Supporting Information

BBr_3-Mediated Dearomative Spirocyclization of Biaryl Ynones: Facile Access to Spiro[5.5]dienones

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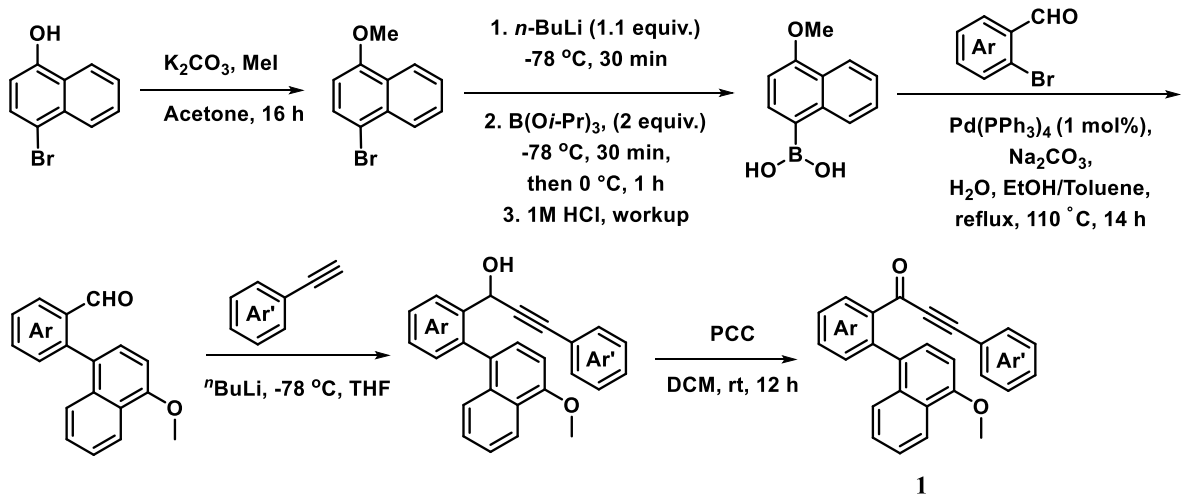
CONTENTS

1. General Information:

All dry solvents were dried using activated 4Å molecular sieves and stored under argon. For thin layer chromatography (TLC), silica gel plates with fluorescence indicator 254 nm were used and compounds were visualized by irradiation with UV light and/or by I2. Celite® 512 medium was used for filtrations. Flash column chromatography was performed using 100-200 or 230-400 mesh silica gel. Petroleum ether and ethyl acetate for flash chromatography were acquired from commercial sources and were used without purification. NMR spectra were acquired on a Bruker 400 MHz, 500 MHz and 600 MHz spectrometer. Chemical shifts (δ) are reported in ppm relative to residual solvent signals (CDCl3, 7.26 ppm for ^{1}H NMR and 77.23 ppm for ^{13}C NMR respectively). 13C spectra were acquired on a broad band decoupled mode. For ^{1}H NMR, data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, dd = double doublet, ddd = doublet of doublet of doublets, t = triplet, q = quartet, dt = doublet of triplets, m = multiplet), coupling constants (Hz) and integration. Using ESI mode, HRMS spectra were recorded.

Unless otherwise stated, raw materials from industrial suppliers were used without any additional purification.

2. Synthesis of starting materials:



1

K_2CO_3 (50.00 mmol, 5.0 equiv.) was added to a solution of 4-bromonaphthalen-1-ol (10.00 mmol, 1.0 equiv.) in acetone (80 mL) and stirred for 10 min. The flask above was filled with iodomethane (13.00 mmol, 1.3 equiv.), and the mixtures were allowed to reflux for 16 h. The mixture was subsequently filtered, and the filtrate was concentrated in vacuo and purified by

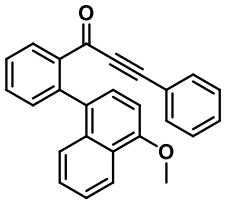
column chromatography (petroleum ether/EtOAc, 100:1) to get product 1-bromo-4-methoxynaphthalene (95%).[1]

1-bromo-4-methoxynaphthalene (5.0 mmol, 1.0 equiv.) was dissolved in 20 mL of THF and cooled to -78 °C using a method that was previously reported.[2] Dropwise addition of n-BuLi (5.5 mmol, 2.43 M, 1.1 equiv.) was followed by 30 min. of stirring the reaction. After that, B(O*i*-Pr)3 (10 mmol, 2.0 equiv.) was added dropwise, and the reaction was agitated for an additional 30 min. The reaction was then allowed to cool to 0 ℃ and agitated for a further hour. After that, the reaction was quenched with 1 M HCl (40 mL) and extracted with EtOAc 3 times. The mixed organic phases were filtered, concentrated under low pressure, and dried on $MgSO_4$. The product was utilized directly without further purification.

Under an atmosphere of N_2, the *o*-bromobenzaldehyde (0.2 mmol, 1.0 equiv.) and (4-methoxynaphthalen-1-yl)boronic acid (0.2 mmol, 1.0 equiv.) were charged into a 100 mL flask with a stir bar. After adding water (50 µL), $Pd(PPh_3)_4$ (0.002 mmol, 0.01 equiv.) and sodium carbonate (0.2 mmol, 1.0 equiv.), in toluene : EtOH (1 : 1, 2 mL), the solution was heated to reflux at 110 ℃ for 14 h. The reaction mixture was diluted with DCM (10 mL) and rinsed with water (5 mL) after being cooled to room temperature. The mixed organic layer was dried over anhydrous Na_2SO_4 and purified on silica gel column chromatography using n-hexane/EtOAc (19:1) as an eluent to produce (68%) 2-(4-methoxynaphthalen-1-yl)benzaldehyde, which was used in the next step.[3]

Phenylacetylene (6 mmol, 1.2 equiv.) was added to a 50 mL two-necked flask, which was then evacuated and backfilled with argon. After that, 20 mL of anhydrous THF was added and cooled to -78 ℃. Following the addition of n-BuLi (6 mmol, 2.5 M in hexane, 1.2 equiv.) to the solution, the reaction was maintained at -78 ℃ for an additional hour. After adding the aforementioned aldehyde (5 mmol, 1.0 equiv.), the mixture was warmed to room temperature and left for an hour. After quenching the solution with saturated aqueous NH_4Cl (20 mL), the solution was extracted with ethyl acetate 3 times. The mixed organic layer was then dried over anhydrous Na_2SO_4 after being rinsed with saturated NaCl. The residue was used without further purification in the step.[4]

PCC (30 mmol, 2.0 equiv.) was gradually added to a stirred solution of the above secondary alcohol (15.0 mmol, 1.0 equiv.) in DCM (45 mL). The final suspension was swirled for 12 h at room temperature. Afterwards, the solution was filtered through celite, DCM was used to clean the filter's residue. The combined filtrate was vacuum-concentrated, and was then purified using flash chromatography on silica gel using EtOAc/petroleum ether (v/v, 1 : 10) as eluent to produce ketone **1** (58%).[5]



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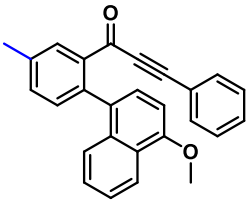

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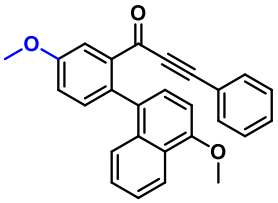

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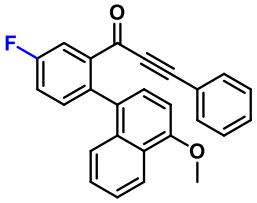

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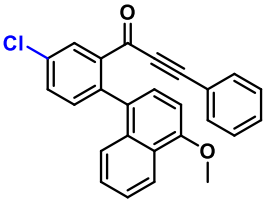

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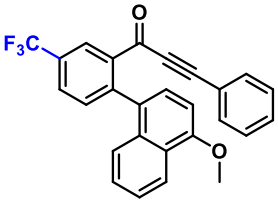

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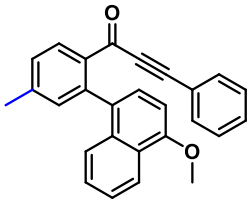

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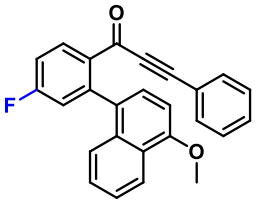

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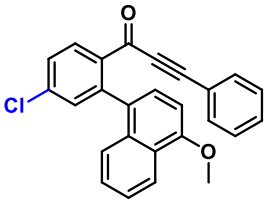

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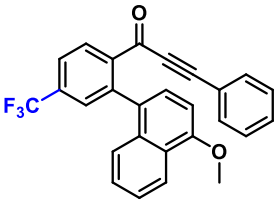

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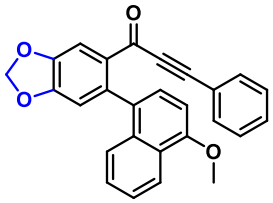

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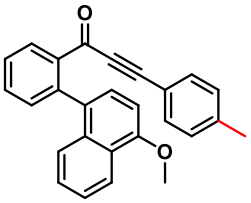

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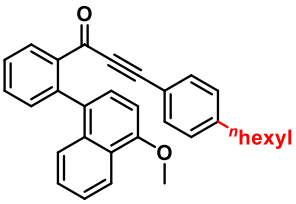

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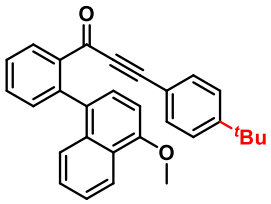

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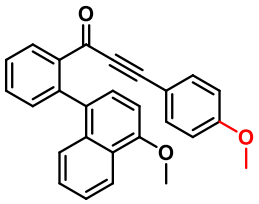

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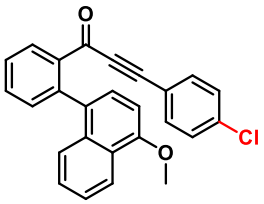

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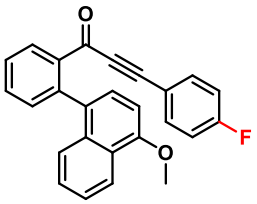

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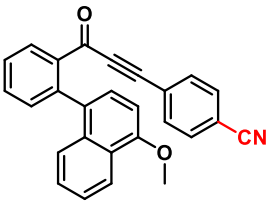

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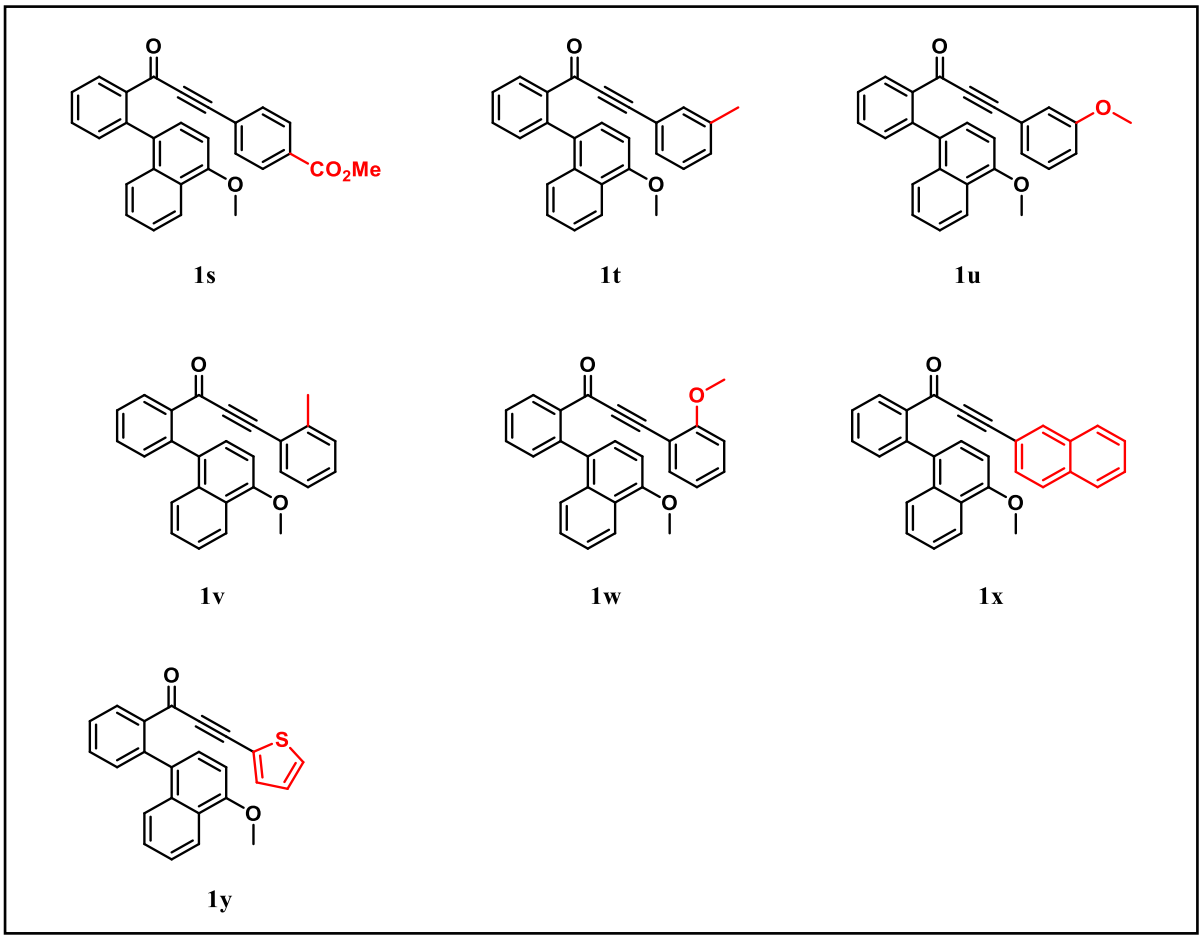
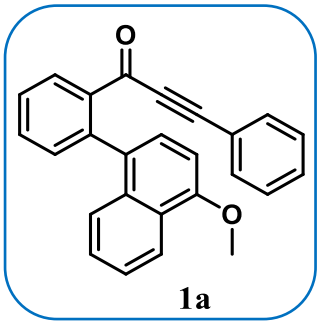


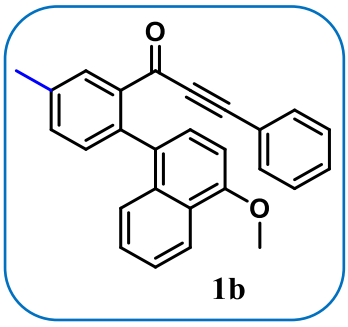
3. Characterization of starting materials:



1-(2-(4-methoxynaphthalen-1-yl)phenyl)-3-phenylprop-2-yn-1-one (1a)

Yellow solid; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.30 (dd, *J* = 8.5, 1.5 Hz, 1H), 8.07 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.74 (dd, *J* = 8.3, 1.4 Hz, 1H), 7.65 (td, *J* = 7.5, 1.4 Hz, 1H), 7.56 (td, *J* = 7.6, 1.3 Hz, 1H), 7.54 – 7.48 (m, 3H), 7.30 – 7.26 (m, 2H), 7.13 (t, *J* = 7.8 Hz, 2H), 6.81 (d, *J* = 7.8 Hz, 1H), 6.69 (dd, *J* = 8.2, 1.4 Hz, 2H), 3.94 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 180.42, 155.75, 141.42, 139.42, 133.35, 132.74, 132.58, 132.08, 130.56, 130.14, 130.02, 128.77, 128.17, 127.71, 127.09, 125.99, 125.97, 125.36, 122.55, 120.15, 103.69, 93.27, 88.79, 55.68;

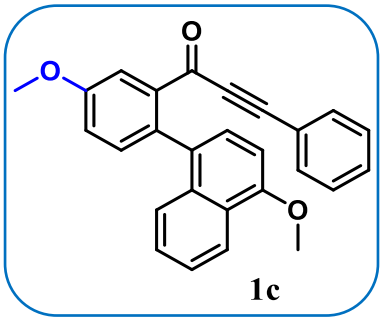
110.6, 109.2, 93.0, 90.6, 55.6, 55.1; **HRMS (ESI) (*m/z*):** calcd for $C_{26}H_{18}O_2$ ($[M+H]^+$), 363.1380; found 363.1381.



1b

1-(2-(4-methoxynaphthalen-1-yl)-5-methylphenyl)-3-phenylprop-2-yn-1-one (1b)

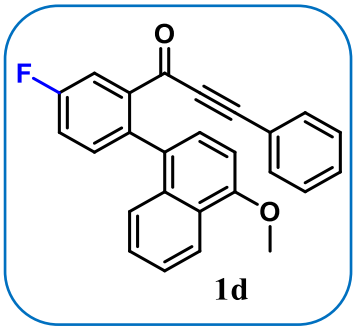
Yellow solid; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.29 (dd, *J* = 8.4, 1.4 Hz, 1H), 7.88 (d, *J* = 1.9 Hz, 1H), 7.75 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.54 – 7.45 (m, 3H), 7.40 (d, *J* = 7.7 Hz, 1H), 7.29 – 7.25 (m, 2H), 7.12 (t, *J* = 7.9 Hz, 2H), 6.81 (d, *J* = 7.8 Hz, 1H), 6.67 (dd, *J* = 8.1, 1.5 Hz, 2H), 3.93 (s, 3H), 2.53 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 180.65, 155.65, 139.27, 138.65, 137.61, 133.53, 132.97, 132.72, 132.51, 130.56, 130.30, 130.07, 128.80, 128.14, 127.00, 126.07, 126.02, 125.31, 122.52, 120.23, 103.73, 93.25, 88.88, 55.67, 21.29; **HRMS (ESI) (*m/z*):** calcd for $C_{27}H_{20}O_2$ ($[M+H]^+$), 377.1536; found 377.1541.



1c

1-(5-methoxy-2-(4-methoxynaphthalen-1-yl)phenyl)-3-phenylprop-2-yn-1-one (1c)

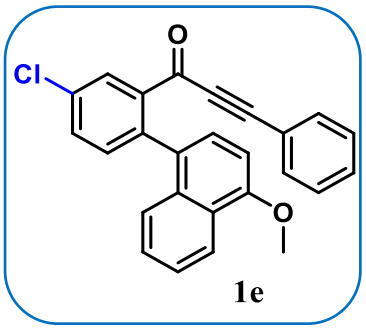
Yellow solid; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.26 (dd, *J* = 7.9, 1.9 Hz, 1H), 7.73 (dd, *J* = 7.8, 1.9 Hz, 1H), 7.56 (d, *J* = 2.8 Hz, 1H), 7.52 – 7.45 (m, 2H), 7.40 (d, *J* = 8.4 Hz, 1H), 7.25 (dd, *J* = 8.1, 6.2 Hz, 2H), 7.19 (dd, *J* = 8.4, 2.8 Hz, 1H), 7.10 (t, *J* = 7.8 Hz, 2H), 6.78 (d, *J* = 7.8 Hz, 1H), 6.62 (dd, *J* = 8.2, 1.4 Hz, 2H), 3.95 (s, 3H), 3.91 (s, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 180.19, 159.10, 155.65, 140.20, 134.09, 133.76, 133.71, 132.74, 130.27, 130.11, 129.08, 128.14, 127.01, 126.12, 126.06, 125.31, 122.53, 120.15, 119.18, 113.56, 103.74, 93.56, 88.79, 55.86, 55.68; **HRMS (ESI) (*m/z*):** calcd for $C_{27}H_{20}O_3$ ($[M+H]^+$), 393.1485; found 393.1493.



1d

1-(5-fluoro-2-(4-methoxynaphthalen-1-yl)phenyl)-3-phenylprop-2-yn-1-one (1d)

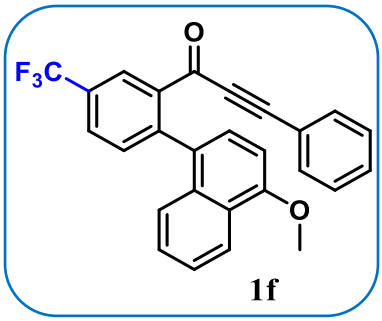
Yellow solid; **^{1}H NMR (500 MHz, $CDCl_3$)** ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.27 (dd, *J* = 7.9, 1.9 Hz, 1H), 7.74 (dd, *J* = 9.1, 2.8 Hz, 1H), 7.66 (dd, *J* = 7.8, 1.9 Hz, 1H), 7.54 – 7.42 (m, 3H), 7.33 (td, *J* = 8.2, 2.8 Hz, 1H), 7.26 – 7.20 (m, 2H), 7.11 (t, *J* = 7.8 Hz, 2H), 6.78 (d, *J* = 7.8 Hz, 1H), 6.64 (dd, *J* = 8.2, 1.4 Hz, 2H), 3.91 (s, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 178.90, 163.08, 161.11, 155.94, 140.82, 140.76, 137.44, 137.41, 134.39, 134.33, 133.46, 132.80, 130.34, 129.42, 129.07, 128.22, 127.24, 126.05, 125.80, 125.46, 122.66, 119.91, 119.32, 119.15, 116.58, 116.40, 103.69, 94.05, 88.41, 55.71; **HRMS (ESI) (*m/z*):** calcd for $C_{26}H_{17}FO_2$ ($[M+H]^+$), 381.1285; found 381.1286.



1e

1-(5-chloro-2-(4-methoxynaphthalen-1-yl)phenyl)-3-phenylprop-2-yn-1-one (1e)

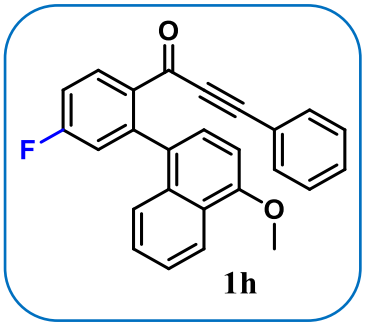
Yellow solid; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.27 (dd, *J* = 8.0, 1.9 Hz, 1H), 8.01 (d, *J* = 2.3 Hz, 1H), 7.70 – 7.64 (m, 1H), 7.59 (dd, *J* = 8.2, 2.3 Hz, 1H), 7.50 (td, *J* = 5.1, 4.6, 2.0 Hz, 2H), 7.43 (d, *J* = 8.2 Hz, 1H), 7.29 – 7.20 (m, 2H), 7.11 (t, *J* = 7.8 Hz, 2H), 6.78 (d, *J* = 7.9 Hz, 1H), 6.64 (dd, *J* = 8.1, 1.4 Hz, 2H), 3.91 (s, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 178.92, 156.03, 140.57, 139.76, 133.95, 133.92, 133.23, 132.81, 131.98, 130.37, 129.78, 129.26, 128.96, 128.22, 127.31, 126.05, 125.72, 125.52, 122.68, 119.87, 103.69, 94.11, 88.40, 55.72; **HRMS (ESI) (*m/z*):** calcd for $C_{26}H_{17}ClO_2$ ($[M+H]^+$), 397.0990; found 397.0990.



1f

1-(2-(4-methoxynaphthalen-1-yl)-5-(trifluoromethyl)phenyl)-3-phenylprop-2-yn-1-one (1f)

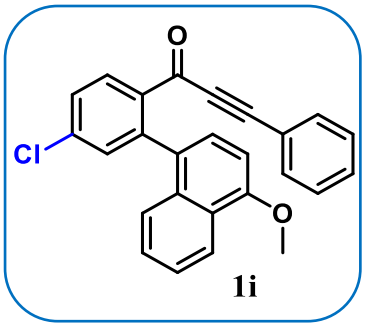
Orange solid; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.35 – 8.30 (m, 2H), 7.88 (dd, *J* = 8.0, 2.1 Hz, 1H), 7.69 (dd, *J* = 7.5, 2.2 Hz, 1H), 7.64 (d, *J* = 8.0 Hz, 1H), 7.53 (m, 2H), 7.30 – 7.24 (m, 2H), 7.12 (t, *J* = 7.8 Hz, 2H), 6.81 (d, *J* = 7.9 Hz, 1H), 6.67 – 6.63 (m, 2H), 3.92 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 178.91, 156.26, 144.87, 139.76, 133.25, 132.93, 132.76, 130.44, 130.20, 129.98, 129.03, 128.98, 128.26, 128.23, 128.21, 127.46, 126.98, 126.96, 126.93, 126.91, 125.99, 125.61, 125.47, 124.86, 123.05, 122.74, 119.65, 103.65, 94.34, 88.32, 55.65; **HRMS (ESI) (*m/z*):** calcd for $C_{27}H_{17}F_3O_2$ ($[M+H]^+$), 431.1253; found 431.1254.



1h

1-(4-fluoro-2-(4-methoxynaphthalen-1-yl)phenyl)-3-phenylprop-2-yn-1-one (1h)

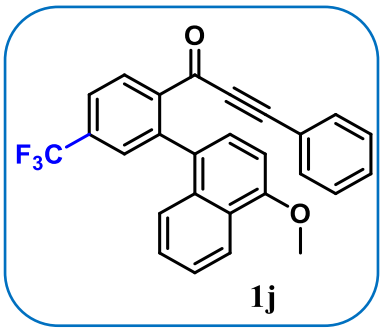
Yellow solid; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.30 – 8.27 (m, 1H), 8.11 (dd, *J* = 8.7, 5.8 Hz, 1H), 7.72 – 7.68 (m, 1H), 7.54 – 7.49 (m, 2H), 7.31 – 7.22 (m, 3H), 7.20 (dd, *J* = 9.2, 2.6 Hz, 1H), 7.13 (t, *J* = 7.5 Hz, 2H), 6.80 (d, *J* = 7.8 Hz, 1H), 6.68 (dd, *J* = 8.2, 1.4 Hz, 2H), 3.93 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 178.73, 165.51, 163.82, 156.08, 144.58, 144.52, 135.66, 135.65, 133.08, 132.88, 132.82, 132.72, 130.23, 129.43, 128.65, 128.21, 127.37, 125.98, 125.58, 125.54, 122.67, 120.05, 119.44, 119.29, 115.10, 114.96, 103.62, 93.51, 88.58, 55.71; **HRMS (ESI) (*m/z*):** calcd for $C_{26}H_{17}FO_2$ ($[M+H]^+$), 381.1285; found 381.1284.



1i

1-(4-chloro-2-(4-methoxynaphthalen-1-yl)phenyl)-3-phenylprop-2-yn-1-one (1i)

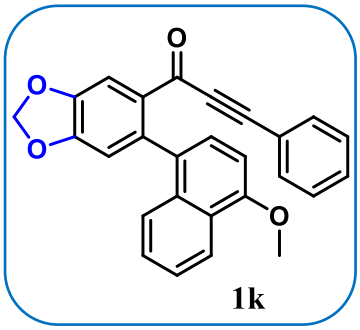
Yellow solid; **^{1}H NMR (500 MHz, $CDCl_3$)** ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.29 – 8.24 (m, 1H), 7.99 (d, *J* = 8.4 Hz, 1H), 7.66 (dt, *J* = 7.9, 2.6 Hz, 1H), 7.52 – 7.45 (m, 4H), 7.27 – 7.20 (m, 2H), 7.10 (t, *J* = 7.9 Hz, 2H), 6.77 (d, *J* = 7.9 Hz, 1H), 6.68 – 6.64 (m, 2H), 3.90 (s, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 178.98, 156.10, 143.19, 138.38, 137.67, 133.11, 132.74, 132.44, 131.53, 130.29, 129.19, 128.79, 128.21, 127.99, 127.39, 125.97, 125.60, 125.54, 122.66, 119.96, 103.64, 93.77, 88.53, 55.70; **HRMS (ESI) (*m/z*):** calcd for $C_{26}H_{17}ClO_2$ ($[M+H]^+$), 397.0990; found 397.1023.



1j

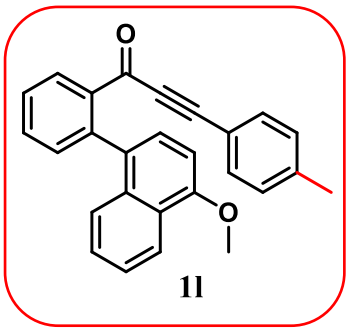
1-(2-(4-methoxynaphthalen-1-yl)-4-(trifluoromethyl)phenyl)-3-phenylprop-2-yn-1-one (1j)

Yellow semi solid; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.31 – 8.27 (m, 1H), 8.10 (d, *J* = 8.1 Hz, 1H), 7.78 (d, *J* = 8.1 Hz, 2H), 7.67 – 7.63 (m, 1H), 7.53 – 7.49 (m, 2H), 7.25 (d, *J* = 7.7 Hz, 2H), 7.10 (t, *J* = 7.7 Hz, 2H), 6.80 (d, *J* = 7.9 Hz, 1H), 6.63 (dd, *J* = 7.9, 1.5 Hz, 2H), 3.92 (s, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 179.42, 156.30, 142.32, 141.89, 133.58, 133.32, 133.05, 132.84, 130.51, 130.37, 129.41, 129.38, 129.22, 128.93, 128.27, 127.59, 126.06, 125.66, 125.47, 124.90, 124.52, 124.49, 124.46, 122.79, 122.73, 119.72, 103.69, 94.38, 88.40, 55.75; **HRMS (ESI) (*m/z*):** calcd for $C_{27}H_{17}F_3O_2$ ($[M+H]^+$), 431.1253; found 431.1258.



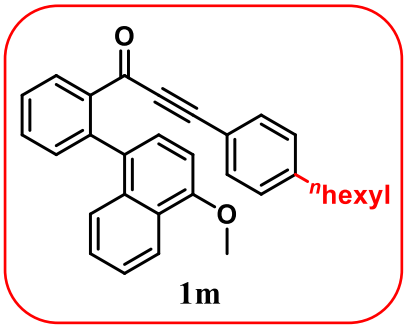
1k

1-(6-(4-methoxynaphthalen-1-yl)benzo[*d*][1,3]dioxol-5-yl)-3-phenylprop-2-yn-1-one (1k) Yellow solid; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.27 – 8.21 (m, 1H), 7.76 – 7.71 (m, 1H), 7.58 (s, 1H), 7.53 – 7.46 (m, 2H), 7.27 – 7.20 (m, 2H), 7.09 (t, *J* = 7.6 Hz, 2H), 6.89 (s, 1H), 6.76 (d, *J* = 7.8 Hz, 1H), 6.61 (d, *J* = 7.3 Hz, 2H), 6.12 (dd, *J* = 12.1, 1.3 Hz, 2H), 3.89 (s, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 178.29, 155.86, 151.04, 147.57, 138.54, 133.58, 133.43, 132.59, 130.35, 129.90, 129.01, 128.09, 127.13, 126.07, 125.95, 125.38, 122.57, 120.36, 112.19, 109.60, 103.69, 102.30, 93.12, 88.81, 55.67; **HRMS (ESI) (*m/z*):** calcd for $C_{27}H_{18}O_4$ ($[M+H]^+$), 407.1278; found 407.1278.



1l

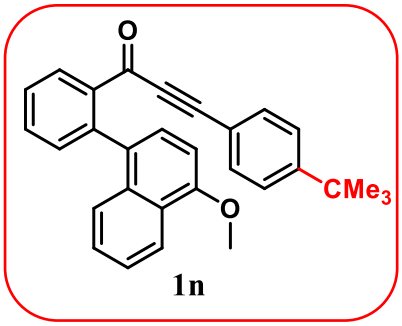
1-(2-(4-methoxynaphthalen-1-yl)phenyl)-3-(*p*-tolyl)prop-2-yn-1-one (1l) Yellow solid; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.32 – 8.27 (m, 1H), 8.07 – 8.02 (m, 1H), 7.72 (dd, *J* = 6.3, 3.2 Hz, 1H), 7.62 (t, *J* = 7.5 Hz, 1H), 7.51 (dt, *J* = 23.1, 7.8 Hz, 4H), 7.25 (d, *J* = 7.1 Hz, 1H), 6.92 (d, *J* = 7.8 Hz, 2H), 6.81 (d, *J* = 7.8 Hz, 1H), 6.57 (dd, *J* = 8.2, 3.5 Hz, 2H), 3.94 (s, 3H), 2.28 (s, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 180.49, 155.75, 141.35, 140.84, 139.60, 133.37, 132.88, 132.60, 131.95, 130.68, 130.05, 129.04, 129.03, 128.76, 127.69, 127.08, 126.05, 125.35, 122.57, 117.11, 103.75, 93.97, 88.76, 55.71, 21.82; **HRMS (ESI) (*m/z*):** calcd for $C_{27}H_{20}O_2$ ($[M+H]^+$), 377.1536; found 377.1537.



1m

3-(4-hexylphenyl)-1-(2-(4-methoxynaphthalen-1-yl)phenyl)prop-2-yn-1-one (1m)

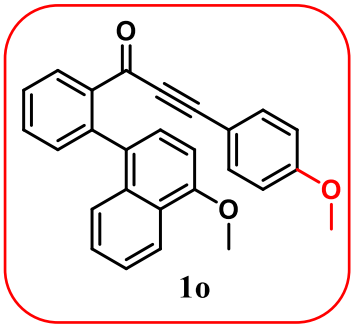
Yellow solid; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.28 (dd, *J* = 7.9, 1.9 Hz, 1H), 8.05 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.72 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.61 (td, *J* = 7.5, 1.5 Hz, 1H), 7.55 – 7.45 (m, 4H), 7.27 – 7.24 (m, 1H), 6.92 (d, *J* = 7.9 Hz, 2H), 6.80 (d, *J* = 7.9 Hz, 1H), 6.59 (d, *J* = 8.1 Hz, 2H), 3.92 (s, 3H), 2.51 (t, *J* = 7.8 Hz, 2H), 1.30 – 1.24 (m, 8H), 0.88 (t, *J* = 6.7 Hz, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 180.45, 155.72, 145.81, 141.34, 139.56, 133.35, 132.86, 132.58, 131.94, 130.67, 130.04, 128.70, 128.35, 127.76, 127.66, 127.05, 126.01, 125.32, 122.55, 117.26, 103.73, 94.06, 88.73, 77.49, 77.23, 76.98, 55.69, 36.16, 31.83, 31.20, 29.05, 22.76, 14.26; **HRMS (ESI) (*m/z*):** calcd for $C_{32}H_{30}O_2$ ($[M+H]^+$), 447.2319; found 447.2319.



1n

3-(4-(*tert*-butyl)phenyl)-1-(2-(4-methoxynaphthalen-1-yl)phenyl)prop-2-yn-1-one (1n)

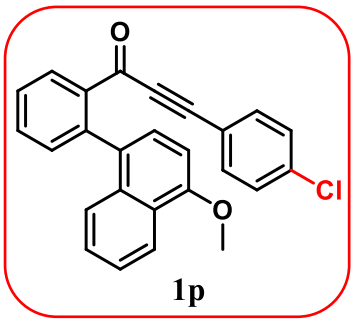
Orange semi solid; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.32 (dd, *J* = 8.2, 1.1 Hz, 1H), 8.08 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.73 (dd, *J* = 8.6, 1.3 Hz, 1H), 7.65 (td, *J* = 7.5, 1.5 Hz, 1H), 7.59 – 7.49 (m, 4H), 7.29 (d, *J* = 7.9 Hz, 1H), 7.19 – 7.14 (m, 2H), 6.82 (d, *J* = 7.8 Hz, 1H), 6.70 – 6.66 (m, 2H), 3.95 (s, 3H), 1.28 (s, 9H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 180.48, 155.68, 153.83, 141.34, 139.50, 133.35, 132.69, 132.57, 131.99, 130.65, 130.04, 128.62, 127.67, 127.06, 125.97, 125.33, 125.25, 122.53, 117.11, 103.72, 93.99, 88.67, 55.68, 35.09, 31.20; **HRMS (ESI) (*m/z*):** calcd for $C_{30}H_{26}O_2$ ($[M+H]^+$), 419.2006; found 419.2040.



1o

1-(2-(4-methoxynaphthalen-1-yl)phenyl)-3-(4-methoxyphenyl)prop-2-yn-1-one (1o)

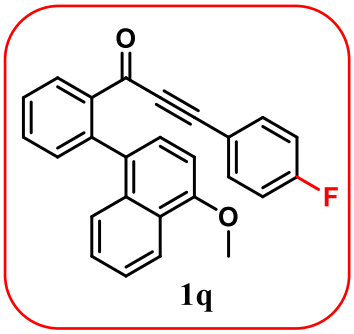
Yellow solid; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.30 (dd, *J* = 7.7, 2.0 Hz, 1H), 8.03 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.75 (dd, *J* = 7.5, 1.9 Hz, 1H), 7.61 (td, *J* = 7.5, 1.5 Hz, 1H), 7.55 – 7.46 (m, 5H), 7.25 (d, *J* = 7.5 Hz, 1H), 6.81 (d, *J* = 7.9 Hz, 1H), 6.60 (d, *J* = 5.6 Hz, 3H), 3.94 (s, 3H), 3.75 (s, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 180.50, 161.27, 155.69, 141.22, 139.70, 134.88, 133.30, 132.57, 131.82, 130.68, 129.97, 128.80, 127.66, 127.04, 126.08, 126.01, 125.32, 122.57, 113.94, 112.02, 103.72, 94.46, 88.84, 55.72, 55.49; **HRMS (ESI) (*m/z*):** calcd for $C_{27}H_{20}O_3$ ($[M+H]^+$), 393.1485; found 393.1492.



1p

3-(4-chlorophenyl)-1-(2-(4-methoxynaphthalen-1-yl)phenyl)prop-2-yn-1-one (1p)

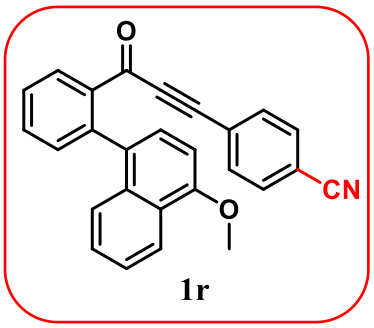
Yellow solid; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.29 (dd, *J* = 8.0, 1.1 Hz, 1H), 8.03 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.75 (dd, *J* = 7.5, 1.3 Hz, 1H), 7.63 (td, *J* = 7.5, 1.4 Hz, 1H), 7.56 – 7.47 (m, 4H), 7.24 (d, *J* = 7.8 Hz, 1H), 7.09 – 7.05 (m, 2H), 6.79 (d, *J* = 7.8 Hz, 1H), 6.51 – 6.47 (m, 2H), 3.93 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 180.25, 155.78, 141.43, 139.33, 136.39, 133.87, 133.29, 132.56, 132.14, 130.42, 129.91, 129.07, 128.58, 127.75, 127.14, 126.03, 125.98, 125.41, 122.58, 118.56, 103.66, 91.74, 89.43, 55.68; **HRMS (ESI) (*m/z*):** calcd for $C_{26}H_{17}ClO_2$ ($[M+H]^+$), 397.0990; found 397.0990.



1q

3-(4-fluorophenyl)-1-(2-(4-methoxynaphthalen-1-yl)phenyl)prop-2-yn-1-one (1q)

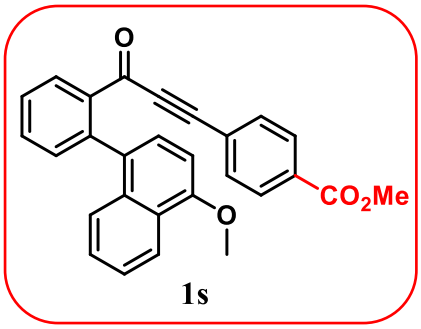
Yellow solid; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.06 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.77 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.66 (td, *J* = 7.5, 1.5 Hz, 1H), 7.59 – 7.49 (m, 4H), 7.30 – 7.26 (m, 1H), 6.82 (td, *J* = 8.3, 2.0 Hz, 3H), 6.63 – 6.58 (m, 2H), 3.96 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 180.34, 164.45, 162.78, 155.80, 141.42, 139.44, 135.00, 134.94, 133.34, 132.60, 132.08, 130.53, 129.95, 129.02, 127.75, 127.13, 126.07, 126.03, 125.40, 122.59, 116.27, 116.24, 115.73, 115.58, 103.71, 92.18, 88.70, 55.72; **HRMS (ESI) (*m/z*):** calcd for $C_{26}H_{17}FO_2$ ($[M+H]^+$), 381.1285; found 381.1285.



1r

4-(3-(2-(4-methoxynaphthalen-1-yl)phenyl)-3-oxoprop-1-yn-1-yl)benzonitrile (1r)

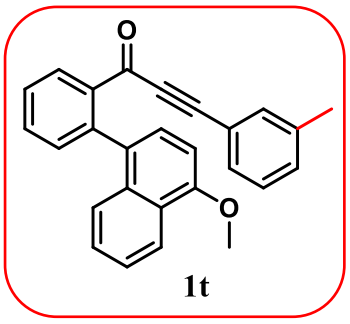
Orange semi solid; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.24 (dd, *J* = 8.7, 1.3 Hz, 1H), 7.88 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.67 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.60 (td, *J* = 7.5, 1.5 Hz, 1H), 7.52 (td, *J* = 7.6, 1.3 Hz, 1H), 7.50 – 7.43 (m, 3H), 7.25 – 7.22 (m, 1H), 7.19 (d, *J* = 7.8 Hz, 1H), 6.71 (d, *J* = 7.8 Hz, 1H), 6.59 – 6.55 (m, 2H), 6.30 (s, 1H), 3.89 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 193.11, 155.93, 143.00, 140.78, 139.96, 132.91, 131.92, 131.82, 131.77, 130.50, 130.40, 129.85, 129.05, 129.01, 128.11, 128.02, 127.81, 125.94, 125.88, 125.68, 122.68, 118.28, 112.97, 103.75, 55.77; **HRMS (ESI) (*m/z*):** calcd for $C_{27}H_{17}NO_2$ ($[M+H]^+$), 388.1332; found 388.1333.



1s

methyl 4-(3-(2-(4-methoxynaphthalen-1-yl)phenyl)-3-oxoprop-1-yn-1-yl)benzoate (1s)

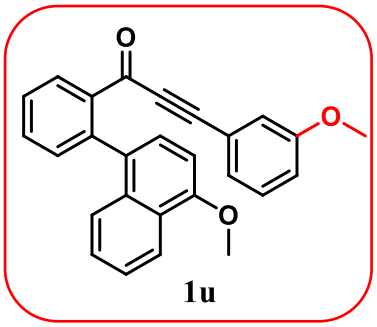
Orange semi solid; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.26 (dd, *J* = 8.0, 1.6 Hz, 1H), 8.03 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.78 – 7.72 (m, 3H), 7.64 (td, *J* = 7.5, 1.4 Hz, 1H), 7.54 (td, *J* = 7.6, 1.3 Hz, 1H), 7.52 – 7.46 (m, 3H), 7.24 (d, *J* = 7.8 Hz, 1H), 6.78 (d, *J* = 7.8 Hz, 1H), 6.64 – 6.61 (m, 2H), 3.90 (s, 3H), 3.89 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 180.11, 166.35, 155.83, 141.57, 139.17, 133.33, 132.55, 132.35, 132.29, 130.94, 130.32, 129.91, 129.14, 129.09, 128.98, 127.77, 127.17, 125.95, 125.48, 124.64, 122.57, 103.62, 91.40, 90.40, 55.65, 52.51; **HRMS (ESI) (*m/z*):** calcd for $C_{28}H_{20}O_4$ ([M+H]$^+$), 421.1434; found 421.1435.



1t

1-(2-(4-methoxynaphthalen-1-yl)phenyl)-3-(*m*-tolyl)prop-2-yn-1-one (1t)

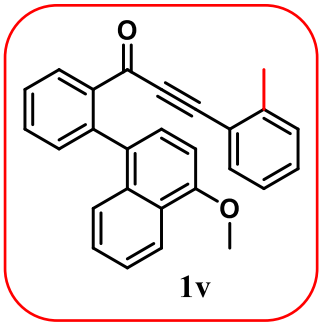
Yellow solid; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.31 (dd, *J* = 8.4, 1.5 Hz, 1H), 8.06 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.77 (dd, *J* = 8.4, 1.4 Hz, 1H), 7.64 (td, *J* = 7.5, 1.5 Hz, 1H), 7.57 – 7.49 (m, 4H), 7.27 (d, *J* = 7.7 Hz, 1H), 7.07 (d, *J* = 7.6 Hz, 1H), 7.02 (t, *J* = 7.6 Hz, 1H), 6.82 (d, *J* = 7.8 Hz, 1H), 6.62 (d, *J* = 7.5 Hz, 1H), 6.31 (s, 1H), 3.94 (s, 3H), 2.20 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 180.49, 155.74, 141.39, 139.50, 137.92, 133.31, 133.22, 132.60, 131.97, 131.14, 130.56, 130.00, 129.94, 128.94, 128.05, 127.68, 127.04, 126.09, 126.05, 125.41, 122.52, 119.92, 103.69, 93.74, 88.59, 55.67, 21.15; **HRMS (ESI) (*m/z*):** calcd for $C_{27}H_{20}O_2$ ([M+H]$^+$), 377.1536; found 377.1538.



1u

1-(2-(4-methoxynaphthalen-1-yl)phenyl)-3-(3-methoxyphenyl)prop-2-yn-1-one (1u)

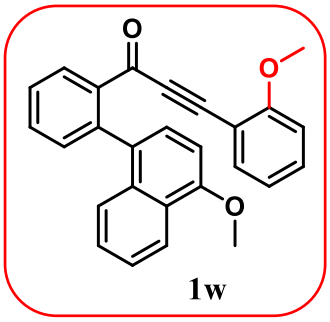
Yellow solid; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.28 (dd, *J* = 6.9, 2.9 Hz, 1H), 8.06 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.73 – 7.69 (m, 1H), 7.63 (td, *J* = 7.5, 1.5 Hz, 1H), 7.54 (td, *J* = 7.6, 1.3 Hz, 1H), 7.51 – 7.44 (m, 3H), 7.27 (d, *J* = 8.3 Hz, 1H), 7.02 (t, *J* = 8.0 Hz, 1H), 6.81 (t, *J* = 7.7 Hz, 2H), 6.32 (d, *J* = 2.1 Hz, 1H), 6.31 – 6.27 (m, 1H), 3.93 (s, 3H), 3.69 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 180.34, 159.12, 155.75, 141.43, 139.29, 133.37, 132.59, 132.15, 130.54, 130.03, 129.26, 128.73, 127.71, 127.04, 125.92, 125.40, 125.37, 122.50, 121.12, 117.21, 116.91, 103.69, 93.26, 88.45, 55.66, 55.52; **HRMS (ESI) (*m/z*):** calcd for $C_{27}H_{20}O_3$ ($[M+H]^+$), 393.1485; found 393.1486.



1v

1-(2-(4-methoxynaphthalen-1-yl)phenyl)-3-(*o*-tolyl)prop-2-yn-1-one (1v)

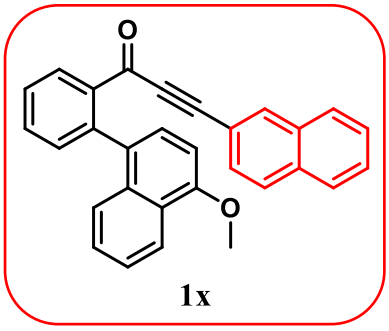
Yellow semi solid; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.30 – 8.23 (m, 1H), 8.15 – 8.08 (m, 1H), 7.63 (t, *J* = 7.5 Hz, 2H), 7.55 (s, 1H), 7.51 – 7.41 (m, 3H), 7.26 (d, *J* = 7.5 Hz, 1H), 7.18 (t, *J* = 7.6 Hz, 1H), 7.06 (d, *J* = 7.7 Hz, 1H), 6.95 (td, *J* = 7.6, 3.7 Hz, 1H), 6.79 (d, *J* = 5.5 Hz, 1H), 6.56 (dd, *J* = 5.7, 3.3 Hz, 1H), 3.91 (s, 3H), 2.15 (s, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 180.24, 155.70, 141.81, 141.39, 139.37, 133.43, 133.04, 132.66, 132.17, 130.74, 130.31, 130.23, 129.52, 128.30, 127.73, 127.04, 125.92, 125.83, 125.50, 125.34, 122.53, 120.14, 103.63, 92.60, 92.32, 55.67, 20.54; **HRMS (ESI) (*m/z*):** calcd for $C_{27}H_{20}O_2$ ($[M+H]^+$), 377.1536; found 377.1540.



1w

1-(2-(4-methoxynaphthalen-1-yl)phenyl)-3-(2-methoxyphenyl)prop-2-yn-1-one (1w)

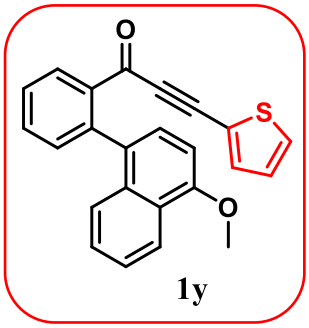
Orange semi solid; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.28 (dd, *J* = 8.8, 1.1 Hz, 1H), 8.19 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.68 – 7.61 (m, 2H), 7.56 (td, *J* = 7.6, 1.3 Hz, 1H), 7.50 – 7.43 (m, 3H), 7.27 (td, *J* = 8.4, 7.9, 2.0 Hz, 2H), 6.81 (d, *J* = 7.8 Hz, 1H), 6.75 (d, *J* = 8.7 Hz, 1H), 6.71 (td, *J* = 7.5, 1.0 Hz, 1H), 6.45 (dd, *J* = 7.6, 1.7 Hz, 1H), 3.95 (s, 3H), 3.78 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 179.99, 161.42, 155.53, 141.32, 139.26, 134.63, 133.28, 132.63, 132.01, 130.88, 130.73, 128.16, 127.63, 126.90, 125.89, 125.87, 125.21, 122.42, 120.28, 110.59, 109.53, 103.64, 92.84, 90.26, 55.86, 55.66; **HRMS (ESI) (*m/z*):** calcd for $C_{27}H_{20}O_3$ ($[M+H]^+$), 393.1485; found 393.1487.



1x

1-(2-(4-methoxynaphthalen-1-yl)phenyl)-3-(naphthalen-2-yl)prop-2-yn-1-one (1x)

Orange semi solid; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.35 (d, *J* = 8.9 Hz, 1H), 8.10 (d, *J* = 7.8 Hz, 1H), 7.84 (d, *J* = 8.2 Hz, 1H), 7.74 – 7.71 (m, 1H), 7.65 (dd, *J* = 8.9, 5.3 Hz, 2H), 7.61 – 7.51 (m, 5H), 7.50 – 7.46 (m, 2H), 7.30 (d, *J* = 7.8 Hz, 1H), 7.00 (s, 1H), 6.81 (d, *J* = 7.8 Hz, 1H), 6.78 (dd, *J* = 8.5, 1.6 Hz, 1H), 3.87 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 180.40, 155.76, 141.41, 139.50, 133.88, 133.60, 133.34, 132.58, 132.49, 131.99, 130.51, 129.93, 129.09, 128.27, 128.24, 127.83, 127.81, 127.76, 127.69, 127.11, 126.77, 126.13, 126.06, 125.49, 122.64, 117.29, 103.69, 93.80, 89.10, 55.59; **HRMS (ESI) (*m/z*):** calcd for $C_{30}H_{20}O_2$ ($[M+H]^+$), 413.1536; found 413.1541.

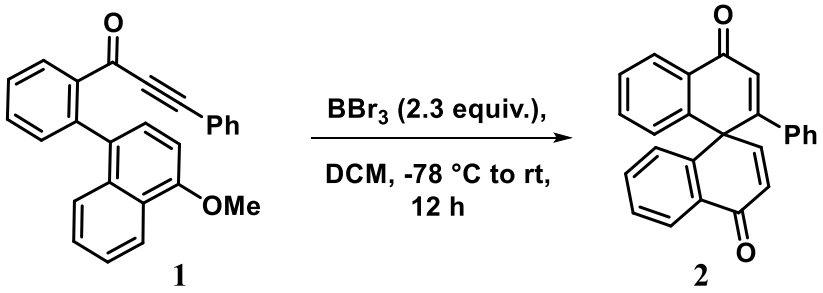


1y

1-(2-(4-methoxynaphthalen-1-yl)phenyl)-3-(thiophen-2-yl)prop-2-yn-1-one (1y)

Orange semi solid; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.32 (dd, *J* = 7.4, 1.3 Hz, 1H), 8.05 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.71 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.63 (td, *J* = 7.5, 1.4 Hz, 1H), 7.57 – 7.46 (m, 4H), 7.28 – 7.25 (m, 2H), 6.84 (d, *J* = 7.8 Hz, 1H), 6.81 (dd, *J* = 5.1, 3.7 Hz, 1H), 6.55 (dd, *J* = 3.7, 1.2 Hz, 1H), 3.97 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 179.78, 155.81, 141.47, 139.11, 136.35, 134.80, 133.32, 132.61, 132.12, 131.39, 130.41, 129.90, 128.85, 127.72, 127.40, 127.12, 125.96, 125.46, 122.60, 120.07, 103.74, 93.45, 87.29, 55.73; **HRMS (ESI) (*m/z*):** calcd for $C_{24}H_{16}O_2S$ ([M+H]$^+$), 369.0944.; found 369.0945.

4. Optimization study:



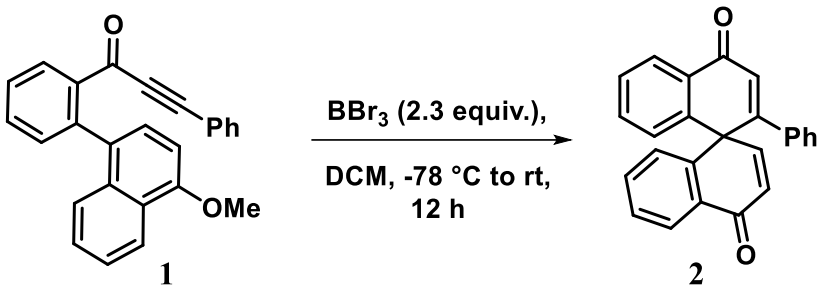
1 2

Table: Optimization of solvents for products

Entry[a]	Solvent	Temperature	Yield[b] (%)
1.	Toluene	-78 °C to rt	15
2.	**DCM**	**-78 °C to rt**	**85**
3.	THF	-78 °C to rt	0
4.	CH_3CN	0 °C to rt	0
5.	EtOAc	-78 °C to rt	75

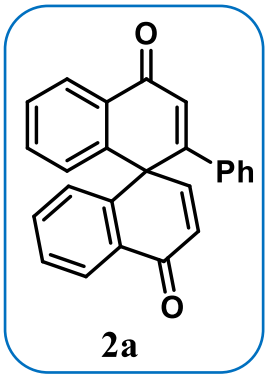
[a] Unless otherwise mentioned, 0.05 mmol of **1** was stirred in 0.5 mL solvent with 2.3 equivalents of BBr_3. [b] Isolated yield after silica gel column chromatography.

