Supporting Information

Palladium-catalyzed cross-coupling of 2-iodobiphenyls with *ortho*-chloroacetophenones through dual C−H arylation for the construction of tribenzo[*a*,*c*,*f*]cyclooctanones

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1. General Information:

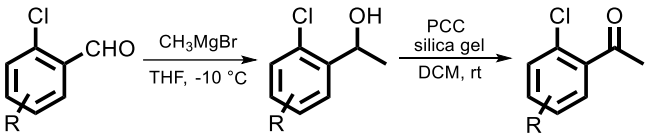
$Pd(OAc)_2$ was purchased from Strem Chemicals. All the solvents were purified by distillation prior to use. Substrates**1a-D5** and **1b-1h** were synthesized according to reported procedures.[1] Unless otherwise noted, the other commercial chemicals were used without further purification.

^1H NMR and ^{13}C NMR spectra were recorded on Bruker ARX400. High resolution mass spectra were measured on Bruker MicroTOF II ESI-TOF mass spectrometer. NMR spectra were recorded in $CDCl_3$. ^1H NMR spectra were referenced to residual $CHCl_3$ at 7.26 ppm, and ^{13}C NMR spectra were referenced to the central peak of $CDCl_3$ at 77.0 ppm. Chemical shifts (δ) are reported in ppm, and coupling constants (J) are in Hertz (Hz). Multiplicities are reported using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet.

2. General Procedures for the Synthesis of *ortho*-Chloroacetophenones

2b, **2m**, **2n** and **2q** were prepared by following method A. **2i-2l** were prepared by following method B. **2h** was prepared by following method C. **2c** and **2o** were prepared by following method D. **2p** was prepared by following method E. All the other *orhto*-chloroacetophenones were purchased.

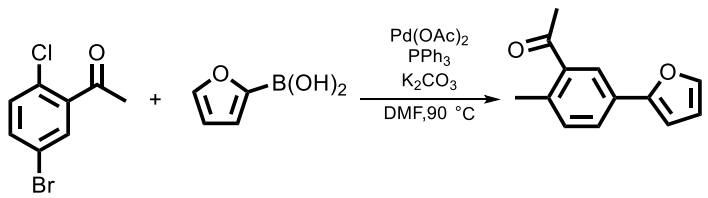
Method A:



Step 1: In a 100 ml round bottom flask, *ortho*-chlorobenzaldehydes (5 mmol) was dissolved in 20 mL of THF. The mixture was cooled to -10 °C and methyl grignard reagent (5 mmol) was added dropwise. The reaction mixture was stirred at -10°C for 5 h. Then the reaction mixture was quenched with sat. aq. NH_4Cl and extracted with EtOAc for three times. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (5:1) to afford corresponding secondary benzylic alcohols.

Step 2: In a 100 ml round bottom flask, secondary benzylic alcohols (4 mmol) was dissolved in 16 mL of DCM. Then PCC (12 mmol) and silica gel (the same mass as PCC) were added. The reaction mixture was stirred at rt for 5 hours, and then the resulting solution/suspension was filtered through a pad of silica gel, eluting with diethyl ether. The solvent was removed under reduced pressure, and the remaining crude residue was purified by flash column chromatography to afford *ortho*-chloroacetophenones.

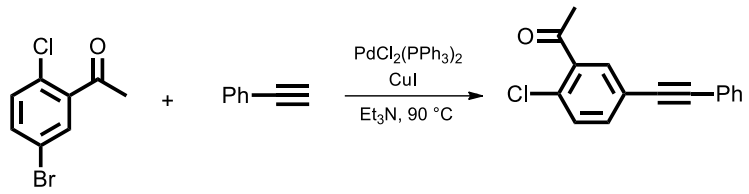
Method B:



Step 1: A 50 mL Schlenk-type round bottom flask quipped with a magnetic stir bar was charged with $Pd(OAc)_2$ (0.125 mmol, 28 mg, 0.05 equiv), PPh_3 (0.625 mmol, 164 mg, 0.25 equiv), K_2CO_3

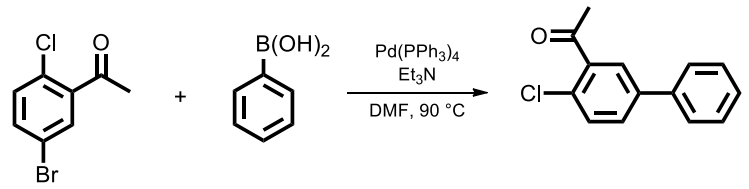
(2.5 mmol, 346 mg, 1.0 equiv), 1-(5-bromo-2-chlorophenyl)ethan-1-one (2.5 mmol, 584 mg, 1.0 equiv), furan-2-ylboronic acid (3.5 mmol, 392 mg, 1.4 equiv) and DMF (5 ml). The flask was evacuated and backfilled with nitrogen. The mixture was stirred at 90 °C (oil bath heating) for 8 hours. Then the reaction mixture was quenched with water and extracted with EtOAc for three times. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (10:1) to afford the corresponding *ortho*-chloroacetophenones.

Method C



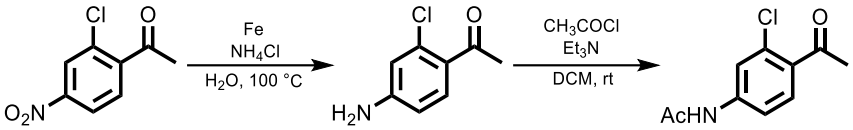
Step 1: A 50 mL Schlenk-type round bottom flask equipped with a magnetic stir bar was charged with $PdCl_2(PPh_3)_2$ (35 mg, 0.05 mmol, 0.02 equiv), CuI (28 mg, 0.15 mmol, 0.06 equiv), 1-(5-bromo-2-chlorophenyl)ethan-1-one (2.5 mmol, 584 mg, 1.0 equiv) and Et_3N (7.5 mL). The mixture was stirred at rt for 20 min. Then ethynylbenzene (307 mg, 3 mmol, 1.2 equiv) was added. Then the flask was evacuated and backfilled with nitrogen and the mixture was stirred at 90 °C (oil bath heating) for 22 h. Then the reaction mixture was quenched with sat. aq. NH_4Cl and extracted with EtOAc for three times. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (5:1) to afford the corresponding *ortho*-chloroacetophenones.

Method D



Step 1: A 50 mL Schlenk-type round bottom flask equipped with a magnetic stir bar was charged with $Pd(PPh_3)_4$ (290 mg, 0.25 mmol, 0.1 equiv), Et_3N (1.04 ml, 7.5 mmol, 3 equiv), 1-(5-bromo-2-chlorophenyl)ethan-1-one (2.5 mmol, 584 mg, 1.0 equiv), phenylboronic acid (366 mg, 3.0 mmol, 1.2 equiv) and DMF (12.5 mL). Then the flask was evacuated and backfilled with nitrogen and the mixture was stirred at 90 °C (oil bath heating) for 12h. Then the reaction mixture was quenched with water and extracted with EtOAc for three times. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (10:1) to afford the corresponding *ortho*-chloroacetophenones.

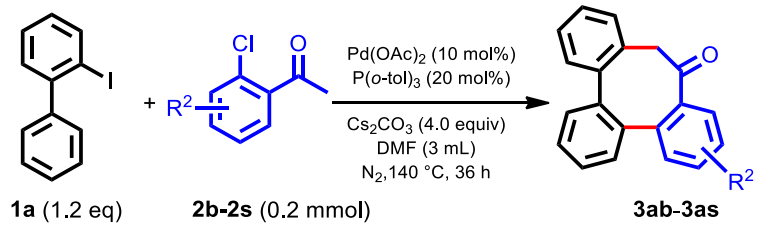
Method E



Step 1: In a 50 ml round bottom flask, Fe (9.55 mmol, 0.55 g, 3.82 equiv), NH_4Cl (1.3 mmol, 0.07 g, 0.52 equiv), H_2O (2.5 ml) was added. The mixture was stirred at 100°C (oil bath heating) for 1 hour. Then 1-(2-chloro-4-nitrophenyl)ethan-1-one (2.5 mmol, 0.5g, 1 equiv) was added to the mixture and stirred at 100°C (oil bath heating) overnight. Then the mixture was diluted by DCM (25 ml), washed by H_2O, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The product was used for the next reaction without purification.

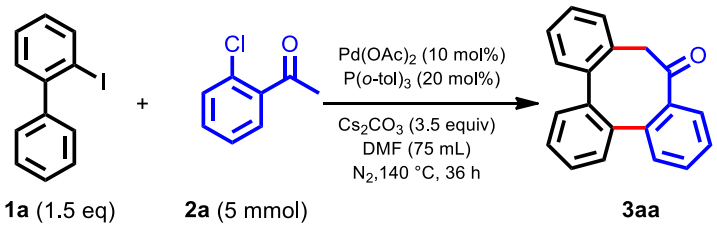
Step 2: In a 50 ml round bottom flask, 1-(4-amino-2-chlorophenyl)ethan-1-one (2 mmol, 0.34 g, 1 equiv) and Et_3N (2.4 mmol, 0.34 ml, 1.2 equiv) were dissolved in dry DCM (20 ml) .The reaction mixture was stirred at 0 °C for 10 min. Then CH_3COCl (2.2 mmol, 0.16 ml, 1.1 equiv) was added dropwise and the mixture was stirred at rt for 4h. Then the mixture was diluted by DCM, washed by HCl (3 N), and extracted with DCM. for dried over Na_2SO_4. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (5:1) to afford corresponding *ortho*-chloroacetophenones.

3. A Typical Procedure for the Intermolecular Dual C–H/C–H Cross-Coupling



A 25 mL Schlenk-type tube (with a Teflon screw cap and a side arm) equipped with a magnetic stir bar was charged with $Pd(OAc)_2$ (0.02 mmol, 4.4 mg, 0.1 equiv), P(*o*-tol)$_3$ (0.04 mmol, 12.2 mg, 0.2 equiv), Cs_2CO_3 (0.8 mmol, 260.4 mg, 4.0 equiv), 2-iodobiphenyls (0.24 mmol, 1.2 equiv), *ortho*-chloroacetophenones (0.2 mmol, 1.0 equiv) and DMF (3 mL). The reaction mixture was frozen with liquid nitrogen and then the tube was evacuated and backfilled with nitrogen (6 times). The mixture was stirred at 140 °C (oil bath heating) for 36 hours. After being cooled down to room temperature, the reaction mixture was diluted with EtOAc (15 mL), washed with brine (3 times), dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by preparative silica gel TLC with petroleum ether/ethyl acetate (using the indicated mobile phase) to afford **3**.

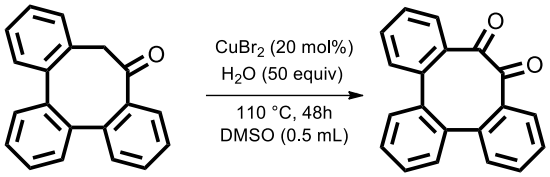
Procedure of the Large-Scale Reaction.



A 250 mL Schlenk-type tube (with a Teflon screw cap and a side arm) equipped with a magnetic

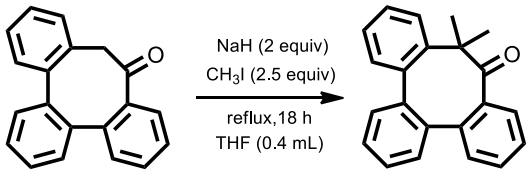
stir bar was charged with $Pd(OAc)_2$ (0.5 mmol, 110 mg, 0.1 equiv), $P(o\text{-}tol)_3$ (1 mmol, 305 mg, 0.2 equiv), Cs_2CO_3 (17.5 mmol, 5.7 g, 3.5 equiv), 2-iodobiphenyl (7.5 mmol, 2.1g, 1.2 equiv), *ortho*-chloroacetophenone (5 mmol, 773 mg, 1.0 equiv) and DMF (75 mL). The reaction mixture was frozen with liquid nitrogen and then the tube was evacuated and backfilled with nitrogen (6 times). The mixture was stirred at 140 °C (oil bath heating) for 36 hours. After being cooled down to room temperature, the reaction mixture was quenched with water and extracted with EtOAc for three times. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (50:1) to afford **3aa** (0.96 g, 70%).

4. Transformation of the Product



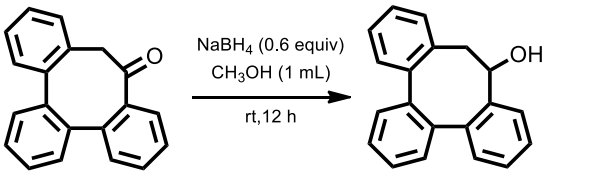
3aa, 0.2 mmol **5aa**, 85%

A 25 mL Schlenk-type tube (with a Teflon screw cap and a side arm) equipped with a magnetic stir bar was charged with $CuBr_2$ (0.04 mmol, 8.9 mg, 0.2 equiv), H_2O (10 mmol, 180 mg, 50 equiv), **3aa** (0.2 mmol, 54 mg, 1.0 equiv) and DMSO (0.5 mL). The reaction mixture was stirred at 110 °C (oil bath heating) for 48 hours. After being cooled down to room temperature, the reaction mixture was diluted with EtOAc (15 mL), washed with brine (3 times), dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by preparative silica gel TLC with petroleum ether/ethyl acetate (10:1) to afford **5aa** (48 mg, 85%).



3aa, 0.2 mmol **6aa**, 73%

An oven-dried 10 mL round bottom flask was charged with 60% dispersion of NaH in mineral oil (16 mg, 0.4 mmol, 2 equiv), anhydrous THF (0.4 mL), **3aa** (54 mg, 0.2 mmol, 1.0 equiv), and methyl iodide (31 ul, 0.5 mmol). The reaction mixture was refluxed overnight. After 18 h the resulting mixture was quenched at 0°C by adding 1 M HCl (0.5 mL) and saturated $NaHCO_3$ (0.5 mL) sequentially, then extracted with ethyl acetate. The combined organic layers were dried over Na_2SO_4, filtered, and concentrated. The residue was purified by preparative silica gel TLC with petroleum ether/ethyl acetate (20:1) to afford **6aa** (44 mg, 73%).

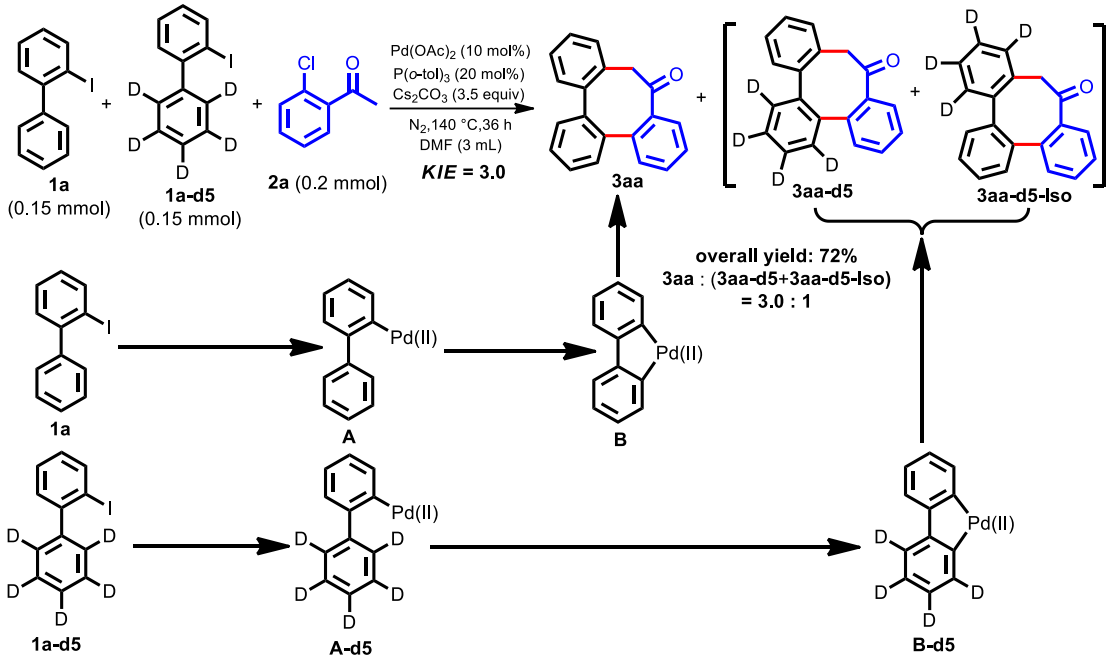


3aa, 0.2 mmol **7aa**, 88%, dr = 53:47

A 10 mL Schlenk-type tube (with a Teflon screw cap and a side arm) equipped with a magnetic stir bar was charged with **3aa** (54 mg, 0.2 mmol, 1.0 equiv) and MeOH (1 ml). then cool down the reaction mixture to 0°C. $NaBH_4$ (4.5 mg, 0.12 mmol, 0.6 equiv) was added to the reaction mixture and then the reaction mixture was stirred at rt for 12h. The reaction mixture was diluted with EtOAc (3 ml) and concentrated in vacuo directly. The residue was purified by preparative silica gel TLC with petroleum ether/ethyl acetate (5:1) to afford **7aa** (48 mg, 88%).

5. Kinetic Isotope Effect Studies

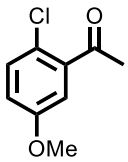
The reaction of 2-iodobiphenyl **1a** and its pentadeuterated derivative **1a-d5** with **2a** was carried out by following the standard procedure. A mixture of three products (**3aa**, **3aa-d5** and **3aa-d5-Iso**) was obtained in an overall yield of 72%. The three products were formed by a mechanism as below. The palladacycle **B-d5** gave **3aa-d5** and **3aa-d5-Iso**. ^{1}H NMR data analysis indicated that the ratio of **3aa** to **3aa-d5** and **3aa-d5-Iso** was 3 to 1, so the KIE value is 3.0.



6. References

[1] Jiang, H.; Zhang, Y.; Chen, D.-S; Zhou, B.; Zhang, Y.-H. *Org. Lett.* **2016**, *18*, 2032-2035.

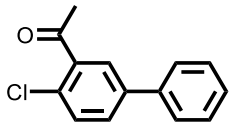
7. Characterization of the Substrates



2b

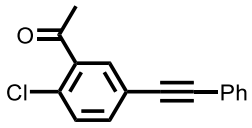
1-(2-chloro-5-methoxyphenyl)ethan-1-one (**2b**): yellowish oil, 0.73 g, 79% yield over two steps. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28 (d, J = 8.8 Hz, 1H), 7.05 (d, J = 3.1 Hz, 1H), 6.92 (dd, J = 8.8, 3.1 Hz, 1H), 3.80 (s, 3H), 2.63 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 200.20, 158.25, 139.68, 131.43,

122.47, 118.12, 114.12, 55.62, 30.64. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_9H_{10}ClO_2$ 185.0364; found 185.0363.



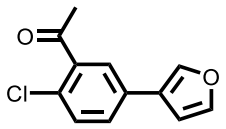
2c

1-(4-chloro-[1,1'-biphenyl]-3-yl)ethan-1-one (**2c**): yellowish oil, 0.40 g, 70% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.74 (d, *J* = 2.2 Hz, 1H), 7.54 (m, 3H), 7.45 – 7.39 (m, 3H), 7.35 (m, 1H), 2.66 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 200.43, 140.20, 139.40, 138.96, 131.07, 130.48, 130.32, 129.07, 128.14, 128.00, 127.00, 30.84. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{14}H_{12}ClO$ 231.0571; found 231.0570.



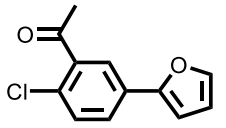
2h

1-(2-chloro-5-(phenylethynyl)phenyl)ethan-1-one (**2h**): yellowish oil, 0.41 g, 64% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.69 (d, *J* = 2.0 Hz, 1H), 7.53 – 7.50 (m, 2H), 7.49 (dd, *J* = 8.3, 2.0 Hz, 1H), 7.36 (d, *J* = 8.3 Hz, 1H), 7.35 – 7.31 (m, 1H), 2.63 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 199.48, 139.12, 134.54, 132.38, 131.69, 131.01, 130.85, 128.82, 128.49, 122.58, 122.55, 91.43, 87.35, 30.62. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{16}H_{12}ClO$ 255.0571; found 255.0561.



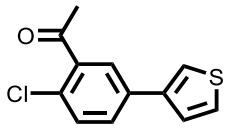
2i

1-(2-chloro-5-(furan-3-yl)phenyl)ethan-1-one (**1d**): brown oil, 0.42 g, 76% yiel. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.74 (m, 1H), 7.62 (d, *J* = 2.2 Hz, 1H), 7.49 – 7.45 (m, 2H), 7.38 (d, *J* = 8.3 Hz, 1H), 6.67 (dd, *J* = 1.7, 0.8 Hz, 1H), 2.67 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 200.46, 144.13, 139.52, 139.05, 131.65, 131.00, 129.49, 129.13, 126.56, 124.74, 108.56, 30.81.
HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{12}H_9ClNaO_2$ 243.0183; found 243.0172.



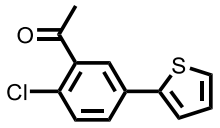
2j

1-(2-chloro-5-(furan-2-yl)phenyl)ethan-1-one (**2j**): brown oil, 0.42 g, 77% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 1.6 Hz, 1H), 7.72 – 7.58 (m, 1H), 7.49 (s, 1H), 7.44 – 7.34 (m, 1H), 6.70 (dd, *J* = 2.5, 0.6 Hz, 1H), 6.54 – 6.27 (m, 1H), 2.68 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.21, 151.92, 142.81, 139.41, 130.98, 129.89, 129.66, 126.86, 124.48, 111.96, 106.40, 30.70. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{12}H_{10}ClO_2$ 221.0364; found 221.0345.



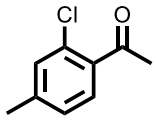
2k

1-(2-chloro-5-(thiophen-3-yl)phenyl)ethan-1-one (**2k**): brown oil, 0.49 g, 82% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.73 (d, *J* = 2.3 Hz, 1H), 7.55 (dd, *J* = 8.3, 2.3 Hz, 1H), 7.44 (dd, *J* = 2.9, 1.3 Hz, 1H), 7.38 (d, *J*= 8.6 Hz, 1H), 7.37 – 7.36 (dd, *J*= 5.7, 2.9 Hz 1H), 7.32 (dd, *J* = 5.0, 1.3 Hz, 1H), 2.66 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 200.41, 140.07, 139.44, 134.84, 131.04, 129.76, 129.68, 127.17, 126.93, 125.96, 121.41, 30.83. HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{12}H_9ClNaOS$ 258.9955; found 258.9965.



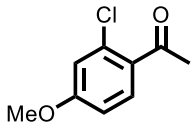
2l

1-(2-chloro-5-(thiophen-2-yl)phenyl)ethan-1-one (**2l**): brown oil, 0.43 g, 72% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.71 (d, *J* = 2.3 Hz, 1H), 7.51 (dd, *J* = 8.3, 2.4 Hz, 1H), 7.32 (d, *J* = 8.4 Hz, 1H), 7.29 – 7.22 (m, 2H), 7.03 (dd, *J* = 5.0, 3.8 Hz, 1H), 2.63 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 200.05, 141.86, 139.47, 133.49, 131.10, 129.90, 128.96, 128.35, 126.45, 125.91, 124.18, 30.77. HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{12}H_9ClNaOS$ 258.9955; found 258.9955.



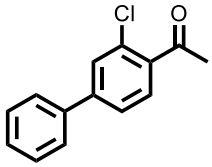
2m

1-(2-chloro-4-methylphenyl)ethan-1-one (**2m**): yellowish oil, 0.67 g, 80% yield over two steps. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.50 (d, *J* = 7.9 Hz, 1H), 7.21 (s, 1H), 7.10 (dd, *J* = 7.9, 0.7 Hz, 1H), 2.62 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 199.66, 143.13, 135.84, 131.51, 131.18, 129.82, 127.66, 30.61, 21.03. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_9H_{10}ClO$ 169.0415; found 169.0401.



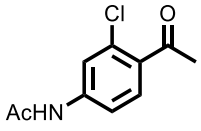
2n

1-(2-chloro-4-methoxyphenyl)ethan-1-one (**2n**): yellowish oil, 0.74 g, 86% yield over two steps. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.49 (d, *J* = 7.9 Hz, 1H), 7.20 (d, *J* = 0.5 Hz, 1H), 7.09 (dd, *J* = 7.9, 0.8 Hz, 1H), 2.61 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 199.47, 143.09, 135.78, 131.45, 131.13, 129.80, 127.64, 30.54, 20.98.HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_9H_9ClNaO_2$ 207.0183; found 207.0199.



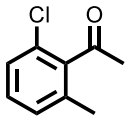
2o

1-(3-chloro-[1,1'-biphenyl]-4-yl)ethan-1-one (**2o**): yellowish oil, 0.44 g, 77% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.0 Hz, 1H), 7.65 (d, *J* = 1.7 Hz, 1H), 7.60 – 7.56 (m, 2H), 7.54 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.47 (m, 2H), 7.43 – 7.35 (m, 1H), 2.69 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 199.82, 145.34, 138.60, 137.18, 132.17, 130.31, 129.24, 129.08, 128.62, 127.18, 125.52, 30.79. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{14}H_{12}ClO$ 231.0571; found 231.0574.



2p

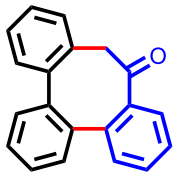
N-(4-acetyl-3-chlorophenyl)acetamide (**2p**): yellow solid, 0.76 g, 72%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.74 (dd, *J* = 8.7, 2.5 Hz, 1H), 7.66 (d, *J* = 2.5 Hz, 1H), 7.36 (d, *J* = 8.7 Hz, 1H), 2.66 (s, 3H), 2.20 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.47, 168.78, 139.14, 137.14, 131.21, 125.99, 123.42, 120.36, 30.77, 24.47. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{10}H_{11}ClNO_2$ 212.0473; found 212.0458.



2q

1-(2-chloro-6-methylphenyl)ethan-1-one (**2q**): yellowish oil, 0.73 g, 86% yield over two steps. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.24 – 7.17 (m, 2H), 7.14 – 7.08 (m, 1H), 2.55 (s, 3H), 2.26 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 204.28, 141.02, 135.14, 129.65, 128.85, 128.80, 126.90, 31.69, 19.11. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_9H_{10}ClO$ 169.0415; found 169.0426.

8. Characterization of the Products

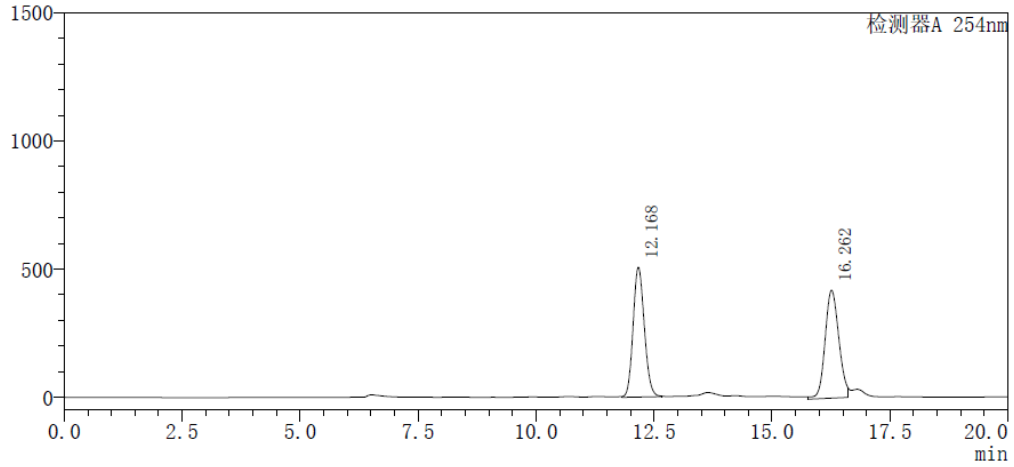


3aa

tribenzo[a,c,e][8]annulen-9(10H)-one (**3aa**): yellowish solid, actual mass 48.7 mg, 90% yield, (eluent: petroleum ether/ethyl acetate = 50:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.53 – 7.43 (m, 2H), 7.39 (td, *J* = 7.5, 1.5 Hz, 1H), 7.36 – 7.27 (m, 4H), 7.23 (m, 3H), 7.06 (dd, *J* = 7.6, 1.0 Hz, 1H), 3.86 – 3.65 (m, 2H).^{13}C NMR (101 MHz, $CDCl_3$) δ 202.21, 141.47, 141.11, 140.16, 139.64, 136.81, 134.12, 131.99, 131.60, 130.97, 128.66, 128.61, 128.45, 128.23, 127.96, 127.83, 127.75, 127.46, 49.89. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{20}H_{15}O$ 271.1117; found 271.1099.

