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Supporting Information

HFIP-promoted formal [2π + 2σ] cycloaddition of *para*-quinone methides with bicyclo[1.1.0]butanes: approach to spiro-bicyclo[2.1.1]hexanes

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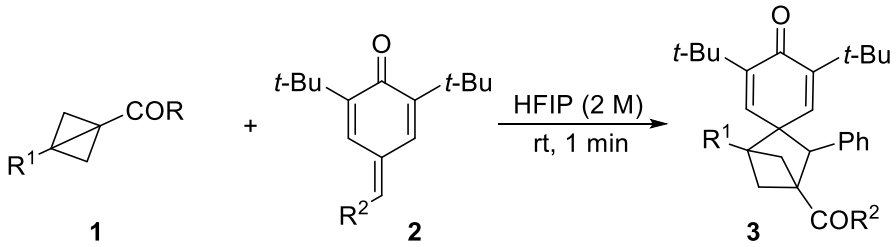
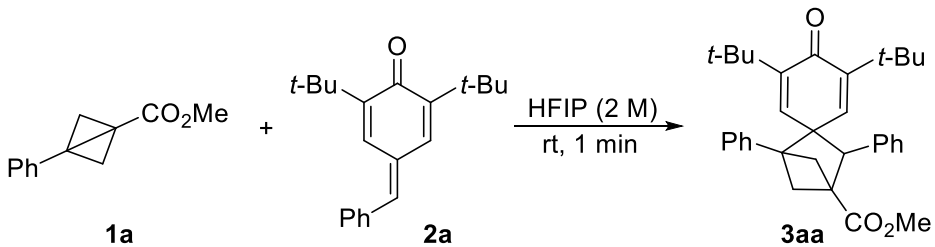
General information ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 400 instrument at 400 (^{1}H NMR), 100 (^{13}C NMR) as well as 376 MHz (^{19}F NMR). Tetramethylsilane (TMS) and $CDCl_3$ (7.26 ppm for ^{1}H NMR, 77.0 ppm for ^{13}C NMR) or THF-*d*8 (1.72 ppm and 3.58 ppm for ^{1}H NMR, 67.2 ppm and 25.3 ppm for ^{13}C NMR) were used as references. Data for ^{1}H NMR were reported as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, m = multiplet), coupling constants (Hz), and integration. Data for ^{13}C NMR were reported as ppm. High-resolution mass spectra (HRMS) analyses were performed by the electrospray ionization (ESI) method on a Waters SYNAPT G2-Si mass spectrometer with a Q-TOF analyzer. Melting points were determined using a X-4 digital micro melting point apparatus. Thin-layer chromatography (TLC) was performed, and visualization of the compounds was accomplished with UV light (254 nm). Flash column chromatography was performed on silica gel (200−300 mesh). Known BCBs **1**[1] and *p*-QMs **2**[2] were prepared according to literature procedures. Other purchased reagents and solvents were used without further purification, if not stated otherwise.

General procedure for preparation of products 3



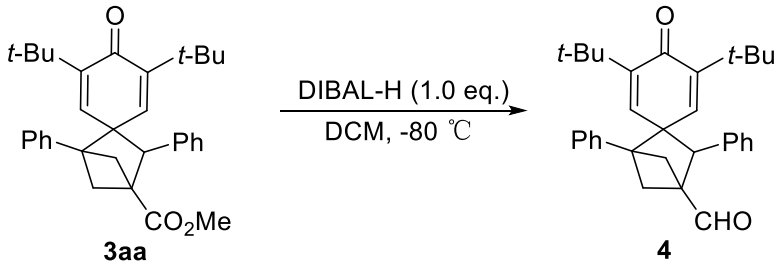
BCBs **1** (0.2 mmol, 1.0 eq.) was added to a mixture of *p*-QMs **2** (0.22 mmol, 1.1 eq.) and HFIP (0.1 mL) under room temperature. The resulting mixture was stirred for 1 min. The residue was purified by silica gel column chromatography (PE/EA = 20/1) to give the pure products **3**.

Procedure for scale-up synthesis of compound 3aa



BCB **1a** (941.2 mg, 5.0 mmol, 1.0 eq.) was added to a mixture of *p*-QM **2a** (1.6 g, 5.5 mmol, 1.1 eq.) and HFIP (2.5 mL) under room temperature. The resulting mixture was stirred for 1 min. After evaporating the solvent under reduced pressure, the crude product was recrystallized with DCM and PE to give the pure product **3aa** (2.0 g, 82% yield) as a white solid.

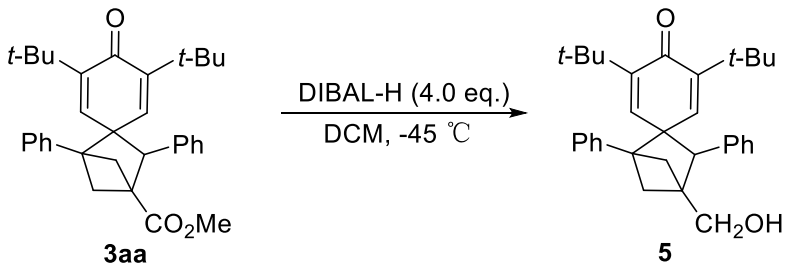
Procedure for preparation of compound 4



3aa **4**

An over-dried 25 mL Schlenk tube was charged with **3aa** (96.5 mg, 0.2 mmol, 1.0 eq.) and dry DCM (2.0 mL) under N_2. The solution was cooled to -80 °C in a dry alcohol bath. A solution of DIBAL-H in toluene (0.2 mL, 0.2 mmol, 1.0 eq., 1.0 M) of was added dropwise to the reaction mixture over 10 min. After stirring at -80 °C for 0.5 h, the reaction was quenched with saturated NH_4Cl aqueous solution (5 mL). The aqueous layer was extracted with ethyl acetate (10 mL × 3), the combined organic layer was dried over Na_2SO_4, filtered and concentrated under the reduced pressure. The residue was purified by silica gel column chromatography (PE/EA = 15/1) to afford product **4** (78.8 mg, 87% yield) as a white solid.

Procedure for preparation of compound 5

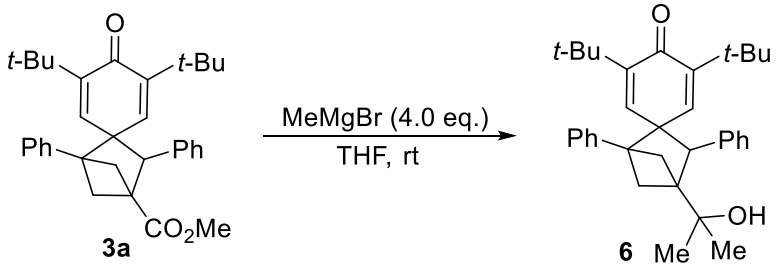


3aa **5**

An over-dried 25 mL Schlenk tube was charged with **3aa** (96.5 mg, 0.2 mmol, 1.0 eq.) and dry

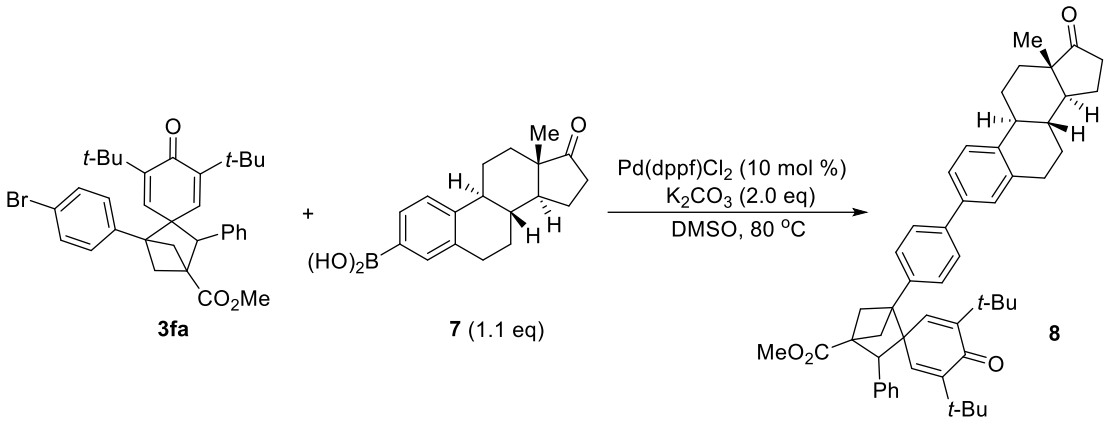
DCM (2.0 mL) under N_2. The solution was cooled to -45 °C in a dry alcohol bath. A solution of DIBAL-H in toluene (0.8 mL, 0.8 mmol, 4.0 eq., 1.0 M) of was added dropwise to the reaction mixture over 0.5 h, and the solution was stirred at -45 °C for 2 h, until reduction was complete (monitored by TLC). Excess hydride was destroyed by the addition of 0.2 mL of a 1 M HCl solution, and the solution was partitioned. The aqueous layer was washed with ethyl acetate (10 mL), and ethyl acetate extracts were washed sequentially with water (10 mL) and saturated NaCl solution (10 mL). The combined organic layer was dried over Na_2SO_4, filtered and concentrated under the reduced pressure. The residue was purified by silica gel column chromatography (PE/EA = 3/1) to afford product **5** (80.9 mg, 89% yield) as a white solid.

Procedure for preparation of compound 6



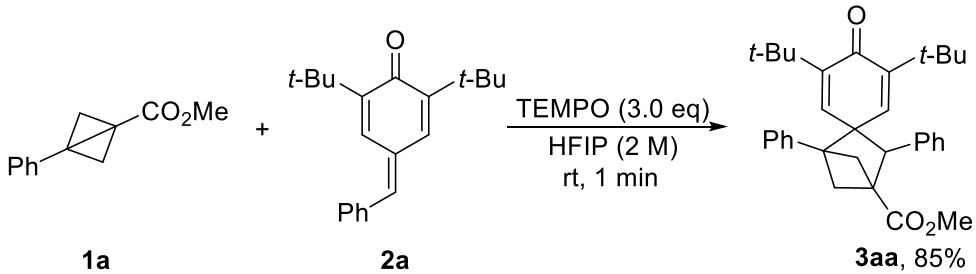
An over-dried 25 mL Schlenk tube was charged with **3aa** (96.5 mg, 0.2 mmol, 1.0 eq.) and dry THF (2.0 mL) under N_2. A solution of methylmagnesium bromide in THF (0.8 mL, 0.8 mmol, 4 eq., 1.0 M) was added dropwise to the reaction mixture. After stirring at room temperature for 1 h, the reaction was quenched with saturated NH_4Cl aqueous solution (5 mL). The aqueous layer was extracted with ethyl acetate (10 mL × 3), the combined organic layer was dried over Na_2SO_4, filtered and concentrated under the reduced pressure. The residue was purified by silica gel column chromatography (PE/EA = 3/1) to afford product **6** (78.2 mg, 81%) as a white solid.

Procedure for preparation of compound 8



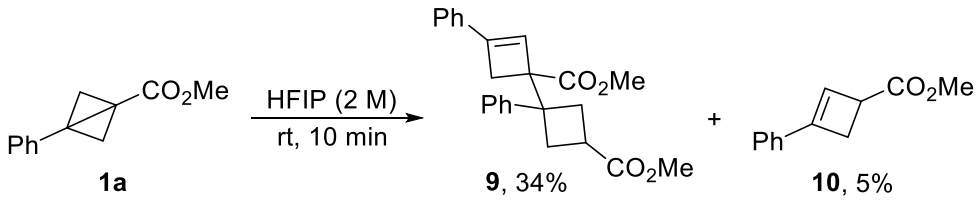
An oven-dried 25 mL Schlenk tube was charged with boronic acid **7** (65.7 mg, 0.22 mmol, 1.1 eq.), $Pd(dppf)Cl_2$ (14.6 mg, 0.02 mmol, 10 mol %), and K_2CO_3 (55.3 mg, 0.4 mmol, 2.0 eq.). After the flask was degassed and refilled with Ar for three times to ensure the complete exclusion of air, **3fa** (112.3 mg, 0.2 mmol, 1.0 eq.) and anhydrous DMSO (2.0 mL) were added sequentially. The resulting mixture was heated in an oil bath at 80 ℃ for 1.5 h, quenched with 5.0 mL of H_2O and extracted with ethyl acetate (10 mL × 3). The combined organic layer was washed sequentially with water (20 mL) and saturated NaCl solution (20 mL), dried with anhydrous Na_2SO_4, filtered and concentrated under the reduced pressure. The residue was purified by silica gel column chromatography (PE/EA = 10:1) to give the pure product **8** (142.6 mg, 97% yield) as a white solid.

Control Experiments



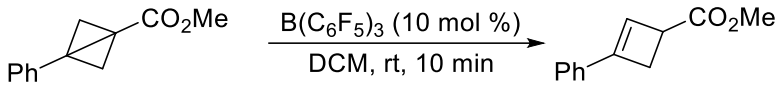
BCB **1a** (37.6 mg, 0.2 mmol, 1.0 eq.) was added to a mixture of *p*-QM **2a** (64.8 mg, 0.22 mmol, 1.1 eq.), TEMPO (93.8 mg, 0.6 mmol, 3.0 eq.) and HFIP (0.1 mL) under room temperature. The

resulting mixture was stirred for 1 min. The residue was purified by silica gel column chromatography (PE/EA = 20/1) to give the pure product **3aa** (82.1 mg, 85% yield).



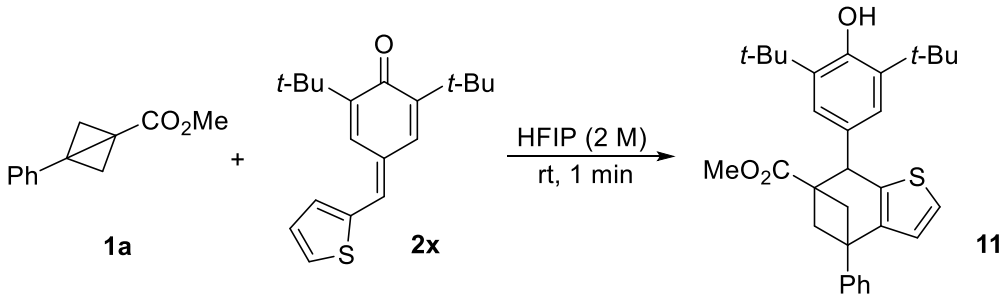
1a **9**, 34% **10**, 5%

A mixture of BCB **1a** (37.6 mg, 0.2 mmol) and HFIP (0.1 mL) was stirred for 10 min under room temperature. The residue was purified by silica gel column chromatography (PE/EA = 20/1) to give product **9** (12.8 mg, 34% yield) and product **10** (1.9 mg, 5% yield).



1a **10**, 92%

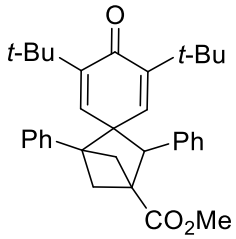
To a mixture of BCB **1a** (37.6 mg, 0.2 mmol) and $B(C_6F_5)_3$ (10.2 mg, 0.02 mmol, 10 mol %) was added DCM (1.0 mL) under room temperature. The resulting mixture was stirred for 10 min. After evaporating the solvent under reduced pressure, the residue was purified by silica gel column chromatography (PE/EA = 20/1) to give the pure product **10** (34.6 mg, 92% yield).



1a **2x** **11**

BCB **1a** (37.6 mg, 0.2 mmol, 1.0 eq.) was added to a mixture of *p*-QM **2x** (66.1 mg, 0.22 mmol, 1.1 eq.) and HFIP (0.1 mL) under room temperature. The resulting mixture was stirred for 1 min. After evaporating the solvent under reduced pressure, the residue was purified by silica gel column chromatography (PE/EA = 20/1) to give the pure product **11** (49.8 mg, 51% yield) as a white solid.

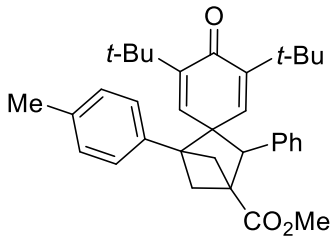
Characterization data



3aa

Methyl

3',5'-di-*tert*-butyl-4'-oxo-1,3-diphenylspiro[bicyclo[2.1.1]hexane-2,1'-cyclohexane]-2',5'-diene-4-carboxylate (3aa). White solid; 84.9 mg, 88% yield, PE/EA = 20/1 as the eluent; mp = 159–160 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.23 (d, J = 7.2 Hz, 2H), 7.19–7.12 (m, 4H), 7.03 (d, J = 2.8 Hz, 1H), 6.99 (d, J = 7.6 Hz, 2H), 6.88–6.86 (m, 2H), 6.11 (d, J = 3.2 Hz, 1H), 4.13 (s, 1H), 3.70 (s, 3H), 2.99 (t, J = 8.8 Hz, 1H), 2.84 (t, J = 7.6 Hz, 1H), 2.52 (d, J = 7.6 Hz, 1H), 2.33 (d, J = 7.2 Hz, 1H), 1.19 (s, 9H), 0.77 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 185.2, 172.3, 148.3, 147.9, 142.4, 141.1, 139.1, 138.1, 128.5, 127.3, 127.0, 126.63, 126.60, 126.2, 60.4, 57.6, 53.2, 52.0, 51.4, 46.2, 40.1, 34.9, 34.7, 29.4, 28.8; **HRMS (ESI)** m/z calcd for $[M + Na]^+$ $C_{33}H_{38}O_3Na$ 505.2713, found 505.2722.

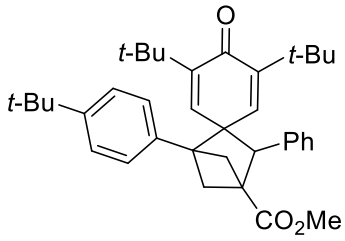


3ba

Methyl

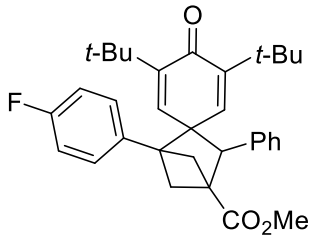
3',5'-di-*tert*-butyl-4'-oxo-3-phenyl-1-(*p*-tolyl)spiro[bicyclo[2.1.1]hexane-2,1'-cyclohexane]-2',5'-diene-4-carboxylate (3ba). White solid; 68.5 mg, 69% yield, PE/EA = 20/1 as the eluent; mp = 172–173 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.23 (d, J = 7.6 Hz, 2H), 7.18–7.15 (m, 1H), 7.03 (d, J = 2.0 Hz, 1H), 6.98 (d, J = 7.2 Hz, 2H), 6.94 (d, J = 8.0 Hz, 2H), 6.77 (d, J = 7.6 Hz, 2H), 6.12

(d, J = 2.0 Hz, 1H), 4.11 (s, 1H), 3.69 (s, 3H), 2.97 (t, J = 9.2 Hz, 1H), 2.81 (t, J = 7.6 Hz, 1H), 2.48 (d, J = 7.6 Hz, 1H), 2.30 (d, J = 7.2 Hz, 1H), 2.23 (s, 3H), 1.20 (s, 9H), 0.78 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 185.3, 172.4, 148.1, 147.8, 142.6, 141.3, 139.1, 136.6, 135.1, 128.4, 128.0, 126.6, 126.1, 60.1, 57.7, 53.2, 52.0, 51.4, 46.4, 40.2, 34.9, 34.7, 29.4, 28.8, 21.1; **HRMS (ESI)** m/z calcd for $[M + Na]^+$ $C_{34}H_{40}O_3Na$ 519.2870, found 519.2874.



3ca

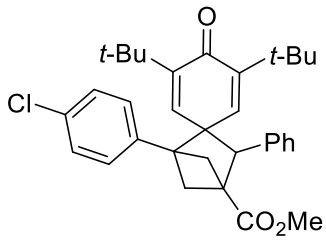
Methyl 3',5'-di-*tert*-butyl-1-(4-(*tert*-butyl)phenyl)-4'-oxo-3-phenylspiro[bicyclo[2.1.1]hexane-2,1'-cyclohexane]-2',5'-diene-4-carboxylate (3ca). White solid; 67.9 mg, 63% yield, PE/EA = 20/1 as the eluent; mp = 171–172 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.23 (d, J = 7.6 Hz, 2H), 7.18–7.14 (m, 3H), 7.01–6.98 (m, 3H), 6.80 (d, J = 8.4 Hz, 2H), 6.09 (d, J = 2.8 Hz, 1H), 4.12 (s, 1H), 3.70 (s, 3H), 2.96 (t, J = 9.6 Hz, 1H), 2.81 (t, J = 7.2 Hz, 1H), 2.51 (d, J = 8.0 Hz, 1H), 2.33 (d, J = 7.2 Hz, 1H), 1.21 (s, 9H), 1.18 (s, 9H), 0.78 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 185.0, 172.4, 150.0, 148.1, 147.7, 142.7, 141.4, 139.2, 134.9, 128.4, 126.61, 126.58, 126.0, 124.0, 60.4, 57.5, 53.4, 52.0, 51.4, 46.3, 40.0, 34.9, 34.6, 34.4, 31.2, 29.3, 28.7; **HRMS (ESI)** m/z calcd for $[M + Na]^+$ $C_{37}H_{46}O_3Na$ 561.3339, found 561.3349.



3da

Methyl

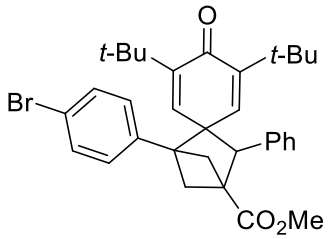
3',5'-di-*tert*-butyl-1-(4-fluorophenyl)-4'-oxo-3-phenylspiro[bicyclo[2.1.1]hexane-2,1'-cyclohexane]-2',5'-diene-4-carboxylate (3da). White solid; 96.1 mg, 96% yield, PE/EA = 20/1 as the eluent; mp = 153–154 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.24 (d, J = 7.6 Hz, 2H), 7.19–7.16 (m, 1H), 7.01–6.97 (m, 3H), 6.83 (d, J = 6.8 Hz, 4H), 6.09 (d, J = 2.8 Hz, 1H), 4.13 (s, 1H), 3.70 (s, 3H), 2.96 (t, J = 9.2 Hz, 1H), 2.81 (t, J = 7.2 Hz, 1H), 2.50 (dd, J = 7.6, 0.8 Hz, 1H), 2.30 (d, J = 7.2 Hz, 1H), 1.20 (s, 9H), 0.78 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 185.0, 172.2, 161.7 (d, J = 244.1 Hz), 148.5, 148.1, 142.1, 140.8, 139.0, 134.0 (d, J = 3.5 Hz), 128.5, 127.8 (d, J = 8.0 Hz), 126.7, 126.6, 114.2 (d, J = 21.5 Hz), 59.7, 57.6, 53.1, 52.1, 51.3, 46.2, 40.1, 34.9, 34.7, 29.4, 28.8; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -115.00 – -115.07 (m, 1F); **HRMS (ESI)** m/z calcd for $[M + Na]^+$ $C_{33}H_{37}FO_3Na$ 523.2619, found 523.2628.



3ea

Methyl 3',5'-di-*tert*-butyl-1-(4-chlorophenyl)-4'-oxo-3-phenylspiro[bicyclo[2.1.1]hexane-2,1'-cyclohexane]-2',5'-diene-4-carboxylate (3ea). White solid; 96.2 mg, 93% yield, PE/EA = 20/1 as the eluent; mp = 149–150 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.23 (d, J = 7.2 Hz, 2H), 7.19–7.16 (m, 1H), 7.12 (d, J = 8.4 Hz, 2H), 7.01–6.96 (m, 3H), 6.81 (d, J = 8.0 Hz, 2H), 6.09 (d, J = 2.8 Hz, 1H), 4.12 (s, 1H), 3.70 (s, 3H), 2.97 (t, J = 9.2 Hz, 1H), 2.81 (t, J = 7.6 Hz, 1H), 2.49 (d, J = 8.0 Hz, 1H), 2.30 (d, J = 7.2 Hz, 1H), 1.20 (s, 9H), 0.78 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 185.1, 172.1, 148.6, 148.2, 141.9, 140.7, 138.8, 136.7, 132.8, 128.5, 127.6, 127.5, 126.7, 126.5, 59.6, 57.7, 53.1, 52.1, 51.3, 46.2, 40.2, 35.0, 34.7, 29.5, 28.9; **HRMS (ESI)** m/z calcd for $[M + Na]^+$

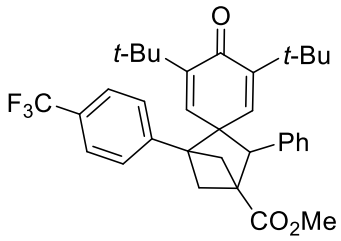
$C_{33}H_{37}ClO_3Na$ 539.2323, found 539.2333.



3fa

Methyl

1-(4-bromophenyl)-3',5'-di-*tert*-butyl-4'-oxo-3-phenylspiro[bicyclo[2.1.1]hexane-2,1'-cyclohexane]-2',5'-diene-4-carboxylate (3fa). White solid; 102.2 mg, 91% yield, PE/EA = 20/1 as the eluent; mp = 174–175 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.28–7.23 (m, 4H), 7.19–7.16 (m, 1H), 7.00–6.96 (m, 3H), 6.76 (d, J = 8.4 Hz, 2H), 6.09 (d, J = 2.4 Hz, 1H), 4.12 (s, 1H), 3.70 (s, 3H), 2.97 (t, J = 9.2 Hz, 1H), 2.81 (t, J = 7.6 Hz, 1H), 2.49 (d, J = 8.0 Hz, 1H), 2.30 (d, J = 7.6 Hz, 1H), 1.20 (s, 9H), 0.78 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 185.1, 172.1, 148.6, 148.3, 141.9, 140.6, 138.8, 137.3, 130.4, 128.5, 127.9, 126.7, 126.5, 120.9, 59.6, 57.7, 53.0, 52.1, 51.3, 46.2, 40.1, 35.0, 34.7, 29.5, 28.8; **HRMS (ESI)** *m/z* calcd for $[M + Na]^+$ $C_{33}H_{37}BrO_3Na$ 583.1818, found 583.1827.

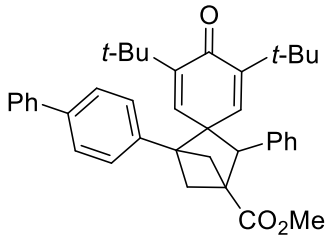


3ga

Methyl

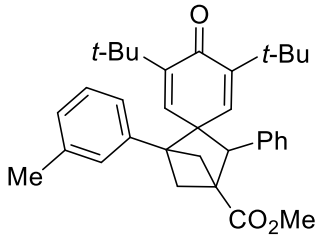
3',5'-di-*tert*-butyl-4'-oxo-3-phenyl-1-(4-(trifluoromethyl)phenyl)spiro[bicyclo[2.1.1]hexane-2,1'-cyclohexane]-2',5'-diene-4-carboxylate (3ga). White solid; 95.8 mg, 87% yield, PE/EA = 20/1 as the eluent; mp = 184–185 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 (d, J = 8.0 Hz, 2H), 7.27–7.24 (m, 2H), 7.20–7.17 (m, 1H), 7.02–6.98 (m, 5H), 6.11 (d, J = 2.8 Hz, 1H), 4.14 (s, 1H), 3.71 (s, 3H), 3.02 (t, J = 9.6 Hz, 1H), 2.86 (dd, J = 9.6, 7.6 Hz, 1H), 2.54 (dd, J = 8.0, 1.6 Hz, 1H), 2.34 (d,

J = 7.2 Hz, 1H), 1.19 (s, 9H), 0.77 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 184.9, 171.9, 148.7, 148.4, 142.2, 141.6, 140.4, 138.7, 129.2 (q, J = 32.3 Hz), 128.5, 126.8, 126.6, 126.5, 124.3 (q, J = 3.7 Hz), 123.9 (q, J = 270.5 Hz), 59.7, 57.7, 53.1, 52.1, 51.4, 46.1, 40.2, 35.0, 34.7, 29.4, 28.8; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.54 (s, 3F); **HRMS (ESI)** m/z calcd for $[M + Na]^+$ $C_{34}H_{37}F_3O_3Na$ 573.2587, found 573.2595.



3ha

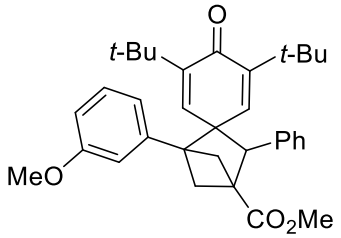
Methyl 1-([1,1'-biphenyl]-4-yl)-3',5'-di-*tert*-butyl-4'-oxo-3-phenylspiro[bicyclo[2.1.1]hexane-2,1'-cyclohexane]-2',5'-diene-4-carboxylate (3ha). White solid; 86.0 mg, 77% yield, PE/EA = 20/1 as the eluent; mp = 153–154 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48 (d, J = 7.6 Hz, 2H), 7.41–7.37 (m, 4H), 7.32–7.23 (m, 3H), 7.20–7.16 (m, 1H), 7.06 (d, J = 2.4 Hz, 1H), 7.00 (d, J = 7.2 Hz, 2H), 6.96 (d, J = 8.0 Hz, 2H), 6.15 (d, J = 2.4 Hz, 1H), 4.15 (s, 1H), 3.71 (s, 3H), 3.02 (t, J = 9.2 Hz, 1H), 2.87 (t, J = 7.6 Hz, 1H), 2.55 (d, J = 7.2 Hz, 1H), 2.36 (d, J = 7.2 Hz, 1H), 1.20 (s, 9H), 0.79 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 185.1, 172.3, 148.3, 148.0, 142.4, 141.1, 140.7, 139.9, 139.0, 137.2, 128.7, 128.5, 127.2, 127.0, 126.70, 126.66, 126.6, 126.0, 60.2, 57.7, 53.3, 52.0, 51.4, 46.3, 40.2, 35.0, 34.7, 29.4, 28.8; **HRMS (ESI)** m/z calcd for $[M + Na]^+$ $C_{39}H_{42}O_3Na$ 581.3026, found 581.3035.



3ia

Methyl

3',5'-di-*tert*-butyl-4'-oxo-3-phenyl-1-(*m*-tolyl)spiro[bicyclo[2.1.1]hexane-2,1'-cyclohexane]-2',5'-diene-4-carboxylate (3ia). White solid; 84.4 mg, 85% yield, PE/EA = 20/1 as the eluent; mp = 109–110 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.23 (d, J = 7.6 Hz, 2H), 7.19–7.15 (m, 1H), 7.05–6.98 (m, 4H), 6.93 (d, J = 7.6 Hz, 1H), 6.67 (d, J = 7.6 Hz, 2H), 6.10 (d, J = 2.8 Hz, 1H), 4.12 (s, 1H), 3.70 (s, 3H), 2.97 (t, J = 9.6 Hz, 1H), 2.82 (t, J = 7.6 Hz, 1H), 2.50 (d, J = 8.0 Hz, 1H), 2.31 (d, J = 7.6 Hz, 1H), 2.21 (s, 3H), 1.19 (s, 9H), 0.78 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 185.2, 172.4, 148.2, 147.8, 142.5, 141.3, 139.1, 138.0, 136.6, 128.4, 127.7, 127.2, 127.0, 126.6, 123.3, 60.5, 57.6, 53.2, 52.0, 51.4, 46.3, 40.1, 34.9, 34.6, 29.4, 28.8, 21.3; **HRMS (ESI)** *m*/*z* calcd for [M + Na]$^+$ $C_{34}H_{40}O_3Na$ 519.2870, found 519.2877.

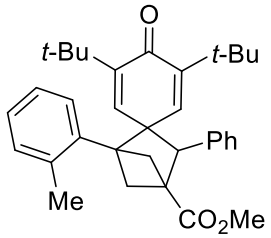


3ja

Methyl

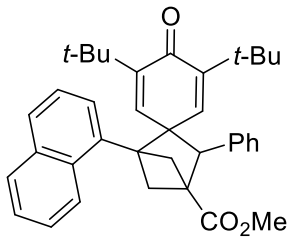
3',5'-di-*tert*-butyl-1-(3-methoxyphenyl)-4'-oxo-3-phenylspiro[bicyclo[2.1.1]hexane-2,1'-cyclohexane]-2',5'-diene-4-carboxylate (3ja). White solid; 92.3 mg, 90% yield, PE/EA = 20/1 as the eluent; mp = 96–97 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.23 (d, J = 7.6 Hz, 2H), 7.19–7.15 (m, 1H), 7.08–7.02 (m, 2H), 6.98 (d, J = 7.6 Hz, 2H), 6.67 (dd, J = 8.4, 2.4 Hz, 1H), 6.47 (d, J = 8.0 Hz, 1H), 6.41 (s, 1H), 6.11 (d, J = 2.8 Hz, 1H), 4.11 (s, 1H), 3.70 (d, J = 2.4 Hz, 6H), 2.98 (t, J = 9.2 Hz, 1H), 2.81 (t, J = 7.6 Hz, 1H), 2.51 (dd, J = 8.0, 1.2 Hz, 1H), 2.32 (d, J = 7.2 Hz, 1H), 1.20 (s, 9H), 0.78 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 185.3, 172.3, 158.7, 148.1, 147.9, 142.4, 141.2, 139.7, 139.0, 128.5, 128.3, 126.64, 126.58, 118.8, 112.7, 111.9, 60.2, 57.7, 55.1, 53.2, 52.0,

51.3, 46.3, 40.2, 34.9, 34.7, 29.4, 28.8; **HRMS (ESI)** *m/z* calcd for $[M + H]^+$ $C_{34}H_{41}O_4$ 513.2999, found 513.2999.



3ka

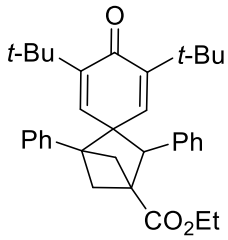
Methyl 3',5'-di-*tert*-butyl-4'-oxo-3-phenyl-1-(*o*-tolyl)spiro[bicyclo[2.1.1]hexane-2,1'-cyclohexane]-2',5'-diene-4-carboxylate (3ka). White solid; 94.4 mg, 95% yield, PE/EA = 20/1 as the eluent; mp = 217–218 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.27–7.23 (m, 2H), 7.20–7.16 (m, 1H), 7.09 (d, J = 2.8 Hz, 1H), 7.04–6.96 (m, 4H), 6.92 (d, J = 7.2 Hz, 1H), 6.75 (dd, J = 7.2, 0.8 Hz, 1H), 6.13 (d, J = 2.8 Hz, 1H), 4.13 (s, 1H), 3.70 (s, 3H), 3.07 (t, J = 9.6 Hz, 1H), 2.93 (dd, J = 9.6, 7.6 Hz, 1H), 2.60 (dd, J = 8.0, 1.6 Hz, 1H), 2.39 (d, J = 7.6 Hz, 1H), 2.22 (s, 3H), 1.20 (s, 9H), 0.77 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 185.1, 172.3, 147.8, 147.0, 142.3, 141.0, 139.1, 135.8, 135.6, 130.9, 128.5, 128.3, 127.3, 126.7, 126.6, 124.7, 61.3, 57.4, 54.4, 52.0, 51.5, 47.9, 41.5, 34.9, 34.6, 29.3, 28.7, 21.1; **HRMS (ESI)** *m/z* calcd for $[M + Na]^+$ $C_{34}H_{40}O_3Na$ 519.2870, found 519.2874.



3la

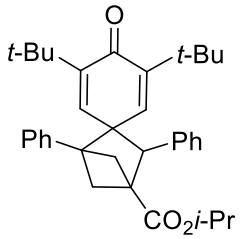
Methyl 3',5'-di-*tert*-butyl-1-(naphthalen-1-yl)-4'-oxo-3-phenylspiro[bicyclo[2.1.1]hexane-2,1'-cyclohexane]-2',5'-diene-4-carboxylate (3la). White solid; 100.2 mg, 94% yield, PE/EA = 20/1 as the eluent; mp = 220–221 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89–7.86 (m, 1H), 7.75–7.72 (m, 1H),

7.63 (d, *J* = 8.4 Hz, 1H), 7.39–7.34 (m, 2H), 7.29–7.24 (m, 3H), 7.21–7.18 (m, 1H), 7.15 (d, *J* = 2.8 Hz, 1H), 7.04 (d, *J* = 7.2 Hz, 2H), 6.99 (d, *J* = 6.8 Hz, 1H), 6.21 (d, *J* = 2.8 Hz, 1H), 4.25 (s, 1H), 3.73 (s, 3H), 3.40 (t, *J* = 9.2 Hz, 1H), 3.26 (t, *J* = 7.6 Hz, 1H), 2.84 (d, *J* = 7.6 Hz, 1H), 2.65 (d, *J* = 7.2 Hz, 1H), 1.02 (s, 9H), 0.61 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 184.6, 172.2, 142.7, 141.5, 139.1, 134.4, 133.6, 131.9, 129.0, 128.5, 128.2, 126.7, 126.7, 126.2, 125.4, 125.3, 125.1, 124.1, 61.3, 57.8, 54.0, 52.1, 51.5, 48.3, 42.1, 34.7, 34.5, 29.1, 28.4; **HRMS (ESI)** *m*/*z* calcd for $[M + Na]^+$ $C_{37}H_{40}O_3Na$ 555.2870, found 555.2876.



3ma

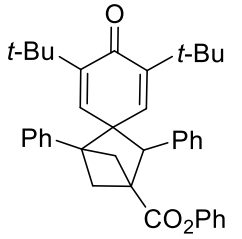
Ethyl 3',5'-di-*tert*-butyl-4'-oxo-1,3-diphenylspiro[bicyclo[2.1.1]hexane-2,1'-cyclohexane]-2',5'-diene-4-carboxylate (3ma). White solid; 73.5 mg, 74% yield, PE/EA = 20/1 as the eluent; mp = 122–123 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.26–7.22 (m, 2H), 7.18–7.12 (m, 4H), 7.04 (d, *J* = 2.8 Hz, 1H), 7.00 (d, *J* = 7.6 Hz, 2H), 6.89–6.86 (m, 2H), 6.13 (d, *J* = 2.8 Hz, 1H), 4.21–4.14 (m, 2H), 4.12 (s, 1H), 2.99 (t, *J* = 9.6 Hz, 1H), 2.83 (dd, *J* = 9.6, 7.2 Hz, 1H), 2.51 (dd, *J* = 8.0, 1.6 Hz, 1H), 2.32 (d, *J* = 7.6 Hz, 1H), 1.20 (m, 12H), 0.78 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 185.2, 171.8, 148.2, 147.8, 142.5, 141.2, 139.1, 138.1, 128.3, 127.2, 127.0, 126.7, 126.6, 126.2, 60.7, 60.4, 57.7, 53.2, 51.5, 46.2, 40.0, 34.9, 34.6, 29.4, 28.8, 14.1; **HRMS (ESI)** *m*/*z* calcd for $[M + Na]^+$ $C_{34}H_{40}O_3Na$ 519.2870, found 519.2877.



3na

Isopropyl

3',5'-di-*tert*-butyl-4'-oxo-1,3-diphenylspiro[bicyclo[2.1.1]hexane-2,1'-cyclohexane]-2',5'-diene -4-carboxylate (3na). White solid; 70.5 mg, 69% yield, PE/EA = 20/1 as the eluent; mp = 118–119 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.25–7.21 (m, 2H), 7.17–7.12 (m, 4H), 7.04 (d, J = 2.8 Hz, 1H), 7.00 (d, J = 7.2 Hz, 2H), 6.89–6.86 (m, 2H), 6.15 (d, J = 2.8 Hz, 1H), 5.10–5.01 (m, 1H), 4.10 (s, 1H), 2.98 (t, J = 9.6 Hz, 1H), 2.82 (dd, J = 9.6, 7.2 Hz, 1H), 2.50 (dd, J = 8.0, 1.6 Hz, 1H), 2.31 (d, J = 7.6 Hz, 1H), 1.23 (d, J = 6.4 Hz, 3H), 1.19 (s, 9H), 1.09 (d, J = 6.0 Hz, 3H), 0.78 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 185.2, 171.4, 148.1, 147.8, 142.6, 141.3, 139.1, 138.2, 128.3, 127.2, 127.0, 126.7, 126.6, 126.2, 68.1, 60.3, 57.7, 53.23 , 51.7, 46.1, 40.0, 34.9, 34.6, 29.4, 28.8, 21.7, 21.6; **HRMS (ESI)** m/z calcd for $[M + Na]^+$ $C_{35}H_{42}O_3Na$ 533.3026, found 533.3036.

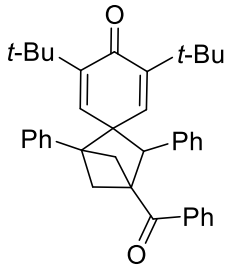


3oa

Phenyl

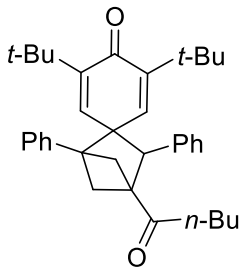
3',5'-di-*tert*-butyl-4'-oxo-1,3-diphenylspiro[bicyclo[2.1.1]hexane-2,1'-cyclohexane]-2',5'-diene -4-carboxylate (3oa). White solid; 91.5 mg, 84% yield, PE/EA = 20/1 as the eluent; mp = 152–153 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36–7.26 (m, 4H), 7.24–7.09 (m, 8H), 6.94–6.92 (m, 4H), 6.20 (d, J = 2.4 Hz, 1H), 4.29 (s, 1H), 3.12 (t, J = 9.6 Hz, 1H), 3.01 (t, J = 7.2 Hz, 1H), 2.65 (dd, J = 8.4, 1.6 Hz, 1H), 2.52 (d, J = 7.2 Hz, 1H), 1.21 (s, 9H), 0.81 (s, 9H); **^{13}C NMR** (100 MHz,

$CDCl_3$) δ 185.1, 170.4, 150.4, 148.4, 148.1, 142.3, 140.9, 138.9, 137.9, 129.4, 128.6, 127.3, 127.1, 126.9, 126.7, 126.2, 126.0, 121.4, 60.6, 57.9, 53.2, 51.6, 46.4, 40.2, 34.9, 34.7, 29.4, 28.8; **HRMS (ESI)** *m*/*z* calcd for $[M + Na]^+$ $C_{38}H_{40}O_3Na$ 567.2870, found 567.2878.



3pa

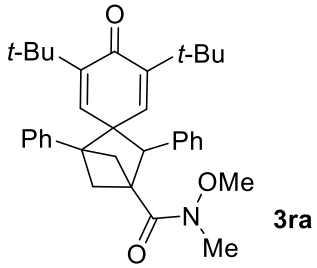
4-Benzoyl-3',5'-di-*tert*-butyl-1,3-diphenylspiro[bicyclo[2.1.1]hexane-2,1'-cyclohexane]-2',5'-dien-4'-one (3pa). White solid; 103.6 mg, 98% yield, PE/EA = 20/1 as the eluent; mp = 211–212 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89–7.87 (m, 2H), 7.54–7.50 (m, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.19–7.08 (m, 7H), 7.02 (d, *J* = 7.2 Hz, 2H), 6.94–6.92 (m, 2H), 6.23 (d, *J* = 3.2 Hz, 1H), 4.34 (s, 1H), 3.24–3.13 (m, 2H), 2.66 (dd, *J* = 8.0, 1.6 Hz, 1H), 2.54 (d, *J* = 7.2 Hz, 1H), 1.22 (s, 9H), 0.78 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 201.0, 185.1, 148.4, 148.0, 142.3, 141.1, 138.8, 138.1, 136.9, 132.8, 128.7, 128.4, 128.1, 127.3, 127.0, 126.9, 126.7, 126.3, 59.9, 59.7, 59.0, 54.2, 48.1, 41.1, 35.0, 34.7, 29.5, 28.8; **HRMS (ESI)** *m*/*z* calcd for $[M + Na]^+$ $C_{38}H_{40}O_2Na$ 551.2921, found 551.2927.



3qa

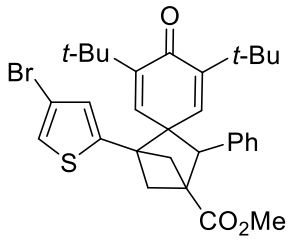
3',5'-Di-*tert*-butyl-4-pentanoyl-1,3-diphenylspiro[bicyclo[2.1.1]hexane-2,1'-cyclohexane]-2',5'-dien-4'-one (3qa). White solid; 97.7 mg, 96% yield, PE/EA = 20/1 as the eluent; mp = 124–125 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.25–7.21 (m, 2H), 7.18–7.11 (m, 4H), 7.04 (d, *J* = 3.2 Hz,

1H), 6.94 (d, J = 7.2 Hz, 2H), 6.89–6.87 (m, 2H), 6.14 (d, J = 2.8 Hz, 1H), 4.15 (s, 1H), 2.93–2.81 (m, 2H), 2.63–2.55 (m, 1H), 2.50 (dd, J = 8.0, 2.0 Hz, 1H), 2.42–2.34 (m, 1H), 2.21 (d, J = 7.2 Hz, 1H), 1.61–1.45 (m, 2H), 1.28–1.20 (m, 11H), 0.84 (t, J = 7.2 Hz, 3H), 0.78 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 209.6, 185.1, 148.2, 148.0, 142.3, 141.0, 138.8, 138.2, 128.5, 127.3, 127.0, 126.8, 126.2, 59.8, 59.1, 57.8, 53.7, 46.8, 39.0, 38.2, 34.9, 34.7, 29.4, 28.8, 25.1, 22.2, 13.8; **HRMS (ESI)** m/z calcd for $[M + Na]^+$ $C_{36}H_{44}O_2Na$ 531.3234, found 531.3242.



3ra

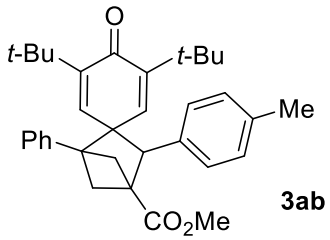
3',5'-Di-*tert*-butyl-*N*-methoxy-*N*-methyl-4'-oxo-1,3-diphenylspiro[bicyclo[2.1.1]hexane-2,1'-cyclohexane]-2',5'-diene-4-carboxamide (3ra). White solid; 74.7 mg, 73% yield, PE/EA = 4/1 as the eluent; mp = 214–215 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.25–7.22 (m, 2H), 7.17–7.11 (m, 6H), 7.02 (d, J = 2.8 Hz, 1H), 6.91–6.89 (m, 2H), 6.21 (d, J = 2.8 Hz, 1H), 4.23 (s, 1H), 3.68 (s, 3H), 3.18 (s, 3H), 3.11 (t, J = 9.2 Hz, 1H), 2.87 (dd, J = 9.6, 7.6 Hz, 1H), 2.49 (dd, J = 8.0, 1.2 Hz, 1H), 2.33 (d, J = 7.2 Hz, 1H), 1.19 (s, 9H), 0.77 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 209.6, 185.1, 148.2, 148.0, 142.3, 141.0, 138.8, 138.2, 128.5, 127.3, 127.0, 126.8, 126.2, 59.8, 59.1, 57.8, 53.7, 46.8, 39.0, 38.2, 34.9, 34.7, 29.4, 28.8, 25.1, 22.2, 13.8; **HRMS (ESI)** m/z calcd for $[M + Na]^+$ $C_{34}H_{41}NO_3Na$ 534.2979, found 534.2980.



3sa

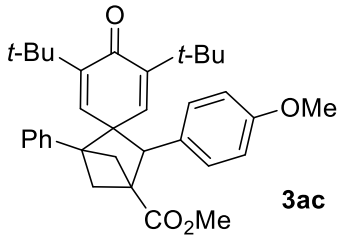
Methyl

1-(4-bromothiophen-2-yl)-3',5'-di-*tert*-butyl-4'-oxo-3-phenylspiro[bicyclo[2.1.1]hexane-2,1'-cyclohexane]-2',5'-diene-4-carboxylate (3sa). White solid; 110.1 mg, 97% yield, PE/EA = 20/1 as the eluent; mp = 133–134 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.26–7.22 (m, 2H), 7.19–7.15 (m, 1H), 6.96–6.93 (m, 4H), 6.56 (d, J = 1.2 Hz, 1H), 6.04 (d, J = 2.8 Hz, 1H), 4.06 (s, 1H), 3.69 (s, 3H), 2.92 (dd, J = 9.6, 8.4 Hz, 1H), 2.74 (dd, J = 10.0, 7.6 Hz, 1H), 2.60 (dd, J = 8.4, 2.0 Hz, 1H), 2.40 (d, J = 7.6 Hz, 1H), 1.26 (s, 9H), 0.82 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 185.5, 171.6, 149.0, 148.9, 142.8, 141.5, 140.3, 138.3, 128.6, 127.6, 126.9, 126.5, 121.4, 108.7, 57.9, 55.4, 52.8, 52.1, 51.5, 47.9, 42.2, 35.1, 34.8, 29.4, 28.7; **HRMS (ESI)** *m*/*z* calcd for $[M + Na]^+$ $C_{31}H_{35}BrSO_3Na$ 589.1382, found 589.1385.



