Supporting Information

[4+1] Annulation of *ortho*-electrophile-substituted *para*-quinone methides to the synthesis of indanes and isoindolines

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1. General Information

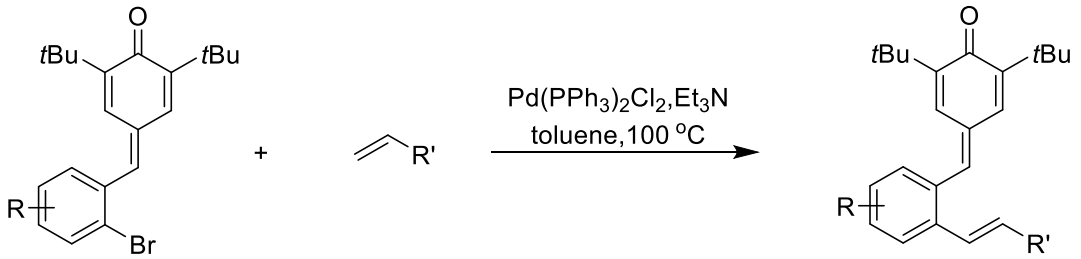
Reagents and Solvents: PE refers to petroleum ether b.p. 60-90 ℃ and EA refers to ethyl acetate. All other starting materials and solvents were commercially available and were used without further purification unless otherwise stated.

Chromatography: Flash column chromatography was carried out using commercially available 200-300 mesh under pressure unless otherwise indicated. Gradient flash chromatography was conducted eluting with PE/EA, they are listed as volume/volume ratios.

Data collection: ^{1}H and ^{13}C NMR spectra were collected on BRUKER AV-300 (300 MHz) spectrometer and AVANCE NEO (400 MHz) using $CDCl_3$ as solvent. Chemical shifts of ^{1}H NMR were recorded in parts per million (ppm, δ) relative to tetramethylsilane (δ = 0.00 ppm) with the solvent resonance as an internal standard ($CDCl_3$: δ = 7.26 ppm). Data are reported as follows: chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, brs = broad singlet, m = multiplet), coupling constant (Hz), and integration. Chemical shifts of ^{13}C NMR were reported in ppm. High Resolution Mass measurement was performed on Agilent Q-TOF 6520 mass spectrometer with electron spray ionization (ESI) as the ion source. Melting point (m.p.) was measured on a microscopic melting point apparatus. Infrared (IR) spectra were recorded using a thin film supported on KBr disks.

2. Preparation of *ortho*-Electrophile-substituted *para*-Quinone Methides

The *ortho*-electrophile-substituted *para*-quinone methides were synthesized from the corresponding *para*-quinone methides as shown in Scheme S1.



Scheme S1. Preparation of *ortho*-electrophile-substituted *para*-quinone methides

The *ortho*-bromobenzyl *para*-quinone methide[1] (1 equiv) was dissolved in toluene (2 mL/mmol *ortho*-bromobenzyl *para*-quinone methide). $Pd(PPh_3)_2Cl_2$ (0.05 equiv), the requisite Heck acceptor (3 equiv) and Et_3N (0.5 mL/mmol *ortho*-bromobenzyl *para*-quinone methide) were added, and the reaction placed under an Ar atmosphere and heated to 100 ℃ (oil bath) for 48 h. The reaction was then cooled to r.t., diluted with H_2O and extracted with CH_2Cl_2. The organic phase was dried (Na_2SO_4), filtered and concentrated, and the crude material was purified by flash chromatography on silica gel (PE/EA = 300/1) to afford the corresponding product. **1a-1r** were synthesized by the general procedure.[2] All the *ortho*-electrophilic *para*-quinone methides were listed in Figure S1.

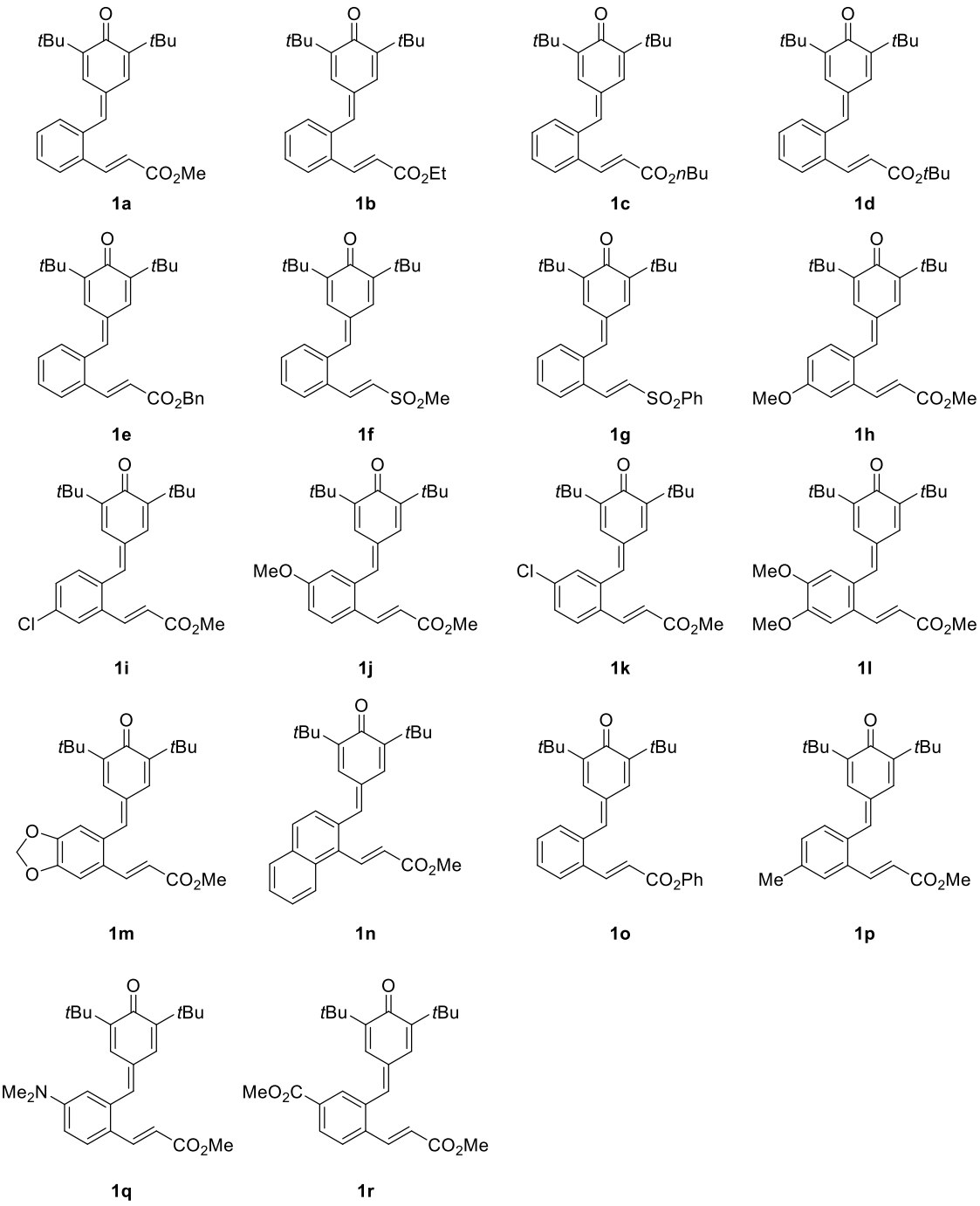
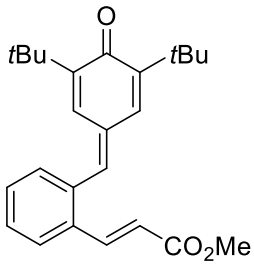
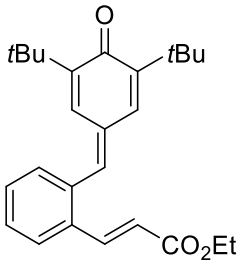


Figure S1. Structures of *ortho*-electrophile-substituted *para*-quinone methides



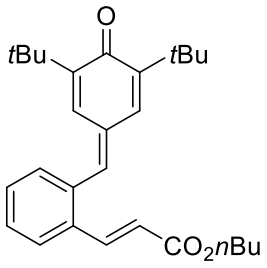
methyl (E)-3-(2-((3,5-di-tert-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)methyl)phenyl)acrylate (1a)

72% yield (1.64 g); yellow solid, m.p. 144 – 145 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.89 (d, *J* = 15.8 Hz, 1H), 7.69 – 7.67 (m, 1H), 7.49 – 7.40 (m, 2H), 7.35 – 7.33 (m, 2H), 7.19 (s, 1H), 7.08 (d, *J* = 2.4 Hz, 1H), 6.42 (d, *J* = 15.9 Hz, 1H), 3.81 (s, 3H), 1.35 (s, 9H), 1.24 (s, 9H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 186.5, 167.0, 149.6, 148.2, 142.2, 139.5, 135.7, 134.5, 134.2, 133.5, 131.6, 129.7, 129.2, 127.8, 127.4, 120.5, 51.9, 35.4, 35.1, 29.5, 29.5 ppm; IR(KBr): 3067, 2999, 2955, 2913, 2866, 1727, 1715, 1695, 1634, 1568, 1557, 1506, 1472, 1456, 1362, 1317, 1277, 1254, 1173, 1088, 1022, 980, 916, 822, 766 cm^{-1}; HRMS (ESI-TOF) calcd for $[C_{25}H_{30}O_3+H]^+$ 379.2268, found 379.2276.



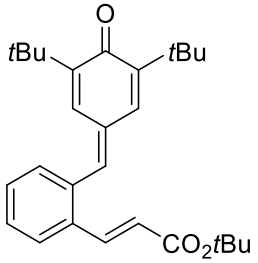
ethyl (E)-3-(2-((3,5-di-tert-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)methyl)phenyl)acrylate (1b)

70% yield (824 mg); yellow solid, m.p. 118 – 119 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.87 (d, *J* = 15.9 Hz, 1H), 7.70 – 7.67 (m, 1H), 7.46 – 7.42 (m, 2H), 7.36 – 7.34 (m, 2H), 7.18 (d, *J* = 2.4 Hz, 1H), 7.08 (d, *J* = 2.5 Hz, 1H), 6.42 (d, *J* = 15.9 Hz, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 1.39 – 1.30 (m, 12H), 1.24 (s, 9H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 186.5, 166.6, 149.6, 148.2, 141.9, 139.6, 135.7, 134.5, 134.2, 133.6, 131.6, 129.7, 129.2, 127.9, 127.4, 120.9, 60.7, 35.4, 35.1, 29.5, 29.5, 14.3 ppm; IR(KBr): 3061, 2995, 2953, 2911, 2866, 1732, 1715, 1699, 1684, 1557, 1472, 1456, 1386, 1362, 1314, 1269, 1221, 1175, 1090, 1038, 1024, 980, 930, 916, 889, 820, 764, 745, 567, 517 cm^{-1}; HRMS (ESI-TOF) calcd for $[C_{26}H_{32}O_3+H]^+$ 393.2424, found 393.2428.



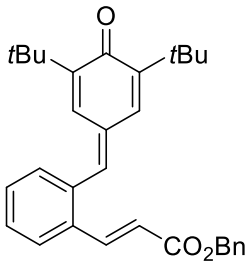
butyl
(E)-3-(2-((3,5-di-tert-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)methyl)phenyl)acrylate (1c)

56% yield (707 mg); yellow solid, m.p. 122 – 124 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.86 (d, *J* = 15.8 Hz, 1H), 7.70 – 7.67 (m, 1H), 7.48 – 7.39 (m, 2H), 7.36 – 7.33 (m, 2H), 7.17 (d, *J* = 2.4 Hz, 1H), 7.07 (d, *J* = 2.4 Hz, 1H), 6.41 (d, *J* = 15.8 Hz, 1H), 4.20 (t, *J* = 6.6 Hz, 2H), 1.67 (dq, *J* = 8.2, 6.7 Hz, 2H), 1.48 – 1.32 (m, 11H), 1.24 (s, 9H), 0.95 (t, *J* = 7.3 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 189.1, 169.2, 152.2, 150.9, 144.5, 142.0, 138.3, 137.0, 136.9, 136.2, 134.1, 132.2, 131.8, 130.4, 129.9, 123.6, 67.2, 38.0, 37.7, 33.3, 32.1, 32.0, 21.8, 16.3 ppm; IR(KBr): 3061, 2999, 2957, 2872, 1715, 1705, 1645, 1614, 1568, 1553, 1485, 1456, 1389, 1362, 1312, 1254, 1219, 1173, 1088, 1024, 980, 947, 930, 916, 889, 881, 822, 766, 746, 515 cm^{-1}; HRMS (ESI-TOF) calcd for $[C_{28}H_{36}O_3+H]^+$ 421.2737, found 421.2738.



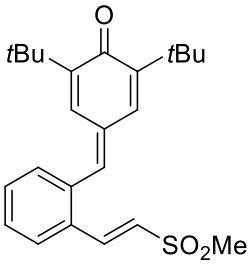
tert-butyl
(E)-3-(2-((3,5-di-tert-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)methyl)phenyl)acrylate (1d)

78% yield (989.3 mg); yellow solid, m.p. 136 – 137 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78 (d, *J* = 15.9 Hz, 1H), 7.70 – 7.67 (m, 1H), 7.46 – 7.37 (m, 2H), 7.36 – 7.32 (m, 2H), 7.17 (d, *J* = 2.4 Hz, 1H), 7.08 (d, *J* = 2.4 Hz, 1H), 6.37 (d, *J* = 15.9 Hz, 1H), 1.52 (s, 9H), 1.35 (s, 9H), 1.24 (s, 9H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 186.5, 166.0, 149.5, 148.1, 140.8, 139.7, 135.6, 134.5, 134.3, 133.5, 131.4, 129.5, 129.2, 127.9, 127.2, 122.5, 80.8, 35.4, 35.1, 29.5, 29.5, 28.2 ppm; IR(KBr): 3061, 3001, 2957, 2922, 2868, 1715, 1699, 1684, 1645, 1568, 15571472, 1456, 1362, 1317, 1254, 1223, 1155, 1090, 1024, 980, 916, 764, 743 cm^{-1}; HRMS (ESI-TOF) calcd for $[C_{28}H_{36}O_3+Na]^+$ 443.2557, found 443.2557.



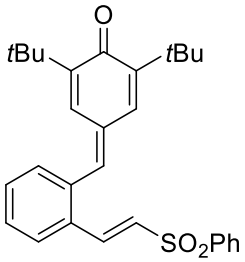
benzyl (E)-3-(2-((3,5-di-tert-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)methyl)phenyl)acrylate (1e)

74 yield (1 g); yellow solid, m.p. 104 – 106 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.92 (d, *J* = 15.8 Hz, 1H), 7.68 – 7.66 (m, 1H), 7.46 – 7.33 (m, 9H), 7.18 (d, *J* = 2.4 Hz, 1H), 7.07 (d, *J* = 2.5 Hz, 1H), 6.47 (d, *J* = 15.9 Hz, 1H), 5.25 (s, 2H), 1.35 (s, 9H), 1.23 (s, 9H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 189.1, 169.0, 152.3, 150.9, 145.1, 141.9, 138.5, 138.4, 137.0, 136.8, 136.2, 134.2, 132.3, 131.8, 131.2, 130.9, 130.9, 130.4, 130.0, 123.2, 69.1, 38.0, 37.7, 32.1, 32.1 ppm; IR(KBr): 3063, 3032, 2999, 2957, 2911, 2866, 1715, 1705, 1643, 1614, 1553, 1485, 1454, 1389, 1360, 1312, 1354, 1219, 1161, 1086, 1022, 980, 947, 930, 916, 889, 880, 822, 764, 746, 513 cm^{-1}; HRMS (ESI-TOF) calcd for $[C_{32}H_{34}O_3+H]^+$ 455.2581, found 455.2580.



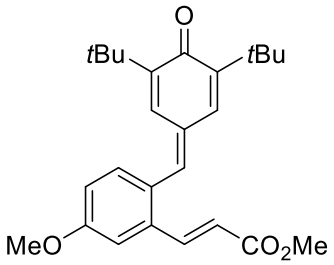
(E)-2,6-di-tert-butyl-4-(2-(2-(methylsulfonyl)vinyl)benzylidene)cyclohexa-2,5-dien-1-one (1f)

33% yield (267 mg); yellow solid, m.p. 186 – 187 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 15.6 Hz, 1H), 7.66 (d, *J* = 7.6 Hz, 1H), 7.52 – 7.47 (m, 2H), 7.38 – 7.30 (m, 2H), 7.16 (s, 1H), 7.07 (s, 1H), 6.93 (d, *J* = 15.3 Hz, 1H), 3.05 (s, 3H), 1.35 – 1.25 (m, 18H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.5, 150.0, 148.6, 141.1, 138.3, 136.3, 134.3, 134.1, 132.0, 131.7, 130.8, 129.4, 128.7, 127.9, 127.5, 43.2, 35.5, 35.2, 29.5 ppm; IR(KBr): 3055, 2999, 2957, 2924, 2866, 1614, 1568, 1483, 1470, 1456, 1362, 1304, 1254, 1136, 968, 822, 758, 511, 498 cm^{-1}; HRMS (ESI-TOF) calcd for $[C_{24}H_{30}O_3S+H]^+$ 399.1988, found 399.1987.



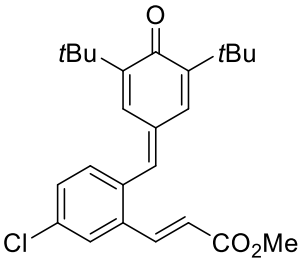
(E)-2,6-di-tert-butyl-4-(2-(2-(phenylsulfonyl)vinyl)benzylidene)cyclohexa-2,5-dien-1-one (1g)

21% yield (192 mg); yellow solid, m.p. 174 – 176 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.97 – 7.93 (m, 2H), 7.87 (d, *J* = 15.0 Hz, 1H), 7.68 – 7.53 (m, 4H), 7.51 – 7.41 (m, 2H), 7.35 (t, *J* = 7.5 Hz, 1H), 7.28 (s, 1H), 7.16 (d, *J* = 2.3 Hz, 1H), 7.05 (d, *J* = 2.4 Hz, 1H), 6.86 (d, *J* = 15.3 Hz, 1H), 1.36 (s, 9H), 1.24 (s, 9H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 186.5, 149.9, 148.5, 140.3, 139.3, 138.4, 136.2, 134.3, 134.0, 133.6, 132.0, 131.9, 130.6, 129.9, 129.4, 129.3, 127.9, 127.8, 127.5, 35.4, 35.2, 29.5, 29.5 ppm; IR(KBr): 3061, 2999, 2957, 2922, 2866, 1614, 1568, 1485, 1447, 1389, 1362, 1308, 1254, 1148, 1086, 1024, 916, 853, 808, 752, 687, 619, 584, 563, 542 cm^{-1}; HRMS (ESI-TOF) calcd for $[C_{29}H_{32}O_3S+H]^+$ 461.2145, found 461.2145.



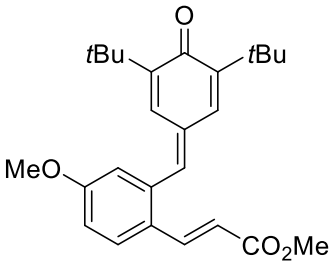
methyl
(E)-3-(2-((3,5-di-tert-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)methyl)-5-methoxyphenyl)acrylate (1h)

77% yield (632 mg); yellow solid, m.p. 150 – 152 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.88 (d, *J* = 15.8 Hz, 1H), 7.33 – 7.28 (m, 2H), 7.23 (d, *J* = 2.4 Hz, 1H), 7.16 (d, *J* = 2.6 Hz, 1H), 7.07 (d, *J* = 2.4 Hz, 1H), 7.01 (dd, *J* = 8.7, 2.6 Hz, 1H), 6.40 (d, *J* = 15.8 Hz, 1H), 3.90 (s, 3H), 3.81 (s, 3H), 1.35 (s, 9H), 1.26 (s, 9H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 186.6, 167.0, 160.3, 149.3, 147.7, 142.2, 139.6, 135.8, 134.7, 133.3, 132.6, 128.4, 128.0, 120.9, 115.8, 112.3, 55.5, 51.9, 35.4, 35.1, 29.5, 29.5 ppm; IR(KBr): 3001, 2953, 2913, 2866, 1715, 1643, 1568, 1454, 1435, 1389, 1360, 1319, 1256, 1225, 1194, 1173, 1086, 1038, 1024, 980, 949, 918, 887, 864, 820, 741, 509 cm^{-1}; HRMS (ESI-TOF) calcd for $[C_{26}H_{32}O_4+H]^+$ 409.2373, found 409.2379.



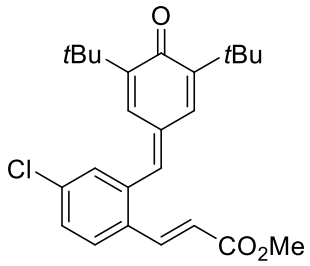
methyl (E)-3-(5-chloro-2-((3,5-di-tert-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)methyl)phenyl)acrylate (1i)

60% yield (495 mg); yellow solid, m.p. 164 – 166 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.80 (d, *J* = 15.9 Hz, 1H), 7.65 (d, *J* = 2.1 Hz, 1H), 7.43 (dd, *J* = 8.3, 2.1 Hz, 1H), 7.29 (d, *J* = 8.3 Hz, 1H), 7.22 (s, 1H), 7.12 (dd, *J* = 2.5, 0.8 Hz, 1H), 7.06 (d, *J* = 2.4 Hz, 1H), 6.42 (d, *J* = 15.9 Hz, 1H), 3.81 (s, 3H), 1.34 (s, 9H), 1.24 (s, 9H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 186.5, 166.7, 150.0, 148.5, 140.8, 137.8, 135.7, 135.3, 134.3, 134.0, 134.0, 132.8, 129.7, 127.3, 127.3, 121.7, 52.0, 35.5, 35.2, 29.5, 29.5 ppm; IR(KBr): 3067, 2997, 2957, 2911, 2866, 1717, 1674, 1614, 1562, 1456, 1435, 1389, 1362, 1319, 1256, 1225, 1196, 1175, 1117, 1082, 1024, 982, 945, 918, 887, 860, 822, 808, 757, 735, 517 cm^{-1}; HRMS (ESI-TOF) calcd for $[C_{25}H_{29}ClO_3+H]^+$ 413.1878, found 413.1883.



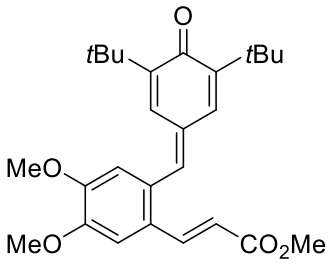
methyl (E)-3-(2-((3,5-di-tert-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)methyl)-4-methoxyphenyl)acrylate (1j)

85% yield (697 mg); yellow solid, m.p. 130 – 132 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83 (d, *J* = 15.8 Hz, 1H), 7.64 (d, *J* = 8.7 Hz, 1H), 7.33 (s, 1H), 7.24 (d, *J* = 2.4 Hz, 1H), 7.08 (d, *J* = 2.4 Hz, 1H), 6.97 (dd, *J* = 8.7, 2.7 Hz, 1H), 6.85 (d, *J* = 2.7 Hz, 1H), 6.32 (d, *J* = 15.8 Hz, 1H), 3.86 (s, 3H), 3.79 (s, 3H), 1.35 (s, 9H), 1.25 (s, 9H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 186.5, 167.4, 160.6, 149.6, 148.3, 141.7, 139.4, 137.3, 134.5, 133.6, 128.9, 127.8, 126.8, 117.9, 116.0, 115.8, 55.5, 51.7, 35.4, 35.1, 29.5 ppm; IR(KBr): 2999, 2955, 2911, 2866, 1719, 1614, 1597, 1555, 1485, 1458, 1437, 1389, 1362, 1298, 1254, 1192, 1165, 1103, 1090, 1038, 1024, 980, 930, 916, 885, 822, 737 cm^{-1}; HRMS (ESI-TOF) calcd for $[C_{26}H_{32}O_4+H]^+$ 409.2373, found 409.2373.



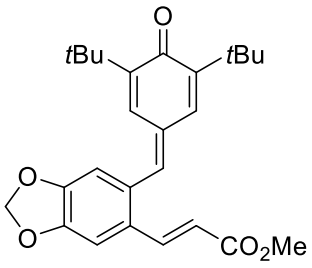
methyl (E)-3-(4-chloro-2-((3,5-di-tert-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)methyl)phenyl)acrylate (1k)

77% yield (640 mg); yellow solid, m.p. 152 – 156 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.80 (d, *J* = 15.9 Hz, 1H), 7.61 (d, *J* = 8.4 Hz, 1H), 7.39 (dd, *J* = 8.4, 2.2 Hz, 1H), 7.35 (d, *J* = 2.2 Hz, 1H), 7.21 (s, 1H), 7.13 (d, *J* = 2.4 Hz, 1H), 7.05 (d, *J* = 2.4 Hz, 1H), 6.40 (d, *J* = 15.9 Hz, 1H), 3.80 (s, 3H), 1.35 (s, 9H), 1.25 (s, 9H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 186.4, 166.8, 150.1, 148.7, 141.0, 137.2, 137.1, 135.7, 134.3, 134.1, 132.5, 131.3, 129.2, 128.6, 127.3, 120.8, 52.0, 35.5, 35.2, 29.5, 29.4 ppm; IR(KBr): 3059, 2999, 2955, 2913, 2866, 1722, 1680, 1630, 1616, 1585, 1564, 1456, 1435, 1389, 1362, 1315, 1254, 1223, 1196, 1173, 1113, 1086, 1024, 982, 951, 912, 881, 822, 741, 515 cm^{-1}; HRMS (ESI-TOF) calcd for $[C_{25}H_{29}ClO_3+H]^+$ 413.1878, found 413.1884.



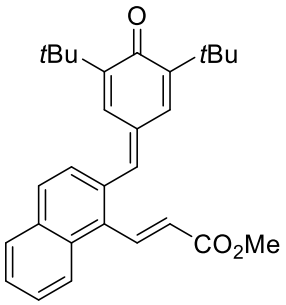
methyl (E)-3-(2-((3,5-di-tert-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)methyl)-4,5-dimethoxyphenyl)acrylate (1l)

84% yield (733 mg); yellow solid, m.p. 168 – 170 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 15.7, 7.5 Hz, 1H), 7.37 (d, *J* = 6.7 Hz, 1H), 7.30 (d, *J* = 4.3 Hz, 1H), 7.17 – 7.08 (m, 2H), 6.88 (d, *J* = 7.3 Hz, 1H), 6.34 (dd, *J* = 16.1, 7.1 Hz, 1H), 3.99 (d, *J* = 6.6 Hz, 3H), 3.94 (d, *J* = 7.0 Hz, 3H), 3.82 (d, *J* = 6.9 Hz, 3H), 1.37 (d, *J* = 6.7 Hz, 9H), 1.27 (d, *J* = 7.1 Hz, 9H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 186.4, 167.2, 150.3, 149.9, 149.5, 148.0, 141.7, 139.4, 134.6, 132.9, 129.4, 127.9, 127.4, 118.3, 114.0, 109.2, 56.1, 51.8, 35.4, 35.1, 29.6, 29.6, 29.5 ppm; IR(KBr): 3001, 2955, 2913, 2866, 1715, 1614, 1549, 1514, 1506, 1485, 1456, 1389, 1360, 1333, 1277, 1192, 1169, 1111, 1086, 1040, 1024, 1005, 978, 949, 932, 916, 895, 822, 737, 559, 529 cm^{-1}; HRMS (ESI-TOF) calcd for $[C_{27}H_{34}O_5+H]^+$ 439.2479, found 439.2480.



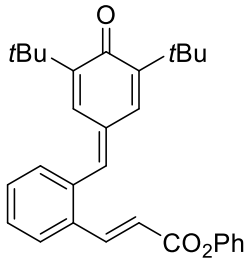
methyl
(E)-3-(6-((3,5-di-tert-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)methyl)benzo[d][1,3]dioxol-5-yl)acrylate (1m)

85% yield (720 mg); yellow solid, m.p. 150 – 152 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.81 (d, *J* = 15.7 Hz, 1H), 7.27 (d, *J* = 2.9 Hz, 1H), 7.18 (d, *J* = 2.4 Hz, 1H), 7.14 (s, 1H), 7.05 (d, *J* = 2.4 Hz, 1H), 6.82 (s, 1H), 6.28 (d, *J* = 15.7 Hz, 1H), 6.08 (s, 2H), 3.79 (s, 3H), 1.34 (s, 9H), 1.25 (s, 9H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 186.5, 167.2, 149.5, 149.4, 148.9, 148.0, 141.6, 139.1, 134.6, 133.2, 130.9, 128.9, 127.6, 118.4, 110.9, 106.5, 102.1, 51.8, 35.4, 35.1, 29.5 ppm; IR(KBr): 2999, 2955, 2909, 2866, 1715, 1614, 1557, 1481, 1456, 1435, 1362, 1288, 1263, 1194, 1173, 1088, 1040, 1024, 932, 914, 891, 822, 741, 501 cm^{-1}; HRMS (ESI-TOF) calcd for $[C_{26}H_{30}O_5+H]^+$ 423.2166, found 423.2170.



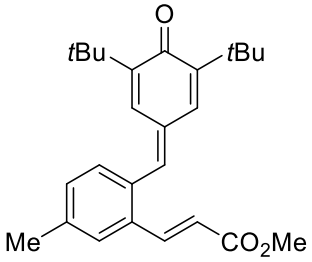
methyl
(E)-3-(2-((3,5-di-tert-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)methyl)naphthalen-1-yl)acrylate (1n)

80% yield (688.7 mg); yellow solid, m.p. 180 – 182 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.34 (d, *J* = 16.0 Hz, 1H), 8.16 – 8.12 (m, 1H), 7.92 – 7.88 (m, 2H), 7.62 – 7.56 (m, 2H), 7.52 (d, *J* = 8.6 Hz, 1H), 7.39 (d, *J* = 2.0 Hz, 1H), 7.35 (s, 1H), 7.08 (d, *J* = 2.4 Hz, 1H), 6.26 (d, *J* = 16.0 Hz, 1H), 3.88 (s, 3H), 1.36 (s, 9H), 1.28 (s, 9H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 186.4, 166.6, 149.7, 148.0, 141.6, 141.2, 134.7, 133.3, 133.1, 132.6, 131.5, 129.0, 128.8, 128.6, 128.4, 127.6, 127.5, 127.3, 124.8, 52.1, 35.5, 35.1, 29.6 ppm; IR(KBr): 3057, 2997, 2955, 2911, 2866, 1719, 1624, 1612, 1560, 1483, 1458, 1435, 1362, 1285, 1269, 1194, 1171, 1086, 1024, 984, 932, 916, 885, 822, 745 cm^{-1}; HRMS (ESI-TOF) calcd for $[C_{29}H_{32}O_3+H]^+$ 429.2424, found 429.2434.



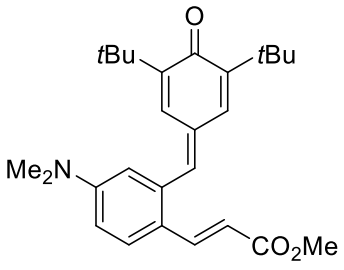
phenyl (E)-3-(2-((3,5-di-tert-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)methyl)phenyl)acrylate (1o)

51% yield (452 mg); yellow solid, m.p. 140 – 141 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 15.9 Hz, 1H), 7.76 (d, *J* = 6.6 Hz, 1H), 7.51 – 7.36 (m, 6H), 7.26 (t, *J* = 5.8 Hz, 1H), 7.19 – 7.14 (m, 3H), 7.09 (s, 1H), 6.62 (d, *J* = 15.8 Hz, 1H).1.34 (s, 9H), 1.25 (s, 9H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.6, 165.0, 150.7, 149.7, 148.4, 143.9, 139.3, 136.0, 134.4, 134.0, 133.9, 131.7, 130.1, 129.5, 129.4, 127.8, 127.6, 125.9, 121.6, 119.9, 35.5, 35.2, 29.5 ppm; IR(KBr): 3061, 2999, 2957, 2866, 1738, 1620, 1609, 1593, 1568, 1493, 1389, 1362, 1312, 1254, 1204, 1132, 1086, 1024, 976, 932, 889, 820, 764, 743, 687, 517 cm^{-1}; HRMS (ESI-TOF) calcd for $[C_{30}H_{32}O_3+Na]^+$ 463.2244, found 463.2244.



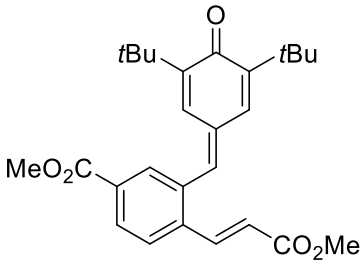
methyl (E)-3-(2-((3,5-di-tert-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)methyl)-5-methylphenyl)acrylate (1p)

68% yield (535 mg); yellow solid, m.p. 178 – 180 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.87 (d, *J* = 15.9 Hz, 1H), 7.48 (s, 1H), 7.32 (s, 1H), 7.26 (s, 2H), 7.22 (d, *J* = 2.5 Hz, 1H), 7.07 (d, *J* = 2.4 Hz, 1H), 6.41 (d, *J* = 15.9 Hz, 1H), 3.80 (s, 3H), 2.43 (s, 3H), 1.35 (s, 9H), 1.25 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 186.5, 167.0, 149.4, 147.9, 142.3, 139.8, 139.5, 134.6, 134.1, 133.1, 132.9, 131.7, 130.7, 128.0, 128.0, 120.3, 51.8, 35.4, 35.1, 29.5, 29.5, 21.4 ppm; IR(KBr): 2997, 2955, 2920, 2866, 1719, 1638, 1614, 1566, 1483, 1458, 1435, 1362, 1317, 1273, 1254, 1192, 1171, 1084, 1022, 980, 916, 887, 820, 501 cm^{-1}; HRMS (ESI-TOF) calcd for $[C_{26}H_{32}O_3+H]^+$ 393.2424, found 393.2424.



methyl (E)-3-(2-((3,5-di-tert-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)methyl)-4-(dimethylamino)phenyl)acrylate (1q)

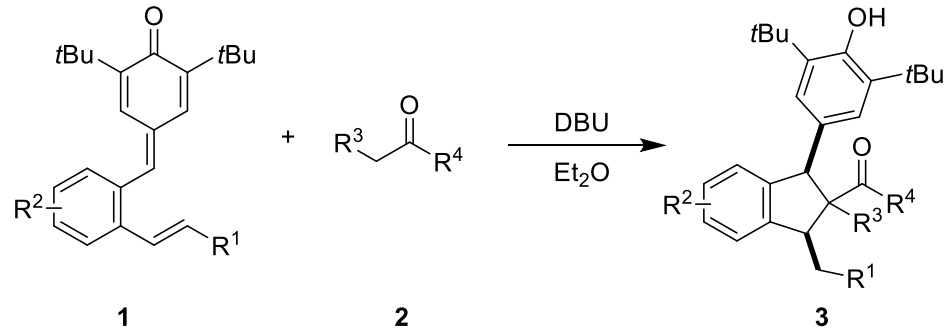
78% yield (660 mg); yellow solid, m.p. 171 – 173 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82 (d, *J* = 15.6 Hz, 1H), 7.60 (d, *J* = 8.7 Hz, 1H), 7.40 (s, 1H), 7.34 (s, 1H), 7.09 (s, 1H), 6.74 (d, *J* = 8.7 Hz, 1H), 6.56 (s, 1H), 6.23 (d, *J* = 15.7 Hz, 1H), 3.77 (s, 3H), 3.04 (s, 6H), 1.36 (s, 9H), 1.26 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 186.7, 167.9, 150.9, 149.2, 148.0, 142.2, 141.2, 137.0, 134.7, 133.2, 128.8, 128.2, 121.7, 114.7, 114.3, 112.7, 51.5, 40.2, 35.4, 35.1, 29.6, 29.5 ppm; IR(KBr): 2997, 2953, 2911, 2866, 1715, 1614, 1593, 1562, 1504, 1456, 1362, 1331, 1292, 1256, 1227, 1173, 1157, 1098, 1024, 980, 932, 881, 822, 806, 735 cm^{-1}; HRMS (ESI-TOF) calcd for $[C_{27}H_{35}NO_3+H]^+$ 422.2690, found 422.2689.



methyl (E)-3-((3,5-di-tert-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)methyl)-4-(3-methoxy-3-oxoprop-1-en-1-yl)benzoate (1r)

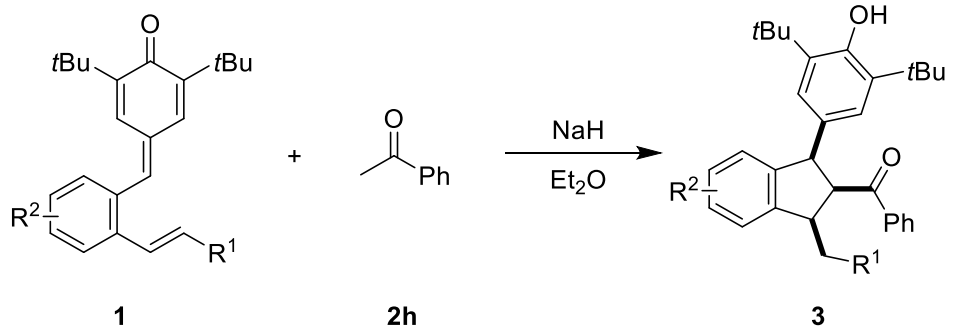
77% yield (672 mg); yellow solid, m.p. 120 – 122 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.07 – 7.75 (m, 4H), 7.29 – 7.09 (m, 3H), 6.49 (d, *J* = 15.3 Hz, 1H), 3.95 – 3.82 (m, 6H), 1.36 – 1.25 (m, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 186.4, 166.5, 165.9, 150.0, 148.6, 141.0, 138.2, 137.6, 135.6, 134.1, 132.8, 131.0, 129.8, 127.4, 127.4, 122.5, 52.4, 51.9, 35.4, 35.1, 29.5, 29.4 ppm; IR(KBr): 2999, 2953, 2913, 2868, 1728, 1715, 1634, 1614, 1568, 1485, 1456, 1435, 1389, 1362, 1296, 1258, 1215, 1173, 1117, 1092, 1024, 986, 914, 883, 845, 822, 772, 735, 648 cm^{-1}; HRMS (ESI-TOF) calcd for $[C_{27}H_{32}O_5+H]^+$ 437.2323, found 437.2320.

3. General Procedure of [4+1] Annulation of *ortho*-Electrophile-substituted *para*-Quinone Methides



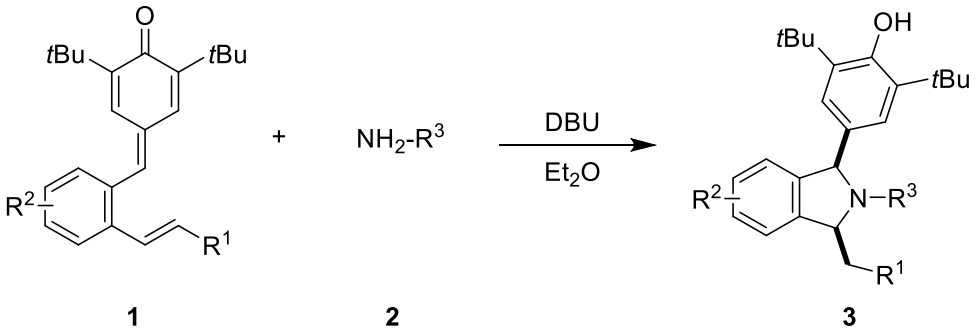
1 **2** **3**

A sealed tube was charged with **1** (0.2 mmol, 1 equiv), **2** (1 equiv), DBU (2.2 equiv), and Et_2O (2 mL). Then the reaction mixture was stirred at a.t. (ambient temperature) for 12 h. The solution was concentrated in *vacuo* and purified by careful chromatography on silica gel (PE/EA = 100/1) to afford the desired product.



1 **2h** **3**

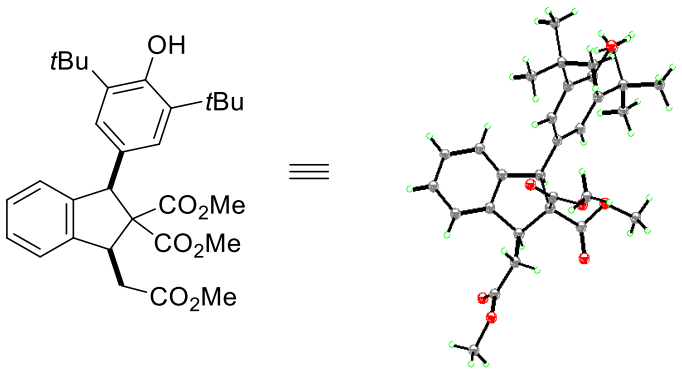
A sealed tube was charged with **2h** (1.2 equiv), NaH (2.5 equiv), and dry Et_2O (1 mL), and the reaction mixture was stirred at a.t. for 10 min. Then, **1** (0.2 mmol, 1 equiv) in dry Et_2O (1 mL) was added to a suspension of **2h**. Then the reaction mixture was stirred at a.t. for 24 h. After hydrolysis with saturated ammonium chloride solution, the water phase was extracted with ethyl acetate for 3 times. The combined organic layers were washed with water and brine sequentially, dried over Na_2SO_4, filtered and concentrated. The crude product was purified by flash chromatography on silica gel (PE/EA = 100/1) to afford the corresponding products.



1 **2** **3**

A sealed tube was charged with **1** (0.2 mmol, 1 equiv), **2** (1 equiv), DBU (2.2 equiv), and solvent (2 mL). Then the reaction mixture was stirred at a.t. for 24 h. The solution was concentrated in *vacuo* and purified by careful chromatography on silica gel (PE/EA = 50/1) to afford the desired product.

4. Crystal Structure of 3aa



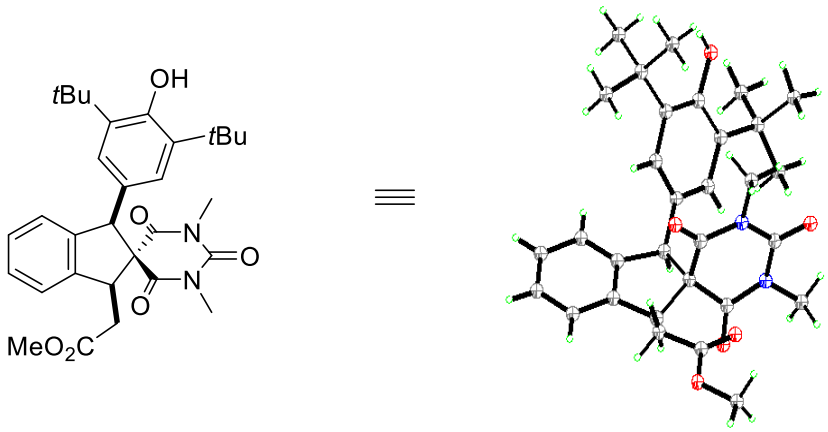
3aa CCDC 1856982

Figure S2. ORTEP plot of the crystal structure of 3aa (50% ellipsoid probability)

X-ray crystallographic data of **3aa**

CCDC number	1856982		
Empirical formula	$C_{30}H_{38}O_7$		
Formula weight	510.60		
Temperature	298 K		
Wavelength	1.54178 Å		
Space group	P 1 21/c 1		
Unit cell dimensions	a=11.8298(2)	Å	=90 °
	b=17.6502(3)	Å	=90.058(1) °
	c=13.5929(2)	Å	=90 °
Volume	2838.17(8) Å		
Z	4		
F(000)	1096.0		
Completeness to theta = 74.530°	99.8%		
Max. and min. transmission	0.750 and 0.370		
R indices (all data)	R= 0.0702(4667) wR2(reflections)= 0.2034(5792)		
S	1.068		

5. Crystal Structure of 3ag



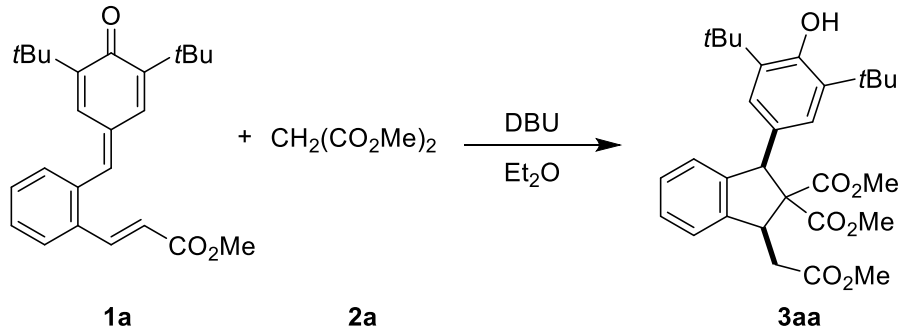
3ag CCDC 1856983

Figure S3. ORTEP plot of the crystal structure of 3ag (50% ellipsoid probability)

X-ray crystallographic data of **3ag**

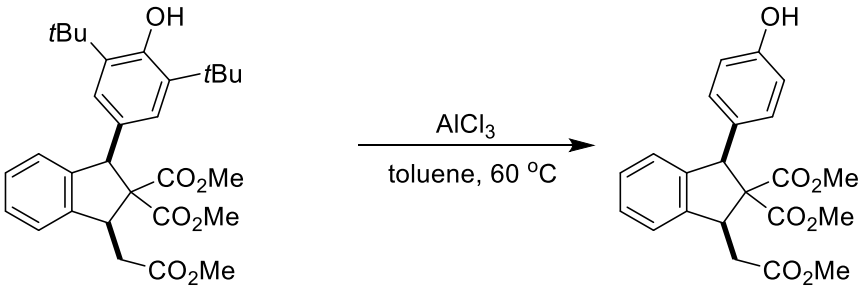
CCDC number	1856983		
Empirical formula	$C_{31}H_{38}N_2O_6$		
Formula weight	534.63		
Temperature	298 K		
Wavelength	1.54178 Å		
Space group	P 1 21/c 1		
Unit cell dimensions	a=11.2677(1)	Å	=90 °
	b=10.9396(1)	Å	=93.117(1) °
	c=24.1210(3)	Å	=90 °
Volume	2968.86(5) Å		
Z	4		
F(000)	1144.0		
Completeness to theta = 72.180°	99.6%		
Max. and min. transmission	0.754 and 0.557		
R indices (all data)	R= 0.0487(5101) wR2(reflections)= 0.1430(5829)		
S	1.047		

6. Scale-up Experiment and Further Functionalization of 3aa



1a **2a** **3aa**

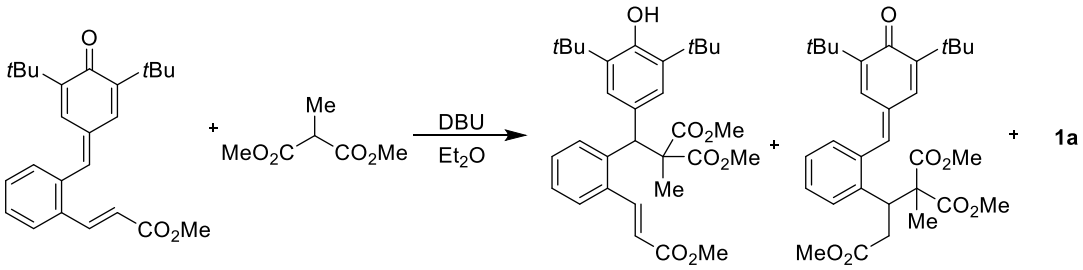
A sealed tube was charged with **1a** (1.136g, 3 mmol), **2a** (0.392 g, 3 mmol, 1 equiv), DBU (2.2 equiv), and Et_2O (30 mL). Then the reaction mixture was stirred at a.t. for 24 h. The solution was concentrated in *vacuo* and purified by careful chromatography on silica gel (PE/EA = 100/1) to afford the desired product 1.45g.



3aa **4aa**

To a solution of **3aa** (102.1mg, 0.2 mmol) in toluene (3 ml) at a.t. was added $AlCl_3$ (5 equiv) in one portion. The mixture was immediately heated to 60 ℃ by using a preheated oil bath and maintained at this temperature for 2 h. The mixture was cooled to r.t. and poured into a separatory funnel containing ice and ethyl acetate (1/1). The layers were separated and the aqueous layer was extracted with ethyl acetate for 3 times. The combined organics were dried (Na_2SO_4), filtered, and concentrated in *vacuo*. The product was purified by column chromatography.

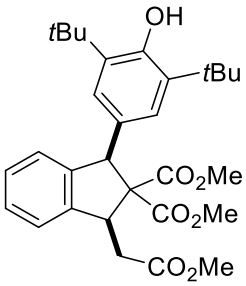
7. Mechanistic Experiments



1a **2l** **5al** **5al'**
(Not observed)

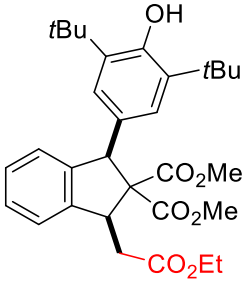
A sealed tube was charged with **1a** (0.2 mmol, 1 equiv), **2l** (1 equiv), DBU (2.2 equiv), and Et_2O (2 mL). Then the reaction mixture was stirred at a.t. for 24 h. The solution was concentrated in *vacuo* and purified by careful chromatography on silica gel (PE/EA = 100/1) to afford the product.

8. Characterization of the Title Products



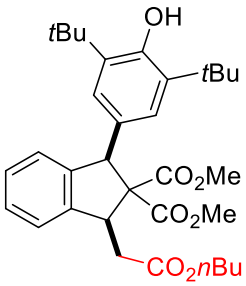
dimethyl (1R,3S)-1-(3,5-di-tert-butyl-4-hydroxyphenyl)-3-(2-methoxy-2-oxoethyl)-1,3-dihydro-2H-indene-2,2-dicarboxylate (3aa)

97% yield (99.1 mg), 9:1 dr; white solid, m.p. 160 – 162 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25 – 7.12 (m, 5H), 7.03 (d, *J* = 7.4 Hz, 1H), 5.29 (s, 1H), 5.14 (s, 1H), 4.09 (t, *J* = 6.0 Hz, 1H), 3.81 – 3.79 (m, 6H), 3.12 – 3.10 (m, 5H), 1.39 (s, 18H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.8, 171.4, 168.5, 153.0, 143.4, 142.0, 135.0, 128.6, 127.5, 126.9, 126.7, 125.1, 122.4, 72.1, 55.9, 52.6, 52.0, 51.5, 46.7, 36.1, 34.3, 30.4 ppm; IR(KBr): 3636, 3460, 3418, 2953, 2914, 2874, 1737, 1732, 1435, 1368, 1303, 1267, 1203, 1169, 1123, 1103, 1051, 1018, 976, 897, 741, 644 cm^{-1}; HRMS (ESI-TOF) calcd for $[C_{30}H_{38}O_7+H]^+$ 511.2690, found 511.2699.



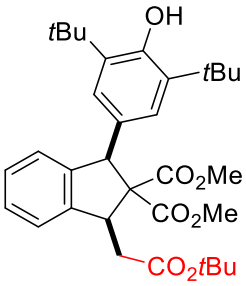
dimethyl (1R,3S)-1-(3,5-di-tert-butyl-4-hydroxyphenyl)-3-(2-ethoxy-2-oxoethyl)-1,3-dihydro-2H-indene-2,2-dicarboxylate (3ba)

88% yield (92.4 mg), 11:1 dr; light yellow solid, m.p. 154 – 156 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25 – 7.13 (m, 5H), 7.03 (d, *J* = 7.4 Hz, 1H), 5.29 (s, 1H), 5.14 (s, 1H), 4.26 (dd, *J* = 7.4, 4.6 Hz, 2H), 4.08 (d, *J* = 6.2 Hz, 1H), 3.81 (s, 3H), 3.10 (s, 5H), 1,40 – 1.30 (m, 21H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.3, 171.4, 168.5, 153.0, 143.5, 142.0, 135.0, 128.6, 127.5, 126.8, 126.7, 125.1, 122.5, 72.1, 60.8, 55.9, 52.6, 51.5, 46.7, 36.4, 34.3, 30.4, 14.3 ppm; IR(KBr): 3638, 3617, 2955, 2913, 2874, 1737, 1732, 1481, 1435, 1393, 1373, 1303, 1267, 1204, 1167, 1123, 1101, 1051, 1030, 976, 895, 808, 743, 646, 592 cm^{-1}; HRMS (ESI-TOF) calcd for $[C_{31}H_{40}O_7+H]^+$ 525.2847, found 525.2848.



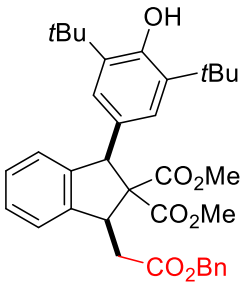
dimethyl (1S,3R)-1-(2-butoxy-2-oxoethyl)-3-(3,5-di-tert-butyl-4-hydroxyphenyl)-1,3-dihydro-2H-indene-2,2-dicarboxylate (3ca)

93% yield (102.4 mg), 5:1 dr; white solid, m.p. 102 – 104 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.26 – 7.13 (m, 5H), 7.03 (d, *J* = 7.4 Hz, 1H), 5.30 (s, 1H), 5.14 (s, 1H), 4.27 – 4.13z (m, 2H), 4.07 (d, *J* = 6.2 Hz, 1H), 3.81 (s, 3H), 3.10 (s, 5H), 1.66 (q, *J* = 7.1 Hz, 2H), 1.49 – 1.39 (m, 20H), 0.96 (t, *J* = 7.4 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.4, 171.4, 168.5, 153.0, 143.5, 142.0, 135.0, 128.6, 127.5, 126.8, 126.7, 125.1, 122.5, 72.1, 64.7, 55.9, 52.6, 51.5, 46.7, 36.4, 34.3, 30.7, 30.4, 19.2, 13.7 ppm; IR(KBr): 3628, 3613, 2957, 2874, 1768, 1732, 1717, 1456, 1435, 1395, 1362, 1308, 1269, 1204, 1169, 1123, 1101, 1051, 976, 893, 808, 745, 644, 592 cm^{-1}; HRMS (ESI-TOF) calcd for $[C_{33}H_{44}O_7+H]^+$ 553.3160, found 553.3161.



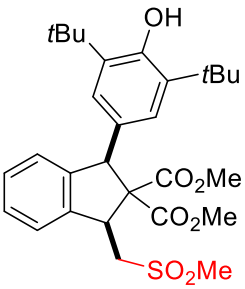
dimethyl (1S,3R)-1-(2-(tert-butoxy)-2-oxoethyl)-3-(3,5-di-tert-butyl-4-hydroxyphenyl)-1,3-dihydro-2H-indene-2,2-dicarboxylate (3da)

71% yield (78.0 mg); >20:1 dr; white solid, m.p. 149 – 150 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.27 – 7.13 (m, 5H), 7.02 (d, *J* = 7.4 Hz, 1H), 5.29 (s, 1H), 5.14 (s, 1H), 4.03 (t, *J* = 6.0 Hz, 1H), 3.82 (s, 3H), 3.09 (s, 3H), 3.02 (d, *J* = 6.0 Hz, 2H), 1.53 (s, 9H), 1.39 (s, 18H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.5, 171.5, 168.5, 153.0, 143.8, 142.0, 135.0, 128.7, 127.4, 126.7, 125.0, 122.6, 80.7, 72.2, 55.9, 52.6, 51.5, 46.7, 37.6, 34.3, 30.4, 28.2 ppm; IR(KBr): 3645, 3613, 2953, 2914, 2874, 1748, 1731, 1715, 1456, 1435, 1393, 1368, 1265, 1211, 1153, 1123, 1101, 1051, 978, 895, 853, 808, 743, 646, 590, 545 cm^{-1}; HRMS (ESI-TOF) calcd for $[C_{33}H_{44}O_7+ Na]^+$ 575.2982, found 575.2979.