HPLC analysis:

<chromatogram>
mV



<Peak table>
检测器A 254nm

Peak#	Ret. Time	Height	Area	Area%
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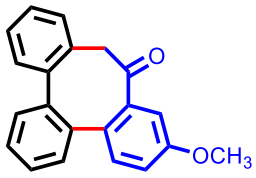
2	16.262	420710	8509460	50.339
总计		927542	16904210	100.000

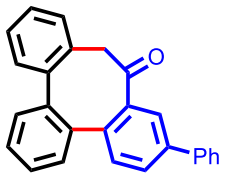


3ab

7-methoxytribenzo[a,c,e][8]annulen-9(10H)-one (**3ab**): yellowish solid, actual mass 49.3 mg, 82% yield, (eluent: petroleum ether/ethyl acetate = 50:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.40 (m, 2H), 7.36 – 7.28 (m, 3H), 7.25 – 7.20 (m, 4H), 6.99 (d, *J* = 8.5 Hz, 1H), 6.94 (dd, *J* = 8.5, 2.7 Hz, 1H), 3.88 – 3.68 (m, 5H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 201.63, 158.89, 141.61, 140.96, 139.83, 137.52, 134.07, 133.65, 132.92, 131.15, 128.59, 128.42, 128.26, 127.92, 127.90, 127.77, 127.47, 118.72, 112.13, 55.36, 49.63.

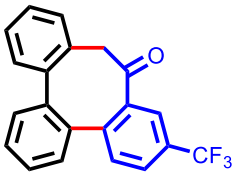
HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{21}H_{17}O_2$ 301.1223; found 301.1221.



3ac

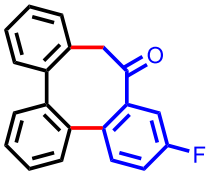
7-phenyltribenzo[a,c,e][8]annulen-9(10H)-one (**3ac**): white solid, actual mass 54.0 mg, 78% yield, (eluent: petroleum ether/ethyl acetate = 50:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 1.9 Hz, 1H), 7.66 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.61 (m, 2H), 7.58 – 7.48 (m, 2H), 7.48 – 7.31 (m, 7H), 7.31 – 7.24 (m, 2H), 7.17 (d, *J* = 8.0 Hz, 1H), 4.00 – 3.52 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.93, 141.48, 140.88, 140.46, 139.73, 139.53, 139.11, 137.00, 134.03, 132.78, 131.01, 130.02, 128.82, 128.72, 128.51, 128.37, 128.28, 128.02, 127.88, 127.74, 127.53, 127.19, 126.99, 49.86.

HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{26}H_{19}O$ 347.1430; found 347.1444.



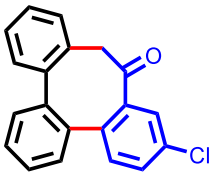
3ad

7-(trifluoromethyl)tribenzo[a,c,e][8]annulen-9(10H)-one (**3ad**): white solid, actual mass 21.7 mg, 32% yield, (eluent: petroleum ether/ethyl acetate = 50:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, J = 0.7 Hz, 1H), 7.62 (dd, J = 8.1, 1.4 Hz, 1H), 7.52 (m, 2H), 7.37 (dd, J = 7.3, 1.3 Hz, 1H), 7.34 – 7.29 (m, 2H), 7.27 (m, 3H), 7.21 (d, J = 8.1 Hz, 1H), 3.94 – 3.41 (m, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 200.549, 143.513 (d, J_{C-F}= 1.0 Hz), 141.004, 139.742, 139.520, 137.181, 133.452, 132.751, 130.766, 130.184 (q, J_{C-F}= 33.0 Hz), 128.925, 128.856, 128.563, 128.540, 128.197 (q, J_{C-F}= 23.4 Hz), 127.916 (q, J_{C-F}=3.4 Hz), 127.802, 125.917 (q, J_{C-F}=3.7 Hz), 123.623 (q, J_{C-F}= 270.8 Hz), 49.625. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{21}H_{14}F_3O$ 339.0991; found 339.1009.



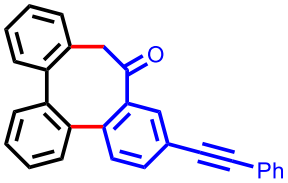
3ae

7-fluorotribenzo[a,c,e][8]annulen-9(10H)-one (**3ae**): white solid, actual mass 25.4 mg, 44% yield, (eluent: petroleum ether/ethyl acetate = 50:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (m, J = 7.5, 2H), 7.42 (dd, J = 9.4, 2.5 Hz, 1H), 7.34 (dd, J = 7.2, 1.7 Hz, 1H), 7.32 – 7.28 (m, 2H), 7.27 – 7.19 (m, 3H), 7.13 – 6.96 (m, 2H), 3.78 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.578, 162.031 (d, J_{C-F}= 246.9 Hz), 141.319, 140.119, 139.733, 138.469 (d, J_{C-F}= 6.3 Hz), 136.226, 136.191, 134.087 (d, J_{C-F}= 7.2 Hz), 133.710, 131.017, 128.691, 128.479, 128.387 (d, J_{C-F}= 3.1), 128.110, 127.914, 127.649, 118.669 (d, J_{C-F}= 21.1 Hz), 115.151 (d, J_{C-F}= 22.8 Hz), 49.442. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{20}H_{14}FO$ 289.1023; found 289.1012..



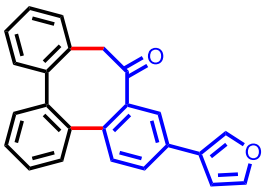
3af

7-chlorotribenzo[a,c,e][8]annulen-9(10H)-one (**2g**): white solid, actual mass 29.9 mg, 49% yield, (eluent: petroleum ether/ethyl acetate = 50:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, J = 2.3 Hz, 1H), 7.54-7.44 (m, 2H), 7.38-7.32 (m, 2H), 7.32 – 7.27 (m, 2H), 7.27-7.21 (m, 3H), 7.01 (d, J = 8.3 Hz, 1H), 4.01 – 3.34 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.62, 141.22, 139.95, 139.65, 138.52, 138.00, 134.06, 133.62, 133.55, 131.52, 130.83, 128.75, 128.57, 128.53, 128.51, 128.43, 128.18, 127.99, 127.71, 49.55. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{20}H_{14}ClO$ 305.0728; found 305.0712.



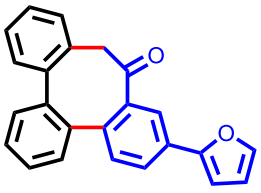
3ah

7-(phenylethynyl)tribenzo[a,c,e][8]annulen-9(10H)-one (**3ah**): white solid, actual mass 47.4 mg, 64% yield, (eluent: petroleum ether/ethyl acetate = 50:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 1.7 Hz, 1H), 7.56 – 7.43 (m, 5H), 7.38 – 7.27 (m, 6H), 7.27 – 7.18 (m, 3H), 7.05 (d, *J* = 8.0 Hz, 1H), 3.80 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.37, 141.29, 140.56, 139.81, 139.66, 137.00, 134.08, 133.78, 132.22, 131.90, 131.66, 130.78, 128.72, 128.53, 128.51, 128.38, 128.35, 128.13, 127.95, 127.62, 123.09, 122.90, 90.77, 88.10, 49.74. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{28}H_{19}O$ 371.1430; found 371.1421.



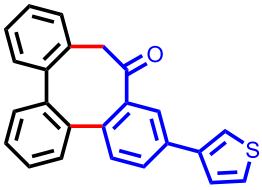
3ai

(*E*)-2-Methyl-1,2,7,8-tetrahydronaphtho[2,1-*b*]furan-9(6*H*)-one *O*-methyl oxime (**4a**): yellow solid, actual mass 47.1 mg, 70% yield, (eluent: petroleum ether/ethyl acetate = 50:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 1.9 Hz, 1H), 7.74 (s, 1H), 7.55 – 7.40 (m, 4H), 7.39 – 7.28 (m, 3H), 7.26-7.22 (m, 3H), 7.07 (d, *J* = 8.0 Hz, 1H), 6.74 – 6.63 (m, 1H), 3.86 – 3.77 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.93, 143.86, 141.45, 140.87, 139.71, 138.98, 138.75, 137.03, 133.95, 132.72, 132.02, 130.92, 128.80, 128.68, 128.47, 128.33, 128.25, 128.01, 127.88, 127.53, 125.81, 125.25, 108.60, 49.82. HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{24}H_{16}NaO_2$ 359.1043; found 359.1032.



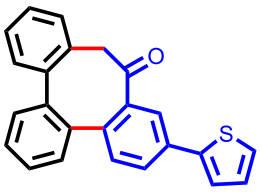
3aj

7-(furan-2-yl)tribenzo[a,c,e][8]annulen-9(10H)-one (**4b**): yellow solid, actual mass 27.6 mg, 41% yield, (eluent: petroleum ether/ethyl acetate = 50:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 1.9 Hz, 1H), 7.68 (dd, *J* = 8.1, 2.0 Hz, 1H), 7.53 – 7.45 (m, 2H), 7.44 (d, *J* = 1.2 Hz, 1H), 7.39 – 7.27 (m, 3H), 7.25 – 7.21 (m, 3H), 7.09 (d, *J* = 8.1 Hz, 1H), 6.68 (d, *J* = 3.3 Hz, 1H), 6.45 (dd, *J* = 3.4, 1.8 Hz, 1H), 3.81 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.87, 152.71, 142.52, 141.42, 140.84, 139.73, 138.84, 137.12, 133.91, 132.63, 130.88, 130.42, 128.69, 128.49, 128.31, 128.30, 128.04, 127.90, 127.55, 126.54, 123.89, 111.78, 106.03, 49.80. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{24}H_{17}O_2$ 337.1223; found 337.1206.



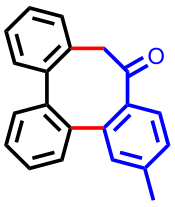
3ak

7-(thiophen-3-yl)tribenzo[a,c,e][8]annulen-9(10H)-one (**4c**): yellow solid, actual mass 51.5 mg, 73% yield, (eluent: petroleum ether/ethyl acetate = 50:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 1.9 Hz, 1H), 7.61 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.54 – 7.44 (m, 3H), 7.41 – 7.29 (m, 5H), 7.27 – 7.19 (m, 3H), 7.10 (d, *J* = 8.0 Hz, 1H), 3.88 – 3.75 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.92, 141.45, 140.87, 140.77, 139.72, 138.85, 137.05, 135.22, 133.97, 132.75, 130.92, 129.30, 128.69, 128.48, 128.33, 128.26, 128.02, 127.88, 127.53, 126.45, 126.41, 126.04, 121.00, 49.84. HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{24}H_{16}NaOS$ 375.0814; found 375.0798.



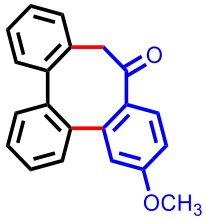
3al

7-(thiophen-2-yl)tribenzo[a,c,e][8]annulen-9(10H)-one (**4d**): yellow solid, actual mass 24.7 mg, 35% yield, (eluent: petroleum ether/ethyl acetate = 50:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 2.0 Hz, 1H), 7.61 (dd, *J* = 8.0, 2.1 Hz, 1H), 7.54 – 7.44 (m, 2H), 7.38 – 7.29 (m, 4H), 7.27 (dd, *J* = 5.1, 1.0 Hz, 1H), 7.26 – 7.22 (m, 2H), 7.11 – 7.02 (m, 2H), 3.87 – 3.77 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.71, 142.78, 141.41, 140.72, 139.71, 139.06, 137.15, 133.95, 133.88, 132.80, 130.87, 128.73, 128.68, 128.49, 128.36, 128.32, 128.10, 128.06, 127.91, 127.57, 125.77, 125.44, 123.79, 49.80. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{24}H_{17}OS$ 353.0995; found 353.1011.



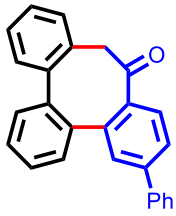
3am

6-methyltribenzo[a,c,e][8]annulen-9(10H)-one (**3am**): white solid, actual mass 45.5 mg, 80% yield, (eluent: petroleum ether/ethyl acetate = 50:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.0 Hz, 1H), 7.54 – 7.39 (m, 2H), 7.37 – 7.27 (m, 3H), 7.26 – 7.17 (m, 3H), 7.10 (d, *J* = 8.0 Hz, 1H), 6.86 (s, 1H), 3.89 – 3.65 (m, 2H), 2.29 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.57, 142.14, 141.45, 141.34, 140.32, 139.65, 134.36, 134.14, 132.85, 131.01, 128.92, 128.59, 128.59, 128.42, 128.27, 128.10, 127.94, 127.75, 127.37, 49.82, 21.33. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{21}H_{17}O$ 285.1274; found 285.1256.



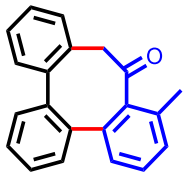
3an

6-methoxytribenzo[a,c,e][8]annulen-9(10H)-one (**4e-2**): white solid, actual mass 48.1 mg, 80% yield, (eluent: petroleum ether/ethyl acetate = 40:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.8 Hz, 1H), 7.54 – 7.41 (m, 2H), 7.38 – 7.28 (m, 3H), 7.25 – 7.17 (m, 3H), 6.82 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.53 (d, *J* = 2.5 Hz, 1H), 3.82 – 3.68 (m, 5H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.31, 161.84, 142.67, 141.22, 139.59, 134.58, 131.29, 130.94, 129.76, 128.47, 128.34, 128.22, 127.98, 127.76, 127.33, 117.32, 113.32, 55.35, 49.63. HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{21}H_{16}NaO_2$ 323.1043; found 323.1048.



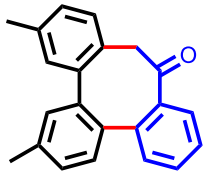
3ao

6-phenyltribenzo[a,c,e][8]annulen-9(10H)-one (**3ao**): white solid, actual mass 50.6 mg, 73% yield, (eluent: petroleum ether/ethyl acetate = 40:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.2 Hz, 1H), 7.56 – 7.44 (m, 5H), 7.42 – 7.28 (m, 7H), 7.25 – 7.17 (m, 3H), 3.91 – 3.70 (m, 2H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 201.48, 144.23, 141.43, 141.22, 140.87, 139.73, 139.52, 135.39, 134.18, 131.14, 130.92, 129.56, 128.88, 128.71, 128.59, 128.43, 128.36, 128.17, 128.08, 127.94, 127.55, 127.24, 126.32, 49.88.
HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{26}H_{18}NaO$ 369.1250; found 369.1246.



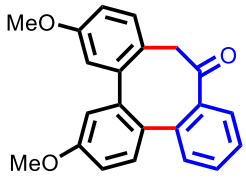
3aq

8-methyltribenzo[a,c,e][8]annulen-9(10H)-one (**4g**): yellowish solid, actual mass 29.5 mg, 52% yield, (eluent: petroleum ether/ethyl acetate = 50:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.37 (m, 2H), 7.33 – 7.27 (m, 2H), 7.22 – 7.09 (m, 5H), 7.05 (d, *J* = 7.3 Hz, 1H), 6.83 (d, *J* = 7.4 Hz, 1H), 3.69 (s, 2H), 2.26 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 208.08, 142.15, 140.46, 139.63, 139.47, 138.18, 134.24, 133.70, 130.11, 129.87, 129.04, 129.01, 128.80, 128.28, 128.03, 127.99, 127.80, 127.39, 127.19, 50.95, 19.85. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{21}H_{17}O$ 285.1274; found 285.1259. Melting point: 130 - 131 ℃.



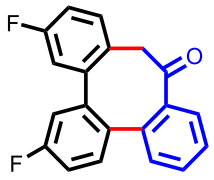
3ba

2,13-dimethyltribenzo[a,c,e][8]annulen-9(10H)-one (**3ba**): white solid, actual mass 43.0 mg, 72% yield, (eluent: petroleum ether/ethyl acetate = 50:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.37 (td, *J* = 7.5, 1.5 Hz, 1H), 7.32 – 7.26 (m, 2H), 7.20 (d, *J* = 7.8 Hz, 1H), 7.15 – 7.06 (m, 3H), 7.04 (dd, *J* = 7.6, 1.0 Hz, 1H), 7.01 (dd, *J* = 7.8, 1.0 Hz, 1H), 3.80 – 3.64 (m, 2H), 2.46 (s, 3H), 2.28 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.46, 141.41, 140.39, 139.61, 138.27, 137.97, 137.01, 136.91, 132.17, 131.51, 131.08, 130.92, 129.10, 128.92, 128.69, 128.62, 128.48, 128.45, 127.53, 49.45, 21.15, 21.10. HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{22}H_{18}NaO$ 321.1250; found 321.1232.



3ca

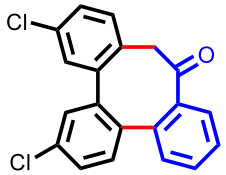
2,13-dimethoxytribenzo[a,c,e][8]annulen-9(10H)-one (**4i**): white solid, actual mass 48.9 mg, 74% yield, (eluent: petroleum ether/ethyl acetate = 50:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (dd, *J* = 7.7, 1.1 Hz, 1H), 7.37 (td, *J* = 7.5, 1.4 Hz, 1H), 7.30 (dd, *J* = 7.6, 1.1 Hz, 1H), 7.24 (d, *J* = 8.5 Hz, 1H), 7.13 (d, *J* = 8.4 Hz, 1H), 7.08 – 6.96 (m, 2H), 6.91 – 6.81 (m, 2H), 6.76 (dd, *J* = 8.4, 2.7 Hz, 1H), 3.89 (s, 3H), 3.79 – 3.67 (m, 5H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.57, 159.33, 158.67, 142.53, 140.82, 139.96, 137.07, 133.51, 132.29, 132.26, 131.51, 129.72, 128.71, 127.50, 126.32, 113.88, 113.62, 113.45, 113.26, 55.47, 55.25, 48.89. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{22}H_{19}O_3$ 331.1329; found 331.1326.



3da

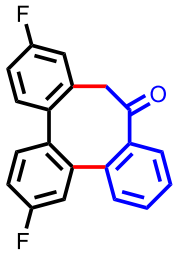
2,13-difluorotribenzo[a,c,e][8]annulen-9(10H)-one (**3da**): white solid, actual mass 26.3 mg, 43% yield, (eluent: petroleum ether/ethyl acetate = 50:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.41 (td, *J* = 7.5, 1.5 Hz, 1H), 7.37 – 7.28 (m, 2H), 7.23 – 7.15 (m, 2H), 7.09 – 6.97 (m, 3H), 6.94 (td, *J* = 8.4, 2.7 Hz, 1H), 3.90 – 3.46 (m, 2H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 201.611 (d, $J_{C\text{-}F}$= 1.5 Hz), 162.326 (d, $J_{C\text{-}F}$= 247.8 Hz), 161.753 (d, $J_{C\text{-}F}$= 245.7 Hz), 142.118 (dd, $J_{C\text{-}F}$= 7.8, 1.8 Hz), 140.521 (dd, $J_{C\text{-}F}$= 8.2, 1.7 Hz), 138.761, 136.996 (d, $J_{C\text{-}F}$= 3.4 Hz), 136.806, 132.932 (d, $J_{C\text{-}F}$= 8.2 Hz), 131.998, 131.784, 130.464 (d, $J_{C\text{-}F}$= 8.4 Hz), 129.860 (d, $J_{C\text{-}F}$= 3.2 Hz), 128.788, 128.132, 115.390 (d, $J_{C\text{-}F}$= 1.7 Hz), 115.364 (d, $J_{C\text{-}F}$= 21.1 Hz), 115.175 (d, $J_{C\text{-}F}$= 2.8 Hz), 114.946(d, $J_{C\text{-}F}$= 21.9 Hz), 48.942. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{20}H_{13}F_2O$ 307.0929; found 307.0939.



3ea

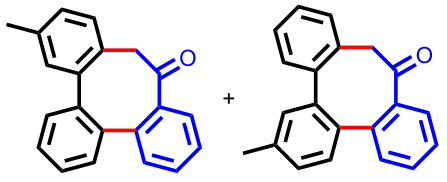
2,13-dichlorotribenzo[a,c,e][8]annulen-9(10H)-one (**4k-2**): white solid, actual mass 20.4 mg, 30% yield, (eluent: petroleum ether/ethyl acetate = 50:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, J = 7.8 Hz, 1H), 7.47 (dd, J = 8.3, 2.2 Hz, 1H), 7.43 (td, J = 7.5, 1.2 Hz, 1H), 7.38 – 7.31 (m, 2H), 7.30 – 7.26 (m, 2H), 7.22 (dd, J = 8.2, 2.1 Hz, 1H), 7.16 (d, J = 8.2 Hz, 1H), 7.03 (d, J = 7.3 Hz, 1H), 3.80 – 3.69 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.01, 141.67, 139.87, 139.48, 138.56, 136.61, 134.31, 133.23, 132.54, 132.44, 131.92, 131.86, 130.16, 128.87, 128.57, 128.45, 128.32, 128.30, 128.03, 49.12. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{20}H_{13}Cl_2O$ 339.0338; found 339.0321.



3ga

3,12-difluorotribenzo[a,c,e][8]annulen-9(10H)-one (**3ga**): white solid, actual mass 31.2 mg, 51% yield, (eluent: petroleum ether/ethyl acetate = 50:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (dd, J = 7.7, 1.3 Hz, 1H), 7.42 (td, J = 7.5, 1.4 Hz, 1H), 7.35 (td, J = 7.6, 1.1 Hz, 1H), 7.31 – 7.16 (m, 3H), 7.10 – 7.01 (m, 2H), 6.97 – 6.87 (m, 2H), 3.76 (s, 2H).

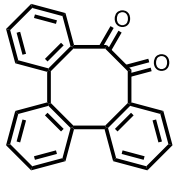
^{13}C NMR (151 MHz, Chloroform-*d*) δ 201.03, 162.264 (d, $J_{C\text{-}F}$= 228.7 Hz), 162.260 (d, $J_{C\text{-}F}$= 264.0 Hz), 143.08 (d, $J_{C\text{-}F}$= 7.9 Hz), 138.81 (d, $J_{C\text{-}F}$= 1.6 Hz), 136.55, 136.35 (d, $J_{C\text{-}F}$= 19.0 Hz), 136.29 (d, $J_{C\text{-}F}$= 23.7 Hz), 134.86 (d, $J_{C\text{-}F}$= 3.3 Hz), 131.877, 131.605, 130.071 (d, $J_{C\text{-}F}$= 18.1 Hz), 130.070, 128.873, 128.330, 117.90 (d, $J_{C\text{-}F}$= 21.8 Hz), 115.56 (d, $J_{C\text{-}F}$= 21.6 Hz), 115.30 (d, $J_{C\text{-}F}$= 21.0 Hz), 114.55 (d, $J_{C\text{-}F}$= 21.2 Hz), 49.835. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{20}H_{13}F_2O$ 307.0929; found 307.0934.



3ha + 3ha-Iso

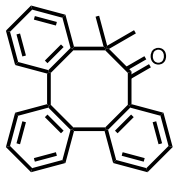
13-methyltribenzo[a,c,e][8]annulen-9(10H)-one (**3ha**) + 2-methyltribenzo[a,c,e][8]annulen-9(10H)-one (**3ha-Iso**): white solid, actual mass 29.6 mg, 52% yield, (eluent: petroleum ether/ethyl acetate = 50:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 – 7.68 (m, 1H), 7.50 – 7.40 (m, 1H), 7.40 – 7.20 (m, 6H), 7.16 – 6.97 (m, 3H), 3.86 – 3.71 (m, 1.11H), 3.74 (s, 0.89H), 2.45 (s, 1.67H), 2.27 (s, 1.33H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.41, 202.22, 141.59, 141.31, 141.11, 140.31, 140.28, 139.80, 139.49, 138.32, 138.07, 137.10, 136.89, 136.87, 134.11, 132.14, 132.06, 131.61, 131.53, 131.12, 130.97, 130.95, 129.16, 128.94, 128.75, 128.68, 128.66, 128.62, 128.60, 128.54, 128.43, 128.26, 128.18, 127.89, 127.73, 127.58, 127.43, 49.94, 49.42, 21.17, 21.11. HRMS (ESI) m/z: [M

+ H]$^+$ calcd for $C_{21}H_{17}O$ 285.1274; found 285.1259.



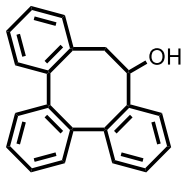
5aa

tribenzo[a,c,e][8]annulene-9,10-dione (**5aa**) : chartreuse solid, actual mass 48.3 mg, 85% yield, (eluent: petroleum ether/ethyl acetate = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.34 (m, 8H), 7.28 (dd, *J* = 6.4, 3.0 Hz, 2H), 7.22 (d, *J* = 7.6 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.94, 138.88, 137.62, 136.29, 131.80, 130.61, 129.94, 129.03, 128.17, 126.93. HRMS (ESI) m/z: [M + H]$^+$ calcd for $C_{20}H_{13}O_2$ 285.0910; found 285.0896.



6aa

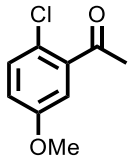
10,10-dimethyltribenzo[a,c,e][8]annulen-9(10H)-one (**6aa**) : white solid, actual mass 43.6 mg, 73% yield, (eluent: petroleum ether/ethyl acetate = 20:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 – 7.35 (m, 2H), 7.27 – 7.10 (m, 9H), 7.07 (d, *J* = 7.5 Hz, 1H), 3.12 (s, 3H), 1.95 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 148.61, 141.78, 140.90, 140.82, 140.64, 139.68, 134.09, 128.27, 128.04, 127.79, 127.51, 126.94, 126.71, 126.18, 126.08, 126.00, 126.00, 125.27, 118.12, 55.79, 16.52. HRMS (ESI) m/z: [M + Na]$^+$ calcd for $C_{22}H_{18}NaO$ 321.1250; found 321.1267.



