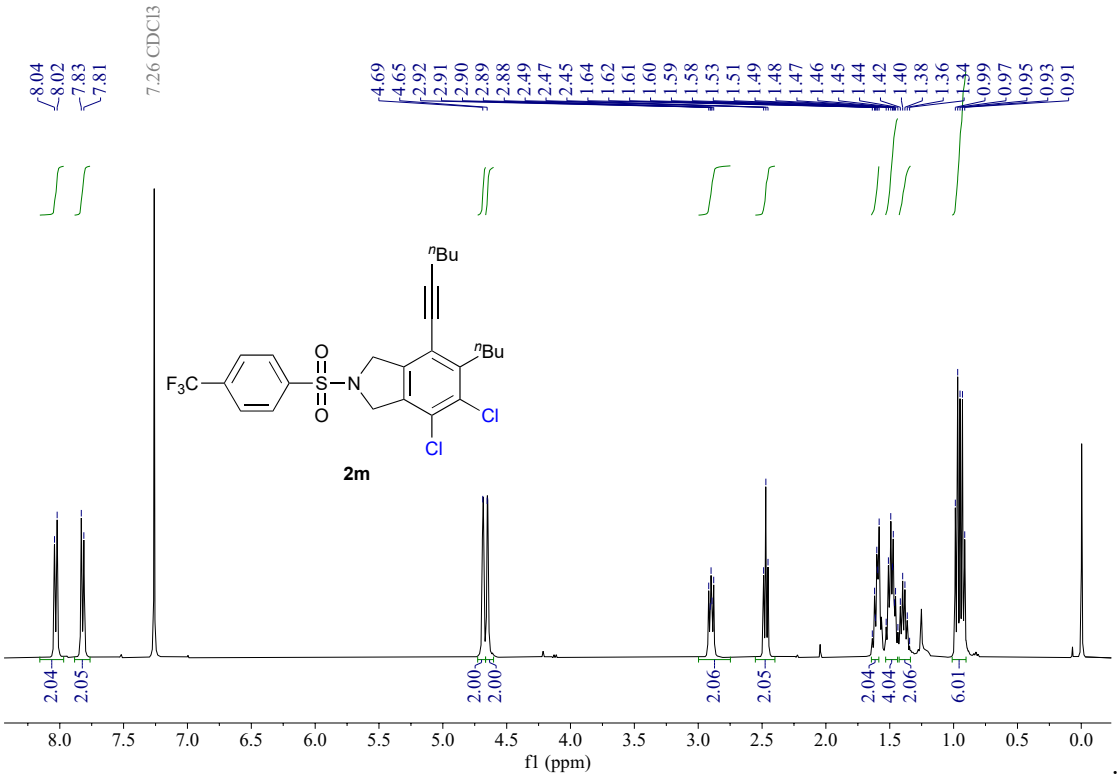

7.29
7.27
7.26
7.26 CDCl3
7.26
7.24
7.24
7.24
7.24
7.06
3.84
3.81
3.77
2.44
2.32
Me
Me
MeOOC
MeOOC
Cl
Cl
2k
4.07
4.00
2.02
6.03
2.00
3.05
3.00
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

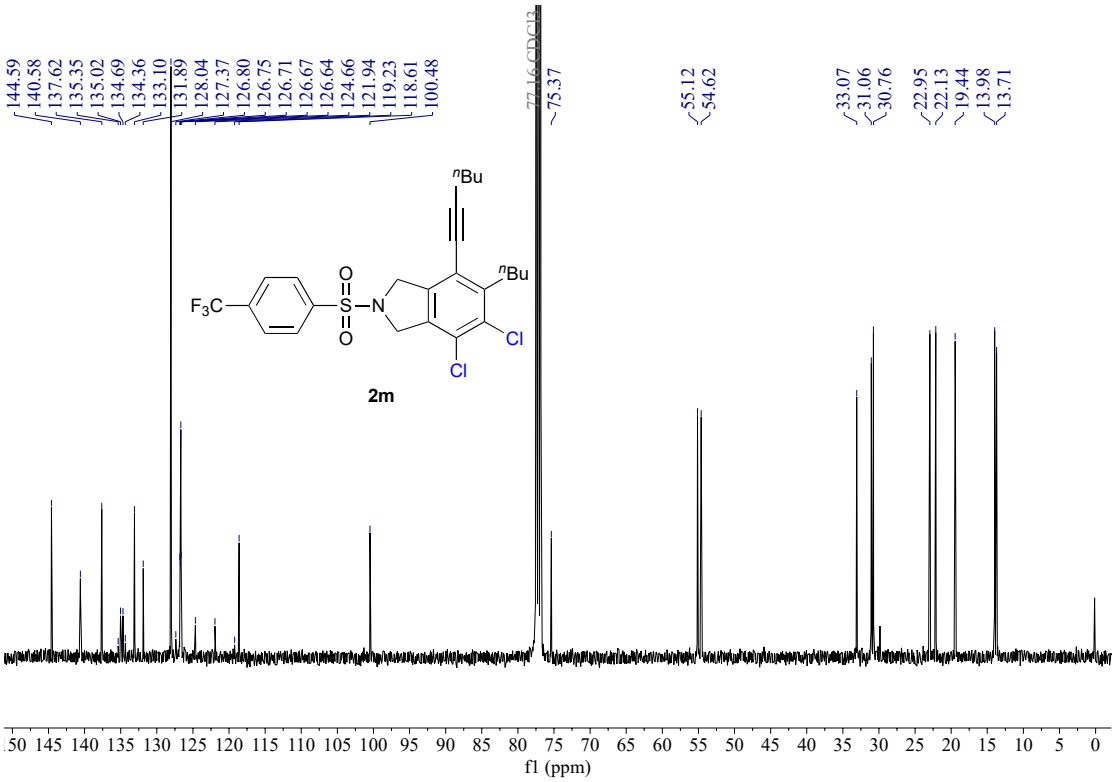

171.67
143.41
141.64
138.92
138.86
137.73
135.50
132.64
131.48
130.71
129.82
129.13
129.01
128.71
119.79
119.77
98.00
85.41
77.16 CDCl3
58.91
53.39
41.68
41.46
21.63
21.51
Me
Me
MeOOC
MeOOC
Cl
Cl
2k
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

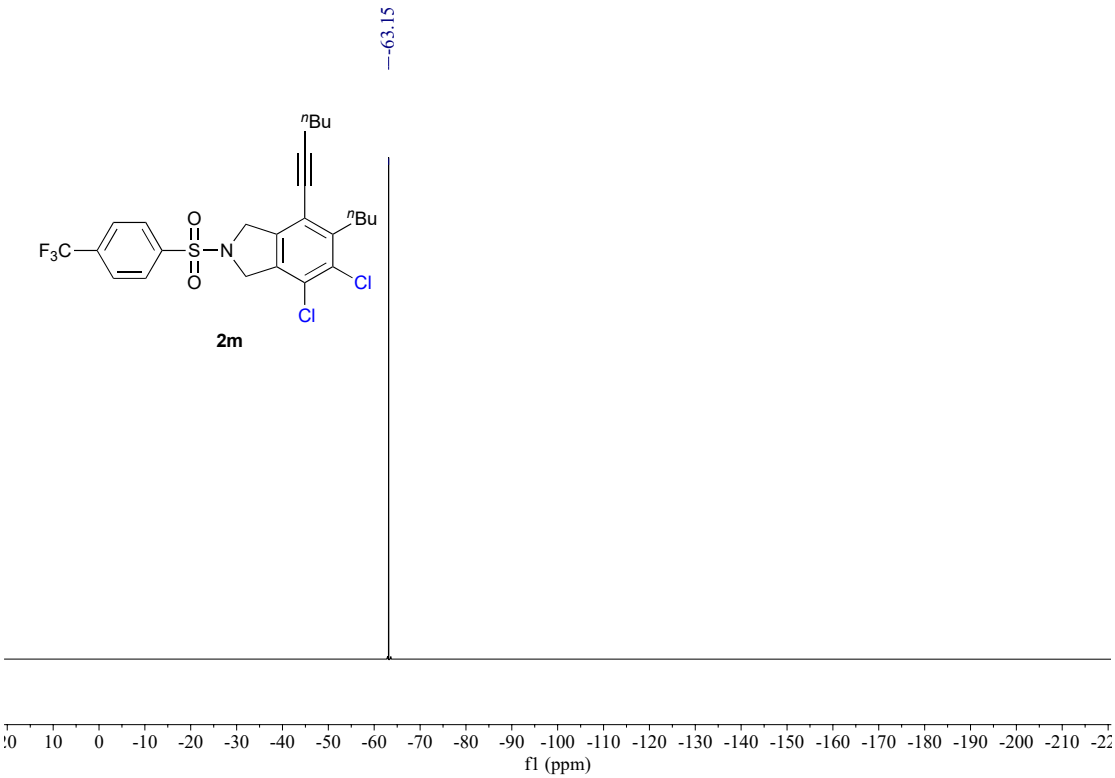

7.34
7.34
7.33
7.32
7.31
7.31
7.26 CDCl3
7.18
7.18
7.17
7.16
7.15
7.15
7.14
7.14
7.13
7.12
7.12
6.99
6.98
6.97
6.96
6.96
6.95
6.94
3.82
3.81
3.77
F
F
MeOOC
MeOOC
Cl
Cl
2l
2.03
4.03
2.03
8.00
2.00
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

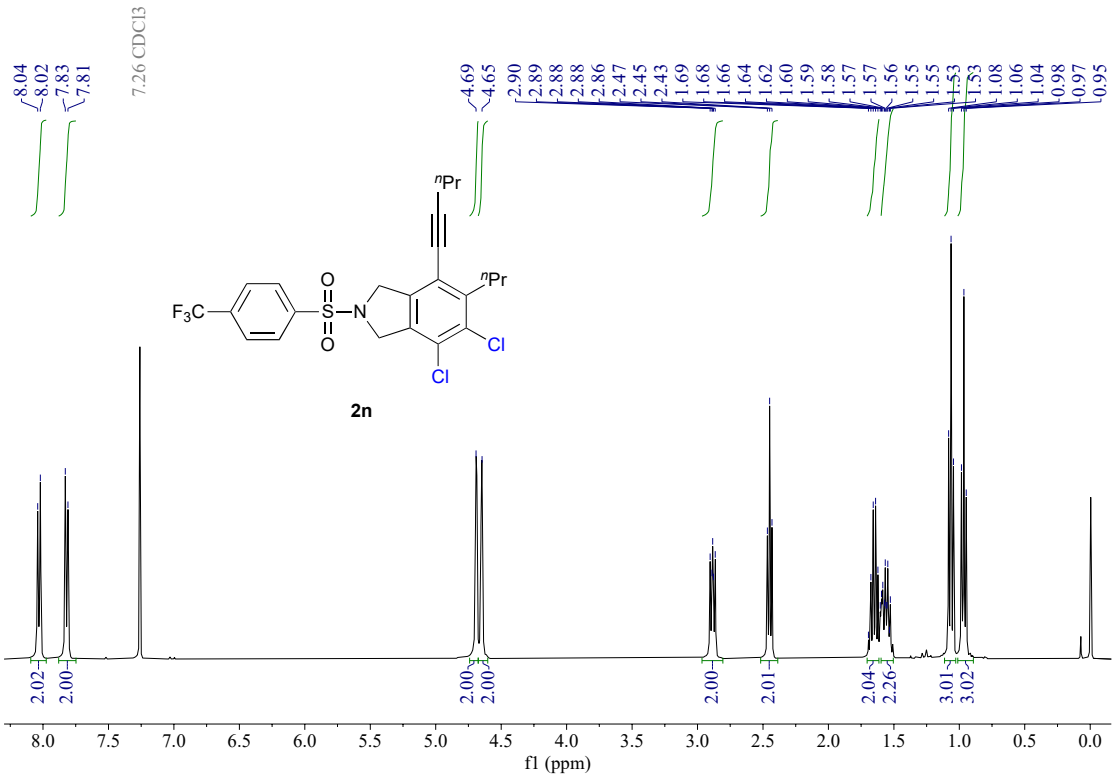

171.59
164.10
161.37
142.32
141.80
139.41
134.28
134.24
133.52
133.44
131.84
131.76
130.84
118.69
118.66
115.96
115.74
115.23
115.01
96.91
85.32
77.16 CDCl3
58.87
53.49
41.61
41.44
F
F
MeOOC
MeOOC
Cl
Cl
2l
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

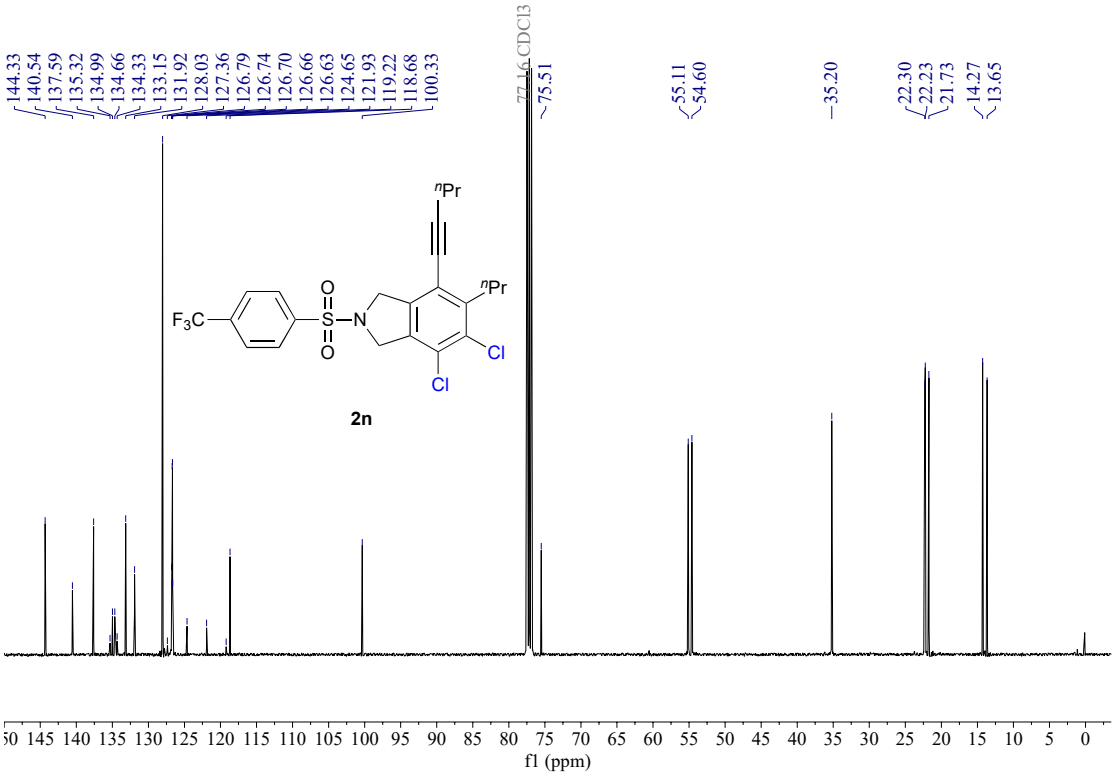

-109.79
-113.66
F
F
MeOOC
MeOOC
Cl
Cl
2l
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

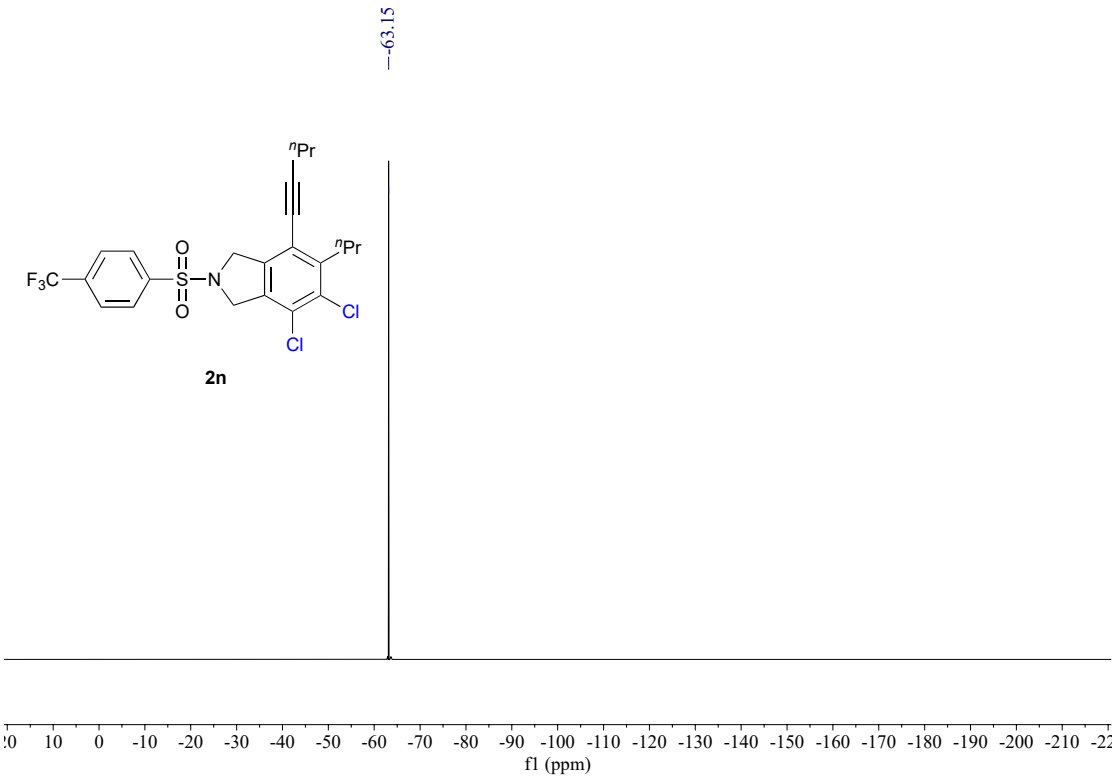

8.04
8.02
7.83
7.81
7.26 CDCl3
4.69
4.65
2.92
2.91
2.90
2.89
2.88
2.49
2.47
2.45
1.64
1.62
1.61
1.60
1.59
1.58
1.53
1.51
1.49
1.48
1.47
1.46
1.45
1.44
1.42
1.40
1.38
1.36
1.34
0.99
0.97
0.95
0.93
0.91
nBu
nBu
F3C
S
N
O
O
Cl
Cl
2m
2.04
2.05
2.00
2.00
2.06
2.05
2.04
4.04
2.06
6.01
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

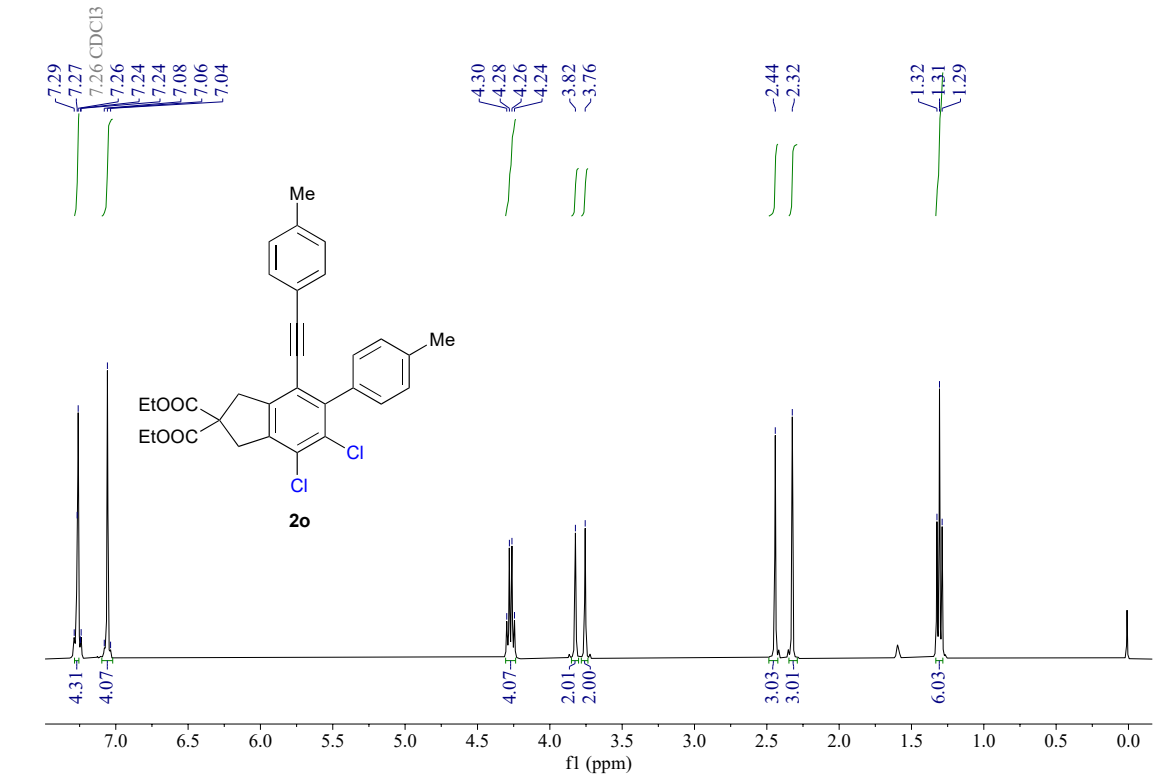

144.59
140.58
137.62
135.35
135.02
134.69
134.36
133.10
131.89
128.04
127.37
126.80
126.75
126.71
126.67
126.64
124.66
121.94
119.23
118.61
100.48
77.16 CDCl3
75.37
55.12
54.62
33.07
31.06
30.76
22.95
22.13
19.44
13.98
13.71
nBu
nBu
F3C
S
N
O
O
Cl
Cl
2m
50 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)

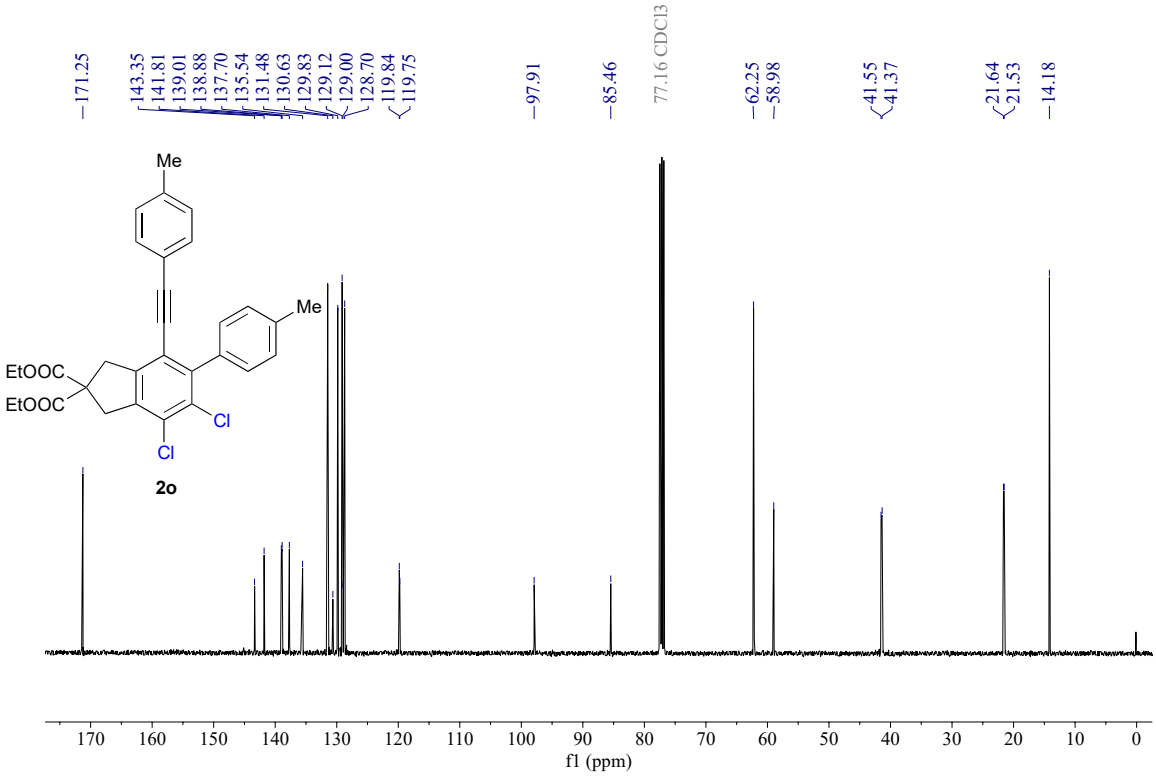

-63.15
nBu
nBu
F3C
O
S
N
O
Cl
Cl
2m
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

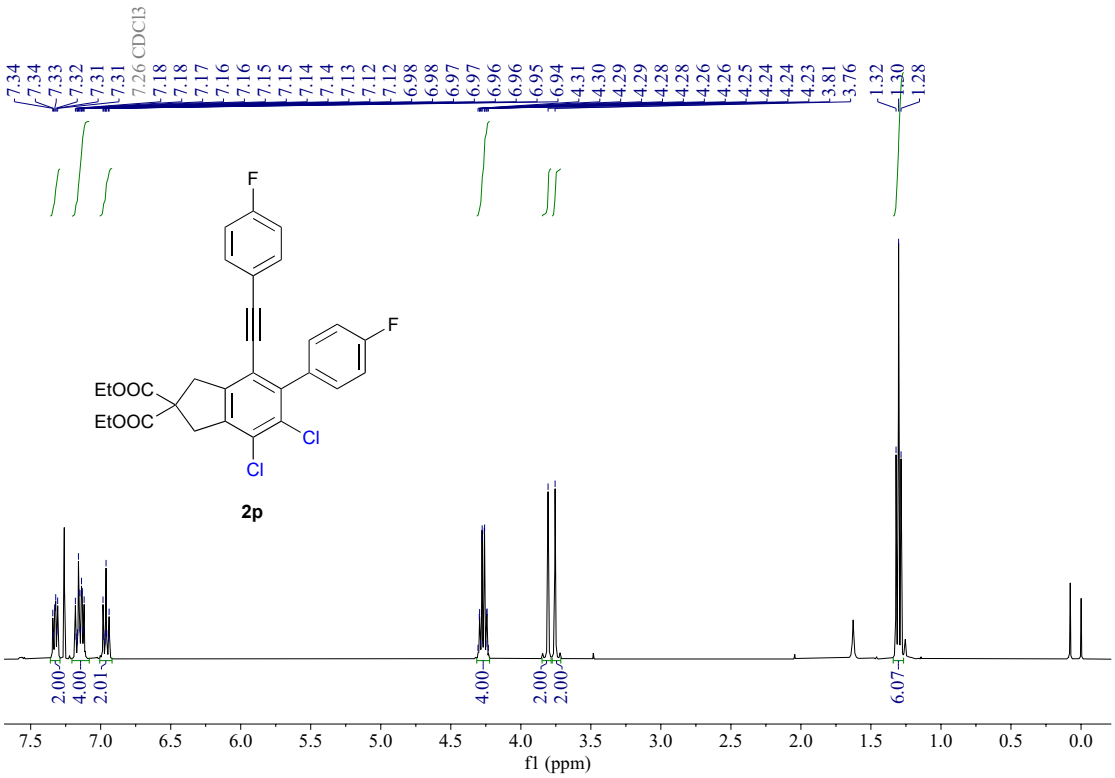

8.04
8.02
7.83
7.81
7.26 CDCl3
4.69
4.65
2.90
2.89
2.88
2.88
2.86
2.47
2.45
2.43
1.69
1.68
1.66
1.64
1.62
1.60
1.59
1.58
1.57
1.57
1.56
1.55
1.55
1.53
1.53
1.08
1.06
1.04
0.98
0.97
0.95
nPr
nPr
F3C
S
N
O
O
Cl
Cl
2n
2.02
2.00
2.00
2.00
2.00
2.01
2.04
2.26
3.01
3.02
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

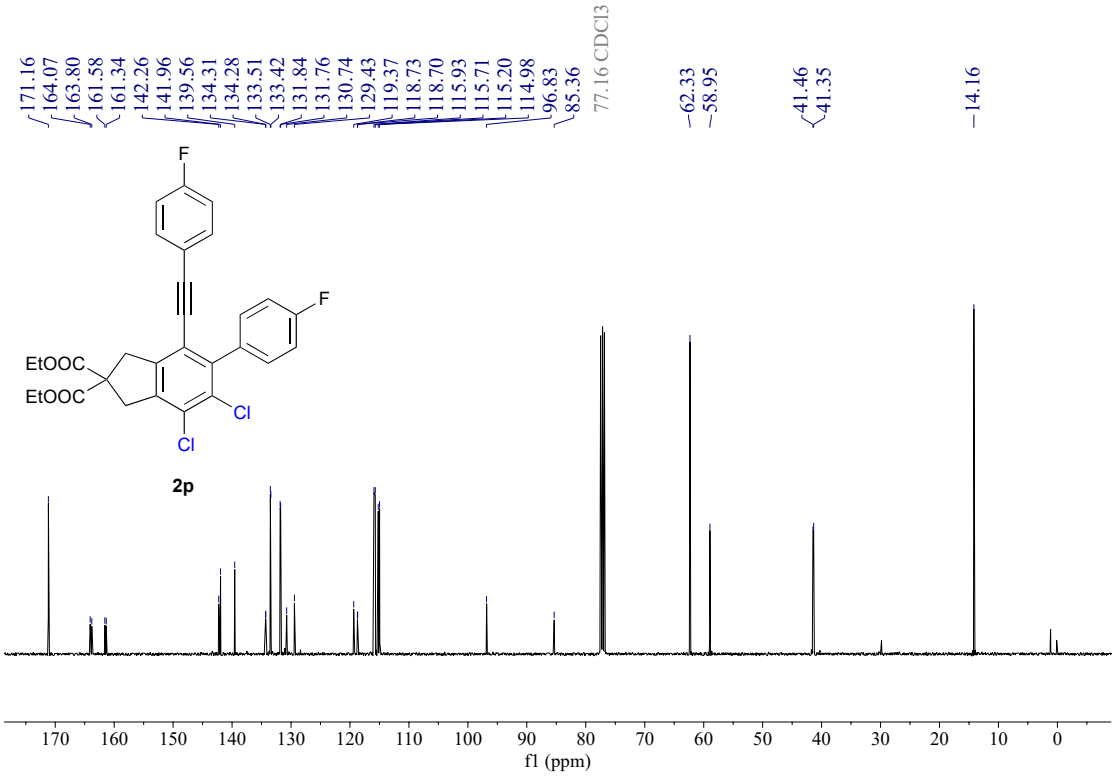

144.33
140.54
137.59
135.32
134.99
134.66
134.33
133.15
131.92
128.03
127.36
126.79
126.74
126.70
126.66
126.63
124.65
121.93
119.22
118.68
100.33
77.16 CDCl3
75.51
55.11
54.60
35.20
22.30
22.23
21.73
14.27
13.65
nPr
nPr
F3C
S
N
O
O
Cl
Cl
2n
50 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)


