Supporting Information

Tf_2O-Induced Selective 1,3-Transposition/Cyclization of Ynones in DMF

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I. General information

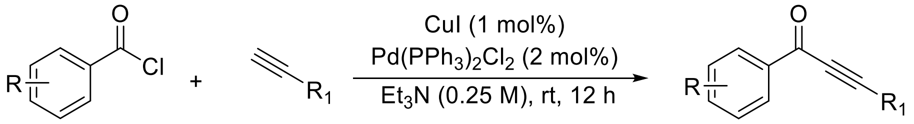
General procedures. Unless specifically stated, all reagents were commercially obtained and where appropriate, purified prior to use. For example, dichloromethane (DCM) was freshly distilled from CaH_2. Other commercially available reagents and solvents were used directly without purification. Reactions were monitored by thin layer chromatography (TLC) using silica gel plates. Flash column chromatography was performed over silica (200 – 300 mesh). ^1H, ^{13}C, ^{19}F NMR spectra were recorded on a Bruker 400 MHz or 500 MHz spectrometer in $CDCl_3$ or d_6-DMSO. Multiplicities were given as: s (singlet); d (doublet); dd (doublets of doublet); t (triplet); q (quartet); td (triplet of doublets); tt (triplet of triplets) ddd (doublet of doublet of doublets) or m (multiplets). High resolution mass spectra (**HRMS**) of the products were obtained on a Bruker Daltonics micro TOF-spectrometer. of the products were obtained on an Agilent Technologies micro Q-TOF-spectrometer.

Reagents. The following chemicals were used as received: 1-Bromo-3-ethynylbenzene (Bide), Benzoyl chloride (Energy-Chemical), Benzyl bromide (Energy-Chemical), Benzoyl chloride (Energy-Chemical), Boron trifluoride etherate (Energy-Chemical), Benzoyl chloride (Energy-Chemical), 3-Benzyloxy-1-propanol (Leyan), 1-Chloro-4-ethynylbenzene (Leyan), Copper(II) trifluoromethanesulfonate (Adamas), Diethyl (bromodifluoromethyl) phosphonate (Leyan), 1-Ethynyl-4-methylbenzene (Leyan), 1-Ethynyl-4-fluorobenzene (Leyan), Ethynyltrimethylsilane (9dingchem), Ethynylcyclopropane (Energy-Chemical), 2-Ethoxybenzoyl Chloride (Adamas), 4-Ethynylbenzonitrile (Leyan), 2-Fluorobenzoyl chloride (Adamas), Flavone (Energy-Chemical), Furan-2-carbonyl chloride (Energy-Chemical), 2-Fluorobenzoyl chloride (Adamas), Hex-1-yne (Energy-Chemical), 4-Hydroxycoumarin (Adamas), 1-Iodonaphthalene (Leyan), 1-Iodo-2-methylbenzene (Energy-Chemical), 2-Iodothiophene (Leyan), 3-Iodothiophene (Energy-Chemical), Isoindoline-1,3-dione (Energy-Chemical), Iodomethane (Energy-

Chemical), Ibuprofen (Energy-Chemical), *m*-Chloroperbenzoic acid (Energy-Chemical), 2-Methoxybenzoyl chloride (Bidei), Methyl 4-Ethynylbenzoate (Leyan), 2-Methyl benzoyl chloride (Adamas), 3-Methylindole (Bide), Manganese dioxide (Leyan), *m*-Anisoyl chloride (Bide), *N*-Chlorosuccinimide (Energy-Chemical), *n*-Butyllithium (Energy-Chemical), Oxalyl chloride (Energy-Chemical), *o*-Anisaldehyde (Leyan), Potassium persulfate (Adamas), *p*-Toluenesulfonyl Hydrazide (Energy-Chemical), Potassium fluoride (Energy-Chemical), Pent-4-yn-1-ol (Leyan), Potassium hydroxide (3A), *p*-Anisoyl chloride (Energy-Chemical), Phenylacetylene (Energy-Chemical), Sodium carbonate anhydrous (3A), Sodium periodate (Energy-Chemical), Sodium sulfate (Energy-Chemical), *tetra*-Butylammonium fluoride hydrate (Energy-Chemical), Triflic anhydride (Heowns), Trimethylchlorosilane (Energy-Chemical).

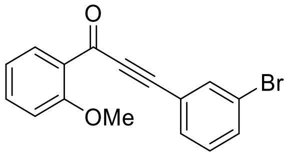
II. Synthesis of starting materials

1. General Method A: Synthesis of alkyne ketone 1a-1i, 1k-1n, 1x, 1ae, 15, 17-19, 31, 32



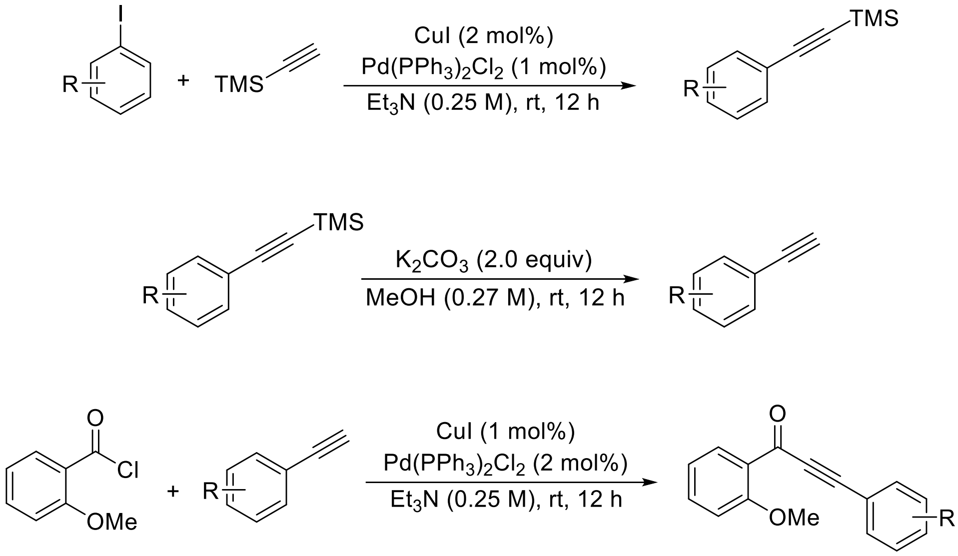
A 120 °C oven-dried 100-mL round-bottom flask, equipped with a stir bar, was charged with alkyne (5.5 mmol, 1.1 equiv), acid chloride (5.0 mmol, 1.0 equiv), CuI (9.5 mg, 0.05 mmol, 0.01 equiv), $Pd(PPh_3)_2Cl_2$ (70.2 mg, 0.10 mmol, 0.02 equiv), the mixture was evacuated and backfilled with nitrogen for three times. Then triethylamine (20.0 mL) was added under nitrogen and the mixture was allowed to stir at room temperature for 12 h. After the completion of reaction, a saturated aqueous solution of NH_4Cl (50.0 mL) was added and the mixture was extracted with ethyl acetate (50.0 mL x 3). The combined organic layers were washed with brine (50.0 mL x 5), dried over by Na_2SO_4 and filtrated. The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography to provide the desired products.

Compound **1a** (prepared on 20.0 mmol scale): a yellow solid, 4.02 g, 17.0 mmol, 85% yield[1]; compound **1b** (prepared on 10.0 mmol scale): a yellow solid, 1.91 g, 7.5 mmol, 75% yield[2]; compound **1c**: a yellow solid, 784.9 mg, 2.9 mmol, 58% yield[3]; compound **1d**: a yellow solid, 857.3 mg, 3.4 mmol, 69% yield[3]; compound **1e**: a yellow liquid, 759.7 mg, 2.9 mmol, 57% yield[3]; compound **1f**: a yellow solid, 1.05 g, 4.0 mmol, 80% yield[4]; compound **1g**: a yellow solid, 1.06 g, 3.6 mmol, 72% yield[5]; compound **1h**: a yellow liquid, 1.10 g, 3.6 mmol, 72% yield[2]; compound **1k**: a yellow solid, 0.99 g, 3.6 mmol, 73.2% yield[3]; compound **1l**: a yellow solid, 1.3 g, 4.2 mmol, 83.2% yield[3]; compound **1m**: a yellow liquid, 939.5 mg, 4.3 mmol, 87% yield[3]; compound **1n**: a yellow liquid, 1.07 g, 4.4 mmol, 88% yield[6]; compound **1x**: a yellow solid, 1.3 g, 4.1 mmol, 81.2% yield[3]; c compound **1ae**: a yellow solid, 593.7 mg, 3.0 mmol, 59.7% yield[3]; compound **15**: a yellow liquid, 1.07 g, 4.3 mmol, 85% yield[7]; compound **17**: a yellow solid, 1.01 g, 4.6 mmol, 92% yield[8]; compound **18** (prepared on 10.0 mmol scale): a yellow liquid, 2.10 g, 9.5 mmol, 95% yield[9]; compound **19** (prepared on 10.0 mmol scale): a yellow liquid, 2.08 g, 9.3 mmol, 93% yield[10]; compound **31**: a yellow liquid, 1.11 g, 4.7 mmol, 94% yield[11]; compound **32**: a yellow solid, 966.0 mg, 4.1 mmol, 82% yield[1]; The spectral data match those previously reported.



3-(3-Bromophenyl)-1-(2-methoxyphenyl)prop-2-yn-1-one 1i: Prepared according to **General Method A** (Eluent: 100:1 to 20:1 petroleum ether: ethyl acetate) and the title compound was isolated as a yellow liquid (2.80 g, 8.9 mmol, 89% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.07 (1H, dd, J = 7.8, 1.8 Hz), 7.77 (1H, s), 7.60 – 7.54 (3H, m), 7.30 – 7.26 (1H, m), 7.08 – 7.02 (2H, m), 3.97 (3H, s); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.5, 160.0, 135.5, 135.4, 133.6, 132.8, 131.5, 130.2, 126.4, 122.8, 122.4, 120.5, 112.3, 89.8, 89.4, 56.0; **HRMS** (ESI$^+$) [M+Na] $^+$ calc'd for $C_{16}H_{11}BrO_2Na$: 336.9835, found: 336.9830.

2. General Method B: Synthesis of alkyne ketone 1j, 1aa-ac



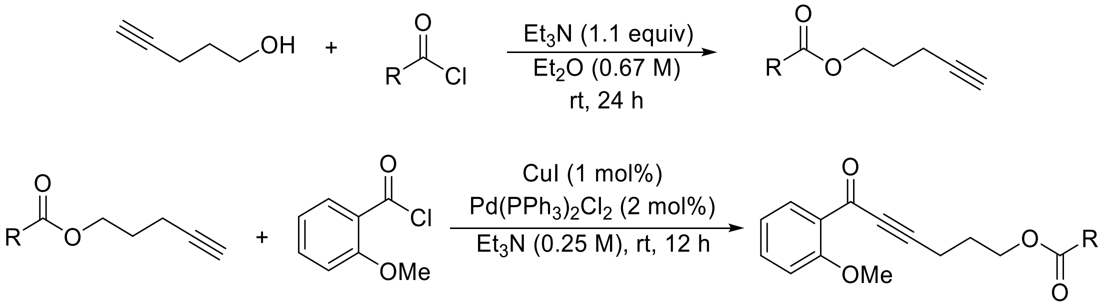
A 120 °C oven-dried 100-mL round-bottom flask, equipped with a stir bar, was charged with ethynyltrimethylsilane (1.18 g, 12.0 mmol, 1.2 equiv), aryl(hetero) iodides (10.0 mmol, 1.0 equiv), CuI (38.1 mg, 0.1 mmol, 0.02 equiv), $Pd(PPh_3)_2Cl_2$ (70.2 mg, 0.10 mmol, 0.01 equiv), the mixture was evacuated and backfilled with nitrogen for three times. Then triethylamine (40.0 mL) was added under nitrogen and the mixture was allowed to stir at room temperature for 12 h. After the completion of reaction, a saturated aqueous solution of NH_4Cl (50.0 mL) was added and the mixture was extracted with ethyl acetate (50.0 mL x 3). The combined organic layers were washed with brine (50.0 mL x 5), dried over by Na_2SO_4 and filtrated. The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography to provide the desired alkyne products.

A 120 °C oven-dried 100-mL round-bottom flask, equipped with a stir bar, was charged with alkyne (8.0 mmol, 1.0 equiv), K_2CO_3 (2.21 g, 16.0 mmol, 2.0 equiv) and MeOH (30.0 mL) under nitrogen. The mixture was allowed to stir at rt for 12 h. After the completion of reaction, a saturated aqueous solution of brine (30.0 mL) was added and the mixture was extracted with dichloromethane (50.0 mL x 3). The combined organic layers were washed with brine (50.0 mL x 5), dried over by Na_2SO_4 and filtrated. The solvent was removed by rotary evaporation and the product don't need further purified, used for next step directly.

A 120 °C oven-dried 100-mL round-bottom flask, equipped with a stir bar, was charged with alkyne (5.5 mmol, 1.1 equiv), 2-methoxybenzoyl chloride (853.0 mg, 5.0 mmol, 1.0 equiv), CuI (9.5 mg, 0.05 mmol, 0.01 equiv), $Pd(PPh_3)_2Cl_2$ (70.2 mg, 0.1 mmol, 0.02 equiv), the mixture was evacuated and backfilled with nitrogen for three times. Then triethylamine (20.0 mL) was added under nitrogen and the mixture was allowed to stir at 50 °C for 12 h. After the completion of reaction, a saturated aqueous solution of NH_4Cl (50.0 mL) was added and the mixture was extracted with ethyl acetate (50.0 mL x 3). The combined organic layers were washed with brine (50.0 mL x 5), dried over by Na_2SO_4 and filtrated. The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography to provide the desired products.

Compound **1j**: a yellow solid, 1.06 g, 4.4 mmol, 87% yield[3]; compound **1aa**: a green liquid, 1.17 g, 4.1 mmol, 82% yield[3]; compound **1ab**: a yellow liquid, 653.3 mg, 2.6 mmol, 52% yield[3]; compound **1ac**: a yellow liquid, 883.5 mg, 3.6 mmol, 73% yield[12]; The spectral data match those previously reported.

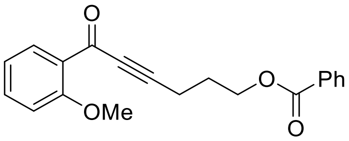
3. General Method C: Synthesis of alkyne ketone 1o-t



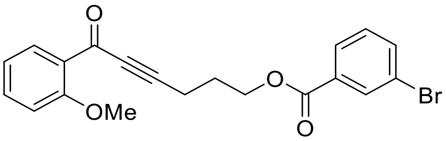
A 120 °C oven-dried 100-mL round-bottom flask, equipped with a stir bar, was charged with pent-4-yn-1-ol (1.26 g, 15.0 mmol, 1.0 equiv), acid chloride (16.5 mmol, 1.1 equiv) were dissolved in Et_2O (22.0 mL), triethylamine (1.67 g, 16.5 mmol, 1.1 equiv) was added slowly, and the reaction mixture was allowed to stir at room temperature for 24 h. The mixture was quenched by water (50.0 mL) then extracted with EtOAc (50.0 mL x 3). The combined organic layers were dried over by Na_2SO_4

then filtered. The solvent was removed by rotary evaporation and purified by flash silica gel chromatography to give desired products.

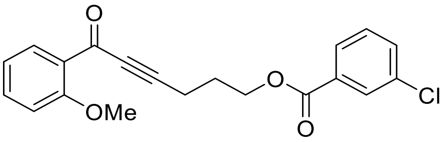
A 120 °C oven-dried 100-mL round-bottom flask, equipped with a stir bar, was charged with alkyne (5.5 mmol, 1.1 equiv), 2-methoxybenzoyl chloride (853.0 mg, 5.0 mmol, 1.0 equiv), CuI (9.5 mg, 0.05 mmol, 0.01 equiv), $Pd(PPh_3)_2Cl_2$ (70.2 mg, 0.1 mmol, 0.02 equiv). The mixture was evacuated and backfilled with nitrogen for three times. Then triethylamine (20.0 mL) was added under nitrogen and the mixture was allowed to stir at 50 °C for 12 h. After the completion of reaction, a saturated aqueous solution of NH_4Cl (50.0 mL) was added and the mixture was extracted with ethyl acetate (50.0 mL x 3). The combined organic layers were washed with brine (50.0 mL x 5), dried over by Na_2SO_4 and filtrated. The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography to provide the desired products.



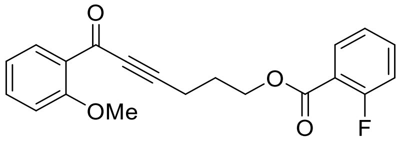
6-(2-Methoxyphenyl)-6-oxohex-4-yn-1-yl benzoate 1o: Prepared according to **General Method C** (Eluent: 80:1 to 10:1 petroleum ether: ethyl acetate) and the title compound was isolated as a yellow liquid (1.39 g, 4.3 mmol, 86% yield); ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 8.05 – 8.03 (2H, m), 8.00 (1H, dd, J = 7.7, 1.8 Hz), 7.58 – 7.48 (2H, m), 7.45 – 7.41 (2H, m), 7.03 – 6.96 (2H, m), 4.47 (2H, t, J = 6.2 Hz), 3.91 (3H, s), 2.66 (2H, t, J = 7.0 Hz), 2.15 – 2.09 (2H, m); ^{13}**C NMR** (101 MHz, $CDCl_3$) δ 177.0, 166.6, 159.8, 135.0, 133.2, 133.0, 130.1, 129.7, 128.5, 126.6, 120.3, 112.2, 93.3, 82.3, 63.5, 55.9, 27.3, 16.4; **HRMS** (ESI$^+$) $[M+Na]^+$ calc'd for $C_{20}H_{18}O_4Na$: 345.1097, found: 345.1092.



6-(2-Methoxyphenyl)-6-oxohex-4-yn-1-yl 3-bromobenzoate 1p: Prepared according to **General Method C** (Eluent: 80:1 to 10:1 petroleum ether: ethyl acetate) and the title compound was isolated as a yellow liquid (1.88 g, 4.7 mmol, 94% yield); **^{1}H NMR** (500 MHz, CDCl$_3$) δ 8.15 (1H, s), 7.99 – 7.96 (2H, m), 7.68 – 7.66 (1H, m), 7.52 – 7.49 (1H, m), 7.32 – 7.29 (1H, m), 7.02 – 6.99 (1H, m), 6.97 (1H, d, J = 8.4 Hz), 4.48 (2H, t, J = 6.2 Hz), 3.91 (3H, s), 2.66 (2H, t, J = 7.0 Hz), 2.15 – 2.10 (2H, m); **^{13}C NMR** (101 MHz, CDCl$_3$) δ 177.0, 165.2, 159.8, 136.1, 135.0, 133.0, 132.6, 132.0, 130.1, 128.3, 126.6, 122.6, 120.3, 112.2, 93.1, 82.4, 64.0, 56.0, 27.2, 16.4; **HRMS** (ESI$^+$) [M+Na]$^+$ calc'd for $C_{20}H_{17}BrO_4Na$: 423.0202, found: 423.0193.

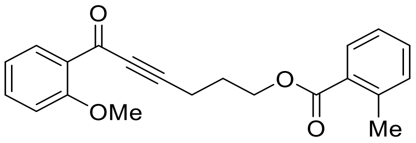


6-(2-Methoxyphenyl)-6-oxohex-4-yn-1-yl 3-bromobenzoate 1q: Prepared according to **General Method C** (Eluent: 80:1 to 10:1 petroleum ether: ethyl acetate) and the title compound was isolated as a yellow liquid (1.52 g, 4.3 mmol, 85% yield); **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.80 – 7.99 (2H, m), 7.93 – 7.91 (1H, m), 7.53 – 7.49 (2H, m), 7.39 – 7.35 (1H, m), 7.03 – 6.99 (1H, m), 6.97 (1H, d, J = 8.5 Hz), 4.47 (2H, t, J = 6.2 Hz), 3.91 (3H, s), 2.66 (2H, t, J = 7.0 Hz), 2.15 – 2.09 (2H, m); **^{13}C NMR** (101 MHz, CDCl$_3$) δ 177.0, 165.4, 159.8, 135.0, 134.6, 133.2, 133.0, 131.8, 129.9, 129.7, 127.8, 126.6, 120.3, 112.2, 93.1, 82.3, 64.0, 56.0, 27.2, 16.4; **HRMS** (ESI$^+$) [M+Na]$^+$ calc'd for $C_{20}H_{17}ClO_4Na$: 379.0708, found: 379.0703.

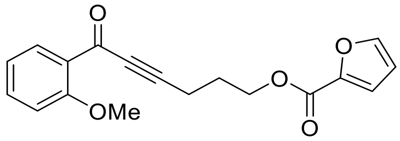


6-(2-Methoxyphenyl)-6-oxohex-4-yn-1-yl 2-fluorobenzoate 1r: Prepared according to **General Method C** (Eluent: 80:1 to 10:1 petroleum ether: ethyl acetate) and the title compound was isolated as a yellow liquid (1.47 g, 4.3 mmol, 86% yield); **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.99 (1H, dd, J = 7.8, 1.9 Hz), 7.96 – 7.92 (1H, m), 7.54 – 7.48 (2H, m), 7.22 – 7.17 (1H, m), 7.15 – 7.10 (1H, m), 7.02 – 6.96 (2H, m), 4.48 (2H, t, J = 6.1 Hz), 3.91 (3H, s), 2.67 (2H, t, J = 6.1 Hz), 2.14 – 2.08 (2H, m); **^{13}C NMR** (101 MHz, CDCl$_3$) δ 177.1, 164.5 (d, $J_{C\text{-}F}$ = 3.8Hz), 162.1 (d, $J_{C\text{-}F}$ = 261.0 Hz), 159.8, 135.0, 134.8 (d, $J_{C\text{-}F}$ = 9.1 Hz), 133.1, 132.3, 126.7, 124.2 (d, $J_{C\text{-}F}$ =

3.8 Hz), 120.3, 118.7 (d, $J_{C\text{-}F}$ = 9.9 Hz), 117.2 (d, $J_{C\text{-}F}$ = 22.6 Hz), 112.2, 93.4, 82.3, 63.8, 56.0, 27.2, 16.4.; **^{19}F NMR** (471 MHz, $CDCl_3$) *δ* –109.1 – –109.2 (m); **HRMS** (ESI$^+$) [M+Na]$^+$ calc'd for $C_{20}H_{17}FO_4Na$: 363.1003, found: 363.0998.

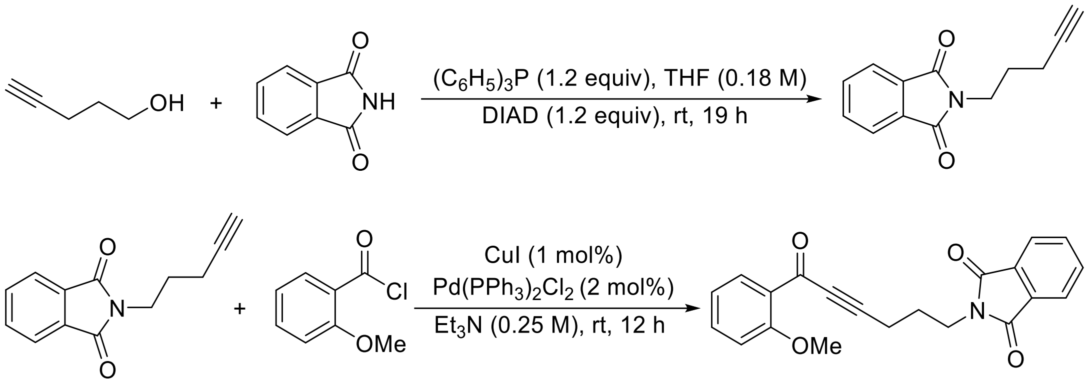


6-(2-Methoxyphenyl)-6-oxohex-4-yn-1-yl 2-methylbenzoate 1s: Prepared according to **General Method C** (Eluent: 80:1 to 10:1 petroleum ether: ethyl acetate) and the title compound was isolated as a yellow liquid (1.62 g, 4.8 mmol, 96% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 8.00 (1H, dd, *J* = 7.8, 1.8 Hz), 7.93 – 7.91 (1H, m), 7.53 – 7.49 (1H, m), 7.42 – 7.39 (1H, m), 7.25 – 7.22 (2H, m), 7.03 – 6.97 (2H, m), 4.44 (2H, t, *J* = 6.2 Hz), 3.92 (3H, s), 2.66 (2H, t, *J* = 7.1 Hz), 2.60 (3H, s), 2.15 – 2.08 (2H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) *δ* 177.0, 167.5, 159.8, 140.3, 135.0, 133.0, 132.2, 131.9, 130.7, 129.4, 126.6, 125.9, 120.3, 112.2, 93.3, 82.3, 63.3, 56.0, 27.3, 21.9, 16.5; **HRMS** (ESI$^+$) [M+Na]$^+$ calc'd for $C_{21}H_{20}O_4Na$: 359.1254, found: 359.1249.



6-(2-Methoxyphenyl)-6-oxohex-4-yn-1-yl furan-2-carboxylate 1t: Prepared according to **General Method C** (Eluent: 80:1 to 10:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colourless liquid (0.78 g, 2.5 mmol, 50% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 7.99 (1H, dd, *J* = 7.8, 1.8 Hz), 7.57 (1H, s), 7.53 – 7.49 (1H, m), 7.18 (1H, d, *J* = 3.4 Hz), 7.03 – 6.99 (1H, m), 6.98 (1H, d, *J* = 8.4 Hz), 6.51 – 6.49 (1H, m), 4.45 (2H, t, *J* = 6.2 Hz), 3.92 (3H, s), 2.64 (2H, t, *J* = 7.0 Hz), 2.13 – 2.06 (2H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) *δ* 177.0, 159.8, 158.7, 146.5, 144.5, 135.0, 133.0, 126.6, 120.3, 118.2, 112.1, 112.0, 93.2, 82.3, 63.4, 55.9, 27.2, 16.3; **HRMS** (ESI$^+$) [M+Na]$^+$ calc'd for $C_{18}H_{16}O_5Na$: 335.0890, found: 335.0888.

4. Synthesis of 2-(6-(2-methoxyphenyl)-6-oxohex-4-yn-1-yl)isoindoline-1,3-dione 1u

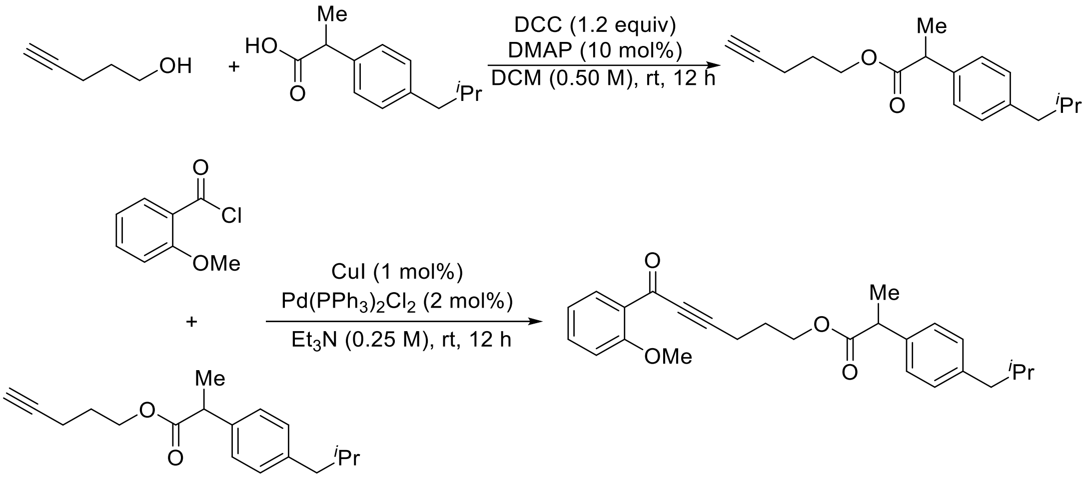


A 120 °C oven-dried 100-mL two-necked round-bottom flask, equipped with a stir bar, was charged with pent-4-yn-1-ol (1.26 g, 15.0 mmol, 1.0 equiv), triphenylphosphine (4.72 g, 18.0 mmol, 1.2 equiv) and phthalimide (2.43 g, 16.5 mmol, 1.1 equiv) in dry THF (84.0 mL). The flask was completely covered with aluminum foiled and DIAD (3.64 g, 18.0 mmol, 1.2 equiv) was added dropwise, and the reaction mixture was allowed to stir at room temperature for 19 h. The mixture was quenched by water (50.0 mL) then extracted with EtOAc (50.0 mL x 3). The combined organic layers were dried over by Na_2SO_4 then filtered. The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography (Eluent: 80:1 to 10:1 petroleum ether: ethyl acetate) to provide the desired products as white solid (2.90 g, 13.6 mmol, 90% yield). The spectral data match those previously reported[13].

A 120 °C oven-dried 100-mL round-bottom flask, equipped with a stir bar, was charged with 2-(pent-4-yn-1-yl)isoindoline-1,3-dione (1.17 g, 5.5 mmol, 1.1 equiv), 2-methoxybenzoyl chloride (853.0 mg, 5.0 mmol, 1.0 equiv), CuI (9.5 mg, 0.05 mmol, 0.01 equiv), $Pd(PPh_3)_2Cl_2$ (70.2 mg, 0.10 mmol, 0.02 equiv), the mixture was evacuated and backfilled with nitrogen for three times. Then triethylamine (20.0 mL) was added under nitrogen and the mixture was allowed to stir at room temperature for 12 h. After the completion of reaction, a saturated aqueous solution of NH_4Cl (50.0 mL) was added and the mixture was extracted with ethyl acetate (50.0 mL x 3).

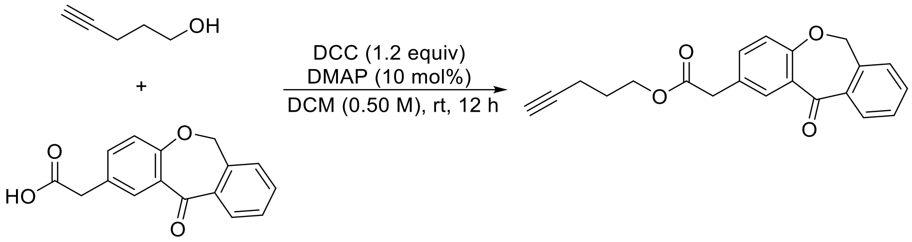
The combined organic layers were washed with brine (50.0 mL x 5), dried over by Na_2SO_4 and filtrated. The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography (Eluent: 80:1 to 10:1 petroleum ether: ethyl acetate) to provide the desired product as a yellow solid (1.06 g, 3.1 mmol, 61% yield); **M.p. =** 76.9 – 77.4 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99 (1H, dd, J = 7.8, 1.8 Hz), 7.79 – 7.77 (2H, m), 7.67 – 7.65 (2H, m), 7.51 – 7.47 (1H, m), 7.03 – 6.99 (1H, m), 6.95 (1H, d, J = 8.3 Hz), 3.90 (3H, s), 3.83 (2H, t, J = 6.9 Hz), 2.54 (2H, t, J = 7.0 Hz), 2.07 – 2.00 (2H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.8, 168.4, 159.7, 134.9, 134.1, 133.2, 132.0, 126.5, 123.3, 120.3, 112.1, 93.3, 82.1, 55.9, 37.3, 26.9, 17.3; **HRMS** (ESI$^+$) $[M+Na]^+$ calc'd for $C_{21}H_{17}NO_4Na$: 370.1050, found: 370.1042.

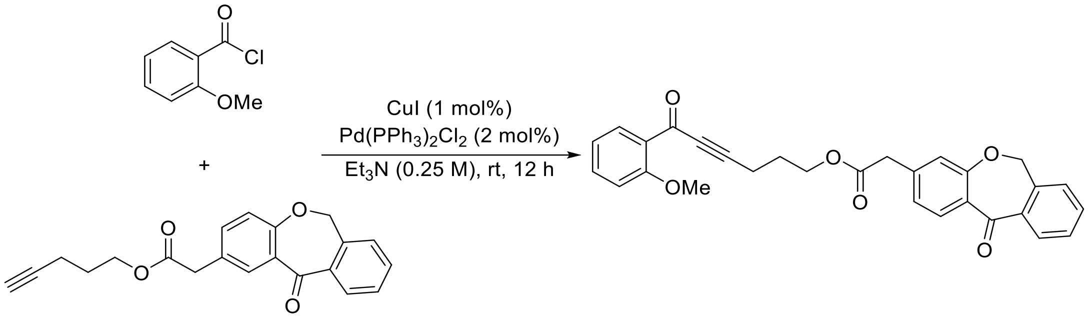
5. General Method D: Synthesis of alkyne ketone 1v, 1w



A 120 °C oven-dried 100-mL round-bottom flask, equipped with a stir bar, was charged with 2-(4-isobutylphenyl)propanoic acid (2.48 g, 12.0 mmol, 1.2 equiv), *N*,*N'*-dicyclohexylcarbodiimide (2.48 g, 12.0 mmol, 1.2 equiv), 4-dimethylaminopyridine (146.4 mg, 1.2 mmol, 0.1 equiv), the mixture was evacuated and backfilled with nitrogen for three times. Then pent-4-yn-1-ol (841.2 mg, 10.0 mmol, 1.0 equiv) and dichloromethane (20.0 mL) were added under nitrogen and the mixture was allowed to stir at 50 °C for 12 h. After the completion of reaction, a saturated aqueous solution of NH_4Cl (50.0 mL) was added and the mixture was extracted with dichloromethane (50.0 mL x 3). The combined organic layers were washed with brine (50.0 mL x 5), dried over by Na_2SO_4 and filtrated. The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography (Eluent: 80:1 to 10:1 petroleum ether: ethyl acetate) to provide the desired product. The spectral data match those previously reported[14].

A 120 ^oC oven-dried 100-mL round-bottom flask, equipped with a stir bar, was charged with pent-4-yn-1-yl 2-(4-isobutylphenyl)propanoate (1.50 g, 5.5 mmol, 1.1 equiv), CuI (9.5 mg, 0.05 mmol, 0.01 equiv), $Pd(PPh_3)_2Cl_2$ (70.2 mg, 0.1 mmol, 0.02 equiv), the mixture was evacuated and backfilled with nitrogen for three times. Then 2-methoxybenzoyl chloride (853.0 mg, 5.0 mmol, 1.0 equiv) and triethylamine (20.0 mL) were added under nitrogen and the mixture was allowed to stir at 50 ^oC for 12 h. After the completion of reaction, a saturated aqueous solution of NH_4Cl (30.0 mL) was added and the mixture was extracted with ethyl acetate (30.0 mL x 3). Thecombined organic layers were washed with brine (30.0 mL x 5), dried over by Na_2SO_4 and filtrated. The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography (Eluent: 80:1 to 10:1 petroleum ether: ethyl acetate) to provide the desired product as a black liquid (1.95 g, 4.8 mmol, 96% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 (1H, dd, J = 7.8, 1.8 Hz), 7.53 – 7.49 (1H, m), 7.19 (2H, d, J = 8.2 Hz), 7.08 (2H, d, J = 8.2 Hz), 7.03 – 6.99 (1H, m), 6.97 (1H, d, J = 8.4 Hz), 4.24 – 4.15 (2H, m), 3.89 (3H, s), 3.73 – 3.67 (1H, m), 2.43 (2H, d, J = 7.2 Hz), 2.40 (2H, t, J = 7.1 Hz), 1.94 – 1.87 (2H, m), 1.86 – 1.78 (1H, m), 1.49 (3H, d, J = 7.2 Hz), 0.88 (6H, d, J = 6.6 Hz); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 177.0, 174.7, 159.8, 140.7, 137.8, 135.0, 133.0, 129.5, 127.2, 126.7, 120.3, 112.2, 93.4, 82.1, 63.1, 55.9, 45.2, 45.1, 30.3, 27.1, 22.5, 18.4, 16.0; **HRMS** (ESI^+) $[M+Na]^+$ calc'd for $C_{26}H_{30}O_4Na$: 429.2036, found: 429.2031.

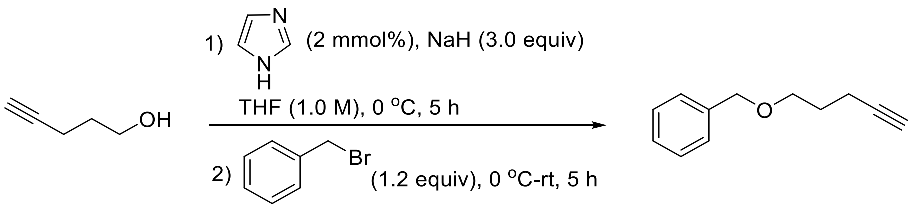


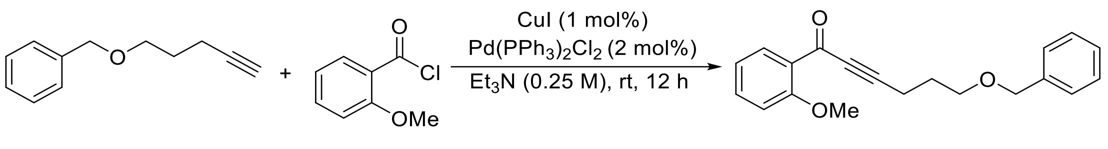


A 120 °C oven-dried 100-mL round-bottom flask, equipped with a stir bar, was charged with 2-(11-oxo-6,11-dihydrodibenzo[*b*,*e*]oxepin-2-yl)acetic acid (3.22 g, 12.0 mmol, 1.2 equiv), *N*,*N'*-dicyclohexylcarbodiimide (2.48 g, 12.0 mmol, 1.2 equiv), 4-dimethylaminopyridine (146.6 mg, 1.2 mmol, 0.1 equiv), the mixture was evacuated and backfilled with nitrogen for three times. Then pent-4-yn-1-ol (841.2 mg, 10.0 mmol, 1.0 equiv) and dichloromethane (20.0 mL) were added under nitrogen and the mixture was allowed to stir at 50 °C for 12 h. After the completion of reaction, a saturated aqueous solution of NH_4Cl (50.0 mL) was added and the mixture was extracted with Dichloromethane (50.0 mL x 3). The combined organic layers were washed with brine (50.0 mL x 5), dried over by Na_2SO_4 and filtrated. The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography (Eluent: 80:1 to 10:1 petroleum ether: ethyl acetate) to provide the desired product as a white solid (1.54 g, 4.6 mmol, 92% yield); **M.p. =** 73.5 – 74.4 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.11 (1H, d, *J* = 2.4 Hz), 7.88 (1H, d, *J* = 7.6 Hz), 7.58 – 7.54 (1H, m), 7.49 – 7.45 (1H, m), 7.42 (1H, dd, *J* = 8.4, 2.2 Hz), 7.36 (1H, d, *J* = 7.4 Hz), 7.03 (1H, d, *J* = 8.4 Hz), 5.18 (2H, s), 4.21 (2H, t, *J* = 6.3 Hz), 3.64 (2H, s), 2.28 – 2.24 (2H, m), 1.96 (1H, t, *J* = 2.6 Hz), 1.89 – 1.82 (2H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 191.0, 171.5, 160.6, 140.6, 136.5, 135.6, 132.9, 132.6, 129.6, 129.4, 127.9, 127.9, 125.2, 121.2, 83.1, 73.7, 69.2, 63.6, 40.3, 27.5, 15.3; **HRMS** (ESI$^+$) $[M+H]^+$ calc'd for $C_{21}H_{19}O_4$: 335.1278, found: 335.1270.

A 120 °C oven-dried 100-mL round-bottom flask, equipped with a stir bar, was charged with pent-4-yn-1-yl 2-(11-oxo-6,11-dihydrodibenzo[*b,e*]oxepin-2-yl)acetate (1.84 g, 5.5 mmol, 1.1 equiv), CuI (9.5 mg, 0.05 mmol, 0.01 equiv), $Pd(PPh_3)_2Cl_2$ (70.2 mg, 0.1 mmol, 0.02 equiv), the mixture was evacuated and backfilled with nitrogen for three times. Then 2-methoxybenzoyl chloride (853.0 mg, 5.0 mmol, 1.0 equiv) and triethylamine (20.0 mL) were added under nitrogen and the mixture was allowed to stir at 50 °C for 12 h. After the completion of reaction, a saturated aqueous solution of NH_4Cl (30.0 mL) was added and the mixture was extracted with ethyl acetate (30.0 mL x 3). The combined organic layers were washed with brine (30.0 mL x 3), dried over by Na_2SO_4 and filtrated. The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography (Eluent: 80:1 to 10:1 petroleum ether: ethyl acetate) to provide the desired product as a yellow liquid (1.01 g, 2.3 mmol, 46% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.11 (1H, d, *J* = 2.4 Hz), 7.98 (1H, dd, *J* = 7.8, 1.8 Hz), 7.88 (1H, d, *J* = 7.6 Hz), 7.58 – 7.53 (1H, m), 7.52 – 7.45 (2H, m), 7.42 (1H, dd, *J* = 8.4, 2.2 Hz), 7.36 (1H, d, *J* = 7.4 Hz), 7.04 – 6.96 (3H, m), 5.19 (2H, s), 4.25 (2H, t, *J* = 6.2 Hz), 3.90 (3H, s), 3.65 (2H, s), 2.54 (2H, t, *J* = 7.0 Hz), 2.01 – 1.94 (2H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 191.0, 177.1, 171.5, 160.6, 159.8, 140.5, 136.4, 135.6, 135.0, 133.1, 132.9, 132.5, 129.6, 129.4, 128.0, 127.8, 126.7, 125.2, 121.3, 120.3, 112.2, 93.3, 82.3, 73.8, 63.6, 56.0, 40.3, 27.1, 16.2; **HRMS** (ESI^+) $[M+Na]^+$ calc'd for $C_{29}H_{24}O_6Na$: 491.1465, found: 491.1450.

6. Synthesis of 6-(benzyloxy)-1-(2-methoxyphenyl)hex-2-yn-1-one 1af





A 120 °C oven-dried 100-mL round-bottom flask, equipped with a stir bar, was charged with pent-4-yn-1-ol (841.0 mg, 10.0 mmol, 1.0 equiv) and imidazole

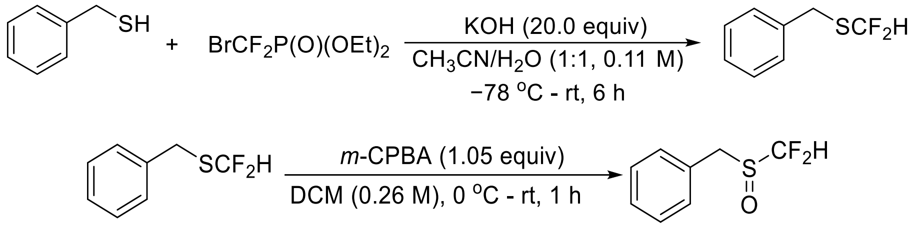
(14.0 mg, 0.2 mmol, 0.02 equiv) were dissolved in dry THF (10.0 mL) under an nitrogen atmosphere. Sodium hydride (60% wt, 1.20 g, 30.0 mmol, 3.0 equiv) was added at 0 °C and the reaction mixture was stirred for 30 min at this temperature. Then, benzyl bromide (2.05 g, 12.0 mmol, 1.2 equiv) was added at 0 °C and the reaction mixture was stirred for 22 h at ambient temperature. After the completion of reaction, a saturated aqueous solution of NH_4Cl (50.0 mL) was added and the mixture was extracted with ethyl acetate (50.0 mL x 3). The combined organic layers were washed with brine (50.0 mL x 3), dried over by Na_2SO_4 and filtrated. The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography (Eluent: 80:1 to 10:1 petroleum ether: ethyl acetate) to provide the desired product as a colourless liquid (1.66 g, 9.5 mmol, 95% yield). The spectral data match those previously reported[15].

A 120 °C oven-dried 100-mL round-bottom flask, equipped with a stir bar, was charged with ((pent-4-yn-1-yloxy)methyl)benzene (1.34 g, 7.7 mmol, 1.1 equiv), 2-methoxybenzoyl chloride (1.19 g, 7.0 mmol, 1.0 equiv), CuI (13.3 mg, 0.07 mmol, 0.01 equiv), $Pd(PPh_3)_2Cl_2$ (98.3 mg, 0.14 mmol, 0.02 equiv), the mixture was evacuated and backfilled with nitrogen for three times. Then triethylamine (20.0 mL) was added under nitrogen and the mixture was allowed to stir at 50 °C for 12 h. After the completion of reaction, a saturated aqueous solution of NH_4Cl (50.0 mL) was added and the mixture was extracted with ethyl acetate (50.0 mL x 3). The combined organic layers were washed with brine (50.0 mL x 3), dried over by Na_2SO_4 and filtrated. The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography (Eluent: 80:1 to 10:1 petroleum ether: ethyl acetate) to provide the desired product as a yellow liquid (2.10 g, 6.8 mmol, 97% yield). The spectral data match those previously reported[16].

7. Synthesis of (((difluoromethyl-*d*)sulfinyl)methyl)benzene 2a

The (((difluoromethyl-*d*)sulfinyl)methyl)benzene **2a** were synthesized according to our previous report, the spectral data match those previously reported[17].

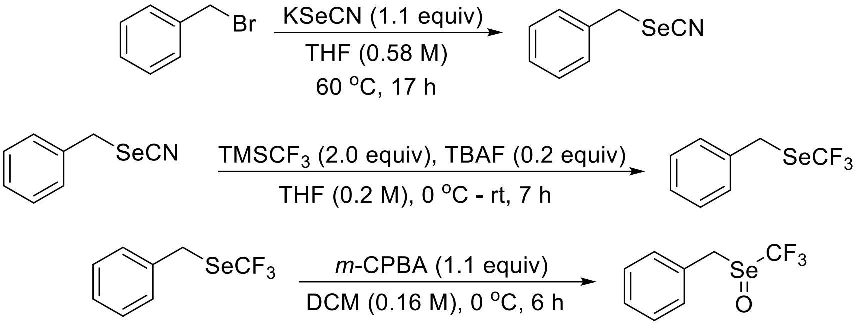
8. Synthesis of (((difluoromethyl)sulfinyl)methyl)benzene 2b



A 120 °C oven-dried 500-mL round-bottom flask, equipped with a stir bar, was charged with phenylmethanethiol (3.73 g, 30.0 mmol, 1.0 equiv) and potassium hydroxide (33.66 g, 600.0 mmol, 20.0 equiv) and acetonitrile/H_2O (280 mL, 1:1) under nitrogen atmosphere. The mixture was cooled to −78 °C, then bromodifluoromethyl diethyl phosphate (16.02 g, 60.0 mmol, 2.0 equiv) was added dropwise to the mixture. Then, the mixture was allowed to stir at room temperature for 6 h. After the reaction was completed, the mixture was extracted with brine (50.0 mL) and ethyl acetate (50.0 mL x 3), then the combined organic layers were extracted with brine (50.0 mL x 3). The combined organic layers were dried over by Na_2SO_4 then filtered. After the completion of reaction, a saturated aqueous solution of NH_4Cl (50.0 mL) was added and the mixture was extracted with ethyl acetate (50.0 mL x 3). The combined organic layers were washed with brine (50.0 mL x 5), dried over by Na_2SO_4 and filtrated. The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography (Eluent: 500:1 to 200:1 petroleum ether: ethyl acetate) to provide the desired product as a colorless liquid (4.36 g, 25.0 mmol, 83% yield). The spectral data match those previously reported[3].

A 120 °C oven-dried 200 mL round-bottom flask, equipped with a stir bar, after exchanging the atmosphere three times with N_2, anhydrous dichloromethane (76.0 mL) and benzyl(difluoromethyl)sulfane (3.48 g, 20.0 mmol, 1.0 equiv) were added to flask under nitrogen protected. The reaction mixture was cooled to 0 °C, and the *m*-CPBA (85.0% wt, 4.26 g, 21.0 mmol, 1.05 equiv) was added in portions quickly to the mixture. Then the reaction mixture was allowed to stir at room temperature for 1 h. After that, the mixture was extracted with dichloromethane (50.0 mL x 3), the combined organic layers were washed by brine (50.0 mL x 5). The organic layer was dried over by Na_2SO_4 then filtered. The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography to provide the desired product **2b** as a white solid (3.23 g, 17.0 mmol, 85% yield). The spectral data match those previously reported[3].

9. Synthesis of (((trifluoromethyl)seleninyl)methyl)benzene 2c

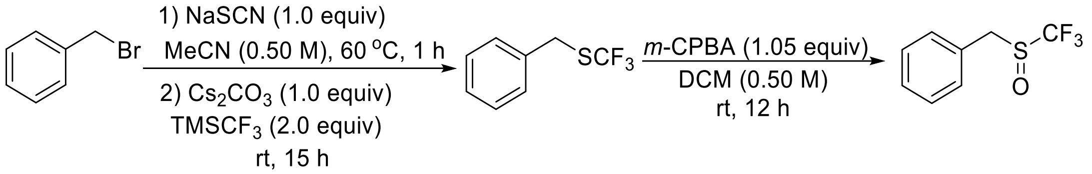


A 120 ^{o}C oven-dried 200-mL round-bottom flask equipped with a stir bar, was charged with (selenocyanatomethyl)benzene (4.63 g, 32.2 mmol, 1.1 equiv), (bromomethyl)benzene (5.00 g, 29.2 mmol, 1.0 equiv) and dry THF (50.0 mL) under nitrogen atmosphere. The reaction mixture was then stirred at 60 ^{o}C for 17 h. After the reaction was completed, the mixture was extracted with brine (50.0 mL) and ethyl acetate (50.0 mL x 3), then the combined organic layers were extracted with brine (50.0 mL x 5). The combined organic layers were dried over by Na_2SO_4 then filtered. The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography to provide the desired product as a yellow solid (5.61 g, 28.6 mmol, 99% yield). The spectral data match those previously reported[18].

A 120 ^{o}C oven-dried 200-mL round-bottom flask, equipped with a stir bar, was charged with (selenocyanatomethyl)benzene (2.31 g, 11.8 mmol, 1.0 equiv) and dry THF (100.0 mL). The flask was evacuated and refilled with nitrogen three times, and then $TMSCF_3$ (3.35 g, 23.6 mmol, 2.0 equiv) was added. The reaction mixture was cooled to 0 °C, and TBAF in 1 M THF was added dropwise. After 10 min at 0 °C under nitrogen, the reaction was allowed to warm to room temperature and stirred for 7 h. After the reaction was completed, the mixture was extracted with brine (30.0 mL) and ethyl acetate (30.0 mL x 3), then the combined organic layers were extracted with brine (30.0 mL x 5). The combined organic layers were dried over by Na_2SO_4 then filtered. The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography to provide the desired product as a colourless liquid (2.09 g, 8.8 mmol, 74% yield). The spectral data match those previously reported[18].

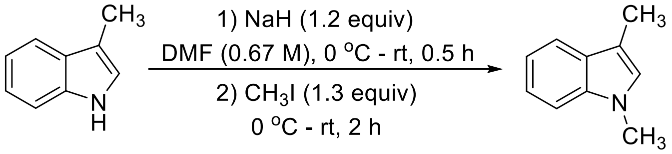
A 120 ^oC oven-dried 200 mL round-bottom flask, equipped with a stir bar, after exchanging the atmosphere three times with nitrogen, anhydrous dichloromethane (50.0 mL) and benzyl(trifluoromethyl)selane (1.91 g, 8.0 mmol, 1.0 equiv) were added to flask under nitrogen protected. The reaction mixture was cooled to 0 ^oC, and the *m*-CPBA (85% wt, 1.79 g, 8.8 mmol, 1.1 equiv) was added in portions quickly to the mixture. Then the reaction mixture was allowed to stir at 0 ^oC for 6 h. After that, the mixture was extracted with dichloromethane (50.0 mL x 3), the combined organic layers were washed by brine (50.0 mL x 5). The organic layer was dried over by Na_2SO_4 then filtered. The solvent was removed by rotary evaporation. The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography to provide the desired product **2c** as a white solid (1.25 g, 4.9 mmol, 61% yield). The spectral data match those previously reported[18].

10. Synthesis of (((trifluoromethyl)sulfinyl)methyl)benzene 2d



An oven-dried 100 mL round-bottom flask, equipped with a stir bar, was charged with NaSCN (1.62 g, 20.0 mmol, 1.0 equiv). After exchanging the atmosphere three times with nitrogen, MeCN (40.0 mL) and benzyl bromide (3.42 g, 20.0 mmol, 1.0 equiv) were added to flask. The reaction mixture was allowed to heat at 60 ^oC for 1 h. Then the reaction mixture was cooled to room temperature, Cs_2CO_3 (6.52 g, 20.0 mmol, 1.0 equiv) and $TMSCF_3$ (5.69 g, 40.0 mmol, 2.0 equiv) were added to the mixture. The reaction mixture was allowed to stir at room temperature for 15 h. When the reaction completed, the mixture was extracted with Et_2O (50.0 mL x 3), the combined organic layers were washed by brine (50.0 mL x 5). The organic layer was dried over by Na_2SO_4 then filtered. The solvent was removed by rotary evaporation and the residue purified by flash silica gel chromatography (Eluent: 200:1 to 50:1 petroleum ether: ethyl ether) to give the corresponding sulfide as a colorless oil. The sulfide was dissolved in dichloromethane (22.0 mL) followed by addition of *m*-CPBA (85.0 wt%, 2.34 g, 11.6 mmol, 1.05 equiv). The reaction mixture was allowed to stir at room temperature for 12 h. The reaction was then quenched with saturated aqueous Na_2CO_3 and extracted with dichloromethane (50.0 mL x 3), the combined organic layers were washed by brine (50.0 mL x 5). The combined organic layers were dried with Na_2SO_4 and the solvent was removed by rotary evaporation. The residue was purified by column chromatography (Eluent: 100:1 to 10:1 petroleum ether: ethyl acetate) to give the desired product **2d** as a white solid (1.52 g, 7.3 mmol, 37% yield). The spectral data match those previously reported[19].

11. Synthesis of 1,3-dimethyl-1*H*-indole 1ag

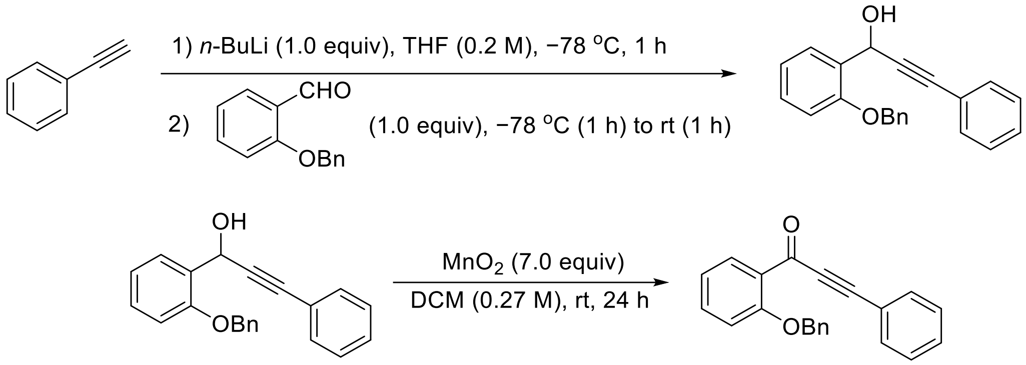


A 120 °C oven-dried 100 mL round-bottom flask, equipped with a stir bar, after exchanging the atmosphere three times with nitrogen, to a solution of 3-methyl-1*H*-indole (656.0 mg, 5.0 mmol, 1.0 equiv) in *N*,*N*-Dimethylformamide (7.5 mL) at 0 °C, was added Sodium hydride (60%, 240.0 mg, 6.0 mmol, 1.2 equiv) portion wise for 5 min and the mixture was stirred for 30 min at room temperature. The reaction mixture was then cooled to 0 °C and was added methyl iodide (923.0 mg, 6.5 mmol, 1.3 equiv) dropwise. The resulting white precipitate was further allowed to stir at room temperature for 2 h. When the reaction completed, the reaction mixture was quenched with saturated ammonium chloride solution (25.0 mL). After that, the mixture was extracted with diethyl ether (25.0 mL x 3), the combined organic layers were washed by brine (25.0 mL x 5). The organic layer was dried over by Na_2SO_4 then filtered. The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography to provide the desired product **1ag** as a colourless liquid (644.0 mg, 4.4 mmol, 89% yield). The spectral data match those previously reported[20].

12. Synthesis of 1-(*p*-tolylthio)pyrrolidine-2,5-dione 1ah

The 1-(*p*-tolylthio)pyrrolidine-2,5-dione **1ah** were synthesized according to our previous report, the spectral data match those previously reported[21].

13. Synthesis of 1-(2-(benzyloxy)phenyl)-3-phenylprop-2-yn-1-one 16

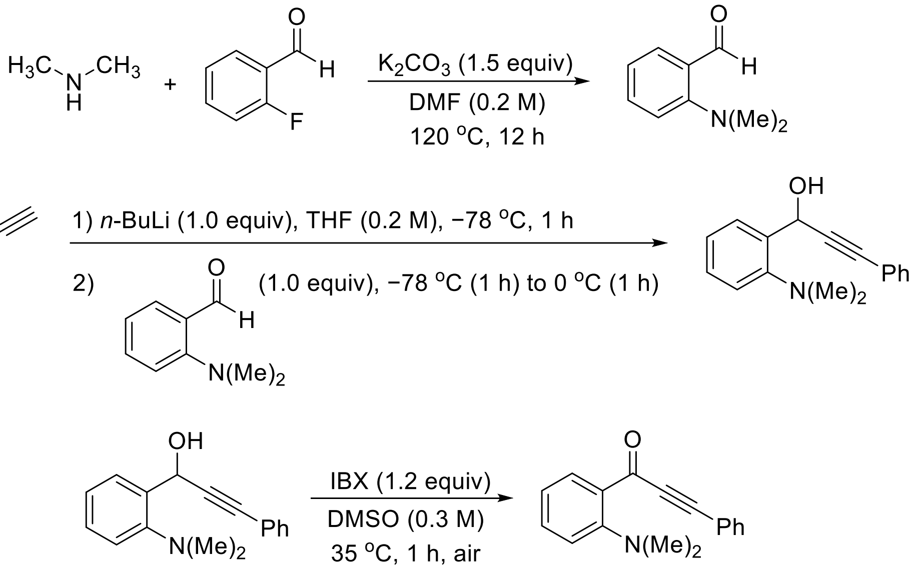


A 120 °C oven-dried 200-mL round-bottom flask equipped with a stir bar, was charged with ethynylbenzene (3.68 g, 36.0 mmol, 1.2 equiv). Then the mixture was evacuated and backfilled with nitrogen for three times. Then dry THF (100.0 mL) under nitrogen atmosphere. The butyllithium (2.5 mol/L, 8 mL, 20.0 mmol, 1.0 equiv) was added dropwise into the mixture at −78 °C. After 1 h at −78 °C, dissolve the 2-(benzyloxy)benzaldehyde (4.24 g, 20.0 mmol, 1.0 equiv) in THF and add dropwise. The reaction mixture was allowed to stir for 1.0 h at −78 °C and room temperature for 1 h. After completion, saturated NH_4Cl solution was added. After the reaction was completed, the mixture was extracted with brine (50.0 mL) and ethyl acetate (50.0 mL x 3), then the combined organic layers were extracted with brine (50.0 mL x 5). The combined organic layers were dried over by Na_2SO_4 then filtered. The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography to provide the desired product as a colourless liquid (5.00 g, 17 mmol, 83% yield). The spectral data match those previously reported[22].

A 120 °C oven-dried 100-mL round-bottom flask equipped with a stir bar, was charged with MnO_2 (1.83 g, 21.0 mmol, 7.0 equiv), 1-(2-(benzyloxy)phenyl)-3-phenylprop-2-yn-1-ol (901.1mg, 3.0 mmol, 1.0 equiv) and dry dichloromethane

(11.0 mL) under nitrogen atmosphere. The reaction mixture was then stirred at room temperature for 24 h. After the reaction was completed, the mixture was extracted with brine (30.0 mL) and ethyl acetate (30.0 mL x 3), then the combined organic layers were extracted with brine (30.0 mL x 5). The combined organic layers were dried over by Na_2SO_4 then filtered. The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography to provide the desired product **16** as a colourless liquid (758.4 mg, 2.4 mmol, 81% yield). The spectral data match those previously reported[23].

14. Synthesis of 1-(2-(dimethylamino)phenyl)-3-phenylprop-2-yn-1-one 20

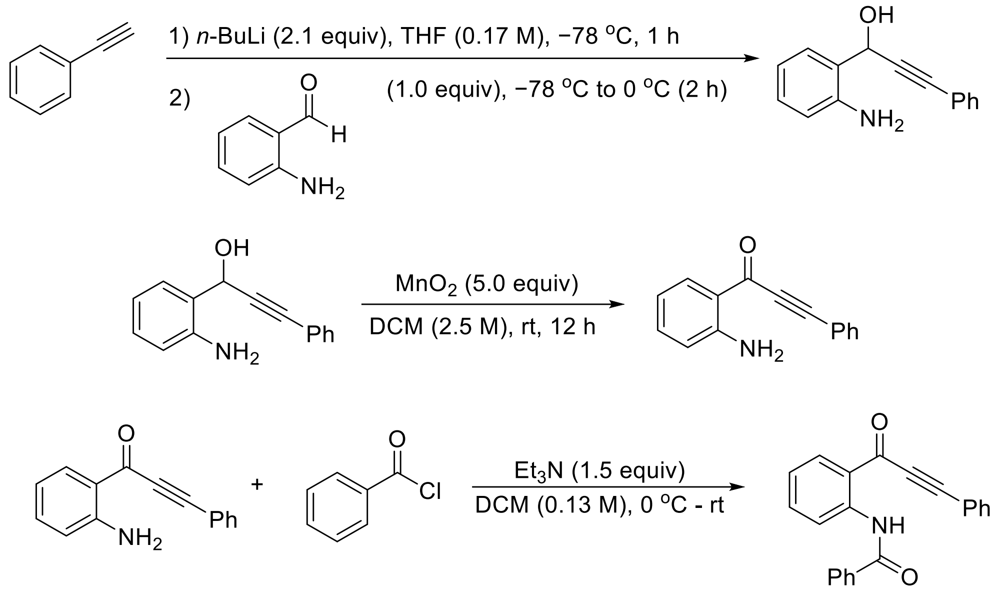


A 120 °C oven-dried 200-mL round-bottom flask, equipped with a stir bar, was charged with K_2CO_3 (2.07 g, 15.0 mmol, 1.5 equiv), 2-fluorobenzaldehyde (1.24 g, 10.0 mmol, 1.0 equiv), dimethylamine (2.0 mol/L, 6.5 mL, 13.0 mmol, 1.3 equiv), the mixture was evacuated and backfilled with nitrogen for three times. Then DMF (50.0 mL) was added under nitrogen and the mixture was allowed to stir at 100 °C for 12 h. After the completion of reaction, a saturated aqueous solution of NH_4Cl (50.0 mL) was added and the mixture was extracted with ethyl acetate (50.0 mL x 3). The combined organic layers were washed with brine (50.0 mL x 5), dried over by Na_2SO_4 and filtrated. The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography (Eluent: 100:1 to 20:1 petroleum ether:

ethyl acetate) to provide the desired product as a yellow liquid (1.27 g, 8.5 mmol, 85% yield).

A 120 ^{o}C oven-dried 100-mL round-bottom flask equipped with a stir bar, was charged with ethynylbenzene (398.3 mg, 3.9 mmol, 1.3 equiv). Then the mixture was evacuated and backfilled with nitrogen for three times. Then dry THF (12.0 mL) under nitrogen atmosphere. The butyllithium (2.5 mol/L, 1.4 mL, 3.6 mmol, 1.2 equiv) was added dropwise into the mixture at −78 ^{o}C. After 1 h at −78 °C, dissolve the 2-(dimethylamino)benzaldehyde (447.6 mg, 3.0 mmol, 1.0 equiv) add dropwise. The reaction mixture was allowed to stir for 1 h at −78 ^{o}C and 0 ^{o}C for 1 h. After completion, saturated NH_4Cl solution was added. After the reaction was completed, the mixture was extracted with brine (30.0 mL) and ethyl acetate (30.0 mL x 3), then the combined organic layers were extracted with brine (30.0 mL x 5), dried over anhydrous $MgSO_4$. After filtration of $MgSO_4$, the filtrate was concentrated under reduced pressure to give the desired alcohol. Without purification, then was added to a solution of IBX (1.01 g, 3.6 mmol, 1.2 equiv) in DMSO (10.0 mL) and the solution was heated to 35 °C (oil bath) for 1 h. The cooled reaction mixture was diluted with ethyl acetate (70.0 mL) and water (30.0 mL) and stirred vigorously for 10 min. Then it was filtered over celite. The organic layer was separated and the aqueous phase was extracted with ethyl acetate (50.0 mL x 3 mL). The combined organic layers were washed with brine (50.0 mL x 5), dried over by Na_2SO_4 and filtrated. The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography (Eluent: 50:1 to 20:1 petroleum ether: ethyl acetate) to provide the desired product as a yellow liquid (158.9 mg, 0.6 mmol, 21% yield). The spectral data match those previously reported[24].

15. Synthesis of N-(2-(3-phenylpropioloyl)phenyl)benzamide 21

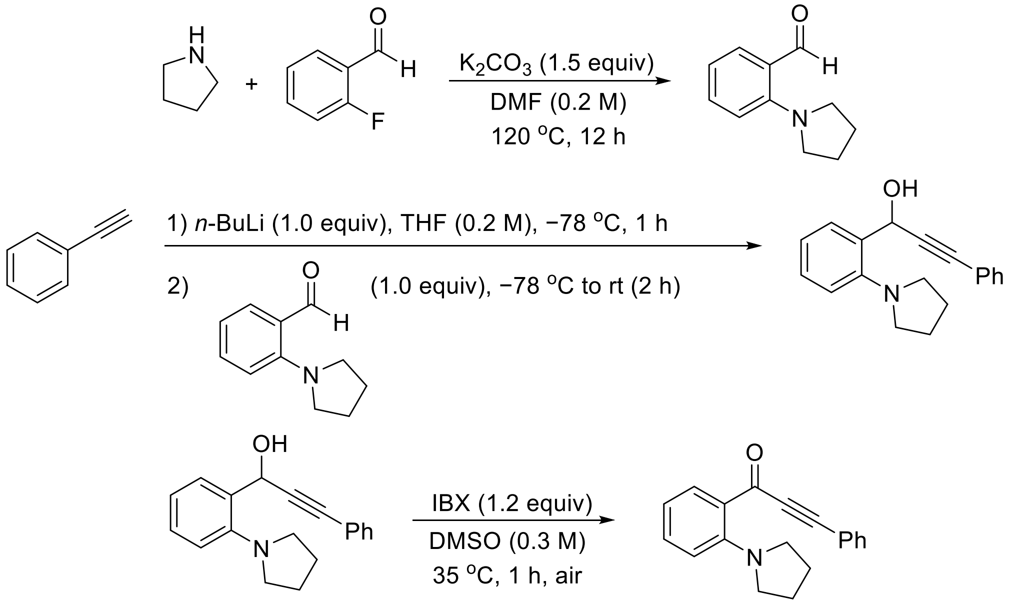


An oven-dried 100-mL two-necked round-bottom flask, equipped with a stir bar, was charged with phenylacetylene (1.07 g, 10.5 mmol, 2.1 equiv) in anhydrous THF (30.0 mL) was dropwise added *n*-BuLi (2.5 mol/L, 4.2 mL, 10.5 mmol, 2.1 equiv) at −78 °C under nitrogen atmosphere and the mixture was allowed to stir for 1 h. A solution of corresponding substituted 2-Aminobenzaldehyde (5.0 mmol in 5 mL anhydrous THF) was dropwise added at −78 °C. The mixture was allowed to stir at −78 °C for 5 min, and then heated up to 0 °C, continue stirred for 2 h. The mixture was quenched by NH_4Cl (50.0 mL) then extracted with ethyl acetate (30.0 mL ×3). The combined organic layers were dried over by Na_2SO_4 then filtered. The solvent was removed by rotary evaporation and purified by flash silica gel chromatography (Eluent: petroleum ether: ethyl acetate) to give desired products.

An oven-dried 50-mL two-necked round-bottom flask, equipped with a stir bar, was charged with 1-(2-aminophenyl)-3-phenylprop-2-yn-1-ol (893.1 mg, 4.0 mmol, 1.0 equiv) in anhydrous DCM (10.0 mL), MnO_2 (434.7 mg, 20 mmol, 5.0 equiv) was added to the mixture under N_2 atmosphere and the mixture was allowed to stir at rt for 12 h (monitored by silica gel TLC plate). After reaction was completed, the mixture was filtered through a pad of celite, and the filtrate was concentrated. The residue was purified by flash silica gel chromatography (Eluent: petroleum ether: ethyl acetate) to give desired products.

An oven-dried 50-mL two-necked round-bottom flask, equipped with a stir bar, was charged with 1-(2-aminophenyl)-3-phenylprop-2-yn-1-one (442.5, 2.0 mmol, 1.0 equiv) in anhydrous DCM (15.0 mL), Et_3N (303.6 mg, 3.0 mmol, 1.5 equiv) was added to the mixture under nitrogen atmosphere and the mixture was cooled in an ice bath, and the corresponding substituted benzoyl chloride (421.7 mg, 3.0 mmol, 1.5 equiv) was added dropwise. Then the solution was stirred at rt for 12 h (monitored by silica gel TLC plate). After reaction was completed, the mixture was washed with dilute hydrochloric acid, saturated $NaHCO_3$, then extracted with ethyl acetate (20.0 mL ×3). The combined organic layers were washed with brine (30.0 mL x 5), dried over by Na_2SO_4 and filtrated. The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography (Eluent: 50:1 to 20:1 petroleum ether: ethyl acetate) to provide the desired product as a yellow solid (501.1 mg, 1.5 mmol, 77% yield). The spectral data match those previously reported[25].

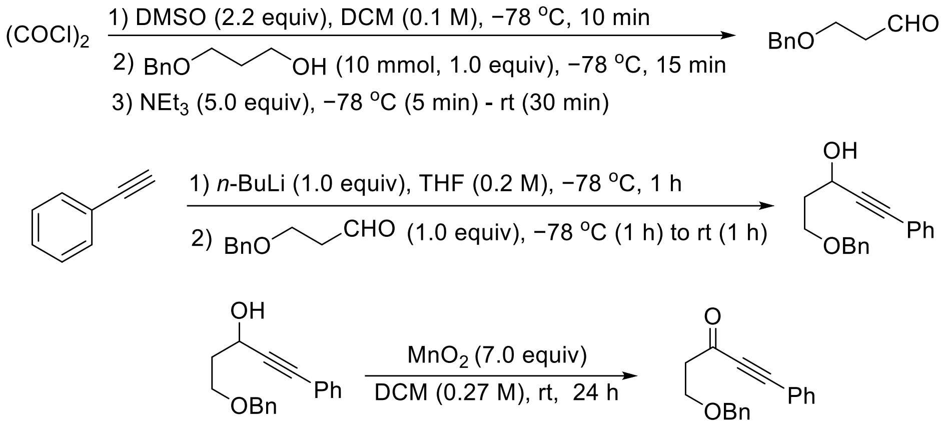
16. Synthesis of 3-phenyl-1-(2-(pyrrolidin-1-yl)phenyl)prop-2-yn-1-one 22



A 120 °C oven-dried 500-mL round-bottom flask, equipped with a stir bar, was charged with K_2CO_3 (4.15 g, 30.0 mmol, 1.5 equiv), 2-fluorobenzaldehyde (2.48 g, 20.0 mmol, 1.0 equiv), pyrrolidine (1.71 g, 24.0 mmol, 1.2 equiv), the mixture was evacuated and backfilled with nitrogen for three times. Then DMF (100.0 mL) was added under nitrogen and the mixture was allowed to stir at 120 °C for 12 h. After the completion of reaction, a saturated aqueous solution of NH_4Cl (50.0 mL) was added and the mixture was extracted with ethyl acetate (50.0 mL x 3). The combined organic layers were washed with brine (50.0 mL x 3), dried over by Na_2SO_4 and filtrated. The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography (Eluent: 100:1 to 20:1 petroleum ether: ethyl acetate) to provide the desired product as a yellow liquid (2.89 g, 16.5 mmol, 82% yield).

A 120 °C oven-dried 100-mL round-bottom flask equipped with a stir bar, was charged with ethynylbenzene (265.5 mg, 2.6 mmol, 1.3 equiv). Then the mixture was evacuated and backfilled with nitrogen for three times. Then dry THF (8.0 mL) under nitrogen atmosphere. The butyllithium (2.5 mol/L, 1.0 mL, 2.4 mmol, 1.2 equiv) was added dropwise into the mixture at −78 °C. After 1 h at −78 °C, dissolve the 2-(pyrrolidin-1-yl)benzaldehyde (350.5 mg, 2.0 mmol, 1.0 equiv) add dropwise. The reaction mixture was allowed to stir for 1 h at −78 °C and 0 °C for 1 h. After completion, saturated NH_4Cl solution was added. After the reaction was completed, the mixture was extracted with brine (30.0 mL) and ethyl acetate (30.0 mL x 3), then the combined organic layers were extracted with brine (30.0 mL x 5), dried over anhydrous $MgSO_4$. After filtration of $MgSO_4$, the filtrate was concentrated under reduced pressure to give the desired alcohol. Without purification, then was added to a solution of IBX (672.0 mg, 2.4 mmol, 1.2 equiv) in DMSO (7.0 mL) and the solution was heated to 35 °C (oil bath) for 1 h. The cooled reaction mixture was diluted with ethyl acetate (50.0 mL) and water (20.0 mL) and stirred vigorously for 10 min. Then it was filtered over celite. The organic layer was separated and the aqueous phase was extracted with ethyl acetate (30.0 mL x 3 mL). The combined organic layers were washed with brine (30.0 mL x 5), dried over by Na_2SO_4 and filtrated. The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography (Eluent: 50:1 to 20:1 petroleum ether: ethyl acetate) to provide the desired product as a yellow liquid (347.1 mg, 1.3 mmol, 63% yield). The spectral data match those previously reported[24].

17. Synthesis of 5-(benzyloxy)-1-phenylpent-1-yn-3-one 36

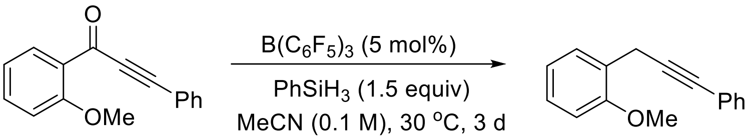


A 120 °C oven-dried 100-mL round-bottom flask equipped with a stir bar, DMSO (1.72 g, 22.0 mmol, 2.2 equiv) was added to a solution of $(COCl)_2$ (1.40 g, 11.0 mmol, 1.1 equiv) in dichloromethane (100.0 mL) at −78 °C. The reaction mixture was stirred for 10 min at which time 3-(benzyloxy)propan-1-ol (1.66 g, 10.0 mmol, 1.0 equiv) was added dropwise into the mixture at −78 °C. After 15 min, triethylamine (5.06 g, 50.0 mmol, 5.0 equiv) was added, the solution was stirred for 5 min at which time the reaction mixture was warmed to room temperature. After stirring for 30 min the reaction was quenched with saturated NH_4Cl (10.0 mL), the mixture was extracted with dichloromethane (50.0 mL x 3), the combined organic layers were washed by brine (50.0 mL x 5). The organic layer was dried over by Na_2SO_4 then filtered. The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography to provide the desired product as a colourless liquid (1.22 g, 7.5 mmol, 75% yield). The spectral data match those previously reported[26].

A 120 °C oven-dried 100-mL round-bottom flask equipped with a stir bar, was charged with ethynylbenzene (367.7 mg, 3.6 mmol, 1.2 equiv). Then it was evacuated and backfilled with nitrogen for three times. Then dry THF (15.0 mL) under nitrogen atmosphere. The butyllithium (2.5 mol/L, 1.2 mL, 3.0 mmol, 1.0 equiv) was added dropwise into the mixture at −78 °C. After 1 h at −78 °C, the 3-(benzyloxy)propanal (492.6 mg, 3.0 mmol, 1.0 equiv) was added dropwise then was added dropwise. The reaction mixture was allowed to stir for 1.0 h at −78 °C and room temperature for 1 h. After completion, saturated NH_4Cl solution was added. After the reaction was completed, the mixture was extracted with brine (30.0 mL) and ethyl acetate (30.0 mL x 3), then the combined organic layers were extracted with brine (30.0 mL x 5). The combined organic layers were dried over by Na_2SO_4 then filtered. The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography to provide the desired product as a colourless liquid (672.3 mg, 2.5 mmol, 85% yield). The spectral data match those previously reported[27].

A 120 °C oven-dried 50-mL round-bottom flask equipped with a stir bar, was charged with MnO_2 (1.52 g, 17.5 mmol, 7.0 equiv), 5-(benzyloxy)-1-phenylpent-1-yn-3-ol (665.9 mg, 2.5 mmol, 1.0 equiv) and dry dichloromethane (9.3 mL) under nitrogen atmosphere. The reaction mixture was then stirred at room temperature for 24 h. After the reaction was completed, the mixture was extracted with brine (30.0 mL) and ethyl acetate (30.0 mL x 3), then the combined organic layers were extracted with brine (30.0 mL x 5). The combined organic layers were dried over by Na_2SO_4 then filtered. The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography to provide the desired product **36** as a colourless liquid (482.1 mg, 1.8 mmol, 73% yield). The spectral data match those previously reported[28].

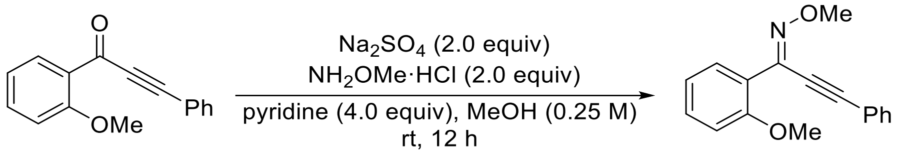
18. Synthesis of 1-methoxy-2-(3-phenylprop-2-yn-1-yl)benzene 38



A 120 °C oven-dried 100-mL round-bottom flask, equipped with a stir bar, was charged with 1-(2-methoxyphenyl)-3-phenylprop-2-yn-1-one (708.8 mg, 3.0 mmol, 1.0 equiv), $B(C_6F_5)_3$ (76.8 mg, 0.15 mmol, 0.05 equiv) and $PhSiH_3$ (486.9 mg, 4.5 mmol, 1.5 equiv) the mixture was evacuated and backfilled with nitrogen for three times. Then MeCN (30.0 mL) was added under nitrogen and the mixture was allowed to stir at 30 °C for 3 d. After the completion of reaction, a saturated aqueous solution of NH_4Cl (30.0 mL) was added and the mixture was extracted with ethyl acetate

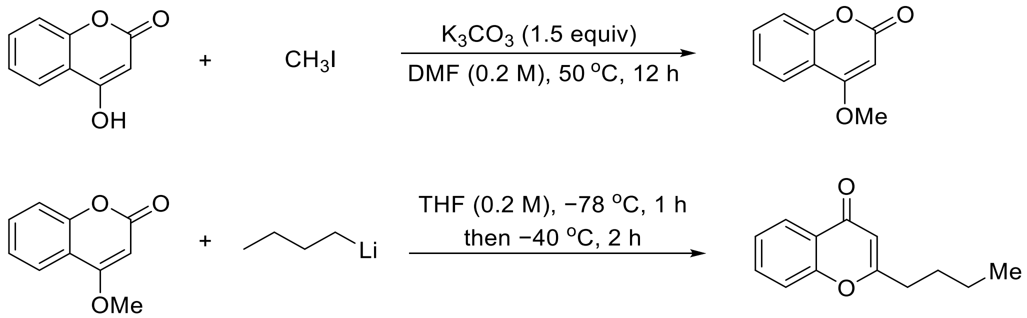
(30.0 mL x 3). The combined organic layers were washed with brine (30.0 mL x 5), dried over by Na_2SO_4 and filtrated. The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography to provide the desired product **38** as a colourless liquid (598.6 mg, 2.7 mmol, 90% yield). The spectral data match those previously reported[29].

19. Synthesis of (*E*)-1-(2-methoxyphenyl)-3-phenylprop-2-yn-1-one *O*-methyl oxime 39



A 120 °C oven-dried 50-mL round-bottom flask equipped with a stir bar, was charged with 1-(2-methoxyphenyl)-3-phenylprop-2-yn-1-one (472.5 mg, 2.0 mmol, 1.0 equiv), methoxylamine hydrochloride (4.0 mmol, 334.1 mg, 2.0 equiv), anhydrous Na_2SO_4 (4.0 mmol, 568.1 mg, 2.0 equiv), pyridine (8.0 mmol, 632.8 mg, 4.0 equiv), and methanol (8.0 mL) under nitrogen atmosphere. The reaction mixture was then stirred at room temperature for 12 h. After the reaction was completed, the mixture was extracted with saturated NH_4Cl solution (20.0 mL) and ethyl acetate (20.0 mL x 3), then the combined organic layers were extracted with brine (20.0 mL x 5). The combined organic layers were dried over by Na_2SO_4 then filtered. The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography (Eluent: 200:1 to 100:1 petroleum ether: ethyl acetate) to provide the desired product **39** as a yellow solid (451.0 mg, 1.7 mmol, 85% yield); The spectral data match those previously reported[28].

20. Synthesis of 2-butyl-4H-chromen-4-one 41



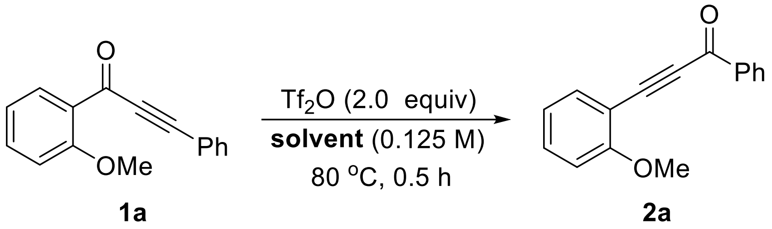
A 120 ^{o}C oven-dried 200-mL round-bottom flask equipped with a stir bar, was charged with 4-hydroxy-2*H*-chromen-2-one (3.24 g, 20.0 mmol, 1.0 equiv) and K_3CO_3 (4.15 g, 30.0 mmol, 1.5 equiv). The mixture was evacuated and backfilled with nitrogen for three times. Then methyl iodide (5.68 g, 40.0 mmol, 2.0 equiv) and dry THF (50.0 mL) under nitrogen atmosphere. The reaction mixture was then stirred at 50 ^{o}C for 12 h. After the reaction was completed, the mixture was extracted with brine (50.0 mL) and ethyl acetate (50.0 mL x 3), then the combined organic layers were extracted with brine (50.0 mL x 5). The combined organic layers were dried over by Na_2SO_4 then filtered. The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography to provide the desired product as a white solid (1.79 g, 10.1 mmol, 51% yield). The spectral data match those previously reported[29].

A 120 ^{o}C oven-dried 100-mL round-bottom flask equipped with a stir bar, was charged with 4-methoxy-2*H*-chromen-2-one (528.5 mg, 3.0 mmol, 1.0 equiv). Then was evacuated and backfilled with nitrogen for three times. Then dry THF (15.0 mL) under nitrogen atmosphere. The butyllithium (2.5 mol/L, 2.4 mL, 2.0 mmol, 2.0 equiv) was added dropwise into the mixture at −78 ^{o}C, and the mixture was allowed to stir for 1.0 h at −78 ^{o}C and −40 ^{o}C for 2 h, the reaction was quenched by slowly adding (15.0 mL) 1 M HCl and the resulting solution was vigorously stirred at rt. for 1 h. After the reaction was completed, the mixture was extracted with brine (30.0 mL) and ethyl acetate (30.0 mL x 3), then the combined organic layers were extracted with brine (30.0 mL x 5). The combined organic layers were dried over by Na_2SO_4 then filtered. The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography to provide the desired product **41** as a yellow liquid (280.9 mg, 1.4 mmol, 46% yield). The spectral data match those previously reported[29].

III. Optimization of the reaction conditions

1. Optimization of 1,3-transposition of 3-(2-methoxyphenyl)-1-phenylprop-2-yn-1-one 2a

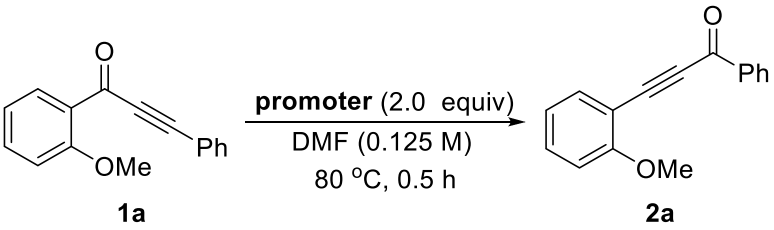
Table S1. Evaluation of different solvents



Entry	**solvent**	Yield of **2a** (%)
1	DMAc	<5
2	1,4-dioxane	<5
3	DMSO	<5
4	NMP	<5
5	Pyridine	<5
6	Toluene	<5
7	DMF	>99
8	CH_2Cl_2	<5
9	MeCN	<5
10	THF	<5

Reaction conditions: **1a** (118.1 mg, 0.5 mmol, 1.0 equiv) and Tf_2O (282.1 mg, 1.0 mmol, 2.0 equiv) in **solvent** (4.0 mL) at 80 °C for 0.5 h. [a]Yield was determined by ^1H NMR spectroscopy in the presence of CH_2Br_2 as an internal standard.

Table S2. Evaluation of different promoters

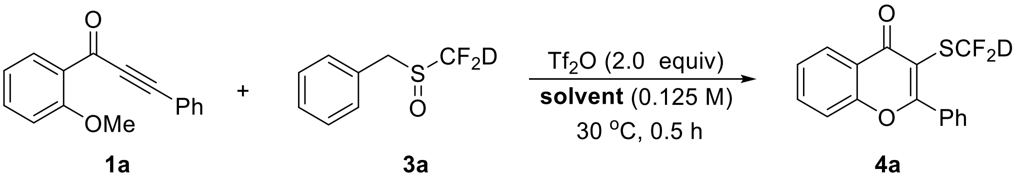


Entry	promoter	Yield of **2a** (%)
1	Tf_2O	>99
2	Ms_2O	<5
3	TFAA	<5
4	phthalic anhyfride	<5
5	$(CH_3CO)_2O$	<5
6	TfOH	<5

Reaction conditions: **1a** (118.1 mg, 0.5 mmol, 1.0 equiv) and promoter (1.0 mmol, 2.0 equiv) in **solvent** (4.0 mL) at 80 °C for 0.5 h. [a]Yield was determined by ^1H NMR spectroscopy in the presence of CH_2Br_2 as an internal standard.

2. Optimization of cyclization of 3-((difluoromethyl-*d*)thio)-2-phenyl-4*H*-chromen-4-one 4a

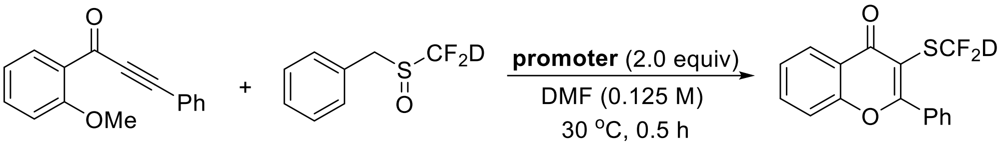
Table S3. Evaluation of different solvents



Entry	**solvent**	Yield of **4a** (%)	D-inc:(%)
1	DCM	74	99
2	MeCN	48	99
3	Toluene	46	99
4	DCE	64	99
5	CCl_4	50	99
6	DMF	>99	99
7	Et_2O	82	99
8	DMAc	<5	99
9	DMSO	<5	99
10	NMP	8	99
11	THF	<5	99
12	1,4-Dioxane	68	99

Reaction conditions: **1a** (23.6 mg, 0.1 mmol, 1.0 equiv) and **3a** (28.7 mg, 0.15 mmol, 1.5 equiv) and Tf_2O (56.4 mg, 0.2 mmol, 2.0 equiv) in **solvent** (0.8 mL) at 30 °C for 0.5 h. [a]Yield was determined by ^1H NMR spectroscopy in the presence of CH_2Br_2 as an internal standard. [b]Deuterium incorporation was determined by ^{19}F NMR.

Table S4. Evaluation of different amount of promoers

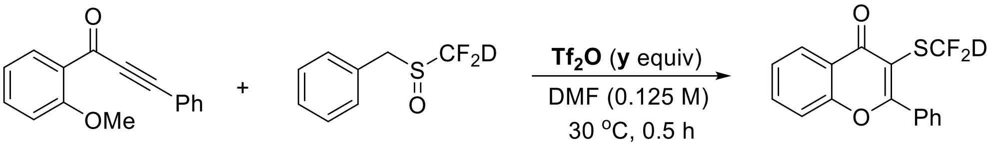


1a **3a** **4a**

Entry	**promoter**	Yield of **4a** (%)	D-inc:(%)
1	Ms_2O	<5	-
2	Ac_2o	<5	-
3	TFAA	8	-
4	TfOH	<5	-
5	Tf_2O	99	-

Reaction conditions: **1a** (23.6 mg, 0.1 mmol, 1.0 equiv) and **3a** (28.7 mg, 0.15 mmol, 1.5 equiv) and **promoter** (2.0 equiv) in DMF (0.8 mL) at 30 °C for 0.5 h. [a]Yield was determined by ^1H NMR spectroscopy in the presence of CH_2Br_2 as an internal standard. [b]Deuterium incorporation was determined by ^{19}F NMR.

Table S5. Evaluation of different amounts of 3a and Tf_2O



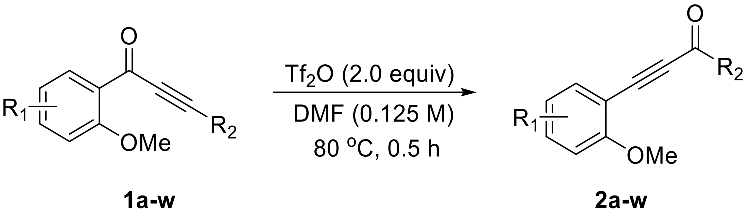
1a **3a** **4a**

Entry	**3a** (**x** equiv)	**Tf_2O** (**y** equiv)	Yield of **4a** (%)	D-inc:(%)
1	1.5	3.0	92	99
2	1.5	1.5	96	99
3	1.5	1.2	88	99
4	1.2	2.0	99	99
5	2.0	2.0	99	99

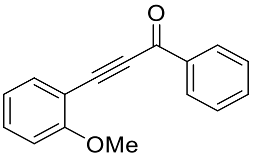
Reaction conditions: **1a** (23.6 mg, 0.1 mmol, 1.0 equiv) and **3a** (**x** equiv) and **Tf_2O** (**y** equiv) in DMF (0.8 mL) at 30 °C for 0.5 h. [a]Yield was determined by ^1H NMR spectroscopy in the presence of CH_2Br_2 as an internal standard. [b]Deuterium incorporation was determined by ^{19}F NMR.

IV. Substrate scope

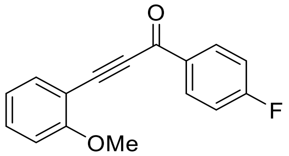
1. General Method E:



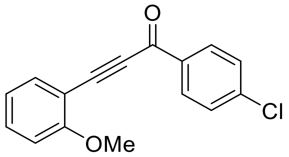
A 120 °C oven-dried 25-mL glass schlenck, equipped with a stir bar, was charged with alkyne ketone (0.5 mmol, 1.0 equiv), and it was evacuated and backfilled with nitrogen for three times. Then dry *N*,*N*-Dimethylformamide (4.0 mL) was added under nitrogen atmosphere. The Tf$_2$O (282.1 mg, 1.0 mmol, 2.0 equiv) was added dropwise into the mixture at room temperature, and the mixture was allowed to stir for 0.5 h at 80 °C. After the completion of reaction, a saturated aqueous solution of NaHCO$_3$ (20.0 mL) was added and the mixture was extracted with ethyl acetate (20.0 mL x 3). The combined organic layers were washed with brine (20.0 mL x 5), dried over by Na$_2$SO$_4$ and filtrated. The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography.



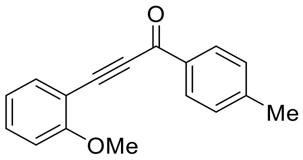
3-(2-Methoxyphenyl)-1-phenylprop-2-yn-1-one 2a: Prepared according to **General Method E** (Eluent: 100:1 to 20:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (109.8 mg, 0.46 mmol, 93% yield); **^{1}H NMR** (500 MHz, CDCl$_3$) δ 8.31 (2H, dd, *J* = 8.4, 1.4 Hz), 7.62 – 7.59 (2H, m), 7.52 – 7.49 (2H, m), 7.45 – 7.41 (1H, m), 6.98 – 6.95 (1H, m), 6.93 (1H, d, *J* = 8.5 Hz), 3.94 (3H, s); **^{13}C NMR** (126 MHz, CDCl$_3$) δ 178.2, 161.9, 137.2, 135.0, 133.9, 132.7, 129.8, 128.6, 120.7, 110.9, 109.4, 91.3, 90.7, 55.9; The spectral data match those previously reported[30].



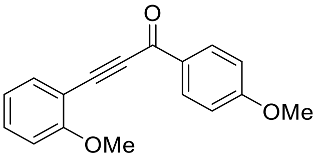
1-(4-Fluorophenyl)-3-(2-methoxyphenyl)prop-2-yn-1-one 2b: Prepared according to **General Method E** (Eluent: 100:1 to 20:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (114.6 mg, 0.45 mmol, 90% yield); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.33 – 8.30 (2H, m), 7.58 (1H, dd, J = 7.6, 1.8 Hz), 7.44 – 7.41 (1H, m), 7.17 – 7.14 (2H, m), 6.97 – 6.94 (1H, m), 6.93 (1H, d, J = 8.4 Hz), 3.94 (3H, s); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 176.5, 167.4, 165.3, 161.9, 135.0, 133.7 (d, $J_{C\text{-}F}$ = 2.7 Hz), 132.8, 132.4 (d, $J_{C\text{-}F}$ = 9.6 Hz), 120.8, 115.7 (d, $J_{C\text{-}F}$ = 22.3 Hz), 110.9, 109.2, 91.0 (d, $J_{C\text{-}F}$ = 8.1 Hz), 55.9; **^{19}F NMR** (471 MHz, $CDCl_3$) δ –103.7 – –103.8 (m); The spectral data match those previously reported[31].



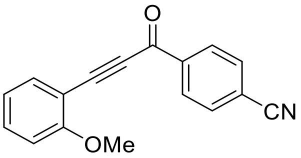
1-(4-Chlorophenyl)-3-(2-methoxyphenyl)prop-2-yn-1-one 2c: Prepared according to **General Method E** (Eluent: 100:1 to 20:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (108.9 mg, 0.40 mmol, 81% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.23 (2H, d, J = 8.6 Hz), 7.59 (1H, dd, J = 7.6, 1.7 Hz), 7.47 – 7.42 (3H, m), 6.99 – 6.95 (1H, m), 6.93 (1H, d, J = 8.5 Hz), 3.95 (3H, s); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.8, 162.0, 140.4, 135.6, 135.1, 132.9, 131.1, 128.9, 120.8, 110.9, 109.2, 91.3, 91.0, 56.0; The spectral data match those previously reported[32].



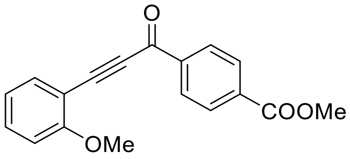
3-(2-Methoxyphenyl)-1-(*p*-tolyl)prop-2-yn-1-one 2d: Prepared according to **General Method E** (Eluent: 100:1 to 20:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (115.2 mg, 0.46 mmol, 92% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.19 (2H, d, J = 8.3 Hz), 7.58 (1H, dd, J = 7.6, 1.7 Hz), 7.43 – 7.38 (1H, m), 7.28 (2H, d, J = 7.9 Hz), 6.96 – 6.93 (1H, m), 6.91 (1H, d, J = 8.4 Hz), 3.92 (3H, s), 2.40 (3H, s); **^{13}C NMR** (101 MHz, CDCl$_3$) *δ* 177.8, 161.8, 144.9, 134.8, 134.8, 132.6, 129.8, 129.2, 120.6, 110.8, 109.3, 91.3, 90.1, 55.8, 21.7; The spectral data match those previously reported[31].



3-(2-Methoxyphenyl)-1-(4-methoxyphenyl)prop-2-yn-1-one 2e: Prepared according to **General Method E** (Eluent: 100:1 to 20:1 petroleum ether: ethyl acetate) and the title compound was isolated as a yellow liquid (114.9 mg, 0.43 mmol, 86% yield); **^{1}H NMR** (400 MHz, CDCl$_3$) *δ* 8.26 (2H, d, *J* = 8.9 Hz), 7.57 (1H, dd, *J* = 7.6, 1.8 Hz), 7.42 – 7.38 (1H, m), 6.96 – 6.90 (4H, m), 3.92 (3H, m), 3.86 (3H, s); **^{13}C NMR** (101 MHz, CDCl$_3$) *δ* 176.8, 164.3, 161.7, 134.8, 132.5, 132.1, 130.5, 120.7, 113.8, 110.8, 109.5, 91.3, 89.8, 55.9, 55.6; The spectral data match those previously reported[32].

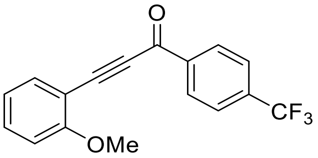


4-(3-(2-Methoxyphenyl)propioloyl)benzonitrile 2f: Prepared according to **General Method E** (Eluent: 100:1 to 10:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (82.9 mg, 0.32 mmol, 63% yield); **^{1}H NMR** (400 MHz, CDCl$_3$) *δ* 8.40 (2H, d, *J* = 8.4 Hz), 7.81 (2H, d, *J* = 8.4 Hz), 7.61 (1H, dd, *J* = 7.6, 1.7 Hz), 7.51 – 7.47 (1H, m), 7.02 – 6.96 (2H, m), 3.98 (3H, s); **^{13}C NMR** (101 MHz, CDCl$_3$) δ 176.3, 162.2, 140.0, 135.3, 133.4, 132.5, 130.1, 121.0, 118.1, 116.9, 111.0, 108.8, 93.0, 91.0, 56.1; The spectral data match those previously reported[33].

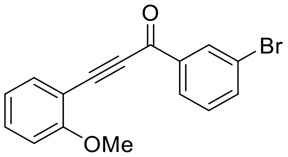


Methyl 4-(3-(2-methoxyphenyl)-3-oxoprop-1-yn-1-yl)benzoate 2g: Prepared according to **General Method E** (Eluent: 100:1 to 10:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (89.9 mg, 0.31 mmol, 61% yield);

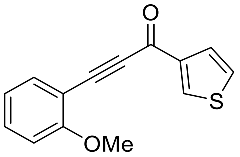
^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.34 (2H, d, *J* = 8.6 Hz), 8.13 (2H, d, *J* = 8.6 Hz), 7.58 (1H, dd, *J* = 7.6, 1.8 Hz), 7.45 – 7.41 (1H, m), 6.98 – 6.92 (2H, m), 3.95 (3H, s), 3.93 (3H, s); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 177.3, 166.3, 162.1, 140.2, 135.1, 134.4, 133.1, 129.7, 129.6, 120.8, 110.9, 109.0, 91.9, 91.3, 56.0, 52.5; The spectral data match those previously reported[34].



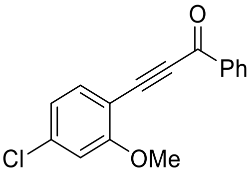
3-(2-Methoxyphenyl)-1-(4-(trifluoromethyl)phenyl)prop-2-yn-1-one 2h: Prepared according to **General Method E** (Eluent: 100:1 to 20:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (80.2 mg, 0.26 mmol, 53% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 8.41 (2H, d, *J* = 8.1 Hz), 7.77 (2H, d, *J* = 8.2 Hz), 7.61 (1H, dd, *J* = 7.6, 1.8 Hz), 7.49 – 7.44 (1H, m), 7.01 – 6.94 (2H, m), 3.98 (3H, s); **^{13}C NMR** (101 MHz, $CDCl_3$) *δ* 176.9, 162.1, 139.7, 135.2, 134.9 (q, J_{C-F} = 32.9 Hz), 133.2, 130.1, 125.7 (q, J_{C-F} = 3.8 Hz), 123.7 (q, J_{C-F} = 274.0 Hz), 120.9, 110.9, 109.0, 92.2, 91.1, 56.0; **^{19}F NMR** (471 MHz, $CDCl_3$) *δ* –63.1(s); The spectral data match those previously reported[31].



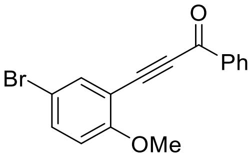
1-(3-Bromophenyl)-3-(2-methoxyphenyl)prop-2-yn-1-one 2i: Prepared according to **General Method E** (Eluent: 100:1 to 20:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (137.9 mg, 0.44 mmol, 88% yield); **M.p. =** 92.3 – 93.2 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 8.50 – 8.49 (1H, m), 8.14 (1H, d, *J* = 7.8 Hz), 7.66 (1H, dd, *J* = 7.9, 1.0 Hz), 7.53 (1H, dd, *J* = 7.6, 1.8 Hz), 7.42 – 7.38 (1H, m), 7.34 – 7.30 (1H, m), 6.94 – 6.88 (2H, m), 3.96 (3H, s); **^{13}C NMR** (101 MHz, $CDCl_3$) *δ* 176.3, 162.1, 138.8, 136.5, 134.9, 133.3, 133.1, 130.0, 127.5, 122.7, 120.7, 110.7, 108.8, 91.9, 90.9, 55.9; **HRMS** (ESI^+) $[M+Na]^+$ calc'd for $C_{16}H_{11}BrO_2Na$: 336.9835, found: 336.9821.



3-(2-Methoxyphenyl)-1-(thiophen-3-yl)prop-2-yn-1-one 2j: Prepared according to **General Method E** (Eluent: 100:1 to 20:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (112.6 mg, 0.46 mmol, 93% yield); **M.p.** = 54.9 – 55.7 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 8.46 (1H, dd, *J* = 3.0, 1.2 Hz), 7.68 (1H, dd, *J* = 5.1, 1.2 Hz), 7.54 (1H, dd, *J* = 7.6, 1.8 Hz), 7.43 – 7.38 (1H, m), 7.32 – 7.30 (1H, m), 6.96 – 6.90 (2H, m), 3.92 (3H, s); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.6, 161.8, 143.3, 135.8, 134.9, 132.7, 126.7, 126.7, 120.7, 110.8, 109.2, 91.7, 88.9, 55.9; **HRMS** (ESI$^+$) [M+Na]$^+$ calc'd for $C_{14}H_{10}O_2SNa$: 265.0294, found: 265.0292.

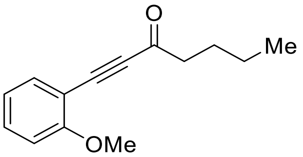


3-(4-Chloro-2-methoxyphenyl)-1-phenylprop-2-yn-1-one 2k: Prepared according to **General Method E** (Eluent: 100:1 to 20:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (108.9 mg, 0.40 mmol, 81% yield); **M.p.** = 77.8 – 78.4 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) *δ* 8.26 (2H, d, *J* = 7.7 Hz), 7.61 – 7.58 (1H, m), 7.50 – 7.47 (3H, m), 6.94 (1H, d, *J* = 8.2 Hz), 6.91 (1H, s), 3.93 (3H, s); **^{13}C NMR** (101 MHz, $CDCl_3$) *δ* 178.0, 162.3, 138.5, 137.0, 135.6, 134.1, 129.8, 128.6, 121.2, 111.9, 108.1, 91.8, 89.2, 56.3; **HRMS** (ESI$^+$) [M+Na]$^+$ calc'd for $C_{16}H_{11}ClO_2Na$: 293.0340, found: 293.0333.

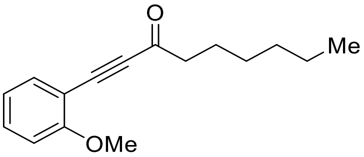


3-(5-Bromo-2-methoxyphenyl)-1-phenylprop-2-yn-1-one 2l: Prepared according to **General Method E** (Eluent: 100:1 to 20:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (57.8 mg, 0.18 mmol, 37% yield); **M.p.** = 103.2 – 104.0 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 8.27 (2H, d, *J* = 7.0 Hz), 7.69 (1H, d, *J* = 2.5 Hz), 7.64 – 6.60 (1H, m), 7.53 – 7.49 (3H, m), 6.82 (1H, d, *J* = 8.9 Hz), 3.94

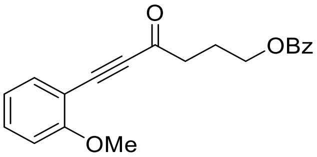
(3H, s); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 177.9, 161.0, 137.0, 137.0, 135.3, 134.2, 129.8, 128.7, 112.6, 112.4, 111.5, 91.8, 88.4, 56.3; **HRMS** (ESI$^+$) [M+Na]$^+$ calc'd for $C_{16}H_{11}BrO_2Na$: 336.9835, found: 336.9837.



1-(2-Methoxyphenyl)hept-1-yn-3-one 2m: Prepared according to **General Method E** (Eluent: 100:1 to 20:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colourless liquid (97.6 mg, 0.45 mmol, 90% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48 (1H, dd, J = 7.6, 1.8 Hz), 7.41 – 7.37 (1H, m), 6.94 – 6.89 (2H, m), 3.87 (3H, s), 2.65 (2H, t, J = 7.4 Hz), 1.77 – 1.70 (2H, m), 1.43 – 1.33 (2H, m), 0.93 (3H, t, J = 7.4 Hz); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 188.5, 161.5, 135.0, 132.5, 120.6, 110.9, 109.2, 92.0, 88.0. 55.8, 45.3, 26.4, 22.2, 13.9; The spectral data match those previously reported[31].

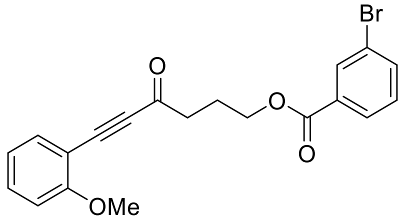


1-(2-Methoxyphenyl)non-1-yn-3-one 2n: Prepared according to **General Method E** (Eluent: 100:1 to 20:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colourless liquid (115.6 mg, 0.47 mmol, 95% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48 (1H, dd, J = 7.6, 1.7 Hz), 7.41 – 7.37 (1H, m), 6.94 – 6.88 (2H, m), 3.87 (3H, s), 2.64 (2H, t, J = 7.5 Hz), 1.78 – 1.71 (2H, m), 1.36 – 1.24 (6H, m), 0.87 (3H, t, J = 6.8 Hz); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 188.5, 161.5, 135.0, 132.5, 120.6, 110.9, 109.3, 92.0, 88.0, 55.8, 45.6, 31.6, 28.7, 24.3, 22.5, 14.1; The spectral data match those previously reported[31].

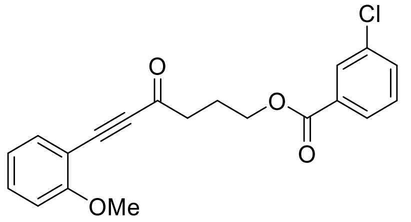


6-(2-Methoxyphenyl)-4-oxohex-5-yn-1-yl benzoate 2o: Prepared according to **General Method E** (Eluent: 80:1 to 10:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (141.6 mg, 0.44 mmol, 88% yield); **M.p. =**

49.5 – 50.2 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 8.03 (2H, d, *J* = 8.5, 1.6 Hz), 7.55 – 7.52 (1H, m), 7.47 (1H, dd, *J* = 7.6, 1.8 Hz), 7.43 – 7.37 (3H, m), 6.93 – 6.90 (1H, m), 6.88 (1H, d, *J* = 8.5 Hz), 4.39 (2H, t, *J* = 6.3 Hz), 3.85 (3H, s), 2.85 (2H, t, *J* = 7.2 Hz), 2.27 – 2.20 (2H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 186.9, 166.5, 161.5, 134.9, 133.0, 132.7, 130.1, 129.6, 128.4, 120.6, 110.8, 108.9, 91.7, 88.8, 64.0, 55.8, 42.1, 23.4; **HRMS** (ESI$^+$) [M+Na]$^+$ calc'd for $C_{20}H_{18}O_4Na$: 345.1097, found: 345.1093.

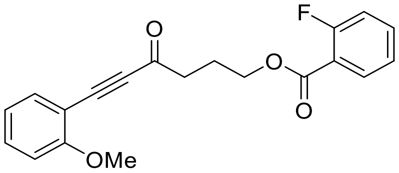


6-(2-Methoxyphenyl)-4-oxohex-5-yn-1-yl 3-bromobenzoate 2p: Prepared according to **General Method E** (Eluent: 80:1 to 10:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (172.3 mg, 0.43 mmol, 86% yield); **M.p. =** 67.8 – 68.6 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 8.16 – 8.15 (1H, m), 7.96 (1H, d, *J* = 7.8 Hz), 7.66 (1H, dd, *J* = 8.2, 1.2 Hz), 7.48 (1H, dd, *J* = 7.6, 1.7 Hz), 7.43 – 7.39 (1H, m), 7.32 – 7.28 (1H, m), 6.95 – 6.88 (2H, m), 4.41 (2H, t, *J* = 6.3 Hz), 3.87 (3H, s), 2.86 (2H, t, *J* = 7.2 Hz), 2.29 – 2.22 (2H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 186.6, 165.0, 161.5, 135.8, 134.9, 132.6, 132.5, 132.0, 130.0, 128.1, 122.4, 120.5, 110.8, 108.8, 91.7, 88.9, 64.4, 55.8, 42.0, 23.3; **HRMS** (ESI$^+$) [M+H]$^+$ calc'd for $C_{20}H_{18}BrO_4$: 400.0305, found: 400.0307.

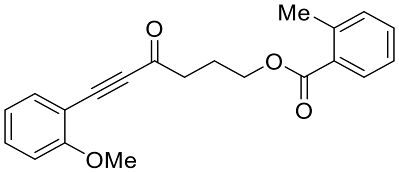


6-(2-Methoxyphenyl)-4-oxohex-5-yn-1-yl 3-chlorobenzoate 2q: Prepared according to **General Method E** (Eluent: 80:1 to 20:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (159.8 mg, 0.45 mmol, 90% yield); **M.p.** = 63.7 – 64.3 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 7.98 – 7.97 (1H, m), 7.89 (1H, d, *J* = 7.8 Hz), 7.50 – 7.45 (2H, m), 7.41 – 7.32 (2H, m), 6.93 – 6.86 (2H, m), 4.39 (2H, t, *J* = 6.3 Hz), 3.85 (3H, s), 2.84 (2H, t, *J* = 7.2 Hz), 2.26 – 2.20 (2H, m); **^{13}C NMR**

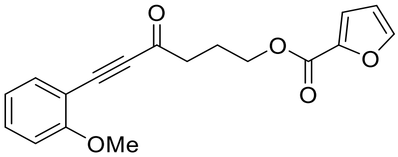
(101 MHz, $CDCl_3$) δ 186.7, 165.2, 161.5, 135.0, 134.5, 133.0, 132.7, 131.8, 129.7, 129.6, 127.7, 120.6, 110.8, 108.9, 91.7, 88.9, 64.4, 55.8, 42.0, 23.4; **HRMS** (ESI$^+$) [M+Na]$^+$ calc'd for $C_{20}H_{17}ClO_4Na$: 379.0708, found: 379.0699.



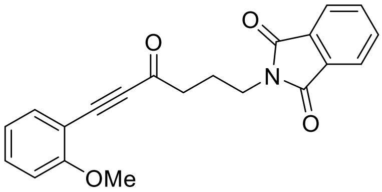
6-(2-Methoxyphenyl)-4-oxohex-5-yn-1-yl 2-fluorobenzoate 2r: Prepared according to **General Method E** (Eluent: 80:1 to 10:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (149.8 mg, 0.44 mmol, 88% yield); **M.p.** = 32.8 – 33.6 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 7.90 – 7.86 (1H, m), 7.48 – 7.41 (2H, m), 7.37 – 7.33 (1H, m), 7.15 – 7.11 (1H, m), 7.09 – 7.04 (1H, m), 6.89 – 6.83 (2H, m), 4.36 (2H, t, *J* = 6.3 Hz), 3.81 (3H, s), 2.83 (2H, t, *J* = 7.3 Hz), 2.22 – 2.15 (2H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 186.7, 164.1 (d, $J_{C\text{-}F}$ = 3.7 Hz), 161.8 (d, $J_{C\text{-}F}$ = 260.9 Hz), 161.4, 134.8, 134.5 (d, $J_{C\text{-}F}$ = 9.3 Hz), 132.6, 132.0, 123.9 (d, $J_{C\text{-}F}$ = 3.9 Hz), 120.4, 118.5 (d, $J_{C\text{-}F}$ = 9.8 Hz), 116.8 (d, $J_{C\text{-}F}$ = 22.2 Hz), 110.7, 108.8, 91.6, 88.7, 64.1, 55.6, 41.8, 23.2; **^{19}F NMR** (471 MHz, $CDCl_3$) *δ* –109.3 – –109.3 (m); **HRMS** (ESI$^+$) [M+Na]$^+$ calc'd for $C_{20}H_{17}FO_4Na$: 363.1003, found: 363.0997.



