

Supporting Information for

Trifluoromethylthiolative spirocyclization of biaryl ynones without leaving groups on the *para*-position of dearomative aryl rings

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1. General considerations

All reactions were carried out under air. ^1H NMR ^{13}C NMR and ^{19}F NMR spectra were measured on a Bruker Avance NMR spectrometer (400 MHz/100 MHz/377 NMR; or 600 MHz/151 MHz/565 NMR) in CDCl_3 as solvent and recorded in ppm relative to internal tetramethylsilane standard. ^1H NMR data are reported as follows: δ , chemical shift; coupling constants (J are given in Hertz, Hz) and integration. Abbreviations to denote the multiplicity of a particular signal were s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets) and m (multiplet). High resolution mass spectroscopy data of the product were collected on an Agilent Technologies 6540 UHD Accurate-Mass Q-TOF LC/MS (ESI).

2. Preparation of the starting materials

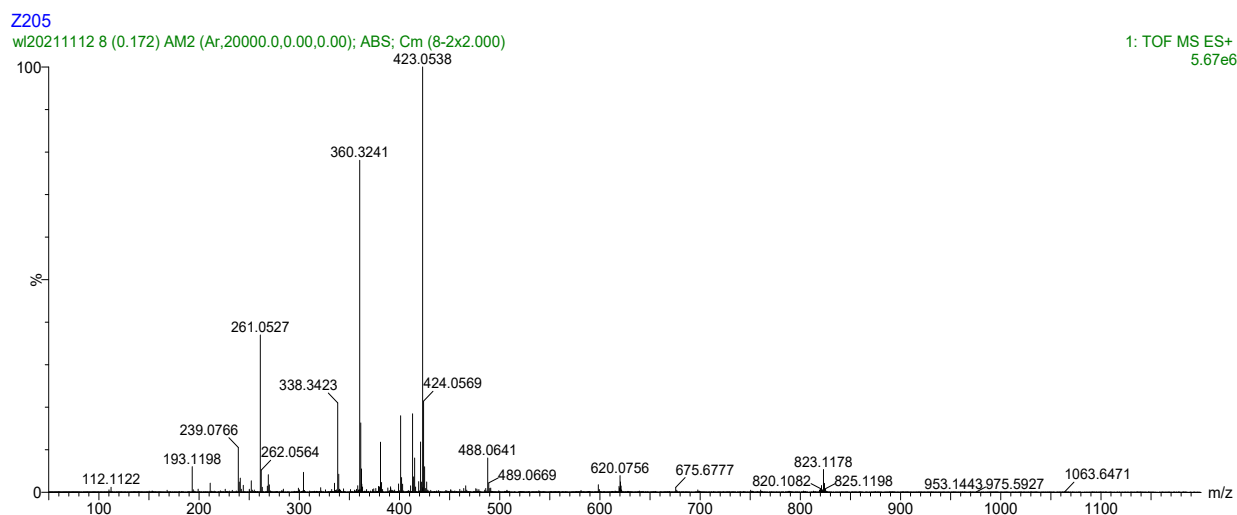
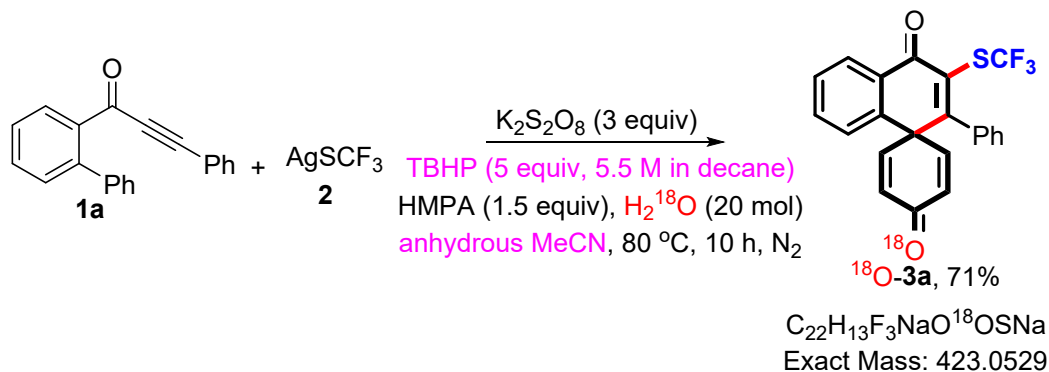
All of biaryl ynones (**1**), and AgSCF₃ (**2**) were prepared according to the reported methods (W.-C. Yang, M.-M. Zhang, Y. Sun, C.-Y. Chen, and L. Wang, *Org. Lett.*, 2021, **23**, 6691–6696).

3. General procedure for the synthesis of **3** and ¹⁸O-labeling experiment.

General procedure for the synthesis of **3:** A 15 mL pressure tube was charged with biaryl ynones (**1a**, 0.2 mmol), AgSCF₃ (**2**, 0.4 mmol), HMPA (0.4 mmol), K₂S₂O₈ (0.6 mmol), TBHP (1.0 mmol, 70% aqueous solution), MeCN (2 mL), and a magnetic stir bar. Then the mixtures were allowed to react at 80 °C for 10 h under nitrogen conditions. After completion of the reaction, the mixture was concentrated to yield the crude product, which was further purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 7:1) to give the desired product **3a**.

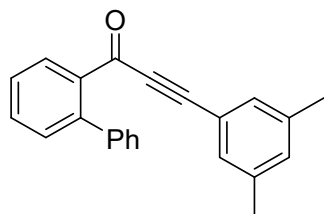
¹⁸O-labeling experiment: A 15 mL pressure tube was charged with biaryl ynones (**1a**, 0.2 mmol), AgSCF₃ (**2**, 0.4 mmol), HMPA (0.4 mmol), K₂S₂O₈ (0.6 mmol), TBHP (1.0 mmol, 5.5 M in decane), anhydrous MeCN (2 mL), and a magnetic stir bar. Then the mixtures were allowed to react at 80 °C for 10 h under nitrogen conditions. After completion of the reaction, the mixture was concentrated to yield the crude product, which was further

purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 7:1) to give the desired product **3a**.



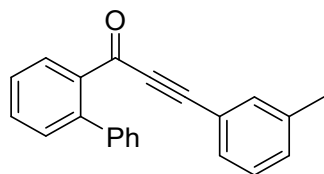
4. Characterization data of raw materials and products

1-([1,1'-biphenyl]-2-yl)-3-(3,5-dimethylphenyl)prop-2-yn-1-one (**1d**)



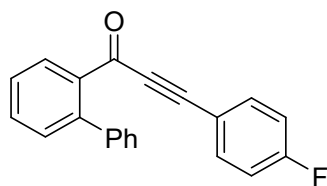
The product purified by flash column chromatography on silica gel (PE/AcOEt = 10:1) to afford the raw material as a yellow liquid (261.1 mg, 84% yield). **¹H NMR (600 MHz, CDCl₃)** δ 7.86 (dd, J = 7.7, 1.0 Hz, 1H), 7.47 – 7.43 (m, 1H), 7.35 (dd, J = 7.7, 0.8 Hz, 1H), 7.34 – 7.29 (m, 5H), 7.24 (d, J = 6.7 Hz, 1H), 6.87 (s, 1H), 6.77 (s, 2H), 2.13 (s, 6H). **¹³C NMR (151 MHz, CDCl₃)** δ 180.6, 142.6, 140.5, 138.1, 137.9, 132.4, 132.1, 131.1, 130.7, 130.1, 129.6, 128.4, 127.8, 127.4, 119.7, 94.6, 88.5, 21.0.

1-([1,1'-biphenyl]-2-yl)-3-(*m*-tolyl)prop-2-yn-1-one (1e)



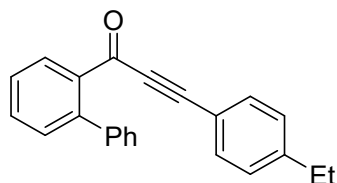
The product purified by flash column chromatography on silica gel (PE/AcOEt = 10:1) to afford the raw material as a yellow liquid (265.8 mg, 91% yield). **¹H NMR (600 MHz, CDCl₃)** δ 7.84 – 7.80 (m, 1H), 7.41 (td, J = 7.5, 1.3 Hz, 1H), 7.31 (dd, J = 7.6, 0.9 Hz, 1H), 7.29 – 7.25 (m, 5H), 7.21 – 7.16 (m, 1H), 7.00 (dd, J = 4.7, 1.7 Hz, 2H), 6.94 – 6.89 (m, 2H), 2.12 (s, 3H). **¹³C NMR (151 MHz, CDCl₃)** δ 180.6, 142.7, 140.5, 138.1, 138.1, 133.6, 132.2, 131.4, 131.1, 130.1, 130.1, 129.6, 128.4, 128.2, 127.8, 127.5, 119.9, 94.2, 88.7, 21.1.

1-([1,1'-biphenyl]-2-yl)-3-(4-fluorophenyl)prop-2-yn-1-one (1g)



The product purified by flash column chromatography on silica gel (PE/AcOEt = 10:1) to afford the raw material as a yellow liquid (271.85 mg, 90% yield). **¹H NMR (600 MHz, CDCl₃)** δ 7.94 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.59 (td, *J* = 7.5, 1.3 Hz, 1H), 7.48 (td, *J* = 7.6, 1.2 Hz, 1H), 7.46 – 7.38 (m, 5H), 7.37 – 7.31 (m, 1H), 7.24 – 7.19 (m, 2H), 7.00 – 6.92 (m, 2H). **¹³C NMR (151 MHz, CDCl₃)** δ 180.5, 164.6, 162.9, 142.7, 140.4, 137.9, 135.22 (d, *J* = 9.0 Hz), 132.2, 131.0, 130.0, 129.6, 128.3, 127.8, 127.4, 116.21 (d, *J* = 3.6 Hz), 115.8, 115.7, 92.7, 88.7.

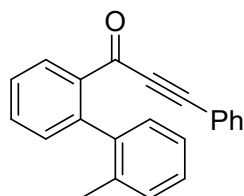
1-([1,1'-biphenyl]-2-yl)-3-(4-ethylphenyl)prop-2-yn-1-one (1i)



The product purified by flash column chromatography on silica gel (PE/AcOEt = 10:1) to afford the raw material as a yellow solid (287.81 mg, 93% yield). **¹H NMR (600 MHz, CDCl₃)** δ 7.95 (dd, *J* = 7.8, 1.1 Hz, 1H), 7.55 (td, *J* = 7.5, 1.3 Hz, 1H), 7.46 – 7.37 (m, 6H), 7.35 – 7.29 (m, 1H), 7.16 (d, *J* = 8.2 Hz, 2H), 7.08 (d, *J* = 8.2 Hz, 2H), 2.60 (q, *J* = 7.6 Hz, 2H), 1.18 (t, *J* = 7.6 Hz, 3H). **¹³C NMR (151 MHz, CDCl₃)** δ 180.7, 147.3,

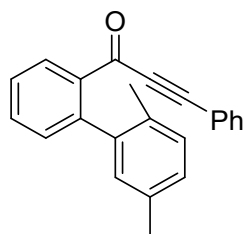
142.7, 140.5, 138.1, 133.1, 132.0, 131.0, 130.0, 129.5, 128.3, 127.9, 127.8, 127.4, 117.2, 94.6, 88.8, 29.0, 15.1.

1-(2'-methyl-[1,1'-biphenyl]-2-yl)-3-phenylprop-2-yn-1-one (1q)



The product purified by flash column chromatography on silica gel (PE/AcOEt = 10:1) to afford the raw material as a yellow liquid (275.7 mg, 91% yield). **¹H NMR (600 MHz, CDCl₃)** δ 8.09 (dd, J = 7.8, 1.2 Hz, 1H), 7.58 (td, J = 7.5, 1.4 Hz, 1H), 7.49 (td, J = 7.6, 1.3 Hz, 1H), 7.38 – 7.33 (m, 3H), 7.31 – 7.27 (m, 3H), 7.23 – 7.19 (m, 3H), 7.18 – 7.15 (m, 1H), 2.15 (s, 3H). **¹³C NMR (151 MHz, CDCl₃)** δ 179.5, 142.4, 140.3, 137.3, 135.8, 132.9, 132.3, 131.3, 130.4, 130.3, 129.9, 129.6, 128.3, 127.8, 127.4, 125.6, 120.2, 93.2, 88.3, 20.3.

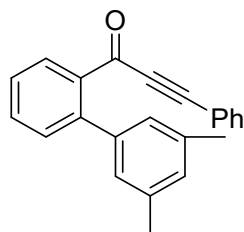
1-(2',5'-dimethyl-[1,1'-biphenyl]-2-yl)-3-phenylprop-2-yn-1-one (1w)



The product purified by flash column chromatography on silica gel (PE/AcOEt = 10:1) to afford the raw material as a yellow liquid (287.81 mg, 93% yield). **¹H NMR (600 MHz, CDCl₃)** δ 8.06 (dd, J = 7.8, 1.1 Hz, 1H),

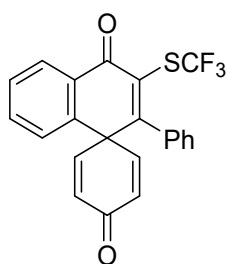
7.58 (td, $J = 7.5, 1.4$ Hz, 1H), 7.48 (td, $J = 7.7, 1.2$ Hz, 1H), 7.40 – 7.37 (m, 1H), 7.35 – 7.32 (m, 2H), 7.33 – 7.26 (m, 3H), 7.10 (d, $J = 7.7$ Hz, 1H), 7.05 – 6.99 (m, 2H), 2.29 (s, 3H), 2.10 (s, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 179.7, 142.6, 140.1, 137.5, 134.9, 132.8, 132.8, 132.2, 131.3, 130.3, 130.0, 129.8, 128.6, 128.3, 127.3, 120.3, 93.2, 88.3, 20.9, 19.7.

1-(3',5'-dimethyl-[1,1'-biphenyl]-2-yl)-3-phenylprop-2-yn-1-one (1x)



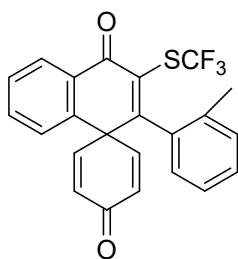
The product purified by flash column chromatography on silica gel (PE/AcOEt = 10:1) to afford the raw material as a yellow liquid (303.88 mg, 98% yield). ^1H NMR (600 MHz, CDCl_3) δ 7.91 (d, $J = 7.8$ Hz, 1H), 7.54 – 7.49 (m, 1H), 7.43 – 7.36 (m, 2H), 7.31 (t, $J = 7.0$ Hz, 1H), 7.25 – 7.17 (m, 4H), 7.01 (s, 2H), 6.92 (s, 1H), 2.29 (s, 6H). ^{13}C NMR (151 MHz, CDCl_3) δ 180.8, 143.2, 140.5, 138.2, 137.8, 132.8, 132.1, 130.9, 130.4, 129.8, 129.6, 128.3, 127.5, 127.2, 120.3, 93.6, 88.9, 21.3.

2'-Phenyl-3'-((trifluoromethyl)thio)-4'*H*-spiro[cyclohexane-1,1'-naphthalene]-2,5-diene-4,4'-dione (3a)¹



The product purified by flash column chromatography on silica gel (PE/AcOEt = 7:1) to afford the **3a** as a yellow solid (65.26 mg, 82% yield). ^1H NMR (400 MHz, CDCl_3) δ 8.36 (dd, $J = 7.7, 1.3$ Hz, 1H), 7.67 – 7.57 (m, 2H), 7.36 (ddd, $J = 16.1, 7.8, 2.3$ Hz, 3H), 7.30 – 7.27 (m, 1H), 7.01 (d, $J = 6.9$ Hz, 2H), 6.75 (d, $J = 10.0$ Hz, 2H), 6.35 (d, $J = 10.0$ Hz, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 184.2, 179.2, 166.7, 147.16, 137.5, 135.9, 134.0, 130.6, 129.9, 129.8, 129.4, 129.2, 128.7, 128.6 (q, $J = 308.1$ Hz), 128.1, 127.8, 127.3, 52.6. ^{19}F NMR (376 MHz, CDCl_3) δ -39.46 (s). The characterization data matched the literature.¹

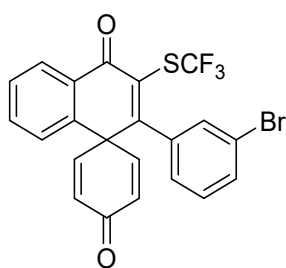
2'-(*o*-Tolyl)-3'-((trifluoromethyl)thio)-4'*H*-spiro[cyclohexane-1,1'-naphthalene]-2,5-diene-4,4'-dione (3b)¹



The product purified by flash column chromatography on silica gel (PE/AcOEt = 7:1) to afford the **3b** as a yellow solid (49.01 mg, 62% yield). ^1H

NMR (400 MHz, CDCl₃) δ 8.29 (dd, $J = 7.7, 1.5$ Hz, 1H), 7.54 (dq, $J = 14.8, 7.4, 1.4$ Hz, 2H), 7.24 – 7.18 (m, 2H), 7.14 (d, $J = 7.5$ Hz, 1H), 7.05 (t, $J = 7.5$ Hz, 1H), 6.81 (d, $J = 7.7$ Hz, 1H), 6.74 (dd, $J = 10.0, 3.1$ Hz, 1H), 6.65 (dd, $J = 9.9, 3.1$ Hz, 1H), 6.34 (dd, $J = 9.9, 1.6$ Hz, 1H), 6.20 (dd, $J = 10.0, 1.6$ Hz, 1H), 2.09 (s, 3H). **¹³C NMR (101 MHz, CDCl₃)** δ 183.0, 178.0, 164.3, 146.8, 144.9, 137.1, 133.7, 133.0, 132.8, 130.1, 129.7, 129.5, 129.4, 128.8 (q, $J = 317.1$ Hz), 128.4, 128.3, 127.7, 126.9, 126.3, 126.1, 123.8, 52.3, 19.2. **¹⁹F NMR (376 MHz, CDCl₃)** δ -38.18 (s). The characterization data matched the literature.¹

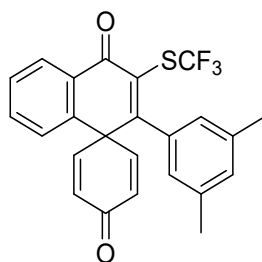
2'-(3-Bromophenyl)-3'-((trifluoromethyl)thio)-4'*H*-spiro[cyclohexane-1,1'-naphthalene]-2,5-diene-4,4'-dione (3c)¹



The product purified by flash column chromatography on silica gel (PE/AcOEt = 7:1) to afford the **3c** as a yellow solid (48.41 mg, 51% yield). **¹H NMR (400 MHz, CDCl₃)** δ 8.33 (dd, $J = 7.8, 1.3$ Hz, 1H), 7.62 (dtd, $J = 25.0, 7.5, 1.3$ Hz, 2H), 7.53 (dd, $J = 8.1, 0.7$ Hz, 1H), 7.31 – 7.17 (m, 3H), 6.97 (d, $J = 7.7$ Hz, 1H), 6.75 (t, $J = 8.5$ Hz, 2H), 6.40 (t, $J = 10.4$ Hz, 2H).

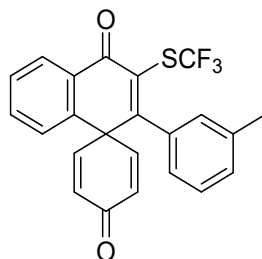
¹³C NMR (101 MHz, CDCl₃) δ 183.9, 178.9, 164.8, 146.8, 146.7, 137.5, 137.3, 134.2, 132.3, 130.8, 130.3, 130.3, 129.7, 129.5, 129.4, 128.7, 128.4 (q, *J* = 311.06 Hz), 128.1, 126.0, 121.9, 52.4. **¹⁹F NMR (376 MHz, CDCl₃) δ** -39.32 (s). The characterization data matched the literature.¹

2'-(3,5-Dimethylphenyl)-3'-((trifluoromethyl)thio)-4'*H*-spiro[cyclohexane-1,1'-naphthalene]-2,5-diene-4,4'-dione (3d)¹



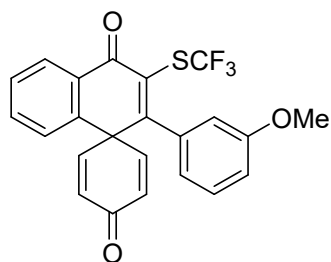
The product purified by flash column chromatography on silica gel (PE/AcOEt = 7:1) to afford the **3d** as a yellow solid (65.55 mg, 77% yield). **¹H NMR (400 MHz, CDCl₃) δ** 8.27 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.52 (dtd, *J* = 20.7, 7.4, 1.4 Hz, 2H), 7.21 (dd, *J* = 7.8, 0.8 Hz, 1H), 6.92 (s, 1H), 6.70 – 6.62 (m, 2H), 6.52 (s, 2H), 6.32 – 6.21 (m, 2H), 2.21 (s, 6H). **¹³C NMR (101 MHz, CDCl₃) δ** 183.3, 178.3, 166.0, 146.3, 136.5, 136.4, 134.9, 132.9, 129.8, 129.3, 128.9, 128.8 (q, *J* = 317.1 Hz), 128.3, 127.6, 127.0, 123.8, 51.6, 20.3. **¹⁹F NMR (376 MHz, CDCl₃) δ** -39.46 (s). The characterization data matched the literature.¹

2'-(*m*-Tolyl)-3'-((trifluoromethyl)thio)-4'*H*-spiro[cyclohexane-1,1'-naphthalene]-2,5-diene-4,4'-dione (3e)¹



The product purified by flash column chromatography on silica gel (PE/AcOEt = 7:1) to afford the **3e** as a yellow solid (45.71 mg, 56% yield). ¹H NMR (400 MHz, CDCl₃) δ 8.35 (dd, J = 7.7, 1.4 Hz, 1H), 7.60 (ddd, J = 13.0, 7.5, 1.4 Hz, 2H), 7.25 (ddd, J = 29.6, 10.3, 2.9 Hz, 3H), 6.80 (d, J = 6.0 Hz, 2H), 6.74 (d, J = 10.0 Hz, 2H), 6.35 (d, J = 10.3 Hz, 2H), 2.33 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 184.3, 179.3, 166.9, 147.2, 137.59, 137.56, 135.9, 133.9, 130.4, 129.9, 129.4, 128.72, 128.7 (q, J = 317.1 Hz), 128.1, 127.78, 127.73, 124.3, 52.6, 21.4. ¹⁹F NMR (376 MHz, CDCl₃) δ -39.46 (s) The characterization data matched the literature.¹

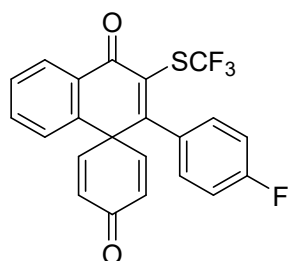
2'-(3-methoxyphenyl)-3'-((trifluoromethyl)thio)-4'*H*-spiro[cyclohexane-1,1'-naphthalene]-2,5-diene-4,4'-dione (3f)



The product purified by flash column chromatography on silica gel (PE/

AcOEt = 4:1) to afford the **3f** as a yellow solid (67.62 mg, 79% yield). ¹H NMR (400 MHz, CDCl₃) δ 8.35 – 8.33 (m, 1H), 7.63 – 7.57 (m, 2H), 7.30 – 7.24 (m, 2H), 6.98 – 6.87 (m, 1H), 6.73 – 6.74 (m, 2H), 6.59 – 6.57 (m, 2H), 6.36 (t, *J* = 9.2 Hz, 2H), 3.77 (d, *J* = 3.1 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 184.3, 179.2, 166.4, 158.8, 147.2, 137.5, 137.1, 134.0, 130.5, 129.9, 129.7, 129.4, 129.1, 128.7, 128.6 (q, *J* = 311.75 Hz), 128.0, 119.6, 114.0, 113.7, 55.3, 52.5. ¹⁹F NMR (377 MHz, CDCl₃) δ -39.39 (d, *J* = 2.1 Hz). HRMS (ESI) calcd for C₂₃H₁₅F₃NaO₃S [M+Na]⁺ 451.0586, found 451.0592.