-63.15
nPr
nPr
F3C
O
S
O
N
Cl
Cl
2n
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


7.29
7.27
7.26 CDCl3
7.26
7.24
7.24
7.08
7.06
7.04
4.30
4.28
4.26
4.24
3.82
3.76
2.44
2.32
1.32
1.31
1.29
Me
Me
EtOOC
EtOOC
Cl
Cl
2o
4.31
4.07
4.07
2.01
2.00
3.03
3.01
6.03
f1 (ppm)


171.25
143.35
141.81
139.01
138.88
137.70
135.54
131.48
130.63
129.83
129.12
129.00
128.70
119.84
119.75
97.91
85.46
77.16 CDCl3
62.25
58.98
41.55
41.37
21.64
21.53
14.18
Me
Me
EtOOC
EtOOC
Cl
Cl
2o
f1 (ppm)


7.34
7.34
7.33
7.32
7.31
7.31
7.26 CDCl3
7.18
7.18
7.17
7.16
7.16
7.15
7.15
7.14
7.14
7.13
7.12
7.12
6.98
6.98
6.97
6.96
6.96
6.95
6.94
4.31
4.30
4.29
4.29
4.28
4.28
4.26
4.26
4.25
4.24
4.24
4.23
3.81
3.76
1.32
1.30
1.28
F
F
EtOOC
EtOOC
Cl
Cl
2p
2.00
4.00
2.01
4.00
2.00
2.00
6.07
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
f1 (ppm)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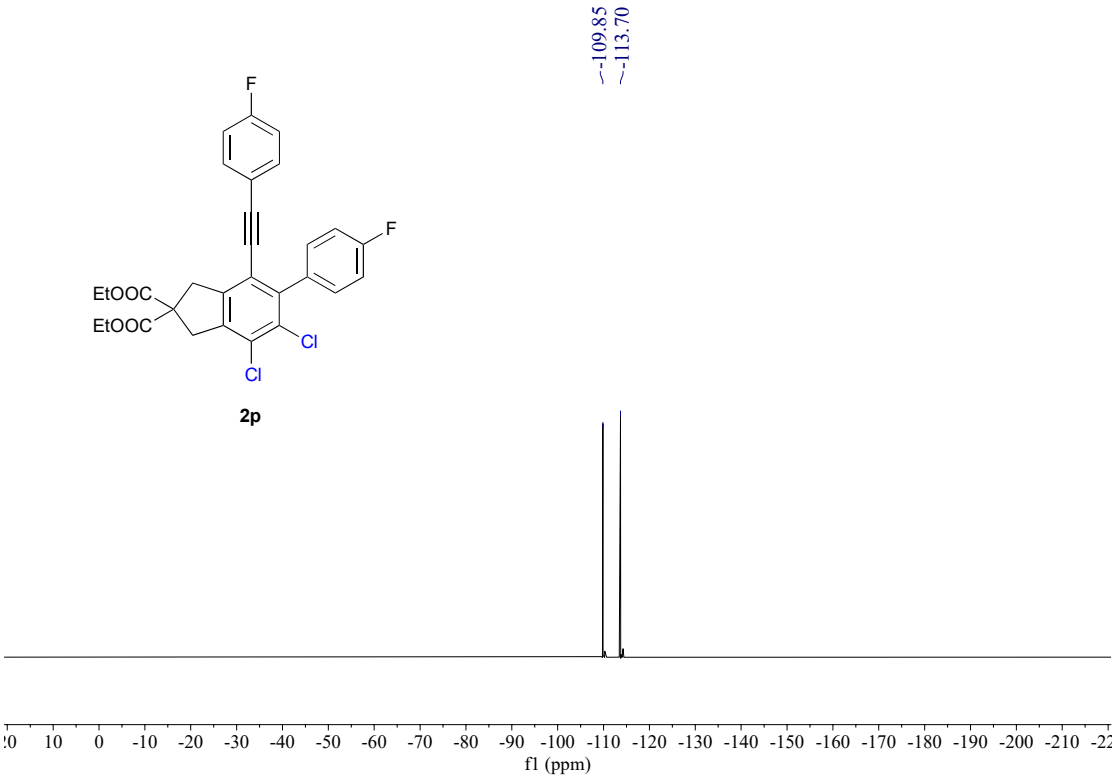
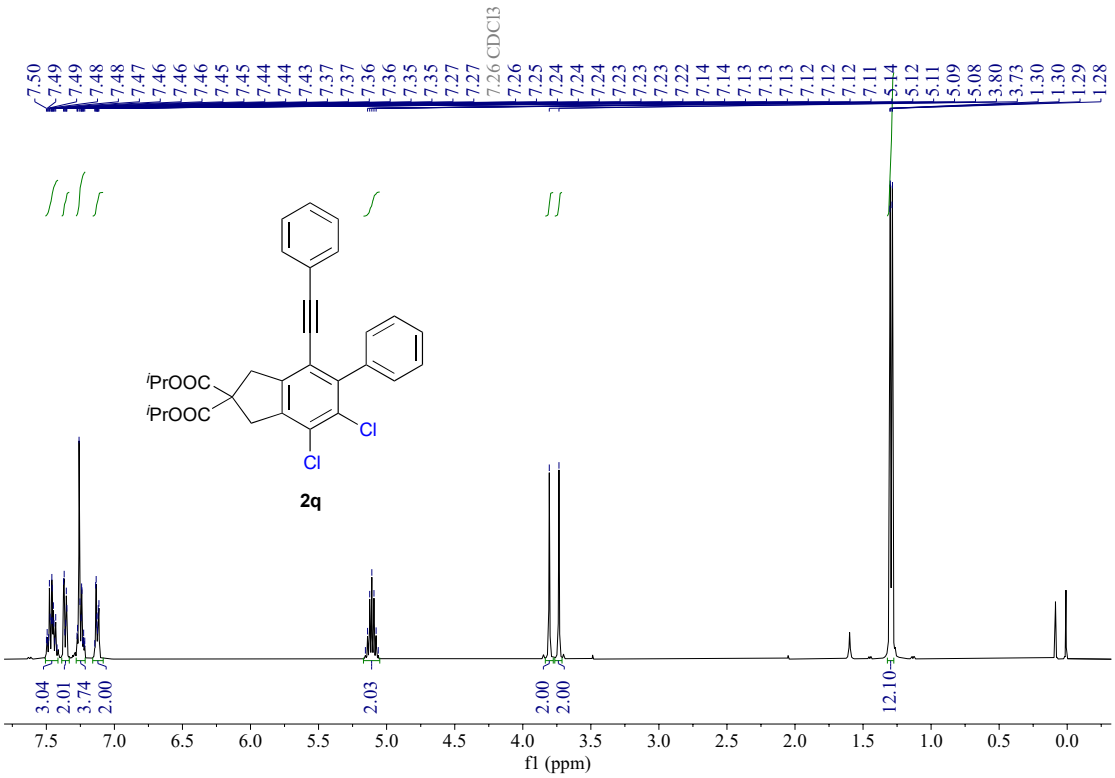
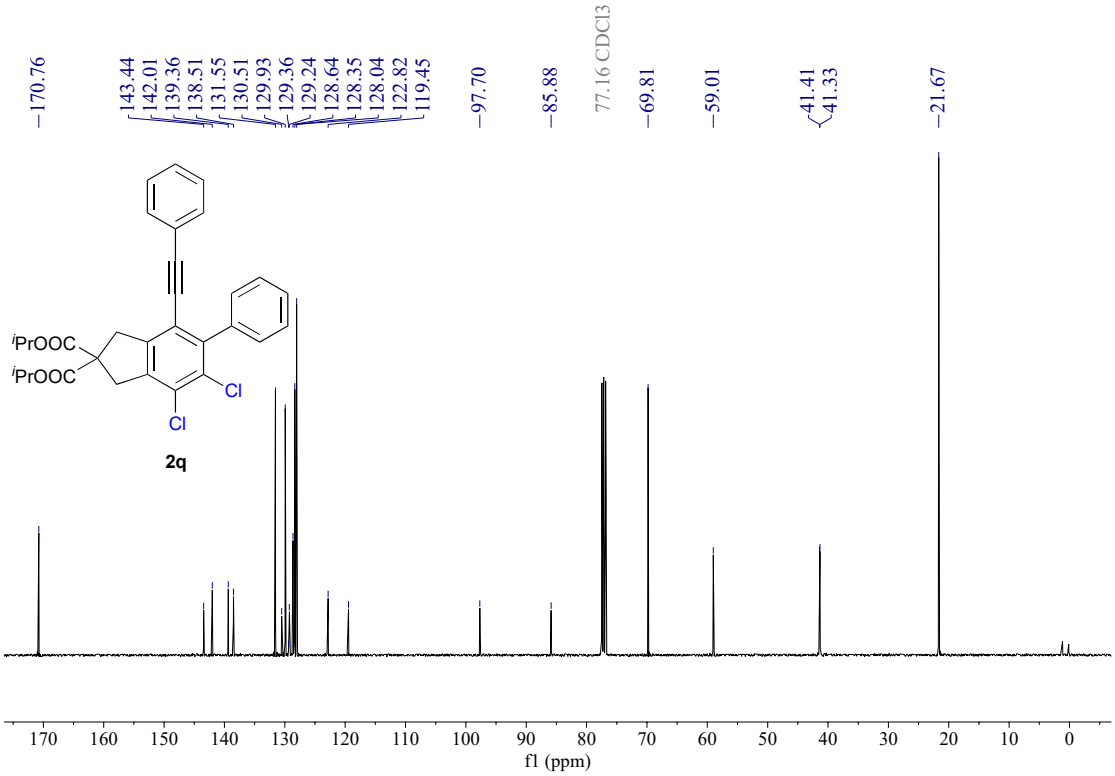
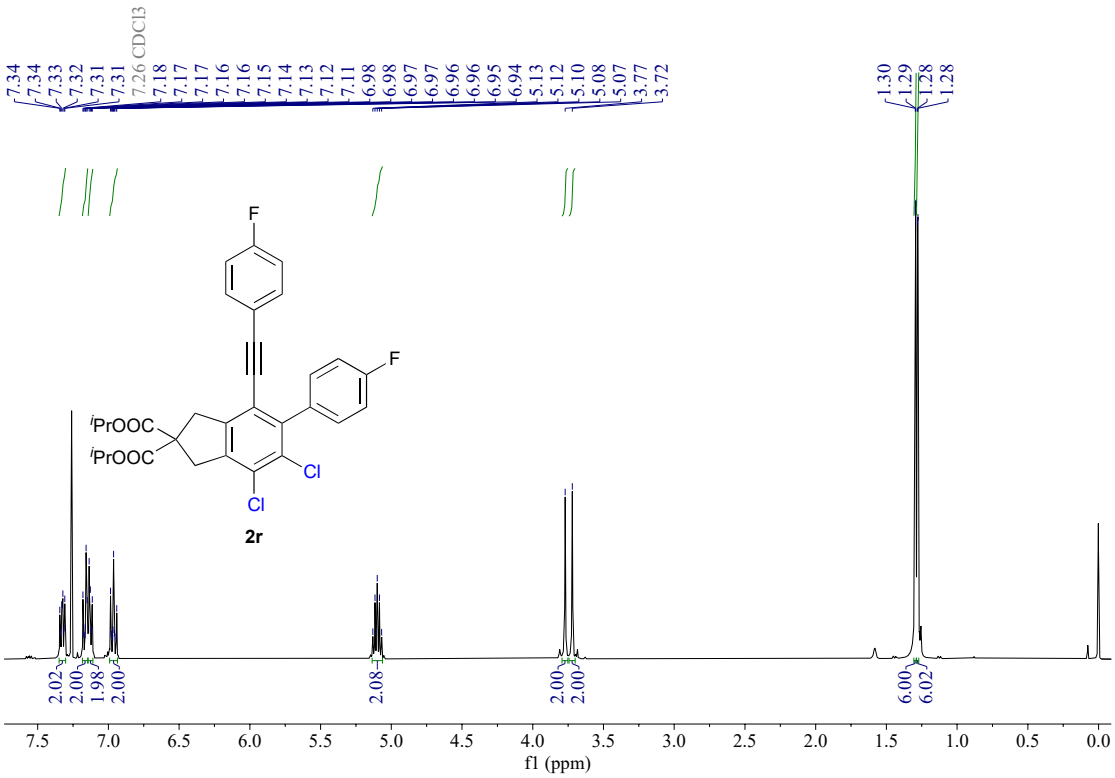
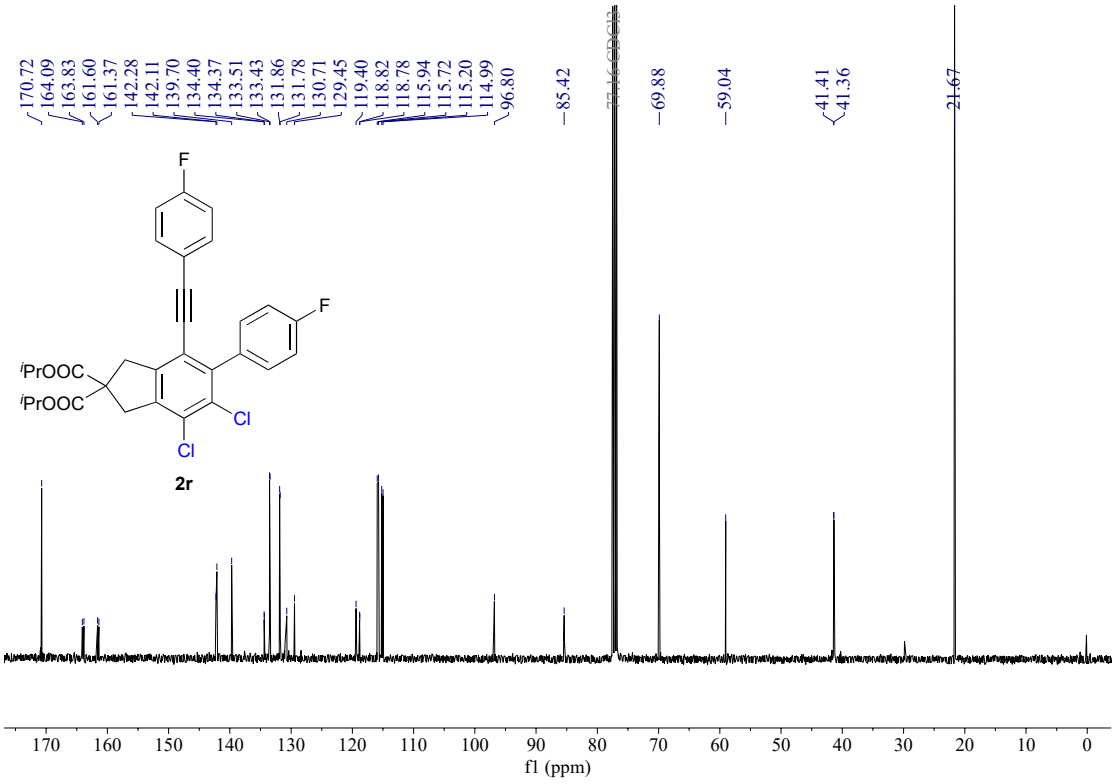
164.07
163.80
161.58
161.34
142.26
141.96
139.56
134.31
134.28
133.51
133.42
131.84
131.76
130.74
129.43
119.37
118.73
118.70
115.93
115.71
115.20
114.98
96.83
85.36
77.16 CDCl3
62.33
58.95
41.46
41.35
14.16
F
F
EtOOC
EtOOC
Cl
Cl
2p
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

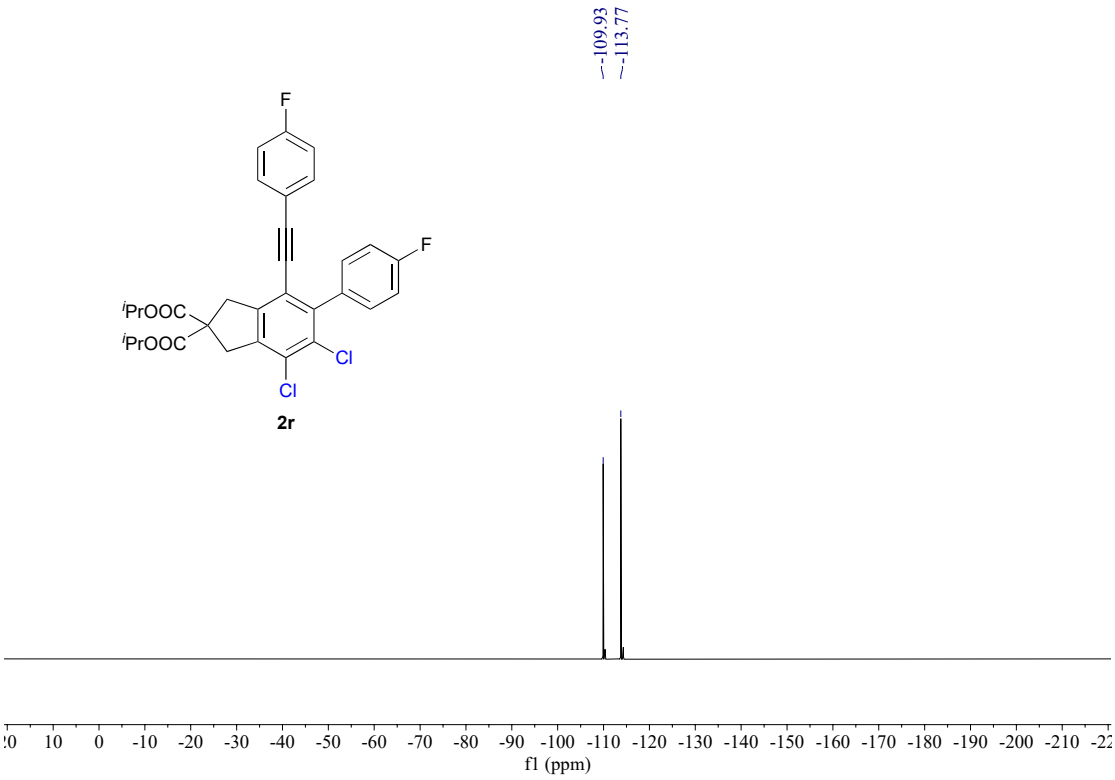

-109.85
-113.70
F
F
EtOOC
EtOOC
Cl
Cl
2p
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

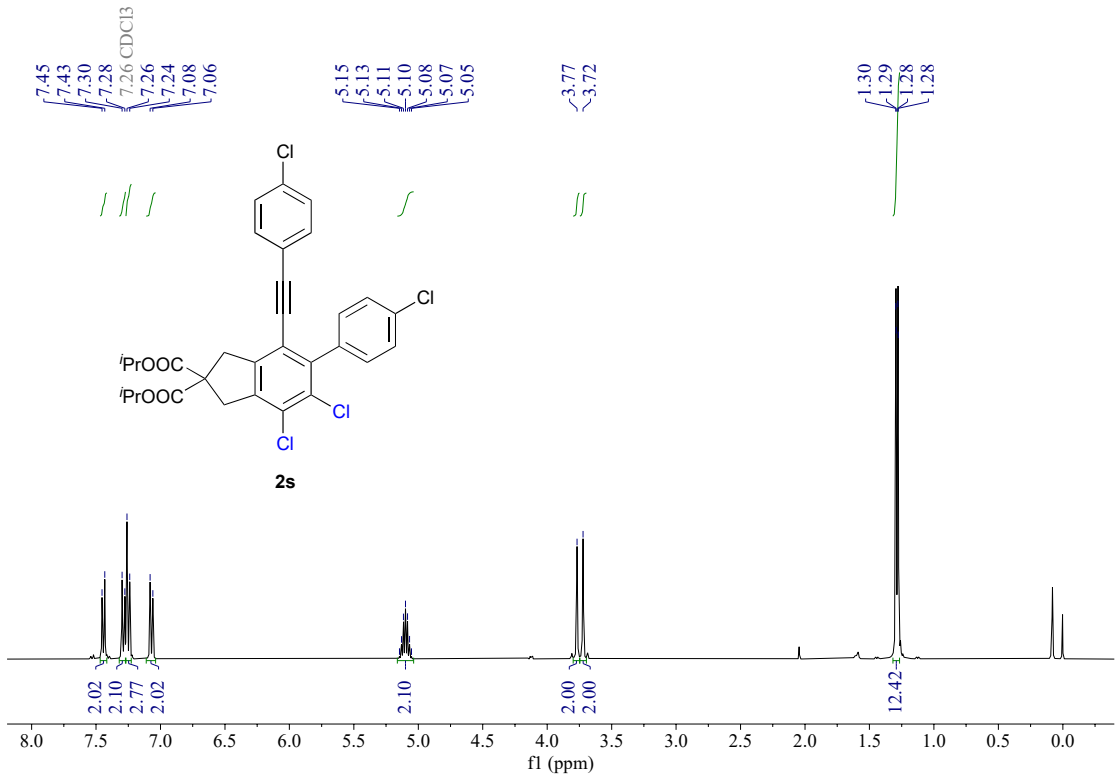

7.50 7.49 7.49 7.48 7.48 7.47 7.46 7.46 7.46 7.45 7.45 7.44 7.44 7.43 7.37 7.37 7.36 7.36 7.35 7.35 7.27 7.27 7.26 CDCl3 7.26 7.25 7.24 7.24 7.24 7.23 7.23 7.23 7.22 7.14 7.14 7.13 7.13 7.13 7.12 7.12 7.12 7.11 5.14 5.12 5.11 5.09 5.08 3.80 3.73 1.30 1.30 1.29 1.28
iPrOOC
iPrOOC
Cl
Cl
2q
3.04 2.01 3.74 2.00 2.03 2.00 2.00 12.10
f1 (ppm)

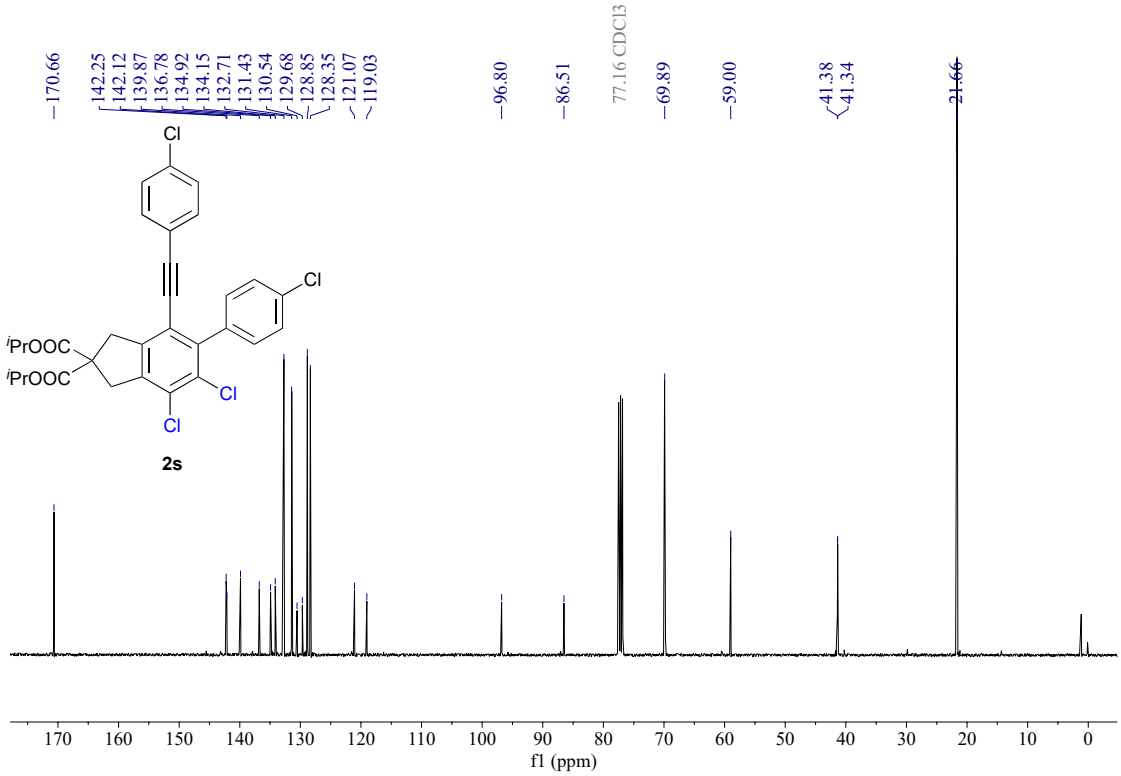

170.76 143.44 142.01 139.36 138.51 131.55 130.51 129.93 129.36 129.24 128.64 128.35 128.04 122.82 119.45 97.70 85.88 77.16 CDCl3 69.81 59.01 41.41 41.33 21.67
iPrOOC
iPrOOC
Cl
Cl
2q
f1 (ppm)

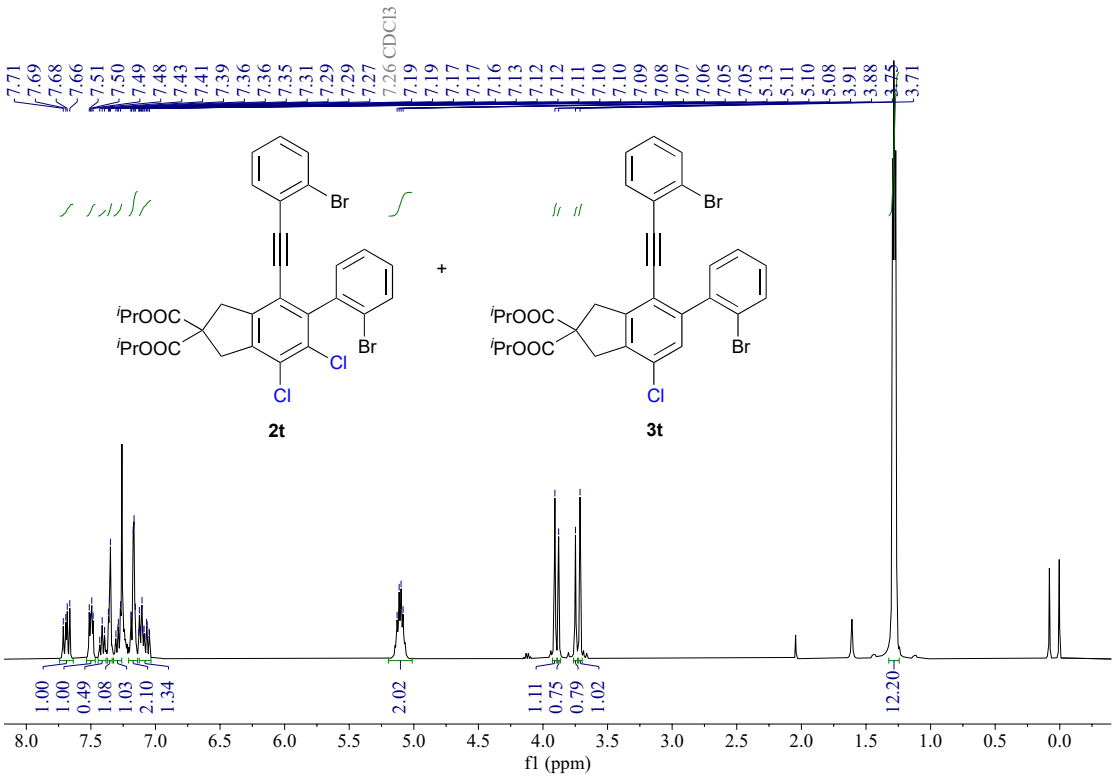

7.34
7.34
7.33
7.32
7.31
7.31
7.26 CDCl3
7.18
7.17
7.17
7.16
7.16
7.15
7.14
7.13
7.12
7.11
6.98
6.98
6.97
6.97
6.96
6.96
6.95
6.94
5.13
5.12
5.10
5.08
5.07
3.77
3.72
1.30
1.29
1.28
1.28
F
F
iPrOOC
iPrOOC
Cl
Cl
2r
2.02
2.00
1.98
2.00
2.08
2.00
2.00
6.00
6.02
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

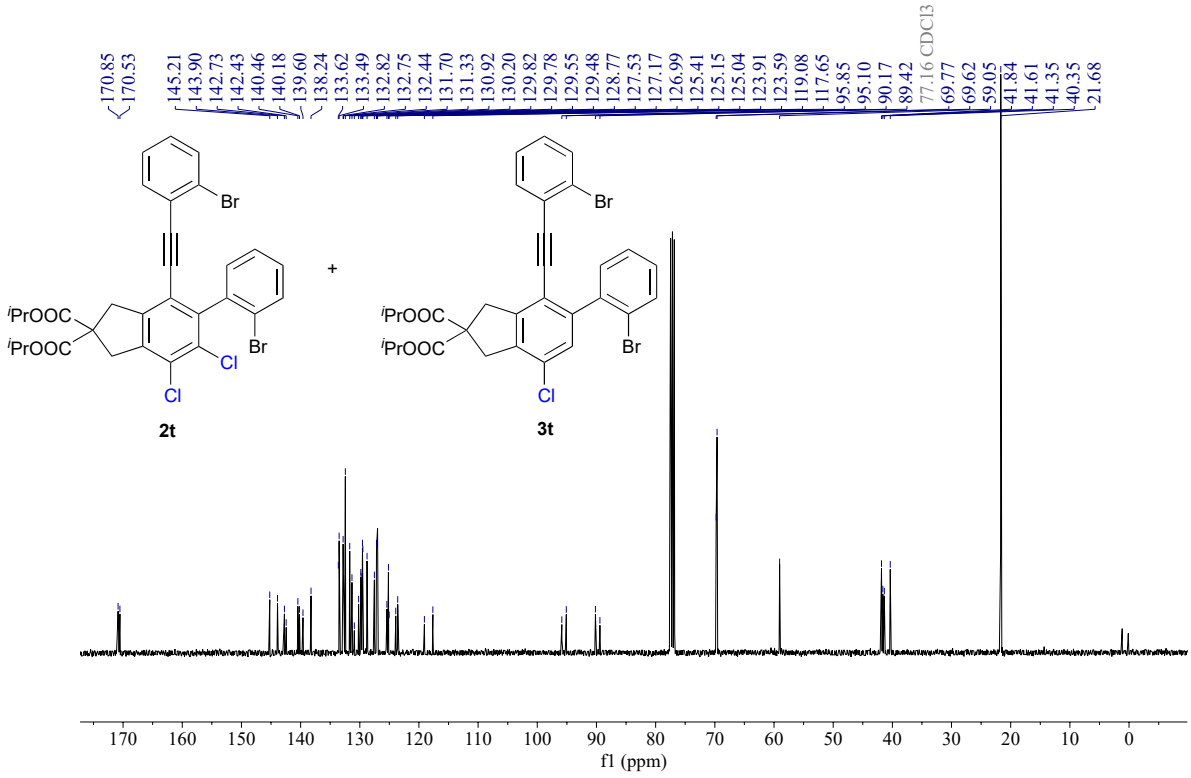

170.72
164.09
163.83
161.60
161.37
142.28
142.11
139.70
134.40
134.37
133.51
133.43
131.86
131.78
130.71
129.45
119.40
118.82
118.78
115.94
115.72
115.20
114.99
96.80
85.42
77.16 CDCl3
69.88
59.04
41.41
41.36
21.67
F
F
iPrOOC
iPrOOC
Cl
Cl
2r
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


