Supplementary Information

Metal-/solvent-free oxidative [4+2]/[3+2] annulation of 2-ethynylbenzaldehydes with arylalkenes: Facile synthesis of benzo[a]fluoren-5-ones

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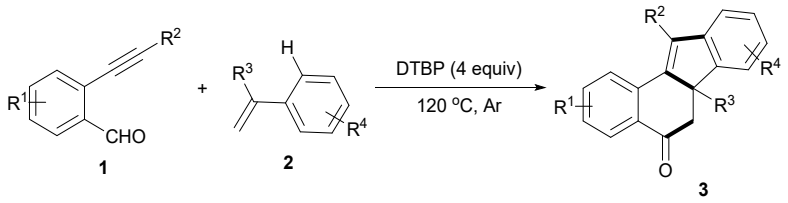
(A) General Experimental Procedure

All ^{1}H and ^{13}C NMR spectras were recorded on a 500 MHz spectrometer at room temperature in $CDCl_3$ with tetramethylsilane as internal standard. Compounds **1**, **1a-D** were prepared according to reported literatures[1], alkenes **2b-c**, **2e-k, 2a-D$_5$** were prepared from corresponding ketones as the reported methods[2], and other materials were purchased from commercial sources and used as received.

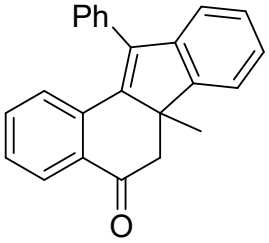
(a) Typical Experimental Procedure for the Synthesis of Benzo[*a*]fluoren-5-ones (3):



A oven-dried Schlenk tube equipped with a magnetic stirring bar was charged with aldehyde **1** (0.3 mmol), alkene **2** (0.9 mmol), DTBP (4 equiv; 1.2 mmol). The tube was evacuated and back-filled with argon for three times and the mixture was stirred at 120 ^{o}C (oil bath) for 24 h until complete consumption of **1** as monitored by TLC and/or GC-MS analysis. After the reaction was finished, the mixture was cool to room temperature and was concentrated to give the crude product. The resulting residue was purified by silica gel column chromatography (hexane/ethyl acetate) to afford the desired product **3**.

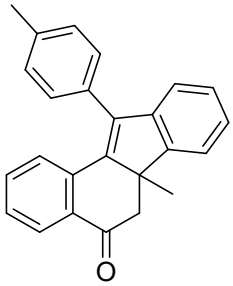
(B) Analytical data

6a-Methyl-11-phenyl-6,6a-dihydro-5*H*-benzo[*a*]fluoren-5-one (3aa):[3]



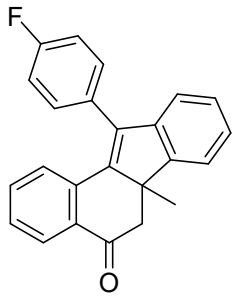
69% yield; White solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.12-8.10 (m, 1H), 7.49-7.46 (m, 3H), 7.45-7.41 (m, 3H), 7.33-7.28 (m, 4H), 7.26-7.24 (m, 1H), 7.17-7.15 (m, 1H), 3.26 (d, *J* = 16.0 Hz, 1H), 2.51 (d, *J* = 16.0 Hz, 1H), 1.38 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 197.59, 151.94, 144.36, 142.92, 137.96, 135.74, 134.62, 133.24, 130.60, 129.06, 128.94, 127.95, 127.66, 127.58, 127.43, 127.35, 126.12, 121.58, 121.56, 52.43, 49.26, 23.16; LRMS (EI 70 ev) m/z (%): 322 (M^+, 82), 307 (100), 277 (17).

6a-Methyl-11-(*p*-tolyl)-6,6a-dihydro-5*H*-benzo[*a*]fluoren-5-one (3ba):[3]



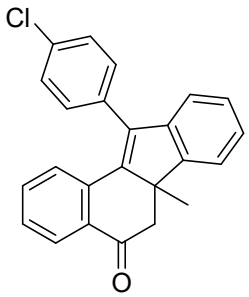
68% yield; Light yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.12-8.10 (m, 1H), 7.47-7.45 (m, 1H), 7.33-7.31 (m, 3H), 7.30-7.28 (m, 4H), 7.28-7.25 (m, 2H), 7.22-7.20 (m, 1H), 3.25 (d, *J* = 16.0 Hz, 1H), 2.51 (d, *J* = 16.0 Hz, 1H), 2.45 (s, 3H), 1.37 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 197.72, 152.02, 144.56, 142.70, 138.04, 137.71, 135.97, 133.25, 131.56, 130.63, 129.67, 128.96, 127.65, 127.59, 127.41, 127.34, 126.08, 121.65, 121.55, 52.39, 49.31, 23.19, 21.39; LRMS (EI 70 ev) *m/z* (%): 336 (M^+, 87), 321 (100), 276 (21).

11-(4-Fluorophenyl)-6a-methyl-6,6a-dihydro-5*H*-benzo[*a*]fluoren-5-one (3ca):[3]



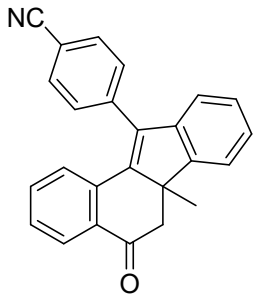
57% yield; Light yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.13-8.11 (m, 1H), 7.48-7.46 (m, 1H), 7.41-7.39 (m, 2H), 7.35-7.31 (m, 4H), 7.24-7.23 (m, 1H), 7.18 (t, *J* = 8.5 Hz, 2H), 7.15-7.13 (m, 1H), 3.26 (d, *J* = 16.0 Hz, 1H), 2.50 (d, *J* = 16.0 Hz, 1H), 1.37 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 197.39, 162.49(d, *J* = 245 Hz), 151.91, 144.18, 143.37, 136.85, 135.55, 133.30, 130.87(d, *J* = 7.5 Hz), 130.68, 130.50 (d, *J* = 3.75 Hz), 127.84, 127.50, 127.48, 127.44, 126.27, 121.65, 121.38, 116.09 (d, *J* = 21.25Hz), 52.46, 49.24, 23.10; ^{19}F NMR (471 MHz, $CDCl_3$) δ -113.41; LRMS (EI 70 ev) *m/z* (%): 340 (M^+, 79), 325 (100), 294 (18).

11-(4-Chlorophenyl)-6a-methyl-6,6a-dihydro-5*H*-benzo[*a*]fluoren-5-one (3da):[3]



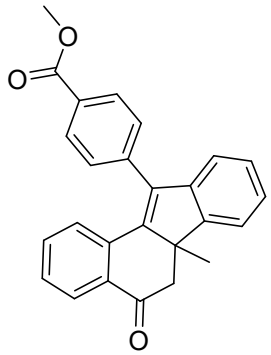
61% yield; Light yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.13-8.11 (m, 1H), 7.48-7.45 (m, 3H), 7.37-7.34 (m, 4H), 7.33-7.31 (m, 2H), 7.25-7.22 (m, 1H), 7.16-7.14 (m, 1H), 3.26 (d, *J* = 16.0 Hz, 1H), 2.49 (d, *J* = 16.0 Hz, 1H), 1.37 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 197.30, 151.90, 143.94, 143.54, 136.60, 135.41, 133.93, 133.36, 133.11, 130.67, 130.54, 129.30, 127.94, 127.52, 127.51, 127.46, 126.32, 121.68, 121.33, 52.55, 49.21, 23.10; LRMS (EI 70 ev) *m/z* (%): 358 (M^++2, 30), 356 (M^+, 73), 343 (35), 341 (100), 276 (38).

4-(6a-Methyl-5-oxo-6,6a-dihydro-5*H*-benzo[*a*]fluoren-11-yl)benzonitrile (3ea)



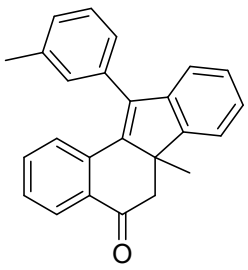
50% yield; Light yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.15-8.13 (m, 1H), 7.80 (d, *J* = 8.5 Hz, 2H), 7.57 (d, *J* = 7.5 Hz, 2H), 7.50-7.49 (m, 1H), 7.40-7.32 (m, 4H), 7.21-7.19 (m, 1H), 7.05-7.03 (m, 1H), 3.28 (d, *J* = 16.5 Hz, 1H), 2.51 (d, *J* = 16.5 Hz, 1H), 1.39 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 196.93, 151.84, 144.61, 143.22, 139.90, 135.82, 134.86, 133.45, 132.82, 130.76, 130.07, 128.37, 127.71, 127.65, 127.31, 126.61, 121.87, 121.07, 118.60, 111.91, 52.85, 49.17, 23.06; IR (KBr, cm^{-1}): 1684; LRMS (EI 70 ev) *m/z* (%): 347 (84), 332 (100), 245 (23); HRMS *m/z* (ESI) calcd for $C_{25}H_{18}NO$ $[M+H]^+$ 348.1383, found 348.1379.

Methyl 4-(6a-methyl-5-oxo-6,6a-dihydro-5*H*-benzo[*a*]fluoren-11-yl)benzoate (3fa)



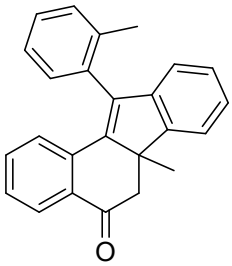
54% yield; Light yellow solid;^{1}H NMR (500 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.0 Hz, 2H), 8.13 (d, *J* = 7.5 Hz, 1H), 7.54-7.49 (m, 3H), 7.37-7.34 (m, 2H), 7.34-7.31 (m, 2H), 7.25-7.23 (m, 1H), 7.09 (d, *J* = 6.5 Hz, 1H), 3.98 (s, 3H), 3.28 (d, *J* = 16.0 Hz, 1H), 2.53 (d, *J* = 16.0 Hz, 1H), 1.39 (s, 3H);^{13}C NMR (125 MHz, $CDCl_3$) δ 197.34, 166.80, 151.82, 143.81, 143.67, 139.64, 136.78, 135.21, 133.38, 130.58, 130.24, 129.65, 129.22, 128.03, 127.53, 127.49, 126.35, 121.71, 121.30, 52.65, 52.25, 49.14, 23.12; LRMS (EI 70 ev) *m/z* (%): 380 (M^+, 100), 365 (97), 276 (32), 138 (37); HRMS *m/z* (ESI) calcd for $C_{26}H_{21}O_3$ $[M+H]^+$ 381.1485, found 381.1487.

6a-Methyl-11-(*m*-tolyl)-6,6a-dihydro-5*H*-benzo[*a*]fluoren-5-one (3ga):[3]



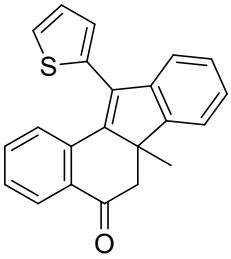
62% yield; White solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.12-8.11 (m, 1H), 7.46-7.45 (m, 1H), 7.36 (t, *J* = 7.5 Hz, 1H), 7.30-7.29 (m, 4H), 7.26-7.23 (m, 3H), 7.21-7.19 (m, 2H), 3.26 (d, *J* = 15.5 Hz, 1H), 2.51 (d, *J* = 16.0 Hz, 1H), 2.39 (s, 3H), 1.37 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 197.52, 151.93, 144.45, 142.70, 138.53, 135.80, 134.54, 133.16, 130.57, 129.53, 128.81, 128.67, 138.13, 127.59, 127.57, 127.37, 127.28, 126.08, 126.06, 121.62, 121.48, 52.34, 49.22, 23.17, 21.42; LRMS (EI 70 ev) *m/z* (%): 336 (M^+, 100), 321 (97), 244 (33).

6a-Methyl-11-(*o*-tolyl)-6,6a-dihydro-5*H*-benzo[*a*]fluoren-5-one (3ha):



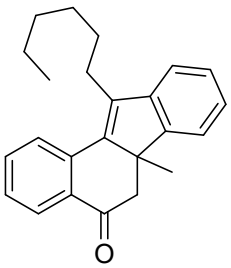
48% yield; Light yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.11-8.09 (m, 1H), 7.49-7.45 (m, 2H), 7.42-7.35 (m, 2H), 7.33-7.26 (m, 5H), 7.08-7.06 (m, 2H), 3.29 (d, *J* = 16.0 Hz, 1H), 2.48 (d, *J* = 16.0 Hz, 1H), 1.84 (s, 3H), 1.42 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 197.60, 152.09, 144.65, 143.39, 137.72, 136.37, 135.81, 133.97, 133.70, 130.81, 130.00, 129.79, 128.09, 127.71, 127.53, 127.33, 126.44, 126.18, 126.13, 121.67, 121.53, 52.53, 49.75, 23.31, 19.29; IR (KBr, cm^{-1}): 1684; LRMS (EI 70 ev) *m/z* (%): 336 (M^+, 100), 321 (99), 276 (21); HRMS *m/z* (ESI) calcd for $C_{25}H_{21}O$ $[M+H]^+$ 337.1587, found 337.1583.

6a-Methyl-11-(thiophen-2-yl)-6,6a-dihydro-5*H*-benzo[*a*]fluoren-5-one (3ia):



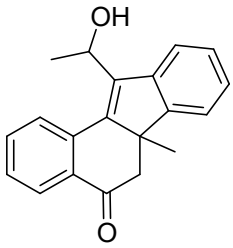
52% yield; Yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.12 (d, *J* = 8.0 Hz, 1H), 7.47-7.45 (m, 2H), 7.43-7.42 (m, 1H), 7.40-7.39 (m, 2H), 7.38-7.35 (m, 1H), 7.35-7.30 (m, 2H), 7.19-7.16 (m, 2H), 3.25 (d, *J* = 16.0 Hz, 1H), 2.50 (d, *J* = 16.0 Hz, 1H), 1.36 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 197.33, 151.47, 145.60, 144.17, 135.36, 134.80, 133.31, 130.73, 130.66, 128.12, 127.64, 127.61, 127.58, 127.54, 127.36, 126.39, 126.35, 121.66, 121.55, 52.60, 49.21, 23.14; IR (KBr, cm^{-1}): 1684; LRMS (EI 70 ev) *m/z* (%): 328 (M^+, 81), 313 (100), 244 (18); HRMS *m/z* (ESI) calcd for $C_{22}H_{17}OS$ $[M+H]^+$ 329.0995, found 329.0994.

11-Hexyl-6a-methyl-6,6a-dihydro-5*H*-benzo[*a*]fluoren-5-one (3ja):



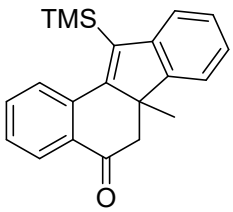
45% yield; Yellow liquid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.15 (d, *J* = 8.0 Hz, 1H), 7.66 (d, *J* = 3.5 Hz, 2H), 7.49 (d, *J* = 7.5 Hz, 1H), 7.43-7.39 (m, 2H), 7.37 (t, *J* = 7.5 Hz, 1H), 7.30-7.28 (m, 1H), 3.16 (d, *J* = 16.0 Hz, 1H), 2.90-2.81 (m, 2H), 2.30 (d, *J* = 15.5 Hz, 1H), 1.88-1.66 (m, 2H), 1.55-1.49 (m, 2H), 1.40-1.32 (m, 4H), 1.28 (s, 3H), 0.90 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 197.88, 152.40, 144.30, 141.62, 138.55, 136.83, 133.79, 130.30, 127.62, 127.31, 127.29, 127.02, 125.87, 121.49, 120.58, 52.41, 49.96, 31.66, 29.73, 29.25, 26.08, 22.62, 22.55, 14.05; IR (KBr, cm^{-1}): 1686; LRMS (EI 70 ev) *m/z* (%): 330 (M^+, 44), 245 (100), 215 (23); HRMS *m/z* (ESI) calcd for $C_{24}H_{27}O$ $[M+H]^+$ 331.2056, found 331.2057.

11-(1-Hydroxyethyl)-6a-methyl-6,6a-dihydro-5*H*-benzo[*a*]fluoren-5-one (3ka):



46% yield*;* Light yellow solid; *d.r.*=1.15:1;^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11-8.08 (m, 2.15H), 8.00 (d, *J* = 7.5 Hz, 1.15H), 7.85-7.82 (m, 2H), 7.67-7.61 (m, 2.2H), 7.42-7.39 (m, 3H), 7.39-7.37 (m, 3.45H), 7.34 (d, *J* = 7.5 Hz, 1.85H), 7.31-7.29 (m, 1.6H), 5.58-5.54 (m, 1H), 5.51-5.47 (m, 1.15H), 3.15 (d, *J* = 7.0 Hz, 1H), 3.11 (d, *J* = 7.0 Hz, 1.15H), 2.47 (s, 2.15H), 2.26 (d, *J* = 7.5 Hz, 1.15H), 2.22 (d, *J* = 7.0 Hz, 1H), 1.85 (d, *J* = 6.5 Hz, 3.45H), 1.64 (d, *J* = 6.5 Hz, 3H), 1.24 (s, 3.45H), 1.22 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.71(2C), 152.46, 152.27, 142.86, 141.73, 141.40, 141.12, 140.41, 139.39, 135.99, 135.81, 133.85, 133.75, 130.53, 130.33, 128.09, 128.05, 127.98, 127.87, 127.65, 127.46, 127.19, 127.13, 125.94, 125.91, 123.89, 122.97, 121.74, 121.64, 65.21, 64.19, 52.90, 52.57, 49.87, 49.82, 22.57, 22.38(2C), 21.90; LRMS (EI 70 ev) *m/z* (%): 290 (M^+, 27), 246 (57), 231 (100), 215 (26), 202 (51); HRMS *m/z* (ESI) calcd for $C_{20}H_{19}O_2$ $[M+H]^+$ 291.1380, found 291.1377.

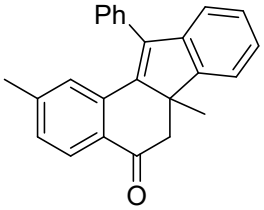
6a-Methyl-11-(trimethylsilyl)-6,6a-dihydro-5*H*-benzo[*a*]fluoren-5-one (3la):



71% yield; Yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.01 (d, *J* = 7.5 Hz, 1H), 7.57 (d, *J* = 7.5 Hz, 1H), 7.53-7.48 (m, 2H), 7.39-7.36 (m, 1H), 7.31 (d, *J* = 7.0 Hz, 1H), 7.26-7.23 (m, 1H), 7.18-7.16 (m, 1H), 3.08 (d, *J* = 16.5 Hz, 1H), 2.23 (d, *J* = 17.0 Hz, 1H), 1.13 (s, 3H), 0.28 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 197.87, 159.52, 152.51, 147.47, 137.84, 136.60, 132.81, 130.72, 129.24, 128.55, 127.02, 126.94, 125.18, 123.97, 121.76, 55.62, 50.41, 22.22, 1.36; IR (KBr, cm^{-1}): 1686; LRMS (EI 70 ev) *m/z* (%): 318 (M^+, 55), 303

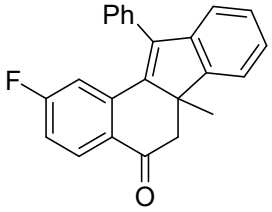
(48), 229 (19) ; HRMS *m/z* (ESI) calcd for $C_{21}H_{23}OSi$ $[M+H]^+$ 319.1513, found 319.1516.

2,6a-Dimethyl-11-phenyl-6,6a-dihydro-5*H*-benzo[*a*]fluoren-5-one (3ma):[3]



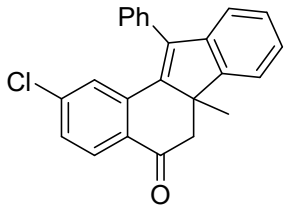
58% yield; Light yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.01 (d, *J* = 8.0 Hz, 1H), 7.49-7.41 (m, 6H), 7.31-7.26 (m, 3H), 7.13 (d, *J* = 8.0 Hz, 1H), 6.94 (s, 1H), 3.23 (d, *J* = 16.0 Hz, 1H), 2.49 (d, *J* = 16.0 Hz, 1H), 2.15 (s, 3H), 1.37 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 197.37, 152.04, 144.38, 143.96, 143.17, 137.75, 135.73, 134.68, 129.09, 128.83, 128.79, 128.45, 127.96, 127.93, 127.45, 127.39, 126.06, 121.56, 121.53, 52.50, 49.24, 23.23, 21.74; LRMS (EI 70 ev) *m/z* (%): 336 (M^+, 87), 321 (100), 276 (16).

2-Fluoro-6a-methyl-11-phenyl-6,6a-dihydro-5*H*-benzo[*a*]fluoren-5-one (3na):



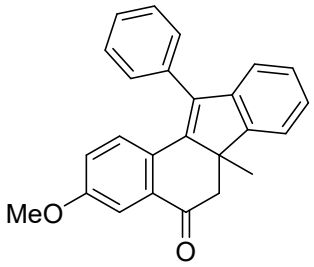
57% yield; White solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.15-8.12 (m, 1H), 7.52-7.49 (m, 2H), 7.48-7.45(m, 2H), 7.41 (d, *J* = 6.5 Hz, 2H), 7.35-7.30 (m, 2H), 7.28-7.24 (m, 1H), 7.01-6.97 (m, 1H), 6.81-6.78 (m, 1H), 3.25 (d, *J* = 16.0 Hz, 1H), 2.49 (d, *J* = 16.0 Hz, 1H), 1.38 (s, 3H);^{13}C NMR (125 MHz, $CDCl_3$): δ 196.14, 166.51(d, *J* = 253.75Hz), 151.93, 144.06, 141.84, 139.45, 138.38 (d, *J* = 9.0 Hz), 133.97, 130.48 (d, *J* = 9.0 Hz), 129.12, 128.89, 128.34, 127.56, 127.33 (d, *J* = 2.5 Hz), 126.56, 121.90, 121.62, 115.33 (d, *J* = 22.5Hz), 113.67 (d, *J* = 22.5Hz), 52.49, 48.99, 23.19; ^{19}F NMR (471 MHz, $CDCl_3$) δ -103.51 (s); IR (KBr, cm^{-1}): 1684; LRMS (EI 70 ev) *m/z* (%): 340 (M^+, 89), 325 (100), 294 (18), 263 (16); HRMS *m/z* (ESI) calcd for $C_{24}H_{18}FO$ $[M+H]^+$ 341.1336, found 341.1339.

2-Chloro-6a-methyl-11-phenyl-6,6a-dihydro-5*H*-benzo[*a*]fluoren-5-one (3oa):[3]



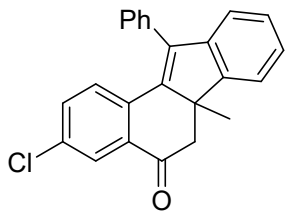
58% yield; Light yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.04 (d, *J* = 8.5 Hz, 1H), 7.53-7.46 (m, 4H), 7.41 (d, *J* = 6.5 Hz, 2H), 7.35-7.31 (m, 2H), 7.30-7.25 (m, 2H), 7.11 (d, *J* = 1.5 Hz, 1H), 3.25 (d, *J* = 16.0 Hz, 1H), 2.49 (d, *J* = 16.0 Hz, 1H), 1.37 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 196.52, 151.95, 144.01, 141.53, 139.69, 139.41, 137.18, 133.91, 129.11, 129.04, 128.94, 128.88, 128.38, 127.94, 127.59, 127.25, 126.57, 121.93, 121.63, 52.44, 49.09, 23.16; LRMS (EI 70 ev) *m/z* (%): 358 (M^++2, 33), 356 (M^+, 90), 343 (33), 341 (100).

3-Methoxy-6a-methyl-11-phenyl-6,6a-dihydro-5*H*-benzo[*a*]fluoren-5-one (3pa):[3]



55% yield; Light yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.59 (d, *J* = 2.5 Hz, 1H), 7.49-7.45 (m, 3H), 7.45-7.41 (m, 3H), 7.28 (t, *J* = 9.0 Hz, 2H), 7.24-7.23 (m, 1H), 7.10 (d, *J* = 8.5 Hz, 1H), 6.90-6.88 (m, 1H), 3.85 (s, 3H), 3.25 (d, *J* = 15.5 Hz, 1H), 2.50 (d, *J* = 16.0 Hz, 1H), 1.37 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 197.59, 159.14, 151.64, 144.61, 142.89, 136.18, 134.86, 131.90, 129.16, 129.07, 128.94, 128.91, 127.84, 127.38, 125.73, 121.62, 121.49, 121.23, 109.33, 55.44, 52.44, 49.18, 23.47; LRMS (EI 70 ev) *m/z* (%): 352 (M^+, 100), 337 (100), 294 (11), 265 (15).

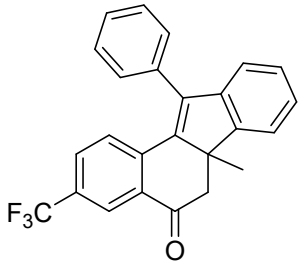
3-Chloro-6a-methyl-11-phenyl-6,6a-dihydro-5*H*-benzo[*a*]fluoren-5-one (3qa):[3]



60% yield; Light yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.07 (d, *J* = 2.0 Hz, 1H), 7.51-7.43 (m, 4H), 7.43-7.40 (m, 2H), 7.34-7.30 (m, 2H), 7.27-7.24 (m, 2H), 7.09 (d, *J* = 8.5 Hz, 1H),

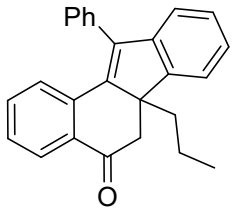
3.27 (d, *J* = 16.0 Hz, 1H), 2.49 (d, *J* = 16.0 Hz, 1H), 1.37 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 196.39, 151.81, 144.16, 141.81, 138.67, 134.32, 134.09, 133.84, 133.28, 131.82, 129.08, 129.05, 128.97, 128.19, 127.58, 127.27, 126.40, 121.75, 121.62, 52.30, 49.11, 23.17; LRMS (EI 70 ev) *m/z* (%): 358 (M^++2, 37), 356 (M^+, 99), 343 (33), 341 (100).

6a-Methyl-11-phenyl-3-(trifluoromethyl)-6,6a-dihydro-5*H*-benzo[*a*]fluoren-5-one (3ra):



52% yield; Yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.38 (s, 1H), 7.53-7.47 (m, 5H), 7.45-7.41 (m, 2H), 7.38-7.32 (m, 2H), 7.31-7.26 (m, 2H), 3.32 (d, *J* =16.0 Hz, 1H), 2.53 (d, *J* = 16.0 Hz, 1H), 1.39 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 196.30, 152.00, 143.96, 141.44, 140.51, 138.85, 134.04, 130.70, 129.65, 129.39 (q, *J* = 3.75Hz), 129.18, 128.90, 128.40, 128.18, 127.71, 126.86, 124.74 (q, *J* = 3.75Hz), 123.66 (q, *J* = 270 Hz), 122.13, 121.71, 52.31, 49.12, 23.06; ^{19}F NMR (471 MHz, $CDCl_3$): δ -62.9; IR (KBr, cm^{-1}): 1692; LRMS (EI 70 ev) *m/z* (%): 390 (M^+, 84), 375 (100), 276 (22); HRMS *m/z* (ESI) calcd for $C_{25}H_{18}F_3O$ $[M+H]^+$ 391.1304, found 391.1300.

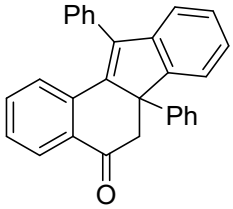
11-Phenyl-6a-propyl-6,6a-dihydro-5*H*-benzo[*a*]fluoren-5-one (3ab):



60% yield; Yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.12-8.10 (m, 1H), 7.49-7.46 (m, 2H), 7.44-7.40 (m, 4H), 7.34-7.28 (m, 4H), 7.24-7.22 (m, 1H), 7.15-7.12 (m, 1H), 3.29 (d, *J* = 16.0 Hz, 1H), 2.53 (d, *J* = 16.0 Hz, 1H), 1.98-1.93 (m, 1H), 1.76-1.70 (m, 1H), 0.93-0.83 (m, 1H),

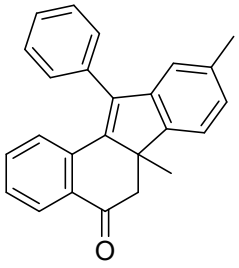
0.79-0.68 (m, 1H), 0.60 (t, J = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 197.76, 150.29, 145.57, 141.46, 139.18, 135.85, 134.71, 133.31, 130.69, 129.10, 128.93, 127.91, 127.67, 127.36 (2C), 127.31, 125.98, 121.60, 121.27, 56.13, 49.11, 38.91, 17.09, 14.08; IR (KBr, cm^{-1}): 1684; LRMS (EI 70 ev) *m/z* (%): 350 (M^+, 53), 307 (100), 276 (23); HRMS *m/z* (ESI) calcd for $C_{26}H_{23}O$ $[M+H]^+$ 351.1743, found 351.1743.

6a,11-Diphenyl-6,6a-dihydro-5*H*-benzo[*a*]fluoren-5-one (3ac):



63% yield; Light yellow solid;^{1}H NMR (500 MHz, $CDCl_3$): δ 7.96-7.94 (m, 1H), 7.53-7.50 (m, 4H), 7.49-7.46 (m, 1H), 7.29-7.26 (m, 3H), 7.26-7.24 (s, 2H), 7.24-7.22 (m, 1H), 7.21-7.18 (m, 2H), 7.16-7.13 (m, 3H), 7.08 (t, J = 7.5 Hz, 1H), 4.07 (d, J = 16.5 Hz, 1H), 2.77 (d, J = 16.5 Hz, 1H);^{13}C NMR (125 MHz, $CDCl_3$): δ 197.01, 152.48, 144.32, 143.03, 140.01, 139.70, 136.27, 134.31, 133.29, 130.74, 129.16, 129.05, 128.81, 128.21, 127.73, 127.56, 127.50, 127.36, 127.00, 126.70, 126.18, 122.90, 121.78, 60.17, 47.52; IR (KBr, cm^{-1}): 1684; LRMS (EI 70 ev) *m/z* (%): 384 (M^+, 100), 306 (20), 276 (24) ; HRMS *m/z* (ESI) calcd for $C_{29}H_{21}O$ $[M+H]^+$ 385.1587, found 385.1587.

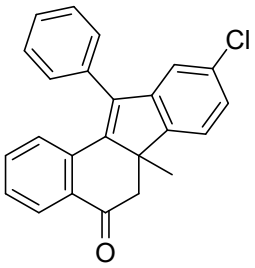
6a,9-Dimethyl-11-phenyl-6,6a-dihydro-5*H*-benzo[*a*]fluoren-5-one (3ae):[3]



64% yield; Light yellow solid;^{1}H NMR (500 MHz, $CDCl_3$): δ 8.11-8.10 (m, 1H), 7.51-7.45 (m, 3H), 7.43-7.41 (m, 2H), 7.36 (d, J = 7.5 Hz, 1H), 7.31-7.29 (m, 2H), 7.13 (d, J = 7.5 Hz, 2H), 7.05 (s, 1H), 3.24 (d, J = 16.0 Hz, 1H), 2.50 (d, J = 16.0 Hz, 1H), 2.36 (s, 3H), 1.37 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 197.77, 149.38, 144.68, 143.32, 138.07, 137.37, 135.92, 134.87, 133.28, 130.70, 129.17, 129.02, 128.47, 127.99, 127.65, 127.41, 127.00, 122.24, 121.37, 52.17, 49.55, 23.33, 21.54; LRMS (EI 70 ev)

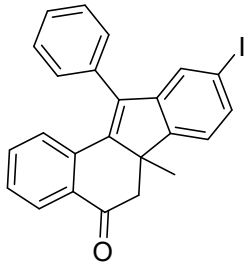
m/z (%): 336 (M^+, 73), 321 (100), 276 (19).

9-Chloro-6a-methyl-11-phenyl-6,6a-dihydro-5*H*-benzo[*a*]fluoren-5-one (3af):[3]



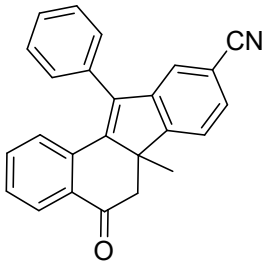
61% yield; White solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.13-8.11 (m, 1H), 7.52-7.48 (m, 2H), 7.47-7.43 (m, 1H), 7.41-7.37 (m, 3H), 7.35-7.31 (m, 2H), 7.29-7.27 (m, 1H), 7.21 (d, *J* = 2.0 Hz, 1H), 7.16-7.14 (m, 1H), 3.24 (d, *J* = 16.0 Hz, 1H), 2.50 (d, *J* = 16.0 Hz, 1H), 1.37 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 197.07, 150.15, 146.16, 144.54, 137.03, 135.32, 133.97, 133.51, 133.39, 130.64, 129.15, 129.01, 128.29, 128.13, 127.66, 127.47, 126.02, 122.56, 121.74, 52.21, 49.10, 23.16; LRMS (EI 70 ev) *m/z* (%): 358 (M^++2, 35), 356 (M^+, 97), 341 (100), 276 (42), 138 (34).

