Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Content

1. General methods

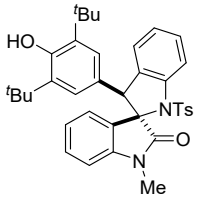
Unless otherwise mentioned, all reagents were purchased from commercial suppliers without further purification. Solvent purification was conducted according to Purification of Laboratory Chemicals (Peerrin, D. D.; Armarego, W. L. and Perrins, D. R., Pergamon Press: Oxford, 1980). Reactions were monitored using Merck Kieselgel $60F_{254}$ aluminium plates. TLC was visualized by UV fluorescence (254 nm) then one of the following: $KMnO_4$, phosphomolybdic acid, ninhydrin, *p*-anisaldehyde, vanillin. The Displacement ellipsoids are scaled to the 30% probability level. If not specially mentioned, flash column chromatography was performed using Yantai xinnuo Chemicals (China) (particle size 0.040–0.063 mm). NMR spectra were recorded on JEOL 400 instruments and calibrated by using residual undeuterated chloroform-d (δ ^{1}H = 7.26 ppm, δ ^{13}C = 77.0 ppm) and residual undeuterated dimethyl sulfoxide-d_6 (δ ^{1}H = 2.54 ppm, δ ^{13}C = 40.0 ppm) as internal references. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, b = broad, td = triple doublet, dt = double triplet, dq = double quartet, m = multiplet. Infrared (IR) spectra were recorded on an iCAN 9-T FT-IR spectrometer. High-resolution mass spectra (HRMS) were recorded on a Thermo Fisher Q Exactive Orbitrap mass spectrometer using ESI (electrosprayionization) as ionization method. *Para*-quinone methide **1**[1] and 3-chlorooxindoles **2**[2] were synthesized according to the literature methods.

2. Experimental procedures and characterization data

Procedure for synthesis of 3

Typical Procedure: To a stirred solution of *para*-quinone methides (0.15 mmol, 1.5 equiv) and 3-chloroooxindoles (0.1 mmol, 1 equiv) in CH_3Cl (1.0 mL) was added TMG (0.25 mmol, 2.5 equiv) at -20 ℃. The reaction was stirred at -20 ℃ for 30 min. The reaction mixture was directly charged to column chromatography on silica gel (PE:DCM:EA = 30:1:1-10:1:1) to give the cycloadduct.

3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-1'-methyl-1-tosyl-2,3'-spirobi[indolin]-2'-one (3aa)



Red solid, isolated yield 94% (64 mg);

dr > 19:1;

mp: 242.0-242.9 °C;

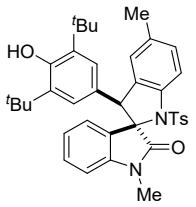
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (d, J = 8.3 Hz, 2H), 7.27 (d, J = 8.5 Hz, 3H), 7.24-7.20 (m, 1H), 7.15 (d, J = 7.4 Hz, 1H), 7.06-7.01 (m, 2H), 6.84 (d, J = 7.3 Hz, 1H), 6.74-6.70 (m, 3H), 6.48 (d, J = 7.8 Hz, 1H), 5.15 (s, 1H), 5.00 (s, 1H), 3.20 (s, 3H), 2.40 (s, 3H), 1.25 (s, 18H);

^{13}C NMR (101 MHz, $CDCl_3$): δ 175.7, 153.1, 144.1, 142.3, 141.7, 136.4, 135.1, 130.2, 129.5, 129.3, 128.4, 128.3, 126.8, 125.8, 125.3, 123.9, 123.4, 122.8, 121.9, 112.4, 107.9, 78.5, 59.0, 34.0, 30.1, 26.5, 21.6;

IR (neat): *v* 3855, 2923, 1719, 1560, 1458, 1349, 1259, 1167, 1091, 749 cm^{-1};

HRMS (ESI): m/z $[M - H]^+$ calcd. for $C_{37}H_{39}N_2O_4S$: 607.2636; found: 607.2635.

3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-1',5-dimethyl-1-tosyl-2,3'-spirobi[indolin]-2'-one (3ba)



White solid, isolated yield 94% (80 mg);

dr > 19:1;

mp: 288.9-289.7 °C;

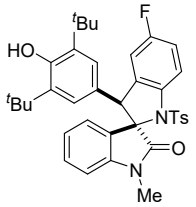
^1H NMR (400 MHz, $CDCl_3$): δ 8.01 (d, J = 8.1 Hz, 2H), 7.27-7.25 (m, 2H), 7.17 (d, J = 8.1 Hz, 1H), 7.06-6.98 (m, 3H), 6.85 (d, J = 7.3 Hz, 1H), 6.74-6.70 (m, 3H), 6.48 (d, J = 7.8 Hz, 1H), 5.12 (s, 1H), 5.01 (s, 1H), 3.19 (s, 3H), 2.39 (s, 3H), 2.27 (s, 3H), 1.25 (s, 18H);

^{13}C NMR (101 MHz, $CDCl_3$): δ 175.6, 153.1, 144.0, 141.7, 140.0, 136.5, 135.0, 132.5, 130.3, 129.5, 129.2, 128.6, 128.3, 126.8, 126.0, 125.8, 123.9, 123.5, 121.6, 112.0, 107.8, 78.5, 59.0, 34.0, 30.1, 26.5, 21.6, 20.8;

IR (neat): *v* 3789, 2960, 1726, 1613, 1438, 1347, 1165, 1050, 809, 750 cm^{-1};

HRMS (ESI): m/z $[M - H]^+$ calcd. for $C_{38}H_{41}N_2O_4S$: 621.2793; found: 621.2788.

3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-5-fluoro-1'-methyl-1-tosyl-2,3'-spirobi[indolin]-2'-one (3ca)



White solid, isolated yield 84% (52 mg);

dr > 19:1;

mp: 262.8-263.7 °C;

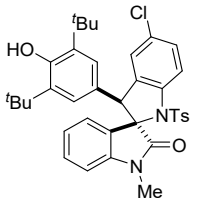
^1H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, J = 8.3 Hz, 2H), 7.29-7.26 (m, 2H), 7.21 (dd, J = 8.7, 4.2 Hz, 1H), 7.06 (t, J = 7.6 Hz, 1H), 6.94-6.84 (m, 3H), 6.77-6.71 (m, 3H), 6.49 (d, J = 7.8 Hz, 1H), 5.11 (s, 1H), 5.02 (s, 1H), 3.19 (s, 3H), 2.40 (s, 3H), 1.25 (s, 18H);

^{13}C NMR (101 MHz, $CDCl_3$): δ 175.3, 160.3 (d, $J_{C\text{-}F}$ = 240.4 Hz), 153.3, 144.3, 141.7, 138.3, 136.3, 135.3, 132.6 (d, $J_{C\text{-}F}$ = 8.0 Hz), 129.6, 129.4, 128.3, 126.6, 125.7, 123.9, 122.8, 122.0, 114.8 (d, $J_{C\text{-}F}$ = 23.5 Hz), 113.0（d, $J_{C\text{-}F}$ = 1.2 Hz), 112.9 (d, $J_{C\text{-}F}$ = 14.6 Hz), 108.0, 78.9, 58.8, 34.0, 30.1, 26.5, 21.6;

IR (neat): *v* 3857, 2920, 1725, 1612, 1440, 1351, 1261, 1165, 1090, 1022, 750 cm^{-1};

HRMS (ESI): m/z [M - H]$^+$ calcd. for $C_{37}H_{38}FN_2O_4S$: 625.2542; found: 625.2541.

5-chloro-3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-1'-methyl-1-tosyl-2,3'-spirobi[indolin]-2'-one (3da)



Red solid, isolated yield >99% (70 mg);

dr > 19:1;

mp: 295.2-296.0 °C;

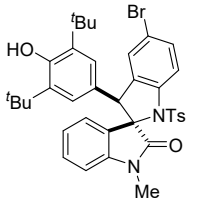
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, J = 8.4 Hz, 2H), 7.28-7.26 (m, 2H), 7.21-7.20 (m, 2H), 7.14-7.13 (m, 1H), 7.06 (td, J = 7.8, 1.2 Hz, 1H), 6.85 (d, J = 7.3 Hz, 1H), 6.75 (t, J = 7.4 Hz, 1H), 6.71 (s, 2H), 6.50 (d, J = 7.8 Hz, 1H), 5.11 (s, 1H), 5.04 (s, 1H), 3.19 (s, 3H), 2.40 (s, 3H), 1.25 (s, 18H);

^{13}C NMR (101 MHz, $CDCl_3$): δ 175.2, 153.3, 144.4, 141.6, 140.9, 136.0, 135.2, 132.4, 129.6, 129.5, 128.3, 128.23, 128.19, 126.3, 125.7, 125.4, 123.8, 122.6, 122.0, 113.2, 108.0, 78.8, 58.8, 34.0, 30.0, 26.5, 21.6;

IR (neat): v 3790, 2923, 1726, 1612, 1468, 1441, 1357, 1165, 749 cm^{-1};

HRMS (ESI): m/z [M - H]$^+$ calcd. for $C_{37}H_{38}ClN_2O_4S$: 641.2246; found: 641.2244.

5-bromo-3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-1'-methyl-1-tosyl-2,3'-spirobi[indolin]-2'-one (3ea)



Red solid, isolated yield >99% (82 mg);

dr > 19:1;

mp: 293.2-294.1 °C;

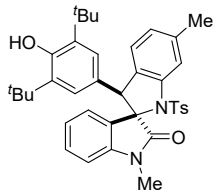
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, J = 8.3 Hz, 2H), 7.34 (d, J = 8.6 Hz, 1H), 7.29-7.26 (m, 3H), 7.16 (d, J = 8.5 Hz, 1H), 7.06 (td, J = 7.7, 1.2 Hz, 1H), 6.85 (d, J = 7.3 Hz, 1H), 6.75 (t, J = 7.5 Hz, 1H), 6.70 (s, 2H), 6.50 (d, J = 7.8 Hz, 1H), 5.12 (s, 1H), 5.04 (s, 1H), 3.19 (s, 3H), 2.40 (s, 3H), 1.25 (s, 18H);

^{13}C NMR (101 MHz, $CDCl_3$): δ 175.2, 153.3, 144.4, 141.7, 141.5, 136.0, 135.3, 132.8, 131.1, 129.6, 129.5, 128.31, 128.30, 126.4, 125.7, 123.8, 122.6, 122.0, 115.5, 113.7, 108.0, 78.7, 58.8, 34.0, 30.1, 26.5, 21.6;

IR (neat): *v* 3638, 2956, 1727, 1613, 1468, 1350, 1164, 1091, 1022, 806, 749 cm^{-1};

HRMS (ESI): m/z $[M - H]^+$ calcd. for $C_{37}H_{38}BrN_2O_4S$: 685.1741; found: 685.1737.

3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-1',6-dimethyl-1-tosyl-2,3'-spirobi[indolin]-2'-one (3fa)



Red solid, isolated yield 90% (56 mg);

dr > 19:1;

mp: 267.9-268.8 °C;

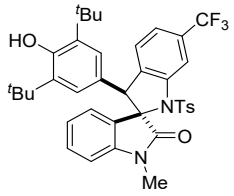
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (d, J = 8.1 Hz, 2H), 7.28-7.26 (m, 2H), 7.10 (s, 1H), 7.05-7.01 (m, 2H), 6.84 (t, J = 7.2 Hz, 2H), 6.74-6.70 (m, 3H), 6.47 (d, J = 7.8 Hz, 1H), 5.10 (s, 1H), 4.99 (s, 1H), 3.19 (s, 3H), 2.40 (s, 3H), 2.35 (s, 3H), 1.24 (s, 18H);

^{13}C NMR (101 MHz, $CDCl_3$): δ 175.7, 153.1, 144.0, 142.5, 141.7, 138.4, 136.5, 135.0, 129.50, 129.49, 129.2, 128.3, 127.3, 126.9, 125.7, 125.0, 123.9, 123.6, 121.9, 113.2, 107.8, 78.7, 58.7, 34.0, 30.1, 26.5, 21.8, 21.6;

IR (neat): *v* 3855, 3650, 2959, 1792, 1718, 1654, 1559, 1507, 1256, 1092, 749 cm^{-1};

HRMS (ESI): m/z $[M - H]^+$ calcd. for $C_{38}H_{41}N_2O_4S$: 621.2793; found: 621.2791.

3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-1'-methyl-1-tosyl-6-(trifluoromethyl)-2,3'-spirobi[indolin]-2'-one (3ga)



White solid, isolated yield 98% (66 mg);

dr > 19:1;

mp: 303.4-304.3 °C;

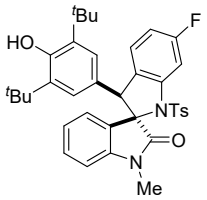
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, J = 8.1 Hz, 2H), 7.53 (s, 1H), 7.30-7.23 (m, 4H), 7.08 (t, J = 7.6 Hz, 1H), 6.81 (d, J = 7.2 Hz, 1H), 6.75 (t, J = 7.4 Hz, 1H), 6.70 (s, 2H), 6.51 (d, J = 7.8 Hz, 1H), 5.14 (s, 1H), 5.04 (s, 1H), 3.21 (s, 3H), 2.41 (s, 3H), 1.25 (s, 18H);

^{13}C NMR (101 MHz, $CDCl_3$): δ 175.2, 153.4, 144.7, 142.8, 141.7, 135.8, 135.3, 134.5, 131.0 (q, $J_{C\text{-}F}$ = 32.2 Hz), 129.7, 129.6, 129.5 (q, $J_{C\text{-}F}$ = 202.4 Hz), 128.3, 126.2, 125.7, 125.4, 123.9, 122.6, 122.1, 120.1 (q, $J_{C\text{-}F}$ = 4.2 Hz), 109.1 (q, $J_{C\text{-}F}$ = 4.0 Hz), 108.1, 78.9, 58.8, 34.0, 30.1, 26.6, 21.6;

IR (neat): ν 3855, 3752, 2921, 1720, 1655, 1431, 1317, 1047, 750, 669 cm^{-1};

HRMS (ESI): m/z $[M - H]^+$ calcd. for $C_{38}H_{38}F_3N_2O_4S$: 675.2510; found: 675.2509.

3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-6-fluoro-1'-methyl-1-tosyl-2,3'-spirobi[indolin]-2'-one (3ha)



White solid, isolated yield >99% (68 mg);

dr > 19:1;

mp: 254.3-255.2 °C;

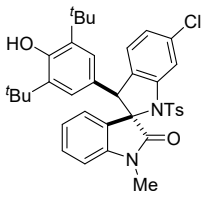
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (d, J = 8.2 Hz, 2H), 7.29 (d, J = 8.0 Hz, 2H), 7.08-7.02 (m, 3H), 6.84 (d, J = 7.2 Hz, 1H), 6.76-6.71 (m, 4H), 6.49 (d, J = 7.8 Hz, 1H), 5.08 (s, 1H), 5.01 (s, 1H), 3.20 (s, 3H), 2.41 (s, 3H), 1.24 (s, 18H);

^{13}C NMR (101 MHz, $CDCl_3$): δ 175.3, 164.1 (d, $J_{C\text{-}F}$ = 243.2 Hz), 153.2, 144.5, 143.6 (d, $J_{C\text{-}F}$ = 11.7 Hz), 141.7, 136.0, 135.2, 129.6, 129.4, 128.3, 126.5, 126.0 (d, $J_{C\text{-}F}$ = 9.8 Hz), 125.7 (d, $J_{C\text{-}F}$ = 2.6 Hz), 125.6, 123.9, 123.2, 122.0, 109.4 (d, $J_{C\text{-}F}$ = 22.6 Hz), 107.9, 101.3 (d, $J_{C\text{-}F}$ = 28.9 Hz), 79.1, 58.3, 34.0, 30.1, 26.5, 21.6;

IR (neat): ν 3855, 2917, 1725, 1612, 1491, 1438, 1355, 1255, 1163, 1091, 750 cm^{-1};

HRMS (ESI): m/z $[M - H]^+$ calcd. for $C_{37}H_{38}FN_2O_4S$: 625.2542; found: 625.2537.

6-chloro-3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-1'-methyl-1-tosyl-2,3'-spirobi[indolin]-2'-one (3ia)



White solid, isolated yield 96% (42 mg);

dr > 19:1;

mp: 285.4-286.3 °C;

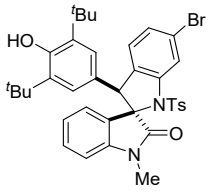
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (d, J = 8.1 Hz, 2H), 7.31-7.26 (m, 3H), 7.08-6.99 (m, 3H), 6.84 (d, J = 7.3 Hz, 1H), 6.75 (t, J = 7.5 Hz, 1H), 6.70 (s, 2H), 6.49 (d, J = 7.8 Hz, 1H), 5.07 (s, 1H), 5.02 (s, 1H), 3.19 (s, 3H), 2.42 (s, 3H), 1.24 (s, 18H);

^{13}C NMR (101 MHz, $CDCl_3$): δ 175.2, 153.2, 144.5, 143.4, 141.7, 136.0, 135.2, 133.9, 129.7, 129.5, 129.0, 128.3, 126.5, 126.0, 125.6, 123.9, 122.91, 122.90, 122.0, 112.9, 108.0, 78.9, 58.5, 34.0, 30.1, 26.5, 21.6;

IR (neat): v 3855, 2922, 1726, 1618, 1474, 1352, 1237, 1166, 1091, 751 cm^{-1};

HRMS (ESI): m/z [M - H]$^+$ calcd. for $C_{37}H_{38}ClN_2O_4S$: 641.2246; found: 641.2244.

6-bromo-3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-1'-methyl-1-tosyl-2,3'-spirobi[indolin]-2'-one (3ja)



White solid, isolated yield >99% (70 mg);

dr > 19:1;

mp: 293.2-294.0 °C;

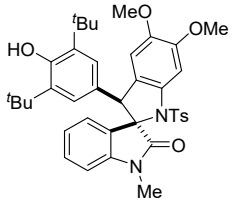
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (d, J = 8.1 Hz, 2H), 7.44 (s, 1H), 7.30 (d, J = 8.0 Hz, 2H), 7.16 (d, J = 7.9 Hz, 1H), 7.06 (t, J = 7.8 Hz, 1H), 7.00 (d, J = 7.9 Hz, 1H), 6.84 (d, J = 7.3 Hz, 1H), 6.75 (t, J = 7.5 Hz, 1H), 6.69 (s, 2H), 6.49 (d, J = 7.8 Hz, 1H), 5.05 (s, 1H), 5.02 (s, 1H), 3.19 (s, 3H), 2.42 (s, 3H), 1.24 (s, 18H);

^{13}C NMR (101 MHz, $CDCl_3$): δ 175.2, 153.3, 144.5, 143.6, 141.6, 136.0, 135.2, 129.7, 129.6, 129.5, 128.3, 126.4, 126.4, 125.9, 125.6, 123.9, 122.8, 122.0, 121.7, 115.7, 108.0, 78.9, 58.6, 34.0, 30.1, 26.5, 21.6;

IR (neat): v 3776, 2921, 1726, 1659, 1598, 1468, 1352, 1165, 750 cm^{-1};

HRMS (ESI): m/z [M - H]$^+$ calcd. for $C_{37}H_{38}BrN_2O_4S$: 685.1741; found: 685.1738.

1-((4-chlorophenyl)sulfonyl)-3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-1'-methyl-2,3'-spirobi[indolin]-2'-one (3ka)



White solid, isolated yield 56% (38 mg);

dr > 19:1;

mp: 232.2-233.0 °C;

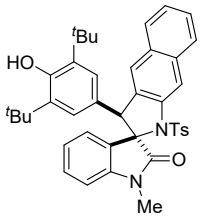
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (d, J = 8.3 Hz, 2H), 7.26-7.24 (m, 2H), 7.03 (td, J = 7.7, 1.1 Hz, 1H), 6.99 (s, 1H), 6.80 (d, J = 7.4 Hz, 1H), 6.75 (s, 2H), 6.71-6.67 (m, 2H), 6.48 (d, J = 7.7 Hz, 1H), 5.12 (s, 1H), 5.00 (s, 1H), 3.88 (s, 3H), 3.74 (s, 3H), 3.21 (s, 3H), 2.40 (s, 3H), 1.25 (s, 18H);

^{13}C NMR (101 MHz, $CDCl_3$): δ 175.5, 153.1, 148.9, 145.1, 144.1, 141.8, 136.7, 135.8, 135.1, 129.5, 129.2, 128.2, 126.7, 125.6, 124.0, 123.9, 121.9, 120.7, 109.0, 107.8, 97.9, 78.5, 58.7, 56.5, 56.1, 34.0, 30.1, 26.5, 21.6;

IR (neat): v 3650, 2923, 1734, 1718, 1507, 1458, 1340, 1164, 1091, 748 cm^{-1};

HRMS (ESI): m/z [M - H]$^+$ calcd. for $C_{39}H_{43}N_2O_6S$: 667.2847; found: 667.2846.

3-(3,5-di-tert-*butyl*-4-hydroxyphenyl)-1'-methyl-1-tosyl-1,3-dihydrospiro[benzo[*f*]indole-2,3'-indolin]-2'-one (3la)



Red solid, isolated yield >99% (72 mg);

dr > 19:1;

mp: 260.8-261.5 °C;

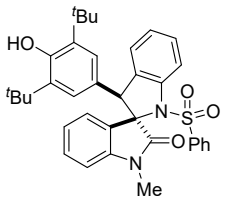
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 (d, J = 8.1 Hz, 2H), 7.79 (d, J = 8.2 Hz, 1H), 7.68 (d, J = 8.0 Hz, 1H), 7.63 (s, 1H), 7.59 (s, 1H), 7.46 (t, J = 7.1 Hz, 1H), 7.36 (t, J = 7.3 Hz, 1H), 7.29 (d, J = 8.1 Hz, 2H), 7.06 (t, J = 7.7 Hz, 1H), 6.85-6.83 (m, 3H), 6.74 (t, J = 7.5 Hz, 1H), 6.50 (d, J = 7.8 Hz, 1H), 5.25 (s, 1H), 5.06 (s, 1H), 3.20 (s, 3H), 2.39 (s, 3H), 1.26 (s, 18H);

^{13}C NMR (101 MHz, $CDCl_3$): δ 175.2, 153.3, 144.3, 141.7, 140.3, 136.1, 135.2, 133.8, 131.7, 130.3, 129.6, 129.4, 128.4, 127.7, 127.5, 126.9, 126.3, 125.9, 124.6, 124.3, 123.7, 122.9, 122.1, 108.6, 108.0, 78.6, 58.9, 34.1, 30.1, 26.5, 21.6;

IR (neat): v 3661, 2967, 1725, 1613, 1349, 1241, 1165, 1051, 896, 749 cm^{-1};

HRMS (ESI): m/z [M - H]$^+$ calcd. for $C_{41}H_{41}N_2O_4S$: 657.2793; found: 657.2789.

3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-1'-methyl-1-(phenylsulfonyl)-2,3'-spirobi[indolin]-2'-one (3ma)



White solid, isolated yield 94% (56 mg);

dr > 19:1;

mp: 198.7-199.3 °C;

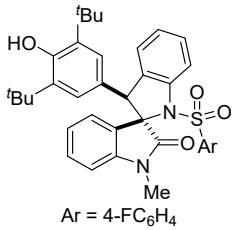
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (d, J = 7.6 Hz, 2H), 7.56 (t, J = 7.2 Hz, 1H), 7.50-7.47 (m, 2H), 7.30-7.26 (m, 2H), 7.16 (d, J = 7.4 Hz, 1H), 7.06-7.02 (m, 2H), 6.83 (d, J = 7.3 Hz, 1H), 6.74-6.70 (m, 3H), 6.49 (d, J = 7.8 Hz, 1H), 5.16 (s, 1H), 5.00 (s, 1H), 3.21 (s, 3H), 1.25 (s, 18H);

^{13}C NMR (101 MHz, $CDCl_3$): δ 175.6, 153.1, 142.2, 141.7, 139.4, 135.1, 133.2, 130.3, 129.3, 128.9, 128.32, 128.30, 126.7, 125.7, 125.4, 123.9, 123.3, 123.0, 122.0, 112.4, 107.9, 78.5, 59.0, 34.0, 30.1, 26.5;

IR (neat): v 3855, 3752, 2961, 1721, 1616, 1474, 1437, 1351, 1166, 1048, 750 cm^{-1};

HRMS (ESI): m/z [M - H]$^+$ calcd. for $C_{36}H_{37}N_2O_4S$: 593.2480; found: 593.2478.

3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-1-((4-fluorophenyl)sulfonyl)-1'-methyl-2,3'-spirobi[indolin]-2'-one (3na)



White solid, isolated yield 85% (52 mg);

dr > 19:1;

mp: 223.5-224.2 °C;

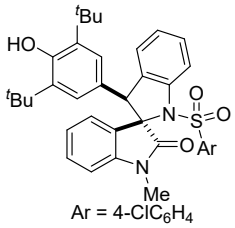
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19 (dd, J = 8.6, 5.1 Hz, 2H), 7.29-7.22 (m, 2H), 7.17-7.13 (m, 3H), 7.05 (t, J = 7.4 Hz, 2H), 6.83 (d, J = 7.3 Hz, 1H), 6.75-6.72 (m, 3H), 6.50 (d, J = 7.8 Hz, 1H), 5.15 (s, 1H), 5.01 (s, 1H), 3.20 (s, 3H), 1.25 (s, 18H);

^{13}C NMR (101 MHz, $CDCl_3$): δ 175.7, 166.7 (d, $J_{C\text{-}F}$ = 254.3 Hz), 153.2, 142.0, 141.7, 135.4 (d, $J_{C\text{-}F}$ = 3.5 Hz), 135.1, 131.3 (d, $J_{C\text{-}F}$ = 9.6 Hz), 130.3, 129.4, 128.4, 126.7, 125.7, 125.5, 123.8, 123.21, 123.16, 122.0, 116.3 (d, $J_{C\text{-}F}$ = 22.4 Hz), 112.3, 108.0, 78.6, 59.0, 34.0, 30.1, 26.5;

IR (neat): v 3855, 3650, 2922, 1718, 1654, 1559, 1507, 1458, 1049, 750 cm^{-1};

HRMS (ESI): m/z [M - H]$^+$ calcd. for $C_{36}H_{36}FN_2O_4S$: 611.2385; found: 611.2383.

1-((4-chlorophenyl)sulfonyl)-3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-1'-methyl-2,3'-spirobi[indolin]-2'-one (3oa)



White solid, isolated yield 72% (46 mg);

mp: 214.7-215.6 °C;

dr > 19:1;

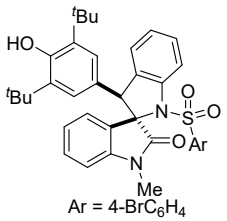
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 (d, J = 8.8 Hz, 2H), 7.44 (d, J = 8.8 Hz, 2H), 7.30-7.26 (m, 2H), 7.17 (d, J = 7.2 Hz, 1H), 7.08-7.03 (m, 2H), 6.81 (dd, J = 7.4, 0.9 Hz, 1H), 6.75-6.71 (m, 3H), 6.50 (d, J = 7.8 Hz, 1H), 5.15 (s, 1H), 5.01 (s, 1H), 3.20 (s, 3H), 1.25 (s, 18H);

^{13}C NMR (101 MHz, $CDCl_3$): δ 175.6, 153.2, 142.0, 141.7, 139.8, 137.9, 135.2, 130.3, 129.8, 129.4, 129.2, 128.4, 126.7, 125.7, 125.5, 123.8, 123.3, 123.2, 122.0, 112.4, 108.0, 78.5, 59.0, 34.0, 30.1, 26.5;

IR (neat): v 3752, 2922, 1735, 1654, 1560, 1458, 1437, 1023, 806, 747 cm^{-1};

HRMS (ESI): m/z $[M - H]^+$ calcd. for $C_{36}H_{36}ClN_2O_4S$: 623.2090; found: 627.2087.

1-((4-chlorophenyl)sulfonyl)-3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-1'-methyl-2,3'-spirobi[indolin]-2'-one (3pa)



White solid, isolated yield 82% (56 mg);

dr > 19:1;

mp: 243.7-244.5 °C;

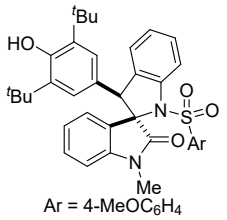
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (d, J = 8.8 Hz, 2H), 7.61 (d, J = 8.8 Hz, 2H), 7.30-7.23 (m, 2H), 7.17 (d, J = 7.1 Hz, 1H), 7.08-7.03 (m, 2H), 6.81 (dd, J = 7.4, 0.9 Hz, 1H), 6.74-6.70 (m, 3H), 6.50 (d, J = 7.8 Hz, 1H), 5.14 (s, 1H), 5.00 (s, 1H), 3.20 (s, 3H), 1.24 (s, 18H);

^{13}C NMR (101 MHz, $CDCl_3$): δ 175.5, 153.2, 141.9, 141.7, 138.4, 135.2, 132.2, 130.3, 129.8, 129.4, 128.44, 128.42, 126.6, 125.7, 125.5, 123.8, 123.3, 123.2, 122.0, 112.4, 108.0, 78.5, 59.0, 34.0, 30.1, 26.5;

IR (neat): v 3650, 2922, 1734, 1717, 1654, 1541, 1458, 1168, 1089, 742 cm^{-1};

HRMS (ESI): m/z [M - H]$^+$ calcd. for $C_{36}H_{36}BrN_2O_4S$: 671.1585; found: 671.1584.

3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-1-((4-methoxyphenyl)sulfonyl)-1'-methyl-2,3'-spirobi[indolin]-2'-one (3qa)



Yellow solid, isolated yield 90% (56 mg);

dr > 19:1;

mp: 216.9-217.7 °C;

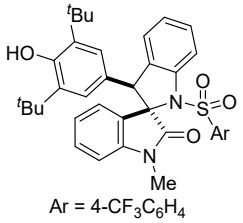
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 (d, J = 8.9 Hz, 2H), 7.27-7.21 (m, 2H), 7.15 (d, J = 7.2 Hz, 1H), 7.06-7.00 (m, 2H), 6.94 (d, J = 8.9 Hz, 2H), 6.84 (d, J = 7.2 Hz, 1H), 6.74-6.71 (m, 3H), 6.48 (d, J = 7.8 Hz, 1H), 5.14 (s, 1H), 5.00 (s, 1H), 3.84 (s, 3H), 3.20 (s, 3H), 1.25 (s, 18H);

^{13}C NMR (101 MHz, $CDCl_3$): δ 175.8, 163.3, 153.1, 142.3, 141.7, 135.1, 130.9, 130.6, 130.2, 129.3, 128.3, 126.8, 125.7, 125.3, 123.9, 123.4, 122.8, 121.9, 114.0, 112.3, 107.9, 78.5, 59.0, 55.6, 34.0, 30.1, 26.5;

IR (neat): v 3855, 3650, 2920, 1718, 1654, 1560, 1458, 1261, 1161, 1028, 750 cm^{-1};

HRMS (ESI): m/z [M - H]$^+$ calcd. for $C_{37}H_{39}N_2O_5S$: 623.2585; found: 623.2584.

3-(3,5-di-tert-butyl-4-hydroxyphenyl)-1'-methyl-1-((4-(trifluoromethyl)phenyl)sulfonyl)-2,3'-spirobi[indolin]-2'-one (3ra)



White solid, isolated yield 68% (46 mg);

dr > 19:1;

mp: 207.5-208.4 °C;

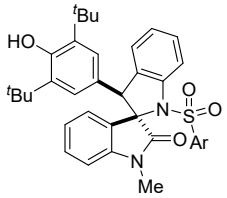
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25 (d, J = 8.2 Hz, 2H), 7.73 (d, J = 8.4 Hz, 2H), 7.35 (d, J = 7.9 Hz, 1H), 7.29 (s, 1H), 7.18 (d, J = 7.4 Hz, 1H), 7.09-7.03 (m, 2H), 6.80-6.65 (m, 4H), 6.51 (d, J = 7.8 Hz, 1H), 5.16 (s, 1H), 5.01 (s, 1H), 3.21 (s, 3H), 1.24 (s, 18H);

^{13}C NMR (101 MHz, $CDCl_3$): δ 175.4, 153.2, 142.9 (q, $J_{C\text{-}F}$ = 31.9 Hz), 141.8, 141.7, 135.2, 130.4, 129.5, 128.8, 128.7, 128.5, 128.0, 126.6, 126.0 (q, $J_{C\text{-}F}$ = 3.9 Hz), 125.7, 125.6 (q, $J_{C\text{-}F}$ = 271.1 Hz), 123.8, 123.5, 123.1, 122.0, 112.4, 108.0, 78.5, 59.0, 34.1, 30.1, 26.6;

IR (neat): ν 3855, 3650, 2922, 1720, 1654, 1580, 1560, 1455, 1260, 1165, 1028, 750 cm^{-1};

HRMS (ESI): m/z [M - H]$^+$ calcd. for $C_{37}H_{36}F_3N_2O_4S$: 661.2353; found: 661.2351.

3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-1'-methyl-1-(naphthalen-2-ylsulfonyl)-2,3'-spirobi[indolin]-2'-one (3sa)



Ar = 2-naphthyl

White solid, isolated yield 80% (54 mg);

dr > 19:1;

mp: 248.0-248.8 °C;

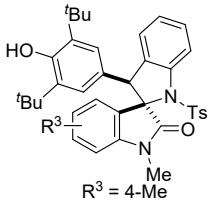
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.57 (d, J = 1.6 Hz, 1H), 8.24 (dd, J = 8.7, 1.9 Hz, 1H), 7.97-7.92 (m, 2H), 7.88 (d, J = 8.0 Hz, 1H), 7.65-7.56 (m, 2H), 7.36 (d, J = 8.0 Hz, 1H), 7.21 (t, J = 7.9 Hz, 1H), 7.15 (d, J = 7.5 Hz, 1H), 7.06-7.00 (m, 2H), 6.81 (d, J = 7.9 Hz, 1H), 6.75 (s, 2H), 6.66 (t, J = 7.0 Hz, 1H), 6.52 (d, J = 7.8 Hz, 1H), 5.19 (s, 1H), 5.00 (s, 1H), 3.24 (s, 3H), 1.25 (s, 18H);

^{13}C NMR (101 MHz, $CDCl_3$): δ 175.7, 153.1, 142.3, 141.8, 136.2, 135.14, 135.12, 131.9, 130.3, 130.0, 129.6, 129.4, 129.3, 129.0, 128.3, 127.8, 127.2, 126.6, 125.9, 125.8, 125.4, 124.0, 123.4, 123.0, 121.9, 112.4, 107.9, 78.5, 59.0, 34.0, 30.1, 26.6;

IR (neat): ν 2920, 1734, 1654, 1559, 1473, 1458, 1341, 1165, 1029, 747 cm^{-1};

HRMS (ESI): m/z [M - H]$^+$ calcd. for $C_{40}H_{39}N_2O_4S$: 643.2636; found: 643.2635.

3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-1',4'-dimethyl-1-tosyl-2,3'-spirobi[indolin]-2'-one (3ab)



R^3 = 4-Me

Yellow solid, isolated yield 98% (70 mg);

dr > 19:1;

mp: 207.5-208.4 °C;

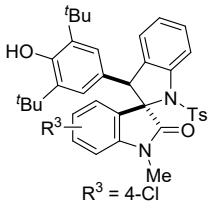
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, J = 8.1 Hz, 2H), 7.53 (d, J = 8.2 Hz, 1H), 7.30-7.22 (m, 4H), 7.13 (d, J = 7.4 Hz, 1H), 7.02 (t, J = 7.4 Hz, 1H), 6.90 (d, J = 7.8 Hz, 1H), 6.57 (s, 2H), 6.49 (d, J = 7.7 Hz, 1H), 5.14 (s, 1H), 4.92 (s, 1H), 2.59 (s, 3H), 2.40 (s, 3H), 2.16 (s, 3H), 1.26 (s, 18H);

^{13}C NMR (101 MHz, $CDCl_3$): δ 171.9, 153.5, 144.0, 143.7, 143.4, 136.6, 135.0, 134.8, 129.7, 129.34, 129.26, 128.4, 127.8, 126.7, 125.9, 125.2, 125.1, 124.2, 122.6, 112.8, 105.4, 77.9, 56.8, 34.1, 30.1, 25.4, 21.6, 17.9;

IR (neat): v 3854, 2922, 1734, 1655, 1606, 1459, 1363, 1243, 1166, 1054, 750 cm^{-1};

HRMS (ESI): m/z [M - H]$^+$ calcd. for $C_{38}H_{41}N_2O_4S$: 621.2793; found: 621.2789.

