Electronic Supplementary Information

Phosphine-Catalyzed [4 + 1] Annulation of 2-Tosylamino-chalcones with Allenoates: Synthesis of trans-2,3-Disubstitued Indolines

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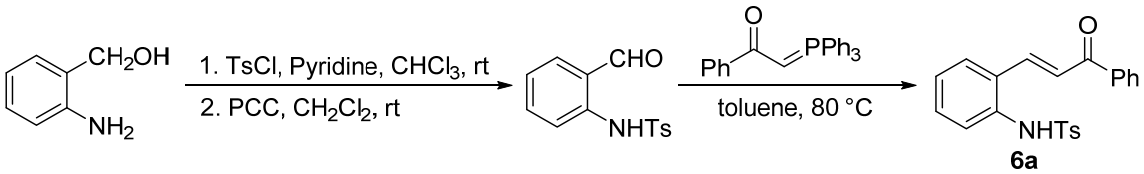
General Information

Unless otherwise indicated, all compounds and reagents were purchased from commercial suppliers and purified by standard techniques. Reactions were monitored through thin-layer chromatography (TLC) on silica gel–precoated glass plates. Chromatograms were visualized by fluorescence quenching under UV light at 254 nm. Flash column chromatography was performed using Qingdao Haiyang flash silica gel (200–300 mesh). Infrared spectra were recorded using a Bruker Optics TENSOR 27 instrument. ^{1}H and ^{13}C NMR spectra were recorded using a Bruker-300 spectrometer. IR spectra were recorded with an FT-IR spectrophotometer and are reported as cm^{-1}. HRMS analyses were carried out on an electrospray ionization (ESI) apparatus using time-of-flight (TOF) mass spectrometry. X-ray crystallographic data were collected using a Bruker SMART CCD-based diffractometer equipped with a low-temperature apparatus operated at 100K.

Preparation of 2-Tosylaminochalcones 6



2-Tosylaminochalcone (**6a**) was prepared according to the literature procedure[1, 2].

(1) Preparation of 2-Tosylaminochalcone (6a)

A dry and nitrogen-flushed 250-mL Schlenk flask, equipped with a magnetic stirring bar and a septum, was charged with a solution of 2-aminobenzyl alcohol (2.46 g, 20 mmol) in $CHCl_3$ (100 mL). TsCl (4.18 g, 1.1 equiv) and pyridine (0.1 mL) was added, and the reaction mixture was stirred for 12 h at room temperature. Thereafter, the

[1] LóPez, M. V.; Bermejo, M. R.; Vázquez, M. E.; Taglietti, A.; Zaragoza, G.; Pedrido, R.; Martínez-Calvo, M. *Org. Biomol. Chem.* **2010**, *8*, 357.

[2] Lee, Y. T.; Jang Y. J.; Syu, S.; Chou, S. C.; Lee, C. J.; Lin, W. W. *Chem. Commun.* **2012**, *48*, 8135.

solvent was removed by evaporation in vacuo. Without purification, the crude product was dissolved in dichloromethane (50 mL) and then PCC (5.173 g, 1.2 equiv) was added. The reaction mixture was stirred for 4 h at room temperature and then filtered through Celite 545 followed by washing with CH_2Cl_2. Thereafter, the solvent was removed by evaporation in vacuo. Purification by flash chromatography (dichloromethane/hexanes: 2/1) furnished 2-tosylaminobenzaldehyde (5.34 g, 97%).

A dry and nitrogen-flushed 100-mL Schlenk flask, equipped with a magnetic stirring bar and a septum, was charged with a solution of N-Ts Benzaldehyde (2.75 g, 10 mmol) in toluene (50 mL). 1-phenyl-2-(triphenylphosphoranylidene)ethanone (4.18 g, 1.1 equiv) was added, and the reaction mixture was stirred for 12 h at 80 °C. Thereafter, the solvent was removed by evaporation in vacuo. Purification by flash chromatography (dichloromethane/hexanes: 6/1) furnished **6a** (3.02 g, 80%).

(2) Preparation of 2-Tosylaminochalcone Derivatives

Other 2-tosylaminochalcone derivatives was synthesized according to the literature procedure [3, 4].

General Procedure for [4 + 1] Cycloaddition Reaction of 2-Tosylaminochalcones with Allenoate

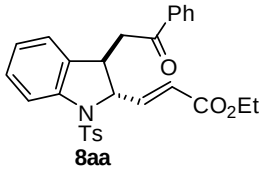
Under a nitrogen atmosphere, to a stirred solution of 2-tosylaminochalcones **6** (0.2 mmol) and benzoic acid (0.04 mmol, 20 mol%) in THF (2 mL) was respectively added fresh 2,3-butadienoate **7** (0.3 mmol) and PBu_3 (0.06 mmol, 30 mol%) via syringes . Then the reaction solution was vigorously stirred at 40 °C and monitored by TLC. After the reaction was complete, the mixture was directly purified by column chromatography on silica gel (petroleum ether/EtOAc as the eluent) to give the corresponding product.

[3] Yang, W.; Du, D. M. *Chem. Commun.* **2013**, *49*, 8842.

[4] Huang, Y. M.; Zheng, C. W.; Zhao, G. *RSC Adv.* **2013**, *3*, 16999.

Characterization Data for the [4 + 1] Cycloaddition Products 8

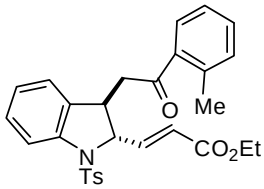
Ethyl (*E*)-3-(3-(2-oxo-2-phenylethyl)-1-tosylindolin-2-yl)acrylate (8aa)



8aa

Prepared according to the general procedure as described above in 71%yield. It was purified by flash chromatography (10% EtOAc/PE) to afford a white solid. mp = 166 – 168 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.81 (m, 1H), 7.65 – 7.56 (m, 3H), 7.55 – 7.40 (m, 4H), 7.36 – 7.29 (m, 1H), 7.17 (dd, *J* = 15.5, 4.7 Hz, 1H), 7.11 – 7.04 (m, 2H), 7.00 (d, *J* = 8.1 Hz, 2H), 6.30 (dd, *J* = 15.5, 1.7 Hz, 1H), 4.64 – 4.52 (m, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.46 (dd, *J* = 10.5, 2.2 Hz, 1H), 2.79 (dd, *J* = 18.6, 4.0 Hz, 1H), 2.25 (s, 3H), 1.75 (dd, *J* = 16.4, 8.4 Hz, 1H), 1.29 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 198.0, 165.5, 146.7, 145.0, 140.4, 136.1, 134.1, 133.9, 133.8, 130.3, 129.0, 127.9, 127.1, 126.0, 125.5, 121.1, 116.6, 67.1, 60.5, 45.1, 42.3, 21.2, 14.3; IR (film) ν_{max} 2981, 1717, 1682, 1597, 1477, 1462, 1449, 1401, 1359, 1302, 1274, 1216,1169, 1092, 1037, 985, 816, 756, 708, 690, 670, 661, 625, 587, 571, 539 cm^{-1}; HRMS (ESI) calcd for $C_{28}H_{27}NO_5S^+$ $[M + Na]^+$ 512.1502, found 512.1502.

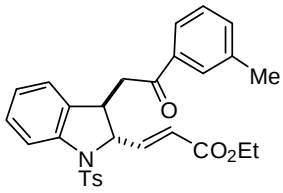
Ethyl (*E*)-3-(3-(2-oxo-2-(*o*-tolyl)ethyl)-1-tosylindolin-2-yl)acrylate (8ba)



8ba

Prepared according to the general procedure as described above in 83%yield. It was purified by flash chromatography (10% EtOAc/PE) to afford a white solid. mp = 121 – 123 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.2 Hz, 1H), 7.51 (m, 3H), 7.33 (m, 4H), 7.21 – 6.93 (m, 5H), 6.28 (dd, *J* = 15.5, 1.6 Hz, 1H), 4.64 – 4.49 (m, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.43 (m, 1H), 2.78 (dd, *J* = 18.5, 4.0 Hz, 1H), 2.40 (s, 3H), 2.22 (s, 3H), 1.76 (dd, *J* = 18.6, 10.6 Hz, 1H), 1.28 (t, *J* = 7.1 Hz, 3H).; ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.3, 166.2, 145.5, 144.2, 140.8, 138.8, 136.2, 135.0, 134.8, 133.6, 129.7, 129.6, 128.7, 128.4, 126.8, 125.5, 125.1, 124.9, 121.8, 117.4, 67.4, 60.4, 47.5, 42.9, 21.7, 21.3, 14.2; IR (film) ν_{max} 2982, 1717, 1680, 1602, 1478, 1462, 1359, 1302, 1274, 1169, 1092, 1034, 982, 815, 757, 708, 690, 662, 626, 571, 541 cm^{-1}; HRMS (ESI) calcd for $C_{29}H_{29}NO_5S^+$ $[M + Na]^+$ 526.1659, found 526.1660.

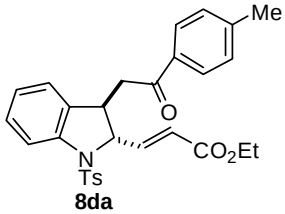
Ethyl (*E*)-3-(3-(2-oxo-2-(*m*-tolyl)ethyl)-1-tosylindolin-2-yl)acrylate (8ca)



8ca

Prepared according to the general procedure as described above in 87%yield. It was purified by flash chromatography (10% EtOAc/PE) to afford a white solid. mp = 158 – 160°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79 (m, 1H), 7.51 (m, 3H), 7.45 – 7.36 (m, 1H), 7.35 – 7.25 (m, 3H), 7.17 (m, 1H), 7.09 (m, 2H), 7.00 (d, J = 8.0 Hz, 2H), 6.29 (dd, J = 15.5, 1.7 Hz, 1H), 4.58 (m, 1H), 4.18 (q, J = 7.1 Hz, 2H), 3.54 – 3.33 (m, 1H), 2.80 (dd, J = 18.6, 4.0 Hz, 1H), 2.41 (s, 3H), 2.23 (s, 3H), 1.75 (dd, J = 18.6, 10.7 Hz, 1H), 1.28 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.3, 166.2, 145.5, 144.1, 140.7, 138.5 136.0, 134.8, 134.2, 133.6, 129.7, 128.7, 128.3, 128.1, 127.0, 125.1, 125.0, 124.9, 121.9, 117.4, 67.3, 60.4, 45.3, 42.7, 21.4, 21.3, 14.2; IR (film) ν_{max} 2981, 1717, 1681, 1602, 1478, 1462, 1359, 1303, 1274,1169, 1092, 1034, 982, 815, 757, 708, 690, 662, 626, 571, 541 cm^{-1}; HRMS (ESI) calcd for $C_{29}H_{29}NO_5S^+$ $[M + Na]^+$ 526.1659, found 526.1656.

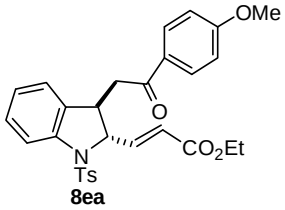
Ethyl (*E*)-3-(3-(2-oxo-2-(*p*-tolyl)ethyl)-1-tosylindolin-2-yl)acrylate (8da)



8da

Prepared according to the general procedure as described above in 81%yield. It was purified by flash chromatography (10% EtOAc/PE) to afford a white solid. mp = 168 – 170 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.1 Hz, 1H), 7.49 (m, 4H), 7.35 – 7.27 (m, 1H), 7.19 (m, 3H), 7.15 – 7.02 (m, 3H), 6.99 (d, *J* = 8.1 Hz, 2H), 6.27 (dd, *J* = 15.5, 1.7 Hz, 1H), 4.61 – 4.47 (m, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 3.43 (m, 1H), 2.74 (dd, *J* = 18.5, 4.0 Hz, 1H), 2.42 (s, 3H), 2.24 (s, 3H), 1.71 (dd, *J* = 18.6, 10.7 Hz, 1H), 1.27 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.3, 166.2, 145.5, 144.1, 140.7, 138.5 136.0, 134.8, 134.2, 133.6, 129.7, 128.7, 128.3, 128.1, 127.0, 125.1, 125.0, 124.9, 121.9, 117.4, 67.3, 60.4, 45.3, 42.7, 21.4, 21.3, 14.2; IR (film) ν_{max} 2981, 1717, 1681, 1602, 1478, 1462, 1359, 1303, 1274,1169, 1092, 1034, 982, 815, 757, 708, 690, 662, 626, 571, 541 cm^{-1}; HRMS (ESI) calcd for $C_{29}H_{29}NO_5S^+$ $[M + Na]^+$ 526.1659, found 526.1656.