9-Iodo-6a-methyl-11-phenyl-6,6a-dihydro-5*H*-benzo[*a*]fluoren-5-one (3ag):



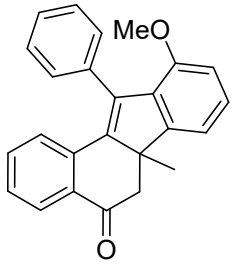
60% yield; Light yellow solid;^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12-8.10 (m, 1H), 7.64-7.62 (m, 1H), 7.55 (s, 1H), 7.51-7.49 (m, 2H), 7.47-7.44 (m, 1H), 7.39-7.38 (m, 2H), 7.36-7.30 (m, 2H), 7.22 (d, *J* = 7.5 Hz, 1H), 7.14-7.13 (m, 1H), 3.23 (d, *J* = 16.0 Hz, 1H), 2.49 (d, *J* = 16.5 Hz, 1H), 1.36 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.95, 151.32, 146.62, 144.09, 136.81, 135.20, 134.82, 133.91, 133.35, 130.60, 130.49, 129.14, 128.97, 128.25, 128.09, 127.63, 127.44, 123.36, 92.91, 52.30, 48.92, 23.02; LRMS (EI 70 ev) *m/z* (%): 448 (M^+, 88), 433 (53), 276 (65), 215 (28), 138 (83); HRMS *m/z* (ESI) calcd for $C_{24}H_{18}IO$ $[M+H]^+$ 449.0397, found 449.0402.

6a-Methyl-5-oxo-11-phenyl-6,6a-dihydro-5*H*-benzo[*a*]fluorene-9-carbonitrile (3ah):



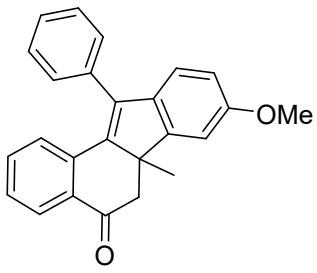
58% yield; Light yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.14-8.12 (m, 1H), 7.62-7.60 (m, 1H), 7.56-7.51 (m, 3H), 7.51-7.49 (m, 2H), 7.40-7.37 (m, 3H), 7.37-7.34 (m, 1H), 7.20-7.18 (m, 1H), 3.27 (d, *J* = 16.0 Hz, 1H), 2.51 (d, *J* = 16.0 Hz, 1H), 1.40 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 196.33, 156.21, 145.35, 145.02, 136.39, 134.82, 133.55, 133.32, 130.63, 130.02, 129.32, 128.90, 128.60, 128.57, 127.72, 127.57, 124.99, 122.34, 119.09, 111.51, 52.94, 48.48, 22.90; LRMS (EI 70 ev) *m/z* (%): 347 (M^+, 91), 332 (100), 314 (18), 269 (32); HRMS *m/z* (ESI) calcd for $C_{25}H_{18}NO$ $[M+H]^+$ 348.1383, found 348.1390.

10-Methoxy-6a-methyl-11-phenyl-6,6a-dihydro-5*H*-benzo[*a*]fluoren-5-one (3ai)



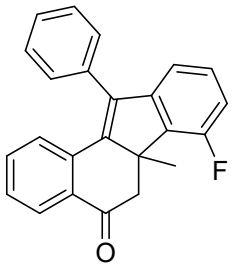
25% yield; Light yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.5 Hz, 1H), 7.52-7.32 (m, 4H), 7.29-7.21 (m, 4H), 7.09 (d, *J* = 7.5 Hz, 1H), 6.92 (d, *J* = 7.5 Hz, 1H), 6.80 (d, *J* = 8.0 Hz, 1H), 3.54 (s, 3H), 3.21 (d, *J* = 16.0 Hz, 1H), 2.50 (d, *J* = 16.0 Hz, 1H), 1.36 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.70, 155.59, 154.43, 142.35, 137.84, 137.06, 136.07, 133.14, 131.59, 130.55, 127.89(2C), 127.63, 127.59, 127.24, 127.21, 127.13, 114.42, 110.70, 55.46, 52.32, 49.38, 23.32; LRMS (EI 70 ev) *m/z* (%): 352 (M^+, 77), 337 (84), 322 (15), 265 (15).

8-Methoxy-6a-methyl-11-phenyl-6,6a-dihydro-5*H*-benzo[*a*]fluoren-5-one (3ai')



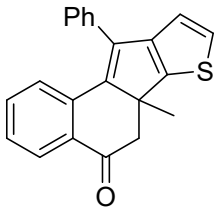
43% yield; Yellow solid;[1]H NMR (500 MHz, $CDCl_3$) δ 8.10-8.08 (m, 1H), 7.49-7.46 (m, 2H), 7.42 (t, *J* = 8.5 Hz, 3H), 7.29-7.28 (m, 2H), 7.16 (d, *J* = 8.5 Hz, 1H), 7.14-7.12 (m, 1H), 7.03 (d, *J* = 2.0 Hz, 1H), 6.85-6.83 (m, 1H), 3.87 (s, 3H), 3.21 (d, *J* = 16.0 Hz, 1H), 2.53 (d, *J* = 16.0 Hz, 1H), 1.37 (s, 3H). [13]C NMR (125 MHz, $CDCl_3$) δ 197.6, 159.0, 153.9, 141.0, 137.8, 137.5, 136.1, 134.9, 133.2, 130.4, 129.0, 128.9, 127.9, 127.4, 127.3, 127.2, 122.3, 112.6, 108.2, 55.6, 52.2, 49.4, 23.4; LRMS (EI 70 ev) *m/z* (%): 352 (M^+, 79), 337 (100), 265 (27); HRMS *m/z* (ESI) calcd for $C_{25}H_{21}O_2$ $[M+H]^+$ 353.1536, found 353.1534.

7-Fluoro-6a-methyl-11-phenyl-6,6a-dihydro-5*H*-benzo[*a*]fluoren-5-one (3aj):



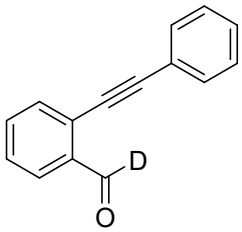
41% yield; Yellow solid; [1]H NMR (500 MHz, $CDCl_3$): δ 8.13-8.11 (m, 1H), 7.49-7.44 (m, 3H), 7.43-7.38 (m, 2H), 7.35-7.29 (m, 2H), 7.28-7.24 (m, 1H), 7.15-7.13 (m, 1H), 7.03 (d, *J* = 7.5 Hz, 1H), 6.95 (t, *J* = 8.5 Hz, 1H), 3.53 (d, *J* = 16.0 Hz, 1H), 2.59 (d, *J* = 16.5 Hz, 1H), 1.49 (s, 3H); [13]C NMR (125 MHz, $CDCl_3$): δ 197.09, 158.86 (d, *J* = 246.25 Hz), 147.31 (d, *J* = 6.8 Hz), 143.99, 137.38 (d, *J* = 2.5 Hz), 136.40 (d, *J* = 16.5 Hz), 135.10, 134.27, 133.29, 131.65, 130.70, 129.29 (d, *J* = 6.25 Hz), 129.03, 128.49, 128.11 (d, *J* = 12.5 Hz), 127.67, 127.41, 117.47 (d, *J* = 2.5 Hz), 113.27 (d, *J* = 21.25 Hz), 52.29 (d, *J* = 1.25 Hz), 47.73, 21.46; [19]F NMR (471 MHz, $CDCl_3$): δ -122.19; IR (KBr, cm^{-1}): 1686; LRMS (EI 70 ev) *m/z* (%): 340 (M^+, 100), 325 (91), 294 (21), 262 (28) ; HRMS *m/z* (ESI) calcd for $C_{24}H_{18}FO$ $[M+H]^+$ 341.1336, found 341.1337.

6a-Methyl-10-phenyl-6,6a-dihydro-5*H*-benzo[4,5]indeno[1,2-*b*]thiophen-5-one (3ak):



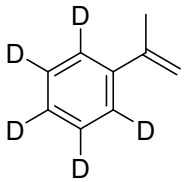
44% yield; Yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.11-8.09 (m, 1H), 7.52-7.50 (m, 2H), 7.46-7.43 (m, 2H), 7.42-7.39 (m, 1H), 7.34-7.33 (m, 1H), 7.33-7.29 (m, 2H), 7.24-7.22 (m, 1H), 6.97 (d, *J* = 5.0 Hz, 1H), 3.21 (d, *J* = 16.0 Hz, 1H), 2.62 (d, *J* = 16.5 Hz, 1H), 1.40 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 197.26, 153.34, 148.86, 144.44, 136.23, 135.22, 135.27, 133.31, 130.08, 128.87, 128.55, 128.09, 127.85, 127.46, 127.24, 126.90, 119.64, 51.98, 50.08, 24.22; IR (KBr, cm^{-1}): 1682; LRMS (EI 70 ev) *m/z* (%): 328 (M^+, 88), 313 (100), 252 (36), 207 (52); HRMS *m/z* (ESI) calcd for $C_{22}H_{17}OS$ $[M+H]^+$ 329.0995, found 329.0994.

1a-D (>99%D): [1d]



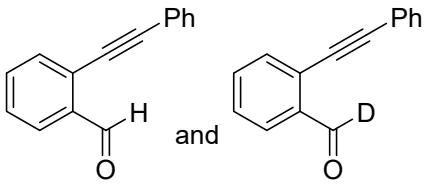
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8 Hz, 1H), 7.61(d, *J* = 8 Hz, 1H), 7.55-7.52 (m, 3H), 7.40 (t, *J* = 7.5Hz, 1H), 7.36-7.35 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 191.14 (t, $J_{C\text{-}D}$ = 27.5 Hz), 135.51, 133.65, 133.02, 131.52, 128.92, 128.45, 128.37, 127.04, 126.67, 122.11, 96.15, 84.75.

2a-D$_5$ (>98%D):[4]



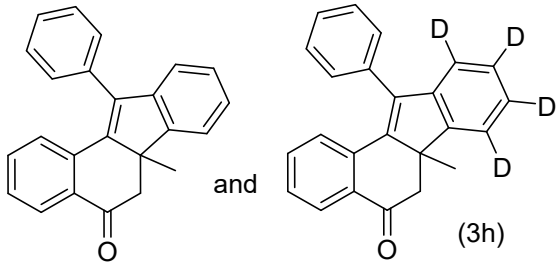
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (s, 0.02H), 7.31(s, 0.02H), 7.16 (s, 0.02H), 5.37 (s, 1H), 5.07 (s, 1H), 2.14 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.12, 140.93, 127.67 (t, $J_{C\text{-}D}$ = 25 Hz), 126.85 (t, $J_{C\text{-}D}$ = 23.75 Hz), 125.01 (t, $J_{C\text{-}D}$ = 25 Hz), 112, 21.8.

1a and **1a-D$_1$**



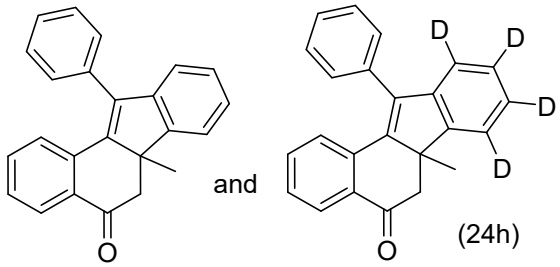
^{1}H NMR (500 MHz, $CDCl_3$) δ 10.65 (s, 0.42H), 7.95 (d, *J* = 7.5 Hz, 1H), 7.64 (d, *J* = 7.5 Hz, 1H), 7.60-7.56 (m, 3H), 7.45 (d, *J* = 7.5 Hz, 1H), 7.39-7.38 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 191.71, 135.68, 133.78, 133.14, 133.13, 131.61, 129.02, 128.56, 128.47, 127.16, 126.81, 122.20, 96.25, 96.22, 84.80.

3aa and 3aa-D_4 (3h)



^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13-8.11 (m, 1H), 7.50-7.45 (m, 3H), 7.45-7.40 (m, 2.62H), 7.34-7.30 (m, 3.24H), 7.27-7.26 (m, 0.62H), 7.17-7.16 (m, 1.02H), 3.27 (d, *J* = 16.0 Hz, 1H), 2.52 (d, *J* = 16.0Hz, 1H), 1.38 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.70, 151.92, 151.84, 144.35, 144.27, 142.89, 137.95, 135.74, 134.59, 133.27, 130.56, 129.06, 128.95, 127.96, 127.67, 127.59, 127.43, 127.35, 126.13, 121.58, 52.42, 49.24, 23.17.

3aa and 3aa-D_4 (24h)

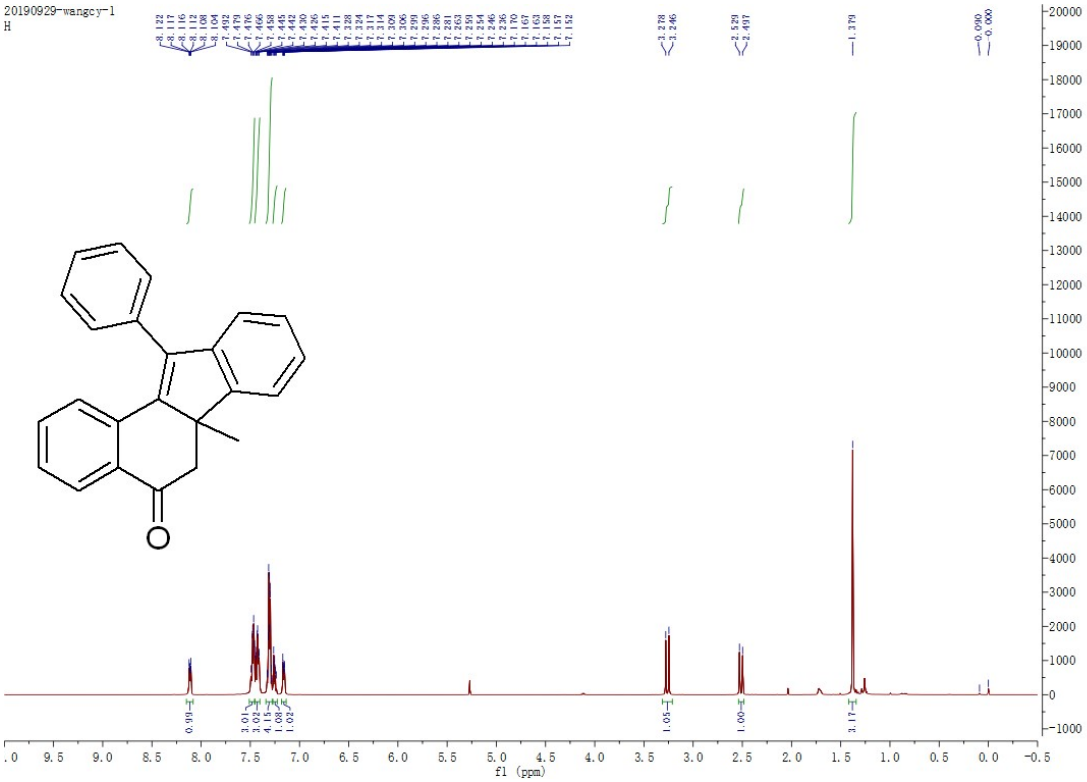


^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13-8.11 (m, 0.98H), 7.50-7.45 (m, 3.07H), 7.45-7.40 (m, 2.69H), 7.33-7.29 (m, 3.28H), 7.27-7.25 (m, 0.64H), 7.17-7.16 (m, 1.02H), 3.27 (d, *J* = 16.0 Hz, 1H), 2.52 (d, *J* = 16.0Hz, 1H), 1.38 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) 197.66, 151.90, 151.82, 144.32, 144.24, 142.87, 137.93, 135.72,

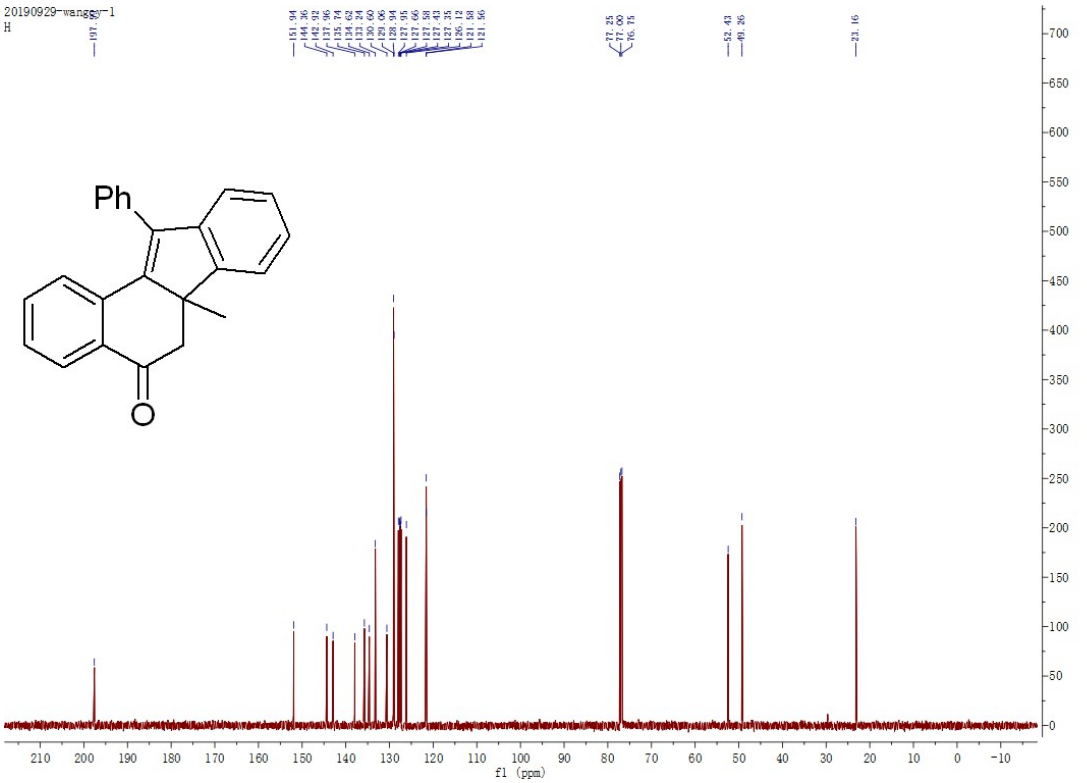
134.57, 133.25, 130.54, 129.04, 128.93, 127.94, 127.66, 127.57, 127.42, 127.34, 126.11, 121.56, 52.40, 49.22, 23.15.

(C) Spectra (NMR Spectra)

6a-Methyl-11-phenyl-6,6a-dihydro-5*H*-benzo[*a*]fluoren-5-one (3aa)

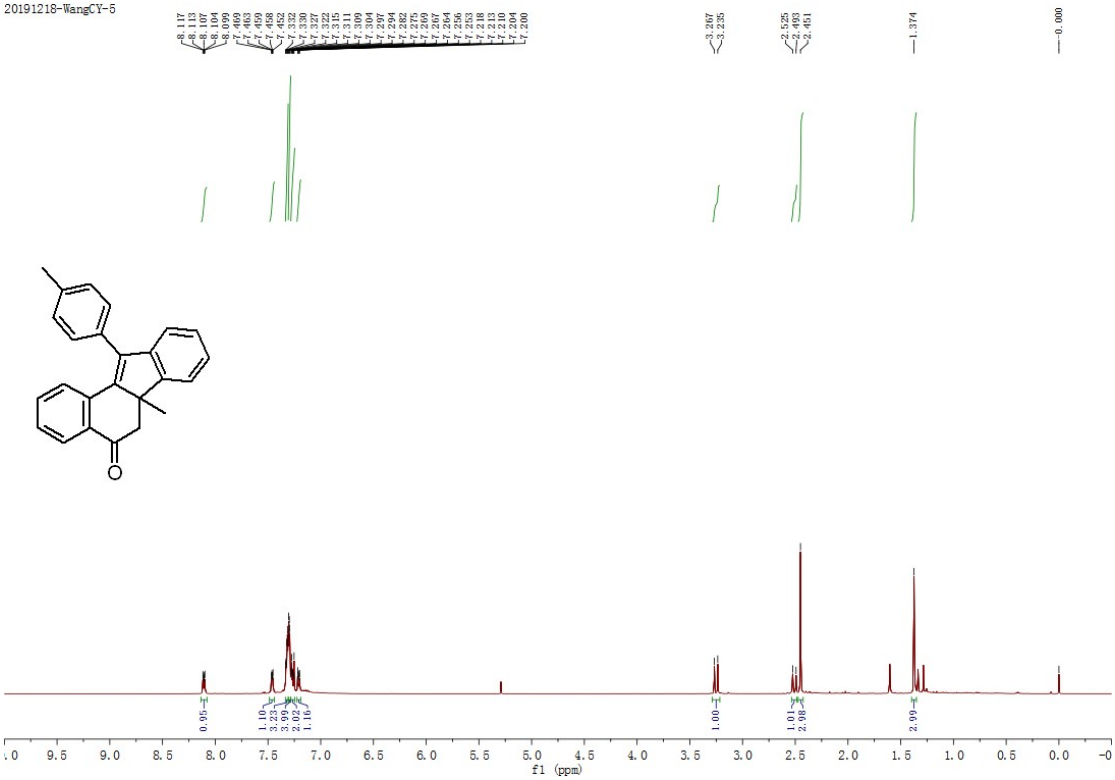


^{1}H NMR (500 MHz, $CDCl_3$)

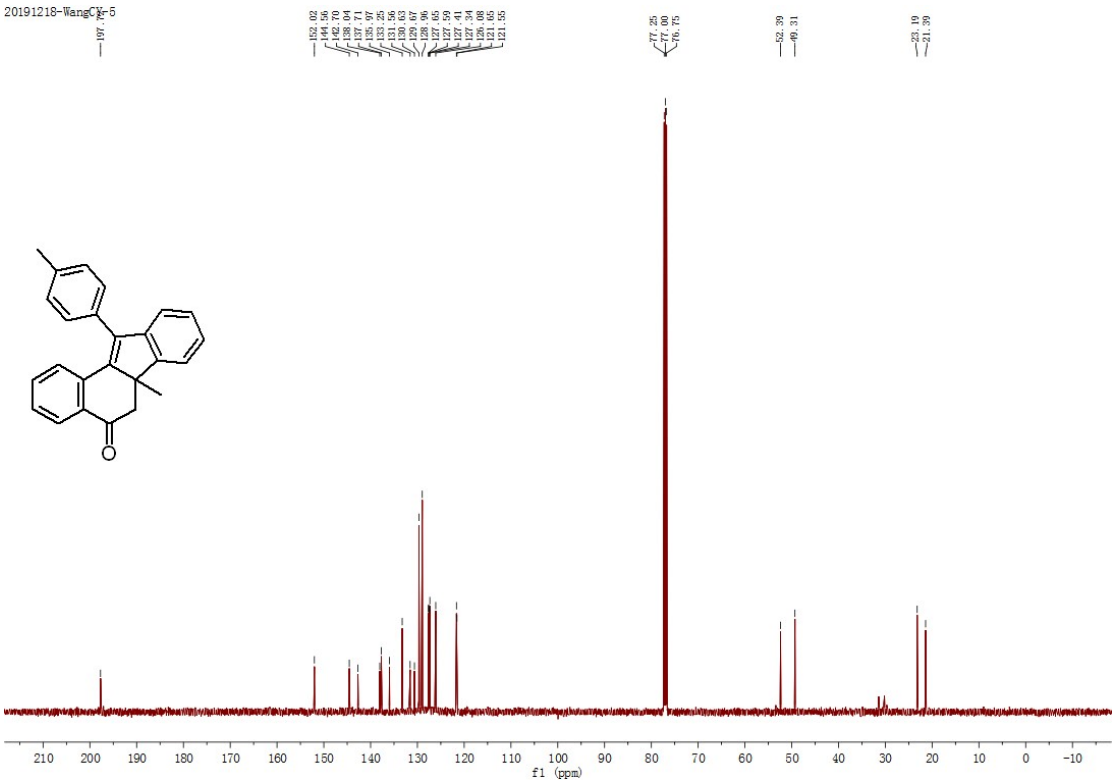


^{13}C NMR (125 MHz, $CDCl_3$)

6a-Methyl-11-(*p*-tolyl)-6,6a-dihydro-5*H*-benzo[*a*]fluoren-5-one (3ba)

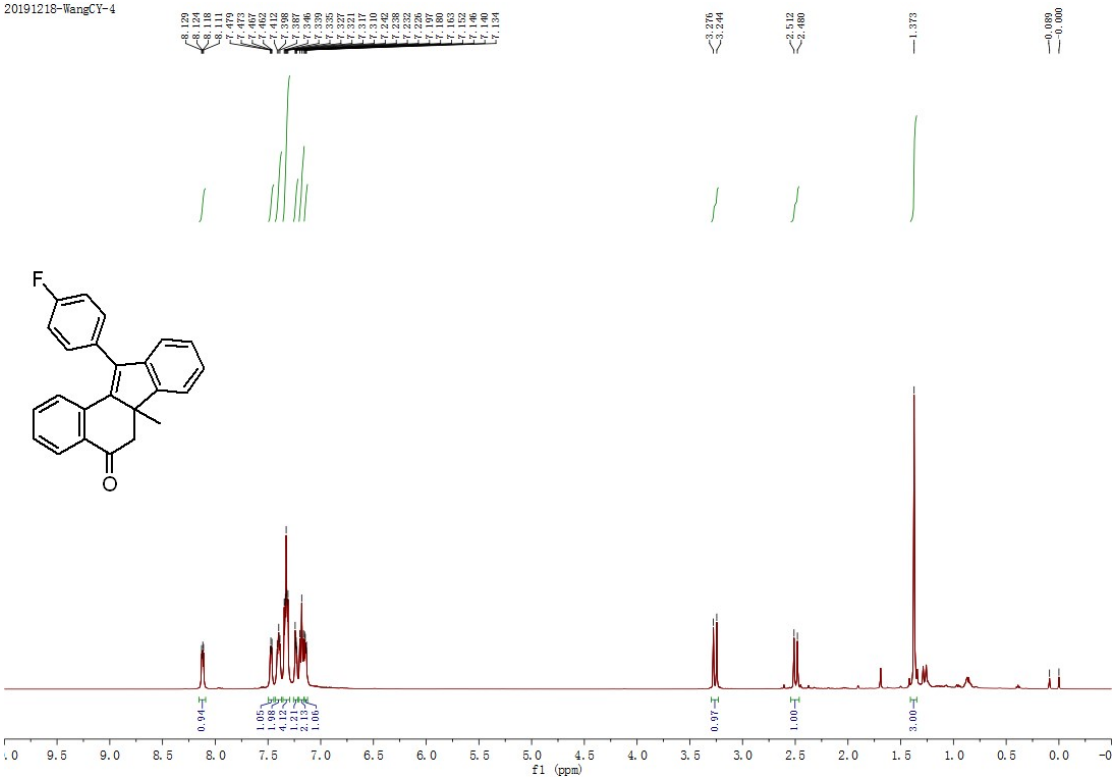


^{1}H NMR (500 MHz, $CDCl_3$)

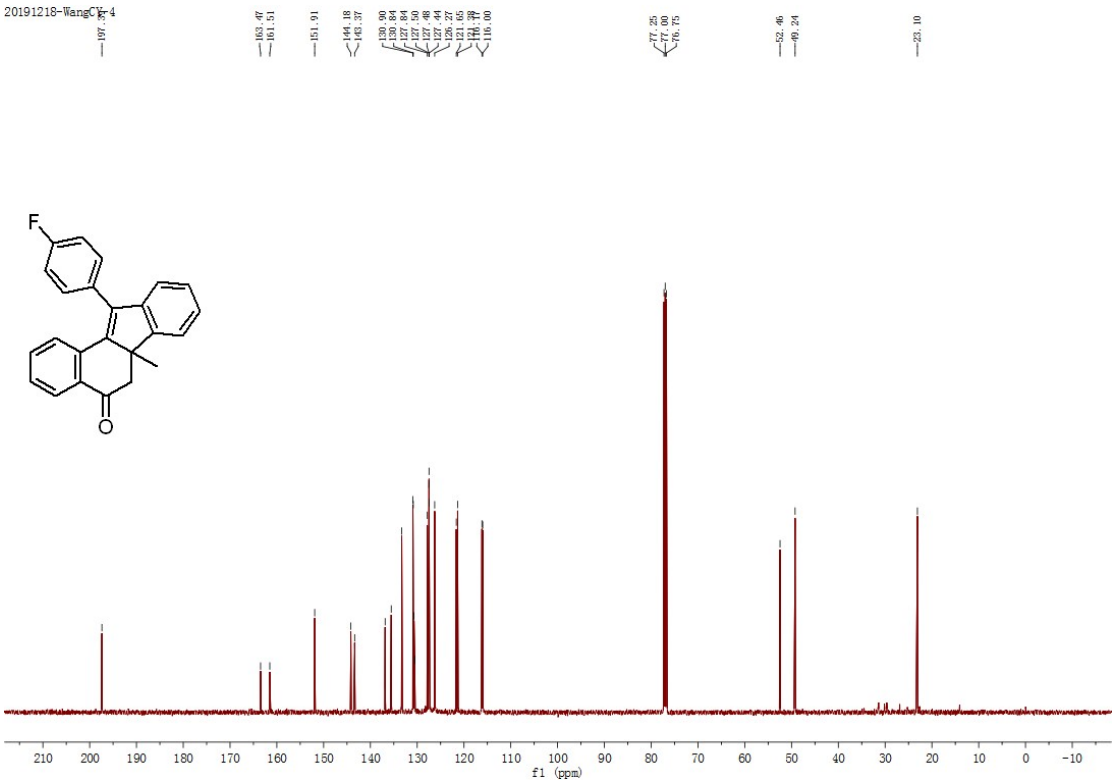


^{13}C NMR (125 MHz, $CDCl_3$)

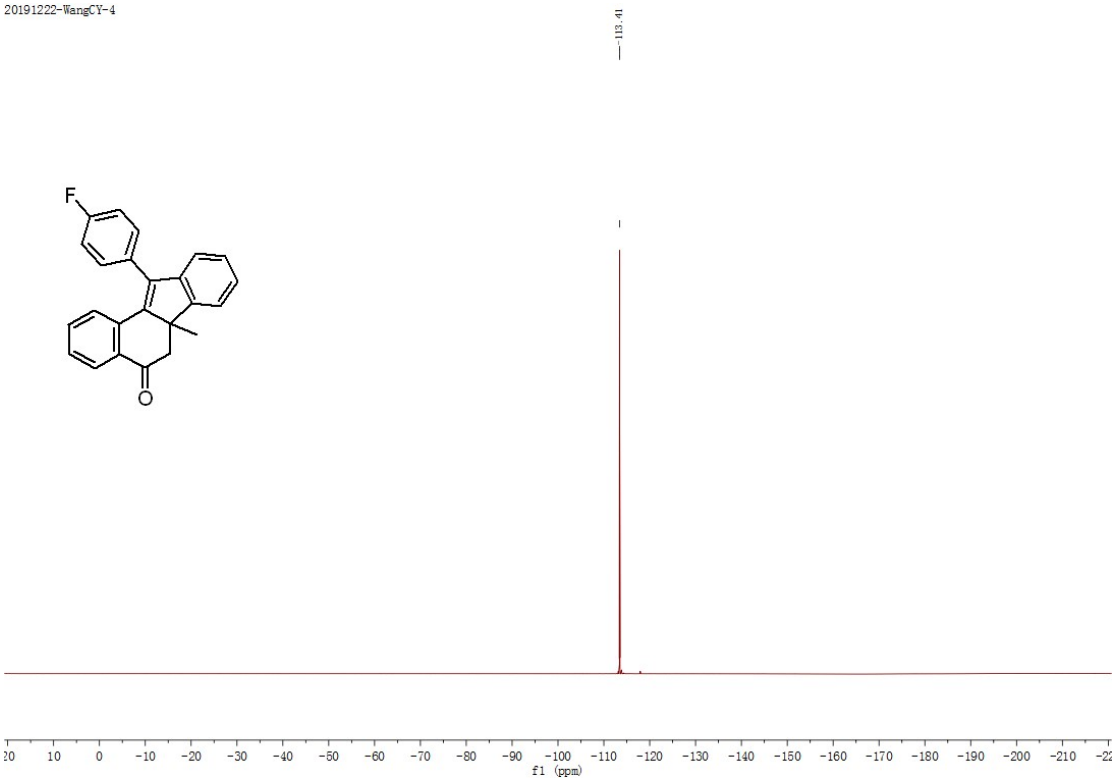
11-(4-Fluorophenyl)-6a-methyl-6,6a-dihydro-5*H*-benzo[*a*]fluoren-5-one (3ca)



