

Supporting Information

Intramolecular Cyclizations of Cyclopropenes with Indole

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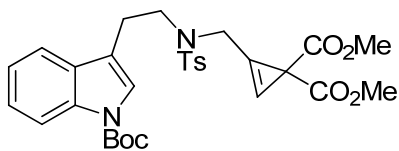
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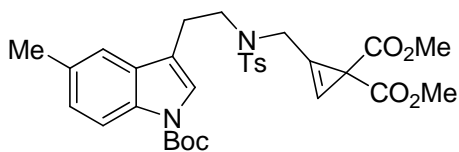
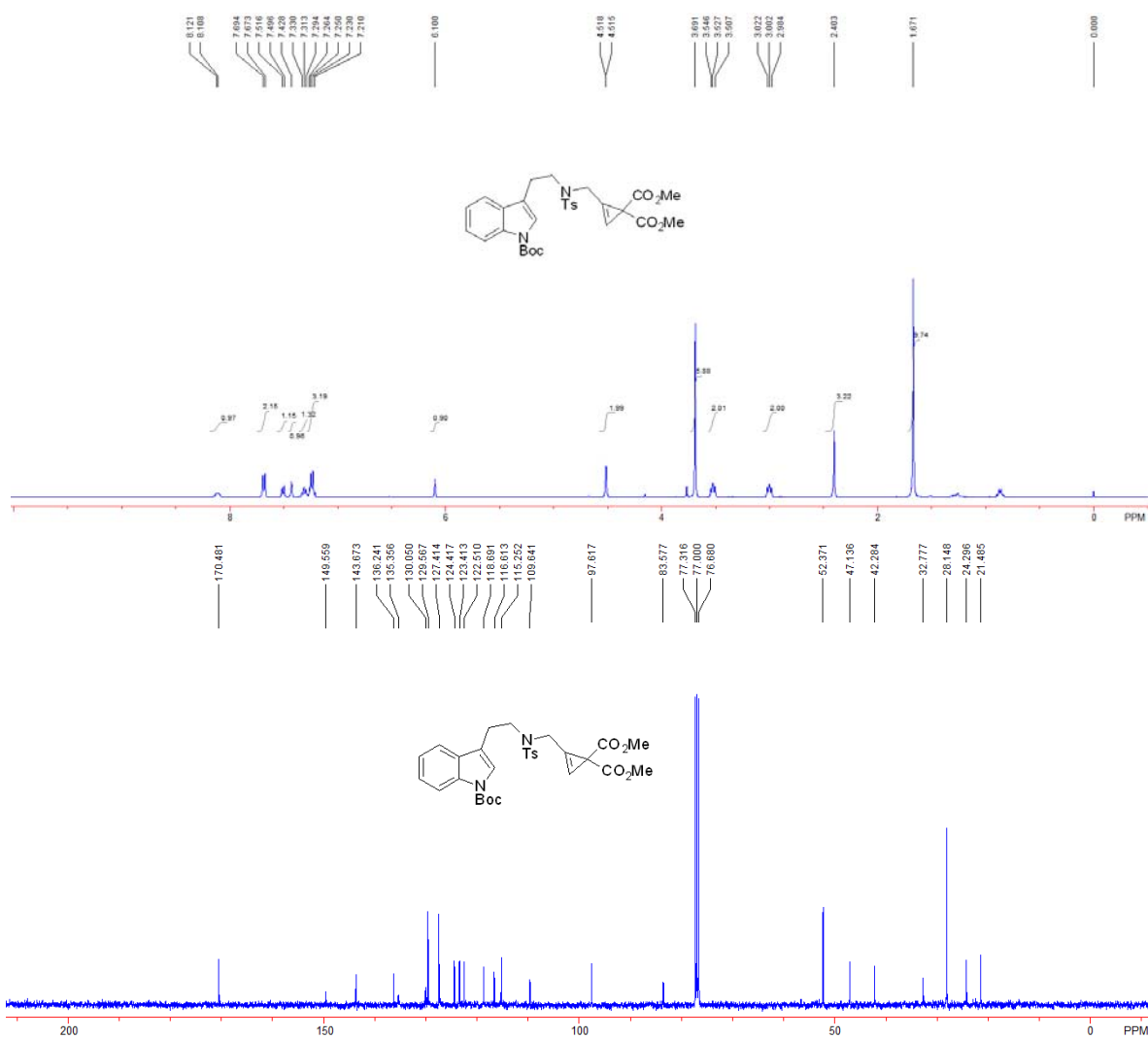
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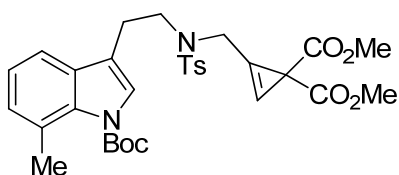
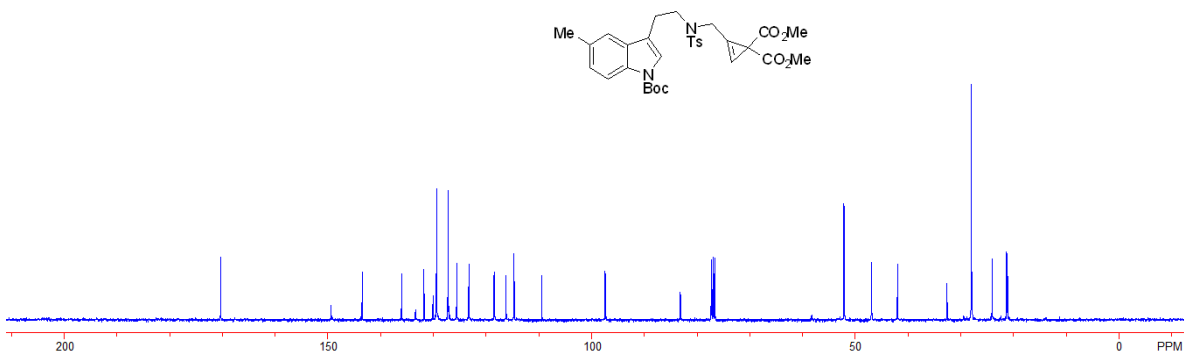
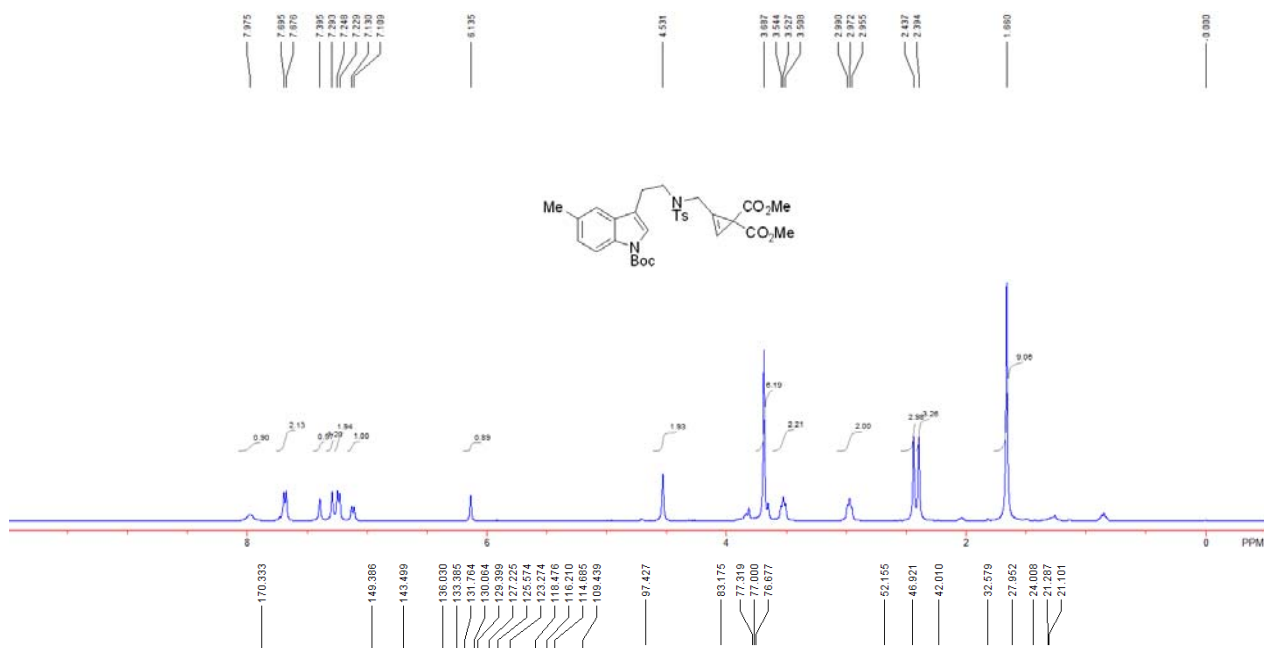
General remarks: ^1H NMR spectra were recorded on a Bruker AM-300 or AM-400 spectrometer for solution in CDCl_3 with tetramethylsilane (TMS) as internal standard; J-values are in Hz. High resolution mass spectra were obtained by using Agilent Technologies 6224 TOF LC/MS (ESI). All of the compounds reported in this paper gave satisfactory HRMS analytic data. Melting points were obtained with a Yanagimoto micro melting point apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer PE-983 spectrometer with absorption in cm^{-1} . THF, toluene and Et_2O were distilled from sodium (Na) under argon (Ar) atmosphere. CH_3CN , 1, 2-dichloroethane and dichloromethane were distilled from CaH_2 under argon (Ar) atmosphere. Commercially obtained reagents were used without further purification. All reactions were monitored by TLC with Huanghai GF254 silica gel coated plates. Flash column chromatography was carried out using 300-400 mesh silica gel at increased pressure.



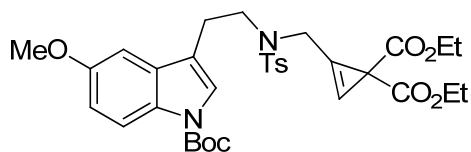
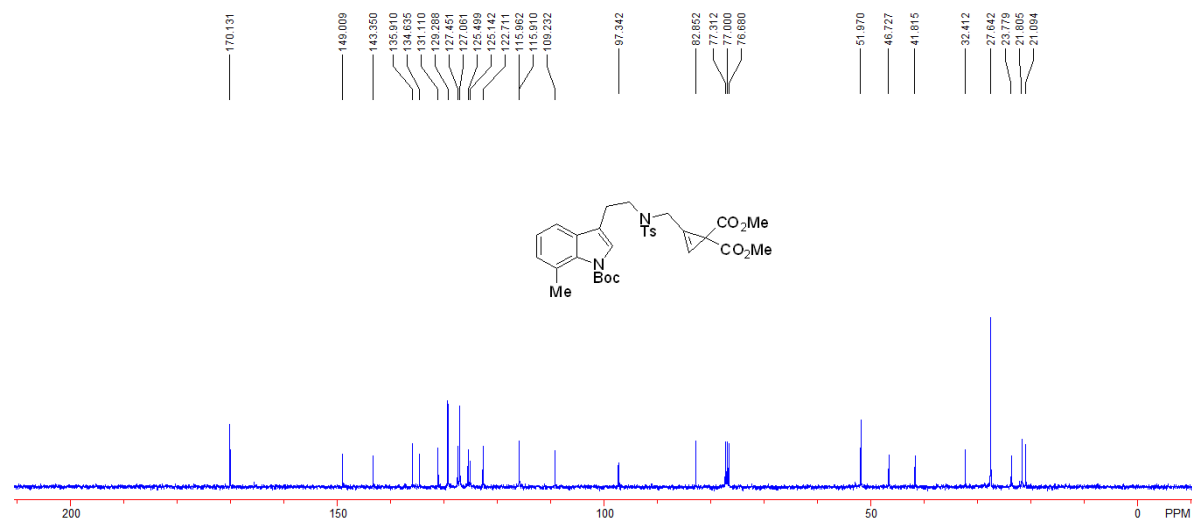
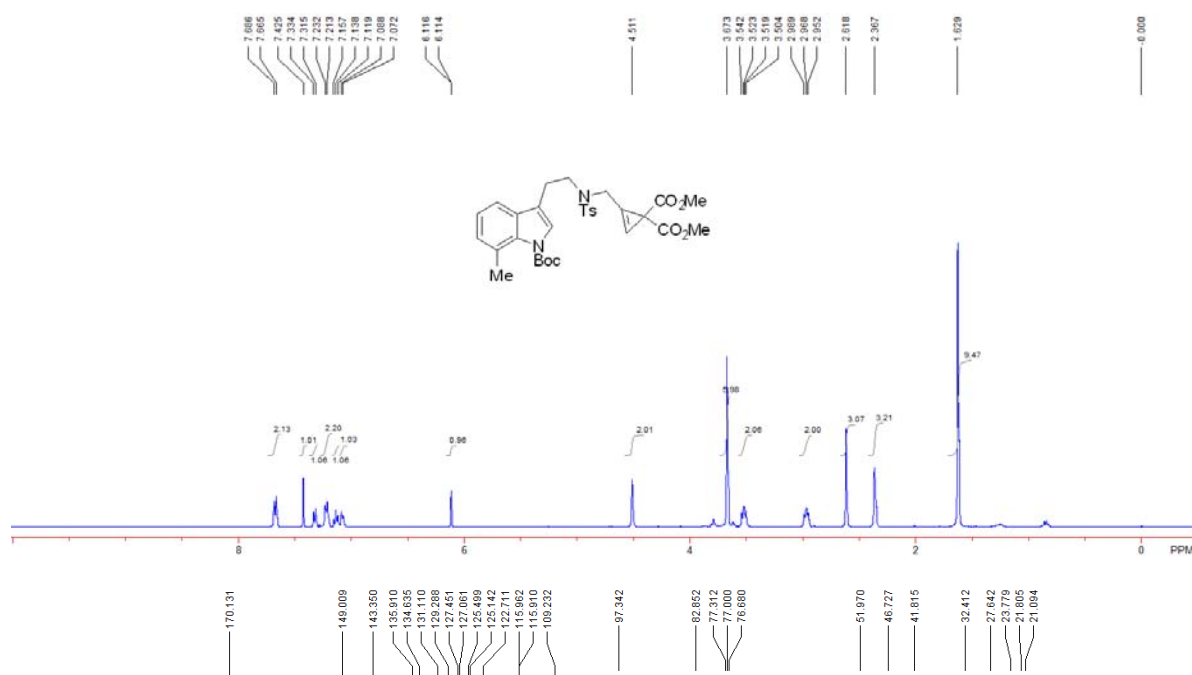
Compound **1a**: 676 mg, 58% yield; a colorless oil; IR (neat) ν 2962, 1726, 1259, 1093, 1017, 797 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz, TMS) δ 1.67 (9H, s), 2.40 (3H, s), 3.00 (2H, t, $J = 8.0$ Hz), 3.53 (2H, t, $J = 8.0$ Hz), 3.69 (6H, s), 4.52 (2H, d, $J = 1.2$ Hz), 6.10 (1H, s), 7.21–7.26 (3H, m), 7.31 (1H, t, $J = 7.2$ Hz), 7.43 (1H, s), 7.51 (1H, d, $J = 8.0$ Hz), 7.68 (2H, d, $J = 8.4$ Hz), 8.11–8.12 (1H, m); ^{13}C NMR (CDCl_3 , 100 MHz, TMS) δ 21.5, 24.3, 28.1, 32.8, 42.3, 47.1, 52.4, 83.6, 97.6, 109.6, 115.3, 116.6, 118.7, 122.5, 123.4, 124.4, 127.4, 129.6, 130.1, 135.4, 136.2, 143.7, 149.6, 170.5; HRMS (ESI) Calcd. for $\text{C}_{30}\text{H}_{34}\text{N}_2\text{O}_8\text{S}$: 582.2036, found: 582.2017.



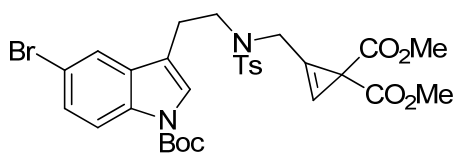
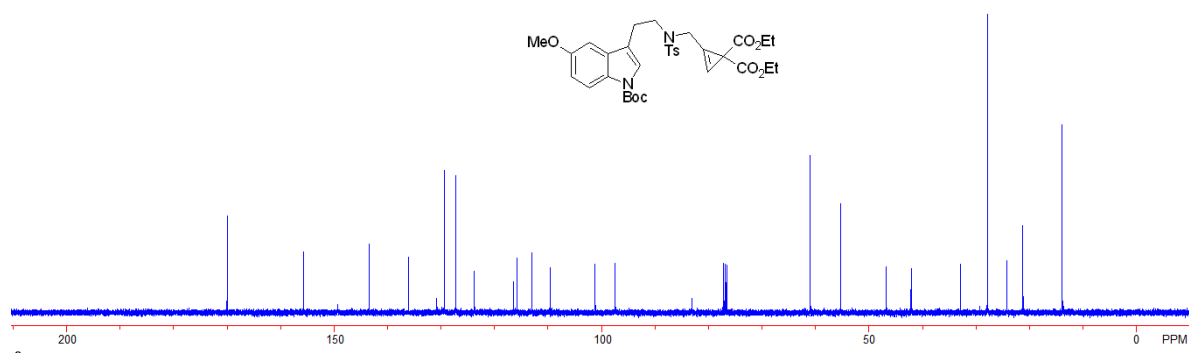
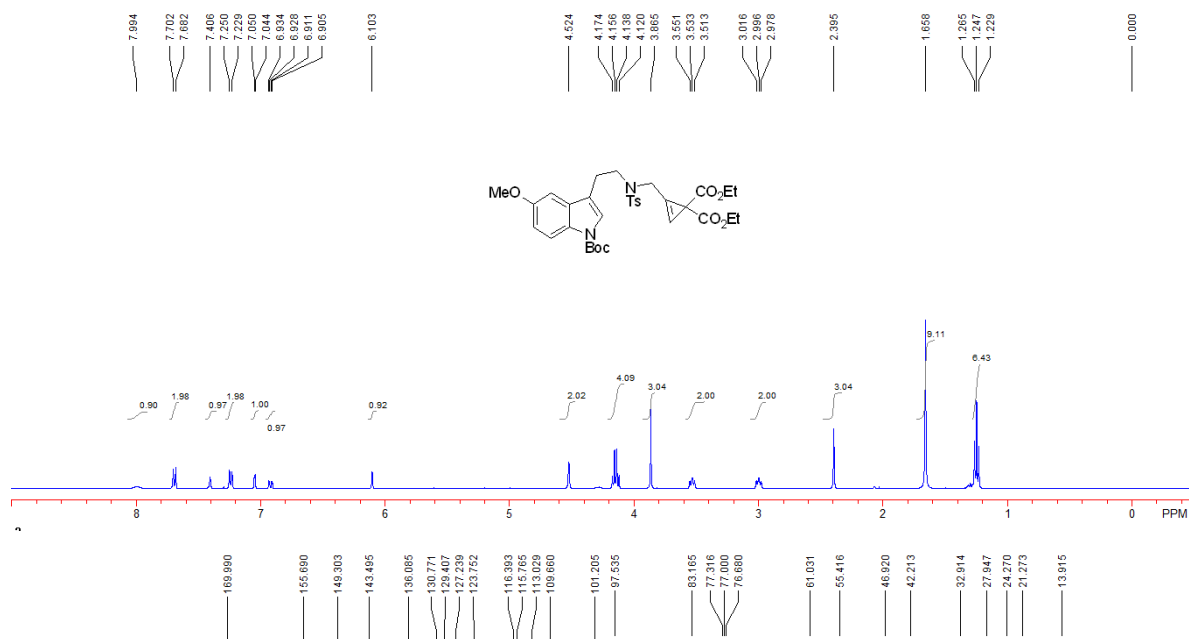
Compound **1b**: 1.684 g, 41% yield; a colorless oil; IR (neat) ν 2954, 2924, 2854, 1732, 1457, 1379, 1258, 1160, 1095 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz, TMS) δ 1.66 (9H, s), 2.39 (3H, s), 2.44 (3H, s), 2.97 (2H, t, $J = 7.2$ Hz), 3.53 (2H, t, $J = 7.2$ Hz), 3.69 (6H, s), 4.53 (2H, s), 6.14 (1H, s), 7.12 (1H, d, $J = 8.4$ Hz), 7.24 (2H, d, $J = 7.6$ Hz), 7.29 (1H, s), 7.40 (1H, s), 7.69 (2H, d, $J = 7.6$ Hz), 7.98 (1H, s); ^{13}C NMR (CDCl_3 , 100 MHz, TMS) δ 21.1, 21.3, 24.0, 28.0, 32.6, 42.0, 46.9, 52.2, 83.2, 97.4, 109.4, 114.7, 116.2, 118.5, 123.3, 125.6, 127.2, 129.4, 130.1, 131.8, 133.4, 136.0, 143.5, 149.4, 170.3; HRMS (ESI) Calcd. for $\text{C}_{31}\text{H}_{36}\text{N}_2\text{O}_8\text{S}$: 596.2192, found: 596.2184.



Compound **1c**: 1.895 g, 76% yield; a colorless oil; IR (neat) ν 2956, 2929, 1739, 1349, 1258, 1156, 1047, 737 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz, TMS) δ 1.63 (9H, s), 2.37 (3H, s), 2.62 (3H, s), 2.95–2.99 (2H, m), 3.50–3.54 (2H, m), 3.67 (6H, s), 4.51 (2H, s), 6.12 (1H, d, $J = 0.8$ Hz), 7.08 (1H, d, $J = 6.4$ Hz), 7.14 (1H, t, $J = 7.6$ Hz), 7.22 (2H, d, $J = 8.0$ Hz), 7.32 (1H, d, $J = 7.6$ Hz), 7.43 (1H, s), 7.68 (2H, d, $J = 8.0$ Hz); ^{13}C NMR (CDCl_3 , 100 MHz, TMS) δ 21.1, 21.8, 23.8, 27.6, 32.4, 41.8, 46.7, 52.0, 82.9, 97.3, 109.2, 115.9, 116.0, 122.7, 125.1, 125.5, 127.1, 127.5, 129.3, 131.1, 134.6, 135.9, 143.4, 149.0, 170.1; HRMS (ESI) Calcd. for $\text{C}_{31}\text{H}_{36}\text{N}_2\text{O}_8\text{S}$: 596.2192, found: 596.2192.

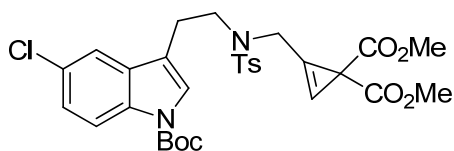
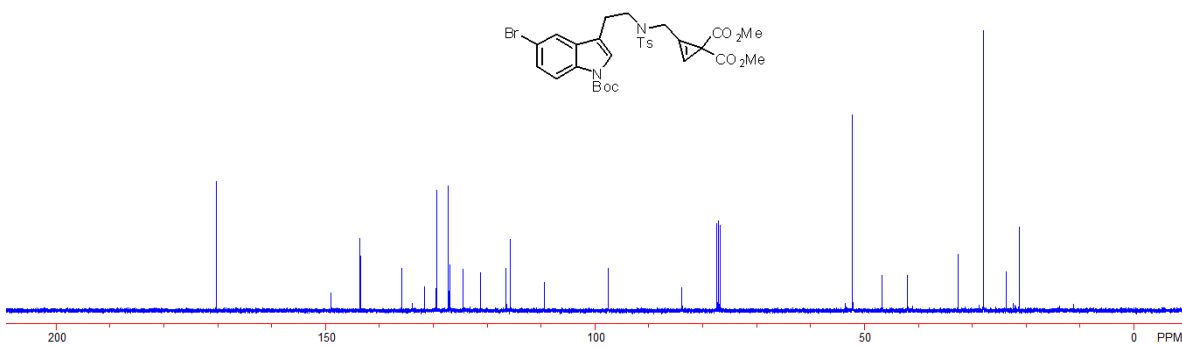
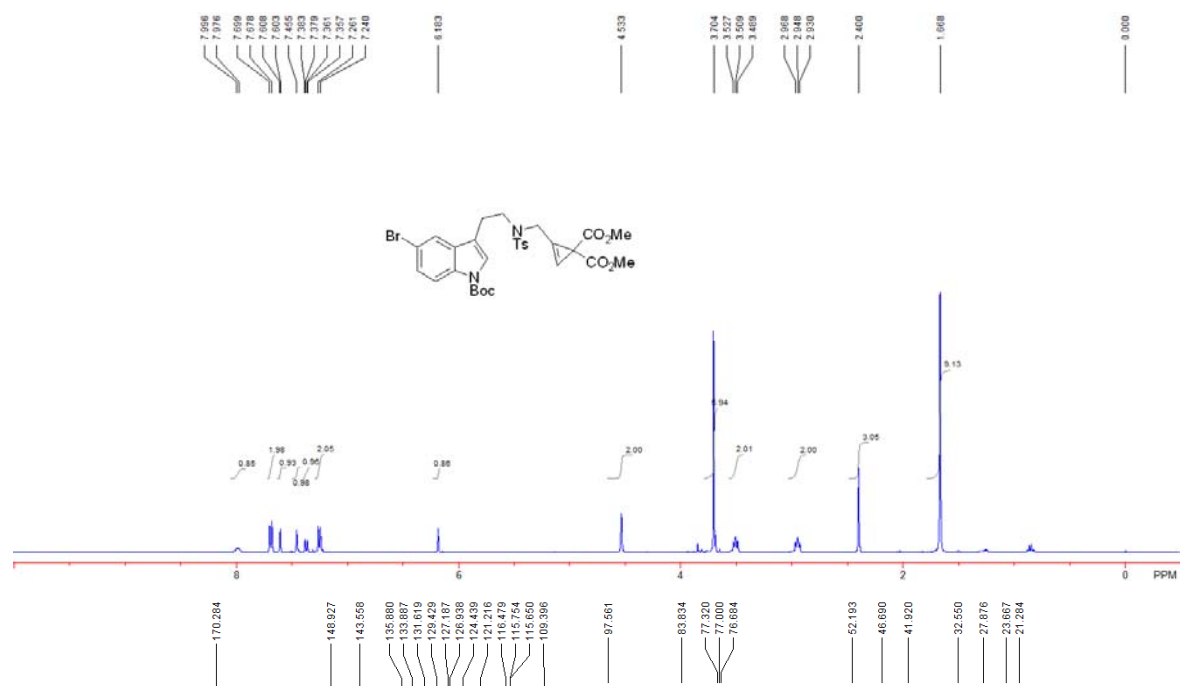


Compound **1d**: 439 mg, 51% yield; a colorless oil; IR (neat) ν 3139, 2974, 2930, 1723, 1478, 1449, 1386, 1369, 1274, 1257, 1156, 1094, 1061 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz, TMS) δ 1.25 (6H, t, $J = 7.2$ Hz), 1.66 (9H, s), 2.40 (3H, s), 3.00 (2H, t, $J = 7.6$ Hz), 3.53 (2H, t, $J = 7.6$ Hz), 3.87 (3H, s), 4.15 (4H, q, $J = 7.2$ Hz), 4.52 (2H, s), 6.10 (1H, s), 6.92 (1H, dd, $J = 2.4, 9.2$ Hz), 7.05 (1H, d, $J = 2.4$ Hz), 7.24 (2H, d, $J = 8.4$ Hz), 7.41 (1H, s), 7.69 (2H, d, $J = 8.4$ Hz), 8.00 (1H, s); ^{13}C NMR (CDCl_3 , 100 MHz, TMS) δ 13.9, 21.3, 24.3, 27.9, 32.9, 42.2, 46.9, 55.4, 61.0, 83.2, 97.5, 101.2, 109.7, 113.0, 115.8, 116.4, 123.8, 127.2, 129.4, 130.8, 136.1, 143.5, 149.3, 155.7, 170.0; HRMS (ESI) Calcd. for $\text{C}_{33}\text{H}_{44}\text{N}_3\text{O}_9\text{S}^{1+}$ ($\text{M}^+ + \text{NH}_4$):, 658.2793, found: 658.2774.



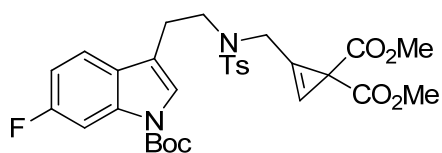
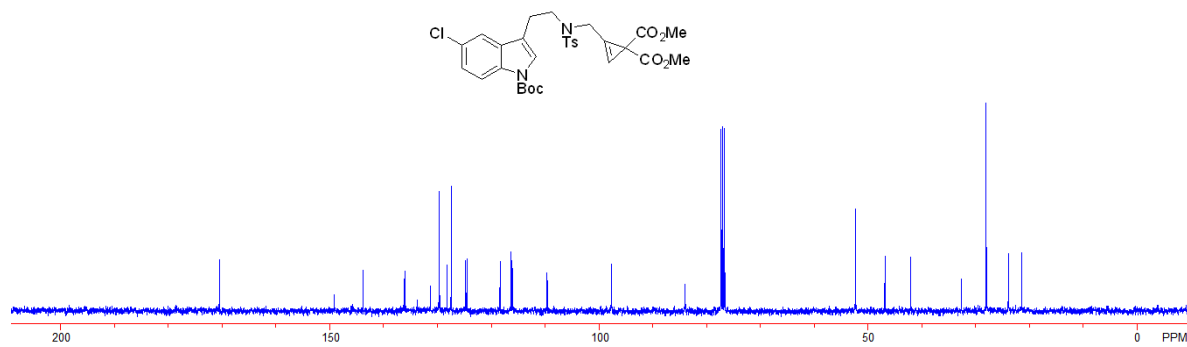
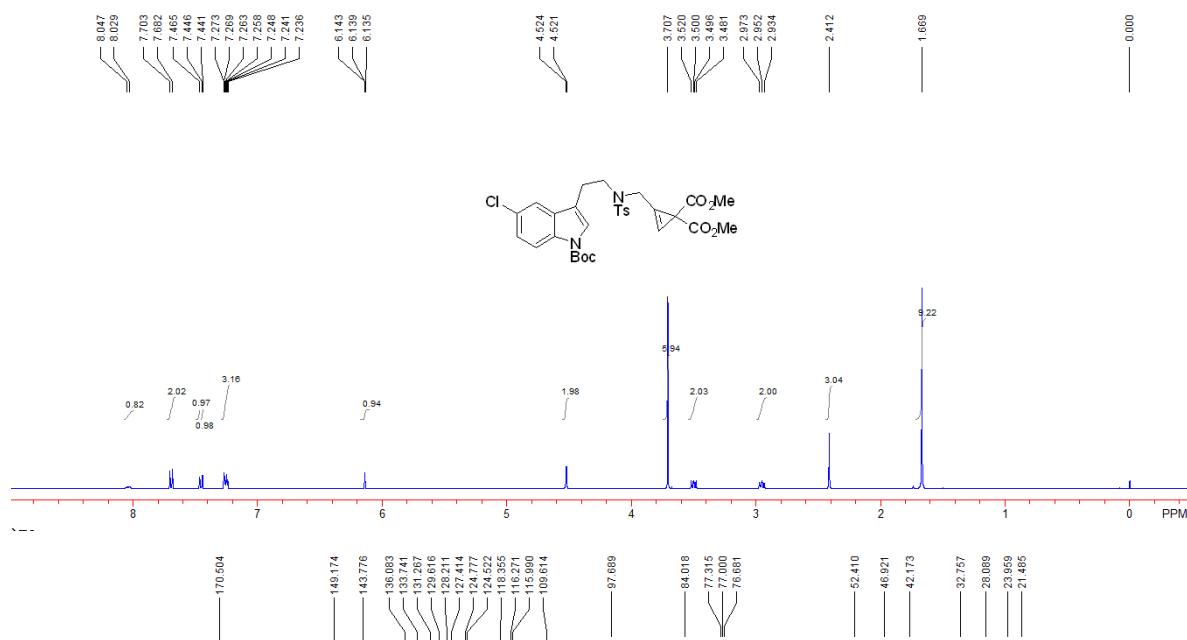
Compound **1e**: 681 mg, 53% yield; a colorless oil; IR (neat) ν 3145, 2979, 2952, 2930, 1728, 1450, 1371, 1277, 1255, 1156, 1103, 1057 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz, TMS) δ 1.67 (9H, s), 2.40 (3H, s), 2.95 (2H, t, $J =$

7.6 Hz), 3.51 (2H, t, $J = 7.6$ Hz), 3.70 (6H, s), 4.53 (2H, s), 6.18 (1H, s), 7.25 (2H, d, $J = 8.4$ Hz), 7.37 (1H, dd, $J = 2.0, 8.8$ Hz), 7.46 (1H, s), 7.61 (1H, d, $J = 2.0$ Hz), 7.69 (2H, d, $J = 8.4$ Hz), 7.98–8.00 (1H, m); ^{13}C NMR (CDCl_3 , 100 MHz, TMS) δ 21.3, 23.7, 27.9, 32.6, 41.9, 46.7, 52.2, 83.8, 97.6, 109.4, 115.7, 115.8, 116.5, 121.2, 124.4, 126.9, 127.2, 129.4, 131.6, 133.9, 135.9, 143.6, 148.9, 170.3; HRMS (ESI) Calcd. for $\text{C}_{30}\text{H}_{33}\text{BrN}_2\text{O}_8\text{S}$: 660.1141, found: 660.1128.