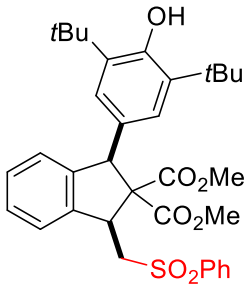
dimethyl (1S,3R)-1-(2-(benzyloxy)-2-oxoethyl)-3-(3,5-di-tert-butyl-4-hydroxyphenyl)-1,3-dihydro-2H-indene-2,2-dicarboxylate (3ea)

82% yield (96.5 mg), 5:1 dr; white solid, m.p. 128 – 130 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 – 7.31 (m, 5H), 7.20 – 7.17 (m, 2H), 7.12 (s, 2H), 7.06 – 7.01 (m, 2H), 5.30 – 5.19 (m, 3H), 5.14 (s, 1H), 4.11 (t, *J* = 6.1 Hz, 1H), 3.77 (s, 3H), 3.17 (d, *J* = 6.0 Hz, 2H), 3.08 (s, 3H), 1.39 (s, 18H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.1, 171.4, 168.5, 153.0, 143.3, 142.0, 135.9, 135.1, 128.6, 128.6, 128.3, 128.3, 127.5, 126.8, 126.7, 125.1, 122.5, 72.1, 66.6, 56.0, 52.6, 51.5, 46.7, 36.4, 34.3, 30.4 ppm; IR(KBr): 3647, 3614, 2953, 2914, 2874, 1748, 1732, 1717, 1472, 1456, 1435, 1317, 1267, 1238, 1211, 1163, 1123, 1101, 1051, 975, 895, 743, 644 cm^{-1}; HRMS (ESI-TOF) calcd for $[C_{36}H_{42}O_7+H]^+$ 587.3003, found 587.3004.



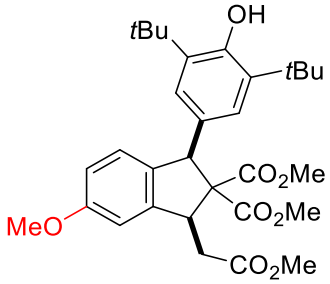
dimethyl (1R,3S)-1-(3,5-di-tert-butyl-4-hydroxyphenyl)-3-((methylsulfonyl)methyl)-1,3-dihydro-2H-indene-2,2-dicarboxylate (3fa)

86% yield (91.7 mg), 10:1 dr; white solid, m.p. 188 – 190 ^{o}C, ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.6 Hz, 1H), 7.72 (t, *J* = 7.5 Hz, 1H), 7.63 (t, *J* = 7.5 Hz, 1H), 7.51 (s, 2H), 7.42 (d, *J* = 7.5 Hz, 1H), 5.69 (s, 1H), 5.58 (s, 1H), 4.47 (d, *J* = 7.0 Hz, 1H), 4.31 – 4.17 (m, 5H), 3.51 (s, 3H), 3.44 (s, 3H), 1.81 (s, 18H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.8, 168.4, 153.1, 141.7, 141.5, 135.3, 128.3, 128.0, 127.3, 126.5, 125.0, 123.7, 72.9, 58.5, 55.7, 52.8, 51.8, 44.4, 41.4, 34.3, 30.4 ppm; IR(KBr): 3636, 3626, 2999, 2955, 2874, 1728, 1456, 1435, 1360, 1292, 1271, 1215, 1142, 1125, 1099, 1047, 970, 922, 893, 806, 737, 644, 602, 503, 480 cm^{-1}; HRMS (ESI-TOF) calcd for $[C_{29}H_{38}O_7S+ Na]^+$ 553.2231, found 553.2233.



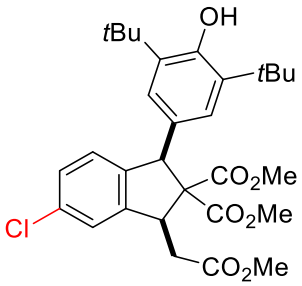
dimethyl (1R,3S)-1-(3,5-di-tert-butyl-4-hydroxyphenyl)-3-((phenylsulfonyl)methyl)-1,3-dihydro-2H-indene-2,2-dicarboxylate (3ga)

91% yield (108.1 mg), 10:1 dr; white solid, m.p. 236 – 238 ^{o}C, ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.42 (d, 2H), 8.12 – 7.99 (m, 4H), 7.68 (dt, *J* = 25.6, 7.4 Hz, 2H), 7.49 – 7.42 (m, 3H), 5.72 (s, 1H), 5.56 (s, 1H), 4.45 – 4.38 (m, 2H), 4.25 (d, *J* = 13.0 Hz, 1H), 4.02 (s, 3H), 3.44 (s, 3H), 1.79 (s, 18H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.2, 168.3, 153.1, 141.7, 141.4, 139.7, 135.3, 133.7, 129.4, 128.3, 128.3, 127.9, 127.2, 126.3, 125.0, 123.7, 73.1, 60.1, 55.6, 52.6, 51.6, 44.6, 34.2, 30.3 ppm; IR(KBr): 3626, 3001, 2955, 2872, 1749, 1732, 1479, 1456, 1435, 1296, 1271, 1171, 1086, 1043, 961, 920, 891, 797, 741, 691, 548, 527 cm^{-1}; HRMS (ESI-TOF) calcd for $[C_{34}H_{40}O_7S+ Na]^+$ 615.2387, found 615.2385.



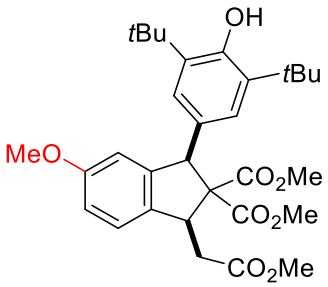
dimethyl (1R,3S)-1-(3,5-di-tert-butyl-4-hydroxyphenyl)-5-methoxy-3-(2-methoxy-2-oxoethyl)-1,3-dihydro-2H-indene-2,2-dicarboxylate (3ha)

85% yield (91.9 mg), 7:1 dr; white solid, m.p. 152 – 155 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.12 (s, 2H), 6.93 (dd, *J* = 8.3, 1.2 Hz, 1H), 6.73 (ddd, *J* = 8.4, 2.4, 1.0 Hz, 1H), 6.68 (dd, *J* = 2.4, 1.2 Hz, 1H), 5.23 (s, 1H), 5.14 (s, 1H), 4.05 (t, *J* = 6.0 Hz, 1H), 3.80 – 3.78 (m, 9H), 3.11 – 3.09 (m, 5H), 1.40 (s, 18H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.7, 171.4, 168.5, 159.4, 153.0, 144.9, 135.0, 133.9, 128.9, 126.6, 125.8, 112.3, 108.5, 72.3, 55.3, 55.2, 52.6, 52.0, 51.5, 46.6, 36.0, 34.3, 30.4; IR(KBr): 3647, 3615, 2953, 2913, 2876, 1771, 1748, 1715, 1472, 1456, 1339, 1317, 1269, 986, 891, 741, 704, 644 cm^{-1}; HRMS (ESI-TOF) calcd for $[C_{31}H_{40}O_8+H]^+$ 541.2796, found 541.2790.



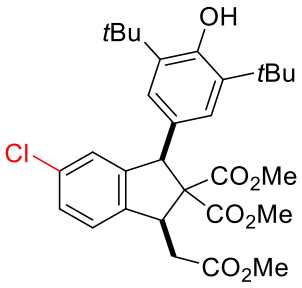
dimethyl (1R,3S)-5-chloro-1-(3,5-di-tert-butyl-4-hydroxyphenyl)-3-(2-methoxy-2-oxoethyl)-1,3-dihydro-2H-indene-2,2-dicarboxylate (3ia)

90% yield (98.2 mg), 8:1 dr; white solid, m.p. 168 – 170 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.16 (d, *J* = 8.1 Hz, 1H), 7.09 (s, 3H), 6.95 (dd, *J* = 8.1, 1.3 Hz, 1H), 5.22 (s, 1H), 5.17 (s, 1H), 4.05 (t, *J* = 6.0 Hz, 1H), 3.81 (s, 6H), 3.11 – 3.08 (m, 5H), 1.39 (s, 18H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.5, 171.0, 168.3, 153.2, 145.4, 140.7, 135.2, 133.1, 128.1, 127.1, 126.6, 126.2, 123.0, 72.3, 55.4, 52.7, 52.1, 51.7, 46.3, 35.9, 34.3, 30.4 ppm; IR(KBr): 3636, 3472, 3460, 3416, 2953, 1741, 1732, 1476, 1435, 1269, 1254, 1206, 1167, 1051, 870, 739 cm^{-1}; HRMS (ESI-TOF) calcd for $[C_{30}H_{37}ClO_7+ H]^+$ 545.2301, found 545.2295.



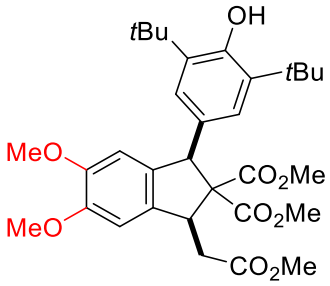
dimethyl (1S,3R)-3-(3,5-di-tert-butyl-4-hydroxyphenyl)-5-methoxy-1-(2-methoxy-2-oxoethyl)-1,3-dihydro-2H-indene-2,2-dicarboxylate (3ja)

91% yield (98.8 mg), 9:1 dr; white solid, m.p. 160 – 162 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.14 (s, 2H), 7.01 (dd, *J* = 8.4, 1.2 Hz, 1H), 6.80 (dd, *J* = 8.4, 1.6 Hz, 1H), 6.58 (s, 1H), 5.26 (s, 1H), 5.16 (s, 1H), 4.02 (t, *J* = 6.0 Hz, 1H), 3.80 (s, 3H), 3.78 (s, 3H), 3.70 (s, 3H), 3.11 (s, 3H), 3.09 – 3.06 (m, 2H), 1.40 (s, 18H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.8, 171.5, 168.5, 159.1, 153.1, 143.5, 135.5, 135.1, 128.4, 126.7, 123.2, 114.0, 110.2, 72.2, 55.9, 55.5, 52.6, 51.9, 51.5, 46.1, 36.3, 34.3, 30.4 ppm; IR(KBr): 3645, 3631, 3617, 2953, 2920, 2876, 1759, 1748, 1732, 1715, 1418, 1373, 1269, 1229, 1152, 1121, 1022, 773, 745, 708, 644, 571 cm^{-1}; HRMS (ESI-TOF) calcd for $[C_{31}H_{40}O_8+H]^+$ 541.2796, found 541.2800.



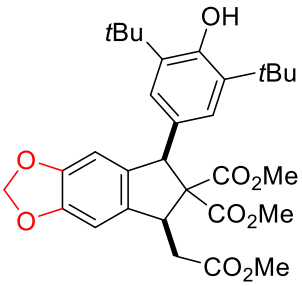
dimethyl (1S,3R)-5-chloro-3-(3,5-di-tert-butyl-4-hydroxyphenyl)-1-(2-methoxy-2-oxoethyl)-1,3-dihydro-2H-indene-2,2-dicarboxylate (3ka)

90% yield (97.7 mg), 7:1 dr; white solid, m.p. 146 – 148 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.21 (d, J = 8.1 Hz, 1H), 7.10 (s, 2H), 7.06 – 7.02 (m, 2H), 5.24 (s, 1H), 5.19 (s, 1H), 4.03 (t, *J* = 6.0 Hz, 1H), 3.81 (s, 3H), 3.79 (s, 3H), 3.13 (s, 3H), 3.10 – 3.07 (m, 2H), 1.40 (s, 18H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.6, 171.1, 168.3, 153.3, 144.2, 141.9, 135.3, 132.7, 127.8, 127.7, 126.6, 125.3, 123.7, 72.2, 55.7, 52.8, 52.1, 51.7, 46.2, 36.0, 34.3, 30.4 ppm; IR(KBr): 3618, 3599, 2955, 2914, 2874, 1748, 1732, 1474, 1435, 1373, 1362, 1260, 1207, 1167, 1123, 1105, 1051, 1020, 976, 901, 739, 669, 550 cm^{-1}; HRMS (ESI-TOF) calcd for $[C_{30}H_{37}ClO_7+H]^+$ 545.2301, found 545.2310.



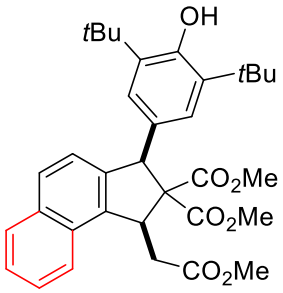
dimethyl (1R,3S)-1-(3,5-di-tert-butyl-4-hydroxyphenyl)-5,6-dimethoxy-3-(2-methoxy-2-oxoethyl)-1,3-dihydro-2H-indene-2,2-dicarboxylate (3la)

95% yield (108.1 mg), 5:1 dr; light yellow solid, m.p. 170 – 171 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.15 (s, 2H), 6.71 (s, 1H), 6.58 (s, 1H), 5.27 (s, 1H), 5.17 (s, 1H), 4.04 (t, *J* = 6.0 Hz, 1H), 3.89 (s, 3H), 3.82 (s, 3H), 3.80 (s, 3H), 3.76 (s, 3H), 3.15 – 3.06 (m, 5H), 1.41 (s, 18H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.9, 171.5, 168.4, 153.0, 148.8, 148.4, 135.1, 133.5, 128.9, 126.6, 108.3, 105.9, 72.0, 56.1, 55.9, 55.6, 52.6, 51.9, 51.5, 46.6, 36.4, 34.3, 30.4 ppm; IR(KBr): 3645, 3617, 2953, 2932, 2872, 1771, 1748, 1715, 1506, 1472, 1339, 1274, 895, 862, 745, 648, 517 cm^{-1}; HRMS (ESI-TOF) calcd for $[C_{32}H_{42}O_9+H]^+$ 571.2902, found 571.2908.



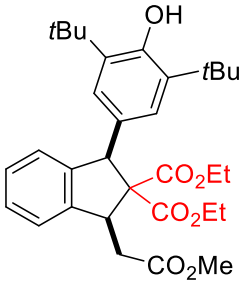
dimethyl (5R,7S)-5-(3,5-di-tert-butyl-4-hydroxyphenyl)-7-(2-methoxy-2-oxoethyl)-5,7-dihydro-6H-indeno[5,6-d][1,3]dioxole-6,6-dicarboxylate (3ma)

81% yield (90.3 mg), 7:1 dr; white solid, m.p. 168 – 170 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.10 (s, 2H), 6.60 (s, 1H), 6.48 (s, 1H), 5.95 (d, *J* = 1.4 Hz, 1H), 5.89 (d, 1H), 5.17 (s, 1H), 5.14 (s, 1H), 3.98 (t, *J* = 6.0 Hz, 1H), 3.79 (s, 3H), 3.77 (s, 3H), 3.12 (s, 3H), 3.07 – 3.04 (m, 2H), 1.40 (s, 18H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.7, 171.3, 168.4, 153.1, 147.3, 147.0, 136.2, 135.1, 135.0, 128.7, 126.6, 105.6, 103.5, 101.1, 72.0, 55.6, 52.6, 52.0, 51.5, 46.3, 36.3, 34.3, 30.4 ppm; IR(KBr): 3647, 3616, 2955, 2926, 2870, 1749, 1734, 1717, 1456, 1338, 1157, 1115, 1045, 1022, 972, 935, 893, 843, 741, 644 cm^{-1}; HRMS (ESI-TOF) calcd for $[C_{31}H_{38}O_9+H]^+$ 555.2589, found 555.2593.



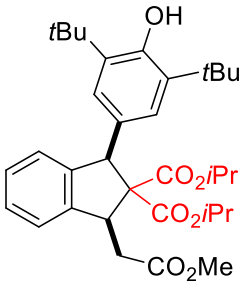
dimethyl (1S,3R)-3-(3,5-di-tert-butyl-4-hydroxyphenyl)-1-(2-methoxy-2-oxoethyl)-1,3-dihydro-2H-cyclopenta[a]naphthalene-2,2-dicarboxylate (3na)

81% yield (91.1 mg), >20:1 dr; light yellow solid, m.p. 108 – 112 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.2 Hz, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.71 (d, *J* = 8.4 Hz, 1H), 7.59 – 7.54 (m, 1H), 7.51 – 7.45 (m, 1H), 7.13 (d, *J* = 8.4 Hz, 1H), 7.05 (s, 2H), 5.64 (s, 1H), 5.15 (s, 1H), 5.03 (dd, *J* = 8.1, 3.1 Hz, 1H), 3.74 (s, 3H), 3.69 (s, 3H), 3.04 (s, 3H), 2.71 – 2.55 (m, 2H), 1.38 (s, 18H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.0, 170.5, 170.0, 153.0, 140.4, 138.5, 135.3, 133.7, 129.2, 128.9, 128.6, 128.1, 126.7, 126.3, 125.5, 123.7, 123.5, 71.8, 55.9, 52.4, 51.9, 45.6, 36.8, 34.3, 30.4 ppm; IR(KBr): 3647, 3617, 3055, 2953, 2911, 2872, 1771, 1748, 1715, 1472, 1456, 1435, 1418, 1395, 1373, 1362, 1269, 1244, 1080, 1024, 986, 918, 891, 768, 741, 704, 640, 546 cm^{-1}; HRMS (ESI-TOF) calcd for $[C_{34}H_{40}O_7+H]^+$ 561.284, found 561.2845.



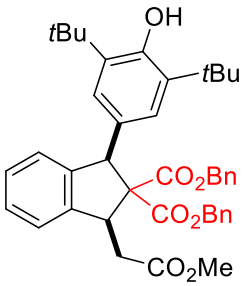
diethyl (1R,3S)-1-(3,5-di-tert-butyl-4-hydroxyphenyl)-3-(2-methoxy-2-oxoethyl)-1,3-dihydro-2H-indene-2,2-dicarboxylate (3ab)

85% yield (92 mg), 10:1 dr; white solid, m.p. 84 – 86 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25 – 7.11 (m, 5H), 7.03 (d, *J* = 7.4 Hz, 1H), 5.32 (s, 1H), 5.14 (s, 1H), 4.33 – 4.23 (m, 2H), 4.05 (dd, *J* = 7.6, 3.9 Hz, 1H), 3.79 (s, 3H), 3.66 (dd, *J* = 10.7, 7.0 Hz, 1H), 3.35 (dd, *J* = 10.6, 7.0 Hz, 1H), 3.17 (t, *J* = 5.4 Hz, 2H), 1.39 (s, 18H), 1.27 (t, *J* = 7.1 Hz, 3H), 0.68 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.9, 170.8, 168.1, 153.0, 143.6, 141.9, 135.0, 128.9, 127.5, 126.7, 126.7, 125.1, 122.4, 72.2, 61.4, 60.5, 55.7, 51.9, 46.6, 36.0, 34.3, 30.4, 14.0, 13.2 ppm; IR(KBr): 3645, 3626, 3607, 2955, 2872, 1732, 1472, 1435, 1366, 1256, 1198, 1169, 1121, 1101, 1049, 1018, 773, 745, 644 cm^{-1}; HRMS (ESI-TOF) calcd for $[C_{32}H_{42}O_7+H]^+$ 539.3003, found 539.3003.



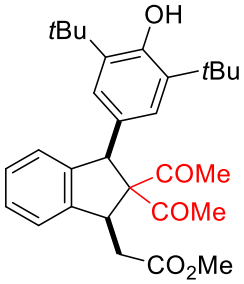
methyl 2-((1R,3S)-3-(3,5-di-tert-butyl-4-hydroxyphenyl)-2,2-diisopropyl-2,3-dihydro-1H-inden-1-yl)acetate (3ac)

83% yield (94.4 mg); 13:1 dr; white solid, m.p. 142 – 143 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.26 – 7.11 (m, 5H), 7.01 (d, *J* = 7.5 Hz, 1H), 5.31 (s, 1H), 5.14 (d, *J* = 11.1 Hz, 2H), 4.30 (p, *J* = 6.4 Hz, 1H), 4.01 (d, *J* = 8.4 Hz, 1H), 3.80 (s, 3H), 3.26 – 3.08 (m, 2H), 1.39 (s, 18H), 1.28 – 1.25 (m, 6H), 1.01 (d, *J* = 6.1 Hz, 3H), 0.39 (d, *J* = 6.3 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.0, 170.4, 167.6, 153.0, 143.8, 142.2, 134.9, 129.0, 127.4, 126.9, 126.7, 125.0, 122.4, 72.2, 68.7, 68.2, 55.5, 51.9, 46.8, 36.4, 34.3, 30.4, 21.7, 21.5, 21.4, 20.7 ppm; IR(KBr): 3630, 3601, 2955, 2876, 1740, 1722, 1541, 1508, 1456, 1435, 1373, 1267, 1204, 1169, 1107, 1043, 922, 899, 833, 771, 752, 644, 592 cm^{-1}; HRMS (ESI-TOF) calcd for $[C_{34}H_{46}O_7+H]^+$ 567.3316, found 567.3321.



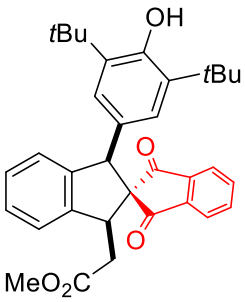
dibenzyl (1R,3S)-1-(3,5-di-tert-butyl-4-hydroxyphenyl)-3-(2-methoxy-2-oxoethyl)-1,3-dihydro-2H-indene-2,2-dicarboxylate (3ad)

90% yield (119.6 mg), 8:1 dr; light yellow solid, m.p. 58 – 60 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.26 – 7.14 (m, 13H), 7.03 (d, *J* = 7.7 Hz, 1H), 6.68 (d, *J* = 6.9 Hz, 2H), 5.38 (s, 1H), 5.16 (s, 3H), 4.73 (d, *J* = 12.6 Hz, 1H), 4.22 (d, *J* = 12.5 Hz, 1H), 4.13 (s, 1H), 3.69 (s, 3H), 3.16 (d, *J* = 8.2 Hz, 2H), 1.34 (s, 18H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.7, 170.5, 168.0, 153.3, 143.5, 142.0, 135.4, 135.3, 134.8, 128.7, 128.5, 128.3, 128.1, 128.0, 127.9, 127.6, 127.4, 126.9, 126.8, 125.1, 122.4, 72.6, 67.4, 66.6, 56.2, 51.9, 46.9, 36.0, 34.3, 30.4 ppm; IR(KBr): 3628, 3618, 3067, 3032, 2953, 2874, 1748, 1732, 1717, 1603, 1588, 1541, 1456, 1435, 1373, 1313, 1269, 1121, 1098, 1045, 895, 799, 743, 696, 646, 601, 489, 459 cm^{-1}; HRMS (ESI-TOF) calcd for $[C_{42}H_{46}O_7+H]^+$ 663.3316, found 663.3314.



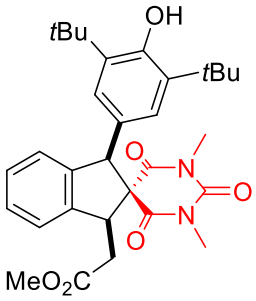
methyl 2-((1S,3R)-2,2-diacetyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl)-2,3-dihydro-1H-inden-1-yl)acetate (3ae)

75% yield (71.7 mg), 6:1 dr; white solid, m.p. 148 – 152 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25 – 7.18 (m, 3H), 7.11 (d, 1H), 6.91 (s, 2H), 5.15 (s, 1H), 5.01 (s, 1H), 4.71 (dd, *J* = 10.8, 3.3 Hz, 1H), 3.76 (s, 3H), 2.59 (dd, *J* = 16.0, 3.3 Hz, 1H), 2.28 (dd, *J* = 16.0, 10.7 Hz, 1H), 2.05 (s, 3H), 1.59 (s, 3H), 1.36 (s, 18H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 207.1, 204.3, 172.4, 153.1, 143.8, 143.1, 135.8, 129.3, 127.9, 125.8, 125.3, 123.7, 82.1, 54.9, 52.0, 44.0, 35.8, 34.3, 30.3, 29.4, 28.9 ppm; IR(KBr): 3647, 3617, 3599, 3566, 3071, 2955, 2922, 2874, 1748, 1732, 1715, 1697, 1682, 1472, 1456, 1435, 1417, 1362, 1211, 1123, 1063, 1022, 997, 887, 756, 741, 660, 625 cm^{-1}; HRMS (ESI-TOF) calcd for $[C_{30}H_{38}O_5+H]^+$ 479.2792, found 479.2789.



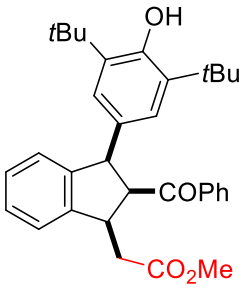
methyl 2-((1R,3S)-1-(3,5-di-tert-butyl-4-hydroxyphenyl)-1',3'-dioxo-1,1',3,3'-tetrahydro-2,2'-spirobi[inden]-3-yl)acetate (3af)

70% yield (73 mg), >20:1 dr; white solid, m.p. 170 – 171 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.6 Hz, 1H), 7.65 (t, *J* = 7.5 Hz, 1H), 7.51 (t, *J* = 7.5 Hz, 1H), 7.38 – 7.24 (m, 4H), 7.09 (d, *J* = 7.4 Hz, 1H), 6.66 (s, 2H), 4.94 (d, *J* = 14.5 Hz, 2H), 4.35 (dd, *J* = 11.1, 4.7 Hz, 1H), 3.30 (s, 3H), 3.12 (dd, *J* = 16.3, 4.8 Hz, 1H), 2.91 (dd, *J* = 16.2, 11.0 Hz, 1H), 1.20 (s, 18H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.0, 200.0, 172.5, 152.8, 143.8, 142.5, 141.4, 135.2, 134.6, 134.5, 127.9, 127.5, 126.3, 126.2, 124.6, 122.8, 122.1, 122.1, 72.3, 62.0, 51.3, 43.4, 34.0, 33.8, 30.1 ppm; IR(KBr): 3645, 3630, 3608, 2954, 2924, 2870, 1740, 1705, 1595, 1541, 1456, 1435, 1362, 1271, 1236, 1163, 908, 874, 750 cm^{-1}; HRMS (ESI-TOF) calcd for $[C_{34}H_{36}O_5+H]^+$ 525.2636, found 525.2634.



methyl 2-((1R,3S)-1-(3,5-di-tert-butyl-4-hydroxyphenyl)-1',3'-dimethyl-2',4',6'-trioxo-1,1',3,3',4',6'-hexahydro-2'H-spiro[indene-2,5'-pyrimidin]-3-yl)acetate (3ag)

81% yield (86.7 mg); >20:1 dr; white solid, m.p. 148 – 149 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33 (t, *J* = 7.4 Hz, 1H), 7.26 (d, *J* = 7.2 Hz, 1H), 7.20 (t, *J* = 6.6 Hz, 1H), 7.03 (d, *J* = 7.5 Hz, 1H), 6.85 (s, 2H), 5.28 (s, 1H), 4.93 (s, 1H), 4.74 (dd, *J* = 11.5, 5.4 Hz, 1H), 3.56 (s, 3H), 3.42 (s, 3H), 3.13 (dd, *J* = 15.1, 8.5 Hz, 2H), 2.61 (s, 3H), 1.37 (s, 18H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.1, 172.1, 167.9, 154.0, 151.0, 144.4, 139.4, 136.0, 128.0, 127.3, 126.0, 125.4, 124.8, 122.1, 69.3, 64.7, 51.8, 45.5, 34.3, 32.6, 30.2, 29.0, 27.7 ppm; IR(KBr): 3630, 3614, 3595, 3588, 2957, 2926, 2872, 1748, 1732, 1682, 1645, 1456, 1435, 1361, 1302, 1238, 1177, 1119, 1059,1034, 1002, 976, 754, 634, 600 cm^{-1}; HRMS (ESI-TOF) calcd for $[C_{31}H_{38}N_2O_6+H]^+$ 535.2798, found 535.2803.



methyl 2-((1R,3R)-2-benzoyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl)-2,3-dihydro-1H-inden-1-yl)acetate (3ah)

67% yield (66.6 mg), >20:1 dr; white solid, m.p. 100 – 102 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.7 Hz, 2H), 7.41 (t, *J* = 7.4 Hz, 1H), 7.30 – 7.20 (m, 5H), 6.99 (d, *J* = 7.5 Hz, 1H), 6.78 (s, 2H), 5.05 (s, 1H), 4.38 – 4.27 (m, 2H), 4.14 (t, *J* = 9.1 Hz, 1H), 3.41 (s, 3H), 2.97 (dd, *J* = 14.8, 5.0 Hz, 1H), 2.60 (dd, *J* = 14.9, 8.8 Hz, 1H), 1.28 (s, 18H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.7, 172.3, 152.7, 144.2, 144.1, 137.5, 136.0, 133.0, 132.7, 128.6, 128.1, 127.5, 127.3, 125.1, 125.0, 123.1, 63.8, 57.2, 51.5, 43.6, 38.9, 34.2, 30.2 ppm; IR(KBr): 3628, 2953, 2920, 2872, 1734, 1674, 1447, 1435, 1362, 1250, 1234, 1200, 1155, 1119, 1024, 901, 748, 702, 685 cm^{-1}; HRMS (ESI-TOF) calcd for $[C_{33}H_{38}O_4+H]^+$ 499.2843, found 499.2842.

The NOE result of **3ah (Figure S4** and **Figure S5)**.

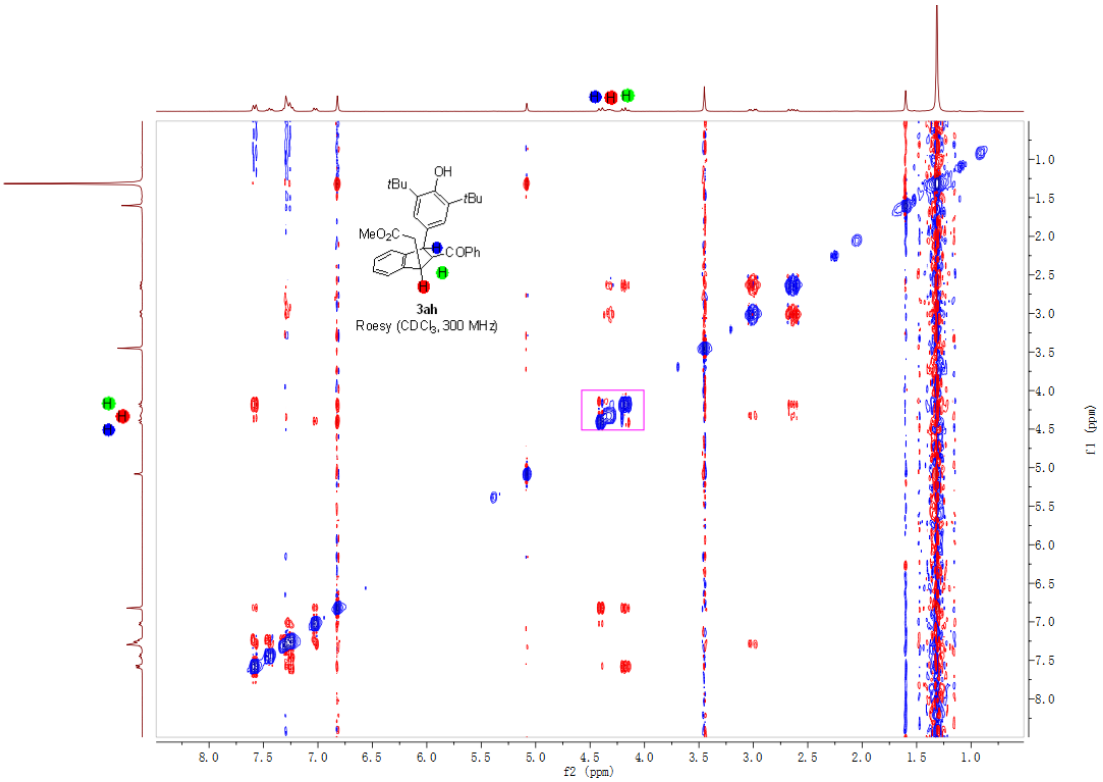


Figure S4 NOE spectrum of 3ah

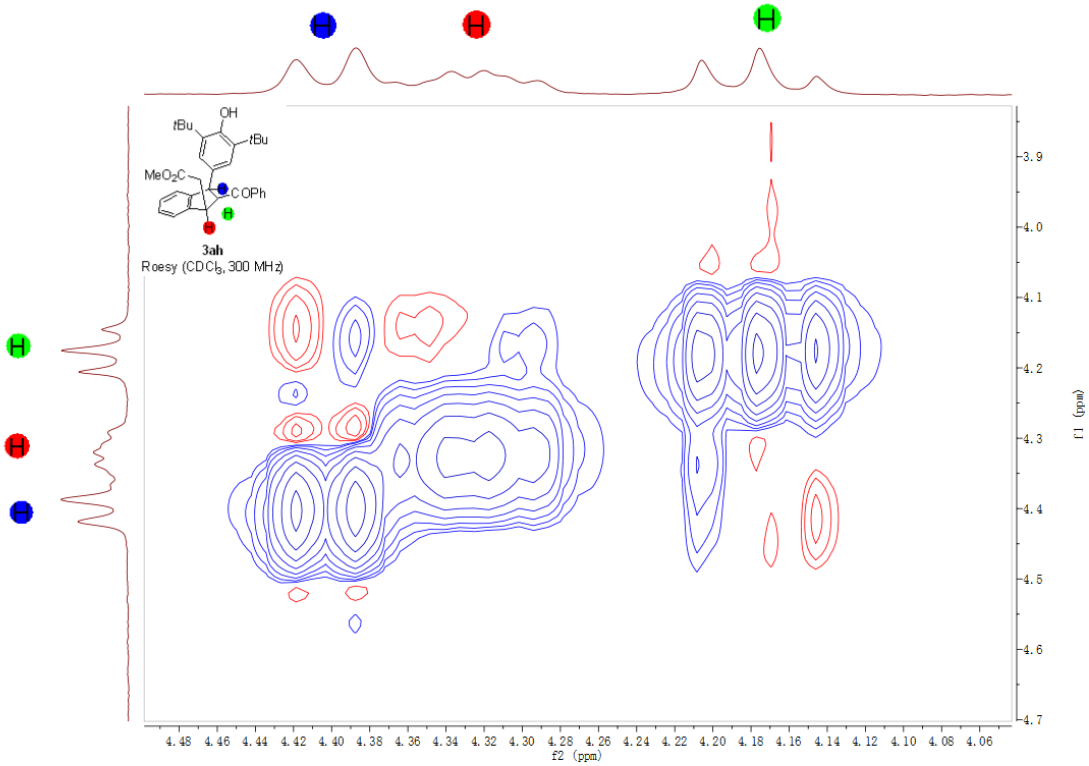
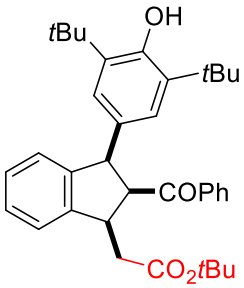


Figure S5 NOE spectrum of 3ah



tert-butyl 2-((1R,3R)-2-benzoyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl)-2,3-dihydro-1H-inden-1-yl)acetate (3dh)

68% yield (73.8 mg), >20:1 dr; white solid, m.p. 100 – 102 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.0 Hz, 2H), 7.41 (t, *J* = 7.0 Hz, 1H), 7.30 – 7.19 (m, 5H), 6.99 (d, *J* = 7.2 Hz, 1H), 6.79 (s, 2H), 5.05 (s, 1H), 4.38 (d, *J* = 9.0 Hz, 1H), 4.30 – 4.18 (m, 2H), 2.77 (dd, *J* = 14.8, 5.0 Hz, 1H), 2.59 (dd, *J* = 14.7, 7.5 Hz, 1H), 1.27 (s, 27H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.8, 171.3, 152.6, 144.3, 144.1, 137.7, 135.9, 133.1, 132.7, 128.7, 128.1, 127.3, 127.1, 125.0, 125.0, 123.5, 80.7, 63.2, 57.1, 43.8, 39.9, 34.2, 30.3, 27.9 ppm; IR(KBr): 3640, 3067, 2959, 2872, 1728, 1715, 1674, 1597, 1580, 1479, 1435, 1393, 1368, 1288, 1250, 1234, 1146, 1121, 1024, 964, 905, 839, 770, 745, 700, 685 cm^{-1}; HRMS (ESI-TOF) calcd for $[C_{36}H_{44}O_4+Na]^+$ 563.3132, found 563.3128.

The NOE result of **3dh (Figure S6** and **Figure S7)**.

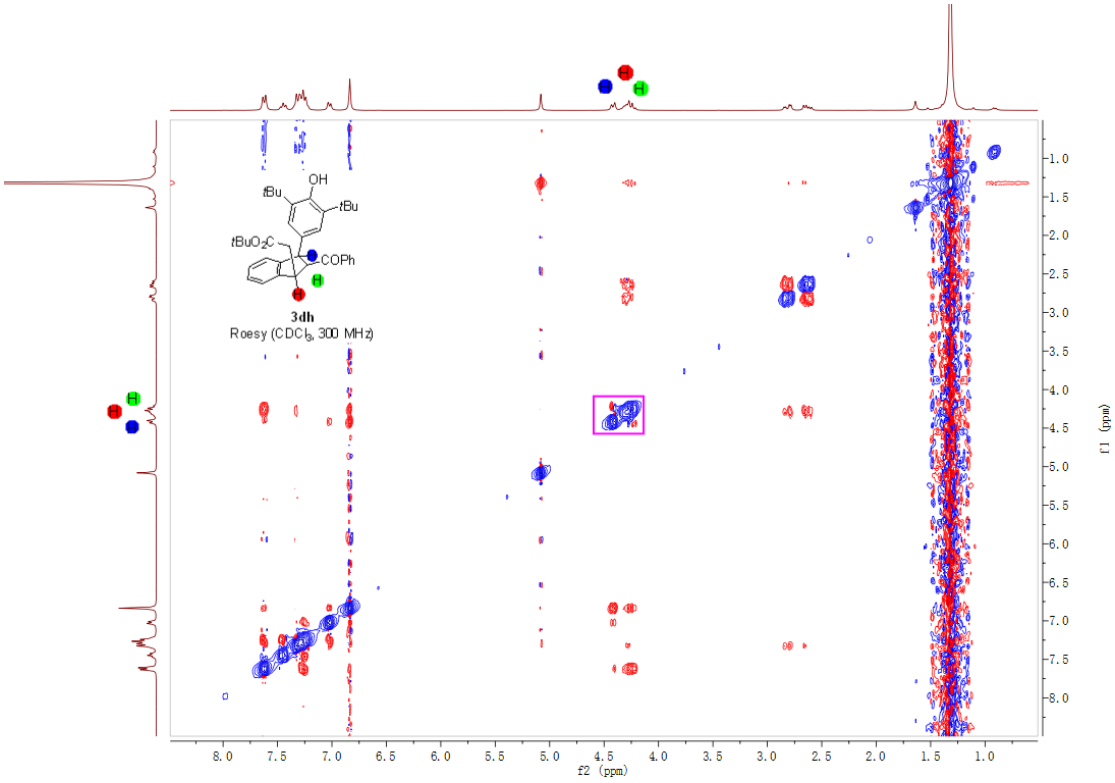


Figure S6 NOE spectrum of 3dh

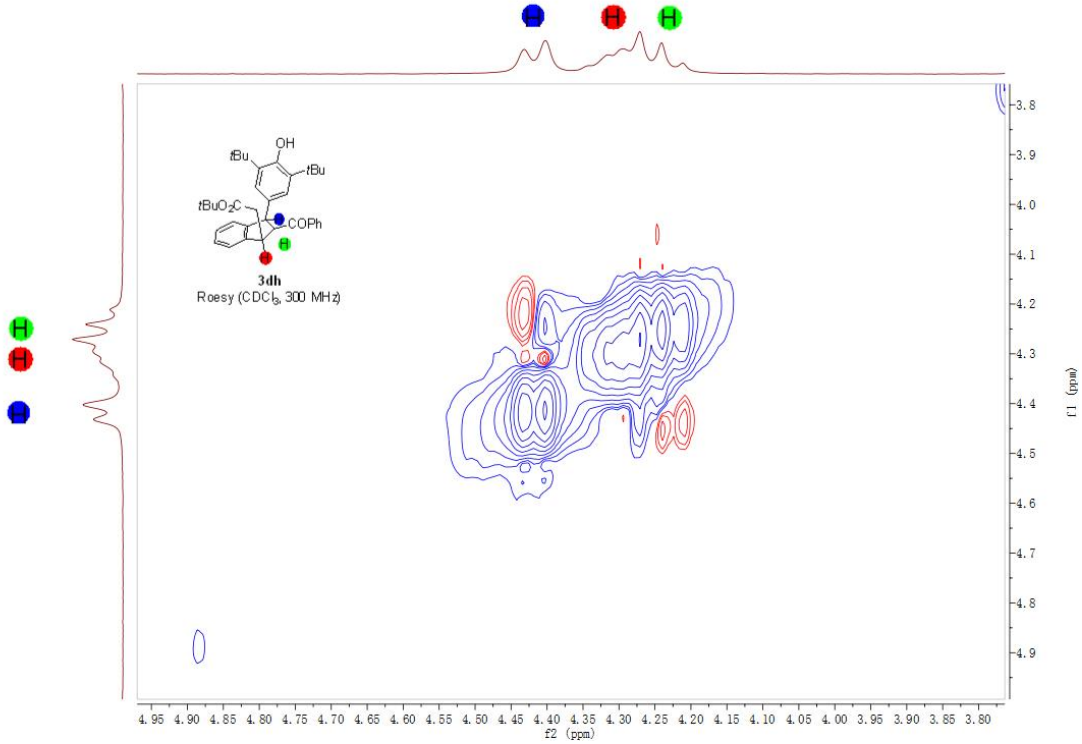
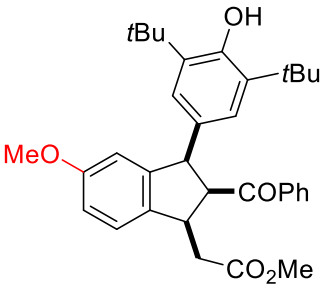
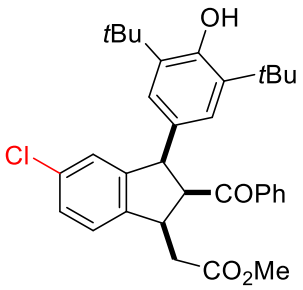


Figure S7 NOE spectrum of 3dh



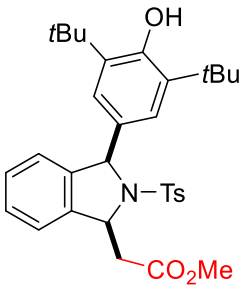
methyl 2-((1R,3R)-2-benzoyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl)-5-methoxy-2,3-dihydro-1H-inden-1-yl)acetate (3jh)

71% yield (75.1 mg), >20:1 dr; white solid, m.p. 86 – 88 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.2 Hz, 2H), 7.41 (t, *J* = 7.4 Hz, 1H), 7.26 – 7.21 (m, 2H), 7.14 (d, *J* = 8.3 Hz, 1H), 6.84 – 6.80 (m, 3H), 6.53 (d, *J* = 2.4 Hz, 1H), 5.06 (s, 1H), 4.35 (d, *J* = 9.2 Hz, 1H), 4.20 (td, *J* = 8.6, 4.9 Hz, 1H), 4.12 (t, *J* = 8.9 Hz, 1H), 3.72 (s, 3H), 3.40 (s, 3H), 2.92 (dd, *J* = 14.8, 5.0 Hz, 1H), 2.57 (dd, *J* = 14.8, 8.7 Hz, 1H), 1.28 (s, 18H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.7, 172.4, 159.7, 152.7, 145.7, 137.5, 136.2, 136.0, 132.7, 128.6, 128.1, 125.0, 123.8, 113.7, 110.1, 64.0, 57.1, 55.6, 51.4, 43.1, 39.2, 34.2, 30.3 ppm; IR(KBr): 3645, 3626, 2953, 2922, 2872, 1738, 1674, 1609, 1595, 1493, 1435, 1360, 1281, 1238, 1207, 1196, 1155, 1117, 1034, 806, 785, 694 cm^{-1}; HRMS (ESI-TOF) calcd for $[C_{34}H_{40}O_5+H]^+$ 529.2949, found 529.2948.



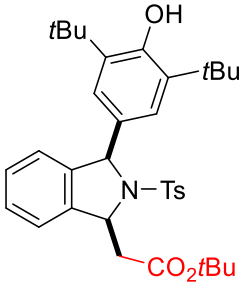
methyl 2-((1R,3R)-2-benzoyl-5-chloro-3-(3,5-di-tert-butyl-4-hydroxyphenyl)-2,3-dihydro-1 H-inden-1-yl)acetate (3kh)

54% yield (57.9 mg), >20:1 dr; white solid, m.p. 150 – 151 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54 (dd, *J* = 8.4, 1.3 Hz, 2H), 7.42 (t, *J* = 7.4 Hz, 1H), 7.26 – 7.16 (m, 4H), 6.96 (s, 1H), 6.77 (s, 2H), 5.10 (s, 1H), 4.34 – 4.16 (m, 3H), 3.44 (s, 3H), 2.91 (dd, *J* = 15.0, 4.7 Hz, 1H), 2.62 (dd, *J* = 15.0, 7.9 Hz, 1H), 1.29 (s, 18H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.1, 172.0, 152.9, 146.3, 142.5, 137.3, 136.1, 133.3, 132.9, 132.2, 128.6, 128.1, 127.6, 125.2, 125.0, 124.3, 63.6, 56.7, 51.5, 43.0, 38.5, 34.2, 30.2 ppm; IR(KBr): 3636, 3626, 3061, 2955, 2924, 2872, 1738, 1674, 1597, 1580, 1472, 1435, 1362, 1250, 1236, 1200, 1157, 1121, 1072, 1016, 916, 874, 814, 772, 704, 687 cm^{-1}; HRMS (ESI-TOF) calcd for $[C_{33}H_{37}ClO_4+H]^+$ 533.2453, found 533.2450.



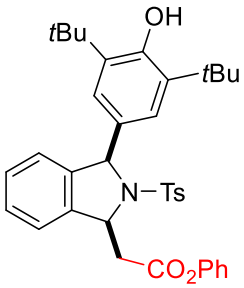
methyl
2-((1S,3R)-3-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-tosylisoindolin-1-yl)acetate (3ai)

82% yield (90.0 mg), >20:1 dr; white solid, m.p. 188 – 189 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.3 Hz, 2H), 7.23 – 7.16 (m, 5H), 7.07 (s, 2H), 7.01 – 6.98 (m, 1H), 5.92 (s, 1H), 5.61 (dd, *J* = 8.7, 4.3 Hz, 1H), 5.17 (s, 1H), 3.81 (s, 3H), 3.38 (dd, *J* = 15.8, 4.3 Hz, 1H), 2.85 (dd, *J* = 15.8, 8.7 Hz, 1H), 2.34 (s, 3H), 1.42 (s, 18H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.3, 153.3, 143.4, 140.4, 138.5, 135.7, 135.6, 132.4, 129.5, 128.3, 128.1, 127.6, 124.2, 123.7, 122.6, 69.6, 61.9, 51.9, 43.9, 34.4, 30.3, 21.5 ppm; IR(KBr): 3626, 2953, 2922, 2874, 1746, 1738, 1597, 1485, 1435, 1352, 1304, 1165, 1092, 1055, 1015, 988, 918, 897, 812, 785, 752, 706, 671, 602, 561 cm^{-1}; HRMS (ESI-TOF) calcd for $[C_{32}H_{39}NO_5S+H]^+$ 550.2622, found 550.2619.



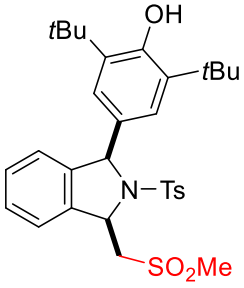
tert-butyl
2-((1S,3R)-3-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-tosylisoindolin-1-yl)acetate (3di)

86% yield (101.3 mg), >20:1 dr; white solid, m.p. 152 – 154 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 7.9 Hz, 2H), 7.26 – 7.14 (m, 5H), 7.03 (s, 2H), 6.95 (d, *J* = 6.5 Hz, 1H), 5.87 (s, 1H), 5.53 (dd, *J* = 9.7, 3.6 Hz, 1H), 5.12 (s, 1H), 3.35 (dd, *J* = 15.8, 3.7 Hz, 1H), 2.67 (dd, *J* = 15.8, 9.7 Hz, 1H), 2.32 (s, 3H), 1.53 (s, 9H), 1.38 (s, 18H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.2, 153.3, 143.3, 140.4, 139.0, 135.7, 135.6, 132.6, 129.5, 128.2, 128.0, 127.6, 124.2, 123.7, 122.7, 81.3, 69.5, 62.0, 45.3, 34.3, 30.3, 28.2, 21.5 ppm; IR(KBr): 3636, 2961, 2928, 2872, 1728, 1597, 1483, 1435, 1393, 1352, 1306, 1234, 1159, 1121, 1094, 1047, 970, 899, 839, 814, 750, 671, 658, 559, 548 cm^{-1}; HRMS (ESI-TOF) calcd for $[C_{35}H_{45}NO_5S+Na]^+$ 614.2911, found 614.2906.



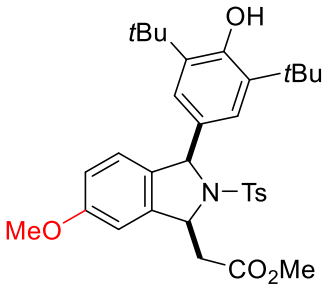
phenyl 2-((1S,3R)-3-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-tosylisoindolin-1-yl)acetate (3oi)

59% yield (72.8 mg), >20:1 dr; white solid, m.p. 132 – 133 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 7.9 Hz, 2H), 7.39 (t, *J* = 7.7 Hz, 2H), 7.32 – 7.12 (m, 8H), 7.06 (s, 2H), 6.98 (d, *J* = 7.1 Hz, 1H), 5.91 (s, 1H), 5.68 (t, *J* = 6.0 Hz, 1H), 5.13 (s, 1H), 3.57 (dd, *J* = 15.9, 4.6 Hz, 1H), 3.12 (dd, *J* = 15.9, 8.0 Hz, 1H), 2.31 (s, 3H), 1.37 (s, 18H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.4, 153.4, 150.6, 143.5, 140.6, 138.3, 135.7, 135.6, 132.2, 129.6, 129.5, 128.5, 128.2, 127.8, 126.0, 124.3, 123.8, 122.7, 121.7, 69.8, 61.9, 44.1, 34.4, 30.3, 21.5 ppm; IR(KBr): 3628, 3065, 2957, 2920, 2872, 1755, 1593, 1493, 1435, 1352, 1294, 1234, 1196, 1163, 1094, 1069, 943, 897, 814, 748, 689, 660, 561, 548 cm^{-1}; HRMS (ESI-TOF) calcd for $[C_{37}H_{41}NO_5S+H]^+$ 612.2778, found 612.2775.



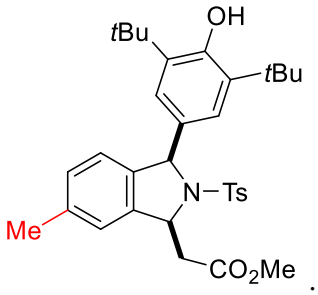
2,6-di-tert-butyl-4-((1R,3R)-3-((methylsulfonyl)methyl)-2-tosylisoindolin-1-yl)phenol (3fi)

84% yield (96.0 mg), >20:1 dr; white solid, m.p. 196 – 197 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.60 (m, 3H), 7.28 (t, *J* = 7.5 Hz, 1H), 7.22 (t, *J* = 7.3 Hz, 1H), 7.16 (d, *J* = 8.0 Hz, 2H), 6.98 – 6.94 (m, 3H), 5.86 (s, 1H), 5.53 (dd, *J* = 7.4, 3.0 Hz, 1H), 5.19 (s, 1H), 3.88 (dd, *J* = 15.0, 3.1 Hz, 1H), 3.48 (dd, *J* = 14.9, 7.3 Hz, 1H), 3.16 (s, 3H), 2.32 (s, 3H), 1.37 (s, 18H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.5, 144.1, 139.7, 137.5, 135.8, 134.3, 131.5, 129.7, 128.7, 128.6, 127.6, 124.3, 123.7, 123.5, 69.4, 62.7, 60.4, 42.4, 34.3, 30.2, 21.5 ppm; IR(KBr): 3626, 3046, 2957, 2872, 1732, 1597, 1485, 1435, 1350, 1306, 1236, 1161, 1119, 1092, 1047, 970, 922, 891, 843, 814, 741, 706, 671, 615, 561, 503 cm^{-1}; HRMS (ESI-TOF) calcd for $[C_{31}H_{39}NO_5S_2+Na]^+$ 592.2162, found 592.2159.



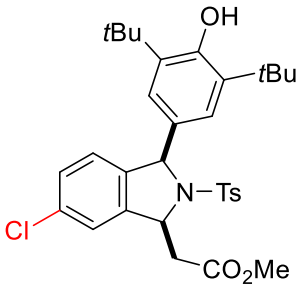
methyl 2-((1S,3R)-3-(3,5-di-tert-butyl-4-hydroxyphenyl)-6-methoxy-2-tosylisoindolin-1-yl)acetate (3hi)

84% yield (97.5 mg), >20:1 dr; white solid, m.p. 153 – 155 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.9 Hz, 2H), 7.14 (d, *J* = 7.9 Hz, 2H), 7.03 (s, 2H), 6.85 (d, *J* = 8.8 Hz, 1H), 6.74 – 6.72 (m, 2H), 5.81 (s, 1H), 5.51 (dd, *J* = 8.9, 4.2 Hz, 1H), 5.12 (s, 1H), 3.77 – 3.73 (m, 6H), 3.33 (dd, *J* = 16.0, 4.3 Hz, 1H), 2.81 (dd, *J* = 15.9, 8.8 Hz, 1H), 2.31 (s, 3H), 1.38 (s, 18H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.8, 159.3, 152.7, 142.8, 139.5, 135.1, 132.2, 132.0, 129.0, 127.1, 124.0, 123.6, 114.5, 106.7, 68.7, 61.4, 54.9, 51.3, 43.4, 33.8, 29.8, 20.9 ppm; IR(KBr): 3626, 3617, 2955, 2916, 2872, 1738, 1614, 1597, 1495, 1435, 1350, 1325, 1306, 1288, 1261, 1234, 1163, 1119, 1094, 1034, 1016, 889, 812, 739, 669, 588, 550 cm^{-1}; HRMS (ESI-TOF) calcd for $[C_{33}H_{41}NO_6S+H]^+$ 580.2727, found 580.2721.