4'-chloro-3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-1'-methyl-1-tosyl-2,3'-spirobi[indolin]-2'-one (3ac)



Foam, isolated yield 96% (62 mg);

dr > 19:1;

mp: 214.5-215.3 °C;

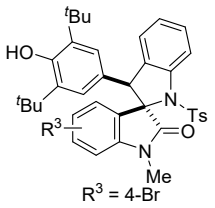
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, J = 8.2 Hz, 2H), 7.53 (d, J = 8.1 Hz, 1H), 7.34-7.28 (m, 2H), 7.26-7.24 (m, 2H), 7.13 (d, J = 7.4 Hz, 1H), 7.08-7.01 (m, 2H), 6.62-6.57 (m, 3H), 5.23 (s, 1H), 5.16 (s, 1H), 2.62 (s, 3H), 2.41 (s, 3H), 1.26 (s, 18H);

^{13}C NMR (101 MHz, $CDCl_3$): δ 171.7, 153.6, 145.8, 144.0, 143.4, 136.7, 135.2, 130.9, 130.7, 129.7, 129.3, 128.3, 127.7, 126.0, 125.5, 124.9, 123.8, 123.5, 122.7, 112.9, 106.3, 77.9, 55.6, 34.1, 30.1, 25.6, 21.6;

IR (neat): v 3637, 2957, 1738, 1611, 1461, 1611, 1461, 1358, 1167, 931, 748 cm^{-1};

HRMS (ESI): m/z [M - H]$^+$ calcd. for $C_{37}H_{38}ClN_2O_4S$: 641.2246; found: 641.2245.

4'-bromo-3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-1'-methyl-1-tosyl-2,3'-spirobi[indolin]-2'-one (3ad)



White solid, isolated yield >99% (70 mg);

dr > 19:1;

mp: 149.1-150.0 °C;

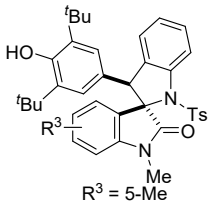
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, J = 8.2 Hz, 2H), 7.52 (d, J = 8.2 Hz, 1H), 7.30-7.22 (m, 5H), 7.13 (d, J = 7.4 Hz, 1H), 7.03 (t, J = 7.4 Hz, 1H), 6.63-6.61 (m, 3H), 5.29 (s, 1H), 5.16 (s, 1H), 2.62 (s, 3H), 2.41 (s, 3H), 1.26 (s, 18H);

^{13}C NMR (101 MHz, $CDCl_3$): δ 171.6, 153.6, 146.0, 144.0, 143.4, 136.7, 135.2, 130.8, 129.7, 129.4, 128.3, 127.9, 127.2, 126.6, 126.0, 124.9, 123.8, 122.7, 119.4, 112.9, 106.8, 78.5, 55.6, 34.1, 30.1, 25.5, 21.6;

IR (neat): v 3632, 2958, 1730, 1606, 1460, 1359, 1239, 1167, 1115, 1091, 931, 749 cm^{-1};

HRMS (ESI): m/z [M - H]$^+$ calcd. for $C_{37}H_{38}BrN_2O_4S$: 685.1741; found: 685.1740.

3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-1',5'-dimethyl-1-tosyl-2,3'-spirobi[indolin]-2'-one (3ae)



White solid, isolated yield 96% (60 mg);

dr > 19:1;

mp: 238.7-239.5 °C;

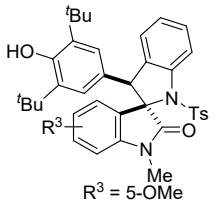
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (d, J = 8.2 Hz, 2H), 7.35 (d, J = 8.1 Hz, 1H), 7.26-7.22 (m, 3H), 7.16 (d, J = 7.3 Hz, 1H), 7.04 (t, J = 7.4 Hz, 1H), 6.82 (d, J = 7.8 Hz, 1H), 6.74 (s, 2H), 6.50 (s, 1H), 6.38 (d, J = 7.9 Hz, 1H), 5.14 (s, 1H), 4.99 (s, 1H), 3.19 (s, 3H), 2.39 (s, 3H), 2.05 (s, 3H), 1.24 (s, 18H);

^{13}C NMR (101 MHz, $CDCl_3$): δ 175.6, 153.1, 144.0, 142.4, 139.5, 136.4, 135.1, 131.0, 130.2, 129.7, 129.4, 128.29, 128.27, 126.3, 125.7, 125.4, 124.8, 123.6, 122.8, 112.4, 107.6, 78.3, 58.8, 34.0, 30.1, 26.6, 21.6, 20.9;

IR (neat): v 3855, 3631, 2921, 1720, 1499, 1459, 1363, 1166, 1091, 932, 750 cm^{-1};

HRMS (ESI): m/z [M - H]$^+$ calcd. for $C_{38}H_{41}N_2O_4S$: 621.2793; found: 621.2791.

3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-5'-methoxy-1'-methyl-1-tosyl-2,3'-spirobi[indolin]-2'-one (3af)



White solid, isolated yield >99% (68 mg);

dr > 19:1;

mp: 207.6-208.3 °C;

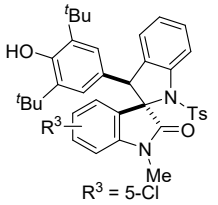
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, J = 8.1 Hz, 2H), 7.33 (d, J = 8.1 Hz, 1H), 7.26-7.21 (m, 3H), 7.15 (d, J = 7.3 Hz, 1H), 7.02 (t, J = 7.4 Hz, 1H), 6.75 (s, 2H), 6.53 (dd, J = 8.3, 2.0 Hz, 1H), 6.39-6.34 (m, 2H), 5.14 (s, 1H), 5.01 (s, 1H), 3.54 (s, 3H), 3.18 (s, 3H), 2.38 (s, 3H), 1.25 (s, 18H);

^{13}C NMR (101 MHz, $CDCl_3$): δ 175.2, 155.0, 153.1, 144.1, 142.3, 136.5, 135.3, 135.1, 130.0, 129.4, 128.3, 128.2, 127.7, 125.7, 125.4, 123.5, 122.9, 112.6, 112.5, 112.0, 108.0, 78.5, 58.8, 55.1, 34.0, 30.1, 26.6, 21.6;

IR (neat): v 3855, 3650, 2958, 1718, 1654, 1458, 1363, 1235, 1165, 1046, 750 cm^{-1};

HRMS (ESI): m/z $[M - H]^+$ calcd. for $C_{38}H_{41}N_2O_5S$: 637.2742; found: 637.2740.

3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-1',5'-dimethyl-1-tosyl-2,3'-spirobi[indolin]-2'-one (3ag)



Red solid, isolated yield 98% (62 mg);

dr > 19:1;

mp: 216.7-217.4 °C;

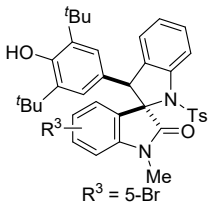
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, J = 8.2 Hz, 2H), 7.39 (d, J = 8.0 Hz, 1H), 7.30-7.23 (m, 3H), 7.17 (d, J = 7.4 Hz, 1H), 7.06 (t, J = 7.4 Hz, 1H), 7.00 (d, J = 8.3 Hz, 1H), 6.73 (s, 2H), 6.59 (s, 1H), 6.42 (d, J = 8.3 Hz, 1H), 5.15 (s, 1H), 5.04 (s, 1H), 3.21 (s, 3H), 2.39 (s, 3H), 1.26 (s, 18H);

^{13}C NMR (101 MHz, $CDCl_3$): δ 175.3, 153.3, 144.4, 142.2, 140.5, 136.1, 135.4, 129.6, 129.5, 129.1, 128.6, 128.1, 127.8, 127.1, 125.6, 125.5, 124.6, 123.3, 123.2, 112.6, 108.8, 77.8, 58.9, 34.0, 30.1, 26.7, 21.6;

IR (neat): v 3752,, 2922, 1734, 1654, 1560, 1458, 1363, 1166, 1028, 804, 667 cm^{-1};

HRMS (ESI): m/z $[M - H]^+$ calcd. for $C_{37}H_{38}ClN_2O_4S$: 641.2246; found: 641.2243.

5'-bromo-3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-1'-methyl-1-tosyl-2,3'-spirobi[indolin]-2'-one (3ah)



White solid, isolated yield >99% (72 mg);

dr > 19:1;

mp: 256.1-257.0 °C;

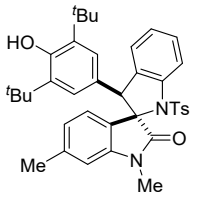
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (d, J = 8.1 Hz, 2H), 7.42 (d, J = 8.1 Hz, 1H), 7.30 (d, J = 7.7 Hz, 1H), 7.23 (d, J = 8.0 Hz, 2H), 7.16 (t, J = 8.1 Hz, 2H), 7.06 (t, J = 7.4 Hz, 1H), 6.73 (s, 2H), 6.67 (s, 1H), 6.38 (d, J = 8.3 Hz, 1H), 5.15 (s, 1H), 5.04 (s, 1H), 3.21 (s, 3H), 2.40 (s, 3H), 1.27 (s, 18H);

^{13}C NMR (101 MHz, $CDCl_3$): δ 175.3, 153.3, 144.4, 142.2, 141.0, 136.1, 135.4, 132.0, 129.6, 129.5, 128.6, 128.02, 128.00, 127.3, 125.51, 125.47, 123.3, 123.2, 114.5, 112.7, 109.3, 77.6, 58.9, 34.0, 30.1, 26.7, 21.6;

IR (neat): v 3854, 3630, 2961, 1734, 1654, 1559, 1458, 1362, 1167, 1121, 807, 738 cm^{-1};

HRMS (ESI): m/z $[M - H]^+$ calcd. for $C_{37}H_{38}BrN_2O_4S$: 685.1741; found: 685.1738.

3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-1',6'-dimethyl-1-tosyl-2,3'-spirobi[indolin]-2'-one (3ai)



Yellow solid, isolated yield 74% (46 mg);

dr > 19:1;

mp: 234.2-235.0 °C;

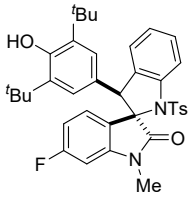
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (d, J = 8.1 Hz, 2H), 7.29-7.26 (m, 2H), 7.24-7.19 (m, 2H), 7.13 (d, J = 7.3 Hz, 1H), 7.01 (t, J = 7.1 Hz, 1H), 6.74-6.73 (m, 3H), 6.55 (d, J = 7.6 Hz, 1H), 6.30 (s, 1H), 5.10 (s, 1H), 5.00 (s, 1H), 3.17 (s, 3H), 2.40 (s, 3H), 2.19 (s, 3H), 1.25 (s, 18H);

^{13}C NMR (101 MHz, $CDCl_3$): δ 175.9, 153.1, 144.1, 142.3, 141.7, 139.5, 136.5, 135.0, 130.4, 129.5, 128.4, 128.2, 125.9, 125.3, 124.0, 123.6, 123.5, 122.8, 122.5, 112.3, 108.7, 78.6, 59.0, 34.0, 30.1, 26.4, 21.7, 21.6;

IR (neat): v 3855, 3752, 2920, 1721, 1618, 1459, 1166, 1029, 750 cm^{-1};

HRMS (ESI): m/z [M - H]$^+$ calcd. for $C_{38}H_{41}N_2O_4S$: 621.2793; found: 621.2788.

3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-6'-fluoro-1'-methyl-1-tosyl-2,3'-spirobi[indolin]-2'-one (3aj)



White solid, isolated yield 93% (58 mg);

dr > 19:1;

mp: 231.7-232.7 °C;

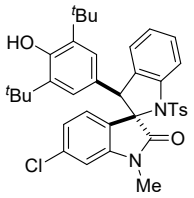
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 (d, J = 8.0 Hz, 2H), 7.29 (d, J = 8.0 Hz, 2H), 7.26-7.20 (m, 2H), 7.15 (d, J = 7.2 Hz, 1H), 7.03 (t, J = 7.2 Hz, 1H), 6.80 (dd, J = 7.9, 5.6 Hz, 1H), 6.73 (s, 2H), 6.41 (d, J = 9.0 Hz, 1H), 6.24 (d, J = 8.8 Hz, 1H), 5.12 (s, 1H), 5.05 (s, 1H), 3.18 (s, 3H), 2.40 (s, 3H), 1.27 (s, 18H);

^{13}C NMR (101 MHz, $CDCl_3$): δ 176.1, 164.9 (d, $J_{C\text{-}F}$ = 245.3 Hz), 153.2, 144.3, 143.5 (d, $J_{C\text{-}F}$ = 11.7 Hz), 142.1, 136.2, 135.3, 129.9, 129.6, 128.4, 128.3, 125.7, 125.4, 125.1 (d, $J_{C\text{-}F}$ = 9.8 Hz), 123.2, 123.0, 122.4 (d, $J_{C\text{-}F}$ = 2.7 Hz), 112.4, 108.0 (d, $J_{C\text{-}F}$ = 22.3 Hz), 96.8 (d, $J_{C\text{-}F}$ = 27.6 Hz), 78.0, 59.0, 34.0, 30.1, 26.6, 21.6;

IR (neat): ν 3855, 3753, 2919, 1735, 1719, 1655, 1560, 1459, 1166, 1031, 750 cm^{-1};

HRMS (ESI): m/z [M - H]$^+$ calcd. for $C_{37}H_{38}FN_2O_4S$: 625.2542; found: 625.2540.

6'-chloro-3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-1'-methyl-1-tosyl-2,3'-spirobi[indolin]-2'-one (3ak)



White solid, isolated yield 96% (62 mg);

dr > 19:1;

mp: 211.5-212.4 °C;

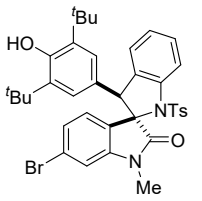
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 (d, J = 8.2 Hz, 2H), 7.30 (d, J = 8.1 Hz, 2H), 7.24-7.20 (m, 2H), 7.14 (d, J = 7.4 Hz, 1H), 7.03 (t, J = 7.5 Hz, 1H), 6.88 (d, J = 7.9 Hz, 1H), 6.74-6.71 (m, 3H), 6.63 (s, 1H), 5.11 (s, 1H), 5.06 (s, 1H), 3.16 (s, 3H), 2.41 (s, 3H), 1.27 (s, 18H);

^{13}C NMR (101 MHz, $CDCl_3$): δ 175.5, 153.3, 144.4, 143.0, 142.1, 136.2, 135.3, 129.9, 129.6, 128.4, 128.3, 126.0, 125.7, 125.3, 125.0, 124.7, 123.0, 122.95, 122.90, 112.4, 111.4, 78.2, 59.1, 34.1, 30.1, 26.6, 21.6;

IR (neat): ν 3637, 2957, 1727, 1607, 1440, 1347, 1240, 1166, 1091, 749, 669 cm^{-1};

HRMS (ESI): m/z $[M - H]^+$ calcd. for $C_{37}H_{38}ClN_2O_4S$: 641.2246; found: 641.2245.

6'-bromo-3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-1'-methyl-1-tosyl-2,3'-spirobi[indolin]-2'-one (3al)



Red solid, isolated yield 96% (62 mg);

dr > 19:1;

mp: 220.1-221.0 °C;

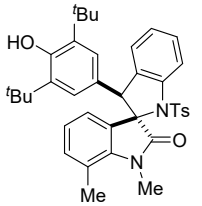
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 (d, J = 8.1 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 7.26-7.21 (m, 2H), 7.14 (d, J = 7.4 Hz, 1H), 7.03 (t, J = 7.2 Hz, 1H), 6.79 (d, J = 7.9 Hz, 1H), 6.73-6.72 (m, 3H), 6.49 (s, 1H), 5.11 (s, 1H), 5.06 (s, 1H), 3.17 (s, 3H), 2.41 (s, 3H), 1.27 (s, 18H);

^{13}C NMR (101 MHz, $CDCl_3$): δ 175.7, 153.3, 144.4, 142.9, 142.1, 136.2, 135.3, 135.0, 129.9, 129.6, 128.4, 128.3, 125.7, 125.5, 125.3, 124.7, 123.04, 122.99, 121.7, 112.4, 108.6, 78.1, 59.1, 34.1, 30.1, 26.6, 21.6;

IR (neat): ν 3854, 3650, 2927, 1734, 1636, 1559, 1541, 1458, 1437, 1166, 669 cm^{-1};

HRMS (ESI): m/z $[M - H]^+$ calcd. for $C_{37}H_{38}BrN_2O_4S$: 685.1741; found: 685.1738.

3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-1',7'-dimethyl-1-tosyl-2,3'-spirobi[indolin]-2'-one (3am)



White solid, isolated yield >99% (68 mg);

dr > 19:1;

mp: 230.2-231.1 °C;

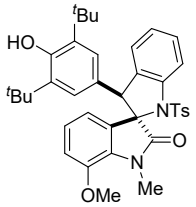
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (d, J = 8.1 Hz, 2H), 7.29 (d, J = 8.2 Hz, 2H), 7.24-7.19 (m, 2H), 7.14 (d, J = 7.3 Hz, 1H), 7.01 (t, J = 7.2 Hz, 1H), 6.76-6.70 (m, 4H), 6.61 (t, J = 7.5 Hz, 1H), 5.12 (s, 1H), 5.02 (s, 1H), 3.50 (s, 3H), 2.40 (s, 3H), 2.29 (s, 3H), 1.27 (s, 18H);

^{13}C NMR (101 MHz, $CDCl_3$): δ 176.6, 153.1, 144.1, 142.4, 139.2, 136.4, 135.0, 132.9, 130.1, 129.5, 128.4, 128.2, 127.6, 125.7, 125.4, 123.4, 122.8, 121.9, 121.7, 119.4, 112.2, 78.2, 59.4, 34.0, 30.1, 30.0, 21.6, 18.7;

IR (neat): v 3855, 3631, 2920, 1720, 1655, 1459, 1438, 1364, 1166, 750 cm^{-1};

HRMS (ESI): m/z [M - H]$^+$ calcd. for $C_{38}H_{41}N_2O_4S$: 621.2793; found: 621.2790.

3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-7'-methoxy-1'-methyl-1-tosyl-2,3'-spirobi[indolin]-2'-one (3an)



Yellow solid, isolated yield 75% (48 mg);

dr > 19:1;

mp: 259.3-260.1 °C;

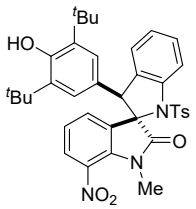
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 (d, J = 8.1 Hz, 2H), 7.28 (d, J = 8.0 Hz, 2H), 7.24-7.18 (m, 2H), 7.14 (d, J = 7.3 Hz, 1H), 7.01 (t, J = 6.9 Hz, 1H), 6.74 (s, 2H), 6.66 (t, J = 8.1 Hz, 1H), 6.59 (d, J = 8.2 Hz, 1H), 6.50 (d, J = 7.3 Hz, 1H), 5.11 (s, 1H), 5.02 (s, 1H), 3.64 (s, 3H), 3.49 (s, 3H), 2.40 (s, 3H), 1.27 (s, 18H);

^{13}C NMR (101 MHz, $CDCl_3$): δ 176.0, 153.1, 145.2, 144.1, 142.4, 136.5, 135.0, 130.2, 129.52, 129.51, 128.8, 128.5, 128.2, 125.7, 125.4, 123.5, 122.8, 122.6, 116.7, 113.4, 112.3, 78.6, 59.3, 56.1, 34.1, 30.1, 29.9, 21.6;

IR (neat): v 3854, 3745, 3650, 2918, 1654, 1559, 1541, 1458, 1437, 1375, 1046 cm^{-1};

HRMS (ESI): m/z [M - H]$^+$ calcd. for $C_{38}H_{41}N_2O_5S$: 637.2742; found: 637.2739.

3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-1'-methyl-7'-nitro-1-tosyl-2,3'-spirobi[indolin]-2'-one (3ao)



White solid, isolated yield 74% (48 mg);

dr > 19:1;

mp: 231.6-232.6 °C;

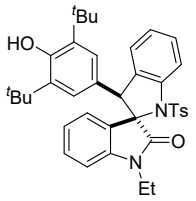
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 (d, J = 8.1 Hz, 2H), 7.47 (d, J = 8.3 Hz, 1H), 7.34 (d, J = 8.0 Hz, 2H), 7.25-7.14 (m, 4H), 7.06 (t, J = 7.1 Hz, 1H), 6.84 (t, J = 8.0 Hz, 1H), 6.72 (s, 2H), 5.19 (s, 1H), 5.08 (s, 1H), 3.28 (s, 3H), 2.43 (s, 3H), 1.26 (s, 18H);

^{13}C NMR (101 MHz, $CDCl_3$): δ 177.3, 153.5, 144.7, 142.1, 135.9, 135.7, 135.4, 135.0, 131.8, 129.8, 129.3, 128.7, 128.4, 127.4, 125.6, 125.5, 124.9, 123.3, 122.6, 121.6, 112.3, 76.8, 59.6, 34.1, 30.5, 30.0, 21.7;

IR (neat): v 3854, 3650, 2922, 1734, 1654, 1559, 1540, 1458, 1166, 1118, 742 cm^{-1};

HRMS (ESI): m/z [M - H]$^+$ calcd. for $C_{37}H_{38}N_3O_6S$: 652.2487; found: 652.2485.

3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-1'-ethyl-1-tosyl-2,3'-spirobi[indolin]-2'-one (3ap)



Yellow solid, isolated yield 74% (46 mg);

dr > 19:1;

mp: 188.1-189.0 °C;

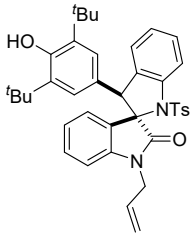
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 (d, J = 8.1 Hz, 2H), 7.28-7.26 (m, 2H), 7.23-7.19 (m, 1H), 7.11-6.99 (m, 4H), 6.88 (d, J = 7.3 Hz, 1H), 6.75-6.70 (m, 3H), 6.52 (d, J = 7.8 Hz, 1H), 5.14 (s, 1H), 5.00 (s, 1H), 3.91-3.82 (m, 1H), 3.67-3.58 (m, 1H), 2.39 (s, 3H), 1.24 (s, 18H);

^{13}C NMR (101 MHz, $CDCl_3$): δ 175.3, 153.1, 144.1, 142.2, 141.0, 136.5, 135.0, 130.7, 129.5, 129.2, 128.3, 128.2, 127.1, 126.1, 125.3, 124.2, 123.4, 122.8, 121.7, 112.3, 108.0, 78.4, 58.9, 35.0, 34.0, 30.0, 21.6, 12.5;

IR (neat): v 3855, 3752, 2923, 1735, 1719, 1654, 1560, 1459, 1167, 1020, 750, 669 cm^{-1};

HRMS (ESI): m/z [M - H]$^+$ calcd. for $C_{38}H_{41}N_2O_4S$: 621.2793; found: 621.2791.

1'-allyl-3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-1-tosyl-2,3'-spirobi[indolin]-2'-one (3aq)



White solid, isolated yield 88% (56 mg);

dr > 19:1;

mp: 203.9-204.6 °C;

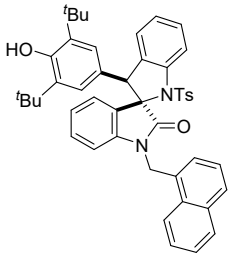
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 (d, J = 8.2 Hz, 2H), 7.30-7.26 (m, 3H), 7.24-7.20 (m, 1H), 7.09 (d, J = 7.1 Hz, 1H), 7.05-6.99 (m, 2H), 6.91 (d, J = 7.3 Hz, 1H), 6.76-6.73 (m, 3H), 6.49 (d, J = 7.8 Hz, 1H), 5.80-5.71 (m, 1H), 5.18-5.14 (m, 3H), 5.01 (s, 1H), 4.46 (d, J = 16.6 Hz, 1H), 4.19 (dd, J = 16.5, 5.2 Hz, 1H), 2.39 (s, 3H), 1.25 (s, 18H);

^{13}C NMR (101 MHz, $CDCl_3$): δ 175.5, 153.2, 144.1, 142.2, 141.1, 136.4, 135.0, 130.8, 129.5, 129.2, 128.34, 128.25, 127.2, 126.8, 126.2, 125.2, 124.0, 123.3, 122.9, 121.9, 117.6, 112.3, 109.1, 78.6, 59.2, 42.7, 34.0, 30.1, 21.6;

IR (neat): ν 3854, 3745, 3650, 2922, 1734, 1654, 1559, 1507, 1166, 750 cm^{-1};

HRMS (ESI): m/z [M - H]$^+$ calcd. for $C_{39}H_{41}N_2O_4S$: 633.2793; found: 633.2791.

3-(3,5-di-tert-butyl-4-hydroxyphenyl)-1'-(naphthalen-1-ylmethyl)-1-tosyl-2,3'-spirobi[indolin]-2'-one (3ar)



White solid, isolated yield 87% (64 mg);

dr = 4:1;

mp: 212.7-213.6 °C;

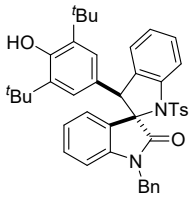
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 (d, J = 8.0 Hz, 2H), 8.03 (d, J = 8.3 Hz, 1H), 7.88 (d, J = 8.0 Hz, 1H), 7.72 (d, J = 8.0 Hz, 1H), 7.59 (t, J = 7.1 Hz, 1H), 7.53 (t, J = 7.8 Hz, 1H), 7.35-7.27 (m, 6H), 7.12 (d, J = 7.8 Hz, 2H), 7.05 (d, J = 7.3 Hz, 1H), 6.97 (d, J = 7.3 Hz, 1H), 6.90 (t, J = 7.7 Hz, 1H), 6.81-6.75 (m, 3H), 6.20 (d, J = 7.8 Hz, 1H), 5.62 (d, J = 16.8 Hz, 1H), 5.22 (s, 1H), 5.10 (s, 1H), 2.40 (s, 3H), 1.28 (s, 18H);

^{13}C NMR (101 MHz, $CDCl_3$): δ 176.0, 153.4, 144.2, 142.2, 141.3, 136.5, 135.3, 133.7, 130.9, 130.6, 129.6, 129.5, 129.3, 129.0, 128.4, 128.3, 127.7, 127.0, 126.3, 125.9, 125.8, 125.7, 125.2, 123.9, 123.7, 123.4, 122.9, 122.3, 122.2, 112.4, 109.6, 79.1, 59.7, 42.1, 34.1, 30.2, 21.6;

IR (neat): ν 3855, 2920, 1734, 1654, 1560, 1457, 1360, 1027, 799, 665 cm^{-1};

HRMS (ESI): m/z [M - H]$^+$ calcd. for $C_{47}H_{45}N_2O_4S$: 733.3106; found: 733.3104.

1'-benzyl-3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-1-tosyl-2,3'-spirobi[indolin]-2'-one (3as)



Yellow solid, isolated yield 64% (44 mg);

dr > 19:1;

mp: 232.2-233.0 °C;

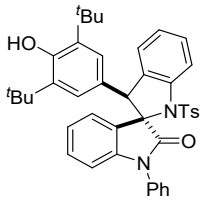
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 (d, J = 8.0 Hz, 2H), 7.33-7.20 (m, 9H), 7.10 (d, J = 7.4 Hz, 1H), 7.02 (t, J = 7.3 Hz, 1H), 6.92-6.88 (m, 2H), 6.76 (s, 2H), 6.71 (t, J = 7.5 Hz, 1H), 6.23 (d, J = 8.0 Hz, 1H), 5.32 (d, J = 16.0 Hz, 1H), 5.18 (s, 1H), 5.05 (s, 1H), 4.47 (d, J = 16.0 Hz, 1H), 2.40 (s, 3H), 1.25 (s, 18H);

^{13}C NMR (101 MHz, $CDCl_3$): δ 175.8, 153.3, 144.1, 142.2, 141.0, 136.5, 135.1, 135.0, 130.8, 129.5, 129.2, 128.7, 128.4, 128.3, 127.3, 126.9, 126.8, 126.2, 125.2, 123.9, 123.3, 122.9, 122.1, 112.4, 109.5, 78.8, 59.5, 44.3, 34.1, 30.2, 21.6;

IR (neat): ν 3855, 3650, 2924, 1734, 1718, 1654, 1559, 1458, 1363, 1090, 750 cm^{-1};

HRMS (ESI): m/z [M - H]$^+$ calcd. for $C_{43}H_{43}N_2O_4S$: 683.2949; found: 683.2947.

3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-1'-phenyl-1-tosyl-2,3'-spirobi[indolin]-2'-one (3at)



White solid, isolated yield 81% (54 mg);

dr > 19:1;

mp: 121.9-122.7 °C;

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (d, J = 8.1 Hz, 2H), 7.50 (t, J = 7.4 Hz, 2H), 7.42-7.39 (m, 1H), 7.34 (d, J = 7.6 Hz, 2H), 7.28-7.22 (m, 4H), 7.13 (d, J = 7.6 Hz, 1H), 7.05-6.98 (m, 3H), 6.85 (s, 2H), 6.80 (t, J = 7.4 Hz, 1H), 6.47 (d, J = 8.0 Hz, 1H), 5.23 (s, 1H), 5.07 (s, 1H), 2.39 (s, 3H), 1.27 (s, 18H);

^{13}C NMR (101 MHz, $CDCl_3$): δ 175.2, 153.3, 144.2, 142.1, 142.0, 136.4, 135.2, 134.4, 130.9, 129.6, 129.54, 129.49, 129.2, 128.4, 128.3, 128.1, 126.6, 126.4, 125.3, 124.3, 123.3, 122.9, 122.4, 112.3, 109.3, 78.7, 59.4, 34.1, 30.1, 21.6;

IR (neat): ν 3855, 3631, 2920, 1736, 1597, 1459, 1364, 1236, 1028, 750 cm^{-1};

HRMS (ESI): m/z [M - H]$^+$ calcd. for $C_{42}H_{41}N_2O_4S$: 669.2793; found: 669.2792.

Procedure for one-pot reaction

To a solution of compound **4** (70 mg, 0.15 mmol) in $CHCl_3$ (1.5 mL) was added MnO_2 (65 mg, 0.75 mmol), then the reaction mixture was stirred at 60 ℃ for 4 h. The reaction mixture was directly cooled to -20 ℃ and was added **2a** (18 mg, 0.1 mmol) and TMG (29 mg, 0.25 mmol). The reaction was stirred at -20 ℃ for 30 min. The reaction mixture was directly charged to column chromatography on silica gel (PE:DCM:EA = 30:1:1-10:1:1) to give the cycloadduct (47 mg, 77% yield).

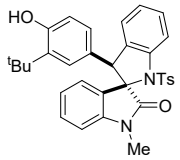
Procedure for synthesis of 5

To a solution of compound **3aa** (200 mg, 0.33 mmol) in dry toluene (16 mL) was added $AlCl_3$ (432 mg, 3.3 mmol) in one portion. The reaction mixture was stirred at 0 ℃ for 2 h and H_2O was added to quench the reaction and extracted with DCM (3 × 20 mL). The organic layer was dried with anhydrous Na_2SO_4 and solvent was concentrated under reduced pressure to give a residue, which was purified by column chromatography (PE:EA = 10:1-4:1) to afford the product **5** (166 mg, 91% yield).

Procedure for synthesis of 6

To a solution of compound **3aa** (30 mg, 0.05 mmol) in dry toluene (0.3 mL) was added a solution of $AlCl_3$ (80 mg, 0.6 mmol) in $MeNO_2$ (0.3 mL) in one portion. The reaction mixture was stirred at 60 ℃ for 1 h and H_2O was added to quench the reaction and extracted with DCM (3 × 5 mL). The organic layer was dried with anhydrous Na_2SO_4 and solvent was concentrated under reduced pressure to give a residue, which was purified by column chromatography (PE:EA = 4:1) to afford the product **6** (20 mg, 79% yield).

3-(3-(tert-butyl)-4-hydroxyphenyl)-1'-methyl-1-tosyl-2,3'-spirobi[indolin]-2'-one (5)



5

White solid, isolated yield 91% (166 mg);

dr > 19:1;

mp: 207.9-208.5 °C;

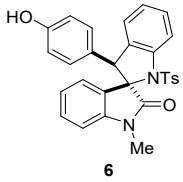
^{1}H NMR (400 MHz, DMSO-D_6): δ 9.23 (s, 1H), 7.84 (d, J = 8.3 Hz, 2H), 7.37 (d, J = 8.2 Hz, 2H), 7.31-7.24 (m, 2H), 7.12-7.06 (m, 3H), 6.79 (d, J = 7.8 Hz, 1H), 6.69 (t, J = 7.5 Hz, 1H), 6.63 (s, 1H), 6.56-6.53 (m, 2H), 6.46 (d, J = 8.2 Hz, 1H), 4.96 (s, 1H), 3.14 (s, 3H), 2.37 (s, 3H), 1.12 (s, 9H);

^{13}C NMR (101 MHz, DMSO-D_6): δ 175.4, 155.7, 145.0, 142.5, 142.1, 136.2, 135.0, 130.6, 130.21, 130.20, 130.0, 129.0, 128.4, 127.7, 126.3, 125.8, 124.1, 123.6, 122.9, 122.1, 116.0, 112.5, 109.1, 78.1, 58.3, 34.5, 29.5, 27.0, 21.6;

IR (neat): ν 3855, 3650, 2922, 1718, 1654, 1560, 1457, 1360, 1090, 750 cm^{-1};

HRMS (ESI): m/z $[M - H]^+$ calcd. for $C_{33}H_{31}N_2O_4S$: 551.2010; found: 551.2009.

3-(4-hydroxyphenyl)-1'-methyl-1-tosyl-2,3'-spirobi[indolin]-2'-one (6)



6

White solid, isolated yield 79% (20 mg);

dr > 19:1;

mp: 223.7-224.4 °C;

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (d, J = 8.1 Hz, 2H), 7.26-7.20 (m, 4H), 7.10-6.98 (m, 3H), 6.88-6.84 (m, 3H), 6.72 (t, J = 7.5 Hz, 1H), 6.57-6.52 (m, 3H), 5.15 (s, 1H), 5.09 (s, 1H), 3.21 (s, 3H), 2.39 (s, 3H);

^{13}C NMR (101 MHz, $CDCl_3$): δ 175.9, 155.2, 144.2, 142.1, 142.0, 136.3, 130.7, 130.3, 129.6, 129.5, 128.4, 128.3, 126.3, 125.3, 125.2, 124.1, 122.9, 122.1, 114.8, 112.4, 108.3, 78.2, 57.9, 26.7, 21.6;

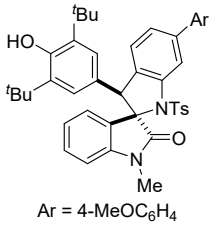
IR (neat): ν 3854, 2920, 1733, 1717, 1652, 1559, 1459, 1091, 750 cm^{-1};

HRMS (ESI): m/z [M - H]$^+$ calcd. for $C_{29}H_{23}N_2O_4S$: 495.1384; found: 495.1383.

Procedure for synthesis of 8

To a solution of the compound **3ja** (34 mg, 0.05 mmol), 4-methoxyphenylboronic acid **7** (9 mg, 0.06 mmol), K_2CO_3 (21 mg, 0.15 mmol) in DMF/H_2O (4:1, 1.5 mL) was added $Pd(PPh_3)_4$ (6 mg, 0.005 mmol) and N_2 was bubbled through the mixture for 2 min. The mixture was stirred at 80 °C for 4h, then cooled to room temperature. The reaction mixture was diluted with water (5 mL), and then extracted with EA (3 x 15 mL). The combined organic layer was washed with water, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to give a residue, which was purified by column chromatography (PE:EA = 4:1) to afford the product **8** (31 mg, 87% yield).