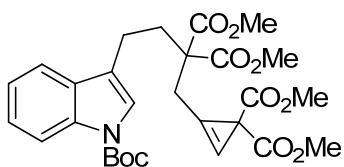


Compound **1f**: 231 mg, 52% yield; a yellow oil; IR (neat) ν 3145, 2979, 2952, 2930, 1731, 1452, 1372, 1278, 1257, 1158, 1064 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz, TMS) δ 1.67 (9H, s), 2.41 (3H, s), 2.93–2.97 (2H, m), 3.48–3.52 (2H, m), 3.71 (6H, s), 4.52 (2H, d, $J = 1.2$ Hz), 6.14 (1H, t, $J = 1.2$ Hz), 7.24–7.27 (3H, m), 7.44 (1H,

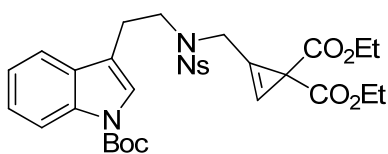
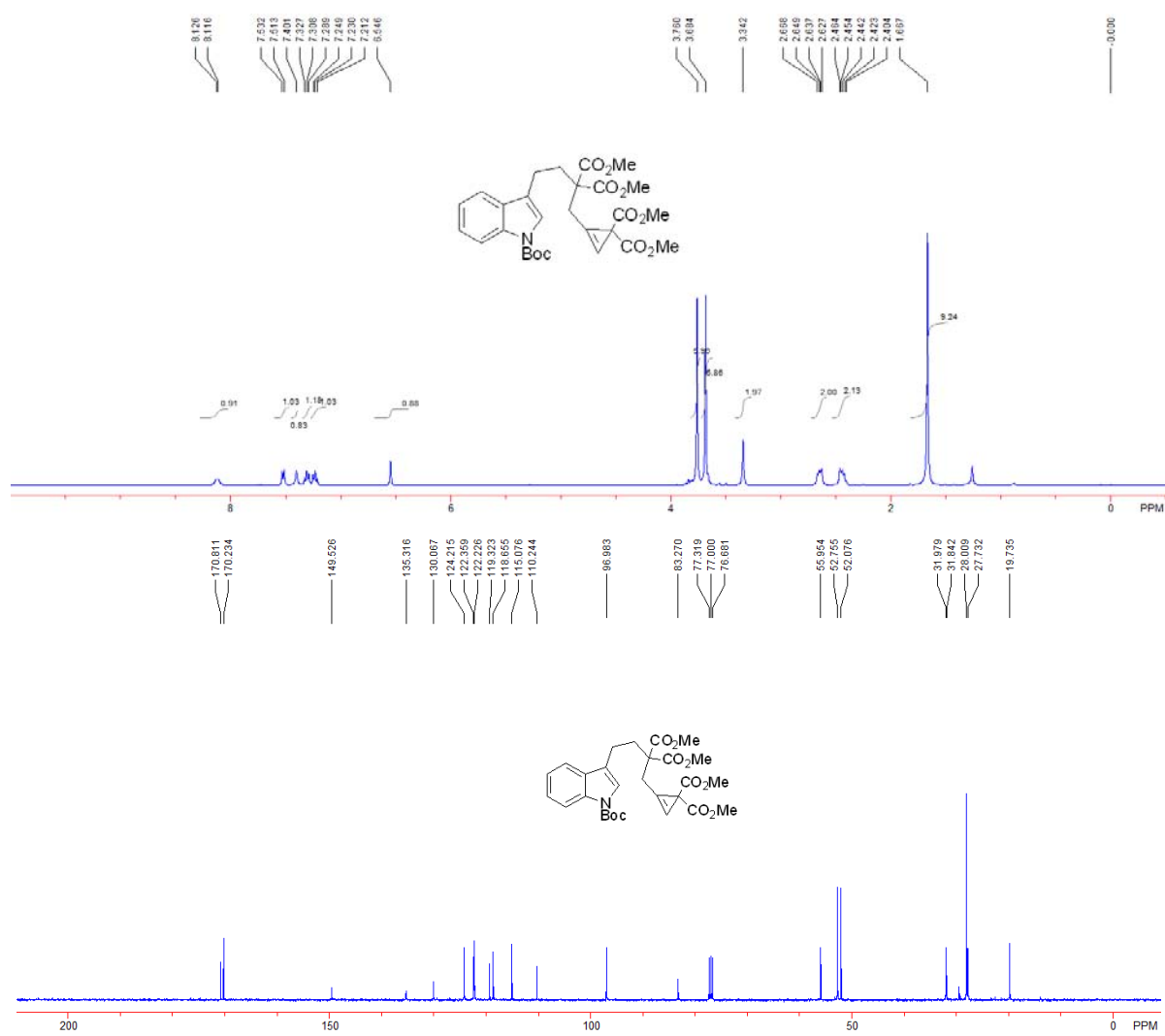
d, $J = 2.0$ Hz), 7.47 (1H, s), 7.69 (2H, d, $J = 8.4$ Hz), 8.03–8.05 (1H, m); ^{13}C NMR (CDCl_3 , 100 MHz, TMS) δ 21.5, 24.0, 28.1, 32.8, 42.2, 46.9, 52.4, 84.0, 97.7, 109.6, 116.0, 116.3, 118.4, 124.5, 124.8, 127.4, 128.2, 129.6, 131.3, 133.7, 136.1, 143.8, 149.2, 170.5; HRMS (ESI) Calcd. for $\text{C}_{30}\text{H}_{33}\text{ClN}_2\text{O}_8\text{S}$: 616.1646, found: 616.1663.



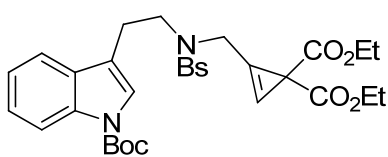
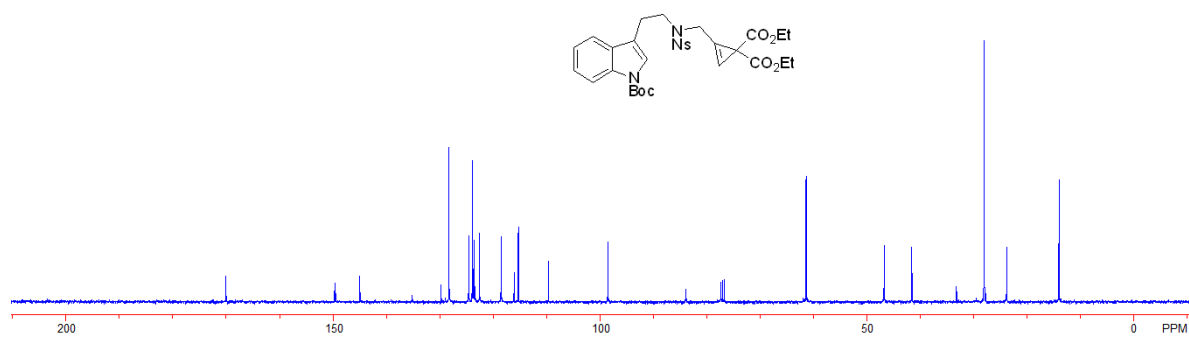
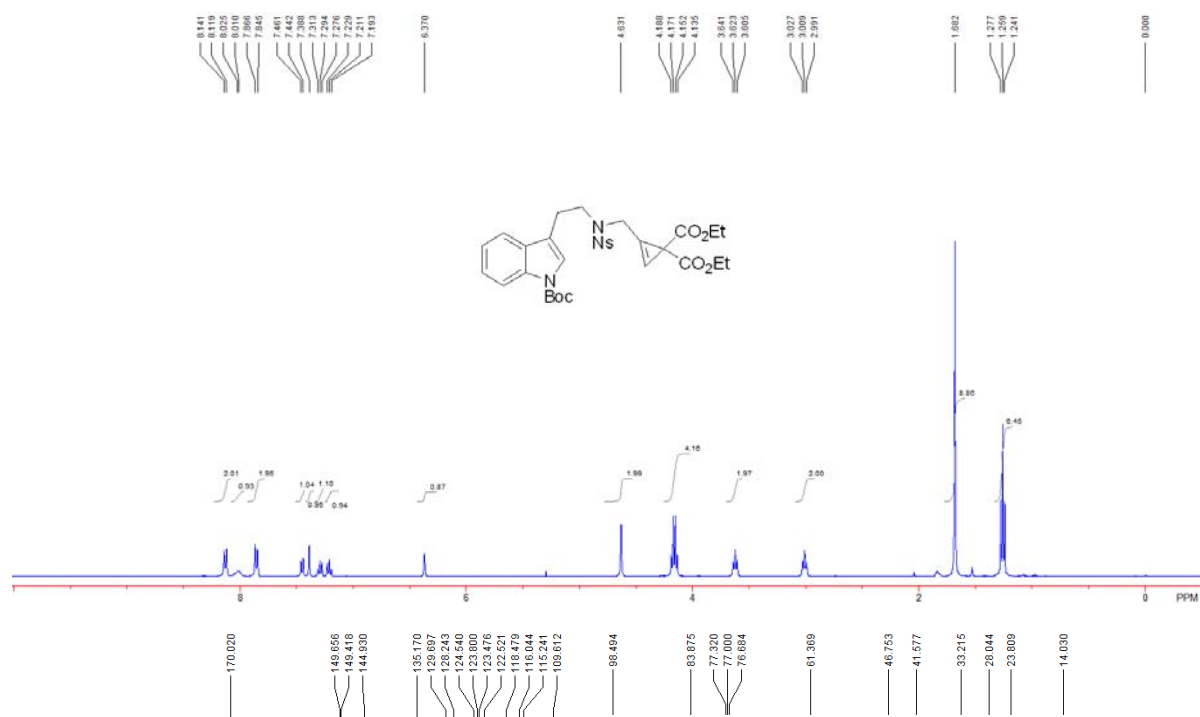
Compound **1g**: 1.194 g, 74% yield; a yellow oil; IR (neat) ν 3139, 2980, 2953, 2930, 1726, 1441, 1370, 1274, 1252, 1156, 1095, 1067, 734 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz, TMS) δ 1.67 (9H, s), 2.41 (3H, s), 2.97–3.00 (2H, m), 3.50–3.54 (2H, m), 3.70 (6H, s), 4.51 (2H, s), 6.13 (1H, s), 6.95–7.00 (1H, m), 7.24 (2H, d, $J = 8.4$ Hz), 7.41–7.45 (2H, m), 7.68 (2H, d, $J = 8.4$ Hz), 7.83–7.85 (1H, m); ^{13}C NMR (CDCl_3 , 100 MHz, TMS) δ 21.4, 24.1, 28.0, 32.7, 42.1, 47.0, 52.3, 83.9, 97.6, 102.5 (d, $J = 28.5$ Hz), 109.5, 110.6 (d, $J = 23.9$ Hz), 116.4 (d, $J = 0.8$ Hz), 119.3 (d, $J = 10.3$ Hz), 123.5 (d, $J = 3.8$ Hz), 126.3, 127.3, 129.5, 136.1, 143.6, 149.2, 160.8 (d,



Compound **1h**: 143 mg, 53% yield; a white solid; mp.103–105 °C; IR (neat) ν 3139, 2954, 1728, 1453, 1435, 1372, 1273, 1254, 1158, 1065, 749 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz, TMS) δ 1.67 (9H, s), 2.40–2.46 (2H, m), 2.63–2.67 (2H, m), 3.34 (2H, s), 3.68 (6H, s), 3.76 (6H, s), 6.55 (1H, s), 7.23 (1H, t, $J = 7.6$ Hz), 7.31 (1H, t, $J = 7.6$ Hz), 7.40 (1H, s), 7.52 (1H, d, $J = 7.6$ Hz), 8.12–8.13 (1H, m); ^{13}C NMR (CDCl_3 , 100 MHz, TMS) δ 19.7, 27.7, 28.0, 31.8, 32.0, 52.1, 52.8, 56.0, 83.3, 97.0, 110.2, 115.1, 118.7, 119.3, 122.2, 122.4, 124.2, 130.1, 135.3, 149.5, 170.2, 170.8; HRMS (ESI) Calcd. for $\text{C}_{28}\text{H}_{37}\text{N}_2\text{O}_{10}^+$ ($\text{M}^+ + \text{NH}_4$): 561.2443, found: 561.2429.

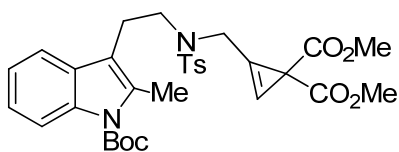
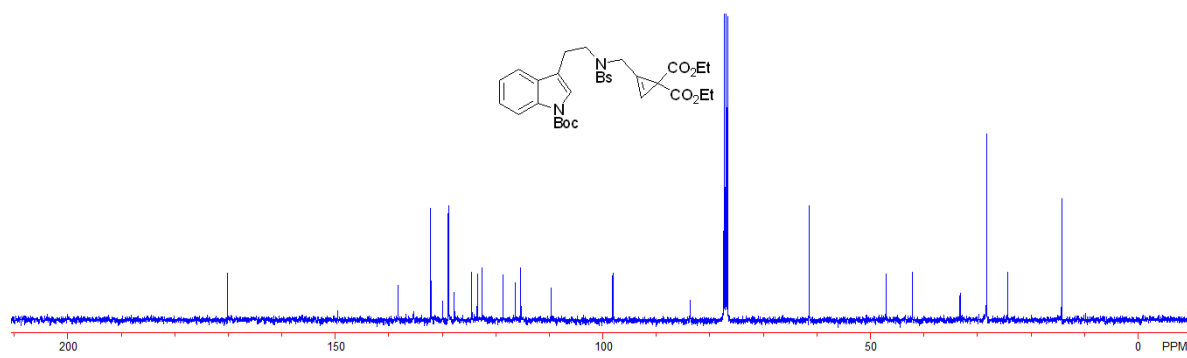
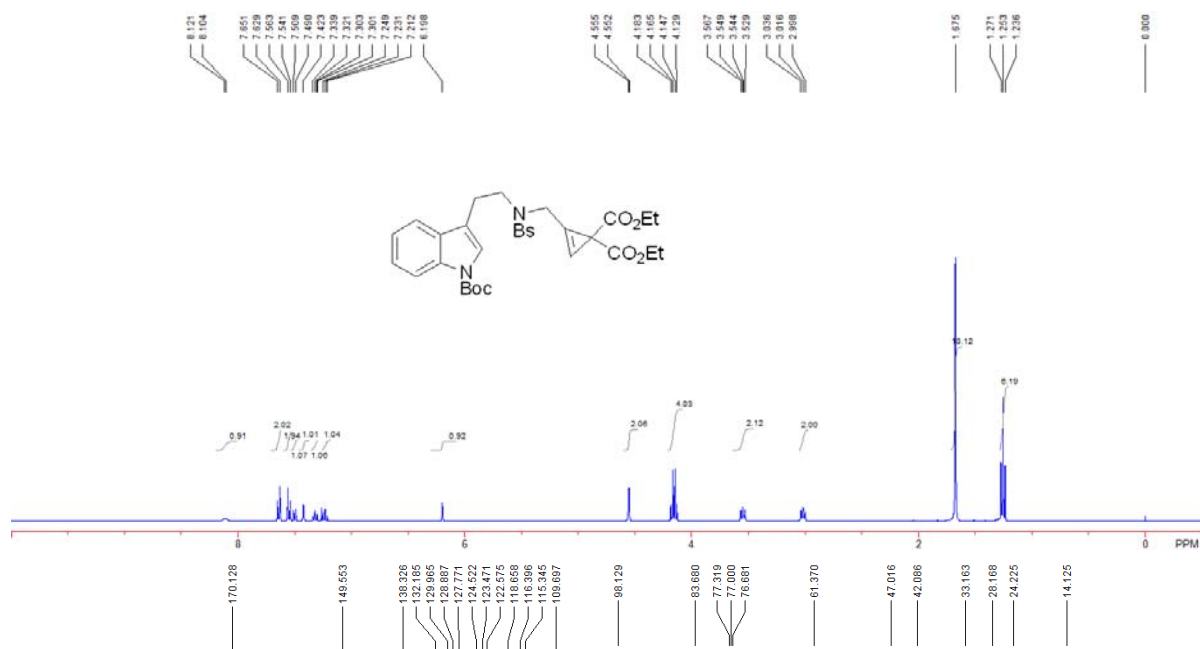


Compound **1i**: 126 mg, 15% yield; a colorless oil; IR (neat) ν 2960, 2925, 2871, 2855, 1724, 1530, 1452, 1367, 1349, 1258, 1158, 1097, 1060, 1017, 742 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz, TMS) δ 1.26 (6H, t, $J = 7.2$ Hz), 1.68 (9H, s), 3.01 (2H, t, $J = 7.2$ Hz), 3.62 (2H, t, $J = 7.2$ Hz), 4.16 (4H, q, $J = 7.2$ Hz), 4.63 (2H, s), 6.37 (1H, s), 7.21 (1H, t, $J = 7.2$ Hz), 7.29 (1H, t, $J = 7.2$ Hz), 7.39 (1H, s), 7.45 (1H, d, $J = 7.6$ Hz), 7.86 (2H, d, $J = 8.4$ Hz), 8.01–8.03 (1H, m), 8.13 (2H, d, $J = 8.4$ Hz); ^{13}C NMR (CDCl_3 , 100 MHz, TMS) δ 14.0, 23.8, 28.0, 33.2, 41.6, 46.8, 61.4, 83.9, 98.5, 109.6, 115.2, 116.0, 118.5, 122.5, 123.5, 123.8, 124.5, 128.2, 129.7, 135.2, 144.9, 149.4, 149.7, 170.0; HRMS (ESI) Calcd. for $\text{C}_{31}\text{H}_{39}\text{N}_4\text{O}_{10}\text{S}^{1+}$ ($\text{M}^+ + \text{NH}_4$): 659.2381, found: 659.2374.



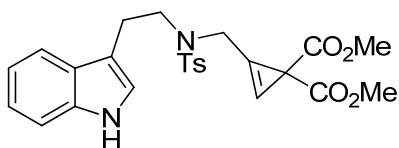
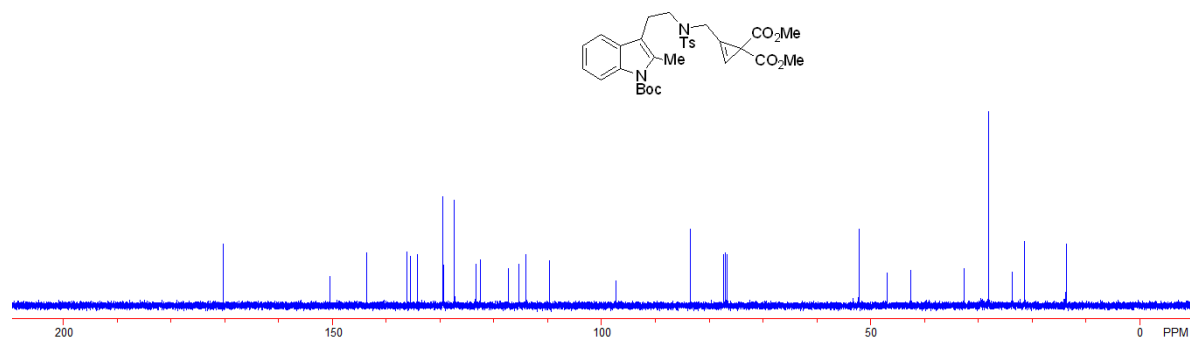
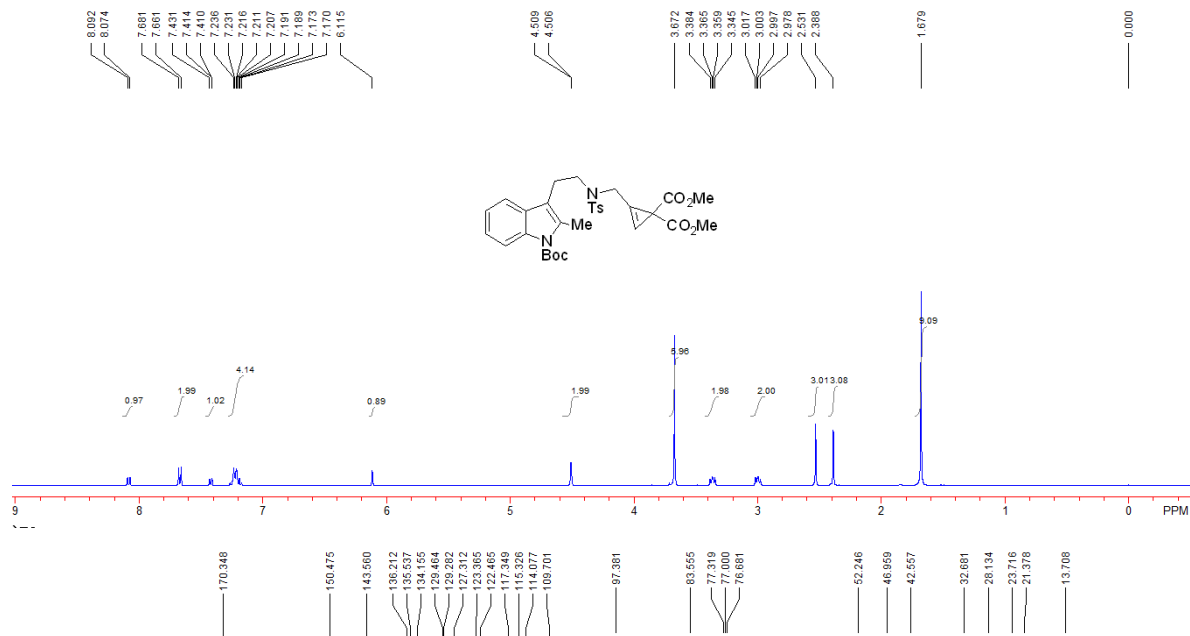
Compound **1j**: 26 mg, 16% yield; a colorless oil; IR (neat) ν 2983, 2929, 2874, 2854, 1735, 1453, 1369, 1257,

1155, 1097, 1020, 749 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz, TMS) δ 1.25 (6H, t, $J = 7.2$ Hz), 1.68 (9H, s), 3.02 (2H, t, $J = 7.6$ Hz), 3.53–3.57 (2H, m), 4.16 (4H, q, $J = 7.2$ Hz), 4.55 (2H, d, $J = 1.2$ Hz), 6.20 (1H, s), 7.23 (1H, dd, $J = 7.2, 7.6$ Hz), 7.30–7.34 (1H, m), 7.42 (1H, s), 7.50 (1H, d, $J = 7.6$ Hz), 7.55 (2H, d, $J = 8.4$ Hz), 7.64 (2H, d, $J = 8.4$ Hz), 8.10–8.12 (1H, m); ^{13}C NMR (CDCl_3 , 100 MHz, TMS) δ 14.1, 24.2, 28.2, 33.2, 42.1, 47.0, 61.4, 83.7, 98.1, 109.7, 115.3, 116.4, 118.7, 122.6, 123.5, 124.5, 127.8, 128.9, 130.0, 132.2, 138.3, 149.6, 170.1; HRMS (ESI) Calcd. for $\text{C}_{31}\text{H}_{39}\text{BrN}_3\text{O}_8\text{S}^{1+}$ ($\text{M}^+ + \text{NH}_4$): 692.1636, found: 692.1623.



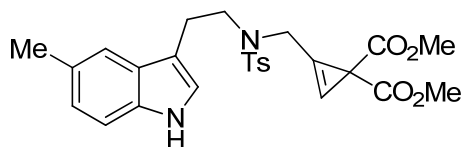
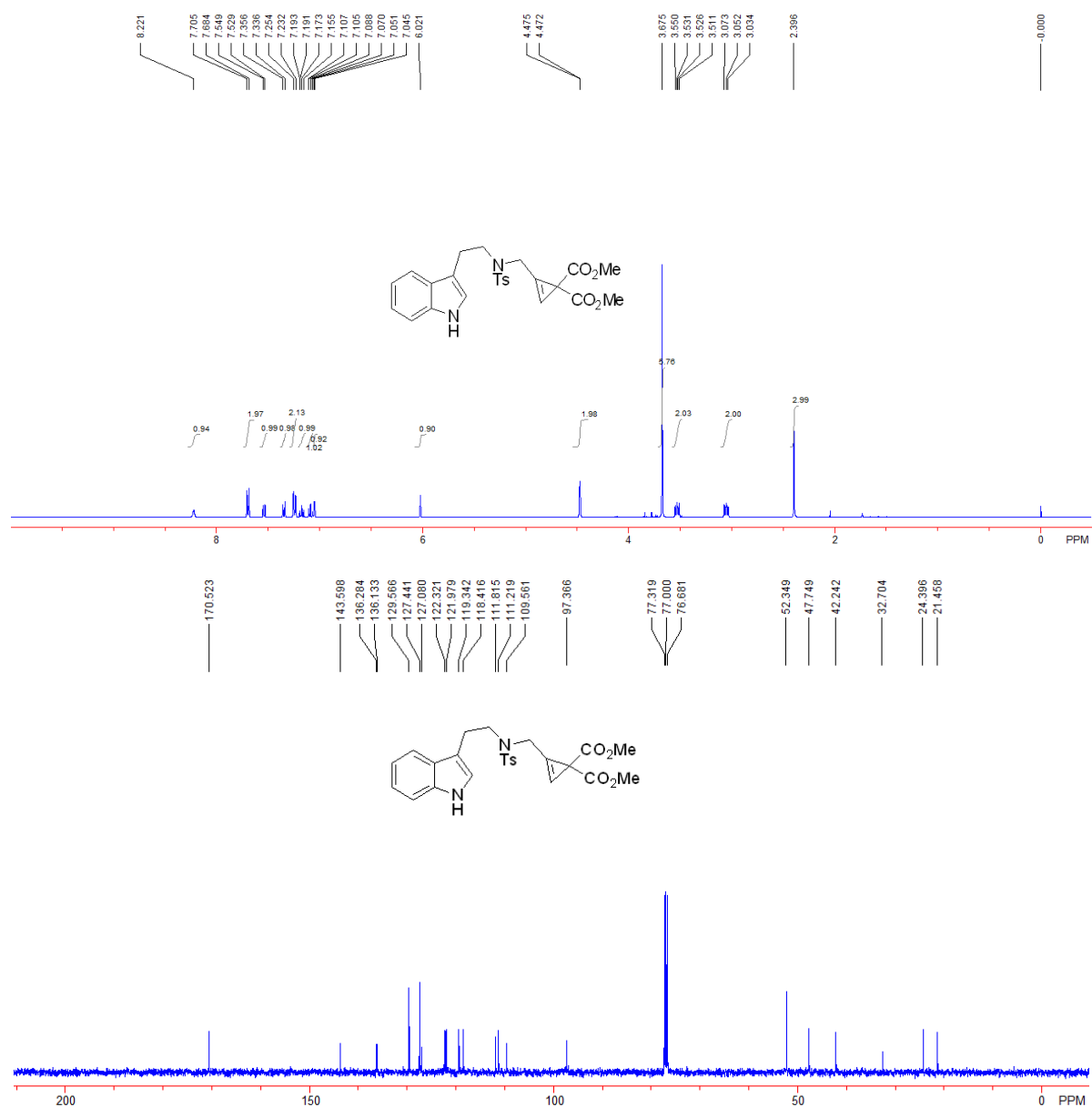
Compound **1k**: 429 mg, 55% yield; a colorless oil; IR (neat) ν 2953, 2929, 1727, 1458, 1356, 1322, 1253, 1158, 1137, 748 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz, TMS) δ 1.68 (9H, s), 2.39 (3H, s), 2.53 (3H, s), 2.98–3.02 (2H,

m), 3.35–3.38 (2H, m), 3.67 (6H, s), 4.51 (2H, d, $J = 1.2$ Hz), 6.12 (1H, s), 7.17–7.24 (4H, m), 7.41–7.43 (1H, m), 7.67 (2H, d, $J = 8.0$ Hz), 8.08 (1H, d, $J = 7.2$ Hz); ^{13}C NMR (CDCl_3 , 100 MHz, TMS) δ 13.7, 21.4, 23.7, 28.1, 32.7, 42.6, 47.0, 52.2, 83.6, 97.4, 109.7, 114.1, 115.3, 117.3, 122.5, 123.4, 127.3, 129.3, 129.5, 134.2, 135.5, 136.2, 143.6, 150.5, 170.3; HRMS (ESI) Calcd. for $\text{C}_{31}\text{H}_{36}\text{N}_2\text{O}_8\text{S}$: 596.2192, found: 596.2192.



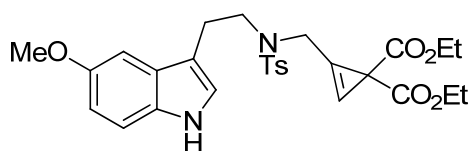
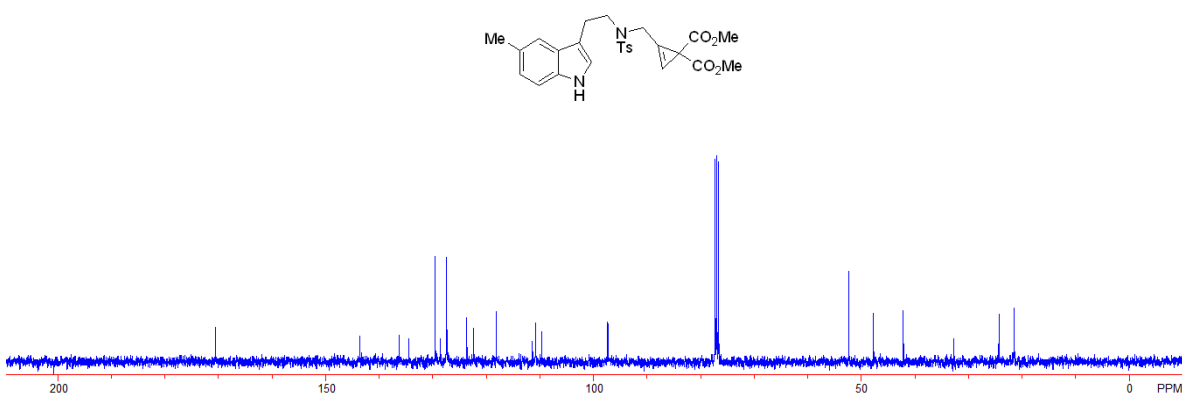
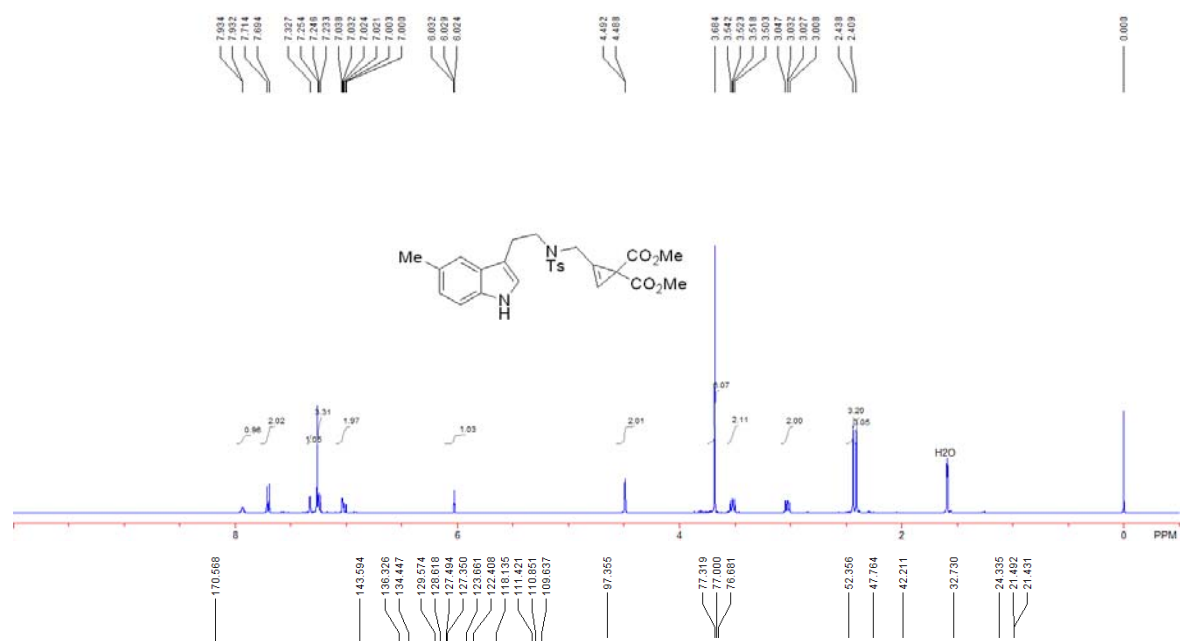
Compound **1a'**: 1.05 g, 81% yield; a colorless oil; IR (neat) ν 3398, 2953, 2924, 2853, 1735, 1457, 1435, 1339, 1288, 1265, 1067, 735, 654 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz, TMS) δ 2.40 (3H, s), 3.03–3.07 (2H, m), 3.51–3.55 (2H, m), 3.68 (6H, s), 4.47 (2H, d, $J = 1.2$ Hz), 6.02 (1H, s), 7.05 (1H, d, $J = 2.4$ Hz), 7.07–7.11 (1H, m), 7.16–7.19 (1H, m), 7.24 (2H, d, $J = 8.4$ Hz), 7.35 (1H, d, $J = 8.0$ Hz), 7.54 (1H, d, $J = 8.0$ Hz), 7.69 (2H, d, $J = 8.4$ Hz), 8.22 (1H, s); ^{13}C NMR (CDCl_3 , 100 MHz, TMS) δ 21.5, 24.4, 32.7, 42.2, 47.7, 52.3, 97.4, 109.6,

111.2, 111.8, 118.4, 119.3, 122.0, 122.3, 127.1, 127.4, 129.6, 136.1, 136.3, 143.6, 170.5; HRMS (ESI) Calcd. for C₂₅H₂₆N₂O₆S: 482.1512, found: 482.1521.