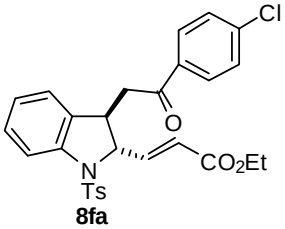
Ethyl (*E*)-3-(3-(2-(4-methoxyphenyl)-2-oxoethyl)-1-tosylindolin-2-yl)acrylate (8ea)



8ea

Prepared according to the general procedure as described above in 73%yield. It was purified by flash chromatography (10% EtOAc/PE) to afford a white solid. mp = 173 – 175 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.0 Hz, 1H), 7.62 – 7.48 (m, 4H), 7.35 – 7.27 (m, 1H), 7.15 (dd, *J* = 15.5, 4.8 Hz, 1H), 7.09 – 6.98 (m, 3H), 6.89 (d, *J* = 8.9 Hz, 2H), 6.28 (dd, *J* = 15.5, 1.7 Hz, 1H), 4.60 – 4.52 (m, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.89 (s, 3H), 3.49 – 3.40 (m, 1H), 2.72 (dd, *J* = 18.4, 4.1 Hz, 1H), 2.28 (s, 3H), 1.73 (dd, *J* = 18.4, 10.6 Hz, 1H), 1.28 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 195.5, 166.2, 163.7, 145.5, 144.0, 140.8, 135.0, 133.8, 130.1, 129.8, 129.1, 128.7, 127.0, 125.1, 124.9, 121.9, 117.4, 113.7, 67.4, 60.4, 55.5, 44.9, 42.8, 21.5, 14.2; IR (film) ν_{max} 2963, 1717, 1672, 1600, 1575, 1511, 1477, 1461, 1421, 1359, 1305, 1261, 1219 ,1168, 1092, 1029, 987, 814, 757, 666, 586, 570 cm^{-1}; HRMS (ESI) calcd for $C_{29}H_{29}NO_6S^+$ $[M + Na]^+$ 542.1608, found 542.1604.

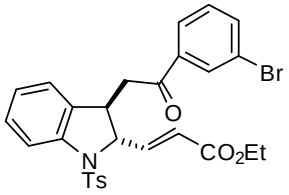
Ethyl (*E*)-3-(3-(2-(4-chlorophenyl)-2-oxoethyl)-1-tosylindolin-2-yl)acrylate (8fa)



8fa

Prepared according to the general procedure as described above in 78%yield. It was purified by flash chromatography (11% EtOAc/PE) to afford a white solid. mp = 168 – 171 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79 (m, 1H), 7.60 – 7.46 (m, 4H), 7.46 – 7.36 (m, 2H), 7.36 – 7.27 (m, 1H), 7.20 – 6.96 (m, 5H), 6.28 (dd, *J* = 15.5, 1.6 Hz, 1H), 4.54 (m, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.54 – 3.37 (m, 1H), 2.75 (dd, *J* = 18.6, 4.0 Hz, 1H), 2.26 (s, 3H), 1.73 (dd, *J* = 18.6, 10.6 Hz, 1H), 1.28 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.0, 144.9, 144.5, 139.5, 135.8, 135.6, 134.6, 133.6, 130.4, 129.9, 128.9, 128.6, 127.8, 127.0, 125.3, 122.1, 118.5, 67.6, 60.5, 45.0, 42.5, 21.5, 14.2; IR (film) ν_{max} 1717, 1682.8, 1590, 1478, 1462, 1401, 1360, 1303, 1275, 1214, 1169, 1092, 1035, 988, 816, 757, 708, 666, 629, 586, 572, 541, 529 cm^{-1}; HRMS (ESI) calcd for $C_{28}H_{25}ClNO_5S^+$ $[M + Na]^+$ 546.1112, found 546.1115.

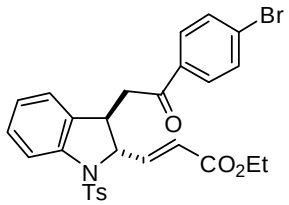
Ethyl (*E*)-3-(3-(2-(3-bromophenyl)-2-oxoethyl)-1-tosylindolin-2-yl)acrylate (8ga)



8ga

Prepared according to the general procedure as described above in 56%yield. It was purified by flash chromatography (11% EtOAc/PE) to afford a white solid. mp = 122 – 124 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.80 (m, 1H), 7.76 – 7.69 (m, 2H), 7.61 – 7.48 (m, 3H), 7.39 – 7.29 (m, 2H), 7.20 – 7.01 (m, 5H), 6.29 (dd, *J* = 15.5, 1.7 Hz, 1H), 4.56 (dt, *J* = 4.8, 1.8 Hz, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.44 (dd, *J* = 10.6, 2.1 Hz, 1H), 2.76 (dd, *J* = 18.7, 4.0 Hz, 1H), 2.28 (s, 3H), 1.75 (dd, *J* = 18.7, 10.5 Hz, 1H), 1.29 (t, *J* = 7.1 Hz, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.8, 166.2, 145.2, 144.4, 140.8, 137.7, 136.4, 134.9, 133.3, 130.8, 130.2, 129.7, 128.9, 127.0, 126.3, 125.2, 124.9, 122.9, 122.1, 117.5, 67.3, 60.5, 45.3, 42.5, 21.6, 14.2; IR (film) ν_{max} 3066, 2980,1716, 1687, 1596, 1567, 1477, 1462, 1422, 1359, 1303, 1262, 1211, 1169, 1092, 1036, 981, 905, 870, 800, 757, 740, 707, 681, 666, 625, 570, 541, 496 cm^{-1}; HRMS (ESI) calcd for $C_{28}H_{26}BrlNO_5S^+$ $[M + Na]^+$ 590.0607, found 590.0610.

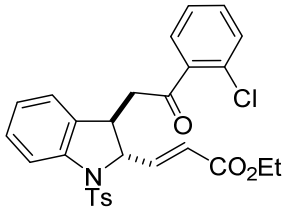
Ethyl (*E*)-3-(3-(2-(4-bromophenyl)-2-oxoethyl)-1-tosylindolin-2-yl)acrylate (8ha)



8ha

Prepared according to the general procedure as described above in 64%yield. It was purified by flash chromatography (11% EtOAc/PE) to afford a pale yellow solid. mp = 158 – 160 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.1 Hz, 1H), 7.51 (m, 6H), 7.31 (m, 1H), 7.19 – 7.04 (m, 3H), 7.01 (d, *J* = 8.1 Hz, 2H), 6.27 (dd, *J* = 15.5, 1.7 Hz, 1H), 4.58 – 4.48 (m, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.50 – 3.36 (m, 1H), 2.73 (dd, *J* = 18.6, 4.0 Hz, 1H), 2.26 (s, 3H), 1.72 (dd, *J* = 18.6, 10.6 Hz, 1H), 1.27 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.8, 166.2, 145.2, 144.4, 140.8, 137.7, 136.4, 134.9, 133.3, 130.8, 130.2, 129.7, 128.9, 127.0, 126.3, 125.2, 124.9, 122.9, 122.1, 117.5, 67.3, 60.5, 45.3, 42.5, 21.6, 14.2; IR (film) ν_{max} 3065, 2981, 2928,1716, 1684, 1586, 1478, 1462, 1397, 1360, 1274, 1213, 1168, 1092, 1071, 1034, 1010, 988, 903, 815, 756, 738, 708, 665, 628, 572 cm^{-1}; HRMS (ESI) calcd for $C_{28}H_{26}BrNO_5S^+$ $[M + Na]^+$ 590.0607, found 590.0601.

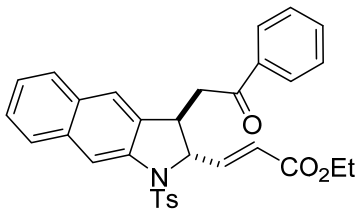
Ethyl (*E*)-3-(3-(2-(2-chlorophenyl)-2-oxoethyl)-1-tosylindolin-2-yl)acrylate (8ia)



8ia

Prepared according to the general procedure as described above in 61%yield. It was purified by flash chromatography (11% EtOAc/PE) to afford a white solid. mp = 168 – 171 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79 (m, 1H), 7.60 – 7.48 (m, 4H), 7.45 – 7.38 (m, 2H), 7.36 – 7.28 (m, 1H), 7.19 – 7.06 (m, 3H), 7.05 – 7.00 (m, 2H), 6.28 (dd, *J* = 15.5, 1.7 Hz, 1H), 4.55 (m, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.57 – 3.34 (m, 1H), 2.76 (dd, *J* = 18.6, 4.1 Hz, 1H), 2.27 (s, 3H), 1.88 – 1.63 (m, 1H), 1.28 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.0, 144.9, 144.5, 139.5, 135.8, 135.6, 134.6, 133.6, 130.4, 129.9, 128.9, 128.6, 127.8, 127.0, 125.5, 122.1, 118.5, 67.6, 60.5, 45.0, 42.5, 21.5, 14.2; IR (film) ν_{max} 1717, 1683, 1590, 1478, 1462, 1401, 1360, 1303, 1275, 1214, 1169, 1092, 1035, 988, 816, 757, 708, 666, 629, 586, 573, 541, 529 cm^{-1}; HRMS (ESI) calcd for $C_{28}H_{25}ClNO_5S^+$ $[M + Na]^+$ 546.1112, found 546.1115.

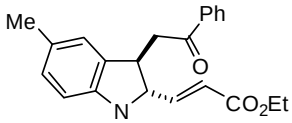
Ethyl (*E*)-3-(3-(2-oxo-2-phenylethyl)-1-tosyl-2,3-dihydro-1H-benzo[f]indol-2-yl)-acrylate (8ja)



8ja

Prepared according to the general procedure as described above in 58%yield. It was purified by flash chromatography (11% EtOAc/PE) to afford a white solid. mp = 173 – 175 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.94 – 7.84 (m, 4H), 7.78 (m, 3H), 7.60 (m, 8.3 Hz, 3H), 7.51 (m, 2H), 7.37 – 7.28 (m, 1H), 7.20 (m, 1H), 7.11 (m, 2H), 6.92 (d, *J* = 8.0 Hz, 2H), 6.32 (m, 1H), 6.32 (dd, *J* = 15.5, 1.4 Hz, 1H), 4.64 (d, *J* = 4.7 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.50 (m, 1H), 2.97 (dd, *J* = 18.6, 3.9 Hz, 1H), 2.05 (s, 3H), 1.91 (dd, *J* = 18.5, 10.8 Hz, 1H), 1.28 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.1, 166.2, 145.5, 144.2, 140.8, 135.7, 134.9, 133.6, 133.3, 132.3, 129.7, 129.4, 128.8, 128.5, 127.9, 127.0, 127, 125.1, 124.9, 123.4, 121.9, 117.4, 67.3, 60.4, 45.4, 42.8, 21.3, 14.2; IR (film) ν_{max} 3060, 2980, 2926, 1715, 1677, 1627, 1596, 1525, 1477,1463, 1358, 1303, 1274, 1213, 1169, 1124, 1092, 1037, 982, 943, 919, 862, 815, 755, 736, 707, 666, 639, 626, 584, 570, 540, 478 cm^{-1}; HRMS (ESI) calcd for $C_{32}H_{29}NO_5S^+$ $[M + Na]^+$ 562.1659, found 562.1660.

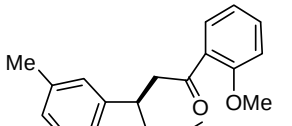
Ethyl (*E*)-3-(5-methyl-3-(2-oxo-2-phenylethyl)-1-tosylindolin-2-yl)acrylate (8ka)



8ka

Prepared according to the general procedure as described above in 69%yield. It was purified by flash chromatography (11% EtOAc/PE) to afford a white solid. mp = 153 – 155 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67 (m, 1H), 7.63 – 7.54 (m, 3H), 7.53 – 7.39 (m, 4H), 7.18 (d, *J* = 4.7 Hz, 1H), 7.15 – 7.07 (m, 2H), 6.99 (d, *J* = 8.0 Hz, 2H), 6.90 – 6.82 (m, 1H), 6.29 (dd, *J* = 15.5, 1.7 Hz, 1H), 4.61 – 4.45 (m, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.47 – 3.32 (m, 1H), 2.77 (dd, *J* = 18.6, 4.1 Hz, 1H), 2.30 (s, 3H), 2.24 (s, 3H), 1.70 (dd, *J* = 18.6, 10.6 Hz, 2H), 1.28 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.2, 166.2, 145.5, 144.0, 138.4, 136.0, 135.0, 134.8, 133.7, 133.4, 129.7, 129.4, 128.5, 127.8, 127.0, 125.4, 121.8, 117.3, 67.4, 60.3, 45.2, 42.6, 21.4, 21.0, 14.2; IR (film) ν_{max} 2963, 2926, 1718, 1683, 1597, 1581, 1489, 1449, 1402, 1358, 1303, 1274, 1230, 1205, 1168, 1140, 1091, 1039, 985, 878, 816, 760, 739, 706, 690, 670, 657, 604, 576, 542 cm^{-1}; HRMS (ESI) calcd for $C_{29}H_{29}NO_5S^+$ $[M + Na]^+$ 526.1659, found 526.1660.