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

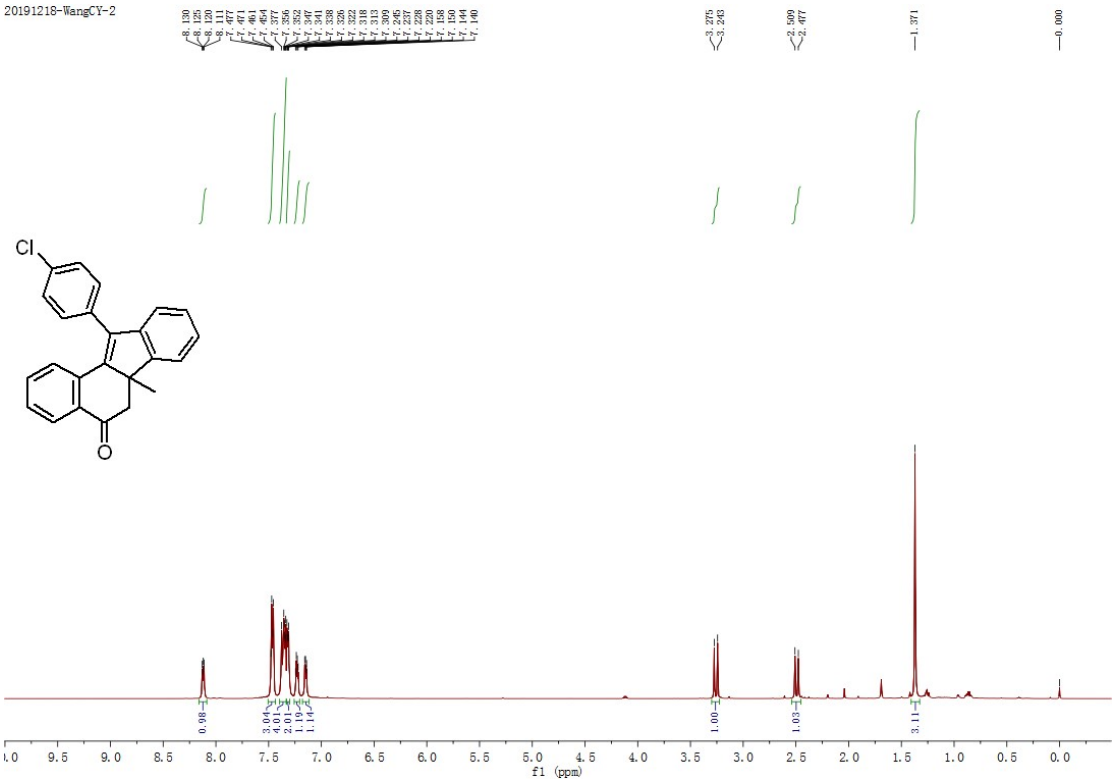


^{13}C NMR (125 MHz, $CDCl_3$)

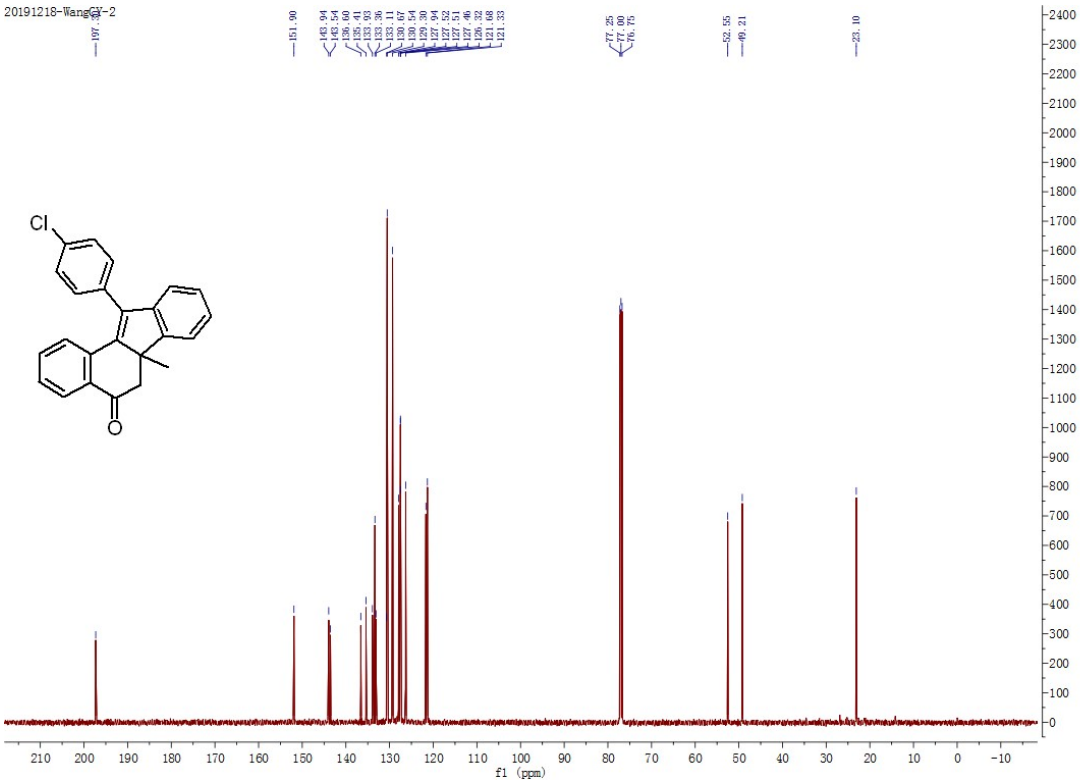


^{19}F NMR (471 MHz, $CDCl_3$)

11-(4-Chlorophenyl)-6a-methyl-6,6a-dihydro-5*H*-benzo[*a*]fluoren-5-one (3da)

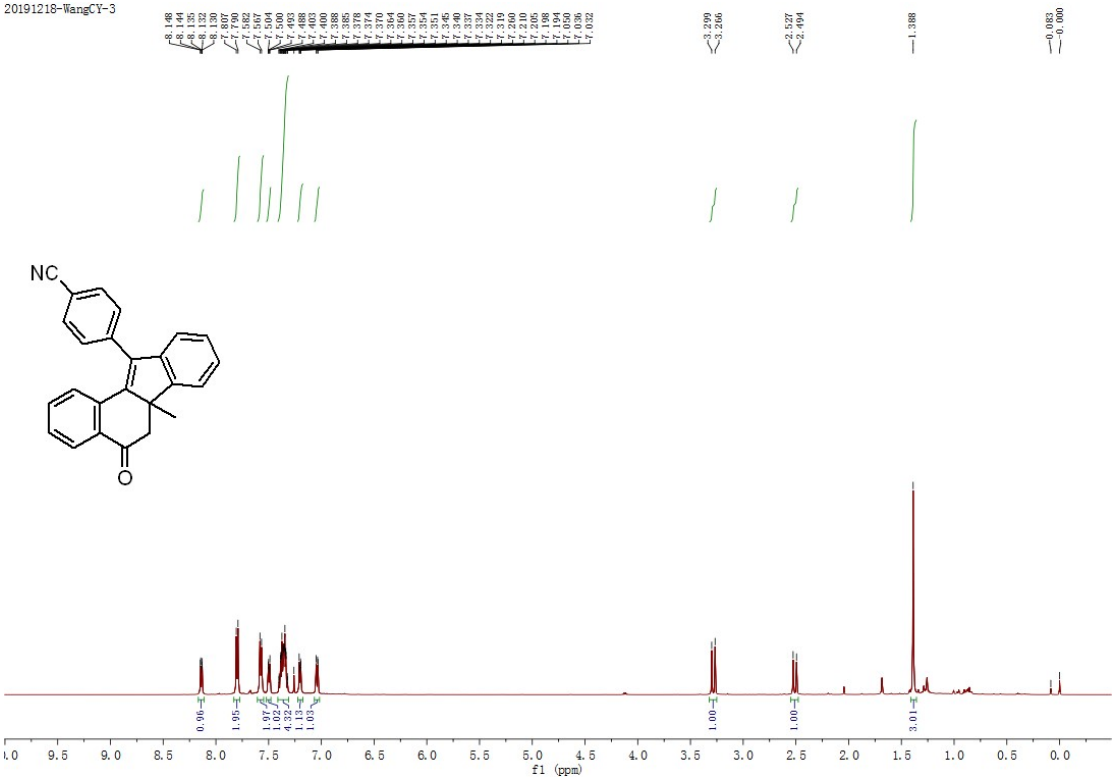


^{1}H NMR (500 MHz, $CDCl_3$)

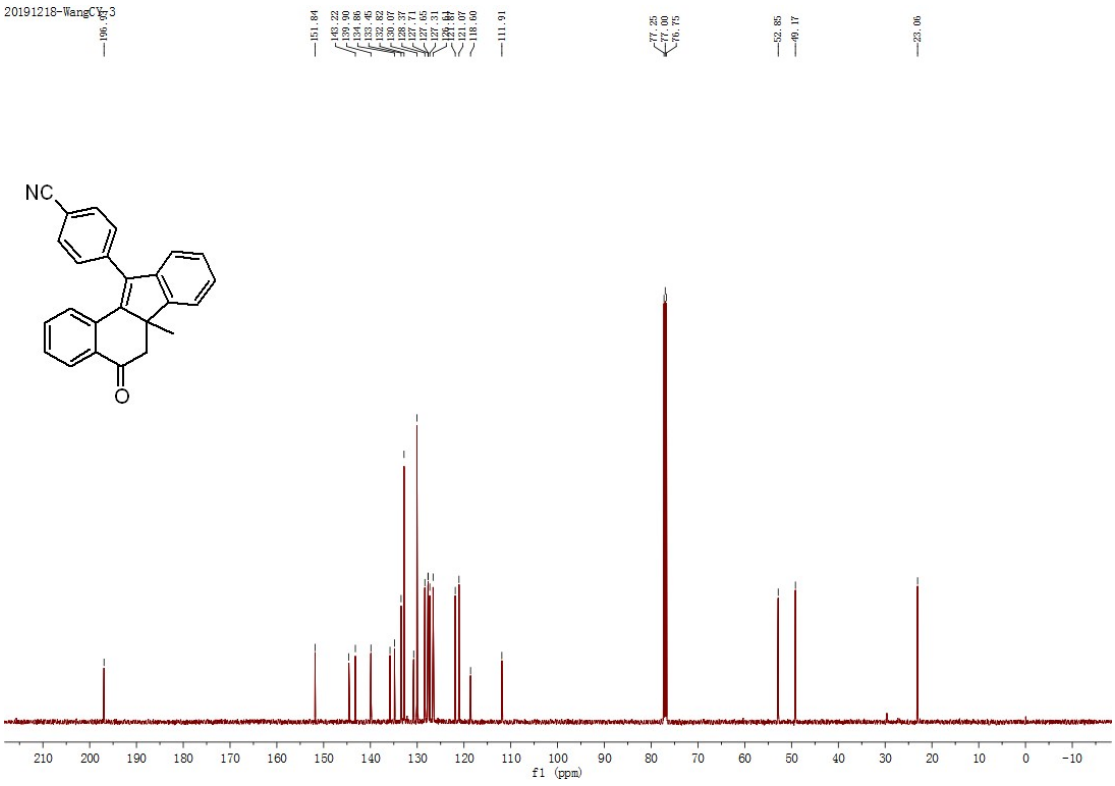


^{13}C NMR (125 MHz, $CDCl_3$)

4-(6a-Methyl-5-oxo-6,6a-dihydro-5*H*-benzo[*a*]fluoren-11-yl)benzonitrile (3ea)

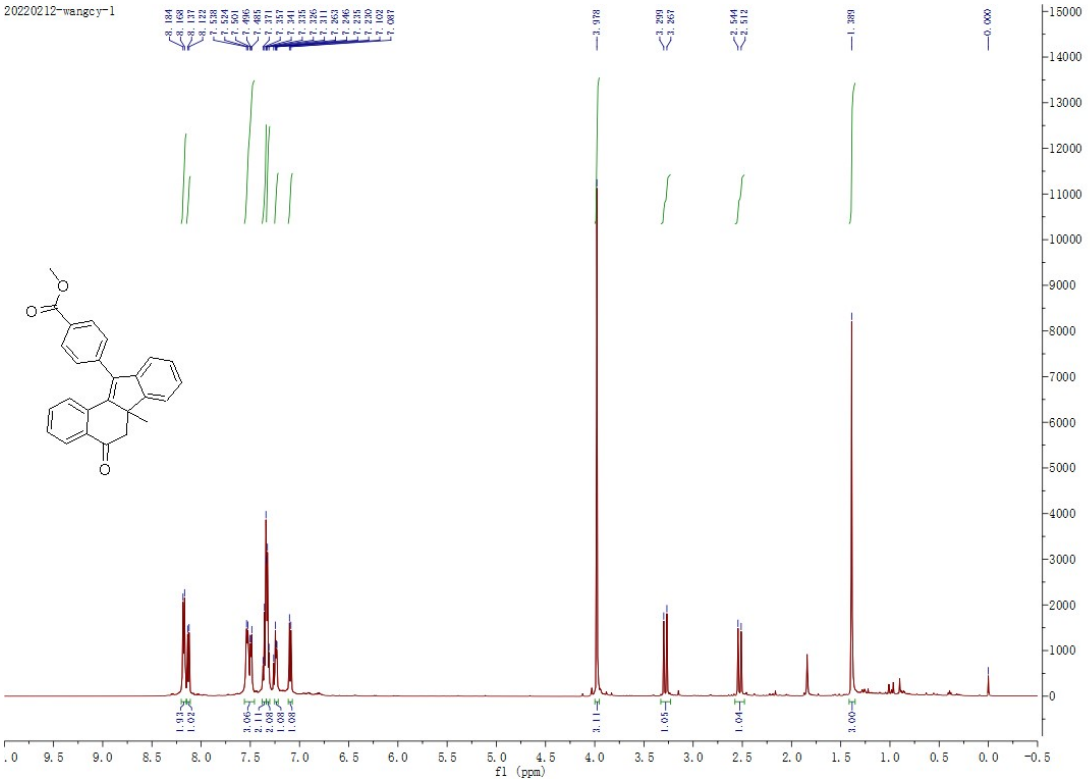


^{1}H NMR (500 MHz, $CDCl_3$)

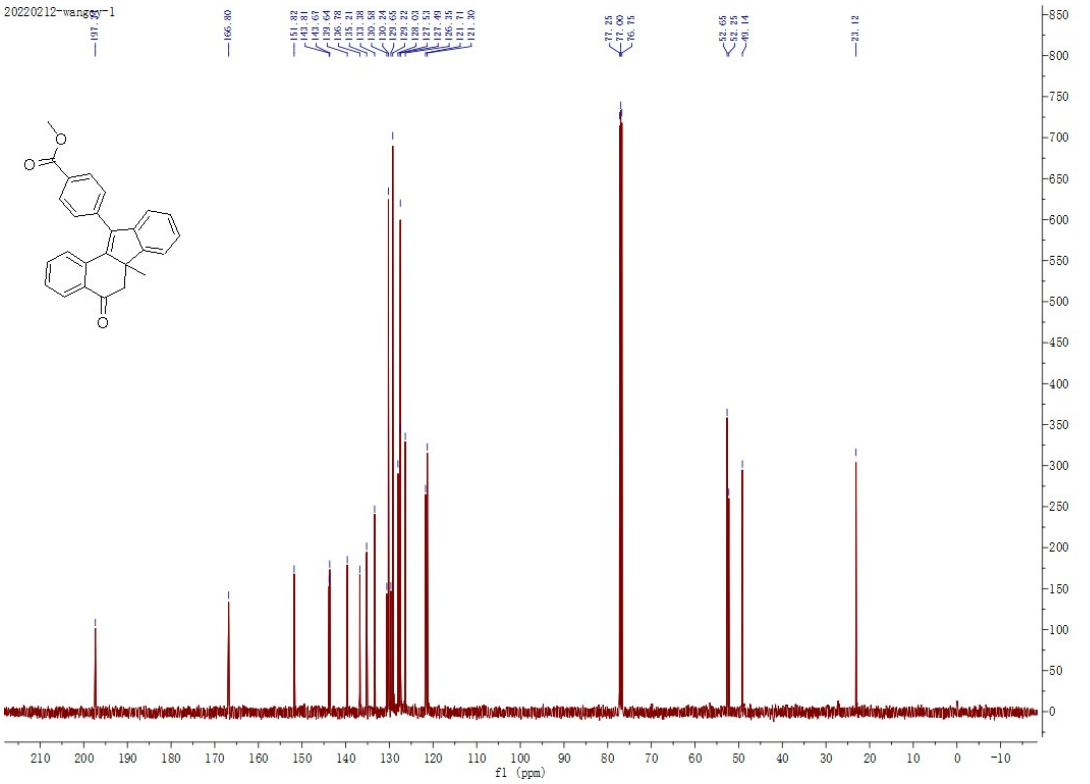


^{13}C NMR (125 MHz, $CDCl_3$)

Methyl 4-(6a-methyl-5-oxo-6,6a-dihydro-5*H*-benzo[*a*]fluoren-11-yl)benzoate (3fa)

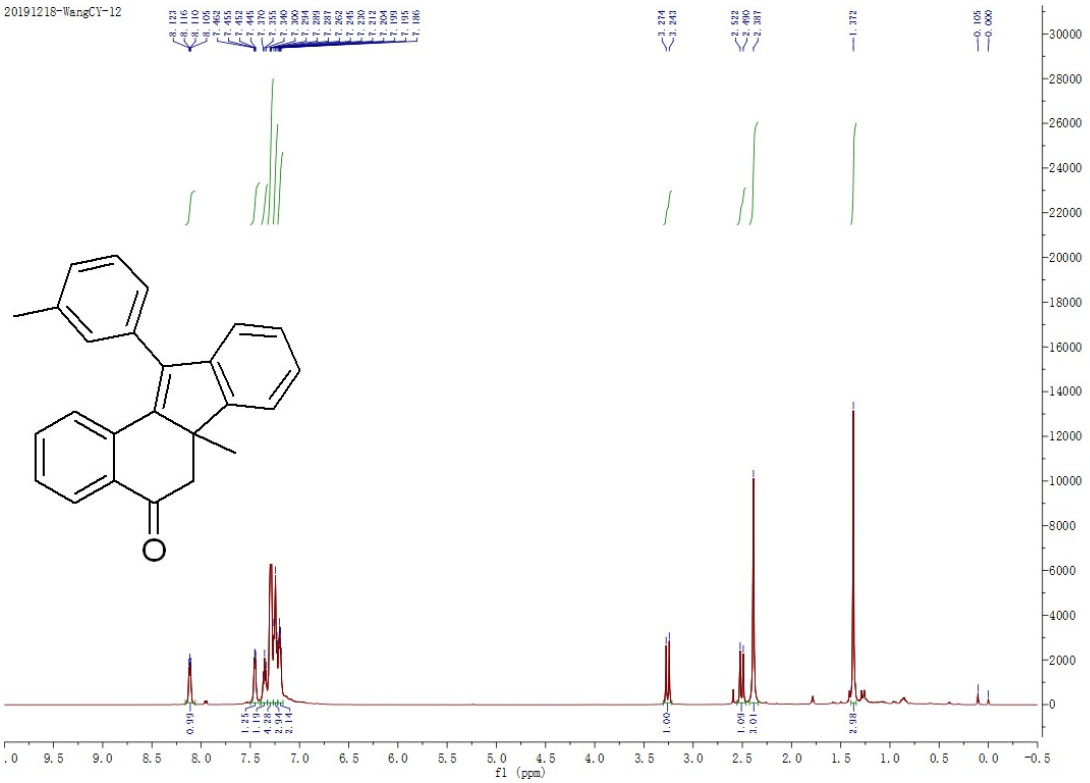


^{1}H NMR (500 MHz, $CDCl_3$)

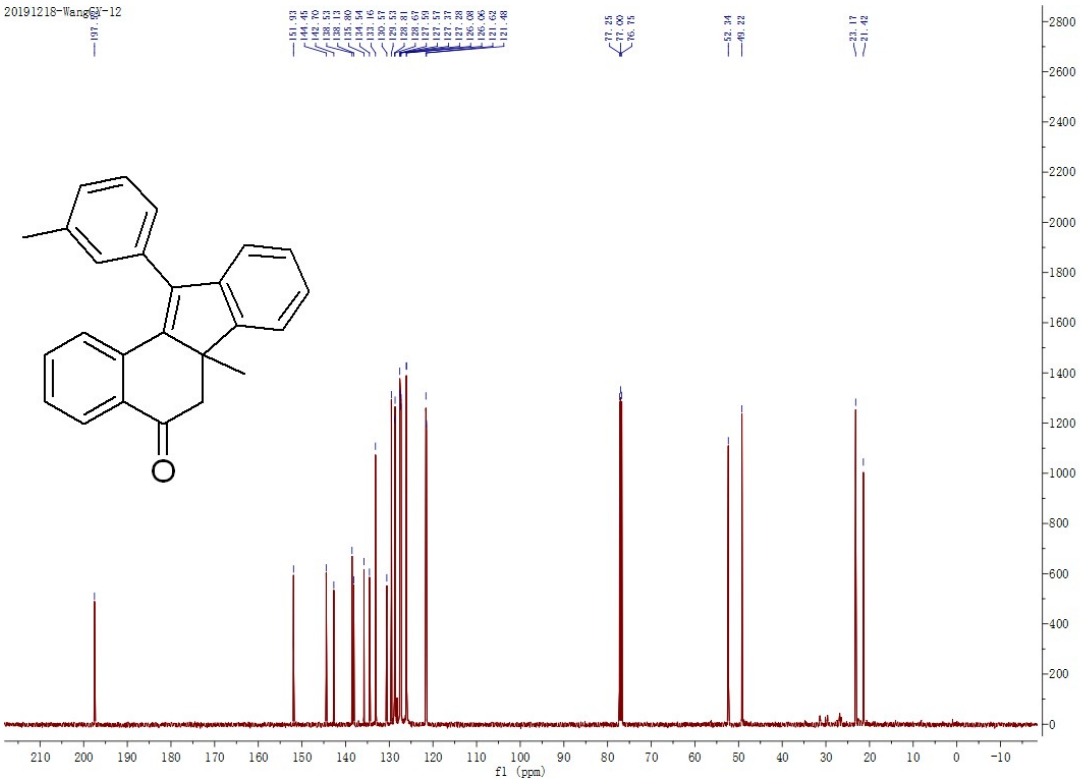


^{13}C NMR (125 MHz, $CDCl_3$)

6a-Methyl-11-(*m*-tolyl)-6,6a-dihydro-5*H*-benzo[*a*]fluoren-5-one (3ga)

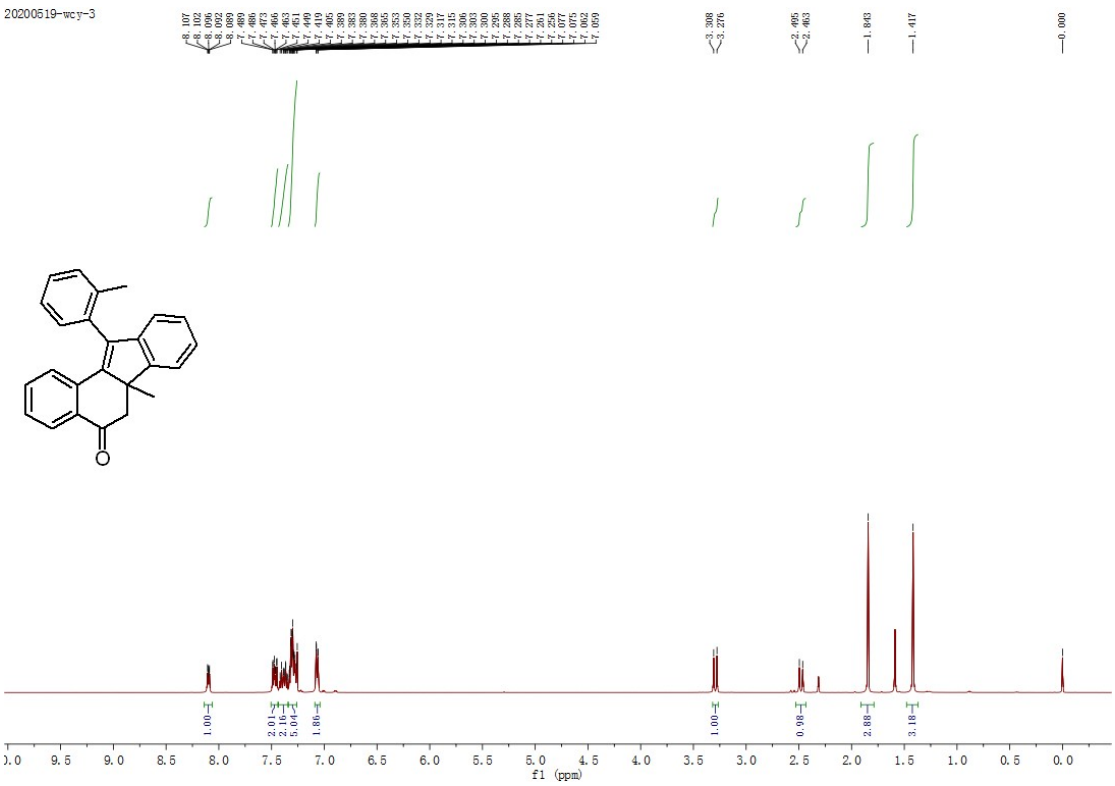


^{1}H NMR (500 MHz, $CDCl_3$)

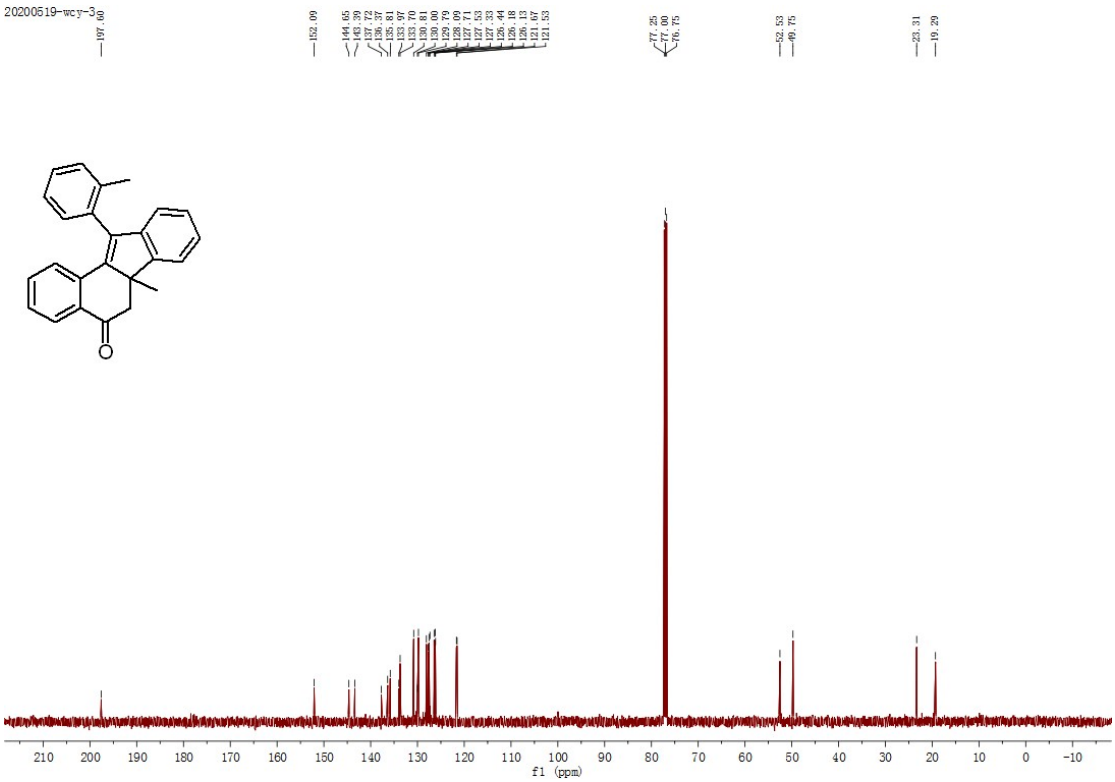


^{13}C NMR (125 MHz, $CDCl_3$)

6a-Methyl-11-(*o*-tolyl)-6,6a-dihydro-5*H*-benzo[*a*]fluoren-5-one (3ha)

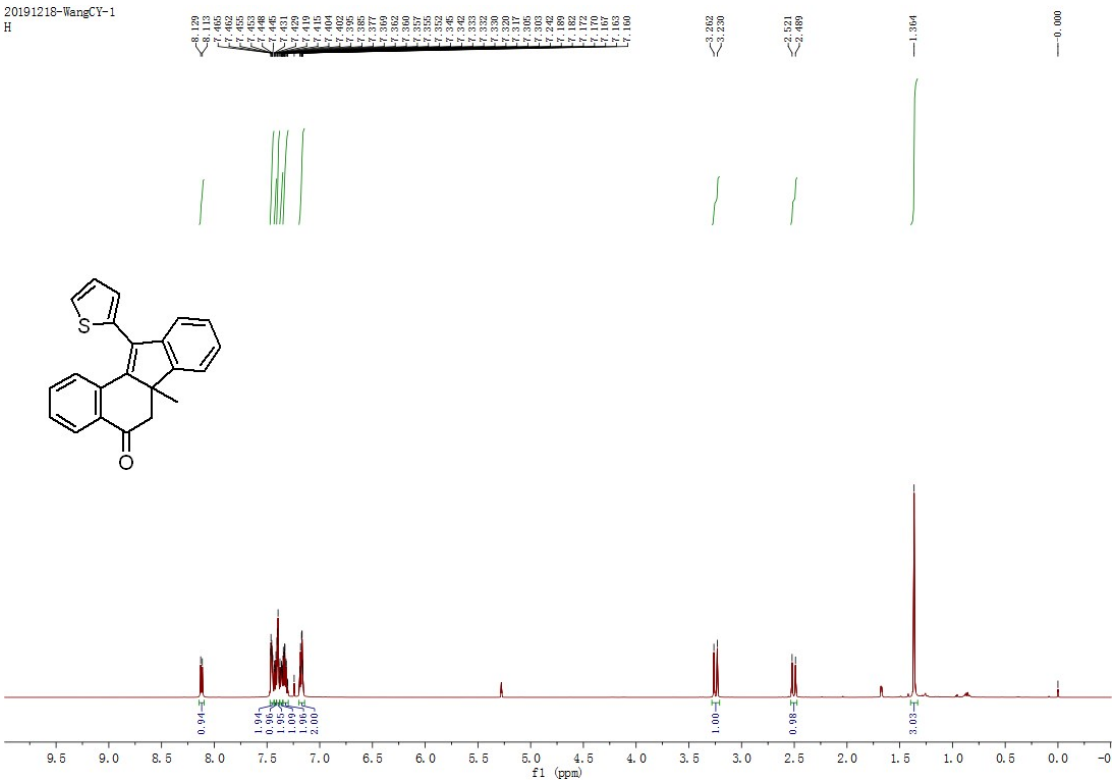


^{1}H NMR (500 MHz, $CDCl_3$)

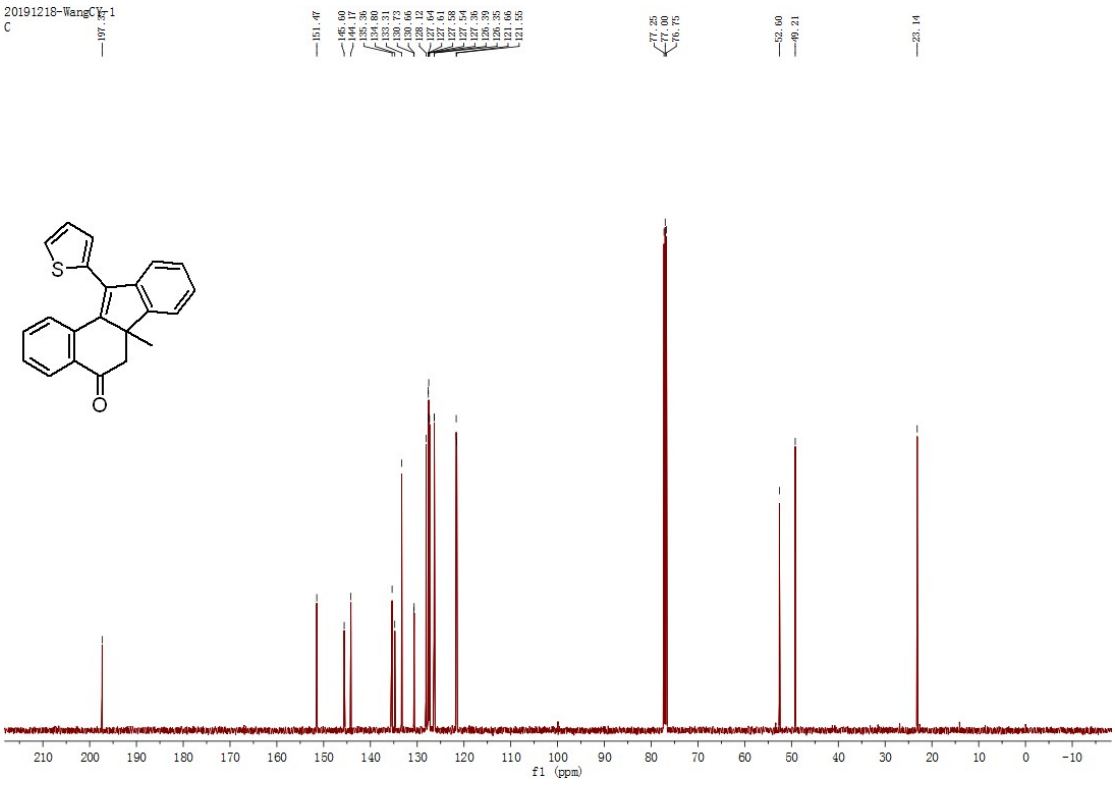


^{13}C NMR (125 MHz, $CDCl_3$)