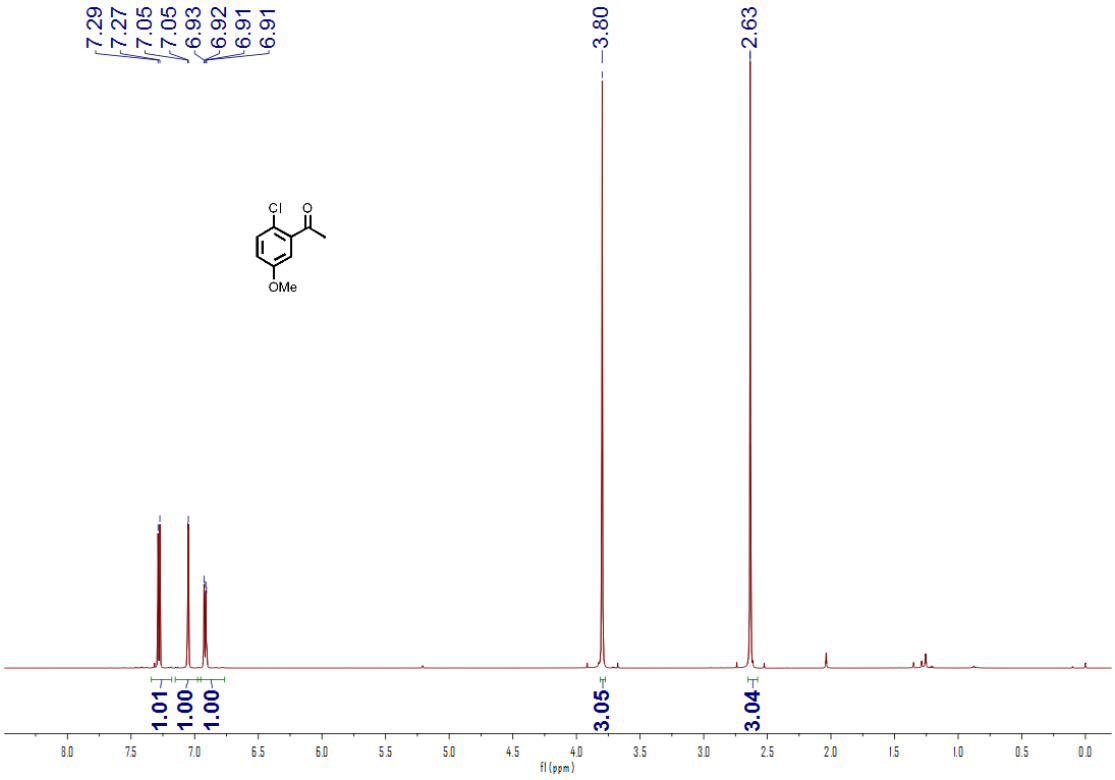
7aa^1+ 7aa^2

9,10-dihydrotribenzo[a,c,e][8]annulen-9-ol (**7aa^1+ 7aa^2**) : white solid, actual mass 48.0 mg, 88% yield, (eluent: petroleum ether/ethyl acetate = 20:1). **7aa^1**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.38 (m, 3H), 7.29 – 7.26 (m, 1H), 7.21 – 7.08 (m, 7H), 7.02 – 6.94 (m, 1H), 5.05 (t, *J* = 9.1 Hz, 1H), 3.28 (dd, *J* = 13.1, 8.6 Hz, 1H), 2.83 (dd, *J* = 13.1, 9.7 Hz, 1H), 1.70 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.11, 141.84, 140.66, 139.71, 139.60, 137.01, 132.86, 130.98, 129.81, 128.28, 128.07, 128.00, 127.79, 127.73, 127.72, 127.64, 127.47, 126.56, 77.90, 41.04. **7aa^2**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.8 Hz, 1H), 7.48 – 7.40 (m, 2H), 7.36 – 7.26 (m, 3H), 7.15 (td, *J* = 7.5, 1.0 Hz, 1H), 7.11 – 7.00 (m, 4H), 6.99 – 6.92 (m, 1H), 5.10 (t, *J* = 8.1 Hz, 3H), 3.61 (dd, *J* = 15.2, 8.1 Hz, 1H), 2.88 (dd, *J* = 15.2, 8.1 Hz, 1H), 1.92 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.24, 142.35, 140.95, 140.70, 139.35, 137.09, 130.90, 130.21, 129.20, 128.43, 128.11, 127.79, 127.68, 127.52, 127.22, 126.77, 126.06, 123.10, 70.04, 45.33. HRMS (ESI) m/z: [M + Na]$^+$ calcd for $C_{20}H_{16}NaO$ 295.1093; found 295.1089.

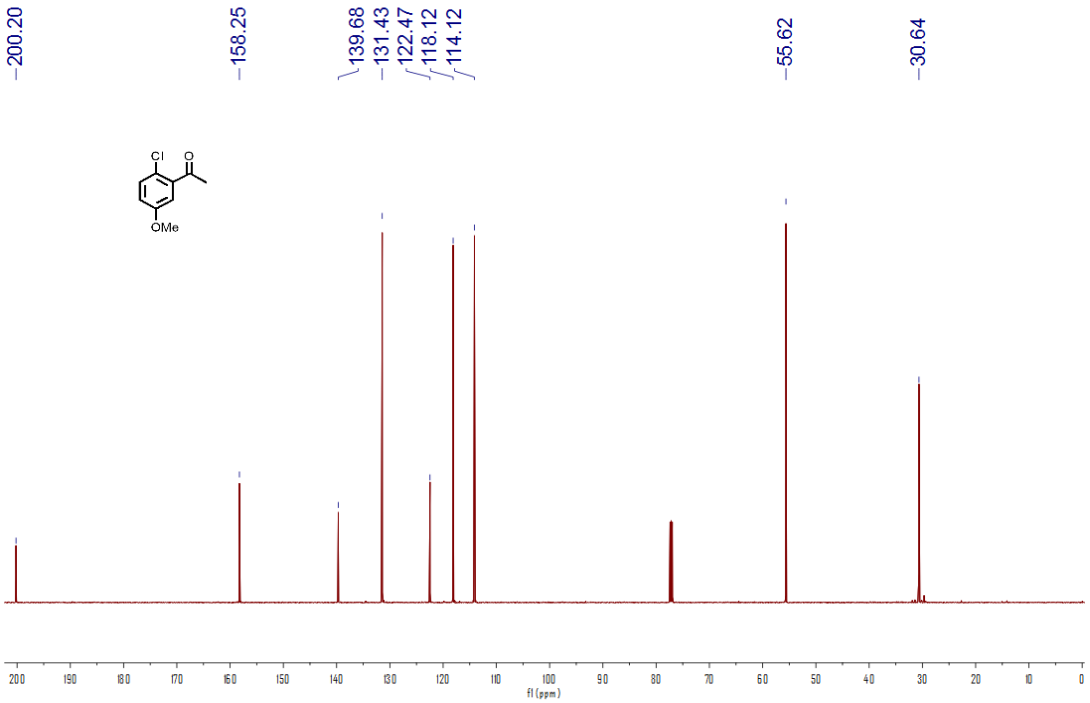
9. NMR Spectra



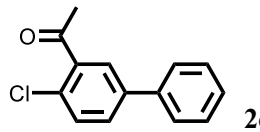
2b



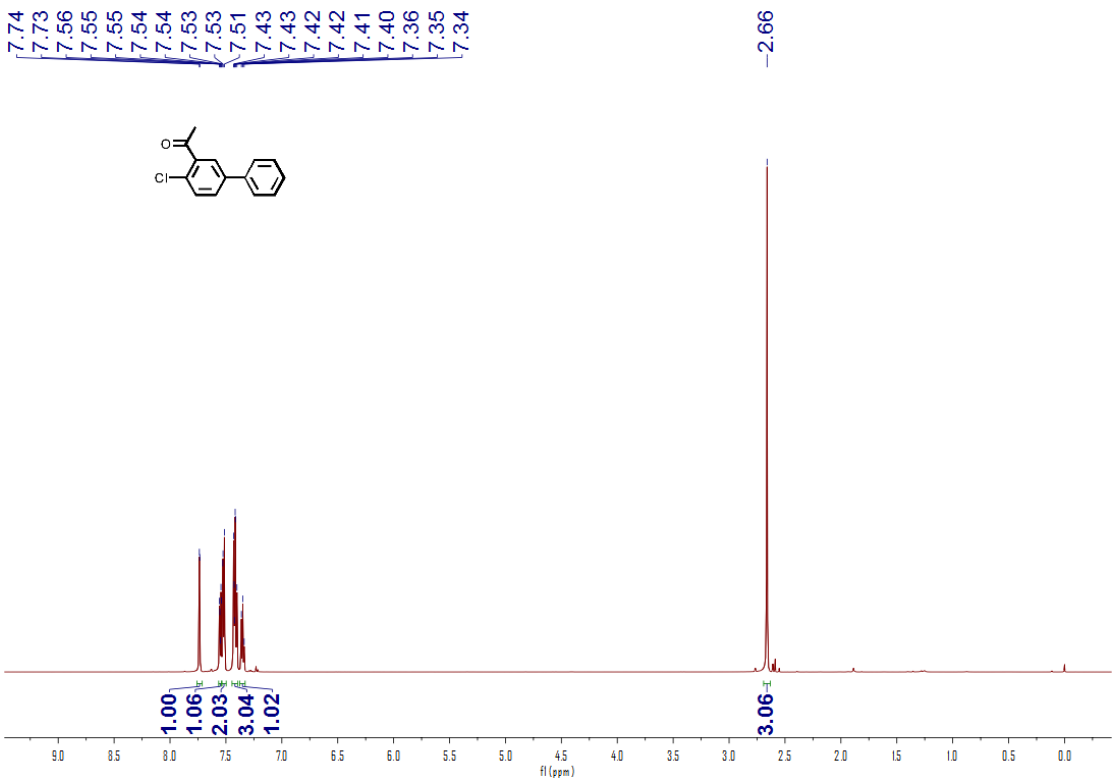
^{1}H NMR (600 MHz, $CDCl_3$)



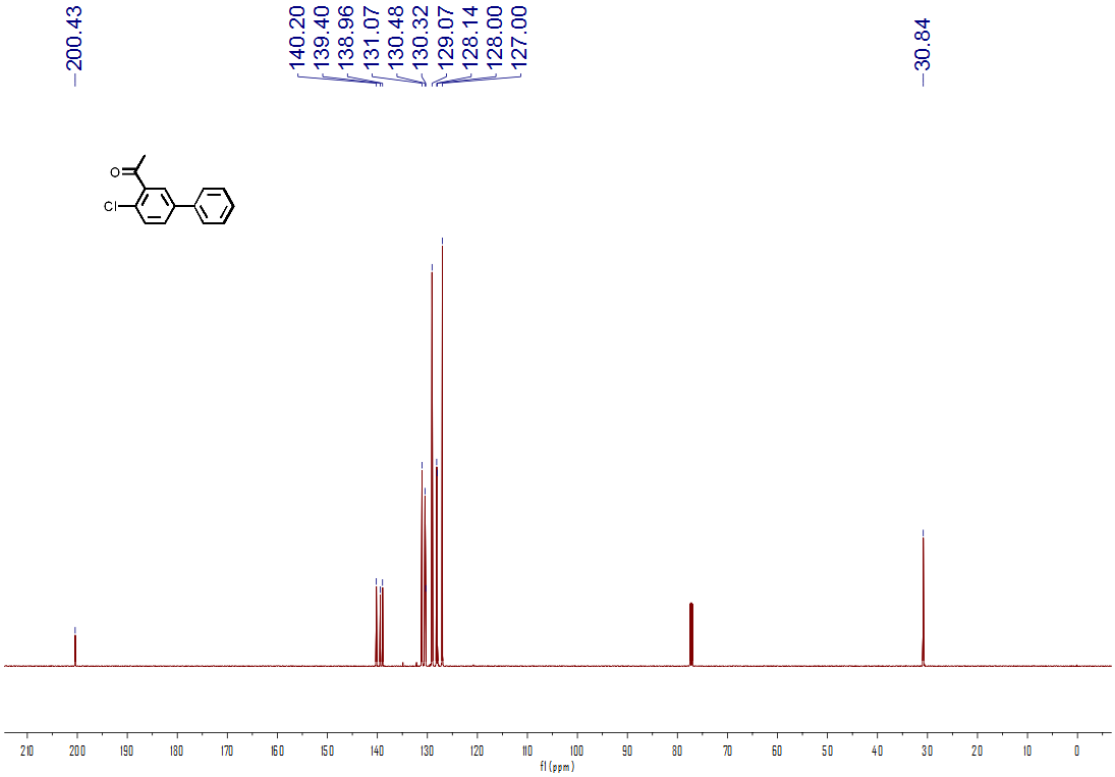
^{13}C NMR (151 MHz, $CDCl_3$)



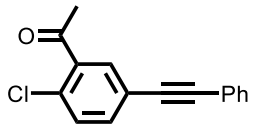
2c



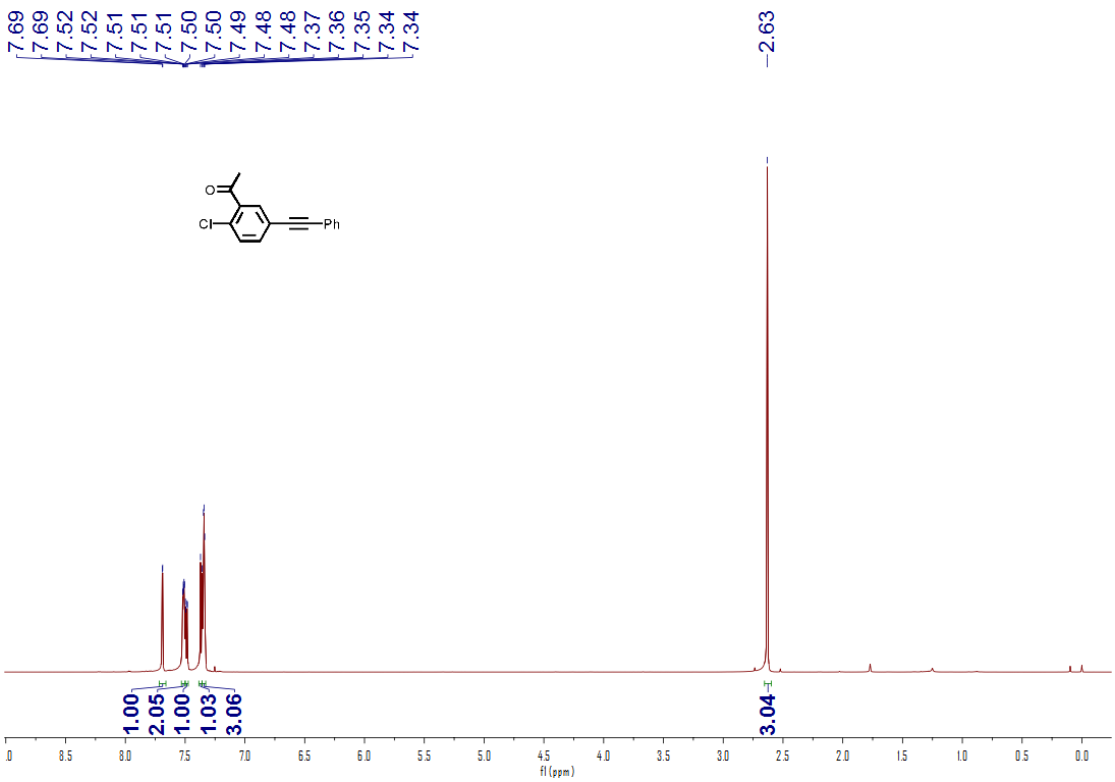
^{1}H NMR (600 MHz, $CDCl_3$)



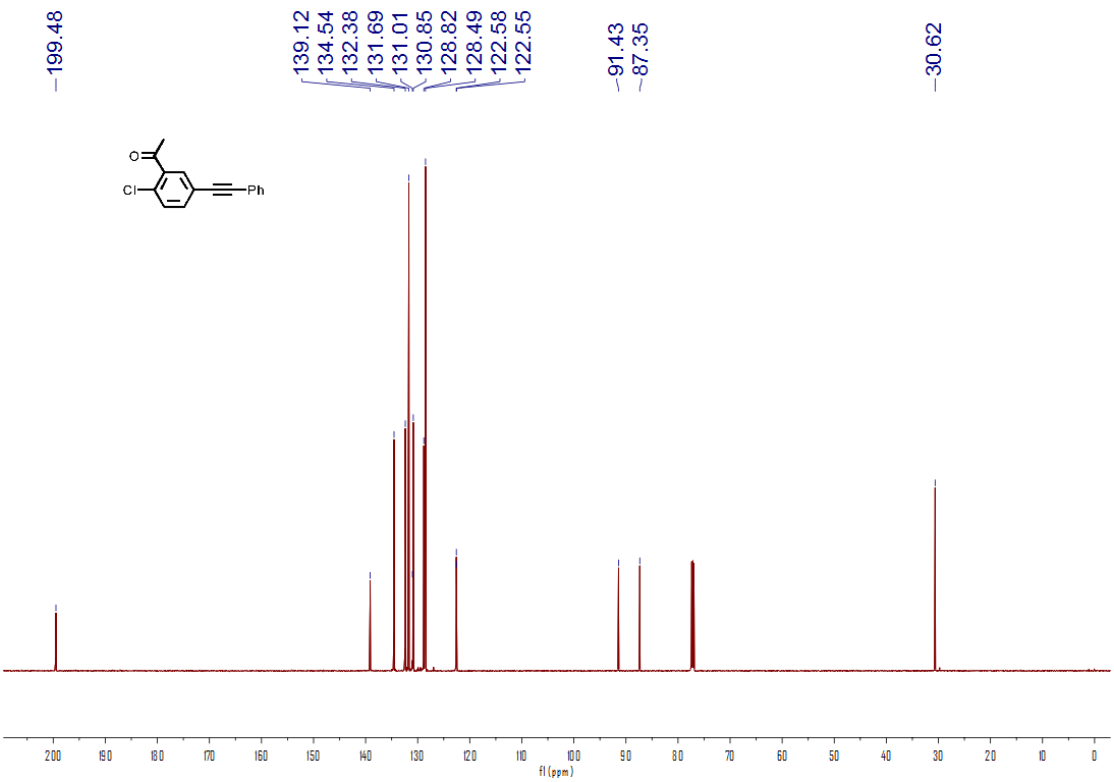
^{13}C NMR (151 MHz, $CDCl_3$)



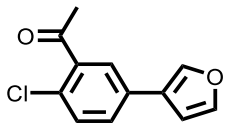
2h



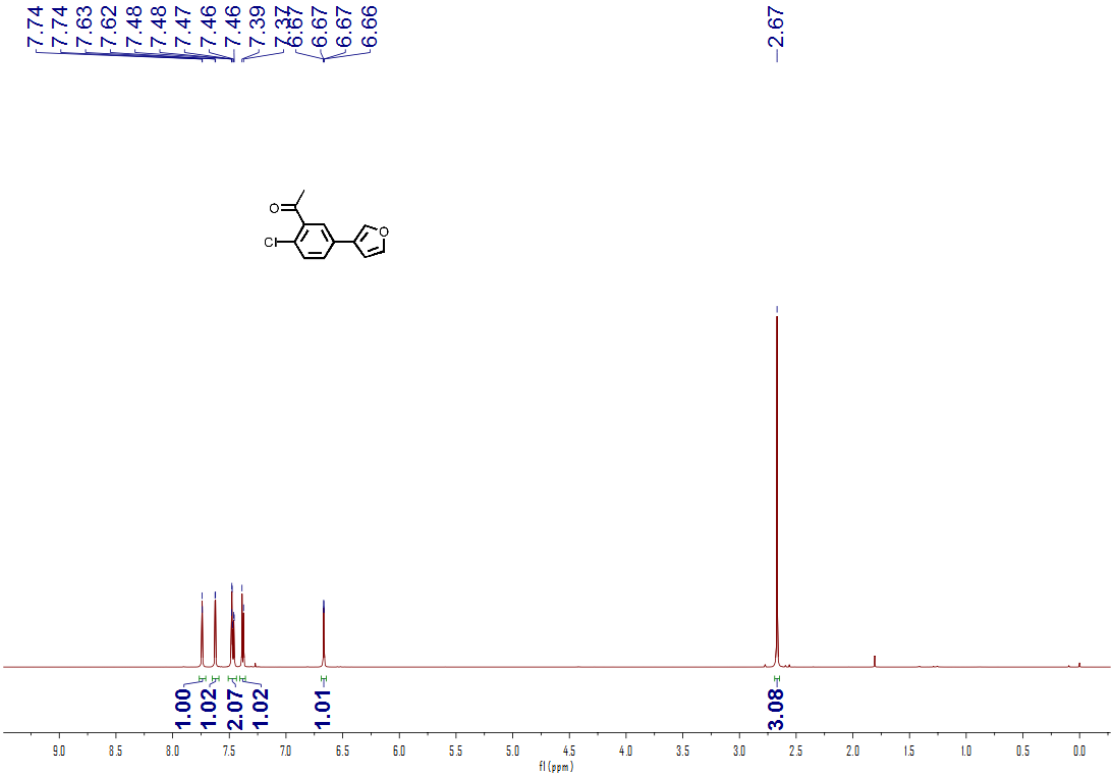
^{1}H NMR (600 MHz, $CDCl_3$)



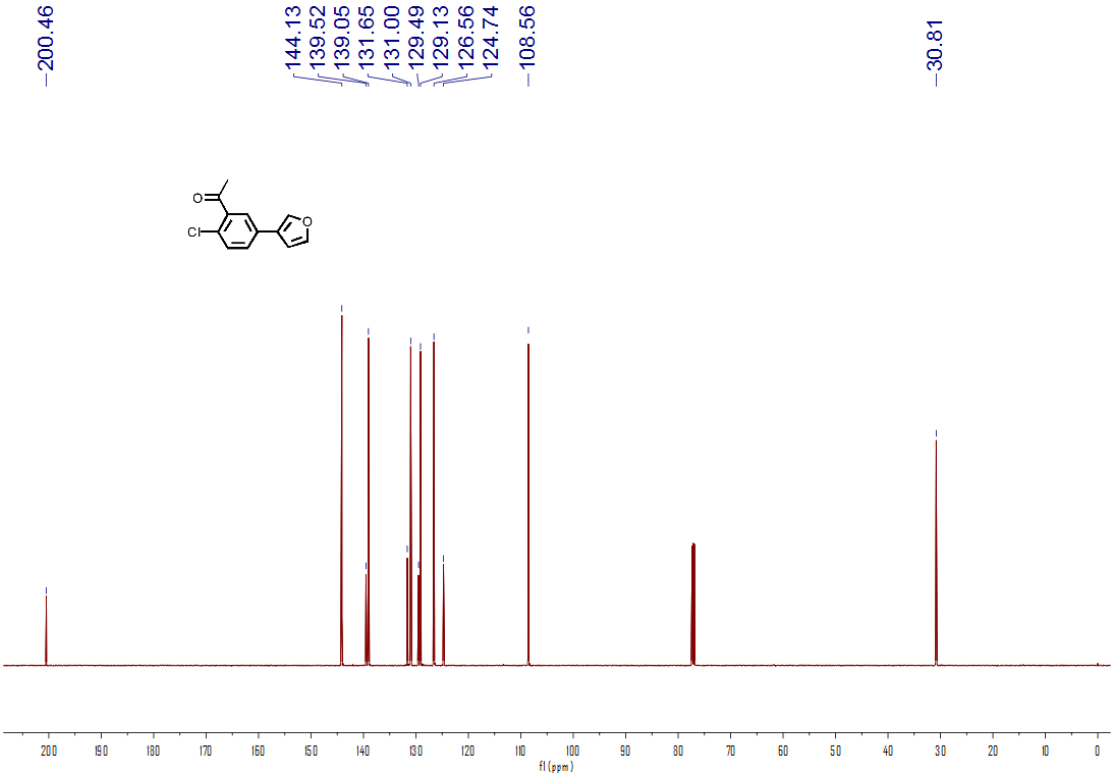
^{13}C NMR (151 MHz, $CDCl_3$)



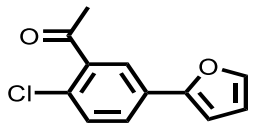
2i



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



^{13}C NMR (151 MHz, $CDCl_3$)



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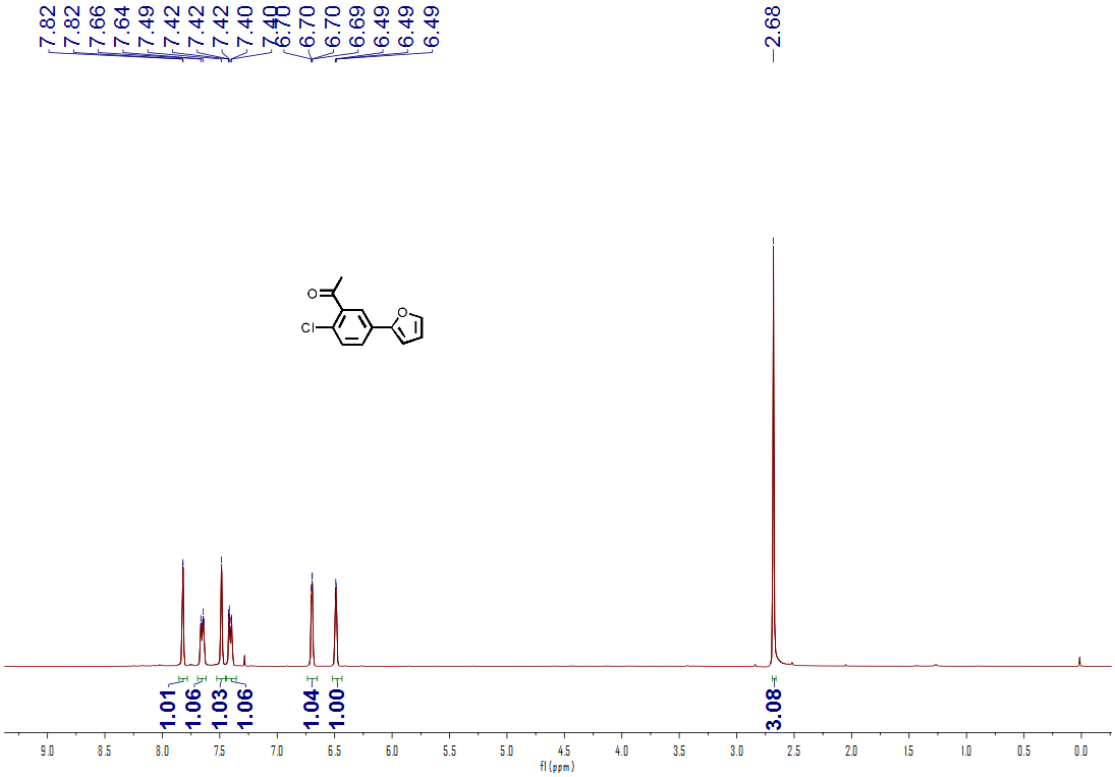
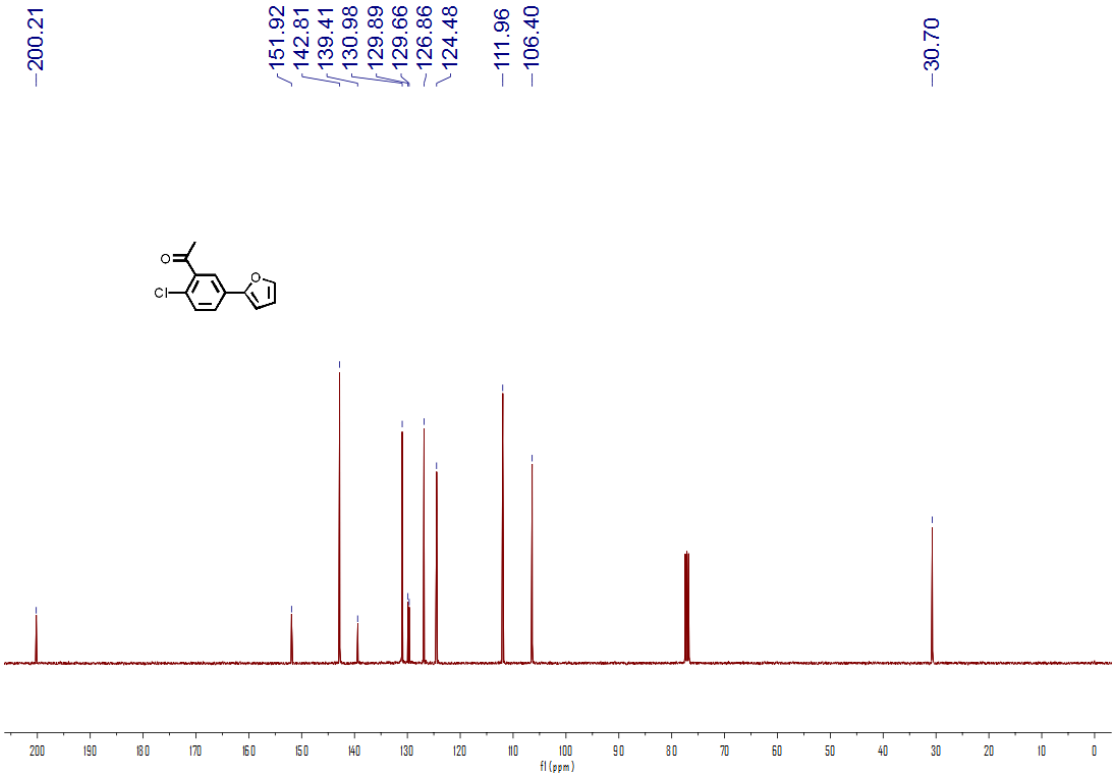
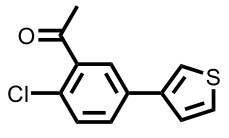