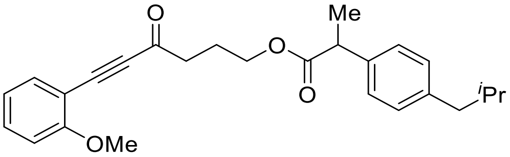
6-(2-Methoxyphenyl)-4-oxohex-5-yn-1-yl 2-methylbenzoate 2s: Prepared according to **General Method E** (Eluent: 80:1 to 10:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (137.8 mg, 0.41 mmol, 82% yield); **M.p.** = 38.0 – 38.6 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 7.92 (1H, dd, *J* = 7.9, 1.3 Hz), 7.47 (1H, dd, *J* = 7.6, 1.8 Hz), 7.41 – 7.35 (2H, m), 7.24 – 7.20 (2H, m), 6.94 – 6.90 (1H, m), 6.88 (1H, d, *J* = 8.5 Hz), 4.36 (2H, t, *J* = 6.3 Hz), 3.85 (3H, s), 2.85 (2H, t, *J* = 7.4 Hz), 2.59 (3H, s), 2.26 – 2.19 (2H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 186.7, 167.4, 161.5, 140.2, 134.9, 132.6, 132.0, 131.7, 130.6, 129.4, 125.7, 120.5, 110.8, 108.9, 91.7, 88.8, 63.7, 55.7, 42.1, 23.4, 21.8; **HRMS** (ESI$^+$) [M+Na]$^+$ calc'd for $C_{21}H_{20}O_4Na$: 359.1254, found: 359.1249.



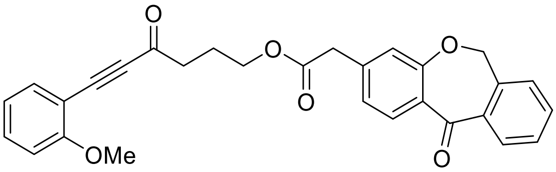
6-(2-Methoxyphenyl)-4-oxohex-5-yn-1-yl furan-2-carboxylate 2t: Prepared according to **General Method E** (Eluent: 80:1 to 10:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (132.9 mg, 0.43 mmol, 85% yield); **M.p. =** 48.5 – 49.3 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 7.56 – 7.55 (1H, m), 7.47 (1H, dd, *J* = 7.6, 1.8 Hz), 7.42 – 7.37 (1H, m), 7.17 (1H, dd, *J* = 3.5, 0.9 Hz), 6.94 – 6.87 (2H, m), 6.49 – 6.47 (1H, m), 4.36 (2H, t, *J* = 6.3 Hz), 3.86 (3H, s), 2.82 (2H, t, *J* = 7.2 Hz), 2.23 – 2.17 (2H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 186.8, 161.6, 158.7, 146.4, 144.6, 135.0, 132.7, 120.6, 118.1, 111.9, 110.9, 109.0, 91.7, 88.9, 63.9, 55.8, 42.0, 23.4; **HRMS** (ESI$^+$) [M+Na]$^+$ calc'd for $C_{18}H_{16}O_5Na$: 335.0890, found: 335.0886.



2-(6-(2-Methoxyphenyl)-4-oxohex-5-yn-1-yl)isoindoline-1,3-dione 2u: Prepared according to **General Method E** (Eluent: 80:1 to 10:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (136.9 mg, 0.39 mmol, 79% yield); **M.p. =** 83.8 – 84.4 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 7.83 – 7.80 (2H, m), 7.73 – 7.70 (2H, m), 7.47 (1H, dd, *J* = 7.7, 1.8 Hz), 7.43 – 7.39 (1H, m), 6.95 – 6.89 (2H, m), 3.87 (3H, s), 3.78 (2H, t, *J* = 6.9 Hz), 2.76 (2H, t, *J* = 7.5 Hz), 2.19 – 2.12 (2H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 186.4, 168.2, 161.4, 134.9, 133.9, 132.5, 131.9, 123.1, 120.4, 110.7, 108.8, 91.6, 88.7, 55.7, 42.6, 37.1, 23.2; **HRMS** (ESI$^+$) [M+Na]$^+$ calc'd for $C_{21}H_{17}NO_4Na$: 370.1050, found: 370.1043.

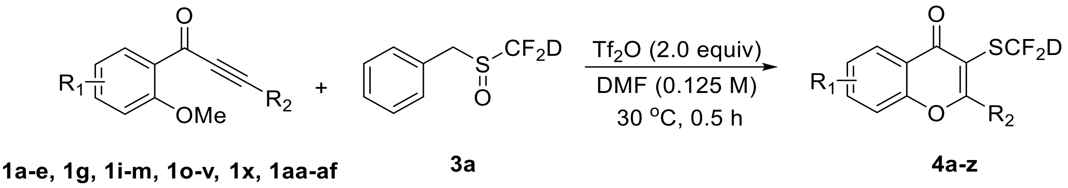


6-(2-Methoxyphenyl)-4-oxohex-5-yn-1-yl 2-(4-isobutylphenyl)propanoate 2v: Prepared according to **General Method E** (Eluent: 80:1 to 10:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colourless liquid (186.9 mg, 0.46 mmol, 92% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 7.49 (1H, dd, *J* = 7.6, 1.8 Hz), 7.44 – 7.39 (1H, m), 7.21 (2H, d, *J* = 8.0 Hz), 7.07 (2H, d, *J* = 8.0 Hz), 6.96 – 6.89 (2H, m), 4.14 (2H, t, *J* = 6.2 Hz), 3.87 (3H, s), 3.73 – 3.68 (1H, m), 2.64 (2H, t, *J* = 7.3 Hz), 2.41 (2H, d, *J* = 7.1 Hz), 2.08 – 2.01 (2H, m), 1.86 – 1.76 (1H, m), 1.49 (3H, d, *J* = 7.2 Hz), 0.87 (6H, d, *J* = 6.7 Hz); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 186.7, 174.6, 161.5, 140.5, 137.7, 134.9, 132.6, 129.3, 127.1, 120.5, 110.8, 109.0, 91.7, 88.5, 63.5, 55.7, 45.1, 44.9, 41.7, 30.1, 23.2, 22.3, 18.3; **HRMS** (ESI$^+$) $[M+Na]^+$ calc'd for $C_{26}H_{30}O_4Na$: 429.2036, found: 429.2032.

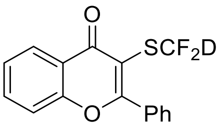


6-(2-Methoxyphenyl)-4-oxohex-5-yn-1-yl 2-(11-oxo-6,11-dihydrodibenzo[*b,e*]oxepin-3-yl)acetate 2w: Prepared according to **General Method E** (Eluent: 50:1 to 5:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colourless liquid (201.5 mg, 0.43 mmol, 86% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 8.10 (1H, d, *J* = 2.4 Hz), 7.86 (1H, d, *J* = 7.5 Hz), 7.55 – 7.51 (1H, m), 7.48 (1H, dd, *J* = 7.6, 1.5 Hz), 7.45 – 7.37 (3H, m), 7.33 (1H, d, *J* = 7.4 Hz), 7.00 (1H, d, *J* = 8.4 Hz), 6.94 – 6.90 (1H, m), 6.88 (1H, d, *J* = 8.5 Hz), 5.14 (2H, s), 4.18 (2H, t, *J* = 6.3 Hz), 3.86 (3H, s), 3.64 (2H, s), 2.74 (2H, t, *J* = 7.2 Hz), 2.13 – 2.06 (2H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) *δ* 190.8, 186.8, 171.4, 161.5, 160.5, 140.4, 136.4, 135.6, 135.0, 132.8, 132.7, 132.5, 129.5, 129.3, 127.8, 127.8, 125.1, 121.1, 120.6, 110.8, 108.9, 91.7, 88.8, 73.6, 64.0, 55.8, 41.9, 40.2, 23.3; **HRMS** (ESI$^+$) $[M+Na]^+$ calc'd for $C_{29}H_{24}O_6Na$: 491.1465, found: 491.1455.

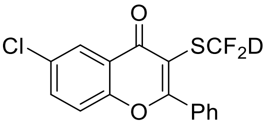
2. General Method F:



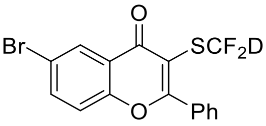
A 120 °C oven-dried 25-mL glass schlenck, equipped with a stir bar, was charged with (((difluoromethyl-*d*)sulfinyl)methyl)benzene (114.7 mg, 0.6 mmol, 1.2 equiv) and alkyne ketone (0.5 mmol, 1.0 equiv). The mixture was evacuated and backfilled with nitrogen for three times. Then dry *N,N*-Dimethylformamide (4.0 mL) was added under nitrogen atmosphere. The Tf_2O (282.1 mg, 1.0 mmol, 2.0 equiv) was added dropwise into the mixture at 30 °C, and the mixture was allowed to stir for 0.5 h at 30 °C. After the completion of reaction, a saturated aqueous solution of $NaHCO_3$ (20.0 mL) was added and the mixture was extracted with ethyl acetate (20.0 mL x 3). The combined organic layers were washed with brine (20.0 mL x 5), dried over by Na_2SO_4 and filtrated. The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography.



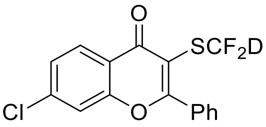
3-((Difluoromethyl-*d*)thio)-2-phenyl-4*H*-chromen-4-one 4a: Prepared according to **General Method F** (Eluent: 100:1 to 20:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (131.3 mg, 0.43 mmol, 86% yield); **M.p** = 94.5 – 95.3 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.28 (1H, dd, J = 8.1, 1.7 Hz), 7.78 (2H, dd, J = 8.1, 1.6 Hz), 7.76 – 7.73 (1H, m), 7.58 – 7.47 (5H, m); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 176.2, 168.9, 156.0, 134.7, 132.5, 131.4, 129.8, 128.4, 126.4, 126.2, 122.5, 118.7 (tt, $J_{C\text{-}F}$ = 276.3, 32.7 Hz), 118.5, 110.8 (t, $J_{C\text{-}F}$ = 3.8 Hz); **^{19}F NMR** (471 MHz, $CDCl_3$) δ –96.2 (t, J = 9.0 Hz); **HRMS** (ESI$^+$) $[M+Na]^+$ calc'd for $C_{16}H_9DF_2O_2SNa$: 328.0325, found: 328.0323.



6-Chloro-3-((difluoromethyl-*d*)thio)-2-phenyl-4*H*-chromen-4-one 4b: Prepared according to **General Method F** (Eluent: 100:1 to 20:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (136.8 mg, 0.40 mmol, 81% yield); **M.p. =** 123.8 – 124.6 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.16 (1H, d, J = 2.6 Hz), 7.76 (2H, d, J = 6.6 Hz), 7.64 (1H, dd, J = 8.9, 2.6 Hz), 7.58 – 7.51 (3H, m), 7.46 (1H, d, J = 8.9 Hz); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.9, 168.9, 154.2, 134.7, 132.1, 132.0, 131.5, 129.7, 128.4, 125.6, 123.2, 119.9, 118.5 (tt, $J_{C\text{-}F}$ = 273.9, 33.0 Hz), 110.8 (t, $J_{C\text{-}F}$ = 3.7 Hz); **^{19}F NMR** (471 MHz, $CDCl_3$) δ –96.0 (t, J = 8.8 Hz); **HRMS** (ESI$^+$) [M+Na]$^+$ calc'd for $C_{16}H_8DClF_2O_2SNa$: 361.9935, found: 361.9930.

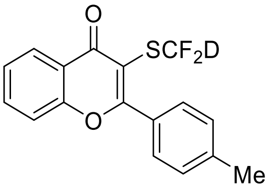


6-Bromo-3-((difluoromethyl-*d*)thio)-2-phenyl-4*H*-chromen-4-one 4c: Prepared according to **General Method F** (Eluent: 100:1 to 20:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (167.4 mg, 0.44 mmol, 87% yield); **M.p. =** 137.5 – 138.4 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.36 (1H, d, J = 2.5 Hz), 7.80 (1H, dd, J = 8.9, 2.5 Hz), 7.76 (2H, d, J = 7.1 Hz), 7.59 – 7.52 (3H, m), 7.41 (1H, d, J = 8.9 Hz); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 174.9, 169.0, 154.6, 137.6, 132.1, 131.6, 129.7, 128.9, 128.4, 123.6, 120.2, 119.5, 118.5 (tt, $J_{C\text{-}F}$ = 276.8, 32.8 Hz), 111.0 (t, $J_{C\text{-}F}$ = 3.7 Hz); **^{19}F NMR** (471 MHz, $CDCl_3$) δ –96.1 (t, J = 9.5 Hz); **HRMS** (ESI$^+$) [M+Na]$^+$ calc'd for $C_{16}H_8DBrF_2O_2SNa$: 405.9430, found: 405.9443.

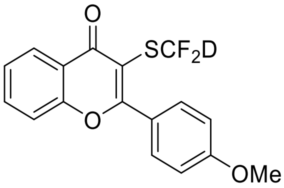


7-Chloro-3-((difluoromethyl-*d*)thio)-2-phenyl-4*H*-chromen-4-one 4d: Prepared according to **General Method F** (Eluent: 100:1 to 20:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (144.8 mg, 0.43 mmol, 85% yield); **M.p. =** 136.7 – 137.5 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.17 (1H, d, J =

8.6 Hz), 7.76 (2H, d, *J* = 7.1 Hz), 7.58 – 7.52 (4H, m), 7.41 (1H, dd, *J* = 8.6, 1.5 Hz); **^{13}C NMR** (126 MHz, $CDCl_3$) *δ* 175.2, 168.8, 155.9, 140.7, 132.0, 131.5, 129.7, 128.4, 127.7, 126.9, 120.9, 118.6 (tt, $J_{C\text{-}F}$ = 276.7, 33.0 Hz), 118.2, 111.2 (t, $J_{C\text{-}F}$ = 3.8 Hz); **^{19}F NMR** (471 MHz, $CDCl_3$) *δ* –96.0 (t, *J* = 9.0 Hz); **HRMS** (ESI$^+$) [M+Na]$^+$ calc'd for $C_{16}H_8DClF_2O_2SNa$: 361.9935, found: 361.9945.

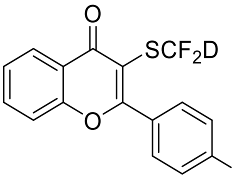


3-((Difluoromethyl-*d*)thio)-2-(*p*-tolyl)-4*H*-chromen-4-one 4e: Prepared according to **General Method F** (Eluent: 100:1 to 20:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (111.9 mg, 0.35 mmol, 70% yield); **M.p.** = 125.3 – 126.1 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) *δ* 8.23 (1H, dd, *J* = 8.0, 1.7 Hz), 7.72 – 7.68 (3H, m), 7.48 (1H, d, *J* = 8.4 Hz), 7.46 – 7.43 (1H, m), 7.32 (2H, d, *J* = 7.9 Hz), 2.44 (3H, s); **^{13}C NMR** (101 MHz, $CDCl_3$) *δ* 176.1, 168.9, 155.8, 141.9, 134.5, 129.7, 129.5, 129.0, 126.2, 126.0, 122.3, 118.8 (tt, $J_{C\text{-}F}$ = 276.9, 33.4 Hz), 110.2 (t, $J_{C\text{-}F}$ = 3.8 Hz), 118.1, 21.6; **^{19}F NMR** (471 MHz, $CDCl_3$) *δ* –96.1 (t, *J* = 9.0 Hz); **HRMS** (ESI$^+$) [M+H]$^+$ calc'd for $C_{17}H_{12}DF_2O_2S$: 319.0583, found: 319.0588.

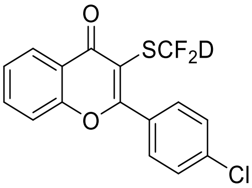


3-((Difluoromethyl-*d*)thio)-2-(4-methoxyphenyl)-4*H*-chromen-4-one 4f: Prepared according to **General Method F** (Eluent: 100:1 to 20:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (78.4 mg, 0.23 mmol, 47% yield); **M.P. =** 105.1 – 106.0 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) *δ* 8.24 (1H, dd, *J* = 8.0, 1.7 Hz), 8.00 (2H, d, *J* = 8.9 Hz), 7.73 – 7.69 (1H, m), 7.50 – 7.44 (2H, m), 7.03 (2H, d, *J* = 8.9 Hz), 3.89 (3H, s); **^{13}C NMR** (101 MHz, $CDCl_3$) *δ* 176.1, 168.5, 161.2, 155.7, 134.4, 131.7, 126.2, 125.9, 124.5, 122.3, 118.9 (tt, $J_{C\text{-}F}$ = 276.4, 32.8 Hz), 118.0, 113.7, 109.6 (t, $J_{C\text{-}F}$ = 3.7 Hz), 55.5, 29.7; **^{19}F NMR** (471 MHz, $CDCl_3$) *δ* –

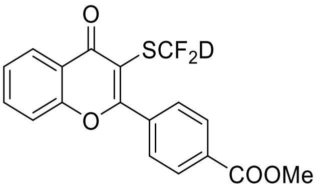
96.2 (t, J = 8.8 Hz); **HRMS** (ESI$^+$) [M+Na]$^+$ calc'd for $C_{17}H_{11}DF_2O_3SNa$: 358.0430, found: 358.0427.



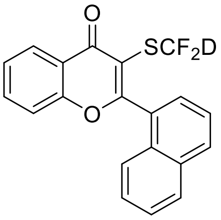
3-((Difluoromethyl-*d*)thio)-2-(4-fluorophenyl)-4*H*-chromen-4-one 4g: Prepared according to **General Method F** (Eluent: 100:1 to 20:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (127.8 mg, 0.40 mmol, 79% yield); **M.p.** = 96.7 – 97.3 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.20 (1H, d, J = 7.9 Hz), 7.80 (2H, dd, J = 8.6, 5.3 Hz), 7.73 – 7.69 (1H, m), 7.49 – 7.42 (2H, m), 7.21 – 7.17 (2H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 175.9, 167.7, 165.5, 163.0, 155.7, 134.6, 132.1 (d, $J_{C\text{-}F}$ = 8.9 Hz), 128.5 (d, $J_{C\text{-}F}$ = 3.5 Hz), 126.2 (d, $J_{C\text{-}F}$ = 9.9 Hz), 122.2, 118.7 (tt, $J_{C\text{-}F}$ = 277.3, 32.6 Hz), 118.0, 115.6 (d, $J_{C\text{-}F}$ = 22.1 Hz), 110.5 (t, $J_{C\text{-}F}$ = 3.7 Hz); **^{19}F NMR** (471 MHz, $CDCl_3$) δ –96.1 (t, J = 2.4 Hz), –107.3 (m); **HRMS** (ESI$^+$) [M+Na]$^+$ calc'd for $C_{16}H_8DF_3O_2S$: 346.0230, found: 346.0236.



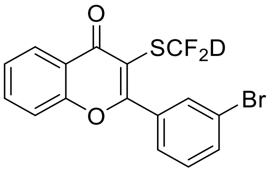
2-(4-Chlorophenyl)-3-((difluoromethyl-*d*)thio)-4*H*-chromen-4-one 4h: Prepared according to **General Method F** (Eluent: 100:1 to 20:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (148.2 mg, 0.44 mmol, 87% yield); **M.p.** = 128.2 – 128.9 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.26 (1H, dd, J = 8.0,1.7 Hz), 7.76 – 7.73 (3H, m), 7.52 – 7.47 (4H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.0, 167.7, 155.9, 137.7, 134.8, 131.2, 130.9, 128.8, 126.4, 126.3, 122.4, 118.7 (tt, $J_{C\text{-}F}$ = 314.2, 33.0 Hz), 118.2, 111.0 (t, $J_{C\text{-}F}$ = 3.8 Hz); **^{19}F NMR** (471 MHz, $CDCl_3$) δ –96.0 (t, J = 8.9 Hz); **HRMS** (ESI$^+$) [M+Na]$^+$ calc'd for $C_{16}H_8DClF_2O_2S$: 361.9935, found: 361.9939.



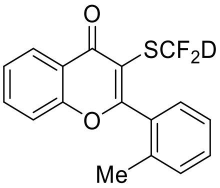
Methyl 4-(3-((difluoromethyl-*d*)thio)-4-oxo-4*H*-chromen-2-yl)benzoate 4i: Prepared according to **General Method F** (Eluent: 100:1 to 20:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (174.7 mg, 0.48 mmol, 96% yield); **M.p. =** 137.8 – 138.7 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.20 (1H, dd, J = 8.0, 1.7 Hz), 8.15 (2H, d, J = 8.4 Hz), 7.82 (2H, d, J = 8.4 Hz), 7.74 – 7.69 (1H, m), 7.50 – 7.43 (2H, m), 3.93 (3H, s); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 175.7, 167.6, 166.0, 155.7, 136.3, 134.7, 132.3, 129.7, 129.4, 126.2, 122.2, 188.5 (tt, J_{C-F} = 277.4, 33.3 Hz), 118.1, 111.1 (t, J_{C-F} = 3.6 Hz), 52.5 (one carbons were missing due to overlap); **^{19}F NMR** (471 MHz, $CDCl_3$) δ –96.0 (t, J = 8.6 Hz); **HRMS** (ESI$^+$) $[M+Na]^+$ calc'd for $C_{18}H_{11}DF_2O_2SNa$: 386.0379, found: 386.0370.



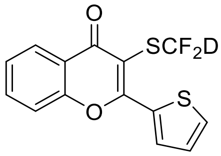
3-((Difluoromethyl-*d*)thio)-2-(naphthalen-1-yl)-4*H*-chromen-4-one 4j: Prepared according to **General Method F** (Eluent: 100:1 to 20:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (88.7 mg, 0.25 mmol, 50% yield); **M.p. =** 117.8 – 118.6 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.37 (1H, dd, J = 8.0, 1.5 Hz), 8.06 (1H, d, J = 8.0 Hz), 7.96 (1H, d, J = 7.5 Hz), 7.75 – 7.71 (1H, m), 7.69 – 7.65 (2H, m), 7.62 (1H, d, J = 7.9 Hz), 7.59 – 7.50 (3H, m), 7.46 (1H, d, J = 8.4 Hz); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 175.7, 169.0, 156.2, 134.7, 133.4, 131.3, 130.5, 130.1, 128.8, 128.2, 127.6, 126.7, 126.4, 126.2, 124.9, 124.5, 122.8, 118.3, 118.2 (tt, J_{C-F} = 267.6, 32.4 Hz), 113.7 (t, J_{C-F} = 3.8 Hz); **^{19}F NMR** (471 MHz, $CDCl_3$) δ –95.4 – –96.7 (m); **HRMS** (ESI$^+$) $[M+Na]^+$ calc'd for $C_{20}H_{11}DF_2O_2SNa$: 378.0481, found: 378.0475.



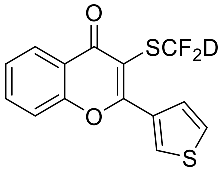
2-(3-Bromophenyl)-3-((difluoromethyl-*d*)thio)-4*H*-chromen-4-one 4k: Prepared according to **General Method F** (Eluent: 100:1 to 20:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (139.8 mg, 0.36 mmol, 73% yield); **M.p. =** 127.6 – 128.0 °C; **^{1}H NMR** (400 MHz, CDCl$_3$) δ 8.23 (1H, dd, J = 8.0, 1.8 Hz), 7.88 (1H, s), 7.76 – 7.72 (2H, m), 7.67 (1H, d, J = 8.1 Hz), 7.52 – 7.45 (2H, m), 7.41 – 7.37 (1H, m); **^{13}C NMR** (101 MHz, CDCl$_3$) δ 176.2, 168.9, 156.0, 134.8, 134.2, 132.3, 129.9, 128.66, 126.3, 126.3, 122.3, 118.5 (tt, $J_{C\text{-}F}$ = 277.1, 32.6 Hz), 118.1, 111.1 (t, $J_{C\text{-}F}$ = 3.7 Hz). **^{19}F NMR** (471 MHz, CDCl$_3$) δ –95.9 (t, J = 9.3 Hz); **HRMS** (ESI$^+$) [M+Na]$^+$ calc'd for $C_{16}H_8BrDF_2O_2SNa$: 405.9430, found: 405.9429.



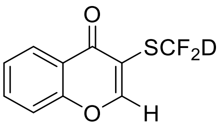
3-((Difluoromethyl-*d*)thio)-2-(*p*-tolyl)-4*H*-chromen-4-one 4l: Prepared according to **General Method F** (Eluent: 100:1 to 20:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (108.8 mg, 0.34 mmol, 68% yield); **M.p. =** 100.3 – 100.9 °C; **^{1}H NMR** (500 MHz, CDCl$_3$) δ 8.31 (1H, dd, J = 8.1, 1.7 Hz), 7.76 – 7.73 (1H, m), 7.52 – 7.45 (3H, m), 7.38 – 7.33 (3H, m), 2.31 (3H, s); **^{13}C NMR** (101 MHz, CDCl$_3$) δ 175.8, 169.9, 156.0, 136.4, 134.7, 132.4, 130.8, 130.6, 129.5, 126.4, 126.2, 125.8, 122.7, 118.4 (tt, $J_{C\text{-}F}$ = 277.2, 32.8 Hz), 118.2, 112.5 (t, $J_{C\text{-}F}$ = 3.7 Hz), 19.4; **^{19}F NMR** (471 MHz, CDCl$_3$) δ –95.2 (s); **HRMS** (ESI$^+$) [M+Na]$^+$ calc'd for $C_{17}H_{11}DF_2O_2SNa$: 342.0481, found: 342.0477.



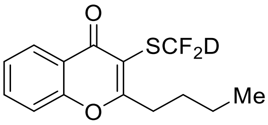
3-((Difluoromethyl-*d*)thio)-2-(thiophen-*2*-yl)-4*H*-chromen-4-one 4m: Prepared according to **General Method F** (Eluent: 100:1 to 20:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (99.8 mg, 0.32 mmol, 64% yield); **M.p. =** 130.1 – 130.9 °C; **^{1}H NMR** (500 MHz, CDCl$_3$) δ 8.26 (1H, d, J = 3.8 Hz), 8.22 (1H, d, J = 7.9 Hz), 7.74 – 7.70 (2H, m), 7.52 (1H, d, J = 8.4 Hz), 7.46 – 7.43 (1H, m), 7.23 – 7.21 (1H, m); **^{13}C NMR** (126 MHz, CDCl$_3$) δ 176.0, 162.2, 155.4, 134.6, 134.3, 133.9, 133.6, 127.7, 126.4, 126.0, 122.1, 119.1 (tt, $J_{\text{C-F}}$ = 278.1, 32.9 Hz), 117.9, 107.1 (t, $J_{\text{C-F}}$ = 3.6 Hz); **^{19}F NMR** (471 MHz, CDCl$_3$) δ –95.0 (t, J = 8.9 Hz); **HRMS** (ESI$^+$) [M+Na]$^+$ calc'd for $C_{14}H_7DF_2O_2S_2Na$: 333.9889, found: 333.9890.



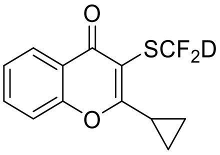
3-((Difluoromethyl-*d*)thio)-2-(thiophen-*3*-yl)-4*H*-chromen-4-one 4n: Prepared according to **General Method F** (Eluent: 100:1 to 20:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (101.8 mg, 0.33 mmol, 65% yield); **M.p. =** 107.5 – 108.3 °C; **^{1}H NMR** (400 MHz, CDCl$_3$) δ 8.34 (1H, dd, J = 3.1, 1.3 Hz), 8.21 (1H, dd, J = 7.9, 1.8 Hz), 7.82 (1H, dd, J = 5.1, 1.4 Hz), 7.74 – 7.69 (1H, m), 7.51 – 7.42 (3H, m); **^{13}C NMR** (101 MHz, CDCl$_3$) δ 176.2, 163.4, 155.6, 134.6, 133.1, 132.1, 128.6, 126.3, 126.1, 125.8, 122.2, 119.2 (tt, $J_{\text{C-F}}$ = 277.0, 32.3 Hz), 118.0, 109.0 (t, $J_{\text{C-F}}$ = 3.7 Hz); **^{19}F NMR** (471 MHz, CDCl$_3$) δ –95.4 (t, J = 9.2 Hz); **HRMS** (ESI$^+$) [M+Na]$^+$ calc'd for $C_{14}H_7DF_2O_2S_2Na$: 333.9889, found: 333.9888.



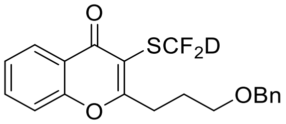
3-((Difluoromethyl-*d*)thio)-4*H*-chromen-4-one 4o: Prepared according to **General Method F** (Eluent: 100:1 to 20:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (63.9 mg, 0.28 mmol, 56% yield); **M.p. =** 92.2 – 93.1 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.28 (1H, s), 8.23 (1H, dd, J = 8.0, 1.5 Hz), 7.73 – 7.70 (1H, m), 7.49 – 7.44 (2H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 175.3, 160.1, 156.4, 134.6, 126.4 (one carbons were missing due to overlap), 123.7, 118.4, 118.3 (tt, $J_{C\text{-}F}$ = 277.0, 32.3 Hz), 112.6 (t, $J_{C\text{-}F}$ = 3.1 Hz); **^{19}F NMR** (471 MHz, $CDCl_3$) δ –95.3 (t, J = 8.8 Hz); **HRMS** (ESI$^+$) $[M+Na]^+$ calc'd for $C_{10}H_5DF_2O_2SNa$: 252.0012, found: 252.0015.



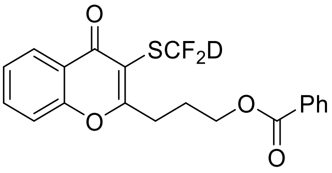
2-Butyl-3-((difluoromethyl-*d*)thio)-4*H*-chromen-4-one 4p: Prepared according to **General Method F** (Eluent: 100:1 to 20:1 petroleum ether: ethyl acetate) and the title compound was isolated as a yellow solid (62.9 mg, 0.22 mmol, 44% yield); **M.p. =** 40.1 – 40.7 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.20 (1H, dd, J = 8.0, 1.7 Hz), 7.71 – 7.68 (1H, m), 7.46 – 7.41 (2H, m), 3.07 (2H, t, J = 7.8 Hz), 1.79 – 1.73 (2H, m), 1.49 – 1.42 (2H, m), 0.98 (3H, t, J = 7.4 Hz); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 175.5, 175.4, 155.7, 134.3, 126.4, 125.9, 122.7, 118.9 (tt, $J_{C\text{-}F}$ = 276.9, 32.3 Hz), 117.9, 109.8 (t, $J_{C\text{-}F}$ = 3.6 Hz), 33.9, 29.7, 22.5, 13.8; **^{19}F NMR** (471 MHz, $CDCl_3$) δ –95.5 (t, J = 8.9 Hz); **HRMS** (ESI$^+$) $[M+Na]^+$ calc'd for $C_{14}H_{13}DF_2O_2SNa$: 308.0638, found: 308.0640.



2-Cyclopropyl-3-((difluoromethyl-*d*)thio)-4*H*-chromen-4-one 4q: Prepared according to **General Method F** (Eluent: 100:1 to 20:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (84.9 mg, 0.32 mmol, 63% yield); **M.p. =** 138.9 – 139.7 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.18 (1H, d, J = 7.9 Hz), 7.66 – 7.63 (1H, m), 7.41 – 7.38 (1H, m), 7.32 (1H, d, *J* = 8.4 Hz), 2.98 – 2.93 (1H, m), 1.37 – 1.34 (2H, m), 1.24 – 1.20 (2H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) *δ* 175.1, 174.9, 155.0, 134.1, 126.5, 125.8, 122.7, 119.3 (tt, J_{C-F} = 277.0, 32.4 Hz), 117.5, 108.4 (t, J_{C-F} = 3.7 Hz), 14.3, 10.4; **^{19}F NMR** (471 MHz, $CDCl_3$) *δ* –95.0 (t, *J* = 8.6 Hz); **HRMS** (ESI$^+$) [M+Na]$^+$ calc'd for $C_{13}H_9DF_2O_2SNa$: 292.0325, found: 292.0324.

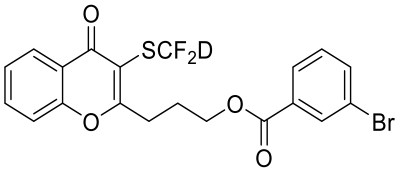


2-(3-(Benzyloxy)propyl)-3-((difluoromethyl-*d*)thio)-4*H*-chromen-4-one 4r: Prepared according to **General Method F** (Eluent: 80:1 to 10:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colourless liquid (101.9 mg, 0.27 mmol, 54% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 8.22 (1H, dd, *J* = 8.4, 1.5 Hz), 7.73 – 7.69 (1H, m), 7.47 – 7.43 (2H, m), 7.35 – 7.28 (5H, m), 4.54 (2H, s), 3.62 (2H, t, *J* = 6.0 Hz), 3.25 (2H, t, *J* = 7.8 Hz), 2.18 – 2.11 (2H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) *δ* 175.4, 174.8, 155.6, 138.2, 134.2, 128.4, 127.7, 127.6, 126.3, 125.8, 122.5, 118.8 (tt, J_{C-F} = 276.7, 32.1 Hz),117.8, 109.8 (t, J_{C-F} = 3.5 Hz), 73.1, 69.1, 31.2, 27.6; **^{19}F NMR** (471 MHz, $CDCl_3$) *δ* –95.3 (t, *J* = 8.6 Hz); **HRMS** (ESI$^+$) [M+Na]$^+$ calc'd for $C_{20}H_{17}DF_2O_3SNa$: 400.0900, found: 400.0895.

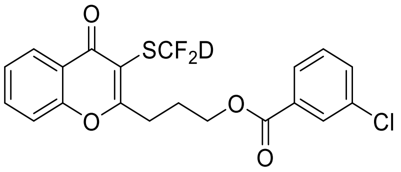


3-(3-((Difluoromethyl-*d*)thio)-4-oxo-4*H*-chromen-2-yl)propyl benzoate 4s: Prepared according to **General Method F** (Eluent: 80:1 to 10:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (117.4 mg, 0.30 mmol, 60% yield); **M.p. =** 84.0 – 84.7 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 8.16 (1H, dd, *J* = 8.1, 1.3 Hz), 7.95 (2H, d, *J* = 7.2 Hz), 7.69 – 7.65 (1H, m), 7.54 – 7.50 (1H, m), 7.43 – 7.35 (4H, m), 4.45 (2H, t, *J* = 6.1 Hz), 3.29 (2H, t, *J* = 7.7 Hz), 2.34 – 2.27 (2H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) *δ* 175.3, 173.9, 166.4, 155.6, 134.4, 133.1, 129.9, 129.5, 128.4, 126.3, 126.0, 122.5, 118.7 (tt, J_{C-F} = 275.3, 32.5 Hz), 117.8, 110.1 (t, J_{C-F} =

3.6 Hz), 63.9, 31.1, 26.5; **^{19}F NMR** (471 MHz, $CDCl_3$) δ –95.3 (t, J = 9.9 Hz); **HRMS** (ESI$^+$) [M+Na]$^+$ calc'd for $C_{20}H_{15}DF_2O_4SNa$: 414.0692, found: 414.0685.

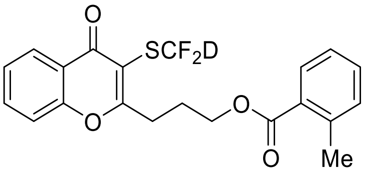


3-(3-((Difluoromethyl-*d*)thio)-4-oxo-4*H*-chromen-2-yl)propyl 3-bromobenzoate 4t: Prepared according to **General Method F** (Eluent: 80:1 to 10:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (120.1 mg, 0.26 mmol, 51% yield); **M.p.** = 95.0 – 95.8 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.18 (1H, dd, J = 8.2, 1.8 Hz), 8.06 – 8.05 (1H, m), 7.85 (1H, d, J = 7.8 Hz), 7.68 – 7.60 (2H, m), 7.41 – 7.37 (2H, m), 7.25 – 7.21 (1H, m), 4.44 (2H, t, J = 6.0 Hz), 3.27 (2H, t, J = 7.6 Hz), 2.33 – 2.26 (2H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 175.2, 173.8, 165.1, 155.5, 136.0, 134.4, 132.5, 131.8, 130.0, 128.1, 126.3, 126.0, 122.5, 122.5, 118.7 (tt, $J_{C\text{-}F}$ = 279.3, 32.3 Hz), 117.8, 111.1 (t, $J_{C\text{-}F}$ = 3.4 Hz), 64.3, 31.1, 26.4; **^{19}F NMR** (471 MHz, $CDCl_3$) δ –95.2 (t, J = 8.9 Hz); **HRMS** (ESI$^+$) [M+Na]$^+$ calc'd for $C_{20}H_{14}DBrF_2O_4SNa$: 491.9797, found: 491.9789.

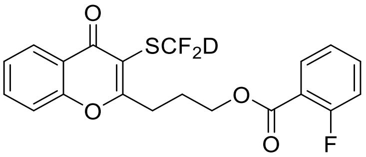


3-(3-((Difluoromethyl-*d*)thio)-4-oxo-4*H*-chromen-2-yl)propyl 3-chlorobenzoate 4u: Prepared according to **General Method F** (Eluent: 80:1 to 10:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (140.7 mg, 0.33 mmol, 66% yield); **M.p.** = 77.7 – 78.6 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.11 (1H, dd, J = 8.0, 1.7 Hz), 7.88 – 7.87 (1H, m), 7.79 (1H, d, J = 7.8 Hz), 7.66 – 7.62 (1H, m), 7.45 – 7.36 (3H, m), 7.29 – 7.25 (1H, m), 4.43 (2H, t, J = 6.0 Hz), 3.26 (2H, t, J = 7.5 Hz), 2.32 – 2.25 (2H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 175.2, 173.7, 165.1, 155.4, 134.5, 134.4, 133.1, 131.5, 129.7, 129.5, 127.6, 126.2, 126.0, 122.4, 118.6 (tt, $J_{C\text{-}F}$ = 276.8, 32.8 Hz), 117.8, 110.0 (t, $J_{C\text{-}F}$ = 3.6 Hz), 64.3, 31.0, 26.3;

^{19}F NMR (471 MHz, $CDCl_3$) δ –95.2 (t, J = 8.8 Hz); **HRMS** (ESI^+) $[M+Na]^+$ calc'd for $C_{20}H_{14}ClDF_2O_4SNa$: 448.0303, found: 448.0318.

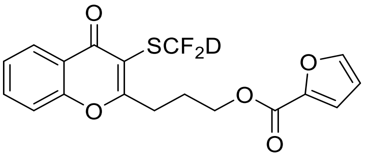


3-(3-((Difluoromethyl-*d*)thio)-4-oxo-4*H*-chromen-2-yl)propyl 2-methylbenzoate 4v: Prepared according to **General Method F** (Eluent: 80:1 to 10:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (108.9 mg, 0.27 mmol, 54% yield); **M.p. =** 96.2 – 96.8 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.17 (1H, dd, J = 8.0, 1.8 Hz), 7.85 (1H, dd, J = 7.9, 1.5 Hz), 7.70 – 7.66 (1H, m), 7.44 – 7.35 (3H, m), 7.22 – 7.15 (2H, m), 4.42 (2H, t, J = 6.1 Hz), 3.29 (2H, t, J = 7.7 Hz), 2.59 (3H, s), 2.32 – 2.26 (2H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 175.3, 174.0, 167.4, 155.6, 140.4, 134.4, 132.2, 131.8, 130.6, 129.2, 126.4, 126.0, 125.8, 122.5, 118.7 (tt, $J_{C\text{-}F}$ = 276.7, 32.6 Hz), 117.8, 110.1 (t, $J_{C\text{-}F}$ = 3.5 Hz), 63.7, 31.2, 26.6, 21.9; **^{19}F NMR** (471 MHz, $CDCl_3$) δ –95.3 (t, J = 8.9 Hz); **HRMS** (ESI^+) $[M+Na]^+$ calc'd for $C_{21}H_{17}DF_2O_4SNa$: 428.0849, found: 428.0842.

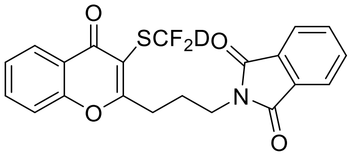


3-(3-((Difluoromethyl-*d*)thio)-4-oxo-4*H*-chromen-2-yl)propyl 2-fluorobenzoate 4w: Prepared according to **General Method F** (Eluent: 80:1 to 10:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (129.1 mg, 0.32 mmol, 63% yield); **M.p. =** 122.7 – 123.4 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.15 (1H, dd, J = 8.0, 1.7 Hz), 7.88 – 7.84 (1H, m), 7.68 – 7.64 (1H, m), 7.50 – 7.45 (1H, m), 7.43 – 7.38 (2H, m), 7.16 – 7.12 (1H, m), 7.09 – 7.04 (1H, m), 4.46 (2H, t, J = 6.0 Hz), 3.29 (2H, t, J = 7.6 Hz), 2.32 – 2.26 (2H, m); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 175.3, 174.0, 164.3 (d, $J_{C\text{-}F}$ = 3.6 Hz), 162.0 (d, $J_{C\text{-}F}$ = 260.3 Hz), 155.6, 134.7 (d, $J_{C\text{-}F}$ = 9.1 Hz), 134.4, 132.1, 126.3, 126.0, 124.1 (d, $J_{C\text{-}F}$ = 3.7 Hz), 122.6, 118.7 (tt, $J_{C\text{-}F}$ = 276.6, 32.7 Hz), 118.5 (d, $J_{C\text{-}F}$ = 9.3 Hz), 117.9, 117.1 (d, $J_{C\text{-}F}$ = 22.7 Hz), 110.1 (t, $J_{C\text{-}F}$ = 3.6 Hz), 64.2, 31.1, 26.5; **^{19}F NMR** (471 MHz, $CDCl_3$) δ –95.3 (2F, t, J =

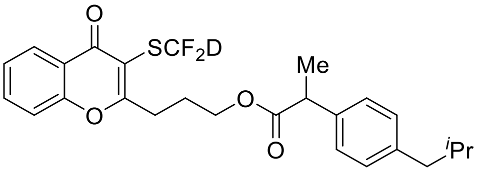
8.9 Hz), –109.0 – –109.1 (1F, m); **HRMS** (ESI$^+$) [M+Na]$^+$ calc'd for $C_{20}H_{14}DF_3O_2SNa$: 432.0598, found: 432.0590.



3-(3-((Difluoromethyl-*d*)thio)-4-oxo-4*H*-chromen-2-yl)propyl furan-2-carboxylate 4x: Prepared according to **General Method F** (Eluent: 80:1 to 10:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (89.5 mg, 0.23 mmol, 47% yield); **M.p. =** 85.8 – 86.7 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.17 (1H, dd, J = 7.9, 1.4 Hz), 7.70 – 7.65 (1H, m), 7.45 – 7.39 (3H, m), 7.08 (1H, dd, J = 3.4, 0.6 Hz), 6.43 – 6.42 (1H, m), 4.43 (2H, t, J = 6.1 Hz), 3.27 (2H, t, J = 7.6 Hz), 2.31 – 2.24 (2H, m); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 175.4, 173.9, 158.5, 155.6, 146.5, 144.3, 134.4, 126.3, 126.0, 122.6, 118.8 (tt, $J_{C\text{-}F}$ = 277.0, 32.4 Hz), 118.2, 117.9, 111.9, 110.1 (t, $J_{C\text{-}F}$ = 3.3 Hz), 63.9, 31.1, 26.4; **^{19}F NMR** (471 MHz, $CDCl_3$) δ –95.3 (t, J = 9.1 Hz); **HRMS** (ESI$^+$) [M+Na]$^+$ calc'd for $C_{18}H_{13}DF_2O_5SNa$: 404.0485, found: 404.0488.

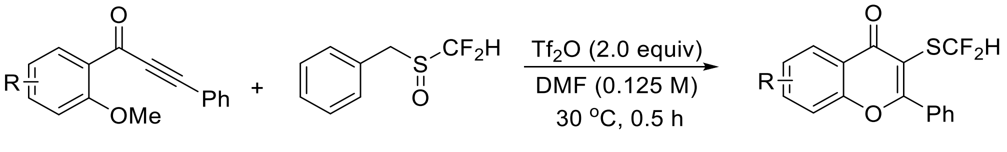


2-(3-(3-((Difluoromethyl-*d*)thio)-4-oxo-4*H*-chromen-2-yl)propyl)isoindoline-1,3-dione 4y: Prepared according to **General Method F** (Eluent: 80:1 to 10:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (122.9 mg, 0.30 mmol, 59% yield); **M.p. =** 148.3 – 148.9 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.12 (1H, dd, J = 8.0, 1.7 Hz), 7.80 – 7.77 (2H, m), 7.70 – 7.64 (3H, m), 7.45 – 7.37 (2H, m), 3.82 (2H, t, J = 7.0 Hz), 3.16 (2H, t, J = 7.7 Hz), 2.23 – 2.16 (2H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 175.2, 173.6, 168.3, 155.5, 134.4, 134.2, 131.9, 126.3, 126.0, 123.4, 122.4, 118.7 (tt, $J_{C\text{-}F}$ = 277.0, 32.7 Hz), 117.9, 110.0 (t, $J_{C\text{-}F}$ = 3.6 Hz), 37.4, 31.5, 25.9; **^{19}F NMR** (471 MHz, $CDCl_3$) δ –95.1 (t, J = 8.8 Hz); **HRMS** (ESI$^+$) [M+Na]$^+$ calc'd for $C_{21}H_{14}DF_2NO_4SNa$: 439.0645, found: 439.0637.



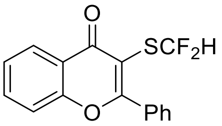
3-(3-((Difluoromethyl-*d*)thio)-4-oxo-4*H*-chromen-2-yl)propyl 2-(4-isobutylphenyl)propanoate 4z: Prepared according to **General Method F** (Eluent: 80:1 to 10:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colourless liquid (159.7 mg, 0.34 mmol, 67% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.18 (1H, dd, J = 7.9, 1.7 Hz), 7.70 – 7.65 (1H, m), 7.43 – 7.38 (2H, m), 7.19 (2H, d, J = 8.1 Hz), 7.08 (2H, d, J = 8.1 Hz), 4.18 (2H, t, J = 6.1 Hz), 3.66 (1H, q, J = 7.2 Hz), 3.13 – 3.00 (2H, m), 2.42 (2H, d, J = 7.2 Hz), 2.12 – 2.05 (2H, m), 1.86 – 1.76 (1H, m), 1.48 (3H, d, J = 7.2 Hz), 0.86 (6H, d, J = 6.6 Hz); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 175.1, 174.5, 173.8, 155.4, 140.5, 137.5, 134.3, 129.3, 127.1, 126.2, 125.9, 122.4, 118.6 (tt, $J_{C\text{-}F}$ = 276.5, 32.5 Hz), 117.8, 109.8 (t, $J_{C\text{-}F}$ = 3.4 Hz), 63.3, 45.0, 44.9, 30.6, 30.1, 26.3, 22.3, 18.3; **^{19}F NMR** (471 MHz, $CDCl_3$) δ –95.4 (q, J = 9.0 Hz); **HRMS** (ESI$^+$) [M+Na]$^+$ calc'd for $C_{26}H_{27}DF_2O_4SNa$: 498.1631, found: 498.1631.

3. General Method G:

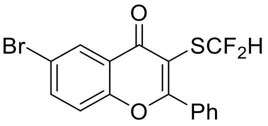


A 120 °C oven-dried 25-mL glass schlenck, equipped with a stir bar, was charged with (((difluoromethyl)sulfinyl)methyl)benzene (114.1 mg, 0.6 mmol, 1.2 equiv) and alkyne ketone (0.5 mmol, 1.0 equiv). The mixture was evacuated and backfilled with nitrogen for three times. Then dry *N,N*-Dimethylformamide (4.0 mL) was added under nitrogen atmosphere. The Tf_2O (282.1 mg, 1.0 mmol, 2.0 equiv) was added dropwise into the mixture at 30 °C, and the mixture was allowed to stir for 0.5 h at 30 °C. After the completion of reaction, a saturated aqueous solution of $NaHCO_3$ (20.0 mL) was added and the mixture was extracted with ethyl acetate (20.0 mL x 3). The combined organic layers were washed with brine (20.0 mL x 5), dried over by

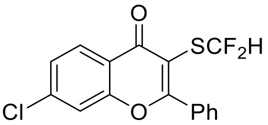
Na_2SO_4 and filtrated. The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography.



3-((Difluoromethyl)thio)-2-phenyl-4*H*-chromen-4-one 4aa: Prepared according to **General Method G** (Eluent: 100:1 to 20:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (131.9 mg, 0.43 mmol, 87% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.26 (1H, dd, J = 8.0, 1.7 Hz), 7.79 – 7.71 (3H, m), 7.59 – 7.45 (5H, m), 7.36 (1H, t, J = 59.7 Hz); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.1, 168.9, 155.9, 134.6, 132.4, 131.3, 129.7, 128.4, 126.3, 126.1 , 122.4, 119.0 (t, $J_{C\text{-}F}$ = 277.9 Hz), 118.2, 110.6 (t, $J_{C\text{-}F}$ = 3.7 Hz); **^{19}F NMR** (471 MHz, $CDCl_3$) δ –95.3 (d, J = 59.8 Hz); The spectral data match those previously reported[3].

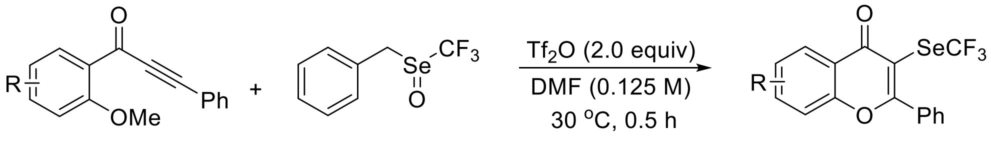


6-Bromo-3-((difluoromethyl)thio)-2-phenyl-4*H*-chromen-4-one 4ab: Prepared according to **General Method G** (Eluent: 100:1 to 20:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (178.4 mg, 0.47 mmol, 93% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.36 (1H, d, J = 2.5 Hz), 7.80 (1H, dd, J = 8.9, 2.4 Hz), 7.78 – 7.75 (2H, m), 7.60 – 7.51 (3H, m), 7.41 (1H, d, J = 8.9 Hz), 7.32 (1H, t, J = 59.6 Hz); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.9, 169.0, 154.6, 137.6, 132.1, 131.6, 129.7, 128.9, 128.4, 123.6, 120.2, 119.5, 118.8 (t, $J_{C\text{-}F}$ = 275.8 Hz), 110.9 (t, $J_{C\text{-}F}$ = 3.7 Hz); **^{19}F NMR** (471 MHz, $CDCl_3$) δ –95.3 (d, J = 57.6 Hz); The spectral data match those previously reported[3].



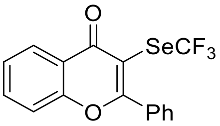
7-Chloro-3-((difluoromethyl)thio)-2-phenyl-4*H*-chromen-4-one 4ac: Prepared according to **General Method G** (Eluent: 100:1 to 20:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (140.2 mg, 0.41 mmol, 83% yield); **^{1}H NMR** (400 MHz, CDCl$_3$) δ 8.17 (1H, d, J = 8.6 Hz), 7.77 – 7.75 (2H, m), 7.59 – 7.50 (4H, m), 7.42 (1H, dd, J = 8.6, 1.9 Hz), 7.33 (1H, t, J = 59.6 Hz); **^{13}C NMR** (101 MHz, CDCl$_3$) δ 175.2, 168.8 (t, $J_{C\text{-}F}$ = 1.6 Hz), 155.9, 140.7, 132.0, 131.5, 129.7, 128.4, 127.7, 126.9, 120.9, 118.9 (t, $J_{C\text{-}F}$ = 278.4 Hz), 118.2, 111.1 (t, $J_{C\text{-}F}$ = 3.8 Hz); **^{19}F NMR** (471 MHz, CDCl$_3$) δ –95.3 (d, J = 59.7 Hz); The spectral data match those previously reported[3].

4. General Method H:

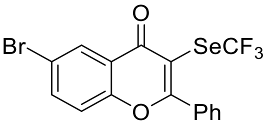


1a, 1l **3c** **4ad, 4ae**

A 120 °C oven-dried 25-mL glass schlenck, equipped with a stir bar, was charged with (((trifluoromethyl)seleninyl)methyl)benzene (153.1 mg, 0.6 mmol, 1.2 equiv) and alkyne ketone (0.5 mmol, 1.0 equiv). The mixture was evacuated and backfilled with nitrogen for three times. Then dry *N,N*-Dimethylformamide (4.0 mL) was added under N$_2$ atmosphere. The Tf$_2$O (282.1 mg, 1.0 mmol, 2.0 equiv) was added dropwise into the mixture at 30 °C, and the mixture was allowed to stir for 0.5 h at 30 °C. After the completion of reaction, a saturated aqueous solution of NaHCO$_3$ (20.0 mL) was added and the mixture was extracted with ethyl acetate (20.0 mL x 3). The combined organic layers were washed with brine (20.0 mL x 5), dried over by Na$_2$SO$_4$ and filtrated. The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography.

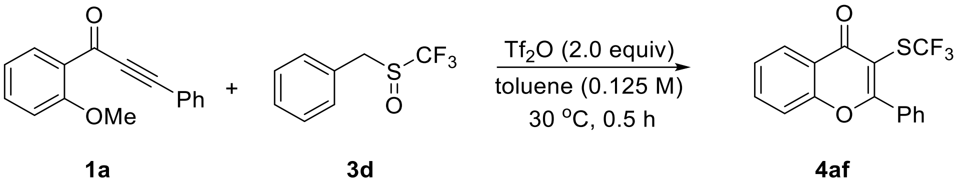


2-Phenyl-3-((trifluoromethyl)selanyl)-4*H*-chromen-4-one 4ad: Prepared according to **General Method H** (Eluent: 100:1 to 20:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (153.9 mg, 0.42 mmol, 83% yield); **M.p.** = 113.9 – 114.6 °C; **^{1}H NMR** (400 MHz, CDCl$_3$) δ 8.28 (1H, dd, J = 8.0, 1.7 Hz), 7.73 – 7.65 (3H, m), 7.58 – 7.44 (5H, m); **^{13}C NMR** (101 MHz, CDCl$_3$) δ 175.2, 170.9, 155.9, 134.6, 133.5, 131.3, 129.4, 128.3, 126.8, 126.2, 122.2, 121.8 (d, $J_{C\text{-}F}$ = 336.6 Hz), 118.0, 109.3; **^{19}F NMR** (471 MHz, $CDCl_3$) *δ* –34.6 (s); **HRMS** (ESI^+) $[M+Na]^+$ calc'd for $C_{16}H_9F_3O_2SeNa$: 386.9672, found: 386.9669.



6-Bromo-2-phenyl-3-((trifluoromethyl)selanyl)-4*H*-chromen-4-one 4ae: Prepared according to **General Method H** (Eluent: 100:1 to 20:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (149.5 mg, 0.33 mmol, 67% yield); **M.p. =** 170.0 – 170.8 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 8.37 (1H, d, *J* = 2.4 Hz), 7.79 (1H, dd, *J* = 8.9, 2.3 Hz), 7.67 – 7.65 (2H, m), 7.60 – 7.50 (3H, m), 7.40 (1H, d, *J* = 8.8 Hz); **^{13}C NMR** (101 MHz, $CDCl_3$) *δ* 174.0, 171.0, 154.7, 137.6, 133.2, 131.5, 129.5, 129.3, 128.4, 123.5, 123.4, 120.1, 119.6, 109.4; **^{19}F NMR** (471 MHz, $CDCl_3$) *δ* –34.5 (s); **HRMS** (ESI^+) $[M+H]^+$ calc'd for $C_{16}H_9BrF_3O_2Se$: 441.8879, found: 441.8886.

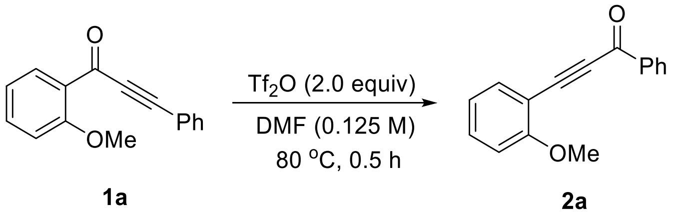
5. Synthesis of 2-phenyl-3-((trifluoromethyl)thio)-4*H*-chromen-4-one 4af



A 120 °C oven-dried 25-mL glass schlenck, equipped with a stir bar, was charged with (((trifluoromethyl)sulfinyl)methyl)benzene (124.9 mg, 0.6 mmol, 1.2 equiv) and 1-(2-methoxyphenyl)-3-phenylprop-2-yn-1-one (118.1 mg, 0.5 mmol, 1.0 equiv). The mixture was evacuated and backfilled with nitrogen for three times. Then dry toluene (4.0 mL) was added under nitrogen atmosphere. The Tf_2O (282.1 mg, 1.0 mmol, 2.0 equiv) was added dropwise into the mixture at 30 °C, and the mixture was allowed to stir for 0.5 h at 30 °C. After the completion of reaction, a saturated aqueous solution of $NaHCO_3$ (20.0 mL) was added and the mixture was extracted with ethyl acetate (20.0 mL x 3). The combined organic layers were washed with brine (20.0 mL x 5), dried over by Na_2SO_4 and filtrated. The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography (Eluent: 100:1 to 20:1 petroleum ether: ethyl acetate). The product was isolated as a yellow solid (77.5 mg, 0.24 mmol, 48% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.31 (1H, dd, J = 8.0, 1.7 Hz), 7.78 – 7.72 (3H, m), 7.62 – 7.48 (5H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 175.5, 172.2, 155.8, 134.8, 132.5, 131.5, 129.6, 128.4, 129.2 (q, $J_{C\text{-}F}$ = 312.6 Hz), 128.5, 126.9, 126.5, 122.8, 108.7; **^{19}F NMR** (471 MHz, $CDCl_3$) δ –42.7 (s); The spectral data match those previously reported[3].

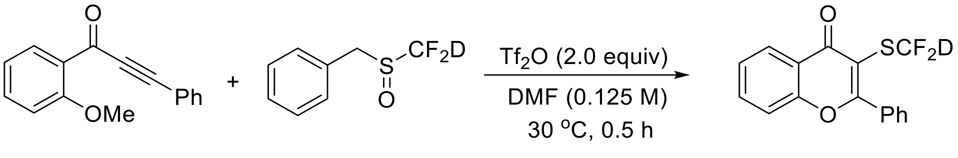
V. Gram-scale reaction

1. Synthesis of 3-(2-methoxyphenyl)-1-phenylprop-2-yn-1-one 3a



A 120 °C oven-dried 200-mL round-bottom flask equipped with a stir bar, was charged with 1-(2-methoxyphenyl)-3-phenylprop-2-yn-1-one **1a** (2.36 g, 10.0 mmol, 1.0 equiv). The mixture was evacuated and backfilled with nitrogen for three times. Then dry *N,N*-Dimethylformamide (80.0 mL) was added under nitrogen atmosphere. The Tf_2O (5.64 g, 20.0 mmol, 2.0 equiv) was added dropwise into the mixture at room temperature, and the mixture was allowed to stir for 0.5 h at 80 °C. After the completion of reaction, a saturated aqueous solution of $NaHCO_3$ (50.0 mL) was added and the mixture was extracted with ethyl acetate (50.0 mL x 3). The combined organic layers were washed with brine (50.0 mL x 5), dried over by Na_2SO_4 and filtrated. The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography to provide the desired product **2a** as a yellow solid (2.02 g, 8.5 mmol, 86% yield).

2. Synthesis of 3-((difluoromethyl-*d*)thio)-2-phenyl-4*H*-chromen-4-one 4a

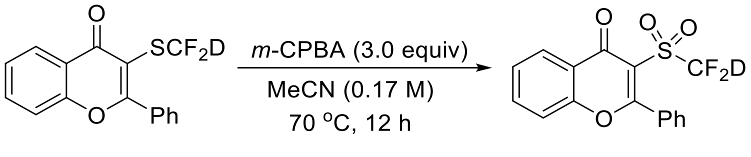


1a **3a** **4a**

A 120 °C oven-dried 100-mL round-bottom flask equipped with a stir bar, was charged with (((difluoromethyl-*d*)sulfinyl)methyl)benzene **3a** (1.15 g, 6.0 mmol, 1.2 equiv) and 1-(2-methoxyphenyl)-3-phenylprop-2-yn-1-one **1a** (1.18 g, 5.0 mmol, 1.0 equiv). The mixture was evacuated and backfilled with nitrogen for three times. Then dry *N,N*-Dimethylformamide (40.0 mL) was added under nitrogen atmosphere. The Tf_2O (2.82 g, 10.0 mmol, 2.0 equiv) was added dropwise into the mixture at 30 °C, and the mixture was allowed to stir for 0.5 h at 30 °C. After the completion of reaction, a saturated aqueous solution of $NaHCO_3$ (50.0 mL) was added and the mixture was extracted with ethyl acetate (50.0 mL x 3). The combined organic layers were washed with brine (50.0 mL x 5), dried over by Na_2SO_4 and filtrated. The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography to provide the desired product **4a** as a white solid (1.31 g, 4.3 mmol, 86% yield).

VI. Synthetic applications of current method

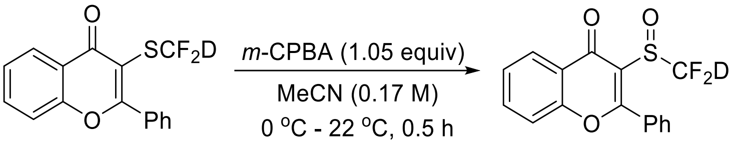
1. Synthesis of 3-((difluoromethyl-*d*)sulfonyl)-*4*H- chromen-4-one 5 from 4a



4a **5**

A 120 °C oven-dried 25-mL glass schlenck, equipped with a stir bar, was charged with 3-((difluoromethyl-*d*)thio)-2-phenyl-4*H*-chromen-4-one **4a** (91.6 mg, 0.3 mmol, 1.0 equiv) and *m*-CPBA (85% wt, 182.7 mg, 0.9 mmol, 3.0 equiv). The mixture was evacuated and backfilled with nitrogen for three times. Then dry acetonitrile (1.8 mL) was added under nitrogen atmosphere. The mixture was allowed to stir for 12 h at 70 °C. After the completion of reaction, a saturated aqueous solution of $NaHCO_3$ (30.0 mL) was added and the mixture was extracted with ethyl acetate (20.0 mL x 3). The combined organic layers were washed with brine (20.0 mL x 5), dried over by Na_2SO_4 and filtrated. The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography (Eluent: 30:1 to 5:1 petroleum ether: ethyl acetate) to provide the desired product as a white solid (75.8 mg, 0.22 mmol, 75% yield); **M.p. =** 170.6 – 171.3 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.25 (1H, dd, J = 7.9, 1.7 Hz), 7.85 – 7.81 (1H, m), 7.72 – 7.70 (2H, m), 7.67 – 7.63 (1H, m), 7.60 – 7.52 (4H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.3, 172.6, 155.5, 136.0, 132.7, 130.4, 129.5, 128.3, 127.3, 126.2, 123.0, 119.9, 118.5, 114.4 (tt, $J_{C\text{-}F}$ = 285.3, 33.6 Hz); **^{19}F NMR** (471 MHz, $CDCl_3$) δ –125.7 (t, J = 8.1 Hz); **HRMS** (ESI$^+$) [M+Na]$^+$ calc'd for $C_{16}H_9DF_2O_4SNa$: 360.0223, found: 360.0221.

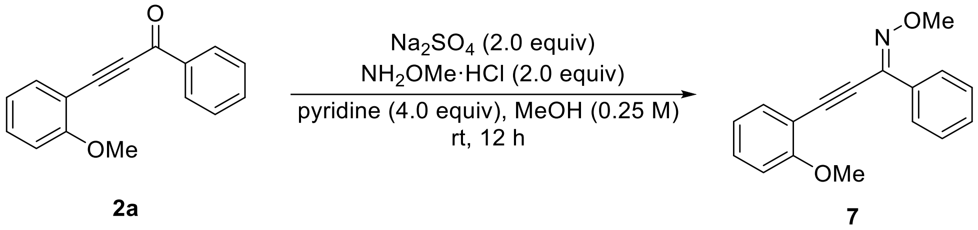
2. Synthesis of 3-((difluoromethyl-*d*)sulfinyl)-4*H*-chromen-4-one 6 from 4a



4a **6**

A 120 °C oven-dried 25-mL glass schlenck, equipped with a stir bar, after exchanging the atmosphere three times with nitrogen, dry acetonitrile (1.8 mL) and 3-((difluoromethyl-*d*)thio)-2-phenyl-4*H*-chromen-4-one **4a** (91.6 mg, 0.3 mmol, 1.0 equiv) were added to flask under nitrogen protected. The reaction mixture was cooled to 0 °C, and the *m*-CPBA (85% wt, 64.0 mg, 0.315 mmol, 1.05 equiv) was added in portions quickly to the mixture. Then the reaction mixture was allowed to stir at 22 °C for 0.5 h. After the completion of reaction, a saturated aqueous solution of $NaHCO_3$ (30.0 mL) was added and the mixture was extracted with ethyl acetate (20.0 mL x 3). The combined organic layers were washed with brine (20.0 mL x 5), dried over by Na_2SO_4 and filtrated. The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography (Eluent: 20:1 to 2:1 petroleum ether: ethyl acetate) to provide the desired product as a white solid (69.8 mg, 0.22 mmol, 72% yield); **M.p. =** 130.2 – 130.9 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.28 (1H, dd, J = 8.0, 1.6 Hz), 7.81 – 7.78 (1H, m), 7.69 – 7.66 (3H, m), 7.60 – 7.51 (4H, m); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.8, 172.0, 155.8, 135.5, 132.9, 130.3, 129.8, 128.9, 126.9, 126.5, 123.8, 120.6, 120.5, 118.4; **^{19}F NMR** (471 MHz, $CDCl_3$) δ –111.3 – –112.0 (1F, m), –121.2 – –121.9 (1F, m); **HRMS** (ESI$^+$) $[M+Na]^+$ calc'd for $C_{16}H_9DF_2O_3SNa$: 344.0274, found: 344.0275.

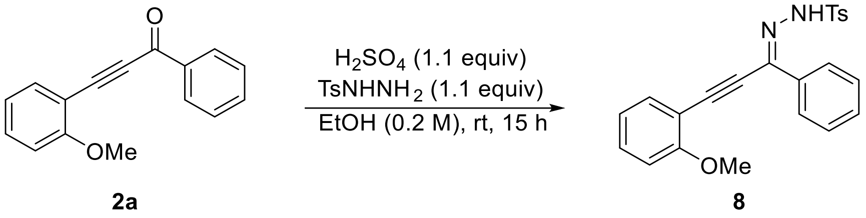
3. Synthesis of (*E*)-3-(2-methoxyphenyl)-1-phenylprop-2-yn-1-one O-methyl oxime 7 from 2a



A 120 °C oven-dried 50-mL round-bottom flask equipped with a stir bar, was charged with 3-(2-methoxyphenyl)-1-phenylprop-2-yn-1-one **2a** (472.5 mg, 2.0 mmol, 1.0 equiv), methoxylamine hydrochloride (4.0 mmol, 334.1 mg, 2.0 equiv), anhydrous Na_2SO_4 (4.0 mmol, 568.1 mg, 2.0 equiv), pyridine (8.0 mmol, 632.8 mg, 4.0 equiv), and methanol (8.0 mL) under nitrogen atmosphere. The reaction mixture was then stirred at room temperature for 12 h. After the reaction was completed, the mixture was extracted with saturated NH_4Cl solution (20.0 mL) and ethyl acetate (20.0 mL x 3), then the combined organic layers were extracted with brine (20.0 mL x 5). The combined organic layers were dried over by Na_2SO_4 then filtered. The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography (Eluent: 200:1 to 100:1 petroleum ether: ethyl acetate) to provide the desired product **7** as a colourless liquid (424.7 mg, 1.6 mmol, 80% yield); **^{1}H NMR**

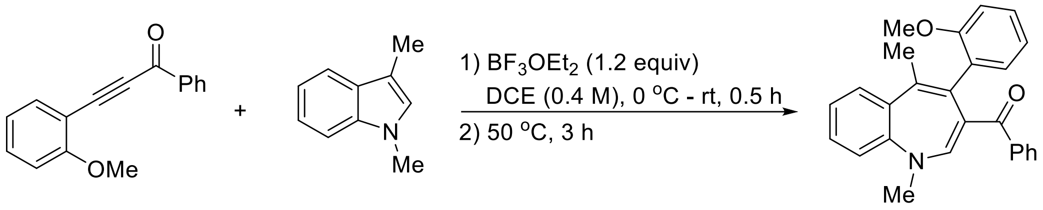
(400 MHz, $CDCl_3$) δ 8.01 – 7.99 (2H, m), 7.58 (1H, dd, J = 7.6, 1.7 Hz), 7.42 – 7.36 (4H, m), 6.98 – 6.94 (1H, m), 6.93 (1H, d, J = 8.4 Hz), 4.15 (3H, s), 3.95 (3H, s); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 157.8, 139.0, 132.2, 131.0, 130.36, 129.4, 128.4, 123.6, 122.3, 120.8, 111.9, 100.3, 80.9, 63.1, 56.0; The spectral data match those previously reported[28].

4. Synthesis of (*E*)-*N'*-(3-(2-methoxyphenyl)-1-phenylprop-2-yn-1-ylidene)-4-methylbenzenesulfonohydrazide 8 from 2a



A 120 °C oven-dried 50-mL round-bottom flask equipped with a stir bar, concentrated sulfuric acid (323.6 mg, 3.3 mmol, 1.1 equiv) was added dropwise over 1 min to a slurry of 3-(2-methoxyphenyl)-1-phenylprop-2-yn-1-one **2a** (708.8 mg, 3.0 mmol, 1.0 equiv) and *p*-toluenesulfonyl hydrazide (614.6 mg, 3.3 mmol, 1.1 equiv) in EtOH (15.0 mL) at room temperature. The reaction mixture was stirred at the same temperature for 15 h. After the reaction was completed, the mixture was extracted with saturated NH_4Cl solution (20.0 mL) and ethyl acetate (20.0 mL x 3), then the combined organic layers were extracted with brine (20.0 mL x 5). The combined organic layers were dried over by Na_2SO_4 then filtered. The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography (Eluent: 200:1 to 100:1 petroleum ether: ethyl acetate) to provide the desired product **8** as a yellow solid (1.03 g, 2.55 mmol, 85% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.49 (1H, s), 7.94 – 7.89 (4H, m), 7.52 (1H, dd, J = 7.5, 1.6 Hz), 7.49 – 7.45 (1H, m), 7.41 – 7.38 (3H, m), 7.30 (2H, d, J = 8.1 Hz), 7.05 – 7.00 (2H, m), 4.16 (3H, s), 2.40 (3H, s); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.8, 144.1, 136.1, 135.8, 133.8, 132.5, 132.3, 130.1, 129.8, 128.5, 127.9, 126.7, 120.9, 110.8, 109.8, 102.4, 83.3, 56.2, 21.7; The spectral data match those previously reported[30].

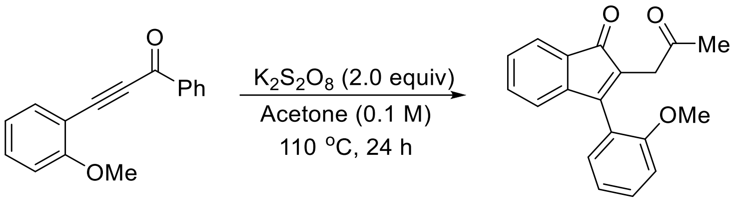
5. Synthesis of (4-(2-methoxyphenyl)-1,5-dimethyl-1*H*-benzo[*b*]azepin-3-yl)(phenyl)methanone 9 from 3a



3a **1ag** **9**

A 120 ^{o}C oven-dried 25-mL glass schlenck, equipped with a stir bar, was charged with 3-(2-methoxyphenyl)-1-phenylprop-2-yn-1-one **3a** (118.1 mg, 0.5 mmol, 1.0 equiv) and 1,3-dimethyl-1*H*-indole **1ag** (108.9 mg, 0.75 mmol, 1.5 equiv). The mixture was evacuated and backfilled with nitrogen for three times. Then dry Dichloroethane (1.25 mL) was added under nitrogen atmosphere. The BF_3OEt_2 (85.2 mg, 0.6 mmol, 1.2 equiv) was added dropwise into the mixture at 0 ^{o}C, and the mixture was allowed to stir for 0.5 h at room temperature. After complete consumption of 3-(2-methoxyphenyl)-1-phenylprop-2-yn-1-one (monitored by TLC), the reaction mixture was heated at 50 ^{o}C for 3 h. After the completion of reaction, a saturated aqueous solution of $NaHCO_3$ (20.0 mL) was added and the mixture was extracted with dichloromethane (20.0 mL x 3). The combined organic layers were washed with brine (20.0 mL x 5), dried over by Na_2SO_4 and filtrated. The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography (Eluent: 100:1 to 10:1 petroleum ether: ethyl acetate) to provide the desired product **9** as a orange solid (168.0 mg, 0.44 mmol, 88% yield) (The analytical data given here is for the atropisomeric mixtures of benzepine); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.93 (1H, d, J = 7.0 Hz), 7.79 (1H, d, J = 7.0 Hz), 7.61 – 6.59 (1H, m), 7.46 – 7.09 (7H, m), 7.01 – 7.67 (4H, m), 3.83 (2H, s), 3.44 (1H, s), 3.38 (2H, s), 3.44 (1H, s), 3.35 (1H, s), 2.38 (2H, s); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 193.6, 191.9, 157.5, 155.9, 139.7, 139.2, 138.3, 138.1, 137.8, 137.8, 137.3, 135.3, 132.6, 132.5, 132.1, 131.3, 130.7, 130.4, 130.0, 129.8, 128.7, 128.3, 128.2, 128.1, 128.0, 128.0, 127.9, 127.4, 122.6, 121.8, 120.8, 120.6, 119.4, 119.2, 118.9, 118.6, 111.9, 111.5, 111.2, 110.6, 109.2, 108.8, 55.8, 54.7, 30.9, 30.6, 9.8, 9.5; The spectral data match those previously reporte[20].

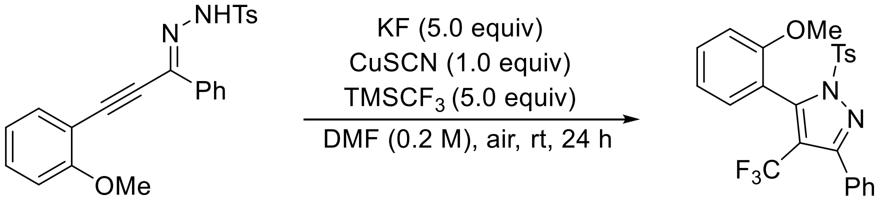
6. Synthesis of 3-(2-methoxyphenyl)-2-(2-oxopropyl)-1*H*-inden-1-one 10 from 2a



2a **10**

A 120 °C oven-dried 25-mL glass schlenck, equipped with a stir bar, was charged with 3-(2-methoxyphenyl)-1-phenylprop-2-yn-1-one **2a** (118.1 mg, 0.5 mmol, 1.0 equiv), potassium persulfate (270.3 mg, 1.0 mmol, 2.0 equiv), and acetone (5.0 mL) under nitrogen atmosphere. The reaction mixture was then stirred at 110 °C for 24 h. After the completion of reaction, a saturated aqueous solution of $NaHCO_3$ (20.0 mL) was added and the mixture was extracted with ethyl acetate (20.0 mL x 3). The combined organic layers were washed with brine (20.0 mL x 5), dried over by Na_2SO_4 and filtrated. The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography (Eluent: 200:1 to 100:1 petroleum ether: ethyl acetate) to provide the desired product **10** as a yellow liquid (68.6 mg, 0.23 mmol, 47% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48 (1H, d, J = 7.0 Hz), 7.46 – 7.42 (1H, m), 7.32 – 7.28 (2H, m), 7.22 – 7.19 (1H, m), 7.08 – 7.02 (2H, m), 6.89 (1H, d, J = 7.2 Hz), 3.77 (3H, s), 3.37 – 3.25 (2H, m), 2.17 (3H, s); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 205.4, 197.3, 156.8, 155.8, 145.8, 133.4, 131.2, 130.7, 130.0, 129.3, 128.6, 122.6, 121.4, 120.9, 120.8, 111.5, 55.4, 39.1, 29.9; The spectral data match those previously reported[31].

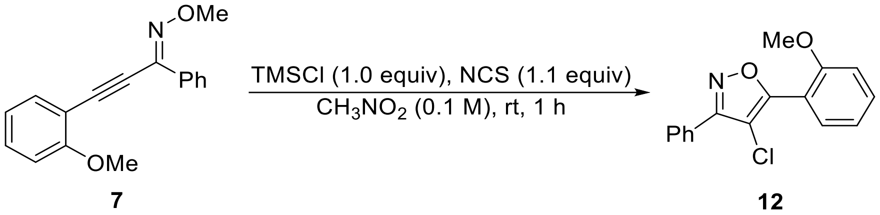
7. Synthesis of 5-(2-methoxyphenyl)-3-phenyl-1-tosyl-4-(trifluoromethyl)-1*H*-pyrazole 11 from 8



8 **11**

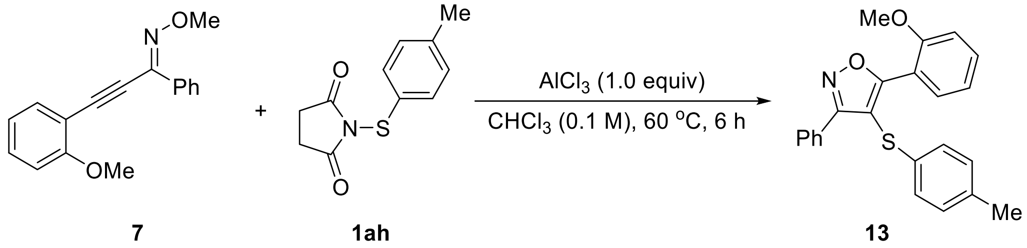
A 120 ^{o}C oven-dried 25-mL glass schlenck, equipped with a stir bar, was charged with (*E*)-*N'*-(3-(2-methoxyphenyl)-1-phenylprop-2-yn-1-ylidene)-4-methylbenzenesulfonohydrazide **8** (202.2 mg, 0.5 mmol, 1.0 equiv), trimethyl(trifluoromethyl)silane (355.5 mg, 2.5 mmol, 5.0 equiv), Copper(I) thiocyanate (61.3 mg, 0.5 mmol, 1.0 equiv), potassium fluoride (147.4 mg, 2.5 mmol, 5.0 equiv), and dry *N,N*-Dimethylformamide (2.5 mL) under air atmosphere. The reaction mixture was then stirred at room temperature for 24 h. After the completion of reaction, a saturated aqueous solution of $NaHCO_3$ (20.0 mL) was added and the mixture was extracted with ethyl acetate (20.0 mL x 3). The combined organic layers were washed with brine (20.0 mL x 5), dried over by Na_2SO_4 and filtrated. The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography (Eluent: 200:1 to 100:1 petroleum ether: ethyl acetate) to provide the desired product **11** as a white solid (140.0 mg, 0.30 mmol, 59% yield); ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.70 – 7.66 (4H, m), 7.50 – 7.46 (1H, m), 7.42 – 7.40 (3H, m), 7.24 (2H, d, J = 8.2 Hz), 7.20 (1H, dd, J = 7.5, 1.7 Hz), 7.05 – 7.01 (1H, m), 6.93 (1H, d, J = 8.3 Hz), 3.66 (3H, s), 2.37 (3H, s); ^{13}**C NMR** (101 MHz, $CDCl_3$) δ 157.7, 152.5, 146.1, 144.0, 143.9 (q, $J_{C\text{-}F}$ = 3.3 Hz), 134.3, 132.0, 131.4, 130.9, 129.8, 129.4, 129.0, 128.7, 128.3, 122.0 (q, $J_{C\text{-}F}$ = 270.1 Hz), 119.9, 116.3, 113.3 (q, $J_{C\text{-}F}$ = 35.9 Hz), 110.6, 55.4, 21.7; ^{19}**F NMR** (471 MHz, $CDCl_3$) δ –54.4 (s); **HRMS** (ESI^{+}) $[M+Na]^{+}$ calc'd for $C_{24}H_{19}F_3N_2O_3S$: 495.0961, found: 495.0965.

8. Synthesis of 4-chloro-5-(2-methoxyphenyl)-3-phenylisoxazole 12 from 7



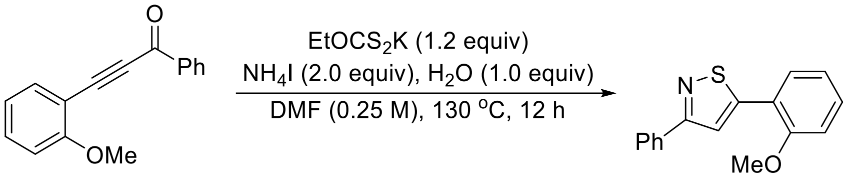
A 120 °C oven-dried 25-mL glass schlenck, equipped with a stir bar, was charged with (*E*)-3-(2-methoxyphenyl)-1-phenylprop-2-yn-1-one *O*-methyl oxime **7** (132.7 mg, 0.5 mmol, 1.0 equiv) and *N*-Chlorosuccinimide (73.4 mg, 0.55 mmol, 1.1 equiv). The mixture was evacuated and backfilled with nitrogen for three times. Then nitromethane (5.0 mL) was added under nitrogen atmosphere. The trimethylchlorosilane (54.3 mg, 0.5 mmol, 1.0 equiv) was added dropwise into the mixture at room temperature, and the mixture was allowed to stir for 1.0 h at room temperature. After the completion of reaction, a saturated aqueous solution of $NaHCO_3$ (20.0 mL) was added and the mixture was extracted with dichloromethane (20.0 mL x 3). The combined organic layers were washed with brine (20.0 mL x 5), dried over by Na_2SO_4 and filtrated. The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography (Eluent: 200:1 to 100:1 petroleum ether: ethyl acetate) to provide the desired product **12** as a colourless liquid (100.7 mg, 0.35 mmol, 70% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 – 7.94 (2H, m), 7.60 – 7.58 (1H, m), 7.54 – 7.49 (4H, m), 7.12 – 7.09 (1H, m), 7.06 (1H, d, *J* = 8.4 Hz), 3.91 (3H, s); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.7, 160.0, 157.5, 132.6, 130.8, 130.2, 128.8, 128.3, 127.8, 120.7, 115.4, 111.8, 107.1, 55.8; **HRMS** (ESI$^+$) $[M+Na]^+$ calc’d for $C_{16}H_{12}ClNO_2Na$: 308.0449, found: 308.0438.

9. Synthesis of 5-(2-methoxyphenyl)-3-phenyl-4-(*p*-tolylthio)isoxazole 13 from 7



A 120 °C oven-dried 25-mL glass schlenck, equipped with a stir bar, was charged with (*E*)-3-(2-methoxyphenyl)-1-phenylprop-2-yn-1-one *O*-methyl oxime **7** (132.7 mg, 0.5 mmol, 1.0 equiv), aluminium chloride (66.7 mg, 0.5 mmol, 1.0 equiv), and 1-(*p*-tolylthio)pyrrolidine-2,5-dione **1ah** (166.0 mg, 0.75 mmol, 1.5 equiv). The mixture was evacuated and backfilled with nitrogen for three times. Then trichloromethane (5.0 mL) was added under nitrogen atmosphere, and the reaction mixture was allowed to stir at 60 °C for 6 h. After the completion of reaction, a saturated aqueous solution of $NaHCO_3$ (20.0 mL) was added and the mixture was extracted with dichloromethane (20.0 mL x 3). The combined organic layers were washed with brine (20.0 mL x 5), dried over by Na_2SO_4 and filtrated. The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography (Eluent: 200:1 to 100:1 petroleum ether: ethyl acetate) to provide the desired product **13** as a yellow liquid (139.6 mg, 0.37 mmol, 75% yield); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.97 (2H, dd, *J* = 7.8, 2.1 Hz), 7.53 – 7.47 (2H, m), 7.45 – 7.39 (3H, m), 7.07 – 7.01 (6H, m), 3.76 (3H, s), 2.27 (3H, s); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.0, 163.7, 157.8, 135.4, 133.2, 132.4, 131.2, 129.9, 129.8, 128.6, 128.5, 128.3, 126.6, 120.5, 116.3, 111.5, 105.3, 55.2, 20.9; **HRMS** (ESI$^+$) $[M+Na]^+$ calc'd for $C_{23}H_{19}NO_2SNa$: 396.1029, found: 396.1023.

10. Synthesis of 3-(2-methoxyphenyl)-5-phenylisothiazole 14 from 2a

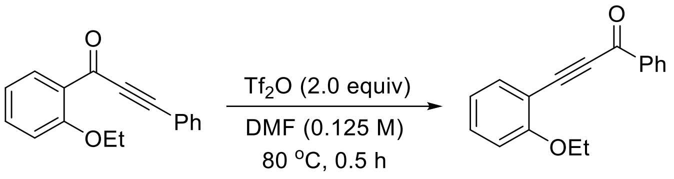


2a **14**

A 120 °C oven-dried 25-mL glass schlenck, equipped with a stir bar, was charged with 3-(2-methoxyphenyl)-1-phenylprop-2-yn-1-one (118.1 mg, 0.5 mmol, 1.0 equiv), potassium ethylxanthate (0.6 mmol, 96.2 mg, 1.2 equiv), ammonium iodide (144.9 mg, 1.0 mmol, 2.0 equiv), water (9.0 mg, 0.5 mmol, 1.0 equiv), and dry *N,N*-Dimethylformamide (2.0 mL) under nitrogen atmosphere. The reaction mixture was then stirred at 130 °C for 12 h. After the completion of reaction, a saturated aqueous solution of $NaHCO_3$ (20.0 mL) was added and the mixture was extracted with ethyl acetate (20.0 mL x 3). The combined organic layers were washed with brine (20.0 mL x 5), dried over by Na_2SO_4 and filtrated. The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography (Eluent: 200:1 to 100:1 petroleum ether: ethyl acetate) to provide the desired product **14** as a red solid (120.0 mg, 0.45 mmol, 90% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.51 (1H, s), 7.99 (1H, dd, J = 8.4, 1.6 Hz), 7.87 – 7.85 (2H, m), 7.55 – 7.50 (4H, m), 7.19 (1H, d, J = 8.7 Hz), 6.88 – 6.84 (1H, m), 1.62 (3H, s); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 178.4, 174.4, 170.7, 135.7, 134.4, 131.6, 129.6, 128.0, 124.5, 124.2, 122.5, 119.5, 116.8, 29.8; The spectral data match those previously reported[32].

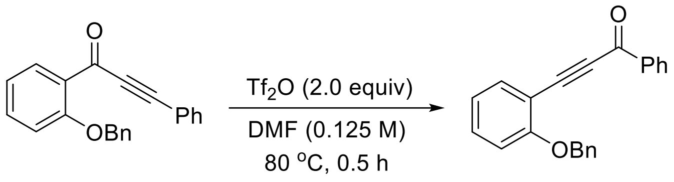
VI. Mechanistic study

1. Effect of OEt, OBn, SMe, Me, F instead of OMe 1,3-transposition



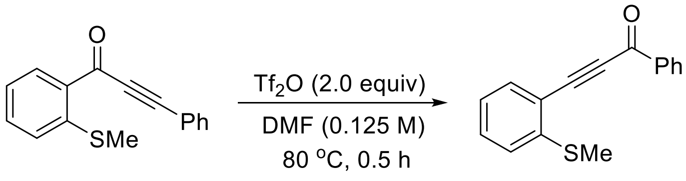
15 **23**

A 120 °C oven-dried 25-mL glass schlenck, equipped with a stir bar, was charged with 1-(2-ethoxyphenyl)-3-phenylprop-2-yn-1-one **15** (125.1 mg, 0.5 mmol, 1.0 equiv). The mixture was evacuated and backfilled with nitrogen for three times. Then dry *N,N*-Dimethylformamide (4.0 mL) was added under nitrogen atmosphere. The Tf_2O (282.1 mg, 1.0 mmol, 2.0 equiv) was added dropwise into the mixture at room temperature, and the mixture was allowed to stir for 0.5 h at 80 °C. After the completion of reaction, a saturated aqueous solution of $NaHCO_3$ (20.0 mL) was added and the mixture was extracted with ethyl acetate (20.0 mL x 3). The combined organic layers were washed with brine (20.0 mL x 5), dried over by Na_2SO_4 and filtrated. The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography (Eluent: 100:1 to 20:1 petroleum ether: ethyl acetate) to provide the desired product **23** as a white solid (108.6 mg, 0.43 mmol, 87% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.36 (2H, d, J = 7.2 Hz), 7.61 – 7.58 (2H, m), 7.49 – 7.46 (2H, m), 7.41 – 7.37 (1H, m), 6.95 – 6.91 (1H, m), 6.89 (1H, d, J = 8.4 Hz), 4.12 (2H, q, J = 7.0 Hz), 1.56 (3H, t, J = 7.0 Hz); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 178.2, 161.5, 137.1, 135.1, 133.9, 132.8, 129.8, 128.4, 120.5, 111.5, 109.3, 91.3, 91.0, 64.2, 14.9; The spectral data match those previously reported[8].



16 **24**

A 120 °C oven-dried 25-mL glass schlenck, equipped with a stir bar, was charged with 1-(2-(benzyloxy)phenyl)-3-phenylprop-2-yn-1-one **16** (156.2 mg, 0.5 mmol, 1.0 equiv). The mixture was evacuated and backfilled with nitrogen for three times. Then dry *N,N*-Dimethylformamide (4.0 mL) was added under nitrogen atmosphere. The Tf_2O (282.1 mg, 1.0 mmol, 2.0 equiv) was added dropwise into the mixture at room temperature, and the mixture was allowed to stir for 0.5 h at 80 °C. After the completion of reaction, a saturated aqueous solution of $NaHCO_3$ (20.0 mL) was added and the mixture was extracted with ethyl acetate (20.0 mL x 3). The combined organic layers were washed with brine (20.0 mL x 5), dried over by Na_2SO_4 and filtrated. The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography (Eluent: 100:1 to 20:1 petroleum ether: ethyl acetate) to provide the desired product **24** as a white solid (139.8 mg, 0.45 mmol, 90% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.18 – 8.15 (2H, m), 7.63 (1H, dd, J = 7.6, 1.8 Hz), 7.51 – 7.46 (3H, m), 7.42 – 7.35 (4H, m), 7.22 – 7.18 (2H, m), 7.00 – 6.95 (2H, m), 5.13 (2H, s); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 178.2, 161.1, 136.9, 136.1, 135.4, 133.8, 132.8, 129.7, 128.8, 128.5, 128.3, 127.9, 121.0, 112.1, 109.8, 91.5, 90.5, 70.7; The spectral data match those previously reported[22].



17 **25**

A 120 °C oven-dried 25-mL glass schlenck, equipped with a stir bar, was charged with 1-(2-(methylthio)phenyl)-3-phenylprop-2-yn-1-one **17** (126.2 mg, 0.5 mmol, 1.0 equiv). The mixture was evacuated and backfilled with nitrogen for three times. Then dry *N,N*-Dimethylformamide (4.0 mL) was added under nitrogen atmosphere. The Tf_2O (282.1 mg, 1.0 mmol, 2.0 equiv) was added dropwise into the mixture at room temperature, and the mixture was allowed to stir for 0.5 h at 80 °C. After the completion of reaction, a saturated aqueous solution of $NaHCO_3$ (20.0 mL) was added and the mixture was extracted with ethyl acetate (20.0 mL x 3). The combined organic layers were washed with brine (20.0 mL x 5), dried over by Na_2SO_4 and filtrated. The solvent was removed by rotary evaporation and 0.5 mmol CH_2Br_2 was added to the residue. The yield was determined by ^{1}H NMR spectroscopy in the presence of CH_2Br_2 (87.8 mg, 0.5 mmol) as an internal standard. Crude ^{1}H NMR yield of **25** is 17%.

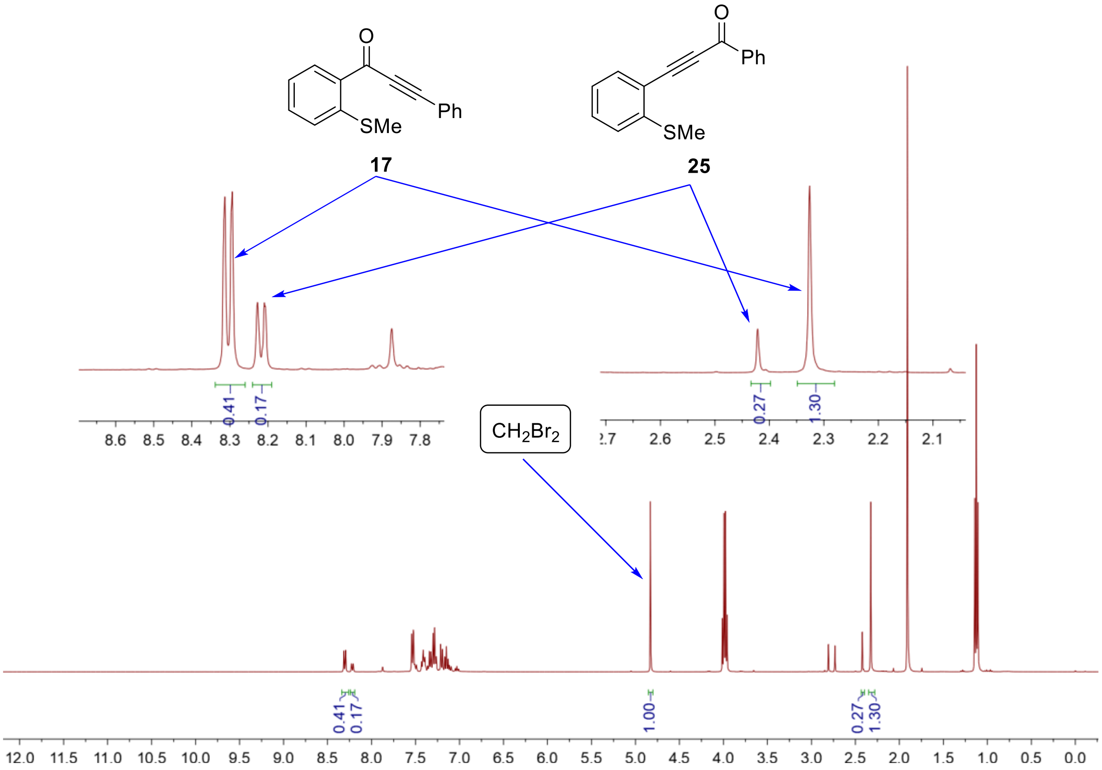
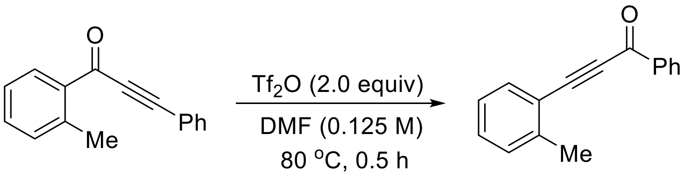


Figure S5. Crude ^{1}H NMR of the reaction between compound **17** and Tf_2O



18

26

A 120 °C oven-dried 25-mL glass schlenck, equipped with a stir bar, was charged with 3-phenyl-1-(*o*-tolyl)prop-2-yn-1-one **18** (110.1 mg, 0.5 mmol, 1.0 equiv). The mixture was evacuated and backfilled with nitrogen for three times. Then dry *N,N*-

Dimethylformamide (4.0 mL) was added under nitrogen atmosphere. The Tf_2O (282.1 mg, 1.0 mmol, 2.0 equiv) was added dropwise into the mixture at room temperature, and the mixture was allowed to stir for 0.5 h at 80 °C. After the completion of reaction, a saturated aqueous solution of $NaHCO_3$ (20.0 mL) was added and the mixture was extracted with ethyl acetate (20.0 mL x 3). The combined organic layers were washed with brine (20.0 mL x 5), dried over by Na_2SO_4 and filtrated. The solvent was removed by rotary evaporation and 0.5 mmol CH_2Br_2 was added to the residue. The yield was determined by ^1H NMR spectroscopy in the presence of CH_2Br_2 (87.8 mg, 0.5 mmol) as an internal standard. Crude ^1H NMR yield of **26** is 8%.

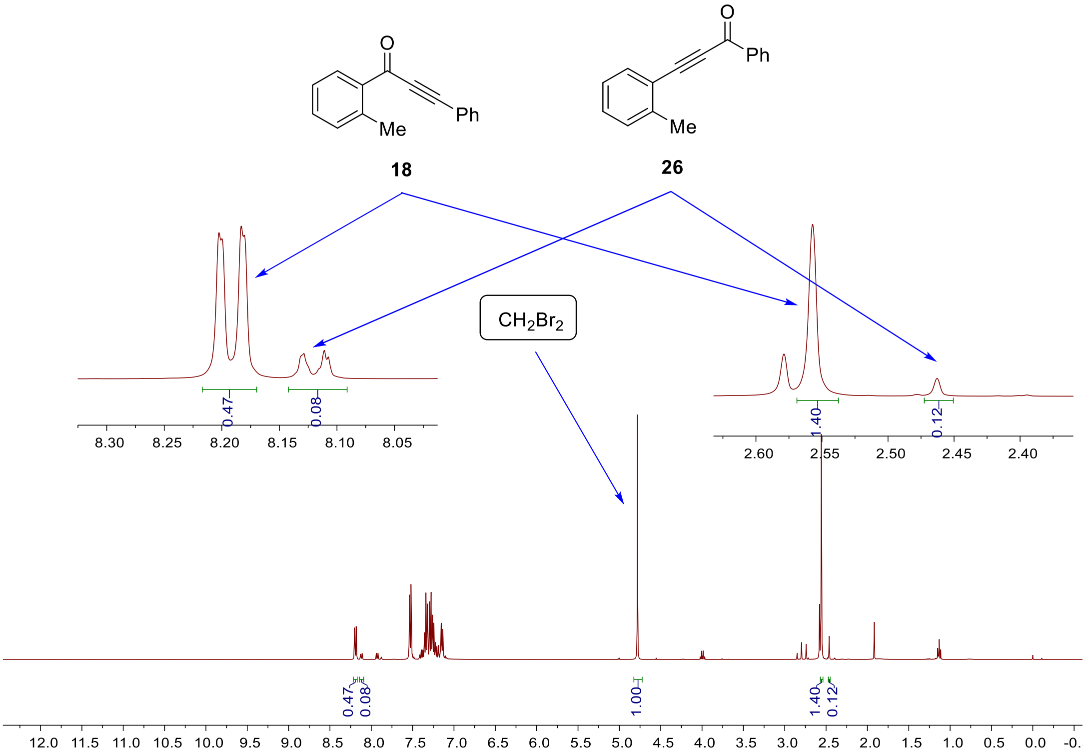
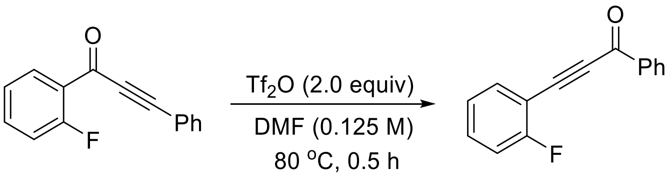


Figure S6. Crude ^1H NMR of the reaction between compound **18** and Tf_2O



19 **27**

A 120 ^{o}C oven-dried 25-mL glass schlenck, equipped with a stir bar, was charged with 1-(2-fluorophenyl)-3-phenylprop-2-yn-1-one **19** (112.1 mg, 0.5 mmol, 1.0 equiv). The mixture was evacuated and backfilled with nitrogen for three times. Then dry *N,N*-Dimethylformamide (4.0 mL) was added under nitrogen atmosphere. The Tf_2O (282.1 mg, 1.0 mmol, 2.0 equiv) was added dropwise into the mixture at room temperature, and the mixture was allowed to stir for 0.5 h at 80 ^{o}C. After the completion of reaction, a saturated aqueous solution of $NaHCO_3$ (20.0 mL) was added and the mixture was extracted with ethyl acetate (20.0 mL x 3). The combined organic layers were washed with brine (20.0 mL x 5), dried over by Na_2SO_4 and filtrated. The solvent was removed by rotary evaporation and 0.5 mmol CH_2Br_2 was added to the residue. The yield was determined by ^{1}H NMR spectroscopy in the presence of CH_2Br_2 (87.8 mg, 0.5 mmol) as an internal standard. The desired product **27** wasn't formed.

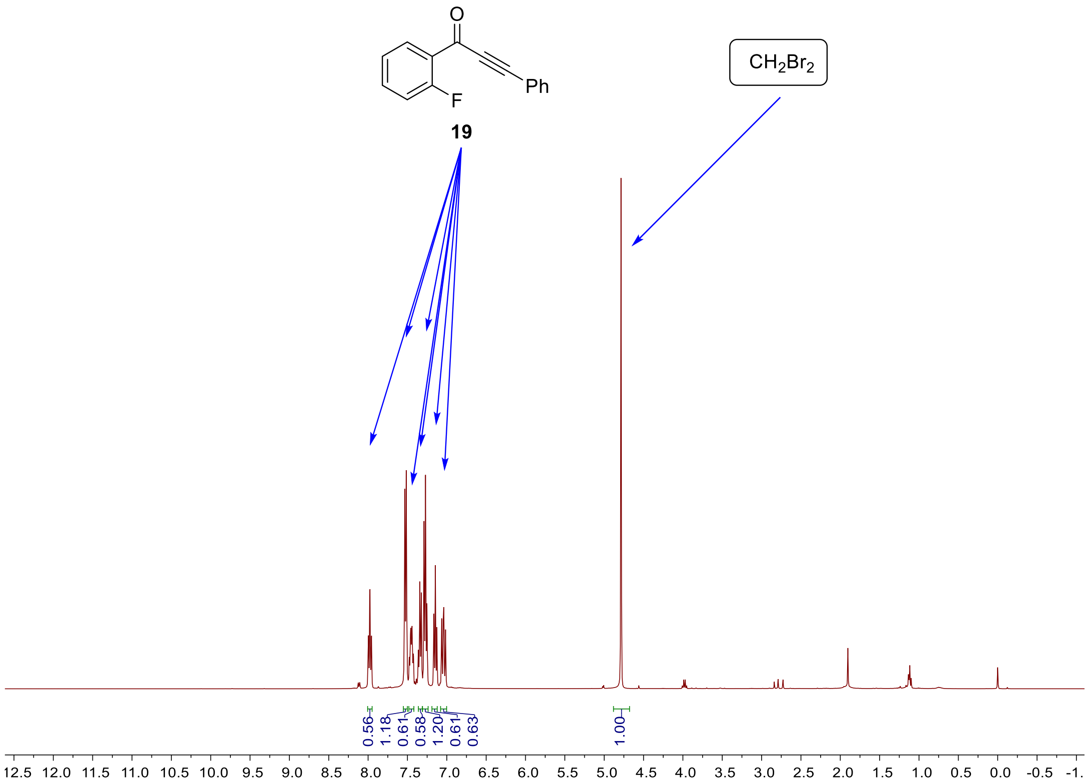
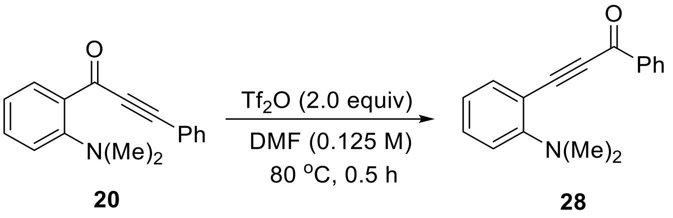
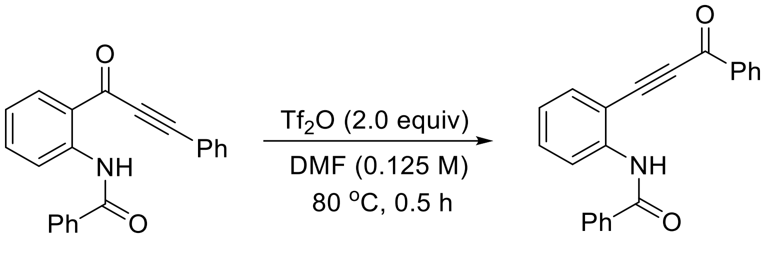


Figure S7. Crude ^{1}H NMR of the reaction between compound **19** and Tf_2O

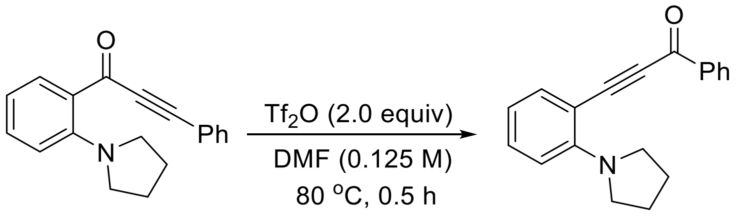


A 120 °C oven-dried 25-mL glass schlenck, equipped with a stir bar, was charged with 1-(2-(dimethylamino)phenyl)-3-phenylprop-2-yn-1-one **20** (124.7 mg, 0.5 mmol, 1.0 equiv). The mixture was evacuated and backfilled with nitrogen for three times. Then dry *N,N*-Dimethylformamide (4.0 mL) was added under nitrogen atmosphere. The Tf_2O (282.1 mg, 1.0 mmol, 2.0 equiv) was added dropwise into the mixture at room temperature, and the mixture was allowed to stir for 0.5 h at 80 °C. After the completion of reaction, a saturated aqueous solution of $NaHCO_3$ (20.0 mL) was added and the mixture was extracted with ethyl acetate (20.0 mL x 3). The combined organic layers were washed with brine (20.0 mL x 5), dried over by Na_2SO_4 and filtrated. The desired product **28** was not observed, and starting material **20** decomposed completely (monitored by silica gel TLC plate).



21 **29**

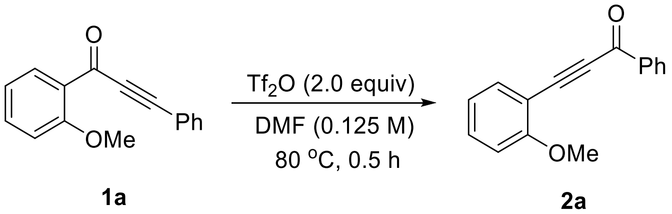
A 120 °C oven-dried 25-mL glass schlenck, equipped with a stir bar, was charged with *N*-(2-(3-phenylpropioloyl)phenyl)benzamide **22** (162.7 mg, 0.5 mmol, 1.0 equiv). The mixture was evacuated and backfilled with nitrogen for three times. Then dry *N,N*-Dimethylformamide (4.0 mL) was added under nitrogen atmosphere. The Tf_2O (282.1 mg, 1.0 mmol, 2.0 equiv) was added dropwise into the mixture at room temperature, and the mixture was allowed to stir for 0.5 h at 80 °C. After the completion of reaction, a saturated aqueous solution of $NaHCO_3$ (20.0 mL) was added and the mixture was extracted with ethyl acetate (20.0 mL x 3). The combined organic layers were washed with brine (20.0 mL x 5), dried over by Na_2SO_4 and filtrated. The desired product **29** was not observed, and starting material **21** decomposed completely (monitored by silica gel TLC plate).



22 **30**

A 120 °C oven-dried 25-mL glass schlenck, equipped with a stir bar, was charged with 3-phenyl-1-(2-(pyrrolidin-1-yl)phenyl)prop-2-yn-1-one **21** (137.7 mg, 0.5 mmol, 1.0 equiv). The mixture was evacuated and backfilled with nitrogen for three times. Then dry *N,N*-Dimethylformamide (4.0 mL) was added under nitrogen atmosphere. The Tf_2O (282.1 mg, 1.0 mmol, 2.0 equiv) was added dropwise into the mixture at room temperature, and the mixture was allowed to stir for 0.5 h at 80 °C. After the completion of reaction, a saturated aqueous solution of $NaHCO_3$ (20.0 mL) was added and the mixture was extracted with ethyl acetate (20.0 mL x 3). The combined organic layers were washed with brine (20.0 mL x 5), dried over by Na_2SO_4 and filtrated. The desired product **30** was not observed, and starting material **22** decomposed completely (monitored by silica gel TLC plate).

2. Reaction of *para*- or *meta*-OMe on benzene ring



A 120 °C oven-dried 25-mL glass schlenck, equipped with a stir bar, was charged with 1-(2-methoxyphenyl)-3-phenylprop-2-yn-1-one **1a** (118.1 mg, 0.5 mmol, 1.0 equiv). The mixture was evacuated and backfilled with nitrogen for three times. Then dry *N,N*-Dimethylformamide (4.0 mL) was added under nitrogen atmosphere. The Tf_2O (282.1 mg, 1.0 mmol, 2.0 equiv) was added dropwise into the mixture at room temperature, and the mixture was allowed to stir for 0.5 h at 80 °C. After the completion of reaction, a saturated aqueous solution of $NaHCO_3$ (20.0 mL) was added and the mixture was extracted with ethyl acetate (20.0 mL x 3). The combined organic layers were washed with brine (20.0 mL x 5), dried over by Na_2SO_4 and filtrated. The solvent was removed by rotary evaporation and 0.5 mmol CH_2Br_2 was added to the residue. The yield was determined by ^1H NMR spectroscopy in the presence of CH_2Br_2 (87.8 mg, 0.5 mmol) as an internal standard. Crude ^1H NMR yield of **2a** is >99%.

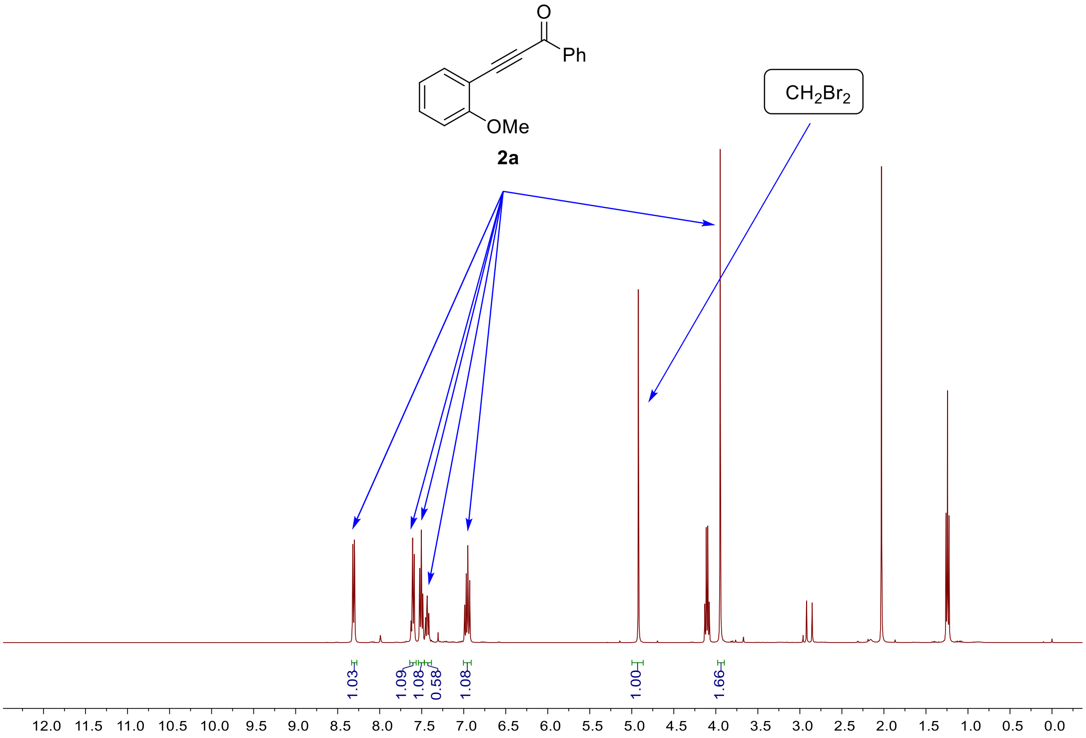
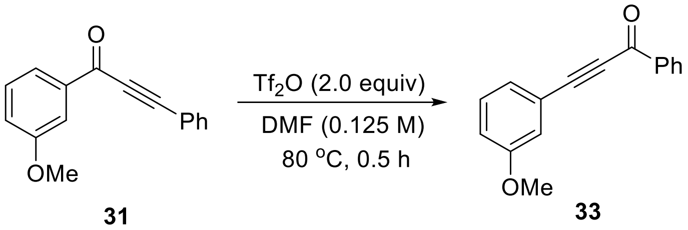


Figure S8. Crude ^{1}H NMR of the reaction between compound **1a** and Tf$_2$O



A 120 ^{o}C oven-dried 25-mL glass schlenck, equipped with a stir bar, was charged with 1-(3-methoxyphenyl)-3-phenylprop-2-yn-1-one **31** (118.1 mg, 0.5 mmol, 1.0 equiv). The mixture was evacuated and backfilled with nitrogen for three times. Then dry *N,N*-Dimethylformamide (4.0 mL) was added under nitrogen atmosphere. The Tf$_2$O (282.1 mg, 1.0 mmol, 2.0 equiv) was added dropwise into the mixture at room temperature, and the mixture was allowed to stir for 0.5 h at 80 ^{o}C. After the completion of reaction, a saturated aqueous solution of NaHCO$_3$ (20.0 mL) was added and the mixture was extracted with ethyl acetate (20.0 mL x 3). The combined organic layers were washed with brine (20.0 mL x 5), dried over by Na$_2$SO$_4$ and filtrated. The solvent was removed by rotary evaporation and 0.5 mmol CH$_2$Br$_2$ was added to the residue. The yield was determined by ^{1}H NMR spectroscopy in the presence of

CH_2Br_2 (87.8 mg, 0.5 mmol) as an internal standard. The desired product **33** was not observed.