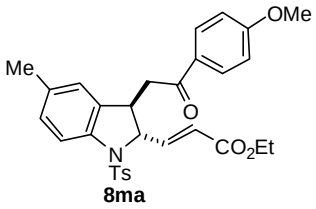
Ethyl (*E*)-3-(3-(2-(2-methoxyphenyl)-2-oxoethyl)-5-methyl-1-tosylindolin-2-yl)-acrylate (8la)



8la

Prepared according to the general procedure as described above in 78%yield. It was purified by flash chromatography (12.5% EtOAc/PE) to afford a white solid. mp = 148 – 150 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.3 Hz, 1H), 7.54 (dd, *J* = 18.6, 8.5 Hz, 4H), 7.19 – 7.06 (m, 2H), 7.02 (d, *J* = 8.1 Hz, 2H), 6.93 – 6.79 (m, 3H), 6.27 (dd, *J* = 15.5, 1.7 Hz, 1H), 4.65 – 4.44 (m, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.89 (s, 3H), 3.38 (m, 1H), 2.69 (dd, *J* = 18.3, 4.0 Hz, 1H), 2.28 (d, *J* = 4.8 Hz, 6H), 1.68 (dd, *J* = 18.2, 10.7 Hz, 1H), 1.27 (t, *J* = 7.0 Hz, 3H).; ^{13}C NMR (75 MHz, DMSO-d_6) δ 199.4, 165.6, 158.6, 146.9, 144.6, 138.0, 134.6, 134.5, 134.2, 133.9, 130.1, 129.9, 129.8, 129.4, 127.2, 127.0, 126.2, 120.9, 120.8, 116.2, 112.7, 67.3, 60.5, 56.0, 50.1, 42.7, 21.2, 20.9, 14.3; IR (film) ν_{max} 2962, 2926, 1717, 1680, 1597, 1486, 1462, 1437, 1397, 1359, 1260, 1167, 1091, 1025, 989, 815, 758, 738, 706, 689, 669, 604, 570, 544 cm^{-1}; HRMS (ESI) calcd for $C_{29}H_{29}NO_5S^+$ $[M + Na]^+$ 556.1764, found 556.1764.

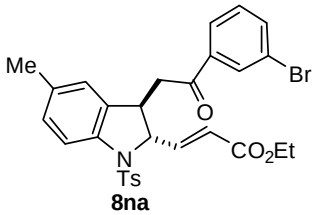
Ethyl (*E*)-3-(3-(2-(4-methoxyphenyl)-2-oxoethyl)-5-methyl-1-tosylindolin-2-yl)-acrylate (8ma)



8ma

Prepared according to the general procedure as described above in 83%yield. It was purified by flash chromatography (12.5% EtOAc/PE) to afford a white solid. mp = 142 – 144 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.58 (m, 2H), 7.52 – 7.43 (m, 3H), 7.18 – 7.07 (m, 3H), 7.06 – 6.97 (m, 4H), 6.07 (dd, *J* = 15.5, 1.7 Hz, 1H), 4.56 – 4.46 (m, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 3.83 (s, 3H), 3.34 (m, 1H), 2.84 (dd, *J* = 18.5, 4.7 Hz, 1H), 2.48 (m, *J* = 3.7, 1.8 Hz, 1H), 2.22 (s, 3H), 2.20 (s, 3H), 1.76 (dd, *J* = 18.5, 9.6 Hz, 1H), 1.20 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 196.3, 165.6, 163.6, 146.9, 144.9, 138.0, 134.7, 134.4, 133.9, 130.3, 129.4, 129.1, 127.0, 126.4, 121.0, 116.5, 114.1, 67.3, 60.5, 55.9, 44.8, 42.4, 21.3, 20.9, 14.3; IR (film) ν_{max} 2962, 1718, 1672, 1600, 1575, 1511, 1489, 1463, 1421, 1358, 1305, 1262, 1234, 1207, 1168, 1111, 1091,1034, 987, 881, 816, 736, 707, 668, 600, 574, 543 cm^{-1} ; HRMS (ESI) calcd for $C_{29}H_{29}NO_5S^+$ $[M + Na]^+$ 556.1764, found 556.1765.

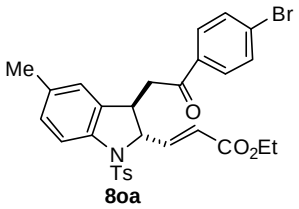
Ethyl (*E*)-3-(3-(2-(3-bromophenyl)-2-oxoethyl)-5-methyl-1-tosylindolin-2-yl)acrylate (8na)



8na

Prepared according to the general procedure as described above in 61%yield. It was purified by flash chromatography (10% EtOAc/PE) to afford a pale yellow solid. mp = 160 – 162 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76 – 7.63 (m, 3H), 7.59 – 7.45 (m, 3H), 7.39 – 7.28 (m, 1H), 7.18 – 7.07 (m, 2H), 7.02 (m, 2H), 6.84 (m, 1H), 6.27 (dd, *J* = 15.5, 1.7 Hz, 1H), 4.67 – 4.41 (m, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.36 (m, 1H), 2.72 (dd, *J* = 18.7, 3.9 Hz, 1H), 2.27 (d, *J* = 8.6 Hz, 6H), 1.67 (dd, *J* = 18.8, 10.6 Hz, 1H), 1.27 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.1, 166.1, 145.3, 143.9, 138.3, 135.0, 134.9, 134.7, 133.5, 131.8, 129.7, 129.5, 129.2, 128.6, 127.0, 125.4, 121.9, 117.3, 67.3, 60.3, 45.1, 42.5, 21.5, 21., 14.2; IR (film) ν_{max} 2981, 1716, 1684, 1586, 1488, 1399, 1359, 1303, 1274, 1229, 1203, 1168, 1091, 1072, 1038, 1011, 987, 816, 737, 707, 666, 605, 576, 542 cm^{-1}; HRMS (ESI) calcd for $C_{29}H_{28}BrNO_5S^+$ $[M + Na]^+$604.0764, found 604.0768.

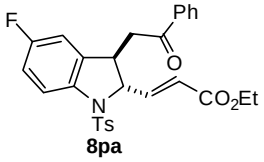
Ethyl (*E*)-3-(3-(2-(4-bromophenyl)-2-oxoethyl)-5-methyl-1-tosylindolin-2-yl)acrylate (8oa)



8oa

Prepared according to the general procedure as described above in 83%yield. It was purified by flash chromatography (10% EtOAc/PE) to afford a pale yellow solid. mp = 160 – 162 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.66 (m, 1H), 7.61 – 7.54 (m, 2H), 7.53 – 7.41 (m, 4H), 7.19 – 7.07 (m, 2H), 7.01 (d, *J* = 8.0 Hz, 2H), 6.85 (s, 1H), 6.27 (dd, *J* = 15.5, 1.7 Hz, 1H), 4.56 – 4.45 (m, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.37 (dd, *J* = 10.4, 2.2 Hz, 1H), 2.73 (dd, *J* = 18.7, 4.0 Hz, 1H), 2.29 (s, 3H), 2.26 (s, 3H), 1.66 (dd, *J* = 18.7, 10.6 Hz, 1H), 1.27 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.1, 166.1, 145.3, 143.9, 138.3, 135.0, 134.9, 134.7, 133.5, 131.8, 129.7, 129.5, 129.2, 128.6, 127.0, 125.4, 121.9, 117.3, 67.3, 60.4, 45.1, 42.5, 21.5, 21.0, 14.2. IR (film) ν_{max} 2981, 1716, 1684, 1586, 1488, 1399, 1359, 1303, 1274, 1229, 1203, 1168, 1091, 1071, 1038, 1011, 987, 816, 737, 707, 666, 605, 576, 542 cm^{-1}; HRMS (ESI) calcd for $C_{29}H_{28}BrNO_5S^+$ $[M + Na]^+$604.0764, found 604.0768.

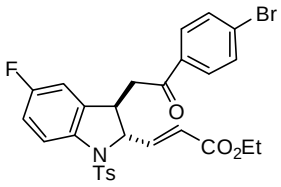
Ethyl (*E*)-3-(5-fluoro-3-(2-oxo-2-phenylethyl)-1-tosylindolin-2-yl)acrylate (8pa)



8pa

Prepared according to the general procedure as described above in 67%yield. It was purified by flash chromatography (10% EtOAc/PE) to afford a white solid. mp = 163 – 165 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.74 (dd, *J* = 8.9, 4.6 Hz, 1H), 7.63 – 7.54 (m, 3H), 7.52 – 7.38 (m, 4H), 7.13 (dd, *J* = 15.5, 4.7 Hz, 1H), 7.06 – 6.94 (m, 3H), 6.77 (dd, *J* = 8.1, 2.5 Hz, 1H), 6.28 (dd, *J* = 15.5, 1.7 Hz, 1H), 4.64 – 4.51 (m, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.41 (d, *J* = 7.7 Hz, 1H), 2.72 (dd, *J* = 18.5, 4.3 Hz, 1H), 2.25 (s, 3H), 1.72 (dd, *J* = 18.6, 10.4 Hz, 1H), 1.28 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.7, 166.1, 162.1, 158.8, 145.0, 144.3, 136.8, 135.8, 135.8, 135.7, 134.6, 133.6, 129.9, 128.6, 127.7, 127.0, 122.1, 118.8, 118.7, 115.7, 115.4, 112.3, 112.0, 67.6, 60.4, 44.9, 42.6, 21.4, 14.2; IR (film) ν_{max} 3063, 2982, 1717, 1683, 1598, 1482, 1449, 1401, 1360,1303, 1275, 1234, 1204, 1168, 1136, 1091, 1038, 986, 926, 868, 817, 749, 706, 690, 671, 657, 604, 578, 542 cm^{-1}; HRMS (ESI) calcd for $C_{28}H_{26}FNO_5S^+$ $[M + Na]^+$ 530.1408, found 530.1404.

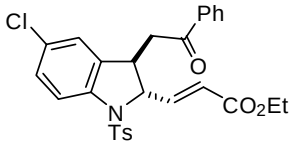
Ethyl (*E*)-3-(3-(2-(4-bromophenyl)-2-oxoethyl)-5-fluoro-1-tosylindolin-2-yl)acrylate (8qa)



8qa

Prepared according to the general procedure as described above in 85%yield. It was purified by flash chromatography (10% EtOAc/PE) to afford a pale yellow solid. mp = 178 – 180 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.73 (dd, *J* = 8.9, 4.6 Hz, 1H), 7.61 – 7.52 (m, 2H), 7.52 – 7.40 (m, 4H), 7.10 (dd, *J* = 15.5, 4.7 Hz, 1H), 7.06 – 6.95 (m, 3H), 6.76 (dd, *J* = 7.9, 2.6 Hz, 1H), 6.26 (dd, *J* = 15.5, 1.6 Hz, 1H), 4.59 – 4.44 (m, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.39 (dd, *J* = 10.0, 2.8 Hz, 1H), 2.68 (dd, *J* = 18.6, 4.3 Hz, 1H), 2.27 (s, 3H), 1.70 (dd, *J* = 18.6, 10.3 Hz, 1H), 1.27 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.7, 166.0, 162.0, 158.8, 144.8, 144.3, 136.7, 135.6, 135.5, 134.6, 134.5, 131.9, 129.8, 129.2, 128.8, 127.0, 122.1, 118.8, 118.7, 115.8, 115.5, 112.3, 112.0, 67.6, 60.5, 44.8, 42.5, 29.6, 21.5, 14.1; IR (film) ν_{max} 2982, 1716, 1685, 1586, 1483, 1398, 1361, 1303, 1275, 1168, 1136, 1092, 1071, 1031, 987, 816, 756, 707, 665, 605, 578, 542 cm^{-1}; HRMS (ESI) calcd for $C_{28}H_{26}BrFNO_5S^+$ [M + Na]$^+$608.0513, found 608.0508.

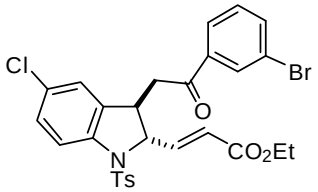
Ethyl (*E*)-3-(5-chloro-3-(2-oxo-2-phenylethyl)-1-tosylindolin-2-yl)acrylate (8ra)



8ra

Prepared according to the general procedure as described above in 70%yield. It was purified by flash chromatography (10% EtOAc/PE) to afford a white solid. mp = 168 – 170 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.72 (m, 1H), 7.65 – 7.56 (m, 3H), 7.53 – 7.39 (m, 4H), 7.32 – 7.23 (m, 1H), 7.13 (dd, 1H), 7.08 – 6.98 (m, 3H), 6.27 (dd, *J* = 15.5, 1.7 Hz, 1H), 4.60 – 4.54 (m, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.47 – 3.37 (m, 1H), 2.75 (dd, *J* = 18.6, 4.2 Hz, 1H), 2.24 (s, 3H), 1.73 (dd, *J* = 18.6, 10.5 Hz, 1H), 1.28 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.0, 144.9, 144.5, 139.5, 135.8, 135.6, 134.6, 133.6, 130.4, 129.9, 128.9, 128.6, 127.8, 127.0, 125.3, 122.1, 118.5, 67.6, 60.5, 45.0, 42.5, 21.5, 14.2; IR (film) ν_{max} 3064, 2981, 1717, 1683, 1597, 1468, 1449, 1402, 1361, 1304, 1274, 1216, 1168, 1115, 1090, 1037, 984, 817, 758, 736, 690, 667, 595, 541 cm^{-1}; HRMS (ESI) calcd for $C_{28}H_{26}ClNO_5S^+$ [M + Na]$^+$ 546.1112, found 546.1110.