2'-(4-Fluorophenyl)-3'-((trifluoromethyl)thio)-4'*H*-spiro[cyclohexane-1,1'-naphthalene]-2,5-diene-4,4'-dione (3g)¹

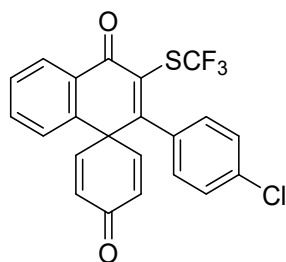


The product purified by flash column chromatography on silica gel (PE/AcOEt = 7:1) to afford the **3g** as a yellow solid (55.7 mg, 67% yield). ¹H NMR (600 MHz, CDCl₃) δ 8.26 (d, *J* = 7.1 Hz, 1H), 7.59 – 7.54 (m, 1H), 7.51 (t, *J* = 7.2 Hz, 1H), 7.22 (d, *J* = 7.8 Hz, 1H), 6.99 – 6.93 (m, 4H), 6.67 (d, *J* = 9.9 Hz, 2H), 6.30 (d, *J* = 9.9 Hz, 2H). ¹³C NMR (151 MHz, CDCl₃) δ 182.9, 178.0, 164.7, 161.87 (d, *J* = 249.9 Hz), 145.9, 136.4, 133.1, 130.8 (d, *J* = 3.4 Hz), 129.7, 129.4, 128.8 (q, *J* = 317.1 Hz), 128.7, 128.46 (dd, *J*

= 16.5, 7.8 Hz), 127.7, 127.1, 126.4, 114.18 (d, $J = 22.0$ Hz), 51.6. ^{19}F NMR (376 MHz, CDCl_3) δ -39.42 (s), -110.99 (s). The characterization data matched the literature.¹

δ 163.70 (d, $J = 305.4$ Hz), 130.87 (d, $J = 3.4$ Hz), 114.18 (d, $J = 22.0$ Hz).

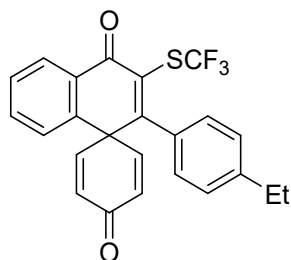
2'-(4-Chlorophenyl)-3'-((trifluoromethyl)thio)-4'*H*-spiro[cyclohexane-1,1'-naphthalene]-2,5-diene-4,4'-dione (3h)¹



The product purified by flash column chromatography on silica gel (PE/AcOEt = 7:1) to afford the **3h** as a yellow solid (49.65 mg, 58% yield). ^1H NMR (400 MHz, CDCl_3) δ 8.33 (dd, $J = 7.7, 1.1$ Hz, 1H), 7.62 (tdd, $J = 15.0, 10.8, 4.0$ Hz, 2H), 7.31 (dd, $J = 17.6, 8.0$ Hz, 3H), 6.97 (d, $J = 8.4$ Hz, 2H), 6.74 (d, $J = 10.0$ Hz, 2H), 6.38 (d, $J = 10.0$ Hz, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 183.9, 179.0, 165.5, 146.8, 137.3, 135.4, 134.2, 134.1, 130.8, 130.2, 129.7, 129.5, 128.8, 128.7, 128.6 (q, $J = 317.1$ Hz), 128.2, 128.1, 52.5. ^{19}F NMR (376 MHz, CDCl_3) δ -39.40 (s). The characterization data matched the literature.¹

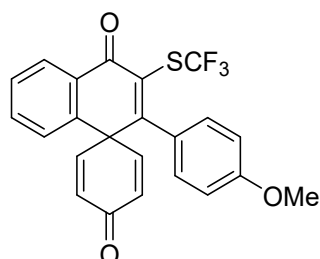
2'-(4-Ethylphenyl)-3'-((trifluoromethyl)thio)-4'*H*-spiro[cyclohexane-

1,1'-naphthalene]-2,5-diene-4,4'-dione (**3i**)¹



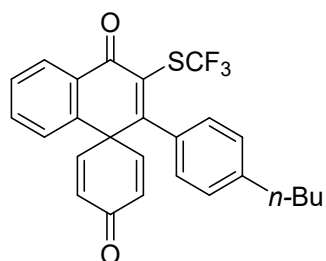
The product purified by flash column chromatography on silica gel (PE/AcOEt = 7:1) to afford the **3i** as a yellow solid (66.38 mg, 78% yield). ¹H NMR (400 MHz, CDCl₃) δ 8.35 (dd, J = 7.7, 1.5 Hz, 1H), 7.60 (ddd, J = 12.9, 7.5, 1.4 Hz, 2H), 7.28 (dd, J = 7.8, 0.8 Hz, 1H), 7.16 (d, J = 8.1 Hz, 2H), 6.91 (d, J = 8.1 Hz, 2H), 6.74 (d, J = 10.0 Hz, 2H), 6.35 (d, J = 10.0 Hz, 2H), 2.66 (t, J = 7.6 Hz, 2H), 1.26 (d, J = 7.6 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 184.3, 179.3, 147.3, 145.3, 137.5, 133.9, 133.3, 130.5, 129.9, 129.3, 128.7, 128.6 (q, J = 311.06 Hz), 128.1, 127.2, 127.1, 52.8, 28.5, 14.8. ¹⁹F NMR (376 MHz, CDCl₃) δ -39.50 (s). The characterization data matched the literature.¹

2'-(4-Methoxyphenyl)-3'-((trifluoromethyl)thio)-4'H-spiro[cyclohexane-1,1'-naphthalene]-2,5-diene-4,4'-dione (**3j**)¹



The product purified by flash column chromatography on silica gel (PE/AcOEt = 5:1) to afford the **3j** as a yellow solid 68.4 mg, 80% yield). **¹H NMR (400 MHz, CDCl₃)** δ 8.33 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.59 (dtd, *J* = 23.5, 7.4, 1.3 Hz, 2H), 7.33 – 7.23 (m, 1H), 6.96 (d, *J* = 8.7 Hz, 2H), 6.88 – 6.83 (m, 2H), 6.74 (t, *J* = 6.4 Hz, 2H), 6.37 (t, *J* = 6.4 Hz, 2H), 3.82 (s, 3H). **¹³C NMR (101 MHz, CDCl₃)** δ 184.3, 179.4, 166.8, 160.0, 147.4, 137.6, 133.9, 130.5, 130.2, 130.0, 129.9, 129.5 (q, *J* = 311.03 Hz), 129.3, 128.7, 128.6, 128.4, 128.1, 113.2, 55.2, 52.9. **¹⁹F NMR (376 MHz, CDCl₃)** δ -39.54 (s). The characterization data matched the literature.¹

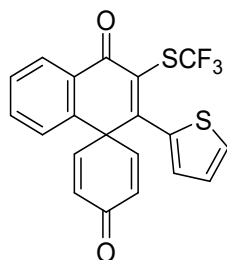
2'-(4-butylphenyl)-3'-((trifluoromethyl)thio)-4'*H*-spiro[cyclohexane-1,1'-naphthalene]-2,5-diene-4,4'-dione (3k)



The product purified by flash column chromatography on silica gel (PE/AcOEt = 4:1) to afford the **3k** as a yellow solid (65.33mg, 72% yield). **¹H NMR (400 MHz, CDCl₃)** δ 8.34 (dd, *J* = 7.7, 1.2 Hz, 1H), 7.65 – 7.49 (m, 2H), 7.31 – 7.27 (m, 1H), 7.13 (d, *J* = 8.0 Hz, 2H), 6.90 (d, *J* = 8.0 Hz, 2H), 6.73 (d, *J* = 10.0 Hz, 2H), 6.35 (d, *J* = 10.0 Hz, 2H), 2.67 – 2.51 (m, 2H), 1.60 (dd, *J* = 15.6, 8.1 Hz, 2H), 1.34 (dt, *J* = 14.5, 7.4 Hz, 2H), 0.93 (t, *J* = 7.3 Hz, 3H). **¹³C NMR (101 MHz, CDCl₃)** δ 184.3, 179.3, 167.0, 147.3,

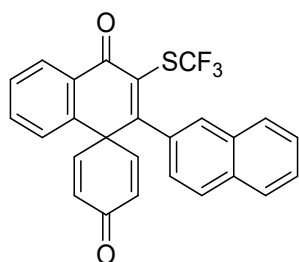
144.1, 137.6, 133.9, 133.3, 130.5, 129.9, 129.7, 129.3, 128.9 (q, $J = 306.06$ Hz), 128.7, 128.1, 127.7, 127.1, 52.8, 35.3, 33.1, 22.4, 13.9. ^{19}F NMR (377 MHz, CDCl_3) δ -39.50 (d, $J = 6.5$ Hz). HRMS (ESI) calcd for $\text{C}_{26}\text{H}_{21}\text{O}_2\text{NaSF}_3$ $[\text{M}+\text{Na}]^+$ 477.1107, found 477.1111.

2'-(Thiophen-2-yl)-3'-((trifluoromethyl)thio)-4'H-spiro[cyclohexane-1,1'-naphthalene]-2,5-diene-4,4'-dione (3l)¹



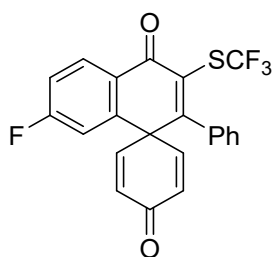
The product purified by flash column chromatography on silica gel (PE/AcOEt = 7:1) to afford the **3l** as a yellow solid (60.61 mg, 75% yield). ^1H NMR (400 MHz, CDCl_3) δ 8.27 (dd, $J = 7.8, 1.4$ Hz, 1H), 7.53 (dtd, $J = 22.4, 7.4, 1.4$ Hz, 2H), 7.36 (dd, $J = 5.1, 1.1$ Hz, 1H), 7.26 – 7.21 (m, 1H), 6.96 (dd, $J = 5.0, 3.6$ Hz, 1H), 6.86 (dd, $J = 3.6, 1.0$ Hz, 1H), 6.67 – 6.60 (m, 2H), 6.40 – 6.33 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 183.3, 177.8, 158.7, 146.0, 136.3, 134.5, 133.09, 129.9, 129.0 (q, $J = 311.3$ Hz), 128.7, 128.4, 128.2, 127.7, 127.1, 125.8, 51.6. ^{19}F NMR (376 MHz, CDCl_3) δ -39.48 (s). The characterization data matched the literature.¹

2'-(Naphthalen-2-yl)-3'-((trifluoromethyl)thio)-4'H-spiro[cyclohexane-1,1'-naphthalene]-2,5-diene-4,4'-dione (3m)¹



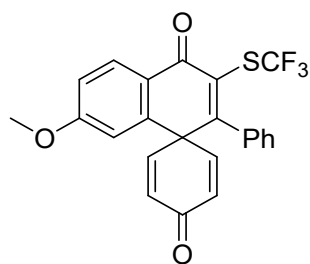
The product purified by flash column chromatography on silica gel (PE/AcOEt = 7:1) to afford the **3m** as a yellow solid (51 mg, 57% yield). **¹H NMR (600 MHz, CDCl₃)** δ 8.38 (d, J = 7.8 Hz, 1H), 7.86 (d, J = 7.7 Hz, 1H), 7.82 (d, J = 8.4 Hz, 1H), 7.79 (d, J = 7.6 Hz, 1H), 7.65 (t, J = 7.5 Hz, 1H), 7.60 (t, J = 7.6 Hz, 1H), 7.57 – 7.51 (m, 2H), 7.47 (s, 1H), 7.31 (d, J = 7.8 Hz, 1H), 7.13 (d, J = 8.4 Hz, 1H), 6.83 (d, J = 9.4 Hz, 2H), 6.34 (t, J = 9.4 Hz, 2H). **¹³C NMR (151 MHz, CDCl₃)** δ 184.1, 179.3, 166.6, 147.2, 137.5, 135.9, 134.0, 133.4, 133.0, 132.0, 130.7, 130.5, 130.1, 130.0, 129.4, 128.8, 128.6 (q, J = 311.15 Hz), 128.3, 128.1, 127.8, 127.2, 127.0, 126.7, 124.8, 52.8. **¹⁹F NMR (565 MHz, CDCl₃)** δ -39.39 (s). The characterization data matched the literature.¹

7'-Fluoro-2'-phenyl-3'-((trifluoromethyl)thio)-4'*H*-spiro[cyclohexane-1,1'-naphthalene]-2,5-diene-4,4'-dione (3n)¹



The product purified by flash column chromatography on silica gel (PE/AcOEt = 7:1) to afford the **3n** as a yellow solid (68.33 mg, 84% yield). **¹H NMR (400 MHz, CDCl₃)** δ 8.38 (dd, J = 8.8, 5.8 Hz, 1H), 7.43 – 7.31 (m, 3H), 7.27 (td, J = 8.4, 2.5 Hz, 1H), 7.04 – 6.98 (m, 2H), 6.96 (dd, J = 9.1, 2.4 Hz, 1H), 6.78 – 6.71 (m, 2H), 6.40 – 6.32 (m, 2H). **¹³C NMR (101 MHz, CDCl₃)** δ 183.7, 178.1, 167.2, 166.5, 164.6, 146.4, 140.7 (d, J = 8.5 Hz), 135.7, 131.9 (d, J = 9.6 Hz), 130.9, 129.3, 128.5 (q, J = 310.6 Hz), 127.9, 127.2, 126.5 (d, J = 2.6 Hz), 117.6, 117.4, 114.9, 114.7, 52.5 (d, J = 1.3 Hz). **¹⁹F NMR (377 MHz, CDCl₃)** δ -39.43 (s), -101.77 (d, J = 2.9 Hz). The characterization data matched the literature.¹

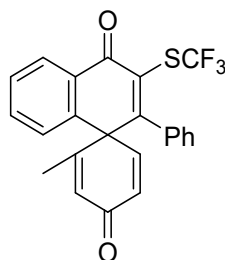
7'-Methoxy-2'-phenyl-3'-((trifluoromethyl)thio)-4'-H-spiro[cyclohexane-1,1'-naphthalene]-2,5-diene-4,4'-dione (3o**)¹**



The product purified by flash column chromatography on silica gel (PE/AcOEt = 7:1) to afford the **3o** as a yellow solid (63.88 mg, 76% yield). **¹H NMR (400 MHz, CDCl₃)** δ 8.24 (d, J = 8.8 Hz, 1H), 7.27 (ddd, J = 16.1, 7.8, 3.7 Hz, 3H), 7.01 (dd, J = 8.8, 2.5 Hz, 1H), 6.94 – 6.90 (m, 2H), 6.68 (t, J = 6.4 Hz, 2H), 6.61 (d, J = 2.4 Hz, 1H), 6.27 (t, J = 6.4 Hz, 2H), 3.76

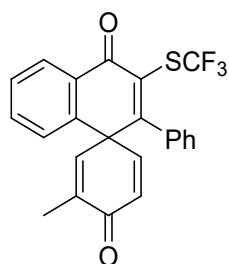
(d, $J = 3.2$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 183.1, 177.2, 164.7, 163.0, 146.3, 138.9, 134.9, 130.2, 129.5, 128.6 (q, $J = 311.06$ Hz), 128.0, 126.7, 126.3, 122.2, 114.6, 111.4, 54.7, 51.6. ^{19}F NMR (376 MHz, CDCl_3) δ -39.49 (s). The characterization data matched the literature.¹

2-Methyl-2'-phenyl-3'-((trifluoromethyl)thio)-4'*H*-spiro[cyclohexane-1,1'-naphthalene]-2,5-diene-4,4'-dione (3p)¹



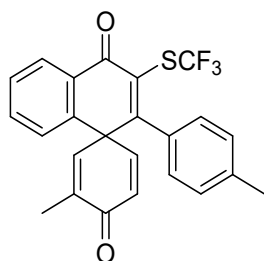
The product purified by flash column chromatography on silica gel (PE/AcOEt = 7:1) to afford the **3p** as a yellow solid (53.61 mg, 65% yield). ^1H NMR (600 MHz, CDCl_3) δ 8.35 (dd, $J = 7.9, 1.3$ Hz, 1H), 7.69 – 7.53 (m, 2H), 7.40 – 7.29 (m, 3H), 7.18 (d, $J = 7.6$ Hz, 1H), 7.00 (s, 2H), 6.73 (d, $J = 9.8$ Hz, 1H), 6.35 – 6.24 (m, 2H), 1.76 (d, $J = 1.2$ Hz, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 185.0, 179.4, 166.9, 155.7, 147.2, 138.7, 135.6, 134.3, 131.1, 130.8, 130.2, 129.7, 129.5, 129.3, 128.7 (q, $J = 309.55$ Hz), 128.4, 127.8, 127.6, 55.8, 20.2. ^{19}F NMR (565 MHz, CDCl_3) δ -39.46 (s). The characterization data matched the literature.¹

3-Methyl-2'-phenyl-3'-((trifluoromethyl)thio)-4'*H*-spiro[cyclohexane-1,1'-naphthalene]-2,5-diene-4,4'-dione (3q)¹



The product purified by flash column chromatography on silica gel (PE/AcOEt = 7:1) to afford the **3q** as a yellow solid (69.74 mg, 85% yield). ^1H NMR (600 MHz, CDCl_3) δ 8.27 (dd, $J = 7.8, 1.2$ Hz, 1H), 7.52 (dtd, $J = 15.0, 7.8, 1.2$ Hz, 2H), 7.27 (dt, $J = 14.4, 7.5$ Hz, 3H), 7.19 (s, 1H), 6.89 (dd, $J = 21.5, 6.9$ Hz, 2H), 6.64 (dd, $J = 9.8, 3.1$ Hz, 1H), 6.44 (dd, $J = 2.9, 1.4$ Hz, 1H), 6.24 (d, $J = 9.8$ Hz, 1H), 1.78 (d, $J = 1.2$ Hz, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 183.8, 178.3, 166.5, 145.6, 141.3, 137.3, 136.7, 134.9, 132.8, 129.4, 128.8, 128.6, 128.3, 128.1, 128.0, 127.6, 127.0, 126.7, 126.5, 126.0, 51.8, 14.7. ^{19}F NMR (565 MHz, CDCl_3) δ -39.79 (s). The characterization data matched the literature.¹

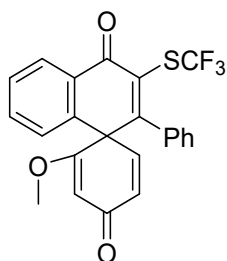
3-Methyl-2'-(*p*-tolyl)-3'-((trifluoromethyl)thio)-4'*H*-spiro[cyclohexane-1,1'-naphthalene]-2,5-diene-4,4'-dione (3r**)¹**



The product purified by flash column chromatography on silica gel (PE/AcOEt = 7:1) to afford the **3r** as a yellow solid (61.29 mg, 73% yield). ^1H

NMR (600 MHz, CDCl₃) δ 8.33 (dd, $J = 7.8, 1.2$ Hz, 1H), 7.60 (td, $J = 7.6, 1.4$ Hz, 1H), 7.57 – 7.53 (m, 1H), 7.28 – 7.23 (m, 1H), 7.11 (d, $J = 7.7$ Hz, 2H), 6.85 (d, $J = 9.6$ Hz, 2H), 6.70 (dd, $J = 9.8, 3.1$ Hz, 1H), 6.50 (dd, $J = 2.9, 1.4$ Hz, 1H), 6.31 (d, $J = 9.8$ Hz, 1H), 2.35 (s, 3H), 1.86 (d, $J = 1.2$ Hz, 3H). **¹³C NMR (151 MHz, CDCl₃)** δ 185.0, 179.4, 167.8, 146.8, 142.5, 139.0, 138.4, 137.7, 133.8, 133.2, 130.3, 129.9, 129.3, 129.1, 128.65 (q, $J = 311.06$ Hz), 128.60, 128.4, 128.2, 128.1, 127.4, 126.9, 53.0, 21.3, 15.7. **¹⁹F NMR (565 MHz, CDCl₃)** δ -39.80 (s). The characterization data matched the literature.¹

2-Methoxy-2'-phenyl-3'-((trifluoromethyl)thio)-4'*H*-spiro[cyclohexane-1,1'-naphthalene]-2,5-diene-4,4'-dione (3s)¹



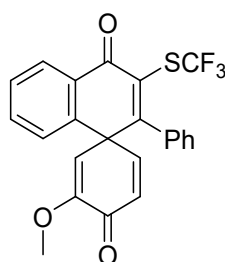
The product purified by flash column chromatography on silica gel (PE/AcOEt = 5:1) to afford the **3s** as a yellow solid (55.61 mg, 65% yield). **¹H NMR (600 MHz, CDCl₃)** δ 8.33 (dd, $J = 7.8, 1.0$ Hz, 1H), 7.61 (td, $J = 7.7, 1.4$ Hz, 1H), 7.57 (dd, $J = 11.0, 4.1$ Hz, 1H), 7.38 – 7.31 (m, 3H), 7.24 (d, $J = 7.8$ Hz, 1H), 7.05 – 6.88 (m, 2H), 6.47 (d, $J = 9.7$ Hz, 1H), 6.30 (dd, $J = 9.7, 0.8$ Hz, 1H), 5.60 (s, 1H), 3.59 (s, 3H). **¹³C NMR (151 MHz, CDCl₃)** δ 186.7, 179.5, 172.3, 166.4, 142.8, 138.3, 135.6, 134.0, 130.38,

130.34, 129.28, 129.23, 128.6 (q, $J = 311.06$ Hz), 128.4, 128.1, 127.8, 127.2, 126.9, 105.1, 56.1, 55.0. ^{19}F NMR (565 MHz, CDCl_3) δ -39.84 (s).