3-(3,5-di-tert-butyl-4-hydroxyphenyl)-6-(4-methoxyphenyl)-1'-methyl-1-tosyl-2,3'-spirobi[indolin]-2'-one (8)



Ar = 4-MeOC$_6$H$_4$

White solid, isolated yield 87% (31 mg);

dr > 19:1;

mp: 214.9-215.7 °C;

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (d, J = 8.1 Hz, 2H), 7.52-7.48 (m, 3H), 7.29-7.26 (m, 2H), 7.19 (d, J = 9.4 Hz, 2H), 7.07-6.98 (m, 3H), 6.91 (d, J = 7.2 Hz, 1H), 6.74-6.72 (m, 3H), 6.49 (d, J = 7.8 Hz, 1H), 5.17 (s, 1H), 5.00 (s, 1H), 3.87 (s, 3H), 3.21 (s, 3H), 2.39 (s, 3H), 1.26 (s, 18H);

^{13}C NMR (101 MHz, $CDCl_3$): δ 175.6, 159.2, 153.1, 144.2, 142.9, 141.7, 141.3, 136.5, 135.1, 133.3, 129.6, 129.3, 128.7, 128.4, 128.2, 126.9, 125.7, 125.4, 124.0, 123.5, 122.0, 121.5, 114.2, 110.8, 107.9, 78.8, 58.8, 55.3, 34.1, 30.1, 26.5, 21.6;

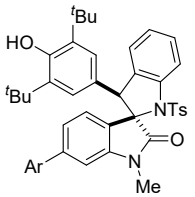
IR (neat): v 3855, 2923, 1730, 1718, 1650, 1559, 1458, 1090, 750 cm^{-1};

HRMS (ESI): m/z [M - H]$^+$ calcd. for $C_{44}H_{45}N_2O_5S$: 713.3055; found: 713.3052.

Procedure for synthesis of 9

To a solution of the compound **3al** (28 mg, 0.04 mmol), 4-methoxyphenylboronic acid **7** (7.3 mg, 0.048 mmol), K_2CO_3 (16.5 mg, 0.12 mmol) in DMF/H_2O (4:1, 1.5 mL) was added $Pd(PPh_3)_4$ (4.7 mg, 0.004 mmol) and N_2 was bubbled through the mixture for 2 min. The mixture was stirred at 80 °C for 4h, then cooled to room temperature. The reaction mixture was diluted with water (5 mL), and then extracted with EA (3 x 15 mL). The combined organic layer was washed with water, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to give a residue, which was purified by column chromatography (PE:EA = 4:1) to afford the product **9** (24 mg, 85% yield).

3-(3,5-di-tert-butyl-4-hydroxyphenyl)-6'-(4-methoxyphenyl)-1'-methyl-1-tosyl-2,3'-spirobi[indolin]-2'-one (9)



Ar = 4-MeOC$_6$H$_4$

White solid, isolated yield 85% (24.3 mg);

dr > 19:1;

mp: 221.5-222.4 °C;

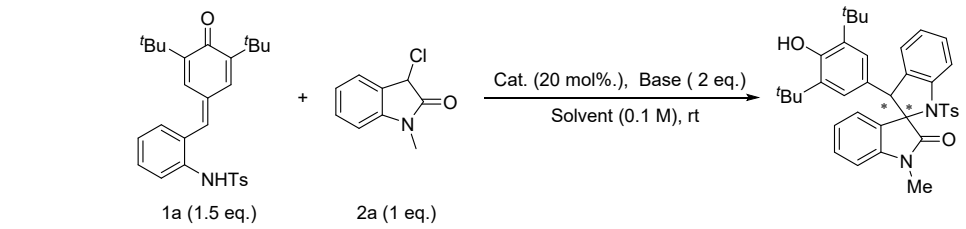
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (d, J = 8.2 Hz, 2H), 7.33-7.26 (m, 5H), 7.23 (d, J = 8.2 Hz, 1H), 7.16 (d, J = 7.5 Hz, 1H), 7.04 (t, J = 7.3 Hz, 1H), 6.91 (d, J = 8.6 Hz, 2H), 6.88 (s, 2H), 6.78 (s, 2H), 6.61 (s, 1H), 5.16 (s, 1H), 4.98 (s, 1H), 3.83 (s, 3H), 3.24 (s, 3H), 2.40 (s, 3H), 1.24 (s, 18H);

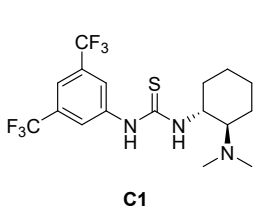
^{13}C NMR (101 MHz, $CDCl_3$): δ 175.9, 159.2, 153.2, 144.2, 142.6, 142.32, 142.26, 136.5, 135.2, 133.6, 130.3, 129.6, 128.4, 128.3, 128.1, 125.8, 125.3, 125.2, 124.0, 123.4, 122.9, 120.6, 114.1, 112.4, 106.5, 78.6, 59.1, 55.3, 34.1, 30.1, 26.6, 21.6;

IR (neat): v 3856, 2922, 1740, 1598, 1559, 1458, 1366, 1089, 750 cm^{-1};

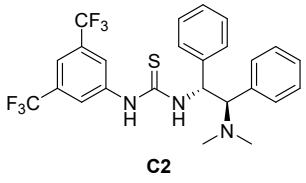
HRMS (ESI): m/z [M - H]$^+$ calcd. for $C_{44}H_{45}N_2O_5S$: 713.3055; found: 713.3052.

Condition screening for asymmetric version

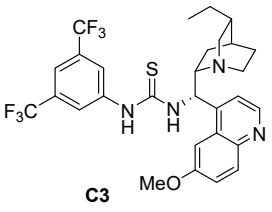




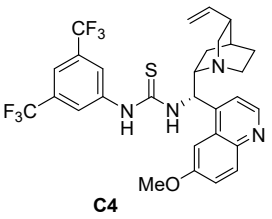
C1



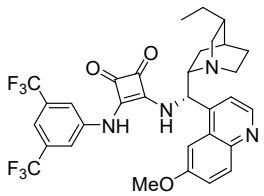
C2



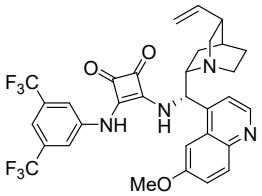
C3



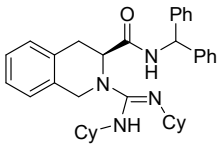
C4



C5



C6



C7

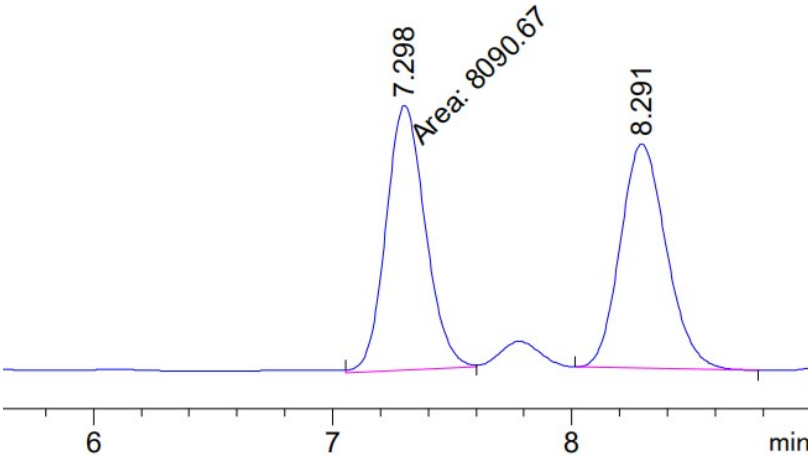
Entry	Cat.	Base	Solvent	dr[a]	yield[b]	ee[c]
1	C1	CH_3COOLi	$CHCl_3$	-	Trace	-
2	C2	CH_3COOLi	$CHCl_3$	-	n.d.	-
3	C3	CH_3COOLi	$CHCl_3$	-	Trace	-
4	C4	CH_3COOLi	$CHCl_3$	-	n.d.	-
5	C5	CH_3COOLi	$CHCl_3$	5:1	11%	24%
6	C6	CH_3COOLi	$CHCl_3$	-	n.d.	-
7	C7	CH_3COOLi	$CHCl_3$	6:1	45%	33%
8	C7	NH_4HCO_3	$CHCl_3$	10:1	85%	67%
9	C7	$NaHCO_3$	$CHCl_3$	4:1	81%	0%
10	C7	NH_4HCO_3	Et_2O	5:1	36%	55%
11	C7	NH_4HCO_3	THF	11:1	84%	4%
12	C7	NH_4HCO_3	DCM	4:1	12%	15%

Reaction condition: **1a** (0.075 mmol), **2a** (0.05 mmol), catalyst (0.01 mmol) and base (0.1 mmol) in solvent (0.5 mL). [a] Dr were determined via the ratio of the integration of the *N*-Me peaks from ^{1}H NMR of the crude product. [b] Isolated yield. [c] Enantiomeric excesses were determined by chiral HPLC analysis.

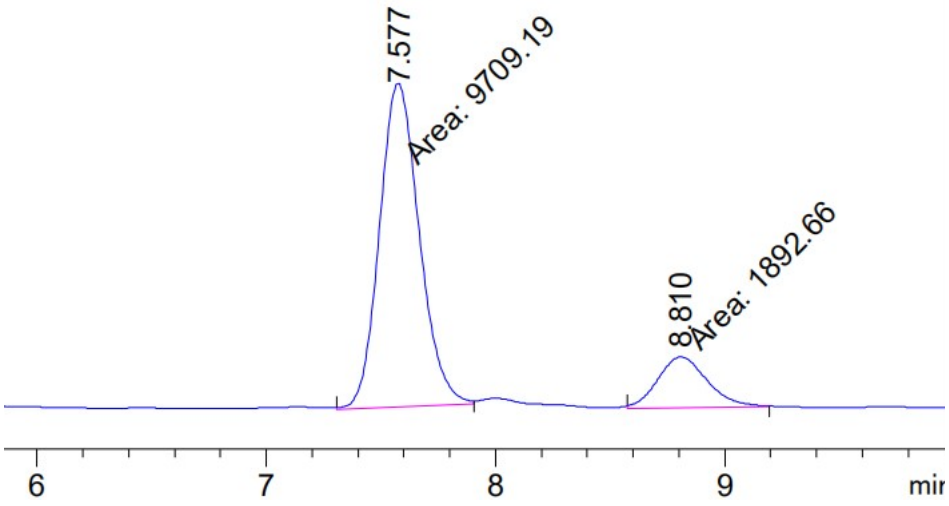
Procedure for synthesis of (+)-3aa

To a solution of the compound **1a** (34.8 mg, 0.075 mmol), **2a** (9.1 mg, 0.05 mmol), NH_4HCO_3 (7.9 mg, 0.1 mmol) in $CHCl_3$ (0.5 mL) was added chiral catalyst (5.5 mg, 0.01 mmol) and the reaction was stirred at room temperature for 3 d. The reaction mixture was directly charged to column chromatography on silica gel to give the **(+)-3aa** (26 mg, 85%).

HPLC of compound 3aa



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.298	MM	0.1903	8090.66504	708.67883	50.1590
2	8.291	BB	0.2060	8039.38037	601.26843	49.8410



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.577	MM	0.2011	9709.19043	804.74359	83.6866
2	8.810	MM	0.2507	1892.66101	125.82281	16.3134

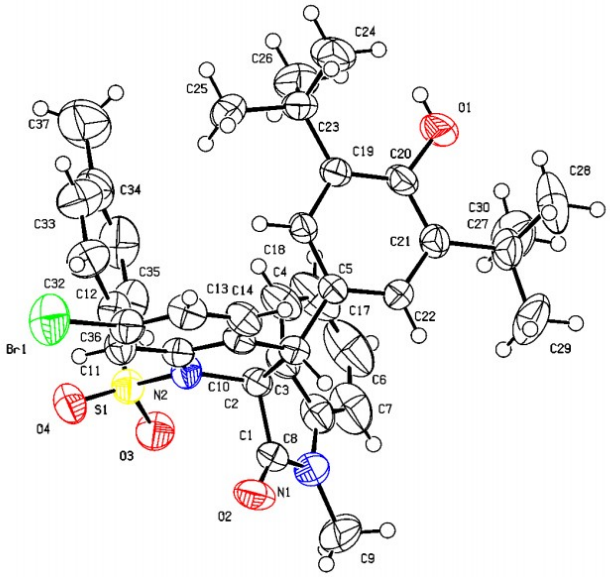
3. Reference

[1] J. Wang, X. Pan, J. Liu, L. Zhao, Y. Zhi, K. Zhao and L. Hu, Diastereoselective Synthesis of Tetrahydroquinolines via [4 + 2] Annulation between in Situ Generated *p*-Quinone Methides and Nitroalkenes, *Org. Lett.* 2018, **20**, 5995.

[2] K. Zhao, Y. Zhi, T. Shu, A. Valkonen, K. Rissanen and D. Enders, Organocatalytic Domino Oxa-Michael/1,6-Addition Reactions: Asymmetric Synthesis of Chromans Bearing Oxindole Scaffolds, *Angew. Chem., Int. Ed.* 2016, **55**, 12104.

4. Crystallographic data of 3ja

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-2110859 (**3ja**), Copies of these data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

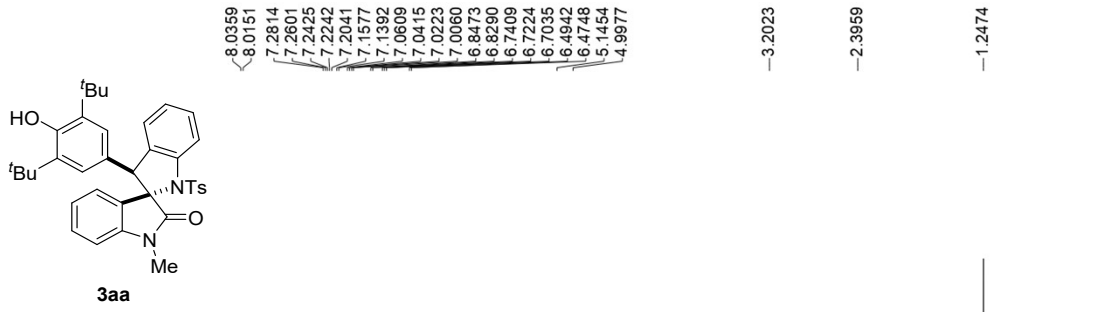


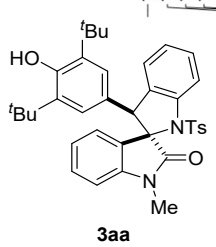
STable 1. Crystal data and structure refinement for **3ja**.

Identification code	**3ja**
Empirical formula	C37H39BrN2O4S
Formula weight	687.67
Temperature/K	293(2)
Crystal system	triclinic
Space group	P-1
a/Å	11.0140(4)
b/Å	11.3559(5)
c/Å	14.3441(7)
α/°	83.796(4)
β/°	86.279(4)
γ/°	75.024(4)
Volume/Å3	1721.70(14)
Z	2
ρcalcg/cm3	1.326
μ/mm-1	2.519
F(000)	716.0
Crystal size/mm3	0.3 × 0.3 × 0.3
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	6.202 to 133.19
Index ranges	-9 ≤ h ≤ 13, -13 ≤ k ≤ 13, -17 ≤ l ≤ 17
Reflections collected	10358

Independent reflections	6079 [Rint = 0.0188, Rsigma = 0.0266]
Data/restraints/parameters	6079/0/415
Goodness-of-fit on F2	1.033
Final R indexes [I>=2σ (I)]	R1 = 0.0438, wR2 = 0.1189
Final R indexes [all data]	R1 = 0.0478, wR2 = 0.1227
Largest diff. peak/hole / e Å-3	0.50/-0.72