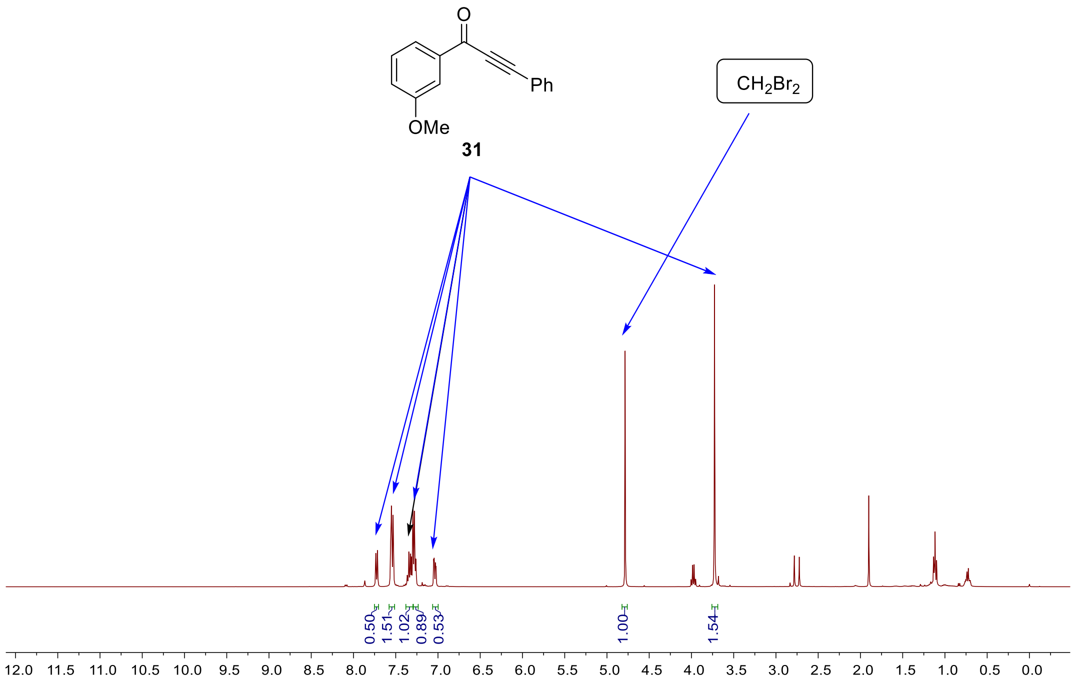
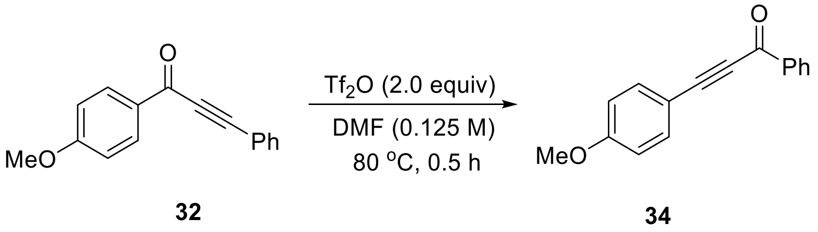


Figure S9. Crude ^{1}H NMR of the reaction between compound **31** and Tf_2O



A 120 °C oven-dried 25-mL glass schlenck, equipped with a stir bar, was charged with 1-(4-methoxyphenyl)-3-phenylprop-2-yn-1-one **32** (118.1 mg, 0.5 mmol, 1.0 equiv). The mixture was evacuated and backfilled with nitrogen for three times. Then dry *N,N*-Dimethylformamide (4.0 mL) was added under nitrogen atmosphere. The Tf_2O (282.1 mg, 1.0 mmol, 2.0 equiv) was added dropwise into the mixture at room temperature, and the mixture was allowed to stir for 0.5 h at 80 °C. After the completion of reaction, a saturated aqueous solution of $NaHCO_3$ (20.0 mL) was added and the mixture was extracted with ethyl acetate (20.0 mL x 3). The combined organic layers were washed with brine (20.0 mL x 5), dried over by Na_2SO_4 and filtrated. The solvent was removed by rotary evaporation and 0.5 mmol CH_2Br_2 was added to the residue. The yield was determined by ^{1}H NMR spectroscopy in the presence of CH_2Br_2 (87.8 mg, 0.5 mmol) as an internal standard. Crude ^{1}H NMR yield of **34** is 29%.

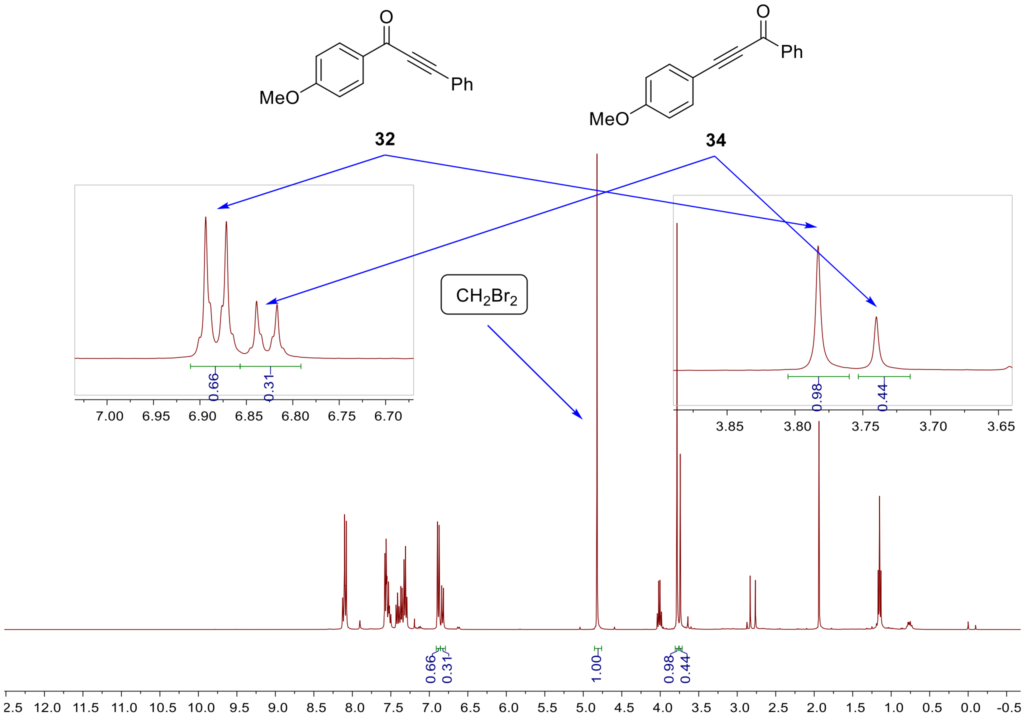
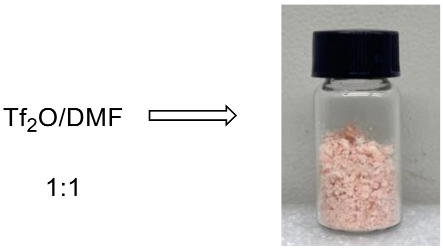


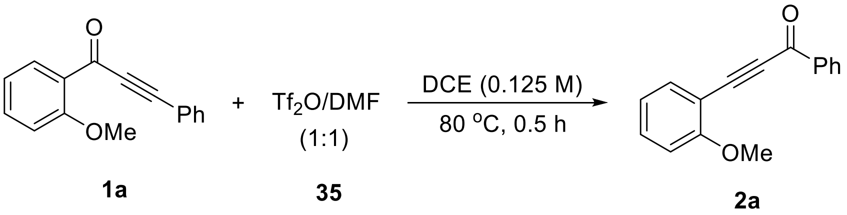
Figure S10. Crude ^{1}H NMR of the reaction between compound **32** and Tf_2O

3. Tow-step reaction: the interaction between Tf₂O and DMF



35

A 120 °C oven-dried 10-mL round-bottom flask, equipped with a stir bar, was charged with Tf_2O (1.41 g, 5.0 mmol, 1.0 equiv) under nitrogen atmosphere. The dry *N,N*-Dimethylformamide (365.5 mg, 5.0 mmol, 1.0 equiv) was added dropwise into at room temperature, it immediately produce **35** as a pink solid.



A 120 °C oven-dried 25-mL glass schlenck, equipped with a stir bar, was charged with 1-(2-methoxyphenyl)-3-phenylprop-2-yn-1-one **1a** (118.1 mg, 0.5 mmol, 1.0 equiv) and **35** (355.2 mg, 1.0 mmol, 2.0 equiv). The mixture was evacuated and backfilled with nitrogen for three times. Then dry DCE (4.0 mL) was added under nitrogen atmosphere. The the mixture was allowed to stir for 0.5 h at 80 °C. After the completion of reaction, a saturated aqueous solution of $NaHCO_3$ (20.0 mL) was added and the mixture was extracted with ethyl acetate (20.0 mL x 3). The combined organic layers were washed with brine (20.0 mL x 5), dried over by Na_2SO_4 and filtrated. The solvent was removed by rotary evaporation and 0.5 mmol CH_2Br_2 was added to the residue. The yield was determined by ^1H NMR spectroscopy in the presence of CH_2Br_2 (87.8 mg, 0.5 mmol) as an internal standard. Crude ^1H NMR yield of **2a** is 17%.

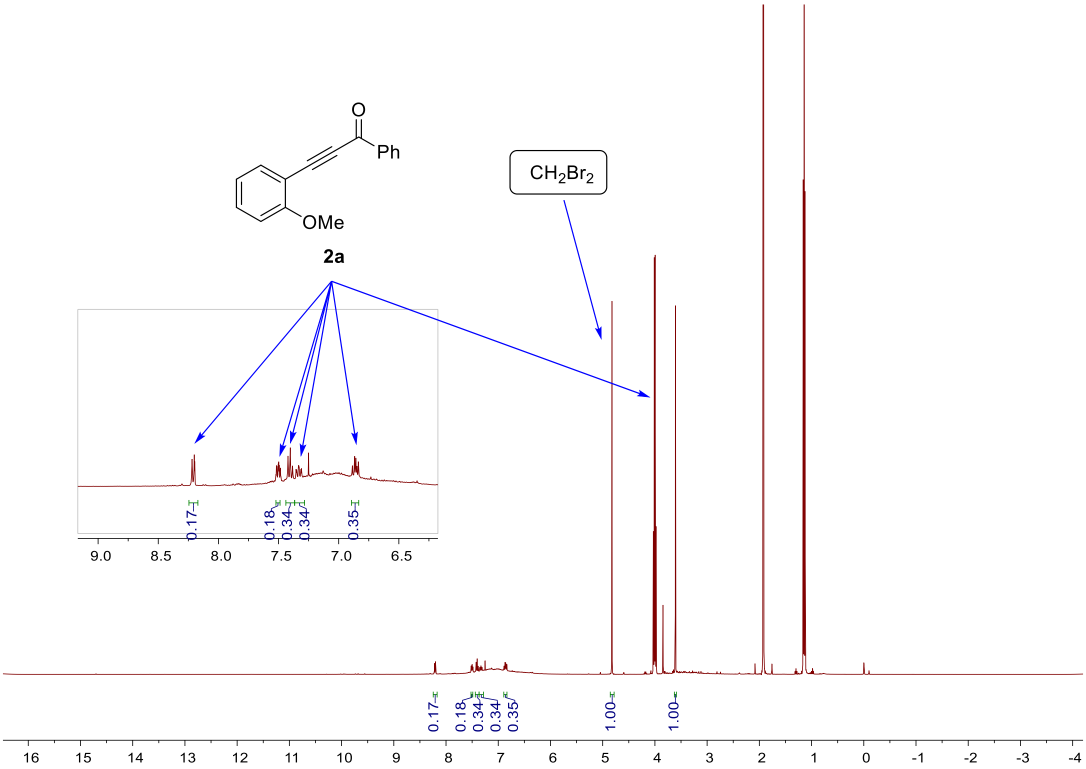
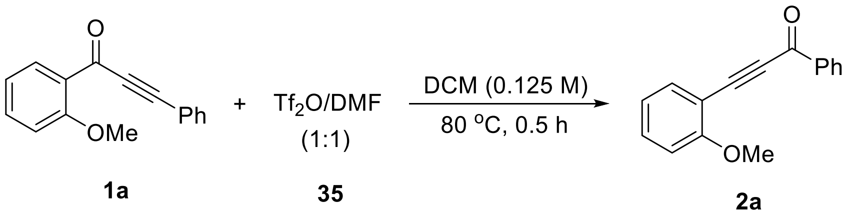


Figure S11. Crude ^1H NMR in DCE solvent



A 120 °C oven-dried 25-mL glass schlenck, equipped with a stir bar, was charged with 1-(2-methoxyphenyl)-3-phenylprop-2-yn-1-one **1a** (118.1 mg, 0.5 mmol, 1.0 equiv) and **35** (355.2 mg, 1.0 mmol, 2.0 equiv). The mixture was evacuated and backfilled with nitrogen for three times. Then dry DCM (4.0 mL) was added under nitrogen atmosphere. The the mixture was allowed to stir for 0.5 h at 80 °C. After the completion of reaction, a saturated aqueous solution of $NaHCO_3$ (20.0 mL) was added and the mixture was extracted with ethyl acetate (20.0 mL x 3). The combined organic layers were washed with brine (20.0 mL x 5), dried over by Na_2SO_4 and filtrated. The solvent was removed by rotary evaporation and 0.5 mmol CH_2Br_2 was added to the residue. The yield was determined by ^{1}H NMR spectroscopy in the presence of CH_2Br_2 (87.8 mg, 0.5 mmol) as an internal standard. Crude ^{1}H NMR yield of **2a** is 19%.

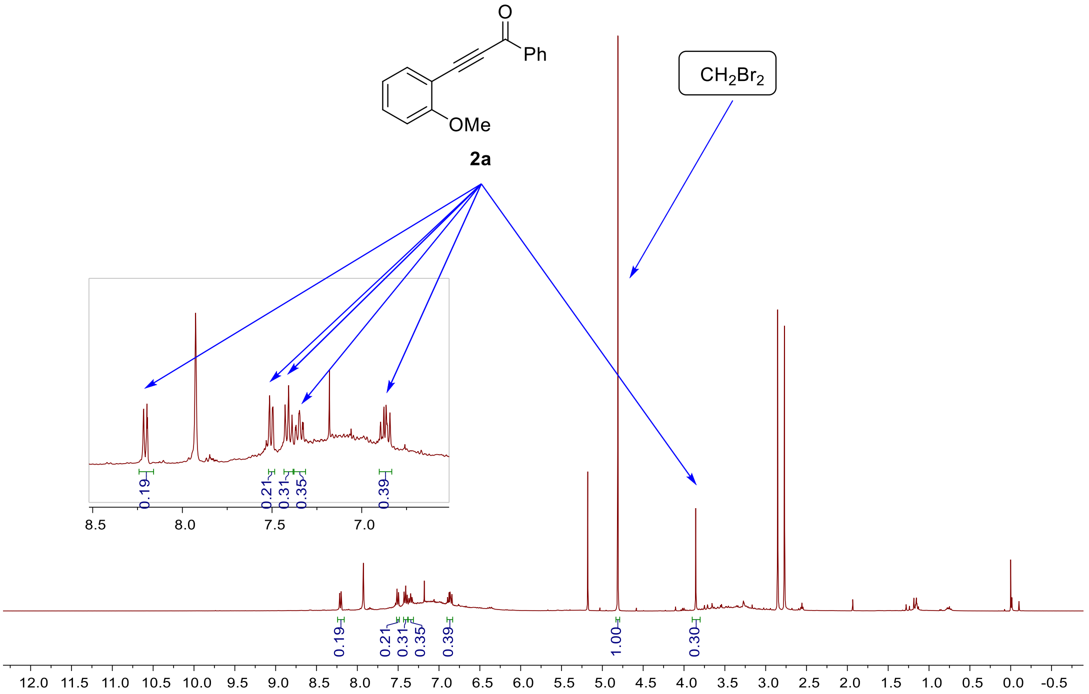
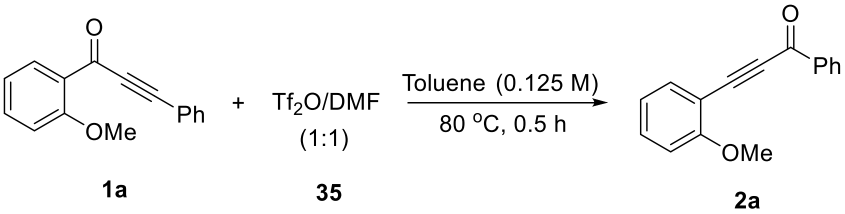


Figure S12. Crude ^{1}H NMR in DCM solvent



A 120 °C oven-dried 25-mL glass schlenck, equipped with a stir bar, was charged with 1-(2-methoxyphenyl)-3-phenylprop-2-yn-1-one **1a** (118.1 mg, 0.5 mmol, 1.0 equiv) and **35** (355.2 mg, 1.0 mmol, 2.0 equiv). The mixture was evacuated and backfilled with nitrogen for three times. Then dry toluene (4.0 mL) was added under nitrogen atmosphere. The the mixture was allowed to stir for 0.5 h at 80 °C. After the completion of reaction, a saturated aqueous solution of $NaHCO_3$ (20.0 mL) was added and the mixture was extracted with ethyl acetate (20.0 mL x 3). The combined organic layers were washed with brine (20.0 mL x 5), dried over by Na_2SO_4 and filtrated. The solvent was removed by rotary evaporation and 0.5 mmol CH_2Br_2 was added to the residue. The yield was determined by ^1H NMR spectroscopy in the presence of CH_2Br_2 (87.8 mg, 0.5 mmol) as an internal standard. Crude ^1H NMR yield of **2a** is 16%.

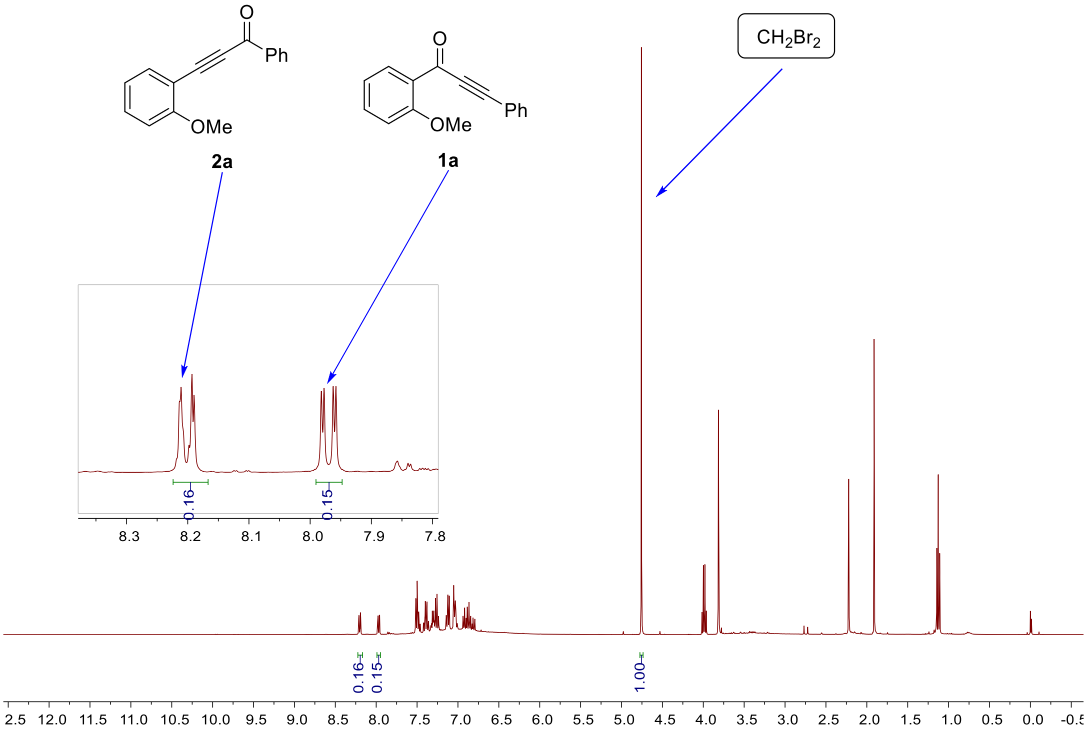
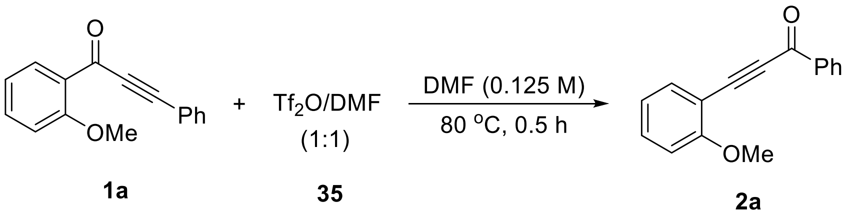


Figure S13. Crude ^1H NMR in Toluene solvent



A 120 ^{o}C oven-dried 25-mL glass schlenck, equipped with a stir bar, was charged with 1-(2-methoxyphenyl)-3-phenylprop-2-yn-1-one **1a** (118.1 mg, 0.5 mmol, 1.0 equiv) and **35** (355.2 mg, 1.0 mmol, 2.0 equiv). The mixture was evacuated and backfilled with nitrogen for three times. Then dry *N,N*-Dimethylformamide (4.0 mL) was added under nitrogen atmosphere. The the mixture was allowed to stir for 0.5 h at 80 ^{o}C. After the completion of reaction, a saturated aqueous solution of NaHCO$_3$ (20.0 mL) was added and the mixture was extracted with ethyl acetate (20.0 mL x 3). The combined organic layers were washed with brine (20.0 mL x 5), dried over by Na$_2$SO$_4$ and filtrated. The solvent was removed by rotary evaporation and 0.5 mmol CH$_2$Br$_2$ was added to the residue. The yield was determined by ^{1}H NMR spectroscopy in the presence of CH$_2$Br$_2$ (87.8 mg, 0.5 mmol) as an internal standard. Crude ^{1}H NMR yield of **2a** is >99%.

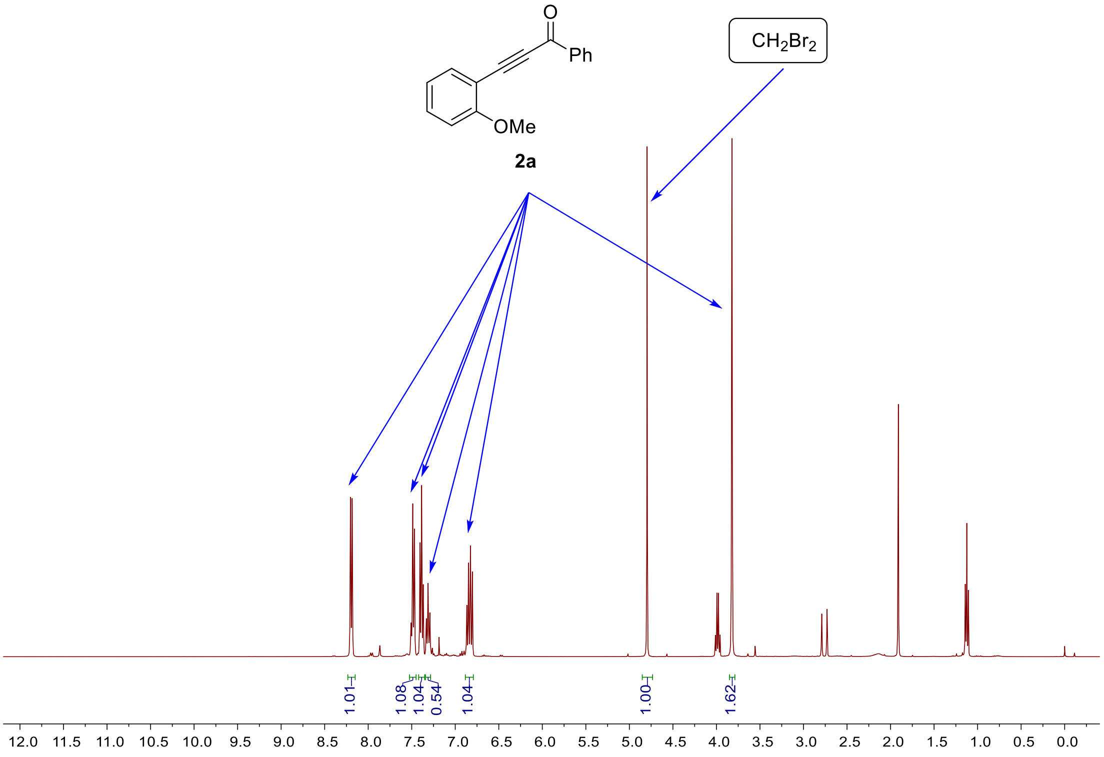
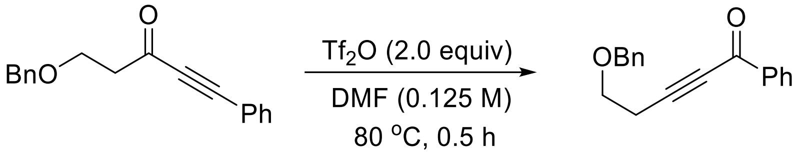


Figure S14. Crude ^{1}H NMR in DMF solvent

4. Control experiments



36 **37**

A 120 °C oven-dried 25-mL glass schlenck, equipped with a stir bar, was charged with 5-(benzyloxy)-1-phenylpent-1-yn-3-one **36** (132.1 mg, 0.5 mmol, 1.0 equiv). The mixture was evacuated and backfilled with nitrogen for three times. Then dry *N,N*-Dimethylformamide (4.0 mL) was added under nitrogen atmosphere. The Tf_2O (282.1 mg, 1.0 mmol, 2.0 equiv) was added dropwise into the mixture at room temperature, and the mixture was allowed to stir for 0.5 h at 80 °C. After the completion of reaction, a saturated aqueous solution of $NaHCO_3$ (20.0 mL) was added and the mixture was extracted with ethyl acetate (20.0 mL x 3). The combined organic layers were washed with brine (20.0 mL x 5), dried over by Na_2SO_4 and filtrated. The solvent was removed by rotary evaporation and 0.5 mmol CH_2Br_2 was added to the residue. The yield was determined by ^{1}H NMR spectroscopy in the presence of CH_2Br_2 (87.8 mg, 0.5 mmol) as an internal standard. The desired product **37** was not observed.

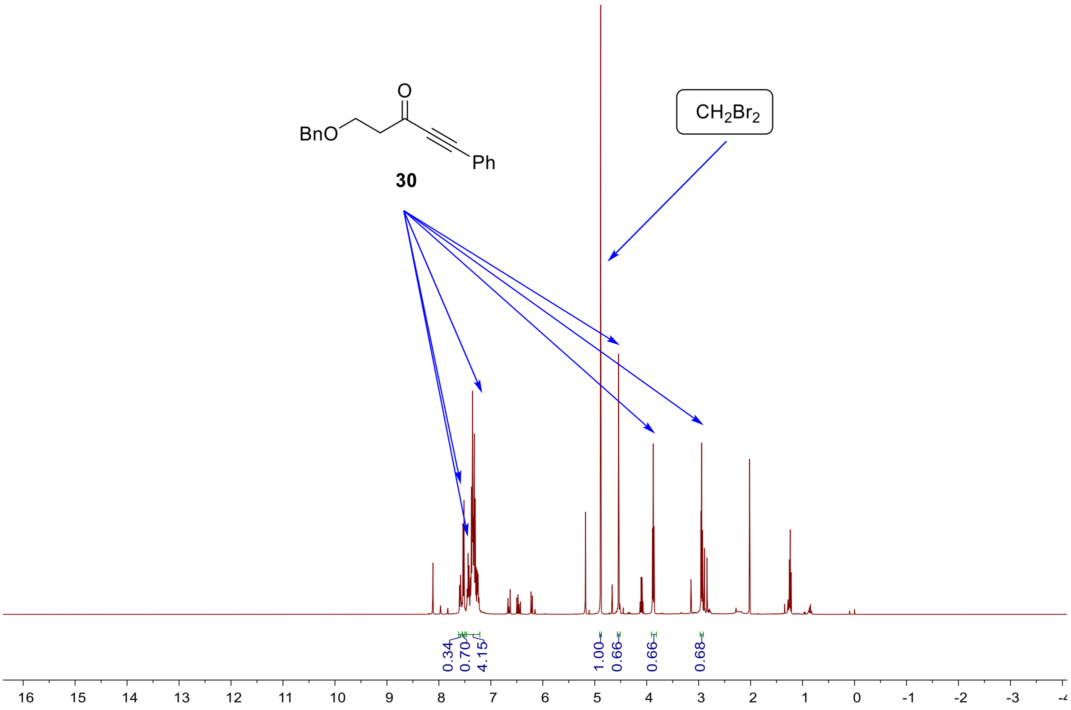
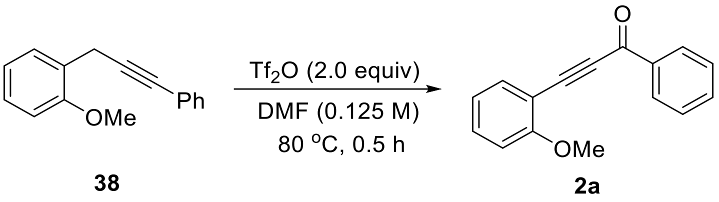


Figure S15. Crude ^{1}H NMR of the reaction between compound **36** and Tf$_2$O



A 120 °C oven-dried 25-mL glass schlenck, equipped with a stir bar, was charged with 1-methoxy-2-(3-phenylprop-2-yn-1-yl)benzene **38** (114.6 mg, 0.5 mmol, 1.0 equiv). The mixture was evacuated and backfilled with nitrogen for three times. Then dry *N,N*-Dimethylformamide (4.0 mL) was added under nitrogen atmosphere. The Tf$_2$O (282.1 mg, 1.0 mmol, 2.0 equiv) was added dropwise into the mixture at room temperature, and the mixture was allowed to stir for 0.5 h at 80 °C. After the completion of reaction, a saturated aqueous solution of NaHCO$_3$ (20.0 mL) was added and the mixture was extracted with ethyl acetate (20.0 mL x 3). The combined organic layers were washed with brine (20.0 mL x 5), dried over by Na$_2$SO$_4$ and filtrated. The solvent was removed by rotary evaporation and 0.5 mmol CH$_2$Br$_2$ was added to the residue. The yield was determined by ^{1}H NMR spectroscopy in the presence of

CH_2Br_2 (87.8 mg, 0.5 mmol) as an internal standard. The desired product **2a** was not observed.

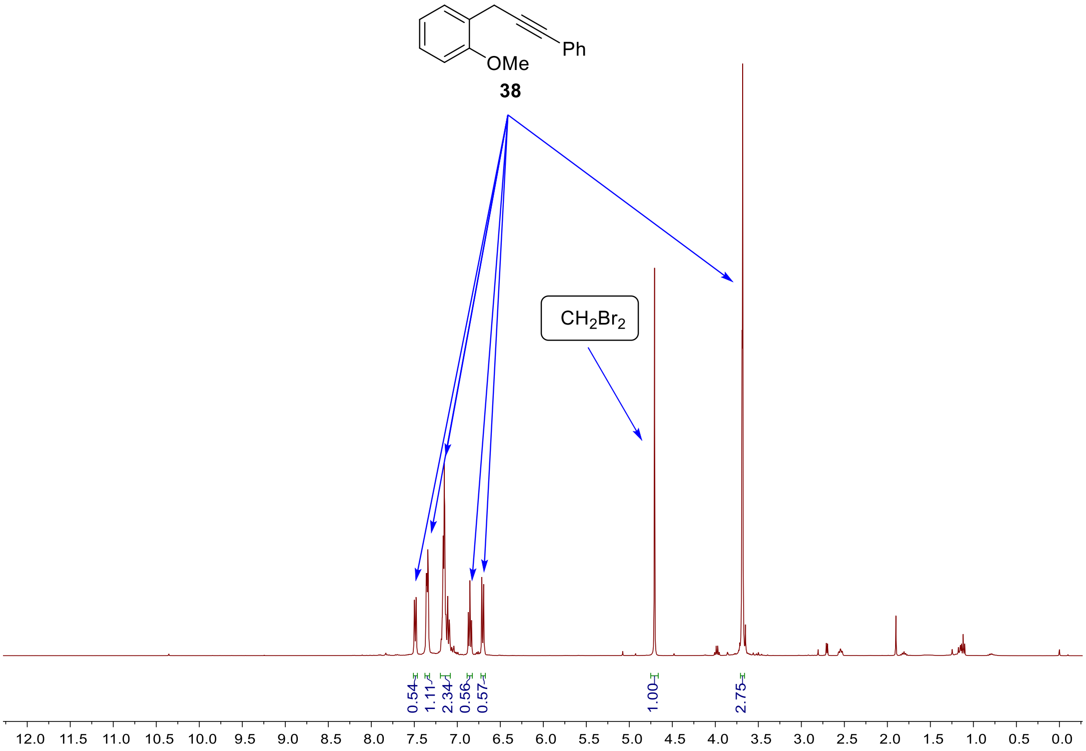
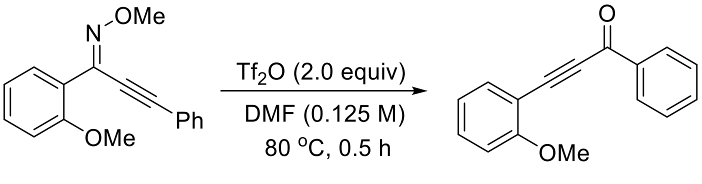


Figure S16. Crude ^{1}H NMR of the reaction between compound **38** and Tf_2O



39 **2a**

A 120 °C oven-dried 25-mL glass schlenck, equipped with a stir bar, was charged with (*E*)-1-(2-methoxyphenyl)-3-phenylprop-2-yn-1-one O-methyl oxime **39** (132.7 mg, 0.5 mmol, 1.0 equiv). The mixture was evacuated and backfilled with nitrogen for three times. Then dry *N,N*-Dimethylformamide (4.0 mL) was added under nitrogen atmosphere. The Tf_2O (282.1 mg, 1.0 mmol, 2.0 equiv) was added dropwise into the mixture at room temperature, and the mixture was allowed to stir for 0.5 h at 80 °C. After the completion of reaction, a saturated aqueous solution of $NaHCO_3$ (20.0 mL) was added and the mixture was extracted with ethyl acetate (20.0 mL x 3). The combined organic layers were washed with brine (20.0 mL x 5), dried over by Na_2SO_4 and filtrated. The solvent was removed by rotary evaporation and 0.5 mmol CH_2Br_2 was added to the residue. The yield was determined by ^1H NMR spectroscopy in the presence of CH_2Br_2 (87.8 mg, 0.5 mmol) as an internal standard. The desired product **2a** was not observed, and starting material **39** decomposed completely.

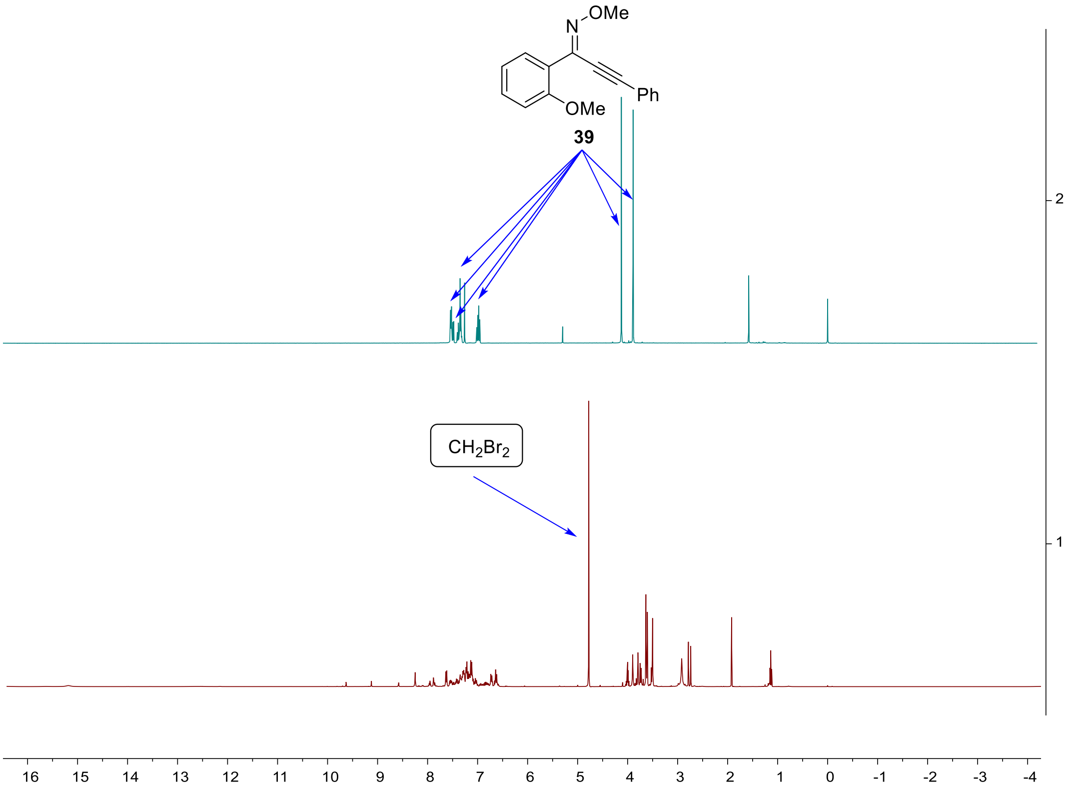
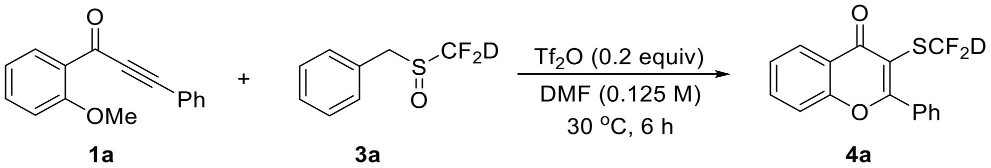


Figure S17. Crude ^1H NMR of the reaction between compound **39** and Tf_2O

5. Catalytic 1,3-transposition and cyclization



A 120 °C oven-dried 25-mL glass schlenck, equipped with a stir bar, was charged with 1-(2-methoxyphenyl)-3-phenylprop-2-yn-1-one **1a** (47.3 mg, 0.2 mmol, 1.0 equiv,) and (((difluoromethyl-d)sulfinyl)methyl)benzene **3a** (45.9 mg, 0.24 mmol, 1.2 equiv). The mixture was evacuated and backfilled with nitrogen for three times. Then dry *N,N*-Dimethylformamide (1.6 mL) was added under nitrogen atmosphere. The Tf_2O (11.3 mg, 0.04 mmol, 0.02 equiv,) was added dropwise into the mixture at

30 °C, and the mixture was allowed to stir for 6 h at 30 °C. After the completion of reaction, a saturated aqueous solution of brine (20.0 mL) was added and the mixture was extracted with ethyl acetate (20.0 mL x 3). The combined organic layers were washed with brine (20.0 mL x 5), dried over by Na_2SO_4 and filtrated. The solvent was removed by rotary evaporation and 0.2 mmol CH_2Br_2 was added to the residue. The yield was determined by ^1H NMR spectroscopy in the presence of CH_2Br_2 (35.1 mg, 0.2 mmol) as an internal standard. Crude ^1H NMR yield of **4a** is 18%.

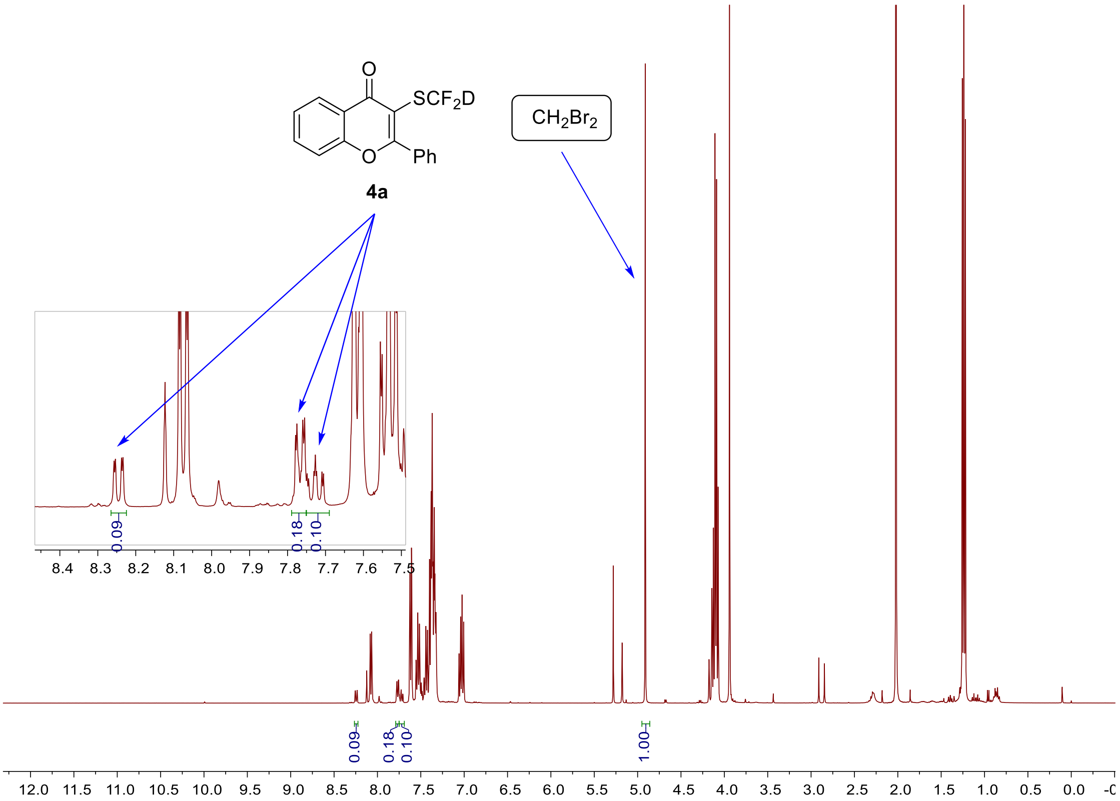
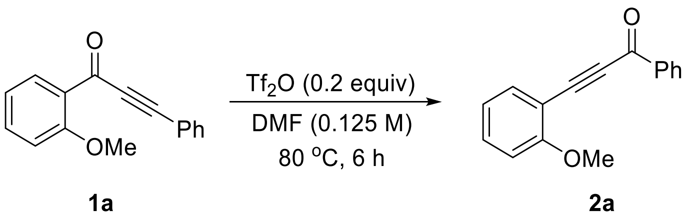


Figure S18. Crude ^1H NMR of the reaction between product **1a**, reagent **2a** with catalytic amount of Tf_2O



A 120 °C oven-dried 25-mL glass schlenck, equipped with a stir bar, was charged with 1-(2-methoxyphenyl)-3-phenylprop-2-yn-1-one **1a** (118.1 mg, 0.5 mmol, 1.0 equiv). The mixture was evacuated and backfilled with nitrogen for three times.

Then dry *N,N*-Dimethylformamide (4.0 mL) was added under nitrogen atmosphere. The Tf_2O (28.2 mg, 0.1 mmol, 0.2 equiv) was added dropwise into the mixture at room temperature, and the mixture was allowed to stir for 6 h at 80 °C. After the completion of reaction, a saturated aqueous solution of $NaHCO_3$ (20.0 mL) was added and the mixture was extracted with ethyl acetate (20.0 mL x 3). The combined organic layers were washed with brine (20.0 mL x 5), dried over by Na_2SO_4 and filtrated. The solvent was removed by rotary evaporation and 0.2 mmol CH_2Br_2 was added to the residue. The yield was determined by ^1H NMR spectroscopy in the presence of CH_2Br_2 (87.8 mg, 0.5 mmol) as an internal standard. Crude ^1H NMR yield of **2a** is 68%.

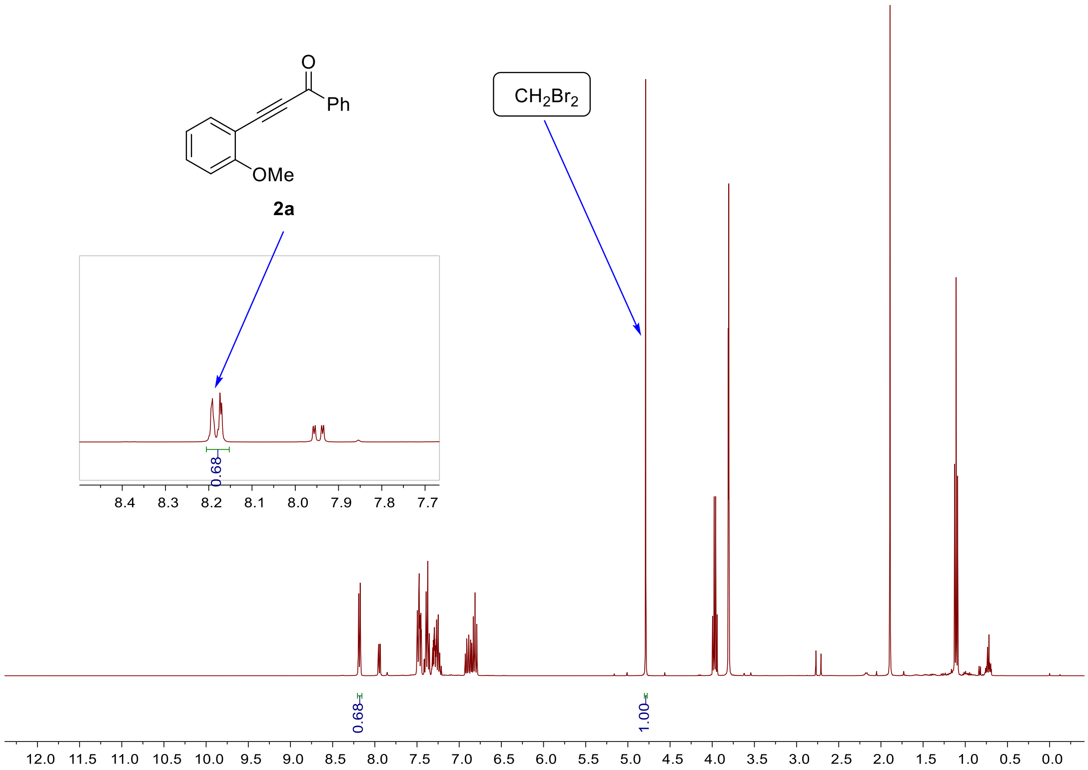
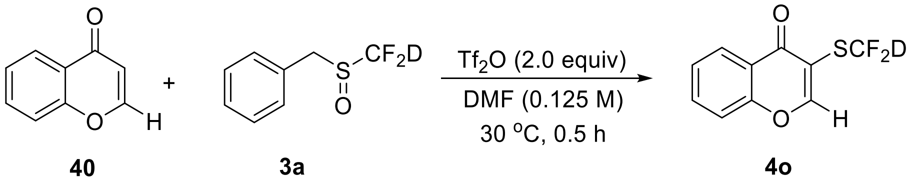


Figure S19. Crude ^1H NMR of the reaction between product **1a** and catalytic amount of Tf_2O

6. Reaction of with non-deuterodifluoromethylthiolated chromones



A 120 °C oven-dried 25-mL glass schlenck, equipped with a stir bar, was charged with 4*H*-chromen-4-one **40** (28.2 mg, 0.2 mmol, 1.0 equiv,) and (((difluoromethyl-d)sulfinyl)methyl)benzene **3a** (45.9 mg, 0.24 mmol, 1.2 equiv). The mixture was evacuated and backfilled with nitrogen for three times. Then dry *N,N*-Dimethylformamide (1.6 mL) was added under nitrogen atmosphere. The Tf_2O (112.9 mg, 0.4 mmol, 2.0 equiv,) was added dropwise into the mixture at 30 °C, and the mixture was allowed to stir for 0.5 h at 30 °C. After the completion of reaction, a saturated aqueous solution of brine (20.0 mL) was added and the mixture was extracted with ethyl acetate (20.0 mL x 3). The combined organic layers were washed with brine (20.0 mL x 5), dried over by Na_2SO_4 and filtrated. The solvent was removed by rotary evaporation and 0.2 mmol CH_2Br_2 was added to the residue. The yield was determined by ^{1}H NMR spectroscopy in the presence of CH_2Br_2 (35.1 mg, 0.2 mmol) as an internal standard. Crude ^{1}H NMR yield of **4o** is 22%.

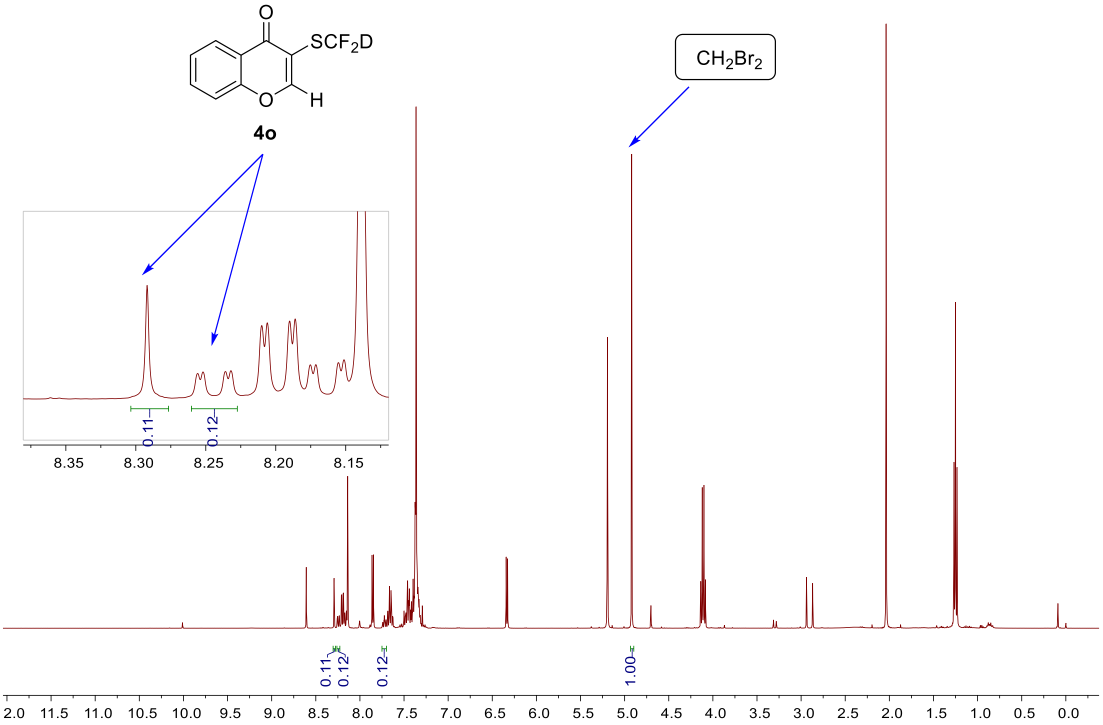
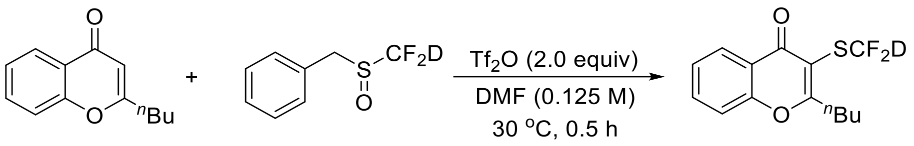


Figure S20. Crude ^{1}H NMR of the reaction between **40**, reagent **3a** and Tf_2O



41 **3a** **4p**

A 120 °C oven-dried 25-mL glass schlenck, equipped with a stir bar, was charged with 2-butyl-4*H*-chromen-4-one **41** (40.5 mg, 0.2 mmol, 1.0 equiv,) and (((difluoromethyl-d)sulfinyl)methyl)benzene **3a** (45.9 mg, 0.24 mmol, 1.2 equiv). The mixture was evacuated and backfilled with nitrogen for three times. Then dry *N,N*-Dimethylformamide (1.6 mL) was added under nitrogen atmosphere. The Tf_2O (112.9 mg, 0.4 mmol, 2.0 equiv,) was added dropwise into the mixture at 30 °C, and the mixture was allowed to stir for 0.5 h at 30 °C. After the completion of reaction, a saturated aqueous solution of brine (20.0 mL) was added and the mixture was extracted with ethyl acetate (20.0 mL x 3). The combined organic layers were washed with brine (20.0 mL x 5), dried over by Na_2SO_4 and filtrated. The solvent was removed by rotary evaporation and 0.2 mmol CH_2Br_2 was added to the residue. The yield was determined by ^{1}H NMR spectroscopy in the presence of CH_2Br_2 (35.1 mg, 0.2 mmol) as an internal standard. Crude ^{1}H NMR yield of **4p** is 11%.

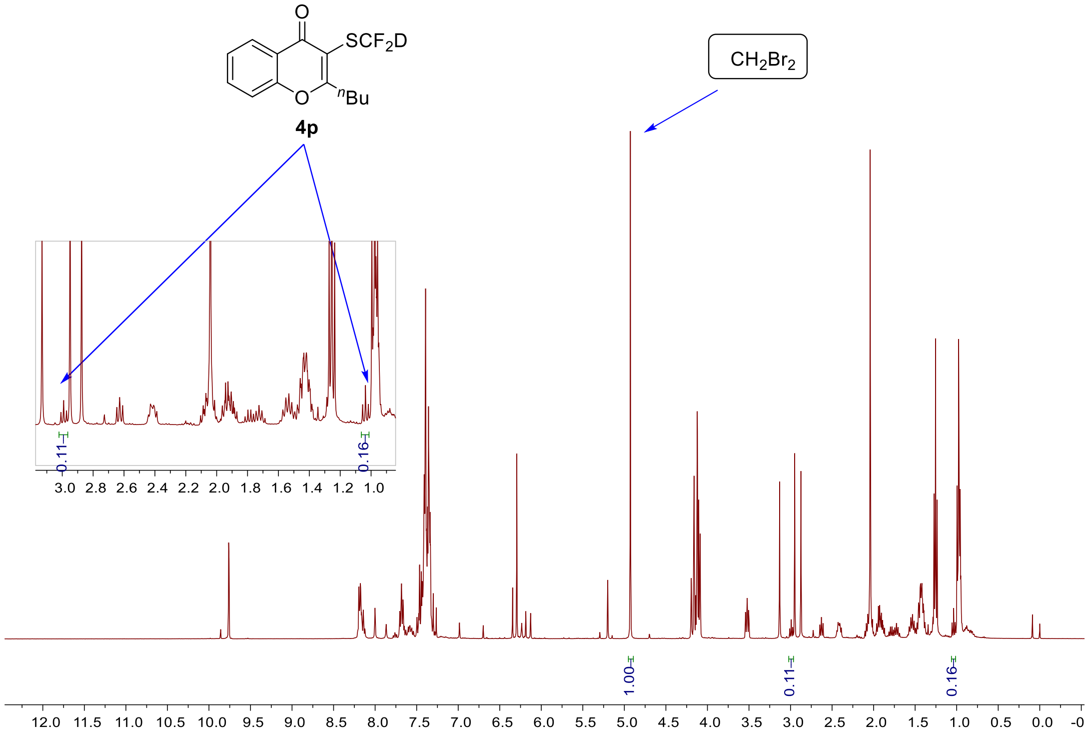


Figure S21. Crude ^{1}H NMR of the reaction between **41**, reagent **3a** and Tf_2O

VII. X-ray crystal structure and data

White crystals of compound **4a** were slowly grown from a mixture of petroleum ether and ethyl acetate solution of the compound at 24 °C. For X-ray structure analyses, the oil-coated crystals were mounted onto a loop, and the diffraction data were collected on a Bruker Smart Apex II CCD diffractometer with graphitemonochromated Mo Kα (λ = 0.71073 Å). An empirical (multi-scan) absorption correction was applied with the program SADABS. The structures were solved by Olex2 with the ShelXT solution program using the intrinsic phasing method and subsequently refined on F2 by using full-matrix least-squares techniques (SHELXL- 2014). If not noted otherwise, all non-hydrogen atoms were refined anisotropically, and hydrogen atoms were located at calculated positions or found in the ΔF map. Figures of the solid-state molecular structures were generated using XP as implemented in the SHELXTL program.

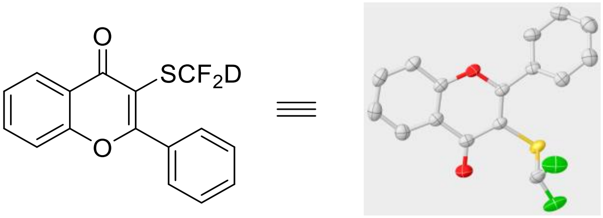


Figure S22. ORTEP drawing of product **4a** with 50% thermal ellipsoid.

Table S6 Crystal data and structure refinement for mo230831a.

Identification code	mo230831a
Empirical formula	$C_{16}H_9DF_2O_2S$
Formula weight	305.31
Temperature/K	296.15
Crystal system	triclinic
Space group	P-1
a/Å	8.9515(17)

b/Å	9.5789(19)
c/Å	16.542(3)
α/°	105.130(4)
β/°	91.474(4)
γ/°	91.176(4)
Volume/Å^3	1368.2(5)
Z	4
ρ_{calc}g/cm^3	1.482
μ/mm^{-1}	0.260
F(000)	624.0
Crystal size/mm^3	0.15 × 0.15 × 0.12
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.406 to 61.054
Index ranges	$-11 \leq h \leq 12$, $-13 \leq k \leq 13$, $-23 \leq l \leq 23$
Reflections collected	28127
Independent reflections	7672 [R_{int} = 0.0316, R_{sigma} = 0.0291]
Data/restraints/parameters	7672/16/416
Goodness-of-fit on F^2	1.039
Final R indexes [I>=2σ (I)]	R_1 = 0.0498, wR_2 = 0.1281
Final R indexes [all data]	R_1 = 0.0783, wR_2 = 0.1471
Largest diff. peak/hole / e Å^{-3}	0.37/-0.37

Table S7 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for mo230831a.

U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	x	y	z	U(eq)
S(1)	1637.0(4)	7827.9(5)	5014.0(3)	53.10(14)
F(1)	1690.7(19)	9967.6(16)	4296.0(10)	100.0(5)
F(2)	-150.4(15)	8476.0(18)	3949.0(10)	95.4(5)
O(1)	6032.0(12)	7447.6(13)	5336.5(8)	51.2(3)
O(2)	2804.4(16)	5509.8(17)	3610.5(9)	71.4(4)

Table S7 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for mo230831a.

U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	x	*y*	*z*	U(eq)
C(1)	6399.4(18)	6346.5(19)	4665.3(11)	47.9(4)
C(2)	7898(2)	5986(2)	4620.4(14)	59.4(5)
C(3)	8337(2)	4923(3)	3945.1(15)	69.2(6)
C(4)	7311(3)	4210(2)	3326.4(15)	71.7(6)
C(5)	5832(2)	4569(2)	3378.4(13)	62.2(5)
C(6)	5348.8(19)	5655.8(19)	4055.6(11)	49.3(4)
C(7)	3787.9(19)	6105.6(19)	4124.8(11)	50.6(4)
C(8)	3508.7(16)	7320.3(18)	4841.1(10)	44.4(4)
C(9)	4619.2(17)	7958.5(18)	5406.8(11)	45.4(4)
C(10)	4564.1(18)	9187.1(19)	6154.9(11)	48.2(4)
C(11)	3766(2)	10423(2)	6160.0(12)	56.2(4)
C(12)	3789(3)	11569(2)	6869.7(14)	67.6(5)
C(13)	4592(3)	11504(3)	7578.2(15)	75.0(6)
C(14)	5392(3)	10294(3)	7579.9(15)	78.3(6)
C(15)	5387(2)	9143(2)	6875.7(13)	63.2(5)
C(16)	1315(2)	8558(2)	4124.5(13)	61.0(5)
D(16)	1856.29	8010.19	3641.25	73
S(2)	3604.6(14)	3082(2)	1138.6(9)	79.2(6)
S(3)	3797.5(13)	1821.0(13)	563.8(8)	82.7(4)
F(3)	6232(12)	2943(15)	1260(8)	127(3)
F(4)	4872(6)	1544(6)	-171(3)	137.9(19)
F(5)	4497(4)	4340(4)	1607(2)	125.9(12)
F(6)	6275(9)	2504(14)	948(7)	209(6)
O(3)	-474.0(15)	2611.4(15)	106.7(8)	58.9(3)
O(4)	3554(2)	3843(3)	-576.9(13)	120.5(8)
C(17)	-381(2)	3091(2)	-604.9(11)	57.4(4)
C(18)	-1701(3)	3100(3)	-1053.5(13)	75.5(6)

Table S7 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for mo230831a.

U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	x	*y*	*z*	U(eq)
C(19)	-1649(3)	3576(3)	-1772.0(14)	85.2(7)
C(20)	-324(3)	4043(3)	-2031.8(14)	79.6(7)
C(21)	968(3)	4040(2)	-1582.5(13)	72.3(6)
C(22)	961(2)	3548(2)	-850.7(12)	59.7(5)
C(23)	2328(3)	3445(3)	-386.8(16)	81.3(7)
C(24)	2148(3)	2777(3)	314.2(17)	86.5(8)
C(25)	777(2)	2454(2)	549.7(13)	59.5(5)
C(26)	371(2)	1855(2)	1258.0(13)	59.8(5)
C(27)	1081(3)	2314(3)	2044.3(15)	77.8(6)
C(28)	645(3)	1734(3)	2687.2(16)	87.3(8)
C(29)	-501(3)	704(3)	2555.2(18)	87.0(8)
C(30)	-1225(3)	281(3)	1789.1(18)	81.8(7)
C(31)	-801(3)	845(2)	1139.5(15)	67.5(5)
C(32)	5012(5)	3387(6)	932(3)	82.1(13)
D(32)	5122.67	3867.47	480.75	99
C(33)	5163(7)	2716(8)	486(4)	79.5(19)
D(33)	5315	3548.32	253.18	95

Table S8 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for mo230831a.

The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S(1)	34.3(2)	71.2(3)	62.0(3)	32.4(2)	-0.25(17)	0.81(18)
F(1)	120.4(12)	91.7(10)	104.4(11)	60.8(9)	-31.6(9)	-30.6(9)

Table S8 Anisotropic Displacement Parameters ($Å^2×10^3$) for mo230831a.

The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+…]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
F(2)	61.0(8)	120.5(12)	121.9(12)	66.1(10)	-32.8(7)	-1.9(7)
O(1)	33.0(5)	58.4(7)	62.9(7)	18.2(6)	-4.0(5)	-1.7(5)
O(2)	56.7(8)	77.9(10)	71.9(9)	8.1(8)	-18.3(7)	-2.2(7)
C(1)	39.9(8)	50.4(9)	60.7(10)	27.3(8)	3.3(7)	0.0(7)
C(2)	40.7(9)	68.7(12)	77.2(13)	34.0(10)	3.9(8)	2.6(8)
C(3)	52.6(11)	76.2(14)	92.3(16)	43.0(13)	19.6(11)	18.4(10)
C(4)	76.8(14)	63.7(13)	80.9(15)	26.7(11)	22.4(12)	19.0(11)
C(5)	67.4(12)	55.0(11)	66.3(12)	19.6(10)	5.0(9)	3.5(9)
C(6)	46.1(9)	48.0(9)	58.6(10)	23.0(8)	1.2(7)	0.0(7)
C(7)	44.6(9)	53.0(10)	58.3(10)	23.0(8)	-5.6(7)	-3.9(7)
C(8)	33.3(7)	52.1(9)	53.6(9)	24.7(8)	-1.7(6)	-1.7(6)
C(9)	35.8(7)	51.1(9)	55.8(9)	25.9(8)	0.0(6)	-3.1(6)
C(10)	39.4(8)	53.4(10)	54.6(9)	19.8(8)	0.0(7)	-8.3(7)
C(11)	58.5(10)	54.5(10)	60.6(11)	23.8(9)	4.9(8)	-2.7(8)
C(12)	74.8(13)	53.4(11)	76.6(14)	19.7(10)	14.3(11)	-2.6(10)
C(13)	82.2(15)	67.2(14)	69.2(13)	7.4(11)	7.6(11)	-15.6(12)
C(14)	80.1(15)	85.0(17)	64.9(13)	14.4(12)	-18.5(11)	-15.4(13)
C(15)	56.6(11)	65.2(12)	67.6(12)	19.1(10)	-14.9(9)	-6.3(9)
C(16)	52.7(10)	74.6(13)	62.1(11)	29.1(10)	-4.2(8)	10.7(9)
S(2)	44.8(7)	139.3(17)	56.9(8)	32.4(10)	-3.3(5)	2.0(7)
S(3)	75.1(7)	85.1(8)	101.3(9)	45.3(7)	19.6(6)	22.3(5)
F(3)	75(5)	169(6)	156(6)	79(5)	-26(4)	13(4)
F(4)	164(5)	124(4)	127(4)	28(3)	40(3)	58(3)
F(5)	98(2)	167(3)	96(2)	6(2)	-3.6(17)	-2(2)
F(6)	58(3)	328(13)	283(12)	145(10)	30(5)	73(5)
O(3)	61.9(8)	65.2(8)	50.9(7)	18.6(6)	-4.2(6)	-3.1(6)

Table S8 Anisotropic Displacement Parameters (Å^2×10^3) for mo230831a.

The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\dots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O(4)	89.6(13)	183(2)	119.7(16)	100.1(16)	-18.9(11)	-51.6(14)
C(17)	74.0(12)	50.7(10)	44.6(9)	8.3(8)	-4.6(8)	-0.4(9)
C(18)	74.8(14)	92.9(17)	57.2(12)	18.0(11)	-8.5(10)	0.7(12)
C(19)	94.9(18)	103.0(19)	57.2(12)	21.0(13)	-16.6(12)	10.5(15)
C(20)	114(2)	75.3(15)	51.8(11)	20.8(11)	-8.6(12)	6.0(14)
C(21)	100.2(17)	63.0(13)	55.8(11)	20.5(10)	-2.0(11)	-6.1(11)
C(22)	80.1(13)	47.9(10)	50.5(10)	13.0(8)	-5.8(9)	-5.0(9)
C(23)	79.0(15)	94.3(17)	84.0(15)	50.9(14)	-12.6(12)	-27.3(13)
C(24)	64.8(13)	118(2)	99.2(17)	72.2(16)	-17.2(12)	-21.1(13)
C(25)	63.1(11)	56.8(11)	62.5(11)	24.0(9)	-6.3(9)	-5.0(9)
C(26)	61.7(11)	59.3(11)	66.4(11)	30.2(9)	4.5(9)	3.3(9)
C(27)	69.6(13)	96.7(17)	79.4(14)	46.6(13)	-10.4(11)	-1.3(12)
C(28)	82.6(16)	121(2)	72.0(14)	48.4(15)	4.5(12)	29.0(16)
C(29)	88.2(17)	100.3(19)	95.0(18)	60.8(16)	33.2(15)	31.4(15)
C(30)	87.1(17)	66.1(14)	101.2(19)	35.1(13)	31.2(15)	3.4(12)
C(31)	73.0(13)	56.3(11)	75.5(13)	20.9(10)	12.2(11)	-1.1(10)
C(32)	64(2)	110(4)	79(3)	33(3)	16(2)	21(3)
C(33)	67(4)	89(5)	88(5)	30(4)	20(4)	29(3)

Table S9 Bond Lengths for mo230831a.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S(1)	C(8)	1.7638(16)	S(3)	C(32)	1.796(6)
S(1)	C(16)	1.8054(19)	F(3)	C(33)	1.546(11)
F(1)	C(16)	1.340(3)	F(4)	C(33)	1.358(7)

Table S9 Bond Lengths for mo230831a.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
F(2)	C(16)	1.332(2)	F(5)	C(32)	1.343(5)
O(1)	C(1)	1.369(2)	F(6)	C(32)	1.429(9)
O(1)	C(9)	1.3622(19)	O(3)	C(17)	1.375(2)
O(2)	C(7)	1.230(2)	O(3)	C(25)	1.355(2)
C(1)	C(2)	1.391(2)	O(4)	C(23)	1.230(3)
C(1)	C(6)	1.384(2)	C(17)	C(18)	1.381(3)
C(2)	C(3)	1.373(3)	C(17)	C(22)	1.377(3)
C(3)	C(4)	1.385(3)	C(18)	C(19)	1.381(3)
C(4)	C(5)	1.374(3)	C(19)	C(20)	1.377(4)
C(5)	C(6)	1.400(3)	C(20)	C(21)	1.359(3)
C(6)	C(7)	1.469(2)	C(21)	C(22)	1.409(3)
C(7)	C(8)	1.459(3)	C(22)	C(23)	1.446(3)
C(8)	C(9)	1.366(2)	C(23)	C(24)	1.474(3)
C(9)	C(10)	1.471(3)	C(24)	C(25)	1.350(3)
C(10)	C(11)	1.394(3)	C(25)	C(26)	1.483(3)
C(10)	C(15)	1.396(3)	C(26)	C(27)	1.392(3)
C(11)	C(12)	1.382(3)	C(26)	C(31)	1.387(3)
C(12)	C(13)	1.375(3)	C(27)	C(28)	1.383(3)
C(13)	C(14)	1.375(4)	C(28)	C(29)	1.382(4)
C(14)	C(15)	1.379(3)	C(29)	C(30)	1.367(4)
C(16)	D(16)	0.9800	C(30)	C(31)	1.381(3)
S(2)	C(24)	1.825(3)	C(32)	D(32)	0.9800
S(2)	C(33)	1.771(6)	C(33)	D(33)	0.9800
S(3)	C(24)	1.847(3)			

Table S10 Bond Angles for mo230831a.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C(8)	S(1)	C(16)	99.07(8)	C(22)	C(17)	C(18)	121.99(19)
C(9)	O(1)	C(1)	120.80(13)	C(17)	C(18)	C(19)	118.1(2)
O(1)	C(1)	C(2)	116.10(16)	C(20)	C(19)	C(18)	121.2(2)
O(1)	C(1)	C(6)	122.01(15)	C(21)	C(20)	C(19)	120.3(2)
C(6)	C(1)	C(2)	121.88(18)	C(20)	C(21)	C(22)	120.1(2)
C(3)	C(2)	C(1)	118.5(2)	C(17)	C(22)	C(21)	118.3(2)
C(2)	C(3)	C(4)	120.90(19)	C(17)	C(22)	C(23)	120.01(18)
C(5)	C(4)	C(3)	120.1(2)	C(21)	C(22)	C(23)	121.6(2)
C(4)	C(5)	C(6)	120.4(2)	O(4)	C(23)	C(22)	122.7(2)
C(1)	C(6)	C(5)	118.15(17)	O(4)	C(23)	C(24)	122.4(2)
C(1)	C(6)	C(7)	119.53(17)	C(22)	C(23)	C(24)	114.88(19)
C(5)	C(6)	C(7)	122.30(17)	C(23)	C(24)	S(2)	119.09(17)
O(2)	C(7)	C(6)	122.21(18)	C(23)	C(24)	S(3)	114.91(19)
O(2)	C(7)	C(8)	123.04(16)	C(25)	C(24)	S(2)	114.79(18)
C(8)	C(7)	C(6)	114.75(15)	C(25)	C(24)	S(3)	120.27(17)
C(7)	C(8)	S(1)	117.34(12)	C(25)	C(24)	C(23)	121.0(2)
C(9)	C(8)	S(1)	120.45(14)	O(3)	C(25)	C(26)	109.74(17)
C(9)	C(8)	C(7)	121.92(15)	C(24)	C(25)	O(3)	121.36(18)
O(1)	C(9)	C(8)	120.84(16)	C(24)	C(25)	C(26)	128.86(19)
O(1)	C(9)	C(10)	109.22(14)	C(27)	C(26)	C(25)	122.36(19)
C(8)	C(9)	C(10)	129.92(15)	C(31)	C(26)	C(25)	118.57(19)
C(11)	C(10)	C(9)	122.29(16)	C(31)	C(26)	C(27)	119.01(19)
C(11)	C(10)	C(15)	118.60(18)	C(28)	C(27)	C(26)	120.1(2)
C(15)	C(10)	C(9)	119.05(16)	C(29)	C(28)	C(27)	120.3(2)
C(12)	C(11)	C(10)	120.15(19)	C(30)	C(29)	C(28)	119.6(2)
C(13)	C(12)	C(11)	120.6(2)	C(29)	C(30)	C(31)	120.8(2)
C(12)	C(13)	C(14)	119.9(2)	C(30)	C(31)	C(26)	120.1(2)
C(13)	C(14)	C(15)	120.3(2)	S(3)	C(32)	D(32)	108.8
C(14)	C(15)	C(10)	120.5(2)	F(5)	C(32)	S(3)	112.8(3)

Table S10 Bond Angles for mo230831a.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
S(1)	C(16)	D(16)	110.4	F(5)	C(32)	F(6)	124.4(6)
F(1)	C(16)	S(1)	112.23(14)	F(5)	C(32)	D(32)	108.8
F(1)	C(16)	D(16)	110.4	F(6)	C(32)	S(3)	91.5(6)
F(2)	C(16)	S(1)	107.92(14)	F(6)	C(32)	D(32)	108.8
F(2)	C(16)	F(1)	105.33(17)	S(2)	C(33)	D(33)	107.1
F(2)	C(16)	D(16)	110.4	F(3)	C(33)	S(2)	90.7(6)
C(33)	S(2)	C(24)	97.8(2)	F(3)	C(33)	D(33)	107.1
C(32)	S(3)	C(24)	97.07(18)	F(4)	C(33)	S(2)	110.7(5)
C(25)	O(3)	C(17)	120.68(16)	F(4)	C(33)	F(3)	131.5(7)
O(3)	C(17)	C(18)	116.53(19)	F(4)	C(33)	D(33)	107.1
O(3)	C(17)	C(22)	121.48(17)				

Table S11 Torsion Angles for mo230831a.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
S(1)	C(8)	C(9)	O(1)	171.40(11)	O(3)	C(17)	C(18)	C(19)	180.0(2)
S(1)	C(8)	C(9)	C(10)	-7.1(2)	O(3)	C(17)	C(22)	C(21)	-179.33(18)
O(1)	C(1)	C(2)	C(3)	-177.78(16)	O(3)	C(17)	C(22)	C(23)	3.9(3)
O(1)	C(1)	C(6)	C(5)	178.18(15)	O(3)	C(25)	C(26)	C(27)	-141.2(2)
O(1)	C(1)	C(6)	C(7)	-0.2(2)	O(3)	C(25)	C(26)	C(31)	36.1(3)
O(1)	C(9)	C(10)	C(11)	139.57(16)	O(4)	C(23)	C(24)	S(2)	21.3(4)
O(1)	C(9)	C(10)	C(15)	-37.8(2)	O(4)	C(23)	C(24)	S(3)	-27.1(4)
O(2)	C(7)	C(8)	S(1)	5.8(2)	O(4)	C(23)	C(24)	C(25)	174.7(3)
O(2)	C(7)	C(8)	C(9)	179.60(17)	C(17)	O(3)	C(25)	C(24)	0.7(3)
C(1)	O(1)	C(9)	C(8)	4.6(2)	C(17)	O(3)	C(25)	C(26)	-177.12(15)
C(1)	O(1)	C(9)	C(10)	-176.64(13)	C(17)	C(18)	C(19)	C(20)	-0.7(4)
C(1)	C(2)	C(3)	C(4)	-0.8(3)	C(17)	C(22)	C(23)	O(4)	-179.7(3)
C(1)	C(6)	C(7)	O(2)	-178.48(16)	C(17)	C(22)	C(23)	C(24)	2.4(3)

Table S11 Torsion Angles for mo230831a.

A	B	C	D	Angle/˚	A	B	C	D	Angle/˚
C(1)	C(6)	C(7)	C(8)	2.4(2)	C(18)	C(17)	C(22)	C(21)	0.2(3)
C(2)	C(1)	C(6)	C(5)	-0.2(2)	C(18)	C(17)	C(22)	C(23)	-176.6(2)
C(2)	C(1)	C(6)	C(7)	-178.53(15)	C(18)	C(19)	C(20)	C(21)	0.2(4)
C(2)	C(3)	C(4)	C(5)	0.5(3)	C(19)	C(20)	C(21)	C(22)	0.5(4)
C(3)	C(4)	C(5)	C(6)	0.0(3)	C(20)	C(21)	C(22)	C(17)	-0.6(3)
C(4)	C(5)	C(6)	C(1)	-0.1(3)	C(20)	C(21)	C(22)	C(23)	176.1(2)
C(4)	C(5)	C(6)	C(7)	178.15(17)	C(21)	C(22)	C(23)	O(4)	3.7(4)
C(5)	C(6)	C(7)	O(2)	3.2(3)	C(21)	C(22)	C(23)	C(24)	-174.2(2)
C(5)	C(6)	C(7)	C(8)	-175.91(15)	C(22)	C(17)	C(18)	C(19)	0.5(3)
C(6)	C(1)	C(2)	C(3)	0.7(3)	C(22)	C(23)	C(24)	S(2)	-160.8(2)
C(6)	C(7)	C(8)	S(1)	-175.01(11)	C(22)	C(23)	C(24)	S(3)	150.8(2)
C(6)	C(7)	C(8)	C(9)	-1.3(2)	C(22)	C(23)	C(24)	C(25)	-7.3(4)
C(7)	C(8)	C(9)	O(1)	-2.2(2)	C(23)	C(24)	C(25)	O(3)	6.0(4)
C(7)	C(8)	C(9)	C(10)	179.33(15)	C(23)	C(24)	C(25)	C(26)	-176.6(2)
C(8)	S(1)	C(16)	F(1)	-88.66(16)	C(24)	S(2)	C(33)	F(3)	-177.4(5)
C(8)	S(1)	C(16)	F(2)	155.73(15)	C(24)	S(2)	C(33)	F(4)	-42.0(5)
C(8)	C(9)	C(10)	C(11)	-41.8(3)	C(24)	S(3)	C(32)	F(5)	61.6(4)
C(8)	C(9)	C(10)	C(15)	140.87(18)	C(24)	S(3)	C(32)	F(6)	-169.8(5)
C(9)	O(1)	C(1)	C(2)	175.05(14)	C(24)	C(25)	C(26)	C(27)	41.2(4)
C(9)	O(1)	C(1)	C(6)	-3.4(2)	C(24)	C(25)	C(26)	C(31)	-141.6(3)
C(9)	C(10)	C(11)	C(12)	-177.80(16)	C(25)	O(3)	C(17)	C(18)	174.67(19)
C(9)	C(10)	C(15)	C(14)	178.23(18)	C(25)	O(3)	C(17)	C(22)	-5.8(3)
C(10)	C(11)	C(12)	C(13)	-0.3(3)	C(25)	C(26)	C(27)	C(28)	179.1(2)
C(11)	C(10)	C(15)	C(14)	0.8(3)	C(25)	C(26)	C(31)	C(30)	-179.0(2)
C(11)	C(12)	C(13)	C(14)	0.7(3)	C(26)	C(27)	C(28)	C(29)	-0.3(4)
C(12)	C(13)	C(14)	C(15)	-0.3(4)	C(27)	C(26)	C(31)	C(30)	-1.6(3)
C(13)	C(14)	C(15)	C(10)	-0.4(3)	C(27)	C(28)	C(29)	C(30)	-1.4(4)
C(15)	C(10)	C(11)	C(12)	-0.5(3)	C(28)	C(29)	C(30)	C(31)	1.6(4)
C(16)	S(1)	C(8)	C(7)	-69.52(14)	C(29)	C(30)	C(31)	C(26)	-0.1(4)

Table S11 Torsion Angles for mo230831a.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C(16)	S(1)	C(8)	C(9)	116.63(14)	C(31)	C(26)	C(27)	C(28)	1.8(3)
S(2)	C(24)	C(25)	O(3)	160.51(18)	C(32)	S(3)	C(24)	C(23)	67.1(3)
S(2)	C(24)	C(25)	C(26)	-22.1(4)	C(32)	S(3)	C(24)	C(25)	-134.6(3)
S(3)	C(24)	C(25)	O(3)	-151.05(18)	C(33)	S(2)	C(24)	C(23)	-47.4(4)
S(3)	C(24)	C(25)	C(26)	26.4(4)	C(33)	S(2)	C(24)	C(25)	157.5(3)

Table S12 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for mo230831a.

Atom	*x*	*y*	*z*	U(eq)
H(2)	8586.76	6453.85	5038.73	71
H(3)	9337.73	4678.41	3902.37	83
H(4)	7624.15	3486.81	2874.89	86
H(5)	5147.44	4087.55	2961.18	75
H(11)	3216.18	10476.48	5684.77	67
H(12)	3257.33	12392.59	6868.13	81
H(13)	4593.85	12276.01	8055.23	90
H(14)	5938.35	10252.25	8058.29	94
H(15)	5936.84	8331.91	6881.12	76
H(18)	-2599.77	2794.78	-876.94	91
H(19)	-2524.25	3580.55	-2086.21	102
H(20)	-313.7	4361.7	-2516.72	96
H(21)	1858.25	4363.36	-1758.42	87
H(27)	1850.14	3010.56	2137.38	93
H(28)	1126.04	2039.96	3211.05	105
H(29)	-777.8	299.99	2984.88	104
H(30)	-2012.56	-394.32	1704.55	98
H(31)	-1302.59	547.66	621.33	81

Table S13 Atomic Occupancy for mo230831a.

Atom	*Occupancy*	Atom	*Occupancy*	Atom	*Occupancy*
S(2)	0.4108(19)	S(3)	0.5892(19)	F(3)	0.4108(19)
F(4)	0.4108(19)	F(5)	0.5892(19)	F(6)	0.5892(19)
C(32)	0.5892(19)	D(32)	0.5892(19)	C(33)	0.4108(19)
D(33)	0.4108(19)				

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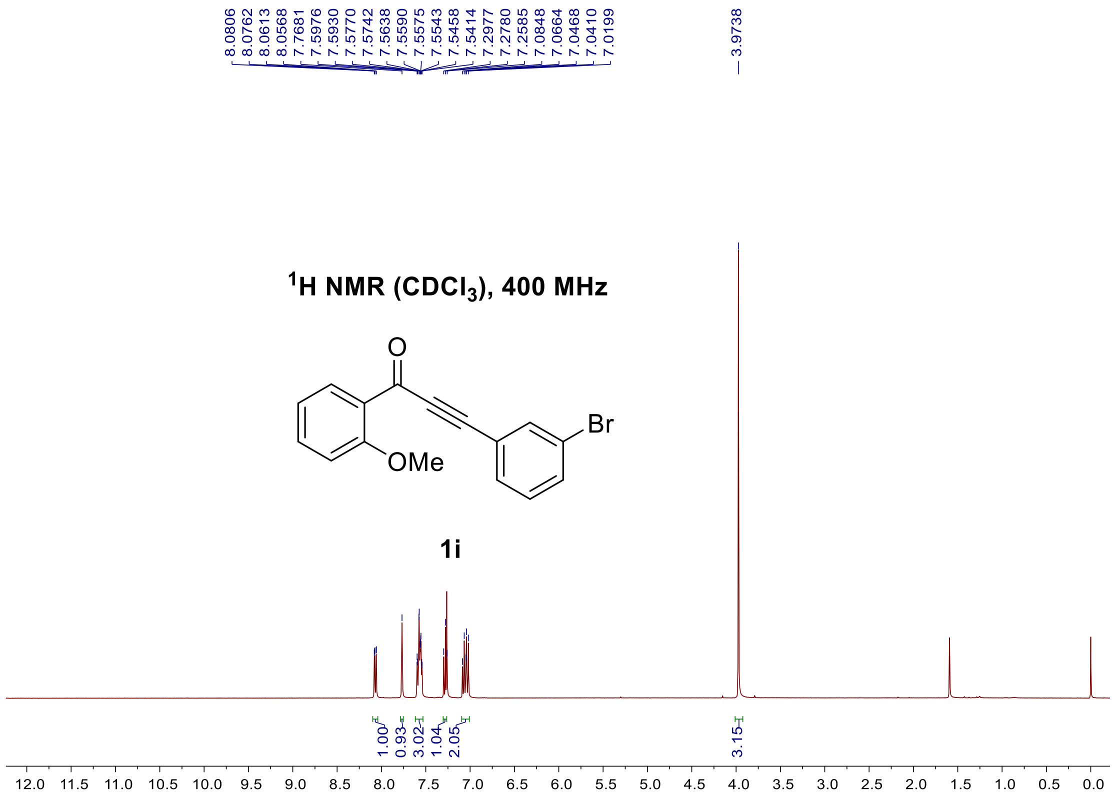
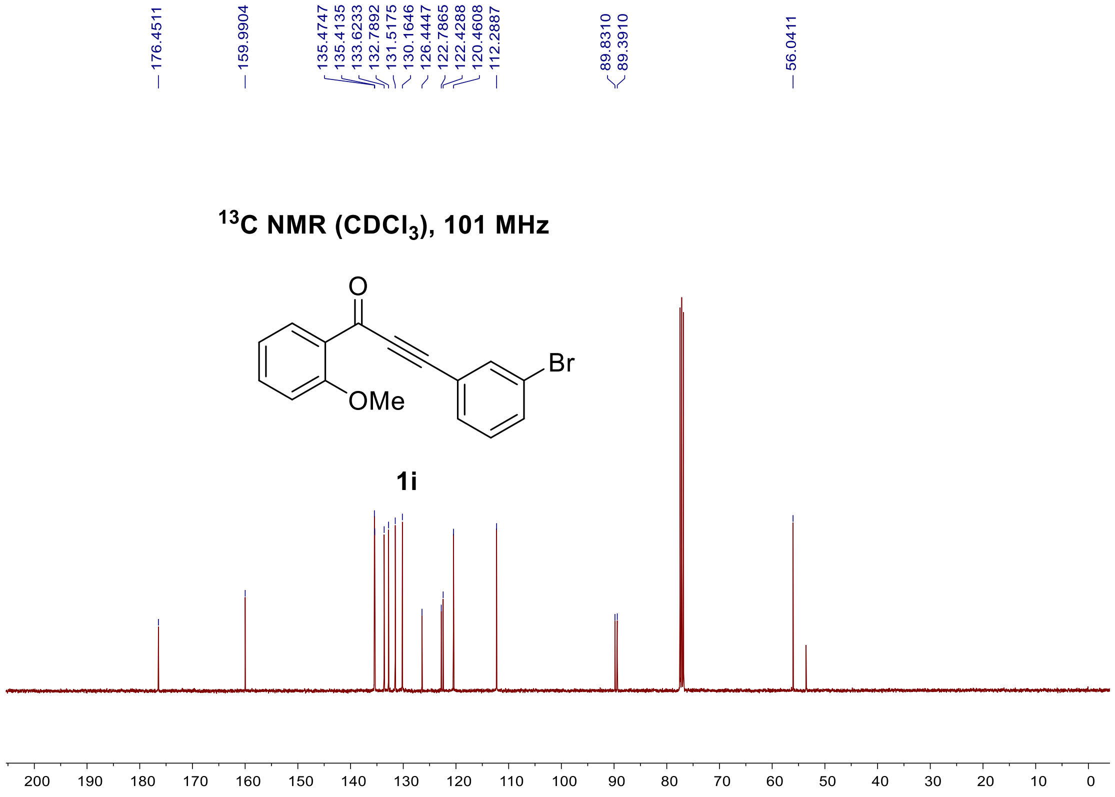
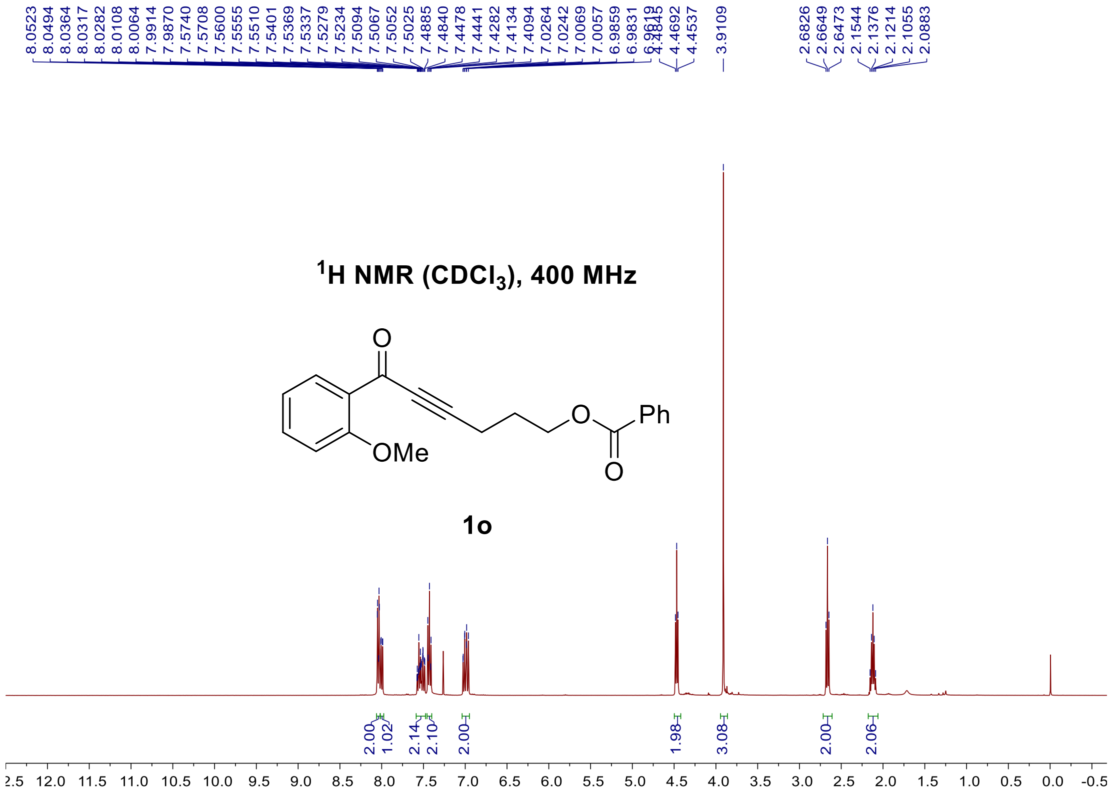
IX. NMR spectra



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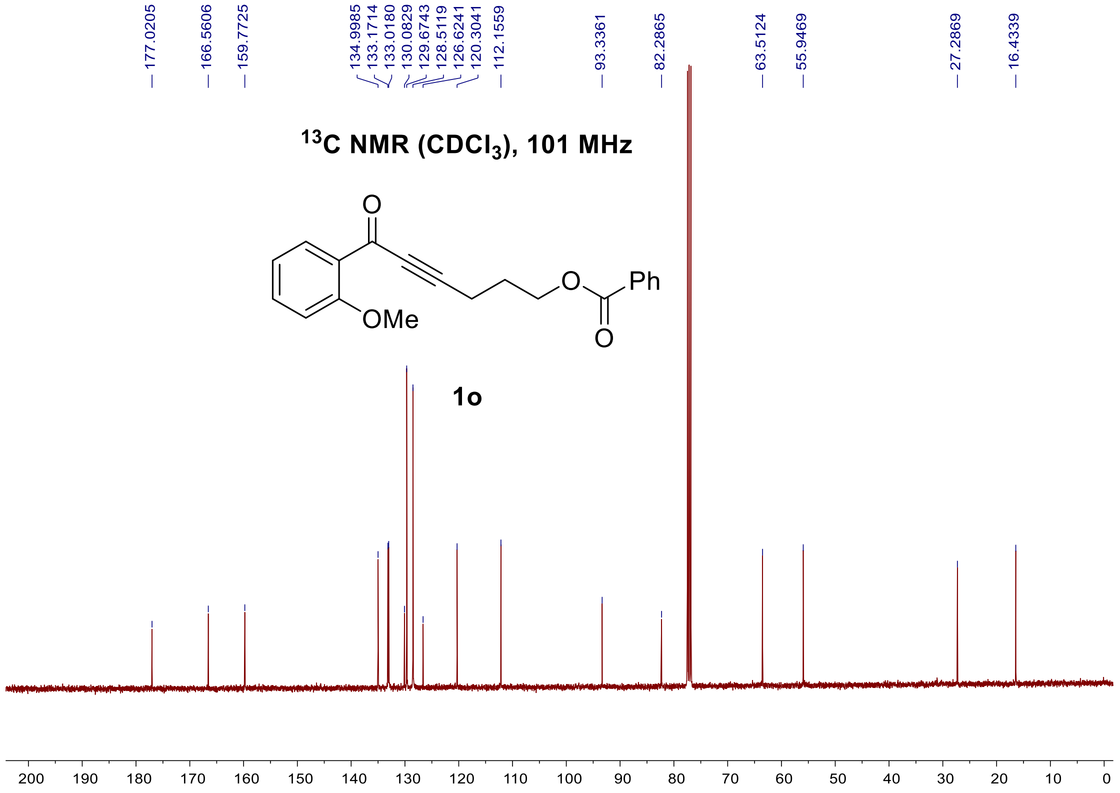
8.0494
8.0364
8.0317
8.0282
8.0108
8.0064
7.9914
7.9870
7.5740
7.5708
7.5600
7.5555
7.5510
7.5401
7.5369
7.5337
7.5279
7.5234
7.5094
7.5067
7.5052
7.5025
7.4885
7.4840
7.4478
7.4441
7.4282
7.4134
7.4094
7.0264
7.0242
7.0069
7.0057
6.9859
6.9831
6.9619
4.4845
4.4692
4.4537
3.9109
2.6826
2.6649
2.6473
2.1544
2.1376
2.1214
2.1055
2.0883
¹H NMR (CDCl₃), 400 MHz
O
OMe
O
Ph
O
1o
2.00
1.02
2.14
2.10
2.00
1.98
3.08
2.00
2.06
2.5
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5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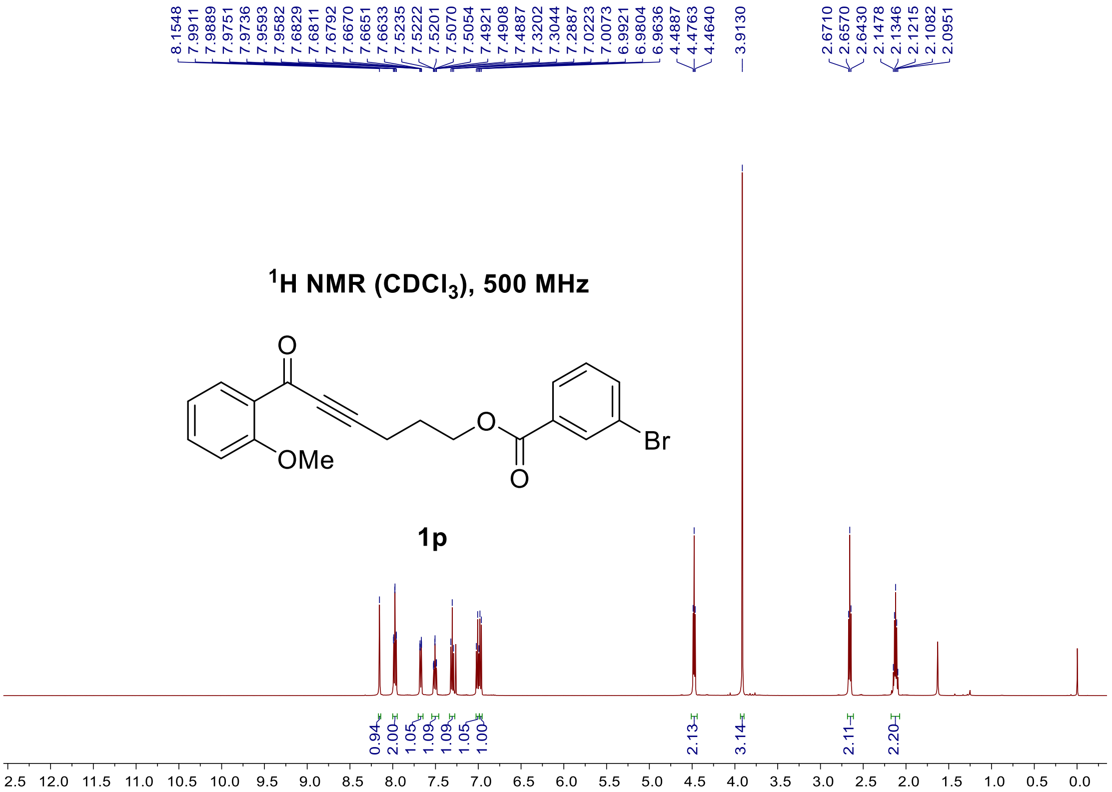
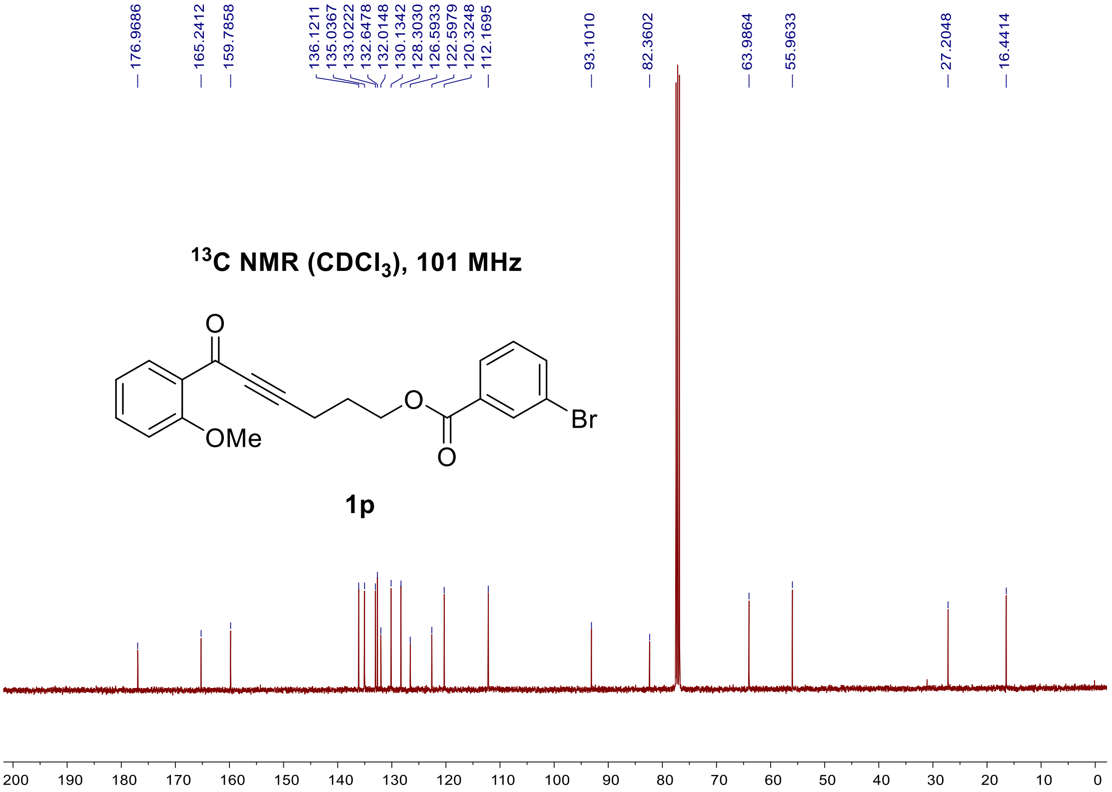
166.5606
159.7725
134.9985
133.1714
133.0180
130.0829
129.6743
128.5119
126.6241
120.3041
112.1559
93.3361
82.2865
63.5124
55.9469
27.2869
16.4339
¹³C NMR (CDCl₃), 101 MHz
O
OMe
O
Ph
O
1o
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


8.1548
7.9911
7.9889
7.9751
7.9736
7.9593
7.9582
7.6829
7.6811
7.6792
7.6670
7.6651
7.6633
7.5235
7.5222
7.5201
7.5070
7.5054
7.4921
7.4908
7.4887
7.3202
7.3044
7.2887
7.0223
7.0073
6.9921
6.9804
6.9636
4.4887
4.4763
4.4640
3.9130
2.6710
2.6570
2.6430
2.1478
2.1346
2.1215
2.1082
2.0951
^{1}H NMR (CDCl$_3$), 500 MHz
O
OMe
O
Br
O
1p
0.94
2.00
1.05
1.09
1.09
1.05
1.00
2.13
3.14
2.11
2.20
2.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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159.7858
136.1211
135.0367
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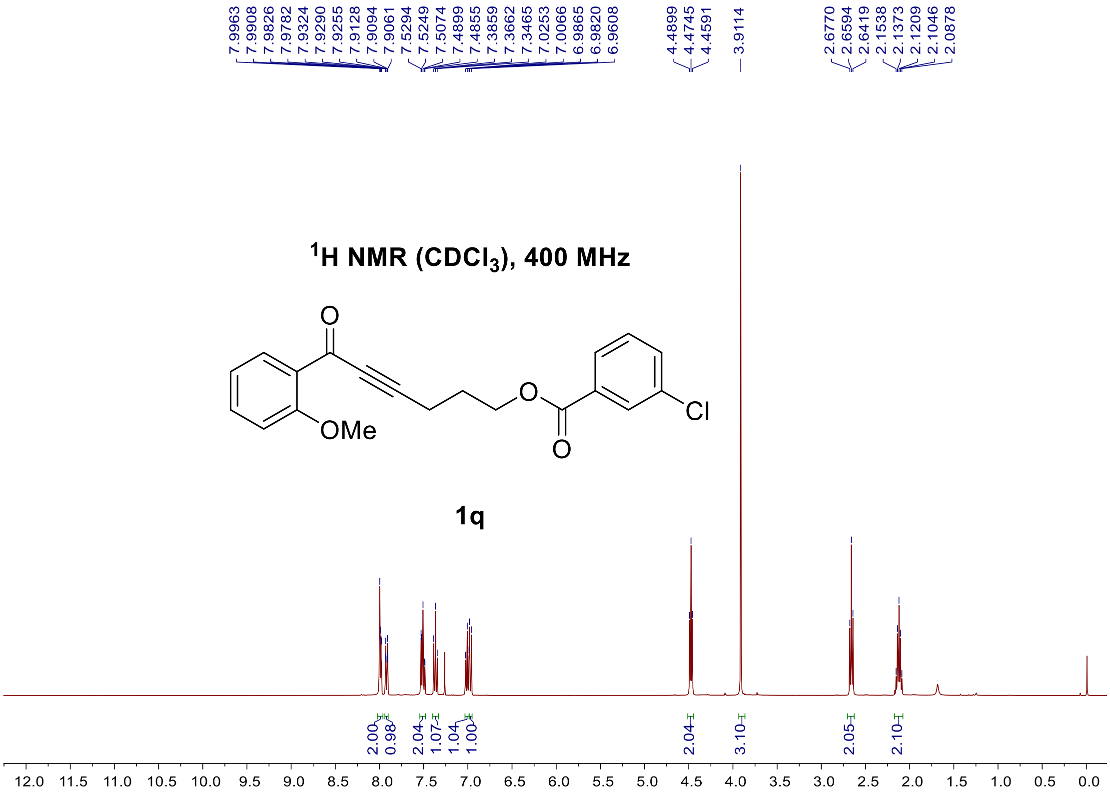
132.6478
132.0148
130.1342
128.3030
126.5933
122.5979
120.3248
112.1695
93.1010
82.3602
63.9864
55.9633
27.2048
16.4414
^{13}C NMR (CDCl$_3$), 101 MHz
O
OMe
O
Br
O
1p
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0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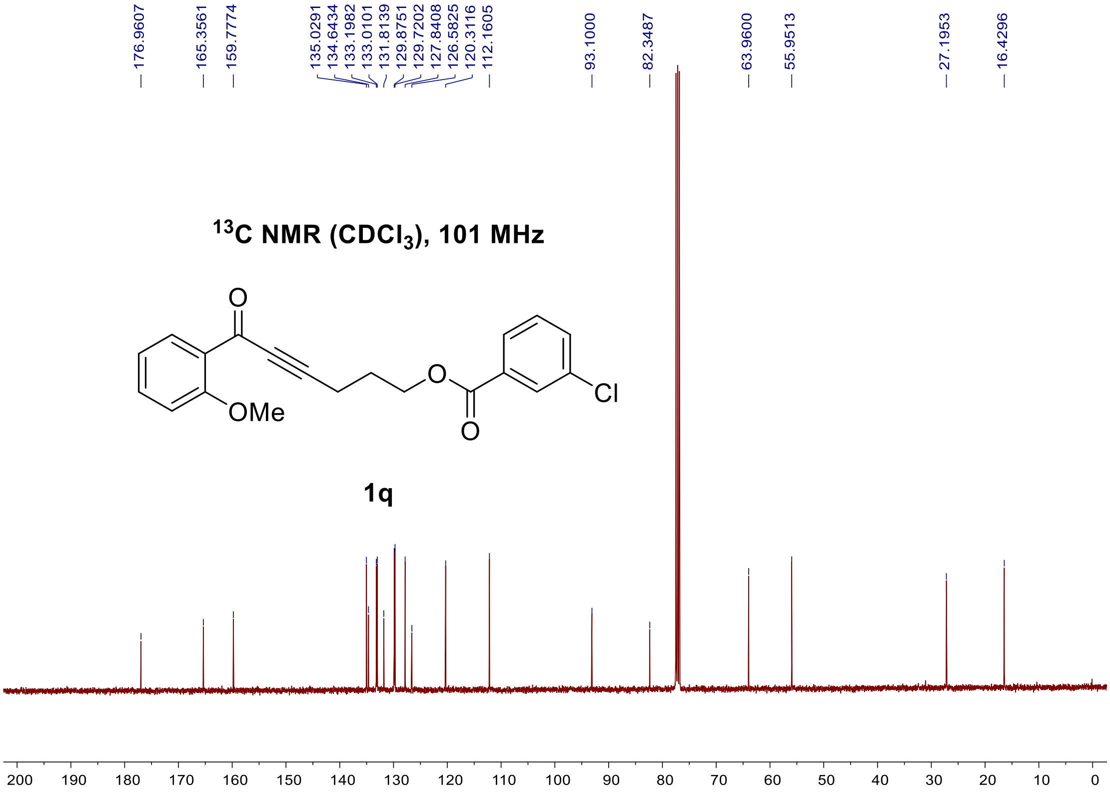
7.9908
7.9826
7.9782
7.9324
7.9290
7.9255
7.9128
7.9094
7.9061
7.5294
7.5249
7.5074
7.4899
7.4855
7.3859
7.3662
7.3465
7.0253
7.0066
6.9865
6.9820
6.9608
4.4899
4.4745
4.4591
3.9114
2.6770
2.6594
2.6419
2.1538
2.1373
2.1209
2.1046
2.0878
^{1}H NMR (CDCl$_3$), 400 MHz
O
OMe
O
O
Cl
1q
2.00
0.98
2.04
1.07
1.04
1.00
2.04
3.10
2.05
2.10
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0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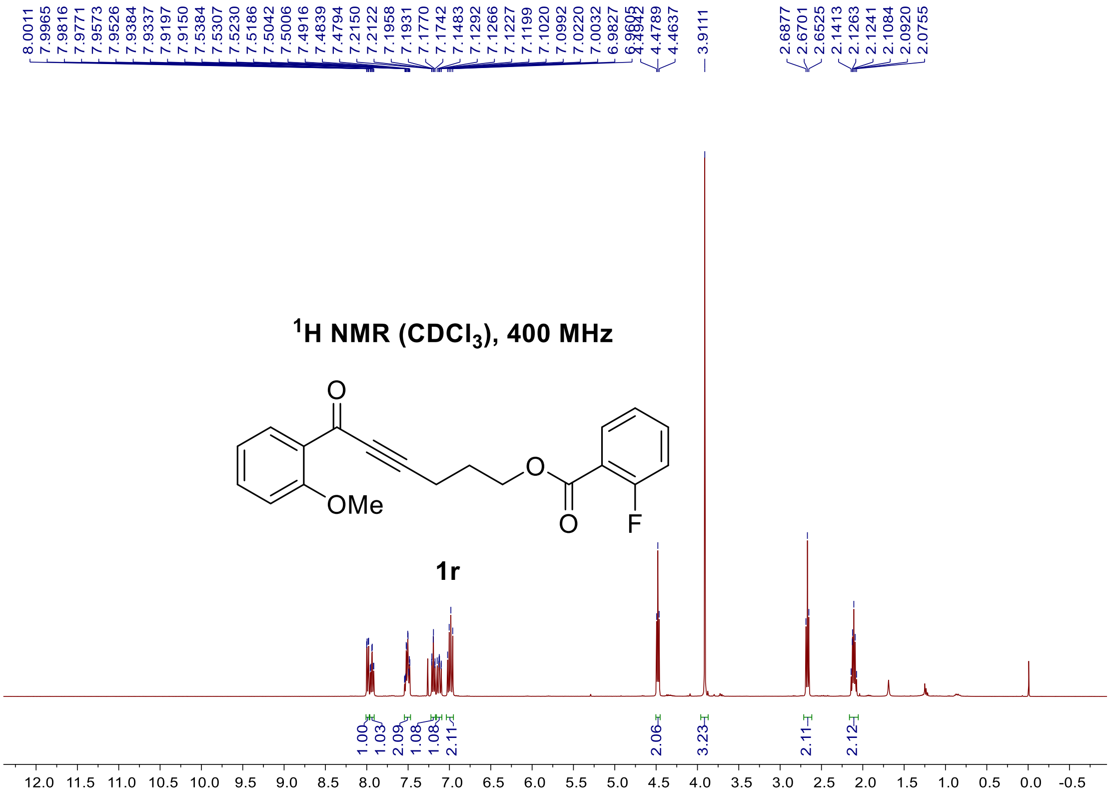
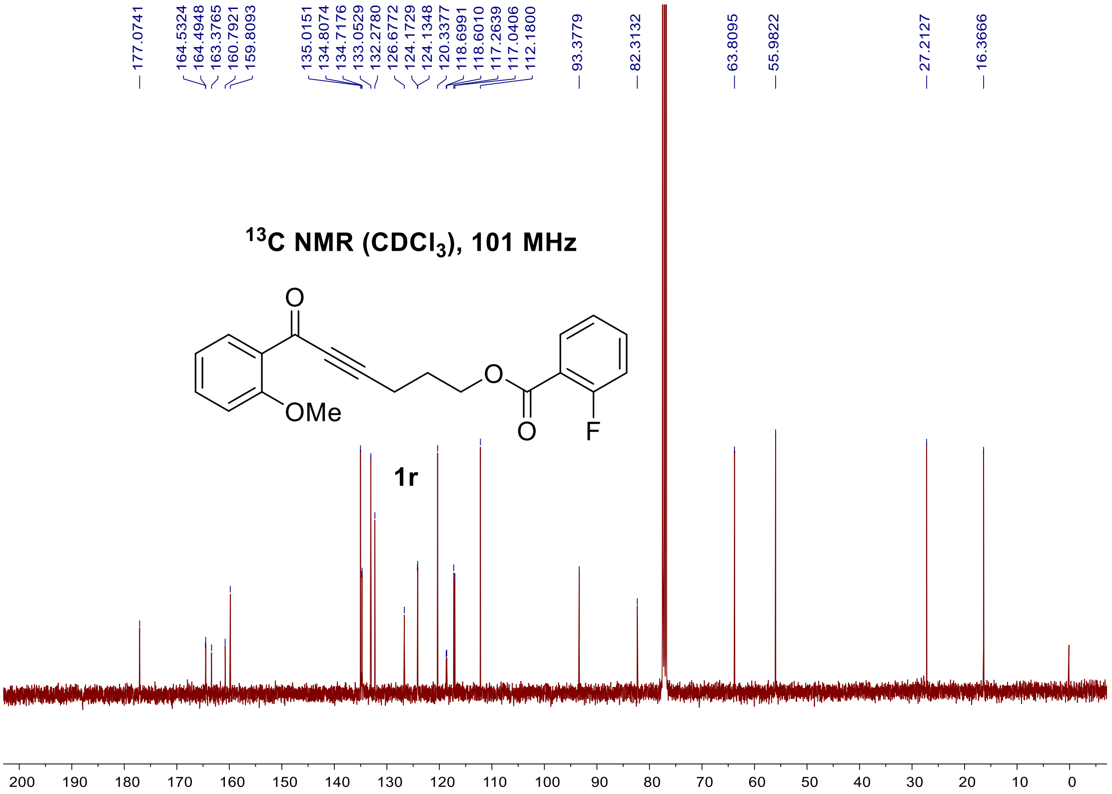
165.3561
159.7774
135.0291
134.6434
133.1982
133.0101
131.8139
129.8751
129.7202
127.8408
126.5825
120.3116
112.1605
93.1000
82.3487
63.9600
55.9513
27.1953
16.4296
^{13}C NMR (CDCl$_3$), 101 MHz
O
OMe
O
O
Cl
1q
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0