The characterization data matched the literature.¹

3-Methoxy-2'-phenyl-3'-((trifluoromethyl)thio)-4'*H*-

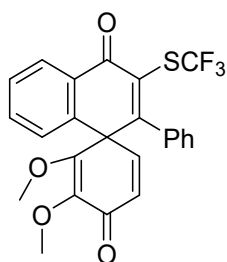
spiro[cyclohexane-1,1'-naphthalene]-2,5-diene-4,4'-dione (3t)¹



The product purified by flash column chromatography on silica gel (PE/AcOEt = 5:1) to afford the **3t** as a yellow solid (68.2 mg, 80% yield). ^1H NMR (600 MHz, CDCl_3) δ 8.27 (d, $J = 7.8$ Hz, 1H), 7.54 (td, $J = 7.6, 1.5$ Hz, 1H), 7.49 (t, $J = 7.2$ Hz, 1H), 7.27 (dt, $J = 14.0, 7.7$ Hz, 3H), 7.23 – 7.21 (m, 1H), 6.94 – 6.87 (m, 2H), 6.66 (dd, $J = 9.8, 2.7$ Hz, 1H), 6.29 (d, $J = 9.7$ Hz, 1H), 5.61 (d, $J = 2.7$ Hz, 1H), 3.55 (s, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 179.4, 179.3, 167.9, 152.4, 147.2, 139.0, 135.8, 134.0, 130.4, 129.7, 129.2, 129.1, 128.65, 128.62 (q, $J = 332.2$ Hz), 128.0, 127.8, 127.4, 127.2, 115.3, 55.2, 52.8. ^{19}F NMR (565 MHz, CDCl_3) δ -39.50 (s). The characterization data matched the literature.¹

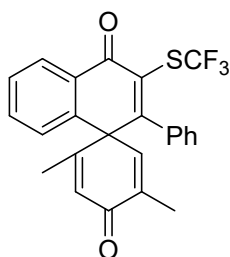
2,3-Dimethoxy-2'-phenyl-3'-((trifluoromethyl)thio)-4'*H*-

spiro[cyclohexane-1,1'-naphthalene]-2,5-diene-4,4'-dione (3u)¹



The product purified by flash column chromatography on silica gel (PE/AcOEt = 4:1) to afford the **3u** as a yellow solid (55.89 mg, 61% yield). ¹H NMR (600 MHz, CDCl₃) δ 8.26 (dd, J = 7.8, 1.1 Hz, 1H), 7.56 – 7.46 (m, 2H), 7.34 – 7.24 (m, 3H), 7.20 (d, J = 7.3 Hz, 1H), 7.05 – 6.93 (m, 2H), 6.32 (d, J = 9.7 Hz, 1H), 6.21 (d, J = 9.7 Hz, 1H), 3.78 (s, 3H), 3.38 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 182.7, 178.5, 165.7, 158.2, 140.9, 138.8, 137.4, 134.6, 132.8, 129.5, 129.1, 128.5, 128.18, 128.16, 127.6 (q, J = 309.55 Hz), 127.5, 126.9, 126.7, 126.4, 126.1, 125.6, 60.2, 59.6, 55.8. ¹⁹F NMR (565 MHz, CDCl₃) δ -39.88 (s). The characterization data matched the literature.¹

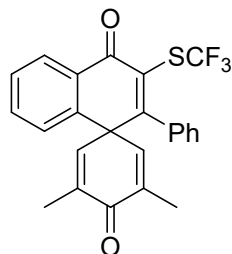
2,5-dimethyl-2'-phenyl-3'-((trifluoromethyl)thio)-4'*H*-spiro[cyclohexane-1,1'-naphthalene]-2,5-diene-4,4'-dione (3v)



The product purified by flash column chromatography on silica gel (PE/AcOEt = 7:1) to afford the **3w** as a yellow solid (41.08 mg, 48% yield). ¹H

NMR (600 MHz, CDCl₃) δ 8.35 (d, J = 7.8 Hz, 1H), 7.62 (t, J = 7.5 Hz, 1H), 7.56 (t, J = 7.5 Hz, 1H), 7.37 – 7.28 (m, 3H), 7.13 (d, J = 7.8 Hz, 1H), 6.93 (d, J = 6.8 Hz, 2H), 6.47 (s, 1H), 6.25 (s, 1H), 1.83 (s, 3H), 1.72 (s, 3H). **¹³C NMR (151 MHz, CDCl₃)** δ 185.5, 179.5, 167.8, 155.1, 142.3, 139.5, 136.7, 135.6, 134.2, 131.1, 130.8, 130.4, 130.2, 129.1, 128.7 (q, J = 310.56 Hz), 128.4, 127.8, 127.6, 126.5, 56.1, 20.0, 15.3. **¹⁹F NMR (565 MHz, CDCl₃)** δ -39.55 (s). HRMS (ESI) calcd for C₂₄H₁₇F₃NaO₂S [M+Na]⁺ 449.0794, found 449.0803.

3,5-dimethyl-2'-phenyl-3'-((trifluoromethyl)thio)-4'H-spiro[cyclohexane-1,1'-naphthalene]-2,5-diene-4,4'-dione (3w)



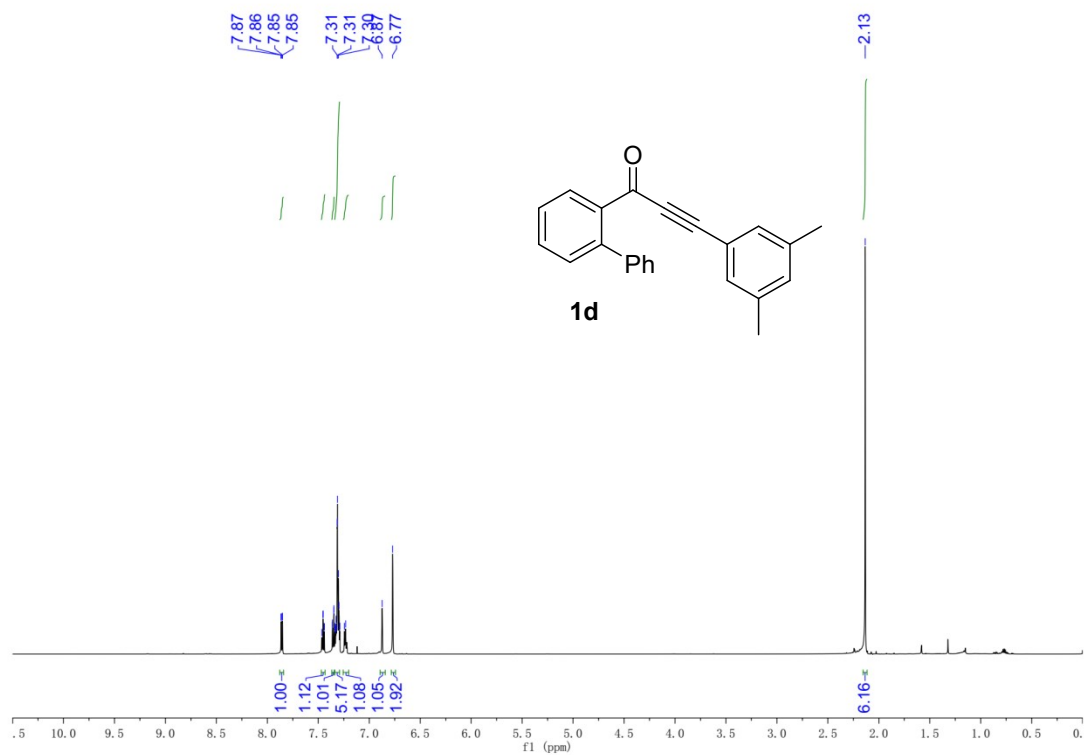
The product purified by flash column chromatography on silica gel (PE/AcOEt = 7:1) to afford the **3x** as a yellow solid (62.19 mg, 73% yield). **¹H NMR (600 MHz, CDCl₃)** δ 8.33 (d, J = 7.8 Hz, 1H), 7.59 (t, J = 7.5 Hz, 1H), 7.54 (t, J = 7.5 Hz, 1H), 7.35 – 7.28 (m, 3H), 7.23 (d, J = 7.8 Hz, 1H), 6.93 (d, J = 7.5 Hz, 2H), 6.49 (s, 2H), 1.83 (s, 6H). **¹³C NMR (151 MHz, CDCl₃)** δ 185.4, 179.6, 168.5, 141.9, 139.2, 137.4, 136.1, 133.8, 129.8, 128.9, 128.7 (q, J = 310.56 Hz), 128.8, 128.5, 128.1, 127.4, 127.3, 52.5,

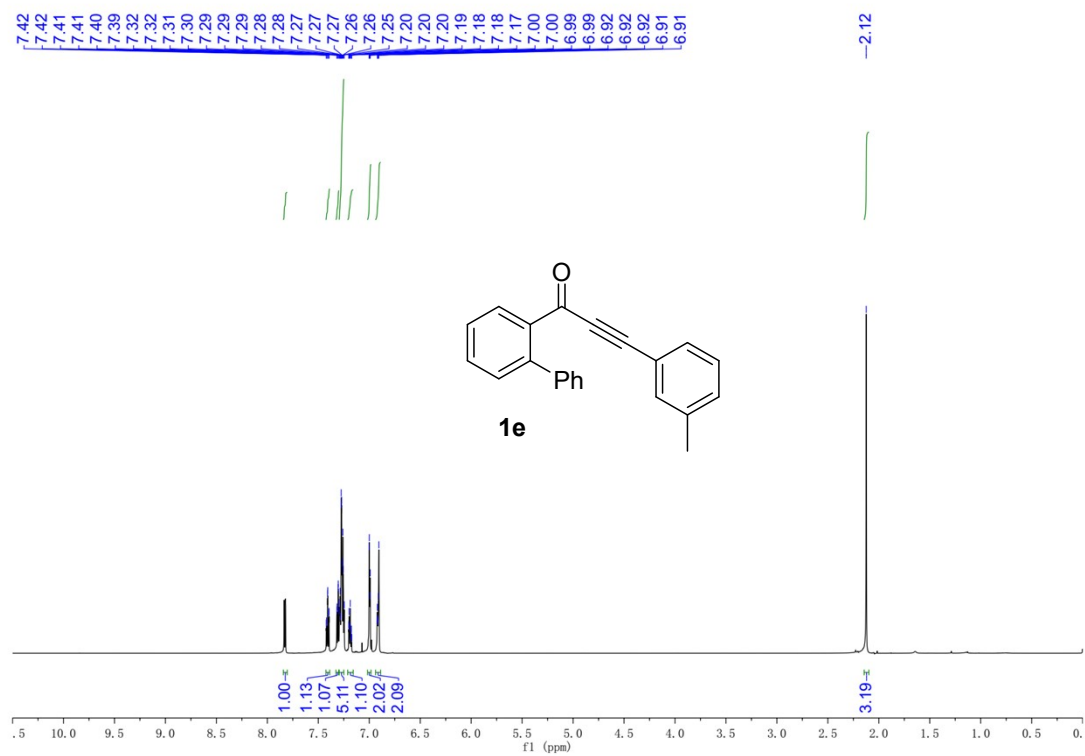
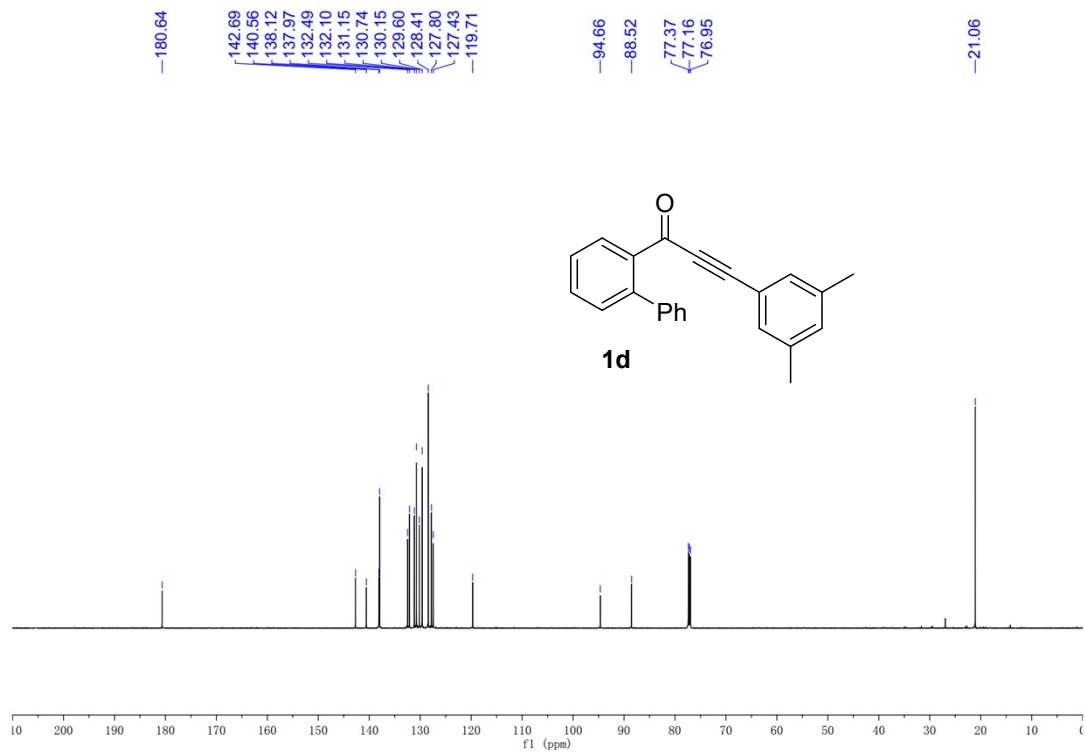
15.9. ^{19}F NMR (565 MHz, CDCl_3) δ -39.64 (s). HRMS (ESI) calcd for $\text{C}_{24}\text{H}_{17}\text{F}_3\text{NaO}_2\text{S}$ $[\text{M}+\text{Na}]^+$ 449.0794 , found 449.080

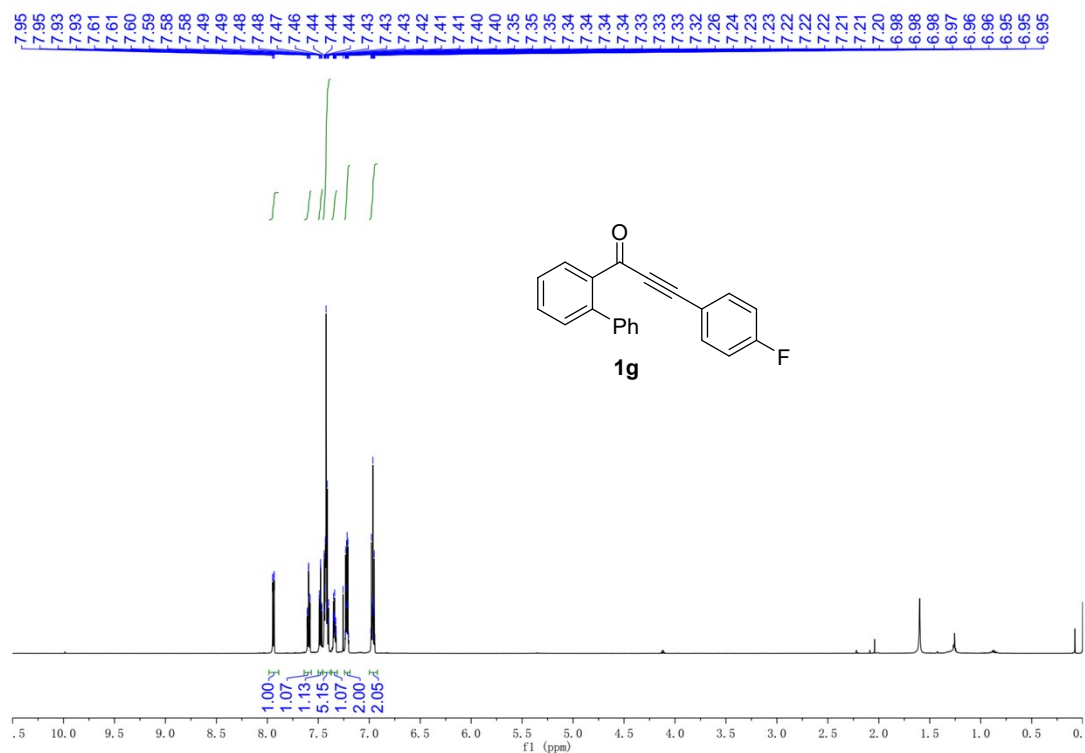
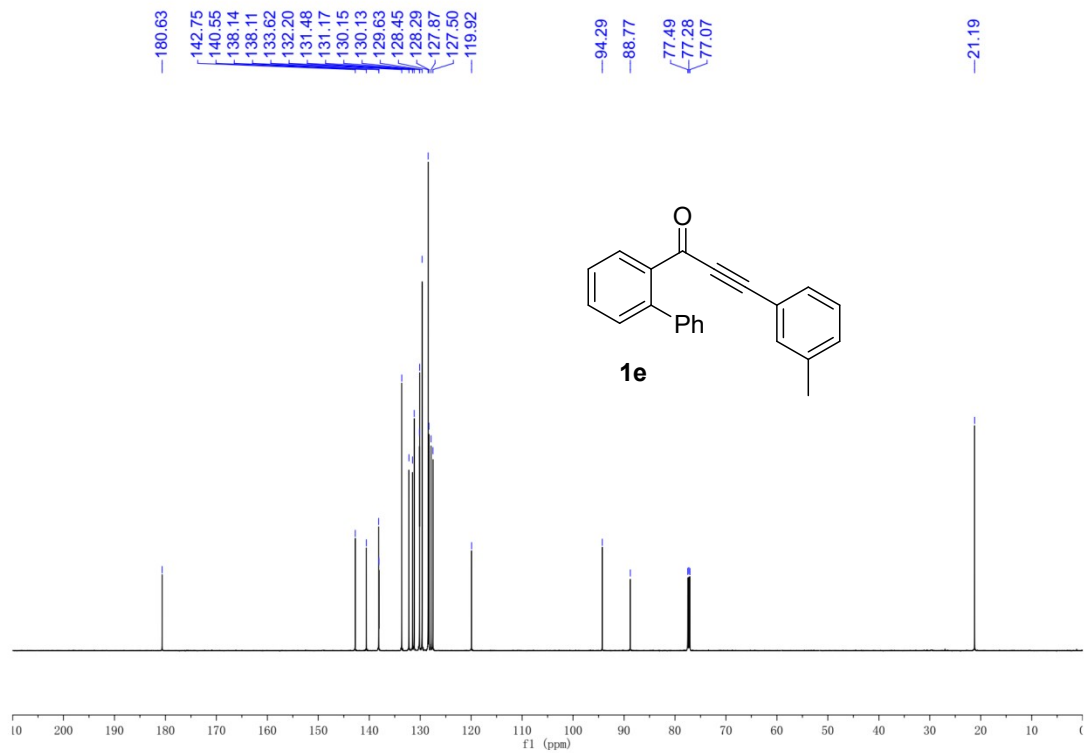
References for known compounds:

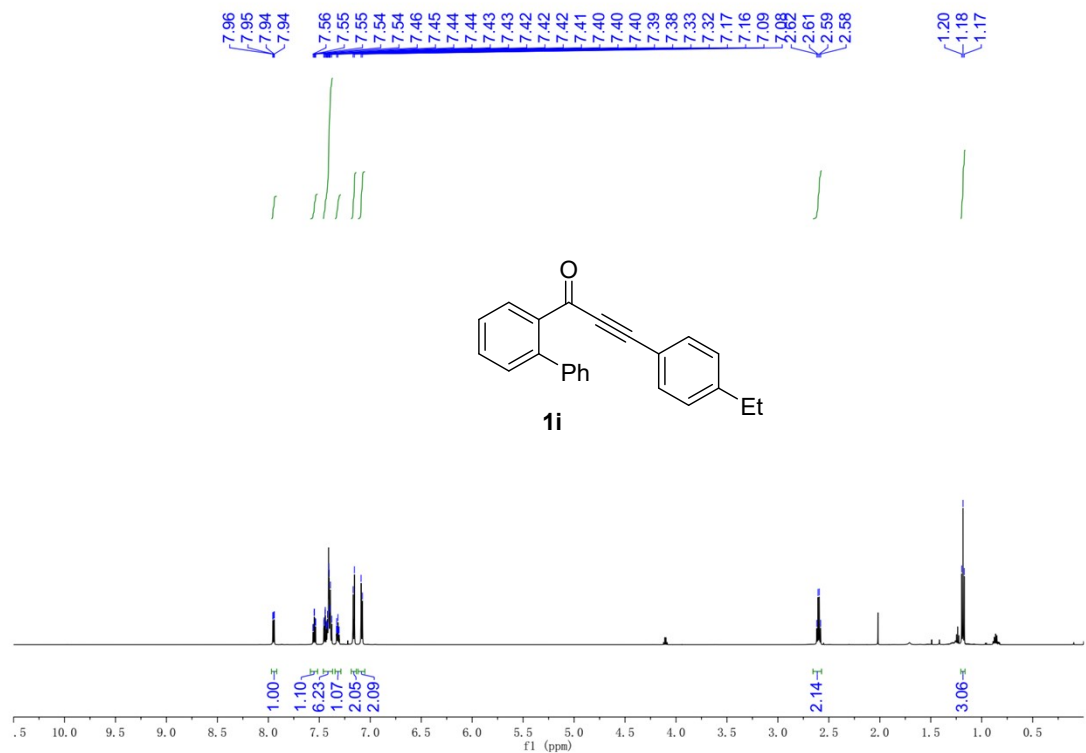
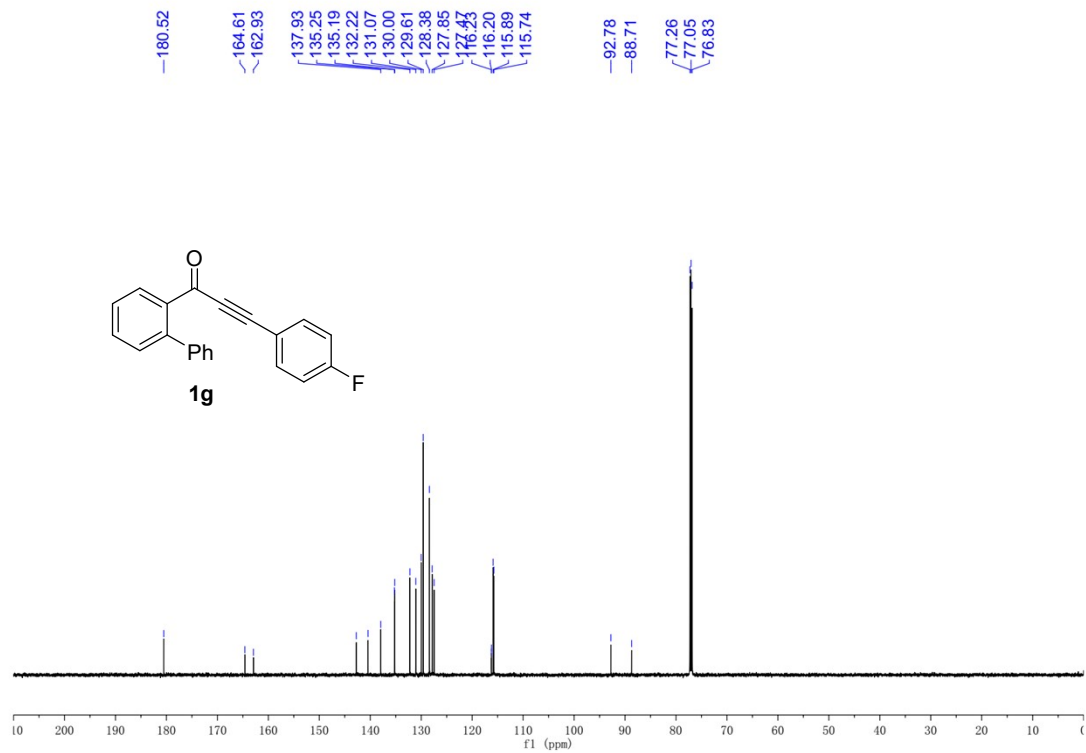
[1] W.-C. Yang, M.-M. Zhang, Y. Sun, C.-Y. Chen, and L. Wang, *Org. Lett.*, 2021, **23**, 6691–6696