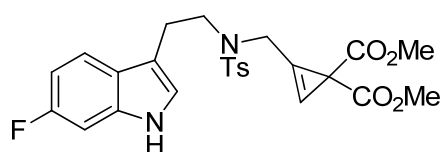
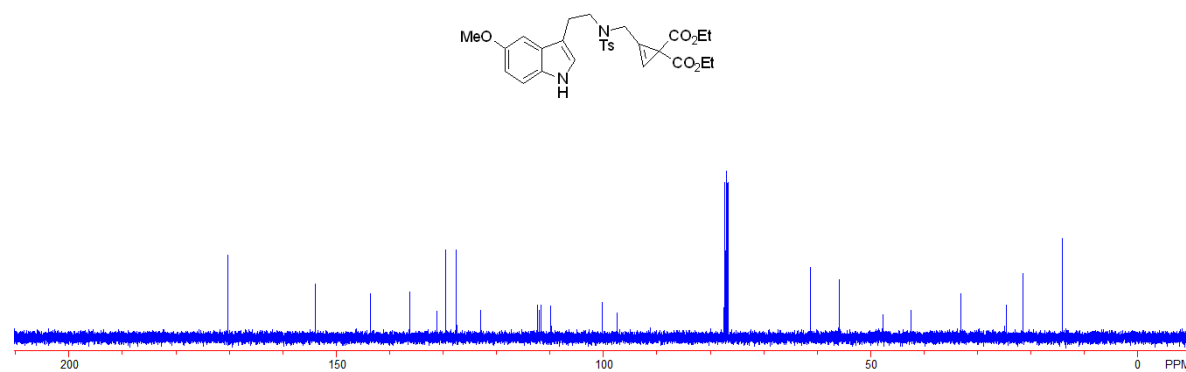
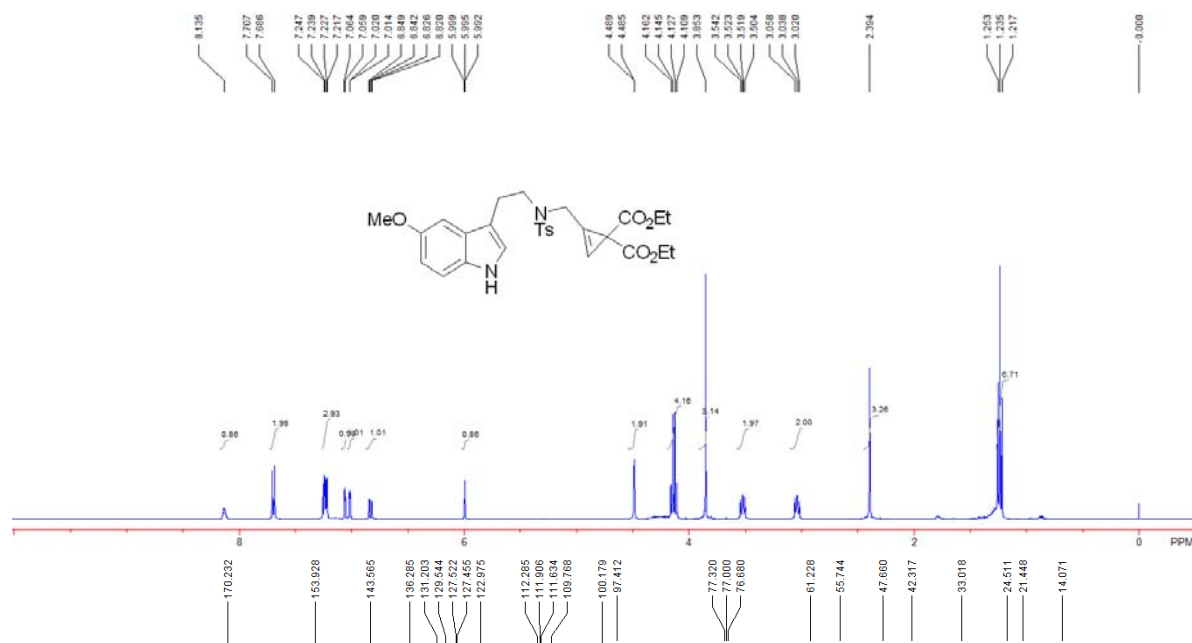
Compound **1b'**: 920 mg, 57% yield; a colorless oil; IR (neat) ν 3395, 2949, 2916, 2857, 1733, 1596, 1435, 1340, 1288, 1159, 1093, 1067, 915, 813, 736, 662 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz, TMS) δ 2.41 (3H, s), 2.44 (3H, s), 3.01–3.05 (2H, m), 3.50–3.54 (2H, m), 3.68 (6H, s), 4.49 (2H, d, J = 1.6 Hz), 6.03 (1H, t, J = 1.6 Hz), 7.00–7.04 (2H, m), 7.23–7.27 (3H, m), 7.33 (1H, s), 7.70 (2H, d, J = 8.0 Hz), 7.93 (1H, m); ¹³C NMR (CDCl₃,

100 MHz, TMS) δ 21.4, 21.5, 24.3, 32.7, 42.2, 47.8, 52.4, 97.4, 109.6, 110.9, 111.4, 118.1, 122.4, 123.7, 127.4, 127.5, 128.6, 129.6, 134.4, 136.3, 143.6, 170.6; HRMS (ESI) Calcd. for $C_{28}H_{32}N_2O_6S$: 524.1981, found: 524.1989.



Compound **1d'**: 46mg, 15% yield; a colorless oil; IR (neat) ν 2961, 2928, 2856, 2364, 1734, 1260, 1159, 1093, 1018, 799 cm^{-1} ; 1H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.24 (6H, t, $J = 7.2$ Hz), 2.39 (3H, s), 3.02–3.06 (2H, m), 3.50–3.54 (2H, m), 3.85 (3H, s), 4.14 (4H, q, $J = 7.2$ Hz), 4.49 (2H, d, $J = 1.6$ Hz), 6.00 (1H, t, $J = 1.6$ Hz), 6.83 (1H, dd, $J = 2.4, 8.8$ Hz), 7.02 (1H, d, $J = 2.4$ Hz), 7.06 (1H, d, $J = 2.4$ Hz), 7.22–7.25 (3H, m), 7.70 (2H, d, $J = 8.4$ Hz), 8.14 (1H, m); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 14.1, 21.4, 24.5, 33.0, 42.3, 47.7, 55.7, 61.2,

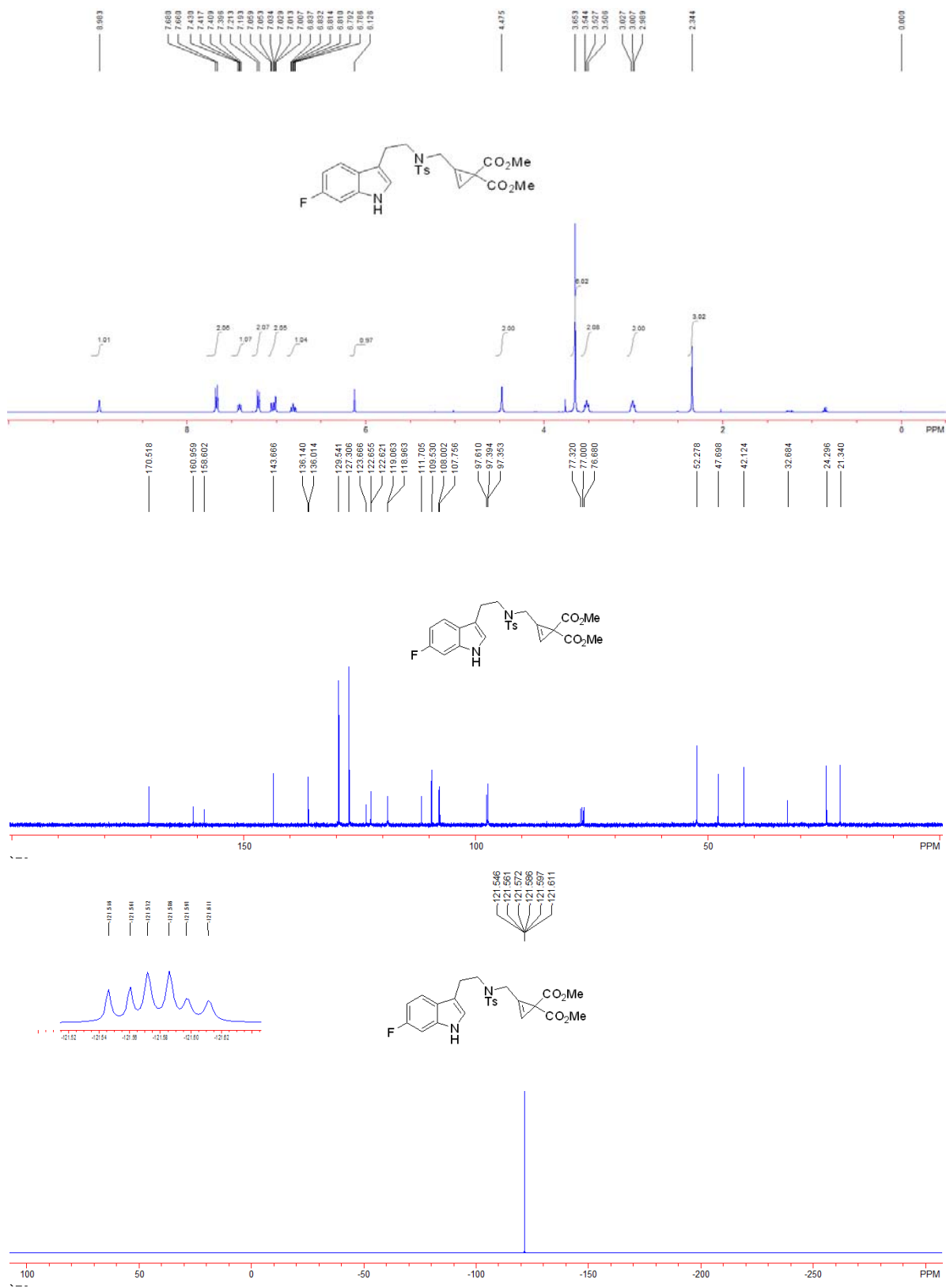
97.4, 100.2, 109.8, 111.6, 111.9, 112.3, 123.0, 131.2, 136.3, 143.6, 153.9, 170.2; HRMS (ESI) Calcd. for $C_{28}H_{32}N_2O_7S$: 540.1930, found: 540.1919.



Compound **1g'**: 832 mg, 84% yield; a colorless oil; IR (neat) ν 3377, 3146, 2953, 2925, 1736, 1628, 1456, 1436, 1343, 1290, 1254, 1158, 1095, 1068, 951, 812 cm^{-1} ; 1H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.34 (3H, s), 2.99–3.03 (2H, m), 3.51–3.54 (2H, m), 3.65 (6H, s), 4.48 (2H, s), 6.13 (1H, s), 6.79–6.84 (1H, m), 7.01–7.06 (2H, m), 7.20 (2H, d, $J = 8.0$ Hz), 7.41 (1H, dd, $J = 5.2, 8.4$ Hz), 7.67 (2H, d, $J = 8.0$ Hz), 8.98 (1H, m); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.3, 24.3, 32.7, 42.1, 47.7, 52.3, 97.4 (d, $J = 4.1$ Hz), 97.6, 107.9 (d, $J = 24.6$ Hz), 109.5, 111.7, 119.0 (d, $J = 10.0$ Hz), 122.6 (d, $J = 3.4$ Hz), 123.7, 127.3, 129.5, 136.0 (d, $J = 12.6$ Hz),

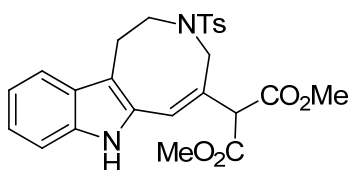
143.7, 159.8 (d, $J = 235.7$ Hz), 170.5; ^{19}F NMR (376 MHz, CDCl_3 , CFCl_3): -121.61– -121.55 (m); HRMS (ESI)

Calcd. for $\text{C}_{25}\text{H}_{25}\text{FN}_2\text{O}_6\text{S}$: 500.1417, found: 500.1429.

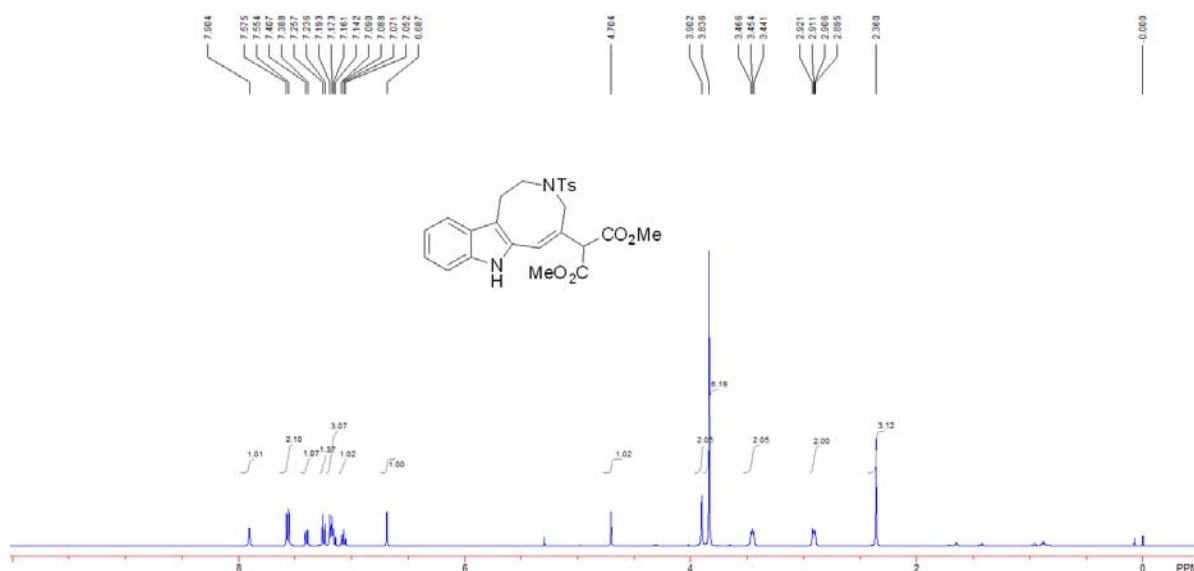


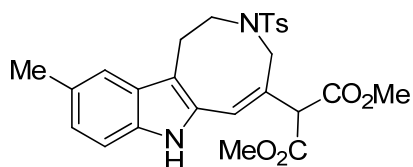
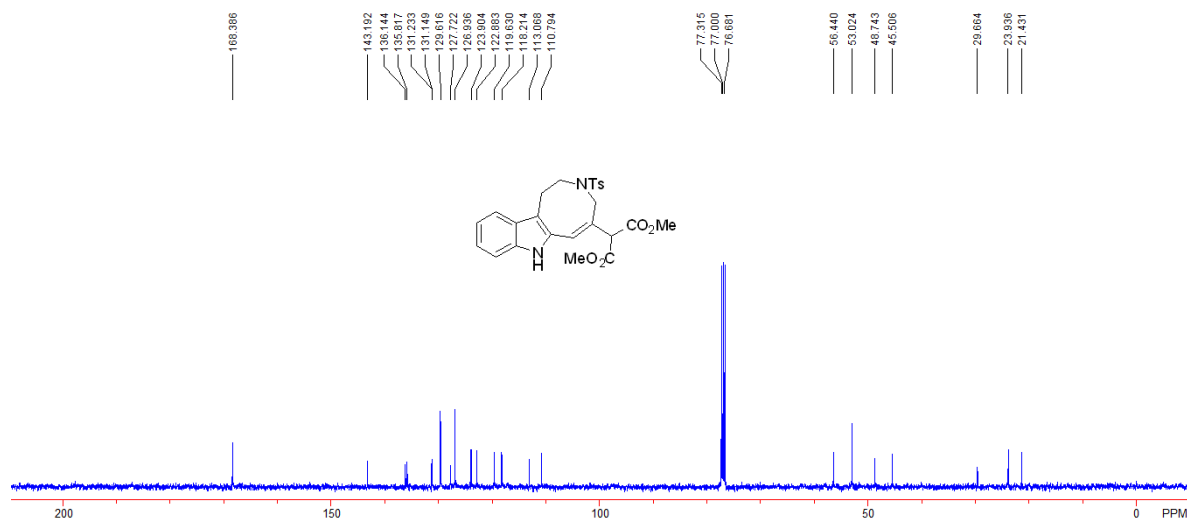
General Procedure and Spectroscopic Data of the Products 2

A solution of compound **1** (0.1 mmol) was stirred at ambient temperature in the mixed solvent of TFA and DCM (1:1). The reaction was monitored by TLC. When the deprotected compound was observed, then 1.5 eq of HOTf was added into the reaction system. Once the reaction was complete, the solvent was removed under reduced pressure and the residue was chromatographed on silica gel (elution with petroleum ether/ethyl acetate = 3/1) to provide the corresponding product **2**.

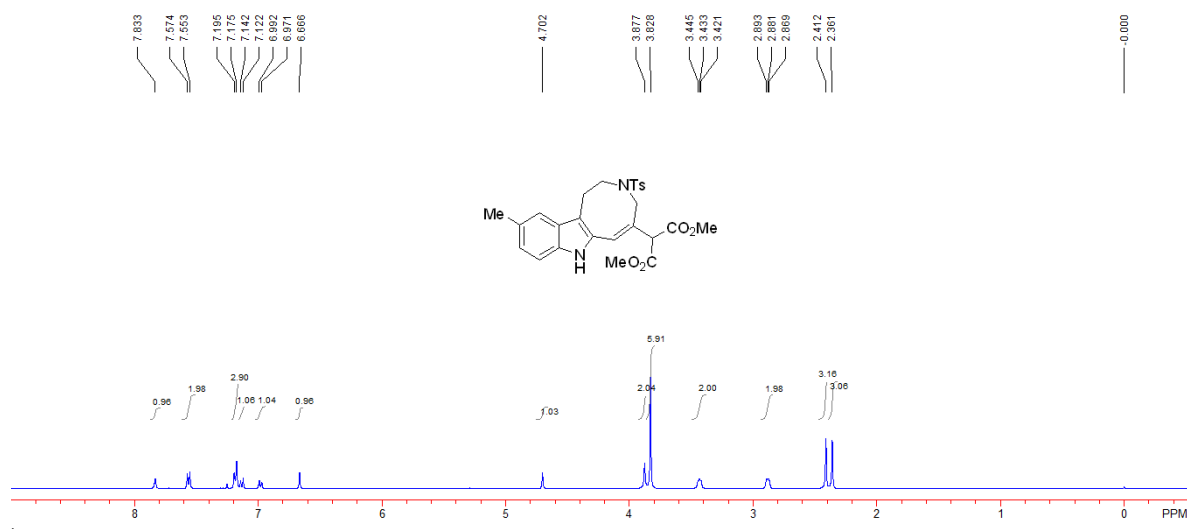


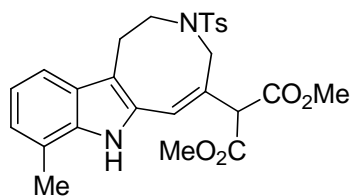
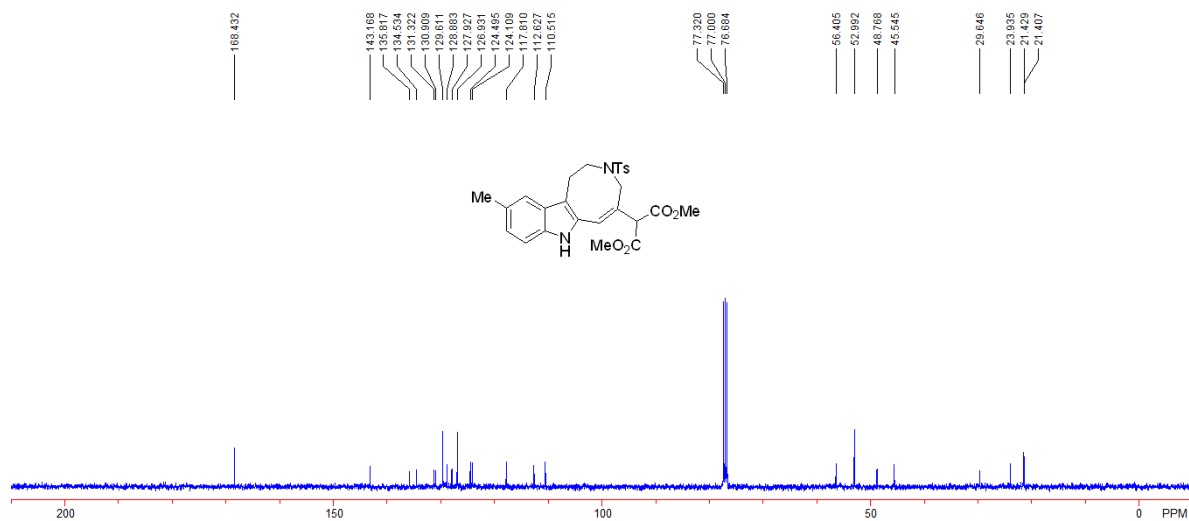
Compound **2a**: 36 mg, 62% yield; a white solid; mp. 75–77 °C; IR (neat) ν 3374, 2954, 2924, 2854, 1734, 1457, 1436, 1334, 1157, 1093, 740 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz, TMS) δ 2.36 (3H, s), 2.90–2.92 (2H, m), 3.45 (2H, t, $J = 4.8$ Hz), 3.84 (6H, s), 3.90 (2H, s), 4.70 (1H, s), 6.69 (1H, s), 7.05–7.09 (1H, m), 7.14–7.19 (3H, m), 7.25 (1H, d, $J = 8.4$ Hz), 7.40 (1H, d, $J = 7.6$ Hz), 7.56 (2H, d, $J = 8.4$ Hz), 7.90 (1H, s); ^{13}C NMR (CDCl_3 , 100 MHz, TMS) δ 21.4, 23.9, 29.7, 45.5, 48.7, 53.0, 56.4, 110.8, 113.1, 118.2, 119.6, 122.9, 123.9, 126.9, 127.7, 129.6, 131.1, 131.2, 135.8, 136.1, 143.2, 168.4; HRMS (ESI) Calcd. for $\text{C}_{25}\text{H}_{26}\text{N}_2\text{O}_6\text{S}$: 482.1512, found: 482.1525.



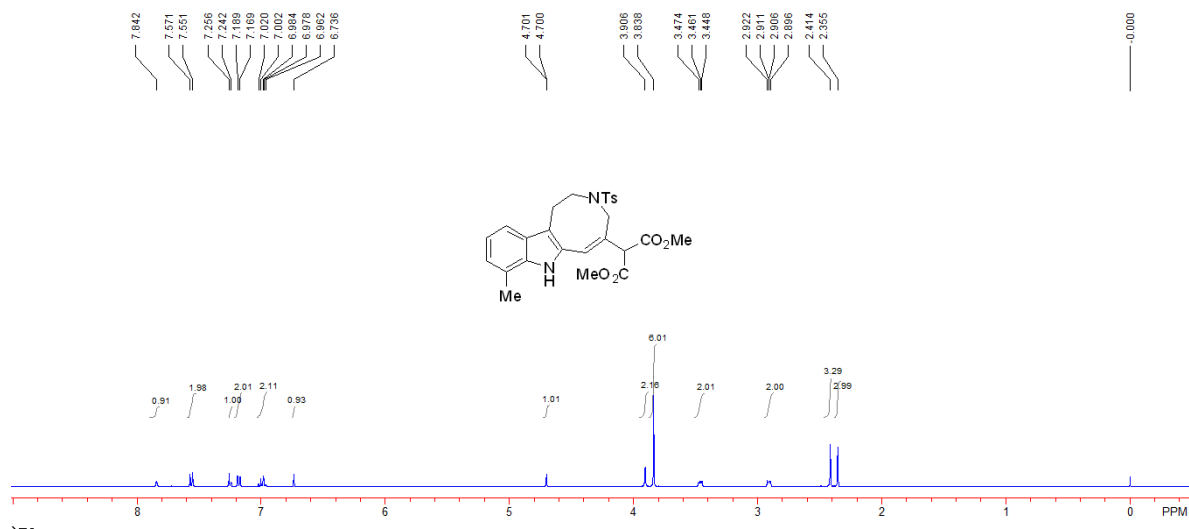


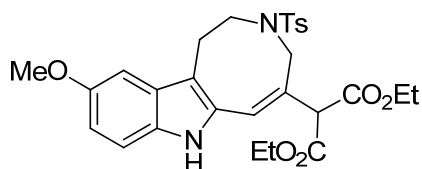
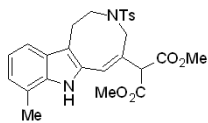
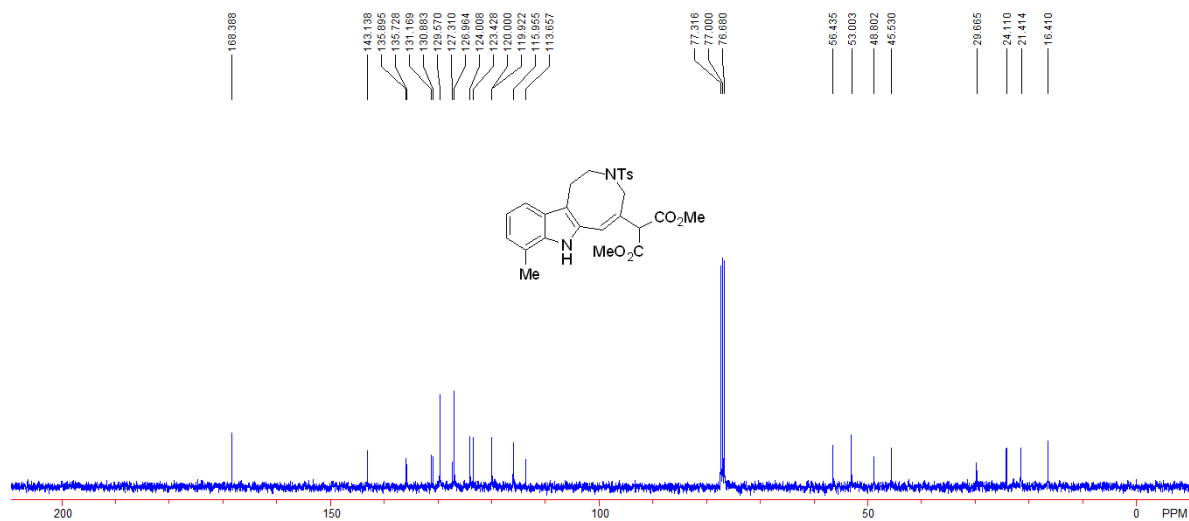
Compound **2b**: 35 mg, 81% yield; a white solid; mp. 75–77 °C; IR (neat) ν 3384, 2955, 2923, 2854, 1737, 1457, 1328, 1260, 1156, 1092, 1018, 800 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz, TMS) δ 2.36 (3H, s), 2.41 (3H, s), 2.88 (2H, t, $J = 4.8$ Hz), 3.43 (2H, t, $J = 4.8$ Hz), 3.83 (6H, s), 3.88 (2H, s), 4.70 (1H, s), 6.67 (1H, s), 6.98 (1H, d, $J = 8.4$ Hz), 7.13 (1H, d, $J = 8.0$ Hz), 7.19 (3H, d, $J = 8.0$ Hz), 7.56 (2H, d, $J = 8.4$ Hz), 7.83 (1H, s); ^{13}C NMR (CDCl_3 , 100 MHz, TMS) δ 21.41, 21.43, 23.9, 29.6, 45.5, 48.8, 53.0, 56.4, 110.5, 112.6, 117.8, 124.1, 124.5, 126.9, 127.9, 128.9, 129.6, 130.9, 131.3, 134.5, 135.8, 143.2, 168.4; HRMS (ESI) Calcd. for $\text{C}_{26}\text{H}_{29}\text{N}_2\text{O}_6\text{S}$: 496.1668, found: 496.1667.



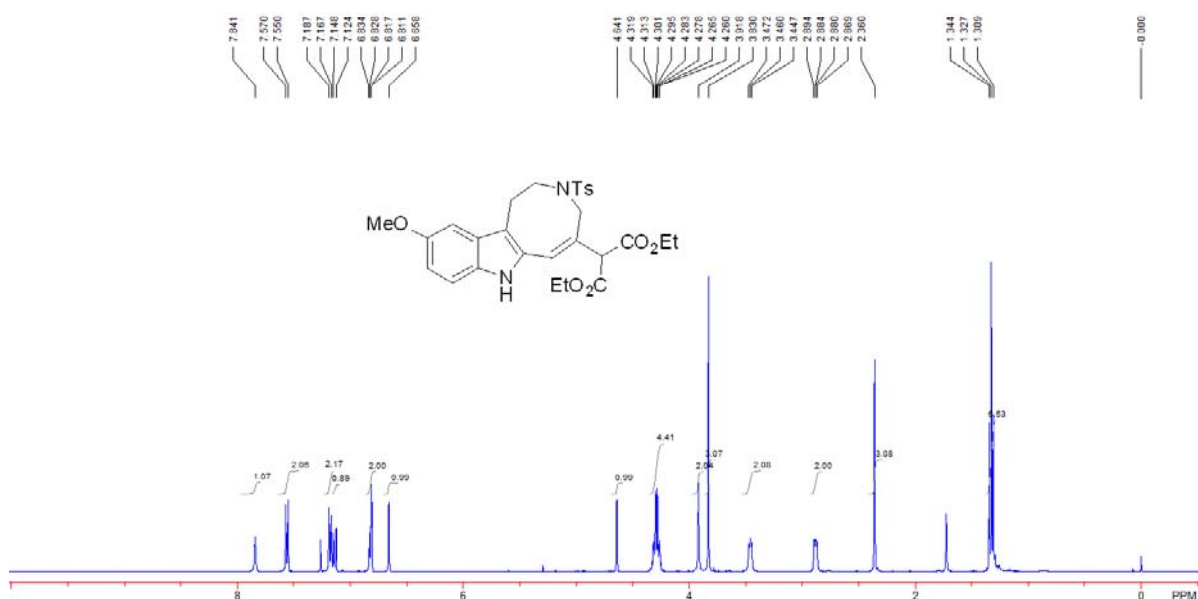


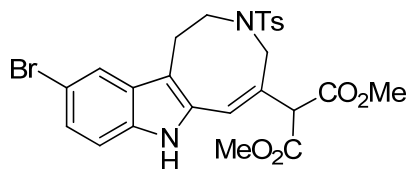
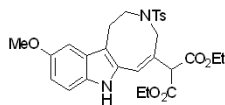
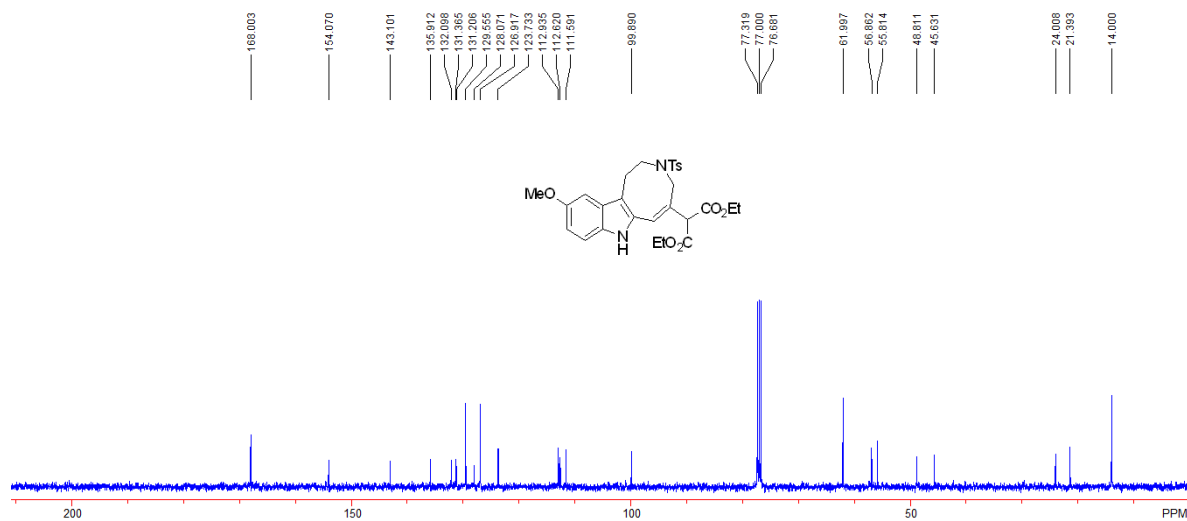
Compound **2c**: 111 mg, 93% yield; a white solid; mp. 75–77 °C; IR (neat) ν 3380, 2954, 2924, 2854, 1735, 1435, 1333, 1156, 1092, 738 cm^{-1} ; ¹H NMR (CDCl₃, 400 MHz, TMS) δ 2.36 (3H, s), 2.41 (3H, s), 2.90–2.92 (2H, m), 3.46 (2H, t, J = 5.2 Hz), 3.84 (6H, s), 3.91 (2H, s), 4.70 (1H, d, J = 0.4 Hz), 6.74 (1H, s), 6.96–7.02 (2H, m), 7.18 (2H, d, J = 8.0 Hz), 7.25 (1H, d, J = 5.6 Hz), 7.56 (2H, d, J = 8.0 Hz), 7.84 (1H, s); ¹³C NMR (CDCl₃, 100 MHz, TMS) δ 16.4, 21.4, 24.1, 29.7, 45.5, 48.8, 53.0, 56.4, 113.7, 116.0, 119.9, 120.0, 123.4, 124.0, 127.0, 127.3, 129.6, 130.9, 131.2, 135.7, 135.9, 143.1, 168.4; HRMS (ESI) Calcd. for C₂₆H₂₈N₂O₆S: 496.1668, found: 496.1680.