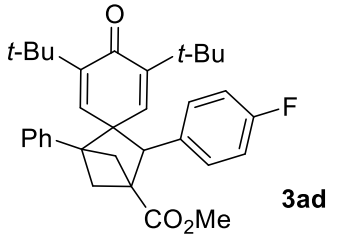
3ab

Methyl 3',5'-di-*tert*-butyl-4'-oxo-1-phenyl-3-(*p*-tolyl)spiro[bicyclo[2.1.1]hexane-2,1'-cyclohexane]-2',5'-diene-4-carboxylate (3ab). White solid; 69.5 mg, 70% yield, PE/EA = 20/1 as the eluent; mp = 162–163 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.16–7.12 (m, 3H), 7.05–7.01 (m, 3H), 6.87 (d, J = 7.6 Hz, 4H), 6.13 (d, J = 2.8 Hz, 1H), 4.09 (s, 1H), 3.69 (s, 3H), 2.98 (t, J = 9.6 Hz, 1H), 2.82 (dd, J = 9.6, 7.2 Hz, 1H), 2.50 (dd, J = 8.0, 1.6 Hz, 1H), 2.31 (d, J = 7.2 Hz, 1H), 2.28 (s, 3H), 1.18 (s, 9H), 0.78 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 185.3, 172.4, 148.1, 147.8, 142.5, 141.3, 138.1, 136.2, 136.0, 129.1, 127.2, 127.0, 126.5, 126.2, 60.4, 57.4, 53.2, 52.0, 51.4, 46.2, 40.1, 34.9, 34.7, 29.4, 28.8, 21.0; **HRMS (ESI)** *m*/*z* calcd for $[M + Na]^+$ $C_{34}H_{40}O_3Na$ 519.2870, found 519.2880.



3ac

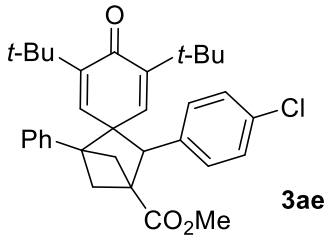
Methyl 3',5'-di-*tert*-butyl-3-(4-methoxyphenyl)-4'-oxo-1-phenylspiro[bicyclo[2.1.1]hexane-2,1'-cyclohexane]-2',5'-diene-4-carboxylate (3ac). White solid; 80.0 mg, 78% yield, PE/EA = 15/1 as the eluent; mp = 119–120 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.17–7.13 (m, 3H), 7.02 (d, J = 2.8 Hz, 1H), 6.92 (d, J = 8.8 Hz, 2H), 6.89–6.86 (m, 2H), 6.79 (d, J = 8.8 Hz, 2H), 6.16 (d, J = 2.8 Hz, 1H), 4.08 (s, 1H), 3.76 (s, 3H), 3.70 (s, 3H), 2.98 (t, J = 9.6 Hz, 1H), 2.82 (dd, J = 10.0, 7.6 Hz, 1H), 2.50 (dd, J = 8.4, 2.0 Hz, 1H), 2.31 (d, J = 7.2 Hz, 1H), 1.18 (s, 9H), 0.80 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 185.2, 172.4, 158.2, 148.1, 147.8, 142.5, 141.3, 138.1, 131.1, 127.6, 127.2, 127.0, 126.2, 113.9, 60.3, 57.1, 55.3, 53.2, 52.0, 51.5, 46.2, 40.1, 34.9, 34.7, 29.4, 28.9; **HRMS (ESI)** *m*/*z* calcd for $[M + Na]^+$ $C_{34}H_{40}O_4Na$ 535.2819, found 535.2827.



3ad

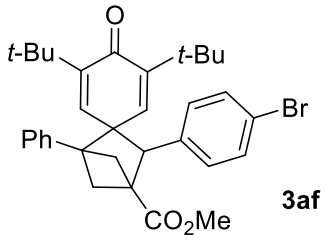
Methyl 3',5'-di-*tert*-butyl-3-(4-fluorophenyl)-4'-oxo-1-phenylspiro[bicyclo[2.1.1]hexane-2,1'-cyclohexane]-2',5'-diene-4-carboxylate (3ad). White solid; 92.1 mg, 92% yield, PE/EA = 20/1 as the eluent; mp = 158–159 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.17–7.13 (m, 3H), 7.01 (d, J = 2.8 Hz, 1H), 6.97–6.93 (m, 4H), 6.88–6.86 (m, 2H), 6.11 (d, J = 2.8 Hz, 1H), 4.09 (s, 1H), 3.71 (s, 3H), 2.95 (t, J = 9.6 Hz, 1H), 2.82 (dd, J = 9.2, 7.6 Hz, 1H), 2.52 (dd, J = 8.0, 1.6 Hz, 1H), 2.33 (d, J =

7.2 Hz, 1H), 1.18 (s, 9H), 0.81 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 185.1, 172.1, 161.5 (d, J = 244.0 Hz), 148.4, 148.2, 142.2, 140.8, 137.9, 134.9 (d, J = 3.4 Hz), 128.2 (d, J = 7.8 Hz), 127.3, 127.1, 126.2, 115.3 (d, J = 21.2 Hz), 60.5, 57.0, 53.1, 52.1, 51.5, 46.2, 40.0, 34.9, 34.7, 29.4, 28.9; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -115.69 – -115.75 (m, 1F); **HRMS (ESI)** *m*/*z* calcd for $[M + Na]^+$ $C_{33}H_{37}FO_3Na$ 523.2619, found 523.2622.



3ae

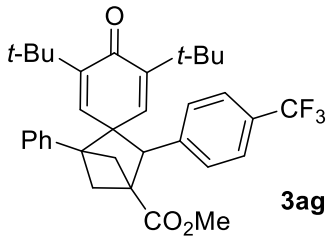
Methyl 3',5'-di-*tert*-butyl-3-(4-chlorophenyl)-4'-oxo-1-phenylspiro[bicyclo[2.1.1]hexane-2,1'-cyclohexane]-2',5'-diene-4-carboxylate (3ae). White solid; 93.1 mg, 90% yield, PE/EA = 20/1 as the eluent; mp = 171–172 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.25–7.21 (m, 2H), 7.17–7.11 (m, 3H), 7.00 (d, J = 3.2 Hz, 1H), 6.93 (d, J = 8.4 Hz, 2H), 6.89–6.85 (m, 2H), 6.11 (d, J = 2.8 Hz, 1H), 4.07 (s, 1H), 3.70 (s, 3H), 2.94 (dd, J = 9.6, 8.4 Hz, 1H), 2.82 (dd, J = 9.6, 7.2 Hz, 1H), 2.52 (dd, J = 8.0, 2.0 Hz, 1H), 2.34 (d, J = 7.2 Hz, 1H), 1.18 (s, 9H), 0.81 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 185.0, 172.0, 148.5, 148.3, 142.0, 140.5, 132.4, 128.6, 128.0, 127.3, 127.1, 126.2, 60.5, 57.1, 53.2, 52.1, 51.4, 46.2, 40.0, 34.9, 34.7, 29.4, 28.9; **HRMS (ESI)** *m*/*z* calcd for $[M + Na]^+$ $C_{33}H_{37}ClO_3Na$ 539.2323, found 539.2333.



3af

Methyl

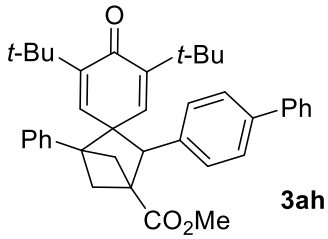
3-(4-bromophenyl)-3',5'-di-*tert*-butyl-4'-oxo-1-phenylspiro[bicyclo[2.1.1]hexane-2,1'-cyclohexane]-2',5'-diene-4-carboxylate (3af). White solid; 85.4 mg, 76% yield, PE/EA = 20/1 as the eluent; mp = 151–152 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 (d, J = 8.4 Hz, 2H), 7.16–7.12 (m, 3H), 7.00 (d, J = 2.8 Hz, 1H), 6.88–6.86 (m, 4H), 6.10 (d, J = 3.2 Hz, 1H), 4.05 (s, 1H), 3.70 (s, 3H), 2.93 (t, J = 9.6 Hz, 1H), 2.82 (dd, J = 9.6, 7.2 Hz, 1H), 2.52 (dd, J = 8.4, 2.0 Hz, 1H), 2.34 (d, J = 7.6 Hz, 1H), 1.18 (s, 9H), 0.81 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 185.0, 172.0, 148.5, 148.4, 142.0, 140.5, 138.2, 137.8, 131.5, 128.4, 127.3, 127.1, 126.2, 120.5, 60.5, 57.2, 53.1, 52.1, 51.3, 46.2, 40.0, 34.9, 34.7, 29.4, 28.9; **HRMS (ESI)** *m*/*z* calcd for $[M + Na]^+$ $C_{33}H_{37}BrO_3Na$ 583.1818, found 583.1819.



3ag

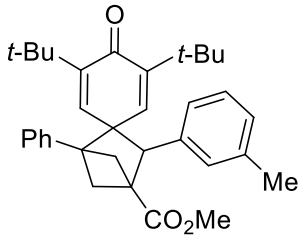
Methyl 3',5'-di-*tert*-butyl-4'-oxo-1-phenyl-3-(4-(trifluoromethyl)phenyl)spiro[bicyclo[2.1.1]hexane-2,1'-cyclohexane]-2',5'-diene-4-carboxylate (3ag). White solid; 60.6 mg, 55% yield, PE/EA = 20/1 as the eluent; mp = 125–126 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53 (d, J = 8.4 Hz, 2H), 7.18–7.11 (m, 5H), 7.03 (d, J = 2.8 Hz, 1H), 6.89–6.87 (m, 2H), 6.05 (d, J = 2.8 Hz, 1H), 4.15 (s, 1H), 3.71 (s, 3H), 2.95 (t, J = 9.6 Hz, 1H), 2.85 (dd, J = 9.6, 7.6 Hz, 1H), 2.55 (dd, J = 8.0, 1.6 Hz, 1H), 2.37 (d, J = 7.6 Hz, 1H), 1.19 (s, 9H), 0.77 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 185.0, 171.9, 148.7, 148.6, 143.42, 143.41, 141.9, 140.2, 137.7, 129.0 (q, J = 32.5 Hz), 127.4, 127.2, 127.0, 126.2, 125.4 (q, J = 3.6 Hz), 124.1 (q, J = 270.2 Hz), 60.5, 57.5, 53.3, 52.1, 51.3, 46.2, 40.1, 35.0, 34.7, 29.4, 28.8; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.67 (s, 3F); **HRMS (ESI)** *m*/*z* calcd for [M +

Na]$^+$ $C_{34}H_{37}F_3O_3Na$ 573.2587, found 573.2593.



3ah

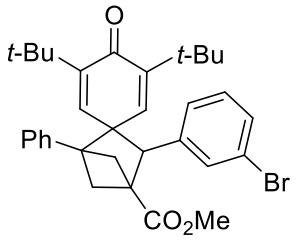
Methyl 3-([1,1'-biphenyl]-4-yl)-3',5'-di-*tert*-butyl-4'-oxo-1-phenylspiro[bicyclo[2.1.1]hexane-2,1'-cyclohexane]-2',5'-diene-4-carboxylate (3ah). White solid; 102.8 mg, 92% yield, PE/EA = 20/1 as the eluent; mp = 212–213 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54–7.52 (m, 2H), 7.48 (d, J = 8.4 Hz, 2H), 7.44–7.41 (m, 2H), 7.36–7.31 (m, 1H), 7.17–7.11 (m, 3H), 7.08–7.05 (m, 3H), 6.91–6.88 (m, 2H), 6.17 (d, J = 2.8 Hz, 1H), 4.16 (s, 1H), 3.73 (s, 3H), 3.03 (t, J = 9.6 Hz, 1H), 2.86 (dd, J = 9.6, 7.6 Hz, 1H), 2.54 (dd, J = 8.0, 1.6 Hz, 1H), 2.36 (d, J = 7.2 Hz, 1H), 1.20 (s, 9H), 0.78 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 185.2, 172.3, 148.3, 148.0, 142.3, 141.1, 140.8, 139.6, 138.2, 138.0, 128.8, 127.3, 127.2, 127.1, 127.03, 127.00, 126.9, 126.2, 60.3, 57.5, 53.3, 52.1, 51.4, 46.3, 40.1, 34.9, 34.7, 29.4, 28.8; **HRMS (ESI)** *m*/*z* calcd for [M + Na]$^+$ $C_{39}H_{42}O_3Na$ 581.3026, found 581.3033.



3ai

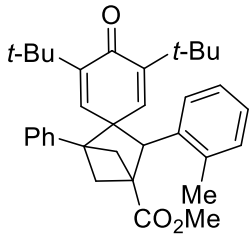
Methyl 3',5'-di-*tert*-butyl-4'-oxo-1-phenyl-3-(*m*-tolyl)spiro[bicyclo[2.1.1]hexane-2,1'-cyclohexane]-2',5'-diene-4-carboxylate (3ai). White solid; 71.5 mg, 72% yield, PE/EA = 20/1 as the eluent; mp = 154–155 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.15–7.10 (m, 4H), 7.03 (d, J = 2.8 Hz, 1H), 6.98 (d,

J = 7.6 Hz, 1H), 6.89–6.87 (m, 2H), 6.82 (d, *J* = 7.6 Hz, 1H), 6.73 (s, 1H), 6.12 (d, *J* = 2.8 Hz, 1H), 4.09 (s, 1H), 3.70 (s, 3H), 2.98 (t, *J* = 9.6 Hz, 1H), 2.82 (dd, *J* = 9.6, 7.6 Hz, 1H), 2.51 (dd, *J* = 8.0, 2.0 Hz, 1H), 2.32 (d, *J* = 7.6 Hz, 1H), 2.25 (s, 3H), 1.19 (s, 9H), 0.78 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 185.2, 172.4, 148.1, 147.8, 142.4, 141.3, 139.0, 138.2, 138.0, 128.3, 127.7, 127.3, 127.3, 127.0, 126.2, 123.1, 60.3, 57.7, 53.2, 52.0, 51.3, 46.2, 40.1, 34.9, 34.6, 29.4, 28.8, 21.4; **HRMS (ESI)** *m*/*z* calcd for $[M + Na]^+$ $C_{34}H_{40}O_3Na$ 519.2870, found 519.2876.



3aj

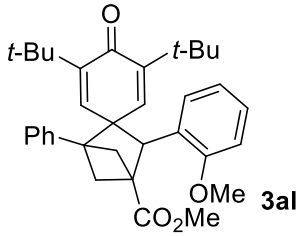
Methyl 3-(3-bromophenyl)-3',5'-di-*tert*-butyl-4'-oxo-1-phenylspiro[bicyclo[2.1.1]hexane-2,1'-cyclohexane]-2',5'-diene-4-carboxylate (3aj). White solid; 77.5 mg, 69% yield, PE/EA = 20/1 as the eluent; mp = 170–171 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8.0 Hz, 1H), 7.17–7.11 (m, 5H), 7.00 (d, *J* = 3.2 Hz, 1H), 6.94 (d, *J* = 7.6 Hz, 1H), 6.89–6.85 (m, 2H), 6.09 (d, *J* = 3.2 Hz, 1H), 4.07 (s, 1H), 3.72 (s, 3H), 2.93 (dd, *J* = 9.6, 8.4 Hz, 1H), 2.82 (dd, *J* = 9.6, 7.2 Hz, 1H), 2.52 (dd, *J* = 8.4, 2.0 Hz, 1H), 2.34 (d, *J* = 7.2 Hz, 1H), 1.19 (s, 9H), 0.82 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 184.9, 172.0, 148.6, 148.4, 141.9, 141.6, 140.4, 137.8, 129.99, 129.97, 129.8, 127.3, 127.1, 126.2, 125.0, 122.6, 60.5, 57.2, 53.2, 52.1, 51.2, 46.2, 40.0, 35.0, 34.7, 29.4, 28.9; **HRMS (ESI)** *m*/*z* calcd for $[M + Na]^+$ $C_{33}H_{37}BrO_3Na$ 583.1818, found 583.1820.



3ak

Methyl

3',5'-di-*tert*-butyl-4'-oxo-1-phenyl-3-(*o*-tolyl)spiro[bicyclo[2.1.1]hexane-2,1'-cyclohexane]-2',5'-diene-4-carboxylate (3ak). White solid; 84.4 mg, 85% yield, PE/EA = 20/1 as the eluent; mp = 177–178 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.28 (d, J = 7.2 Hz, 1H), 7.17–7.10 (m, 5H), 7.08–7.04 (m, 2H), 6.84–6.81 (m, 2H), 6.21 (d, J = 2.8 Hz, 1H), 4.25 (s, 1H), 3.69 (s, 3H), 3.04 (dd, J = 10.0, 8.4 Hz, 1H), 2.85 (dd, J = 9.6, 7.2 Hz, 1H), 2.53 (dd, J = 8.0, 1.6 Hz, 1H), 2.31 (d, J = 7.2 Hz, 1H), 1.97 (s, 3H), 1.13 (s, 9H), 0.79 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 184.5, 172.4, 148.2, 143.5, 140.3, 137.8, 137.7, 137.5, 130.7, 127.1, 127.0, 126.59, 126.55, 125.6, 124.7, 61.0, 55.3, 52.6, 52.1, 52.0, 46.2, 40.2, 34.8, 34.7, 29.1, 28.8, 20.3; **HRMS (ESI)** *m*/*z* calcd for $[M + Na]^+$ $C_{34}H_{40}O_3Na$ 519.2870, found 519.2872.

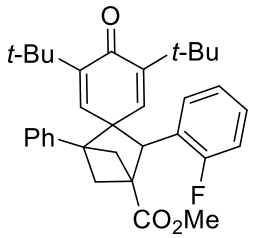


3al

Methyl

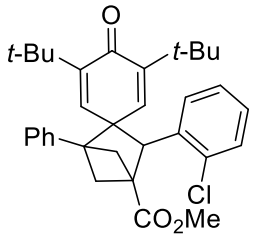
3',5'-di-*tert*-butyl-3-(2-methoxyphenyl)-4'-oxo-1-phenylspiro[bicyclo[2.1.1]hexane-2,1'-cyclohexane]-2',5'-diene-4-carboxylate (3al). White solid; 86.1 mg, 84% yield, PE/EA = 15/1 as the eluent; mp = 117–118 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.21–7.15 (m, 2H), 7.14–7.10 (m, 3H), 7.06 (d, J = 2.8 Hz, 1H), 6.91–6.84 (m, 3H), 6.70 (d, J = 8.0 Hz, 1H), 6.15 (d, J = 3.2 Hz, 1H), 4.30 (s, 1H), 3.70 (s, 3H), 3.47 (s, 3H), 2.95 (dd, J = 9.6, 8.0 Hz, 1H), 2.86 (dd, J = 10.0, 7.2 Hz, 1H), 2.48 (dd, J = 8.0, 2.0 Hz, 1H), 2.31 (d, J = 7.2 Hz, 1H), 1.18 (s, 9H), 0.80 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 185.6, 172.6, 157.8, 147.6, 146.7, 144.1, 140.6, 138.1, 128.1, 127.6, 127.1, 126.9, 126.4, 125.2, 119.8, 109.6, 60.6, 54.3, 52.8, 52.5, 52.0, 51.0, 46.2, 39.9, 34.7, 34.6, 29.5,

29.0; **HRMS (ESI)** *m*/*z* calcd for $[M + Na]^+$ $C_{34}H_{40}O_4Na$ 535.2819, found 535.2826.



3am

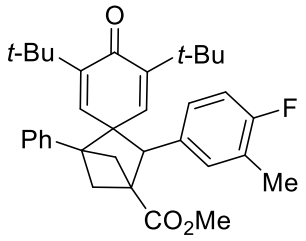
Methyl 3',5'-di-*tert*-butyl-3-(2-fluorophenyl)-4'-oxo-1-phenylspiro[bicyclo[2.1.1]hexane-2,1'-cyclohexane]-2',5'-diene-4-carboxylate (3am). White solid; 85.1 mg, 85% yield, PE/EA = 20/1 as the eluent; mp = 145–146 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.26–7.13 (m, 5H), 7.10–7.06 (m, 1H), 7.01 (d, J = 2.8 Hz, 1H), 6.94–6.87 (m, 3H), 6.16 (d, J = 2.8 Hz, 1H), 4.27 (s, 1H), 3.71 (s, 3H), 2.96 (t, J = 9.6 Hz, 1H), 2.87 (dd, J = 9.6, 7.2 Hz, 1H), 2.53 (dd, J = 8.0, 2.0 Hz, 1H), 2.35 (d, J = 7.2 Hz, 1H), 1.17 (s, 9H), 0.80 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 185.1, 172.1, 161.5 (d, J = 246.1 Hz), 148.4, 147.9, 141.8, 139.2, 137.9, 128.3 (d, J = 8.1 Hz), 127.2, 127.0, 126.9 (d, J = 15.6 Hz), 126.2, 126.0 (d, J = 4.5 Hz), 123.7 (d, J = 3.6 Hz), 115.4 (d, J = 21.3 Hz), 60.3, 52.6, 52.2, 52.1, 51.0, 46.2, 40.0, 34.8, 34.7, 29.3, 28.9; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -111.90 – -111.96 (m, 1F); **HRMS (ESI)** *m*/*z* calcd for $[M + Na]^+$ $C_{33}H_{37}FO_3Na$ 523.2619, found 523.2626.



3an

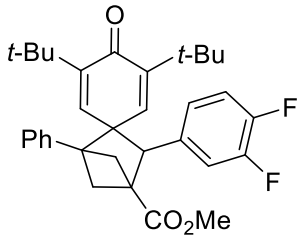
Methyl 3',5'-di-*tert*-butyl-3-(2-chlorophenyl)-4'-oxo-1-phenylspiro[bicyclo[2.1.1]hexane-2,1'-cyclohexane]-2',5'-diene-4-carboxylate (3an). White solid; 77.6 mg, 75% yield, PE/EA = 20/1 as the eluent; mp = 121–122 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36 (d, J = 7.6 Hz, 1H), 7.28 (dd, J =

8.0, 1.2 Hz, 1H), 7.25–7.21 (m, 1H), 7.17–7.11 (m, 4H), 7.06 (d, *J* = 3.2 Hz, 1H), 6.85–6.83 (m, 2H), 6.13 (d, *J* = 2.8 Hz, 1H), 4.40 (s, 1H), 3.69 (s, 3H), 2.99 (t, *J* = 9.6 Hz, 1H), 2.88 (dd, *J* = 9.6, 7.2 Hz, 1H), 2.53 (dd, *J* = 8.0, 1.6 Hz, 1H), 2.33 (d, *J* = 7.2 Hz, 1H), 1.14 (s, 9H), 0.81 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 184.8, 172.1, 148.7, 147.5, 143.1, 138.7, 137.5, 135.9, 130.0, 127.8, 127.1, 127.1, 126.5, 126.4, 60.6, 55.3, 52.6, 52.1, 51.9, 46.1, 40.1, 34.8, 34.7, 29.2, 28.9; **HRMS (ESI)** *m*/*z* calcd for $[M + Na]^+$ $C_{33}H_{37}ClO_3Na$ 539.2323, found 539.2322.



3ao

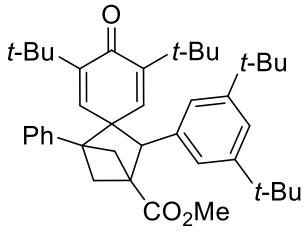
Methyl 3',5'-di-*tert*-butyl-3-(4-fluoro-3-methylphenyl)-4'-oxo-1-phenylspiro[bicyclo[2.1.1]hexane-2,1'-cyclohexane]-2',5'-diene-4-carboxylate (3ao). White solid; 77.2 mg, 75% yield, PE/EA = 20/1 as the eluent; mp = 139–140 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.17–7.10 (m, 3H), 7.01 (d, *J* = 2.8 Hz, 1H), 6.91–6.86 (m, 3H), 6.83–6.79 (m, 1H), 6.74 (dd, *J* = 7.2, 2.0 Hz, 1H), 6.13 (d, *J* = 3.2 Hz, 1H), 4.04 (s, 1H), 3.70 (s, 3H), 2.95 (dd, *J* = 10.0, 8.4 Hz, 1H), 2.81 (dd, *J* = 9.6, 7.6 Hz, 1H), 2.51 (dd, *J* = 8.0, 1.6 Hz, 1H), 2.32 (d, *J* = 7.6 Hz, 1H), 2.18 (d, *J* = 1.6 Hz, 3H), 1.19 (s, 9H), 0.81 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 185.2, 172.2, 160.0 (d, *J* = 242.8 Hz), 148.3, 148.1, 142.2, 140.9, 138.0, 134.5 (d, *J* = 3.7 Hz), 130.1 (d, *J* = 5.0 Hz), 127.3, 127.1, 126.2, 124.870 (d, *J* = 17.1 Hz), 124.866, 114.79 (d, *J* = 22.2 Hz), 60.3, 57.1, 53.2, 52.0, 51.4, 46.2, 40.1, 34.9, 34.7, 29.4, 28.9, 14.6 (d, *J* = 3.4 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -120.21 – -120.27 (m, 1F); **HRMS (ESI)** *m*/*z* calcd for $[M + Na]^+$ $C_{34}H_{39}FO_3Na$ 537.2775, found 537.2773.



3ap

Methyl

3',5'-di-*tert*-butyl-3-(3,4-difluorophenyl)-4'-oxo-1-phenylspiro[bicyclo[2.1.1]hexane-2,1'-cyclohexane]-2',5'-diene-4-carboxylate (3ap). White solid; 60.2 mg, 58% yield, PE/EA = 20/1 as the eluent; mp = 134–135 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.17–7.12 (m, 3H), 7.09–7.03 (m, 1H), 6.98 (d, J = 2.8 Hz, 1H), 6.88–6.81 (m, 3H), 6.74–6.71 (m, 1H), 6.11 (d, J = 2.8 Hz, 1H), 4.05 (s, 1H), 3.72 (s, 3H), 2.92 (t, J = 9.6 Hz, 1H), 2.81 (dd, J = 9.6, 7.2 Hz, 1H), 2.52 (dd, J = 8.0, 1.6 Hz, 1H), 2.34 (d, J = 7.2 Hz, 1H), 1.18 (s, 9H), 0.83 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 184.9, 171.8, 150.8 (dd, J = 122.9, 12.7 Hz), 148.7, 148.6, 148.4 (dd, J = 122.2, 12.7 Hz), 141.8, 140.1, 137.6, 136.3 (dd, J = 5.2, 4.2 Hz), 127.3, 127.2, 126.2, 122.8 (dd, J = 6.1, 3.6 Hz), 117.3 (d, J = 17.0 Hz), 115.7 (d, J = 17.5 Hz), 60.5, 56.8, 53.1, 52.1, 51.4, 46.1, 39.9, 35.0, 34.8, 29.4, 28.9; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -137.10 – -137.22 (m, 1F), -140.04 – -140.16 (m, 1F); **HRMS (ESI)** *m*/*z* calcd for $[M + Na]^+$ $C_{33}H_{36}F_2O_3Na$ 541.2525, found 541.2528.

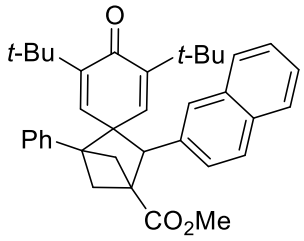


3aq

Methyl

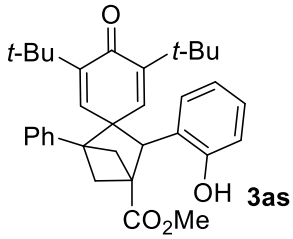
3',5'-di-*tert*-butyl-3-(3,5-di-*tert*-butylphenyl)-4'-oxo-1-phenylspiro[bicyclo[2.1.1]hexane-2,1'-cyclohexane]-2',5'-diene-4-carboxylate (3aq). White solid; 109.5 mg, 92% yield, PE/EA = 20/1 as the eluent; mp = 156–157 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.20 (s, 1H), 7.17–7.10 (m, 3H),

7.03 (d, J = 3.2 Hz, 1H), 6.91–6.89 (m, 2H), 6.86 (s, 2H), 6.18 (d, J = 2.8 Hz, 1H), 4.10 (s, 1H), 3.70 (s, 3H), 3.04 (t, J = 9.6 Hz, 1H), 2.82 (dd, J = 9.6, 7.6 Hz, 1H), 2.51 (dd, J = 8.0, 1.6 Hz, 1H), 2.31 (d, J = 7.2 Hz, 1H), 1.24 (s, 18H), 1.19 (s, 9H), 0.75 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 185.3, 172.5, 150.8, 148.3, 147.8, 142.2, 141.2, 138.2, 137.7, 127.3, 126.9, 126.3, 120.5, 120.4, 60.1, 59.1, 53.2, 52.0, 51.5, 46.5, 40.4, 34.9, 34.7, 34.5, 31.4, 29.4, 28.9; **HRMS (ESI)** m/z calcd for $[M + Na]^+$ $C_{41}H_{54}O_3Na$ 617.3965, found 617.3973.



3ar

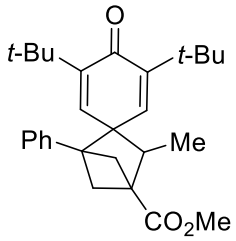
Methyl 3',5'-di-*tert*-butyl-3-(naphthalen-2-yl)-4'-oxo-1-phenylspiro[bicyclo[2.1.1]hexane-2,1'-cyclohexane]-2',5'-diene-4-carboxylate (3ar). White solid; 75.6 mg, 71% yield, PE/EA = 20/1 as the eluent; mp = 217–218 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.77–7.75 (m, 2H), 7.69 (d, J = 8.4 Hz, 1H), 7.53 (s, 1H), 7.48–7.41 (m, 2H), 7.17–7.10 (m, 4H), 6.97 (dd, J = 8.4, 1.2 Hz, 1H), 6.90–6.88 (m, 2H), 6.14 (d, J = 2.8 Hz, 1H), 4.29 (s, 1H), 3.71 (s, 3H), 3.09 (t, J = 9.2 Hz, 1H), 2.90 (dd, J = 9.2, 7.6 Hz, 1H), 2.59 (dd, J = 8.0, 1.2 Hz, 1H), 2.38 (d, J = 7.2 Hz, 1H), 1.22 (s, 9H), 0.65 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 185.1, 172.4, 148.3, 148.1, 142.5, 141.0, 138.0, 136.8, 133.2, 132.2, 128.1, 127.8, 127.5, 127.3, 127.1, 126.3, 126.1, 125.7, 123.9, 60.7, 57.8, 53.2, 52.1, 51.5, 46.3, 40.1, 35.0, 34.6, 29.4, 28.7; **HRMS (ESI)** m/z calcd for $[M + Na]^+$ $C_{37}H_{40}O_3Na$ 555.2870, found 555.2870.



3as

Methyl

3',5'-di-*tert*-butyl-3-(2-hydroxyphenyl)-4'-oxo-1-phenylspiro[bicyclo[2.1.1]hexane-2,1'-cyclohexane]-2',5'-diene-4-carboxylate (3as). White solid; 81.8 mg, 82% yield, PE/EA = 6/1 as the eluent; mp = 231–232 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.18–7.05 (m, 6H), 6.90–6.85 (m, 3H), 6.65 (d, J = 8.0 Hz, 1H), 6.27 (d, J = 2.4 Hz, 1H), 4.59 (s, 1H), 4.25 (s, 1H), 3.70 (s, 3H), 3.02 (t, J = 9.2 Hz, 1H), 2.87 (t, J = 7.6 Hz, 1H), 2.52 (d, J = 7.2 Hz, 1H), 2.34 (d, J = 7.6 Hz, 1H), 1.16 (s, 9H), 0.81 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 185.4, 172.4, 154.7, 148.3, 148.1, 142.5, 139.9, 138.0, 127.8, 127.2, 127.0, 126.2, 126.0, 125.4, 120.4, 115.5, 60.3, 53.0, 52.3, 52.1, 51.2, 46.2, 40.0, 34.9, 34.7, 29.3, 28.9; **HRMS (ESI)** *m*/*z* calcd for $[M + Na]^+$ $C_{33}H_{38}O_4Na$ 521.2662, found 521.2671.

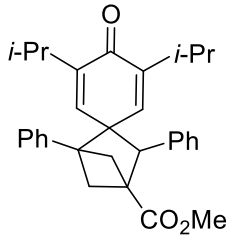


3at

Methyl

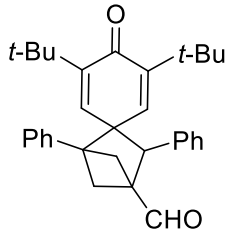
3',5'-di-*tert*-butyl-3-methyl-4'-oxo-1-phenylspiro[bicyclo[2.1.1]hexane-2,1'-cyclohexane]-2',5'-diene-4-carboxylate (3at). White solid; 76.5 mg, 91% yield, PE/EA = 20/1 as the eluent; mp = 135–136 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.17–7.10 (m, 3H), 6.88–6.86 (m, 2H), 6.78 (dd, J = 14.8, 2.4 Hz, 2H), 3.75 (s, 3H), 2.84 (q, J = 6.8 Hz, 1H), 2.71–2.63 (m, 2H), 2.19 (t, J = 5.6 Hz, 2H), 1.13 (d, J = 8.0 Hz, 18H), 1.08 (d, J = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 185.3,

172.3, 149.3, 147.8, 143.0, 139.6, 138.2, 127.2, 126.9, 126.4, 60.9, 52.6, 51.7, 51.1, 48.7, 44.8, 39.1, 35.2, 34.8, 29.3, 14.3; **HRMS (ESI)** m/z calcd for $[M + Na]^+$ $C_{28}H_{36}O_3Na$ 443.2557, found 443.2564.



3au

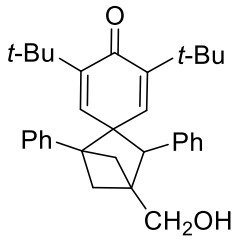
Methyl 3',5'-diisopropyl-4'-oxo-1,3-diphenylspiro[bicyclo[2.1.1]hexane-2,1'-cyclohexane]-2',5'-diene-4-carboxylate (3au). White solid; 50.0 mg, 55% yield, PE/EA = 20/1 as the eluent; mp = 137–138 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.22 (t, J = 6.8 Hz, 2H), 7.17–7.09 (m, 4H), 7.04 (d, J = 2.8 Hz, 1H), 6.98 (d, J = 7.6 Hz, 2H), 6.92–6.89 (m, 2H), 6.18 (d, J = 3.2 Hz, 1H), 4.14 (s, 1H), 3.69 (s, 3H), 3.07 (dd, J = 10.0, 8.4 Hz, 1H), 3.03–2.92 (m, 1H), 2.87 (dd, J = 10.0, 7.6 Hz, 1H), 2.72–2.62 (m, 1H), 2.54 (d, J = 8.0, 1.6 Hz, 1H), 2.34 (d, J = 7.6 Hz, 1H), 1.14 (d, J = 7.2 Hz, 3H), 0.97 (d, J = 6.8 Hz, 3H), 0.68 (d, J = 6.8 Hz, 3H), 0.42 (d, J = 6.8 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 184.1, 172.1, 146.3, 146.1, 142.7, 141.6, 138.8, 138.2, 128.5, 127.3, 127.0, 126.7, 126.5, 126.1, 60.2, 57.7, 53.5, 52.0, 51.5, 46.3, 40.1, 26.3, 25.8, 22.2, 22.0, 21.7, 21.3; **HRMS (ESI)** *m*/*z* calcd for $[M + Na]^+$ $C_{31}H_{34}O_3Na$ 477.2400, found 477.2407.



4

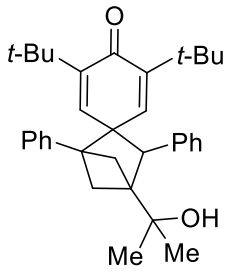
3',5'-Di-*tert*-butyl-4'-oxo-1,3-diphenylspiro[bicyclo[2.1.1]hexane-2,1'-cyclohexane]-2',5'-diene-4-carbaldehyde (4). White solid; 78.8 mg, 87% yield, PE/EA = 15/1 as the eluent; mp = 199–

200 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.96 (s, 1H), 7.27–7.24 (m, 2H), 7.20 (d, J = 7.2 Hz, 1H), 7.17–7.14 (m, 3H), 7.02 (d, J = 3.2 Hz, 1H), 6.95 (d, J = 7.2 Hz, 2H), 6.90–6.88 (m, 2H), 6.13 (d, J = 7.2 Hz, 1H), 4.19 (s, 1H), 2.94 (t, J = 9.6 Hz, 1H), 2.83 (dd, J = 9.6, 7.2 Hz, 1H), 2.52 (dd, J = 8.0, 1.6 Hz, 1H), 2.28 (d, J = 7.2 Hz, 1H), 1.19 (s, 9H), 0.78 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 200.1, 185.1, 148.5, 148.2, 141.9, 140.6, 138.5, 137.8, 128.6, 127.3, 127.1, 127.0, 126.9, 126.2, 60.8, 58.4, 56.3, 53.4, 44.9, 38.9, 34.9, 34.7, 29.4, 28.8; **HRMS (ESI)** m/z calcd for $[M + H]^+$ $C_{32}H_{37}O_2$ 453.2788, found 453.2785.



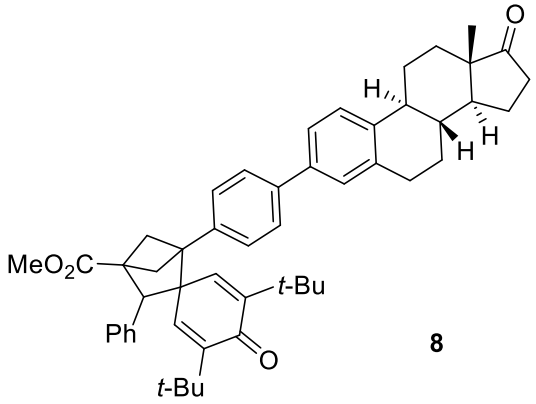
5

3',5'-Di-*tert*-butyl-4-(hydroxymethyl)-1,3-diphenylspiro[bicyclo[2.1.1]hexane-2,1'-cyclohexane]-2',5'-dien-4'-one (5). White solid; 80.9 mg, 89% yield, PE/EA = 3/1 as the eluent; mp = 169–170 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.27–7.24 (m, 2H), 7.19–7.10 (m, 4H), 7.07 (d, J = 7.2 Hz, 2H), 7.03 (d, J = 2.8 Hz, 1H), 6.94–6.91 (m, 2H), 6.34 (d, J = 2.8 Hz, 1H), 3.99 (dd, J = 18.8, 11.6 Hz, 2H), 3.69 (d, J = 1.2 Hz, 1H), 2.95 (dd, J = 10.0, 7.6 Hz, 1H), 2.53 (dd, J = 10.0, 7.6 Hz, 1H), 2.15 (dd, J = 7.6, 2.0 Hz, 1H), 2.09 (d, J = 7.6 Hz, 1H), 1.17 (s, 9H), 0.77 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 185.5, 147.6, 147.5, 142.8, 141.6, 139.2, 139.1, 128.4, 127.6, 127.2, 126.62, 126.55, 126.2, 62.5, 59.9, 57.2, 53.9, 52.0, 43.4, 39.7, 34.8, 34.6, 29.4, 28.9; **HRMS (ESI)** m/z calcd for $[M + Na]^+$ $C_{32}H_{38}O_2Na$ 477.2764, found 477.2774.



6

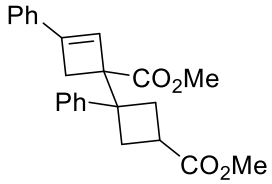
3',5'-Di-*tert*-butyl-4-(2-hydroxypropan-2-yl)-1,3-diphenylspiro[bicyclo[2.1.1]hexane-2,1'-cyclohexane]-2',5'-dien-4'-one (6). White solid; 78.2 mg, 81% yield, PE/EA = 3/1 as the eluent; mp = 116–117 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.23 (d, J = 7.2 Hz, 3H), 7.19–7.10 (m, 5H), 7.01–6.97 (m, 3H), 6.71 (d, J = 3.2 Hz, 1H), 3.58 (d, J = 2.0 Hz, 1H), 3.16 (dd, J = 10.0, 8.4 Hz, 1H), 2.43 (dd, J = 9.6, 7.6 Hz, 1H), 2.31 (dd, J = 8.0, 2.0 Hz, 1H), 2.08 (d, J = 7.2 Hz, 1H), 1.28 (s, 3H), 1.21 (s, 3H), 1.16 (s, 9H), 0.80 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 185.7, 147.6, 147.3, 142.1, 141.3, 139.9, 139.6, 128.4, 127.3, 127.0, 126.6, 126.2, 71.4, 60.4, 59.0, 57.0, 54.5, 43.9, 38.7, 34.8, 34.7, 29.5, 28.9, 27.8, 27.2; **HRMS (ESI)** *m*/*z* calcd for $[M + Na]^+$ $C_{34}H_{42}O_2Na$ 505.3077, found 505.3080.



8

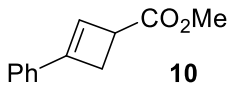
Methyl 3',5'-di-*tert*-butyl-1-(4-((8*R*,9*S*,13*S*,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-3-yl)phenyl)-4'-oxo-3-phenylspiro[bicyclo[2.1.1]hexane-2,1'-cyclohexane]-2',5'-diene-4-carboxylate (8). White solid; 142.6 mg, 97% yield, PE/EA = 10/1 as the eluent; mp = 134–135 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37–7.27 (m, 4H), 7.23–7.16 (m,

4H), 7.06 (d, *J* = 2.4 Hz, 1H), 7.00 (d, *J* = 7.2 Hz, 2H), 6.94 (d, *J* = 8.0 Hz, 2H), 6.14 (d, *J* = 2.4 Hz, 1H), 4.15 (s, 1H), 3.71 (s, 3H), 3.04–2.94 (m, 3H), 2.86 (dd, *J* = 9.6, 7.2 Hz, 1H), 2.56–2.42 (m, 3H), 2.37–2.30 (m, 2H), 2.22–1.94 (m, 4H), 1.68–1.61 (m, 2H), 1.59–1.41 (m, 4H), 1.20 (d, *J* = 1.6 Hz, 9H), 0.91 (s, 3H), 0.79 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) *δ* 220.9, 185.1, 172.3, 148.2, 147.9, 142.4, 141.2, 139.6, 139.0, 138.9, 138.2, 137.0, 136.8, 128.5, 127.5, 126.63, 126.58, 125.79, 125.77, 124.4, 60.2, 57.7, 53.3, 52.0, 51.4, 50.4, 48.0, 46.3, 44.3, 40.2, 38.1, 35.8, 34.9, 34.7, 31.6, 29.5, 29.4, 28.8, 26.5, 25.7, 21.6, 13.8; **HRMS (ESI)** *m*/*z* calcd for $[M + Na]^+$ $C_{51}H_{58}O_4Na$ 757.4227, found 757.4235.



9

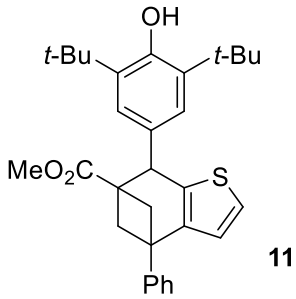
Dimethyl 1',3-diphenyl-[1,1'-bi(cyclobutan)]-2-ene-1,3'-dicarboxylate (9). Colorless liquid; 12.8 mg, 34% yield, PE/EA = 20/1 as the eluent; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43–7.40 (m, 2H), 7.38–7.32 (m, 7H), 7.31–7.28 (m, 1H), 6.39 (s, 1H), 3.67 (s, 3H), 3.46 (s, 3H), 3.02 (dd, *J* = 18.8, 13.6 Hz, 2H), 2.95–2.84 (m, 3H), 2.73–2.64 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) *δ* 175.6, 173.6, 148.1, 143.5, 133.3, 128.6, 128.4, 128.1, 127.0, 126.7, 126.3, 125.0, 58.4, 51.7, 51.4, 46.3, 34.6, 33.2, 32.8, 31.6; **HRMS (ESI)** *m*/*z* calcd for $[M + Na]^+$ $C_{24}H_{24}O_4Na$ 399.1567, found 399.1577.



10

Methyl 3-phenylcyclobut-2-ene-1-carboxylate (10). Colorless liquid; 34.6 mg, 92% yield, PE/EA = 20/1 as the eluent; **^{1}H NMR** (400 MHz, THF-*d*8) *δ* 7.25–7.22 (m, 2H), 7.19–7.16 (m, 2H), 7.13–7.09 (m, 1H), 6.15 (d, *J* = 1.2 Hz, 1H), 3.50 (s, 3H), 3.48–3.45 (m, 1H), 2.91–2.82 (m,

2H); **^{13}C NMR** (100 MHz, THF-*d*8) δ 173.4, 149.0, 134.9, 129.1, 129.0, 125.7, 125.4, 51.7, 42.1, 33.0. Physical and spectral properties of this material were identical to those previously reported in literature.[3]



11

Methyl 7-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-4-phenyl-4,7-dihydro-4,6-methanobenzo[*b*]thiophene-6(5*H*)-carboxylate (11). White solid; 49.8 mg, 51% yield, PE/EA = 20/1 as the eluent; mp = 202–203 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42–7.37 (m, 2H), 7.34–7.29 (m, 3H), 6.92–6.89 (m, 3H), 6.77 (d, J = 5.2 Hz, 1H), 5.08 (s, 1H), 4.74 (s, 1H), 3.62 (s, 3H), 2.71 (dd, J = 8.4, 3.6 Hz, 1H), 2.65 (t, J = 7.6 Hz, 1H), 2.49 (dd, J = 9.2, 7.6 Hz, 1H), 1.38 (s, 18H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.7, 152.7, 149.9, 143.6, 135.2, 134.7, 131.9, 128.5, 127.5, 127.1, 126.0, 125.3, 120.8, 51.6, 49.8, 49.1, 47.7, 44.0, 37.5, 34.2, 30.4; **HRMS (ESI)** *m*/*z* calcd for $[M + Na]^+$ $C_{31}H_{36}SO_3Na$ 511.2277, found 511.2278.