5. General procedure for synthesis of 2:



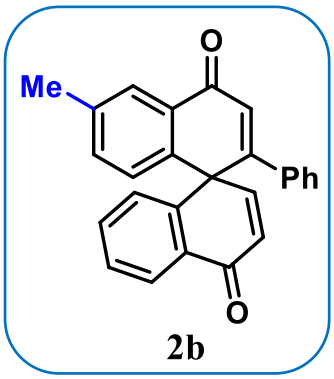
A solution of **1** (0.05 mmol) in 0.5 mL of DCM in a flame-dried flask, under nitrogen atmosphere, was cooled to -78 ℃. 1M BBr_3 in DCM (10.92µL, 2.3 equiv.) was added dropwise. The reaction mixture was allowed to warm to room temperature for 12 h. The reaction was monitored by TLC. After completion of reaction, the reaction mixture was diluted with DCM and washed with water until washings had neutral reaction. The mixed organic layer was dried over anhydrous Na_2SO_4 and the purification was performed by flash column chromatography on silica gel using ethyl acetate/petroleum ether (v/v,1:19) as eluent to give spiro product **2**.

6. Characterization of products:



2-phenyl-4*H*,4'*H*-1,1'-spirobi[naphthalene]-4,4'-dione (2a)

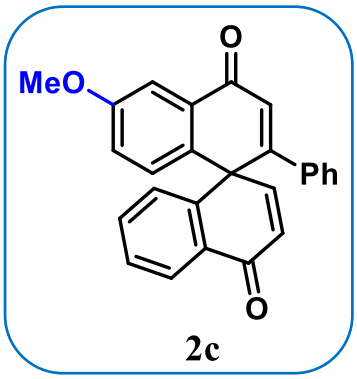
Pink solid, m.p. 203-205 ˚C, 85 % yield, 14.8 mg; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.31 – 8.28 (m, 1H), 8.17 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.47 – 7.39 (m, 4H), 7.23 – 7.19 (m, 1H), 7.14 – 7.06 (m, 3H), 6.97 – 6.94 (m, 1H), 6.80 – 6.76 (m, 4H), 6.55 (d, *J* = 10.0 Hz, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 184.48, 184.44, 159.30, 148.98, 143.54, 143.38, 137.92, 133.66, 132.32, 130.45, 130.30, 129.49, 129.33, 129.33, 129.20, 128.48, 128.36, 128.29, 127.77, 127.31, 127.16, 51.37; **HRMS (ESI) (*m/z*):** calcd for $C_{25}H_{16}O_2$ ($[M+H]^+$), 349.1224; found 349.1222.



2b

6-methyl-2-phenyl-4*H*,4'*H*-1,1'-spirobi[naphthalene]-4,4'-dione (2b)

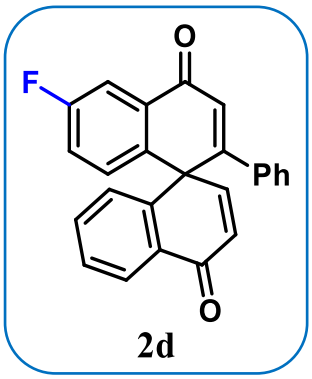
Yellow solid, m.p. 201-203 ˚C, 58 % yield, 10.51 mg; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.16 (dd, *J* = 7.6, 1.8 Hz, 1H), 8.10 (d, *J* = 2.1 Hz, 1H), 7.42 (m, 2H), 7.25 – 7.19 (m, 2H), 7.11 (t, *J* = 7.7 Hz, 2H), 7.06 (dd, *J* = 7.6, 1.6 Hz, 1H), 6.85 (d, *J* = 8.1 Hz, 1H), 6.81 – 6.74 (m, 4H), 6.53 (d, *J* = 10.0 Hz, 1H), 2.41 (s, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 184.71, 184.52, 159.22, 149.22, 143.57, 140.74, 138.48, 137.99, 134.78, 133.59, 132.31, 130.40, 130.23, 129.40, 129.29, 129.15, 129.14, 128.38, 128.27, 127.78, 127.27, 127.14, 51.18, 21.25; **HRMS (ESI) (*m/z*):** calcd for $C_{26}H_{18}O_2$ ([M+H]$^+$), 363.1380; found 363.1380.



2c

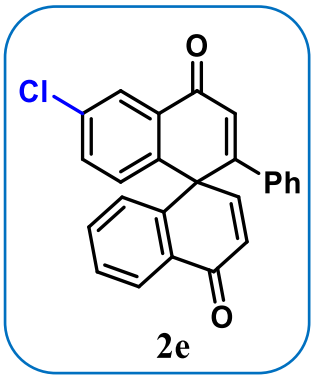
6-methoxy-2-phenyl-4*H*,4'*H*-1,1'-spirobi[naphthalene]-4,4'-dione (2c)

Orange solid, m.p. 206-208 ˚C, 66 % yield, 12.5 mg; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.15 (dd, *J* = 7.6, 1.8 Hz, 1H), 7.73 (d, *J* = 2.9 Hz, 1H), 7.47 – 7.38 (m, 2H), 7.21 (t, *J* = 7.5 Hz, 1H), 7.11 (t, *J* = 7.6 Hz, 2H), 7.07 – 7.04 (m, 1H), 7.00 (dd, *J* = 8.8, 2.9 Hz, 1H), 6.86 (d, *J* = 8.8 Hz, 1H), 6.82 – 6.71 (m, 4H), 6.52 (d, *J* = 10.0 Hz, 1H), 3.89 (s, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 184.49, 184.44, 159.52, 159.47, 149.19, 143.42, 137.93, 135.85, 133.59, 132.30, 131.65, 130.88, 130.15, 129.32, 129.11, 129.08, 128.39, 128.27, 127.77, 127.28, 122.46, 108.54, 55.87, 51.04; **HRMS (ESI) (*m/z*):** calcd for $C_{26}H_{18}O_3$ ([M+H]$^+$), 379.1329; found 379.1332.



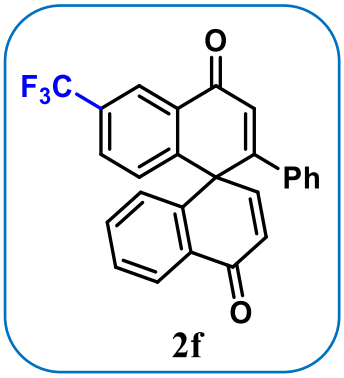
6-fluoro-2-phenyl-4*H*,4'*H*-1,1'-spirobi[naphthalene]-4,4'-dione (2d)

Yellow solid, m.p. 213-215 ˚C, 65 % yield, 12 mg; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.17 (dd, *J* = 7.4, 1.9 Hz, 1H), 7.93 (dd, *J* = 8.7, 2.9 Hz, 1H), 7.50 – 7.40 (m, 2H), 7.22 (t, *J* = 7.4 Hz, 1H), 7.17 – 7.08 (m, 3H), 7.06 (dd, *J* = 7.4, 1.6 Hz, 1H), 6.96 (dd, *J* = 8.8, 4.9 Hz, 1H), 6.79 – 6.74 (m, 4H), 6.55 (d, *J* = 10.0 Hz, 1H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 184.17, 183.40, 163.36, 161.37, 159.81, 148.54, 142.94, 139.37, 139.35, 137.67, 133.73, 132.53, 132.48, 132.27, 131.95, 131.89, 129.90, 129.47, 129.45, 129.08, 128.65, 128.32, 127.74, 127.41, 121.54, 121.36, 113.00, 112.82, 51.06; **^{19}F NMR (565 MHz, $CDCl_3$)** δ -111.84; **HRMS (ESI) (*m/z*):** calcd for $C_{25}H_{15}FO_2$ ($[M+H]^+$), 367.1129; found 367.1129.



6-chloro-2-phenyl-4*H*,4'*H*-1,1'-spirobi[naphthalene]-4,4'-dione (2e)

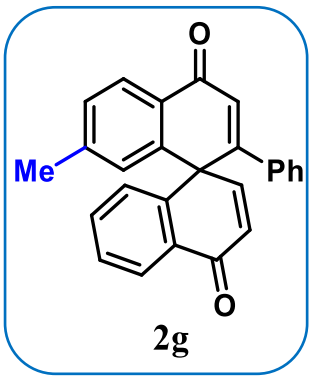
Colourless solid, m.p. 209-211 ˚C, 68 % yield, 13 mg; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.25 (d, *J* = 2.4 Hz, 1H), 8.17 (dd, *J* = 7.6, 1.8 Hz, 1H), 7.49 – 7.42 (m, 2H), 7.39 (dd, *J* = 8.5, 2.5 Hz, 1H), 7.23 (t, *J* = 7.5 Hz, 1H), 7.12 (t, *J* = 7.8 Hz, 2H), 7.06 (dd, *J* = 7.6, 1.5 Hz, 1H), 6.91 (d, *J* = 8.5 Hz, 1H), 6.80 – 6.74 (m, 4H), 6.56 (d, *J* = 10.0 Hz, 1H)**; ^{13}C NMR (125 MHz, $CDCl_3$)** δ 184.14, 183.24, 159.70, 148.30, 142.77, 141.85, 137.62, 135.00, 133.79, 133.77, 132.26, 131.76, 131.22, 130.00, 129.61, 129.52, 129.08, 128.73, 128.36, 127.73, 127.47, 126.86, 51.05; **HRMS (ESI) (*m/z*):** calcd for $C_{25}H_{15}ClO_2$ ($[M+H]^+$), 383.0834; found 383.0835.



2f

2-phenyl-6-(trifluoromethyl)-4*H*,4'*H*-1,1'-spirobi[naphthalene]-4,4'-dione (2f)

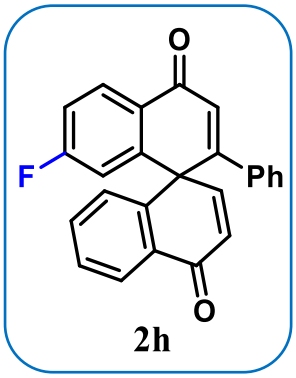
Colourless solid, m.p. 219-221 ˚C, 74 % yield, 15.4 mg; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.57 (s, 1H), 8.20 (dd, *J* = 7.4, 1.9 Hz, 1H), 7.65 (dd, *J* = 8.5, 2.1 Hz, 1H), 7.51 – 7.44 (m, 2H), 7.23 (d, *J* = 7.6 Hz, 1H), 7.12 (q, *J* = 8.5 Hz, 3H), 7.06 (d, *J* = 7.3 Hz, 1H), 6.83 (s, 1H), 6.78 (dd, *J* = 9.0, 5.3 Hz, 3H), 6.59 (d, *J* = 9.9 Hz, 1H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 183.97, 183.11, 159.84, 147.82, 147.00, 142.42, 137.49, 133.91, 132.30, 131.35, 131.09, 130.84, 130.82, 130.51, 129.98, 129.95, 129.78, 129.75, 129.72, 129.65, 129.11, 128.94, 128.42, 127.73, 127.59, 124.69, 124.56, 124.53, 122.52, 51.32; **^{19}F NMR (565 MHz, $CDCl_3$)** δ -63.01; **HRMS (ESI) (*m/z*):** calcd for $C_{26}H_{15}F_3O_2$ ($[M+H]^+$), 417.1097; found 417.1098.



2g

7-methyl-2-phenyl-4*H*,4'*H*-1,1'-spirobi[naphthalene]-4,4'-dione (2g)

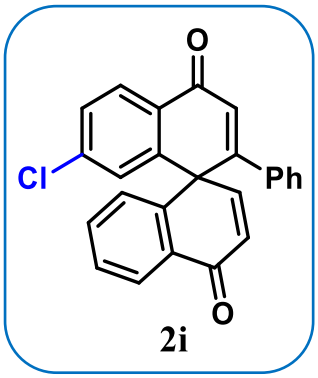
Yellow solid, m.p. 205-207 ˚C, 58 % yield, 10.51 mg; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.20 – 8.16 (m, 2H), 7.44 (m, 2H), 7.25 (dd, *J* = 8.1, 1.7 Hz, 1H), 7.21 (t, *J* = 7.5 Hz, 1H), 7.12 – 7.07 (m, 3H), 6.79 – 6.75 (m, 2H), 6.75 – 6.71 (m, 3H), 6.54 (d, *J* = 10.0 Hz, 1H), 2.25 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 184.57, 184.39, 158.94, 149.13, 144.65, 143.52, 143.49, 137.97, 133.64, 132.27, 130.32, 129.58, 129.54, 129.23, 129.21, 128.41, 128.22, 128.19, 127.77, 127.25, 127.22, 22.00; **HRMS (ESI) (*m/z*):** calcd for $C_{26}H_{18}O_2$ ($[M+H]^+$), 363.1380; found 363.1381.



2h

7-fluoro-2-phenyl-4*H*,4'*H*-1,1'-spirobi[naphthalene]-4,4'-dione (2h)

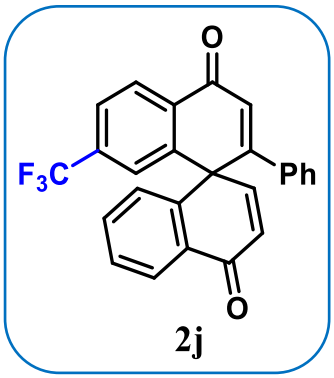
Yellow semi solid, 60 % yield, 11 mg; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.33 (dd, *J* = 8.8, 5.9 Hz, 1H), 8.18 (dd, *J* = 7.5, 1.9 Hz, 1H), 7.52 – 7.43 (m, 2H), 7.25 – 7.19 (m, 1H), 7.16 – 7.07 (m, 4H), 6.80 – 6.74 (m, 4H), 6.62 (dd, *J* = 9.5, 2.5 Hz, 1H), 6.57 (d, *J* = 10.0 Hz, 1H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 184.06, 183.25, 166.83, 164.79, 159.30, 148.22, 146.65, 146.58, 142.72, 137.66, 133.83, 132.18, 130.34, 130.26, 130.10, 129.69, 129.47, 129.07, 128.82, 128.35, 127.74, 127.52, 127.14, 127.12, 116.68, 116.50, 116.00, 115.82, 51.38**; ^{19}F NMR (565 MHz, $CDCl_3$)** δ -103.15; **HRMS (ESI) (*m/z*):** calcd for $C_{25}H_{15}FO_2$ ($[M+H]^+$), 367.1129; found 367.1129.



2i

7-chloro-2-phenyl-4*H*,4'*H*-1,1'-spirobi[naphthalene]-4,4'-dione (2i)

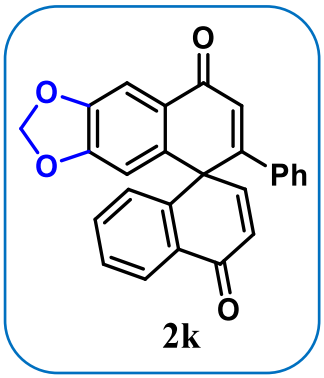
Yellow semi solid, 68 % yield, 13 mg; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.24 (d, *J* = 8.4 Hz, 1H), 8.19 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.48 (m, 2H), 7.42 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.24 – 7.21 (m, 1H), 7.13 – 7.07 (m, 3H), 6.92 (d, *J* = 2.0 Hz, 1H), 6.78 – 6.73 (m, 4H), 6.57 (d, *J* = 10.0 Hz, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 184.06, 183.50, 159.36, 148.02, 145.31, 142.54, 140.25, 137.61, 133.87, 132.25, 130.09, 129.80, 129.49, 129.32, 129.16, 129.13, 128.91, 128.87, 128.34, 127.75, 127.56, 51.19; **HRMS (ESI) (*m/z*):** calcd for $C_{25}H_{15}ClO_2$ ($[M+H]^+$), 383.0834; found 383.0831.



2j

2-phenyl-7-(trifluoromethyl)-4*H*,4'*H*-1,1'-spirobi[naphthalene]-4,4'-dione (2j)

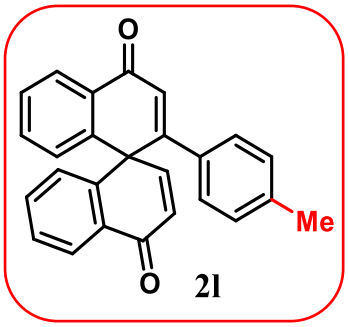
Yellow semi solid, 74 % yield, 15.4 mg; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.42 (d, *J* = 8.2 Hz, 1H), 8.19 (dd, *J* = 7.4, 2.1 Hz, 1H), 7.70 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.48 (m, 2H), 7.26 – 7.22 (m, 1H), 7.18 (s, 1H), 7.12 (t, *J* = 7.7 Hz, 2H), 7.05 (dd, *J* = 7.4, 1.8 Hz, 1H), 6.81 – 6.72 (m, 4H), 6.59 (d, *J* = 10.0 Hz, 1H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 183.84, 183.30, 160.24, 147.56, 144.41, 142.14, 137.44, 135.27, 135.01, 133.90, 132.88, 132.34, 130.09, 130.04, 129.58, 129.09, 129.00, 128.36, 128.07, 127.72, 127.65, 126.55, 126.52, 126.49, 126.46, 125.22, 125.19, 124.38, 122.21, 51.36; **^{19}F NMR (565 MHz, $CDCl_3$)** δ -63.13; **HRMS (ESI) (*m/z*):** calcd for $C_{26}H_{15}F_3O_2$ ($[M+H]^+$), 417.1097; found 417.1097.



2k

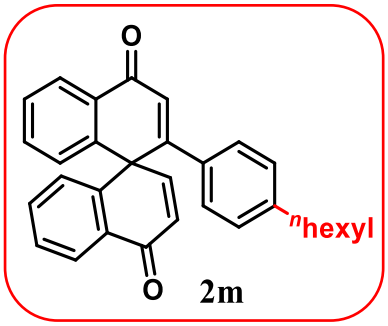
6'-phenyl-4*H*,8'*H*-spiro[naphthalene-1,5'-naphtho[2,3-*d*][1,3]dioxole]-4,8'-dione (2k)

Brown solid, m.p. 217-219 ˚C, 70 % yield, 13.73 mg; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.15 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.67 (s, 1H), 7.45 (m, 2H), 7.23 – 7.18 (m, 1H), 7.12 – 7.07 (m, 3H), 6.76 – 6.71 (m, 4H), 6.53 (d, *J* = 10.0 Hz, 1H), 6.32 (s, 1H), 6.00 (d, *J* = 1.3 Hz, 1H), 5.97 (d, *J* = 1.3 Hz, 1H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 184.29, 183.26, 158.53, 152.52, 149.01, 148.45, 143.18, 140.02, 137.83, 133.68, 132.25, 130.03, 129.34, 129.23, 129.03, 128.56, 128.23, 127.79, 127.33, 126.12, 108.40, 105.58, 102.33, 51.60; **HRMS (ESI) (*m/z*):** calcd for $C_{26}H_{16}O_4$ ($[M+H]^+$), 393.1122; found 393.1122.



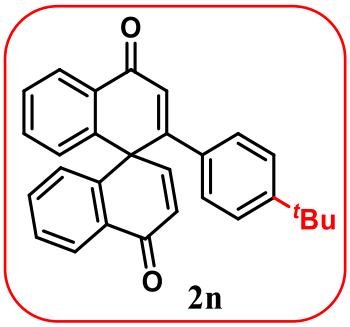
2-(*p*-tolyl)-4*H*,4'*H*-1,1'-spirobi[naphthalene]-4,4'-dione (2l)

Orange solid, m.p. 196-198 ˚C, 45 % yield, 8.15 mg; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.31 – 8.27 (m, 1H), 8.19 (d, *J* = 7.6 Hz, 1H), 7.47 – 7.40 (m, 4H), 7.07 (d, *J* = 7.3 Hz, 1H), 6.94 (dd, *J* = 19.3, 6.3 Hz, 3H), 6.82 – 6.76 (m, 2H), 6.70 (d, *J* = 7.7 Hz, 2H), 6.55 (d, *J* = 9.9 Hz, 1H), 2.24 (s, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 184.58, 184.54, 159.34, 149.31, 143.63, 143.56, 139.53, 135.13, 133.68, 133.58, 132.31, 130.48, 130.00, 129.47, 129.22, 129.16, 129.06, 128.43, 128.29, 127.67, 127.31, 127.14, 51.39, 21.33; **HRMS (ESI) (*m/z*):** calcd for $C_{26}H_{18}O_2$ ($[M+H]^+$), 363.1380; found 363.1380.



2-(4-hexylphenyl)-4*H*,4'*H*-1,1'-spirobi[naphthalene]-4,4'-dione (2m)

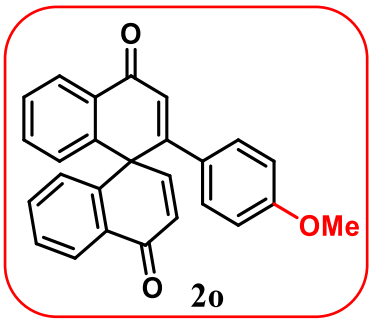
Colourless solid, m.p. 209-211 ˚C, 64 % yield, 13.84 mg; **^{1}H NMR (400 MHz, DMSO)** δ 8.14 (dd, *J* = 7.4, 2.0 Hz, 1H), 8.02 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.56 – 7.44 (m, 4H), 7.17 – 7.10 (m, 2H), 7.01 – 6.93 (m, 3H), 6.79 (d, *J* = 8.2 Hz, 2H), 6.71 (s, 1H), 6.55 (d, *J* = 10.0 Hz, 1H), 2.45 (t, *J* = 7.7 Hz, 2H), 1.45 (m, *J* = 7.9 Hz, 2H), 1.25 – 1.16 (m, 6H), 0.85 – 0.78 (t, 3H); **^{13}C NMR (150 MHz, DMSO)** δ 183.53, 183.34, 158.24, 149.84, 143.42, 143.30, 143.15, 135.15, 133.72, 133.63, 131.47, 129.76, 129.30, 129.26, 129.01, 128.33, 128.12, 127.84, 127.35, 126.41, 126.24, 126.09, 50.63, 34.60, 30.98, 30.41, 28.21, 21.98, 13.89; **HRMS (ESI) (*m/z*):** calcd for $C_{31}H_{28}O_2$ ($[M+H]^+$), 433.2163; found 433.2161.



2n

2-(4-(*tert*-butyl)phenyl)-4*H*,4'*H*-1,1'-spirobi[naphthalene]-4,4'-dione (2n)

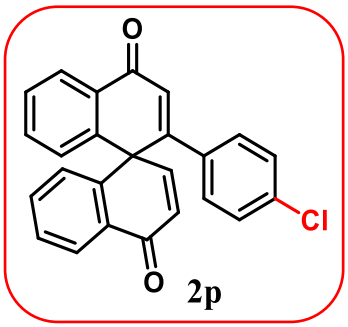
Colourless solid, m.p. 215-217 °C, 62 % yield, 12.54 mg; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.32 – 8.29 (m, 1H), 8.26 – 8.24 (m, 1H), 7.49 – 7.43 (m, 4H), 7.18 – 7.13 (m, 2H), 7.13 – 7.10 (m, 1H), 7.01 – 6.97 (m, 1H), 6.88 (s, 1H), 6.80 (dd, *J* = 9.2, 7.1 Hz, 3H), 6.59 (d, *J* = 10.0 Hz, 1H), 1.24 (s, 9H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 184.71, 184.58, 159.05, 152.82, 149.47, 143.75, 143.47, 135.07, 133.78, 133.57, 132.18, 130.40, 129.95, 129.38, 129.21, 129.00, 128.42, 128.22, 127.49, 127.41, 127.14, 125.38, 51.18, 34.80, 31.28; **HRMS (ESI) (*m/z*):** calcd for $C_{29}H_{24}O_2$ ($[M+H]^+$), 405.1850; found 405.1848.



2o

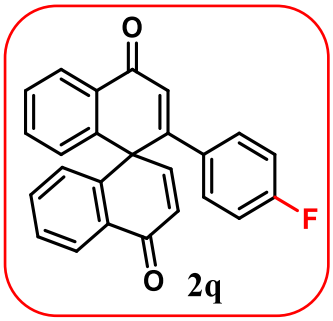
2-(4-methoxyphenyl)-4*H*,4'*H*-1,1'-spirobi[naphthalene]-4,4'-dione (2o)

Brown solid, m.p. 211-213 °C, 78 % yield, 14.76 mg; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.31 – 8.24 (m, 1H), 8.26 – 8.19 (m, 1H), 7.44 – 7.40 (m, 4H), 7.08 – 7.05 (m, 1H), 6.97 – 6.93 (m, 1H), 6.83 – 6.76 (m, 4H), 6.65 – 6.62 (m, 2H), 6.56 (d, *J* = 10.0 Hz, 1H), 3.71 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 184.63, 184.51, 160.51, 158.75, 149.67, 143.84, 143.45, 133.77, 133.52, 132.17, 130.39, 130.33, 129.56, 129.40, 129.17, 129.06, 129.01, 128.42, 128.22, 127.34, 127.08, 113.81, 55.37, 51.33; **HRMS (ESI) (*m/z*):** calcd for $C_{26}H_{18}O_3$ ($[M+H]^+$), 379.1329; found 379.1329.



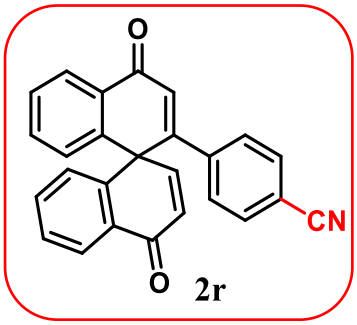
2-(4-chlorophenyl)-4*H*,4'*H*-1,1'-spirobi[naphthalene]-4,4'-dione (2p)

Yellow semi solid, 78 % yield, 14.93 mg; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.31 – 8.27 (m, 1H), 8.18 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.48 – 7.43 (m, 4H), 7.11 – 7.07 (m, 2H), 7.05 (dd, *J* = 7.8, 1.4 Hz, 1H), 6.97 – 6.93 (m, 1H), 6.76 (d, *J* = 11.2 Hz, 2H), 6.72 (d, *J* = 8.6 Hz, 2H), 6.57 (d, *J* = 10.0 Hz, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 184.27, 184.25, 158.00, 148.69, 143.38, 143.08, 136.27, 135.55, 133.82, 133.80, 132.26, 130.53, 130.31, 129.50, 129.47, 129.13, 129.11, 128.69, 128.62, 128.48, 127.45, 127.20, 51.22; **HRMS (ESI) (*m/z*):** calcd for $C_{25}H_{15}ClO_2$ ($[M+H]^+$), 383.0834; found 383.0834.



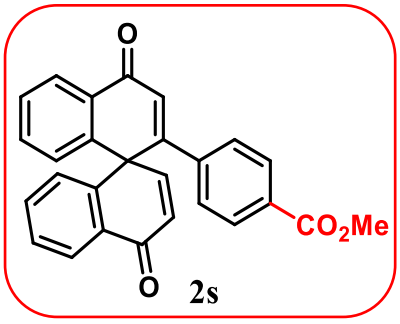
2-(4-fluorophenyl)-4*H*,4'*H*-1,1'-spirobi[naphthalene]-4,4'-dione (2q)

Orange semi solid, 69 % yield, 12.64 mg; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.31 – 8.26 (m, 1H), 8.18 (dd, *J* = 7.3, 2.0 Hz, 1H), 7.48 – 7.41 (m, 4H), 7.06 (d, *J* = 7.5 Hz, 1H), 6.98 – 6.94 (m, 1H), 6.84 – 6.74 (m, 6H), 6.56 (d, *J* = 9.9 Hz, 1H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 184.31, 184.27, 164.18, 162.19, 158.16, 148.83, 143.44, 143.23, 133.94, 133.91, 133.75, 132.32, 131.71, 130.53, 130.37, 129.75, 129.68, 129.51, 129.41, 129.14, 128.63, 128.44, 127.40, 127.19, 126.16, 125.80, 115.54, 115.37, 51.37; **^{19}F NMR (565 MHz, $CDCl_3$)** δ -111.49; **HRMS (ESI) (*m/z*):** calcd for $C_{25}H_{15}FO_2$ ($[M+H]^+$), 367.1129; found 367.1128.



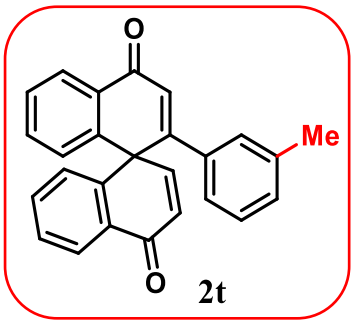
4-(4,4'-dioxo-4*H*,4'*H*-1,1'-spirobi[naphthalen]-2-yl)benzonitrile (2r)

Orange solid, m.p. 222-224 ˚C, 64 % yield, 11.95 mg; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.31 – 8.28 (m, 1H), 8.16 (dd, *J* = 7.6, 1.9 Hz, 1H), 7.50 – 7.45 (m, 4H), 7.42 (d, *J* = 8.4 Hz, 2H), 7.06 (dd, *J* = 7.6, 1.6 Hz, 1H), 6.97 – 6.94 (m, 1H), 6.90 – 6.87 (m, 2H), 6.78 (d, *J* = 10.0 Hz, 1H), 6.73 (s, 1H), 6.57 (d, *J* = 10.0 Hz, 1H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 183.86, 183.84, 157.09, 147.99, 143.20, 142.57, 142.18, 134.05, 133.87, 132.25, 132.04, 130.96, 130.22, 129.74, 129.49, 129.14, 128.91, 128.68, 128.64, 127.54, 127.28, 118.11, 113.22, 51.03; **HRMS (ESI) (*m/z*):** calcd for $C_{26}H_{15}NO_2$ ($[M+H]^+$), 374.1176; found 374.1178.



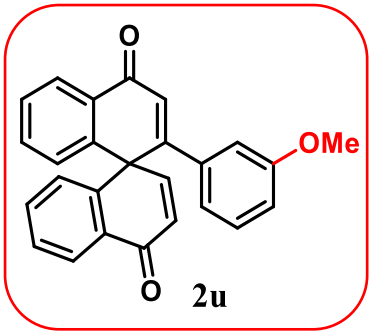
methyl 4-(4,4'-dioxo-4*H*,4'*H*-1,1'-spirobi[naphthalen]-2-yl)benzoate (2s)

Yellow solid, m.p. 193-195 ˚C, 54 % yield, 10.97 mg; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.32 – 8.29 (m, 1H), 8.18 – 8.13 (m, 1H), 7.78 (d, *J* = 8.4 Hz, 2H), 7.49 – 7.40 (m, 4H), 7.07 (d, *J* = 7.7 Hz, 1H), 6.98 – 6.94 (m, 1H), 6.84 (d, *J* = 8.4 Hz, 2H), 6.81 – 6.75 (m, 2H), 6.55 (d, *J* = 10.0 Hz, 1H), 3.86 (s, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 184.14, 184.08, 166.44, 158.24, 148.40, 143.41, 142.91, 142.18, 133.86, 133.73, 132.30, 130.80, 130.61, 130.35, 129.54, 129.51, 129.46, 129.21, 128.70, 128.53, 127.94, 127.42, 127.22, 52.43, 51.20; **HRMS (ESI) (*m/z*):** calcd for $C_{27}H_{18}O_4$ ($[M+H]^+$), 407.1278; found 407.1276.



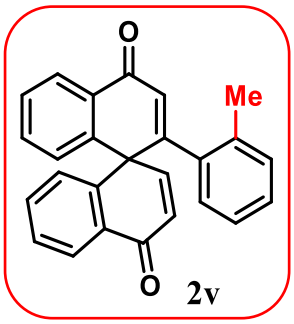
2-(*m*-tolyl)-4*H*,4'*H*-1,1'-spirobi[naphthalene]-4,4'-dione (2t)

Orange solid, m.p. 194-196 ˚C, 48 % yield, 8.7 mg; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.32 – 8.26 (m, 1H), 8.18 (dd, *J* = 7.5, 1.9 Hz, 1H), 7.44 (m, 4H), 7.07 (d, *J* = 7.0 Hz, 1H), 7.03 (d, *J* = 7.7 Hz, 1H), 6.97 (dt, *J* = 7.5, 5.9 Hz, 2H), 6.77 (d, *J* = 8.5 Hz, 2H), 6.58 (s, 1H), 6.53 (dd, *J* = 9.3, 4.0 Hz, 2H), 2.16 (s, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 184.54, 184.49, 159.51, 149.08, 143.61, 143.49, 137.93, 137.90, 133.62, 132.44, 130.50, 130.14, 130.09, 129.52, 129.27, 129.24, 128.64, 128.45, 128.34, 128.13, 127.22, 127.15, 124.75, 51.40, 21.50; **HRMS (ESI) (*m/z*):** calcd for $C_{26}H_{18}O_2$ ([M+H]$^+$), 363.1380; found 363.1379.



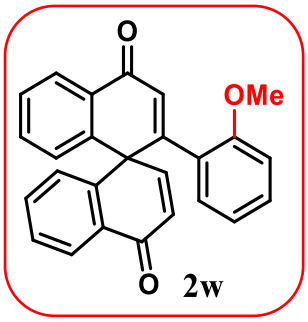
2-(3-methoxyphenyl)-4*H*,4'*H*-1,1'-spirobi[naphthalene]-4,4'-dione (2u)

Brwon semi solid, 79 % yield, 14.95 mg; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.32 – 8.28 (m, 1H), 8.19 (dd, *J* = 7.6, 1.8 Hz, 1H), 7.44 (m, 5H), 7.08 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.04 (t, *J* = 7.9 Hz, 1H), 6.82 – 6.75 (m, 3H), 6.55 (d, *J* = 10.0 Hz, 1H), 6.42 (d, *J* = 8.1 Hz, 1H), 6.25 (s, 1H), 3.54 (s, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 184.52, 184.47, 159.13, 159.02, 149.07, 143.50, 143.47, 139.22, 133.69, 133.67, 132.39, 130.43, 130.22, 129.48, 129.45, 129.24, 128.49, 128.37, 127.32, 127.17, 120.36, 115.53, 115.31, 113.05, 55.24, 51.29; **HRMS (ESI) (*m/z*):** calcd for $C_{26}H_{18}O_3$ ([M+H]$^+$), 379.1329; found 379.1328.



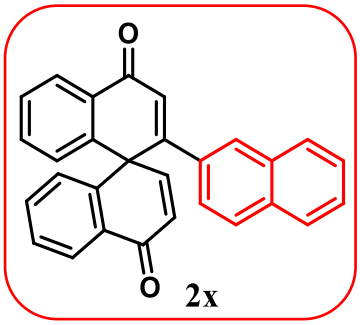
2-(*o*-tolyl)-4*H*,4'*H*-1,1'-spirobi[naphthalene]-4,4'-dione (2v)

Orange semi solid, 44 % yield, 7.97 mg; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.37 – 8.32 (m, 1H), 8.09 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.54 – 7.42 (m, 4H), 7.08 (m, 3H), 7.03 – 6.98 (m, 1H), 6.87 (d, *J* = 10.1 Hz, 1H), 6.73 (m, 1H), 6.58 (s, 1H), 6.47 (d, *J* = 10.1 Hz, 1H), 5.94 (d, *J* = 7.9 Hz, 1H), 2.17 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 184.36, 184.02, 158.45, 147.53, 144.27, 142.92, 136.05, 135.27, 133.71, 133.20, 132.80, 131.73, 130.77, 130.65, 129.79, 129.66, 129.58, 128.76, 128.57, 128.50, 127.47, 127.10, 127.07, 124.80, 52.36, 20.59; **HRMS (ESI) (*m/z*):** calcd for $C_{26}H_{18}O_2$ ([M+H]$^+$), 363.1380; found 363.1380.



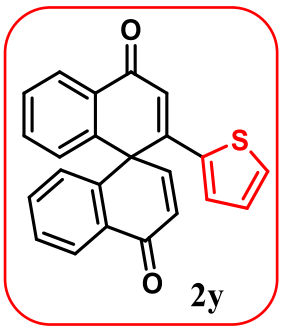
2-(2-methoxyphenyl)-4*H*,4'*H*-1,1'-spirobi[naphthalene]-4,4'-dione (2w)

Brown solid, m.p. 207-209 ˚C, 75 % yield, 14.19 mg; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.32 (dd, *J* = 7.5, 1.8 Hz, 1H), 8.04 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.45 (m, 3H), 7.38 (td, *J* = 7.5, 1.3 Hz, 1H), 7.14 (m, 1H), 7.07 (dd, *J* = 7.9, 1.2 Hz, 1H), 6.97 (dd, *J* = 7.5, 1.5 Hz, 1H), 6.93 (d, *J* = 10.0 Hz, 1H), 6.74 (dd, *J* = 8.4, 1.0 Hz, 1H), 6.60 (s, 1H), 6.52 (td, *J* = 7.5, 1.0 Hz, 1H), 6.44 (d, *J* = 10.0 Hz, 1H), 6.05 (dd, *J* = 7.6, 1.7 Hz, 1H), 3.63 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 184.54, 184.38, 156.31, 156.05, 148.79, 144.07, 143.05, 133.46, 132.82, 132.39, 131.85, 130.74, 130.16, 129.76, 129.59, 128.93, 128.36, 128.34, 128.18, 127.04, 126.76, 125.72, 119.66, 110.89, 55.34, 52.22; **HRMS (ESI) (*m/z*):** calcd for $C_{26}H_{18}O_3$ ([M+H]$^+$), 379.1329; found 379.1332.



2-(naphthalen-2-yl)-4*H*,4'*H*-1,1'-spirobi[naphthalene]-4,4'-dione (2x)

Brown solid, m.p. 219-221 ˚C, 77 % yield, 15.34 mg; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.35 – 8.29 (m, 1H), 8.19 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.72 (d, *J* = 7.2 Hz, 1H), 7.58 (t, *J* = 7.6 Hz, 2H), 7.50 – 7.40 (m, 6H), 7.32 (d, *J* = 1.9 Hz, 1H), 7.16 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.01 – 6.98 (m, 1H), 6.92 (s, 1H), 6.86 (t, *J* = 9.3 Hz, 2H), 6.54 (d, *J* = 10.0 Hz, 1H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 184.44, 184.38, 159.22, 149.16, 143.59, 143.52, 135.44, 133.75, 133.69, 133.35, 132.64, 132.36, 130.59, 130.47, 129.47, 129.27, 129.25, 128.55, 128.54, 128.37, 128.04, 127.72, 127.69, 127.36, 127.19, 126.79, 125.00, 51.44; **HRMS (ESI) (*m/z*):** calcd for $C_{29}H_{18}O_2$ ($[M+H]^+$), 399.1380; found 399.1378.

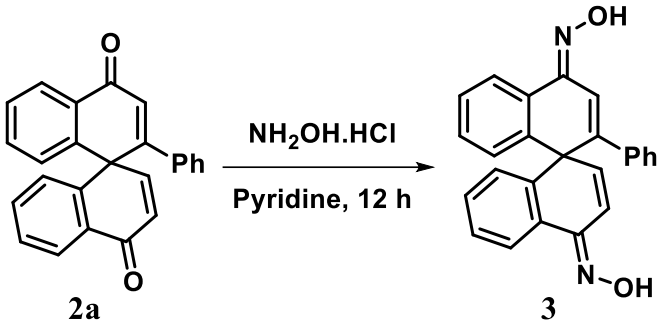


2-(thiophen-2-yl)-4*H*,4'*H*-1,1'-spirobi[naphthalene]-4,4'-dione (2y)

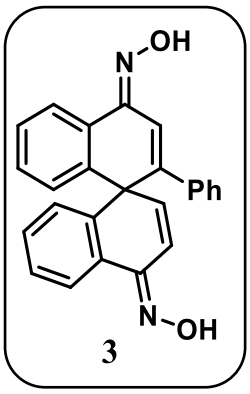
Brown solid, m.p. 197-199 ˚C, 52 % yield, 9.21 mg; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.32 (d, *J* = 7.8 Hz, 1H), 8.28 – 8.25 (m, 1H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.44 – 7.40 (m, 2H), 7.24 (d, *J* = 5.2 Hz, 1H), 7.15 (s, 1H), 7.07 (d, *J* = 7.8 Hz, 1H), 6.97 – 6.91 (m, 2H), 6.86 (t, *J* = 4.5 Hz, 1H), 6.80 (s, 1H), 6.64 (d, *J* = 10.0 Hz, 1H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 184.80, 184.07, 151.30, 149.87, 143.86, 142.80, 139.79, 134.13, 133.65, 132.51, 130.21, 129.65, 129.34, 129.23, 129.11, 128.89, 128.82, 128.25, 127.85, 127.53, 127.48, 127.04, 50.60; **HRMS (ESI) (*m/z*):** calcd for $C_{23}H_{14}O_2S$ ($[M+H]^+$), 355.0788; found 355.0784.

7. Synthetic transformation of 2a:

7.1. Synthetic transformation of 2a to 3:

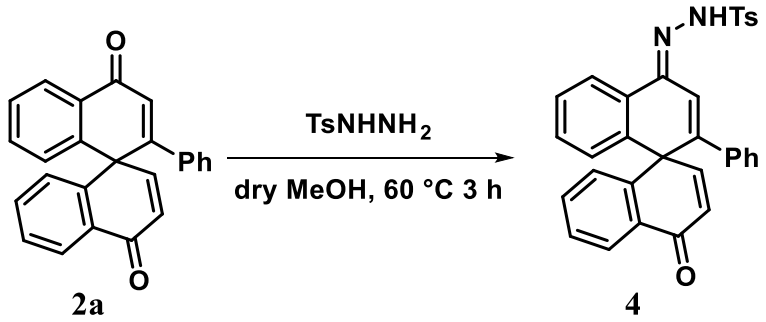


In an oven dried 10 mL round-bottom flask, **2a** (0.05 mmol, 1.0 equiv) was taken along with hydroxylamine hydrochloride (0.2 mmol, 4.0 equiv) and pyridine (0.25 mL) under argon atmosphere. For 12 h, the reaction mixture was agitated at 90 °C. EtOAc (5 mL) was added to the reaction system once the reaction was finished. Then, the mixture was washed with 2 M hydrochloric acid and dried over anhydrous Na_2SO_4. The solvent was removed under vacuo and the residue was purified with chromatography column on silica gel (gradient eluent of EtOAc/petroleum ether: 1/20 to 1/5) to give the product **3** (17.78 mg, 94% yield).[6]

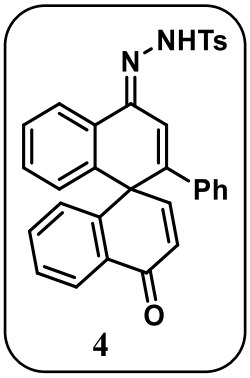


Orange semi liquid, 94 % yield, 17.78 mg; **^{1}H NMR (600 MHz, DMSO)** δ 11.72 (s, 1H), 11.55 (s, 1H), 8.08 – 8.04 (m, 1H), 8.00 – 7.96 (m, 1H), 7.29 – 7.21 (m, 5H), 7.21 – 7.17 (m, 1H), 7.15 (dd, *J* = 8.2, 6.5 Hz, 2H), 7.09 (d, *J* = 10.2 Hz, 1H), 6.96 – 6.91 (m, 3H), 6.81 (dd, *J* = 7.6, 1.7 Hz, 1H), 6.22 (d, *J* = 10.2 Hz, 1H); **^{13}C NMR (150 MHz, DMSO)** δ 147.74, 145.55, 145.17, 140.48, 140.13, 139.62, 139.01, 129.53, 129.29, 129.18, 129.09, 127.92, 127.79, 127.76, 127.68, 127.36, 127.17, 126.99, 122.44, 122.15, 115.79, 114.32, 50.40; **HRMS (ESI) (*m/z*):** calcd for $C_{25}H_{18}N_2O_2$ ($[M+H]^+$), 379.1442; found 379.1442.

7.2. Synthetic transformation of 2a to 4:

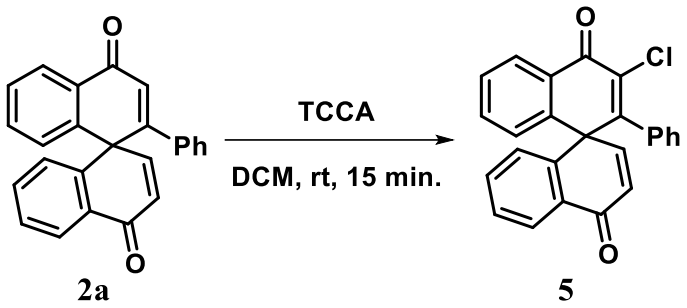


To an oven dried round-bottom flask previously equipped with a magnetic stir bar, was charged with hydrazide (0.05 mmol) in dry methanol (0.25 mL) at 60 °C, **2a** (0.05 mmol, 1.0 equiv) was added. After the completion of reaction, the product began to precipitate. The crude product was filtered and purified by silica gel column chromatography with hexane/ethyl acetate (20-30) % and dried to afford the pure hydrazone **4** (11 mg, 43% yield).[7]



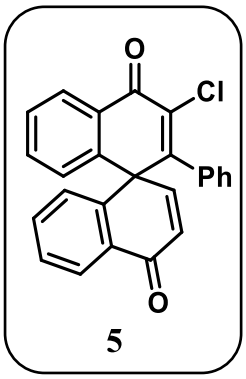
Yellow semi solid, 43 % yield, 11 mg; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.22 (dd, *J* = 8.1, 1.4 Hz, 1H), 8.11 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.98 (d, *J* = 8.3 Hz, 2H), 7.41 – 7.33 (m, 4H), 7.33 – 7.28 (m, 1H), 7.22 – 7.15 (m, 2H), 7.07 (t, *J* = 7.7 Hz, 2H), 7.01 (dd, *J* = 7.7, 1.4 Hz, 1H), 6.89 (s, 1H), 6.79 – 6.72 (m, 4H), 6.44 (d, *J* = 10.0 Hz, 1H), 2.45 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 184.66, 151.71, 150.05, 145.28, 144.63, 144.61, 138.83, 138.35, 135.41, 133.50, 131.87, 130.45, 129.90, 129.67, 129.23, 129.02, 128.92, 128.53, 128.28, 128.26, 128.13, 128.00, 127.87, 126.96, 124.60, 116.61, 51.33, 29.91; **HRMS (ESI) (*m/z*):** calcd for $C_{32}H_{24}N_2O_3S$ ($[M+H]^+$), 517.1581; found 517.1581.

7.3. Synthetic transformation of 2a to 5:



2a **5**

In an oven dried 5 mL vial, **2a** (0.05 mmol) was taken in 0.25 ml DCM. In that resulting solution, trichloroisocyanuric acid (TCCA) (0.05 mmol, 1.0 equiv) was added and stirred at room temperature until **2a** fully consumed. At the end of the reaction, the solvent was removed in vacuum. The residue was purified by flash column chromatography with (gradient eluent of EtOAc/petroleum ether: 95/5) to afford product **5** as white solid (16 mg, 92% yield).[8]



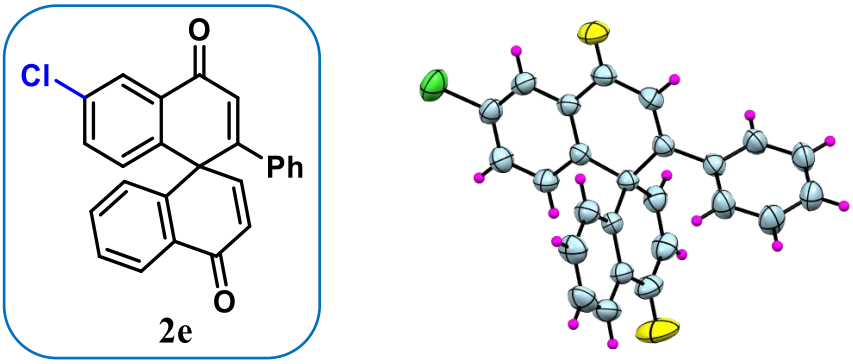
5

Colourless solid, 92 % yield, 16 mg; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.03 (d, *J* = 7.1 Hz, 1H), 7.94 (d, *J* = 6.5 Hz, 1H), 7.54 – 7.48 (m, 2H), 7.44 (t, *J* = 7.5 Hz, 1H), 7.35 (t, *J* = 7.6 Hz, 1H), 7.18 (t, *J* = 7.5 Hz, 1H), 7.01 (t, *J* = 7.7 Hz, 2H), 6.92 (d, *J* = 7.9 Hz, 1H), 6.89 (d, *J* = 7.1 Hz, 1H), 6.66 (d, *J* = 10.0 Hz, 1H), 6.61 (d, *J* = 7.6 Hz, 2H), 6.16 (d, *J* = 10.0 Hz, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 184.06, 183.50, 159.36, 148.02, 145.31, 142.54, 140.25, 137.61, 133.87, 132.25, 130.09, 129.80, 129.49, 129.32, 129.16, 129.13, 128.91, 128.87, 128.34, 127.75, 127.56, 51.19; **HRMS (ESI) (*m/z*):** calcd for $C_{25}H_{15}ClO_2$ ($[M+H]^+$), 383.0834; found 383.0834.

8. Single crystal X-ray diffraction analysis:

The compound **2d** was dissolved in minimum amount of *n*-hexane/DCM (3:1) and kept the solution at room temperature for 2 days to give block like crystal. The crystallographic refinement parameters are given below:

CCDC No.	**2331763**
Empirical formula	$C_{25}H_{15}ClO_2$
Formula weight	382.82
Crystal habit, colour	Block, clear colourless
Temperature, (T)	297 K
Bond precision	C-C = 0.0027 Å
Wavelength (λ)	0.71073 Å
Space group	P 1 21/c 1
Unit cell dimensions	a = 16.591 (10) Å α = 90° b = 7.190 (4) Å β = 93.373 (17)° c = 15.695 (9) Å γ = 90°
Volume	1868.9 (19) $Å^3$
Z	4
Density (calculated)	1.361 g/cm^3
Absorption coefficient (μ)	0.223 mm^{-1}
F(000)	792.0
T_{min}, T_{max}	0.939, 0.952
$T_{min'}$	0.939
Theta (max)	26.322°
R (reflections)	0.0432 (3032)
WR2 (reflections)	0.1019 (3785)

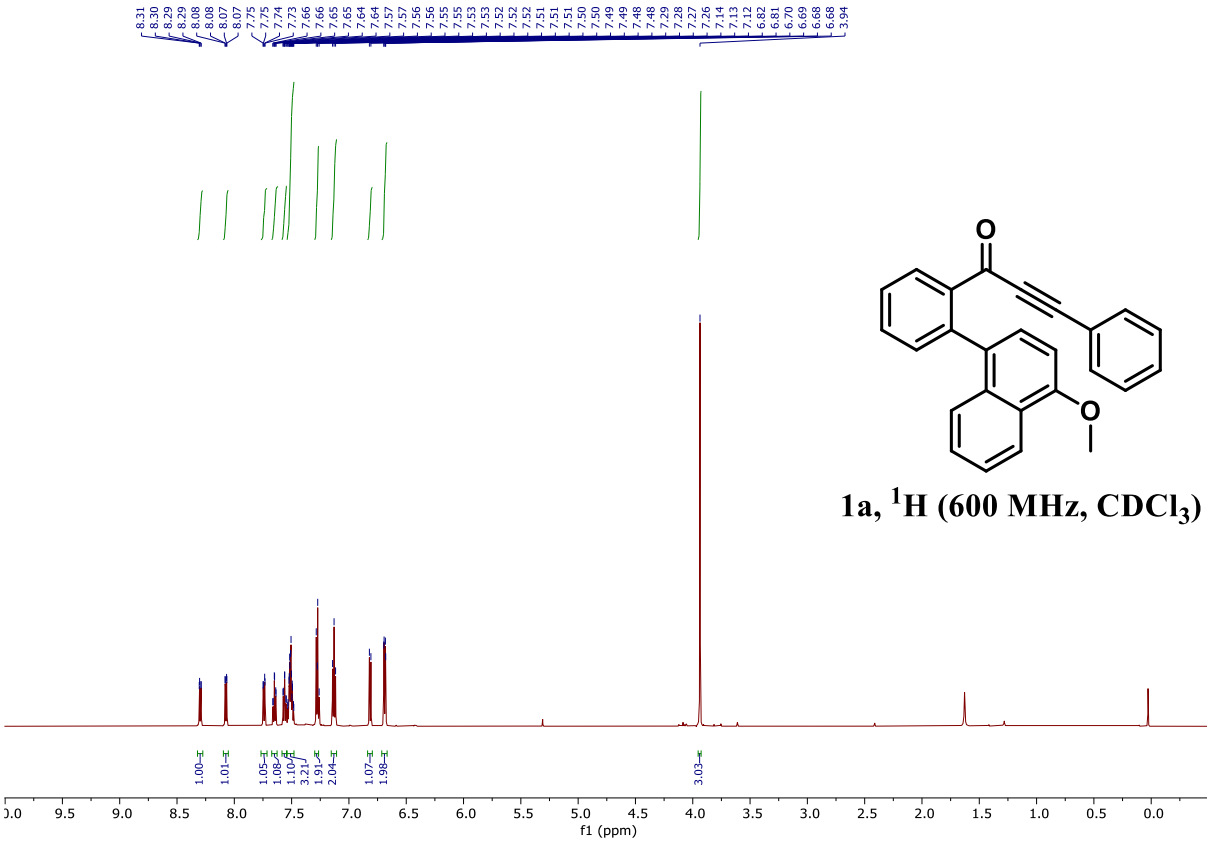


[Fig: ORTEP of the X-ray structure of compound 2e.]