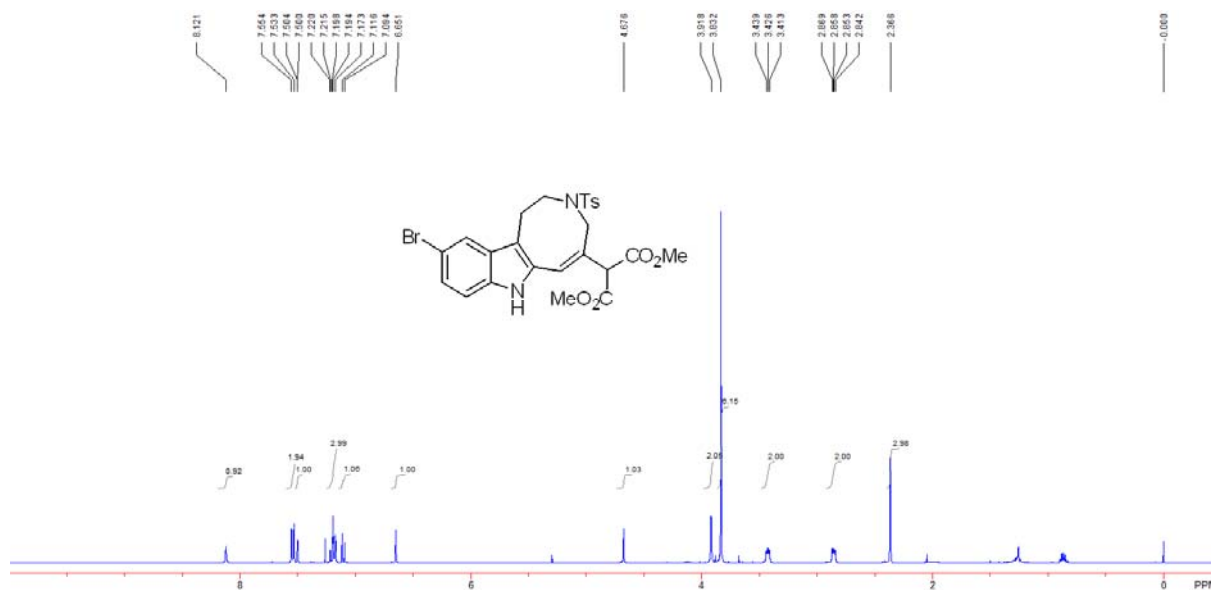


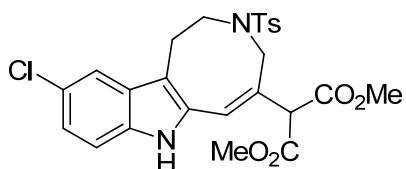
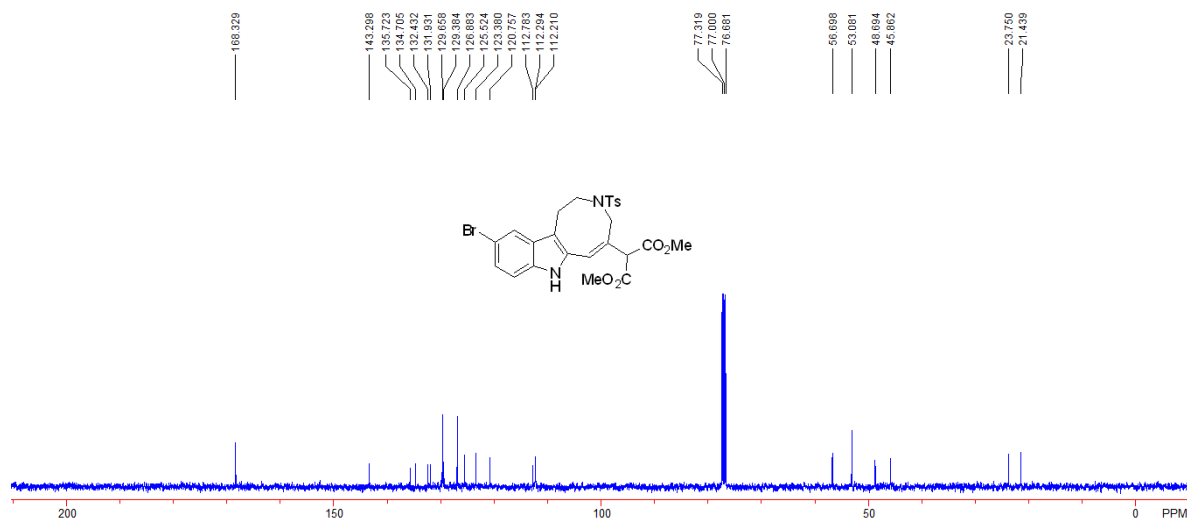
Compound **2d**: 36 mg, 67% yield; a white solid; mp. 55–57 °C; IR (neat) ν 3388, 2958, 2925, 2853, 1731, 1455, 1305, 1217, 1155, 1029, 656 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz, TMS) δ 1.33 (6H, t, $J = 7.2$ Hz), 2.36 (3H, s), 2.87–2.89 (2H, m), 3.46 (2H, t, $J = 5.2$ Hz), 3.83 (3H, s), 3.92 (2H, s), 4.26–4.32 (4H, m), 4.64 (1H, s), 6.66 (1H, s), 6.81–6.83 (2H, m), 7.14 (1H, d, $J = 9.6$ Hz), 7.18 (2H, d, $J = 8.0$ Hz), 7.56 (2H, d, $J = 8.0$ Hz), 7.84 (1H, s); ^{13}C NMR (CDCl_3 , 100 MHz, TMS) δ 14.0, 21.4, 24.0, 45.6, 48.8, 55.8, 56.9, 62.0, 99.9, 111.6, 112.6, 112.9, 123.7, 126.9, 128.1, 129.6, 131.2, 131.4, 132.1, 135.9, 143.1, 154.1, 168.0; HRMS (ESI) Calcd. for $\text{C}_{28}\text{H}_{32}\text{N}_2\text{O}_7\text{S}$: 540.1930, found: 540.1937.



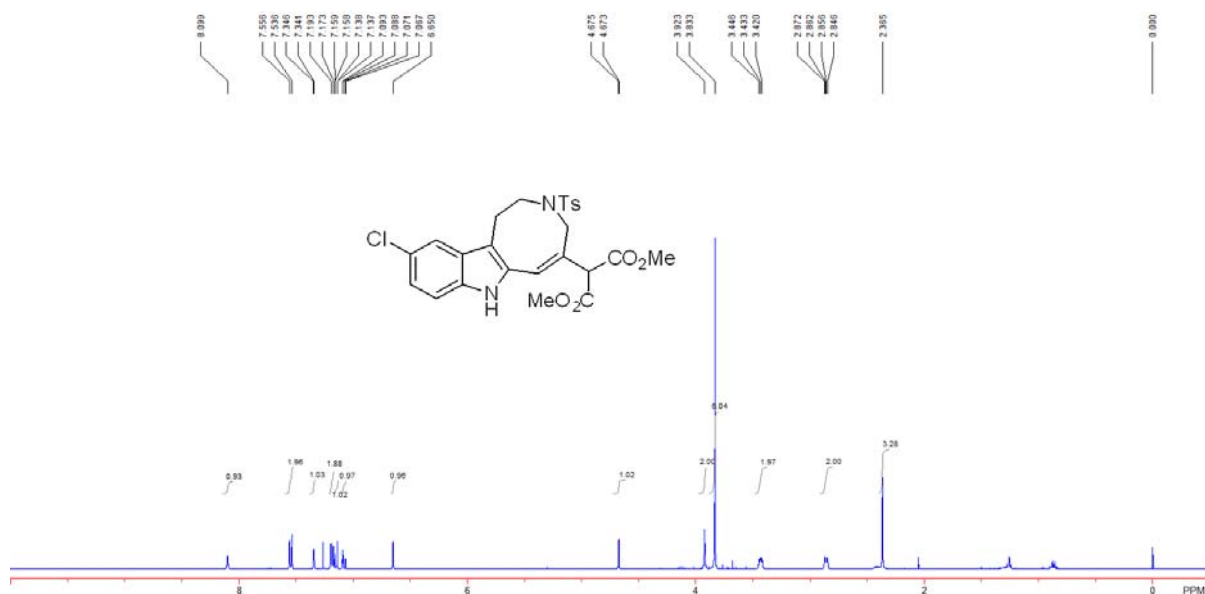


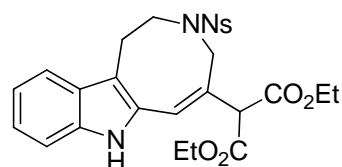
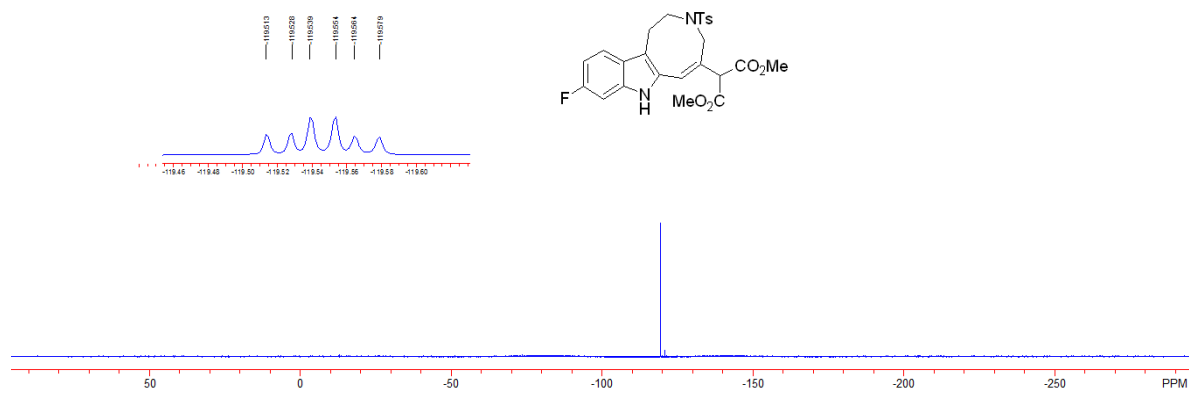
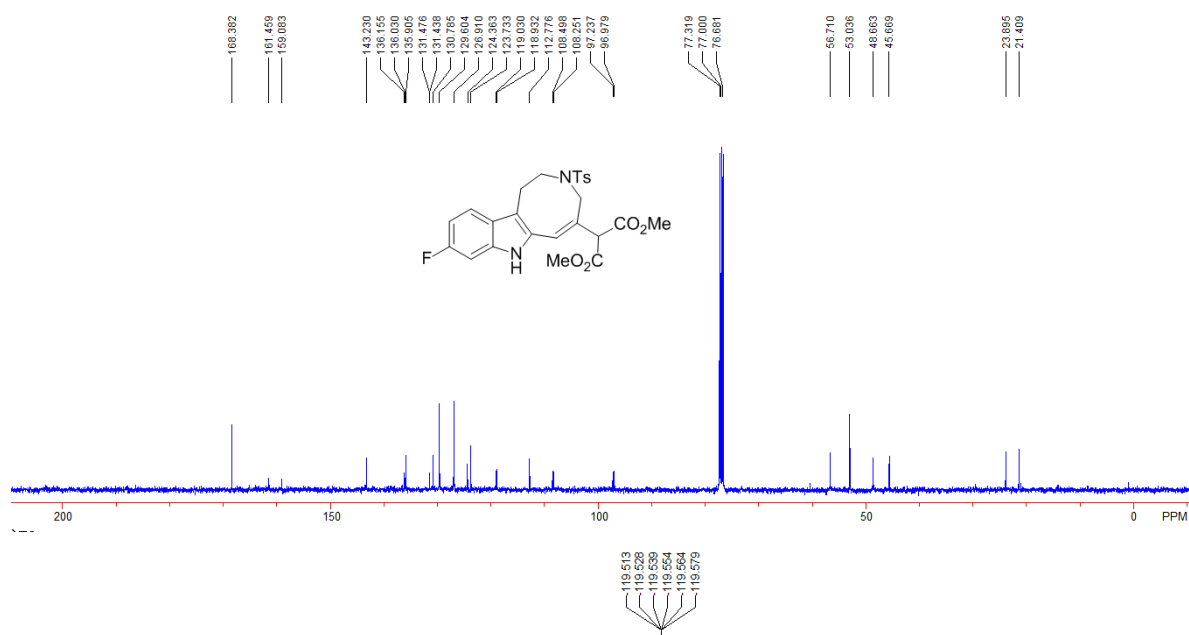
Compound **2e**: 35 mg, 62% yield; a white solid; mp. 74–76 °C; IR (neat) ν 3366, 2955, 2925, 2855, 1738, 1435, 1325, 1325, 1260, 1157, 1092, 1019, 812, 796, 657 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz, TMS) δ 2.37 (3H, s), 2.84–2.87 (2H, m), 3.43 (2H, t, $J = 5.2$ Hz), 3.83 (6H, s), 3.92 (2H, s), 4.68 (1H, s), 6.65 (1H, s), 7.11 (1H, d, $J = 8.8$ Hz), 7.17–7.22 (3H, m), 7.50 (1H, d, $J = 2.0$ Hz), 7.54 (2H, d, $J = 8.4$ Hz), 8.12 (1H, s); ^{13}C NMR (CDCl_3 , 100 MHz, TMS) δ 21.4, 23.8, 45.9, 48.7, 53.1, 56.7, 112.2, 112.3, 112.8, 120.8, 123.4, 125.5, 126.9, 129.4, 129.7, 131.9, 132.4, 134.7, 135.7, 143.3, 168.3; HRMS (ESI) Calcd. for $\text{C}_{25}\text{H}_{25}\text{BrN}_2\text{O}_6\text{S}$: 560.0617, found: 560.0602.



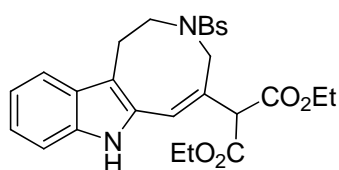
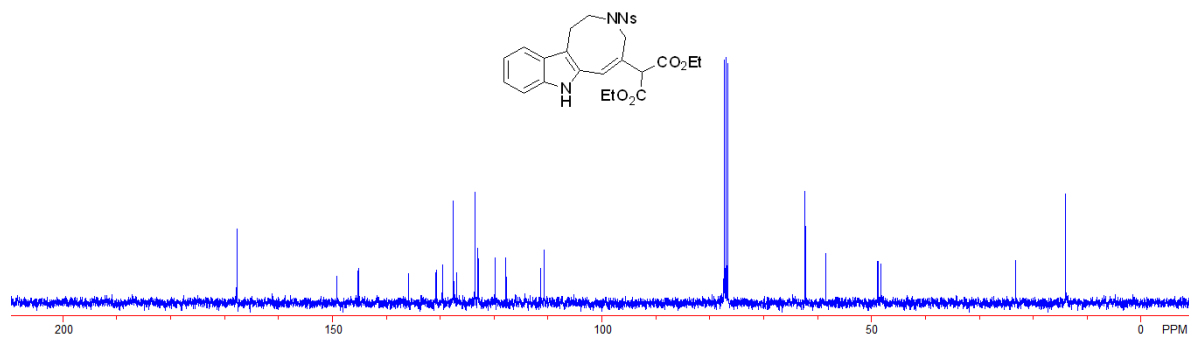
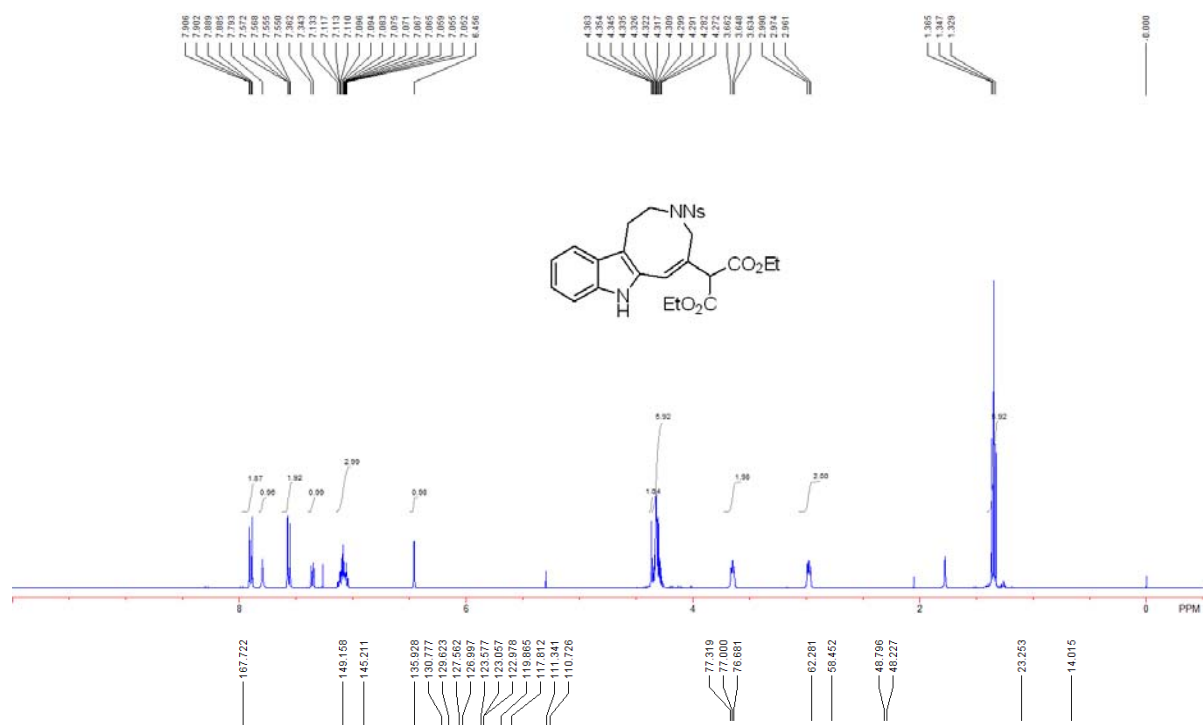


Compound **2f**: 33 mg, 67% yield; a white solid; mp. 80–82 °C; IR (neat) ν 3371, 2953, 2924, 2854, 2360, 1736, 1436, 1326, 1156, 1092, 1031, 661 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz, TMS) δ 2.37 (3H, s), 2.85–2.87 (2H, m), 3.43 (2H, t, $J = 5.2$ Hz), 3.83 (6H, s), 3.92 (2H, s), 4.67 (1H, d, $J = 0.8$ Hz), 6.65 (1H, s), 7.07–7.09 (1H, m), 7.14–7.16 (1H, m), 7.18 (2H, d, $J = 8.0$ Hz), 7.34 (1H, d, $J = 2.0$ Hz), 7.55 (2H, d, $J = 8.0$ Hz), 8.10 (1H, s); ^{13}C NMR (CDCl_3 , 100 MHz, TMS) δ 21.4, 23.8, 45.9, 48.7, 53.1, 56.7, 111.9, 112.3, 117.7, 123.0, 123.4, 125.3, 126.9, 128.7, 129.7, 131.9, 132.6, 134.4, 135.7, 143.3, 168.3; HRMS (ESI) Calcd. for $\text{C}_{25}\text{H}_{25}\text{ClN}_2\text{O}_6\text{S}$: 516.1122, found: 516.1141.

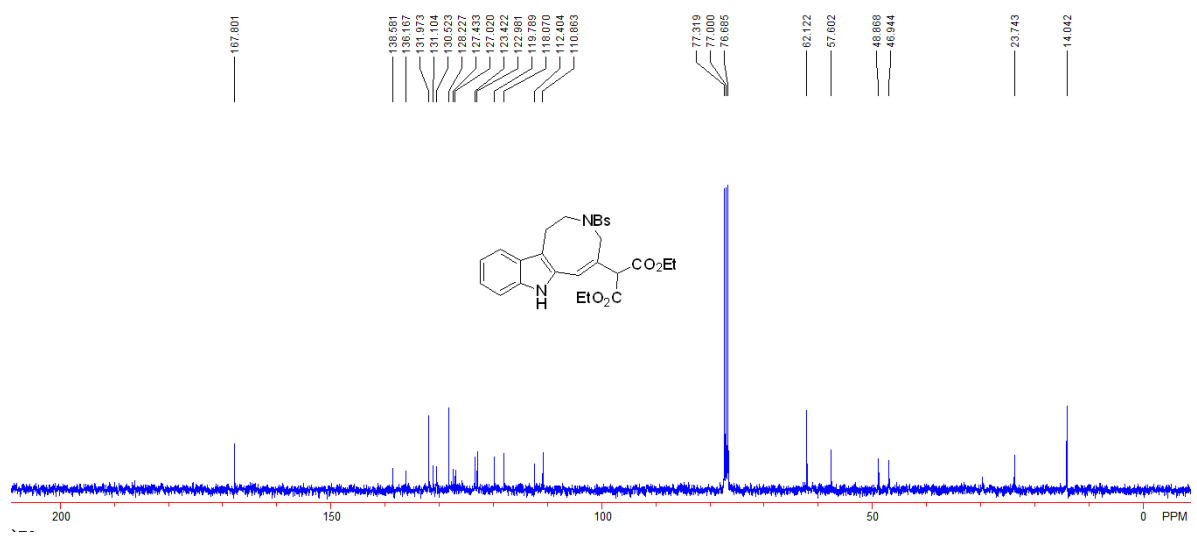
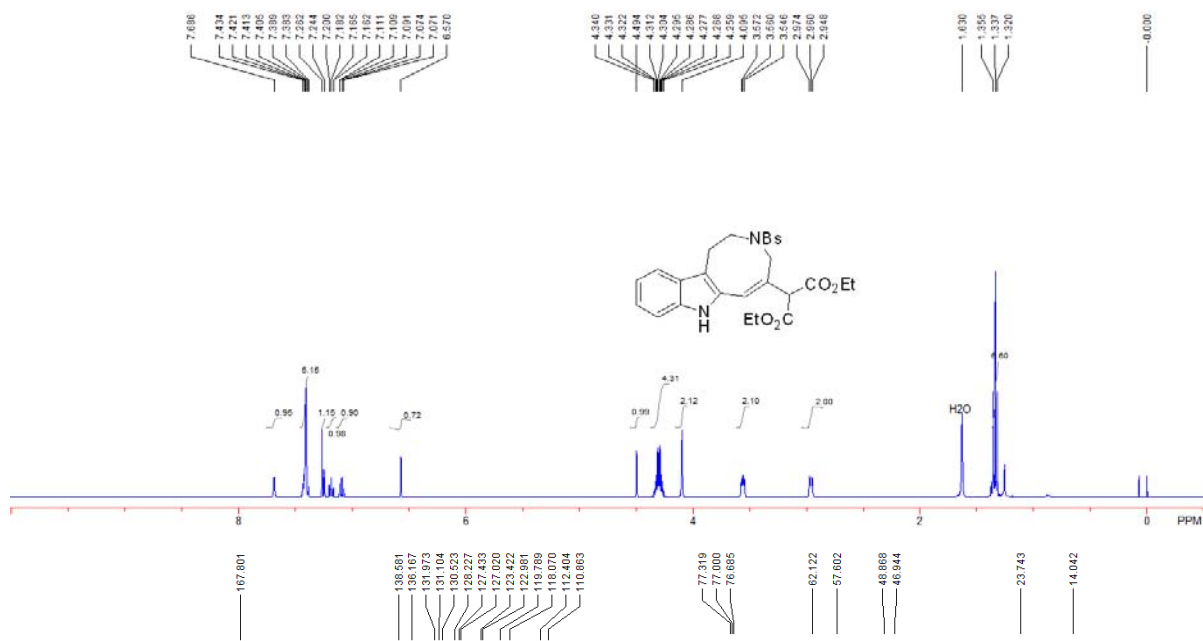




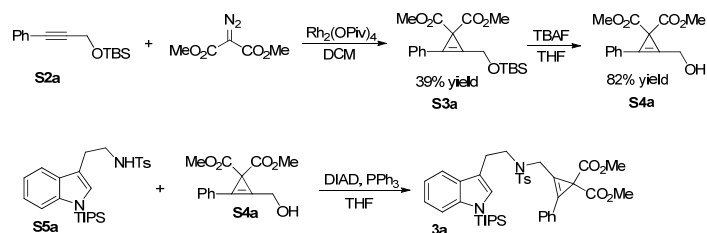
Compound **2i**: 45 mg, 71% yield; a yellow solid; mp. 72–74 °C; IR (neat) ν 3384, 2955, 2925, 2870, 2853, 1729, 1529, 1459, 1347, 1310, 1159, 1031, 741 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz, TMS) δ 1.35 (6H, t, $J = 7.2$ Hz), 2.97 (2H, t, $J = 5.6$ Hz), 3.65 (2H, t, $J = 5.6$ Hz), 4.27–4.35 (6H, m), 4.36 (1H, s), 6.46 (1H, s), 7.05–7.13 (3H, m), 7.35 (1H, d, $J = 7.6$ Hz), 7.55–7.57 (2H, m), 7.79 (1H, s), 7.89–7.91 (2H, m); ^{13}C NMR (CDCl_3 , 100 MHz, TMS) δ 14.0, 23.3, 48.2, 48.8, 58.5, 62.3, 110.7, 111.3, 117.8, 119.9, 123.0, 123.1, 123.6, 127.0, 127.6, 129.6, 130.8, 135.9, 145.2, 149.2, 167.7; HRMS (ESI) Calcd. for $\text{C}_{26}\text{H}_{28}\text{N}_3\text{O}_8\text{S}^{1+}$ ($\text{M}^+ + \text{H}$): 542.1592, found: 542.1586.



Compound **2j**: 16 mg, 73% yield; a yellow solid; mp. 65–67 °C; IR (neat) ν 3384, 2961, 2925, 2854, 1728, 1462, 1339, 1259, 1157, 1090, 1068, 1009, 798, 741 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz, TMS) δ 1.34 (6H, t, $J = 7.2$ Hz), 2.96 (2H, t, $J = 5.2$ Hz), 3.56 (2H, t, $J = 5.2$ Hz), 4.10 (2H, s), 4.26–4.34 (4H, m), 4.49 (1H, s), 6.57 (1H, s), 7.07–7.11 (1H, m), 7.16–7.20 (1H, m), 7.25 (1H, d, $J = 7.2$ Hz), 7.38–7.43 (5H, m), 7.69 (1H, s); ^{13}C NMR (CDCl_3 , 100 MHz, TMS) δ 14.0, 23.7, 46.9, 48.9, 57.6, 62.1, 110.9, 112.4, 118.1, 119.8, 123.0, 123.4, 127.0, 127.4, 128.2, 130.5, 131.1, 132.0, 136.2, 138.6, 167.8; HRMS (ESI) Calcd. for $\text{C}_{26}\text{H}_{28}\text{BrN}_2\text{O}_6\text{S}^{1+}$ ($\text{M}^+ + \text{H}$): 575.0846, found: 575.0836.



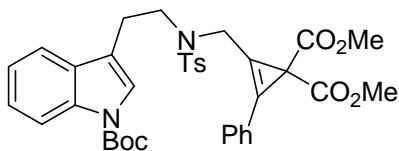
General procedures and spectroscopic data of compounds 3



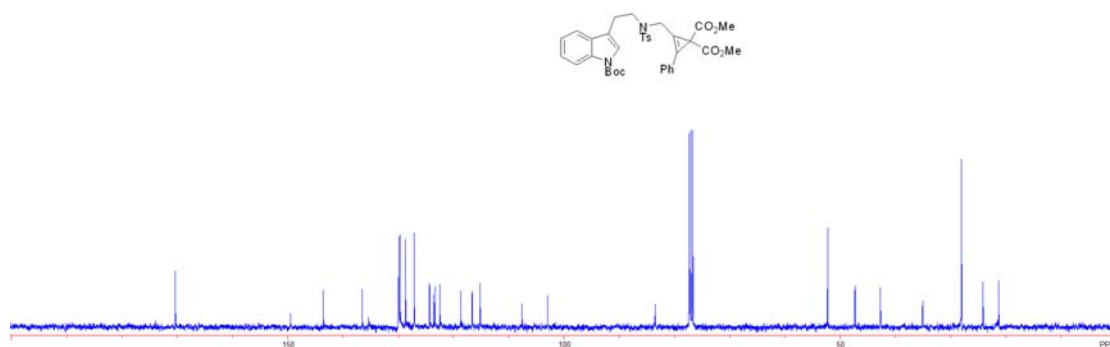
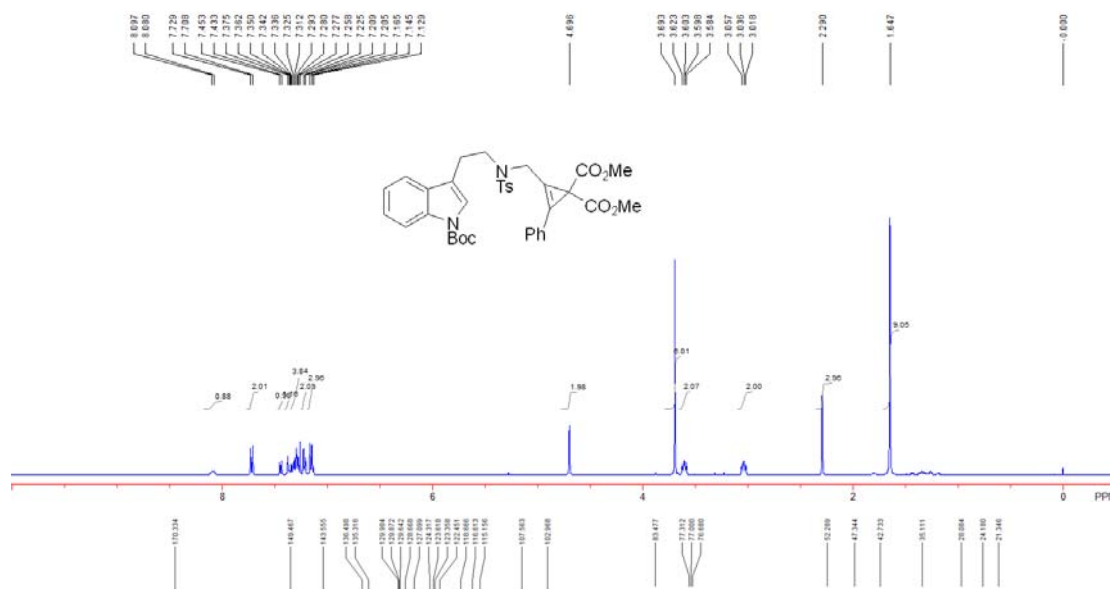
Typical Procedure for the Preparation of S3a. A solution of dimethyl diazomalonate (2.77 g, 17.5 mmol) in dry dichloromethane (2 mL) was added via a syringe pump over 3 hrs to a stirred solution of $\text{Rh}_2(\text{OPiv})_4$ (34 mg, 0.055 mmol) and S2a (2.7 g, 11.0 mmol) in dry dichloromethane (10 mL) at room temperature. After the addition was complete, the reaction mixture was stirred for additional 3 hrs. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography.

Typical Procedure for the Preparation of S4a. A solution of S3a (1.62 g, 4.3 mmol) in dry THF (10 mL) was added tetrabutylammonium fluoride (1.36 g, 4.3 mmol) at room temperature. The reaction mixture was stirred for 2 hrs. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography.

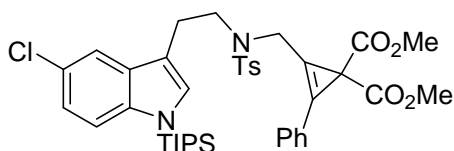
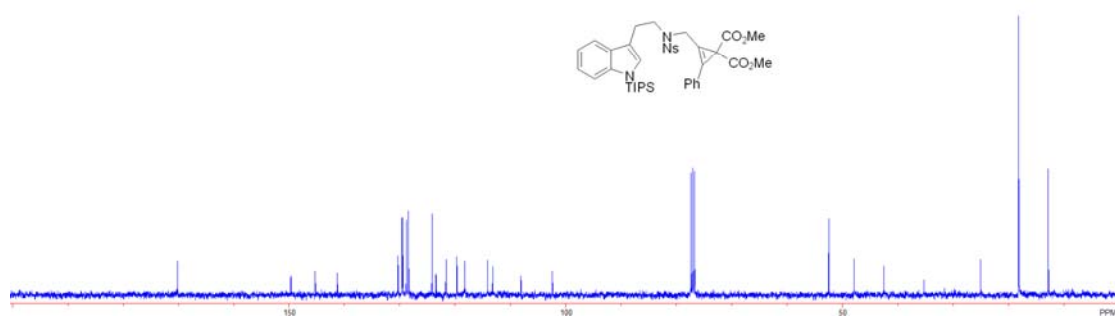
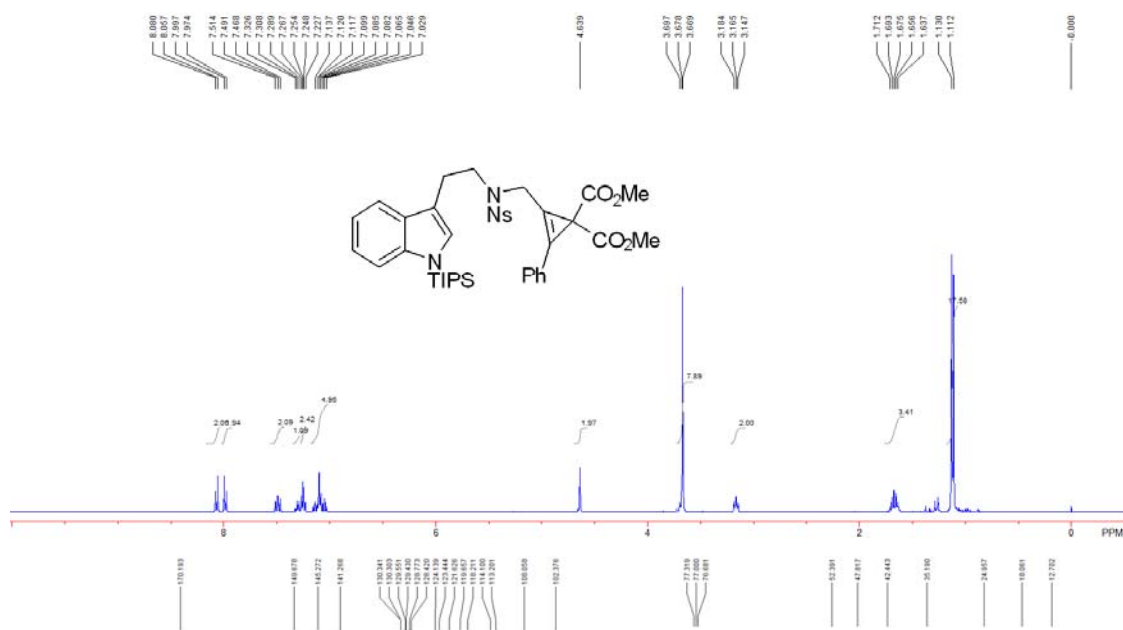
Compound 3a was produced according to the typical Mitsunobu reaction procedure.



Compound **3a'**: 262 mg, 40% yield; a colorless oil; IR (neat) ν 2980.6, 2952.1, 2921.3, 2849.4, 1726.6, 1452.6, 1369.4, 1340.8, 1254.5, 1156.0, 1097.6, 1064.6, 762.2, 748.1 cm^{-1} ; ¹H NMR (CDCl₃, 400 MHz, TMS) δ 1.65 (9H, s), 2.29 (3H, s), 3.04 (2H, t, *J* = 7.2 Hz), 3.58–3.62 (2H, m), 3.69 (6H, s), 4.70 (2H, s), 7.13–7.17 (3H, m), 7.21–7.23 (2H, m), 7.26–7.35 (4H, m), 7.38 (1H, s), 7.44 (1H, d, *J* = 8.0 Hz), 7.72 (2H, d, *J* = 8.0 Hz), 8.09 (1H, d, *J* = 6.8 Hz); ¹³C NMR (CDCl₃, 100 MHz, TMS) δ 21.3, 24.2, 28.1, 35.1, 42.7, 47.3, 52.3, 83.5, 103.0, 107.6, 115.2, 116.6, 118.7, 122.5, 123.4, 123.6, 124.3, 127.1, 128.7, 129.6, 129.9, 130.0, 135.3, 136.5, 143.6, 149.5, 170.3; HRMS (ESI) Calcd. for C₃₆H₄₂N₃O₈S⁺ (M⁺+NH₄): 676.2687, found: 676.2694.