-109.93
-113.77
F
F
iPrOOC
iPrOOC
Cl
Cl
2r
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


7.45
7.43
7.30
7.28
7.26 CDCl3
7.26
7.24
7.08
7.06
5.15
5.13
5.11
5.10
5.08
5.07
5.05
3.77
3.72
1.30
1.29
1.28
1.28
Cl
Cl
iPrOOC
iPrOOC
Cl
Cl
2s
2.02
2.10
2.77
2.02
2.10
2.00
2.00
12.42
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
f1 (ppm)


170.66
142.25
142.12
139.87
136.78
134.92
134.15
132.71
131.43
130.54
129.68
128.85
128.35
121.07
119.03
96.80
86.51
77.16 CDCl3
69.89
59.00
41.38
41.34
21.66
Cl
Cl
iPrOOC
iPrOOC
Cl
Cl
2s
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.71
7.69
7.68
7.66
7.51
7.50
7.49
7.48
7.43
7.41
7.39
7.36
7.36
7.35
7.31
7.29
7.29
7.27
7.26 CDCl3
7.19
7.19
7.17
7.17
7.16
7.13
7.12
7.12
7.11
7.10
7.10
7.09
7.08
7.07
7.06
7.05
7.05
5.13
5.11
5.10
5.08
3.91
3.88
3.75
3.71
Br
iPrOOC
iPrOOC
Cl
Br
Cl
2t
+
Br
iPrOOC
iPrOOC
Br
Cl
3t
1.00
1.00
0.49
1.08
1.03
2.10
1.34
2.02
1.11
0.75
0.79
1.02
12.20
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
f1 (ppm)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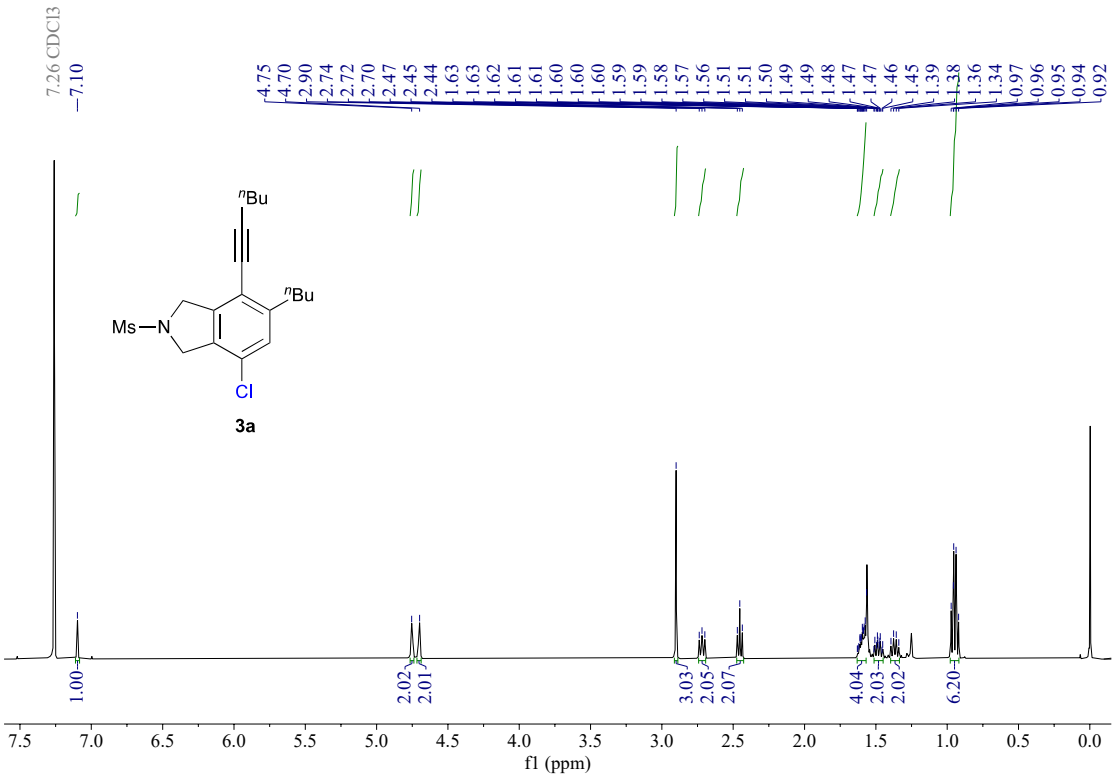
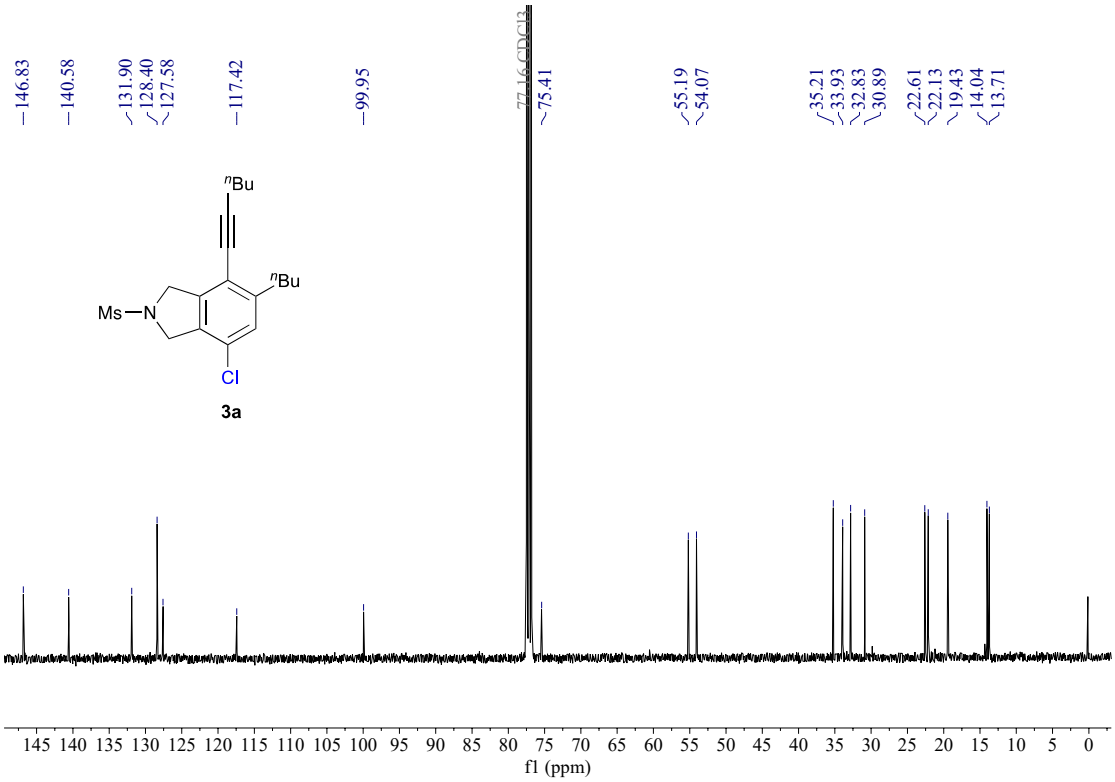
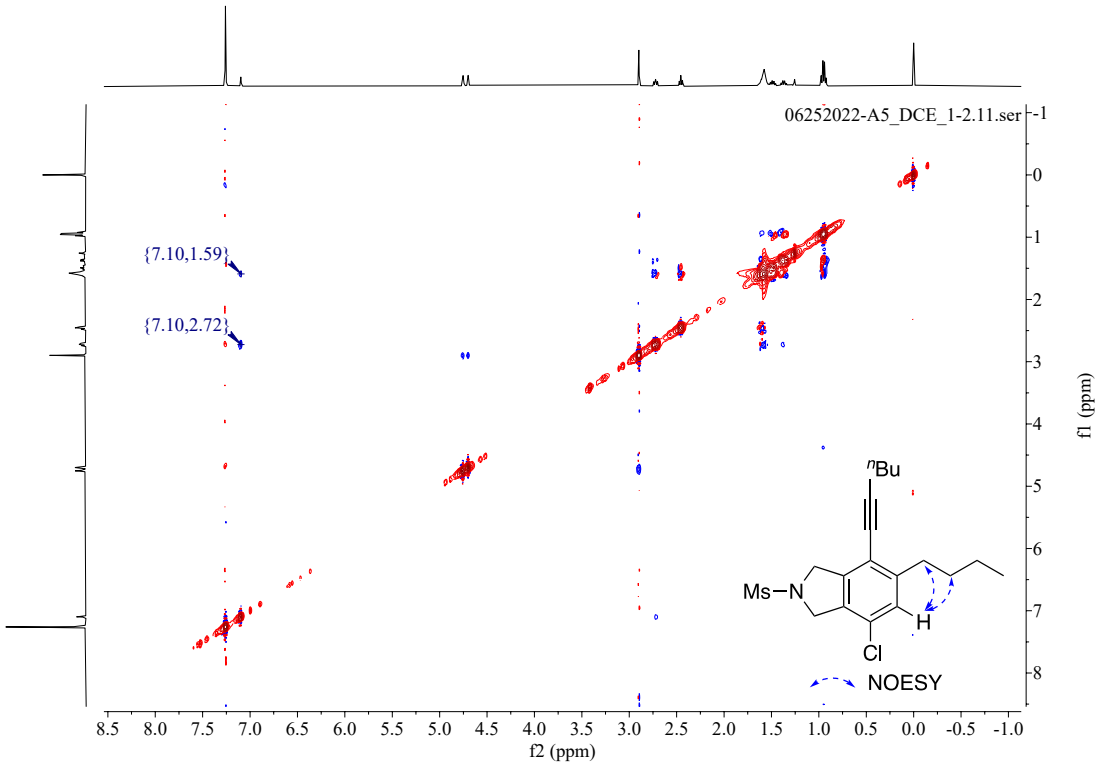
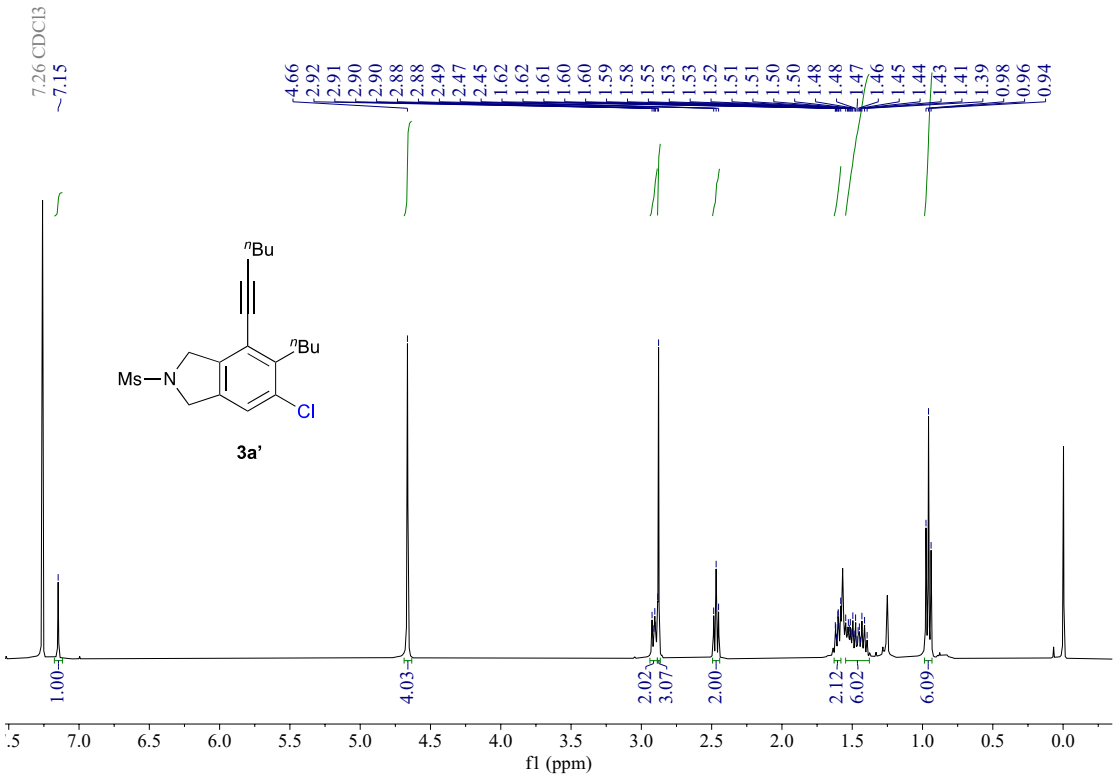
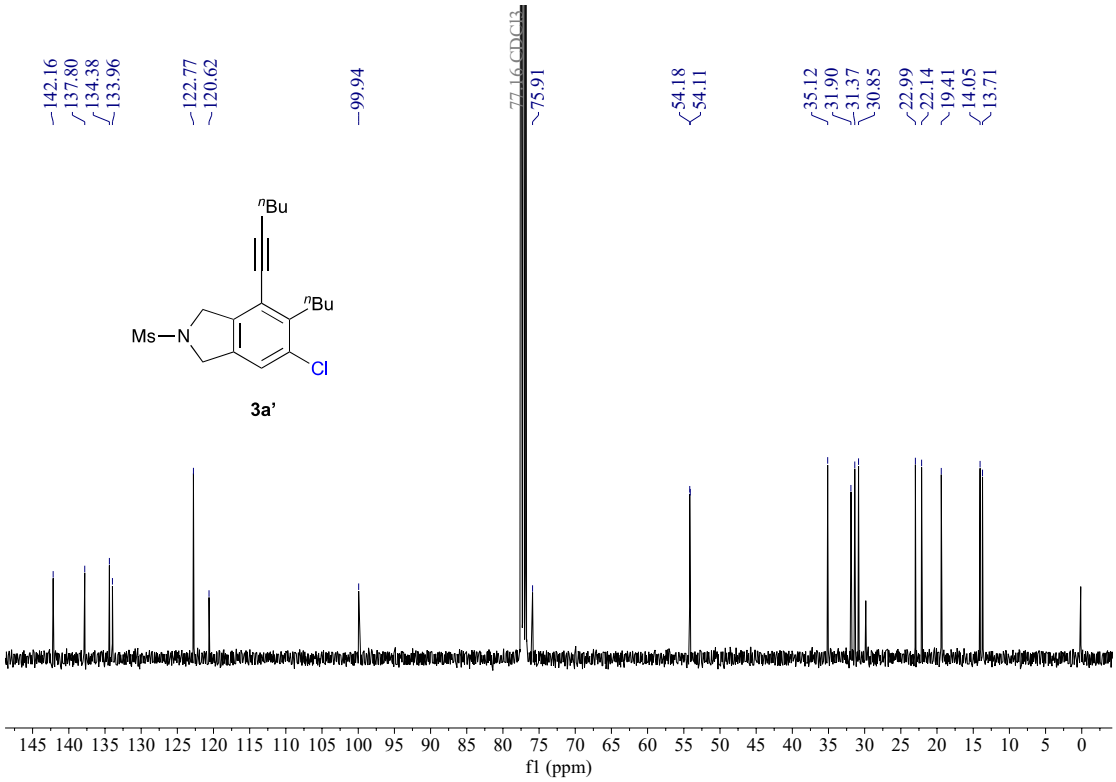
170.53
145.21
143.90
142.73
142.43
140.46
140.18
139.60
138.24
133.62
133.49
132.82
132.75
132.44
131.70
131.33
130.92
130.20
129.82
129.78
129.55
129.48
128.77
127.53
127.17
126.99
125.41
125.15
125.04
123.91
123.59
119.08
117.65
95.85
95.10
90.17
89.42
77.16 CDCl3
69.77
69.62
59.05
41.84
41.61
41.35
40.35
21.68
Br
iPrOOC
iPrOOC
Cl
Br
Cl
2t
+
Br
iPrOOC
iPrOOC
Br
Cl
3t
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

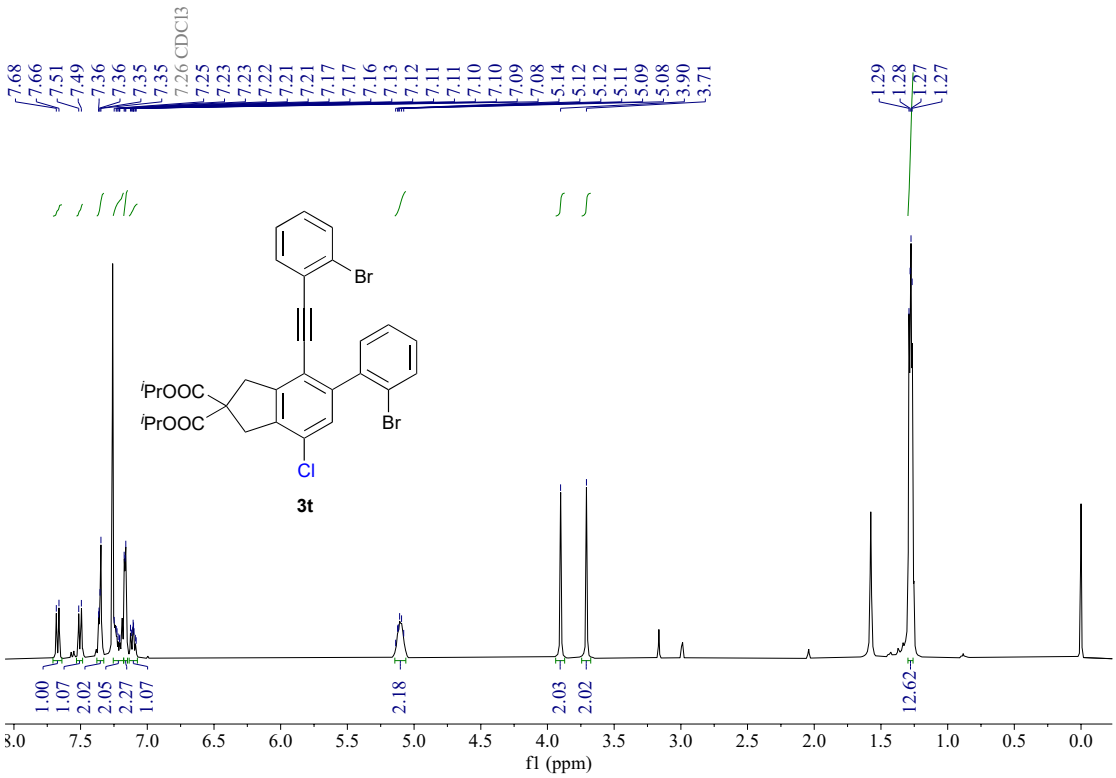

7.26 CDCl3
7.10
4.75
4.70
2.90
2.74
2.72
2.70
2.47
2.45
2.44
1.63
1.63
1.62
1.61
1.61
1.60
1.60
1.60
1.59
1.59
1.58
1.57
1.56
1.51
1.51
1.50
1.49
1.49
1.48
1.47
1.47
1.46
1.45
1.39
1.38
1.36
1.34
0.97
0.96
0.95
0.94
0.92
nBu
nBu
Ms—N
Cl
3a
1.00
2.02
2.01
3.03
2.05
2.07
4.04
2.03
2.02
6.20
7.5 7.0 6.5 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
f1 (ppm)

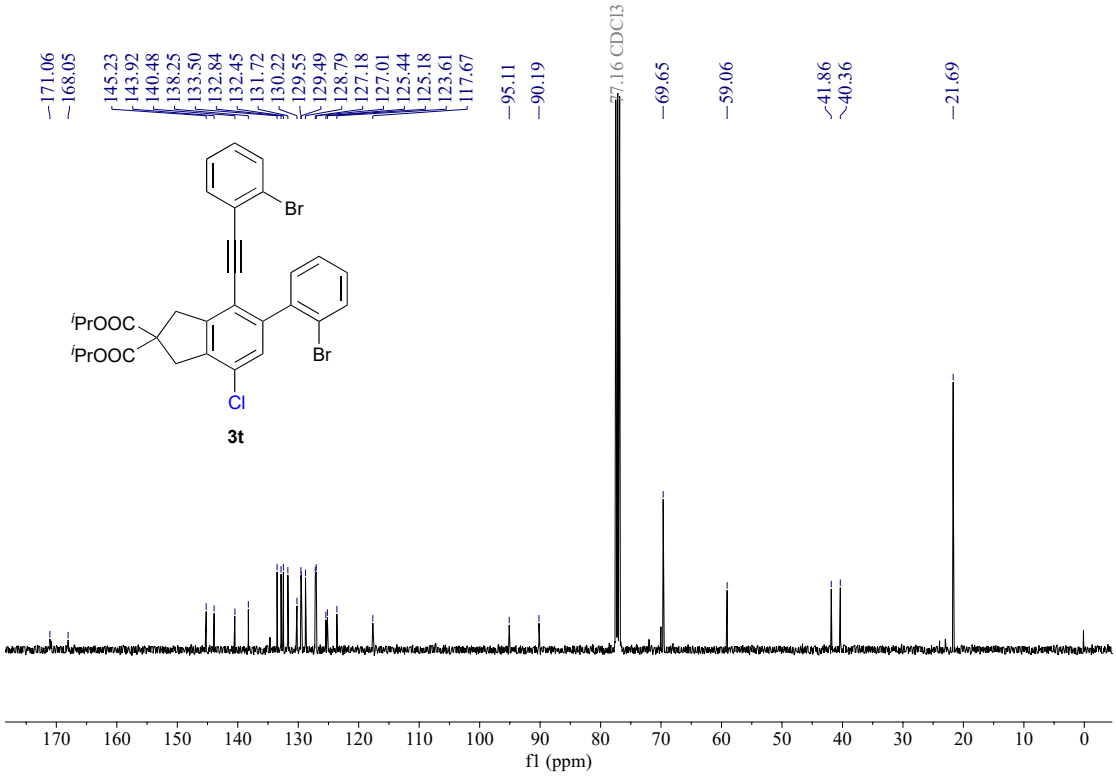

146.83
140.58
131.90
128.40
127.58
117.42
99.95
77.16 CDCl3
75.41
55.19
54.07
35.21
33.93
32.83
30.89
22.61
22.13
19.43
14.04
13.71
nBu
nBu
Ms—N
Cl
3a
145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)

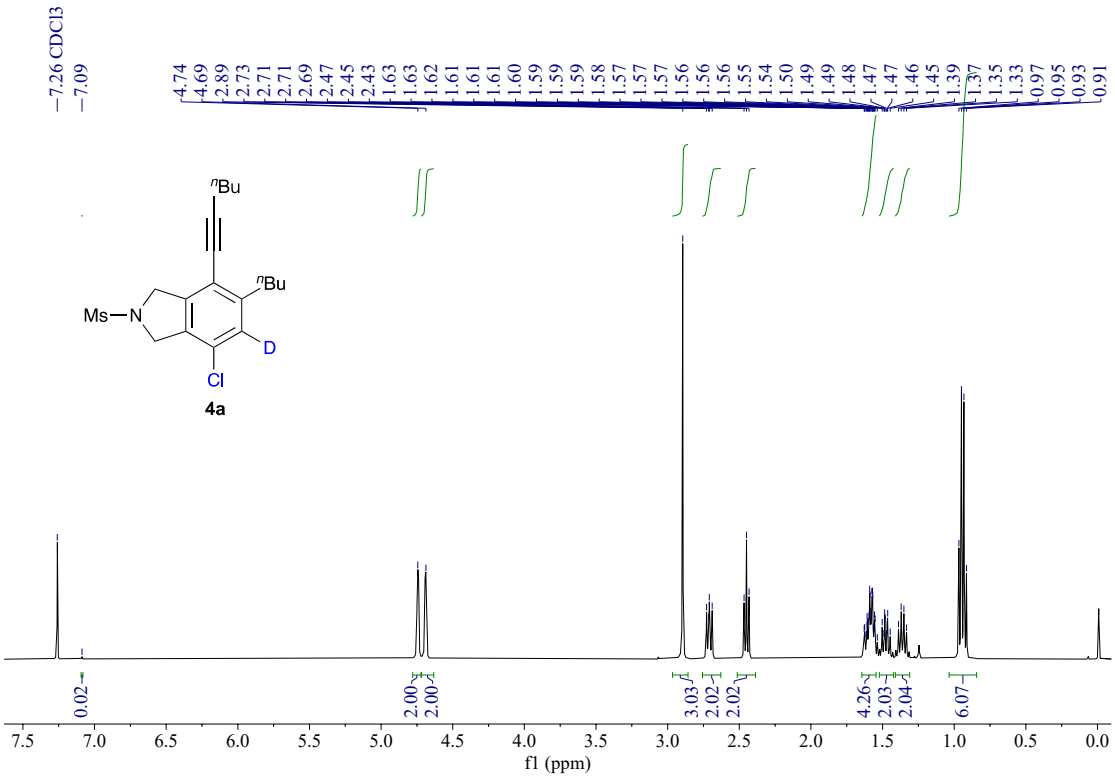

06252022-A5_DCE_1-2.11.ser
{7.10,1.59}
{7.10,2.72}
nBu
Ms–N
H
Cl
NOESY
f2 (ppm)
f1 (ppm)

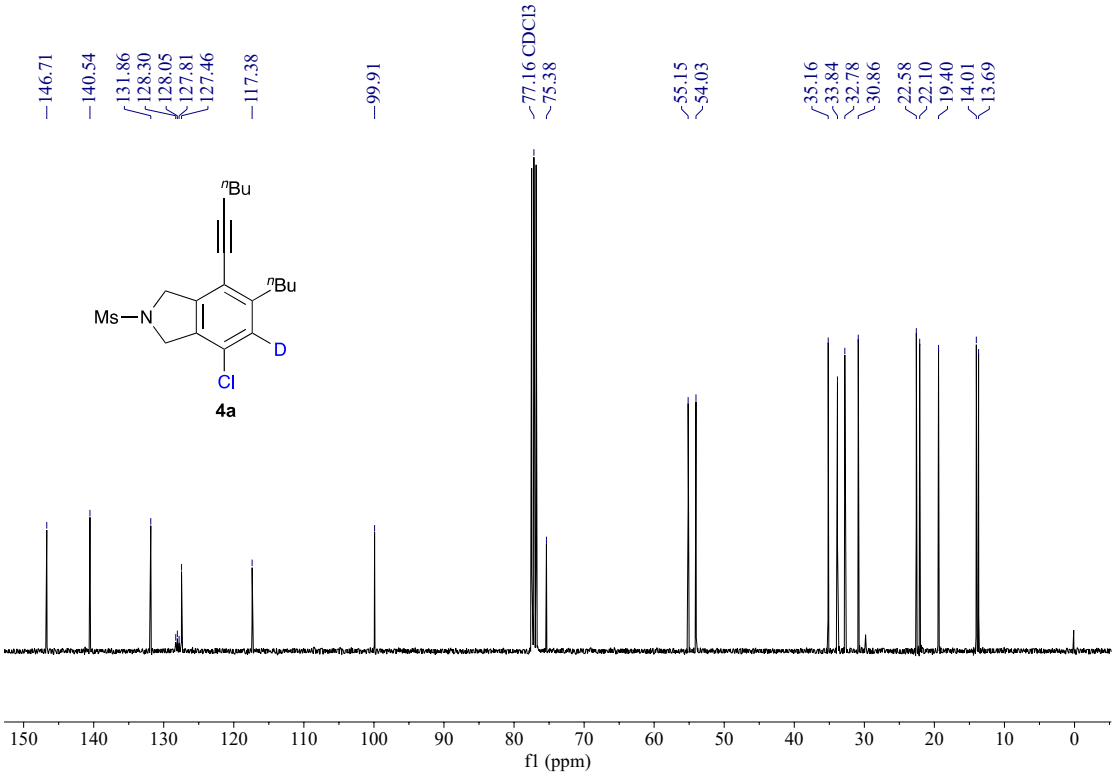

7.26 CDCl3
~7.15
4.66
2.92
2.91
2.90
2.90
2.88
2.88
2.49
2.47
2.45
1.62
1.62
1.61
1.60
1.60
1.59
1.58
1.55
1.53
1.53
1.52
1.51
1.51
1.50
1.50
1.48
1.48
1.47
1.46
1.45
1.44
1.43
1.41
1.39
0.98
0.96
0.94
nBu
nBu
Ms—N
Cl
3a'
1.00
4.03
2.02
3.07
2.00
2.12
6.02
6.09
fl (ppm)

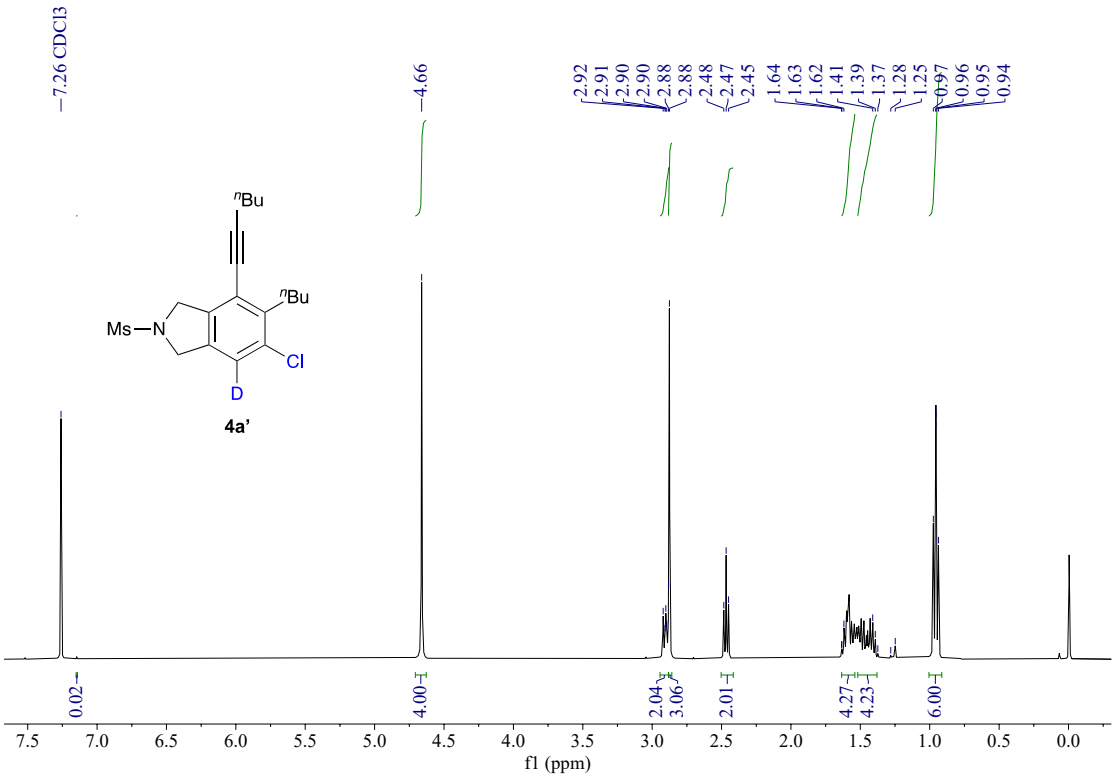

142.16
137.80
134.38
133.96
122.77
120.62
99.94
77.16 CDCl3
75.91
54.18
54.11
35.12
31.90
31.37
30.85
22.99
22.14
19.41
14.05
13.71
nBu
nBu
Ms—N
Cl
3a'
fl (ppm)