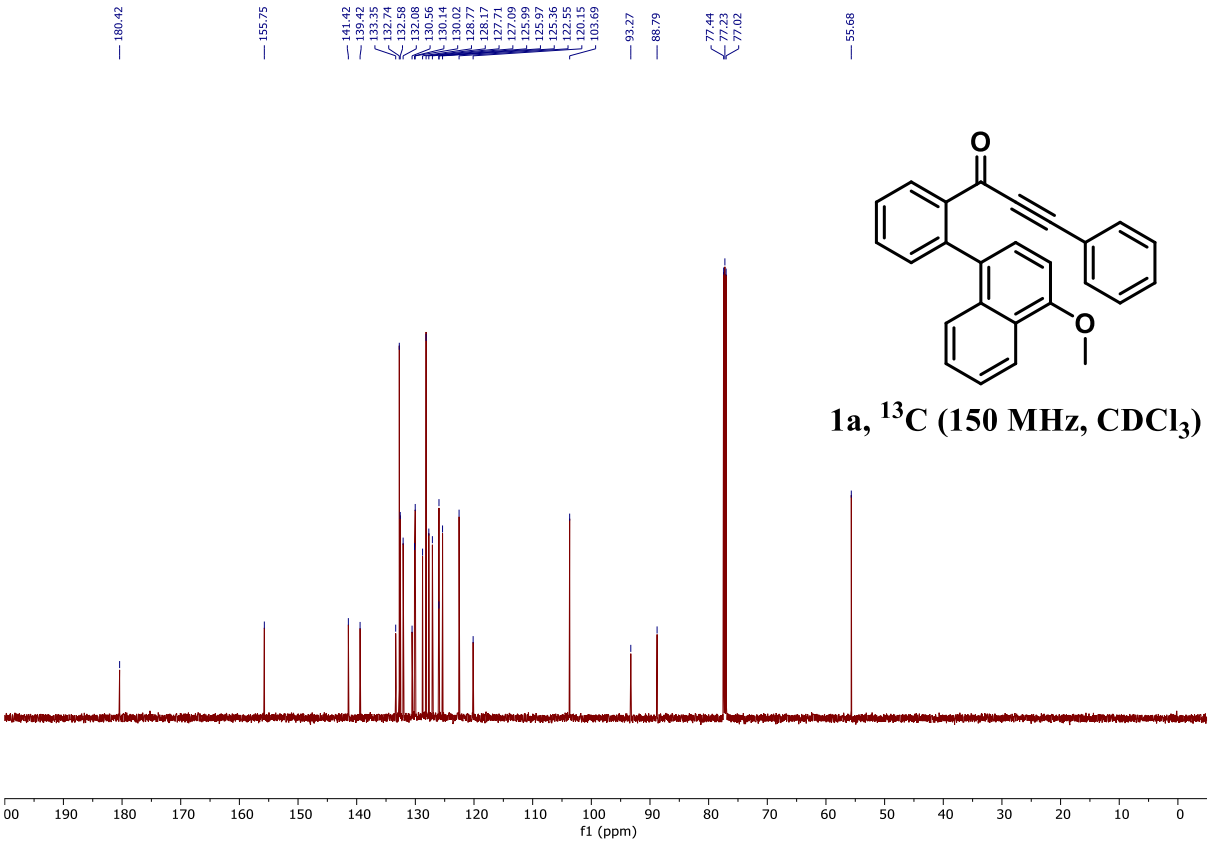
9. References:

1. Shi, Z. F.; Wang, L. J.; Wang, H.; Cao, X. P.; Zhang, H. L. *Org. Lett.* **2007**, *9*, 595.
2. Darses, S.; Michaud, G.; Genet, J.-P. *Eur. J. Org. Chem.* **1999**, 1875−1883.
3. a) Prieto, M.; Zurita, E.; Rosa, E.; Muñoz, L.; Lloyd-Williams, P.; Giralt, E. *J. Org. Chem*., **2004**, *69*, 6812; b) Hoque E.; Bisht R.; Haldar C.; Chattopadhyay B. *J. Am. Chem. Soc*., **2017**, *139*, 7745; c) Roy S.; Das S.K.; Chattopadhyay B. *Angew. Chem. Int. Ed*., **2018**, *57*, 2238.
4. Zhang Y.; Guo D.; Ye S.; Liu Z.; Zhu G. *Org. Lett*.**2017**, *19*, 1302.
5. Zhou M.; Dong D.; Zhu B.; Geng H; Wang Y.; Zhang X. *Org. Lett.* **2013**, *15* (21), 5524-5527.
6. Manna S.; Ashwathappa P. K. S.; Prabhu K. R.; *Chem. Commun.* **2020**, *56*, 13165–13168.
7. Zhang B.H.; Lei L.S.; Liu S.Z.; Mou X.Q.; Liu W.T.; Wang S.H.; Wang J.; Bao W.; Zhang K. *Chem. Commun.*, **2017**, *53*, 8545.

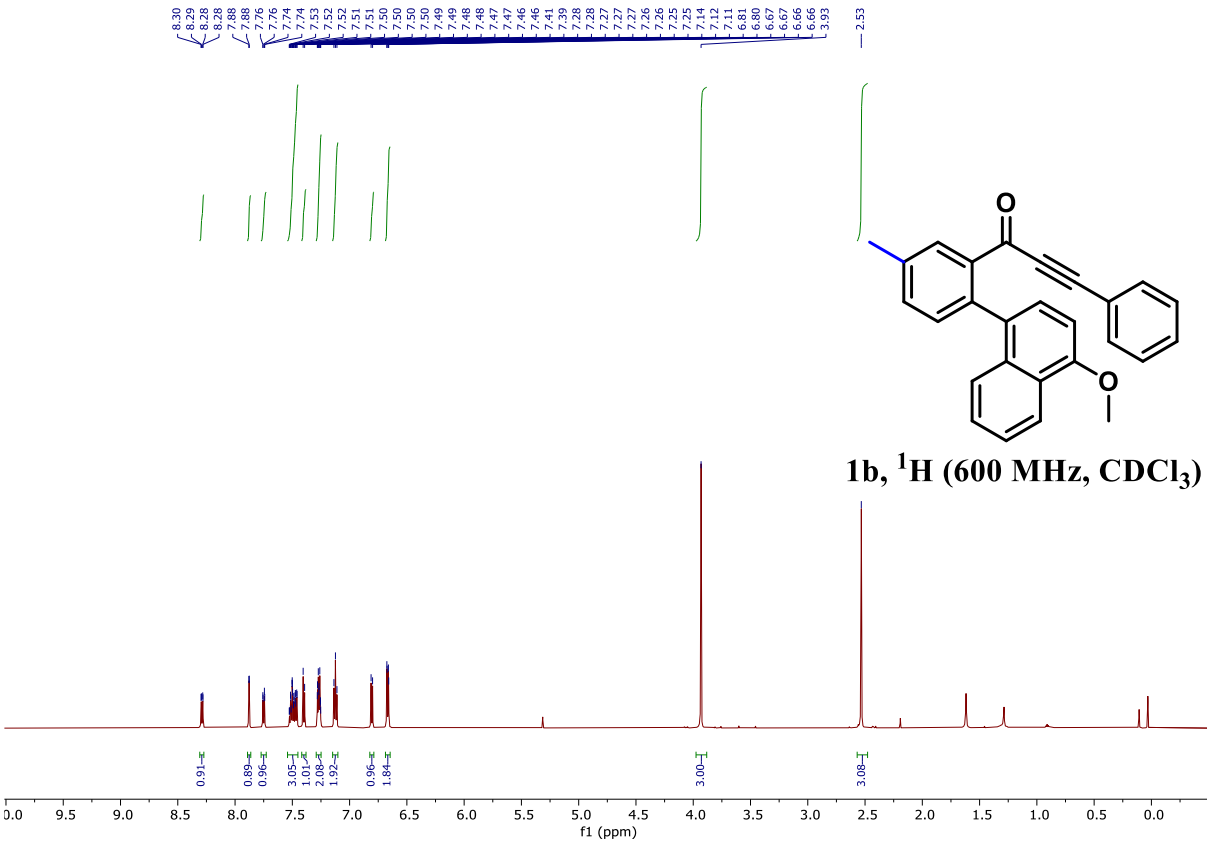
10.^{1}H-NMR & ^{13}C NMR Spectra of starting materials:



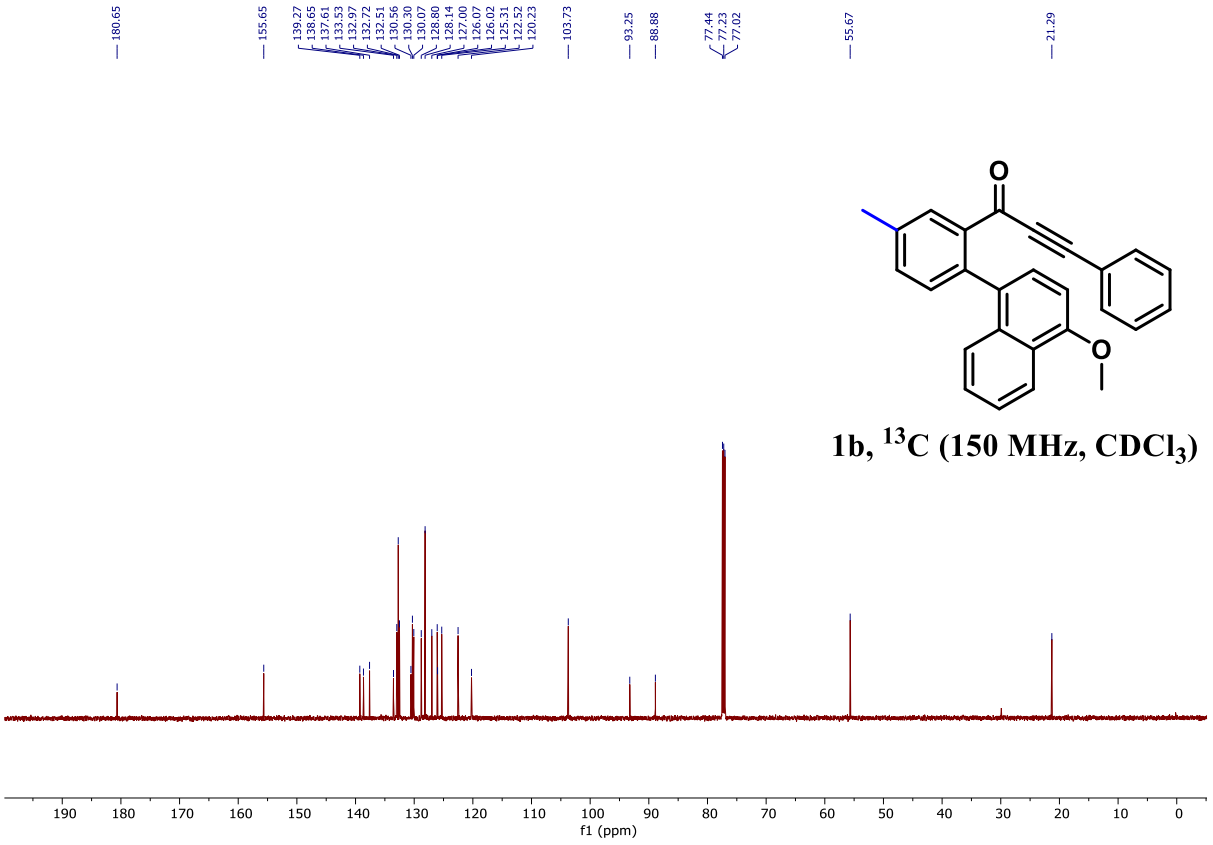
1a, ^{1}H (600 MHz, $CDCl_3$)



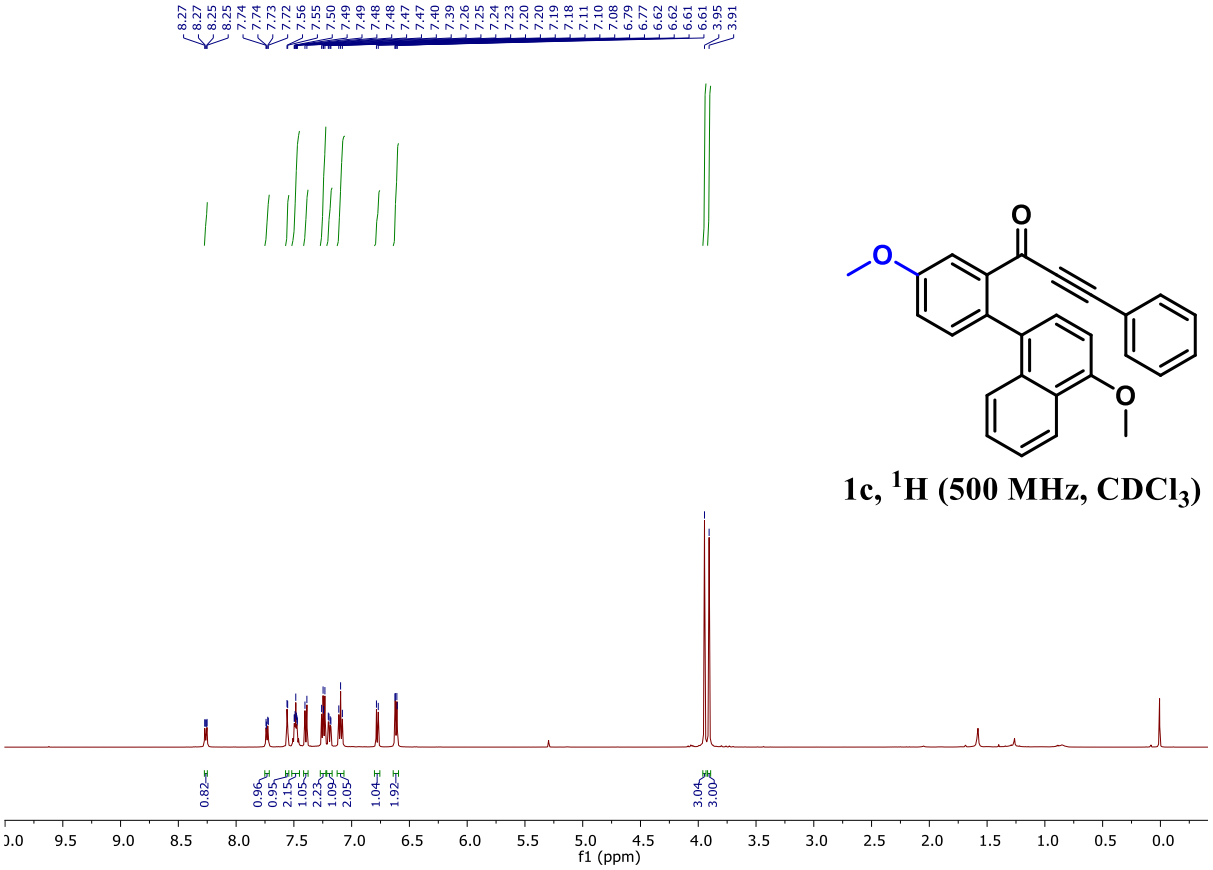
1a, ^{13}C (150 MHz, $CDCl_3$)



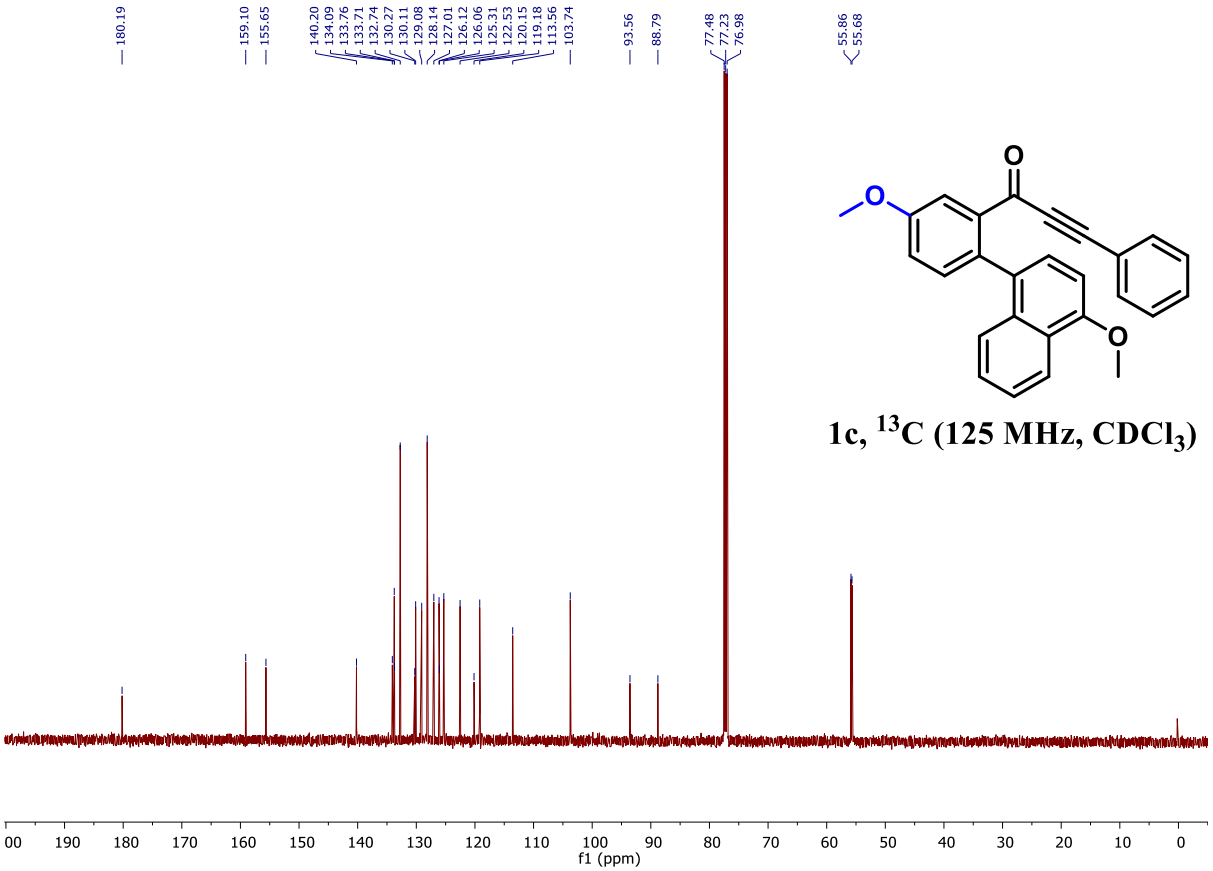
1b, ^{1}H (600 MHz, $CDCl_3$)



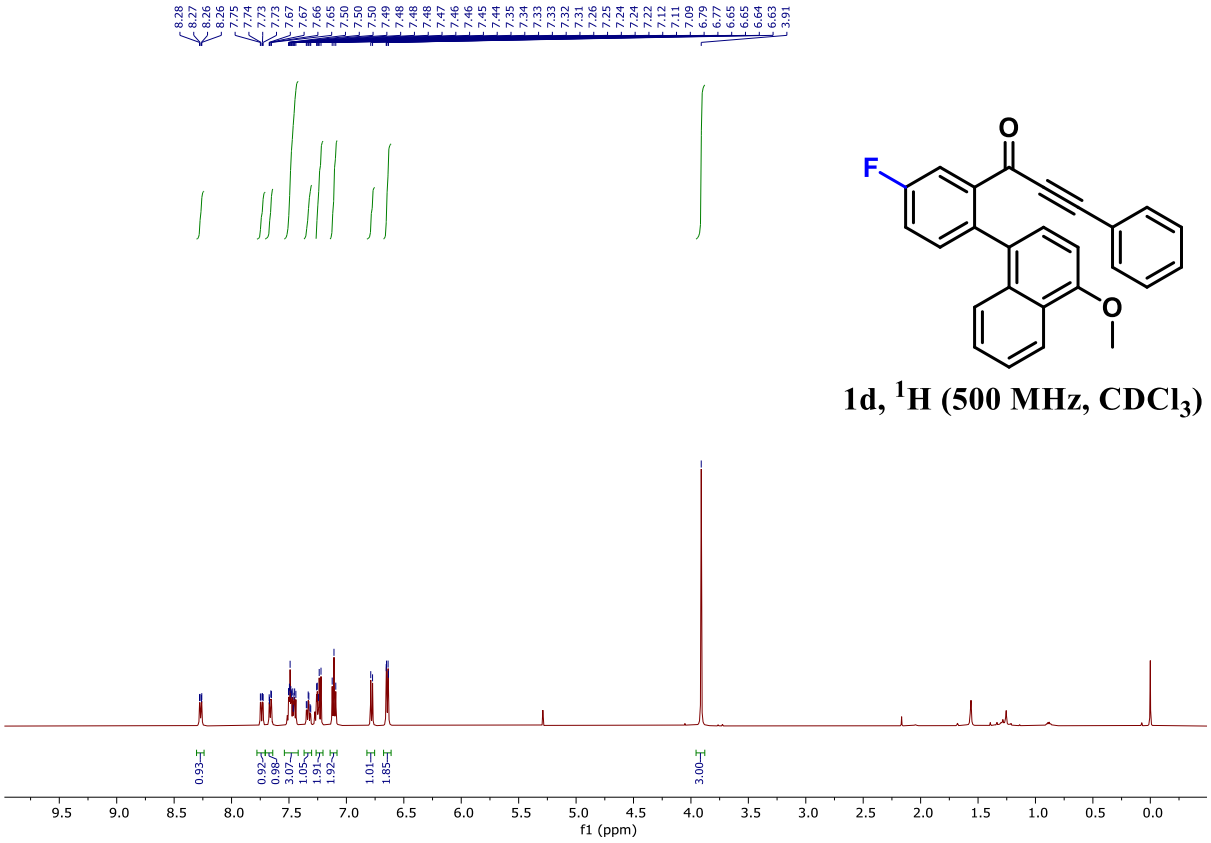
1b, ^{13}C (150 MHz, $CDCl_3$)



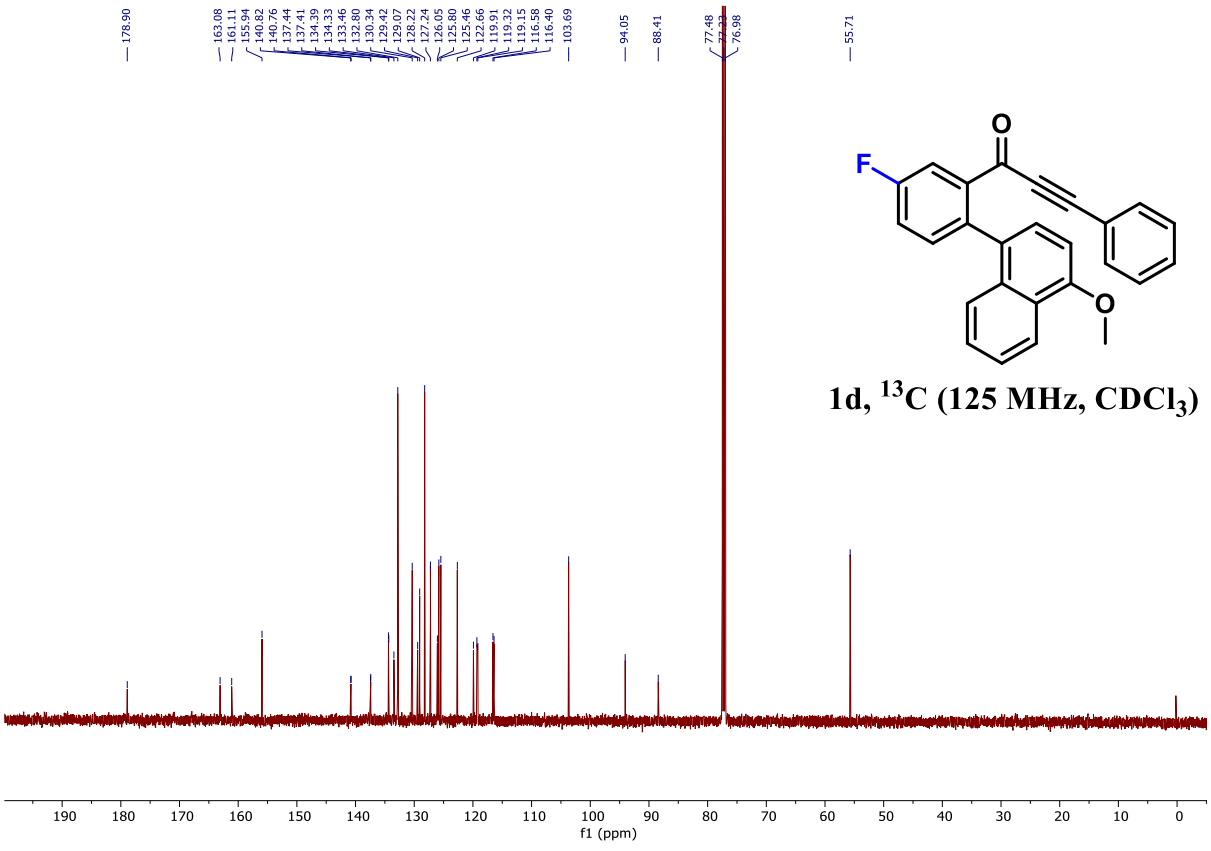
1c, ^{1}H (500 MHz, $CDCl_3$)



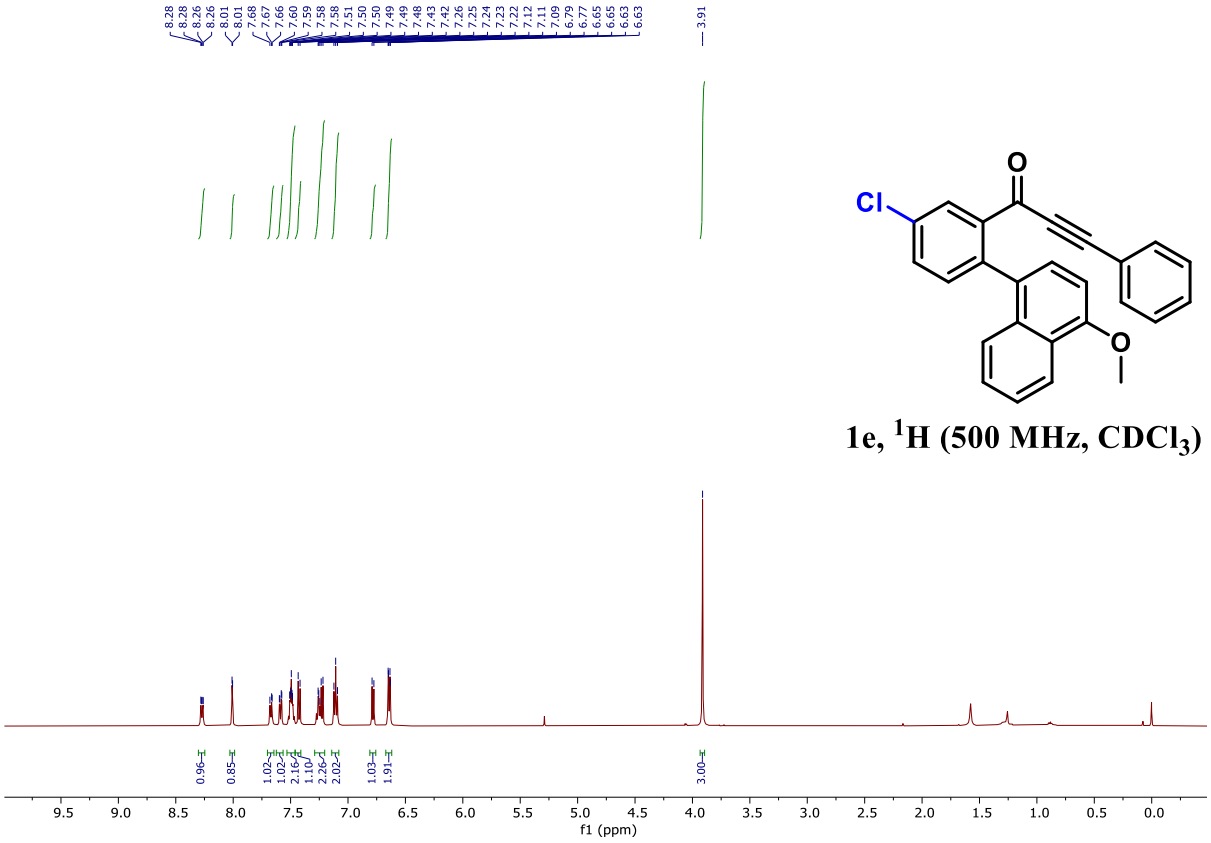
1c, ^{13}C (125 MHz, $CDCl_3$)



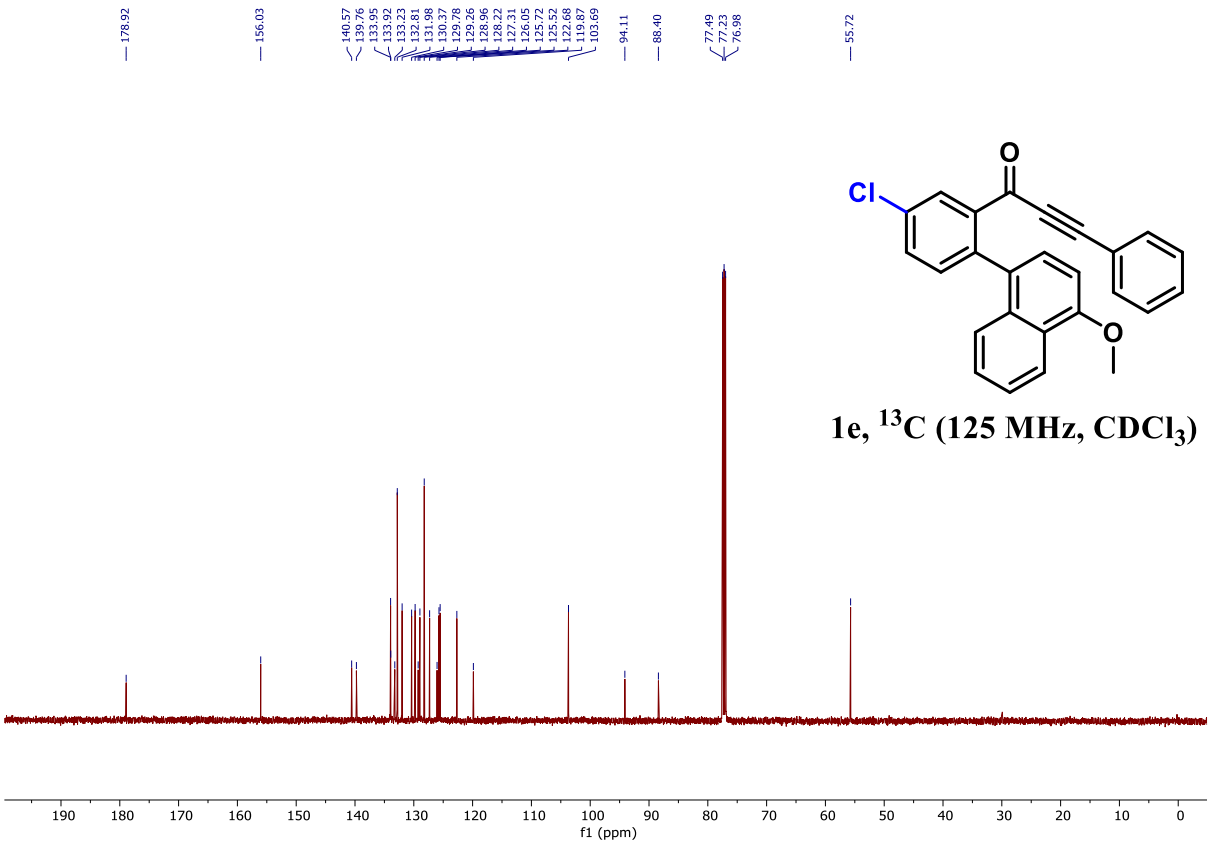
1d, ^{1}H (500 MHz, $CDCl_3$)



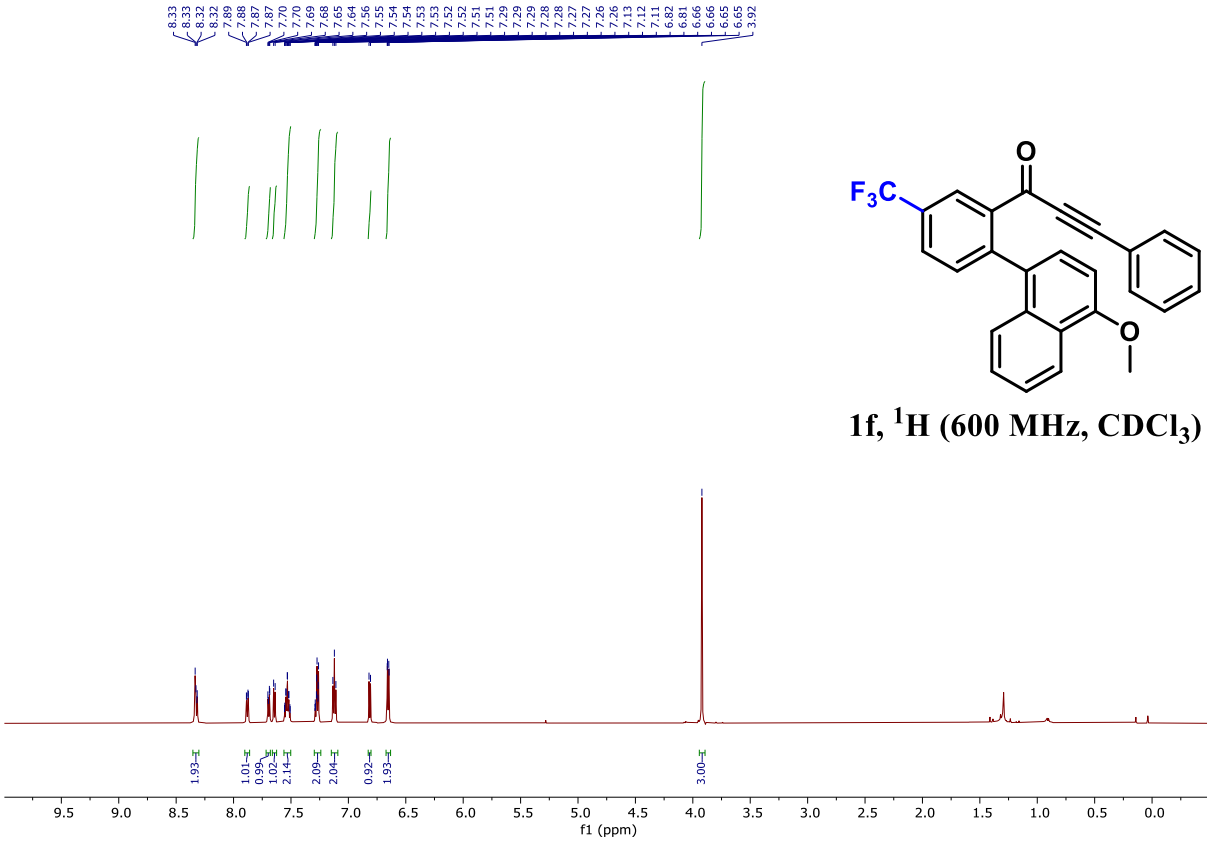
1d, ^{13}C (125 MHz, $CDCl_3$)



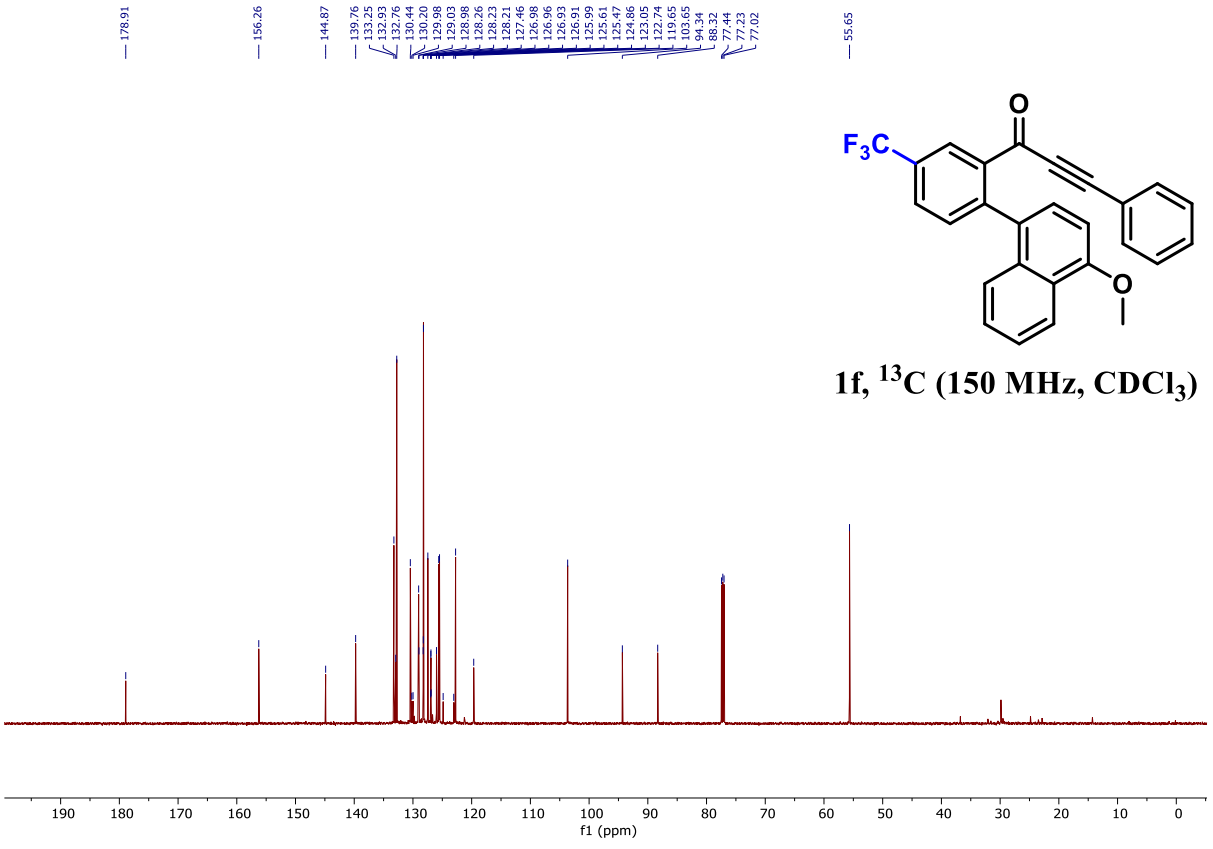
1e, ^{1}H (500 MHz, $CDCl_3$)



1e, ^{13}C (125 MHz, $CDCl_3$)

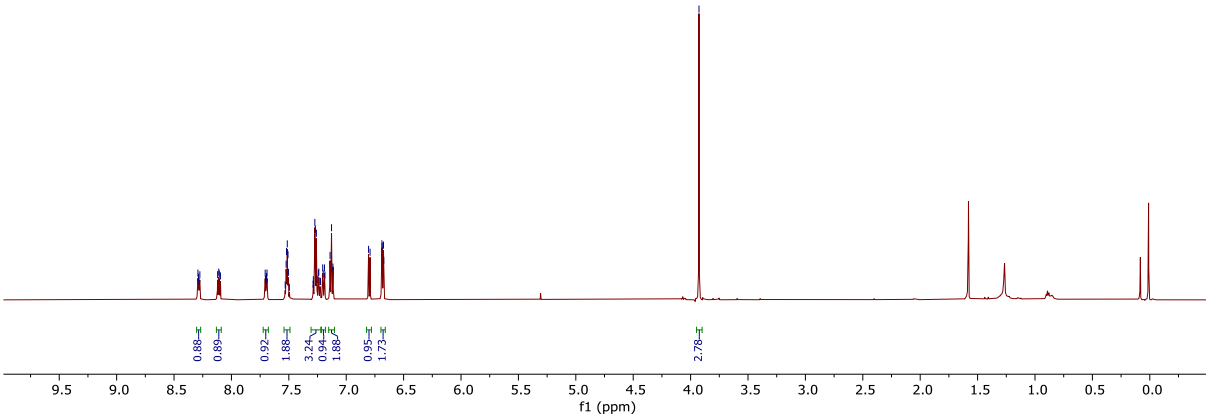


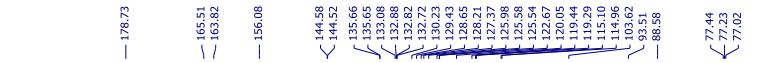
1f, ^{1}H (600 MHz, $CDCl_3$)

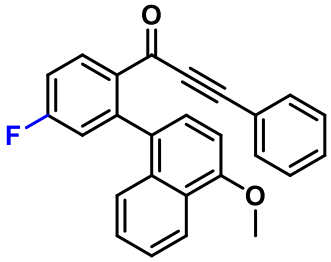


1f, ^{13}C (150 MHz, $CDCl_3$)

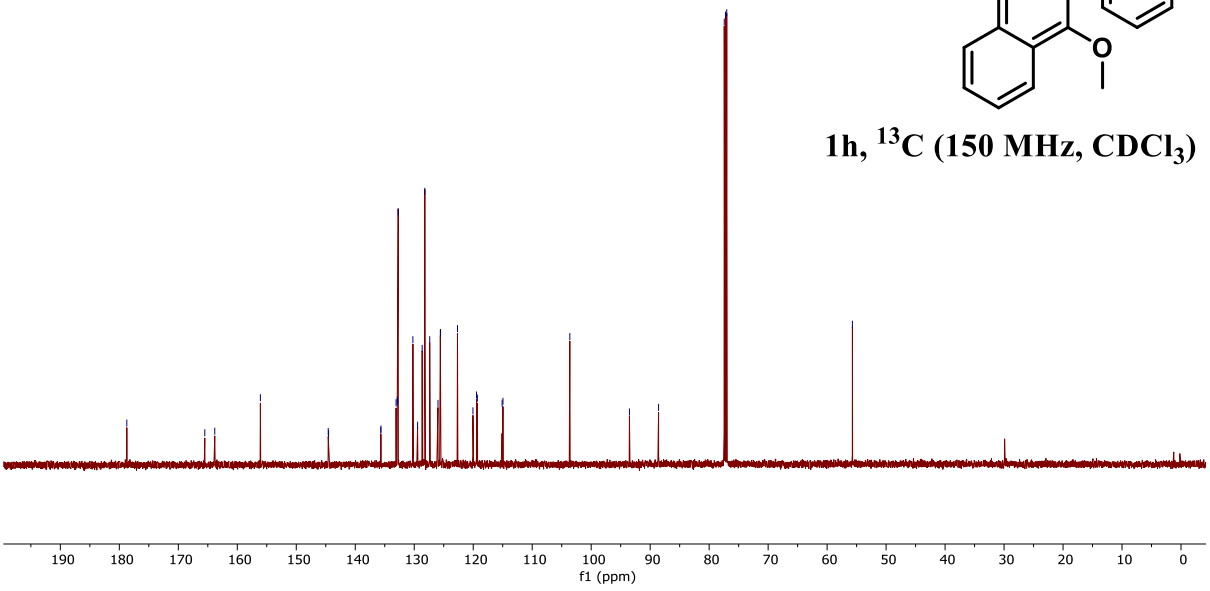
1h, ^{1}H (600 MHz, $CDCl_3$)

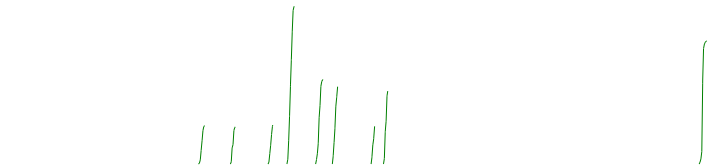


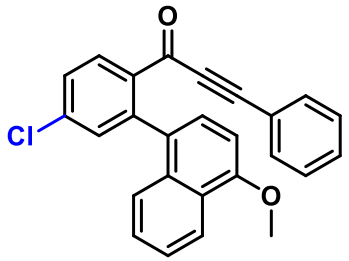




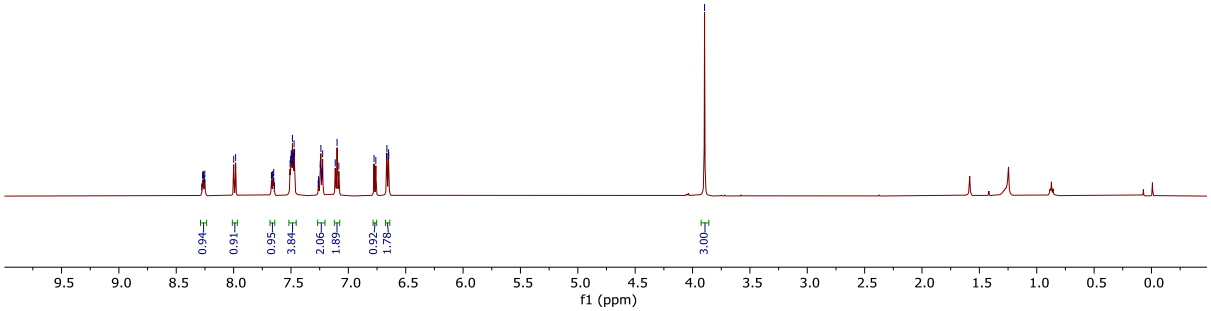
1h, ^{13}C (150 MHz, $CDCl_3$)

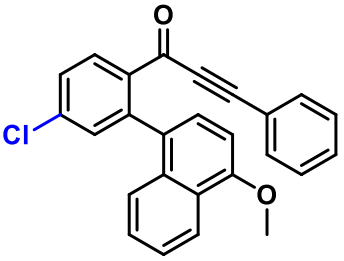




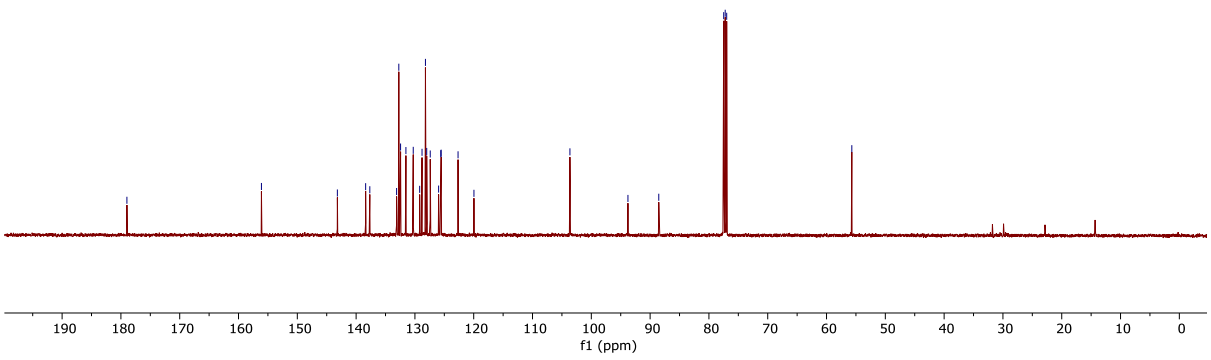


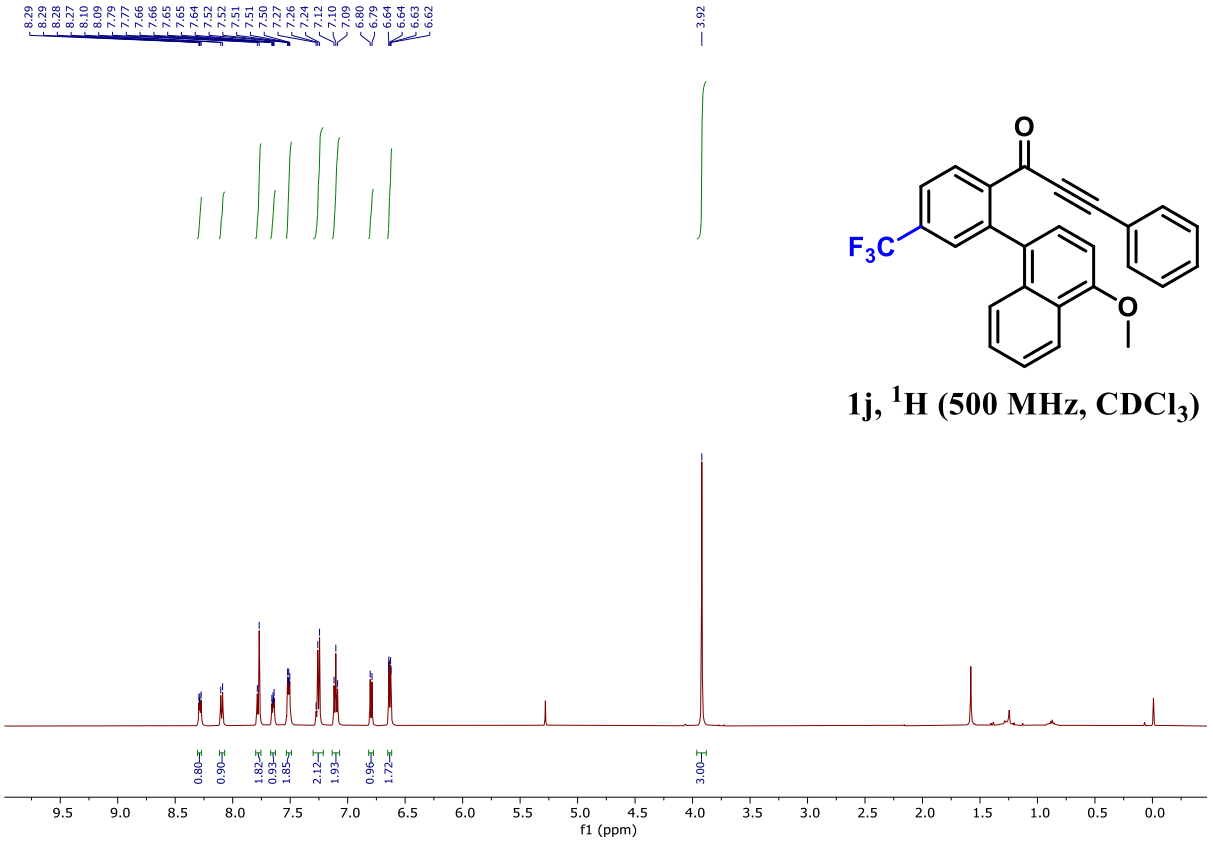
1i, ^{1}H (500 MHz, $CDCl_3$)



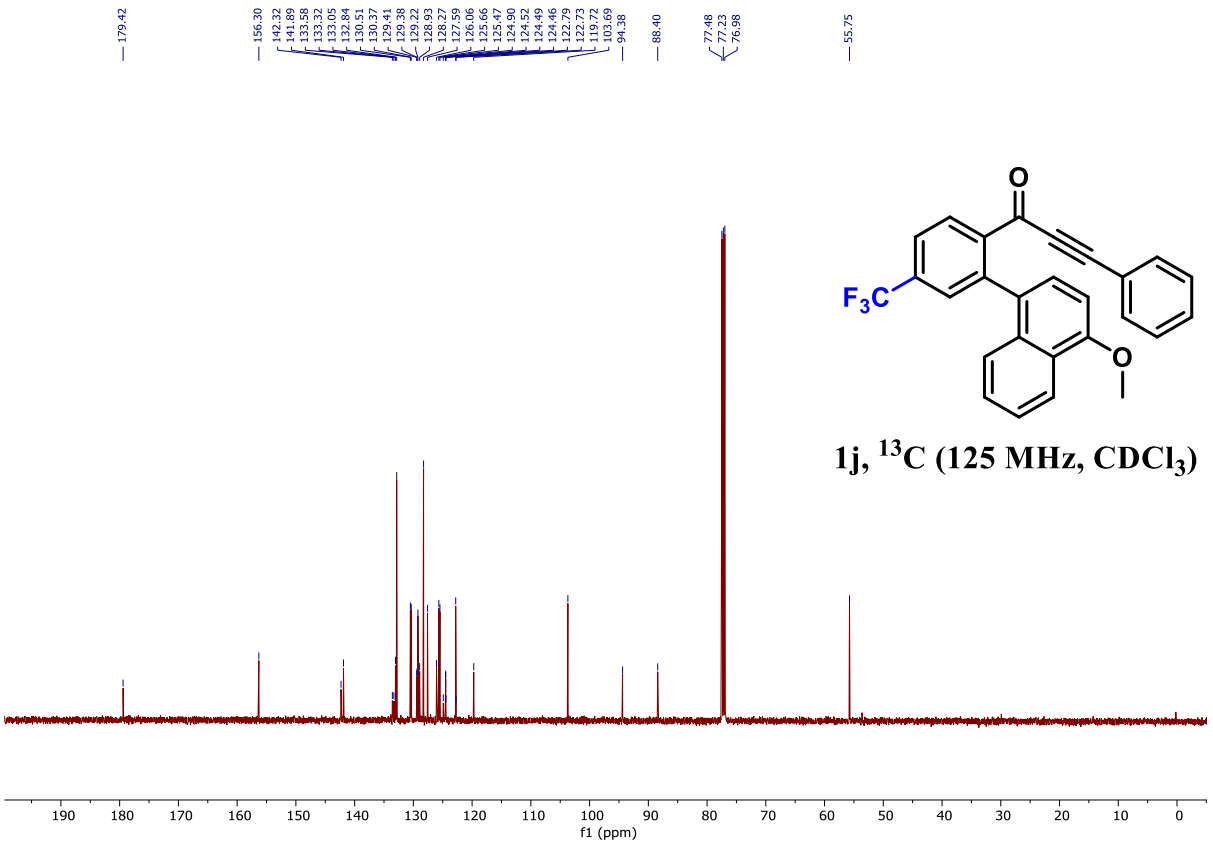


1i, ^{13}C (125 MHz, $CDCl_3$)