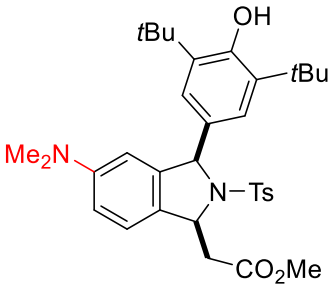
methyl 2-((1S,3R)-3-(3,5-di-tert-butyl-4-hydroxyphenyl)-6-methyl-2-tosylisoindolin-1-yl)acetate (3pi)

83% yield (93.1 mg), >20:1 dr; white solid, m.p. 196 – 198 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.9 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.04 (s, 2H), 7.00 – 6.98 (m, 2H), 6.83 (d, *J* = 8.1 Hz, 1H), 5.83 (s, 1H), 5.52 (dd, *J* = 8.6, 4.3 Hz, 1H), 5.11 (s, 1H), 3.78 (s, 3H), 3.33 (dd, *J* = 15.8, 4.3 Hz, 1H), 2.81 (dd, *J* = 15.8, 8.6 Hz, 1H), 2.31 – 2.28 (m, 6H), 1.38 (s, 18H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.3, 153.2, 143.3, 138.7, 137.9, 137.6, 135.8, 135.6, 132.6, 129.5, 129.3, 127.6, 124.1, 123.4, 122.9, 69.5, 61.9, 51.8, 44.0, 34.3, 30.3, 21.4, 21.4 ppm; IR(KBr): 3626, 2955, 2924, 2872, 1736, 1597, 1497, 1435, 1352, 1306, 1234, 1163, 1121, 1094, 1045, 1016, 887, 810, 669, 584, 550 cm^{-1}; HRMS (ESI-TOF) calcd for $[C_{33}H_{41}NO_5S+H]^+$ 564.2778, found 564.2780.



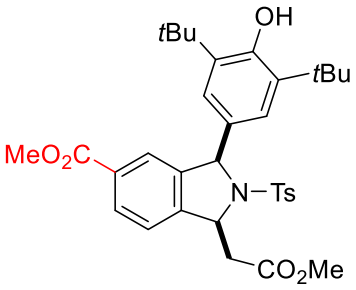
methyl 2-((1S,3R)-6-chloro-3-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-tosylisoindolin-1-yl)acetate (3ii)

87% yield (101.6 mg), >20:1 dr; white solid, m.p. 187 – 189 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.0 Hz, 2H), 7.23 (s, 1H), 7.16 – 7.13 (m, 3H), 7.00 (s, 2H), 6.88 (d, *J* = 8.2 Hz, 1H), 5.83 (s, 1H), 5.53 (dd, *J* = 9.0, 4.0 Hz, 1H), 5.16 (s, 1H), 3.78 (s, 3H), 3.34 (dd, *J* = 16.2, 4.1 Hz, 1H), 2.82 (dd, *J* = 16.2, 9.0 Hz, 1H), 2.32 (s, 3H), 1.38 (s, 18H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.1, 153.5, 143.5, 140.4, 139.0, 135.8, 135.5, 133.9, 131.8, 129.6, 128.8, 127.6, 124.9, 124.2, 123.0, 69.2, 61.5, 52.0, 43.5, 34.3, 30.2, 21.5 ppm; IR(KBr): 3632, 2955, 2872, 1736, 1599, 1477, 1435, 1354, 1319, 1306, 1234, 1207, 1163, 1121, 1094, 1045, 910, 812, 735, 687, 667, 575, 550 cm^{-1}; HRMS (ESI-TOF) calcd for $[C_{32}H_{38}ClNO_5S+Na]^+$ 606.2051, found 606.2051.



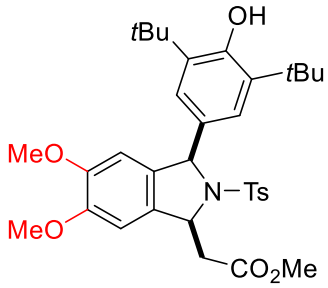
methyl 2-((1S,3R)-3-(3,5-di-tert-butyl-4-hydroxyphenyl)-5-(dimethylamino)-2-tosylisoindolin-1-yl)acetate (3qi)

84% yield (99.5 mg), >20:1 dr; yellow solid, m.p. 110 – 112 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64 (d, *J* = 7.9 Hz, 2H), 7.16 – 7.11 (m, 4H), 7.01 (d, *J* = 8.6 Hz, 1H), 6.57 (d, *J* = 7.9 Hz, 1H), 6.27 (s, 1H), 5.81 (s, 1H), 5.43 (dd, *J* = 8.9, 4.4 Hz, 1H), 5.11 (s, 1H), 3.76 (s, 3H), 3.32 (dd, *J* = 15.5, 4.4 Hz, 1H), 2.83 – 2.71 (m, 7H), 2.31 (s, 3H), 1.40 (s, 18H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.5, 153.2, 150.8, 143.2, 141.5, 135.7, 135.5, 132.7, 129.5, 127.6, 126.6, 123.9, 123.0, 112.8, 106.7, 69.7, 61.7, 51.7, 44.4, 40.6, 34.4, 30.3, 21.5 ppm; IR(KBr): 3626, 2955, 2922, 2872, 1738, 1732, 1620, 1514, 1435, 1352, 1306, 1233, 1163, 1119, 1094, 1047, 972, 910, 812, 735, 679, 662, 586, 550 cm^{-1}; HRMS (ESI-TOF) calcd for $[C_{34}H_{44}N_2O_5S+H]^+$ 593.3044, found 593.3040.



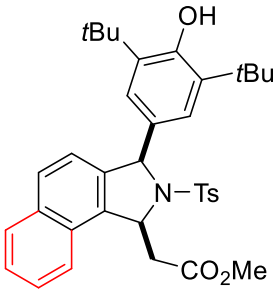
methyl 2-((1S,3R)-3-(3,5-di-tert-butyl-4-hydroxyphenyl)-5-methyl-2-tosylisoindolin-1-yl)acetate compound with carbon dioxide (3ri)

87% yield (105.5 mg), >20:1 dr; white solid, m.p. 121 – 123 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.1 Hz, 1H), 7.64 – 7.57 (m, 3H), 7.31 (d, *J* = 8.2 Hz, 1H), 7.12 (d, *J* = 7.9 Hz, 2H), 7.02 (s, 2H), 5.91 (s, 1H), 5.62 (dd, *J* = 9.0, 4.1 Hz, 1H), 5.17 (s, 1H), 3.84 – 3.77 (m, 6H), 3.35 (dd, *J* = 16.1, 4.2 Hz, 1H), 2.85 (dd, *J* = 16.0, 8.8 Hz, 1H), 2.30 (s, 3H), 1.38 (s, 18H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.5, 169.0, 156.1, 146.1, 146.0, 143.6, 138.4, 134.3, 133.2, 132.2, 132.1, 130.1, 127.7, 127.0, 125.3, 72.0, 64.3, 54.8, 54.5, 46.0, 36.9, 32.8, 24.0 ppm; IR(KBr): 3626, 2955, 2926, 2872, 1726, 1597, 1435, 1354, 1300, 1250, 1206, 1163, 1094, 1043, 986, 889, 814, 766, 739, 687, 664, 615, 573, 548 cm^{-1}; HRMS (ESI-TOF) calcd for $[C_{34}H_{41}NO_7S+Na]^+$ 630.2496, found 630.2490.



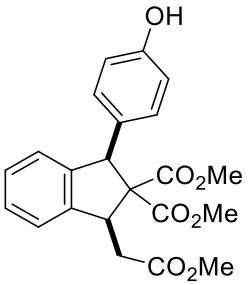
methyl 2-((1S,3R)-3-(3,5-di-tert-butyl-4-hydroxyphenyl)-5,6-dimethoxy-2-tosylisoindolin-1-yl)acetate (3li)

79% yield (95.9 mg), >20:1 dr; white solid, m.p. 156 – 157 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.9 Hz, 2H), 7.16 (d, *J* = 7.9 Hz, 2H), 7.05 (s, 2H), 6.73 (s, 1H), 6.42 (s, 1H), 5.82 (s, 1H), 5.45 (dd, *J* = 9.0, 4.3 Hz, 1H), 5.16 (s, 1H), 3.82 – 3.74 (m, 9H), 3.30 (dd, *J* = 15.9, 4.3 Hz, 1H), 2.77 (dd, *J* = 15.9, 8.9 Hz, 1H), 2.33 (s, 3H), 1.39 (s, 18H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.6, 153.3, 149.6, 149.4, 143.3, 135.7, 135.6, 132.4, 132.0, 130.5, 129.5, 127.5, 124.3, 106.0, 105.1, 69.6, 62.0, 56.0, 55.9, 51.8, 44.1, 34.4, 30.3, 21.5 ppm; IR(KBr): 3628, 2997, 2955, 2872, 2835, 1736, 1611, 1599, 1508, 1464, 1437, 1410, 1348, 1223, 1209, 1163, 1117, 1094, 1042, 891, 847, 814, 737, 706, 669, 602, 550 cm^{-1}; HRMS (ESI-TOF) calcd for $[C_{34}H_{43}NO_7S+Na]^+$ 632.2652, found 632.2649.



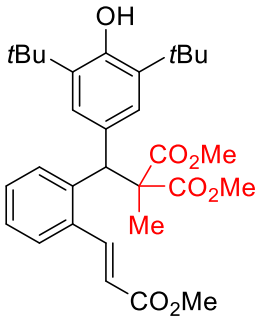
methyl 2-((1S,3R)-3-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-tosyl-2,3-dihydro-1H-benzo[e]isoindol-1-yl)acetate (3ni)

86% yield (103.2 mg), >20:1 dr; white solid, m.p. 170 – 172 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.85 (t, *J* = 8.9 Hz, 2H), 7.72 – 7.68 (m, 3H), 7.51 (dt, *J* = 22.3, 7.3 Hz, 2H), 7.13 – 7.08 (m, 5H), 6.09 (d, *J* = 3.8 Hz, 1H), 6.02 (s, 1H), 5.15 (s, 1H), 3.82 (s, 3H), 3.25 (dd, *J* = 15.7, 3.2 Hz, 1H), 3.03 (dd, *J* = 15.7, 6.8 Hz, 1H), 2.26 (s, 3H), 1.39 (s, 18H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.2, 152.9, 142.8, 137.3, 135.3, 133.2, 132.9, 131.4, 129.0, 128.9, 128.5, 127.2, 127.0, 126.7, 125.5, 124.0, 122.9, 120.7, 70.3, 61.9, 51.6, 43.8, 33.9, 29.8, 20.9 ppm; IR(KBr): 3628, 3059, 2955, 2916, 2872, 1738, 1597, 1518, 1435, 1352, 1234, 1209, 1163, 1119, 1094, 1047, 1016, 889, 827, 812, 768, 739, 704, 665, 583, 550 cm^{-1}; HRMS (ESI-TOF) calcd for $[C_{34}H_{41}NO_5S+H]^+$ 600.2778, found 600.2774.



dimethyl (1R,3S)-1-(4-hydroxyphenyl)-3-(2-methoxy-2-oxoethyl)-1,3-dihydro-2H-indene-2,2-dicarboxylate (4aa)

65% yield (51.4 mg), >20:1 dr; Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28 – 7.15 (m, 4H), 7.11 (d, *J* = 7.5 Hz, 1H), 6.95 (d, *J* = 7.3 Hz, 1H), 6.72 (dd, *J* = 8.7, 2.1 Hz, 2H), 5.72 (s, 1H), 5.30 (s, 1H), 4.10 (t, *J* = 6.1 Hz, 1H), 3.80 (s, 6H), 3.19 (d, *J* = 2.0 Hz, 3H), 3.14 – 3.11 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.8, 171.5, 168.7, 155.3, 143.3, 141.7, 131.2, 130.1, 127.7, 127.1, 124.9, 122.4, 114.9, 72.2, 55.4, 52.8, 52.1, 51.8, 46.5, 36.0 ppm; IR(KBr): 3644, 3612, 2953, 2926, 2853, 1748, 1732, 1715, 1541, 1506, 1456, 1435, 1339, 1269, 1209, 1173, 113, 1051, 845, 808, 758, 592 cm^{-1}; HRMS (ESI-TOF) calcd for $[C_{22}H_{22}O_7+H]^+$ 399.1438, found 399.1432.



dimethyl (E)-2-((3,5-di-tert-butyl-4-hydroxyphenyl)(2-(3-methoxy-3-oxoprop-1-en-1-yl)phenyl)methyl)-2-methylmalonate (5al)

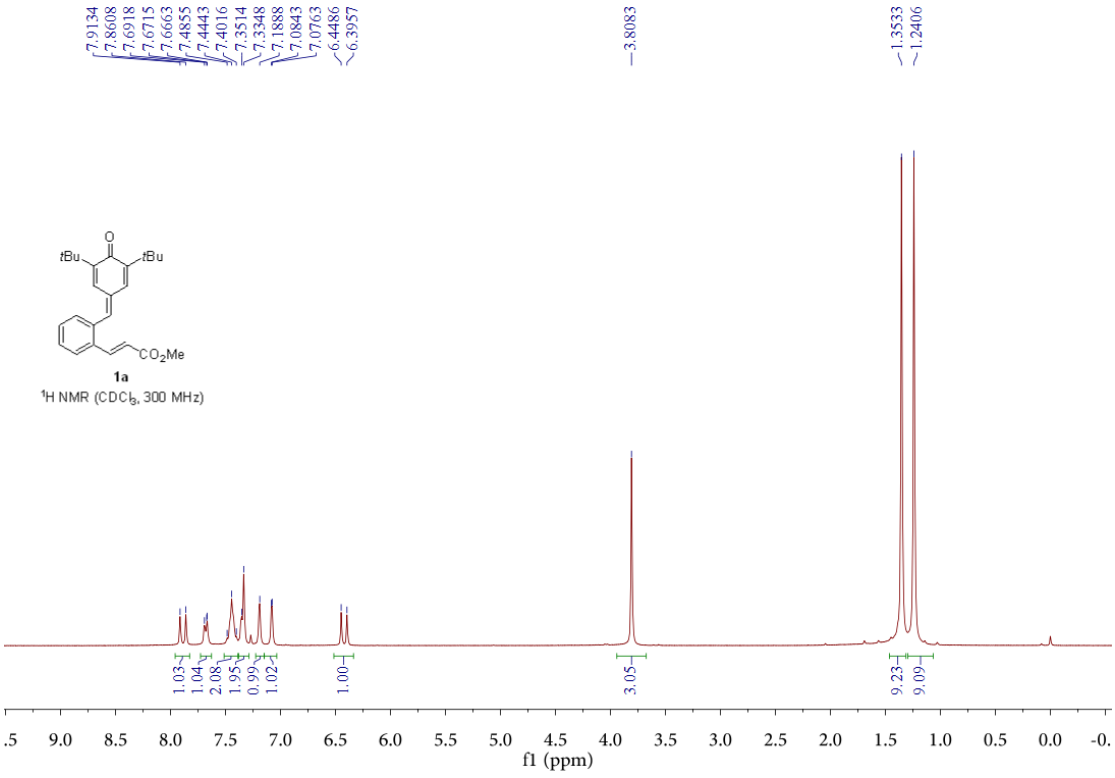
53% yield (55.8 mg); yellow solid, m.p. 56 – 58 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 15.7 Hz, 1H), 7.58 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.40 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.32 (td, *J* = 7.7, 1.5 Hz, 1H), 7.20 (td, *J* = 7.6, 1.2 Hz, 1H), 7.00 (s, 2H), 6.12 (d, *J* = 15.7 Hz, 1H), 5.30 (s, 1H), 5.06 (s, 1H), 3.78 (s, 3H), 3.66 (s, 3H), 3.48 (s, 3H), 1.65 (s, 3H), 1.35 (s, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.0, 171.5, 167.0, 152.4, 143.7, 141.0, 135.1, 134.9, 129.9, 129.2, 127.7, 127.6, 127.1, 126.7, 120.1, 59.0, 52.7, 52.5, 51.6, 50.7, 34.3, 30.3, 20.0; IR(KBr): 3636, 2997, 2953, 2914, 2874, 1728, 1634, 1481, 1435, 1315, 1240, 1211, 1196, 1171, 1111, 1038, 978, 885, 770, 739 cm^{-1}; HRMS (ESI-TOF) calcd for $[C_{31}H_{40}O_7+Na]^+$ 547.2672, found. 547.2663.

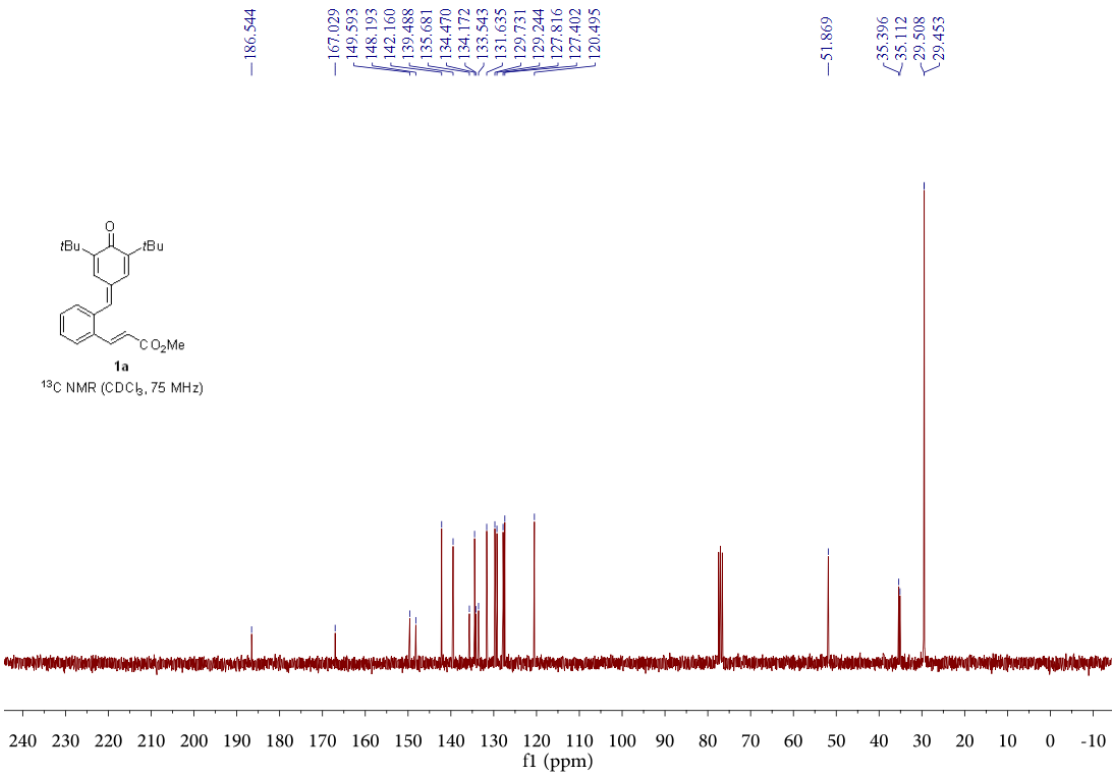
9. References

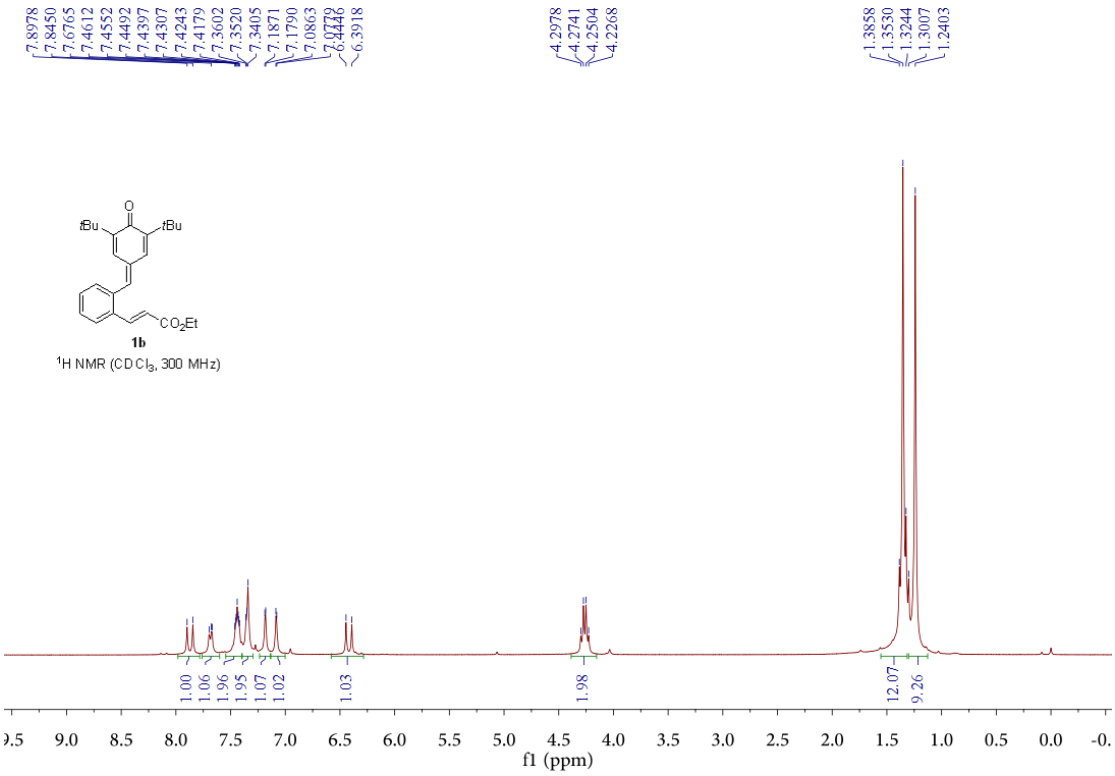
[1] R. Pan, L. Hu, C. Han, A. Lin and H. Yao, *Org. Lett.*, 2018, **20**, 1974.

[2] B. G. Das, A. Chirila, M. Tromp, J. N. H. Reek and B. de Bruin, *J. Am. Chem. Soc.*, 2016, **138**, 8968.

10. ^{1}H NMR and ^{13}C NMR Spectra of the Titled Compounds



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tBu
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1b
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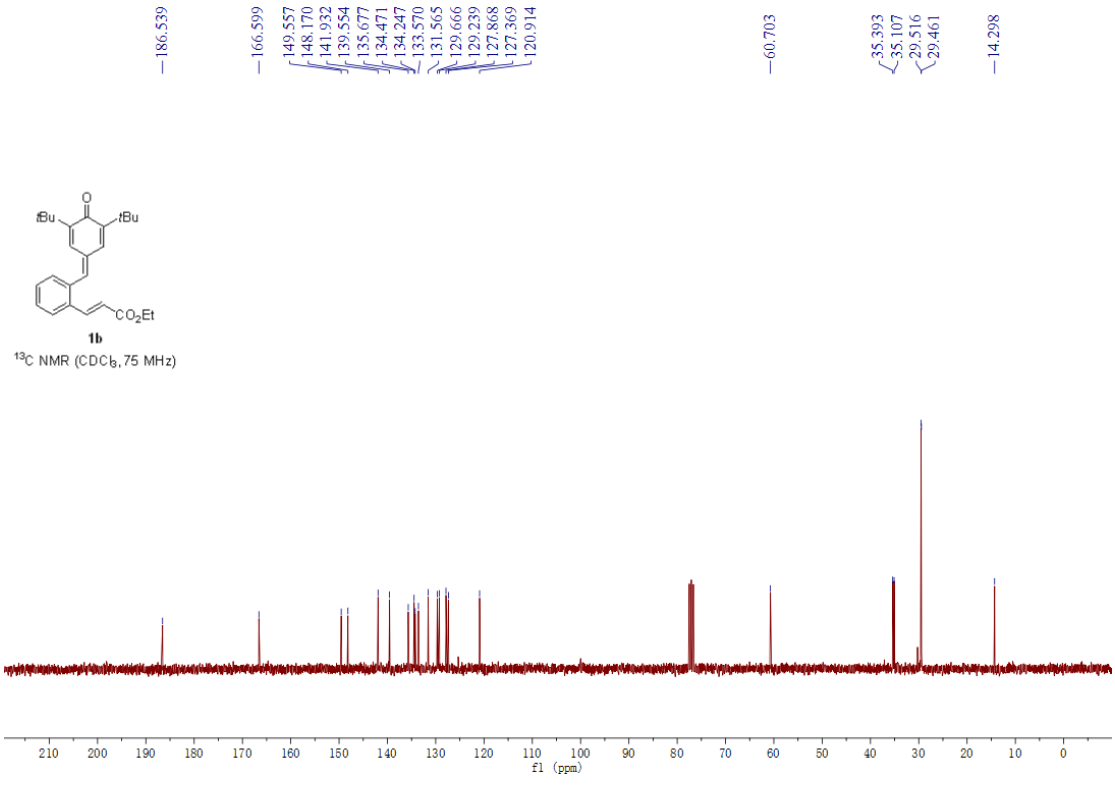
9.26
f1 (ppm)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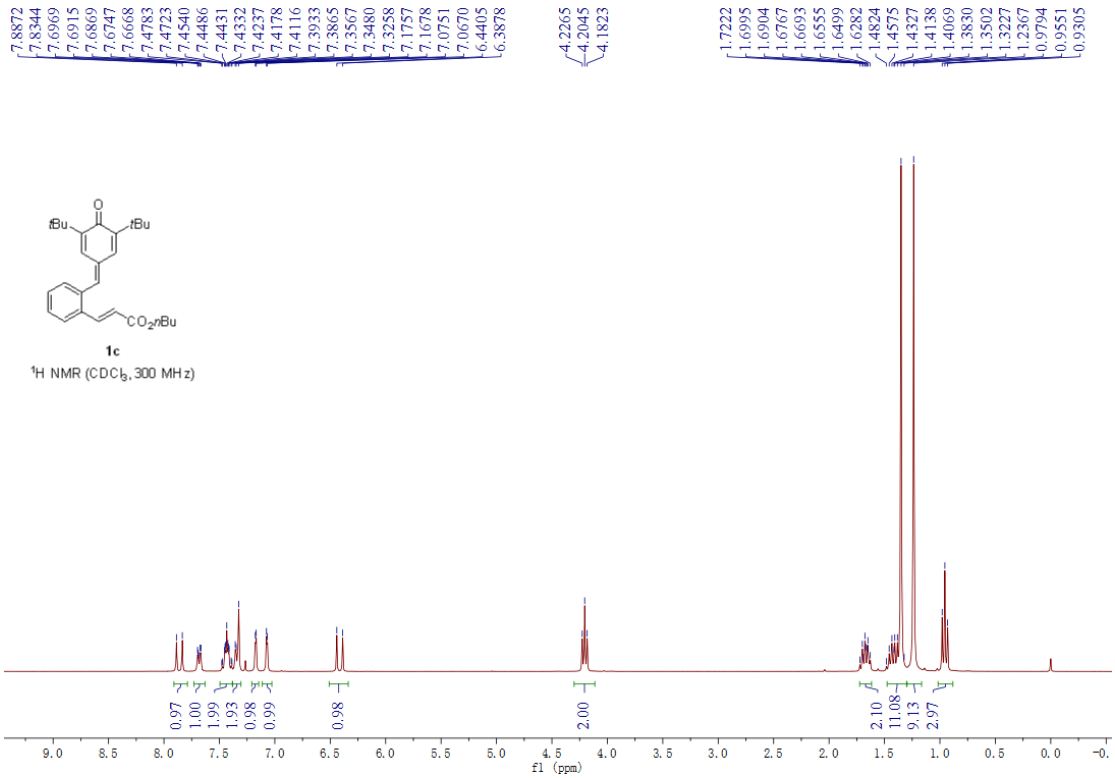
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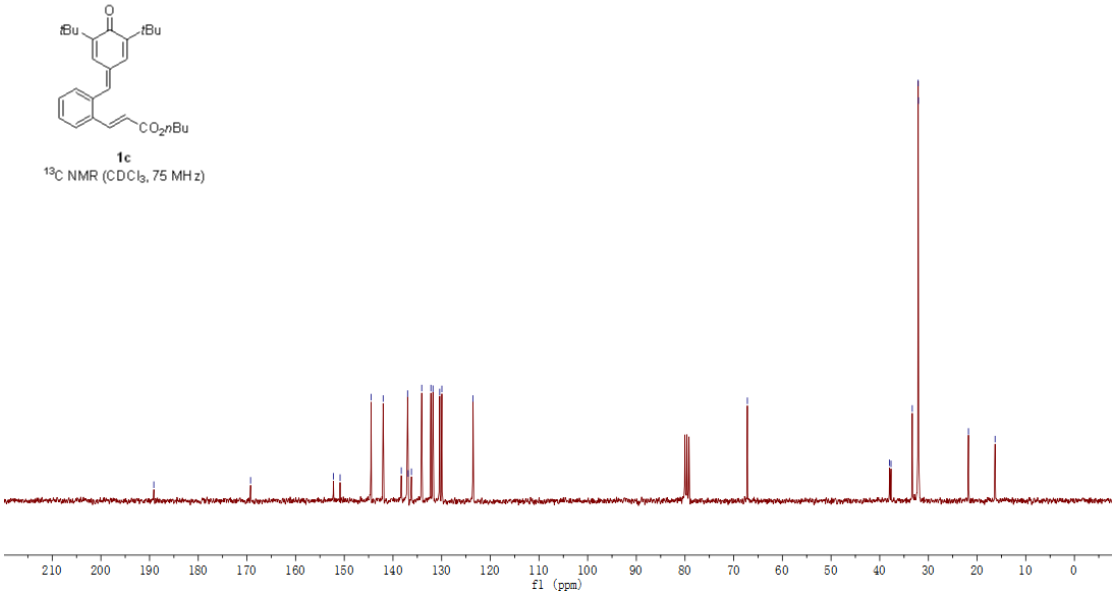
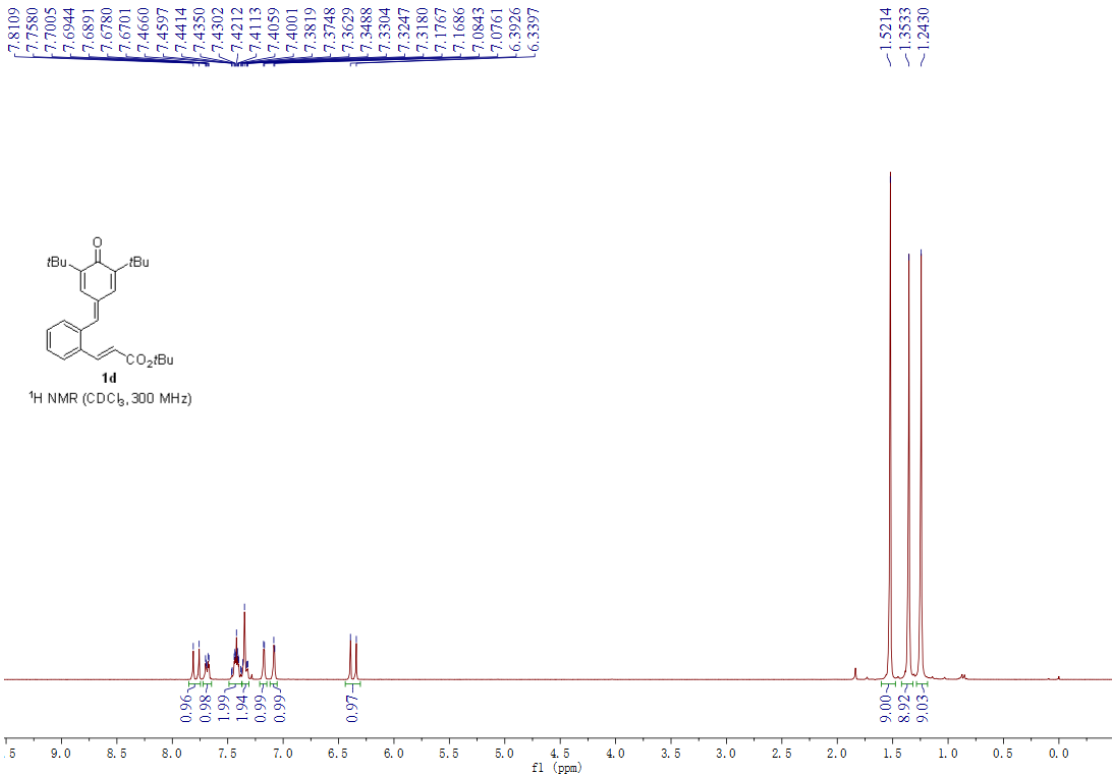
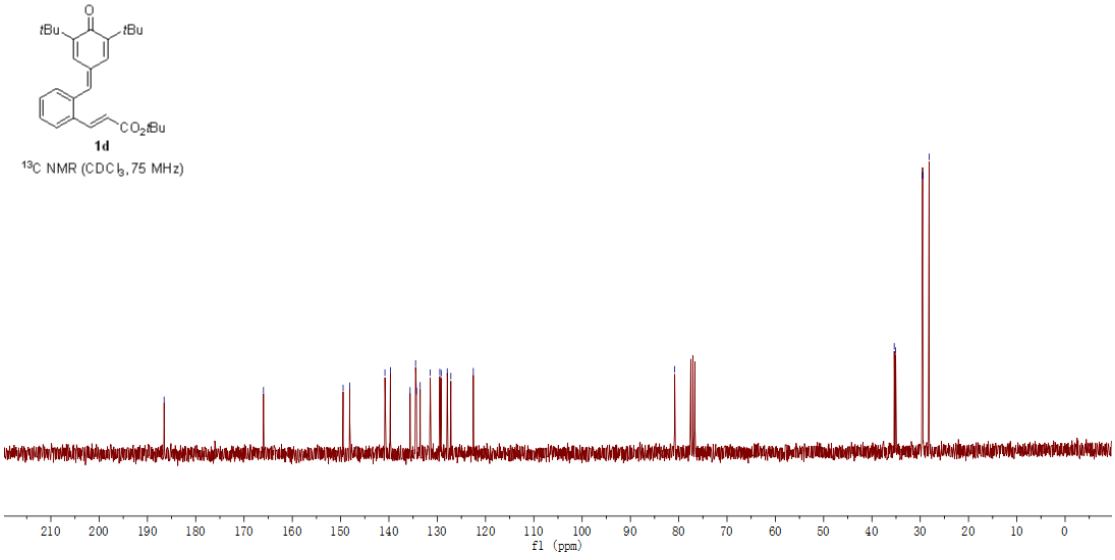
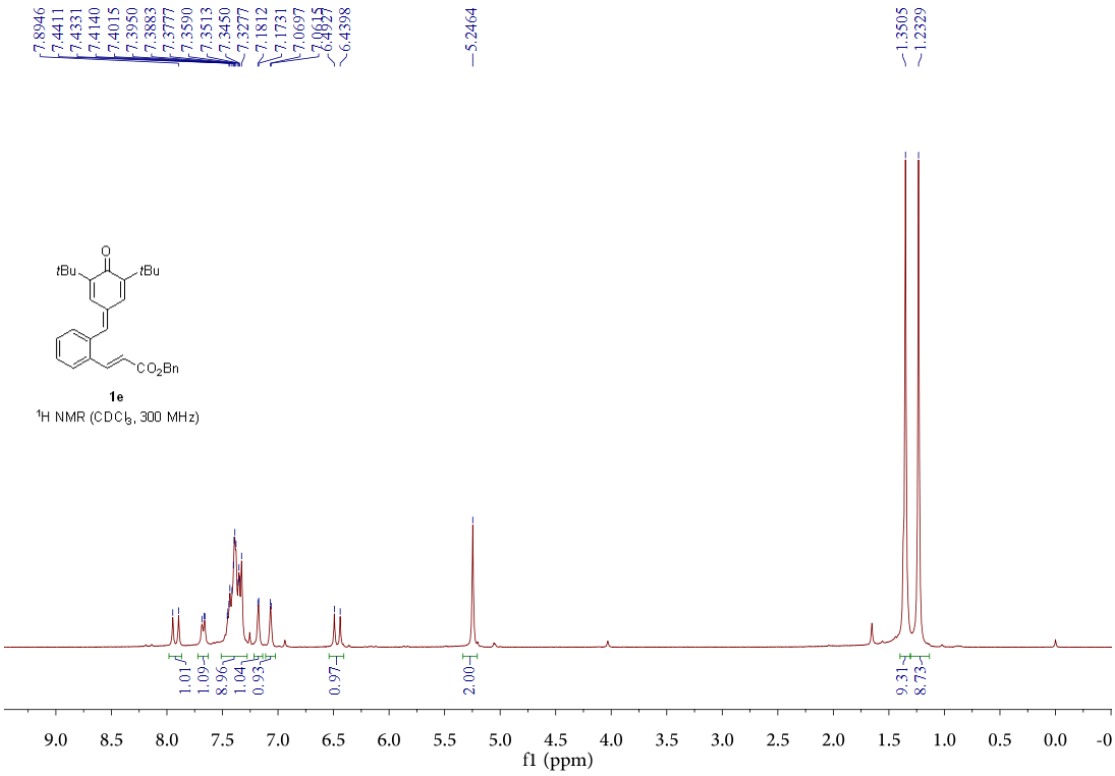
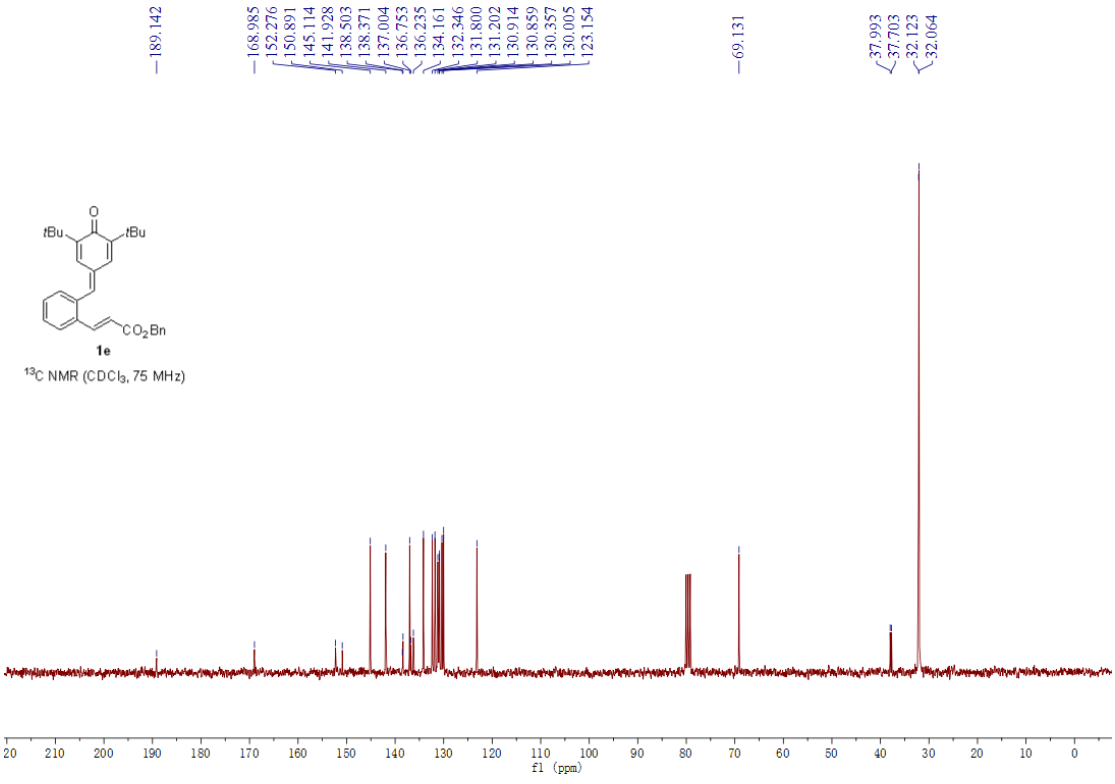
7.6915
7.6869
7.6747
7.6668
7.4783
7.4723
7.4540
7.4486
7.4431
7.4332
7.4237
7.4178
7.4116
7.3933
7.3865
7.3567
7.3480
7.3258
7.1757
7.1678
7.0751
7.0670
6.4405
6.3878
4.2265
4.2045
4.1823
1.7222
1.6995
1.6904
1.6767
1.6693
1.6555
1.6499
1.6282
1.4824
1.4575
1.4327
1.4138
1.4069
1.3830
1.3502
1.3227
1.2367
0.9794
0.9551
0.9305
tBu
tBu
CO2nBu
1c
1H NMR (CDCl3, 300 MHz)
0.97
1.00
1.99
1.93
0.98
0.99
0.98
2.00
2.10
11.08
9.13
2.97
f1 (ppm)

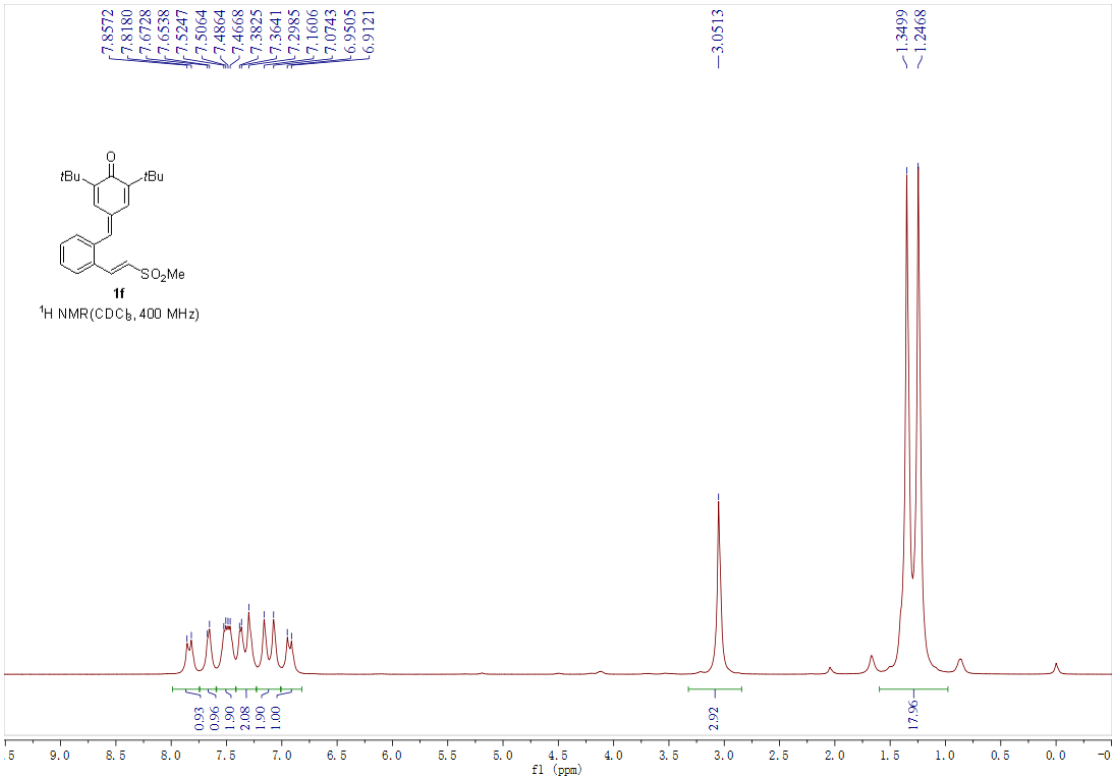

189.128
169.248
152.227
150.862
144.497
142.016
138.289
136.993
136.872
136.203
134.088
132.209
131.777
130.395
129.948
123.555
67.191
37.982
37.682
33.313
32.103
32.050
21.773
16.300
tBu
tBu
CO2nBu
1c
13C NMR (CDCl3, 75 MHz)
f1 (ppm)


7.8109
7.7580
7.7005
7.6944
7.6891
7.6780
7.6701
7.4660
7.4597
7.4414
7.4350
7.4302
7.4212
7.4113
7.4059
7.4001
7.3819
7.3748
7.3629
7.3488
7.3304
7.3247
7.3180
7.1767
7.1686
7.0843
7.0761
6.3926
6.3397
1.5214
1.3533
1.2430
tBu
tBu
CO2tBu
1d
1H NMR (CDCl3, 300 MHz)
0.96
0.98
1.99
1.94
0.99
0.99
0.97
9.00
8.92
9.03
f1 (ppm)


186.548
165.972
149.486
148.110
140.827
139.700
135.618
134.484
134.306
133.528
131.443
129.466
129.180
127.923
127.177
122.527
80.832
35.380
35.087
29.518
29.478
28.169
tBu
tBu
CO2tBu
1d
13C NMR (CDCl3, 75 MHz)
f1 (ppm)

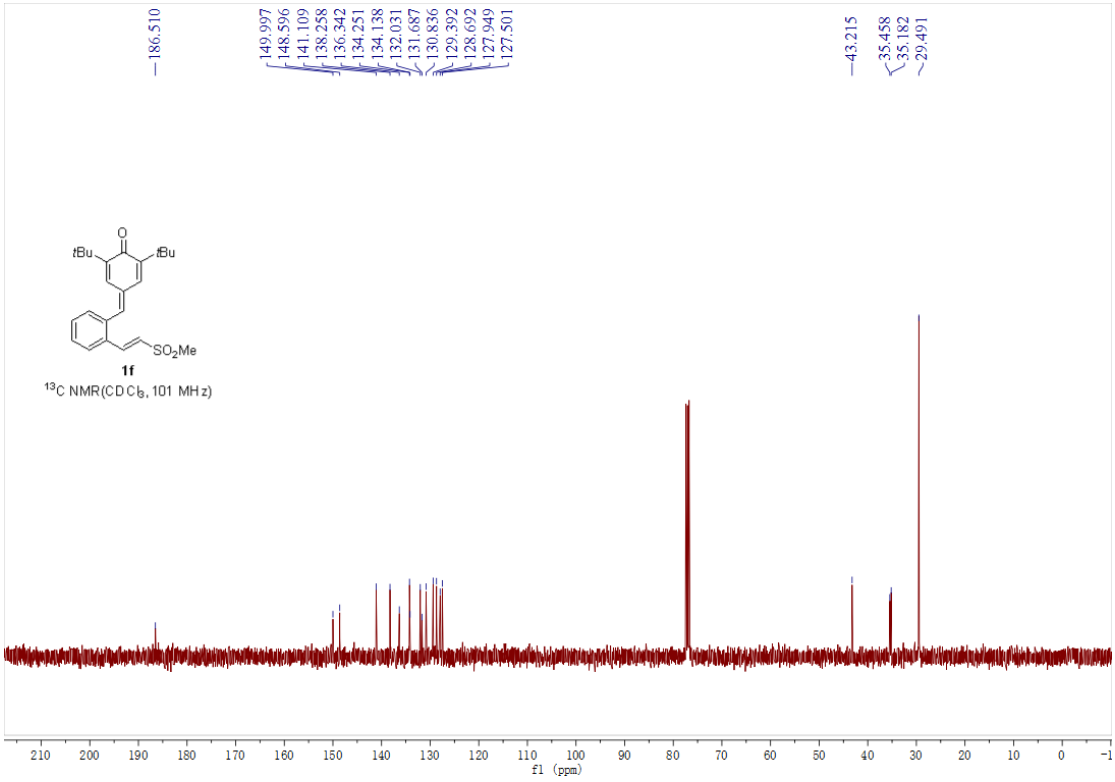

7.8946
7.4411
7.4331
7.4140
7.4015
7.3950
7.3883
7.3777
7.3590
7.3513
7.3450
7.3277
7.1812
7.1731
7.0697
7.0615
6.9927
6.4398
5.2464
1.3505
1.2329
tBu
tBu
CO2Bn
1e
1H NMR (CDCl3, 300 MHz)
1.01
1.09
8.96
1.04
0.93
0.97
2.00
9.31
8.73
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)


189.142
168.985
152.276
150.891
145.114
141.928
138.503
138.371
137.004
136.753
136.235
134.161
132.346
131.800
131.202
130.914
130.859
130.357
130.005
123.154
69.131
37.993
37.703
32.123
32.064
tBu
tBu
CO2Bn
1e
13C NMR (CDCl3, 75 MHz)
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



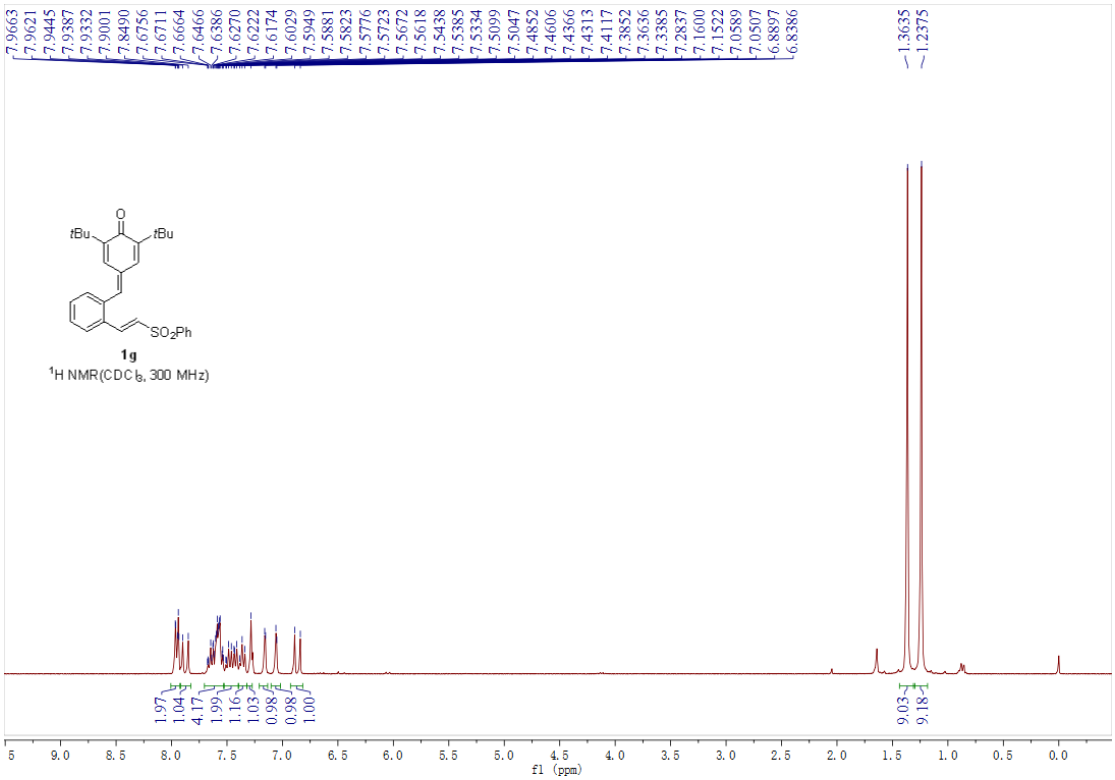
1f

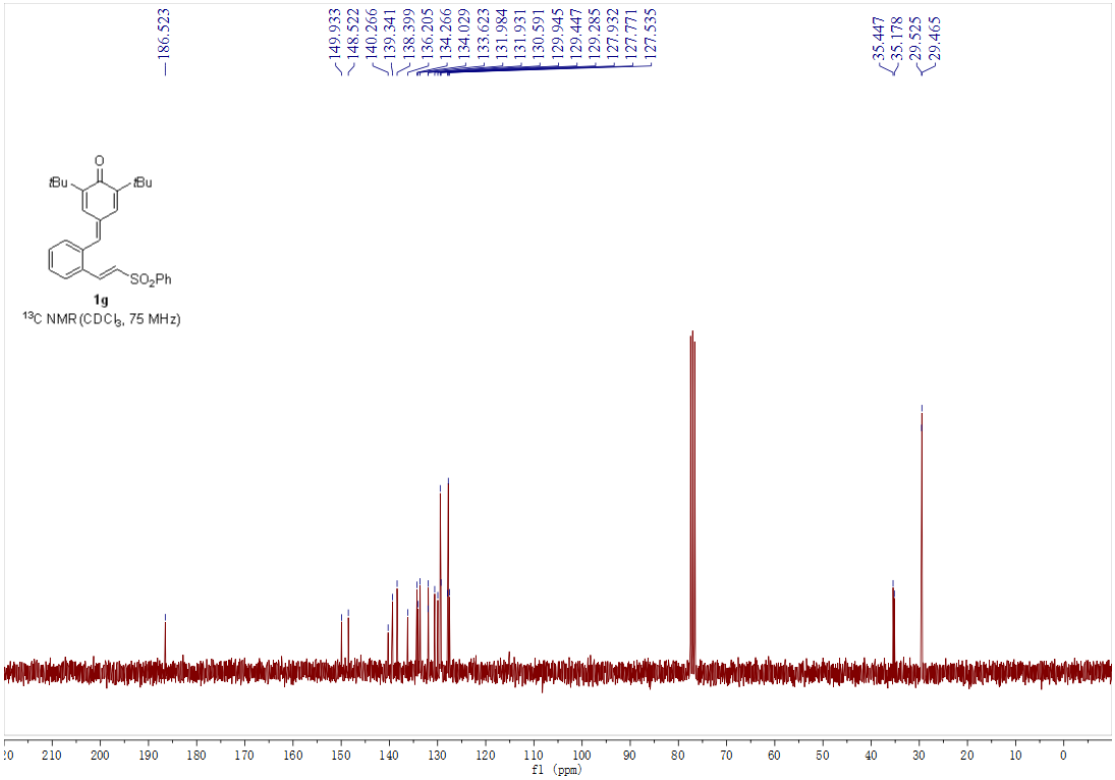
^{1}H NMR($CDCl_3$, 400 MHz)