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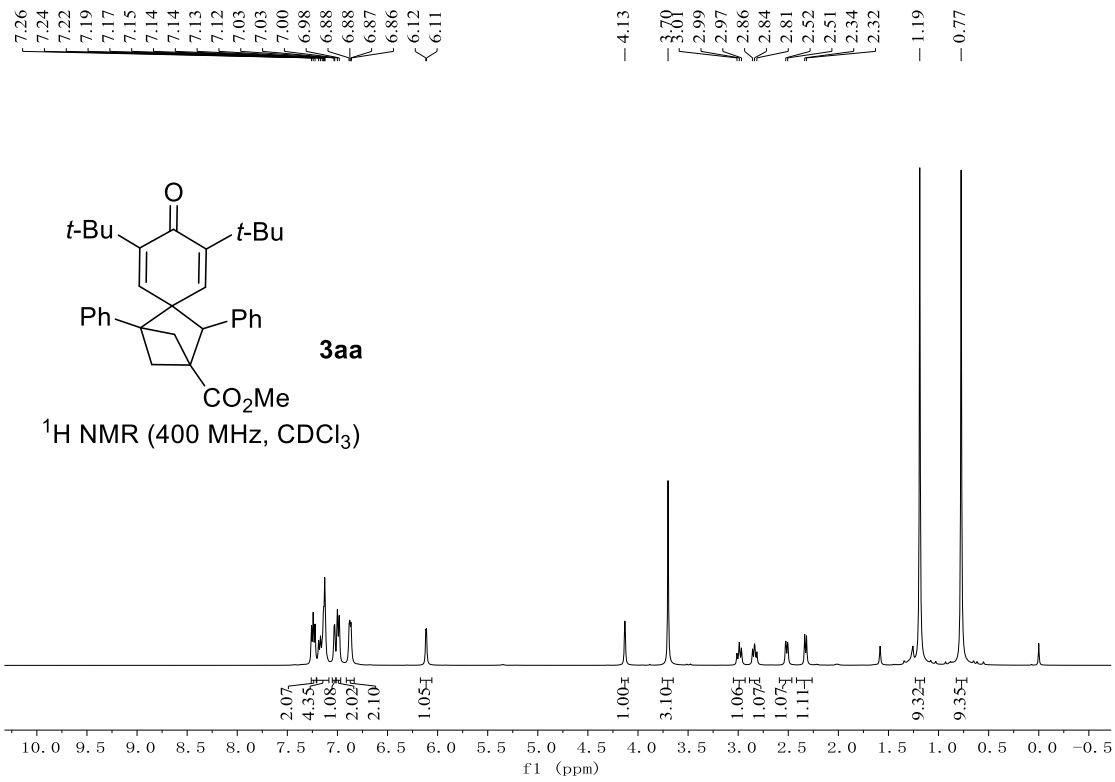
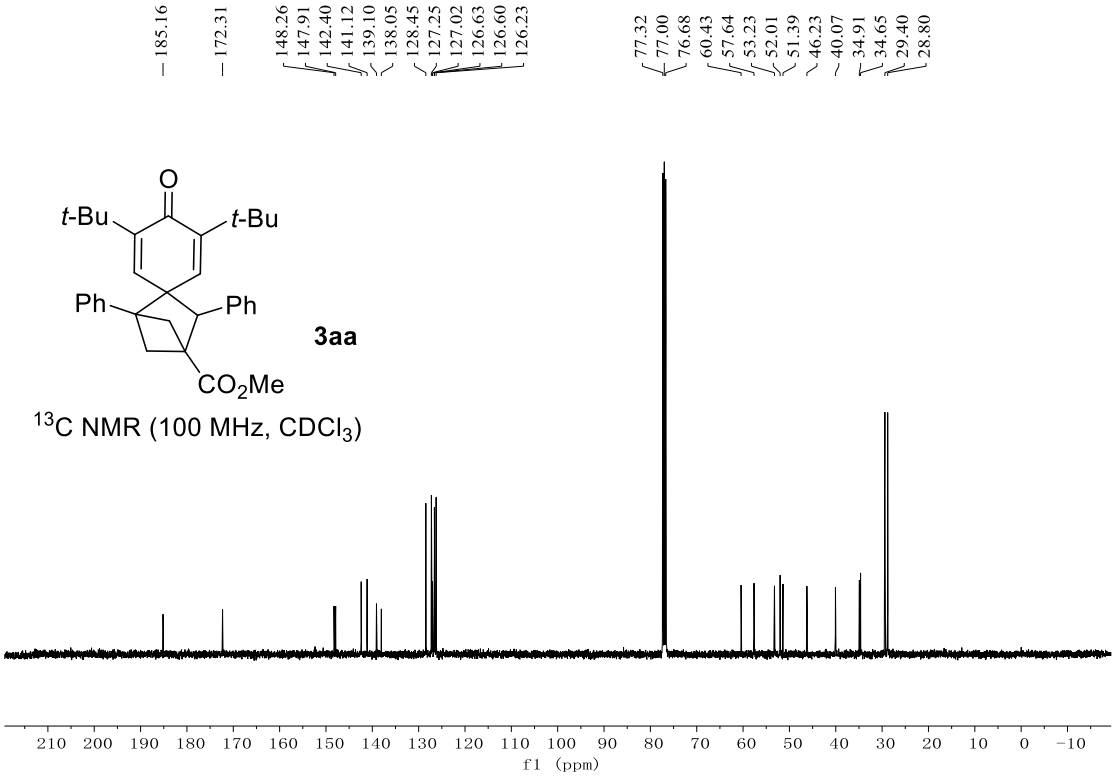
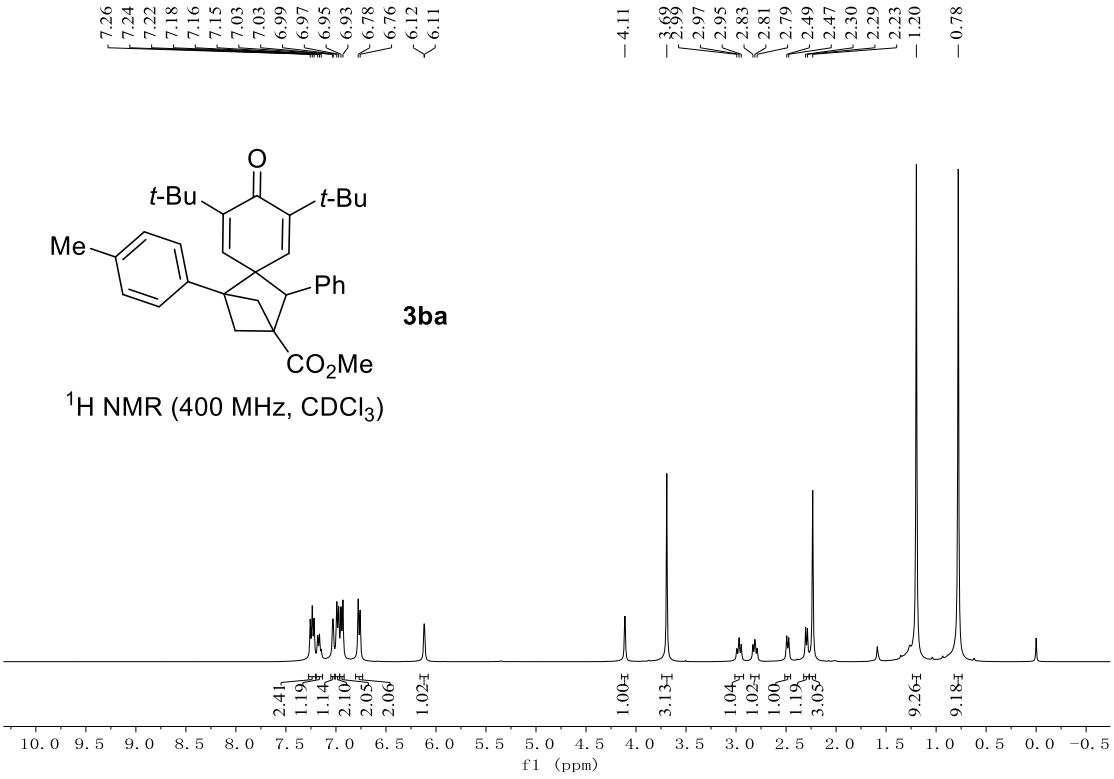
Copies of ^{1}H, ^{13}C and ^{19}F NMR spectra



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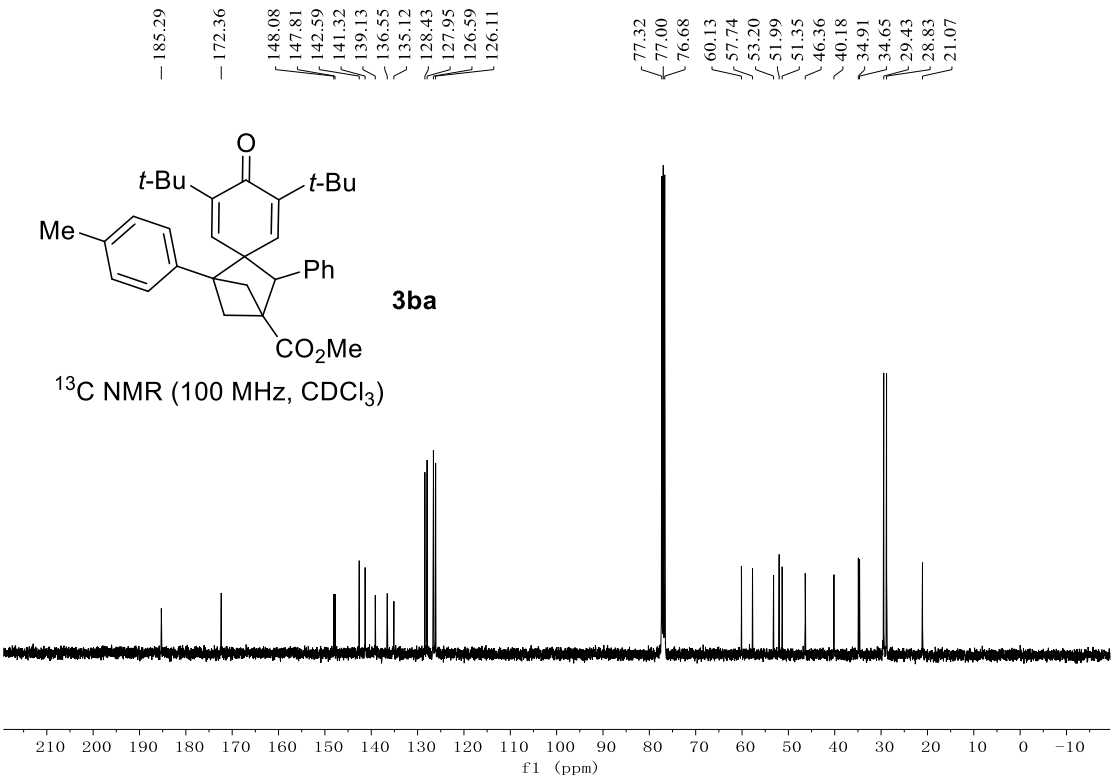
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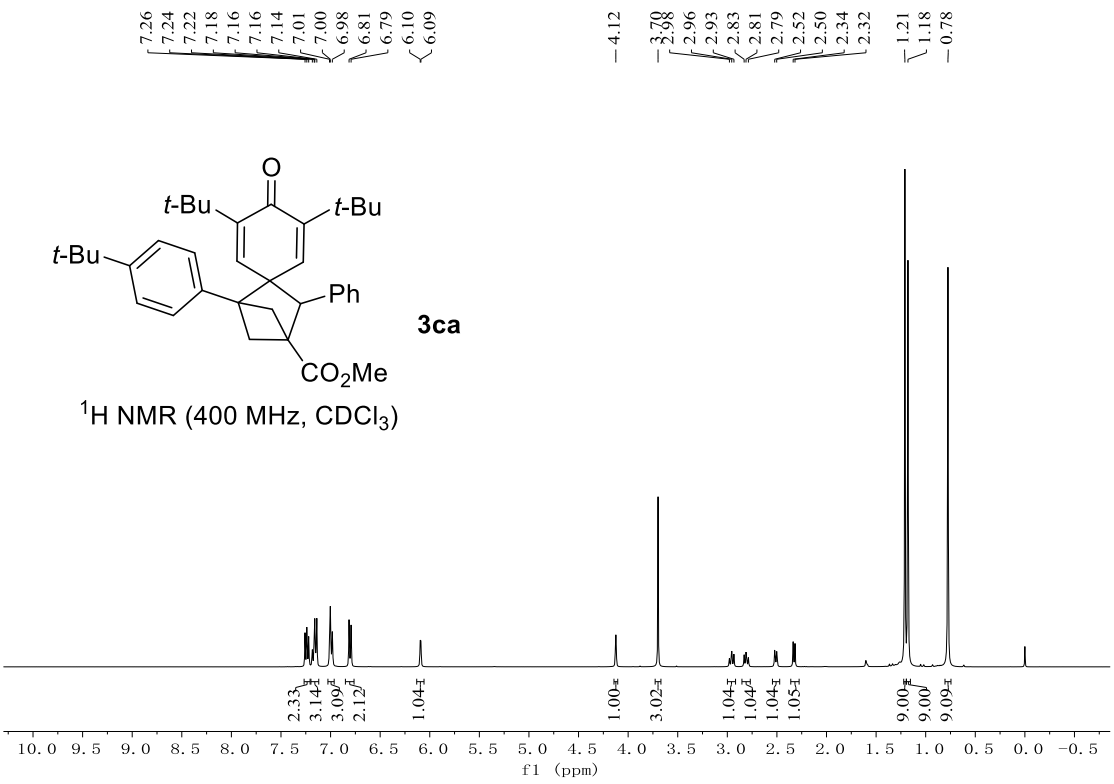
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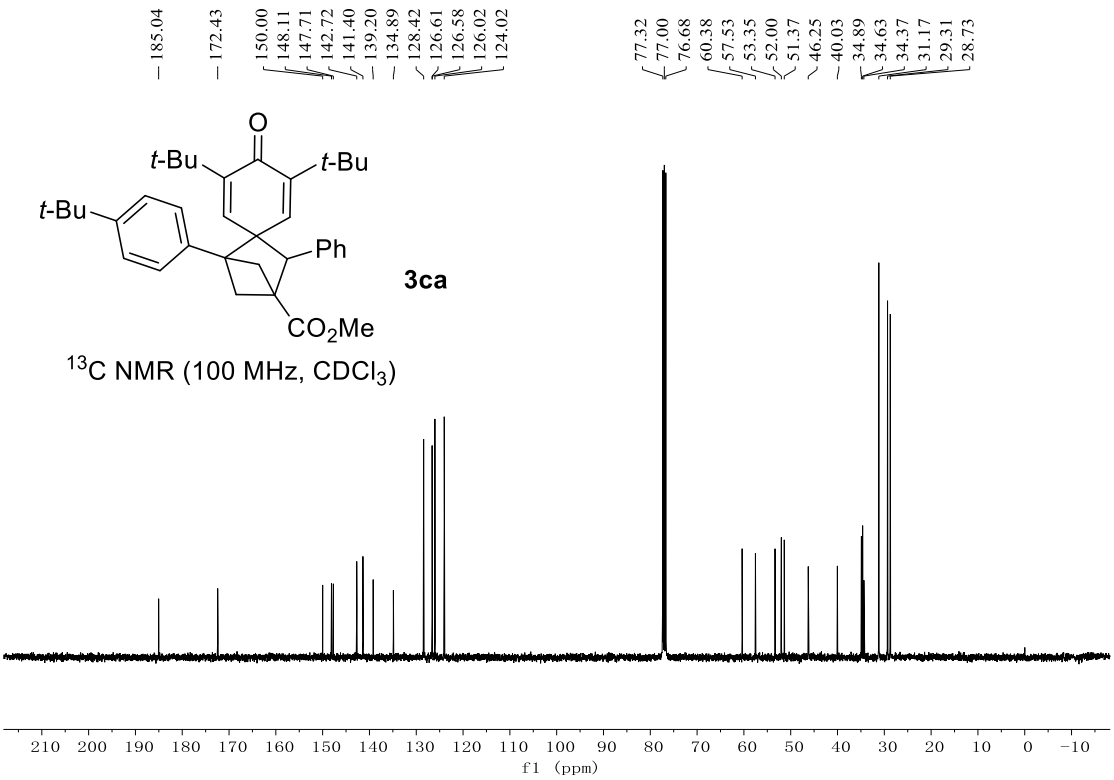
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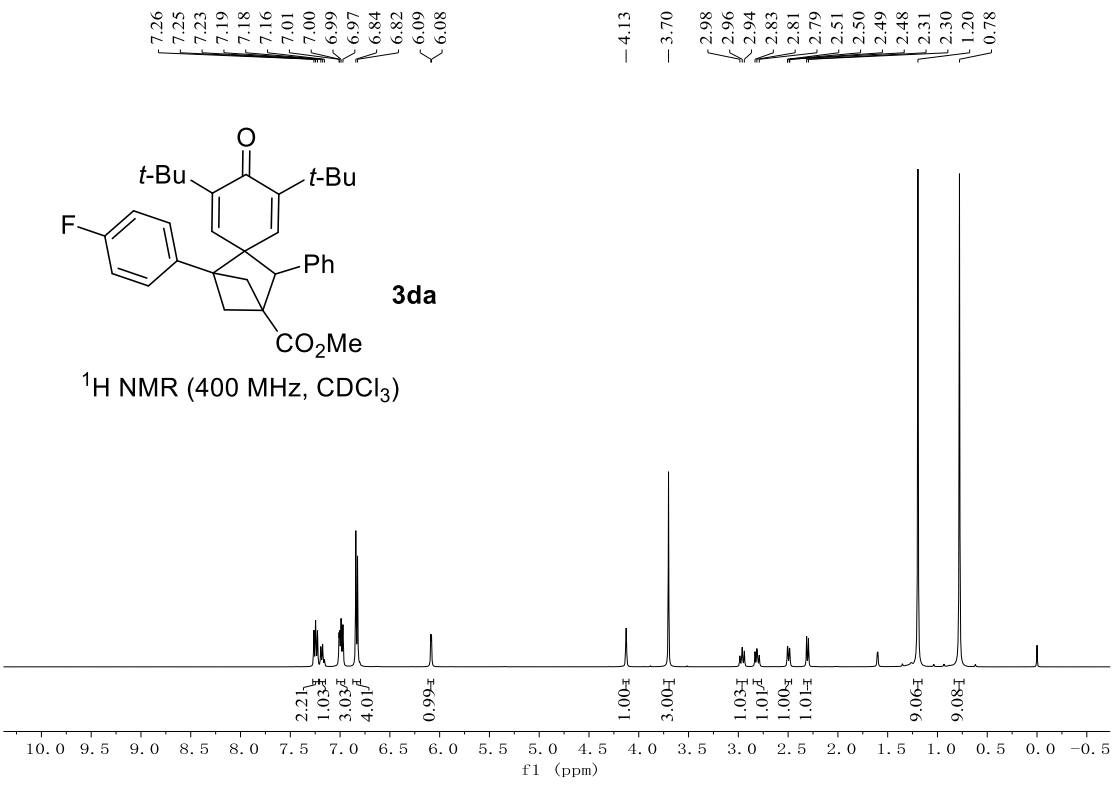
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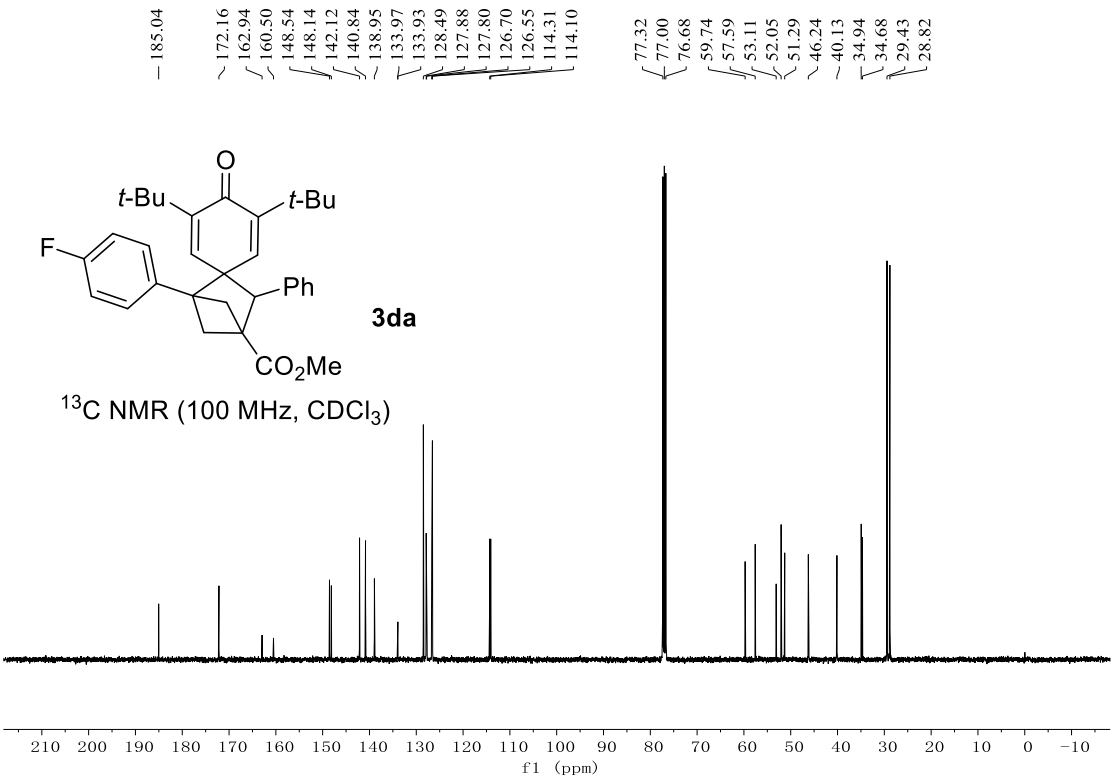
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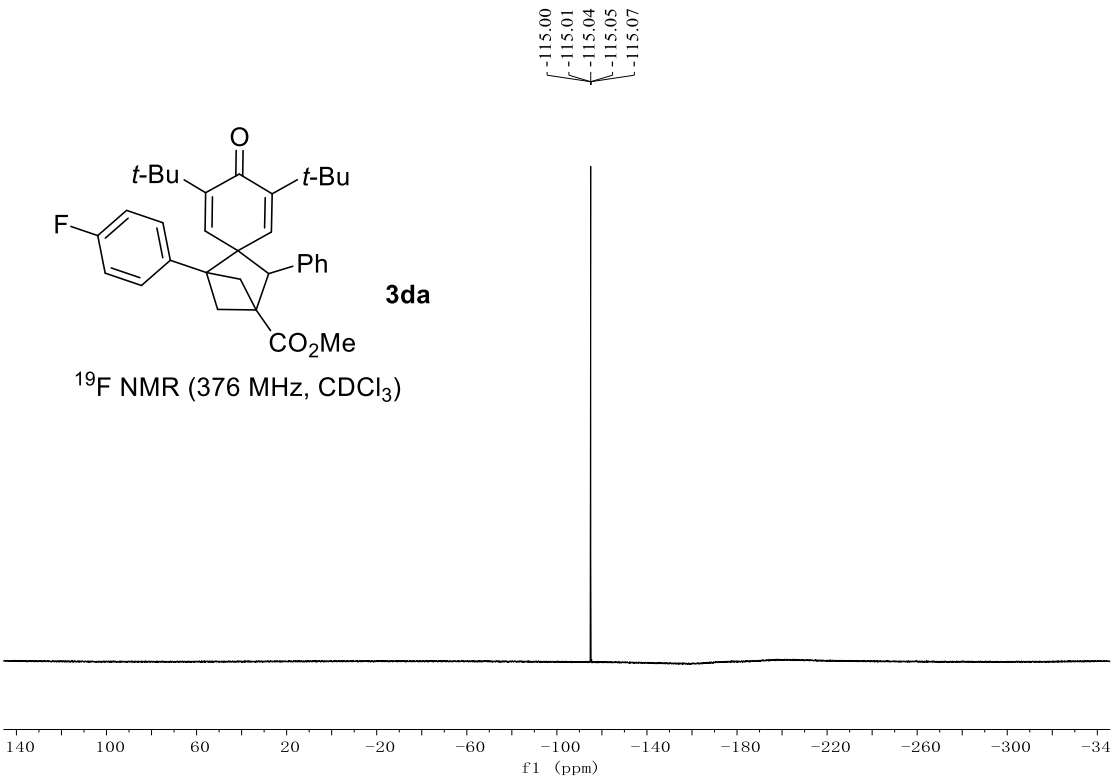
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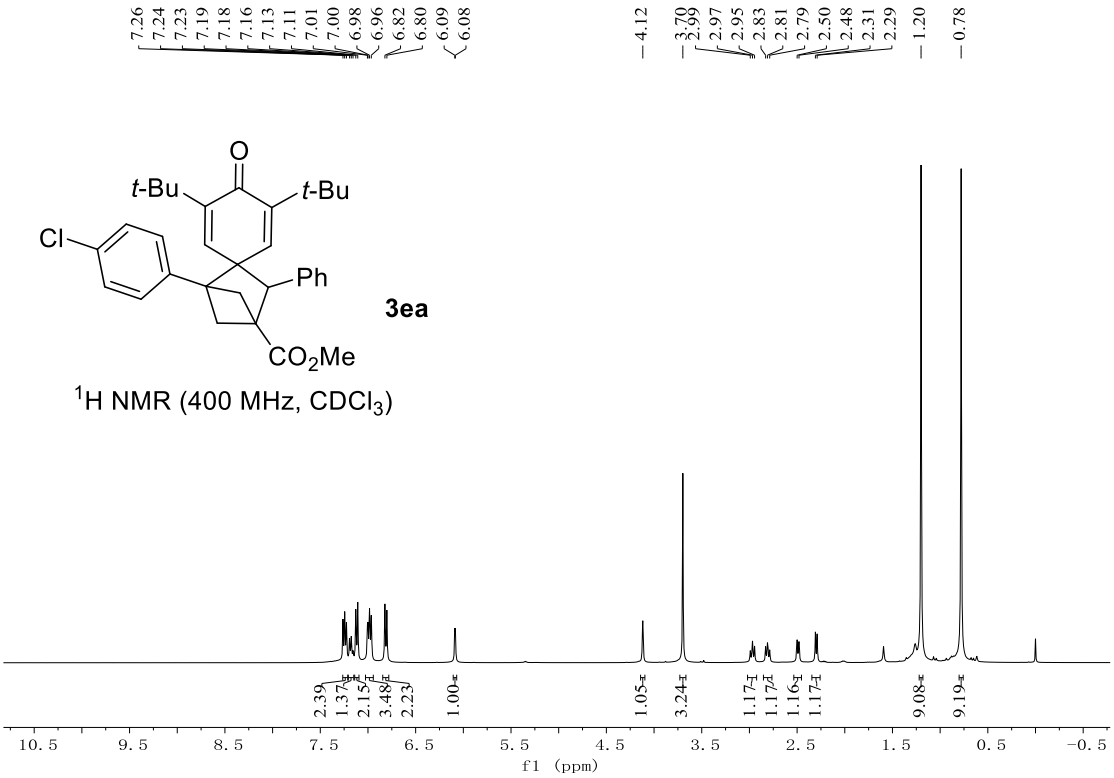
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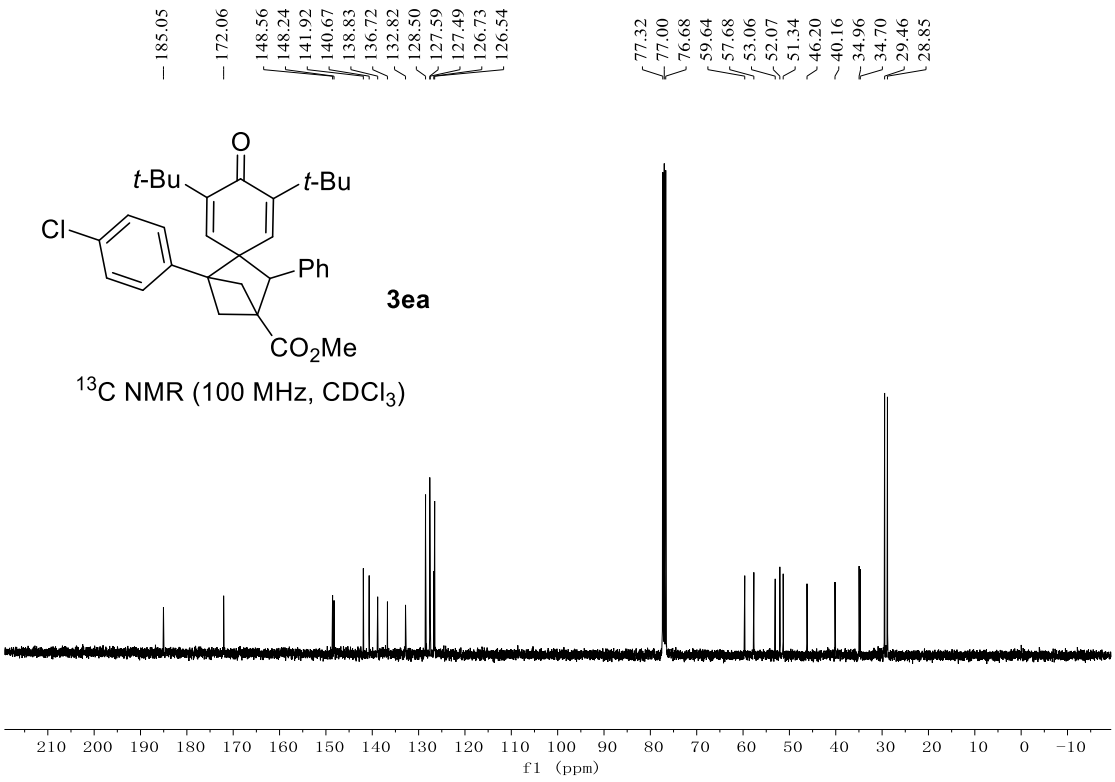
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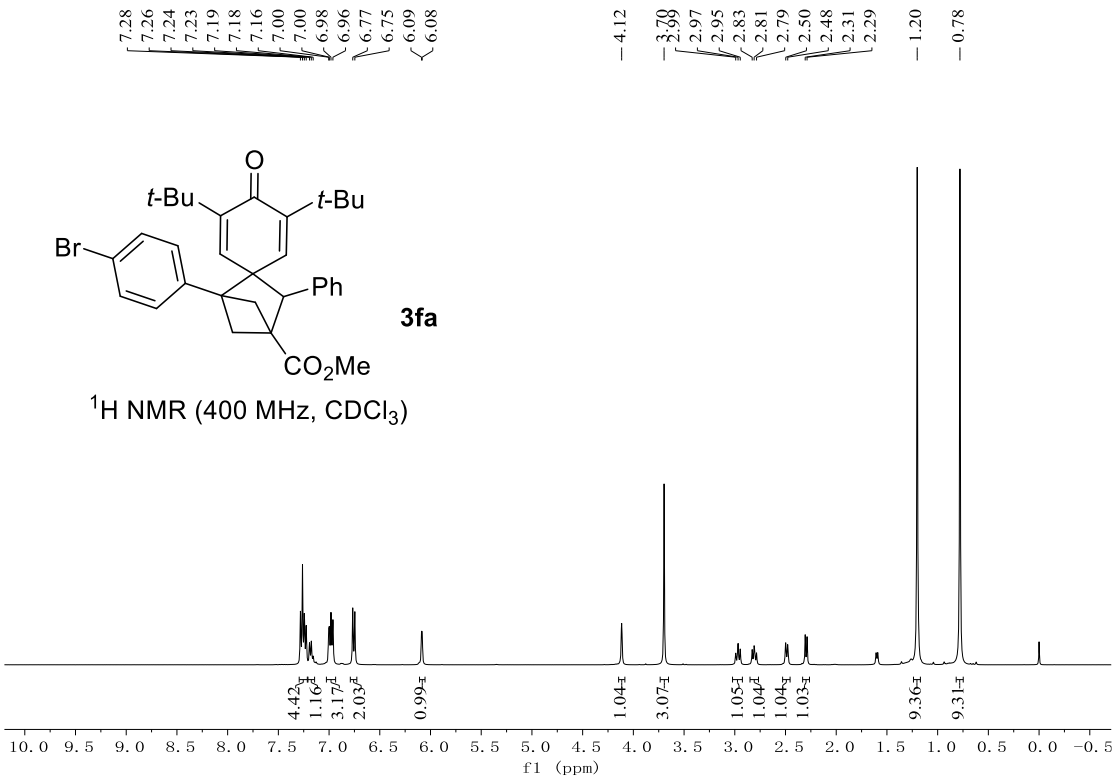
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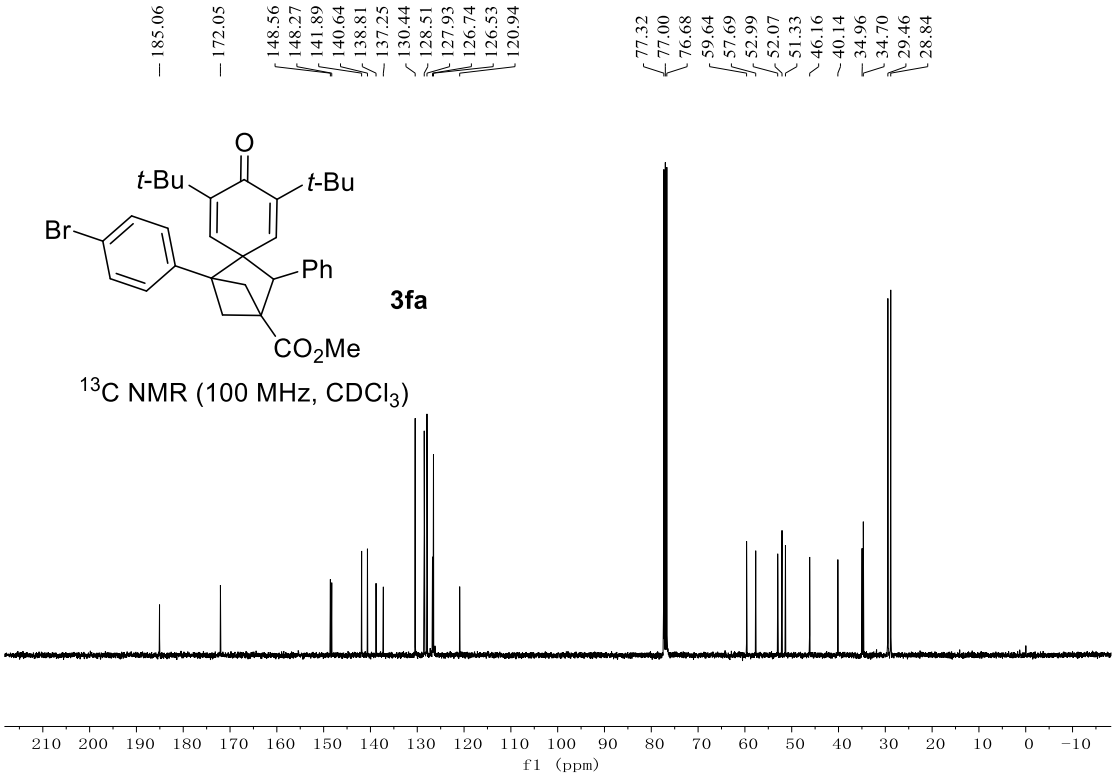
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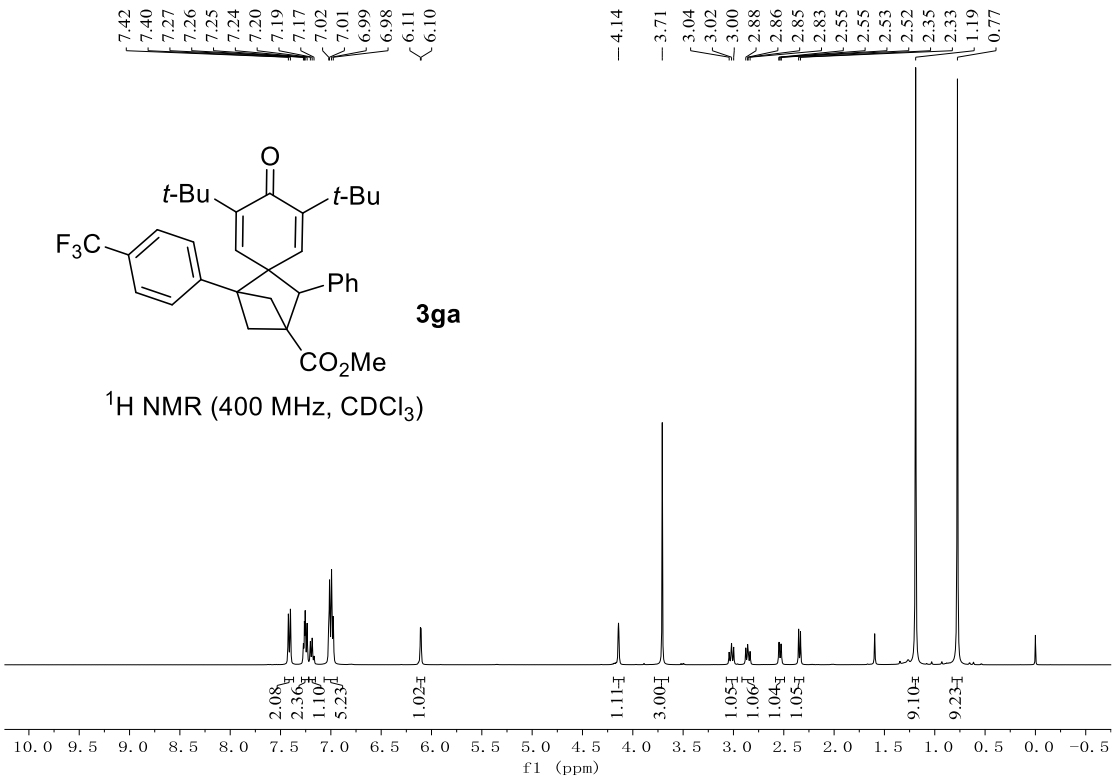
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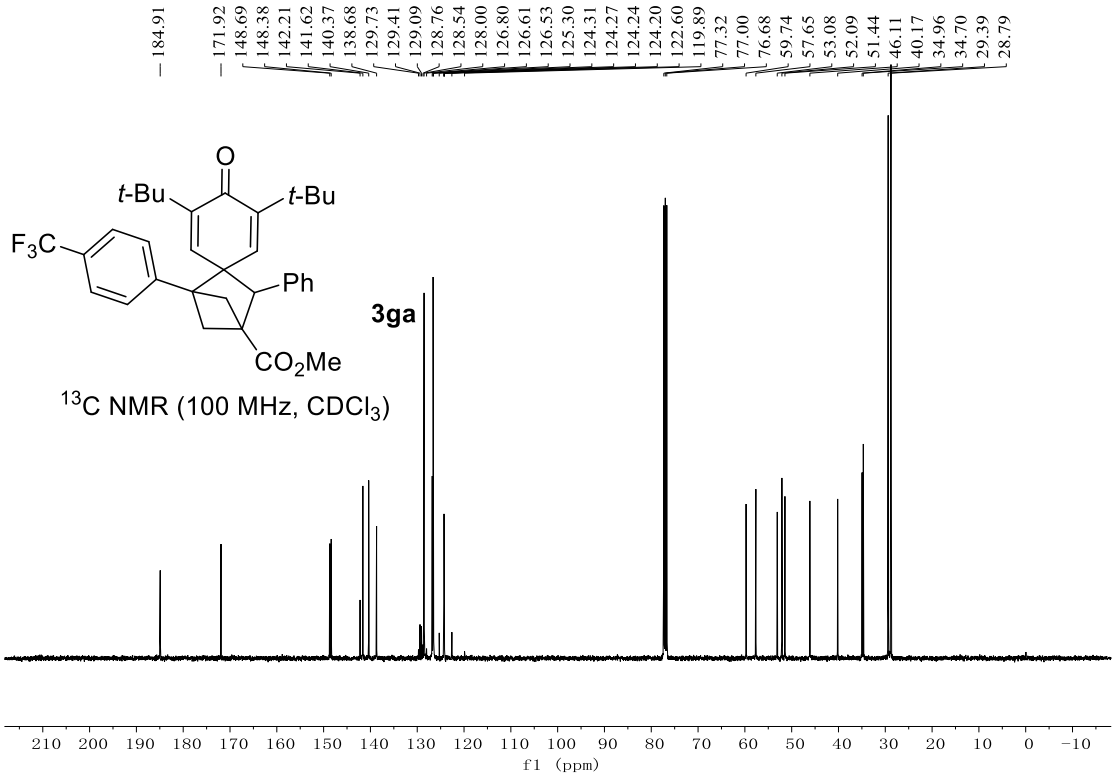
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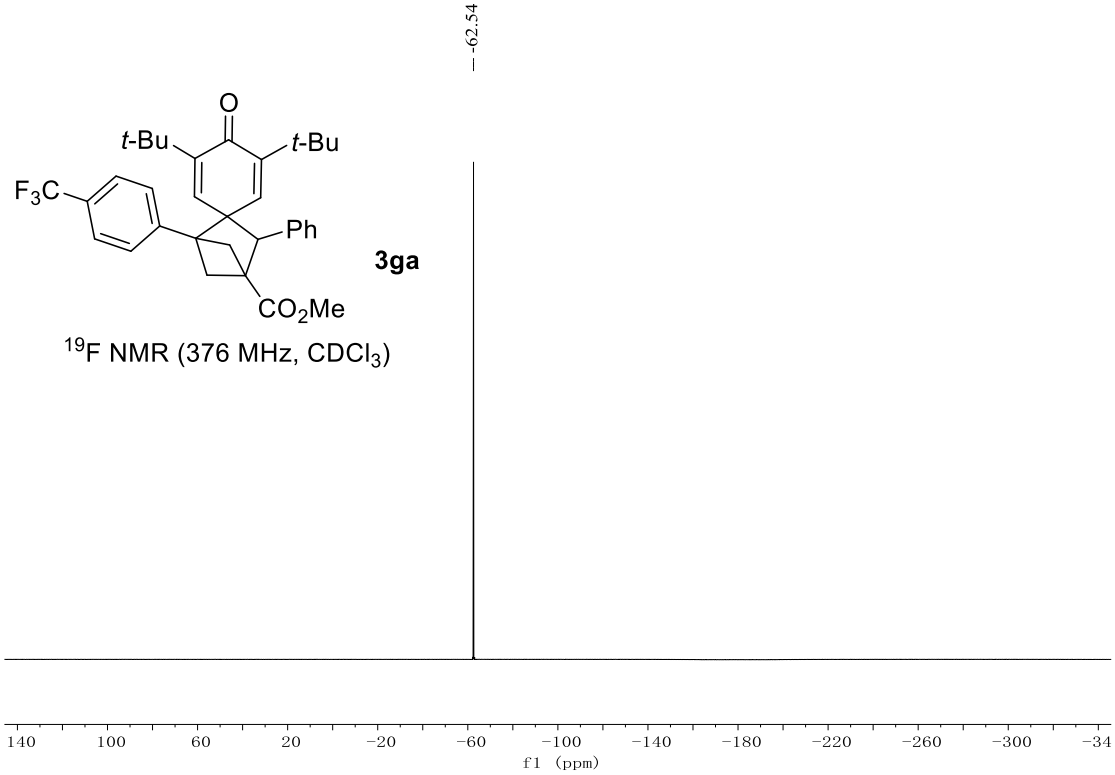
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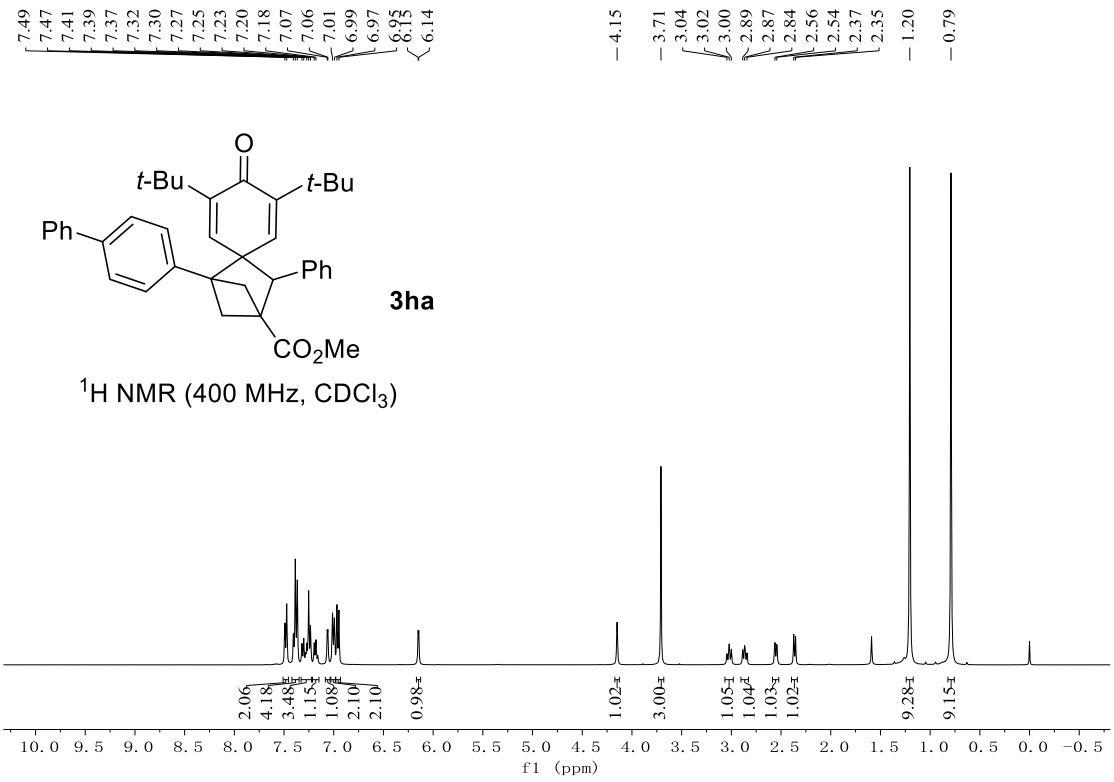
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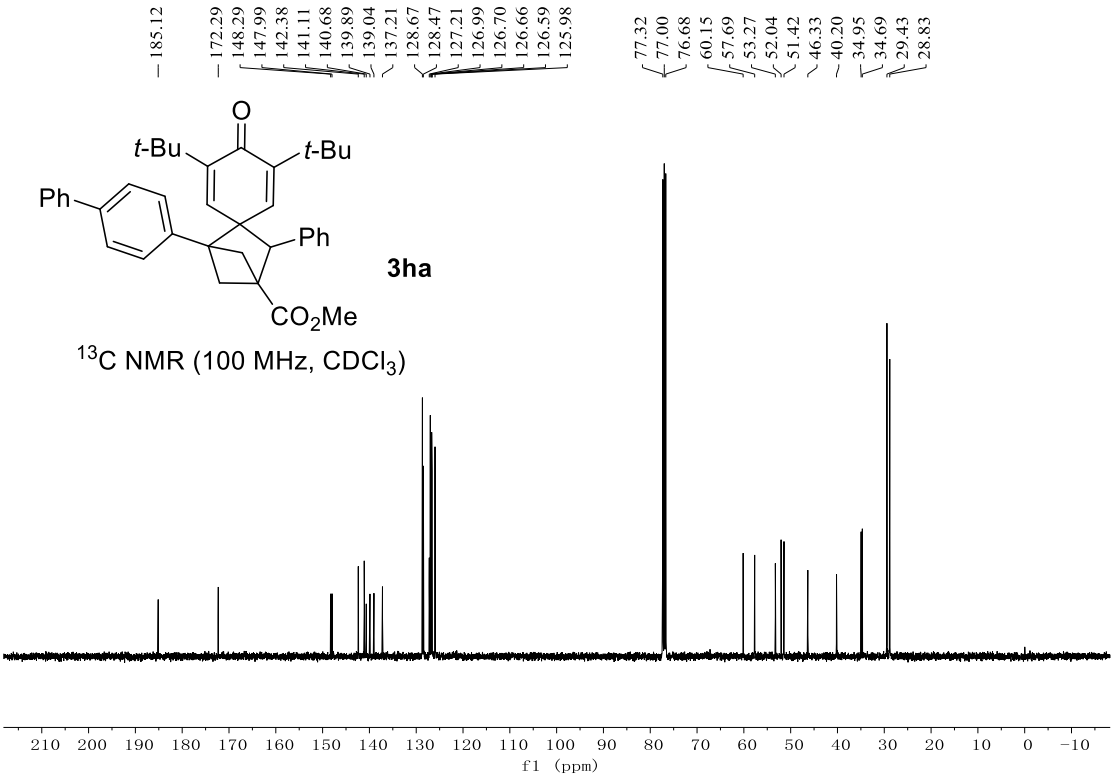
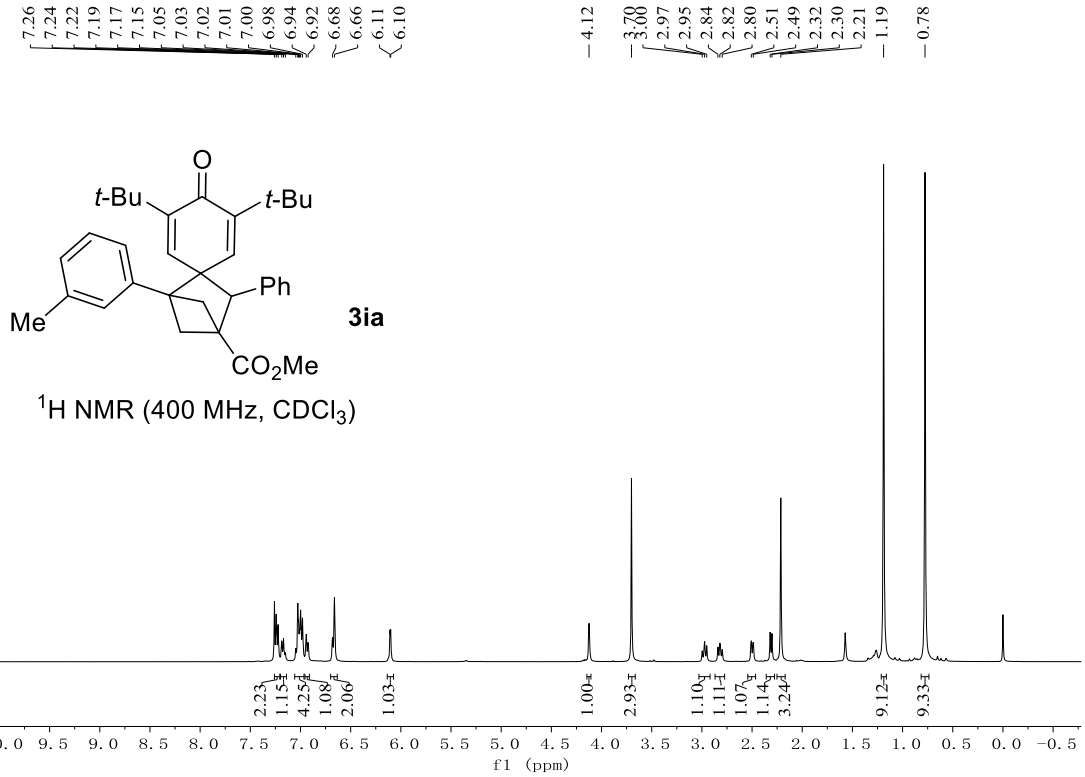
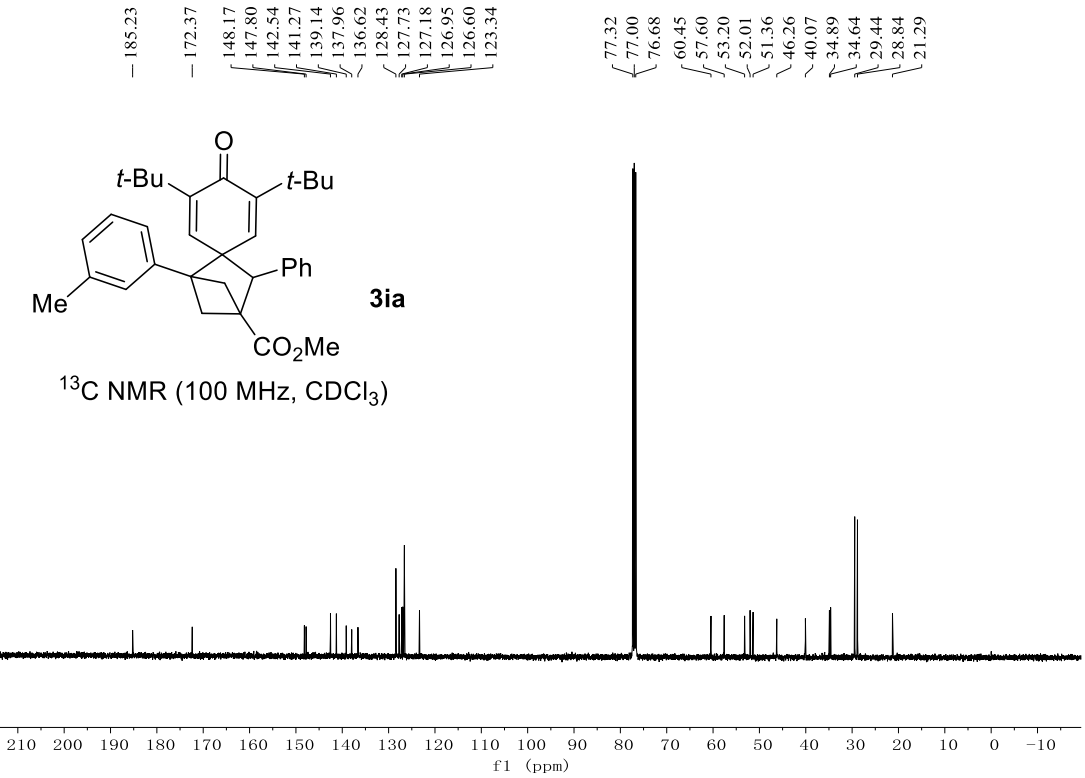
6.97
6.95
6.15
6.14
4.15
3.71
3.04
3.02
3.00
2.89
2.87
2.84
2.56
2.54
2.37
2.35
1.20
0.79
O
t-Bu
t-Bu
Ph
Ph
CO2Me
3ha
1H NMR (400 MHz, CDCl3)
2.06
4.18
3.48
1.15
1.08
2.10
2.10
0.98
1.02
3.00
1.05
1.04
1.03
1.02
9.28
9.15
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)