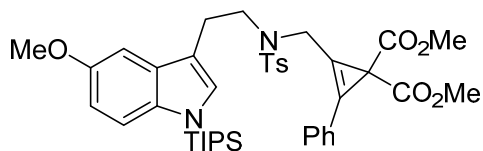
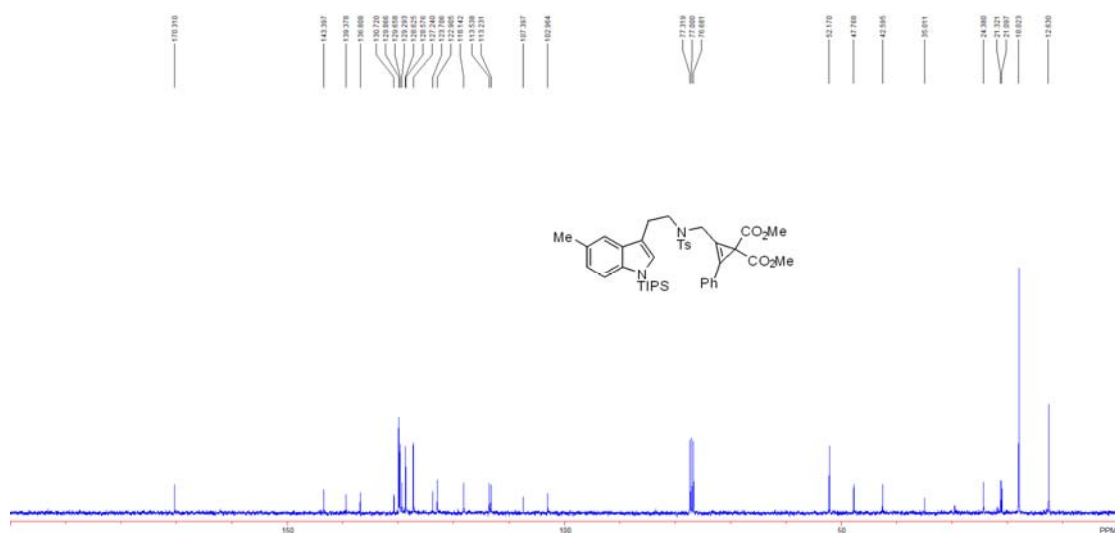
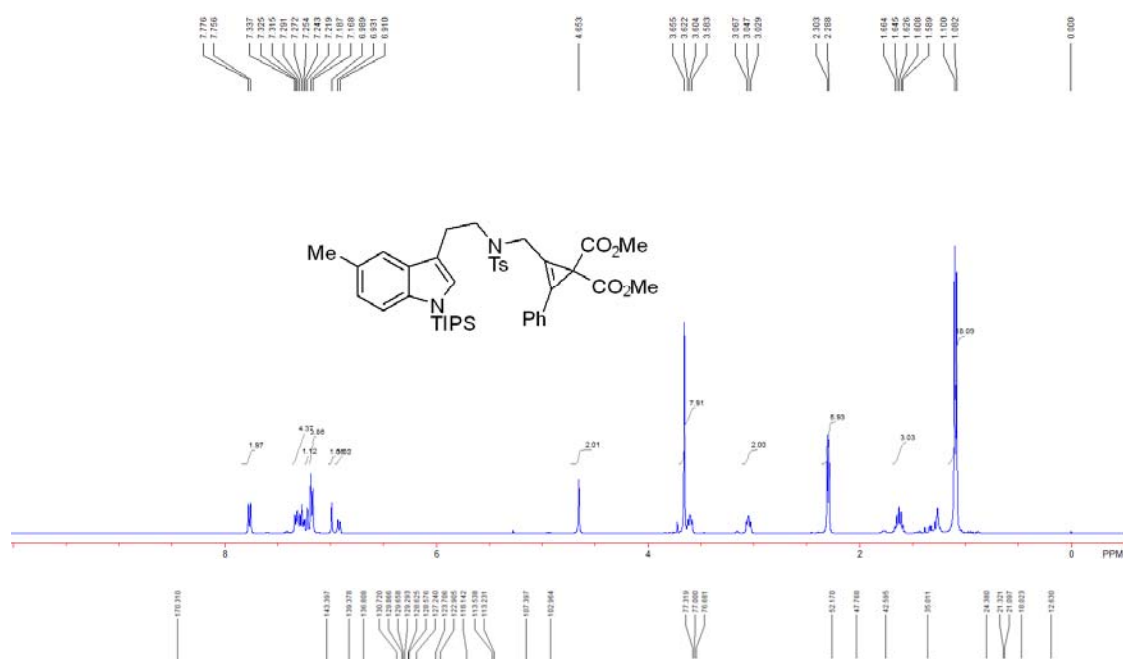


δ 1.12 (18H, d, $J = 7.2$ Hz), 1.64–1.71 (3H, m), 3.17 (2H, t, $J = 7.6$ Hz), 3.67 (6H, s), 3.68 (2H, t, $J = 7.6$ Hz), 4.64 (2H, s), 7.03–7.14 (5H, m), 7.23–7.27 (2H, m), 7.29–7.33 (1H, m), 7.49 (2H, dd, $J_1 = J_2 = 9.2$ Hz), 7.99 (2H, d, $J = 9.2$ Hz), 8.07 (2H, d, $J = 9.2$ Hz); ^{13}C NMR (CDCl_3 , 100 MHz, TMS) δ 12.7, 18.1, 25.0, 35.2, 42.4, 47.8, 52.4, 102.4, 108.1, 113.2, 114.1, 118.2, 119.7, 121.6, 123.4, 124.1, 128.4, 128.8, 129.4, 129.6, 130.30, 130.34, 141.3, 145.3, 149.7, 170.2; HRMS (ESI) Calcd. for $\text{C}_{39}\text{H}_{51}\text{N}_4\text{O}_8\text{SSi}^+$ ($\text{M}^+ + \text{NH}_4$): 763.3191, found: 763.3187.



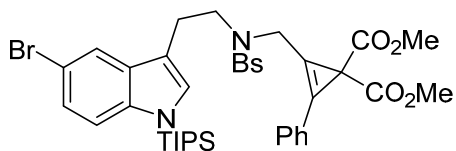
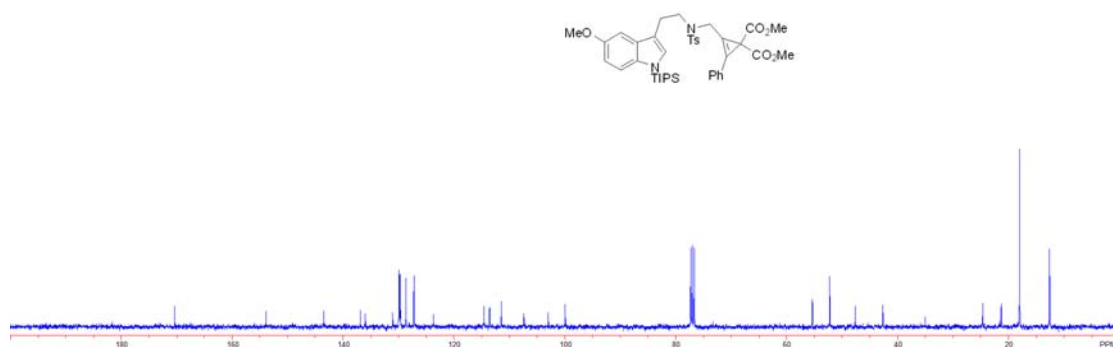
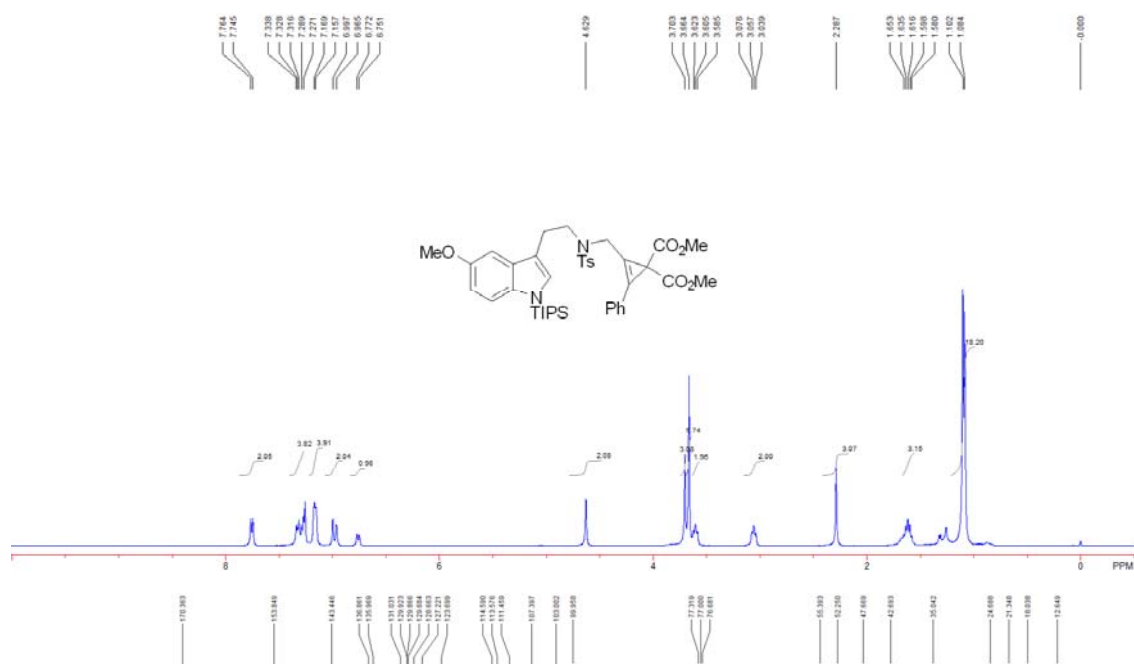
Compound **3d**: 152 mg, 20% yield; a colorless oil; IR (neat) ν 2950.1, 2925.7, 2868.2, 1731.4, 1442.1, 1349.3, 1283.7, 1259.0, 1159.1, 1134.3, 1092.2, 1065.9, 762.4, 691.2 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz, TMS) δ 1.09 (18H, d, $J = 7.2$ Hz), 1.59–1.66 (3H, m), 2.30 (3H, s), 3.03 (2H, t, $J = 7.6$ Hz), 3.58 (2H, t, $J = 7.6$ Hz), 3.68

35.0, 42.6, 47.8, 52.2, 103.0, 107.4, 113.2, 113.5, 118.1, 122.9, 123.7, 127.2, 128.58, 128.63, 129.3, 129.7, 129.9, 130.7, 136.8, 139.4, 143.4, 170.3; HRMS (ESI) Calcd. for $C_{41}H_{56}N_3O_6SSi^+$ ($M^+ + NH_4$): 746.3654, found: 746.3649.



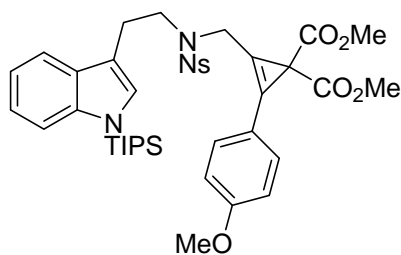
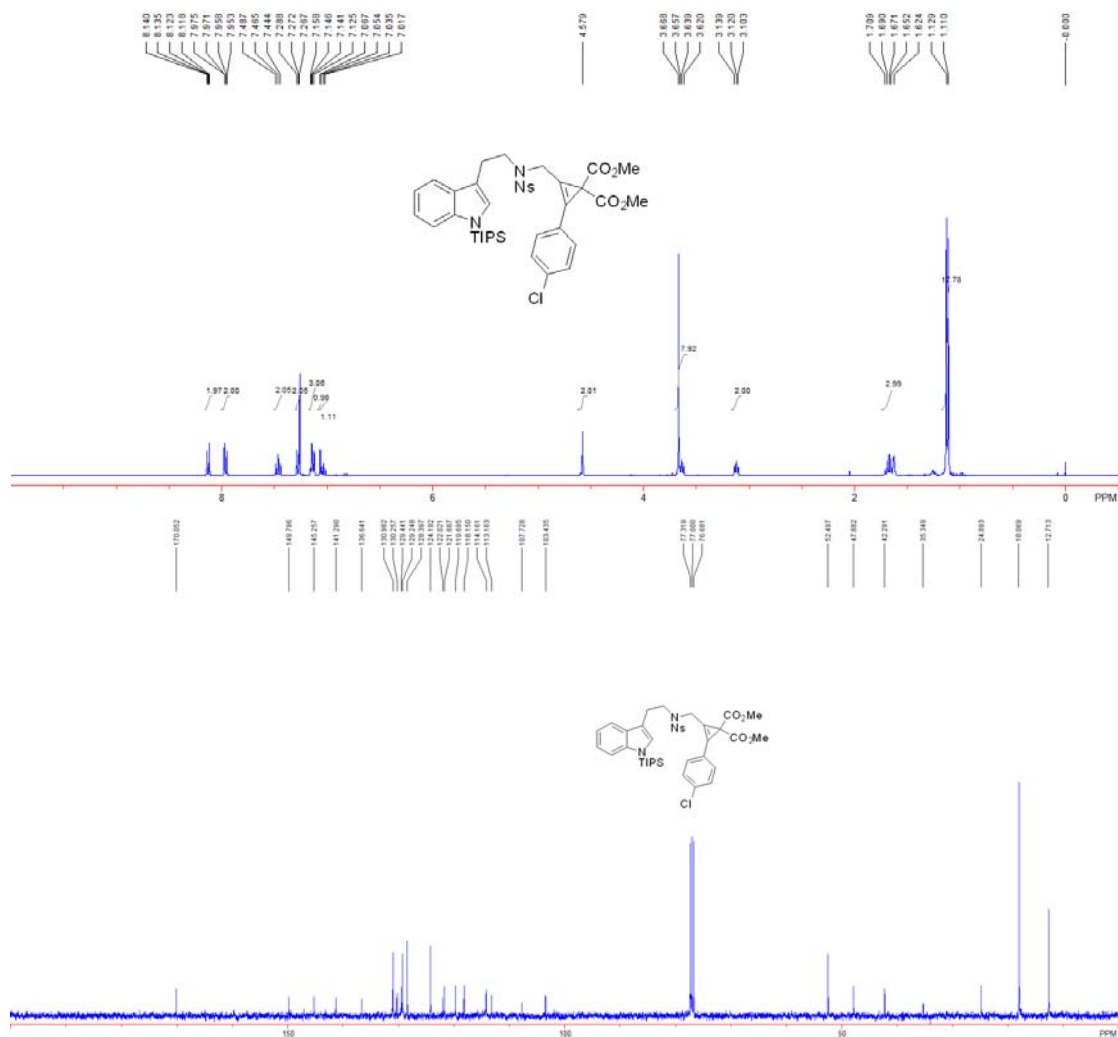
Compound **3f**: 134 mg, 18% yield; a colorless oil; IR (neat) ν 2949.2, 2867.7, 1727.5, 1479.1, 1448.5, 1435.1, 1347.0, 1271.3, 1228.9, 1156.6, 1095.4, 1065.6, 1034.5, 969.3, 882.7 cm^{-1} ; 1H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.09 (18H, d, $J = 7.2$ Hz), 1.58–1.65 (3H, m), 2.29 (3H, s), 3.06 (2H, t, $J = 7.6$ Hz), 3.61 (2H, t, $J = 7.6$ Hz), 3.66 (6H, s), 3.70 (3H, s), 4.63 (2H, s), 6.76 (1H, d, $J = 8.4$ Hz), 6.97–7.00 (2H, m), 7.16–7.17 (4H, m), 7.27–7.34 (4H, m), 7.75 (2H, d, $J = 7.6$ Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 12.6, 18.0, 21.3, 24.7, 35.0,

42.7, 47.7, 52.3, 55.4, 100.0, 103.0, 107.4, 111.5, 113.6, 114.6, 123.7, 127.2, 128.7, 129.7, 129.87, 129.92, 131.0, 136.0, 136.9, 143.4, 153.8, 170.4; HRMS (ESI) Calcd. for $C_{41}H_{56}N_3O_7SSi^+$ ($M^+ + NH_4$): 762.3603, found: 762.3602.



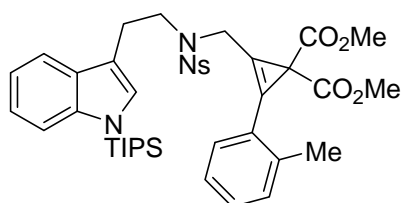
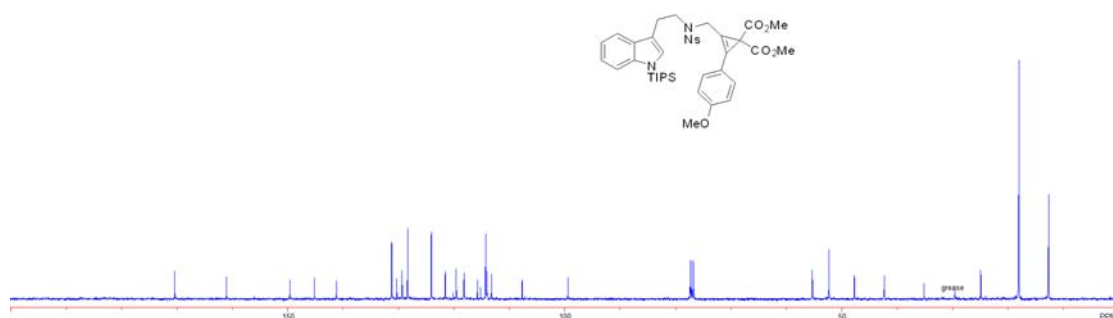
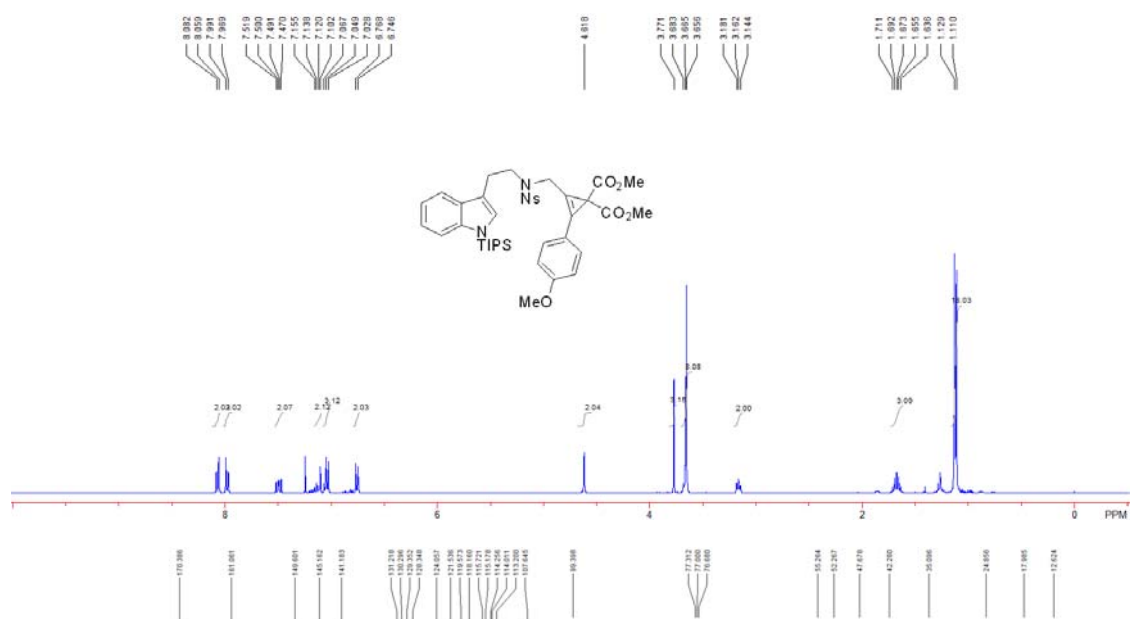
Compound **3g**: 64 mg, 32% yield; a colorless oil; IR (neat) ν 2955.0, 2922.3, 2851.8, 1733.7, 1717.3, 1558.1, 1541.2, 1507.6, 1457.3, 1375.4, 1160.5, 1089.2, 1016.9, 883.2, 749.7 cm^{-1} ; 1H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.10 (18H, d, $J = 7.2$ Hz), 1.59–1.67 (3H, m), 3.06 (2H, t, $J = 7.6$ Hz), 3.59 (2H, t, $J = 7.6$ Hz), 3.69 (6H, s), 4.62 (2H, s), 7.08 (1H, s), 7.19 (3H, d, $J = 7.6$ Hz), 7.31–7.39 (4H, m), 7.51 (2H, d, $J = 8.0$ Hz), 7.57 (1H, s), 7.73 (2H, d, $J = 8.0$ Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 12.6, 18.0, 24.3, 35.1, 42.5, 47.6, 52.4, 102.5,

118.2, 119.7, 121.7, 122.0, 124.2, 128.4, 129.2, 129.4, 130.3, 131.0, 136.6, 141.3, 145.3, 149.8, 170.1; HRMS (ESI) Calcd. for C₃₉H₅₀ClN₄O₈SSi⁺ (M⁺+NH₄): 797.2802, found: 797.2801.



Compound **3i**: 286 mg, 54% yield; a colorless oil; IR (neat) ν 2951.6, 2869.2, 1730.5, 1605.1, 1530.8, 1509.5, 1451.6, 1349.5, 1284.4, 1254.3, 1163.5, 1142.8, 1066.6, 1016.2, 883.0, 740.5 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz, TMS) δ 1.12 (18H, d, J = 7.6 Hz), 1.64–1.71 (3H, m), 3.16 (2H, t, J = 7.6 Hz), 3.66 (6H, s), 3.67 (2H, t, J = 7.6 Hz), 3.77 (3H, s), 4.62 (2H, s), 6.76 (2H, d, J = 8.8 Hz), 7.03–7.07 (3H, m), 7.10–7.16 (2H, m), 7.48 (1H, d, J = 8.4 Hz), 7.51 (1H, d, J = 7.6 Hz), 7.98 (2H, d, J = 8.8 Hz), 8.07 (2H, d, J = 8.8 Hz); ¹³C NMR (CDCl₃, 100 MHz, TMS) δ 12.6, 18.0, 24.9, 35.1, 42.3, 47.7, 52.3, 55.3, 99.4, 107.6, 113.2, 114.0, 114.3, 115.2, 115.7, 118.2,

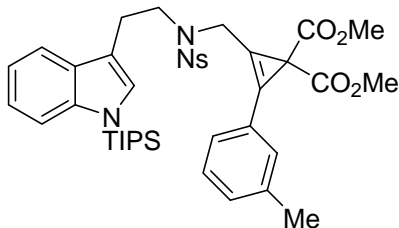
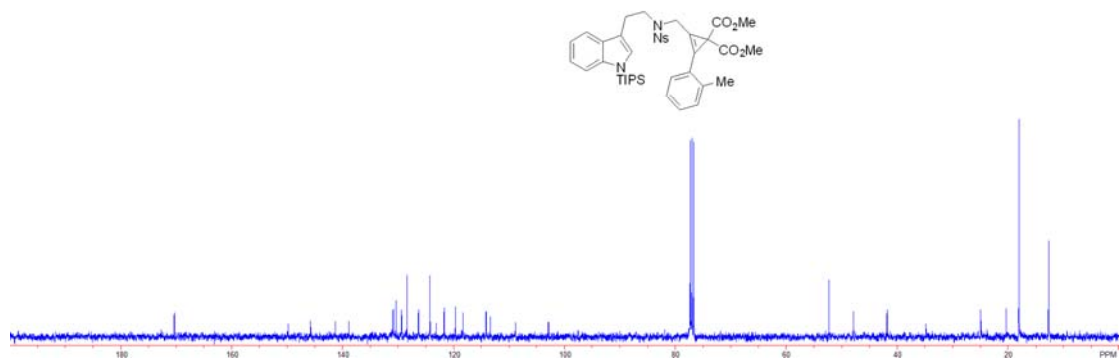
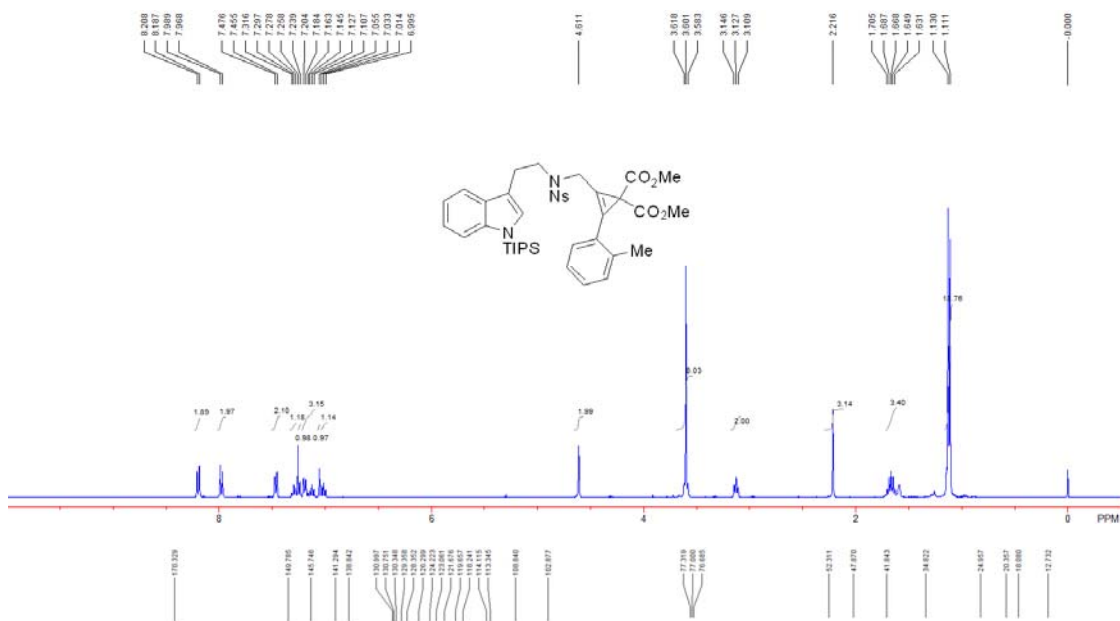
119.6, 121.5, 124.1, 128.3, 129.4, 130.3, 131.2, 141.2, 145.2, 149.6, 161.1, 170.4; HRMS (ESI) Calcd. for $C_{40}H_{53}N_4O_9SSi^+$ ($M^+ + NH_4$): 793.3297, found: 793.3297.



Compound **3j**: 368 mg, 81% yield; a colorless oil; IR (neat) ν 2951.4, 2868.8, 1735.5, 1720.0, 1606.9, 1536.1, 1450.6, 1351.5, 1279.6, 1255.1, 1162.1, 1136.2, 1057.5, 962.0, 738.8 cm^{-1} ; 1H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.12 (18H, d, $J = 7.6$ Hz), 1.63–1.71 (3H, m), 2.22 (3H, s), 3.13 (2H, t, $J = 7.2$ Hz), 3.60 (2H, t, $J = 7.2$ Hz), 3.61 (6H, s), 4.61 (2H, s), 7.01 (1H, dd, $J_1 = J_2 = 7.6$ Hz), 7.06 (1H, s), 7.11–7.20 (3H, m), 7.25 (1H, d, $J = 7.6$ Hz), 7.30 (1H, dd, $J_1 = J_2 = 7.6$ Hz), 7.47 (2H, d, $J = 8.4$ Hz), 7.98 (2H, d, $J = 8.4$ Hz), 8.20 (2H, d, $J = 8.4$ Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 12.7, 18.1, 20.4, 25.0, 34.8, 41.8, 47.9, 52.3, 102.9, 108.8, 113.3, 114.1,

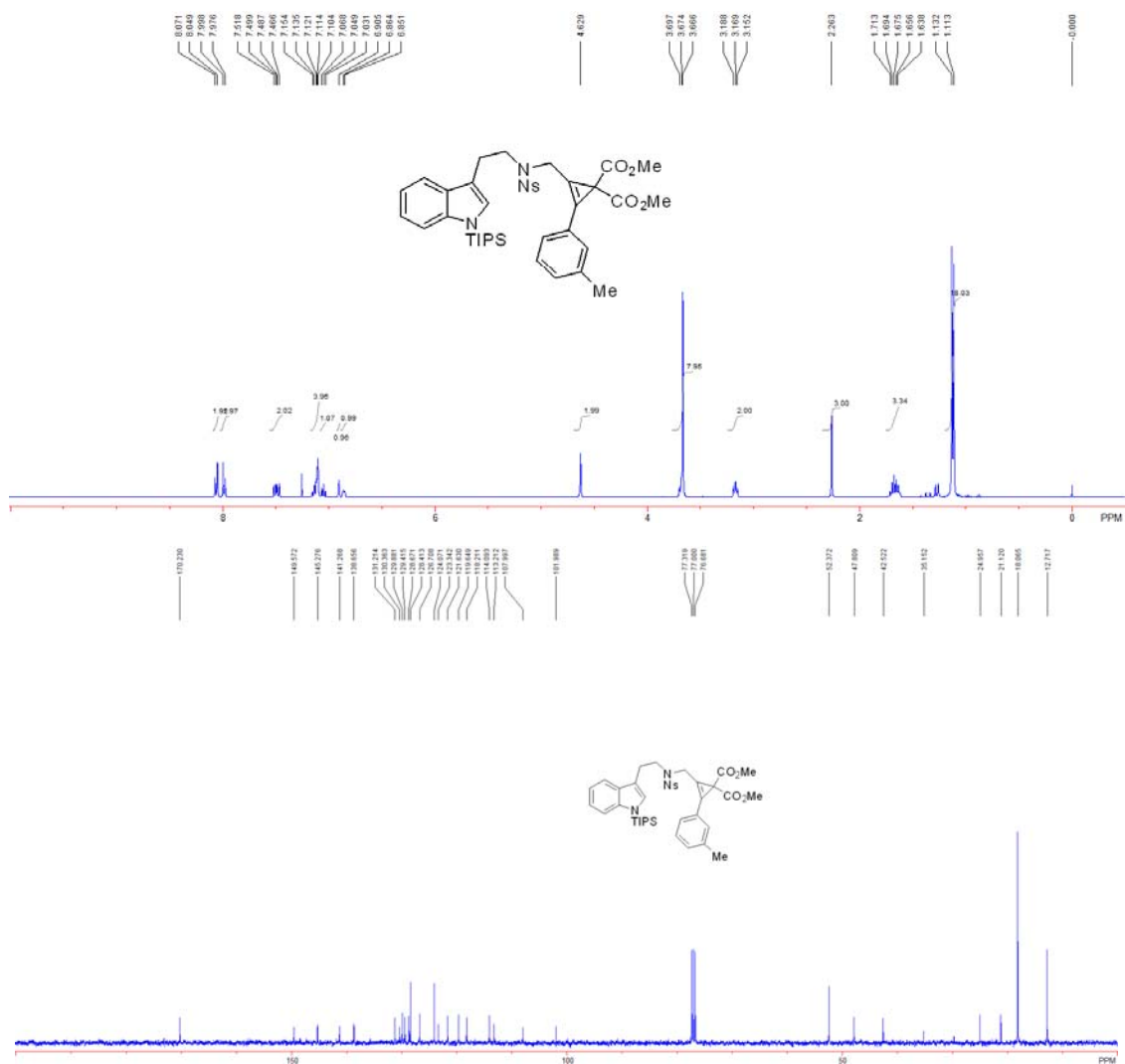
118.2, 119.7, 121.7, 123.1, 124.2, 126.3, 128.4, 129.4, 130.3, 130.8, 131.0, 138.8, 141.3, 145.7, 149.8, 170.3;

HRMS (ESI) Calcd. for $C_{40}H_{53}N_4O_8SSi^+$ ($M^+ + NH_4$): 777.3348, found: 777.3346.



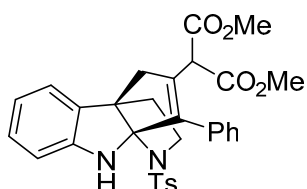
Compound **3k**: 350 mg, 77% yield; a colorless oil; IR (neat) ν 2949.2, 2867.0, 1736.8, 1607.1, 1536.7, 1453.6, 1351.4, 1288.2, 1163.6, 1138.5, 1089.0, 1067.1, 1014.9, 968.4, 741.0 cm^{-1} ; 1H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.12 (18H, d, $J = 7.6$ Hz), 1.64–1.71 (3H, m), 2.26 (3H, s), 3.17 (2H, t, $J = 7.2$ Hz), 3.67 (6H, s), 3.68 (2H, t, $J = 7.2$ Hz), 4.63 (2H, s), 6.86 (1H, d, $J = 5.2$ Hz), 6.91 (1H, s), 7.05 (1H, dd, $J_1 = J_2 = 7.6$ Hz), 7.10–7.15 (4H, m), 7.47 (1H, d, $J = 8.4$ Hz), 7.51 (1H, d, $J = 7.6$ Hz), 7.99 (2H, d, $J = 8.8$ Hz), 8.06 (2H, d, $J = 8.8$ Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 12.7, 18.1, 21.1, 25.0, 35.2, 42.5, 47.8, 52.4, 102.0, 108.0, 113.2, 114.1,

118.2, 119.6, 121.6, 123.3, 124.1, 126.7, 128.4, 128.7, 129.4, 129.9, 130.4, 131.2, 138.7, 141.3, 145.3, 149.6, 170.2; HRMS (ESI) Calcd. for $C_{40}H_{53}N_4O_8SSi^+$ ($M^+ + NH_4$): 777.3348, found: 777.3346.