6a-Methyl-11-(thiophen-2-yl)-6,6a-dihydro-5*H*-benzo[*a*]fluoren-5-one (3ia)

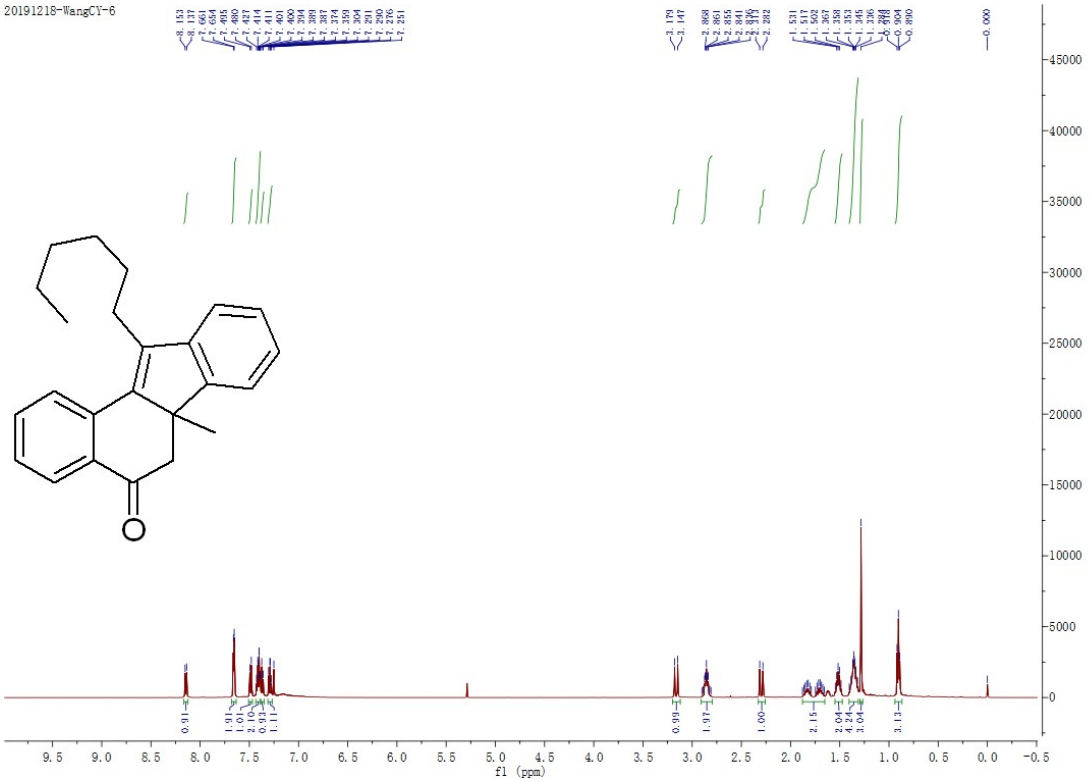


^{1}H NMR (500 MHz, $CDCl_3$)

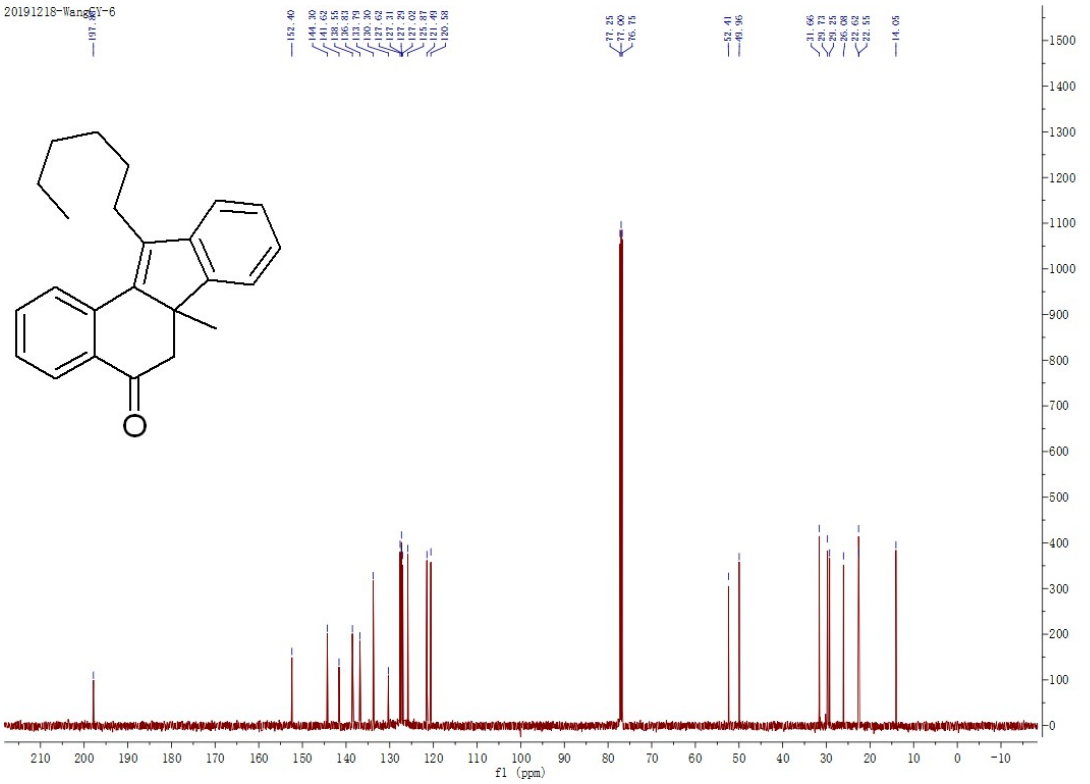


^{13}C NMR (125 MHz, $CDCl_3$)

11-Hexyl-6a-methyl-6,6a-dihydro-5*H*-benzo[*a*]fluoren-5-one (3ja)

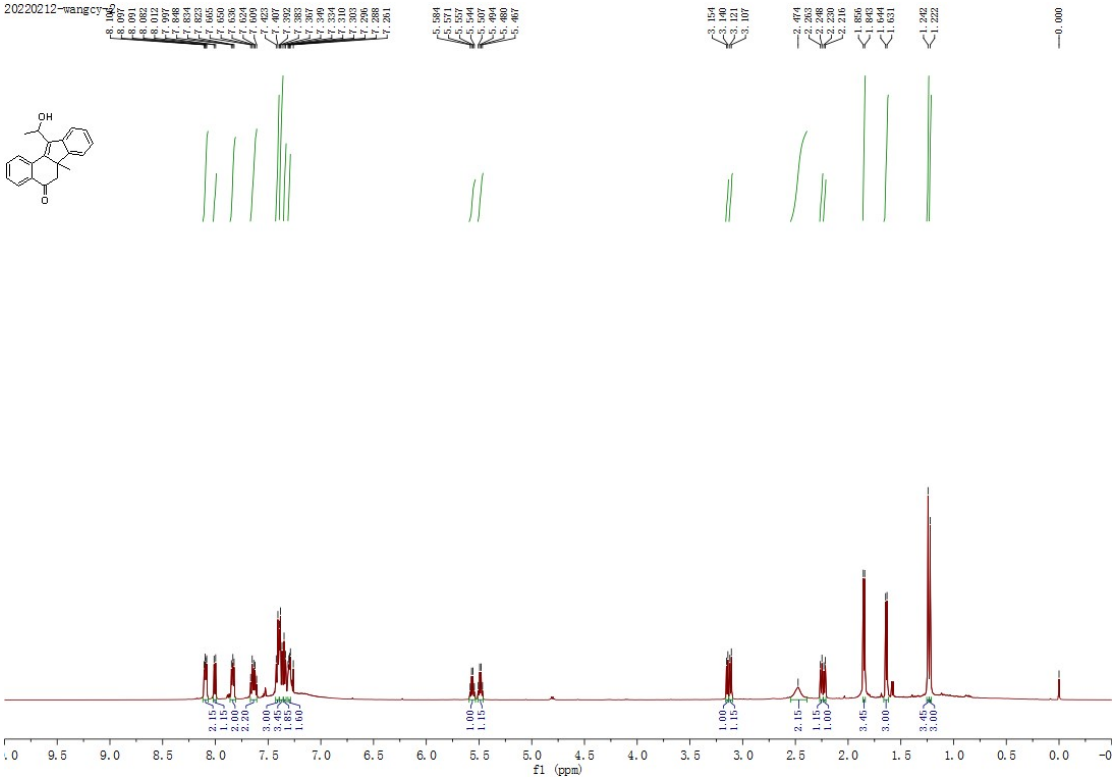


^{1}H NMR (500 MHz, $CDCl_3$)

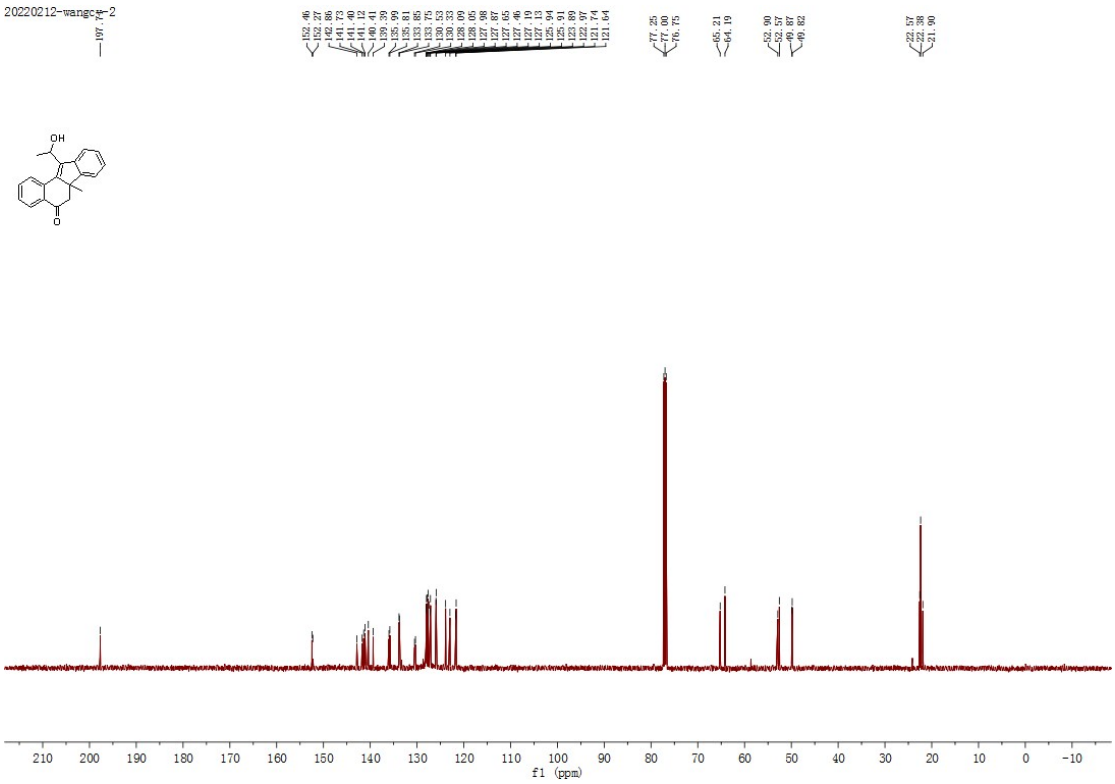


^{13}C NMR (125 MHz, $CDCl_3$)

11-(1-Hydroxyethyl)-6a-methyl-6,6a-dihydro-5*H*-benzo[*a*]fluoren-5-one (3ka)

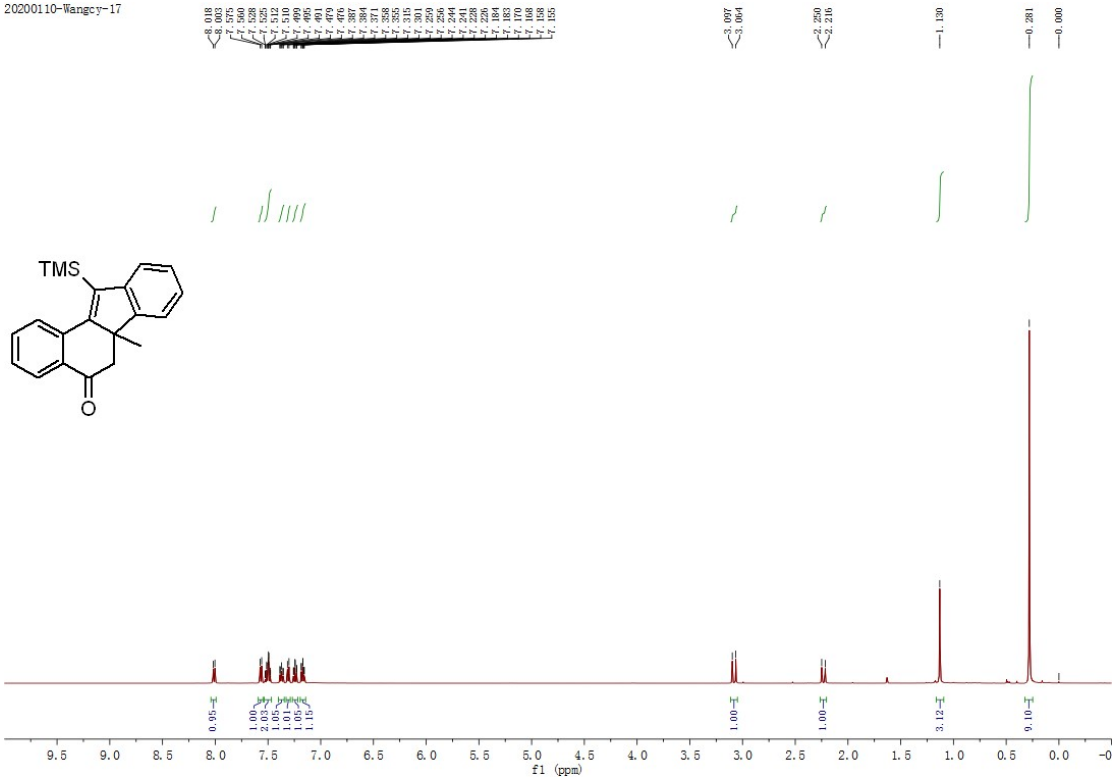


^{1}H NMR (500 MHz, $CDCl_3$)

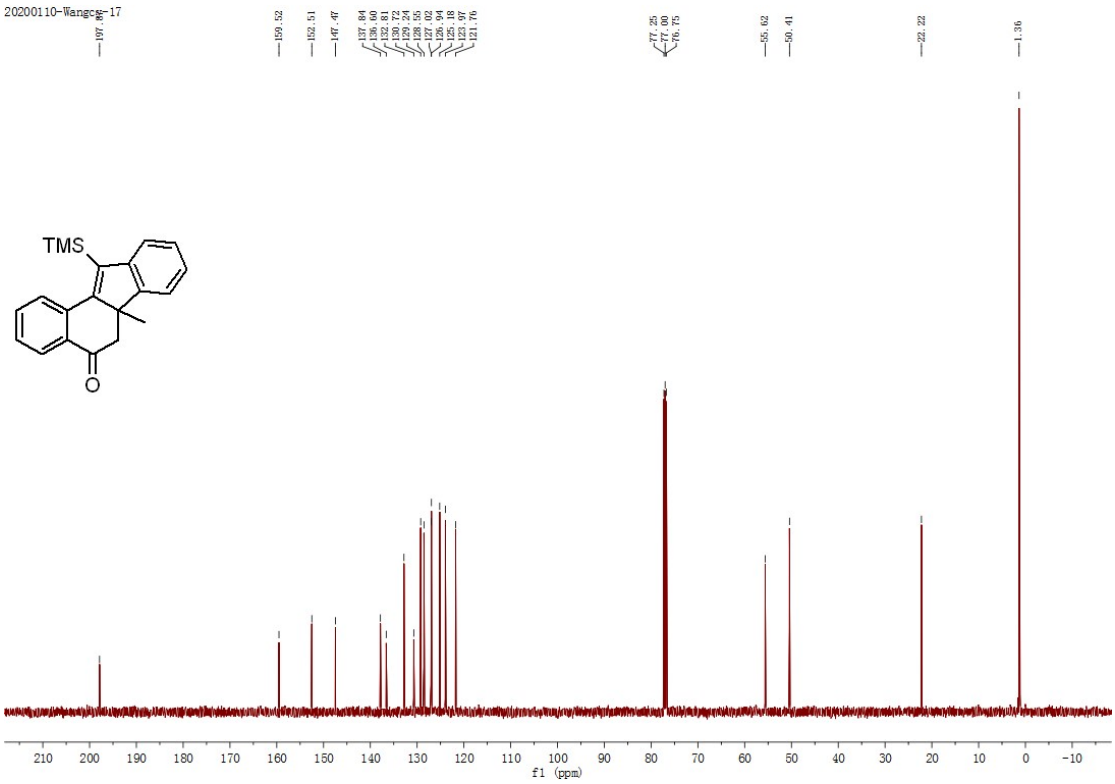


^{13}C NMR (125 MHz, $CDCl_3$)

6a-Methyl-11-(trimethylsilyl)-6,6a-dihydro-5*H*-benzo[*a*]fluoren-5-one (3la)

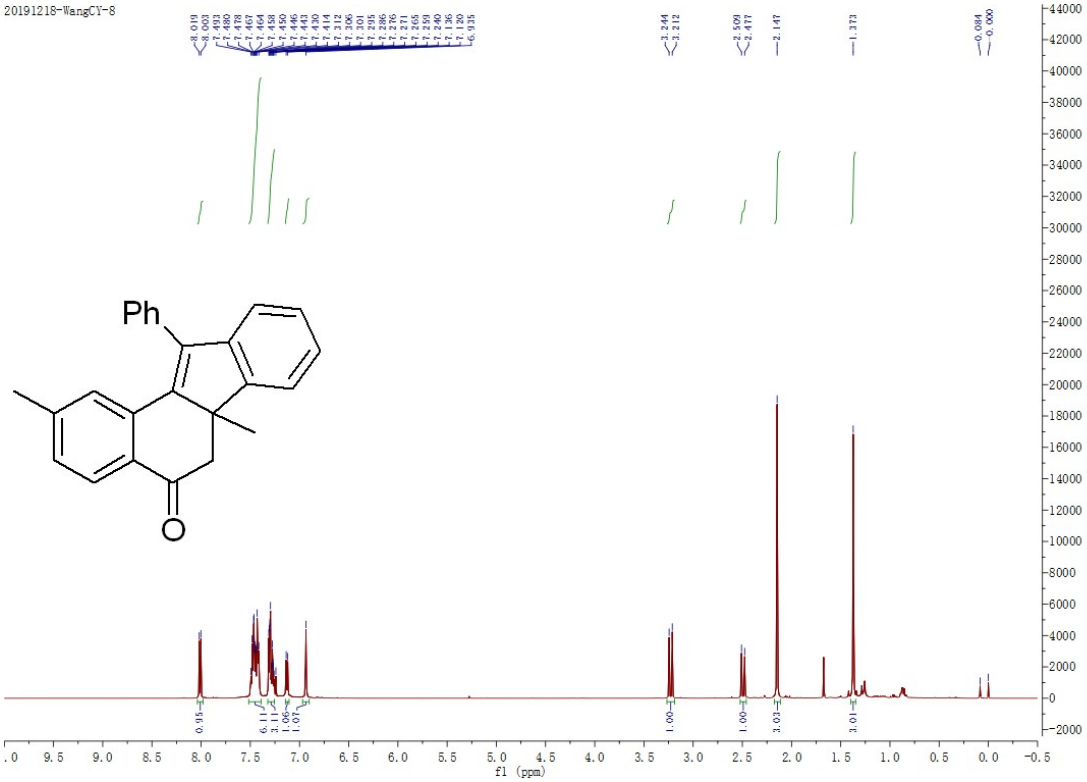


^{1}H NMR (500 MHz, $CDCl_3$)

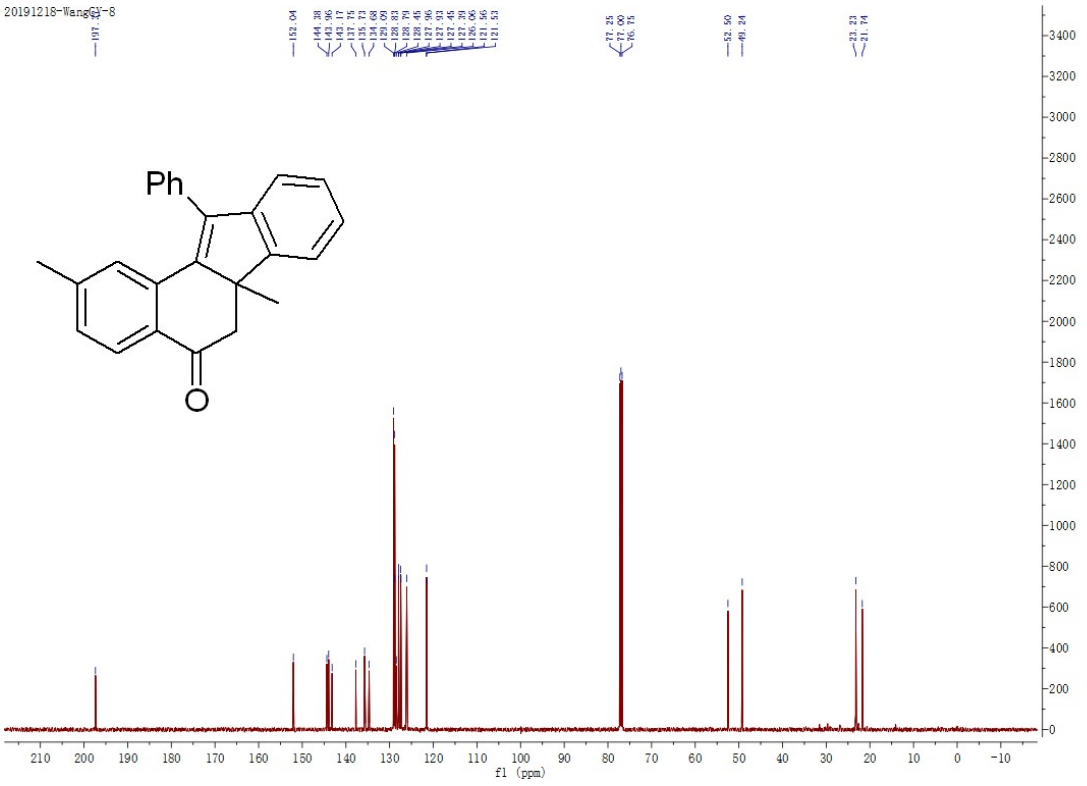


^{13}C NMR (125 MHz, $CDCl_3$)

2,6a-Dimethyl-11-phenyl-6,6a-dihydro-5*H*-benzo[*a*]fluoren-5-one (3ma)

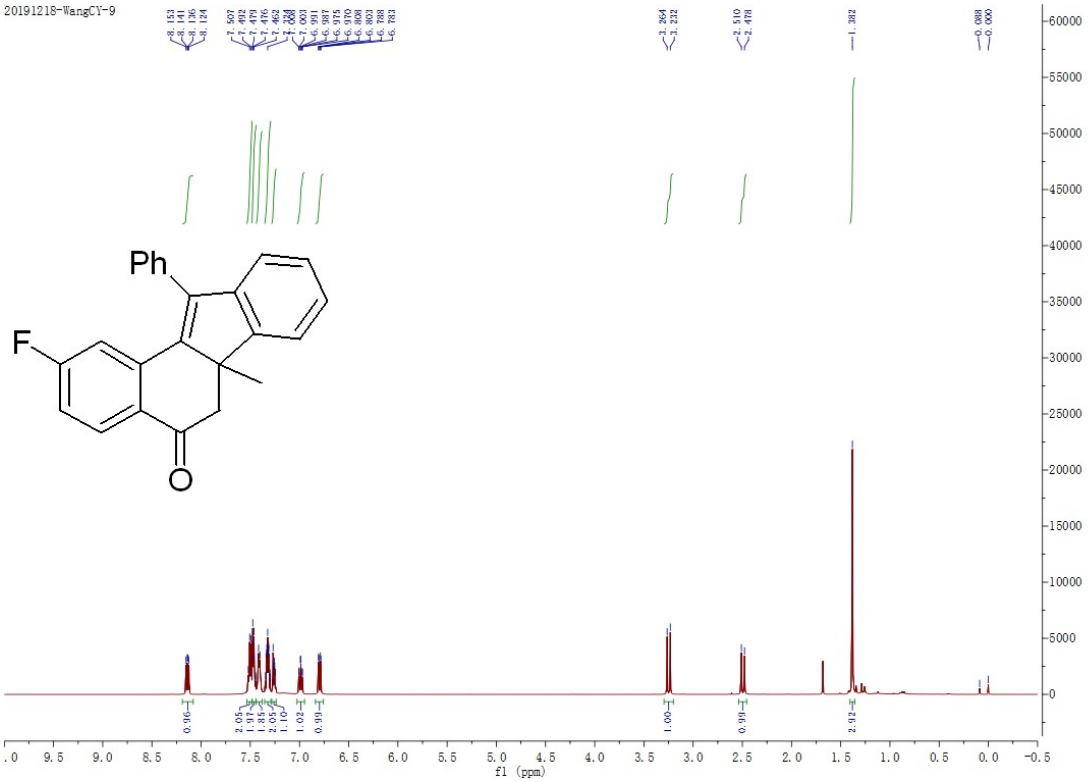


^{1}H NMR (500 MHz, $CDCl_3$)

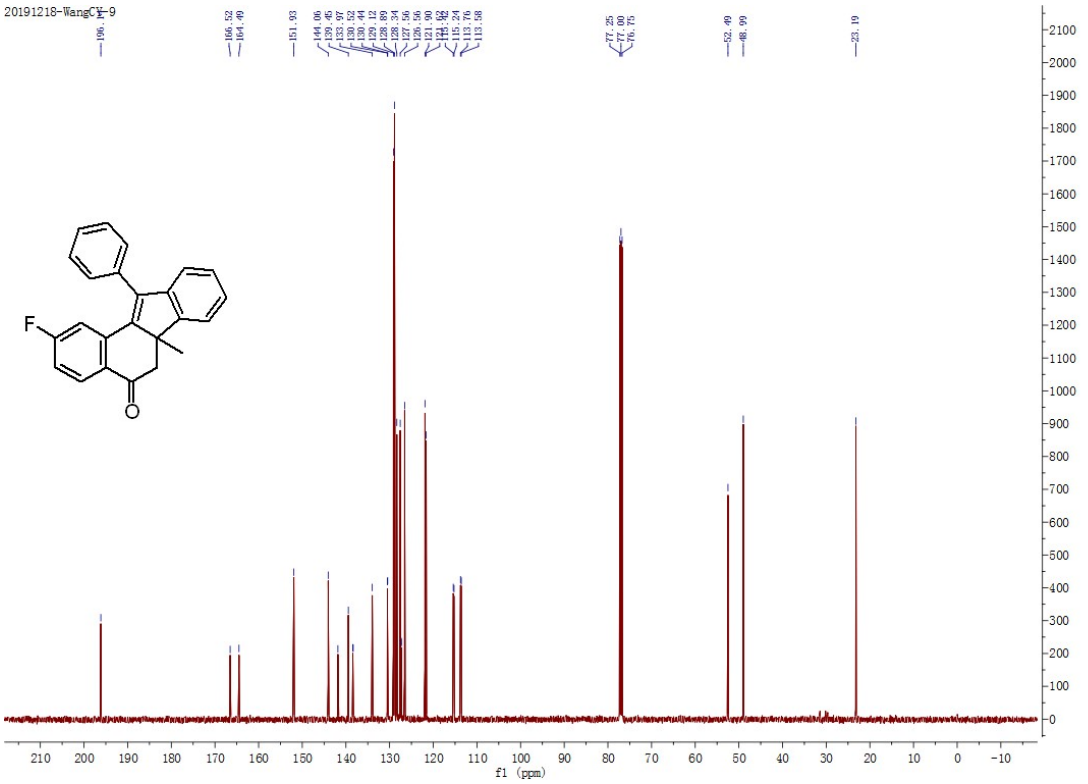


^{13}C NMR (125 MHz, $CDCl_3$)

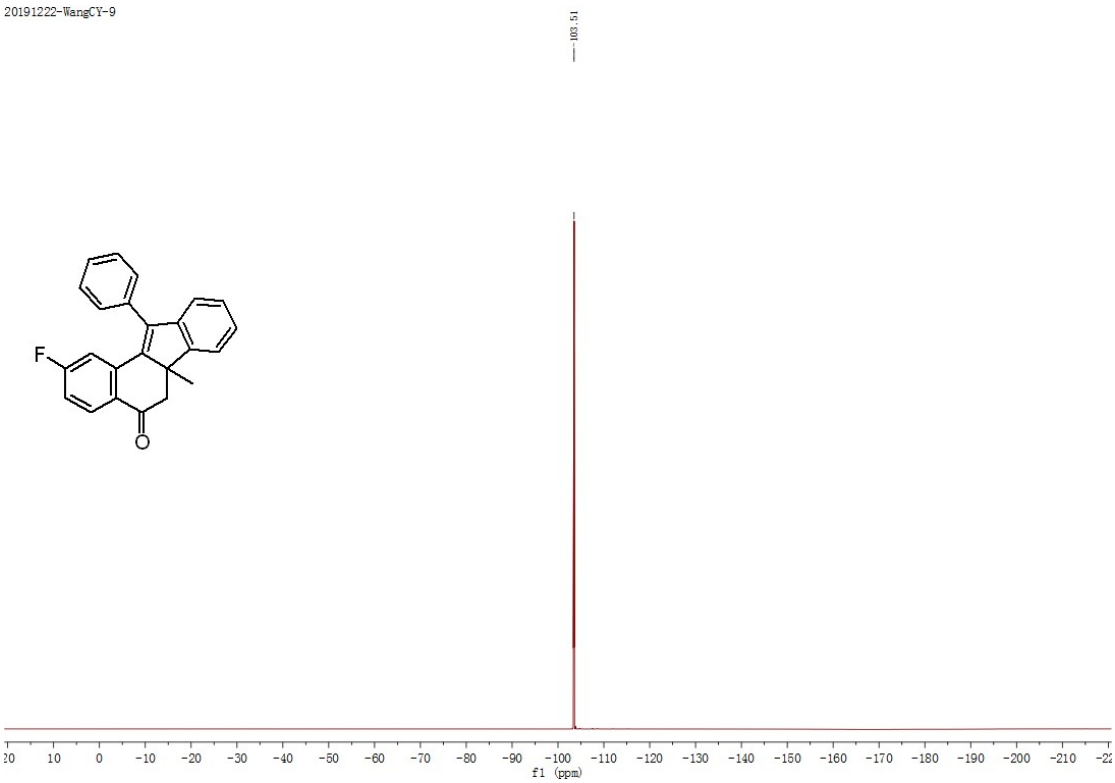
2-Fluoro-6a-methyl-11-phenyl-6,6a-dihydro-5*H*-benzo[*a*]fluoren-5-one (3na)