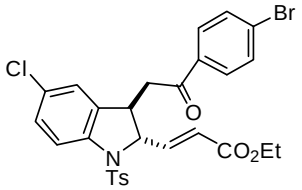
Ethyl (*E*)-3-(3-(2-(3-bromophenyl)-2-oxoethyl)-5-chloro-1-tosylindolin-2-yl)acrylate (8sa)



8sa

Prepared according to the general procedure as described above in 60%yield. It was purified by flash chromatography (11% EtOAc/PE) to afford a pale yellow solid. mp = 158 – 160 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75 – 7.66 (m, 3H), 7.60 – 7.44 (m, 3H), 7.38 – 7.26 (m, 2H), 7.17 – 6.99 (m, 4H), 6.25 (dd, *J* = 15.5, 1.7 Hz, 1H), 4.59 – 4.49 (m, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.47 – 3.33 (m, 1H), 2.71 (dd, *J* = 18.7, 4.1 Hz, 1H), 2.26 (s, 3H), 1.71 (dd, *J* = 18.8, 10.4 Hz, 1H), 1.26 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.6, 166.0, 144.7, 144.4, 139.5, 135.3, 134.7, 134.5, 131.9, 130.4, 129.9, 129.2, 129.0, 128.9, 127.0, 125.2, 122.2, 118.4, 67.5, 60.5, 44.9, 42.4, 21.5, 14.2; IR (film) ν_{max} 1717, 1687, 1597, 1566, 1470, 1422, 1361, 1304, 1275, 1261, 1211, 1167, 1115, 1090, 1036, 816, 764, 750, 666, 592, 542 cm^{-1}; HRMS (ESI) calcd for $C_{28}H_{25}BrClNO_5S^+$ $[M + Na]^+$ 626.0198, found 626.0198.

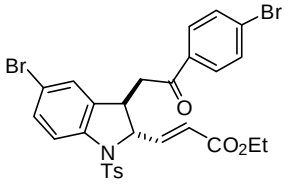
Ethyl (*E*)-3-(3-(2-(4-bromophenyl)-2-oxoethyl)-5-chloro-1-tosylindolin-2-yl)acrylate (8ta)



8ta

Prepared according to the general procedure as described above in 67%yield. It was purified by flash chromatography (11% EtOAc/PE) to afford a pale yellow solid. mp = 198 – 200 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.6 Hz, 1H), 7.62 – 7.54 (m, 2H), 7.52 – 7.41 (m, 3H), 7.32 – 7.26 (m, 1H), 7.15 – 6.99 (m, 4H), 6.24 (dd, *J* = 15.5, 1.6 Hz, 1H), 4.61 – 4.46 (m, 1H), 4.18 (q, *J* = 7.1 Hz, 1H), 3.40 (d, *J* = 7.9 Hz, 1H), 2.70 (dd, *J* = 18.6, 4.1 Hz, 1H), 2.26 (s, 3H), 1.71 (dd, *J* = 18.6, 10.4 Hz, 1H), 1.27 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.6, 166.0, 144.7, 144.4, 139.5, 135.3, 134.7, 134.5, 131.9, 130.4, 129.9, 129.2, 129.0, 128.9, 127.0, 125.2, 122.2, 118.5, 67.5, 60.5, 44.9, 42.4, 21.5 14.2; IR (film) ν_{max} 2980, 1717, 1685, 1585, 1470, 1399, 1362, 1304, 1274, 1214, 1167, 1115, 1091, 1071, 1036, 987, 873, 816, 738, 666, 595, 542 cm^{-1}; HRMS (ESI) calcd for $C_{28}H_{25}BrClNO_5S^+$ $[M + Na]^+$ 626.0198, found 626.0198.

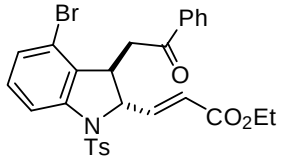
Ethyl (*E*)-3-(5-bromo-3-(2-(4-bromophenyl)-2-oxoethyl)-1-tosylindolin-2-yl)acrylate (8ua)



8ua

Prepared according to the general procedure as described above in 69%yield. It was purified by flash chromatography (11% EtOAc/PE) to afford a pale yellow solid. mp = 203 – 205 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.6 Hz, 1H), 7.58 (m, 2H), 7.53 – 7.38 (m, 4H), 7.18 (d, *J* = 1.7 Hz, 1H), 7.09 (m, 1H), 7.03 (m, 1H), 6.24 (dd, *J* = 15.5, 1.6 Hz, 1H), 4.61 – 4.46 (m, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.40 (d, *J* = 7.7 Hz, 1H), 2.71 (dd, *J* = 18.7, 4.1 Hz, 1H), 2.26 (s, 2H), 1.70 (dd, *J* = 18.7, 10.5 Hz, 1H), 1.27 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.6, 165.9, 144.6, 144.4, 140.0, 135.7, 134.7, 134.5, 131.9, 129.9, 129.2, 128.8, 128.1, 127.0, 122.2, 118.8, 117.9, 67.4, 60.5, 44.9, 42.4, 21.5, 14.2; IR (film) ν_{max} 2981, 1717, 1684, 1585, 1468, 1399, 1362, 1304, 1274, 1213, 1167, 1115, 1092, 1070, 1031, 987, 815, 737, 708, 666, 585 cm^{-1}; HRMS (ESI) calcd for $C_{28}H_{25}Br_2NO_5S^+$ $[M + Na]^+$ 669.9694, found 669.9690.

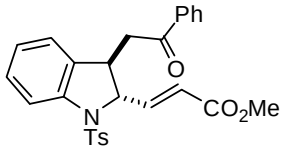
Ehyl (*E*)-3-(4-bromo-3-(2-oxo-2-phenylethyl)-1-tosylindolin-2-yl)acrylate (8ua)



8va

Prepared according to the general procedure as described above in 55%yield. It was purified by flash chromatography (11% EtOAc/PE) to afford a pale yellow solid. mp = 158 – 160 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.73 (dd, *J* = 8.9, 4.6 Hz, 1H), 7.61 – 7.52 (m, 2H), 7.52 – 7.40 (m, 4H), 7.10 (dd, *J* = 15.5, 4.7 Hz, 1H), 7.06 – 6.95 (m, 3H), 6.76 (dd, *J* = 7.9, 2.6 Hz, 1H), 6.26 (dd, *J* = 15.5, 1.6 Hz, 1H), 4.59 – 4.44 (m, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.39 (dd, *J* = 10.0, 2.8 Hz, 1H), 2.68 (dd, *J* = 18.6, 4.3 Hz, 1H), 2.27 (s, 3H), 1.70 (dd, *J* = 18.6, 10.3 Hz, 1H), 1.27 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.6, 166.0, 144.7, 144.4, 139.5, 135.3, 134.7, 134.5, 131.9, 130.4, 129.9, 129.2, 129.0, 128.9, 127.0, 125.2, 122.2, 118.5, 67.5, 60.5, 44.9, 42.4, 21.5, 14.2; IR (film) ν_{max} 1717, 1687, 1597, 1566, 1470, 1421, 1361, 1304, 1275, 1261, 1211, 1167, 1115, 1090, 1036, 816, 764, 750, 666, 592, 542 cm^{-1}; HRMS (ESI) calcd for $C_{28}H_{25}BrClNO_5S^+$ $[M + Na]^+$ 626.0198, found 626.0198.

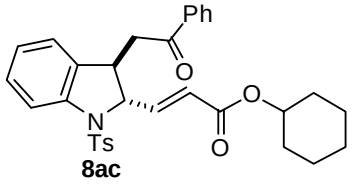
Methyl (*E*)-3-(3-(2-oxo-2-phenylethyl)-1-tosylindolin-2-yl)acrylate (8ab)



8ab

Prepared according to the general procedure as described above in 59%yield. It was purified by flash chromatography (11% EtOAc/PE) to afford a white solid. mp = 182 – 185 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.2 Hz, 1H), 7.65 – 7.54 (m, 3H), 7.53 – 7.38 (m, 4H), 7.36 – 7.24 (m, 1H), 7.18 (dd, *J* = 15.5, 4.8 Hz, 1H), 7.10 – 7.03 (m, 2H), 6.99 (d, *J* = 8.0 Hz, 2H), 6.30 (dd, *J* = 15.5, 1.7 Hz, 1H), 4.58 – 4.50 (m, 1H), 3.71 (s, 3H), 3.48 – 3.37 (m, 1H), 2.79 (dd, *J* = 18.6, 4.0 Hz, 1H), 2.23 (s, 3H), 1.73 (dd, *J* = 18.6, 10.7 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.1, 166.6, 145.8, 144.1, 140.7, 135.9, 134.8, 133.5, 133.4, 129.7, 128.7, 128.5, 127.7, 126.9, 125.2, 124.9, 121.4, 117.4, 67.2, 51.5, 45.2, 42.6, 21.4; IR (film) ν_{max} 1723, 1682, 1597, 1477, 1461, 1449, 1359, 1306, 1276, 1216, 1169, 1092, 1028, 987, 815, 756, 708, 690, 671, 661, 623, 586, 572, 540.31 cm^{-1}; HRMS (ESI) calcd for $C_{27}H_{25}NO_5S^+$ $[M + Na]^+$ 498.1346, found 498.1343.

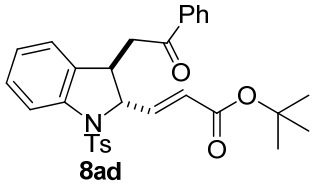
Cyclohexyl (*E*)-3-(3-(2-oxo-2-phenylethyl)-1-tosylindolin-2-yl)acrylate (8ac)



8ac

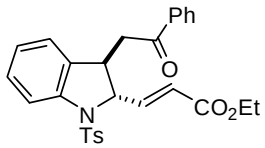
Prepared according to the general procedure as described above in 65%yield. It was purified by flash chromatography (11% EtOAc/PE) to afford a white solid. mp = 162 – 165 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.1 Hz, 1H), 7.64 – 7.54 (m, 3H), 7.53 – 7.38 (m, 4H), 7.35 – 7.27 (m, 1H), 7.16 – 7.03 (m, 3H), 6.99 (d, *J* = 8.0 Hz, 2H), 6.26 (dd, *J* = 15.5, 1.7 Hz, 1H), 4.86 – 4.69 (m, 1H), 4.62 – 4.47 (m, 1H), 3.55 – 3.34 (m, 1H), 2.76 (dd, *J* = 18.6, 4.1 Hz, 1H), 2.23 (s, 3H), 1.92 – 1.78 (m, 2H), 1.78 – 1.68 (m, 2H), 1.61 (s, 1H), 1.58 – 1.16 (m, 7H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.1, 165.6, 145.0, 144.1, 140.7, 135.9, 134.8, 133.7, 133.4, 129.7, 128.7, 128.5, 127.7, 126.9, 125.1, 124.9, 122.4, 117.4, 72.7, 67.3, 45.2, 42.6, 31.6, 25.3, 23.7, 21.4; IR (film) ν_{max} 2938, 2860, 1714, 1683, 1597, 1478, 1450, 1361, 1260, 1216, 1170, 1092, 1017, 986, 932, 814, 756, 708, 690, 670, 662, 626, 571, 542 cm^{-1}; HRMS (ESI) calcd for $C_{32}H_{33}NO_5S^+$ $[M + Na]^+$ 566.1972, found 566.1963.

***tert*-Butyl (E)-3-(3-(2-oxo-2-phenylethyl)-1-tosylindolin-2-yl)acrylate (8ad)**

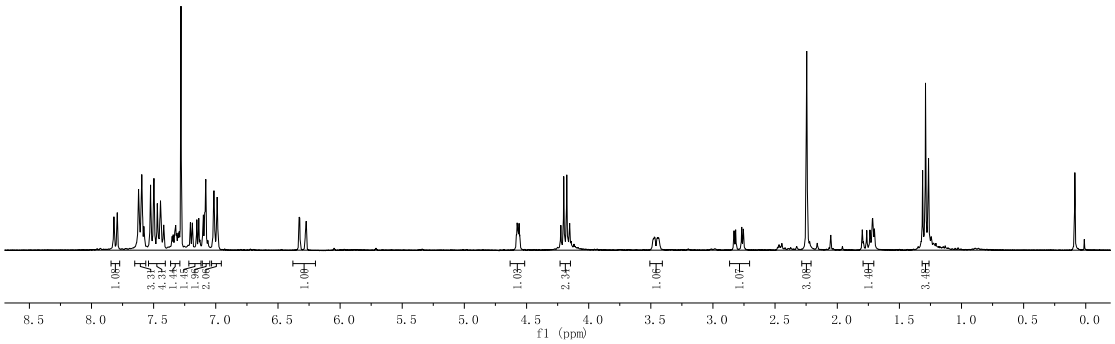


8ad

Prepared according to the general procedure as described above in 68%yield. It was purified by flash chromatography (11% EtOAc/PE) to afford a white solid. mp = 171 – 173 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79 (m, 1H), 7.64 – 7.54 (m, 3H), 7.54 – 7.39 (m, 4H), 7.35 – 7.26 (m, 1H), 7.10 – 7.06 (m, 2H), 7.06 – 6.96 (m, 3H), 6.20 (dd, *J* = 15.5, 1.7 Hz, 1H), 4.54 (dt, *J* = 4.7, 1.8 Hz, 1H), 3.51 – 3.37 (m, 1H), 2.76 (dd, *J* = 18.6, 4.2 Hz, 1H), 2.23 (s, 3H), 1.74 (dd, *J* = 18.6, 10.5 Hz, 1H), 1.47 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.0, 165.5, 144.2, 144.1, 140.8, 136.0, 134.9, 133.8, 133.4, 129.7, 128.7, 128.5, 127.7, 126.9, 125.1, 125.0, 123.6, 117.4, 80.4, 77.4, 77.0, 76.6, 67.3, 45.2, 42.6, 28.0, 21.4; IR (film) ν_{max} 2978, 2932, 1711, 1683, 1597, 1477, 1461, 1450, 1393, 1361, 1310, 1255, 1216, 1168, 1092, 1027, 984, 931, 902, 848, 815, 757, 738, 707, 690, 670, 661, 627, 587, 571, 541 cm^{-1}; HRMS (ESI) calcd for $C_{30}H_{31}NO_5S^+$ $[M + Na]^+$ 540.1815, found 540.1809.