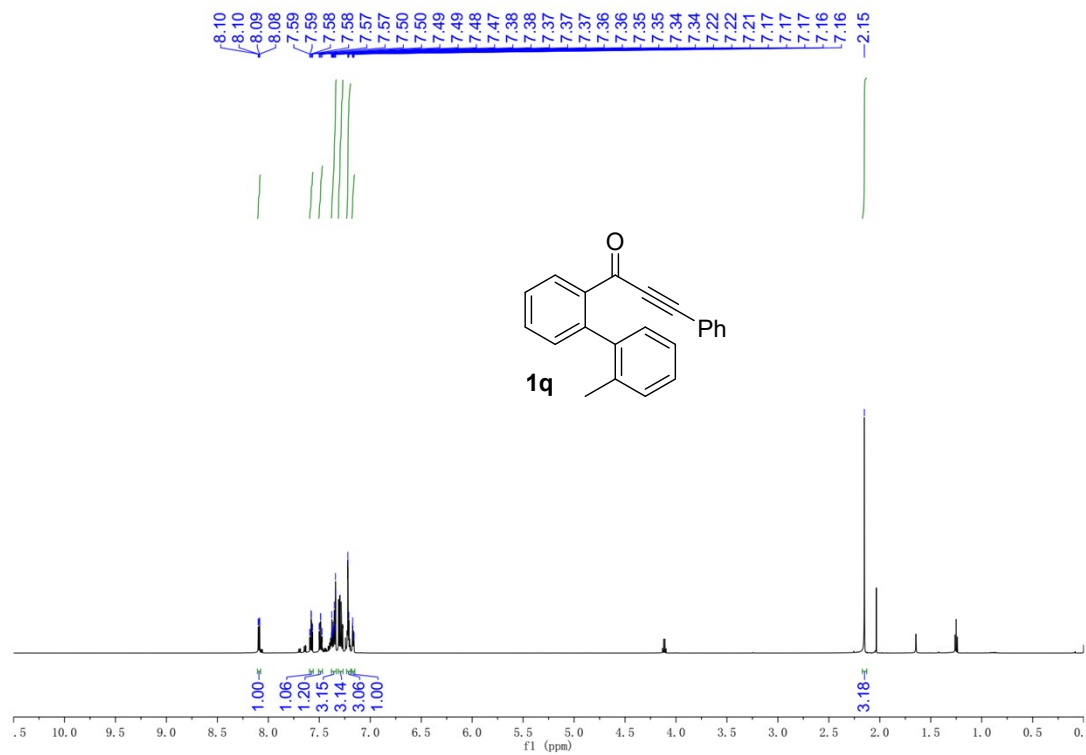
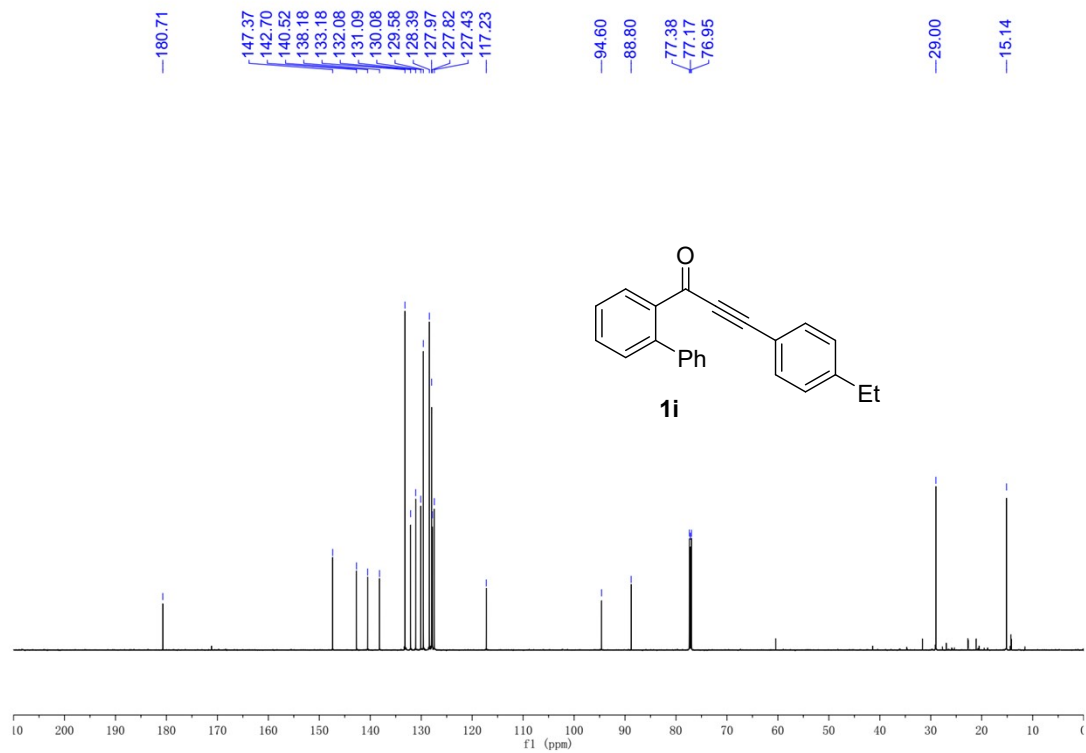
5 ^1H NMR , ^{13}C NMR and ^{19}F NMR of the products

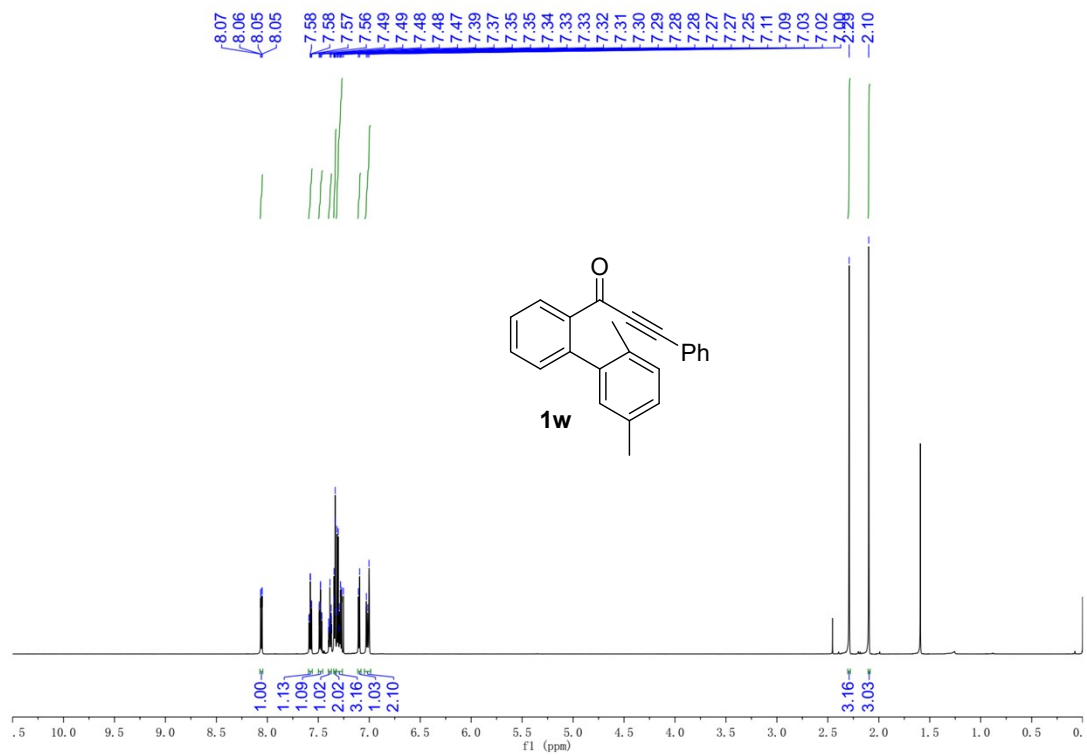
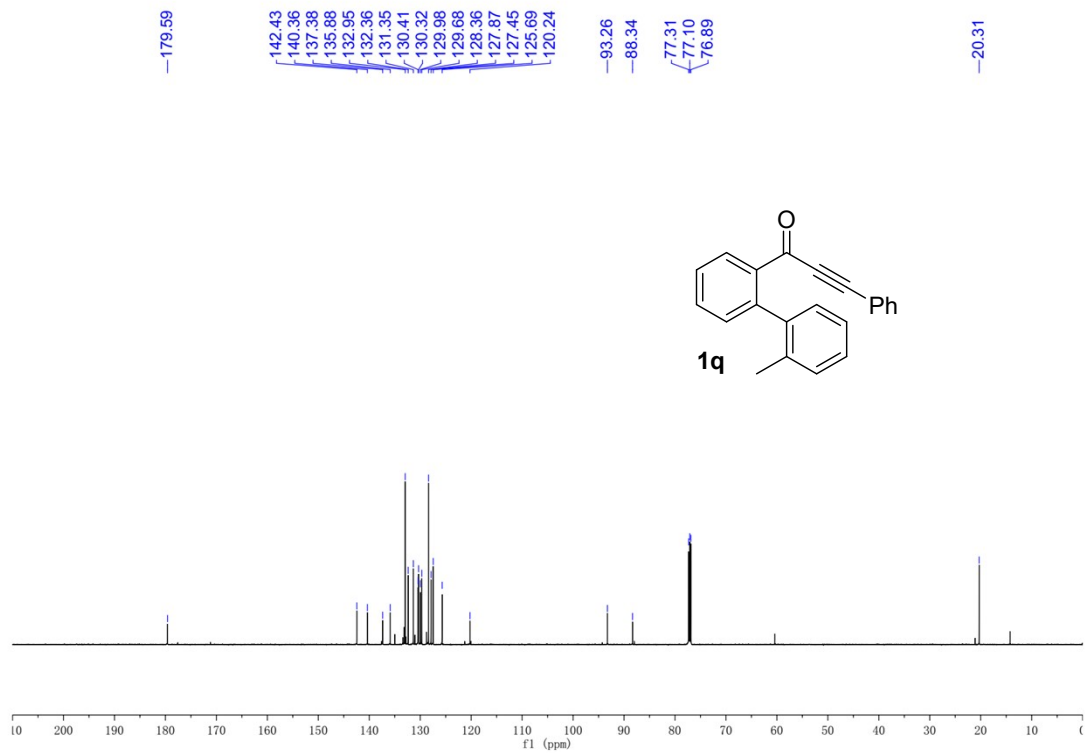


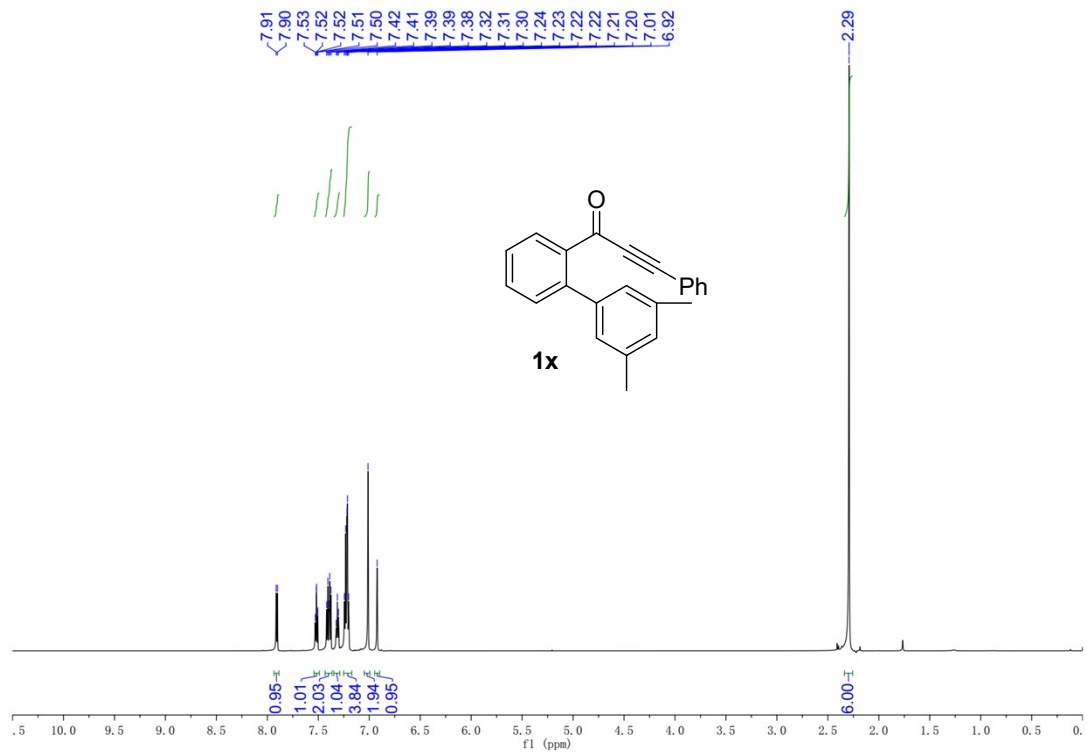
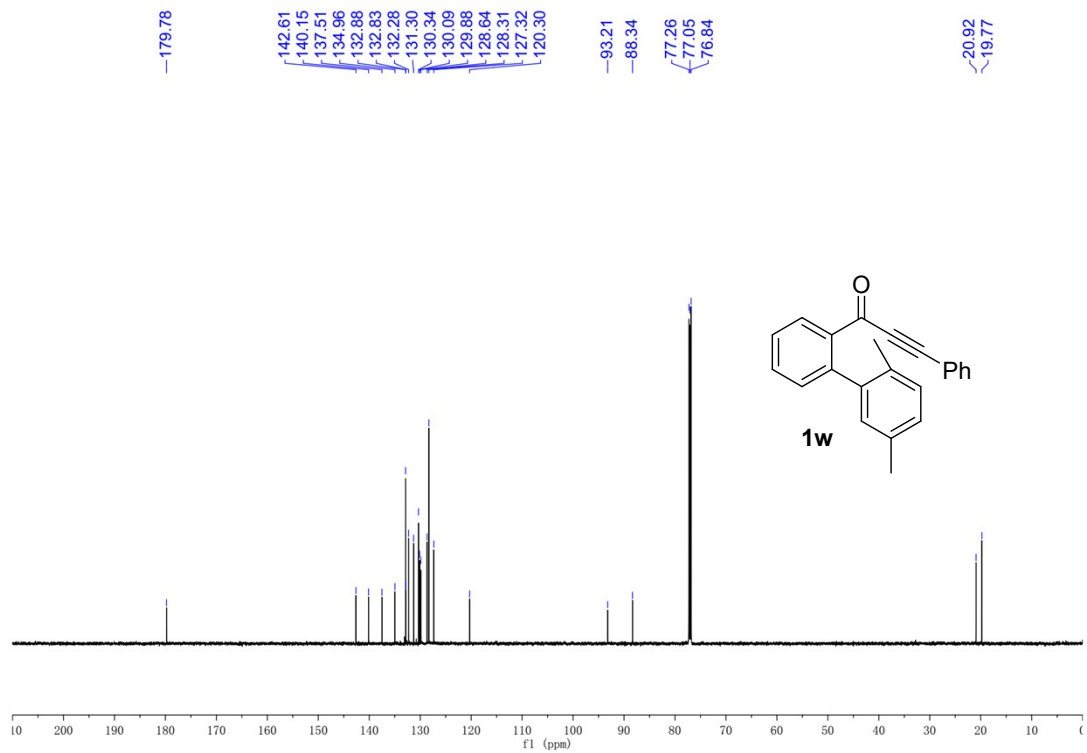


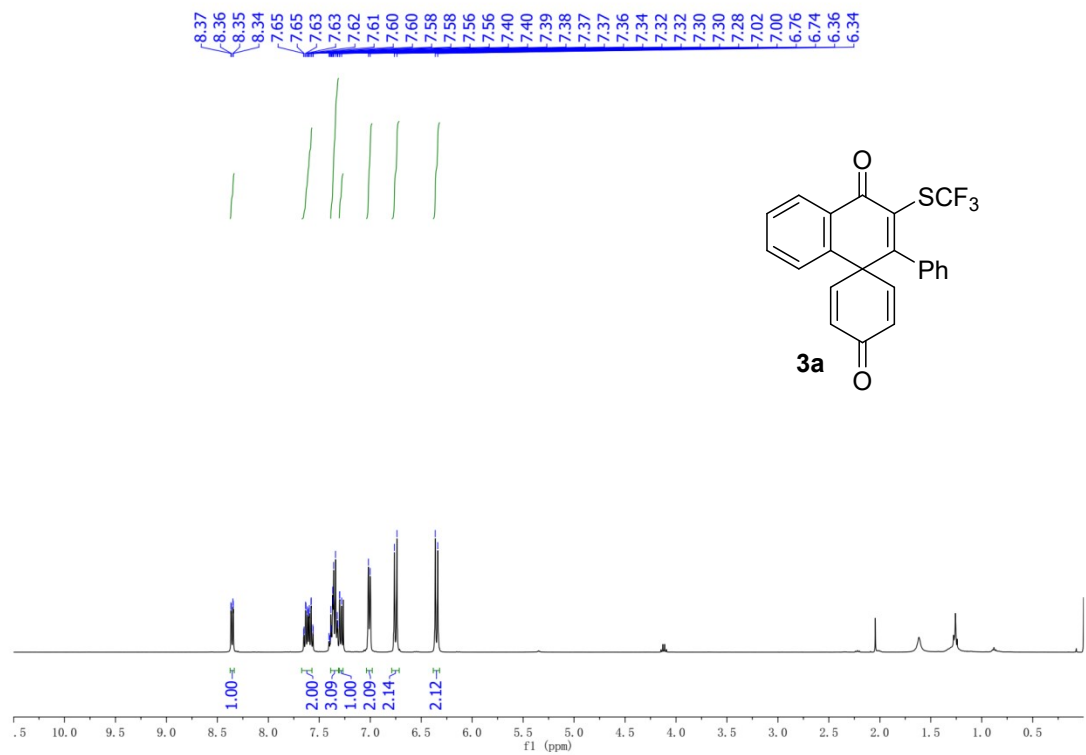
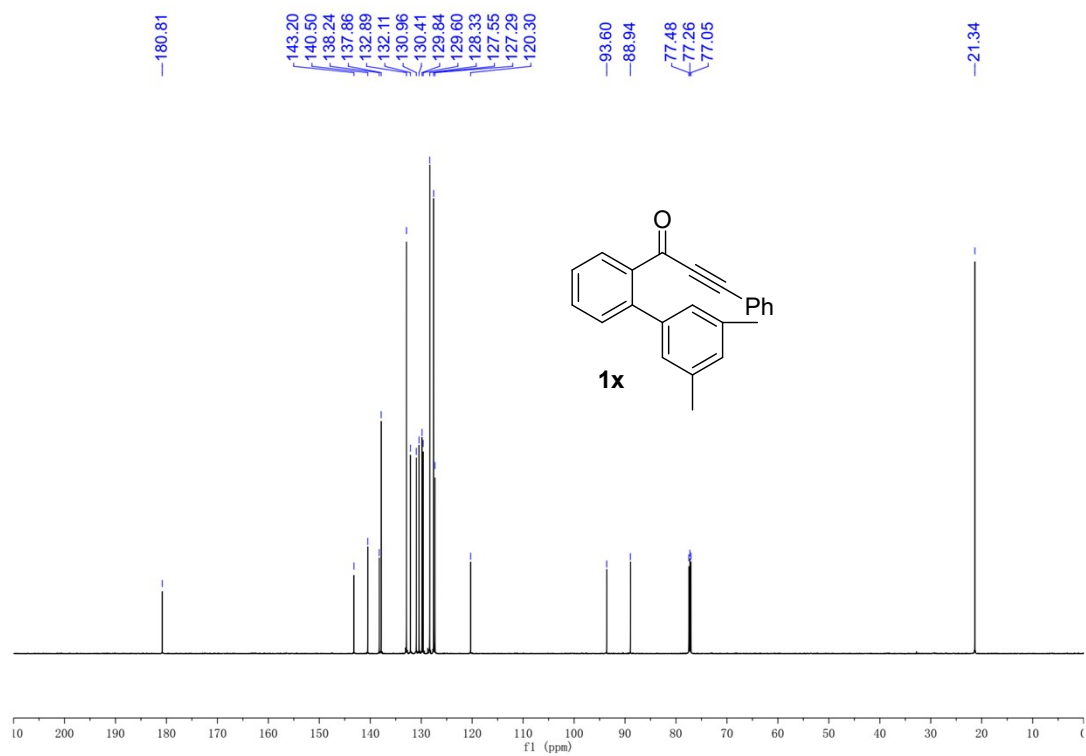


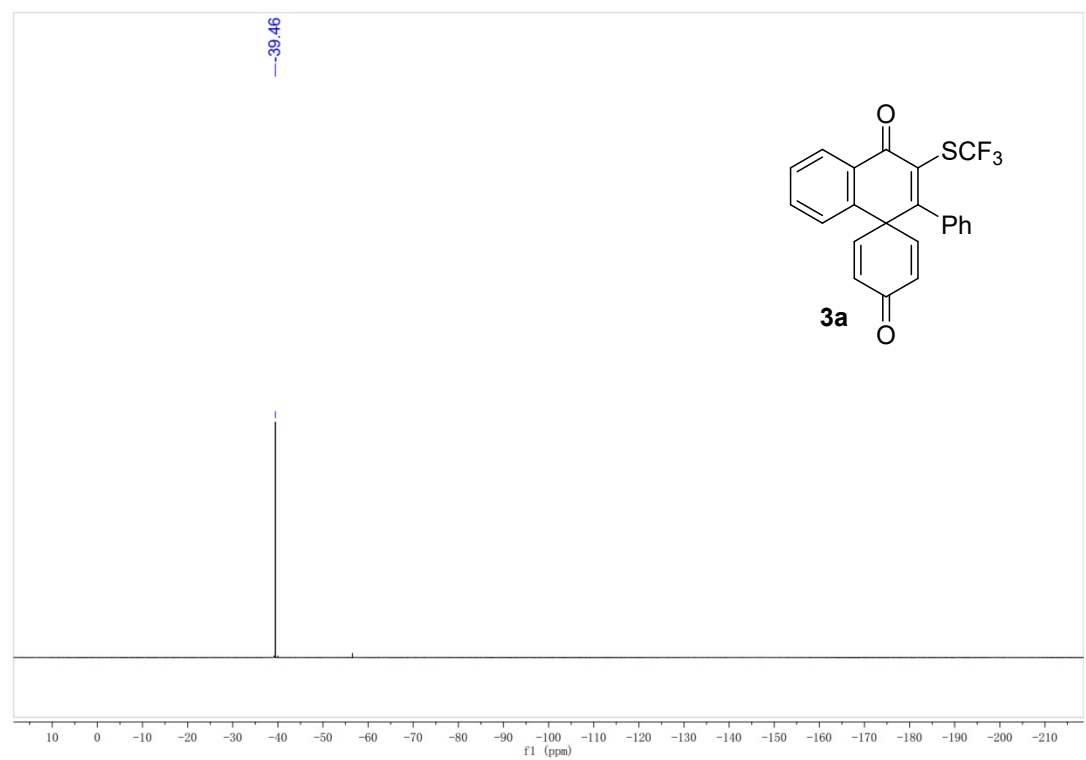
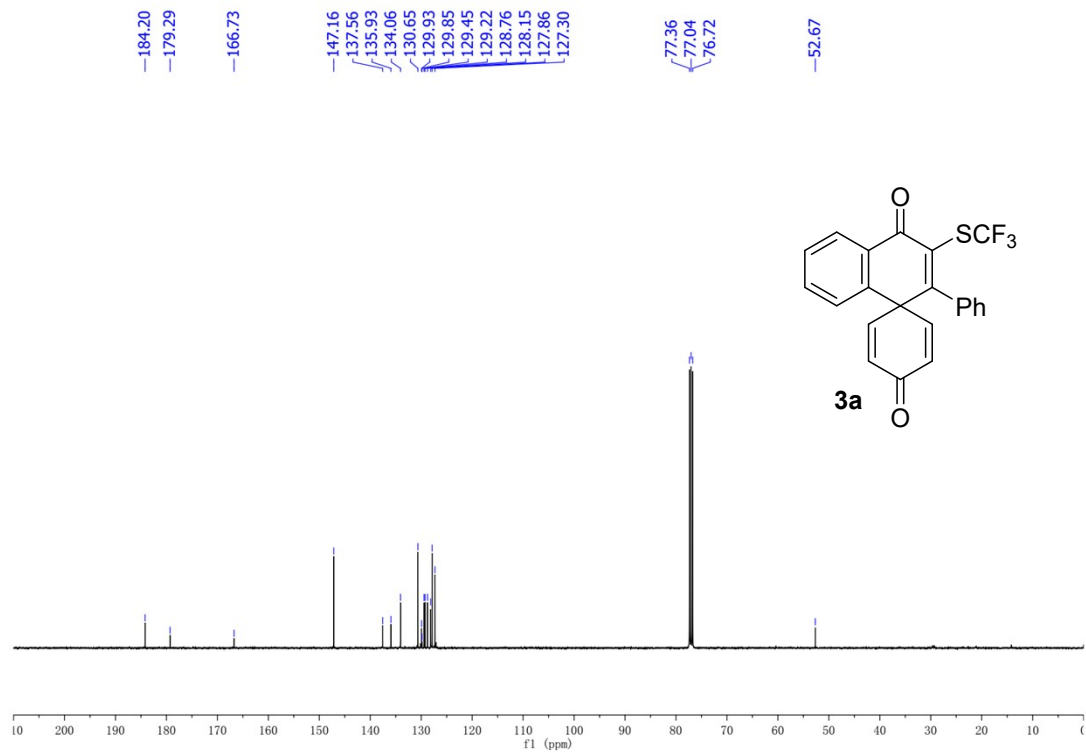