^{1}H NMR (400 MHz, $CDCl_3$)



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



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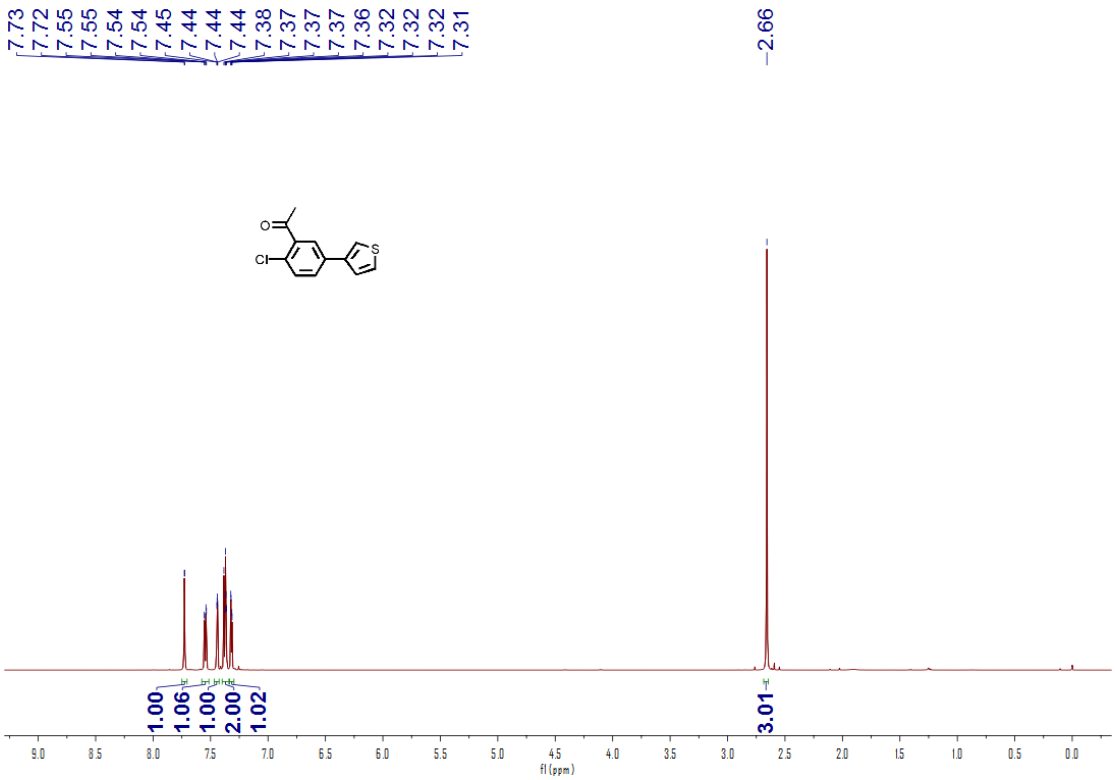
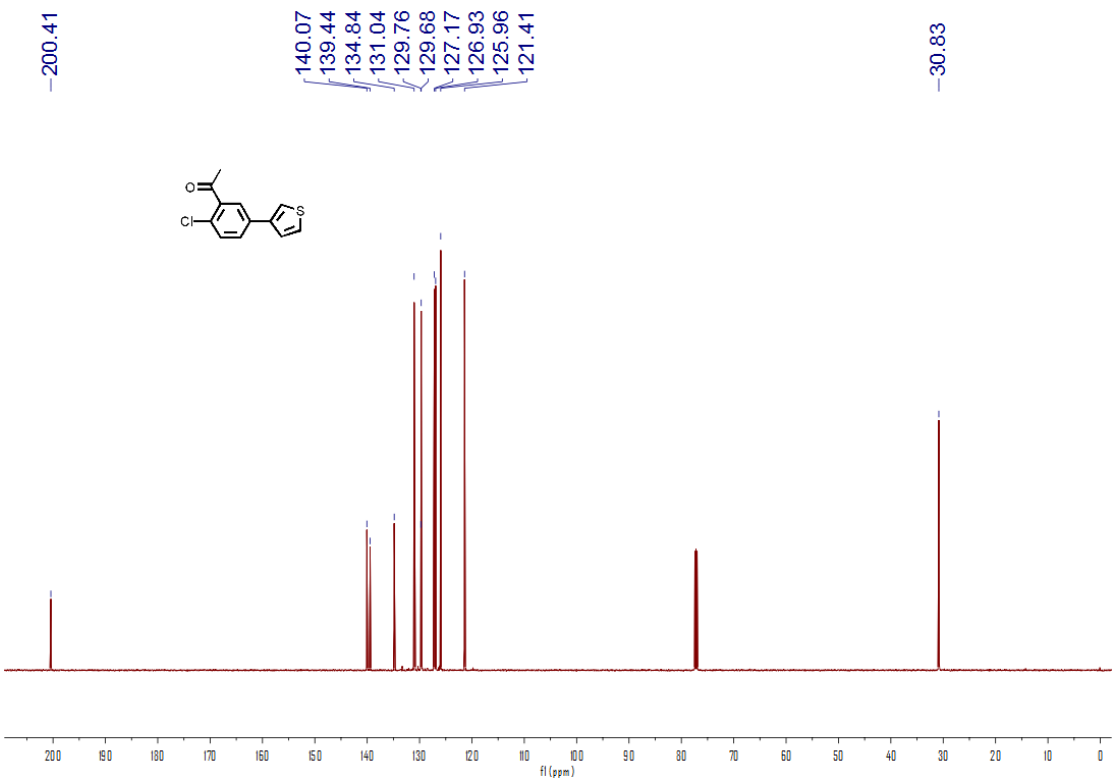
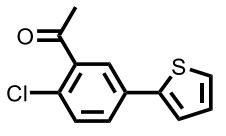


^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C NMR (151 MHz, $CDCl_3$)



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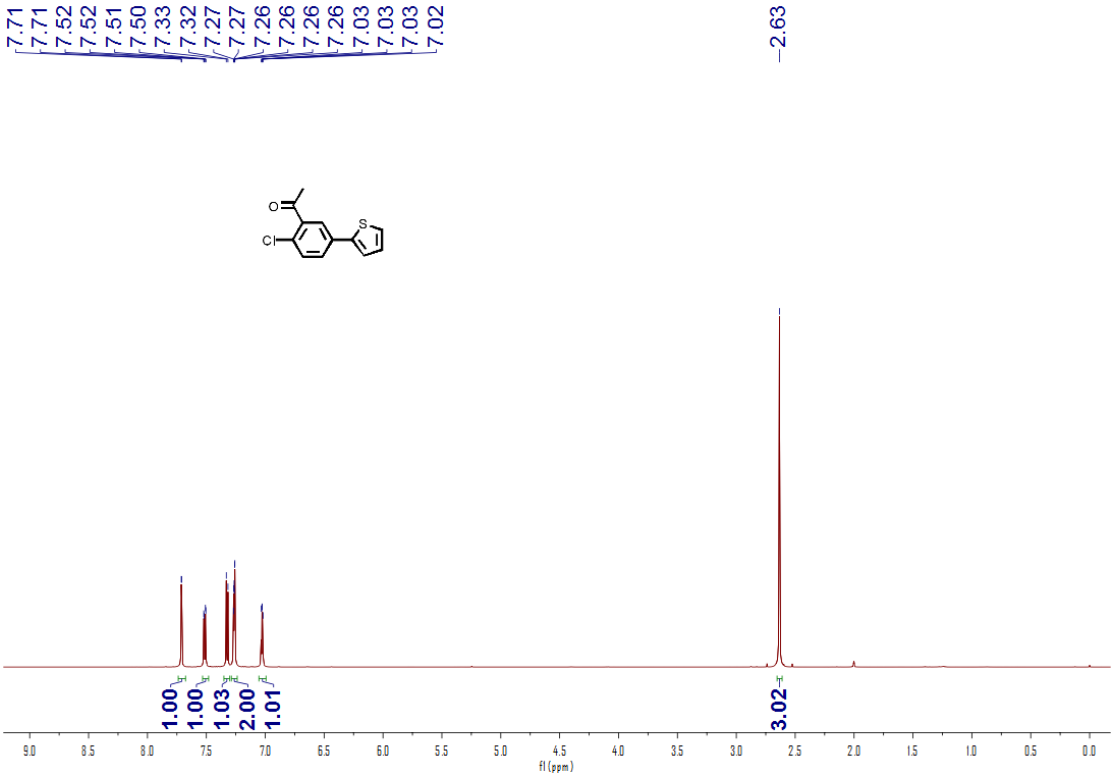
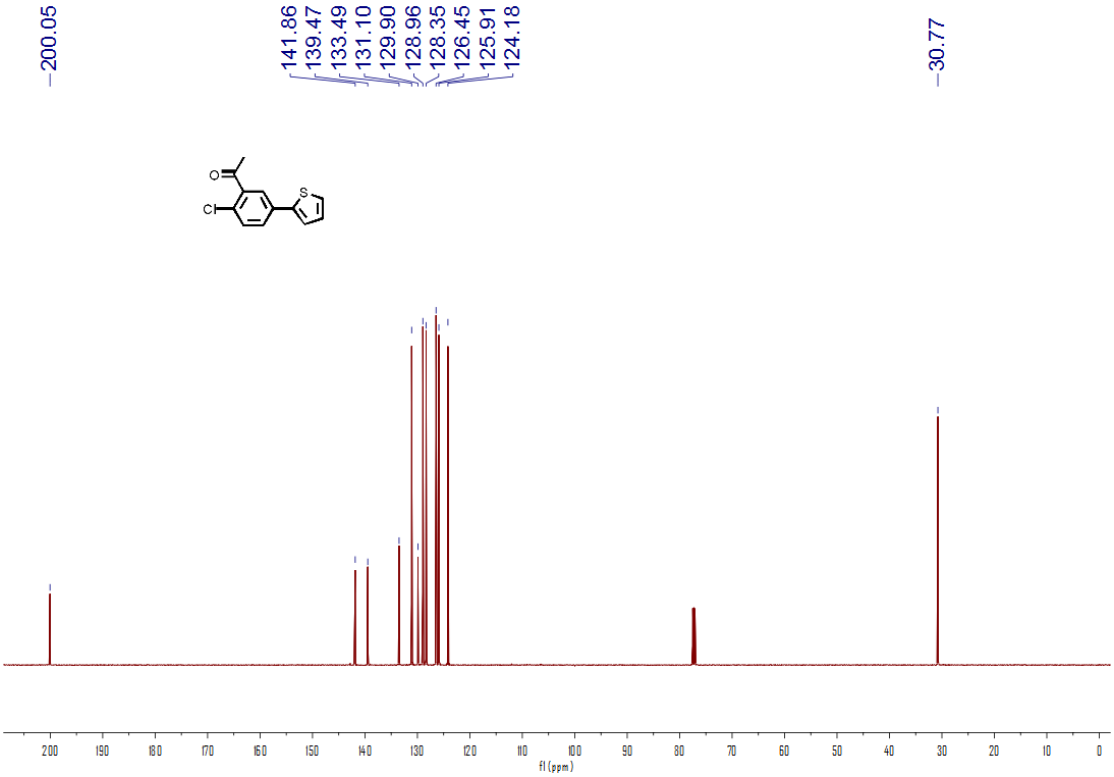
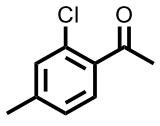


^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C NMR (151 MHz, $CDCl_3$)



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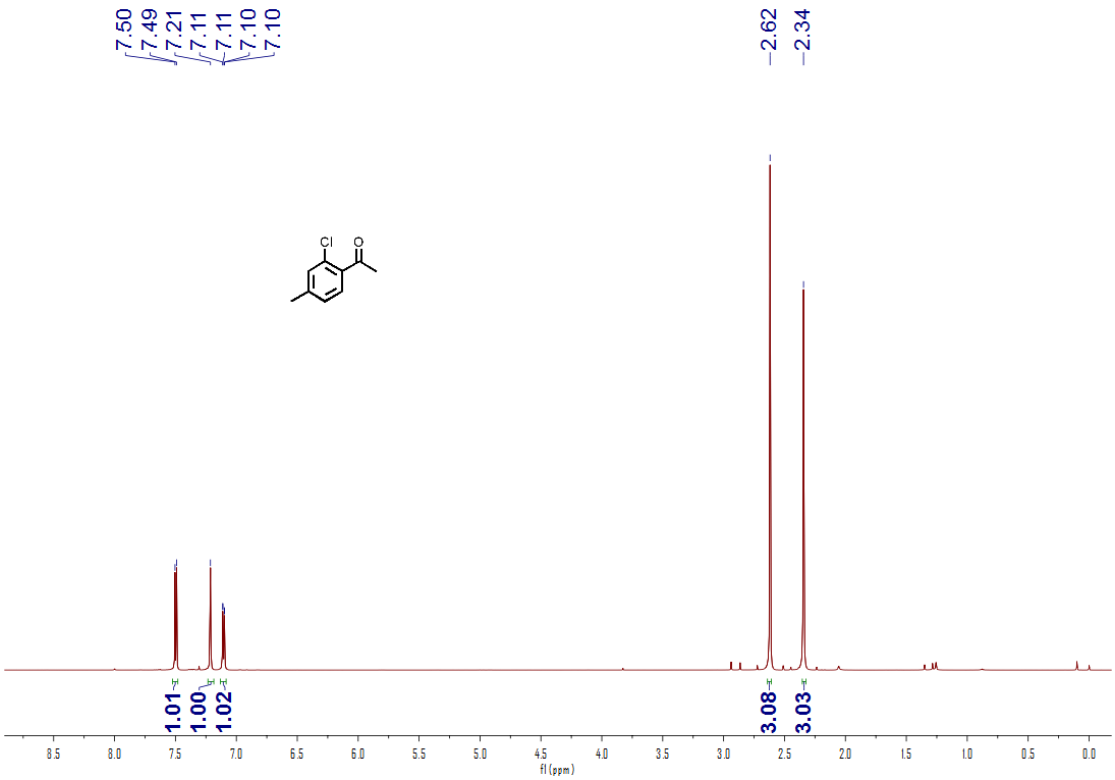
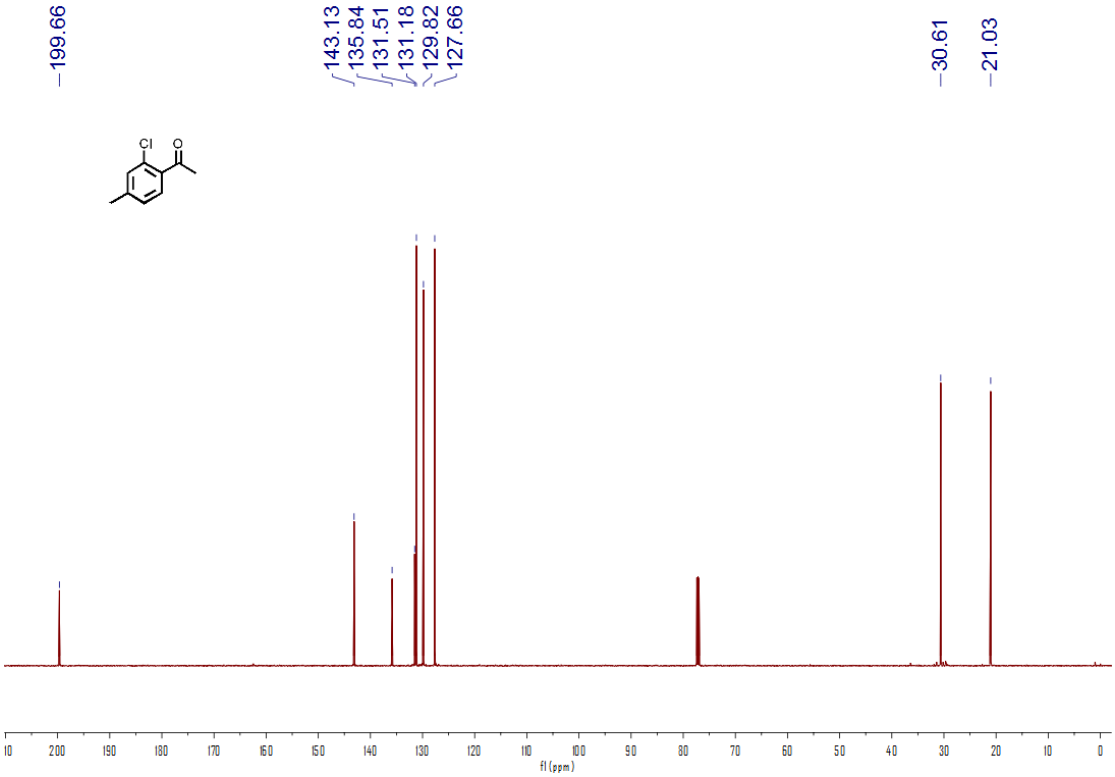
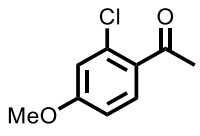


^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C NMR (151 MHz, $CDCl_3$)



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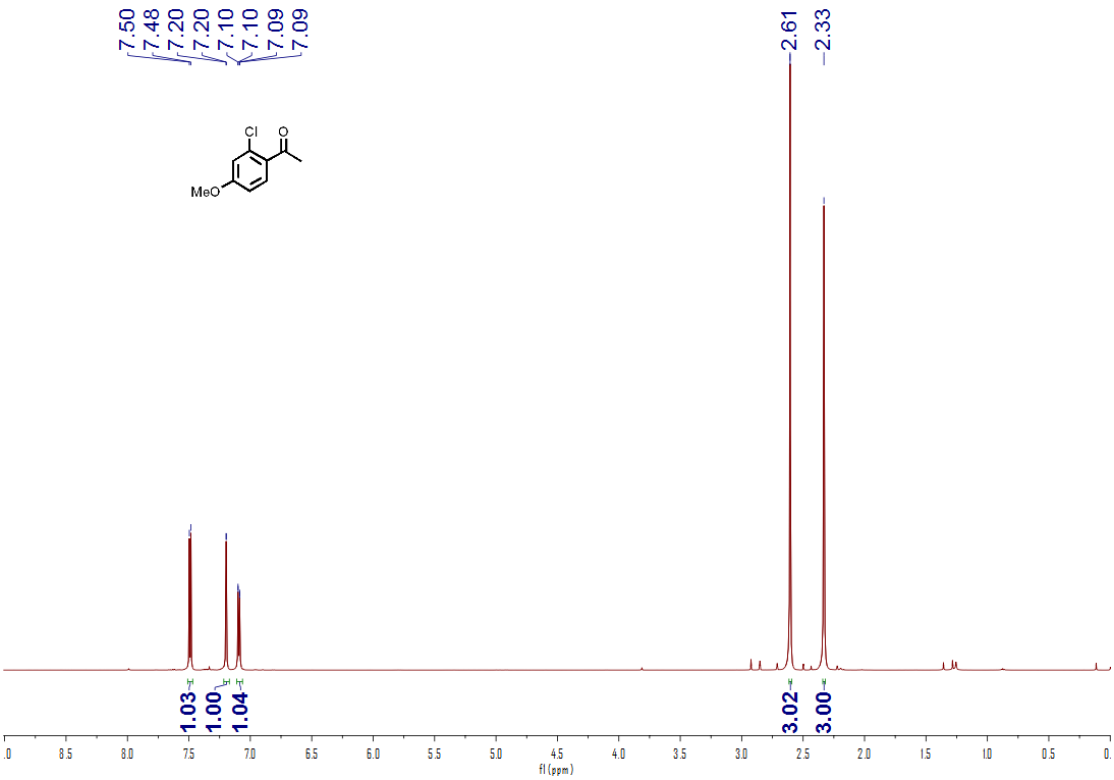
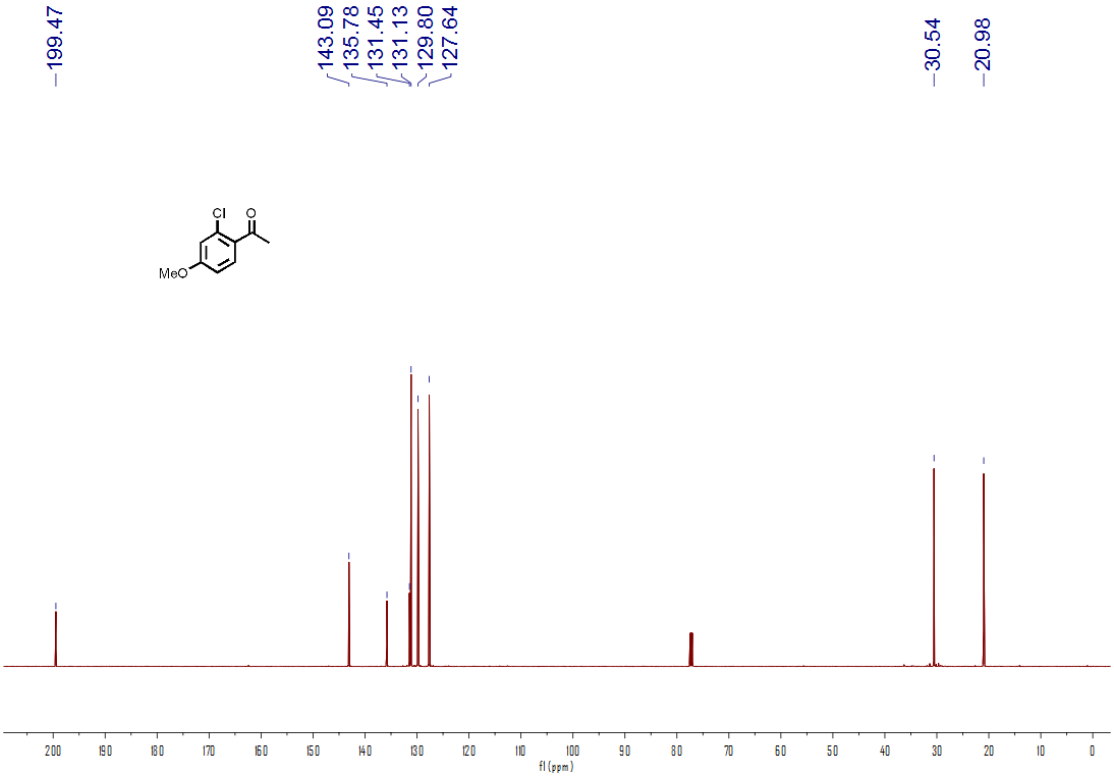
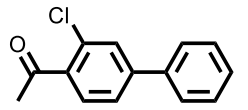


^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C NMR (151 MHz, $CDCl_3$)



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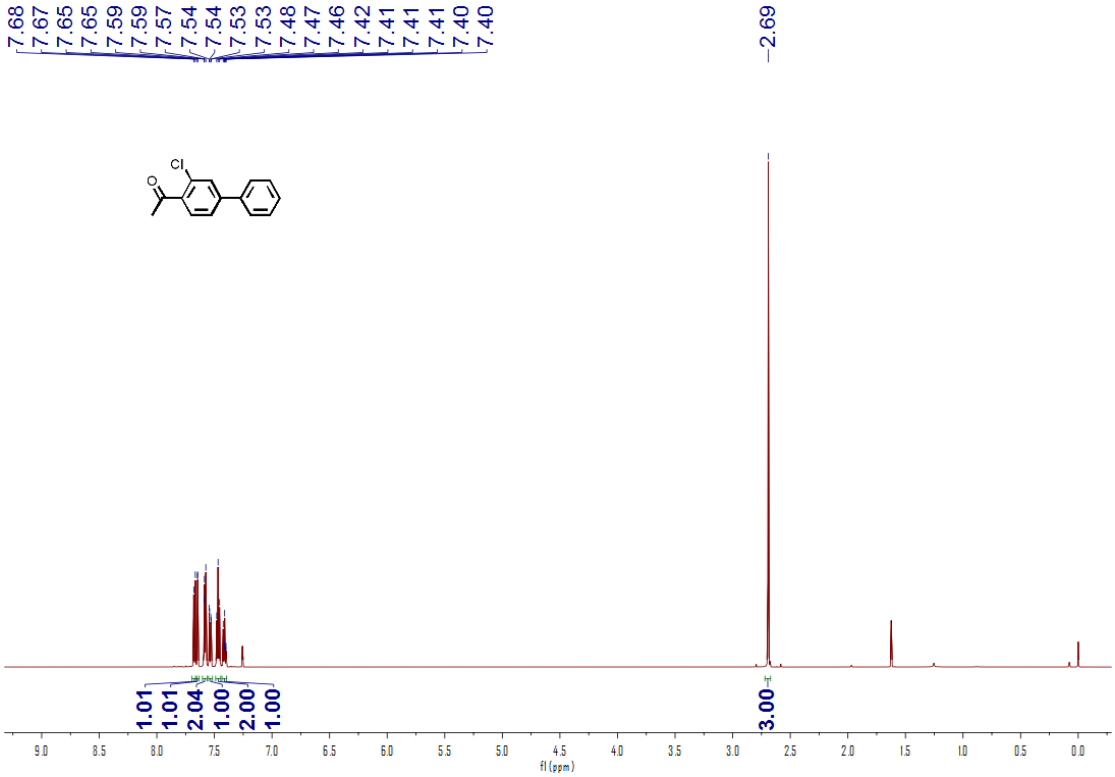
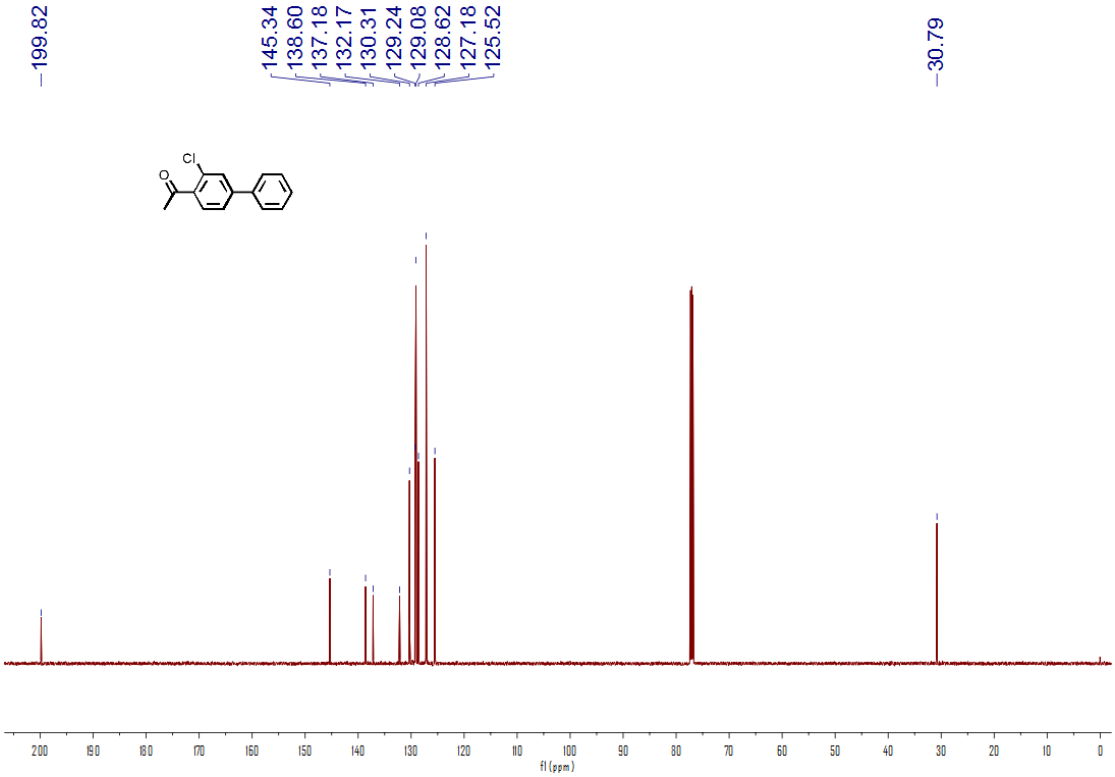
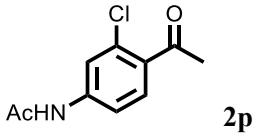