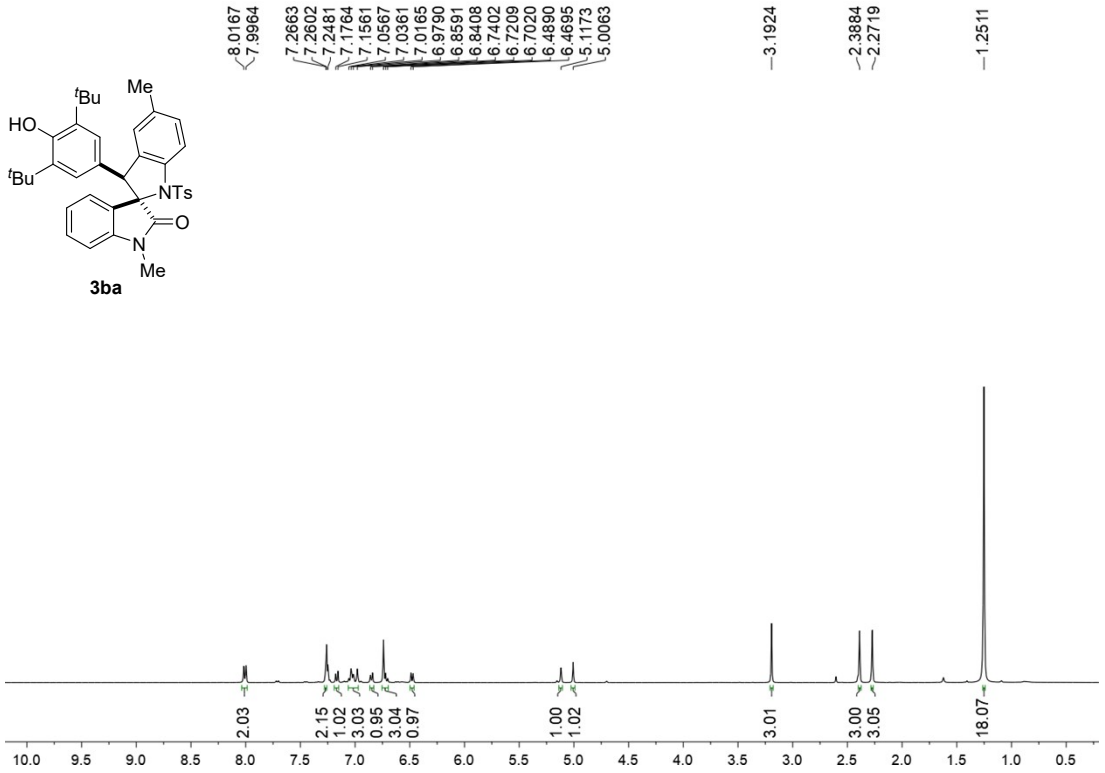
5. Copies of NMR spectra





3aa

3aa


8.0167
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7.2663
7.2602
7.2481
7.1764
7.1561
7.0567
7.0361
7.0165
6.9790
6.8591
6.8408
6.7402
6.7209
6.7020
6.4890
6.4695
5.1173
5.0063
3.1924
2.3884
2.2719
1.2511
tBu
Me
HO
tBu
NTs
O
N
Me
3ba
2.03
2.15
1.02
3.03
0.95
3.04
0.97
1.00
1.02
3.01
3.00
3.05
18.07
10.0
9.5
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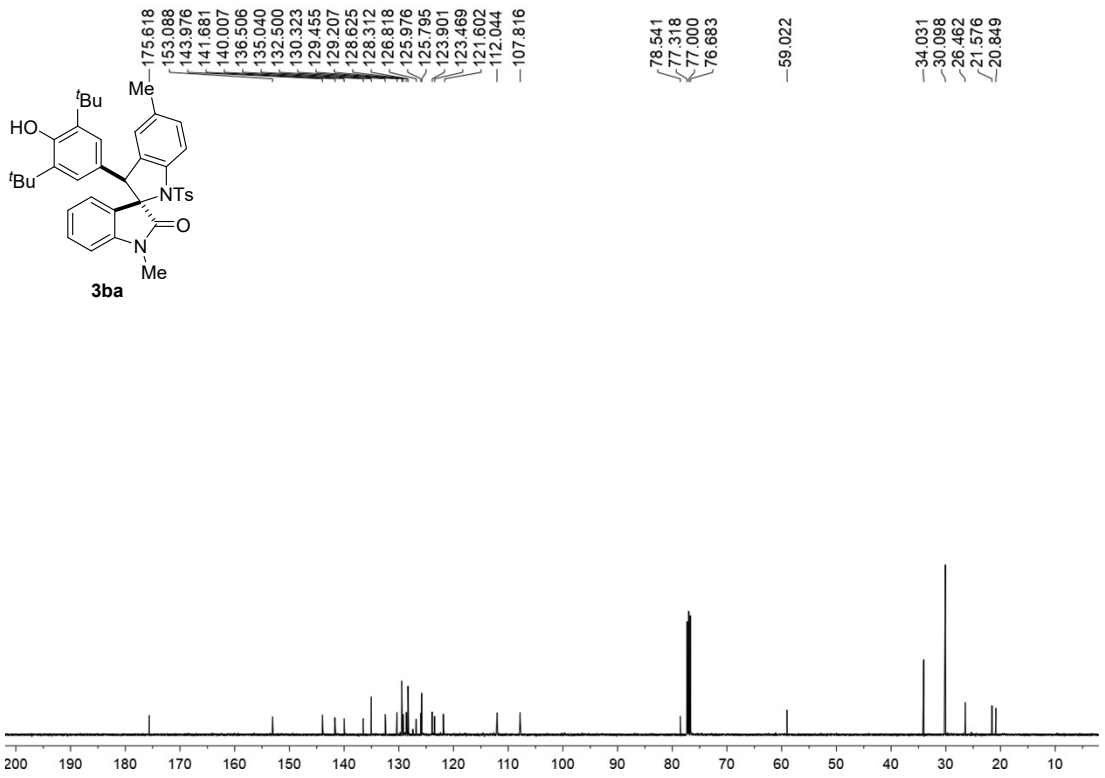
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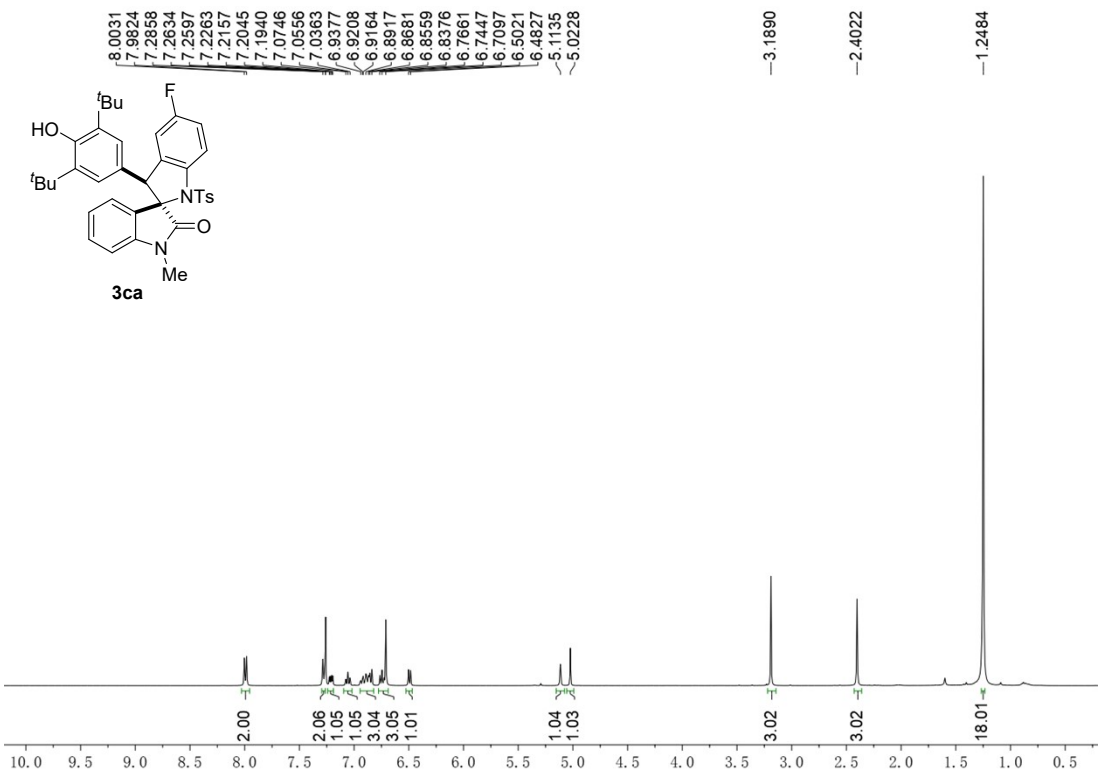
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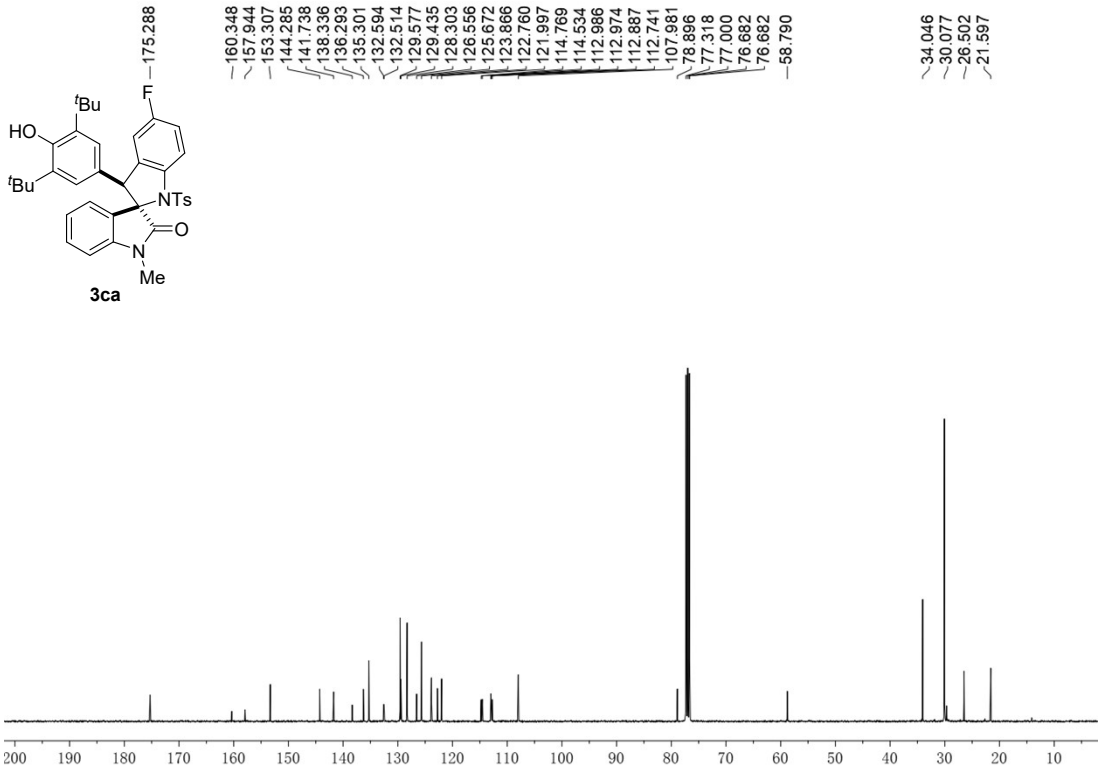
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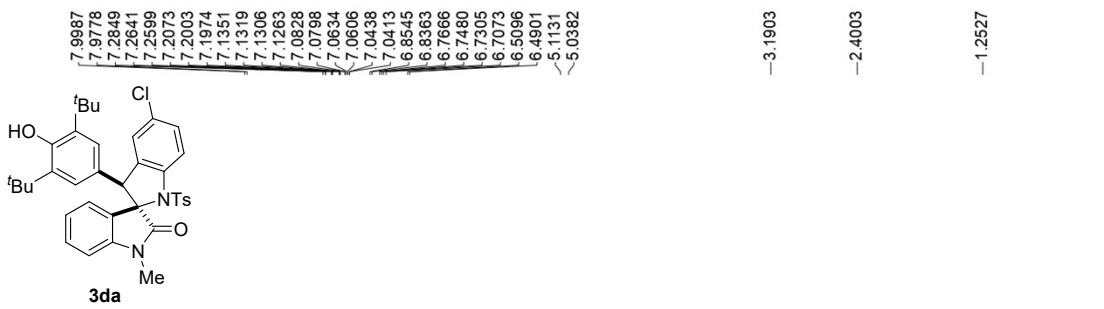
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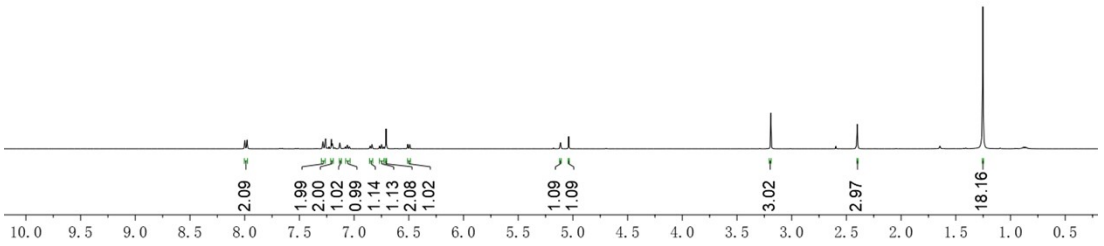
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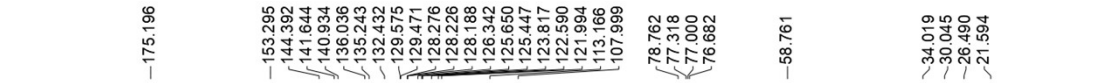
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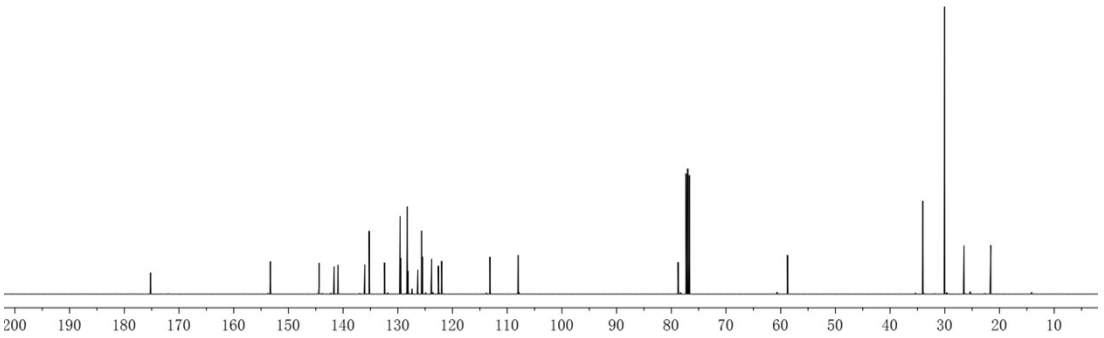
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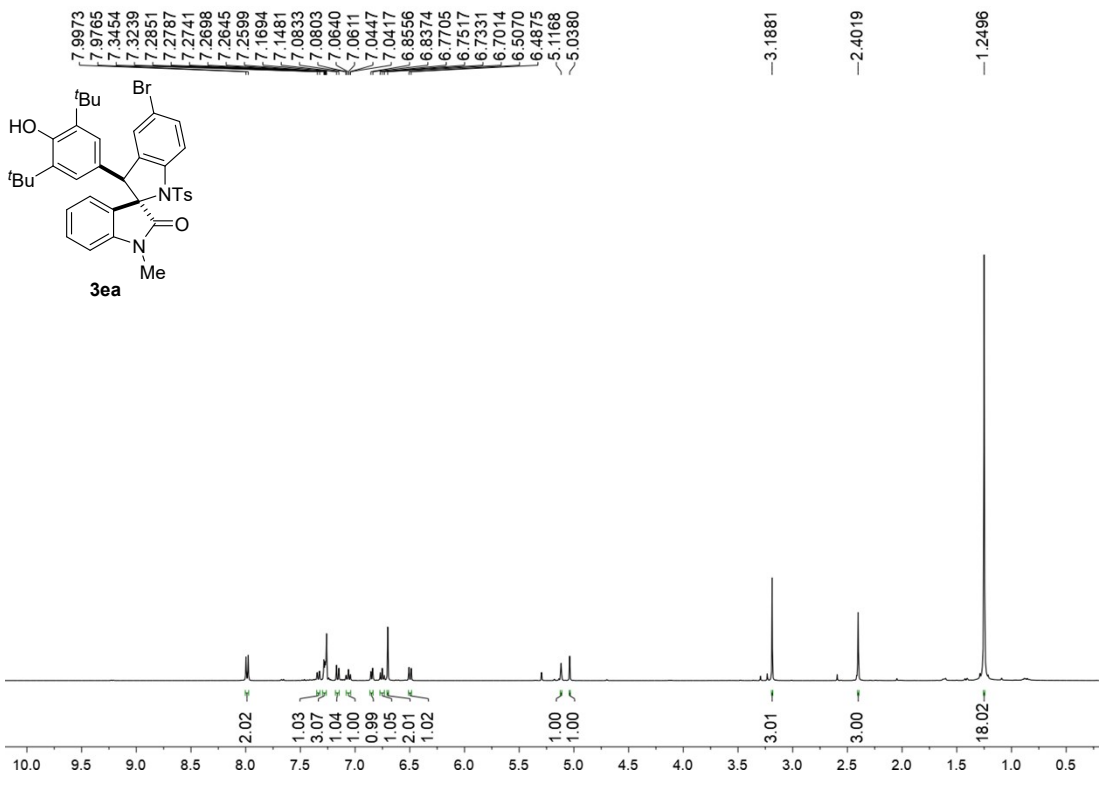
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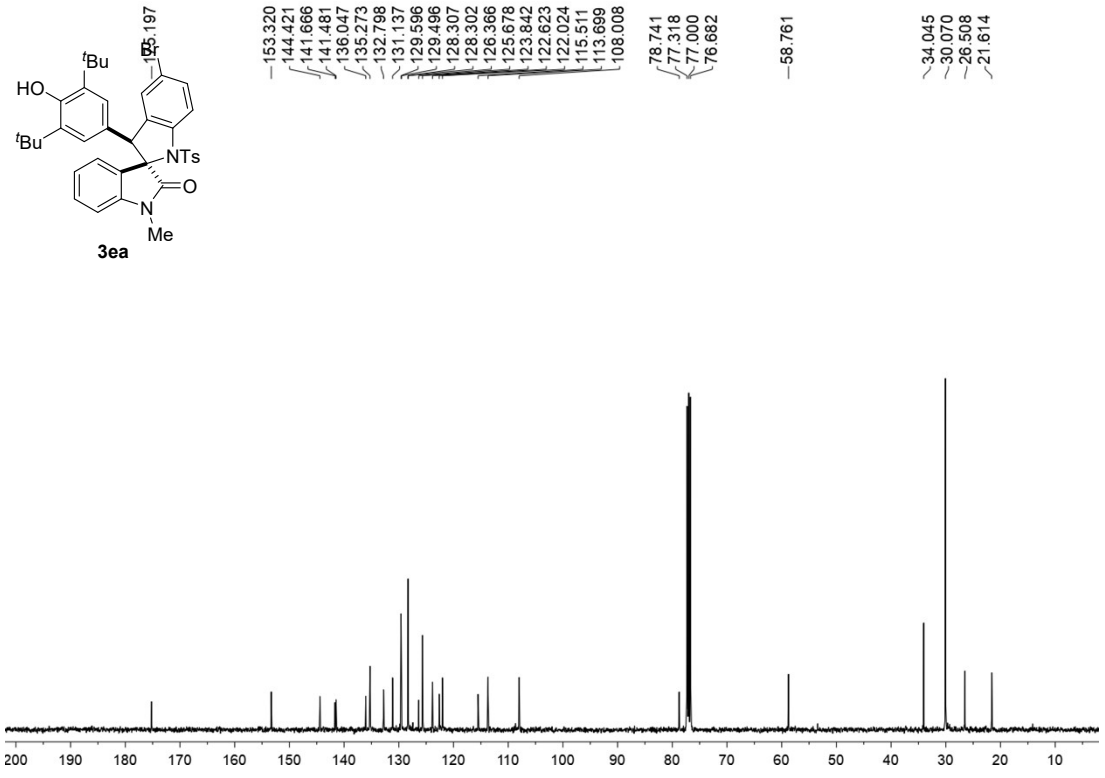
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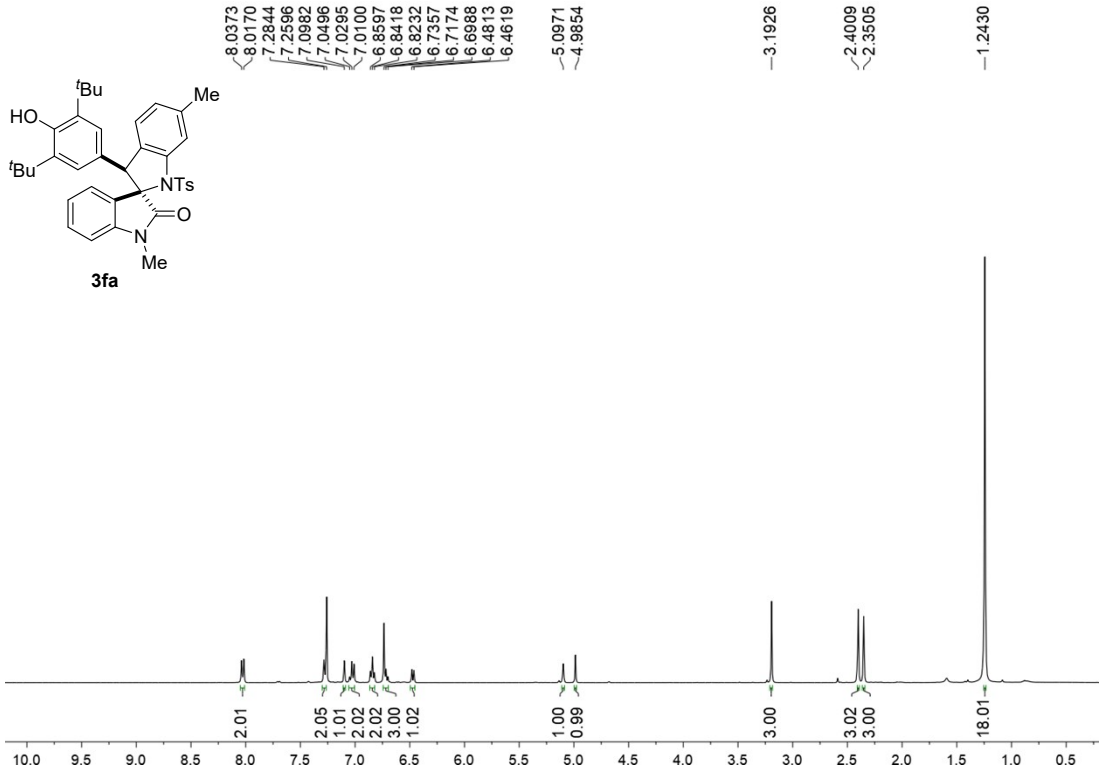
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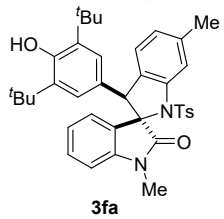
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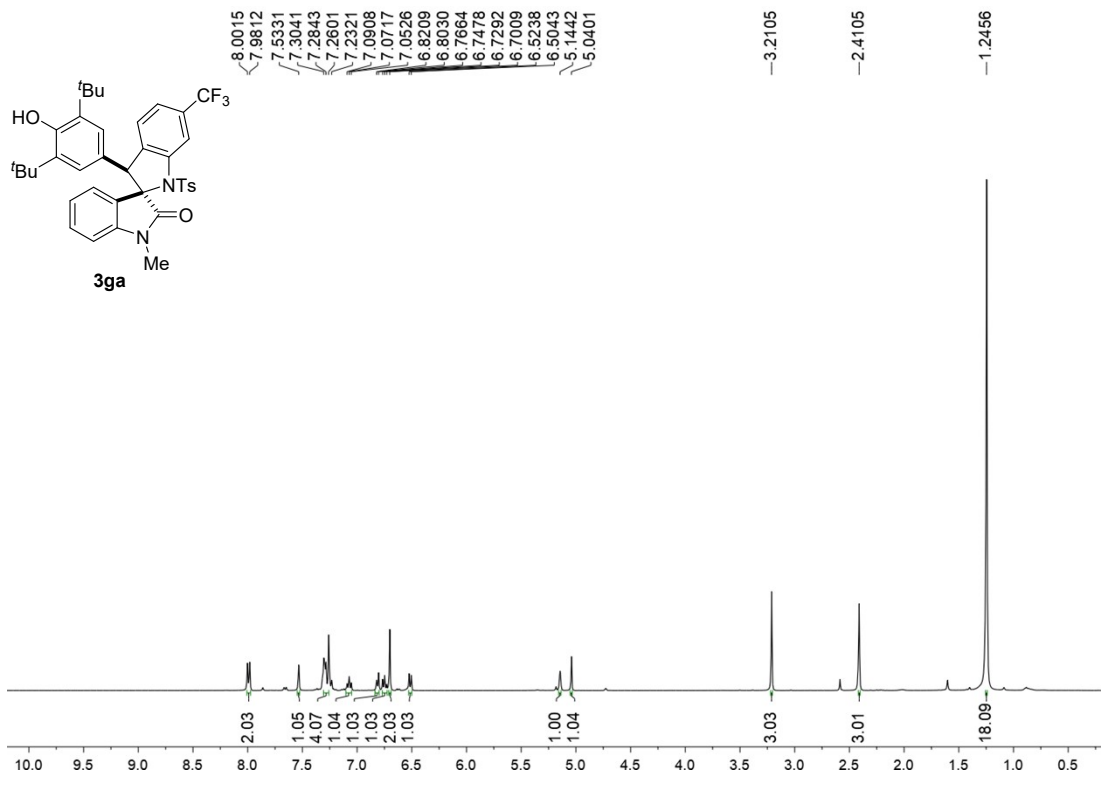
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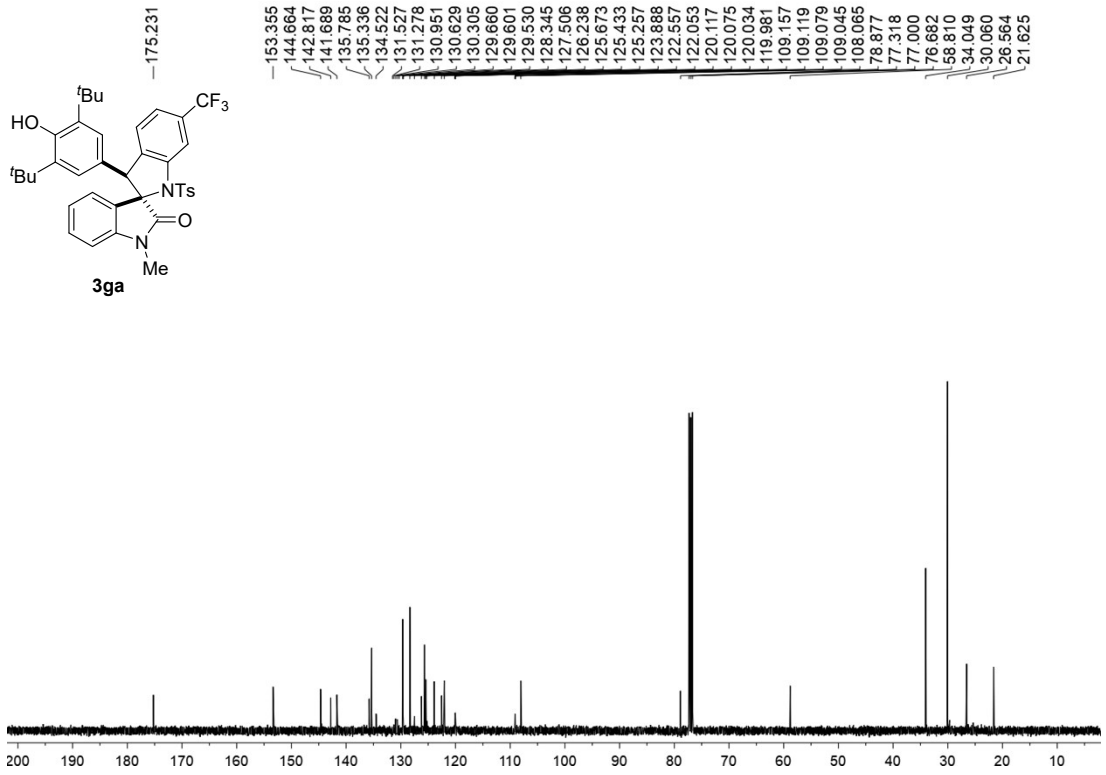
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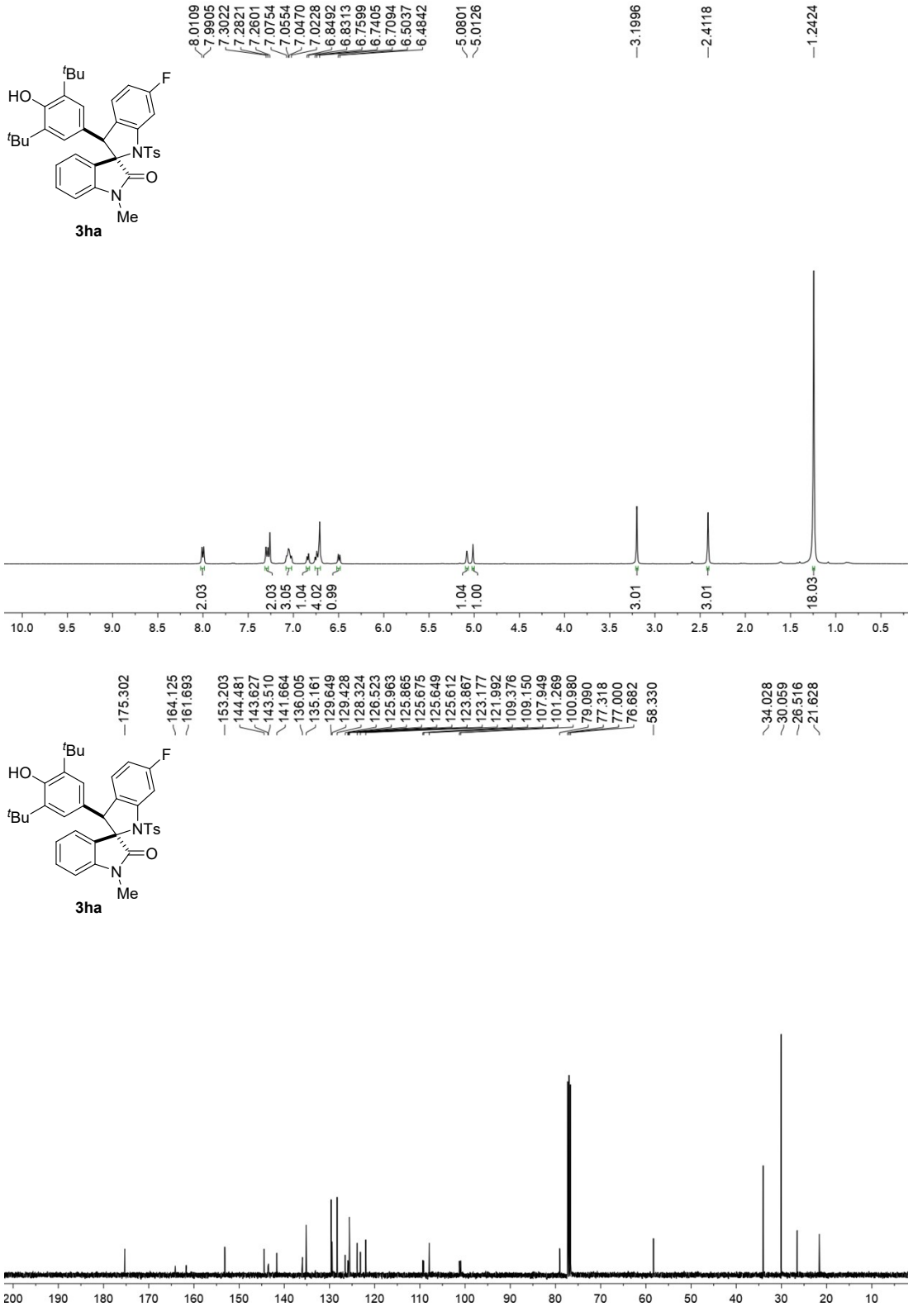
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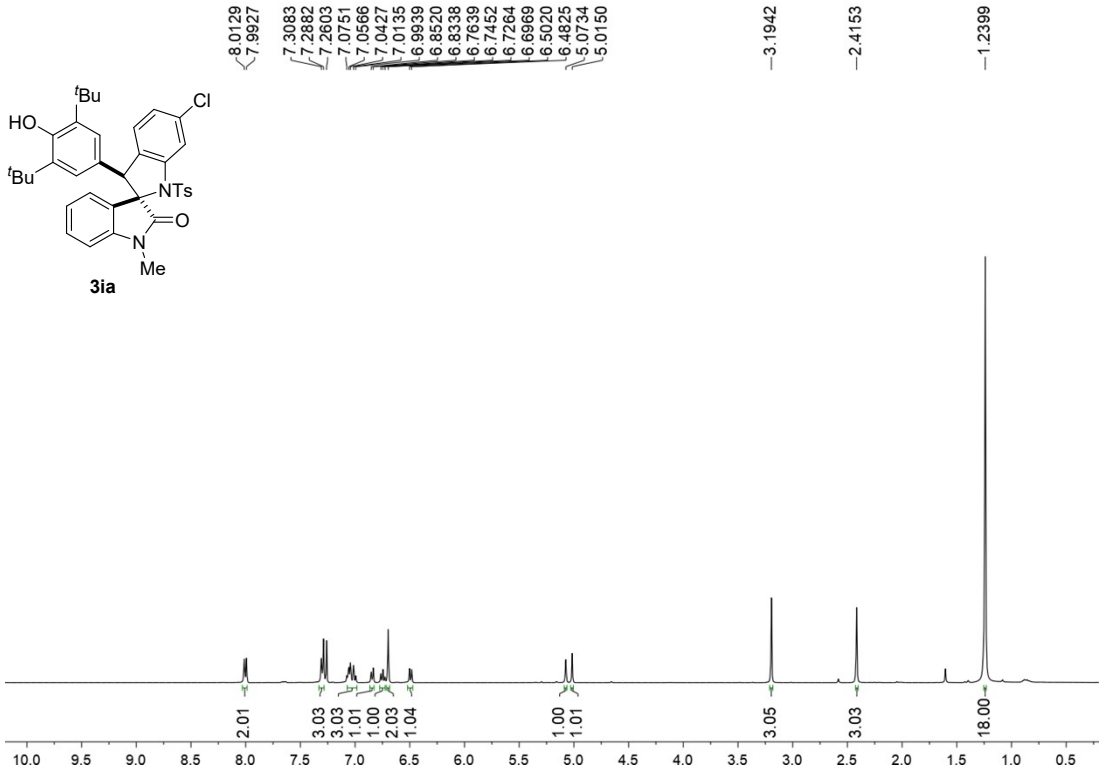
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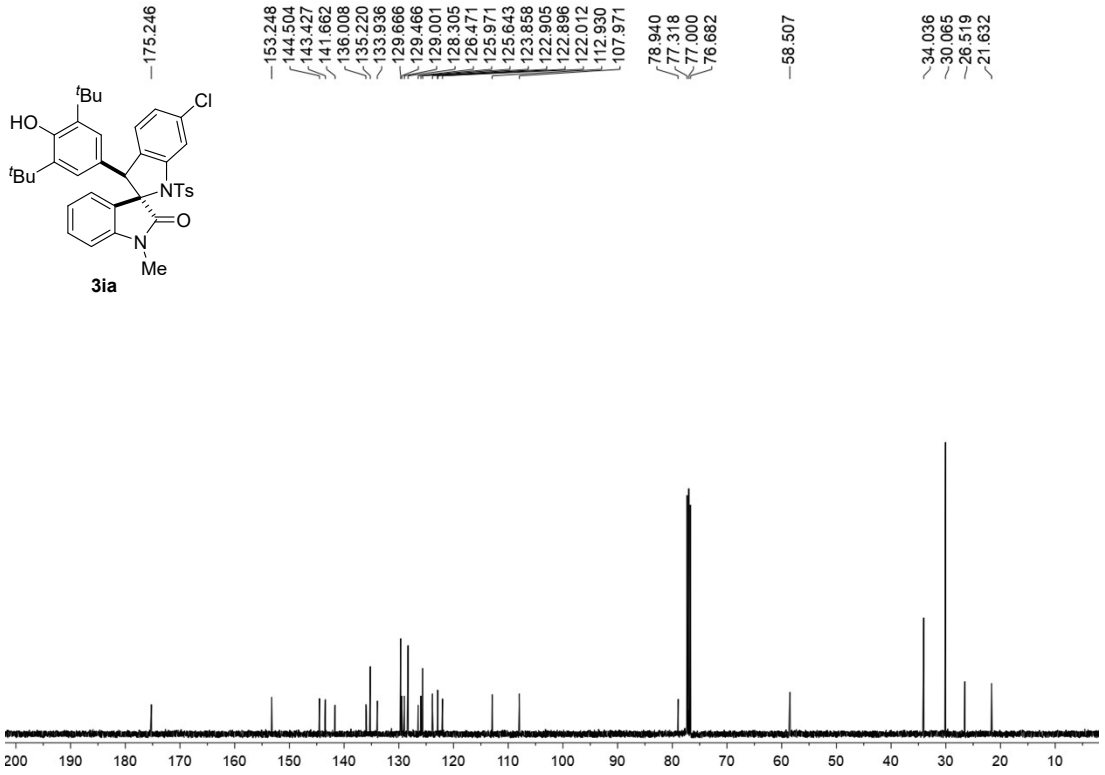
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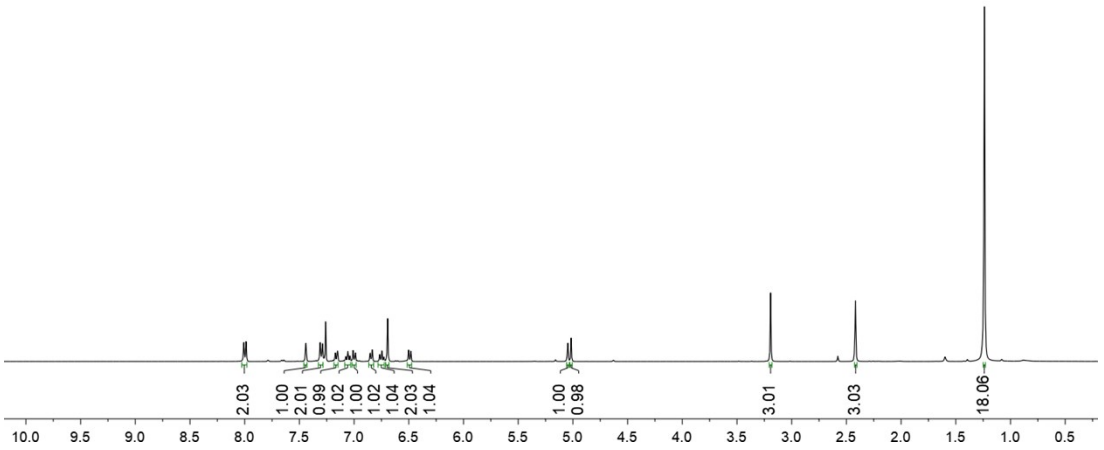
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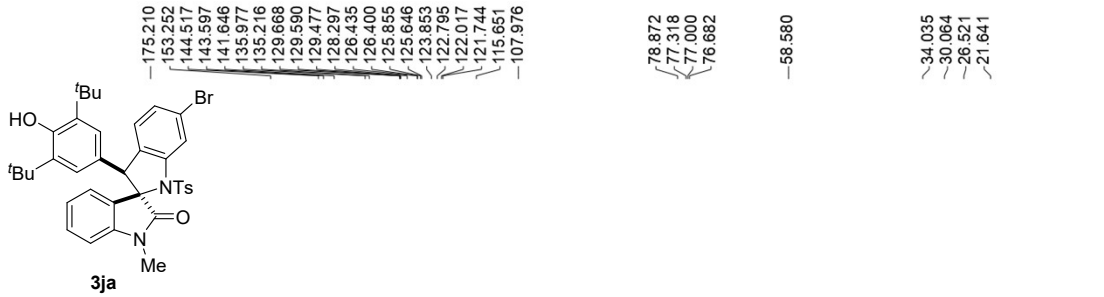
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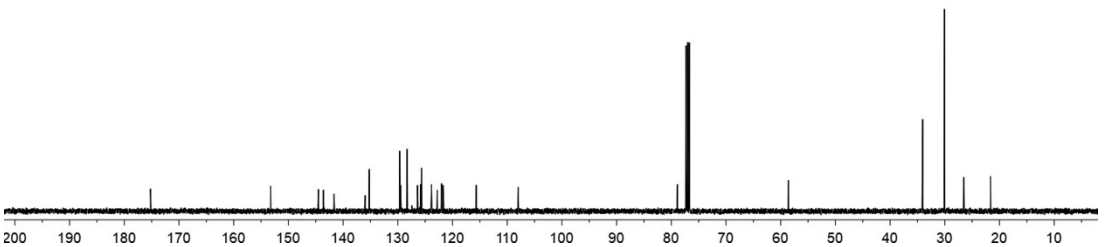
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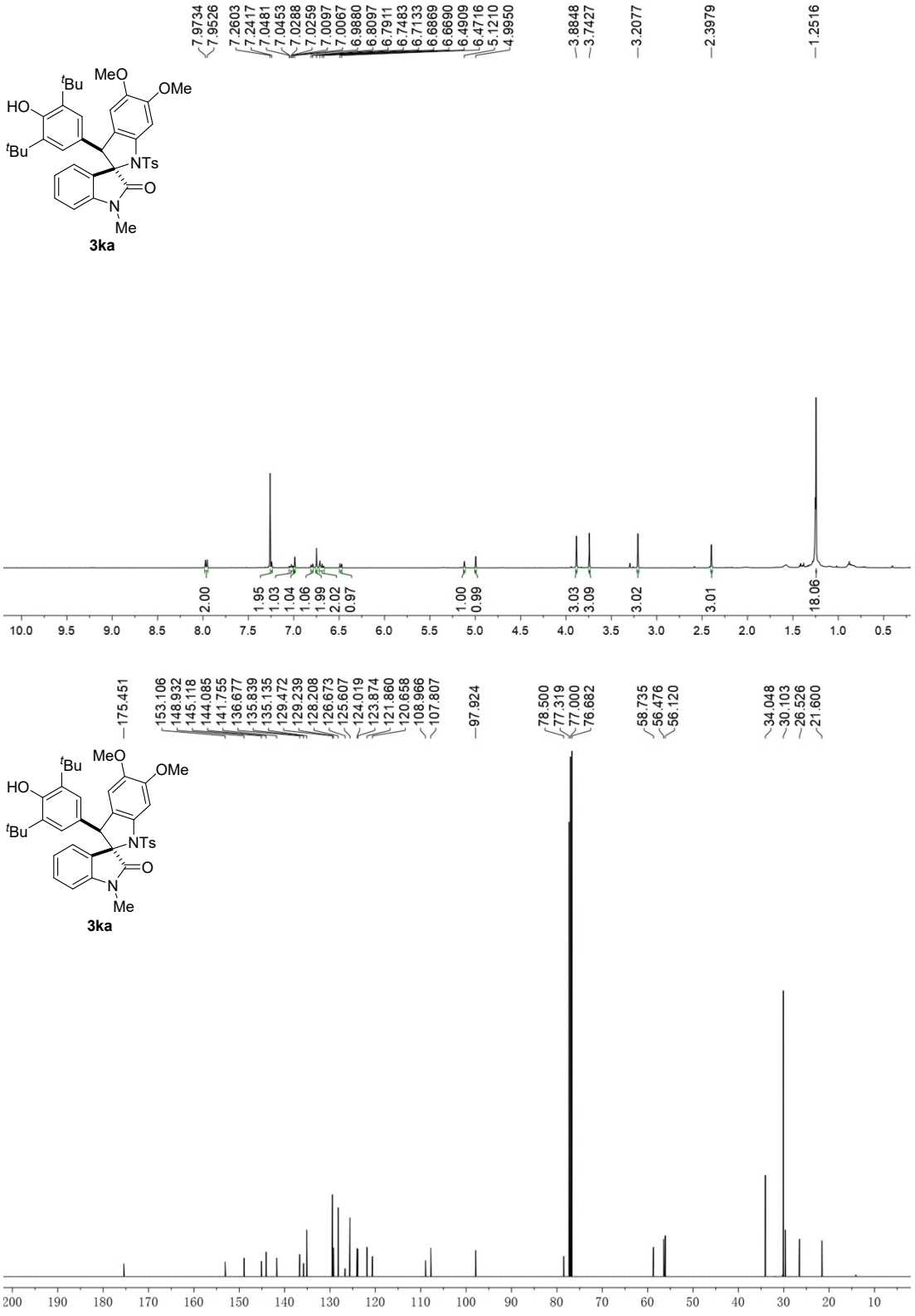
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30
20
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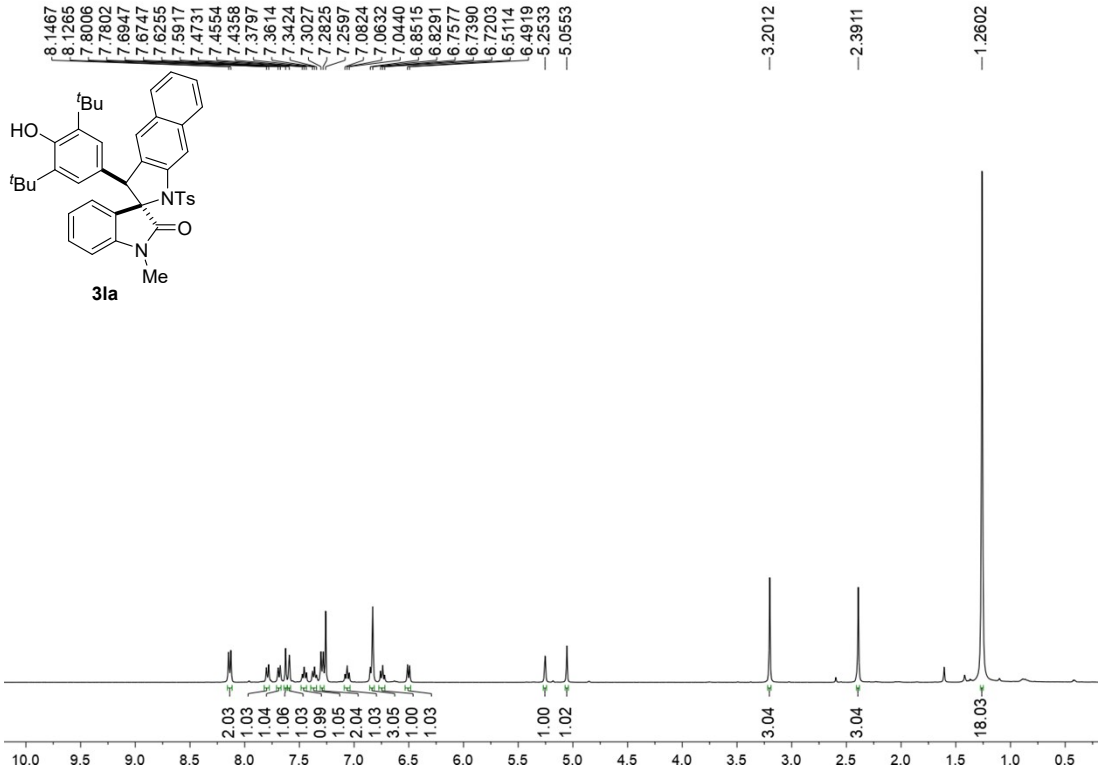
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8.0006
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7.6747
7.6255
7.5917
7.4731
7.4554
7.4358
7.3797
7.3614
7.3424
7.3027
7.2825
7.2597
7.0824
7.0632
7.0440
6.8515
6.8291
6.7577
6.7390
6.7203
6.5114
6.4919
5.2533
5.0553
3.2012
2.3911
1.2602
tBu
HO
tBu
NTs
O
N
Me
3la
2.03
1.03
1.04
1.06
1.03
0.99
1.05
2.04
1.03
3.05
1.00
1.03
1.00
1.02
3.04
3.04
18.03
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
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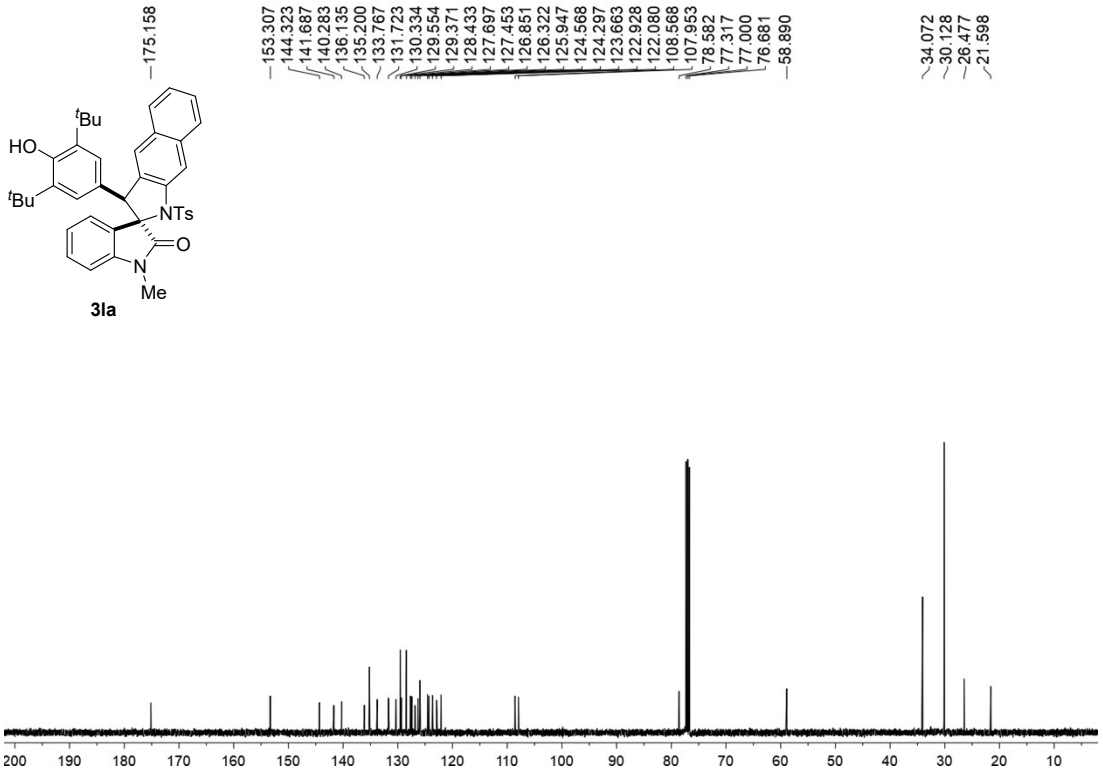
3.5
3.0
2.5
2.0
1.5
1.0
0.5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144.323
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136.135
135.200
133.767
131.723
130.334
129.554
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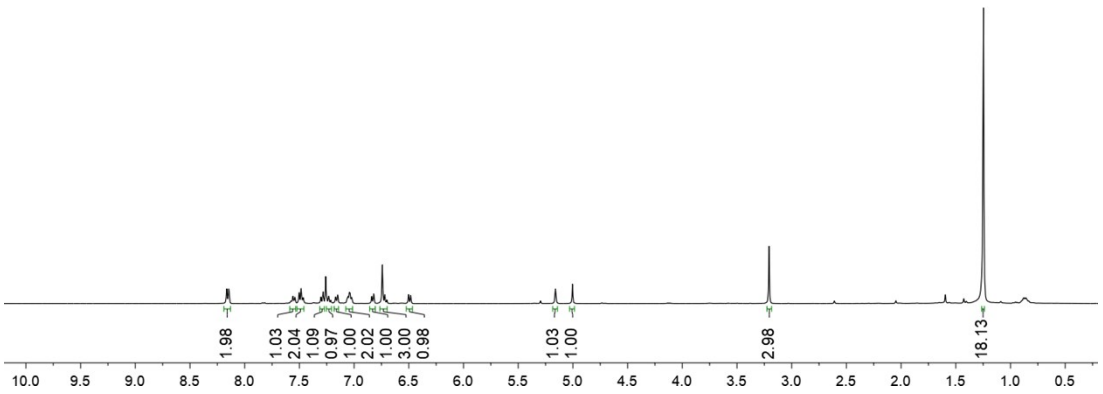
128.433
127.697
127.453
126.851
126.322
125.947
124.568
124.297
123.663
122.928
122.080
108.568
107.953
78.582
77.317
77.000
76.681
58.890
34.072
30.128
26.477
21.598
tBu
HO
tBu
NTs
O
N
Me
3la
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10


8.1638
8.1447
7.5768
7.5587
7.5407
7.5027
7.4836
7.4651
7.3031
7.2831
7.2595
7.2320
7.2123
7.1680
7.1496
7.0612
7.0546
7.0426
7.0239
6.8385
6.8203
6.7417
6.7186
6.6999
6.5019
6.4824
5.1589
5.0034
3.2064
1.2472

tBu
HO
tBu
N
S
O
O
O
Ph
N
Me

3ma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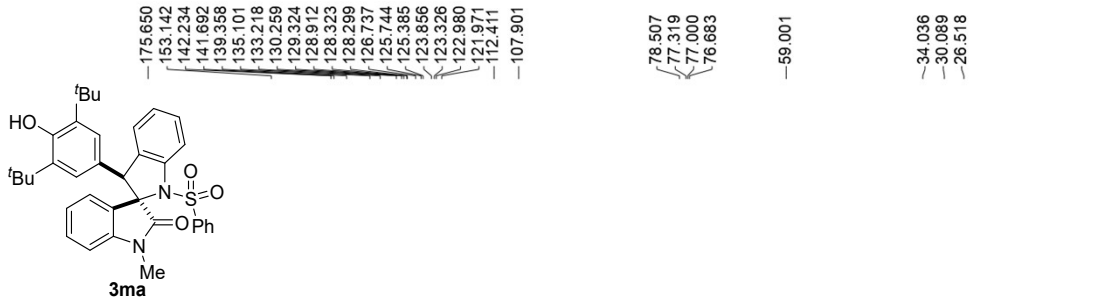
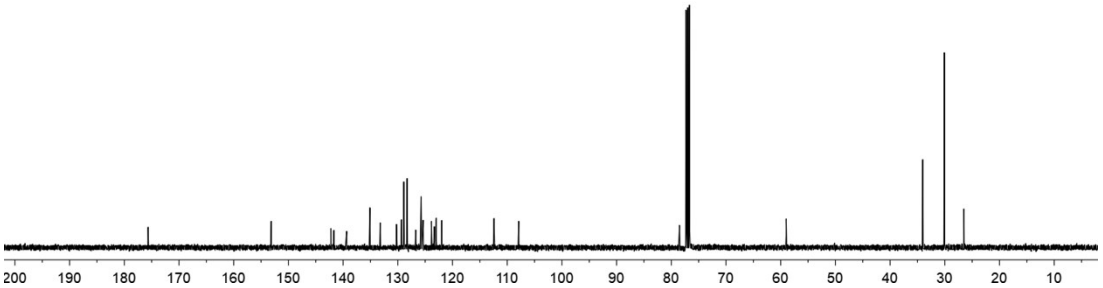
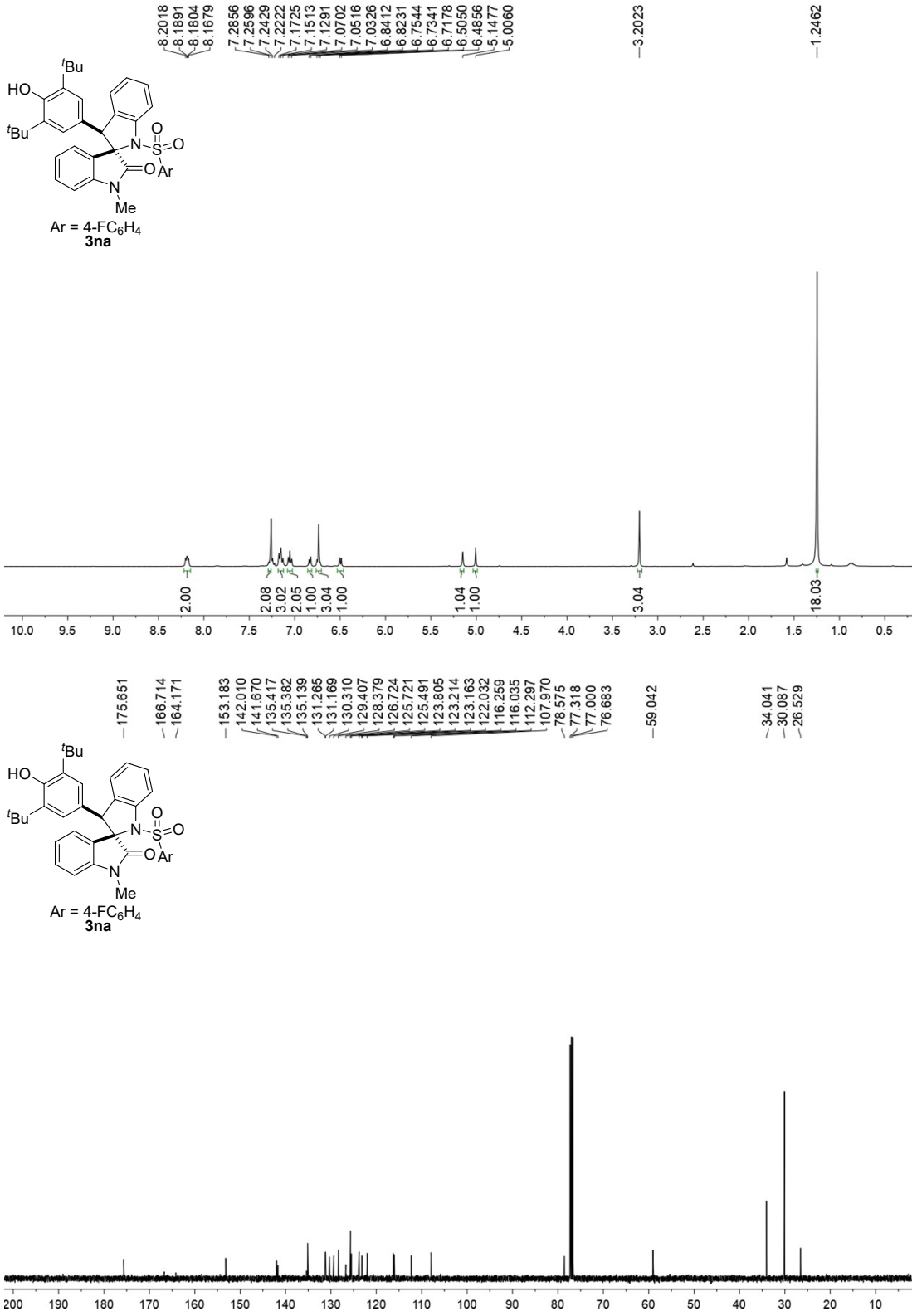
1.03
2.04
1.09
0.97
1.00
2.02
1.00
3.00
0.98
1.03
1.00
2.98
18.13
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5