Ph
O
CO2Et
N
Ts

8aa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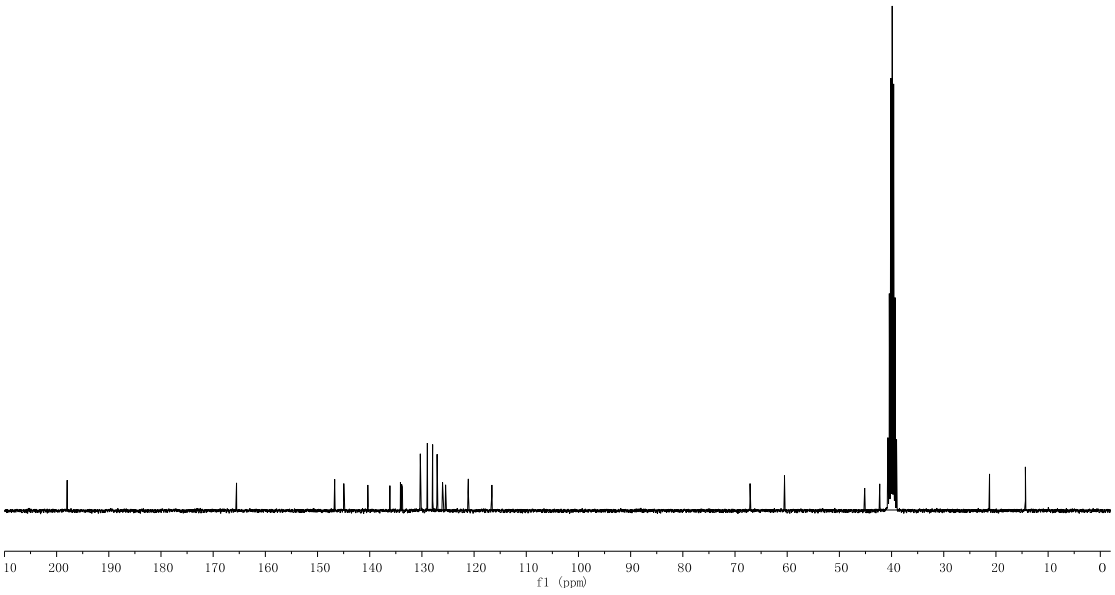
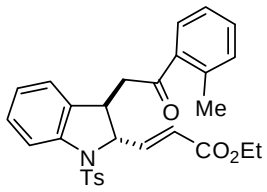
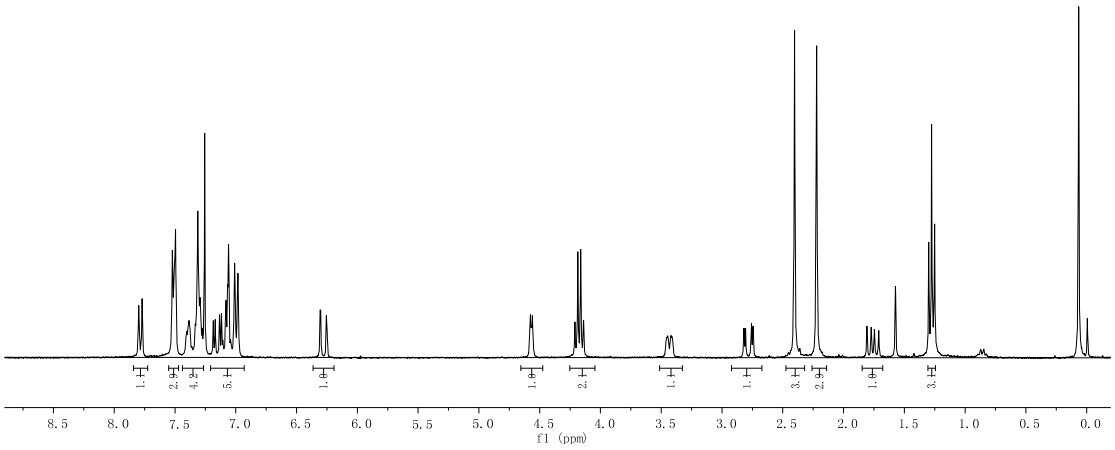
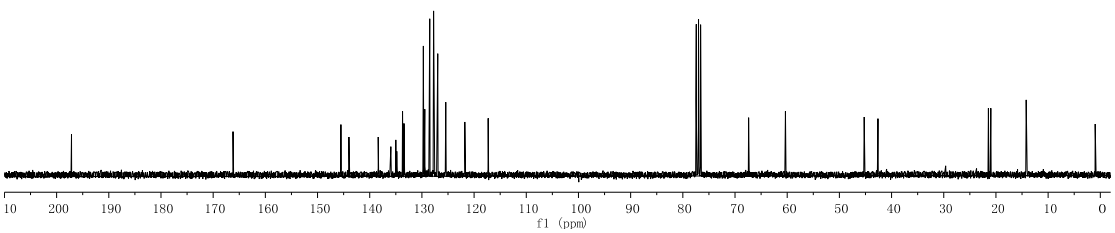
3.37
4.37
1.45
1.45
2.00
1.00
1.03
2.34
1.06
1.07
3.00
1.40
3.48
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

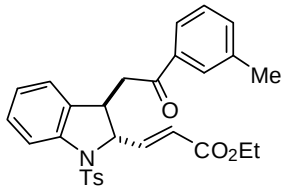

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



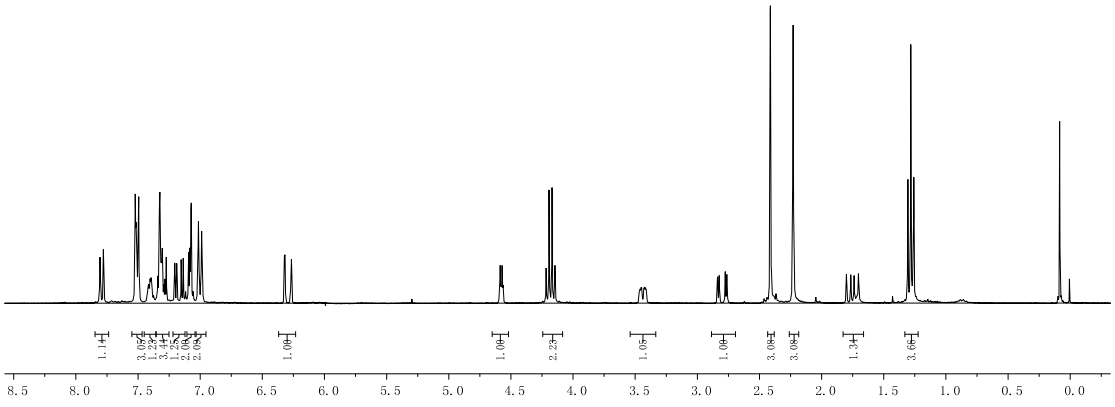
8ba

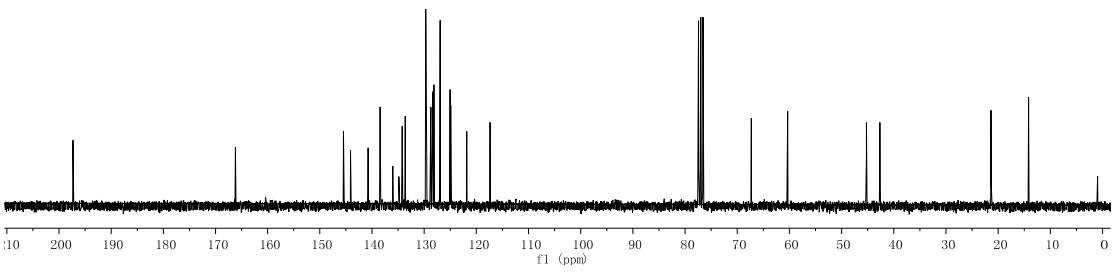


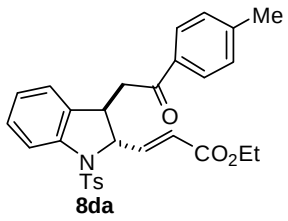



Me
O
N
Ts
CO2Et

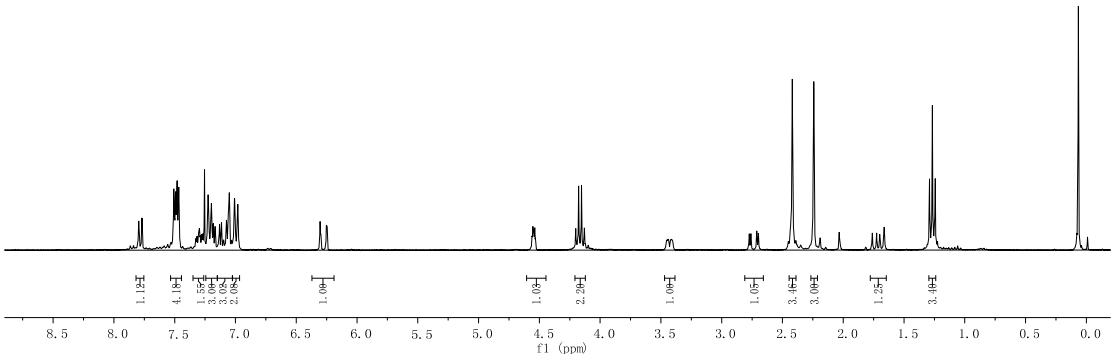
8ca


8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Me
O
N
Ts
CO2Et

8da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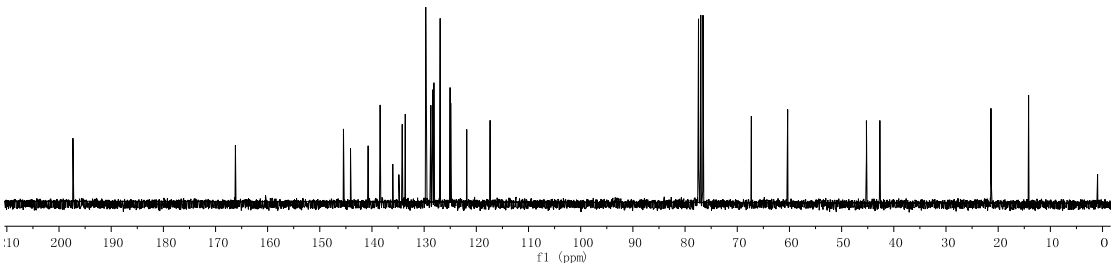
4.18H
1.85H
3.09H
2.08H
1.00H
1.03H
2.29H
1.00H
1.05H
3.46H
3.00H
1.25H
3.40H
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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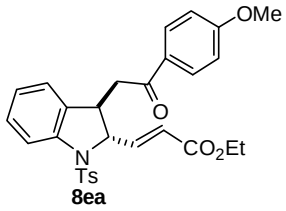
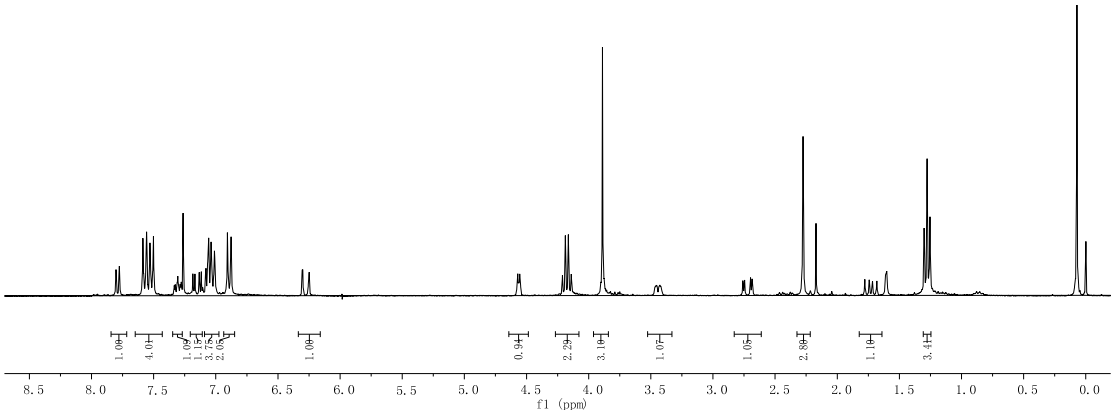
f1 (ppm)