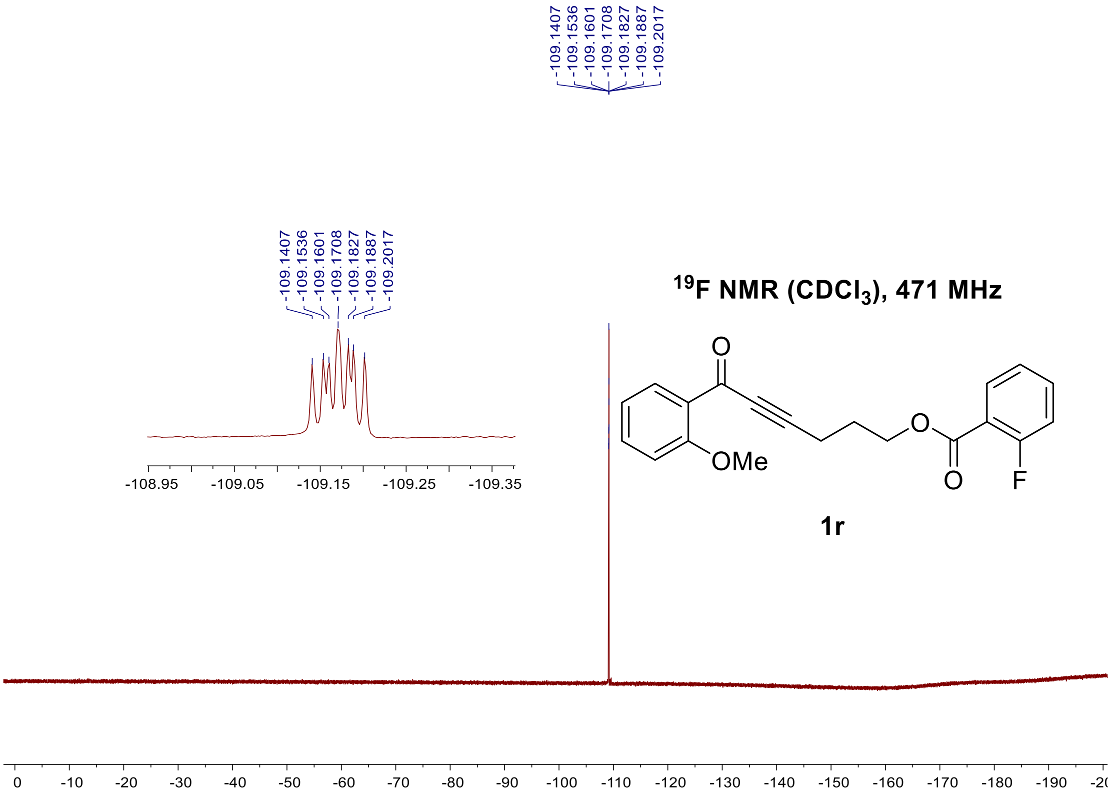
^{1}H NMR (CDCl$_3$), 400 MHz

1r



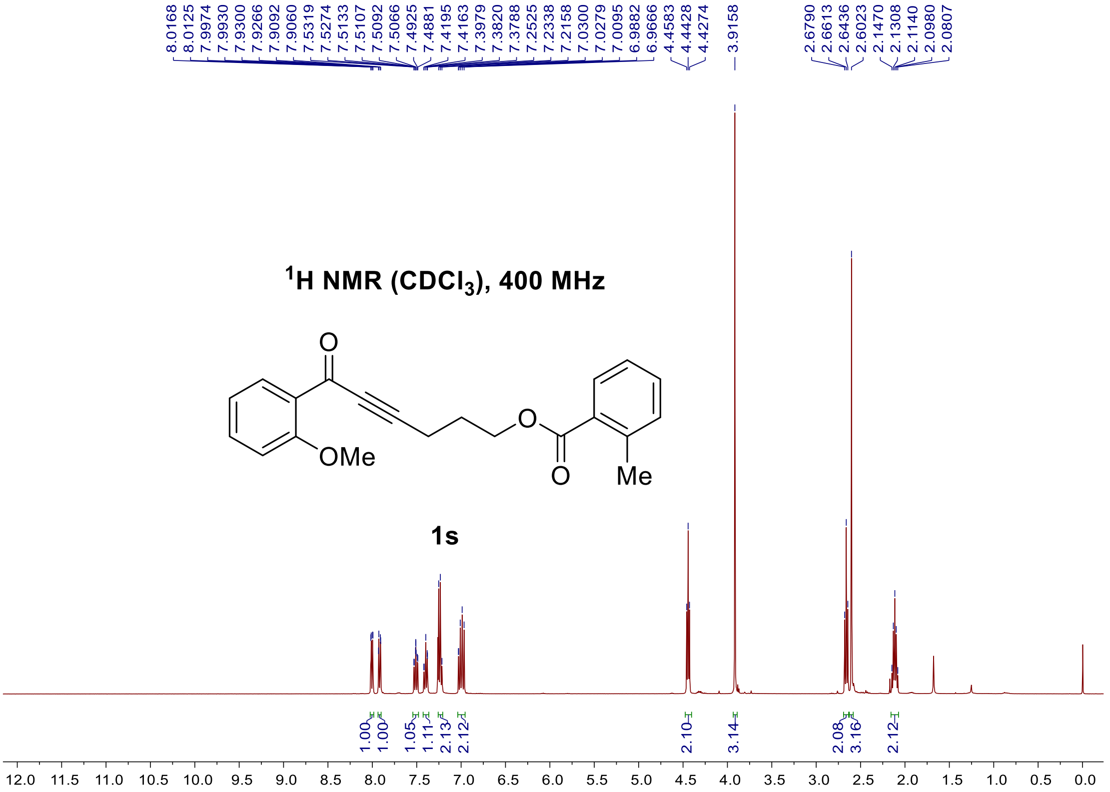
^{13}C NMR (CDCl$_3$), 101 MHz

1r



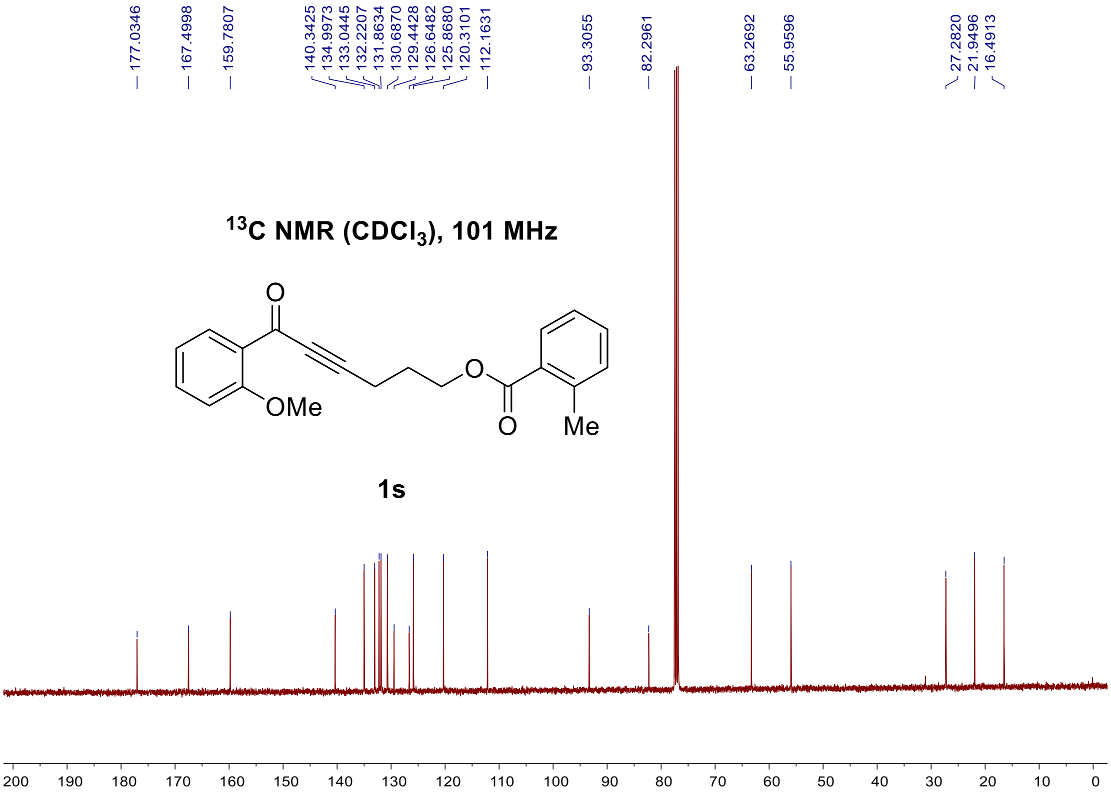
^{19}F NMR (CDCl$_3$), 471 MHz

1r



^{1}H NMR (CDCl$_3$), 400 MHz

1s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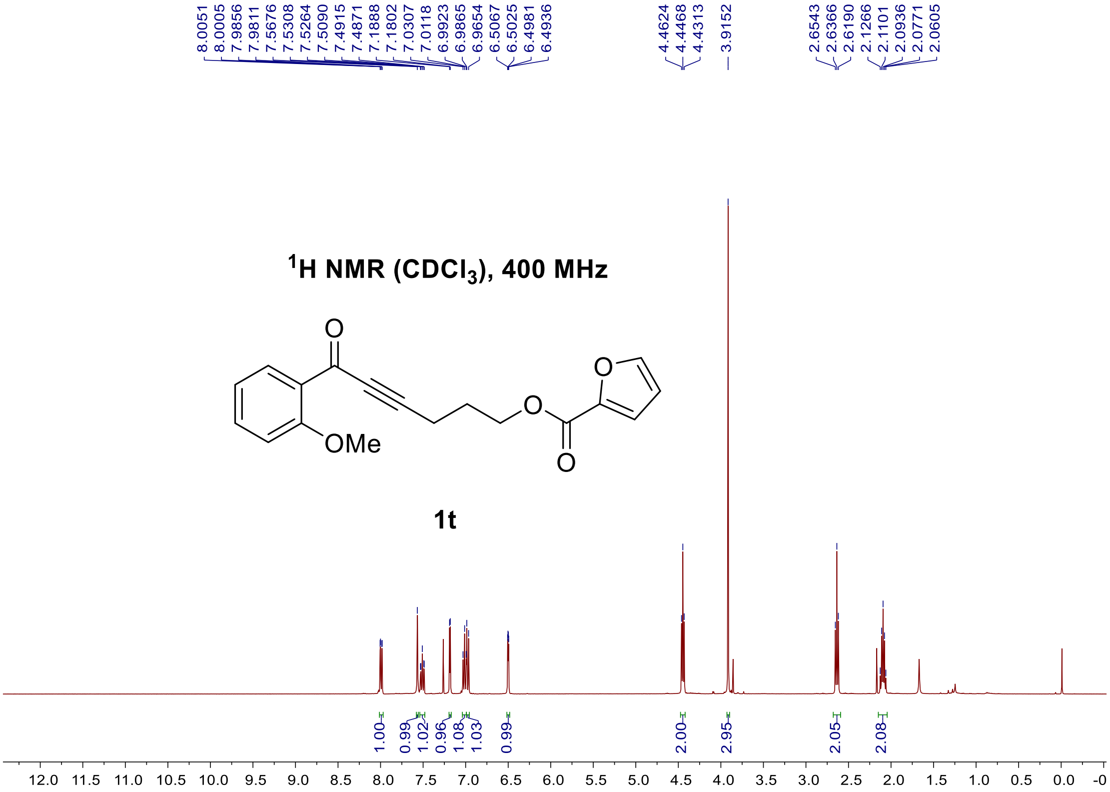
159.7807
140.3425
134.9973
133.0445
132.2207
131.8634
130.6870
129.4428
126.6482
125.8680
120.3101
112.1631
93.3055
82.2961
63.2692
55.9596
27.2820
21.9496
16.4913
^{13}C NMR (CDCl$_3$), 101 MHz
O
OMe
O
O
Me
1s
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0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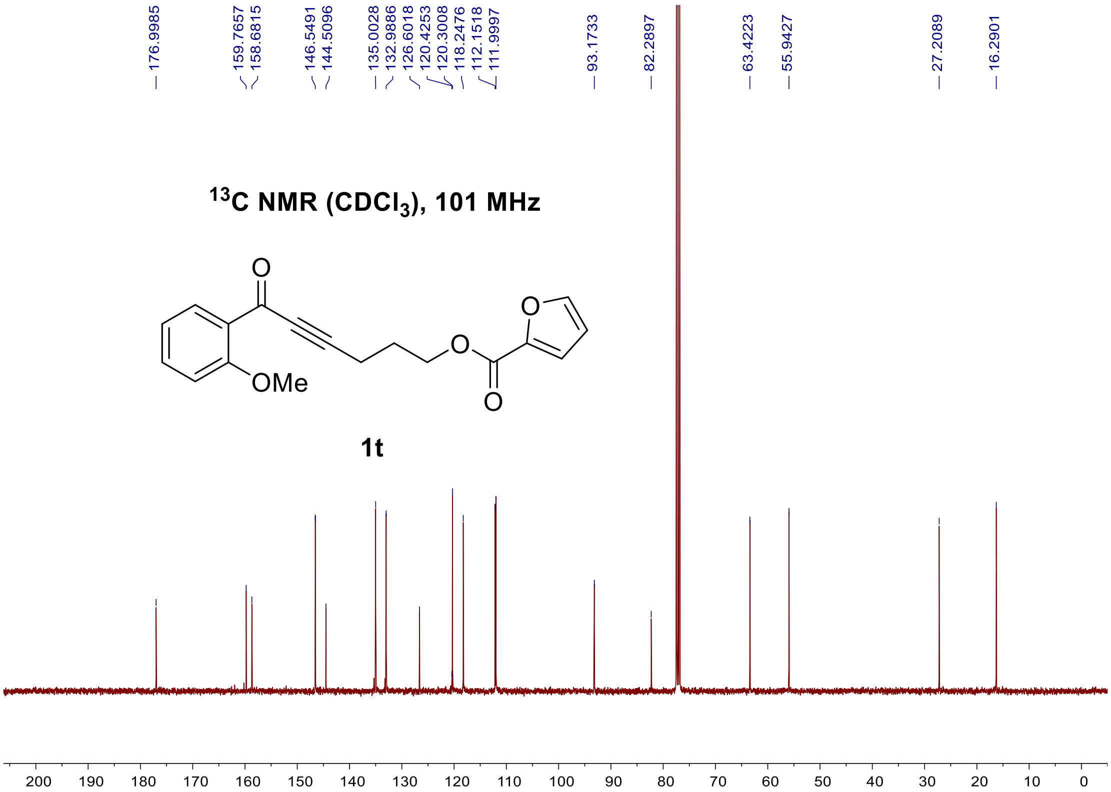
7.9856
7.9811
7.5676
7.5308
7.5264
7.5090
7.4915
7.4871
7.1888
7.1802
7.0307
7.0118
6.9923
6.9865
6.9654
6.5067
6.5025
6.4981
6.4936
4.4624
4.4468
4.4313
3.9152
2.6543
2.6366
2.6190
2.1266
2.1101
2.0936
2.0771
2.0605
^{1}H NMR (CDCl$_3$), 400 MHz
O
O
OMe
O
O
1t
1.00
0.99
1.02
0.96
1.08
1.03
0.99
2.00
2.95
2.05
2.08
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0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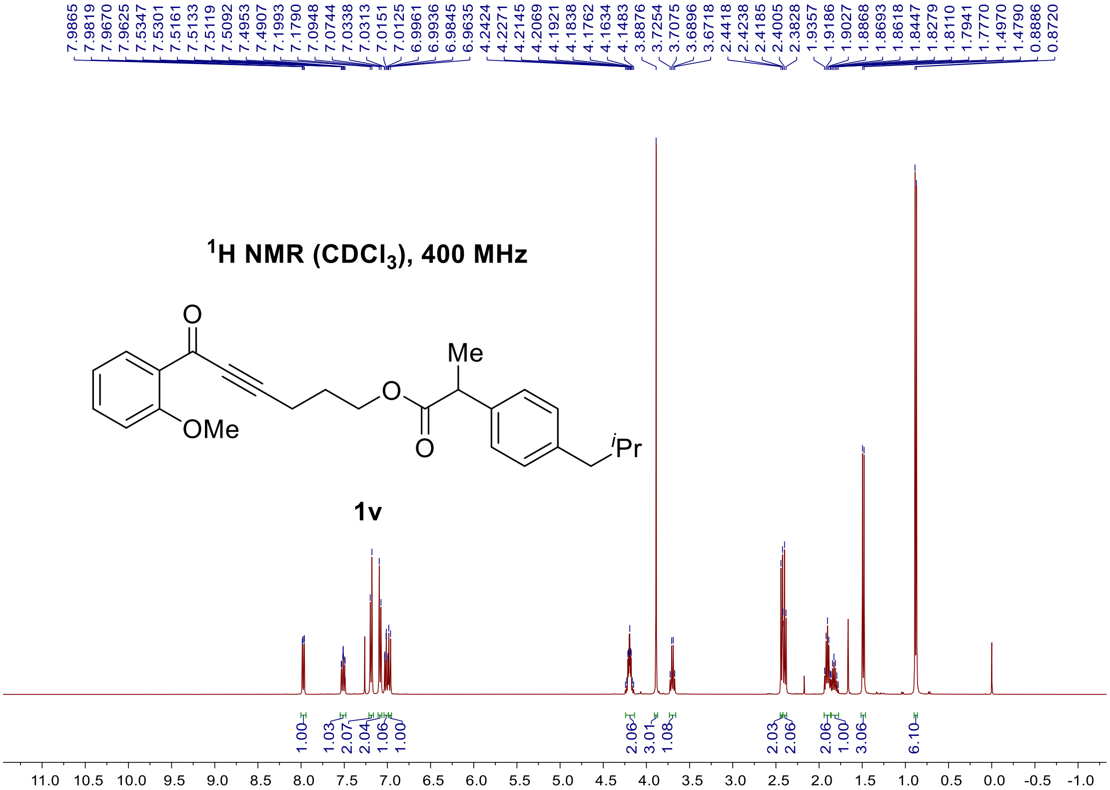
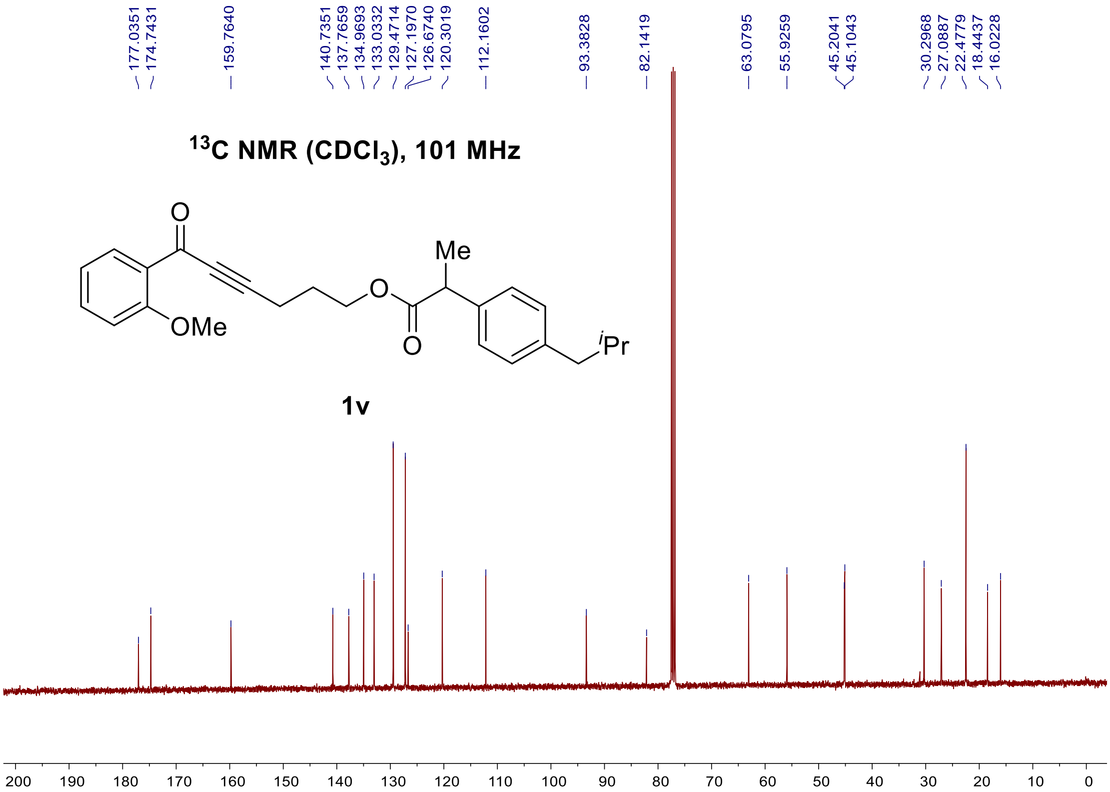
158.6815
146.5491
144.5096
135.0028
132.9886
126.6018
120.4253
120.3008
118.2476
112.1518
111.9997
93.1733
82.2897
63.4223
55.9427
27.2089
16.2901
^{13}C NMR (CDCl$_3$), 101 MHz
O
OMe
O
O
O
1t
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


7.9865
7.9819
7.9670
7.9625
7.5347
7.5301
7.5161
7.5133
7.5119
7.5092
7.4953
7.4907
7.1993
7.1790
7.0948
7.0744
7.0338
7.0313
7.0151
7.0125
6.9961
6.9936
6.9845
6.9635
4.2424
4.2271
4.2145
4.2069
4.1921
4.1838
4.1762
4.1634
4.1483
3.8876
3.7254
3.7075
3.6896
3.6718
2.4418
2.4238
2.4185
2.4005
2.3828
1.9357
1.9186
1.9027
1.8868
1.8693
1.8618
1.8447
1.8279
1.8110
1.7941
1.7770
1.4970
1.4790
0.8886
0.8720
^{1}H NMR (CDCl$_3$), 400 MHz
O
Me
OMe
O
O
^{i}Pr
1v
1.00
1.03
2.07
2.04
1.06
1.00
2.06
3.01
1.08
2.03
2.06
2.06
1.00
3.06
6.10
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0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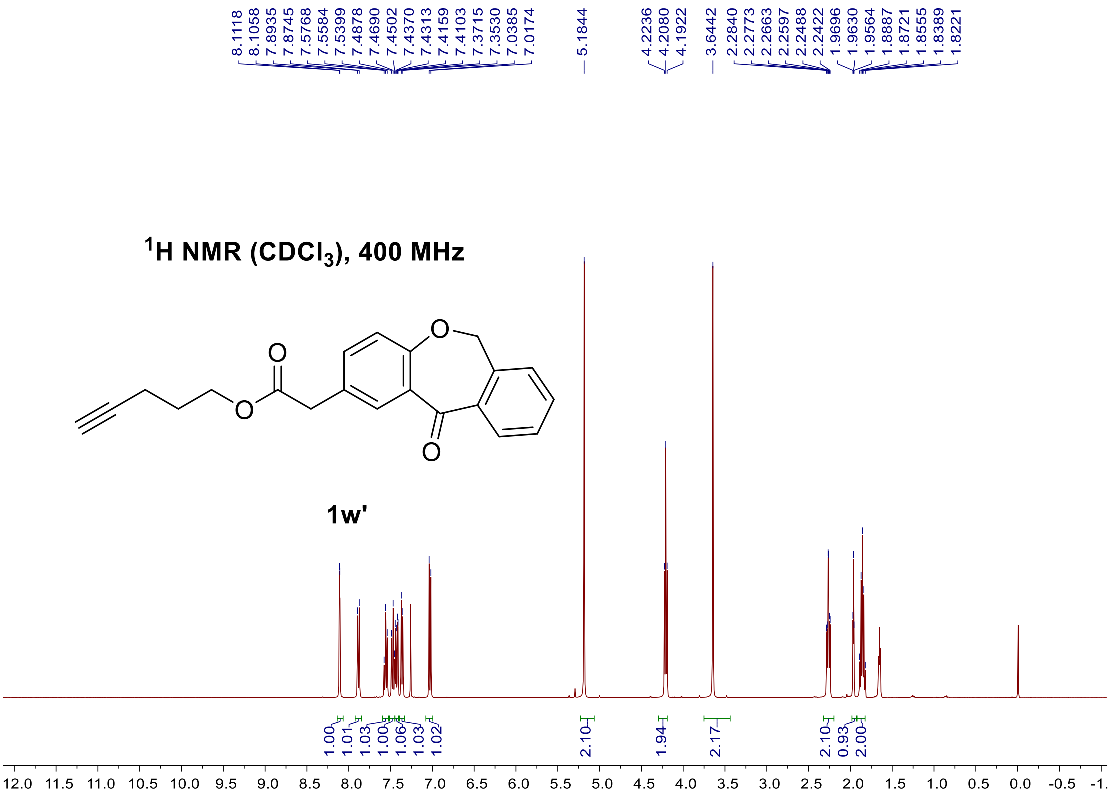
174.7431
159.7640
140.7351
137.7659
134.9693
133.0332
129.4714
127.1970
126.6740
120.3019
112.1602
93.3828
82.1419
63.0795
55.9259
45.2041
45.1043
30.2968
27.0887
22.4779
18.4437
16.0228
13C NMR (CDCl3), 101 MHz
O
Me
O
OMe
O
iPr
1v
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


8.1118
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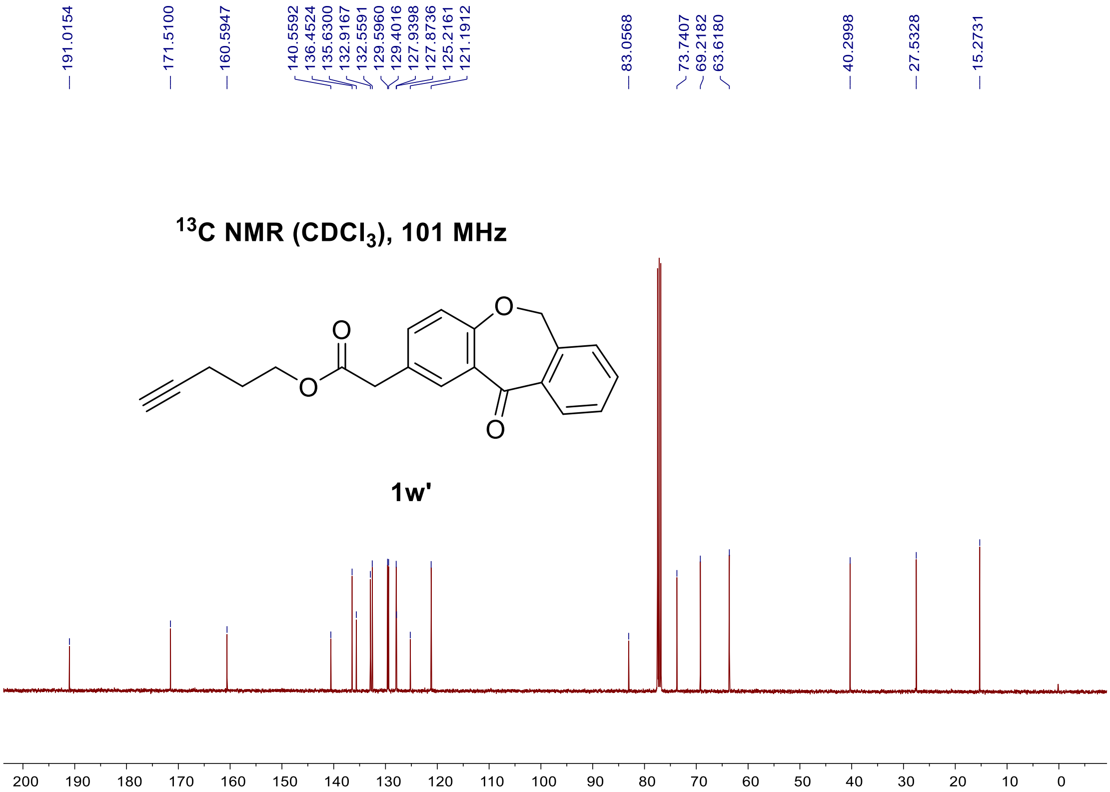
7.8935
7.8745
7.5768
7.5584
7.5399
7.4878
7.4690
7.4502
7.4370
7.4313
7.4159
7.4103
7.3715
7.3530
7.0385
7.0174
5.1844
4.2236
4.2080
4.1922
3.6442
2.2840
2.2773
2.2663
2.2597
2.2488
2.2422
1.9696
1.9630
1.9564
1.8887
1.8721
1.8555
1.8389
1.8221
1H NMR (CDCl3), 400 MHz
O
O
O
O
1w'
1.00
1.01
1.03
1.00
1.06
1.03
1.02
2.10
1.94
2.17
2.10
0.93
2.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.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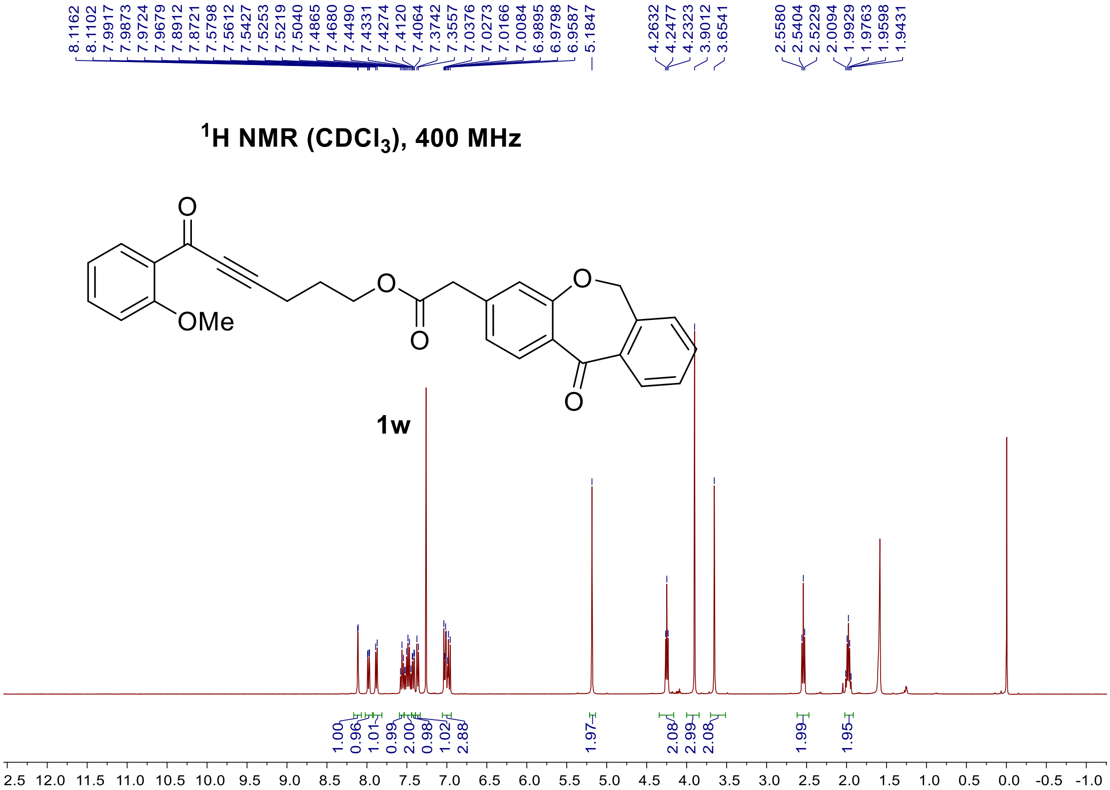
160.5947
140.5592
136.4524
135.6300
132.9167
132.5591
129.5960
129.4016
127.9398
127.8736
125.2161
121.1912
83.0568
73.7407
69.2182
63.6180
40.2998
27.5328
15.2731
^{13}C NMR (CDCl$_3$), 101 MHz
O
O
O
O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

1w'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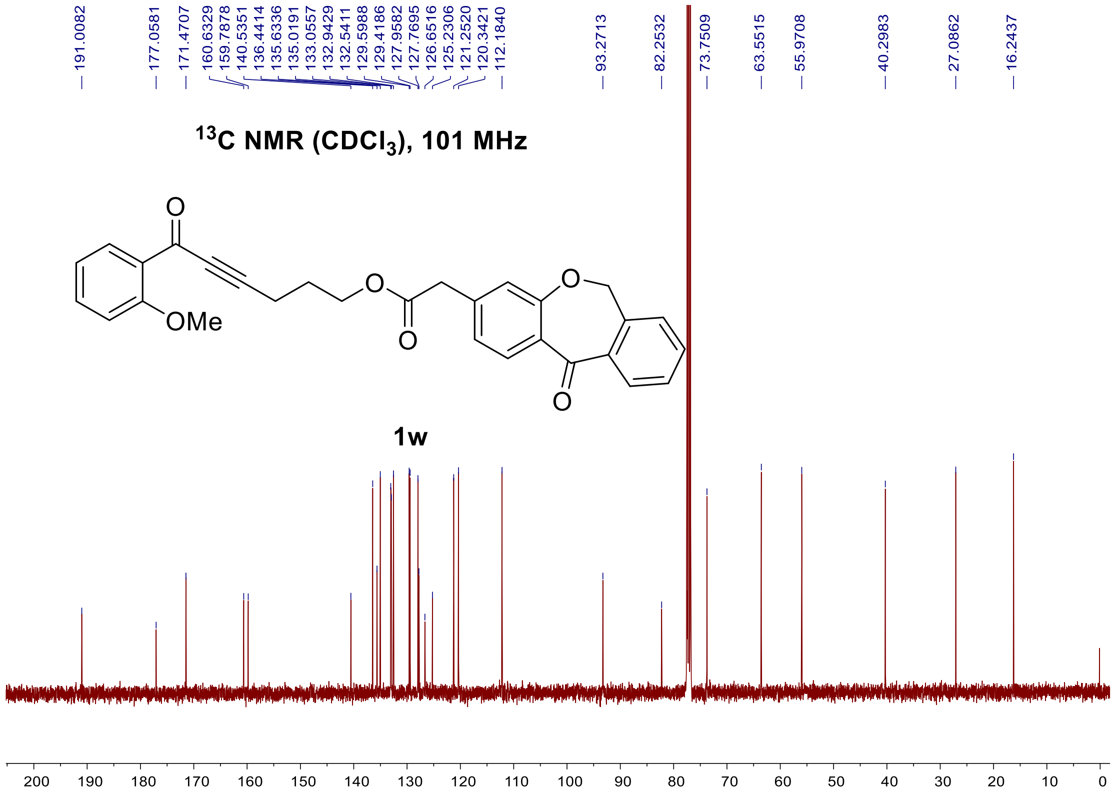
8.1102
7.9917
7.9873
7.9724
7.9679
7.8912
7.8721
7.5798
7.5612
7.5427
7.5253
7.5219
7.5040
7.4865
7.4680
7.4490
7.4331
7.4274
7.4120
7.4064
7.3742
7.3557
7.0376
7.0273
7.0166
7.0084
6.9895
6.9798
6.9587
5.1847
4.2632
4.2477
4.2323
3.9012
3.6541
2.5580
2.5404
2.5229
2.0094
1.9929
1.9763
1.9598
1.9431
^{1}H NMR (CDCl$_3$), 400 MHz
O
OMe
O
O
O
O
1.00
0.96
1.01
0.99
2.00
0.98
1.02
2.88
1.97
2.08
2.99
2.08
1.99
1.95
2.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0

1w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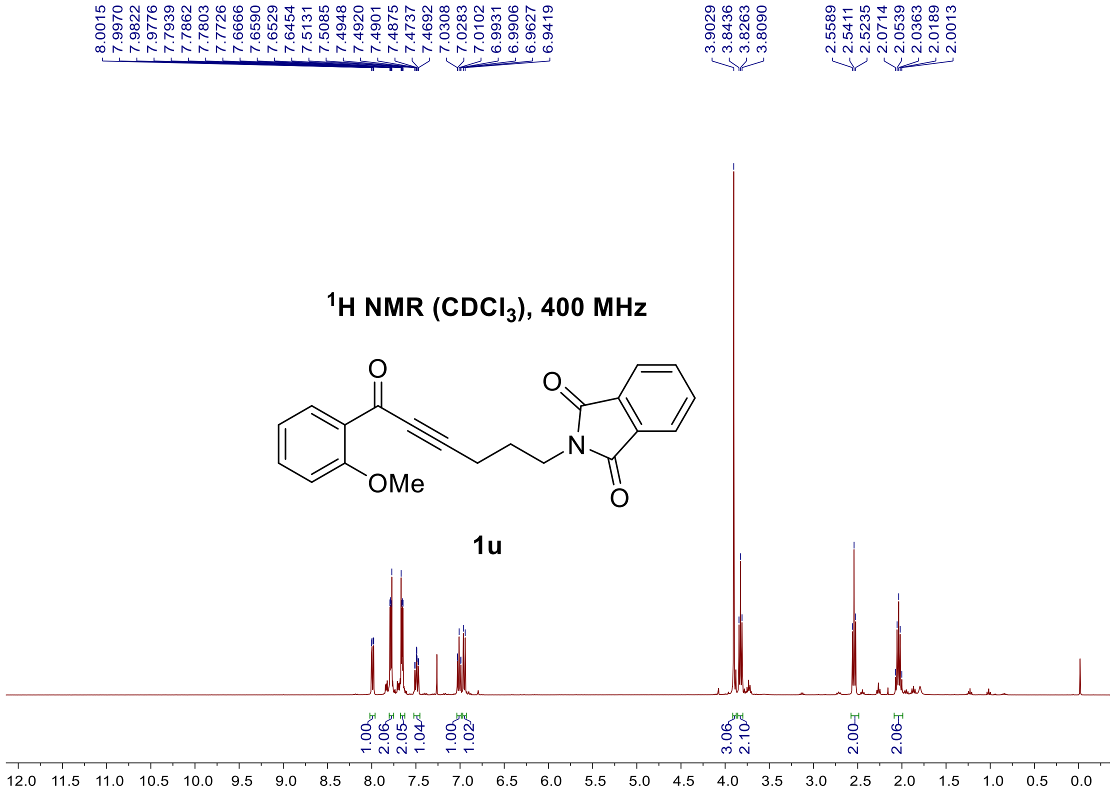
171.4707
160.6329
159.7878
140.5351
136.4414
135.6336
135.0191
133.0557
132.9429
132.5411
129.5988
129.4186
127.9582
127.7695
126.6516
125.2306
121.2520
120.3421
112.1840
93.2713
82.2532
73.7509
63.5515
55.9708
40.2983
27.0862
16.2437
^{13}C NMR (CDCl$_3$), 101 MHz
O
OMe
O
O
O
O
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

1w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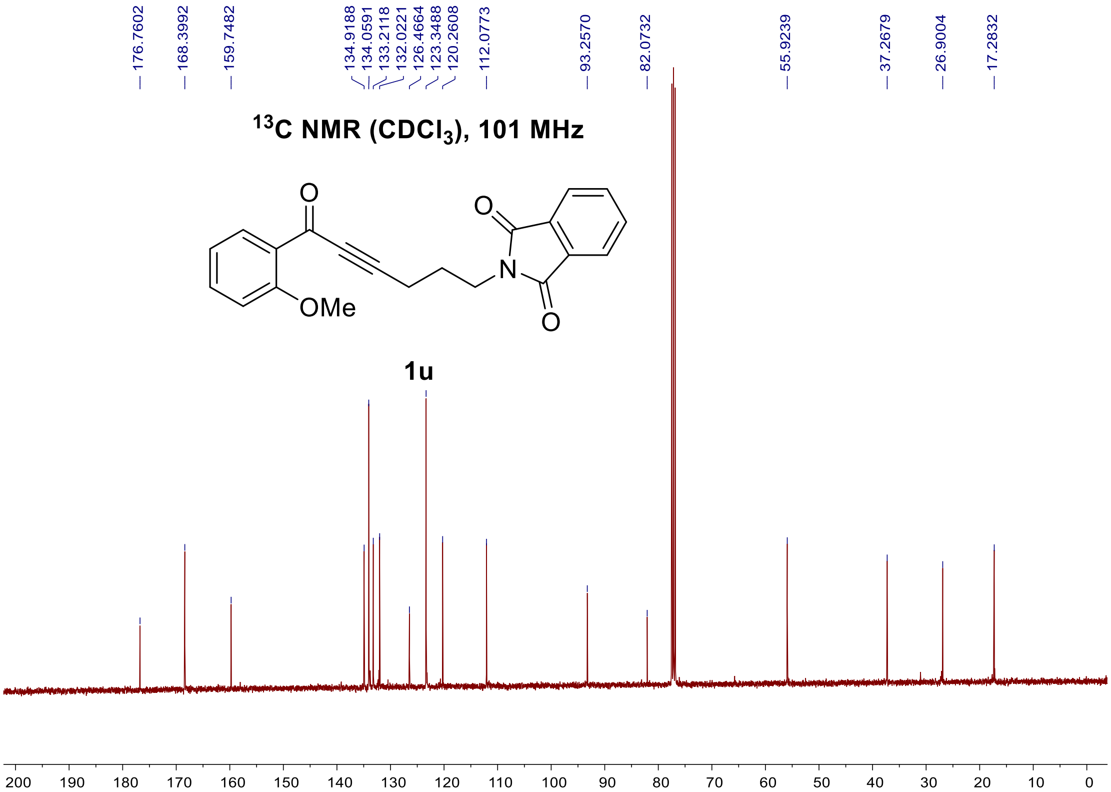
7.9822
7.9776
7.7939
7.7862
7.7803
7.7726
7.6666
7.6590
7.6529
7.6454
7.5131
7.5085
7.4948
7.4920
7.4901
7.4875
7.4737
7.4692
7.0308
7.0283
7.0102
6.9931
6.9906
6.9627
6.9419
3.9029
3.8436
3.8263
3.8090
2.5589
2.5411
2.5235
2.0714
2.0539
2.0363
2.0189
2.0013
^{1}H NMR (CDCl$_3$), 400 MHz
O
O
N
O
OMe
1.00
2.06
2.05
1.04
1.00
1.02
3.06
2.10
2.00
2.06
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

1u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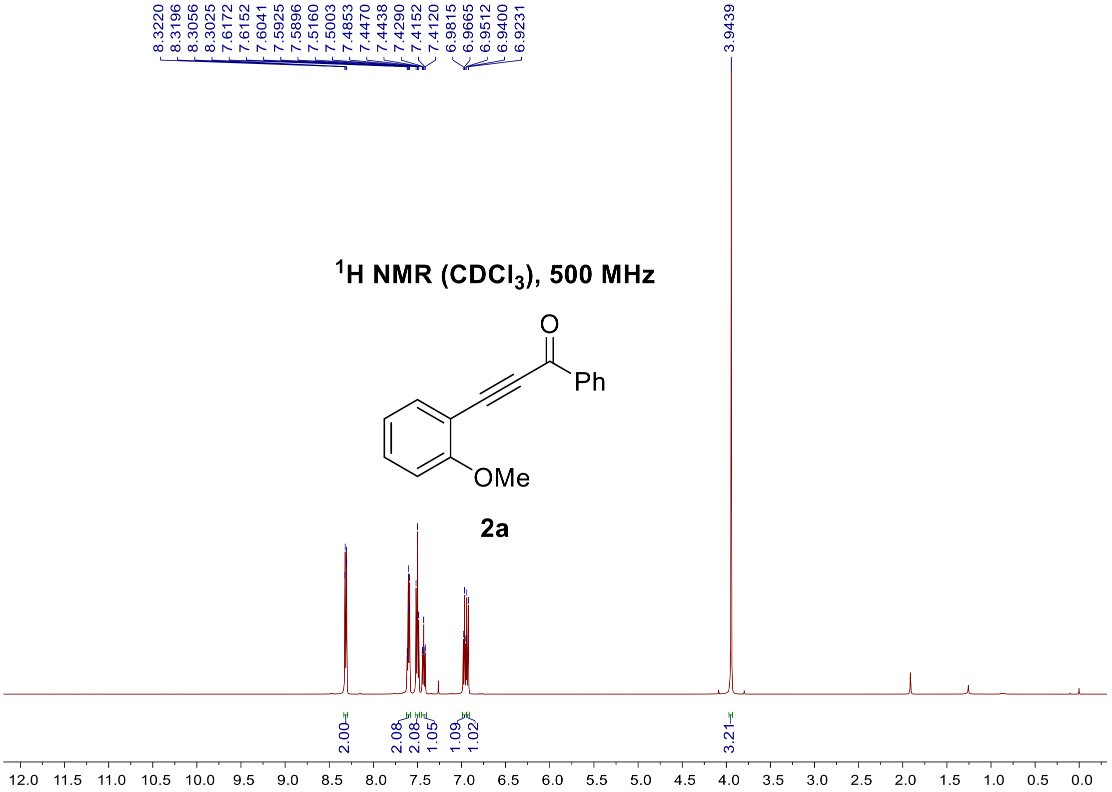
159.7482
134.9188
134.0591
133.2118
132.0221
126.4664
123.3488
120.2608
112.0773
93.2570
82.0732
55.9239
37.2679
26.9004
17.2832
^{13}C NMR (CDCl$_3$), 101 MHz
O
O
N
O
OMe
1u
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0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8.3056
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7.6172
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7.6041
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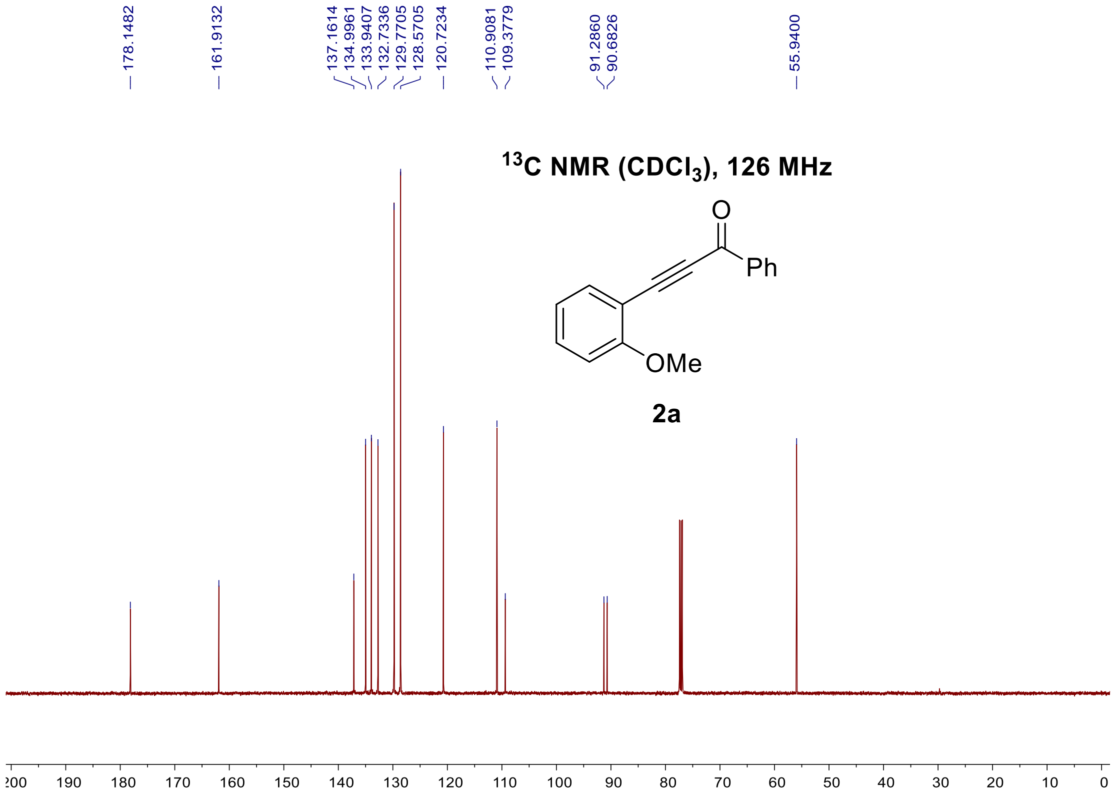
7.5003
7.4853
7.4470
7.4438
7.4290
7.4152
7.4120
6.9815
6.9665
6.9512
6.9400
6.9231
3.9439
^{1}H NMR (CDCl$_3$), 500 MHz
O
Ph
OMe
2a
2.00
2.08
2.08
1.05
1.09
1.02
3.21
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0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161.9132
137.1614
134.9961
133.9407
132.7336
129.7705
128.5705
120.7234
110.9081
109.3779
91.2860
90.6826
55.9400
13C NMR (CDCl3), 126 MHz
O
Ph
OMe
2a
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
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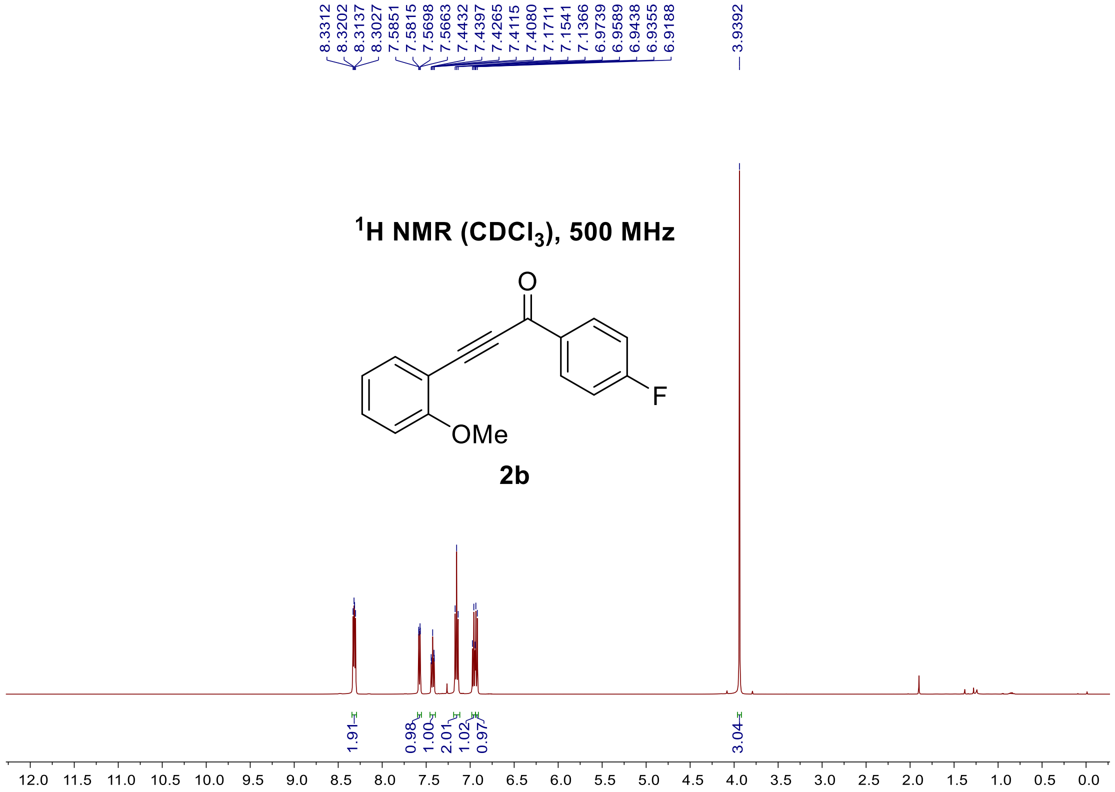
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8.3202
8.3137
8.3027
7.5851
7.5815
7.5698
7.5663
7.4432
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7.4265
7.4115
7.4080
7.1711
7.1541
7.1366
6.9739
6.9589
6.9438
6.9355
6.9188
3.9392
1H NMR (CDCl3), 500 MHz
O
F
OMe
2b
1.91
0.98
1.00
2.01
1.02
0.97
3.04
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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2.5
2.0
1.5
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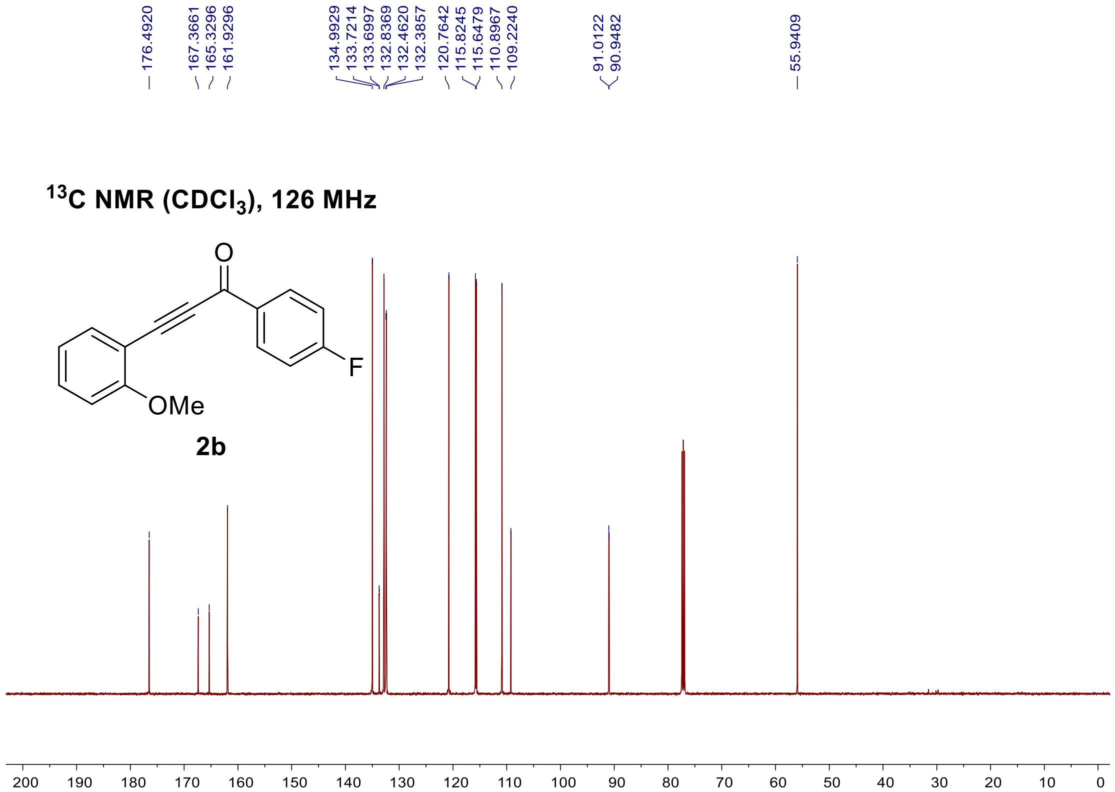
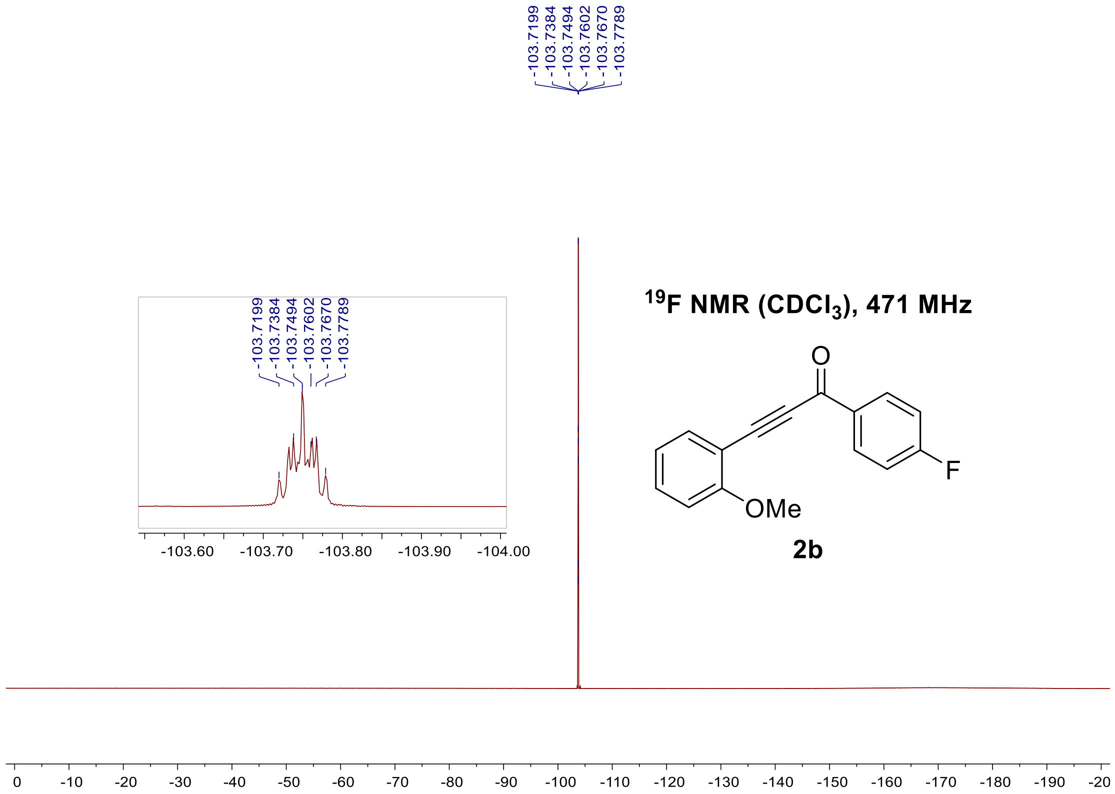
0.0



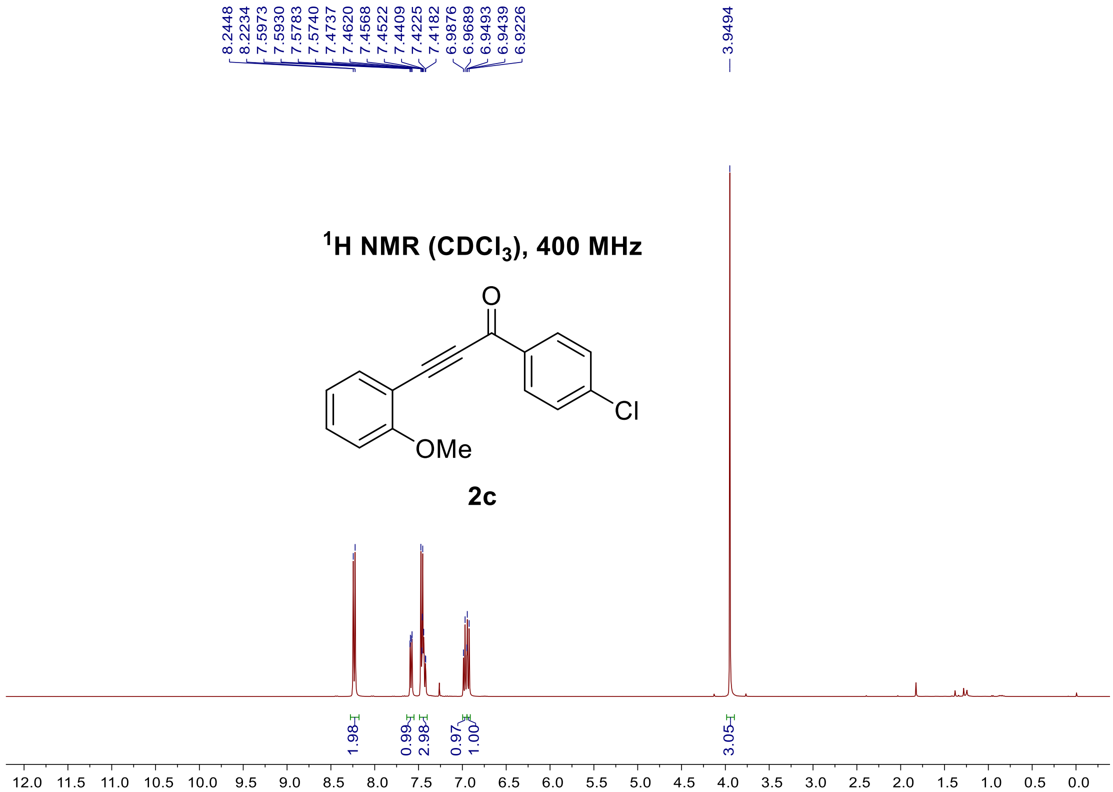
^{13}C NMR (CDCl$_3$), 126 MHz

2b



^{19}F NMR (CDCl$_3$), 471 MHz

2b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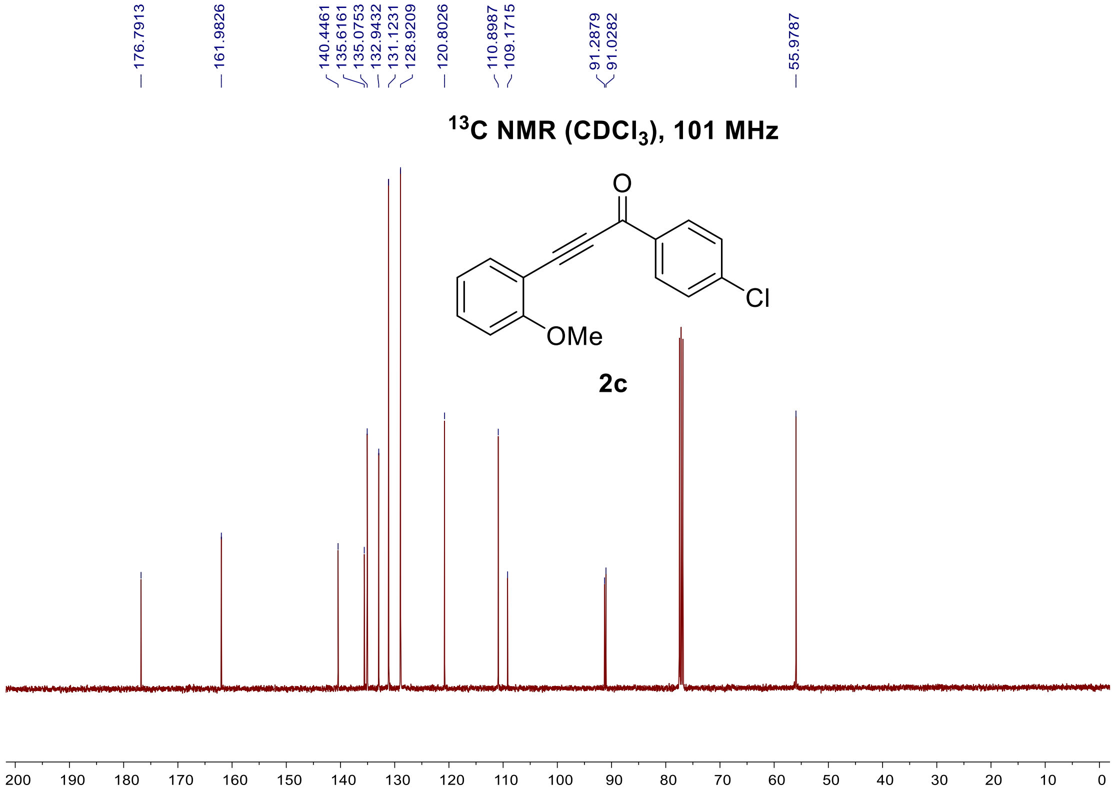
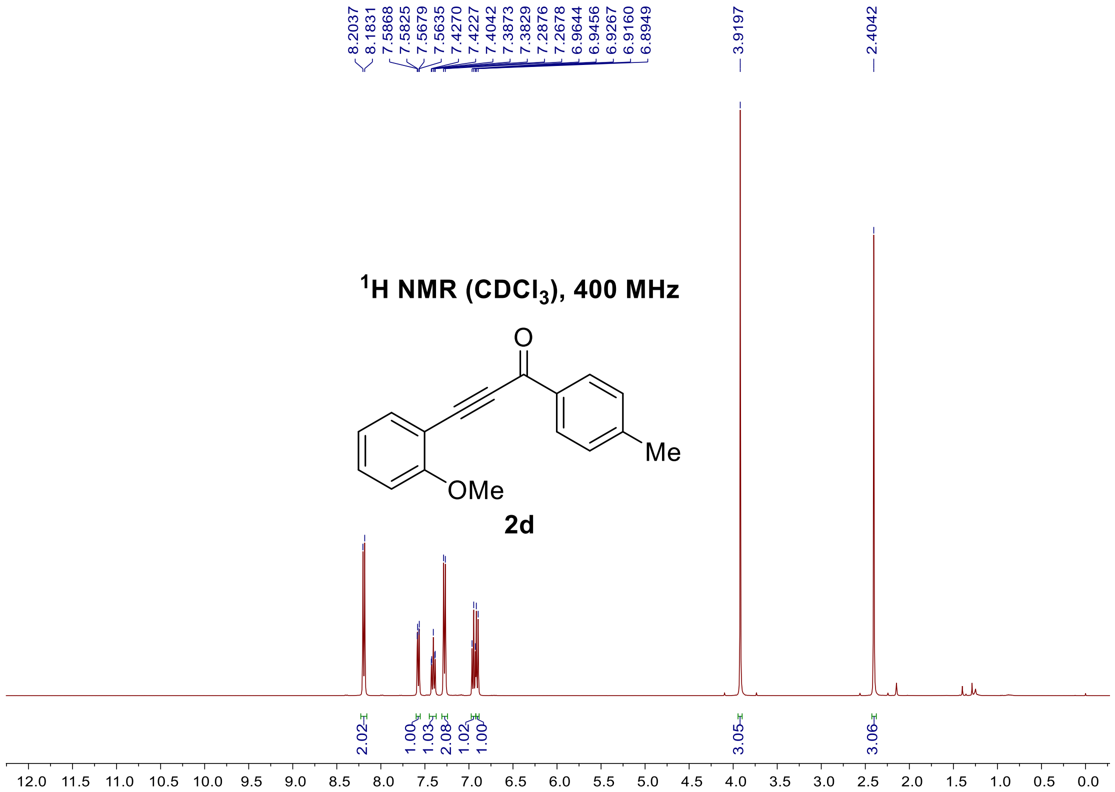
8.2234
7.5973
7.5930
7.5783
7.5740
7.4737
7.4620
7.4568
7.4522
7.4409
7.4225
7.4182
6.9876
6.9689
6.9493
6.9439
6.9226
3.9494
^{1}H NMR (CDCl$_3$), 400 MHz
O
Cl
OMe
2c
1.98
0.99
2.98
0.97
1.00
3.05
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


176.7913
161.9826
140.4461
135.6161
135.0753
132.9432
131.1231
128.9209
120.8026
110.8987
109.1715
91.2879
91.0282
55.9787
^{13}C NMR (CDCl$_3$), 101 MHz
O
Cl
OMe
2c
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0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8.1831
7.5868
7.5825
7.5679
7.5635
7.4270
7.4227
7.4042
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7.3829
7.2876
7.2678
6.9644
6.9456
6.9267
6.9160
6.8949
3.9197
2.4042
^{1}H NMR (CDCl$_3$), 400 MHz
O
Me
OMe
2d
2.02
1.00
1.03
2.08
1.02
1.00
3.05
3.06
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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4.0
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2.5
2.0
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1.0
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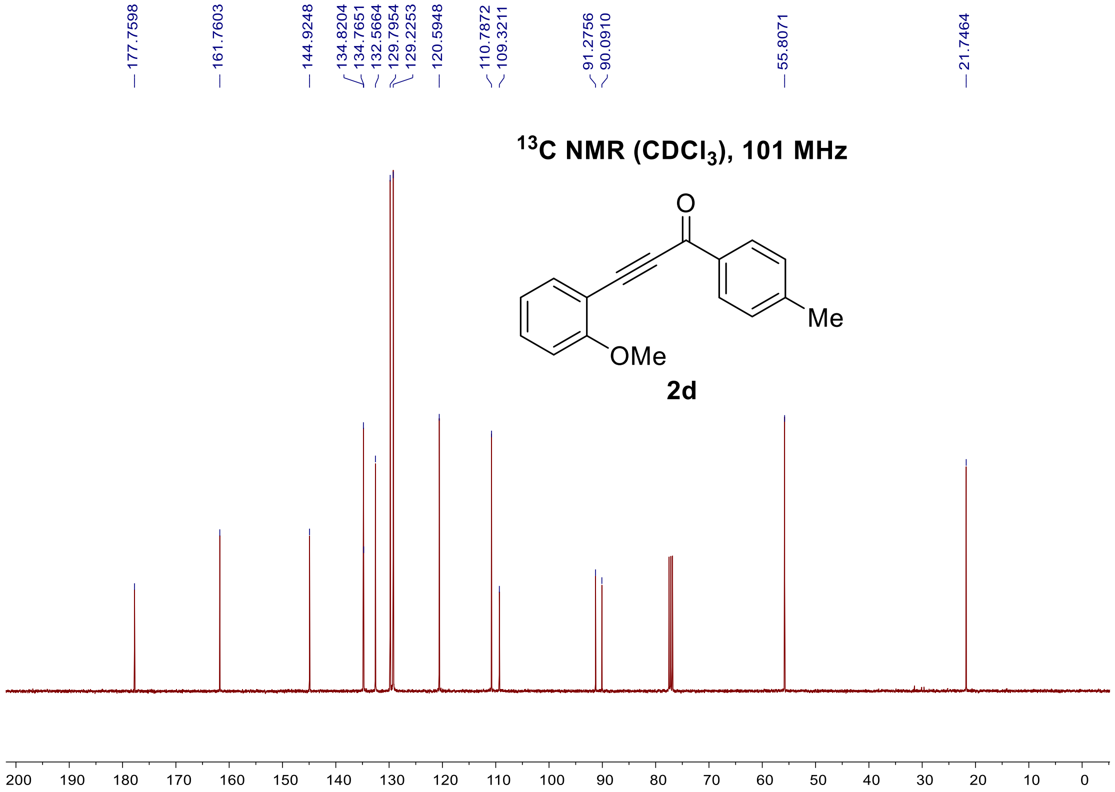
0.0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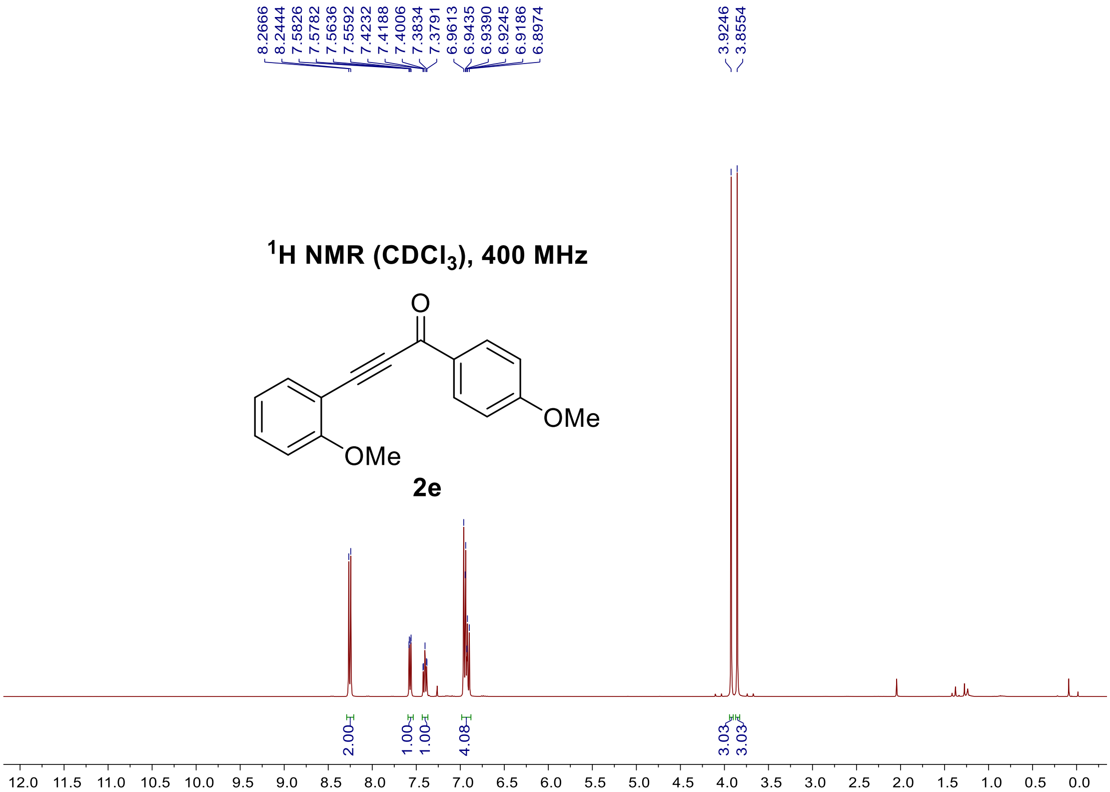
144.9248
134.8204
134.7651
132.5664
129.7954
129.2253
120.5948
110.7872
109.3211
91.2756
90.0910
55.8071
21.7464
^{13}C NMR (CDCl$_3$), 101 MHz
O
Me
OMe
2d
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0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8.2444
7.5826
7.5782
7.5636
7.5592
7.4232
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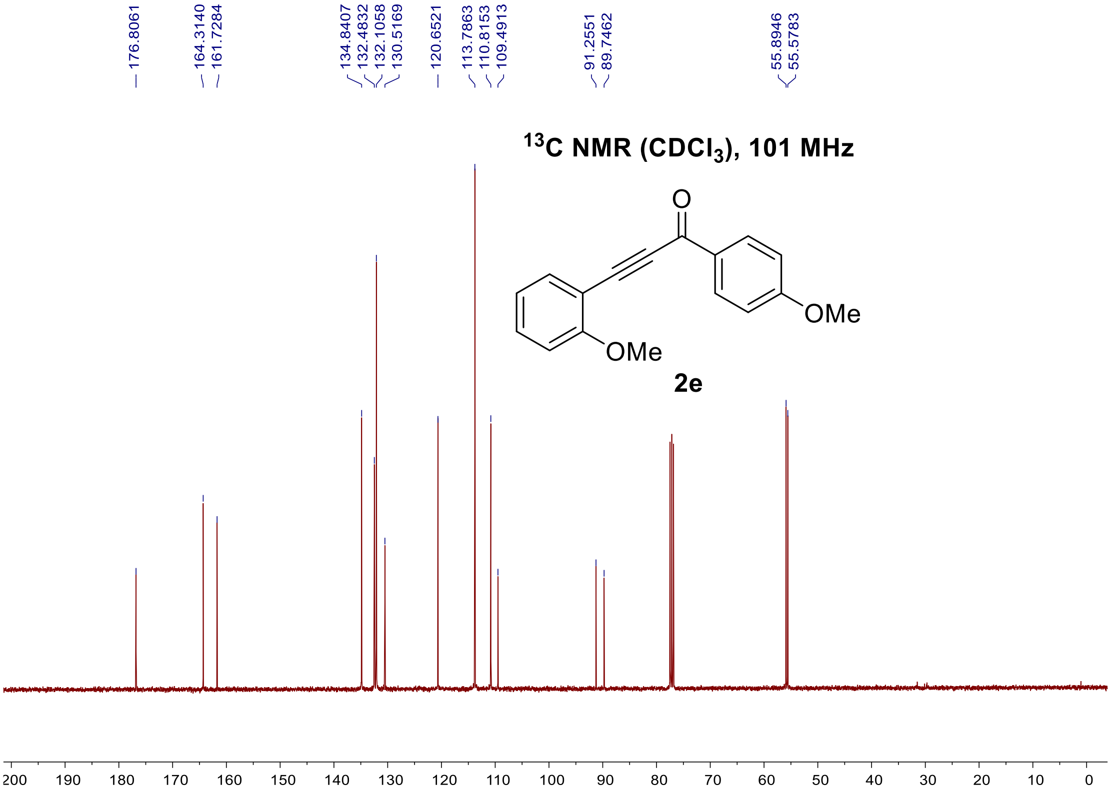
7.4006
7.3834
7.3791
6.9613
6.9435
6.9390
6.9245
6.9186
6.8974
3.9246
3.8554
^{1}H NMR (CDCl$_3$), 400 MHz
O
OMe
OMe
2e
2.00
1.00
1.00
4.08
3.03
3.03
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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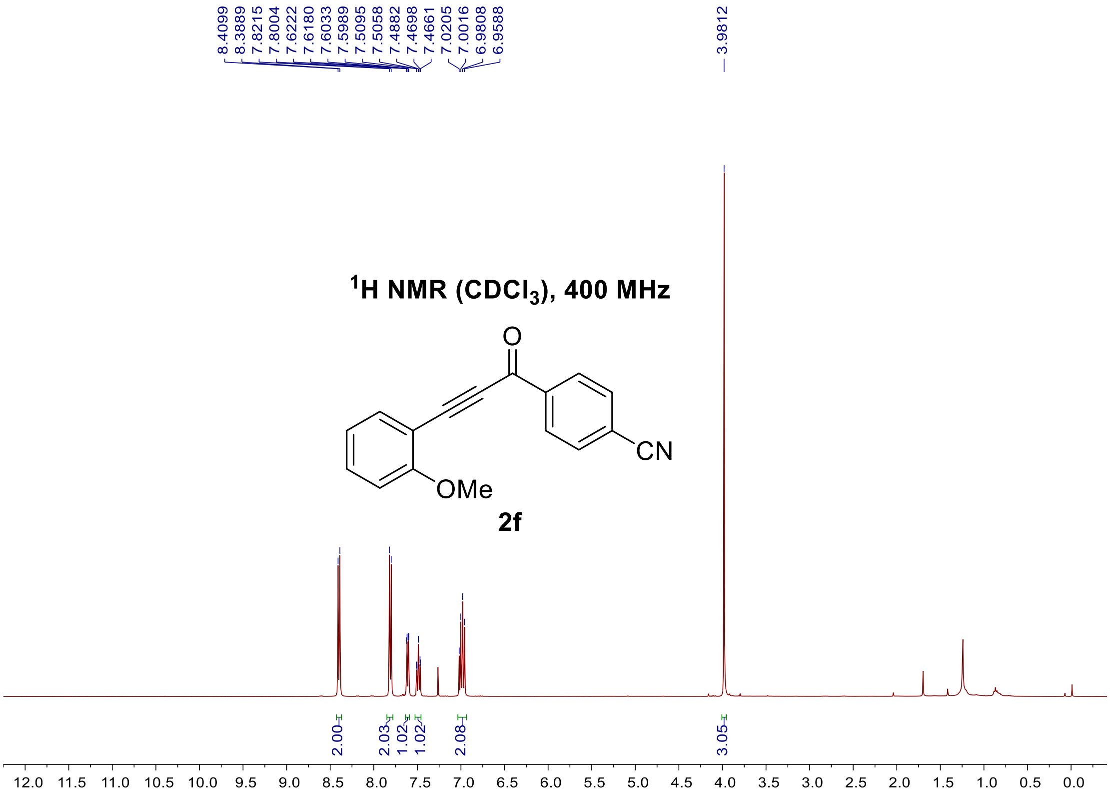
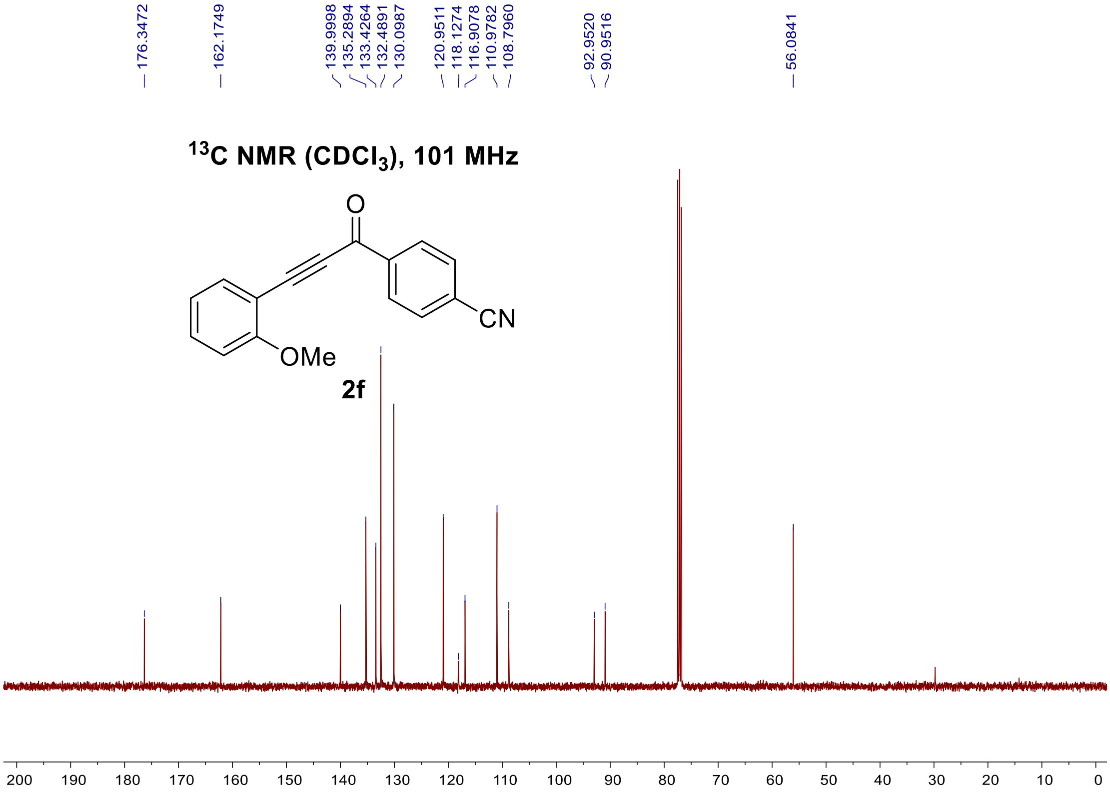
161.7284
134.8407
132.4832
132.1058
130.5169
120.6521
113.7863
110.8153
109.4913
91.2551
89.7462
55.8946
55.5783
^{13}C NMR (CDCl$_3$), 101 MHz
O
OMe
OMe
2e
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0



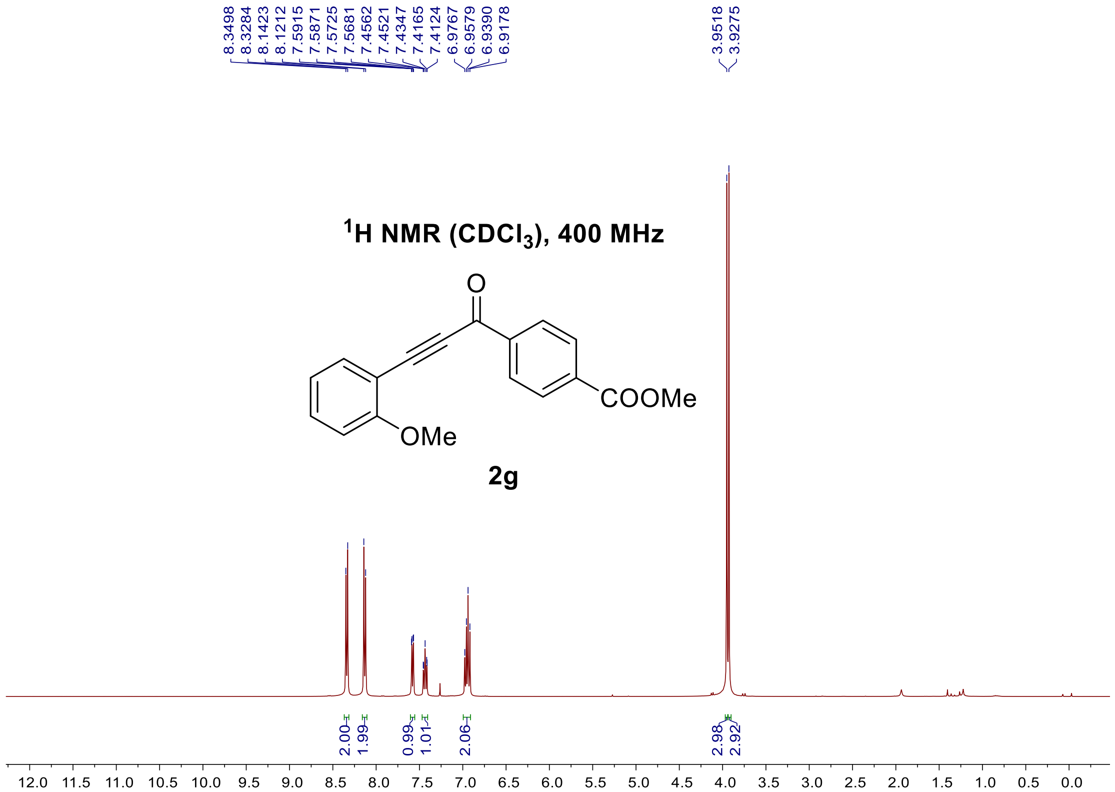
^{1}H NMR (CDCl$_3$), 400 MHz

2f



^{13}C NMR (CDCl$_3$), 101 MHz

2f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8.3284
8.1423
8.1212
7.5915
7.5871
7.5725
7.5681
7.4562
7.4521
7.4347
7.4165
7.4124
6.9767
6.9579
6.9390
6.9178
3.9518
3.9275
^{1}H NMR (CDCl$_3$), 400 MHz
O
COOMe
OMe
2g
2.00
1.99
0.99
1.01
2.06
2.98
2.92
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
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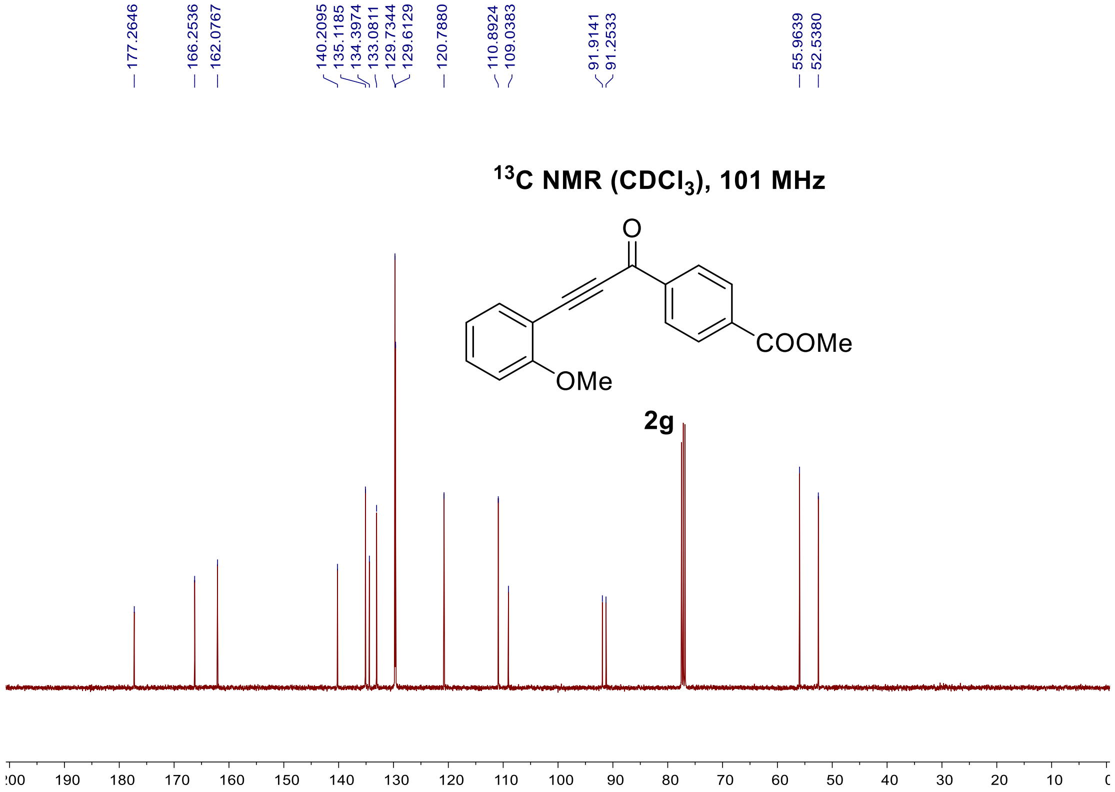
0.0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162.0767
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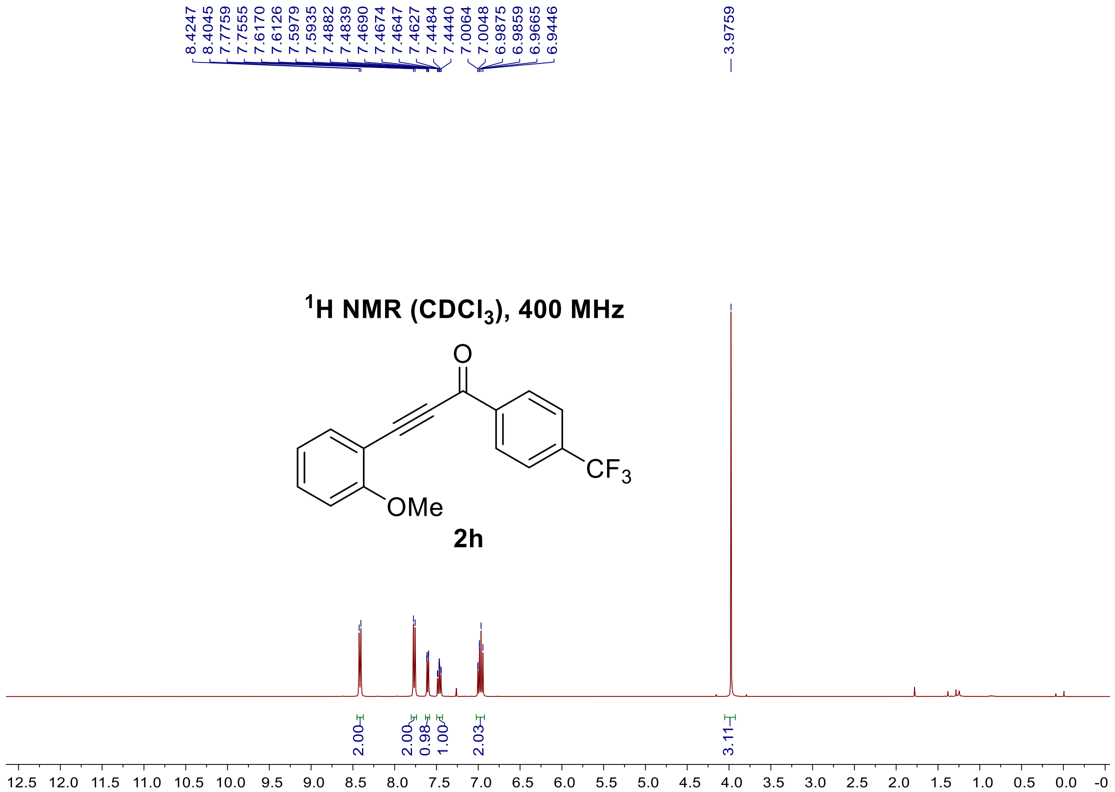
135.1185
134.3974
133.0811
129.7344
129.6129
120.7880
110.8924
109.0383
91.9141
91.2533
55.9639
52.5380
^{13}C NMR (CDCl$_3$), 101 MHz
O
COOMe
OMe
2g
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0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7.7555
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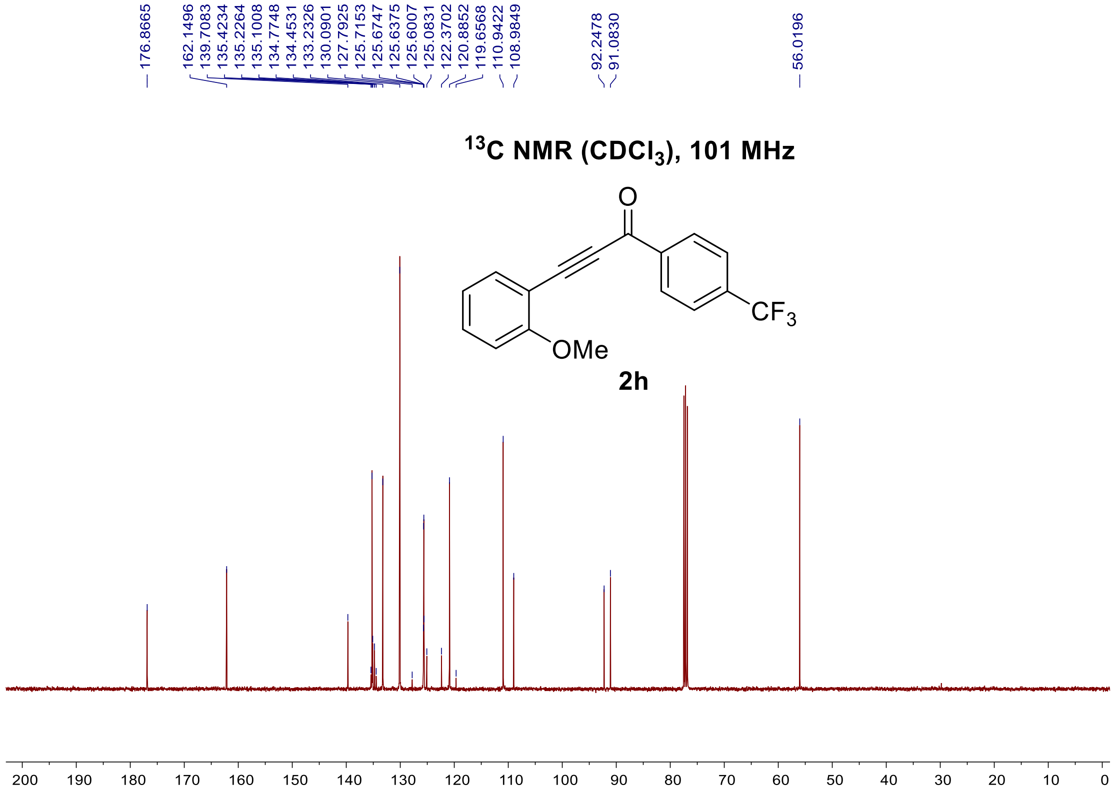
7.6126
7.5979
7.5935
7.4882
7.4839
7.4690
7.4674
7.4647
7.4627
7.4484
7.4440
7.0064
7.0048
6.9875
6.9859
6.9665
6.9446
3.9759
¹H NMR (CDCl₃), 400 MHz
O
CF₃
OMe
2h
2.00
2.00
0.98
1.00
2.03
3.11
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.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162.1496
139.7083
135.4234
135.2264
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134.7748
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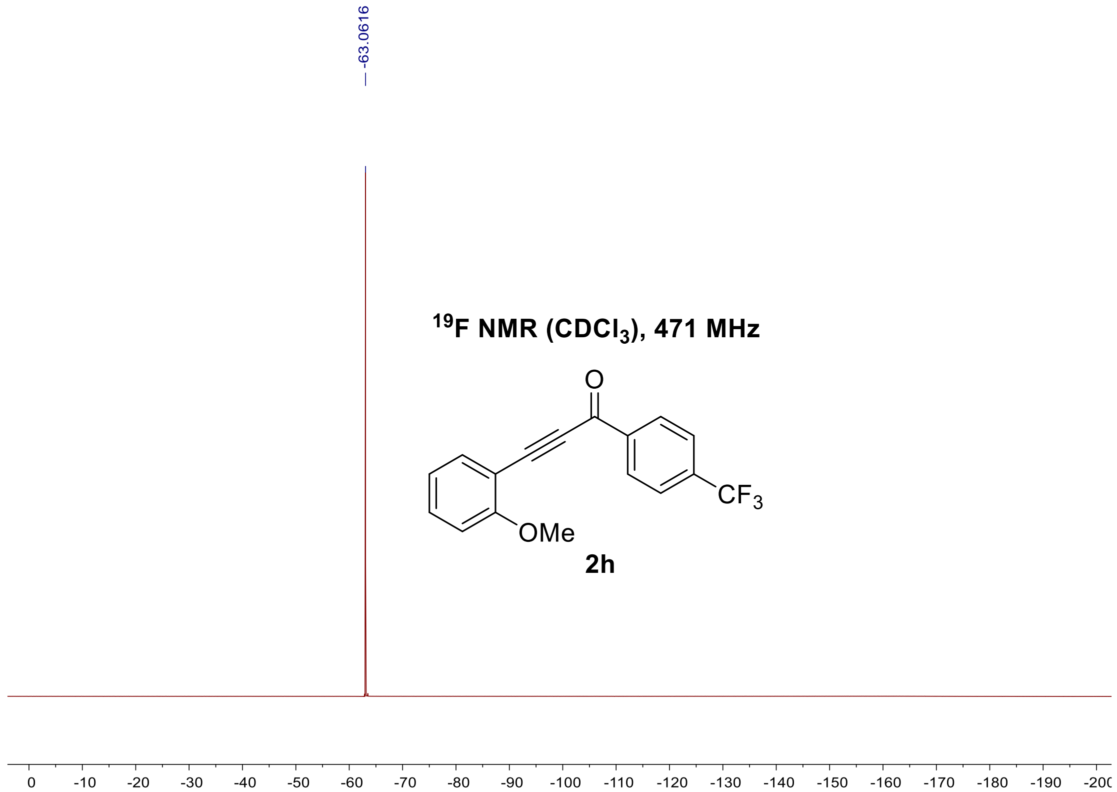
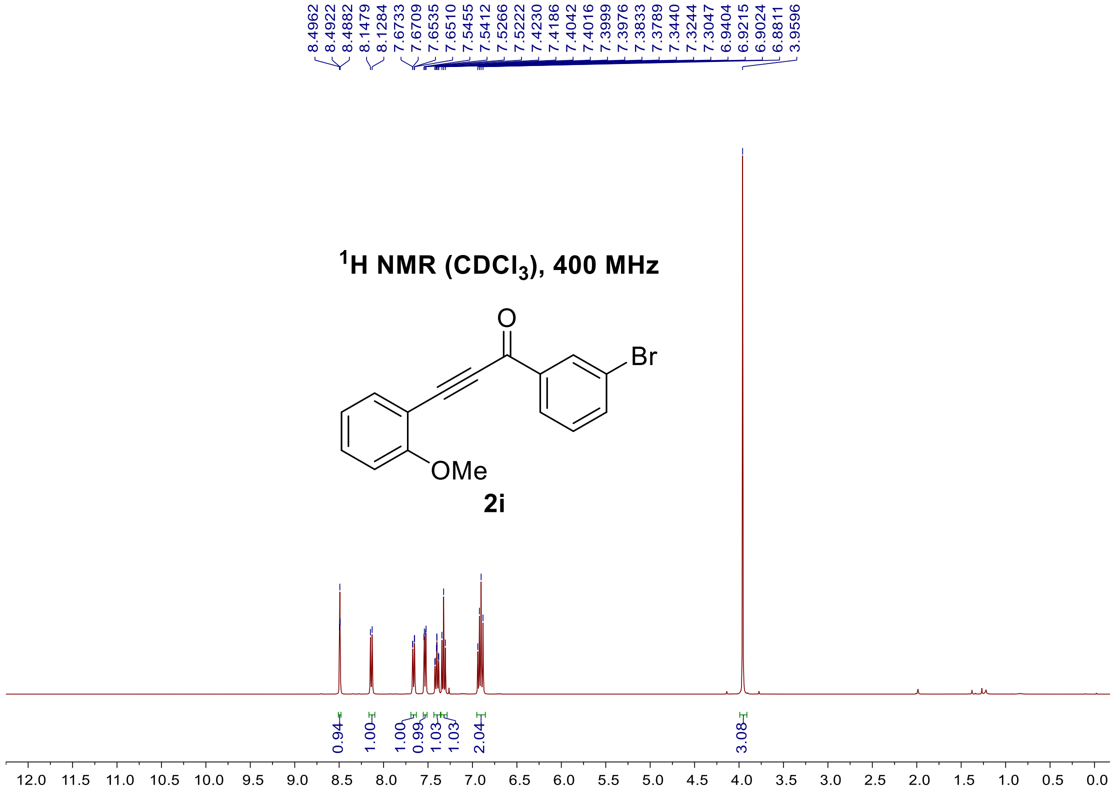
127.7925
125.7153
125.6747
125.6375
125.6007
125.0831
122.3702
120.8852
119.6568
110.9422
108.9849
92.2478
91.0830
56.0196
¹³C NMR (CDCl₃), 101 MHz
O
CF₃
OMe
2h
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0



-63.0616
^{19}F NMR (CDCl$_3$), 471 MHz
O
CF$_3$
OMe
2h
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200



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8.4882
8.1479
8.1284
7.6733
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7.6510
7.5455
7.5412
7.5266
7.5222
7.4230
7.4186
7.4042
7.4016
7.3999
7.3976
7.3833
7.3789
7.3440
7.3244
7.3047
6.9404
6.9215
6.9024
6.8811
3.9596
^{1}H NMR (CDCl$_3$), 400 MHz
O
Br
OMe
2i
0.94
1.00
1.00
0.99
1.03
1.03
2.04
3.08
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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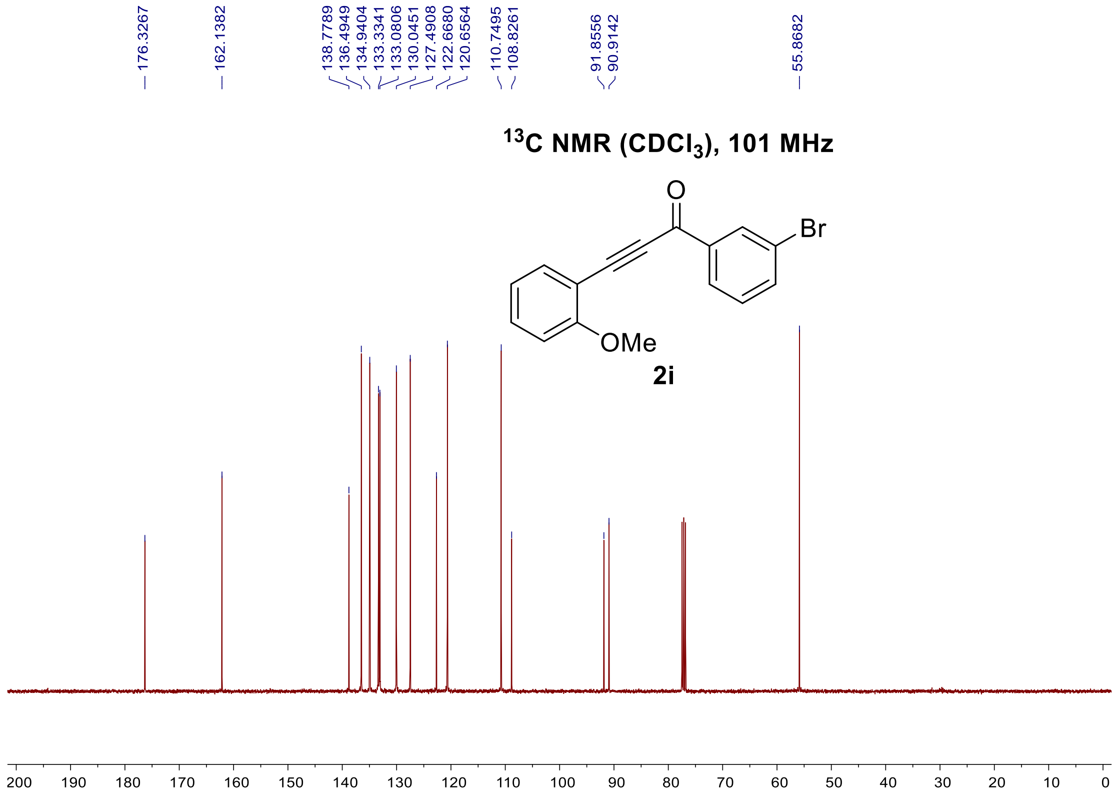
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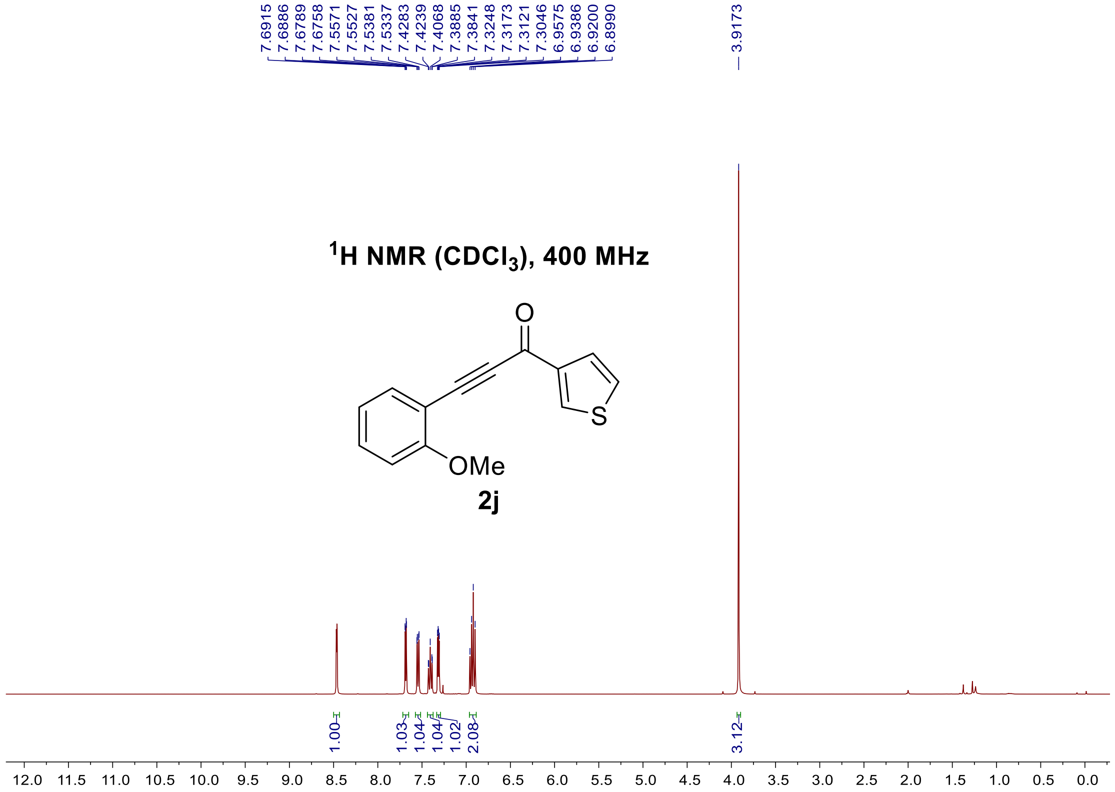
122.6680
120.6564
110.7495
108.8261
91.8556
90.9142
55.8682
^{13}C NMR (CDCl$_3$), 101 MHz
O
Br
OMe
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

2i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7.4068
7.3885
7.3841
7.3248
7.3173
7.3121
7.3046
6.9575
6.9386
6.9200
6.8990
3.9173
^{1}H NMR (CDCl$_3$), 400 MHz
O
S
OMe
1.00
1.03
1.04
1.04
1.02
2.08
3.12
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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4.0
3.5
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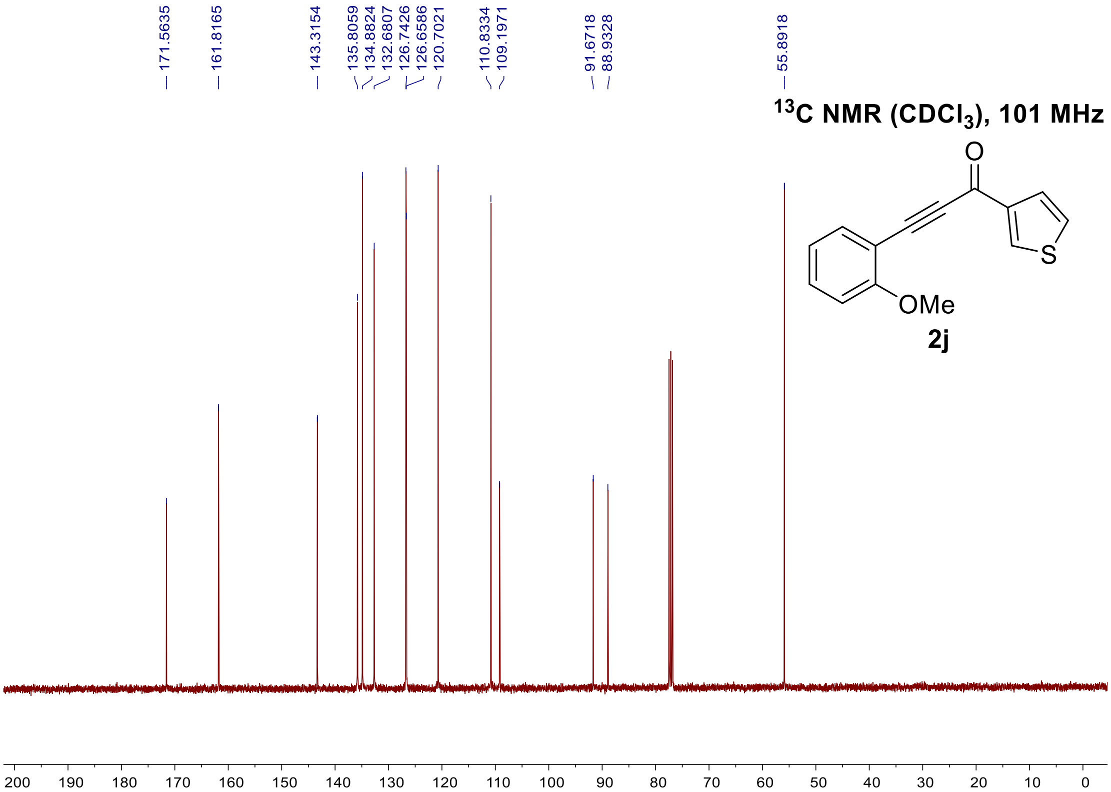
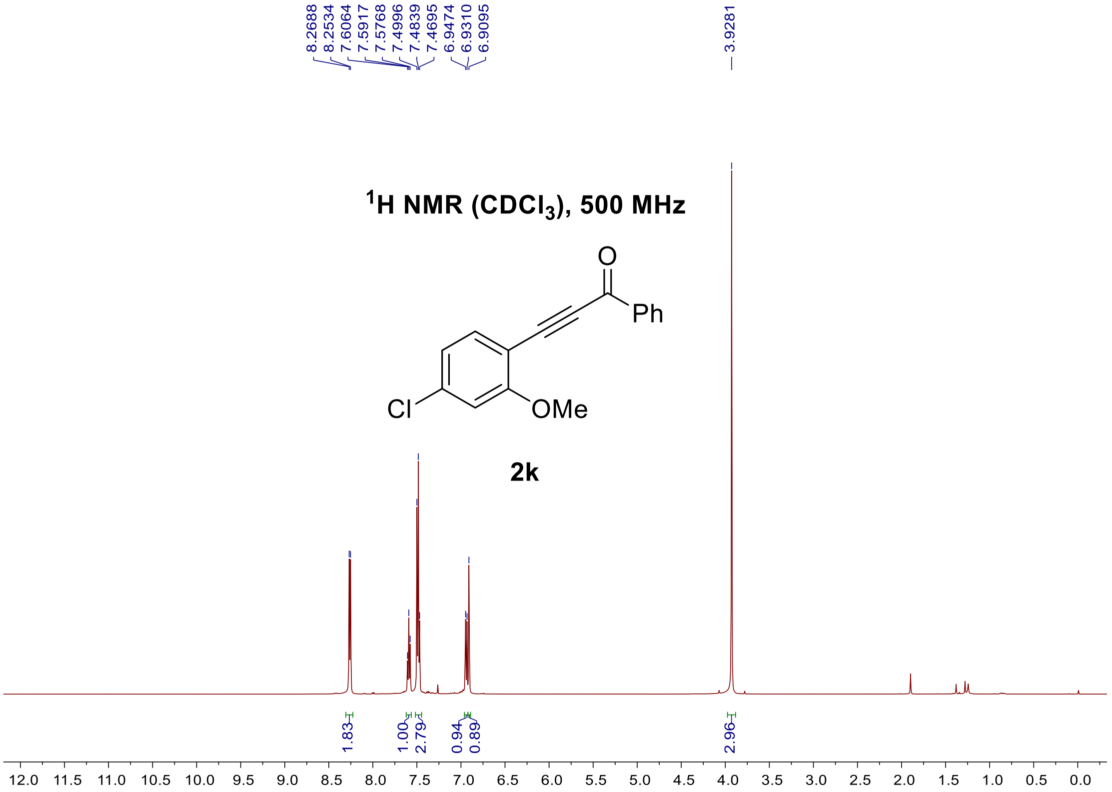
2j