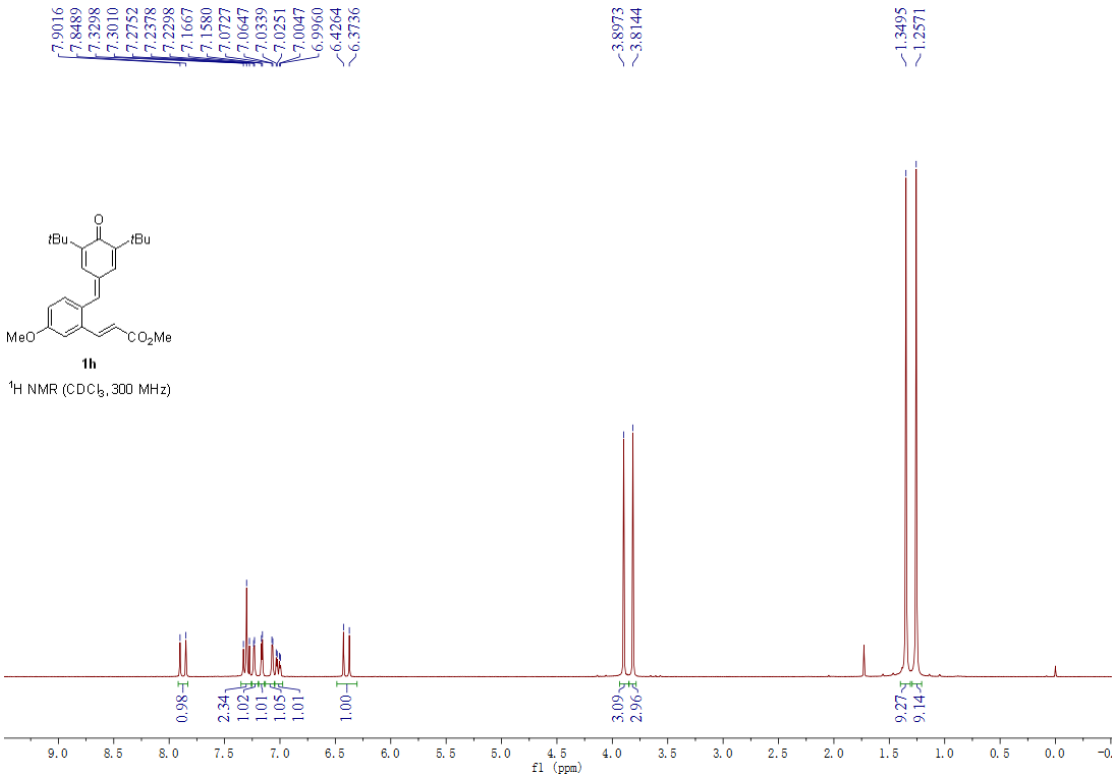


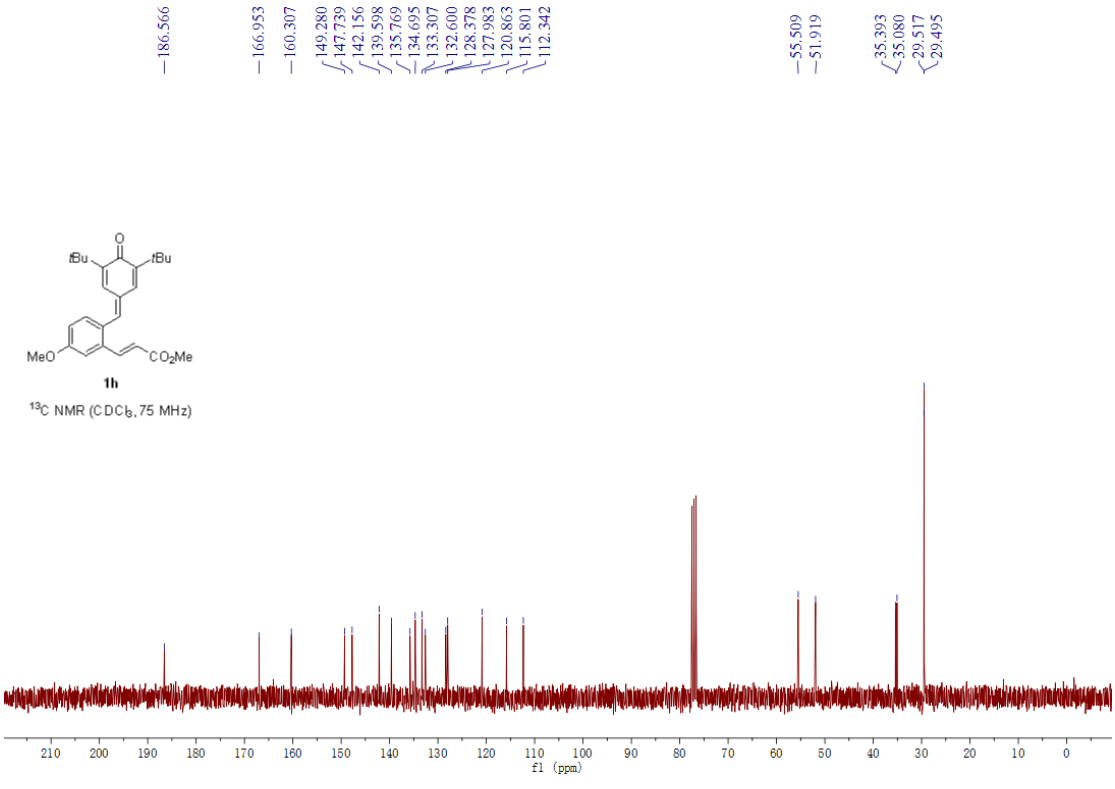
1f

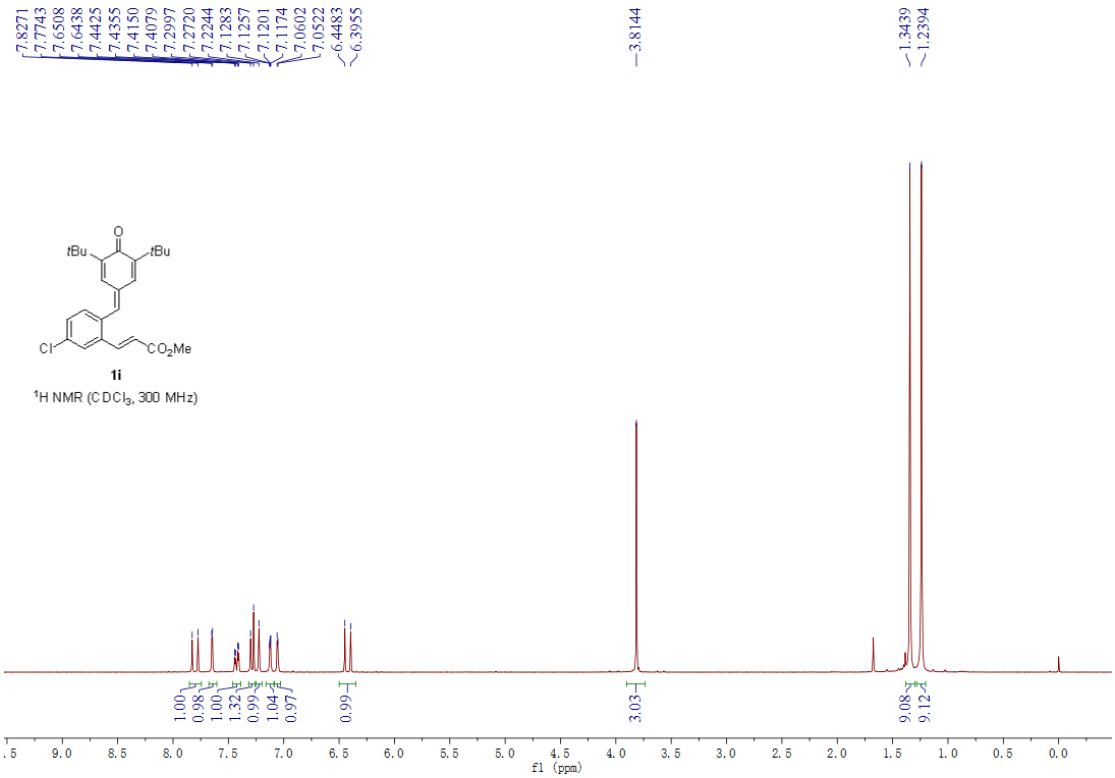
^{13}C NMR($CDCl_3$, 101 MHz)


7.9663
7.9621
7.9445
7.9387
7.9332
7.9001
7.8490
7.6756
7.6711
7.6664
7.6466
7.6386
7.6270
7.6222
7.6174
7.6029
7.5949
7.5881
7.5823
7.5776
7.5723
7.5672
7.5618
7.5438
7.5385
7.5334
7.5099
7.5047
7.4852
7.4606
7.4366
7.4313
7.4117
7.3852
7.3636
7.3385
7.2837
7.1600
7.1522
7.0589
7.0507
6.8897
6.8386
1.3635
1.2375
tBu
tBu
SO2Ph
1g
1H NMR(CDCl3, 300 MHz)
1.97
1.04
4.17
1.99
1.16
1.03
0.98
0.98
1.00
9.03
9.18
f1 (ppm)


186.523
149.933
148.522
140.266
139.341
138.399
136.205
134.266
134.029
133.623
131.984
131.931
130.591
129.945
129.447
129.285
127.932
127.771
127.535
35.447
35.178
29.525
29.465
tBu
tBu
SO2Ph
1g
13C NMR(CDCl3, 75 MHz)
f1 (ppm)

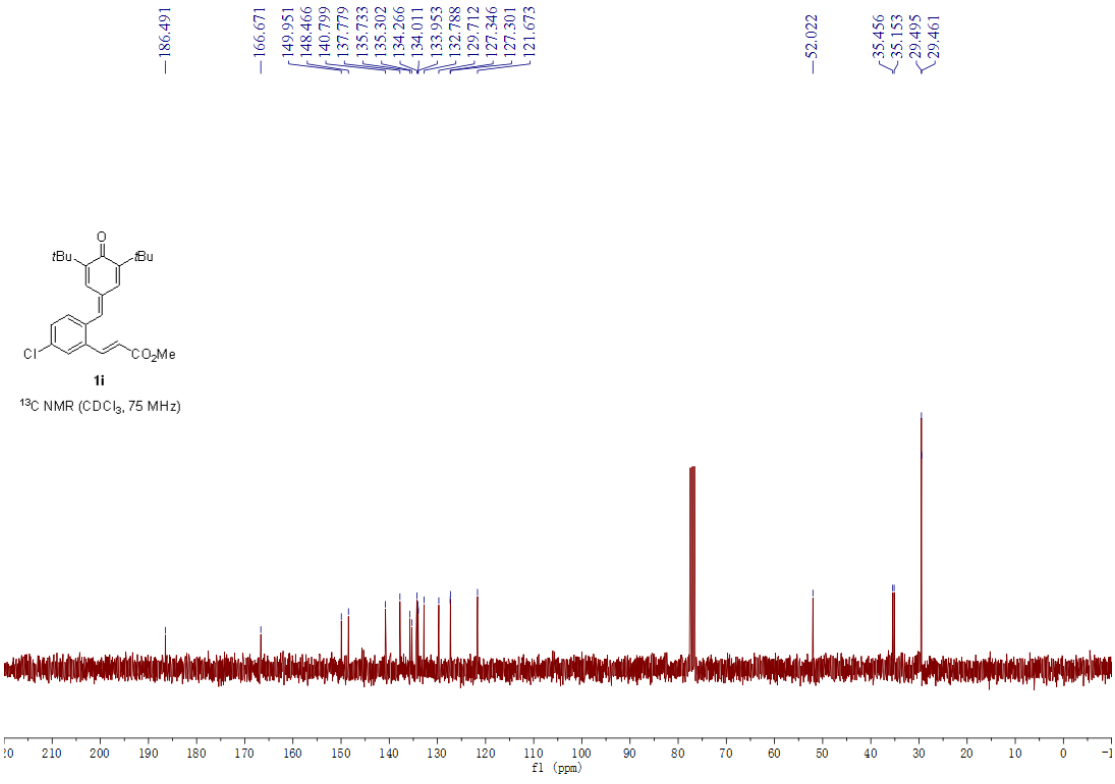

7.9016
7.8489
7.3298
7.3010
7.2752
7.2378
7.2298
7.1667
7.1580
7.0727
7.0647
7.0339
7.0251
7.0047
6.9960
6.4264
6.3736
3.8973
3.8144
1.3495
1.2571
tBu
tBu
MeO
CO2Me
1h
1H NMR (CDCl3, 300 MHz)
0.98
2.34
1.02
1.01
1.05
1.01
1.00
3.09
2.96
9.27
9.14
f1 (ppm)


186.566
166.953
160.307
149.280
147.739
142.156
139.598
135.769
134.695
133.307
132.600
128.378
127.983
120.863
115.801
112.342
55.509
51.919
35.393
35.080
29.517
29.495
tBu
tBu
MeO
CO2Me
1h
13C NMR (CDCl3, 75 MHz)
f1 (ppm)



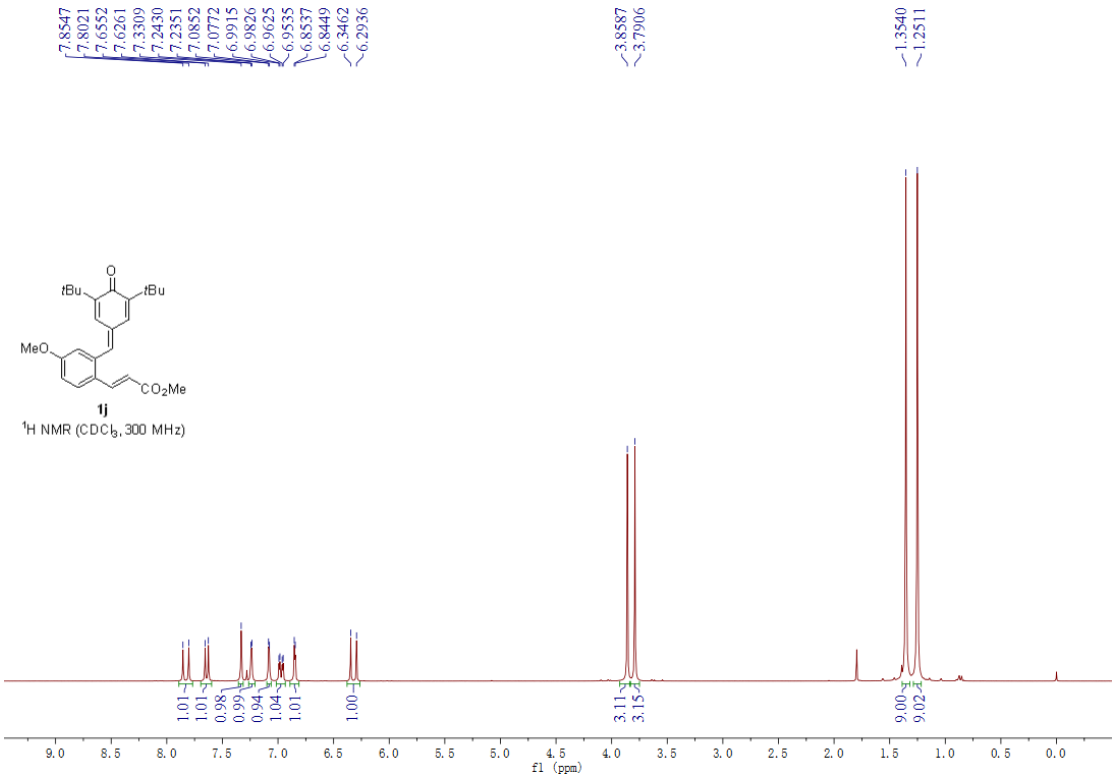
1i

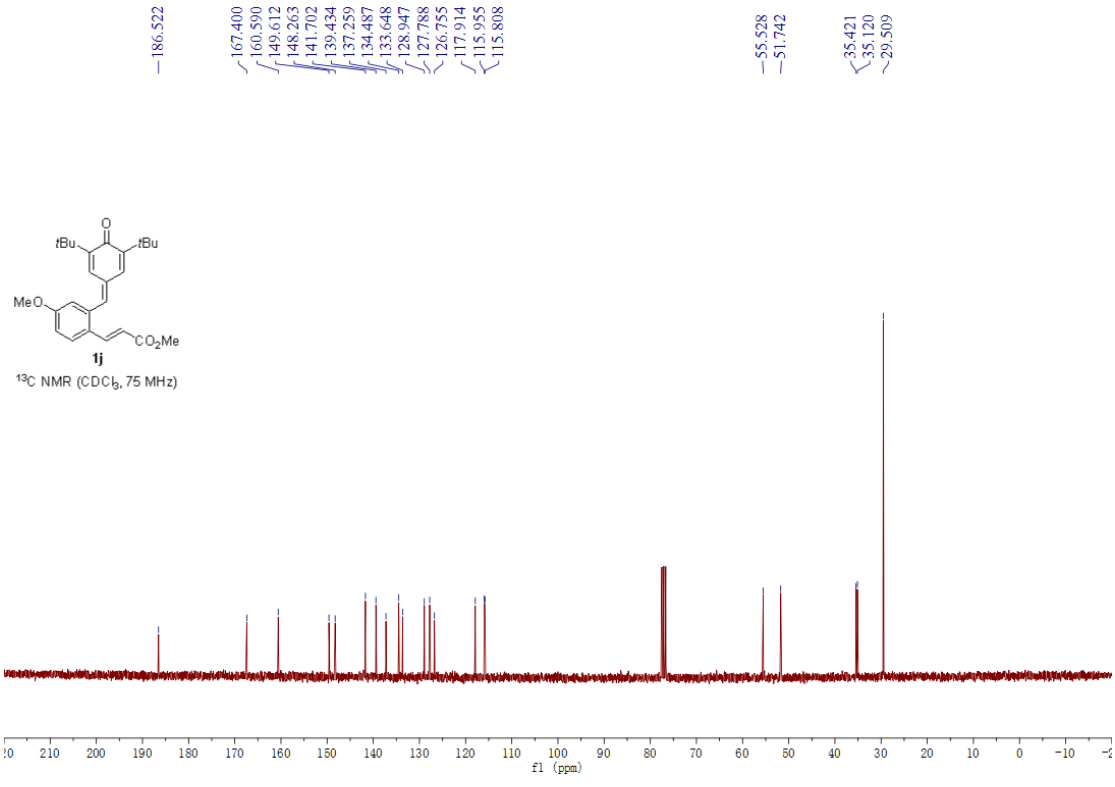
^{1}H NMR ($CDCl_3$, 300 MHz)

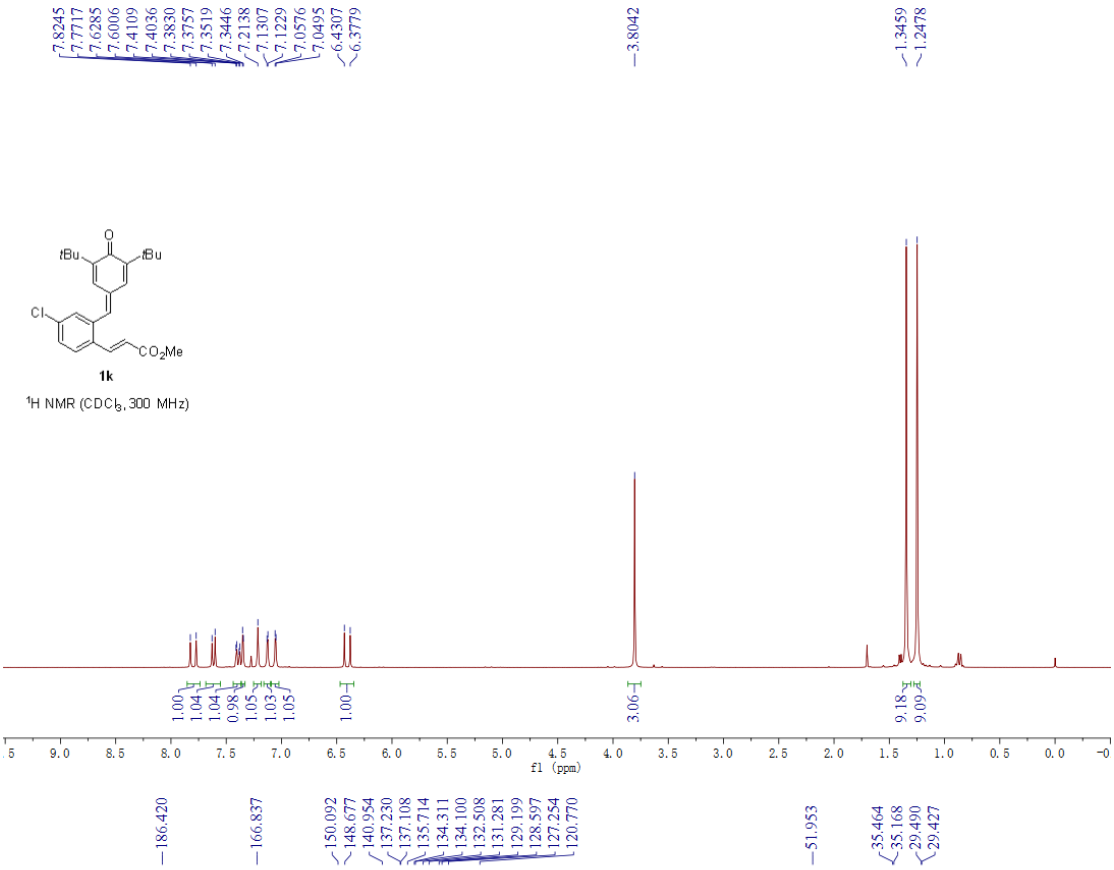


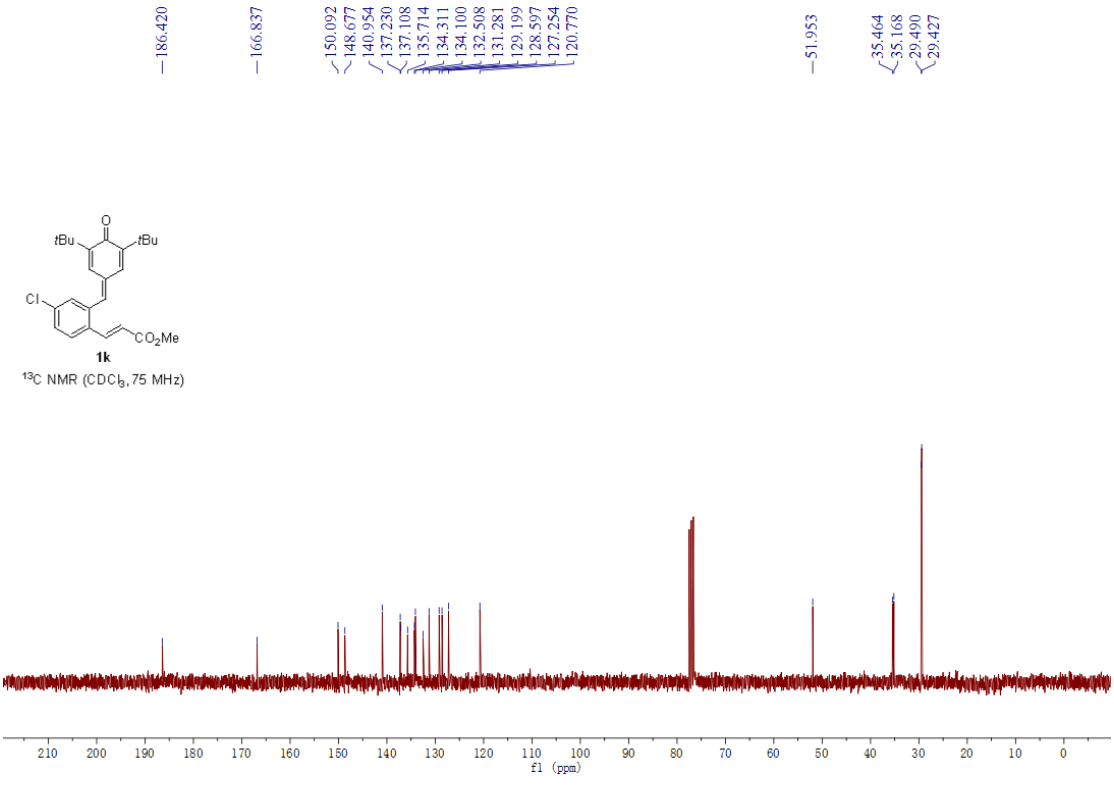
1i

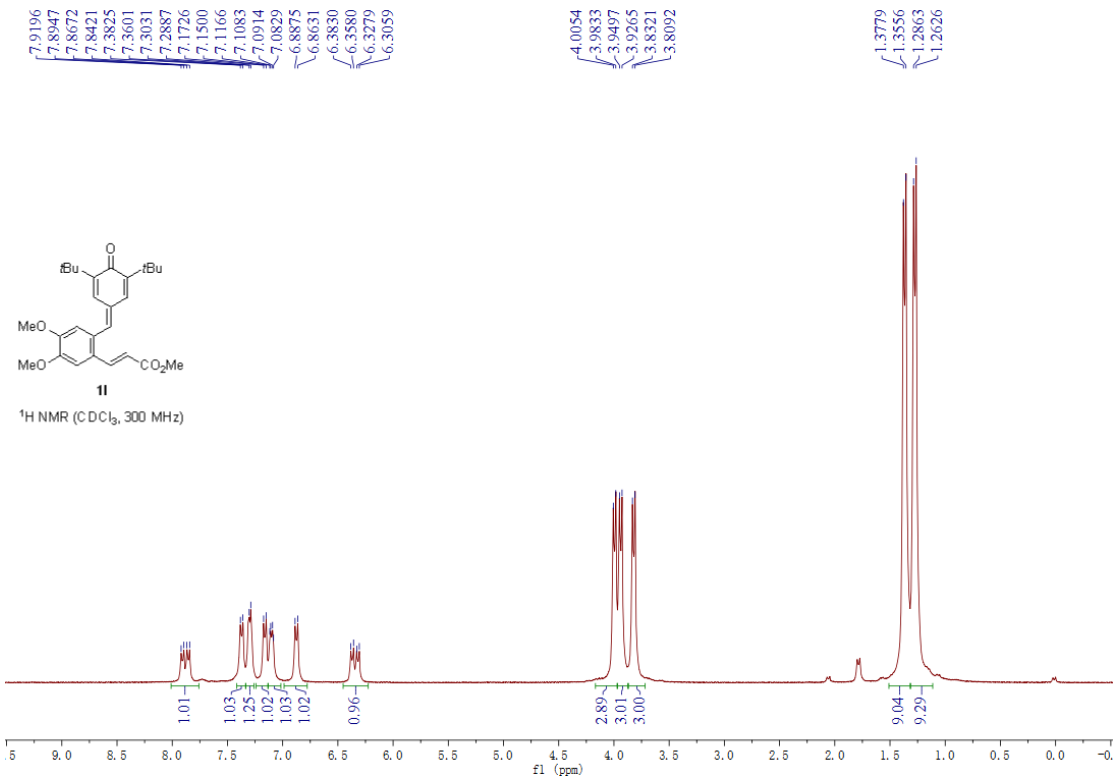
^{13}C NMR ($CDCl_3$, 75 MHz)

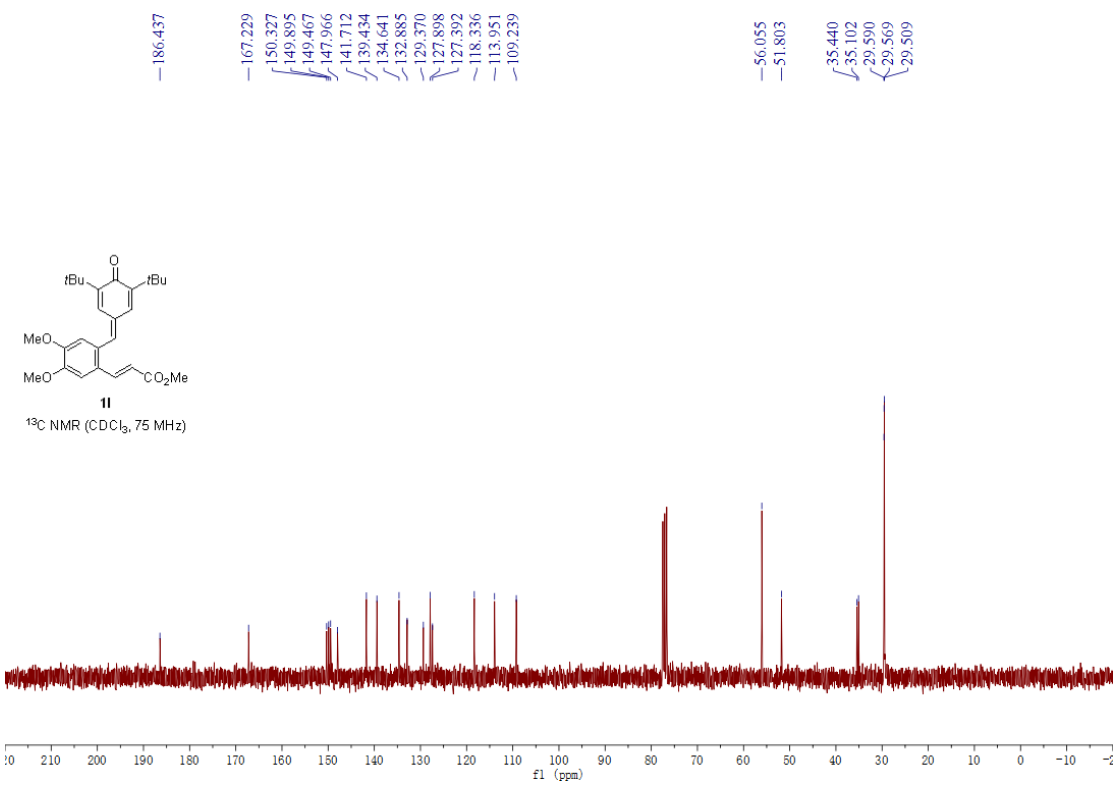

7.8547
7.8021
7.6552
7.6261
7.3309
7.2430
7.2351
7.0852
7.0772
6.9915
6.9826
6.9625
6.9535
6.8537
6.8449
6.3462
6.2936
3.8587
3.7906
1.3540
1.2511
tBu
tBu
O
MeO
CO2Me
1j
1H NMR (CDCl3, 300 MHz)
1.01
1.01
0.98
0.99
0.94
1.04
1.01
1.00
3.11
3.15
9.00
9.02
f1 (ppm)

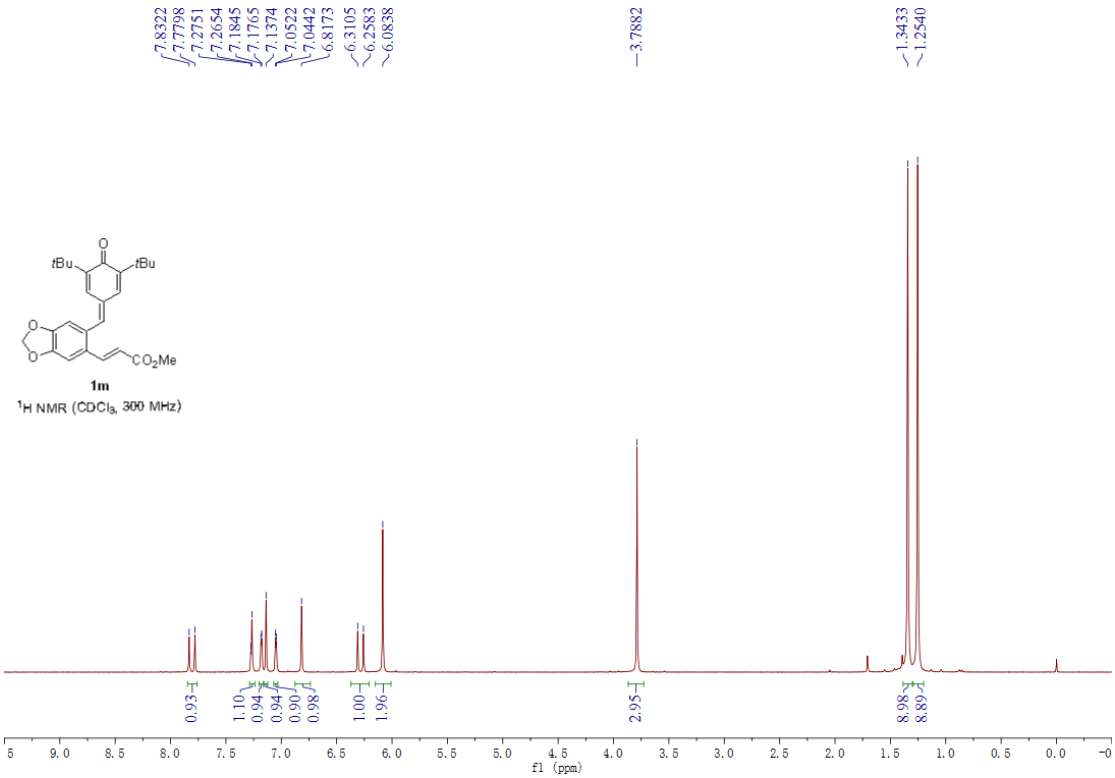

186.522
167.400
160.590
149.612
148.263
141.702
139.434
137.259
134.487
133.648
128.947
127.788
126.755
117.914
115.955
115.808
55.528
51.742
35.421
35.120
29.509
tBu
tBu
O
MeO
CO2Me
1j
13C NMR (CDCl3, 75 MHz)
f1 (ppm)

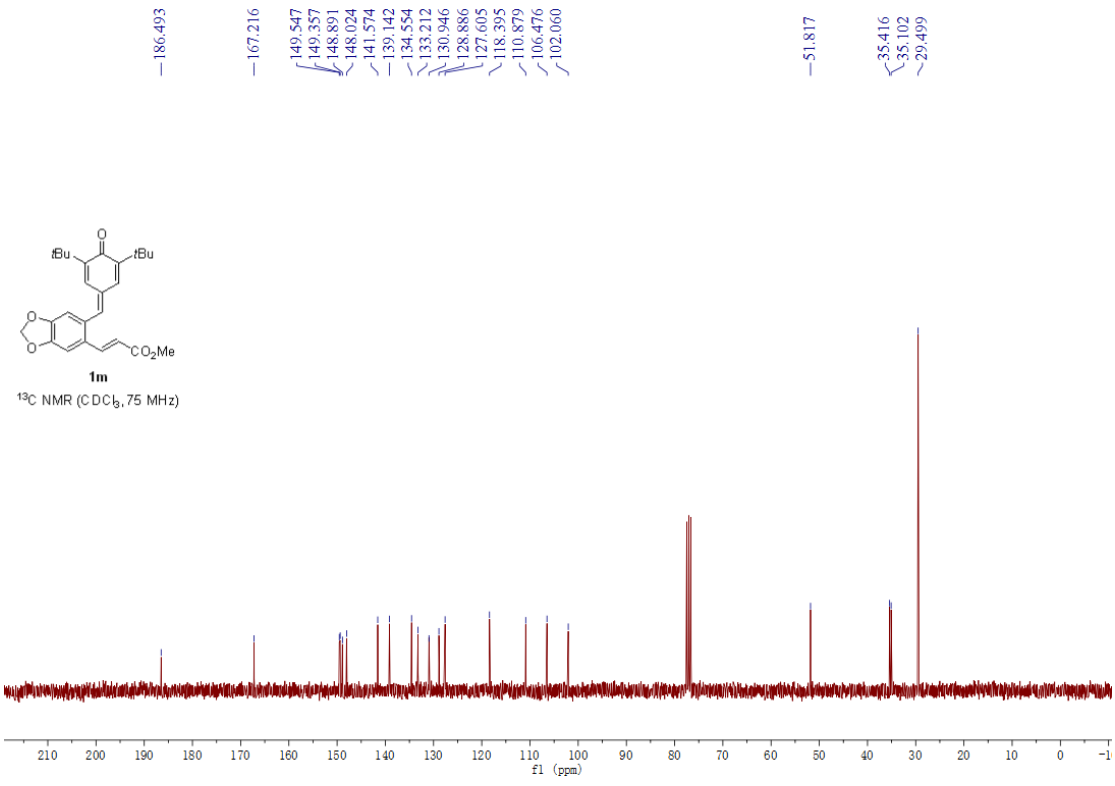

7.8245
7.7717
7.6285
7.6006
7.4109
7.4036
7.3830
7.3757
7.3519
7.3446
7.2138
7.1307
7.1229
7.0576
7.0495
6.4307
6.3779
3.8042
1.3459
1.2478
tBu
tBu
Cl
CO2Me
1k
1H NMR (CDCl3, 300 MHz)
1.00
1.04
1.04
0.98
1.05
1.03
1.05
1.00
3.06
9.18
9.09
f1 (ppm)

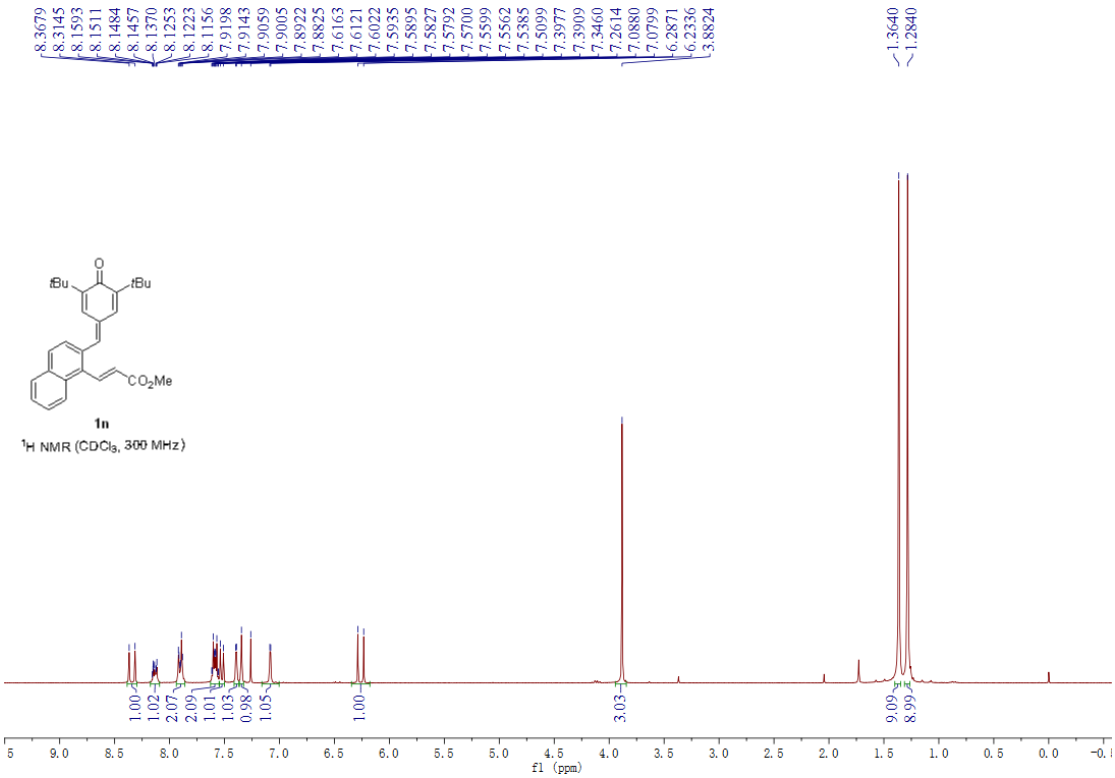

186.420
166.837
150.092
148.677
140.954
137.230
137.108
135.714
134.311
134.100
132.508
131.281
129.199
128.597
127.254
120.770
51.953
35.464
35.168
29.490
29.427
tBu
tBu
Cl
CO2Me
1k
13C NMR (CDCl3, 75 MHz)
f1 (ppm)

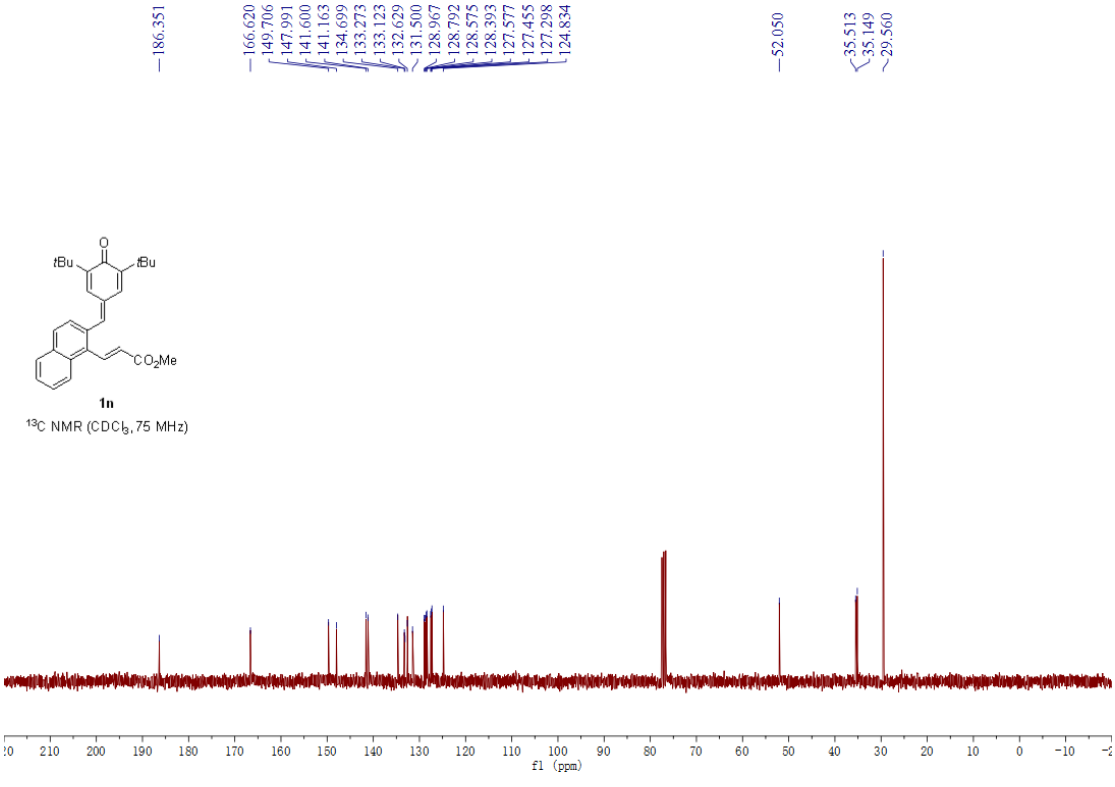

7.9196
7.8947
7.8672
7.8421
7.3825
7.3601
7.3031
7.2887
7.1726
7.1500
7.1166
7.1083
7.0914
7.0829
6.8875
6.8631
6.3830
6.3580
6.3279
6.3059
4.0054
3.9833
3.9497
3.9265
3.8321
3.8092
1.3779
1.3556
1.2863
1.2626
tBu
tBu
MeO
MeO
CO2Me
1l
1H NMR (CDCl3, 300 MHz)
1.01
1.03
1.25
1.02
1.03
1.02
0.96
2.89
3.01
3.00
9.04
9.29
f1 (ppm)

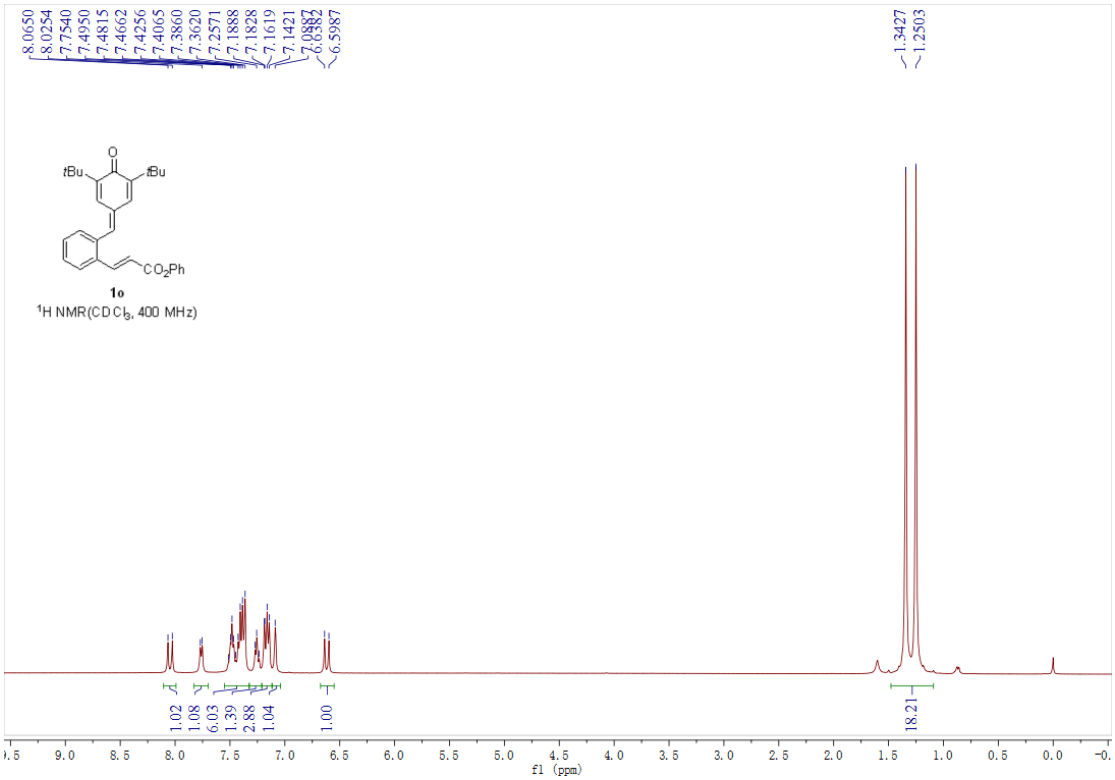

186.437
167.229
150.327
149.895
149.467
147.966
141.712
139.434
134.641
132.885
129.370
127.898
127.392
118.336
113.951
109.239
56.055
51.803
35.440
35.102
29.590
29.569
29.509
tBu
tBu
MeO
MeO
CO2Me
1l
13C NMR (CDCl3, 75 MHz)
f1 (ppm)

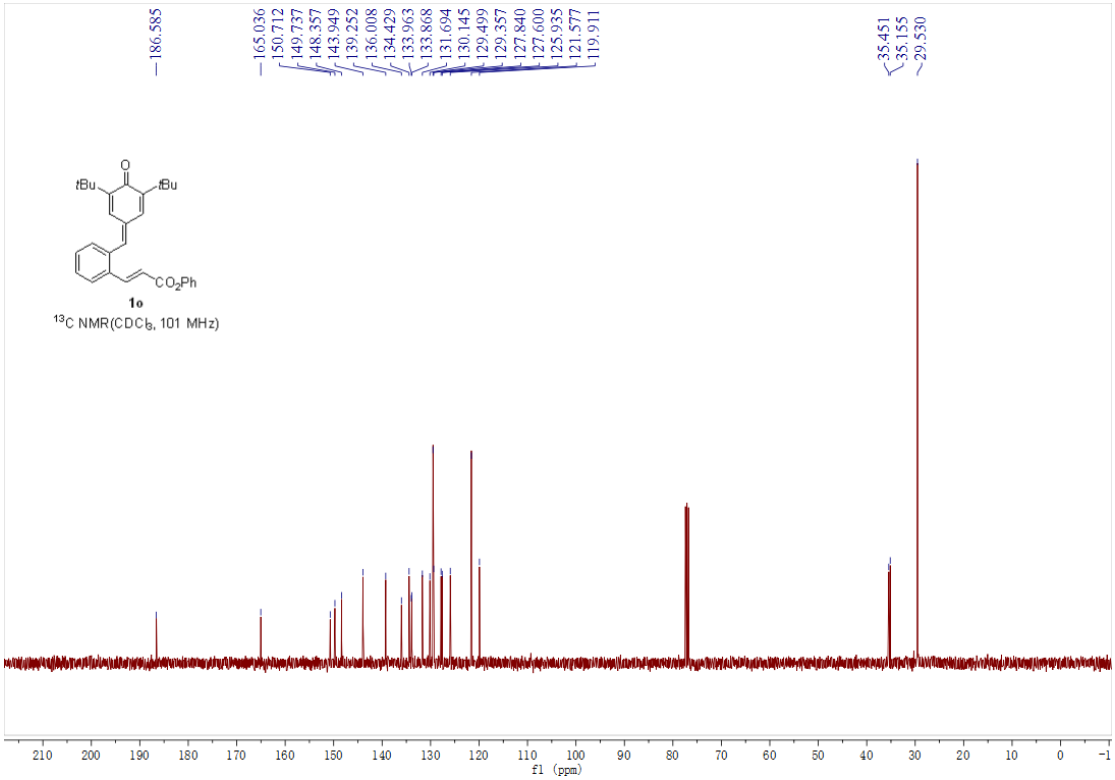

7.8322
7.7798
7.2751
7.2654
7.1845
7.1765
7.1374
7.0522
7.0442
6.8173
6.3105
6.2583
6.0838
3.7882
1.3433
1.2540
tBu
tBu
O
O
O
CO2Me
1m
1H NMR (CDCl3, 300 MHz)
0.93
1.10
0.94
0.94
0.90
0.98
1.00
1.96
2.95
8.98
8.89
f1 (ppm)

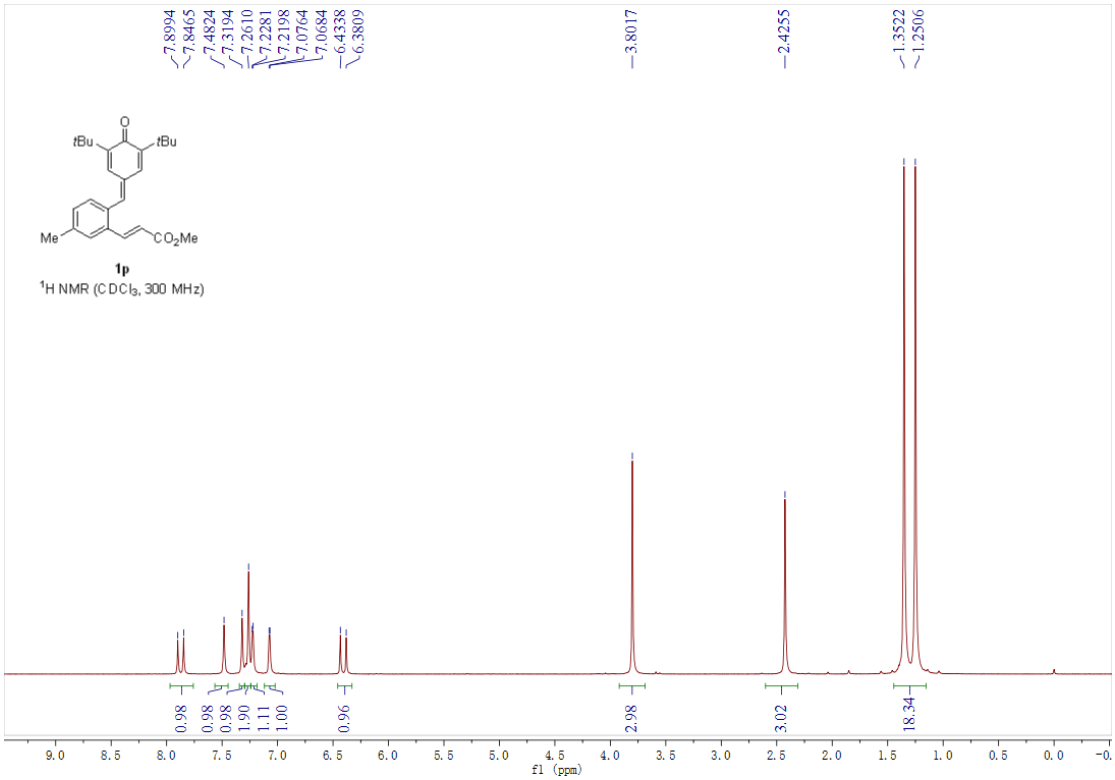

186.493
167.216
149.547
149.357
148.891
148.024
141.574
139.142
134.554
133.212
130.946
128.886
127.605
118.395
110.879
106.476
102.060
51.817
35.416
35.102
29.499
tBu
tBu
O
O
O
CO2Me
1m
13C NMR (CDCl3, 75 MHz)
f1 (ppm)


8.3679
8.3145
8.1593
8.1511
8.1484
8.1457
8.1370
8.1253
8.1223
8.1156
7.9198
7.9143
7.9059
7.9005
7.8922
7.8825
7.6163
7.6121
7.6022
7.5935
7.5895
7.5827
7.5792
7.5700
7.5599
7.5562
7.5385
7.5099
7.3977
7.3909
7.3460
7.2614
7.0880
7.0799
6.2871
6.2336
3.8824
1.3640
1.2840
tBu
tBu
CO2Me
1n
1H NMR (CDCl3, 300 MHz)
1.00
1.02
2.07
2.09
1.01
1.03
0.98
1.05
1.00
3.03
9.09
8.99
f1 (ppm)


186.351
166.620
149.706
147.991
141.600
141.163
134.699
133.273
133.123
132.629
131.500
128.967
128.792
128.575
128.393
127.577
127.455
127.298
124.834
52.050
35.513
35.149
29.560
tBu
tBu
CO2Me
1n
13C NMR (CDCl3, 75 MHz)
f1 (ppm)

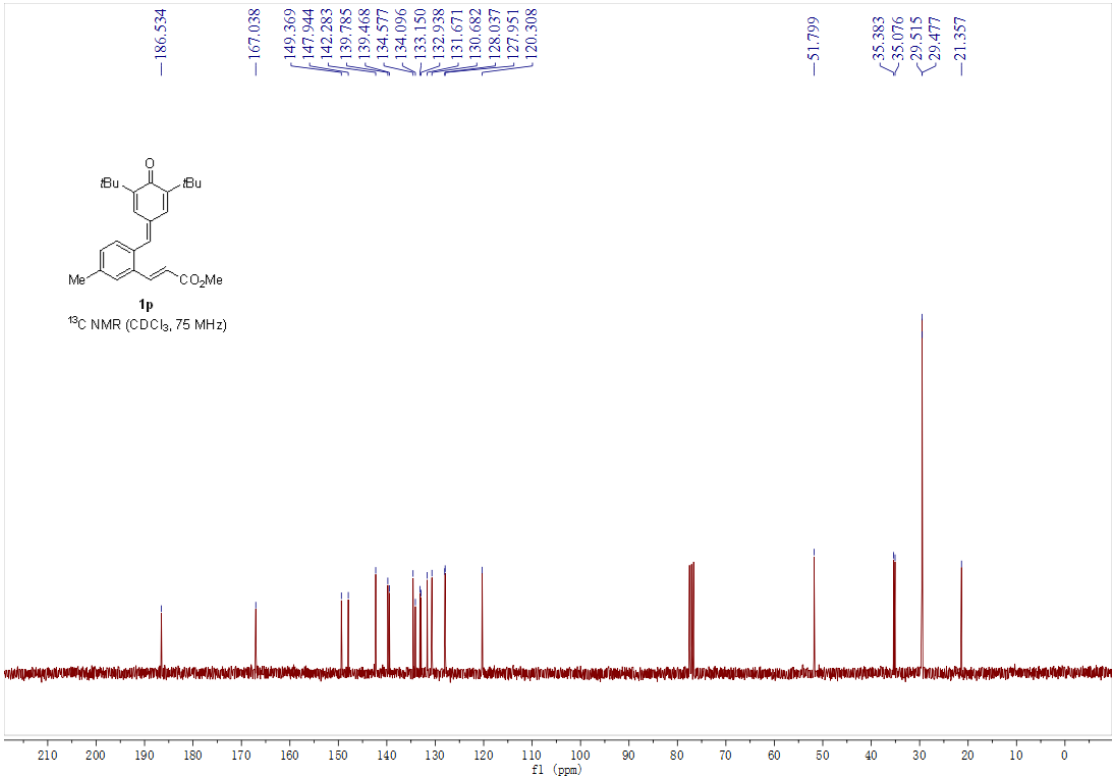

8.0650
8.0254
7.7540
7.4950
7.4815
7.4662
7.4256
7.4065
7.3860
7.3620
7.2571
7.1888
7.1828
7.1619
7.1421
7.0887
6.6382
6.5987
1.3427
1.2503
tBu
tBu
CO2Ph
1o
1H NMR(CDCl3, 400 MHz)
1.02
1.08
6.03
1.39
2.88
1.04
1.00
18.21
f1 (ppm)