175.650
153.142
142.234
141.692
139.358
135.101
133.218
130.259
129.324
128.912
128.323
128.299
126.737
125.744
125.385
123.856
123.326
122.980
121.971
112.411
107.901
78.507
77.319
77.000
76.683
59.001
34.036
30.089
26.518

tBu
HO
tBu
N
S
O
O
O
Ph
N
Me

3ma


200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10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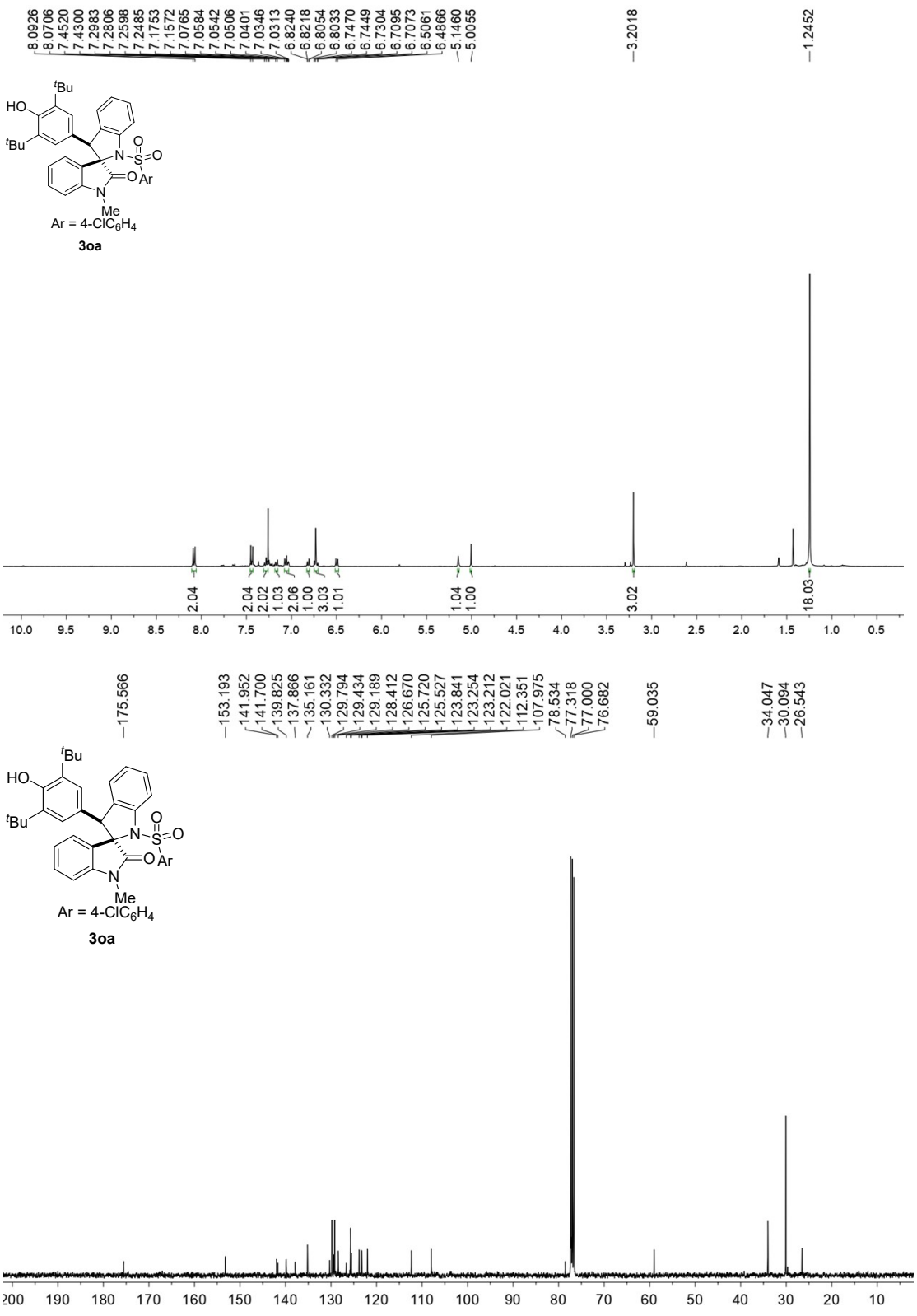
8.1891
8.1804
8.1679
7.2856
7.2596
7.2429
7.2222
7.1725
7.1513
7.1291
7.0702
7.0516
7.0326
6.8412
6.8231
6.7544
6.7341
6.7178
6.5050
6.4856
5.1477
5.0060
3.2023
1.2462
tBu
HO
tBu
O
N
S
O
O
Ar
N
Me
Ar = 4-FC6H4
3na
2.00
2.08
3.02
2.05
1.00
3.04
1.00
1.04
1.00
3.04
18.03
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
175.651
166.714
164.171
153.183
142.010
141.670
135.417
135.382
135.139
131.265
131.169
130.310
129.407
128.379
126.724
125.721
125.491
123.805
123.214
123.163
122.032
116.259
116.035
112.297
107.970
78.575
77.318
77.000
76.683
59.042
34.041
30.087
26.529
tBu
HO
tBu
O
N
S
O
O
Ar
N
Me
Ar = 4-FC6H4
3na
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10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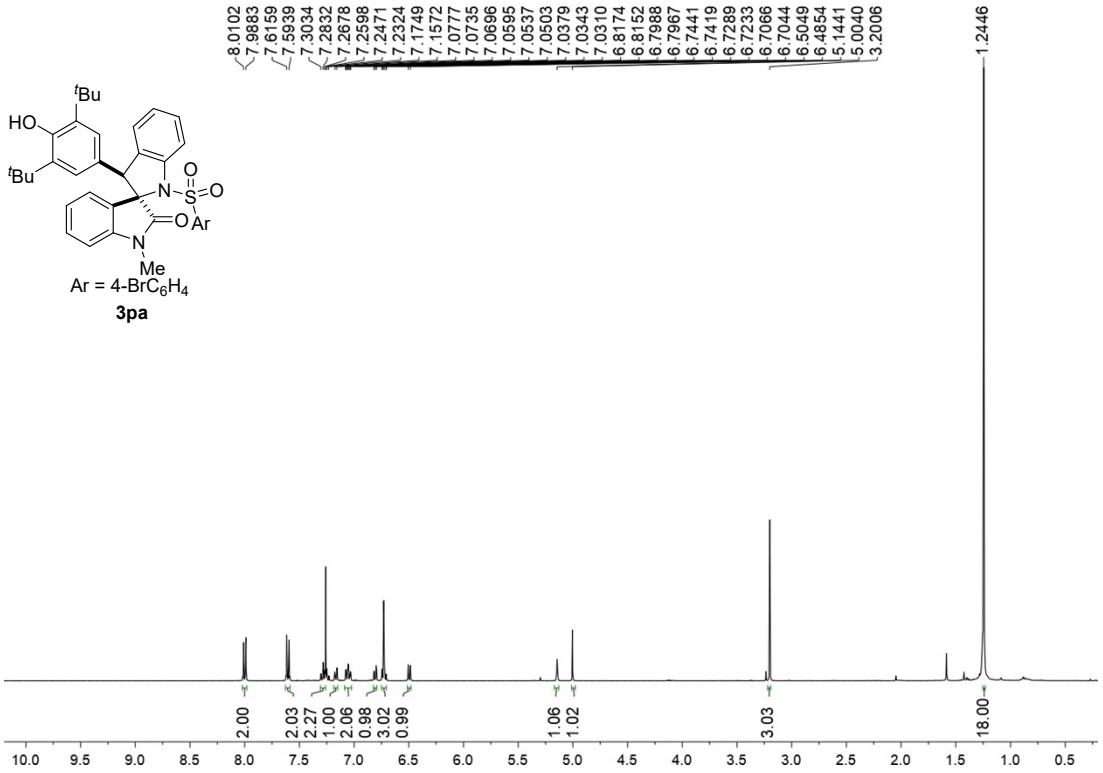
8.0706
7.4520
7.4300
7.2983
7.2806
7.2598
7.2485
7.1753
7.1572
7.0765
7.0584
7.0542
7.0506
7.0401
7.0346
7.0313
6.8240
6.8218
6.8054
6.8033
6.7470
6.7449
6.7304
6.7095
6.7073
6.5061
6.4866
5.1460
5.0055
3.2018
1.2452
tBu
HO
tBu
O
N
S
O
O
Ar
N
Me
Ar = 4-ClC6H4
3oa
2.04
2.04
2.02
1.03
2.06
1.00
3.03
1.01
1.04
1.00
3.02
18.03
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
175.566
153.193
141.952
141.700
139.825
137.866
135.161
130.332
129.794
129.434
129.189
128.412
126.670
125.720
125.527
123.841
123.254
123.212
122.021
112.351
107.975
78.534
77.318
77.000
76.682
59.035
34.047
30.094
26.543
tBu
HO
tBu
O
N
S
O
O
Ar
N
Me
Ar = 4-ClC6H4
3oa
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10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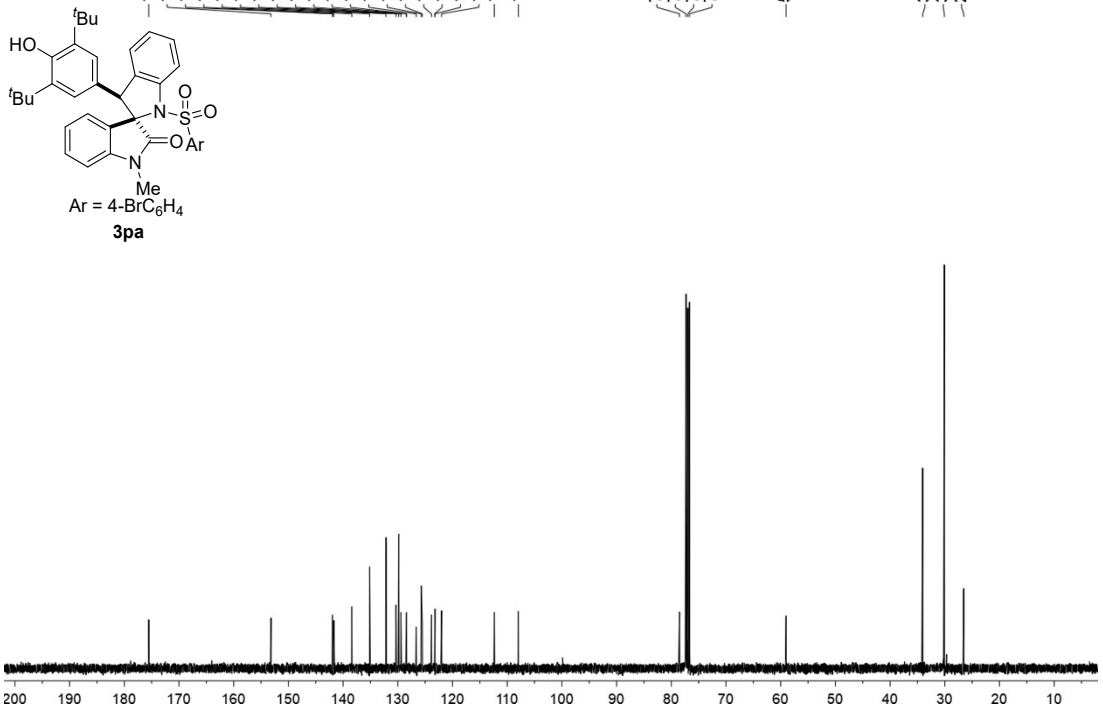
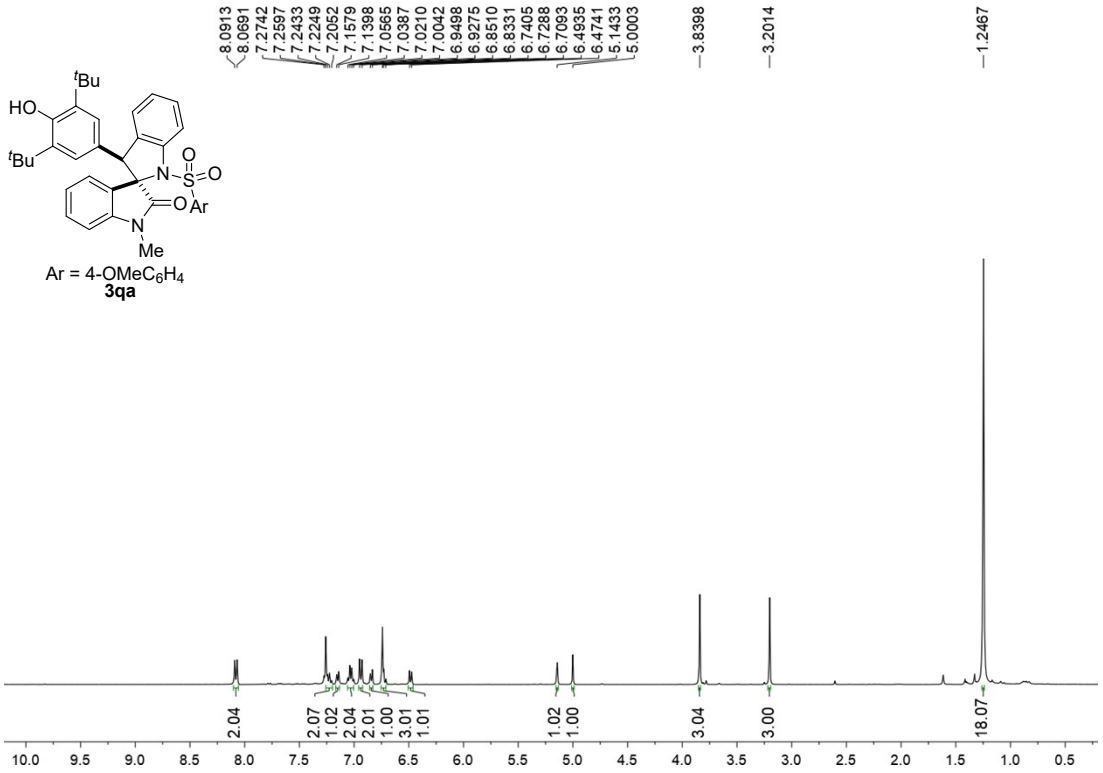
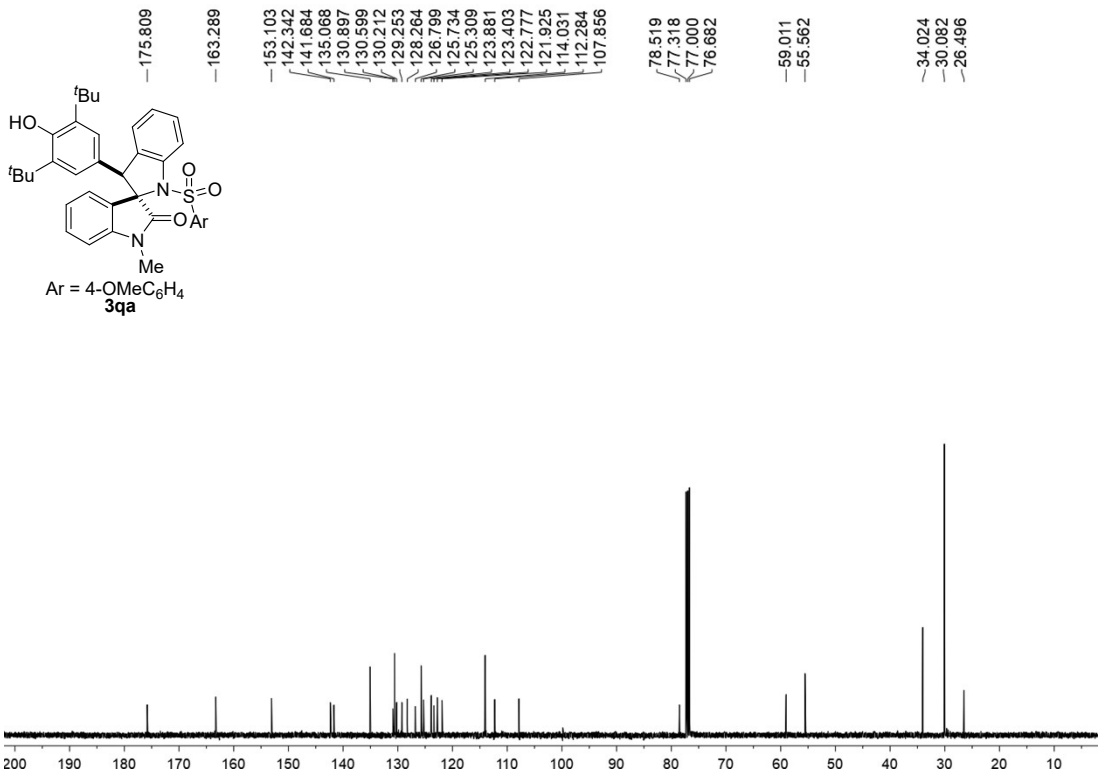
7.9883
7.6159
7.5939
7.3034
7.2832
7.2678
7.2598
7.2471
7.2324
7.1749
7.1572
7.0777
7.0735
7.0696
7.0595
7.0537
7.0503
7.0379
7.0343
7.0310
6.8174
6.8152
6.7988
6.7967
6.7441
6.7419
6.7289
6.7233
6.7066
6.7044
6.5049
6.4854
5.1441
5.0040
3.2006
1.2446
2.00
2.03
2.27
1.00
2.06
0.98
3.02
0.99
1.06
1.02
3.03
18.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5


175.534
153.189
141.937
141.704
138.411
135.164
132.167
130.333
129.844
129.432
128.437
128.416
126.635
125.712
125.529
123.845
123.268
123.208
122.011
112.361
107.968
78.511
77.318
77.000
76.682
59.022
34.043
30.090
26.540
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10


8.0913
8.0691
7.2742
7.2597
7.2433
7.2249
7.2052
7.1579
7.1398
7.0565
7.0387
7.0210
7.0042
6.9498
6.9275
6.8510
6.8331
6.7405
6.7288
6.7093
6.4935
6.4741
5.1433
5.0003
3.8398
3.2014
1.2467
tBu
HO
tBu
N
S
O
O
O
Ar
N
Me
Ar = 4-OMeC6H4
3qa
2.04
2.07
1.02
2.04
2.01
1.00
3.01
1.01
1.02
1.00
3.04
3.00
18.07
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5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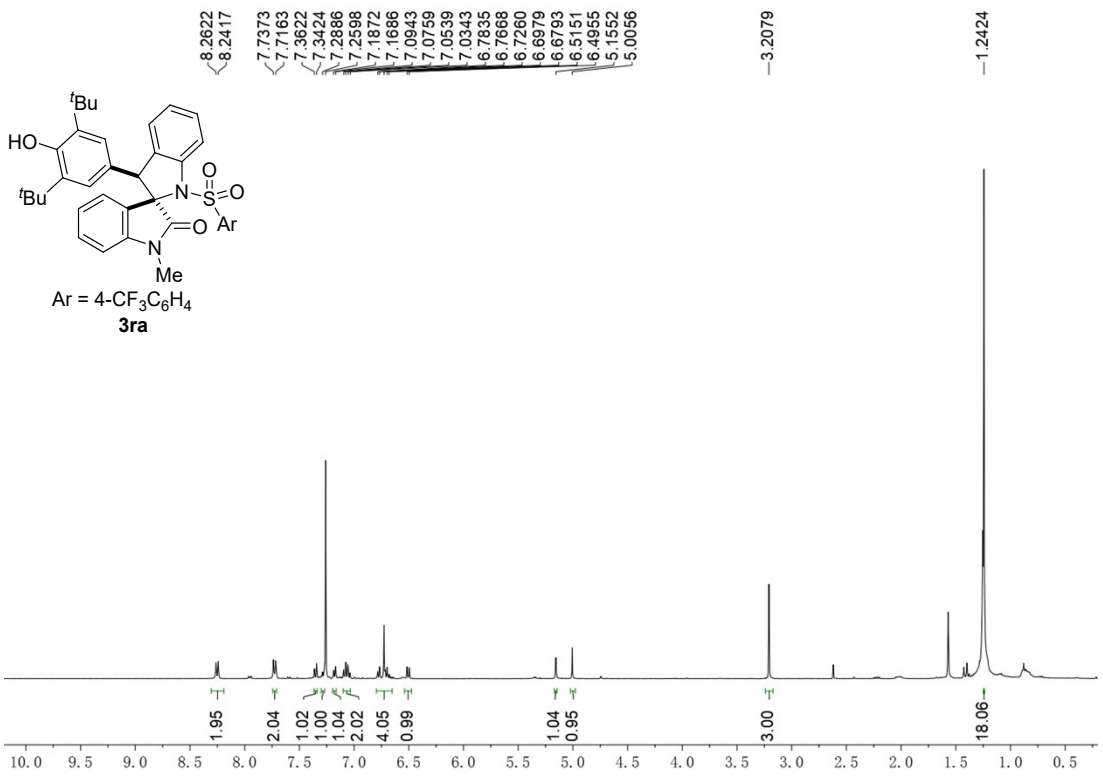
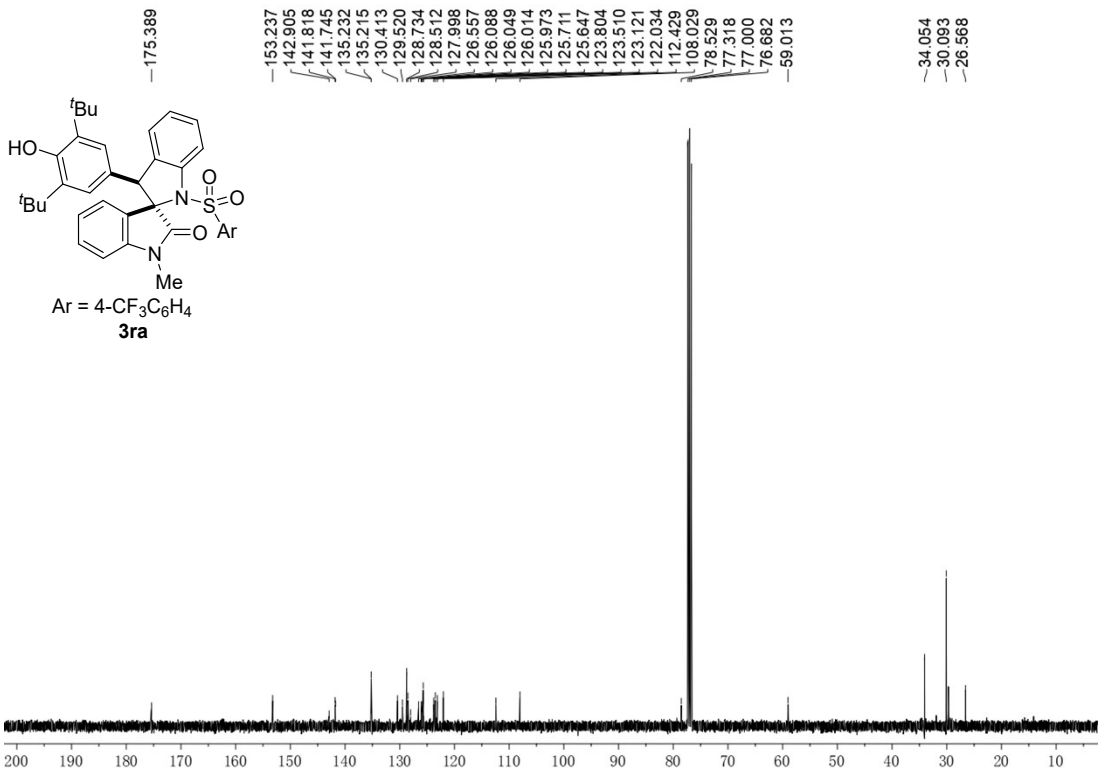
153.103
142.342
141.684
135.068
130.897
130.599
130.212
129.253
128.264
126.799
125.734
125.309
123.881
123.403
122.777
121.925
114.031
112.284
107.856
78.519
77.318
77.000
76.682
59.011
55.562
34.024
30.082
26.496
tBu
HO
tBu
N
S
O
O
O
Ar
N
Me
Ar = 4-OMeC6H4
3qa
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10



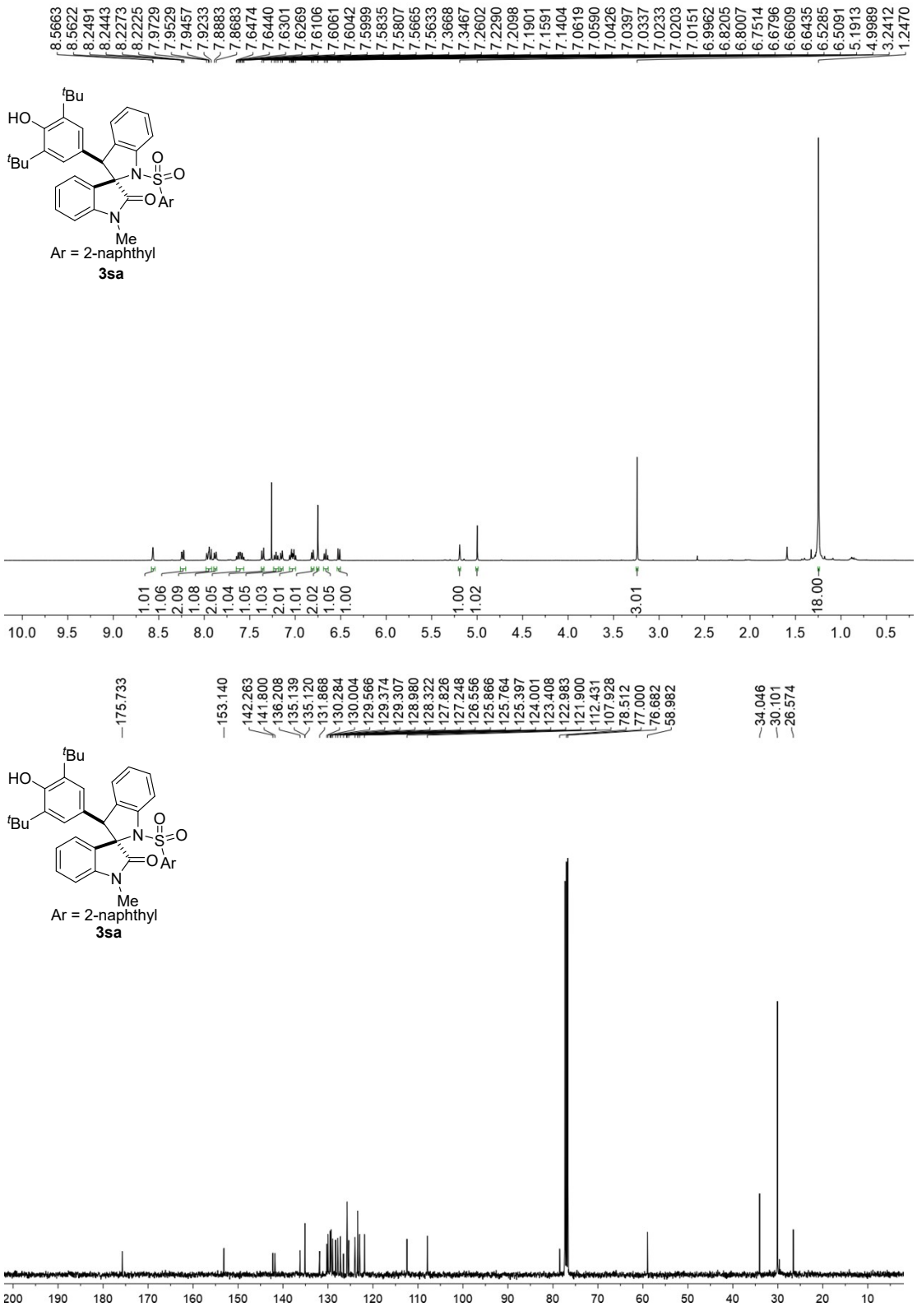


Ar = 4-$CF_3C_6H_4$

3ra

Ar = 4-$CF_3C_6H_4$

3ra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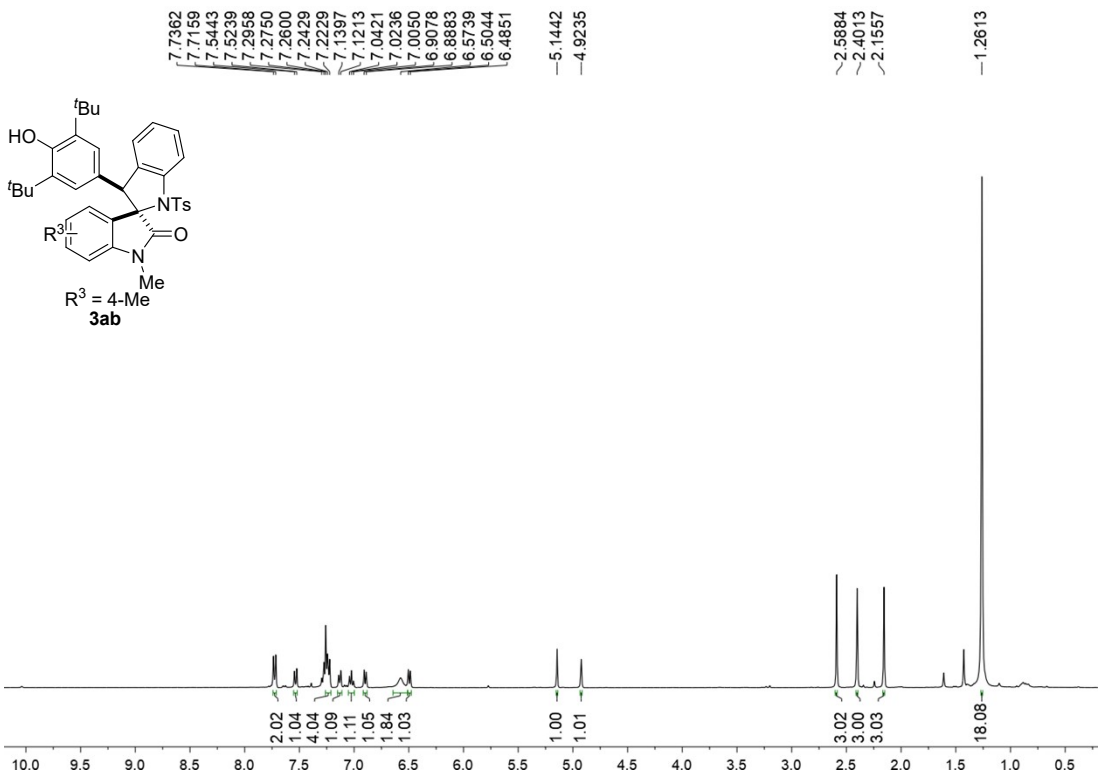
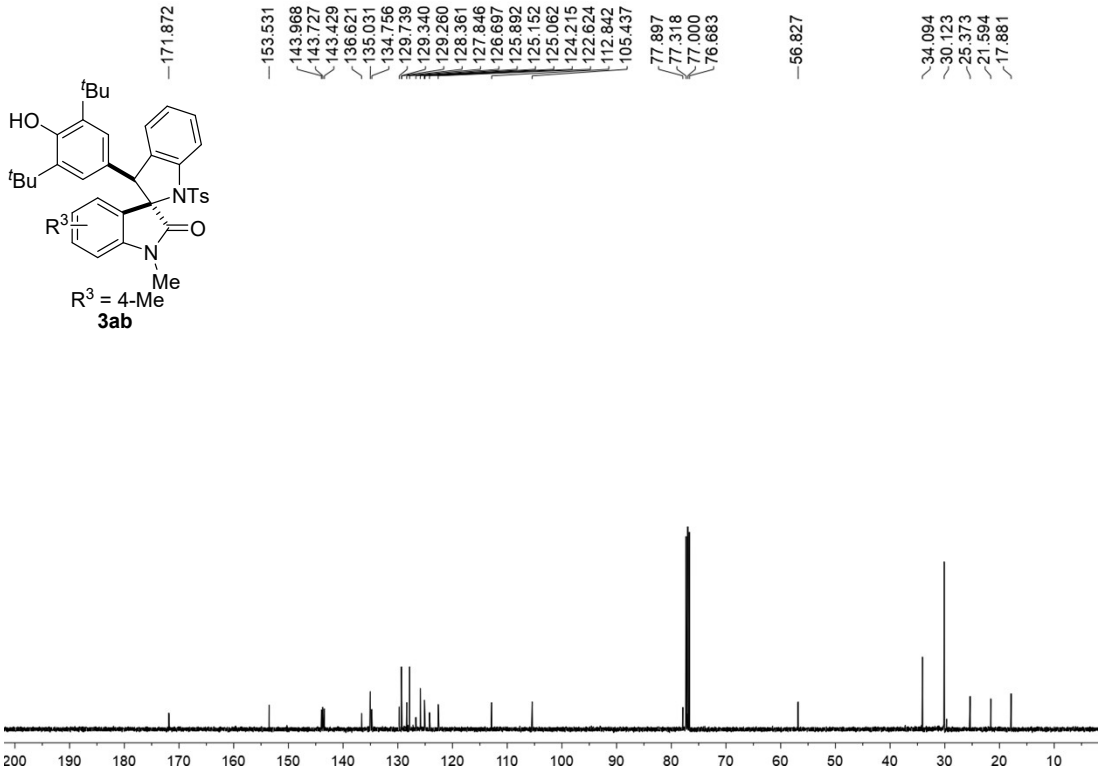
8.5622
8.2491
8.2443
8.2273
8.2225
7.9729
7.9529
7.9457
7.9233
7.8883
7.8683
7.6474
7.6440
7.6301
7.6269
7.6106
7.6061
7.6042
7.5999
7.5835
7.5807
7.5665
7.5633
7.3668
7.3467
7.2602
7.2290
7.2098
7.1901
7.1591
7.1404
7.0619
7.0590
7.0426
7.0397
7.0337
7.0233
7.0203
7.0151
6.9962
6.8205
6.8007
6.7514
6.6796
6.6609
6.6435
6.5285
6.5091
5.1913
4.9989
3.2412
1.2470
tBu
HO
tBu
O
N
S
O
O
Ar
N
Me
Ar = 2-naphthyl
3sa
1.01
1.06
2.09
1.08
2.05
1.04
1.05
1.03
2.01
1.01
2.02
1.05
1.00
1.00
1.02
3.01
18.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
175.733
153.140
142.263
141.800
136.208
135.139
135.120
131.868
130.284
130.004
129.566
129.374
129.307
128.980
128.322
127.826
127.248
126.556
125.866
125.764
125.397
124.001
123.408
122.983
121.900
112.431
107.928
78.512
77.000
76.682
58.982
34.046
30.101
26.574
tBu
HO
tBu
O
N
S
O
O
Ar
N
Me
Ar = 2-naphthyl
3sa
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10