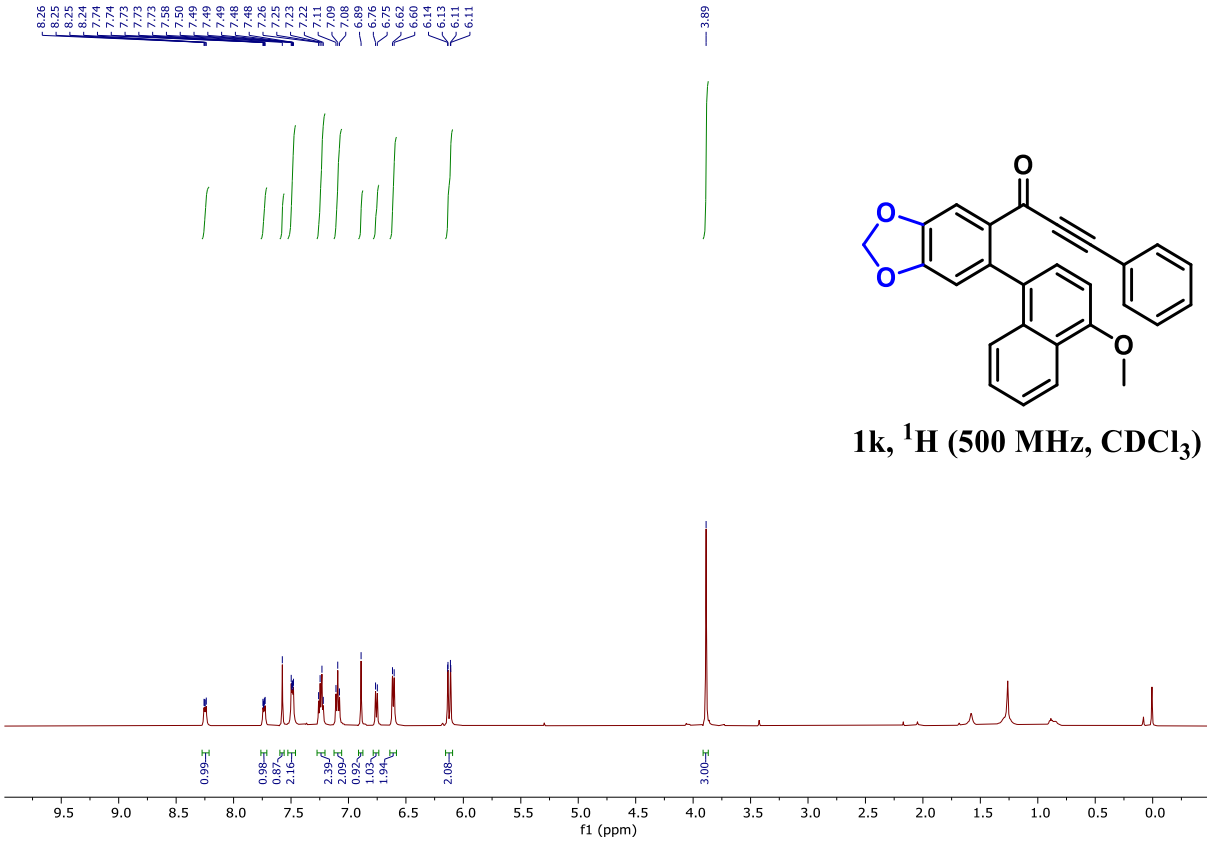




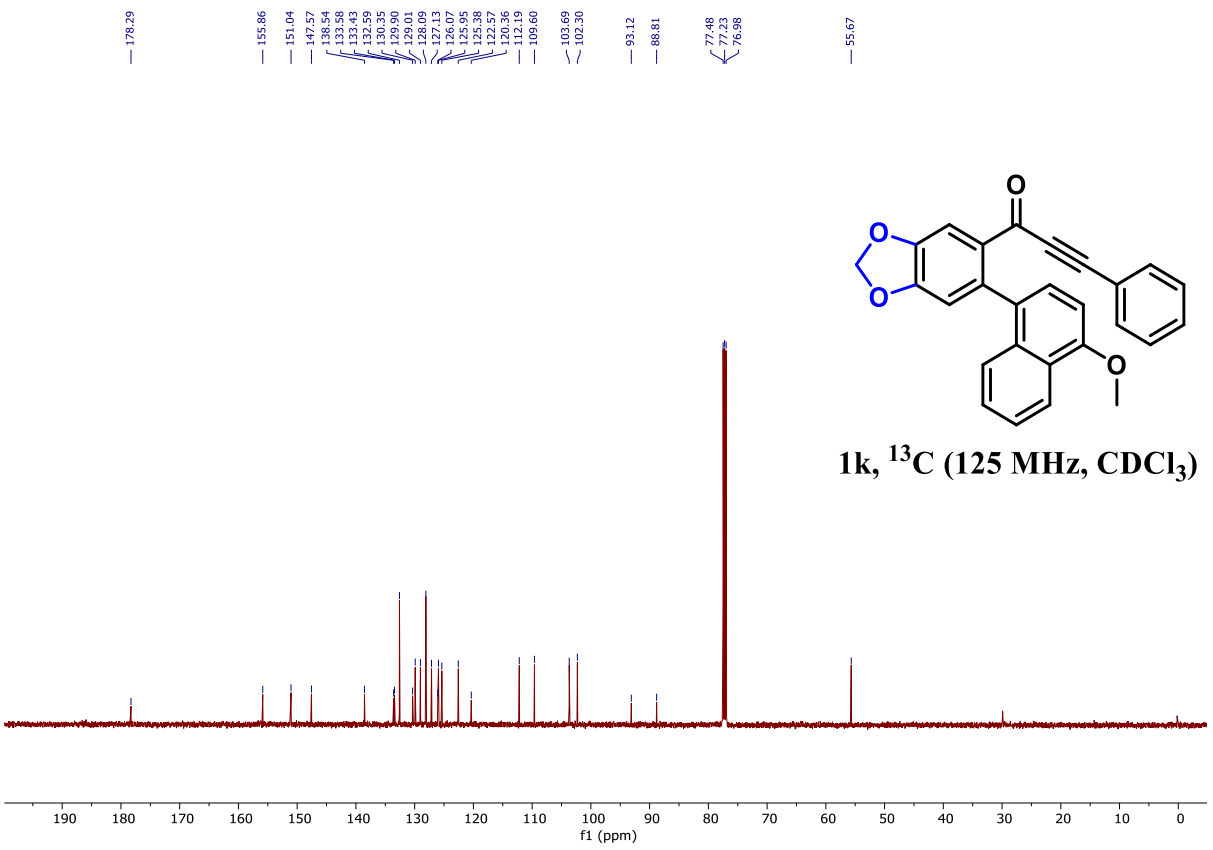
1j, ^{1}H (500 MHz, $CDCl_3$)



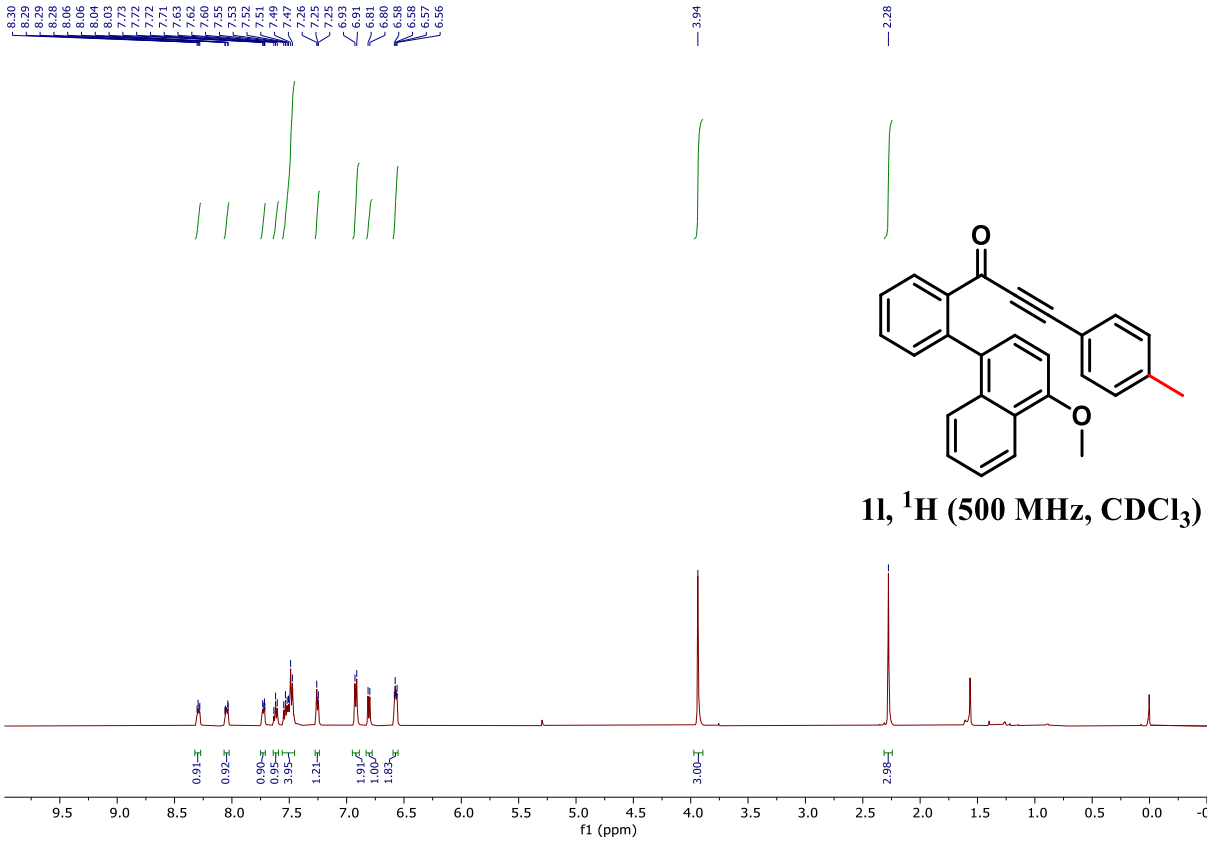
1j, ^{13}C (125 MHz, $CDCl_3$)



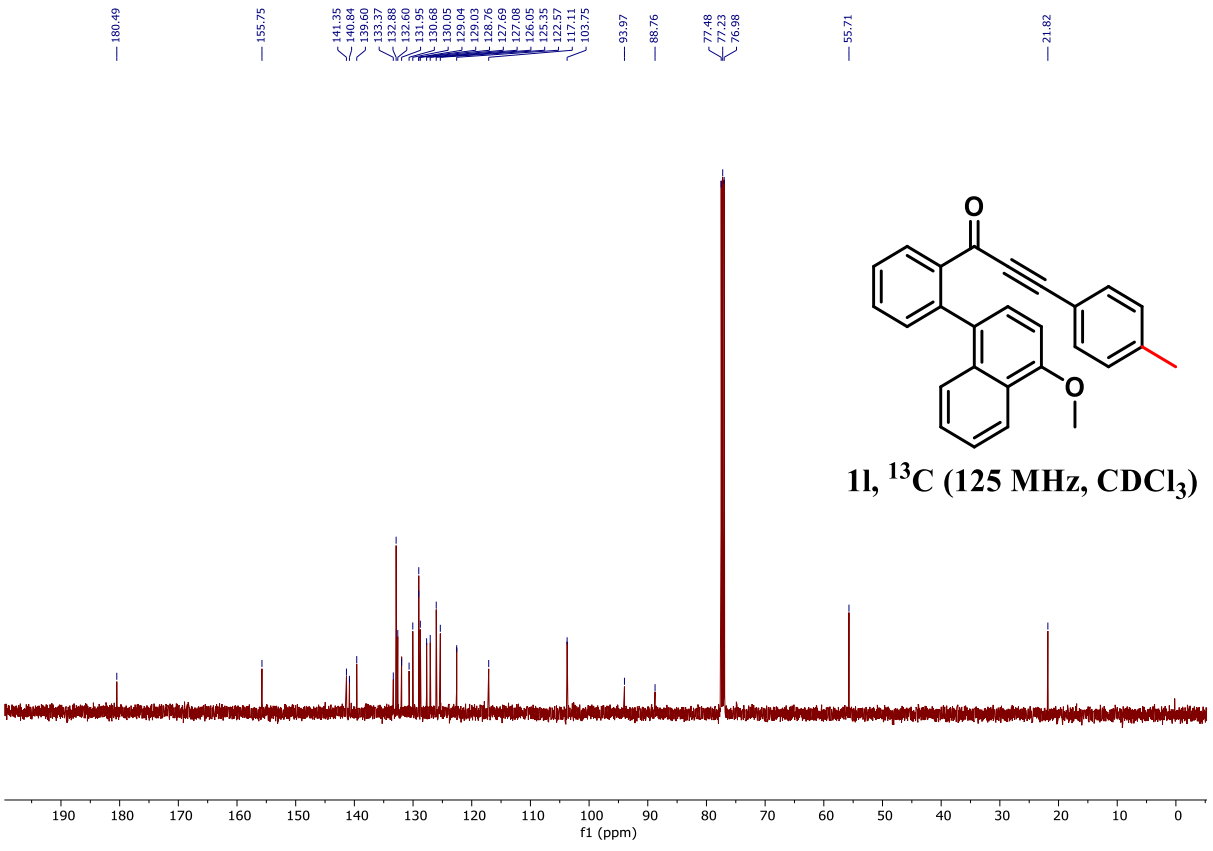
1k, ^{1}H (500 MHz, $CDCl_3$)



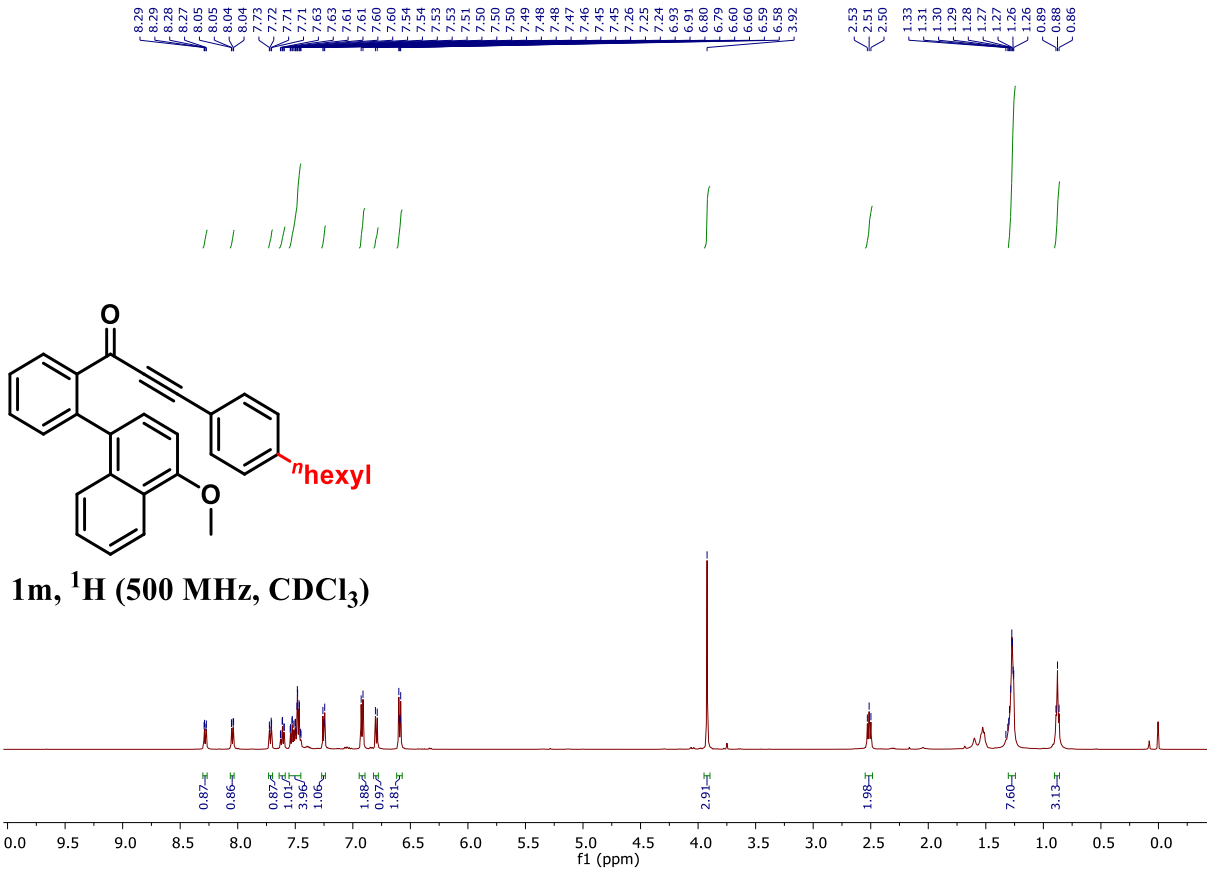
1k, ^{13}C (125 MHz, $CDCl_3$)

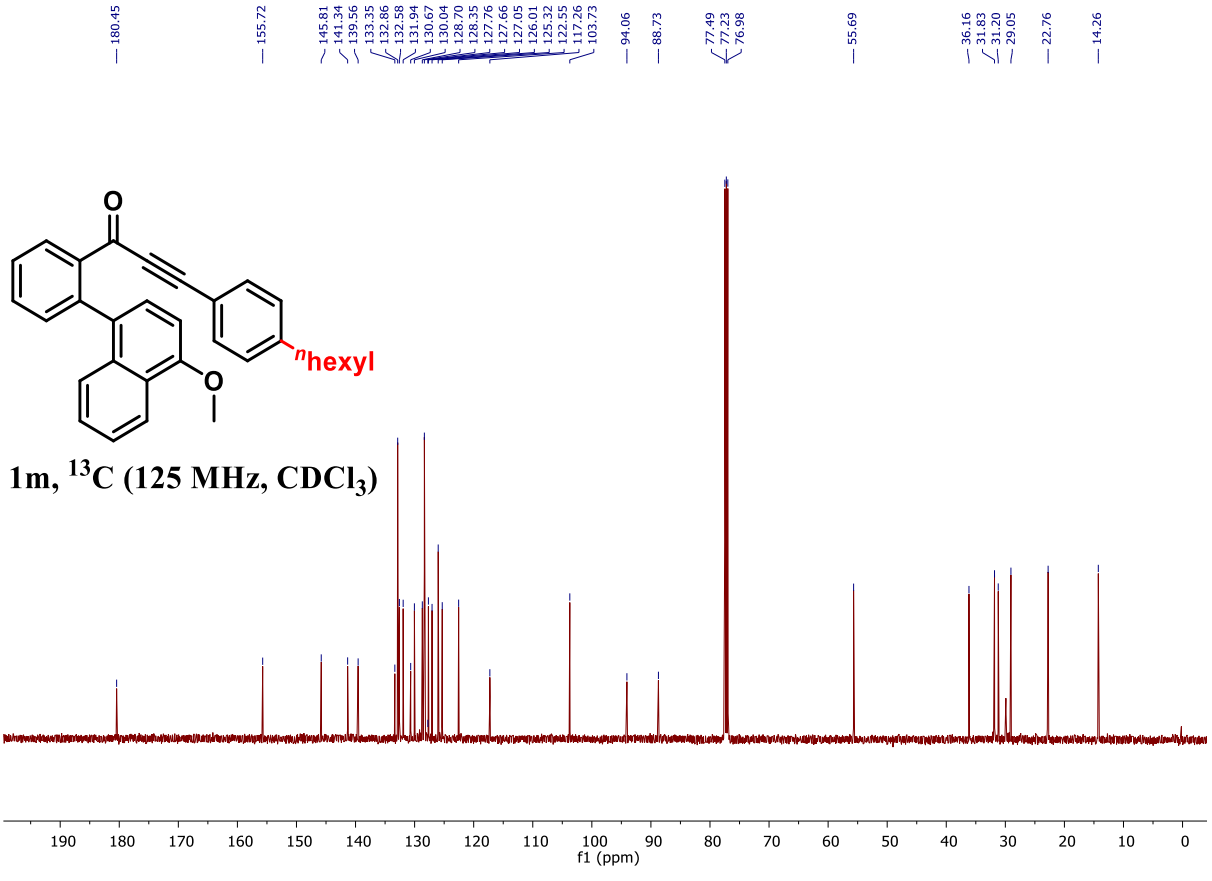


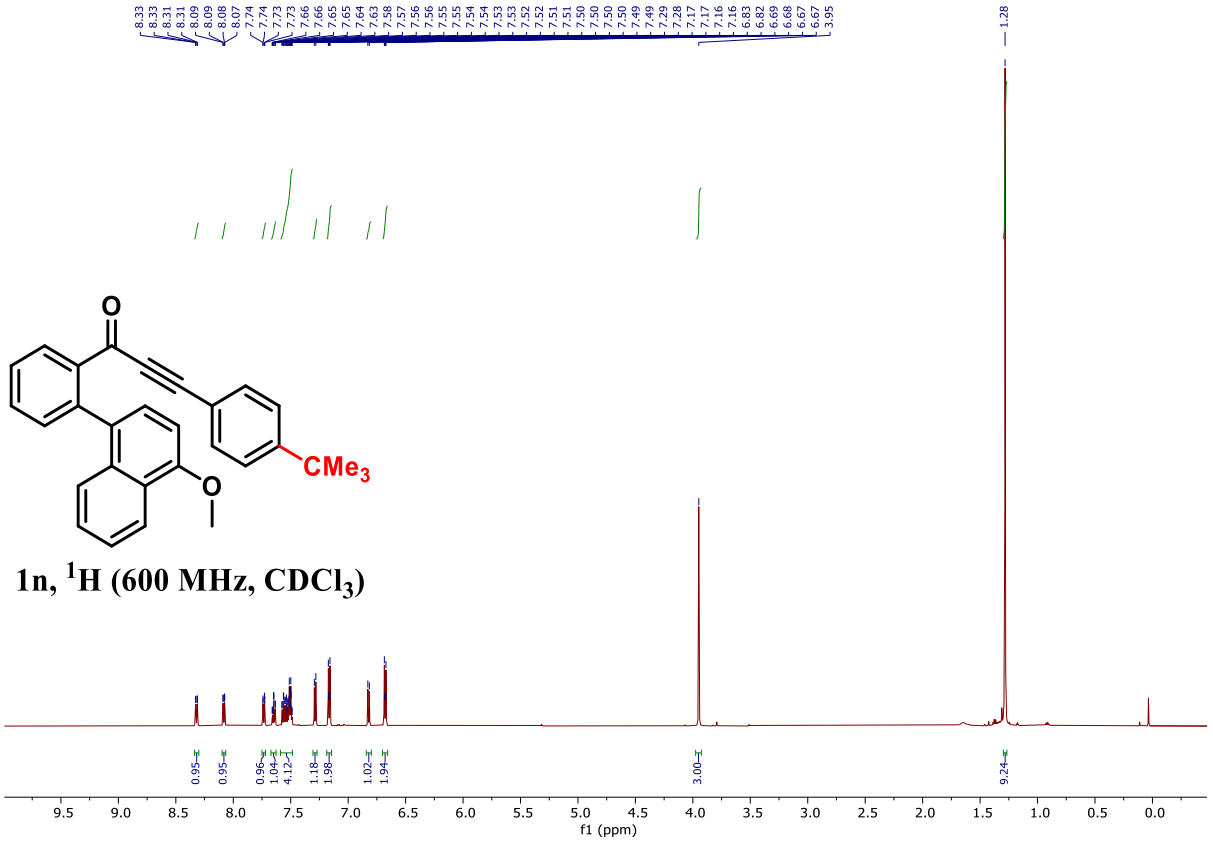
1l, ^{1}H (500 MHz, $CDCl_3$)



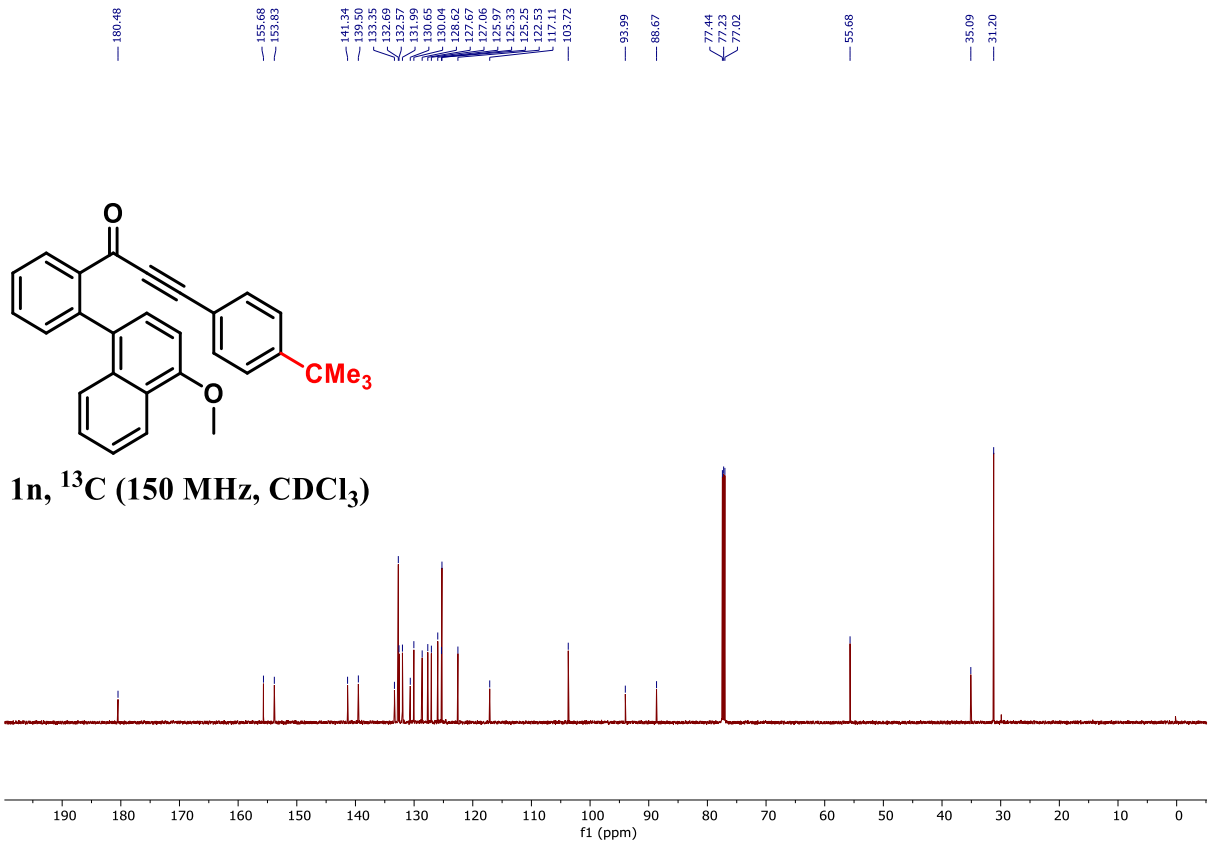
1l, ^{13}C (125 MHz, $CDCl_3$)


8.29 8.29 8.28 8.27 8.05 8.05 8.04 8.04 7.73 7.72 7.71 7.71 7.63 7.63 7.61 7.61 7.60 7.60 7.54 7.54 7.53 7.53 7.51 7.50 7.50 7.50 7.49 7.48 7.48 7.47 7.46 7.45 7.45 7.26 7.25 7.24 6.93 6.91 6.80 6.79 6.60 6.60 6.59 6.58 3.92
2.53 2.51 2.50
1.33 1.31 1.30 1.29 1.28 1.27 1.27 1.26 1.26 0.89 0.88 0.86
O
O
nhexyl
1m, 1H (500 MHz, CDCl3)
0.87 0.86 0.87 1.01 3.96 1.06 1.88 0.97 1.81 2.91 1.98 7.60 3.13
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

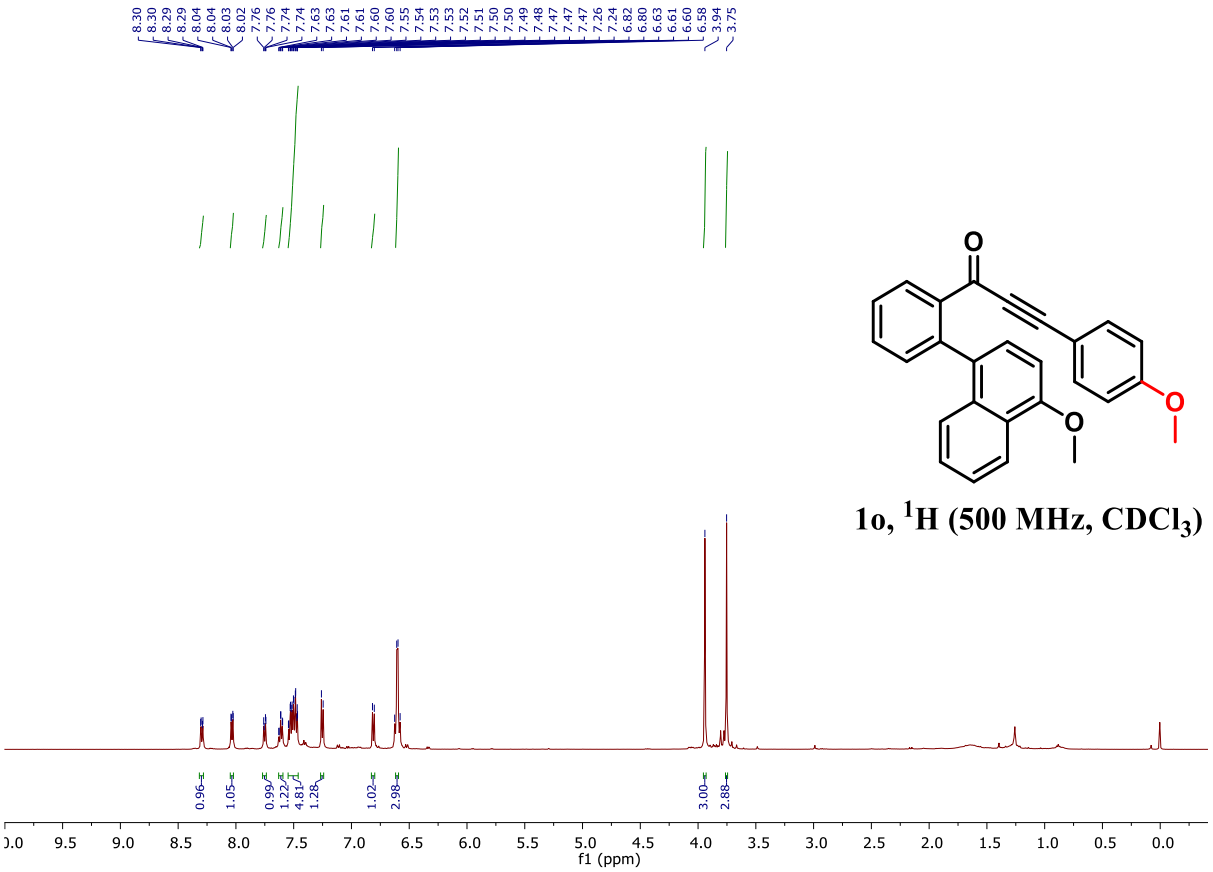

180.45
155.72
145.81 141.34 139.56 133.35 132.86 132.58 131.94 130.67 130.04 128.70 128.35 127.76 127.66 127.05 126.01 125.32 122.55 117.26 103.73
94.06
88.73
77.49 77.23 76.98
55.69
36.16 31.83 31.20 29.05
22.76
14.26
O
O
nhexyl
1m, 13C (125 MHz, CDCl3)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



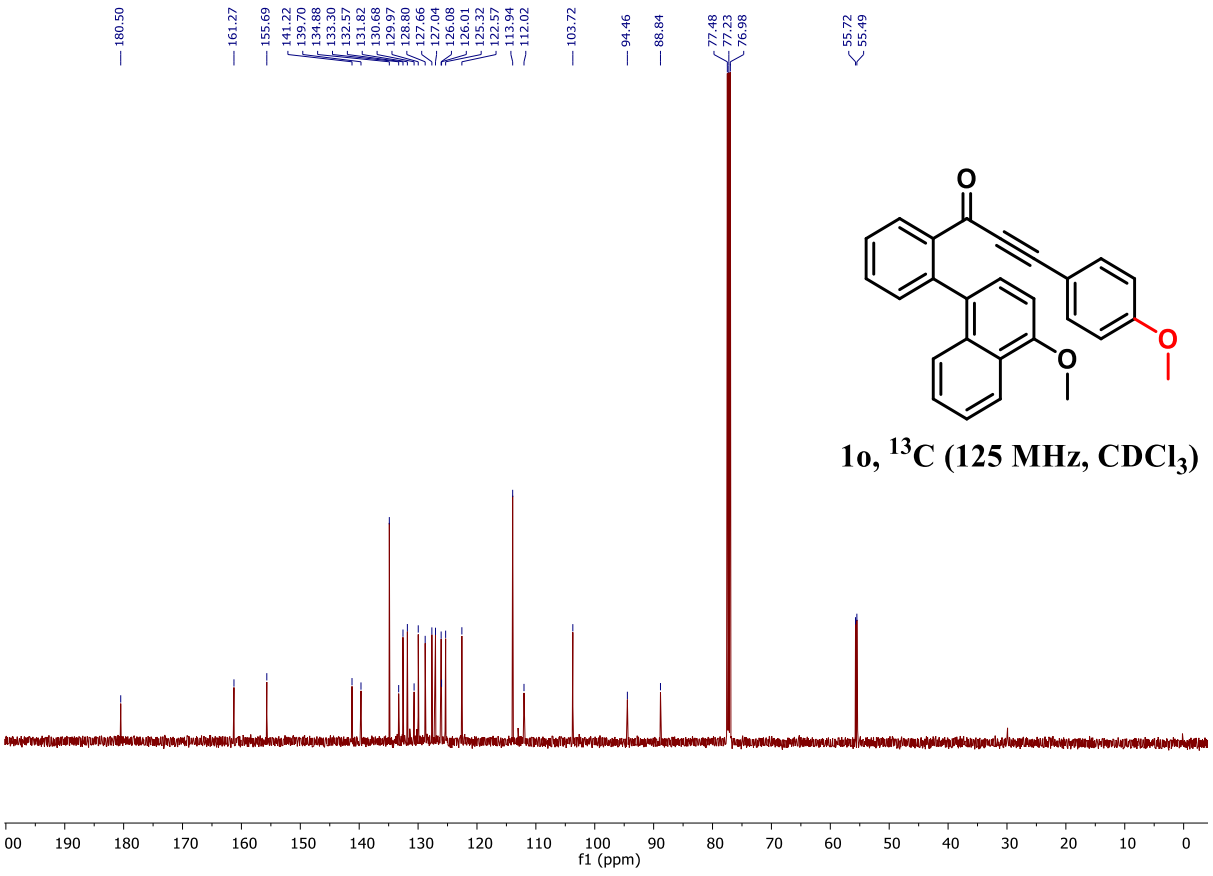
1n, ^{1}H (600 MHz, $CDCl_3$)



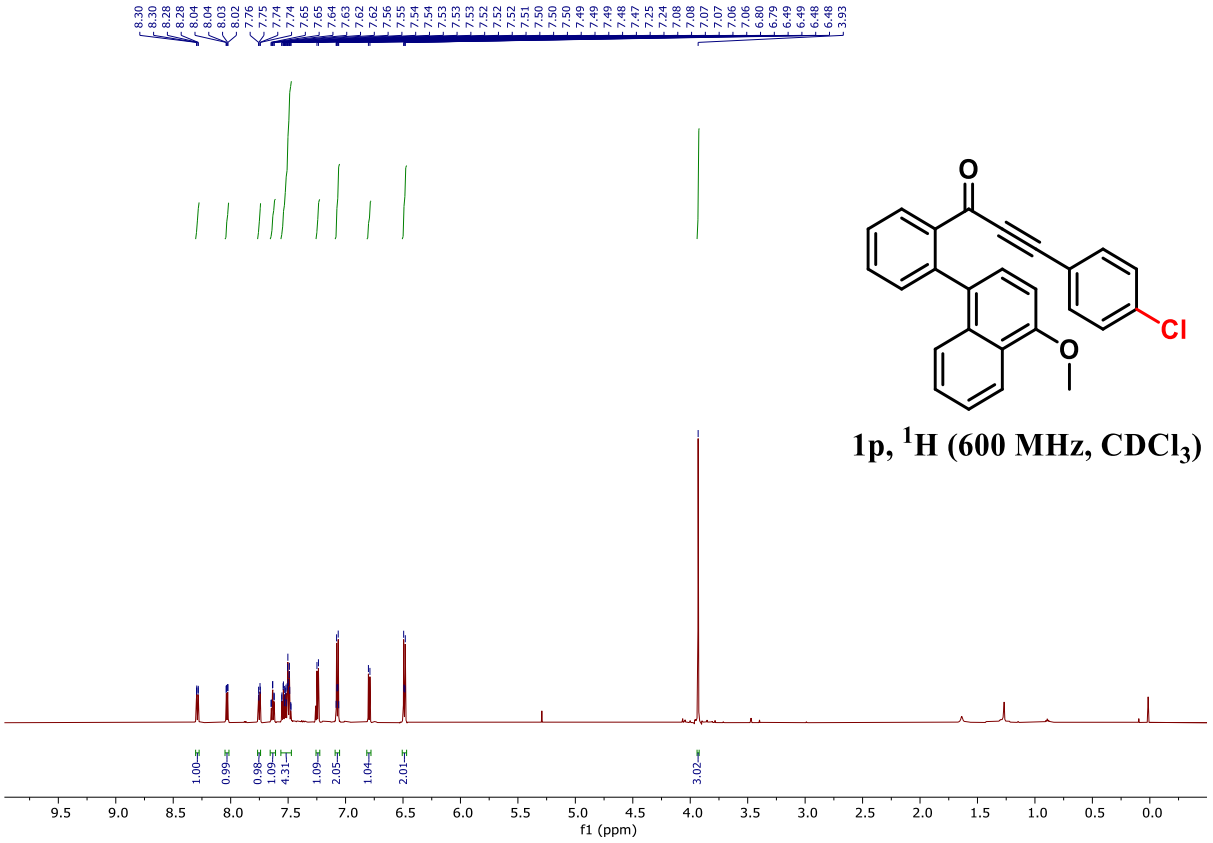
1n, ^{13}C (150 MHz, $CDCl_3$)



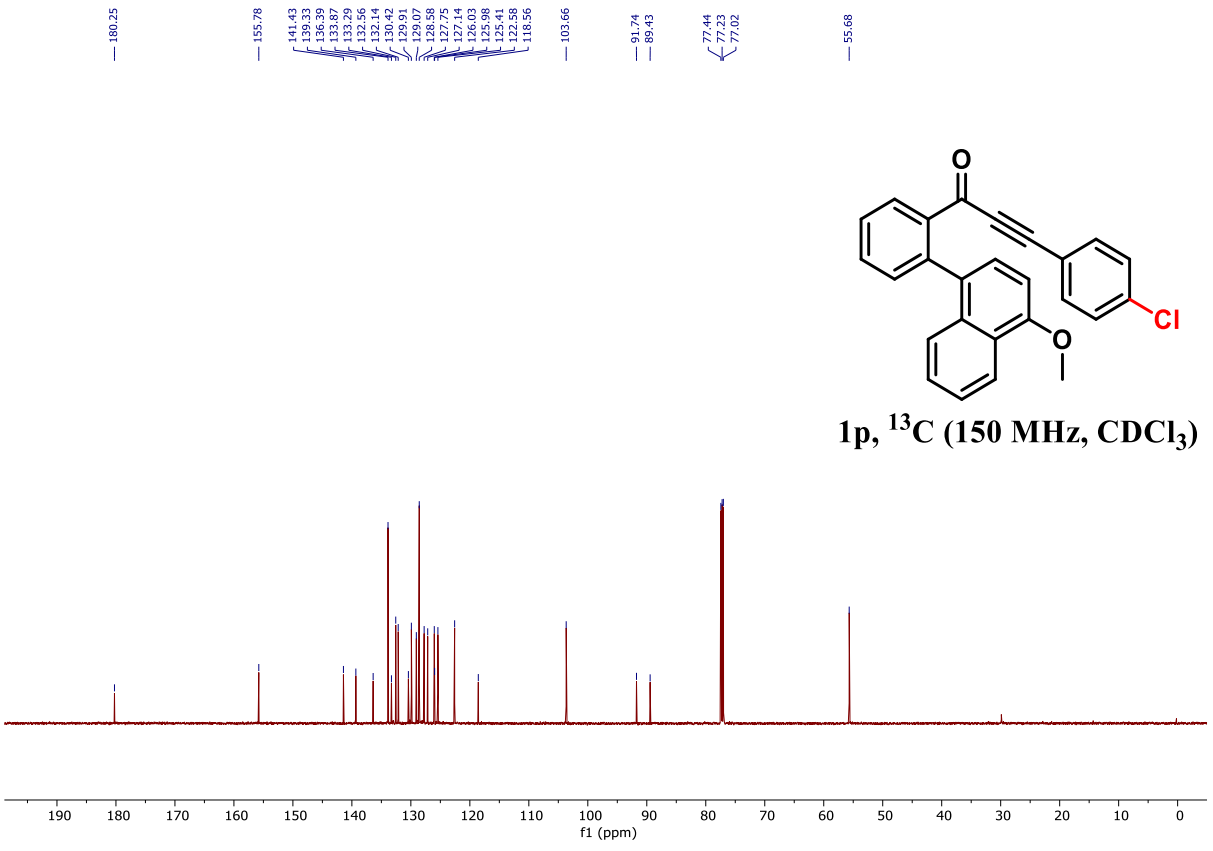
1o, ^{1}H (500 MHz, $CDCl_3$)



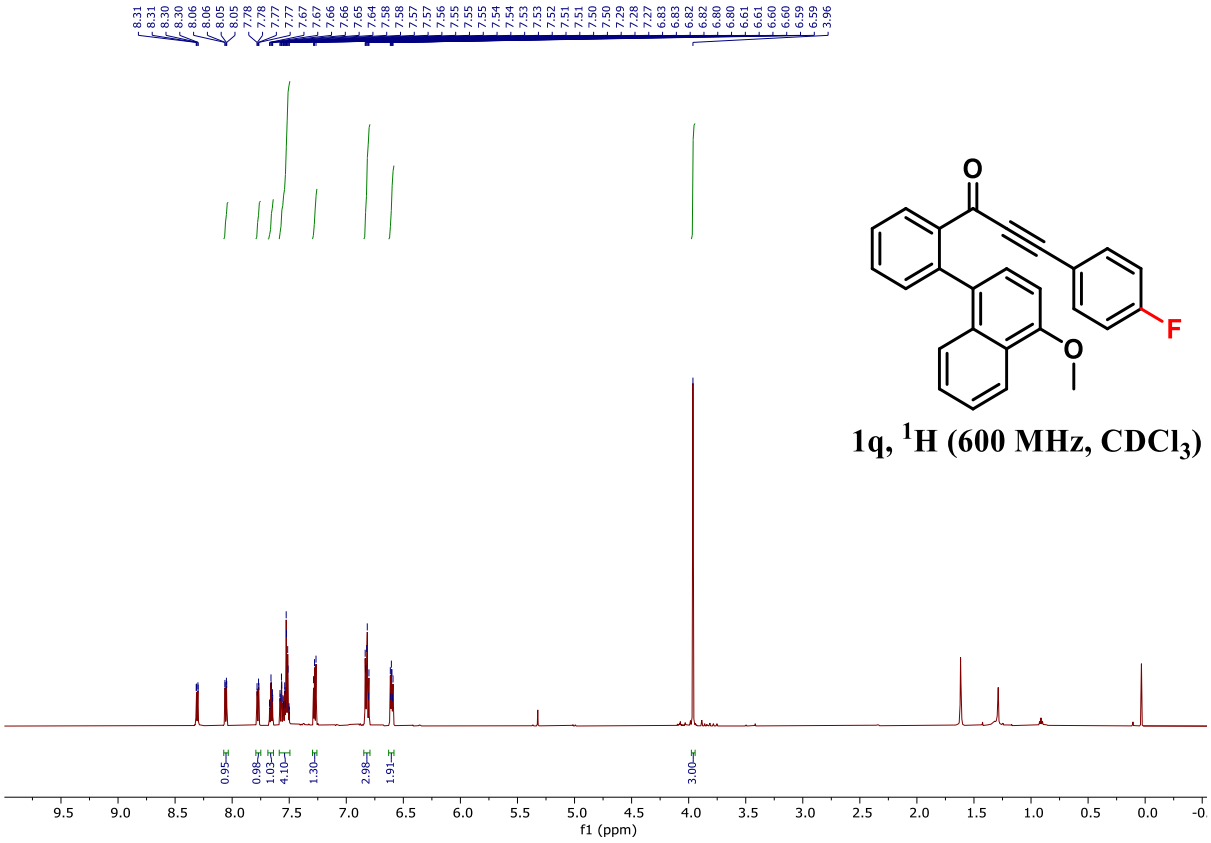
1o, ^{13}C (125 MHz, $CDCl_3$)



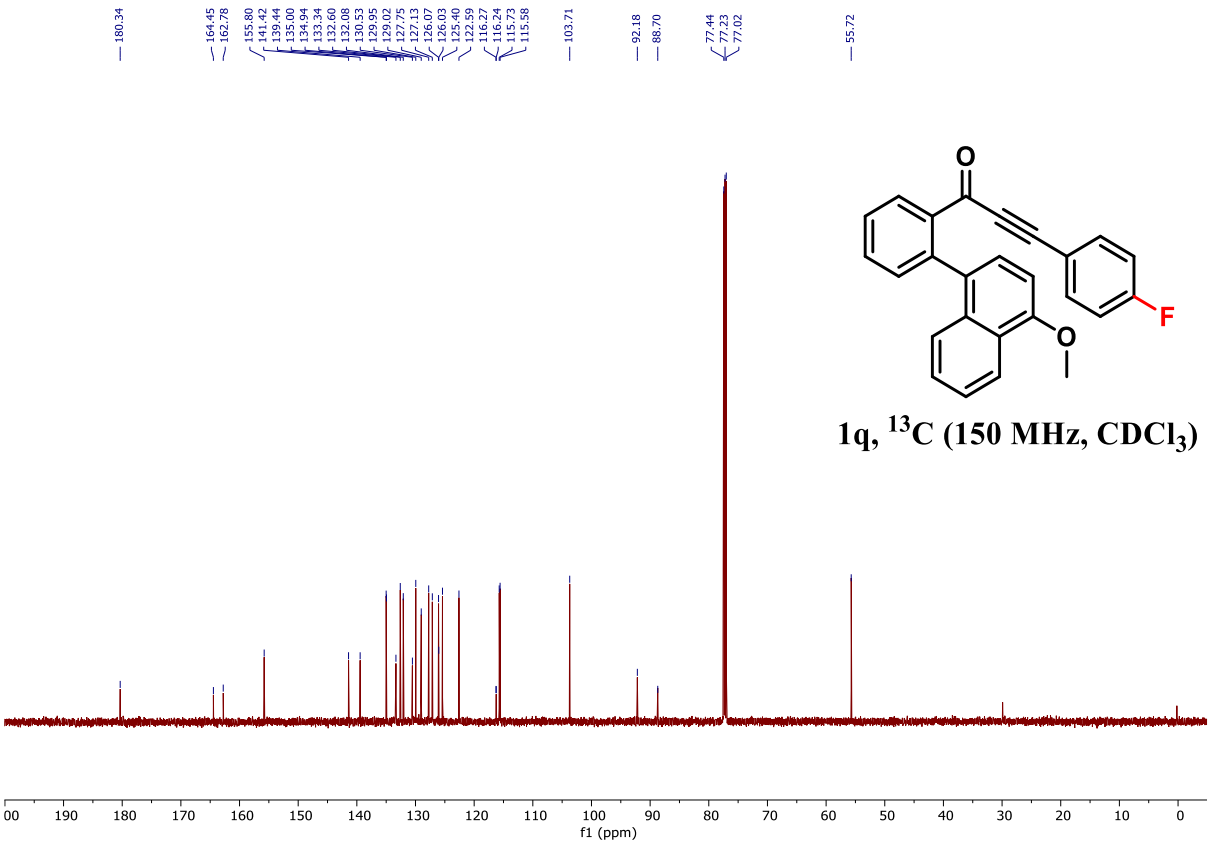
1p, ^{1}H (600 MHz, $CDCl_3$)



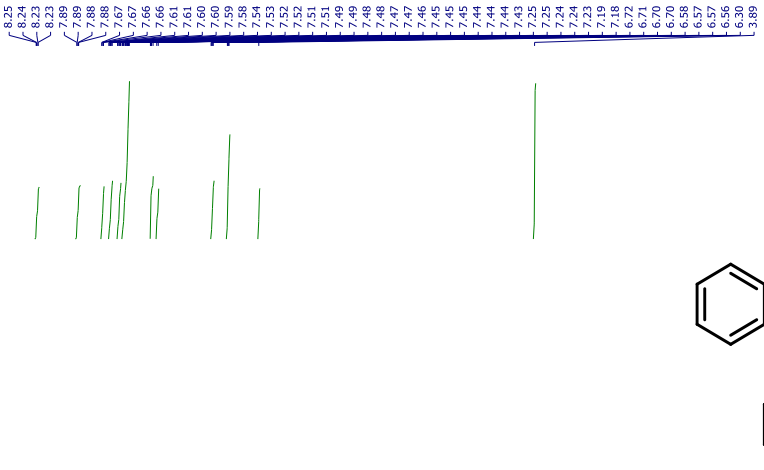
1p, ^{13}C (150 MHz, $CDCl_3$)



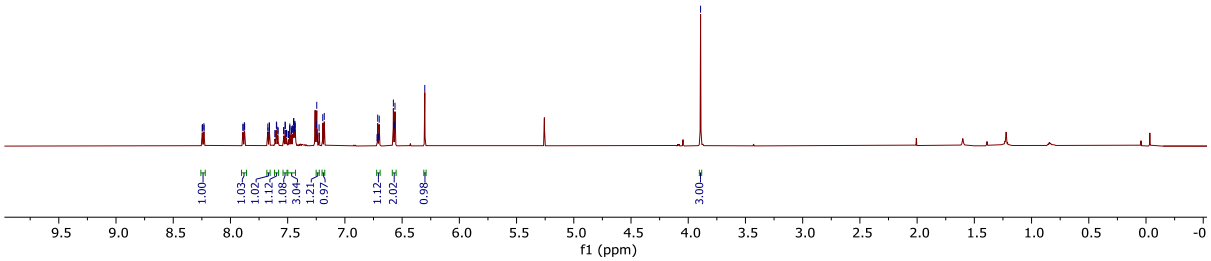
1q, ^{1}H (600 MHz, $CDCl_3$)

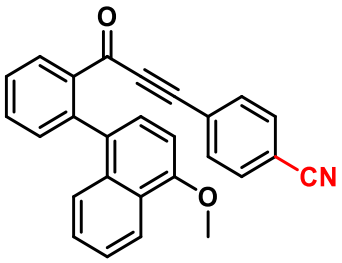


1q, ^{13}C (150 MHz, $CDCl_3$)

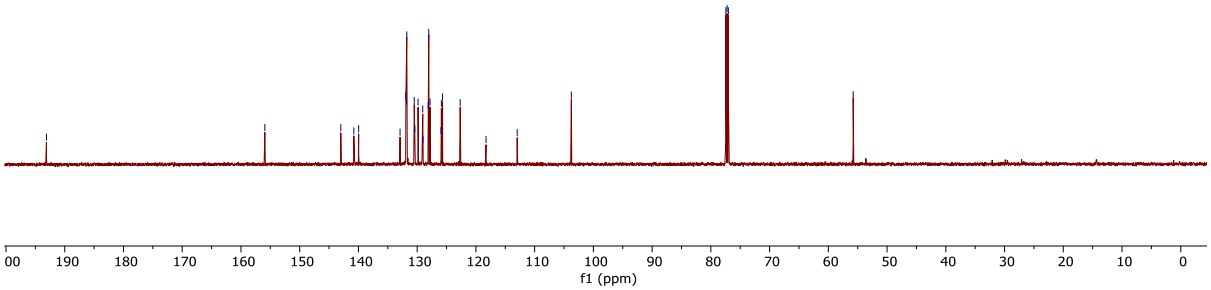


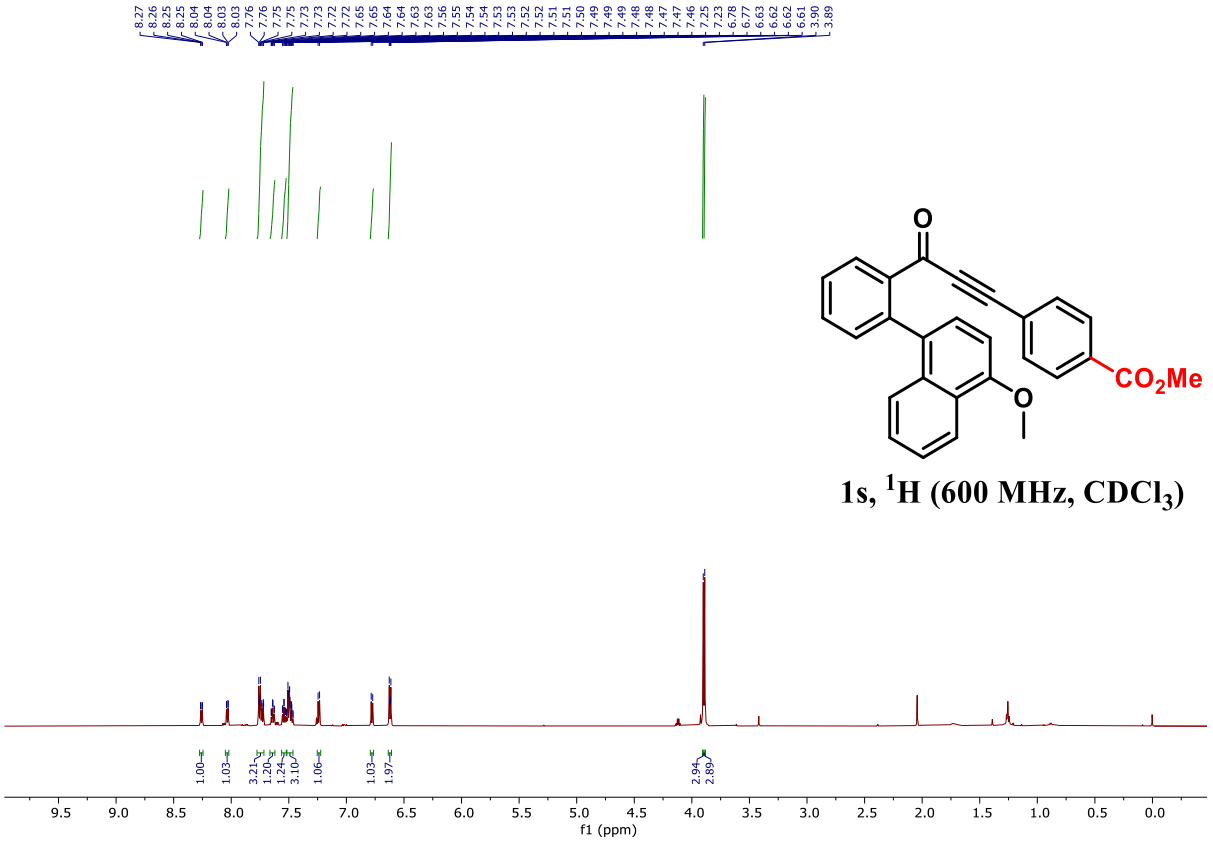
1r, ^{1}H (600 MHz, $CDCl_3$)



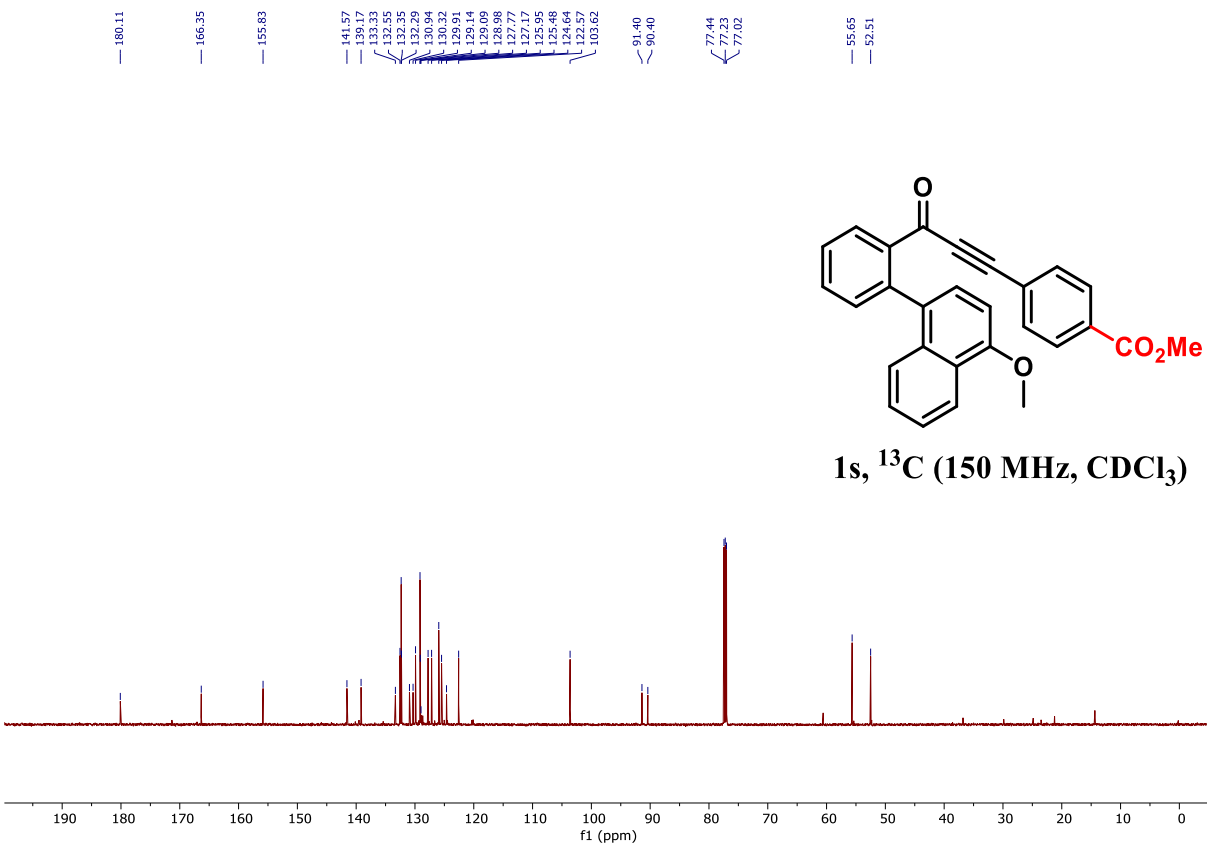


1r, ^{13}C (150 MHz, $CDCl_3$)