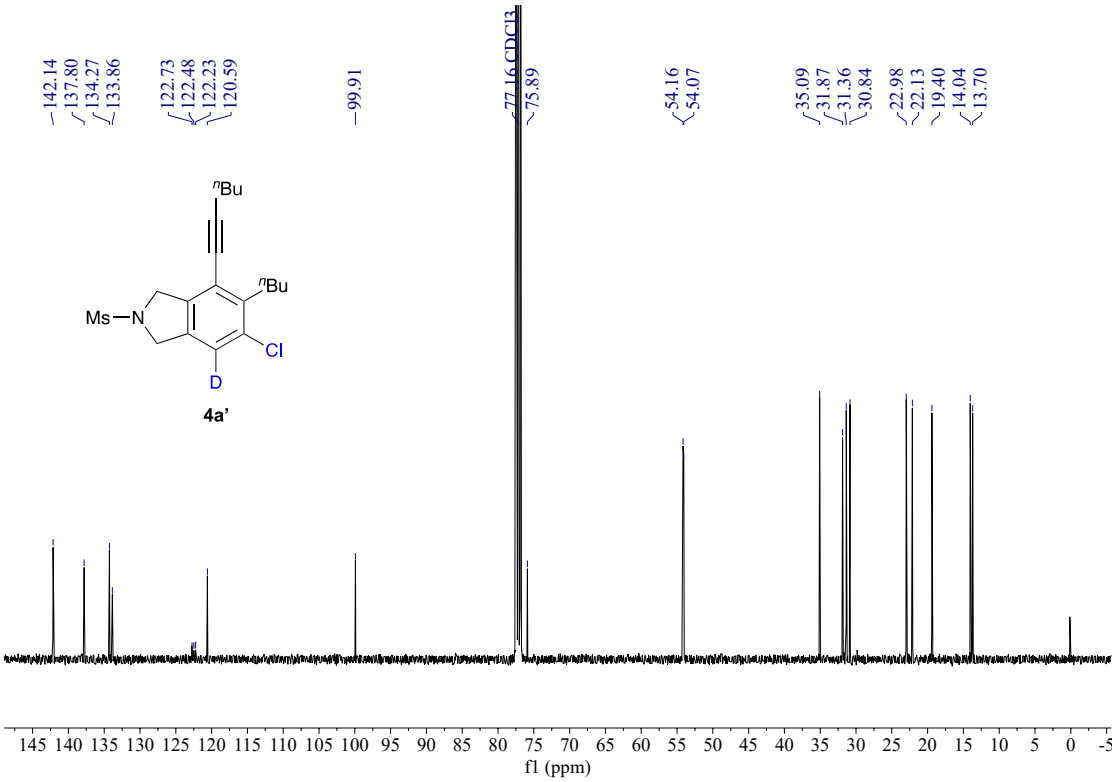

7.68
7.66
7.51
7.49
7.36
7.36
7.35
7.35
7.26 CDCl3
7.25
7.23
7.23
7.22
7.21
7.21
7.17
7.17
7.16
7.13
7.12
7.11
7.11
7.10
7.10
7.09
7.08
5.14
5.12
5.12
5.11
5.09
5.08
3.90
3.71
1.29
1.28
1.27
1.27
Br
iPrOOC
iPrOOC
Br
Cl
3t
1.00
1.07
2.02
2.05
2.27
1.07
2.18
2.03
2.02
12.62
f1 (ppm)

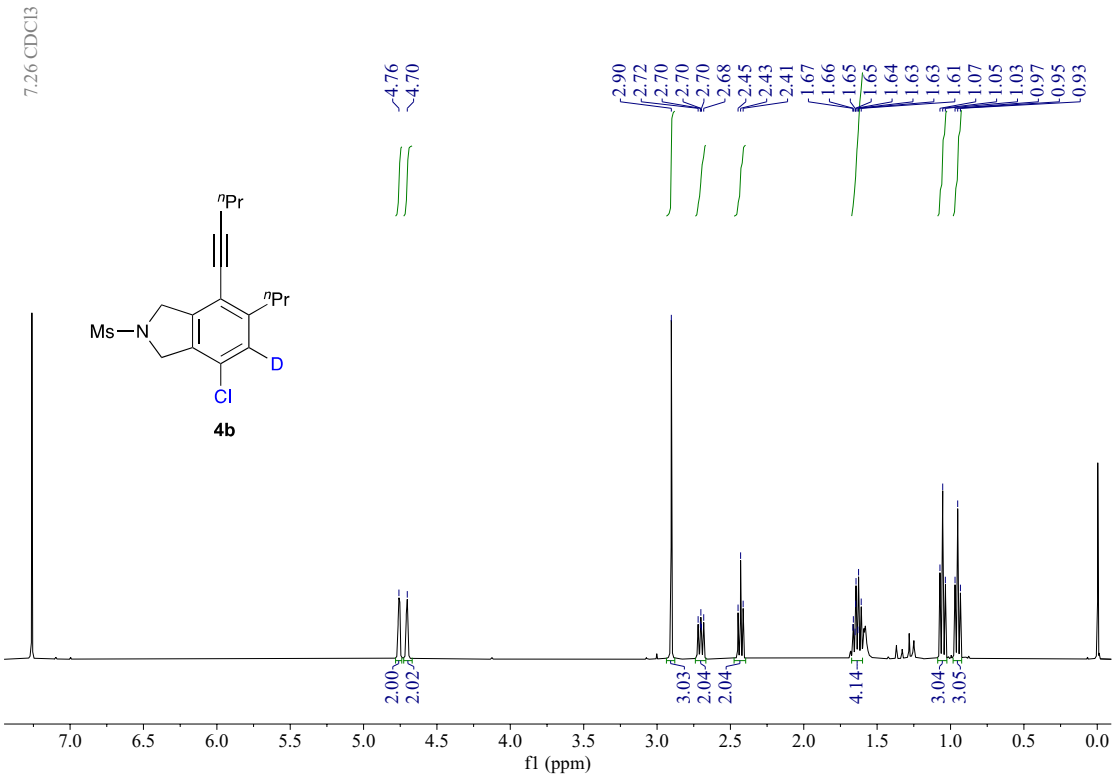

171.06
168.05
145.23
143.92
140.48
138.25
133.50
132.84
132.45
131.72
130.22
129.55
129.49
128.79
127.18
127.01
125.44
125.18
123.61
117.67
95.11
90.19
77.16 CDCl3
69.65
59.06
41.86
40.36
21.69
Br
iPrOOC
iPrOOC
Br
Cl
3t
f1 (ppm)

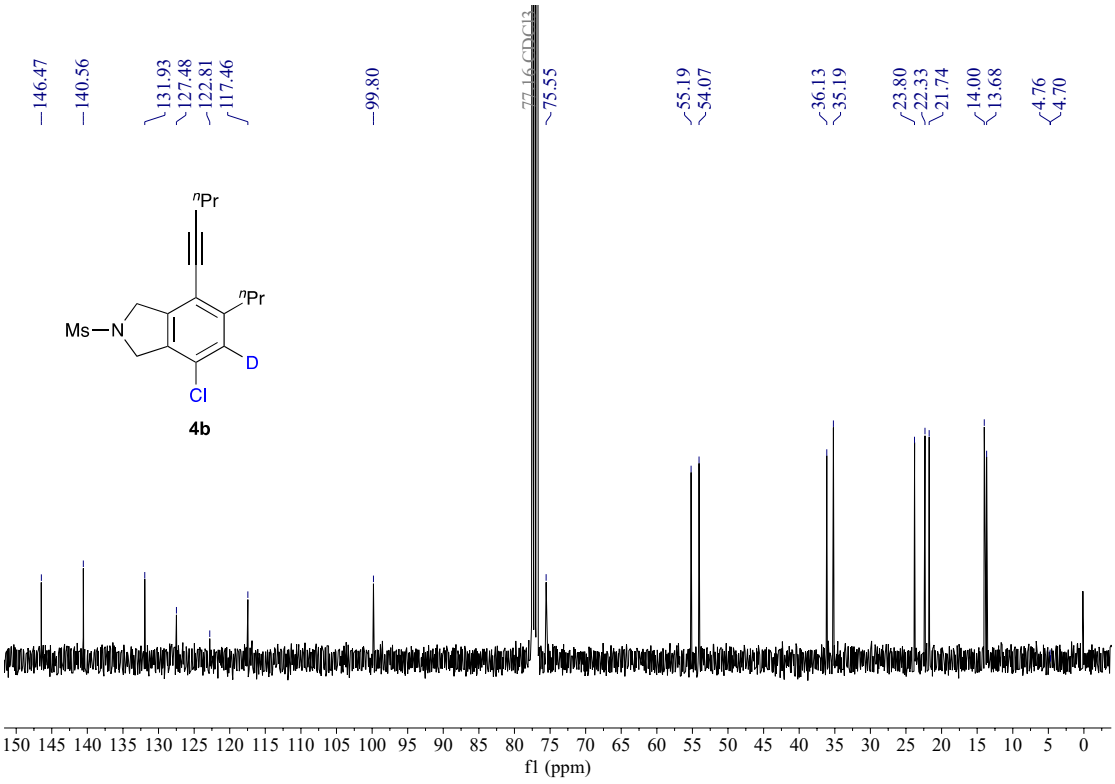

7.26 CDCl3
7.09
4.74
4.69
2.89
2.73
2.71
2.71
2.69
2.47
2.45
2.43
1.63
1.62
1.61
1.61
1.61
1.60
1.59
1.59
1.59
1.58
1.57
1.57
1.57
1.56
1.56
1.56
1.55
1.54
1.50
1.49
1.49
1.48
1.47
1.47
1.46
1.45
1.39
1.37
1.35
1.33
0.97
0.95
0.93
0.91
nBu
nBu
Ms—N
D
Cl
4a
0.02
2.00
2.00
3.03
2.02
2.02
4.26
2.03
2.04
6.07
f1 (ppm)


146.71
140.54
131.86
128.30
128.05
127.81
127.46
117.38
99.91
77.16 CDCl3
75.38
55.15
54.03
35.16
33.84
32.78
30.86
22.58
22.10
19.40
14.01
13.69
nBu
nBu
Ms—N
D
Cl
4a
f1 (ppm)


7.26 CDCl3
4.66
2.92
2.91
2.90
2.90
2.88
2.88
2.48
2.47
2.45
1.64
1.63
1.62
1.41
1.39
1.37
1.28
1.25
0.97
0.96
0.95
0.94
nBu
nBu
Ms—N
Cl
D
4a'
0.02
4.00
2.04
3.06
2.01
4.27
4.23
6.00
f1 (ppm)


142.14
137.80
134.27
133.86
122.73
122.48
122.23
120.59
99.91
77.16 CDCl3
75.89
54.16
54.07
35.09
31.87
31.36
30.84
22.98
22.13
19.40
14.04
13.70
nBu
nBu
Ms—N
Cl
D
4a'
f1 (ppm)


7.26 CDCl3
4.76
4.70
2.90
2.72
2.70
2.70
2.70
2.68
2.45
2.43
2.41
1.67
1.66
1.65
1.65
1.64
1.63
1.63
1.61
1.07
1.05
1.03
0.97
0.95
0.93
nPr
nPr
Ms—N
D
Cl
4b
2.00
2.02
3.03
2.04
2.04
4.14
3.04
3.05
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
f1 (ppm)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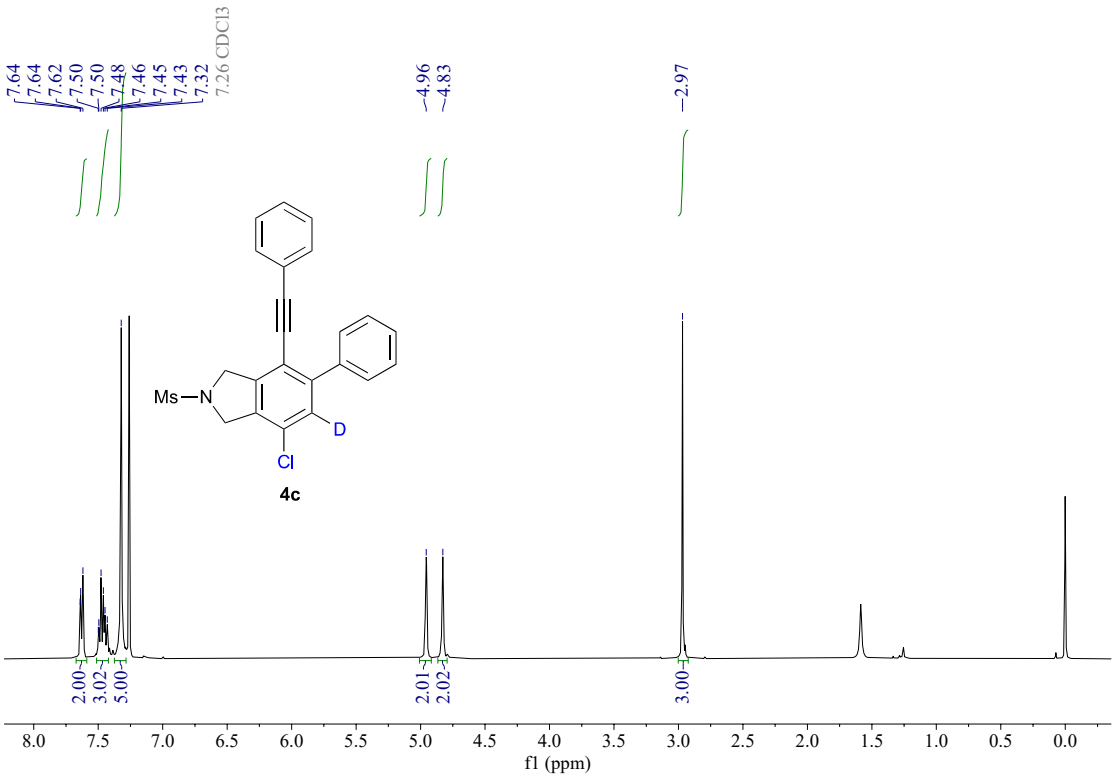
131.93
127.48
122.81
117.46
99.80
77.16 CDCl3
75.55
55.19
54.07
36.13
35.19
23.80
22.33
21.74
14.00
13.68
4.76
4.70
nPr
nPr
Ms—N
D
Cl
4b
150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)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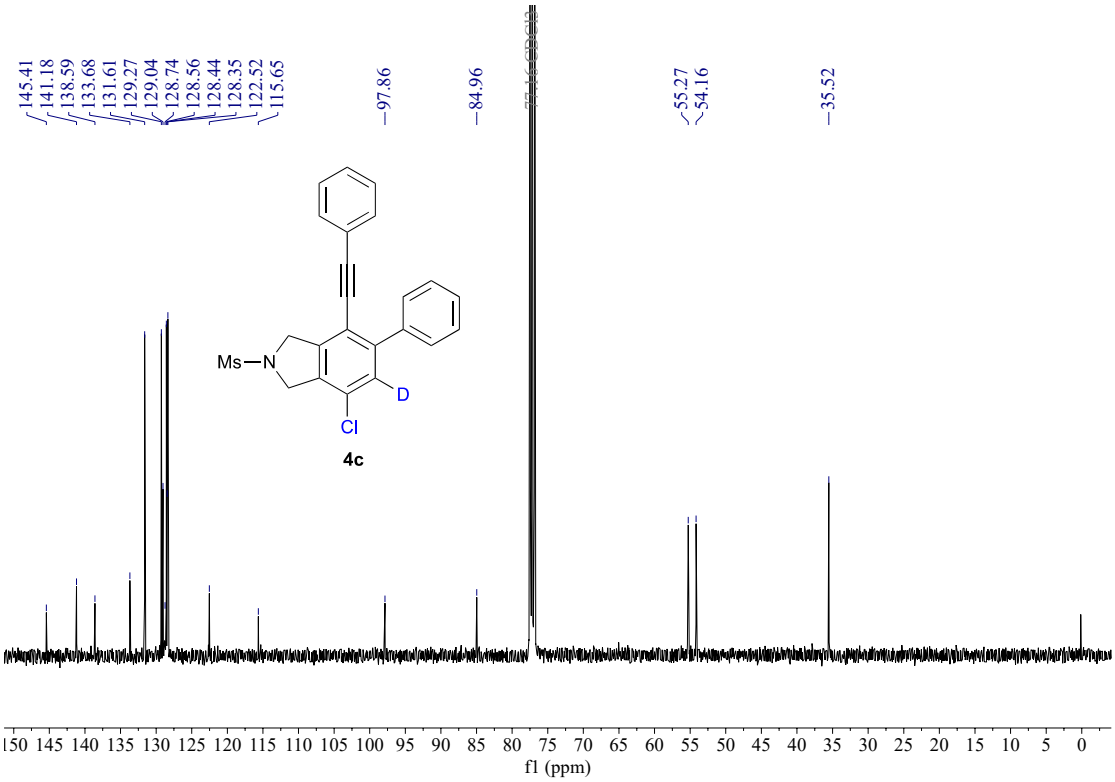
7.64
7.62
7.50
7.50
7.48
7.46
7.45
7.43
7.32
7.26 CDCl3
4.96
4.83
2.97
Ms—N
D
Cl
4c
2.00
3.02
5.00
2.01
2.02
3.00
f1 (ppm)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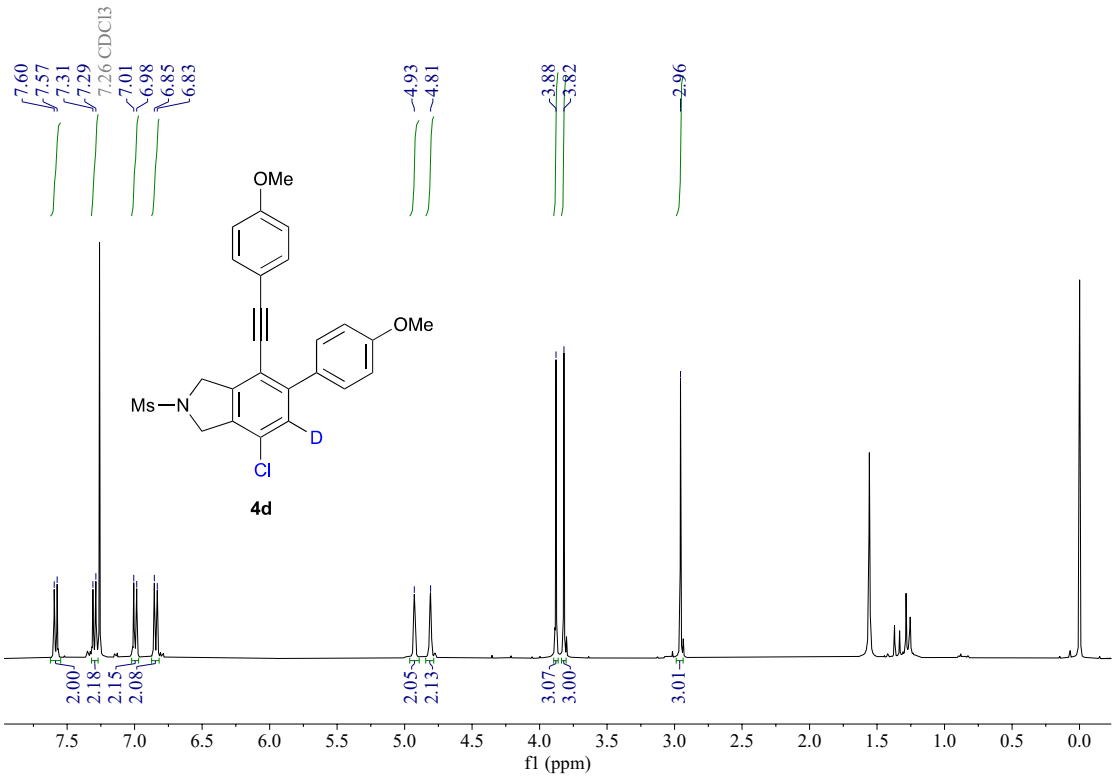
141.18
138.59
133.68
131.61
129.27
129.04
128.74
128.56
128.44
128.35
122.52
115.65
97.86
84.96
77.16 CDCl3
55.27
54.16
35.52
Ms—N
D
Cl
4c
f1 (ppm)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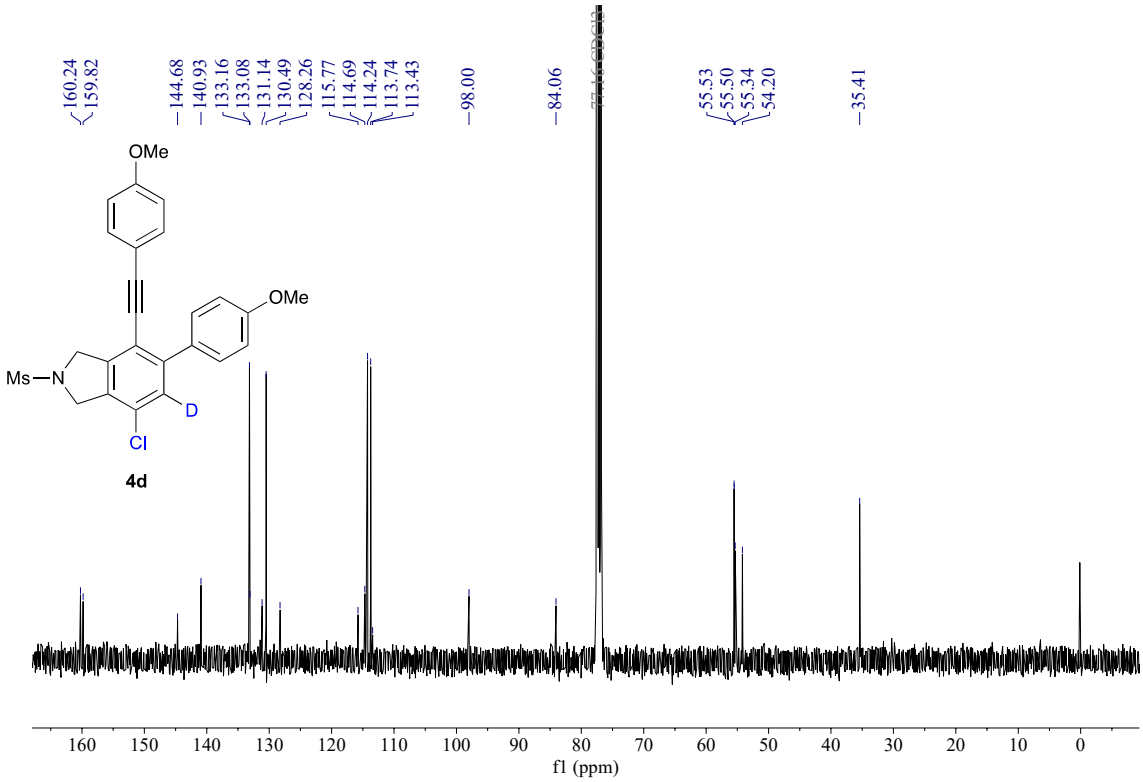
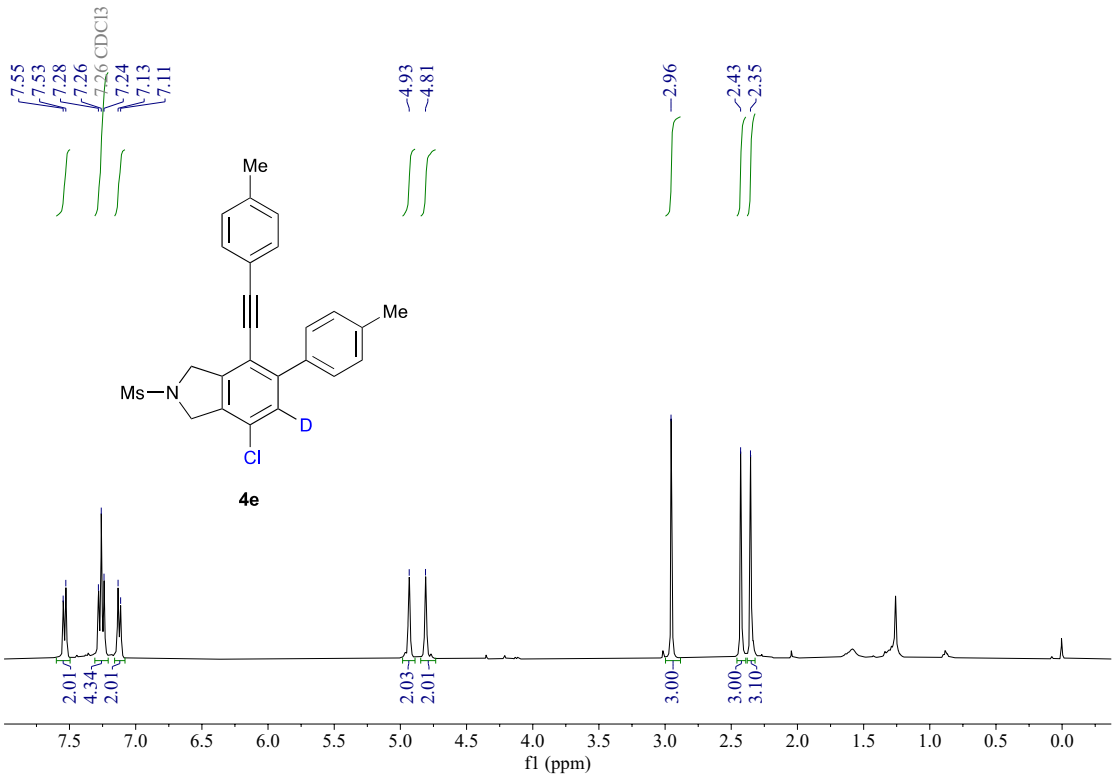
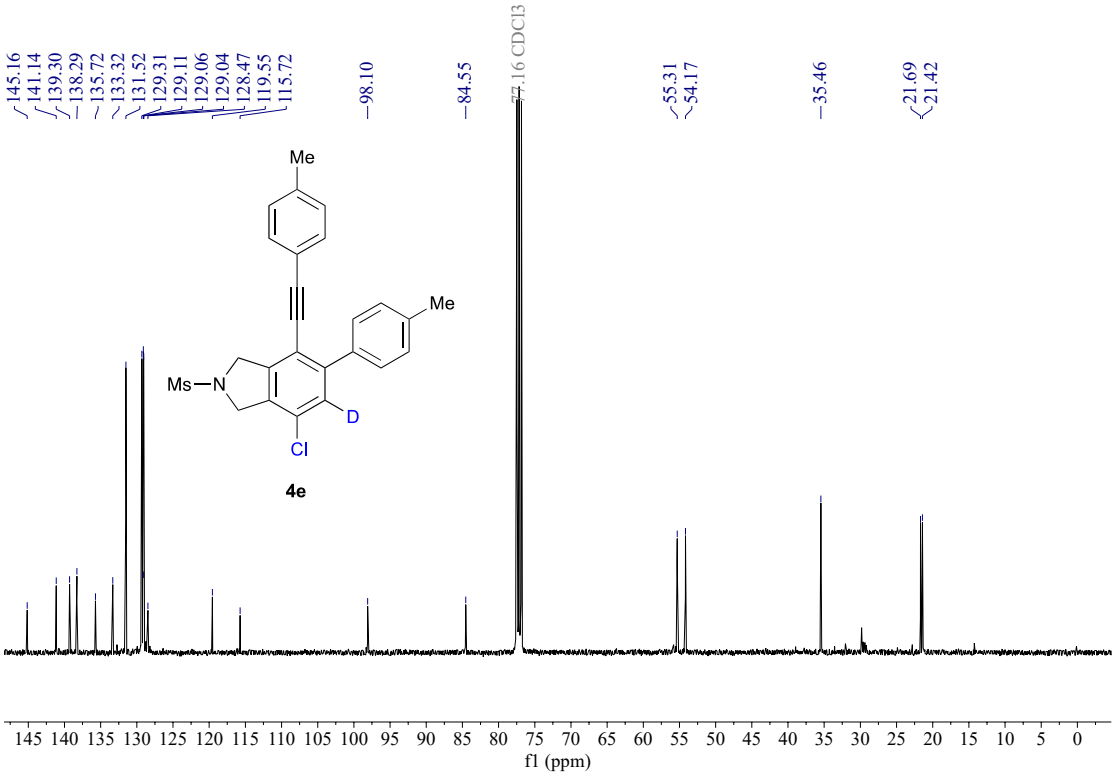
7.57
7.31
7.29
7.26 CDCl3
7.01
6.98
6.85
6.83
4.93
4.81
3.88
3.82
2.96
OMe
OMe
Ms—N
D
Cl
4d
2.00
2.18
2.15
2.08
2.05
2.13
3.07
3.00
3.01
f1 (ppm)


160.24
159.82
144.68
140.93
133.16
133.08
131.14
130.49
128.26
115.77
114.69
114.24
113.74
113.43
98.00
84.06
77.16 CDCl3
55.53
55.50
55.34
54.20
35.41
OMe
OMe
Ms—N
D
Cl
4d
f1 (ppm)