OMe
O
CO2Et
N
Ts

8ea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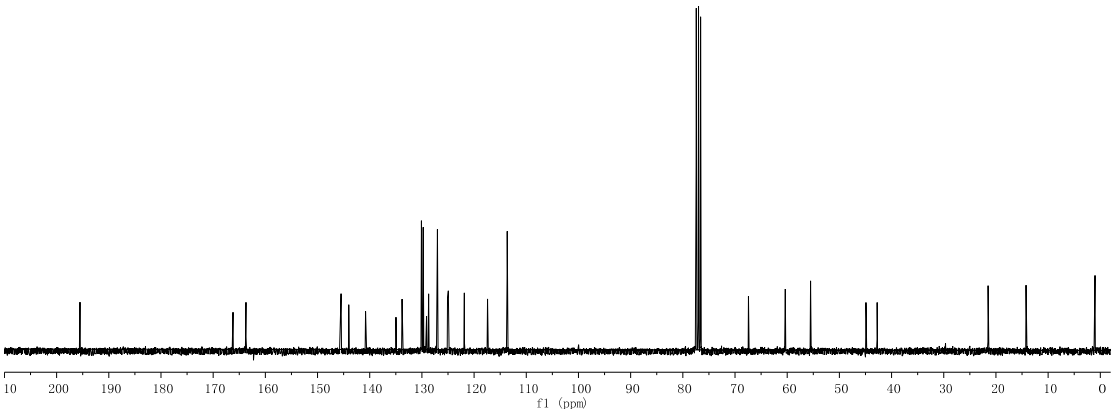
1.05
1.75
3.76
2.05
1.00
0.94
2.29
3.10
1.07
1.06
2.80
1.10
3.44
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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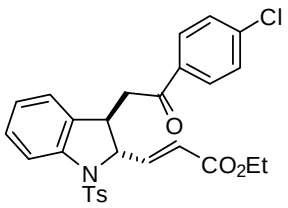
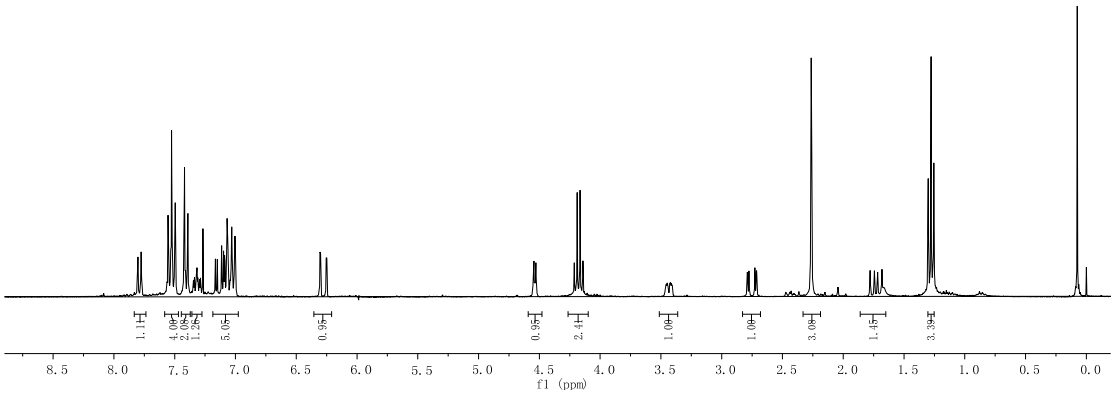
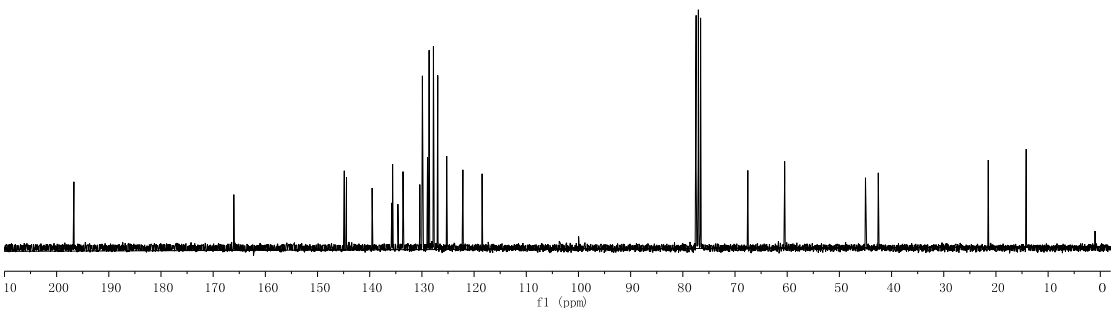
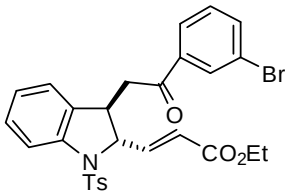
f1 (ppm)


Cl
O
N
Ts
CO2Et

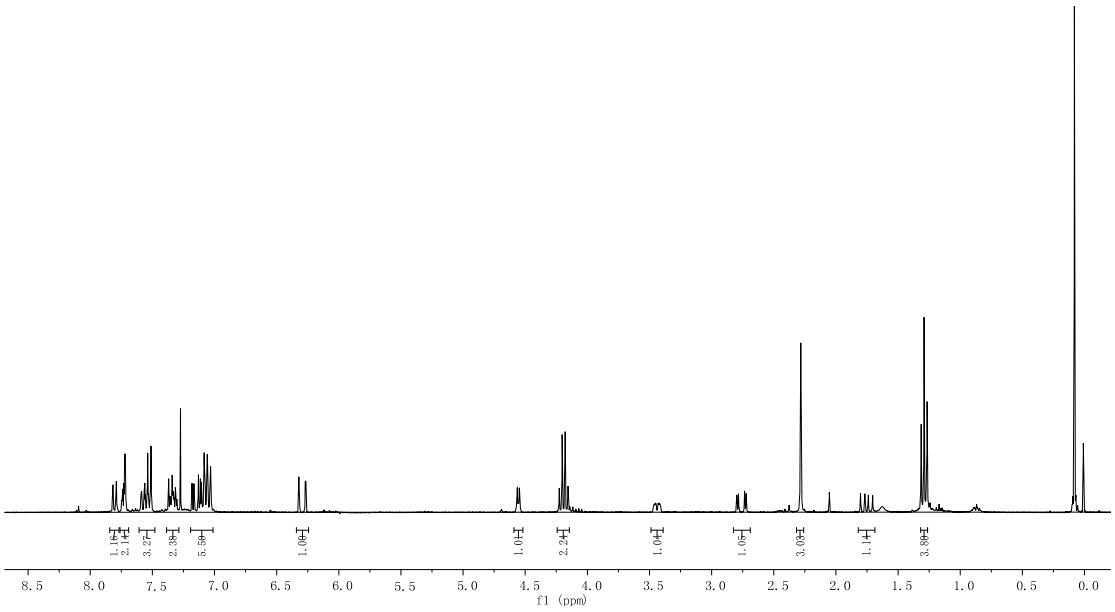
8fa

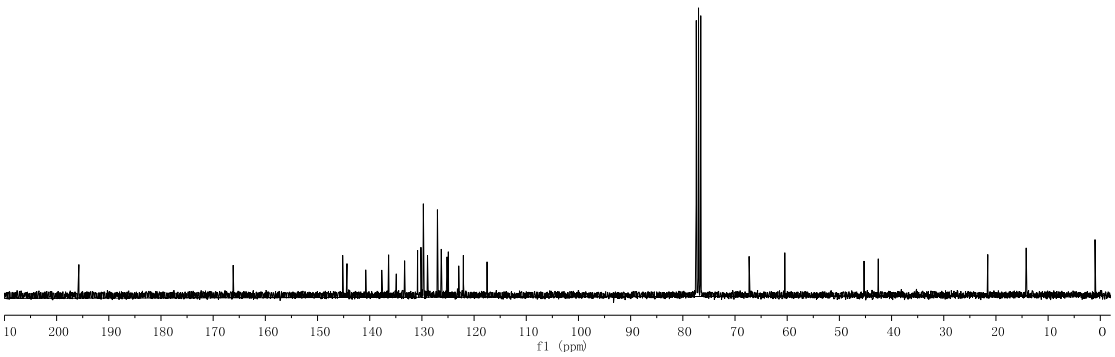

1.11
4.08
2.08
1.25
5.05
0.95
0.95
2.41
1.09
1.09
3.09
1.45
3.39
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

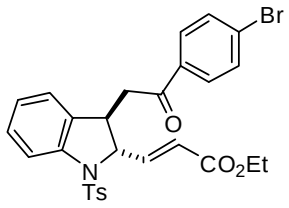

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Br
O
CO2Et
N
Ts

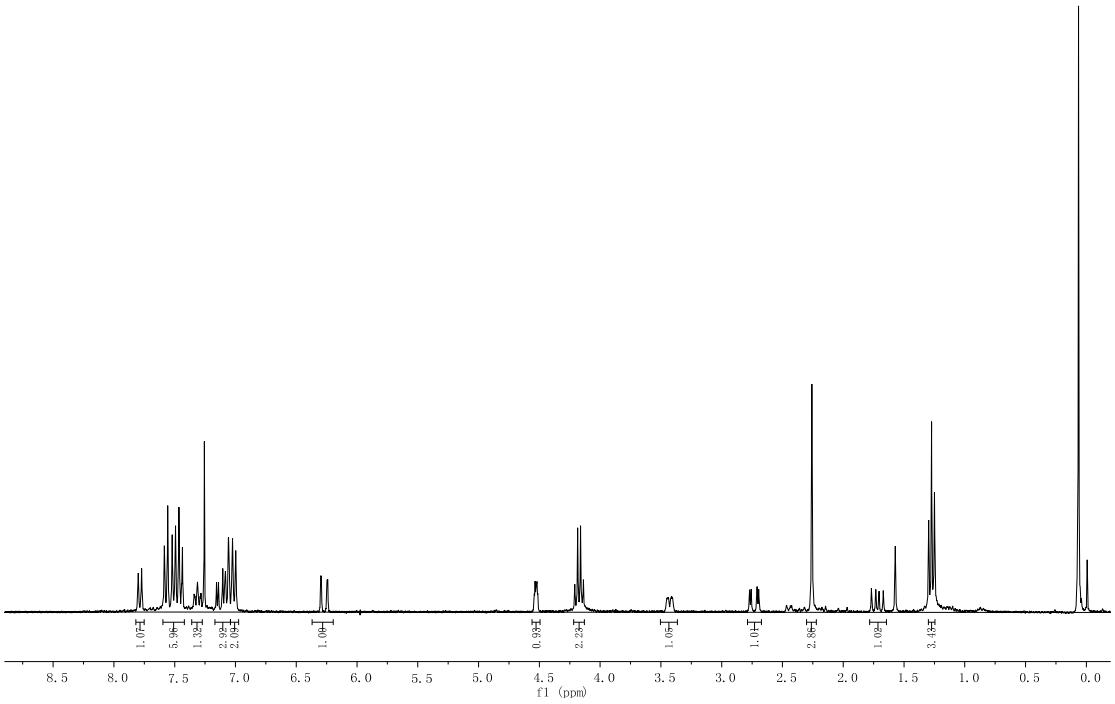
8ga

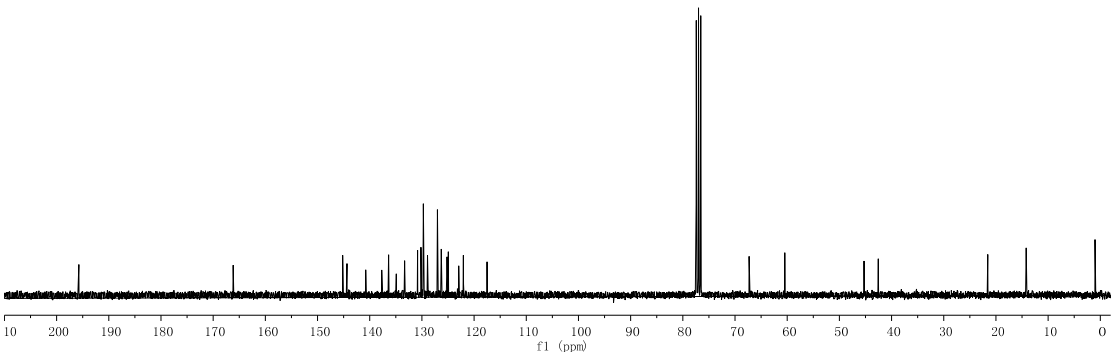

1.16
2.14
3.27
2.38
5.58
1.00
1.04
2.24
1.04
1.05
3.03
1.14
3.80
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