^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C NMR (151 MHz, $CDCl_3$)



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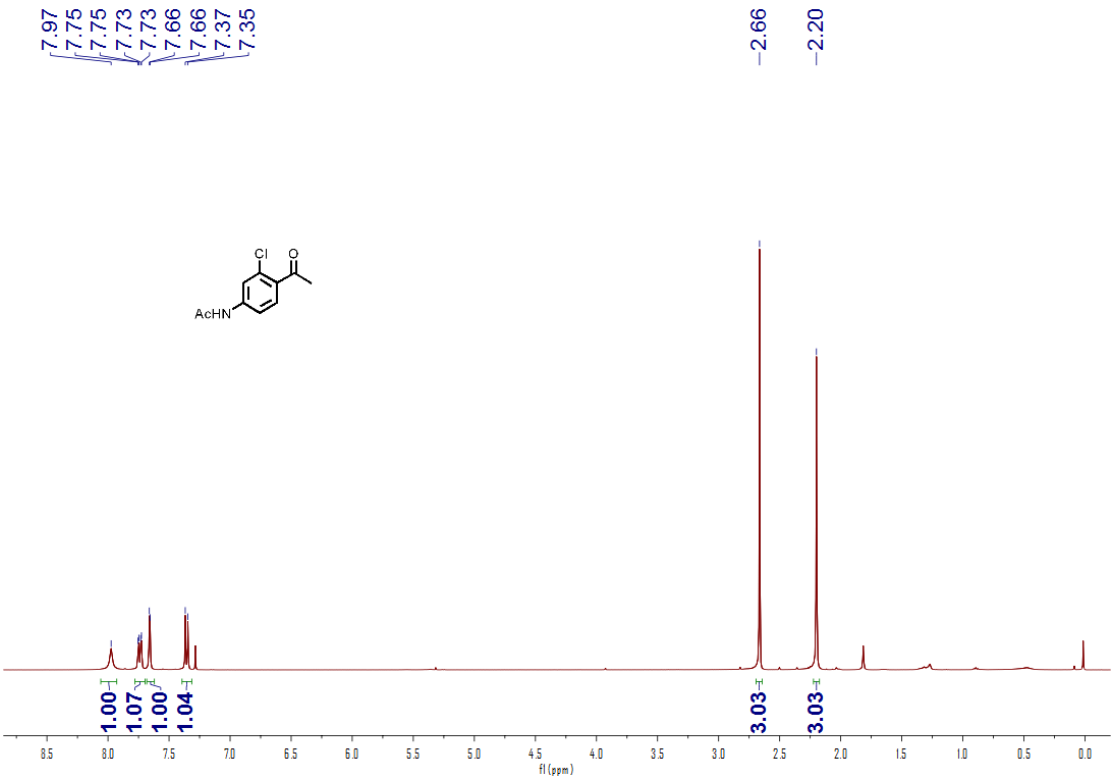
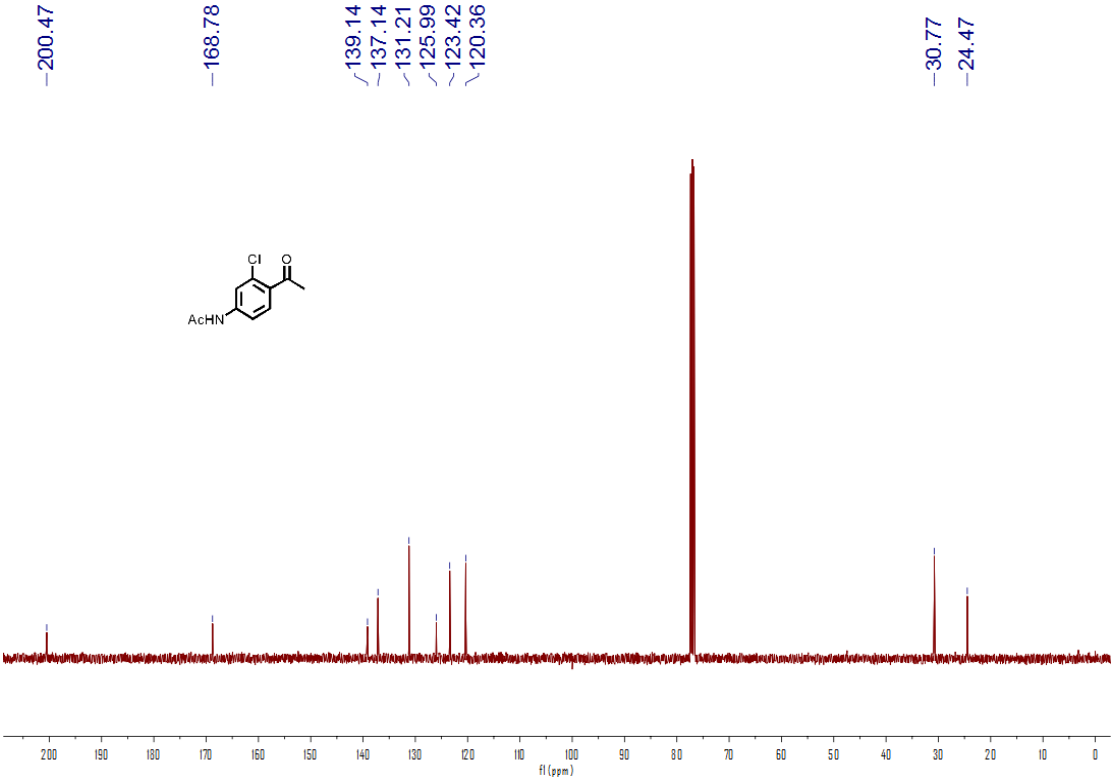
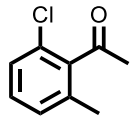


^{1}H NMR (400 MHz, $CDCl_3$)



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



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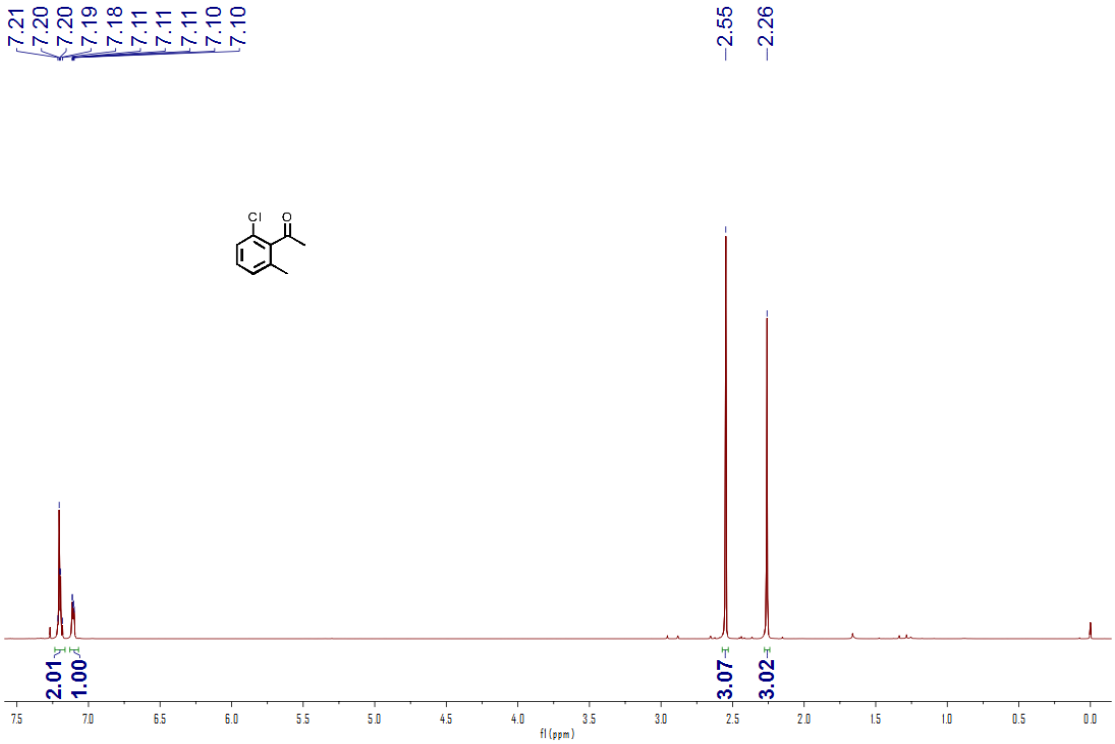
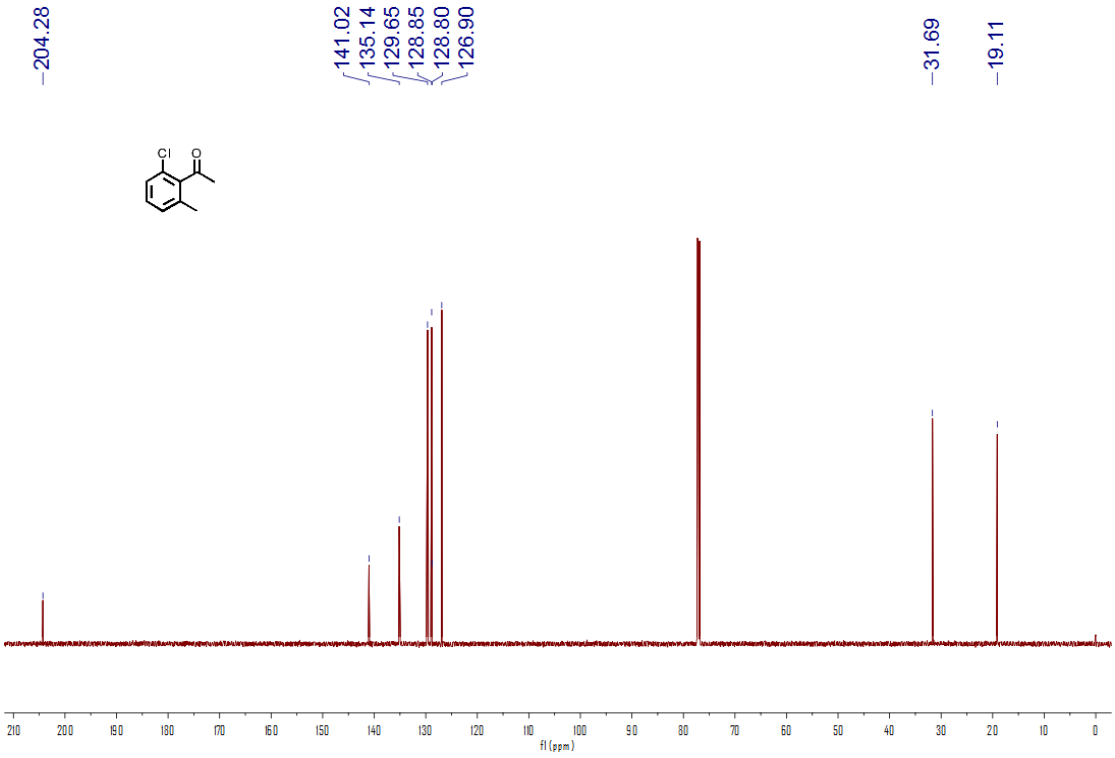
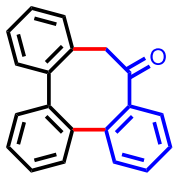


^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C NMR (151 MHz, $CDCl_3$)



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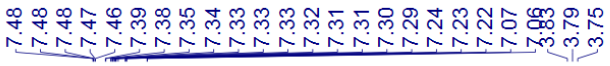
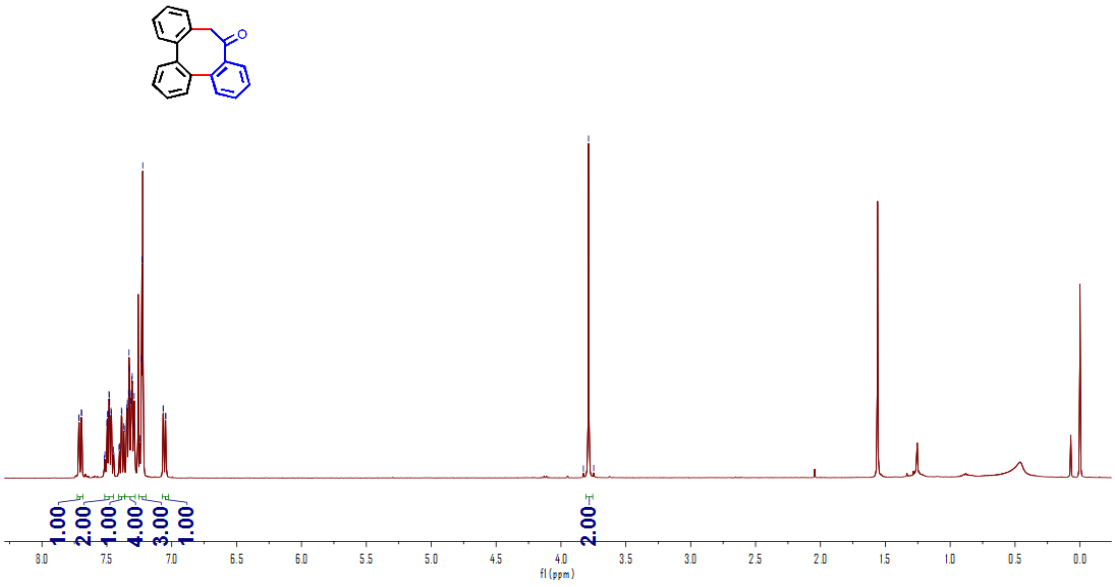
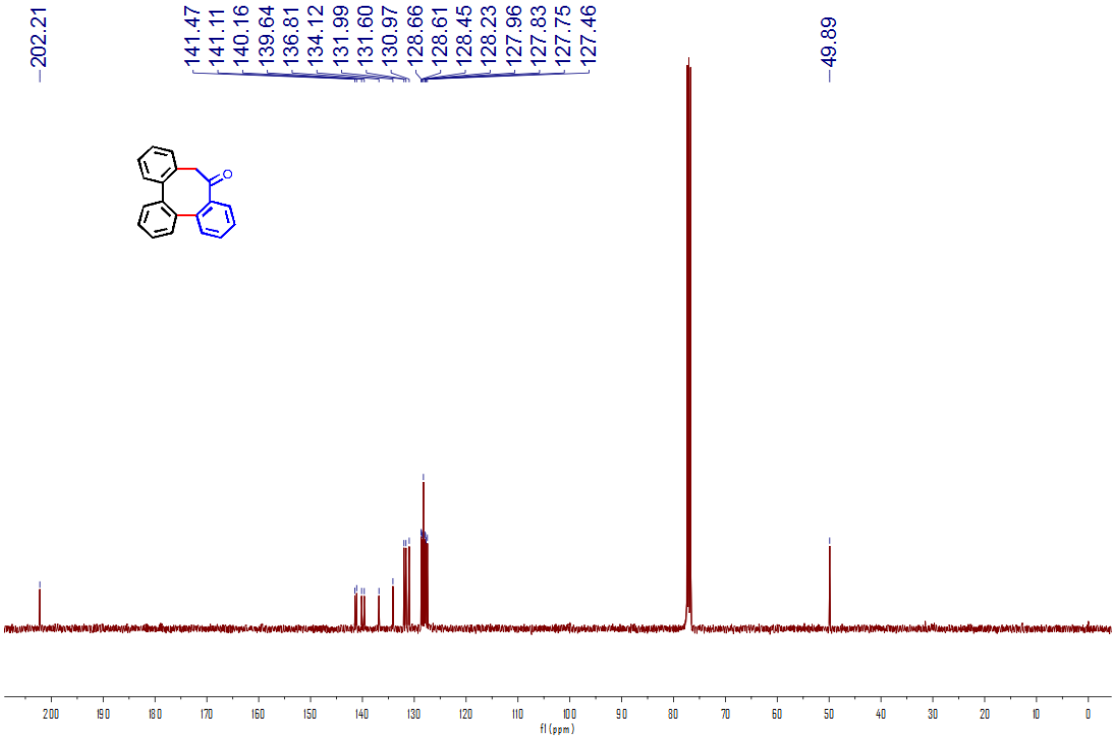
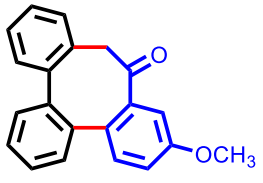




^{1}H NMR (400 MHz, $CDCl_3$)



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



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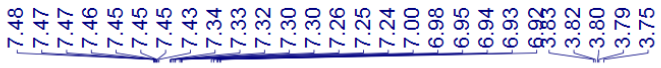
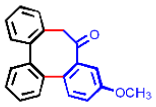
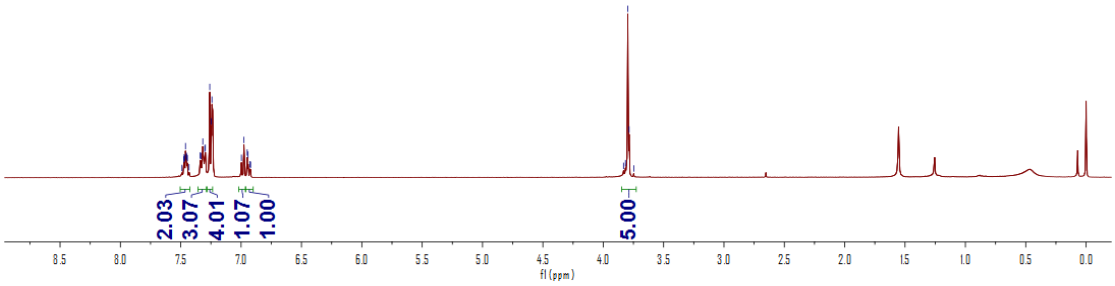
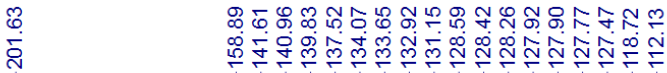
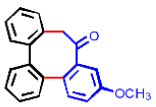




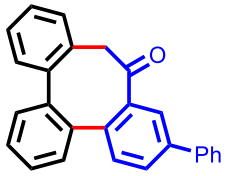


^{1}H NMR (400 MHz, $CDCl_3$)





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



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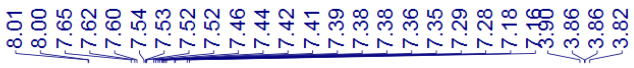
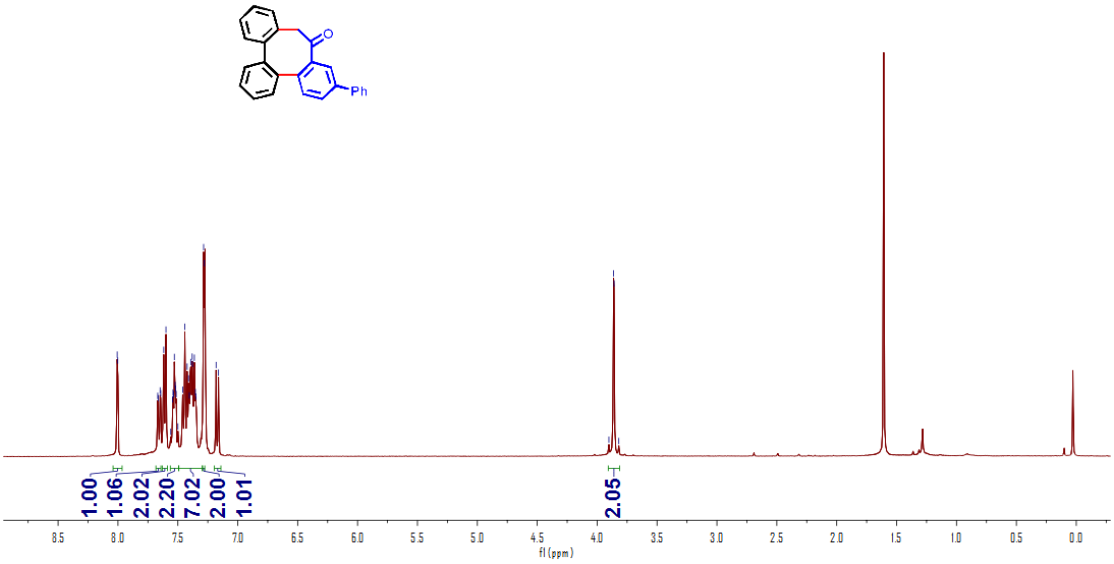
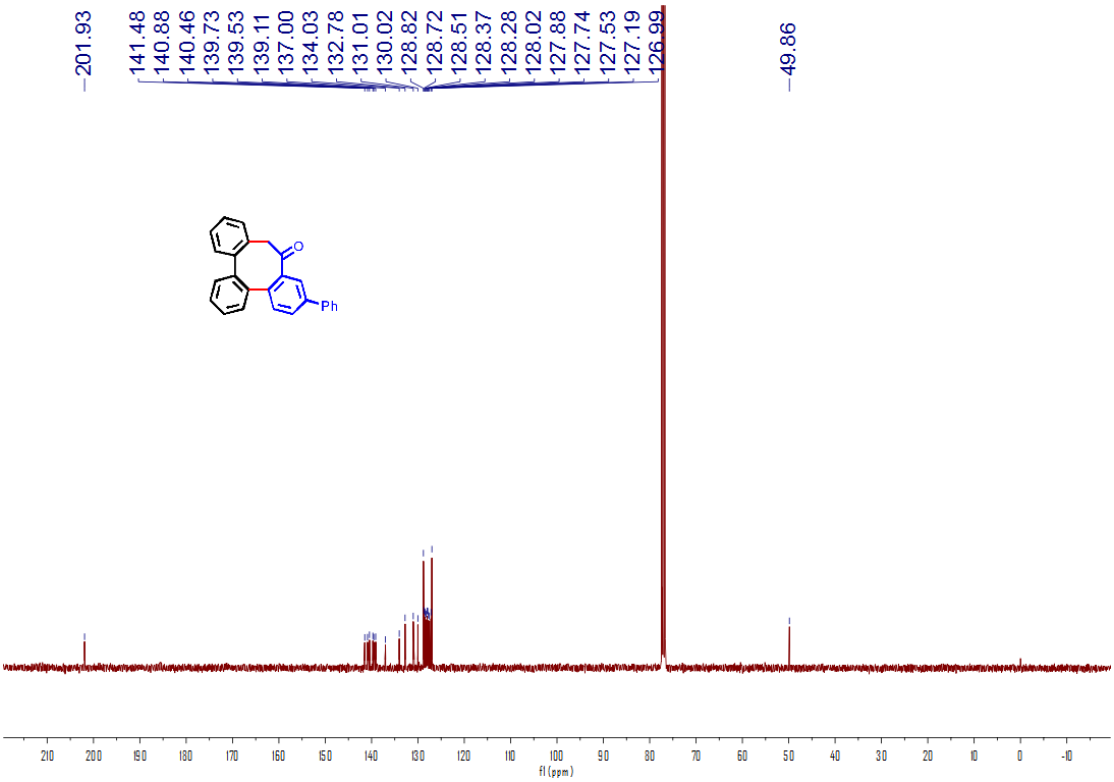
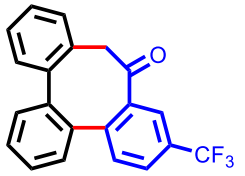




^{1}H NMR (400 MHz, $CDCl_3$)



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



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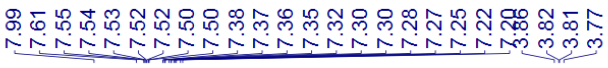
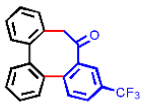
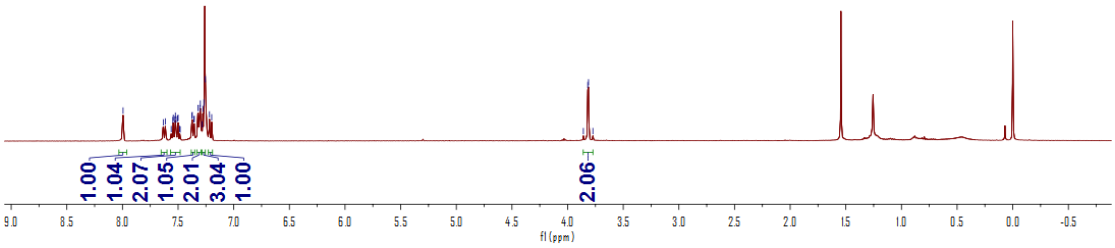
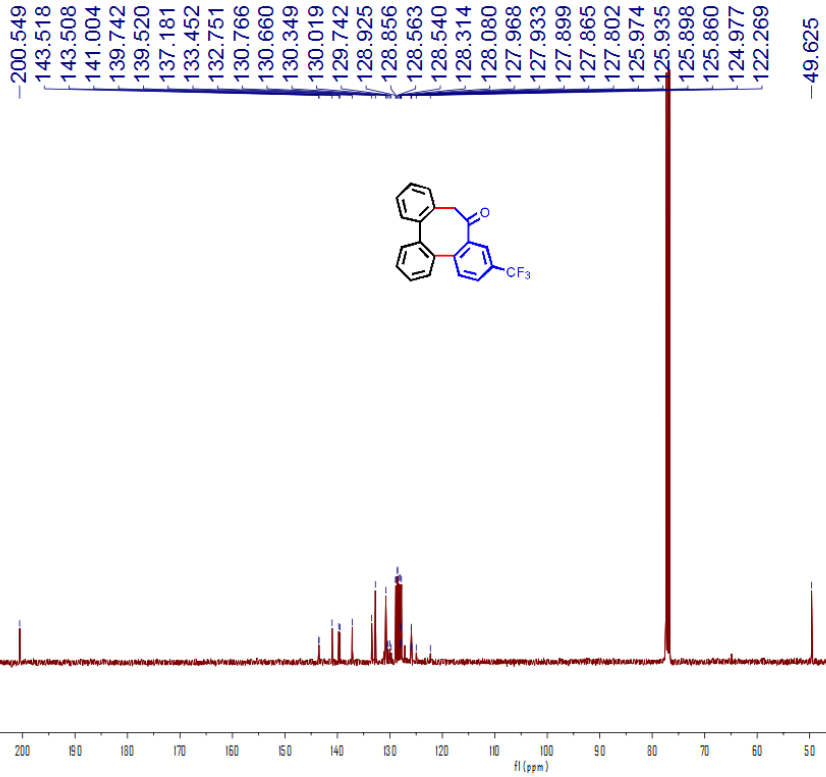


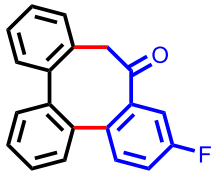




^{1}H NMR (400 MHz, $CDCl_3$)