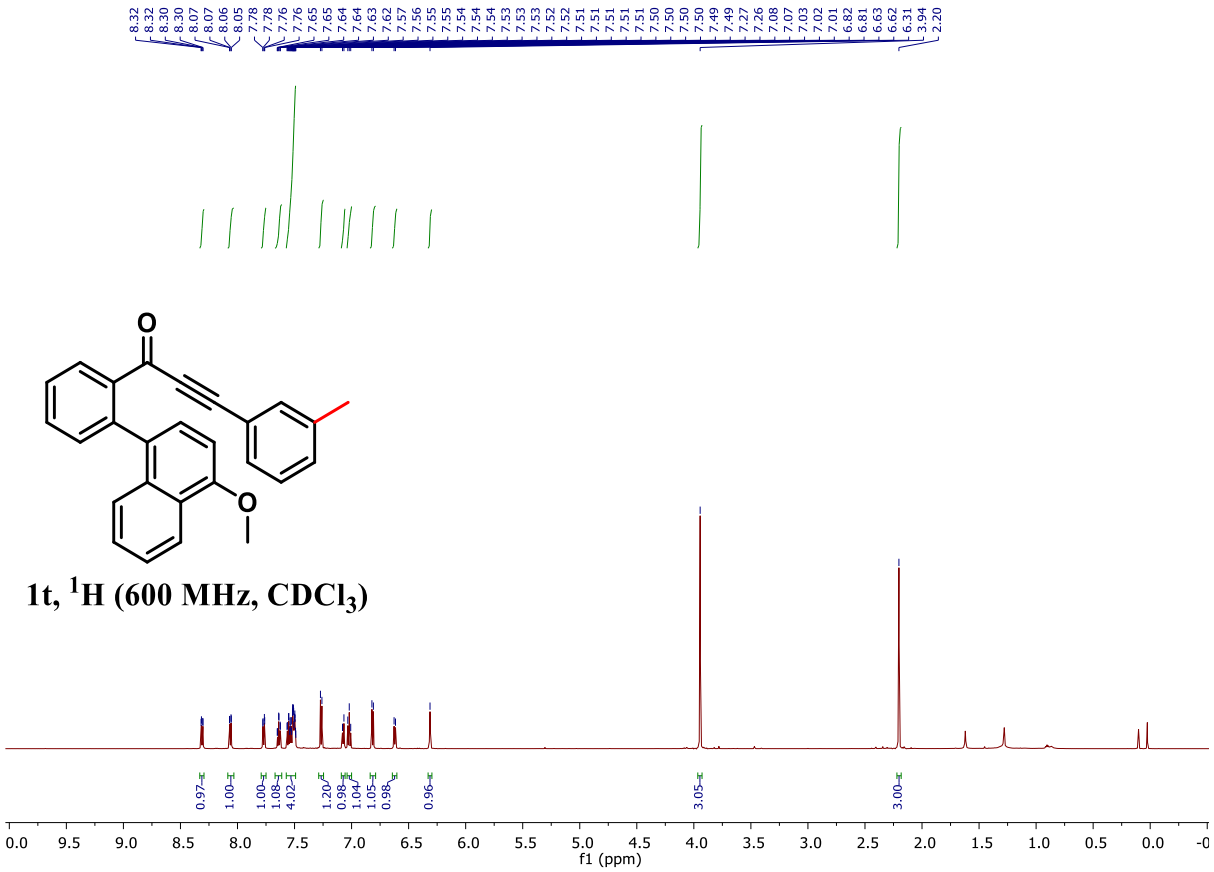




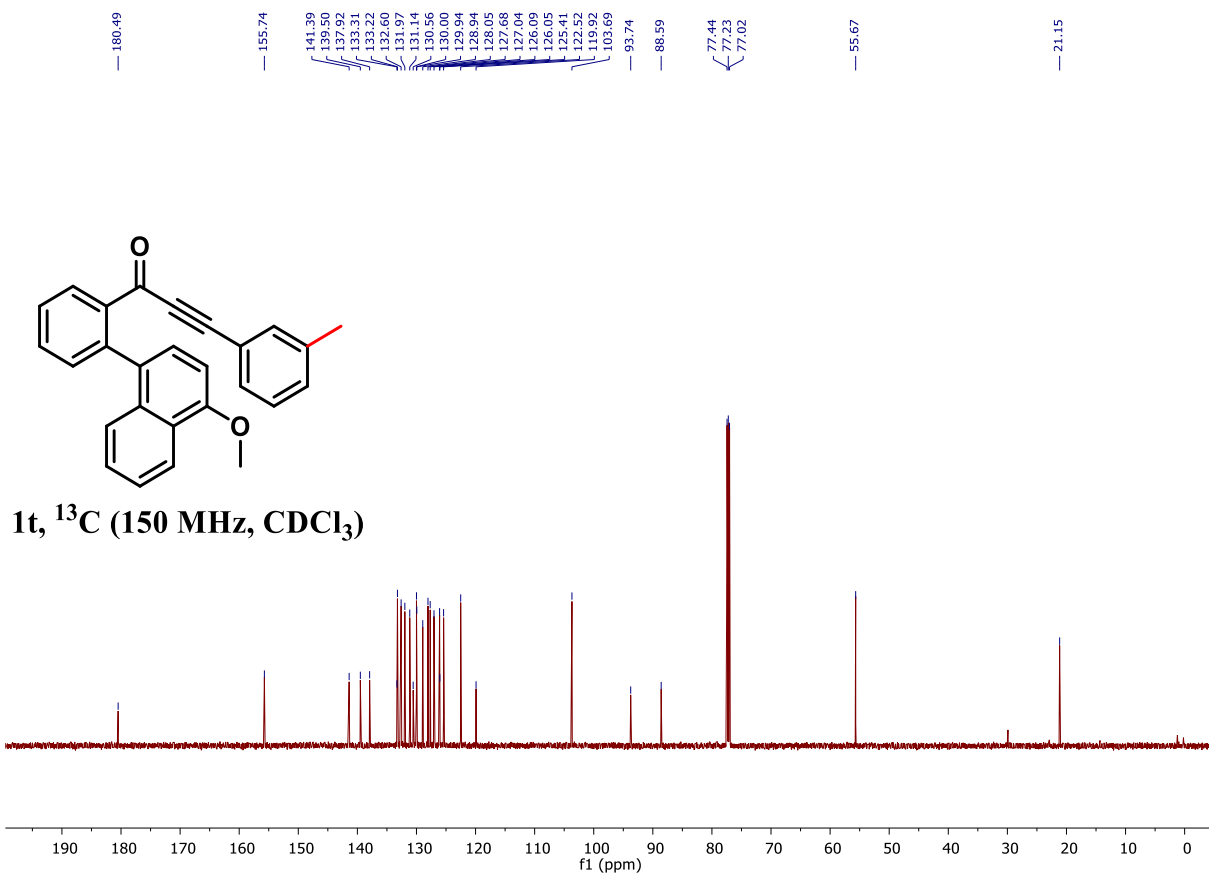
1s, ^{1}H (600 MHz, $CDCl_3$)



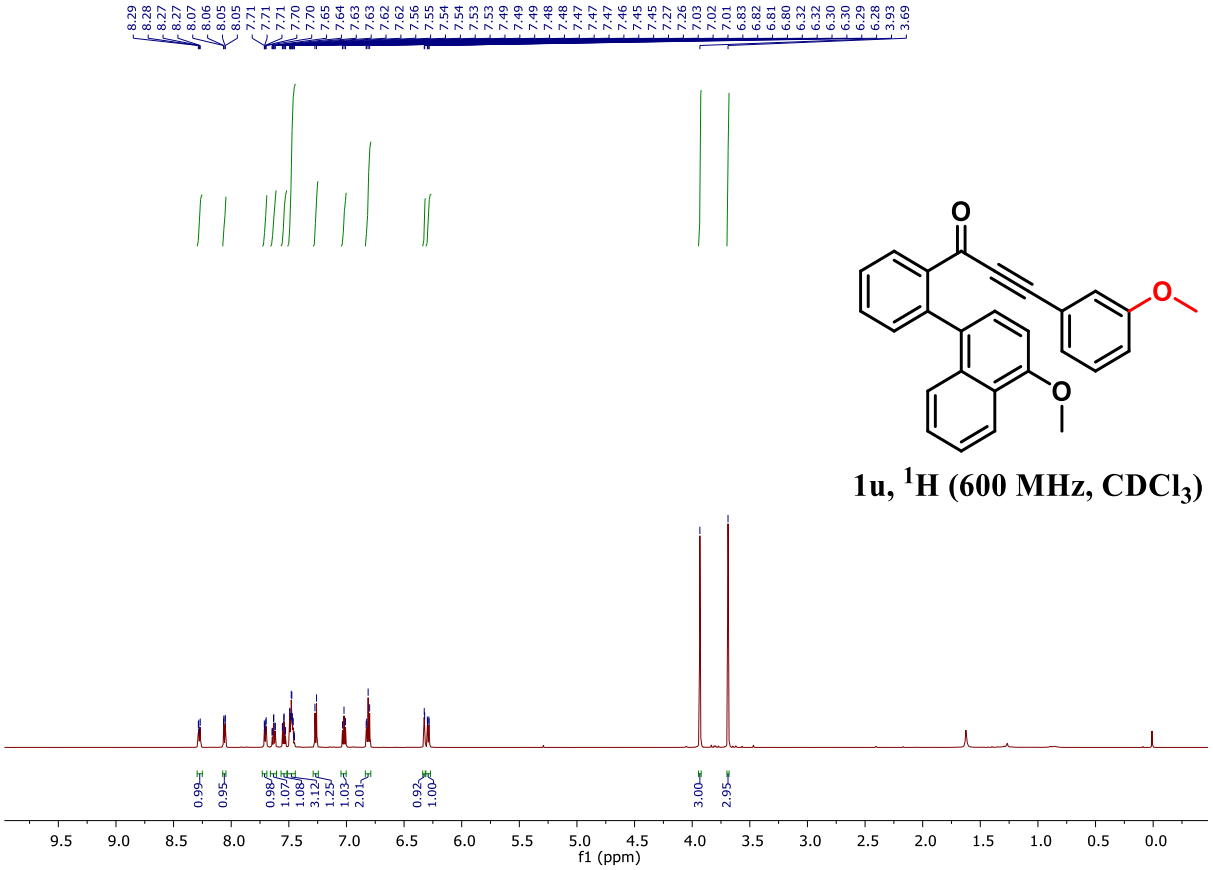
1s, ^{13}C (150 MHz, $CDCl_3$)



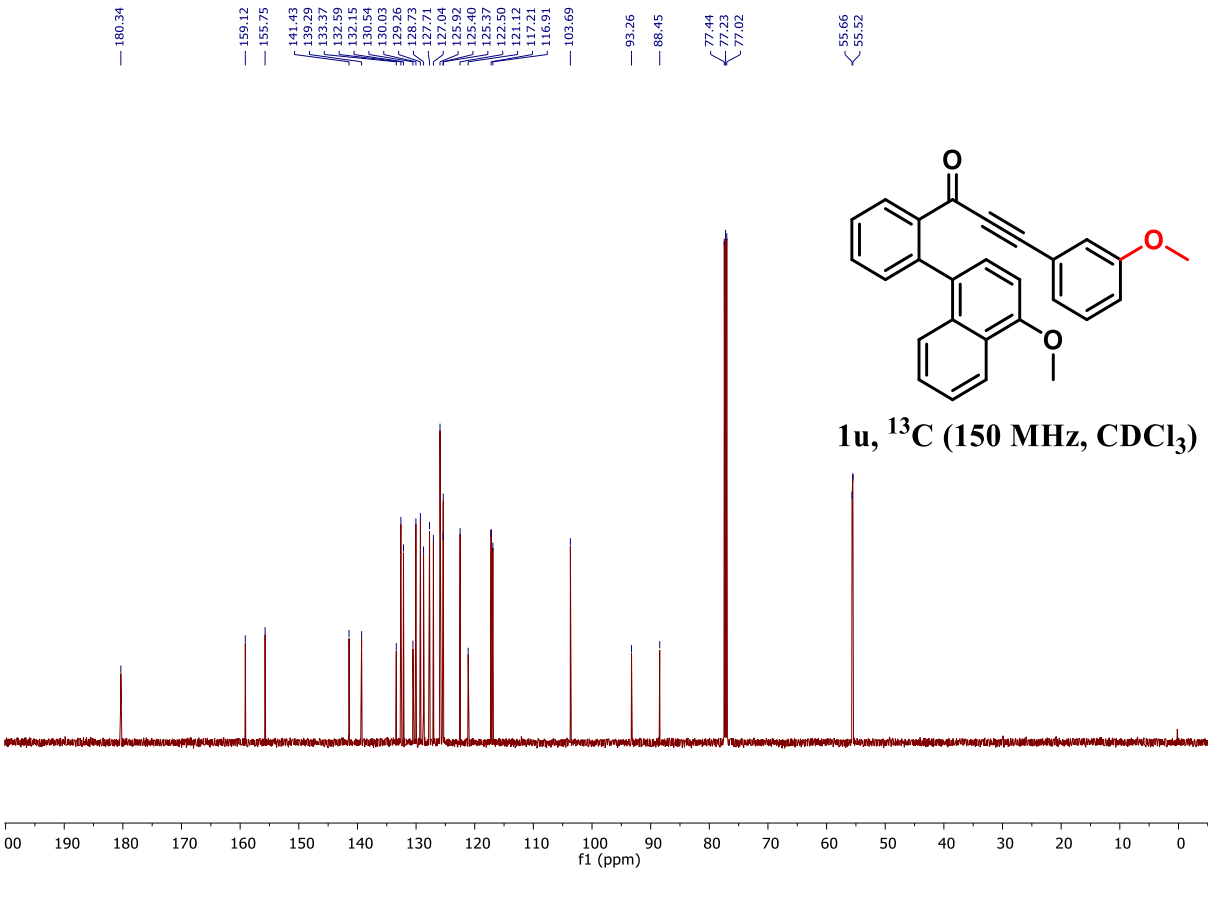
1t, ^{1}H (600 MHz, $CDCl_3$)



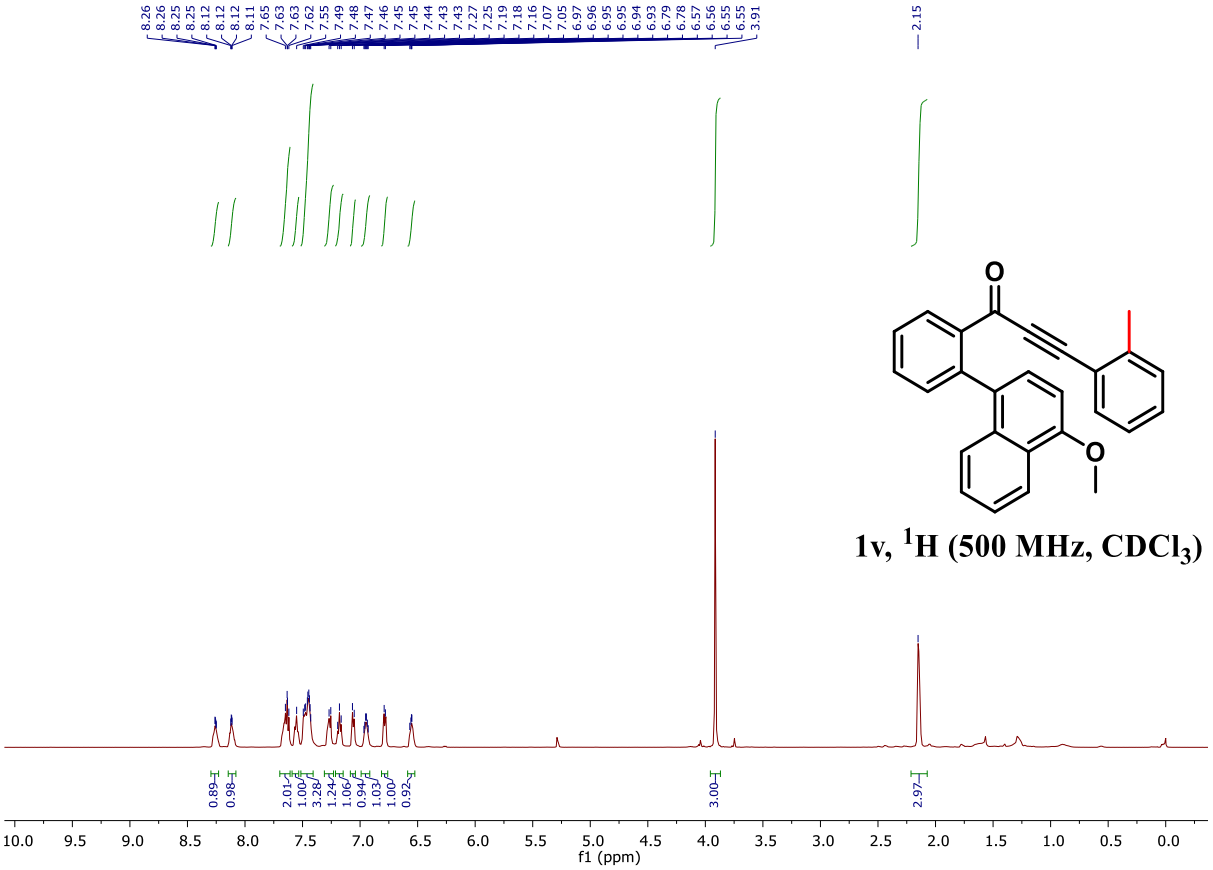
1t, ^{13}C (150 MHz, $CDCl_3$)



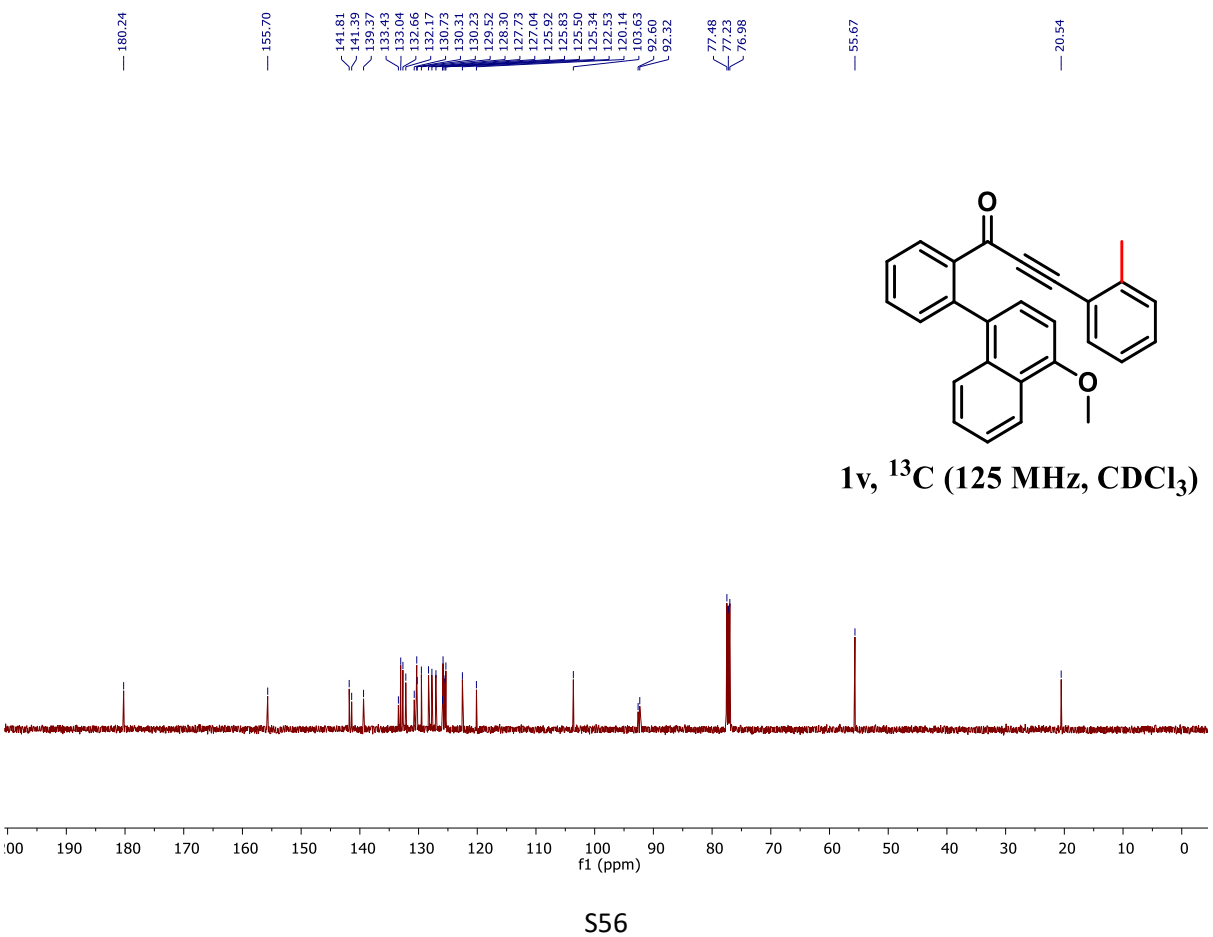
1u, ^{1}H (600 MHz, $CDCl_3$)



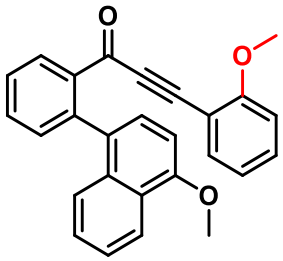
1u, ^{13}C (150 MHz, $CDCl_3$)



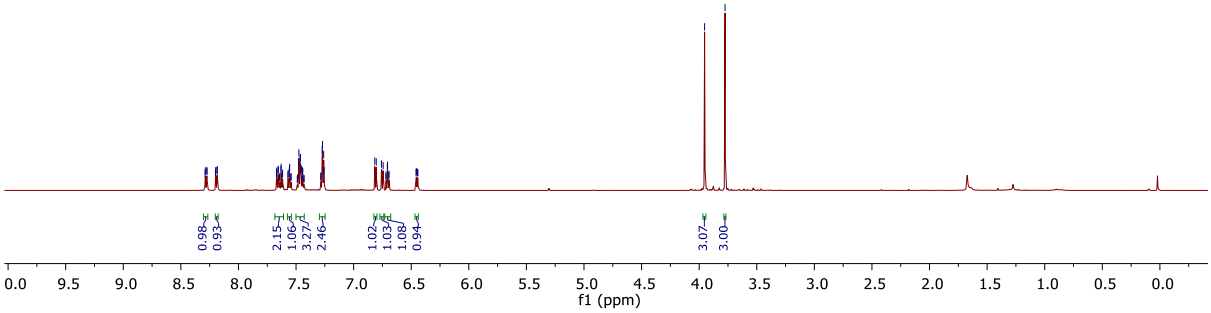
1v, ^{1}H (500 MHz, $CDCl_3$)

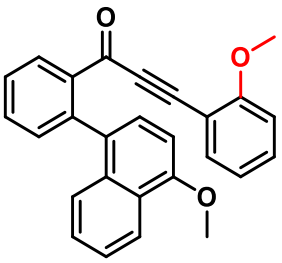


1v, ^{13}C (125 MHz, $CDCl_3$)

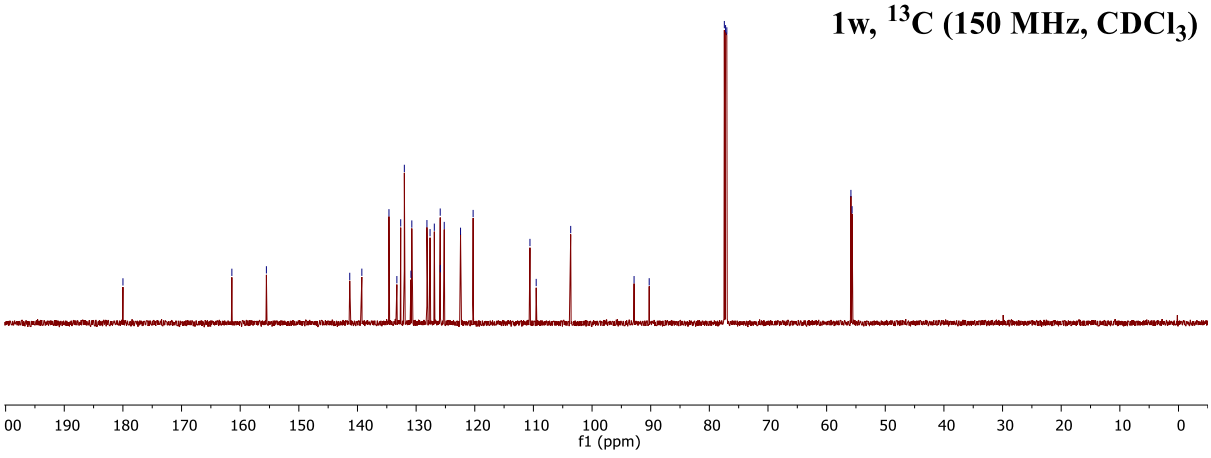


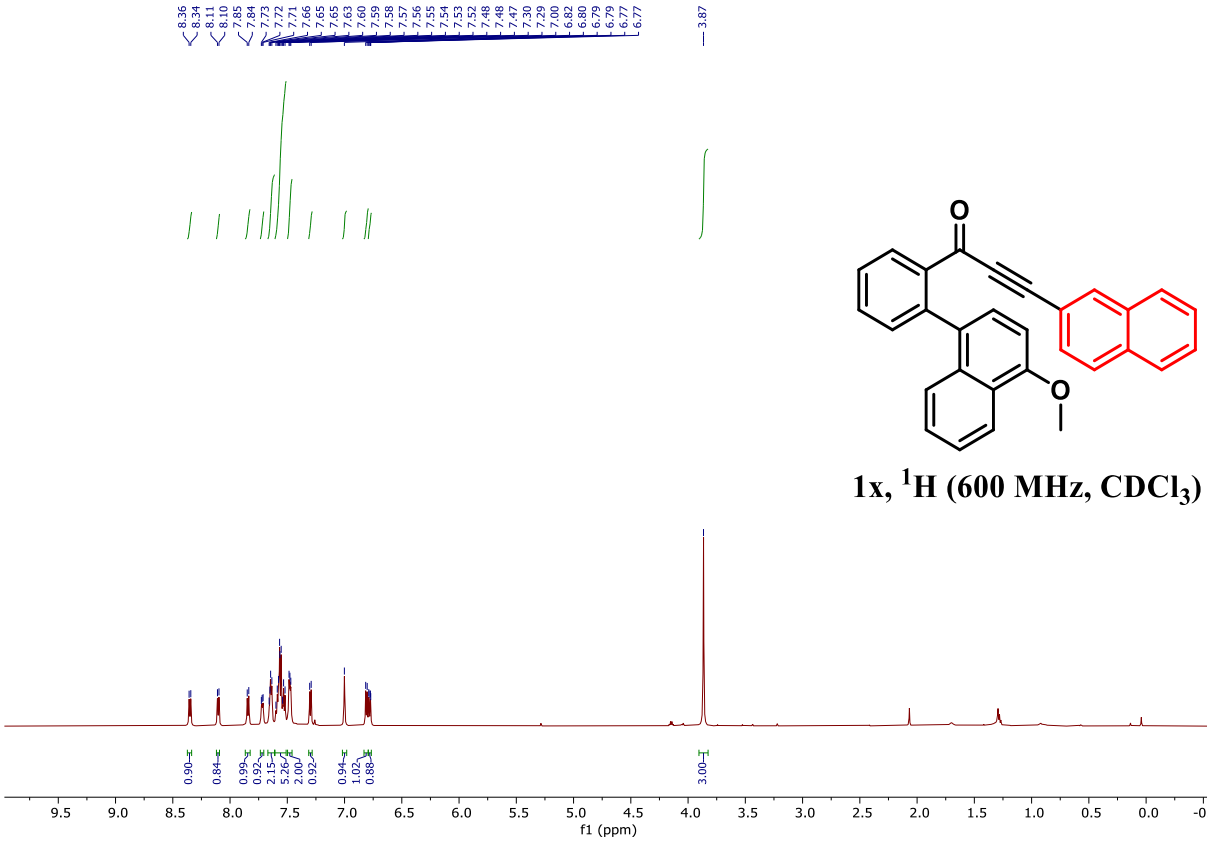
1w, ^{1}H (600 MHz, $CDCl_3$)



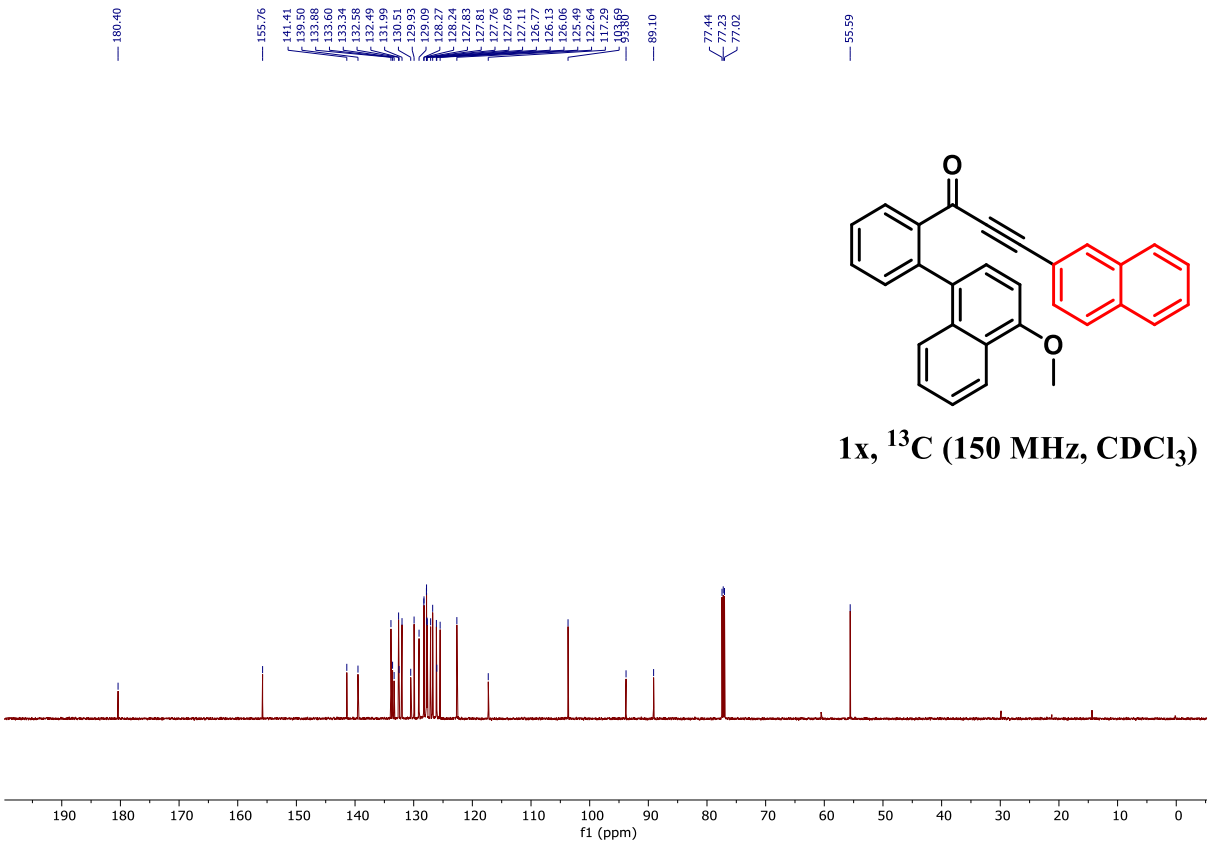


1w, ^{13}C (150 MHz, $CDCl_3$)

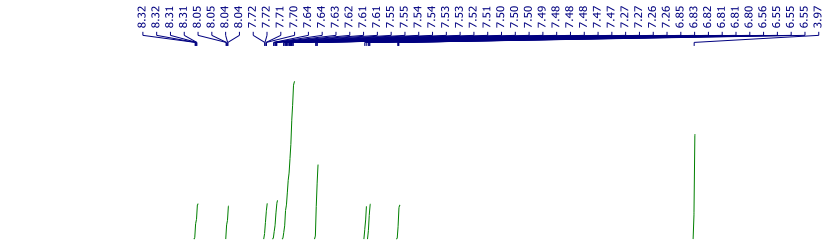


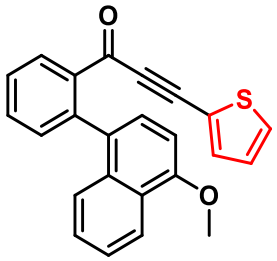


1x, ^{1}H (600 MHz, $CDCl_3$)

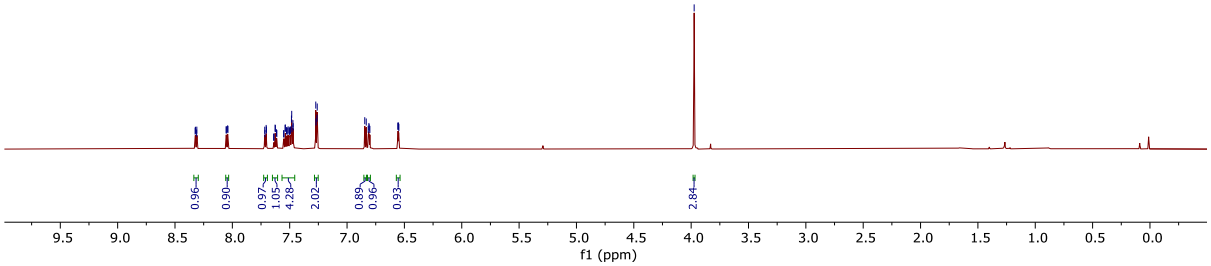


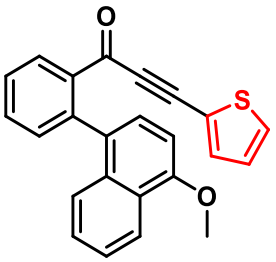
1x, ^{13}C (150 MHz, $CDCl_3$)



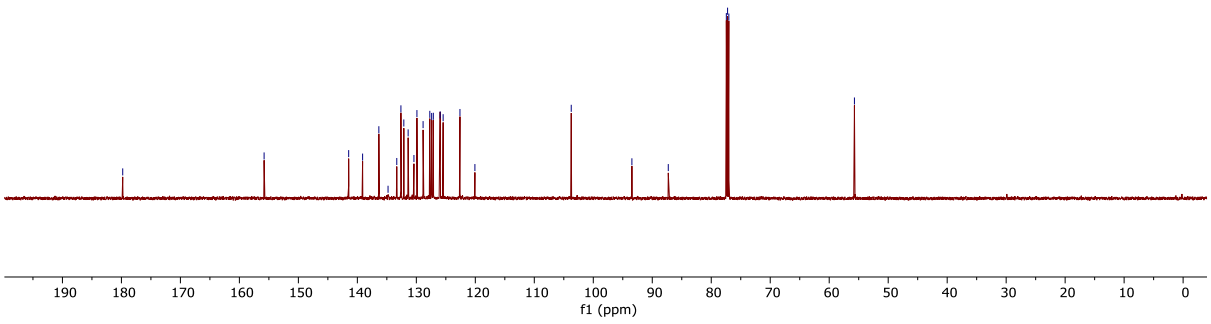


1y, ^{1}H (600 MHz, $CDCl_3$)

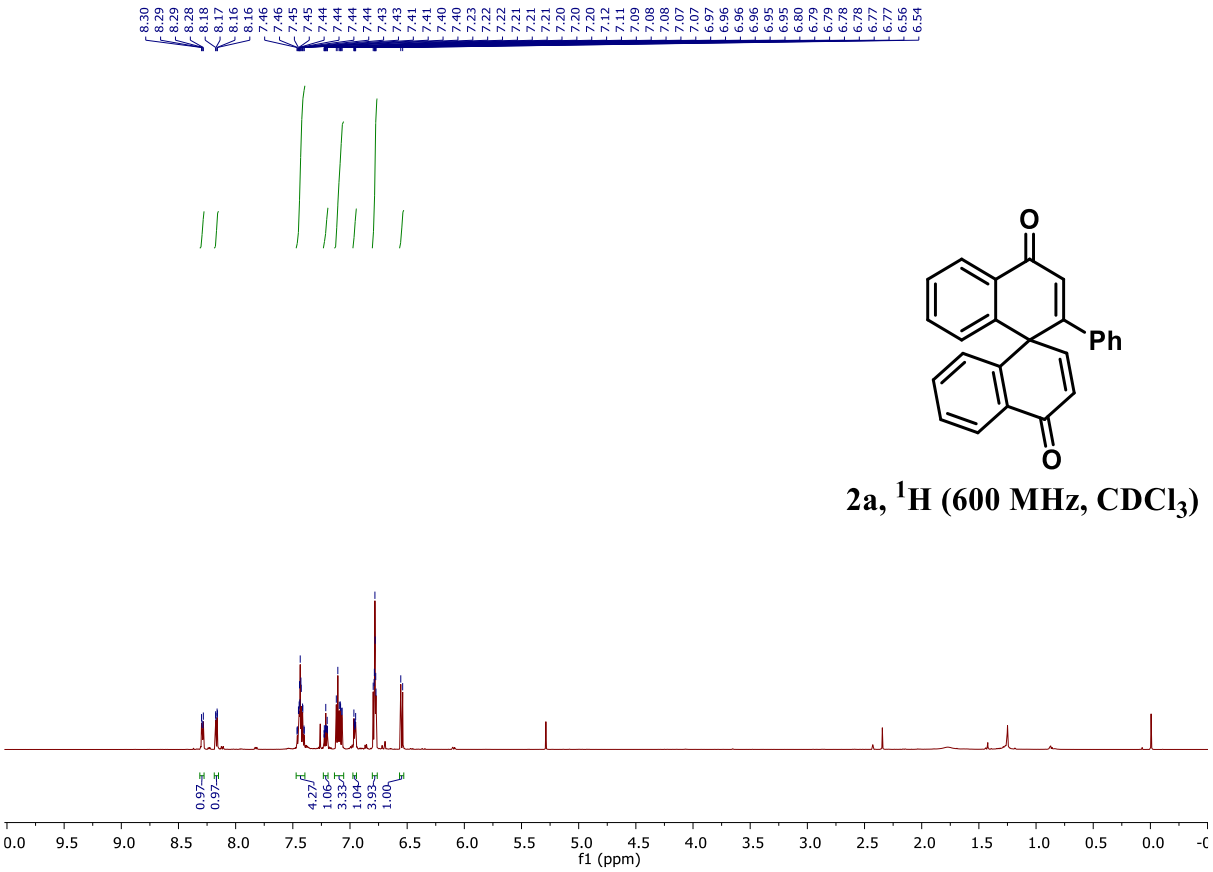




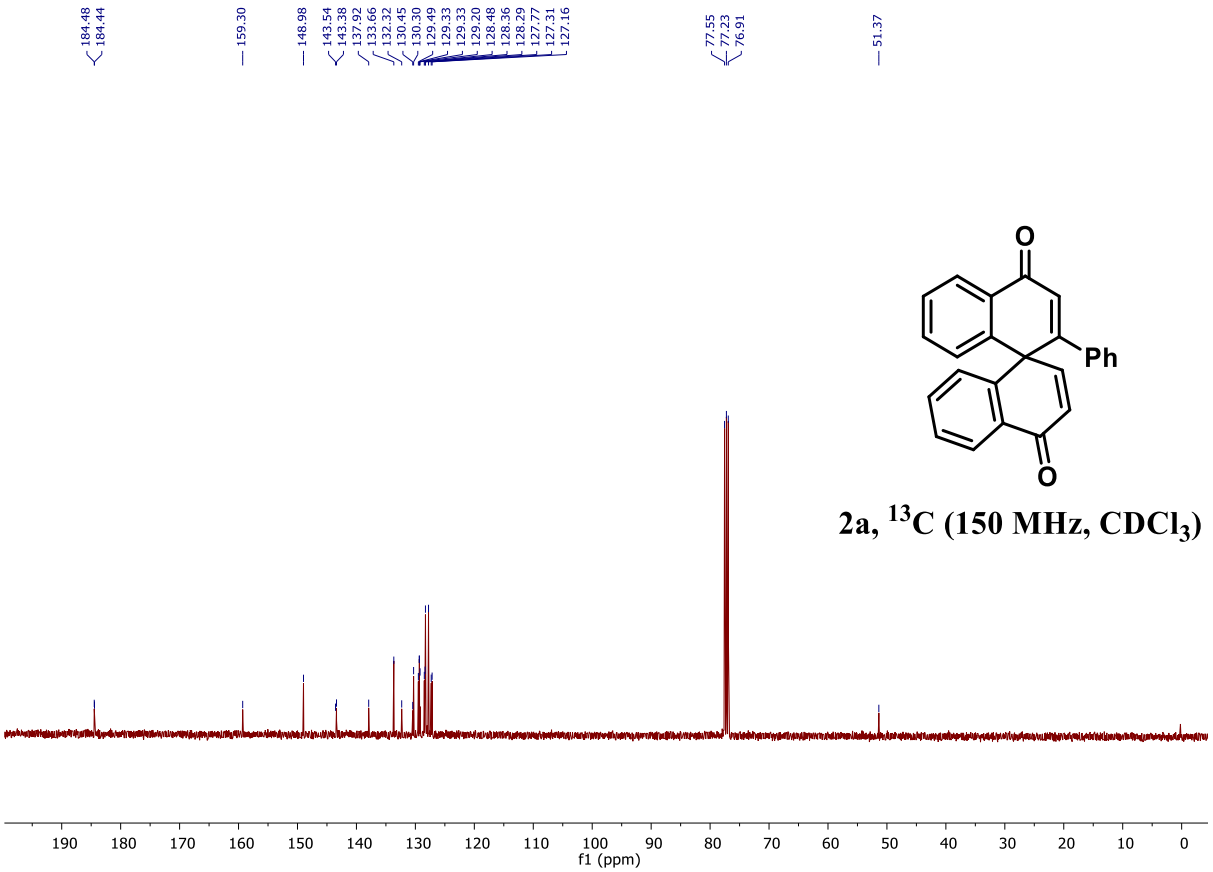
1y, ^{13}C (150 MHz, $CDCl_3$)



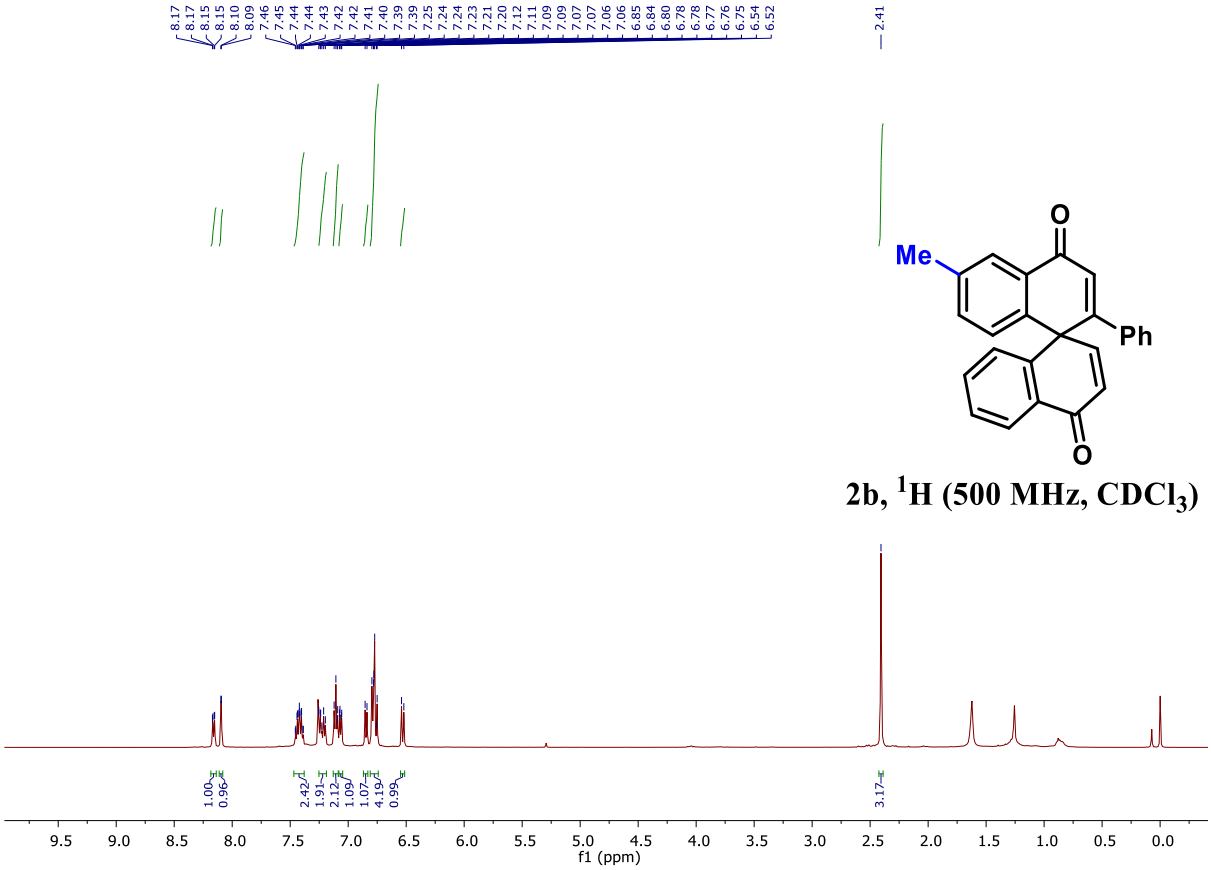
11.[1]H-NMR, [13]C NMR & [19]F NMR Spectra of products:



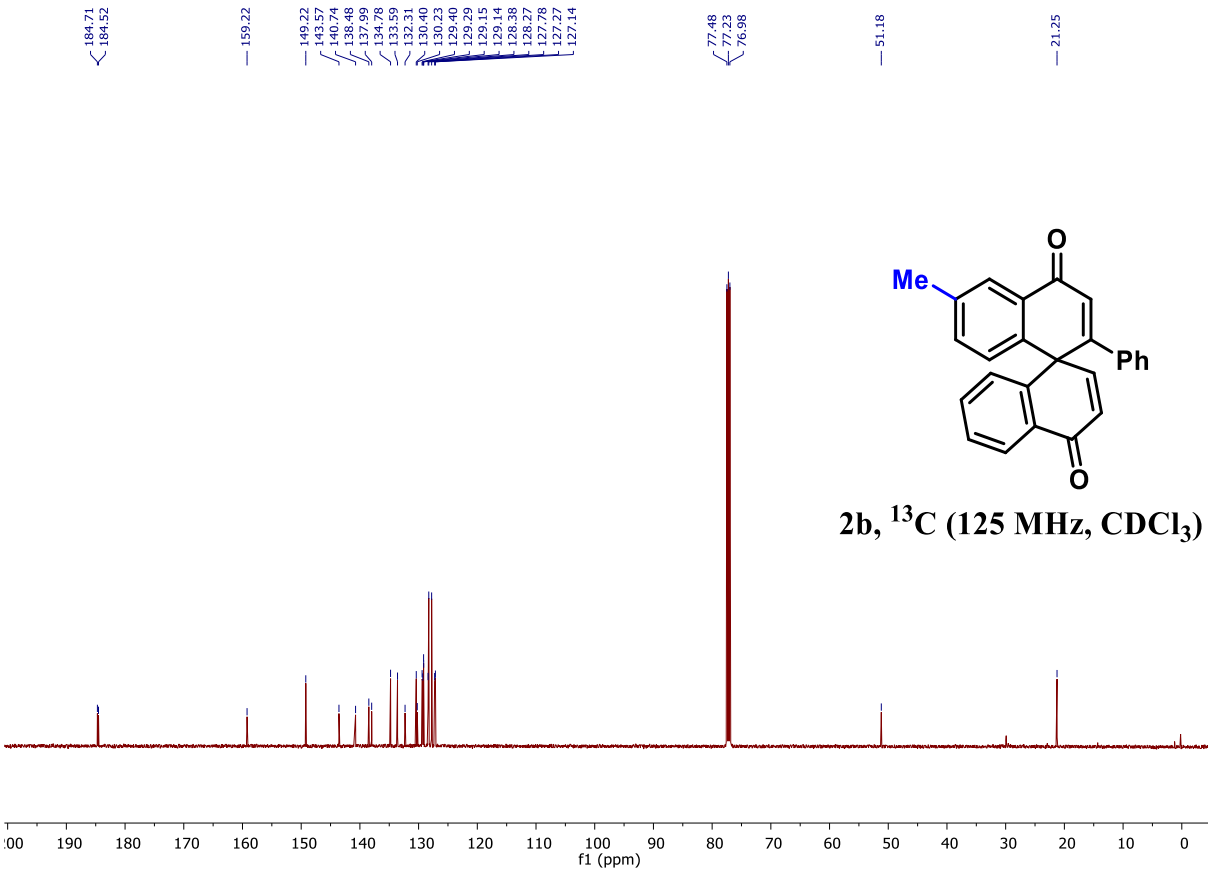
2a, [1]H (600 MHz, $CDCl_3$)



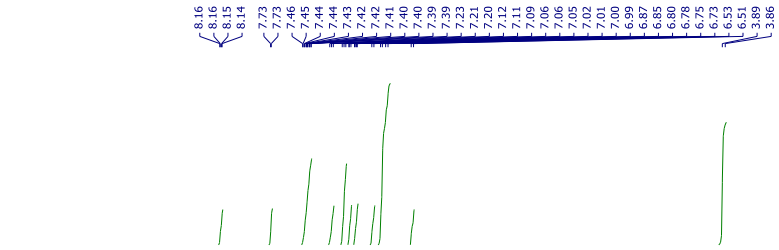
2a, [13]C (150 MHz, $CDCl_3$)

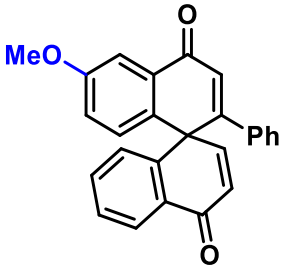


2b, ^{1}H (500 MHz, $CDCl_3$)

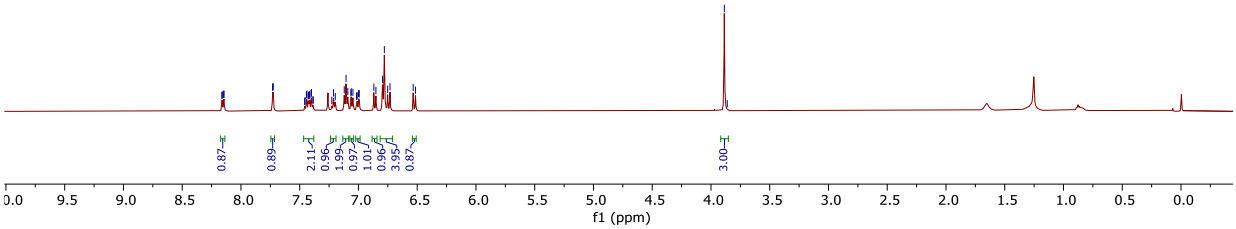


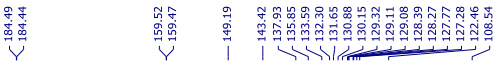
2b, ^{13}C (125 MHz, $CDCl_3$)

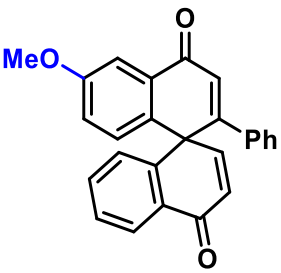




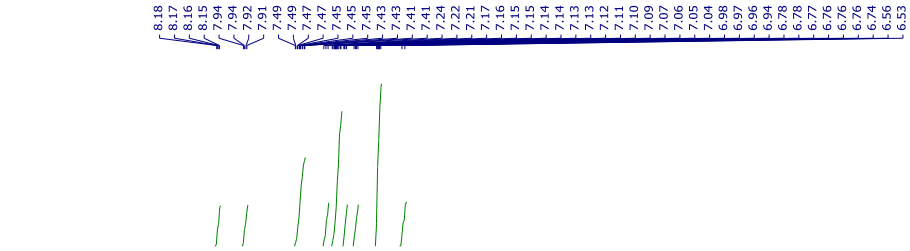
2c, ^{1}H (500 MHz, $CDCl_3$)

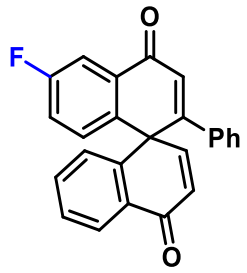




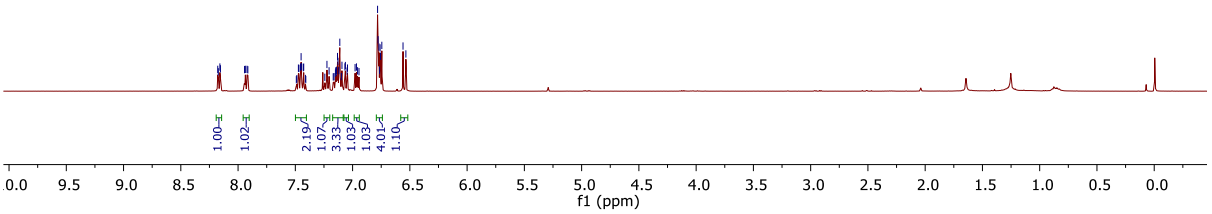


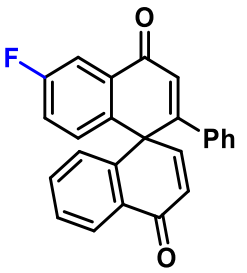
2c, ^{13}C (125 MHz, $CDCl_3$)