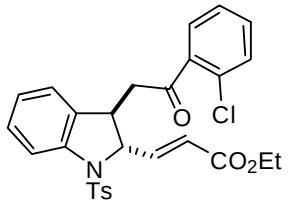

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Br
O
N
Ts
CO2Et

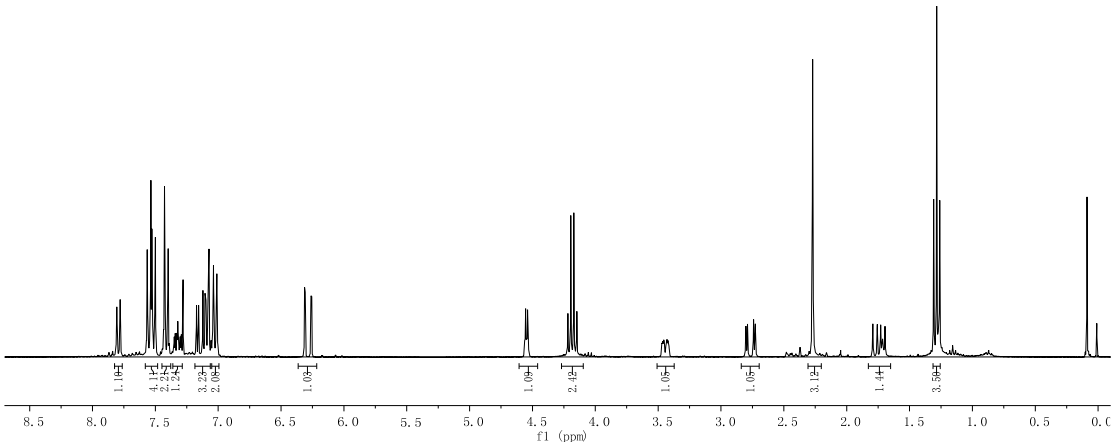
8ha

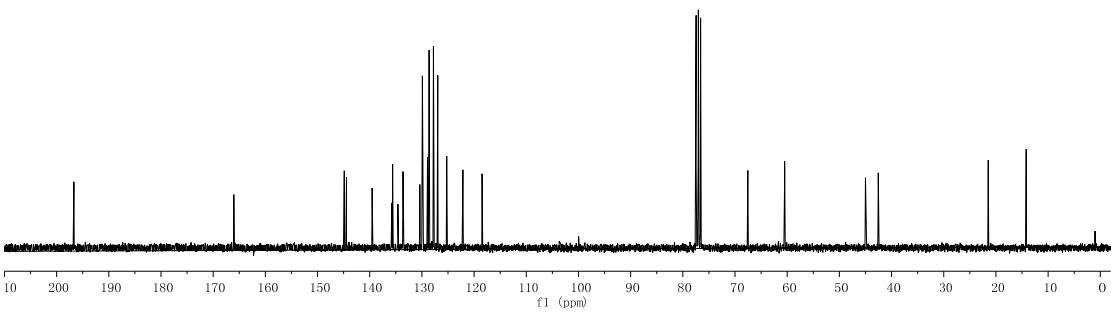

1.07
5.96
1.32
2.99
2.09
1.09
0.93
2.23
1.05
1.01
2.86
1.09
3.43
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

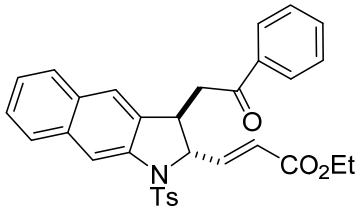

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



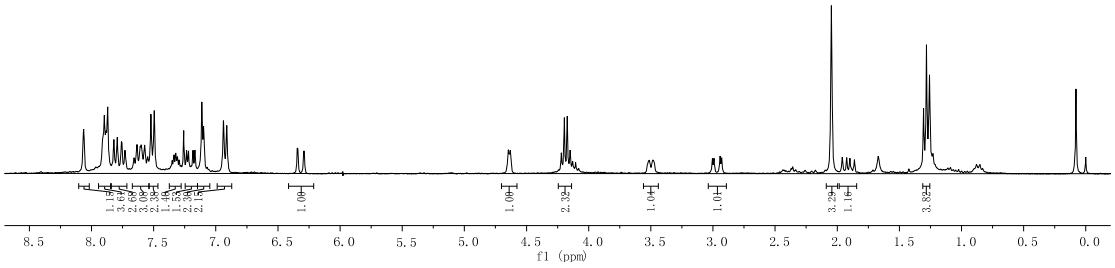
8ia

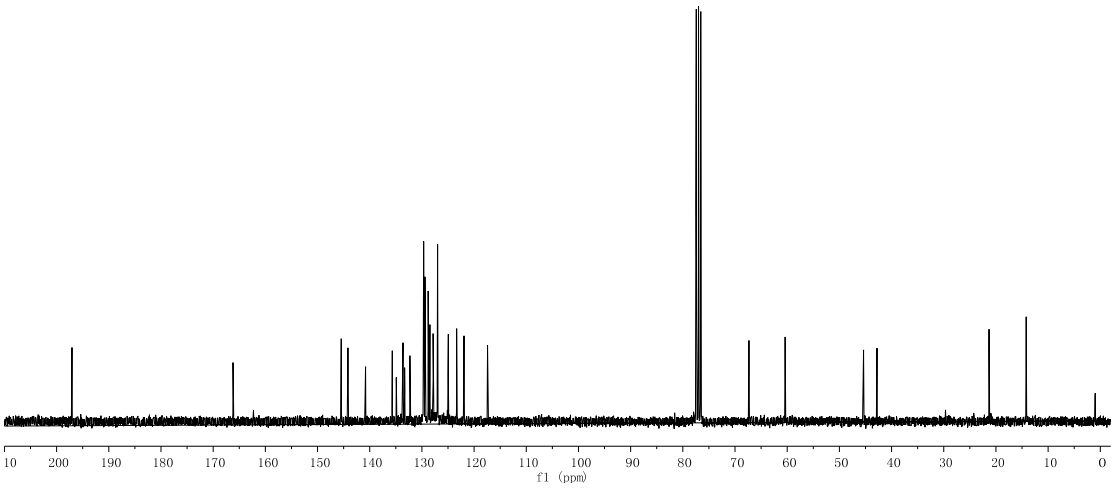





O
CO2Et
N
Ts

8ja


1.00
1.04
1.04
2.32
1.04
1.01
3.23
1.16
3.82
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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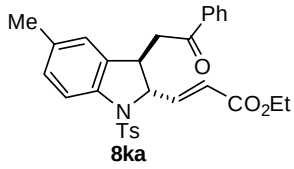
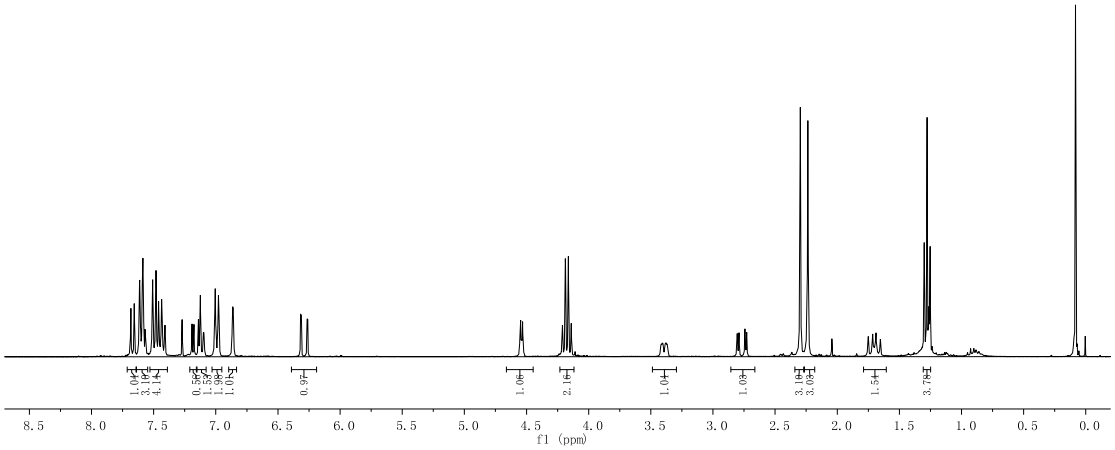
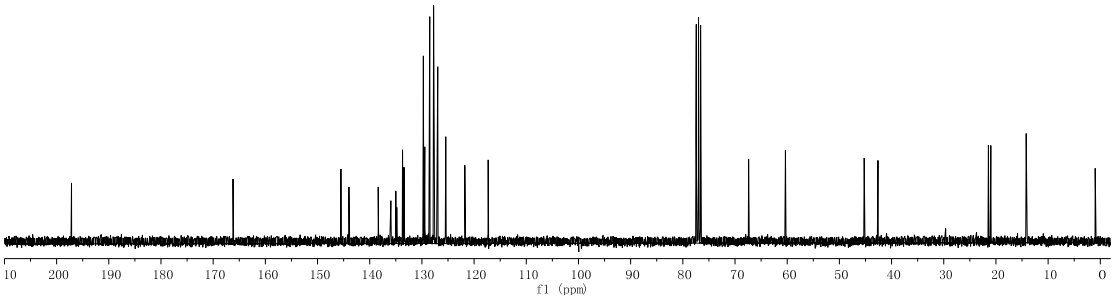
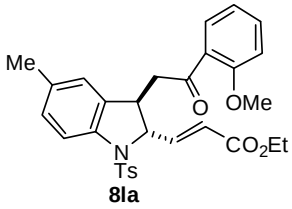
f1 (ppm)


Me
Ph
O
N
Ts
CO2Et

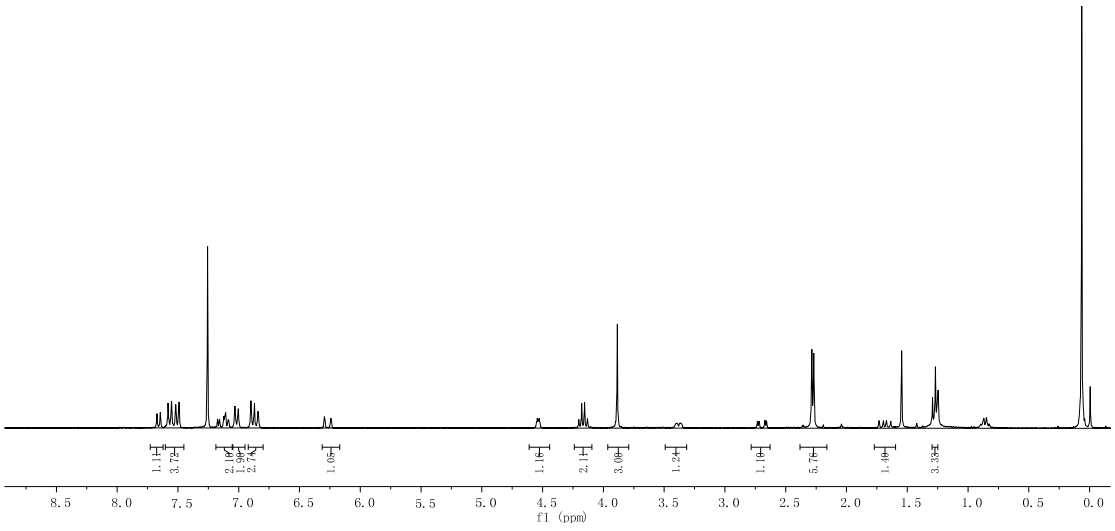
8ka

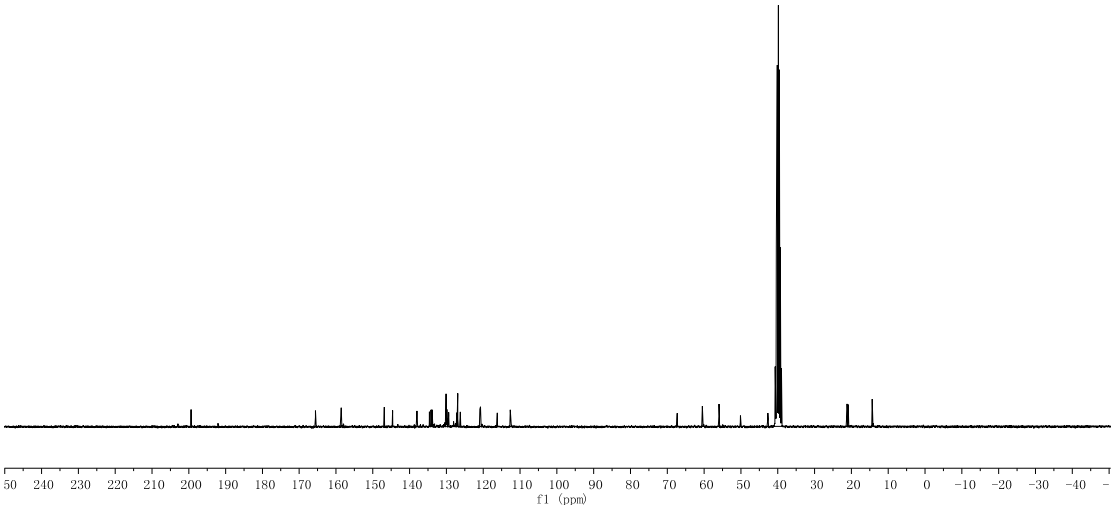

1.04
3.18
4.14
0.58
1.55
1.98
1.10
0.94
1.06
2.16
1.04
1.03
3.10
3.00
1.54
3.78
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