7.55
7.53
7.28
7.26
7.26 CDCl3
7.24
7.13
7.11
4.93
4.81
2.96
2.43
2.35
Me
Me
Ms—N
D
Cl
4e
2.01
4.34
2.01
2.03
2.01
3.00
3.00
3.10
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
f1 (ppm)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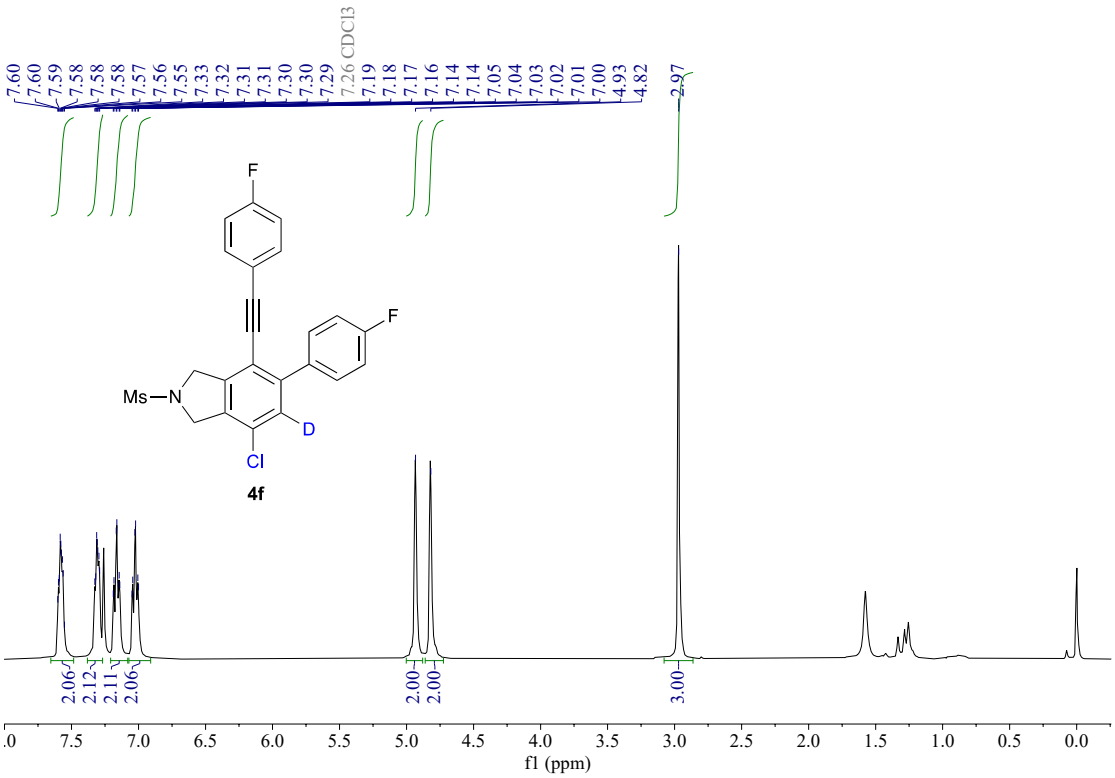
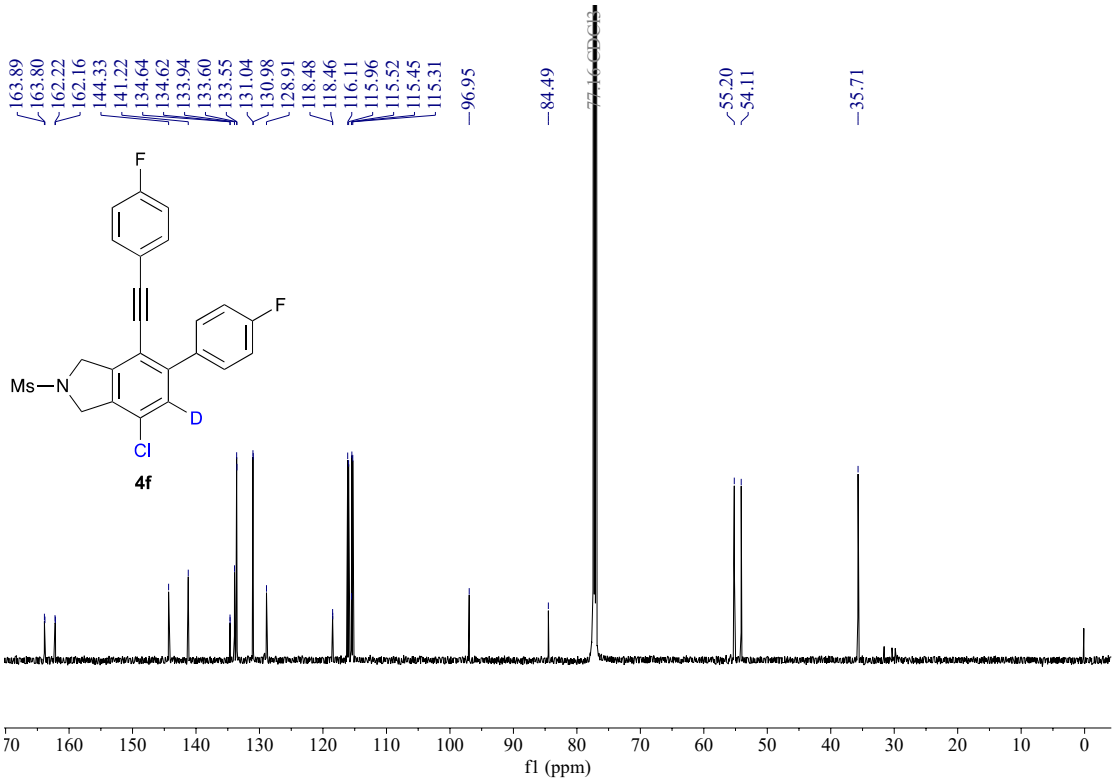
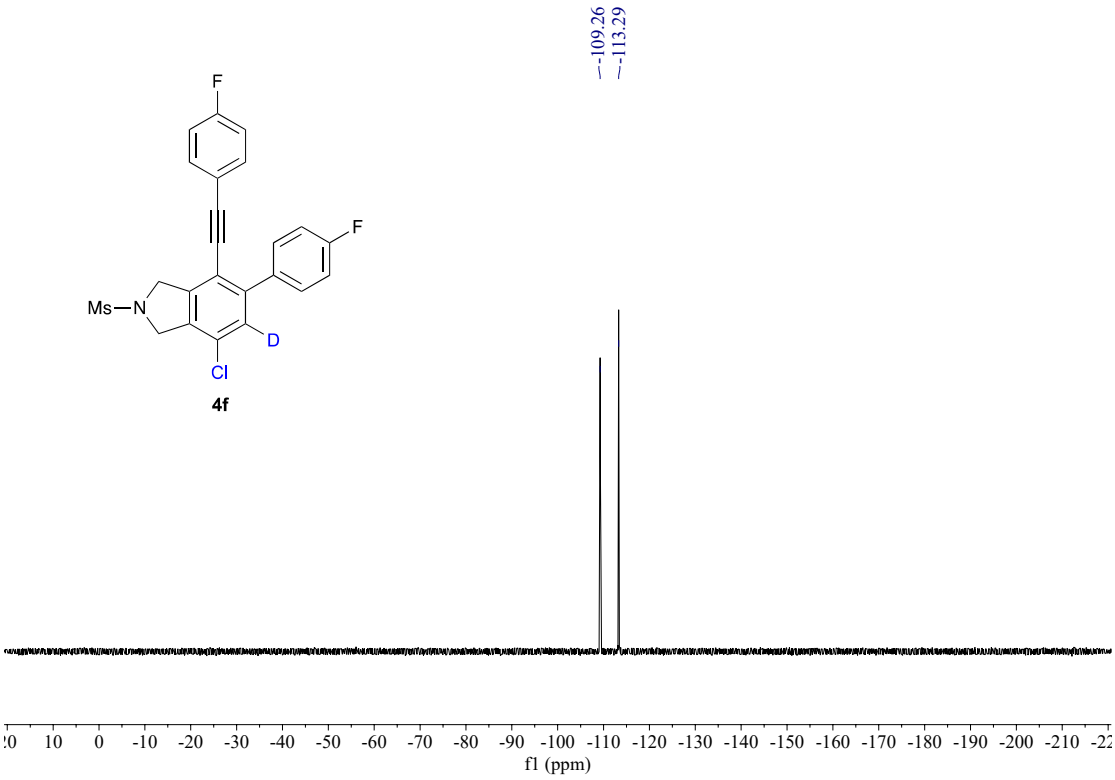
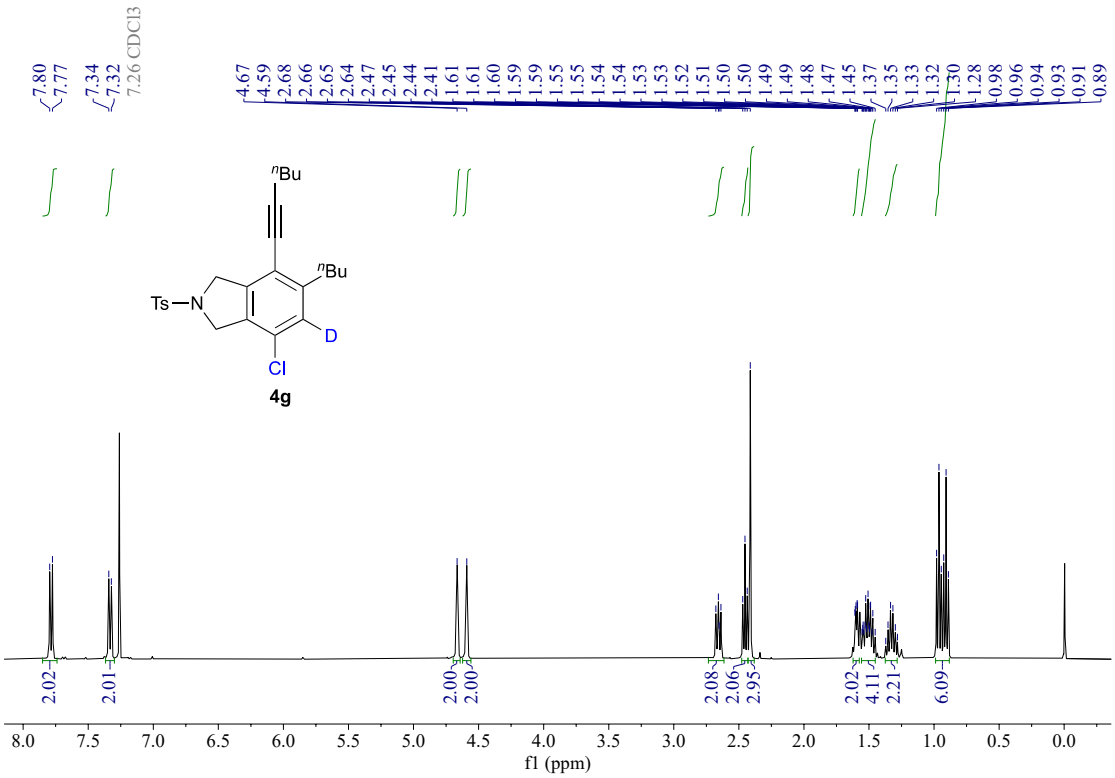
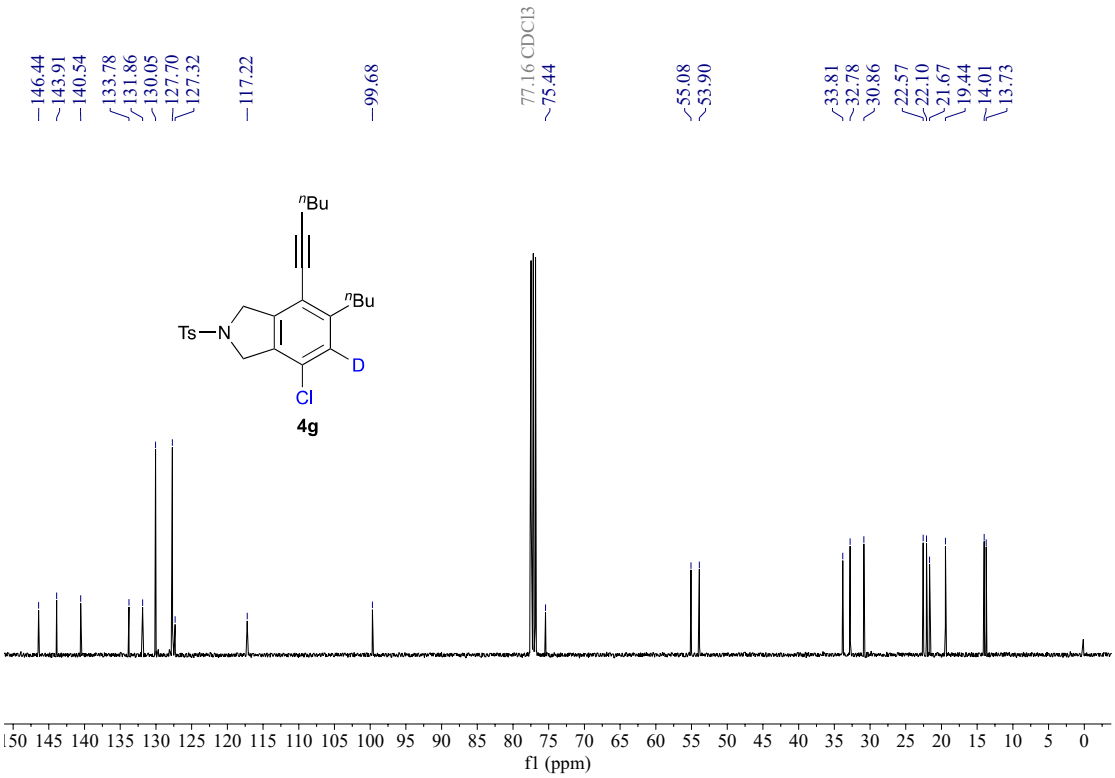
141.14
139.30
138.29
135.72
133.32
131.52
129.31
129.11
129.06
129.04
128.47
119.55
115.72
98.10
84.55
77.16 CDCl3
55.31
54.17
35.46
21.69
21.42
Me
Me
Ms—N
D
Cl
4e
145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)


7.60
7.60
7.59
7.58
7.58
7.58
7.57
7.56
7.55
7.33
7.32
7.31
7.31
7.30
7.30
7.29
7.26 CDCl3
7.19
7.18
7.17
7.16
7.14
7.14
7.05
7.04
7.03
7.02
7.01
7.00
4.93
4.82
2.97
F
F
Ms—N
D
Cl
4f
2.06
2.12
2.11
2.06
2.00
2.00
3.00
f1 (ppm)


163.89
163.80
162.22
162.16
144.33
141.22
134.64
134.62
133.94
133.60
133.55
131.04
130.98
128.91
118.48
118.46
116.11
115.96
115.52
115.45
115.31
96.95
84.49
77.16 CDCl3
55.20
54.11
35.71
F
F
Ms—N
D
Cl
4f
f1 (ppm)


F
F
Ms—N
D
Cl
4f
-109.26
-113.29
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


7.80
7.77
7.34
7.32
7.26 CDCl3
4.67
4.59
2.68
2.66
2.65
2.64
2.47
2.45
2.44
2.41
1.61
1.61
1.60
1.59
1.59
1.55
1.55
1.54
1.54
1.53
1.53
1.52
1.51
1.50
1.50
1.49
1.49
1.48
1.47
1.45
1.37
1.35
1.33
1.32
1.30
1.28
0.98
0.96
0.94
0.93
0.91
0.89
nBu
nBu
Ts—N
D
Cl
4g
2.02
2.01
2.00
2.00
2.08
2.06
2.95
2.02
4.11
2.21
6.09
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
f1 (ppm)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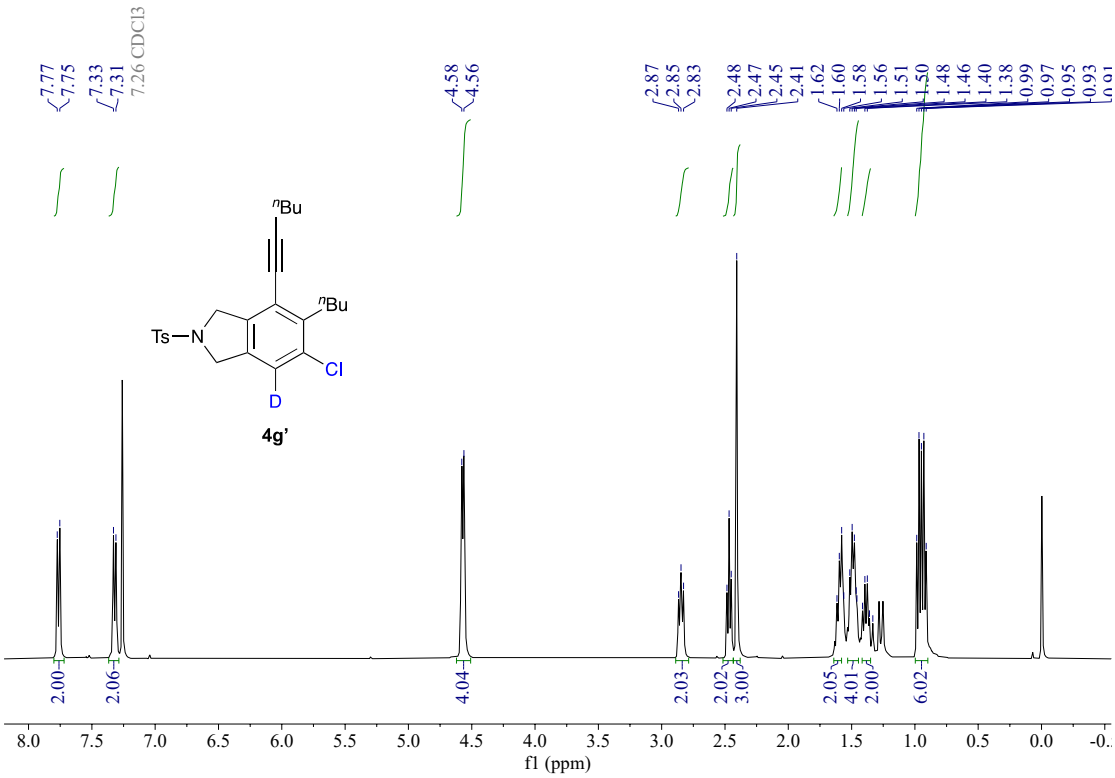
143.91
140.54
133.78
131.86
130.05
127.70
127.32
117.22
99.68
77.16 CDCl3
75.44
55.08
53.90
33.81
32.78
30.86
22.57
22.10
21.67
19.44
14.01
13.73
nBu
nBu
Ts—N
D
Cl
4g
150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)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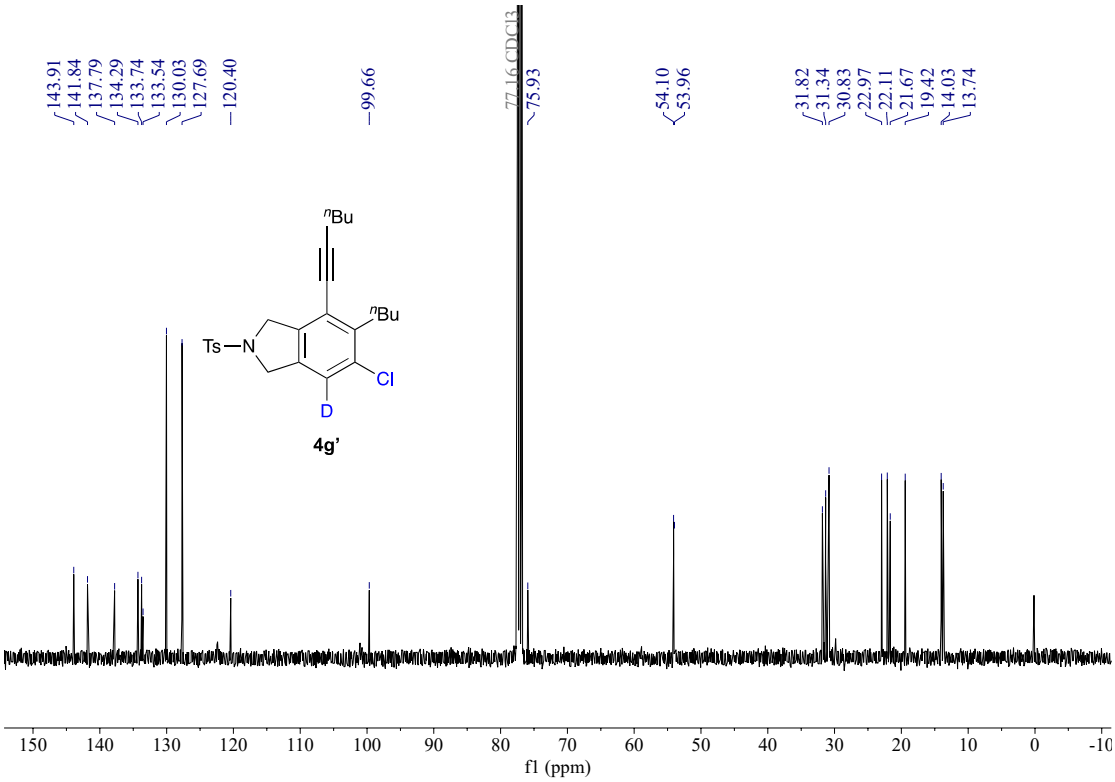
7.75
7.33
7.31
7.26 CDCl3
4.58
4.56
2.87
2.85
2.83
2.48
2.47
2.45
2.41
1.62
1.60
1.58
1.56
1.51
1.50
1.48
1.46
1.40
1.38
0.99
0.97
0.95
0.93
nBu
nBu
Ts—N
Cl
D
4g'
2.00
2.06
4.04
2.03
2.02
3.00
2.05
4.01
2.00
6.02
f1 (ppm)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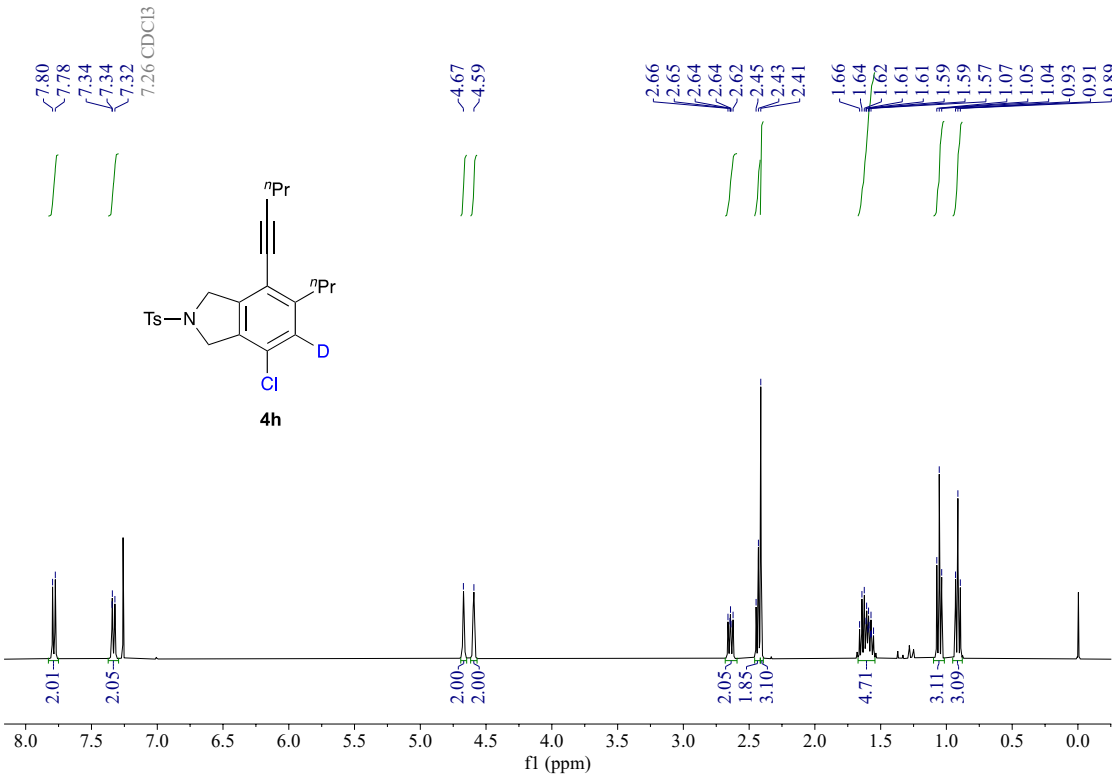
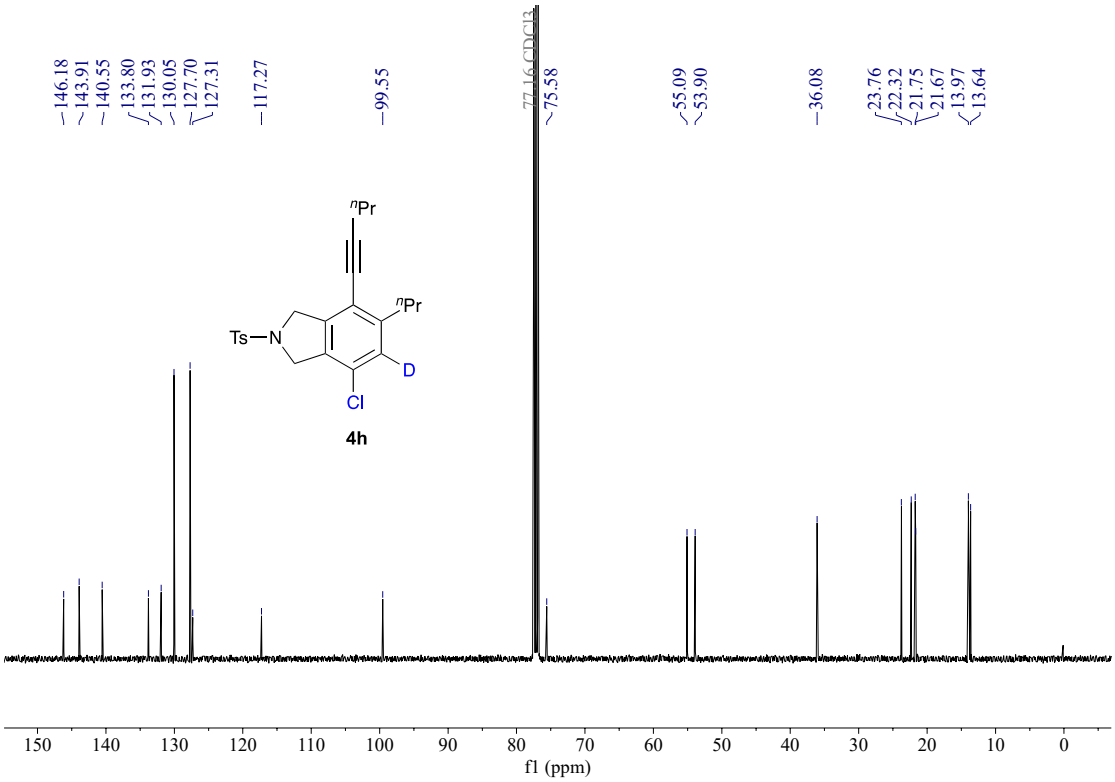
141.84
137.79
134.29
133.74
133.54
130.03
127.69
120.40
99.66
77.16 CDCl3
75.93
54.10
53.96
31.82
31.34
30.83
22.97
22.11
21.67
19.42
14.03
13.74
nBu
nBu
Ts—N
Cl
D
4g'
f1 (ppm)


7.80
7.78
7.34
7.34
7.32
7.26 CDCl3
4.67
4.59
2.66
2.65
2.64
2.64
2.62
2.45
2.43
2.41
1.66
1.64
1.62
1.61
1.61
1.59
1.59
1.57
1.07
1.05
1.04
0.93
0.91
nPr
nPr
Ts—N
D
Cl
4h
2.01
2.05
2.00
2.00
2.05
1.85
3.10
4.71
3.11
3.09
f1 (ppm)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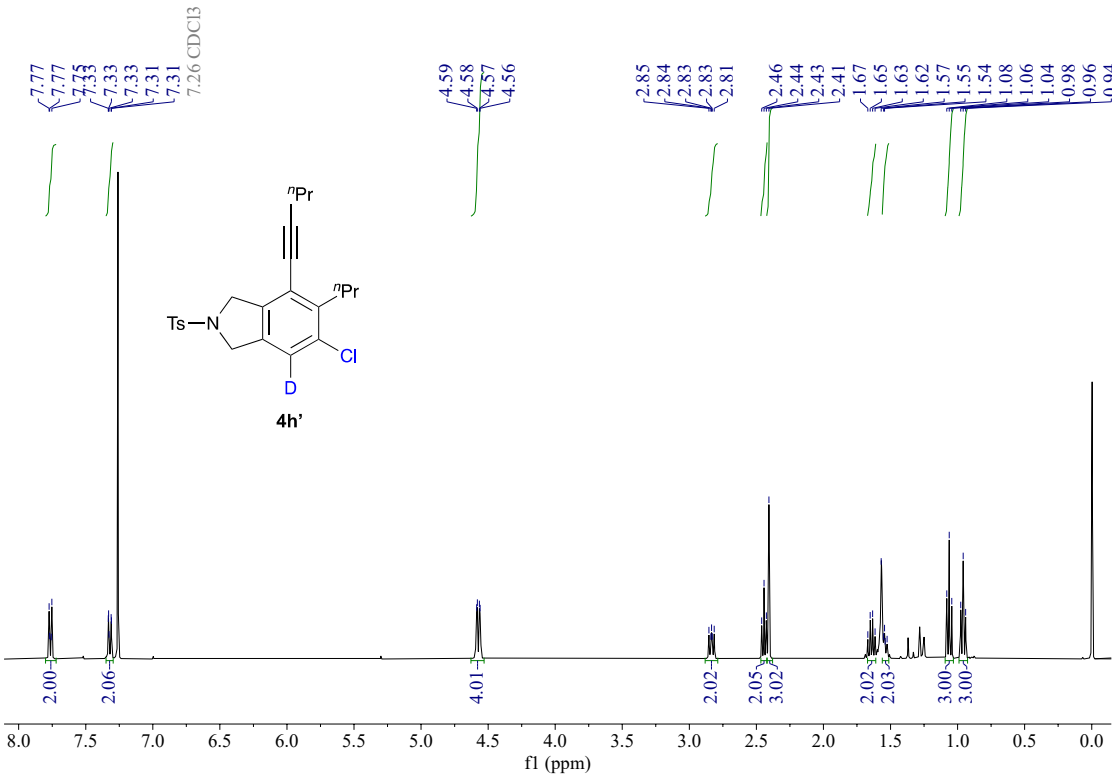
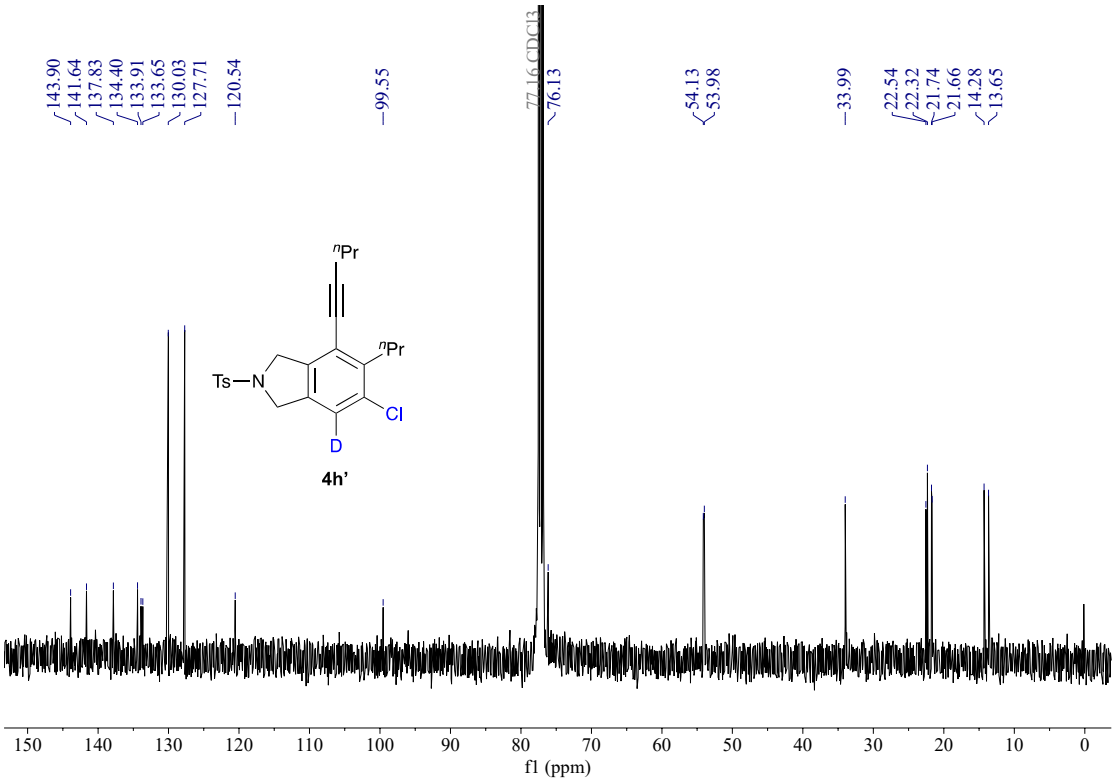
143.91
140.55
133.80
131.93
130.05
127.70
127.31
117.27
99.55
77.16 CDCl3
75.58
55.09
53.90
36.08
23.76
22.32
21.75
21.67
13.97
13.64
nPr
nPr
Ts—N
D
Cl
4h
f1 (ppm)