186.585
165.036
150.712
149.737
148.357
143.949
139.252
136.008
134.429
133.963
133.868
131.694
130.145
129.499
129.357
127.840
127.600
125.935
121.577
119.911
35.451
35.155
29.530
tBu
tBu
CO2Ph
1o
13C NMR(CDCl3, 101 MHz)
f1 (ppm)



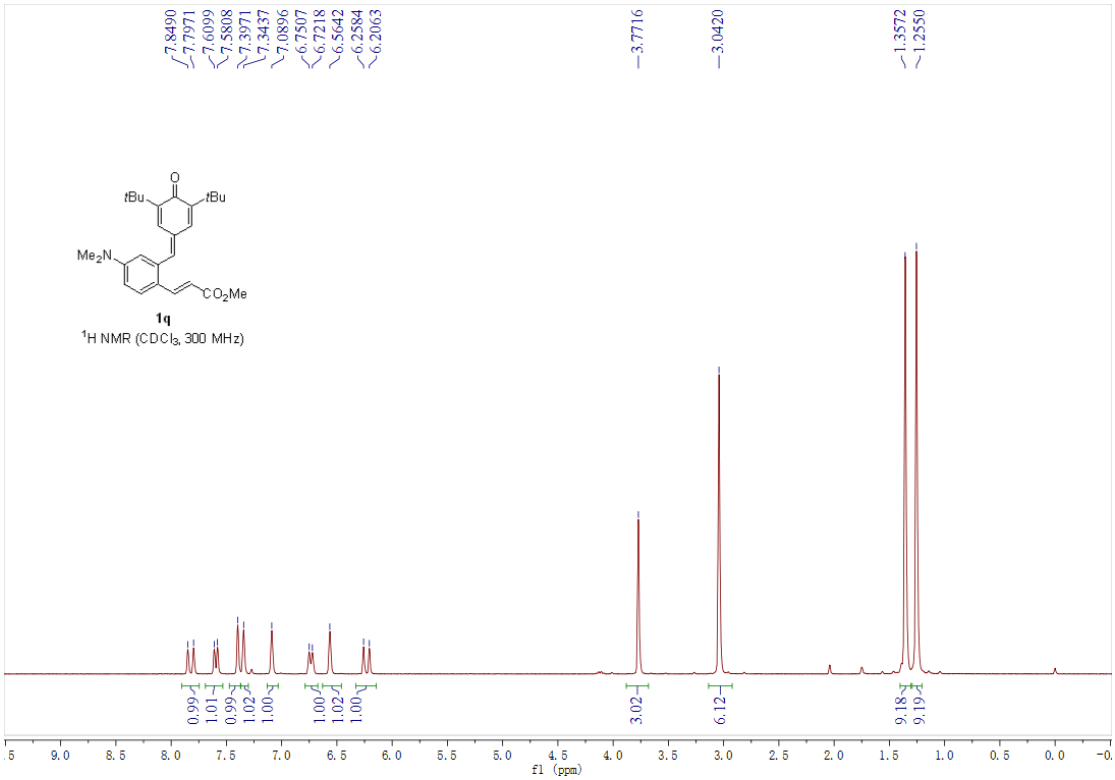
1p

^{1}H NMR ($CDCl_3$, 300 MHz)



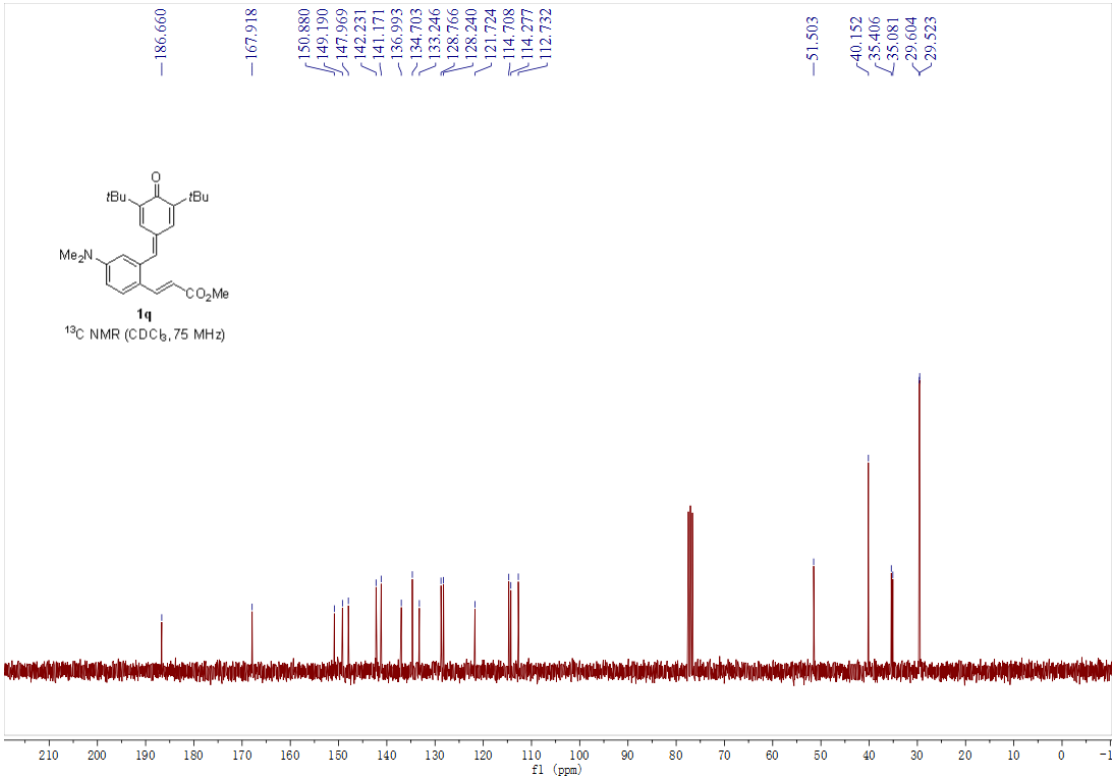
1p

^{13}C NMR ($CDCl_3$, 75 MHz)



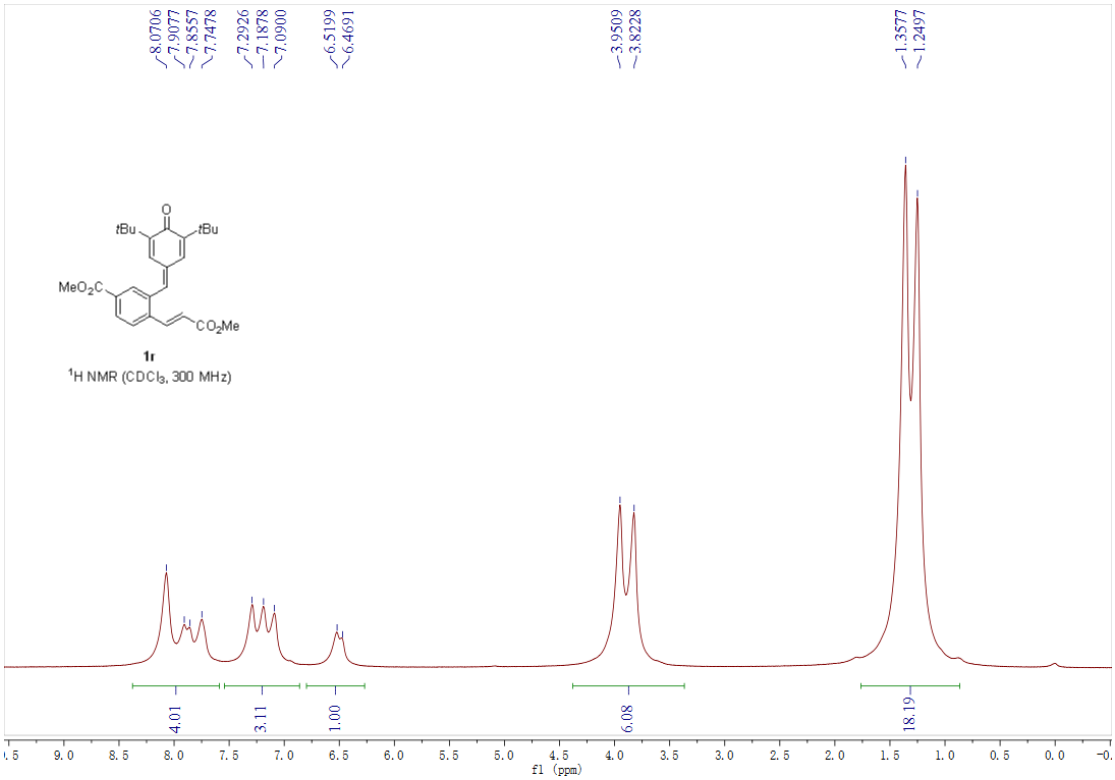
1q

^{1}H NMR ($CDCl_3$, 300 MHz)



1q

^{13}C NMR ($CDCl_3$, 75 MHz)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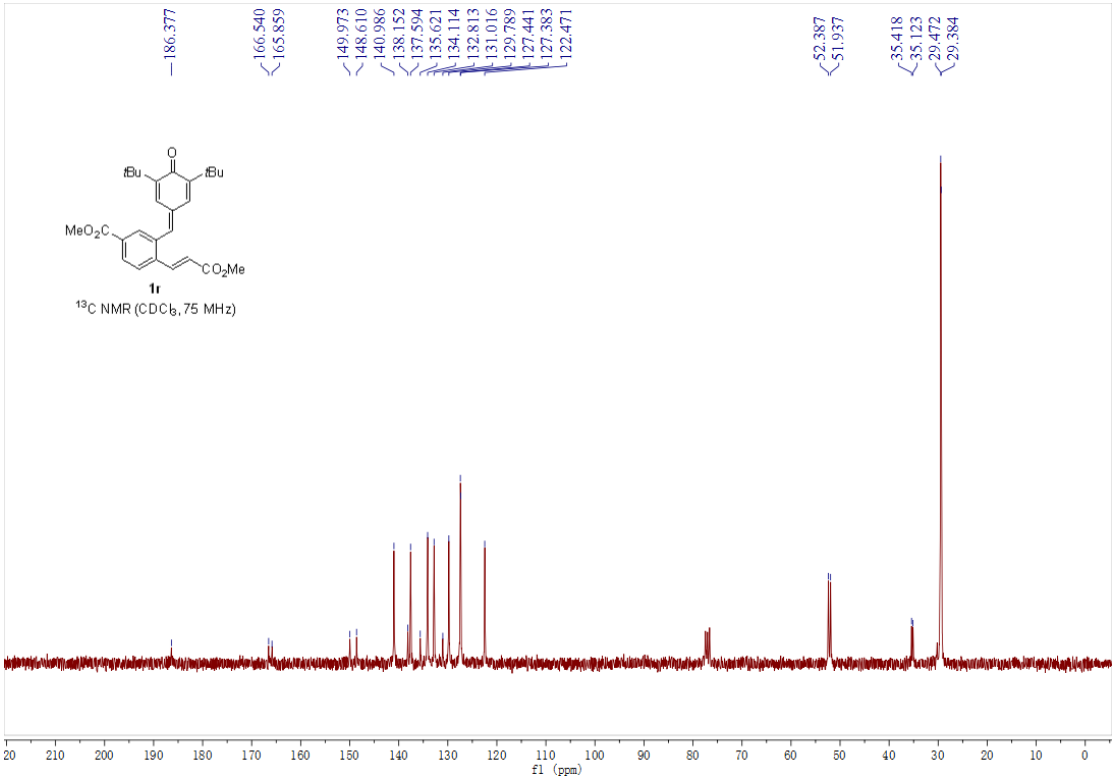
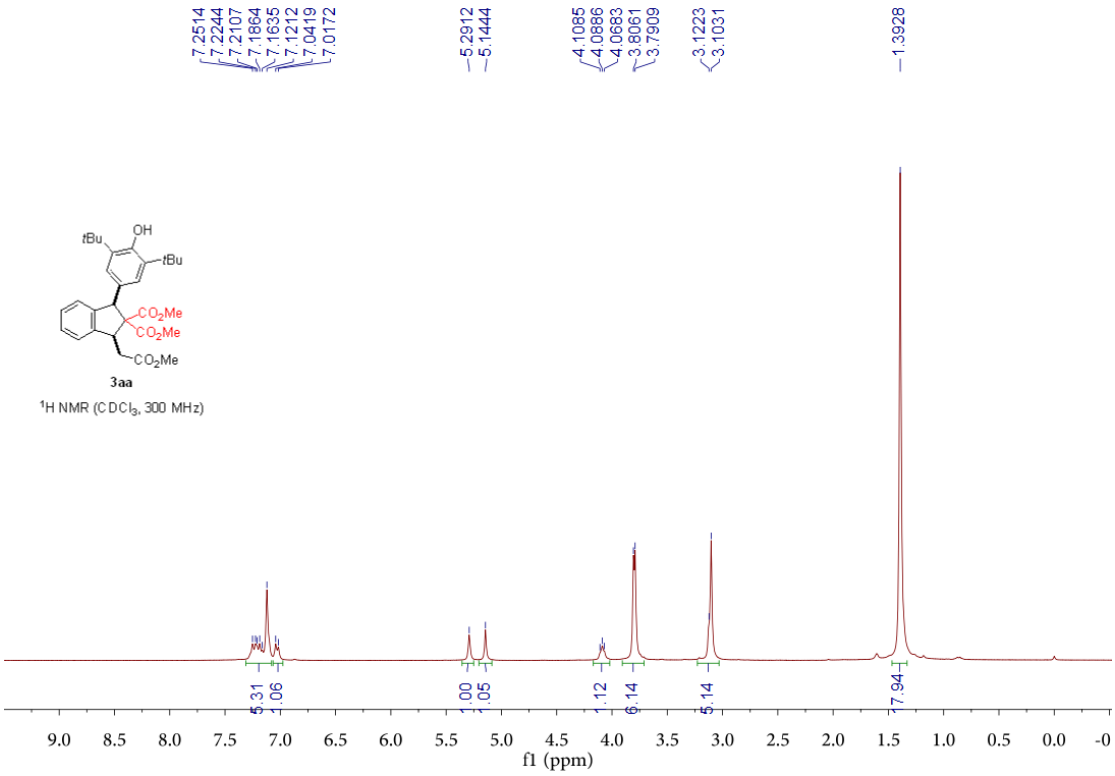
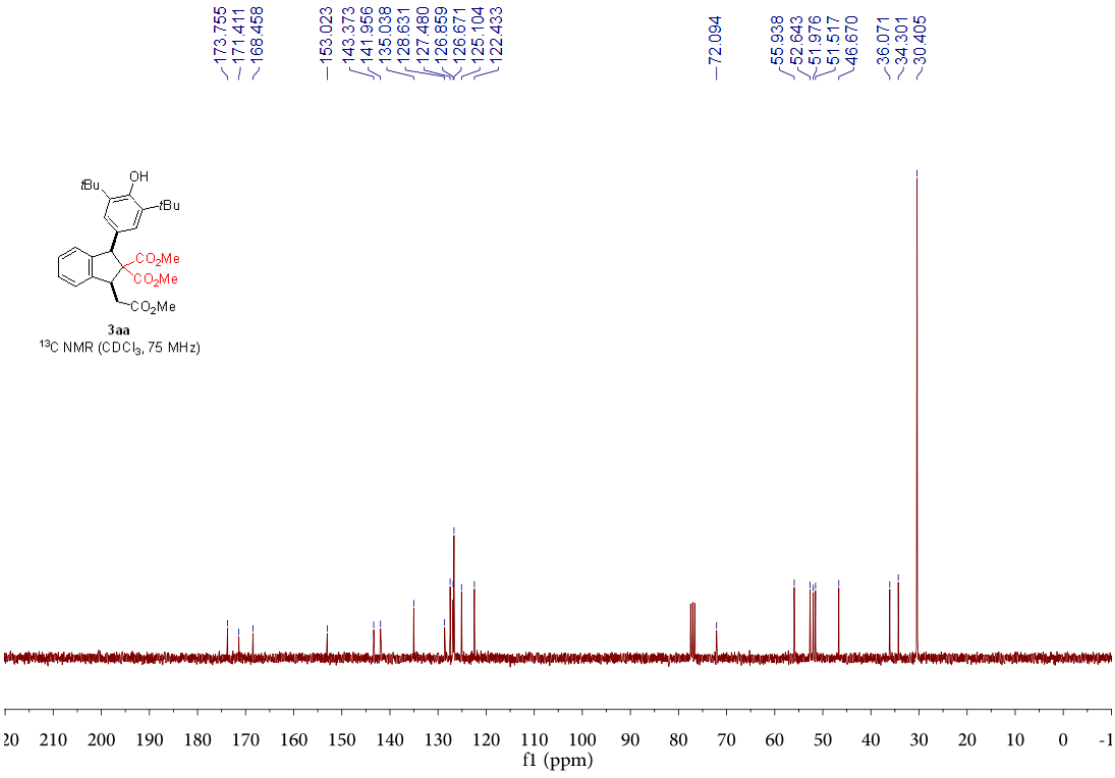
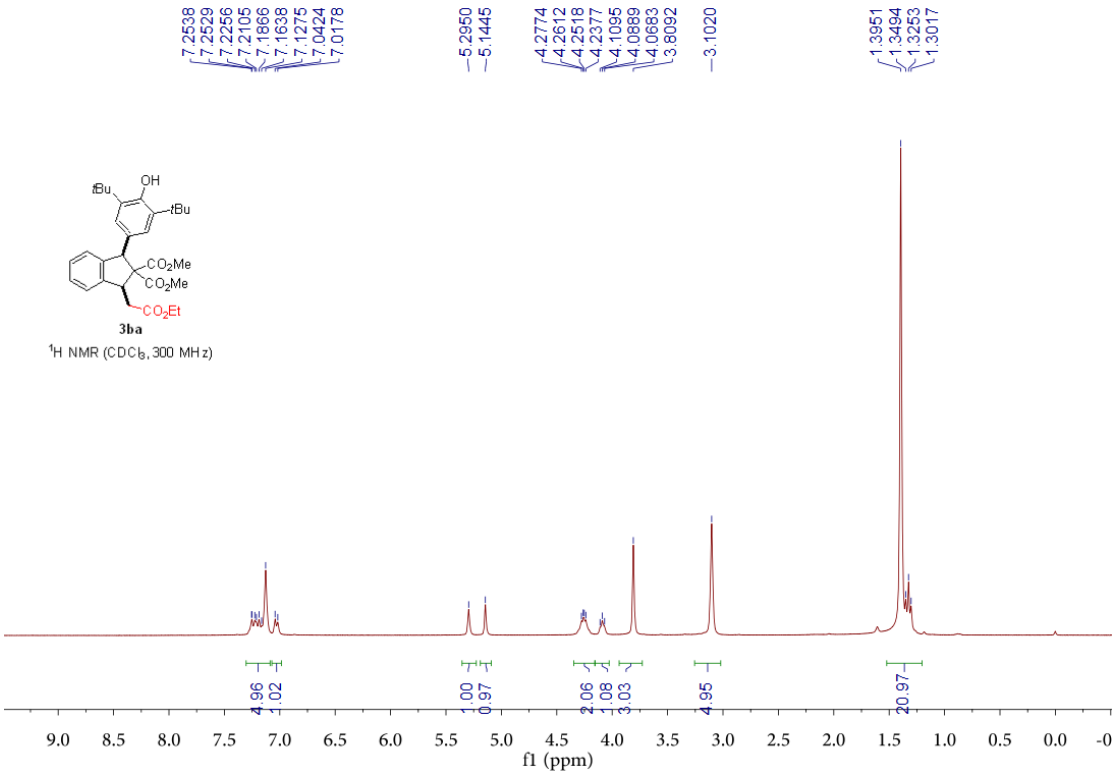
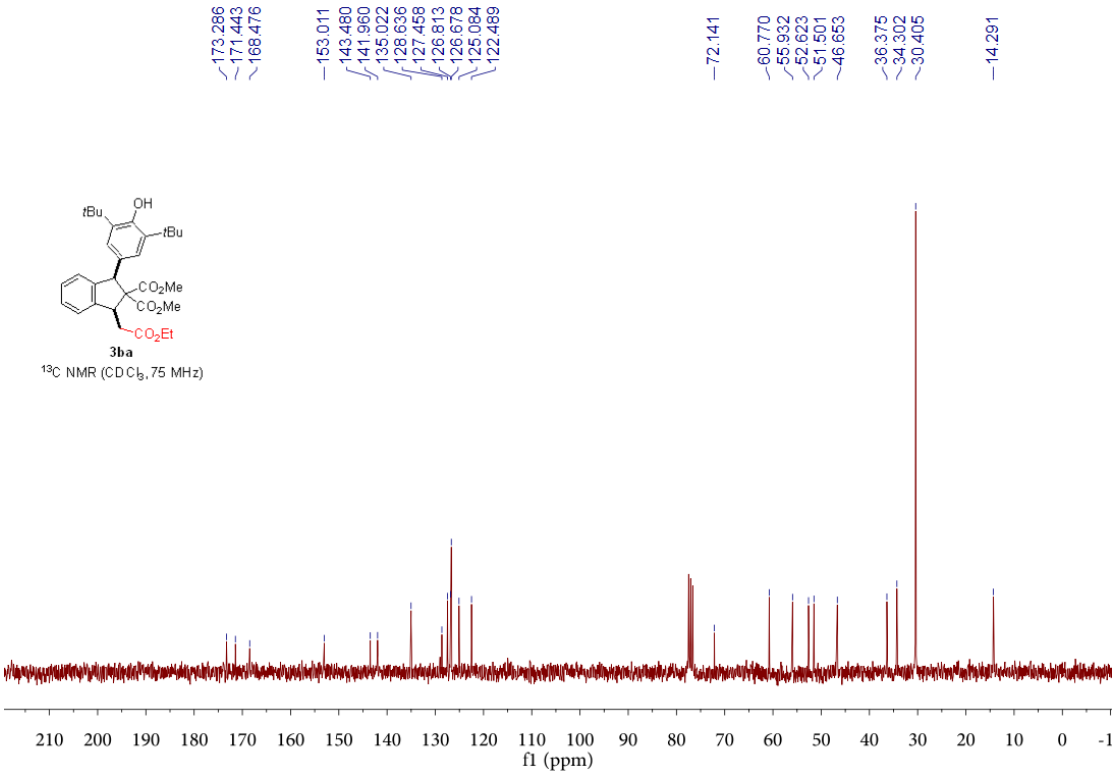
7.9077
7.8557
7.7478
7.2926
7.1878
7.0900
6.5199
6.4691
3.9509
3.8228
1.3577
1.2497
tBu
tBu
MeO2C
CO2Me
1r
1H NMR (CDCl3, 300 MHz)
4.01
3.11
1.00
6.08
18.19
f1 (ppm)

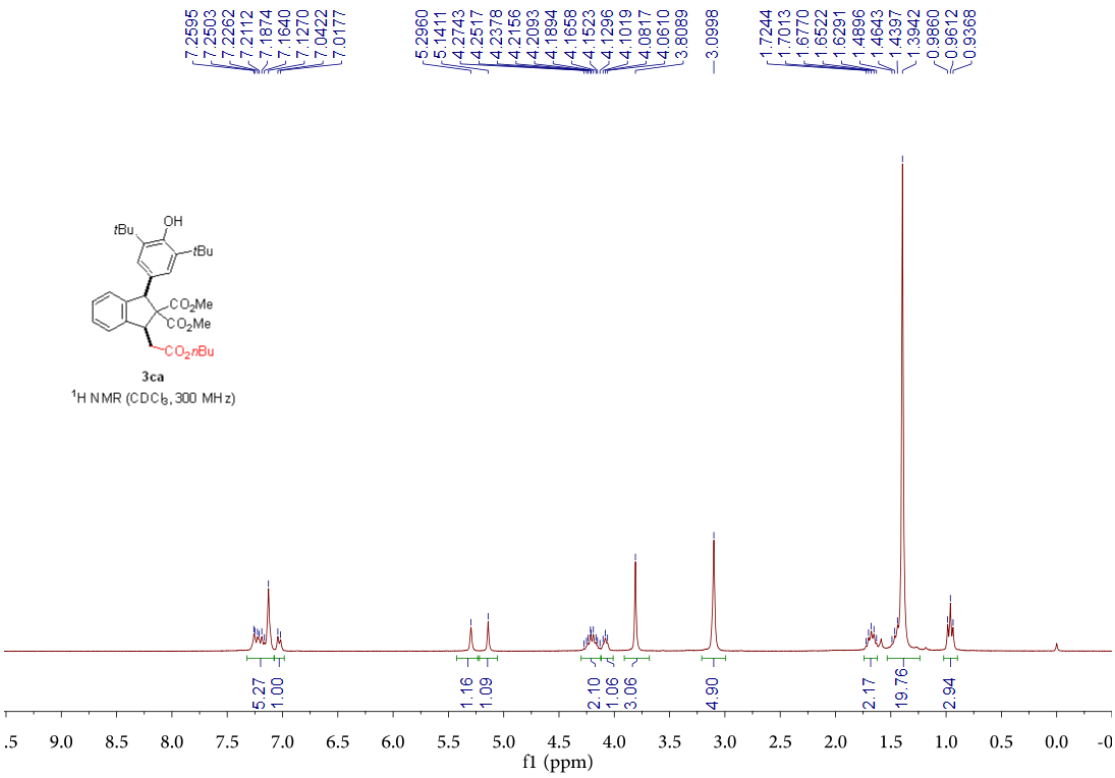

186.377
166.540
165.859
149.973
148.610
140.986
138.152
137.594
135.621
134.114
132.813
131.016
129.789
127.441
127.383
122.471
52.387
51.937
35.418
35.123
29.472
29.384
tBu
tBu
MeO2C
CO2Me
1r
13C NMR (CDCl3, 75 MHz)
f1 (ppm)


7.2514
7.2244
7.2107
7.1864
7.1635
7.1212
7.0419
7.0172
5.2912
5.1444
4.1085
4.0886
4.0683
3.8061
3.7909
3.1223
3.1031
1.3928
tBu
OH
tBu
CO2Me
CO2Me
CO2Me
3aa
1H NMR (CDCl3, 300 MHz)
5.31
1.06
1.00
1.05
1.12
6.14
5.14
7.94
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
f1 (ppm)


173.755
171.411
168.458
153.023
143.373
141.956
135.038
128.631
127.480
126.859
126.671
125.104
122.433
72.094
55.938
52.643
51.976
51.517
46.670
36.071
34.301
30.405
tBu
OH
tBu
CO2Me
CO2Me
CO2Me
3aa
13C NMR (CDCl3, 75 MHz)
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)


7.2538
7.2529
7.2256
7.2105
7.1866
7.1638
7.1275
7.0424
7.0178
5.2950
5.1445
4.2774
4.2612
4.2518
4.2377
4.1095
4.0889
4.0683
3.8092
3.1020
1.3951
1.3494
1.3253
1.3017
tBu
OH
tBu
CO2Me
CO2Me
CO2Et
3ba
1H NMR (CDCl3, 300 MHz)
4.96
1.02
1.00
0.97
2.06
1.08
3.03
4.95
20.97
f1 (ppm)


173.286
171.443
168.476
153.011
143.480
141.960
135.022
128.636
127.458
126.813
126.678
125.084
122.489
72.141
60.770
55.932
52.623
51.501
46.653
36.375
34.302
30.405
14.291
tBu
OH
tBu
CO2Me
CO2Me
CO2Et
3ba
13C NMR (CDCl3, 75 MHz)
f1 (ppm)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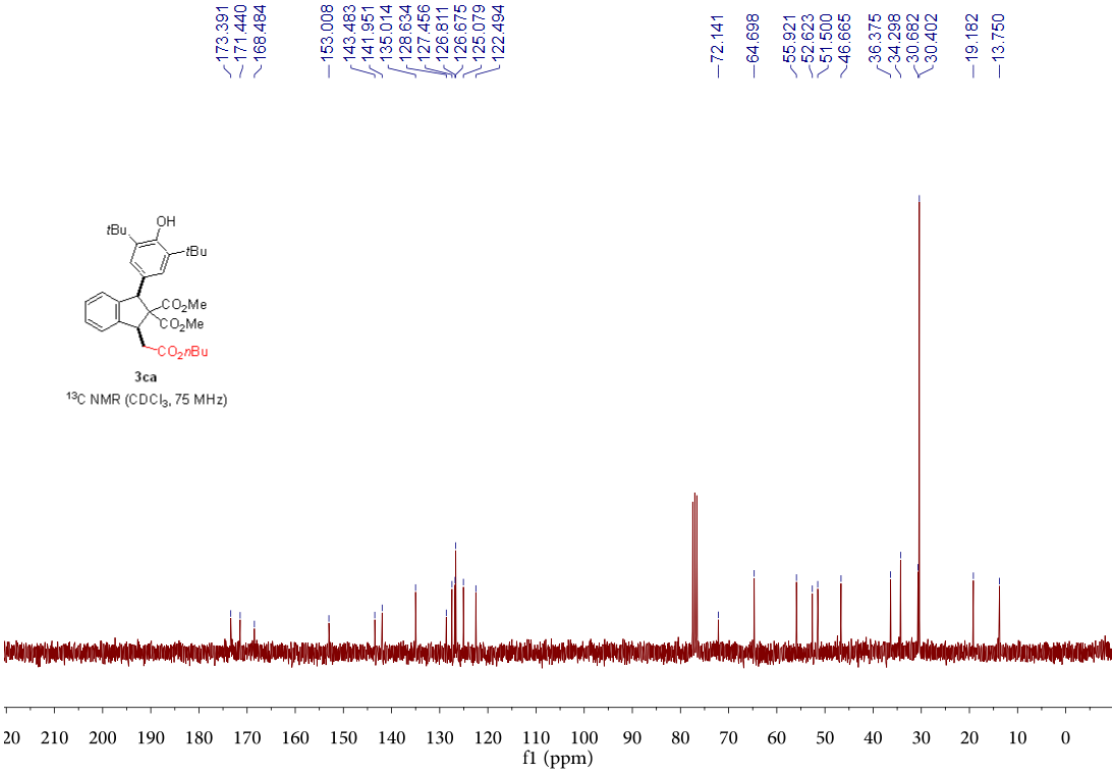
7.2503
7.2262
7.2112
7.1874
7.1640
7.1270
7.0422
7.0177
5.2960
5.1411
4.2743
4.2517
4.2378
4.2156
4.2093
4.1894
4.1658
4.1523
4.1296
4.1019
4.0817
4.0610
3.8089
3.0998
1.7244
1.7013
1.6770
1.6522
1.6291
1.4896
1.4643
1.4397
1.3942
0.9860
0.9612
0.9368
tBu
OH
tBu
CO2Me
CO2Me
CO2nBu
3ca
1H NMR (CDCl3, 300 MHz)
5.27
1.00
1.16
1.09
2.10
1.06
3.06
4.90
2.17
19.76
2.94
f1 (ppm)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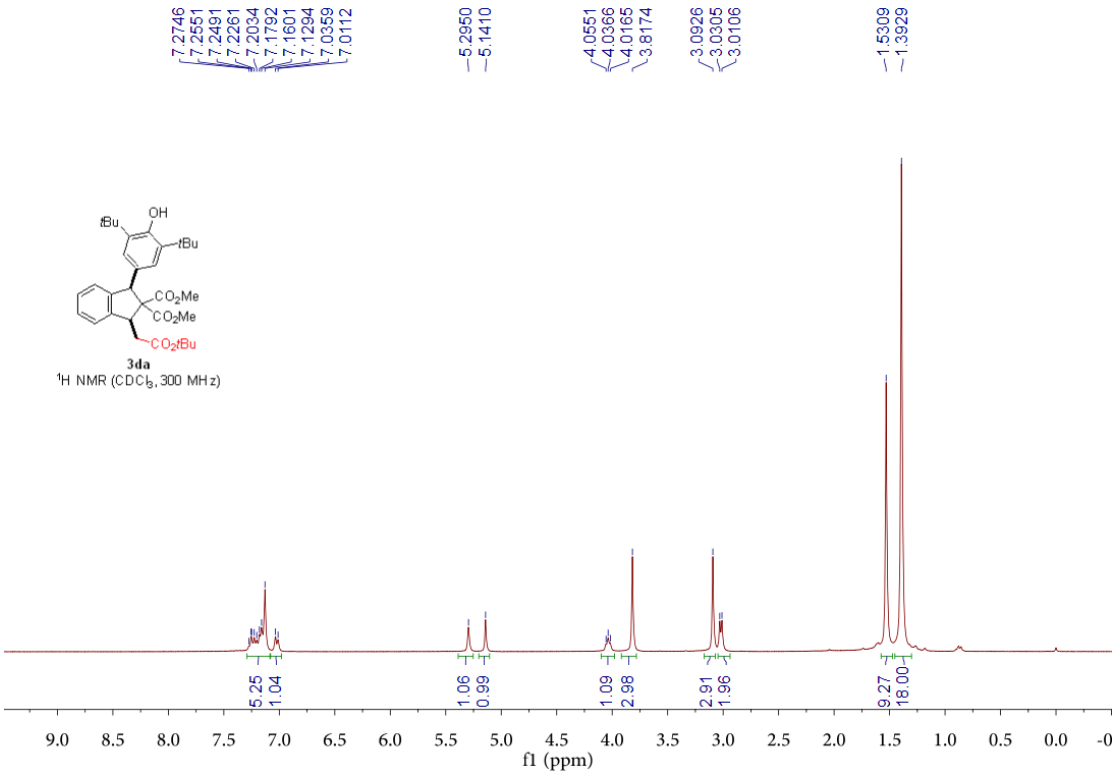
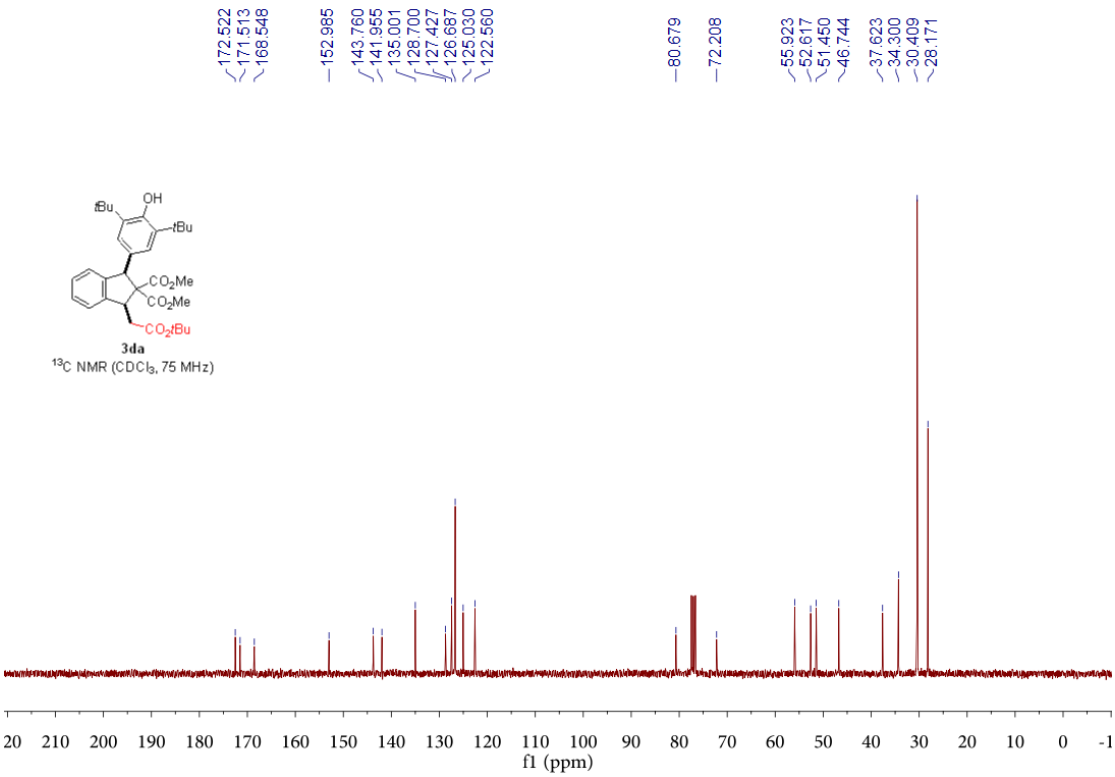
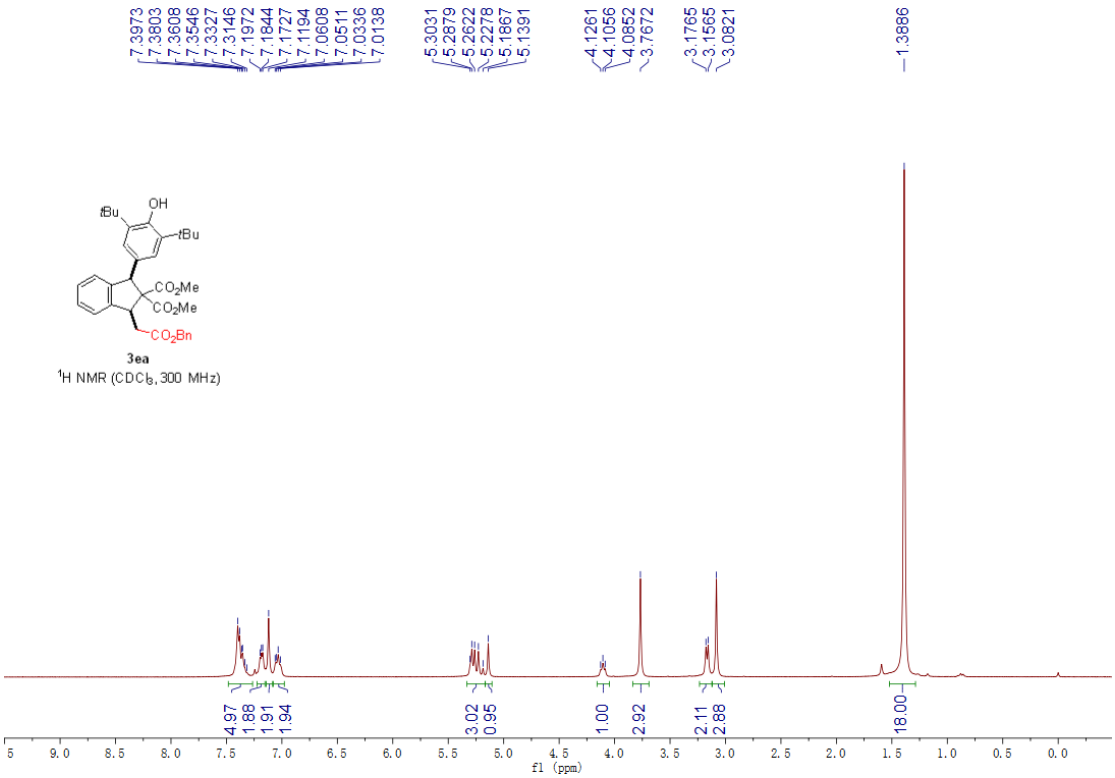
171.440
168.484
153.008
143.483
141.951
135.014
128.634
127.456
126.811
126.675
125.079
122.494
72.141
64.698
55.921
52.623
51.500
46.665
36.375
34.298
30.682
30.402
19.182
13.750
tBu
OH
tBu
CO2Me
CO2Me
CO2nBu
3ca
13C NMR (CDCl3, 75 MHz)
f1 (ppm)

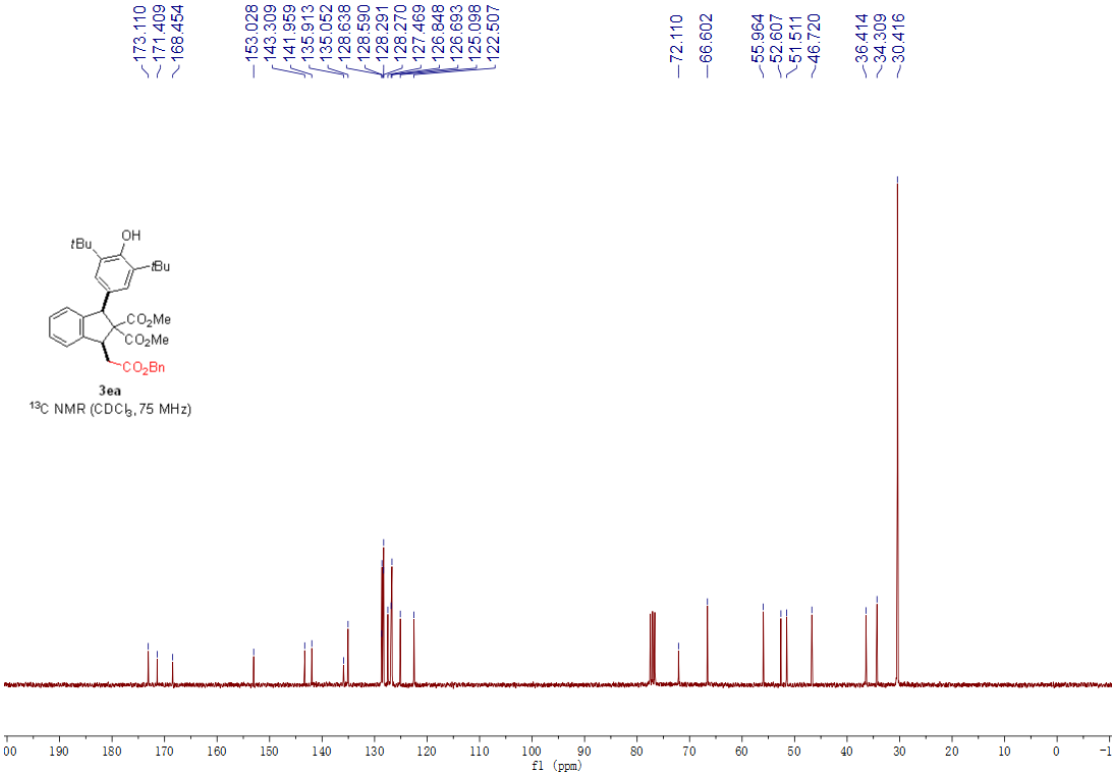

7.2746
7.2551
7.2491
7.2261
7.2034
7.1792
7.1601
7.1294
7.0359
7.0112
5.2950
5.1410
4.0551
4.0366
4.0165
3.8174
3.0926
3.0305
3.0106
1.5309
1.3929
tBu
OH
tBu
CO2Me
CO2Me
CO2tBu
3da
1H NMR (CDCl3, 300 MHz)
5.25
1.04
1.06
0.99
1.09
2.98
2.91
1.96
9.27
18.00
f1 (ppm)


172.522
171.513
168.548
152.985
143.760
141.955
135.001
128.700
127.427
126.687
125.030
122.560
80.679
72.208
55.923
52.617
51.450
46.744
37.623
34.300
30.409
28.171
tBu
OH
tBu
CO2Me
CO2Me
CO2tBu
3da
13C NMR (CDCl3, 75 MHz)
f1 (ppm)



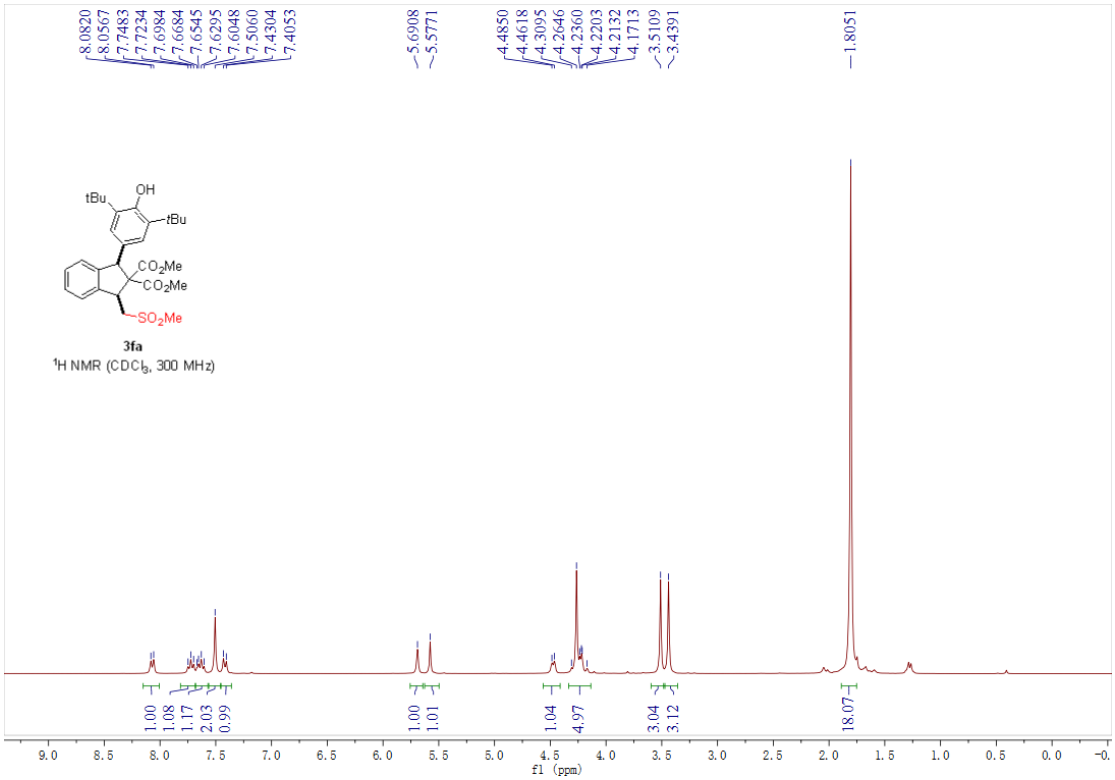
3ea

^{1}H NMR ($CDCl_3$, 300 MHz)



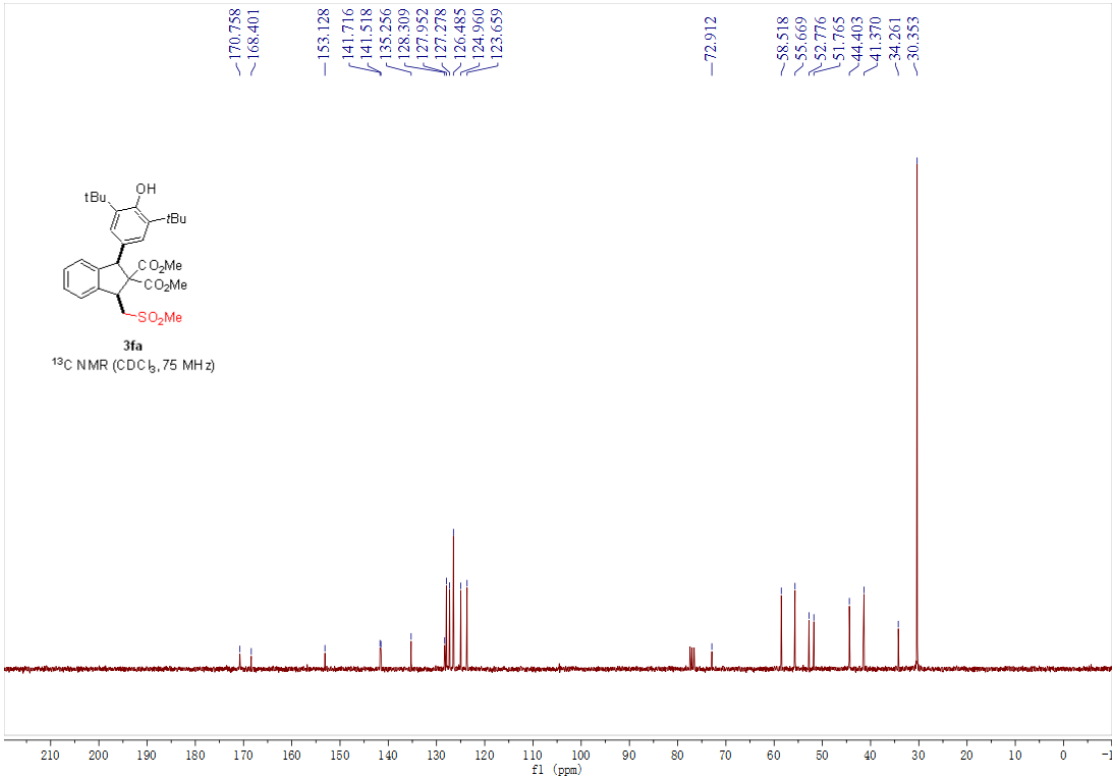
3ea

^{13}C NMR ($CDCl_3$, 75 MHz)



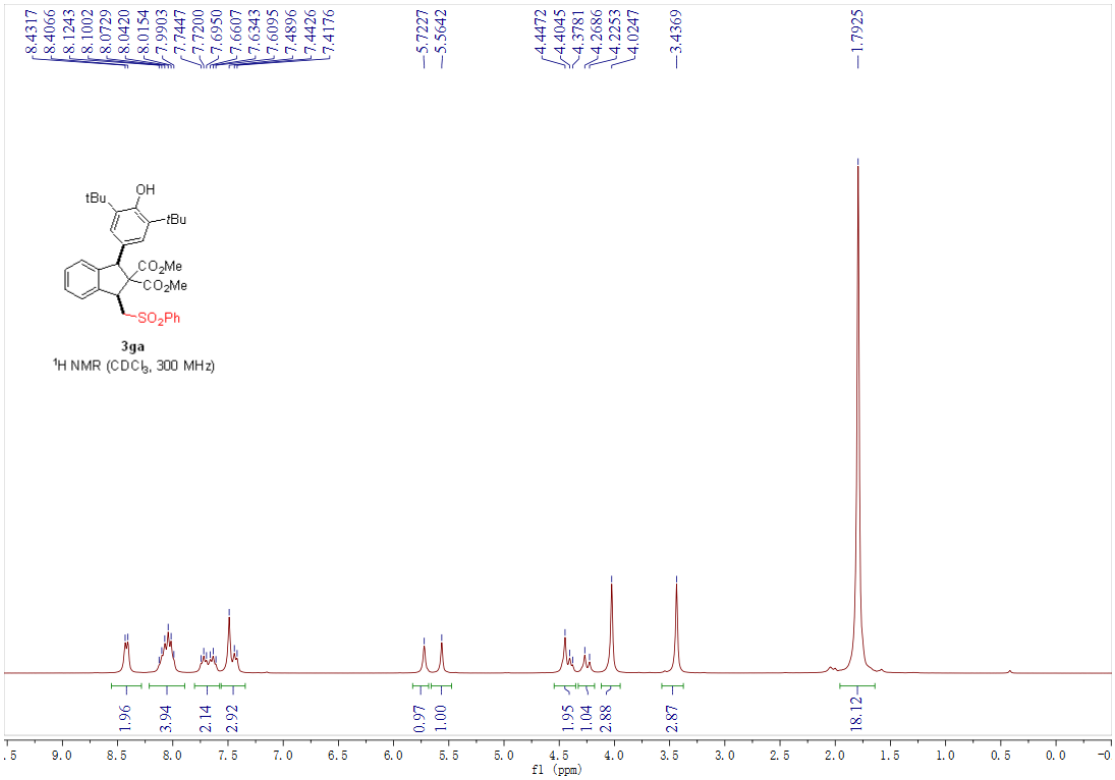
3fa

^{1}H NMR ($CDCl_3$, 300 MHz)



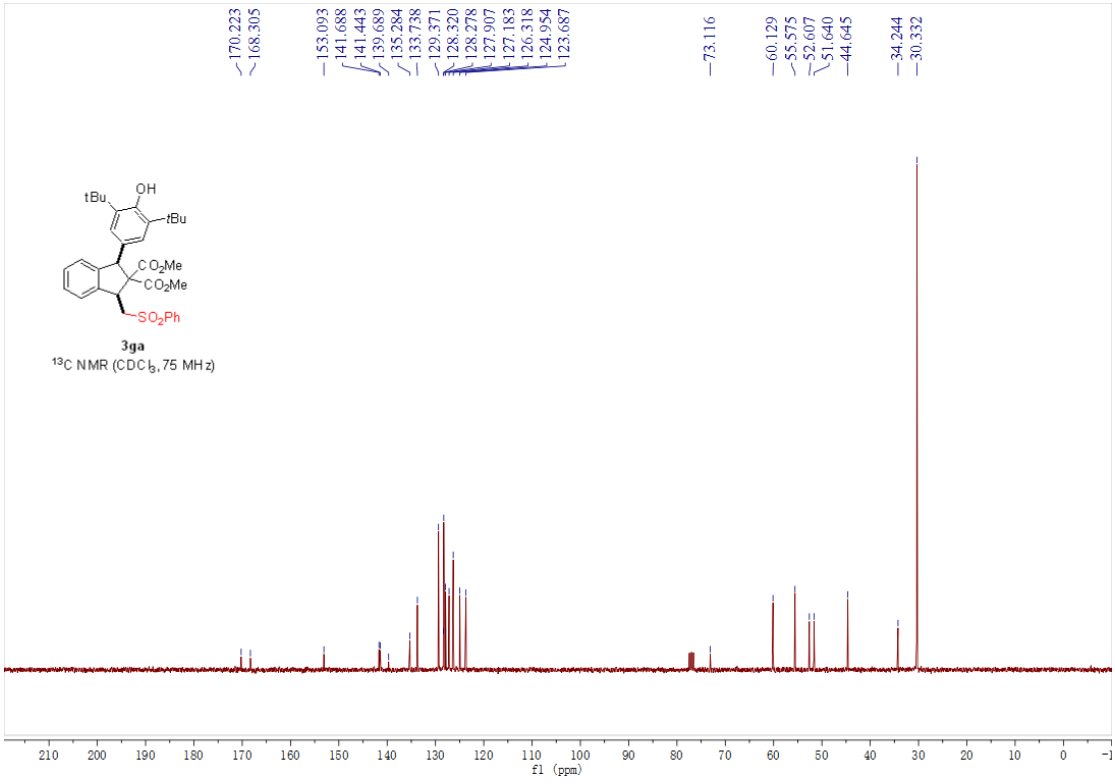
3fa

^{13}C NMR ($CDCl_3$, 75 MHz)