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

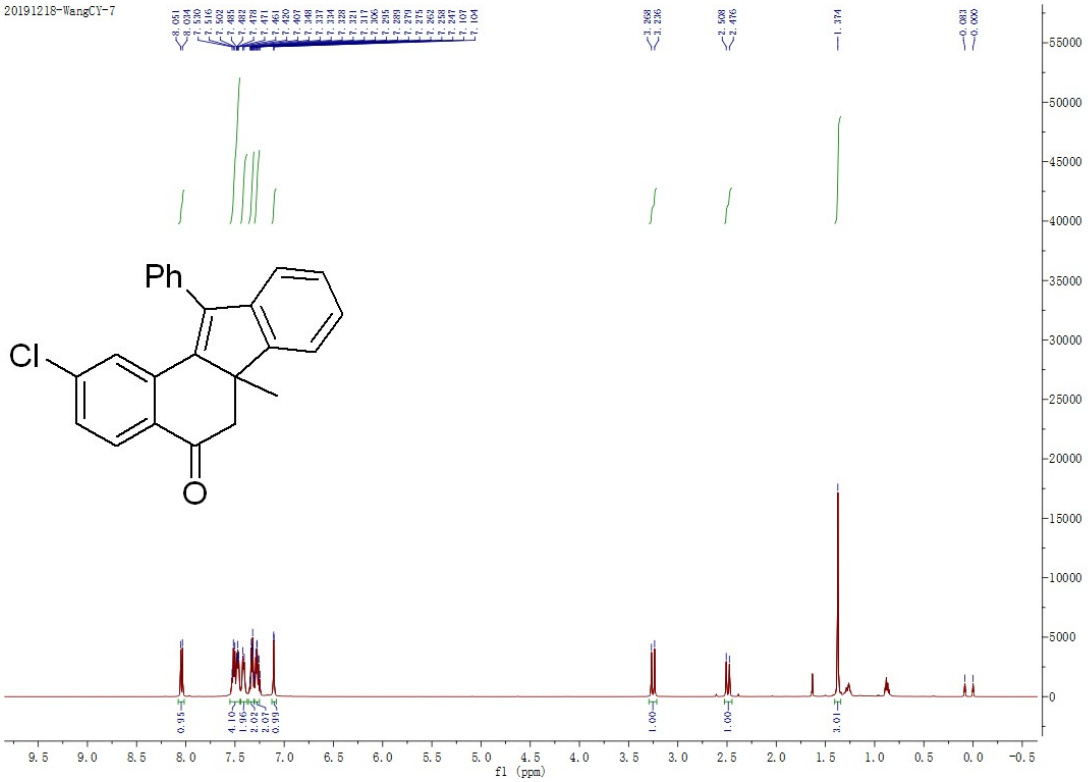


^{13}C NMR (125 MHz, $CDCl_3$)

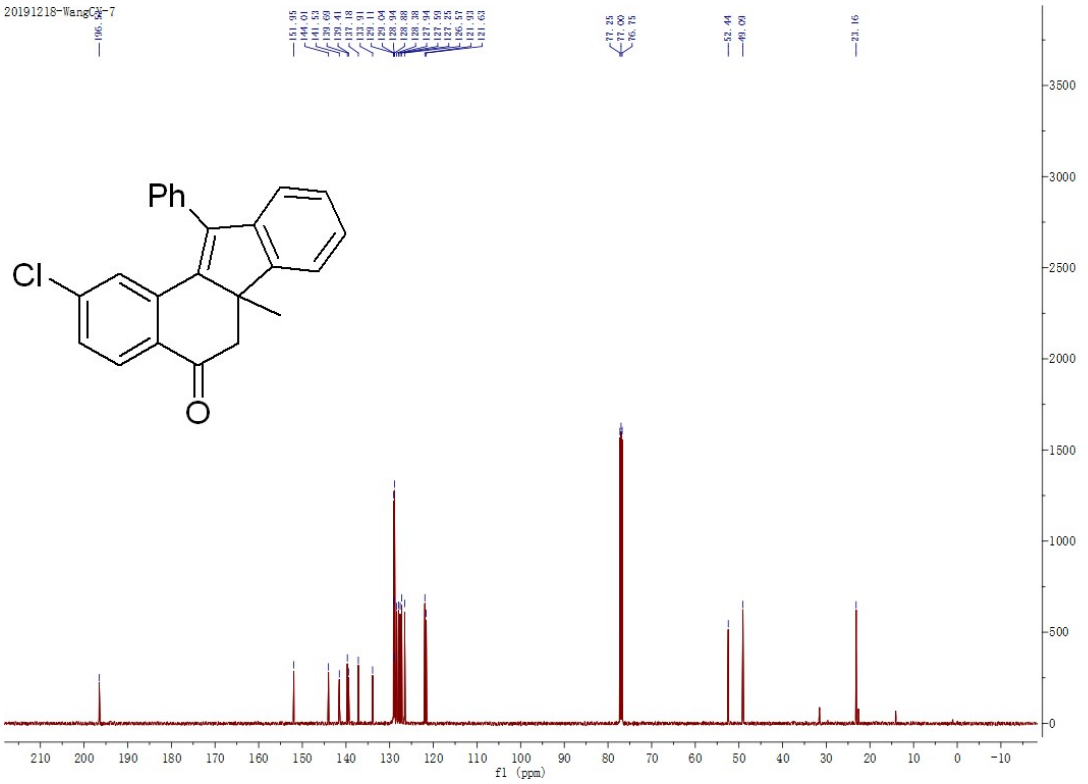


^{19}F NMR (471 MHz, $CDCl_3$)

2-Chloro-6a-methyl-11-phenyl-6,6a-dihydro-5*H*-benzo[*a*]fluoren-5-one (3oa)

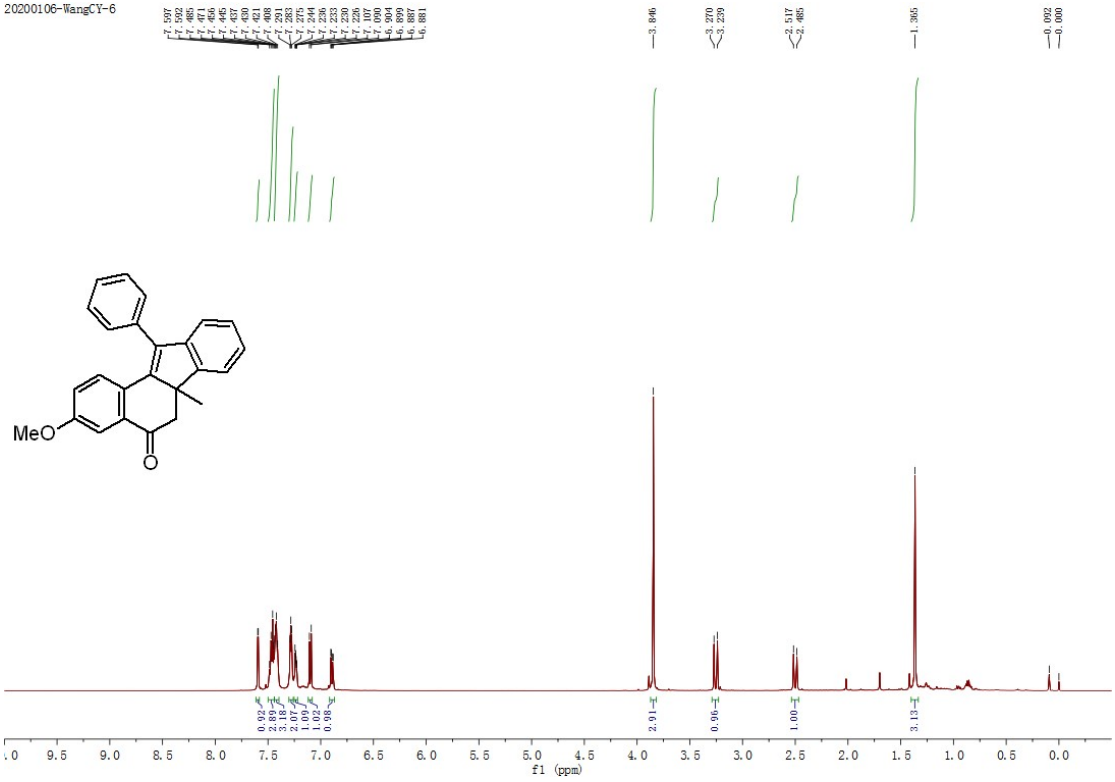


^{1}H NMR (500 MHz, $CDCl_3$)

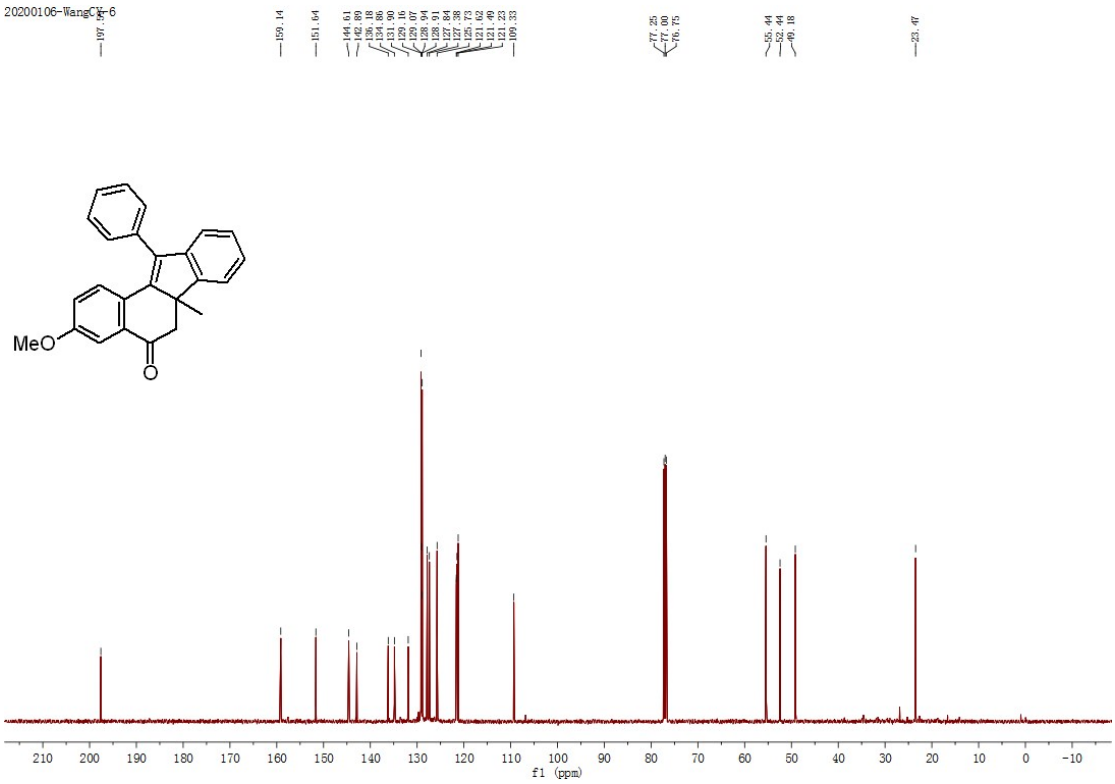


^{13}C NMR (125 MHz, $CDCl_3$)

3-Methoxy-6a-methyl-11-phenyl-6,6a-dihydro-5*H*-benzo[*a*]fluoren-5-one (3pa)

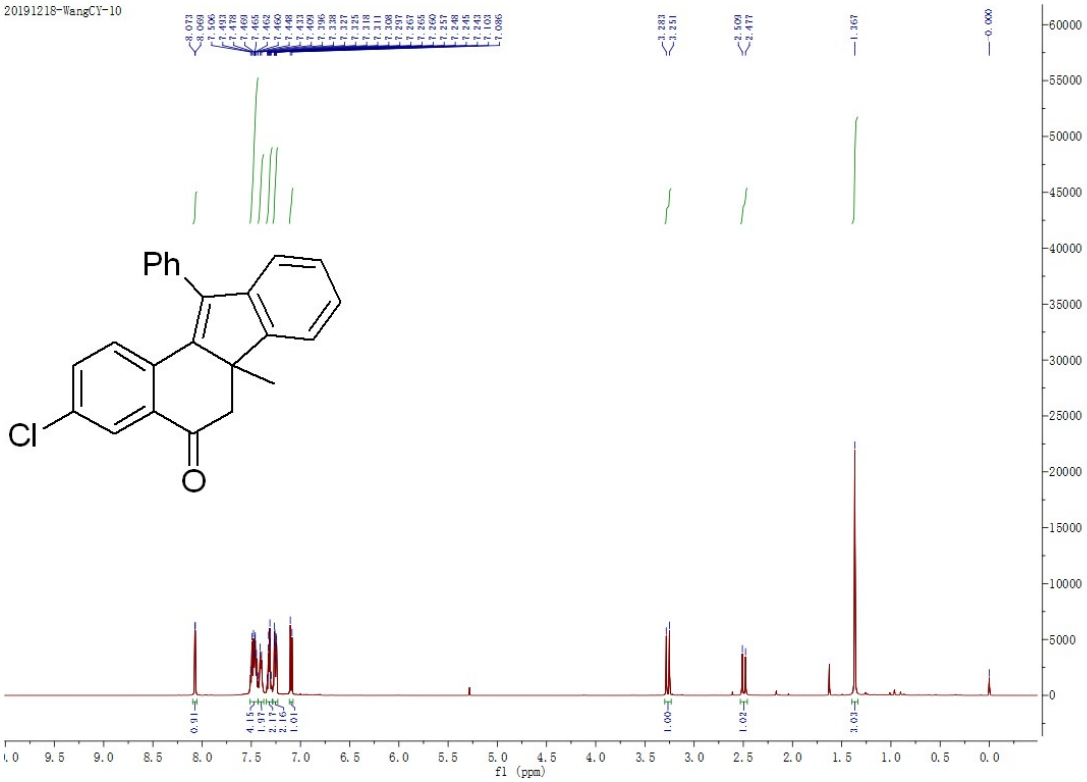


^{1}H NMR (500 MHz, $CDCl_3$)

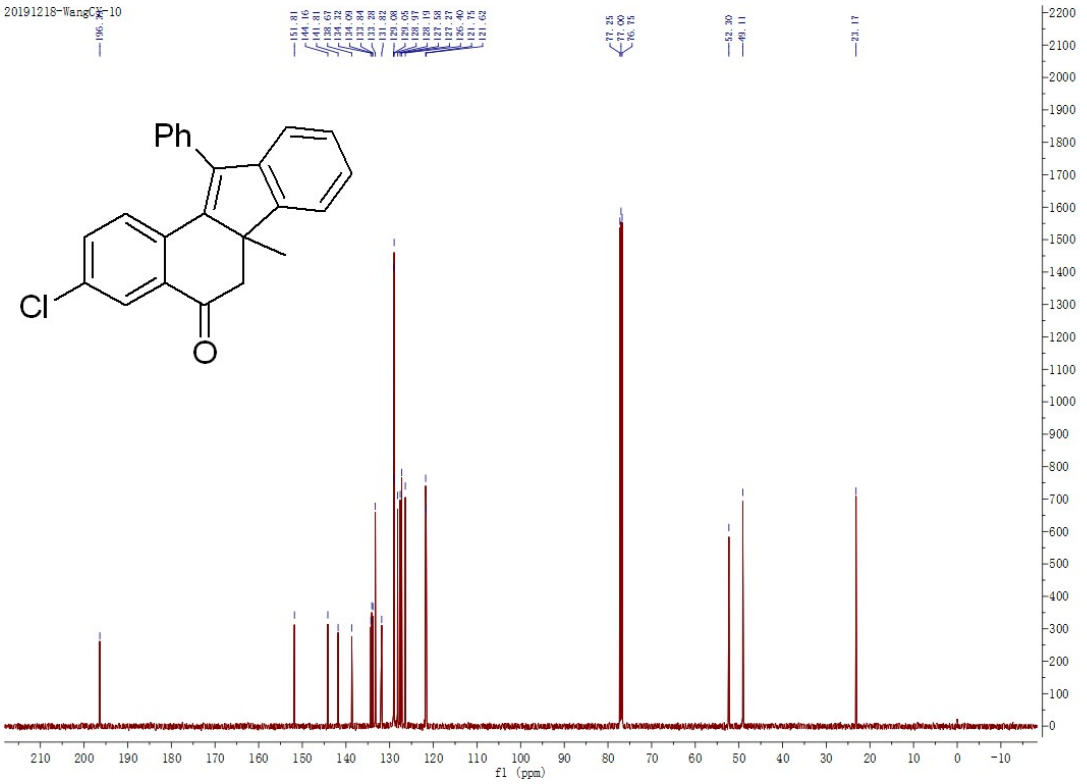


^{13}C NMR (125 MHz, $CDCl_3$)

3-Chloro-6a-methyl-11-phenyl-6,6a-dihydro-5*H*-benzo[*a*]fluoren-5-one (3qa)

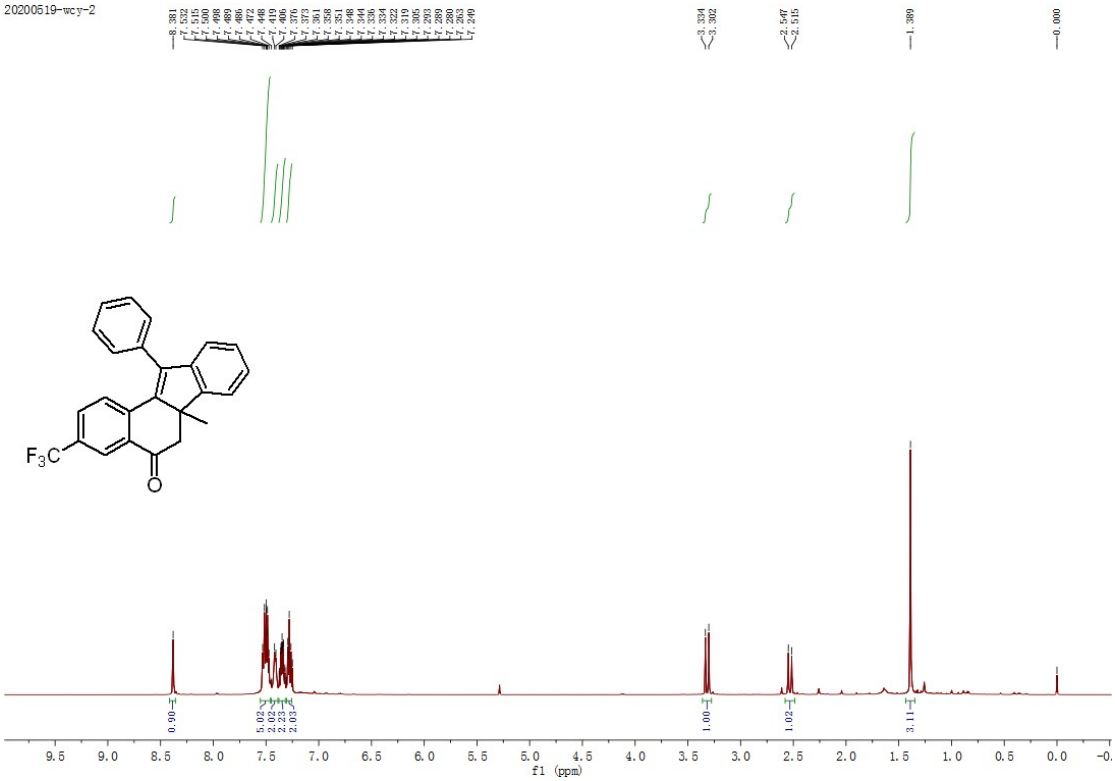


^{1}H NMR (500 MHz, $CDCl_3$)

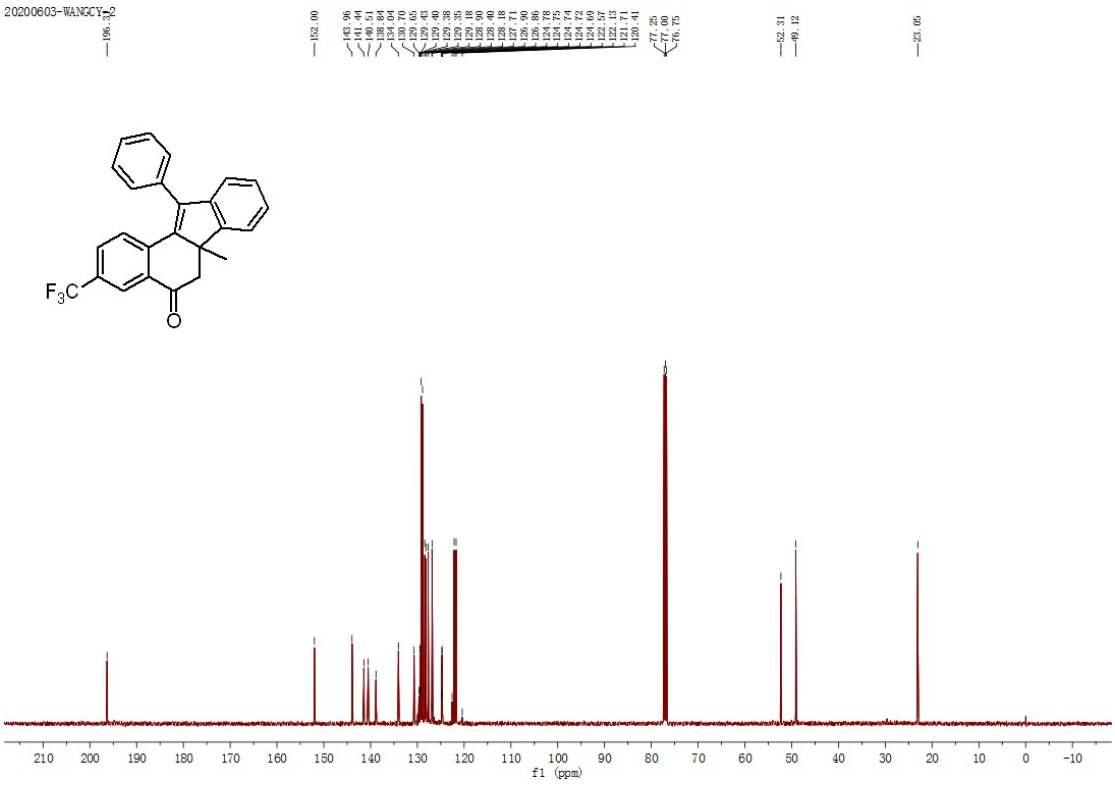


^{13}C NMR (125 MHz, $CDCl_3$)

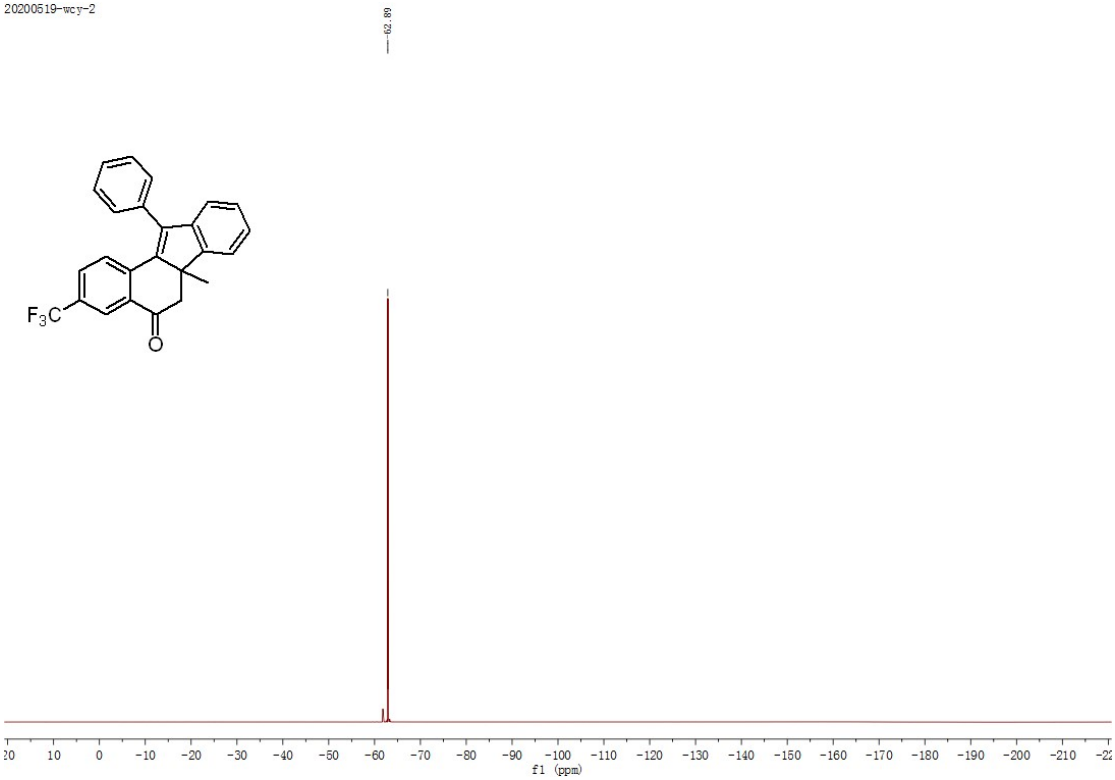
6a-Methyl-11-phenyl-3-(trifluoromethyl)-6,6a-dihydro-5*H*-benzo[*a*]fluoren-5-one (3ra)



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

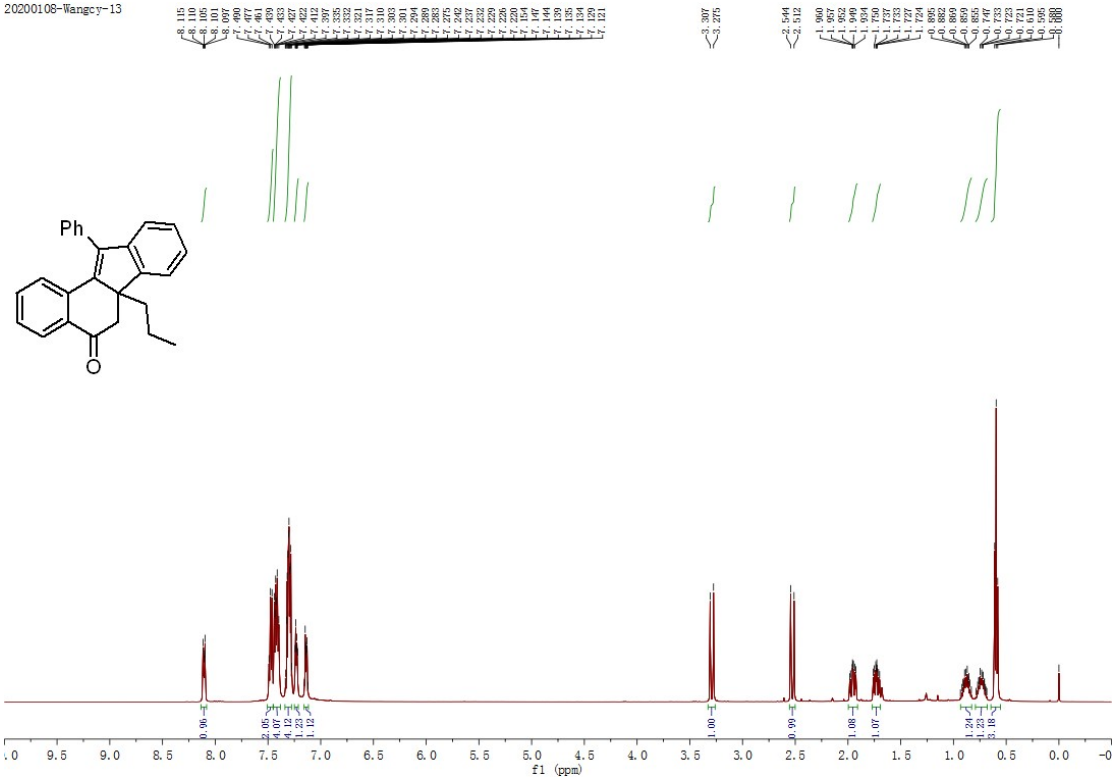


^{13}C NMR (125 MHz, $CDCl_3$)

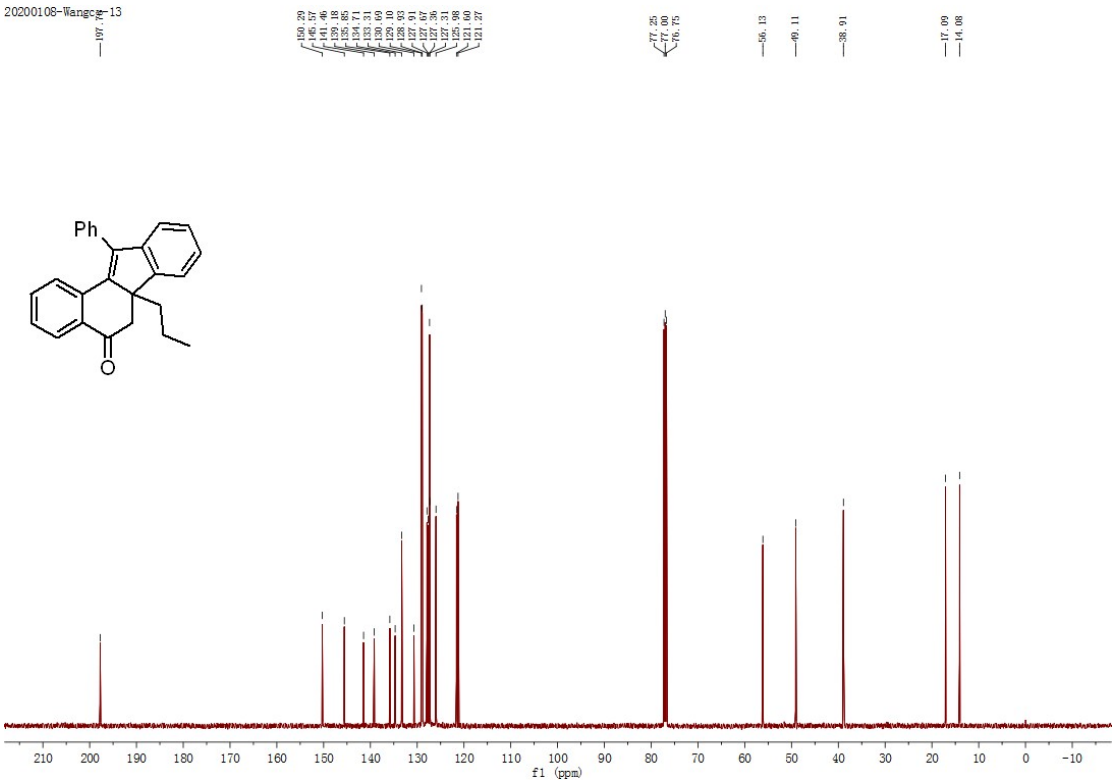


^{19}F NMR (471 MHz, $CDCl_3$)

11-Phenyl-6a-propyl-6,6a-dihydro-5*H*-benzo[*a*]fluoren-5-one (3ab)

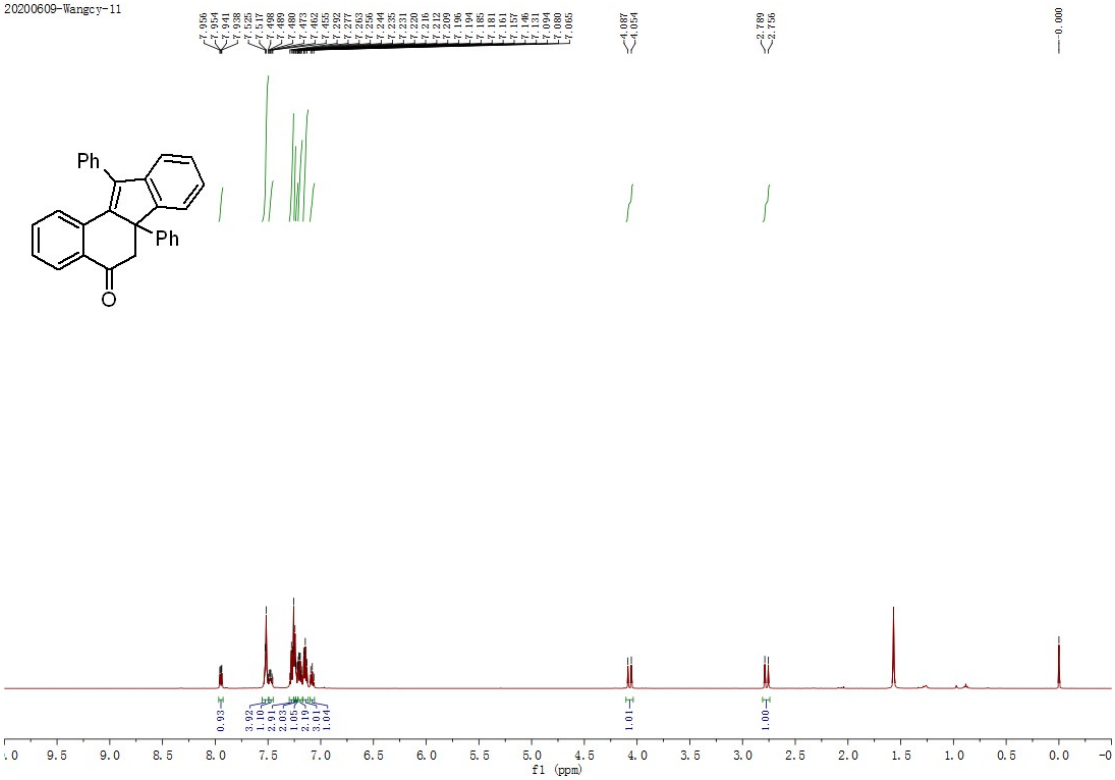


^{1}H NMR (500 MHz, $CDCl_3$)