7.77
7.77
7.75
7.33
7.33
7.31
7.31
7.26 CDCl3
4.59
4.58
4.57
4.56
2.85
2.84
2.83
2.83
2.81
2.46
2.44
2.43
2.41
1.67
1.65
1.63
1.62
1.57
1.55
1.54
1.08
1.06
1.04
0.98
0.96
nPr
nPr
Ts—N
Cl
D
4h'
2.00
2.06
4.01
2.02
2.05
3.02
2.02
2.03
3.00
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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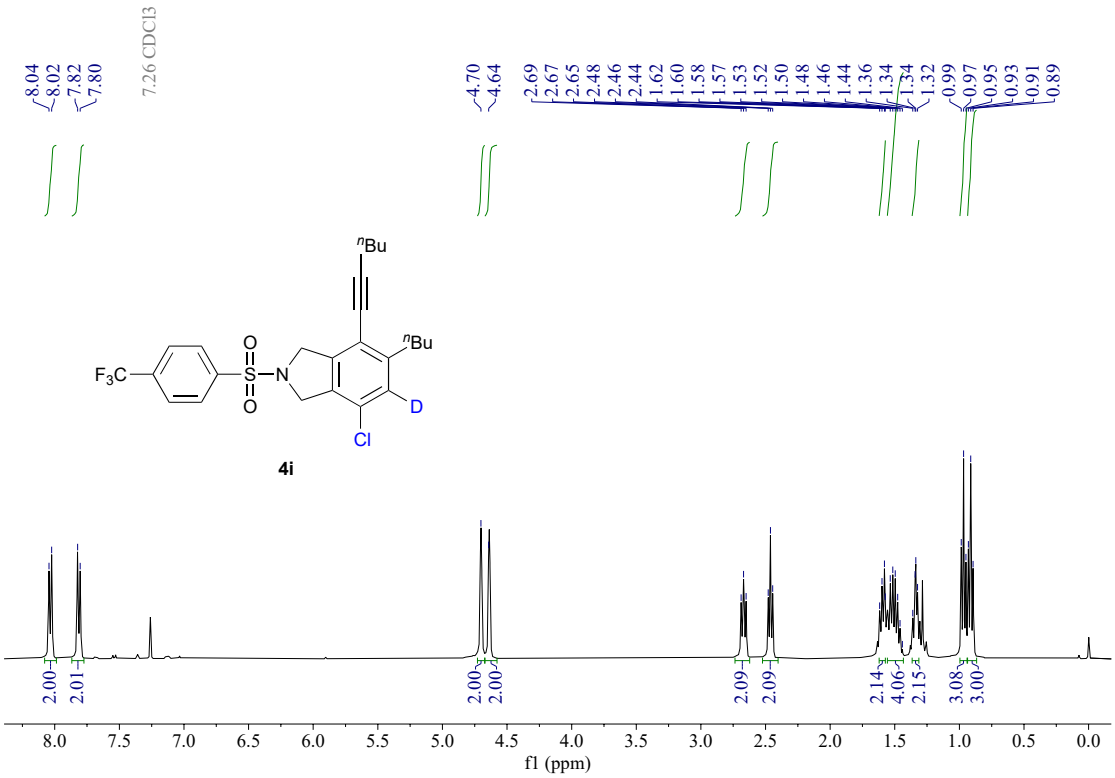
141.64
137.83
134.40
133.91
133.65
130.03
127.71
120.54
99.55
77.16 CDCl3
76.13
54.13
53.98
33.99
22.54
22.32
21.74
21.66
14.28
13.65
nPr
nPr
Ts—N
Cl
D
4h'
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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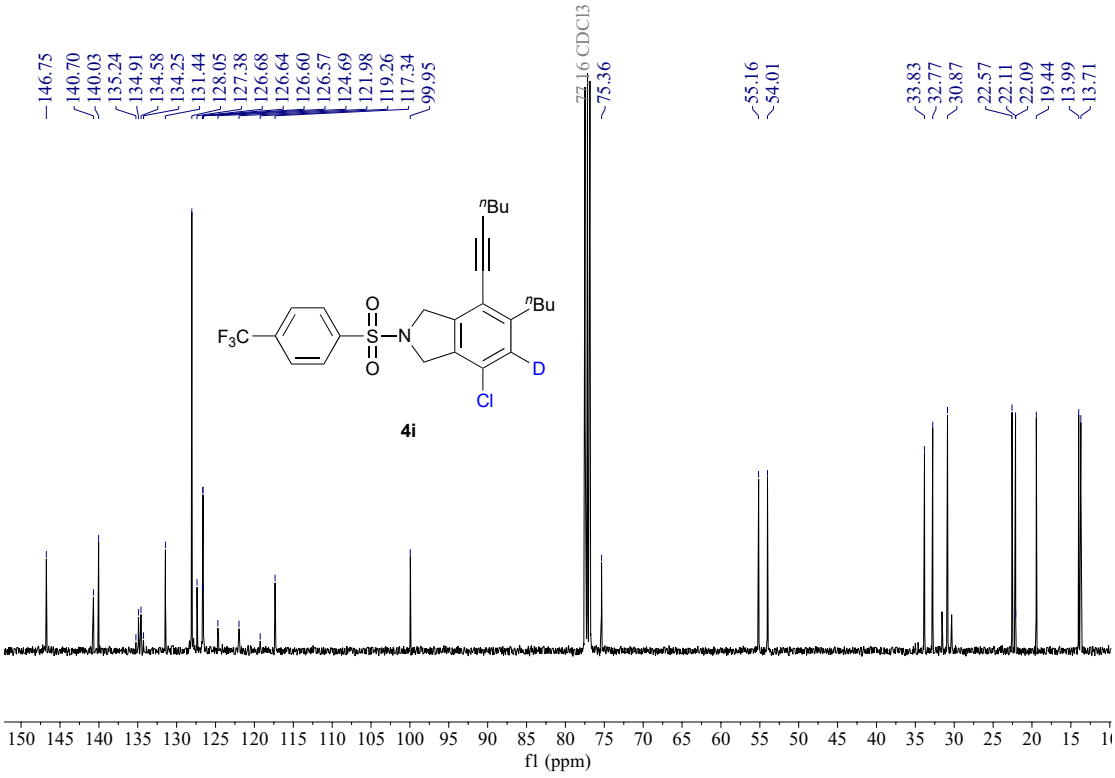
8.02
7.82
7.80
7.26 CDCl3
4.70
4.64
2.69
2.67
2.65
2.48
2.46
2.44
1.62
1.60
1.58
1.57
1.53
1.52
1.50
1.48
1.46
1.44
1.36
1.34
1.34
1.32
0.99
0.97
0.95
0.93
0.91
0.89
nBu
nBu
F3C
S
N
O
O
D
Cl
4i
2.00
2.01
2.00
2.00
2.09
2.09
2.14
4.06
2.15
3.08
3.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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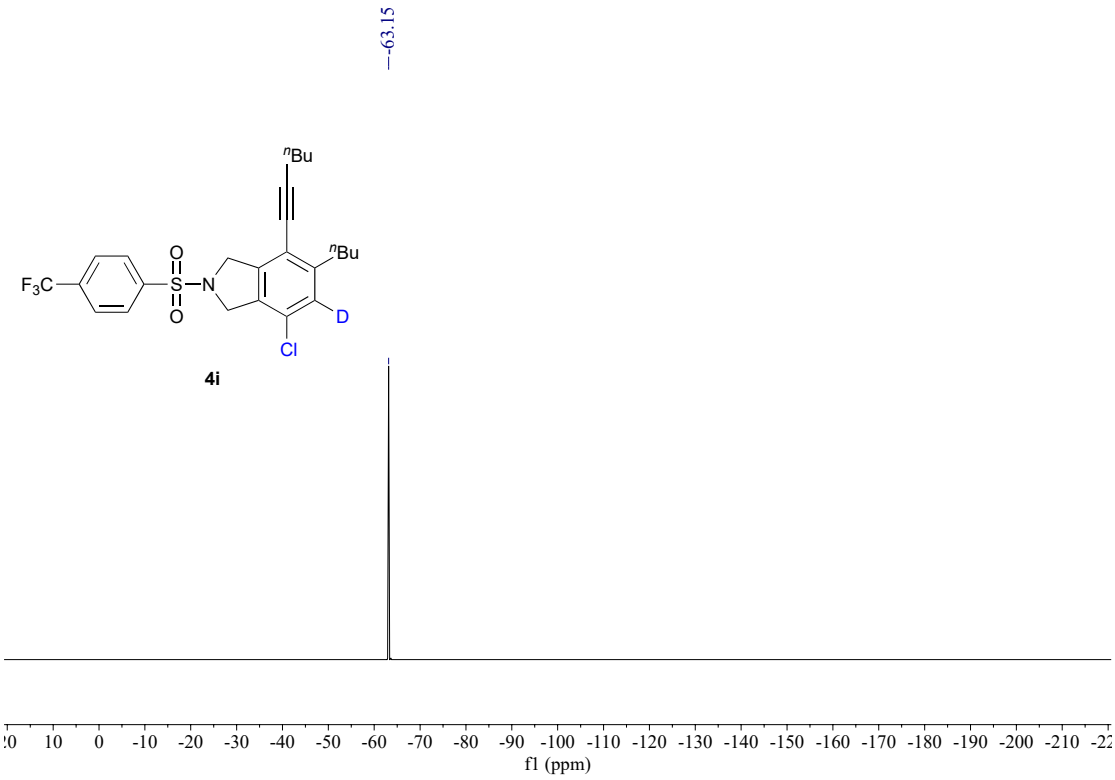
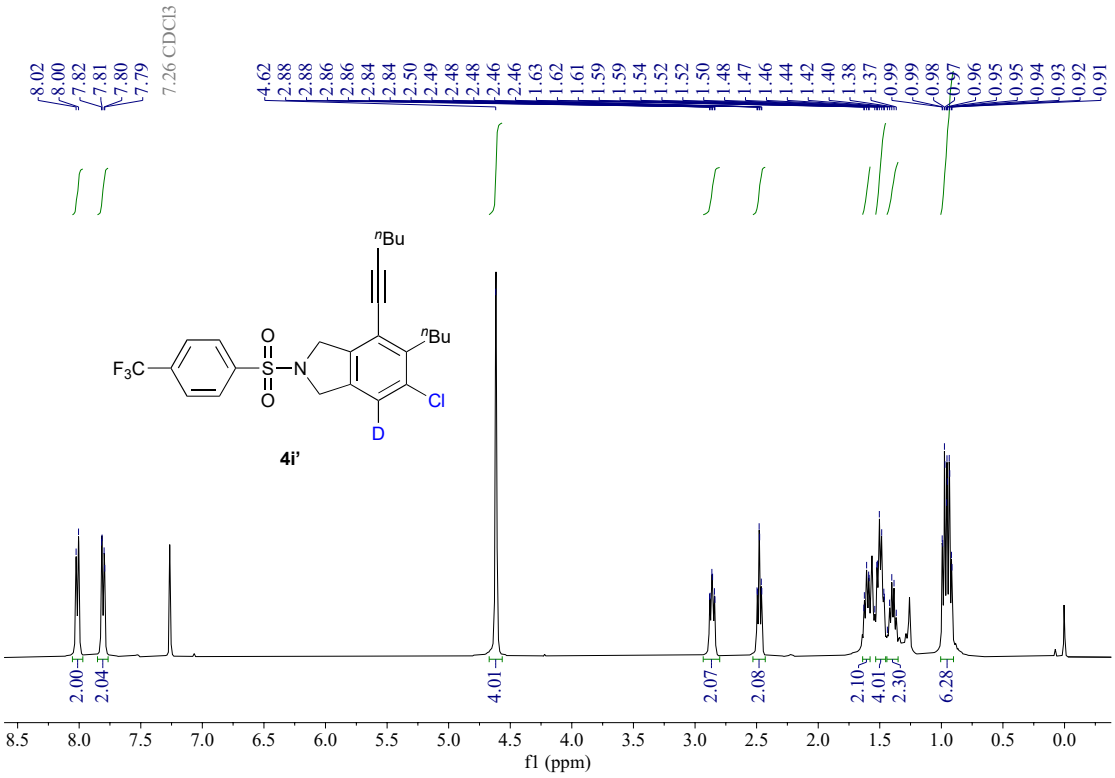
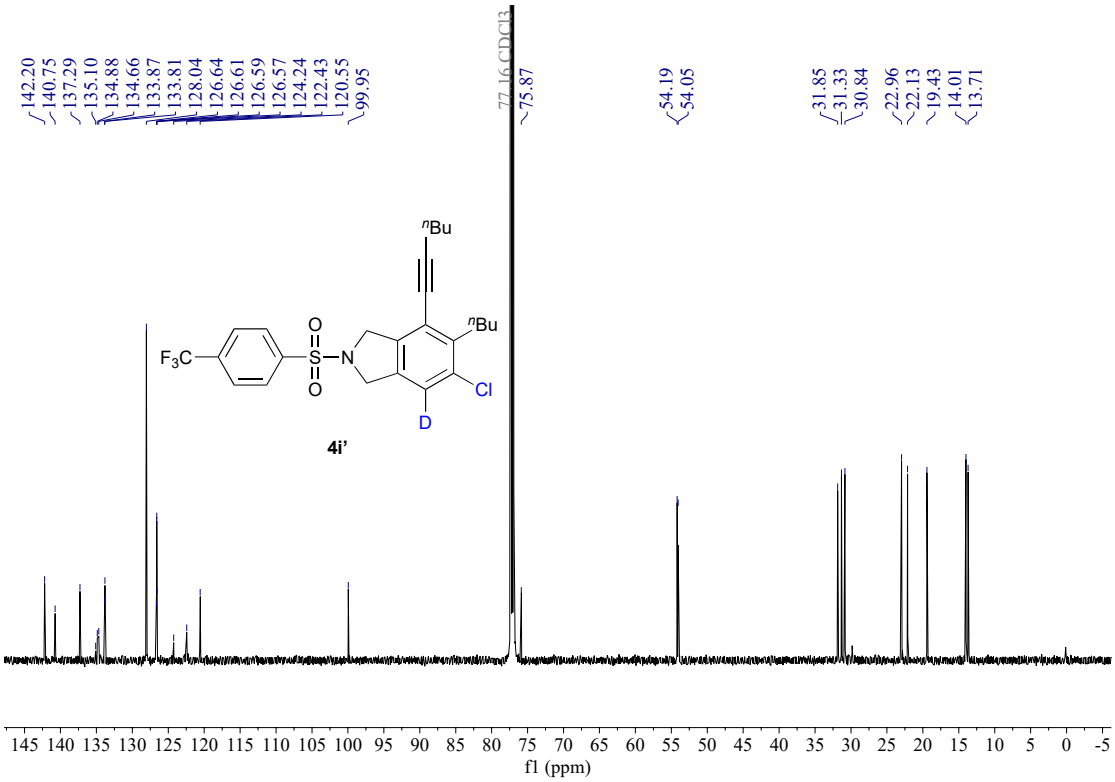
140.70
140.03
135.24
134.91
134.58
134.25
131.44
128.05
127.38
126.68
126.64
126.60
126.57
124.69
121.98
119.26
117.34
99.95
77.16 CDCl3
75.36
55.16
54.01
33.83
32.77
30.87
22.57
22.11
22.09
19.44
13.99
13.71
nBu
nBu
F3C
S
N
O
O
D
Cl
4i
150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15
f1 (ppm)


-63.15
nBu
nBu
F3C
O
S
N
O
D
Cl
4i
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


8.02
8.00
7.82
7.81
7.80
7.79
7.26 CDCl3
4.62
2.88
2.88
2.86
2.86
2.84
2.84
2.50
2.49
2.48
2.48
2.46
2.46
1.63
1.62
1.61
1.59
1.59
1.54
1.52
1.52
1.50
1.48
1.47
1.46
1.44
1.42
1.40
1.38
1.37
0.99
0.99
0.98
0.97
0.96
0.95
0.95
0.94
0.93
0.92
0.91
nBu
nBu
F3C
S
N
O
O
Cl
D
4i'
2.00
2.04
4.01
2.07
2.08
2.10
4.01
2.30
6.28
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
f1 (ppm)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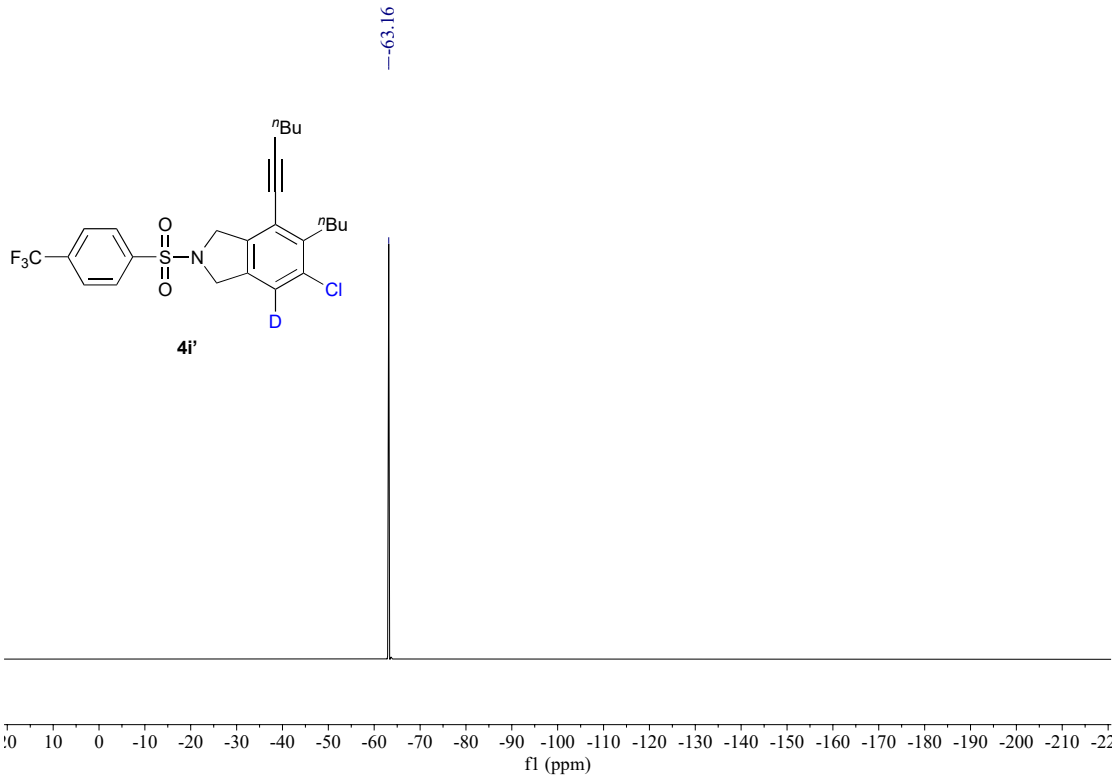
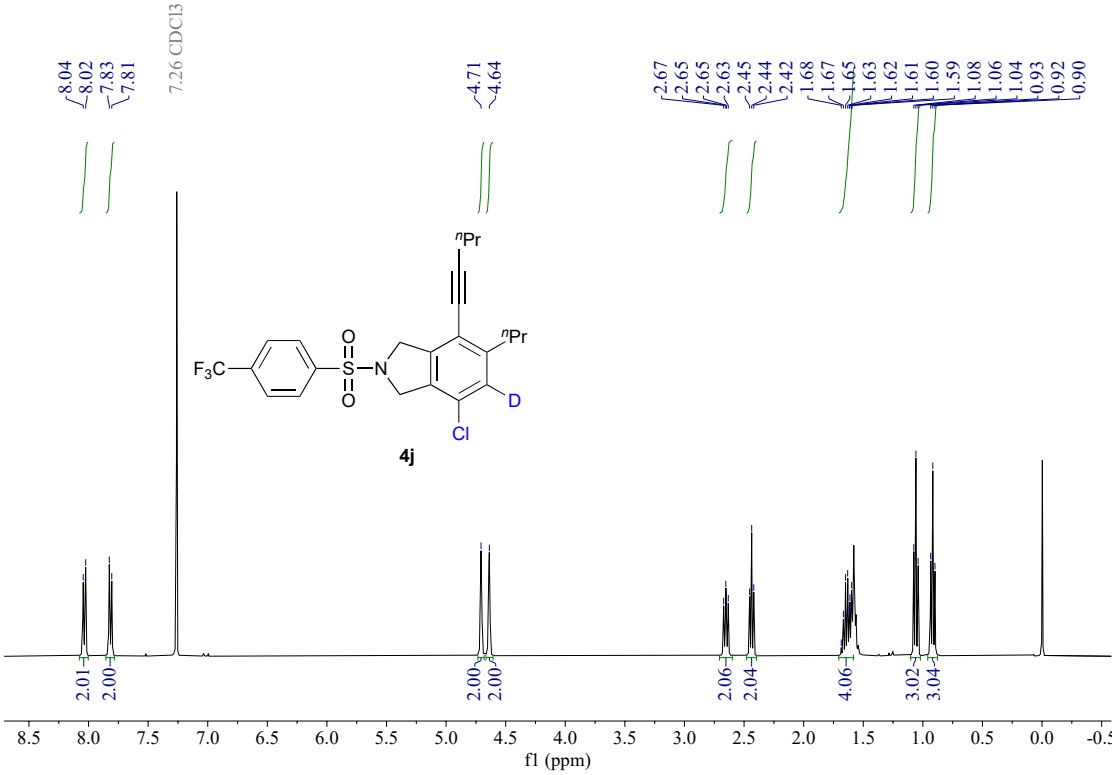
140.75
137.29
135.10
134.88
134.66
133.87
133.81
128.04
126.64
126.61
126.59
126.57
124.24
122.43
120.55
99.95
77.16 CDCl3
75.87
54.19
54.05
31.85
31.33
30.84
22.96
22.13
19.43
14.01
13.71
nBu
nBu
F3C
S
N
O
O
Cl
D
4i'
145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5
f1 (ppm)


-63.16
nBu
nBu
F3C
O
S
N
O
O
Cl
D
4i'
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