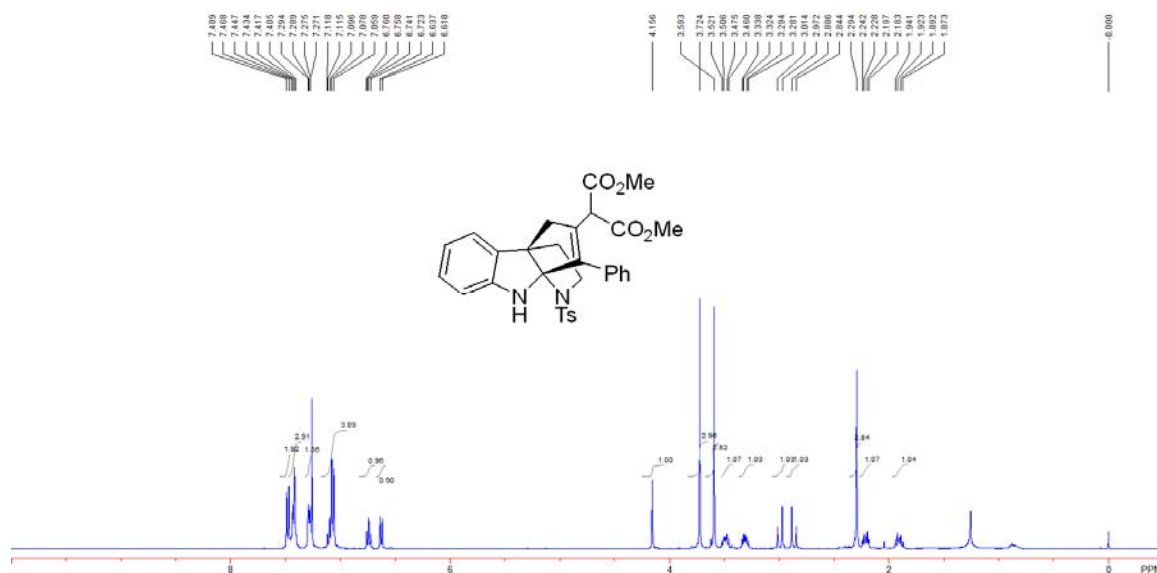


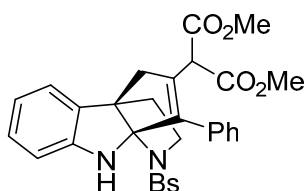
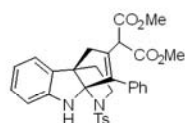
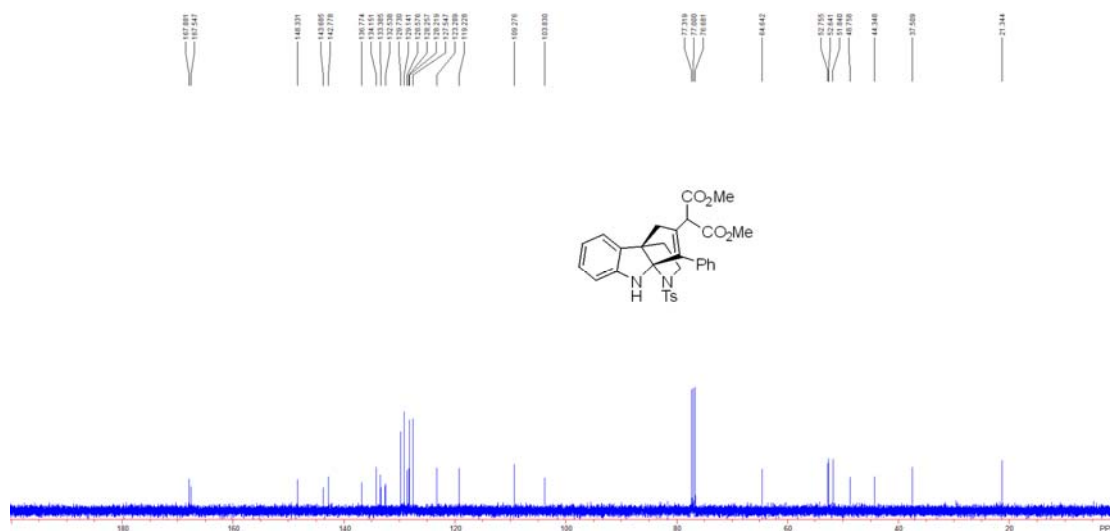
General Procedure and Spectroscopic Data of the Products 4

A solution of compound **3** (0.1 mmol) was stirred at ambient temperature in the mixed solvent of TFA and DCM (1:1). Then 10 mol% of HOTf was added into the reaction system. Once the reaction was complete, the solvent was removed under reduced pressure and the residue was chromatographed on silica gel (elution with petroleum ether/ethyl acetate = 5/1) to provide the corresponding product **4**.

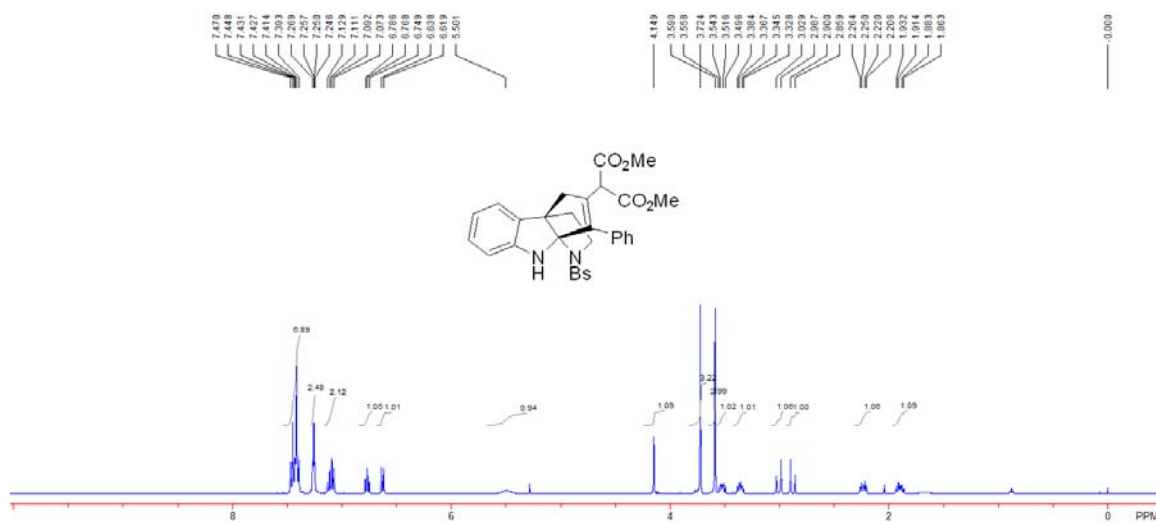


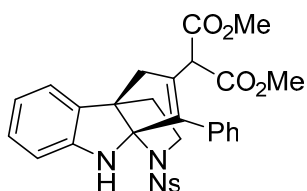
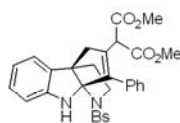
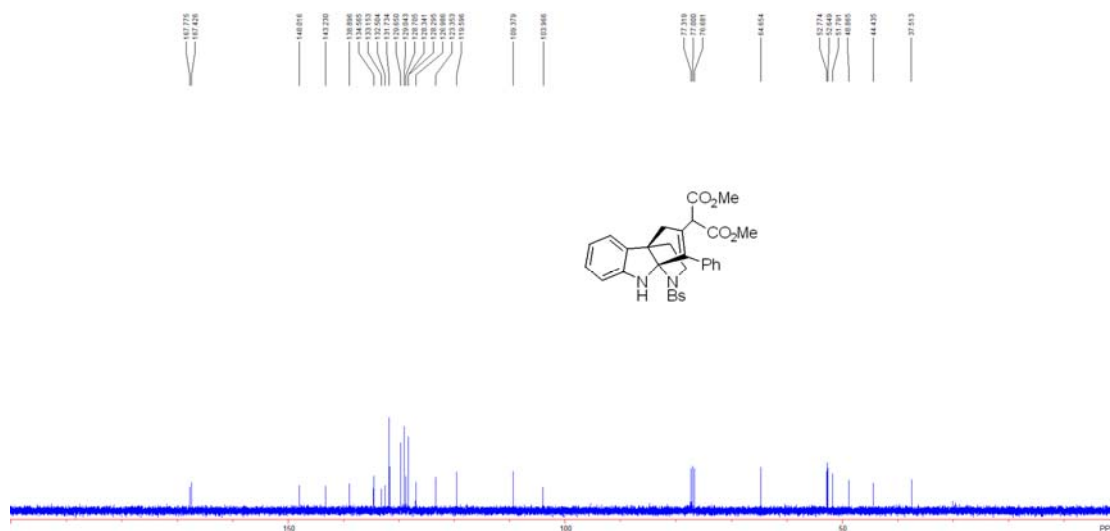
Compound **4a**: 45 mg, 81% yield; a green solid; mp. 92–94 °C; IR (neat) ν 2953.3, 2922.8, 2852.9, 1734.5, 1609.9, 1484.5, 1465.3, 1435.4, 1330.8, 1197.6, 1150.5, 1087.5, 1029.5, 814.9, 702.8 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz, TMS) δ 1.87–1.94 (1H, m), 2.18–2.24 (1H, m), 2.29 (3H, s), 2.87 (1H, d, $J = 16.8$ Hz), 2.99 (1H, d, $J = 16.8$ Hz), 3.28–3.34 (1H, m), 3.46–3.52 (1H, m), 3.59 (3H, s), 3.72 (3H, s), 4.16 (1H, s), 6.63 (1H, d, $J = 7.6$ Hz), 6.72–6.76 (1H, m), 7.06–7.12 (4H, m), 7.28 (2H, dd, $J = 1.6, 7.2$ Hz), 7.41–7.45 (3H, m), 7.48 (2H, d, $J = 8.4$ Hz); ^{13}C NMR (CDCl_3 , 100 MHz, TMS) δ 21.3, 37.5, 44.3, 48.8, 51.8, 52.6, 52.8, 64.6, 103.8, 109.3, 119.2, 123.3, 127.5, 128.2, 128.3, 128.6, 129.1, 129.7, 132.5, 133.4, 134.2, 136.8, 142.8, 143.7, 148.3, 167.5, 167.9; HRMS (ESI) Calcd. for $\text{C}_{31}\text{H}_{31}\text{N}_2\text{O}_6\text{S}^+$ (M^++H): 559.1897, found: 559.1902.



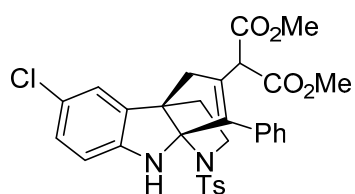
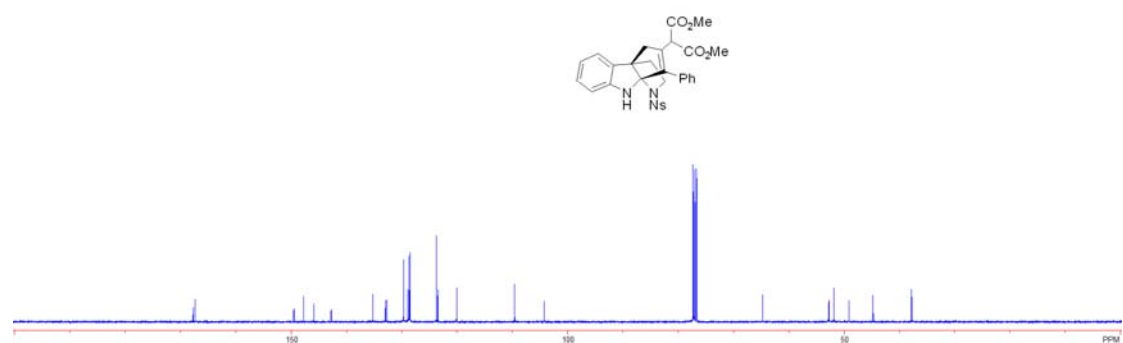
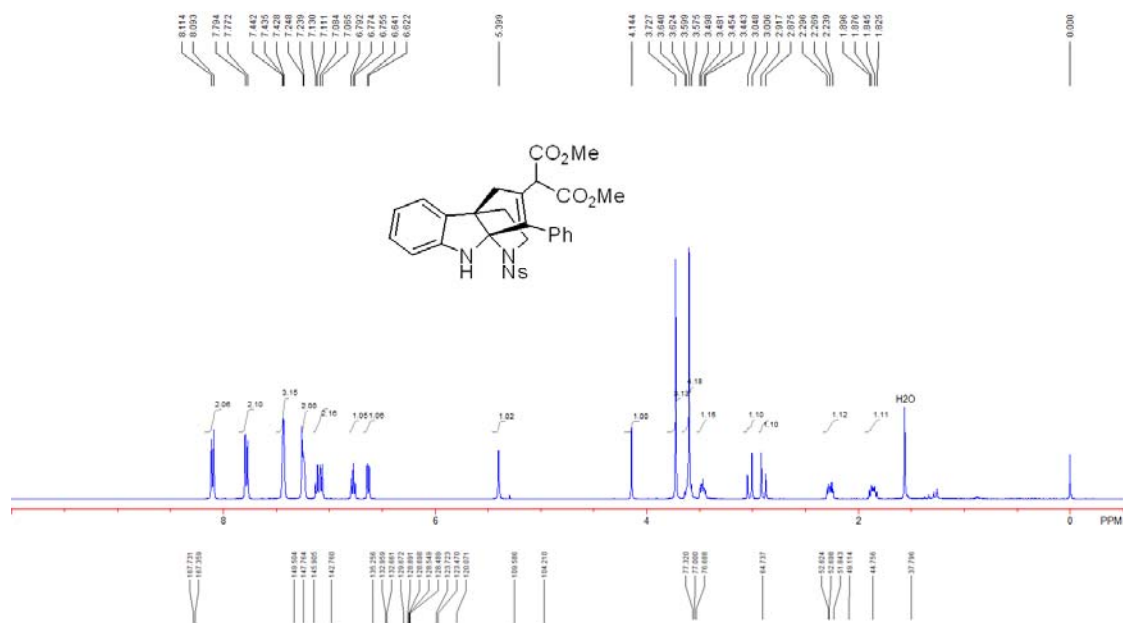


Compound **4b**: 52 mg, 84% yield; a green solid; mp. 98–100 °C; IR (neat) ν 3406.8, 2953.6, 2924.2, 2852.3, 1733.2, 1609.9, 1574.2, 1484.2, 1465.4, 1435.1, 1332.2, 1265.7, 1195.9, 1149.7, 1084.8, 1068.0, 1029.0, 1008.2, 735.1, 701.3 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz, TMS) δ 1.87–1.93 (1H, m), 2.21–2.26 (1H, m), 2.88 (1H, d, $J = 16.8$ Hz), 3.01 (1H, d, $J = 16.8$ Hz), 3.33–3.38 (1H, m), 3.50–3.56 (1H, m), 3.59 (3H, s), 3.72 (3H, s), 4.15 (1H, s), 5.50 (1H, s), 6.63 (1H, d, $J = 7.6$ Hz), 6.77 (1H, dd, $J_1 = J_2 = 7.2$ Hz), 7.07–7.13 (2H, m), 7.25–7.27 (2H, m), 7.39–7.47 (7H, m); ^{13}C NMR (CDCl_3 , 100 MHz, TMS) δ 37.5, 44.4, 48.9, 51.8, 52.6, 52.8, 64.7, 104.0, 109.4, 119.6, 123.4, 127.0, 128.30, 128.34, 128.7, 129.0, 129.7, 131.7, 132.5, 133.2, 134.6, 138.9, 143.2, 148.0, 167.4, 167.8; HRMS (ESI) Calcd. for $\text{C}_{30}\text{H}_{28}\text{BrN}_2\text{O}_6\text{S}^+$ ($\text{M}^+ + \text{H}$): 623.0846, found: 623.0845.

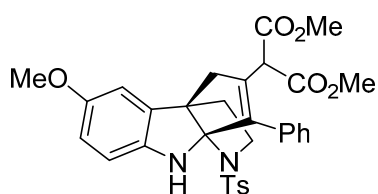
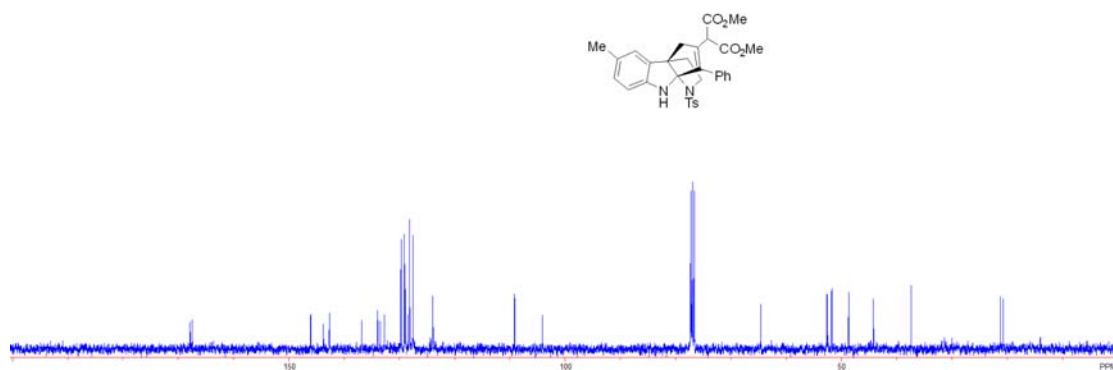
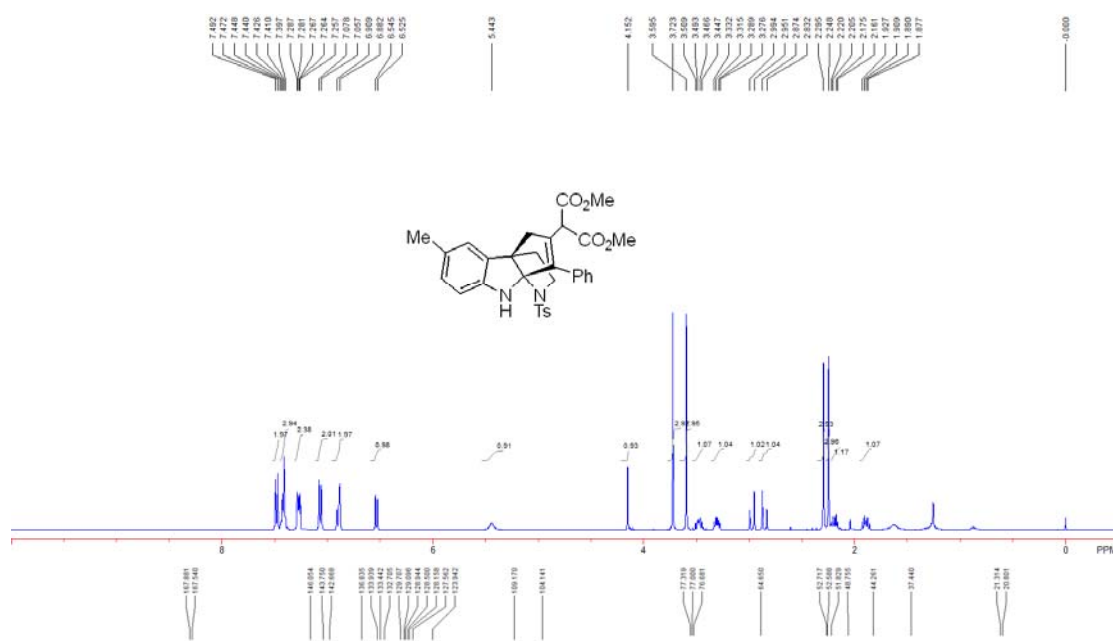




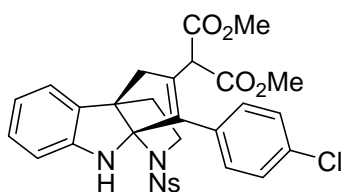
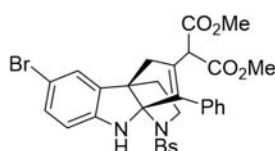
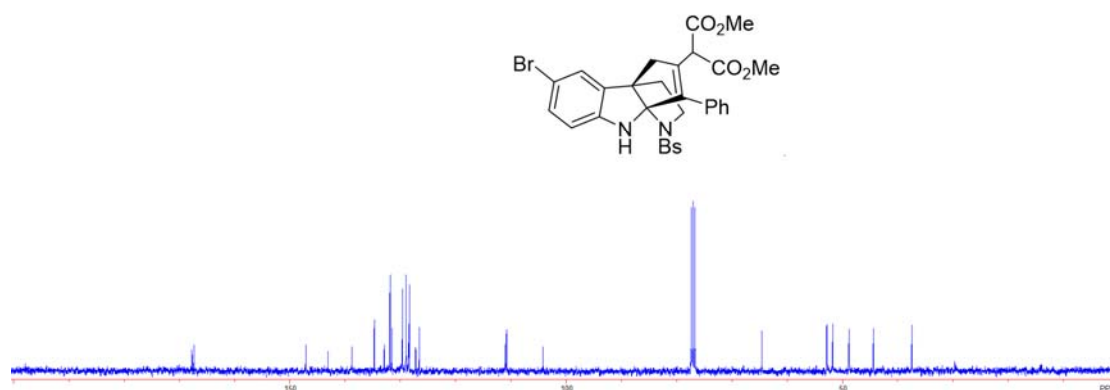
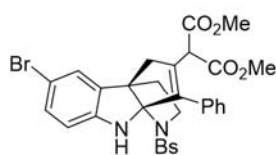
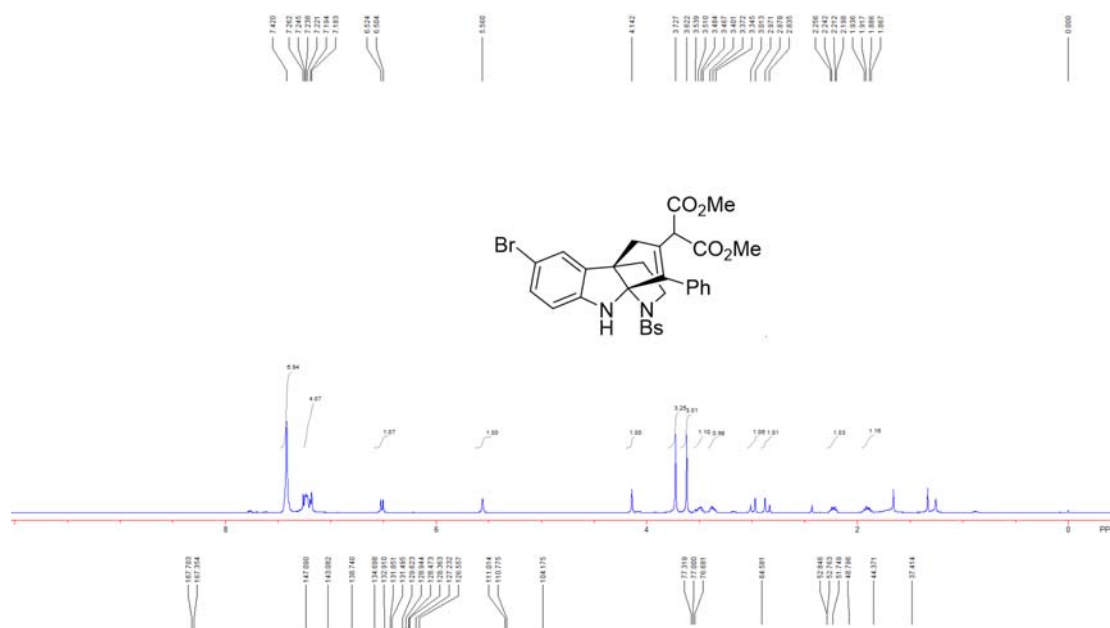
Compound **4c**: 44 mg, 99% yield; a green solid; mp. 105–107 °C; IR (neat) ν 3402.9, 2953.6, 1732.6, 1608.4, 1528.4, 1484.3, 1465.6, 1435.5, 1348.0, 1307.9, 1232.6, 1197.0, 1152.0, 1117.1, 1085.9, 1044.3, 909.8, 732.4 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz, TMS) δ 1.83–1.90 (1H, m), 2.24–2.30 (1H, m), 2.90 (1H, d, $J = 16.8$ Hz), 3.03 (1H, d, $J = 16.8$ Hz), 3.44–3.50 (1H, m), 3.58–3.64 (1H, m), 3.60 (3H, s), 3.73 (3H, s), 4.14 (1H, s), 5.40 (1H, s), 6.63 (1H, d, $J = 7.6$ Hz), 6.77 (1H, dd, $J_1 = J_2 = 7.2$ Hz), 7.07–7.13 (2H, m), 7.24–7.25 (2H, m), 7.43–7.44 (3H, m), 7.78 (2H, d, $J = 8.4$ Hz), 8.10 (2H, d, $J = 8.4$ Hz); ^{13}C NMR (CDCl_3 , 100 MHz, TMS) δ 37.8, 44.8, 49.1, 51.8, 52.7, 52.8, 64.7, 104.2, 109.6, 120.1, 123.5, 123.7, 128.49, 128.55, 128.7, 128.9, 129.7, 132.7, 133.0, 135.3, 142.8, 145.9, 147.8, 149.5, 167.4, 167.7; HRMS (ESI) Calcd. for $\text{C}_{30}\text{H}_{38}\text{N}_3\text{O}_8\text{S}^+$ ($\text{M}^+\text{+H}$): 590.1592, found: 590.1590.



Compound **4d**: 37 mg, 62% yield; a yellow solid; mp. 96–98 °C; IR (neat) ν 3404.9, 2953.1, 2925.1, 2853.8, 1934.8, 1479.0, 1434.2, 1329.9, 1270.0, 1196.5, 1151.6, 1087.2, 1029.8, 705.4, 673.1 cm^{-1} ; ¹H NMR (CDCl₃, 400 MHz, TMS) δ 1.88–1.92 (1H, m), 2.19–2.23 (1H, m), 2.31 (3H, s), 2.84 (1H, d, $J = 16.4$ Hz), 2.98 (1H, d, $J = 16.4$ Hz), 3.31–3.34 (1H, m), 3.44–3.50 (1H, m), 3.62 (3H, s), 3.73 (3H, s), 4.16 (1H, s), 5.60 (1H, s), 6.54 (1H, d, $J = 8.0$ Hz), 7.02–7.10 (4H, m), 7.26 (2H, s), 7.42–7.46 (5H, m); ¹³C NMR (CDCl₃, 100 MHz, TMS) δ 21.4, 37.4, 44.3, 48.7, 51.8, 52.7, 52.8, 64.5, 104.1, 110.1, 123.6, 127.5, 128.3, 128.4, 128.5, 129.2, 129.7, 133.1, 134.2, 136.6, 143.0, 143.5, 146.9, 167.4, 167.8; HRMS (ESI) Calcd. for C₃₁H₃₀ClN₂O₆S⁺ (M⁺+H): 593.1508, found: 593.1510.

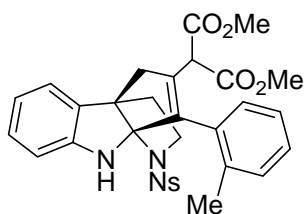
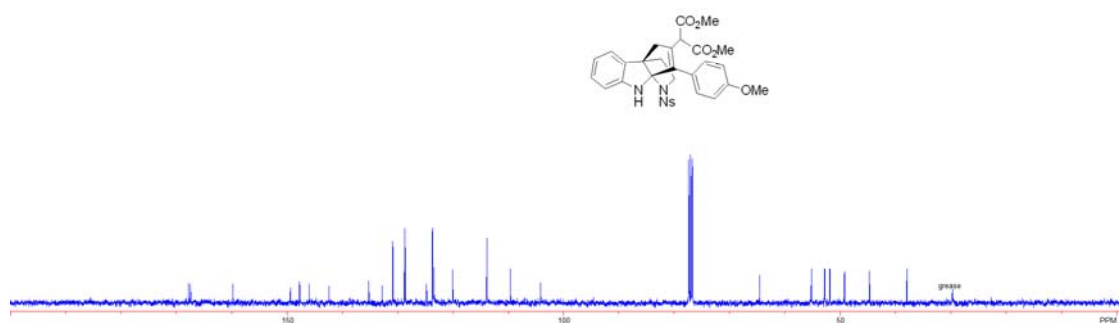
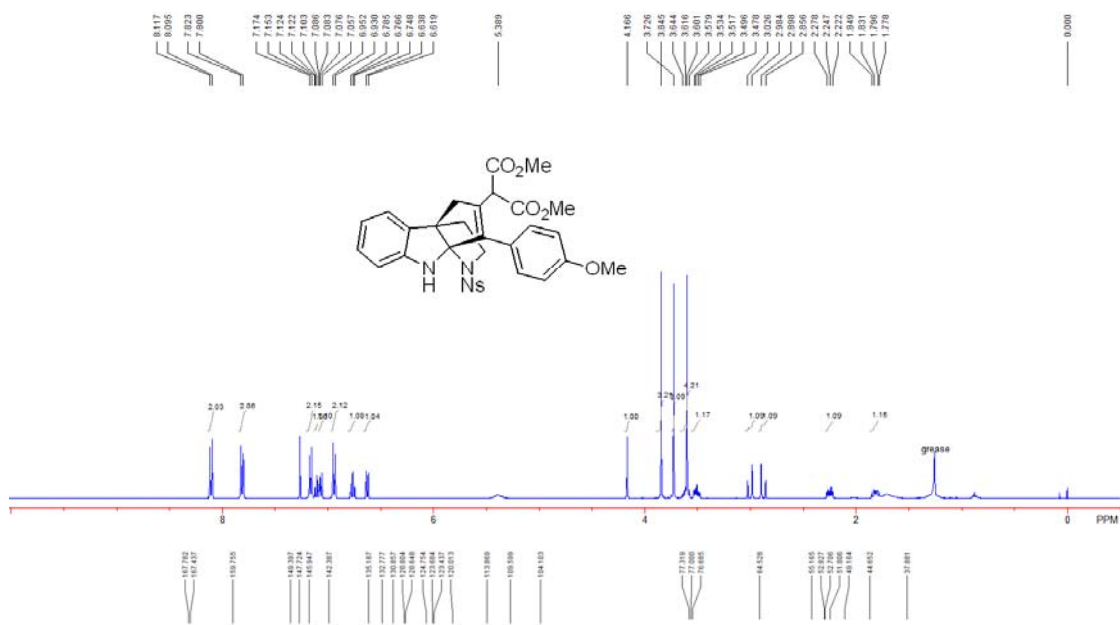


Compound **4f**: 33 mg, 84% yield; a yellow solid; mp. 110–112 °C; IR (neat) ν 2953.9, 2921.6, 2851.3, 1735.5, 1490.8, 1462.8, 1435.7, 1330.1, 1152.2, 1028.8, 811.6, 675.0 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz, TMS) δ 1.88–1.94 (1H, m), 2.18–2.22 (1H, m), 2.30 (3H, s), 2.85 (1H, d, $J = 16.8$ Hz), 2.97 (1H, d, $J = 16.8$ Hz), 3.28–3.32 (1H, m), 3.45–3.51 (1H, m), 3.61 (3H, s), 3.73 (3H, s), 3.74 (3H, s), 4.16 (1H, s), 6.54–6.57 (1H, m), 6.66–6.68 (2H, m), 7.07 (2H, d, $J = 8.0$ Hz), 7.28–7.29 (2H, m), 7.41–7.43 (3H, m), 7.48 (2H, d, $J = 8.0$ Hz); ^{13}C NMR (CDCl_3 , 100 MHz, TMS) δ 21.3, 37.3, 44.1, 48.8, 51.8, 52.6, 52.7, 55.9, 65.0, 104.5, 109.91, 110.00, 113.5, 127.6, 128.18, 128.23, 129.1, 129.7, 133.4, 133.8, 136.8, 142.4, 142.7, 143.8, 153.7, 167.5, 167.9; HRMS (ESI) Calcd. for $\text{C}_{32}\text{H}_{33}\text{N}_2\text{O}_7\text{S}^+$ (M^++H): 589.2003, found: 589.2005.