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



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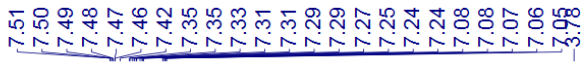
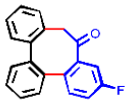
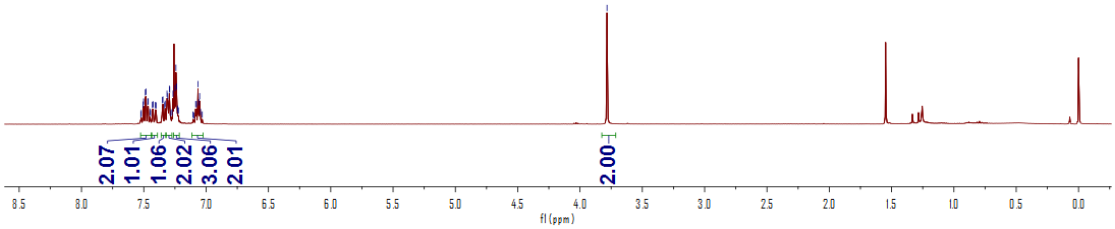
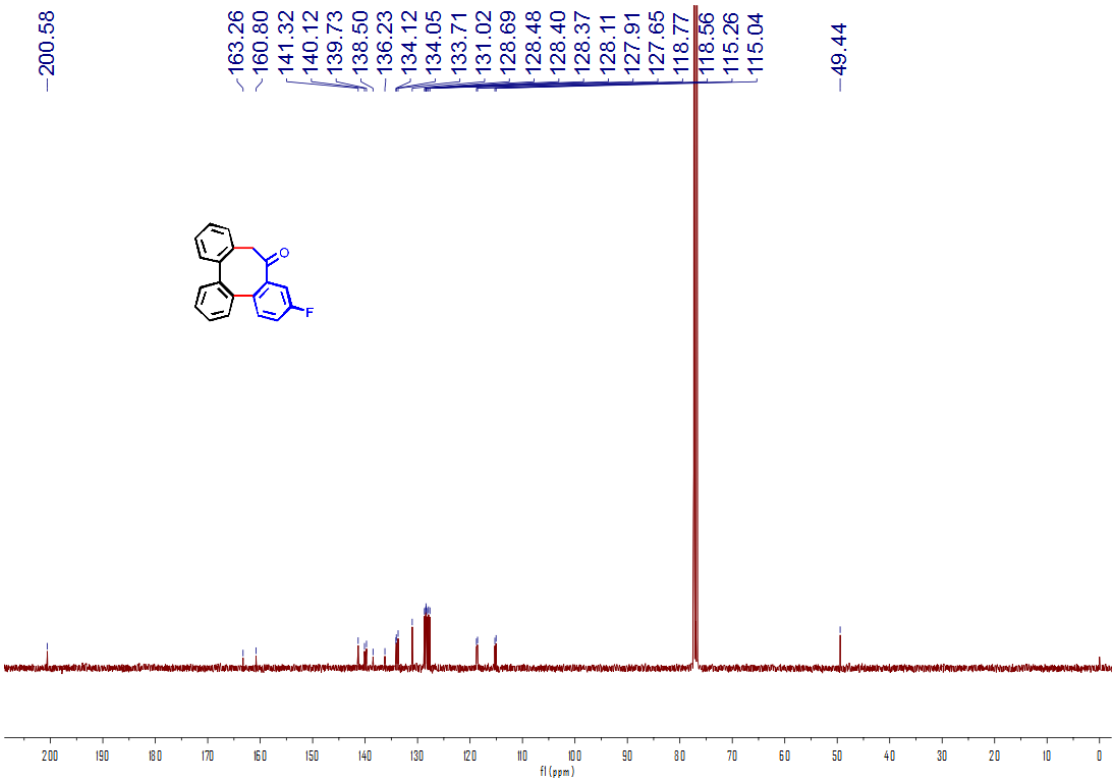


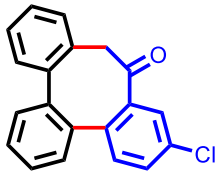




^{1}H NMR (400 MHz, $CDCl_3$)



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



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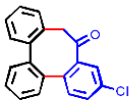
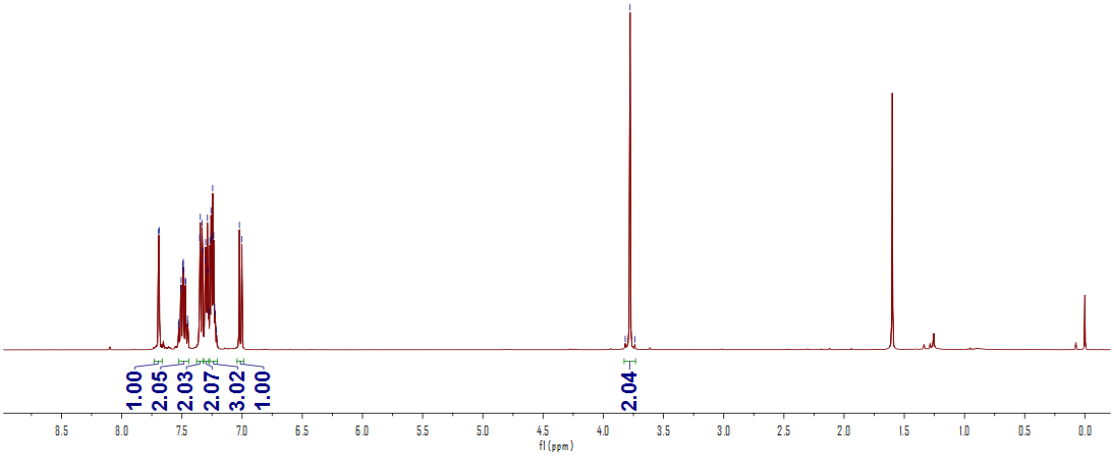
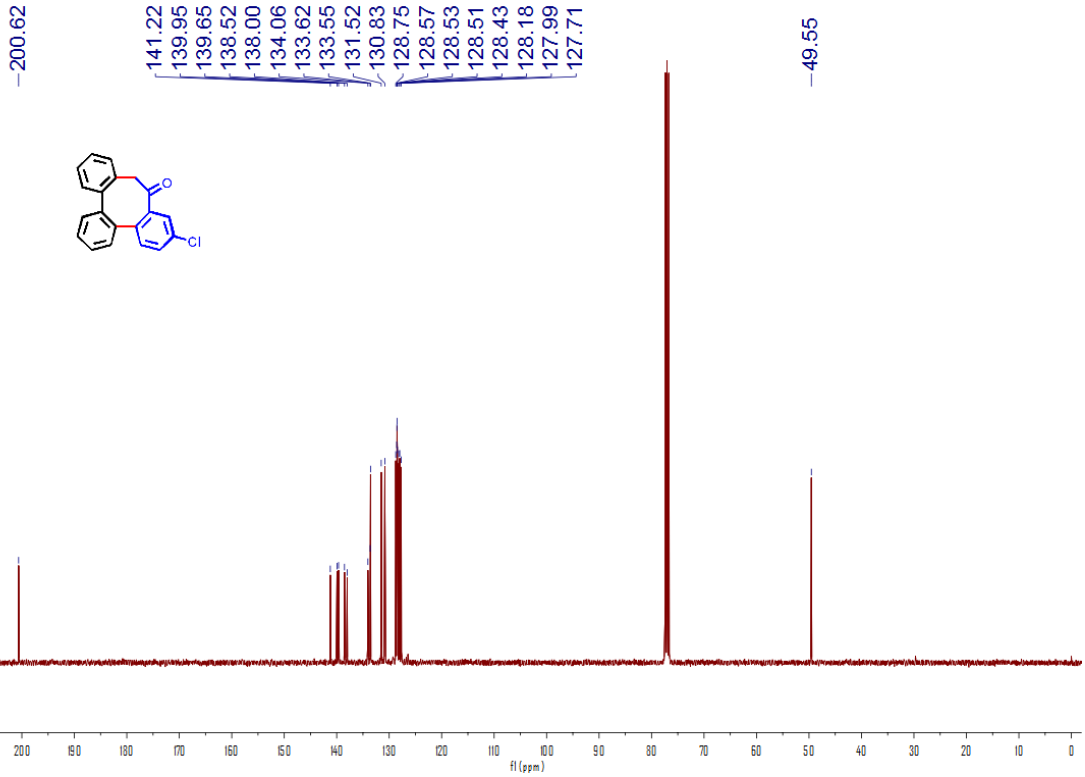
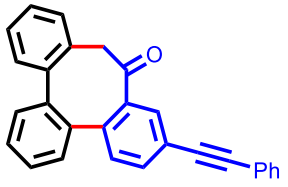




^{1}H NMR (400 MHz, $CDCl_3$)



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



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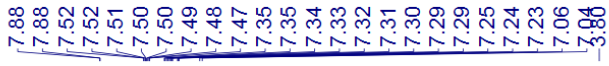
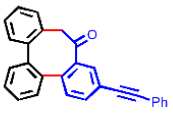
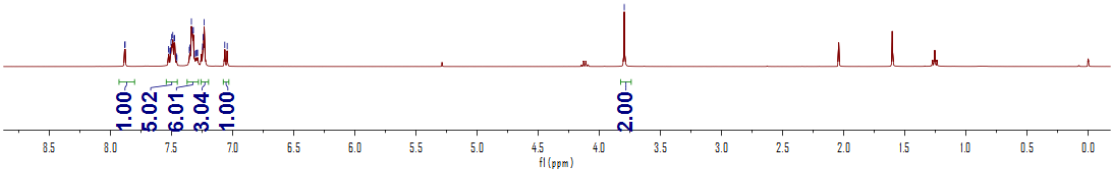
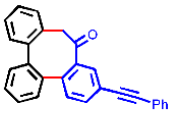


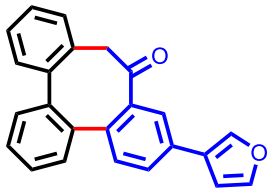




^{1}H NMR (400 MHz, $CDCl_3$)



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



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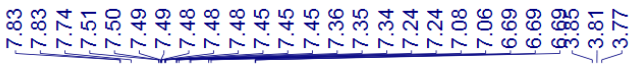
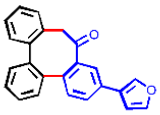
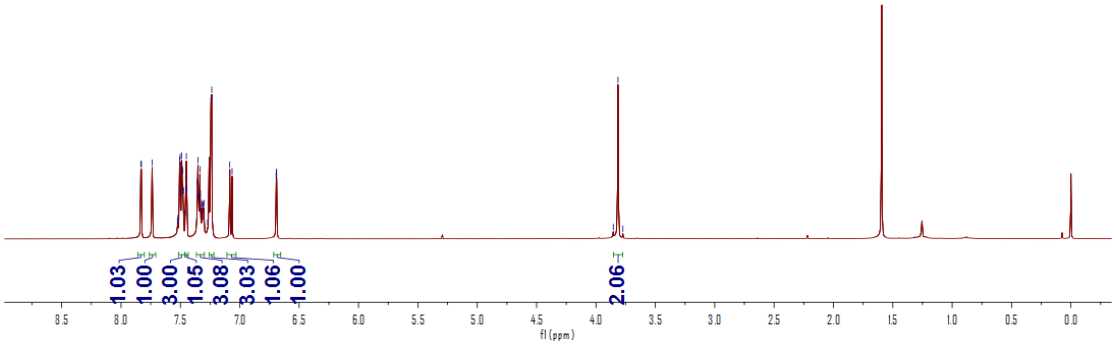
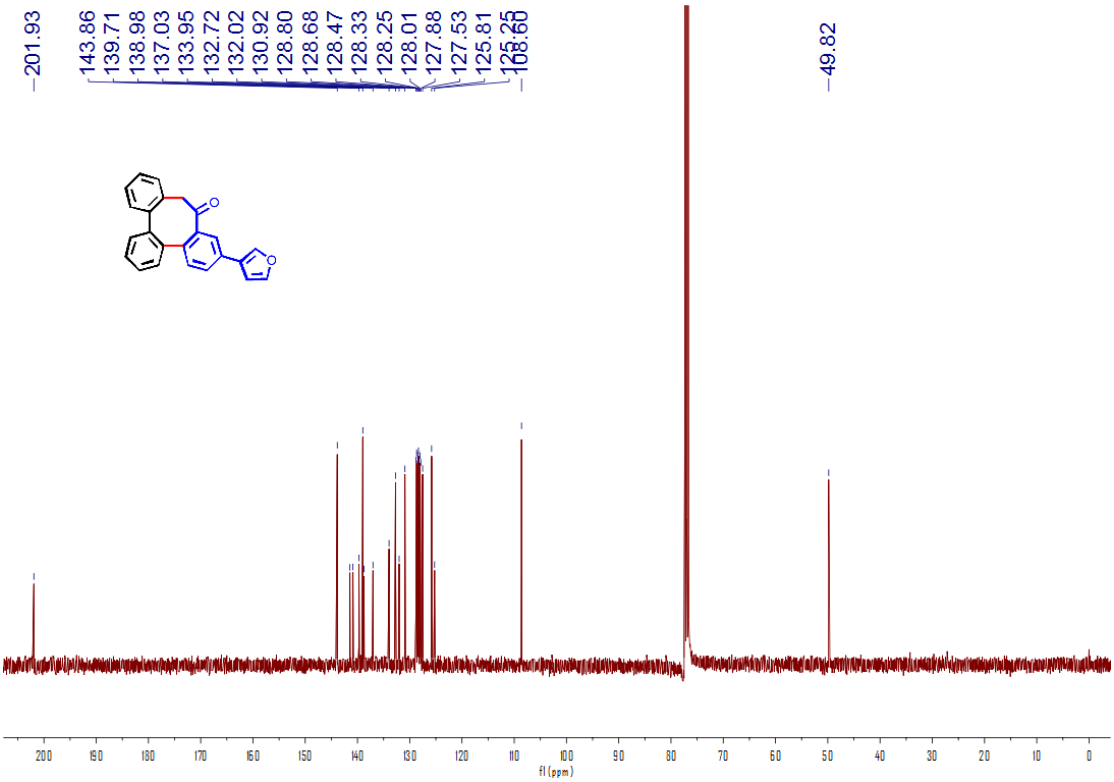


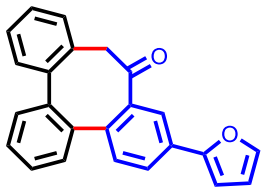




^{1}H NMR (400 MHz, $CDCl_3$)



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



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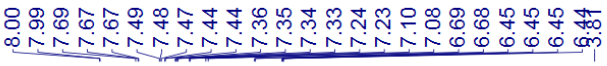
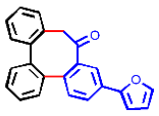
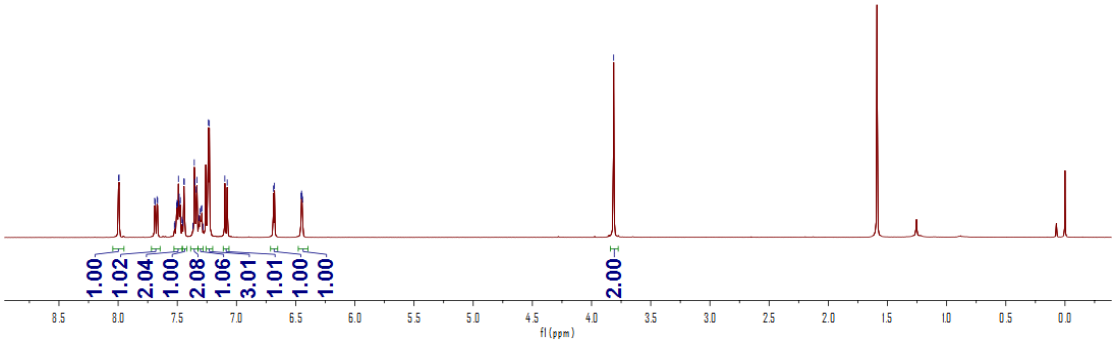
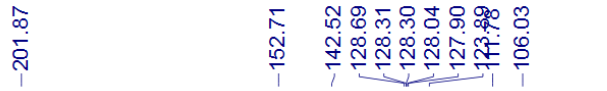
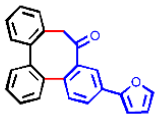




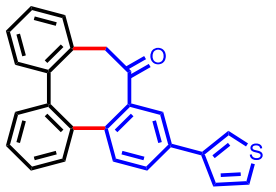


^{1}H NMR (400 MHz, $CDCl_3$)





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



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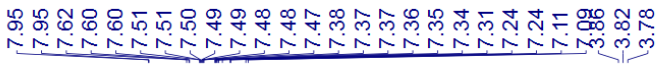
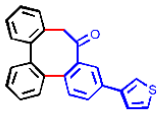
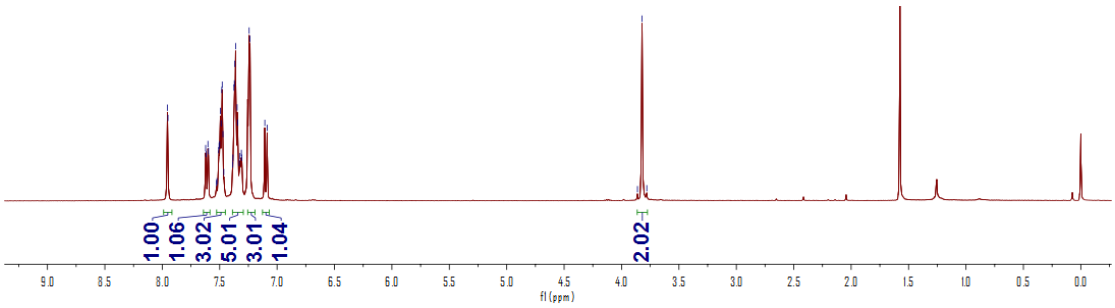
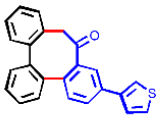


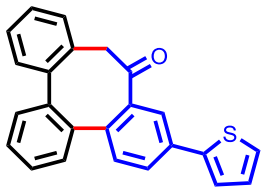




^{1}H NMR (400 MHz, $CDCl_3$)



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



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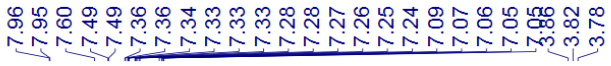
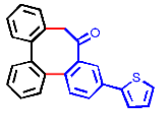
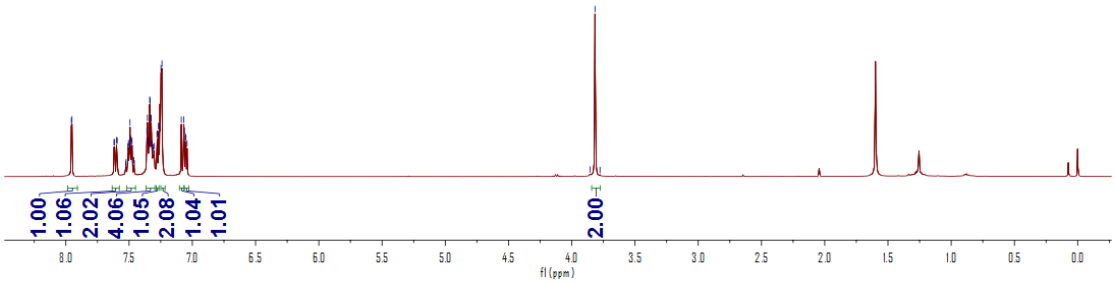
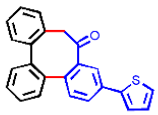


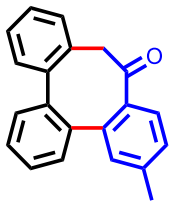




^{1}H NMR (400 MHz, $CDCl_3$)



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



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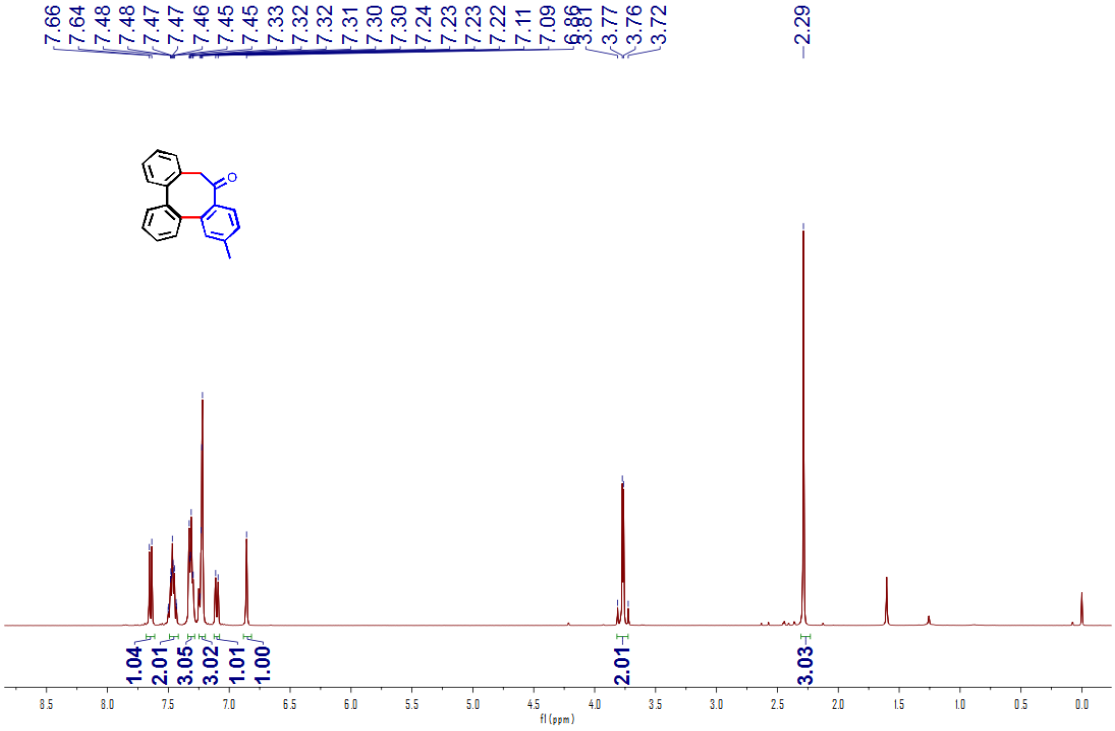
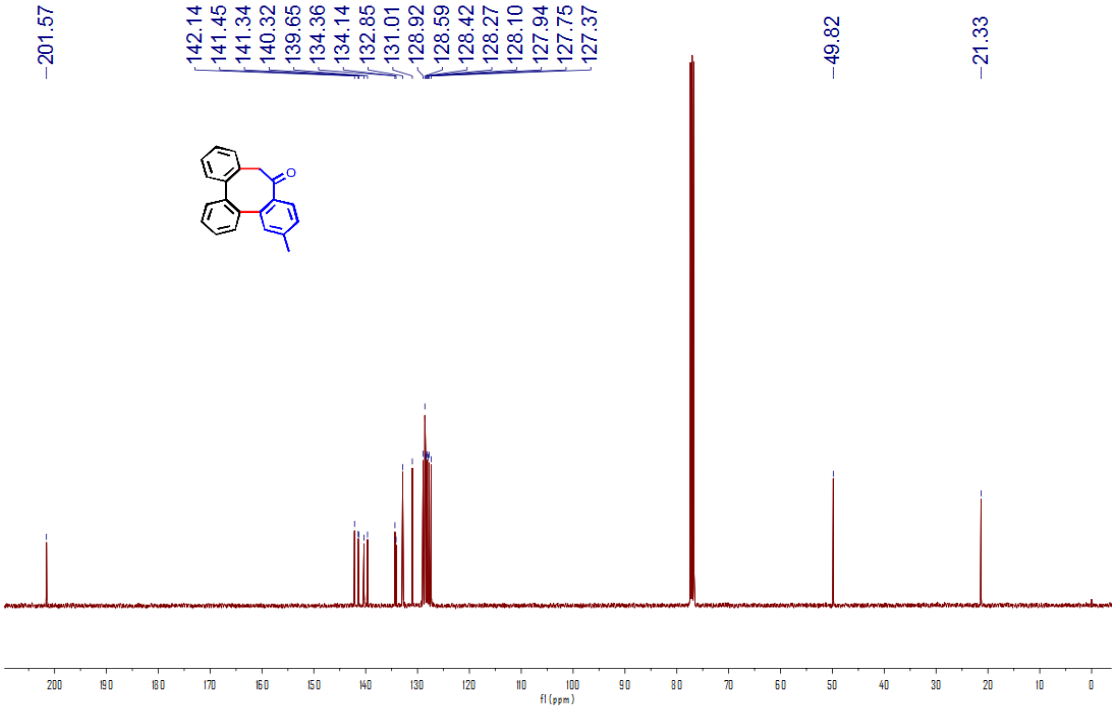
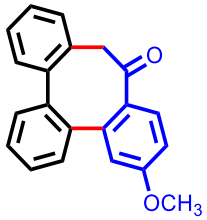


^{1}H NMR (400 MHz, $CDCl_3$)



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



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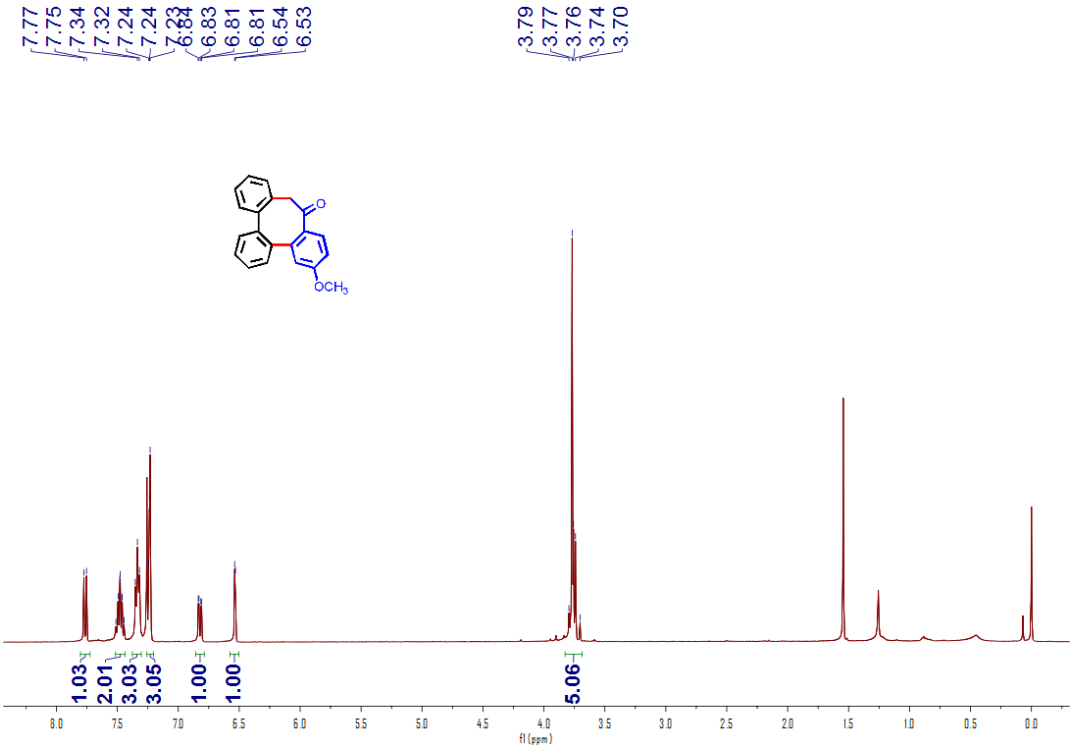
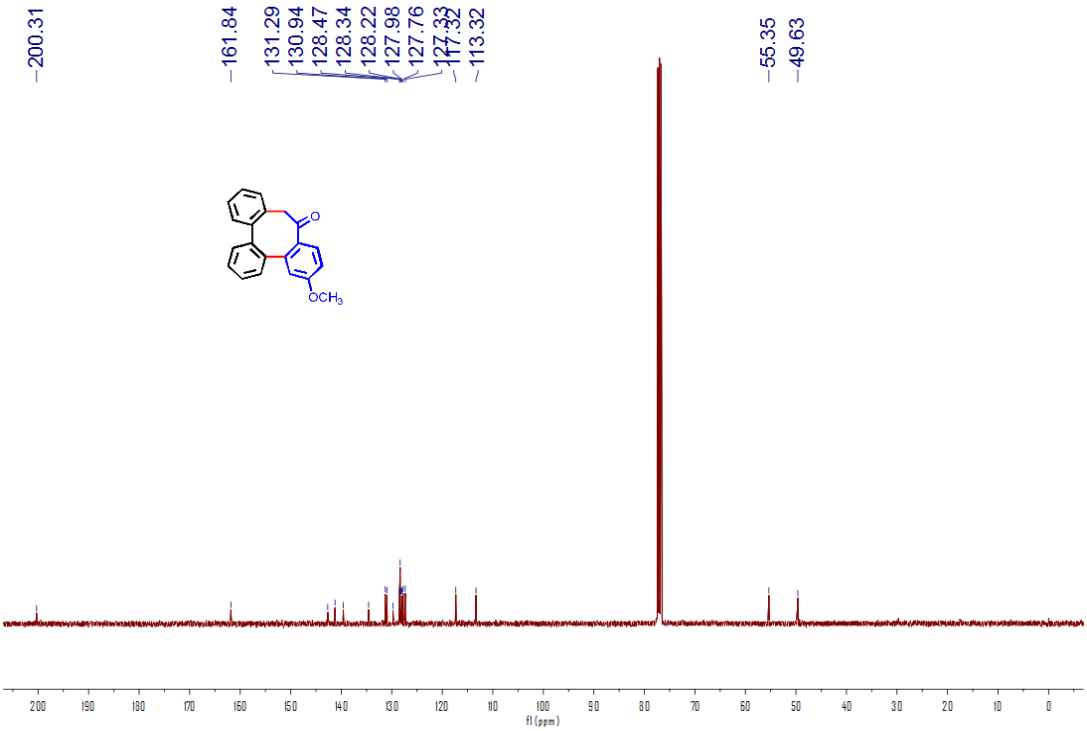
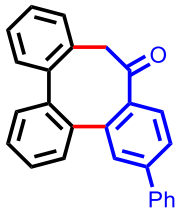