8.04
8.02
7.83
7.81
7.26 CDCl3
4.71
4.64
2.67
2.65
2.65
2.63
2.45
2.44
2.42
1.68
1.67
1.65
1.63
1.62
1.61
1.60
1.59
1.08
1.06
1.04
0.93
0.92
0.90
nPr
nPr
F3C
S
N
O
O
D
Cl
4j
2.01
2.00
2.00
2.00
2.06
2.04
4.06
3.02
3.04
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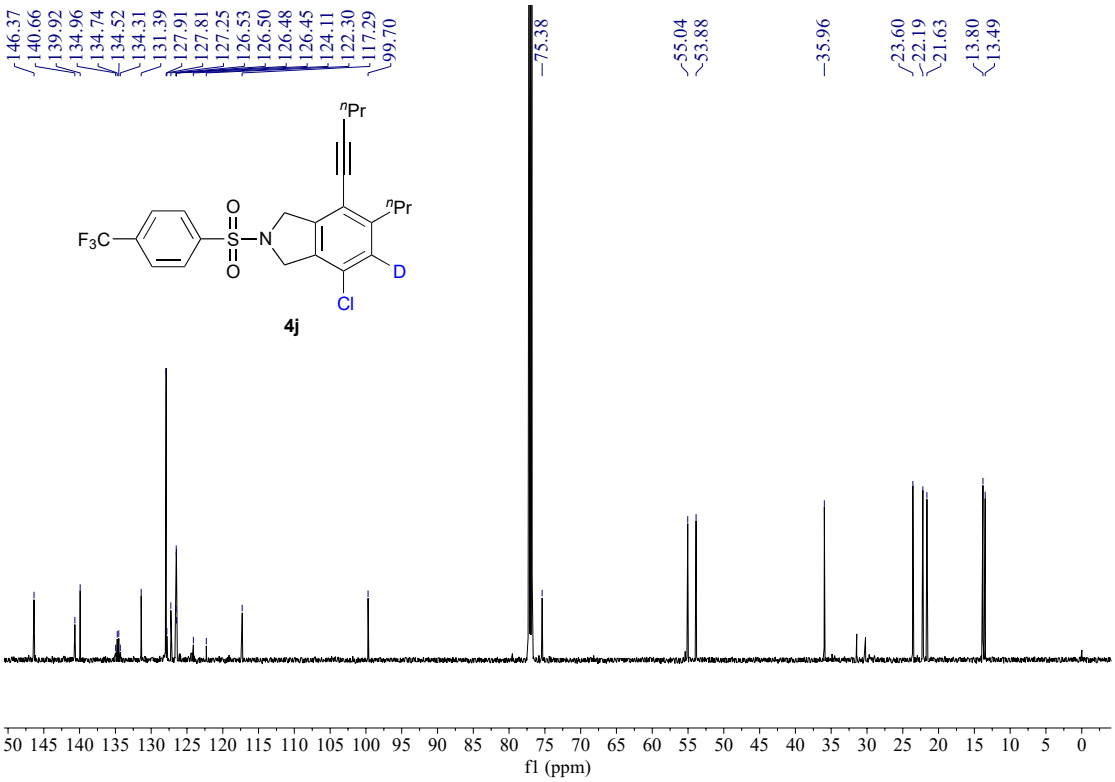
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124.11
122.30
117.29
99.70
75.38
55.04
53.88
35.96
23.60
22.19
21.63
13.80
13.49
nPr
nPr
F3C
S
N
O
O
D
Cl
4j
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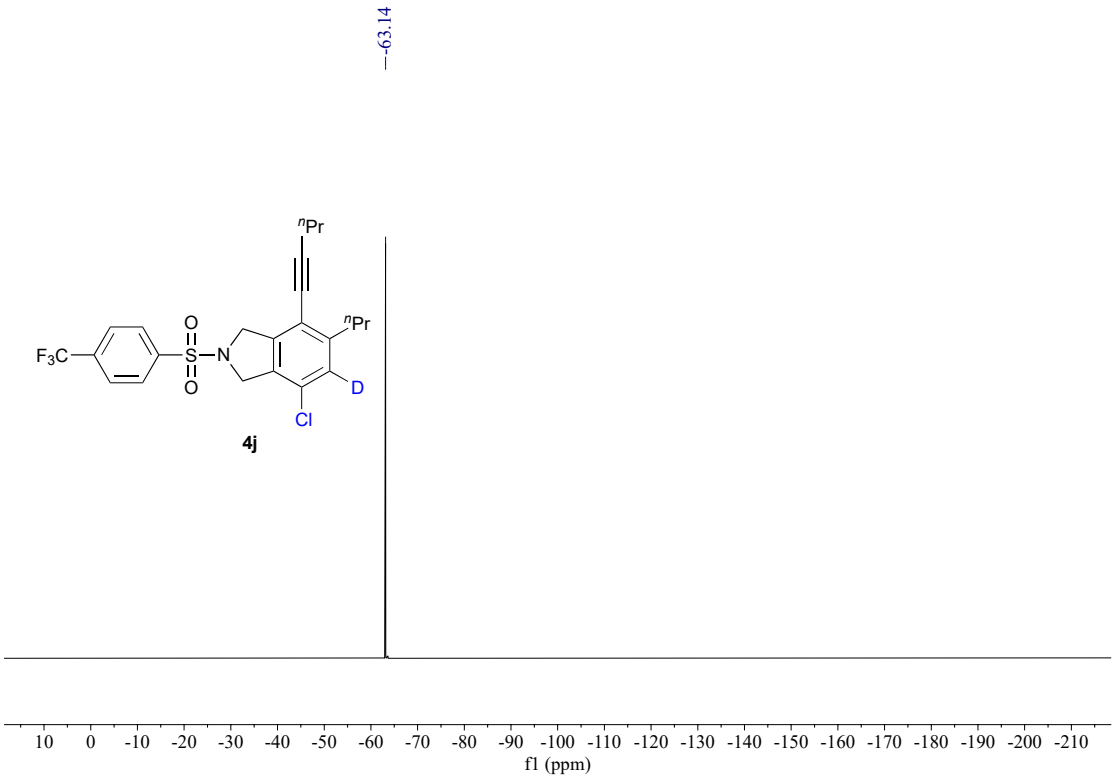
f1 (ppm)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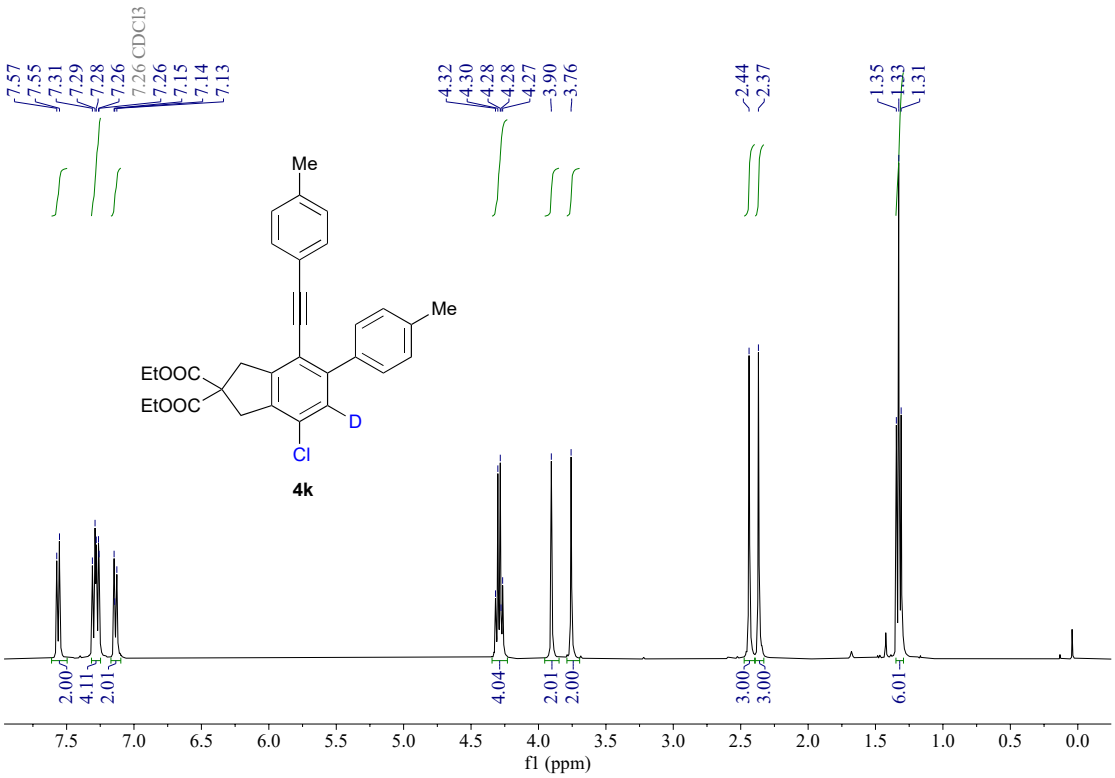
f1 (ppm)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4.28
4.28
4.27
3.90
3.76
2.44
2.37
1.35
1.33
1.31
Me
Me
EtOOC
EtOOC
D
Cl
4k
2.00
4.11
2.01
4.04
2.01
2.00
3.00
3.00
6.01
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6.5
6.0
5.5
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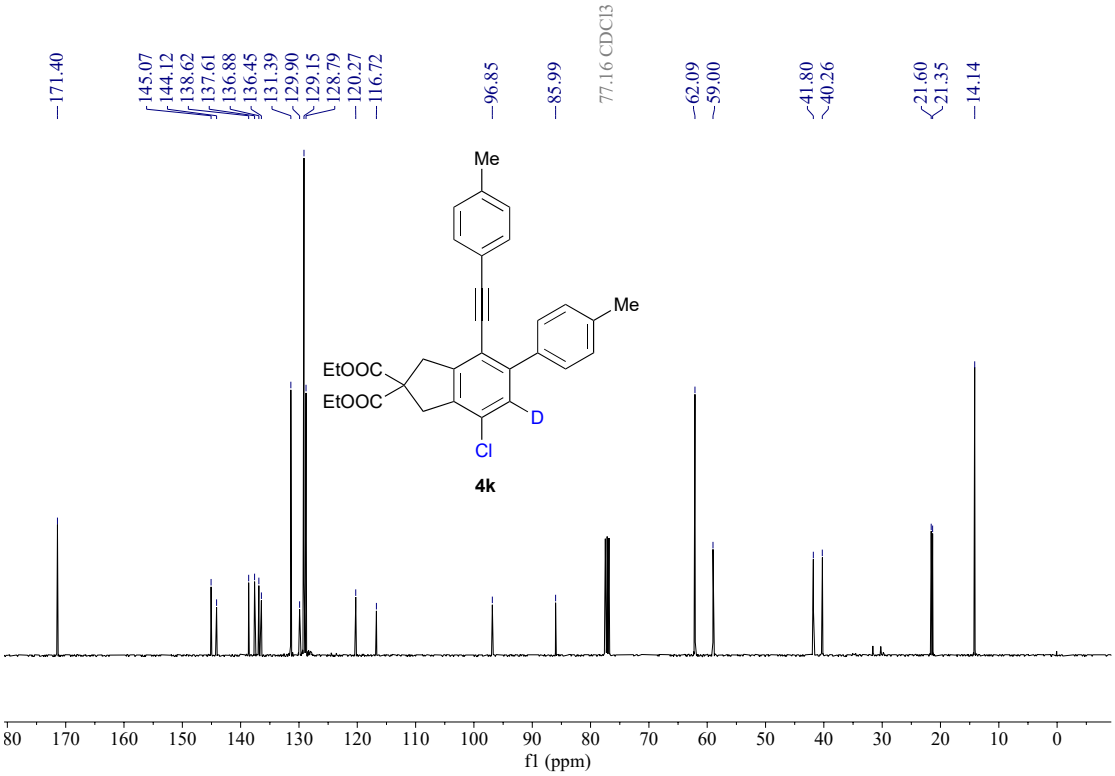
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116.72
96.85
85.99
77.16 CDCl3
62.09
59.00
41.80
40.26
21.60
21.35
14.14
Me
Me
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EtOOC
D
Cl
4k
80
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90
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50
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10
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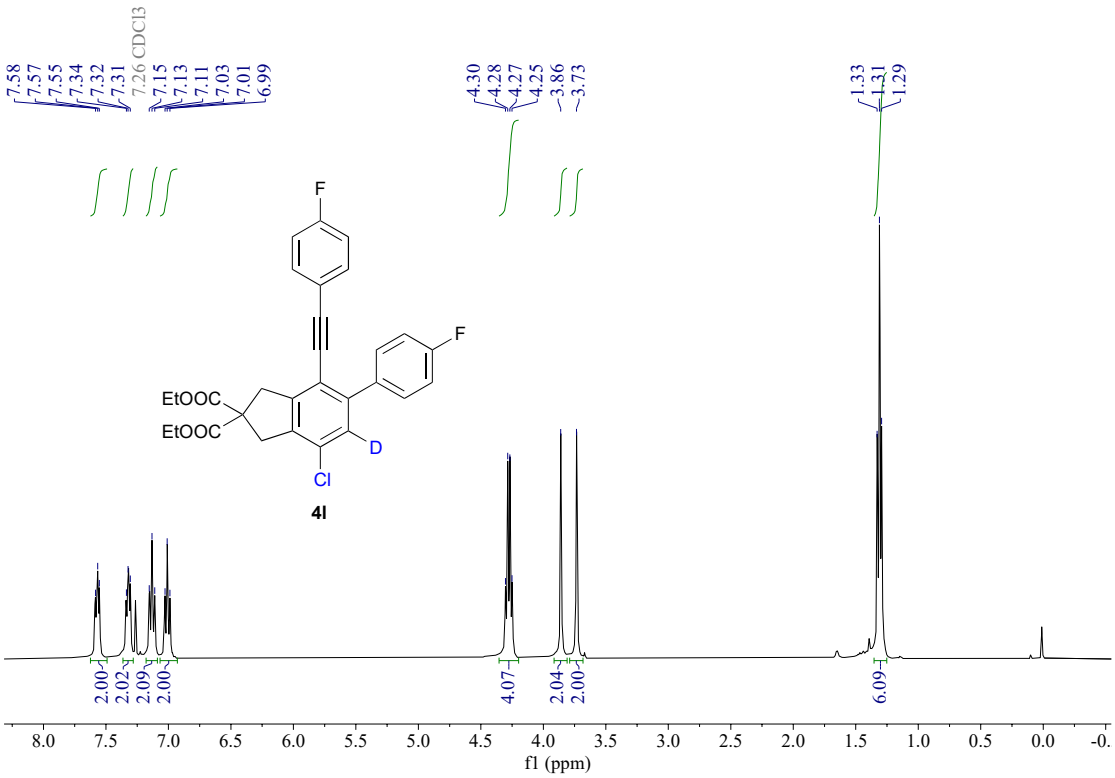
f1 (ppm)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7.01
6.99
4.30
4.28
4.27
4.25
3.86
3.73
1.33
1.31
1.29
F
F
EtOOC
EtOOC
D
Cl
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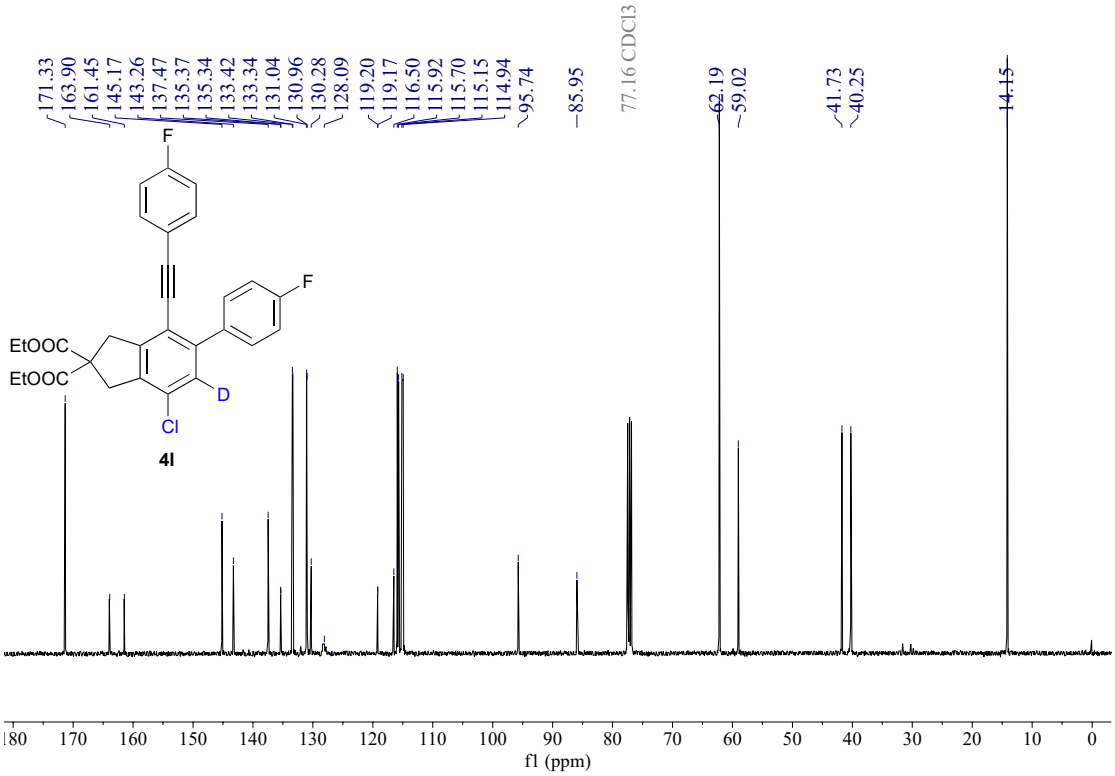
2.02
2.09
2.00
4.07
2.04
2.00
6.09
f1 (ppm)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128.09
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119.17
116.50
115.92
115.70
115.15
114.94
95.74
85.95
77.16 CDCl3
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F
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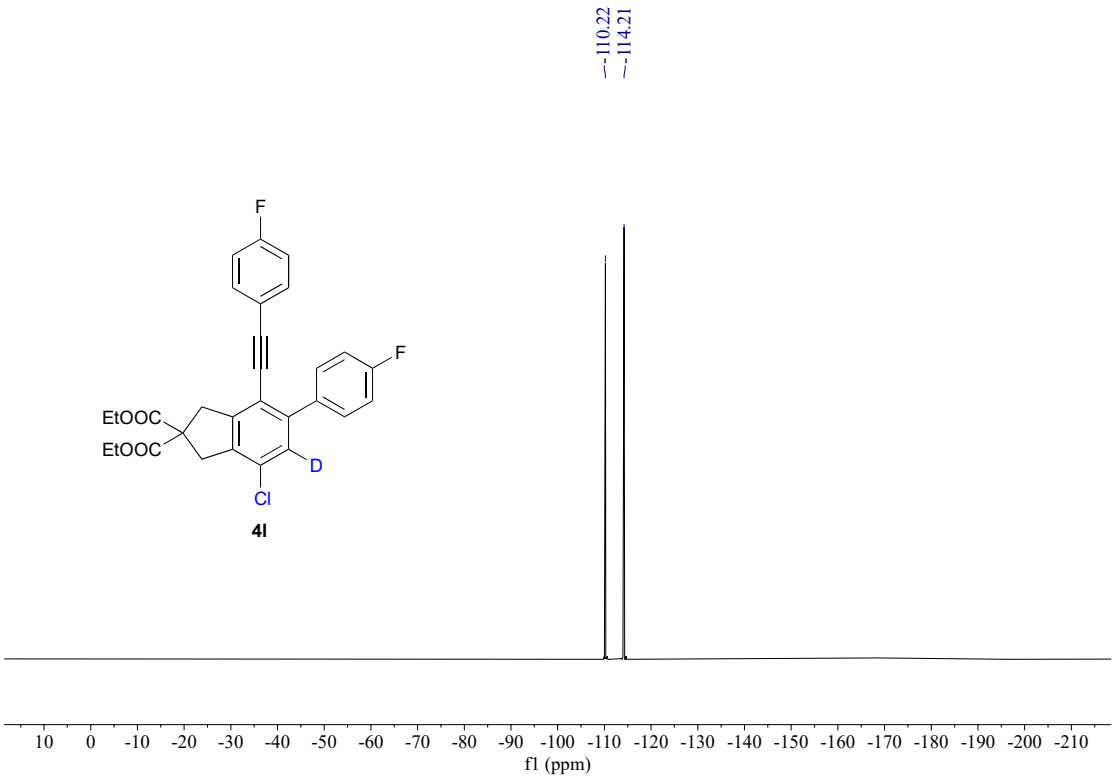
EtOOC
D
Cl
4l
f1 (ppm)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-114.21
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F
EtOOC
EtOOC
D
Cl
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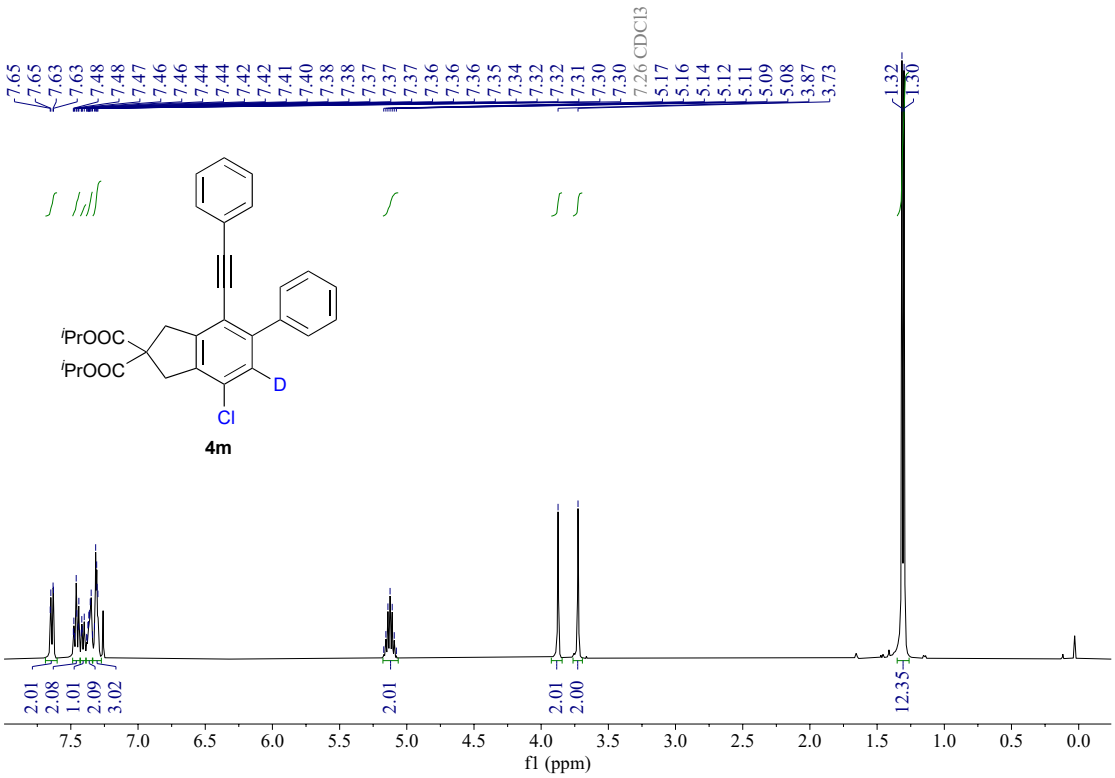
f1 (ppm)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7.40
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7.38
7.37
7.37
7.37
7.36
7.36
7.36
7.35
7.34
7.32
7.32
7.31
7.30
7.30
7.26 CDCl3
5.17
5.16
5.14
5.12
5.11
5.09
5.08
3.87
3.73
1.32
1.30
iPrOOC
iPrOOC
D
Cl
4m
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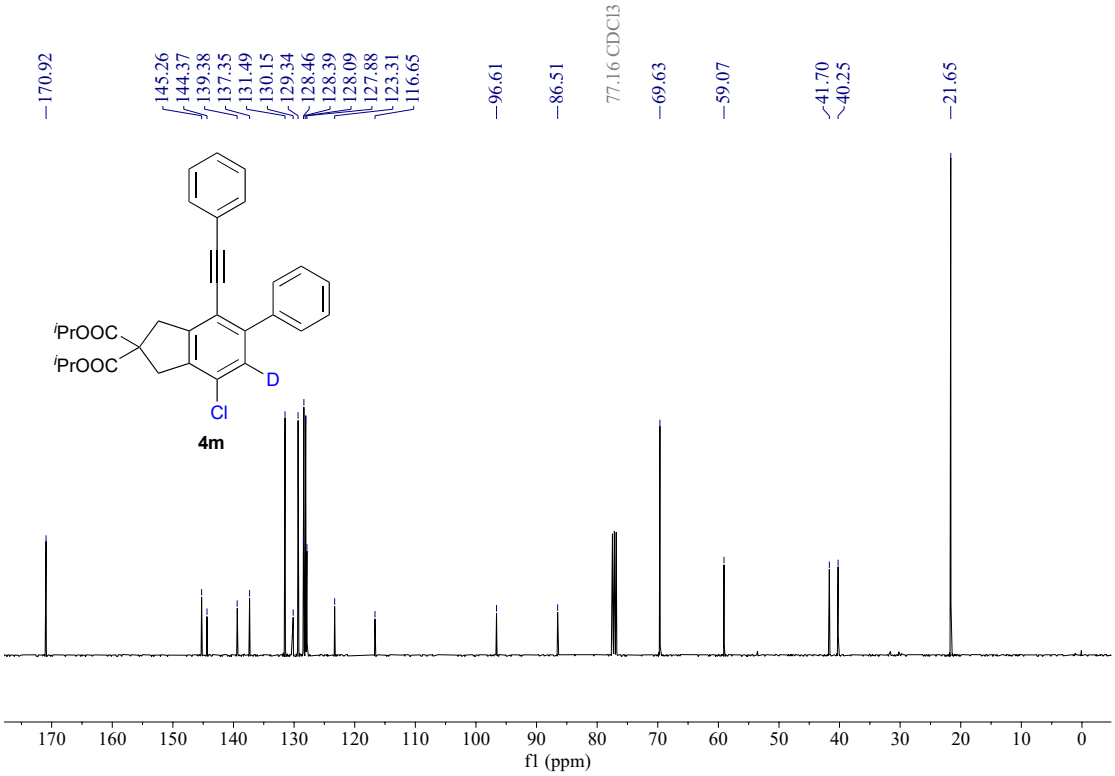
2.08
1.01
2.09
3.02
2.01
2.01
2.00
12.35
f1 (ppm)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128.09
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116.65
96.61
86.51
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59.07
41.70
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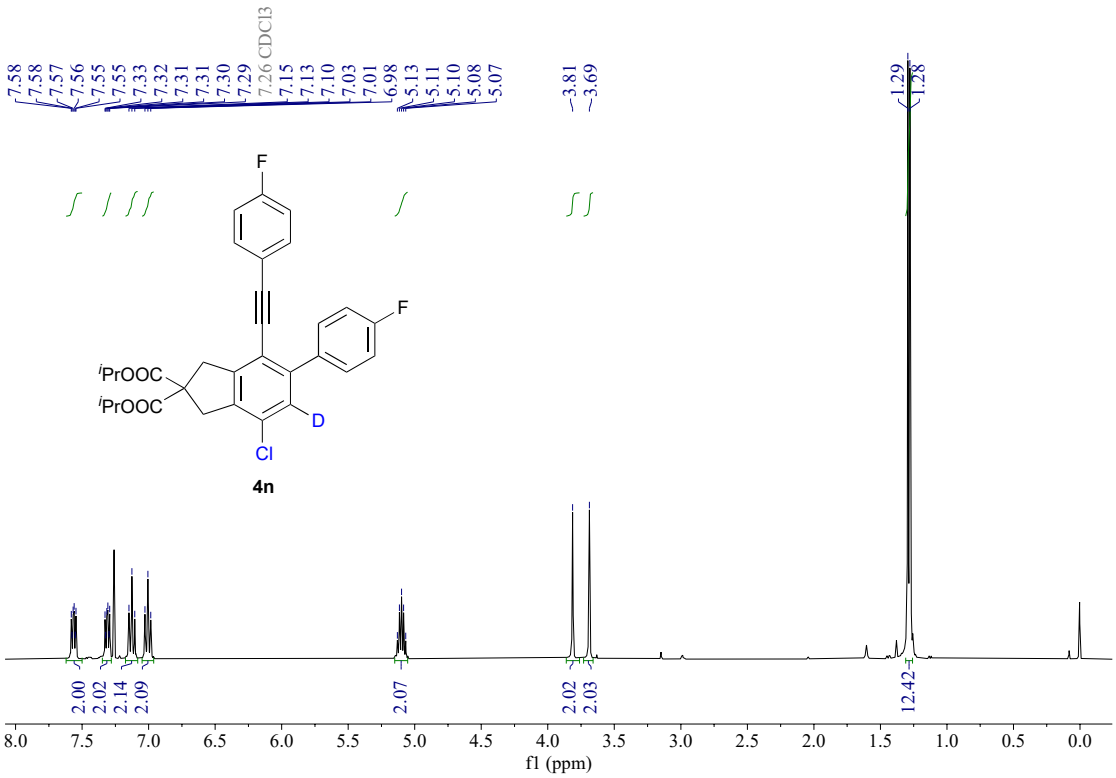
21.65
iPrOOC
iPrOOC
D
Cl
4m
f1 (ppm)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7.10
7.03
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5.13
5.11
5.10
5.08
5.07
3.81
3.69
1.29
1.28
F
F
iPrOOC
iPrOOC
D
Cl
4n
2.00
2.02
2.14
2.09
2.07
2.02
2.03
12.42
8.0
7.5
7.0
6.5
6.0
5.5
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3.5
3.0
2.5
2.0
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1.0
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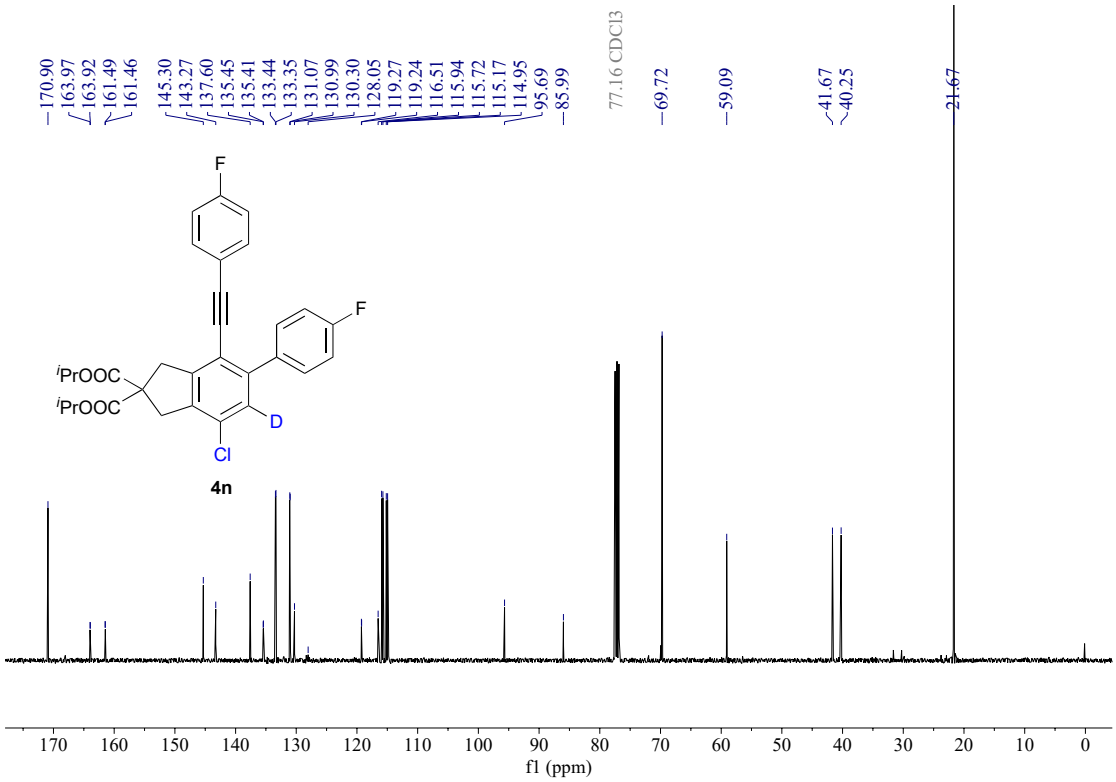
0.0
f1 (ppm)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131.07
130.99
130.30
128.05
119.27
119.24
116.51
115.94
115.72
115.17
114.95
95.69
85.99
77.16 CDCl3
69.72
59.09
41.67
40.25
21.67
F
F
iPrOOC
iPrOOC
D
Cl
4n
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100
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80