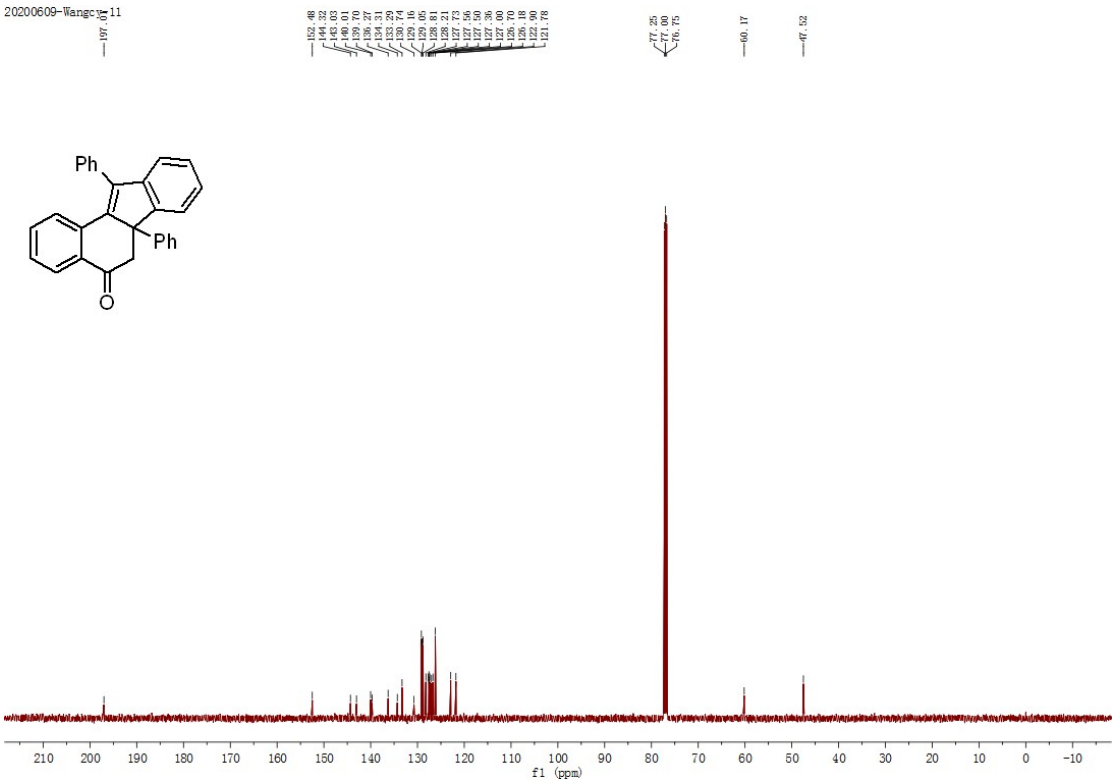


^{13}C NMR (125 MHz, $CDCl_3$)

6a,11-Diphenyl-6,6a-dihydro-5*H*-benzo[*a*]fluoren-5-one (3ac)

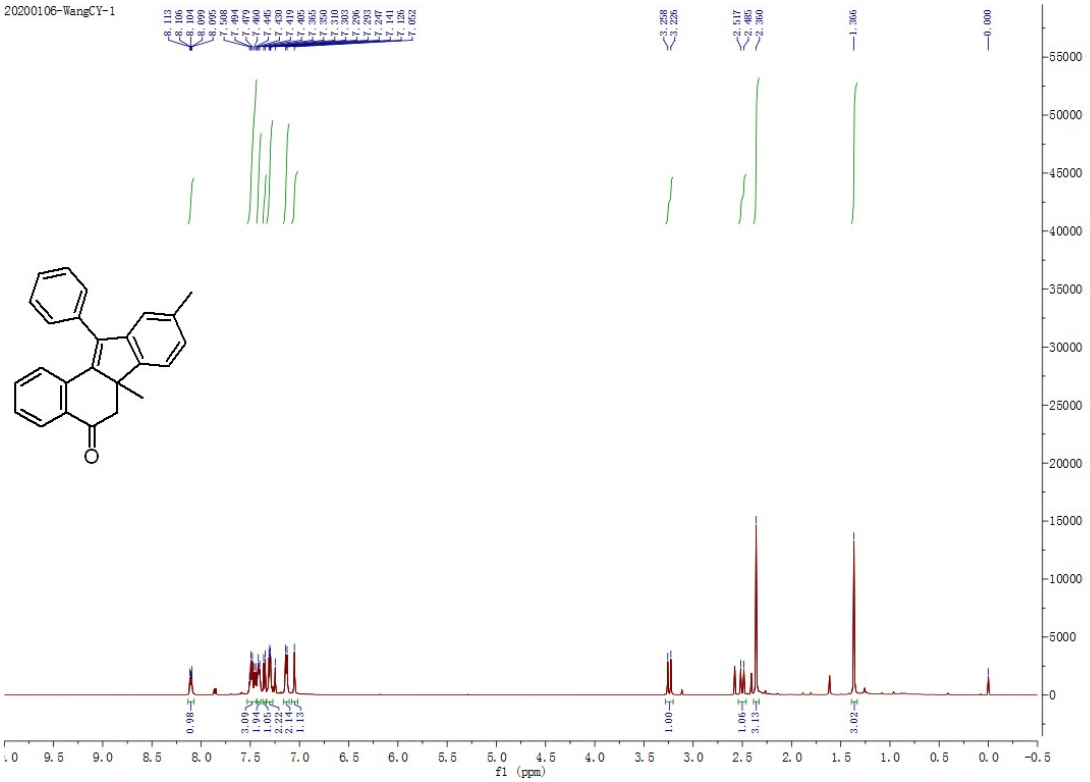


^{1}H NMR (500 MHz, $CDCl_3$)

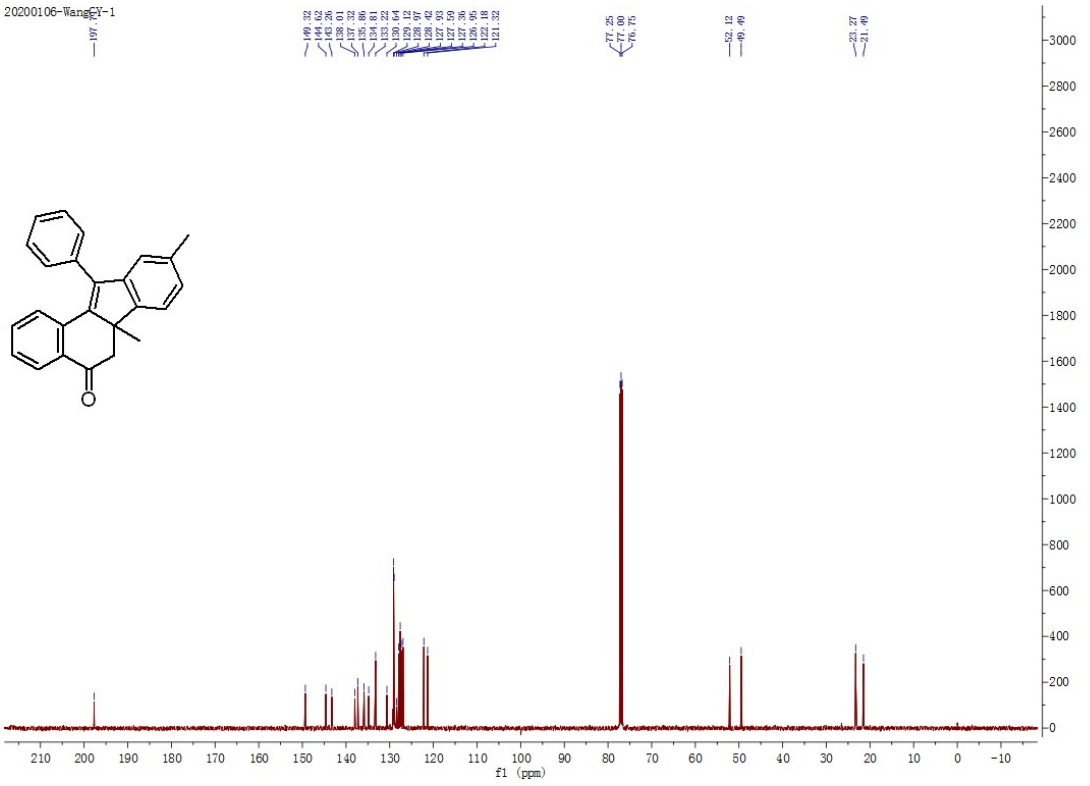


^{13}C NMR (125 MHz, $CDCl_3$)

6a,9-Dimethyl-11-phenyl-6,6a-dihydro-5*H*-benzo[*a*]fluoren-5-one (3ae)

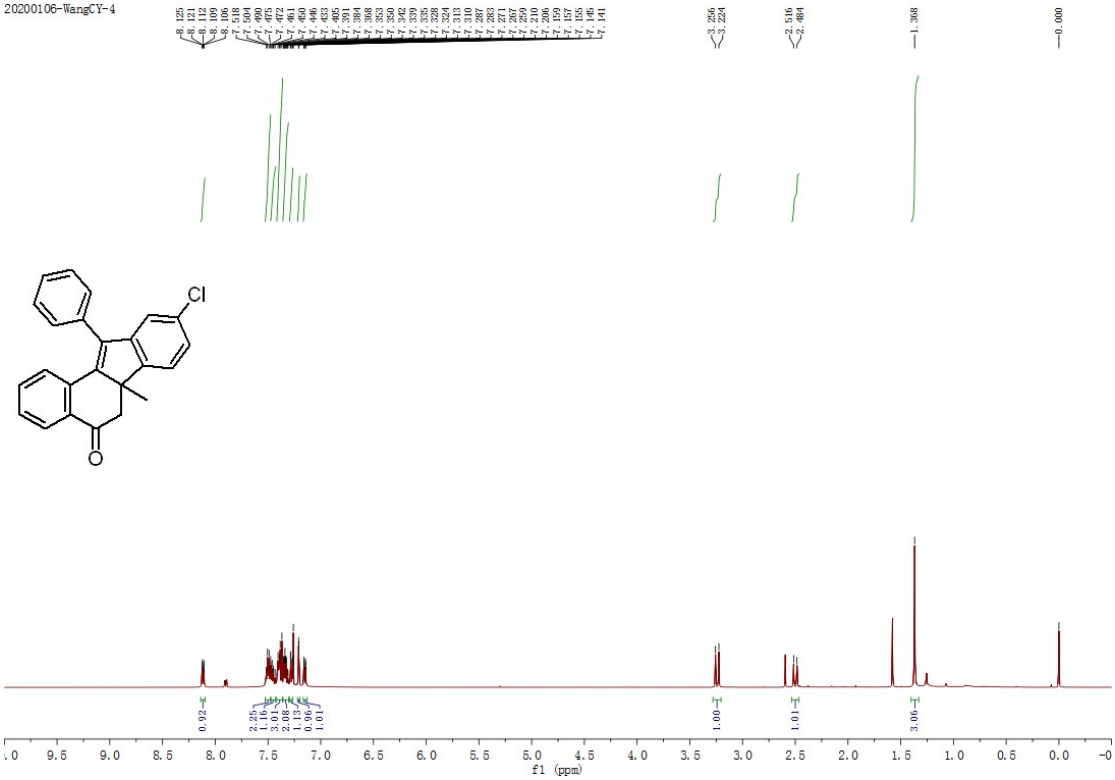


^{1}H NMR (500 MHz, $CDCl_3$)

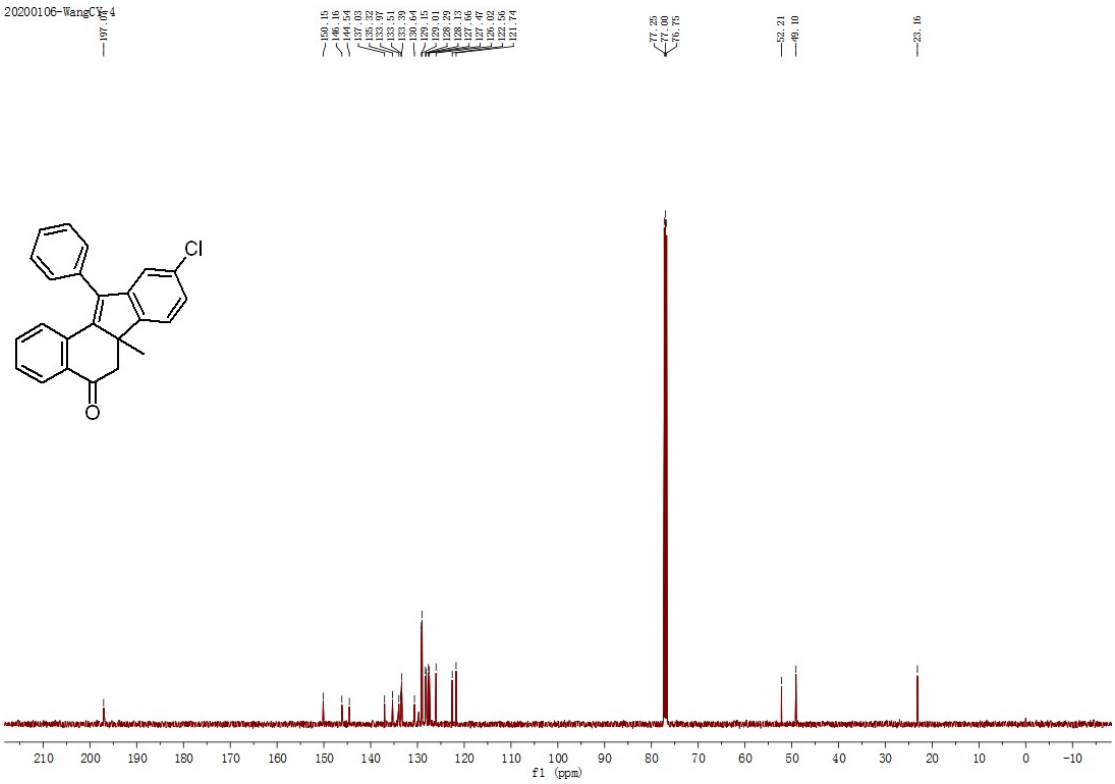


^{13}C NMR (125 MHz, $CDCl_3$)

9-Chloro-6a-methyl-11-phenyl-6,6a-dihydro-5*H*-benzo[*a*]fluoren-5-one (3af)

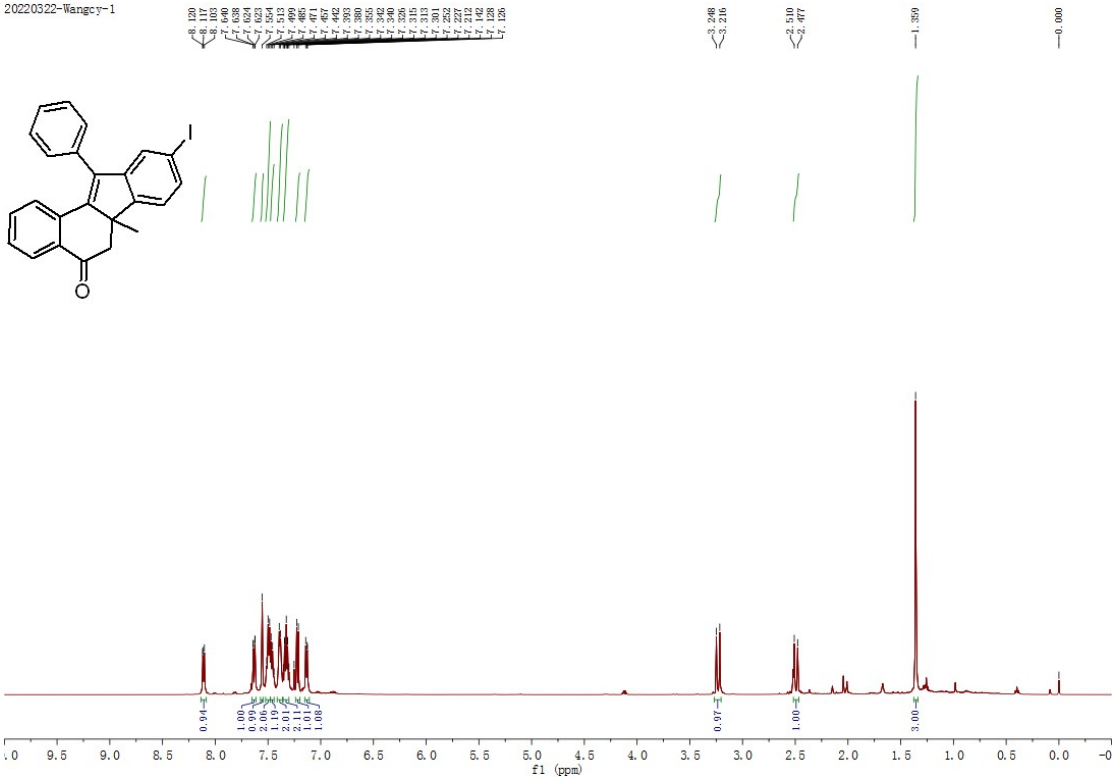


^{1}H NMR (500 MHz, $CDCl_3$)

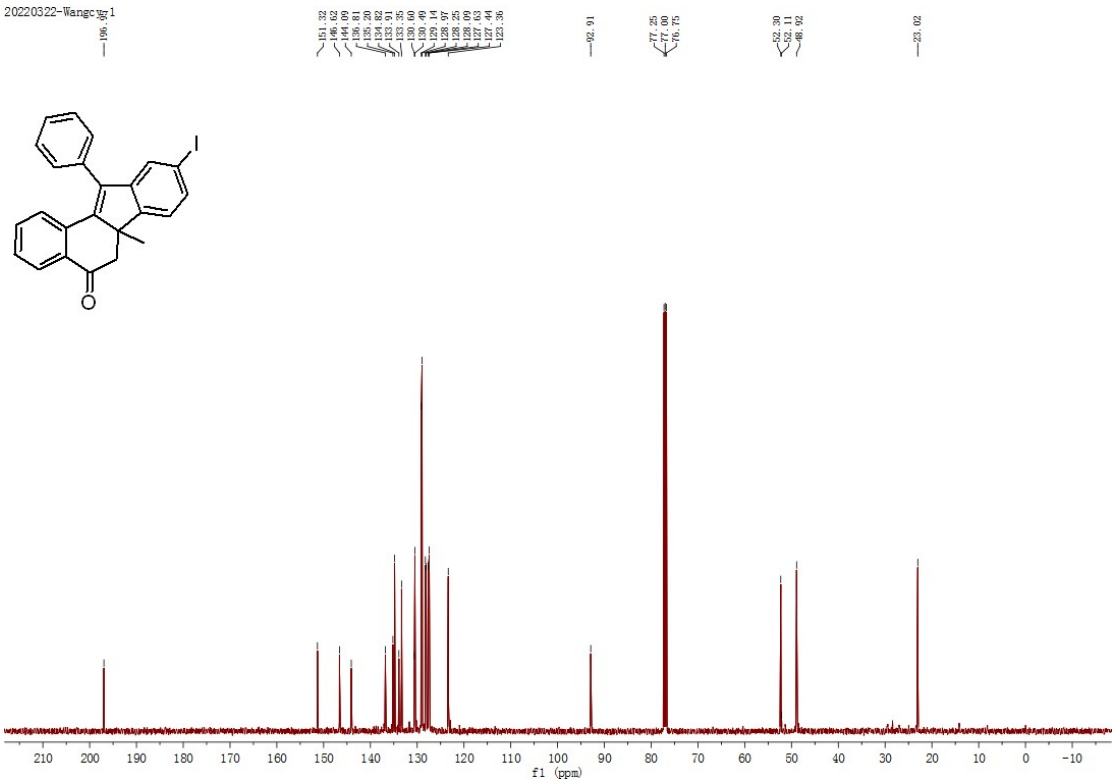


^{13}C NMR (125 MHz, $CDCl_3$)

9-Iodo-6a-methyl-11-phenyl-6,6a-dihydro-5*H*-benzo[*a*]fluoren-5-one (3ag)

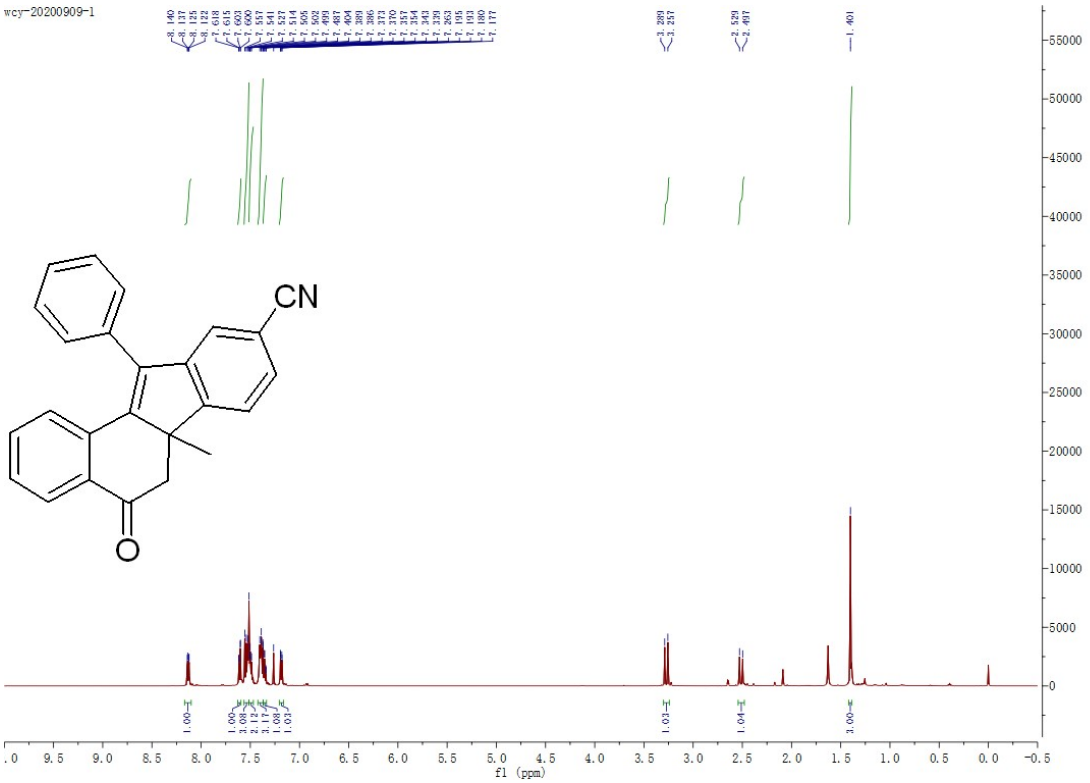


^{1}H NMR (500 MHz, $CDCl_3$)

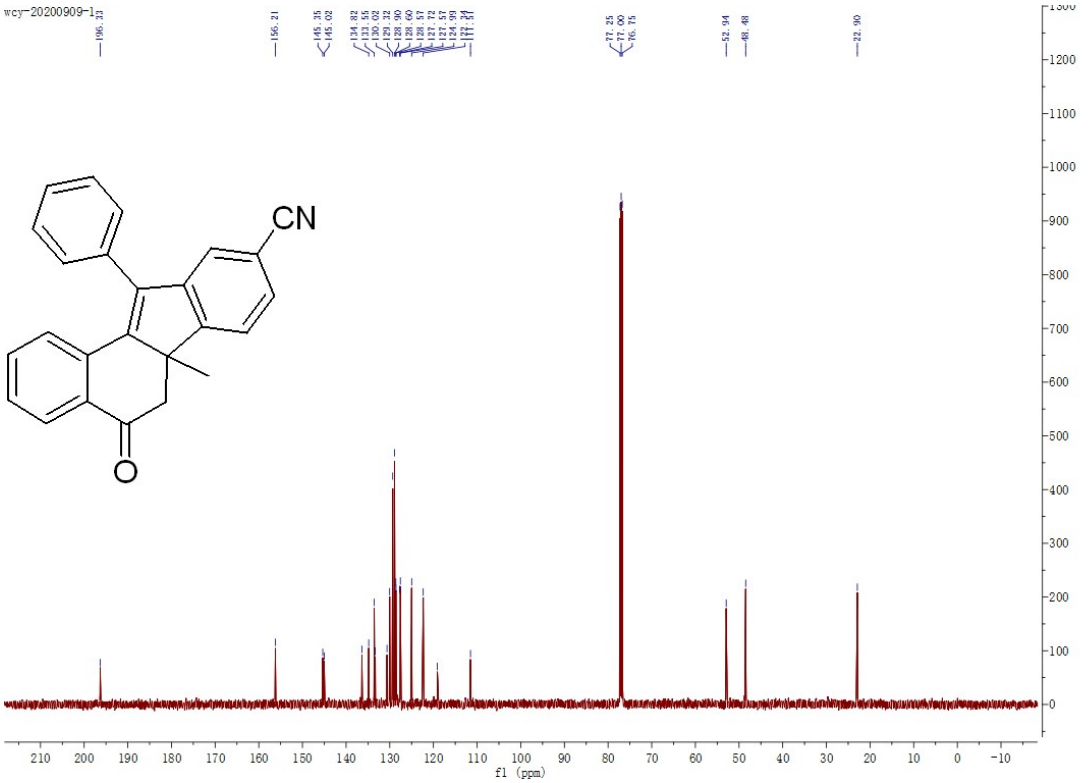


^{13}C NMR (125 MHz, $CDCl_3$)

6a-Methyl-5-oxo-11-phenyl-6,6a-dihydro-5*H*-benzo[*a*]fluorene-9-carbonitrile (3ah)

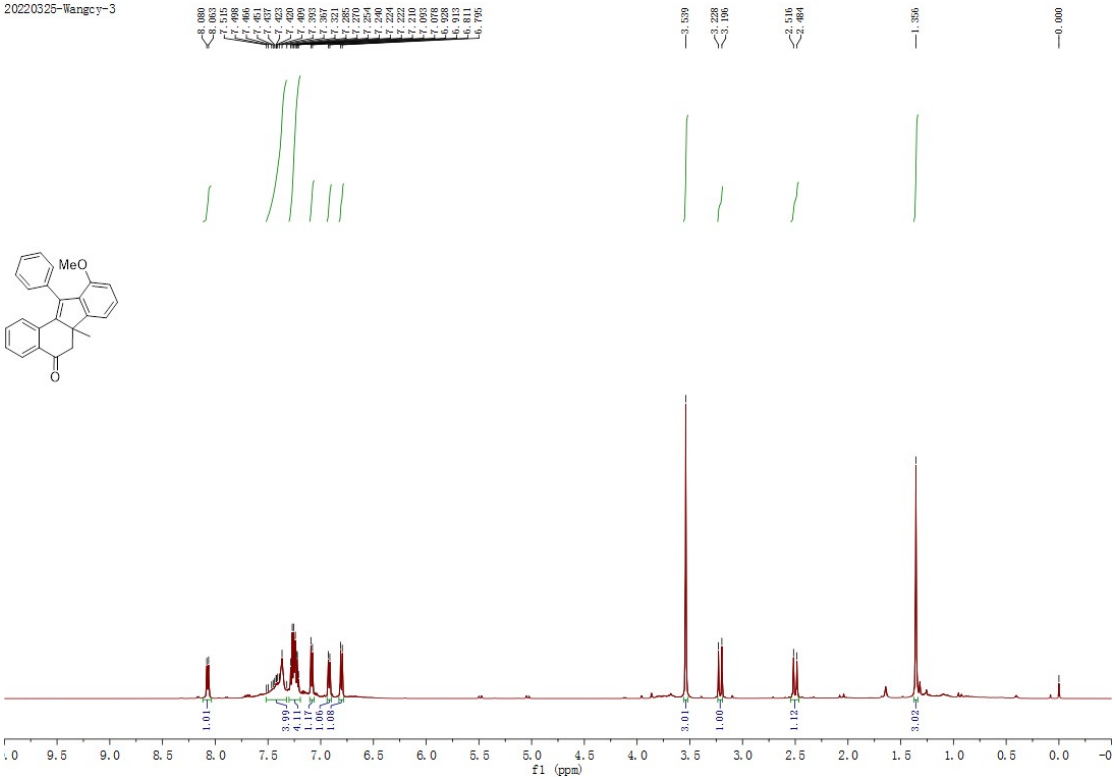


^{1}H NMR (500 MHz, $CDCl_3$)

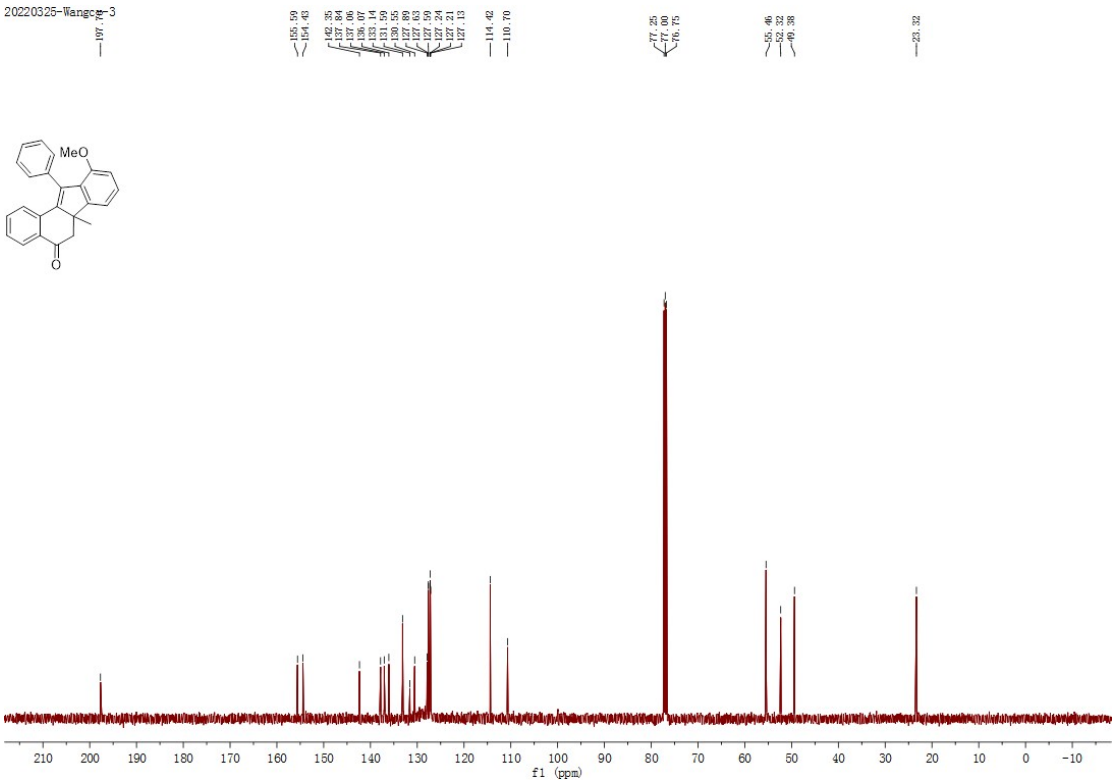


^{13}C NMR (125 MHz, $CDCl_3$)

10-Methoxy-6a-methyl-11-phenyl-6,6a-dihydro-5*H*-benzo[*a*]fluoren-5-one (3ai)

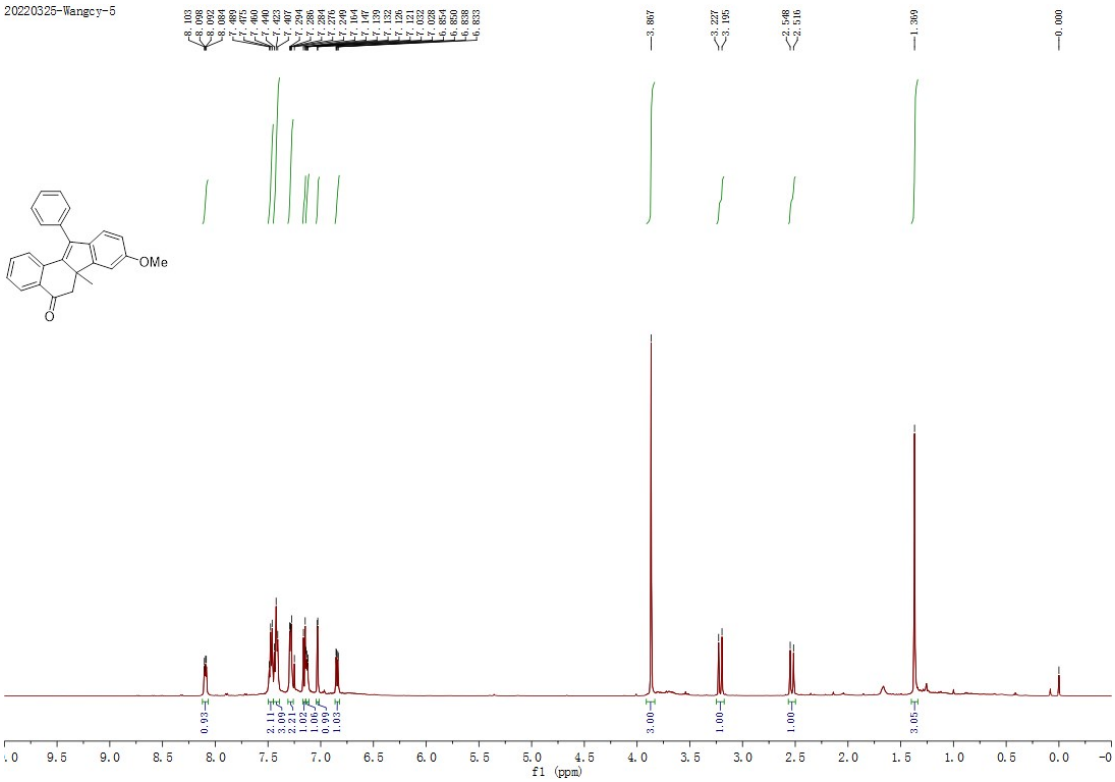


^{1}H NMR (500 MHz, $CDCl_3$)