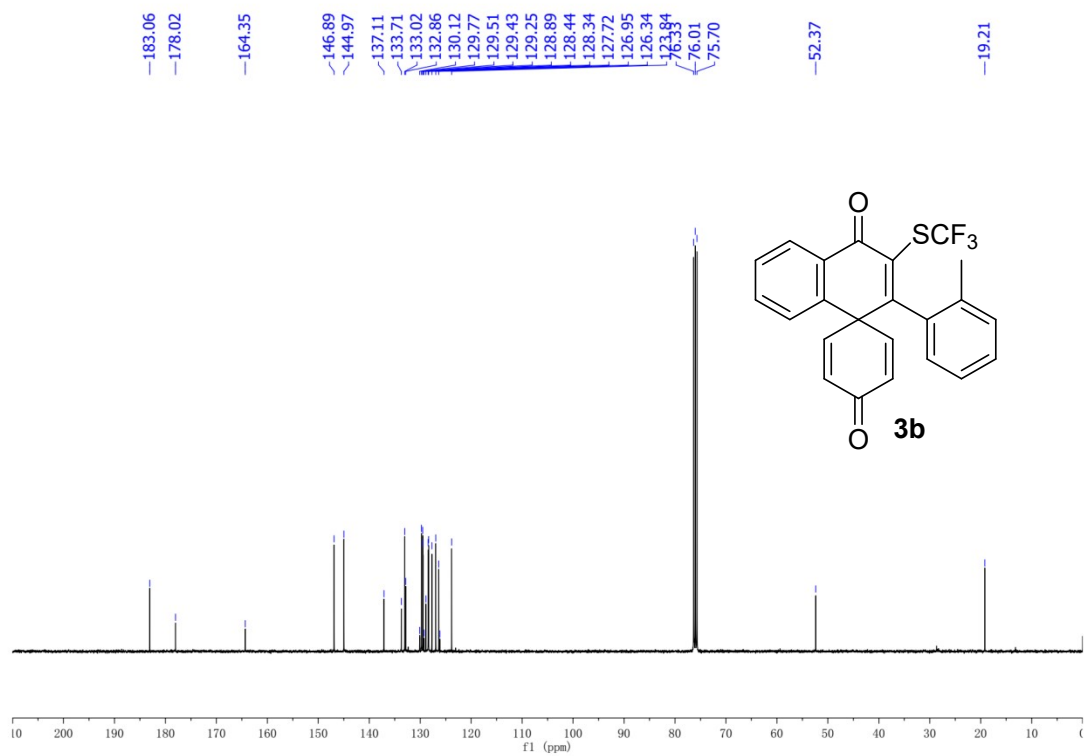
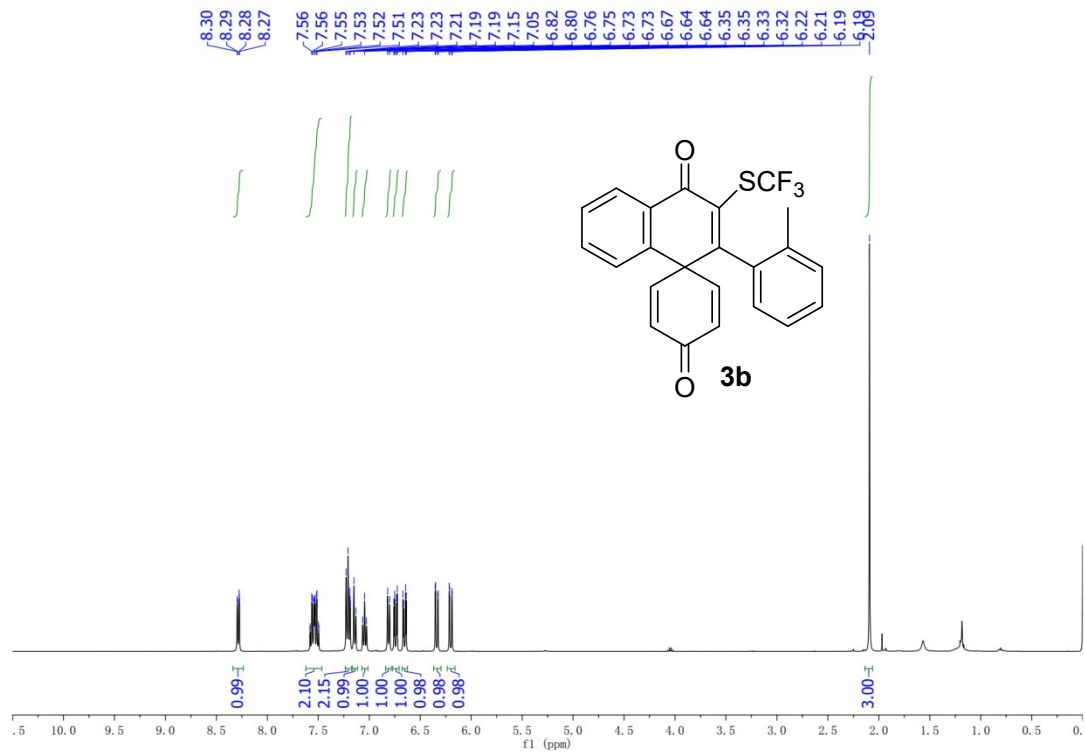


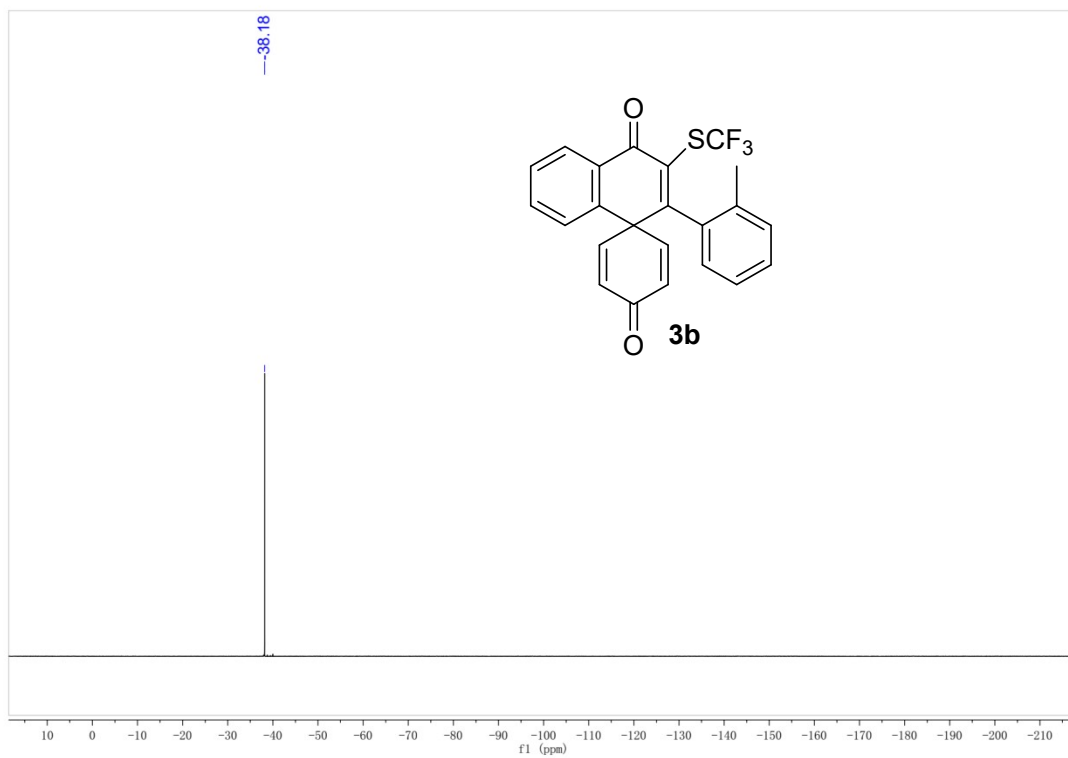




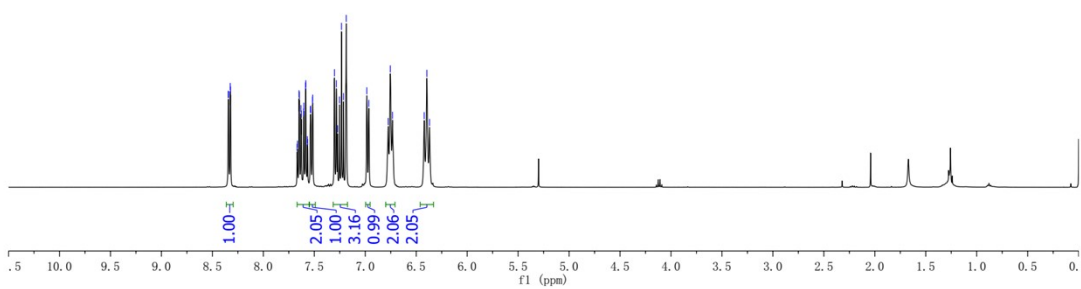
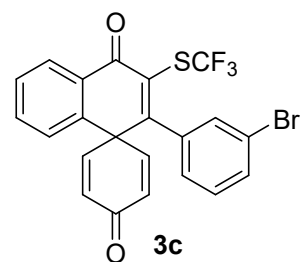
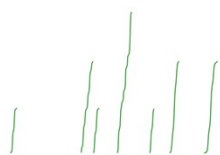


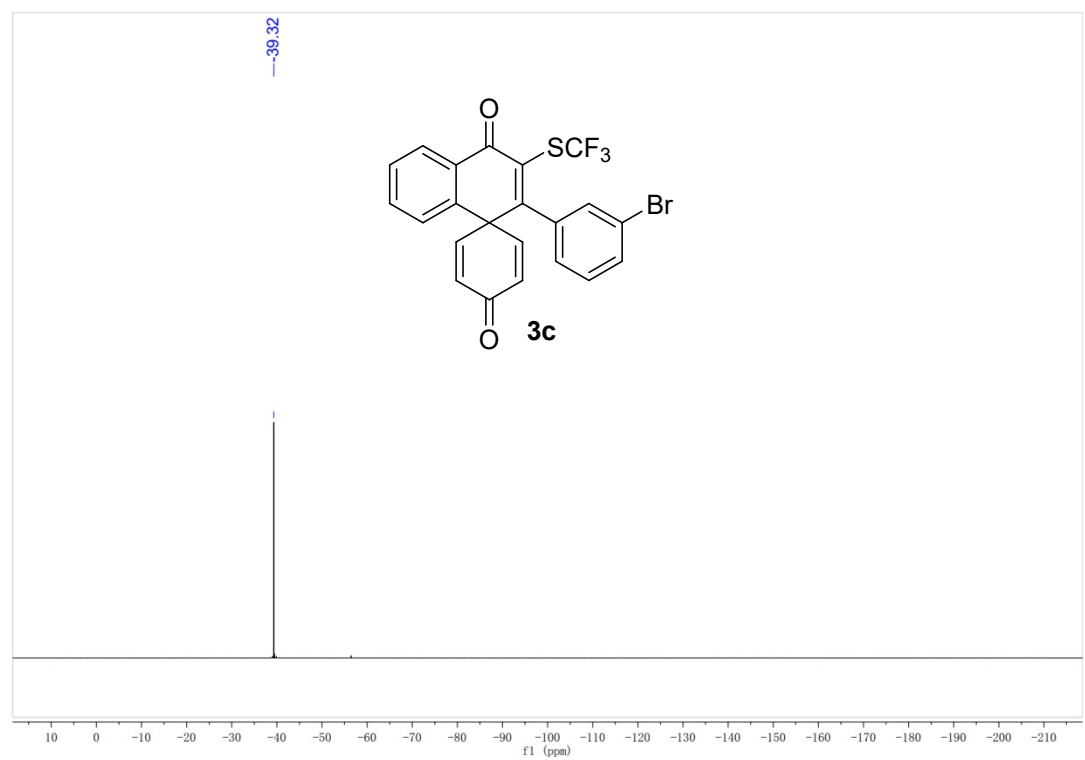
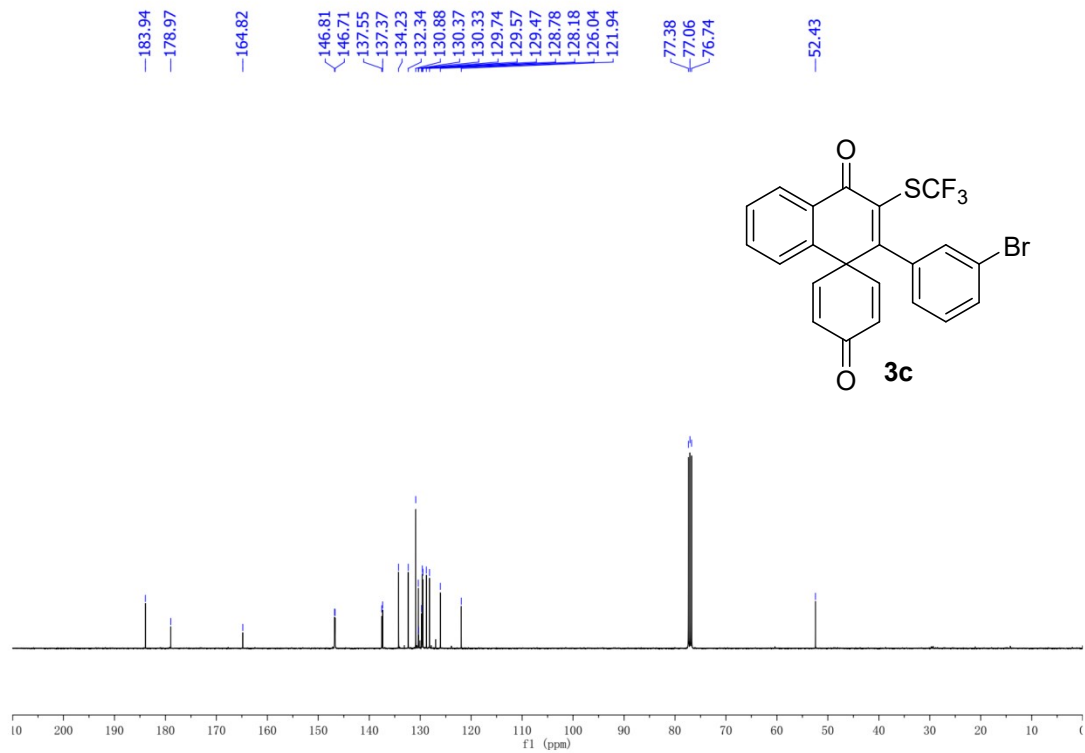


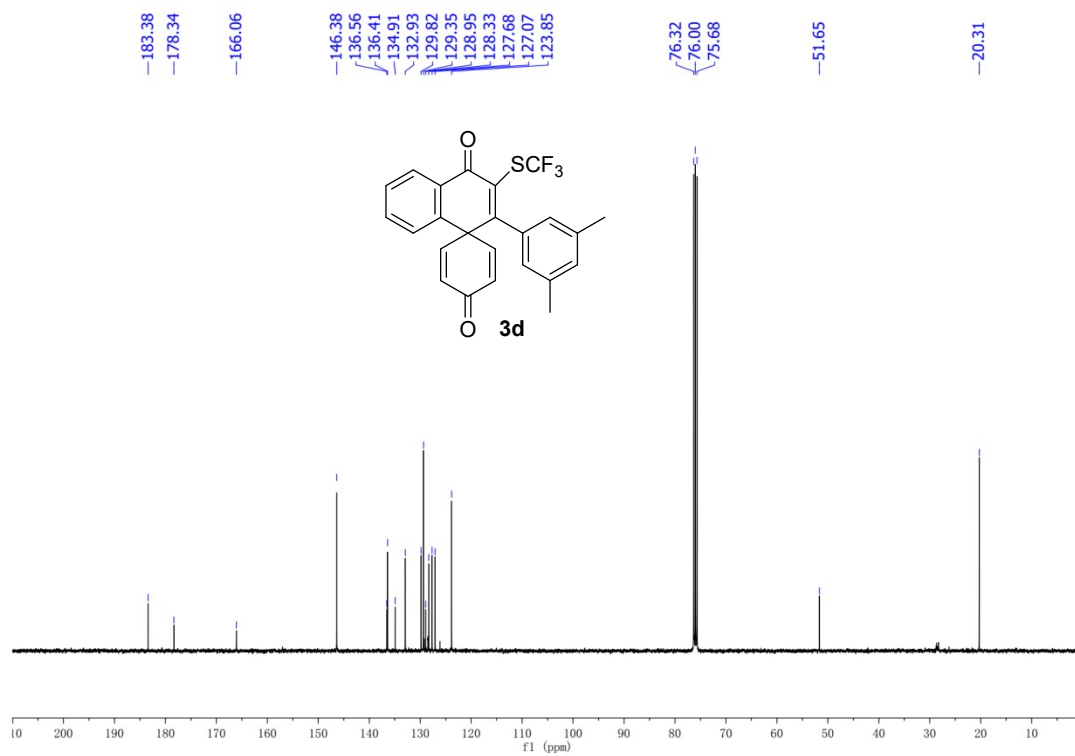
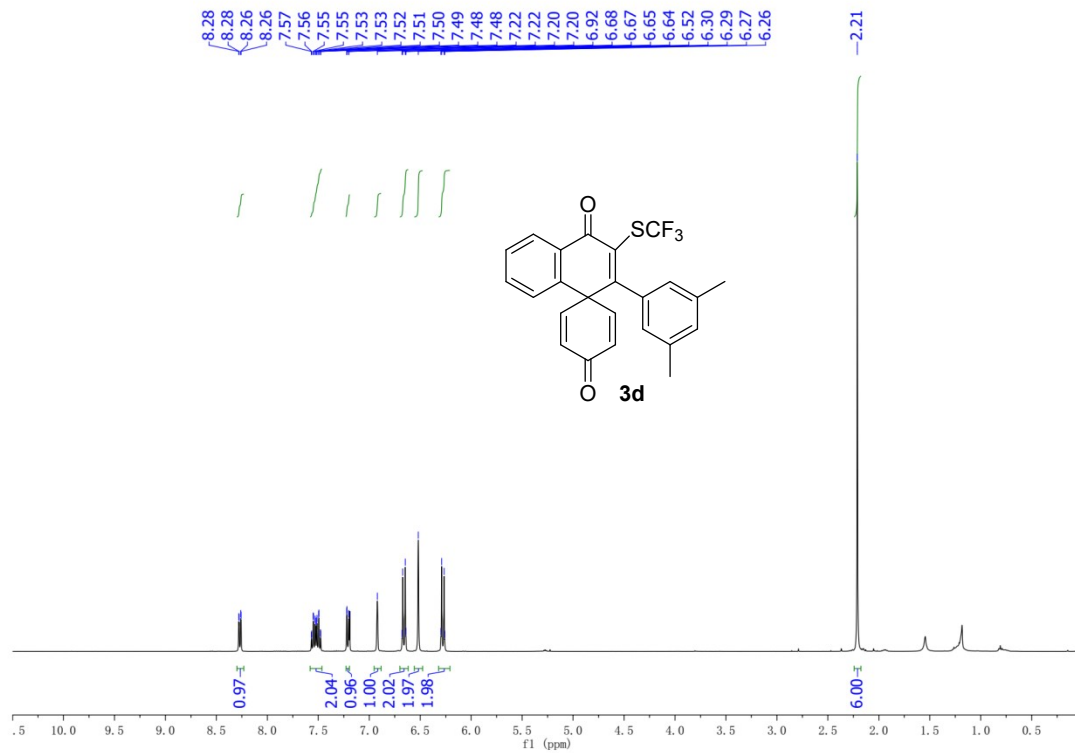


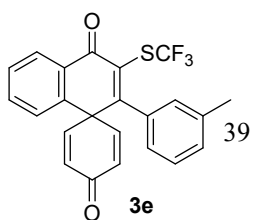
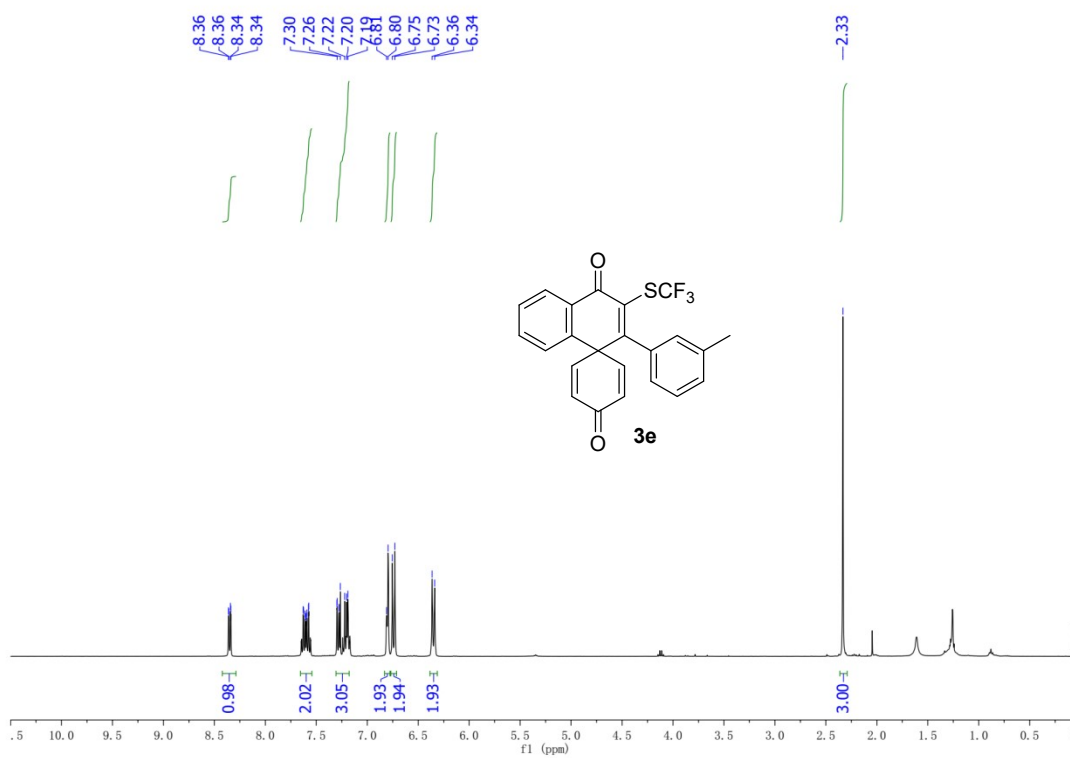