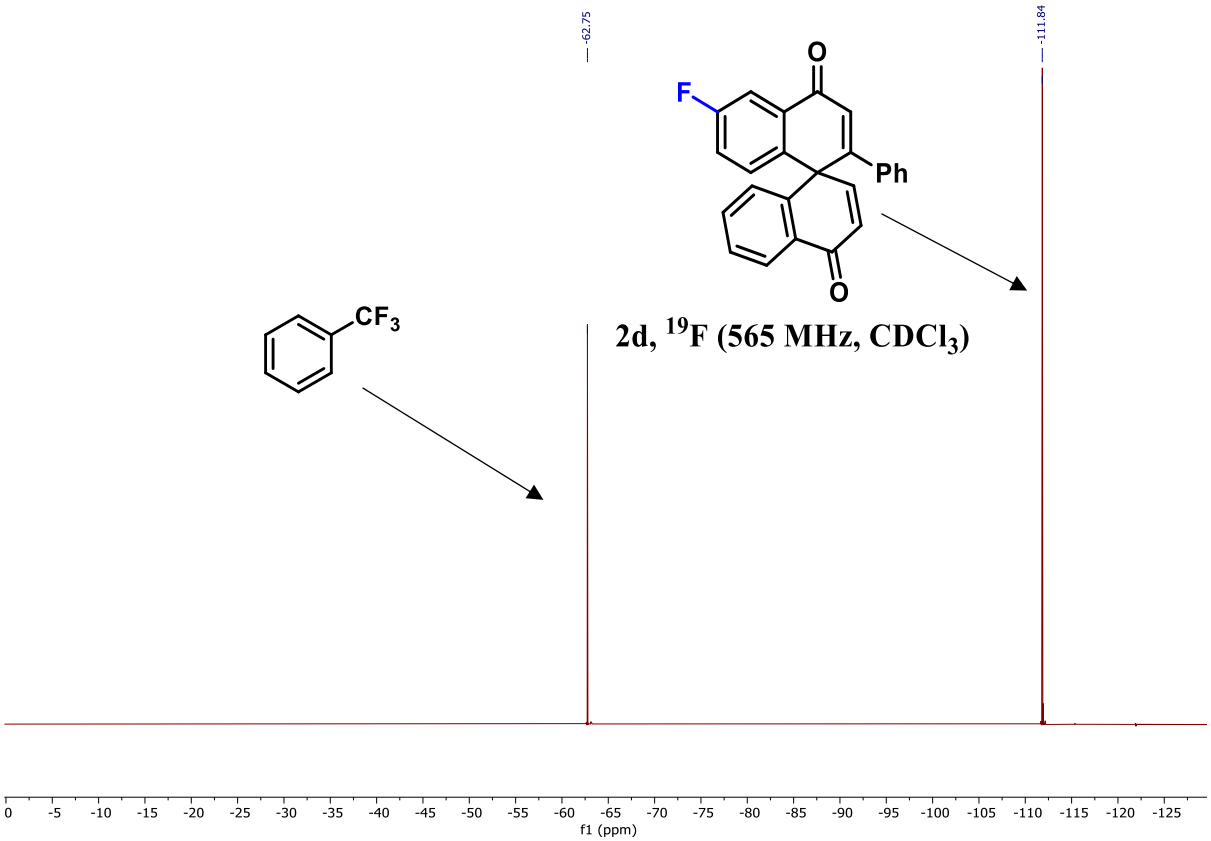


2d, ^{1}H (400 MHz, $CDCl_3$)

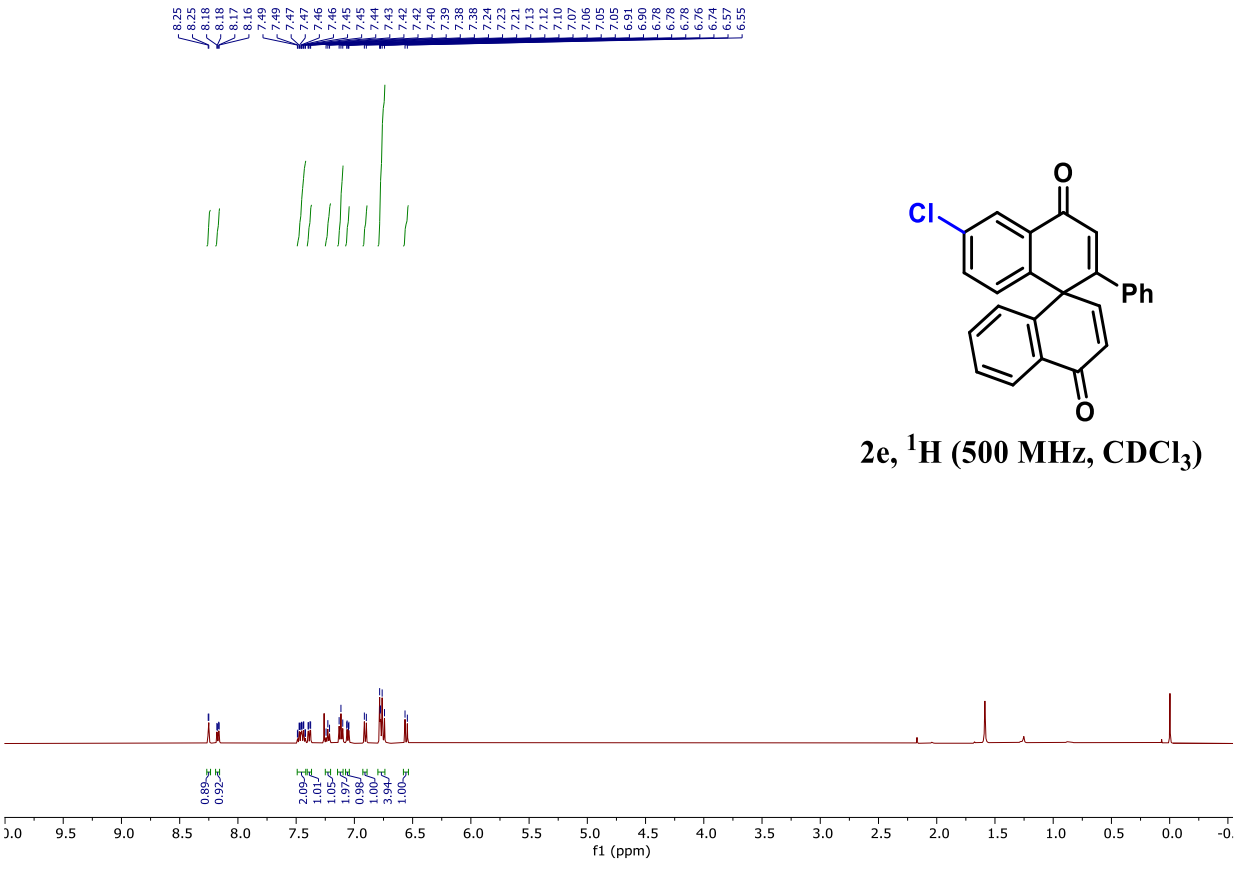




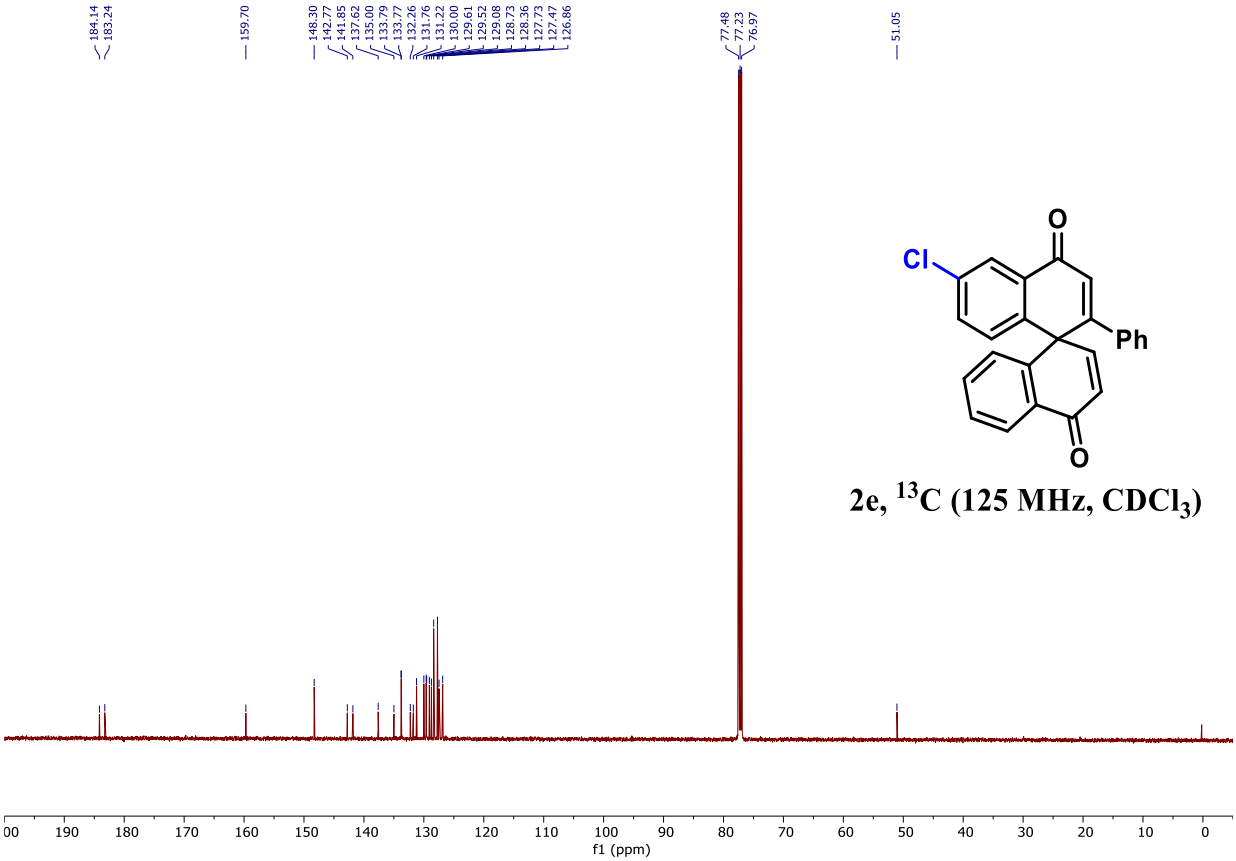
2d, ^{13}C (125 MHz, $CDCl_3$)



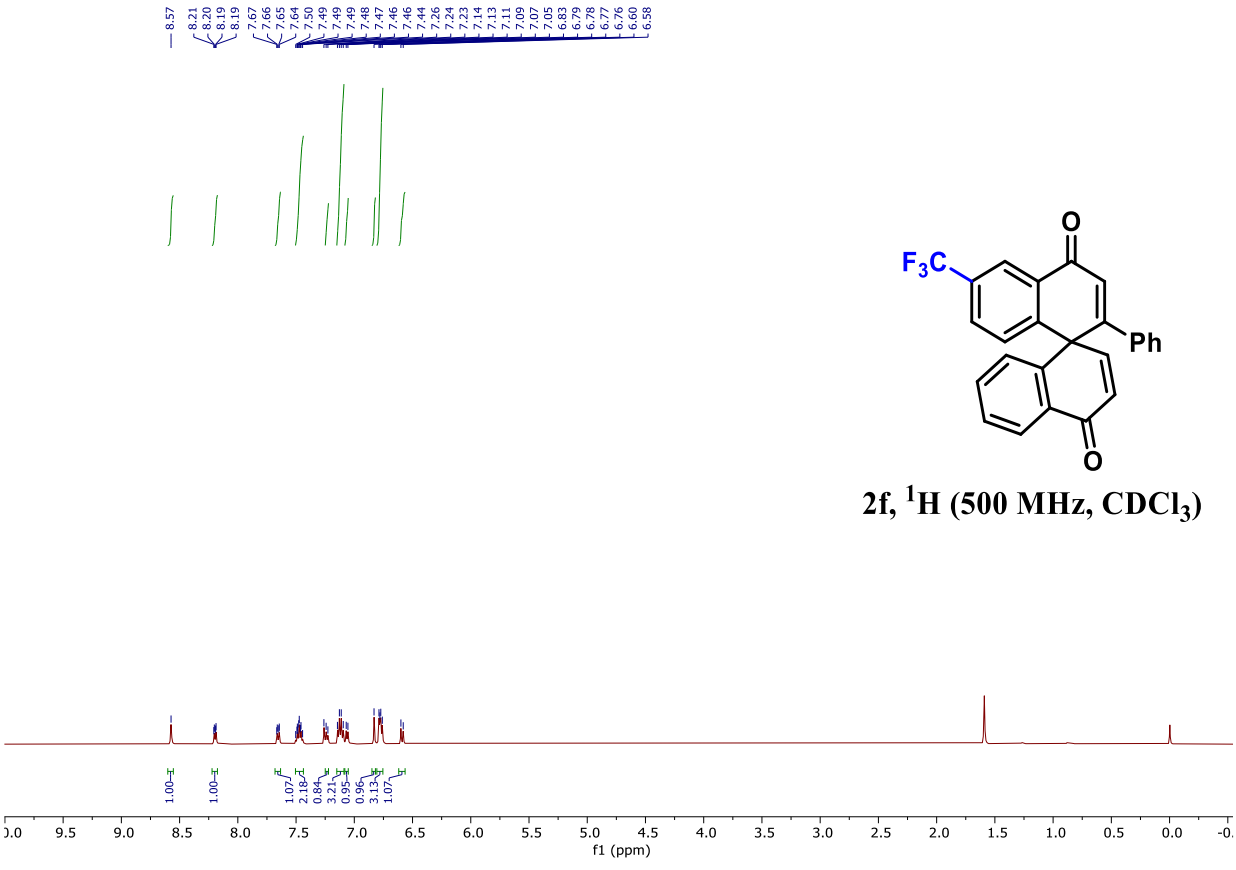
2d, ^{19}F (565 MHz, $CDCl_3$)



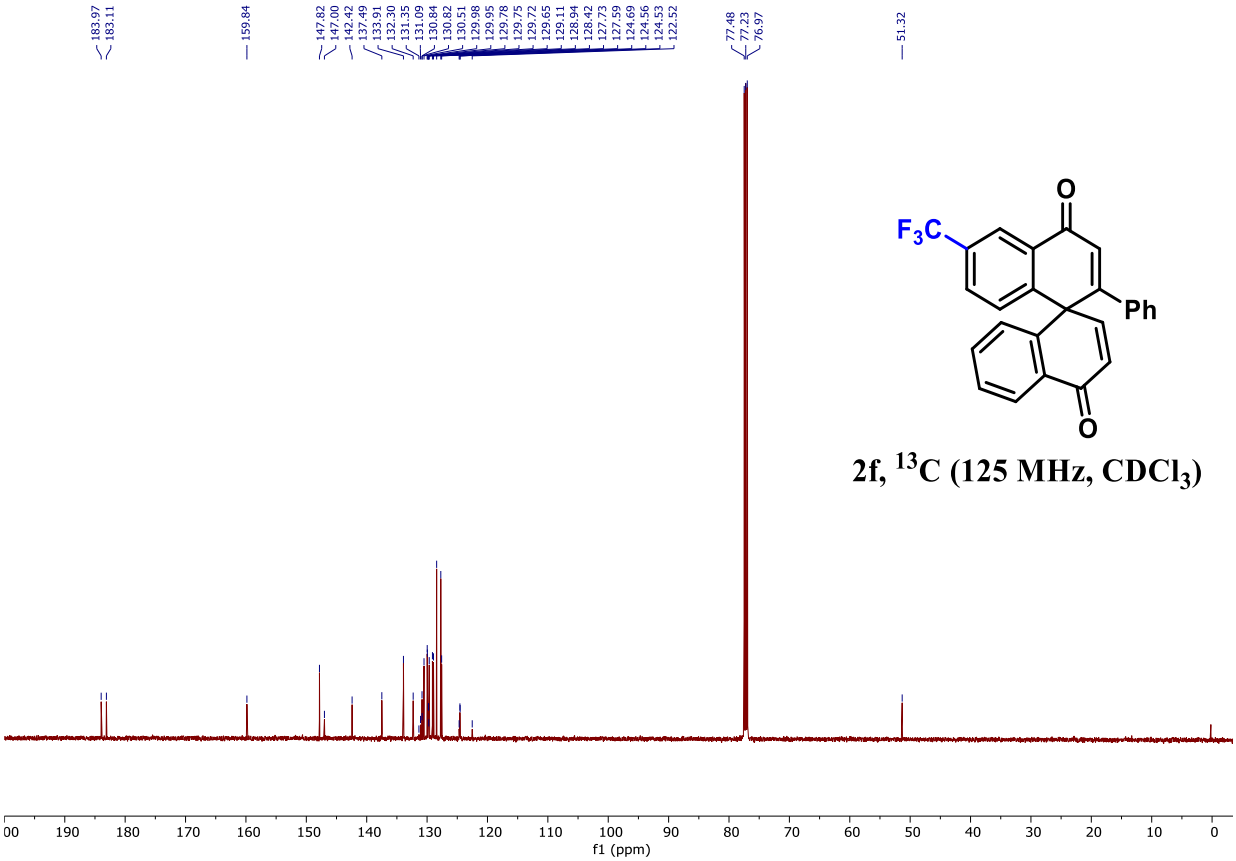
2e, ^{1}H (500 MHz, $CDCl_3$)



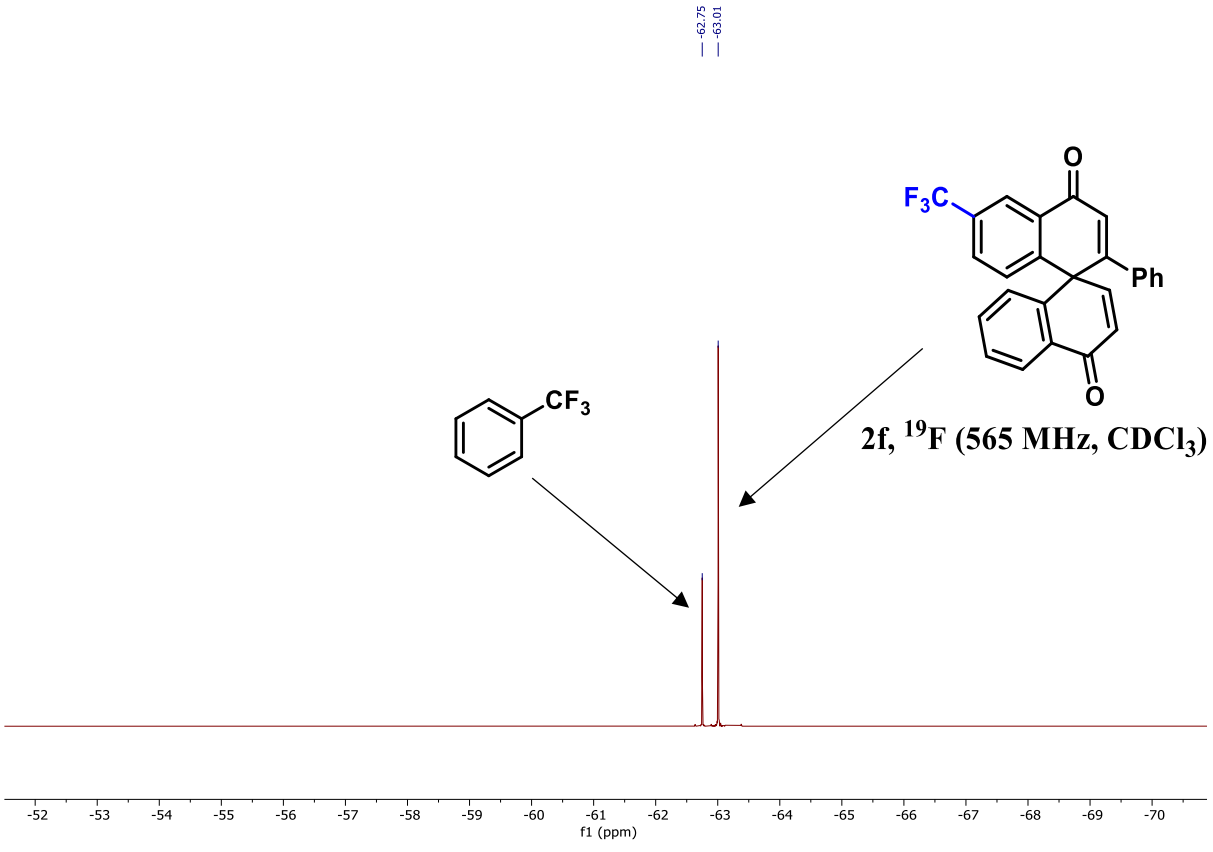
2e, ^{13}C (125 MHz, $CDCl_3$)



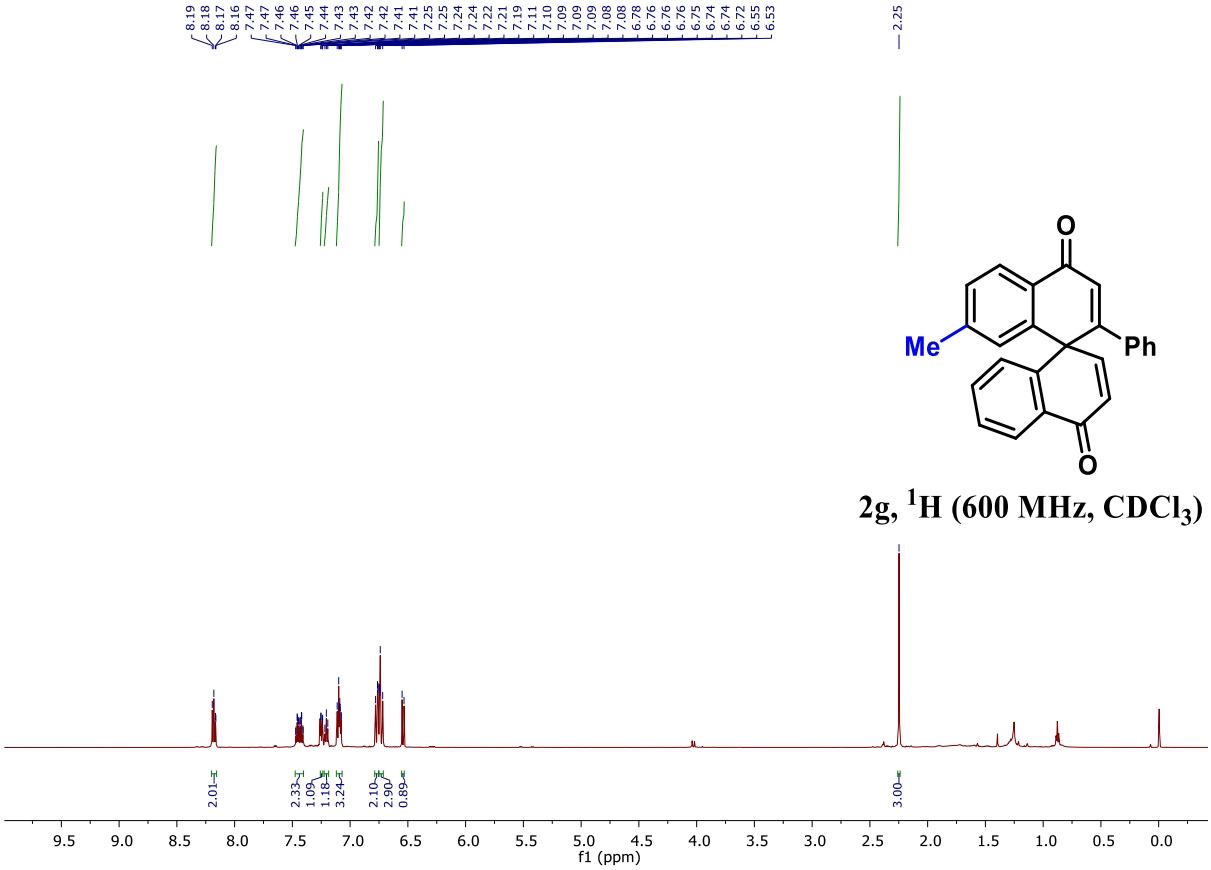
2f, ^{1}H (500 MHz, $CDCl_3$)



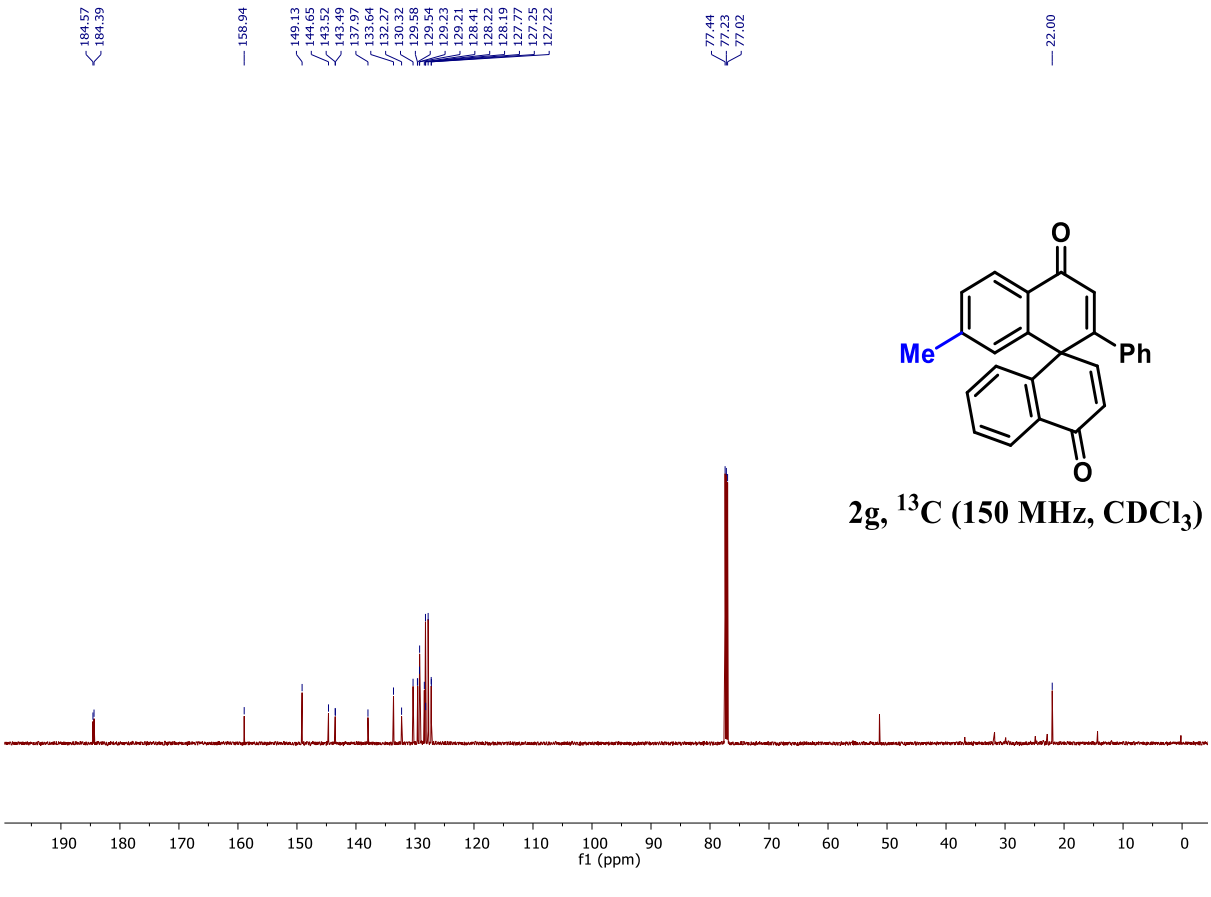
2f, ^{13}C (125 MHz, $CDCl_3$)



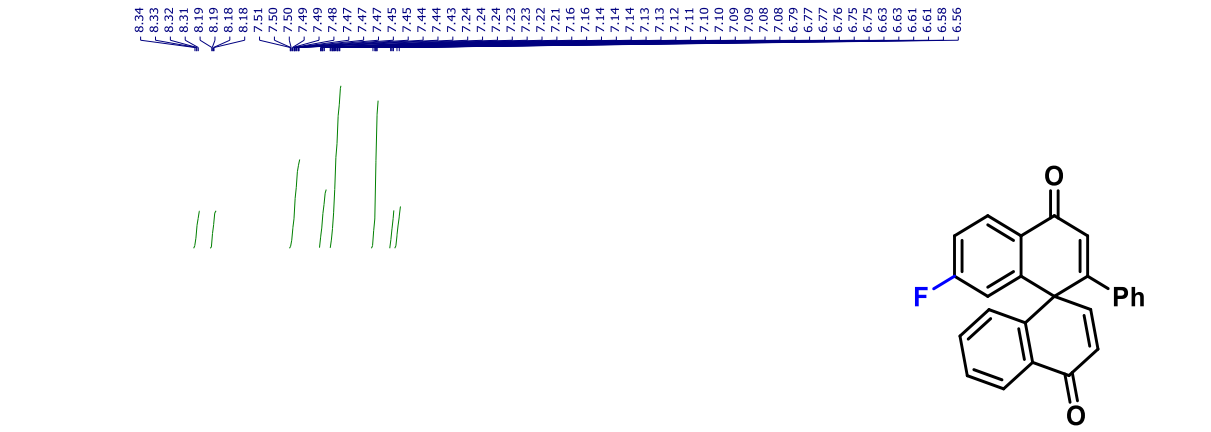
2f, ^{19}F (565 MHz, $CDCl_3$)



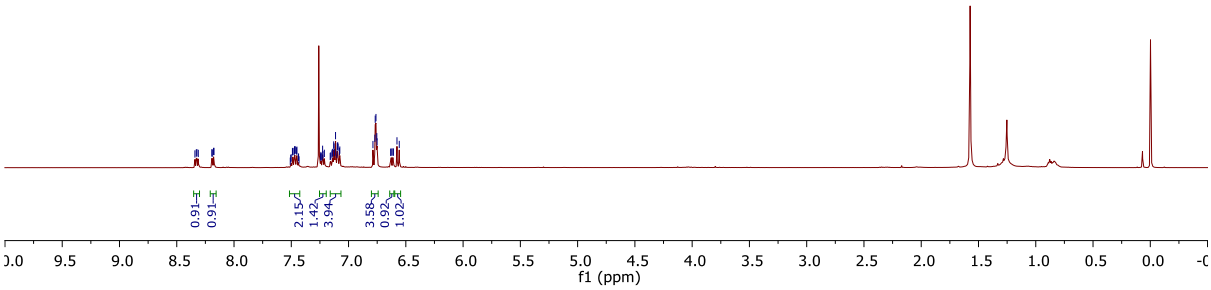
2g, ^{1}H (600 MHz, $CDCl_3$)

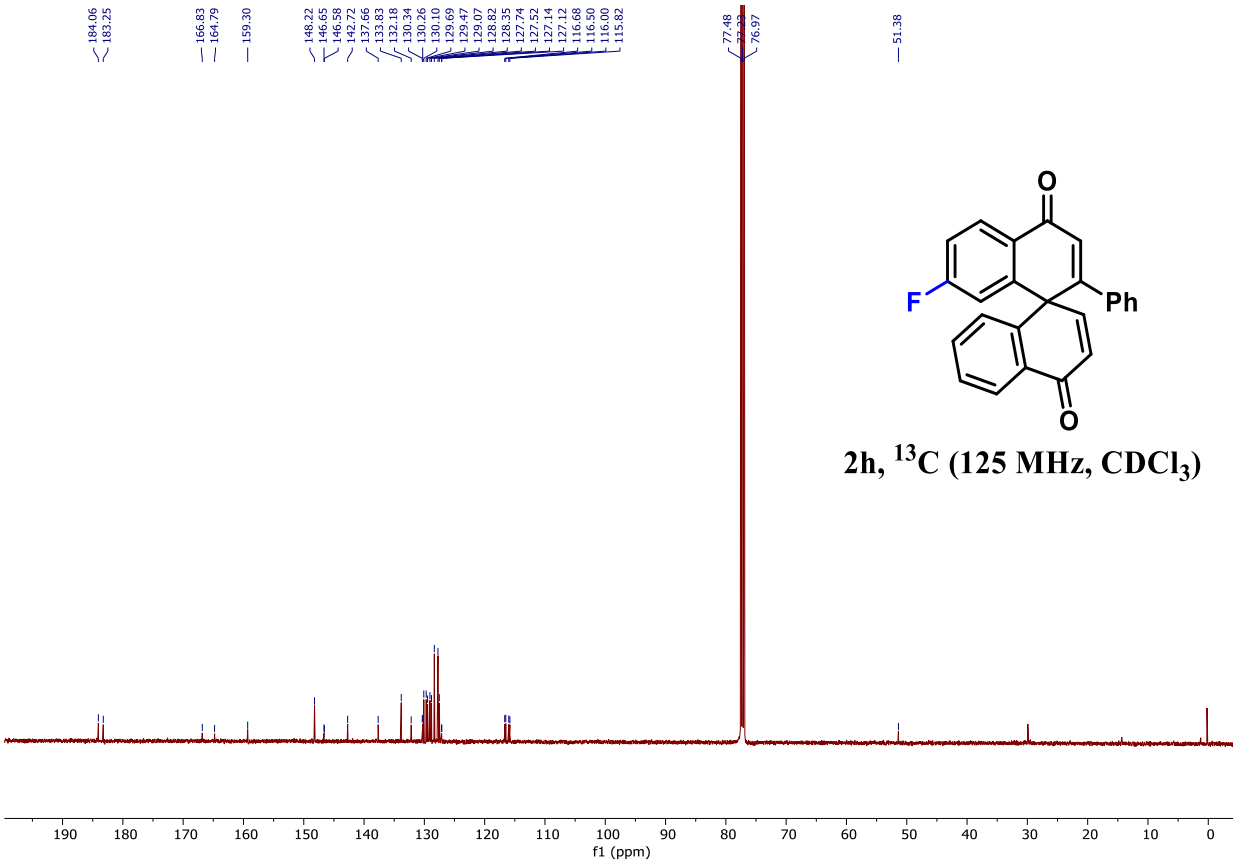


2g, ^{13}C (150 MHz, $CDCl_3$)

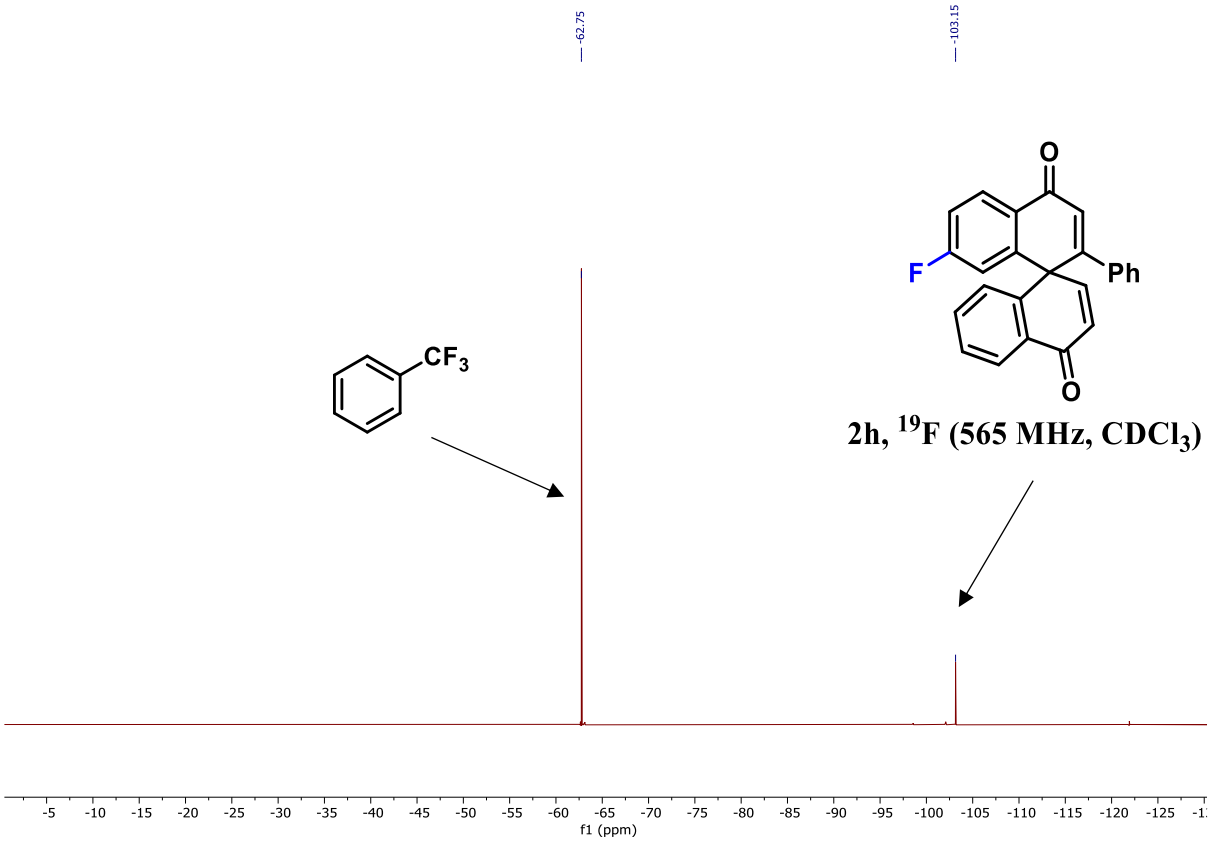


2h, ^{1}H (500 MHz, $CDCl_3$)

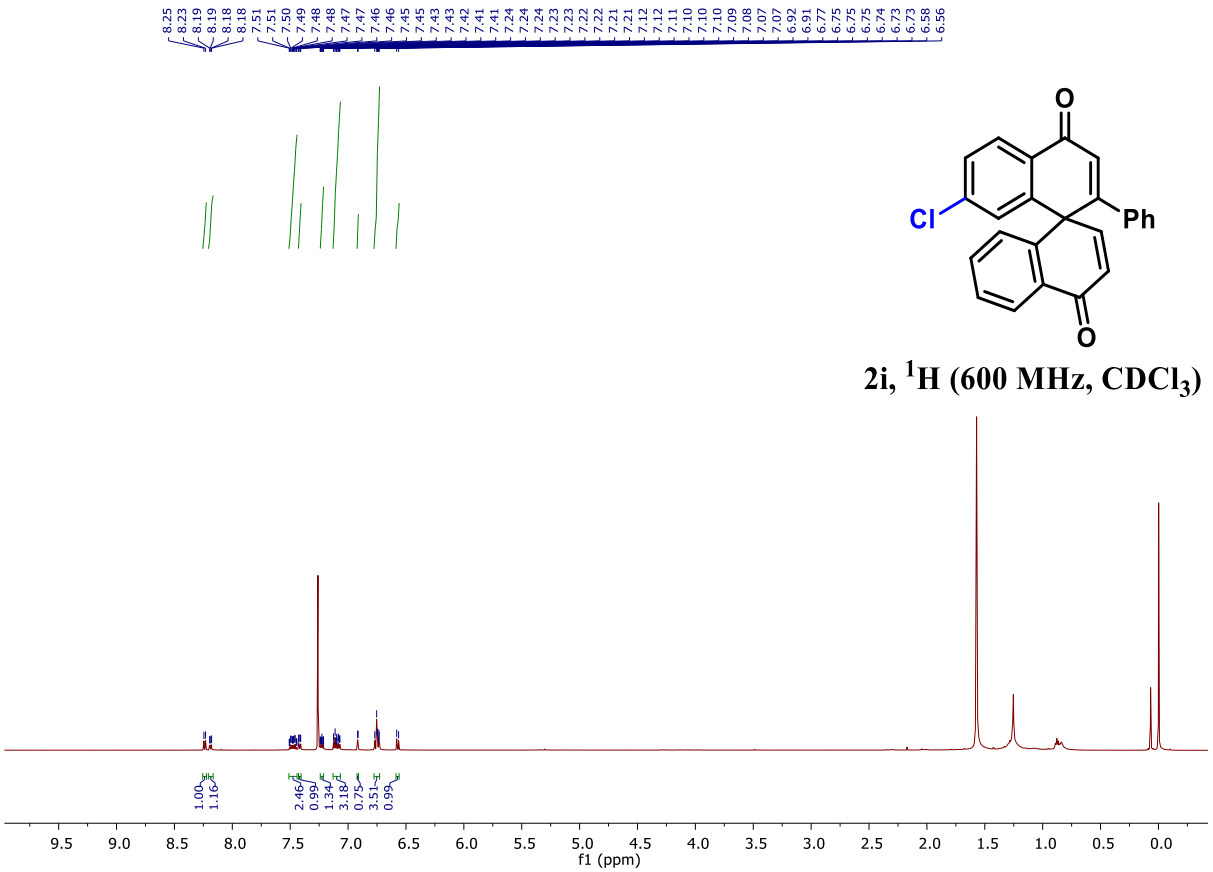




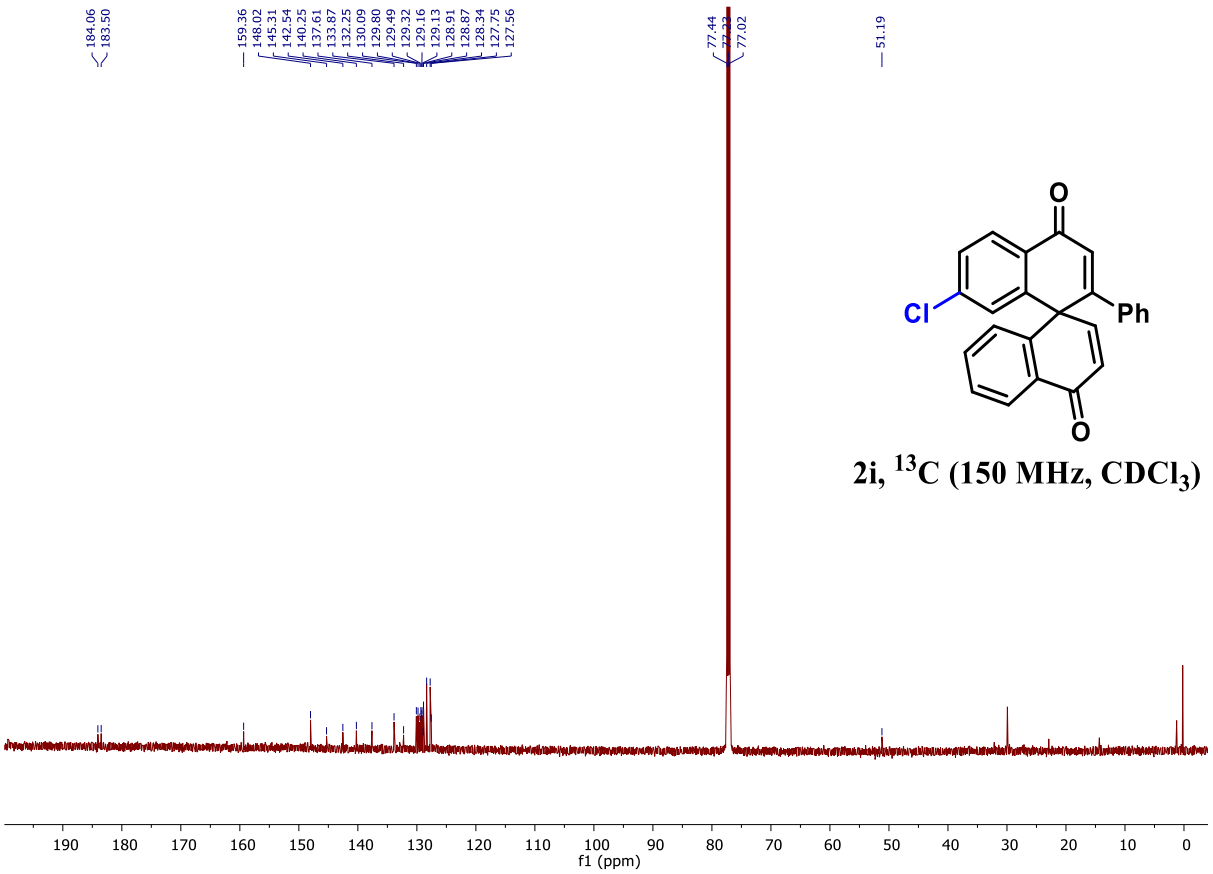
2h, ^{13}C (125 MHz, $CDCl_3$)



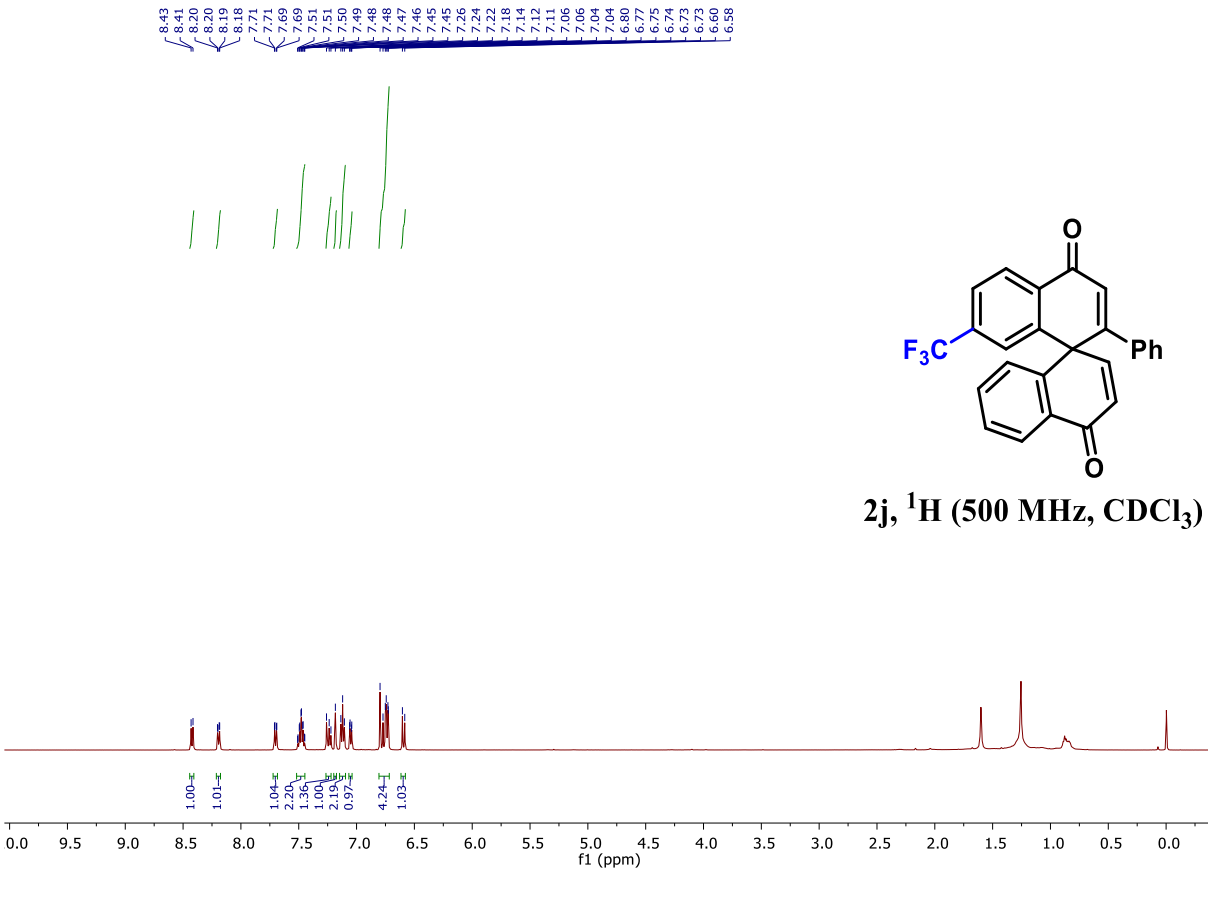
2h, ^{19}F (565 MHz, $CDCl_3$)



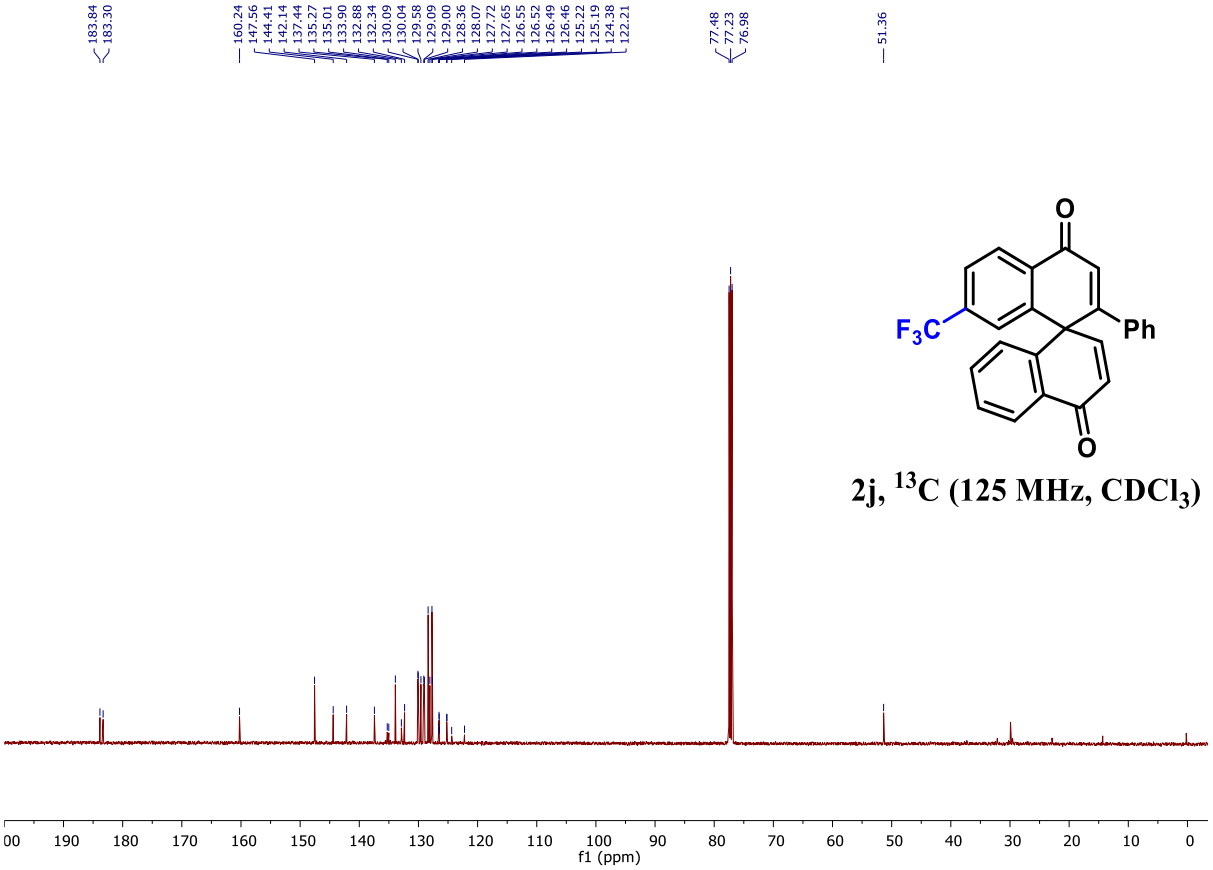
2i, ^{1}H (600 MHz, $CDCl_3$)



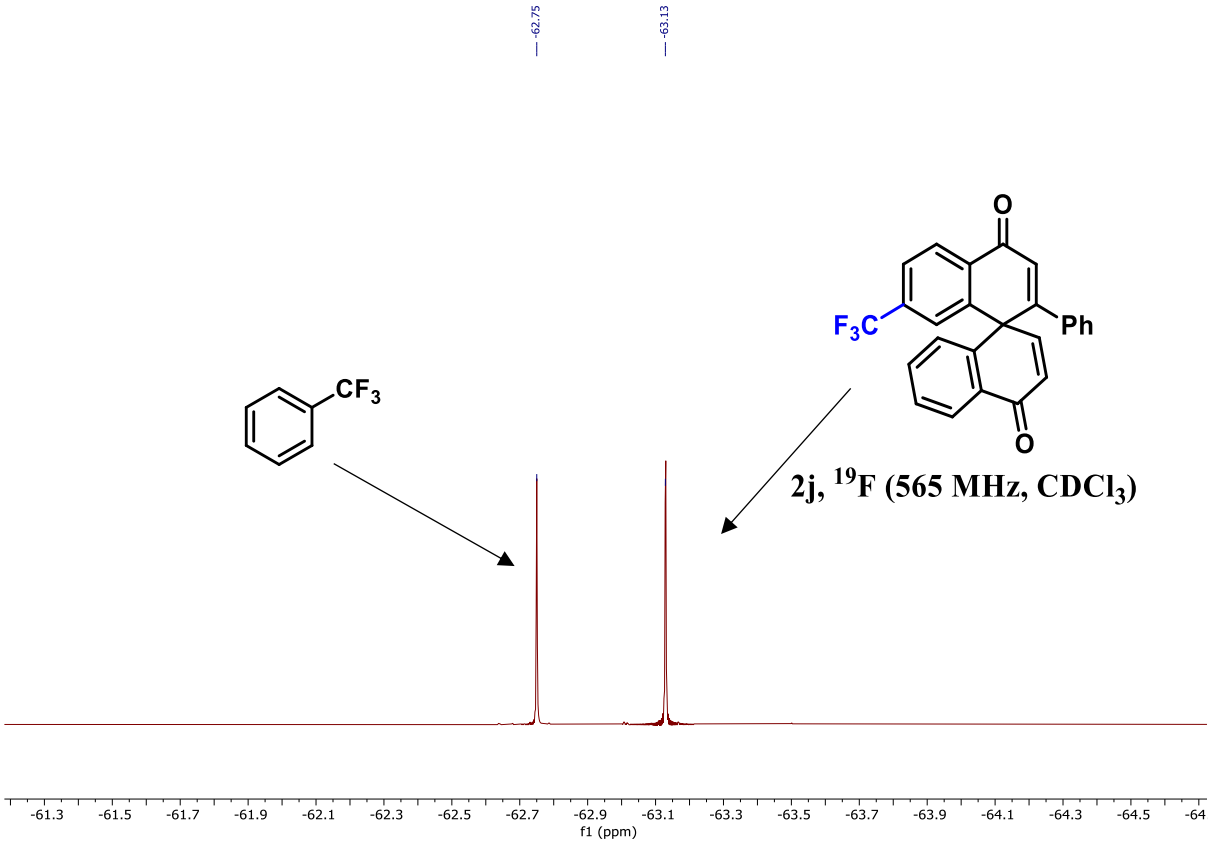
2i, ^{13}C (150 MHz, $CDCl_3$)



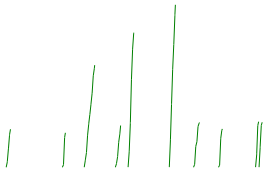
2j, ^{1}H (500 MHz, $CDCl_3$)

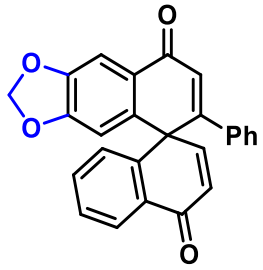


2j, ^{13}C (125 MHz, $CDCl_3$)