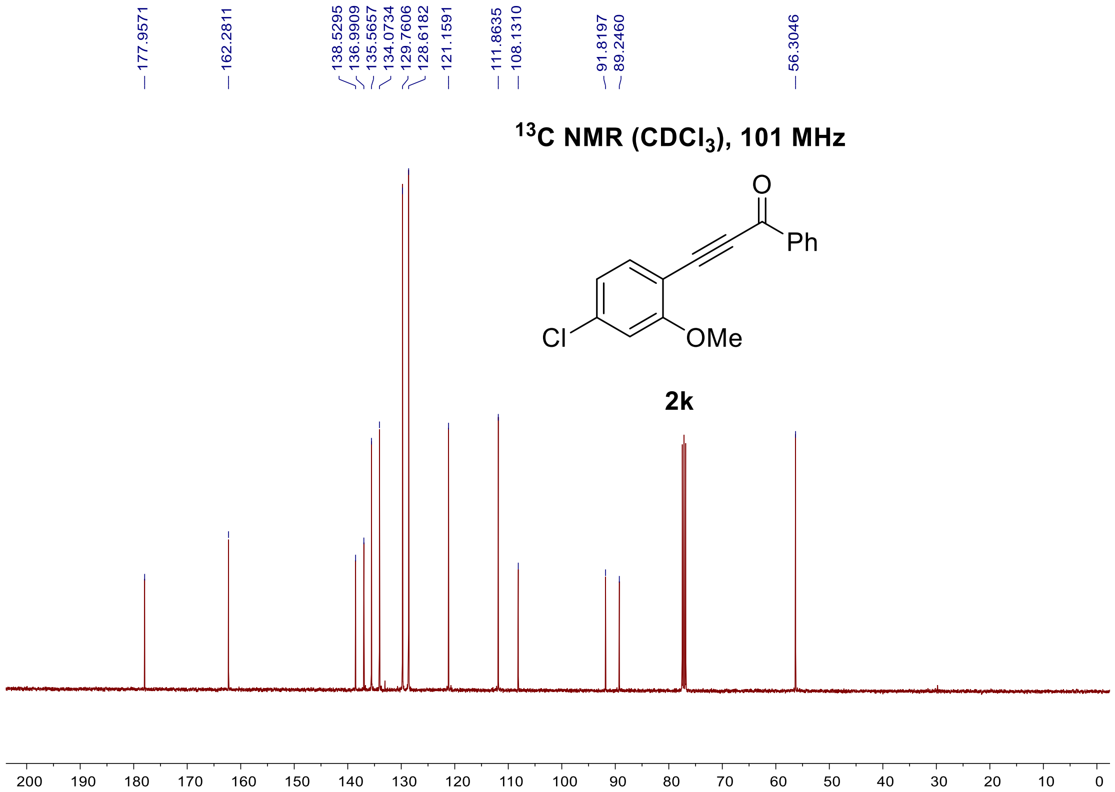
^{13}C NMR (CDCl$_3$), 101 MHz

2j



^{1}H NMR (CDCl$_3$), 500 MHz

2k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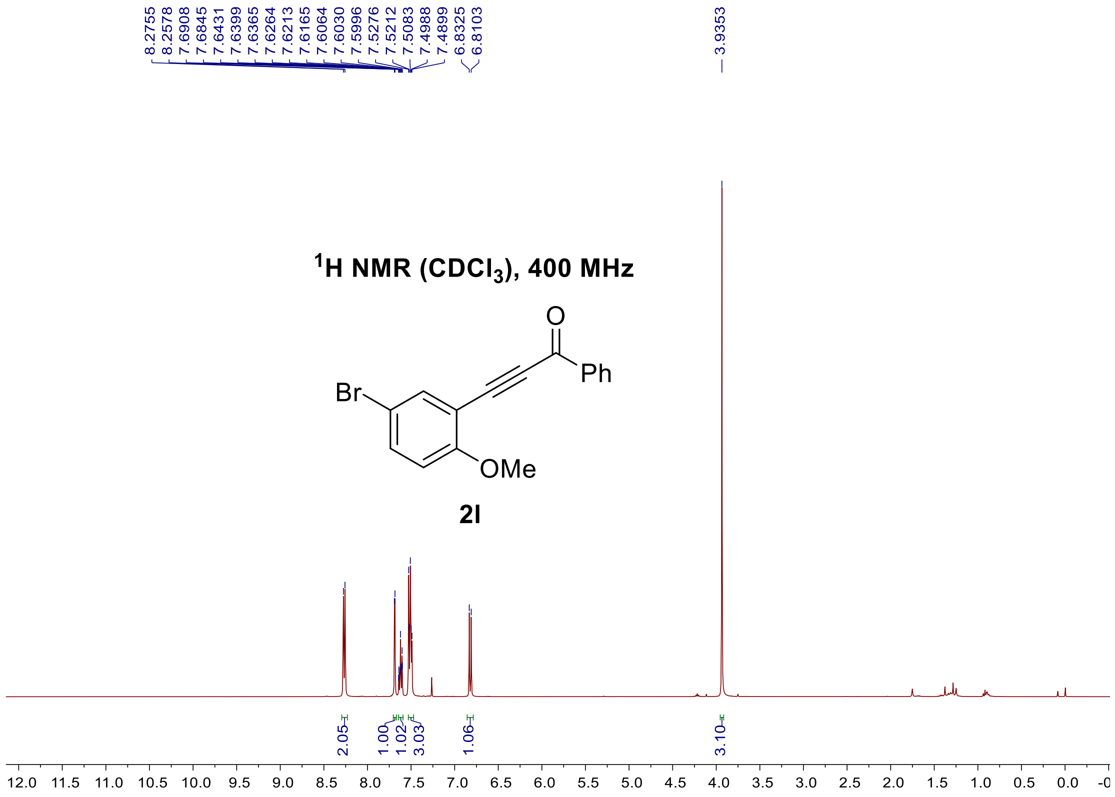
138.5295
136.9909
135.5657
134.0734
129.7606
128.6182
121.1591
111.8635
108.1310
91.8197
89.2460
56.3046
^{13}C NMR (CDCl$_3$), 101 MHz
O
Ph
Cl
OMe
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

2k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7.6431
7.6399
7.6365
7.6264
7.6213
7.6165
7.6064
7.6030
7.5996
7.5276
7.5212
7.5083
7.4988
7.4899
6.8325
6.8103
3.9353
^{1}H NMR (CDCl$_3$), 400 MHz
O
Ph
Br
OMe
2.05
1.00
1.02
3.03
1.06
3.10
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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3.5
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2.5
2.0
1.5
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0.5
0.0
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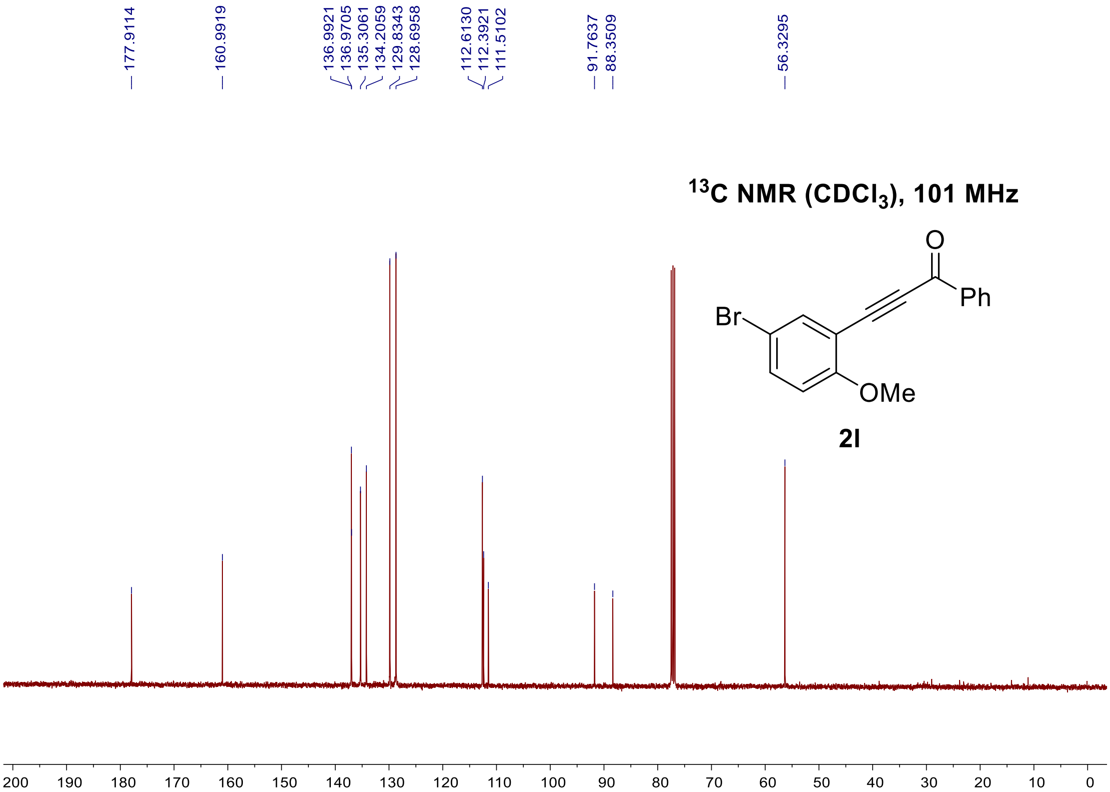
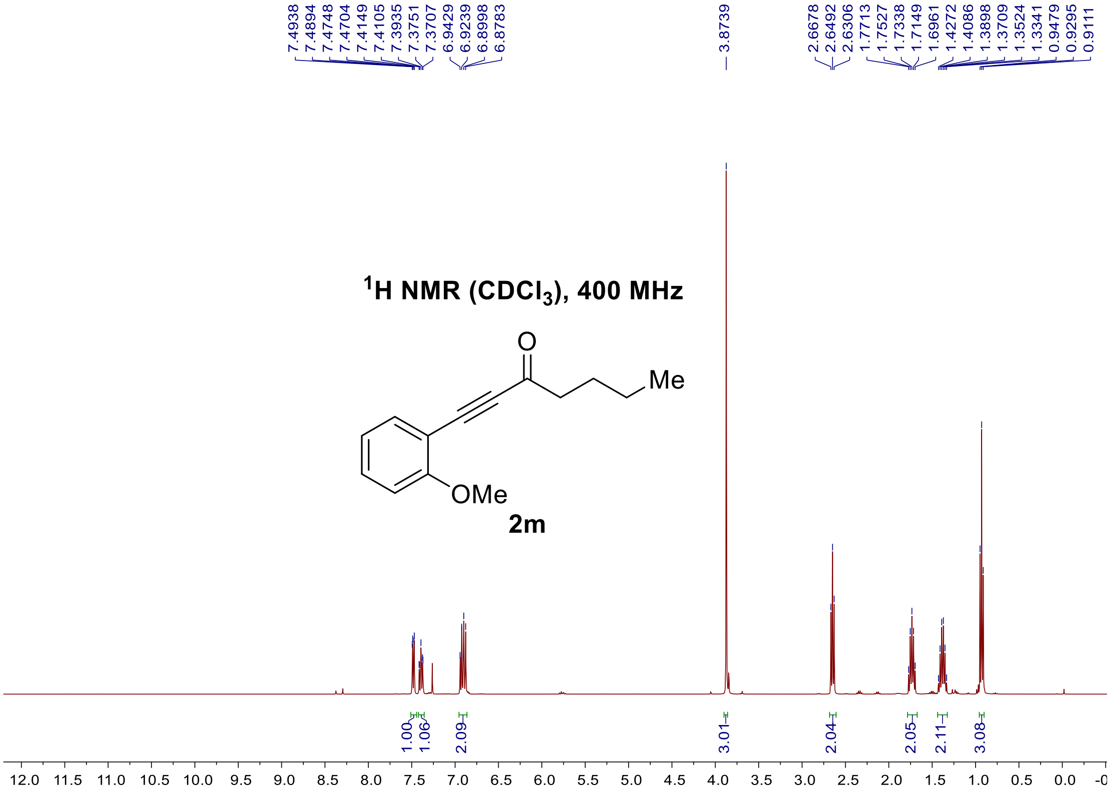
2l



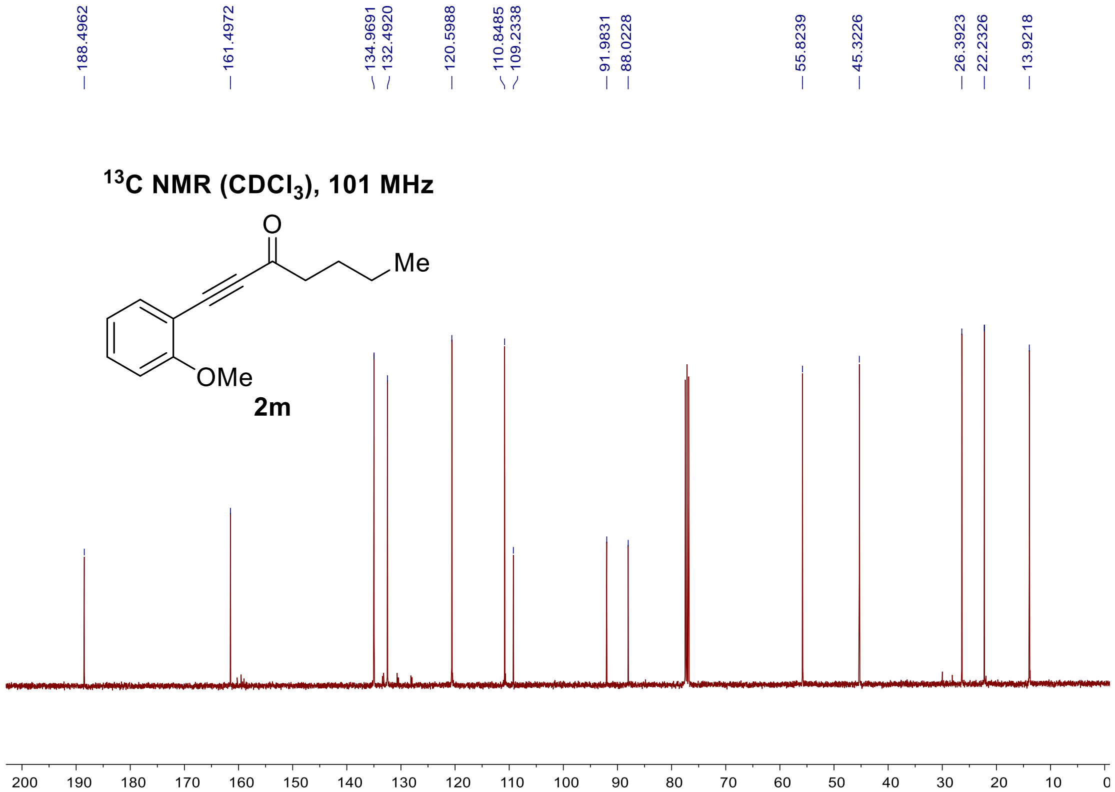
^{13}C NMR ($CDCl_3$), 101 MHz

2l



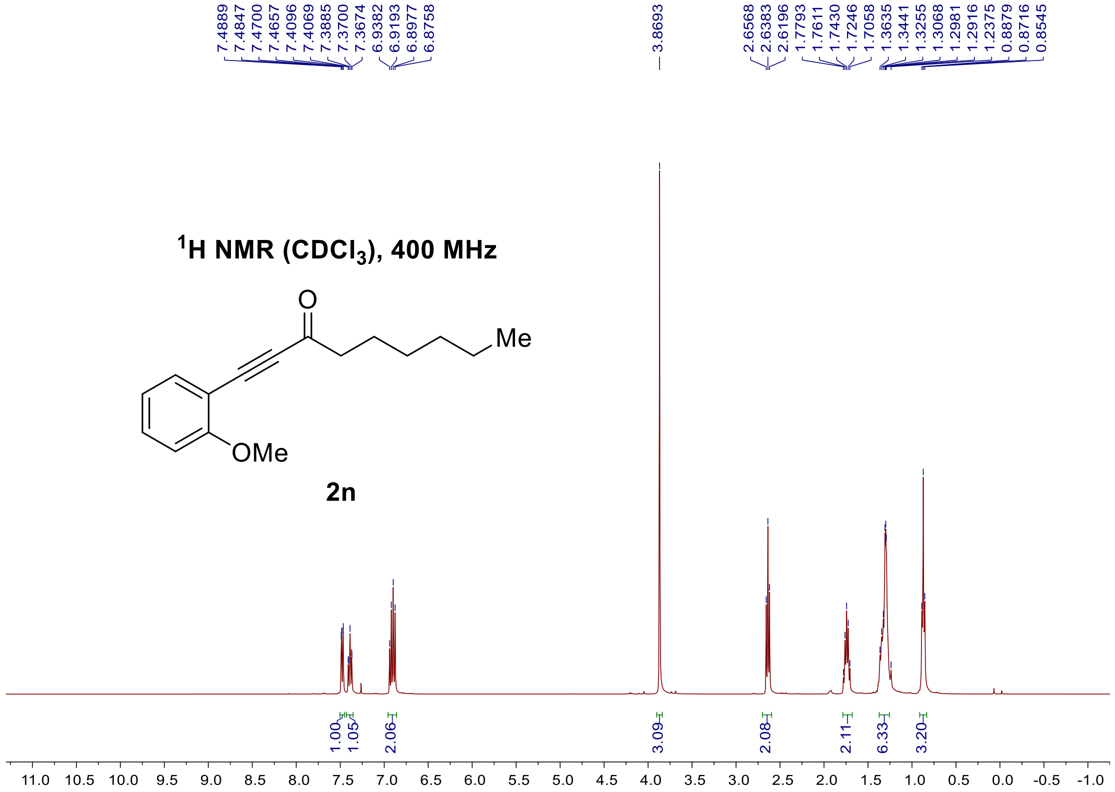
^{1}H NMR ($CDCl_3$), 400 MHz

2m



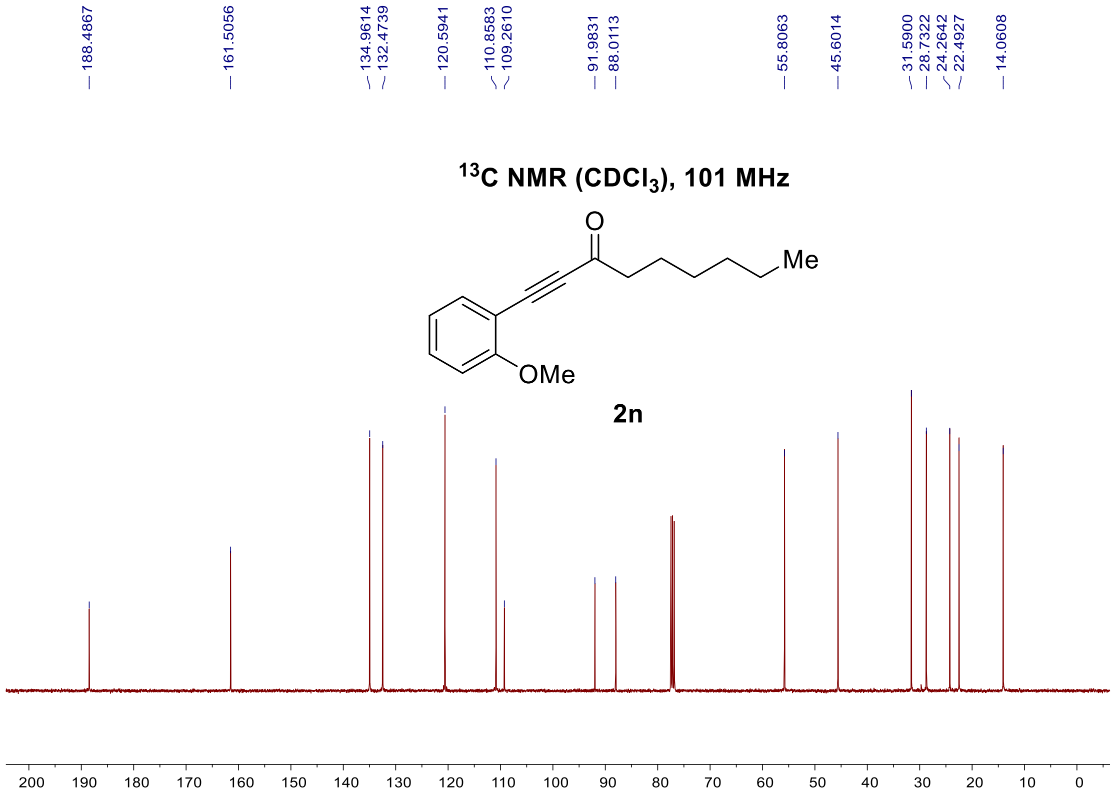
^{13}C NMR (CDCl$_3$), 101 MHz

2m



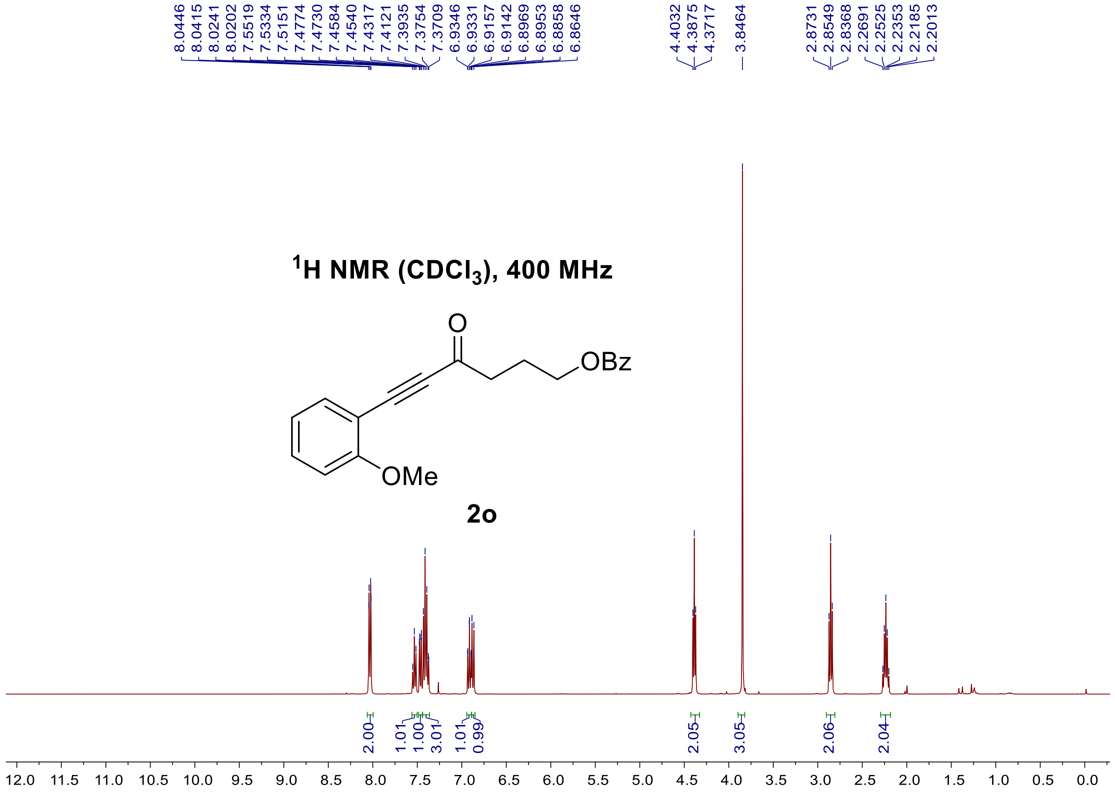
^{1}H NMR (CDCl$_3$), 400 MHz

2n



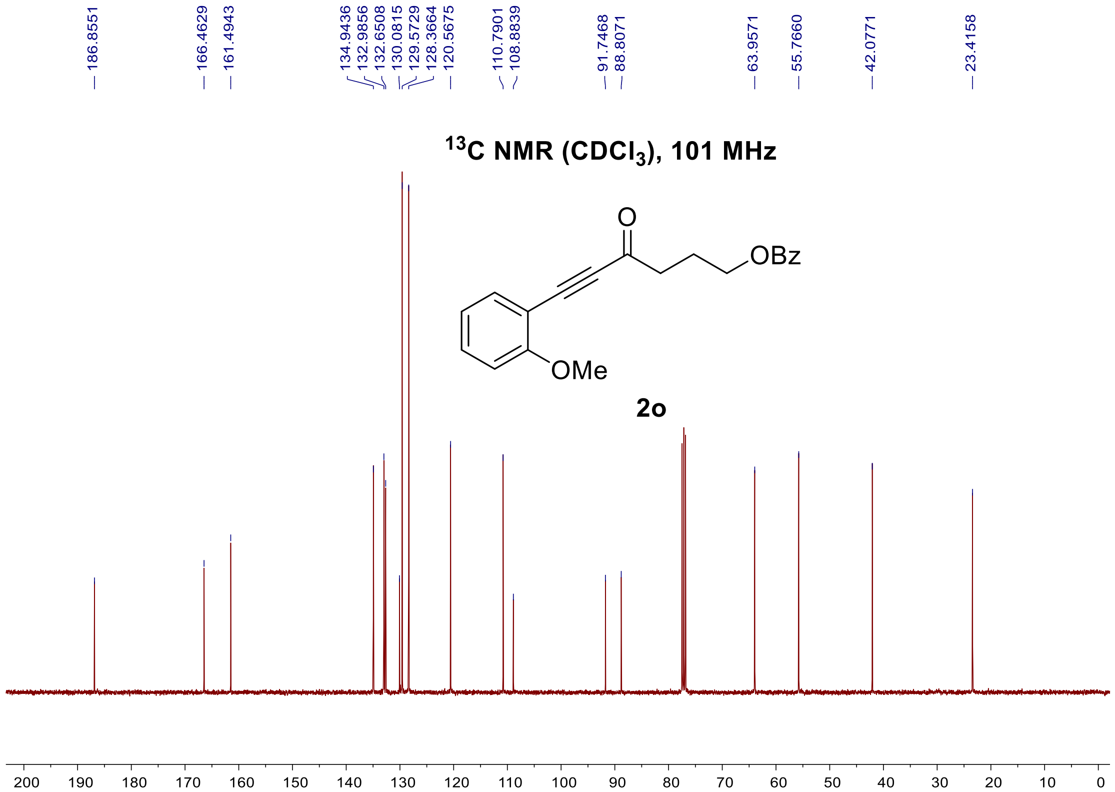
^{13}C NMR ($CDCl_3$), 101 MHz

2n



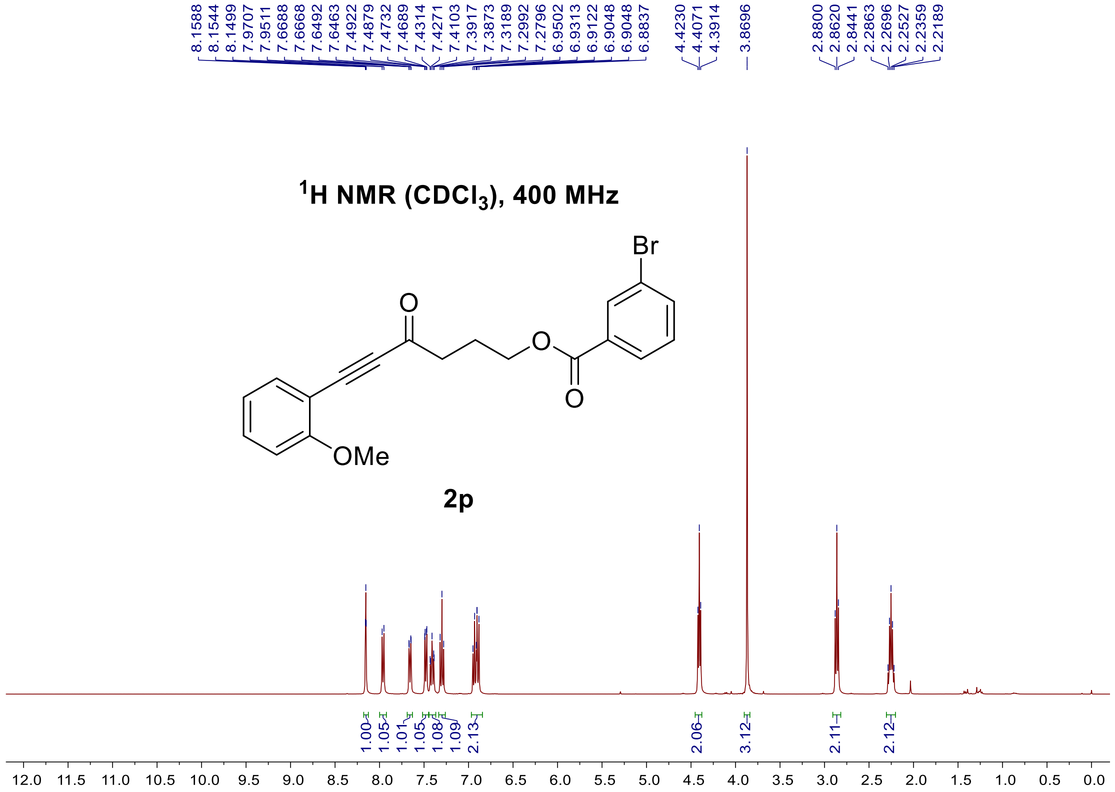
^{1}H NMR ($CDCl_3$), 400 MHz

2o



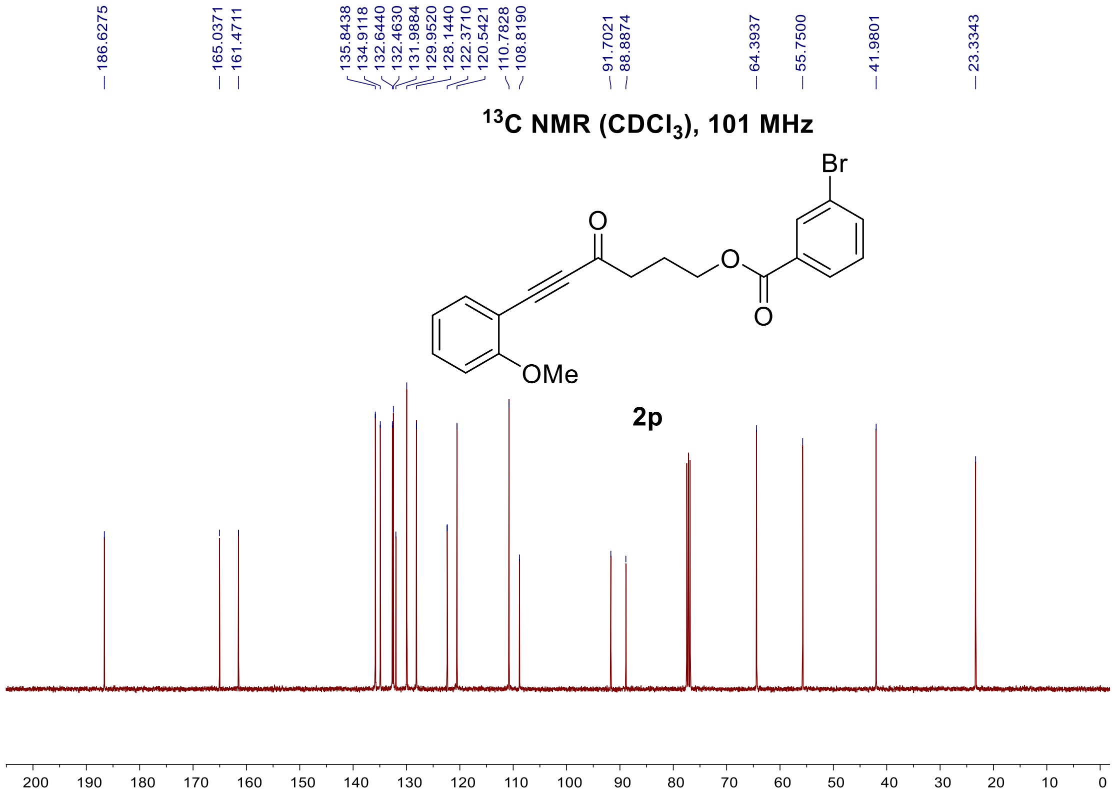
^{13}C NMR (CDCl$_3$), 101 MHz

2o



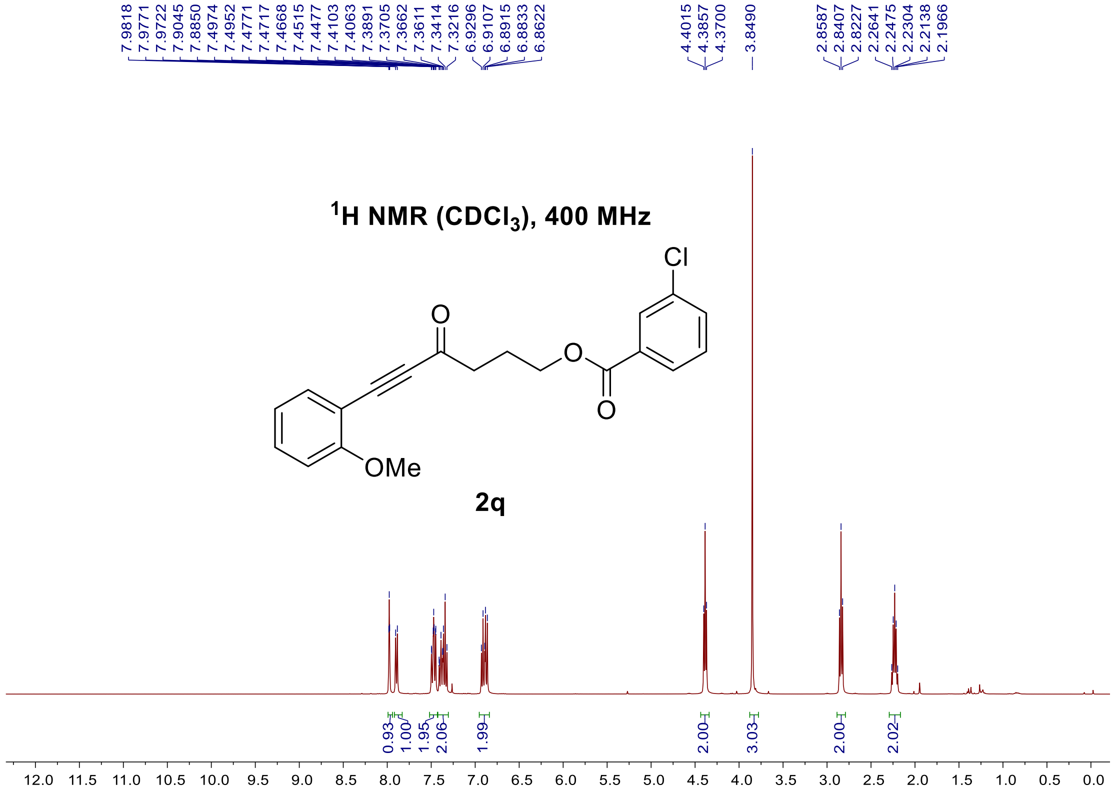
^{1}H NMR (CDCl$_3$), 400 MHz

2p



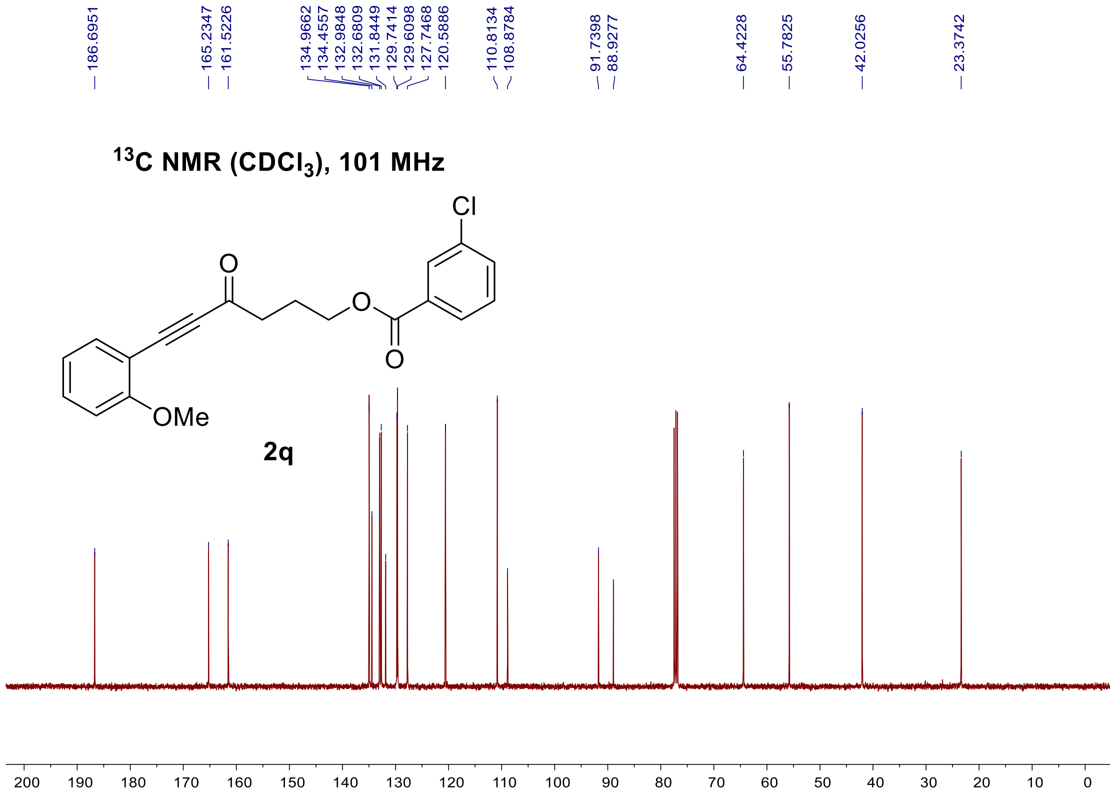
^{13}C NMR ($CDCl_3$), 101 MHz

2p



^{1}H NMR ($CDCl_3$), 400 MHz

2q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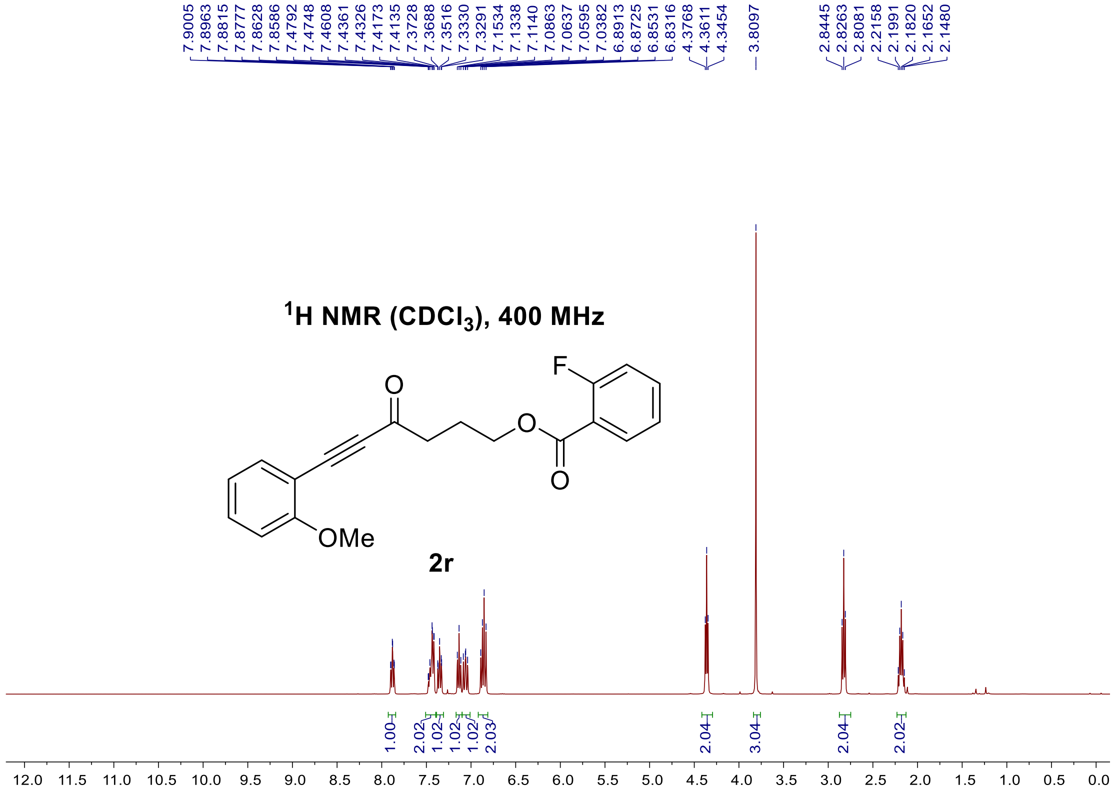
165.2347
161.5226
134.9662
134.4557
132.9848
132.6809
131.8449
129.7414
129.6098
127.7468
120.5886
110.8134
108.8784
91.7398
88.9277
64.4228
55.7825
42.0256
23.3742
^{13}C NMR (CDCl$_3$), 101 MHz
Cl
O
O
O
OMe
2q
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0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7.8963
7.8815
7.8777
7.8628
7.8586
7.4792
7.4748
7.4608
7.4361
7.4326
7.4173
7.4135
7.3728
7.3688
7.3516
7.3330
7.3291
7.1534
7.1338
7.1140
7.0863
7.0637
7.0595
7.0382
6.8913
6.8725
6.8531
6.8316
4.3768
4.3611
4.3454
3.8097
2.8445
2.8263
2.8081
2.2158
2.1991
2.1820
2.1652
2.1480
^{1}H NMR (CDCl$_3$), 400 MHz
F
O
O
O
OMe
2r
1.00
2.02
1.02
1.02
1.02
2.03
2.04
3.04
2.04
2.02
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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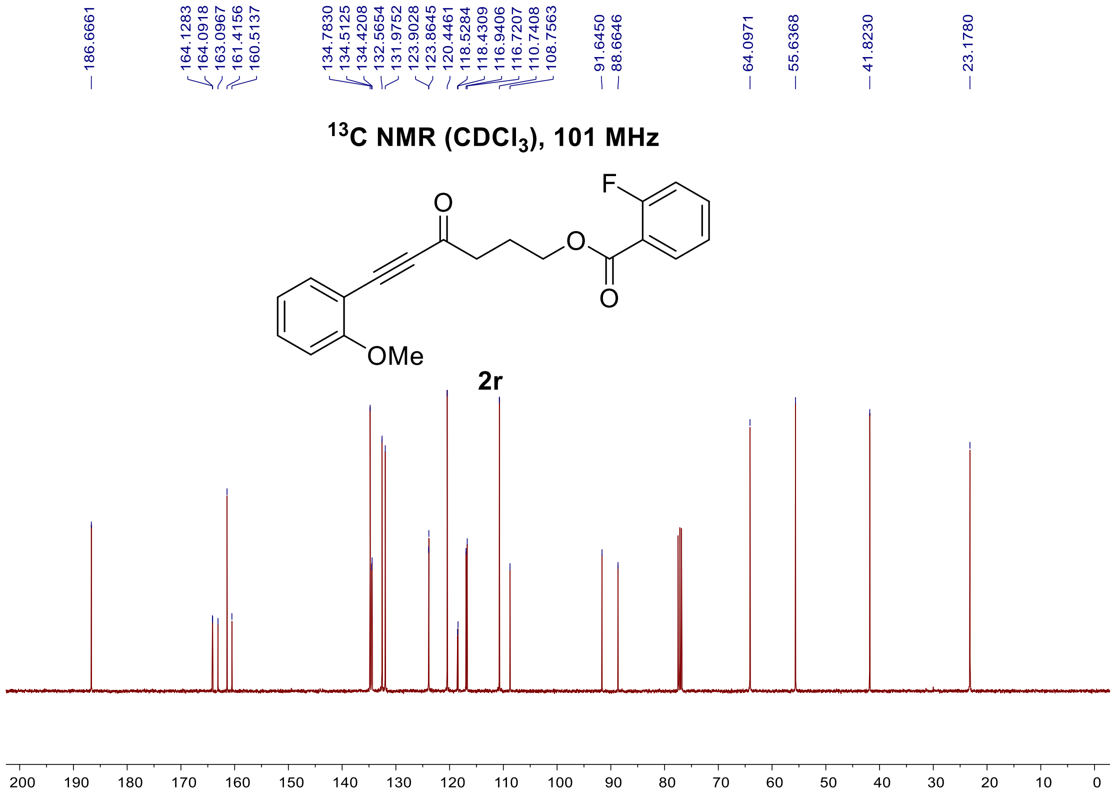
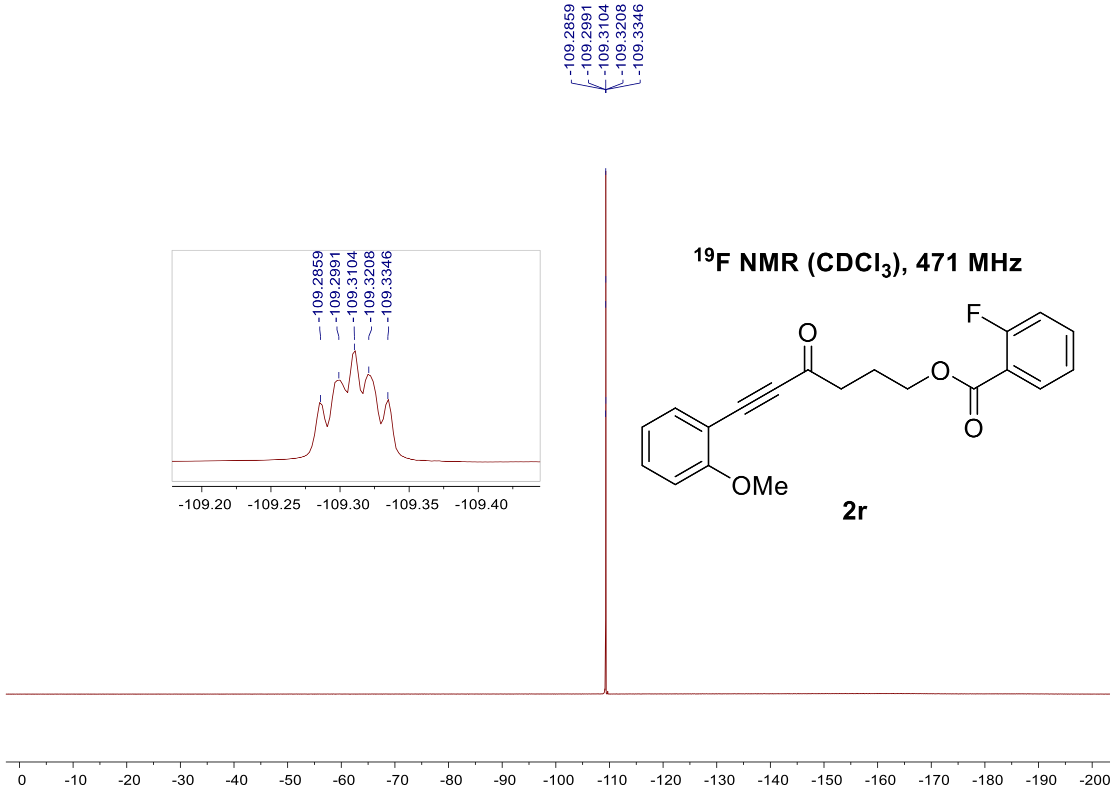
0.0



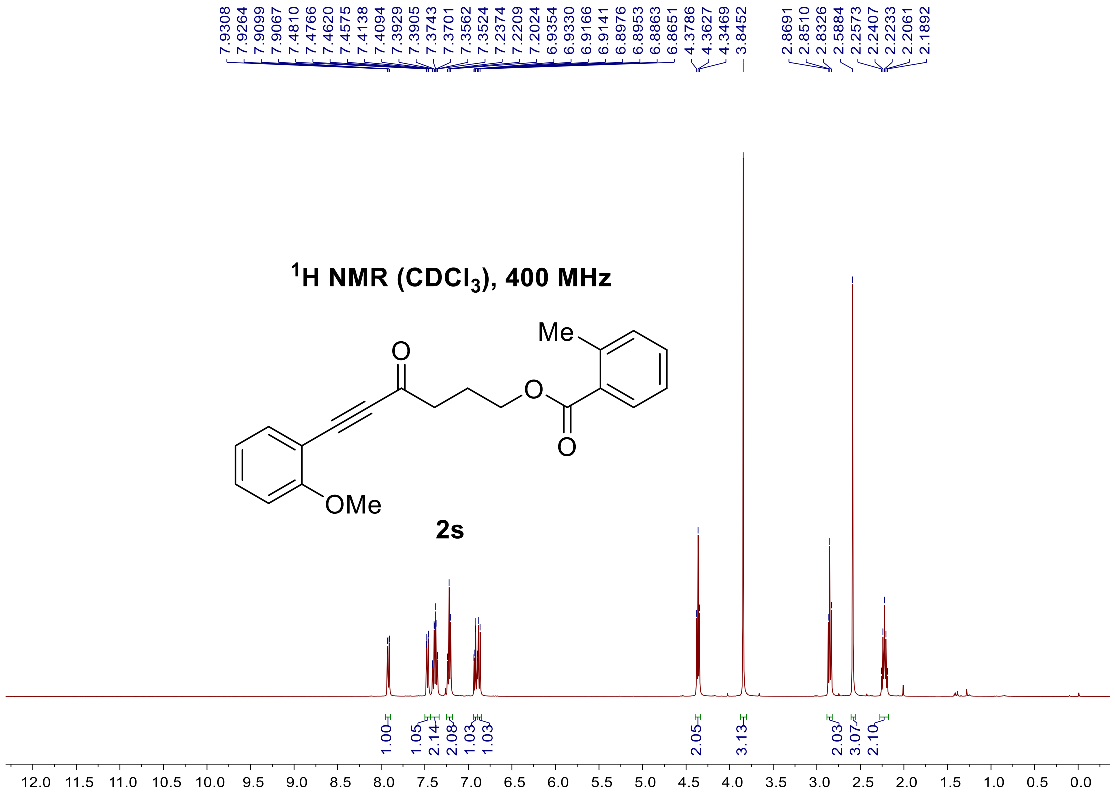
^{13}C NMR (CDCl$_3$), 101 MHz

2r



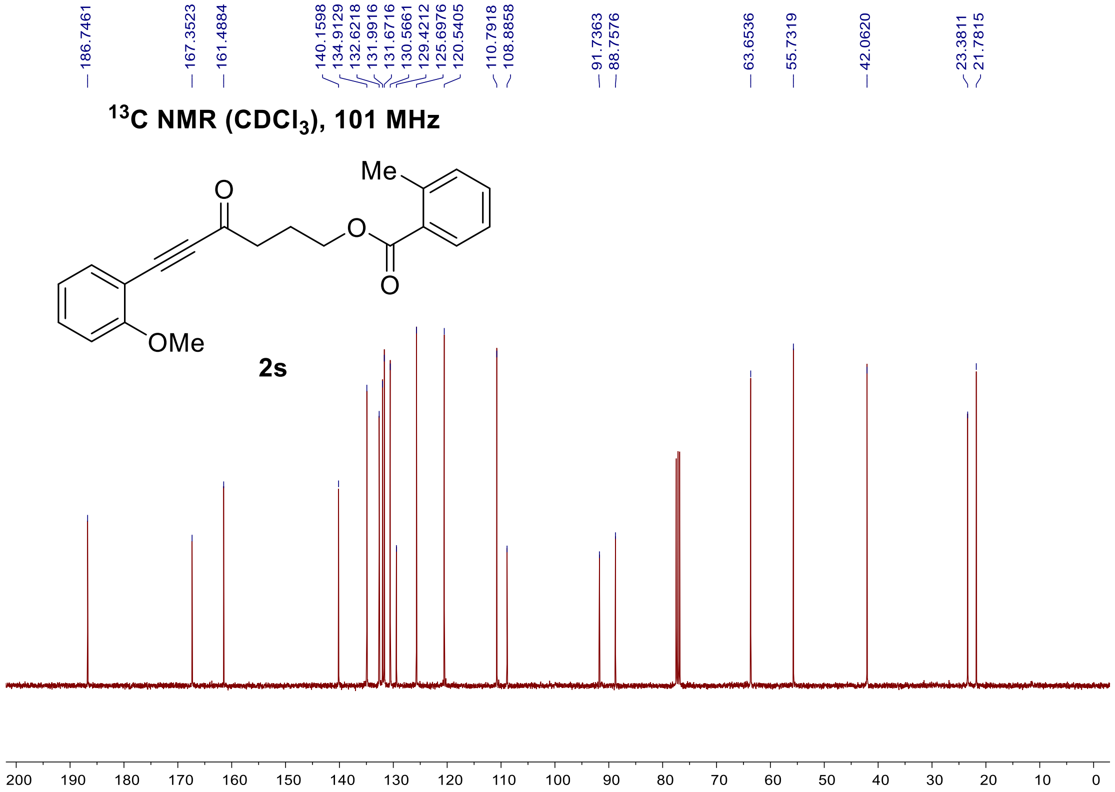
^{19}F NMR (CDCl$_3$), 471 MHz

2r



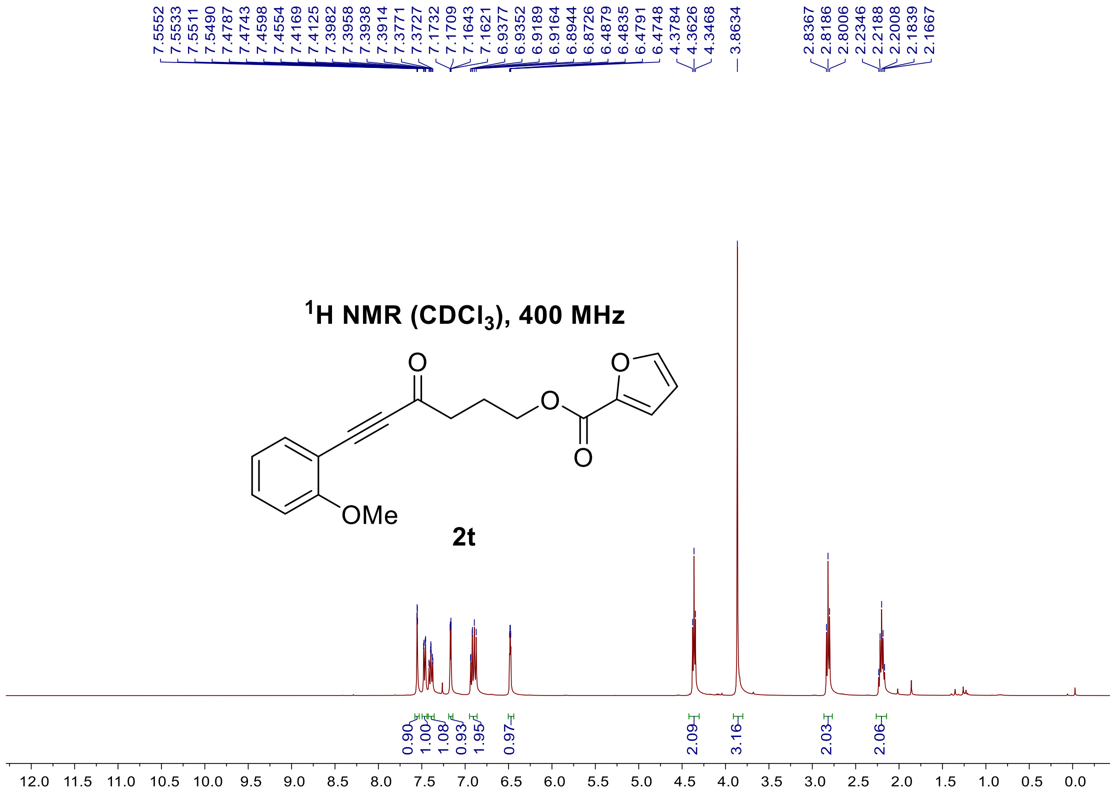
^{1}H NMR (CDCl$_3$), 400 MHz

2s



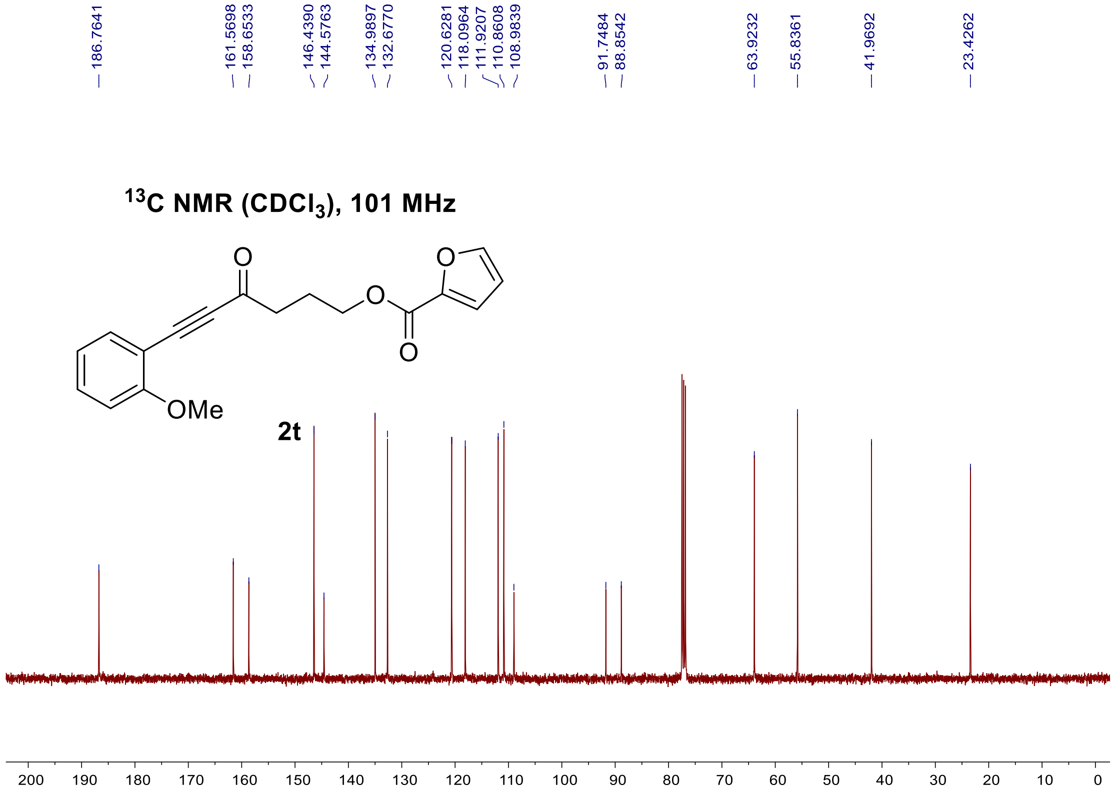
^{13}C NMR (CDCl$_3$), 101 MHz

2s



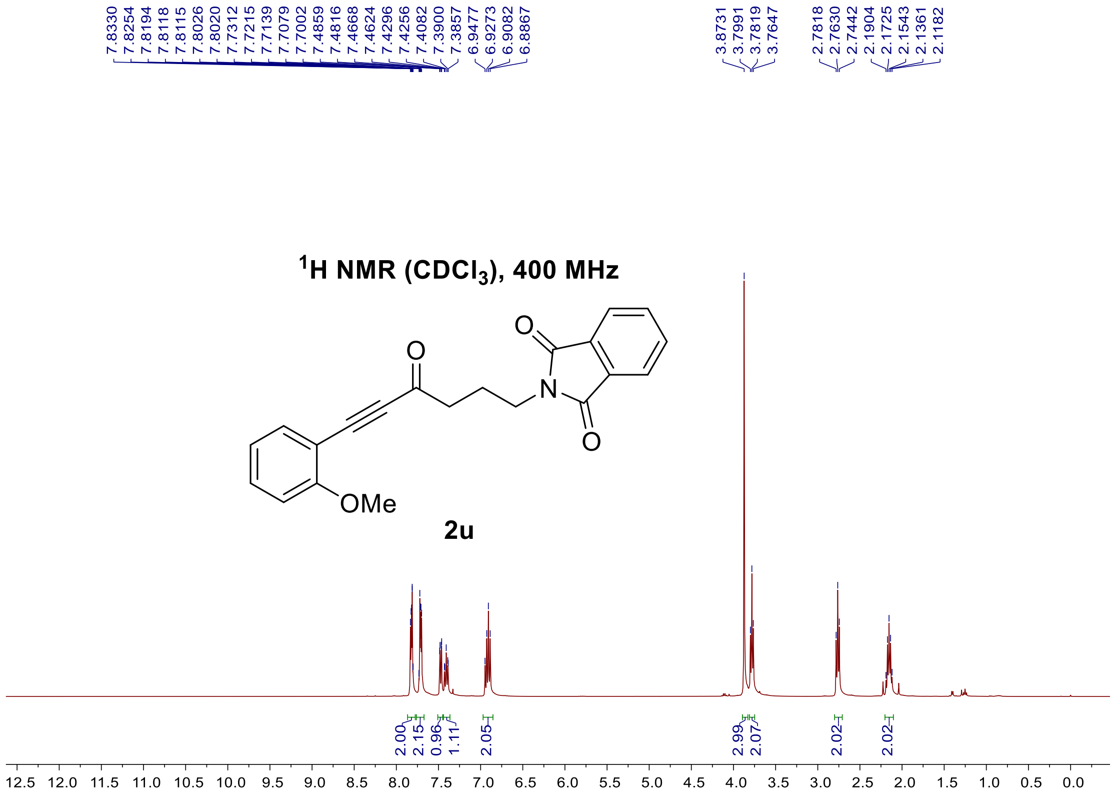
^{1}H NMR (CDCl$_3$), 400 MHz

2t



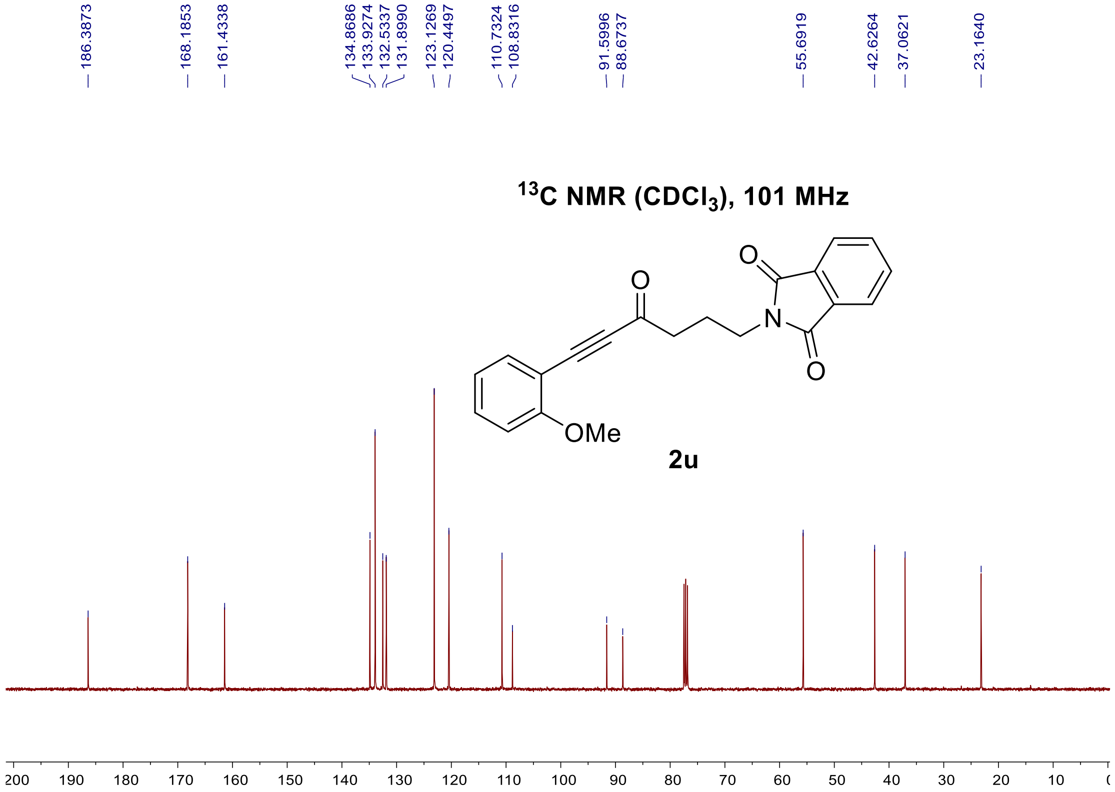
^{13}C NMR (CDCl$_3$), 101 MHz

2t



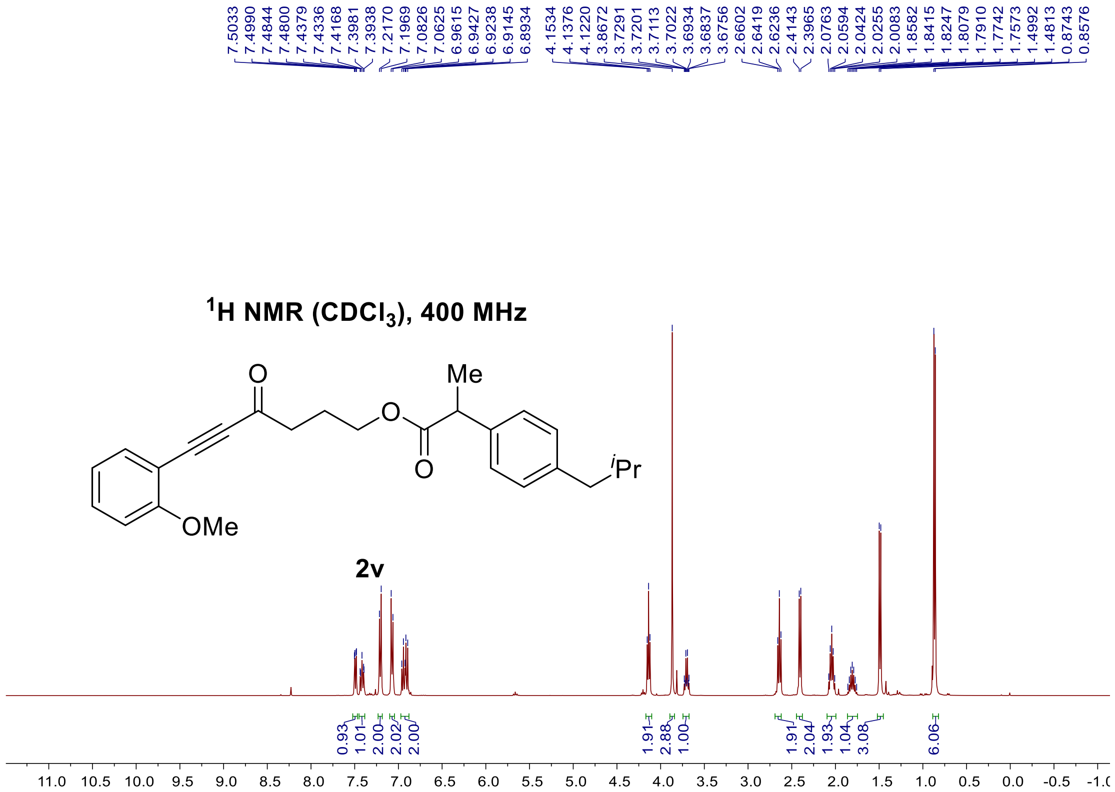
^{1}H NMR (CDCl$_3$), 400 MHz

2u



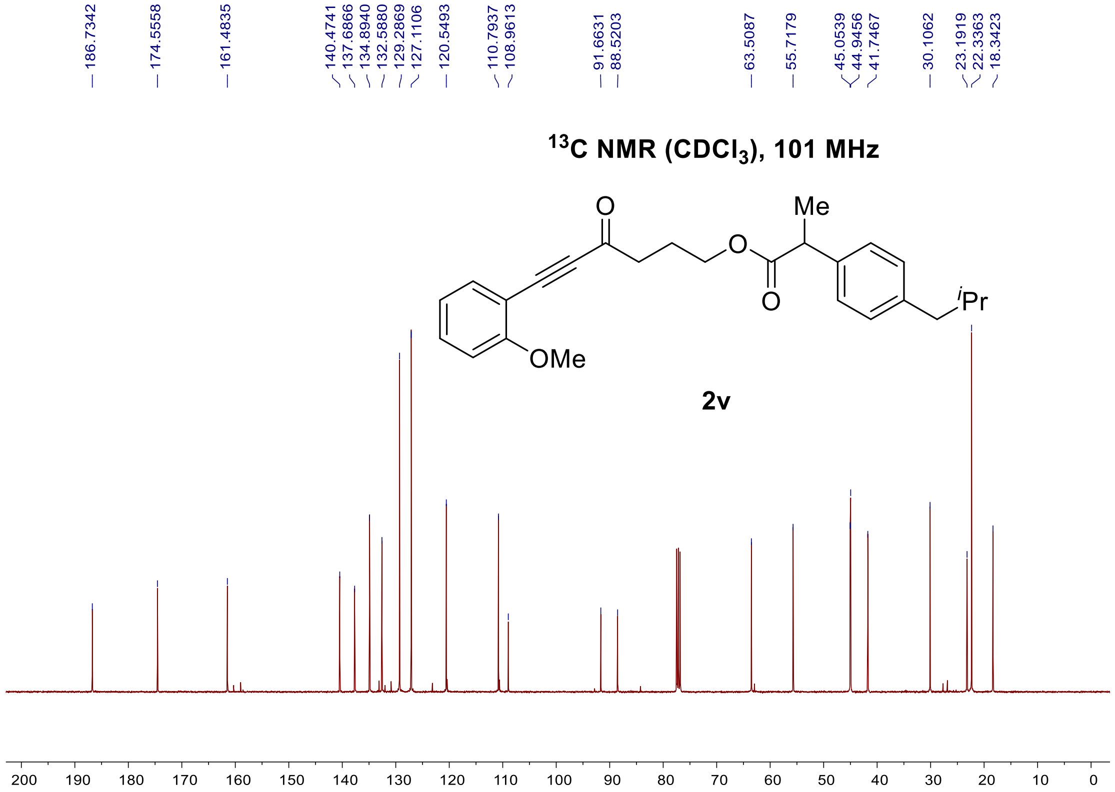
^{13}C NMR (CDCl$_3$), 101 MHz

2u



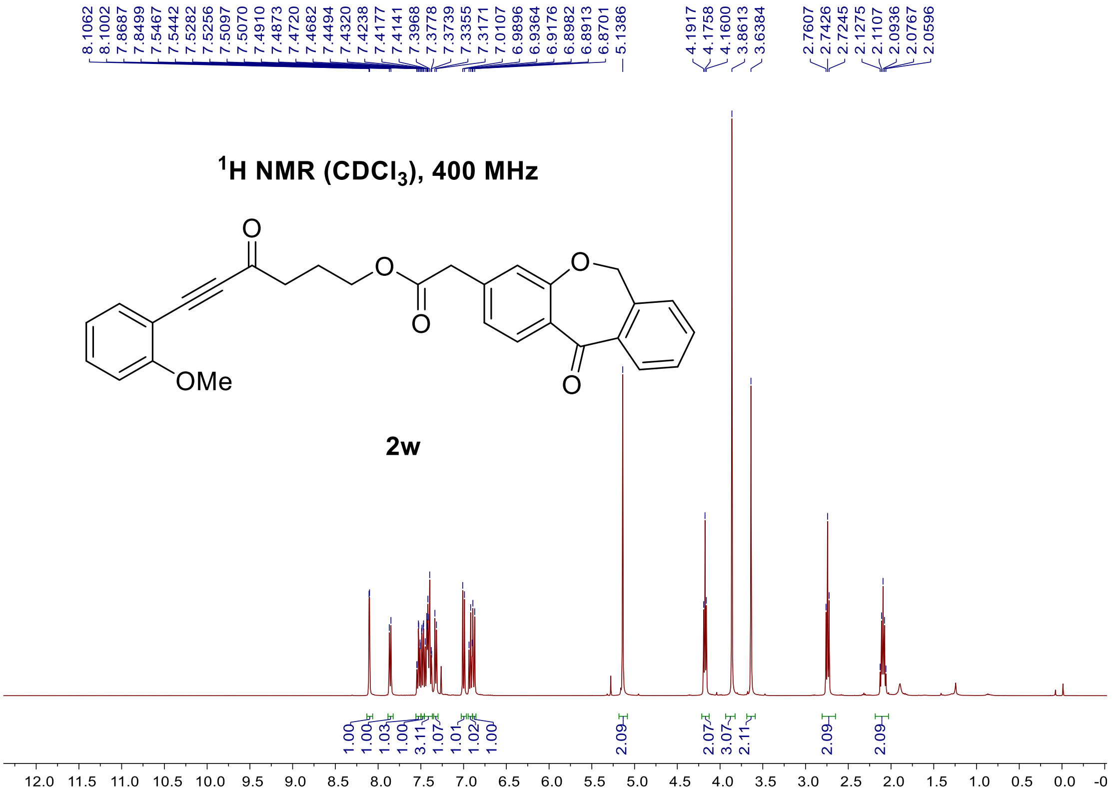
^{1}H NMR (CDCl$_3$), 400 MHz

2v



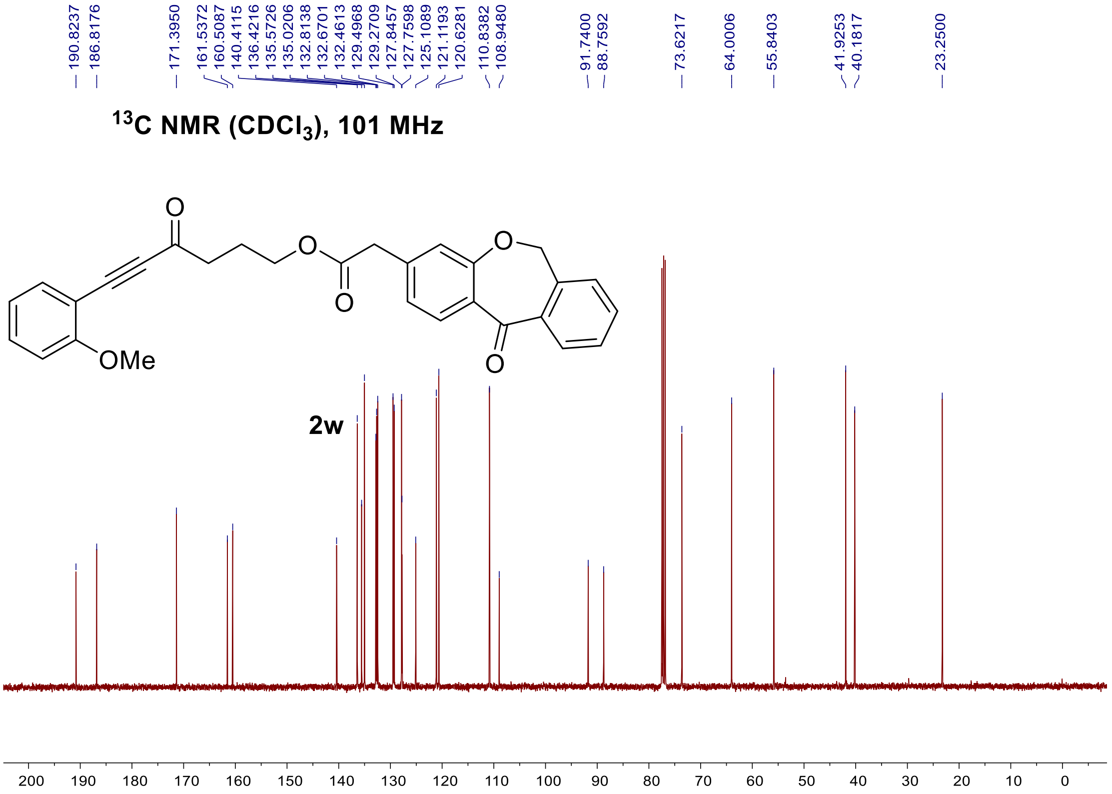
^{13}C NMR (CDCl$_3$), 101 MHz

2v



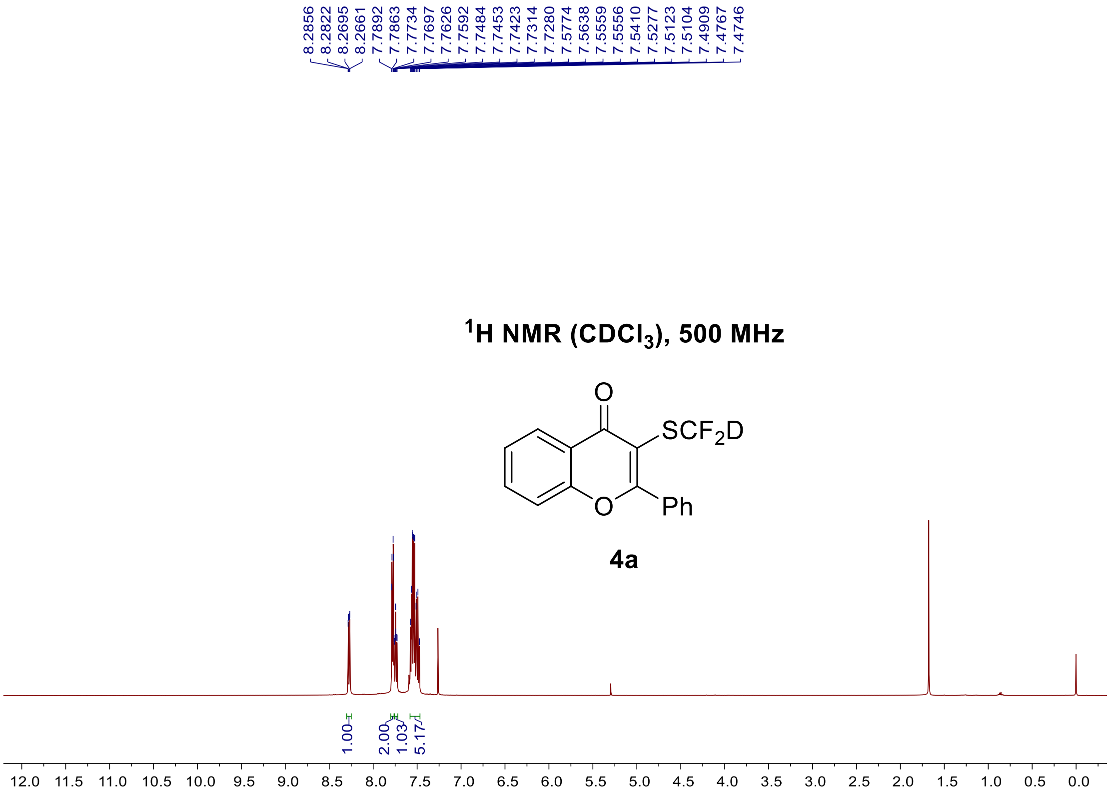
^{1}H NMR (CDCl$_3$), 400 MHz

2w



^{13}C NMR (CDCl$_3$), 101 MHz

2w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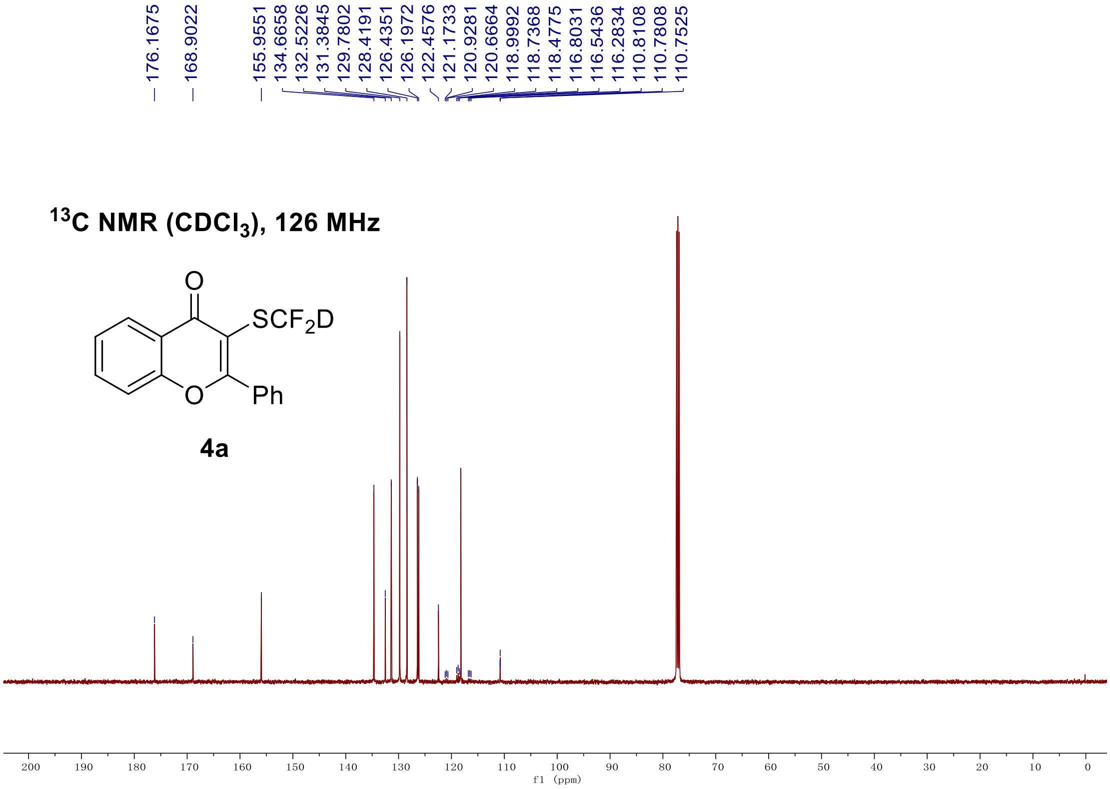
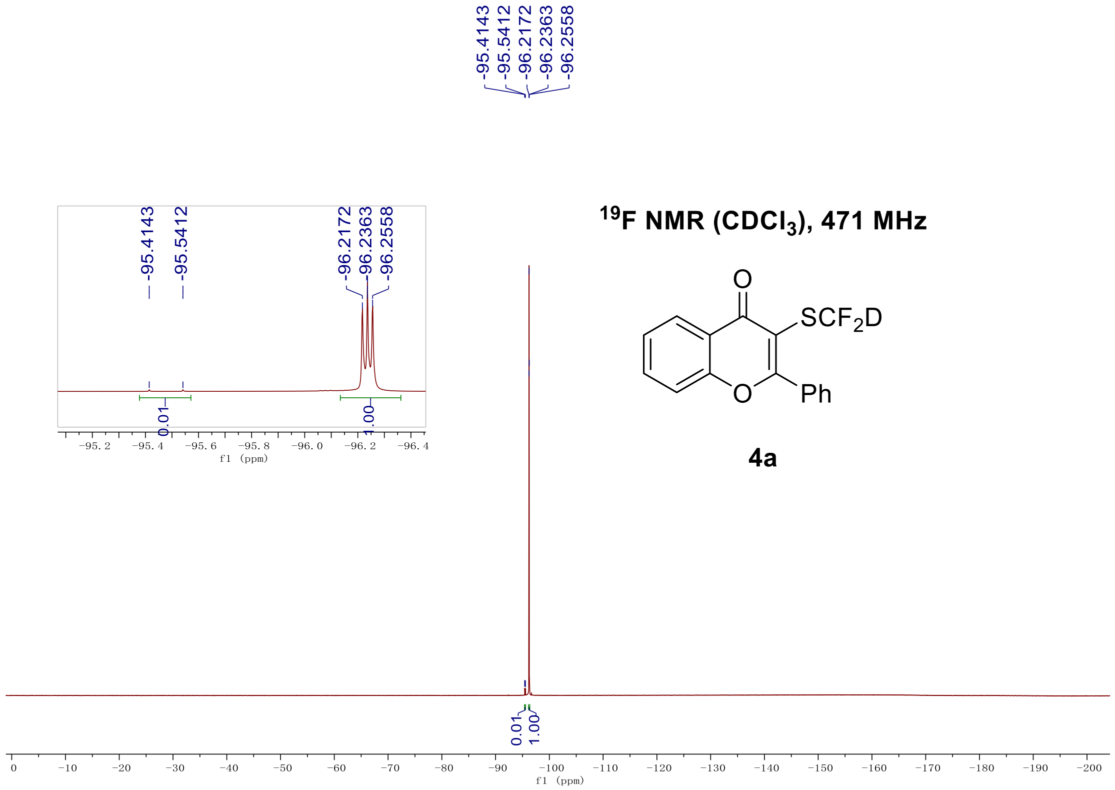
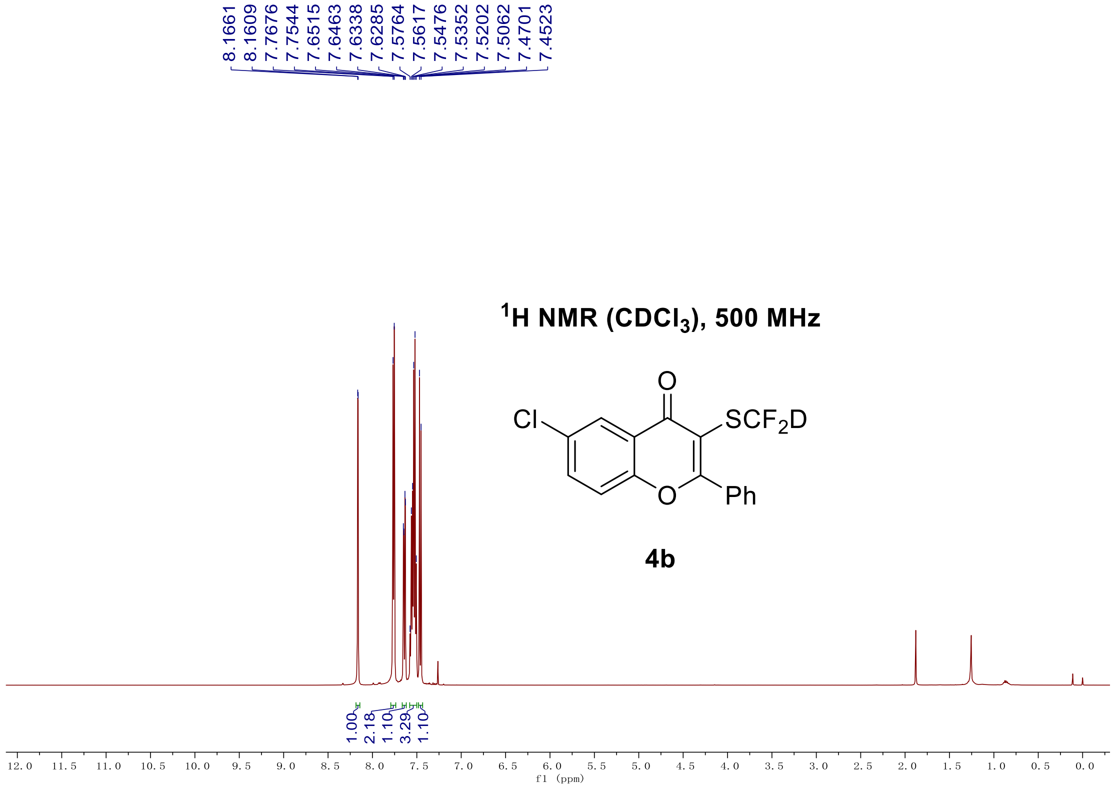
8.2822
8.2695
8.2661
7.7892
7.7863
7.7734
7.7697
7.7626
7.7592
7.7484
7.7453
7.7423
7.7314
7.7280
7.5774
7.5638
7.5559
7.5556
7.5410
7.5277
7.5123
7.5104
7.4909
7.4767
7.4746
^{1}H NMR (CDCl$_3$), 500 MHz
O
SCF$_2$D
O
Ph
4a
1.00
2.00
1.03
5.17
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

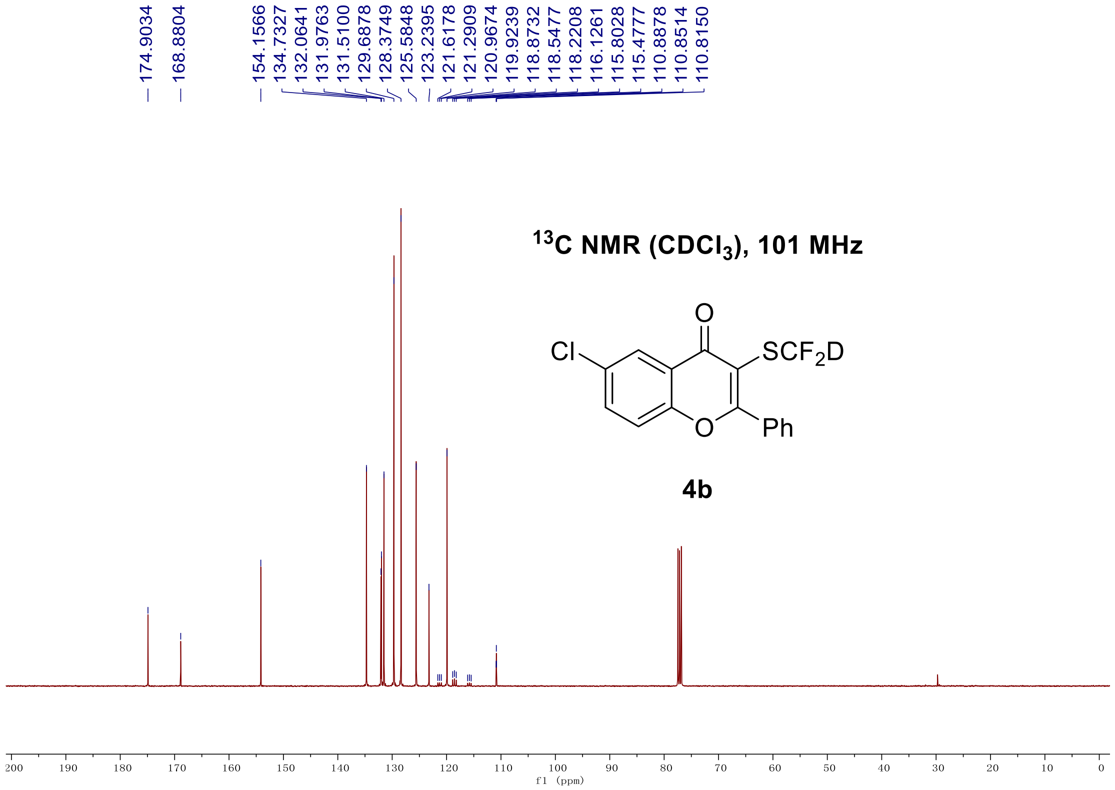

176.1675
168.9022
155.9551
134.6658
132.5226
131.3845
129.7802
128.4191
126.4351
126.1972
122.4576
121.1733
120.9281
120.6664
118.9992
118.7368
118.4775
116.8031
116.5436
116.2834
110.8108
110.7808
110.7525
^{13}C NMR (CDCl$_3$), 126 MHz
O
SCF$_2$D
O
Ph
4a
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

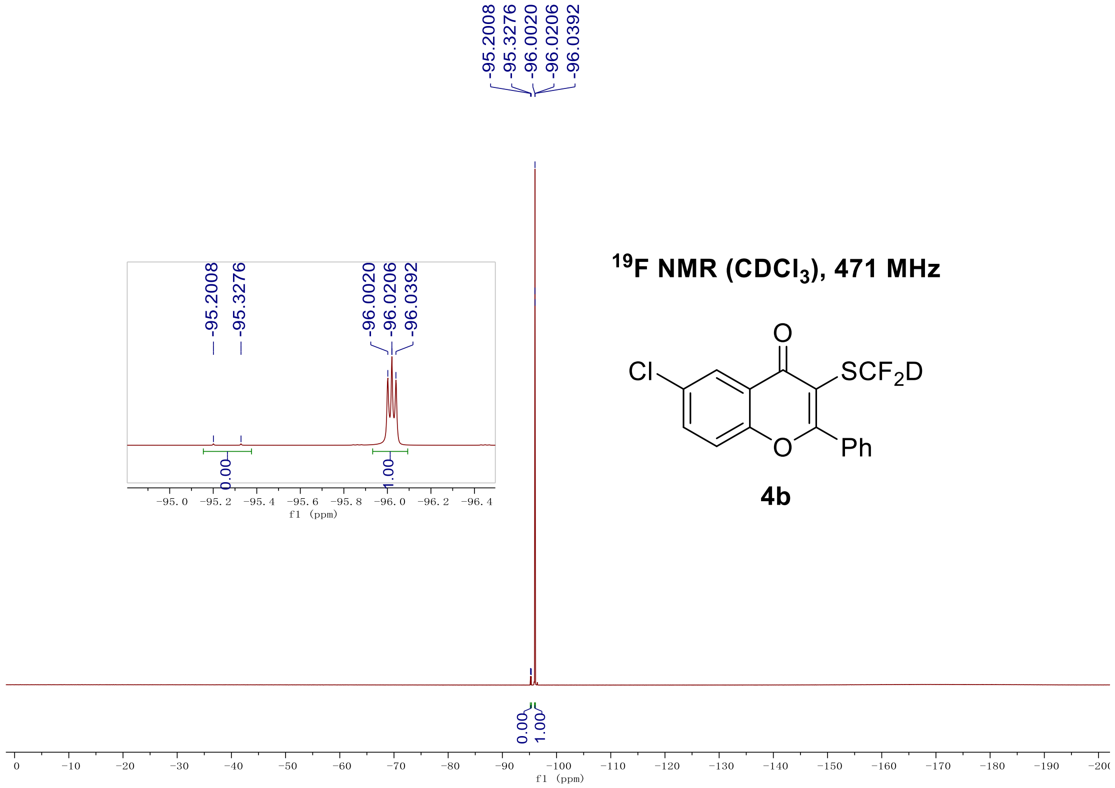

-95.4143
-95.5412
-96.2172
-96.2363
-96.2558
^{19}F NMR ($CDCl_3$), 471 MHz
O
SCF$_2$D
O
Ph
0.01
1.00
-95.2 -95.4 -95.6 -95.8 -96.0 -96.2 -96.4
f1 (ppm)
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

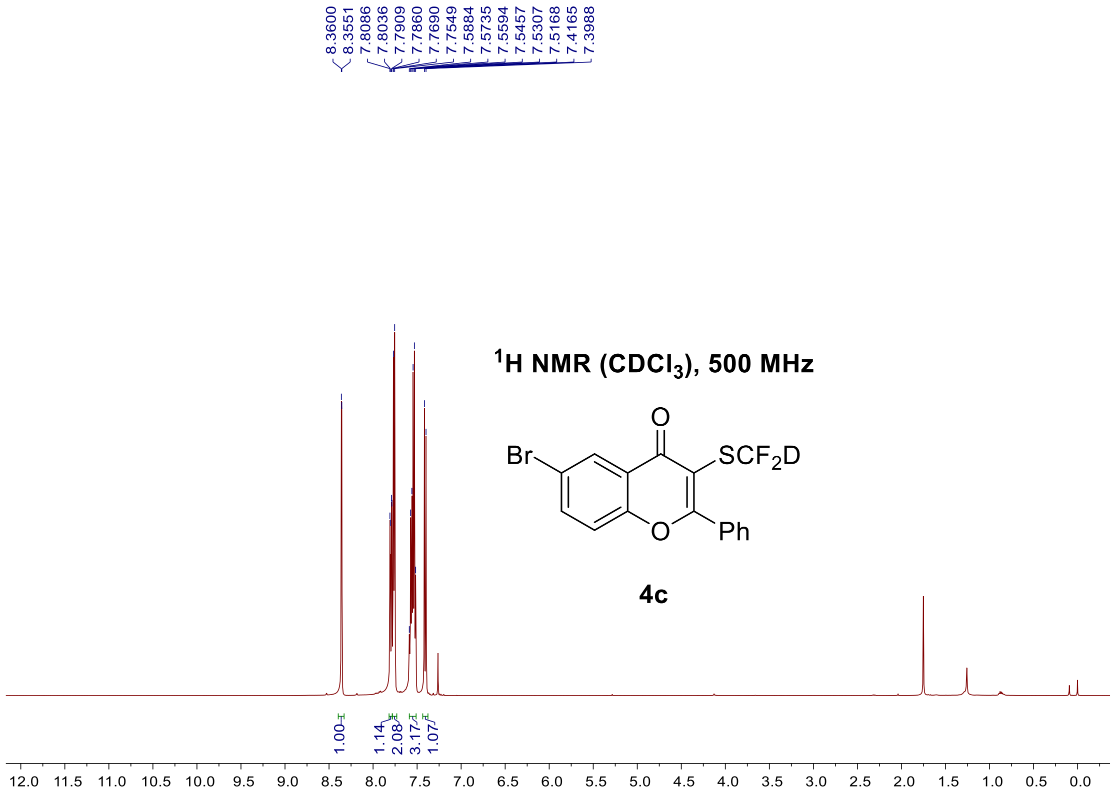
4a


8.1661
8.1609
7.7676
7.7544
7.6515
7.6463
7.6338
7.6285
7.5764
7.5617
7.5476
7.5352
7.5202
7.5062
7.4701
7.4523
^{1}H NMR ($CDCl_3$), 500 MHz
O
Cl
SCF$_2$D
O
Ph
1.00
2.18
1.10
3.29
1.10
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

4b


174.9034
168.8804
154.1566
134.7327
132.0641
131.9763
131.5100
129.6878
128.3749
125.5848
123.2395
121.6178
121.2909
120.9674
119.9239
118.8732
118.5477
118.2208
116.1261
115.8028
115.4777
110.8878
110.8514
110.8150
^{13}C NMR (CDCl$_3$), 101 MHz
O
Cl
SCF$_2$D
O
Ph
4b
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-95.2008
-95.3276
-96.0020
-96.0206
-96.0392
0.00
1.00
−95.0 −95.2 −95.4 −95.6 −95.8 −96.0 −96.2 −96.4
f1 (ppm)
^{19}F NMR (CDCl$_3$), 471 MHz
O
Cl
SCF$_2$D
O
Ph
4b
0.00
1.00
0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200
f1 (ppm)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8.3551
7.8086
7.8036
7.7909
7.7860
7.7690
7.7549
7.5884
7.5735
7.5594
7.5457
7.5307
7.5168
7.4165
7.3988
^{1}H NMR (CDCl$_3$), 500 MHz
O
Br
SCF$_2$D
O
Ph
4c
1.00
1.14
2.08
3.17
1.07
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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4.5
4.0
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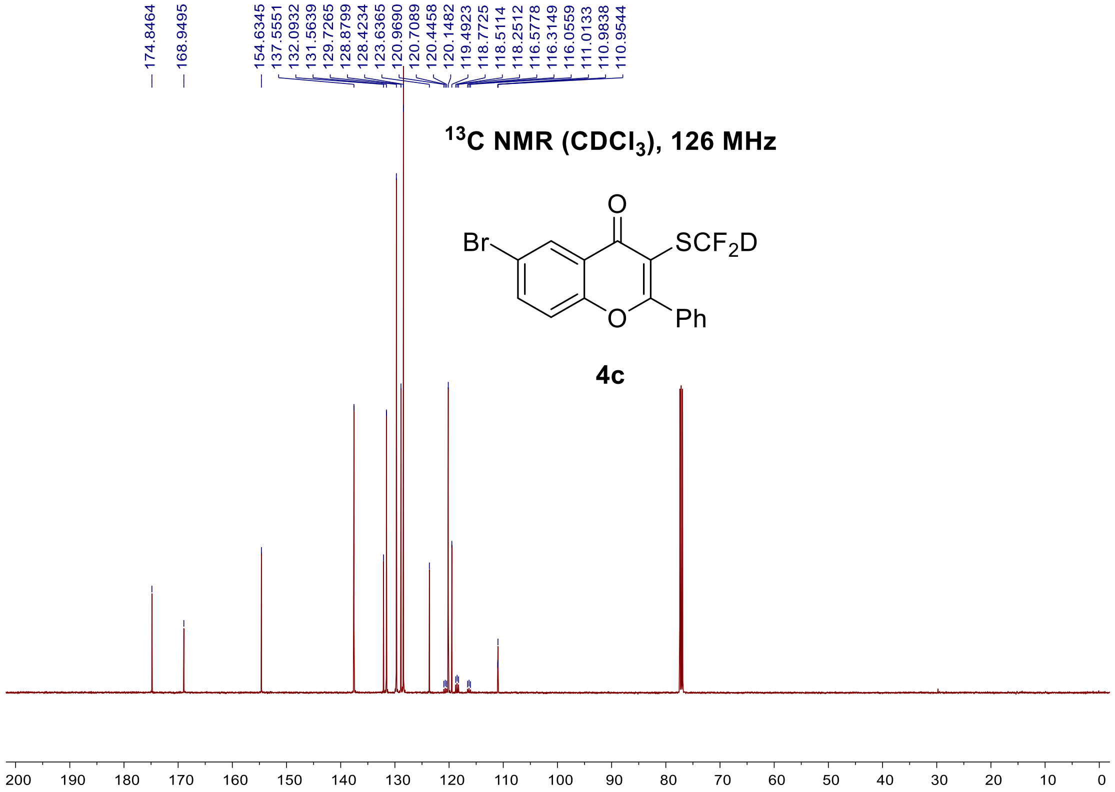
2.5
2.0
1.5
1.0
0.5
0.0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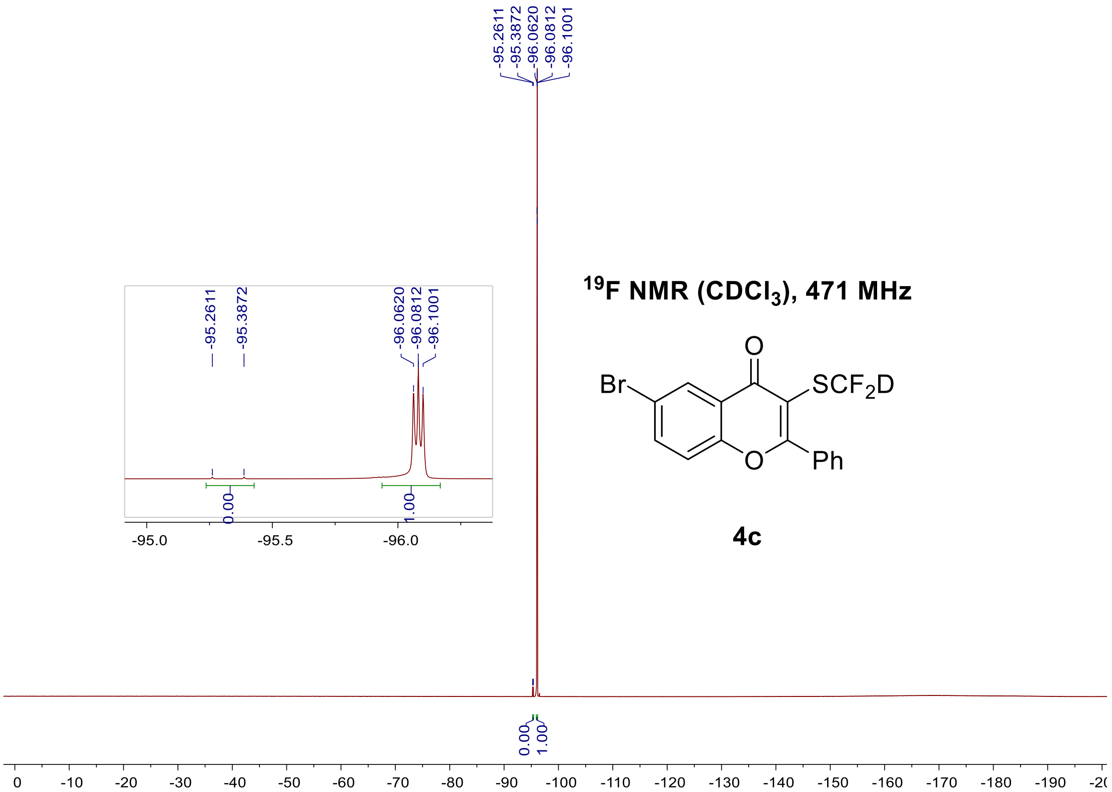
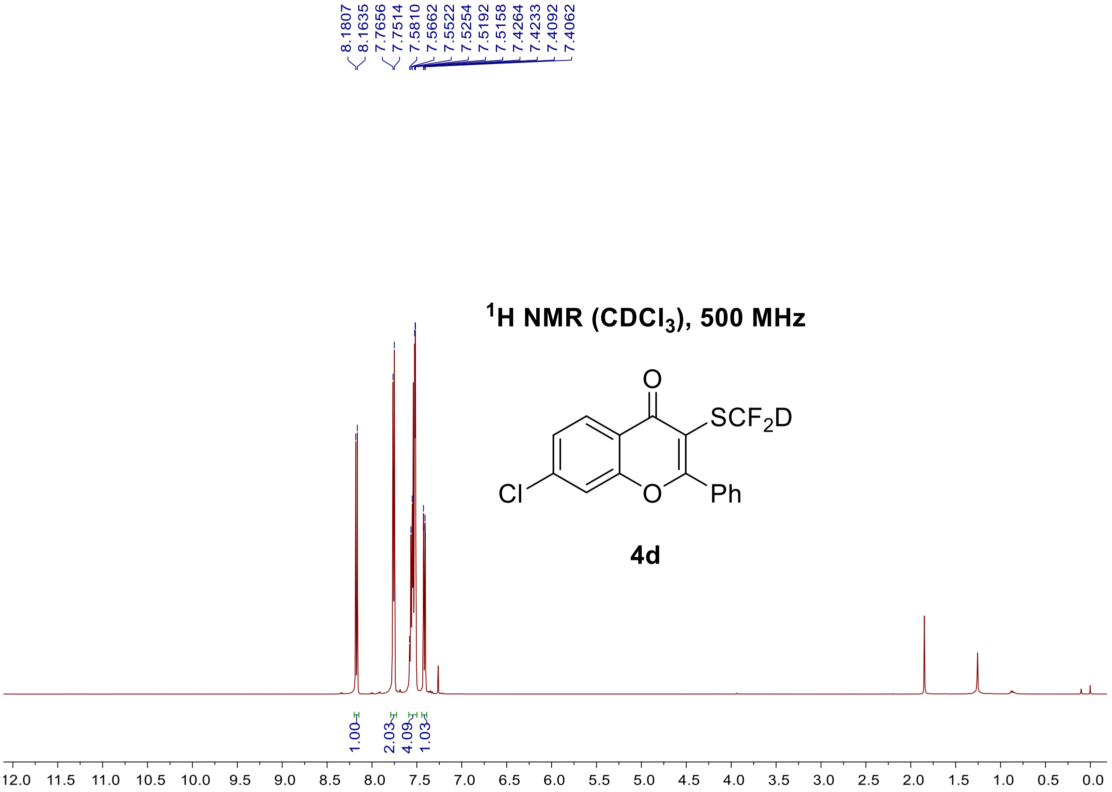
132.0932
131.5639
129.7265
128.8799
128.4234
123.6365
120.9690
120.7089
120.4458
120.1482
119.4923
118.7725
118.5114
118.2512
116.5778
116.3149
116.0559
111.0133
110.9838
110.9544
^{13}C NMR (CDCl$_3$), 126 MHz
O
Br
SCF$_2$D
O
Ph
4c
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0