7.7362
7.7159
7.5443
7.5239
7.2958
7.2750
7.2600
7.2429
7.2229
7.1397
7.1213
7.0421
7.0236
7.0050
6.9078
6.8883
6.5739
6.5044
6.4851
5.1442
4.9235
2.5884
2.4013
2.1557
1.2613
tBu
HO
tBu
NTs
R3
O
N
Me
R3 = 4-Me
3ab
2.02
1.04
4.04
1.09
1.11
1.05
1.84
1.03
1.00
1.01
3.02
3.00
3.03
18.08
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5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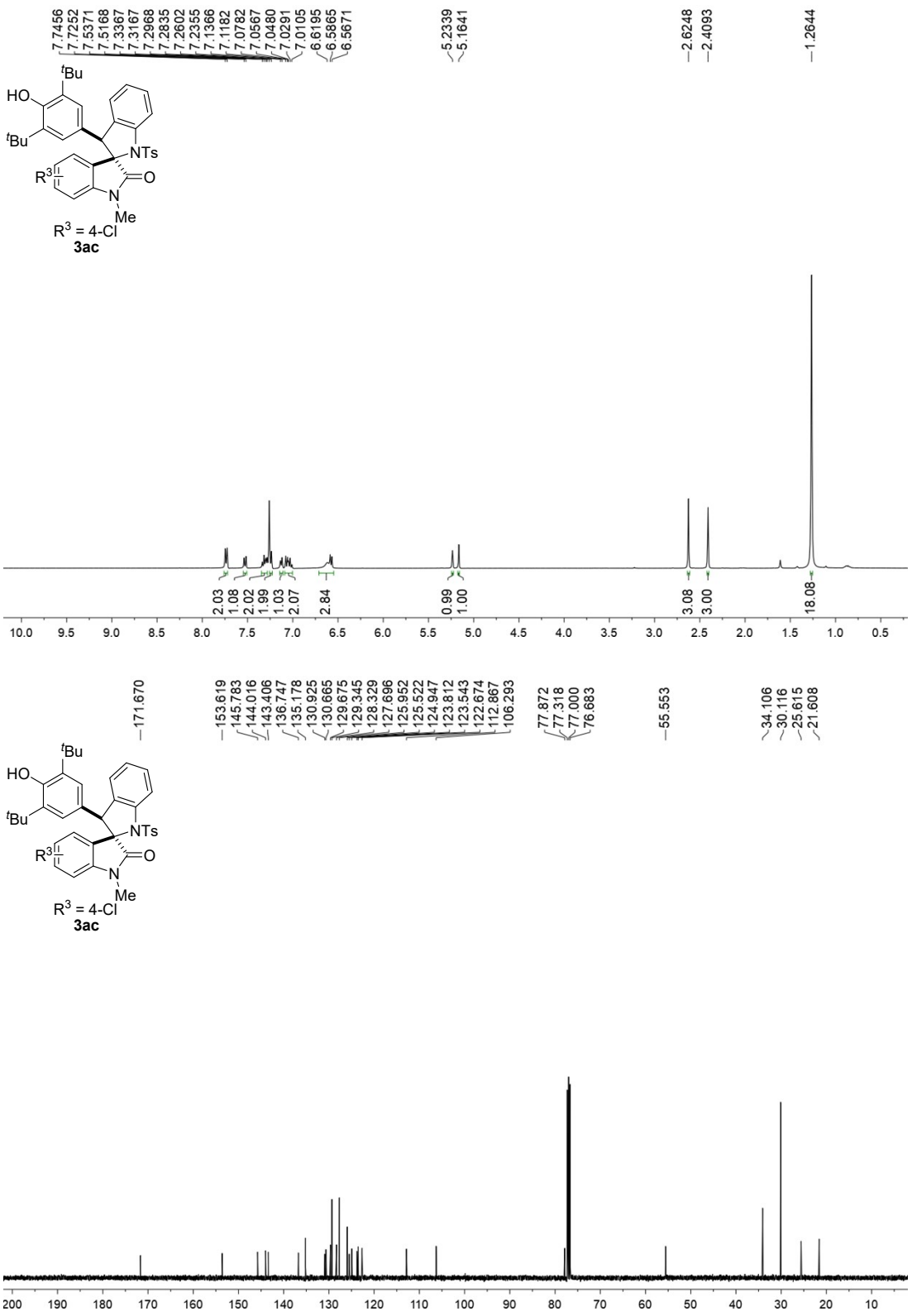
143.968
143.727
143.429
136.621
135.031
134.756
129.739
129.340
129.260
128.361
127.846
126.697
125.892
125.152
125.062
124.215
122.624
112.842
105.437
77.897
77.318
77.000
76.683
56.827
34.094
30.123
25.373
21.594
17.881
tBu
HO
tBu
NTs
R3
O
N
Me
R3 = 4-Me
3ab
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10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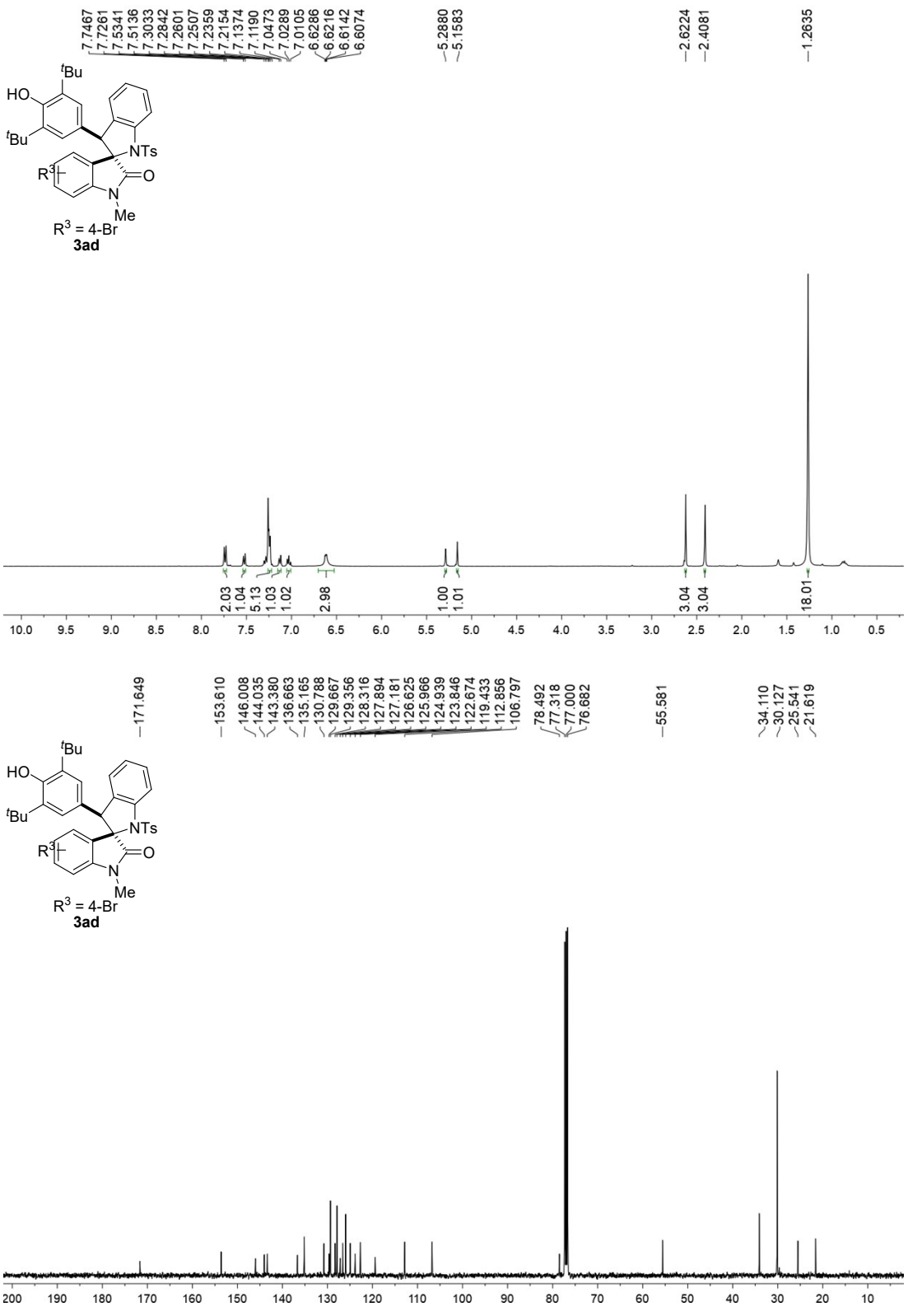
7.7252
7.5371
7.5168
7.3367
7.3167
7.2968
7.2835
7.2602
7.2355
7.1366
7.1182
7.0782
7.0567
7.0480
7.0291
7.0105
6.6195
6.5865
6.5671
5.2339
5.1641
2.6248
2.4093
1.2644
tBu
HO
tBu
NTs
R3
O
N
Me
R3 = 4-Cl
3ac
2.03
1.08
2.02
1.99
1.03
2.07
2.84
0.99
1.00
3.08
3.00
18.08
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
171.670
153.619
145.783
144.016
143.406
136.747
135.178
130.925
130.665
129.675
129.345
128.329
127.696
125.952
125.522
124.947
123.812
123.543
122.674
112.867
106.293
77.872
77.318
77.000
76.683
55.553
34.106
30.116
25.615
21.608
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10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7.3033
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7.2601
7.2507
7.2359
7.2154
7.1374
7.1190
7.0473
7.0289
7.0105
6.6286
6.6216
6.6142
6.6074
5.2880
5.1583
2.6224
2.4081
1.2635
tBu
HO
tBu
NTs
R3
O
N
Me
R3 = 4-Br
3ad
2.03
1.04
5.13
1.03
1.02
2.98
1.00
1.01
3.04
3.04
18.01
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
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153.610
146.008
144.035
143.380
136.663
135.165
130.788
129.667
129.356
128.316
127.894
127.181
126.625
125.966
124.939
123.846
122.674
119.433
112.856
106.797
78.492
77.318
77.000
76.682
55.581
34.110
30.127
25.541
21.619
200
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100
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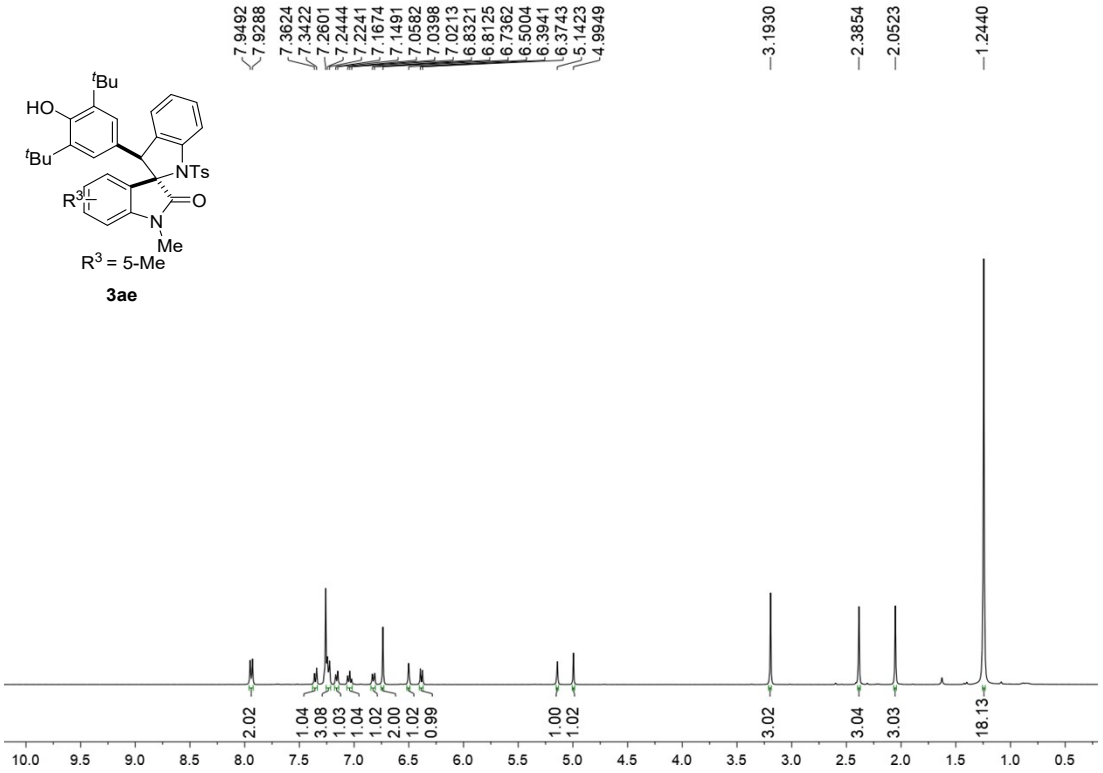
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7.2444
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7.0398
7.0213
6.8321
6.8125
6.7362
6.5004
6.3941
6.3743
5.1423
4.9949
3.1930
2.3854
2.0523
1.2440
tBu
HO
tBu
NTs
R3
O
N
Me
R3 = 5-Me
3ae
2.02
1.04
3.08
1.03
1.04
1.02
2.00
1.02
0.99
1.00
1.02
3.02
3.04
3.03
18.13
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
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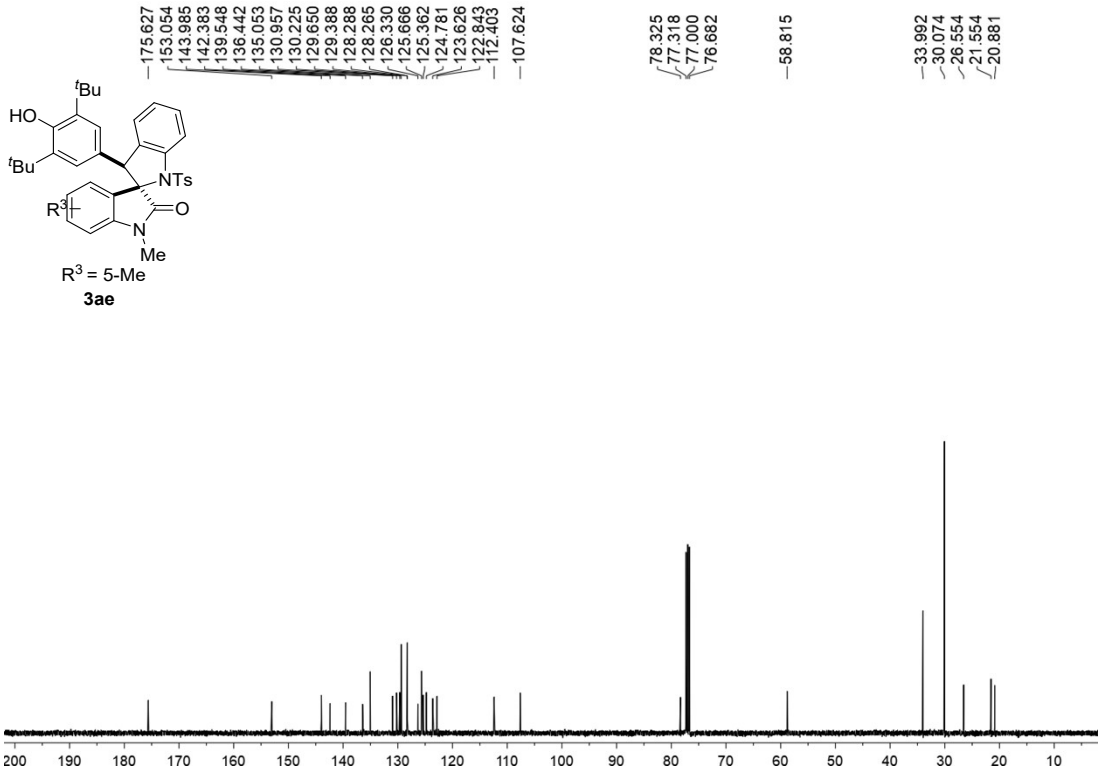
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135.053
130.957
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129.388
128.288
128.265
126.330
125.666
125.362
124.781
123.626
122.843
112.403
107.624
78.325
77.318
77.000
76.682
58.815
33.992
30.074
26.554
21.554
20.881
tBu
HO
tBu
NTs
R3
O
N
Me
R3 = 5-Me
3ae
200
190
180
170
160
150
140
130
120
110
100
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80
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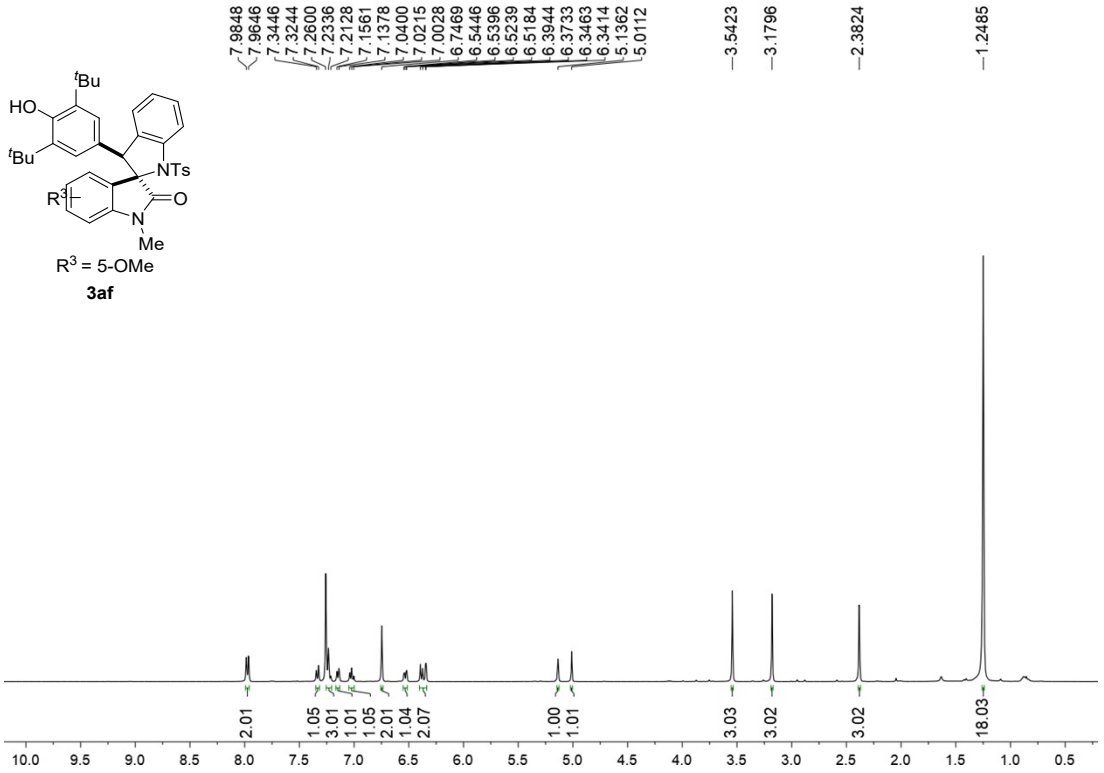
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7.1378
7.0400
7.0215
7.0028
6.7469
6.5446
6.5396
6.5239
6.5184
6.3944
6.3733
6.3463
6.3414
5.1362
5.0112
3.5423
3.1796
2.3824
1.2485
2.01
1.05
3.01
1.01
1.05
2.01
1.04
2.07
1.00
1.01
3.03
3.02
3.02
18.03
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9.0
8.5
8.0
7.5
7.0
6.5
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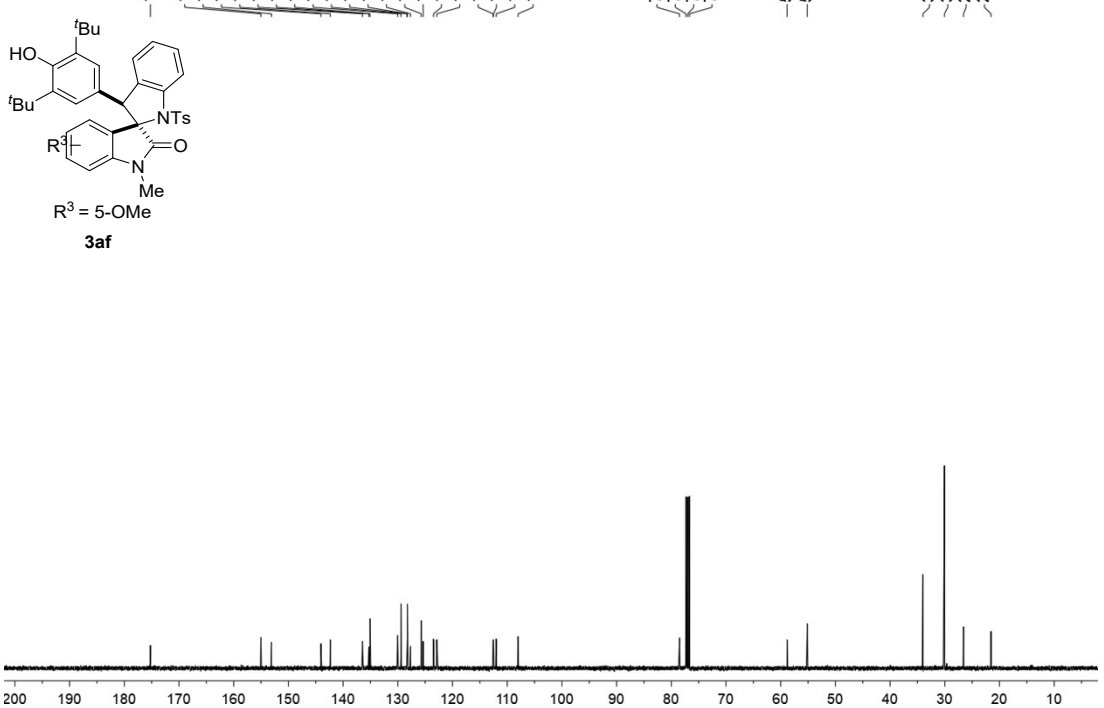
0.5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130.033
129.421
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128.248
127.675
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125.366
123.488
122.877
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112.495
112.010
108.016
78.507
77.318
77.000
76.682
58.823
55.141
34.002
30.069
26.590
21.555
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100
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80
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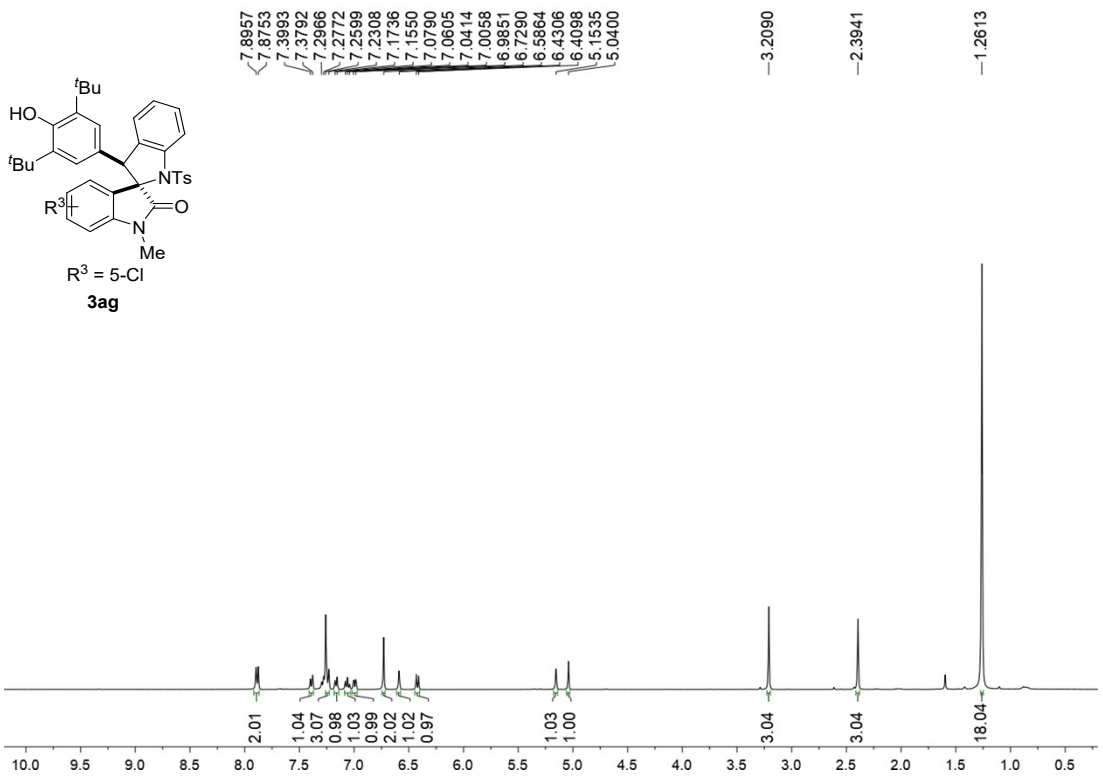
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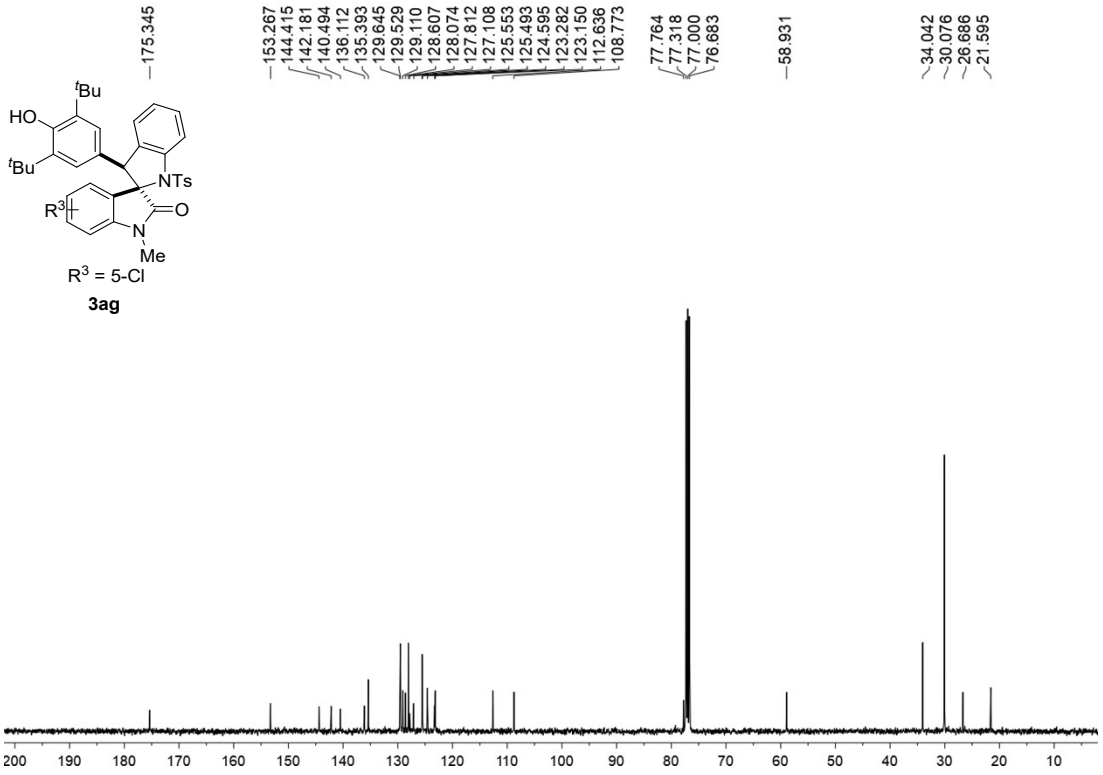
7.2599
7.2308
7.1736
7.1550
7.0790
7.0605
7.0414
7.0058
6.9851
6.7290
6.5864
6.4306
6.4098
5.1535
5.0400
3.2090
2.3941
1.2613
tBu
HO
tBu
NTs
R3
O
N
Me
R3 = 5-Cl
3ag
2.01
1.04
3.07
0.98
1.03
0.99
2.02
1.02
0.97
1.03
1.00
3.04
3.04
18.04
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5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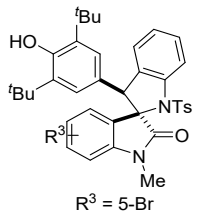
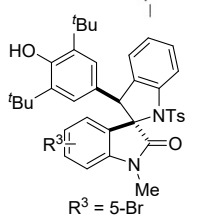
129.645
129.529
129.110
128.607
128.074
127.812
127.108
125.553
125.493
124.595
123.282
123.150
112.636
108.773
77.764
77.318
77.000
76.683
58.931
34.042
30.076
26.686
21.595
tBu
HO
tBu
NTs
R3
O
N
Me
R3 = 5-Cl
3ag
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10



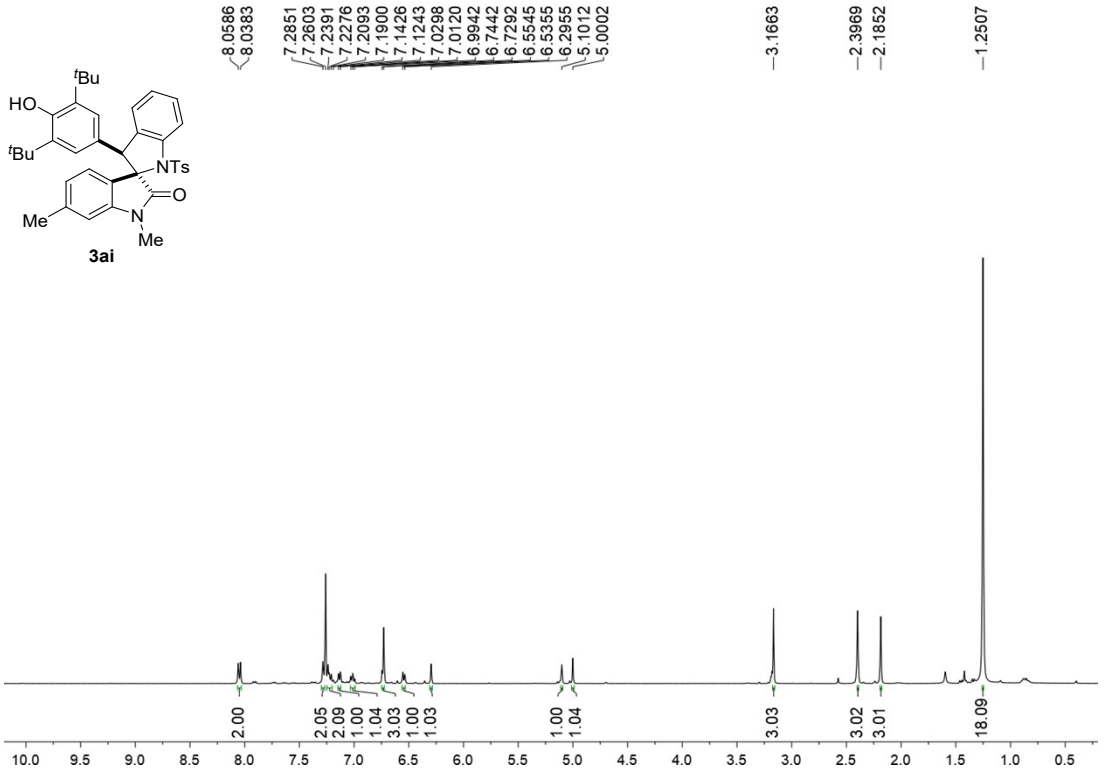
R^3 = 5-Br

3ah



R^3 = 5-Br

3ah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7.2093
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7.1243
7.0298
7.0120
6.9942
6.7442
6.7292
6.5545
6.5355
6.2955
5.1012
5.0002
3.1663
2.3969
2.1852
1.2507
2.00
2.05
2.09
1.00
1.04
3.03
1.00
1.03
1.00
1.04
3.03
3.02
3.01
18.09
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
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5.0
4.5
4.0
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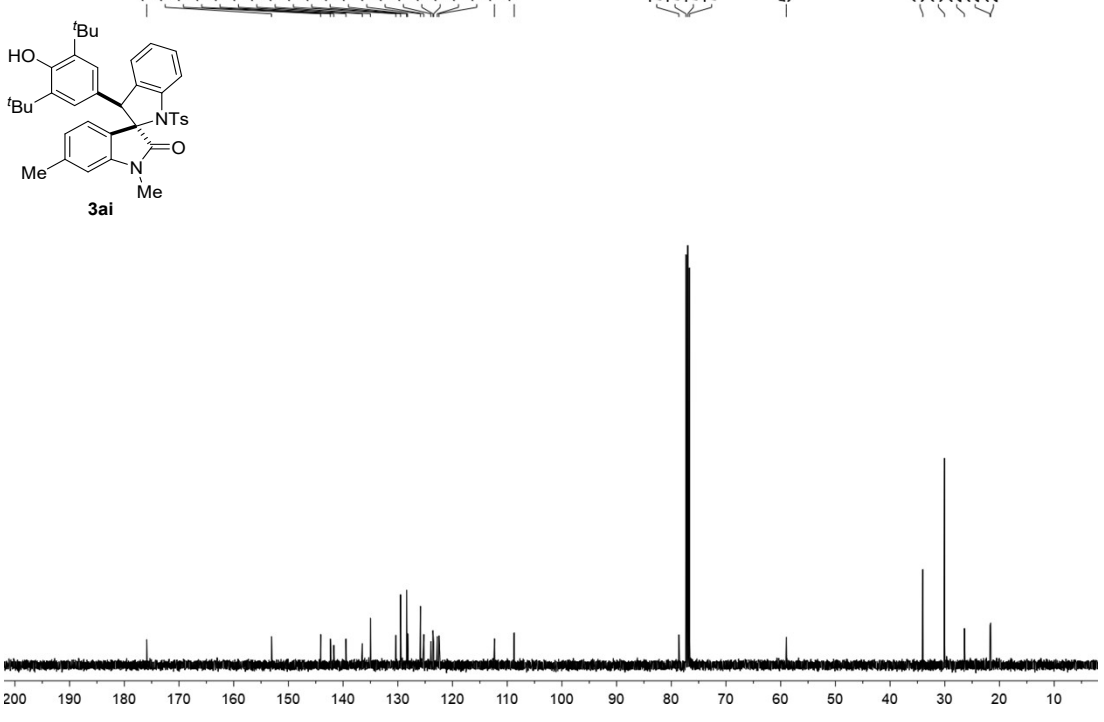
1.0
0.5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135.002
130.362
129.502
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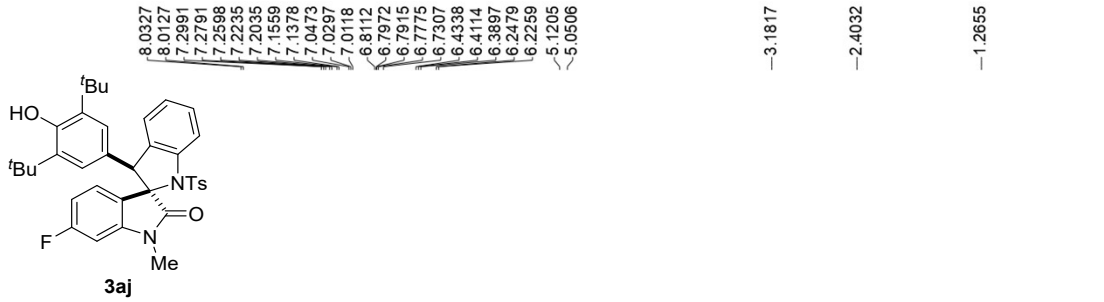
128.201
125.862
125.252
123.969
123.591
123.454
122.792
122.482
112.329
108.734
78.624
77.317
77.000
76.682
58.974
34.022
30.058
26.426
21.723
21.609
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10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7.2791
7.2598
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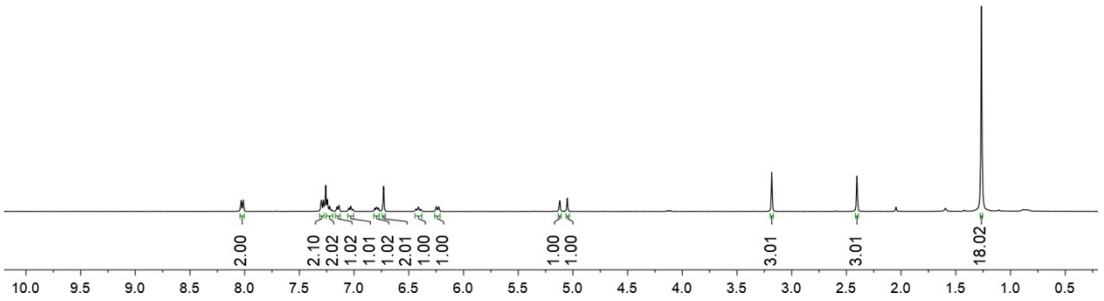
7.2035
7.1559
7.1378
7.0473
7.0297
7.0118
6.8112
6.7972
6.7915
6.7775
6.7307
6.4338
6.4114
6.3897
6.2479
6.2259
5.1205
5.0506
3.1817
2.4032
1.2655
tBu
HO
tBu
NTs
O
F
N
Me