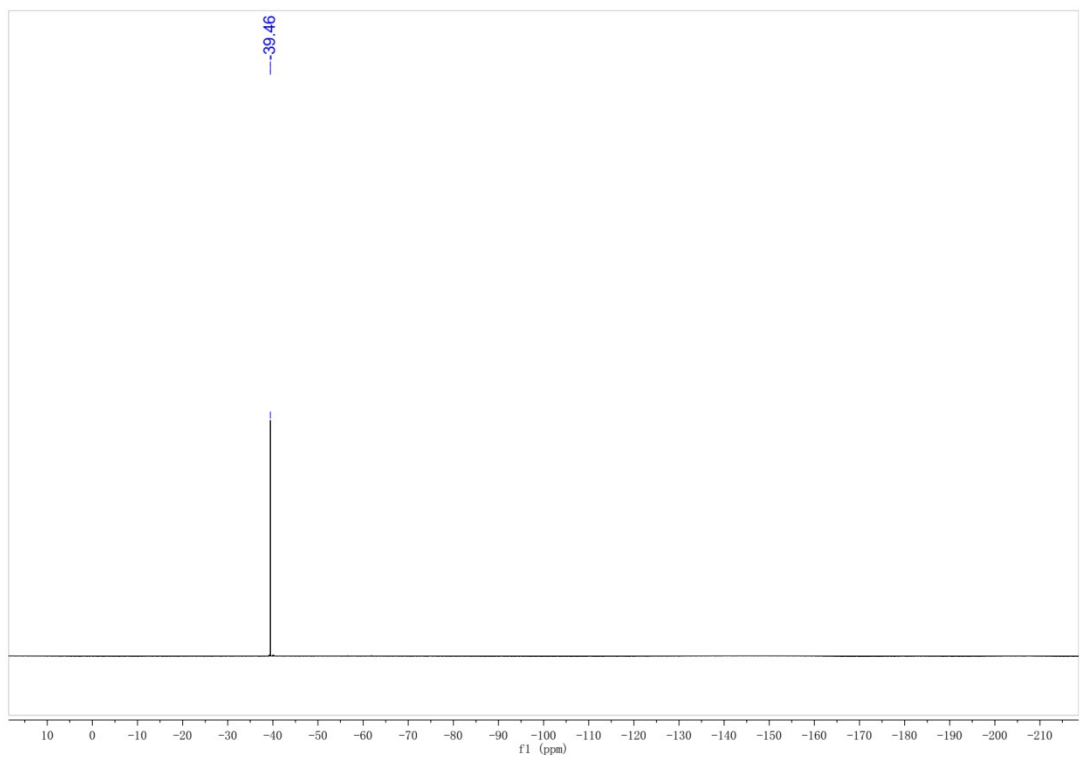
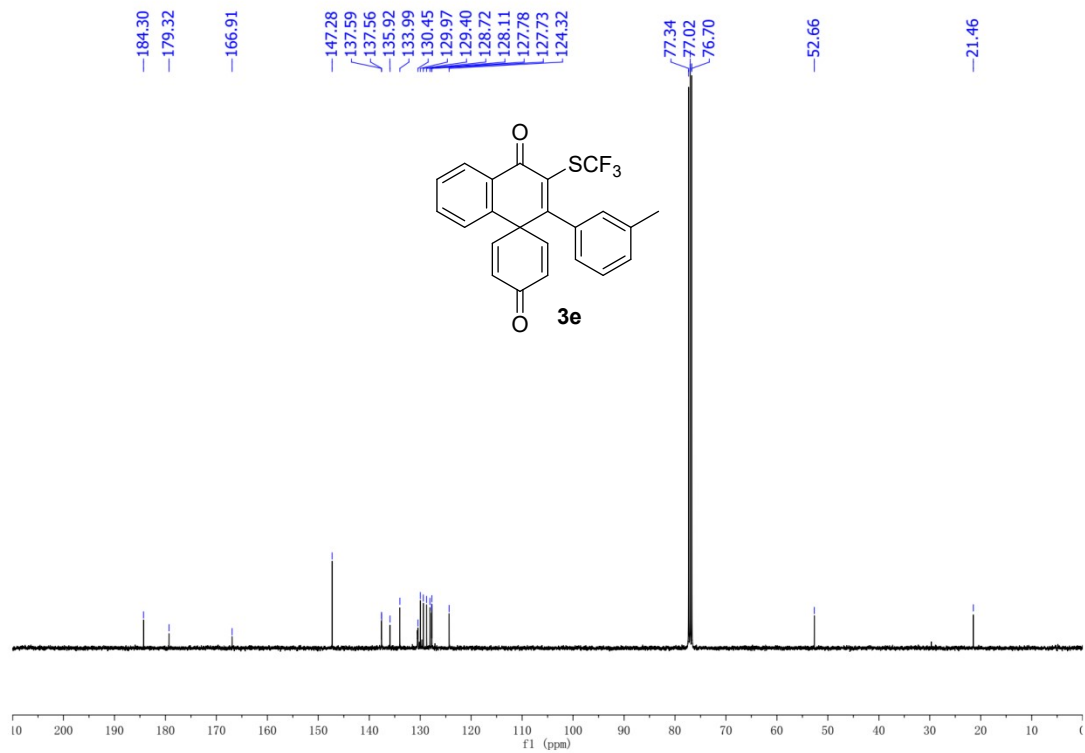
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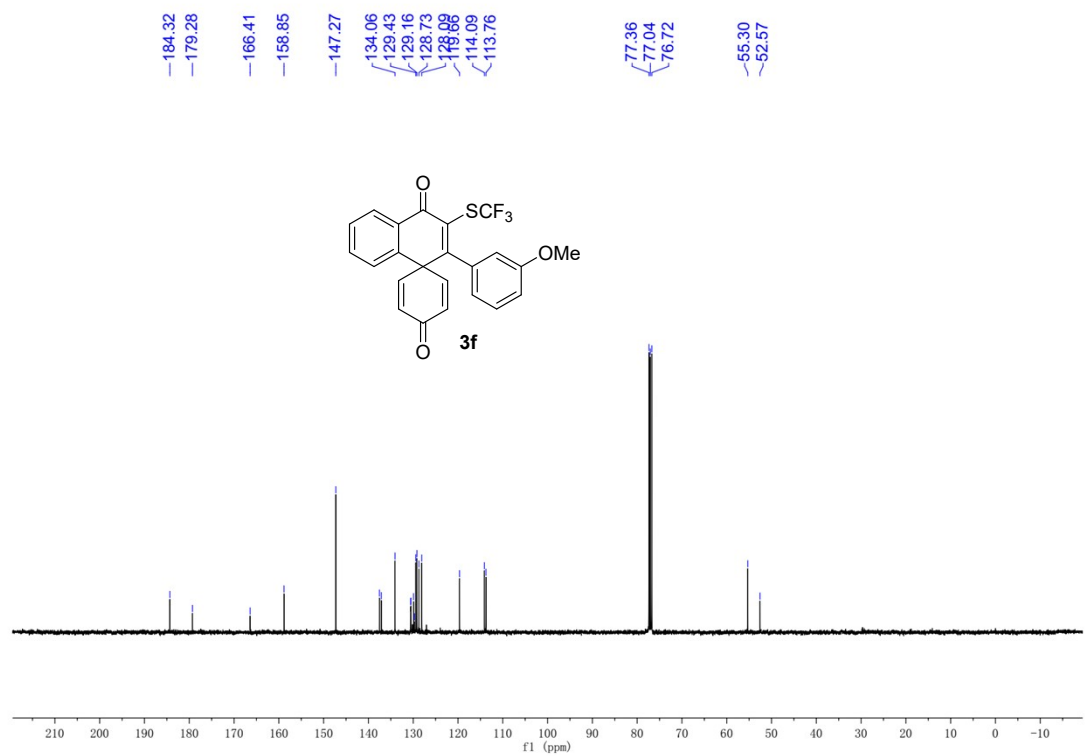
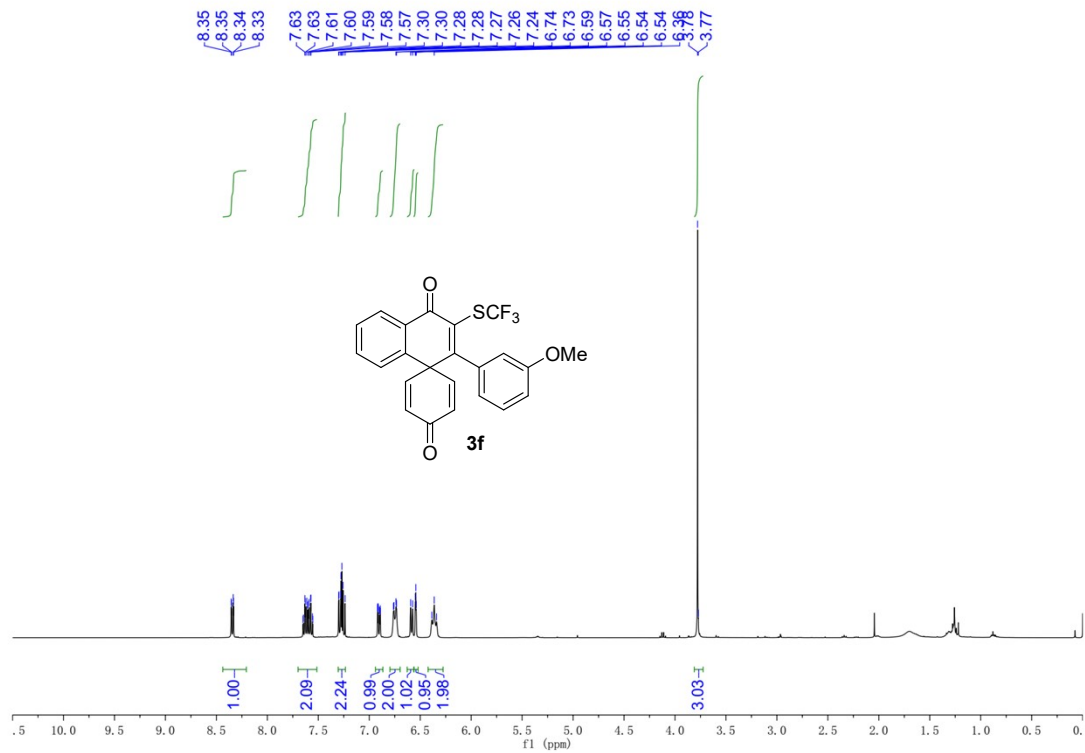


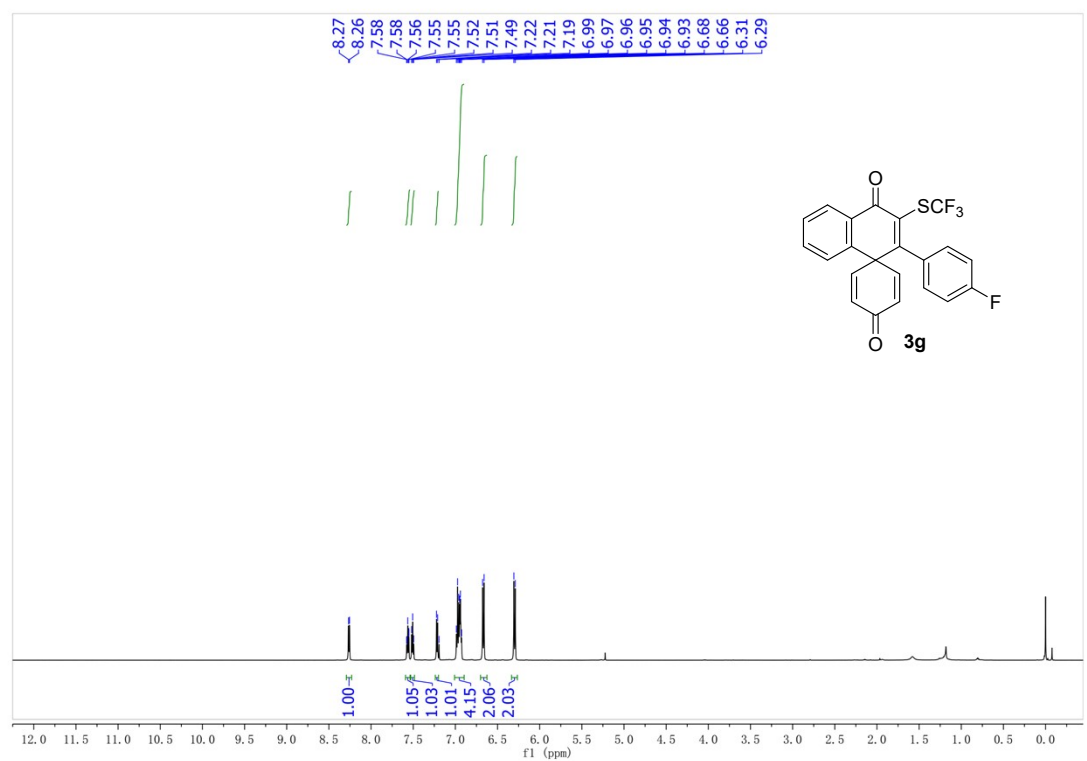
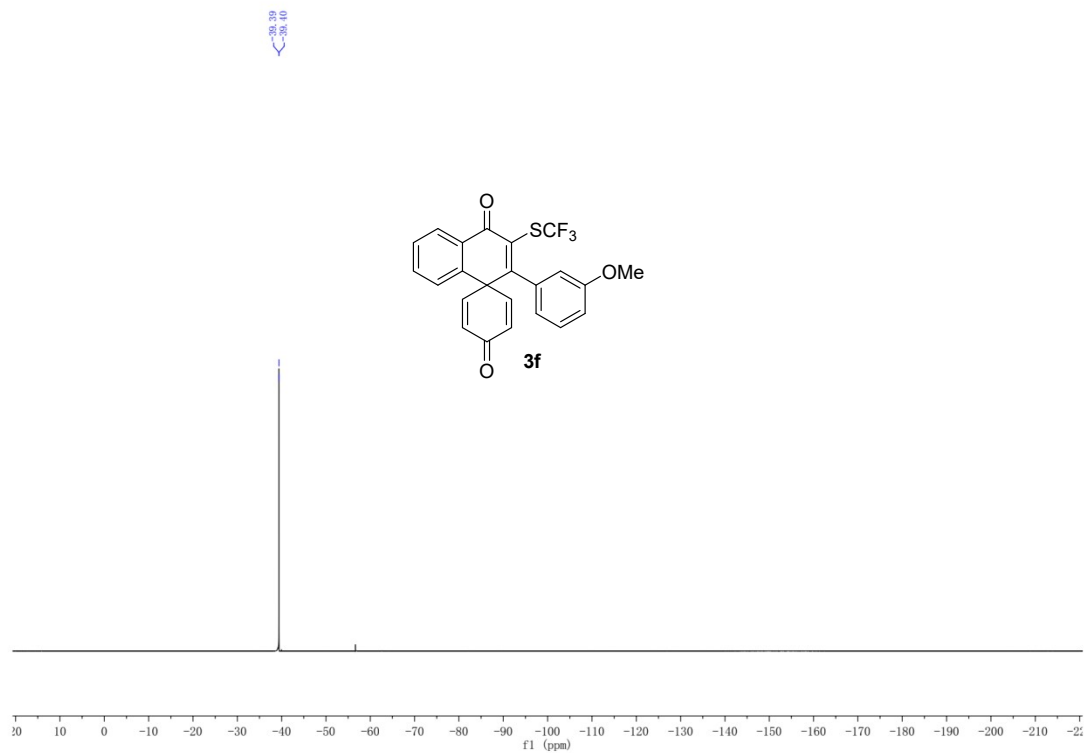


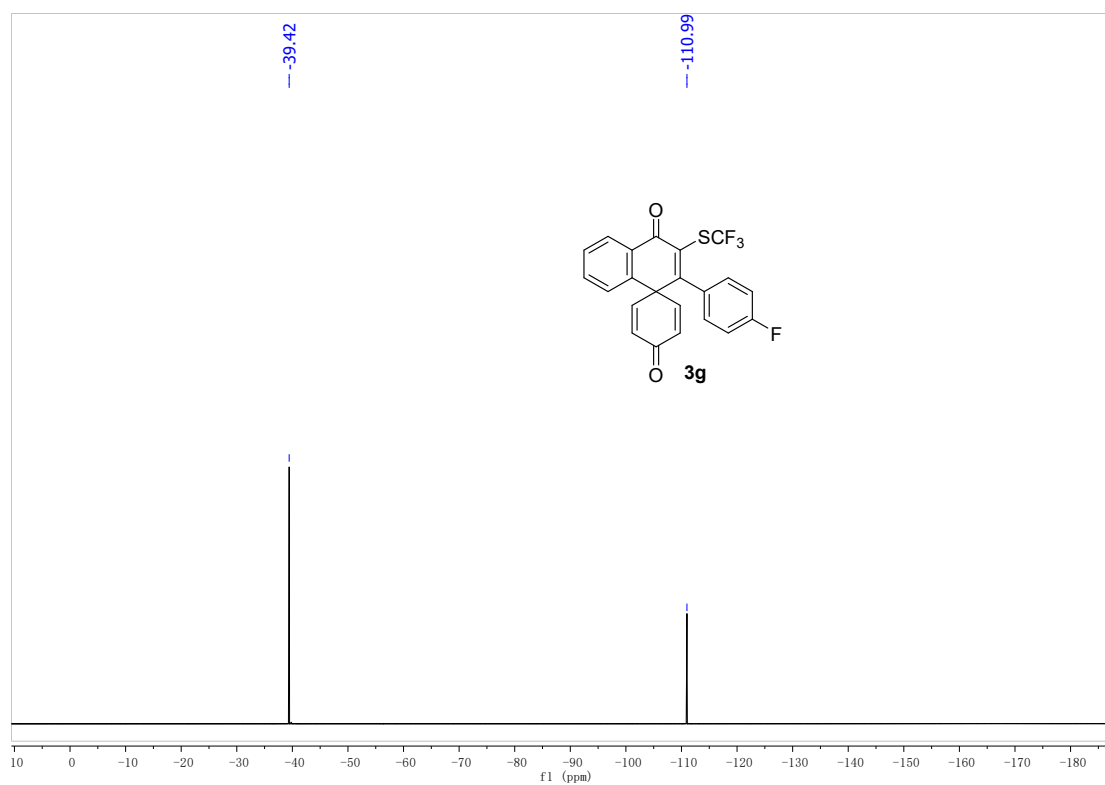
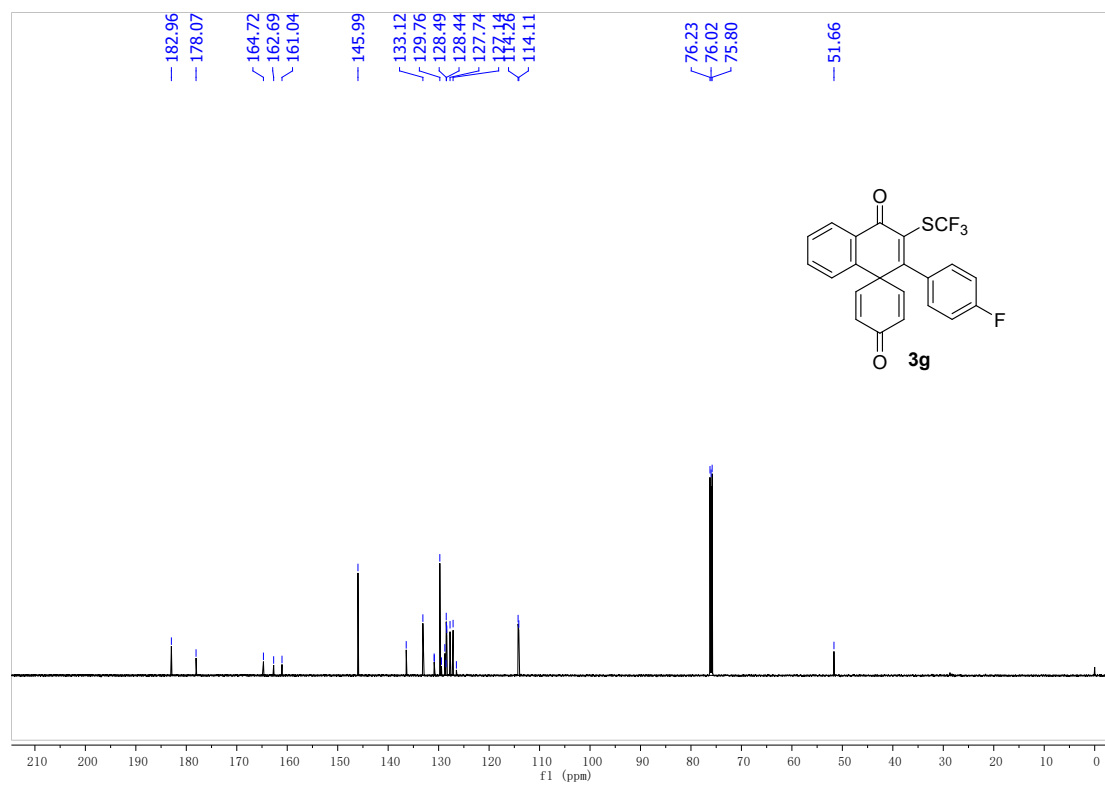


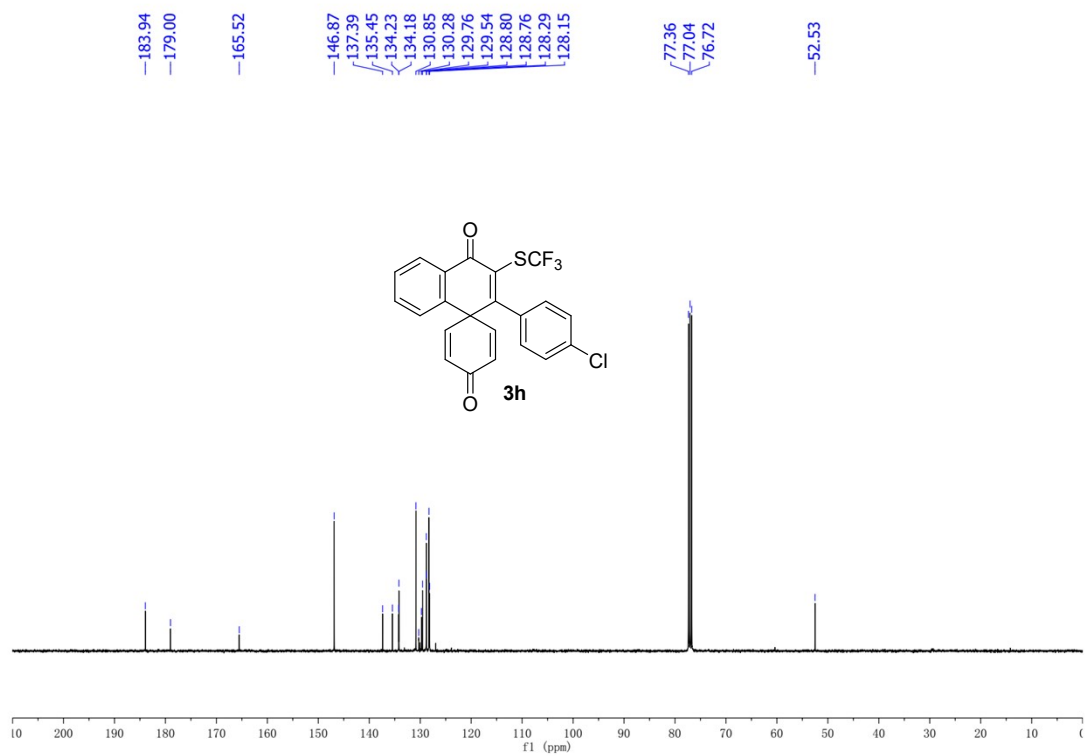
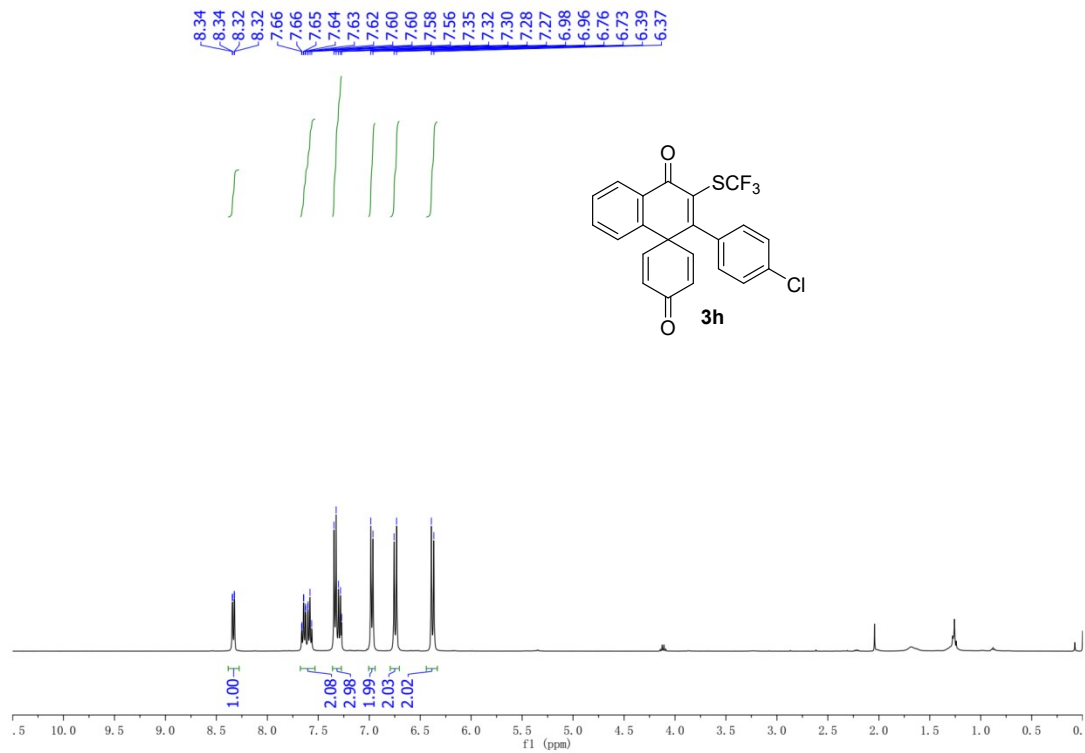