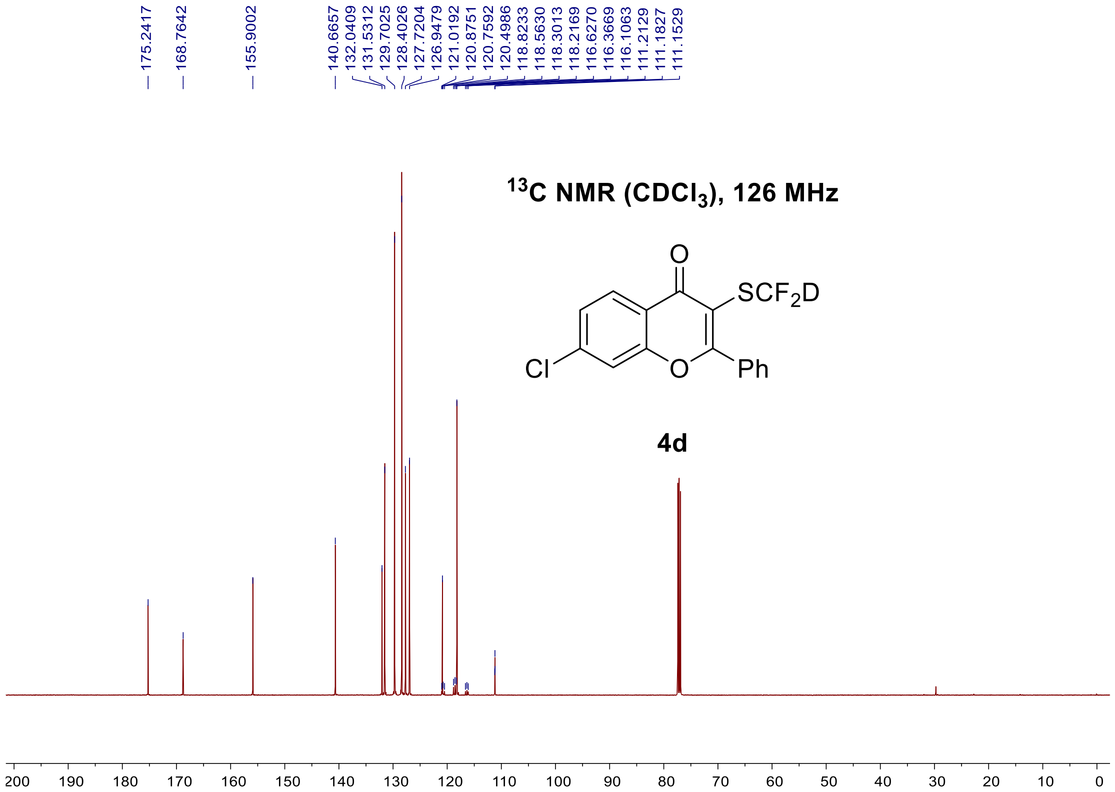
^{19}F NMR (CDCl$_3$), 471 MHz

4c



^{1}H NMR (CDCl$_3$), 500 MHz

4d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155.9002
140.6657
132.0409
131.5312
129.7025
128.4026
127.7204
126.9479
121.0192
120.8751
120.7592
120.4986
118.8233
118.5630
118.3013
118.2169
116.6270
116.3669
116.1063
111.2129
111.1827
111.1529
^{13}C NMR (CDCl$_3$), 126 MHz
O
SCF$_2$D
Cl
O
Ph
4d
200
190
180
170
160
150
140
130
120
110
100
90
80
70
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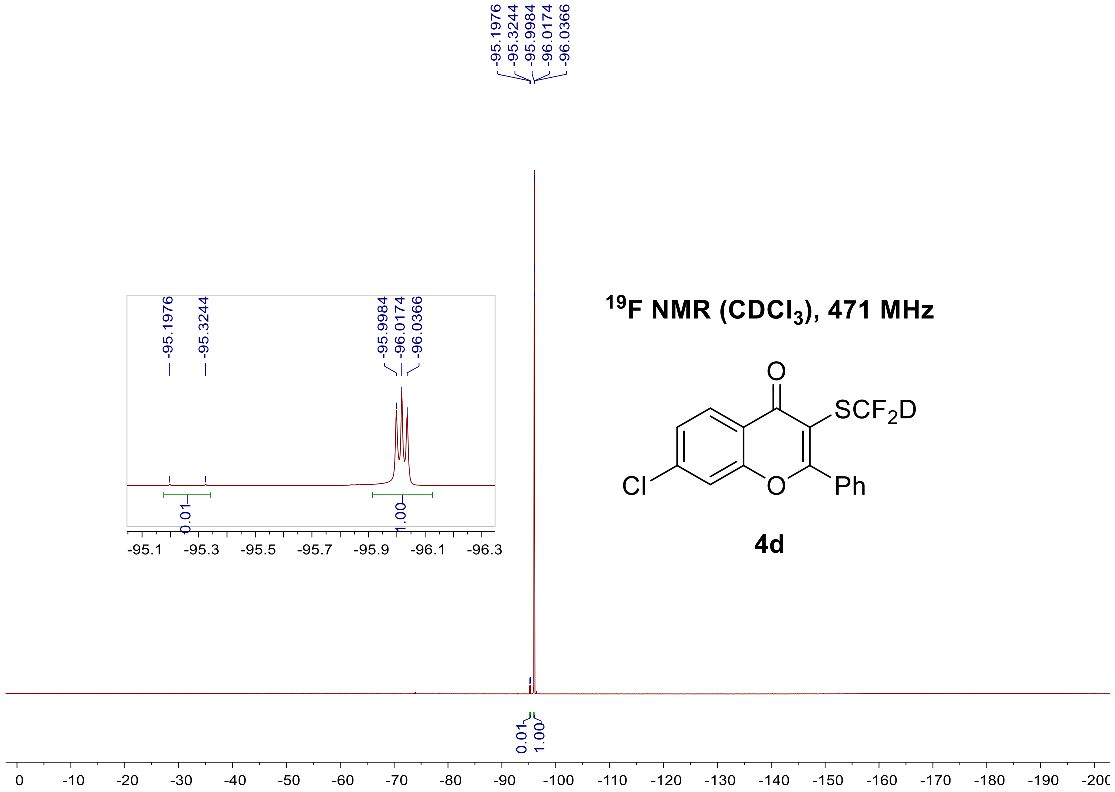
50
40
30
20
10
0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-95.9984
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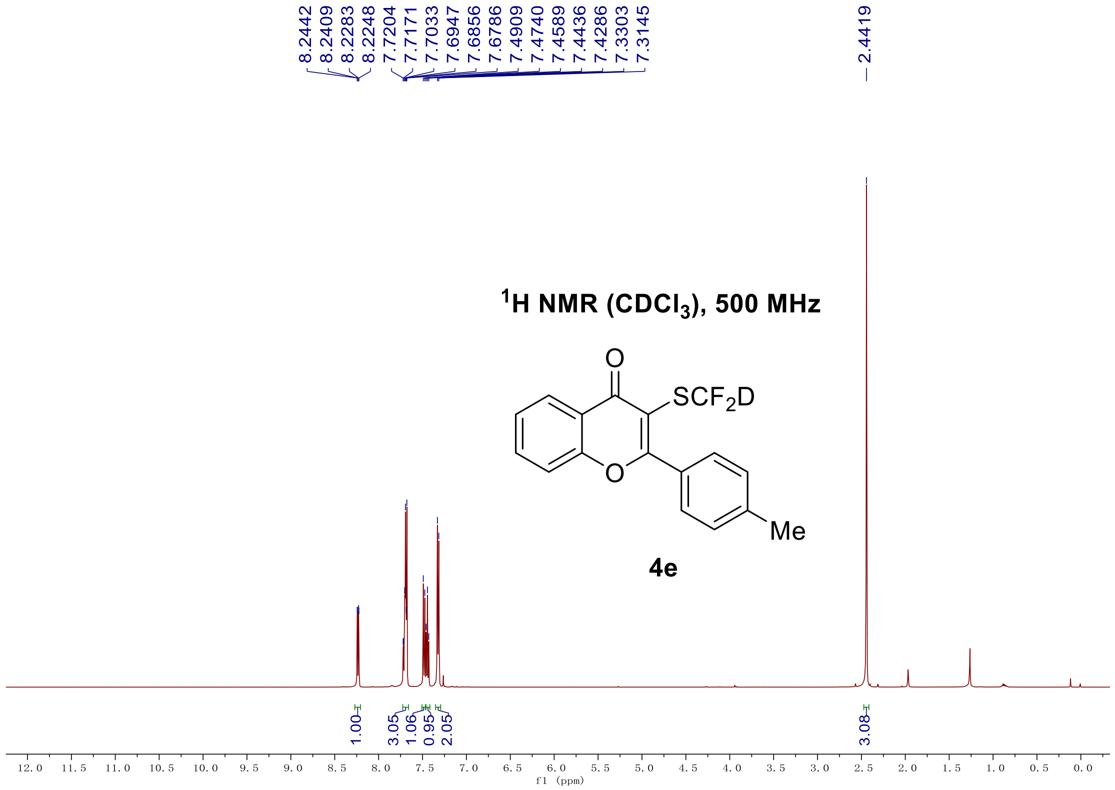
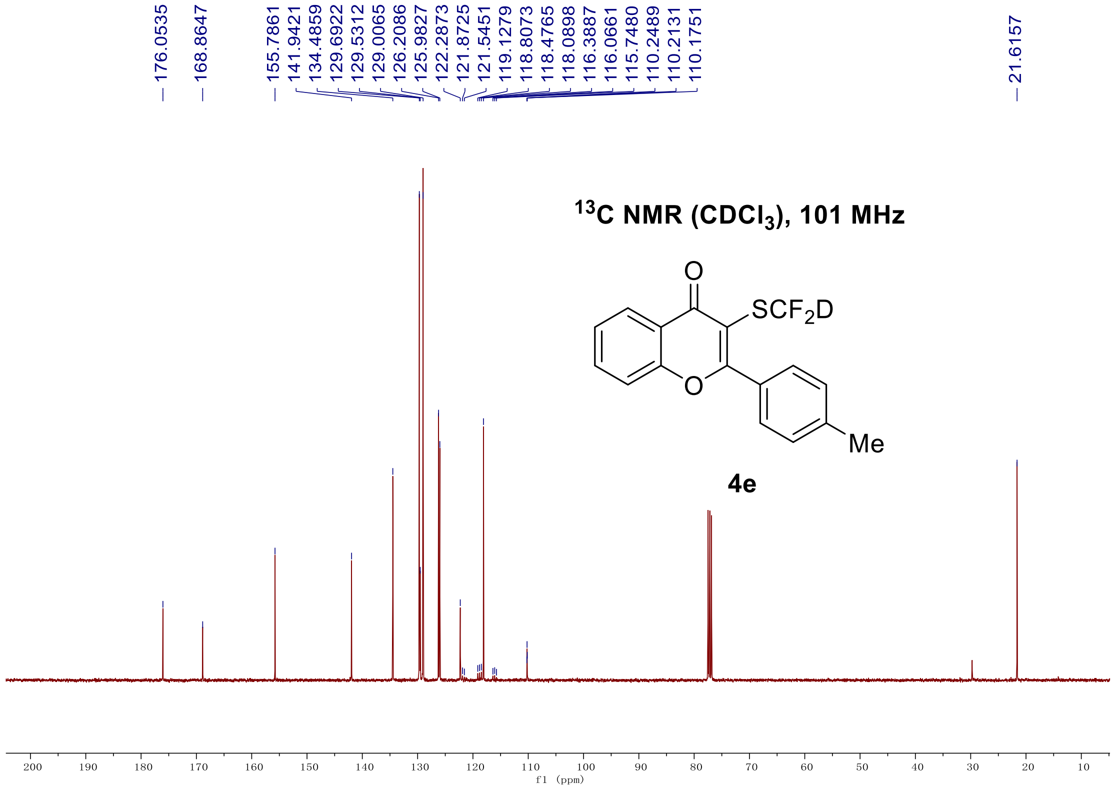
-96.0366
^{19}F NMR (CDCl$_3$), 471 MHz
O
SCF$_2$D
Cl
O
Ph
4d
0.01
1.00
-95.1
-95.3
-95.5
-95.7
-95.9
-96.1
-96.3
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200


8.2442
8.2409
8.2283
8.2248
7.7204
7.7171
7.7033
7.6947
7.6856
7.6786
7.4909
7.4740
7.4589
7.4436
7.4286
7.3303
7.3145
2.4419
^{1}H NMR (CDCl$_3$), 500 MHz
O
SCF$_2$D
O
Me
4e
1.00
3.05
1.06
0.95
2.05
3.08
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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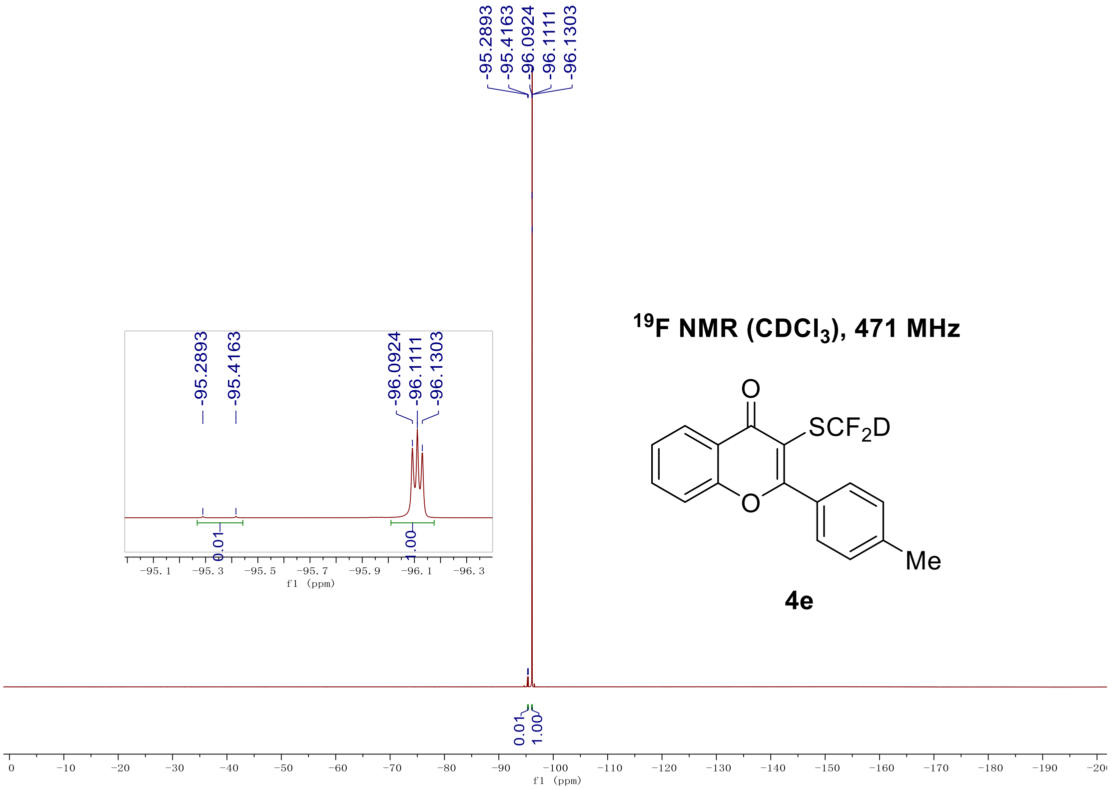
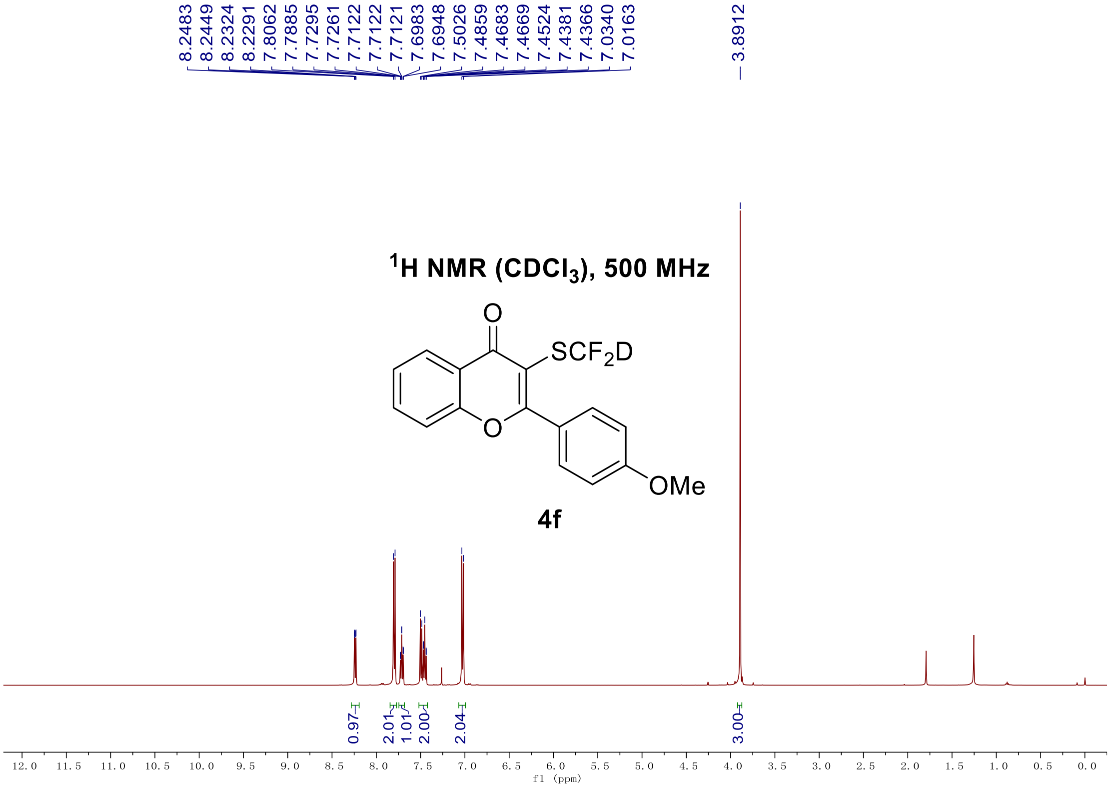
141.9421
134.4859
129.6922
129.5312
129.0065
126.2086
125.9827
122.2873
121.8725
121.5451
119.1279
118.8073
118.4765
118.0898
116.3887
116.0661
115.7480
110.2489
110.2131
110.1751
21.6157
^{13}C NMR (CDCl$_3$), 101 MHz
O
SCF$_2$D
O
Me
4e
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)



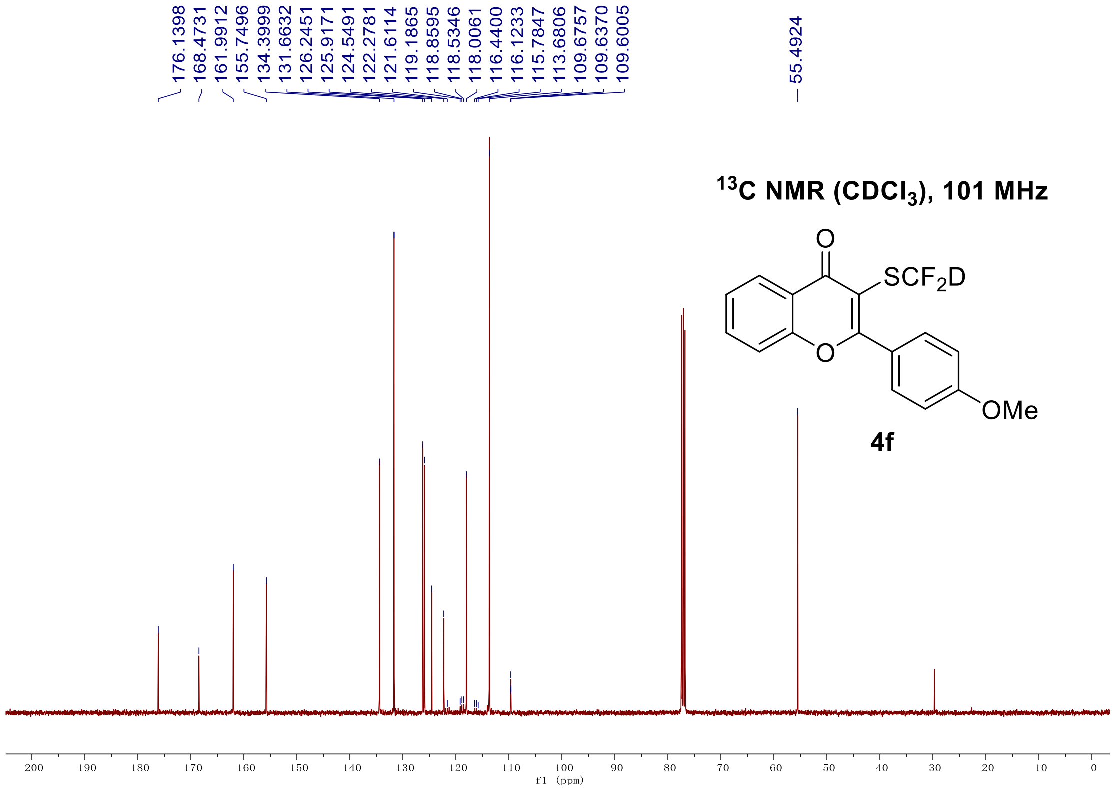
^{19}F NMR ($CDCl_3$), 471 MHz

4e



^{1}H NMR ($CDCl_3$), 500 MHz

4f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134.3999
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126.2451
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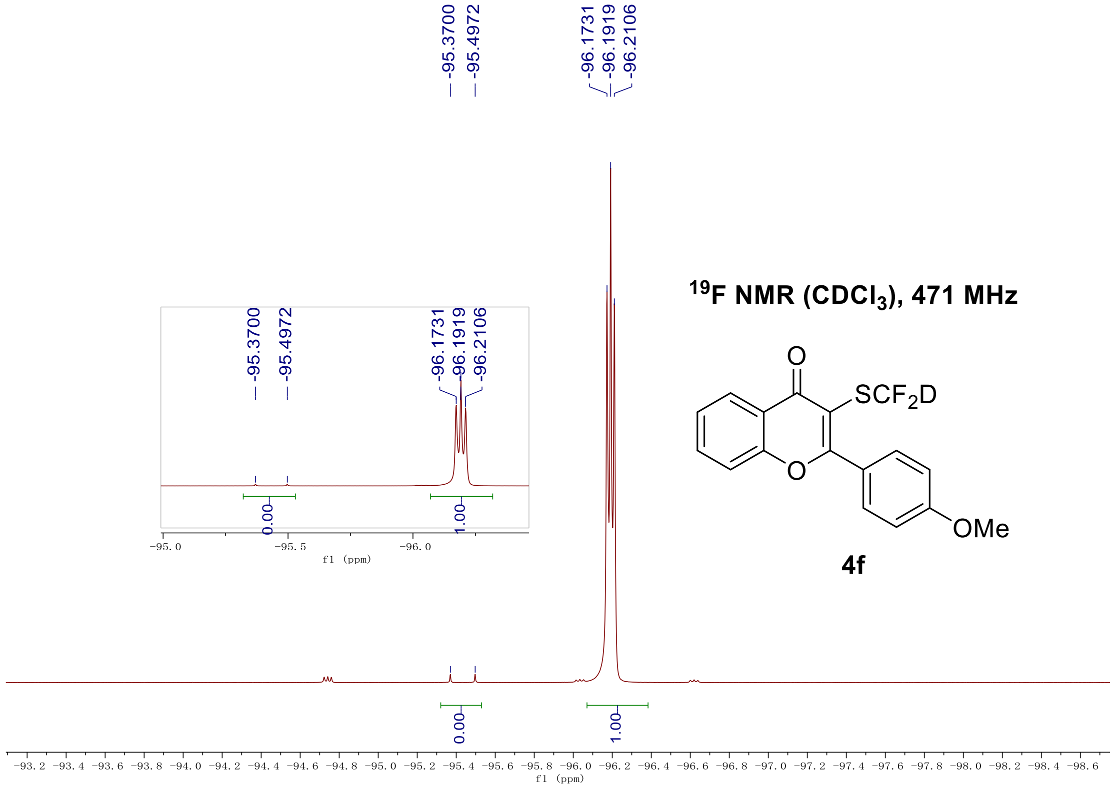
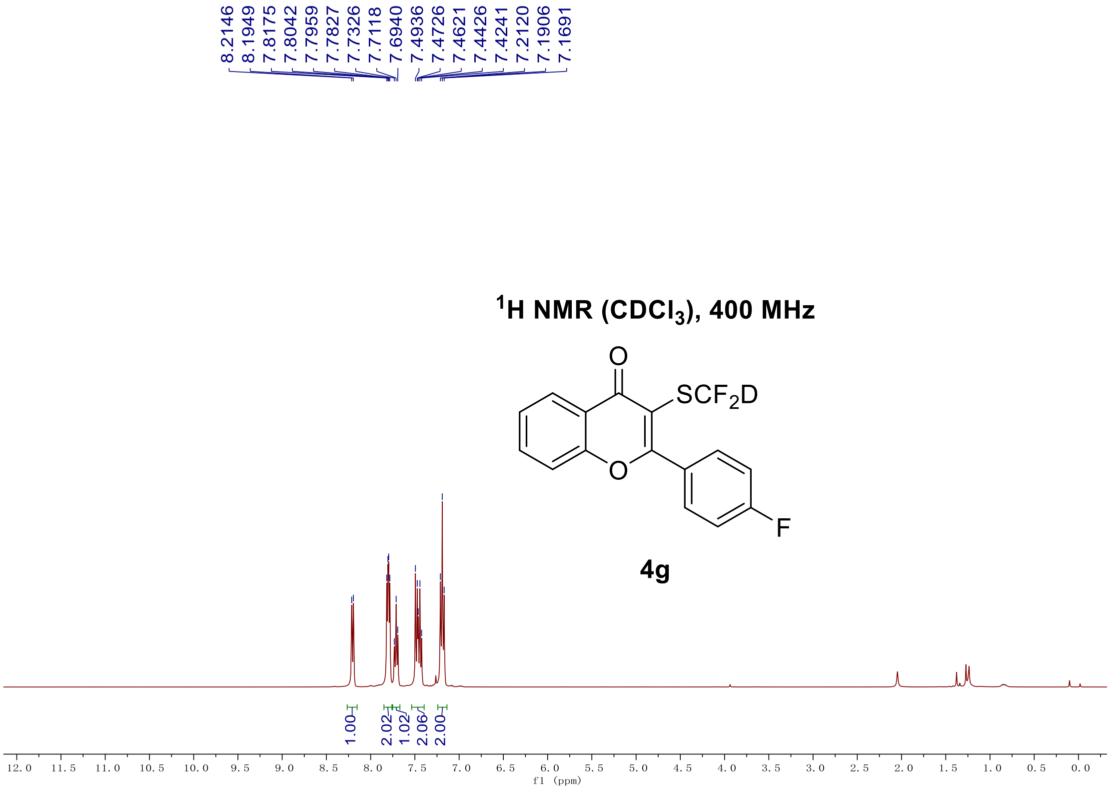
124.5491
122.2781
121.6114
119.1865
118.8595
118.5346
118.0061
116.4400
116.1233
115.7847
113.6806
109.6757
109.6370
109.6005
55.4924
^{13}C NMR (CDCl$_3$), 101 MHz
O
SCF$_2$D
O
OMe
4f
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-95.3700
-95.4972
-96.1731
-96.1919
-96.2106
^{19}F NMR (CDCl$_3$), 471 MHz
O
SCF$_2$D
O
OMe
4f
0.00
1.00
-95.0 -95.5 -96.0
f1 (ppm)
-93.2 -93.4 -93.6 -93.8 -94.0 -94.2 -94.4 -94.6 -94.8 -95.0 -95.2 -95.4 -95.6 -95.8 -96.0 -96.2 -96.4 -96.6 -96.8 -97.0 -97.2 -97.4 -97.6 -97.8 -98.0 -98.2 -98.4 -98.6
f1 (ppm)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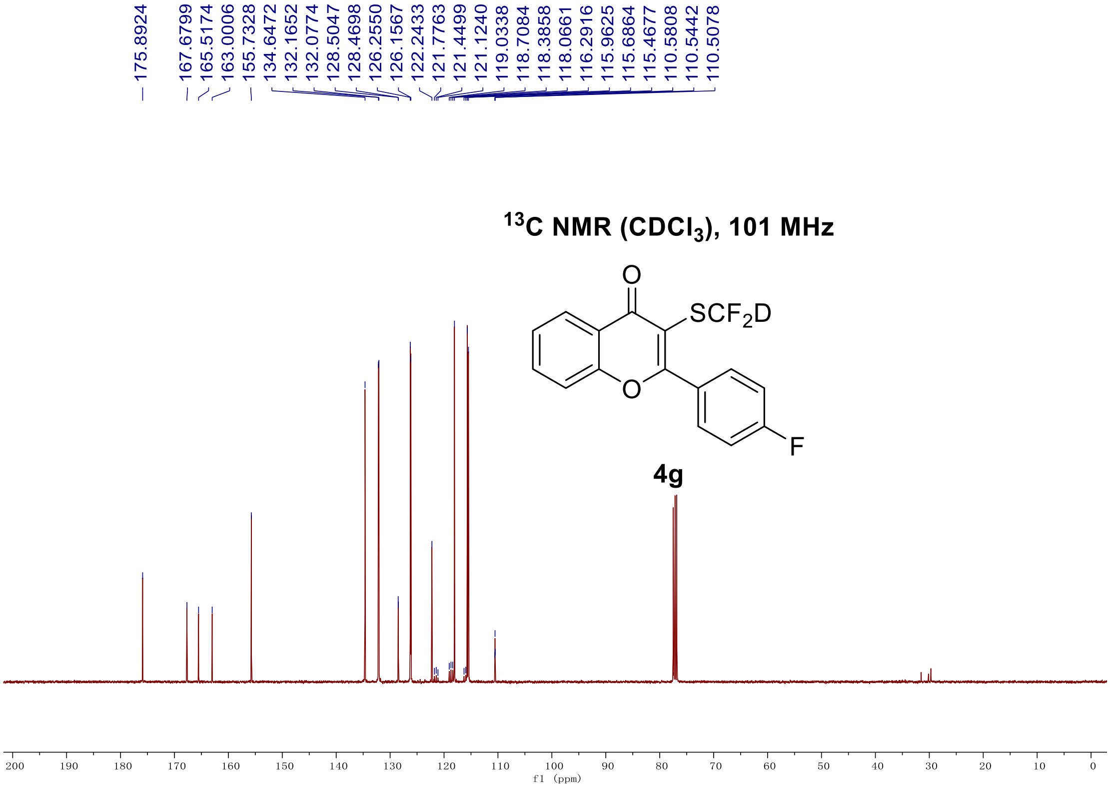
8.1949
7.8175
7.8042
7.7959
7.7827
7.7326
7.7118
7.6940
7.4936
7.4726
7.4621
7.4426
7.4241
7.2120
7.1906
7.1691
1H NMR (CDCl3), 400 MHz
O
SCF2D
O
F
1.00
2.02
1.02
2.06
2.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

4g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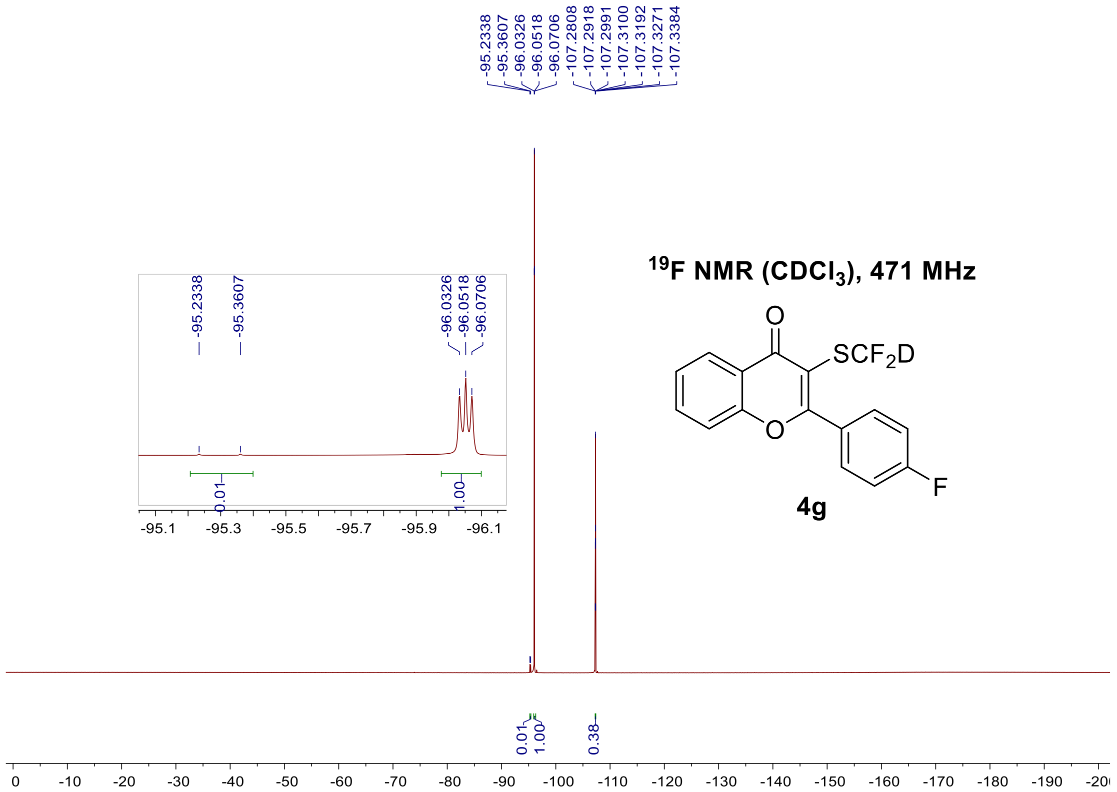
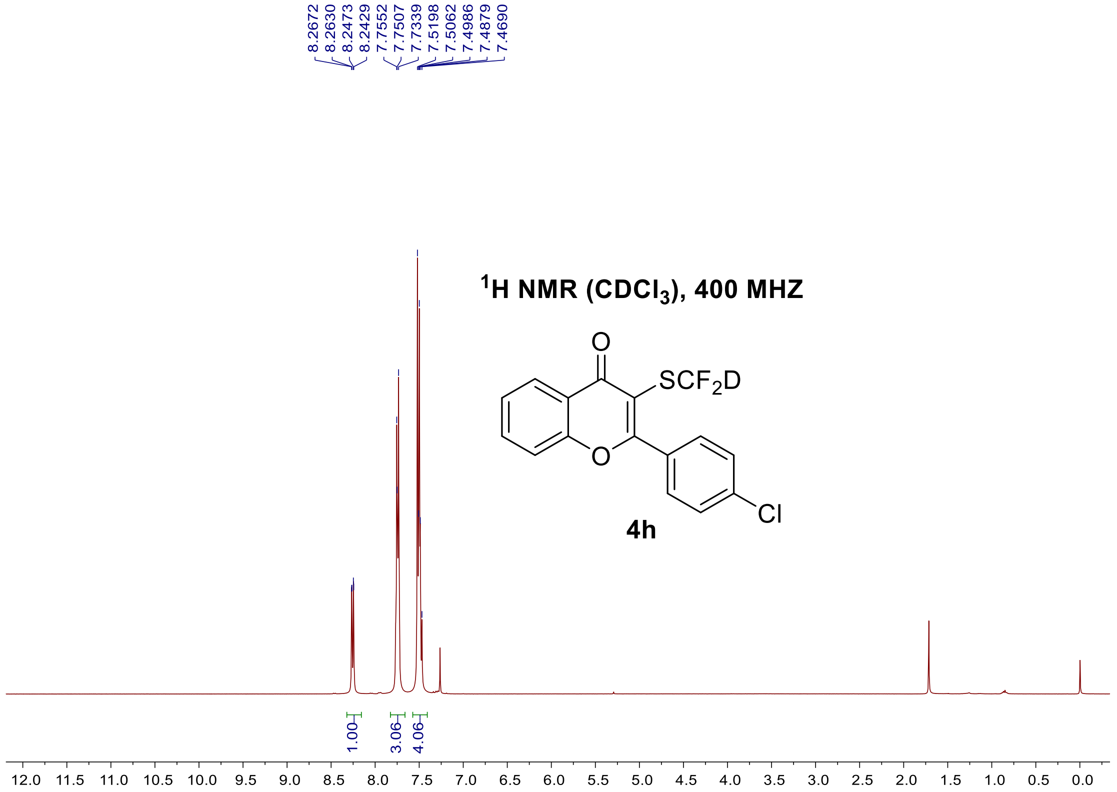
165.5174
163.0006
155.7328
134.6472
132.1652
132.0774
128.5047
128.4698
126.2550
126.1567
122.2433
121.7763
121.4499
121.1240
119.0338
118.7084
118.3858
118.0661
116.2916
115.9625
115.6864
115.4677
110.5808
110.5442
110.5078
13C NMR (CDCl3), 101 MHz
O
SCF2D
O
F
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

4g



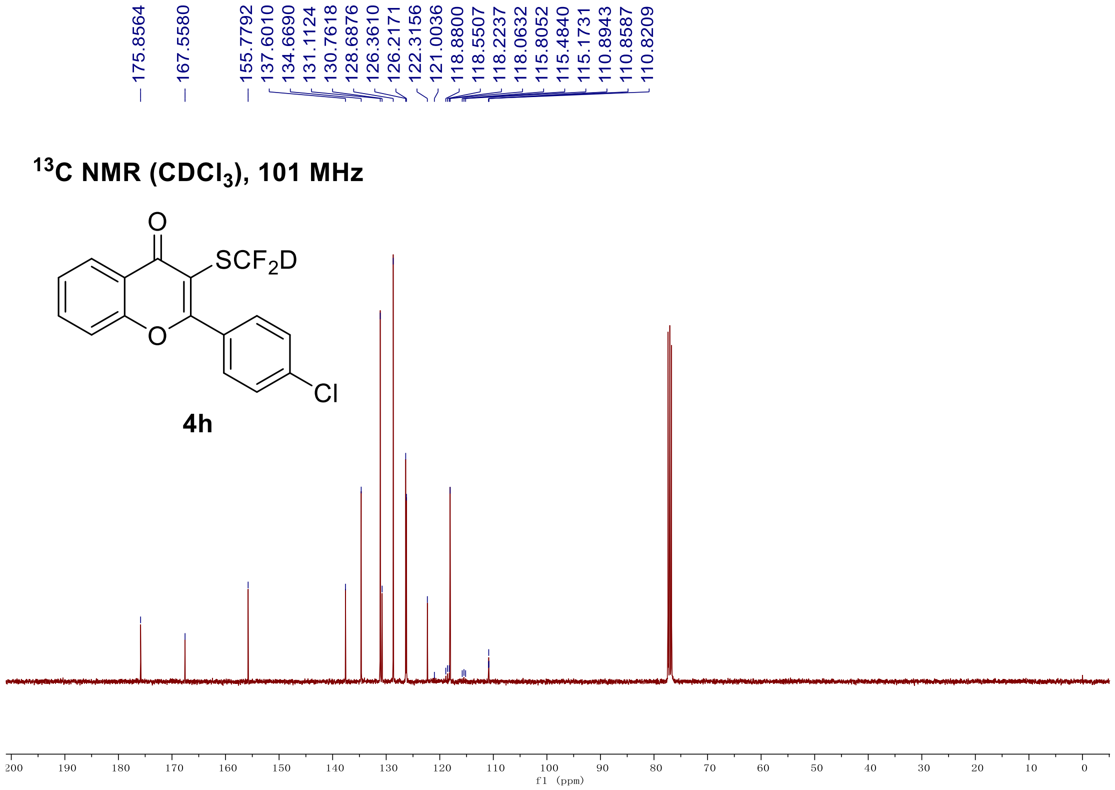
^{19}F NMR (CDCl$_3$), 471 MHz

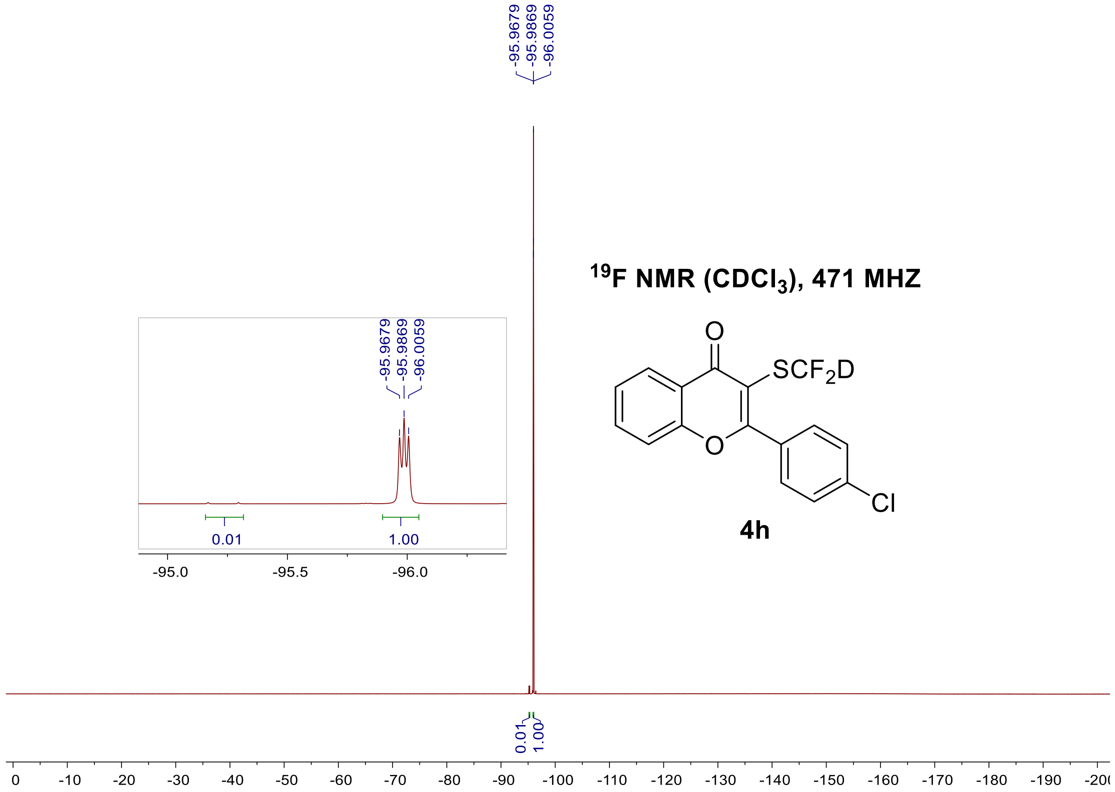
4g

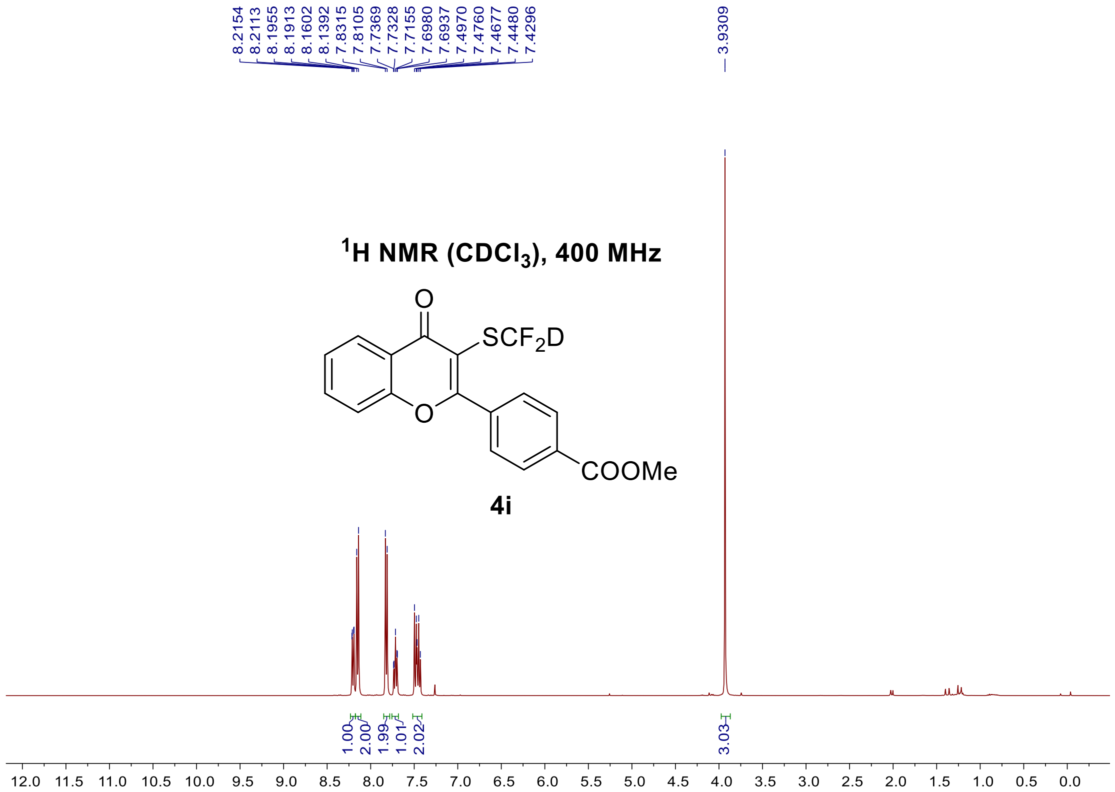


^{1}H NMR (CDCl$_3$), 400 MHZ

4h

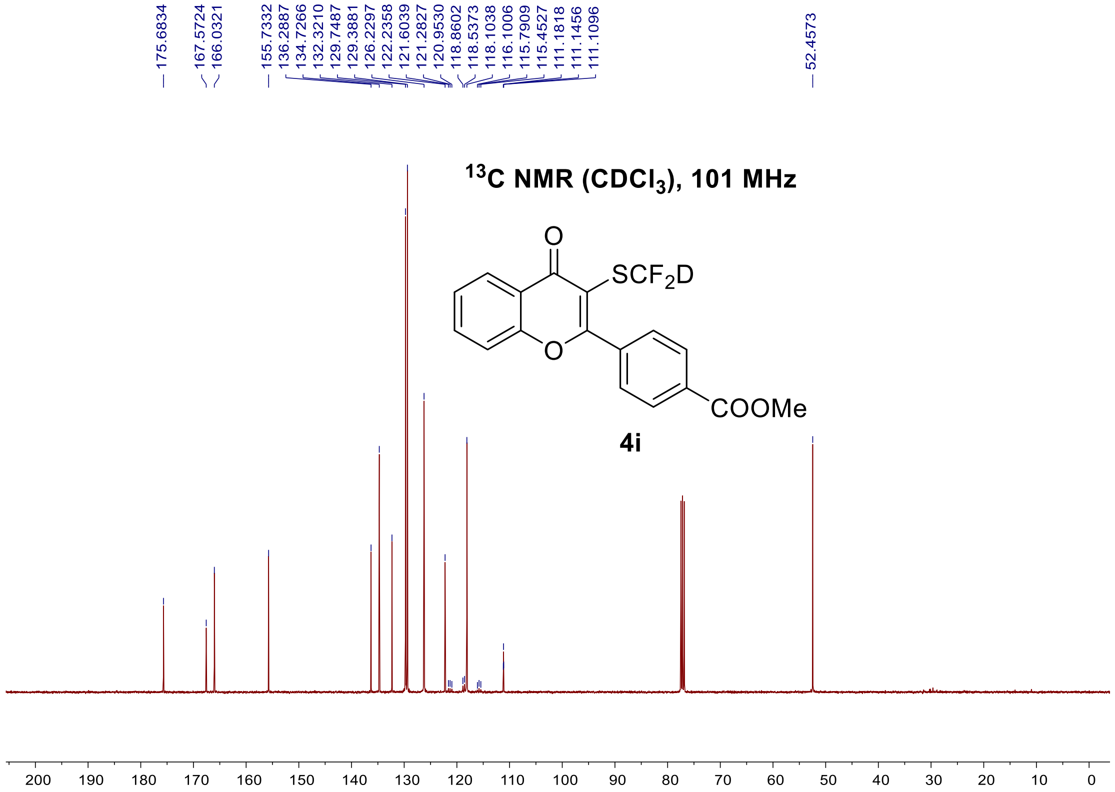

175.8564
167.5580
155.7792
137.6010
134.6690
131.1124
130.7618
128.6876
126.3610
126.2171
122.3156
121.0036
118.8800
118.5507
118.2237
118.0632
115.8052
115.4840
115.1731
110.8943
110.8587
110.8209
^{13}C NMR (CDCl$_3$), 101 MHz
O
SCF$_2$D
O
Cl
4h
f1 (ppm)


-95.9679
-95.9869
-96.0059
^{19}F NMR (CDCl$_3$), 471 MHZ
O
SCF$_2$D
O
Cl
4h
0.01
1.00
-95.0
-95.5
-96.0



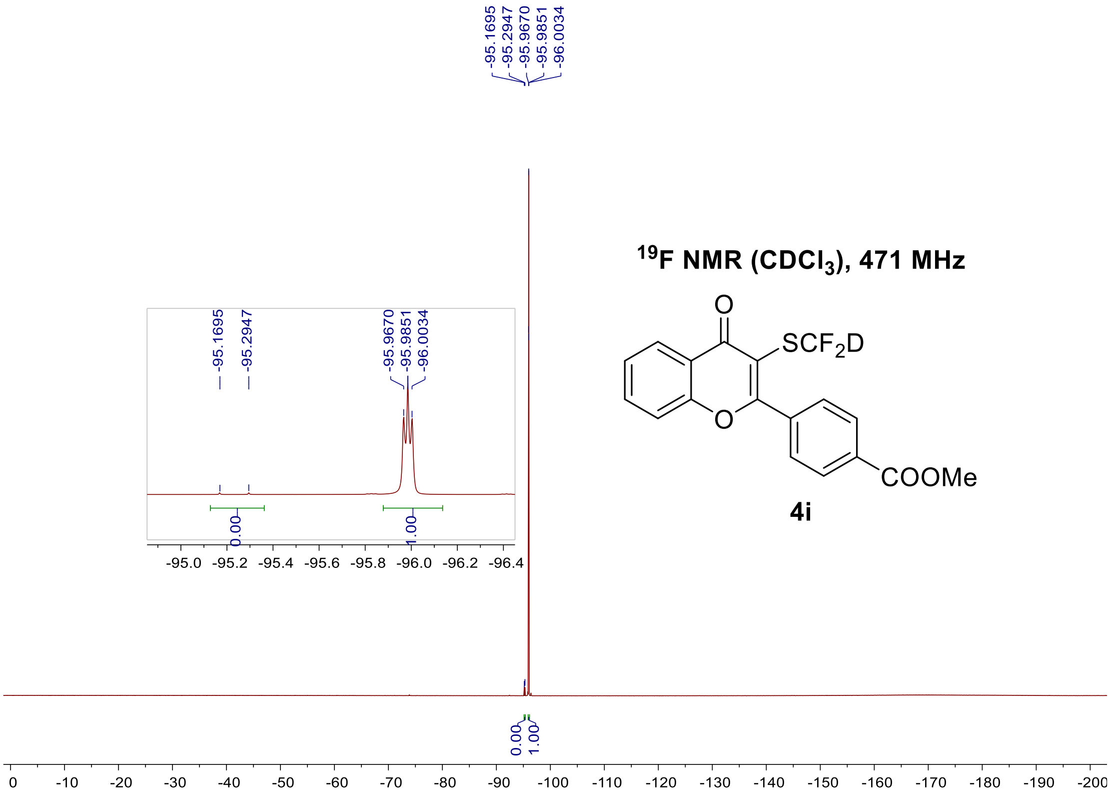
^{1}H NMR (CDCl$_3$), 400 MHz

4i



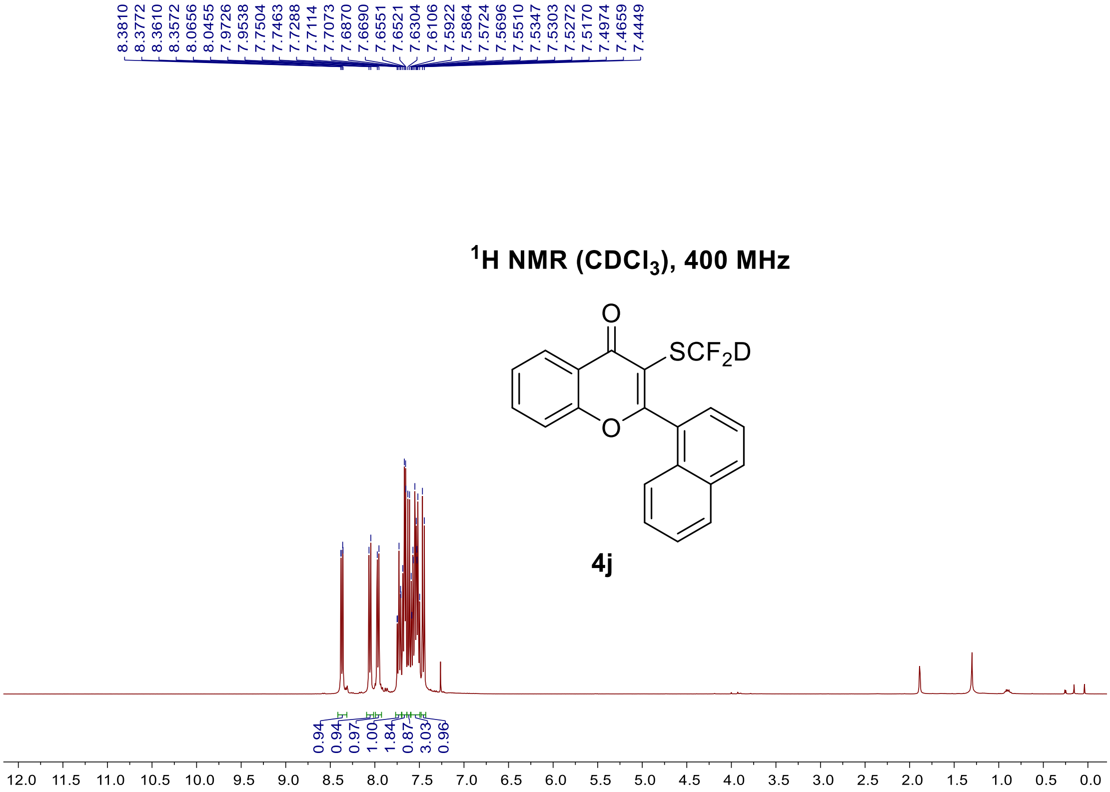
^{13}C NMR (CDCl$_3$), 101 MHz

4i



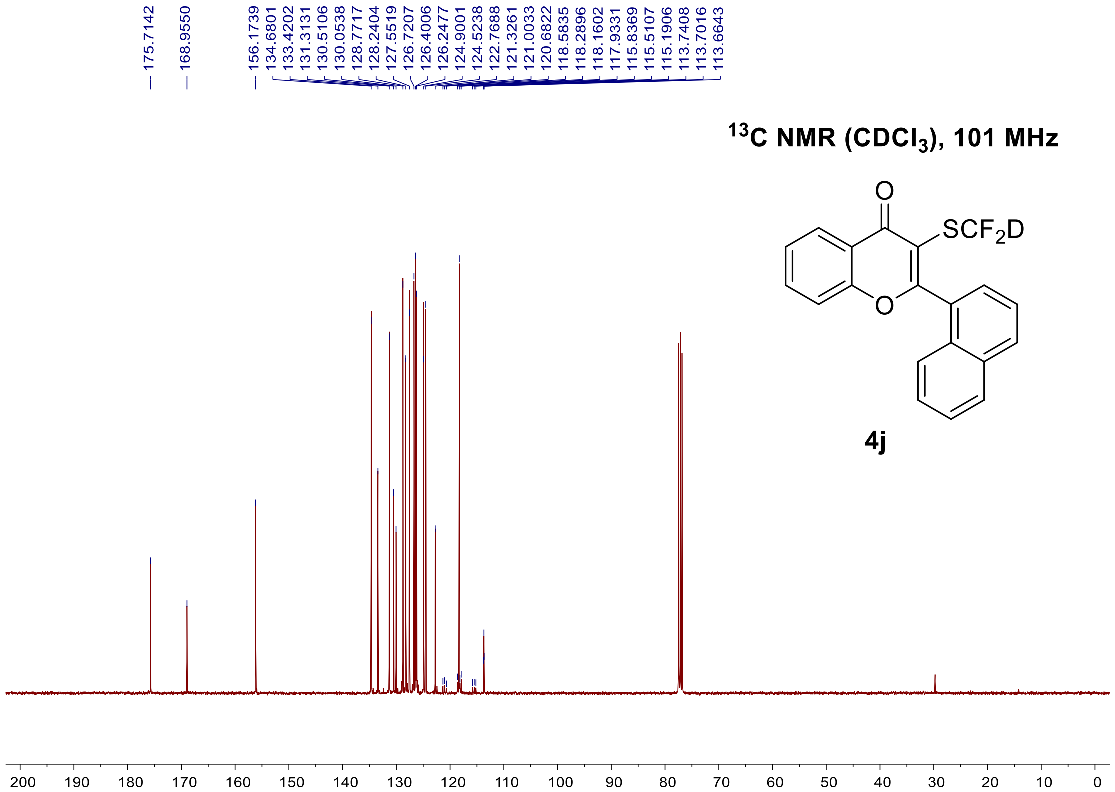
-95.1695
-95.2947
-95.9670
-95.9851
-96.0034
¹⁹F NMR (CDCl₃), 471 MHz
O
SCF₂D
O
COOMe
-95.1695
-95.2947
-95.9670
-95.9851
-96.0034
0.00
1.00
-95.0 -95.2 -95.4 -95.6 -95.8 -96.0 -96.2 -96.4
0.00
1.00
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200

4i



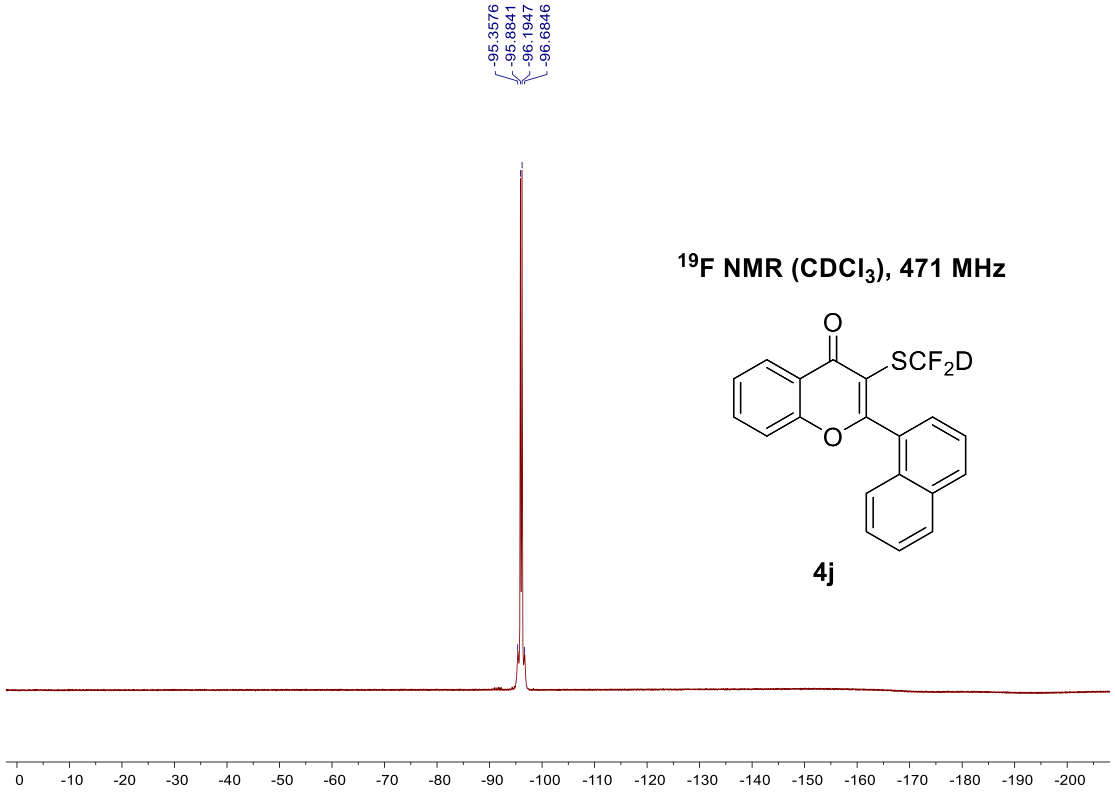
8.3810
8.3772
8.3610
8.3572
8.0656
8.0455
7.9726
7.9538
7.7504
7.7463
7.7288
7.7114
7.7073
7.6870
7.6690
7.6551
7.6521
7.6304
7.6106
7.5922
7.5864
7.5724
7.5696
7.5510
7.5347
7.5303
7.5272
7.5170
7.4974
7.4659
7.4449
¹H NMR (CDCl₃), 400 MHz
O
SCF₂D
O
0.94
0.94
0.97
1.00
1.84
0.87
3.03
0.96
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

4j



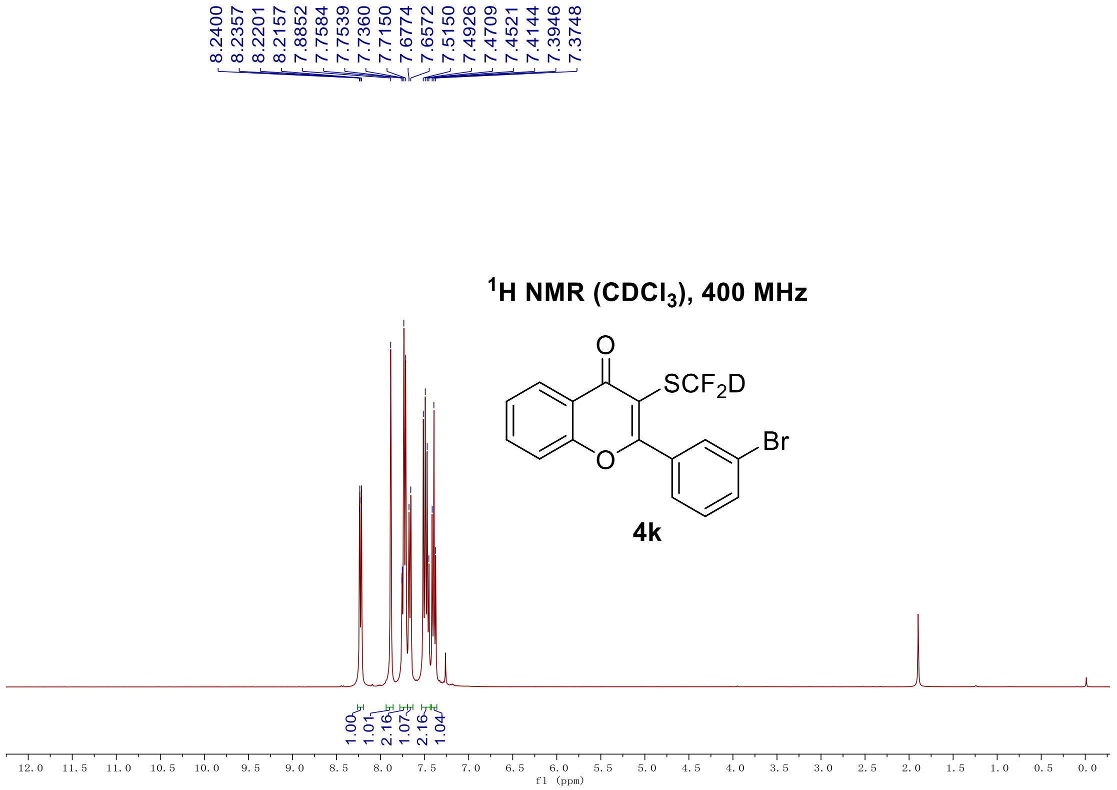
^{13}C NMR (CDCl$_3$), 101 MHz

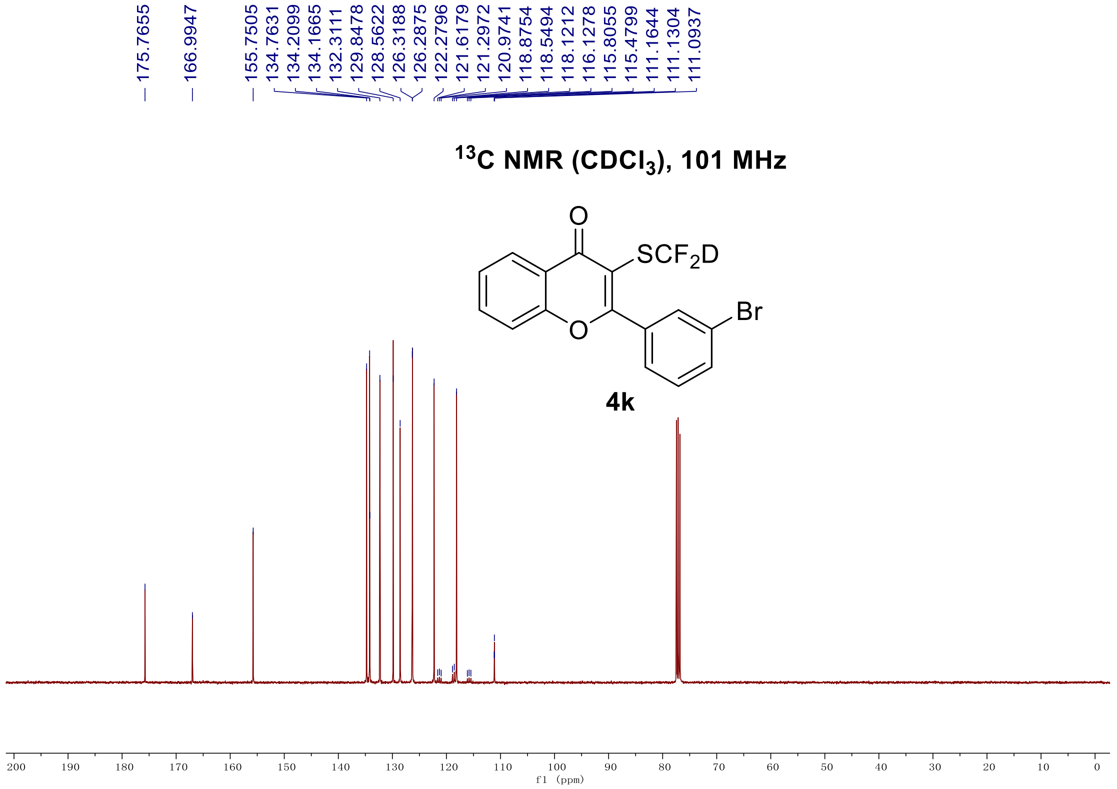
4j

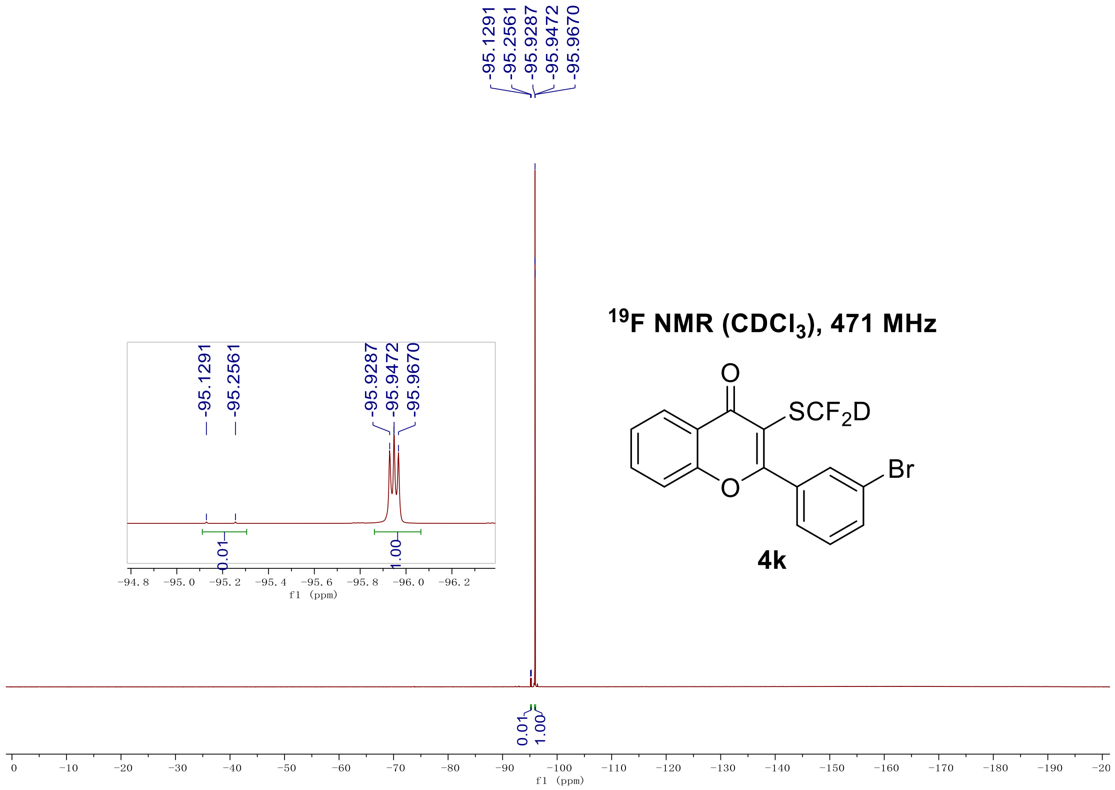


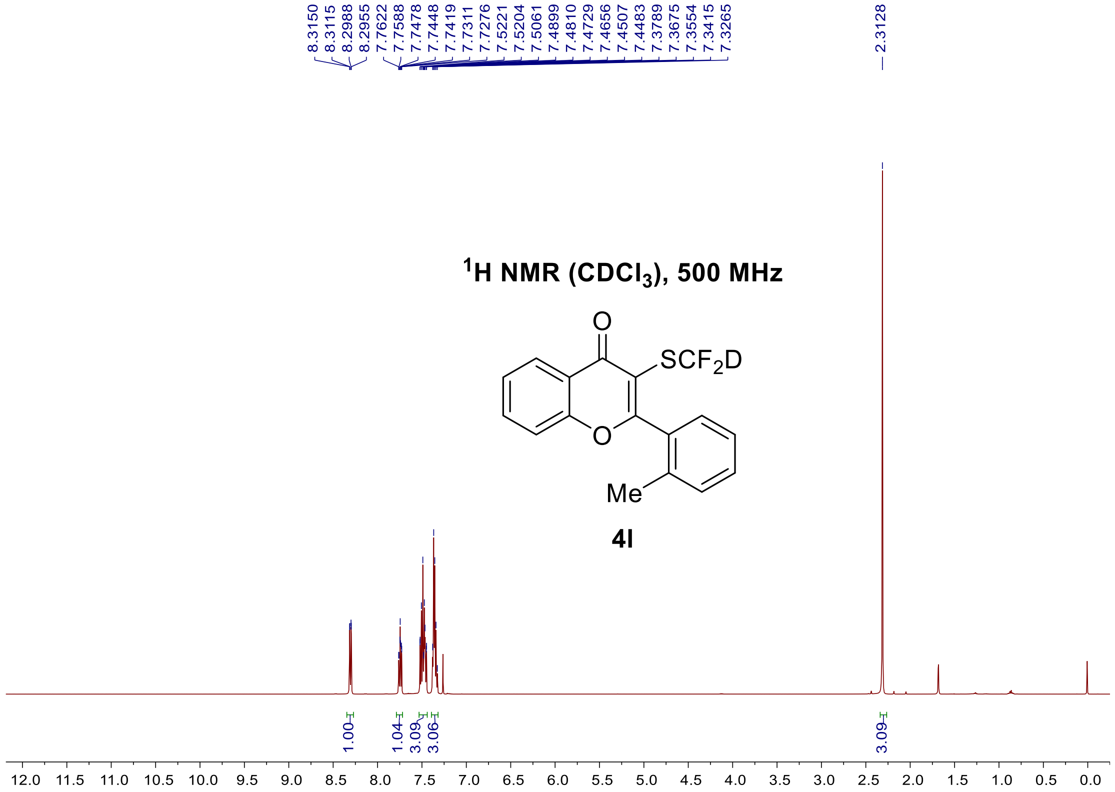
^{19}F NMR (CDCl$_3$), 471 MHz

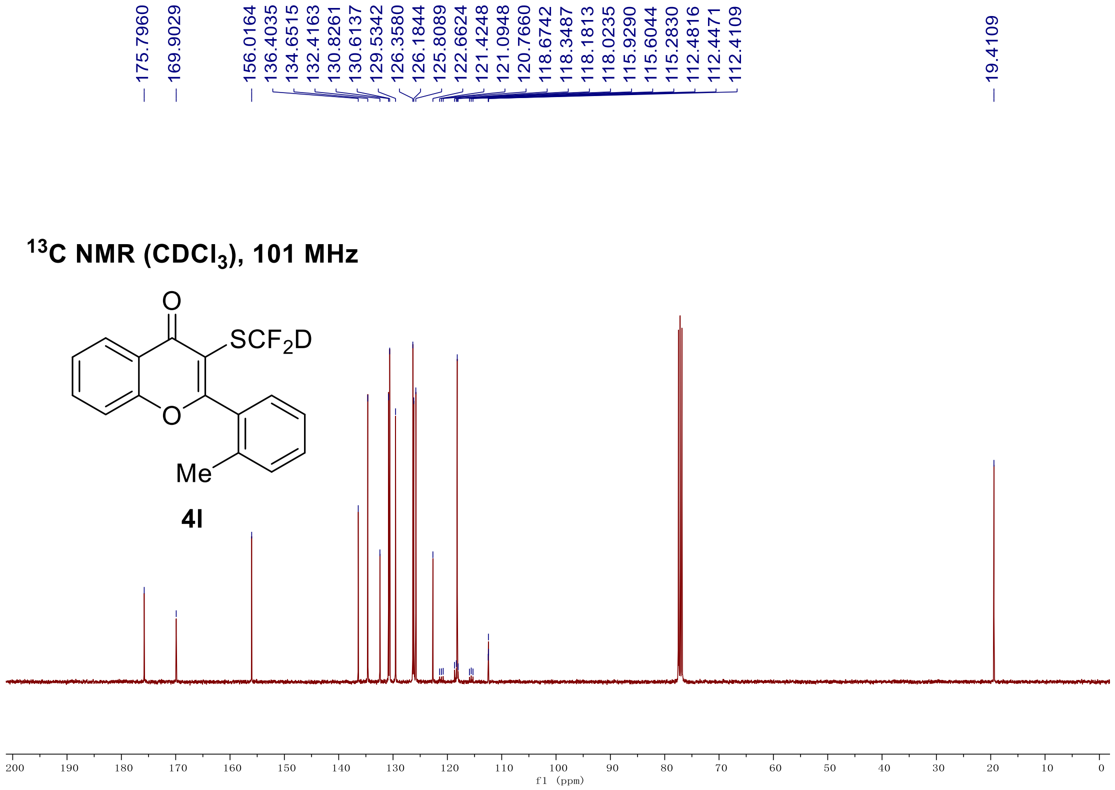
4j

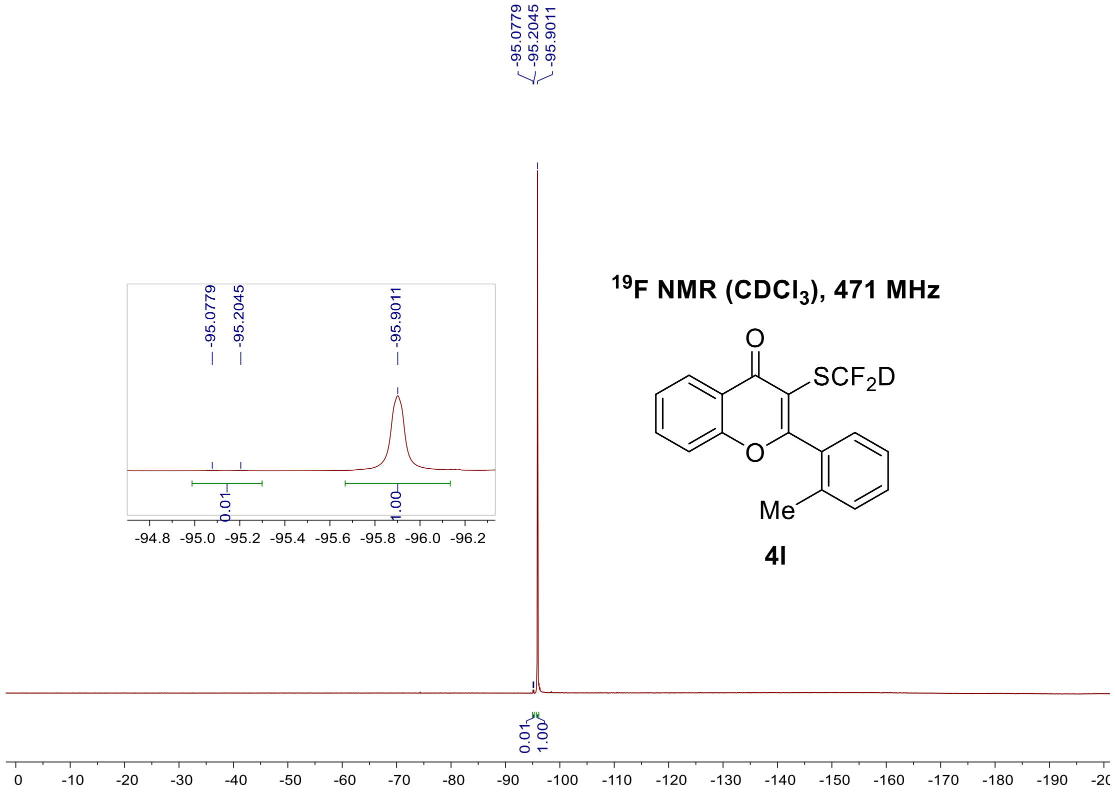

8.2400
8.2357
8.2201
8.2157
7.8852
7.7584
7.7539
7.7360
7.7150
7.6774
7.6572
7.5150
7.4926
7.4709
7.4521
7.4144
7.3946
7.3748
^{1}H NMR (CDCl$_3$), 400 MHz
O
SCF$_2$D
Br
O
4k
1.00
1.01
2.16
1.07
2.16
1.04
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

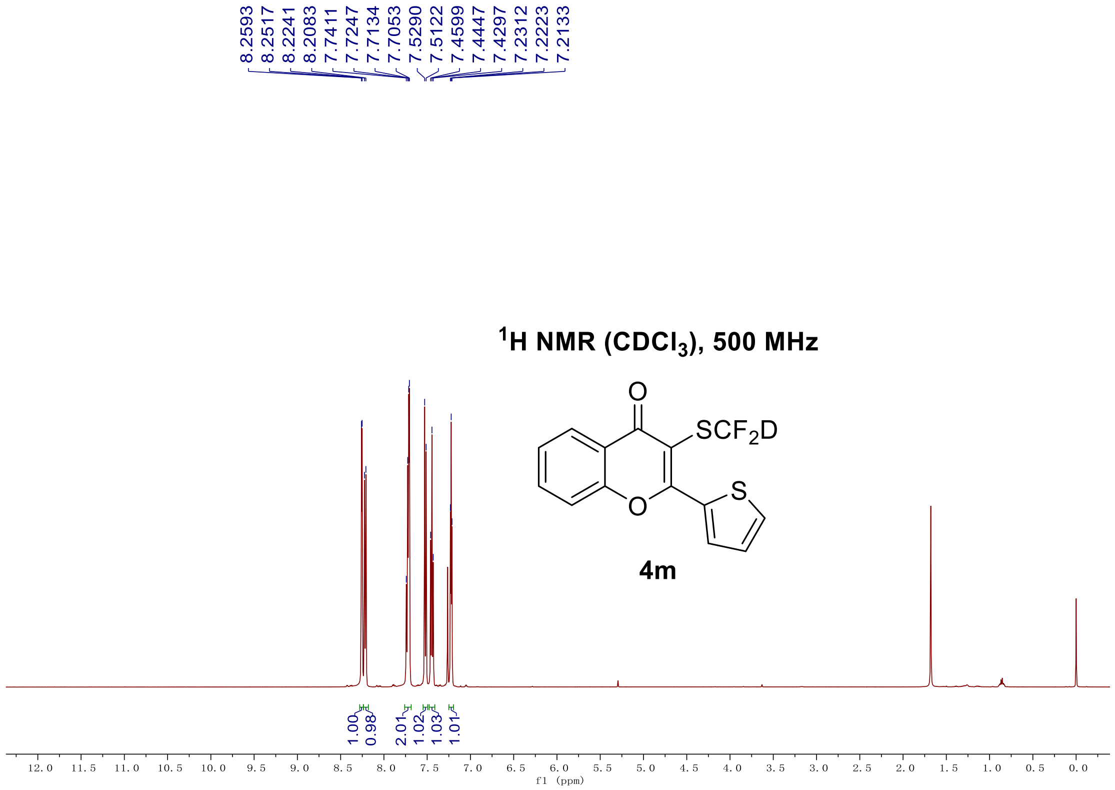

175.7655
166.9947
155.7505
134.7631
134.2099
134.1665
132.3111
129.8478
128.5622
126.3188
126.2875
122.2796
121.6179
121.2972
120.9741
118.8754
118.5494
118.1212
116.1278
115.8055
115.4799
111.1644
111.1304
111.0937
^{13}C NMR (CDCl$_3$), 101 MHz
O
SCF$_2$D
Br
O
4k
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

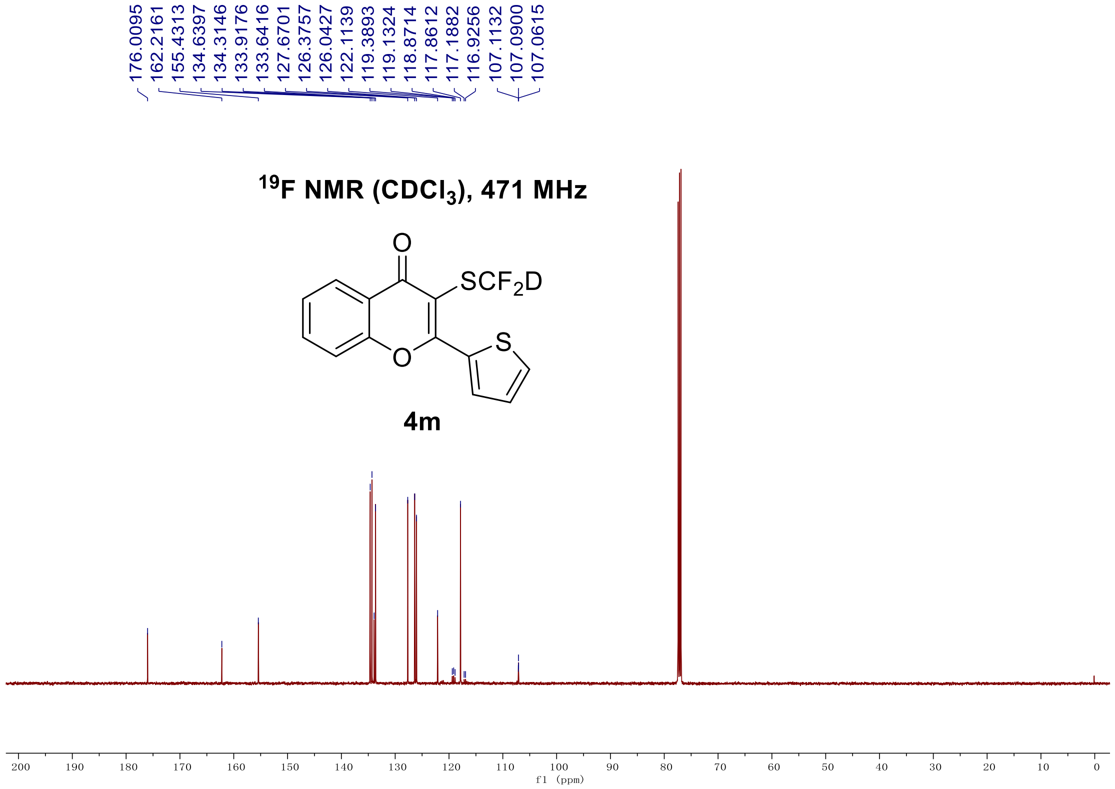

-95.1291
-95.2561
-95.9287
-95.9472
-95.9670
19F NMR (CDCl3), 471 MHz
O
SCF2D
O
Br
4k
0.01
1.00
-94.8 -95.0 -95.2 -95.4 -95.6 -95.8 -96.0 -96.2
f1 (ppm)
0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −20
f1 (ppm)

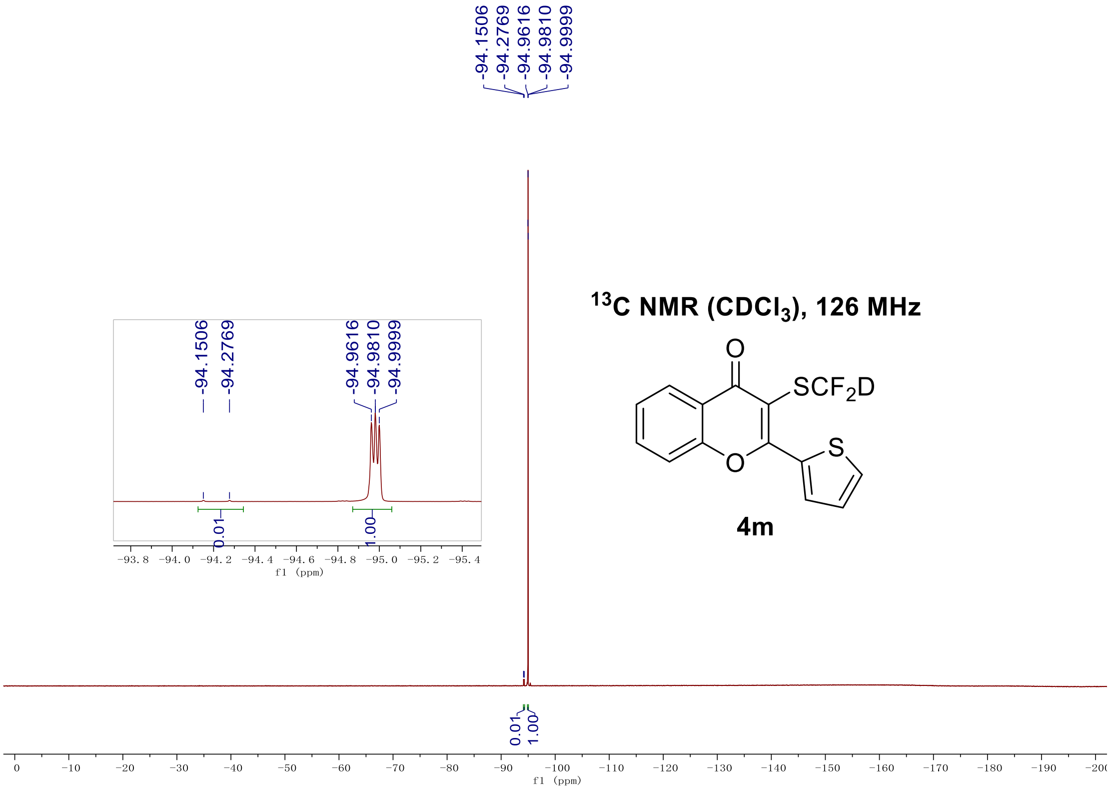

8.3150
8.3115
8.2988
8.2955
7.7622
7.7588
7.7478
7.7448
7.7419
7.7311
7.7276
7.5221
7.5204
7.5061
7.4899
7.4810
7.4729
7.4656
7.4507
7.4483
7.3789
7.3675
7.3554
7.3415
7.3265
2.3128
1H NMR (CDCl3), 500 MHz
O
SCF2D
O
Me
4l
1.00
1.04
3.09
3.06
3.09
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0


175.7960
169.9029
156.0164
136.4035
134.6515
132.4163
130.8261
130.6137
129.5342
126.3580
126.1844
125.8089
122.6624
121.4248
121.0948
120.7660
118.6742
118.3487
118.1813
118.0235
115.9290
115.6044
115.2830
112.4816
112.4471
112.4109
19.4109
^{13}C NMR (CDCl$_3$), 101 MHz
O
SCF$_2$D
O
Me
4l
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-95.0779
-95.2045
-95.9011
0.01
1.00
-94.8 -95.0 -95.2 -95.4 -95.6 -95.8 -96.0 -96.2
^{19}F NMR (CDCl$_3$), 471 MHz
O
SCF$_2$D
O
Me
4l
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -20

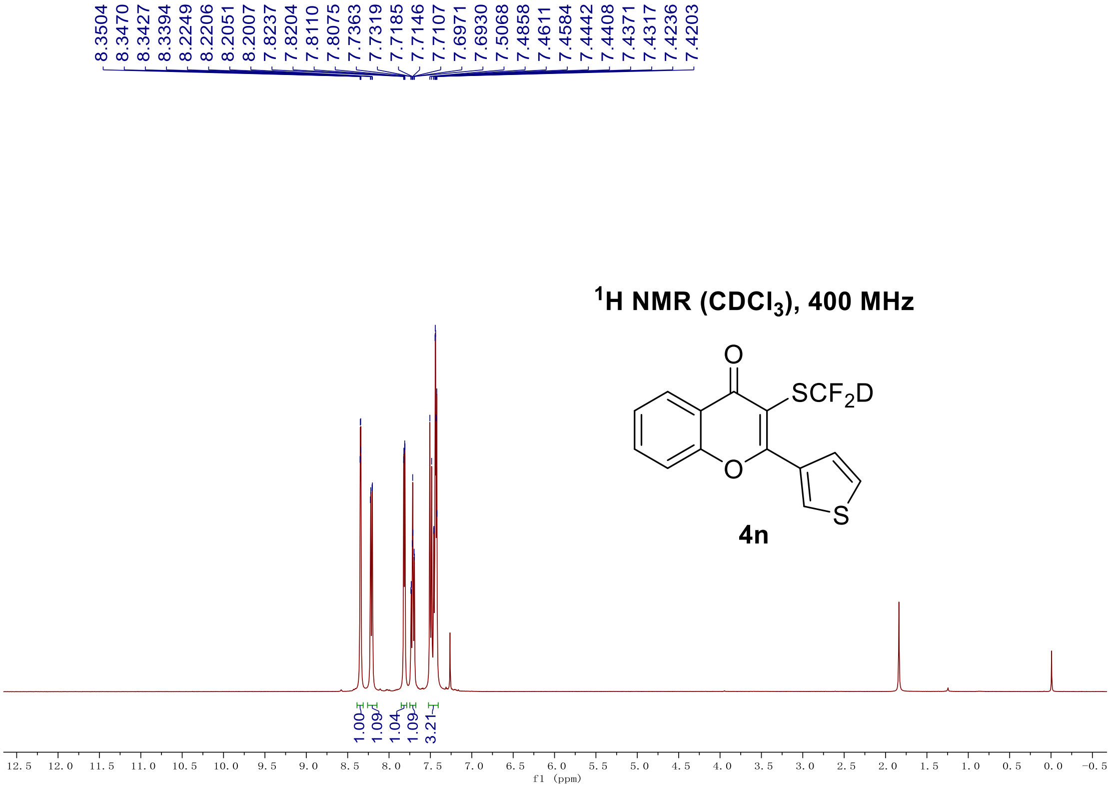

8.2593
8.2517
8.2241
8.2083
7.7411
7.7247
7.7134
7.7053
7.5290
7.5122
7.4599
7.4447
7.4297
7.2312
7.2223
7.2133
^{1}H NMR (CDCl$_3$), 500 MHz
O
SCF$_2$D
S
O
4m
1.00
0.98
2.01
1.02
1.03
1.01
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


176.0095
162.2161
155.4313
134.6397
134.3146
133.9176
133.6416
127.6701
126.3757
126.0427
122.1139
119.3893
119.1324
118.8714
117.8612
117.1882
116.9256
107.1132
107.0900
107.0615
^{19}F NMR (CDCl$_3$), 471 MHz
O
SCF$_2$D
S
O
4m
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



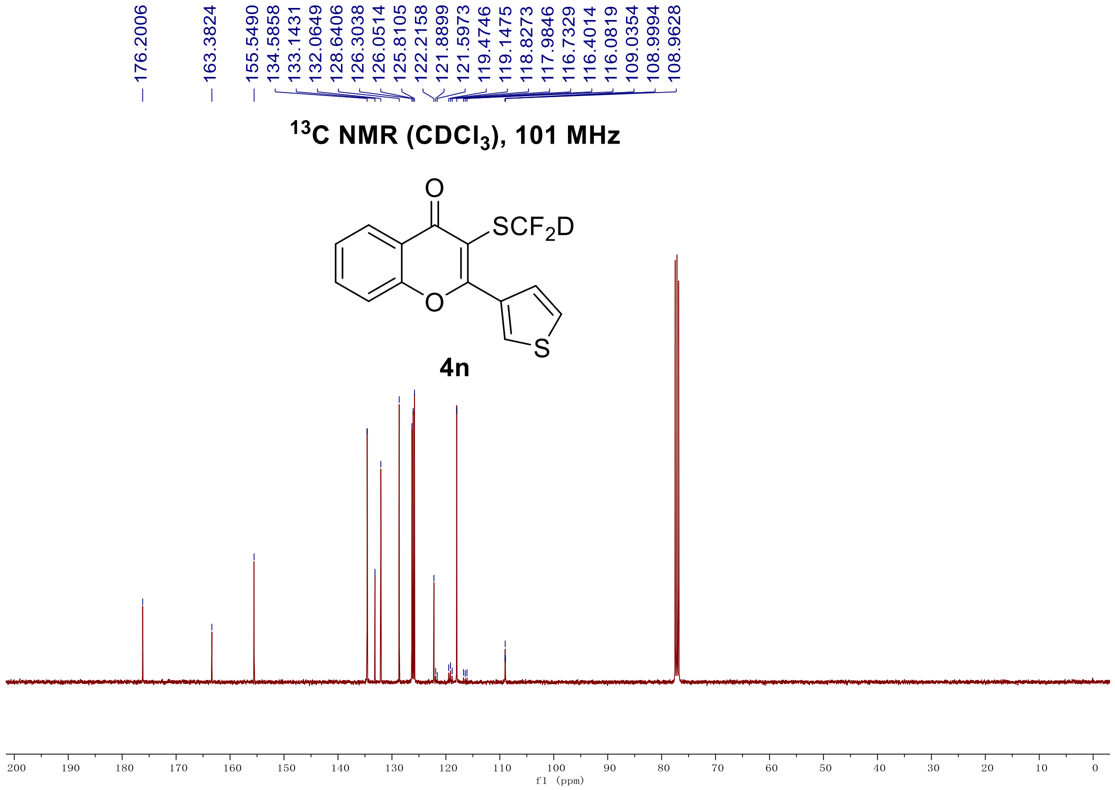
^{13}C NMR (CDCl$_3$), 126 MHz

4m

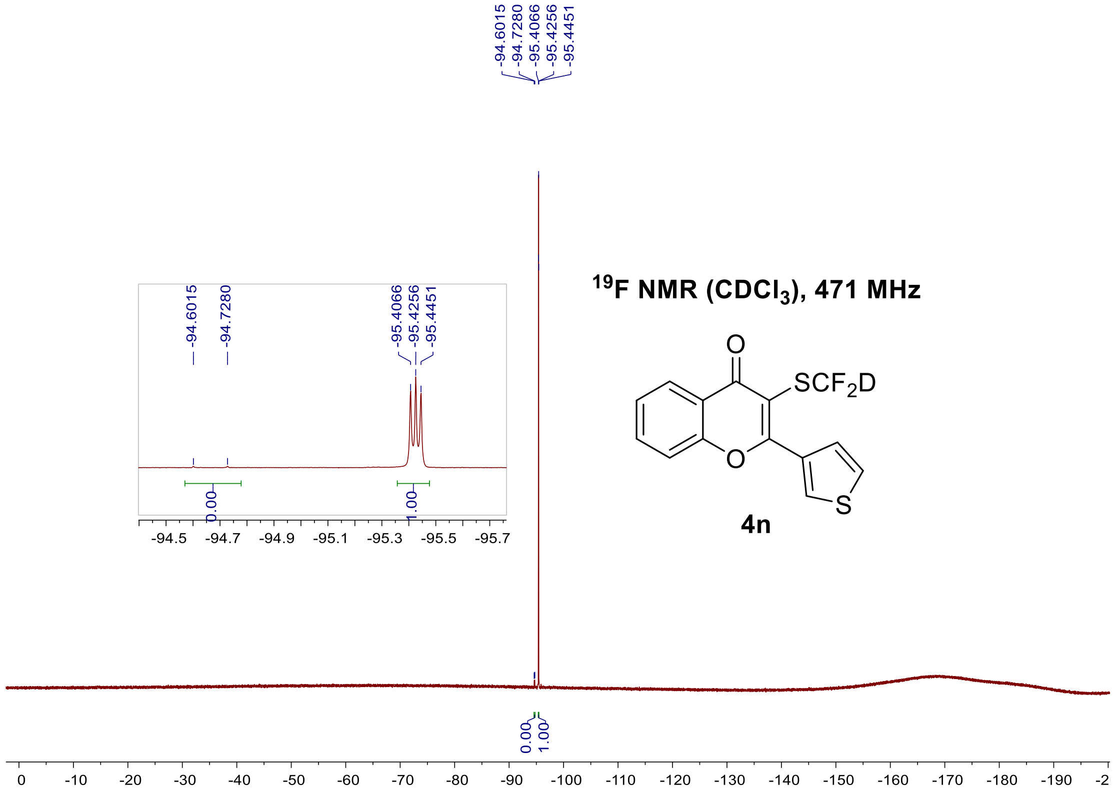


^{1}H NMR (CDCl$_3$), 400 MHz

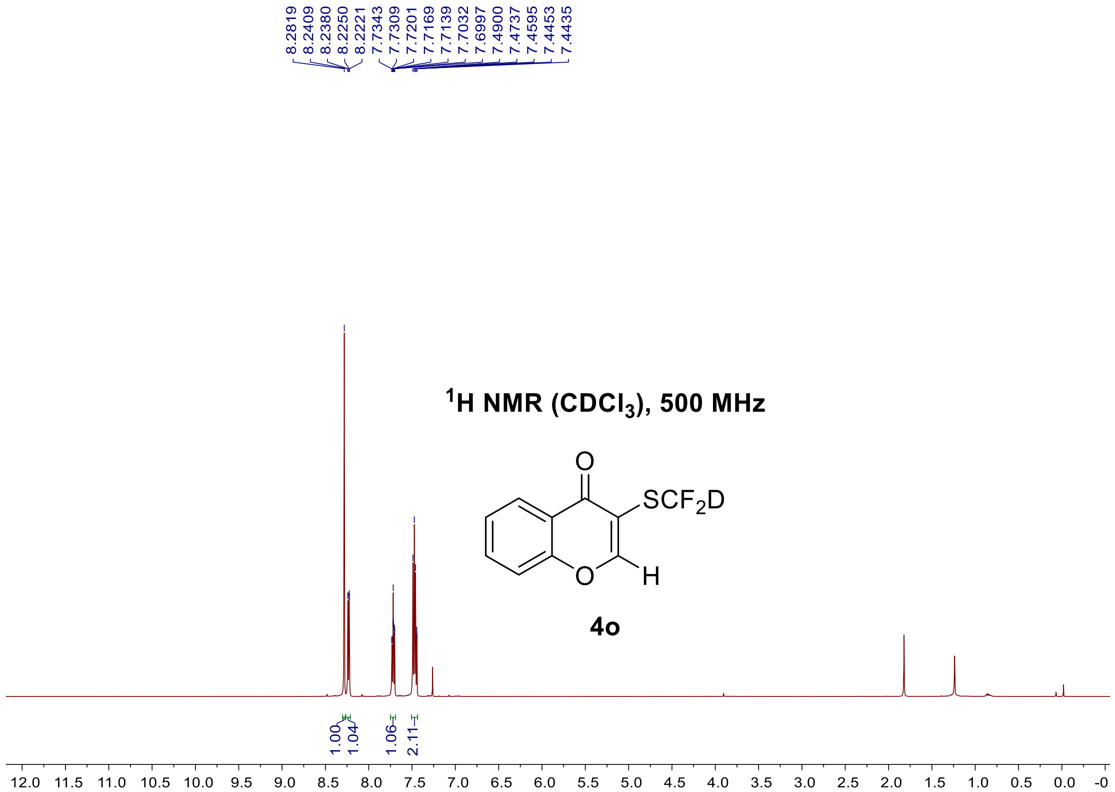
4n



176.2006
163.3824
155.5490
134.5858
133.1431
132.0649
128.6406
126.3038
126.0514
125.8105
122.2158
121.8899
121.5973
119.4746
119.1475
118.8273
117.9846
116.7329
116.4014
116.0819
109.0354
108.9994
108.9628
^{13}C NMR (CDCl$_3$), 101 MHz
O
SCF$_2$D
O
S
4n
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

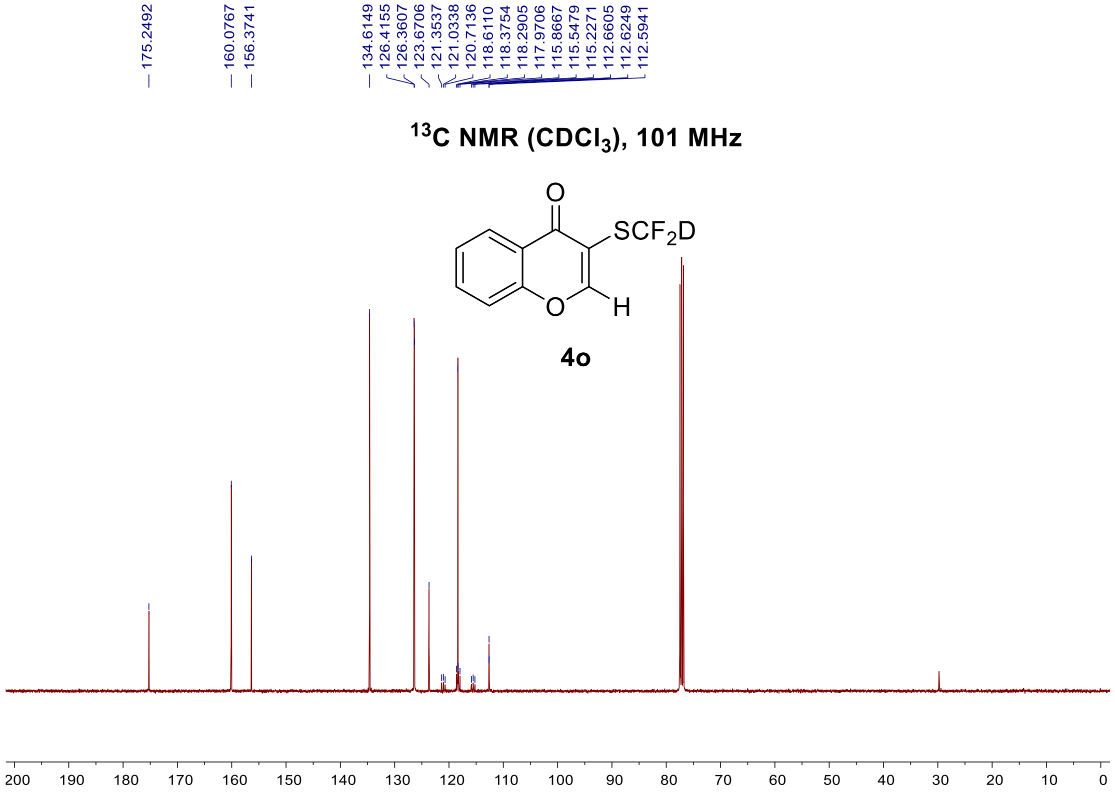


-94.6015
-94.7280
-95.4066
-95.4256
-95.4451
^{19}F NMR (CDCl$_3$), 471 MHz
O
SCF$_2$D
O
S
4n
0.00
1.00
-94.5 -94.7 -94.9 -95.1 -95.3 -95.5 -95.7
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -2



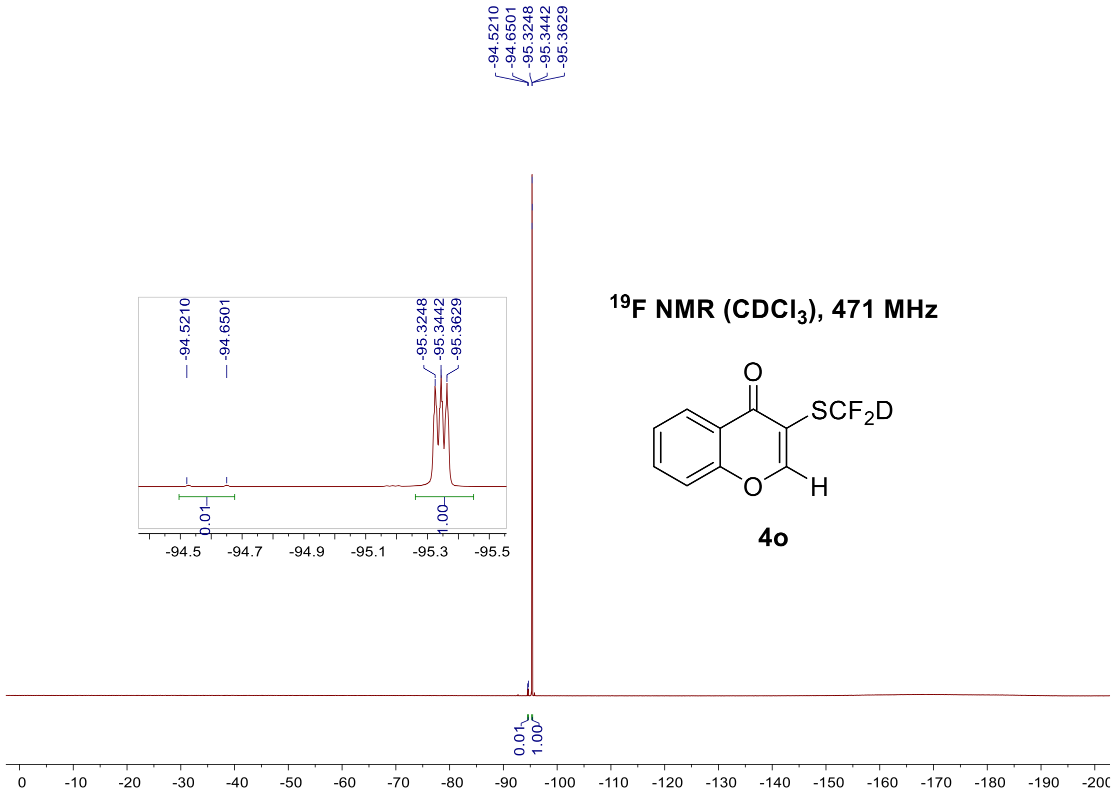
^{1}H NMR (CDCl$_3$), 500 MHz

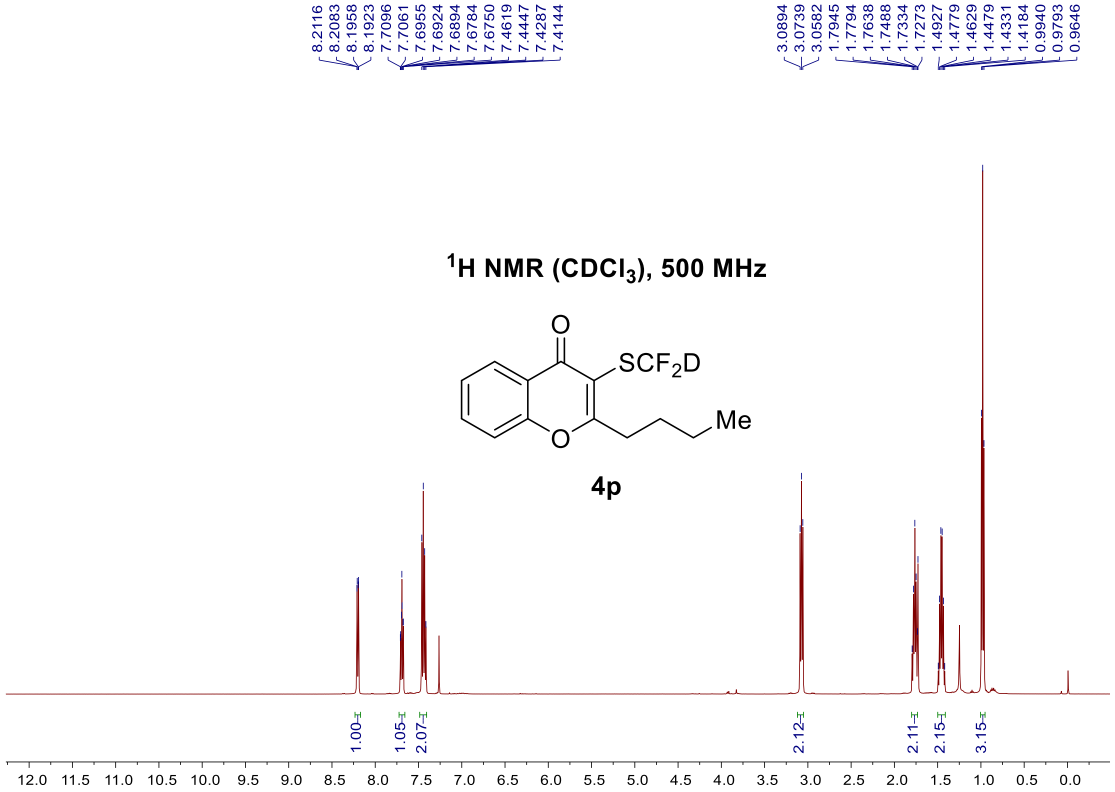
4o

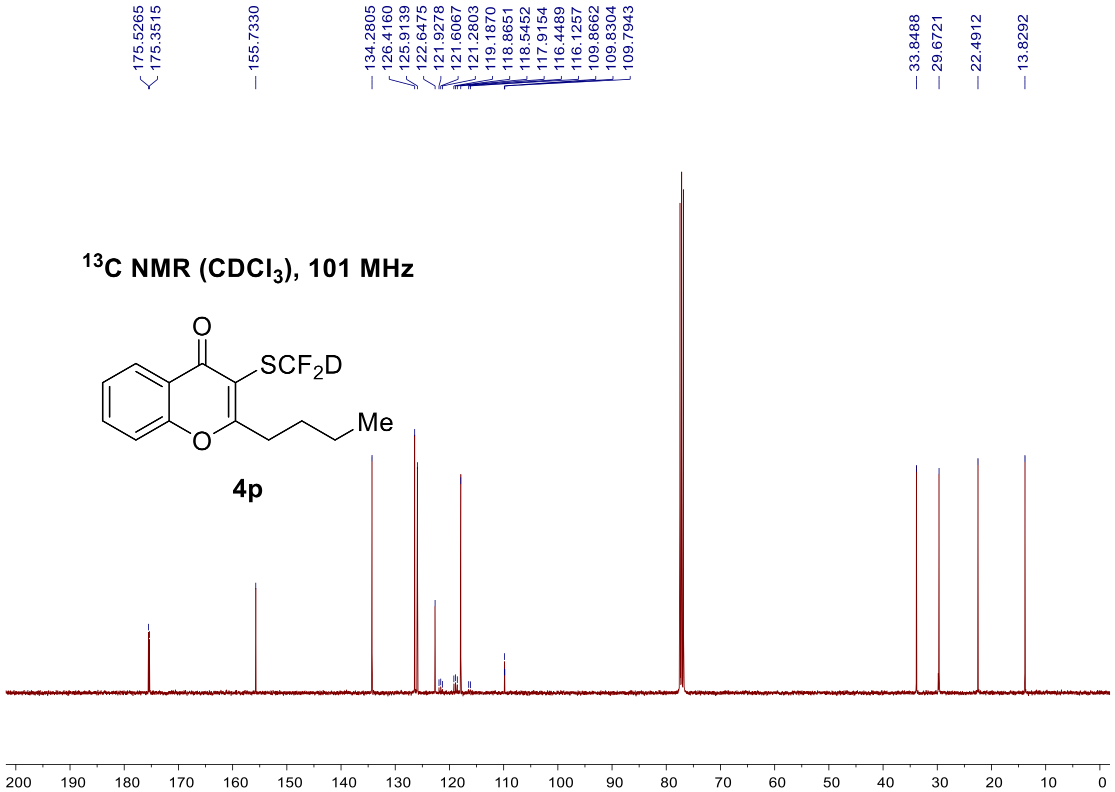


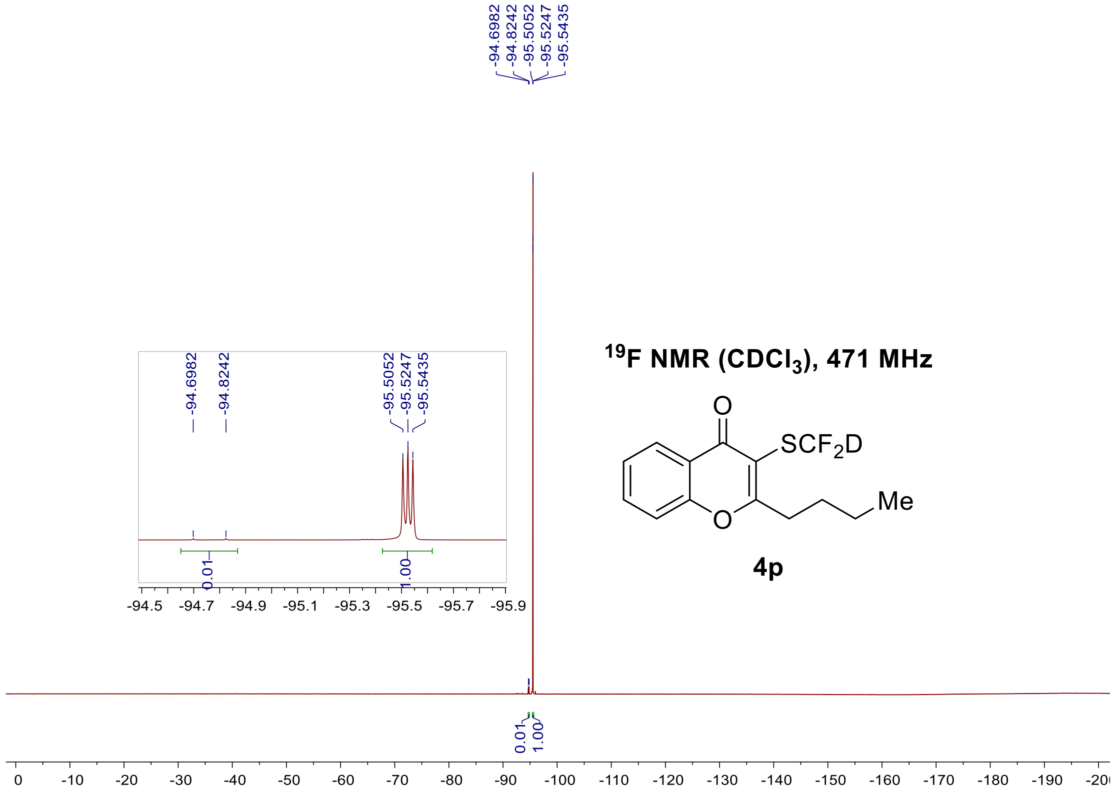
^{13}C NMR (CDCl$_3$), 101 MHz

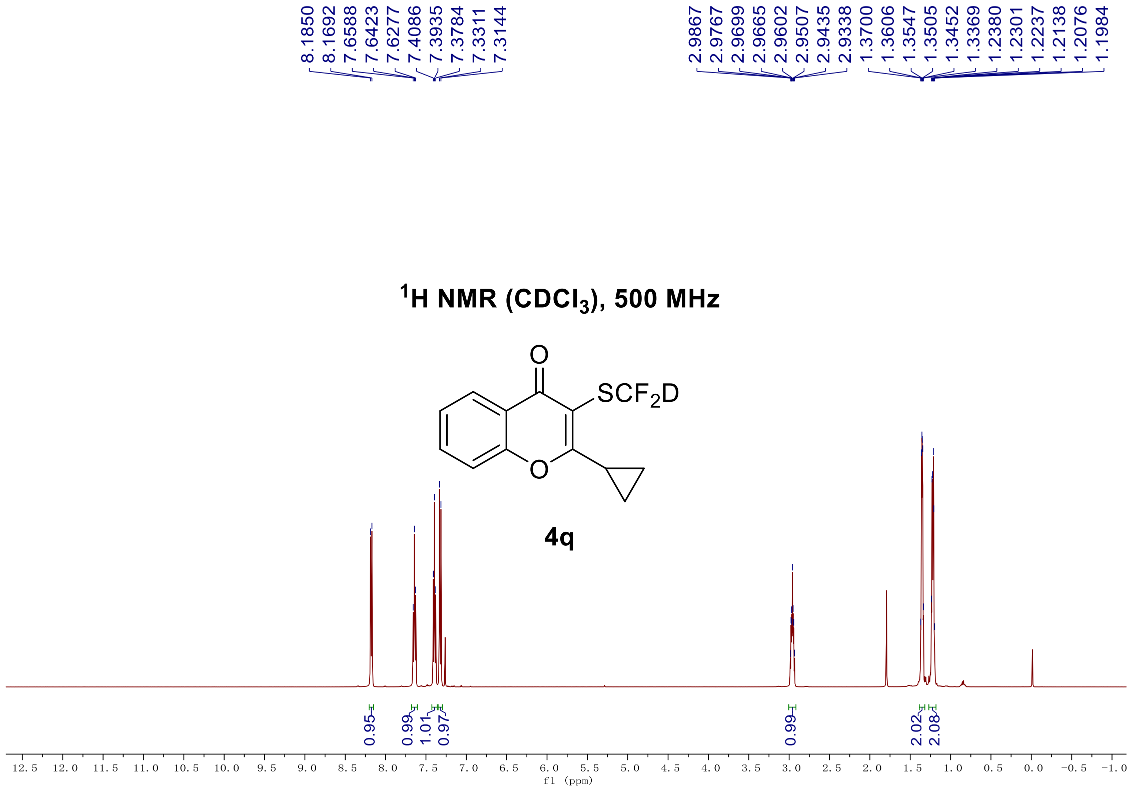
4o


-94.5210
-94.6501
-95.3248
-95.3442
-95.3629
^{19}F NMR (CDCl$_3$), 471 MHz
O
SCF$_2$D
O
H
4o
0.01
1.00
-94.5
-94.7
-94.9
-95.1
-95.3
-95.5
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200