185.12
172.29
148.29
147.99
142.38
141.11
140.68
139.89
139.04
137.21
128.67
128.47
127.21
126.99
126.70
126.66
126.59
125.98
77.32
77.00
76.68
60.15
57.69
53.27
52.04
51.42
46.33
40.20
34.95
34.69
29.43
28.83
O
t-Bu
t-Bu
Ph
Ph
CO2Me
3ha
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


7.26
7.24
7.22
7.19
7.17
7.15
7.05
7.03
7.02
7.01
7.00
6.98
6.94
6.92
6.68
6.66
6.11
6.10
4.12
3.70
3.00
2.97
2.95
2.84
2.82
2.80
2.51
2.49
2.32
2.30
2.21
1.19
0.78
O
t-Bu
t-Bu
Ph
Me
CO2Me
3ia
1H NMR (400 MHz, CDCl3)
2.23
1.15
4.25
1.08
2.06
1.03
1.00
2.93
1.10
1.11
1.07
1.14
3.24
9.12
9.33
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)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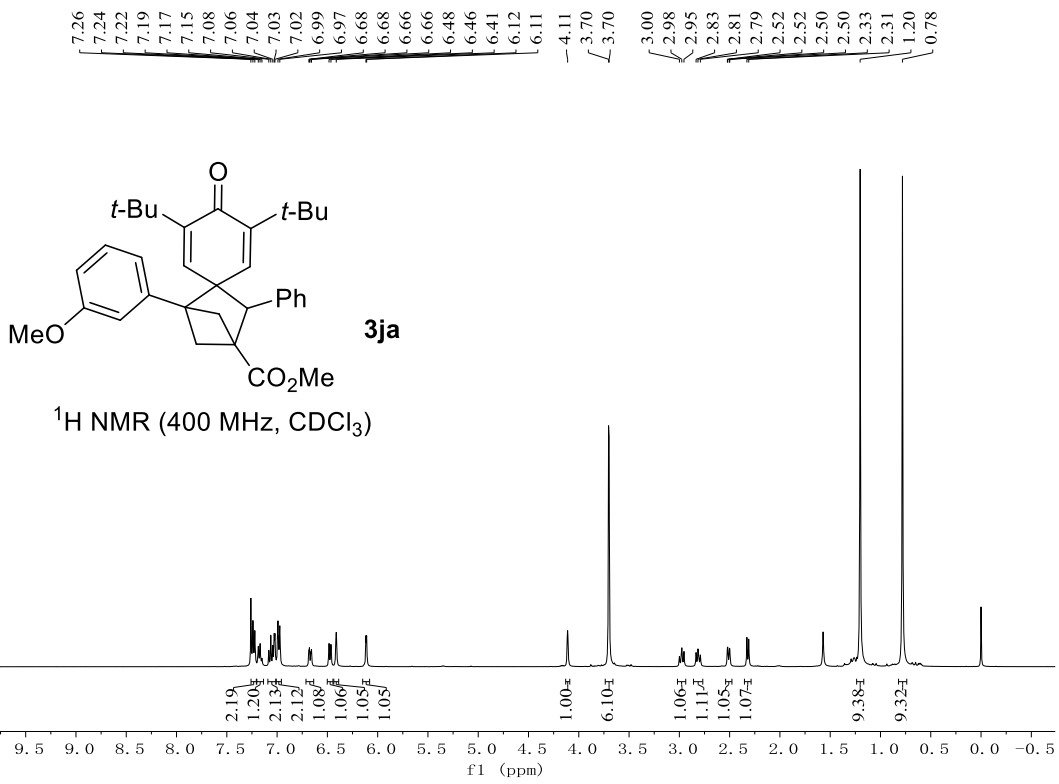
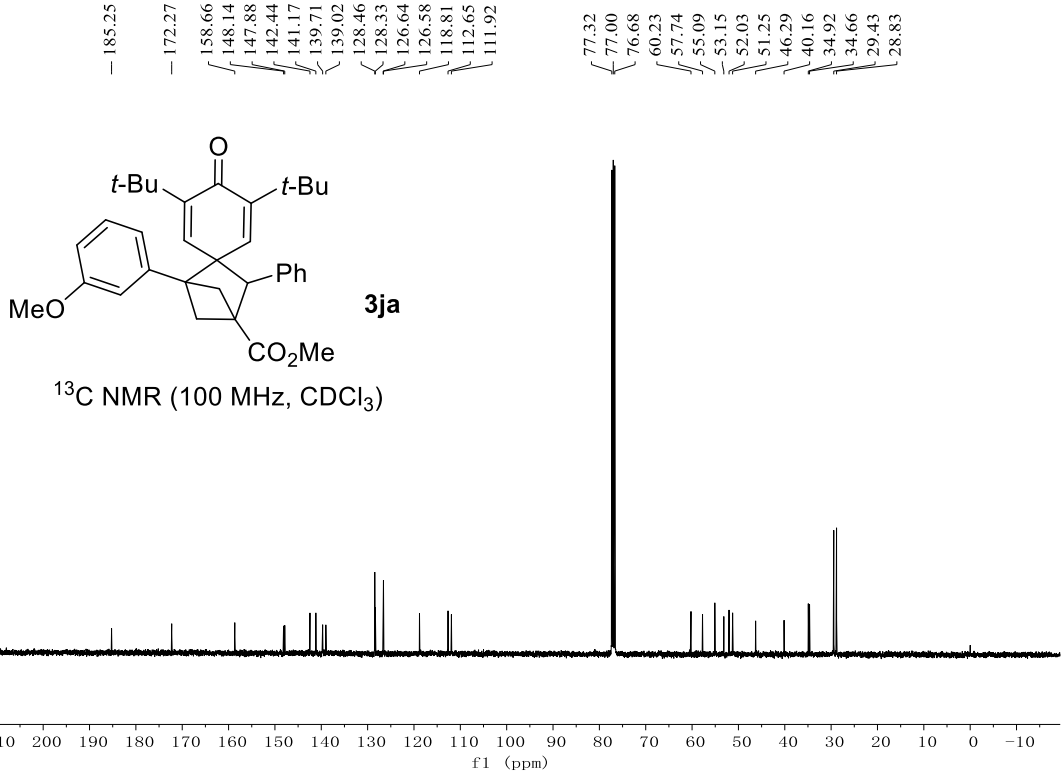
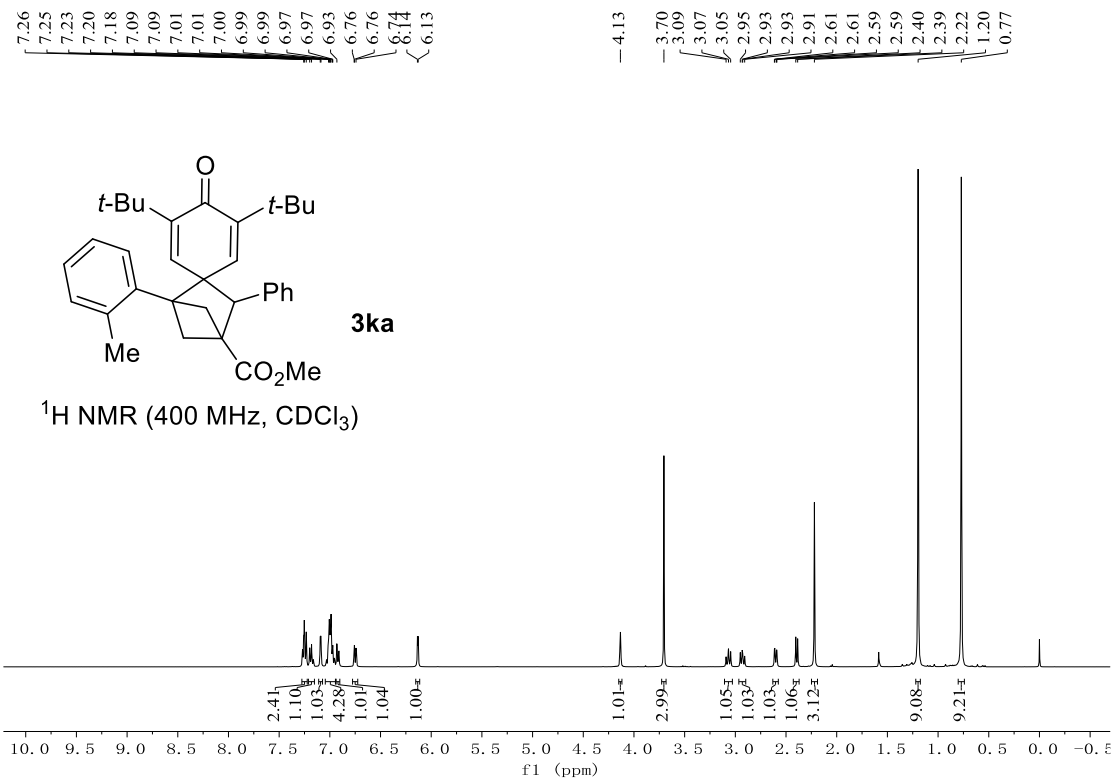
148.17
147.80
142.54
141.27
139.14
137.96
136.62
128.43
127.73
127.18
126.95
126.60
123.34
77.32
77.00
76.68
60.45
57.60
53.20
52.01
51.36
46.26
40.07
34.89
34.64
29.44
28.84
21.29
O
t-Bu
t-Bu
Ph
Me
CO2Me
3ia
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


7.26 7.24 7.22 7.19 7.17 7.15 7.08 7.06 7.04 7.03 7.02 6.99 6.97 6.68 6.68 6.66 6.66 6.48 6.46 6.41 6.12 6.11 4.11 3.70 3.70 3.00 2.98 2.95 2.83 2.81 2.79 2.52 2.52 2.50 2.50 2.33 2.31 1.20 0.78
O
t-Bu
t-Bu
Ph
MeO
CO2Me
3ja
1H NMR (400 MHz, CDCl3)
2.19 1.20 2.13 2.12 1.08 1.06 1.05 1.05 1.00 6.10 1.06 1.11 1.05 1.07 9.38 9.32
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)


185.25 172.27 158.66 148.14 147.88 142.44 141.17 139.71 139.02 128.46 128.33 126.64 126.58 118.81 112.65 111.92 77.32 77.00 76.68 60.23 57.74 55.09 53.15 52.03 51.25 46.29 40.16 34.92 34.66 29.43 28.83
O
t-Bu
t-Bu
Ph
MeO
CO2Me
3ja
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)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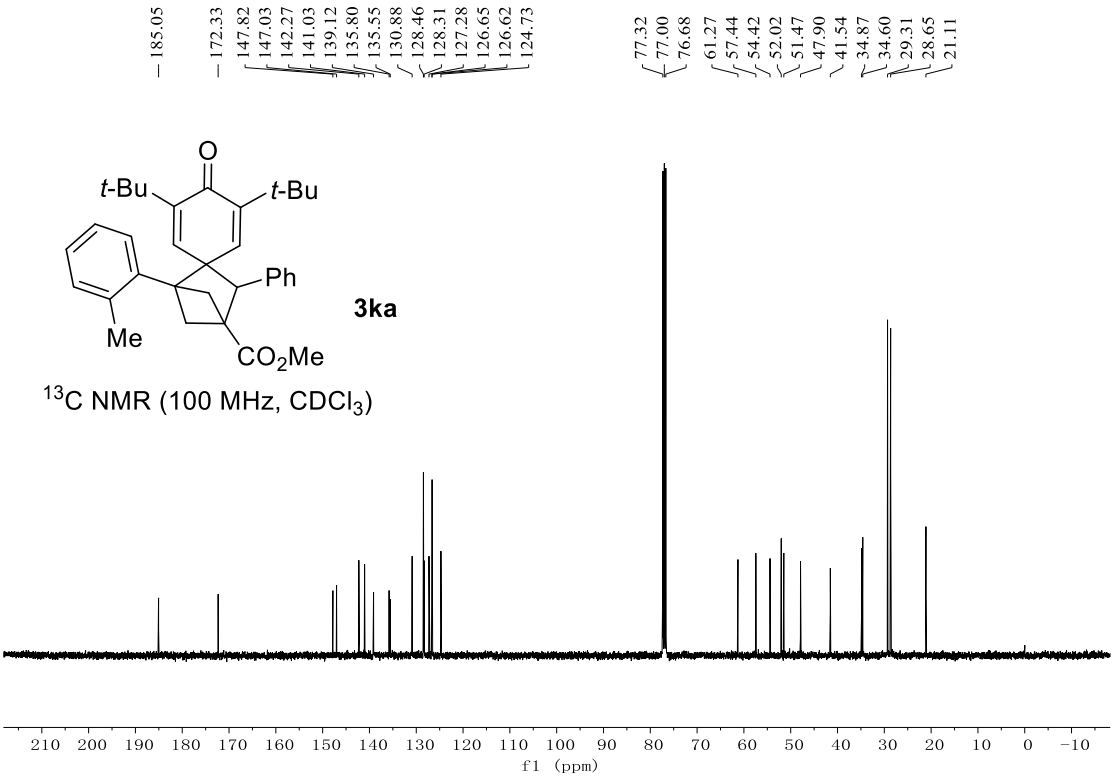
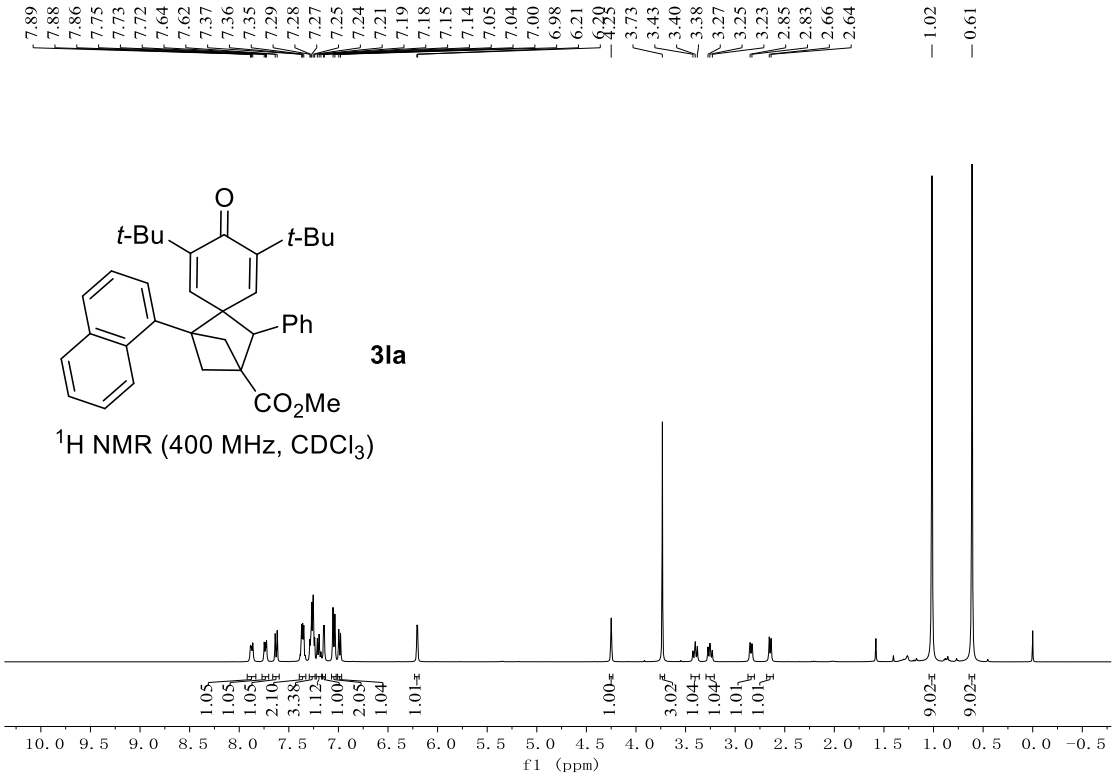
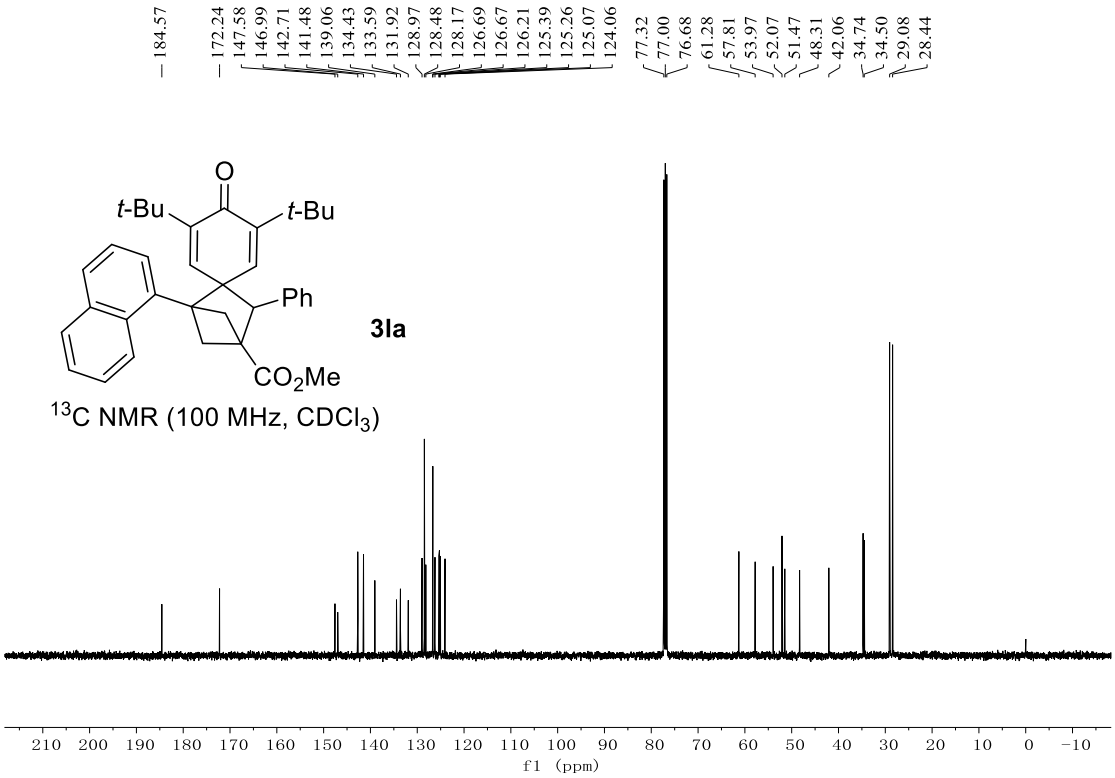
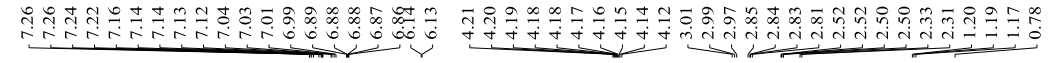
7.25
7.23
7.20
7.18
7.09
7.09
7.01
7.01
7.00
6.99
6.99
6.97
6.97
6.93
6.76
6.76
6.74
6.14
6.13
4.13
3.70
3.09
3.07
3.05
2.95
2.93
2.93
2.91
2.61
2.61
2.59
2.59
2.40
2.39
2.22
1.20
0.77
O
t-Bu
t-Bu
Ph
Me
CO2Me
3ka
1H NMR (400 MHz, CDCl3)
2.41
1.10
1.03
4.28
1.01
1.04
1.00
1.01
2.99
1.05
1.03
1.03
1.06
3.12
9.08
9.21
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)


185.05
172.33
147.82
147.03
142.27
141.03
139.12
135.80
135.55
130.88
128.46
128.31
127.28
126.65
126.62
124.73
77.32
77.00
76.68
61.27
57.44
54.42
52.02
51.47
47.90
41.54
34.87
34.60
29.31
28.65
21.11
O
t-Bu
t-Bu
Ph
Me
CO2Me
3ka
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

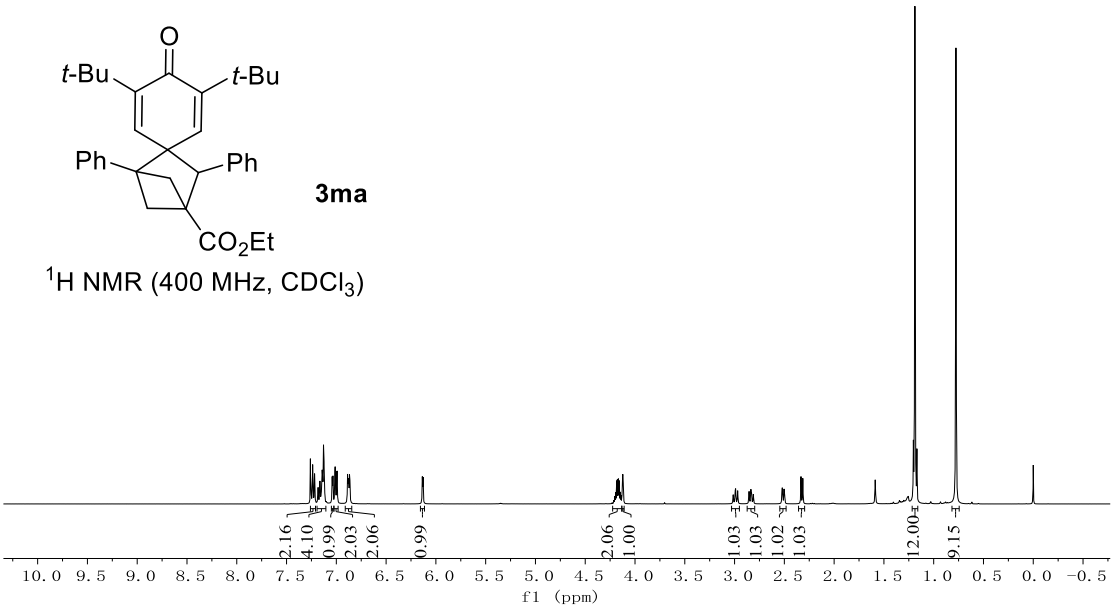

7.89
7.88
7.86
7.75
7.73
7.72
7.64
7.62
7.37
7.36
7.35
7.29
7.28
7.27
7.25
7.24
7.21
7.19
7.18
7.15
7.14
7.05
7.04
7.00
6.98
6.21
6.20
4.25
3.73
3.43
3.40
3.38
3.27
3.25
3.23
2.85
2.83
2.66
2.64
1.02
0.61
O
t-Bu
t-Bu
Ph
CO2Me
3la
1H NMR (400 MHz, CDCl3)
1.05
1.05
1.05
2.10
3.38
1.12
1.00
2.05
1.04
1.01
1.00
3.02
1.04
1.04
1.01
1.01
9.02
9.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)

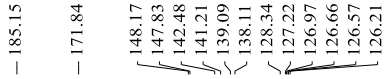

184.57
172.24
147.58
146.99
142.71
141.48
139.06
134.43
133.59
131.92
128.97
128.48
128.17
126.69
126.67
126.21
125.39
125.26
125.07
124.06
77.32
77.00
76.68
61.28
57.81
53.97
52.07
51.47
48.31
42.06
34.74
34.50
29.08
28.44
O
t-Bu
t-Bu
Ph
CO2Me
3la
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)



3ma

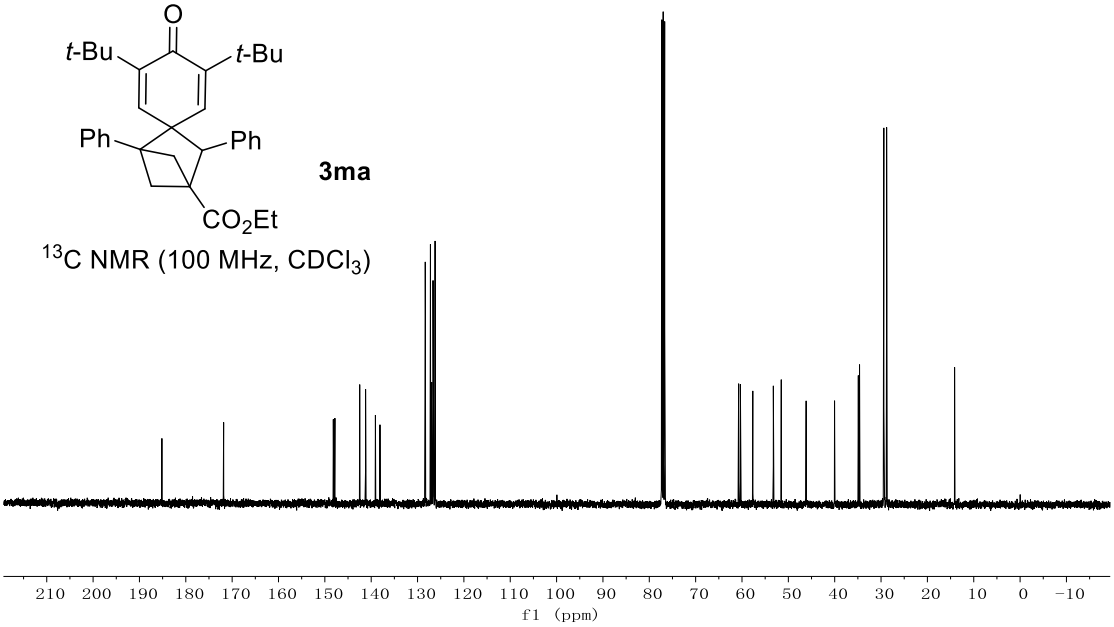
^{1}H NMR (400 MHz, $CDCl_3$)

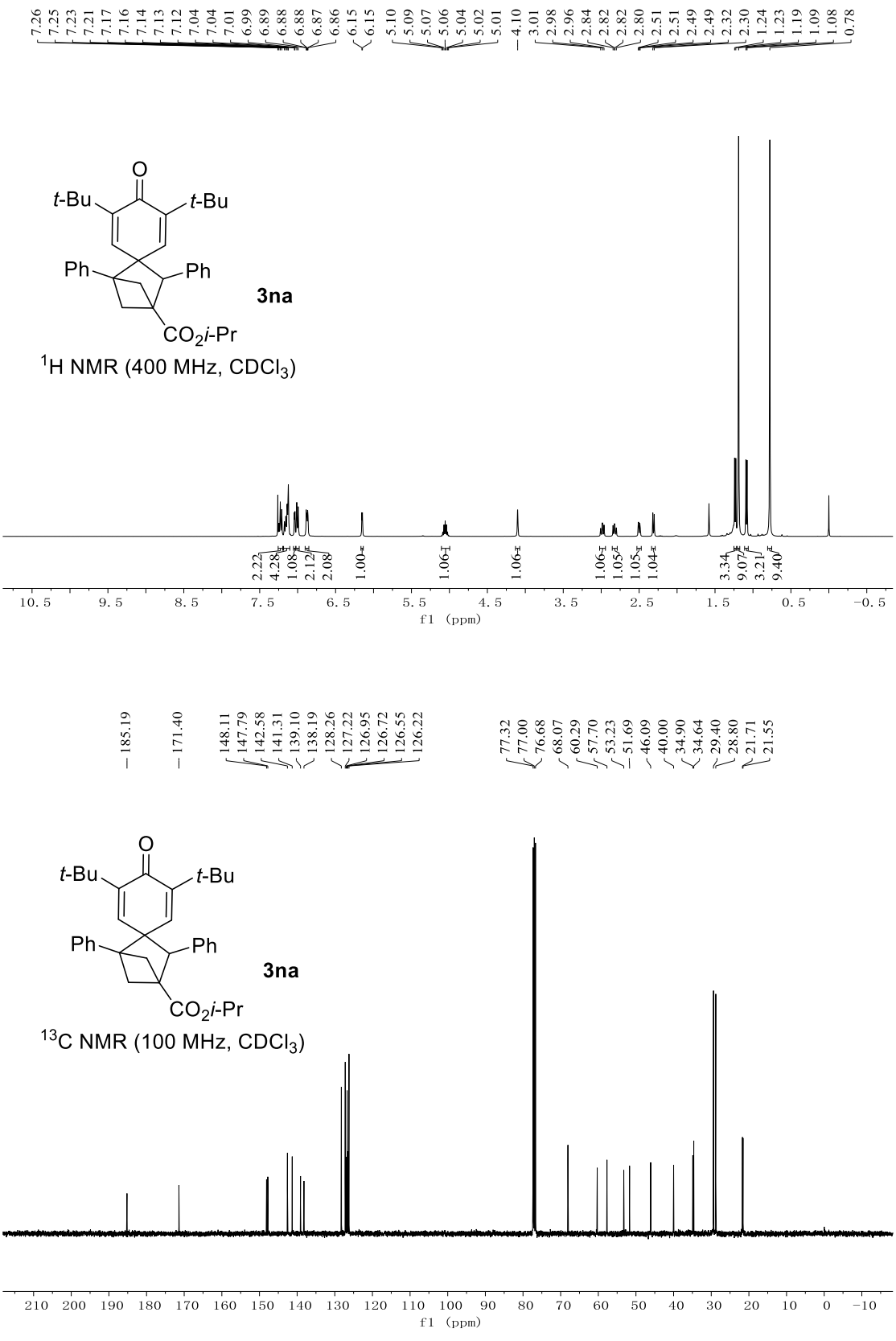


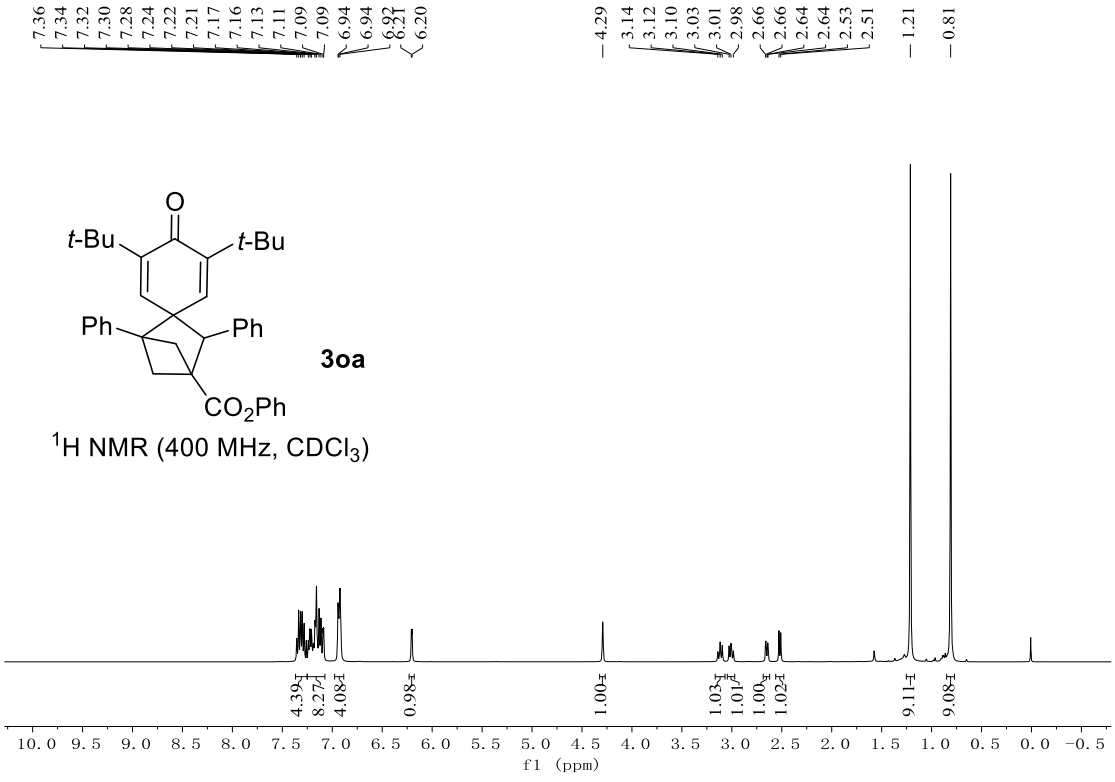


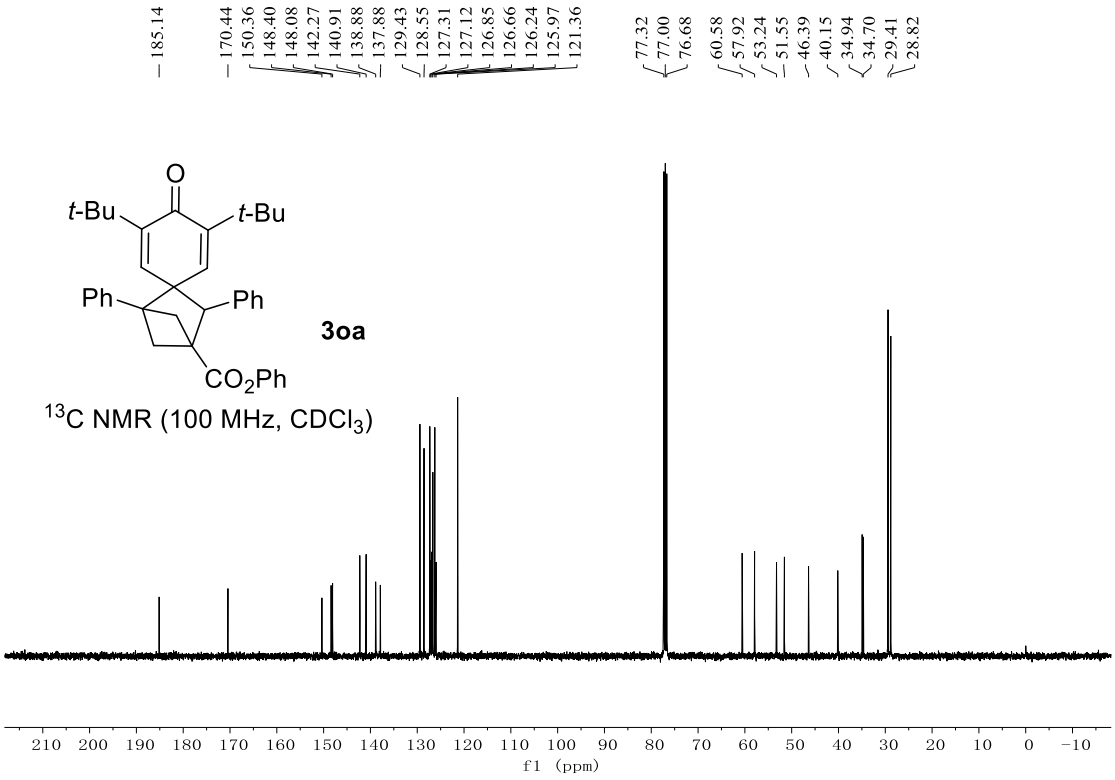
3ma

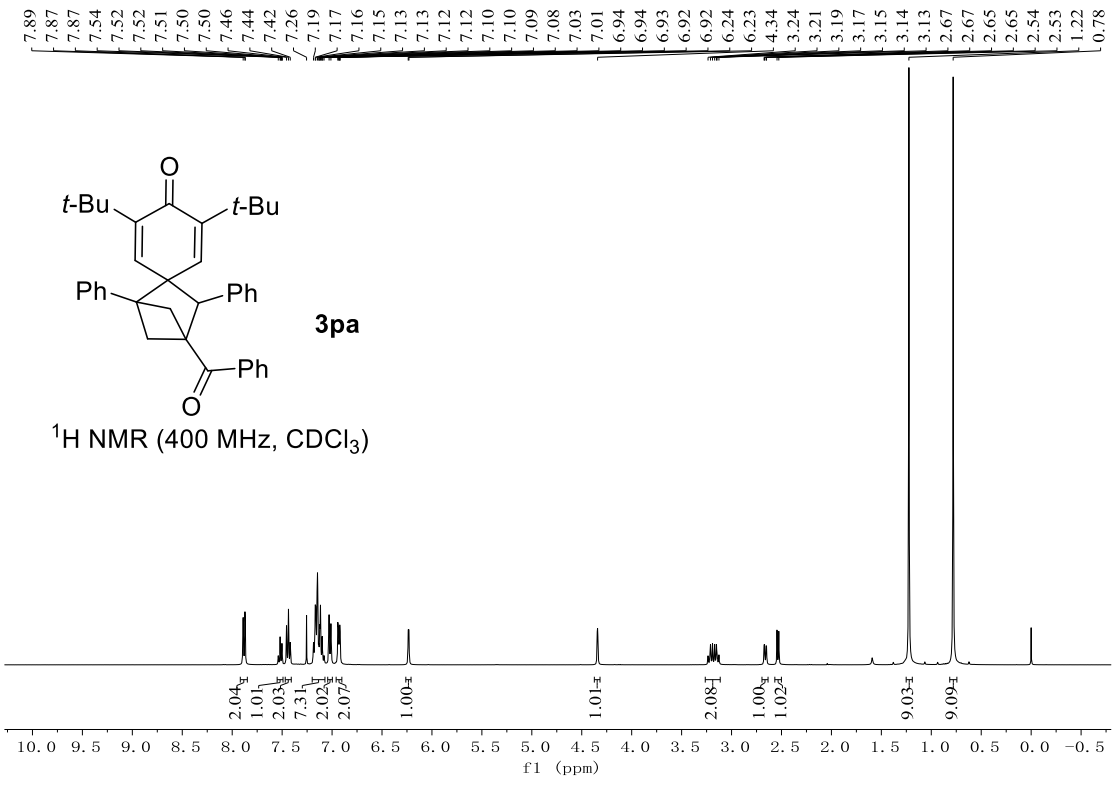
^{13}C NMR (100 MHz, $CDCl_3$)

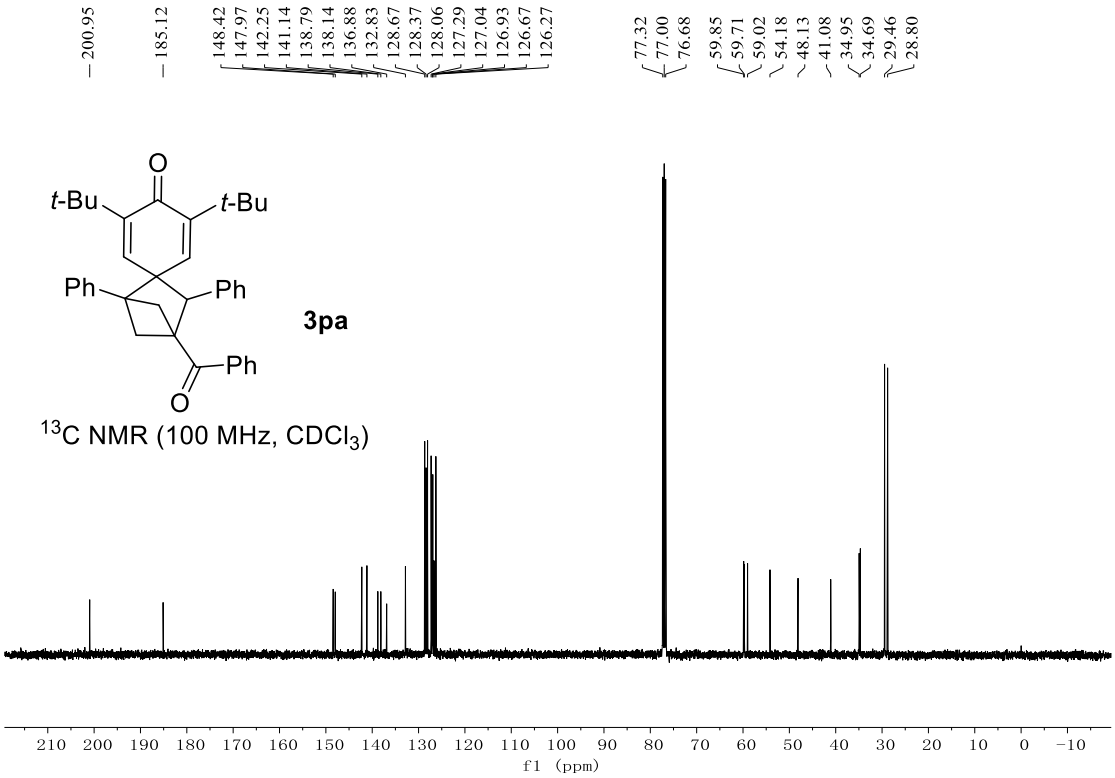


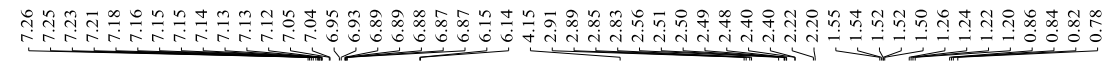

7.26 7.25 7.23 7.21 7.17 7.16 7.14 7.13 7.12 7.04 7.04 7.01 6.99 6.89 6.88 6.88 6.87 6.86 6.15 6.15 5.10 5.09 5.07 5.06 5.04 5.02 5.01 4.10 3.01 2.98 2.96 2.84 2.82 2.82 2.80 2.51 2.51 2.49 2.49 2.32 2.30 1.24 1.23 1.19 1.09 1.08 0.78
O
t-Bu
t-Bu
Ph
Ph
CO2i-Pr
3na
1H NMR (400 MHz, CDCl3)
2.22 4.28 1.08 2.12 2.08 1.00 1.06 1.06 1.06 1.05 1.05 1.04 3.34 9.07 3.21 9.40
10.5 9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5 −0.5
f1 (ppm)
185.19 171.40 148.11 147.79 142.58 141.31 139.10 138.19 128.26 127.22 126.95 126.72 126.55 126.22 77.32 77.00 76.68 68.07 60.29 57.70 53.23 51.69 46.09 40.00 34.90 34.64 29.40 28.80 21.71 21.55
O
t-Bu
t-Bu
Ph
Ph
CO2i-Pr
3na
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

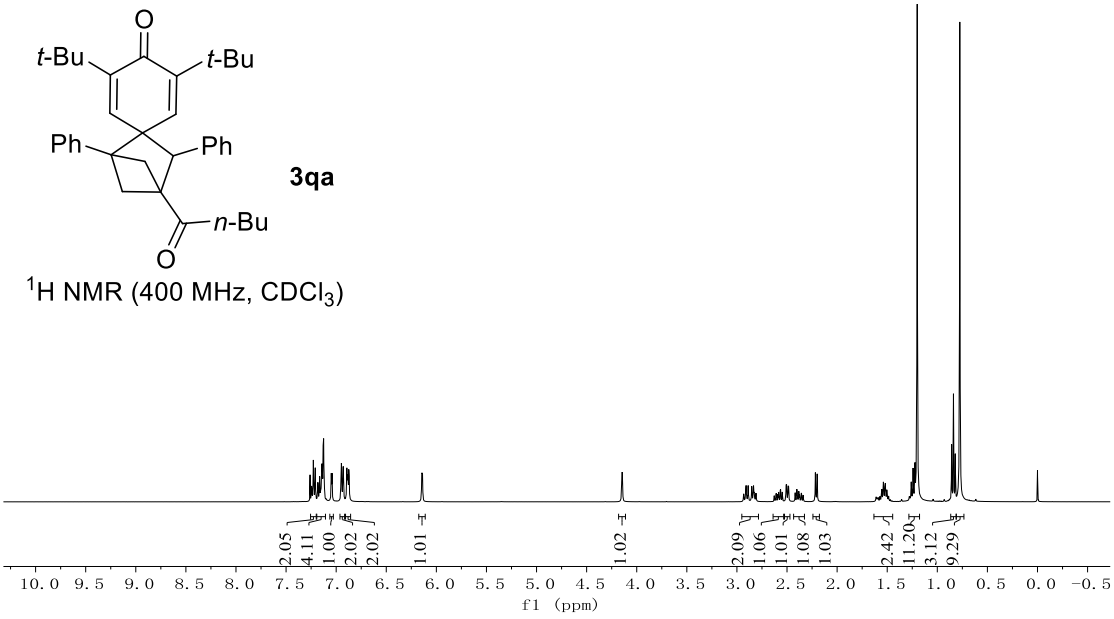

7.36
7.34
7.32
7.30
7.28
7.24
7.22
7.21
7.17
7.16
7.13
7.11
7.09
7.09
6.94
6.94
6.92
6.21
6.20
4.29
3.14
3.12
3.10
3.03
3.01
2.98
2.66
2.66
2.64
2.64
2.53
2.51
1.21
0.81
O
t-Bu
t-Bu
Ph
Ph
CO2Ph
3oa
1H NMR (400 MHz, CDCl3)
4.39
8.27
4.08
0.98
1.00
1.03
1.01
1.00
1.02
9.11
9.08
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)

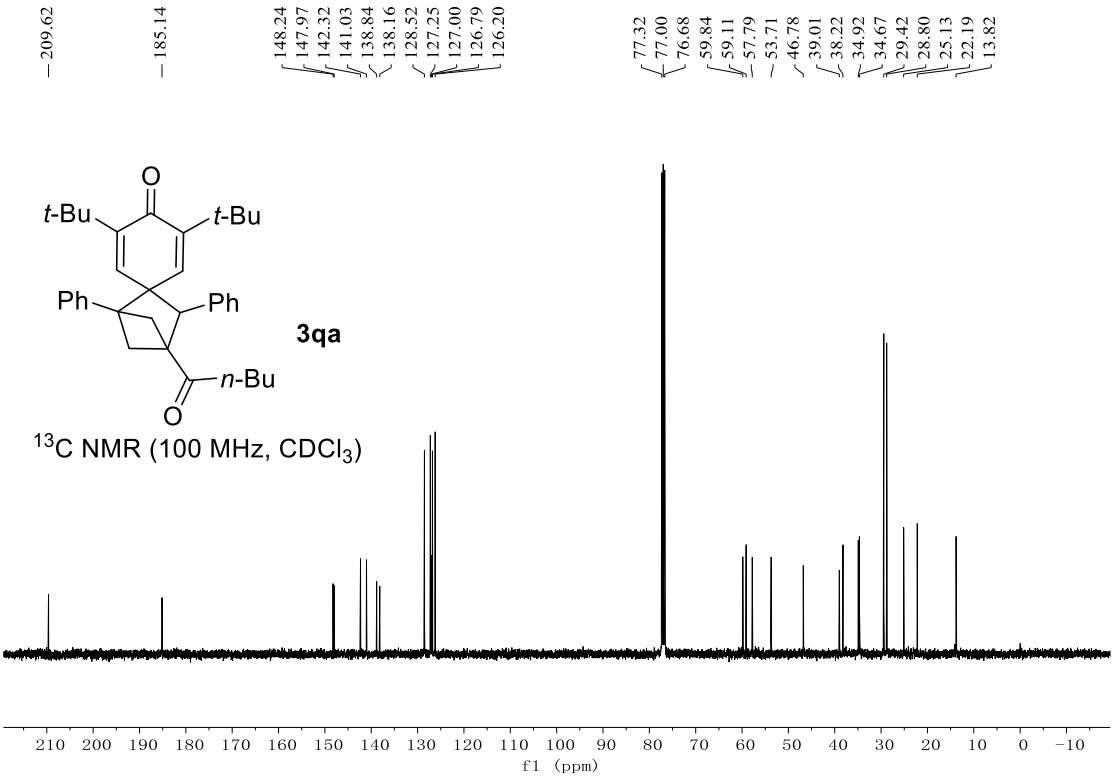

185.14
170.44
150.36
148.40
148.08
142.27
140.91
138.88
137.88
129.43
128.55
127.31
127.12
126.85
126.66
126.24
125.97
121.36
77.32
77.00
76.68
60.58
57.92
53.24
51.55
46.39
40.15
34.94
34.70
29.41
28.82
O
t-Bu
t-Bu
Ph
Ph
CO2Ph
3oa
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

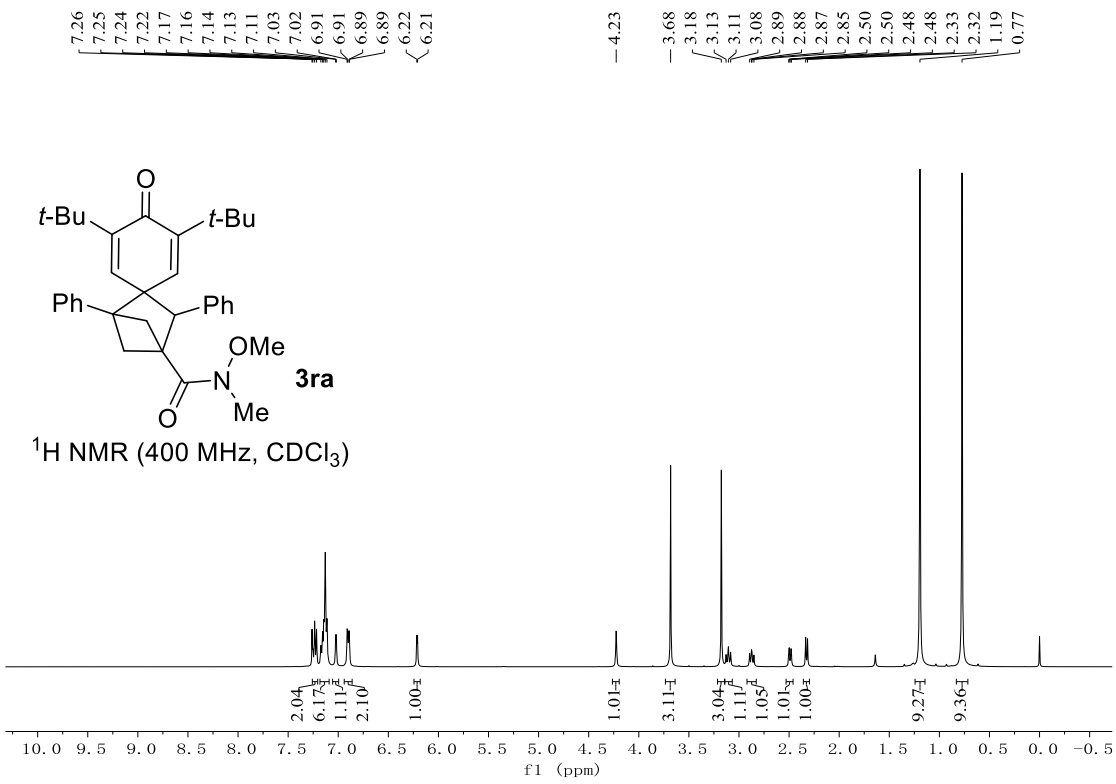

7.89 7.87 7.87 7.54 7.52 7.52 7.51 7.50 7.50 7.46 7.44 7.42 7.26 7.19 7.17 7.16 7.15 7.13 7.13 7.12 7.12 7.10 7.10 7.09 7.08 7.03 7.01 6.94 6.94 6.93 6.92 6.92 6.24 6.23 4.34 3.24 3.21 3.19 3.17 3.15 3.14 3.13 2.67 2.67 2.65 2.65 2.54 2.53 1.22 0.78
t-Bu
t-Bu
Ph
Ph
Ph
O
O
3pa
1H NMR (400 MHz, CDCl3)
2.04 1.01 2.03 7.31 2.02 2.07 1.00 1.01 2.08 1.00 1.02 9.03 9.09
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)