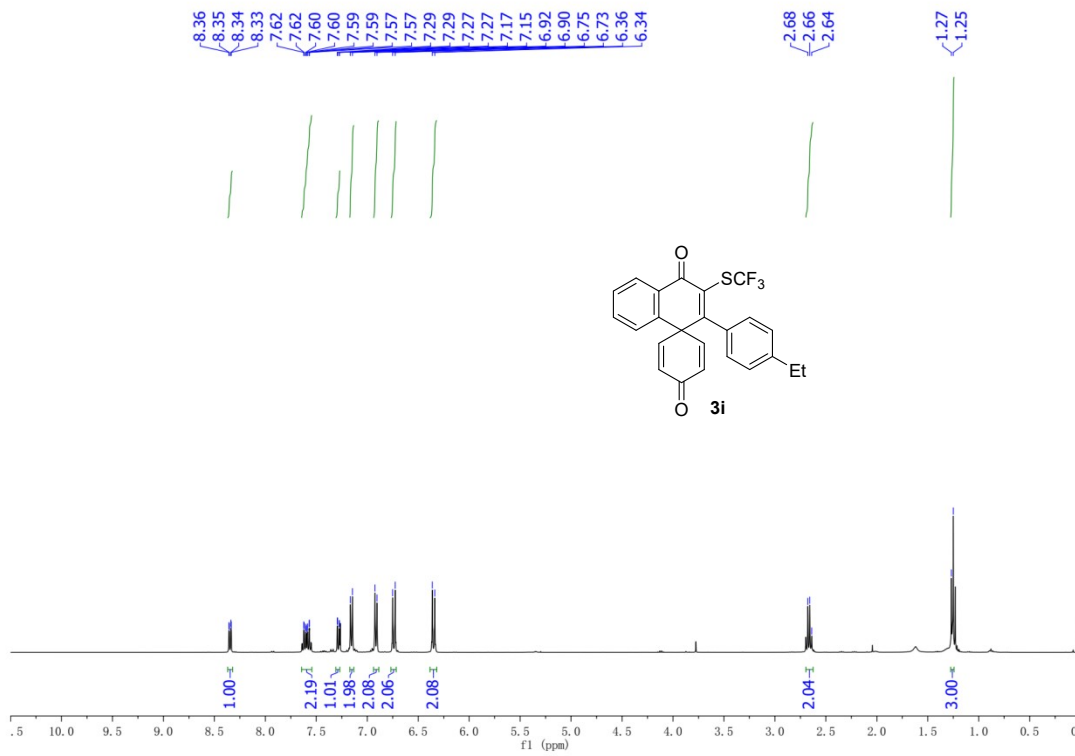
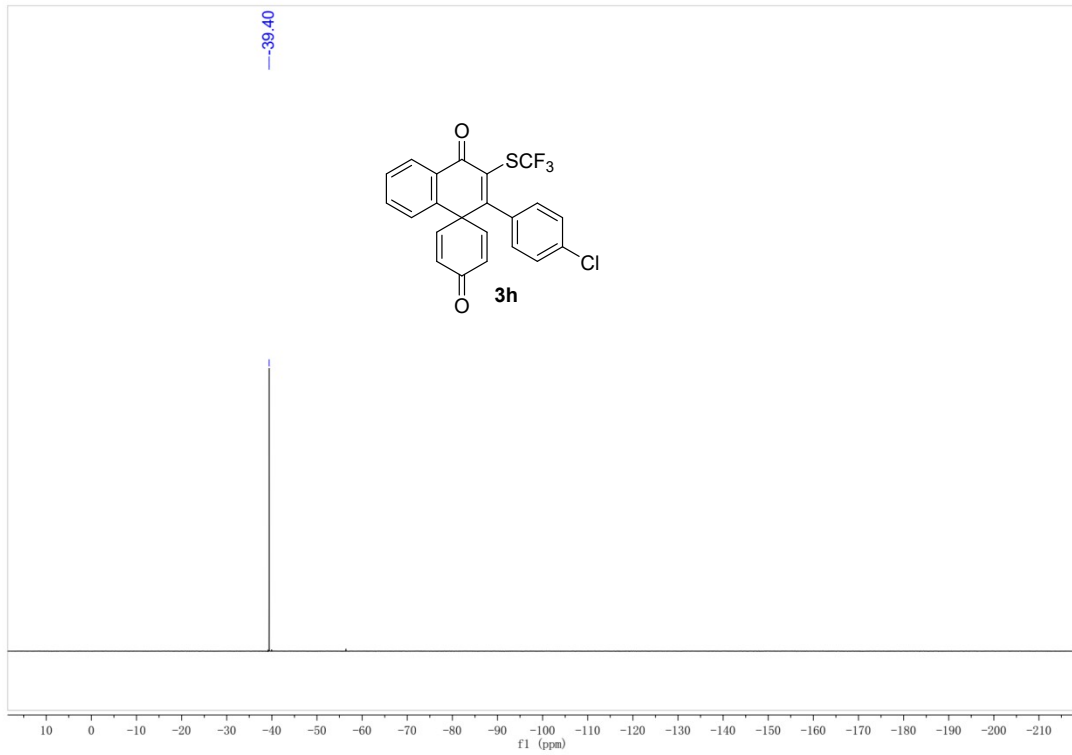


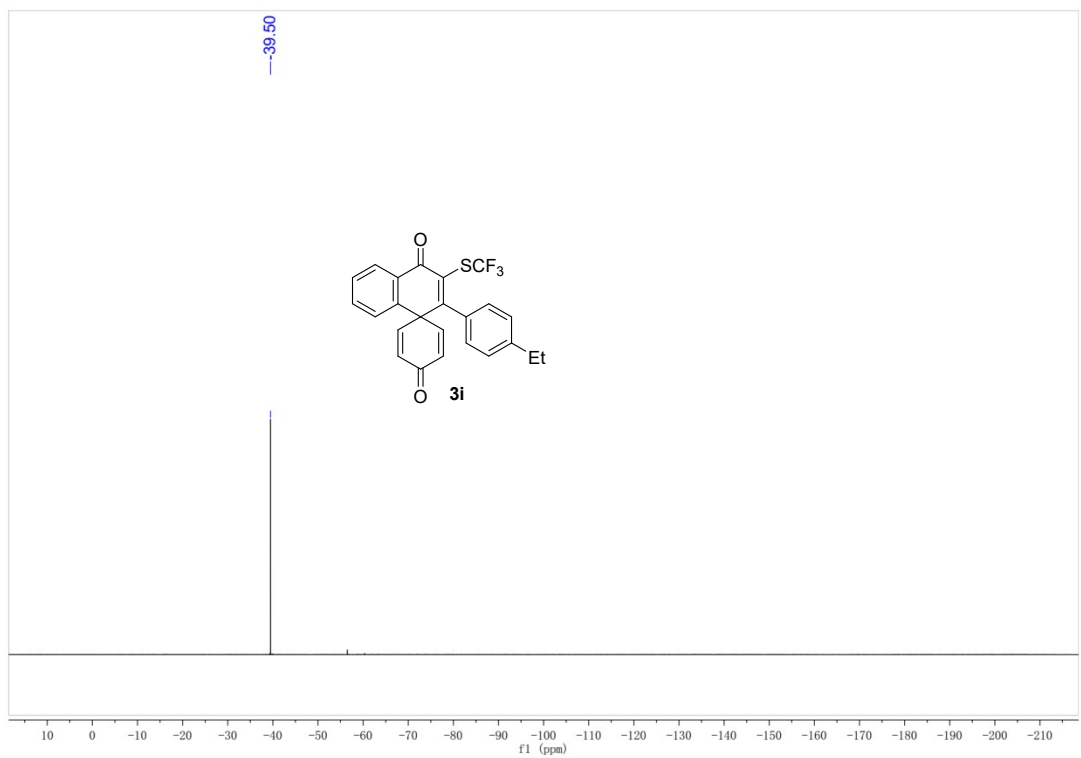
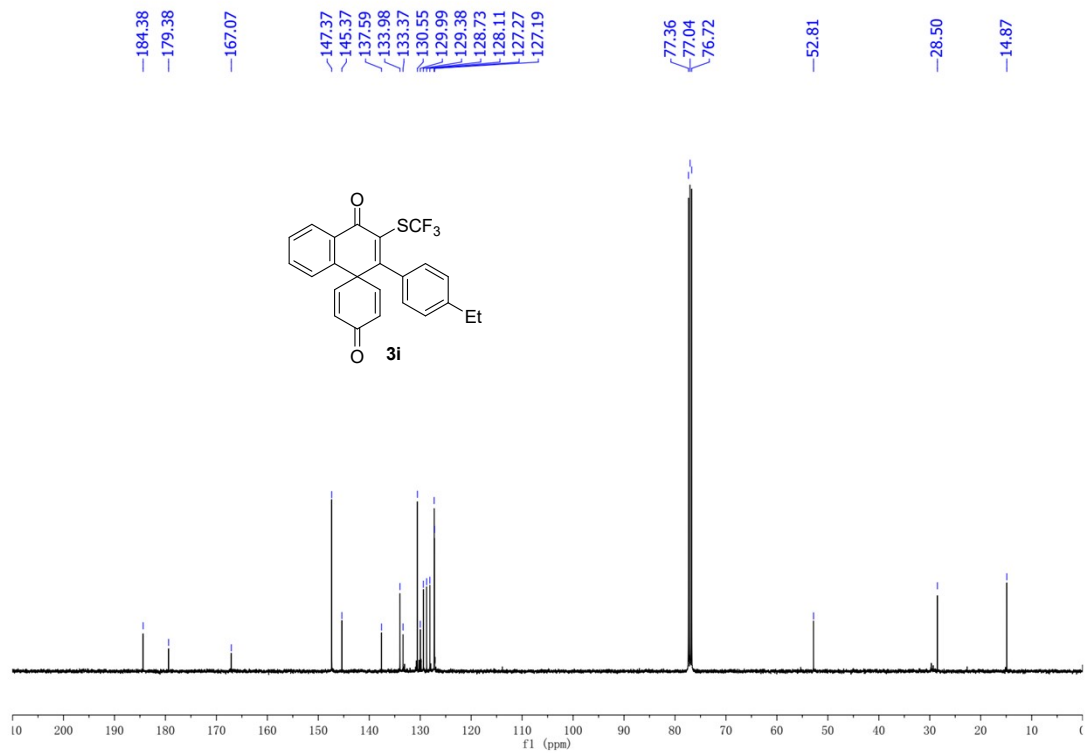


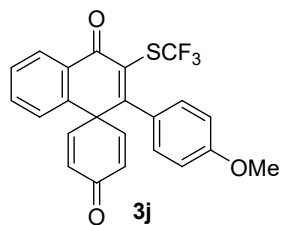
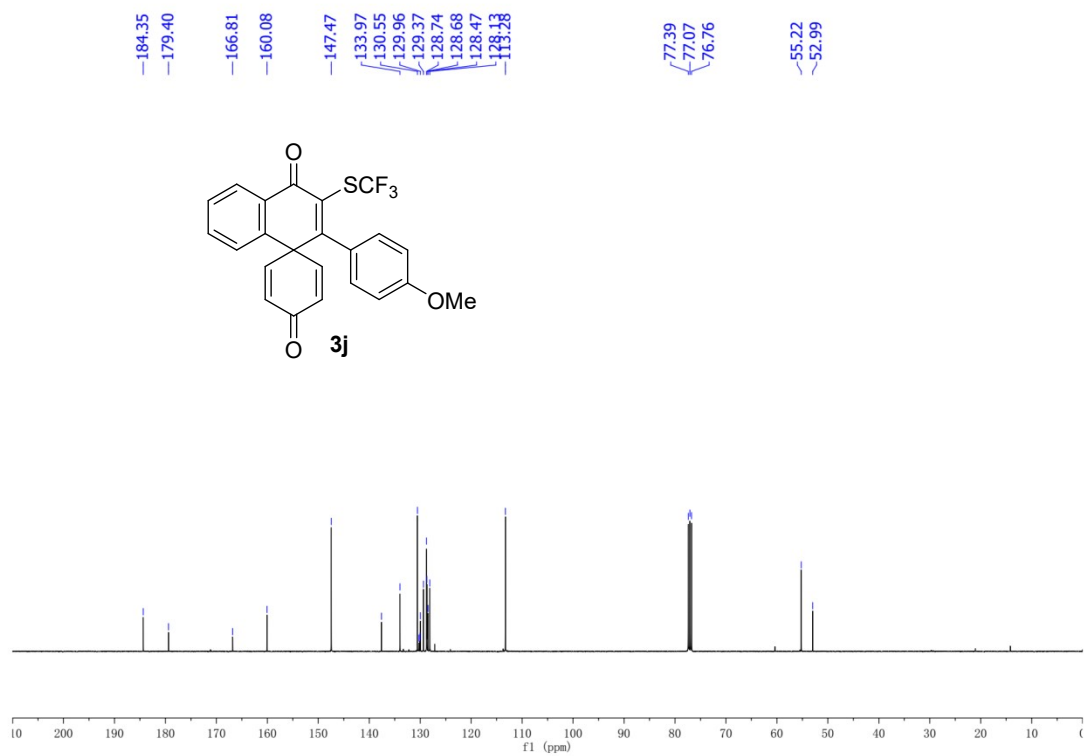
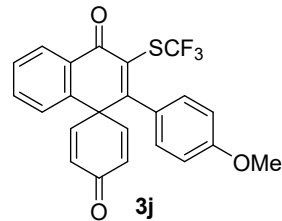
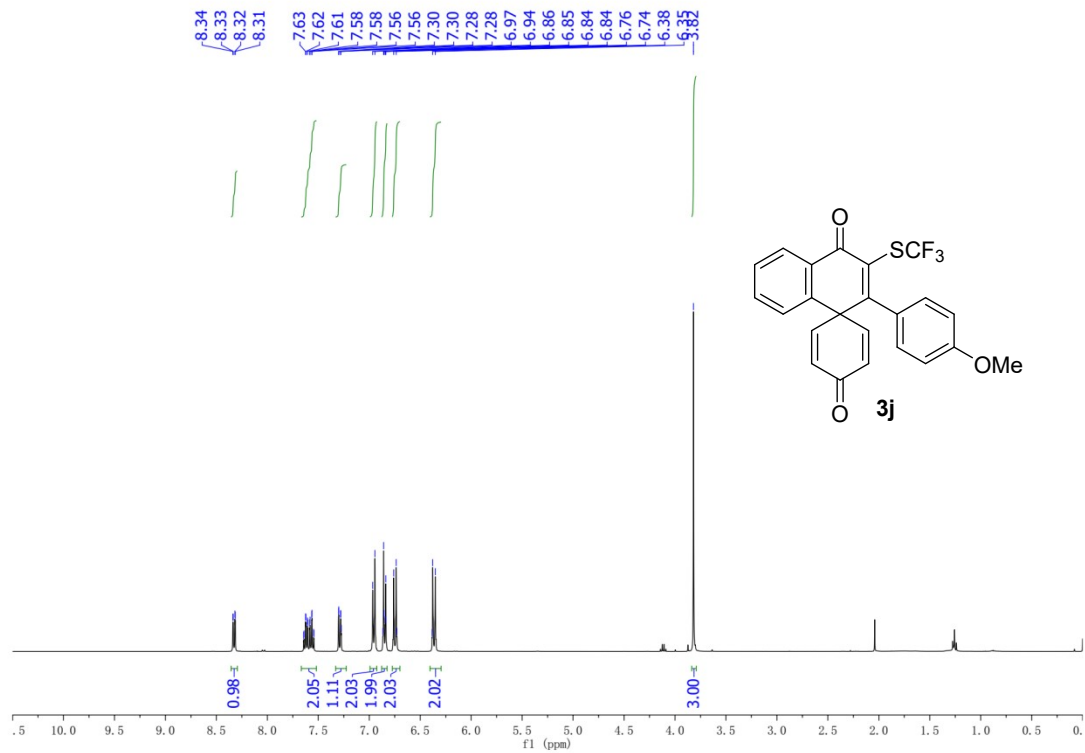


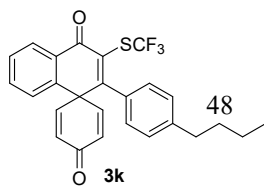
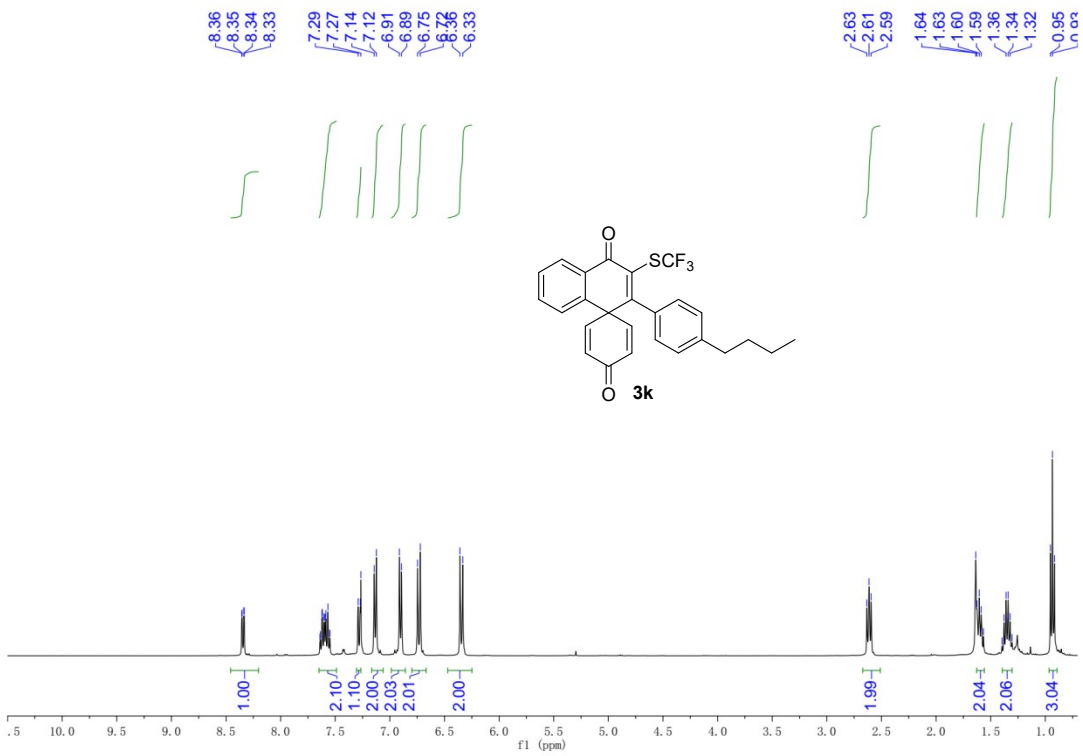
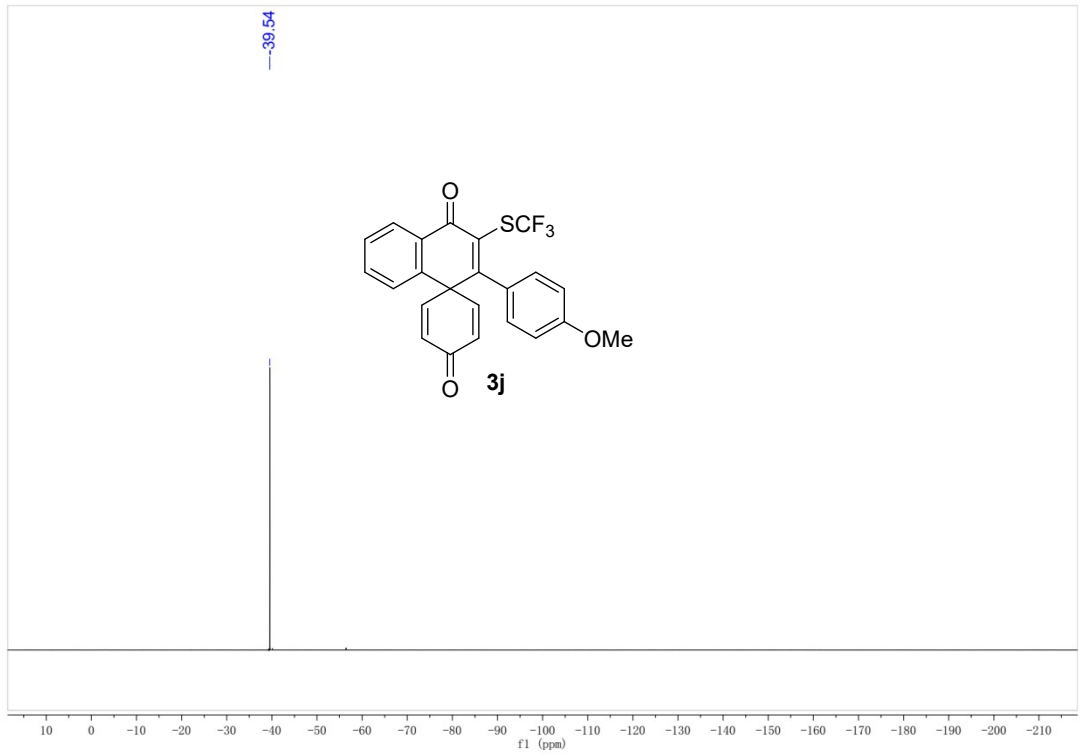




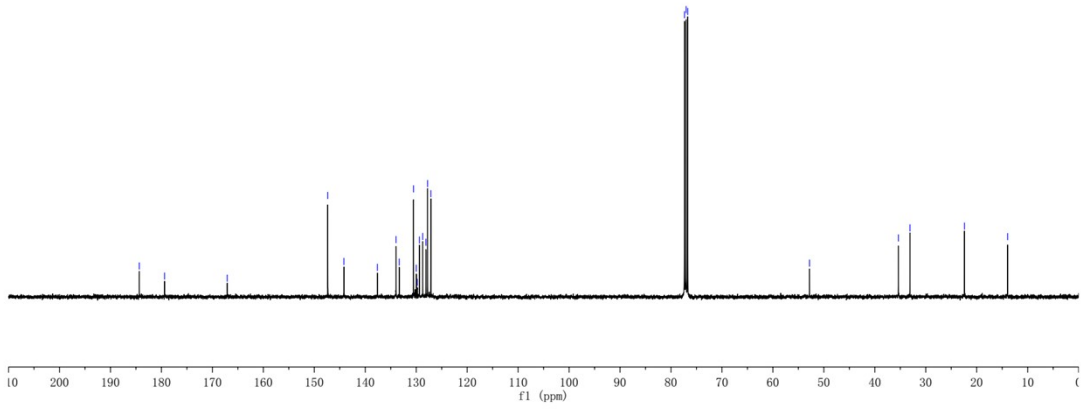
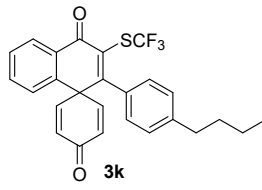