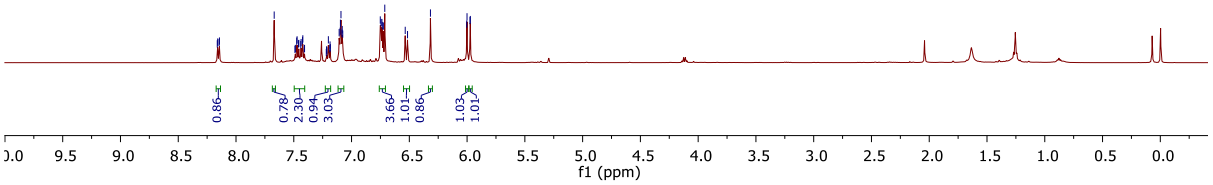


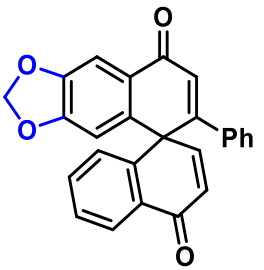
2j, ^{19}F (565 MHz, $CDCl_3$)



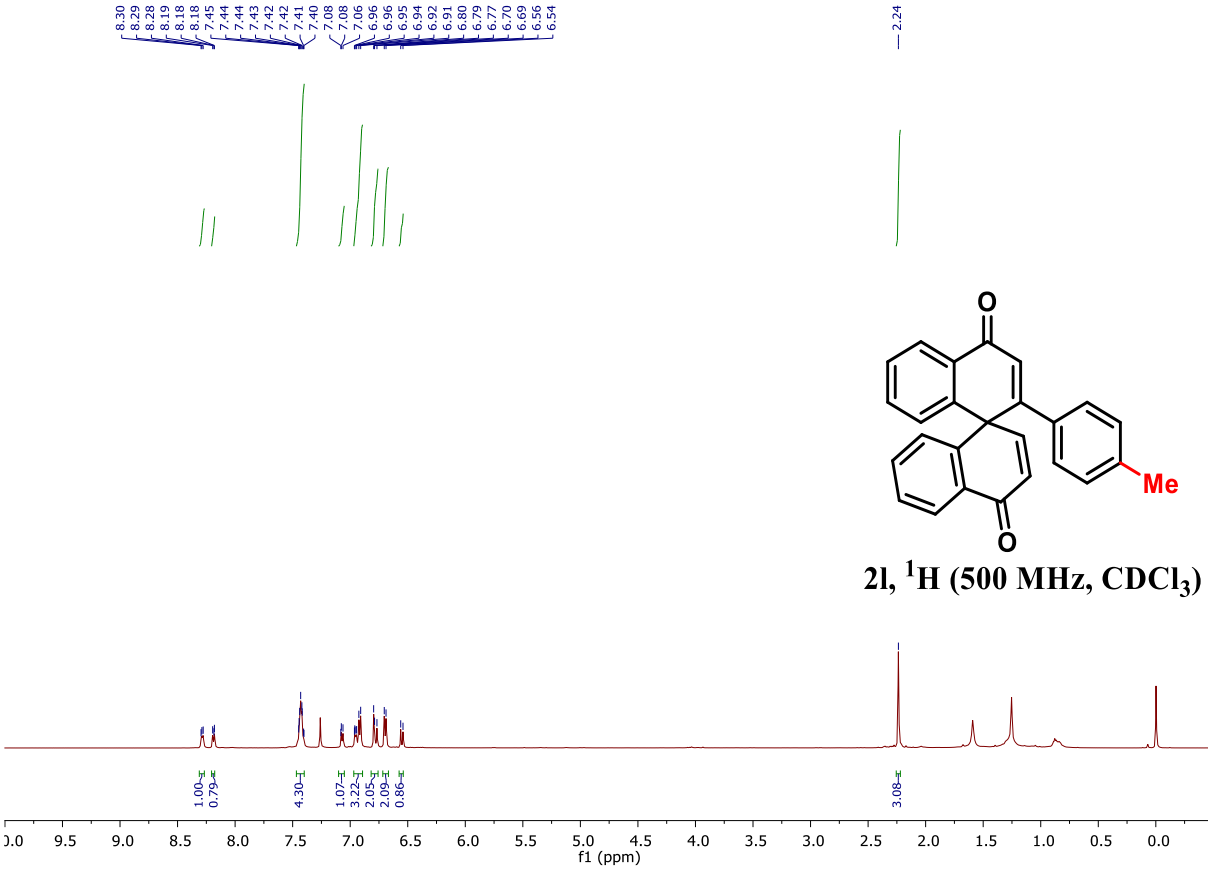


2k, ^{1}H (500 MHz, $CDCl_3$)

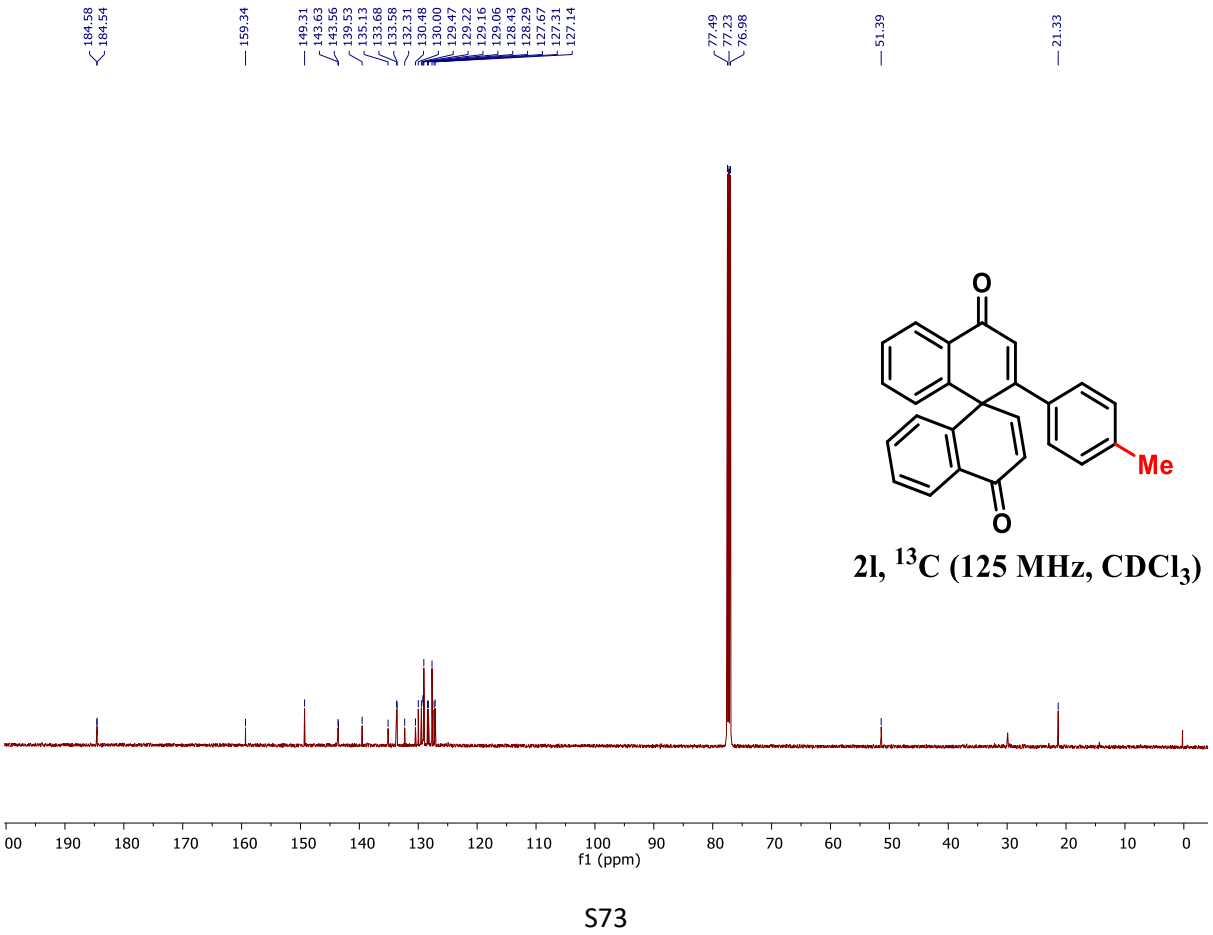




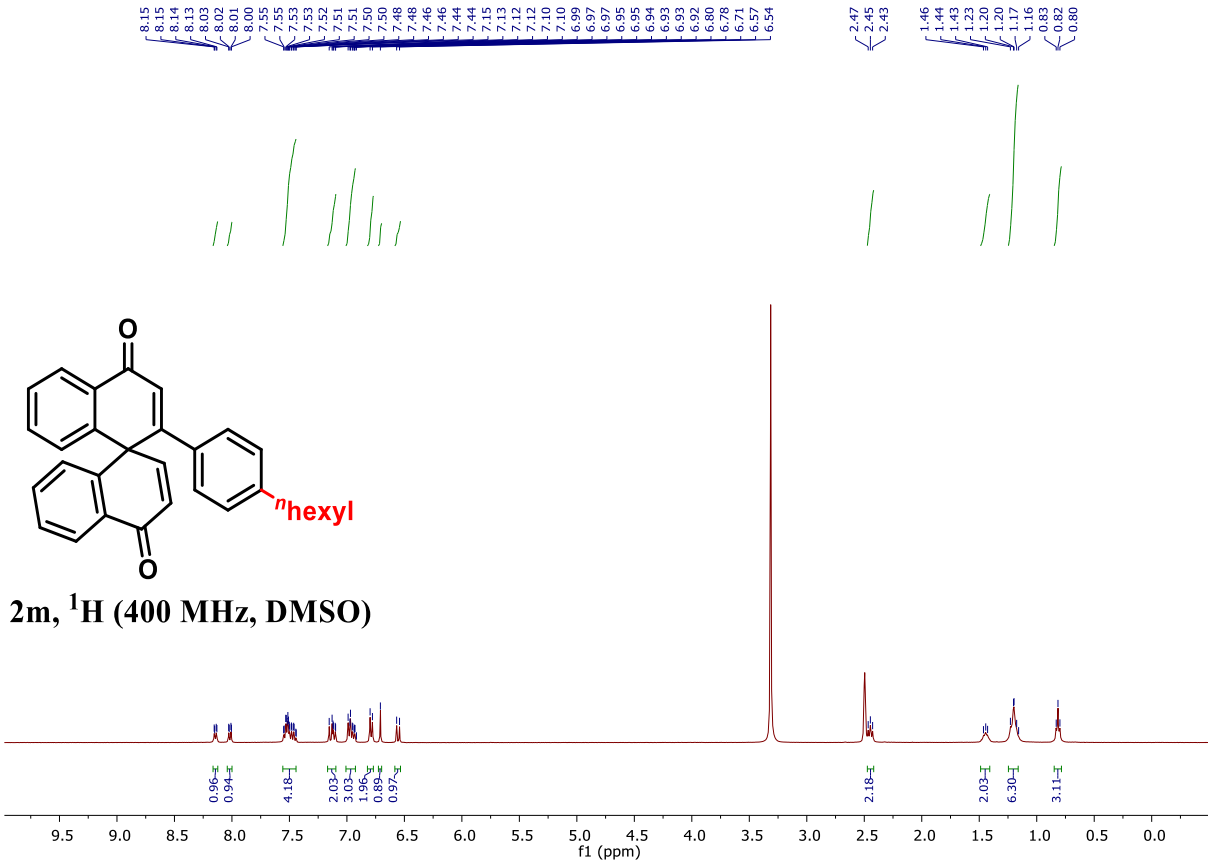
2k, ^{13}C (125 MHz, $CDCl_3$)



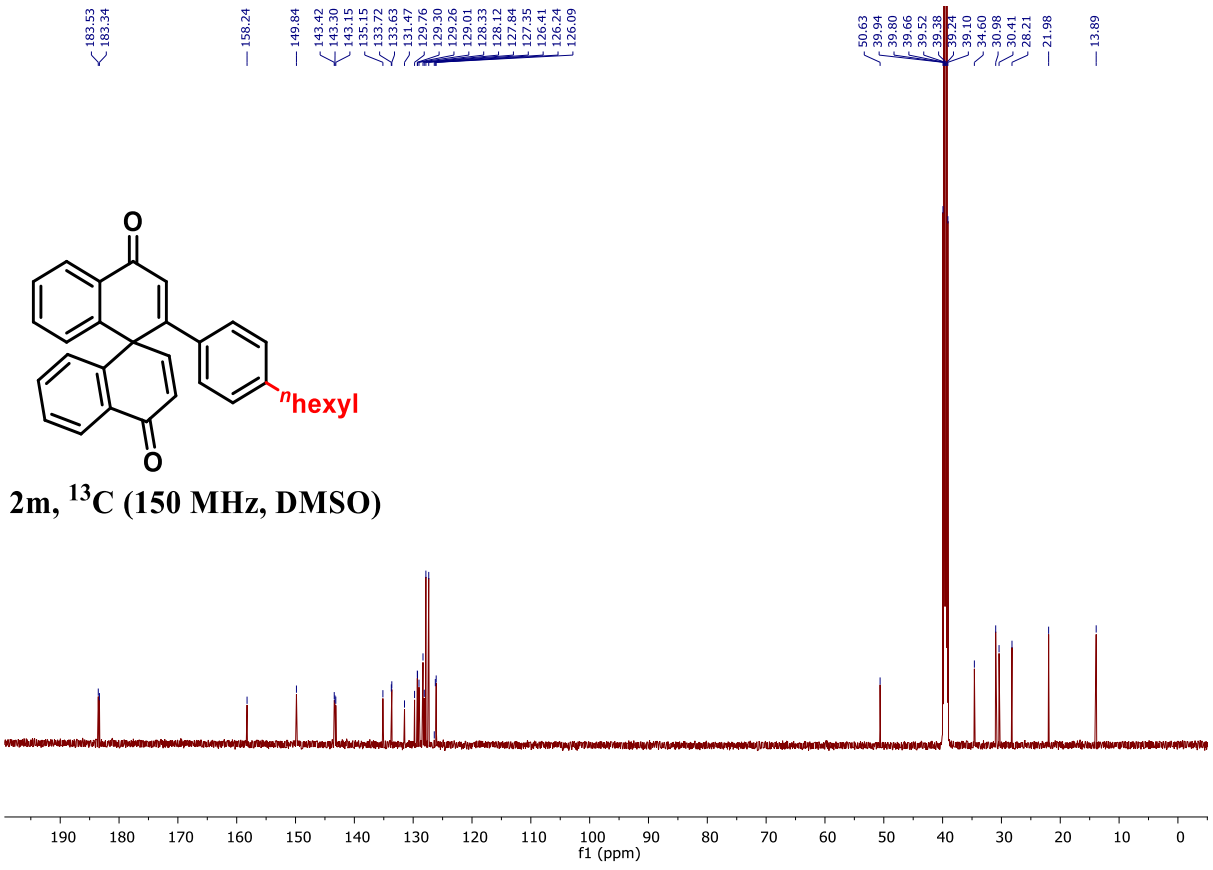
2l, ^{1}H (500 MHz, $CDCl_3$)



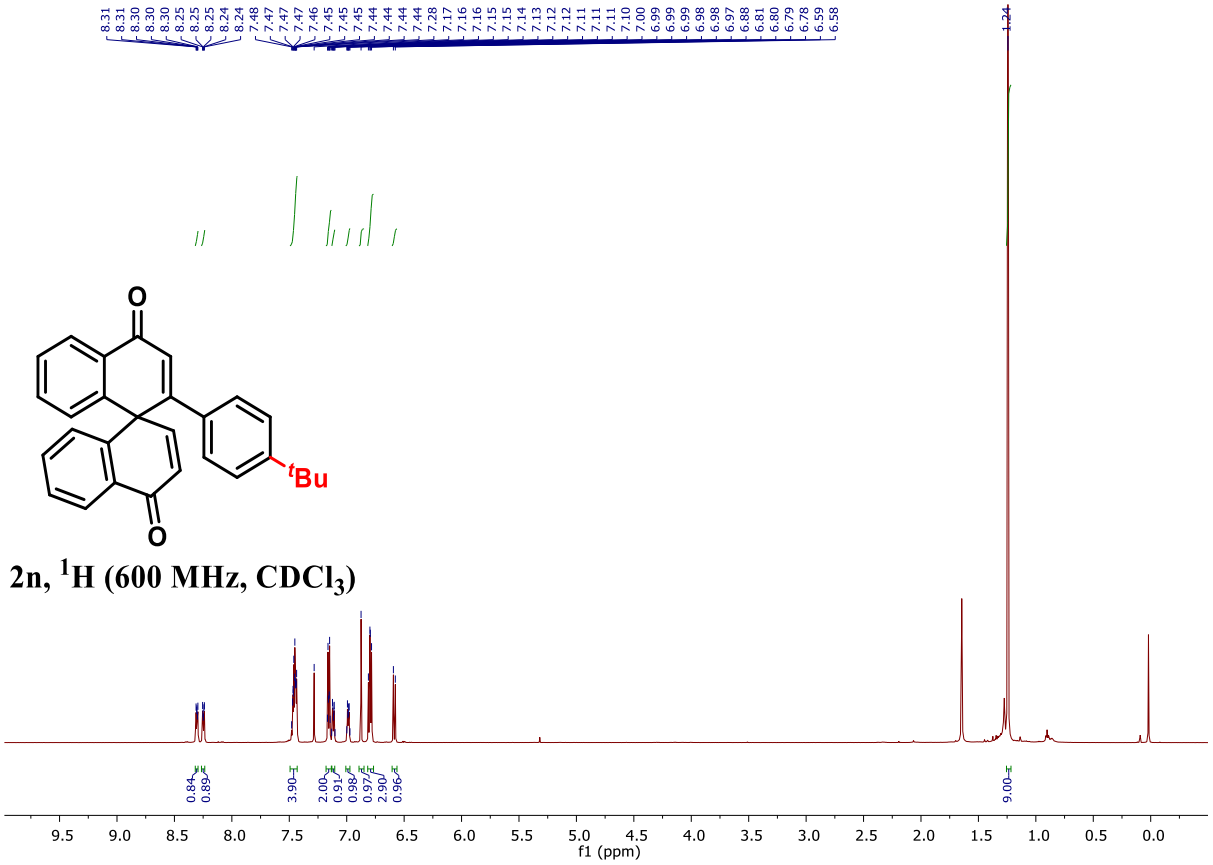
2l, ^{13}C (125 MHz, $CDCl_3$)



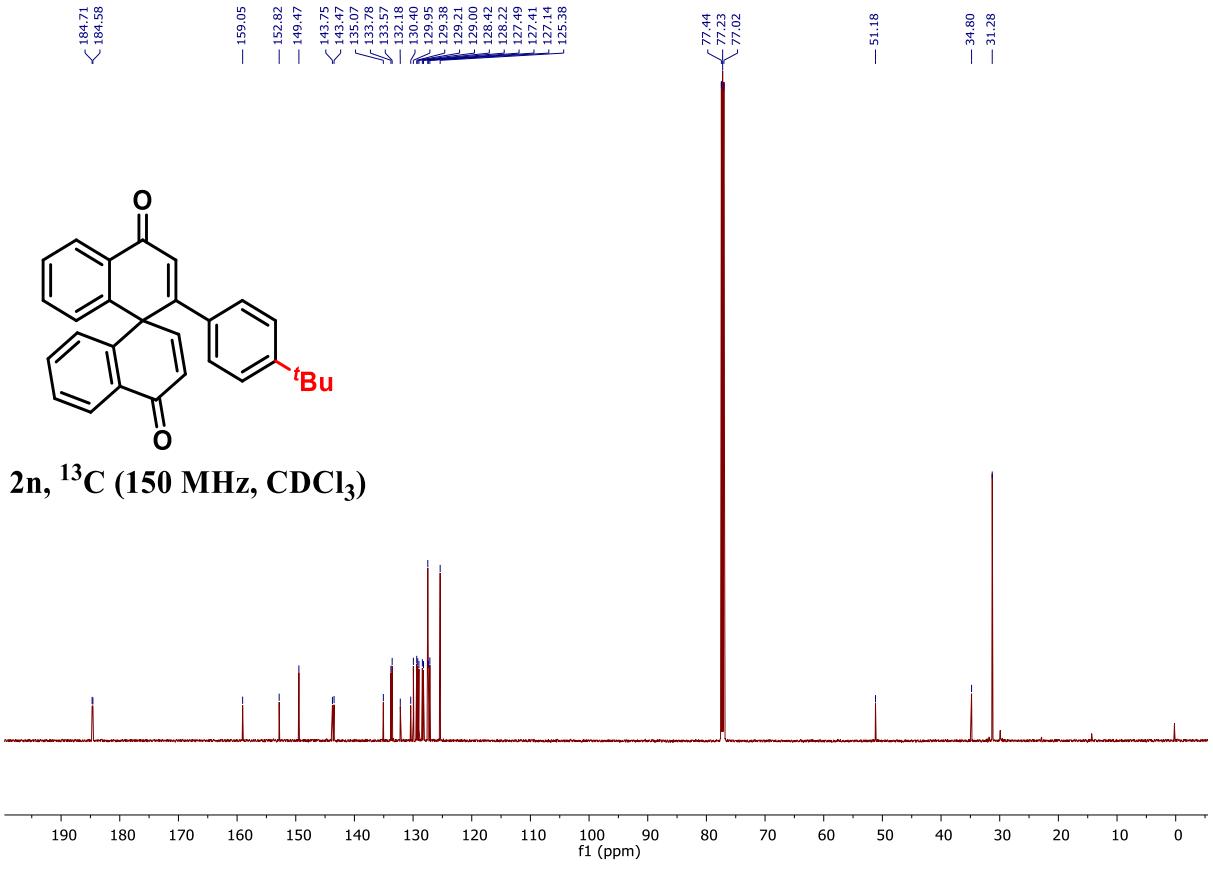
2m, ^{1}H (400 MHz, DMSO)



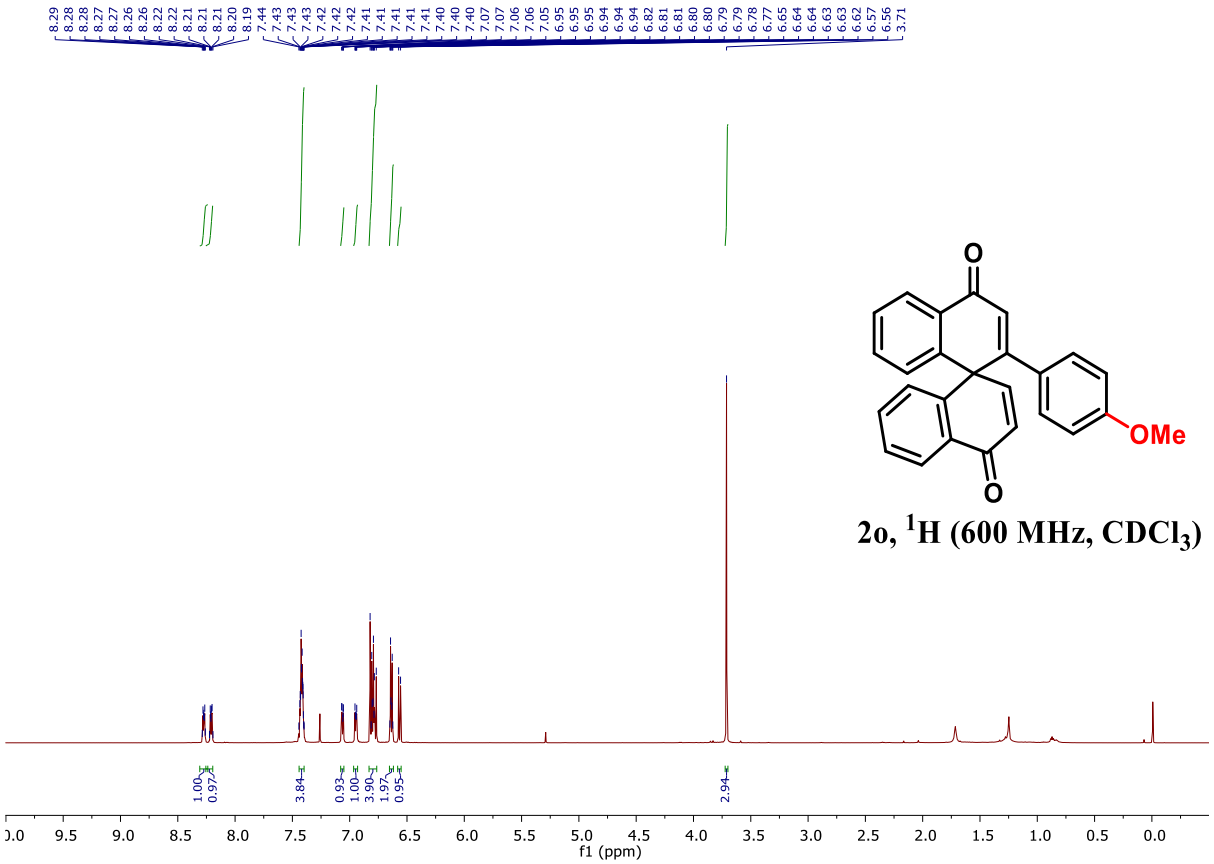
2m, ^{13}C (150 MHz, DMSO)



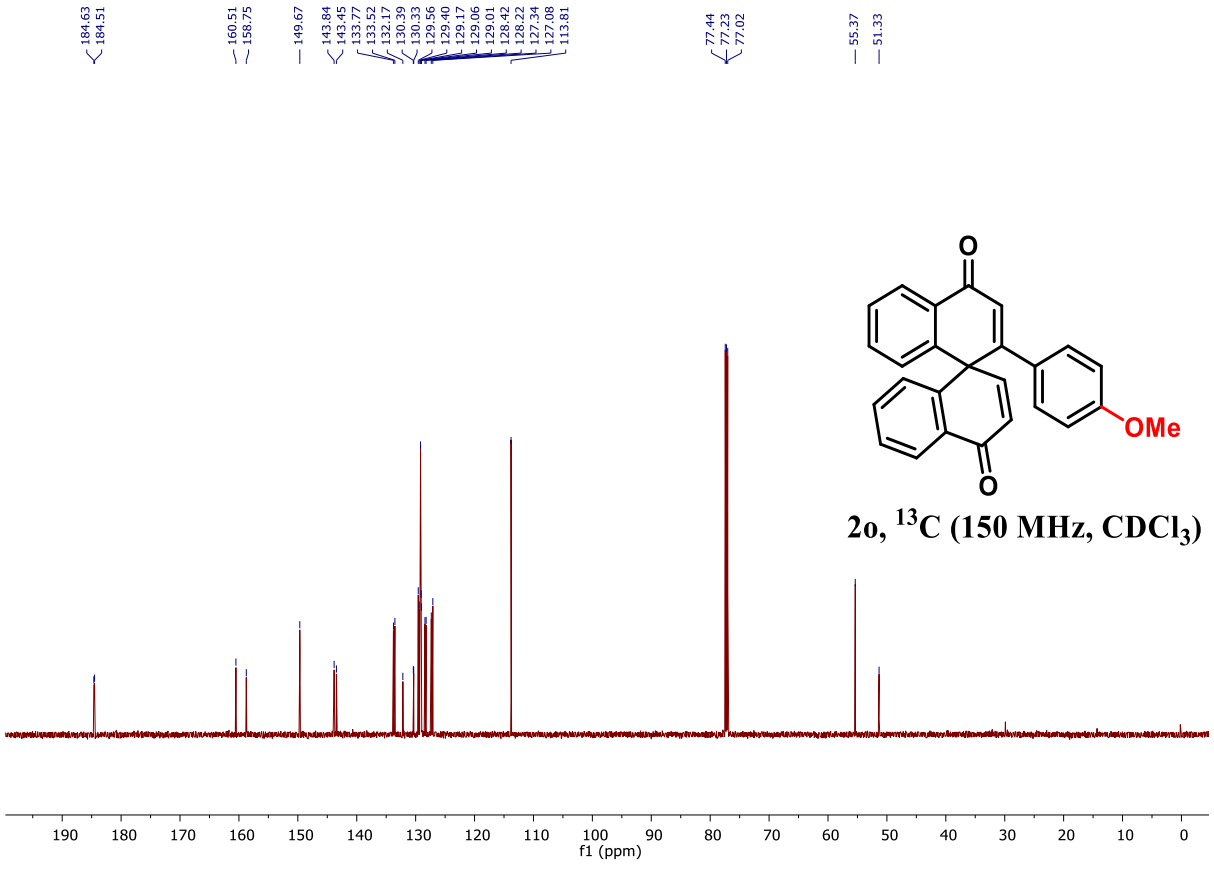
2n, ^{1}H (600 MHz, $CDCl_3$)



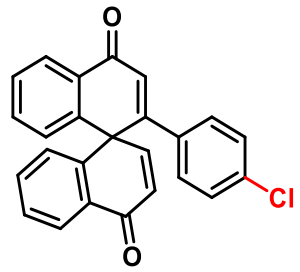
2n, ^{13}C (150 MHz, $CDCl_3$)



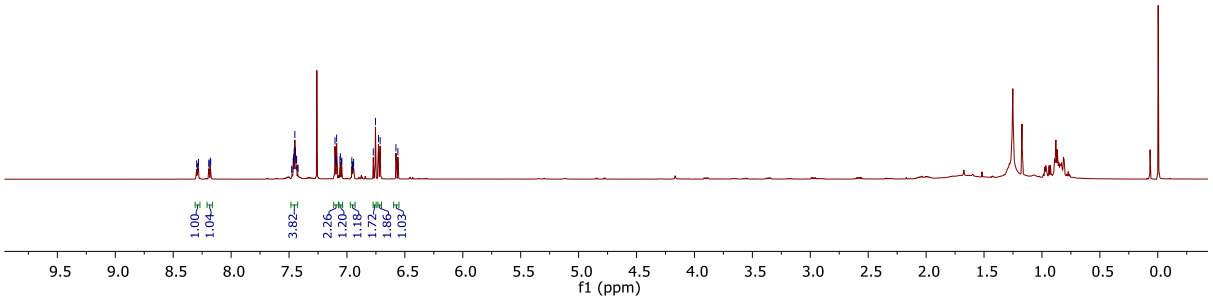
2o, ^{1}H (600 MHz, $CDCl_3$)

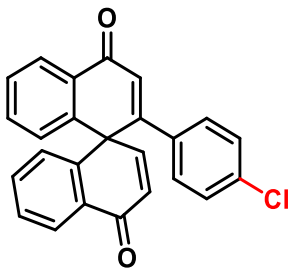


2o, ^{13}C (150 MHz, $CDCl_3$)

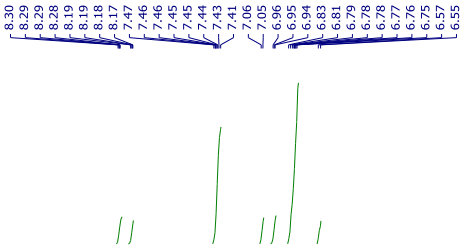


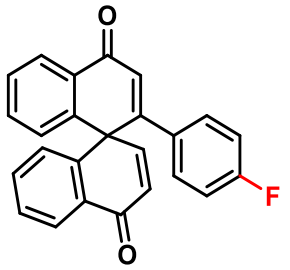
2p, ^{1}H (600 MHz, $CDCl_3$)



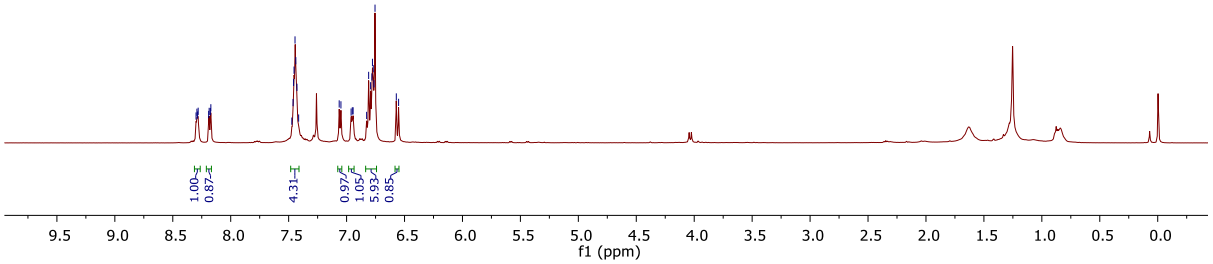


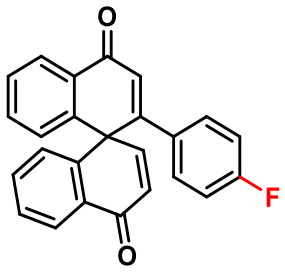
2p, ^{13}C (150 MHz, $CDCl_3$)



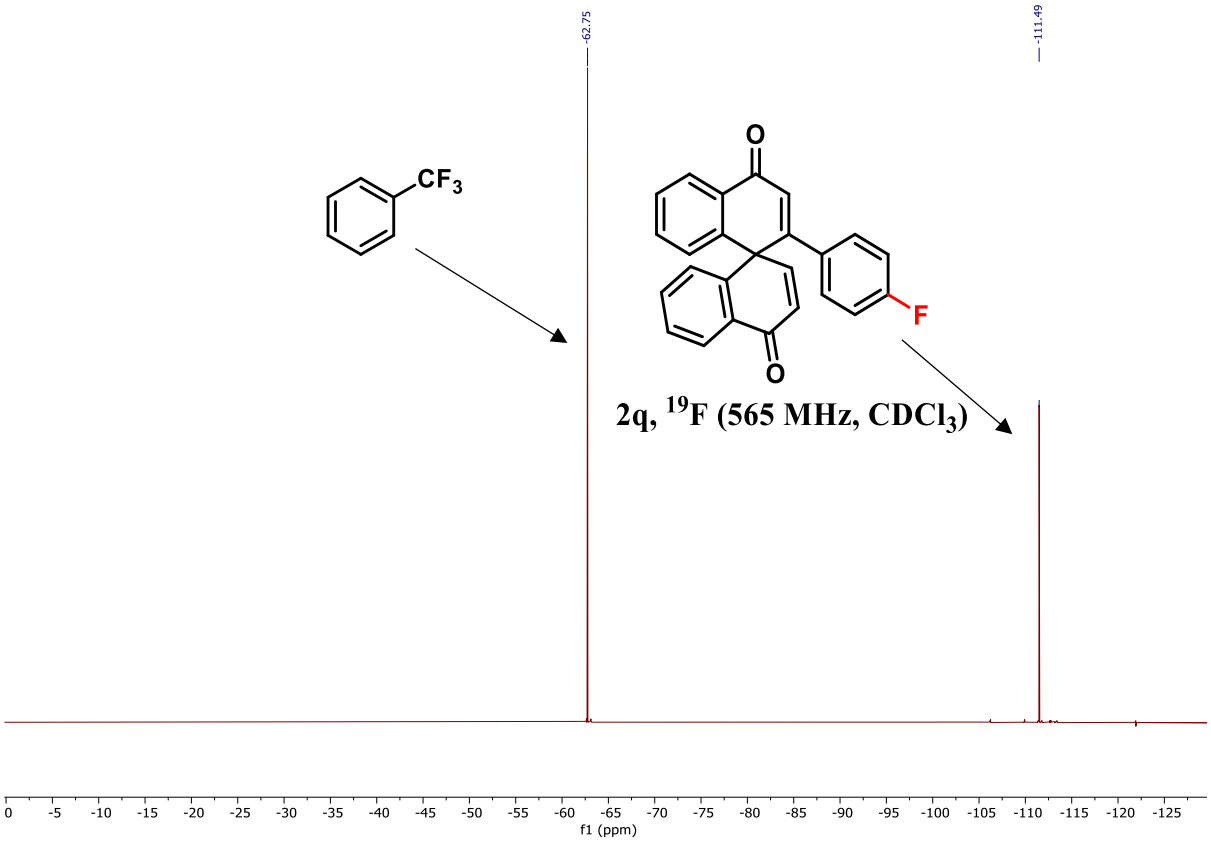


2q, ^{1}H (500 MHz, $CDCl_3$)

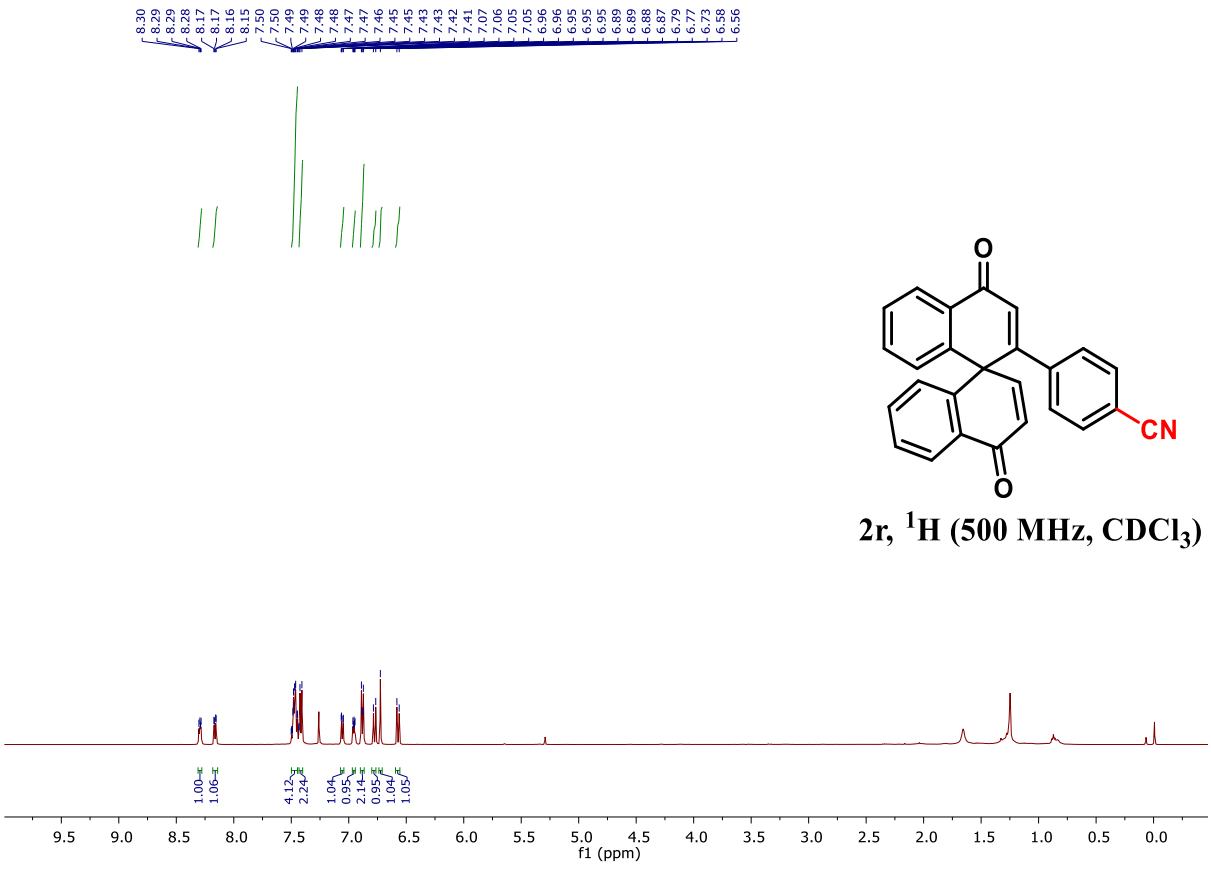




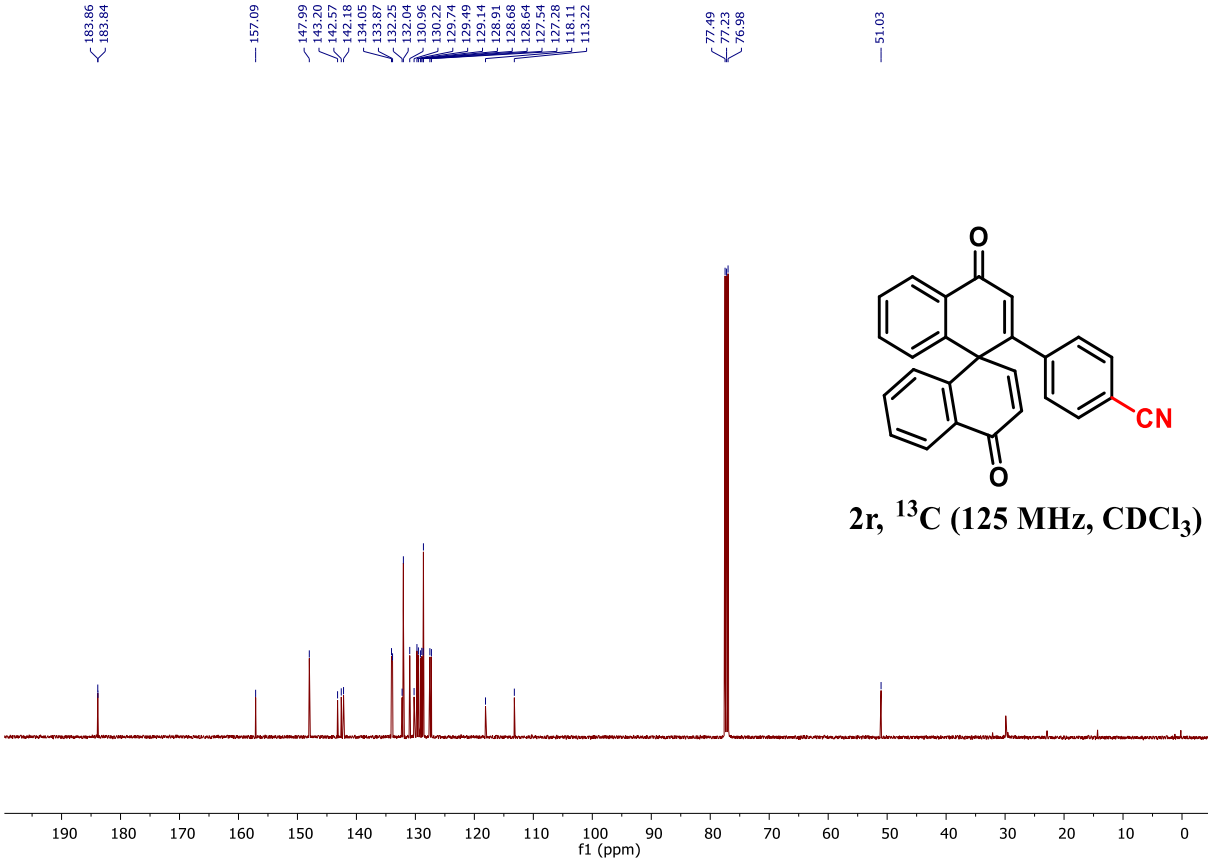
2q, ^{13}C (125 MHz, $CDCl_3$)



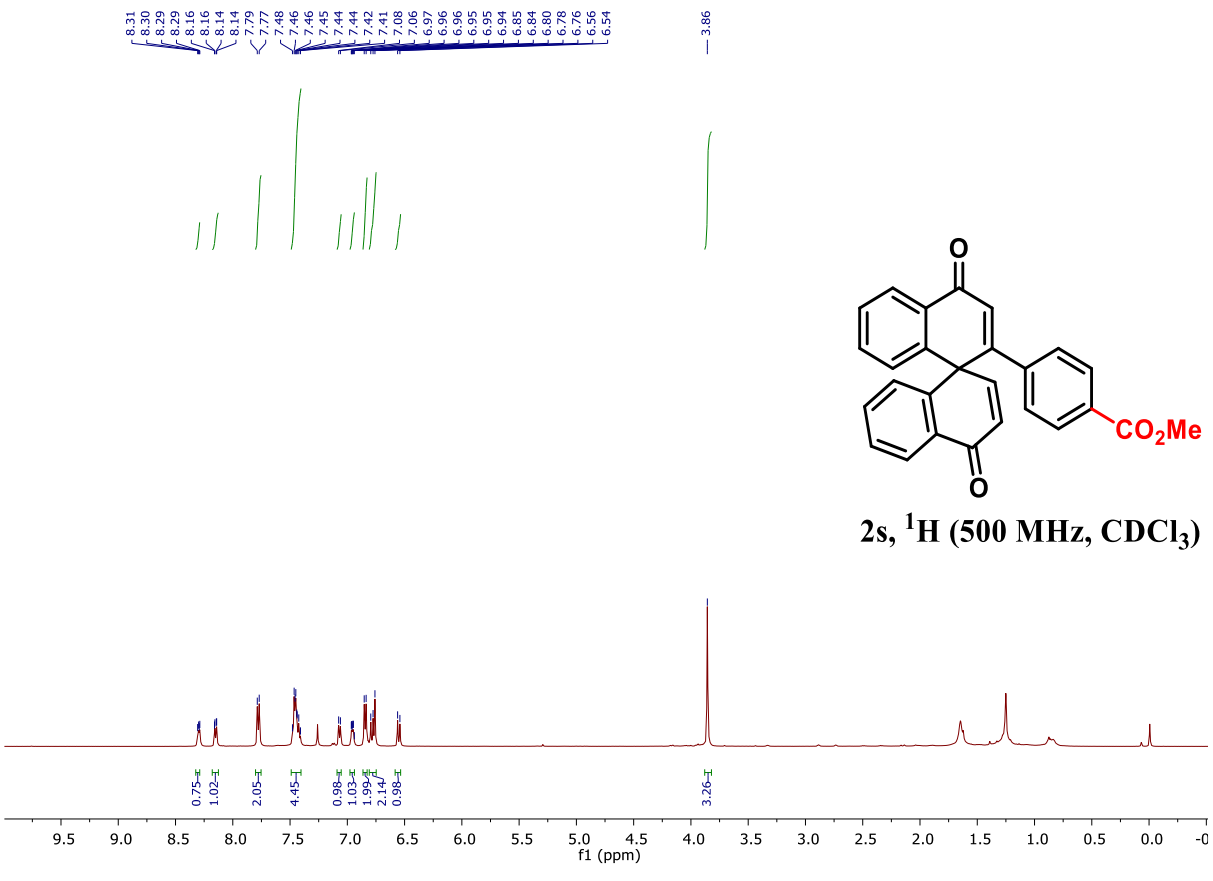
2q, ^{19}F (565 MHz, $CDCl_3$)



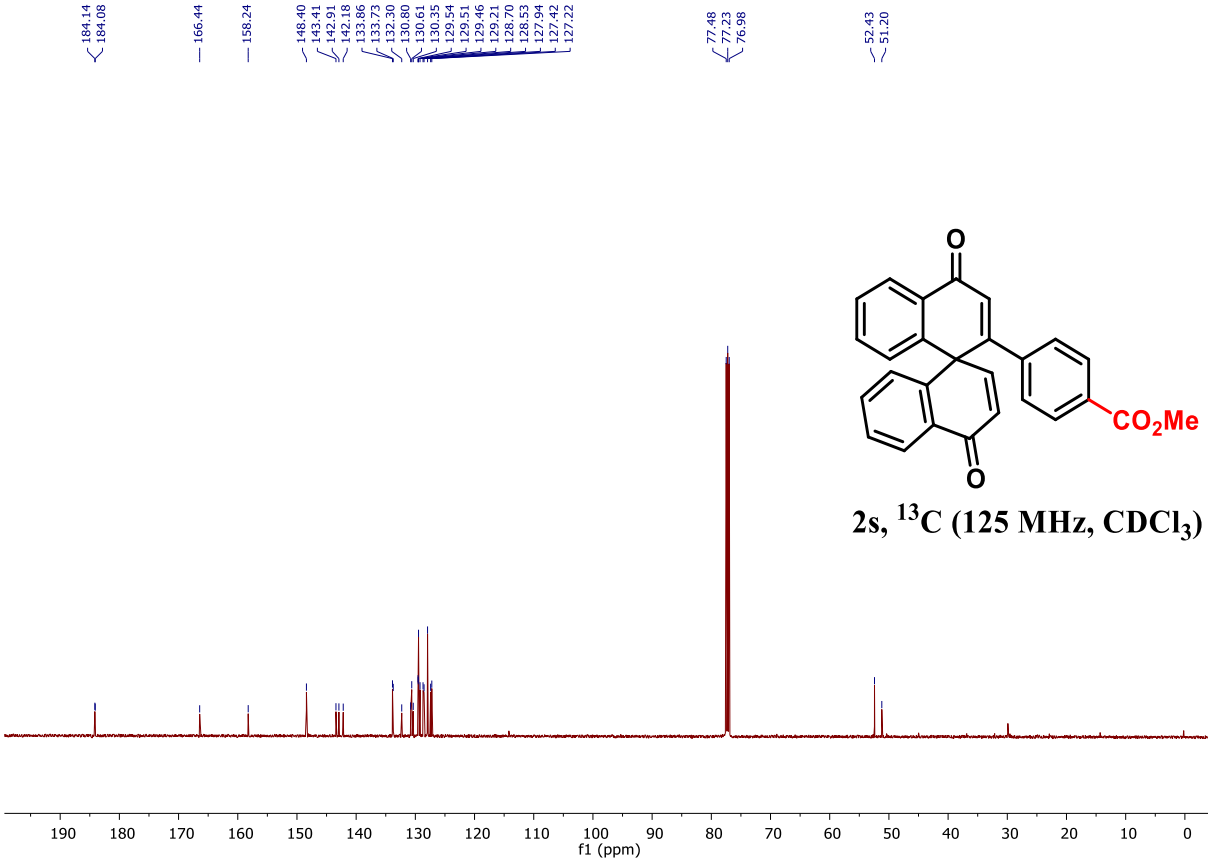
2r, ^{1}H (500 MHz, $CDCl_3$)



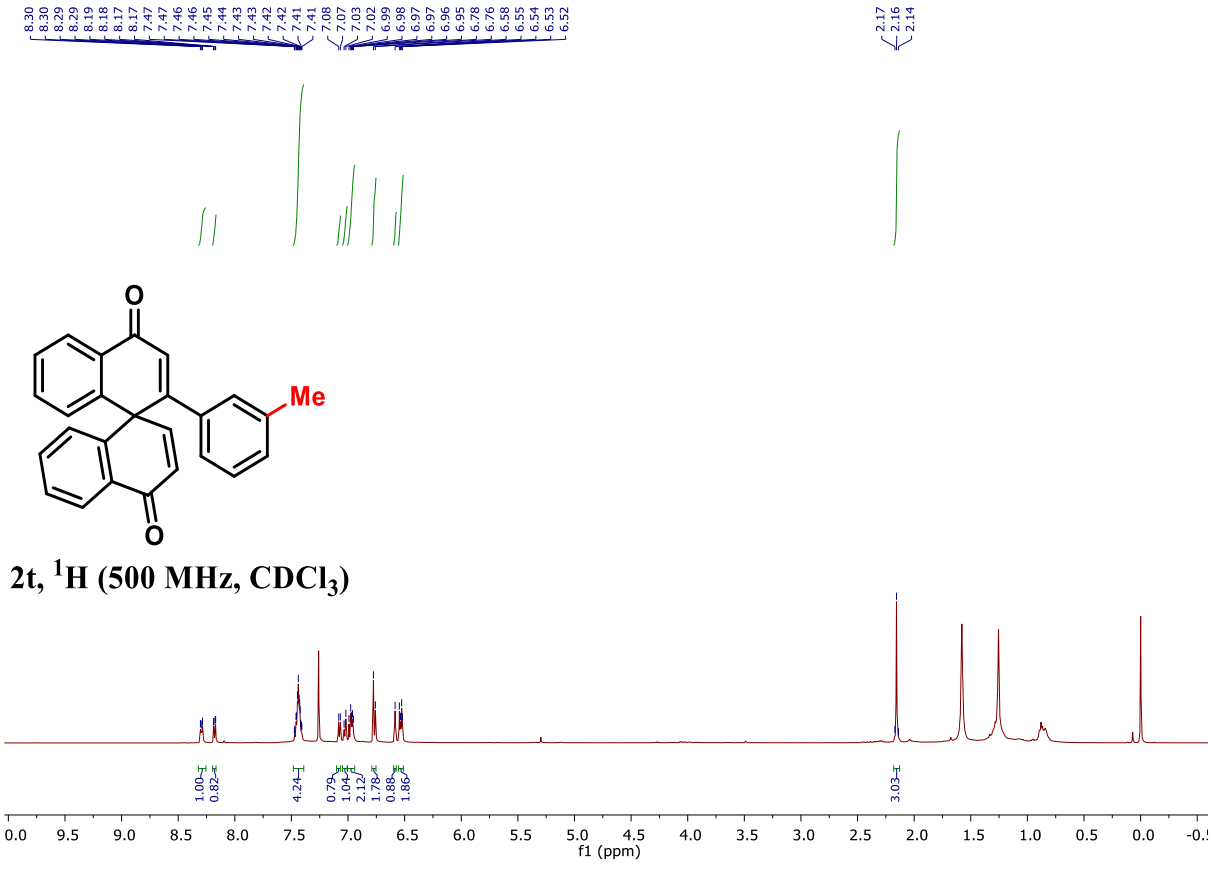
2r, ^{13}C (125 MHz, $CDCl_3$)



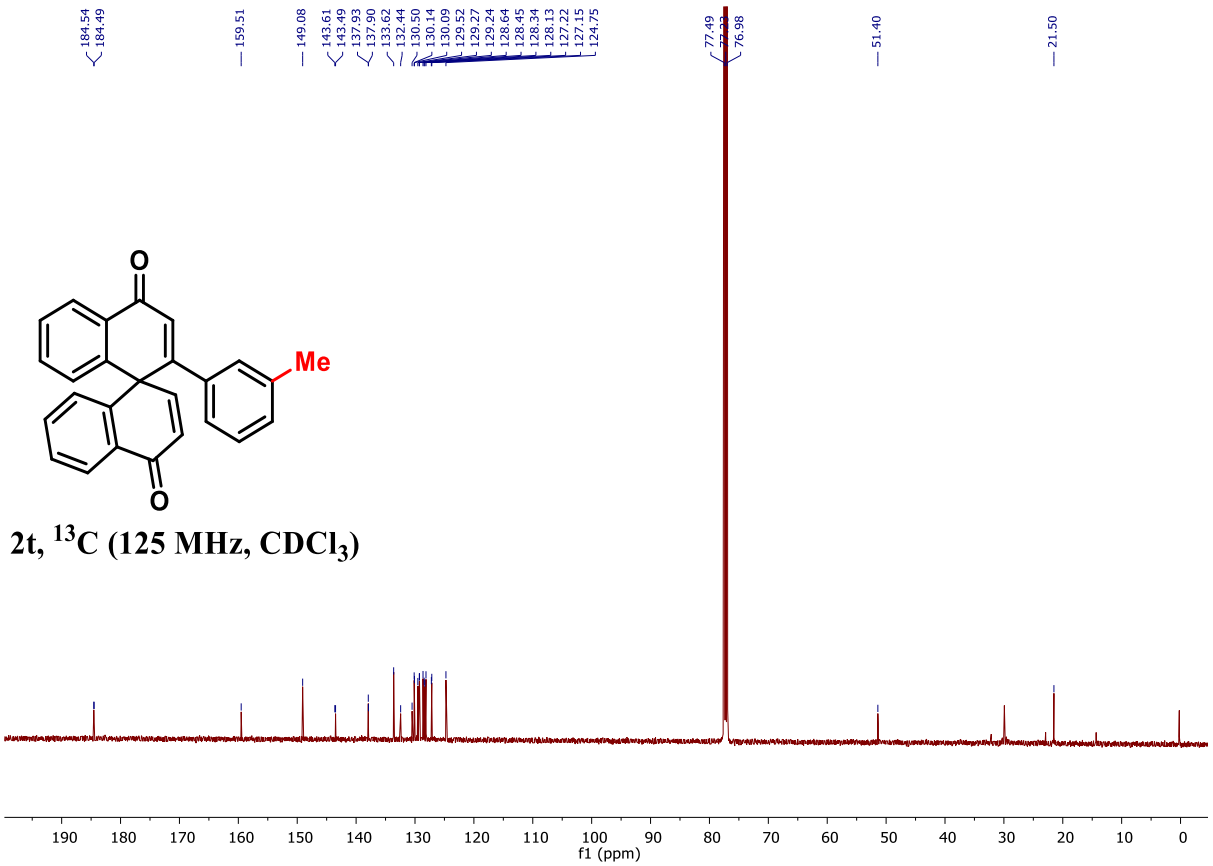
2s, ^{1}H (500 MHz, $CDCl_3$)