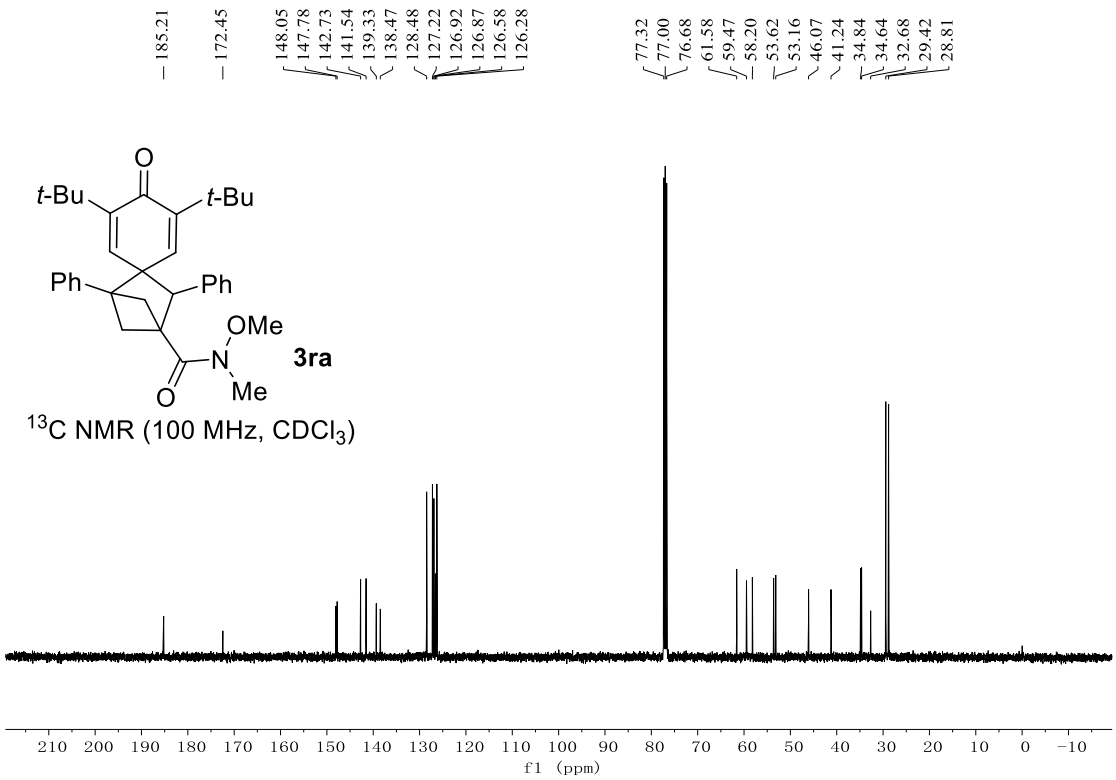

200.95
185.12
148.42 147.97 142.25 141.14 138.79 138.14 136.88 132.83 128.67 128.37 128.06 127.29 127.04 126.93 126.67 126.27
77.32 77.00 76.68
59.85 59.71 59.02 54.18 48.13 41.08 34.95 34.69 29.46 28.80
t-Bu
t-Bu
Ph
Ph
Ph
O
O
3pa
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


7.26
7.25
7.23
7.21
7.18
7.16
7.15
7.15
7.14
7.13
7.13
7.12
7.05
7.04
6.95
6.93
6.89
6.89
6.88
6.87
6.87
6.15
6.14
4.15
2.91
2.89
2.85
2.83
2.56
2.51
2.50
2.49
2.48
2.40
2.40
2.22
2.20
1.55
1.54
1.52
1.52
1.50
1.26
1.24
1.22
1.20
0.86
0.84
0.82
0.78


O
t-Bu
t-Bu
Ph
Ph
n-Bu
O
3qa
1H NMR (400 MHz, CDCl3)
2.05
4.11
1.00
2.02
2.02
1.01
1.02
2.09
1.06
1.01
1.08
1.03
2.42
11.20
3.12
9.29
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)


209.62
185.14
148.24
147.97
142.32
141.03
138.84
138.16
128.52
127.25
127.00
126.79
126.20
77.32
77.00
76.68
59.84
59.11
57.79
53.71
46.78
39.01
38.22
34.92
34.67
29.42
28.80
25.13
22.19
13.82
O
t-Bu
t-Bu
Ph
Ph
n-Bu
O
3qa
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


7.26
7.25
7.24
7.22
7.17
7.16
7.14
7.13
7.11
7.03
7.02
6.91
6.91
6.89
6.89
6.22
6.21
4.23
3.68
3.18
3.13
3.11
3.08
2.89
2.88
2.87
2.85
2.50
2.50
2.48
2.48
2.33
2.32
1.19
0.77
t-Bu
t-Bu
Ph
Ph
OMe
N
Me
O
O
3ra
1H NMR (400 MHz, CDCl3)
2.04
6.17
1.11
2.10
1.00
1.01
3.11
3.04
1.11
1.05
1.01
1.00
9.27
9.36
f1 (ppm)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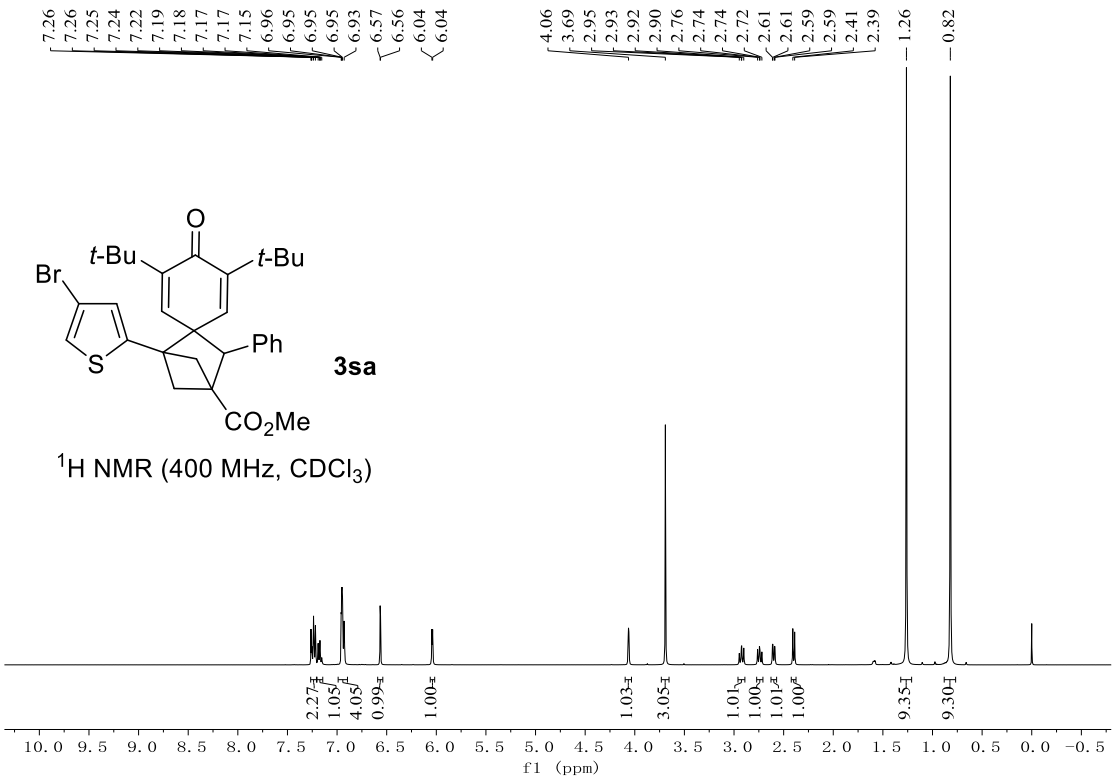
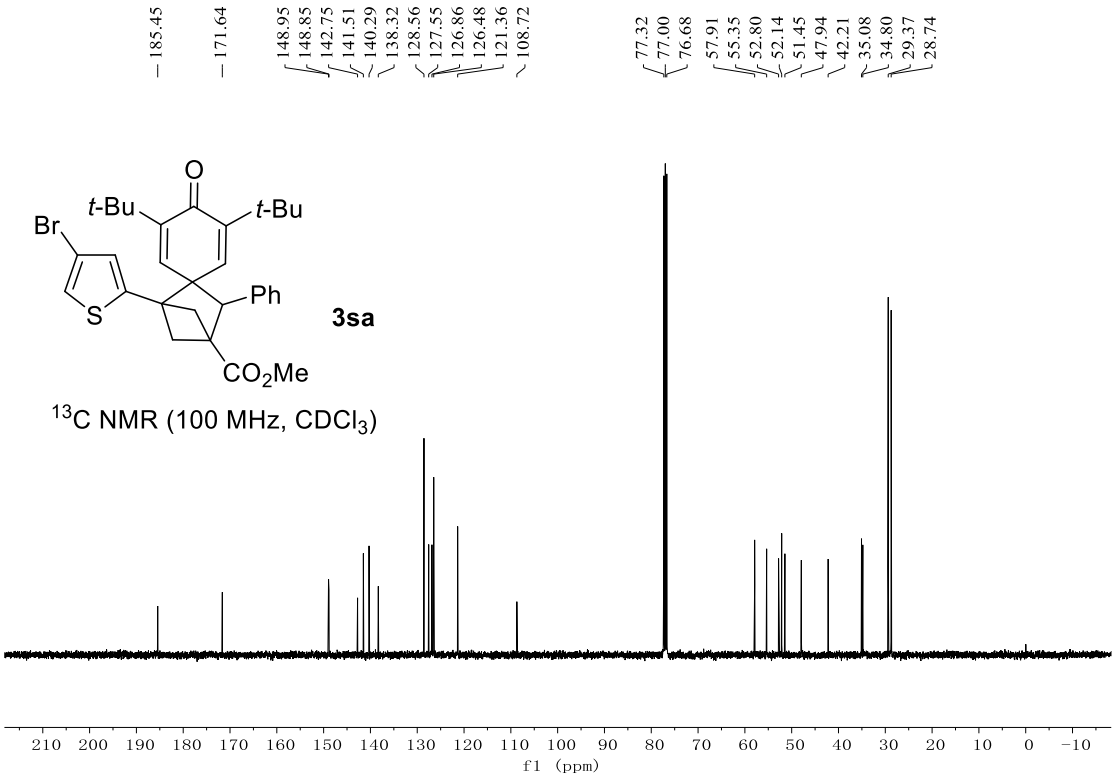
172.45
148.05
147.78
142.73
141.54
139.33
138.47
128.48
127.22
126.92
126.87
126.58
126.28
77.32
77.00
76.68
61.58
59.47
58.20
53.62
53.16
46.07
41.24
34.84
34.64
32.68
29.42
28.81
t-Bu
t-Bu
Ph
Ph
OMe
N
Me
O
O
3ra
13C NMR (100 MHz, CDCl3)
f1 (ppm)


7.26
7.26
7.25
7.24
7.22
7.19
7.18
7.17
7.17
7.15
6.96
6.95
6.95
6.93
6.57
6.56
6.04
6.04
4.06
3.69
2.95
2.93
2.92
2.90
2.76
2.74
2.74
2.72
2.61
2.61
2.59
2.59
2.41
2.39
1.26
0.82
O
t-Bu
t-Bu
Br
Ph
S
CO2Me
3sa
1H NMR (400 MHz, CDCl3)
2.27
1.05
4.05
0.99
1.00
1.03
3.05
1.01
1.00
1.01
1.00
9.35
9.30
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)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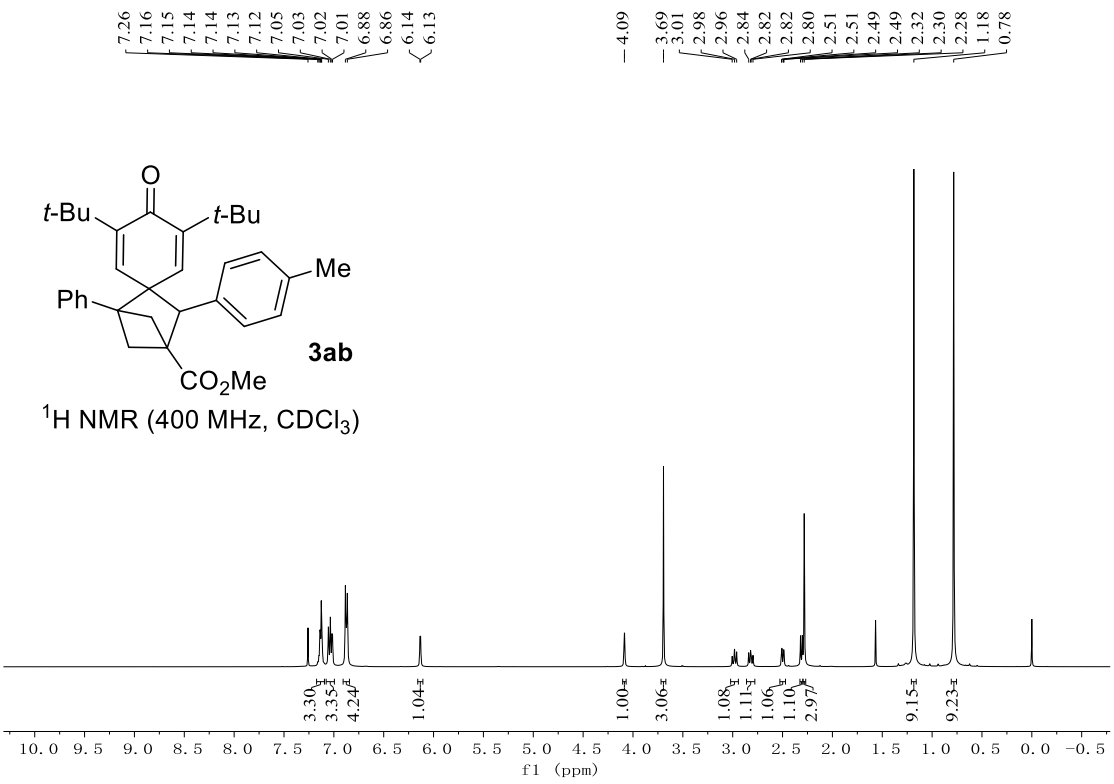
171.64
148.95
148.85
142.75
141.51
140.29
138.32
128.56
127.55
126.86
126.48
121.36
108.72
77.32
77.00
76.68
57.91
55.35
52.80
52.14
51.45
47.94
42.21
35.08
34.80
29.37
28.74
O
t-Bu
t-Bu
Br
Ph
S
CO2Me
3sa
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)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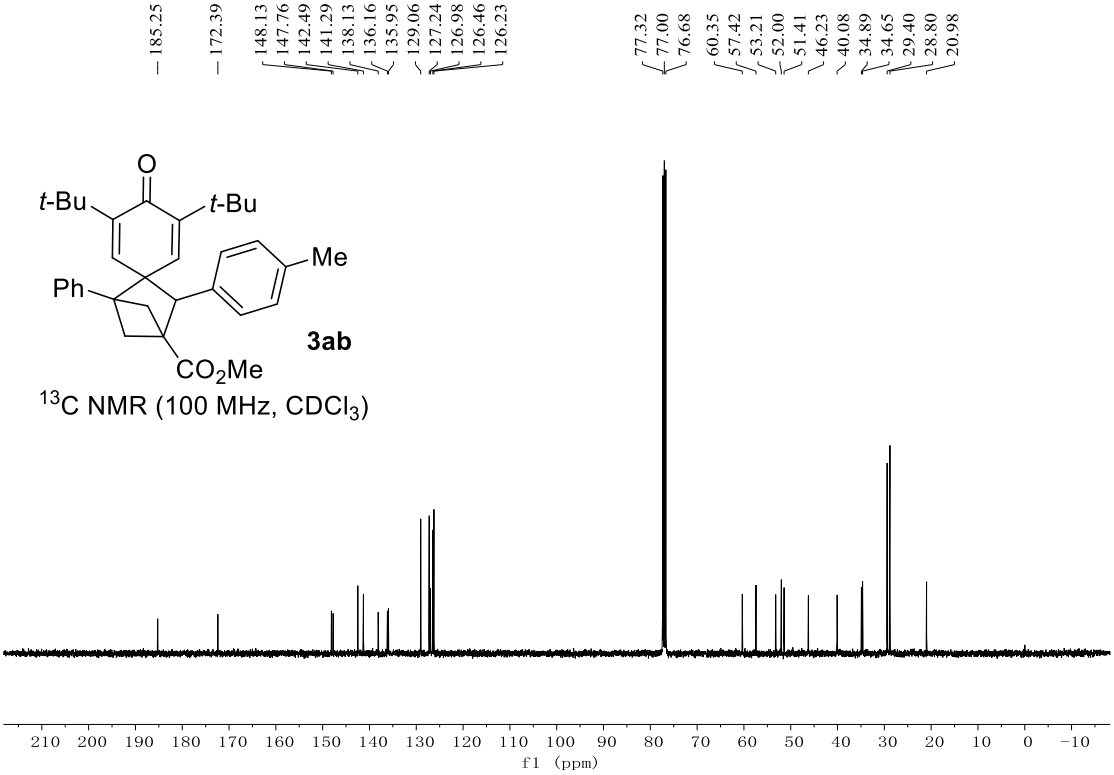
7.16
7.15
7.14
7.14
7.13
7.12
7.05
7.03
7.02
7.01
6.88
6.86
6.14
6.13
4.09
3.69
3.01
2.98
2.96
2.84
2.82
2.82
2.80
2.51
2.51
2.49
2.49
2.32
2.30
2.28
1.18
0.78
O
t-Bu
t-Bu
Me
Ph
CO2Me
3ab
1H NMR (400 MHz, CDCl3)
3.30
3.35
4.24
1.04
1.00
3.06
1.08
1.11
1.06
1.10
2.97
9.15
9.23
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)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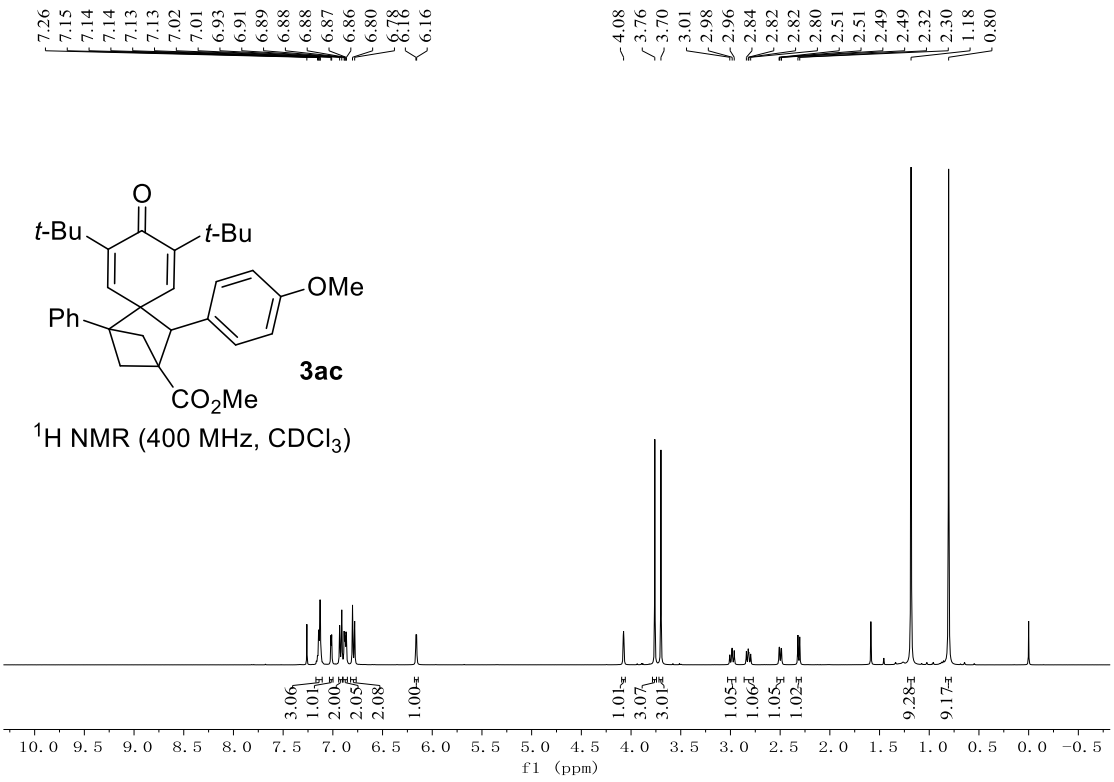
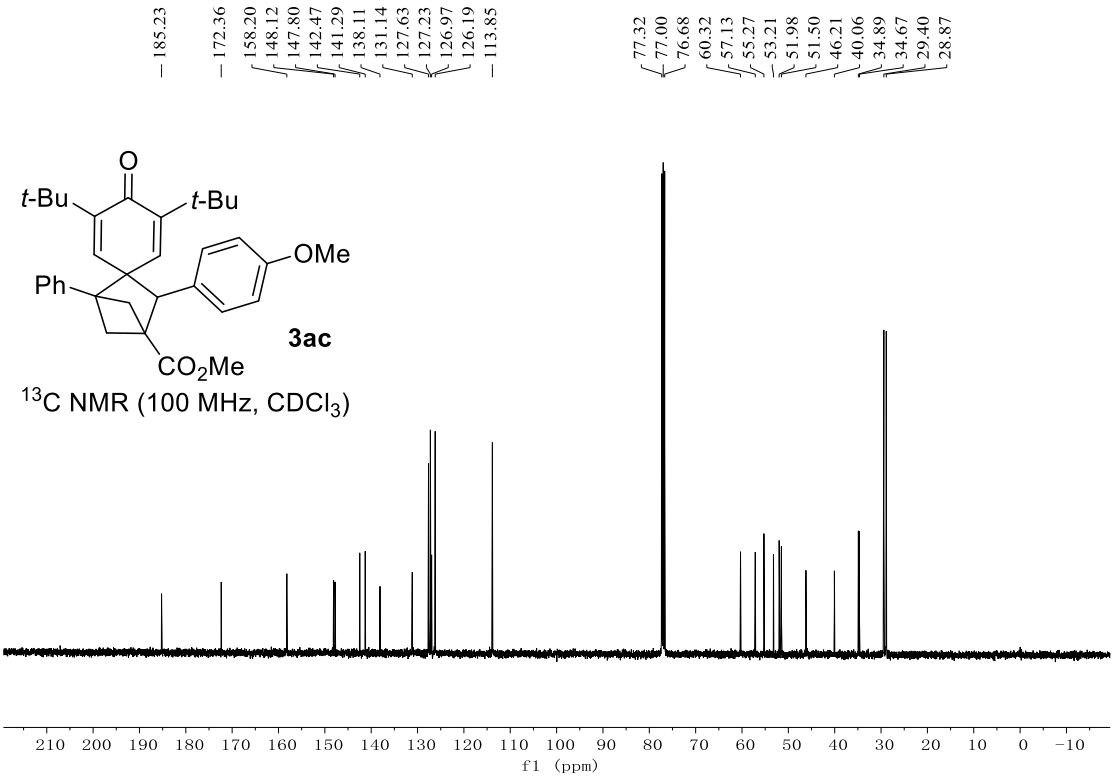
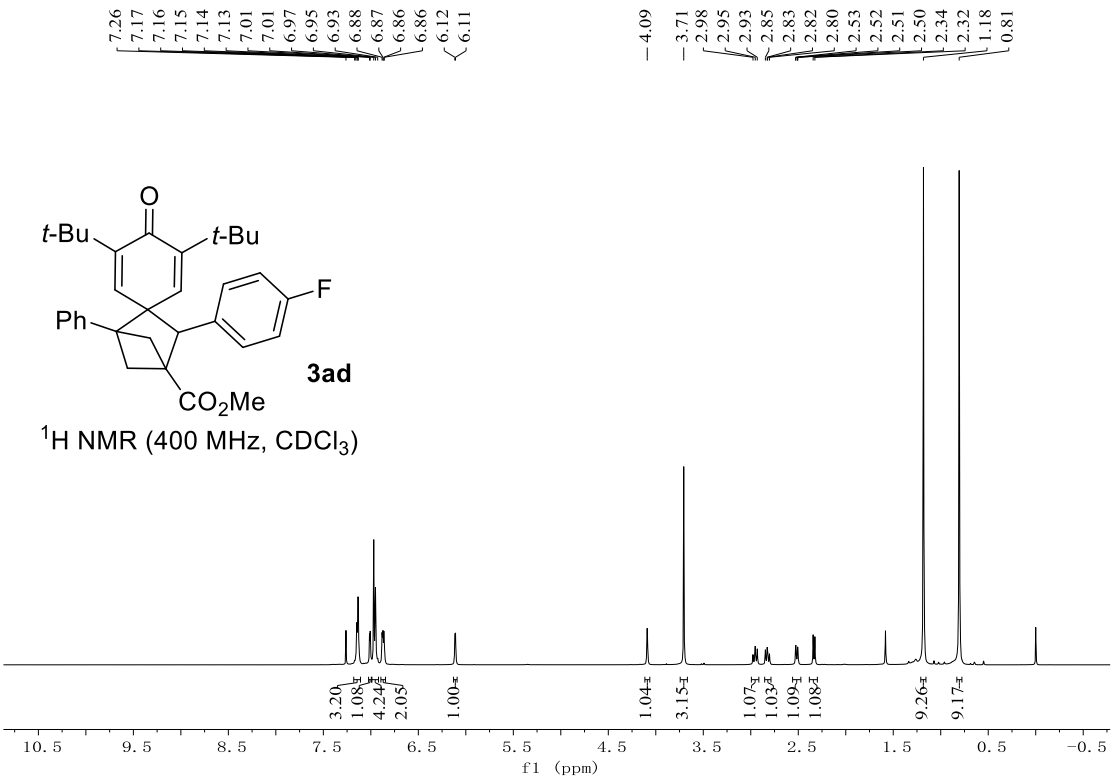
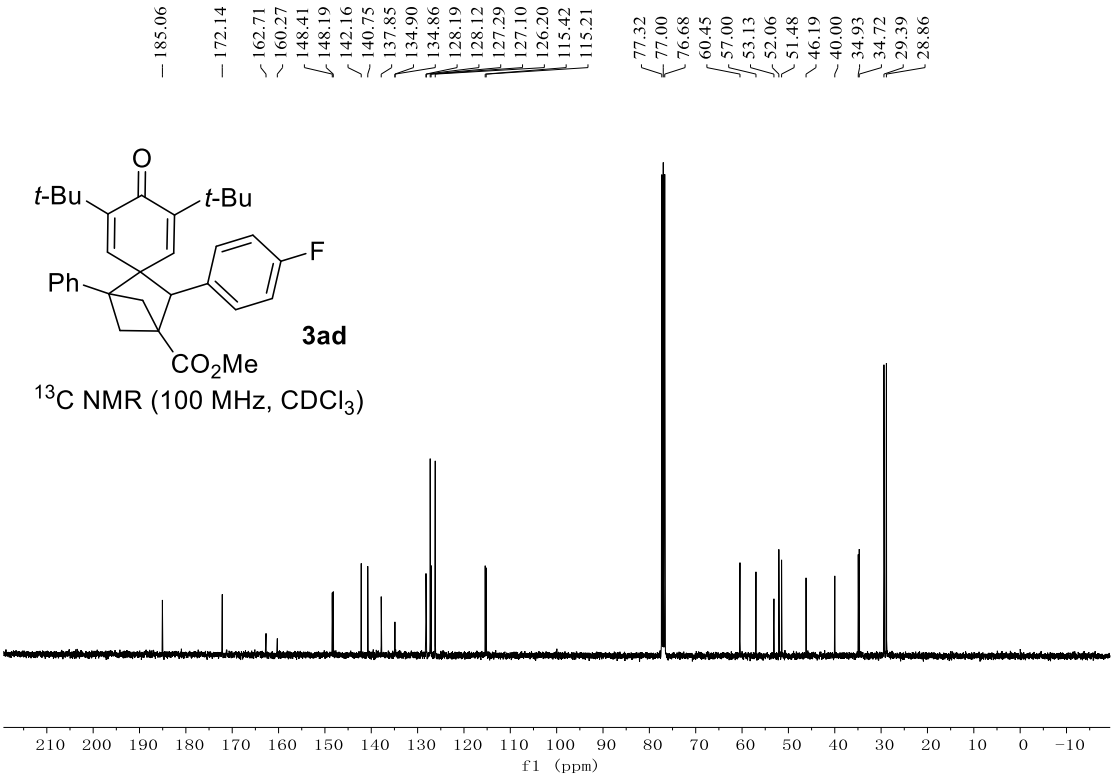
172.39
148.13
147.76
142.49
141.29
138.13
136.16
135.95
129.06
127.24
126.98
126.46
126.23
77.32
77.00
76.68
60.35
57.42
53.21
52.00
51.41
46.23
40.08
34.89
34.65
29.40
28.80
20.98
O
t-Bu
t-Bu
Me
Ph
CO2Me
3ab
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


7.26 7.15 7.14 7.14 7.13 7.13 7.02 7.01 6.93 6.91 6.89 6.88 6.88 6.87 6.86 6.80 6.78 6.16
4.08 3.76 3.70 3.01 2.98 2.96 2.84 2.82 2.82 2.80 2.51 2.51 2.49 2.49 2.32 2.30 1.18 0.80
O
t-Bu
t-Bu
OMe
Ph
CO2Me
3ac
1H NMR (400 MHz, CDCl3)
3.06 1.01 2.00 2.05 2.08 1.00 1.01 3.07 3.01 1.05 1.06 1.05 1.02 9.28 9.17
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)

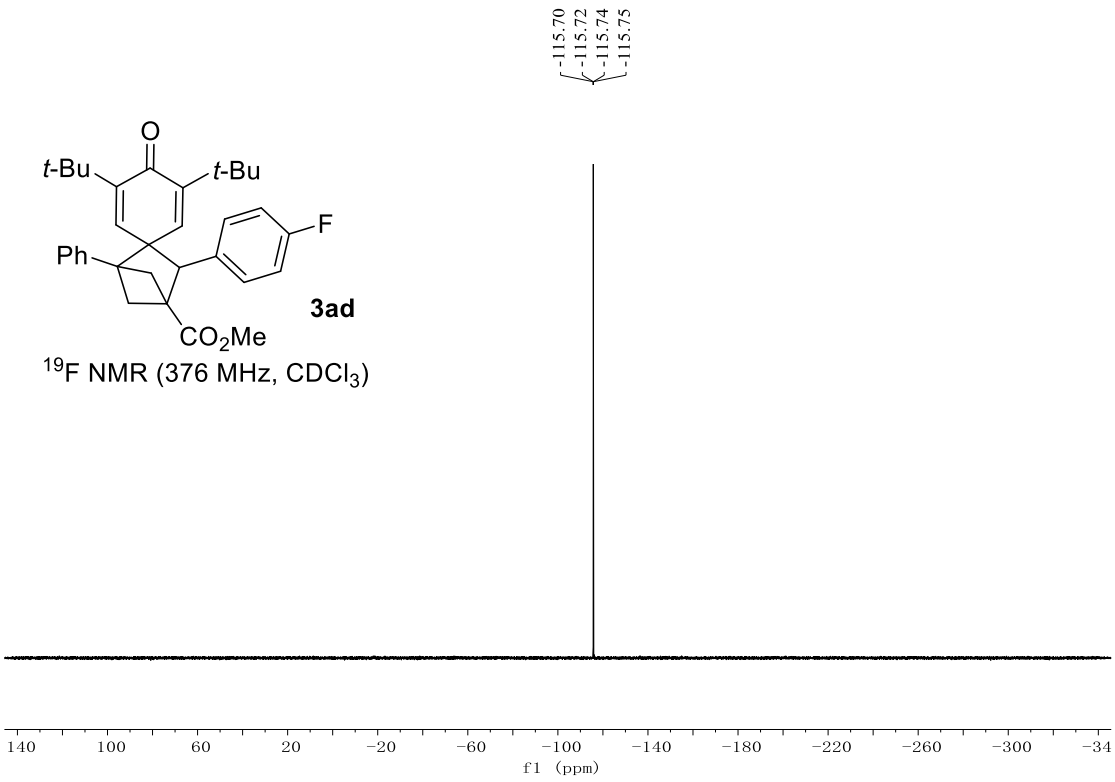

185.23 172.36 158.20 148.12 147.80 142.47 141.29 138.11 131.14 127.63 127.23 126.97 126.19 113.85
77.32 77.00 76.68 60.32 57.13 55.27 53.21 51.98 51.50 46.21 40.06 34.89 34.67 29.40 28.87
O
t-Bu
t-Bu
OMe
Ph
CO2Me
3ac
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


7.26
7.17
7.16
7.15
7.14
7.13
7.01
7.01
6.97
6.95
6.93
6.88
6.87
6.86
6.86
6.12
6.11
4.09
3.71
2.98
2.95
2.93
2.85
2.83
2.82
2.80
2.53
2.52
2.51
2.50
2.34
2.32
1.18
0.81
O
t-Bu
t-Bu
F
Ph
CO2Me
3ad
1H NMR (400 MHz, CDCl3)
3.20
1.08
4.24
2.05
1.00
1.04
3.15
1.07
1.03
1.09
1.08
9.26
9.17
10.5 9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5 −0.5
f1 (ppm)


185.06
172.14
162.71
160.27
148.41
148.19
142.16
140.75
137.85
134.90
134.86
128.19
128.12
127.29
127.10
126.20
115.42
115.21
77.32
77.00
76.68
60.45
57.00
53.13
52.06
51.48
46.19
40.00
34.93
34.72
29.39
28.86
O
t-Bu
t-Bu
F
Ph
CO2Me
3ad
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

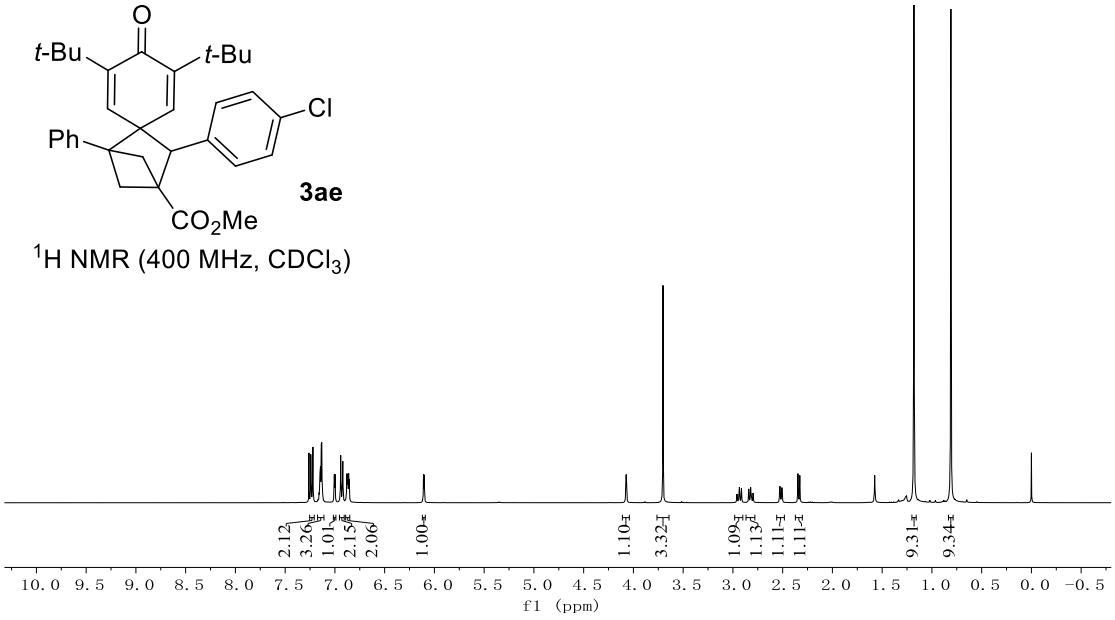
3ad

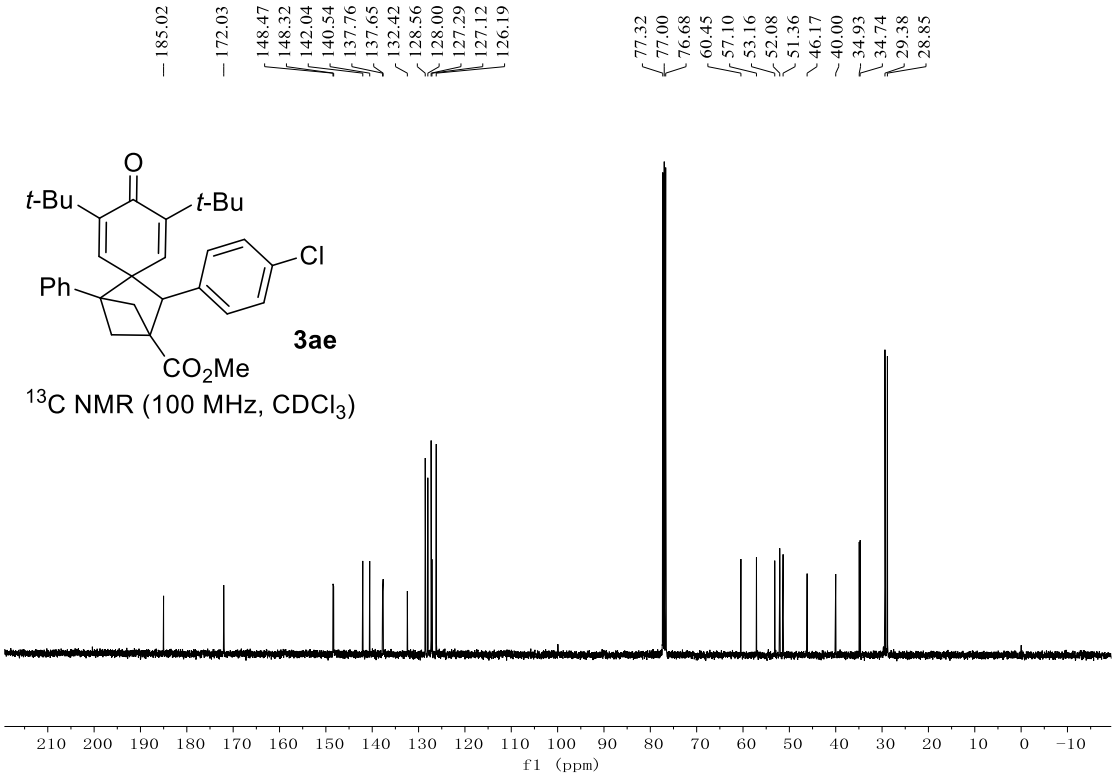
^{19}F NMR (376 MHz, $CDCl_3$)



3ae

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

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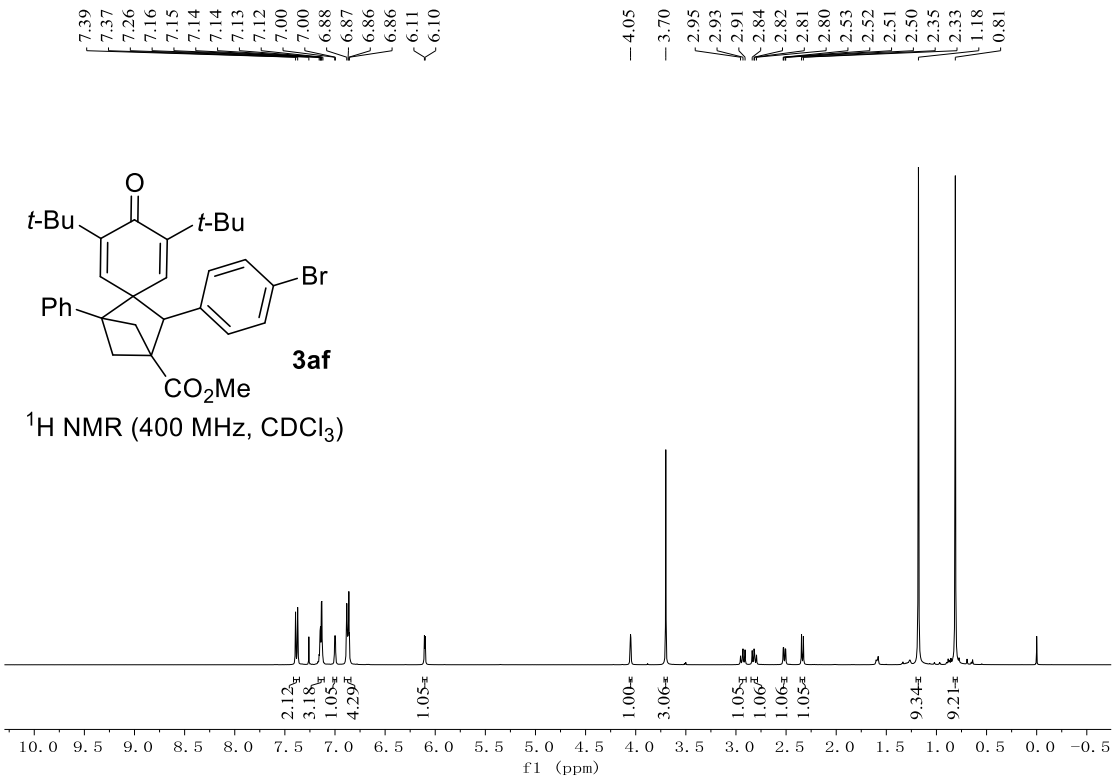
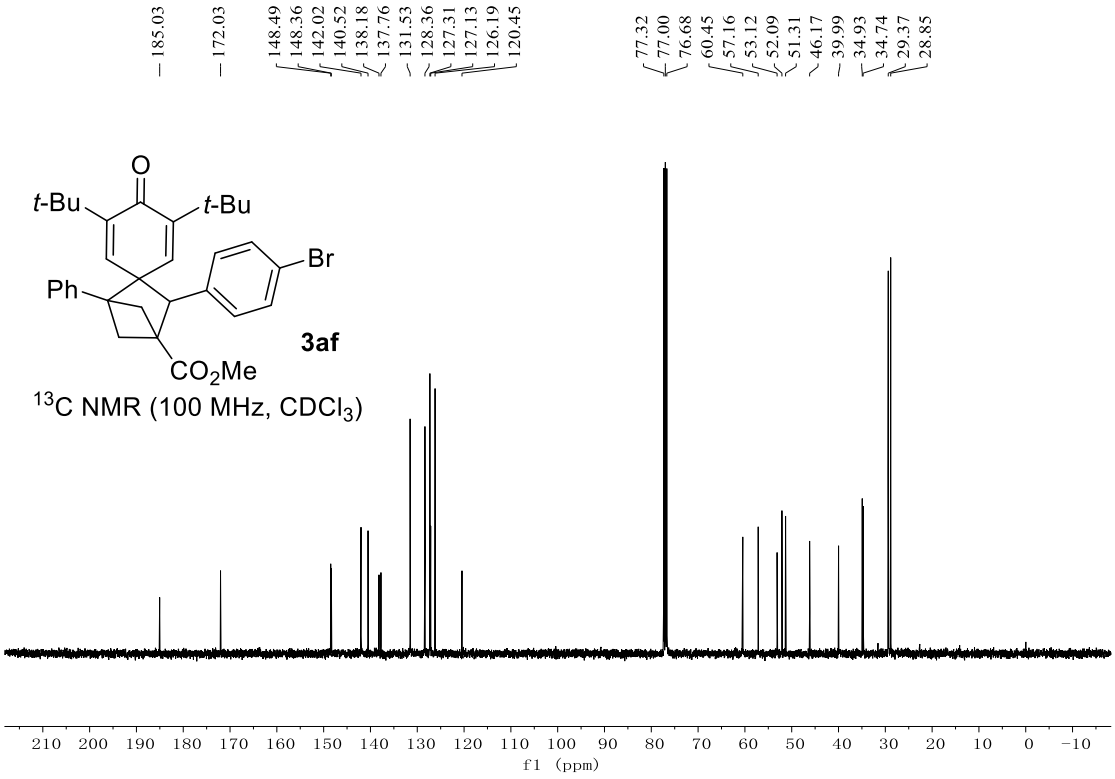
172.03
148.47
148.32
142.04
140.54
137.76
137.65
132.42
128.56
128.00
127.29
127.12
126.19
77.32
77.00
76.68
60.45
57.10
53.16
52.08
51.36
46.17
40.00
34.93
34.74
29.38
28.85
O
t-Bu
t-Bu
Cl
Ph
CO2Me
3ae
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


7.39
7.37
7.26
7.16
7.15
7.14
7.14
7.13
7.12
7.00
7.00
6.88
6.87
6.86
6.86
6.11
6.10
4.05
3.70
2.95
2.93
2.91
2.84
2.82
2.81
2.80
2.53
2.52
2.51
2.50
2.35
2.33
1.18
0.81
O
t-Bu
t-Bu
Br
Ph
CO2Me
3af
1H NMR (400 MHz, CDCl3)
2.12
3.18
1.05
4.29
1.05
1.00
3.06
1.05
1.06
1.06
1.05
9.34
9.21
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)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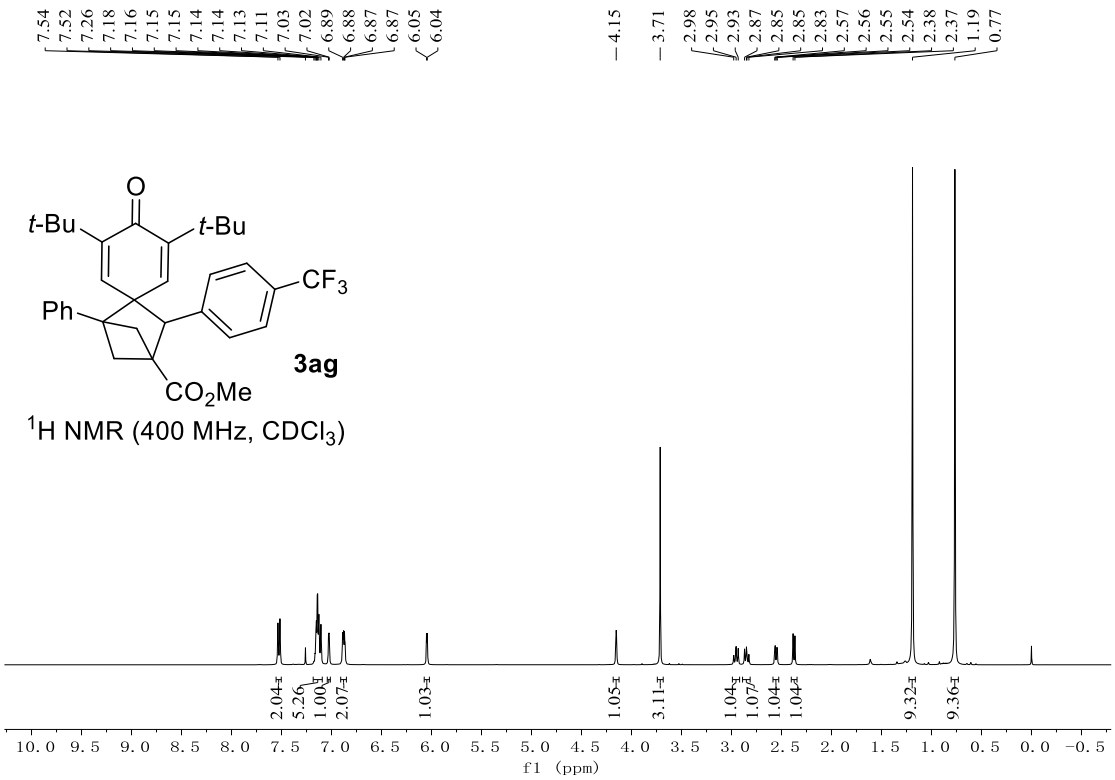
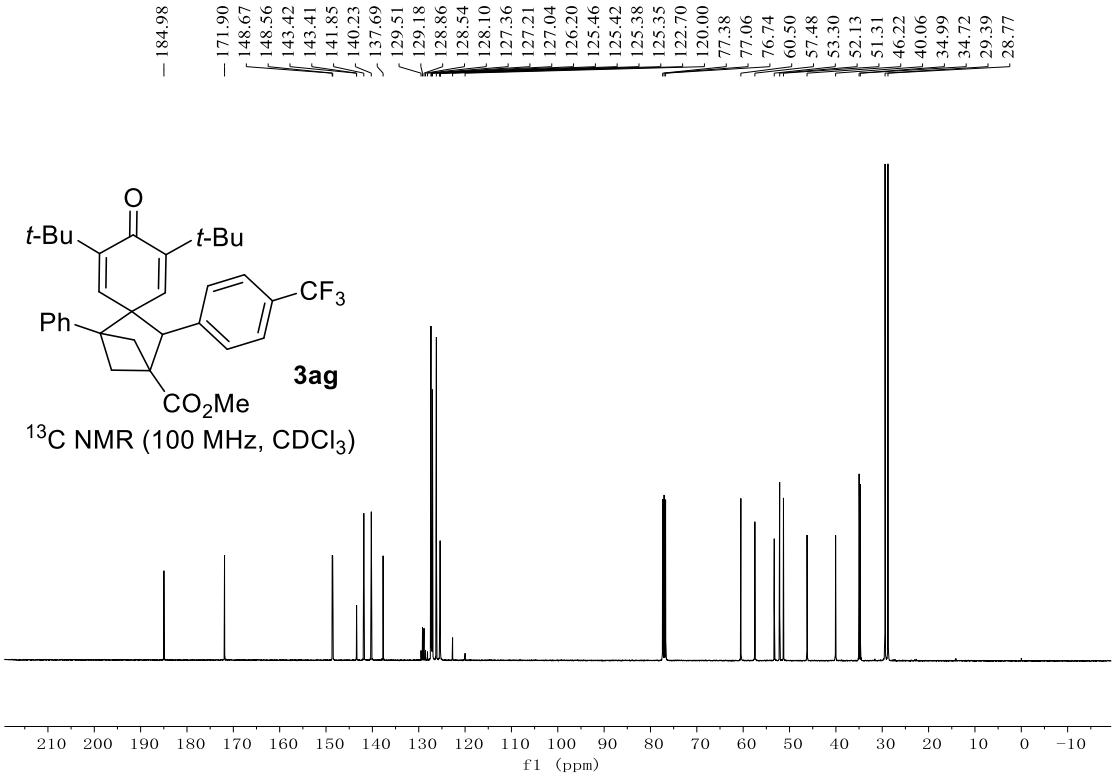
172.03
148.49
148.36
142.02
140.52
138.18
137.76
131.53
128.36
127.31
127.13
126.19
120.45
77.32
77.00
76.68
60.45
57.16
53.12
52.09
51.31
46.17
39.99
34.93
34.74
29.37
28.85
O
t-Bu
t-Bu
Br
Ph
CO2Me
3af
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