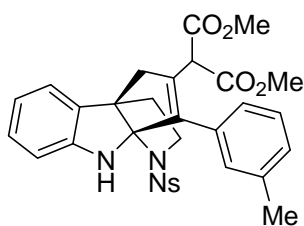
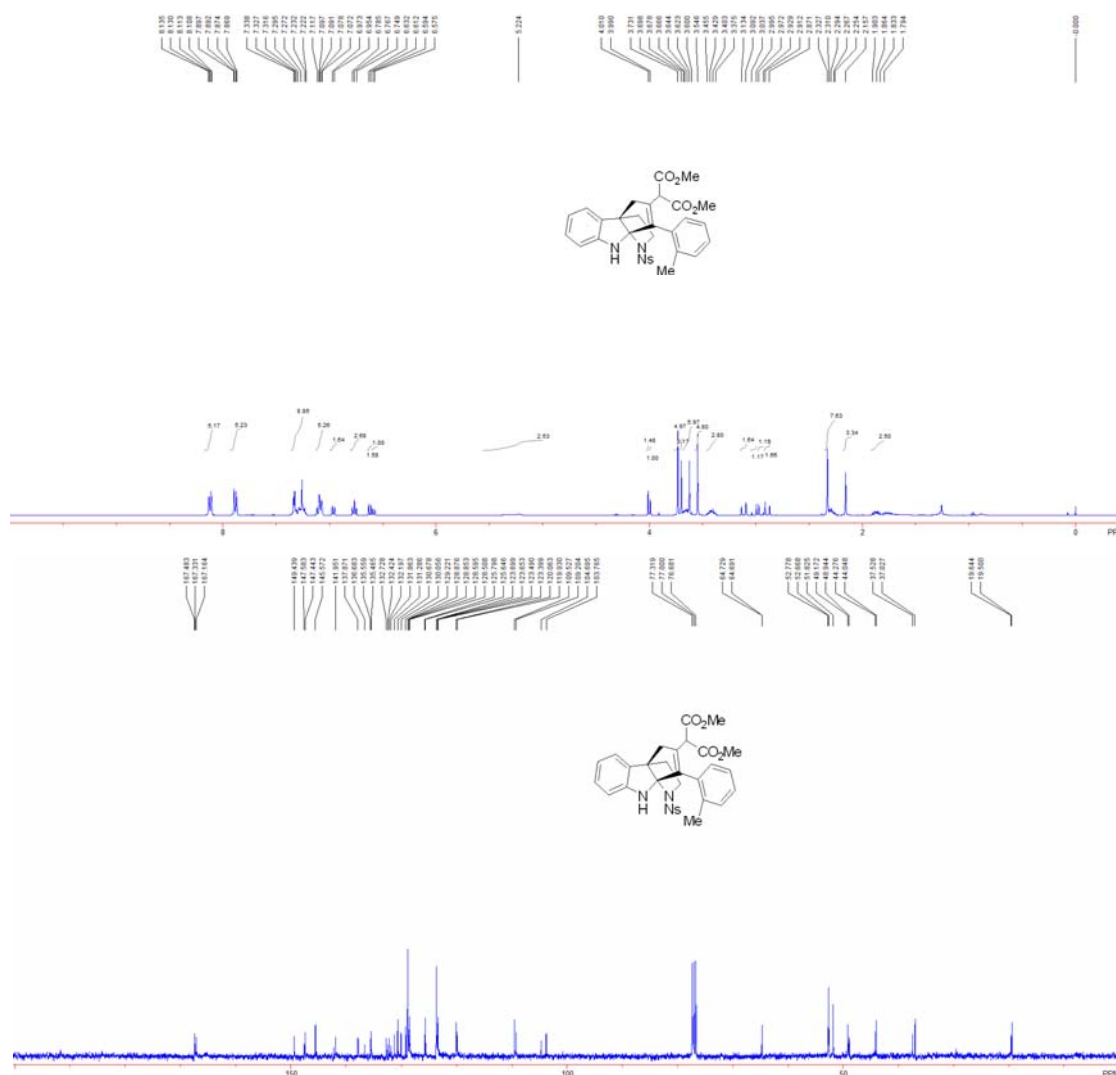
Compound **4h**: 55 mg, 88% yield; a yellow solid; mp. 111–113 °C; IR (neat) ν 2954.3, 2925.1, 2854.1, 1736.9, 1607.4, 1529.3, 1484.3, 1466.6, 1351.0, 1309.7, 1262.7, 1166.5, 1088.3, 1025.6, 911.3, 734.8 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz, TMS) δ 1.80–1.87 (1H, m), 2.24–2.30 (1H, m), 2.90 (1H, d, $J = 17.2$ Hz), 3.00 (1H, d, $J = 17.2$ Hz), 3.43–3.49 (1H, m), 3.59–3.65 (1H, m), 3.61 (3H, s), 3.73 (3H, s), 4.09 (1H, s), 5.36 (1H, s), 6.63 (1H, d, $J = 7.6$ Hz), 6.77 (1H, dd, $J_1 = J_2 = 7.6$ Hz), 7.06–7.12 (2H, m), 7.20 (2H, d, $J = 8.0$ Hz), 7.40 (2H, d, $J = 8.0$ Hz), 7.83 (2H, d, $J = 8.8$ Hz), 8.12 (2H, d, $J = 8.8$ Hz); ^{13}C NMR (CDCl_3 , 100 MHz, TMS) δ 37.8, 44.7, 49.1, 51.7, 52.8, 52.9, 64.7, 103.9, 109.5, 120.1, 123.4, 123.7, 128.67, 128.74, 128.9, 131.0, 131.2, 132.5, 134.7,

(CDCl₃, 100 MHz, TMS) δ 37.9, 44.7, 49.2, 51.8, 52.7, 52.8, 55.2, 64.5, 104.1, 109.6, 113.9, 120.0, 123.4, 123.7, 124.8, 128.6, 128.8, 130.9, 132.8, 135.2, 142.4, 145.9, 147.7, 149.4, 159.8, 167.4, 167.8; HRMS (ESI) Calcd. for C₃₁H₃₀N₃O₉S⁺ (M⁺+H): 620.1697, found: 620.1698.



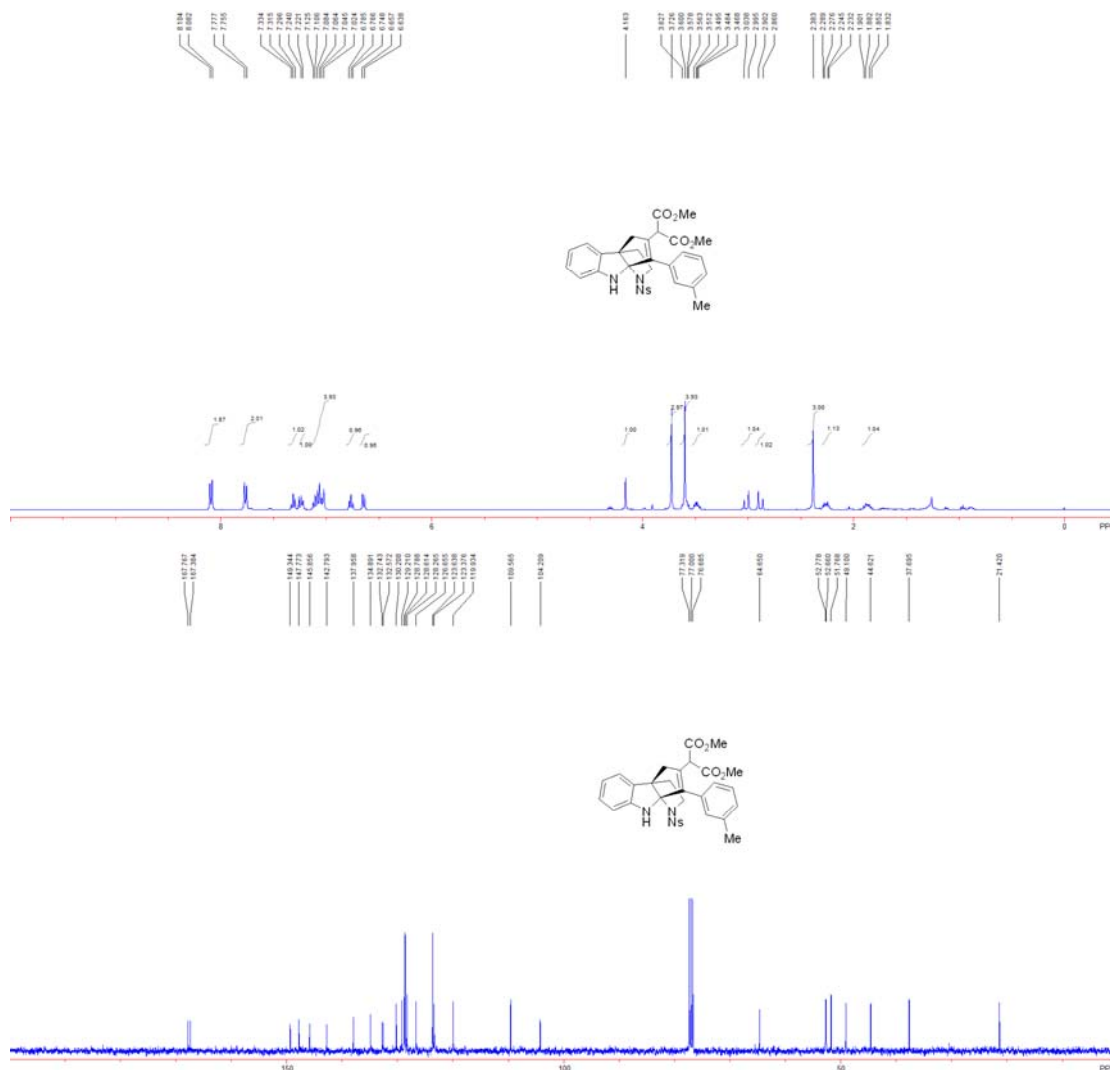
Compound **4j**: 43 mg, 71% yield; a yellow solid; mp. 120–122 °C; IR (neat) ν 3731.6, 2924.0, 2850.4, 1732.1, 1609.8, 1524.0, 1466.4, 1349.7, 1315.3, 1260.6, 1153.9, 1088.6, 1039.7, 745.9, 620.4 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz, TMS) δ 1.79–1.90 (2.6H, m), 2.16 (3H, s), 2.25–2.33 (2.6H, m), 2.33 (4.8H, s), 2.89 (1.6H, d, *J* = 16.8 Hz), 2.95 (1H, d, *J* = 16.8 Hz), 3.02 (1H, d, *J* = 16.8 Hz), 3.11 (1.6H, d, *J* = 16.8 Hz), 3.38–3.46 (2.6H, m), 3.55 (4.8H, s), 3.60–3.68 (2.6H, m), 3.62 (3H, s), 3.70 (3H, s), 3.73 (4.8H, s), 3.99 (1H, s), 4.01 (1.6H, s), 5.22

(2.6H, s), 6.59 (1H, d, $J = 7.6$ Hz), 6.62 (1.6H, d, $J = 7.6$ Hz), 6.77 (2.6H, dd, $J_1 = J_2 = 7.2$ Hz), 6.96 (1.6H, d, $J = 7.6$ Hz), 7.07–7.12 (5.2H, m), 7.22–7.34 (8.8H, m), 7.87–7.90 (5.2H, m), 8.11–8.14 (5.2H, m); ^{13}C NMR (CDCl_3 , 100 MHz, TMS) δ 19.5, 19.6, 37.0, 37.5, 44.0, 44.3, 48.9, 49.2, 51.8, 52.7, 52.8, 64.69, 64.73, 103.8, 104.7, 109.2, 109.5, 119.9, 120.1, 123.4, 123.5, 123.65, 123.70, 125.6, 125.8, 128.5, 128.6, 128.85, 128.88, 129.2, 130.1, 130.7, 131.3, 131.9, 132.2, 132.4, 132.7, 135.5, 135.6, 136.7, 137.9, 142.0, 145.6, 147.4, 147.6, 149.4, 167.2, 167.3, 167.5; HRMS (ESI) Calcd. for $\text{C}_{31}\text{H}_{30}\text{N}_3\text{O}_8\text{S}^+$ ($\text{M}^+\text{+H}$): 604.1748, found: 604.1748.

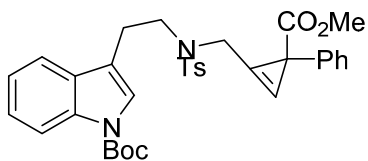


Compound **4k**: 76 mg, 99% yield; a yellow solid; mp. 125–127 °C; IR (neat) ν 3407.3, 2953.4, 2924.9, 2854.5, 1734.9, 1607.4, 1529.6, 1484.9, 1466.0, 1435.4, 1400.3, 1349.1, 1310.1, 1154.4, 1086.8, 1043.8, 735.8, 618.3

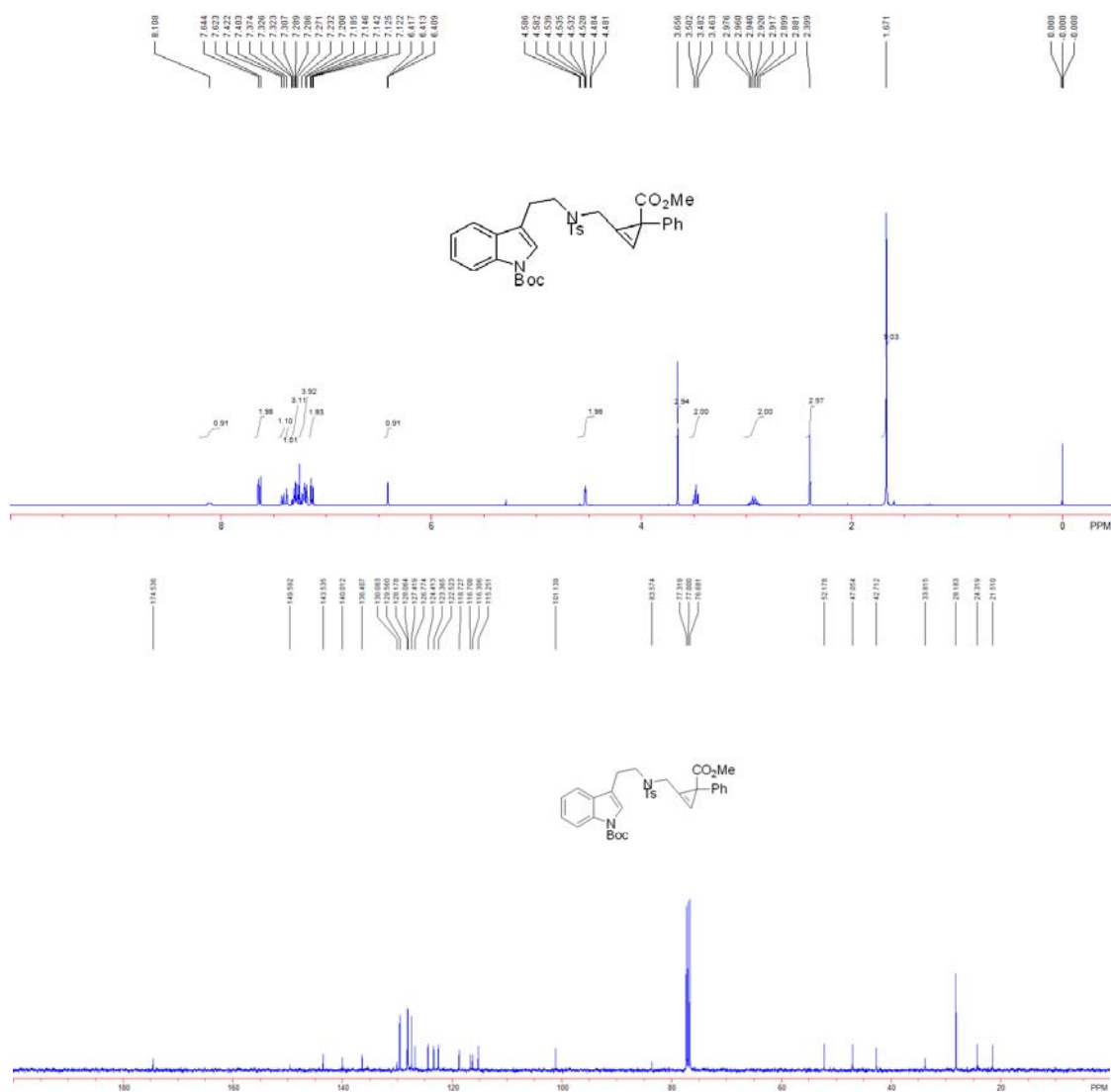
cm⁻¹; ¹H NMR (CDCl₃, 400 MHz, TMS) δ 1.83–1.90 (1H, m), 2.23–2.29 (1H, m), 2.38 (3H, s), 2.88 (1H, d, *J* = 16.8 Hz), 3.02 (1H, d, *J* = 16.8 Hz), 3.47–3.51 (1H, m), 3.56–3.63 (1H, m), 3.60 (3H, s), 3.73 (3H, s), 4.16 (1H, s), 6.65 (1H, d, *J* = 7.6 Hz), 6.77 (1H, dd, *J*₁ = *J*₂ = 7.6 Hz), 7.02–7.13 (4H, m), 7.23 (1H, d, *J* = 7.6 Hz), 7.32 (1H, dd, *J*₁ = *J*₂ = 7.6 Hz), 7.77 (2H, d, *J* = 8.8 Hz), 8.09 (2H, d, *J* = 8.8 Hz); ¹³C NMR (CDCl₃, 100 MHz, TMS) δ 21.4, 37.7, 44.6, 49.1, 51.8, 52.7, 52.8, 64.7, 104.2, 109.6, 119.9, 123.4, 123.6, 126.7, 128.3, 128.6, 128.8, 129.2, 130.2, 132.6, 132.7, 134.9, 138.0, 142.8, 145.9, 147.8, 149.3, 167.4, 167.8; HRMS (ESI) Calcd. for C₃₁H₃₀N₃O₈S⁺ (M⁺+H): 604.1748, found: 604.1748.

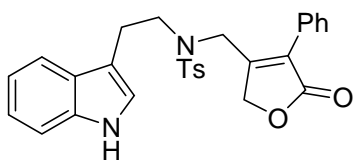


General procedures and spectroscopic data of compounds 5a-8a

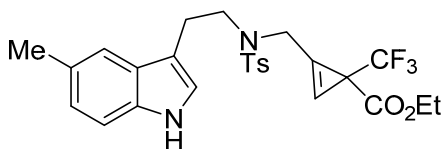
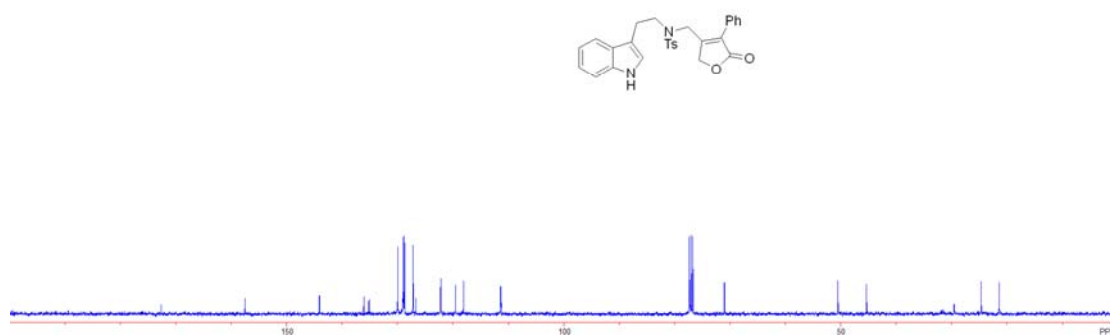
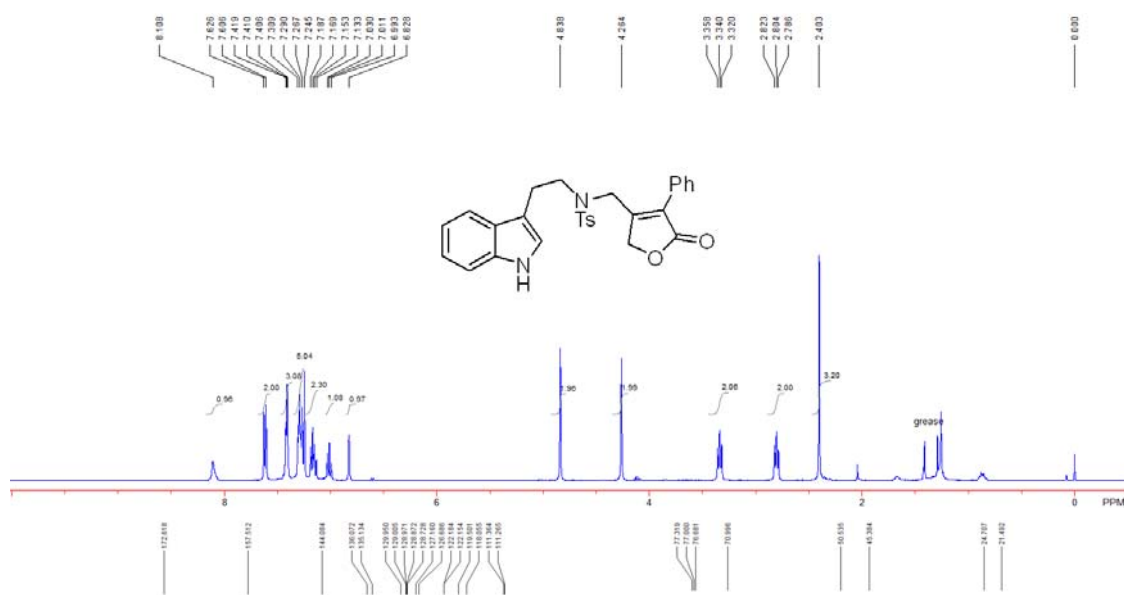


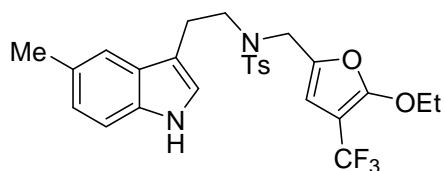
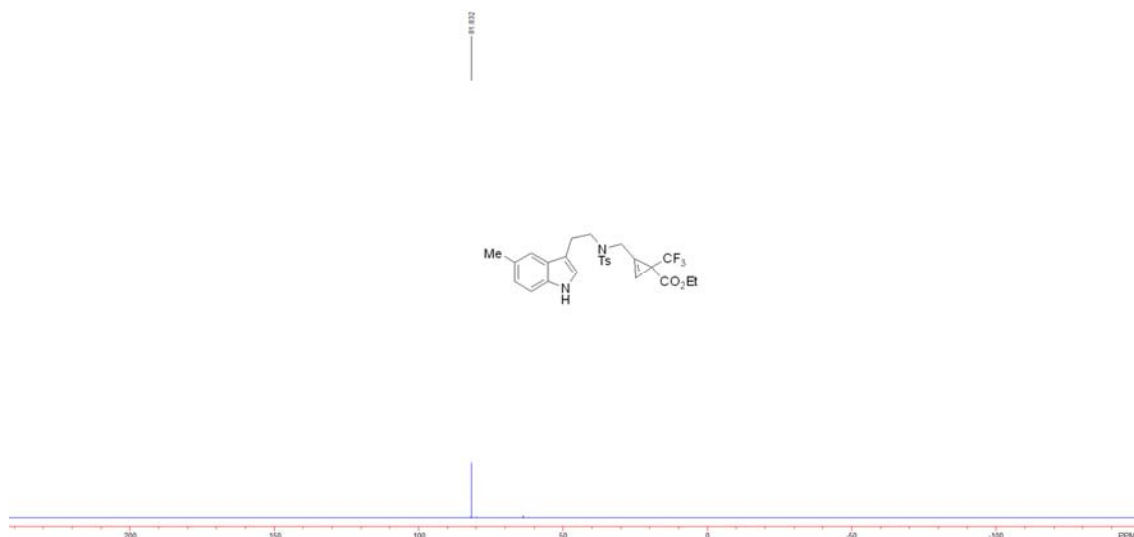
Compound **5a**: 1.01g, 34% yield; a pale yellow oil; IR (neat) ν 3399, 2932, 2924, 2843, 1734, 1458, 1435, 1339, 1299, 1266, 1067, 735, 654 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz, TMS) δ 1.67 (9H, s), 2.40 (3H, s), 2.88–2.98 (2H, m), 3.48 (2H, t, $J = 8.0$ Hz), 3.66 (3H, s), 4.48–4.59 (2H, m), 6.41 (1H, t, $J = 1.6$ Hz), 7.12–7.15 (2H, m), 7.19–7.33 (7H, m), 7.37 (1H, s), 7.41 (1H, d, $J = 7.6$ Hz), 7.63 (2H, d, $J = 8.4$ Hz), 8.11 (1H, s); ^{13}C NMR (CDCl_3 , 100 MHz, TMS) δ 21.5, 24.3, 28.2, 33.8, 42.7, 47.1, 52.2, 83.6, 101.1, 115.3, 116.3, 116.7, 118.7, 122.5, 123.4, 124.4, 126.8, 127.4, 128.1, 128.2, 129.6, 130.1, 136.4, 140.0, 143.5, 149.6, 174.5; HRMS (ESI) Calcd. for $\text{C}_{34}\text{H}_{40}\text{N}_3\text{O}_6\text{S}^+$ ($\text{M}^+ + \text{NH}_4$): 618.2632, found: 618.2623.



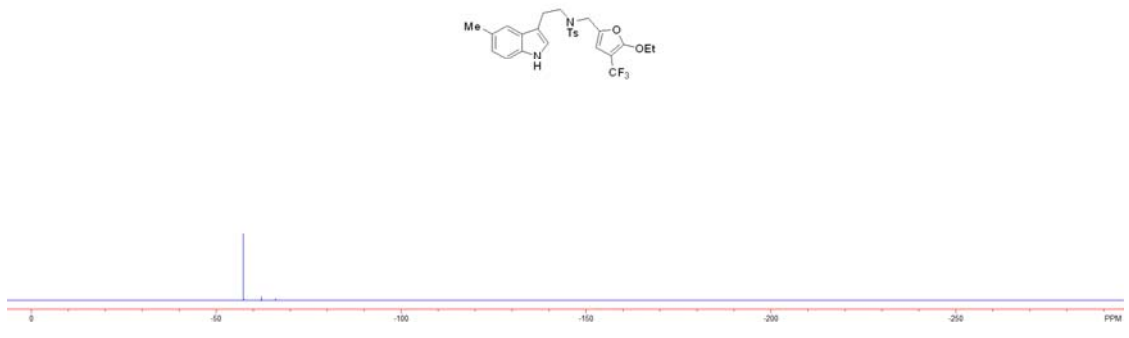
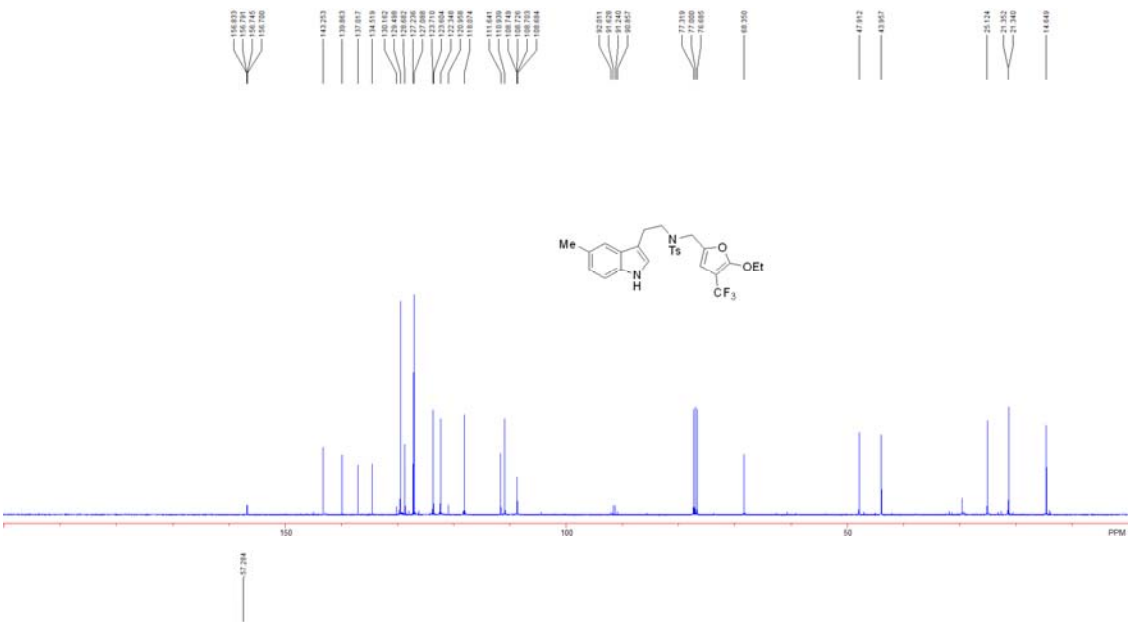
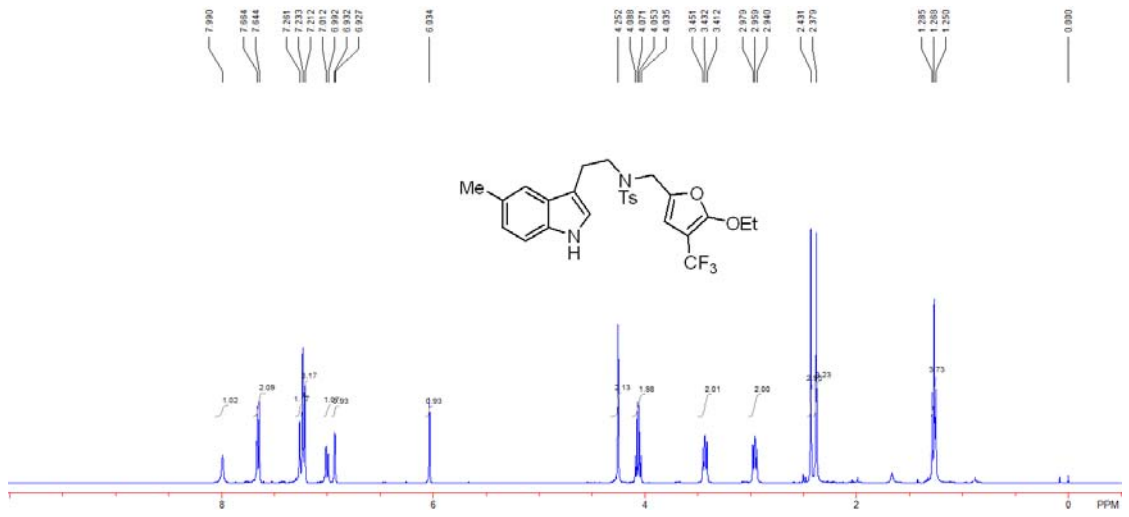


Compound **6a**: 40 mg, 31% yield; a brown solid; mp. 98–100 °C; IR (neat) ν 3405.1, 2922.7, 2851.9, 1729.5, 1457.2, 1340.5, 1157.1, 1093.9, 1038.4, 814.4, 702.9 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz, TMS) δ 2.40 (3H, s), 2.80 (2H, t, $J = 7.6$ Hz), 3.34 (2H, t, $J = 7.6$ Hz), 4.26 (2H, s), 4.84 (2H, s), 6.83 (1H, s), 7.01 (1H, dd, $J_1 = J_2 = 7.6$ Hz), 7.13–7.19 (2H, m), 7.25–7.31 (5H, m), 7.41–7.42 (3H, m), 7.62 (2H, d, $J = 8.0$ Hz), 8.11 (1H, s); ^{13}C NMR (CDCl_3 , 100 MHz, TMS) δ 21.5, 24.7, 45.4, 50.5, 71.0, 111.3, 111.4, 118.1, 119.5, 122.15, 122.18, 126.7, 127.2, 128.7, 128.9, 128.97, 129.00, 130.0, 135.1, 136.1, 144.1, 157.5, 172.6; HRMS (ESI) Calcd. for $\text{C}_{28}\text{H}_{30}\text{N}_3\text{O}_4\text{S}^+$ ($\text{M}^+ + \text{NH}_4$): 504.1952, found: 504.1949.

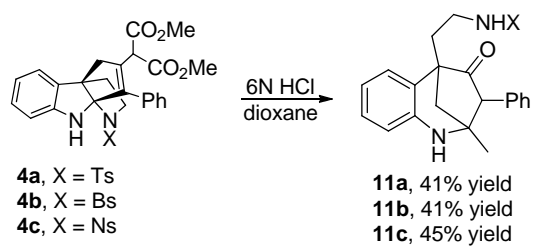
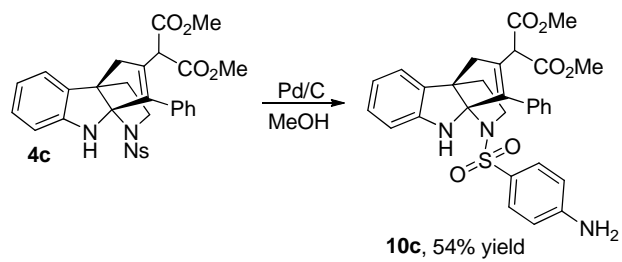
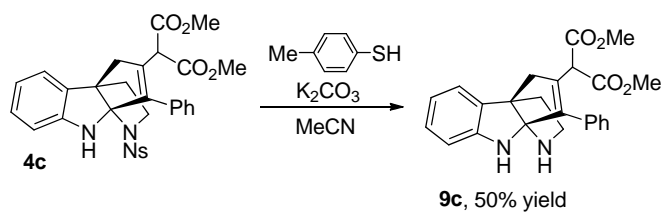


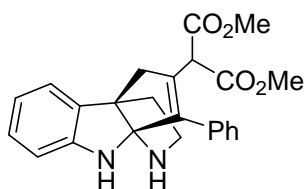


Compound **8a**: 50 mg, 96% yield; a white solid; mp. 108–110 °C; IR (neat) ν 3417.9, 3373.6, 2986.5, 2928.8, 2862.5, 1737.4, 1645.2, 1598.9, 1451.9, 1391.2, 1329.7, 1268.5, 1155.7, 1112.9, 1032.3, 953.8, 796.0 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz, TMS) δ 1.27 (3H, t, $J = 7.2$ Hz), 2.38 (3H, s), 2.43 (3H, s), 2.96 (2H, t, $J = 7.6$ Hz), 3.43 (2H, t, $J = 7.6$ Hz), 4.06 (2H, q, $J = 7.2$ Hz), 4.25 (2H, s), 6.03 (1H, s), 6.93 (1H, d, $J = 2.0$ Hz), 7.00 (1H, d, $J = 8.0$ Hz), 7.22 (3H, d, $J = 8.0$ Hz), 7.26 (1H, s), 7.65 (2H, d, $J = 8.0$ Hz), 7.99 (1H, s); ^{13}C NMR (CDCl_3 , 100 MHz, TMS) δ 14.6, 21.3, 21.4, 25.1, 44.0, 47.9, 68.4, 91.4 (q, $J = 38.3$ Hz), 108.7 (q, $J = 2.3$ Hz), 110.9, 111.6, 118.1, 122.28 (q, $J = 264.6$ Hz), 122.35, 123.7, 127.1, 127.2, 128.7, 129.5, 130.2, 134.5, 137.0, 139.9, 143.3, 156.8 (q, $J = 4.5$ Hz); ^{19}F NMR (376 MHz, CDCl_3 , CFCl_3): -57.28 (s); HRMS (ESI) Calcd. for $\text{C}_{26}\text{H}_{31}\text{F}_3\text{N}_3\text{O}_4\text{S}^+$ ($\text{M}^+ + \text{NH}_4$): 538.1982, found: 538.1980.