^{1}H NMR (400 MHz, $CDCl_3$)



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



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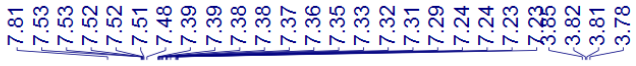
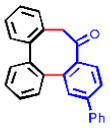
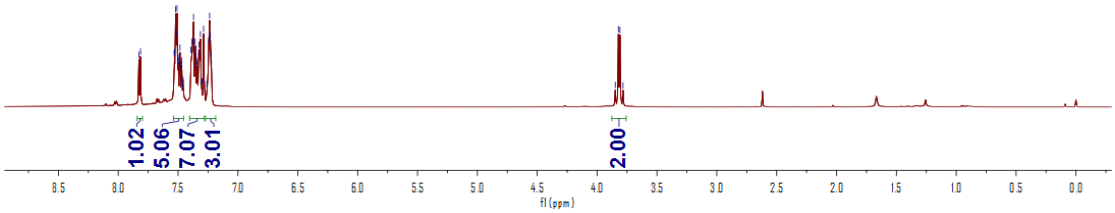
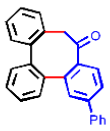
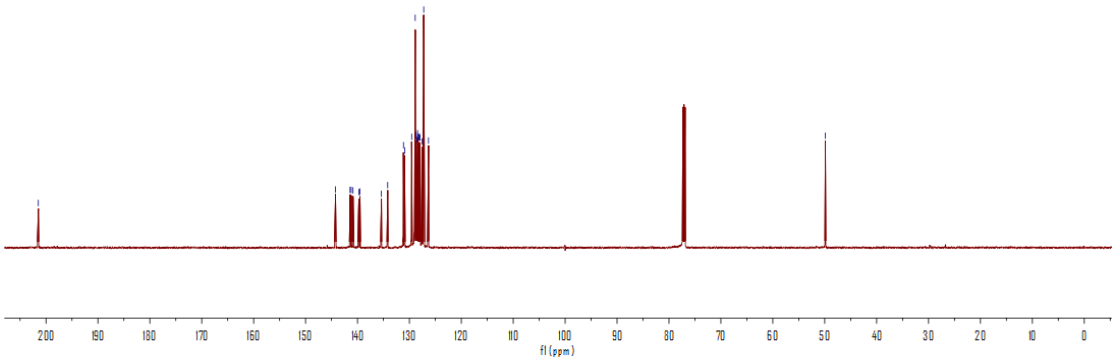




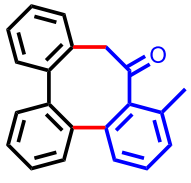


^{1}H NMR (600 MHz, $CDCl_3$)





^{13}C NMR (151 MHz, $CDCl_3$)



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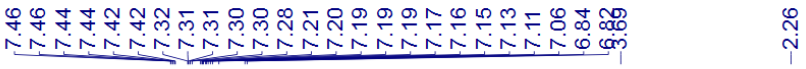
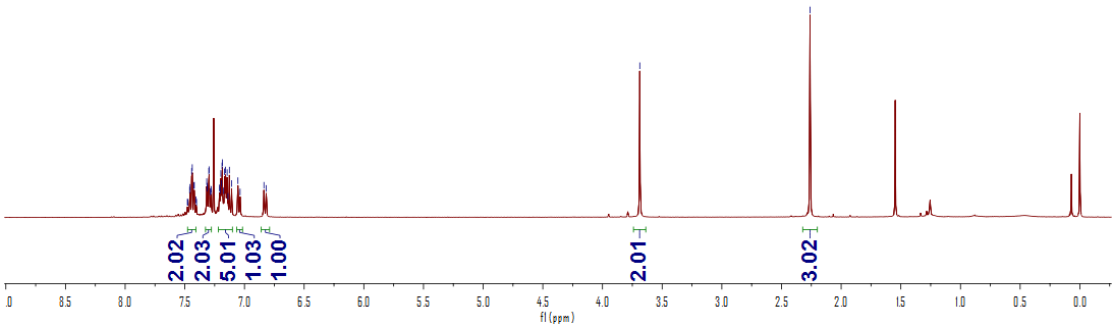
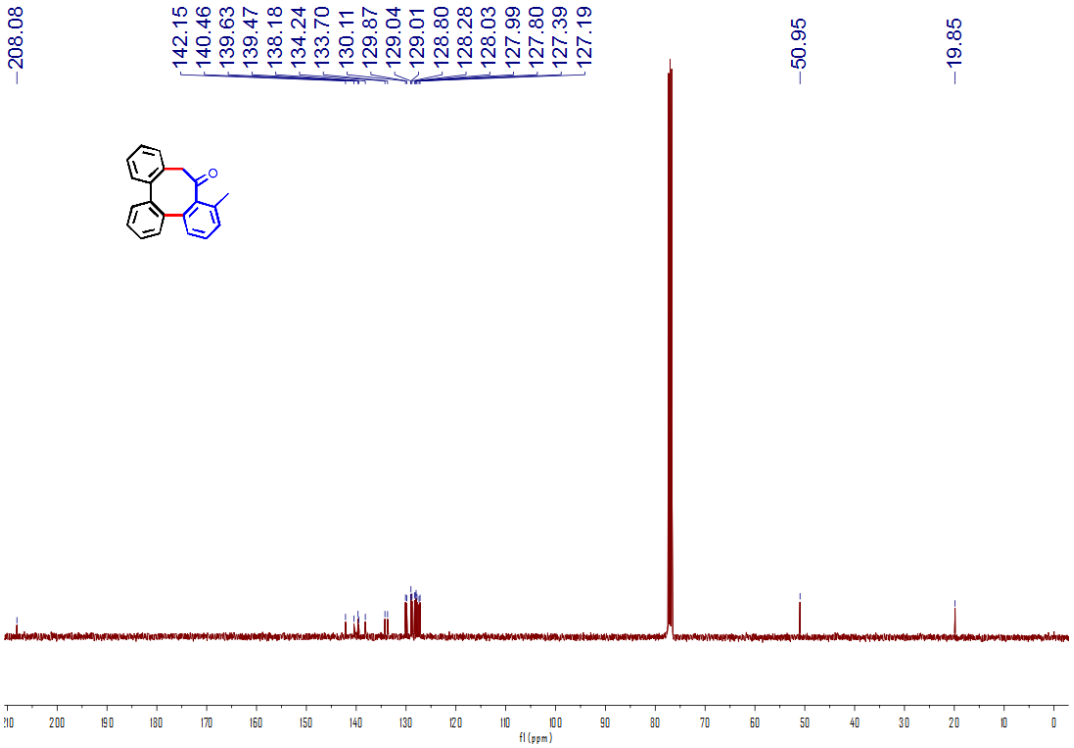
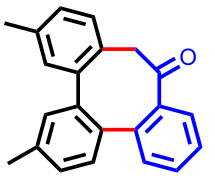




^{1}H NMR (400 MHz, $CDCl_3$)



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



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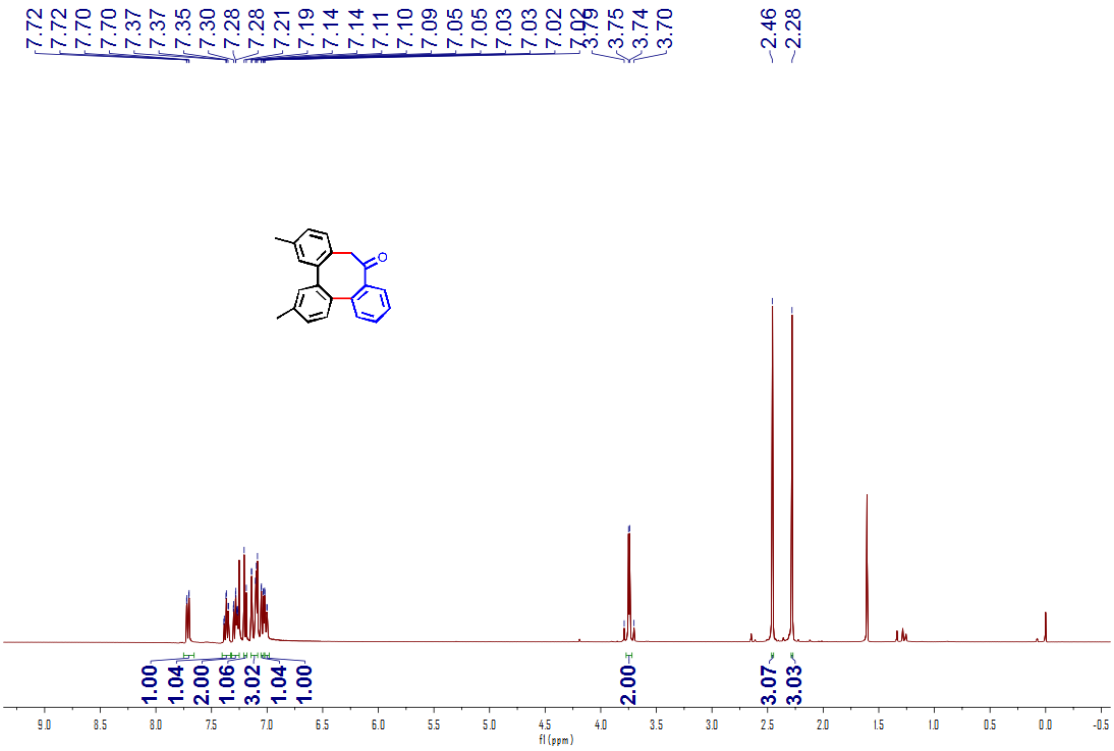
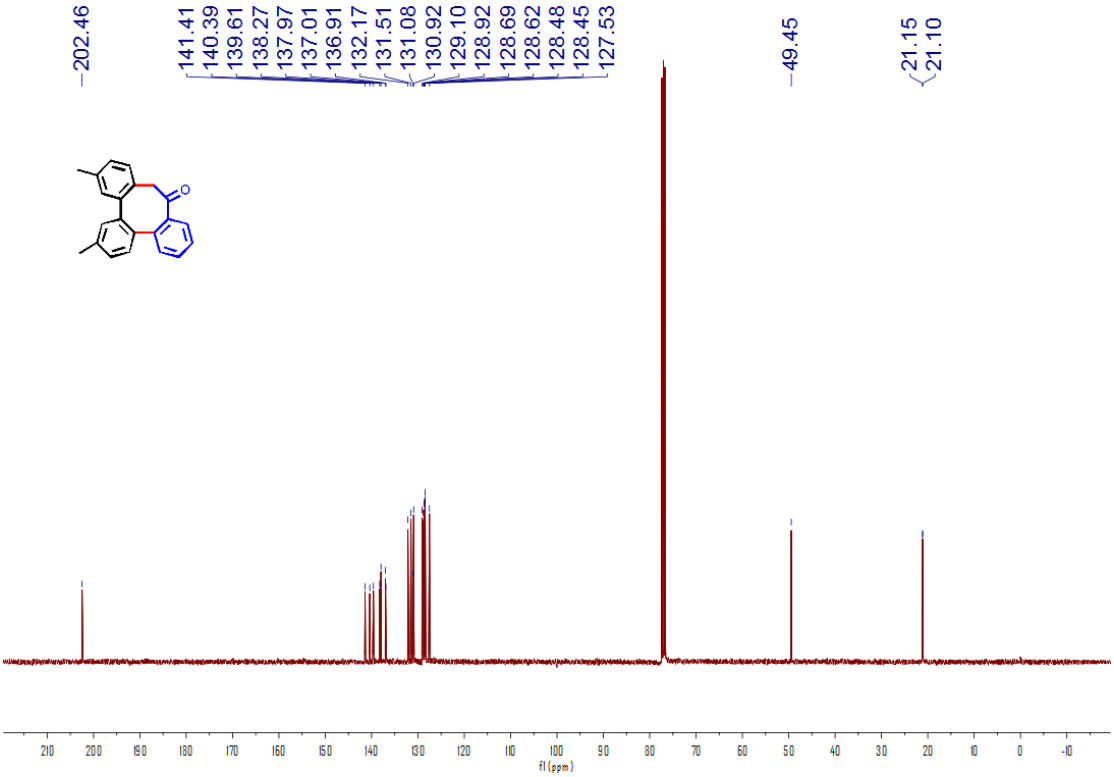
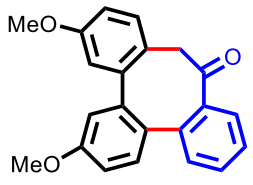


^{1}H NMR (400 MHz, $CDCl_3$)



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



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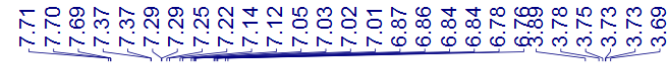
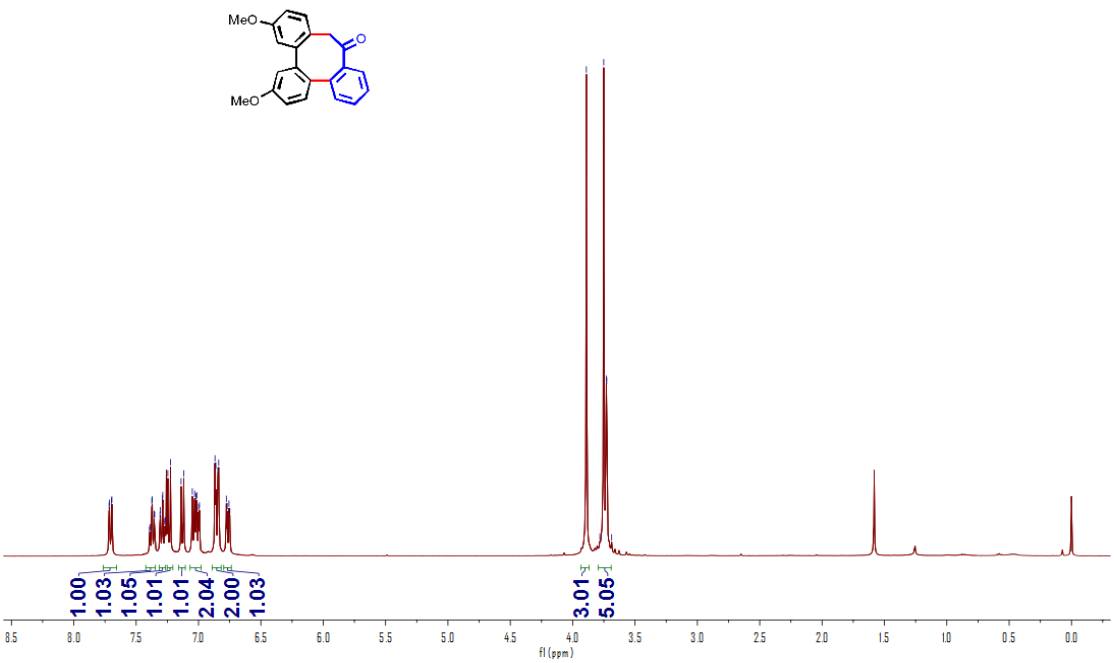
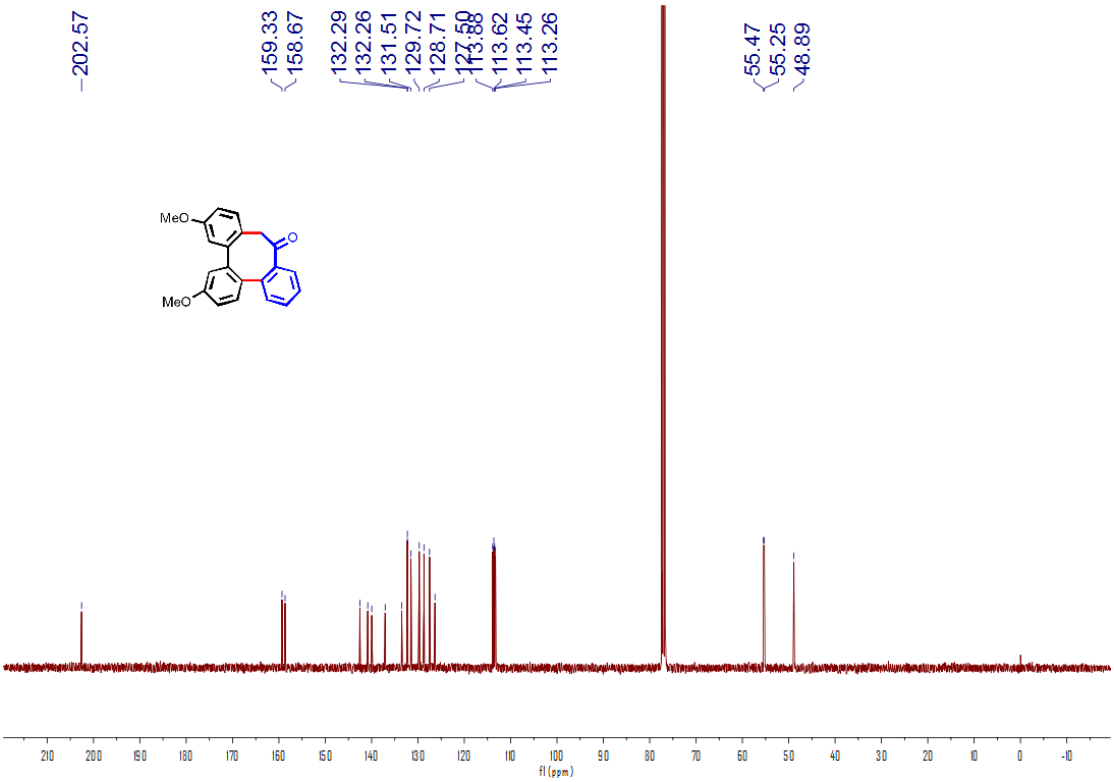
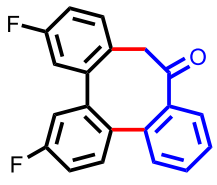




^{1}H NMR (400 MHz, $CDCl_3$)



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



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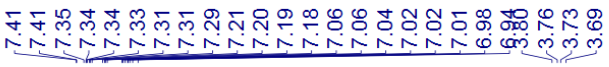
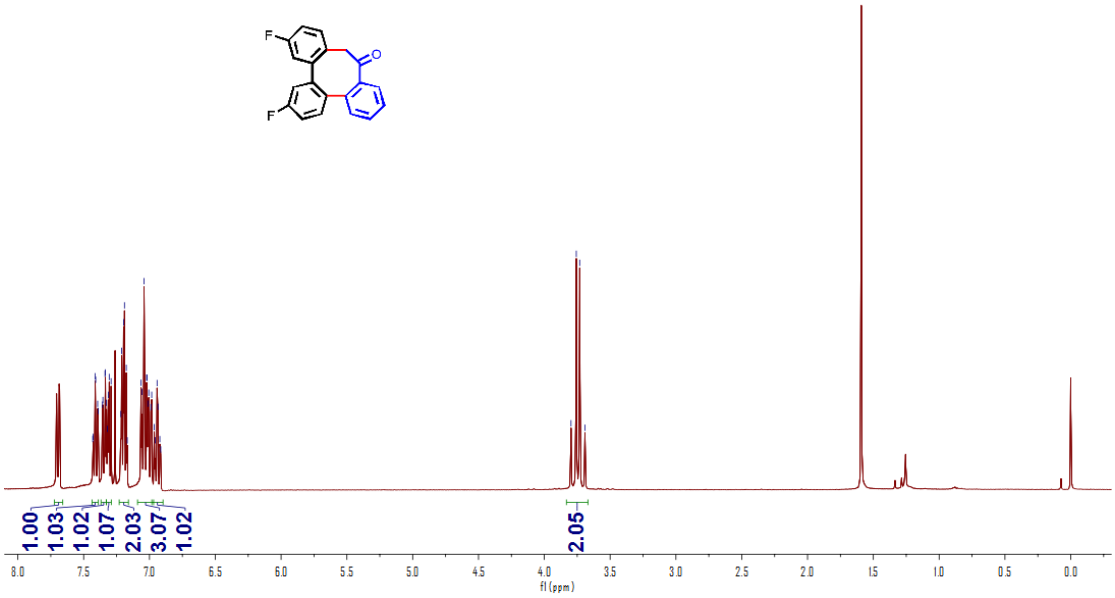
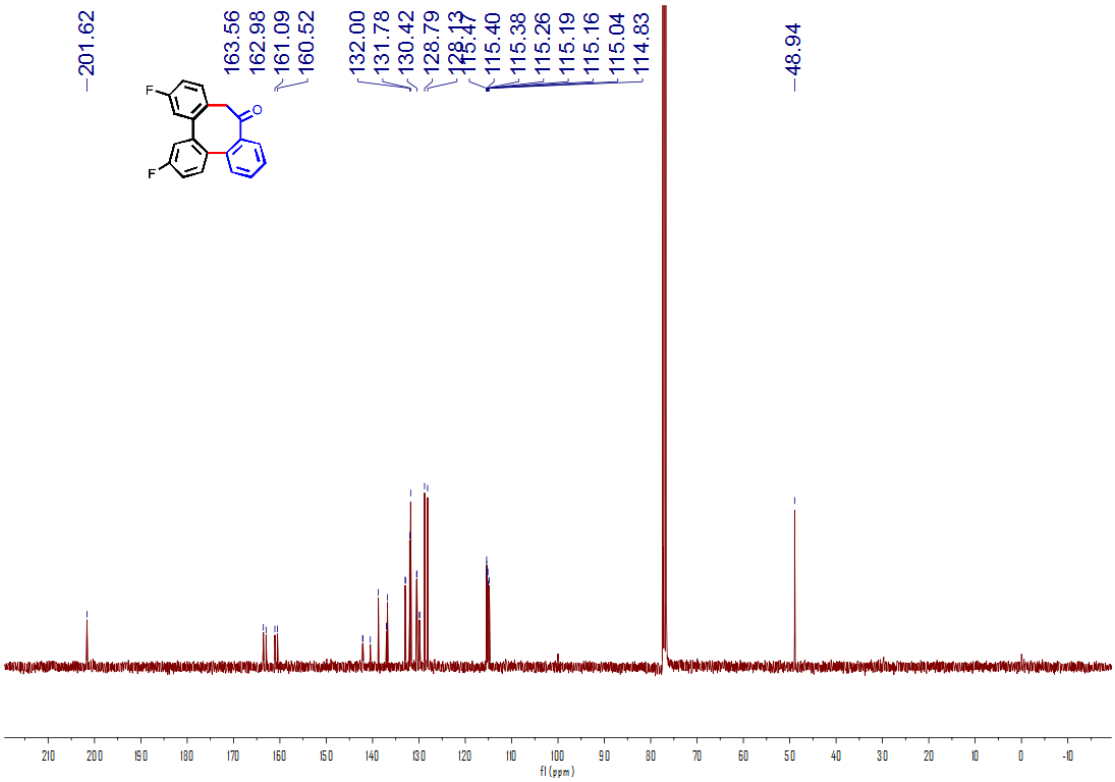
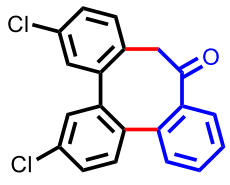




^{1}H NMR (400 MHz, $CDCl_3$)



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



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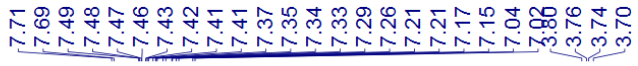
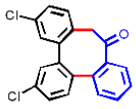
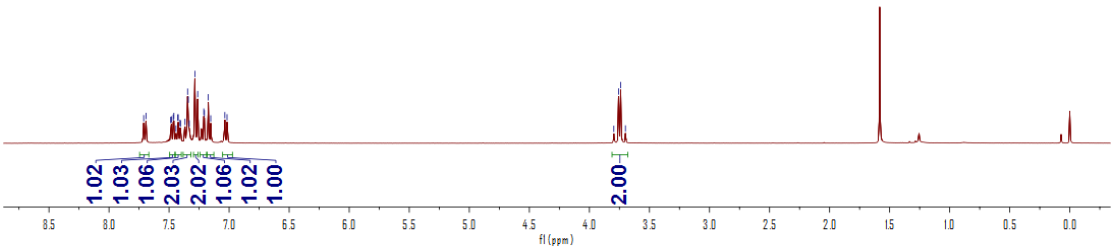
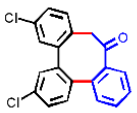
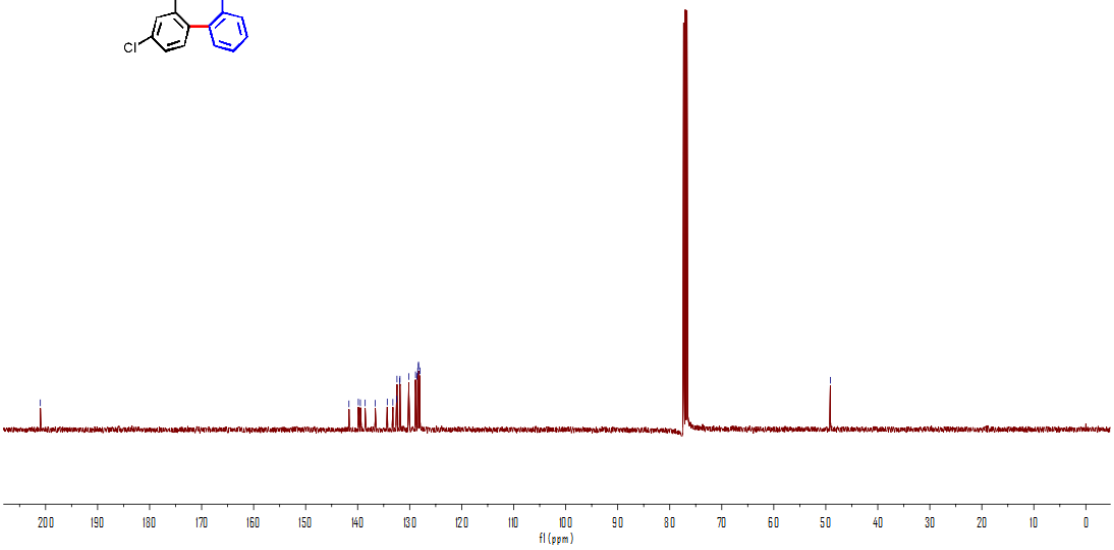




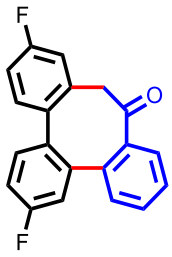


^{1}H NMR (400 MHz, $CDCl_3$)