7.54
7.52
7.26
7.18
7.16
7.15
7.15
7.14
7.14
7.13
7.11
7.03
7.02
6.89
6.88
6.87
6.87
6.05
6.04
4.15
3.71
2.98
2.95
2.93
2.87
2.85
2.85
2.83
2.57
2.56
2.55
2.54
2.38
2.37
1.19
0.77
O
t-Bu
t-Bu
CF3
Ph
CO2Me
3ag
1H NMR (400 MHz, CDCl3)
2.04
5.26
1.00
2.07
1.03
1.05
3.11
1.04
1.07
1.04
1.04
9.32
9.36
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)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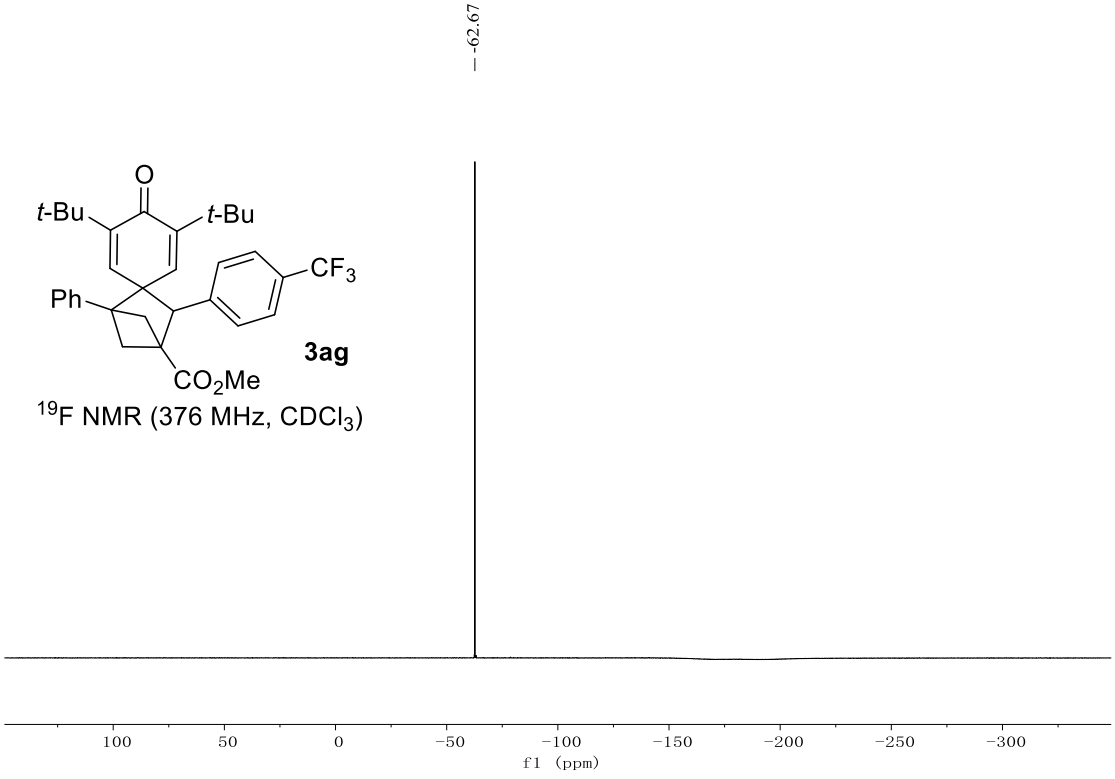
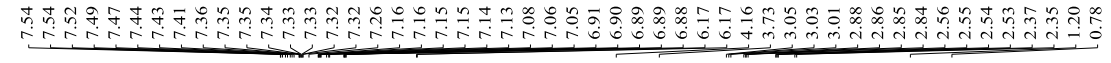
171.90
148.67
148.56
143.42
143.41
141.85
140.23
137.69
129.51
129.18
128.86
128.54
128.10
127.36
127.21
127.04
126.20
125.46
125.42
125.38
125.35
122.70
120.00
77.38
77.06
76.74
60.50
57.48
53.30
52.13
51.31
46.22
40.06
34.99
34.72
29.39
28.77
O
t-Bu
t-Bu
CF3
Ph
CO2Me
3ag
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


-62.67
O
t-Bu
t-Bu
CF3
Ph
CO2Me
3ag
19F NMR (376 MHz, CDCl3)
100 50 0 −50 −100 −150 −200 −250 −300
f1 (ppm)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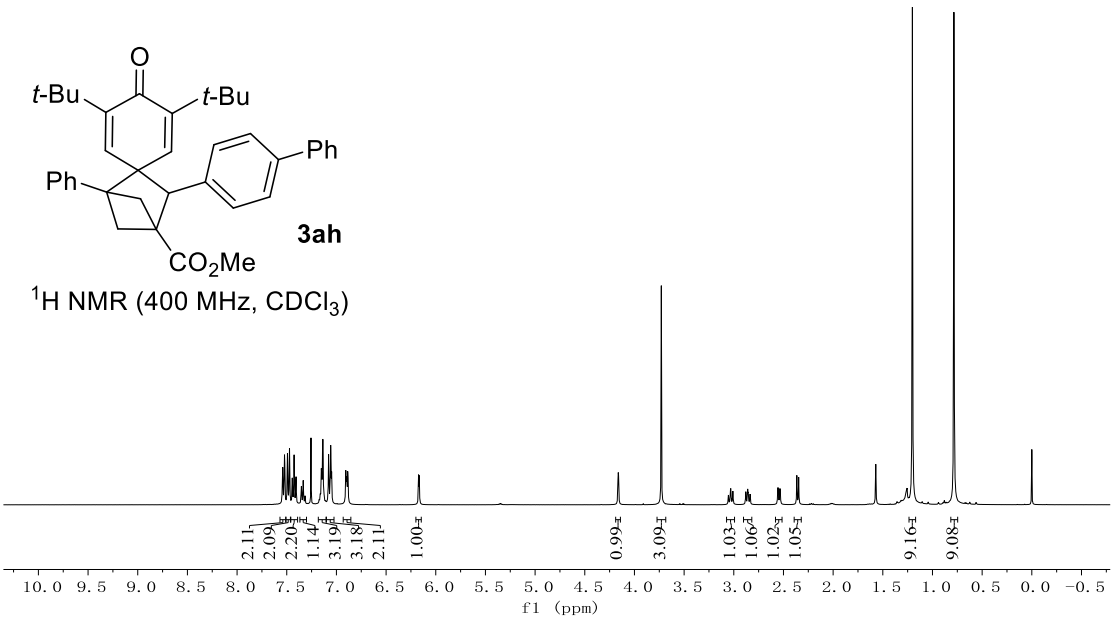
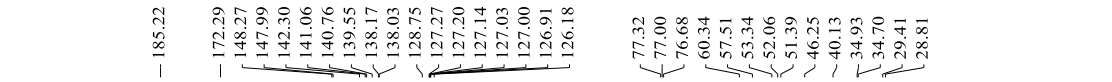
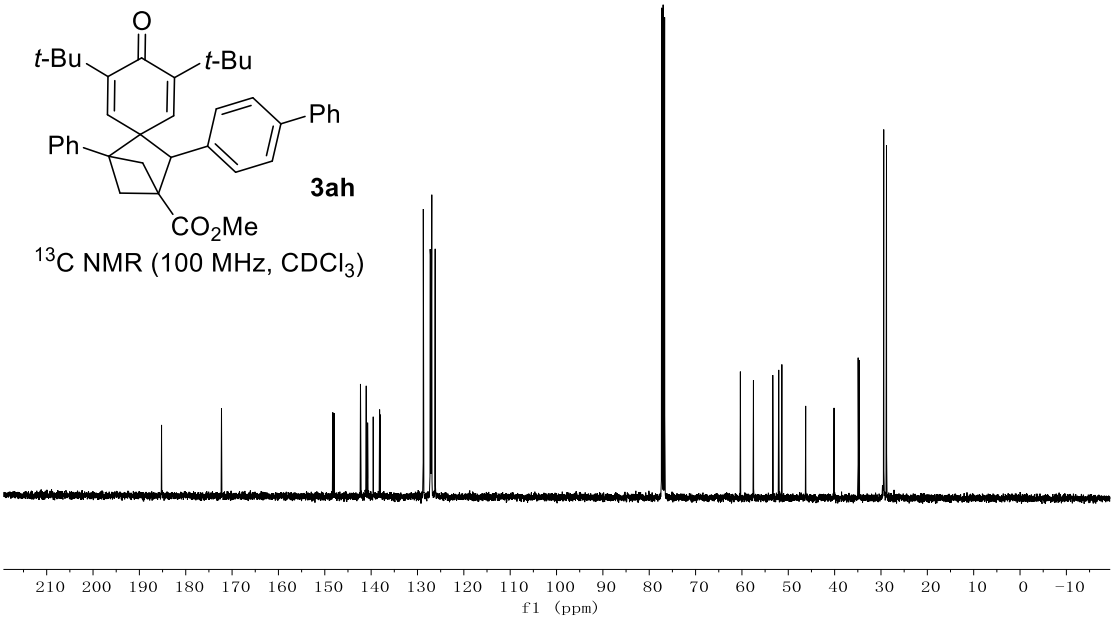
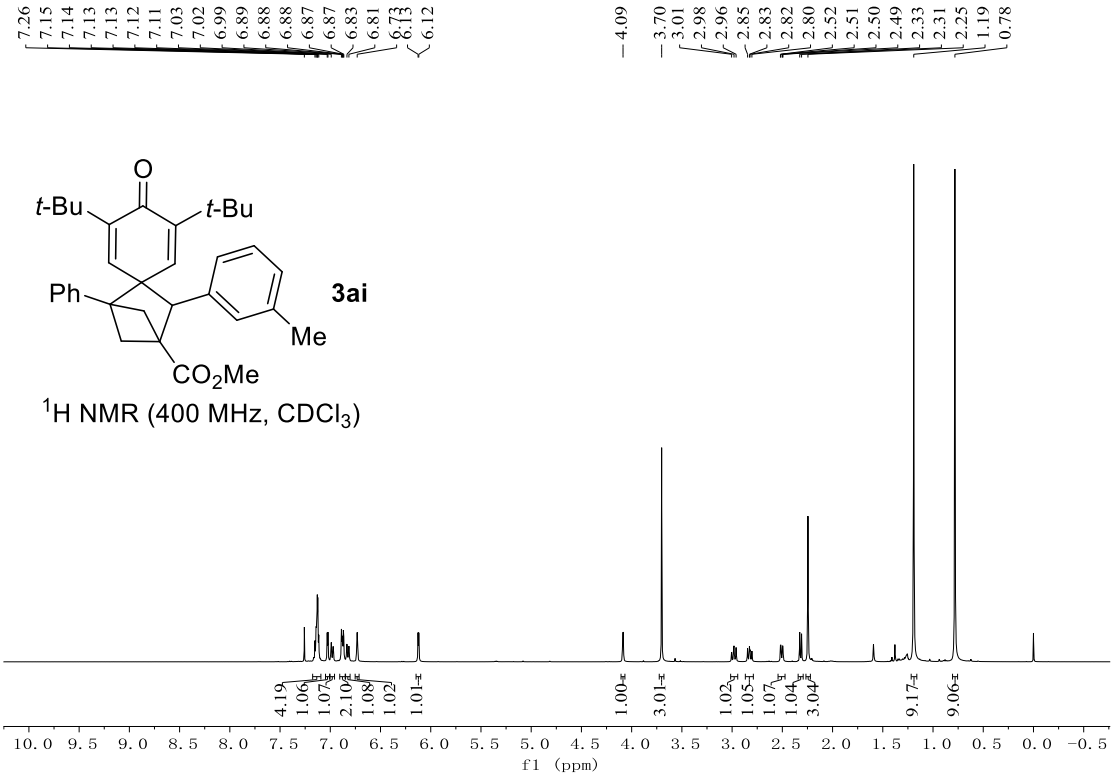
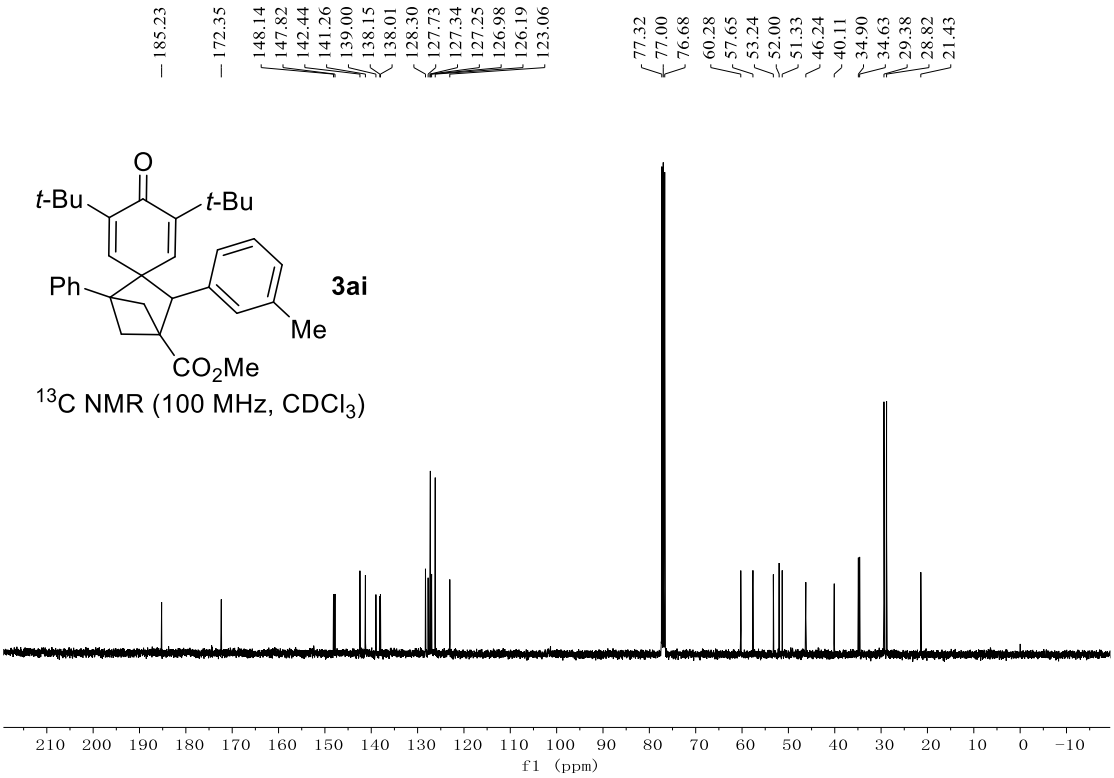
7.54
7.52
7.49
7.47
7.44
7.43
7.41
7.36
7.35
7.35
7.34
7.33
7.33
7.32
7.32
7.26
7.16
7.16
7.15
7.15
7.14
7.13
7.08
7.06
7.05
6.91
6.90
6.89
6.89
6.88
6.17
6.17
4.16
3.73
3.05
3.03
3.01
2.88
2.86
2.85
2.84
2.56
2.55
2.54
2.53
2.37
2.35
1.20
0.78

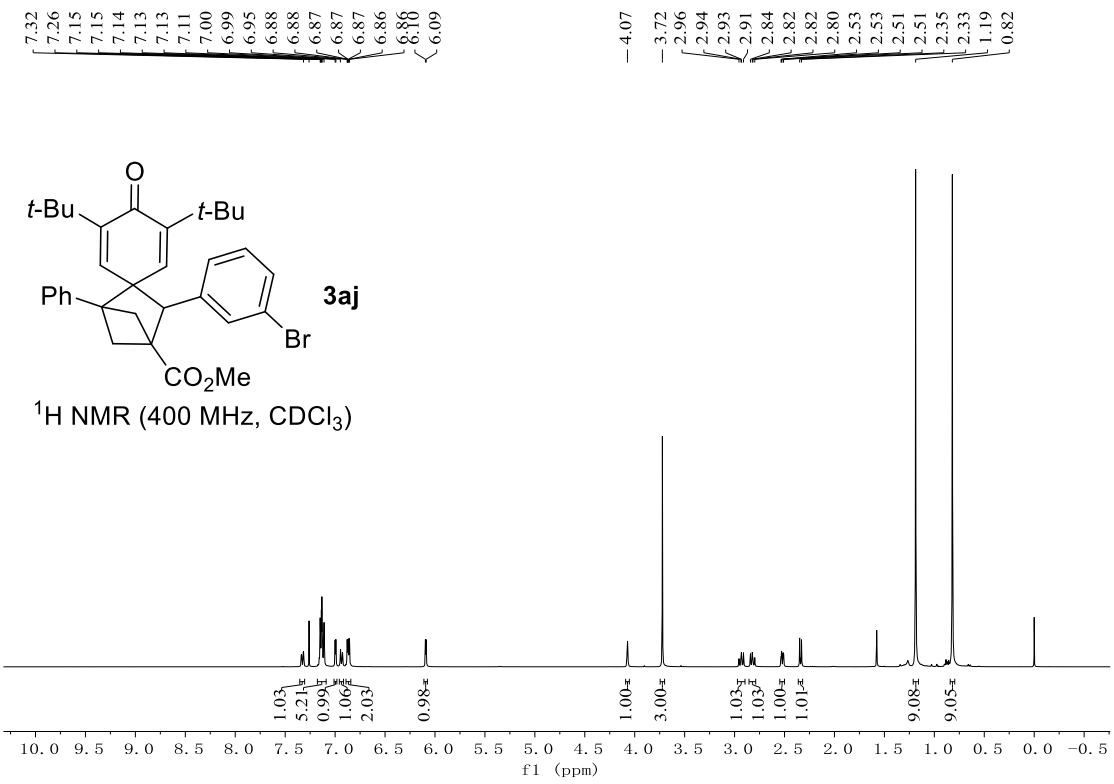

O
t-Bu
t-Bu
Ph
Ph
CO2Me
3ah
1H NMR (400 MHz, CDCl3)
2.11
2.09
2.20
1.14
3.19
3.18
2.11
1.00
0.99
3.09
1.03
1.06
1.02
1.05
9.16
9.08
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)


185.22
172.29
148.27
147.99
142.30
141.06
140.76
139.55
138.17
138.03
128.75
127.27
127.20
127.14
127.03
127.00
126.91
126.18
77.32
77.00
76.68
60.34
57.51
53.34
52.06
51.39
46.25
40.13
34.93
34.70
29.41
28.81


O
t-Bu
t-Bu
Ph
Ph
CO2Me
3ah
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


7.26
7.15
7.14
7.13
7.13
7.12
7.11
7.03
7.02
6.99
6.89
6.88
6.88
6.87
6.87
6.83
6.81
6.73
6.13
6.12
4.09
3.70
3.01
2.98
2.96
2.85
2.83
2.82
2.80
2.52
2.51
2.50
2.49
2.33
2.31
2.25
1.19
0.78
O
t-Bu
t-Bu
Ph
Me
CO2Me
3ai
1H NMR (400 MHz, CDCl3)
4.19
1.06
1.07
2.10
1.08
1.02
1.01
1.00
3.01
1.02
1.05
1.07
1.04
3.04
9.17
9.06
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)


185.23
172.35
148.14
147.82
142.44
141.26
139.00
138.15
138.01
128.30
127.73
127.34
127.25
126.98
126.19
123.06
77.32
77.00
76.68
60.28
57.65
53.24
52.00
51.33
46.24
40.11
34.90
34.63
29.38
28.82
21.43
O
t-Bu
t-Bu
Ph
Me
CO2Me
3ai
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)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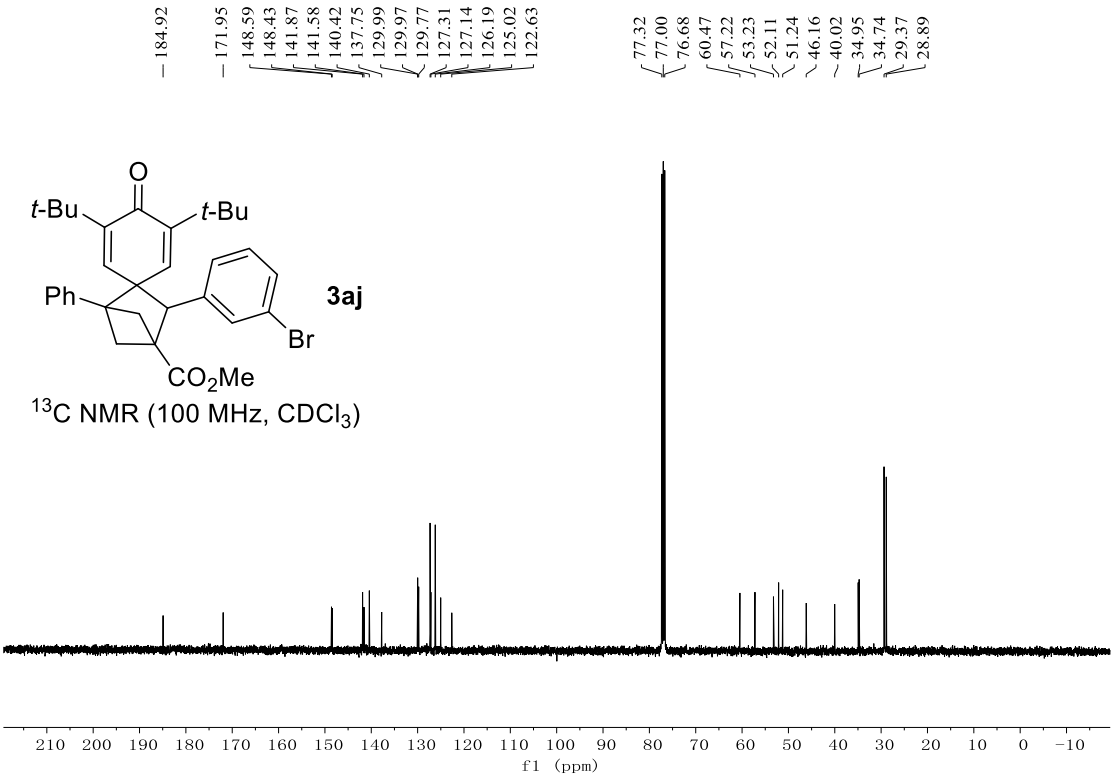
7.26
7.15
7.15
7.14
7.13
7.13
7.11
7.00
6.99
6.95
6.88
6.88
6.87
6.87
6.87
6.86
6.86
6.10
6.09
4.07
3.72
2.96
2.94
2.93
2.91
2.84
2.82
2.82
2.80
2.53
2.53
2.51
2.51
2.35
2.33
1.19
0.82
O
t-Bu
t-Bu
Ph
Br
CO2Me
3aj
1H NMR (400 MHz, CDCl3)
1.03
5.21
0.99
1.06
2.03
0.98
1.00
3.00
1.03
1.03
1.00
1.01
9.08
9.05
f1 (ppm)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148.43
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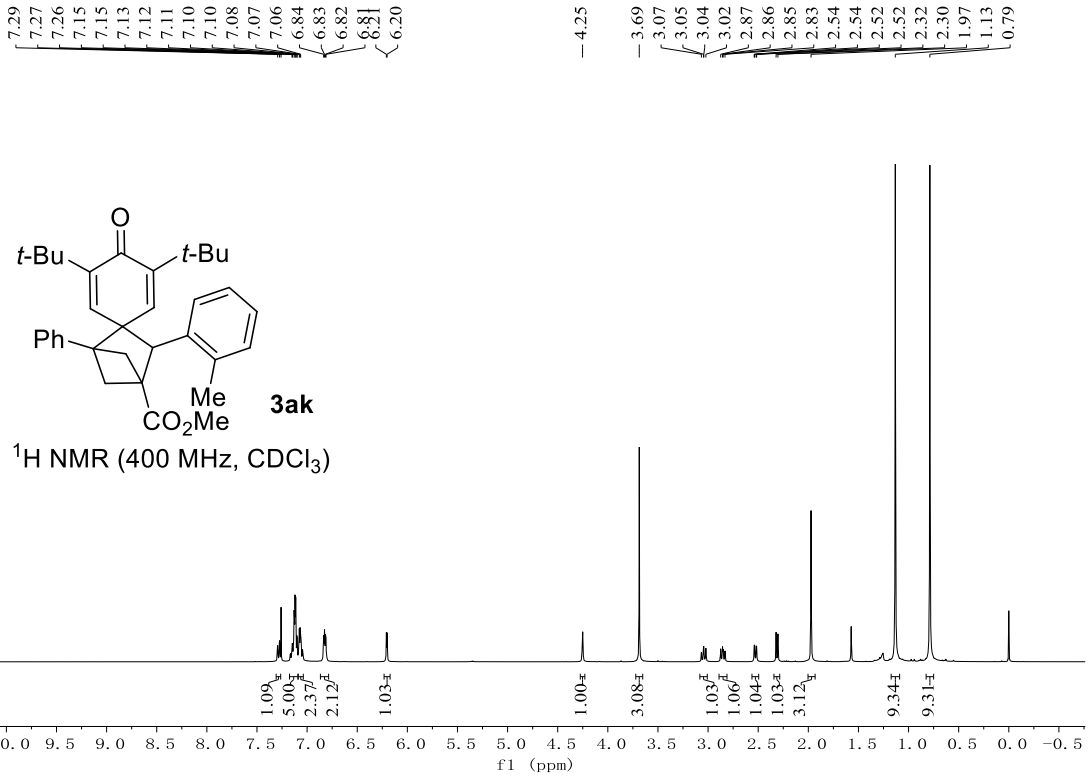
140.42
137.75
129.99
129.97
129.77
127.31
127.14
126.19
125.02
122.63
77.32
77.00
76.68
60.47
57.22
53.23
52.11
51.24
46.16
40.02
34.95
34.74
29.37
28.89
O
t-Bu
t-Bu
Ph
Br
CO2Me
3aj
13C NMR (100 MHz, CDCl3)
f1 (ppm)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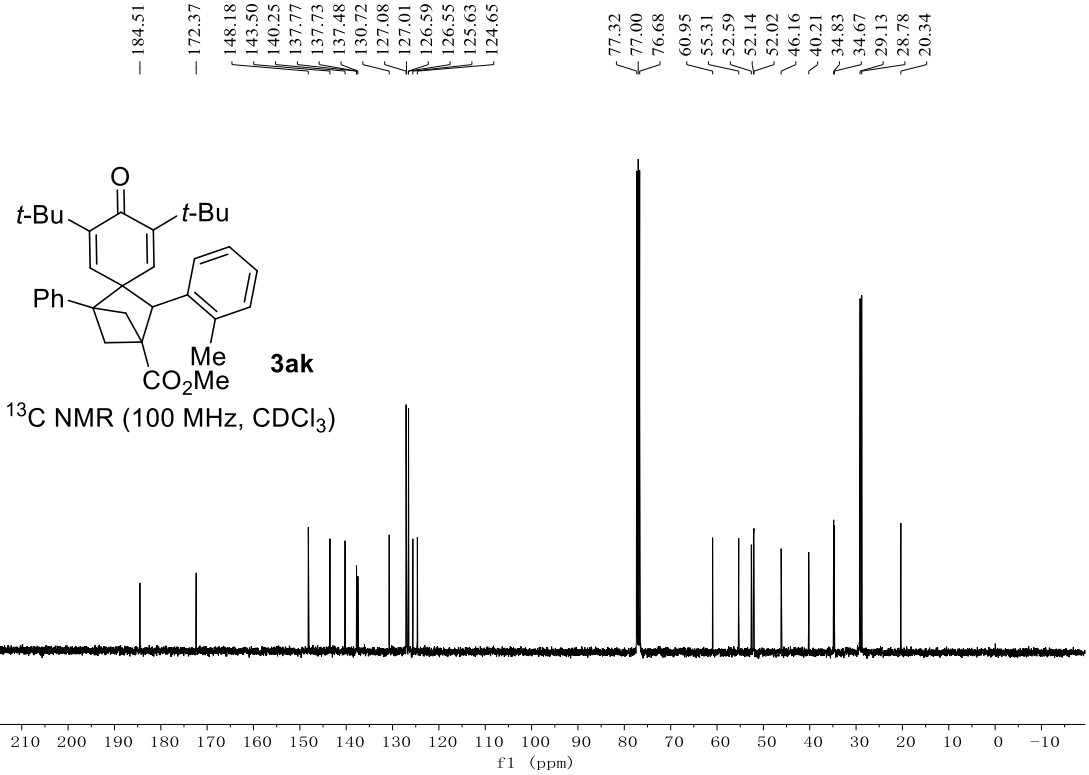
7.11
7.10
7.10
7.08
7.07
7.06
6.84
6.83
6.82
6.81
6.21
6.20
4.25
3.69
3.07
3.05
3.04
3.02
2.87
2.86
2.85
2.83
2.54
2.54
2.52
2.52
2.32
2.30
1.97
1.13
0.79
O
t-Bu
t-Bu
Ph
Me
CO2Me
3ak
1H NMR (400 MHz, CDCl3)
1.09
5.00
2.37
2.12
1.03
1.00
3.08
1.03
1.06
1.04
1.03
3.12
9.34
9.31
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)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172.37
148.18
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137.77
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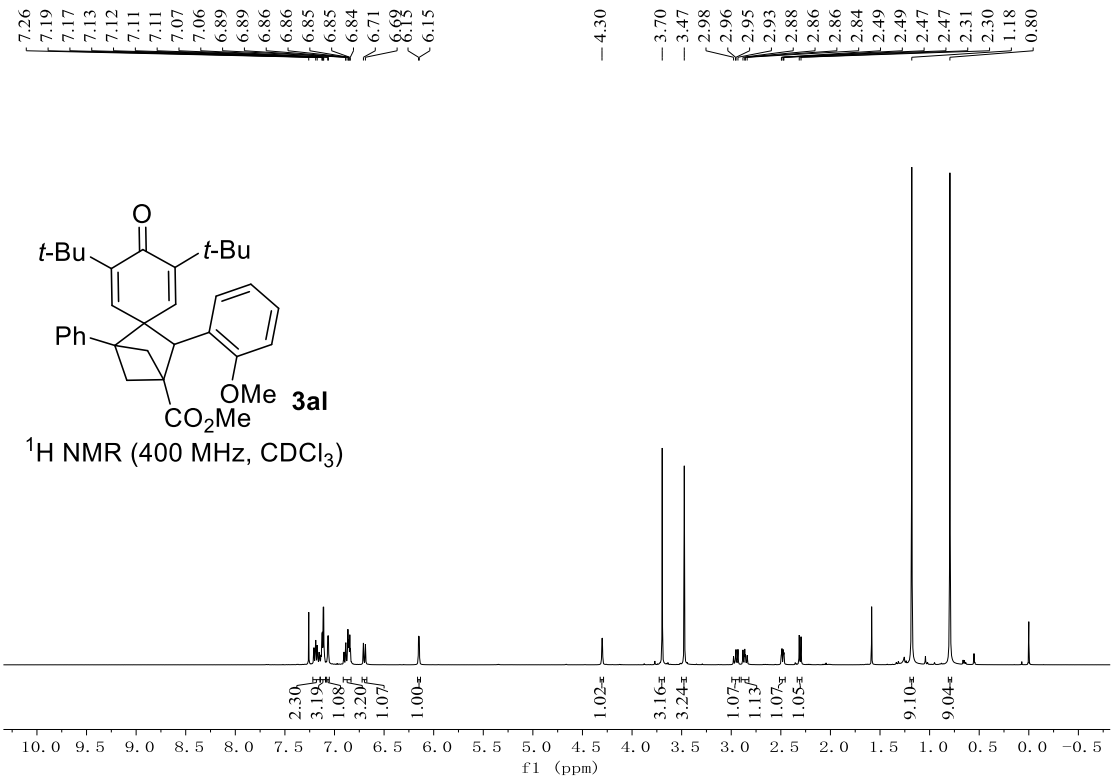
137.48
130.72
127.08
127.01
126.59
126.55
125.63
124.65
77.32
77.00
76.68
60.95
55.31
52.59
52.14
52.02
46.16
40.21
34.83
34.67
29.13
28.78
20.34
O
t-Bu
t-Bu
Ph
Me
CO2Me
3ak
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)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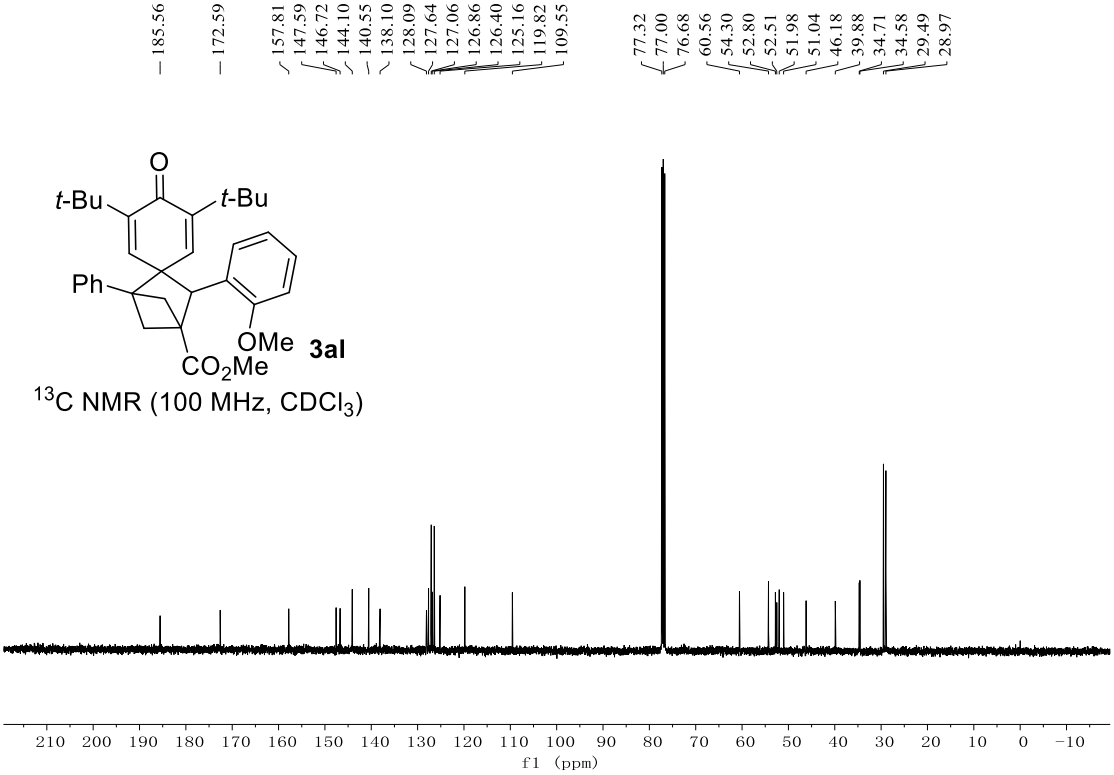
7.19
7.17
7.13
7.12
7.11
7.11
7.07
7.06
6.89
6.89
6.86
6.86
6.85
6.85
6.84
6.71
6.69
6.15
4.30
3.70
3.47
2.98
2.96
2.95
2.93
2.88
2.86
2.86
2.84
2.49
2.49
2.47
2.47
2.31
2.30
1.18
0.80
O
t-Bu
t-Bu
Ph
OMe
CO2Me
3al
1H NMR (400 MHz, CDCl3)
2.30
3.19
1.08
3.20
1.07
1.00
1.02
3.16
3.24
1.07
1.13
1.07
1.05
9.10
9.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)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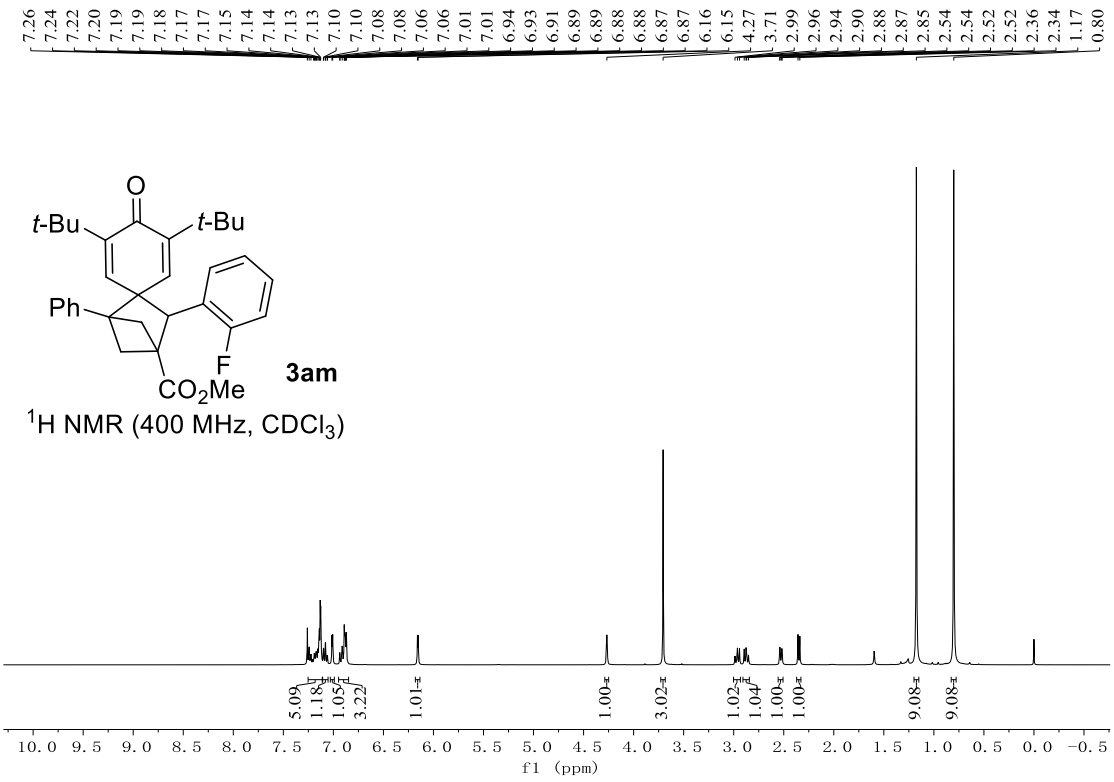
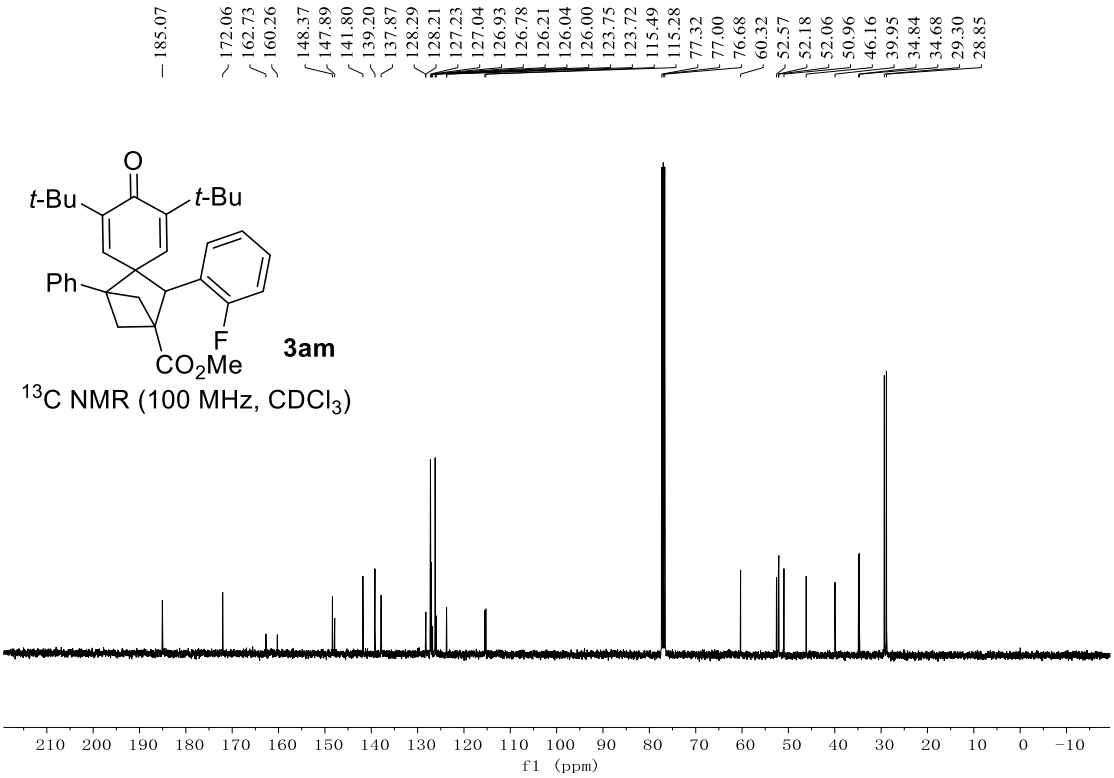
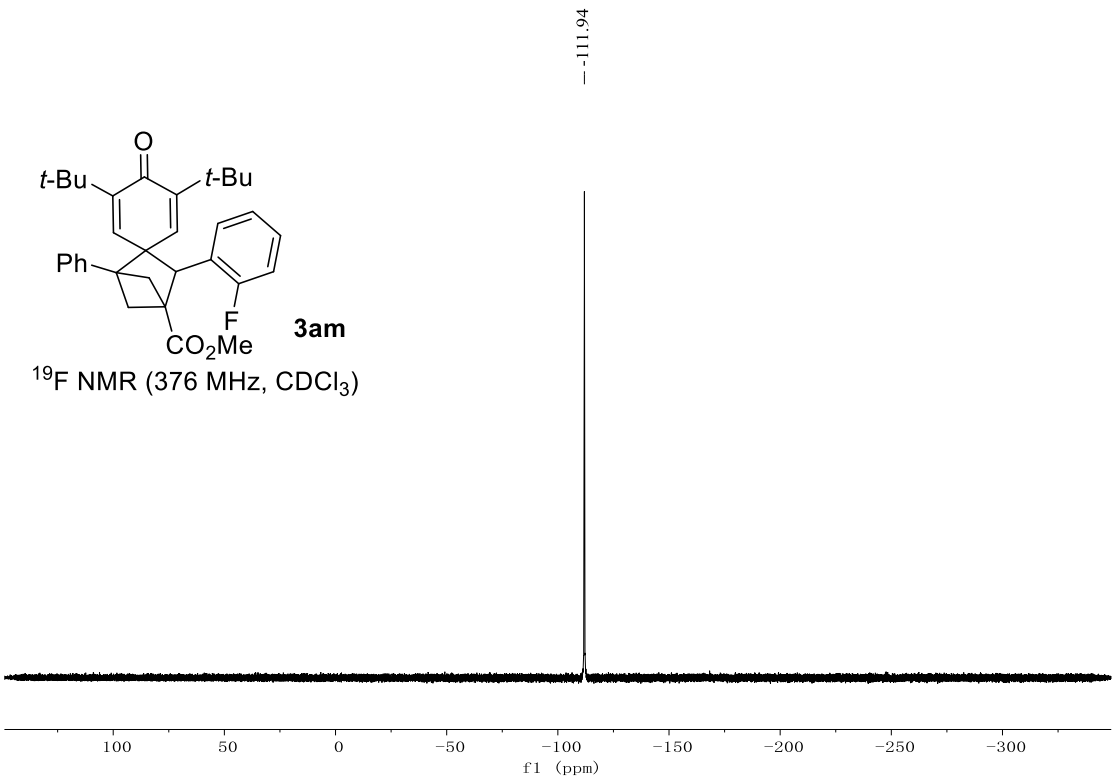
172.59
157.81
147.59
146.72
144.10
140.55
138.10
128.09
127.64
127.06
126.86
126.40
125.16
119.82
109.55
77.32
77.00
76.68
60.56
54.30
52.80
52.51
51.98
51.04
46.18
39.88
34.71
34.58
29.49
28.97
O
t-Bu
t-Bu
Ph
OMe
CO2Me
3al
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


7.26 7.24 7.22 7.20 7.19 7.19 7.18 7.17 7.17 7.15 7.14 7.14 7.13 7.13 7.10 7.10 7.08 7.08 7.06 7.06 7.01 7.01 6.94 6.93 6.91 6.89 6.89 6.88 6.88 6.87 6.87 6.16 6.15 4.27 3.71 2.99 2.96 2.94 2.90 2.88 2.87 2.85 2.54 2.54 2.52 2.52 2.36 2.34 1.17 0.80
O
t-Bu
t-Bu
Ph
F
CO2Me
3am
1H NMR (400 MHz, CDCl3)
5.09 1.18 1.05 3.22 1.01 1.00 3.02 1.02 1.04 1.00 1.00 9.08 9.08
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)


185.07
172.06 162.73 160.26 148.37 147.89 141.80 139.20 137.87 128.29 128.21 127.23 127.04 126.93 126.78 126.21 126.04 126.00 123.75 123.72 115.49 115.28 77.32 77.00 76.68 60.32 52.57 52.18 52.06 50.96 46.16 39.95 34.84 34.68 29.30 28.85
O
t-Bu
t-Bu
Ph
F
CO2Me
3am
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

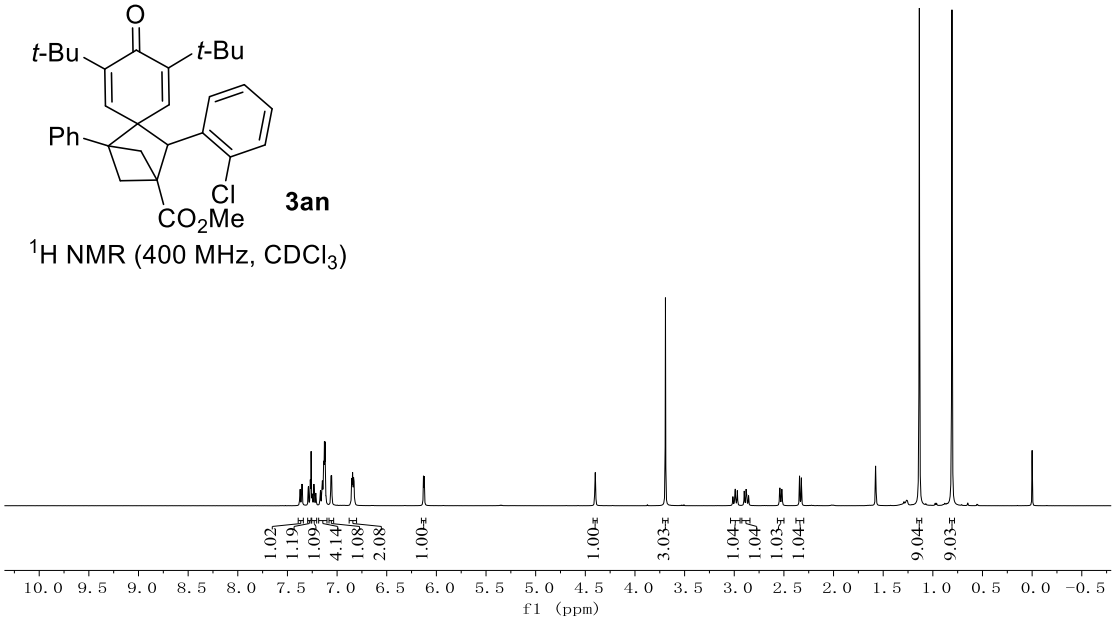
3am

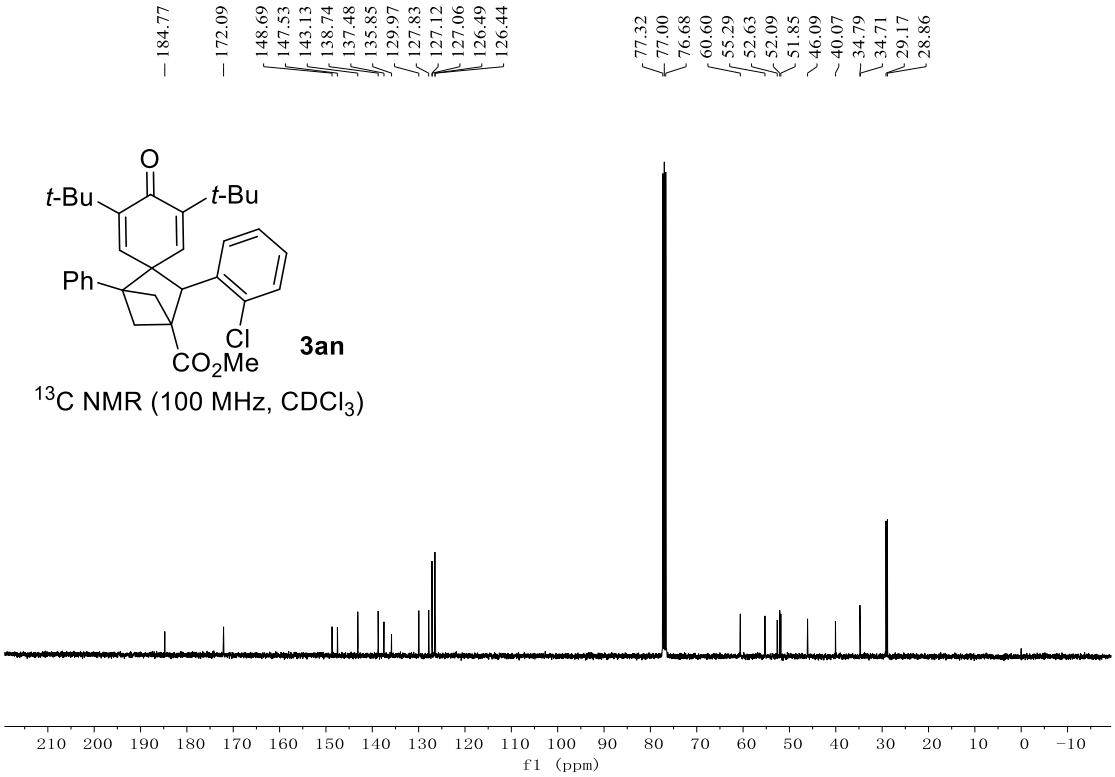
^{19}F NMR (376 MHz, $CDCl_3$)