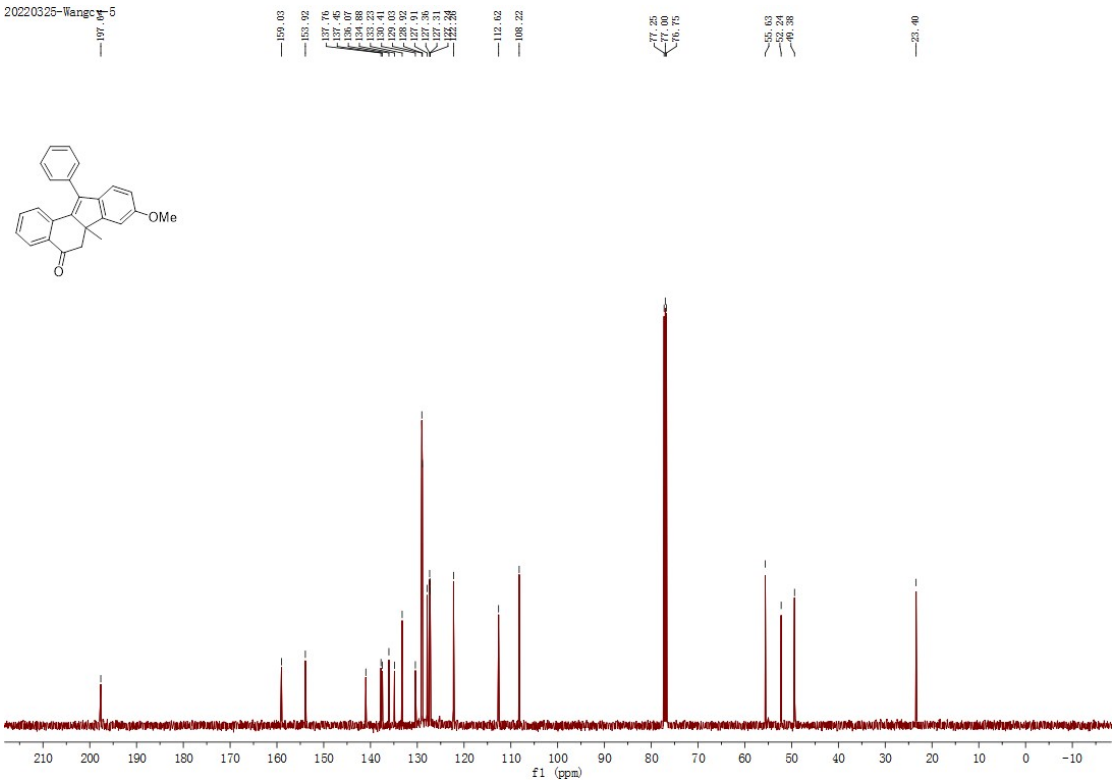


^{13}C NMR (125 MHz, $CDCl_3$)

8-Methoxy-6a-methyl-11-phenyl-6,6a-dihydro-5*H*-benzo[*a*]fluoren-5-one (3ai')

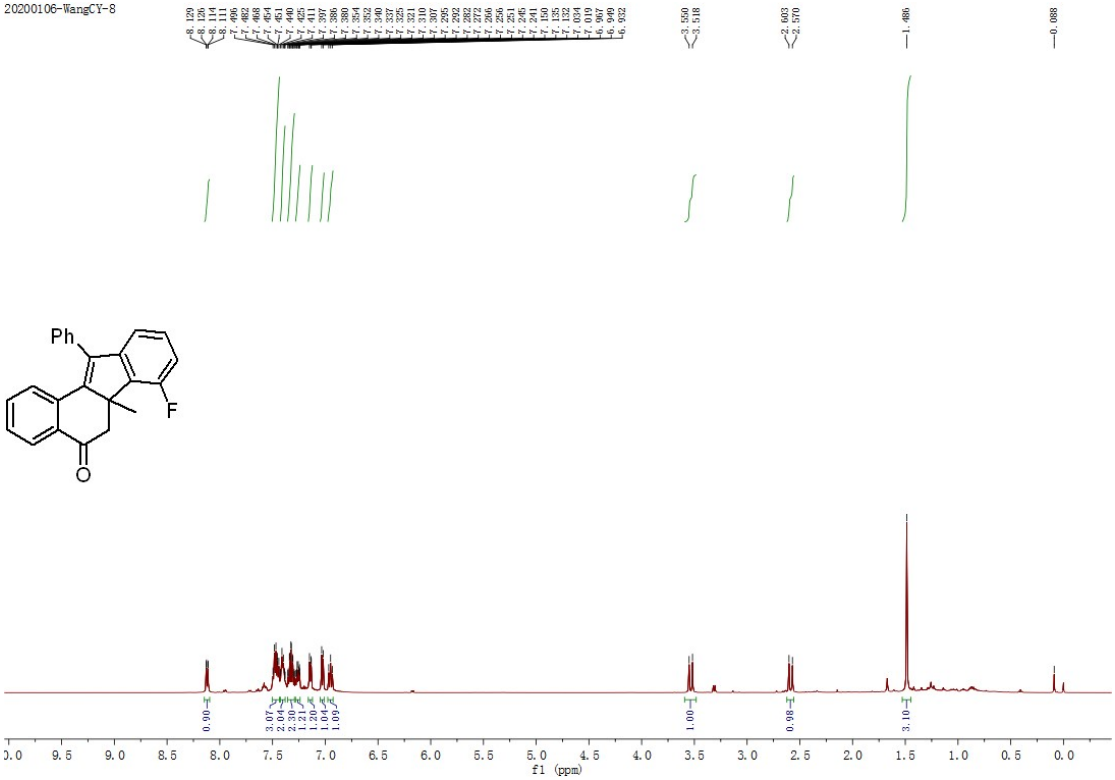


^{1}H NMR (500 MHz, $CDCl_3$)

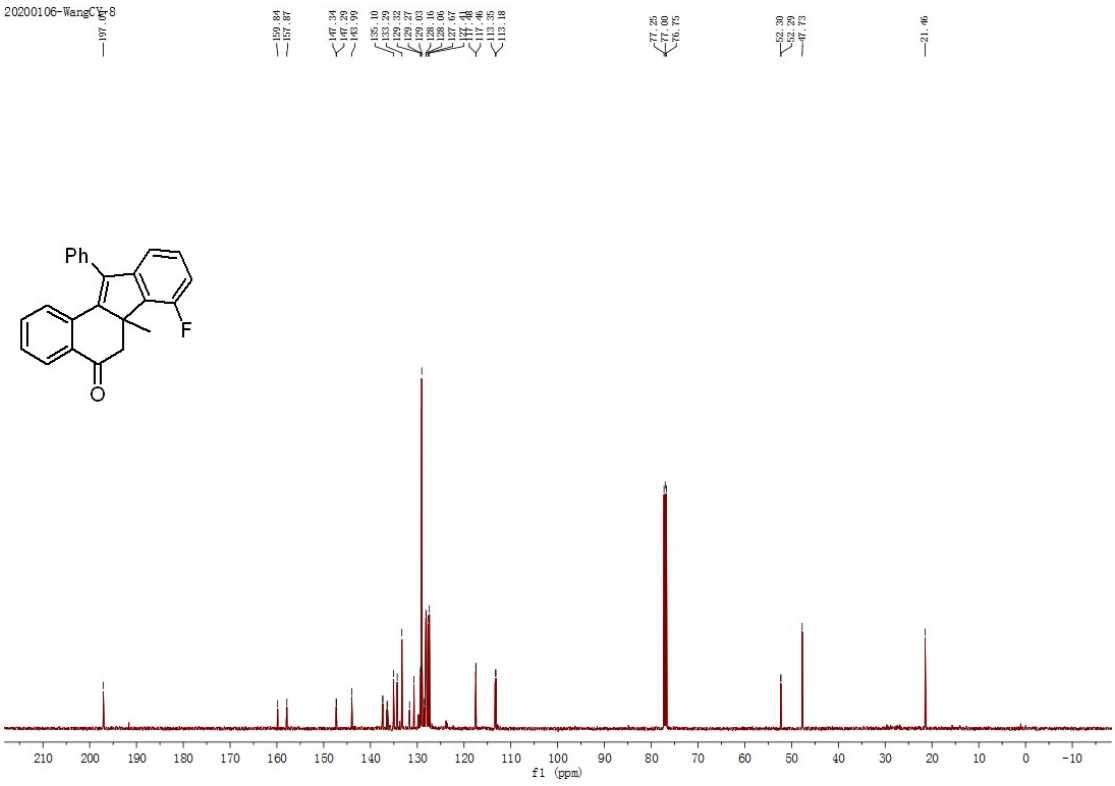


^{13}C NMR (125 MHz, $CDCl_3$)

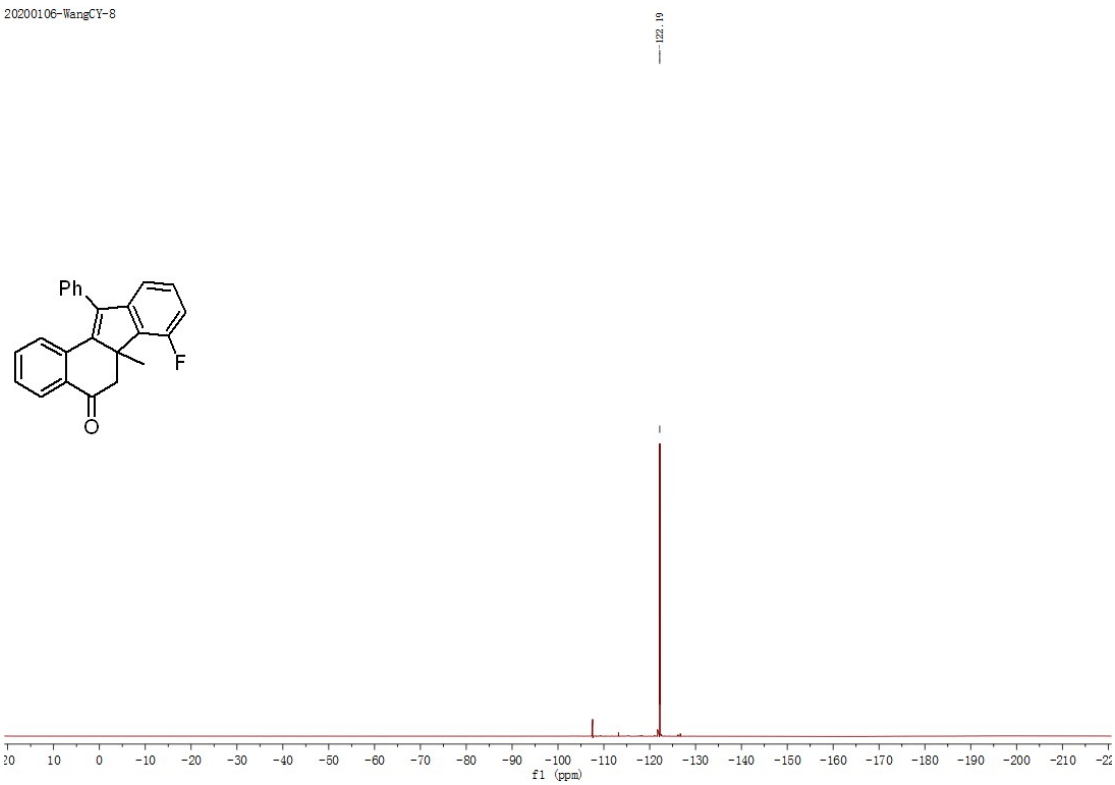
7-Fluoro-6a-methyl-11-phenyl-6,6a-dihydro-5*H*-benzo[*a*]fluoren-5-one (3aj)



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

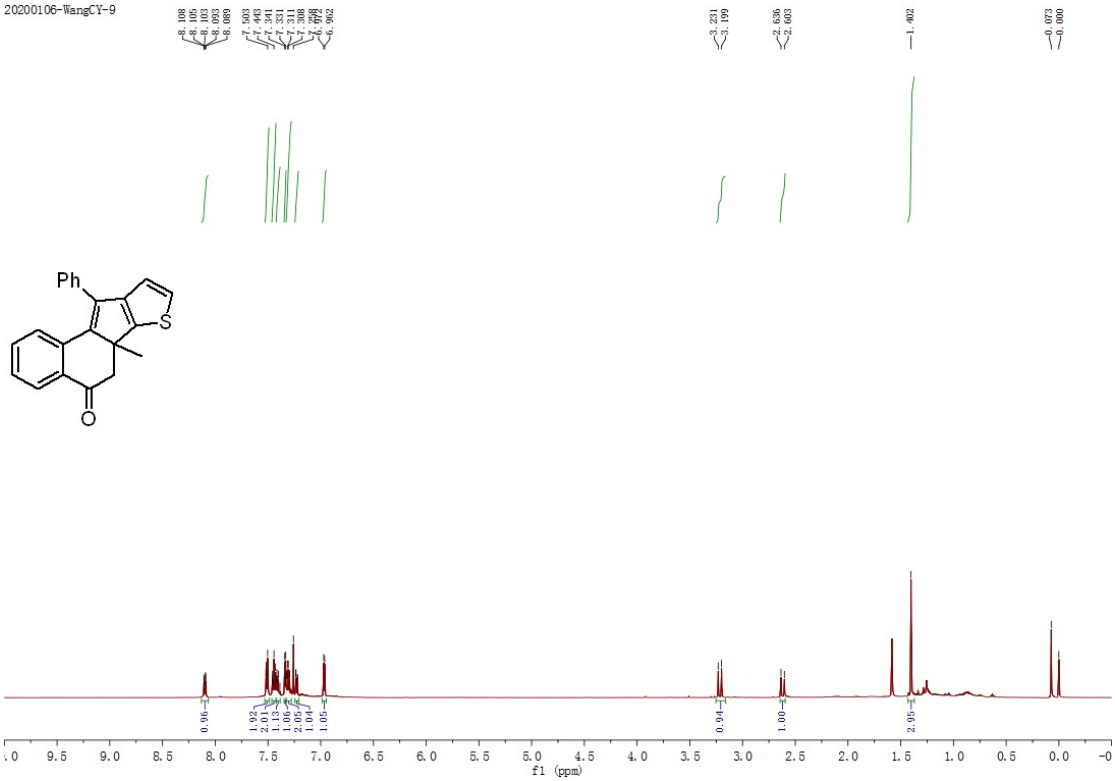


^{13}C NMR (125 MHz, $CDCl_3$)

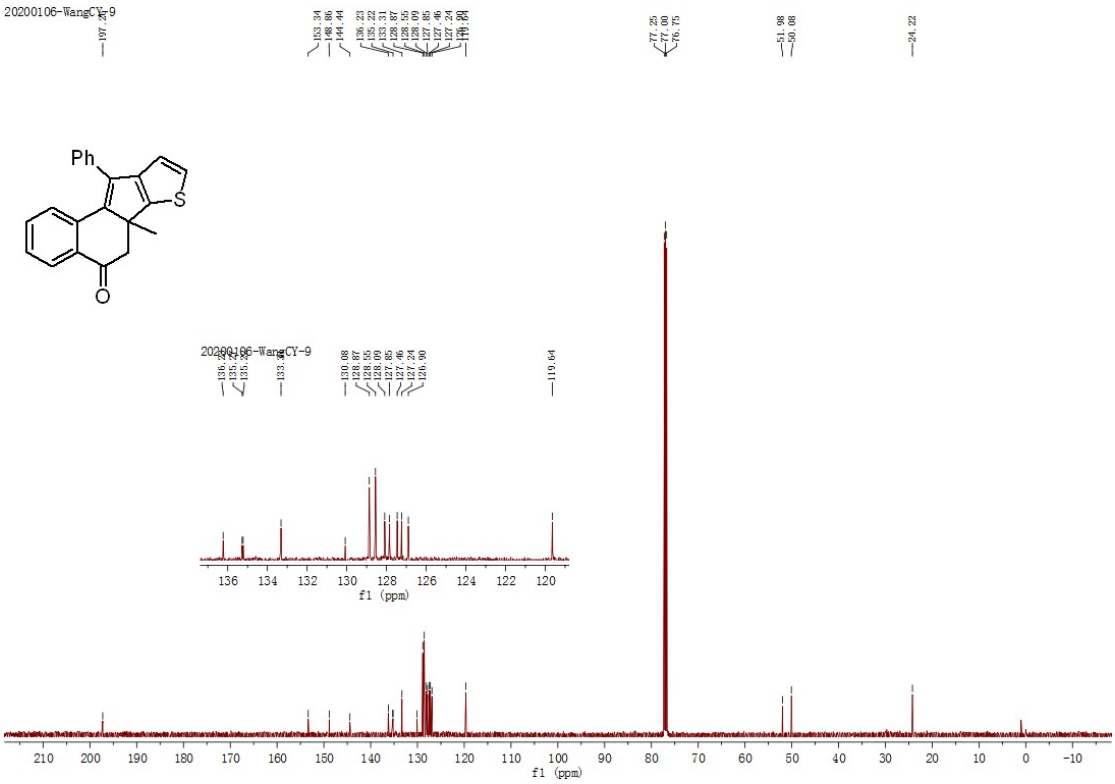


^{19}F NMR (471 MHz, $CDCl_3$)

6a-Methyl-10-phenyl-6,6a-dihydro-5*H*-benzo[4,5]indeno[1,2-*b*]thiophen-5-one (3ak)

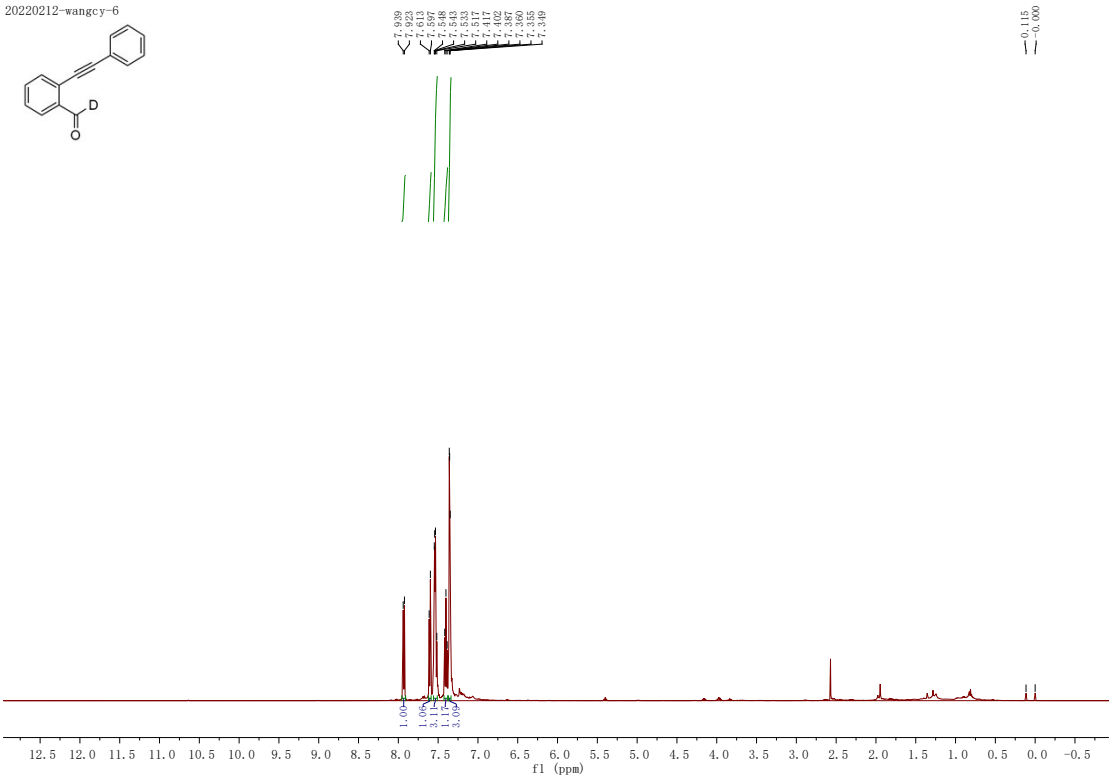


^{1}H NMR (500 MHz, $CDCl_3$)

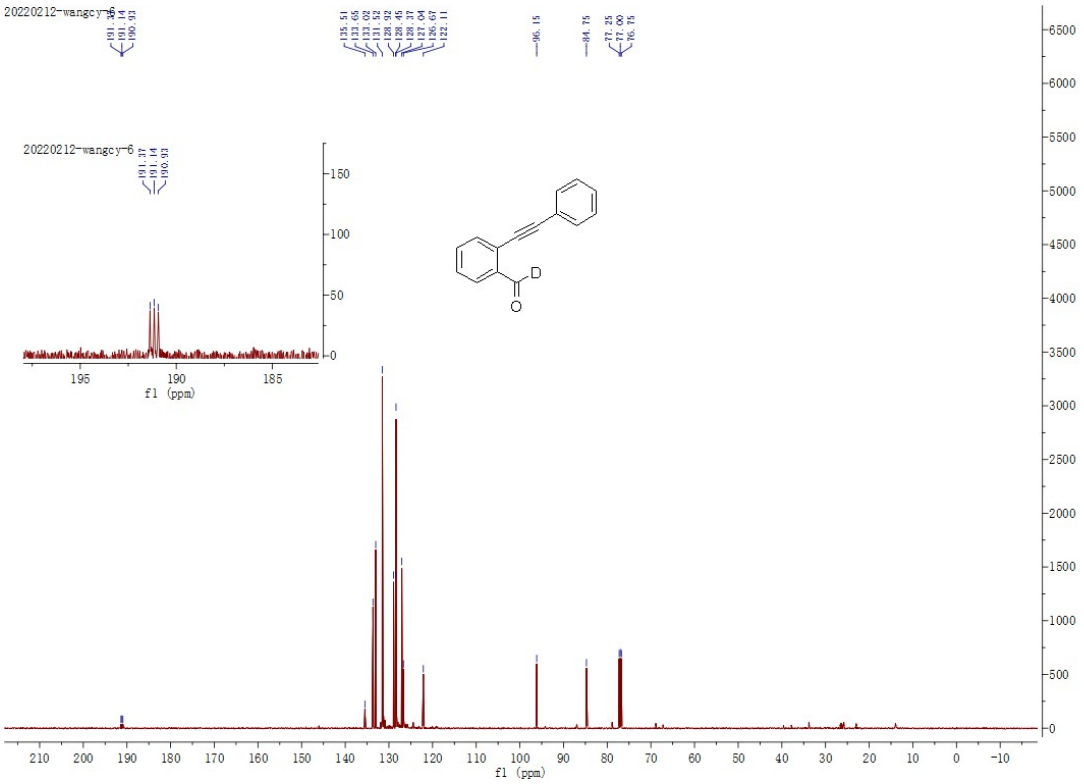


^{13}C NMR (125 MHz, $CDCl_3$)

1a-D_1 (>99%D)

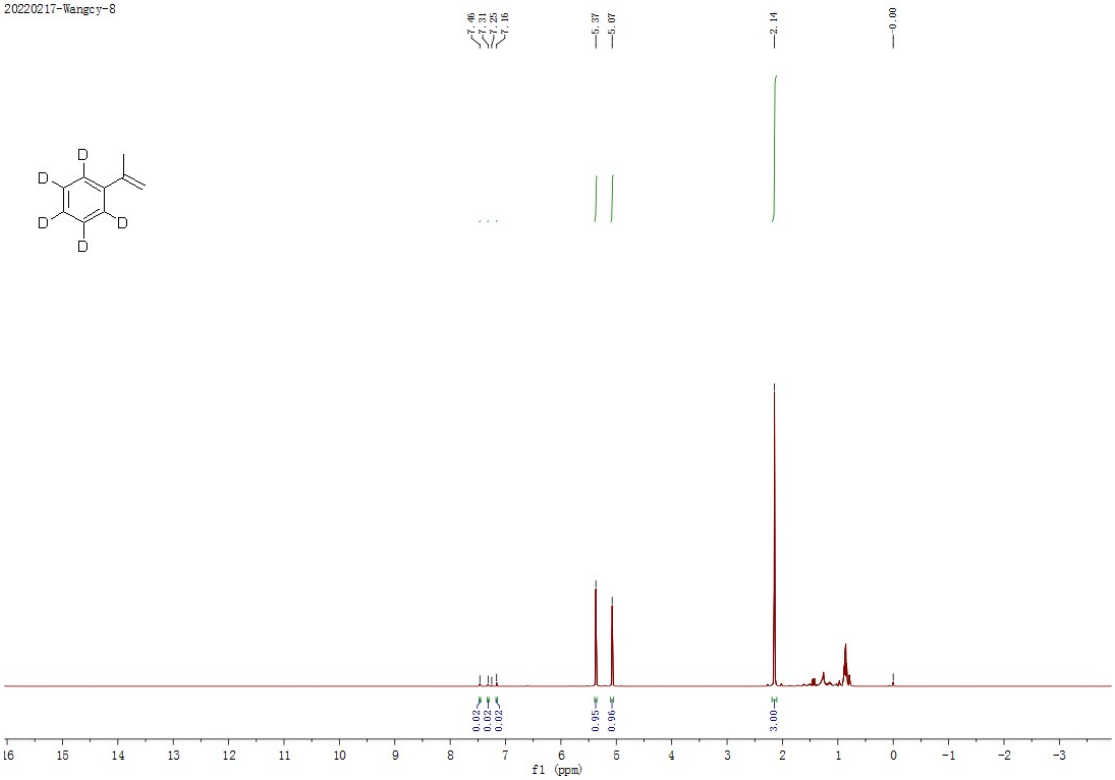


^{1}H NMR (500 MHz, $CDCl_3$)

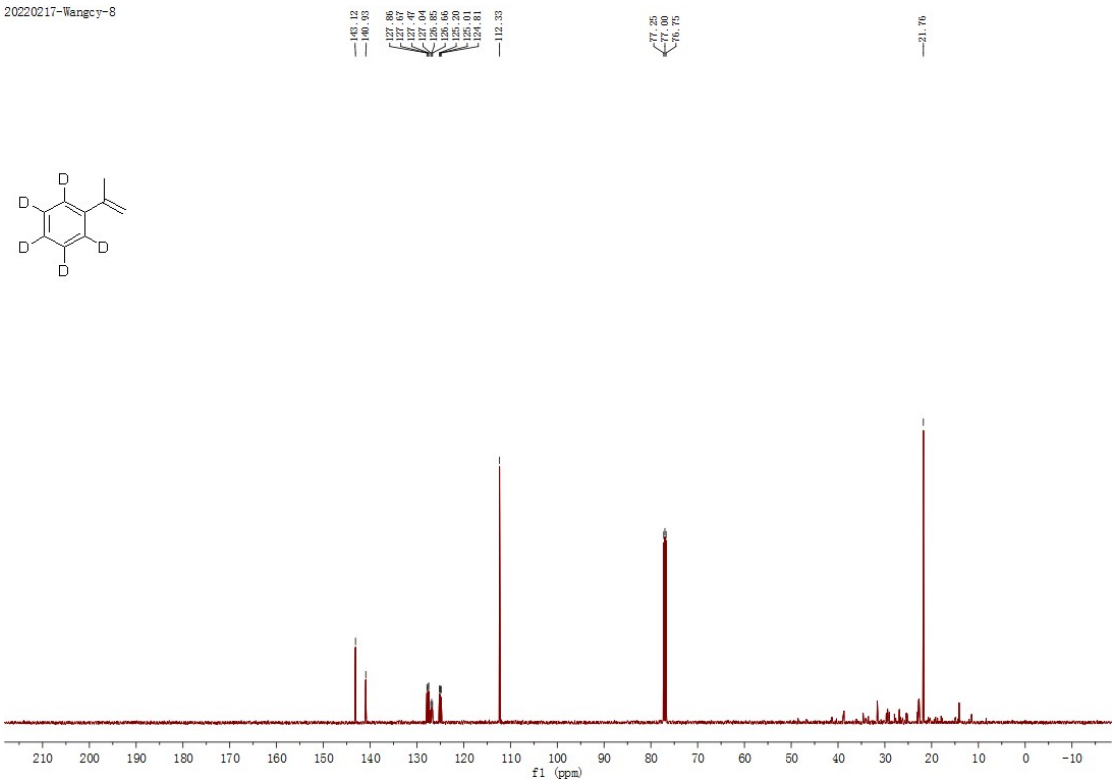


^{13}C NMR (125 MHz, $CDCl_3$)

2a-D_5 (>98%D)

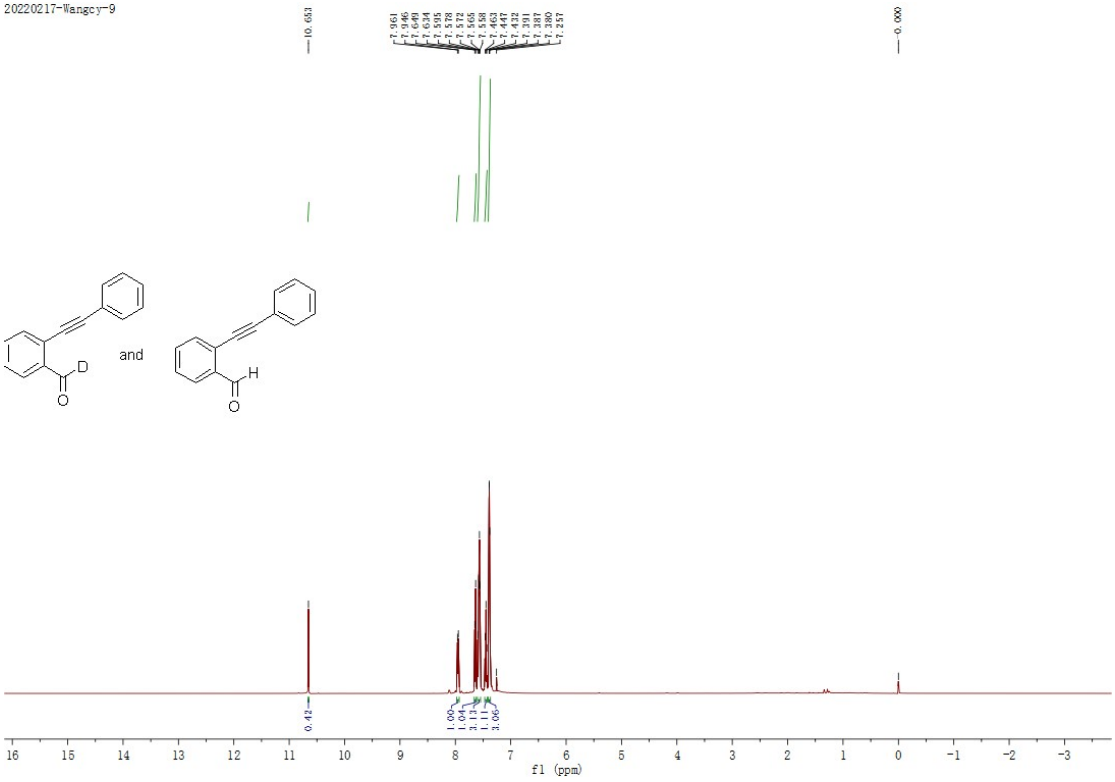


^{1}H NMR (500 MHz, $CDCl_3$)