3aj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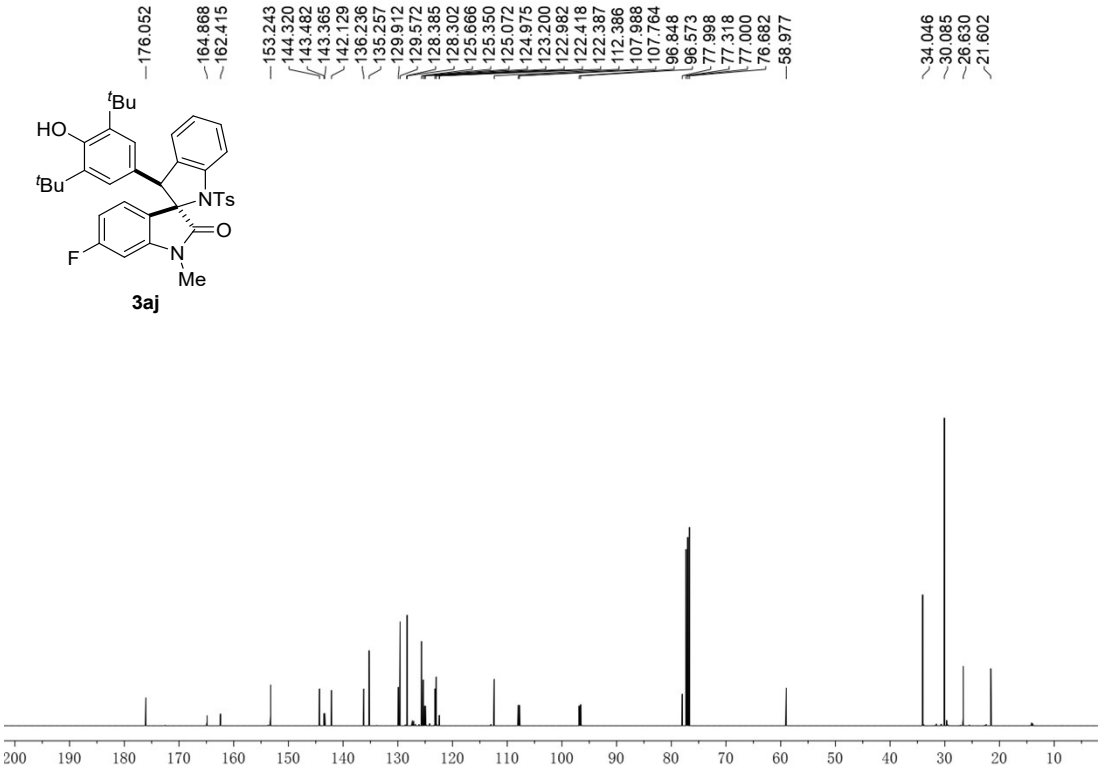
2.02
1.02
1.01
1.02
2.01
1.00
1.00
1.00
1.00
3.01
3.01
18.02
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5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129.572
128.385
128.302
125.666
125.350
125.072
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123.200
122.982
122.418
122.387
112.386
107.988
107.764
96.848
96.573
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77.318
77.000
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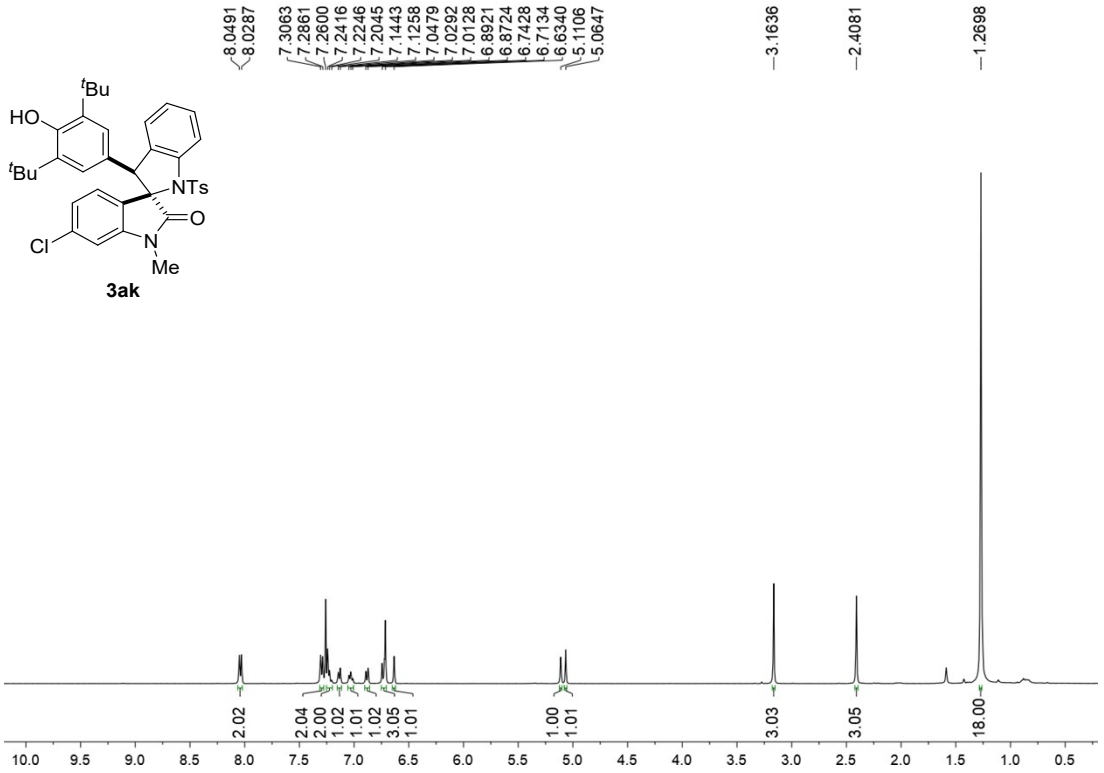
26.630
21.602
tBu
HO
tBu
NTs
O
F
N
Me

3aj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7.1443
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7.0292
7.0128
6.8921
6.8724
6.7428
6.7134
6.6340
5.1106
5.0647
3.1636
2.4081
1.2698
tBu
HO
tBu
NTs
O
Cl
N
Me
3ak
2.02
2.04
2.00
1.02
1.01
1.02
3.05
1.01
1.00
1.01
3.03
3.05
18.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
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3.0
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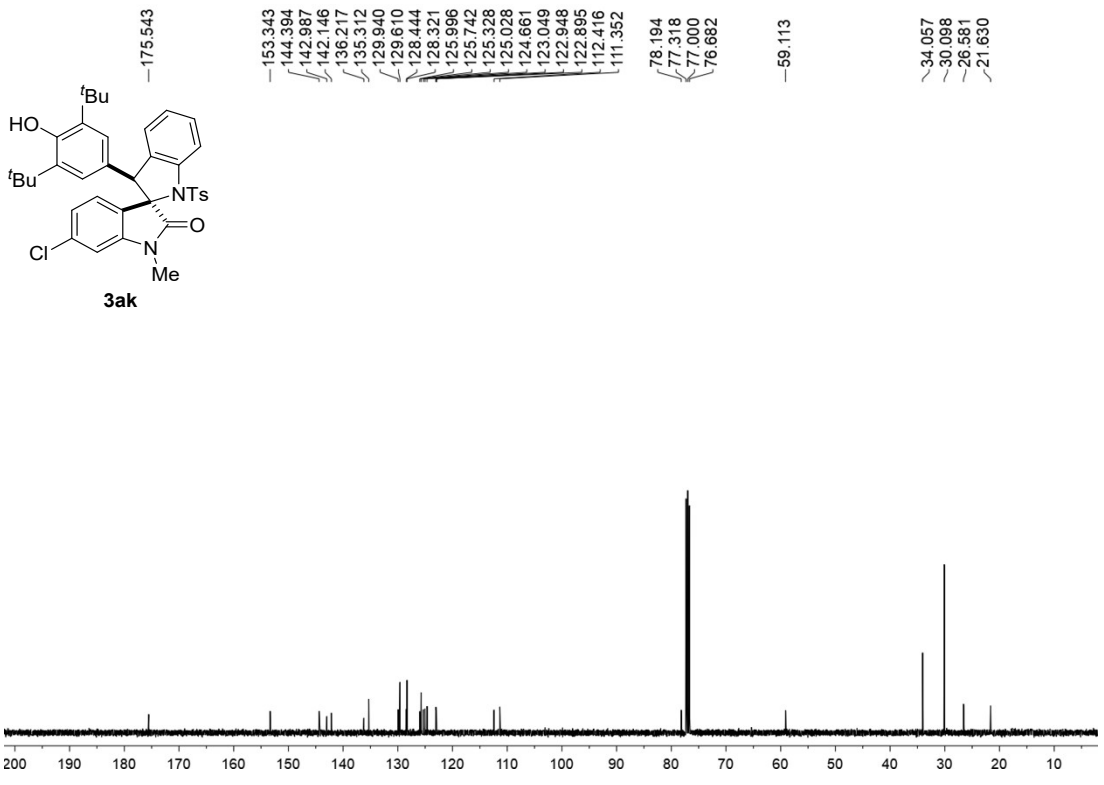
2.0
1.5
1.0
0.5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76.682
59.113
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21.630
tBu
HO
tBu
NTs
O
Cl
N
Me
3ak
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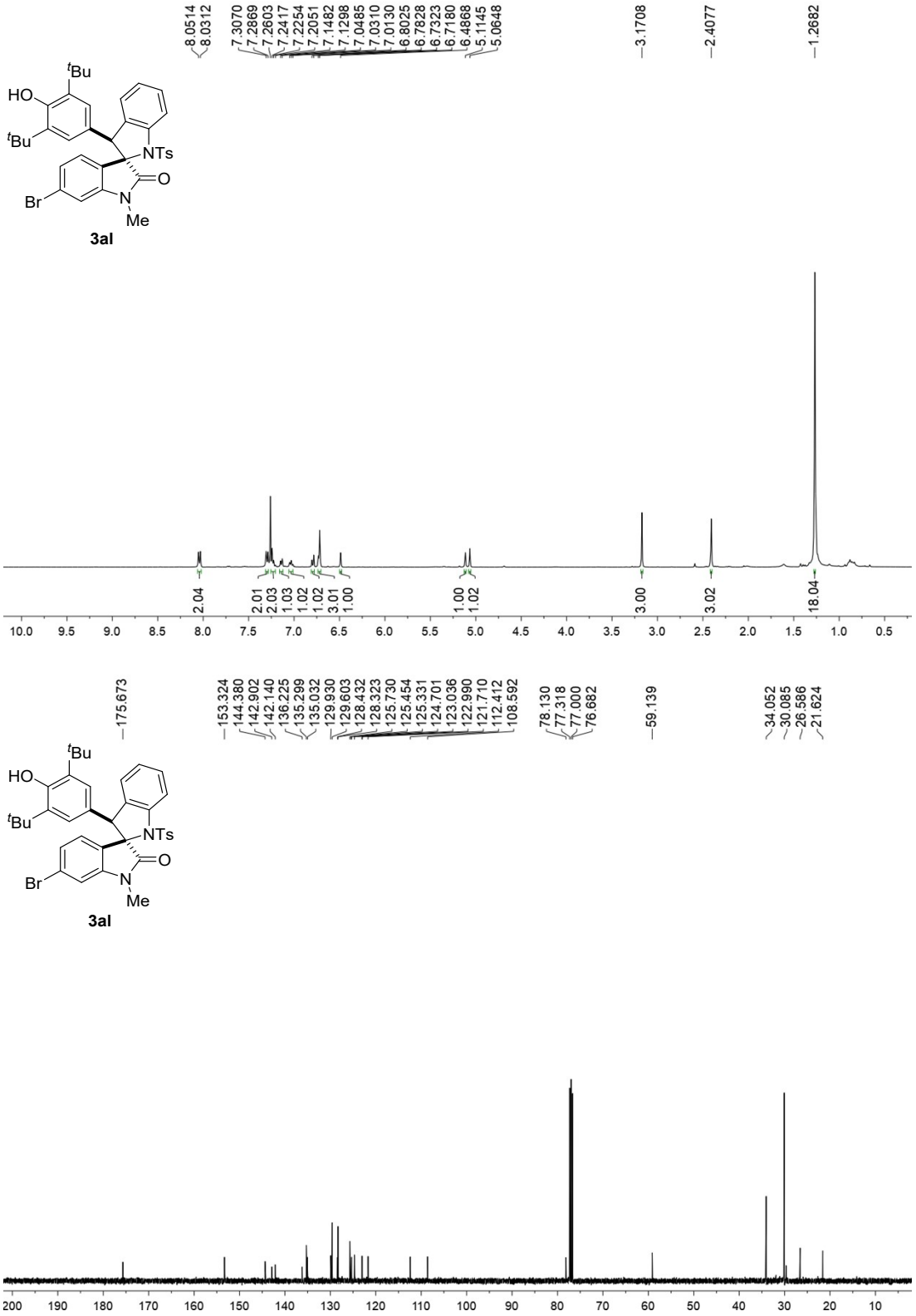
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tBu
HO
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NTs
O
Br
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2.03
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1.02
1.02
3.01
1.00
1.00
1.02
3.00
3.02
18.04
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tBu
NTs
O
Br
N
Me
3al
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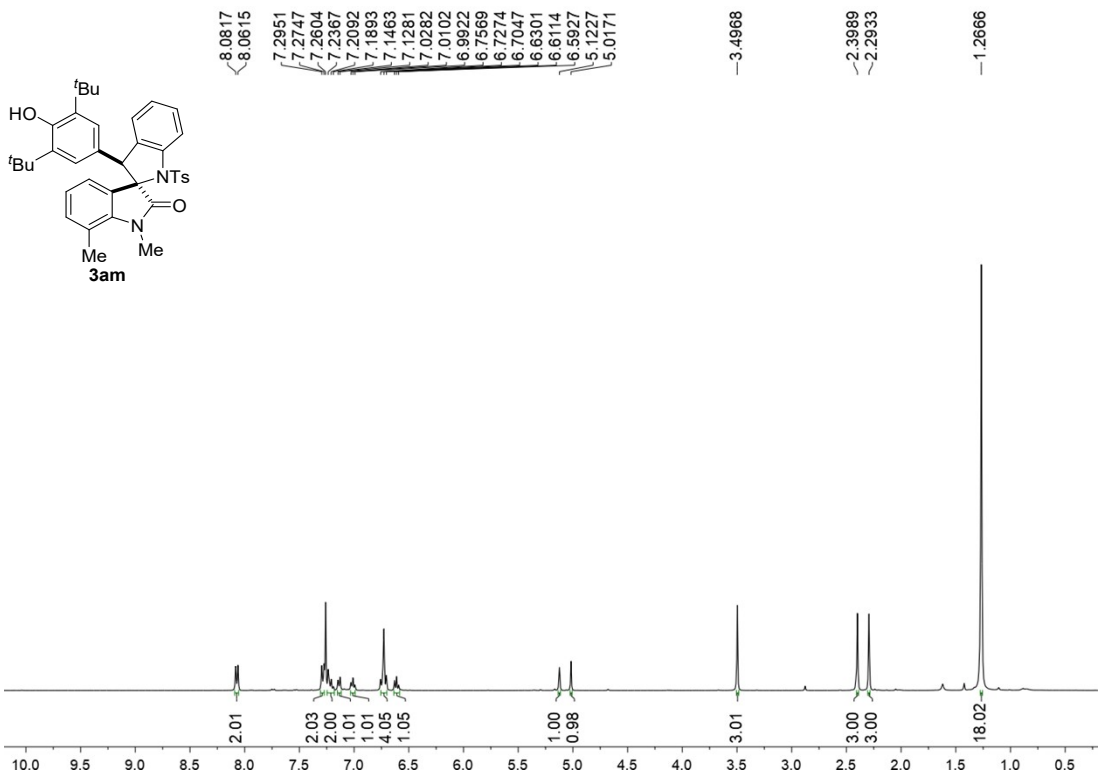
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2.03
2.00
1.01
1.01
4.05
1.05
1.00
0.98
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3.00
3.00
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10.0
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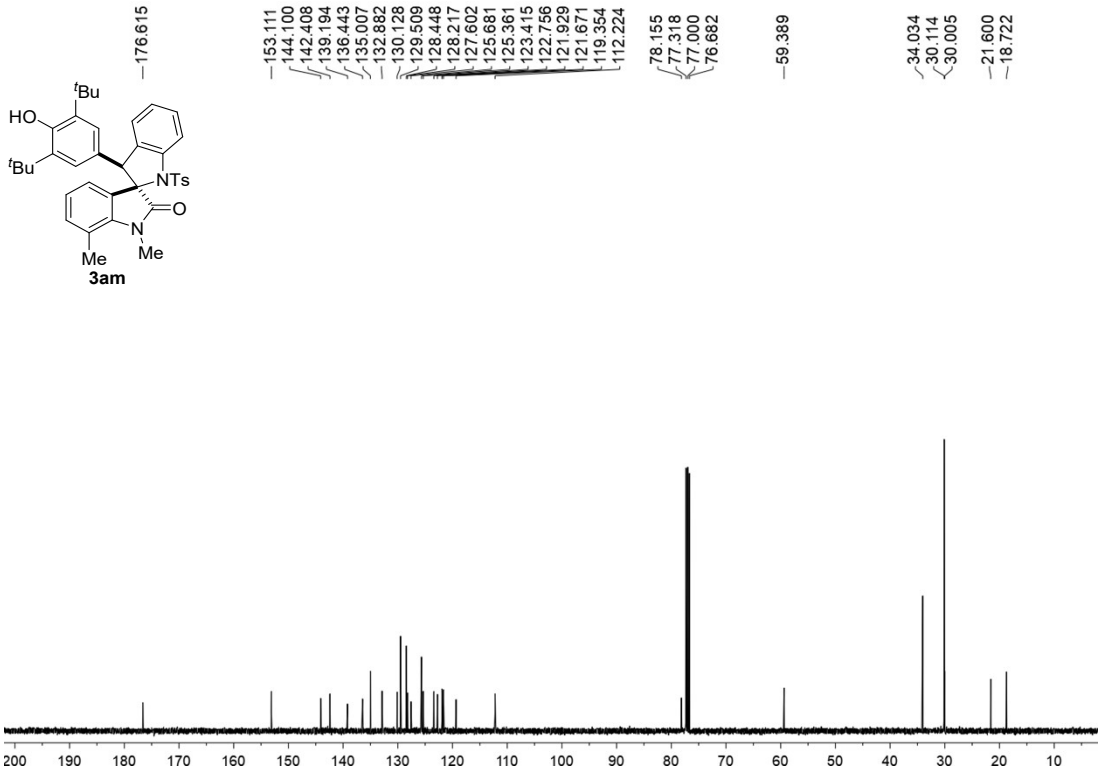
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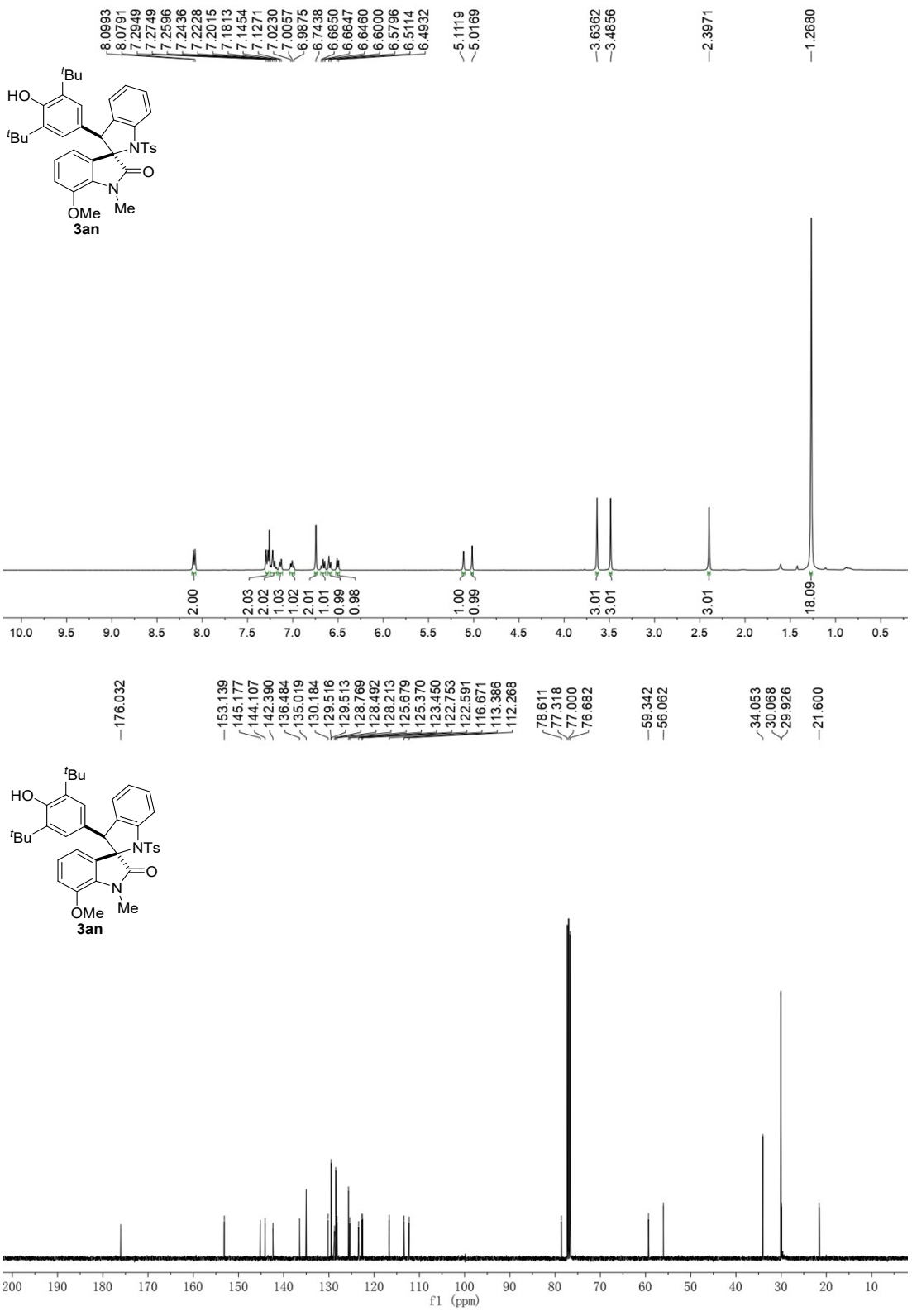
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6.6000
6.5796
6.5114
6.4932
5.1119
5.0169
3.6362
3.4856
2.3971
1.2680
tBu
HO
tBu
NTs
O
N
Me
OMe
3an
2.00
2.03
2.02
1.03
1.02
2.01
1.01
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0.98
1.00
0.99
3.01
3.01
3.01
18.09
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NTs
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Me
OMe
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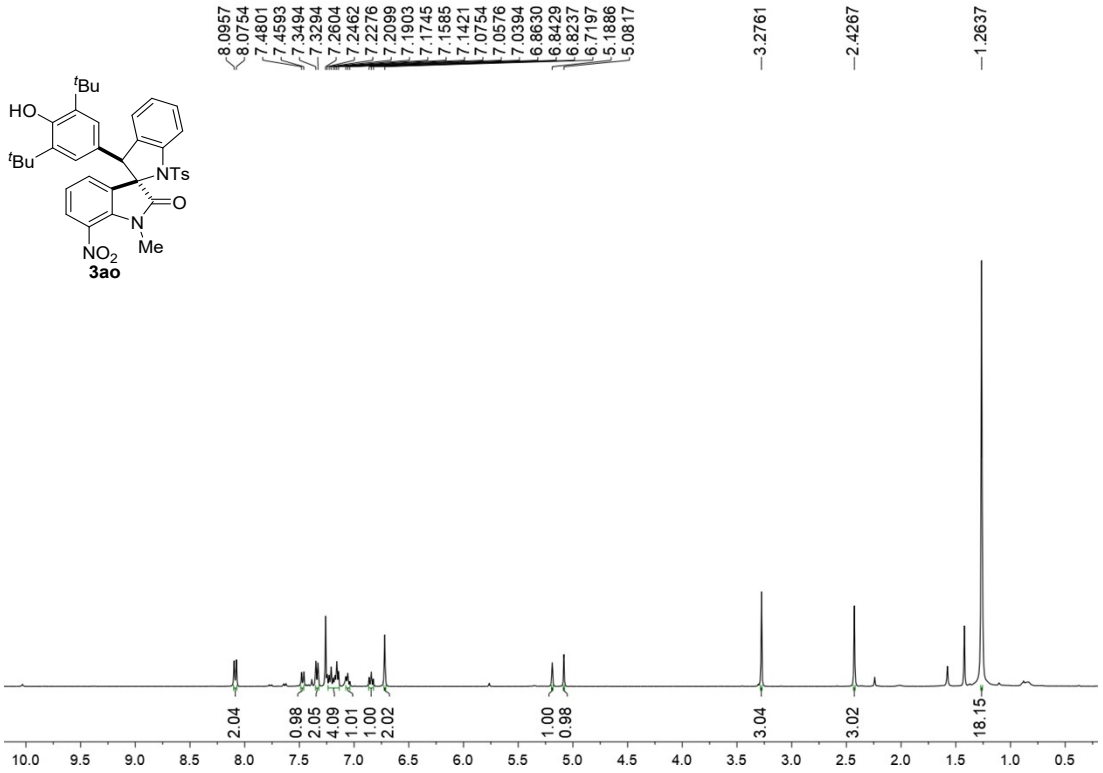
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7.0754
7.0576
7.0394
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6.8429
6.8237
6.7197
5.1886
5.0817
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1.2637
tBu
HO
tBu
NTs
O
N
Me
NO2
3ao
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2.05
4.09
1.01
1.00
2.02
1.00
0.98
3.04
3.02
18.15
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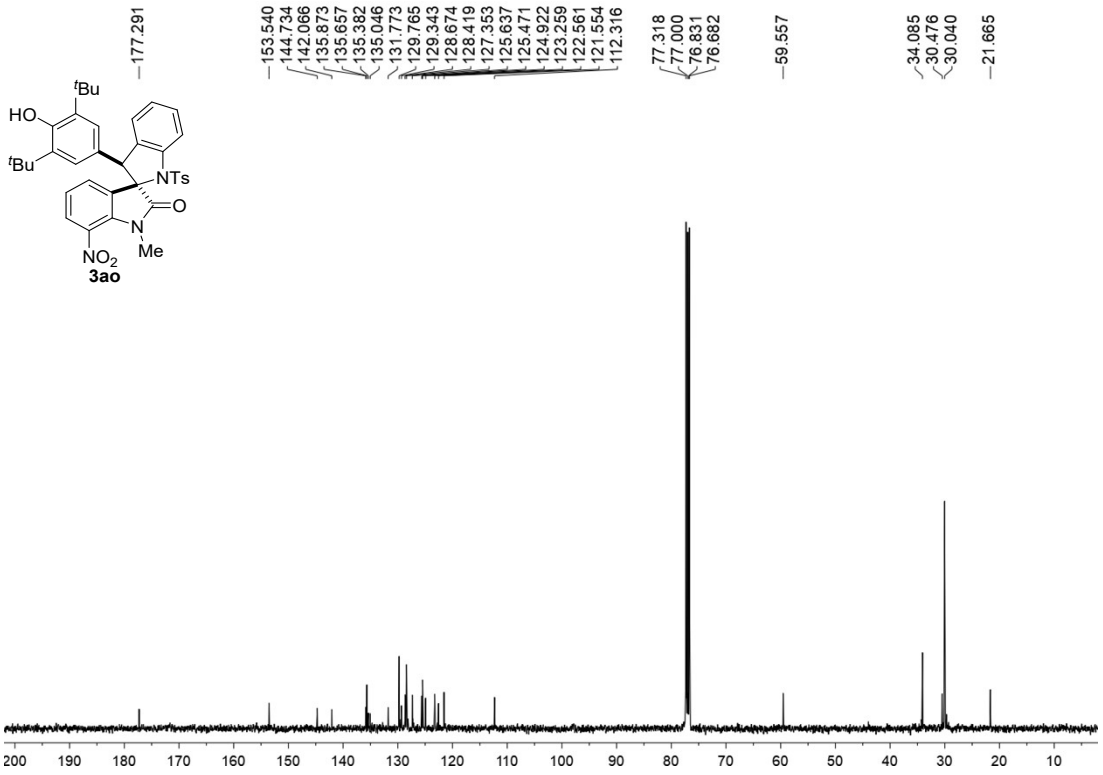
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77.318
77.000
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76.682
59.557
34.085
30.476
30.040
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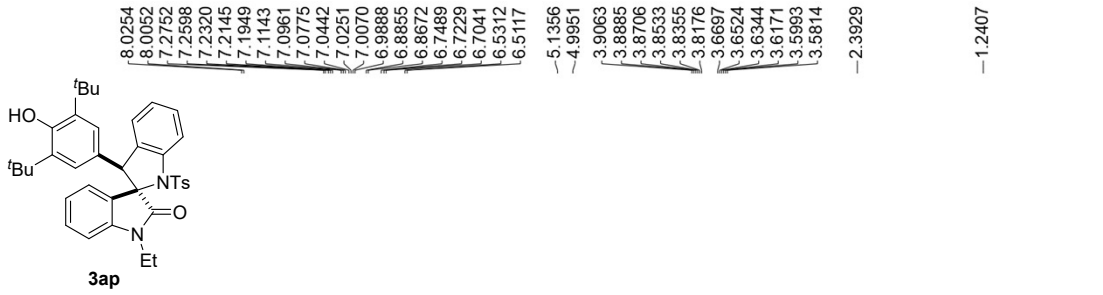
HO
tBu
NTs
O
N
Me
NO2
3ao
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10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6.5117
5.1356
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3.8885
3.8706
3.8533
3.8355
3.8176
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3.6524
3.6344
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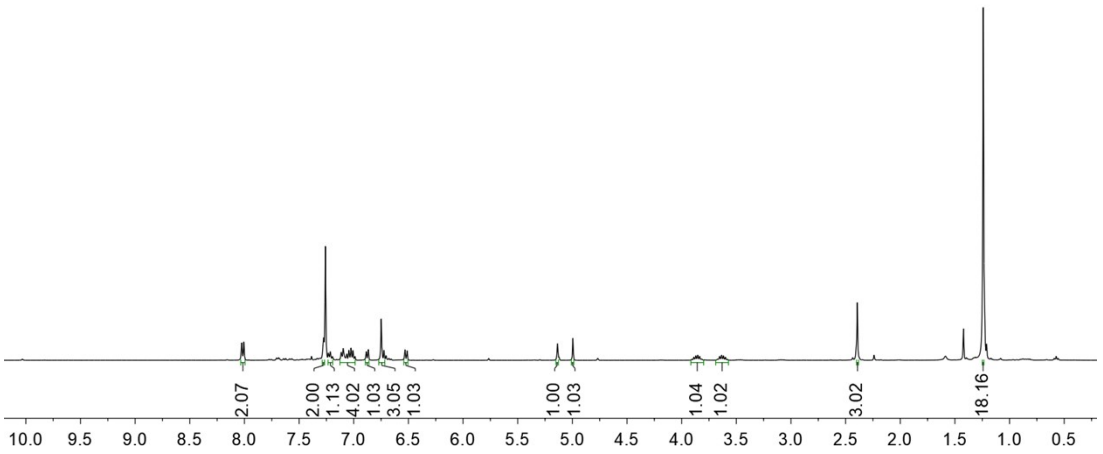
HO
tBu
NTs
O
N
Et

3ap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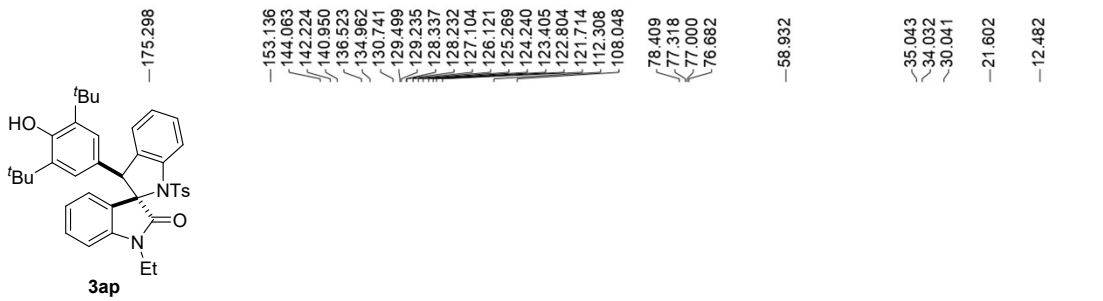
1.03
3.05
1.03
1.00
1.03
1.04
1.02
3.02
18.16
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5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126.121
125.269
124.240
123.405
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121.714
112.308
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78.409
77.318
77.000
76.682
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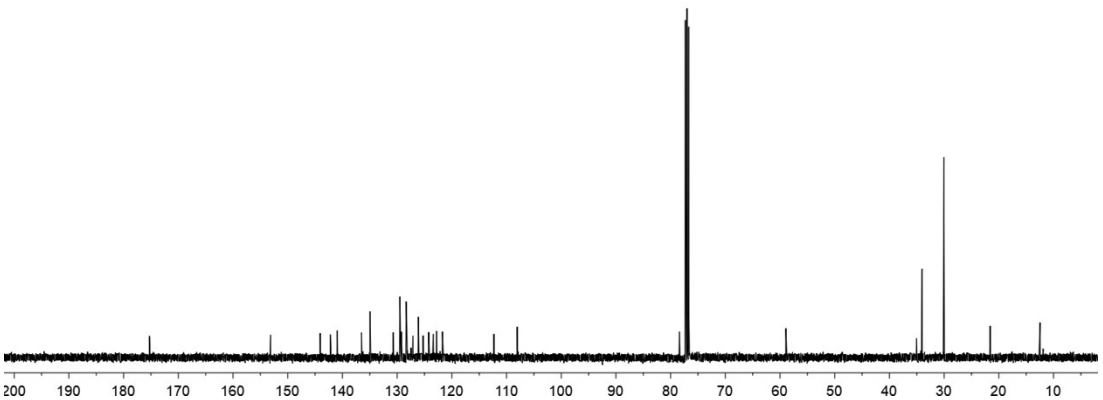
HO
tBu
NTs
O
N
Et