8.2116
8.2083
8.1958
8.1923
7.7096
7.7061
7.6955
7.6924
7.6894
7.6784
7.6750
7.4619
7.4447
7.4287
7.4144
3.0894
3.0739
3.0582
1.7945
1.7794
1.7638
1.7488
1.7334
1.7273
1.4927
1.4779
1.4629
1.4479
1.4331
1.4184
0.9940
0.9793
0.9646
^{1}H NMR (CDCl$_3$), 500 MHz
O
SCF$_2$D
O
Me
4p
1.00
1.05
2.07
2.12
2.11
2.15
3.15
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

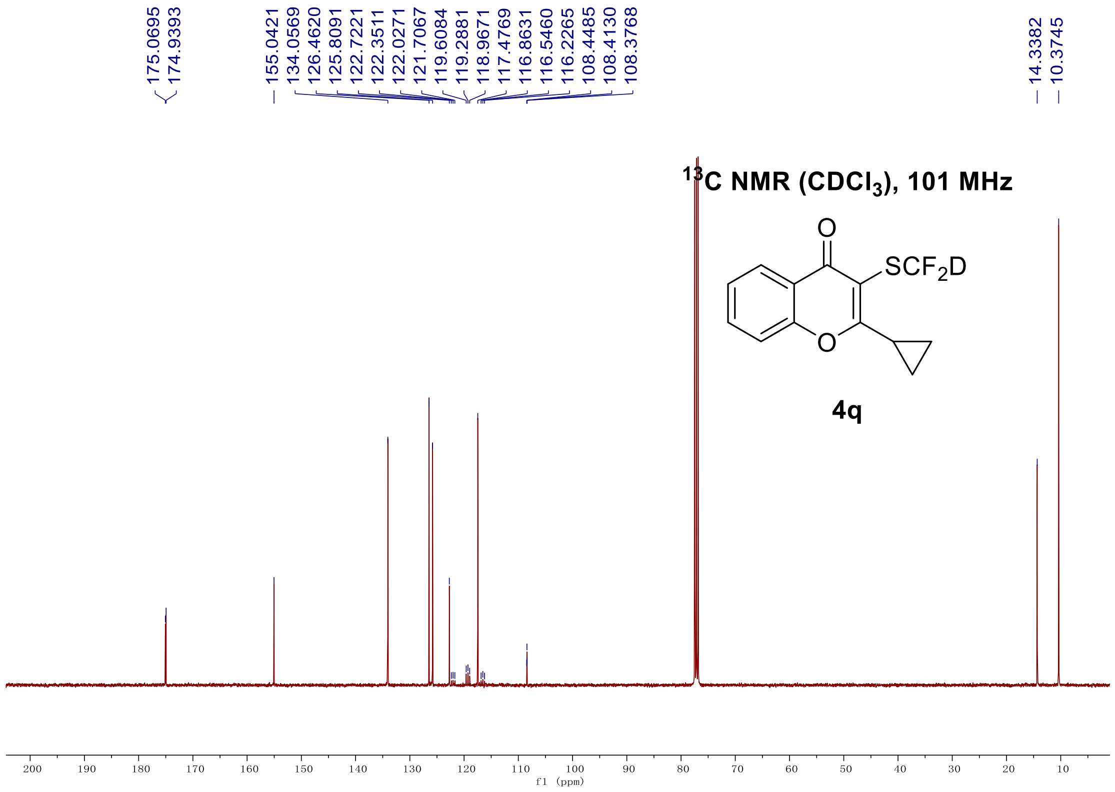

175.5265
175.3515
155.7330
134.2805
126.4160
125.9139
122.6475
121.9278
121.6067
121.2803
119.1870
118.8651
118.5452
117.9154
116.4489
116.1257
109.8662
109.8304
109.7943
33.8488
29.6721
22.4912
13.8292
^{13}C NMR (CDCl$_3$), 101 MHz
O
SCF$_2$D
O
Me
4p
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


-94.6982
-94.8242
-95.5052
-95.5247
-95.5435
^{19}F NMR (CDCl$_3$), 471 MHz
O
SCF$_2$D
O
Me
4p
0.01
1.00
-94.5
-94.7
-94.9
-95.1
-95.3
-95.5
-95.7
-95.9
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200



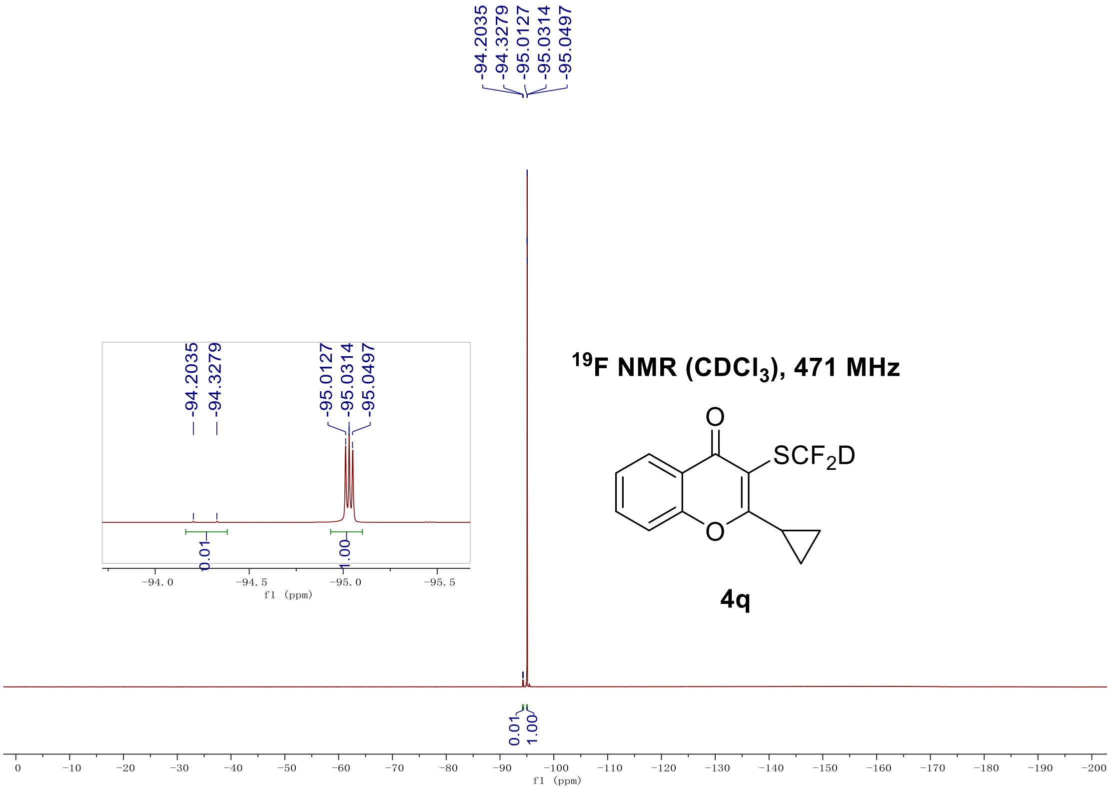
^{1}H NMR ($CDCl_3$), 500 MHz

4q

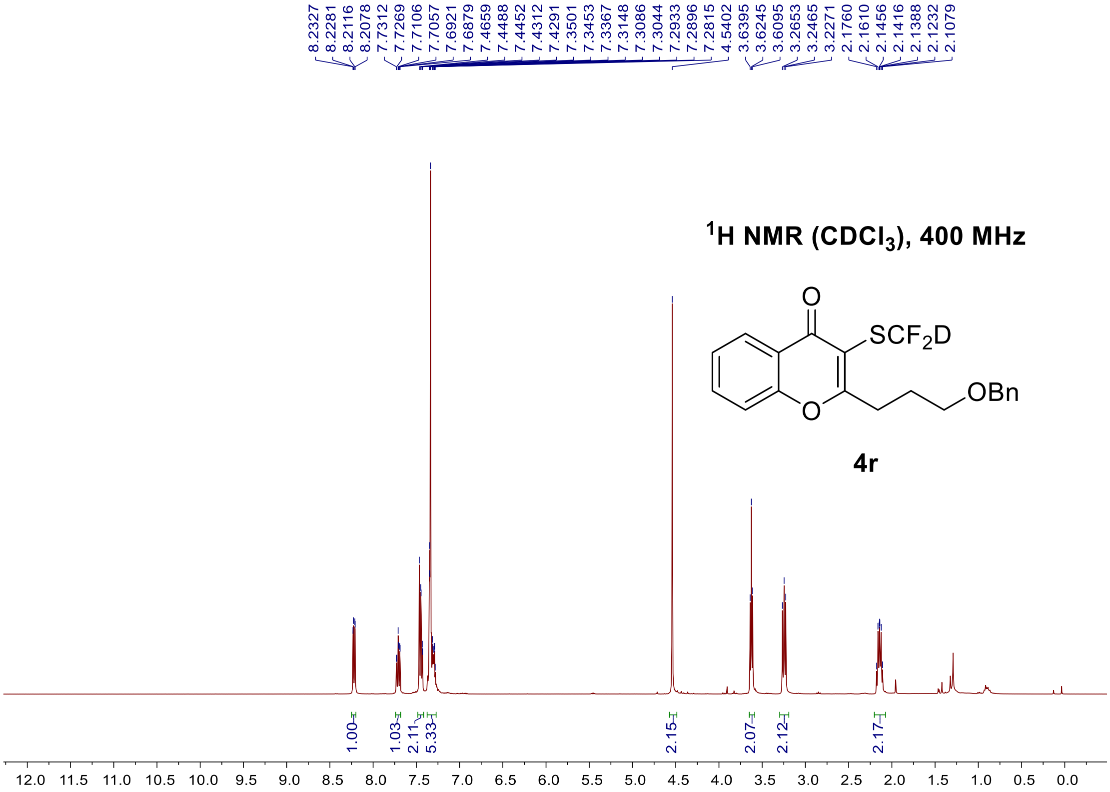


^{13}C NMR ($CDCl_3$), 101 MHz

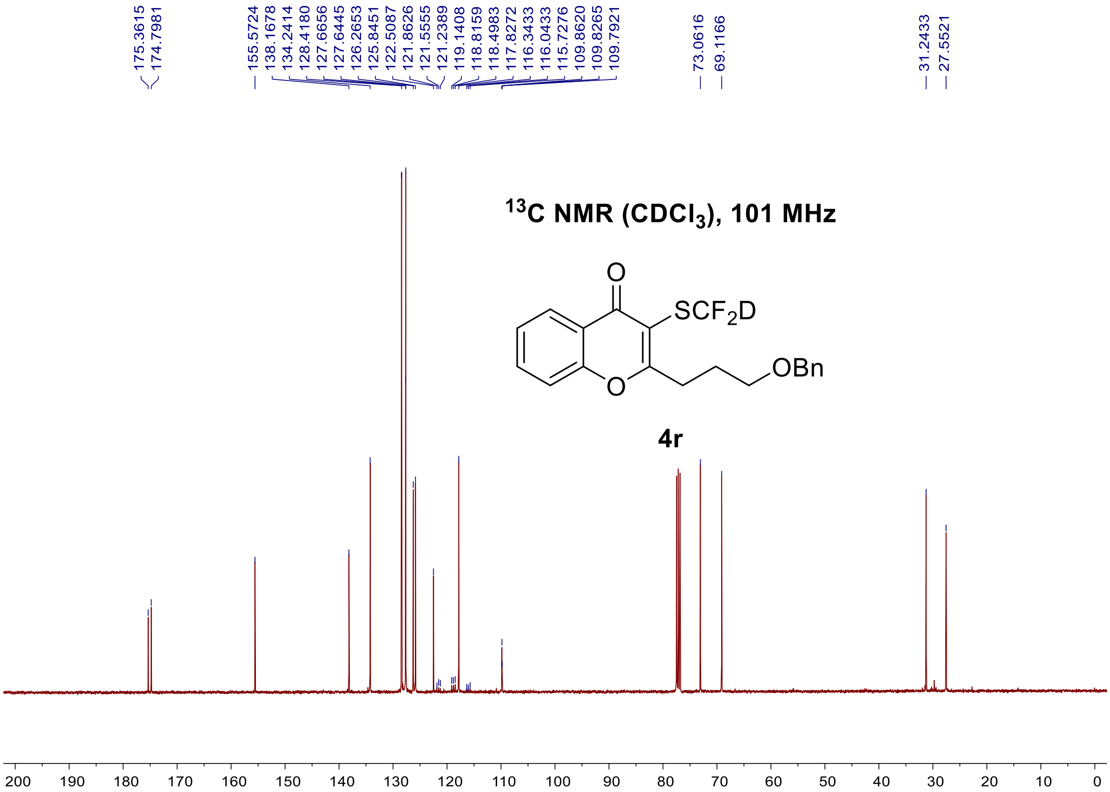
4q



-94.2035
-94.3279
-95.0127
-95.0314
-95.0497
^{19}F NMR (CDCl$_3$), 471 MHz
O
SCF$_2$D
O
4q
0.01
1.00
-94.0
-94.5
-95.0
-95.5
f1 (ppm)
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200

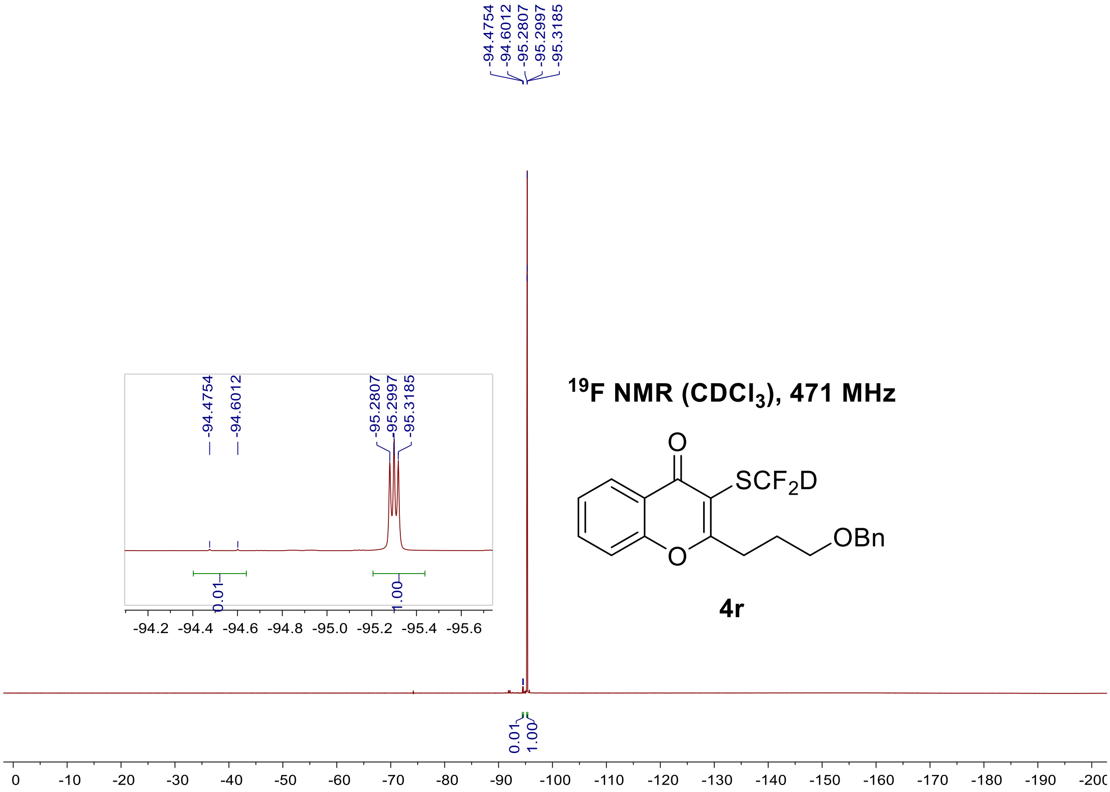


8.2327
8.2281
8.2116
8.2078
7.7312
7.7269
7.7106
7.7057
7.6921
7.6879
7.4659
7.4488
7.4452
7.4312
7.4291
7.3501
7.3453
7.3367
7.3148
7.3086
7.3044
7.2933
7.2896
7.2815
4.5402
3.6395
3.6245
3.6095
3.2653
3.2465
3.2271
2.1760
2.1610
2.1456
2.1416
2.1388
2.1232
2.1079
^{1}H NMR (CDCl$_3$), 400 MHz
O
SCF$_2$D
O
OBn
4r
1.00
1.03
2.11
5.33
2.15
2.07
2.12
2.17
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0



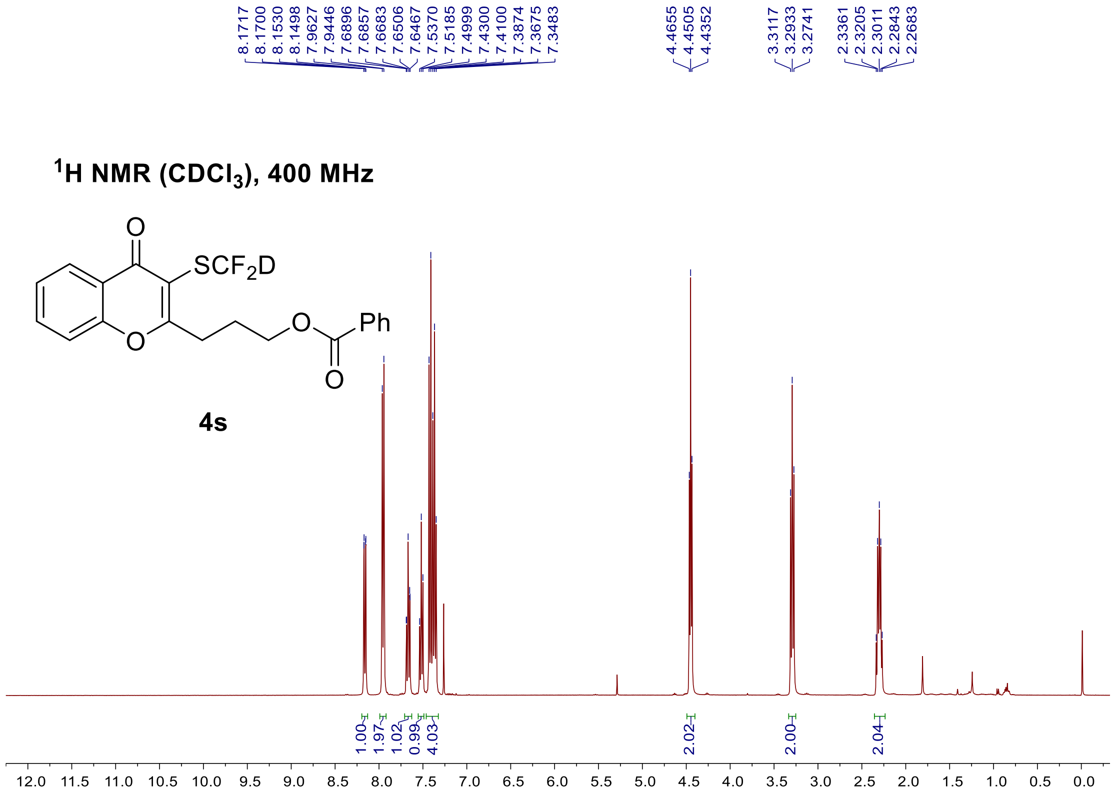
^{13}C NMR (CDCl$_3$), 101 MHz

4r



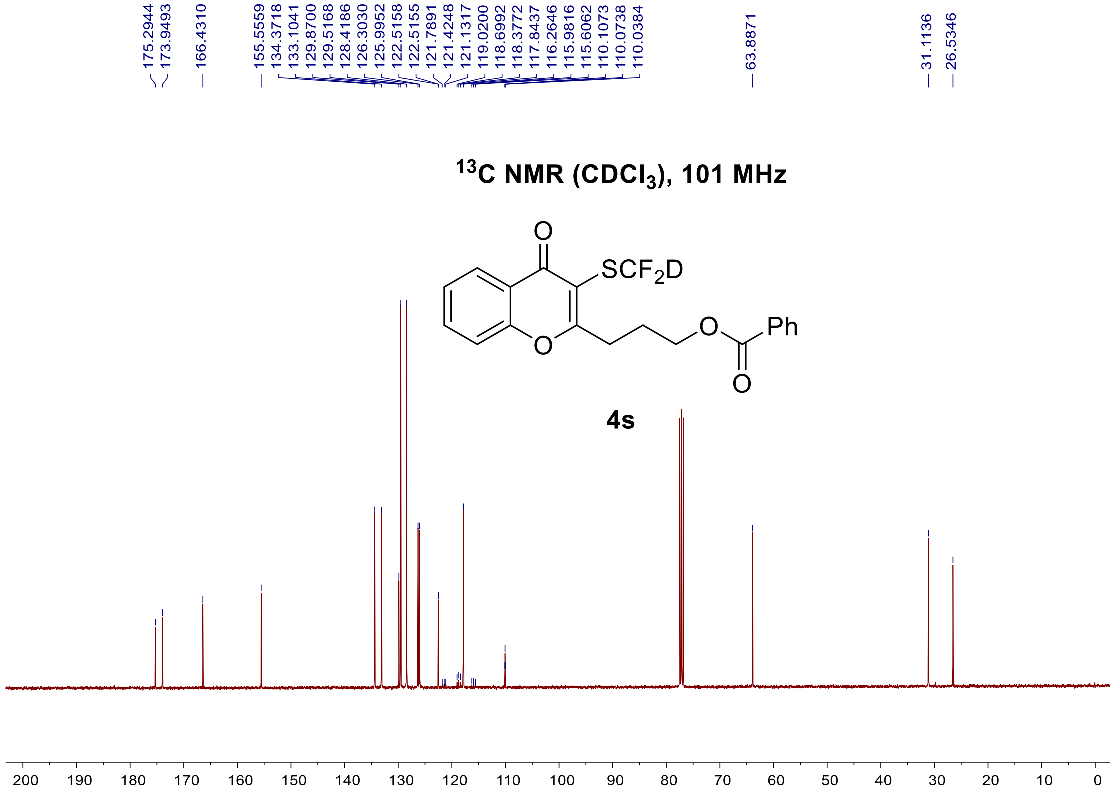
^{19}F NMR (CDCl$_3$), 471 MHz

4r



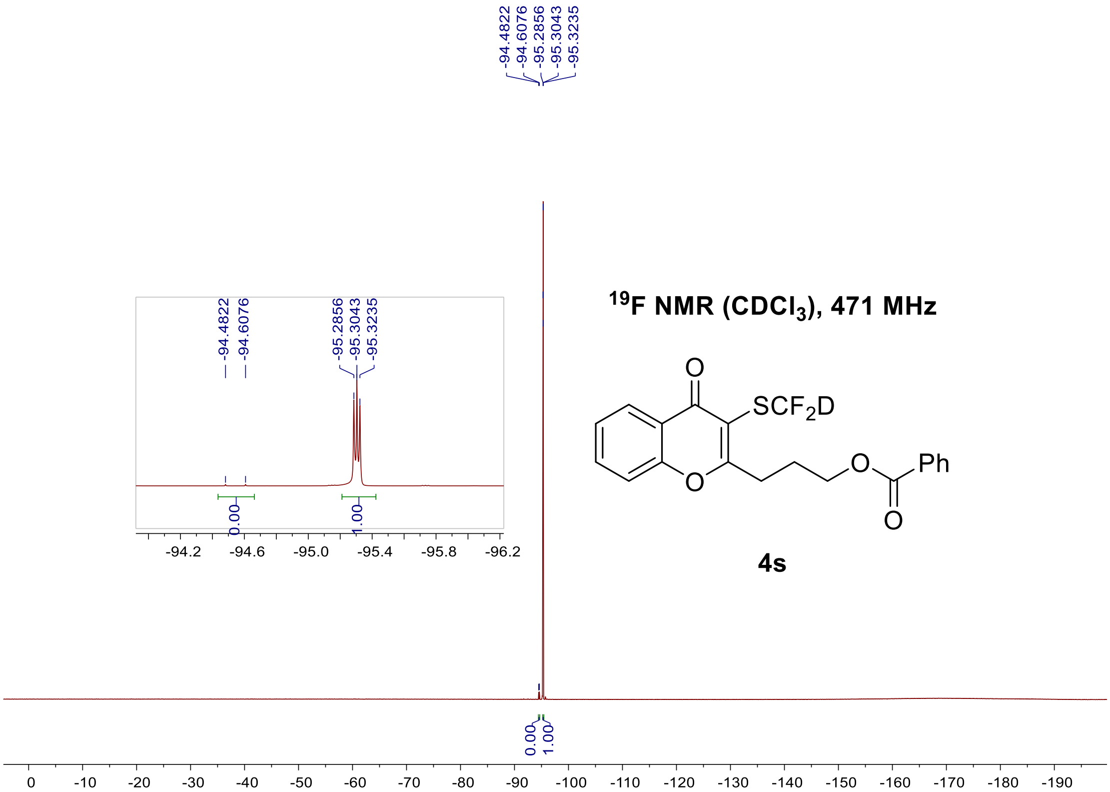
^{1}H NMR (CDCl$_3$), 400 MHz

4s

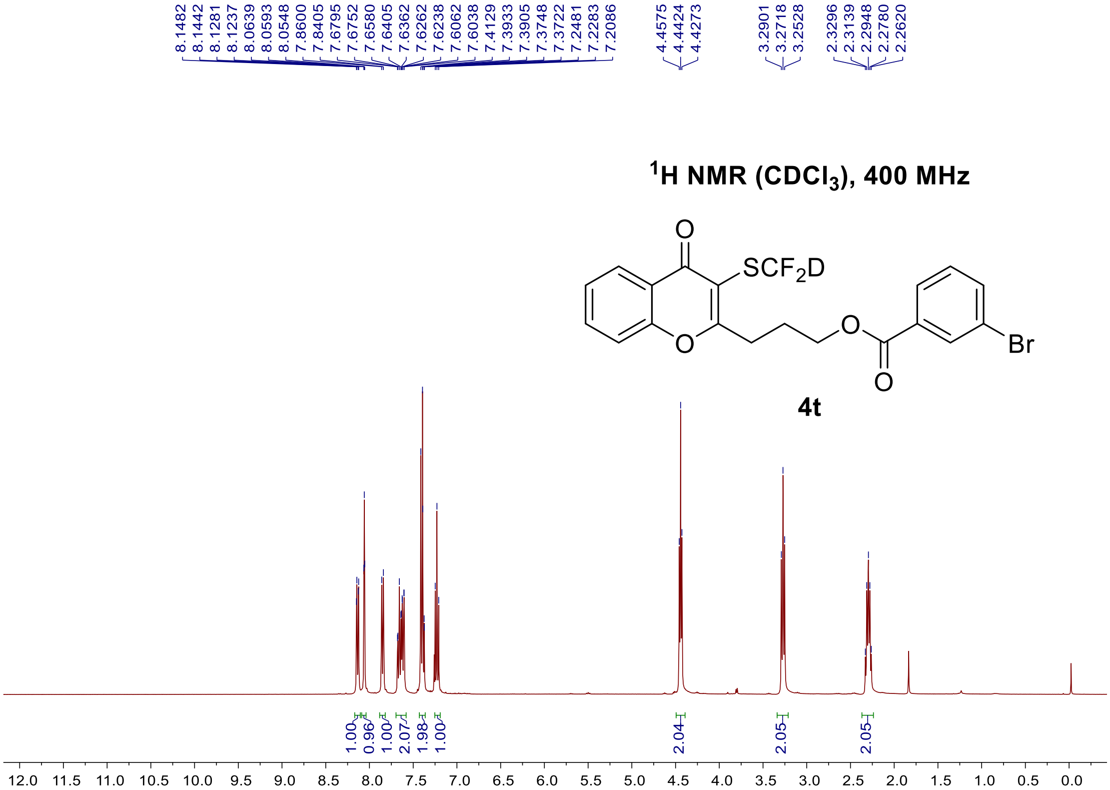


^{13}C NMR (CDCl$_3$), 101 MHz

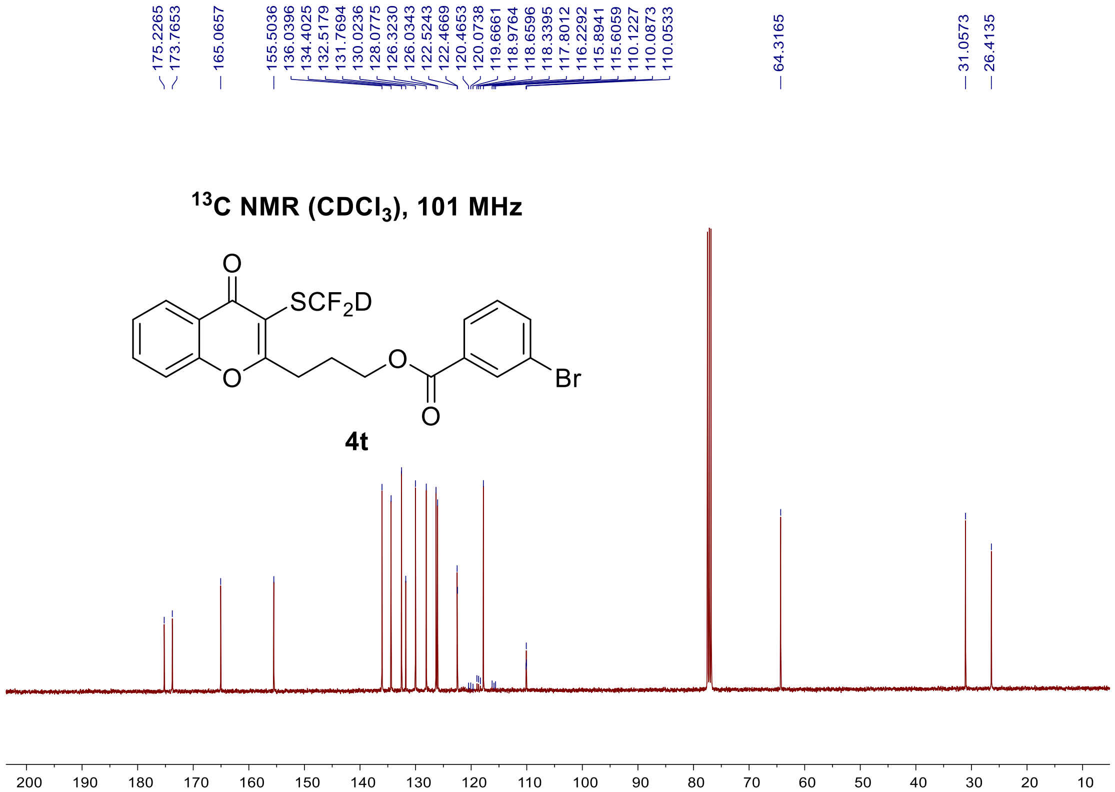
4s

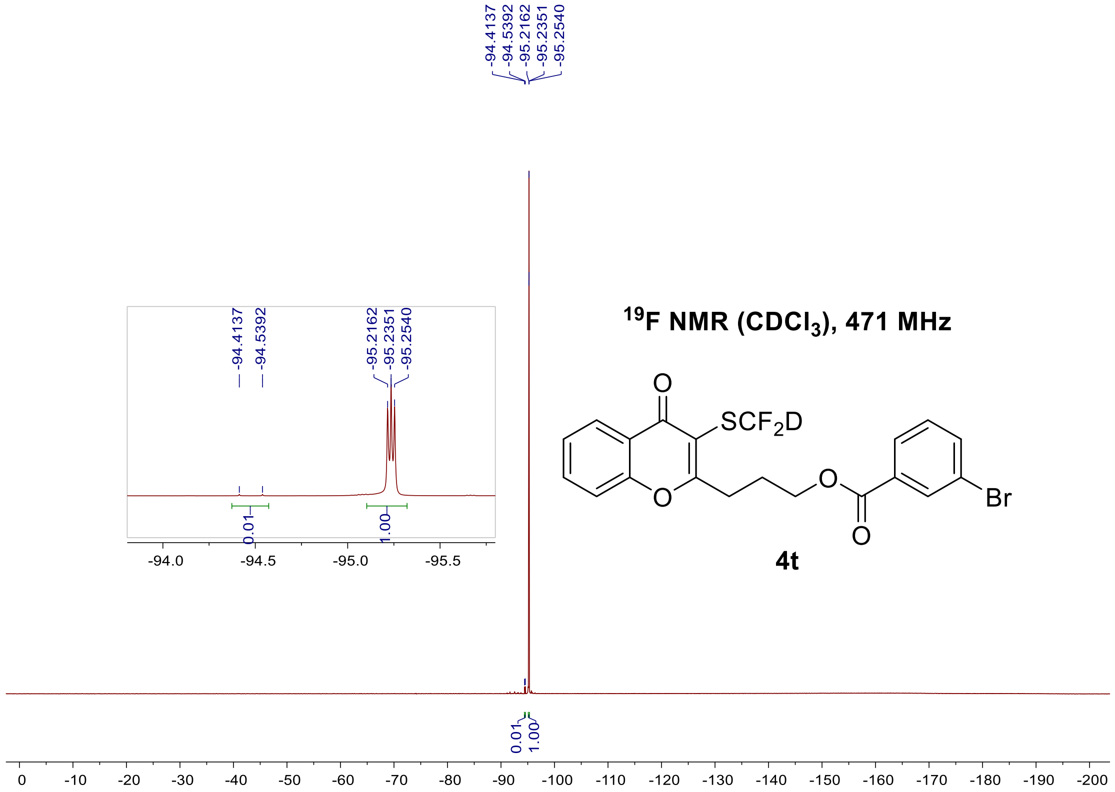

-94.4822
-94.6076
-95.2856
-95.3043
-95.3235
^{19}F NMR (CDCl$_3$), 471 MHz
O
SCF$_2$D
O
O
Ph
O
0.00
1.00
-94.2
-94.6
-95.0
-95.4
-95.8
-96.2
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190

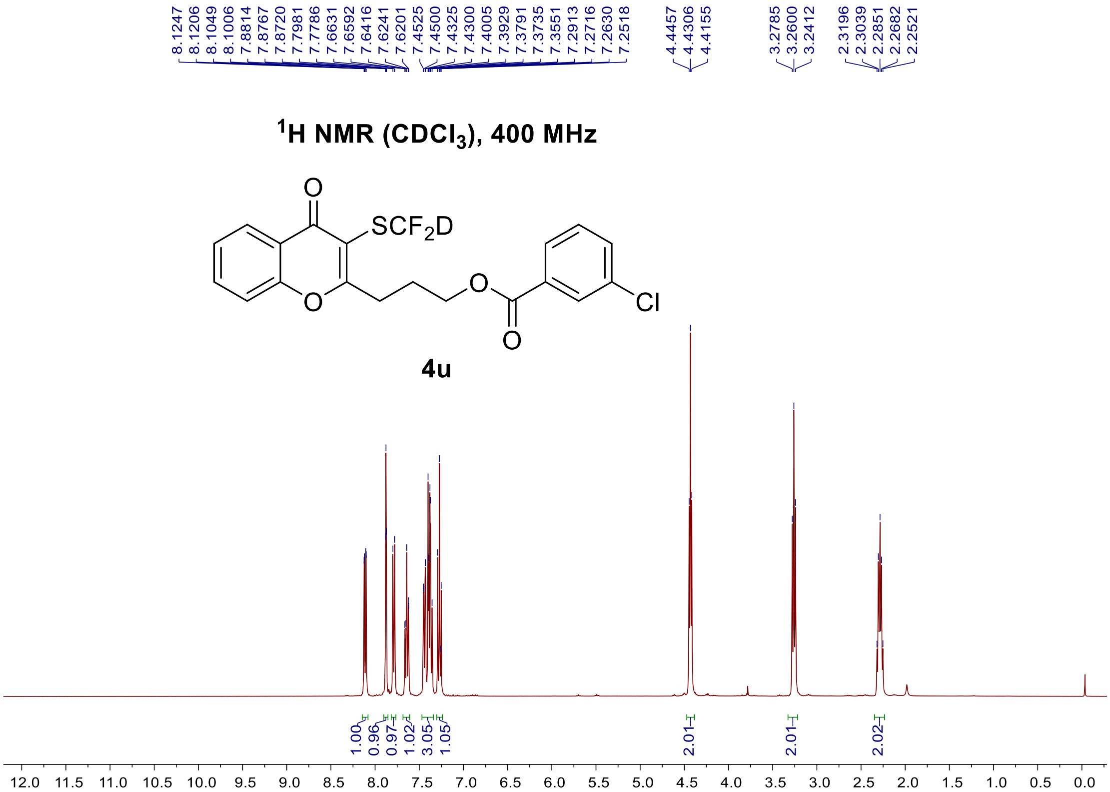
4s


8.1482
8.1442
8.1281
8.1237
8.0639
8.0593
8.0548
7.8600
7.8405
7.6795
7.6752
7.6580
7.6405
7.6362
7.6262
7.6238
7.6062
7.6038
7.4129
7.3933
7.3905
7.3748
7.3722
7.2481
7.2283
7.2086
4.4575
4.4424
4.4273
3.2901
3.2718
3.2528
2.3296
2.3139
2.2948
2.2780
2.2620
^{1}H NMR (CDCl$_3$), 400 MHz
O
SCF$_2$D
O
O
O
Br
1.00
0.96
1.00
2.07
1.98
1.00
2.04
2.05
2.05
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

4t

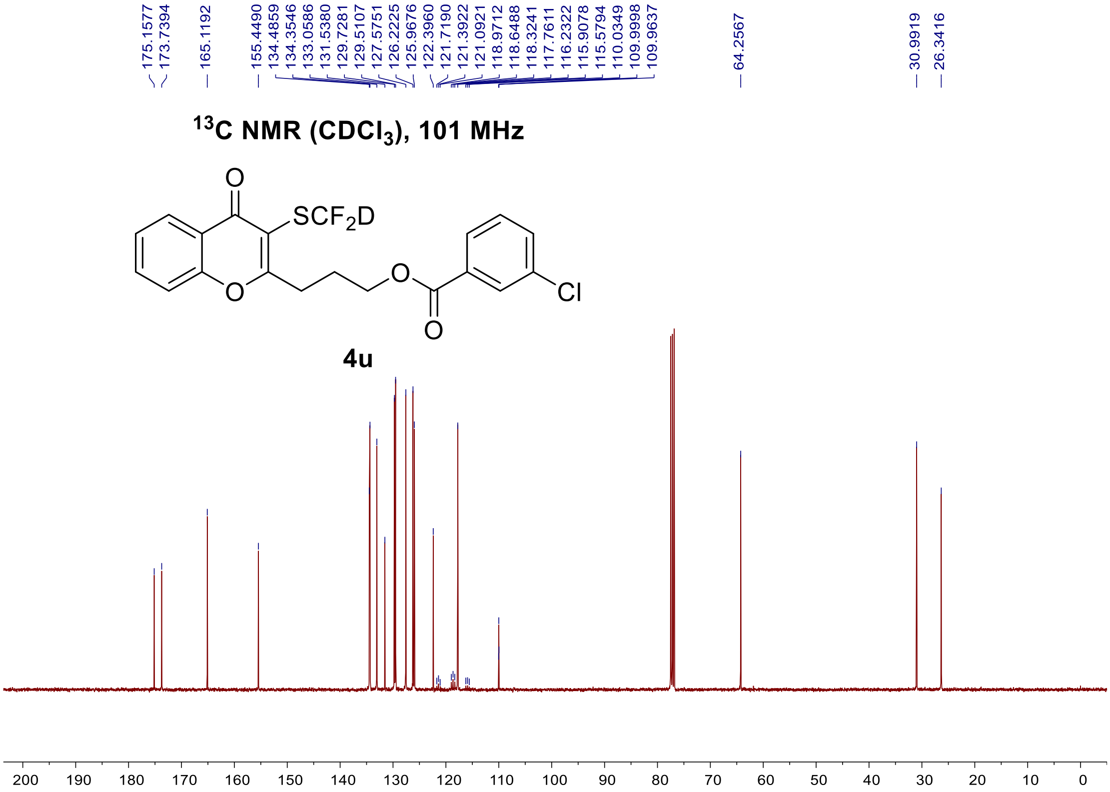

175.2265
173.7653
165.0657
155.5036
136.0396
134.4025
132.5179
131.7694
130.0236
128.0775
126.3230
126.0343
122.5243
122.4669
120.4653
120.0738
119.6661
118.9764
118.6596
118.3395
117.8012
116.2292
115.8941
115.6059
110.1227
110.0873
110.0533
64.3165
31.0573
26.4135
^{13}C NMR (CDCl$_3$), 101 MHz
SCF$_2$D
O
O
O
O
Br
4t
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10


-94.4137
-94.5392
-95.2162
-95.2351
-95.2540
^{19}F NMR (CDCl$_3$), 471 MHz
SCF$_2$D
O
O
O
O
Br
4t
0.01
1.00
-94.0
-94.5
-95.0
-95.5
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200



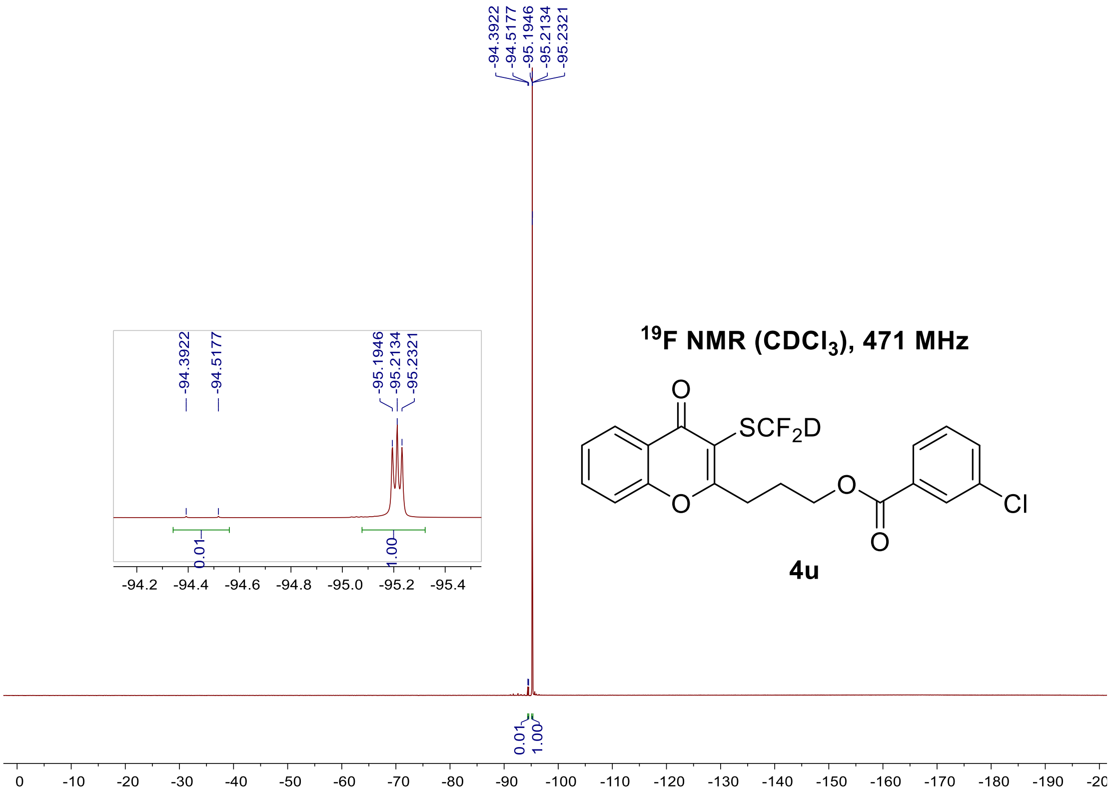
^{1}H NMR ($CDCl_3$), 400 MHz

4u



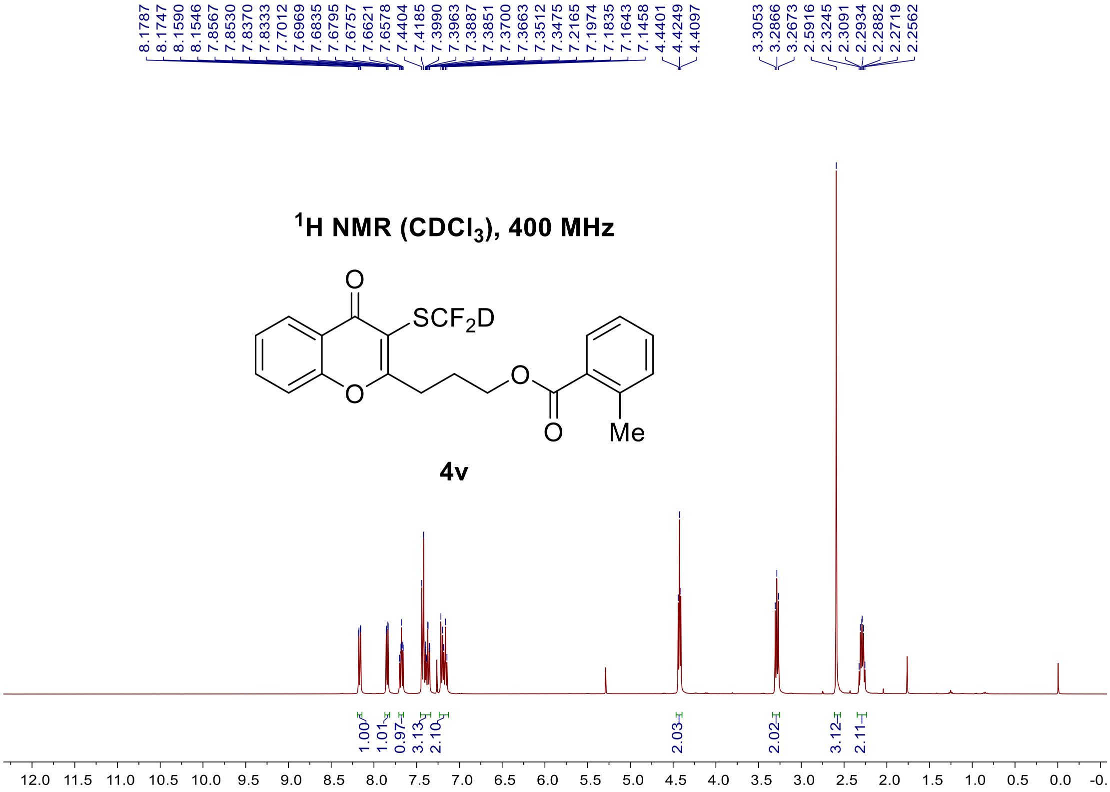
^{13}C NMR ($CDCl_3$), 101 MHz

4u



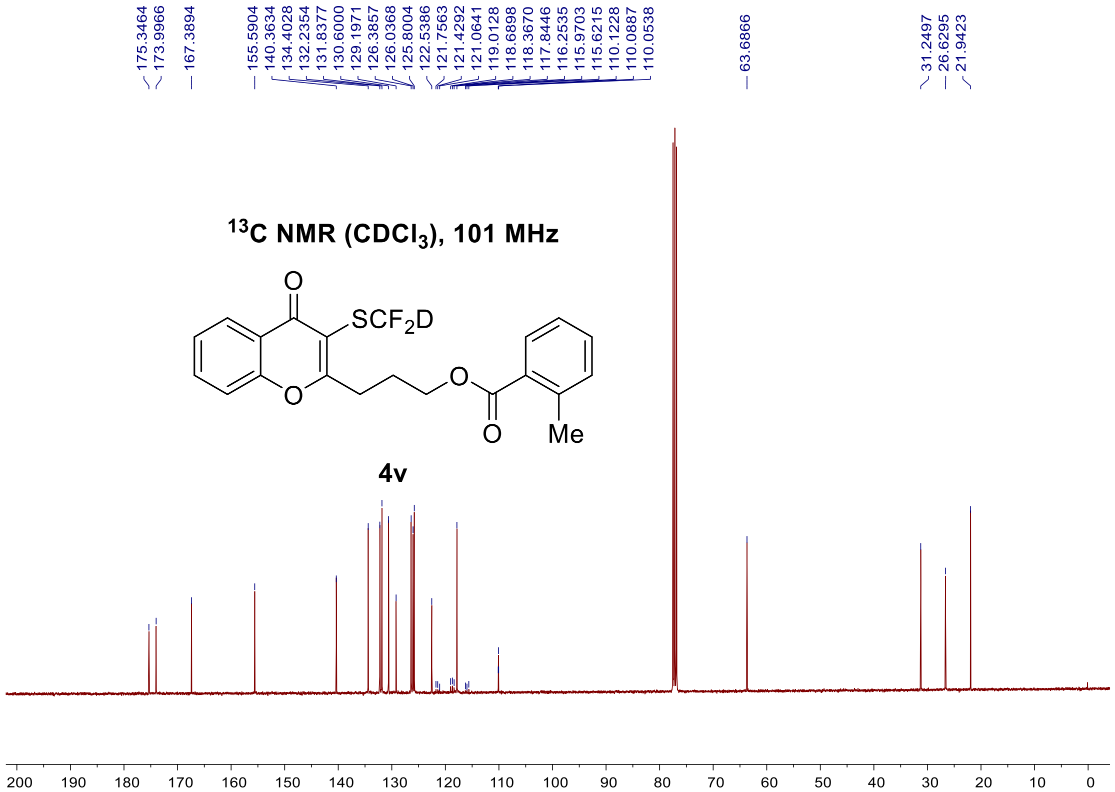
^{19}F NMR ($CDCl_3$), 471 MHz

4u



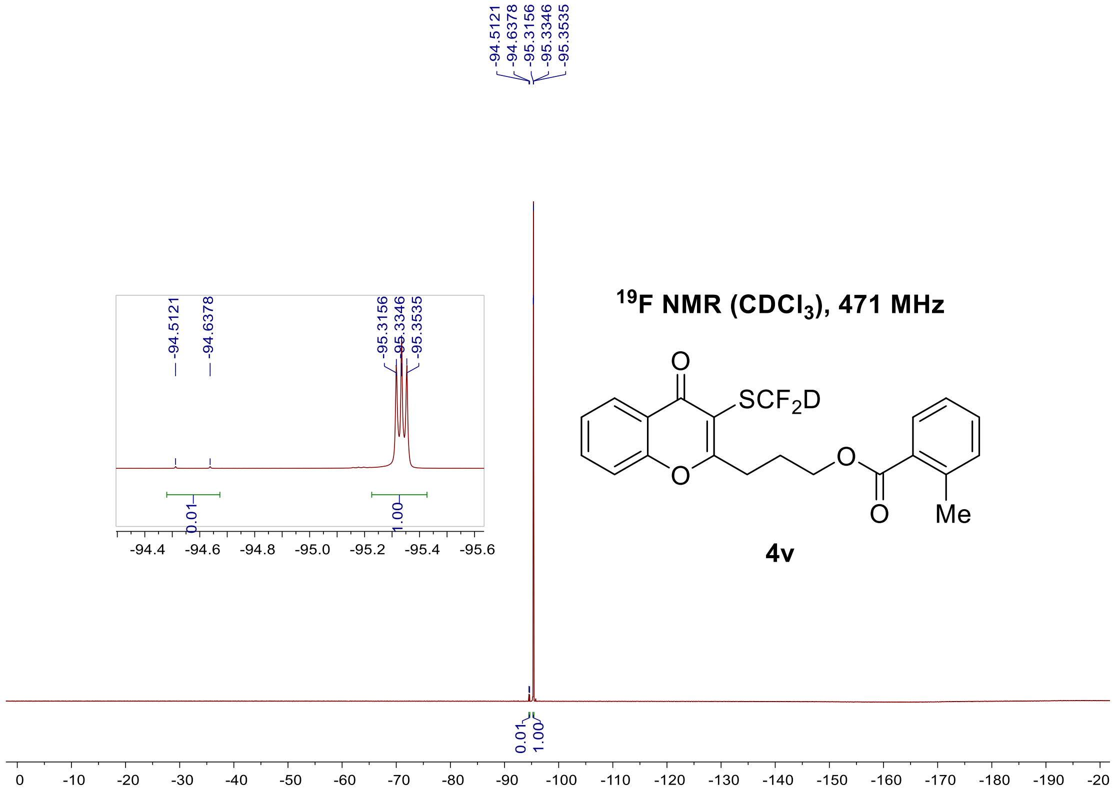
^{1}H NMR ($CDCl_3$), 400 MHz

4v



^{13}C NMR (CDCl$_3$), 101 MHz

4v

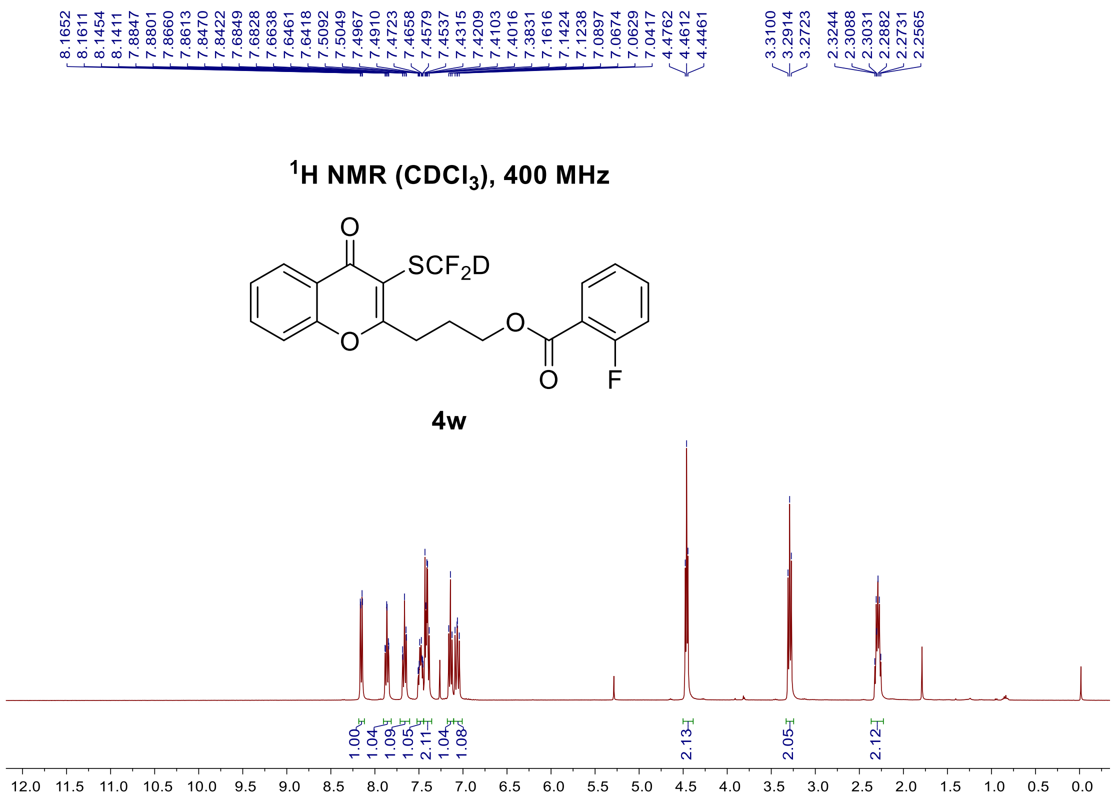


^{19}F NMR (CDCl$_3$), 471 MHz

4v

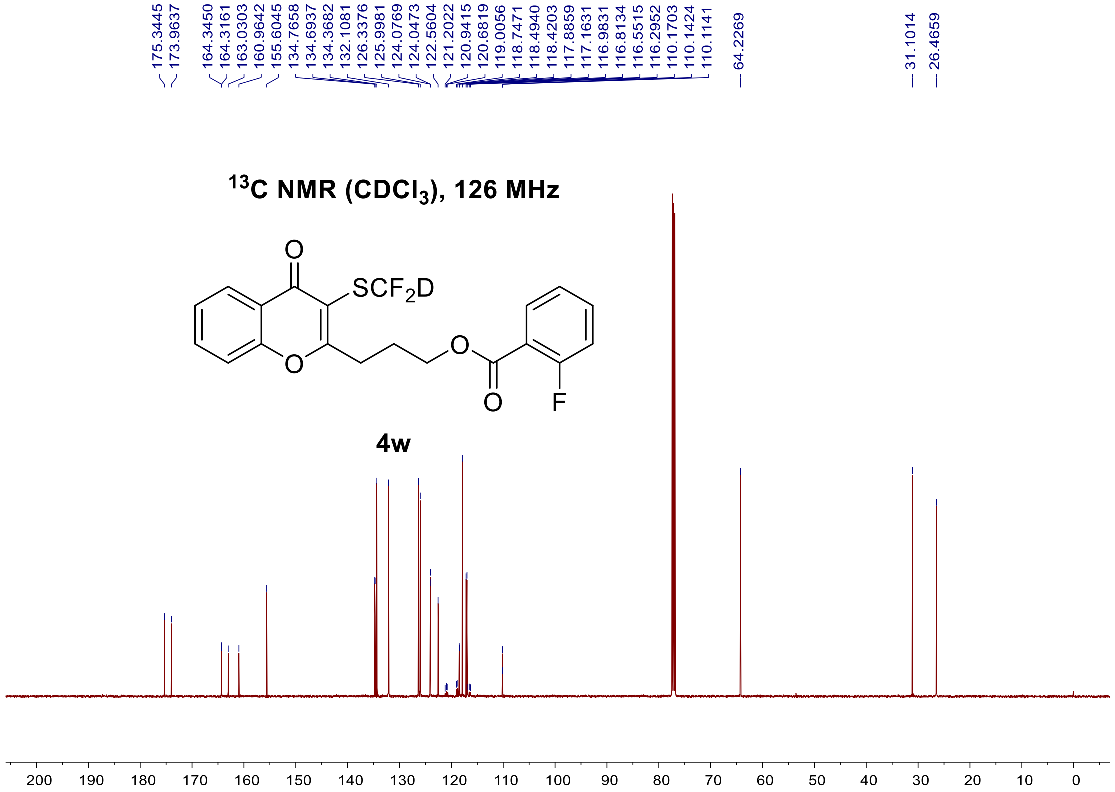
^{1}H NMR (CDCl$_3$), 400 MHz

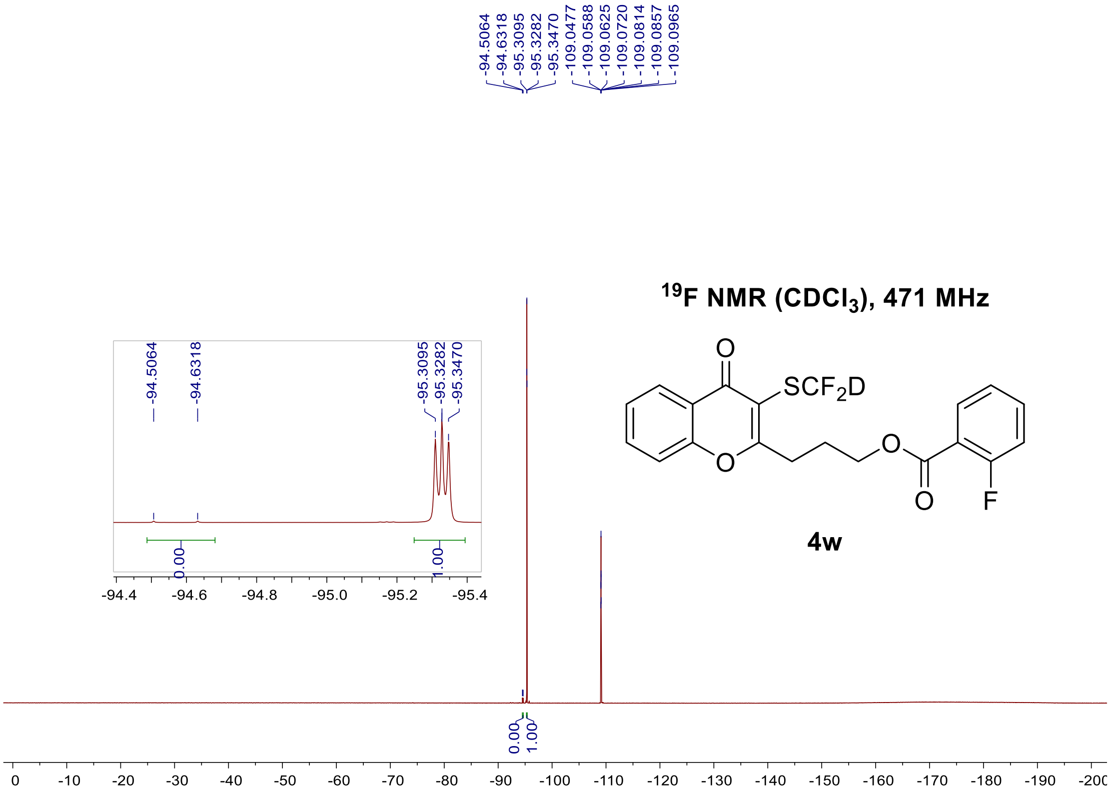
4w



^{13}C NMR (CDCl$_3$), 126 MHz

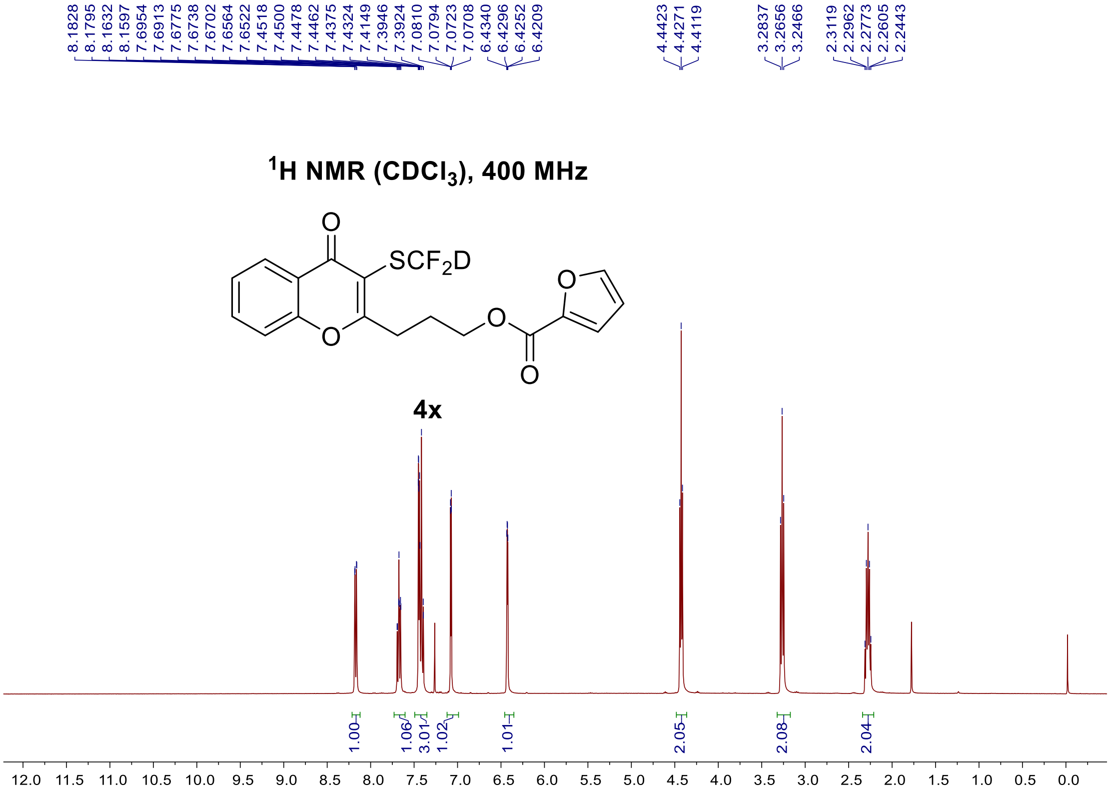
4w





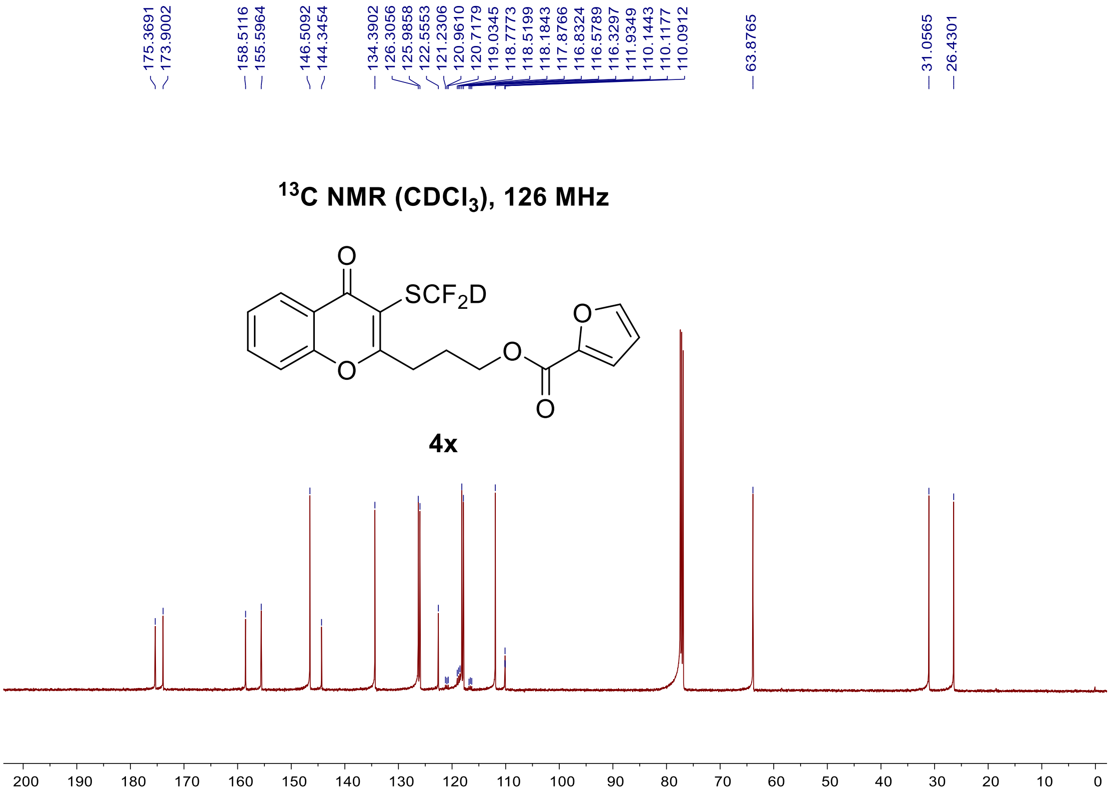
^{19}F NMR (CDCl$_3$), 471 MHz

4w



^{1}H NMR (CDCl$_3$), 400 MHz

4x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173.9002
158.5116
155.5964
146.5092
144.3454
134.3902
126.3056
125.9858
122.5553
121.2306
120.9610
120.7179
119.0345
118.7773
118.5199
118.1843
117.8766
116.8324
116.5789
116.3297
111.9349
110.1443
110.1177
110.0912
63.8765
31.0565
26.4301
13C NMR (CDCl3), 126 MHz
O
SCF2D
O
O
O
O
4x
200
190
180
170
160
150
140
130
120
110
100
90
80
70
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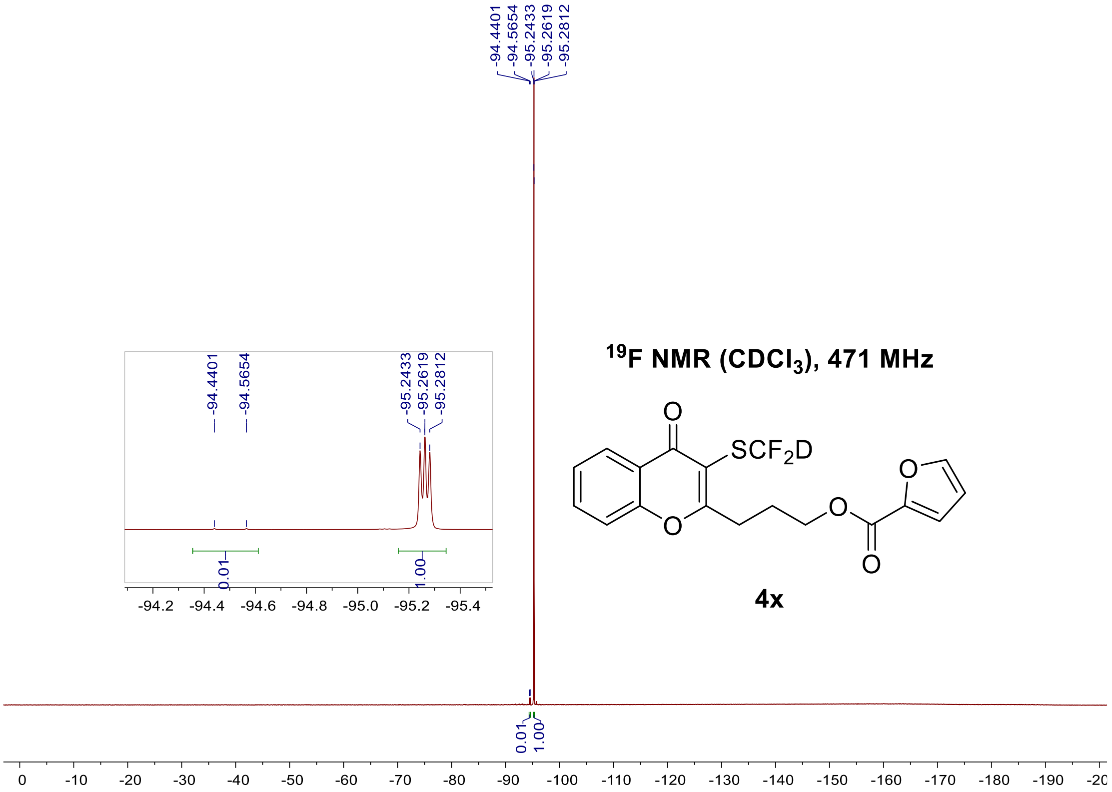
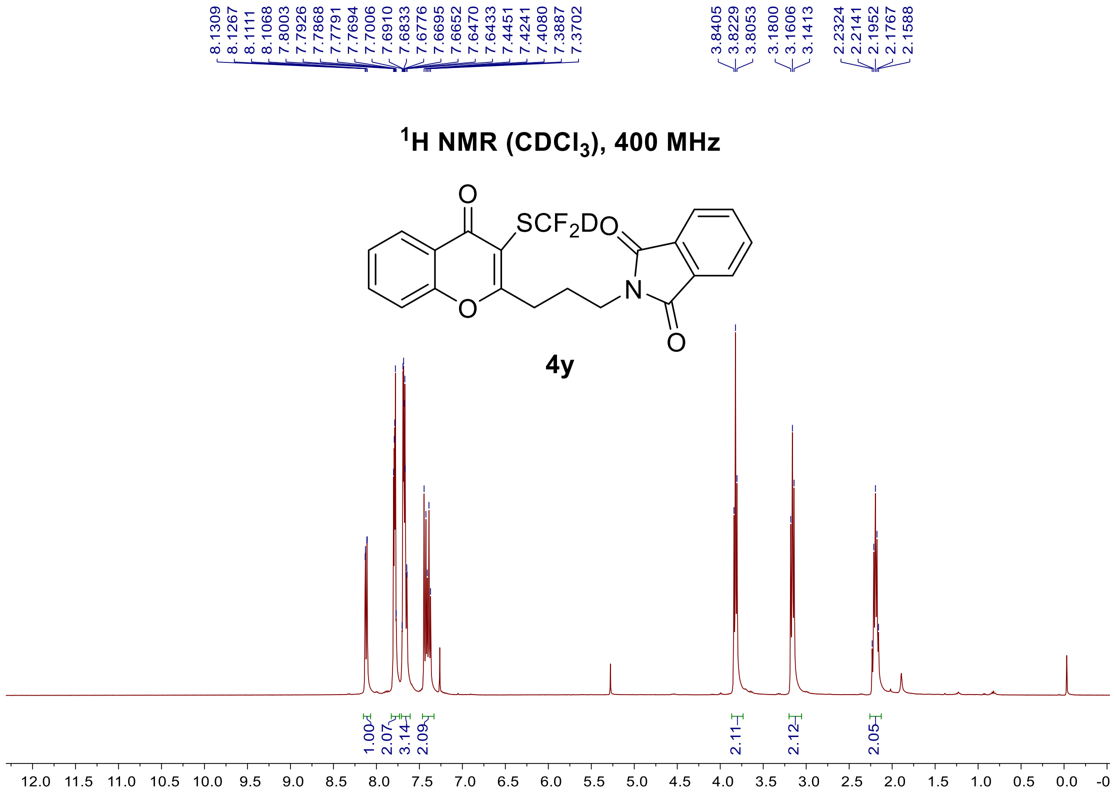
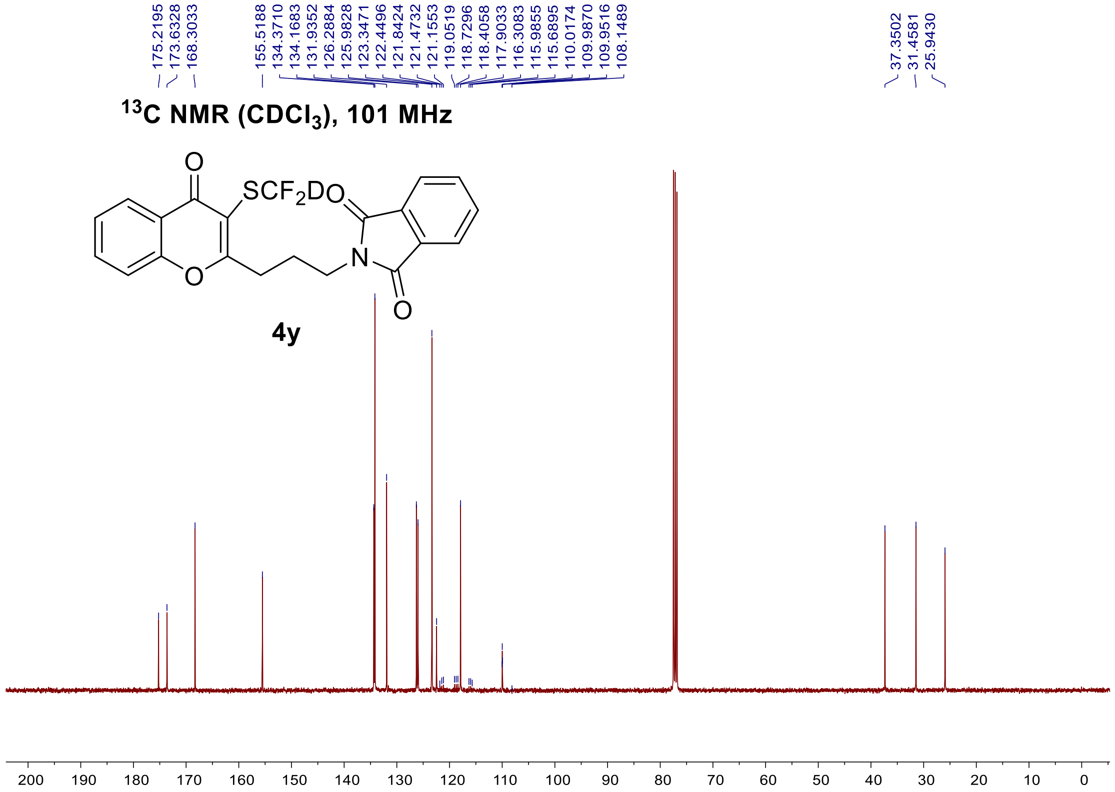
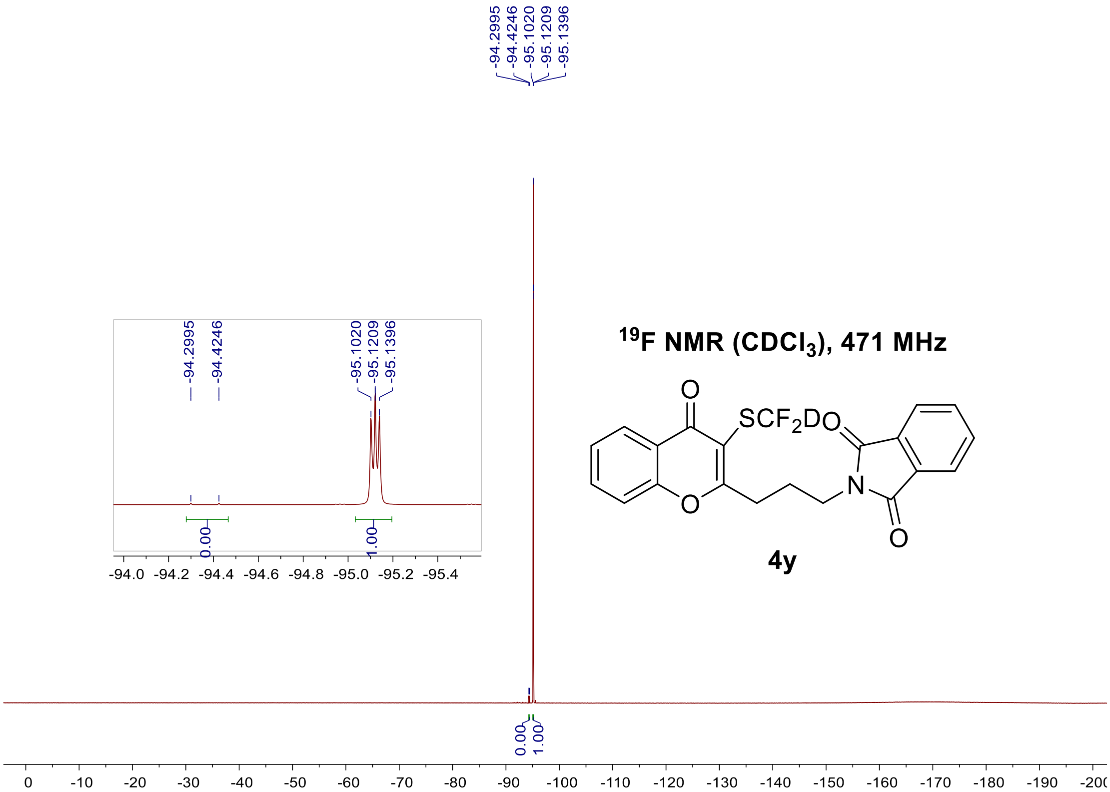
50
40
30
20
10
0


-94.4401
-94.5654
-95.2433
-95.2619
-95.2812
19F NMR (CDCl3), 471 MHz
0.01
1.00
-94.2
-94.4
-94.6
-94.8
-95.0
-95.2
-95.4
O
SCF2D
O
O
O
O
4x
0.01
1.00
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-20

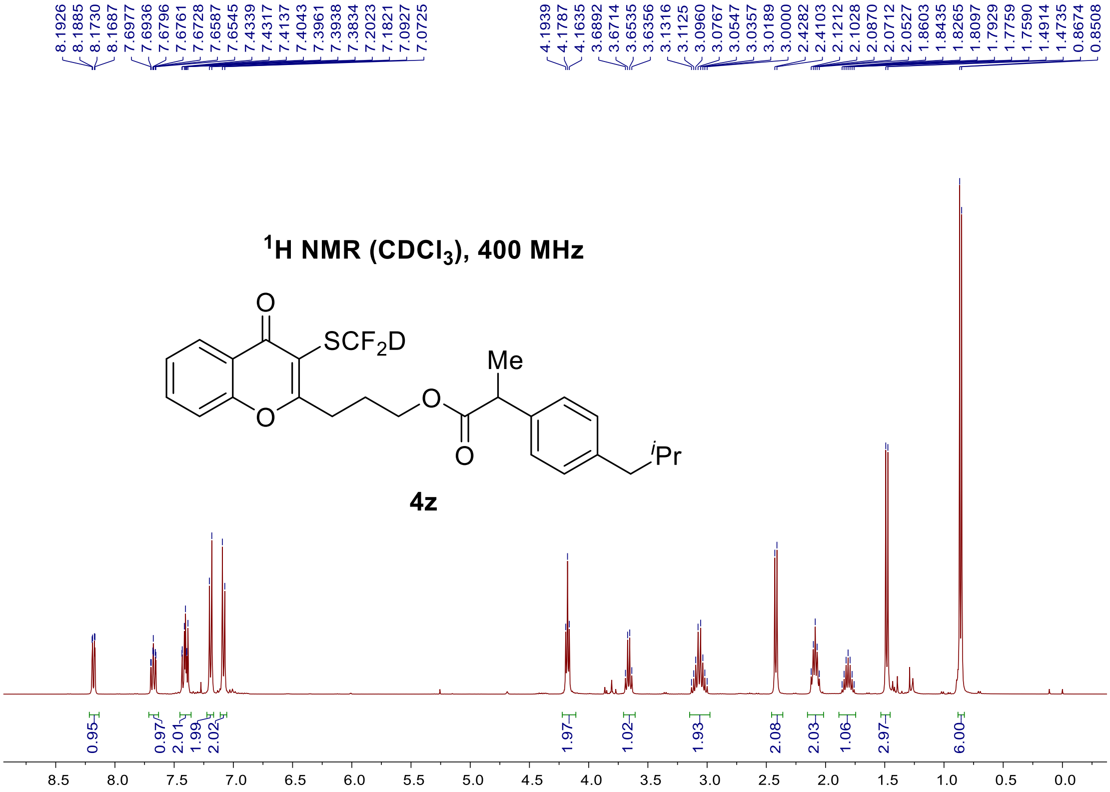

8.1309
8.1267
8.1111
8.1068
7.8003
7.7926
7.7868
7.7791
7.7694
7.7006
7.6910
7.6833
7.6776
7.6695
7.6652
7.6470
7.6433
7.4451
7.4241
7.4080
7.3887
7.3702
3.8405
3.8229
3.8053
3.1800
3.1606
3.1413
2.2324
2.2141
2.1952
2.1767
2.1588
^{1}H NMR (CDCl$_3$), 400 MHz
O
SCF$_2$D
O
N
O
O
4y
1.00
2.07
3.14
2.09
2.11
2.12
2.05
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0


175.2195
173.6328
168.3033
155.5188
134.3710
134.1683
131.9352
126.2884
125.9828
123.3471
122.4496
121.8424
121.4732
121.1553
119.0519
118.7296
118.4058
117.9033
116.3083
115.9855
115.6895
110.0174
109.9870
109.9516
108.1489
37.3502
31.4581
25.9430
^{13}C NMR (CDCl$_3$), 101 MHz
O
SCF$_2$D
O
N
O
O
4y
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0



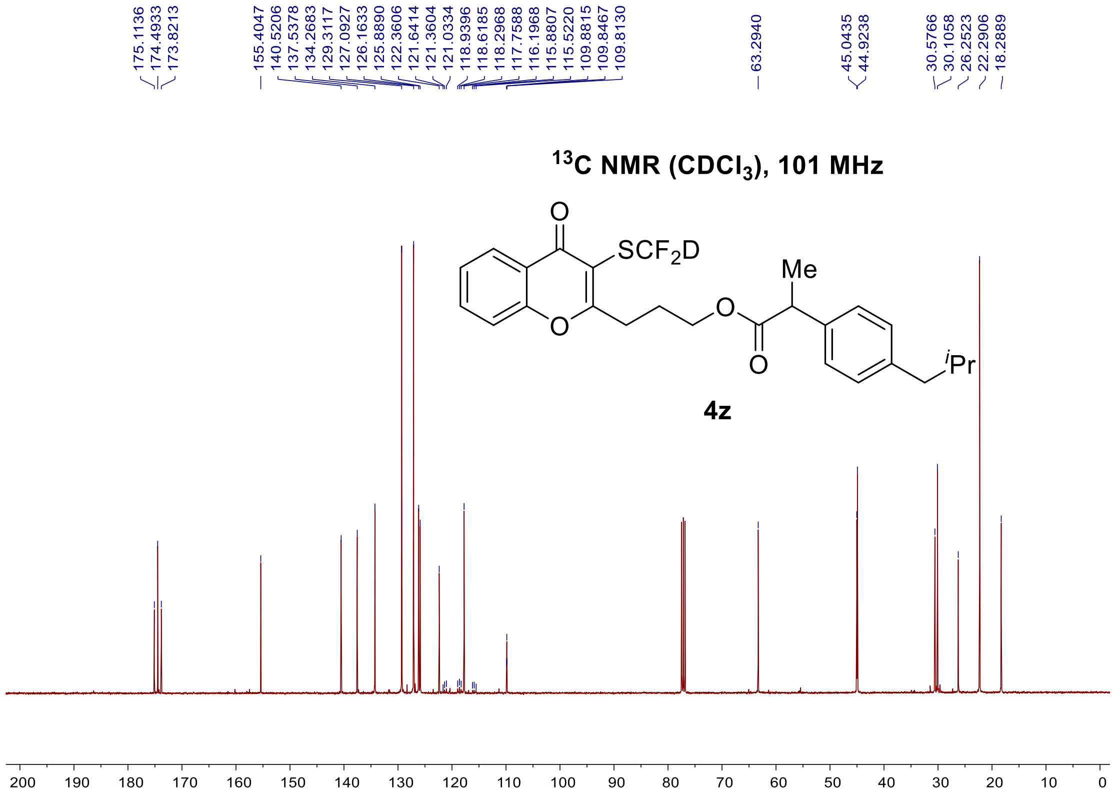
^{19}F NMR (CDCl$_3$), 471 MHz

4y



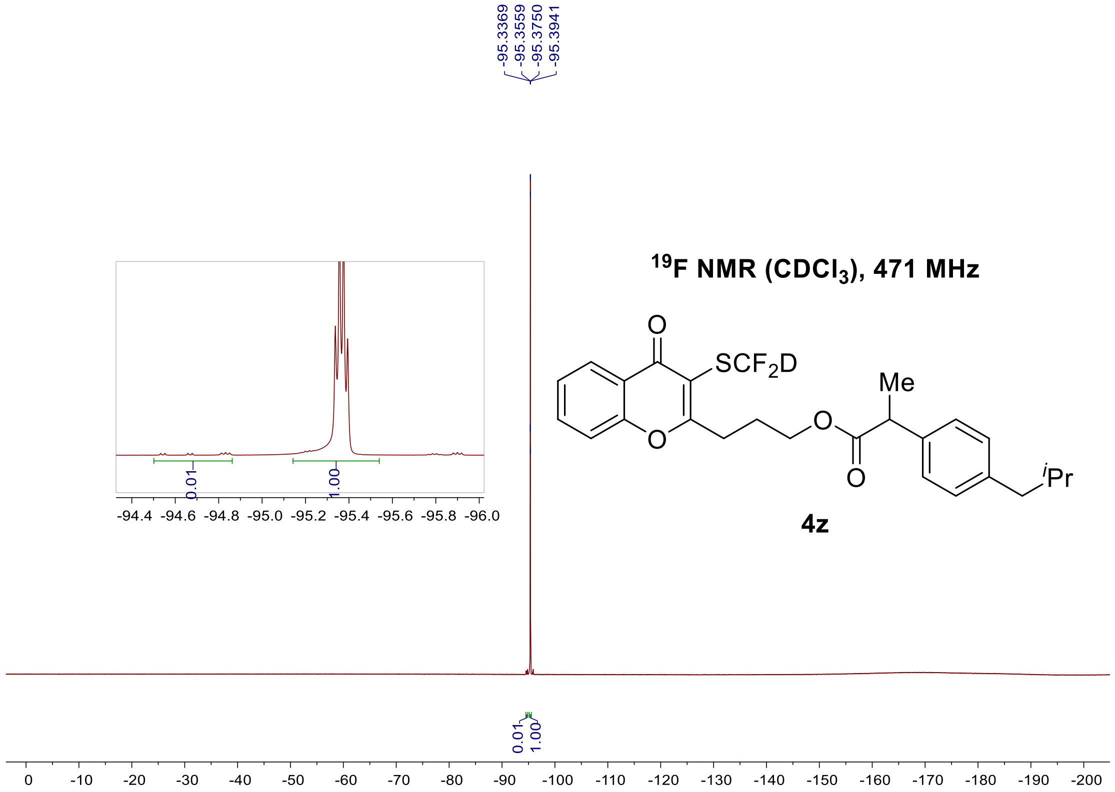
^{1}H NMR (CDCl$_3$), 400 MHz

4z



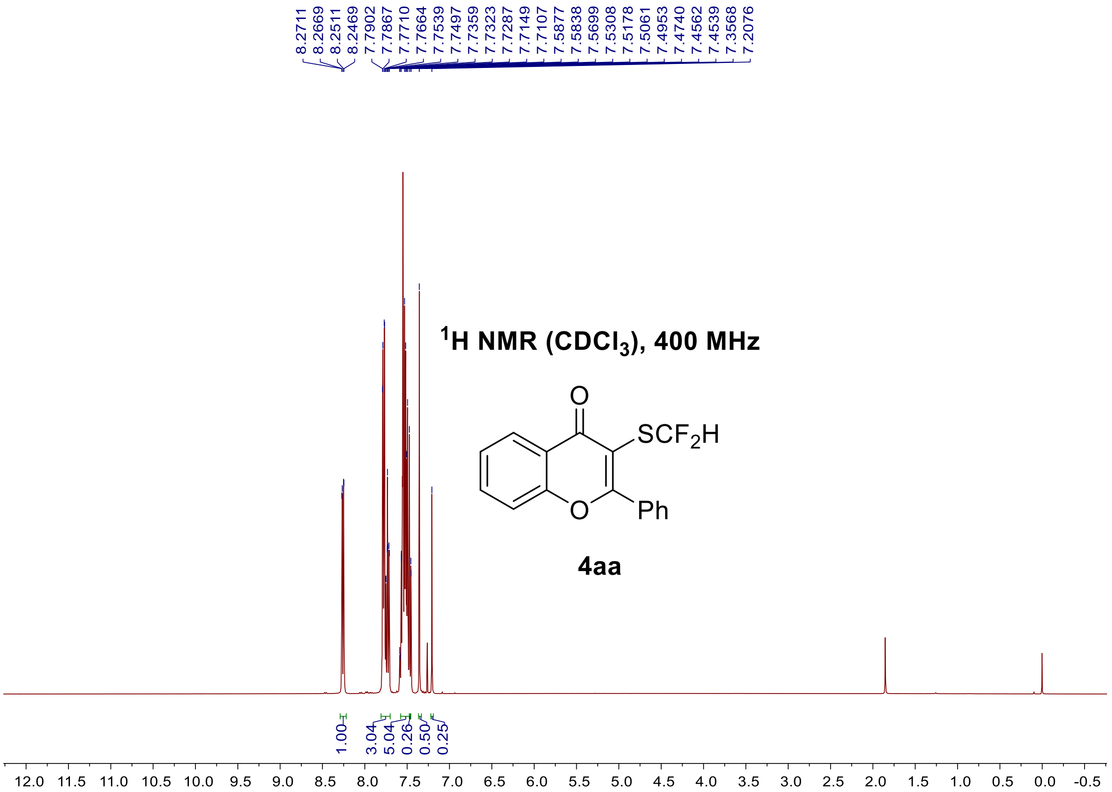
^{13}C NMR ($CDCl_3$), 101 MHz

4z



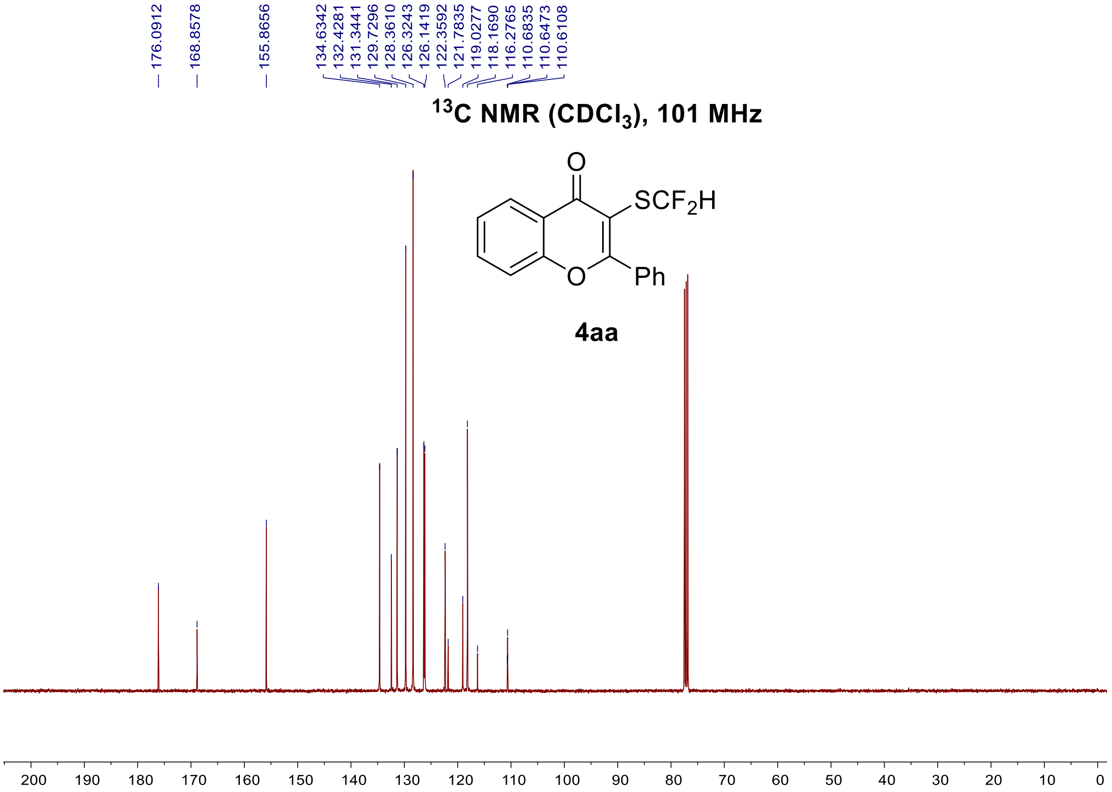
^{19}F NMR ($CDCl_3$), 471 MHz

4z



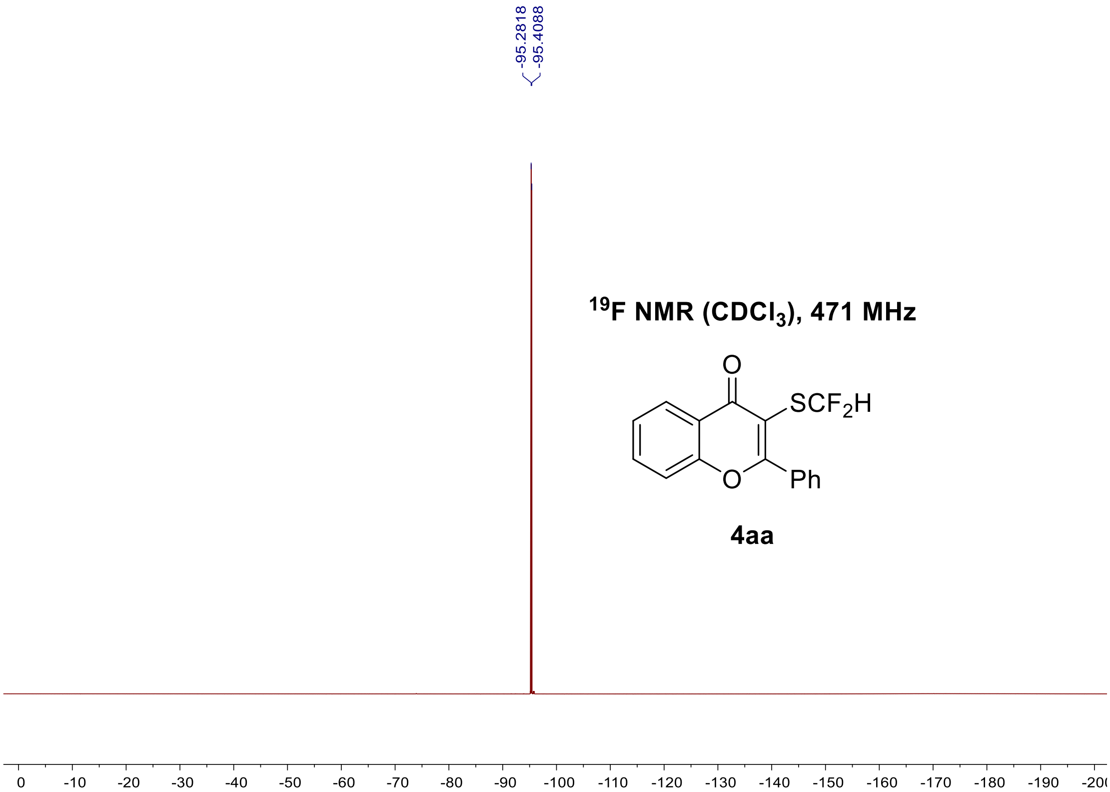
^{1}H NMR ($CDCl_3$), 400 MHz

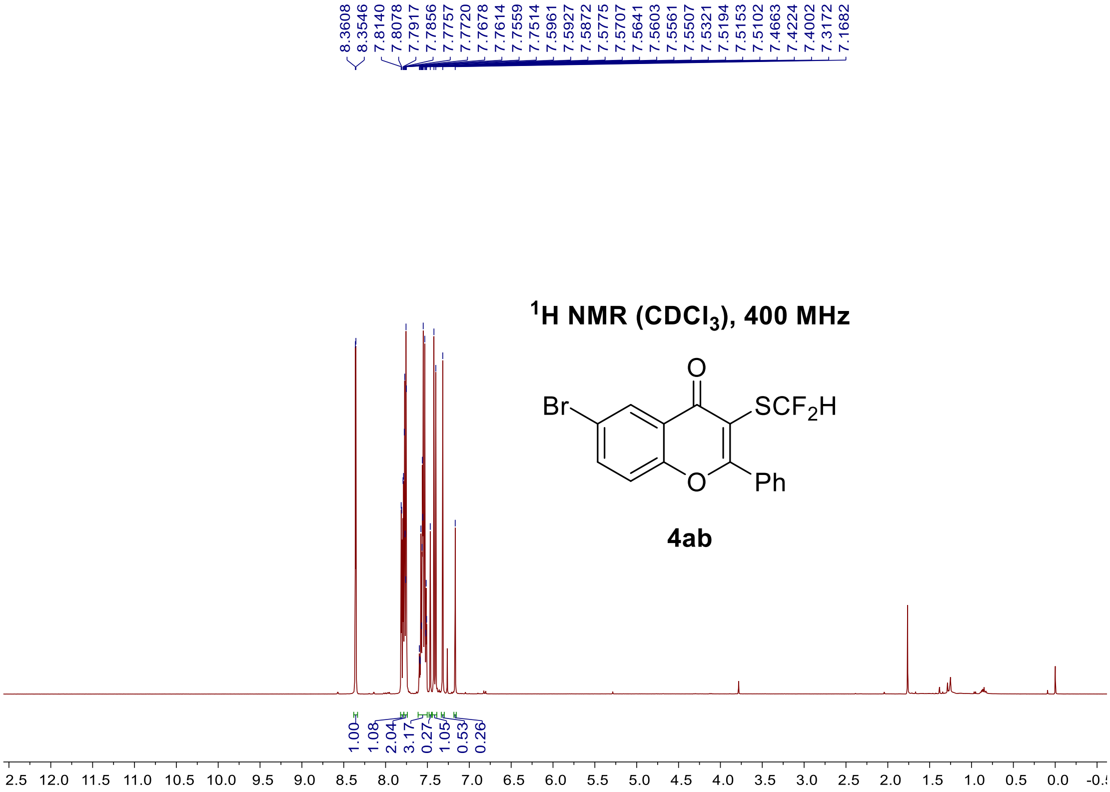
4aa



^{13}C NMR ($CDCl_3$), 101 MHz

4aa


-95.2818
-95.4088
^{19}F NMR ($CDCl_3$), 471 MHz
O
SCF_2H
O
Ph
4aa
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200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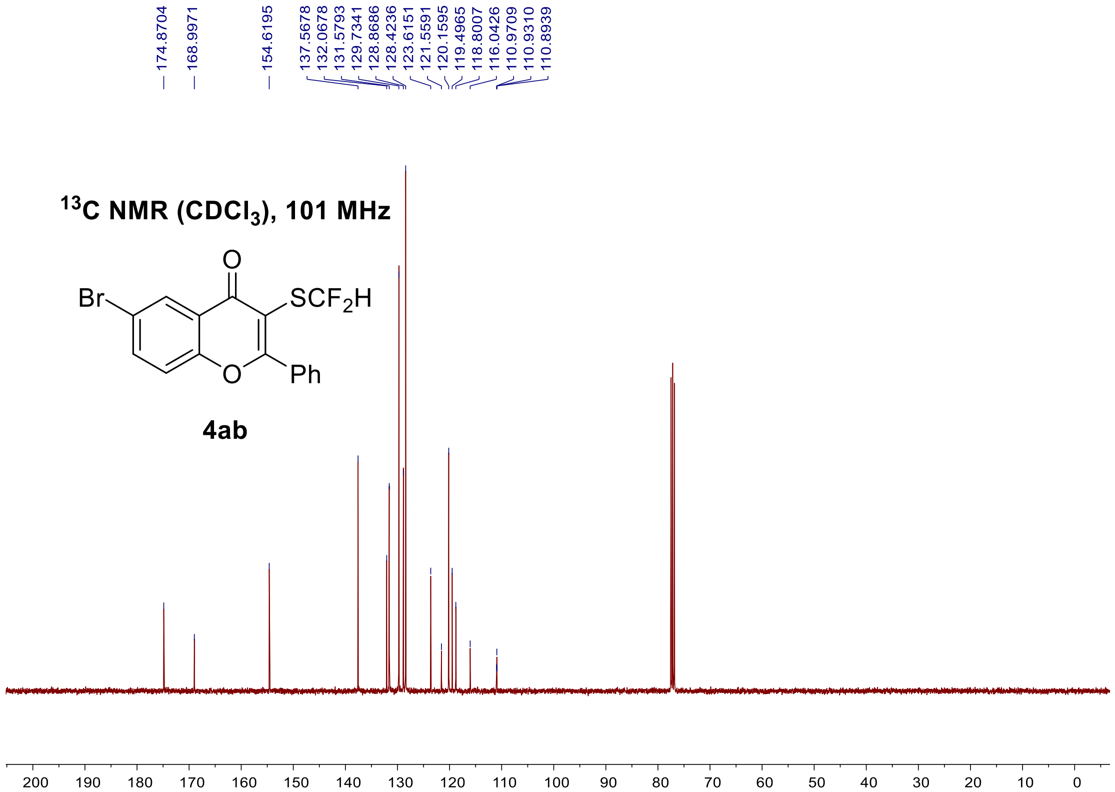
8.3546
7.8140
7.8078
7.7917
7.7856
7.7757
7.7720
7.7678
7.7614
7.7559
7.7514
7.5961
7.5927
7.5872
7.5775
7.5707
7.5641
7.5603
7.5561
7.5507
7.5321
7.5194
7.5153
7.5102
7.4663
7.4224
7.4002
7.3172
7.1682
^{1}H NMR ($CDCl_3$), 400 MHz
O
Br
SCF_2H
O
Ph
4ab
1.00
1.08
2.04
3.17
0.27
1.05
0.53
0.26
12.5
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5



174.8704
168.9971
154.6195
137.5678
132.0678
131.5793
129.7341
128.8686
128.4236
123.6151
121.5591
120.1595
119.4965
118.8007
116.0426
110.9709
110.9310
110.8939
^{13}C NMR ($CDCl_3$), 101 MHz
O
Br
SCF_2H
O
Ph
4ab
200
190
180
170
160
150
140
130
120
110
100
90
80
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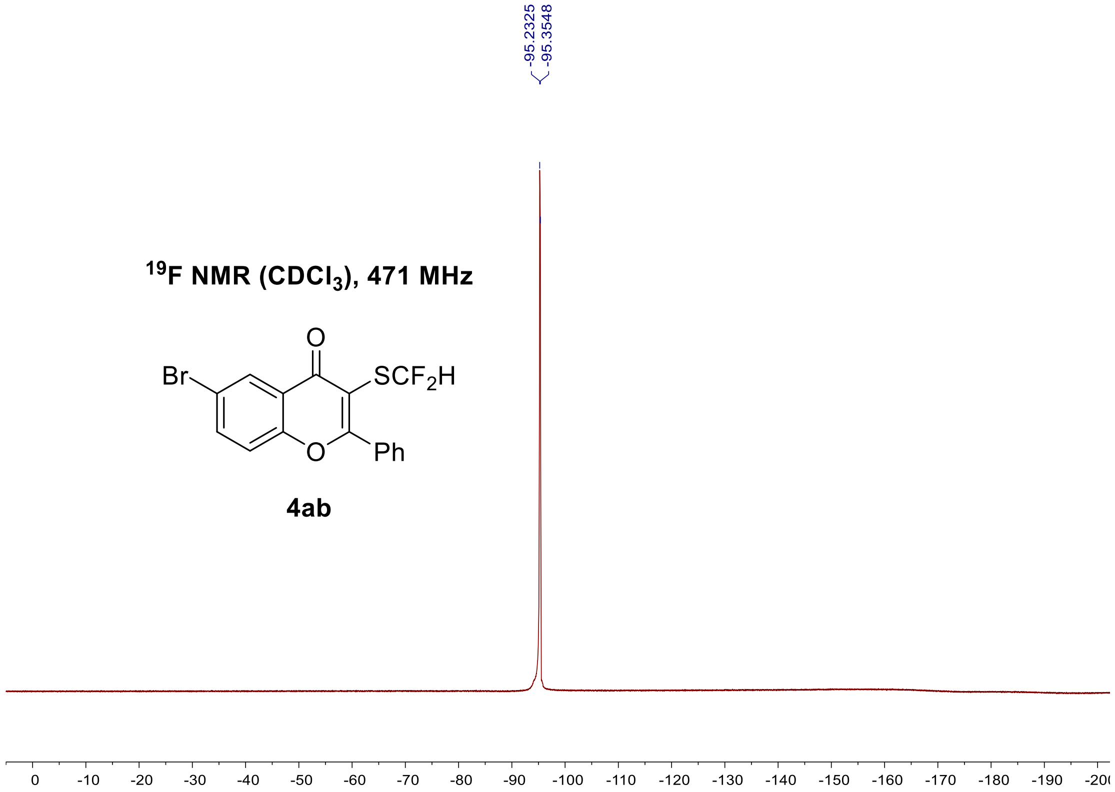
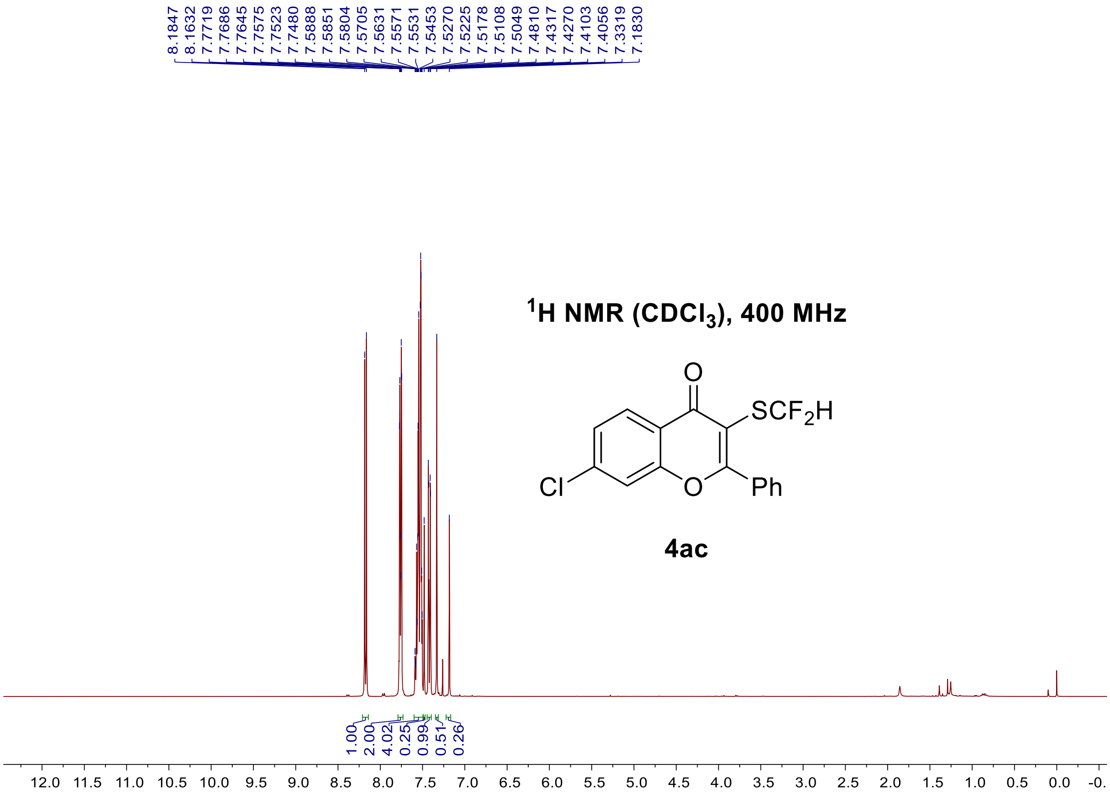
50
40
30
20
10
0



-95.2325
-95.3548
^{19}F NMR ($CDCl_3$), 471 MHz
O
Br
SCF_2H
O
Ph
4ab
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200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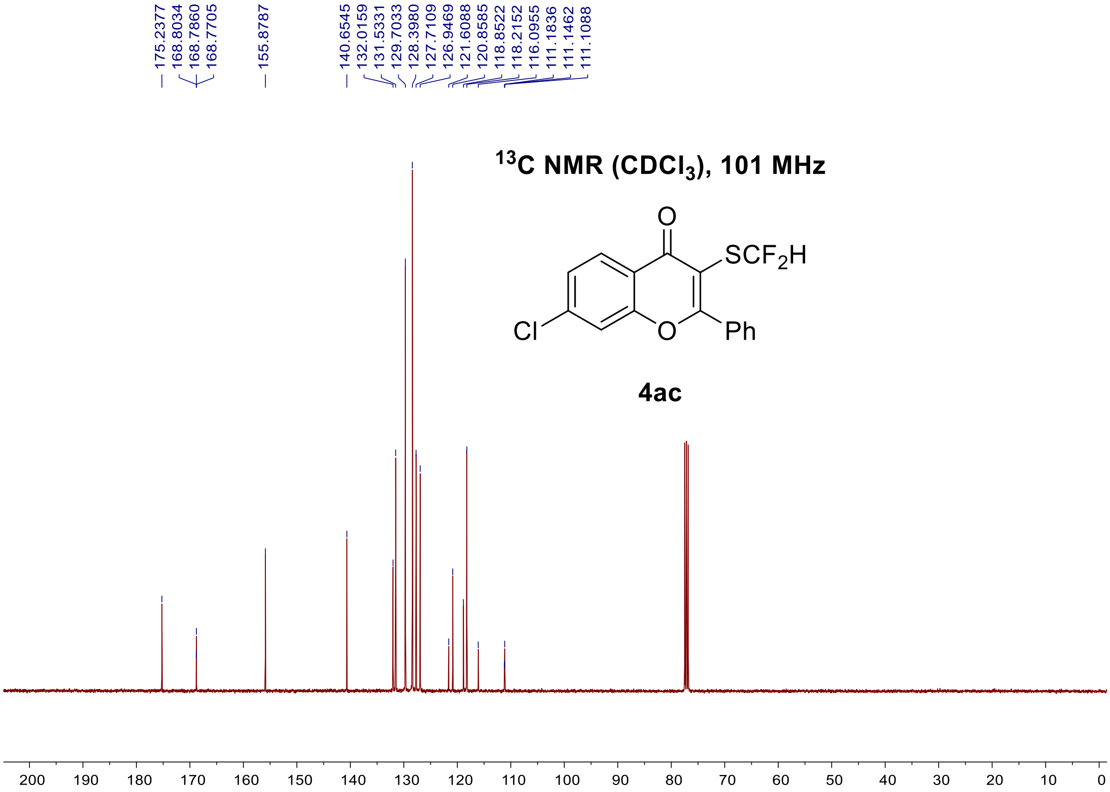
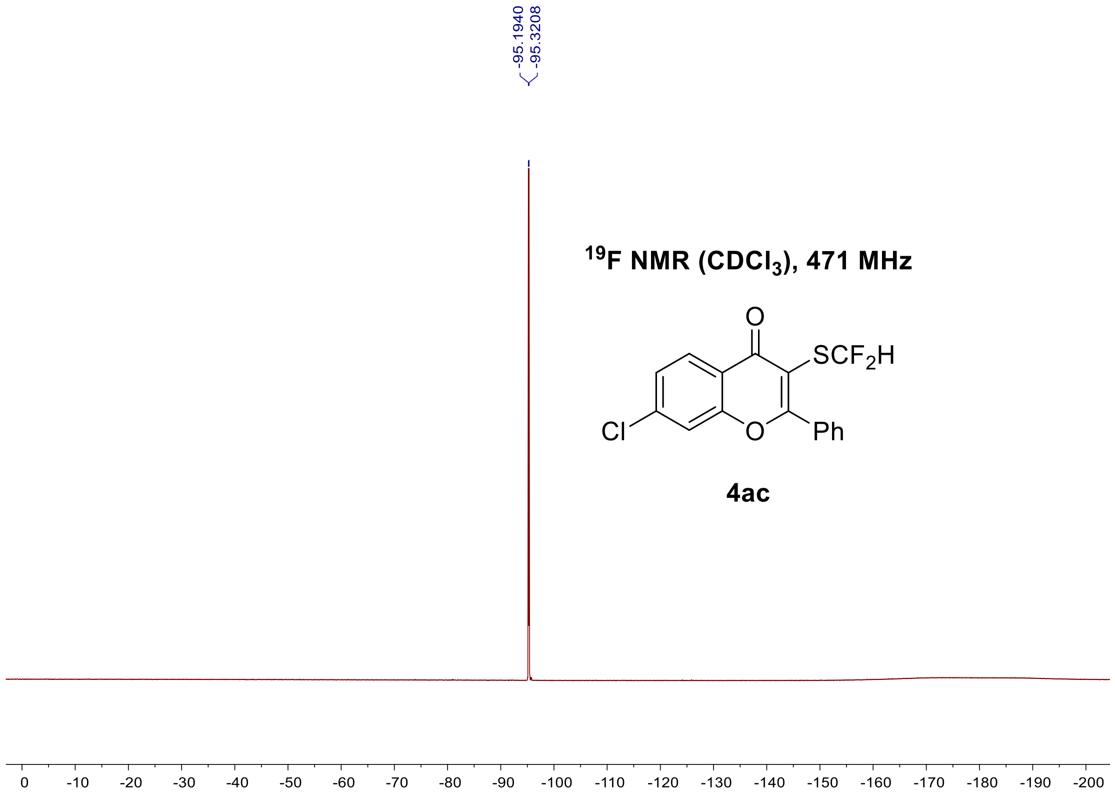
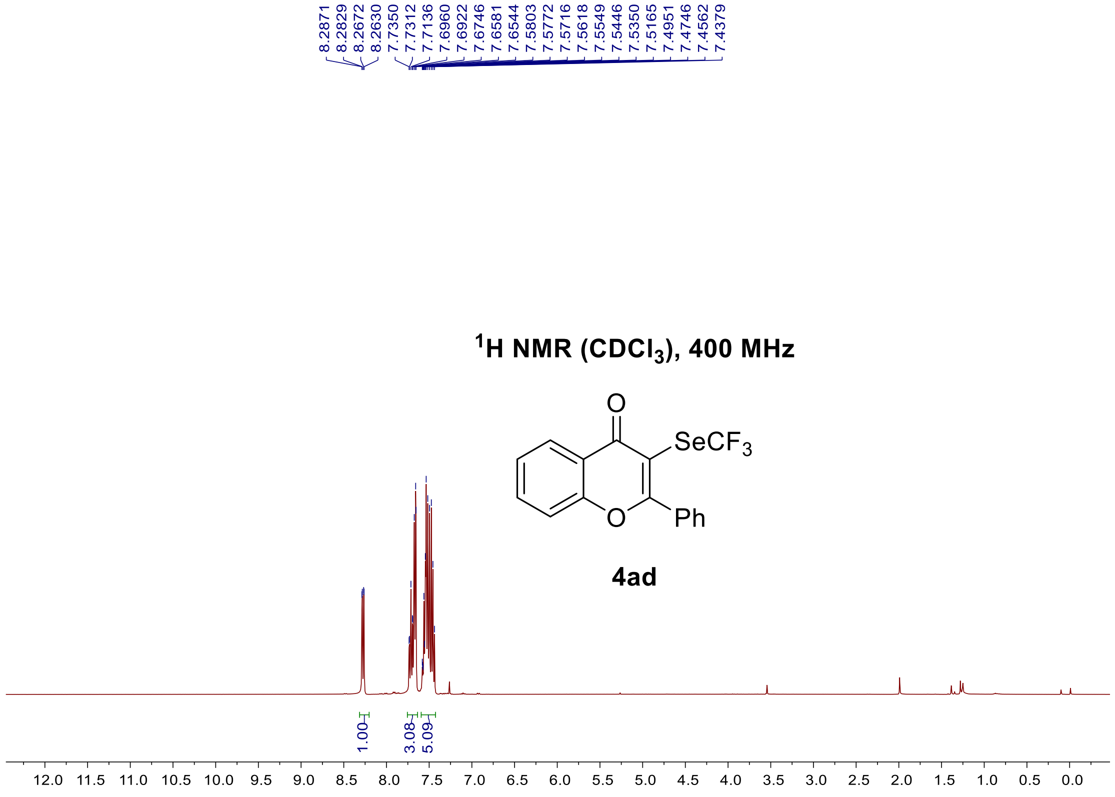
8.1632
7.7719
7.7686
7.7645
7.7575
7.7523
7.7480
7.5888
7.5851
7.5804
7.5705
7.5631
7.5571
7.5531
7.5453
7.5270
7.5225
7.5178
7.5108
7.5049
7.4810
7.4317
7.4270
7.4103
7.4056
7.3319
7.1830
^{1}H NMR (CDCl$_3$), 400 MHz
O
SCF$_2$H
Cl
O
Ph
4ac
1.00
2.00
4.02
0.25
0.99
0.51
0.26
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.