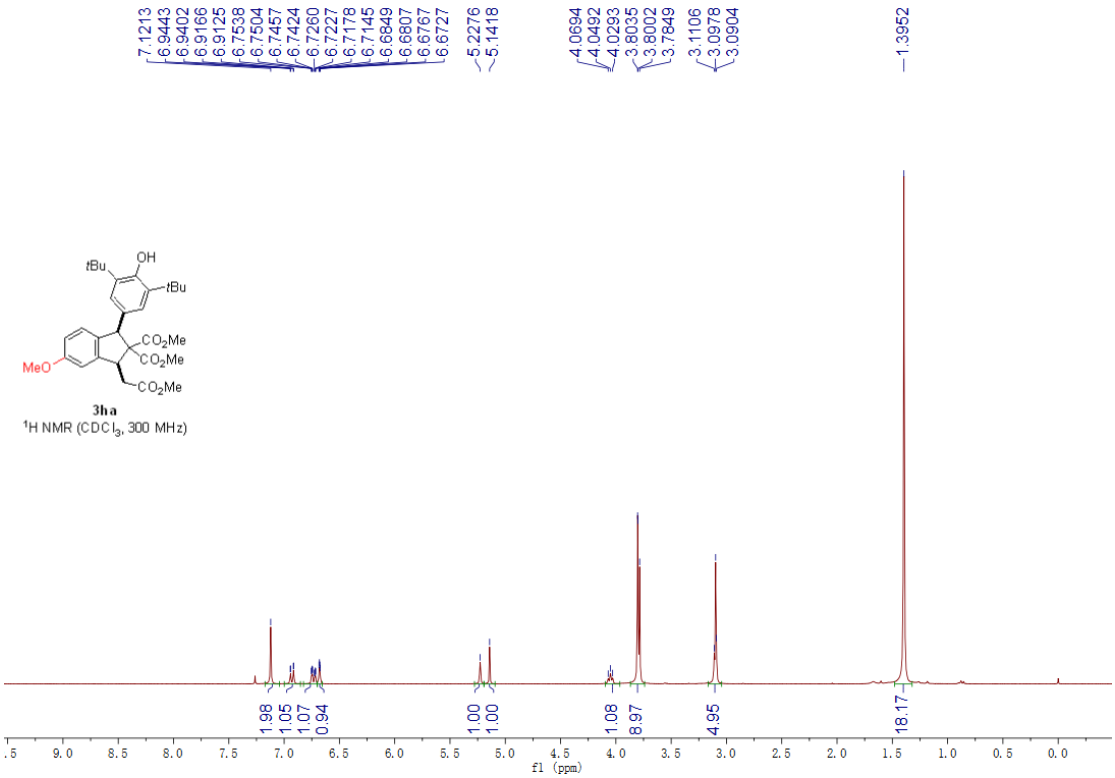
3ga

^{1}H NMR ($CDCl_3$, 300 MHz)



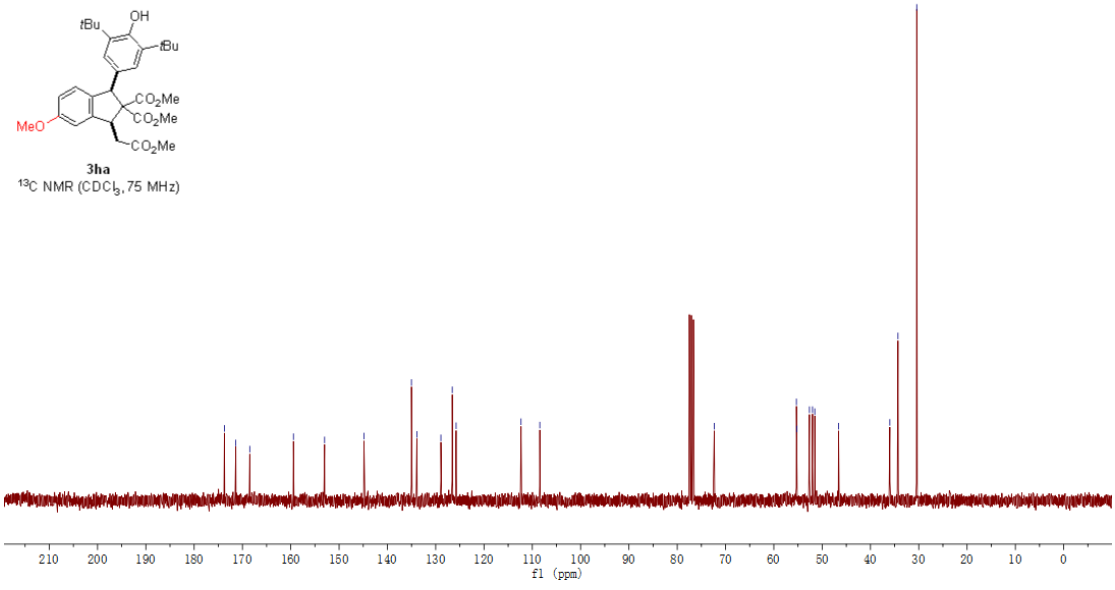
3ga

^{13}C NMR ($CDCl_3$, 75 MHz)



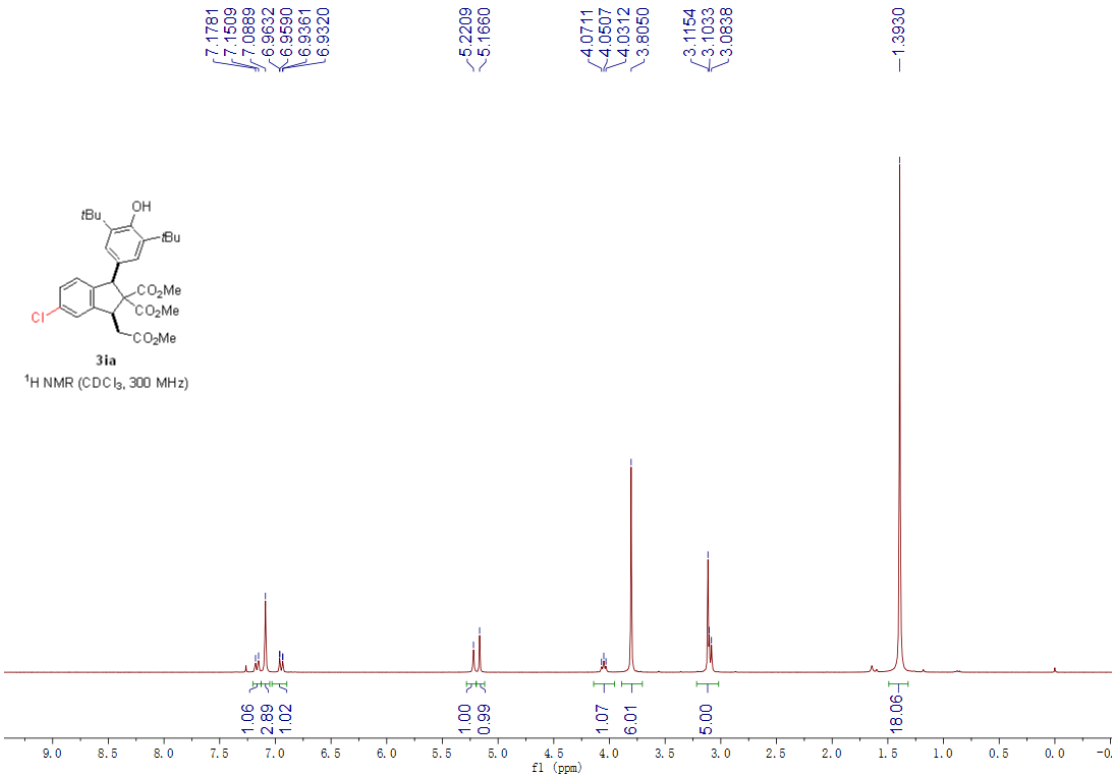
3ha

^{1}H NMR ($CDCl_3$, 300 MHz)



3ha

^{13}C NMR ($CDCl_3$, 75 MHz)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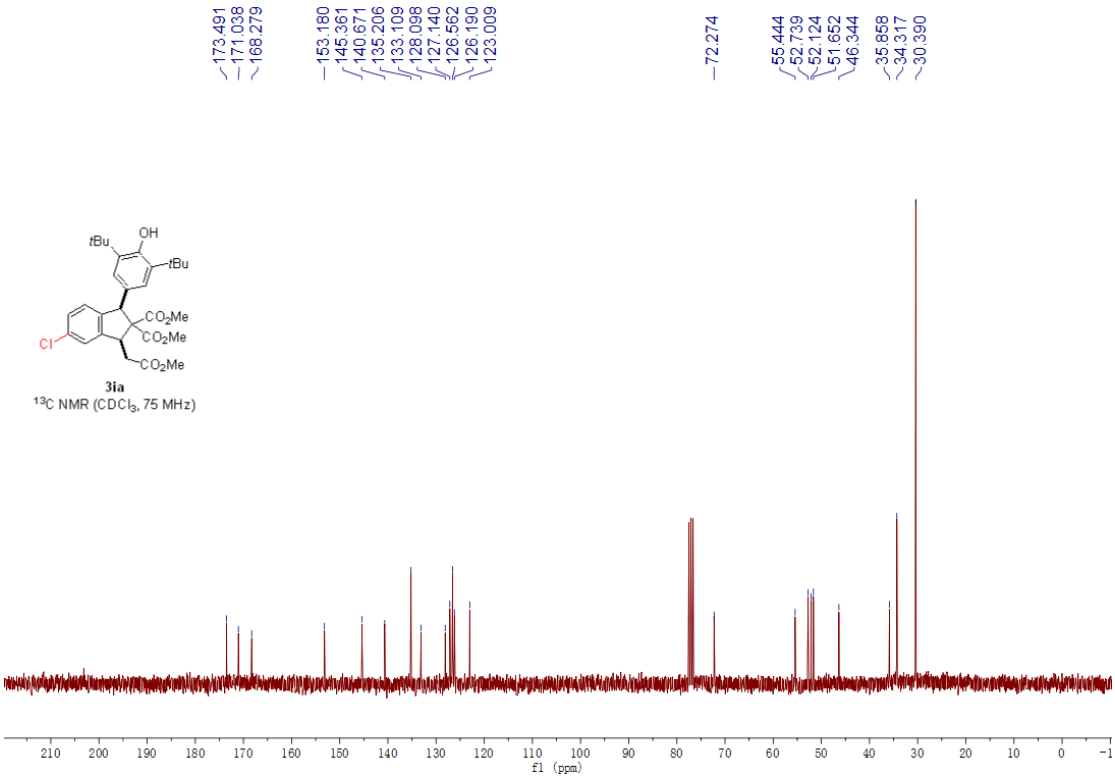
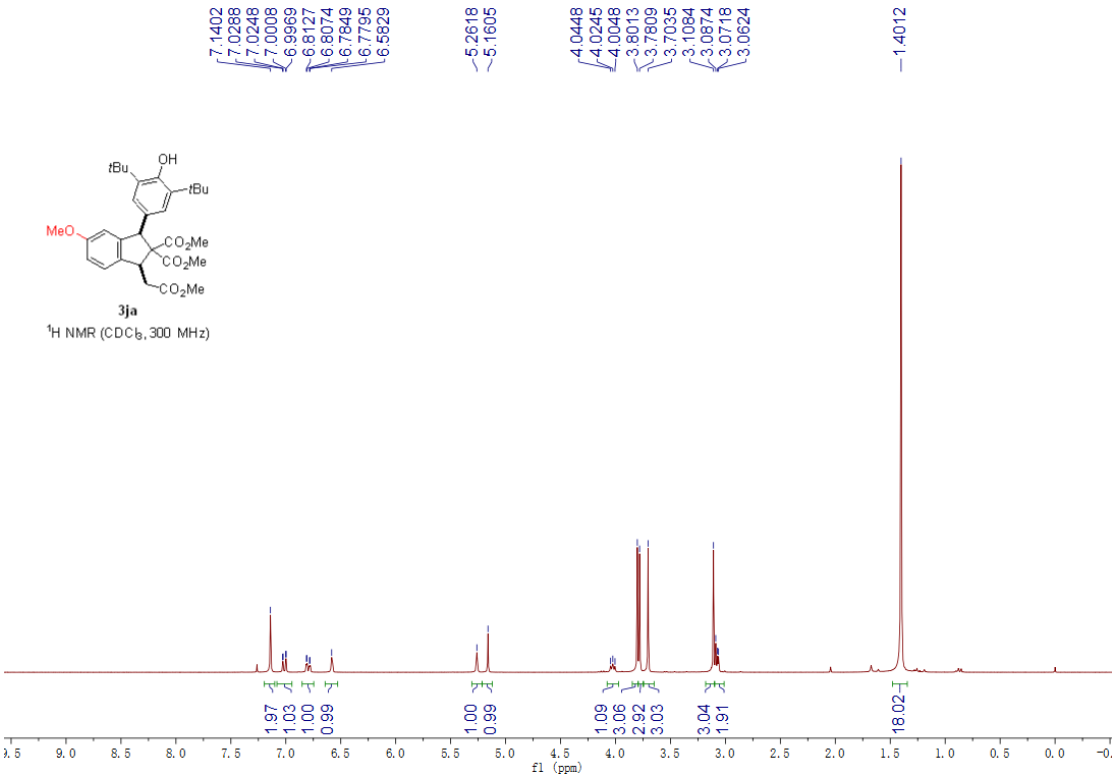
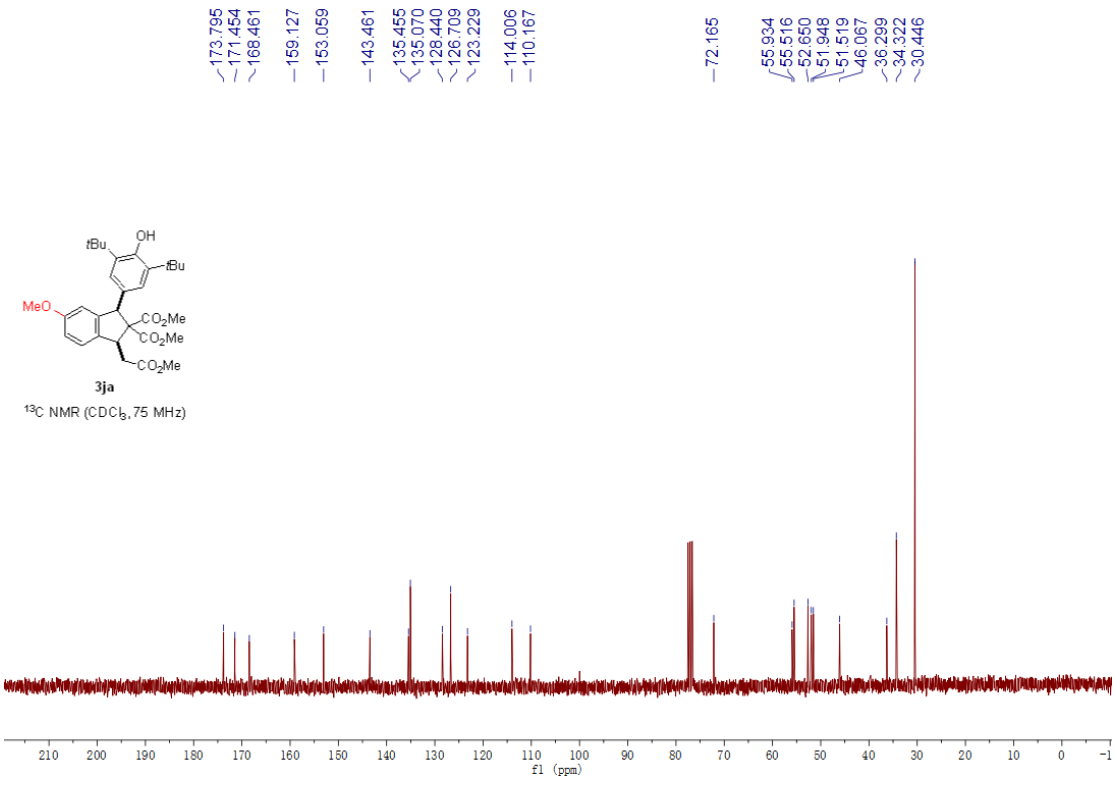
7.0889
6.9632
6.9590
6.9361
6.9320
5.2209
5.1660
4.0711
4.0507
4.0312
3.8050
3.1154
3.1033
3.0838
1.3930
tBu
OH
tBu
CO2Me
CO2Me
CO2Me
Cl
3ia
1H NMR (CDCl3, 300 MHz)
1.06
2.89
1.02
1.00
0.99
1.07
6.01
5.00
18.06
f1 (ppm)


173.491
171.038
168.279
153.180
145.361
140.671
135.206
133.109
128.098
127.140
126.562
126.190
123.009
72.274
55.444
52.739
52.124
51.652
46.344
35.858
34.317
30.390
tBu
OH
tBu
CO2Me
CO2Me
CO2Me
Cl
3ia
13C NMR (CDCl3, 75 MHz)
f1 (ppm)



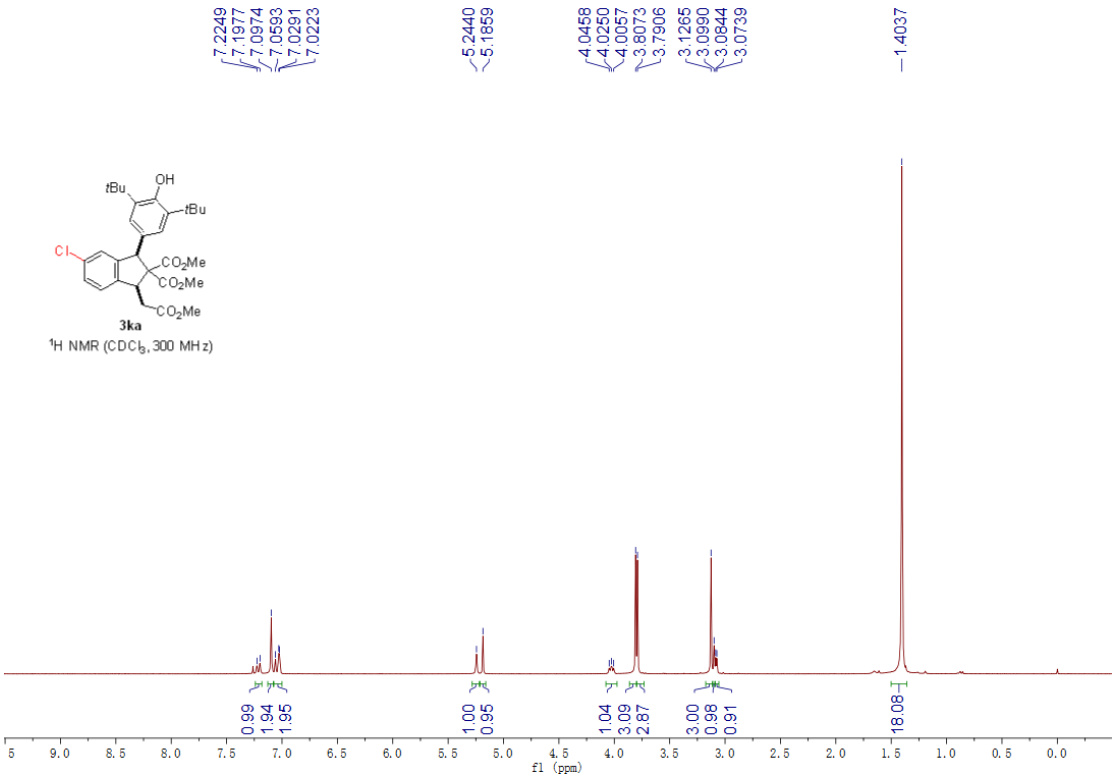
3ja

^{1}H NMR ($CDCl_3$, 300 MHz)



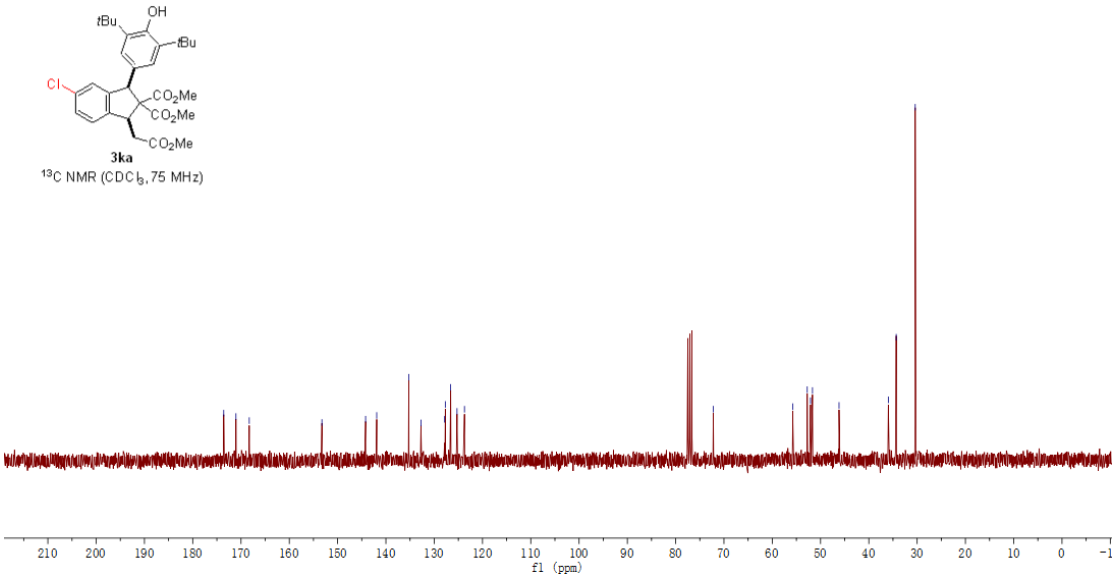
3ja

^{13}C NMR ($CDCl_3$, 75 MHz)



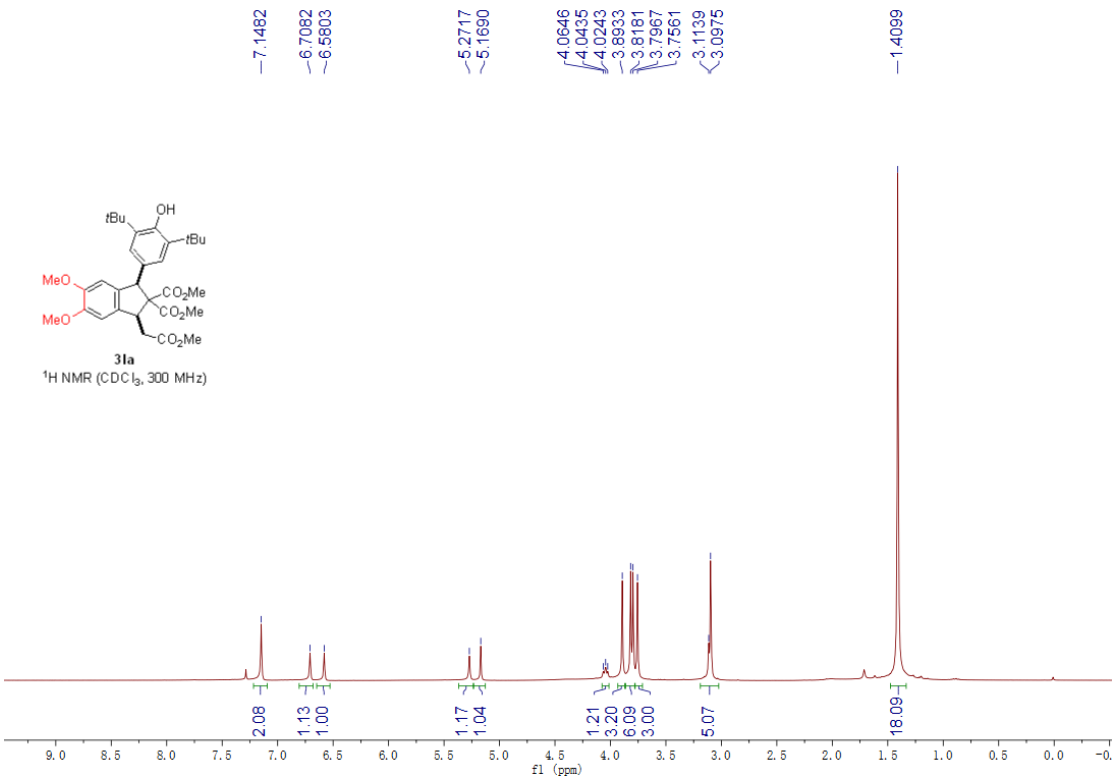
3ka

^{1}H NMR ($CDCl_3$, 300 MHz)



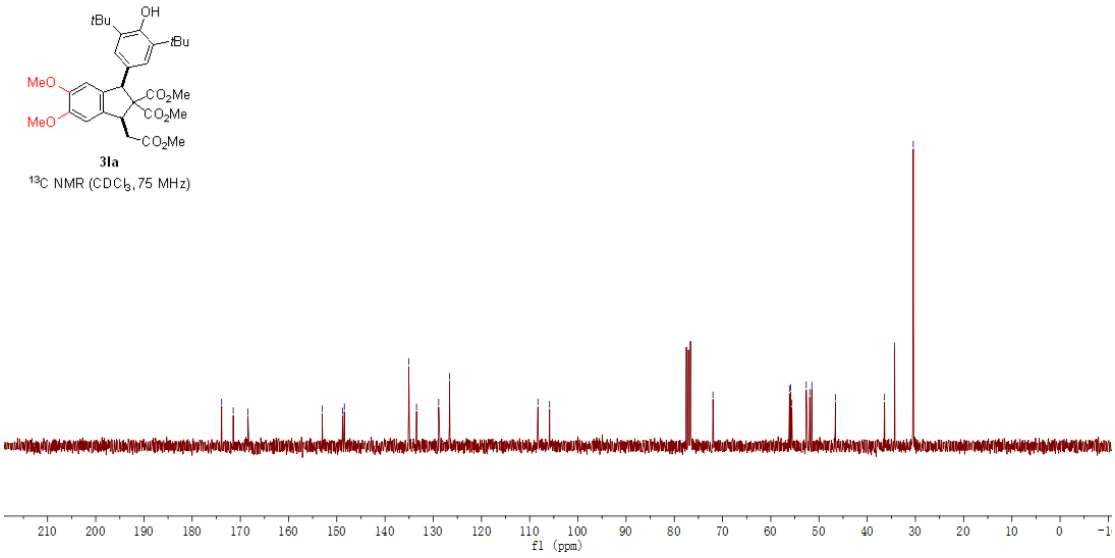
3ka

^{13}C NMR ($CDCl_3$, 75 MHz)



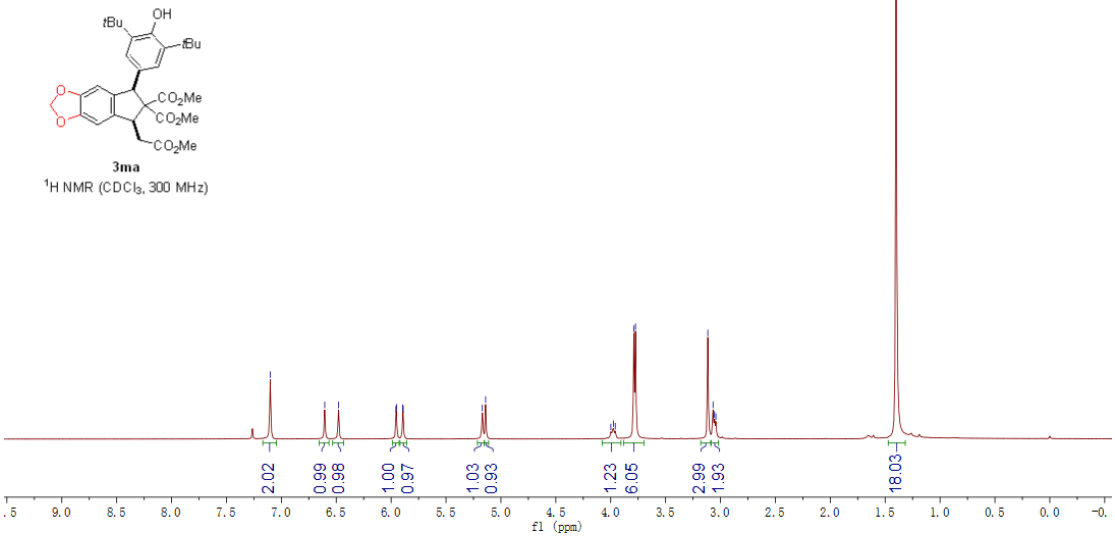
3la

^{1}H NMR ($CDCl_3$, 300 MHz)



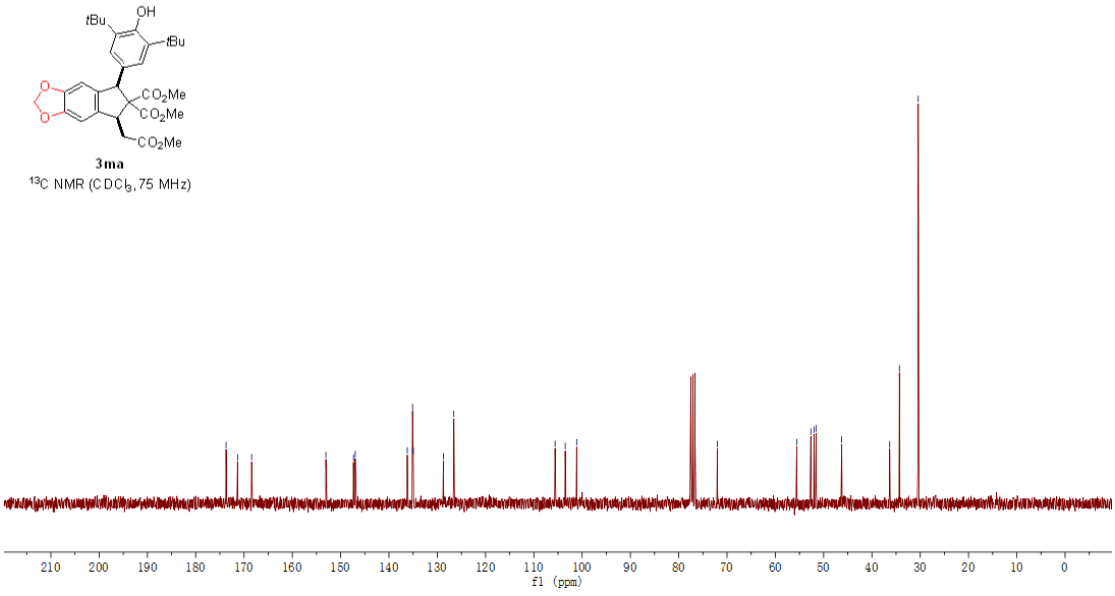
3la

^{13}C NMR ($CDCl_3$, 75 MHz)



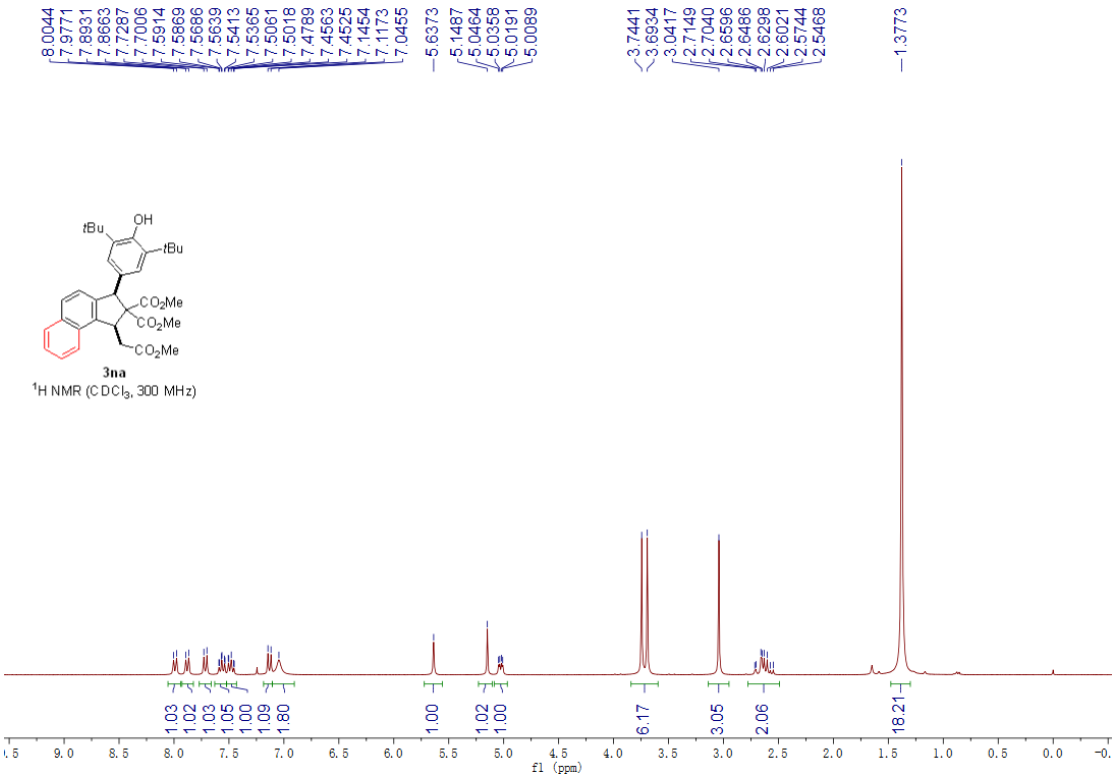
3ma

^{1}H NMR ($CDCl_3$, 300 MHz)



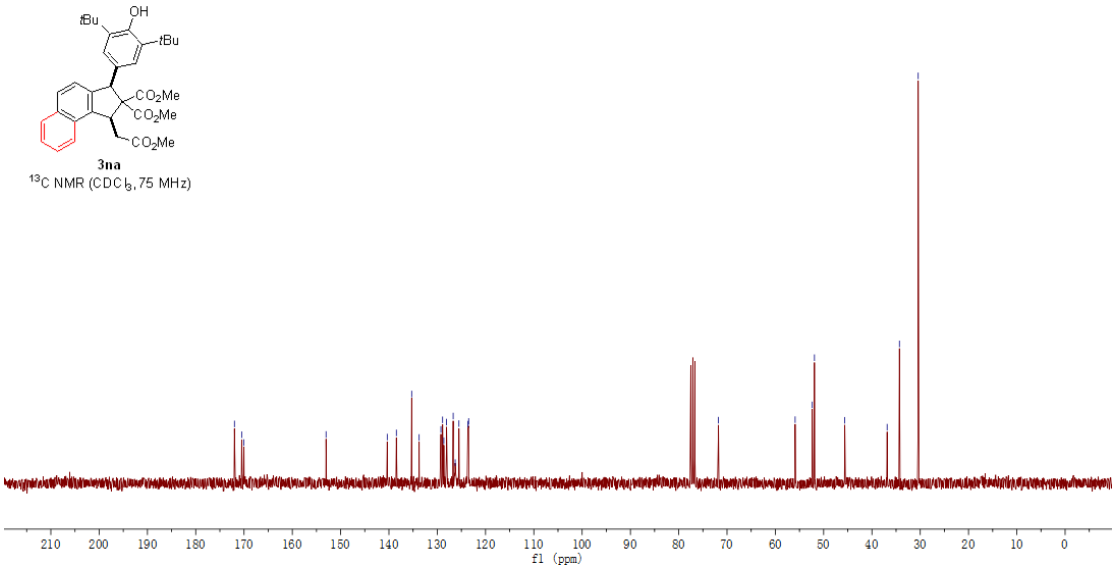
3ma

^{13}C NMR ($CDCl_3$, 75 MHz)



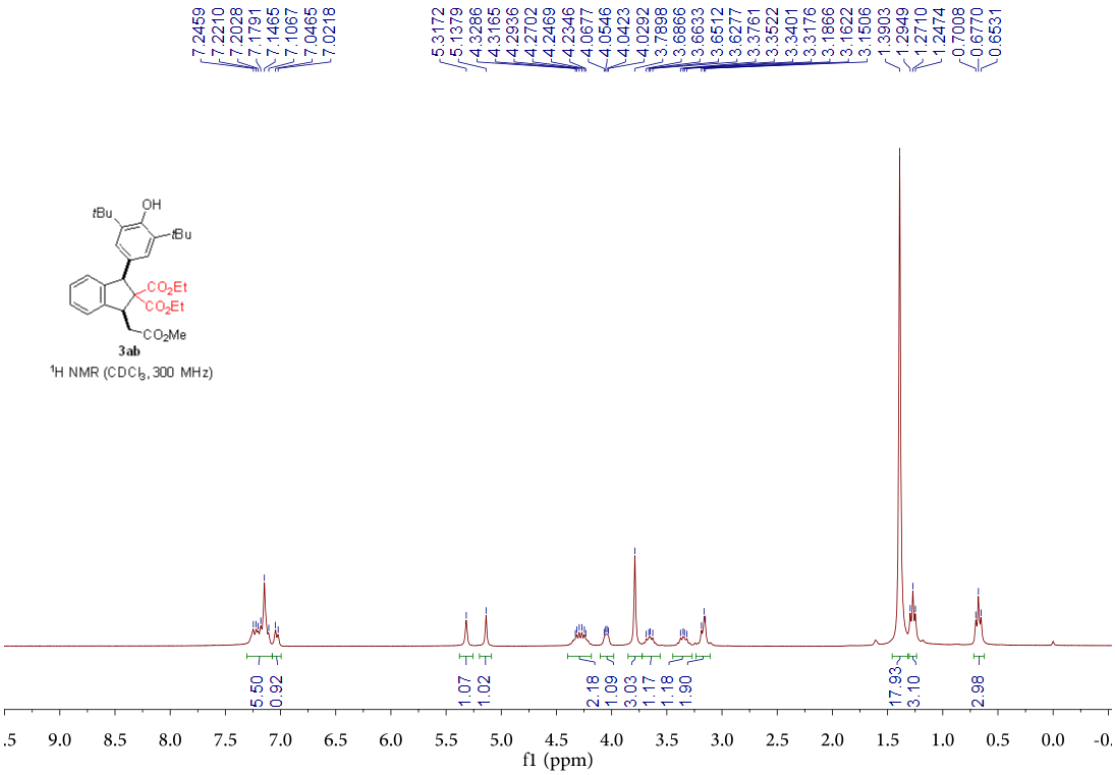
3na

^{1}H NMR ($CDCl_3$, 300 MHz)



3na

^{13}C NMR ($CDCl_3$, 75 MHz)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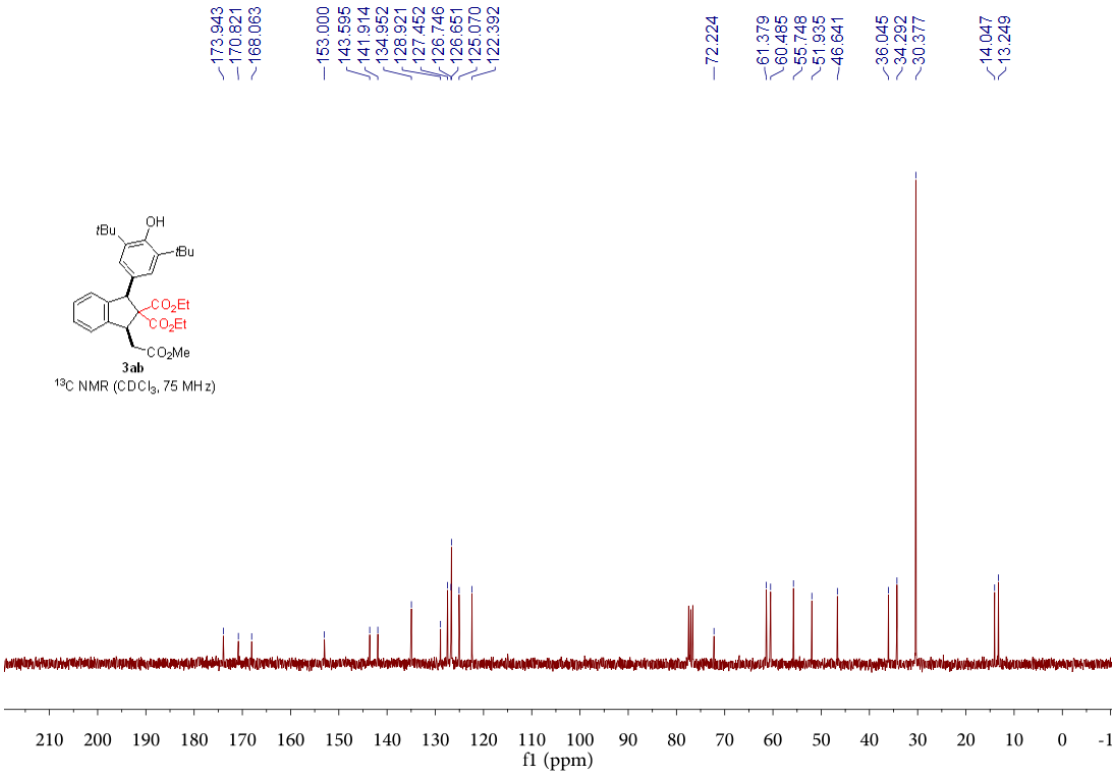
7.2028
7.1791
7.1465
7.1067
7.0465
7.0218
5.3172
5.1379
4.3286
4.3165
4.2936
4.2702
4.2469
4.2346
4.0677
4.0546
4.0423
4.0292
3.7898
3.6866
3.6633
3.6512
3.6277
3.3761
3.3522
3.3401
3.3176
3.1866
3.1622
3.1506
1.3903
1.2949
1.2710
1.2474
0.7008
0.6770
0.6531
tBu
OH
tBu
CO2Et
CO2Et
CO2Me
3ab
1H NMR (CDCl3, 300 MHz)
5.50
0.92
1.07
1.02
2.18
1.09
3.03
1.17
1.18
1.90
17.93
3.10
2.98
f1 (ppm)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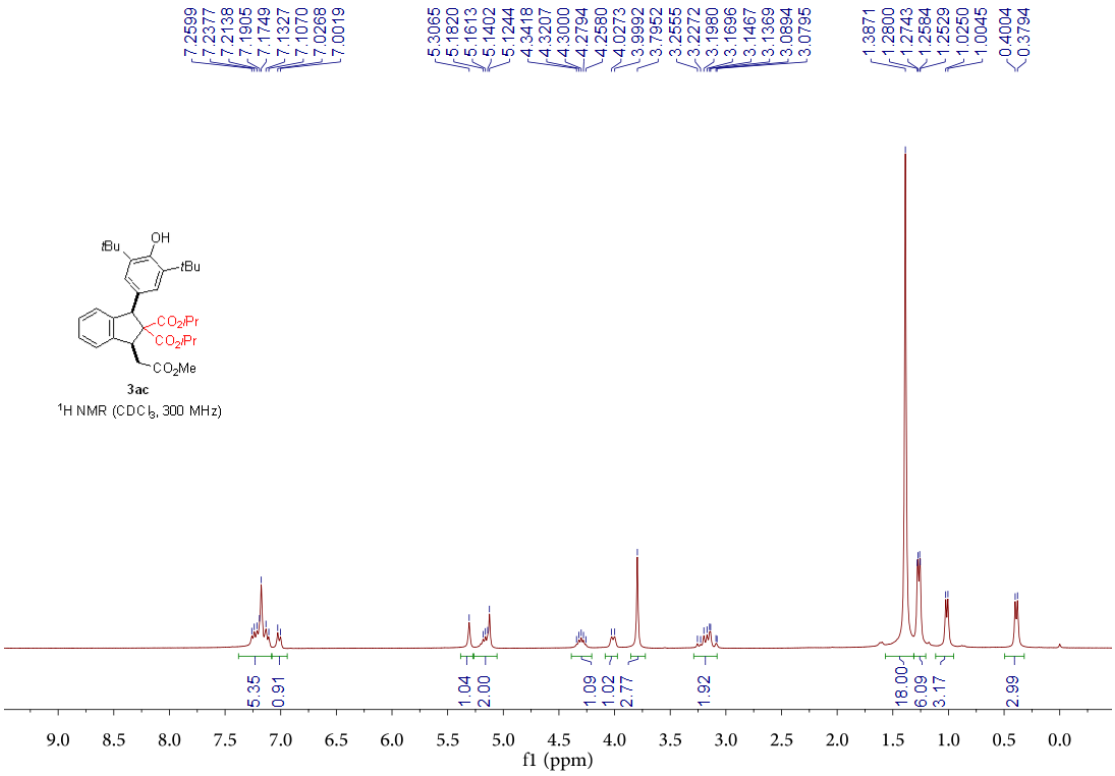
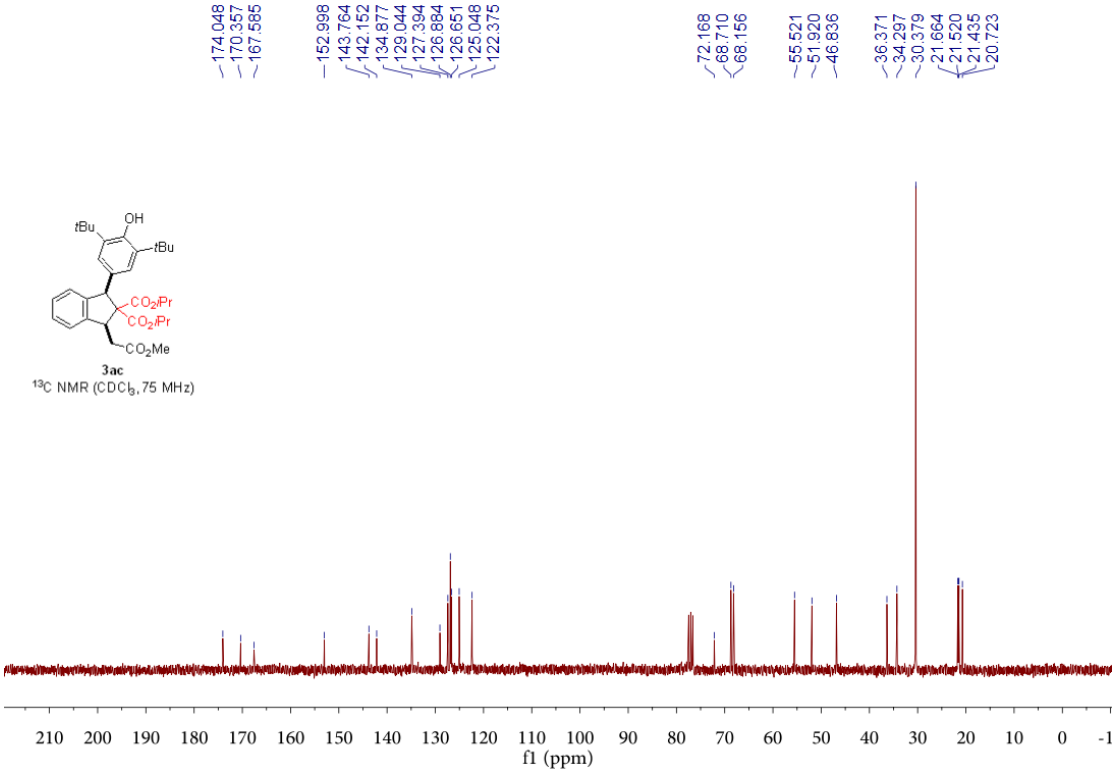
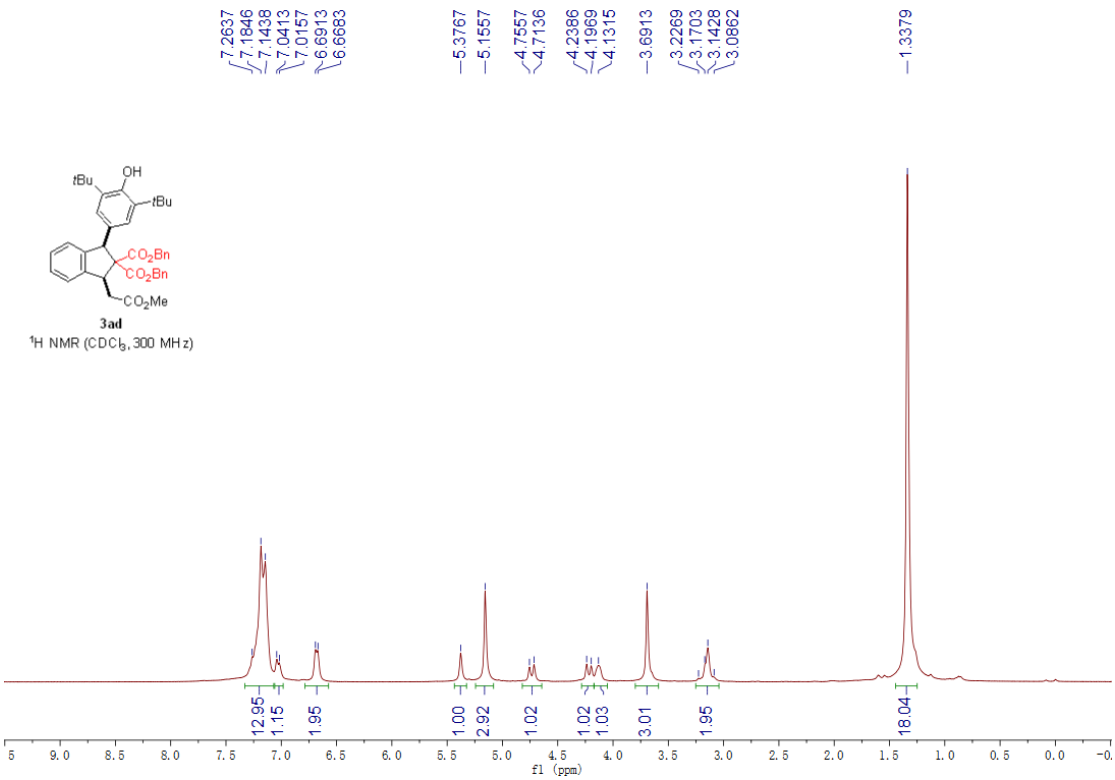
168.063
153.000
143.595
141.914
134.952
128.921
127.452
126.746
126.651
125.070
122.392
72.224
61.379
60.485
55.748
51.935
46.641
36.045
34.292
30.377
14.047
13.249
tBu
OH
tBu
CO2Et
CO2Et
CO2Me
3ab
13C NMR (CDCl3, 75 MHz)
f1 (ppm)

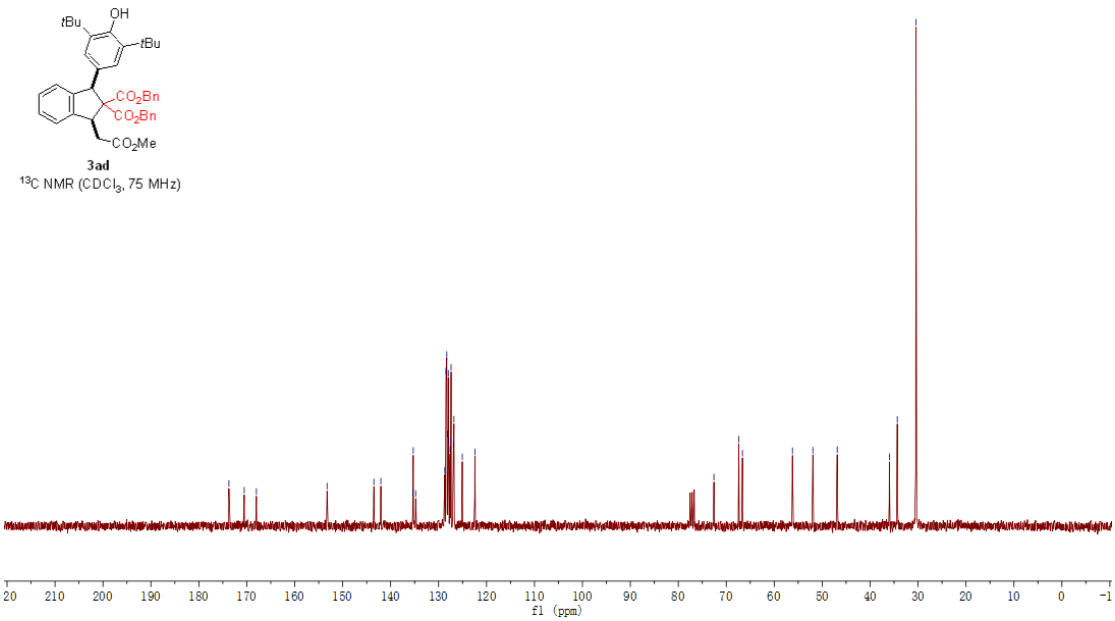

7.2599
7.2377
7.2138
7.1905
7.1749
7.1327
7.1070
7.0268
7.0019
5.3065
5.1820
5.1613
5.1402
5.1244
4.3418
4.3207
4.3000
4.2794
4.2580
4.0273
3.9992
3.7952
3.2555
3.2272
3.1980
3.1696
3.1467
3.1369
3.0894
3.0795
1.3871
1.2800
1.2743
1.2584
1.2529
1.0250
1.0045
0.4004
0.3794
tBu
OH
tBu
CO2iPr
CO2iPr
CO2Me
3ac
1H NMR (CDCl3, 300 MHz)
5.35
0.91
1.04
2.00
1.09
1.02
2.77
1.92
18.00
6.09
3.17
2.99
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


174.048
170.357
167.585
152.998
143.764
142.152
134.877
129.044
127.394
126.884
126.651
125.048
122.375
72.166
68.710
68.156
55.521
51.920
46.836
36.371
34.297
30.379
21.664
21.520
21.435
20.723
tBu
OH
tBu
CO2iPr
CO2iPr
CO2Me
3ac
13C NMR (CDCl3, 75 MHz)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)



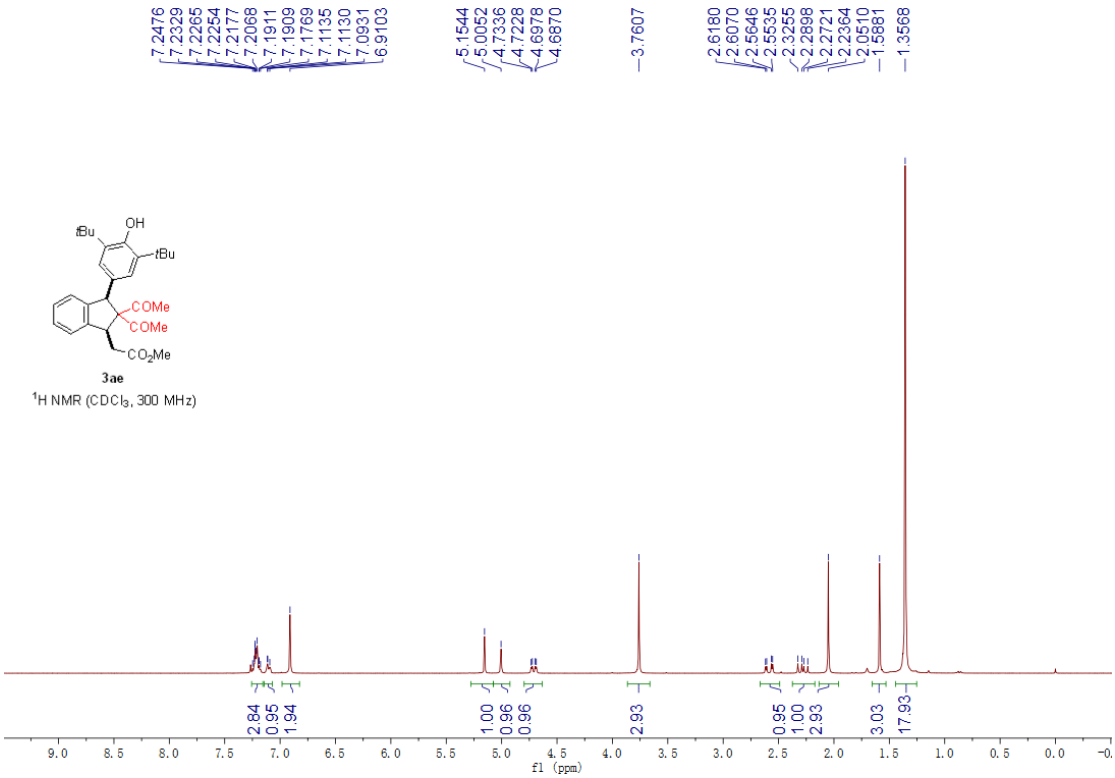
3ad

^{1}H NMR ($CDCl_3$, 300 MHz)