3an

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

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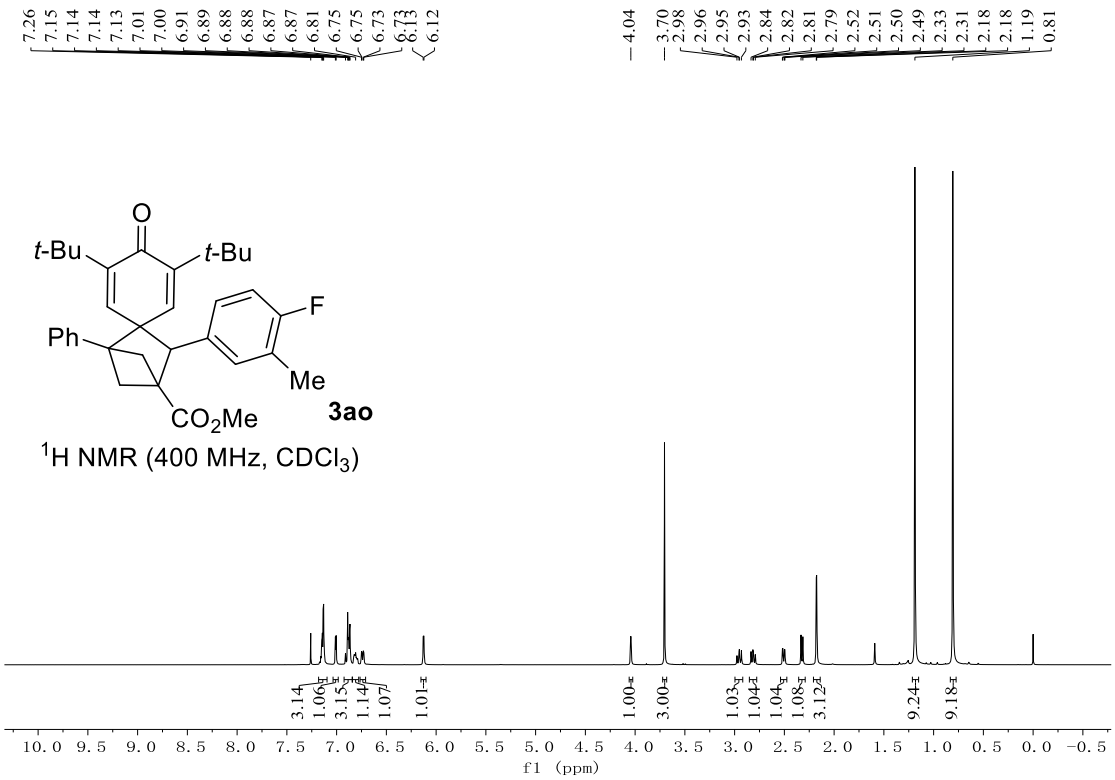
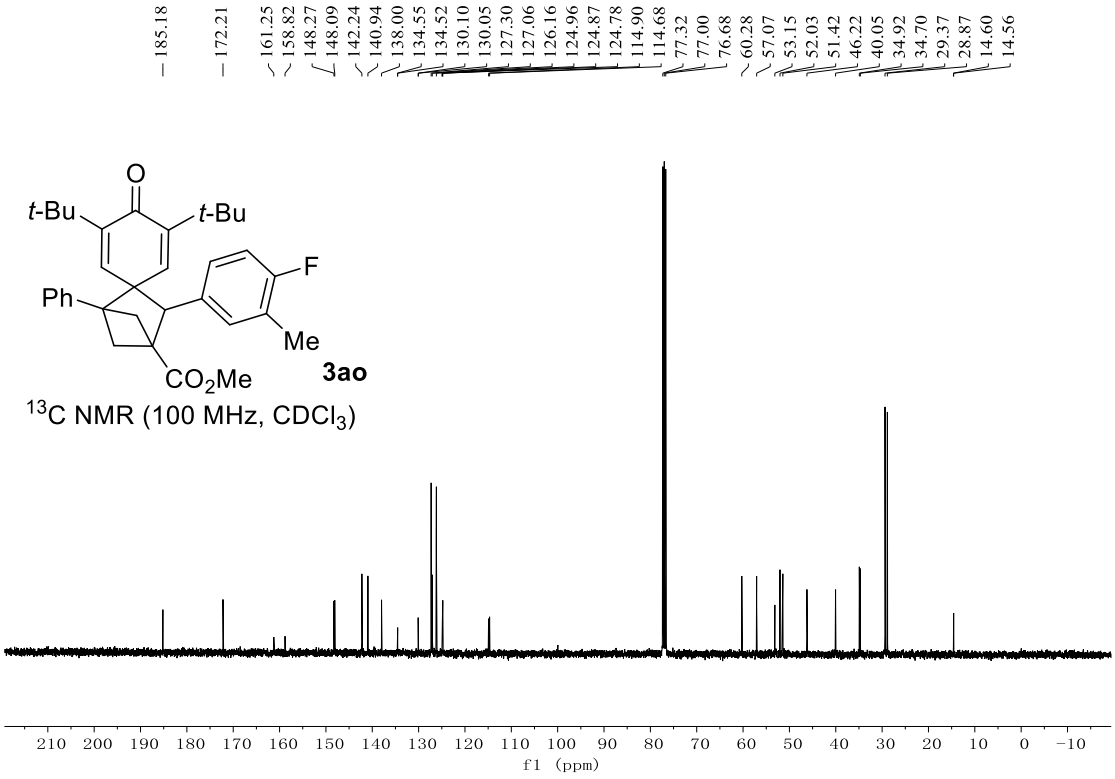
148.69
147.53
143.13
138.74
137.48
135.85
129.97
127.83
127.12
127.06
126.49
126.44
77.32
77.00
76.68
60.60
55.29
52.63
52.09
51.85
46.09
40.07
34.79
34.71
29.17
28.86
O
t-Bu
t-Bu
Ph
Cl
CO2Me
3an
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


7.26
7.15
7.14
7.14
7.13
7.01
7.00
6.91
6.89
6.88
6.88
6.87
6.87
6.81
6.75
6.75
6.73
6.73
6.13
6.12
4.04
3.70
2.98
2.96
2.95
2.93
2.84
2.82
2.81
2.79
2.52
2.51
2.50
2.49
2.33
2.31
2.18
2.18
1.19
0.81
O
t-Bu
t-Bu
Ph
F
Me
CO2Me
3ao
1H NMR (400 MHz, CDCl3)
3.14
1.06
3.15
1.14
1.07
1.01
1.00
3.00
1.03
1.04
1.04
1.08
3.12
9.24
9.18
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)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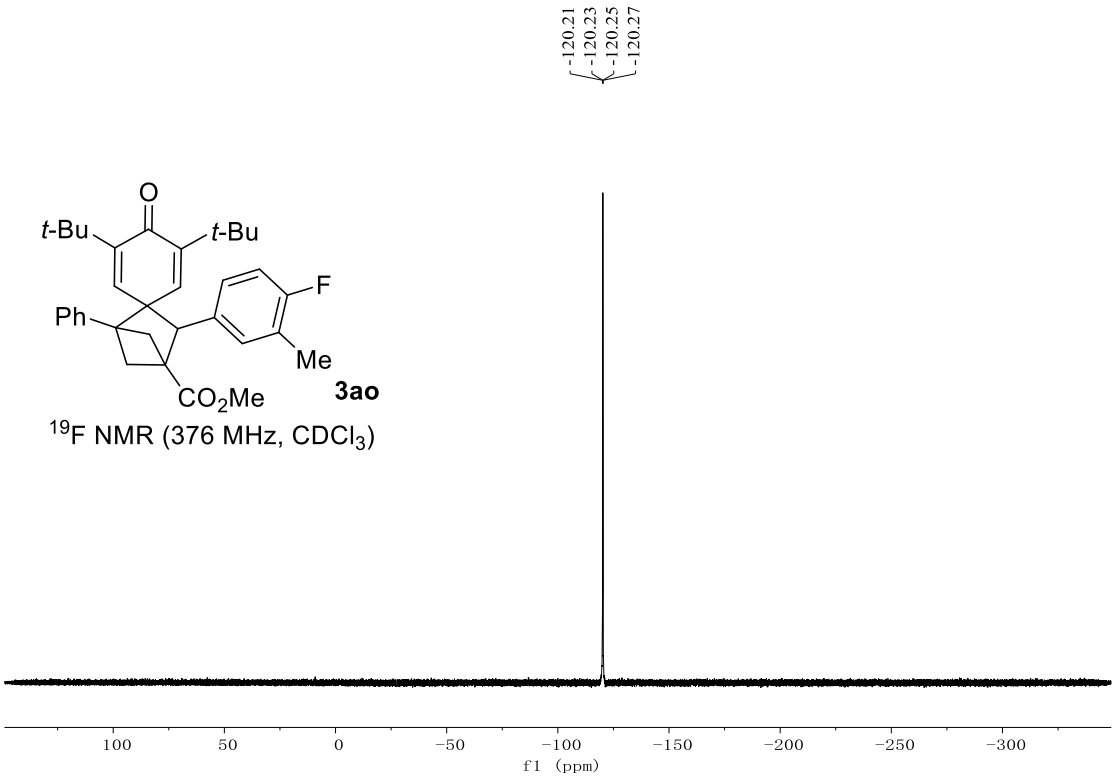
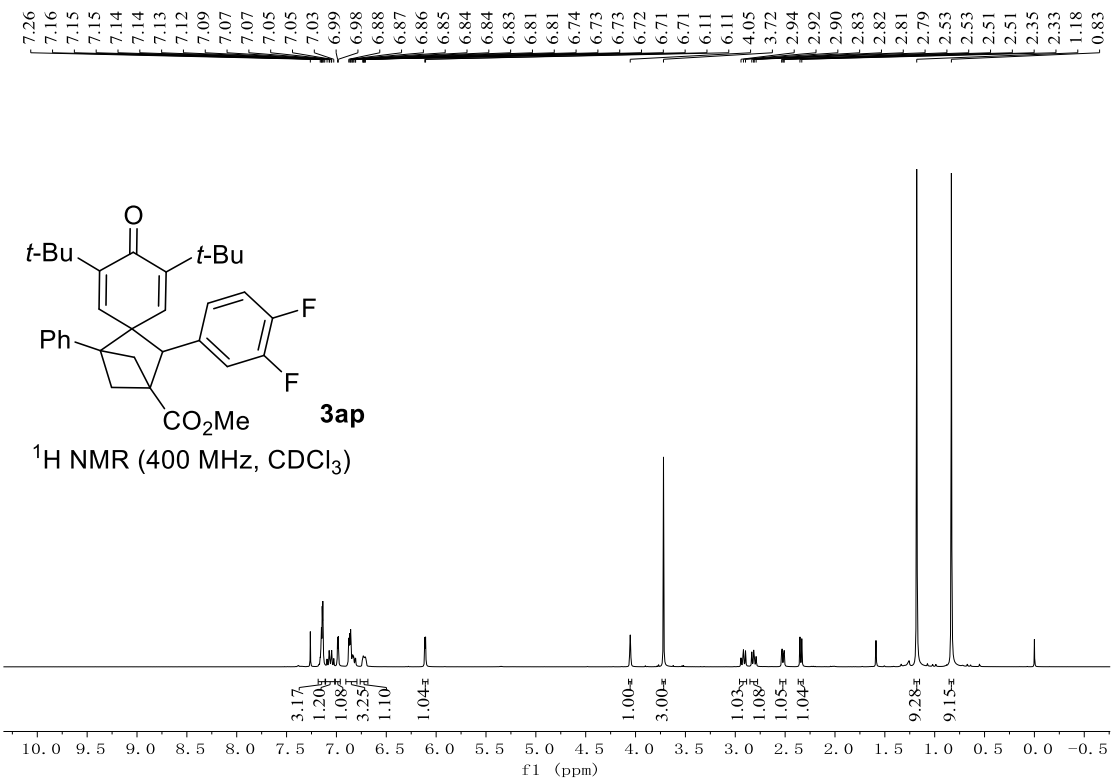
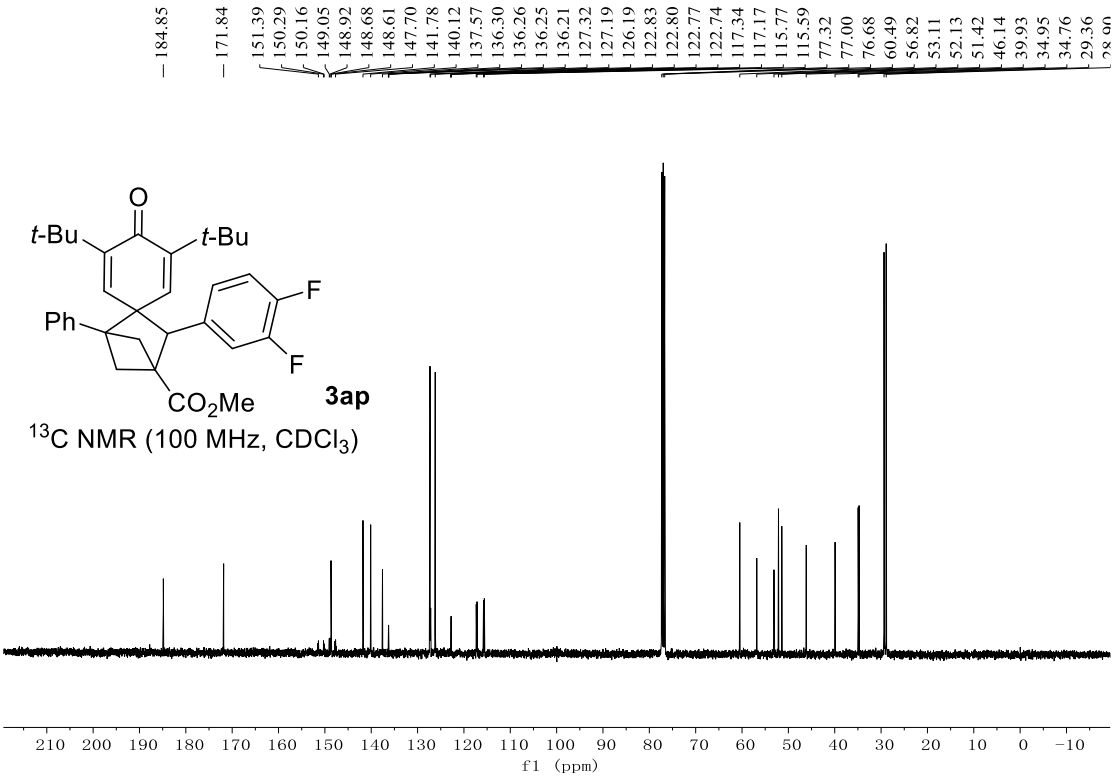
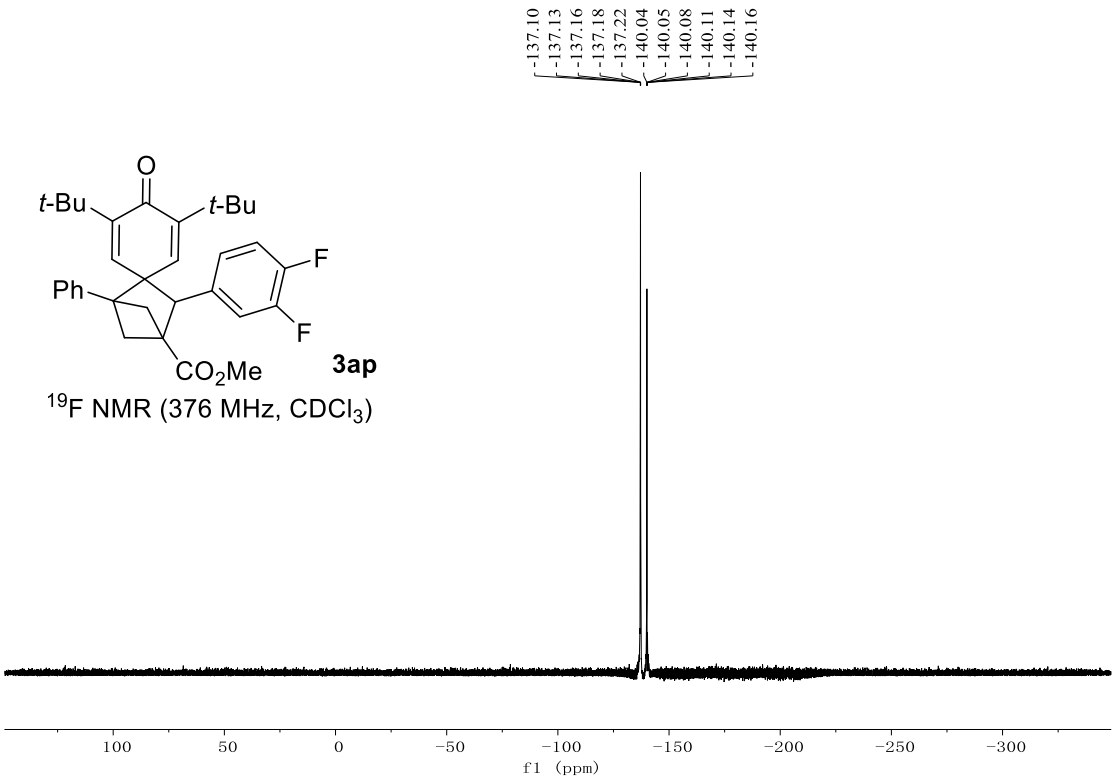
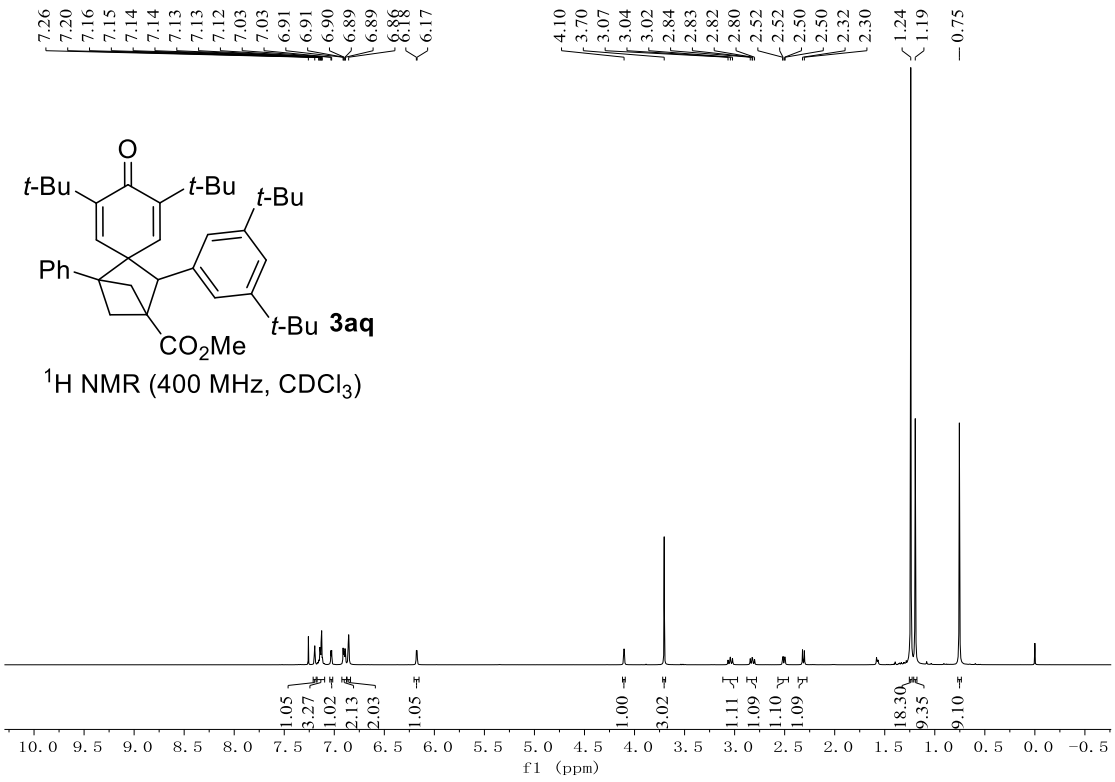
172.21
161.25
158.82
148.27
148.09
142.24
140.94
138.00
134.55
134.52
130.10
130.05
127.30
127.06
126.16
124.96
124.87
124.78
114.90
114.68
77.32
77.00
76.68
60.28
57.07
53.15
52.03
51.42
46.22
40.05
34.92
34.70
29.37
28.87
14.60
14.56
O
t-Bu
t-Bu
F
Ph
Me
CO2Me
3ao
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


-120.21
-120.23
-120.25
-120.27
O
t-Bu
t-Bu
F
Ph
Me
CO2Me
3ao
19F NMR (376 MHz, CDCl3)
100 50 0 −50 −100 −150 −200 −250 −300
f1 (ppm)


7.26 7.16 7.15 7.15 7.14 7.14 7.13 7.12 7.09 7.07 7.07 7.05 7.05 7.03 6.99 6.98 6.88 6.87 6.86 6.85 6.84 6.84 6.83 6.81 6.81 6.74 6.73 6.73 6.72 6.71 6.71 6.11 6.11 4.05 3.72 2.94 2.92 2.90 2.83 2.82 2.81 2.79 2.53 2.53 2.51 2.51 2.35 2.33 1.18 0.83
t-Bu
t-Bu
O
F
F
Ph
CO2Me
3ap
1H NMR (400 MHz, CDCl3)
3.17 1.20 1.08 3.25 1.10 1.04 1.00 3.00 1.03 1.08 1.05 1.04 9.28 9.15
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)


184.85 171.84 151.39 150.29 150.16 149.05 148.92 148.68 148.61 147.70 141.78 140.12 137.57 136.30 136.26 136.25 136.21 127.32 127.19 126.19 122.83 122.80 122.77 122.74 117.34 117.17 115.77 115.59 77.32 77.00 76.68 60.49 56.82 53.11 52.13 51.42 46.14 39.93 34.95 34.76 29.36
t-Bu
t-Bu
O
F
F
Ph
CO2Me
3ap
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


-137.10
-137.13
-137.16
-137.18
-137.22
-140.04
-140.05
-140.08
-140.11
-140.14
-140.16
O
t-Bu
t-Bu
F
F
Ph
CO2Me
3ap
19F NMR (376 MHz, CDCl3)
100
50
0
−50
−100
−150
−200
−250
−300
f1 (ppm)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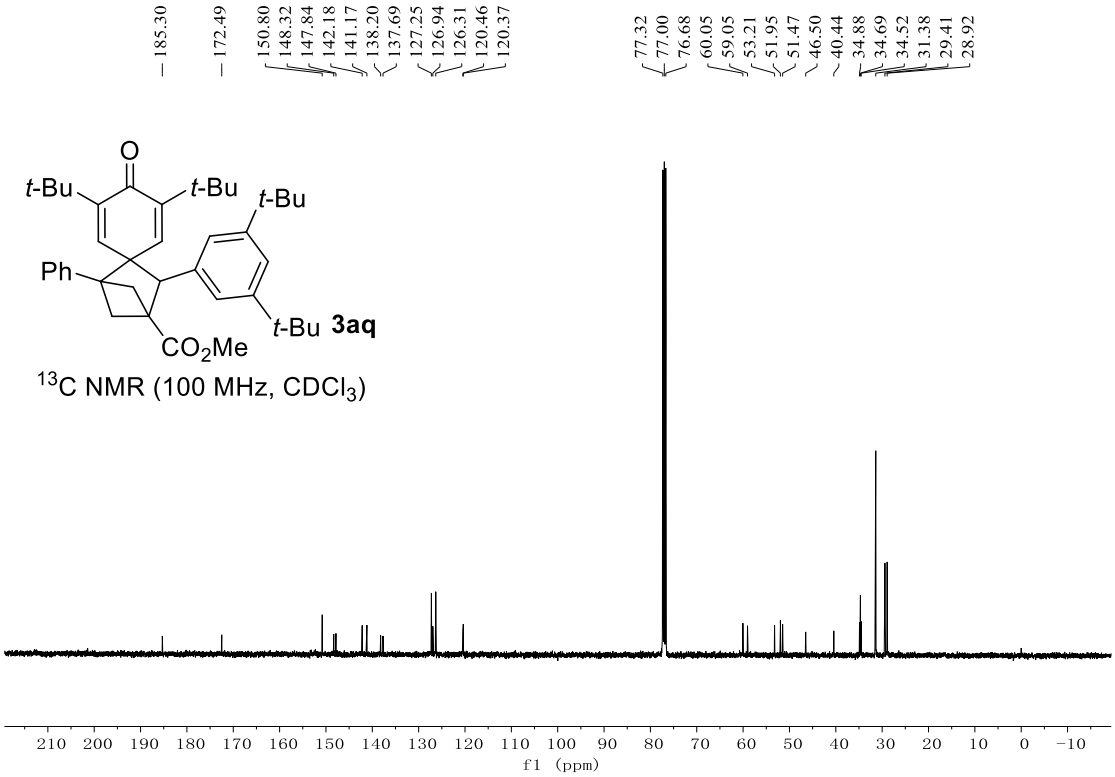
7.20
7.16
7.15
7.14
7.14
7.13
7.13
7.12
7.03
7.03
6.91
6.91
6.90
6.89
6.89
6.88
6.88
6.17
4.10
3.70
3.07
3.04
3.02
2.84
2.83
2.82
2.80
2.52
2.52
2.50
2.50
2.32
2.30
1.24
1.19
0.75
O
t-Bu
t-Bu
t-Bu
Ph
t-Bu
CO2Me
3aq
1H NMR (400 MHz, CDCl3)
1.05
3.27
1.02
2.13
2.03
1.05
1.00
3.02
1.11
1.09
1.10
1.09
18.30
9.35
9.10
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)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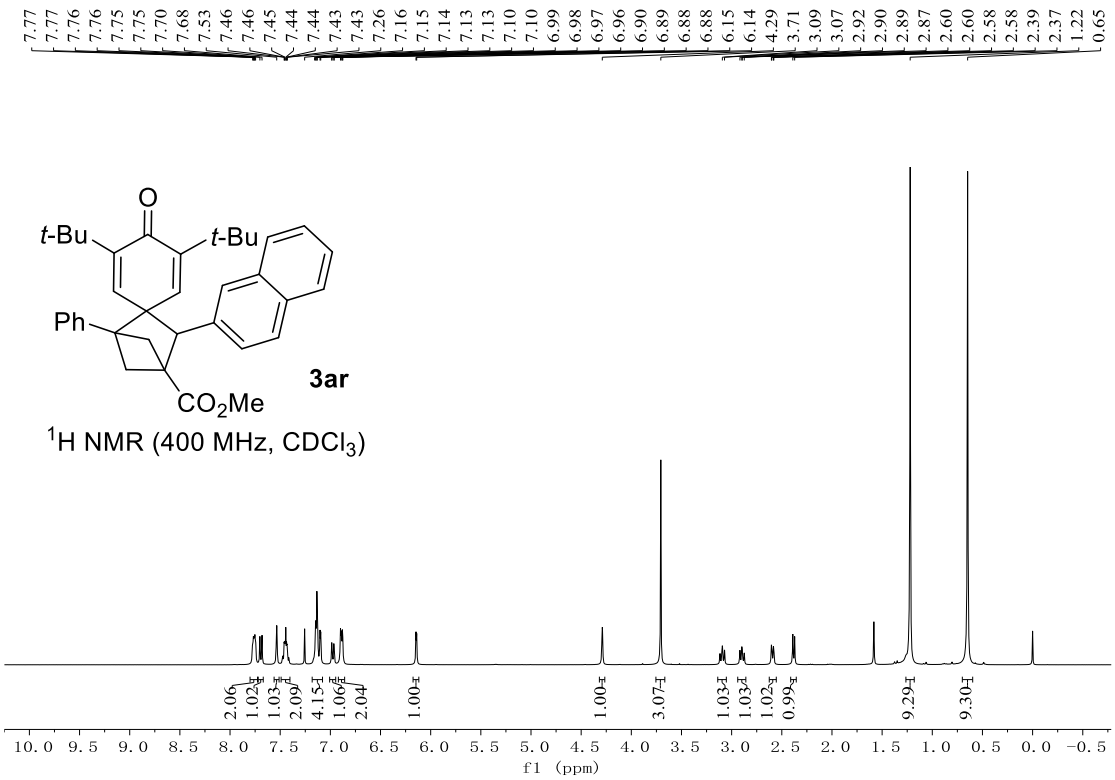
141.17
138.20
137.69
127.25
126.94
126.31
120.46
120.37
77.32
77.00
76.68
60.05
59.05
53.21
51.95
51.47
46.50
40.44
34.88
34.69
34.52
31.38
29.41
28.92
t-Bu
t-Bu
t-Bu
Ph
t-Bu
CO2Me
3aq
13C NMR (100 MHz, CDCl3)
f1 (ppm)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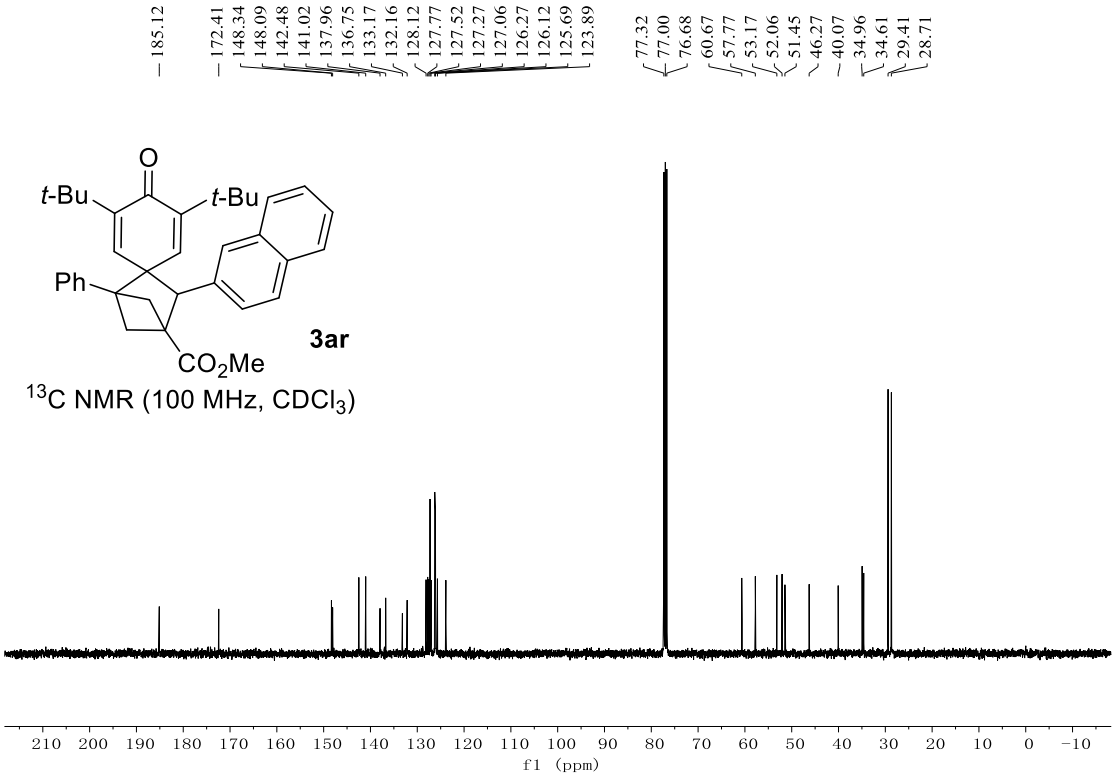
7.77
7.76
7.76
7.75
7.75
7.70
7.68
7.53
7.46
7.46
7.45
7.44
7.44
7.43
7.43
7.26
7.16
7.15
7.14
7.13
7.13
7.10
7.10
6.99
6.98
6.97
6.96
6.90
6.89
6.88
6.88
6.15
6.14
4.29
3.71
3.09
3.07
2.92
2.90
2.89
2.87
2.60
2.60
2.58
2.58
2.39
2.37
1.22
0.65
t-Bu
t-Bu
Ph
CO2Me
3ar
1H NMR (400 MHz, CDCl3)
2.06
1.02
1.03
2.09
4.15
1.06
2.04
1.00
1.00
3.07
1.03
1.03
1.02
0.99
9.29
9.30
f1 (ppm)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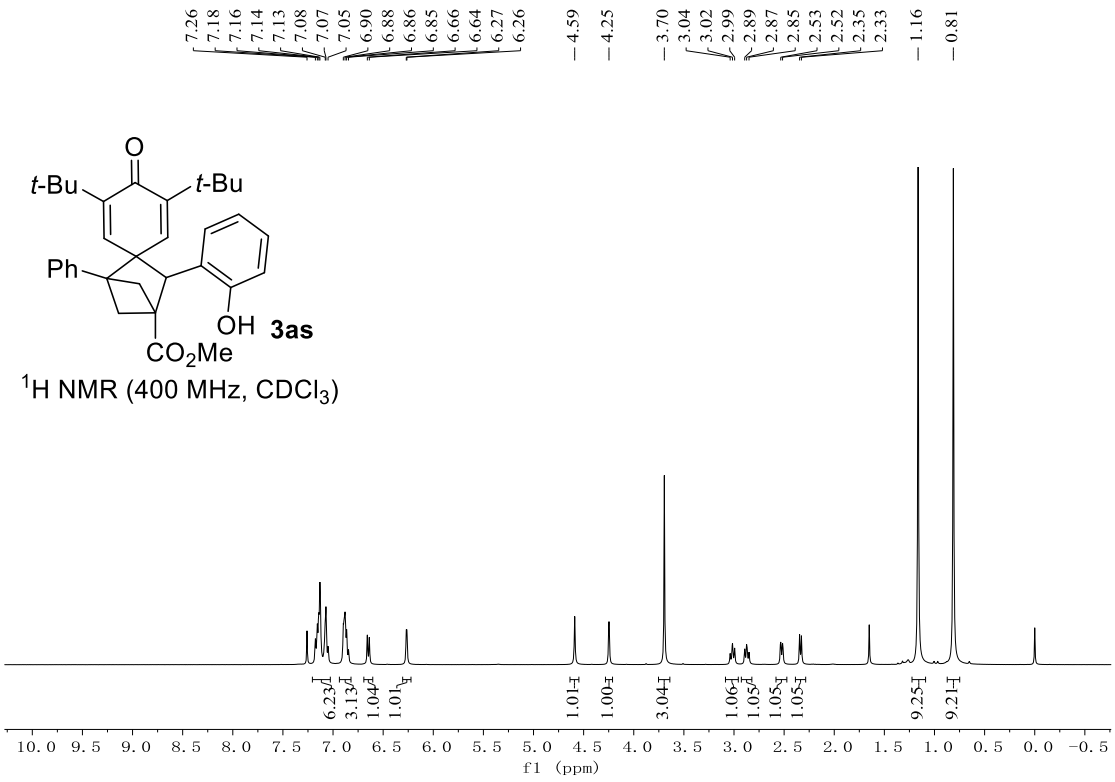
148.09
142.48
141.02
137.96
136.75
133.17
132.16
128.12
127.77
127.52
127.27
127.06
126.27
126.12
125.69
123.89
77.32
77.00
76.68
60.67
57.77
53.17
52.06
51.45
46.27
40.07
34.96
34.61
29.41
28.71
O
t-Bu
t-Bu
Ph
CO2Me
3ar
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


7.26
7.18
7.16
7.14
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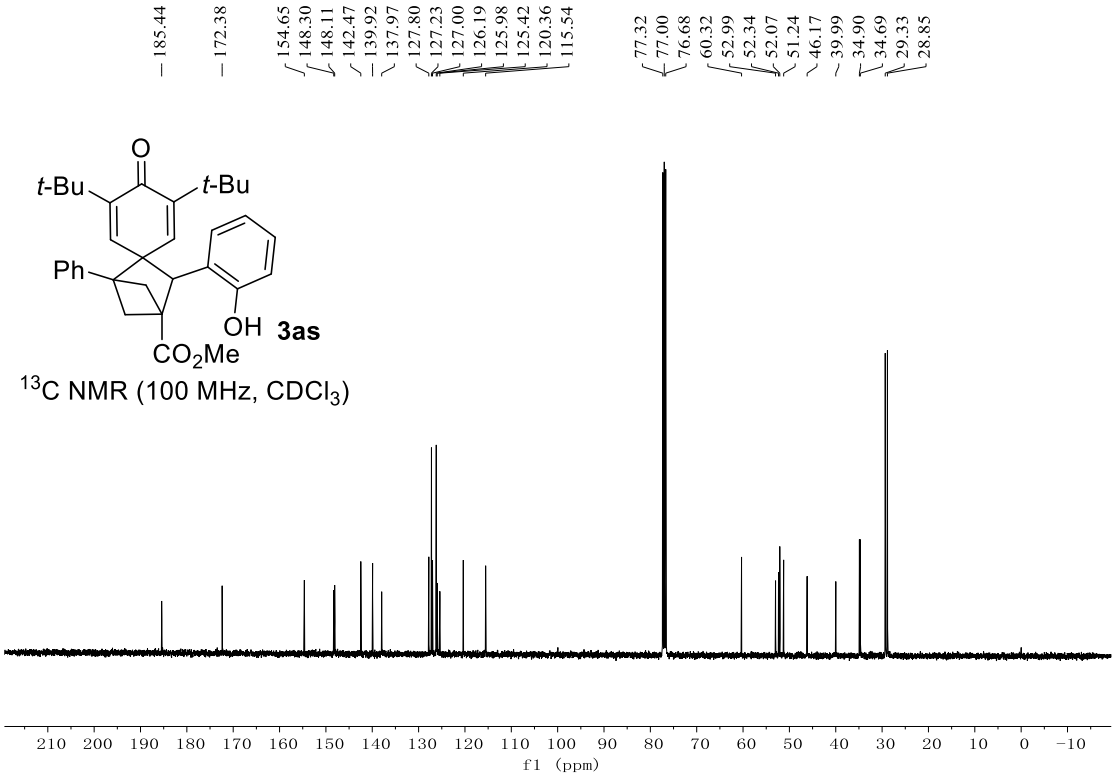
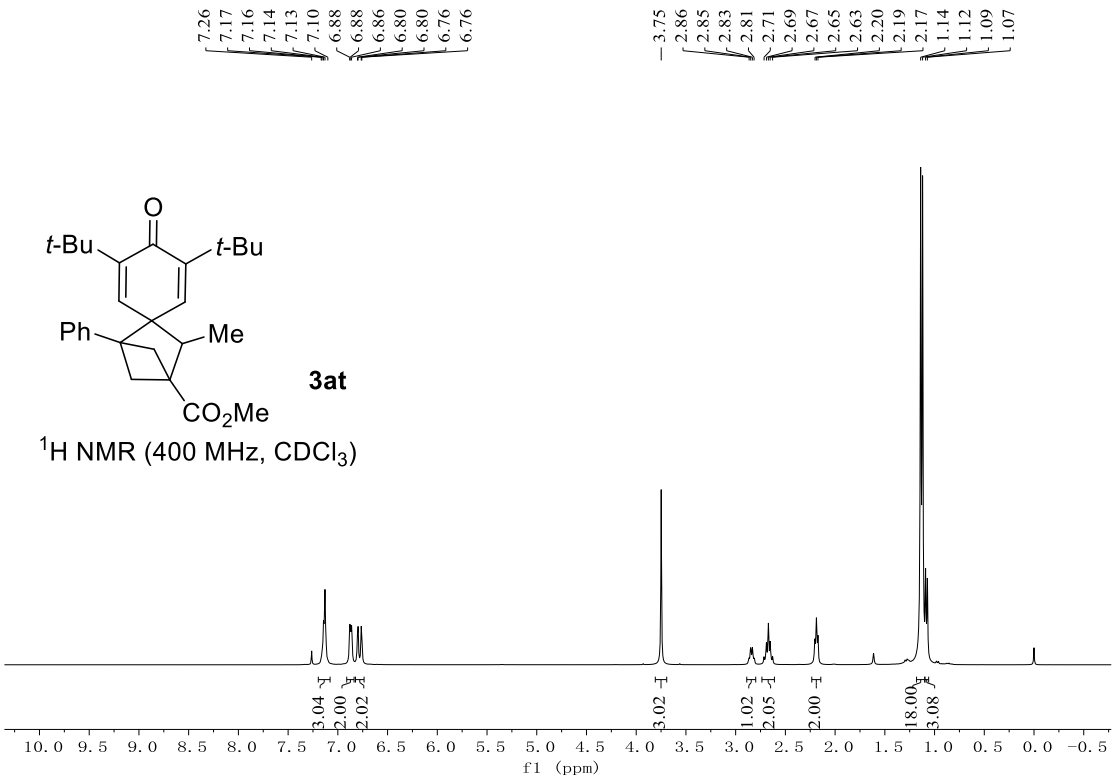
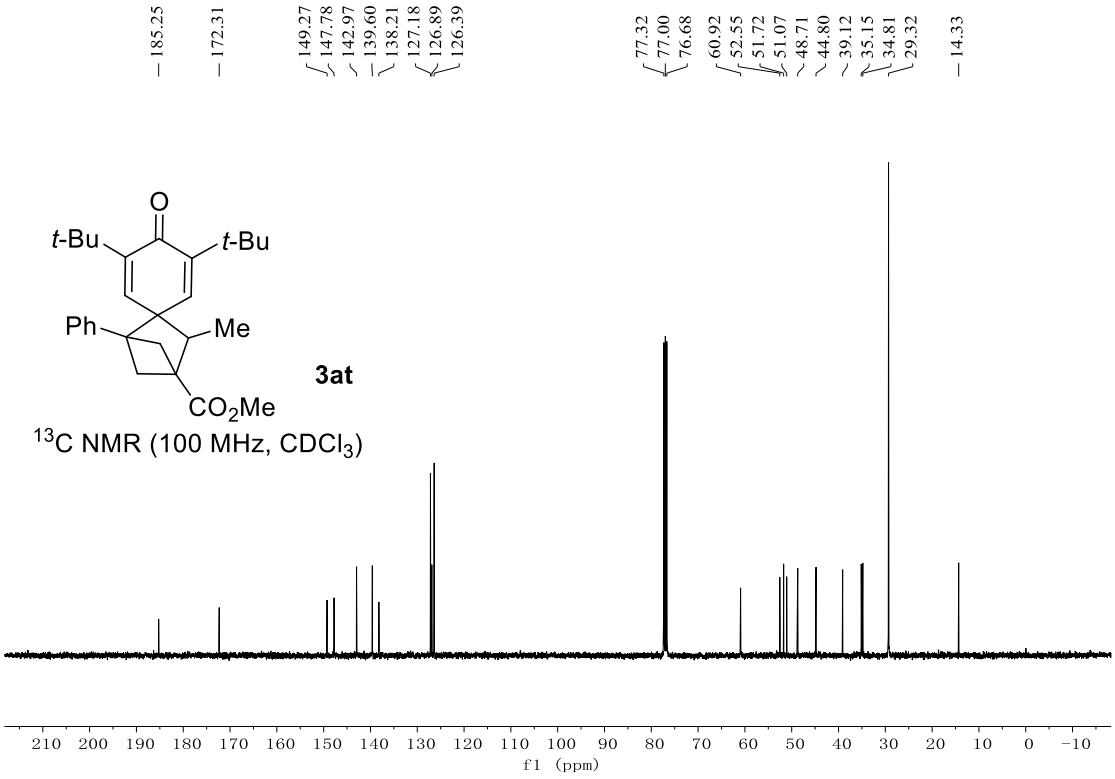
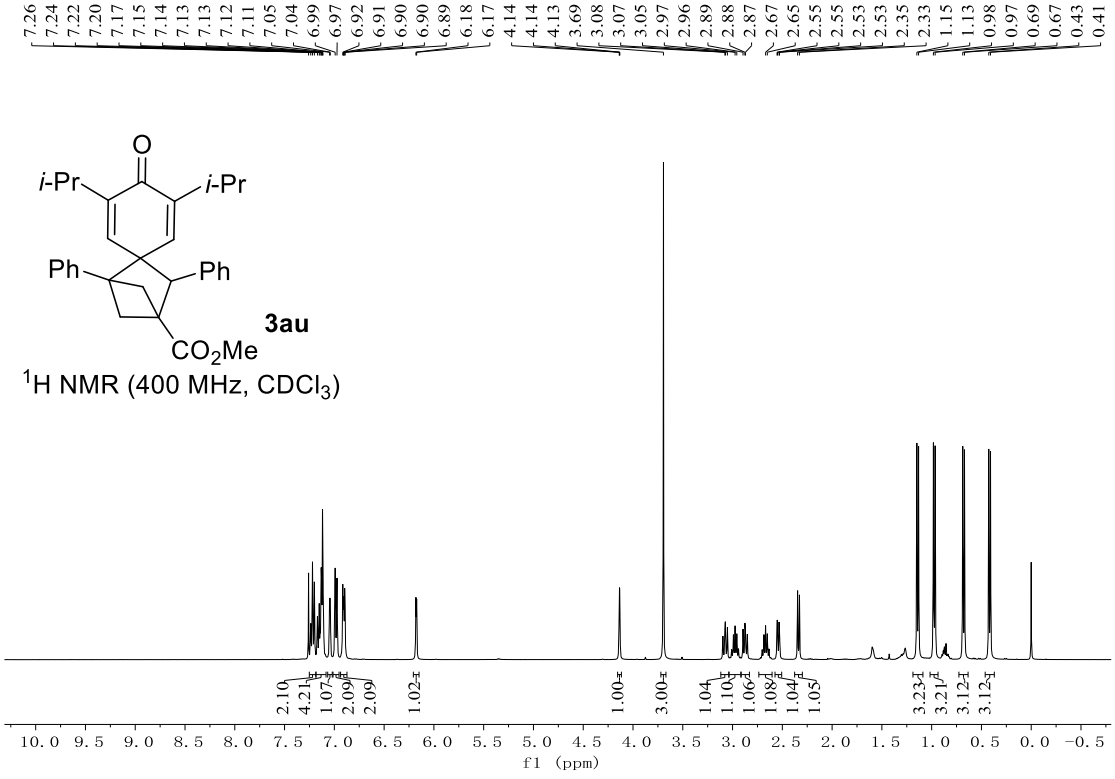
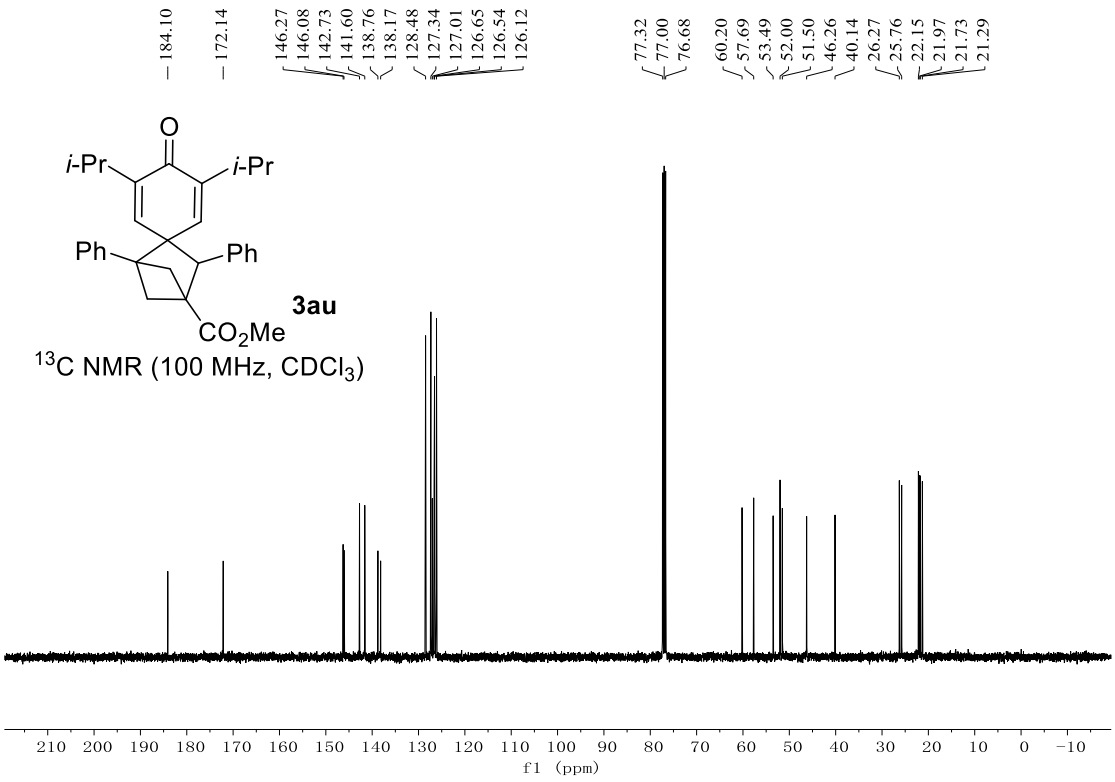
7.08
7.07
7.05
6.90
6.88
6.86
6.85
6.66
6.64
6.27
6.26
4.59
4.25
3.70
3.04
3.02
2.99
2.89
2.87
2.85
2.53
2.52
2.35
2.33
1.16
0.81
O
t-Bu
t-Bu
Ph
OH
CO2Me
3as
1H NMR (400 MHz, CDCl3)
6.23
3.13
1.04
1.01
1.01
1.00
3.04
1.06
1.05
1.05
1.05
9.25
9.21
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)