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



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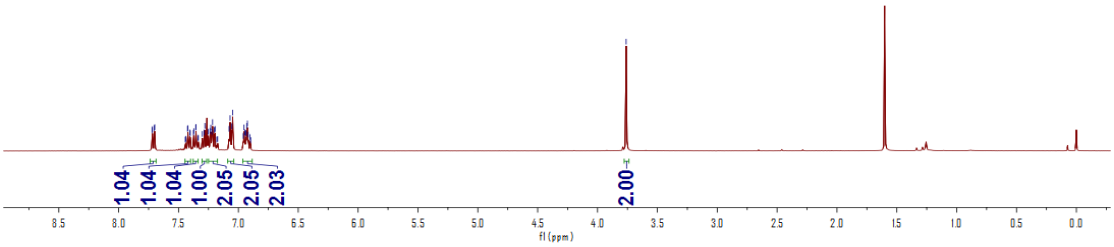
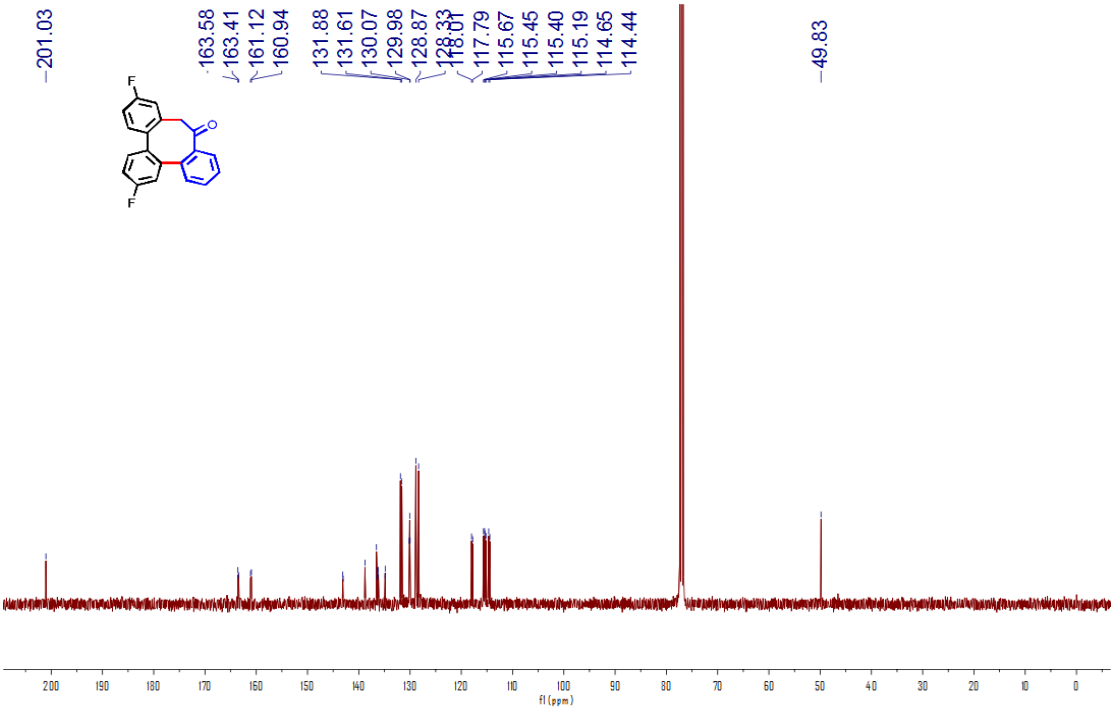
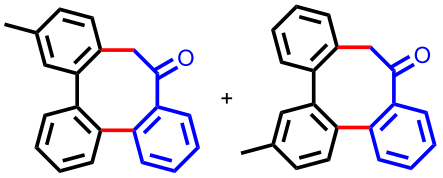


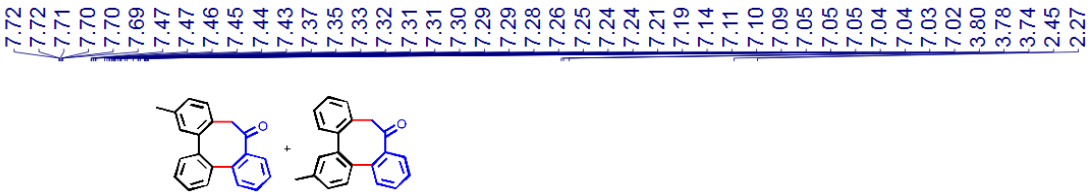
^{1}H NMR (400 MHz, $CDCl_3$)

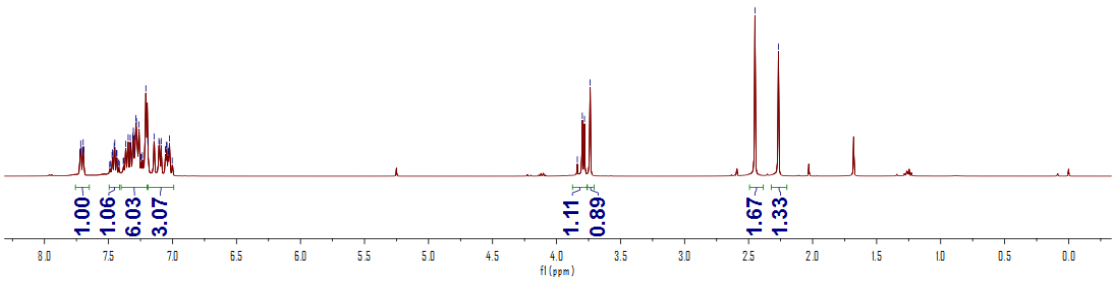


^{13}C NMR (101 MHz, $CDCl_3$)

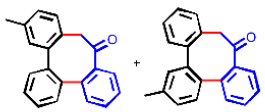


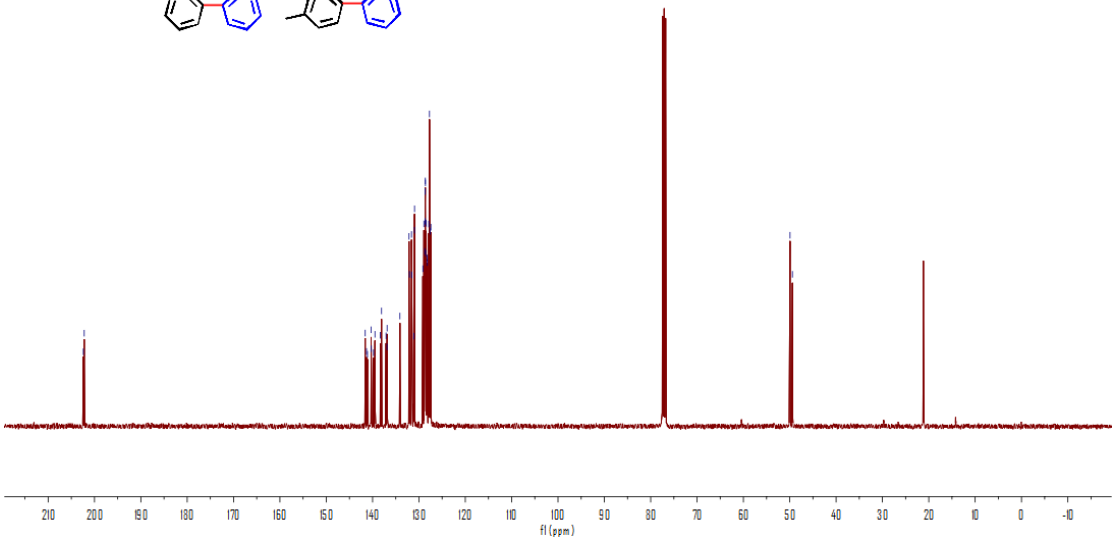
3ha + 3ha-Iso



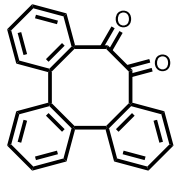


^{1}H NMR (400 MHz, $CDCl_3$)

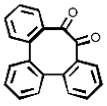


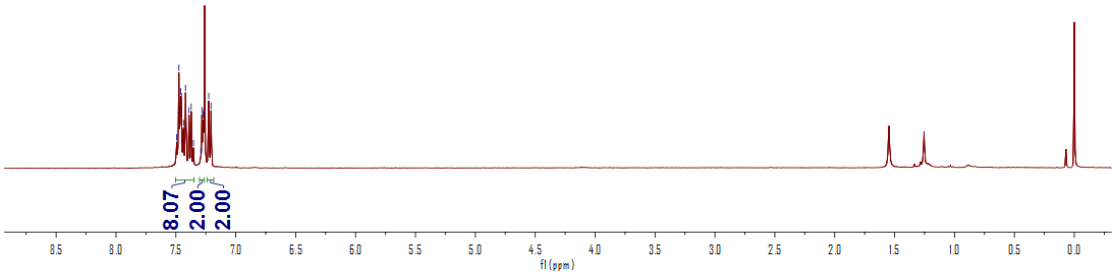


^{13}C NMR (101 MHz, $CDCl_3$)

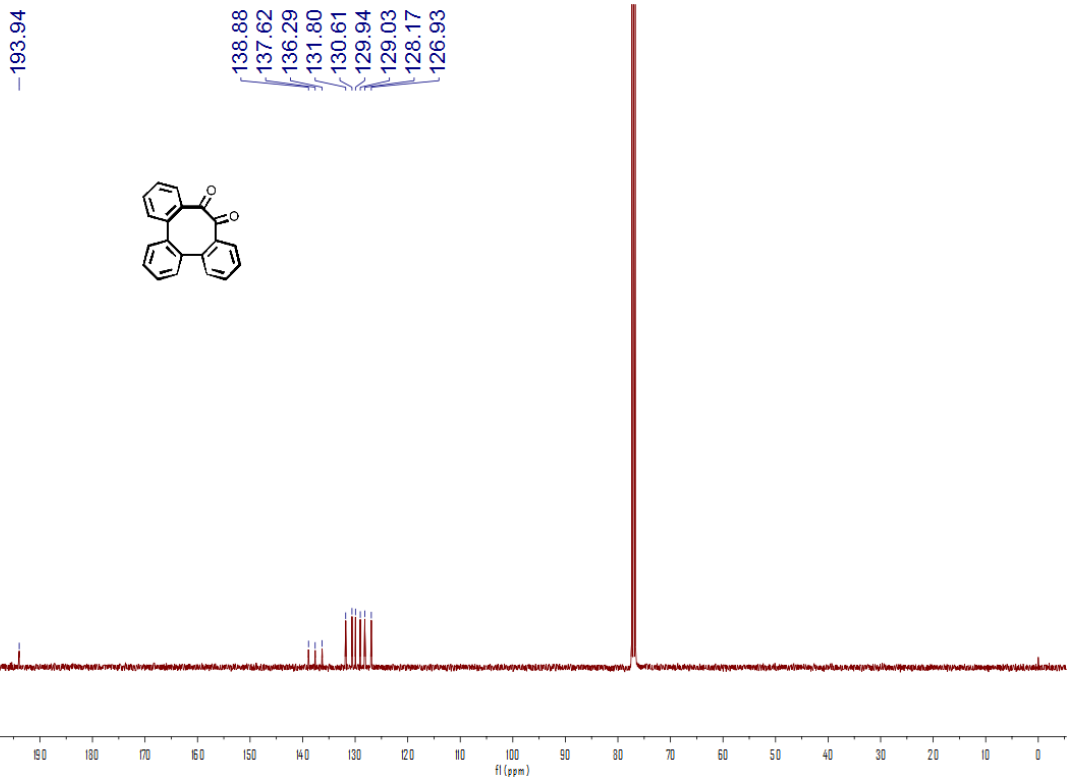


5aa

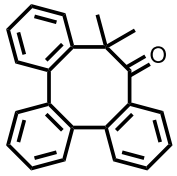




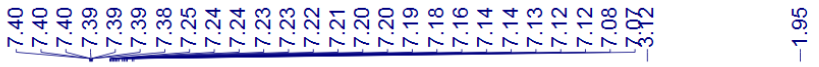
^{1}H NMR (400 MHz, $CDCl_3$)

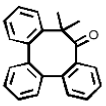


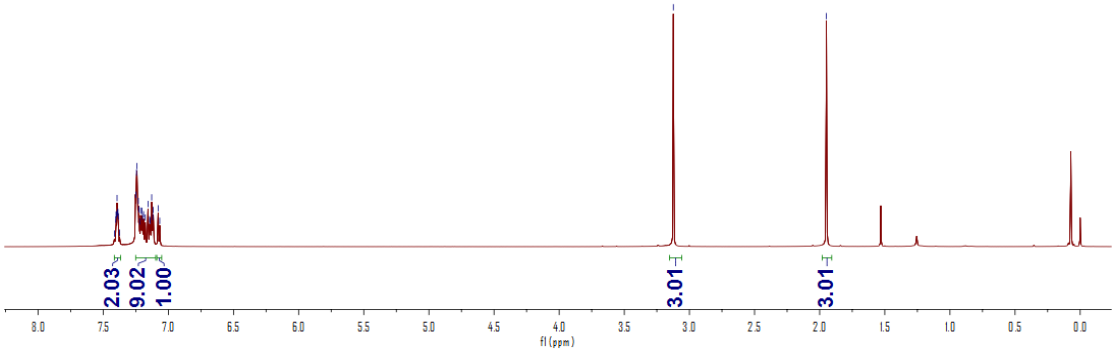
^{13}C NMR (101 MHz, $CDCl_3$)



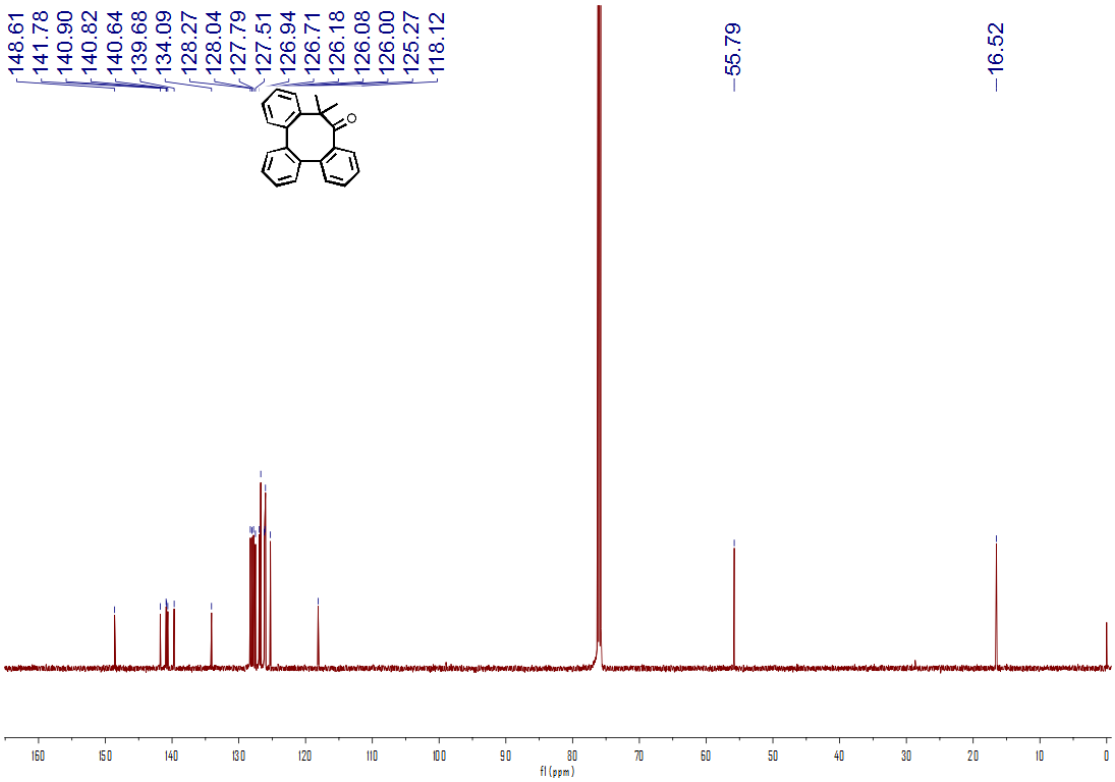
6aa



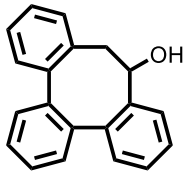




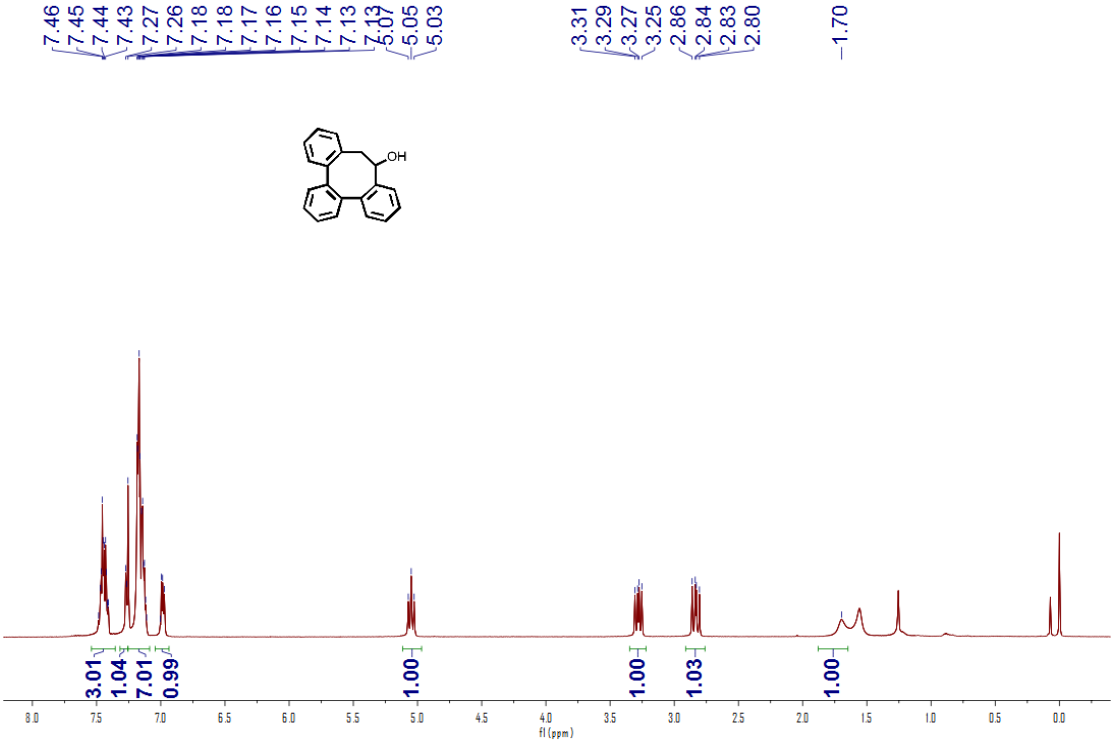
^{1}H NMR (600 MHz, $CDCl_3$)



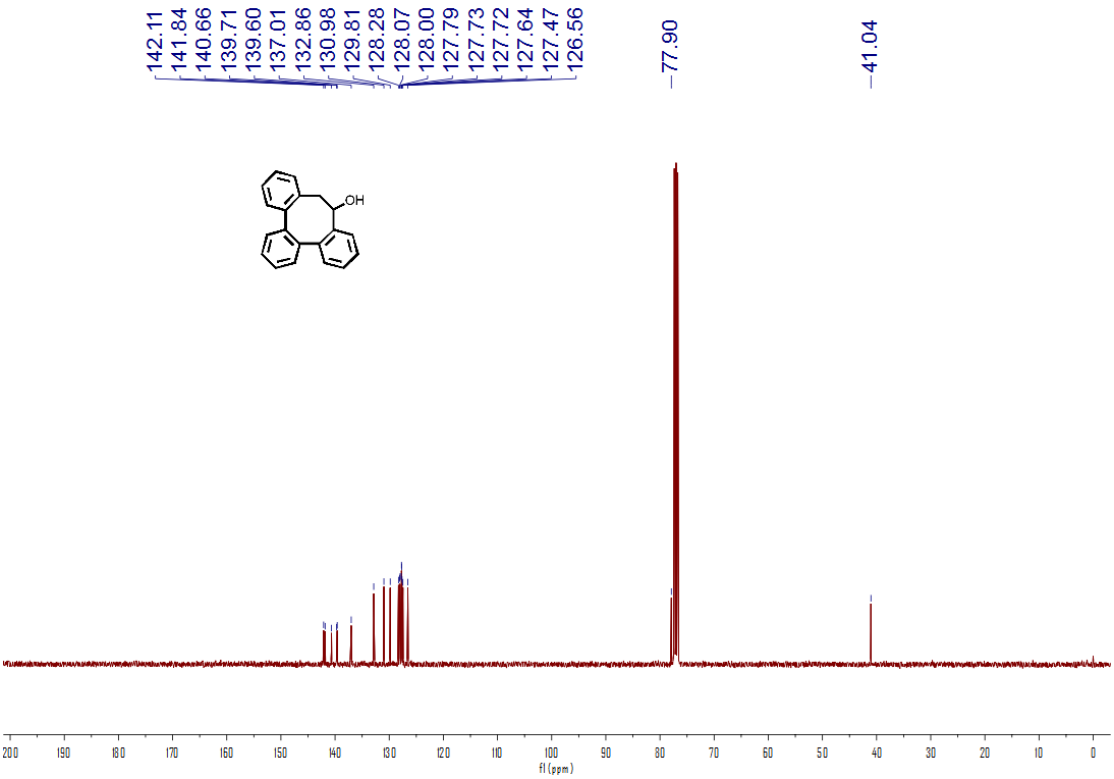
^{13}C NMR (151 MHz, $CDCl_3$)



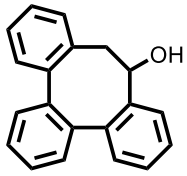
7aa[1]



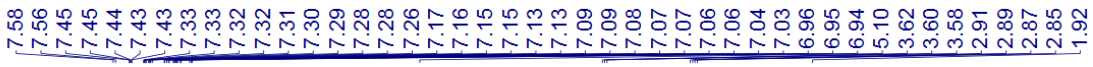
^{1}H NMR (400 MHz, $CDCl_3$)

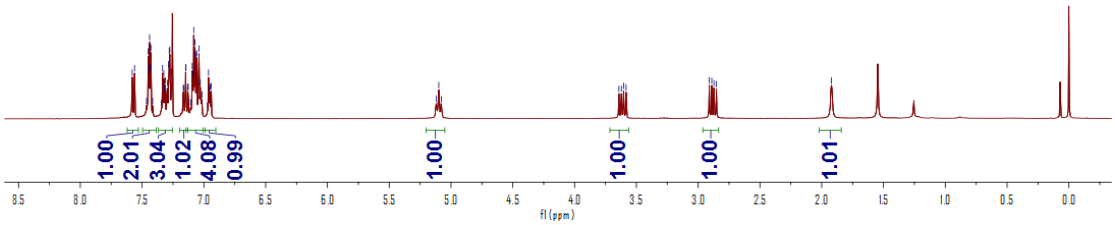


^{13}C NMR (101 MHz, $CDCl_3$)

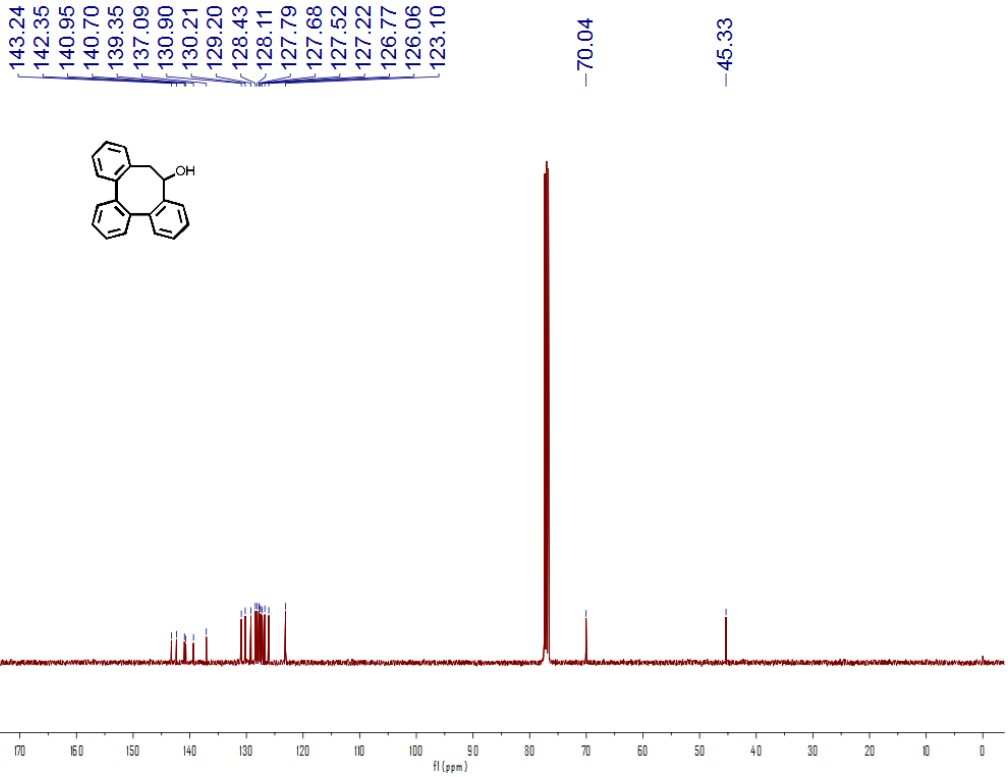


7aa[2]

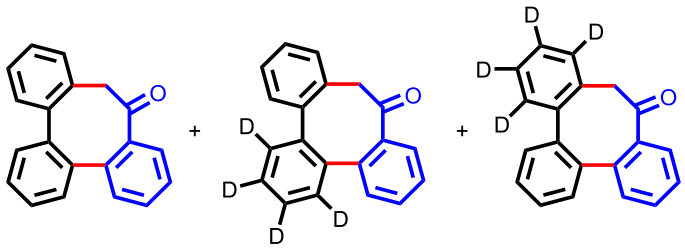




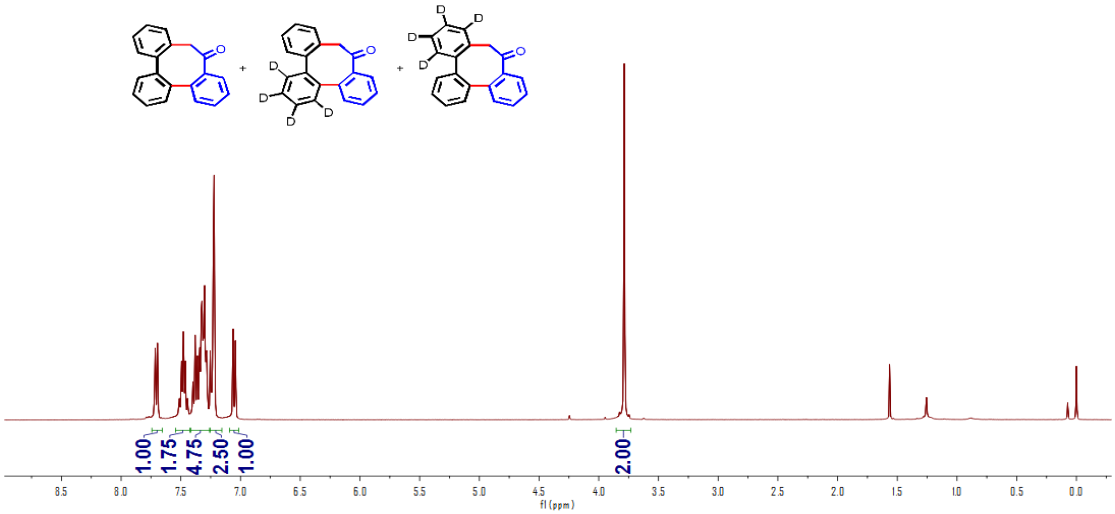
^{1}H NMR (400 MHz, $CDCl_3$)



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



3aa + 3aa-d5 + 3aa-d5-Iso



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

10. Crystal Structure of 3aa

3aa was dissolved with $CDCl_3$ in the NMR tube. The solvent was slowly volatizing under open air to afford crystalline, which was suitable for single crystal X-ray analysis. The CCDC Deposition Number is 2132853.