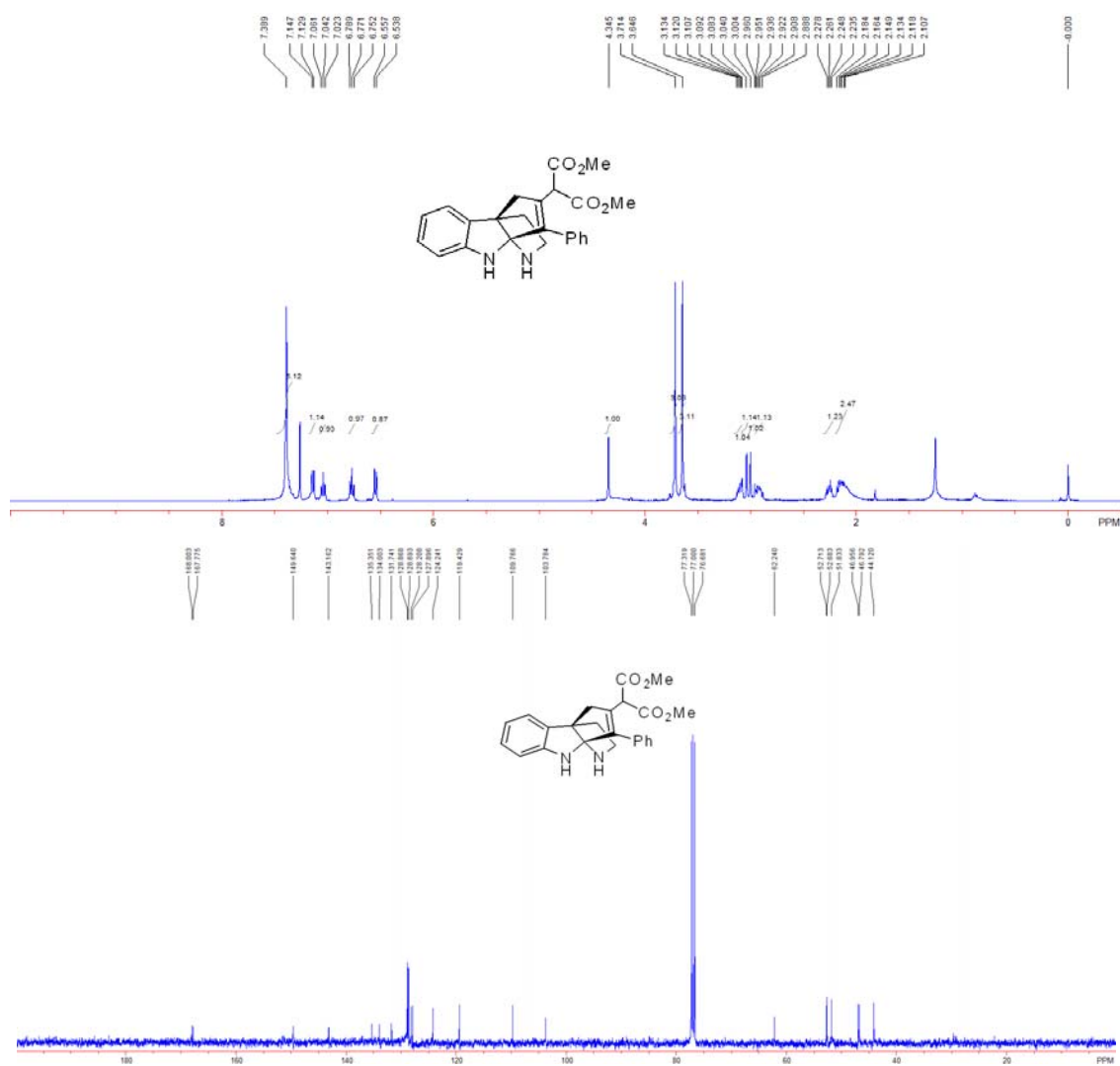


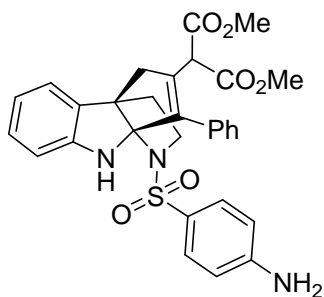
Transformations of product 4c



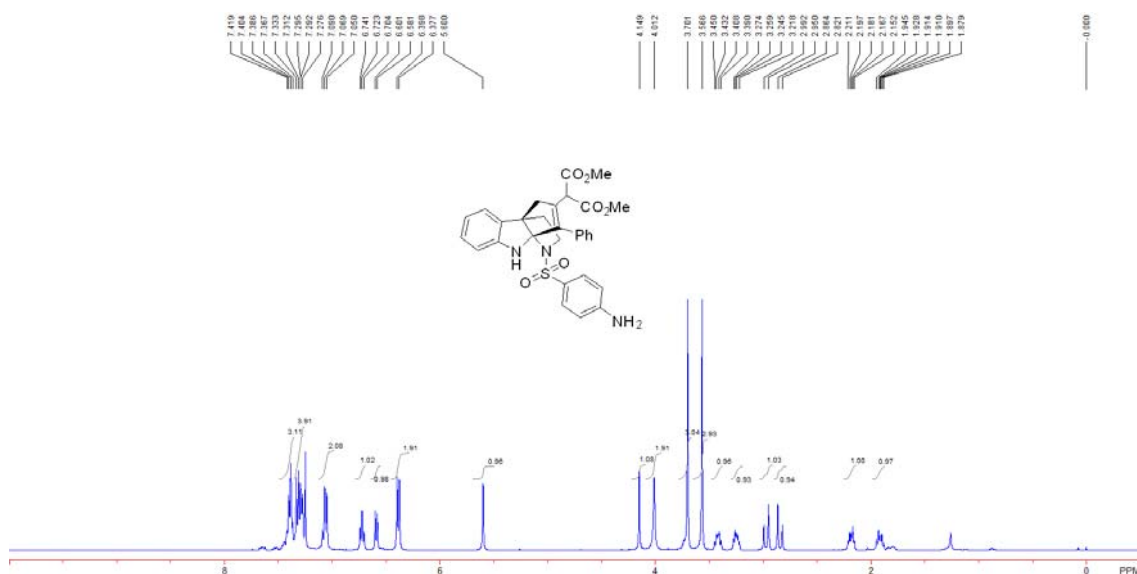


Compound **9c**: 20 mg, 50% yield; a brown oil; IR (neat) ν 3675, 3195, 2956, 2922, 1742, 1608, 1488, 1472, 1435, 1413, 1316, 1280, 1226, 1183, 1151, 1119, 1062, 1017, 727 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz, TMS) δ 2.11–2.18 (2H, m), 2.24–2.28 (1H, m), 2.89–2.95 (1H, m), 2.98 (1H, d, $J = 17.6$ Hz), 3.06 (1H, d, $J = 17.6$ Hz), 3.09–3.13 (1H, m), 3.65 (3H, s), 3.71 (3H, s), 4.35 (1H, s), 6.55 (1H, d, $J = 7.2$ Hz), 6.77 (1H, dd, $J_1 = J_2 = 7.2$ Hz), 7.04 (1H, dd, $J_1 = J_2 = 7.2$ Hz), 7.14 (1H, d, $J = 7.2$ Hz), 7.39 (5H, s); ^{13}C NMR (CDCl_3 , 100 MHz, TMS) δ 44.1, 46.8, 47.0, 51.8, 52.68, 52.71, 62.2, 103.8, 109.8, 119.4, 124.2, 127.9, 128.2, 128.7, 128.9, 131.7, 134.0, 135.4, 143.2, 149.6, 167.8, 168.0; HRMS (ESI) Calcd. for $\text{C}_{24}\text{H}_{25}\text{N}_2\text{O}_4^+$ ($\text{M}^+\text{+H}$): 405.1809, found: 405.1810.

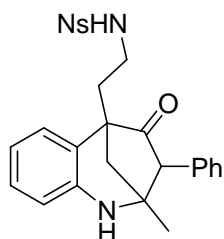
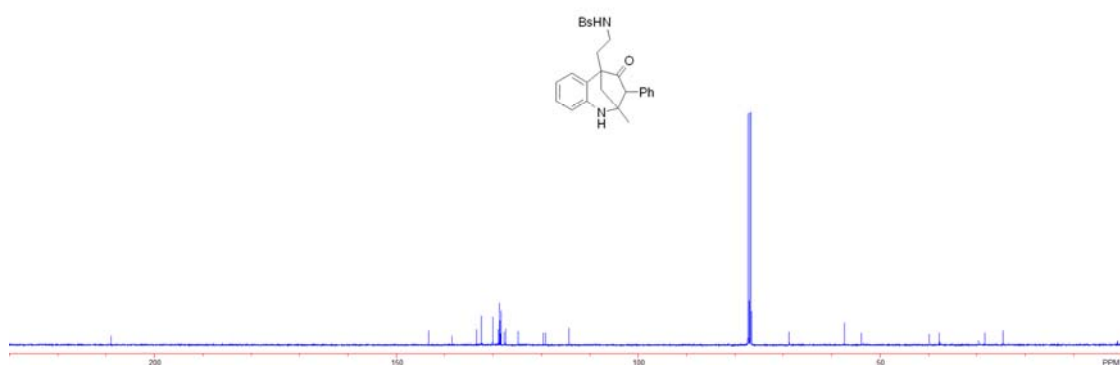
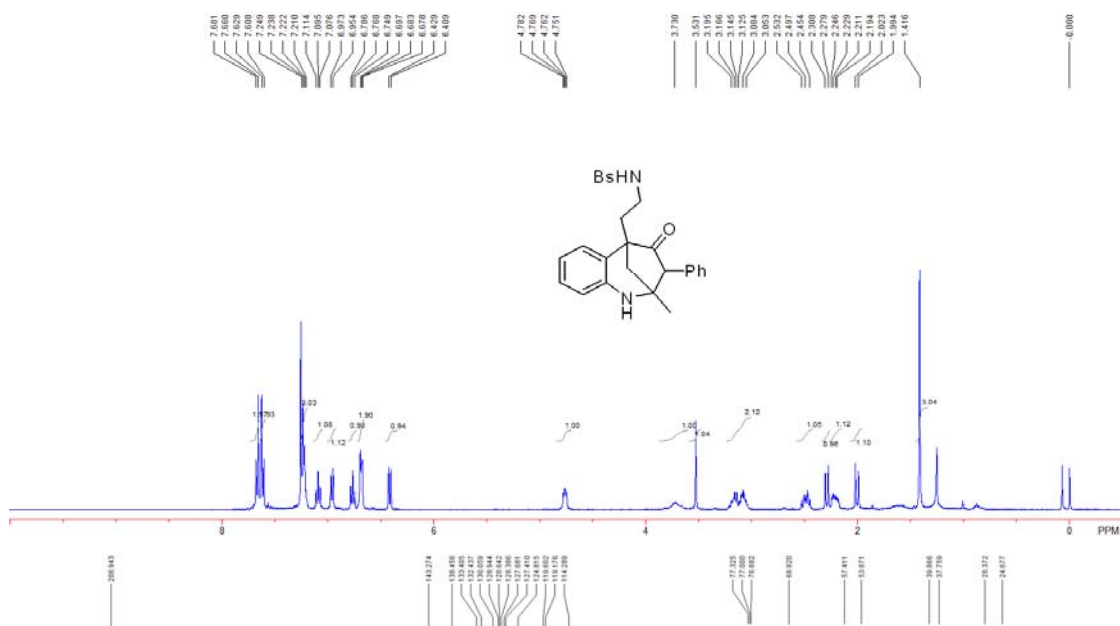




Compound **10c**: 30 mg, 54% yield; a brown oil; IR (neat) ν 3373, 2972, 2927, 2882, 1734, 1597, 1503, 1485, 1436, 1380, 1313, 1147, 1087, 1046, 880, 683 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz, TMS) δ 1.88–1.95 (1H, m), 2.15–2.21 (1H, m), 2.84 (d, $J = 16.8$ Hz), 2.97 (d, $J = 16.8$ Hz), 3.22–3.27 (1H, m), 3.39–3.45 (1H, m), 3.57 (3H, s), 3.70 (3H, s), 4.01 (2H, s), 4.15 (1H, s), 5.60 (1H, s), 6.39 (2H, d, $J = 8.4$ Hz), 6.59 (1H, d, $J = 8.0$ Hz), 6.72 (1H, dd, $J_1 = J_2 = 7.6$ Hz), 7.05–7.09 (2H, m), 7.28–7.33 (4H, m), 7.37–7.42 (3H, m); ^{13}C NMR (CDCl_3 , 100 MHz, TMS) δ 37.3, 44.1, 48.7, 51.7, 52.5, 52.7, 64.5, 103.6, 109.1, 113.4, 119.0, 123.2, 127.4, 128.0, 128.4, 129.5, 129.6, 132.4, 133.5, 133.7, 143.8, 148.3, 150.2, 167.5, 167.8; HRMS (ESI) Calcd. for $\text{C}_{30}\text{H}_{30}\text{N}_3\text{O}_6\text{S}^+$ ($\text{M}^+ + \text{H}$): 560.1850, found: 560.1851.

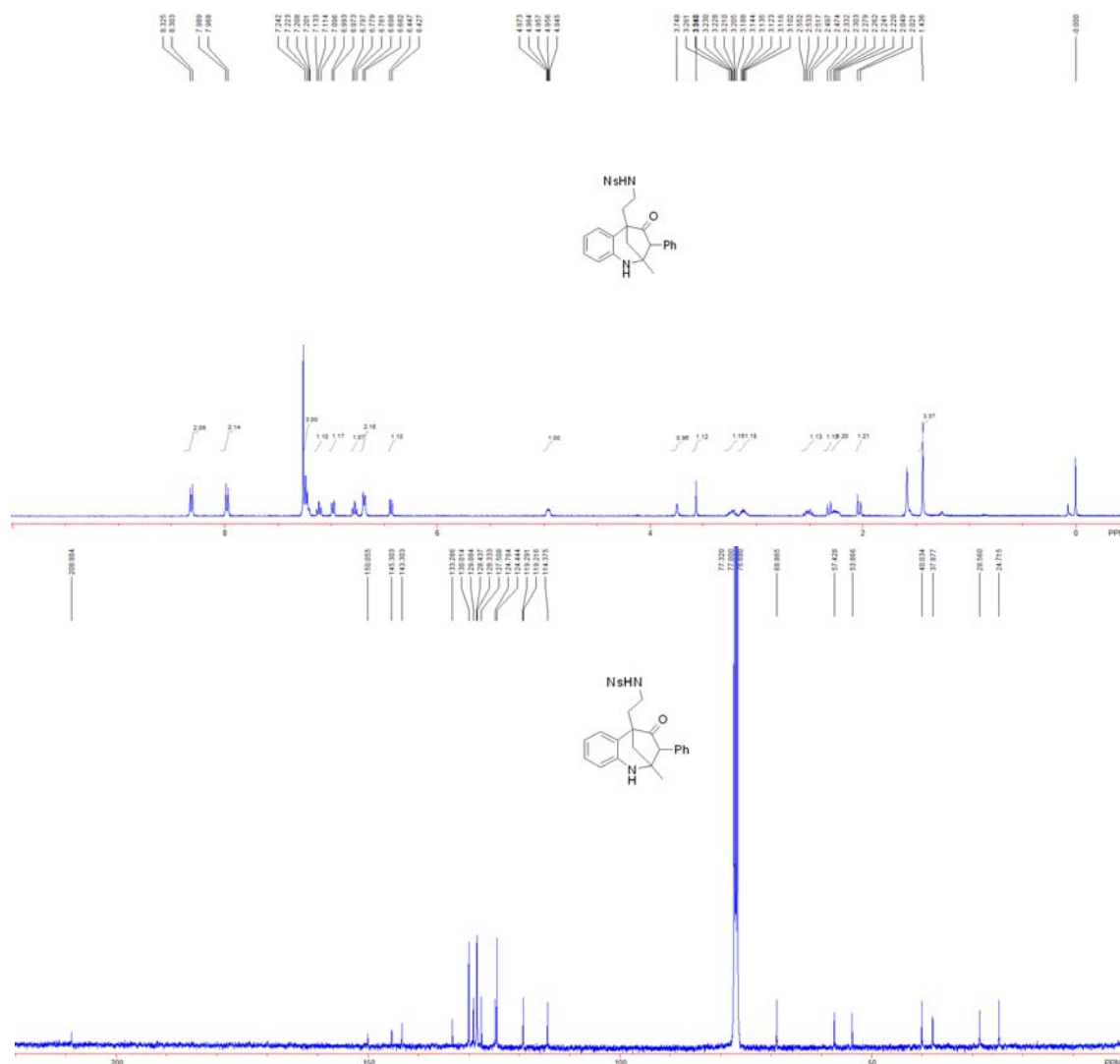


132.4, 133.4, 138.5, 143.3, 208.9; HRMS (ESI) Calcd. for $C_{26}H_{26}BrN_2O_3S^+$ ($M^+ + H$): 525.0842, found: 525.0841.

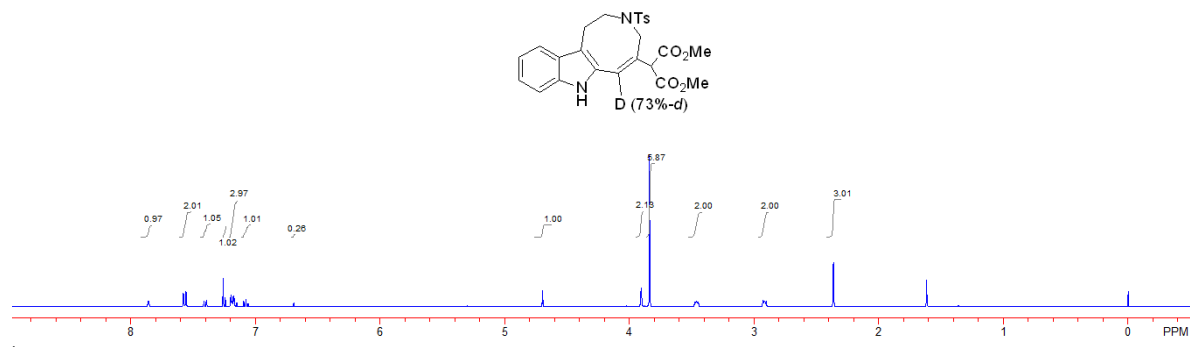
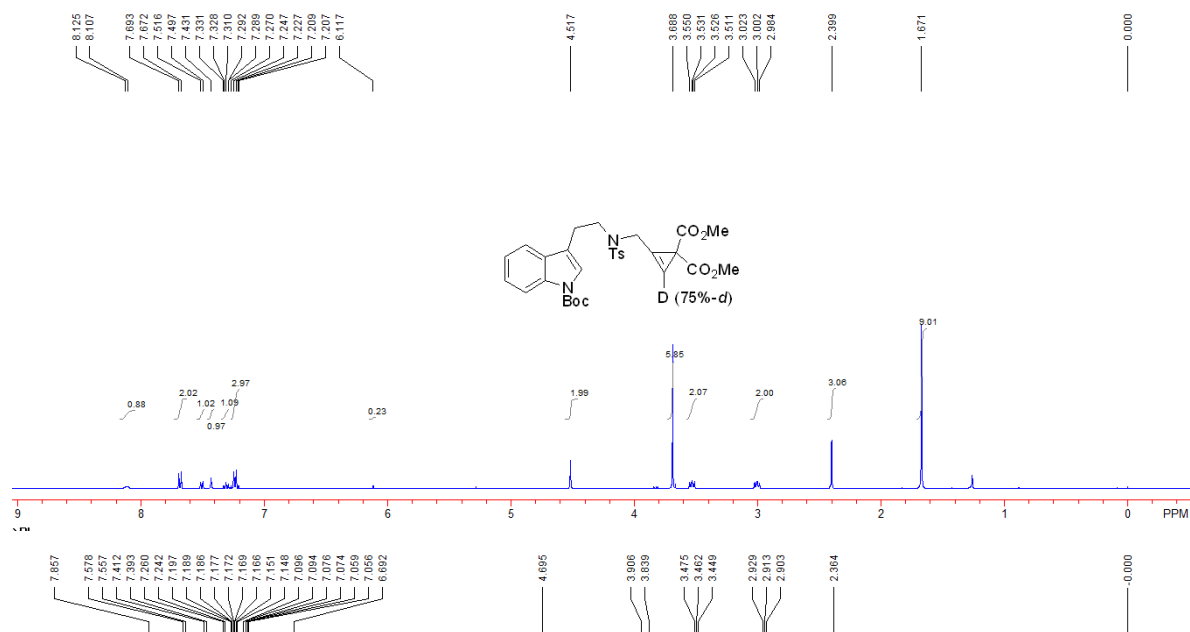


Compound **11c**: 44 mg, 45% yield; a yellow solid; mp. 103–105 °C; IR (neat) ν 2926, 2854, 2362, 1733, 1606, 1529, 1484, 1349, 1310, 1164, 1092, 855, 737 cm^{-1} ; 1H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.44 (3H, s), 2.04 (1H, d, $J = 11.6$ Hz), 2.22–2.28 (1H, m), 2.32 (1H, d, $J = 11.6$ Hz), 2.47–2.55 (1H, m), 3.10–3.14 (1H, m), 3.19–3.26 (1H, m), 3.57 (1H, s), 3.75 (1H, s), 4.95–4.97 (1H, m), 6.44 (1H, d, $J = 8.0$ Hz), 6.69 (2H, d, $J = 6.4$ Hz), 6.78 (1H, dd, $J_1 = J_2 = 7.2$ Hz), 6.98 (1H, d, $J = 8.0$ Hz), 7.11 (1H, dd, $J_1 = J_2 = 7.2$ Hz), 7.20–7.24 (3H, m), 7.98 (2H, d, $J = 8.4$ Hz), 8.31 (2H, d, $J = 8.4$ Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 24.7, 28.6, 37.9,

40.0, 53.9, 57.4, 68.9, 114.4, 119.2, 119.3, 124.4, 124.8, 127.5, 128.3, 128.4, 129.1, 130.0, 133.3, 143.3, 145.3, 150.1, 208.9; HRMS (ESI) Calcd. for C₂₆H₂₆N₃O₅S⁺ (M⁺+H): 492.1588, found: 492.1587.



Deuterium labeling experiment



X-ray Crystal Data of 2b, 4c, 6a, 8a and 11c

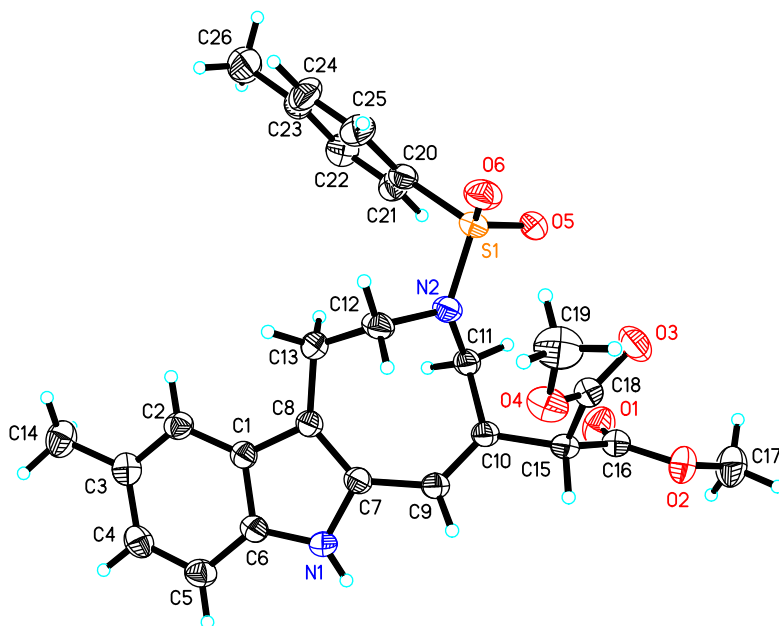


Figure SI-1. ORTEP Drawing of **2b**

The crystal data of **2b** have been deposited in CCDC with number 899936. Empirical Formula: $C_{26}H_{28}N_2O_6S$; Formula Weight: 496.56; Crystal Color, Habit: colorless, Crystal Dimensions: 0.276 x 0.211 x 0.142 mm; Crystal System: Orthorhombic; Lattice Parameters: $a = 19.8378(16)\text{\AA}$, $b = 9.3737(8)\text{\AA}$, $c = 13.4463(12)\text{\AA}$, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$, $V = 2500.4(4)\text{\AA}^3$; Space group: $Pna2(1)/n$; $Z = 4$; $D_{calc} = 1.319\text{ g/cm}^3$; $F_{000} = 1048$; Final R indices $[I > 2\sigma(I)]$ $R1 = 0.0417$, $wR2 = 0.0989$.

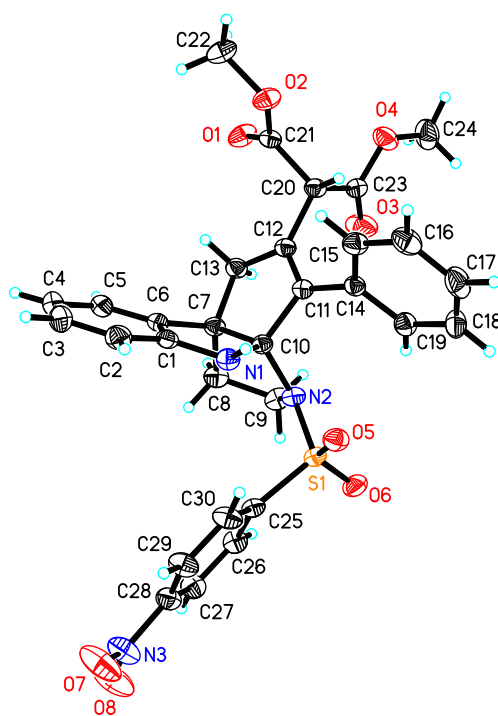


Figure SI-2. ORTEP Drawing of **4c**

The crystal data of **4c** have been deposited in CCDC with number 1409839. Empirical Formula: $C_{30}H_{27}N_3O_8S$; Formula Weight: 589.60; Crystal Color, Habit: colorless, Crystal Dimensions: 0.210 x 0.170 x 0.130 mm³; Crystal System: Monoclinic; Lattice Parameters: $a = 14.3817(15)\text{\AA}$, $b = 10.8082(11)\text{\AA}$, $c = 19.0025(18)\text{\AA}$, $\alpha = 90^\circ$, $\beta = 109.283(2)^\circ$, $\gamma = 90^\circ$, $V = 2788.0(5)\text{\AA}^3$; Space group: P 21/n; Z = 4; $D_{calc} = 1.405\text{ g/cm}^3$; $F_{000} = 1232$; Final R indices [$I > 2\sigma(I)$] R1 = 0.0486, wR2 = 0.1209.

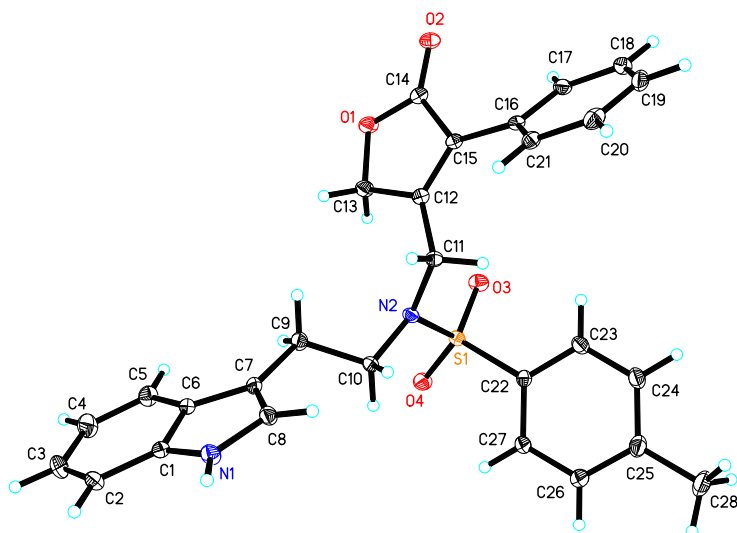


Figure SI-3. ORTEP Drawing of **6a**

The crystal data of **6a** have been deposited in CCDC with number 1401372. Empirical Formula: $C_{28}H_{26}N_2O_4S$; Formula Weight: 486.57; Crystal Color, Habit: colorless, Crystal Dimensions: 0.25 x 0.2 x 0.18 mm³; Crystal System: Orthorhombic; Lattice Parameters: $a = 12.3454(9)\text{\AA}$, $b = 8.6610(6)\text{\AA}$, $c = 22.8626(16)\text{\AA}$, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$, $V = 2444.5(3)\text{\AA}^3$; Space group: $Pn\ a\ 2_1$; $Z = 4$; $D_{calc} = 1.322\text{ g/cm}^3$; $F_{000} = 1024$; Final R indices $[I > 2\sigma(I)]$ $R1 = 0.0411$, $wR2 = 0.0916$.

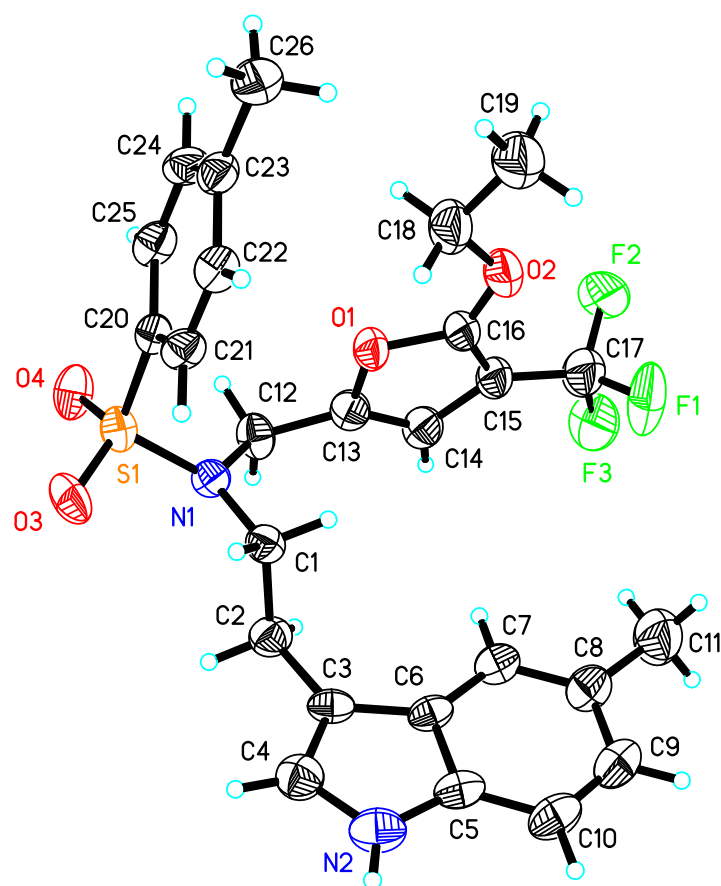


Figure SI-4. ORTEP Drawing of **8a**

The crystal data of **8a** have been deposited in CCDC with number 920329. Empirical Formula: $C_{26}H_{27}F_3N_2O_4S$; Formula Weight: 520.56; Crystal Color, Habit: colorless, Crystal Dimensions: 0.224 x 0.176 x 0.112 mm; Crystal System: Triclinic; Lattice Parameters: $a = 9.9556(15)\text{\AA}$, $b = 14.589(2)\text{\AA}$, $c = 18.274(3)\text{\AA}$, $\alpha = 81.682(3)^\circ$, $\beta = 76.959(4)^\circ$, $\gamma = 88.485(4)^\circ$, $V = 2558.5(6)\text{\AA}^3$; Space group: P-1; $Z = 4$; $D_{calc} = 1.351\text{ g/cm}^3$; $F_{000} = 1088$; Final R indices [$I > 2\sigma(I)$] $R1 = 0.0645$, $wR2 = 0.1423$.

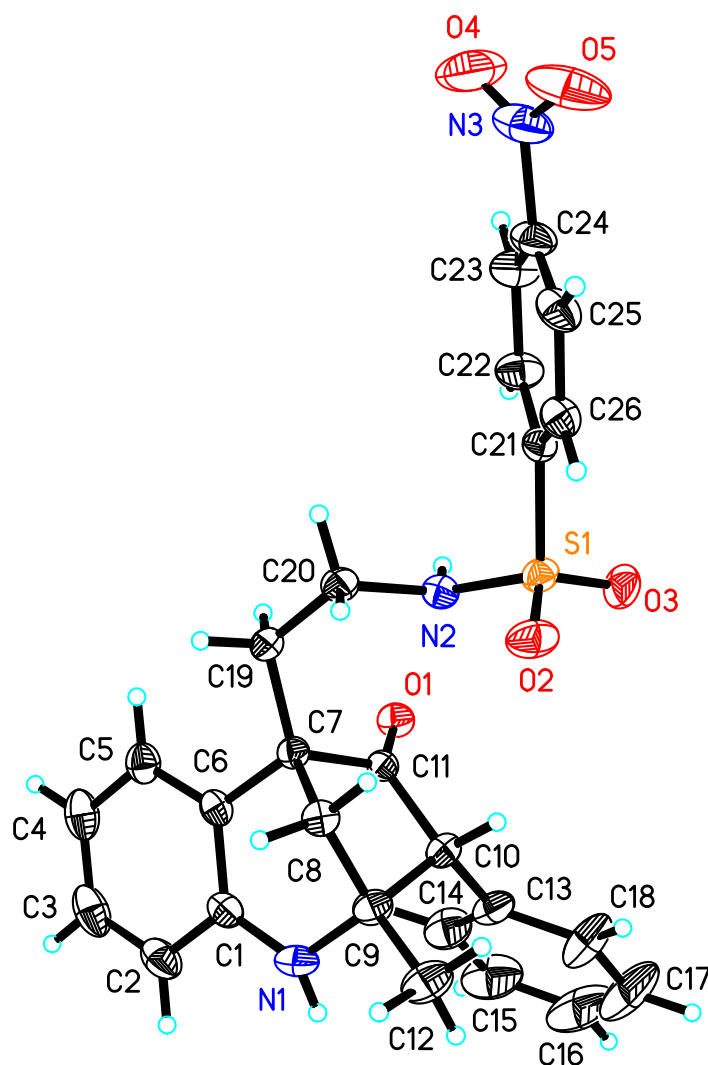


Figure SI-5. ORTEP Drawing of **11c**

The crystal data of **11c** have been deposited in CCDC with number 1439968. Empirical Formula: $C_{26}H_{25}N_3O_5S$; Formula Weight: 491.55; Crystal Color, Habit: colorless, Crystal Dimensions: 0.220 x 0.180 x 0.120 mm³; Crystal System: Triclinic; Lattice Parameters: $a = 9.3636(17)\text{\AA}$, $b = 10.8898(19)\text{\AA}$, $c = 12.521(2)\text{\AA}$, $\alpha = 99.750(4)^\circ$, $\beta = 95.533(4)^\circ$, $\gamma = 107.818(4)^\circ$, $V = 1182.9(4)\text{\AA}^3$; Space group: P -1; $Z = 2$; $D_{calc} = 1.380\text{ g/cm}^3$; $F_{000} = 516$; Final R indices [$I > 2\sigma(I)$] $R1 = 0.0514$, $wR2 = 0.1292$.