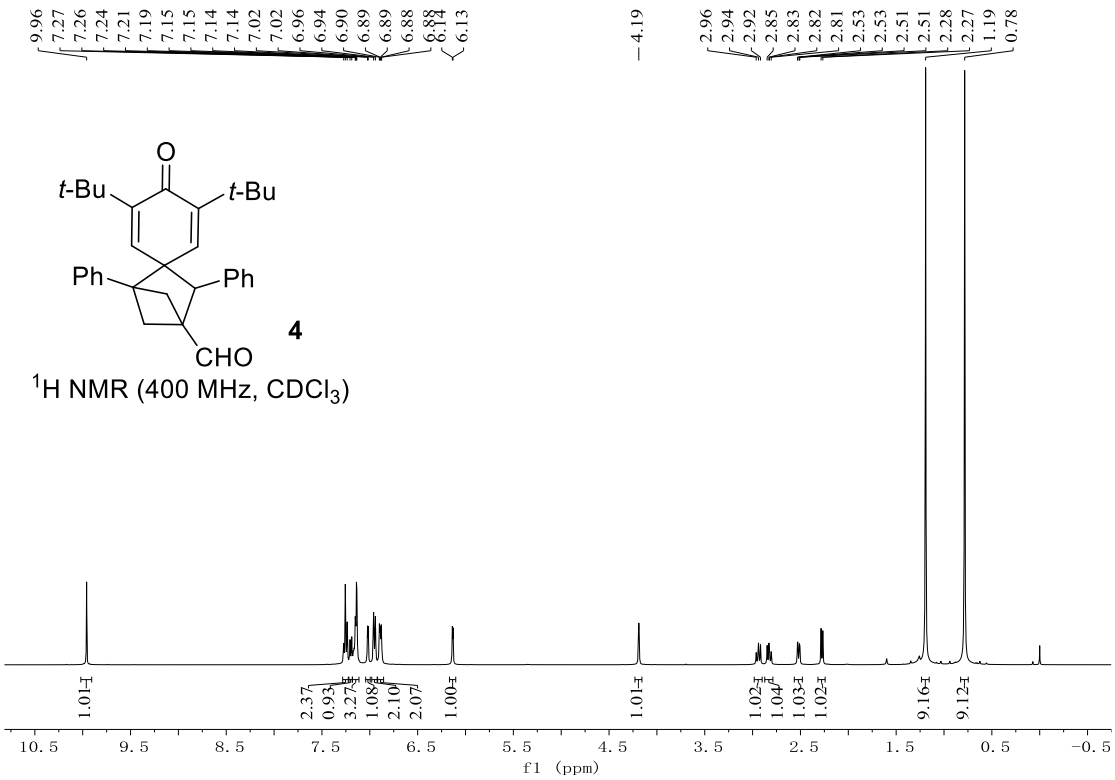

185.44
172.38
154.65
148.30
148.11
142.47
139.92
137.97
127.80
127.23
127.00
126.19
125.98
125.42
120.36
115.54
77.32
77.00
76.68
60.32
52.99
52.34
52.07
51.24
46.17
39.99
34.90
34.69
29.33
28.85
O
t-Bu
t-Bu
Ph
OH
CO2Me
3as
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

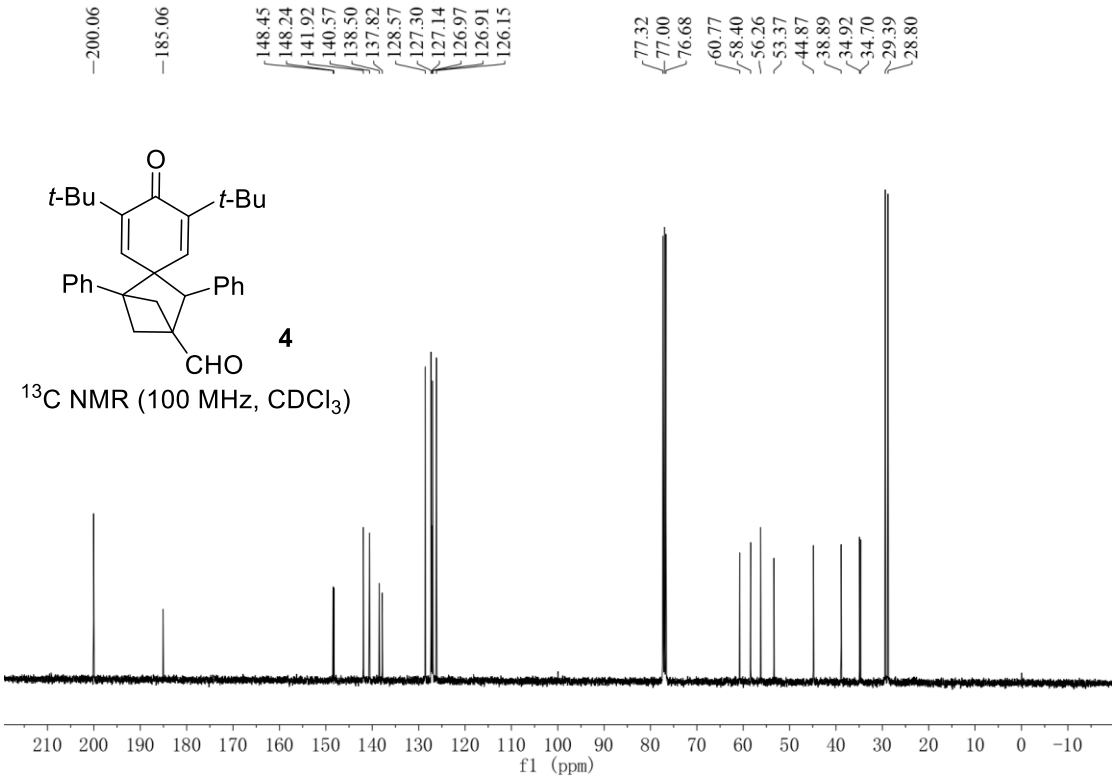

7.26
7.17
7.16
7.14
7.13
7.10
6.88
6.88
6.86
6.80
6.80
6.76
6.76
3.75
2.86
2.85
2.83
2.81
2.71
2.69
2.67
2.65
2.63
2.20
2.19
2.17
1.14
1.12
1.09
1.07
O
t-Bu
t-Bu
Ph
Me
CO2Me
3at
1H NMR (400 MHz, CDCl3)
3.04
2.00
2.02
3.02
1.02
2.05
2.00
18.00
3.08
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)


185.25
172.31
149.27
147.78
142.97
139.60
138.21
127.18
126.89
126.39
77.32
77.00
76.68
60.92
52.55
51.72
51.07
48.71
44.80
39.12
35.15
34.81
29.32
14.33
O
t-Bu
t-Bu
Ph
Me
CO2Me
3at
13C NMR (100 MHz, CDCl3)
f1 (ppm)

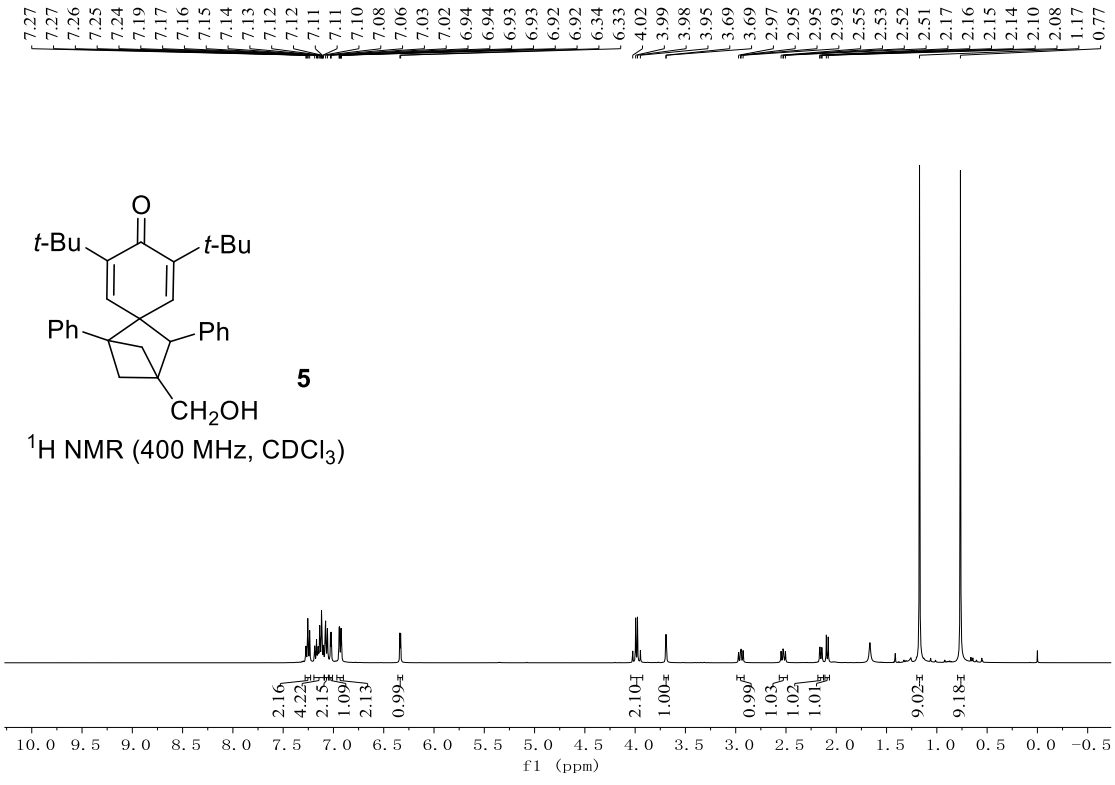

7.26
7.24
7.22
7.20
7.17
7.15
7.14
7.13
7.13
7.12
7.11
7.05
7.04
6.99
6.97
6.92
6.91
6.90
6.90
6.89
6.18
6.17
4.14
4.14
4.13
3.69
3.08
3.07
3.05
2.97
2.96
2.89
2.88
2.87
2.67
2.65
2.55
2.55
2.53
2.53
2.35
2.33
1.15
1.13
0.98
0.97
0.69
0.67
0.43
0.41
O
i-Pr
i-Pr
Ph
Ph
CO2Me
3au
1H NMR (400 MHz, CDCl3)
2.10
4.21
1.07
2.09
2.09
1.02
1.00
3.00
1.04
1.10
1.06
1.08
1.04
1.05
3.23
3.21
3.12
3.12
f1 (ppm)


184.10
172.14
146.27
146.08
142.73
141.60
138.76
138.17
128.48
127.34
127.01
126.65
126.54
126.12
77.32
77.00
76.68
60.20
57.69
53.49
52.00
51.50
46.26
40.14
26.27
25.76
22.15
21.97
21.73
21.29
O
i-Pr
i-Pr
Ph
Ph
CO2Me
3au
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

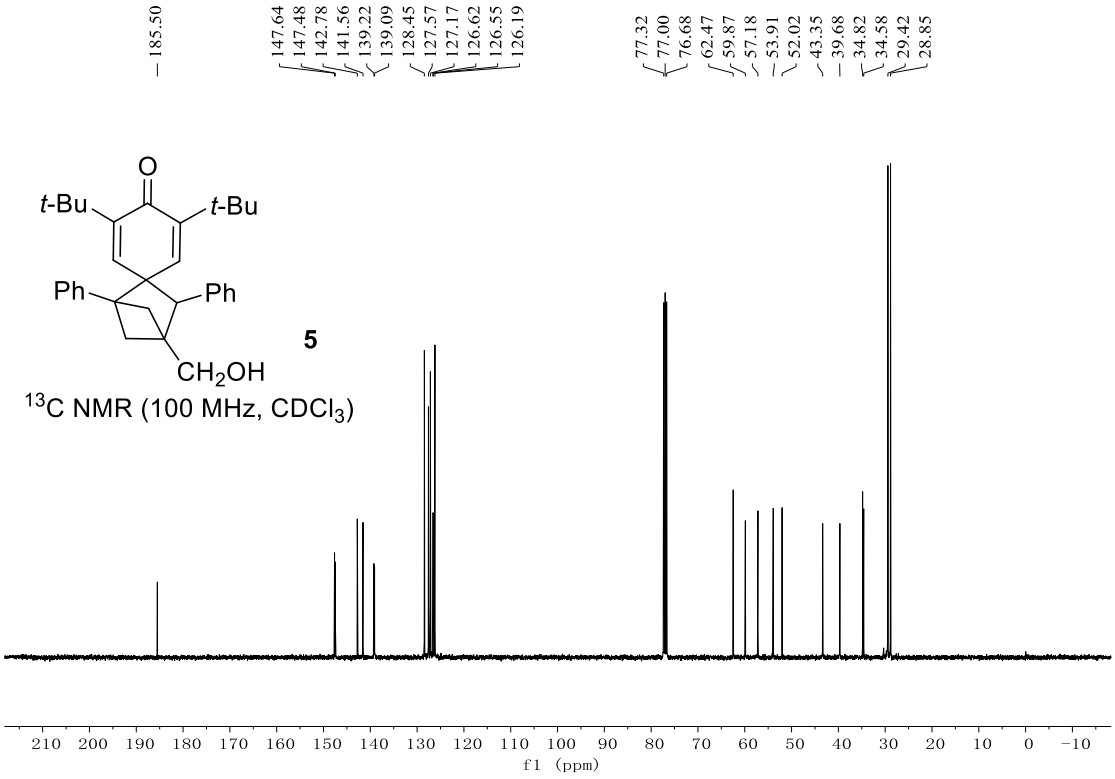

9.96
7.27
7.26
7.24
7.21
7.19
7.15
7.15
7.14
7.14
7.02
7.02
6.96
6.94
6.90
6.89
6.89
6.88
6.88
6.14
6.13
4.19
2.96
2.94
2.92
2.85
2.83
2.82
2.81
2.53
2.53
2.51
2.51
2.28
2.27
1.19
0.78
O
t-Bu
t-Bu
Ph
Ph
CHO
4
1H NMR (400 MHz, CDCl3)
1.01
2.37
0.93
3.27
1.08
2.10
2.07
1.00
1.01
1.02
1.04
1.03
1.02
9.16
9.12
10.5 9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5 −0.5
f1 (ppm)

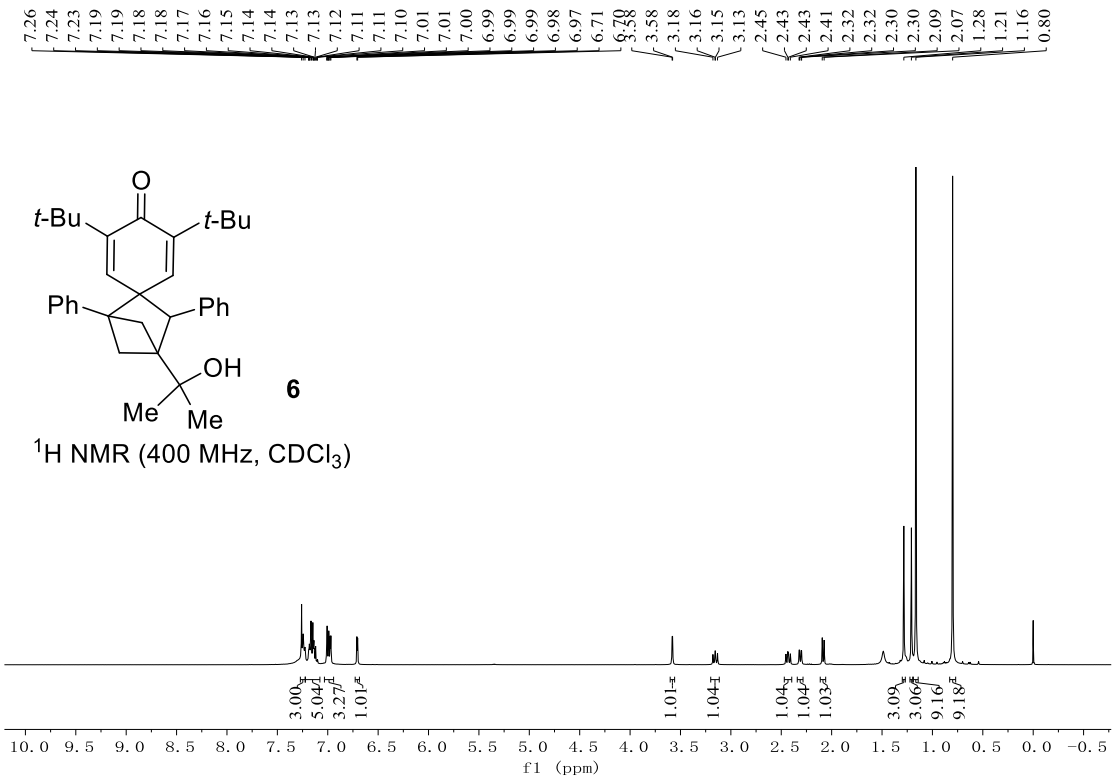


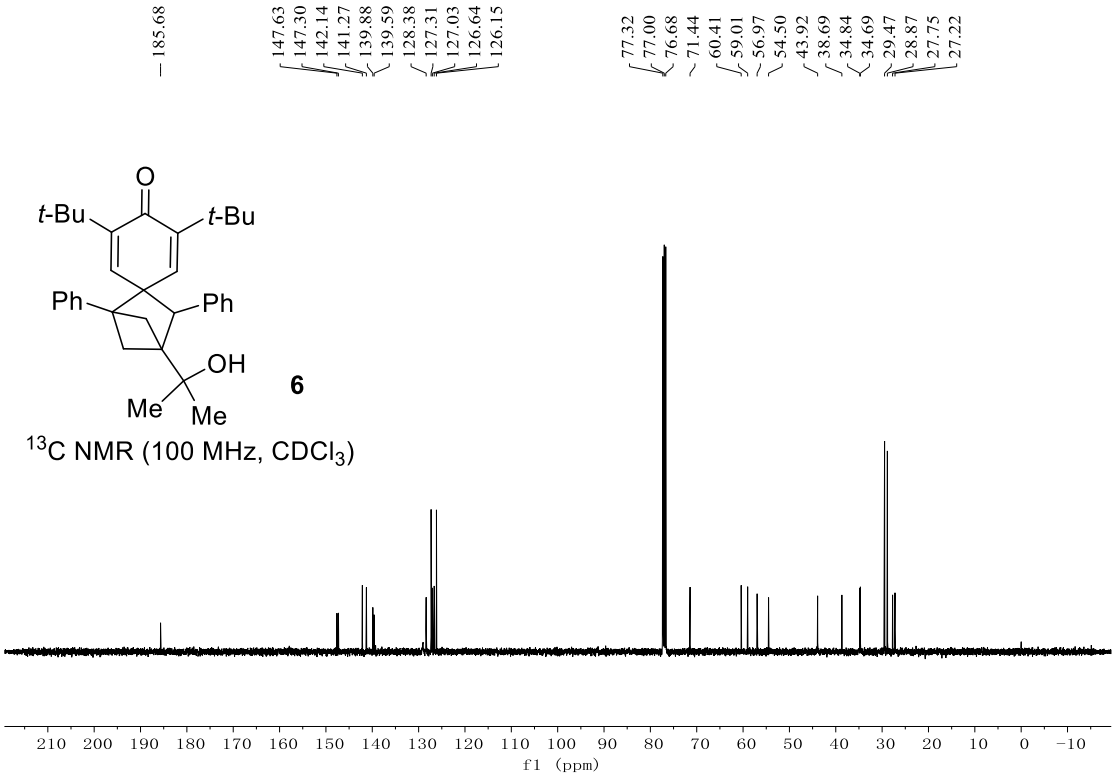
^{13}C NMR (100 MHz, $CDCl_3$)

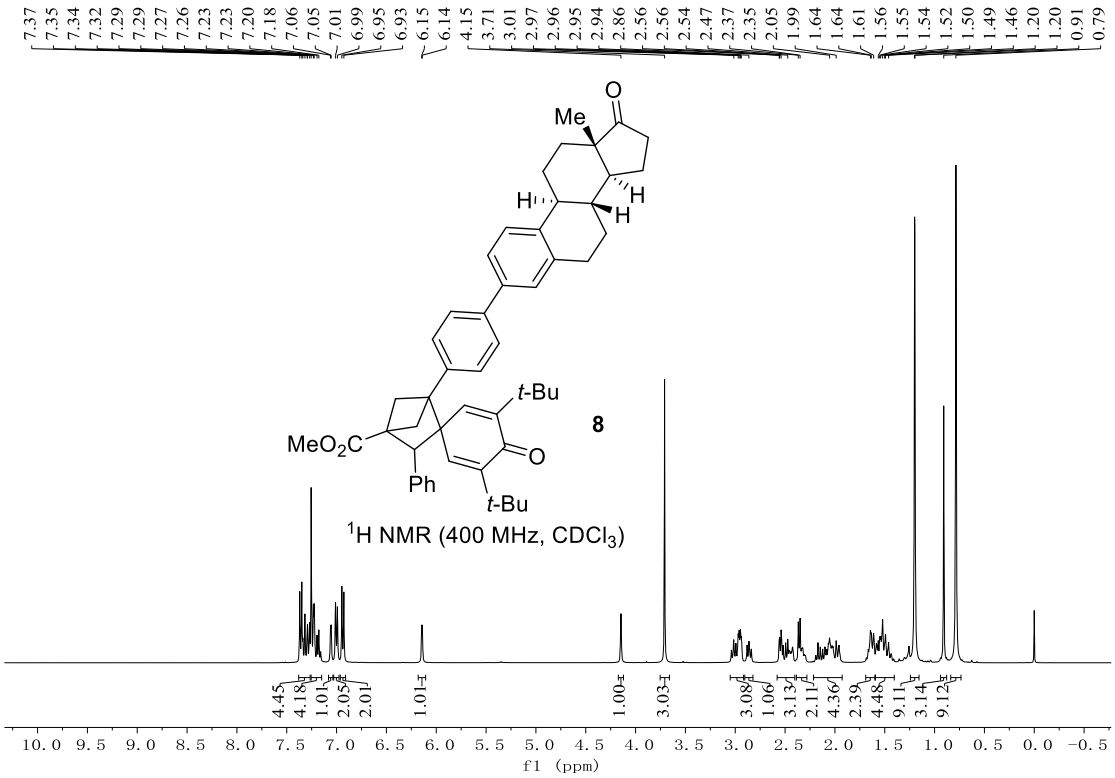


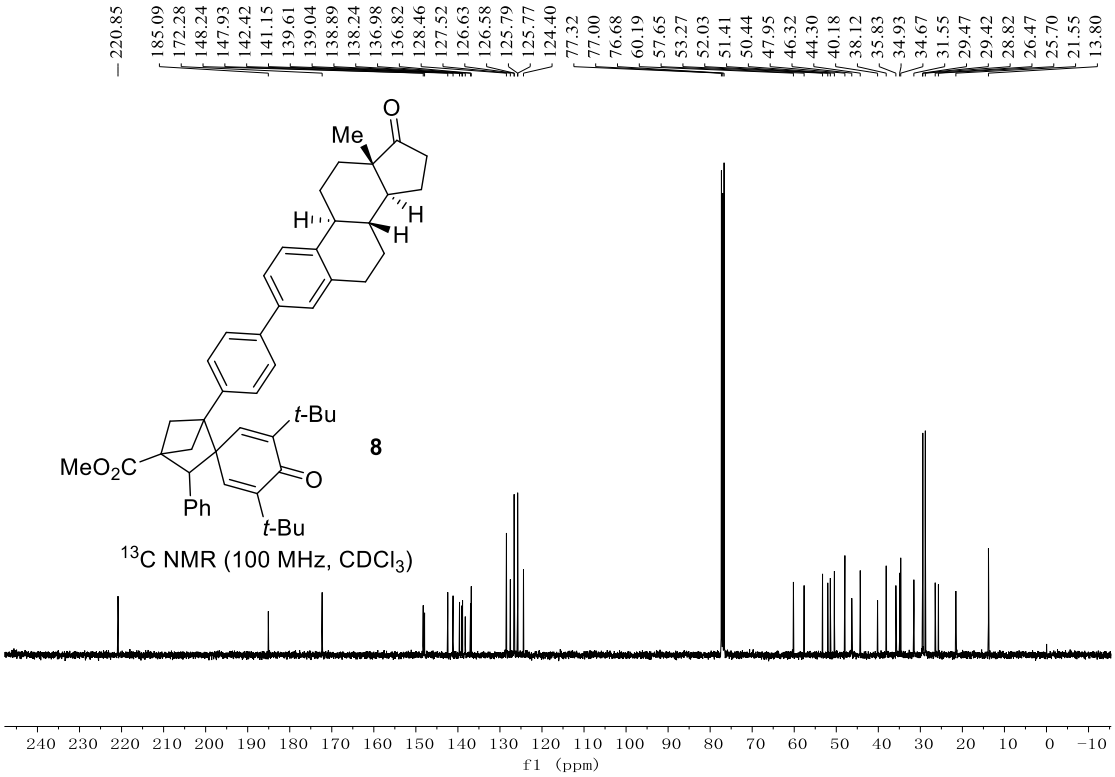
^{1}H NMR (400 MHz, $CDCl_3$)

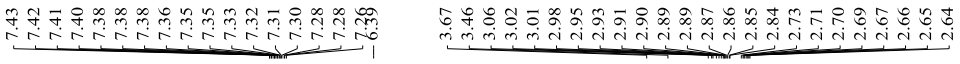

185.50
147.64
147.48
142.78
141.56
139.22
139.09
128.45
127.57
127.17
126.62
126.55
126.19
77.32
77.00
76.68
62.47
59.87
57.18
53.91
52.02
43.35
39.68
34.82
34.58
29.42
28.85
O
t-Bu
t-Bu
Ph
Ph
CH2OH
5
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

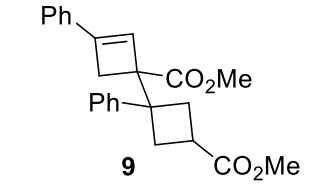

7.26
7.24
7.23
7.19
7.19
7.18
7.18
7.17
7.16
7.15
7.14
7.14
7.13
7.13
7.12
7.11
7.11
7.10
7.01
7.01
7.00
6.99
6.99
6.99
6.98
6.97
6.71
6.70
3.58
3.58
3.18
3.16
3.15
3.13
2.45
2.43
2.43
2.41
2.32
2.32
2.30
2.30
2.09
2.07
1.28
1.21
1.16
0.80
O
t-Bu
t-Bu
Ph
Ph
OH
Me
Me
6
1H NMR (400 MHz, CDCl3)
3.00
5.04
3.27
1.01
1.01
1.04
1.04
1.04
1.03
3.09
3.06
9.16
9.18
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)


185.68
147.63
147.30
142.14
141.27
139.88
139.59
128.38
127.31
127.03
126.64
126.15
77.32
77.00
76.68
71.44
60.41
59.01
56.97
54.50
43.92
38.69
34.84
34.69
29.47
28.87
27.75
27.22
O
t-Bu
t-Bu
Ph
Ph
OH
Me
Me
6
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

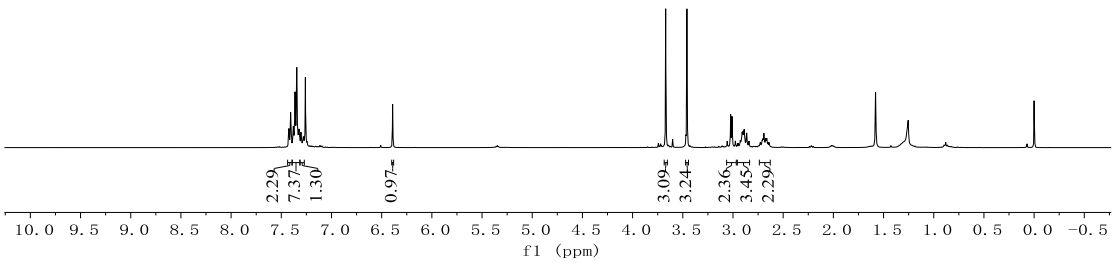

7.37
7.35
7.34
7.32
7.29
7.29
7.27
7.26
7.23
7.23
7.20
7.18
7.06
7.05
7.01
6.99
6.95
6.93
6.15
6.14
4.15
3.71
3.01
2.97
2.96
2.95
2.94
2.86
2.56
2.56
2.54
2.47
2.37
2.35
2.05
1.99
1.64
1.64
1.61
1.56
1.55
1.54
1.52
1.50
1.49
1.46
1.20
1.20
0.91
0.79
Me
O
H
H
H
t-Bu
MeO2C
O
Ph
t-Bu
8
1H NMR (400 MHz, CDCl3)
4.45
4.18
1.01
2.05
2.01
1.01
1.00
3.03
3.08
1.06
3.13
2.11
4.36
2.39
4.48
9.11
3.14
9.12
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)

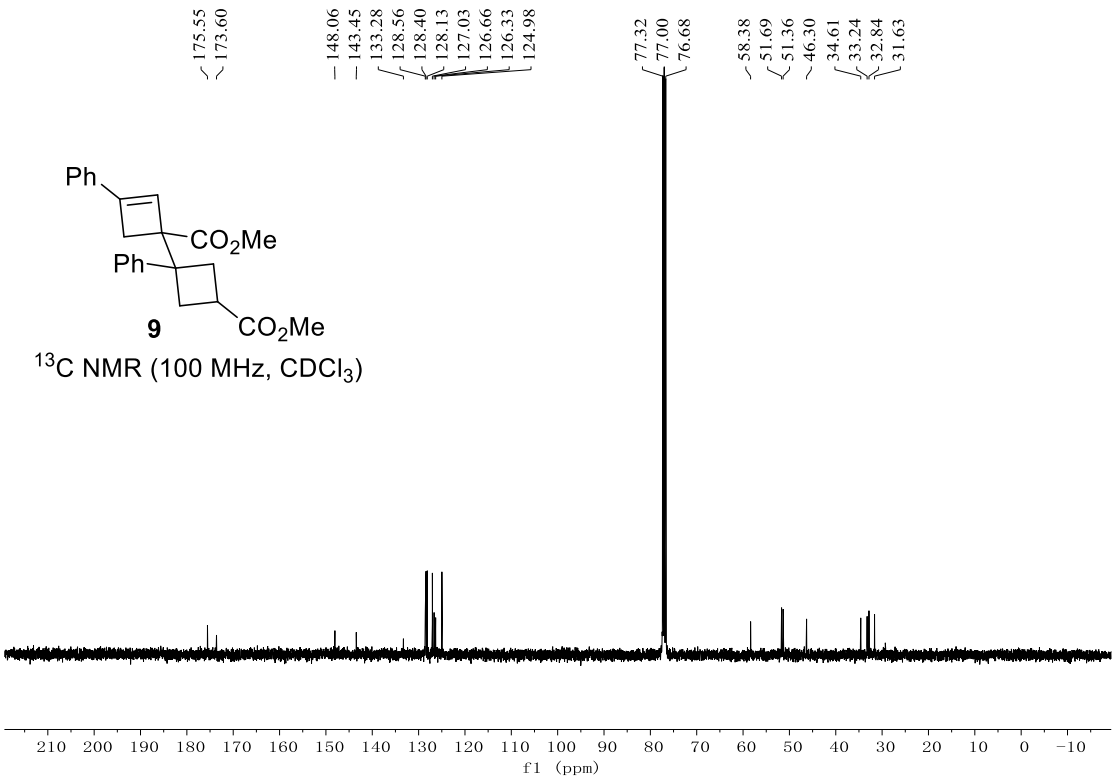


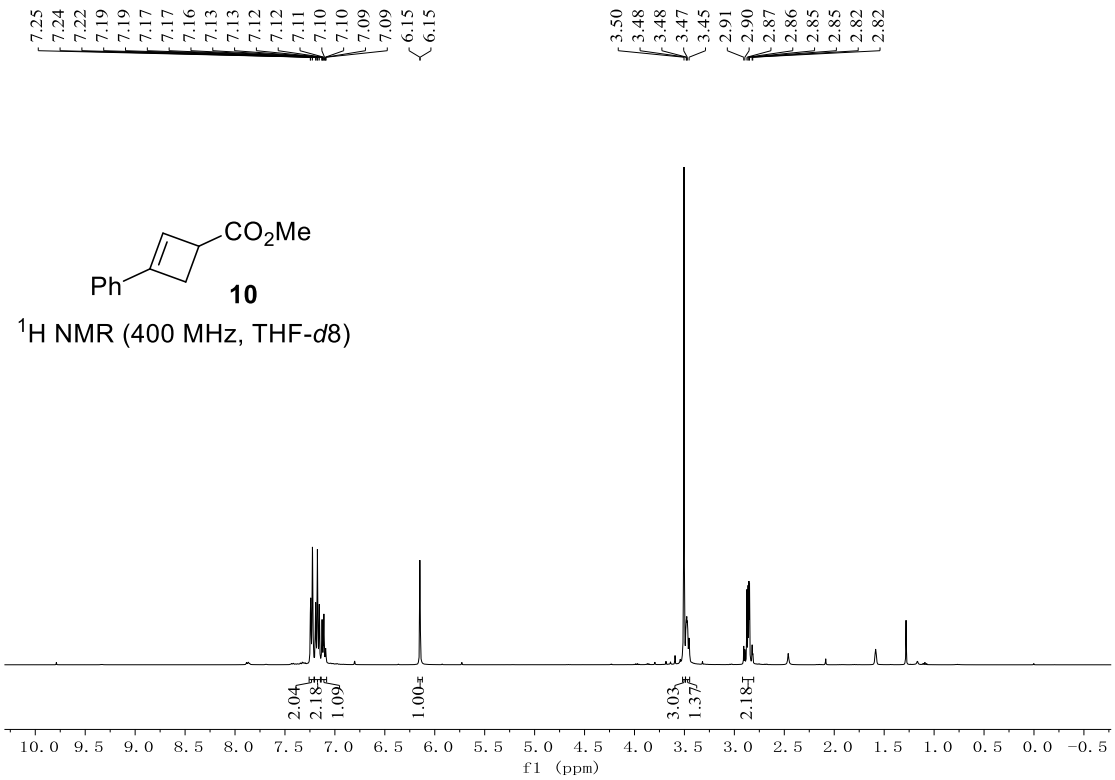


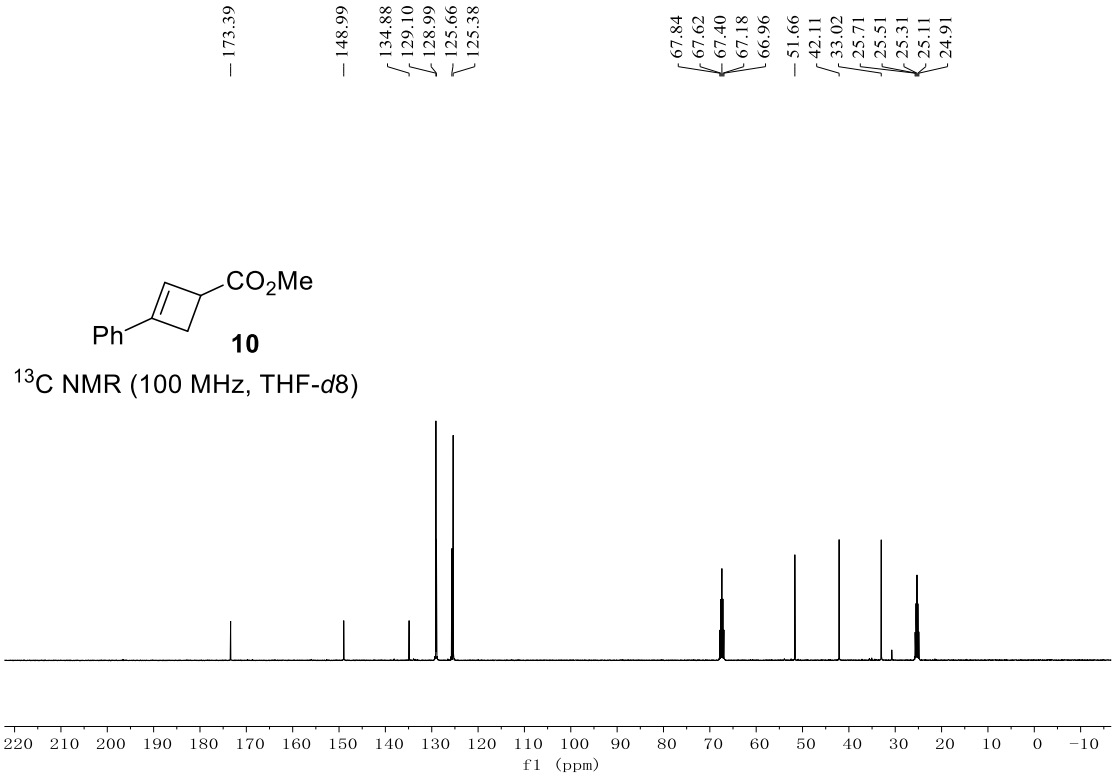


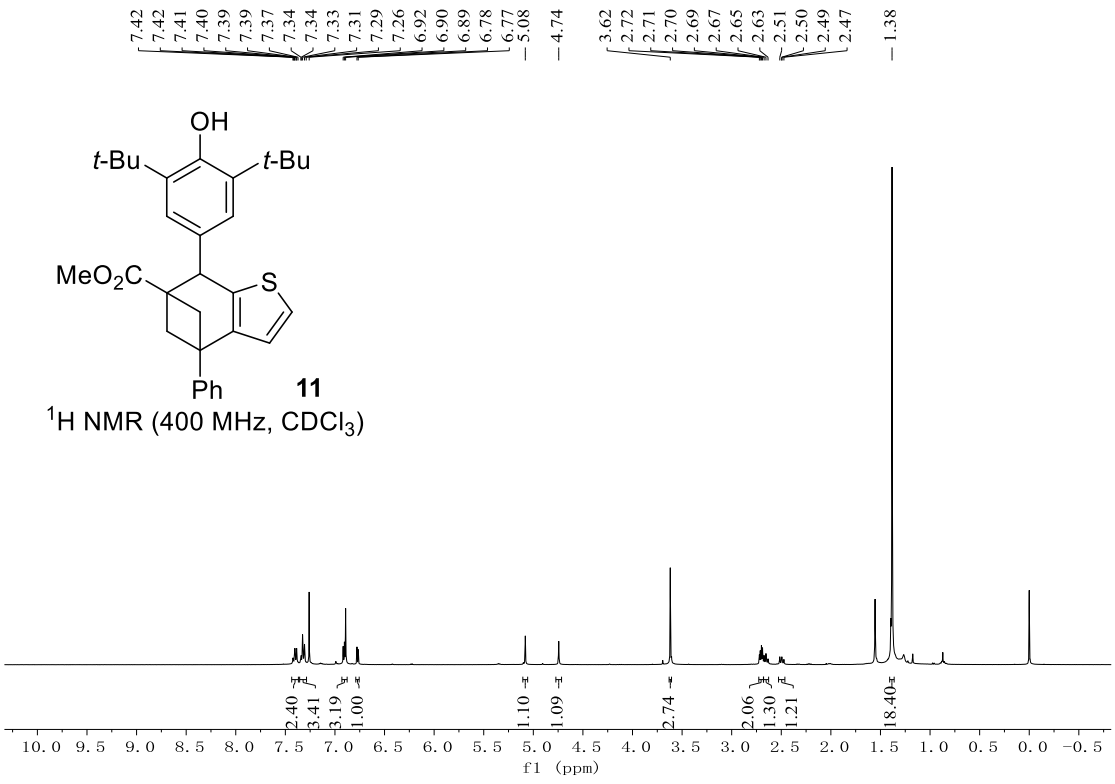
1H NMR (400 MHz, $CDCl_3$)

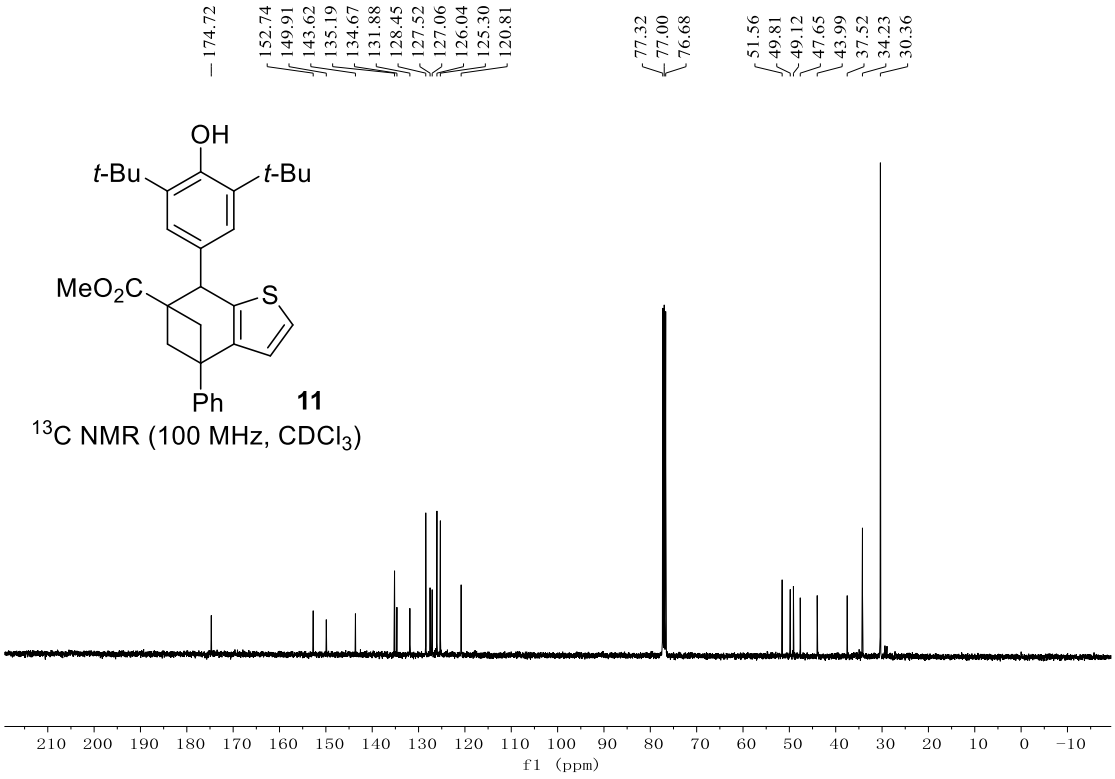



175.55
173.60
148.06
143.45
133.28
128.56
128.40
128.13
127.03
126.66
126.33
124.98
77.32
77.00
76.68
58.38
51.69
51.36
46.30
34.61
33.24
32.84
31.63
Ph
CO2Me
Ph
CO2Me
9
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


7.25
7.24
7.22
7.19
7.19
7.17
7.17
7.16
7.13
7.13
7.12
7.12
7.11
7.10
7.10
7.09
7.09
6.15
6.15
3.50
3.48
3.48
3.47
3.45
2.91
2.90
2.87
2.86
2.85
2.85
2.82
2.82
CO2Me
Ph
10
1H NMR (400 MHz, THF-d8)
2.04
2.18
1.09
1.00
3.03
1.37
2.18
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)

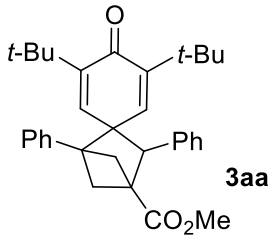

173.39
148.99
134.88
129.10
128.99
125.66
125.38
67.84
67.62
67.40
67.18
66.96
51.66
42.11
33.02
25.71
25.51
25.31
25.11
24.91
CO2Me
Ph
10
13C NMR (100 MHz, THF-d8)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


7.42
7.42
7.41
7.40
7.39
7.39
7.37
7.34
7.34
7.33
7.31
7.29
7.26
6.92
6.90
6.89
6.78
6.77
5.08
4.74
3.62
2.72
2.71
2.70
2.69
2.67
2.65
2.63
2.51
2.50
2.49
2.47
1.38
OH
t-Bu
t-Bu
MeO2C
S
Ph
11
1H NMR (400 MHz, CDCl3)
2.40
3.41
3.19
1.00
1.10
1.09
2.74
2.06
1.30
1.21
18.40
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)

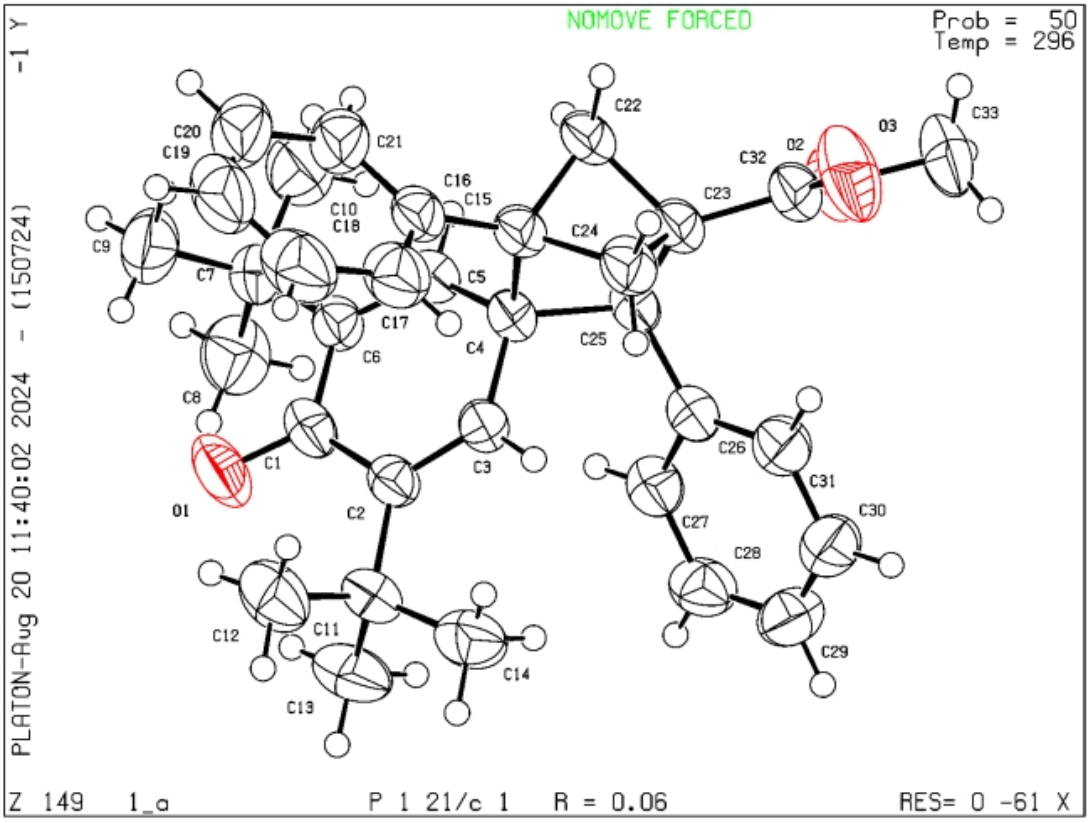

174.72
152.74
149.91
143.62
135.19
134.67
131.88
128.45
127.52
127.06
126.04
125.30
120.81
77.32
77.00
76.68
51.56
49.81
49.12
47.65
43.99
37.52
34.23
30.36
OH
t-Bu
t-Bu
MeO2C
S
Ph
11
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

X-Ray crystallographic data

X-ray structure of product **3aa** (thermal ellipsoids are shown at 50% probability level). The crystal of product **3aa** was obtained by slow evaporation in dichloromethane and petroleum ether. Crystal data have been deposited to CCDC, number 2378832.



3aa



Bond precision:	C-C = 0.0042 A	Wavelength=0.71073	
Cell:	a=12.9177(13)	b=10.0286(10)	c=21.6661(19)
	alpha=90	beta=93.906(2)	gamma=90
Temperature:	296 K		

	Calculated	Reported
Volume	2800.3(5)	2800.2(5)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C33 H38 O3	C33 H38 O3
Sum formula	C33 H38 O3	C33 H38 O3
Mr	482.63	482.63
Dx,g cm-3	1.145	1.145
Z	4	4
Mu (mm-1)	0.072	0.072
F000	1040.0	1040.0
F000'	1040.44	
h,k,lmax	15,11,25	15,11,25
Nref	4950	4934
Tmin,Tmax	0.984,0.987	0.684,0.745
Tmin'	0.984	

Correction method= # Reported T Limits: Tmin=0.684 Tmax=0.745
AbsCorr = NONE

Data completeness= 0.997 Theta(max)= 25.036

R(reflections)= 0.0637(2705) wR2(reflections)= 0.1643(4934)

S = 1.043 Npar= 332