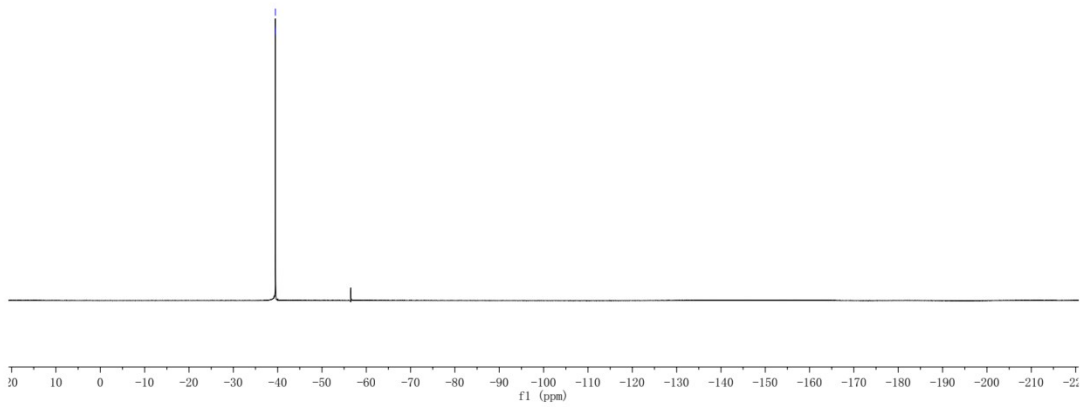


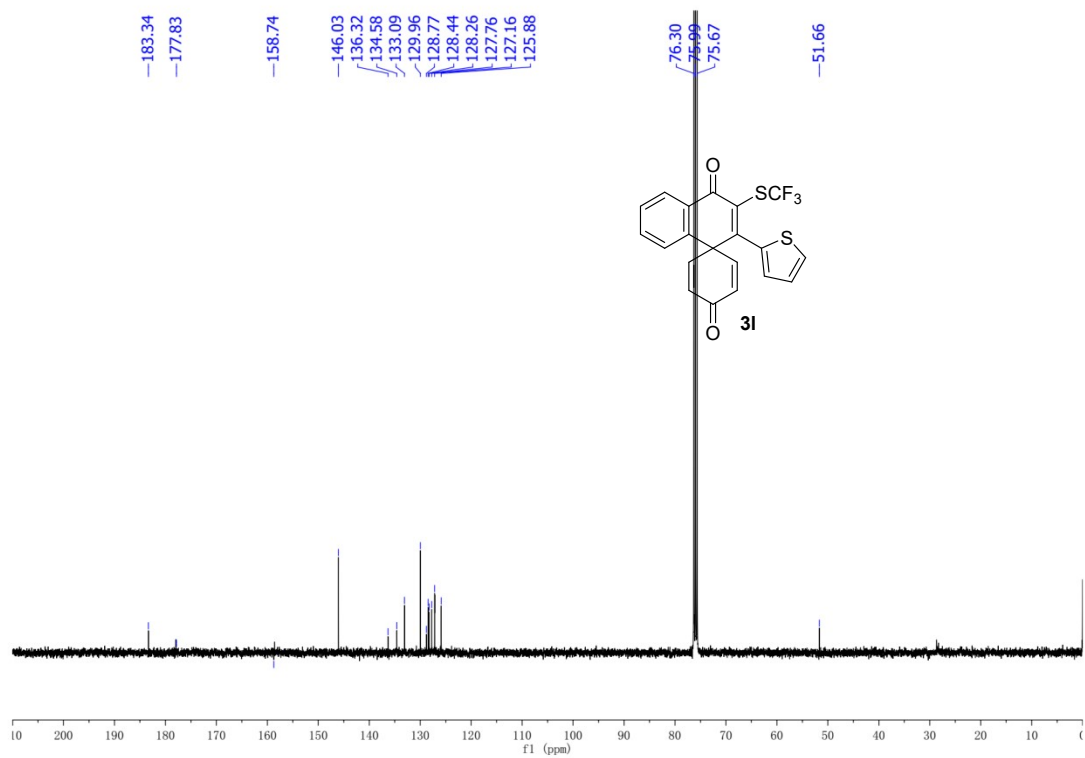
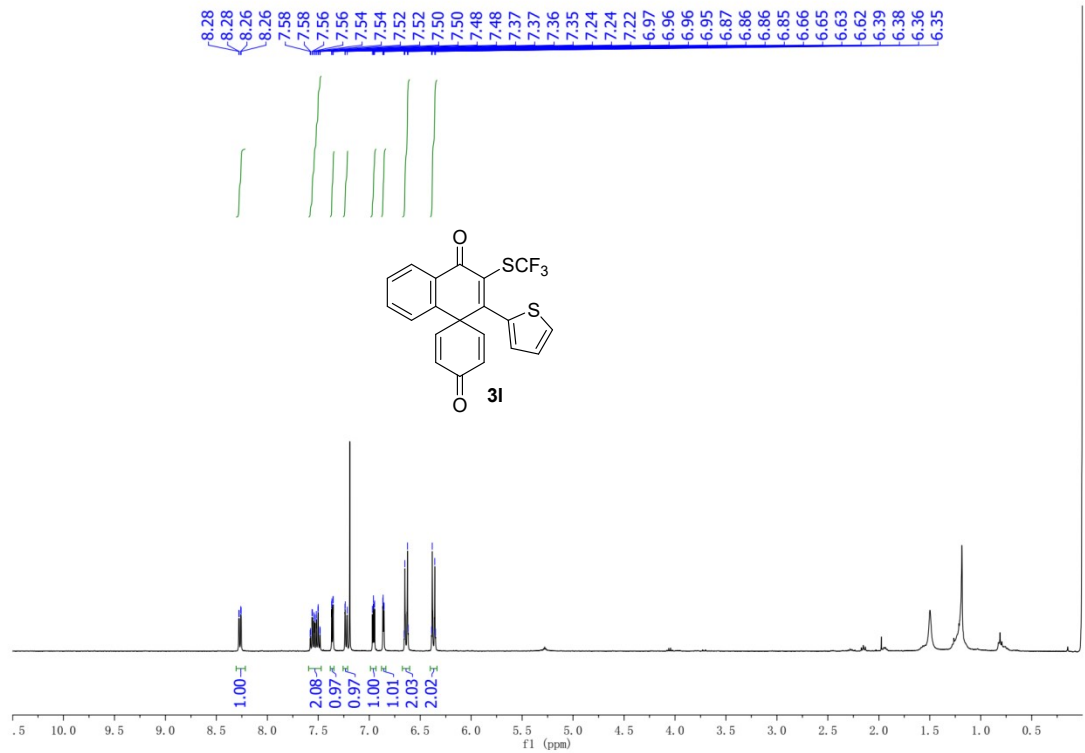


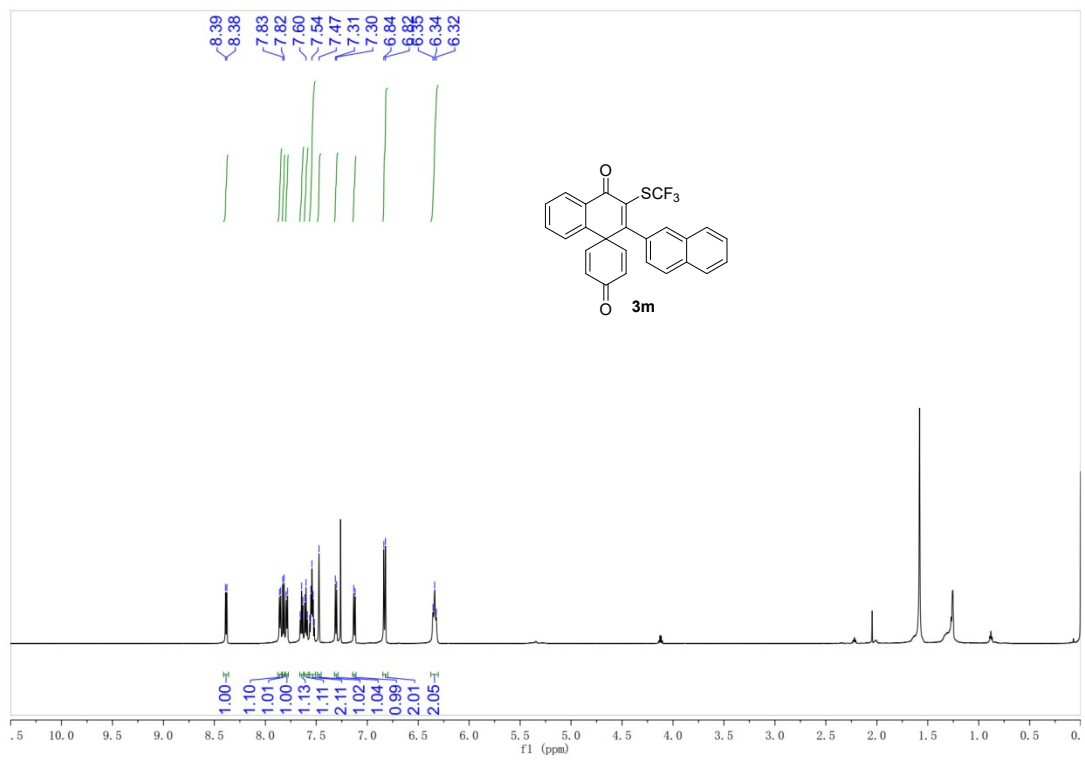
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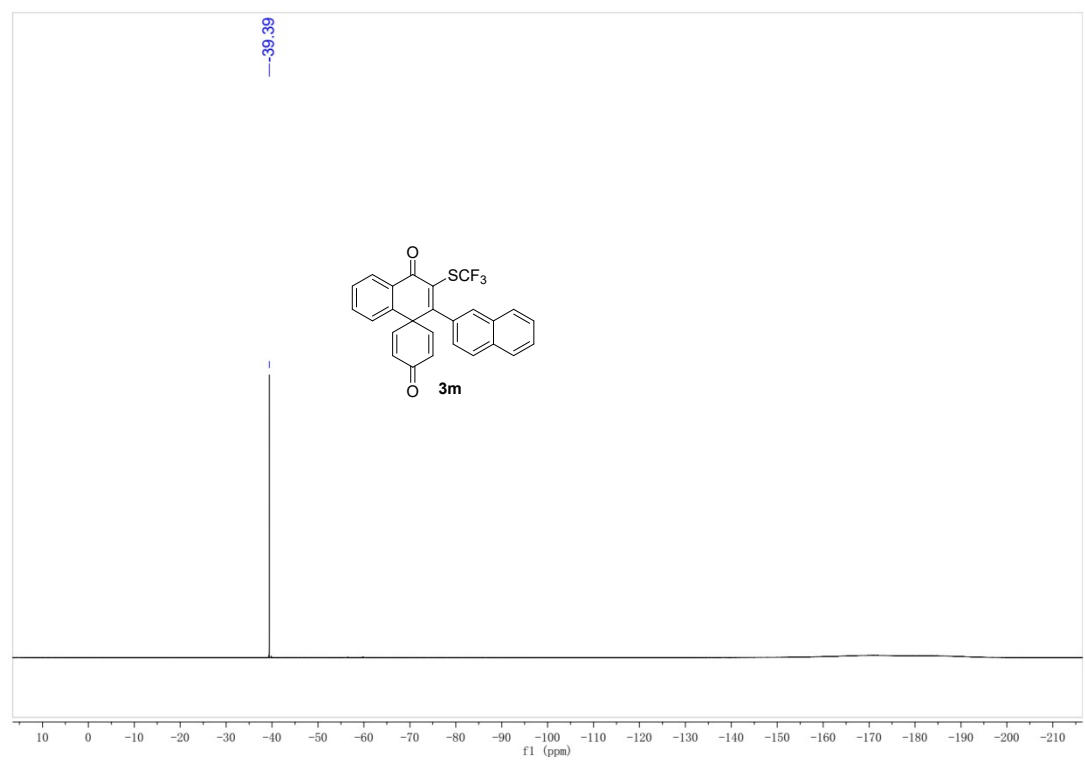
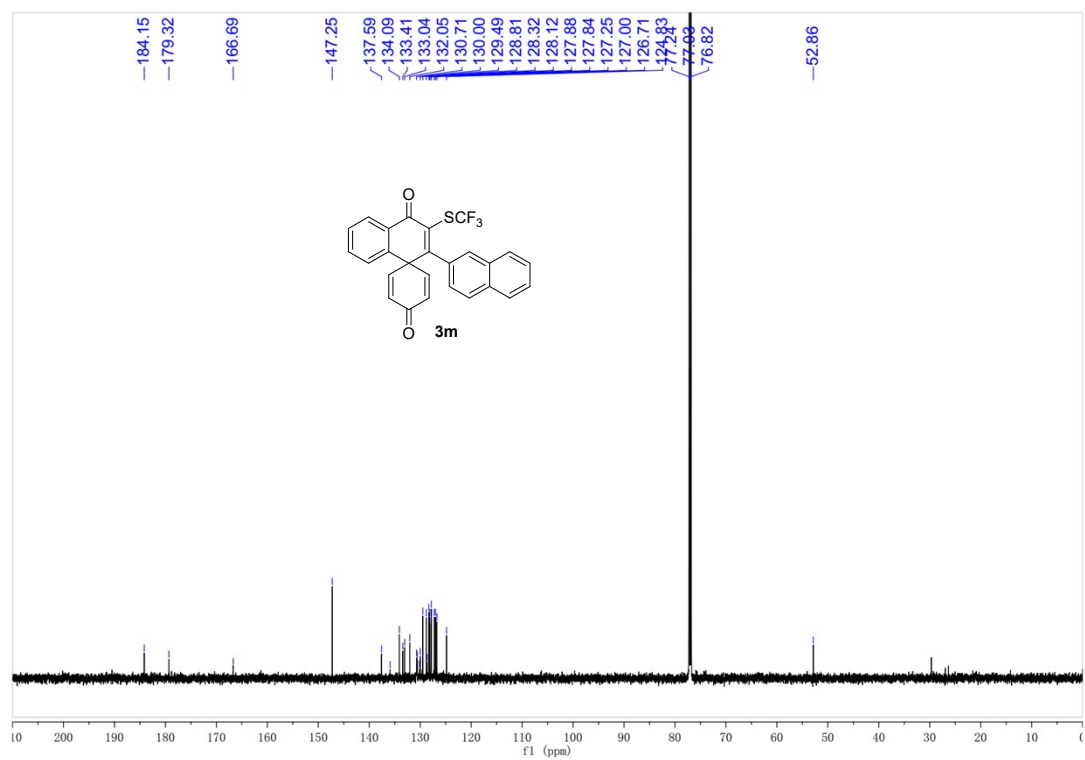


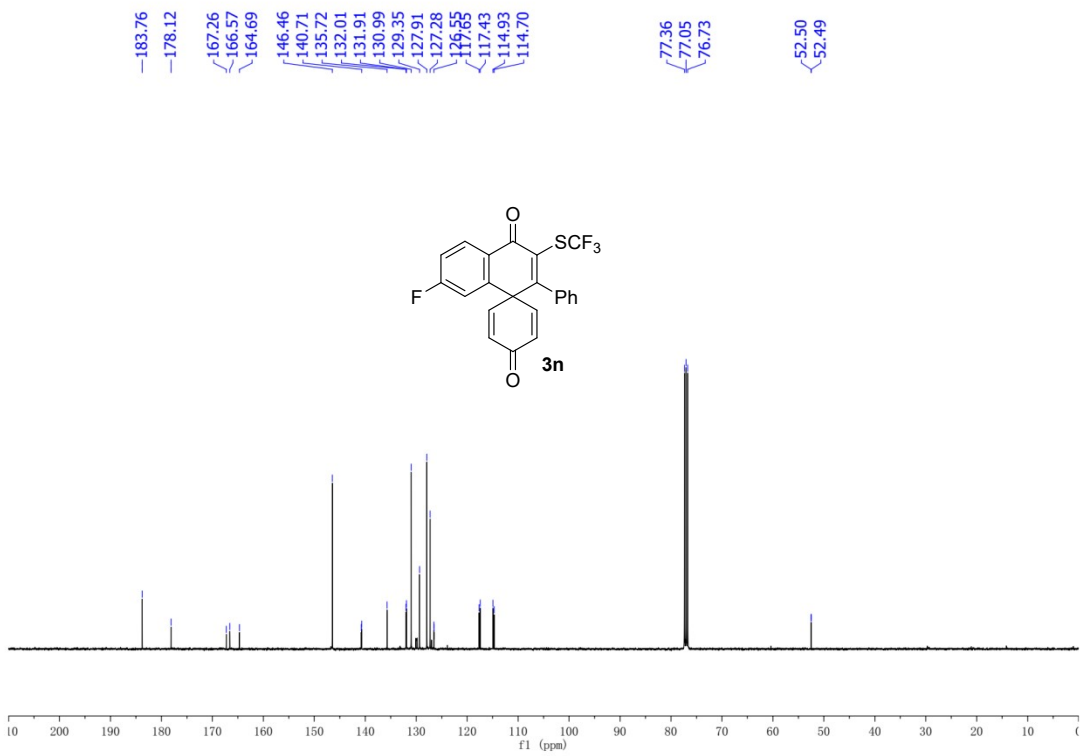
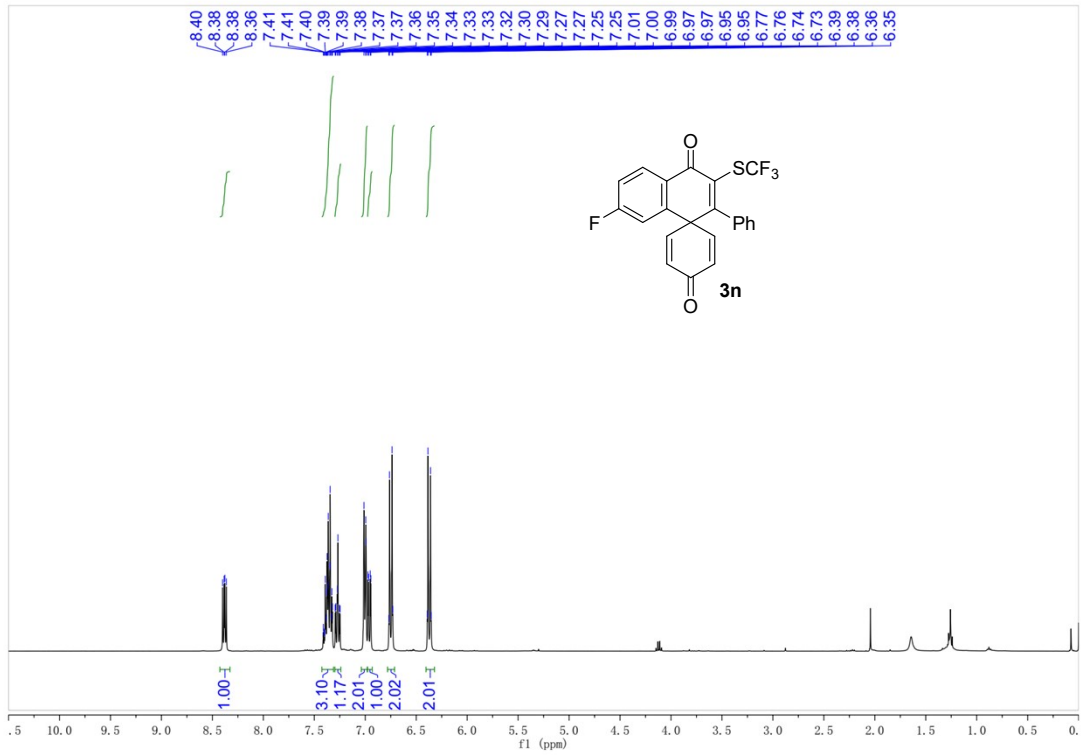
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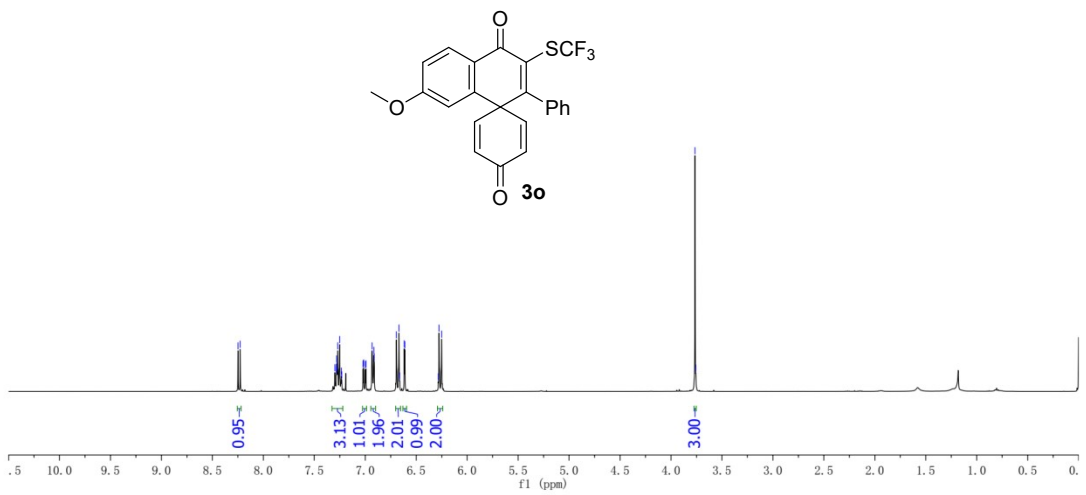
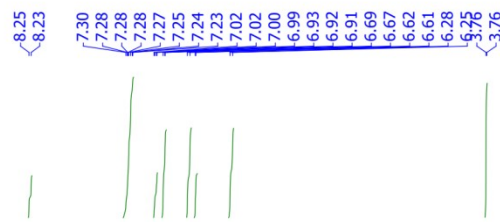
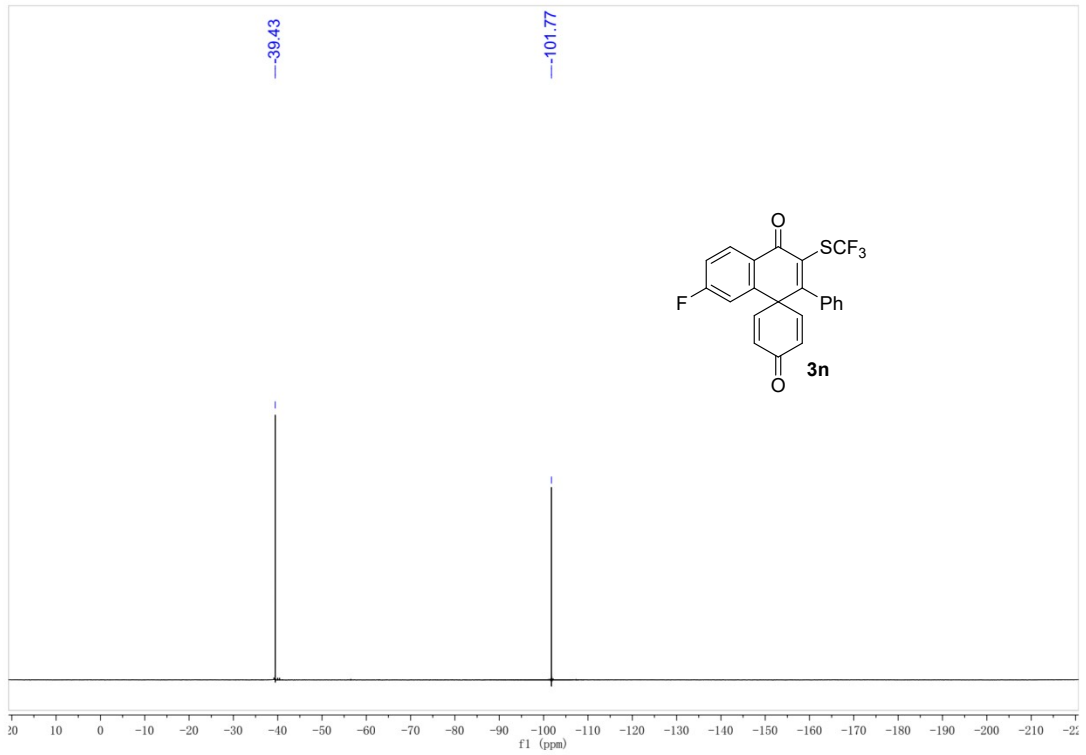












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