175.2377
168.8034
168.7860
168.7705
155.8787
140.6545
132.0159
131.5331
129.7033
128.3980
127.7109
126.9469
121.6088
120.8585
118.8522
118.2152
116.0955
111.1836
111.1462
111.1088
^{13}C NMR (CDCl$_3$), 101 MHz
O
SCF$_2$H
Cl
O
Ph
4ac
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0



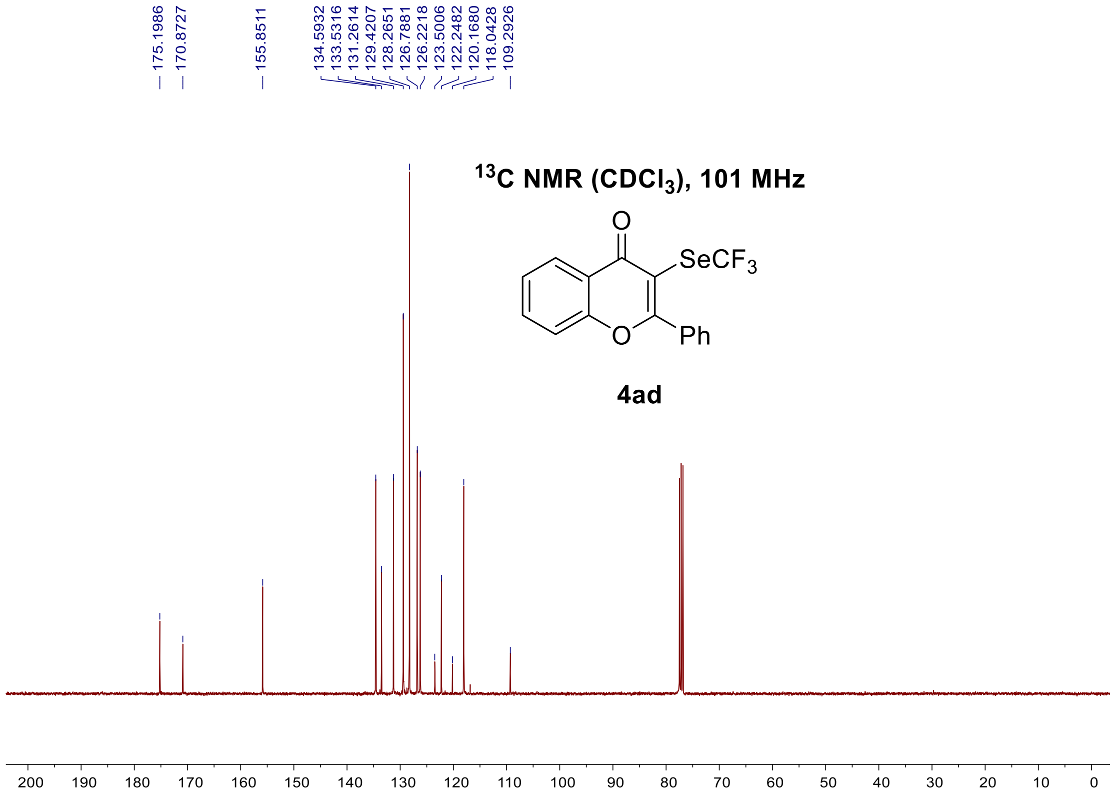
^{19}F NMR (CDCl$_3$), 471 MHz

4ac



^{1}H NMR (CDCl$_3$), 400 MHz

4ad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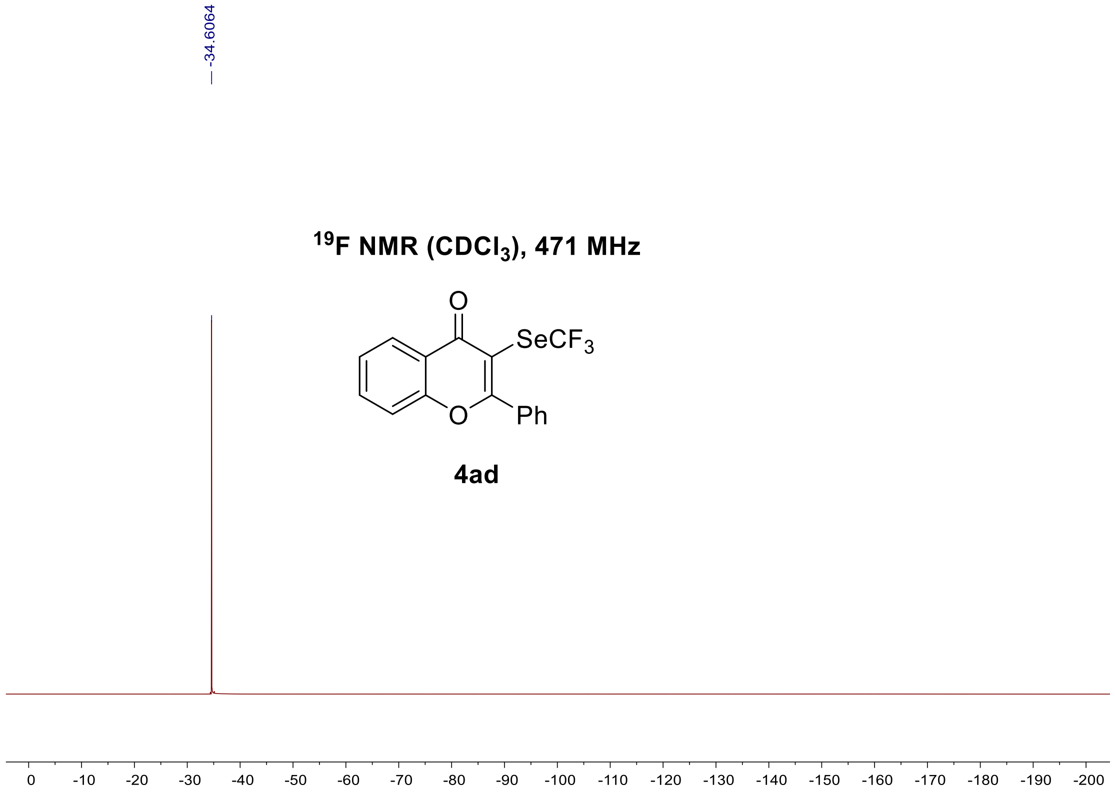
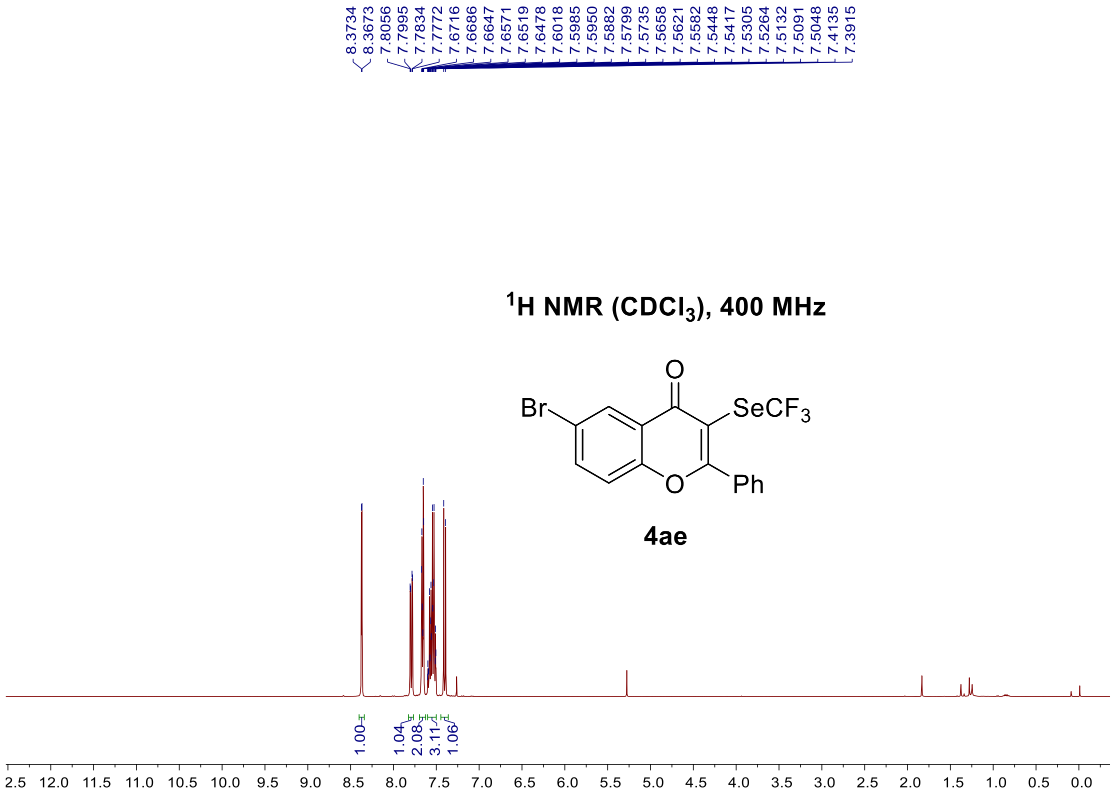
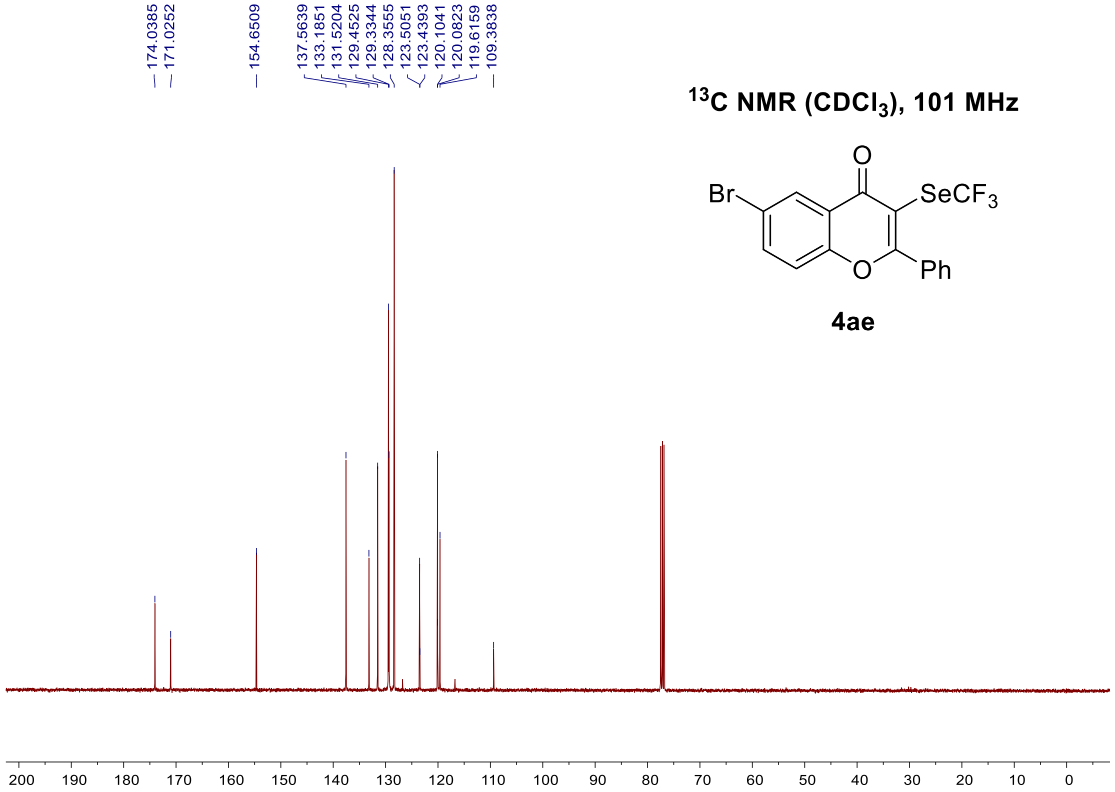
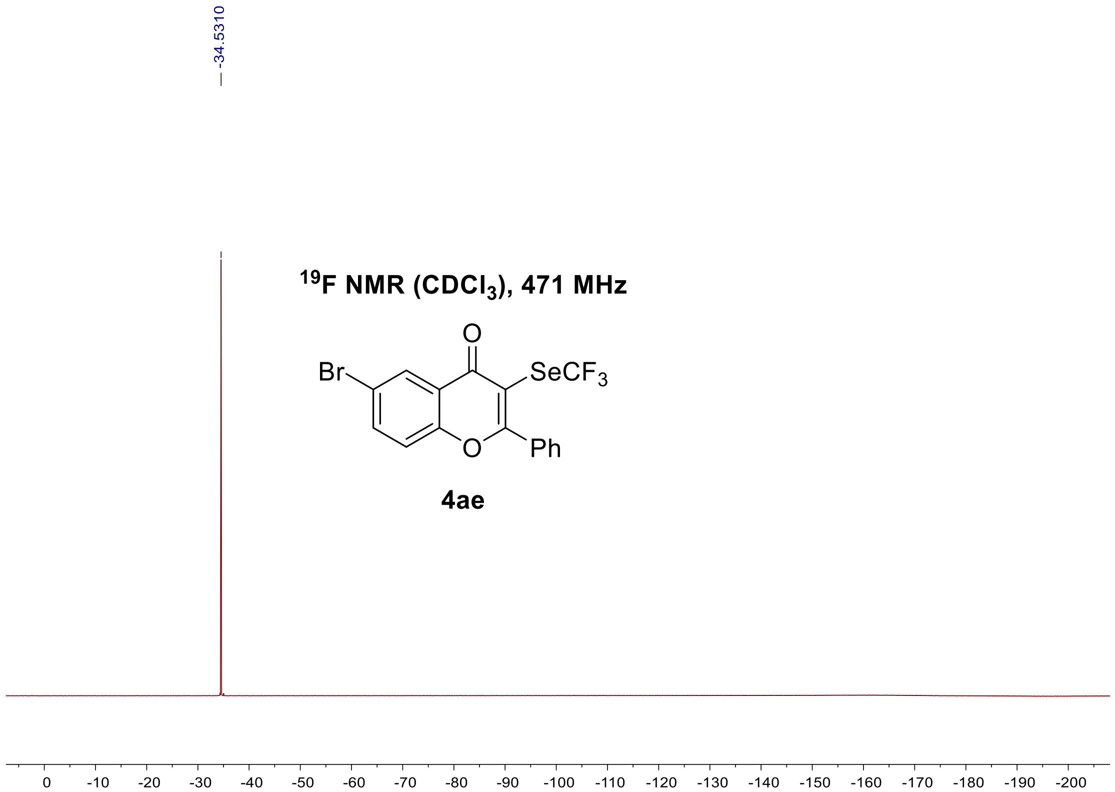
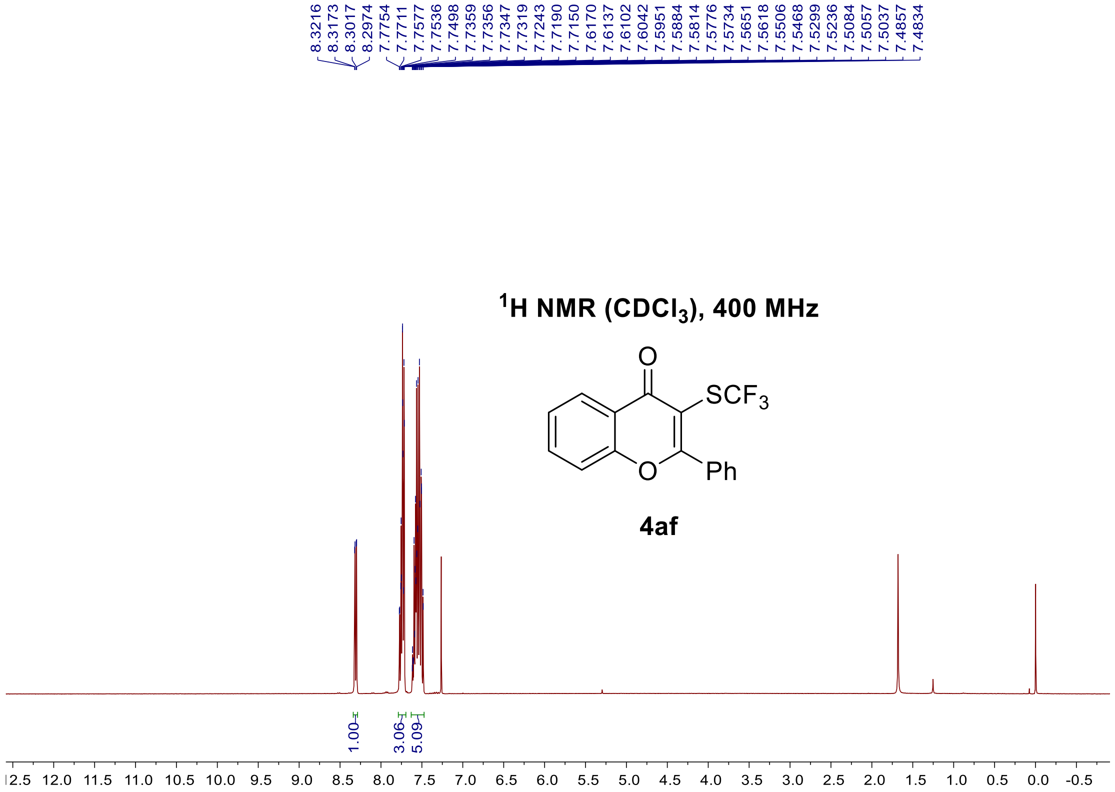
170.8727
155.8511
134.5932
133.5316
131.2614
129.4207
128.2651
126.7881
126.2218
123.5006
122.2482
120.1680
118.0428
109.2926
^{13}C NMR (CDCl$_3$), 101 MHz
O
SeCF$_3$
O
Ph
4ad
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

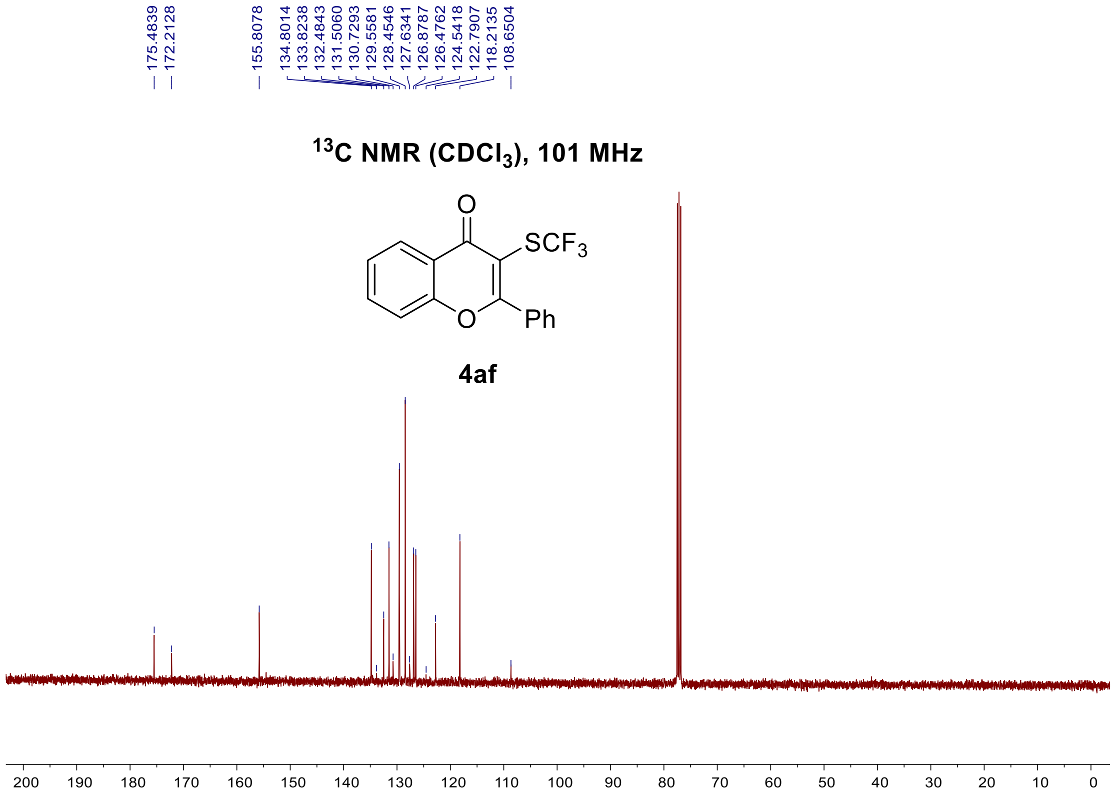

-34.6064
^{19}F NMR (CDCl$_3$), 471 MHz
O
SeCF$_3$
O
Ph
4ad
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200

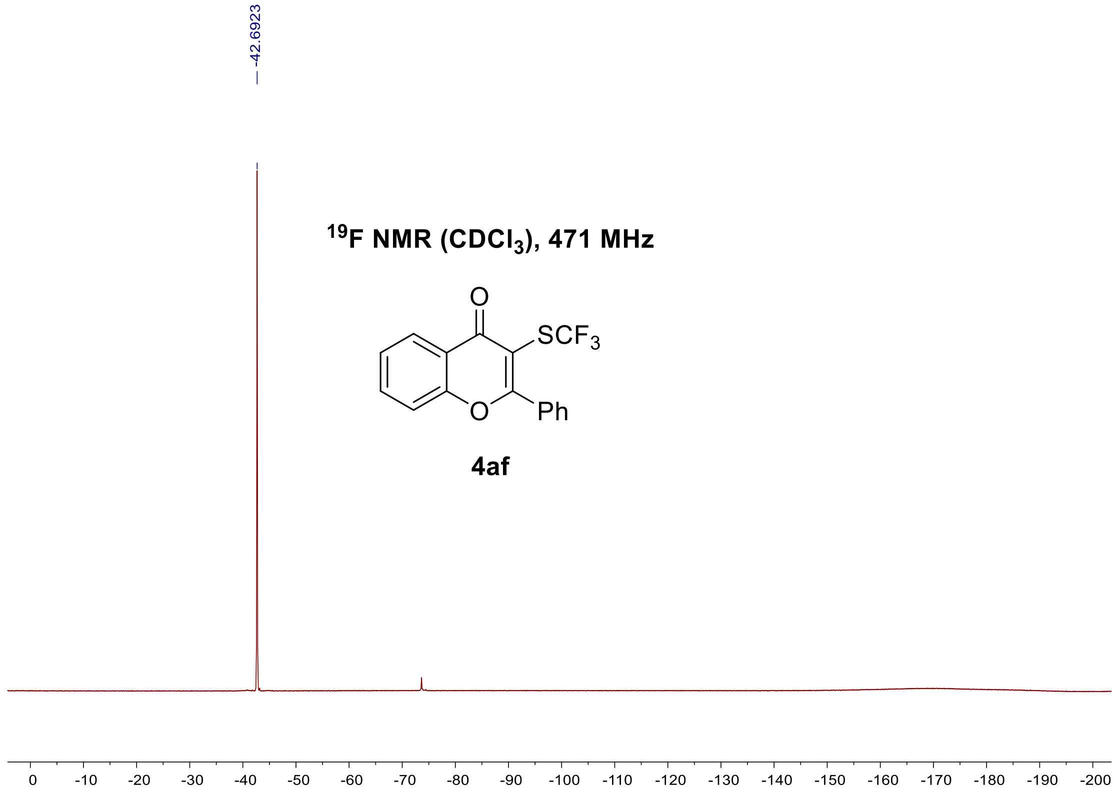

8.3734
8.3673
7.8056
7.7995
7.7834
7.7772
7.6716
7.6686
7.6647
7.6571
7.6519
7.6478
7.6018
7.5985
7.5950
7.5882
7.5799
7.5735
7.5658
7.5621
7.5582
7.5448
7.5417
7.5305
7.5264
7.5132
7.5091
7.5048
7.4135
7.3915
1H NMR (CDCl3), 400 MHz
Br
O
SeCF3
O
Ph
4ae
1.00
1.04
2.08
3.11
1.06
2.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

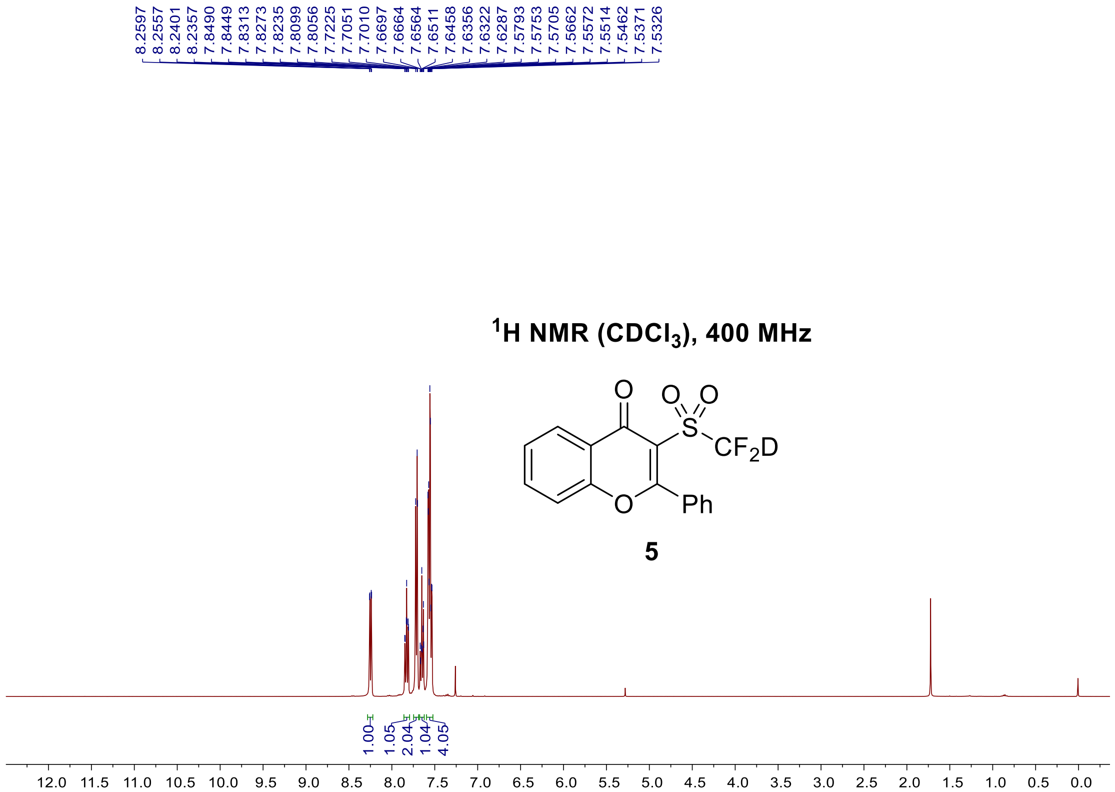

174.0385
171.0252
154.6509
137.5639
133.1851
131.5204
129.4525
129.3344
128.3555
123.5051
123.4393
120.1041
120.0823
119.6159
109.3838
13C NMR (CDCl3), 101 MHz
Br
O
SeCF3
O
Ph
4ae
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

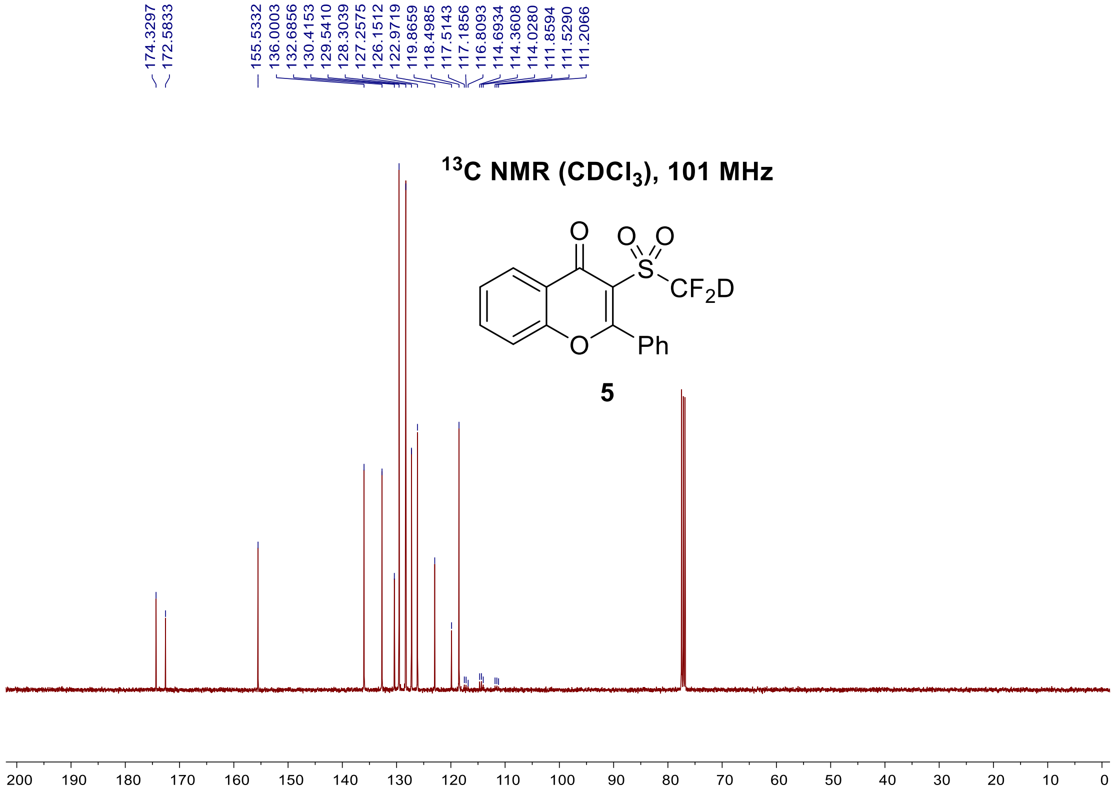

-34.5310
19F NMR (CDCl3), 471 MHz
O
Br
SeCF3
O
Ph
4ae
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200

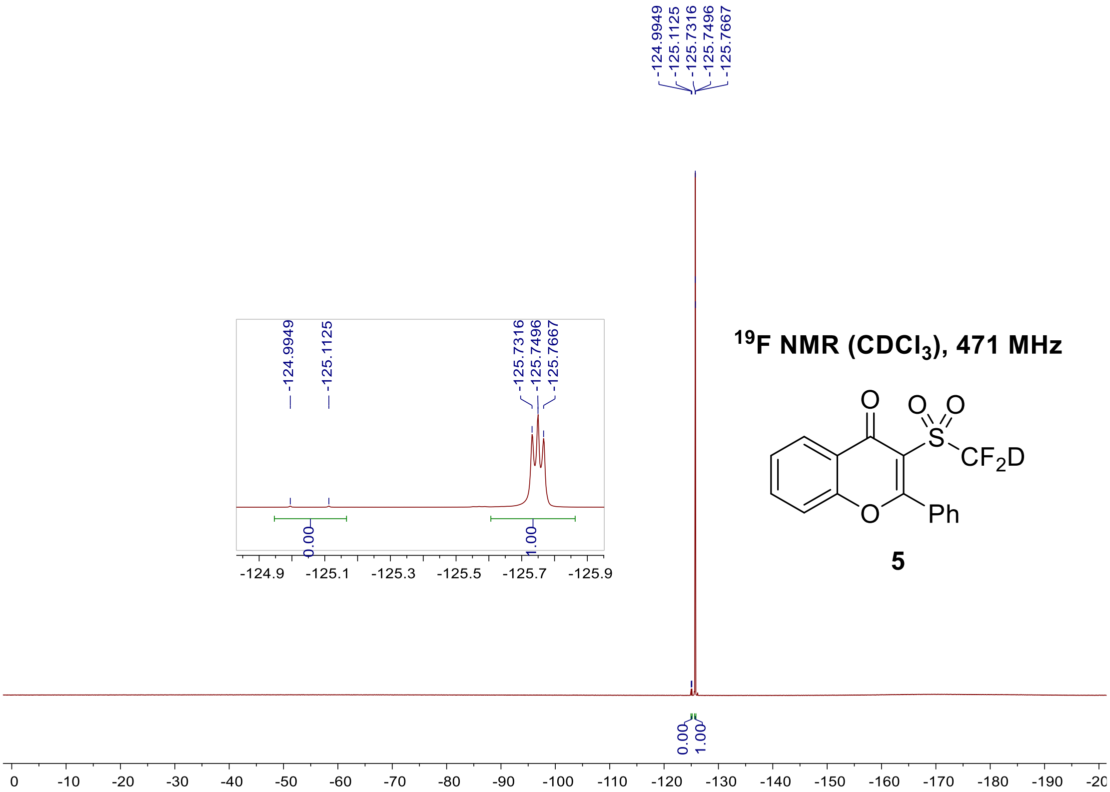

8.3216
8.3173
8.3017
8.2974
7.7754
7.7711
7.7577
7.7536
7.7498
7.7359
7.7356
7.7347
7.7319
7.7243
7.7190
7.7150
7.6170
7.6137
7.6102
7.6042
7.5951
7.5884
7.5814
7.5776
7.5734
7.5651
7.5618
7.5506
7.5468
7.5299
7.5236
7.5084
7.5057
7.5037
7.4857
7.4834
1H NMR (CDCl3), 400 MHz
O
SCF3
O
Ph
4af
1.00
3.06
5.09
12.5
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5


175.4839
172.2128
155.8078
134.8014
133.8238
132.4843
131.5060
130.7293
129.5581
128.4546
127.6341
126.8787
126.4762
124.5418
122.7907
118.2135
108.6504
^{13}C NMR (CDCl$_3$), 101 MHz
O
SCF$_3$
O
Ph
4af
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


-42.6923
^{19}F NMR (CDCl$_3$), 471 MHz
O
SCF$_3$
O
Ph
4af
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200

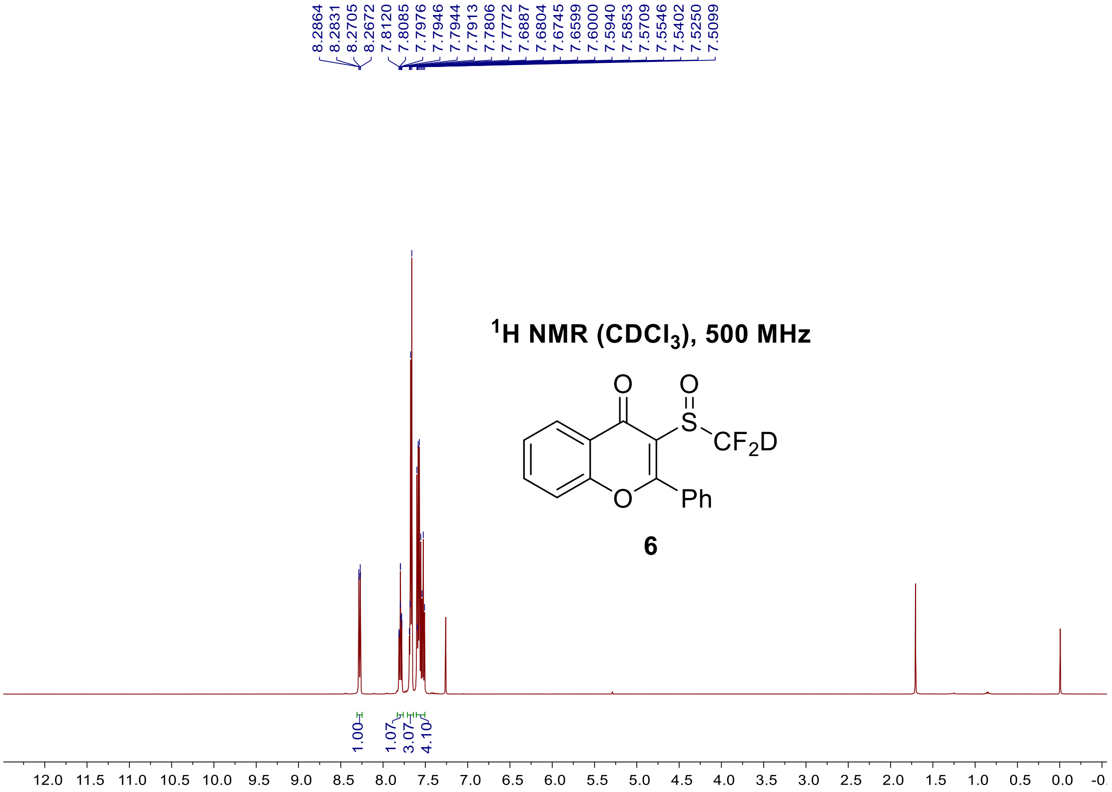

8.2597
8.2557
8.2401
8.2357
7.8490
7.8449
7.8313
7.8273
7.8235
7.8099
7.8056
7.7225
7.7051
7.7010
7.6697
7.6664
7.6564
7.6511
7.6458
7.6356
7.6322
7.6287
7.5793
7.5753
7.5705
7.5662
7.5572
7.5514
7.5462
7.5371
7.5326
¹H NMR (CDCl₃), 400 MHz
O
O
O
S
CF₂D
O
Ph
5
1.00
1.05
2.04
1.04
4.05
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


174.3297
172.5833
155.5332
136.0003
132.6856
130.4153
129.5410
128.3039
127.2575
126.1512
122.9719
119.8659
118.4985
117.5143
117.1856
116.8093
114.6934
114.3608
114.0280
111.8594
111.5290
111.2066
¹³C NMR (CDCl₃), 101 MHz
O
O
O
S
CF₂D
O
Ph
5
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0



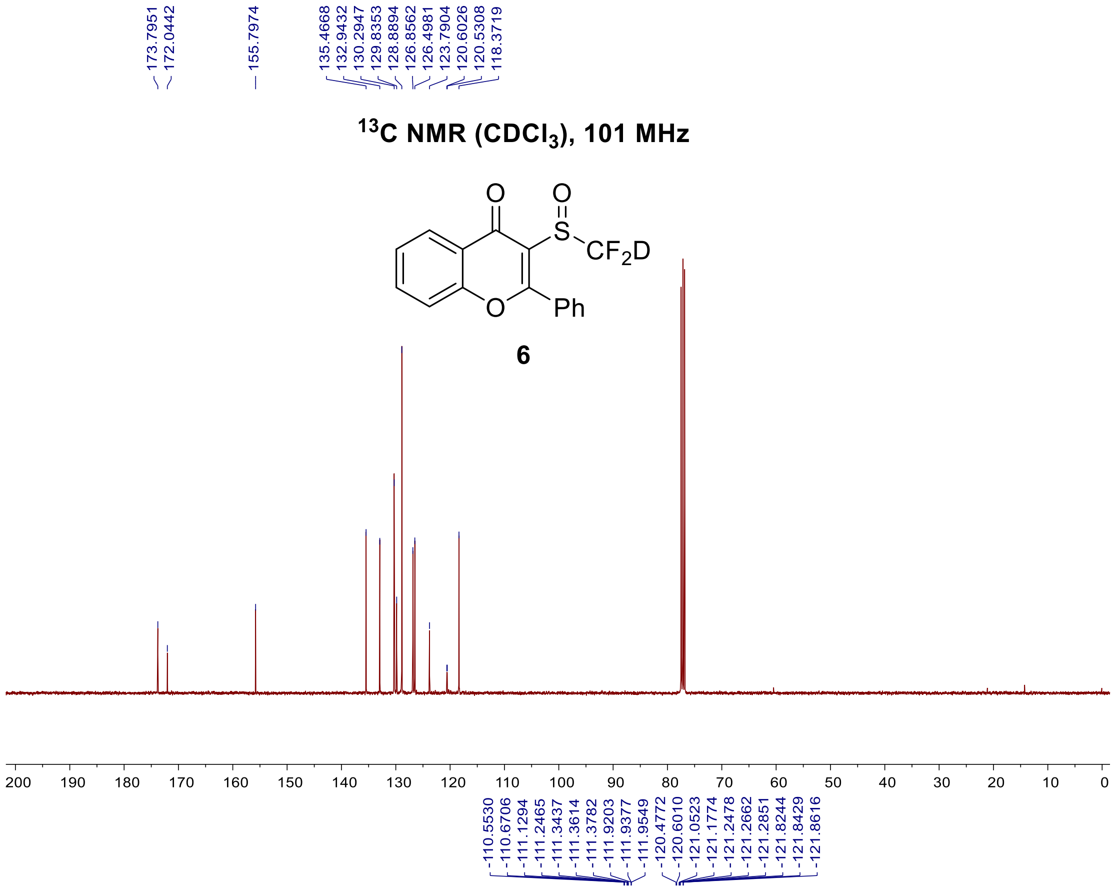
^{19}F NMR (CDCl$_3$), 471 MHz

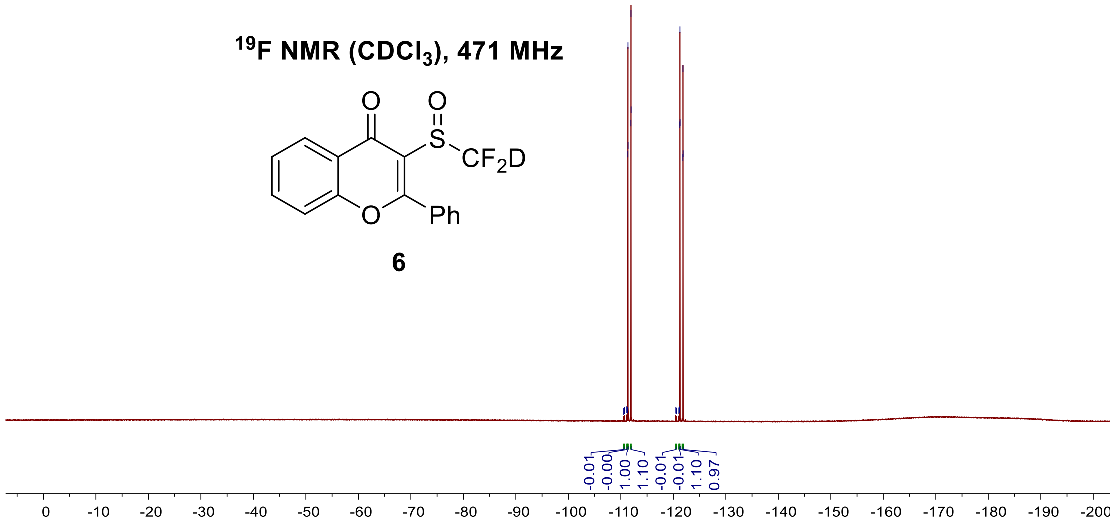
5

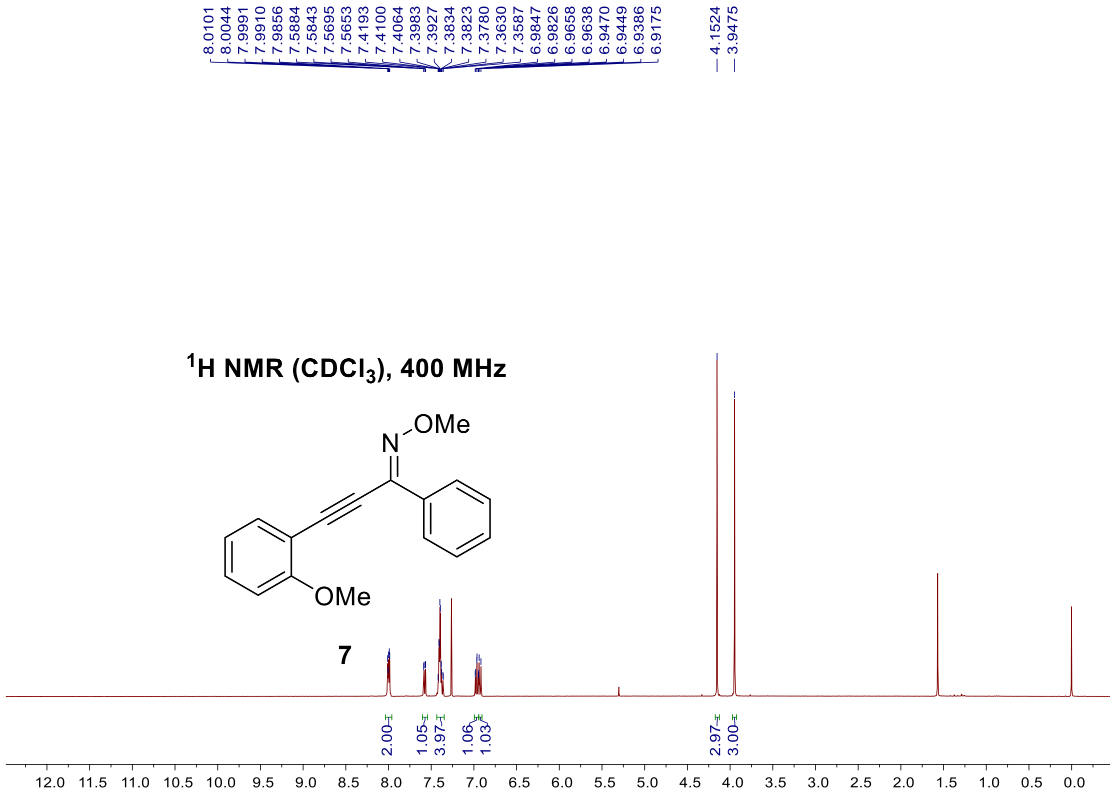


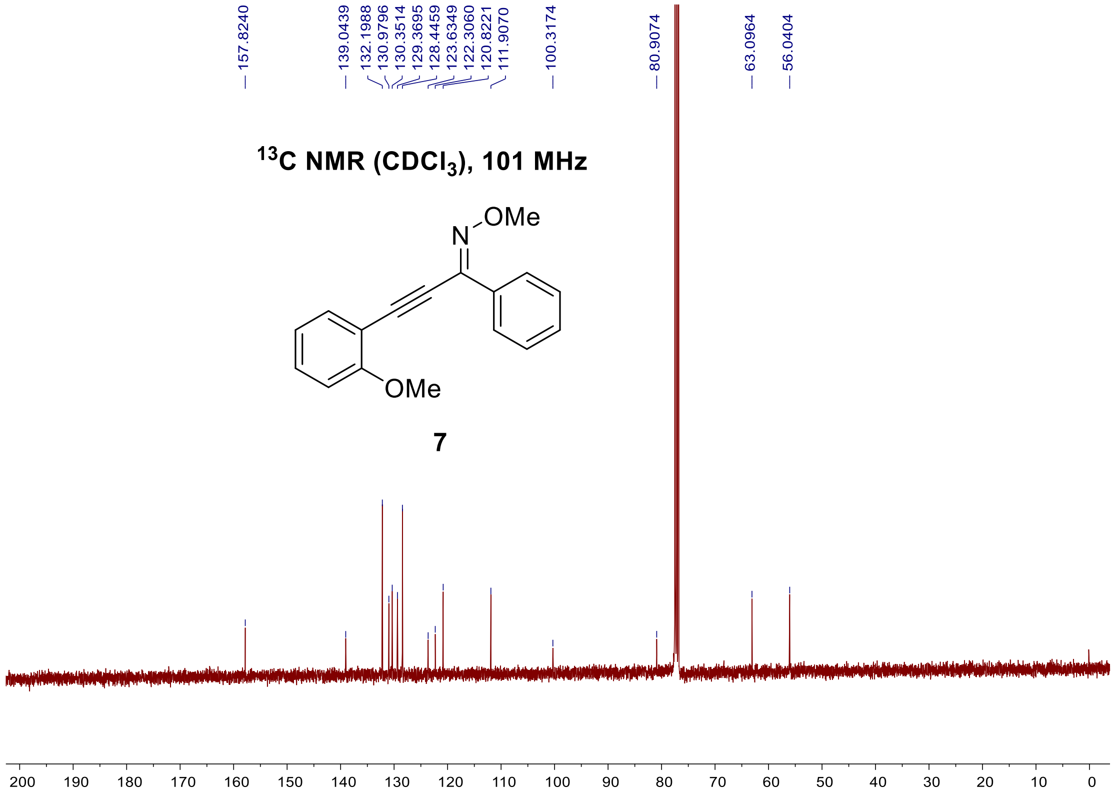
^{1}H NMR (CDCl$_3$), 500 MHz

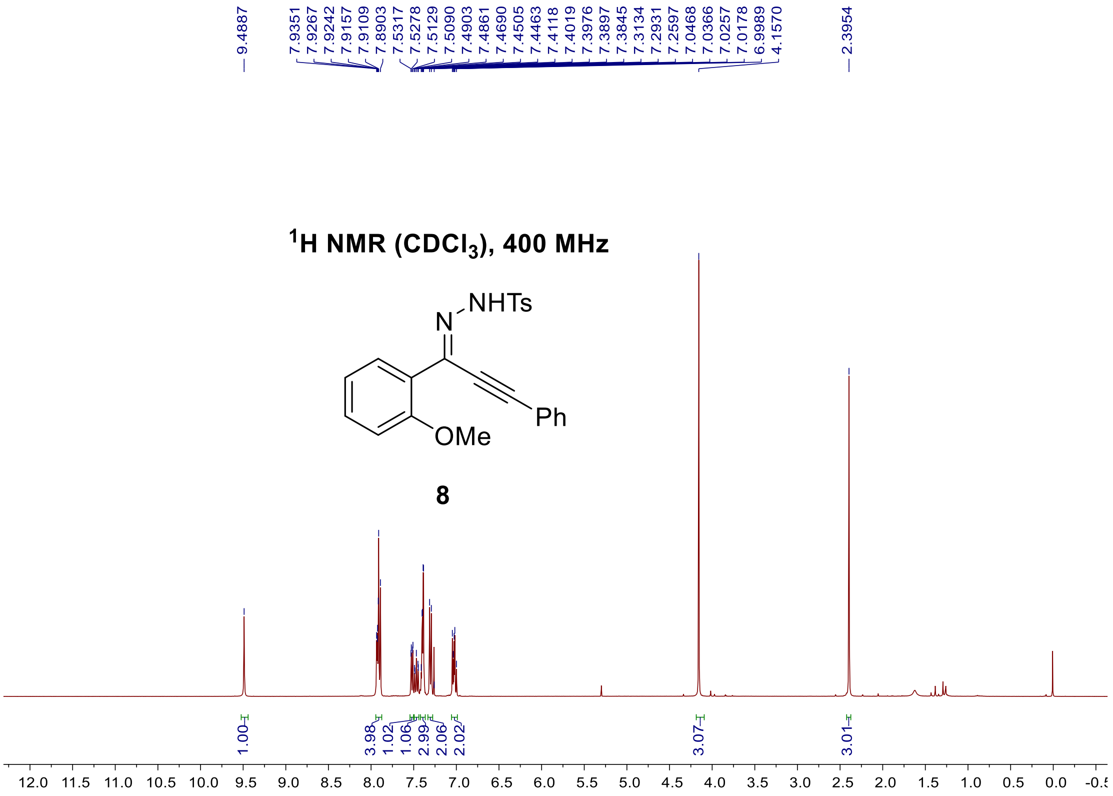
6

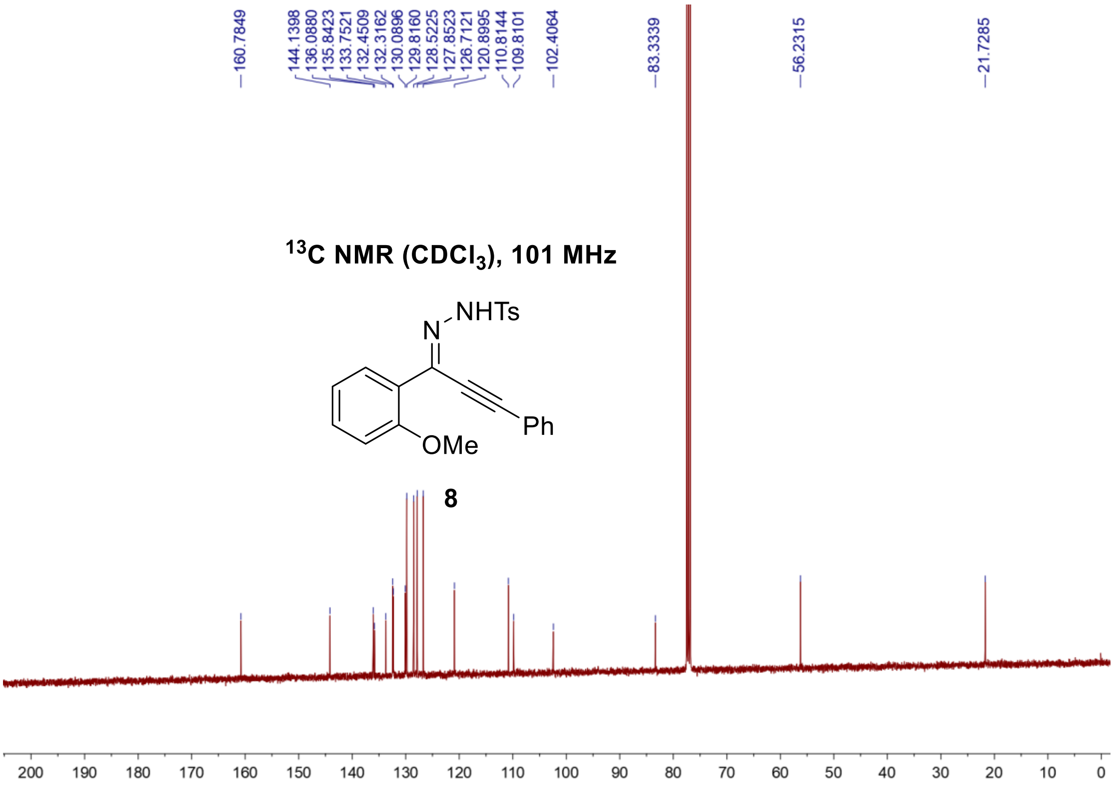

173.7951
172.0442
155.7974
135.4668
132.9432
130.2947
129.8353
128.8894
126.8562
126.4981
123.7904
120.6026
120.5308
118.3719
^{13}C NMR (CDCl$_3$), 101 MHz
O
O
S
CF$_2$D
O
Ph
6
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
-110.5530
-110.6706
-111.1294
-111.2465
-111.3437
-111.3614
-111.3782
-111.9203
-111.9377
-111.9549
-120.4772
-120.6010
-121.0523
-121.1774
-121.2478
-121.2662
-121.2851
-121.8244
-121.8429
-121.8616

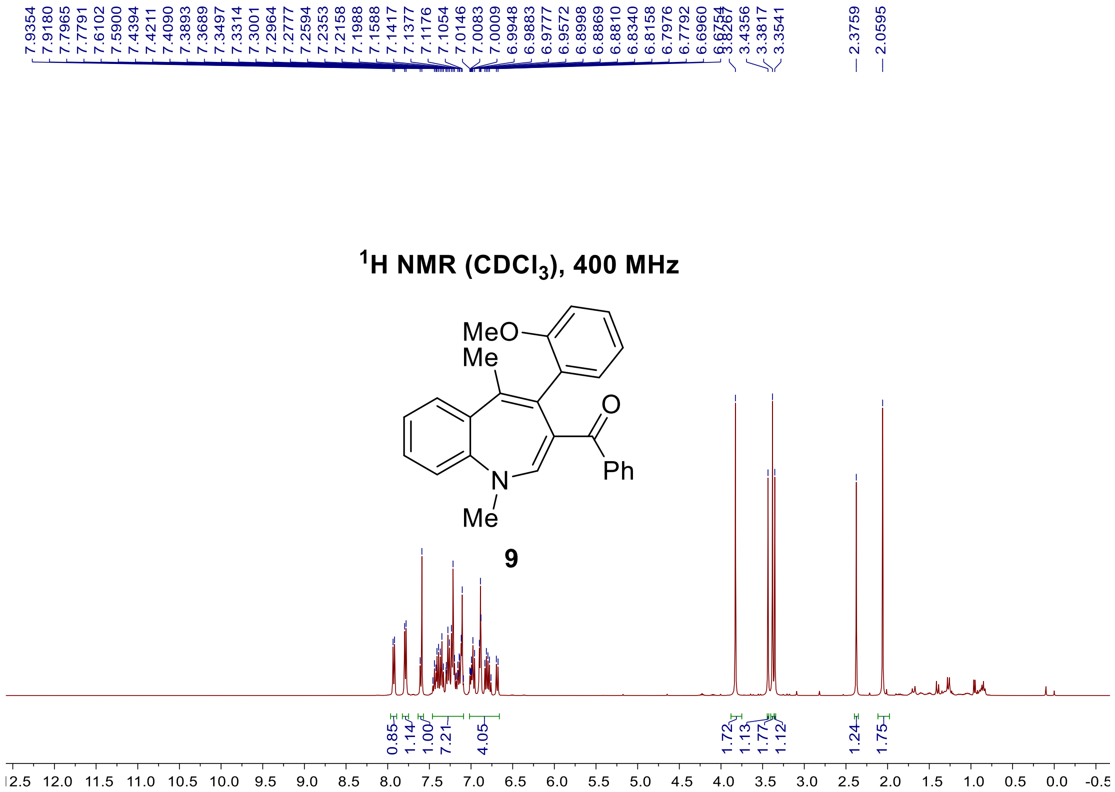

^{19}F NMR (CDCl$_3$), 471 MHz
O
O
S
CF$_2$D
O
Ph
6
-0.01
-0.00
1.00
1.10
-0.01
-0.01
1.10
0.97
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200


8.0101
8.0044
7.9991
7.9910
7.9856
7.5884
7.5843
7.5695
7.5653
7.4193
7.4100
7.4064
7.3983
7.3927
7.3834
7.3823
7.3780
7.3630
7.3587
6.9847
6.9826
6.9658
6.9638
6.9470
6.9449
6.9386
6.9175
4.1524
3.9475
^{1}H NMR (CDCl$_3$), 400 MHz
N
OMe
OMe
7
2.00
1.05
3.97
1.06
1.03
2.97
3.00
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


157.8240
139.0439
132.1988
130.9796
130.3514
129.3695
128.4459
123.6349
122.3060
120.8221
111.9070
100.3174
80.9074
63.0964
56.0404
^{13}C NMR (CDCl$_3$), 101 MHz
N
OMe
OMe
7
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

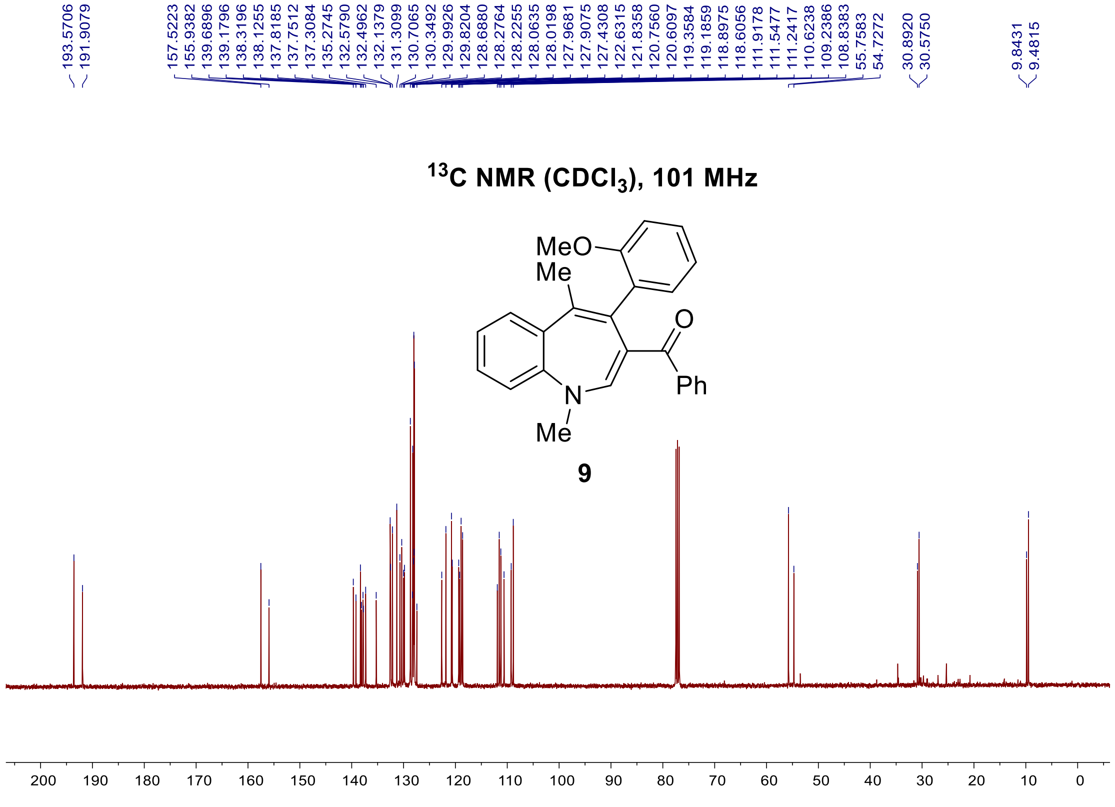

9.4887
7.9351
7.9267
7.9242
7.9157
7.9109
7.8903
7.5317
7.5278
7.5129
7.5090
7.4903
7.4861
7.4690
7.4505
7.4463
7.4118
7.4019
7.3976
7.3897
7.3845
7.3134
7.2931
7.2597
7.0468
7.0366
7.0257
7.0178
6.9989
4.1570
2.3954
¹H NMR (CDCl₃), 400 MHz
NHTs
N
Ph
OMe
8
1.00
3.98
1.02
1.06
2.99
2.06
2.02
3.07
3.01
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5


160.7849
144.1398
136.0880
135.8423
133.7521
132.4509
132.3162
130.0896
129.8160
128.5225
127.8523
126.7121
120.8995
110.8144
109.8101
102.4064
83.3339
56.2315
21.7285
¹³C NMR (CDCl₃), 101 MHz
NHTs
N
Ph
OMe
8
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0



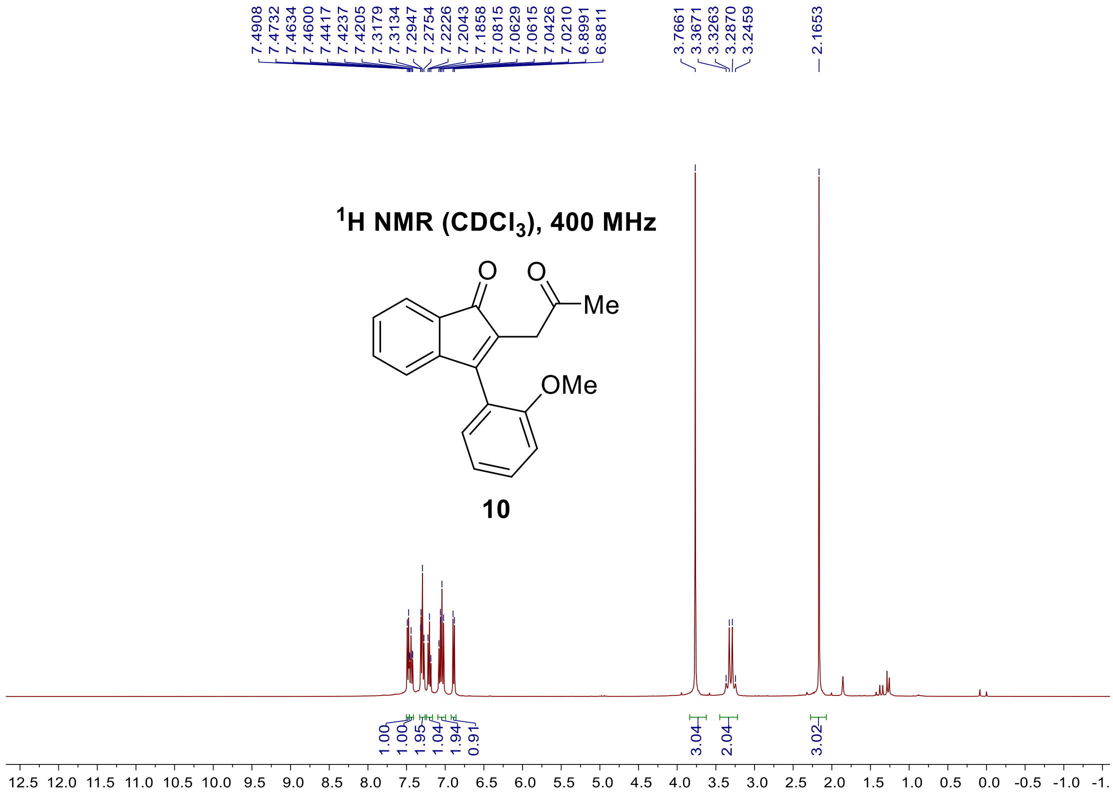
^1H NMR ($CDCl_3$), 400 MHz

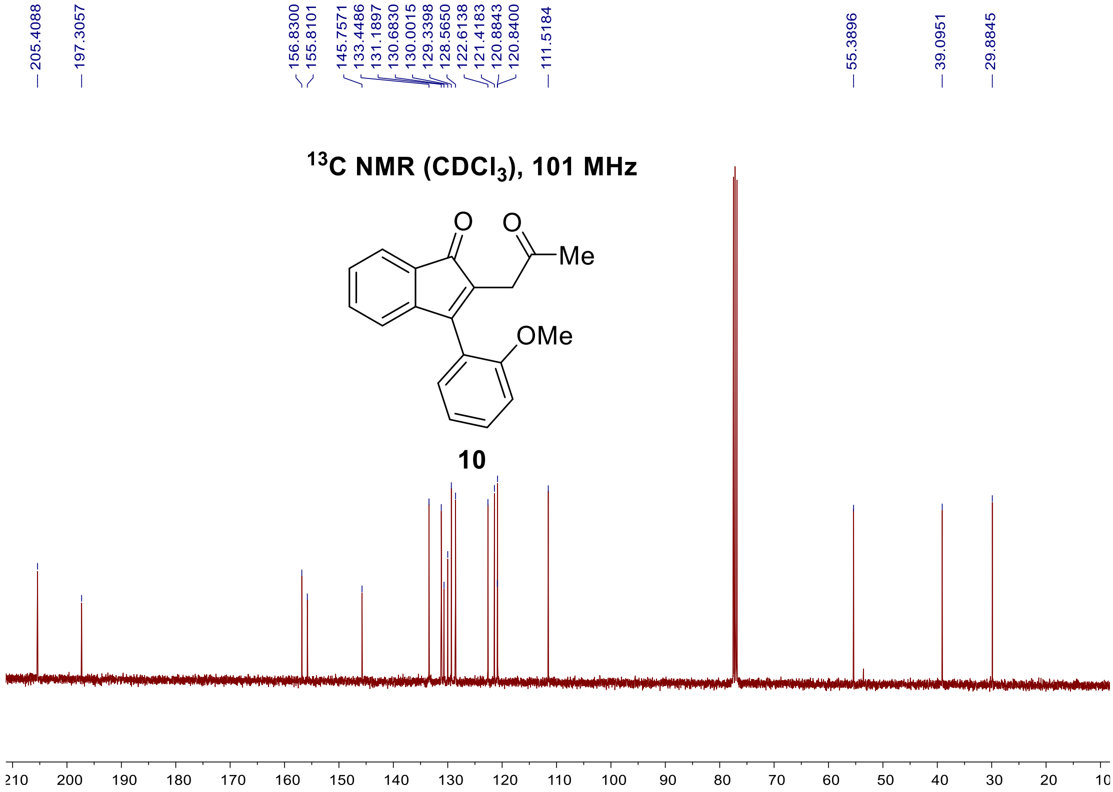
9

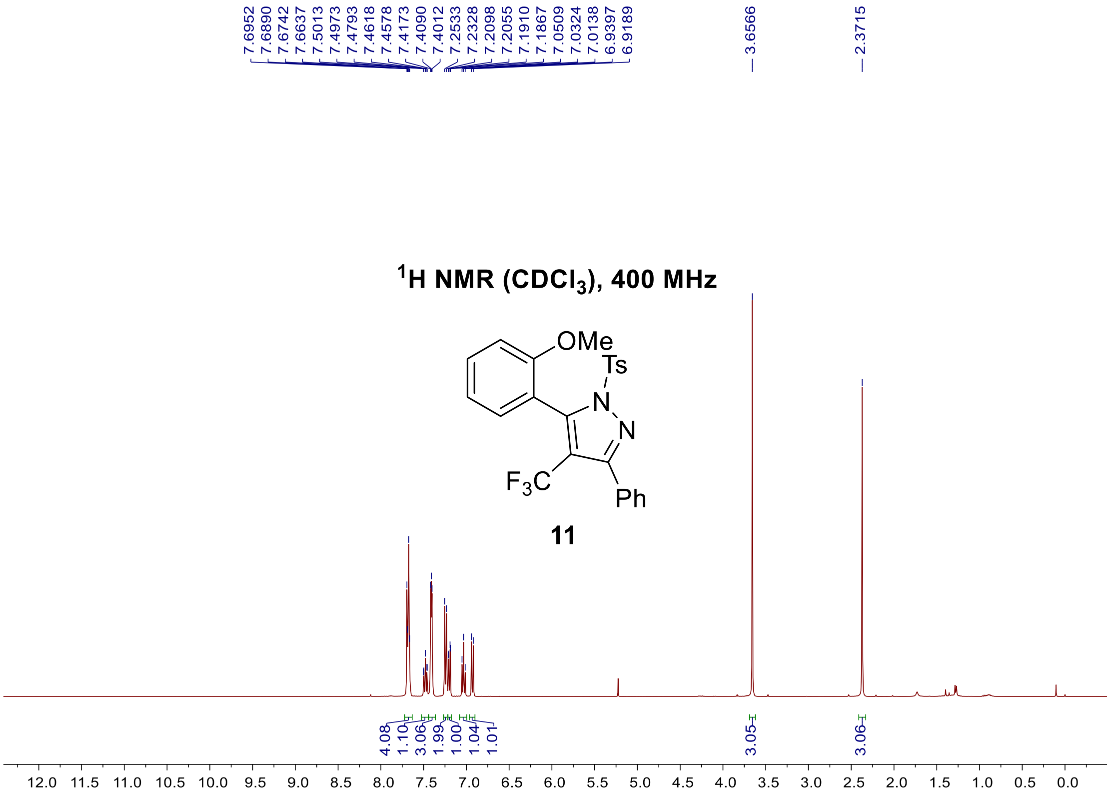


^{13}C NMR ($CDCl_3$), 101 MHz

9


7.4908
7.4732
7.4634
7.4600
7.4417
7.4237
7.4205
7.3179
7.3134
7.2947
7.2754
7.2226
7.2043
7.1858
7.0815
7.0629
7.0615
7.0426
7.0210
6.8991
6.8811
3.7661
3.3671
3.3263
3.2870
3.2459
2.1653
^{1}H NMR (CDCl$_3$), 400 MHz
O
O
Me
OMe
10
1.00
1.00
1.95
1.04
1.94
0.91
3.04
2.04
3.02
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.


205.4088
197.3057
156.8300
155.8101
145.7571
133.4486
131.1897
130.6830
130.0015
129.3398
128.5650
122.6138
121.4183
120.8843
120.8400
111.5184
55.3896
39.0951
29.8845
^{13}C NMR (CDCl$_3$), 101 MHz
O
O
Me
OMe
10
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10


7.6952
7.6890
7.6742
7.6637
7.5013
7.4973
7.4793
7.4618
7.4578
7.4173
7.4090
7.4012
7.2533
7.2328
7.2098
7.2055
7.1910
7.1867
7.0509
7.0324
7.0138
6.9397
6.9189
3.6566
2.3715
^{1}H NMR (CDCl$_3$), 400 MHz
OMe
Ts
N
N
F_3C
Ph
11
4.08
1.10
3.06
1.99
1.00
1.04
1.01
3.05
3.06
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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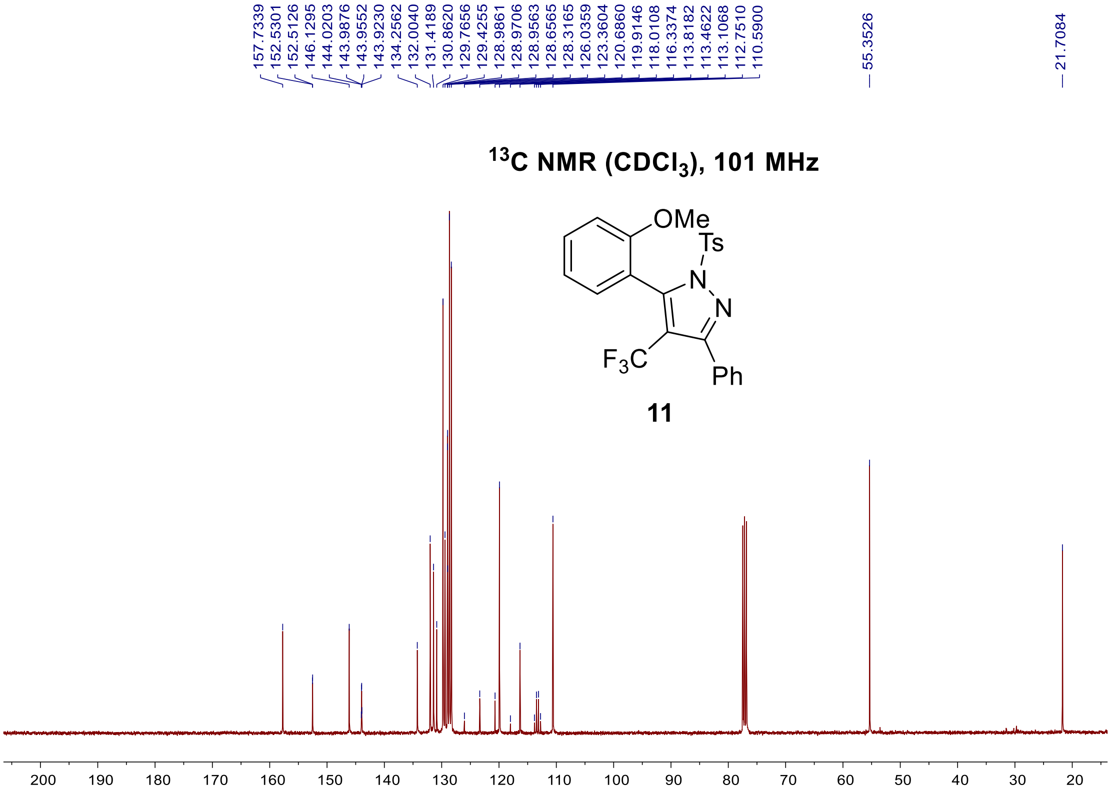
3.0
2.5
2.0
1.5
1.0
0.5
0.0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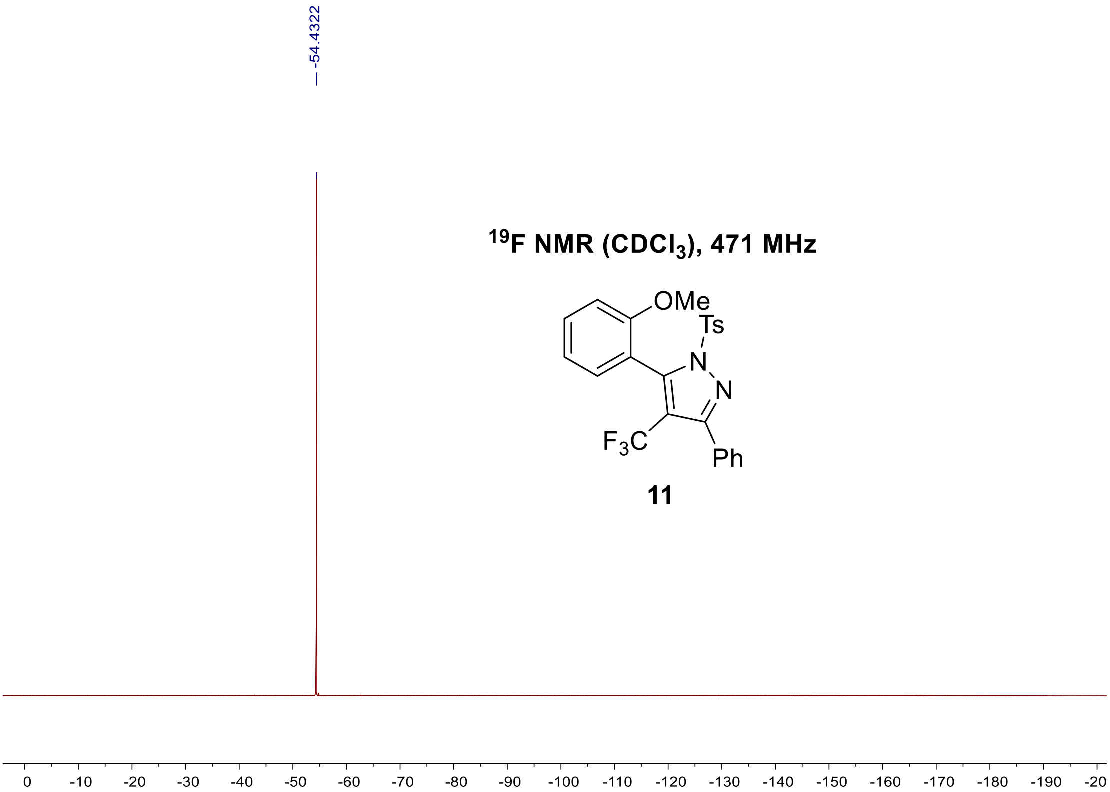
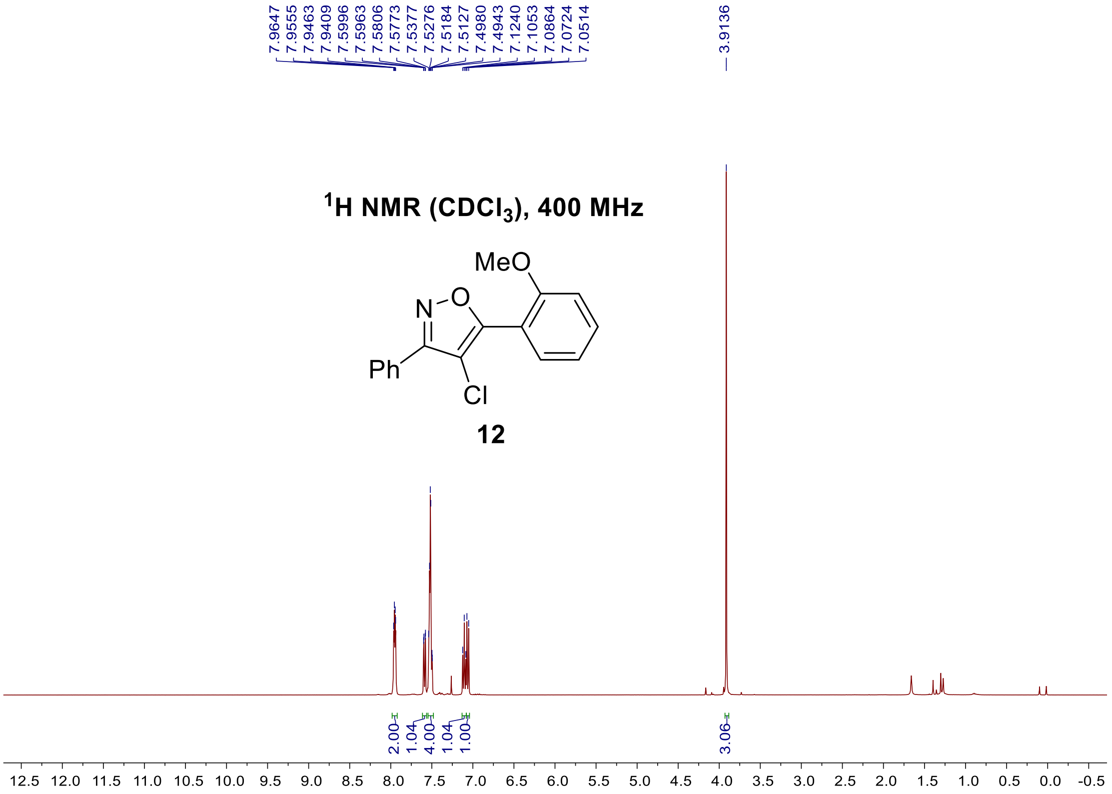
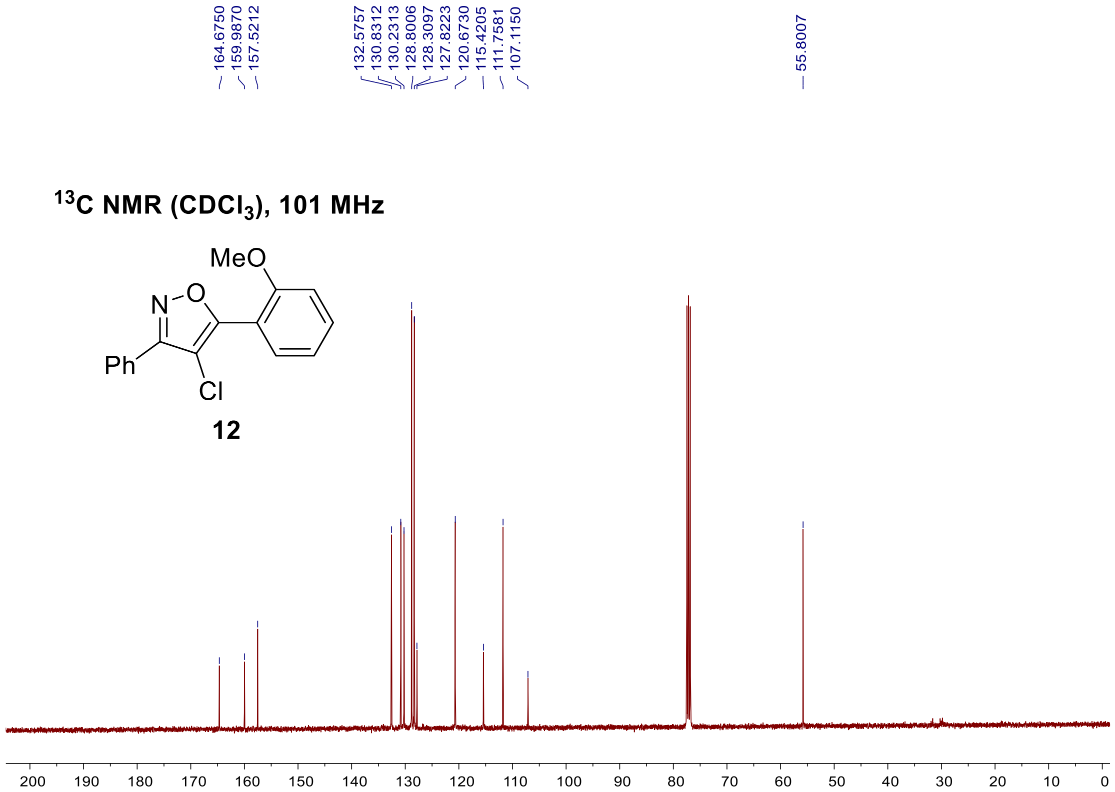
152.5301
152.5126
146.1295
144.0203
143.9876
143.9552
143.9230
134.2562
132.0040
131.4189
130.8620
129.7656
129.4255
128.9861
128.9706
128.9563
128.6565
128.3165
126.0359
123.3604
120.6860
119.9146
118.0108
116.3374
113.8182
113.4622
113.1068
112.7510
110.5900
55.3526
21.7084
^{13}C NMR (CDCl$_3$), 101 MHz
OMe
Ts
N
N
F_3C
Ph
11
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20


-54.4322
^{19}F NMR (CDCl$_3$), 471 MHz
OMe
Ts
N
N
F$_3$C
Ph
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-20

11

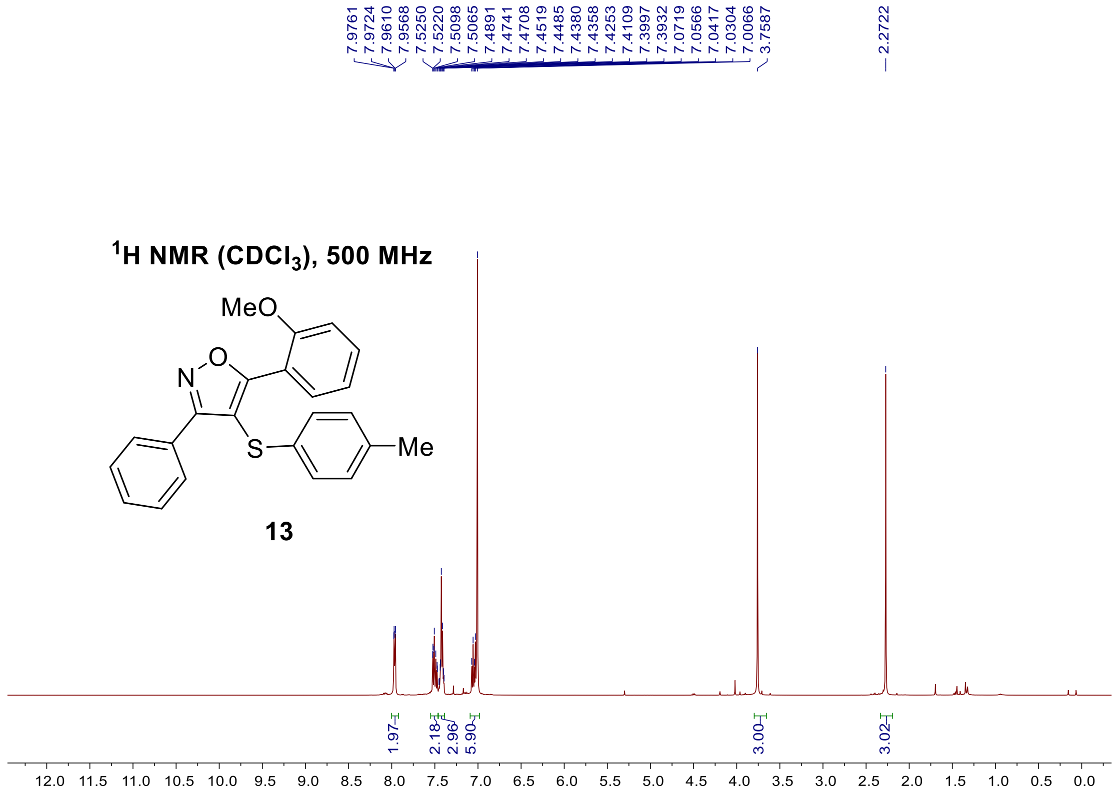

7.9647
7.9555
7.9463
7.9409
7.5996
7.5963
7.5806
7.5773
7.5377
7.5276
7.5184
7.5127
7.4980
7.4943
7.1240
7.1053
7.0864
7.0724
7.0514
3.9136
^{1}H NMR (CDCl$_3$), 400 MHz
MeO
N
O
Ph
Cl
2.00
1.04
4.00
1.04
1.00
3.06
12.5
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5

12



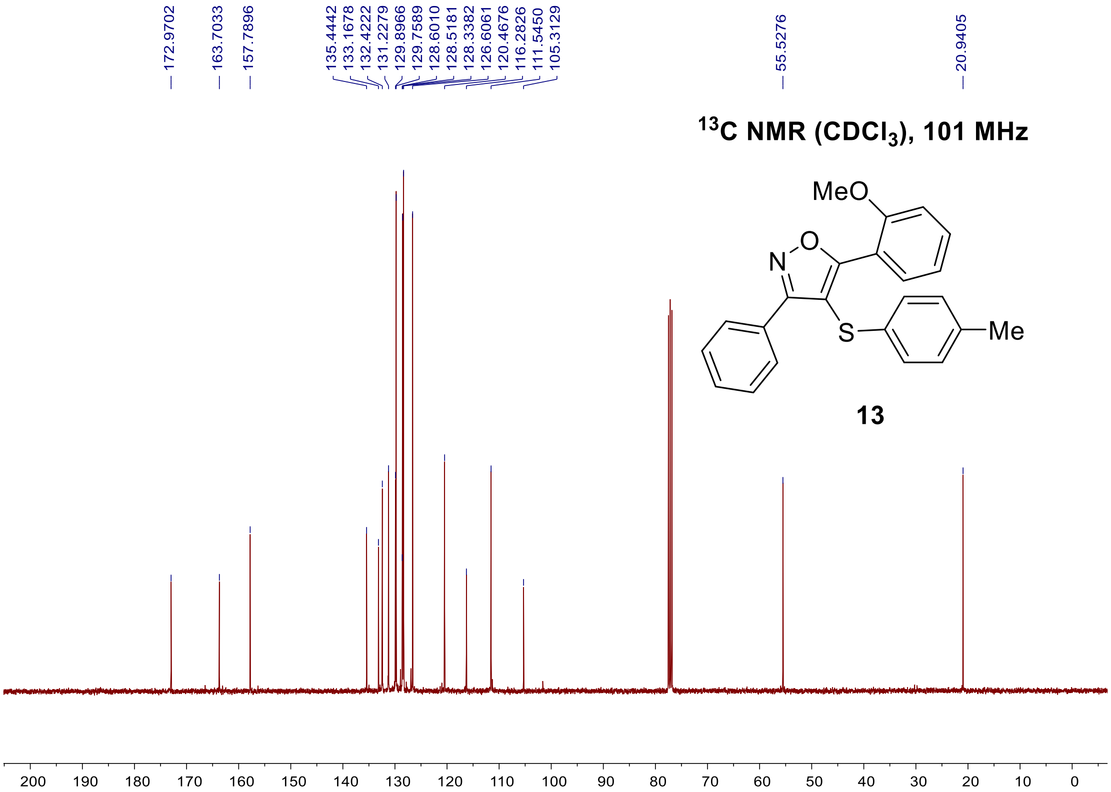
^{13}C NMR (CDCl$_3$), 101 MHz

12

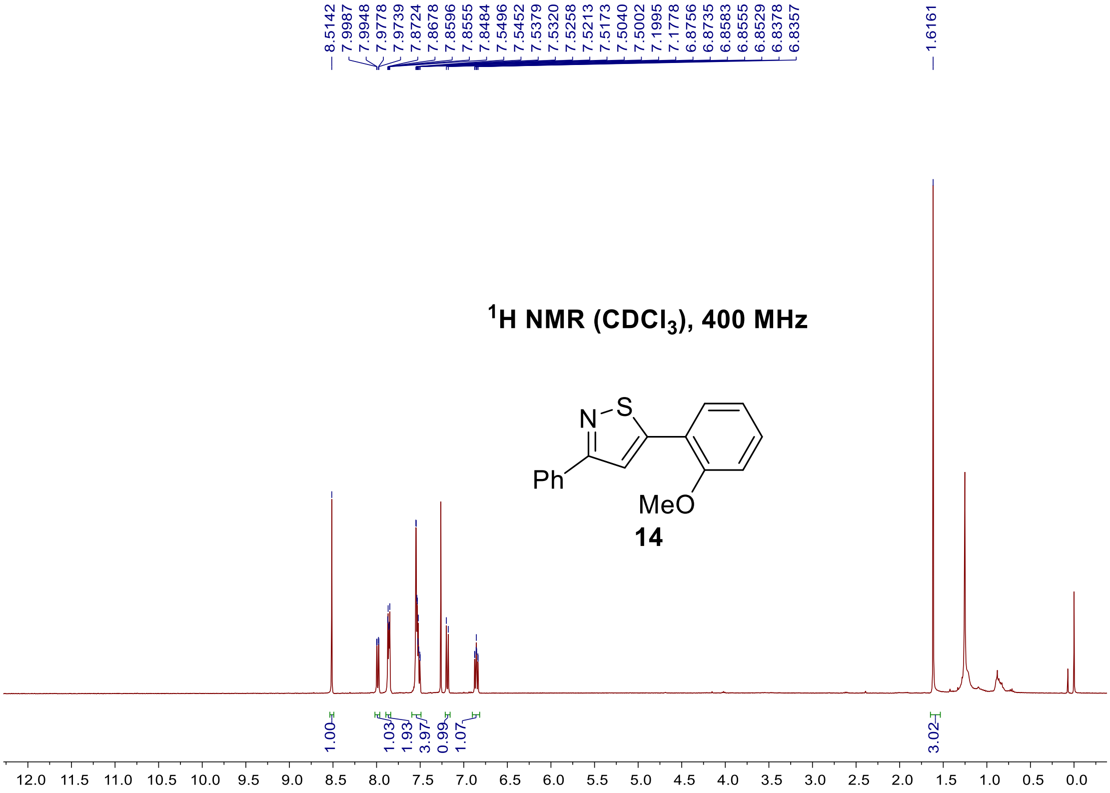


^{1}H NMR (CDCl$_3$), 500 MHz

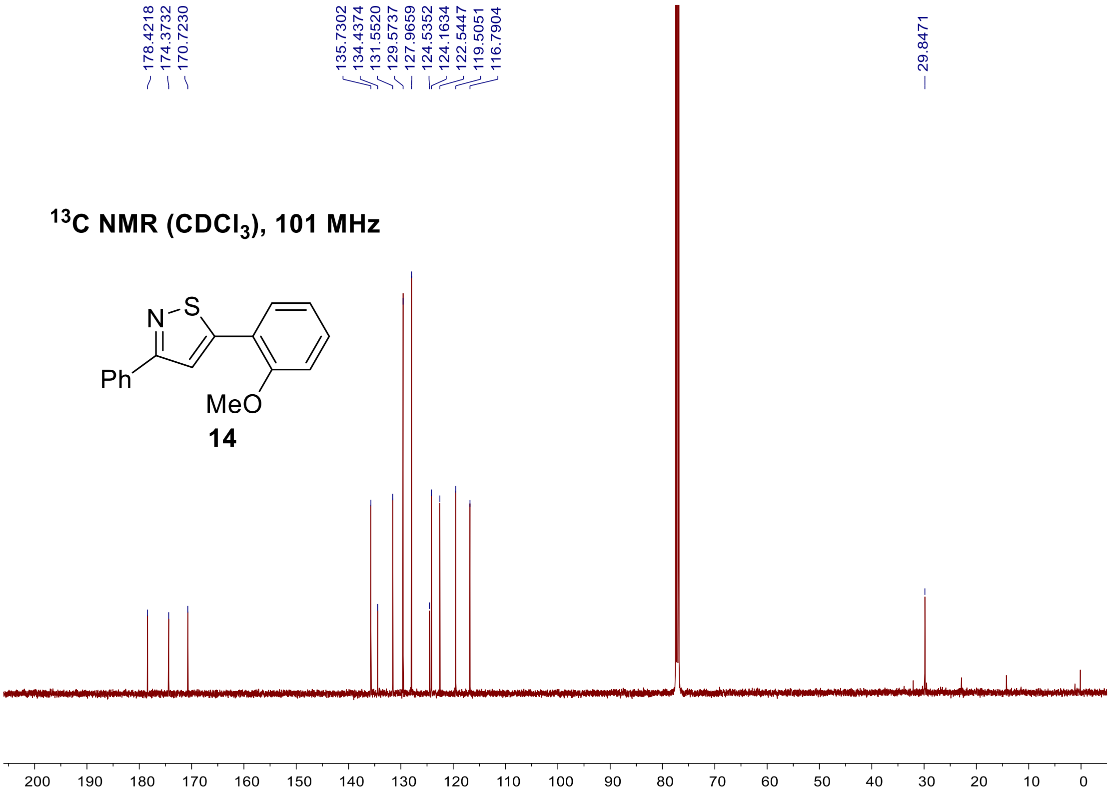
13


172.9702
163.7033
157.7896
135.4442
133.1678
132.4222
131.2279
129.8966
129.7589
128.6010
128.5181
128.3382
126.6061
120.4676
116.2826
111.5450
105.3129
55.5276
20.9405
^{13}C NMR (CDCl$_3$), 101 MHz
MeO
O
N
S
Me
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

13


8.5142
7.9987
7.9948
7.9778
7.9739
7.8724
7.8678
7.8596
7.8555
7.8484
7.5496
7.5452
7.5379
7.5320
7.5258
7.5213
7.5173
7.5040
7.5002
7.1995
7.1778
6.8756
6.8735
6.8583
6.8555
6.8529
6.8378
6.8357
1.6161
^{1}H NMR (CDCl$_3$), 400 MHz
N
S
Ph
MeO
1.00
1.03
1.93
3.97
0.99
1.07
3.02
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

14



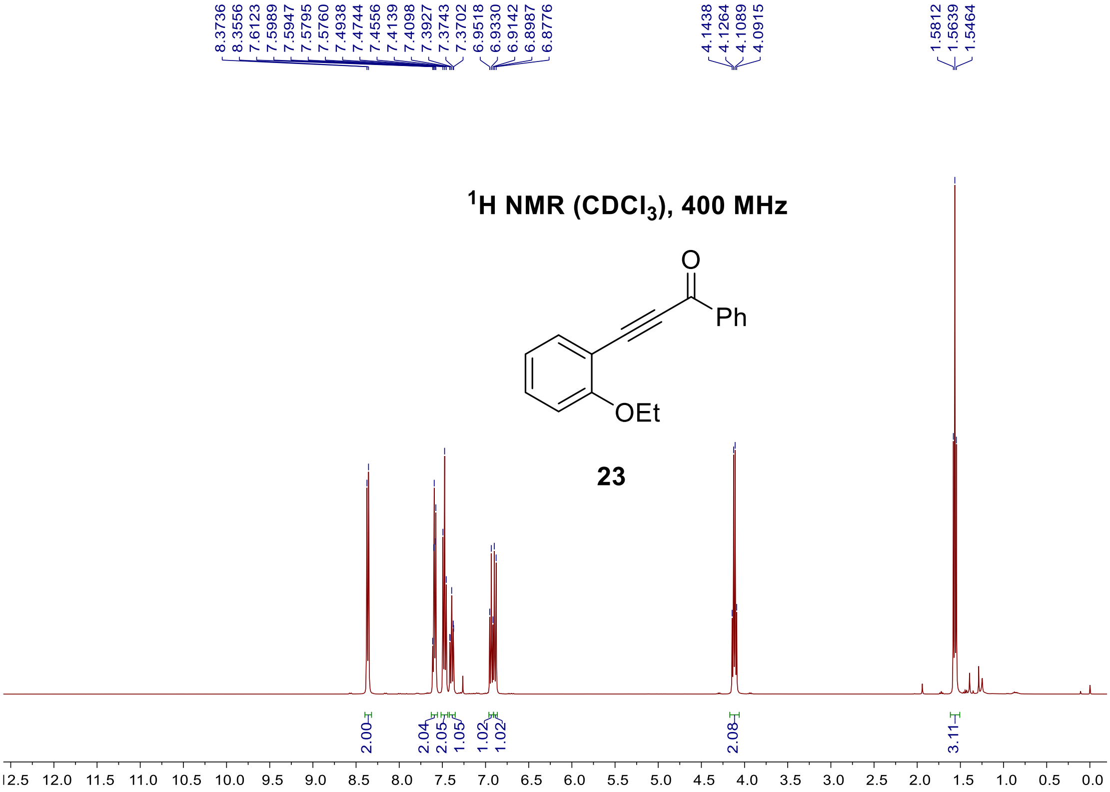


Figure S1. The ^{1}H NMR of compound **23**

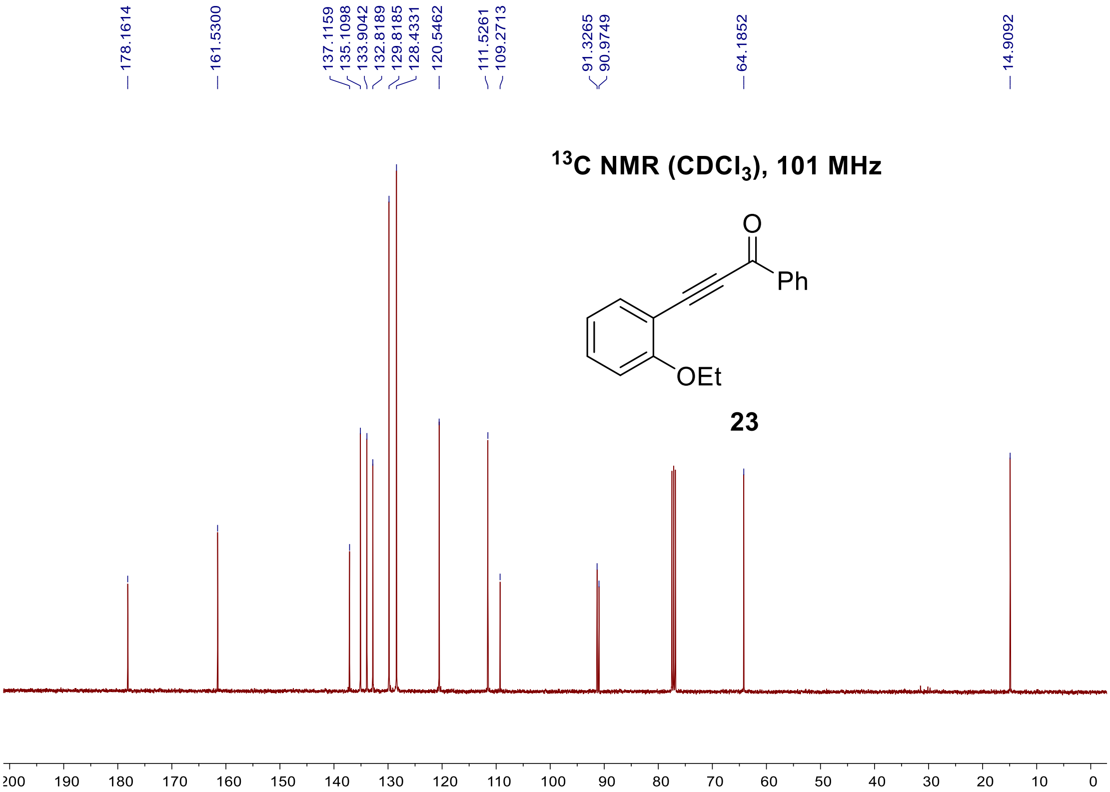


Figure S2. The ^{13}C NMR of compound **23**

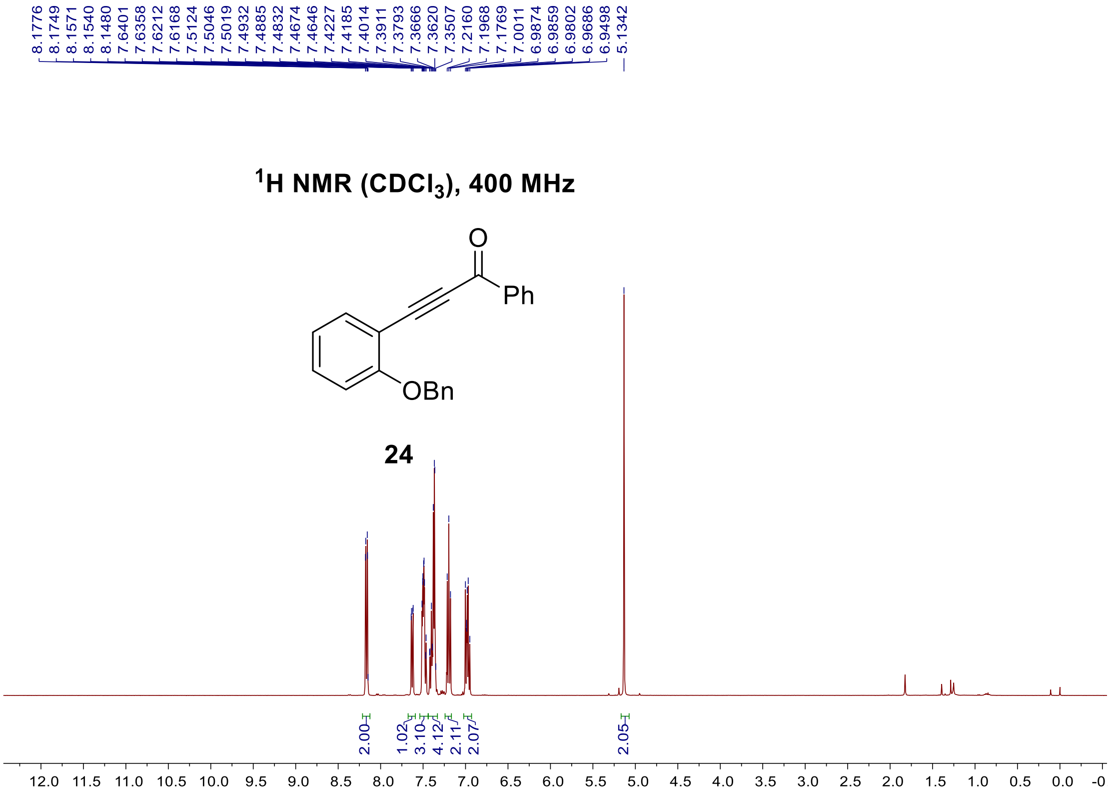


Figure S3. The ^{1}H NMR of compound **24**

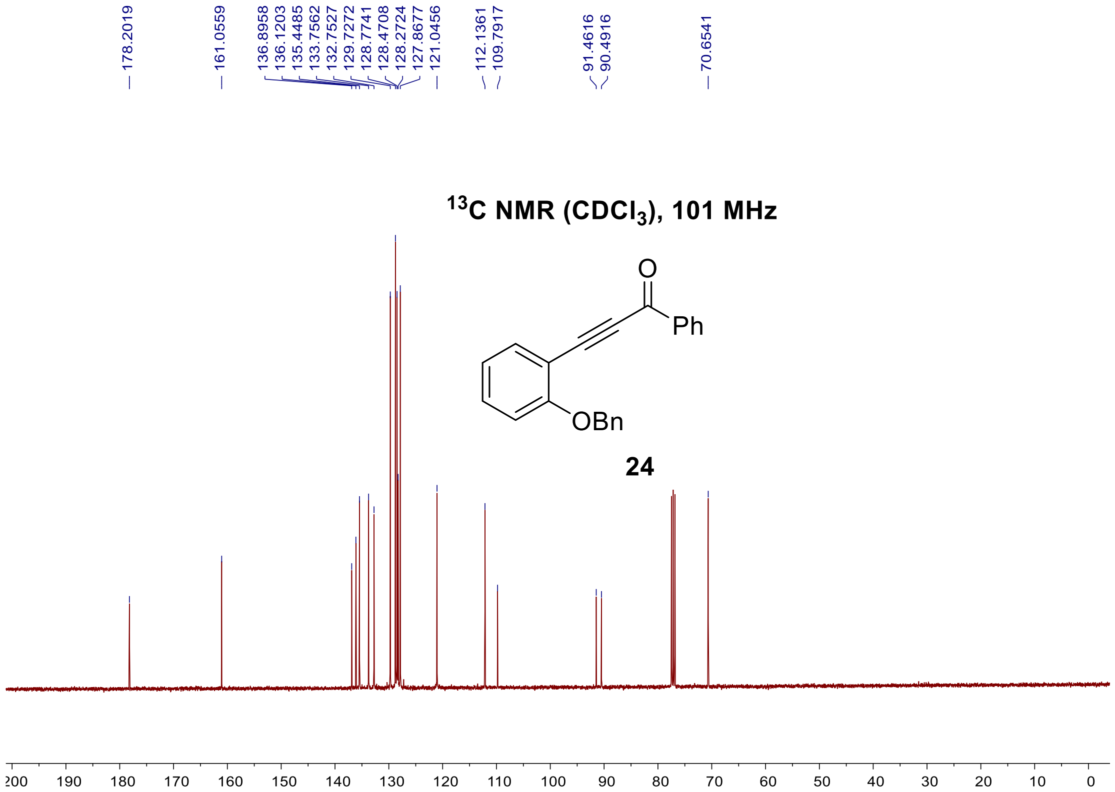


Figure S4. The ^{13}C NMR of compound **24**