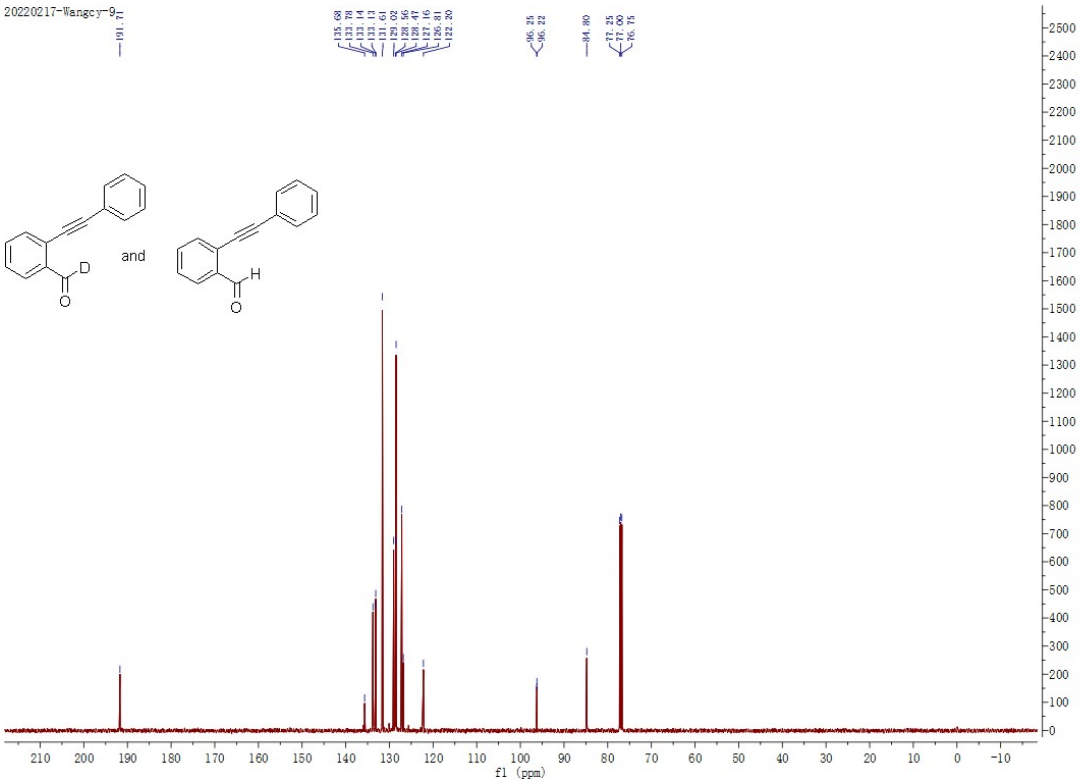


^{13}C NMR (125 MHz, $CDCl_3$)

1a and **1a-D$_1$**

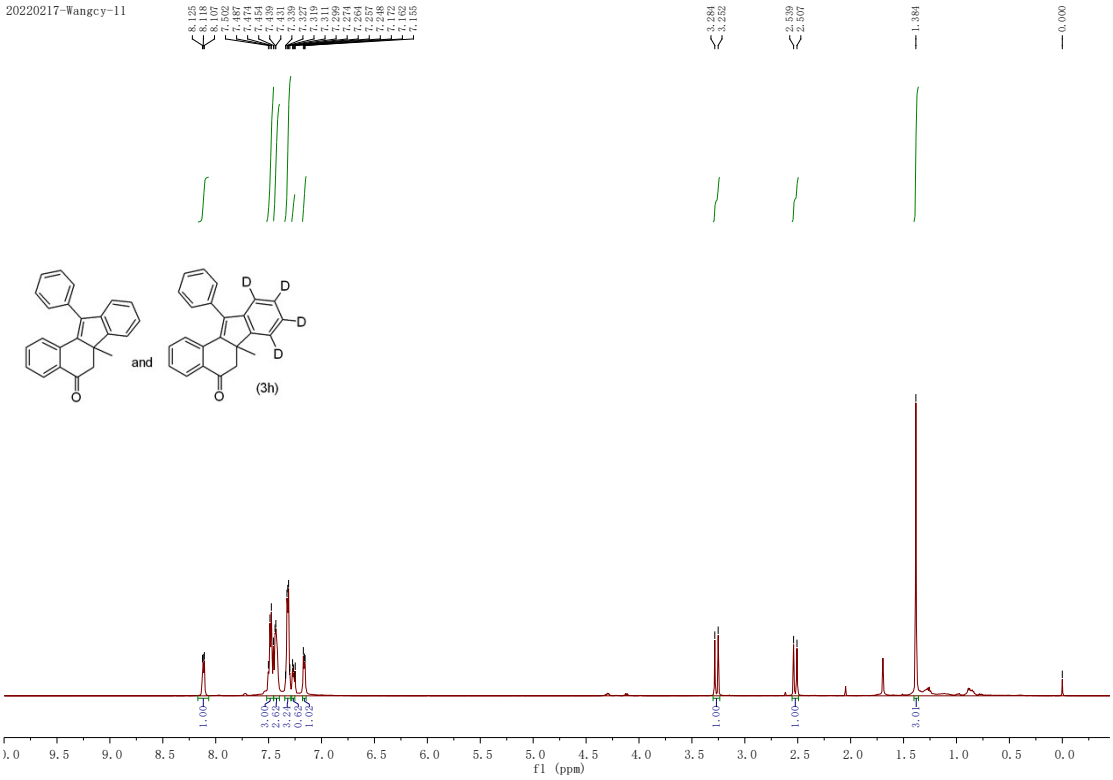


^{1}H NMR (500 MHz, $CDCl_3$)

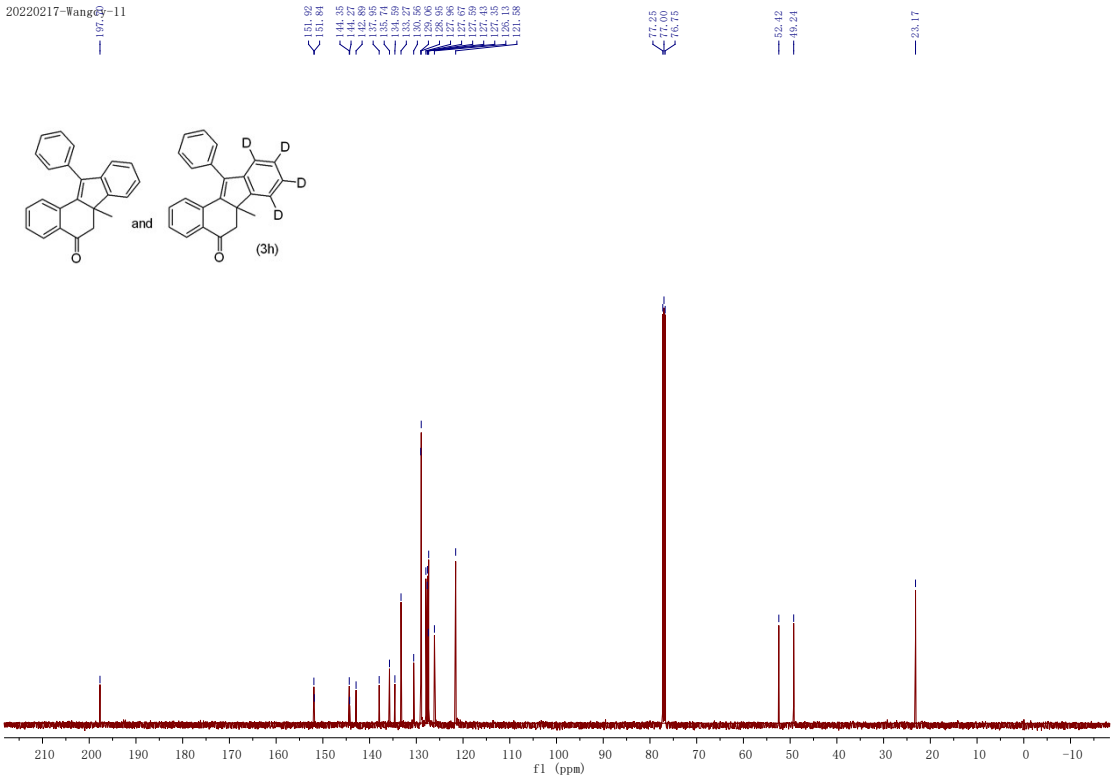


^{13}C NMR (125 MHz, $CDCl_3$)

3aa and 3aa-D_4 (3h)

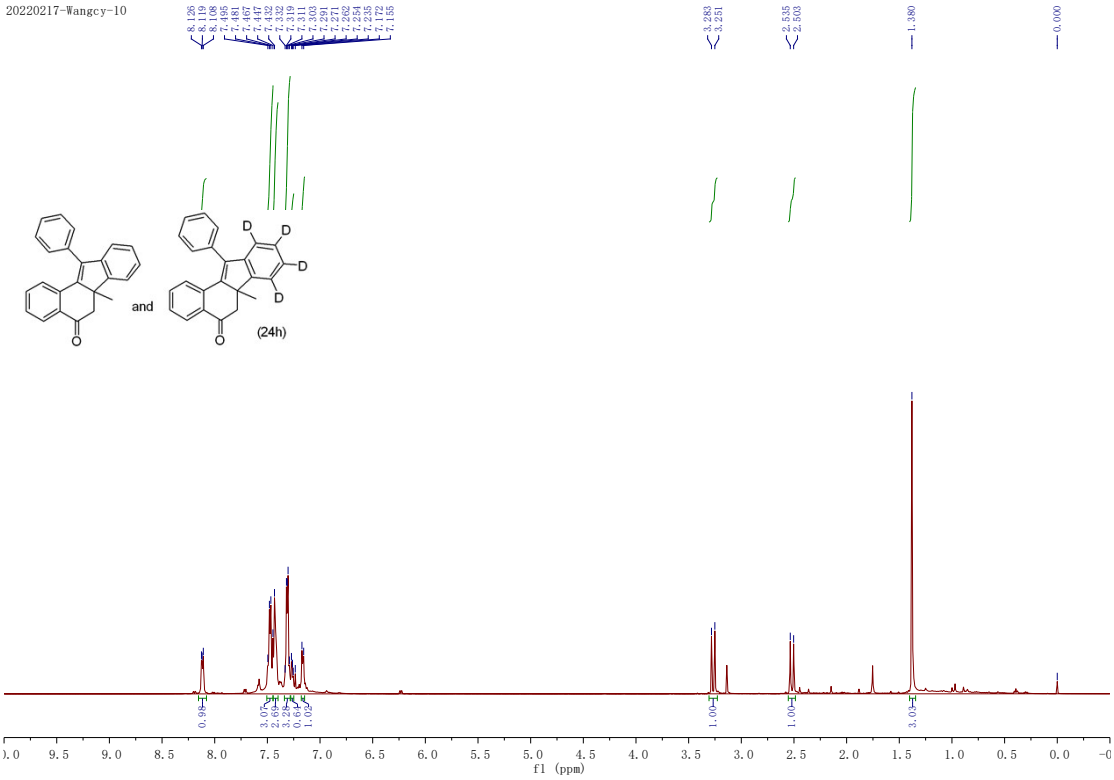


^{1}H NMR (500 MHz, $CDCl_3$)

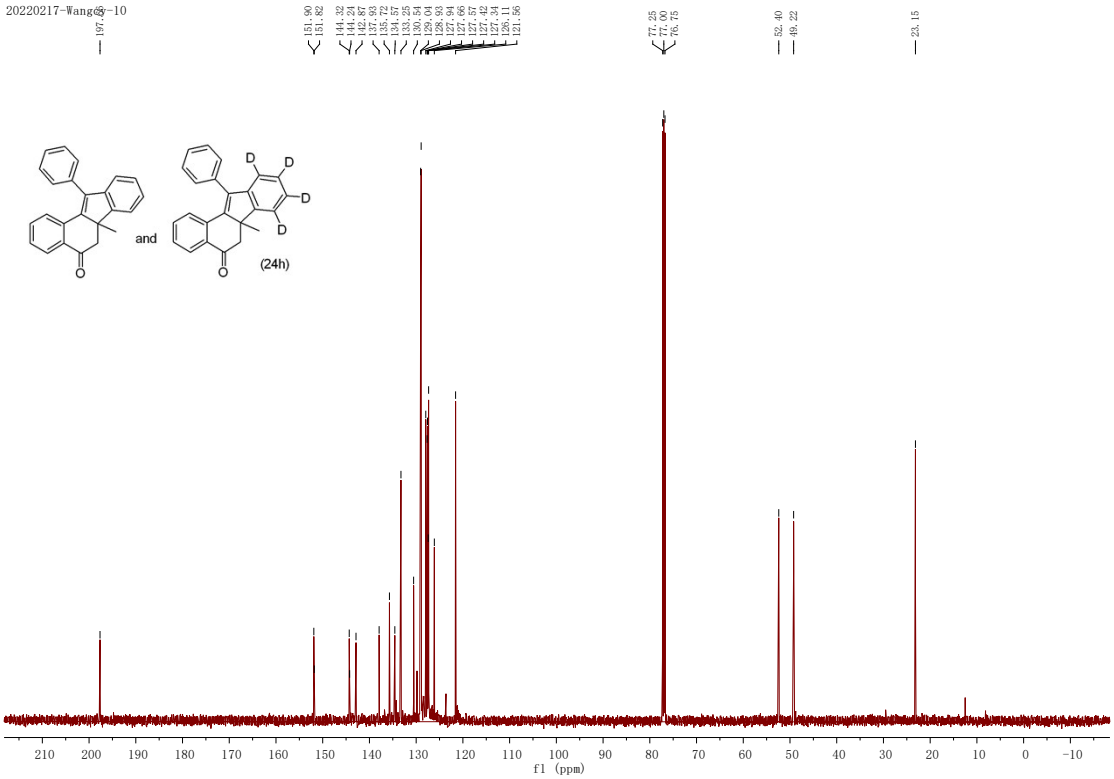


^{13}C NMR (125 MHz, $CDCl_3$)

3aa and 3aa-D_4 (24h)



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



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

(D) The X-ray single-crystal diffraction analysis of 3aa (CCDC: 2122614)

The compound **3aa** was dissolved in a mixed solvent of dichloromethane and hexane (v/v 1:3), and stirred until the compound disappeared completely. Then, the solution was filtered. Colorless crystals were obtained by slow evaporation of the filtrate at room temperature after a few days.

Crystal data of the compound **3aa** was collected at 296 K using the radiation wavelength at 0.71073 Å with a Bruker APEX-II CCD detector at Hengyang normal university (China). A multiscan method was applied for absorption corrections. The structures were solved with direct method and were refined with SHELXL-97 (Sheldrick, 2008)

Molecular structure of the compound with 50% probability ellipsoids

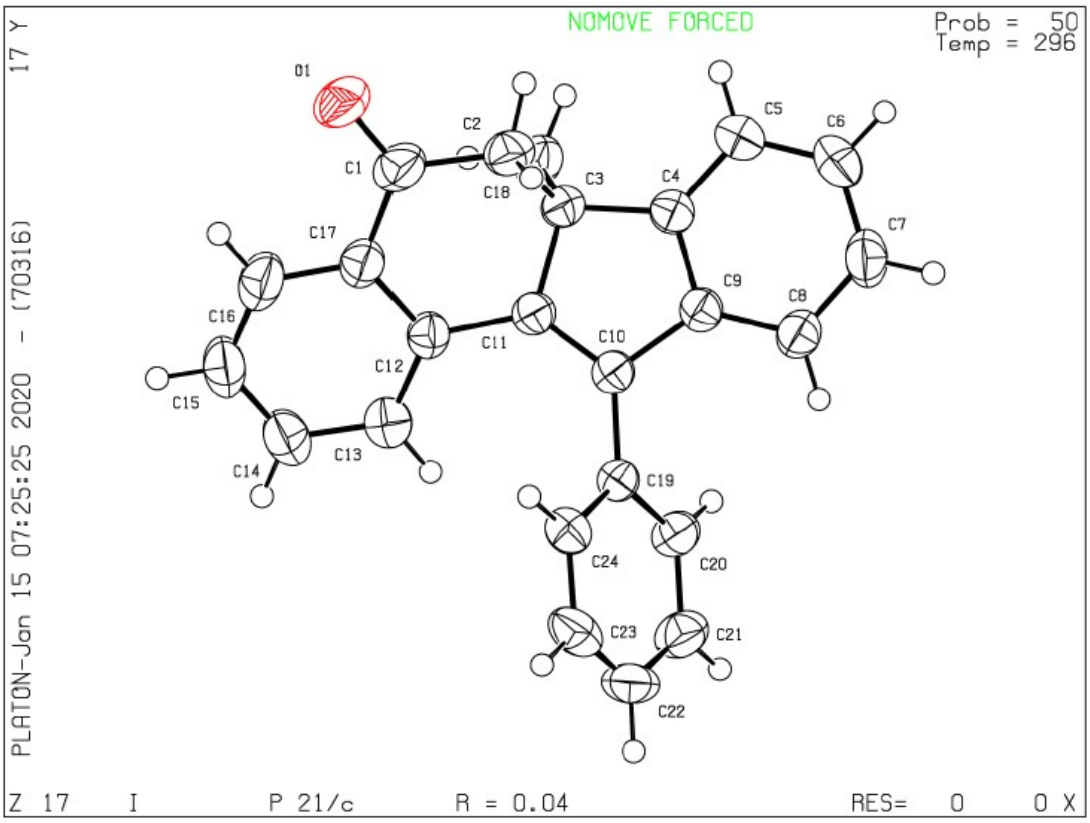


Table S1. Crystal data and structure refinement for wcy001_0m.

Identification code	wcy001_0m	
Empirical formula	C24 H18 O	
Formula weight	322.38	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 9.188(12) Å	α= 90°.
	b = 19.18(2) Å	β= 90.733(16)°.
	c = 9.426(12) Å	γ = 90°.
Volume	1661(4) $Å^3$	
Z	4	
Density (calculated)	1.289 Mg/m^3	
Absorption coefficient	0.077 mm^{-1}	
F(000)	680	
Crystal size	0.230 x 0.220 x 0.210 mm^3	
Theta range for data collection	2.217 to 26.001°.	
Index ranges	-11<=h<=11, -23<=k<=23, -11<=l<=11	
Reflections collected	17892	
Independent reflections	3204 [R(int) = 0.0245]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3204 / 0 / 226	
Goodness-of-fit on F^2	1.049	
Final R indices [I>2sigma(I)]	R1 = 0.0405, wR2 = 0.1027	
R indices (all data)	R1 = 0.0497, wR2 = 0.1100	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.163 and -0.199 $e.Å^{-3}$	

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for wcy001_0m. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	-2899(2)	4076(1)	4524(2)	74(1)
C(1)	-1960(2)	3758(1)	3904(2)	50(1)
C(2)	-514(2)	4086(1)	3610(2)	49(1)
C(3)	75(2)	3844(1)	2191(2)	39(1)
C(4)	1630(2)	4041(1)	1937(2)	39(1)
C(5)	2260(2)	4688(1)	1868(2)	49(1)
C(6)	3727(2)	4733(1)	1602(2)	57(1)
C(7)	4544(2)	4142(1)	1409(2)	56(1)
C(8)	3918(2)	3486(1)	1473(2)	45(1)
C(9)	2445(2)	3440(1)	1733(1)	36(1)
C(10)	1497(2)	2831(1)	1914(1)	35(1)
C(11)	145(2)	3057(1)	2208(1)	36(1)
C(12)	-1183(2)	2686(1)	2594(2)	39(1)
C(13)	-1501(2)	2011(1)	2151(2)	48(1)
C(14)	-2794(2)	1696(1)	2511(2)	56(1)
C(15)	-3782(2)	2036(1)	3337(2)	59(1)
C(16)	-3493(2)	2695(1)	3789(2)	57(1)
C(17)	-2210(2)	3033(1)	3416(2)	45(1)
C(18)	-900(2)	4105(1)	980(2)	52(1)
C(19)	2053(1)	2109(1)	1842(1)	36(1)
C(20)	2769(2)	1873(1)	651(2)	44(1)
C(21)	3296(2)	1206(1)	578(2)	54(1)
C(22)	3136(2)	762(1)	1710(2)	58(1)
C(23)	2464(2)	989(1)	2901(2)	54(1)
C(24)	1912(2)	1657(1)	2970(2)	43(1)

Table S3. Bond lengths [Å] and angles [°] for wcy001_0m.

O(1)-C(1)	1.213(2)
C(1)-C(17)	1.482(3)
C(1)-C(2)	1.499(3)
C(2)-C(3)	1.522(3)
C(2)-H(2A)	0.9700
C(2)-H(2B)	0.9700
C(3)-C(4)	1.500(3)
C(3)-C(11)	1.510(3)
C(3)-C(18)	1.527(2)
C(4)-C(5)	1.371(3)
C(4)-C(9)	1.389(2)
C(5)-C(6)	1.377(3)
C(5)-H(5)	0.9300
C(6)-C(7)	1.374(3)
C(6)-H(6)	0.9300
C(7)-C(8)	1.385(3)
C(7)-H(7)	0.9300
C(8)-C(9)	1.382(3)
C(8)-H(8)	0.9300
C(9)-C(10)	1.468(2)
C(10)-C(11)	1.348(2)
C(10)-C(19)	1.477(2)
C(11)-C(12)	1.463(2)
C(12)-C(13)	1.391(3)
C(12)-C(17)	1.397(2)
C(13)-C(14)	1.379(3)
C(13)-H(13)	0.9300
C(14)-C(15)	1.369(3)
C(14)-H(14)	0.9300
C(15)-C(16)	1.359(3)
C(15)-H(15)	0.9300
C(16)-C(17)	1.394(3)
C(16)-H(16)	0.9300
C(18)-H(18A)	0.9600
C(18)-H(18B)	0.9600
C(18)-H(18C)	0.9600

C(19)-C(24)	1.379(2)
C(19)-C(20)	1.385(2)
C(20)-C(21)	1.370(3)
C(20)-H(20)	0.9300
C(21)-C(22)	1.375(3)
C(21)-H(21)	0.9300
C(22)-C(23)	1.359(3)
C(22)-H(22)	0.9300
C(23)-C(24)	1.381(3)
C(23)-H(23)	0.9300
C(24)-H(24)	0.9300

O(1)-C(1)-C(17)	120.91(16)
O(1)-C(1)-C(2)	121.01(18)
C(17)-C(1)-C(2)	118.08(13)
C(1)-C(2)-C(3)	111.07(14)
C(1)-C(2)-H(2A)	109.4
C(3)-C(2)-H(2A)	109.4
C(1)-C(2)-H(2B)	109.4
C(3)-C(2)-H(2B)	109.4
H(2A)-C(2)-H(2B)	108.0
C(4)-C(3)-C(11)	102.33(11)
C(4)-C(3)-C(2)	114.41(13)
C(11)-C(3)-C(2)	108.18(12)
C(4)-C(3)-C(18)	110.36(14)
C(11)-C(3)-C(18)	111.13(13)
C(2)-C(3)-C(18)	110.18(15)
C(5)-C(4)-C(9)	121.04(16)
C(5)-C(4)-C(3)	129.78(13)
C(9)-C(4)-C(3)	109.17(14)
C(4)-C(5)-C(6)	118.76(15)
C(4)-C(5)-H(5)	120.6
C(6)-C(5)-H(5)	120.6
C(7)-C(6)-C(5)	120.60(16)
C(7)-C(6)-H(6)	119.7
C(5)-C(6)-H(6)	119.7
C(6)-C(7)-C(8)	121.14(17)
C(6)-C(7)-H(7)	119.4

C(8)-C(7)-H(7)	119.4
C(9)-C(8)-C(7)	118.25(15)
C(9)-C(8)-H(8)	120.9
C(7)-C(8)-H(8)	120.9
C(8)-C(9)-C(4)	120.21(14)
C(8)-C(9)-C(10)	130.89(14)
C(4)-C(9)-C(10)	108.84(15)
C(11)-C(10)-C(9)	108.47(14)
C(11)-C(10)-C(19)	129.14(13)
C(9)-C(10)-C(19)	122.32(14)
C(10)-C(11)-C(12)	131.93(15)
C(10)-C(11)-C(3)	111.04(12)
C(12)-C(11)-C(3)	116.95(13)
C(13)-C(12)-C(17)	118.00(15)
C(13)-C(12)-C(11)	123.46(14)
C(17)-C(12)-C(11)	118.51(15)
C(14)-C(13)-C(12)	120.84(16)
C(14)-C(13)-H(13)	119.6
C(12)-C(13)-H(13)	119.6
C(15)-C(14)-C(13)	120.64(18)
C(15)-C(14)-H(14)	119.7
C(13)-C(14)-H(14)	119.7
C(16)-C(15)-C(14)	119.63(16)
C(16)-C(15)-H(15)	120.2
C(14)-C(15)-H(15)	120.2
C(15)-C(16)-C(17)	121.01(17)
C(15)-C(16)-H(16)	119.5
C(17)-C(16)-H(16)	119.5
C(16)-C(17)-C(12)	119.86(17)
C(16)-C(17)-C(1)	119.05(15)
C(12)-C(17)-C(1)	121.09(14)
C(3)-C(18)-H(18A)	109.5
C(3)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5
C(3)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5
C(24)-C(19)-C(20)	118.00(15)

C(24)-C(19)-C(10)	121.20(14)
C(20)-C(19)-C(10)	120.77(13)
C(21)-C(20)-C(19)	121.18(15)
C(21)-C(20)-H(20)	119.4
C(19)-C(20)-H(20)	119.4
C(20)-C(21)-C(22)	119.94(17)
C(20)-C(21)-H(21)	120.0
C(22)-C(21)-H(21)	120.0
C(23)-C(22)-C(21)	119.74(17)
C(23)-C(22)-H(22)	120.1
C(21)-C(22)-H(22)	120.1
C(22)-C(23)-C(24)	120.50(16)
C(22)-C(23)-H(23)	119.7
C(24)-C(23)-H(23)	119.7
C(19)-C(24)-C(23)	120.61(16)
C(19)-C(24)-H(24)	119.7
C(23)-C(24)-H(24)	119.7

Symmetry transformations used to generate equivalent atoms:

Table S4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for wcy001_0m. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	73(1)	60(1)	91(1)	5(1)	41(1)	18(1)
C(1)	50(1)	52(1)	49(1)	7(1)	13(1)	12(1)
C(2)	53(1)	42(1)	52(1)	-3(1)	9(1)	6(1)
C(3)	38(1)	36(1)	44(1)	3(1)	5(1)	5(1)
C(4)	39(1)	37(1)	41(1)	3(1)	1(1)	1(1)
C(5)	51(1)	37(1)	59(1)	2(1)	2(1)	-2(1)
C(6)	54(1)	44(1)	73(1)	2(1)	2(1)	-14(1)
C(7)	38(1)	62(1)	67(1)	4(1)	4(1)	-10(1)
C(8)	38(1)	48(1)	50(1)	3(1)	4(1)	4(1)
C(9)	37(1)	38(1)	34(1)	3(1)	1(1)	1(1)
C(10)	36(1)	36(1)	32(1)	2(1)	1(1)	2(1)
C(11)	37(1)	36(1)	35(1)	2(1)	2(1)	2(1)
C(12)	35(1)	43(1)	39(1)	6(1)	1(1)	0(1)
C(13)	42(1)	47(1)	54(1)	-1(1)	2(1)	-4(1)
C(14)	50(1)	53(1)	64(1)	6(1)	-2(1)	-13(1)
C(15)	43(1)	67(1)	68(1)	13(1)	8(1)	-12(1)
C(16)	41(1)	71(1)	59(1)	11(1)	14(1)	4(1)
C(17)	39(1)	49(1)	48(1)	9(1)	6(1)	4(1)
C(18)	45(1)	53(1)	57(1)	13(1)	2(1)	10(1)
C(19)	33(1)	35(1)	41(1)	1(1)	-1(1)	1(1)
C(20)	45(1)	44(1)	43(1)	3(1)	5(1)	8(1)
C(21)	51(1)	50(1)	61(1)	-12(1)	5(1)	9(1)
C(22)	55(1)	32(1)	85(1)	-4(1)	-11(1)	7(1)
C(23)	62(1)	38(1)	62(1)	12(1)	-7(1)	-7(1)
C(24)	46(1)	40(1)	44(1)	3(1)	2(1)	-4(1)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for wcy001_0m.

	x	y	z	U(eq)
H(2A)	171	3964	4361	59
H(2B)	-617	4589	3601	59
H(5)	1707	5088	2000	59
H(6)	4169	5169	1552	69
H(7)	5533	4182	1232	67
H(8)	4475	3086	1345	54
H(13)	-833	1769	1605	57
H(14)	-2997	1247	2190	67
H(15)	-4645	1818	3587	71
H(16)	-4161	2925	4356	68
H(18A)	-1890	3975	1156	77
H(18B)	-830	4603	918	77
H(18C)	-592	3901	103	77
H(20)	2893	2172	-114	53
H(21)	3761	1054	-235	65
H(22)	3486	308	1661	69
H(23)	2376	692	3674	65
H(24)	1441	1804	3784	52

Table S6. Torsion angles [°] for wcy001_0m.

O(1)-C(1)-C(2)-C(3)	-145.02(16)
C(17)-C(1)-C(2)-C(3)	35.1(2)
C(1)-C(2)-C(3)-C(4)	-169.32(13)
C(1)-C(2)-C(3)-C(11)	-56.01(17)
C(1)-C(2)-C(3)-C(18)	65.65(19)
C(11)-C(3)-C(4)-C(5)	-177.22(15)
C(2)-C(3)-C(4)-C(5)	-60.5(2)
C(18)-C(3)-C(4)-C(5)	64.4(2)
C(11)-C(3)-C(4)-C(9)	3.84(15)
C(2)-C(3)-C(4)-C(9)	120.57(14)
C(18)-C(3)-C(4)-C(9)	-114.50(15)
C(9)-C(4)-C(5)-C(6)	-0.4(2)
C(3)-C(4)-C(5)-C(6)	-179.23(15)
C(4)-C(5)-C(6)-C(7)	0.0(3)
C(5)-C(6)-C(7)-C(8)	0.1(3)
C(6)-C(7)-C(8)-C(9)	0.2(3)
C(7)-C(8)-C(9)-C(4)	-0.6(2)
C(7)-C(8)-C(9)-C(10)	-177.37(15)
C(5)-C(4)-C(9)-C(8)	0.7(2)
C(3)-C(4)-C(9)-C(8)	179.79(13)
C(5)-C(4)-C(9)-C(10)	178.14(13)
C(3)-C(4)-C(9)-C(10)	-2.81(16)
C(8)-C(9)-C(10)-C(11)	177.45(14)
C(4)-C(9)-C(10)-C(11)	0.42(16)
C(8)-C(9)-C(10)-C(19)	0.4(2)
C(4)-C(9)-C(10)-C(19)	-176.62(12)
C(9)-C(10)-C(11)-C(12)	-174.35(14)
C(19)-C(10)-C(11)-C(12)	2.4(3)
C(9)-C(10)-C(11)-C(3)	2.15(16)
C(19)-C(10)-C(11)-C(3)	178.93(13)
C(4)-C(3)-C(11)-C(10)	-3.66(15)
C(2)-C(3)-C(11)-C(10)	-124.79(13)
C(18)-C(3)-C(11)-C(10)	114.13(15)
C(4)-C(3)-C(11)-C(12)	173.42(12)
C(2)-C(3)-C(11)-C(12)	52.29(17)
C(18)-C(3)-C(11)-C(12)	-68.79(18)

C(10)-C(11)-C(12)-C(13)	-29.6(2)
C(3)-C(11)-C(12)-C(13)	154.06(14)
C(10)-C(11)-C(12)-C(17)	152.32(16)
C(3)-C(11)-C(12)-C(17)	-24.01(19)
C(17)-C(12)-C(13)-C(14)	0.2(2)
C(11)-C(12)-C(13)-C(14)	-177.87(14)
C(12)-C(13)-C(14)-C(15)	-1.3(3)
C(13)-C(14)-C(15)-C(16)	0.9(3)
C(14)-C(15)-C(16)-C(17)	0.5(3)
C(15)-C(16)-C(17)-C(12)	-1.6(3)
C(15)-C(16)-C(17)-C(1)	178.44(16)
C(13)-C(12)-C(17)-C(16)	1.2(2)
C(11)-C(12)-C(17)-C(16)	179.37(14)
C(13)-C(12)-C(17)-C(1)	-178.83(14)
C(11)-C(12)-C(17)-C(1)	-0.7(2)
O(1)-C(1)-C(17)-C(16)	-5.7(2)
C(2)-C(1)-C(17)-C(16)	174.20(15)
O(1)-C(1)-C(17)-C(12)	174.33(16)
C(2)-C(1)-C(17)-C(12)	-5.8(2)
C(11)-C(10)-C(19)-C(24)	-55.2(2)
C(9)-C(10)-C(19)-C(24)	121.20(15)
C(11)-C(10)-C(19)-C(20)	126.60(16)
C(9)-C(10)-C(19)-C(20)	-57.01(19)
C(24)-C(19)-C(20)-C(21)	1.3(2)
C(10)-C(19)-C(20)-C(21)	179.58(14)
C(19)-C(20)-C(21)-C(22)	-0.9(3)
C(20)-C(21)-C(22)-C(23)	-0.5(3)
C(21)-C(22)-C(23)-C(24)	1.5(3)
C(20)-C(19)-C(24)-C(23)	-0.3(2)
C(10)-C(19)-C(24)-C(23)	-178.59(14)
C(22)-C(23)-C(24)-C(19)	-1.1(2)

Symmetry transformations used to generate equivalent atoms:

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