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40
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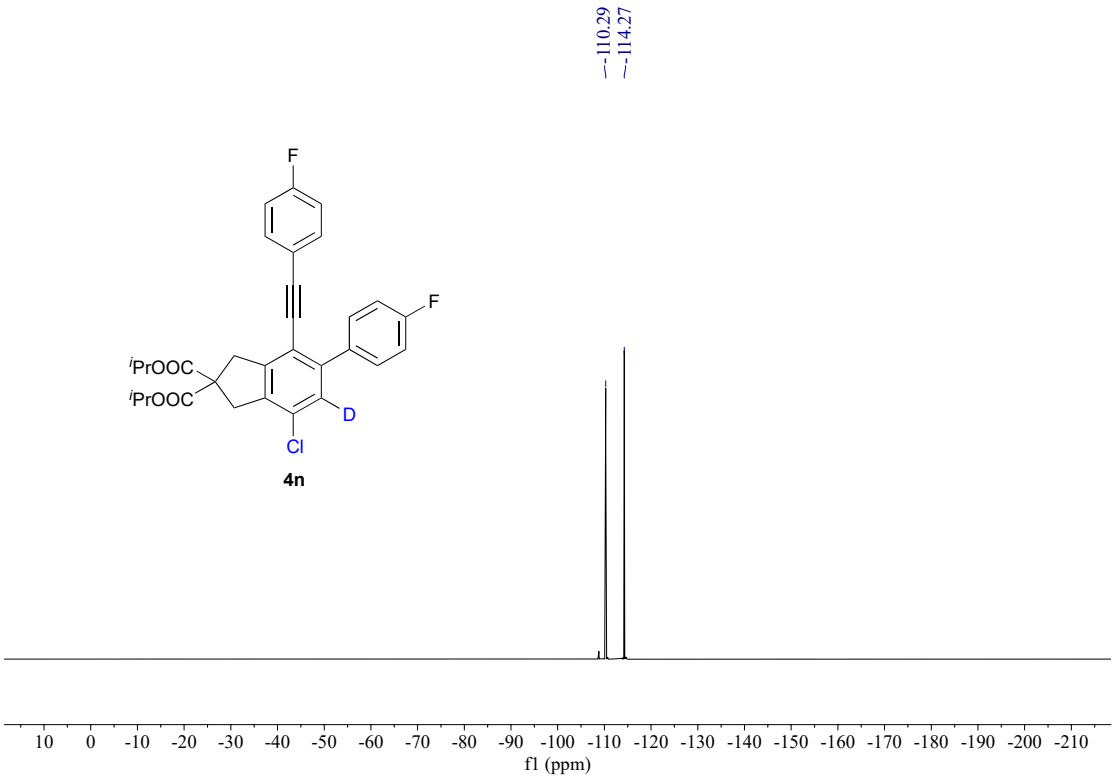
f1 (ppm)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-114.27
F
F
iPrOOC
iPrOOC
D
Cl
4n
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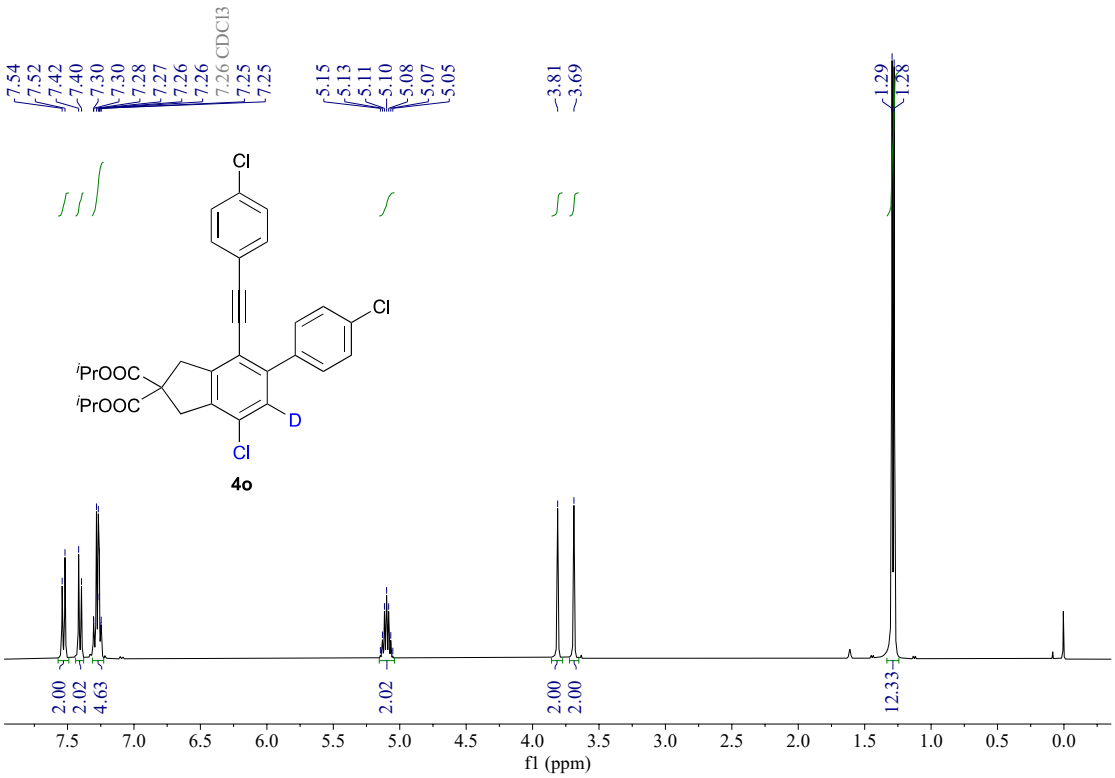
f1 (ppm)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7.25
5.15
5.13
5.11
5.10
5.08
5.07
5.05
3.81
3.69
1.29
1.28
Cl
Cl
iPrOOC
iPrOOC
D
Cl
4o
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2.02
4.63
2.02
2.00
2.00
12.33
7.5
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6.5
6.0
5.5
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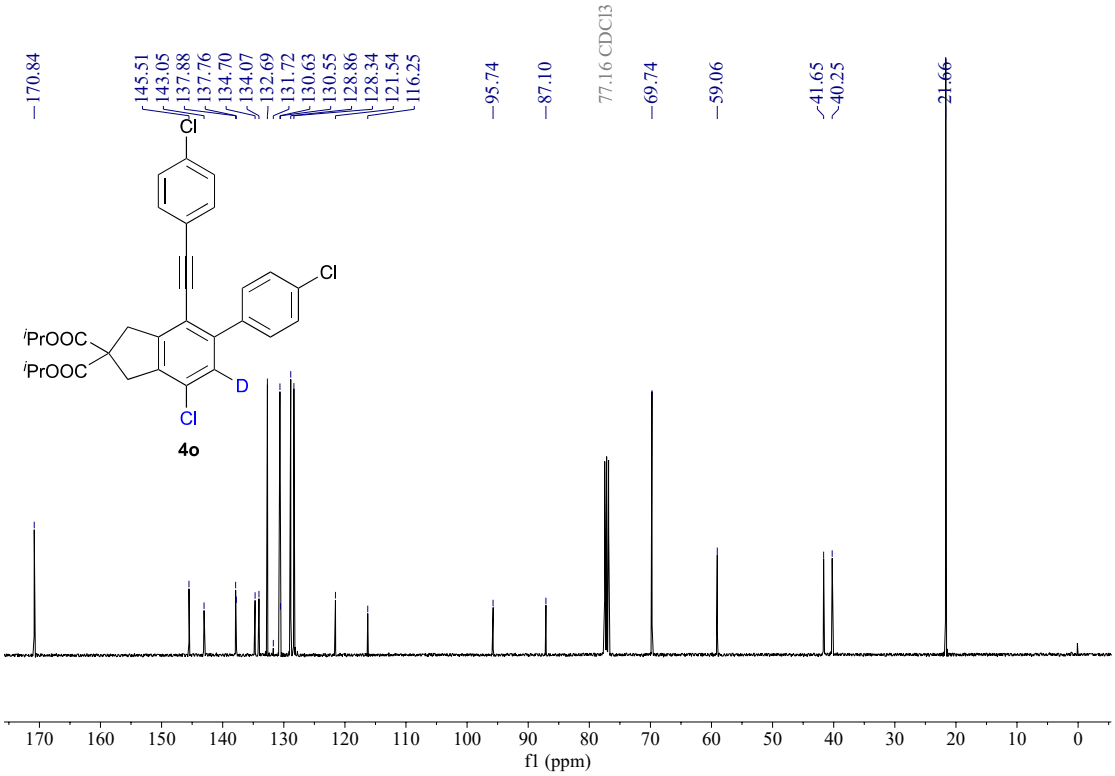
f1 (ppm)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128.34
121.54
116.25
95.74
87.10
77.16 CDCl3
69.74
59.06
41.65
40.25
21.66
Cl
Cl
iPrOOC
iPrOOC
D
Cl
4o
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90
80
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50
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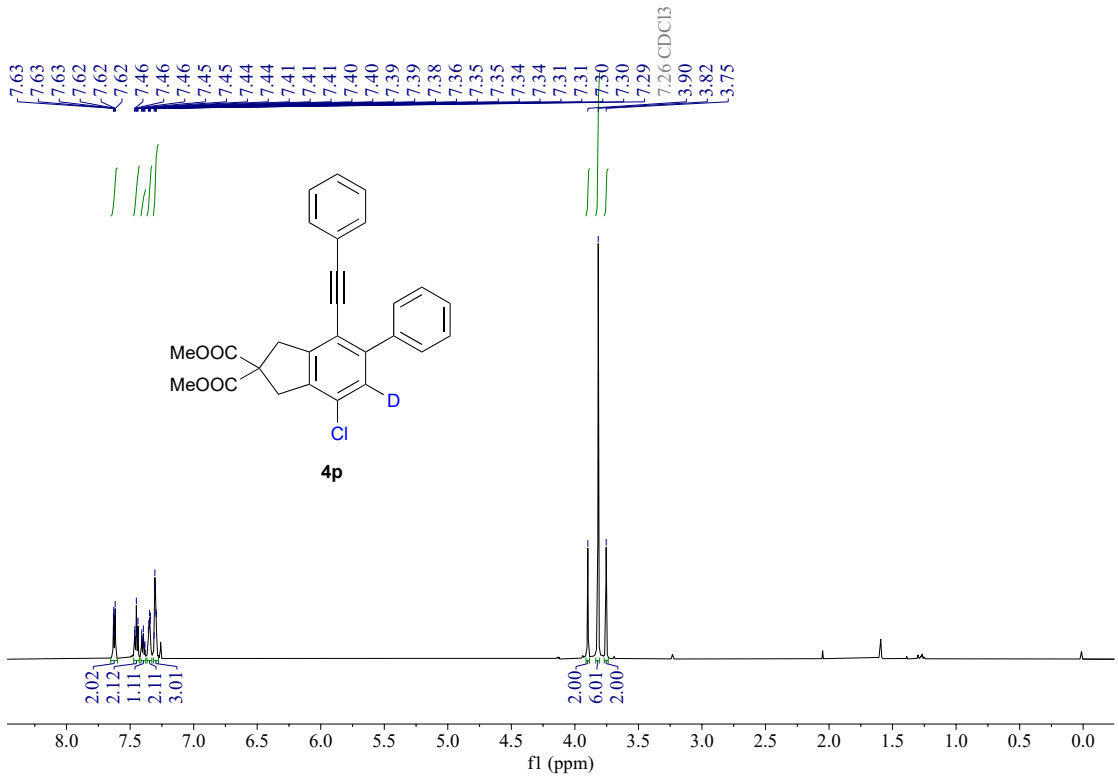
f1 (ppm)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7.31
7.30
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MeOOC
D
Cl
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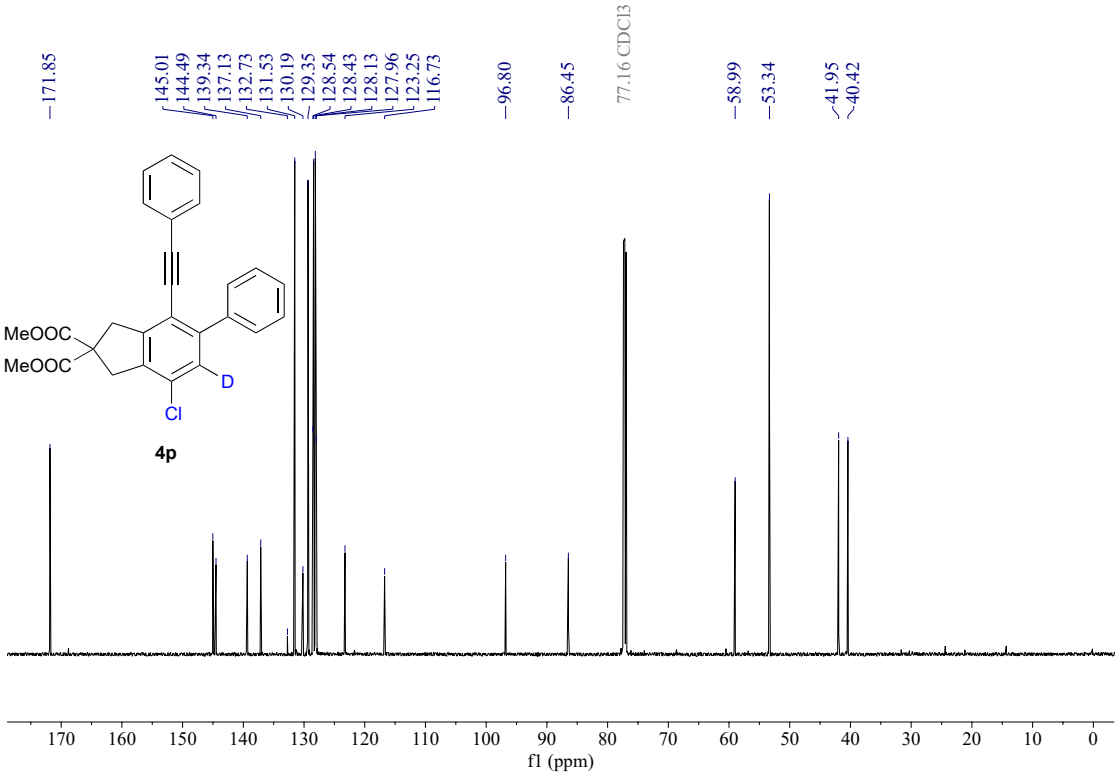
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86.45
77.16 CDCl3
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41.95
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MeOOC
D
Cl
4p
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10
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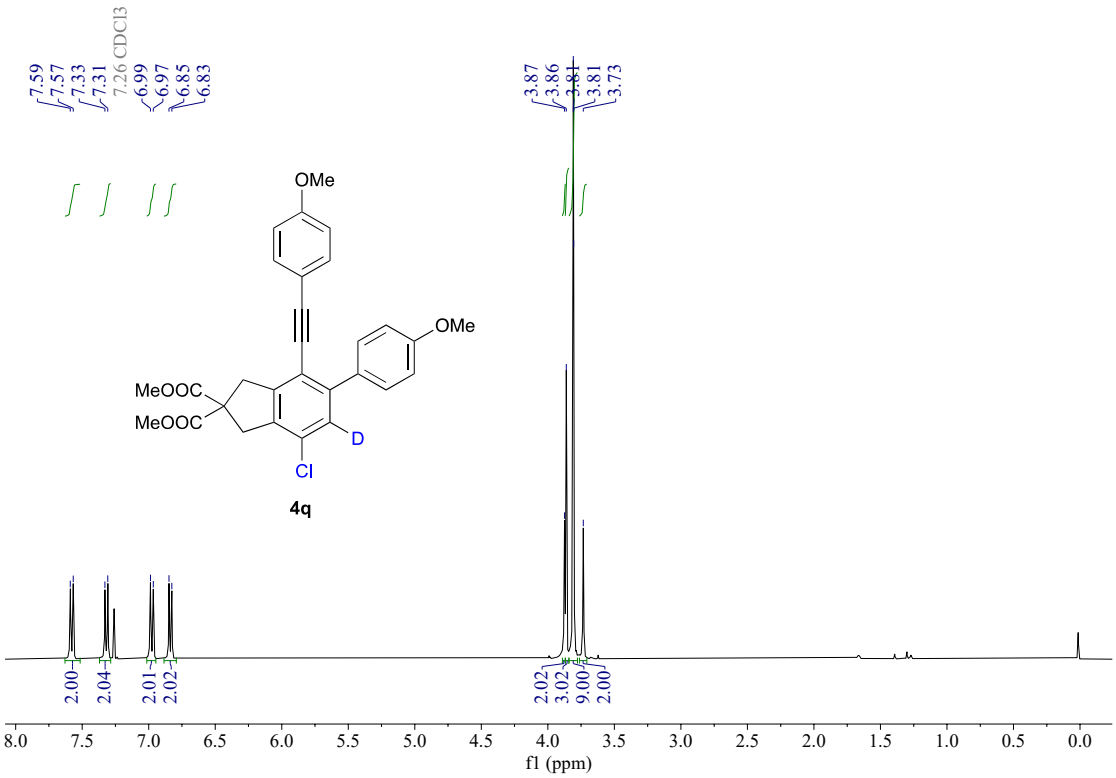
f1 (ppm)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3.81
3.73
OMe
OMe
MeOOC
MeOOC
D
Cl
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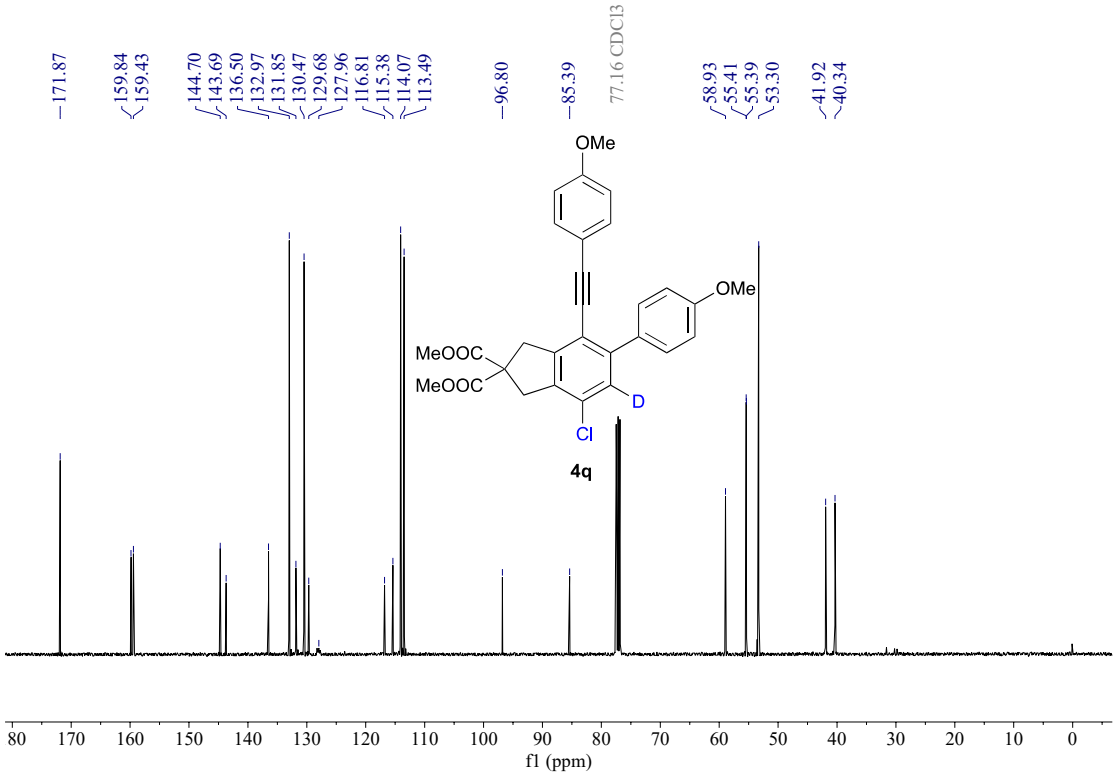
2.04
2.01
2.02
2.02
3.02
9.00
2.00
f1 (ppm)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113.49
96.80
85.39
77.16 CDCl3
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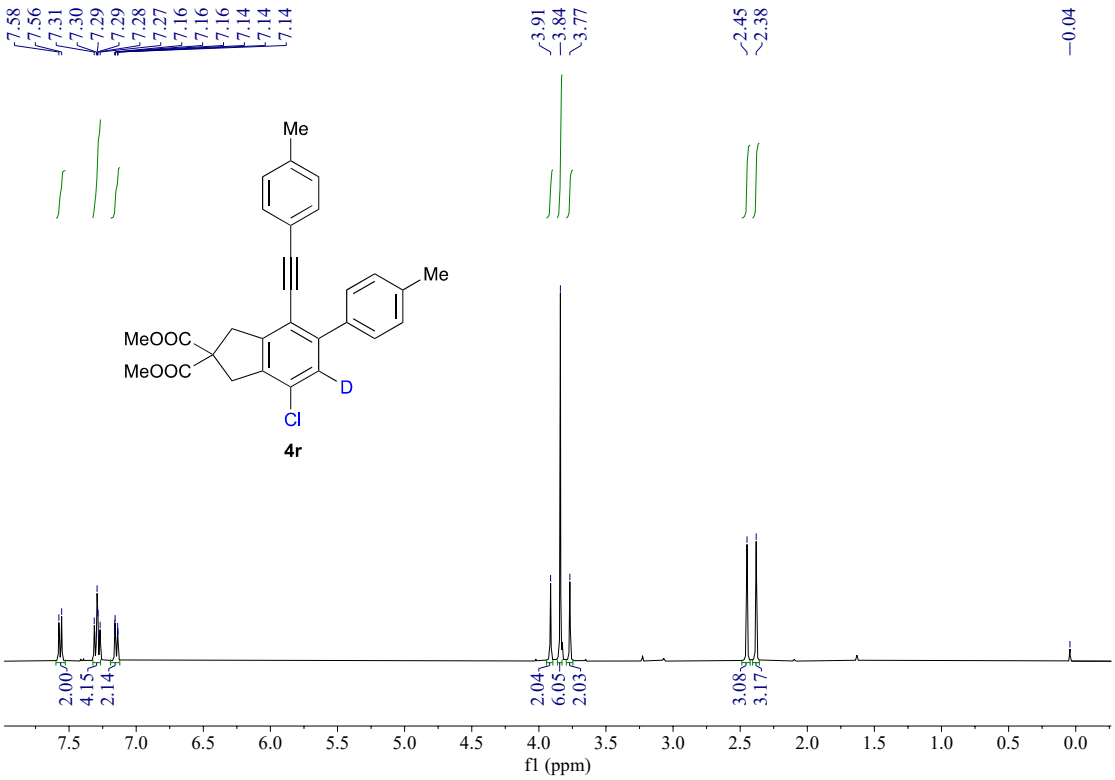
OMe
OMe
MeOOC
MeOOC
D
Cl
4q
f1 (ppm)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Me
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MeOOC
D
Cl
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2.14
2.04
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2.03
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6.5
6.0
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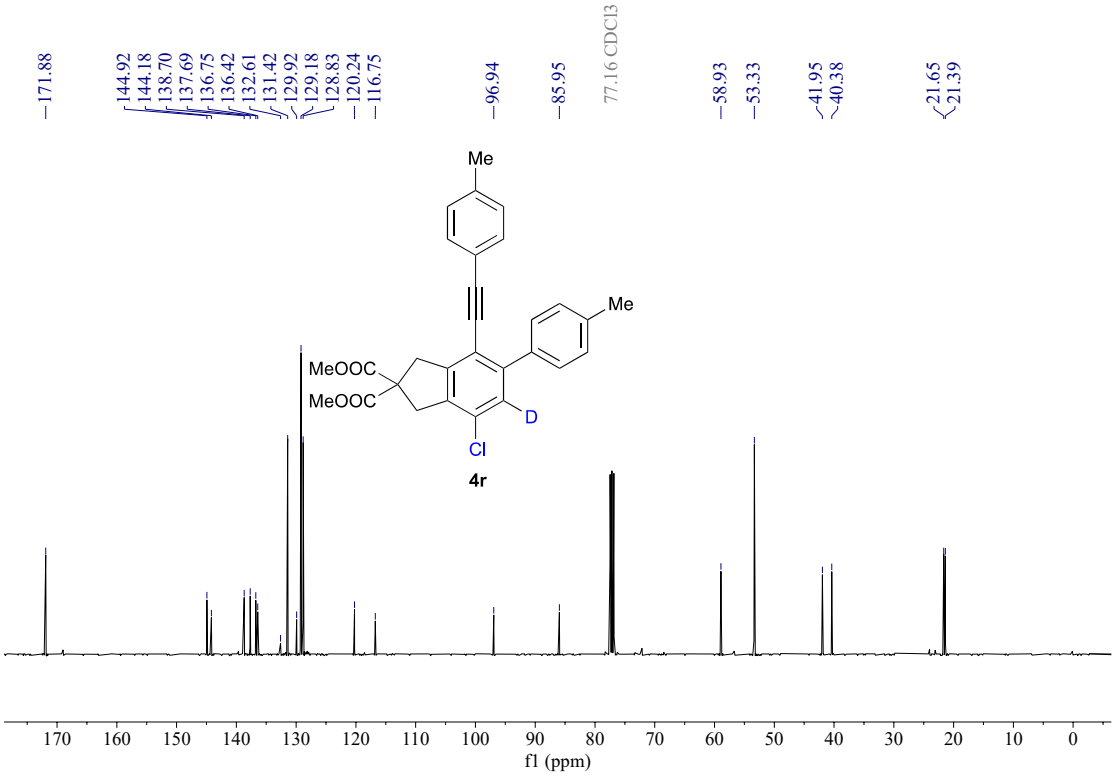
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Me
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MeOOC
D
Cl
4r
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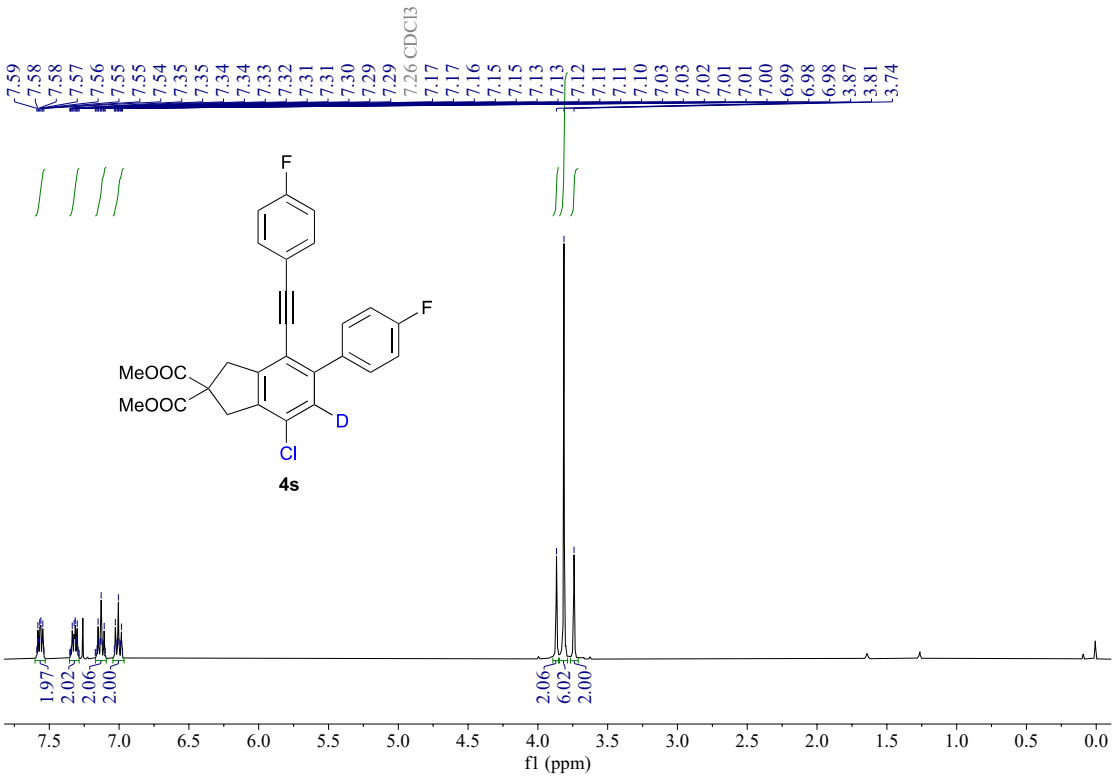
f1 (ppm)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7.29
7.26 CDCl3
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7.02
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7.01
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F
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MeOOC
D
Cl
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2.06
6.02
2.00
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6.0
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2.0
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1.0
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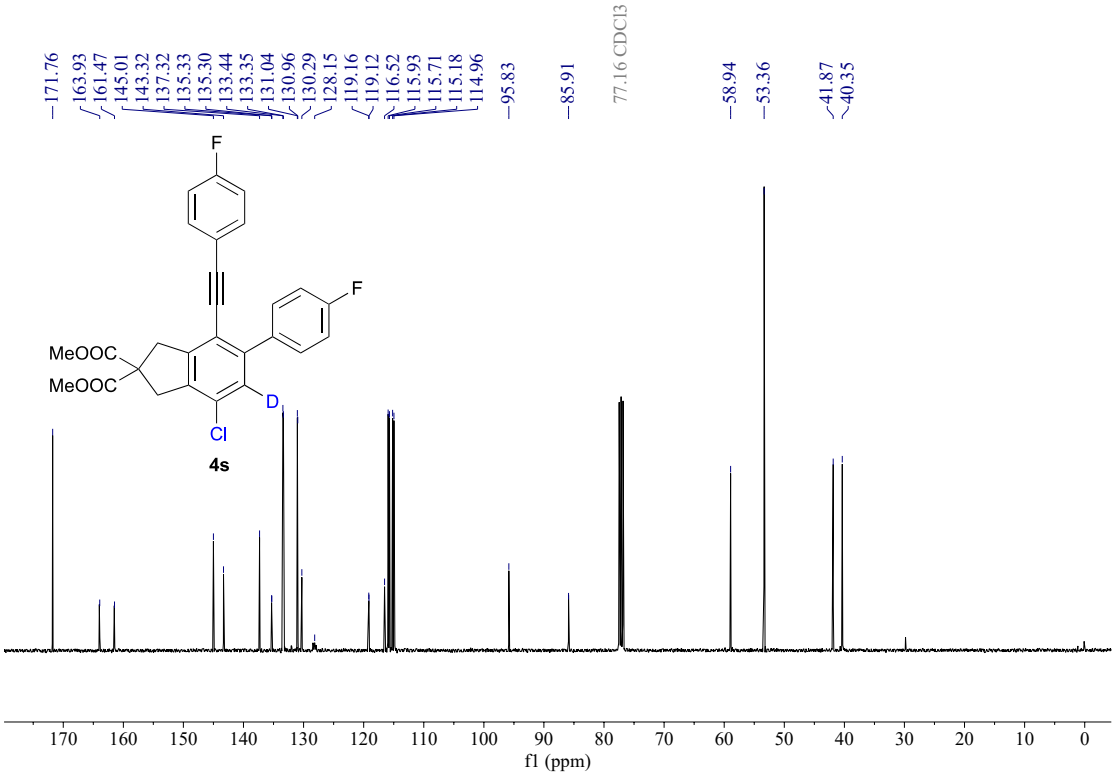
0.0
f1 (ppm)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114.96
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85.91
77.16 CDCl3
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53.36
41.87
40.35
F
F
MeOOC
MeOOC
D
Cl
4s
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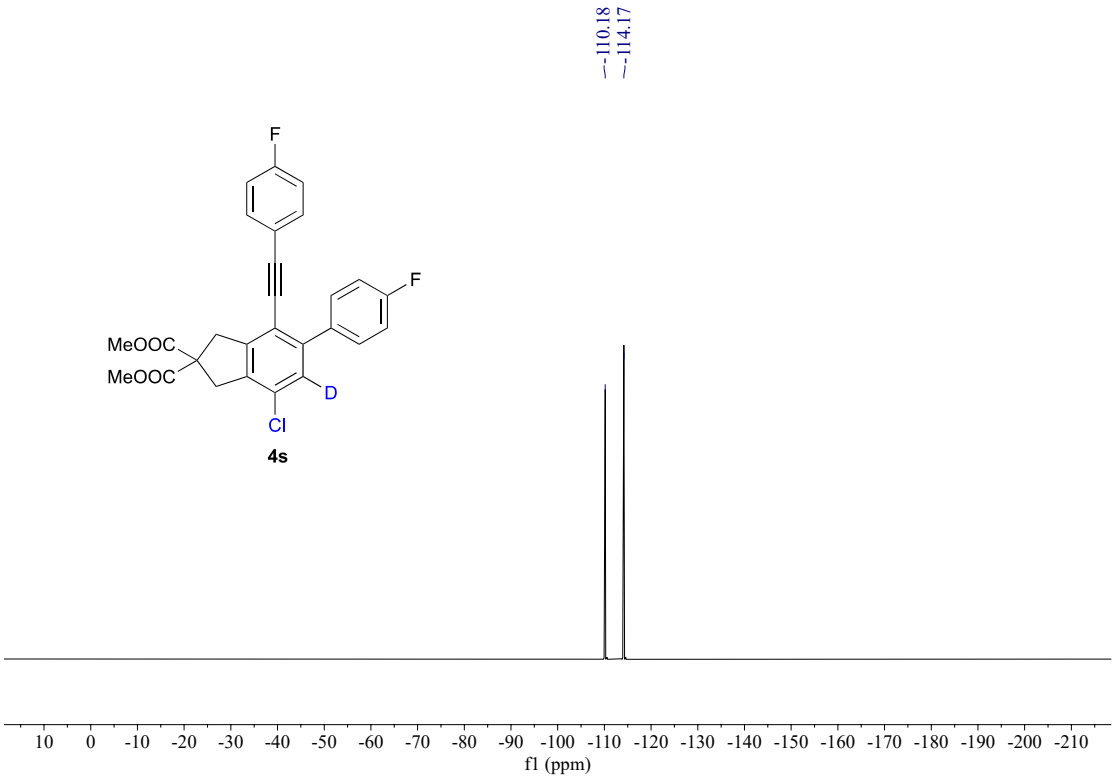
10
0
f1 (ppm)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F
F
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D
Cl
4s
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)