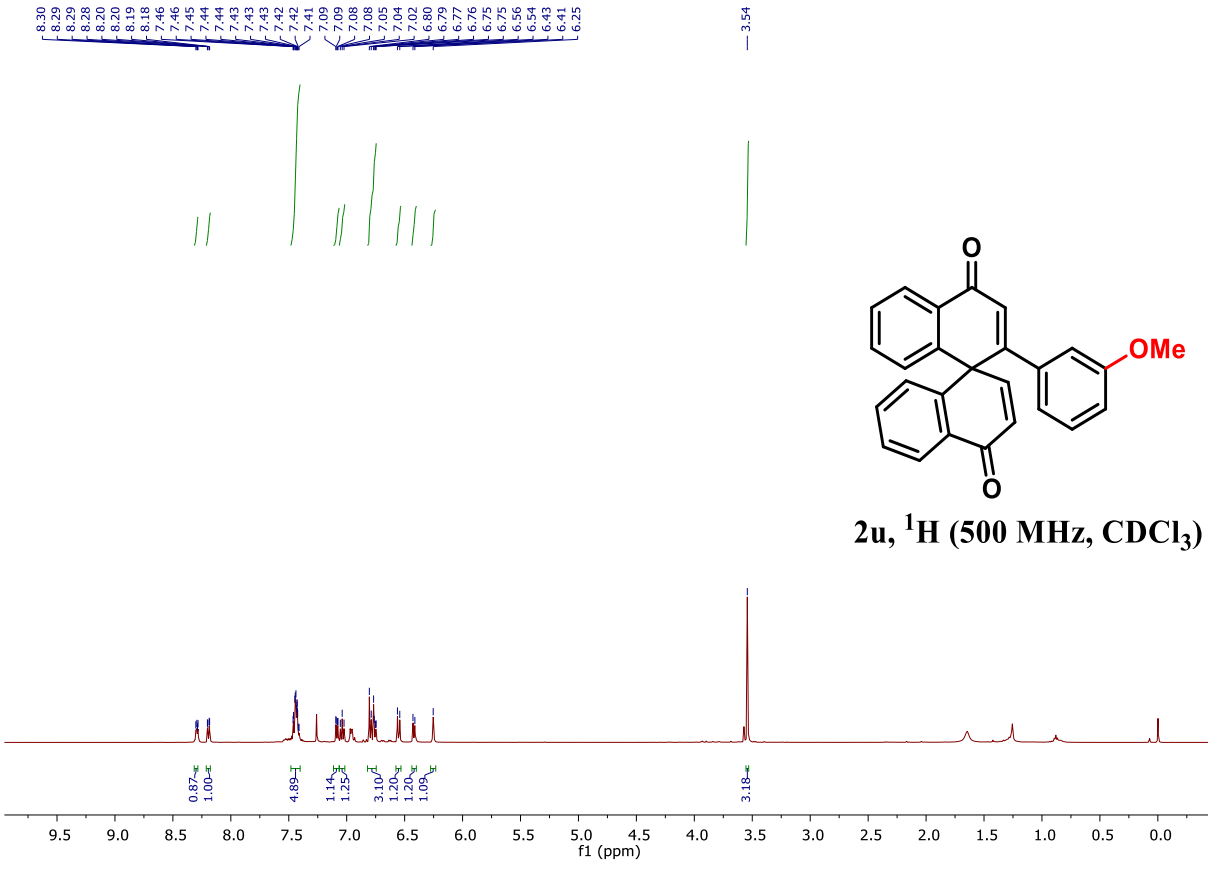
2s, ^{13}C (125 MHz, $CDCl_3$)



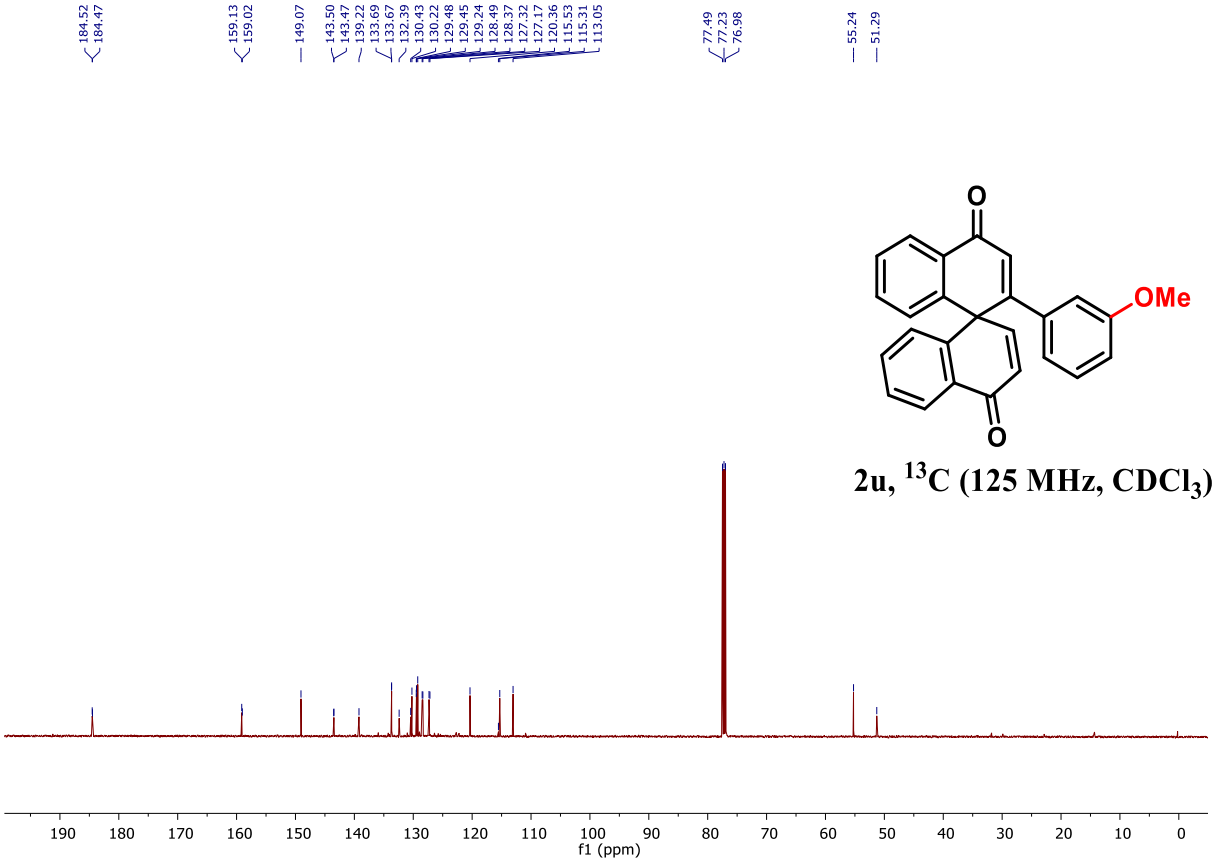
2t, ^{1}H (500 MHz, $CDCl_3$)



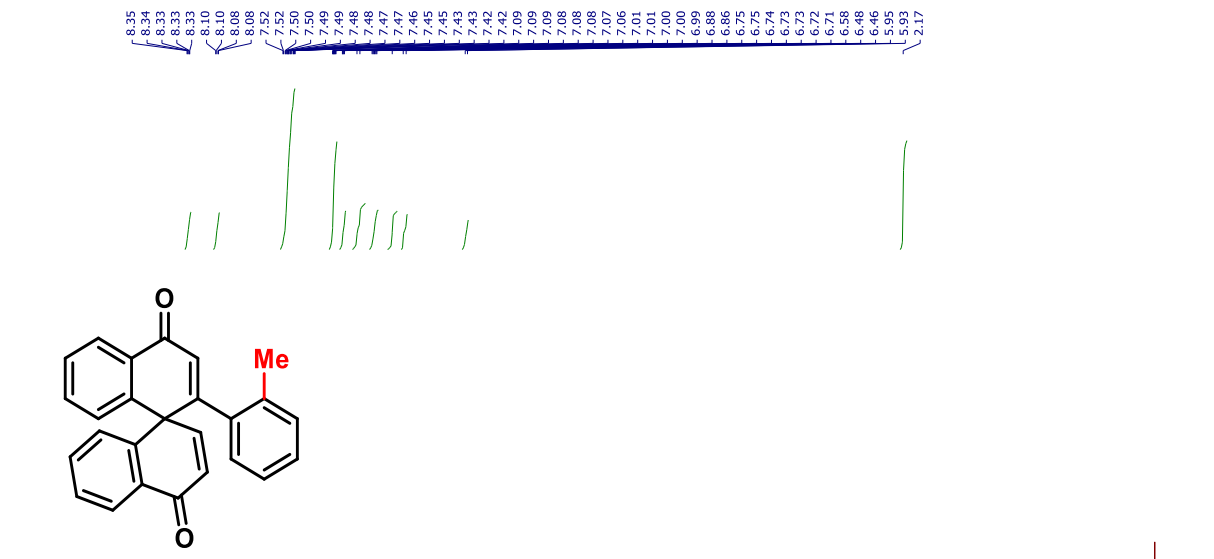
2t, ^{13}C (125 MHz, $CDCl_3$)



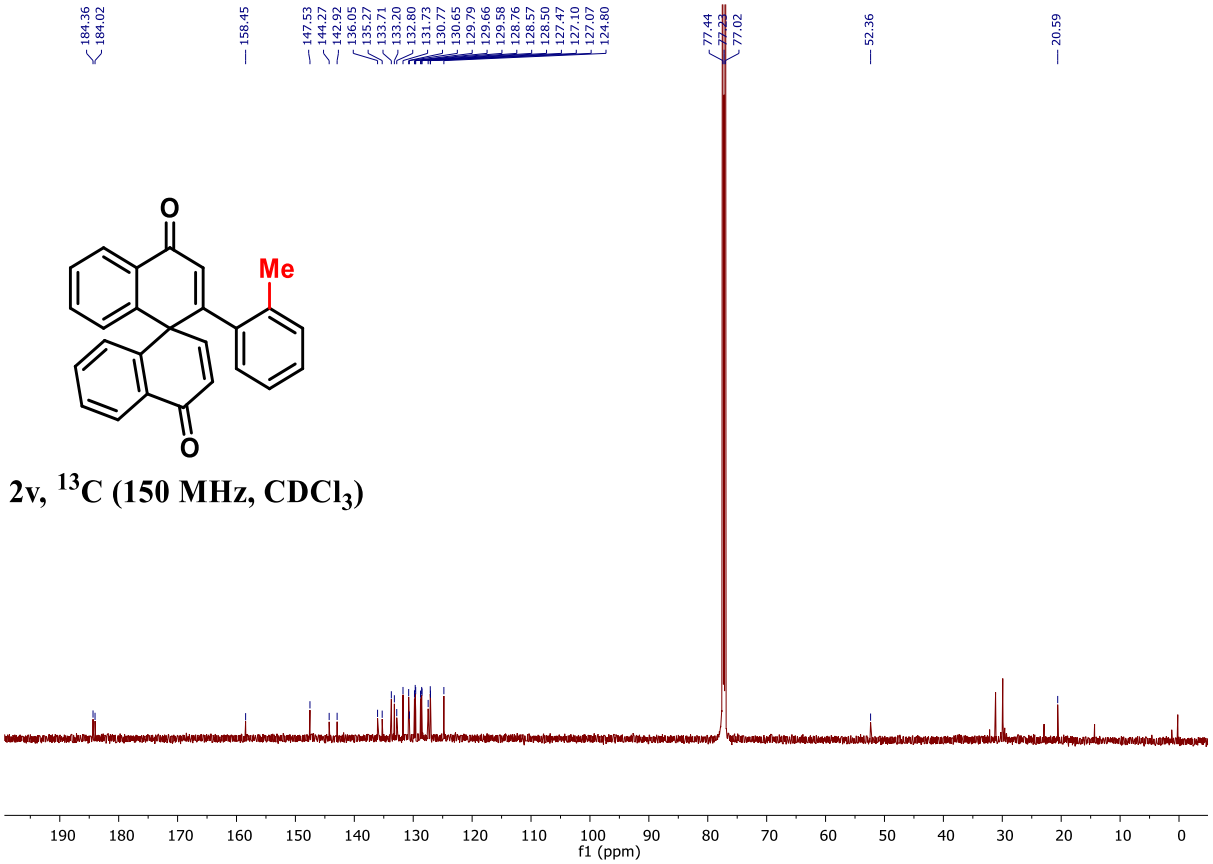
2u, ^{1}H (500 MHz, $CDCl_3$)



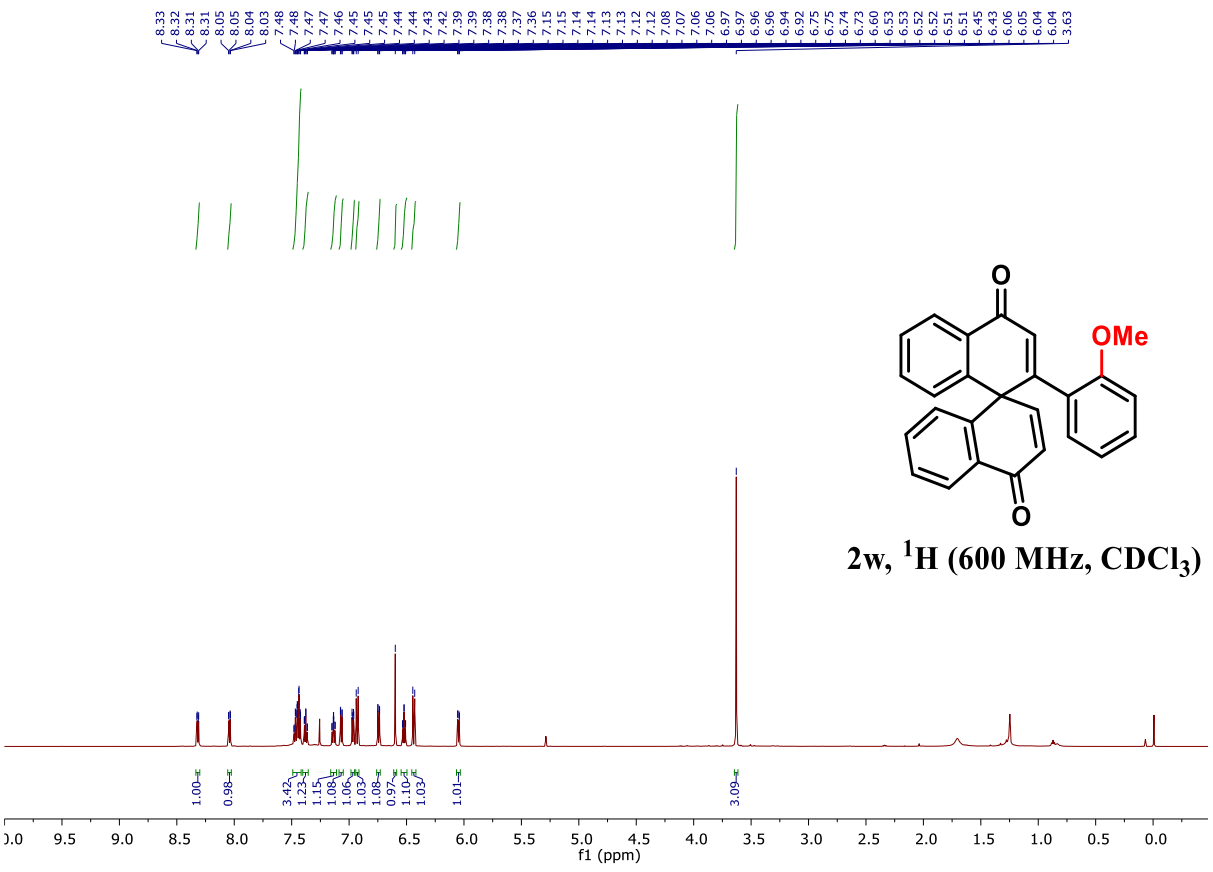
2u, ^{13}C (125 MHz, $CDCl_3$)



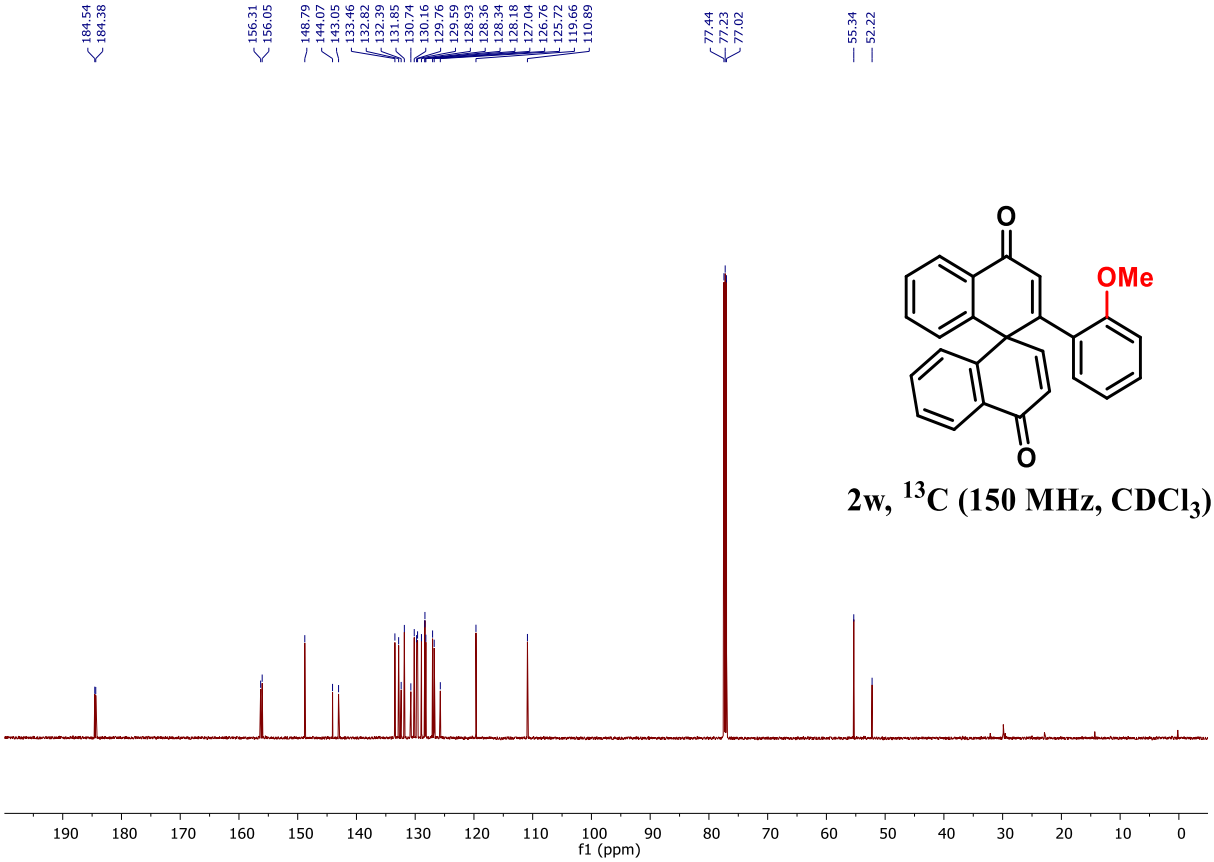
2v, ^{1}H (400 MHz, $CDCl_3$)



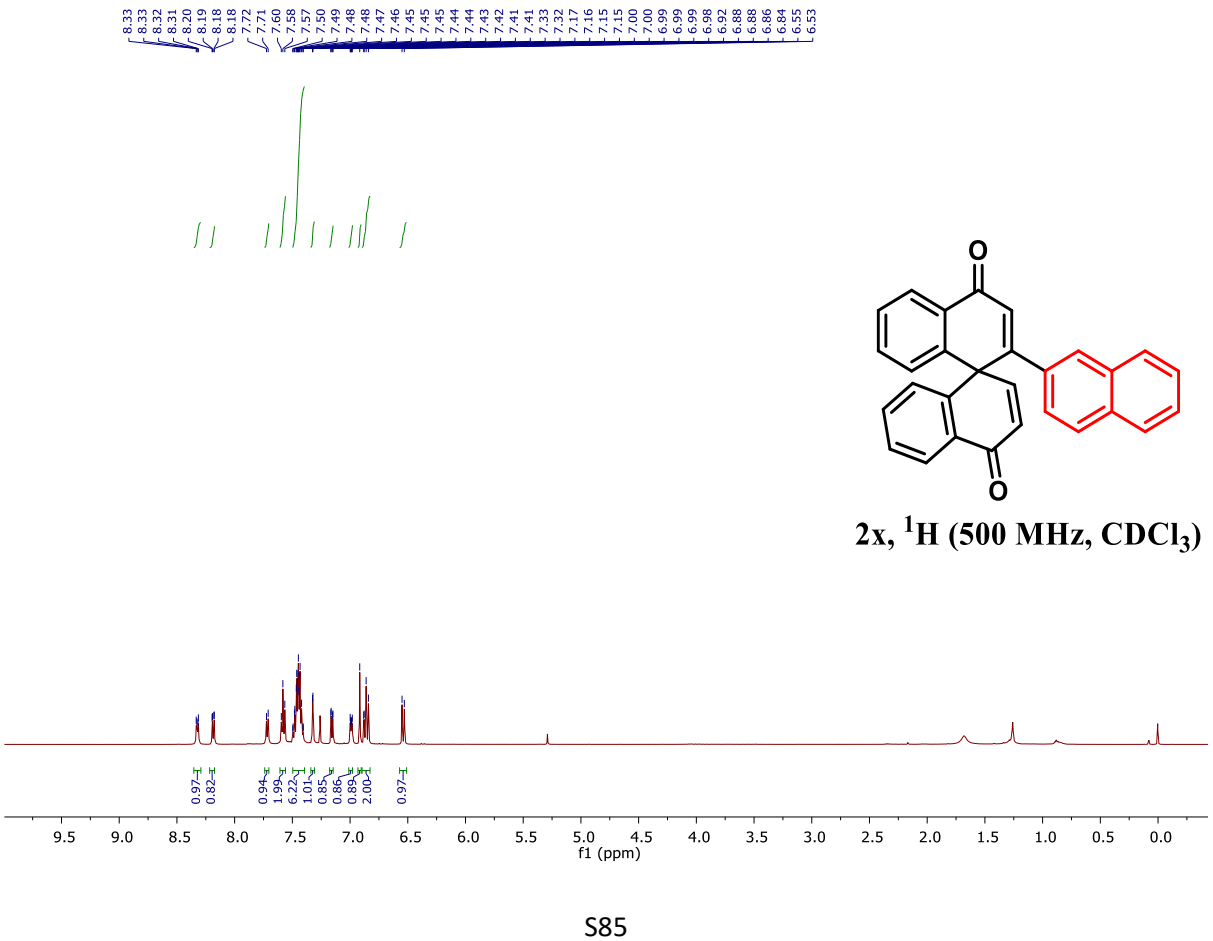
2v, ^{13}C (150 MHz, $CDCl_3$)



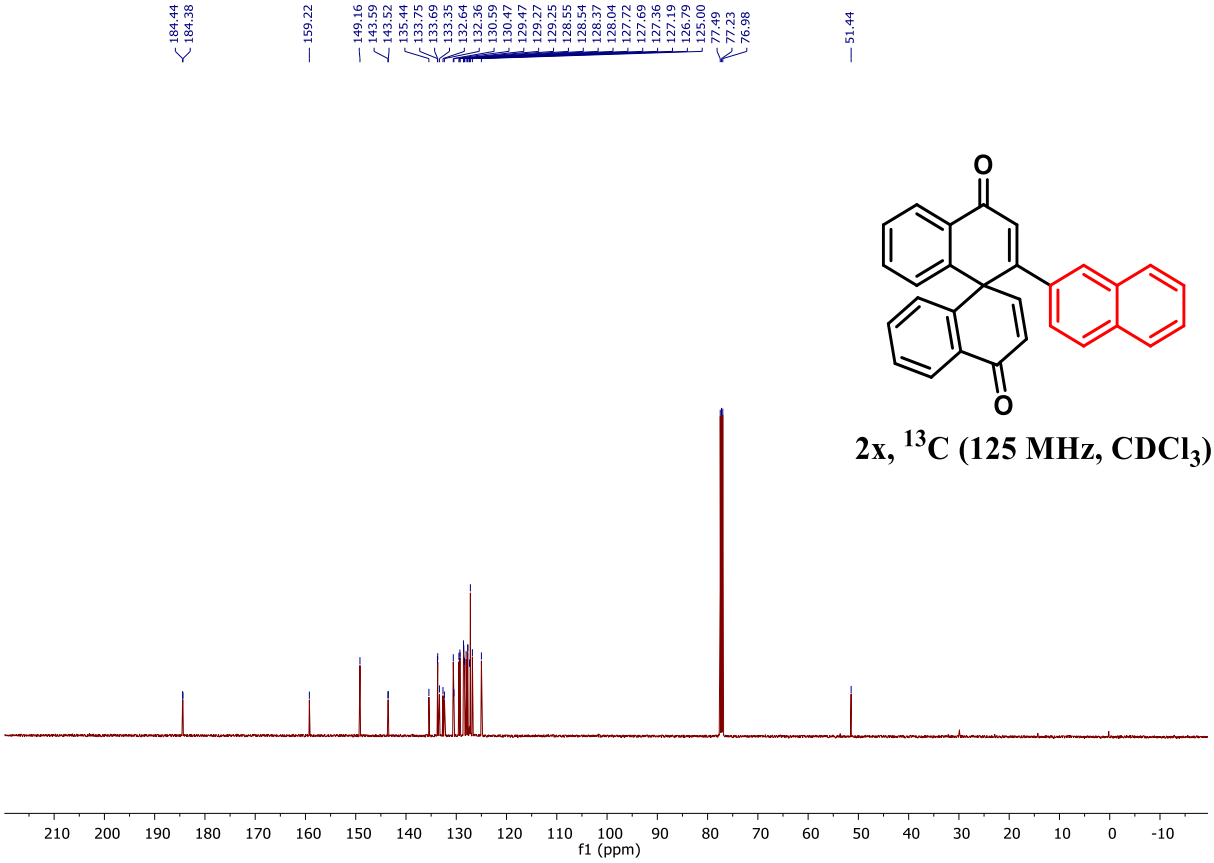
2w, ^{1}H (600 MHz, $CDCl_3$)



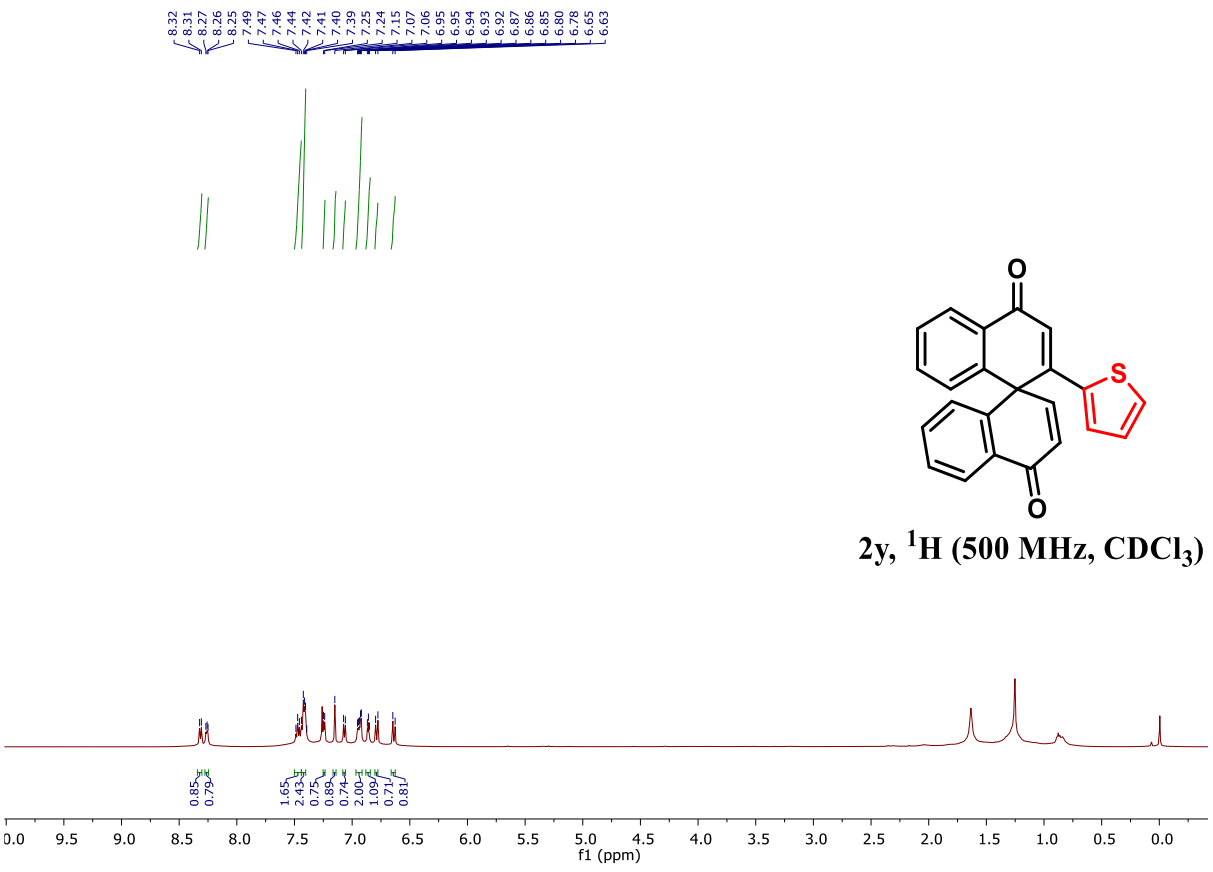
2w, ^{13}C (150 MHz, $CDCl_3$)



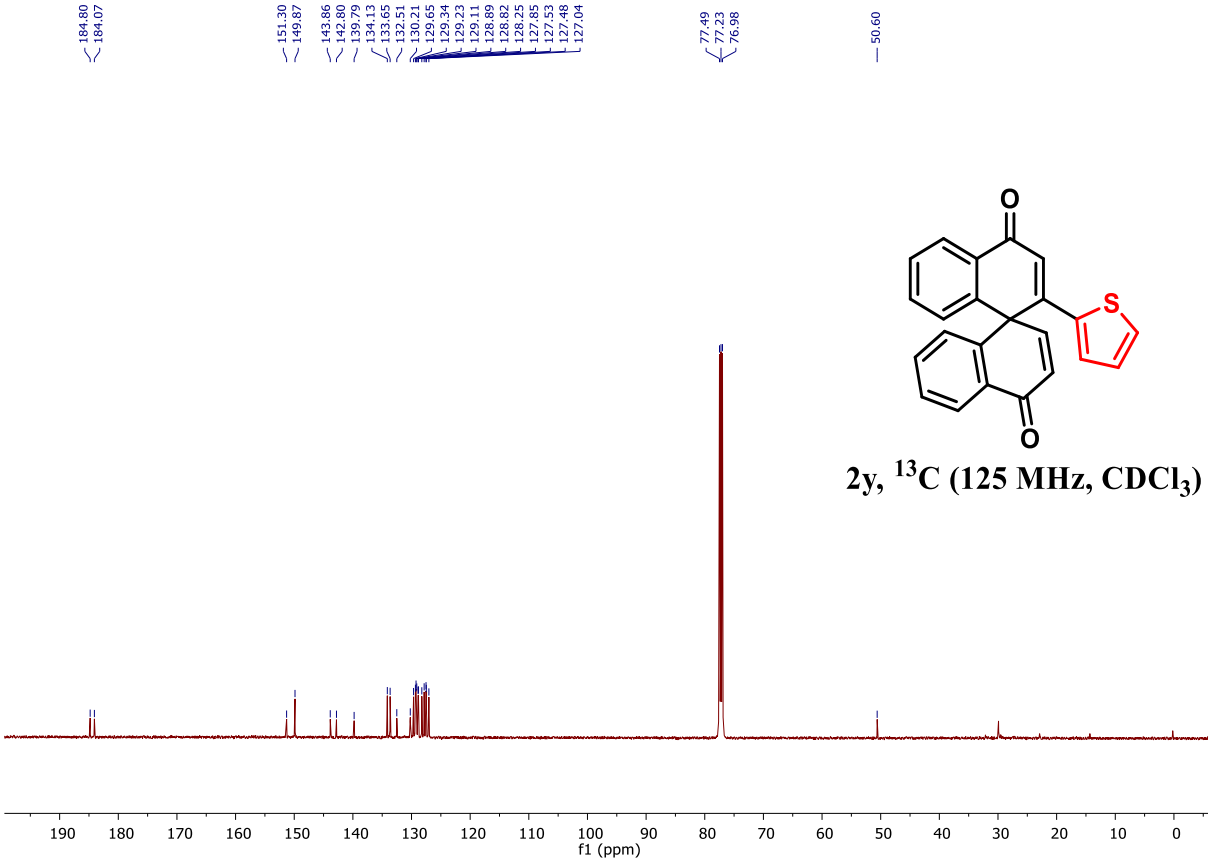
2x, ^{1}H (500 MHz, $CDCl_3$)



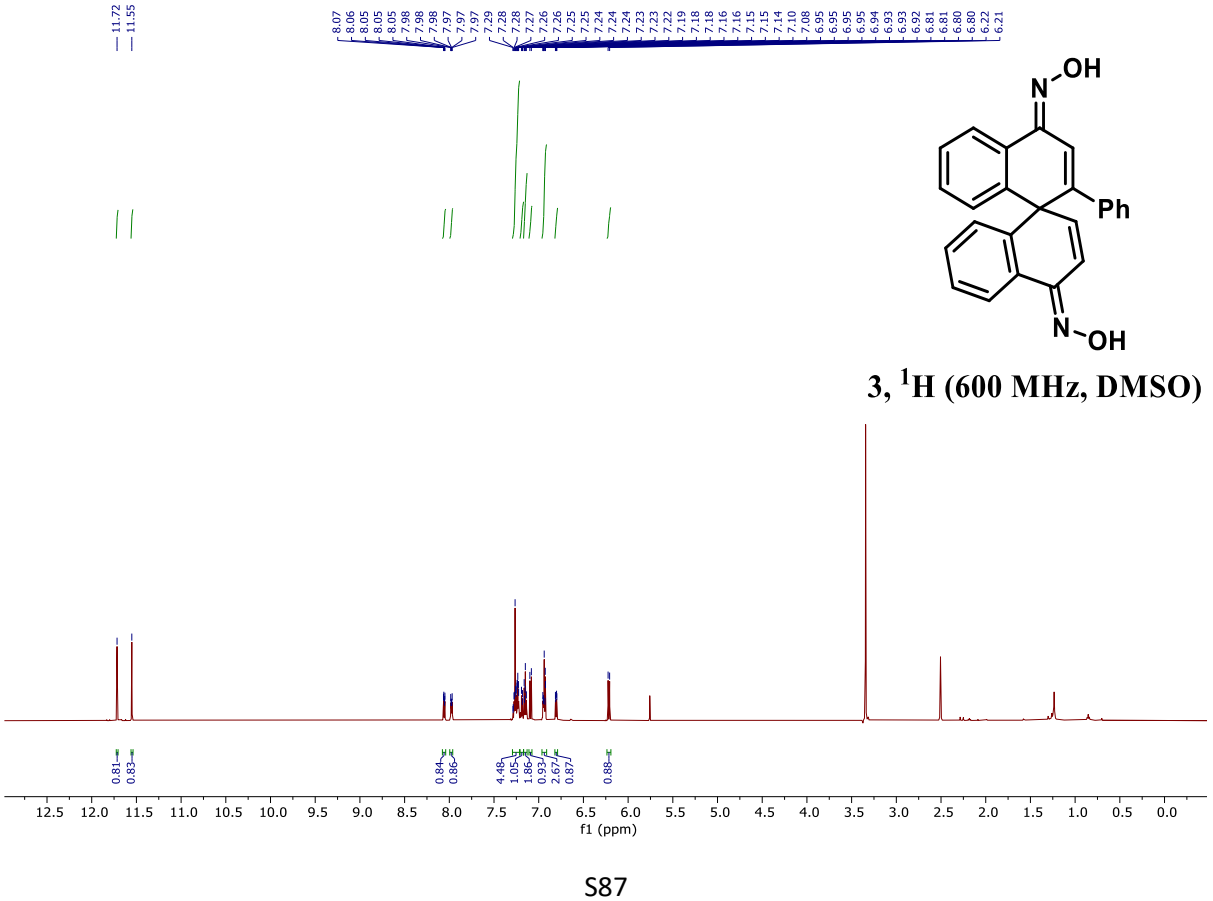
2x, ^{13}C (125 MHz, $CDCl_3$)



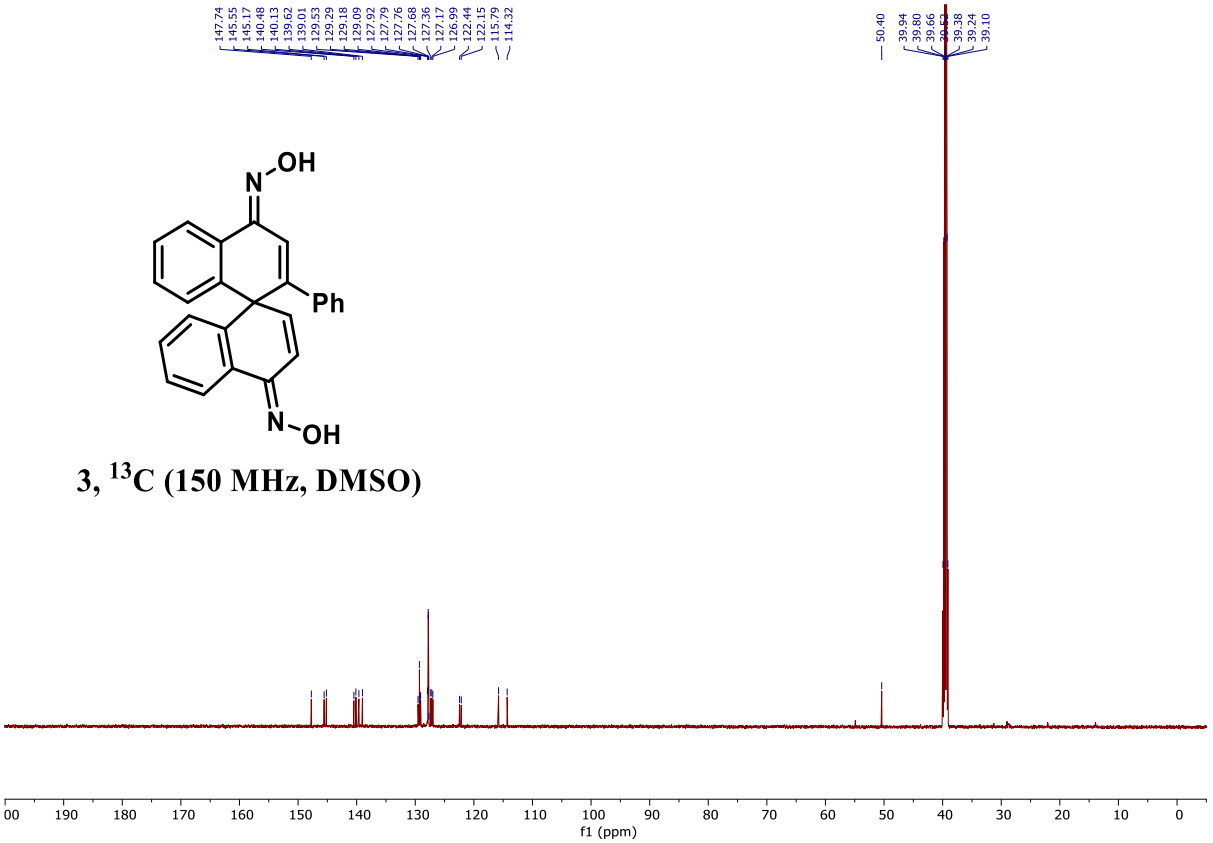
2y, ^{1}H (500 MHz, $CDCl_3$)



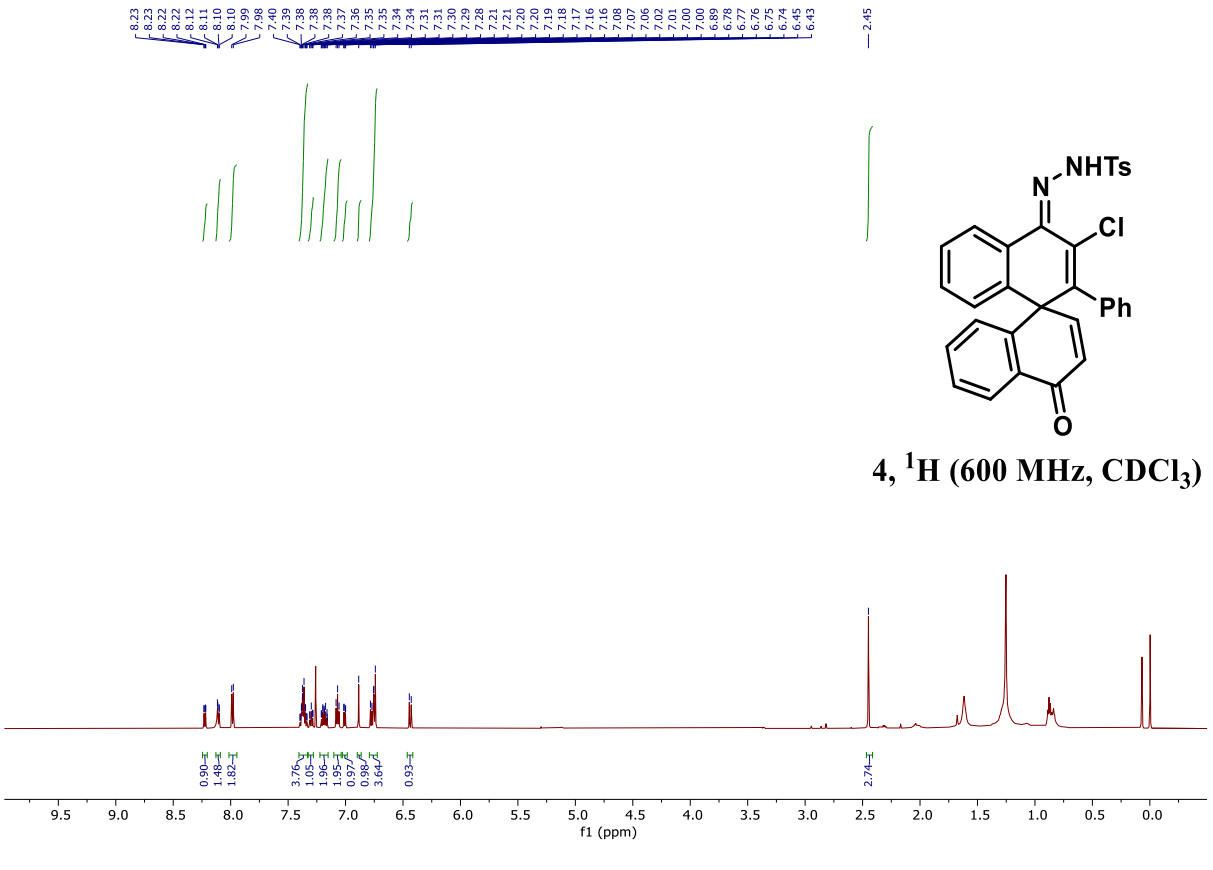
2y, ^{13}C (125 MHz, $CDCl_3$)



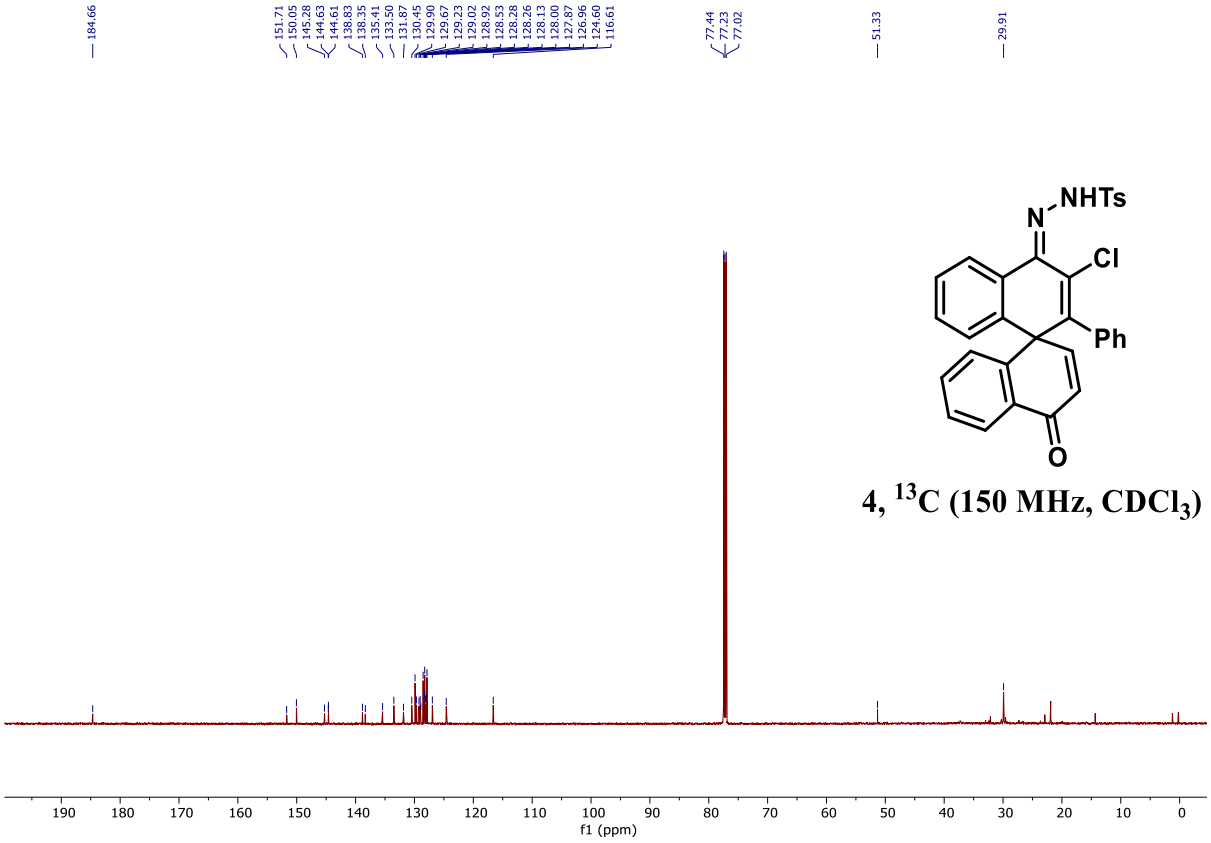
3, ^{1}H (600 MHz, DMSO)



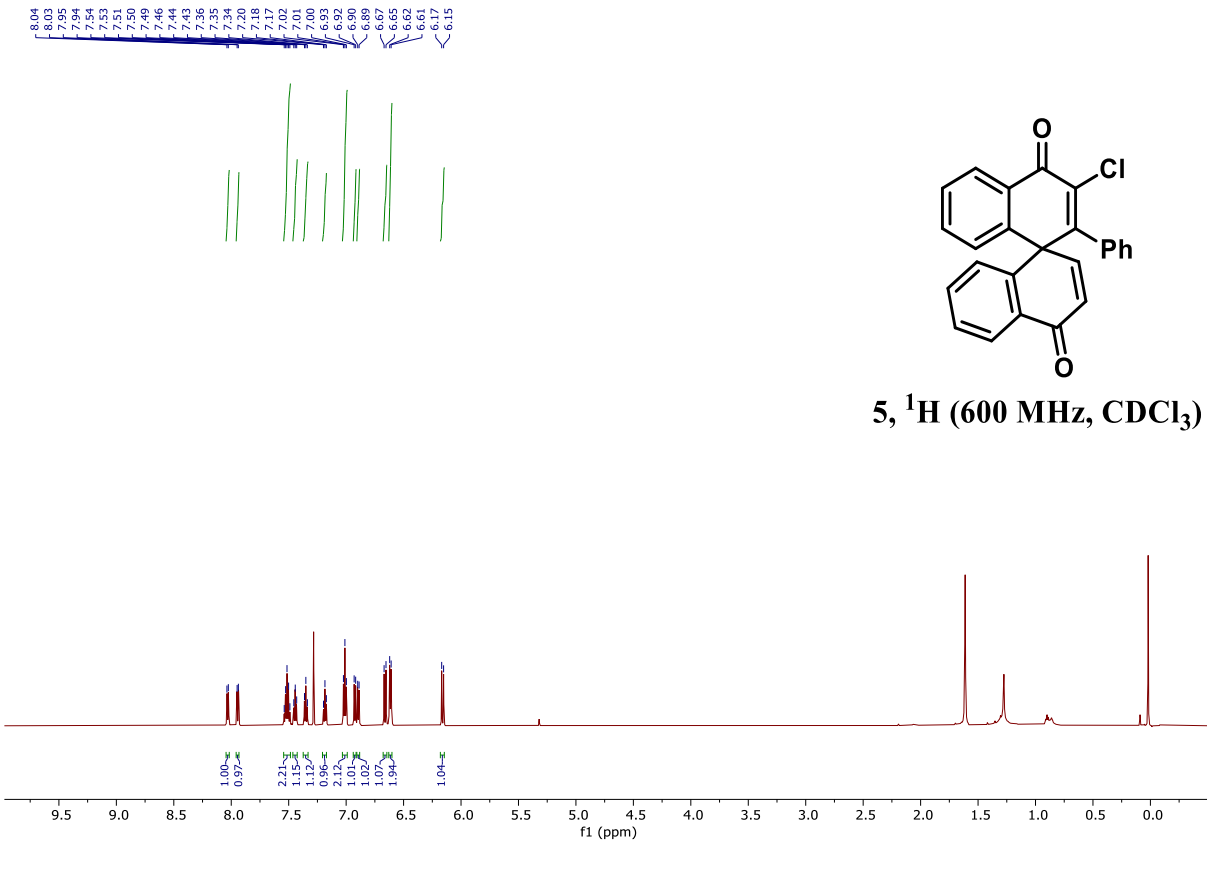
3, ^{13}C (150 MHz, DMSO)



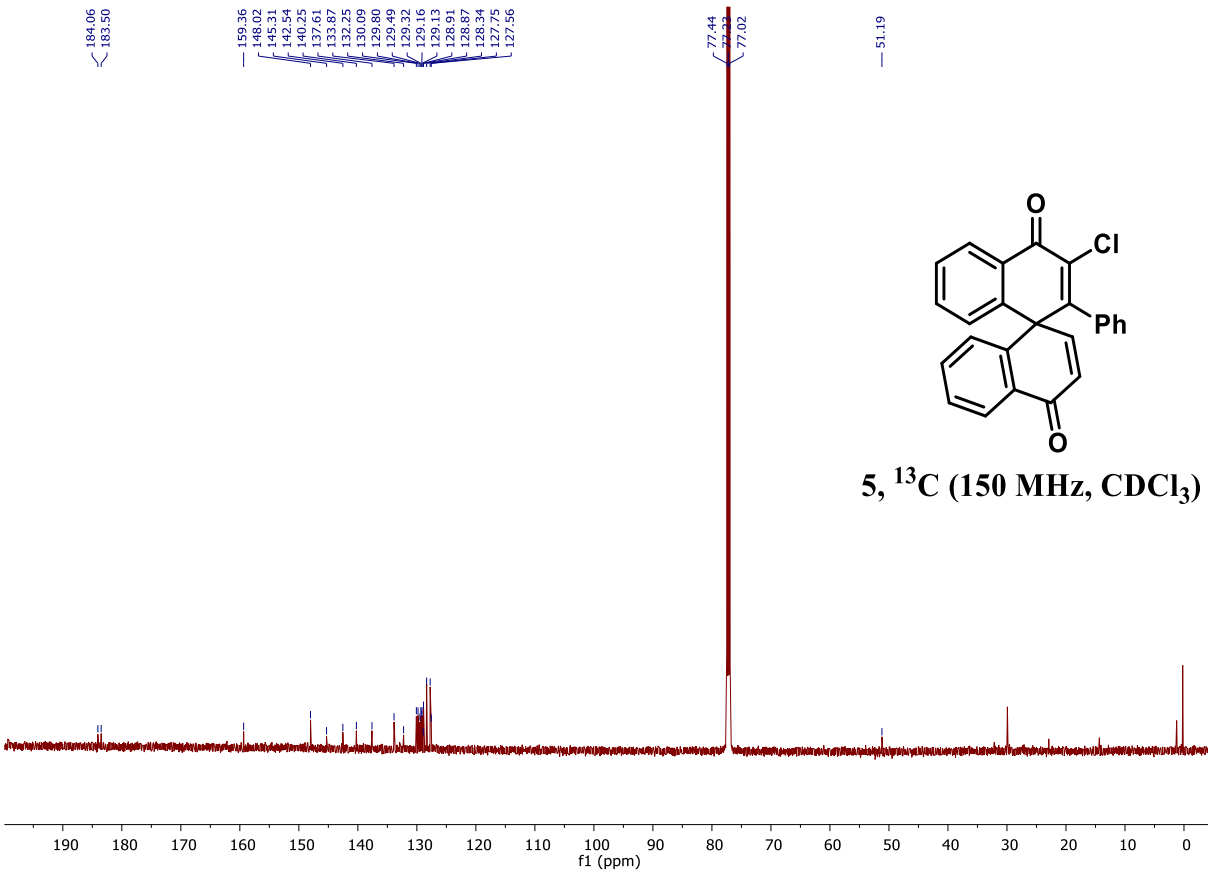
4, ^{1}H (600 MHz, $CDCl_3$)



4, ^{13}C (150 MHz, $CDCl_3$)



5, ^{1}H (600 MHz, $CDCl_3$)



5, ^{13}C (150 MHz, $CDCl_3$)