3ap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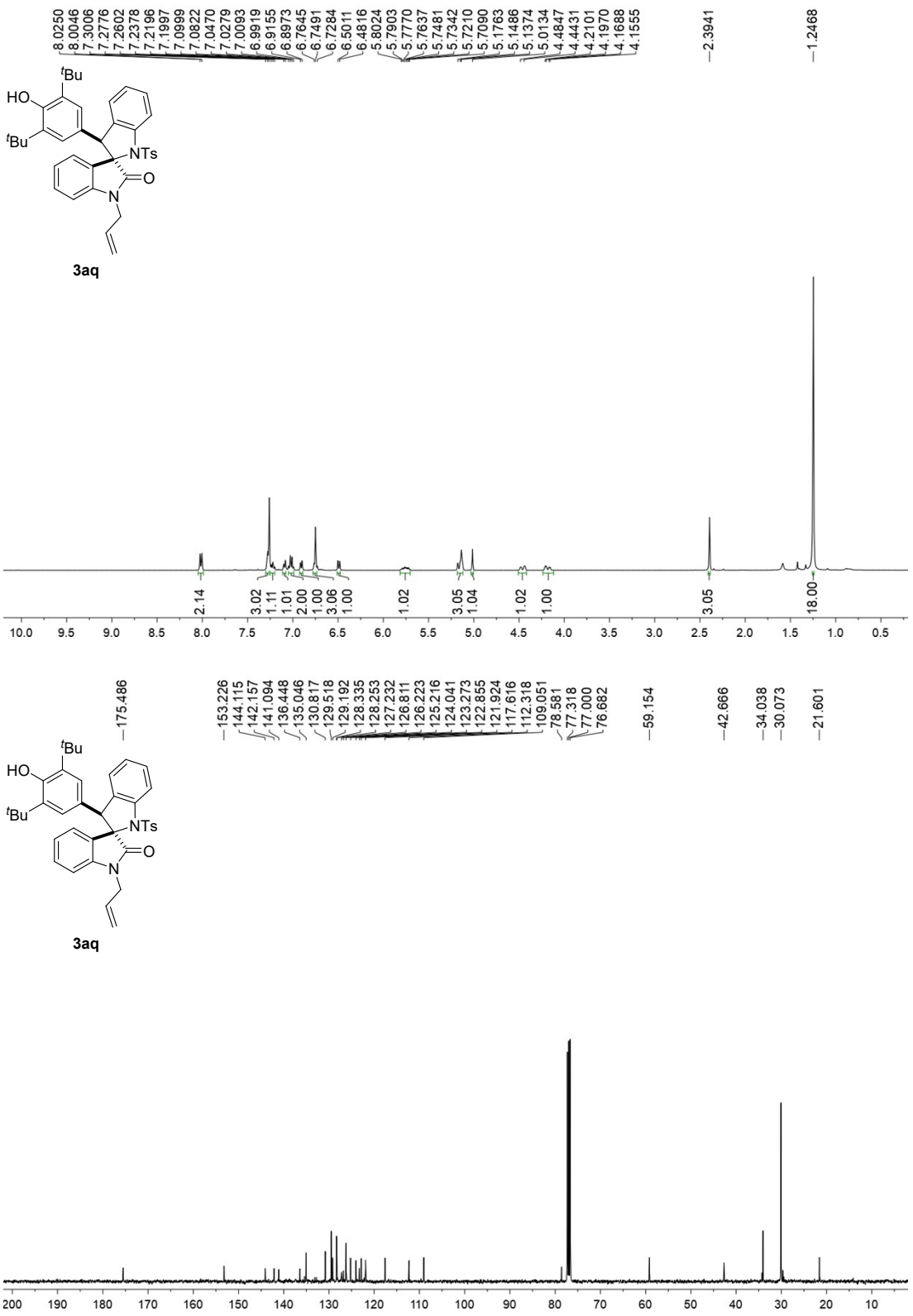
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7.0093
6.9919
6.9155
6.8973
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6.7491
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6.5011
6.4816
5.8024
5.7903
5.7770
5.7637
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5.7342
5.7210
5.7090
5.1763
5.1486
5.1374
5.0134
4.4847
4.4431
4.2101
4.1970
4.1688
4.1555
2.3941
1.2468
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HO
tBu
NTs
O
N
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3.02
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1.01
2.00
1.00
3.06
1.00
1.02
3.05
1.04
1.02
1.00
3.05
18.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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5.0
4.5
4.0
3.5
3.0
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HO
tBu
NTs
O
N
3aq
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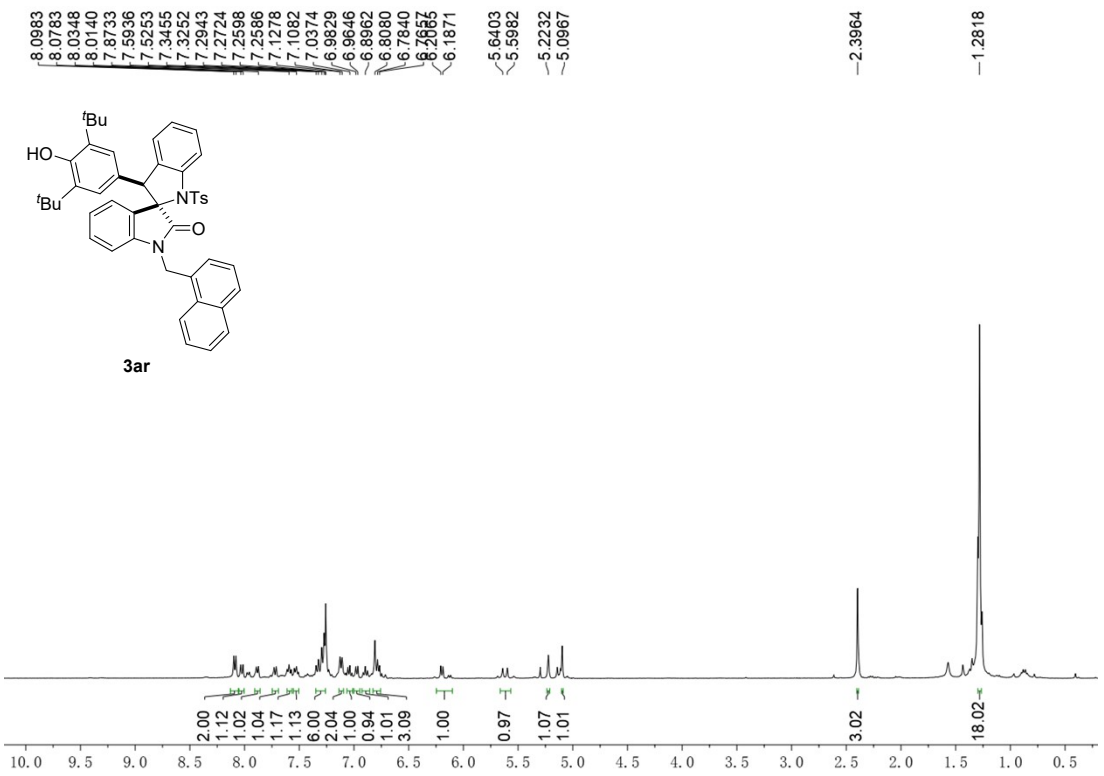
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6.8962
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6.7840
6.1871
5.6403
5.5982
5.2232
5.0967
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1.2818
tBu
HO
tBu
NTs
O
N
3ar
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1.12
1.02
1.04
1.17
1.13
6.00
2.04
1.00
0.94
1.01
3.09
1.00
0.97
1.07
1.01
3.02
18.02
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
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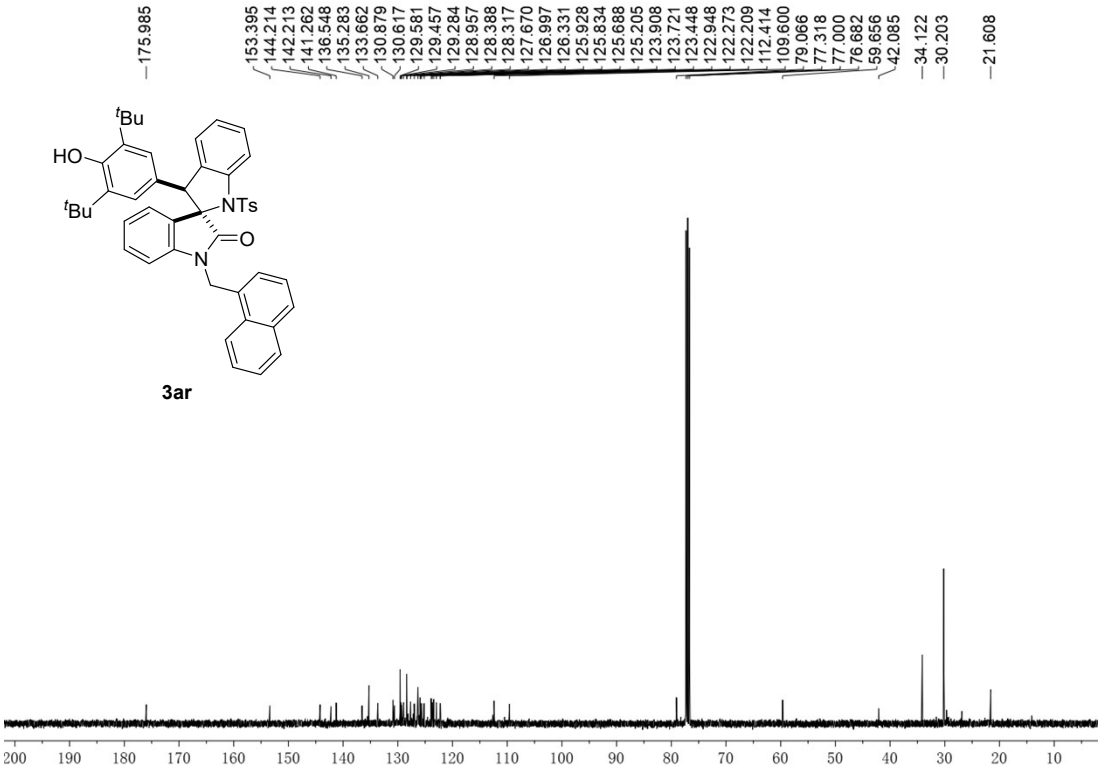
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125.688
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123.721
123.448
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122.273
122.209
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109.600
79.066
77.318
77.000
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59.656
42.085
34.122
30.203
21.608
tBu
HO
tBu
NTs
O
N
3ar
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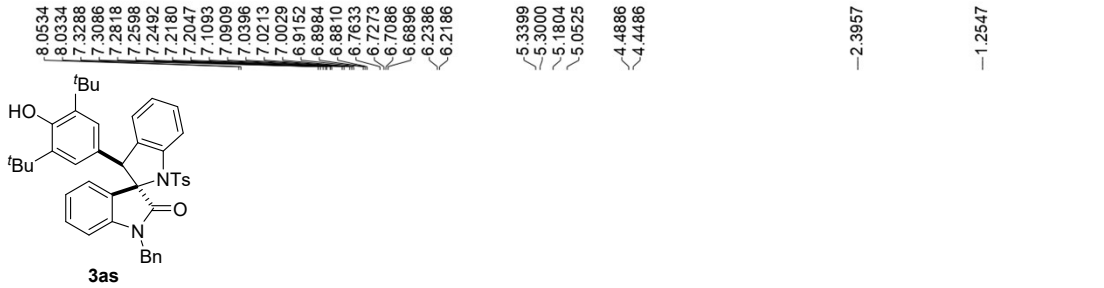
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7.2047
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7.0909
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5.1804
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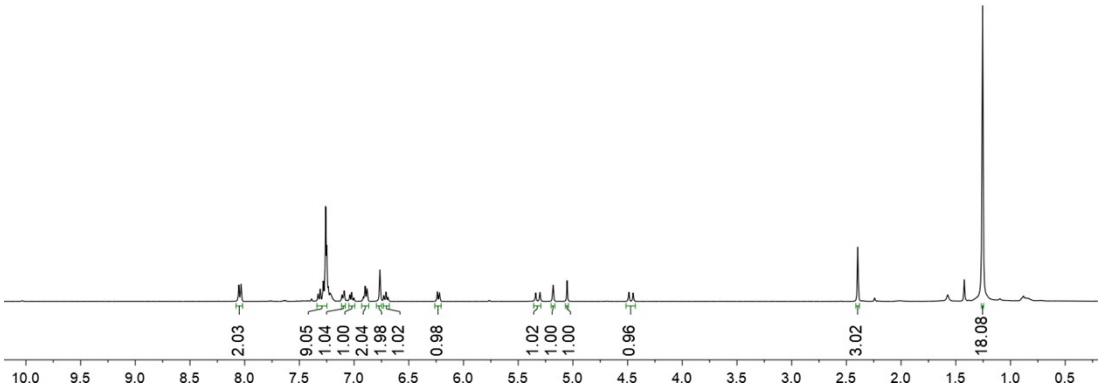
HO
tBu
NTs
O
N
Bn

3as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3.02
18.08
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
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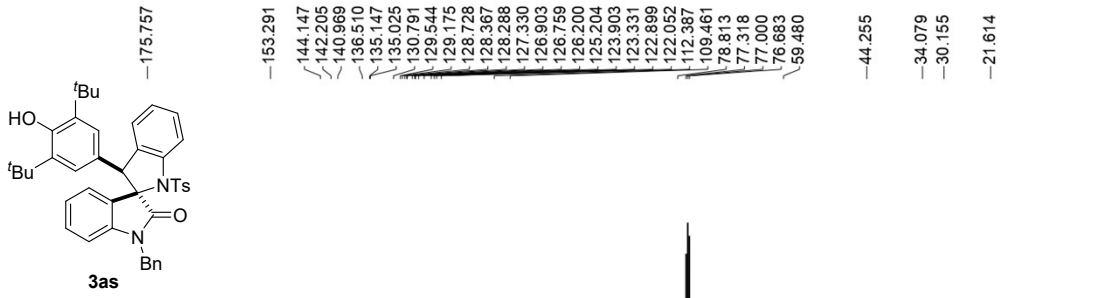
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123.903
123.331
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122.052
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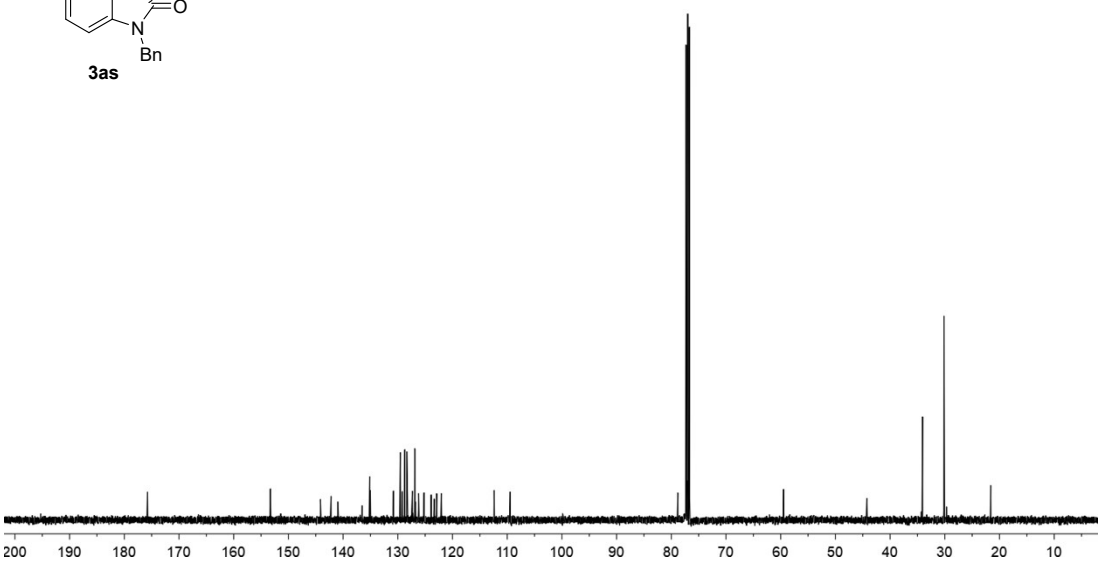
HO
tBu
NTs
O
N
Bn

3as


200
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180
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80
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40
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20
10


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7.3252
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tBu
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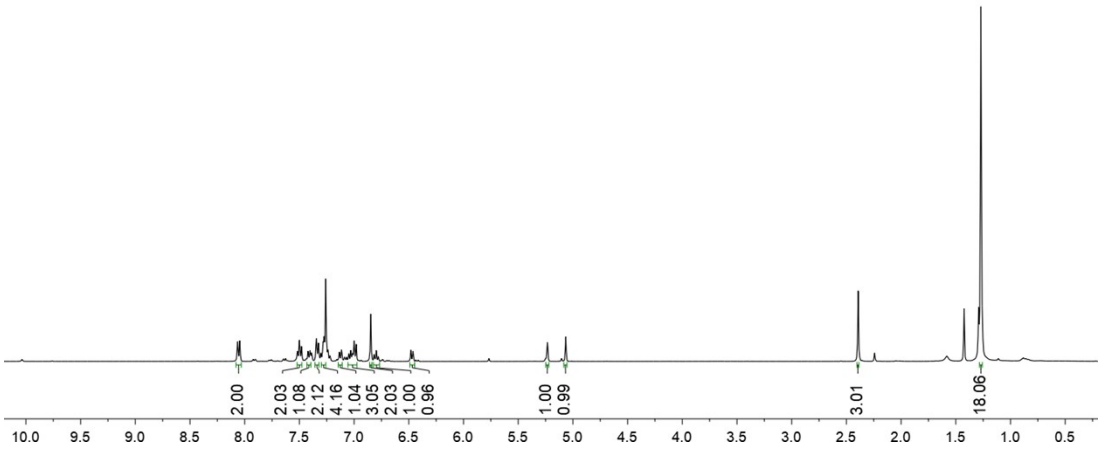
N
Ph

3at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9.0
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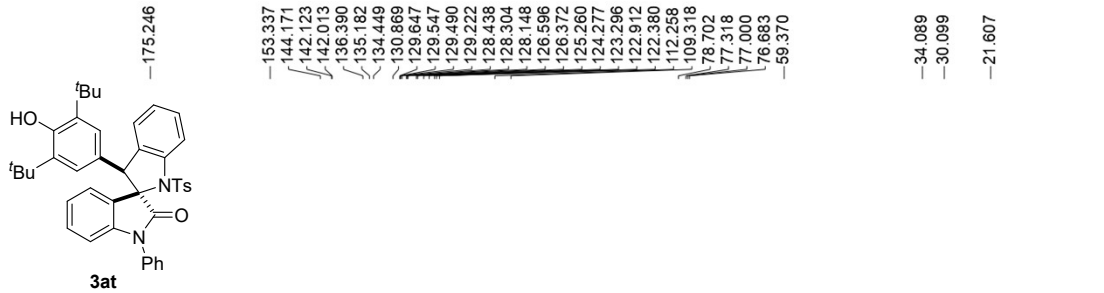
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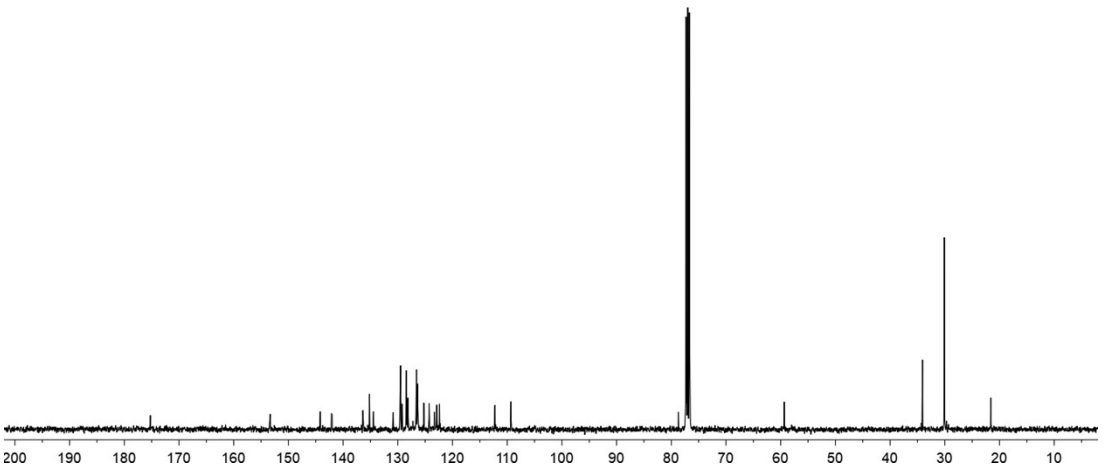
tBu
NTs
O
N
Ph

3at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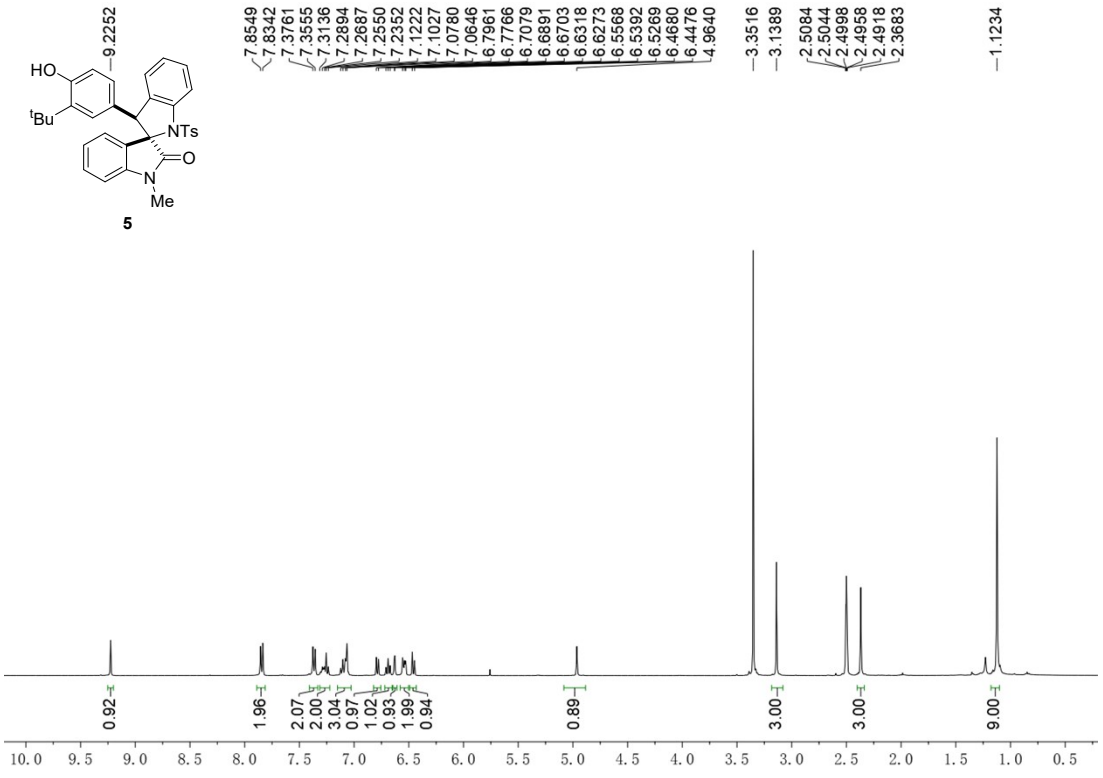
20
10


HO
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NTs
O
N
Me
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6.4680
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3.04
0.97
1.02
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1.99
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0.89
3.00
3.00
9.00
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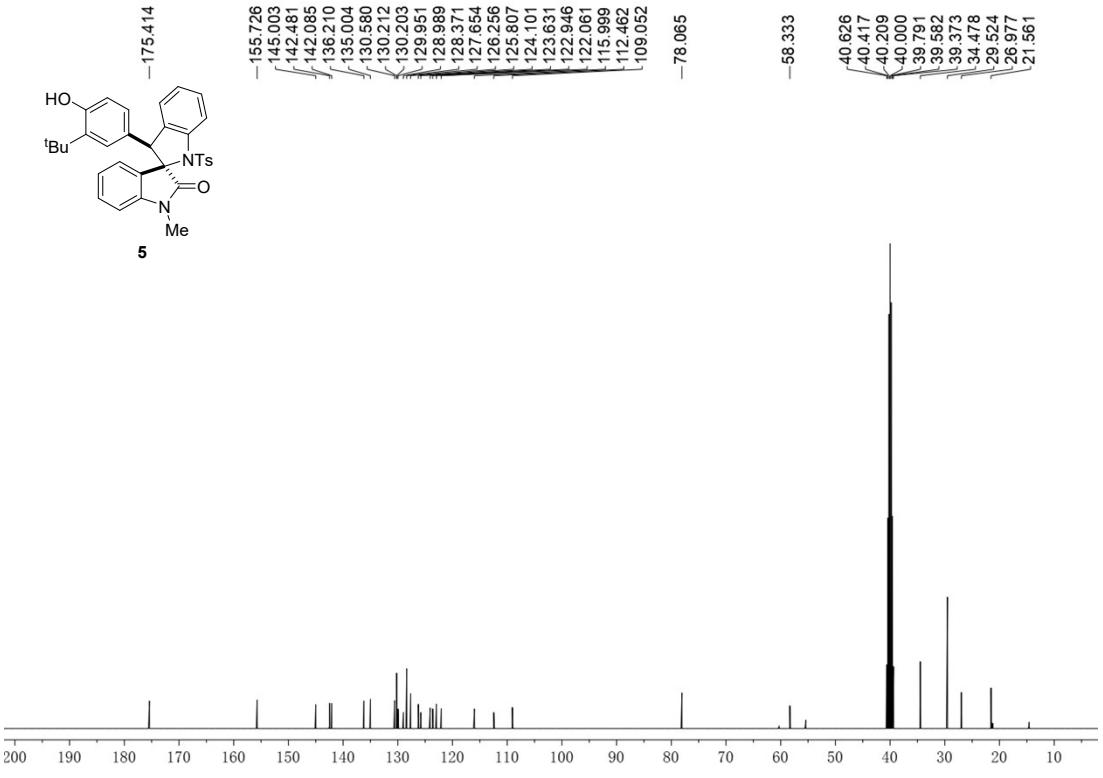
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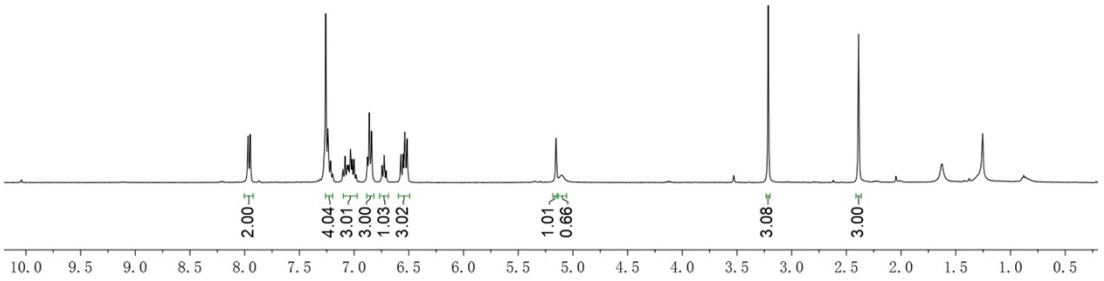
HO
NTs
O
N
Me

6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3.00
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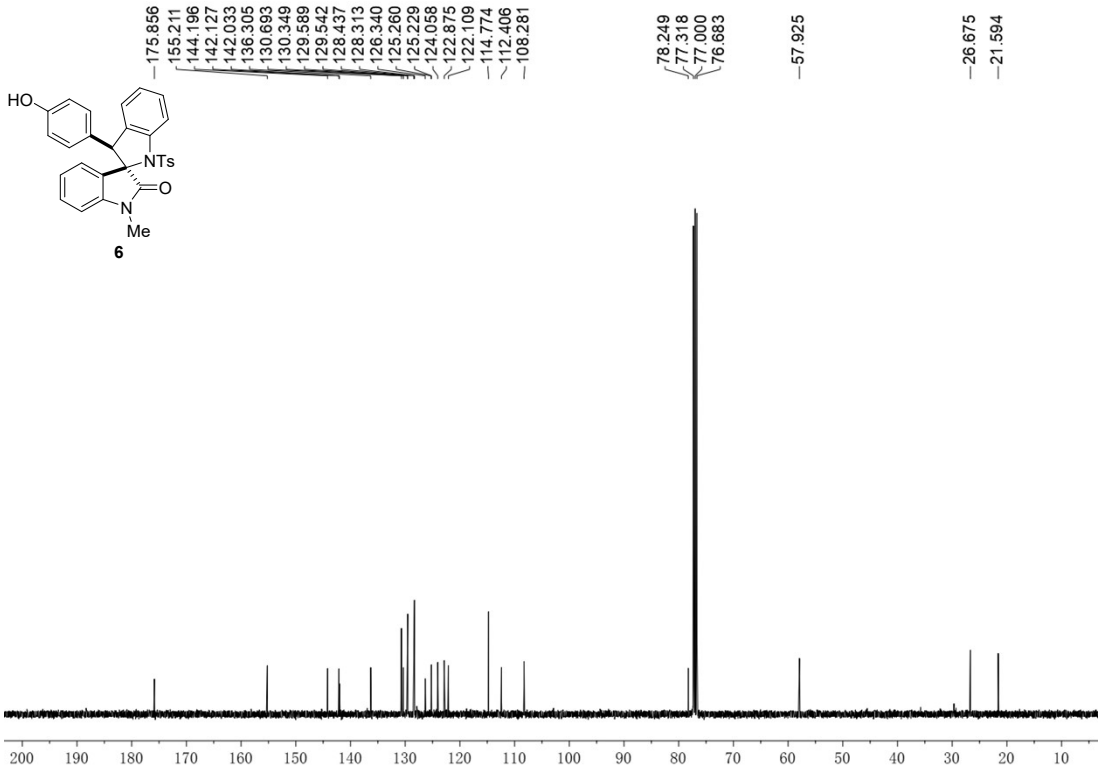
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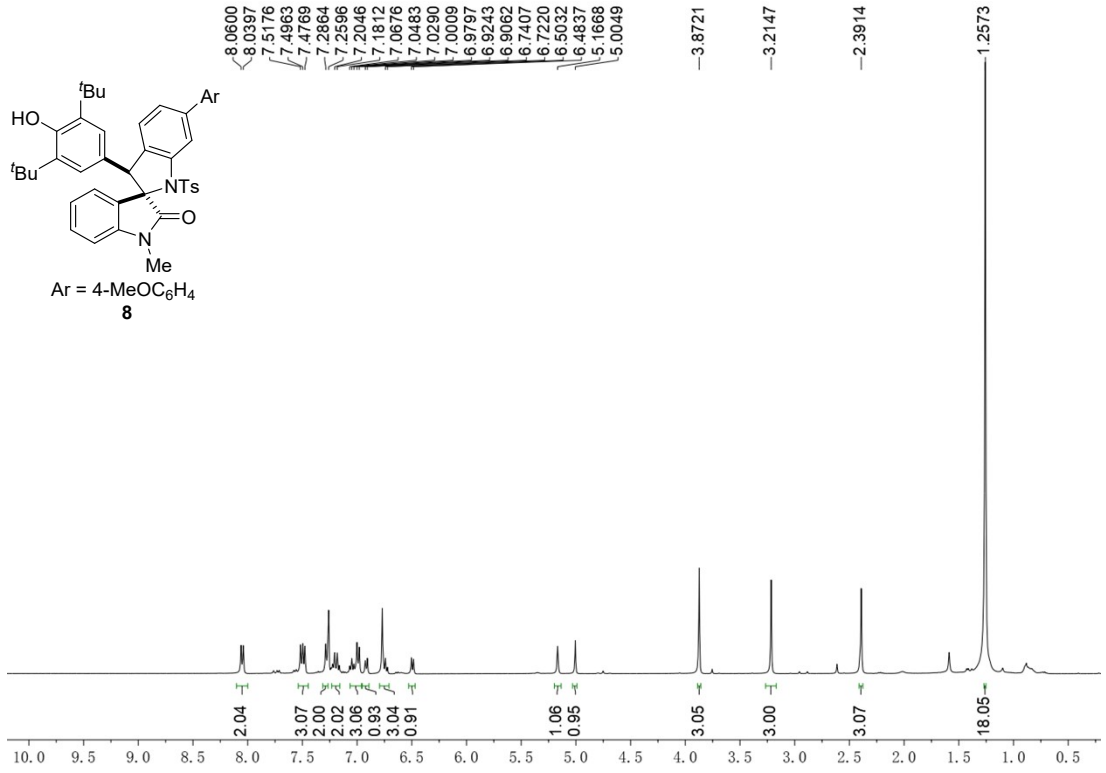
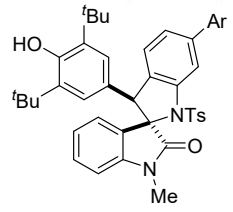
HO
NTs
O
N
Me
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

6



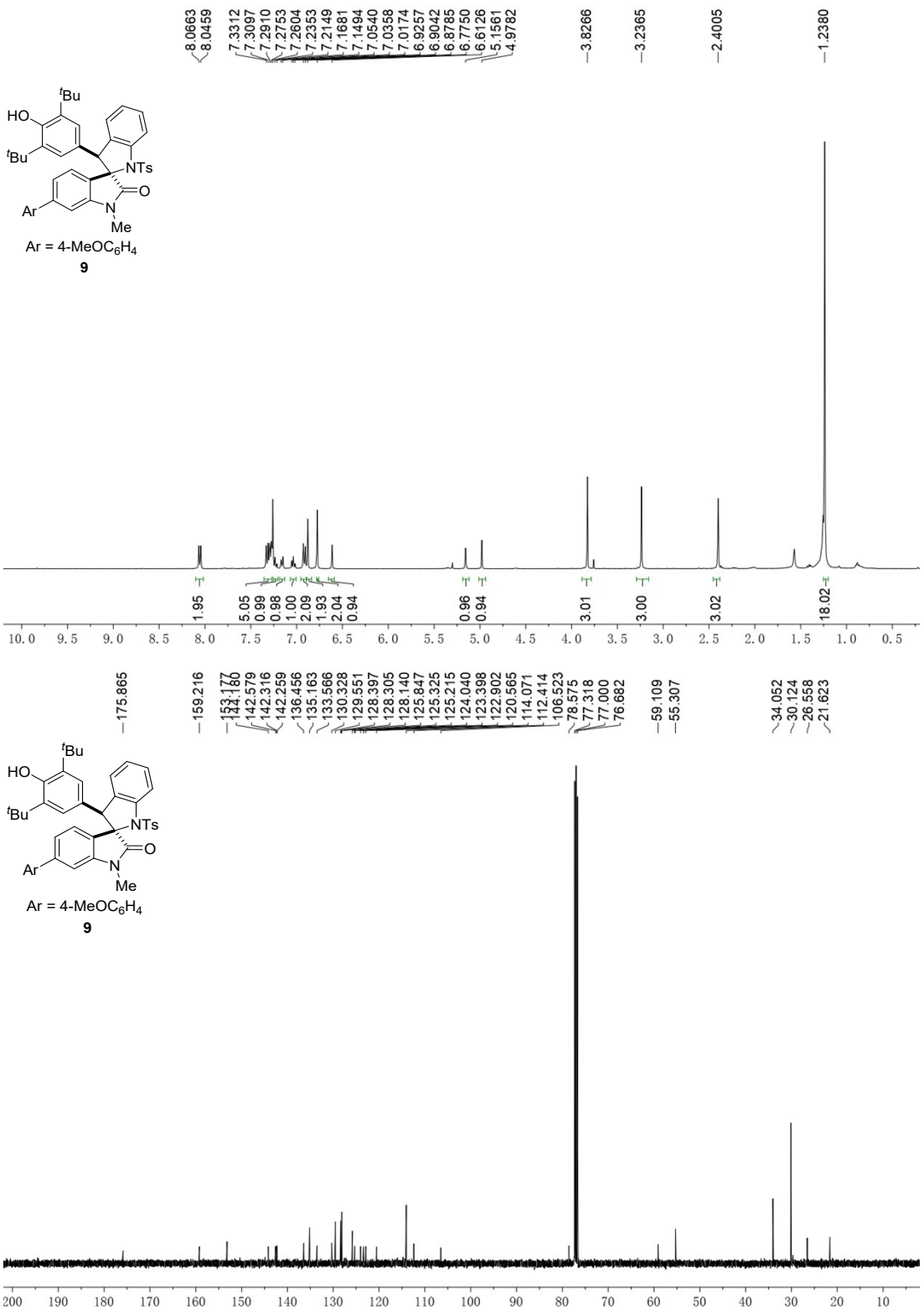


Ar = 4-MeOC$_6$H$_4$

8

Ar = 4-MeOC$_6$H$_4$

8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7.0358
7.0174
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6.9042
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6.7750
6.6126
5.1561
4.9782
3.8266
3.2365
2.4005
1.2380
tBu
HO
tBu
NTs
O
Ar
N
Me
Ar = 4-MeOC6H4
9
1.95
5.05
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10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
175.865
159.216
153.177
142.579
142.316
142.259
136.456
135.163
133.566
130.328
129.551
128.397
128.305
128.140
125.847
125.325
125.215
124.040
123.398
122.902
120.565
114.071
112.414
106.523
78.575
77.318
77.000
76.682
59.109
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30.124
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9
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10