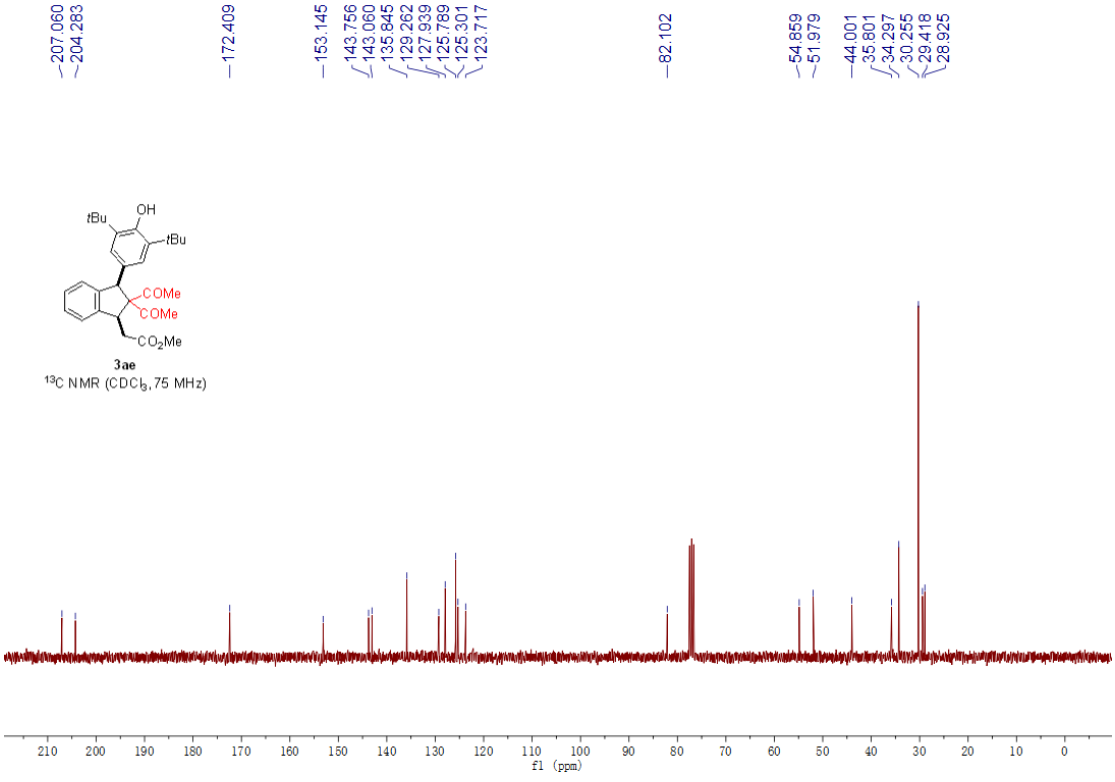
3ad

^{13}C NMR ($CDCl_3$, 75 MHz)



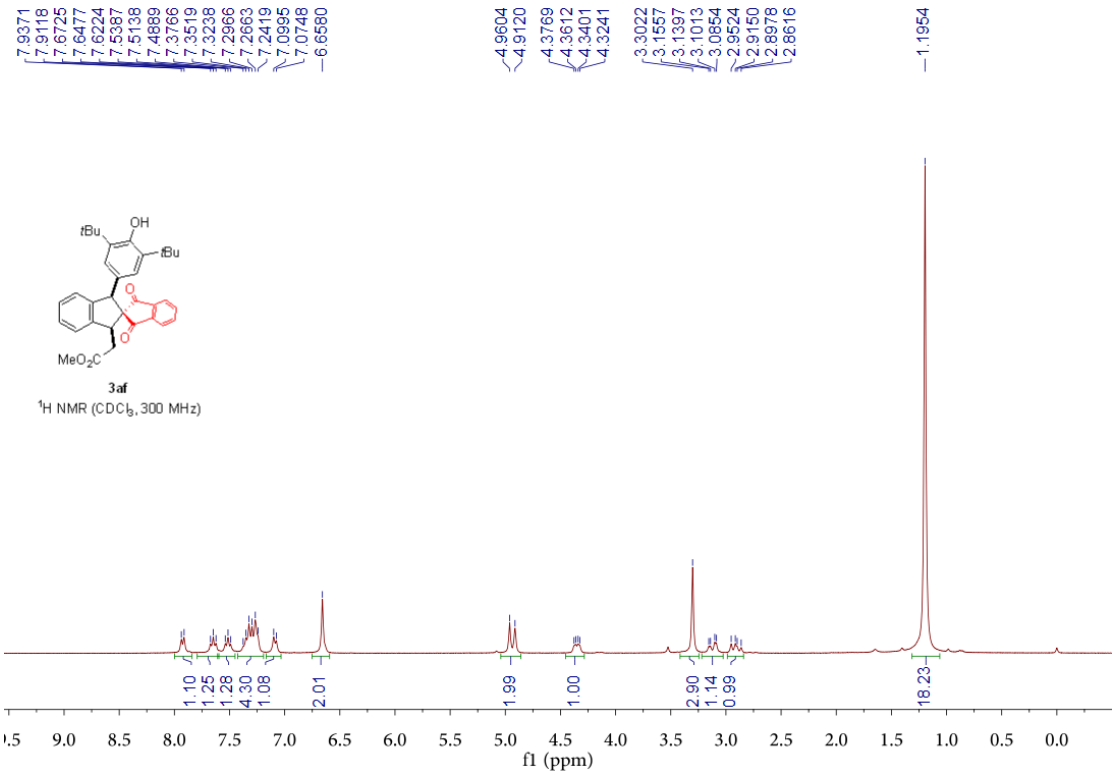
3ae

^{1}H NMR ($CDCl_3$, 300 MHz)



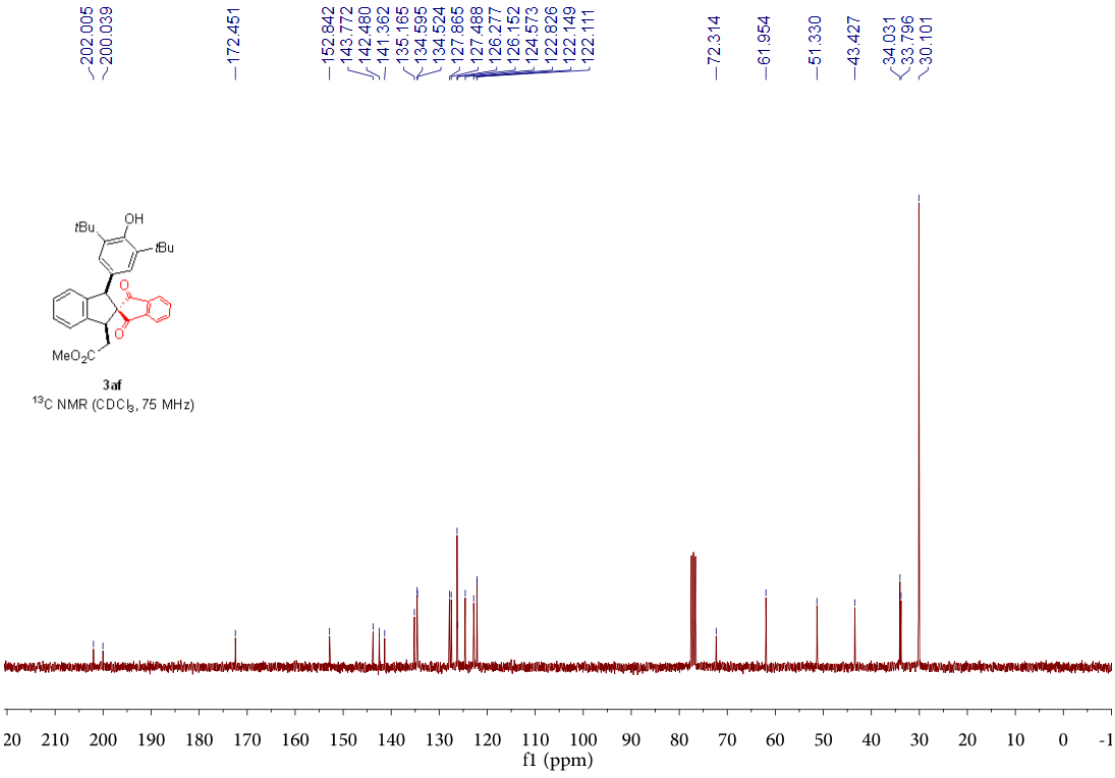
3ae

^{13}C NMR ($CDCl_3$, 75 MHz)



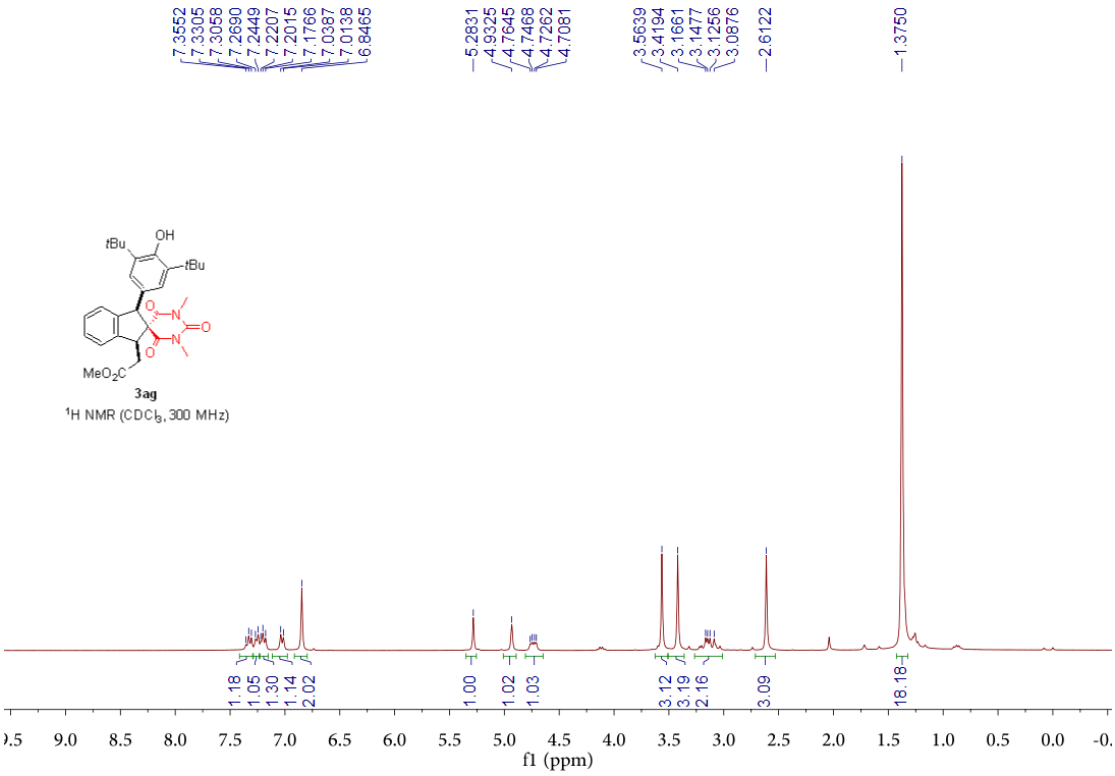
3af

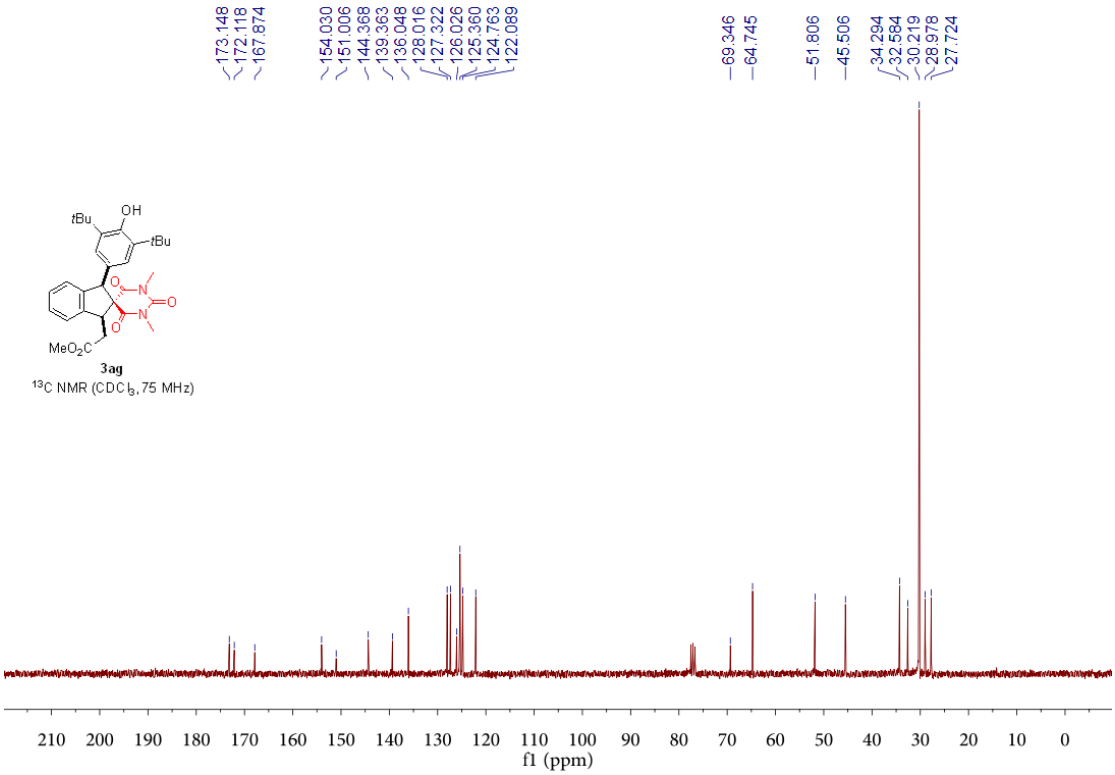
^{1}H NMR ($CDCl_3$, 300 MHz)

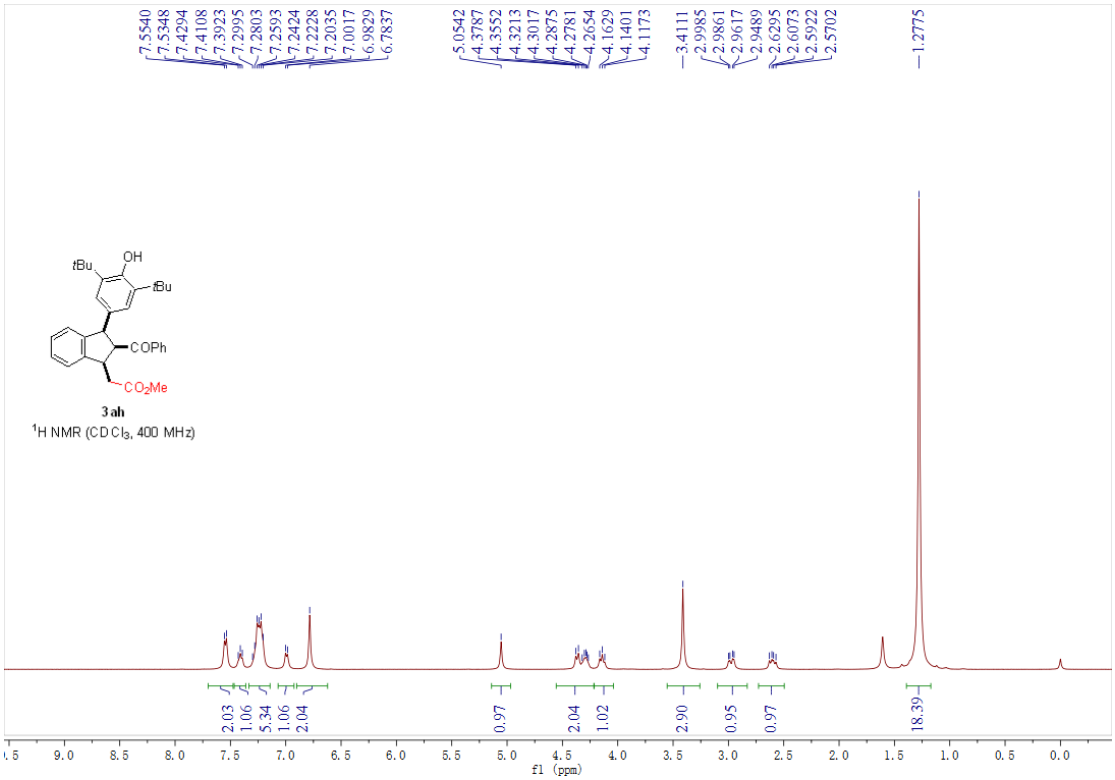


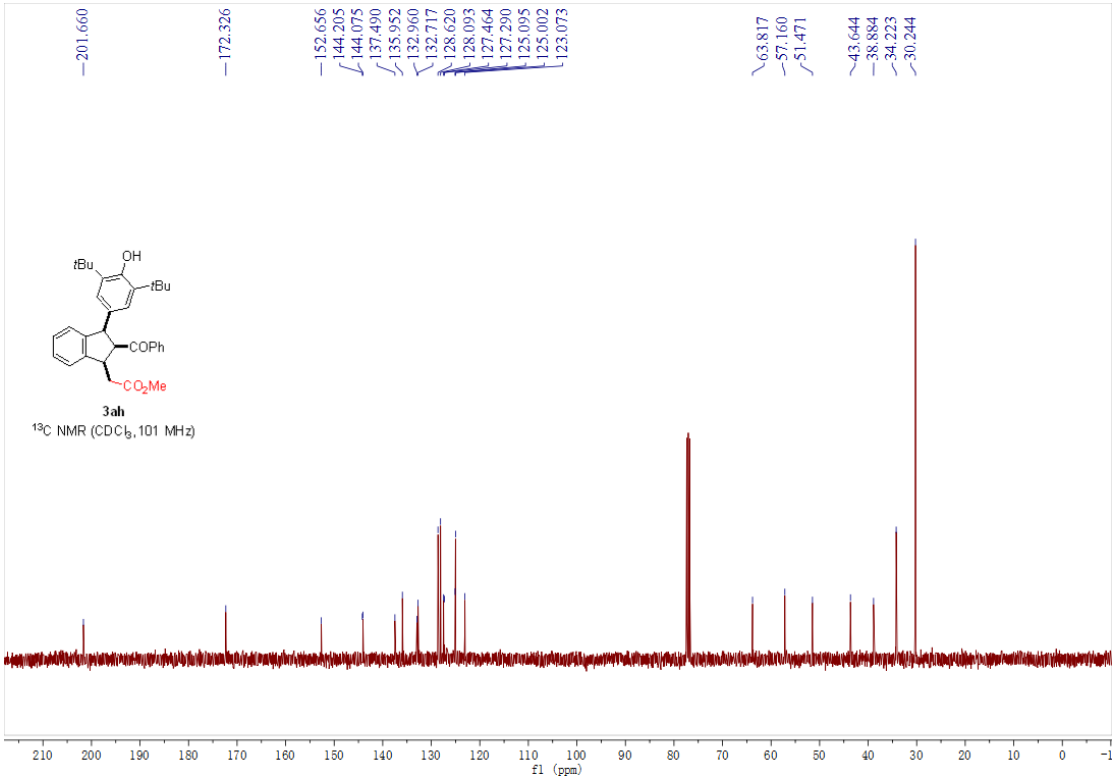
3af

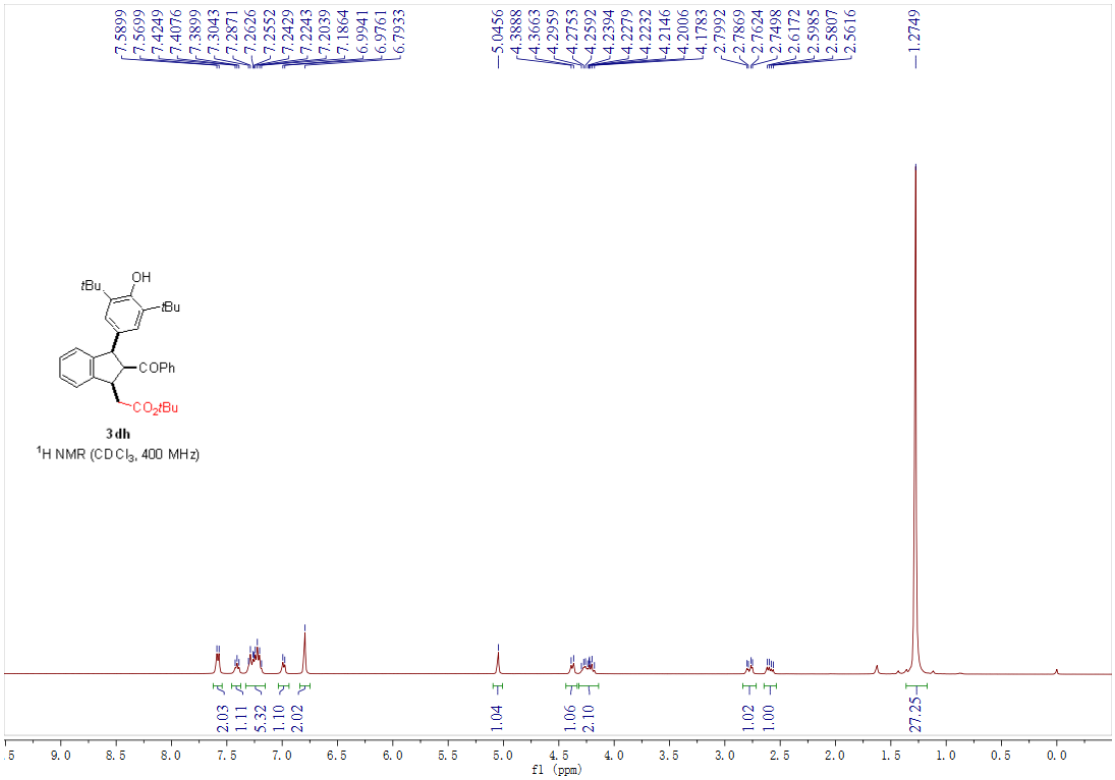
^{13}C NMR ($CDCl_3$, 75 MHz)

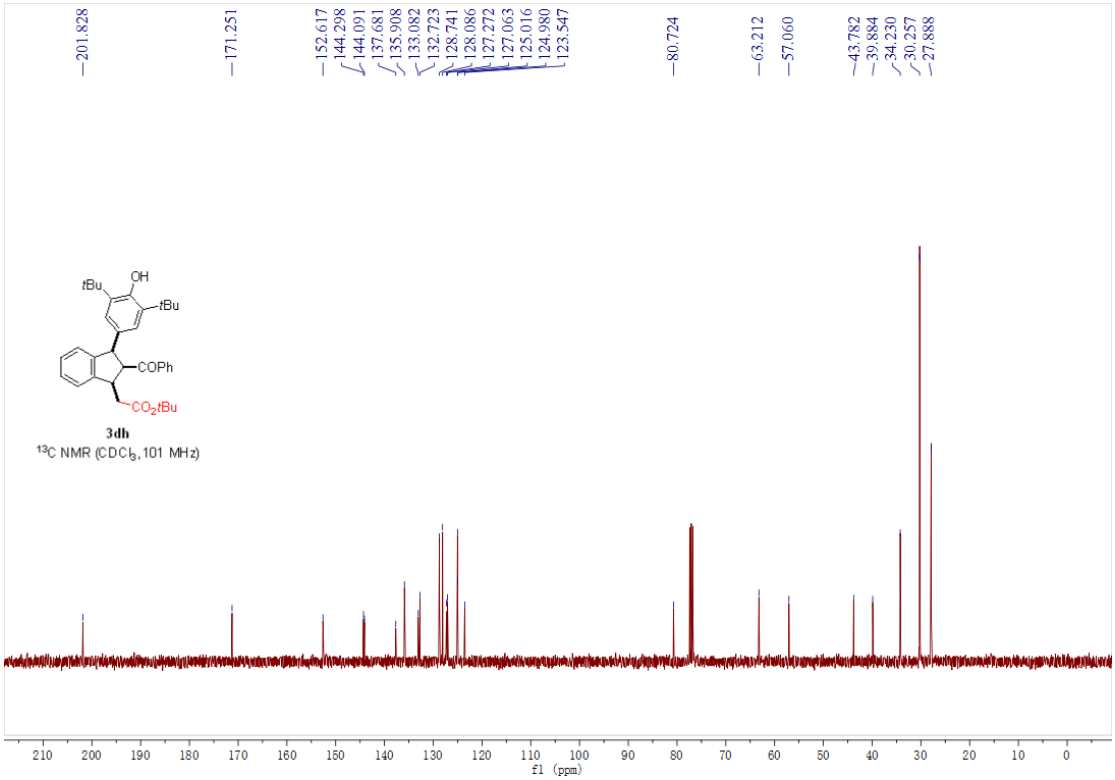

7.3552
7.3305
7.3058
7.2690
7.2449
7.2207
7.2015
7.1766
7.0387
7.0138
6.8465
5.2831
4.9325
4.7645
4.7468
4.7262
4.7081
3.5639
3.4194
3.1661
3.1477
3.1256
3.0876
2.6122
1.3750
tBu
OH
tBu
MeO2C
3ag
1H NMR (CDCl3, 300 MHz)
1.18
1.05
1.30
1.14
2.02
1.00
1.02
1.03
3.12
3.19
2.16
3.09
18.18
f1 (ppm)

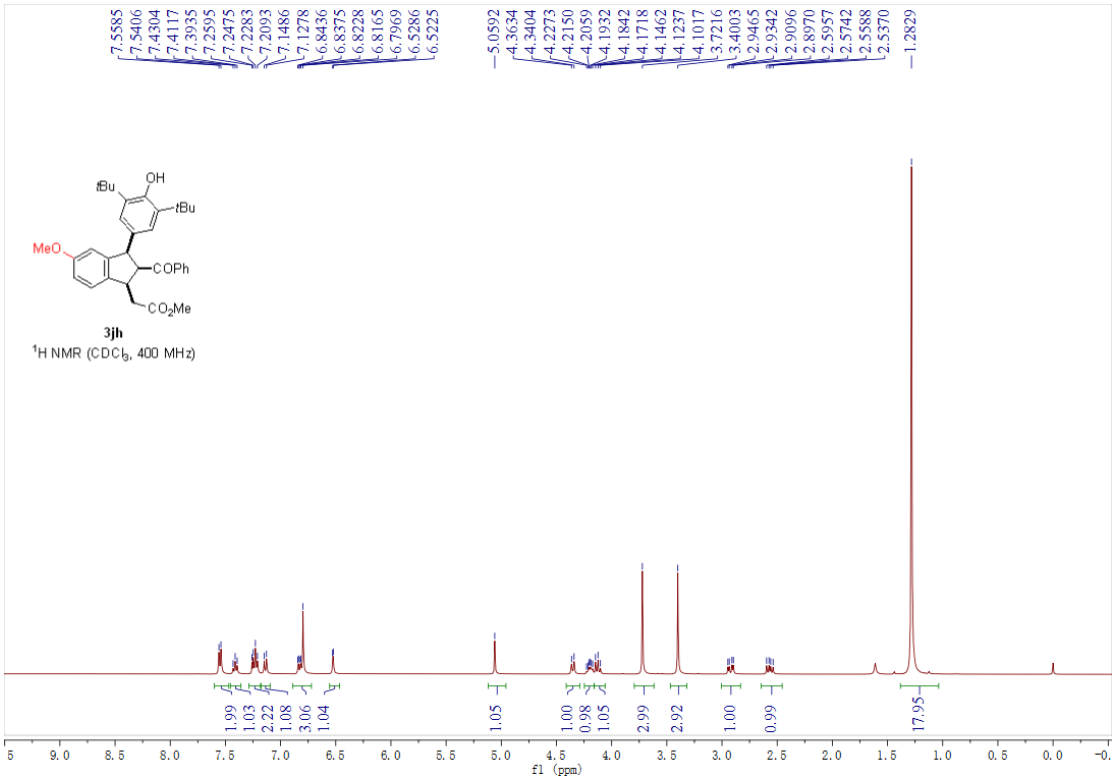

173.148
172.118
167.874
154.030
151.006
144.368
139.363
136.048
128.016
127.322
126.026
125.360
124.763
122.089
69.346
64.745
51.806
45.506
34.294
32.584
30.219
28.978
27.724
tBu
OH
tBu
MeO2C
3ag
13C NMR (CDCl3, 75 MHz)
f1 (ppm)

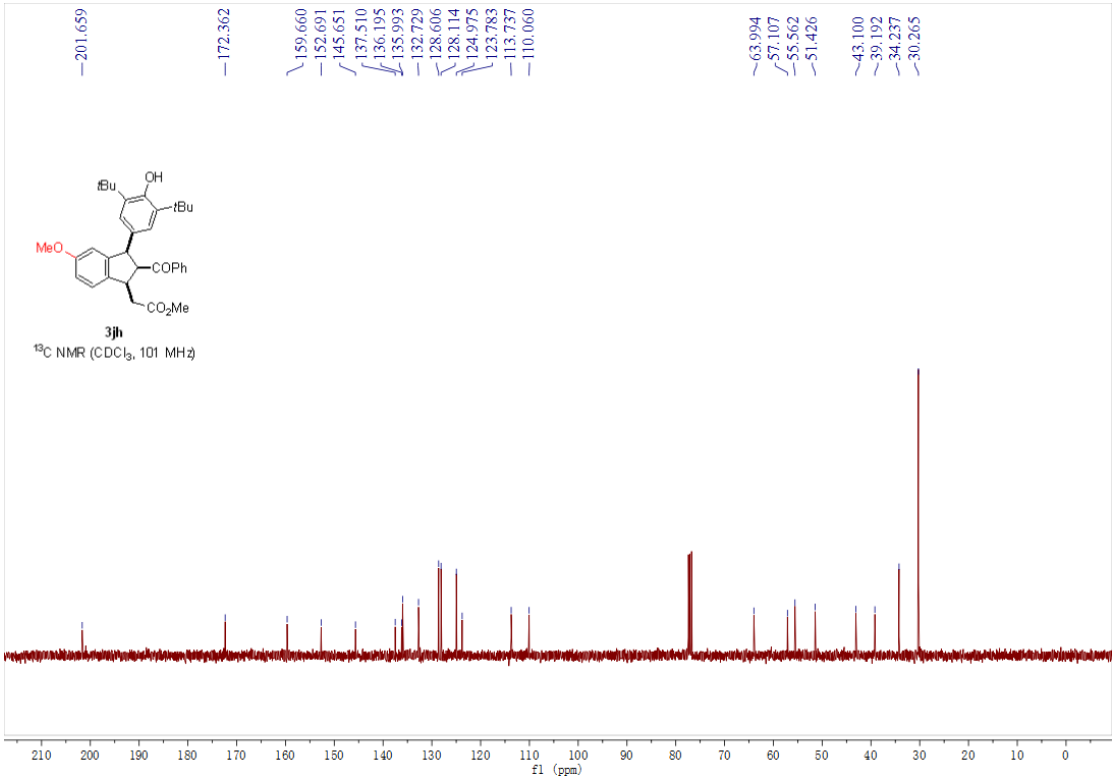

7.5540
7.5348
7.4294
7.4108
7.3923
7.2995
7.2803
7.2593
7.2424
7.2228
7.2035
7.0017
6.9829
6.7837
5.0542
4.3787
4.3552
4.3213
4.3017
4.2875
4.2781
4.2654
4.1629
4.1401
4.1173
3.4111
2.9985
2.9861
2.9617
2.9489
2.6295
2.6073
2.5922
2.5702
1.2775
tBu
OH
tBu
COPh
CO2Me
3ah
1H NMR (CDCl3, 400 MHz)
2.03
1.06
5.34
1.06
2.04
0.97
2.04
1.02
2.90
0.95
0.97
18.39
f1 (ppm)

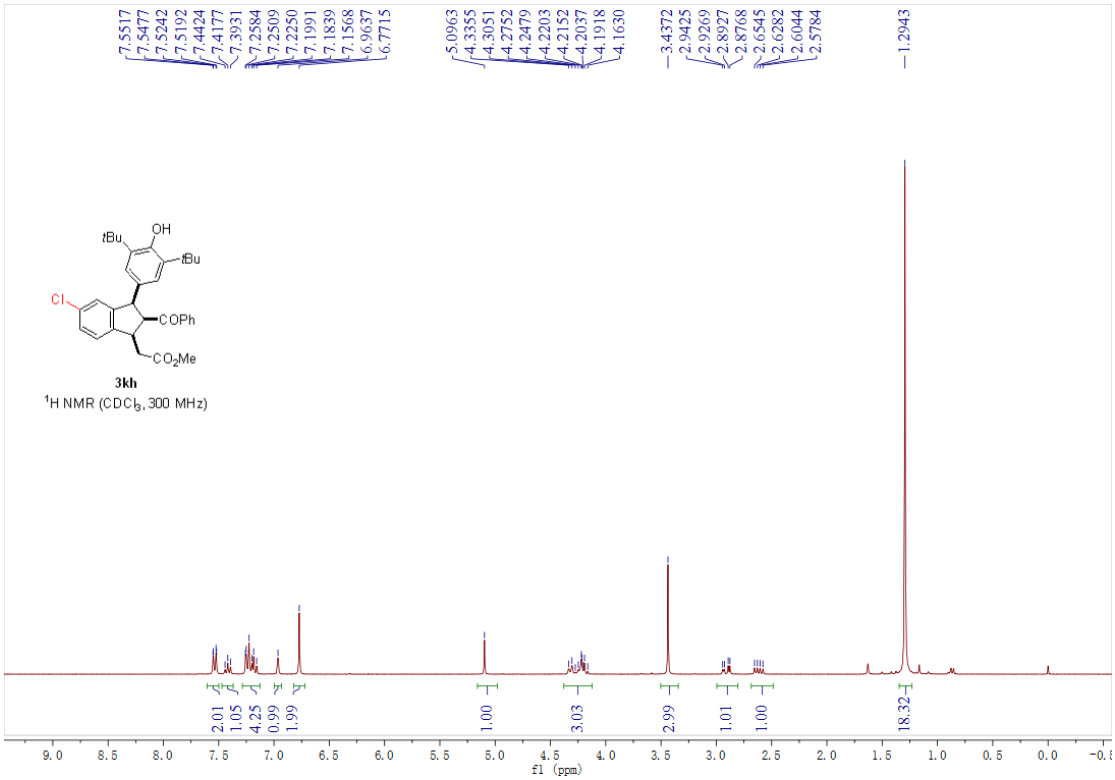

201.660
172.326
152.656
144.205
144.075
137.490
135.952
132.960
132.717
128.620
128.093
127.464
127.290
125.095
125.002
123.073
63.817
57.160
51.471
43.644
38.884
34.223
30.244
tBu
OH
tBu
COPh
CO2Me
3ah
13C NMR (CDCl3, 101 MHz)
f1 (ppm)


7.5899
7.5699
7.4249
7.4076
7.3899
7.3043
7.2871
7.2626
7.2552
7.2429
7.2243
7.2039
7.1864
6.9941
6.9761
6.7933
5.0456
4.3888
4.3663
4.2959
4.2753
4.2592
4.2394
4.2279
4.2232
4.2146
4.2006
4.1783
2.7992
2.7869
2.7624
2.7498
2.6172
2.5985
2.5807
2.5616
1.2749
tBu
OH
tBu
COPh
CO2tBu
3dh
1H NMR (CDCl3, 400 MHz)
2.03
1.11
5.32
1.10
2.02
1.04
1.06
2.10
1.02
1.00
27.25
f1 (ppm)


201.828
171.251
152.617
144.298
144.091
137.681
135.908
133.082
132.723
128.741
128.086
127.272
127.063
125.016
124.980
123.547
80.724
63.212
57.060
43.782
39.884
34.230
30.257
27.888
tBu
OH
tBu
COPh
CO2tBu
3dh
13C NMR (CDCl3, 101 MHz)
f1 (ppm)

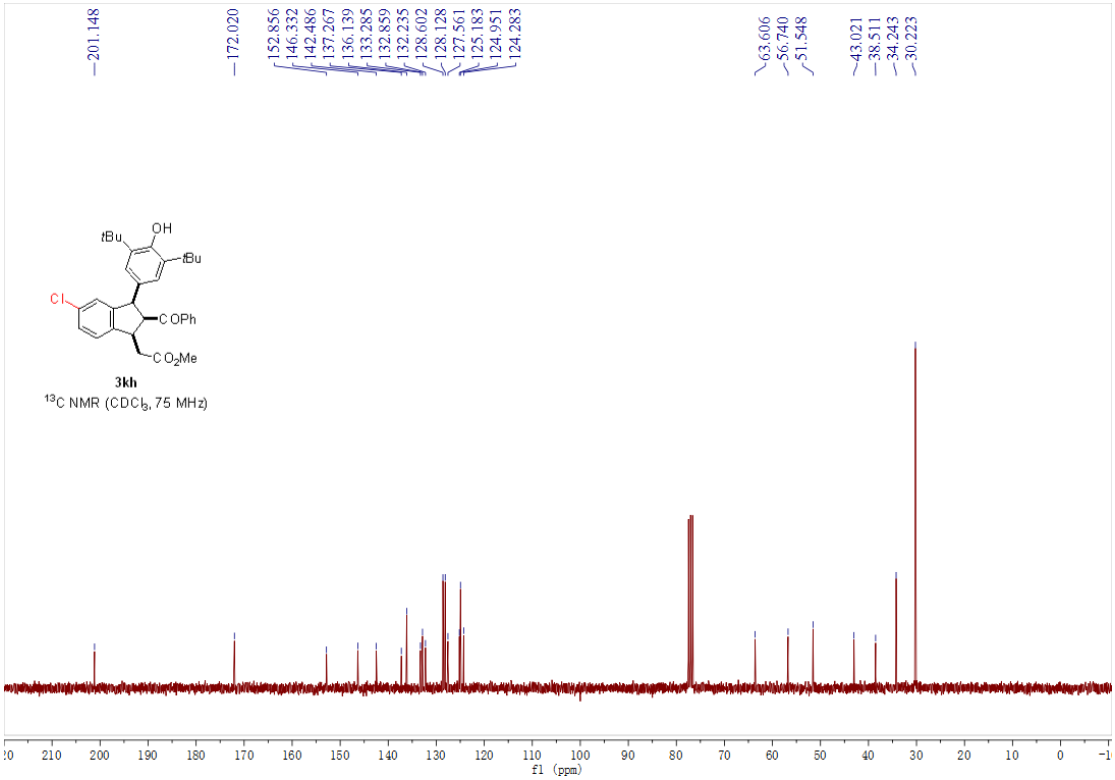

7.5585
7.5406
7.4304
7.4117
7.3935
7.2595
7.2475
7.2283
7.2093
7.1486
7.1278
6.8436
6.8375
6.8228
6.8165
6.7969
6.5286
6.5225
5.0592
4.3634
4.3404
4.2273
4.2150
4.2059
4.1932
4.1842
4.1718
4.1462
4.1237
4.1017
3.7216
3.4003
2.9465
2.9342
2.9096
2.8970
2.5957
2.5742
2.5588
2.5370
1.2829
tBu
OH
tBu
MeO
COPh
CO2Me
3jh
1H NMR (CDCl3, 400 MHz)
1.99
1.03
2.22
1.08
3.06
1.04
1.05
1.00
0.98
1.05
2.99
2.92
1.00
0.99
17.95
f1 (ppm)


201.659
172.362
159.660
152.691
145.651
137.510
136.195
135.993
132.729
128.606
128.114
124.975
123.783
113.737
110.060
63.994
57.107
55.562
51.426
43.100
39.192
34.237
30.265
tBu
OH
tBu
MeO
COPh
CO2Me
3jh
13C NMR (CDCl3, 101 MHz)
f1 (ppm)



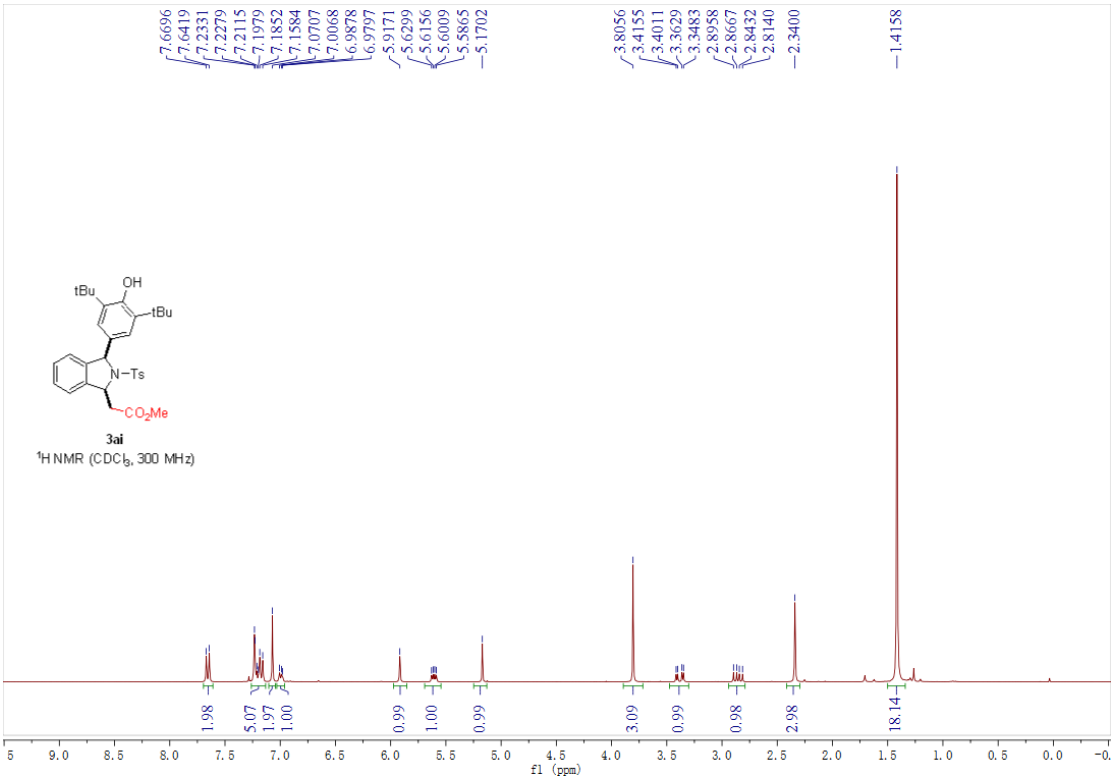
3kh

^{1}H NMR ($CDCl_3$, 300 MHz)



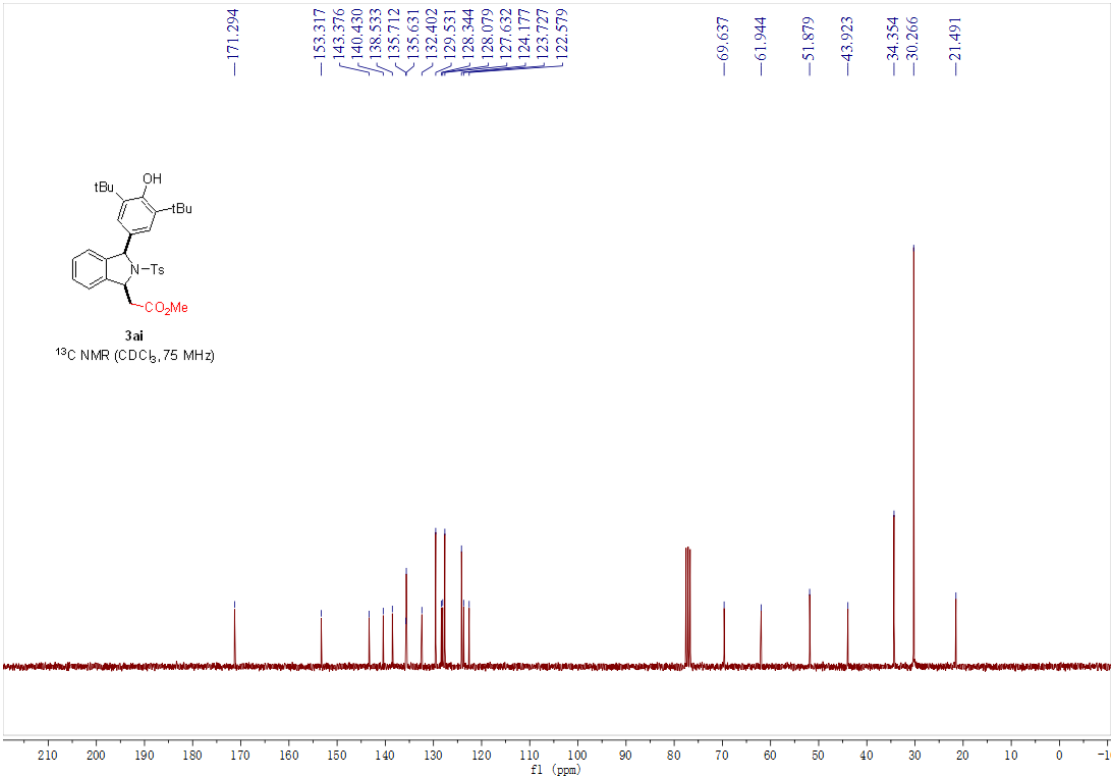
3kh

^{13}C NMR ($CDCl_3$, 75 MHz)



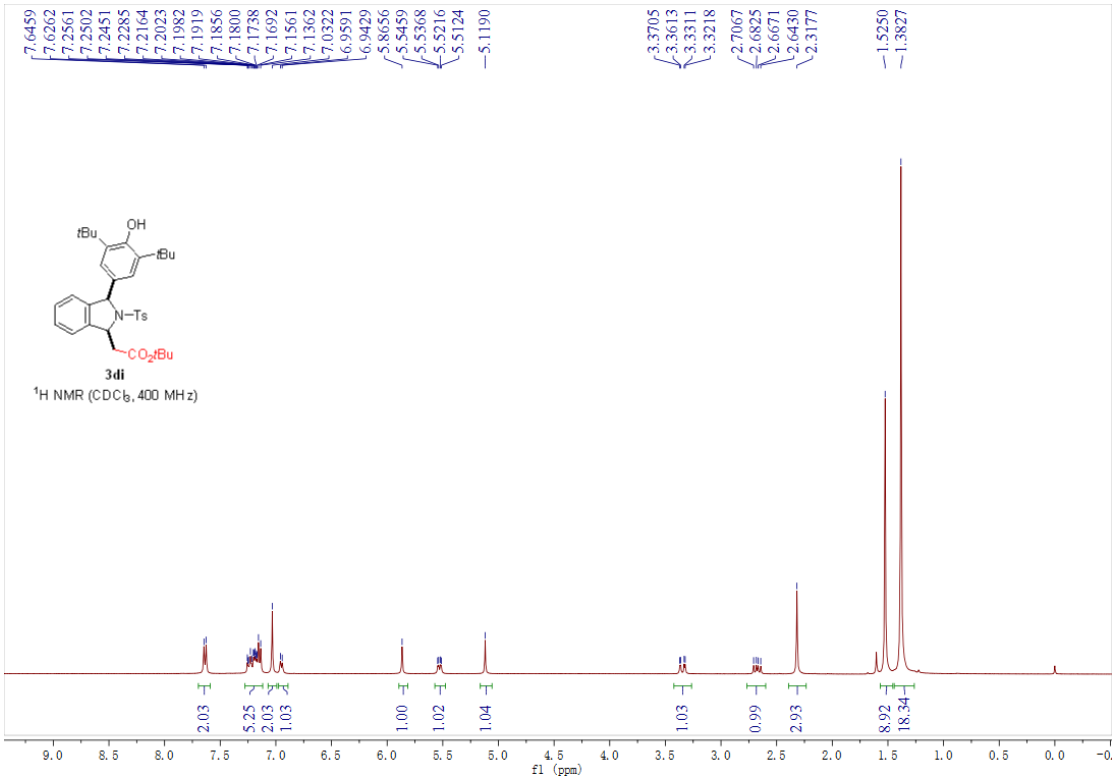
3ai

^{1}H NMR ($CDCl_3$, 300 MHz)



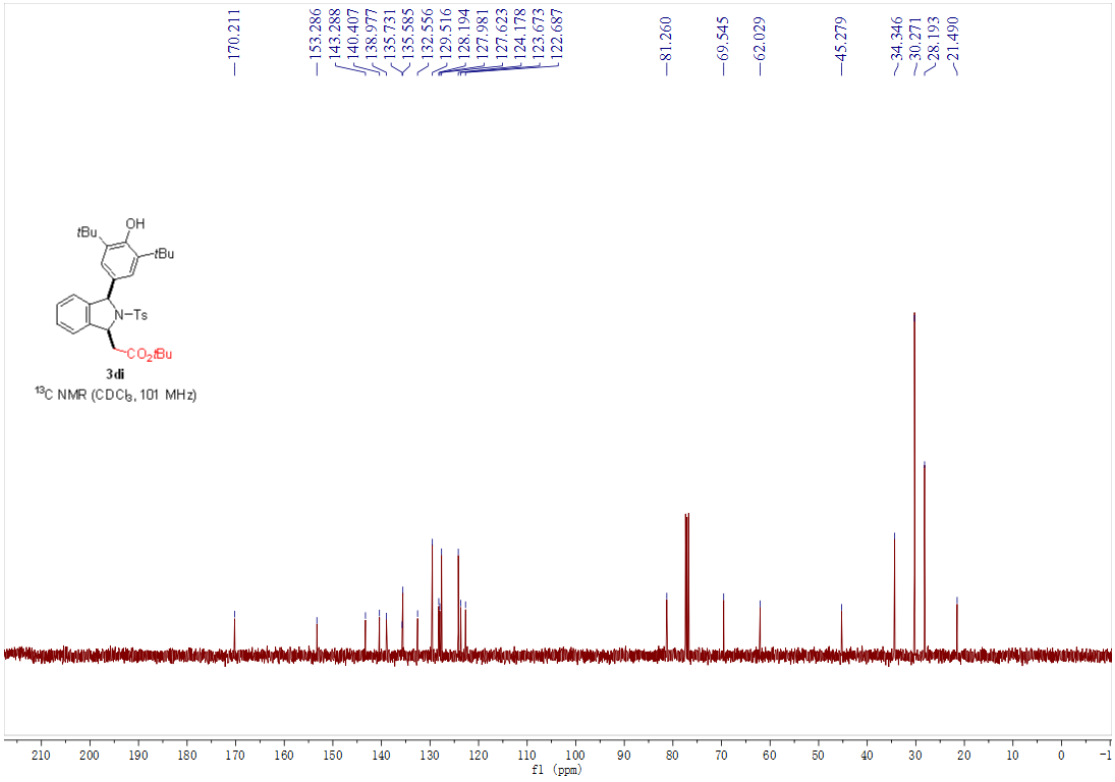
3ai

^{13}C NMR ($CDCl_3$, 75 MHz)



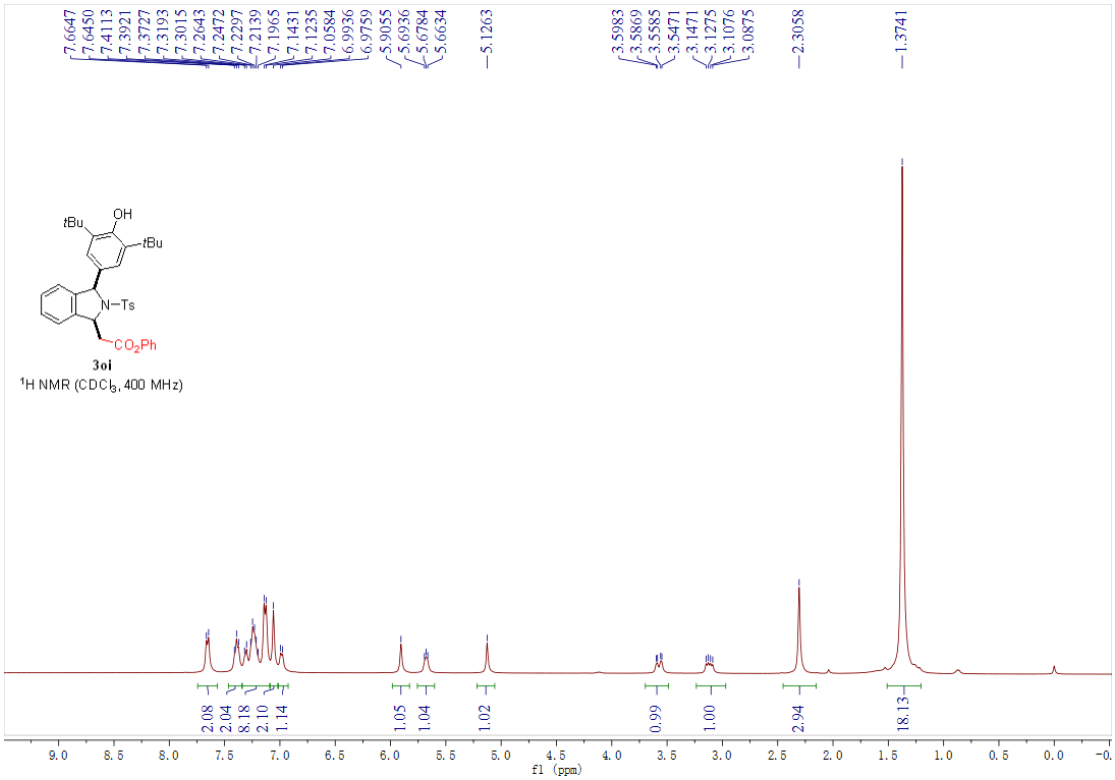
3di

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



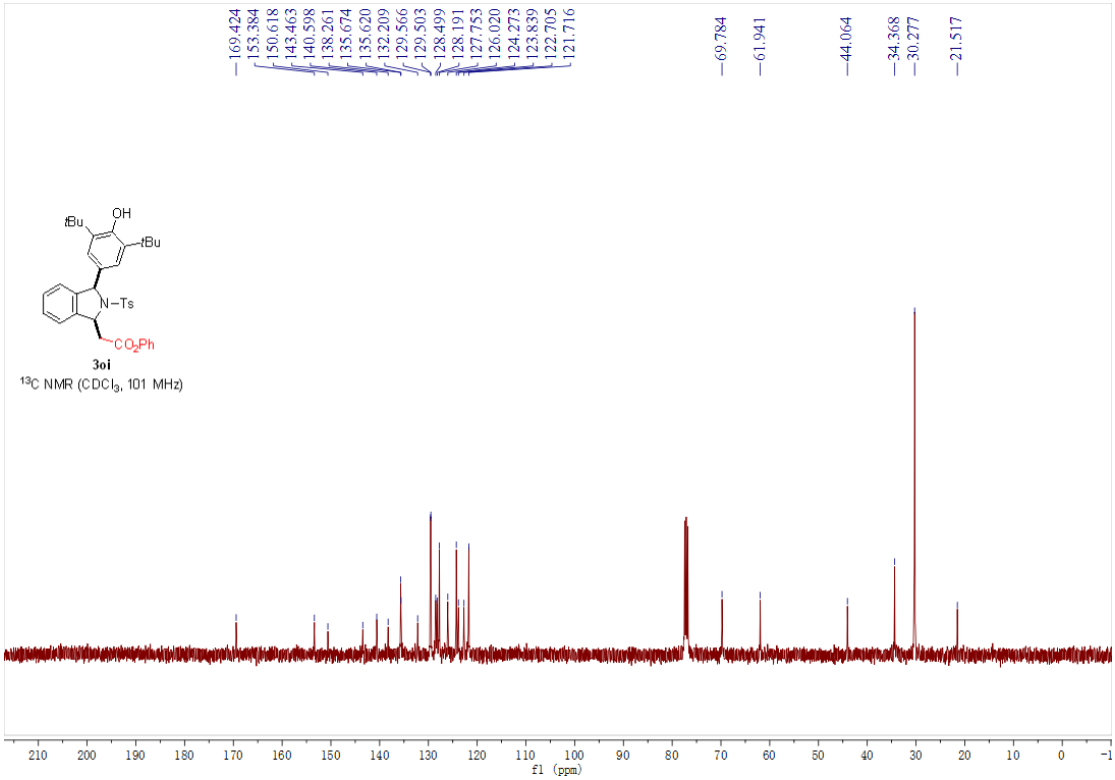
3di

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



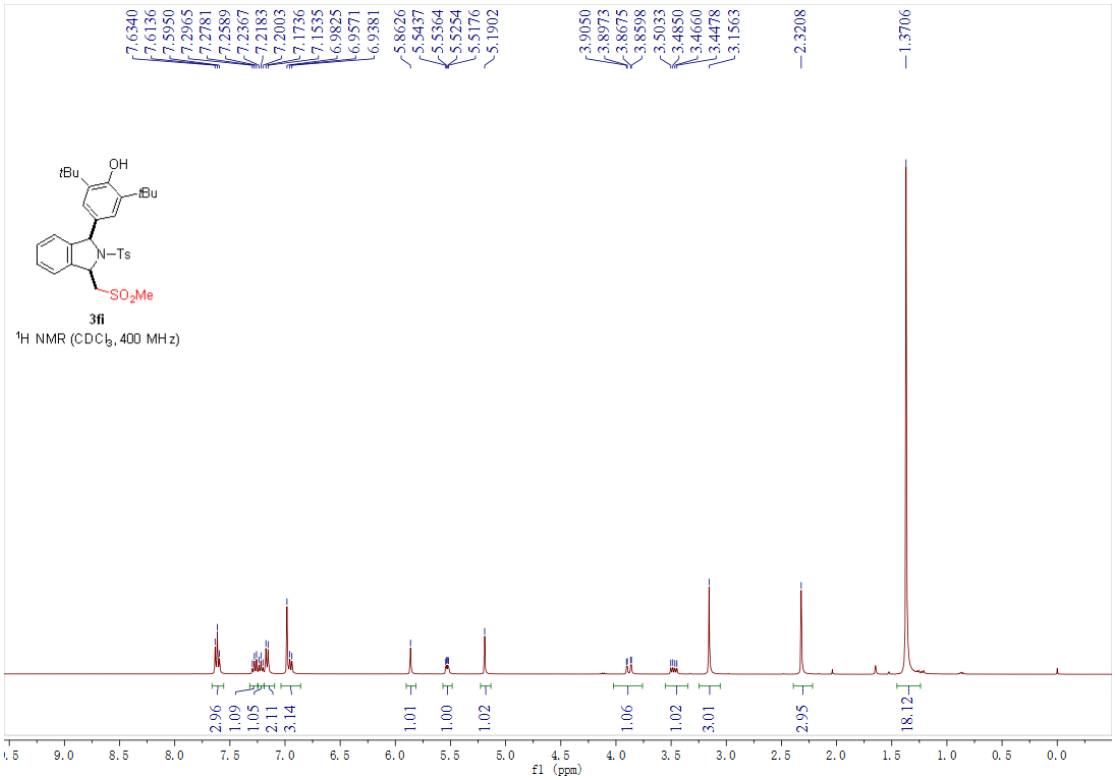
3oi

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



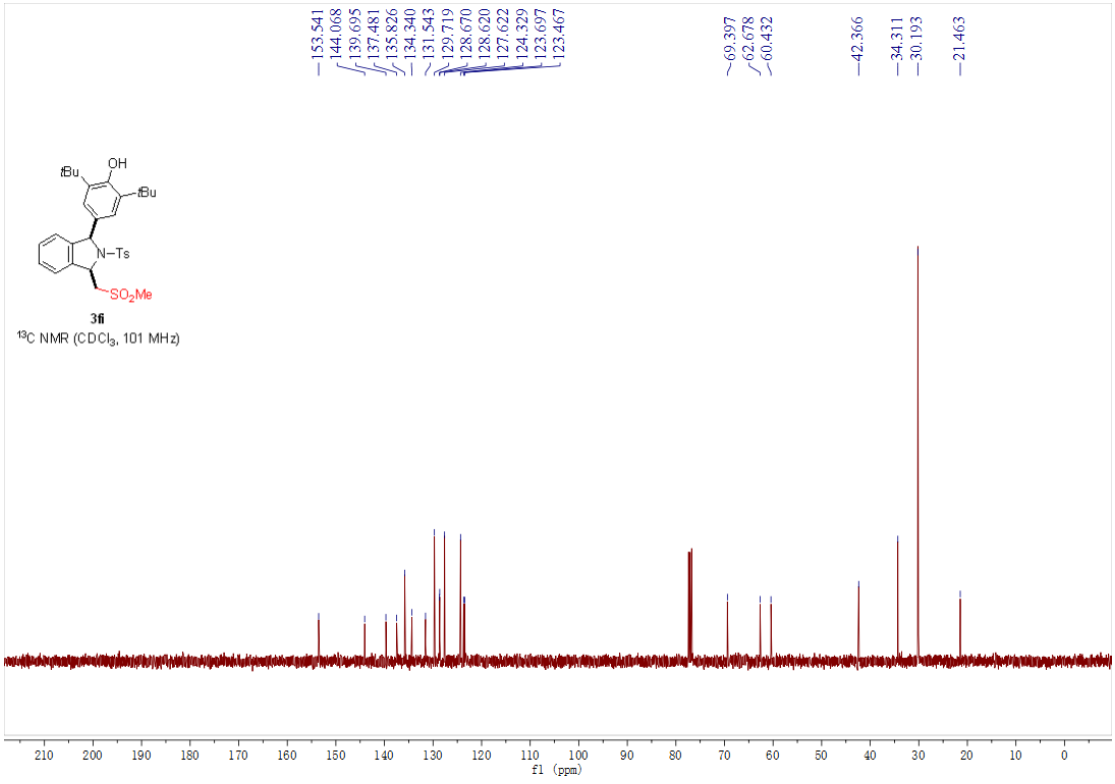
3oi

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



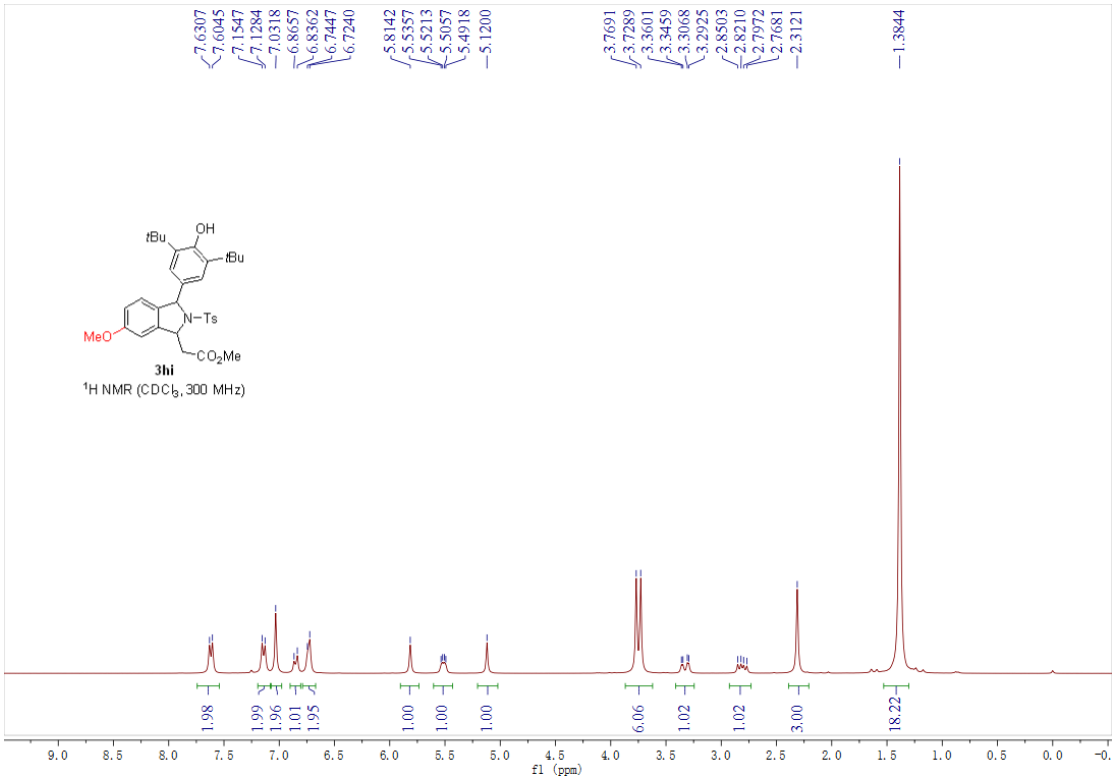
3fi

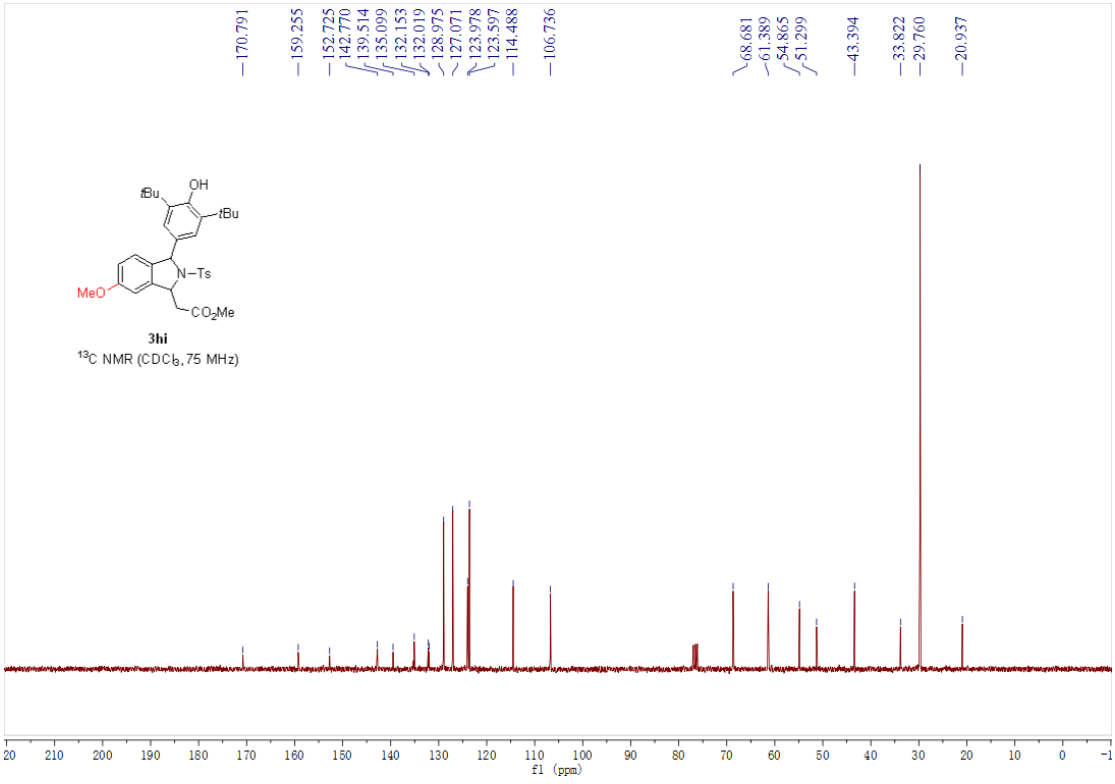
^{1}H NMR ($CDCl_3$, 400 MHz)

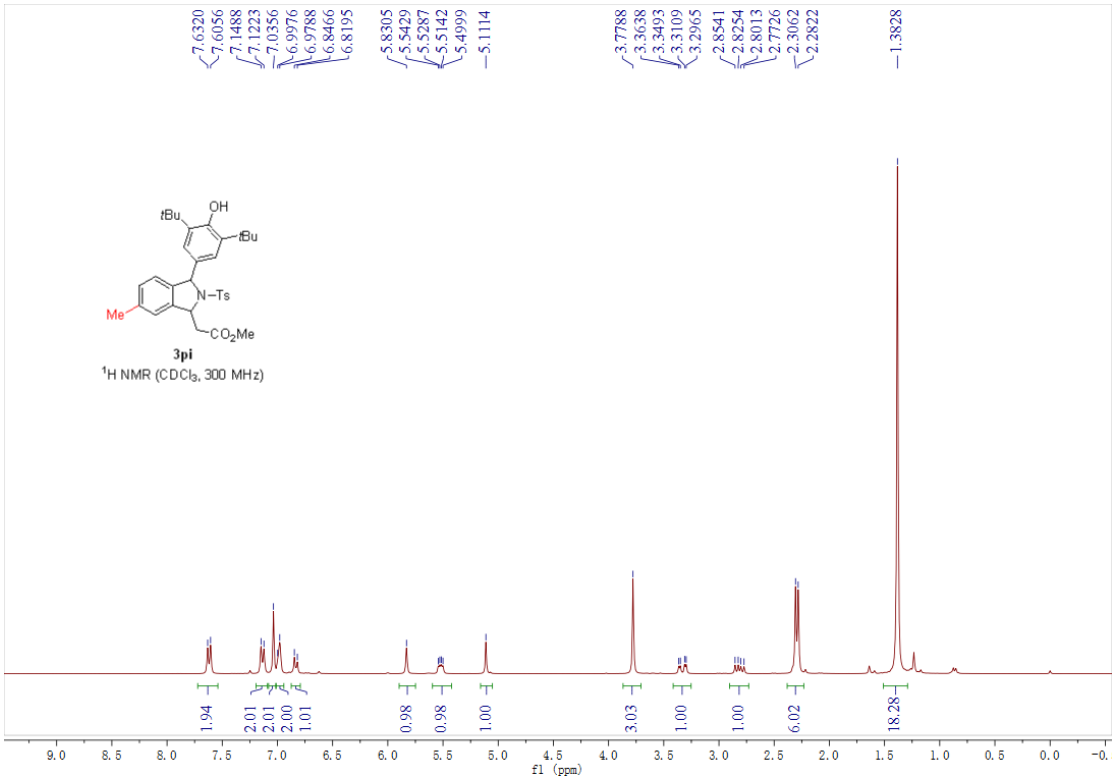


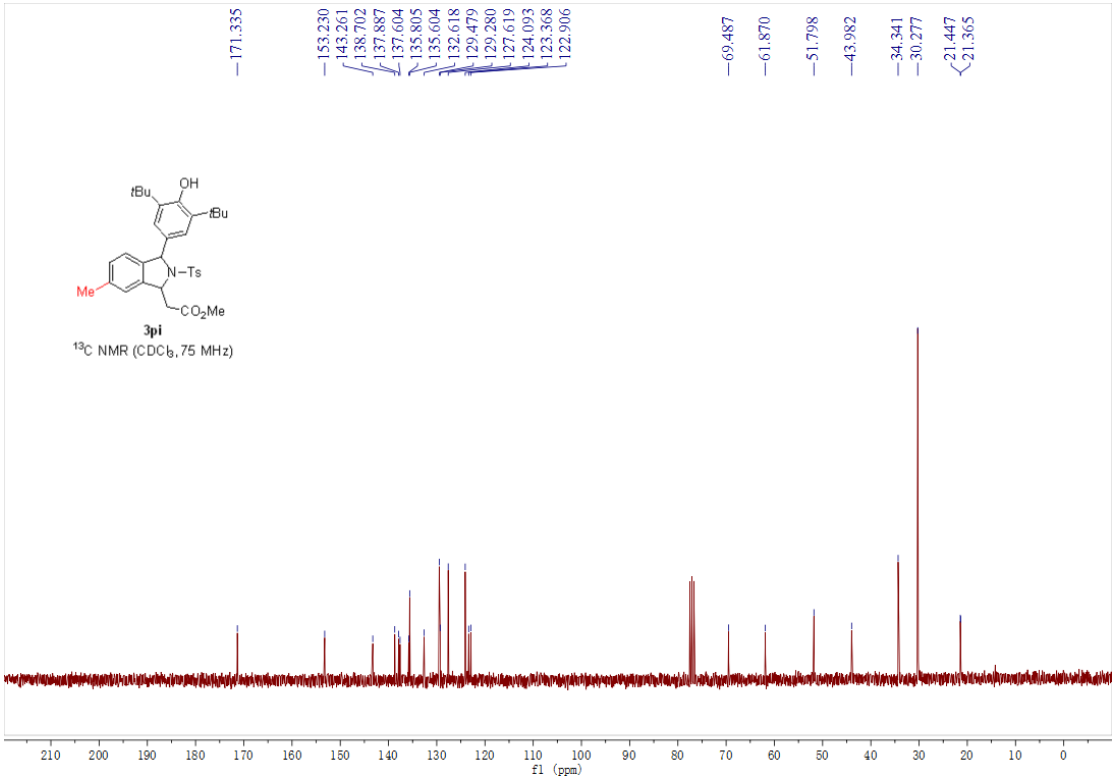
3fi

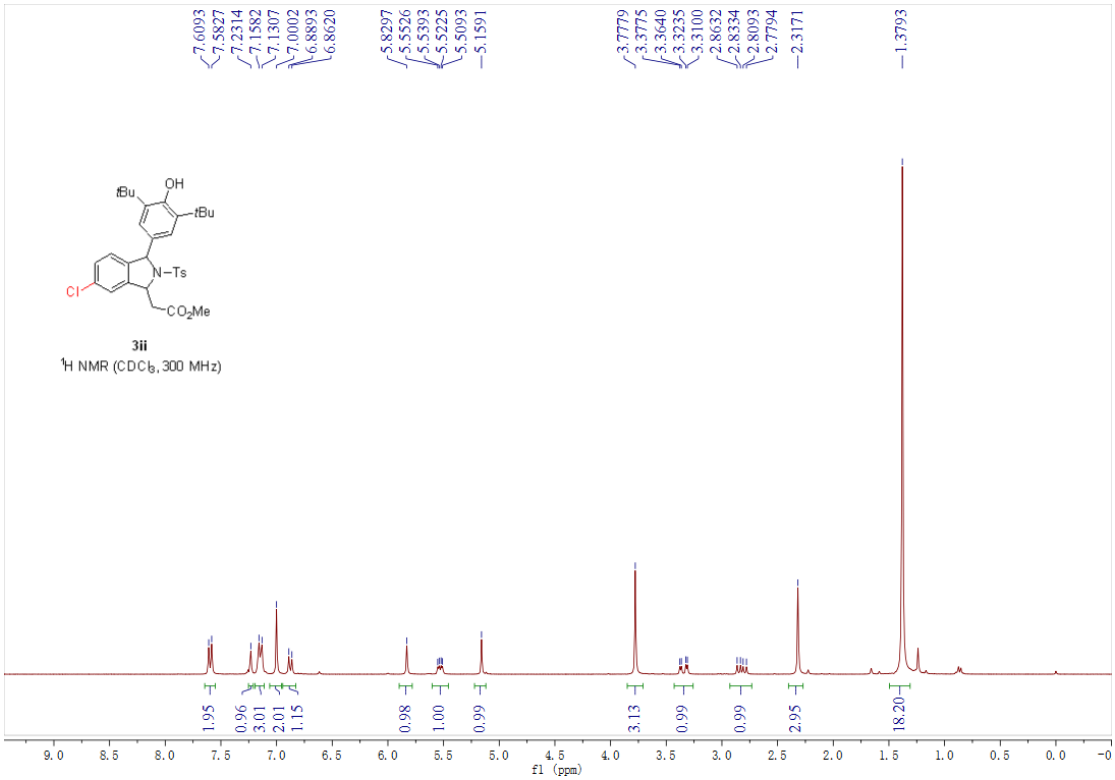
^{13}C NMR ($CDCl_3$, 101 MHz)


7.6307
7.6045
7.1547
7.1284
7.0318
6.8657
6.8362
6.7447
6.7240
5.8142
5.5357
5.5213
5.5057
5.4918
5.1200
3.7691
3.7289
3.3601
3.3459
3.3068
3.2925
2.8503
2.8210
2.7972
2.7681
2.3121
1.3844
tBu
OH
tBu
N–Ts
MeO
CO2Me
3hi
1H NMR (CDCl3, 300 MHz)
1.98
1.99
1.96
1.01
1.95
1.00
1.00
1.00
6.06
1.02
1.02
3.00
18.22
f1 (ppm)


170.791
159.255
152.725
142.770
139.514
135.099
132.153
132.019
128.975
127.071
123.978
123.597
114.488
106.736
68.681
61.389
54.865
51.299
43.394
33.822
29.760
20.937
tBu
OH
tBu
N–Ts
MeO
CO2Me
3hi
13C NMR (CDCl3, 75 MHz)
f1 (ppm)

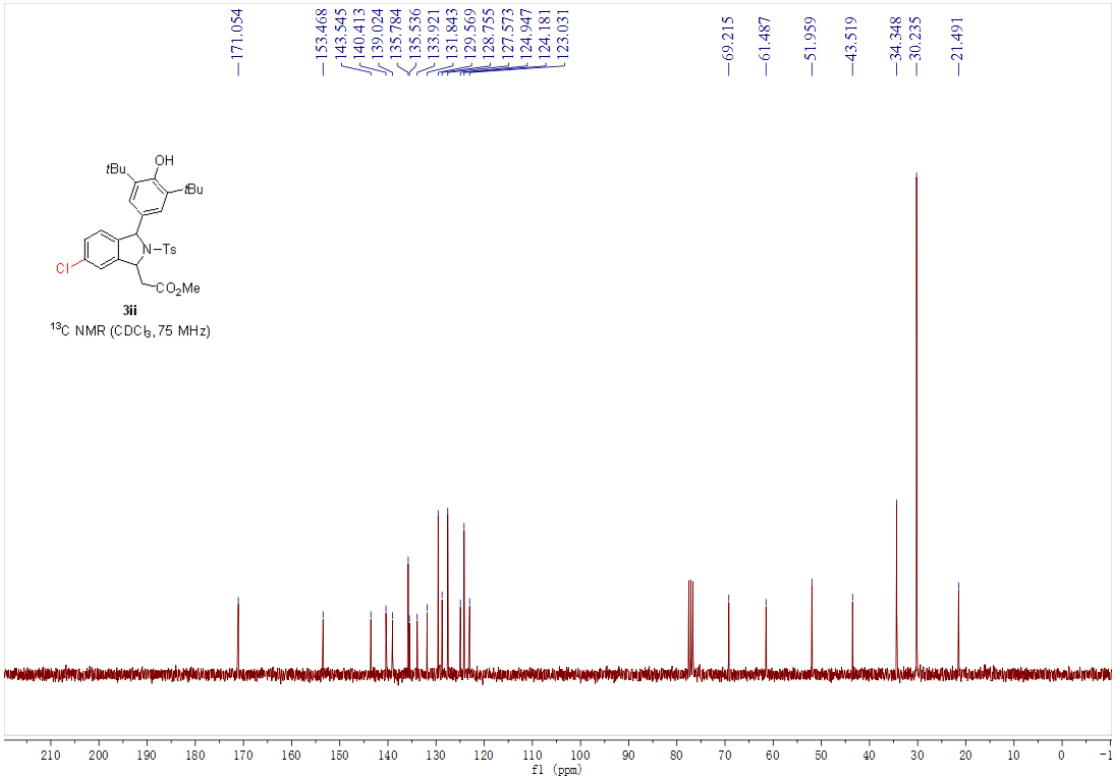

7.6320
7.6056
7.1488
7.1223
7.0356
6.9976
6.9788
6.8466
6.8195
5.8305
5.5429
5.5287
5.5142
5.4999
5.1114
3.7788
3.3638
3.3493
3.3109
3.2965
2.8541
2.8254
2.8013
2.7726
2.3062
2.2822
1.3828
tBu
OH
tBu
N–Ts
Me
CO2Me
3pi
1H NMR (CDCl3, 300 MHz)
1.94
2.01
2.01
2.00
1.01
0.98
0.98
1.00
3.03
1.00
1.00
6.02
18.28
f1 (ppm)


171.335
153.230
143.261
138.702
137.887
137.604
135.805
135.604
132.618
129.479
129.280
127.619
124.093
123.368
122.906
69.487
61.870
51.798
43.982
34.341
30.277
21.447
21.365
tBu
OH
tBu
N–Ts
Me
CO2Me
3pi
13C NMR (CDCl3, 75 MHz)
f1 (ppm)



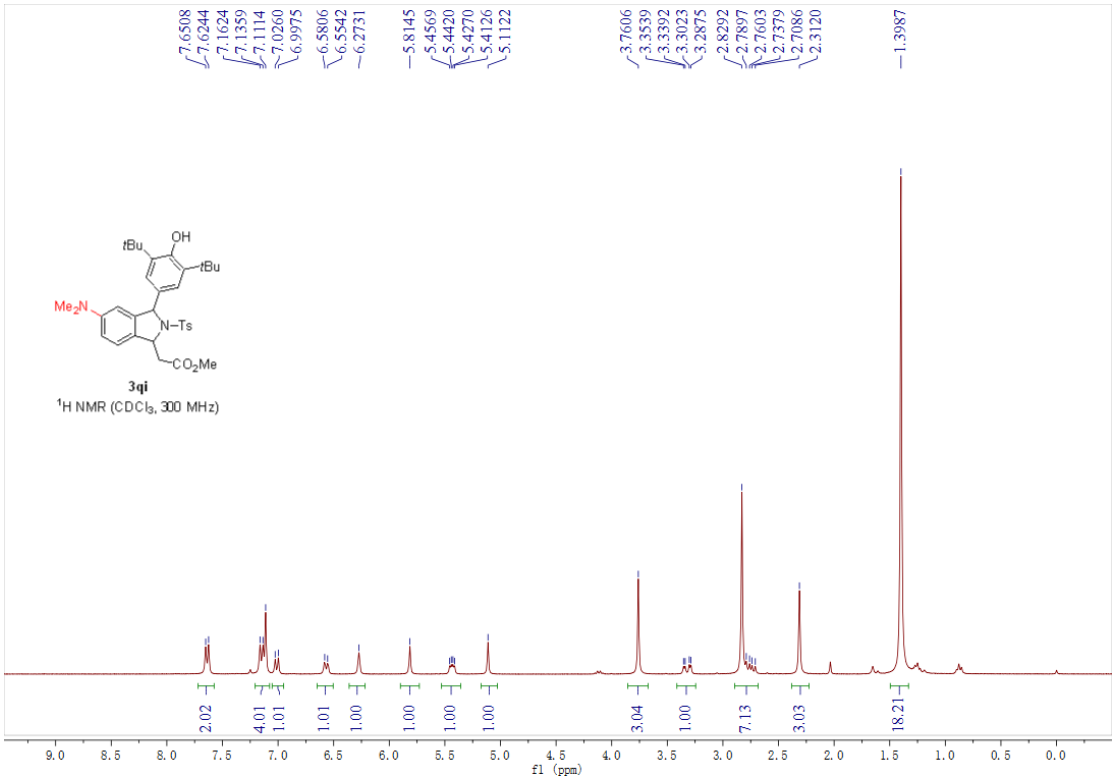
3ii

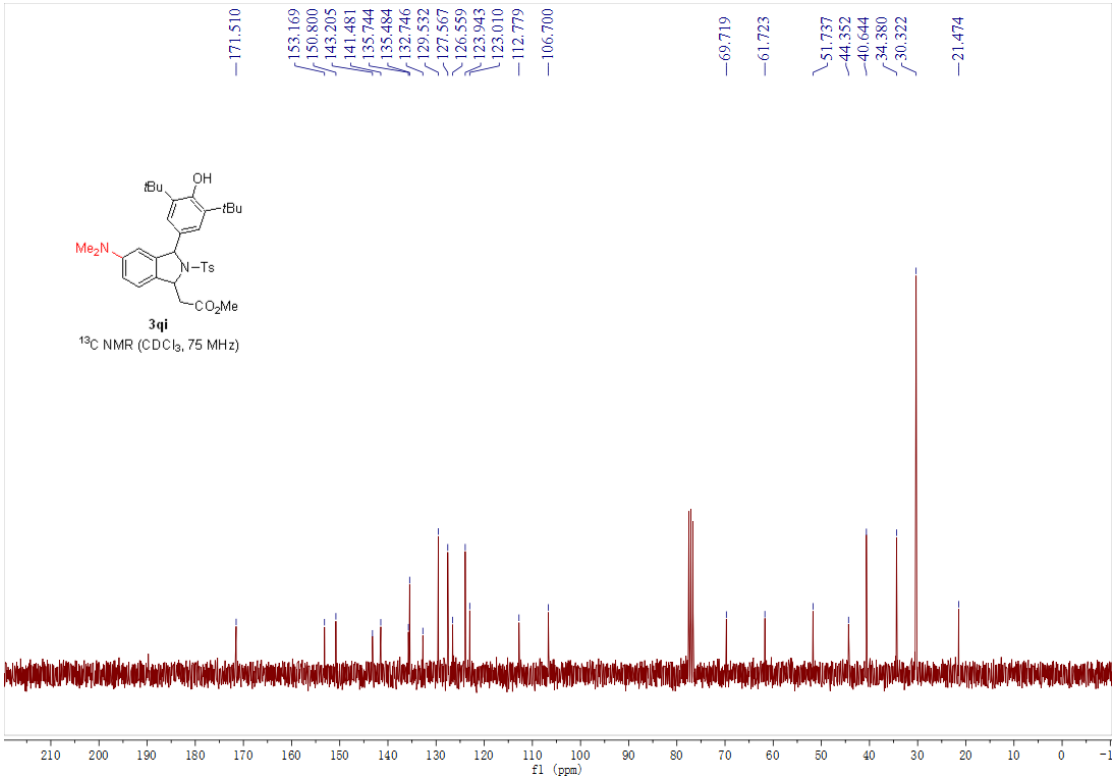
^{1}H NMR ($CDCl_3$, 300 MHz)

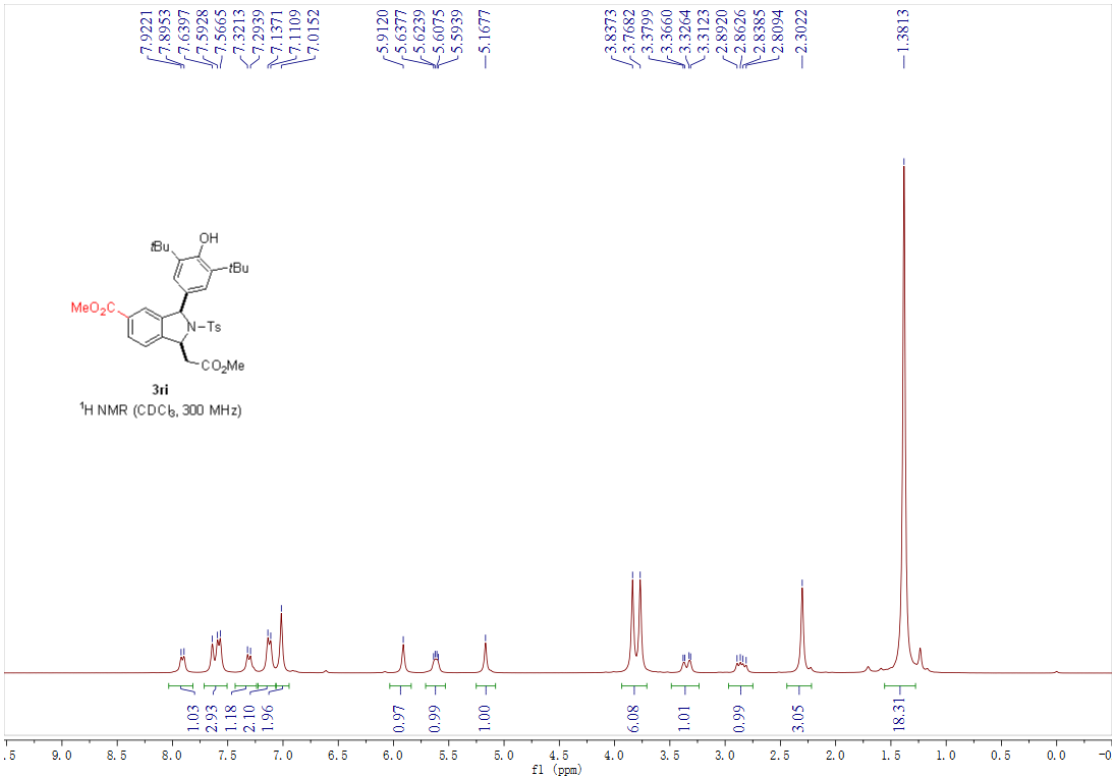


3ii

^{13}C NMR ($CDCl_3$, 75 MHz)

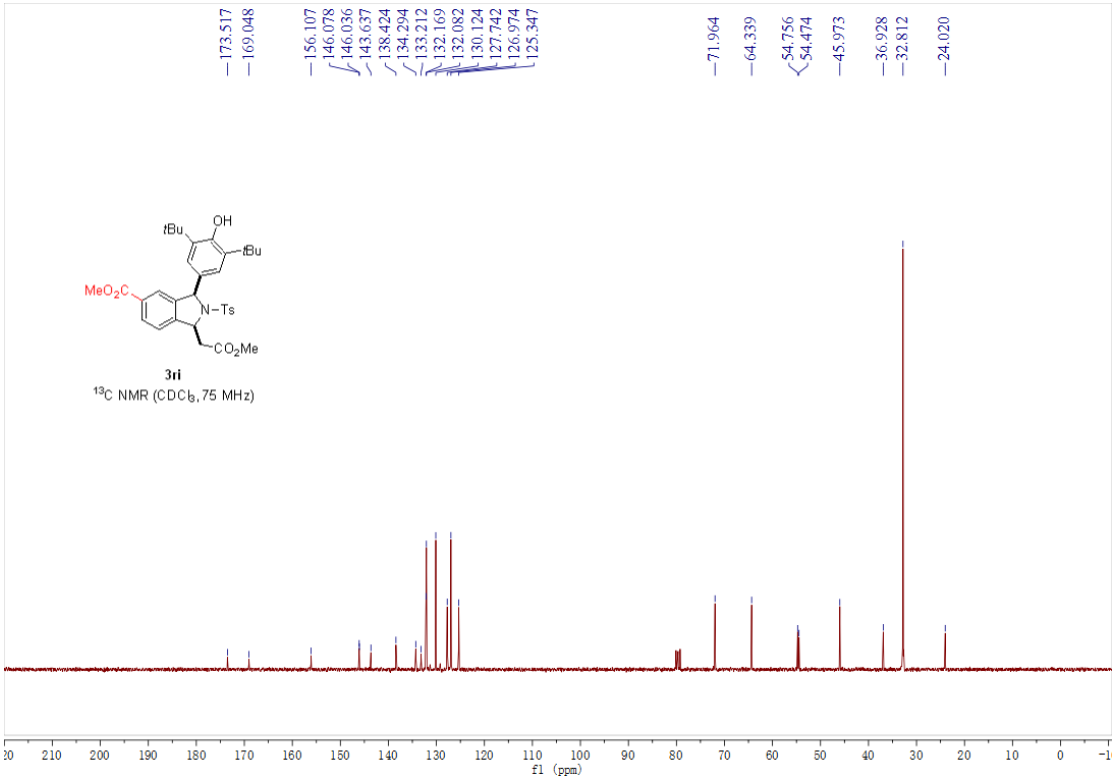

7.6508
7.6244
7.1624
7.1359
7.1114
7.0260
6.9975
6.5806
6.5542
6.2731
5.8145
5.4569
5.4420
5.4270
5.4126
5.1122
3.7606
3.3539
3.3392
3.3023
3.2875
2.8292
2.7897
2.7603
2.7379
2.7086
2.3120
1.3987
tBu
OH
tBu
Me2N
N–Ts
CO2Me
3qi
1H NMR (CDCl3, 300 MHz)
2.02
4.01
1.01
1.01
1.00
1.00
1.00
1.00
3.04
1.00
7.13
3.03
18.21
f1 (ppm)


171.510
153.169
150.800
143.205
141.481
135.744
135.484
132.746
129.532
127.567
126.559
123.943
123.010
112.779
106.700
69.719
61.723
51.737
44.352
40.644
34.380
30.322
21.474
tBu
OH
tBu
Me2N
N–Ts
CO2Me
3qi
13C NMR (CDCl3, 75 MHz)
f1 (ppm)



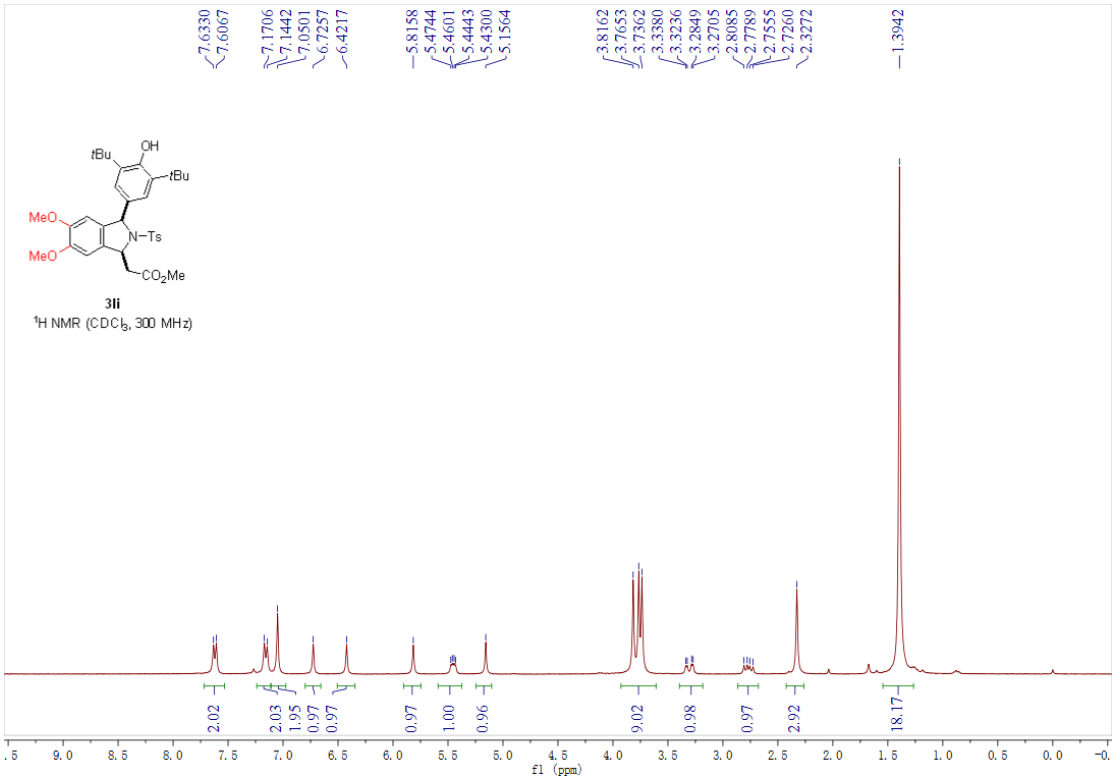
3ri

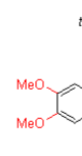
^{1}H NMR ($CDCl_3$, 300 MHz)



3ri

^{13}C NMR ($CDCl_3$, 75 MHz)



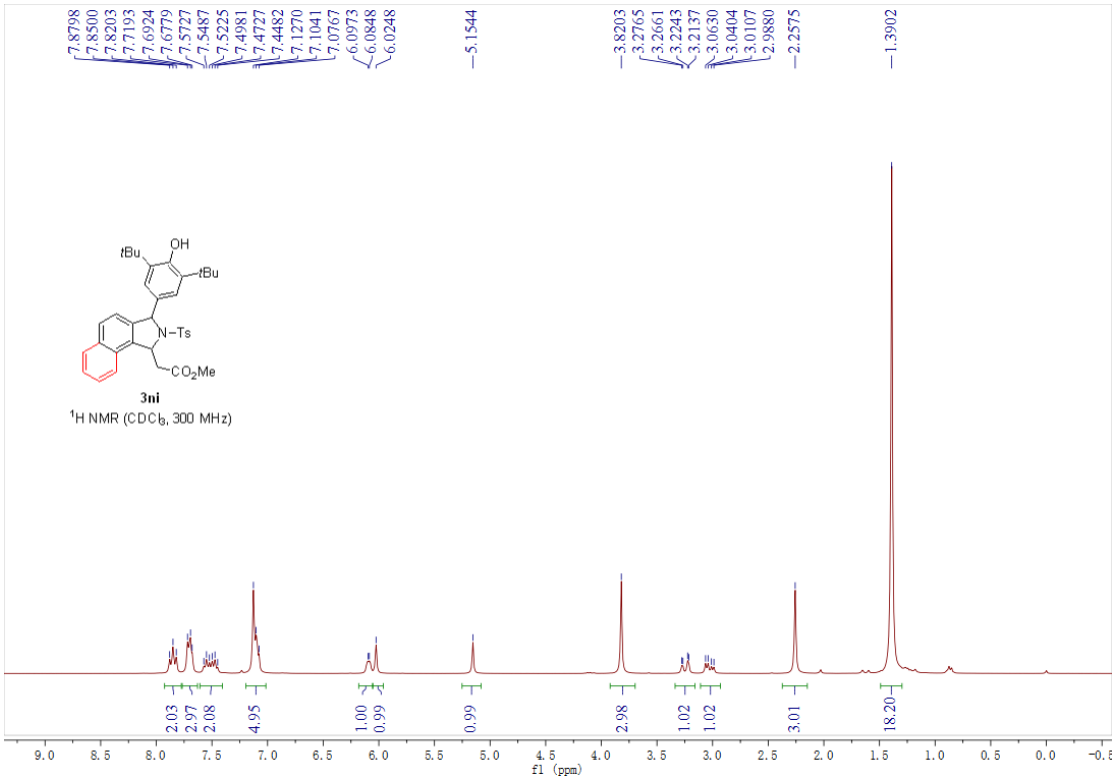


3li

^{1}H NMR ($CDCl_3$, 300 MHz)

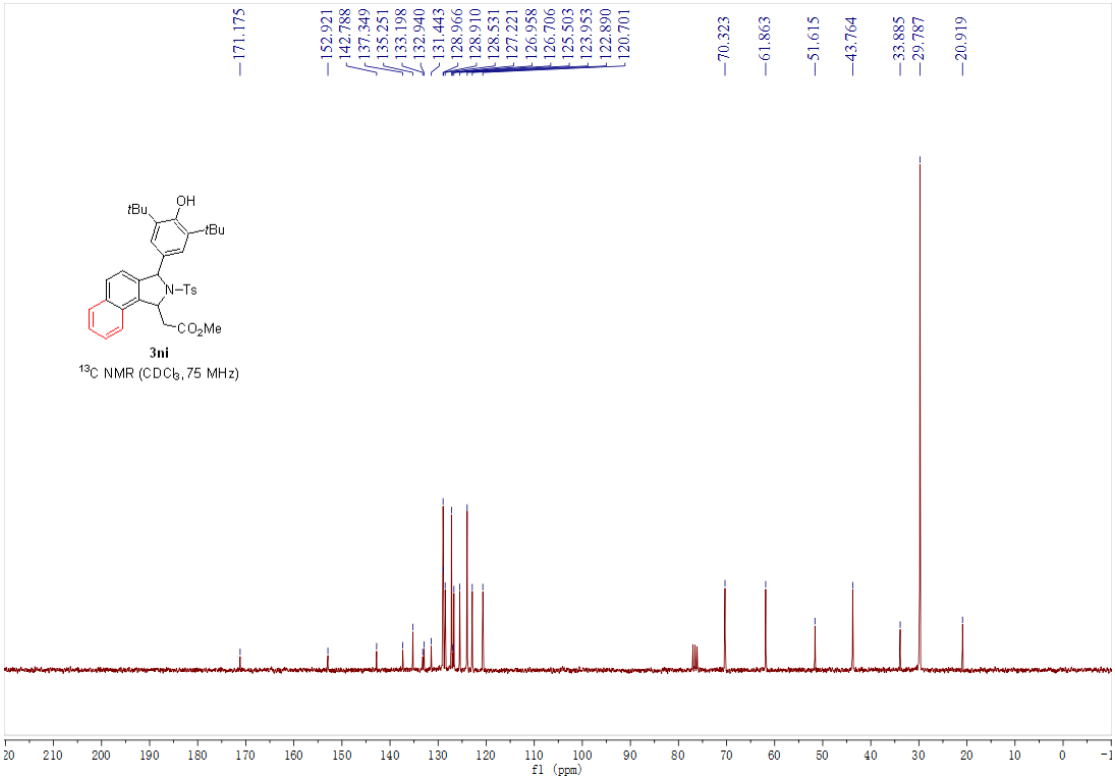
3li

^{13}C NMR ($CDCl_3$, 75 MHz)



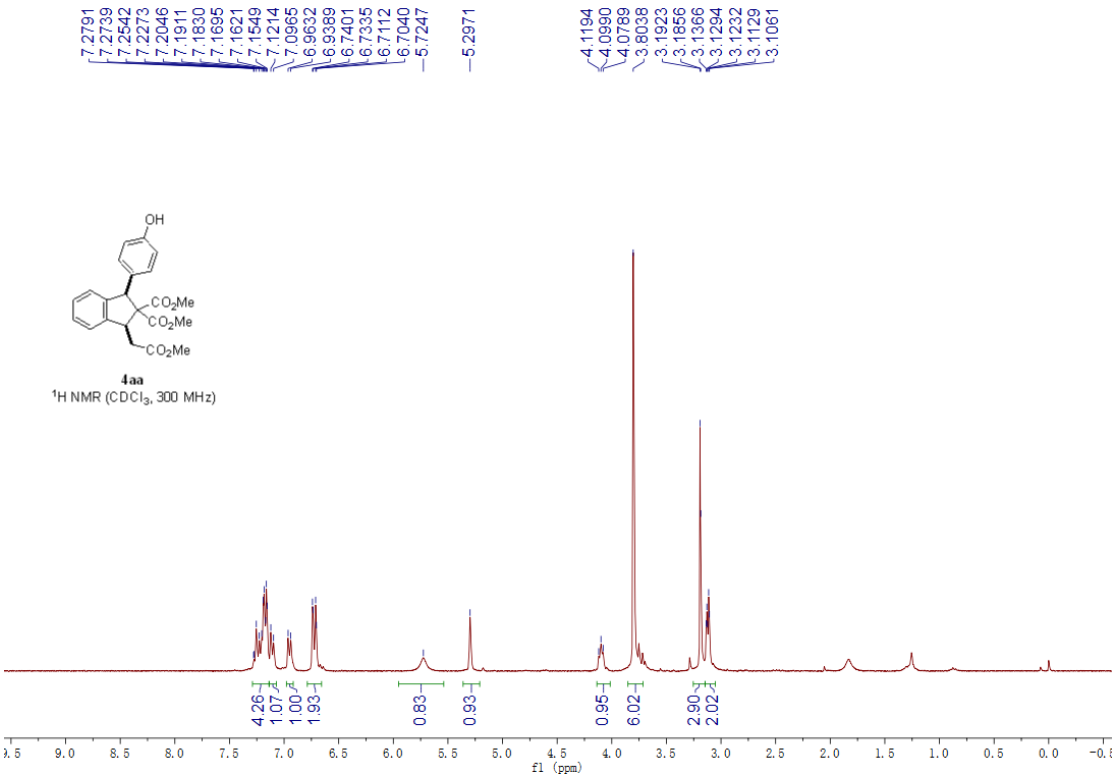
3ni

^{1}H NMR ($CDCl_3$, 300 MHz)



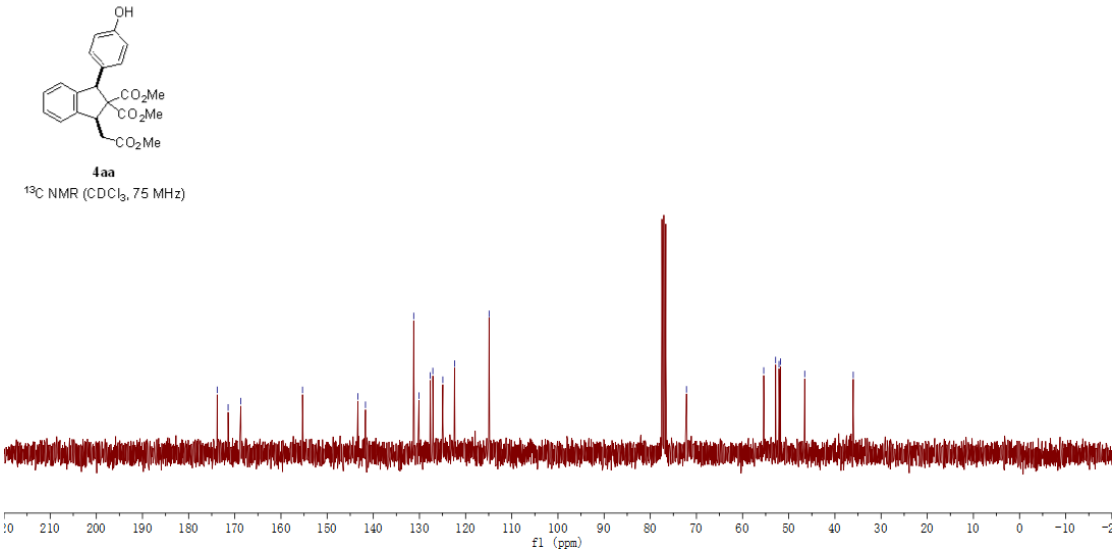
3ni

^{13}C NMR ($CDCl_3$, 75 MHz)



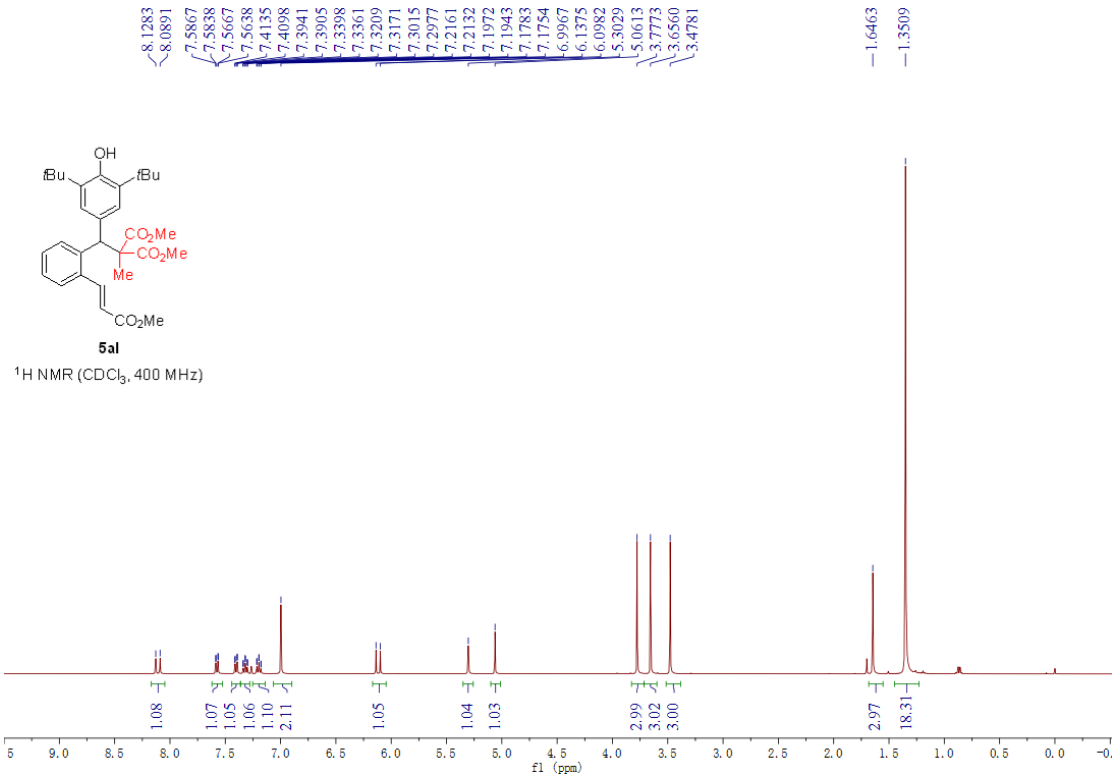
4aa

^{1}H NMR ($CDCl_3$, 300 MHz)



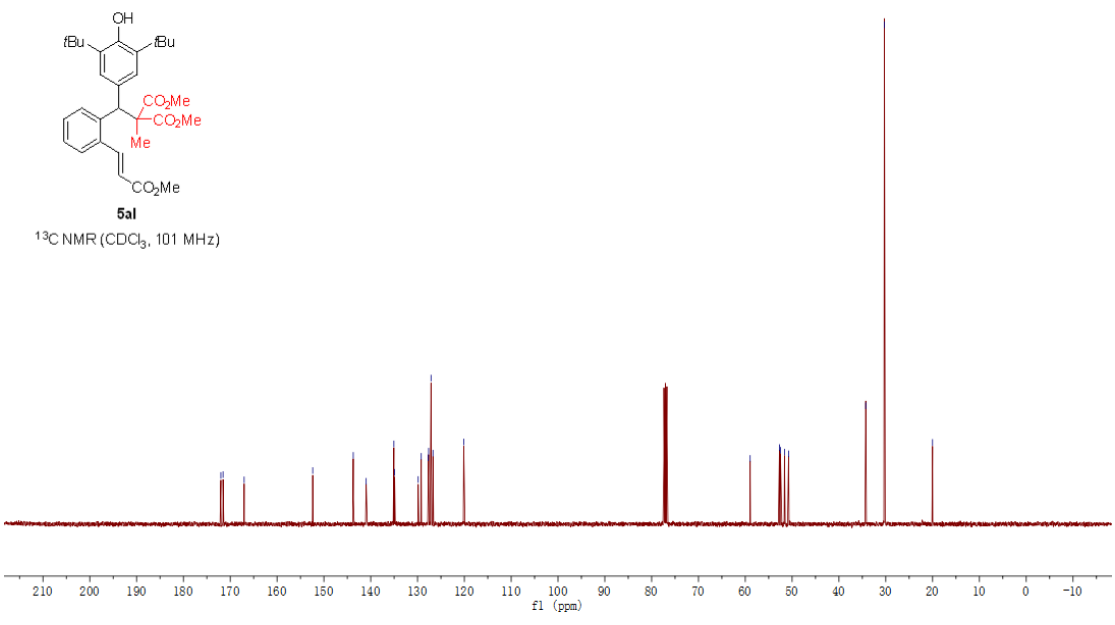
4aa

^{13}C NMR ($CDCl_3$, 75 MHz)



5al

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



5al

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