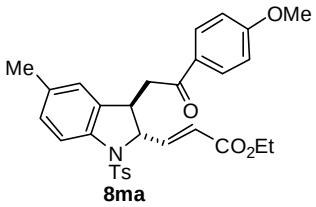

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Me
O
OMe
N
Ts
CO2Et

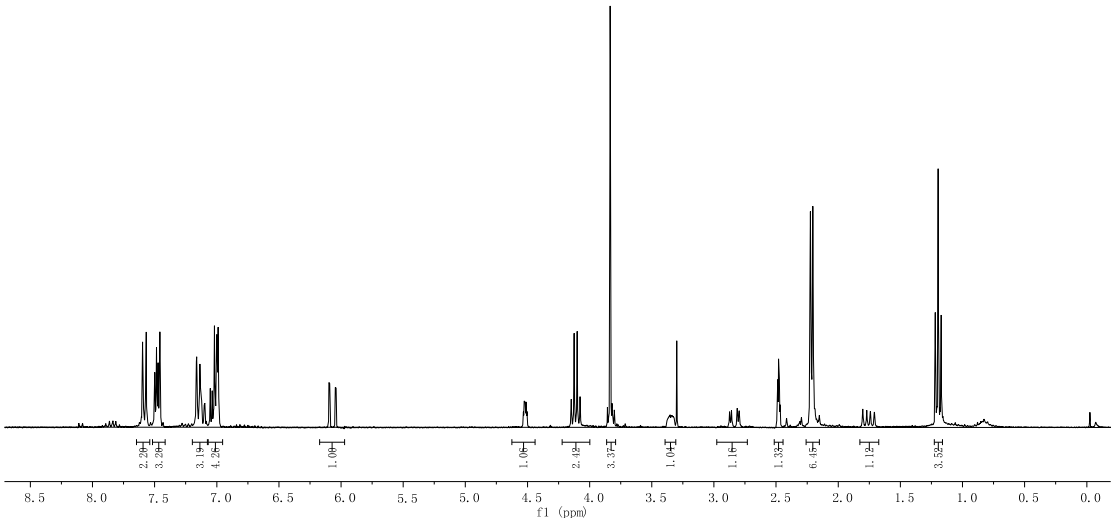
8la

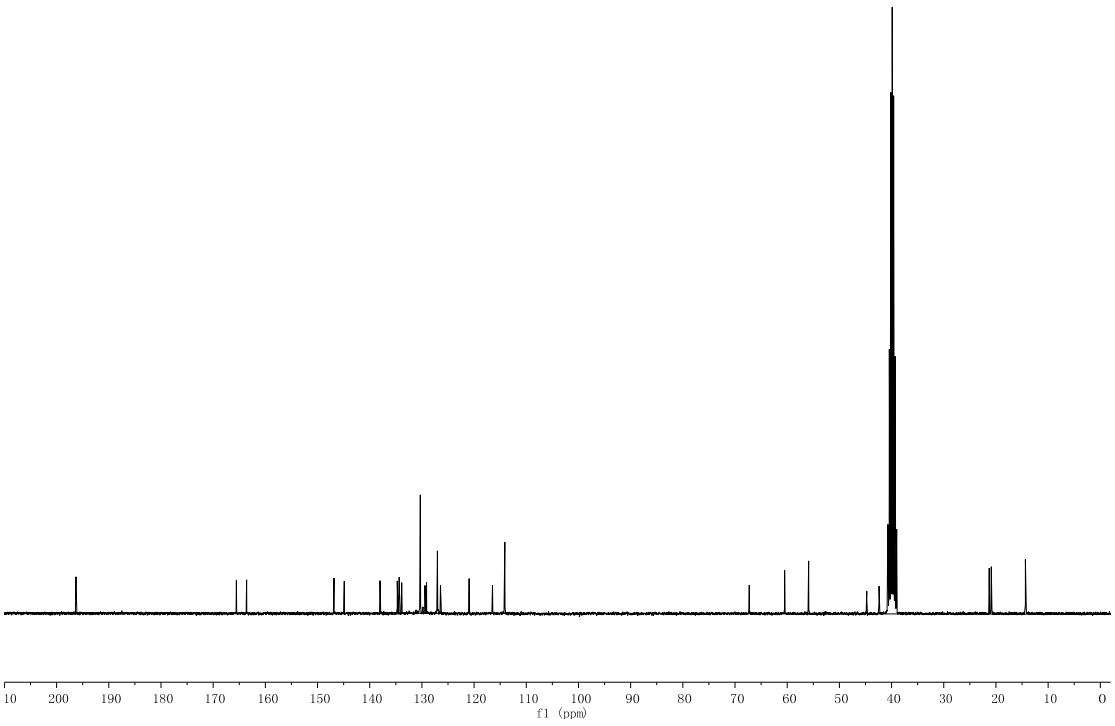

1.11
3.72
2.10
1.94
2.24
1.05
1.16
2.11
3.00
1.24
1.10
5.76
1.10
3.33
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

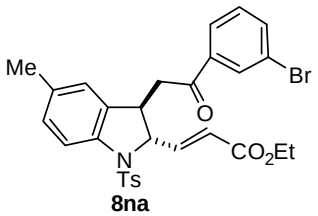

50 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)


OMe
Me
O
CO2Et
N
Ts

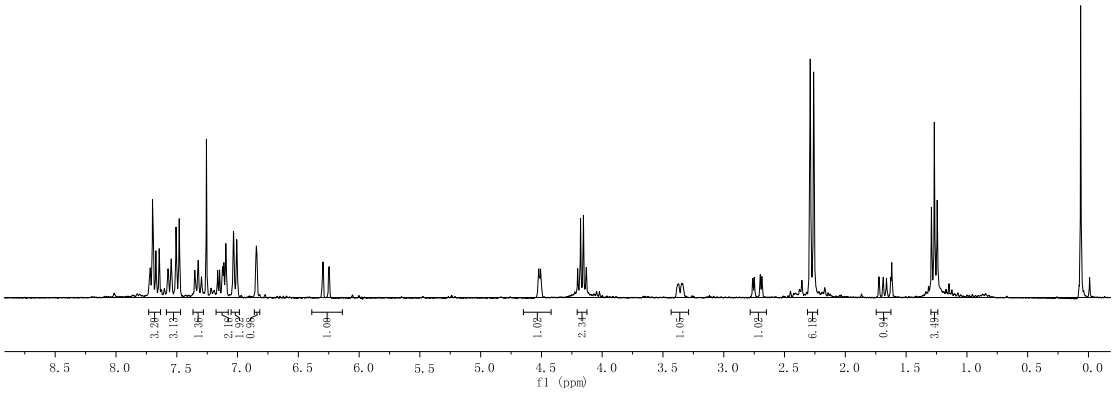
8ma

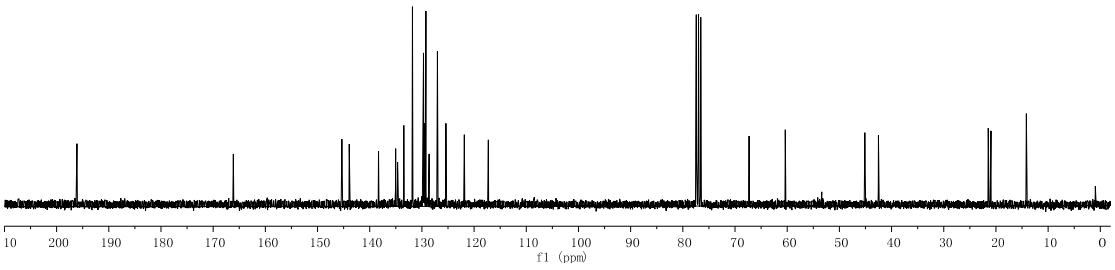

2.20
3.20
3.19
4.26
1.00
1.06
2.12
3.37
1.04
1.16
1.33
6.46
1.12
3.52
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

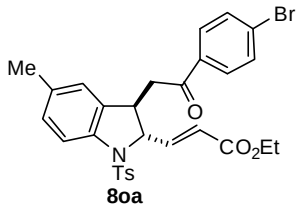

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Me
Br
O
CO2Et
N
Ts

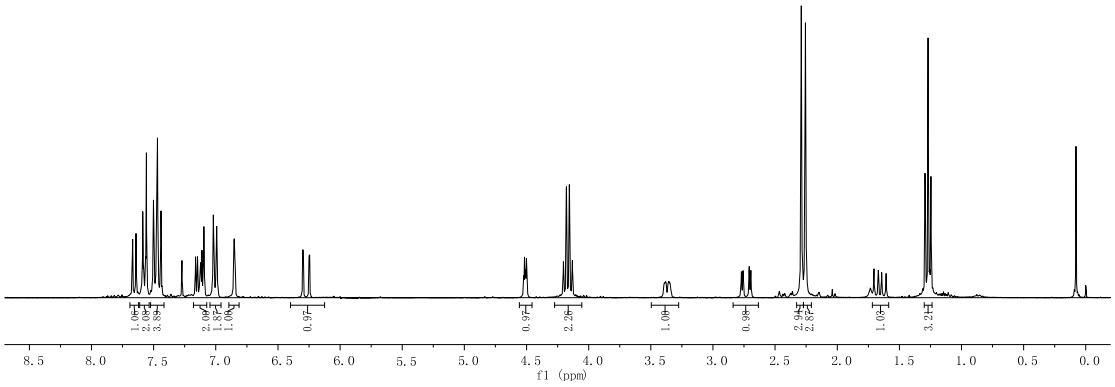
8na

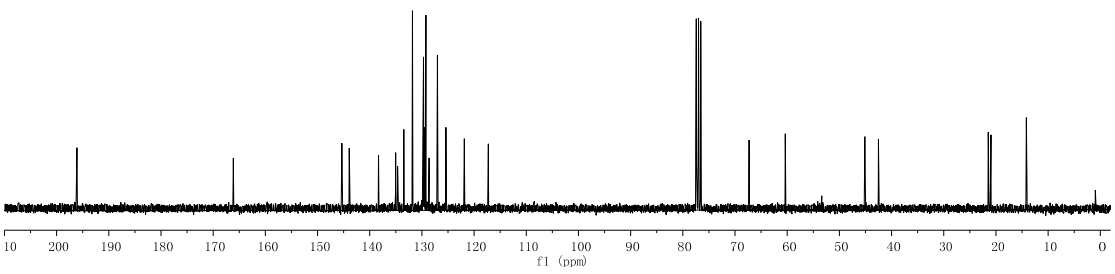

3.39
3.13
1.36
2.04
1.93
0.98
1.00
1.02
2.34
1.05
1.02
6.18
0.94
3.49
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

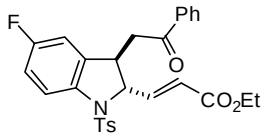

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



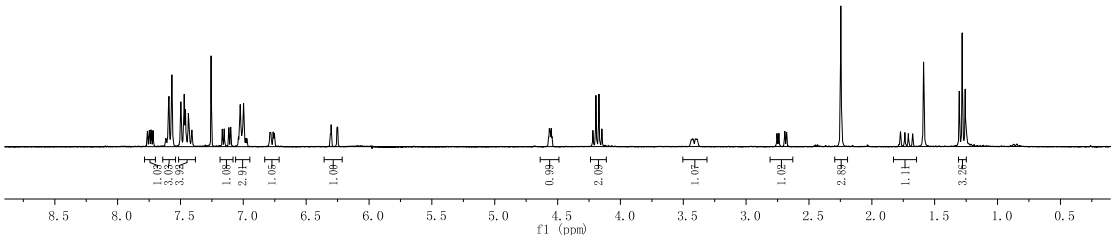
8oa

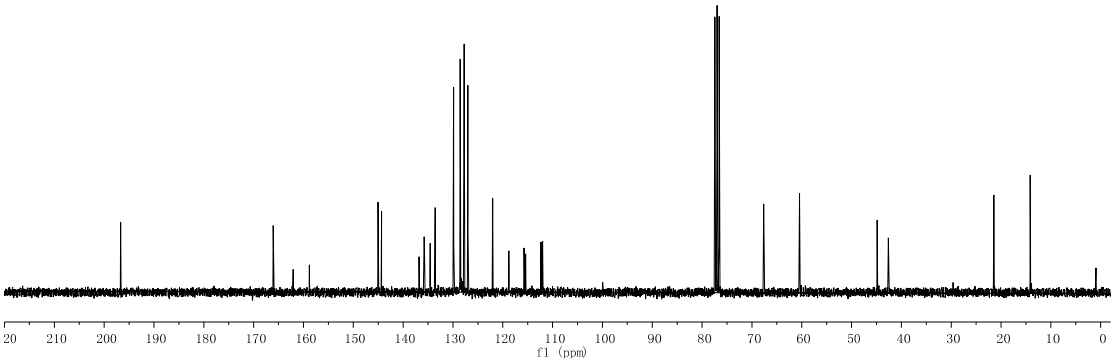


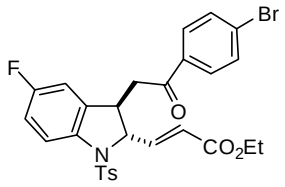



F
Ph
O
N
Ts
CO2Et

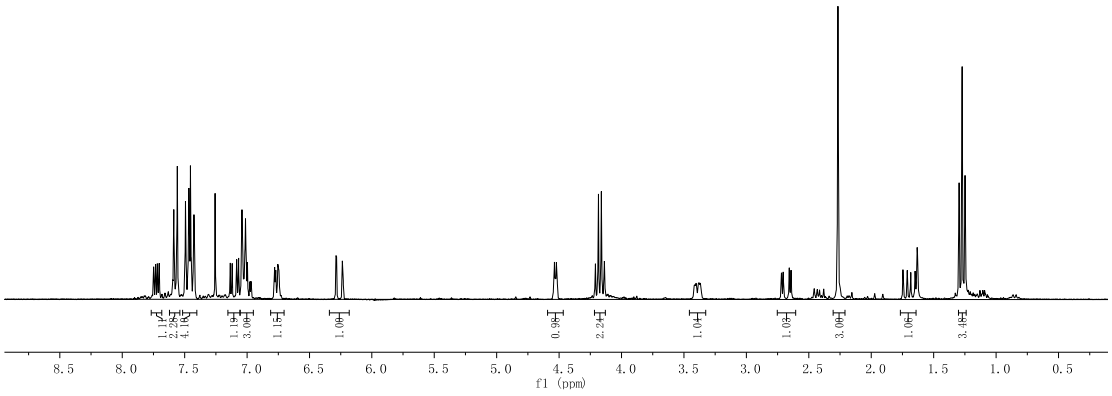
8pa

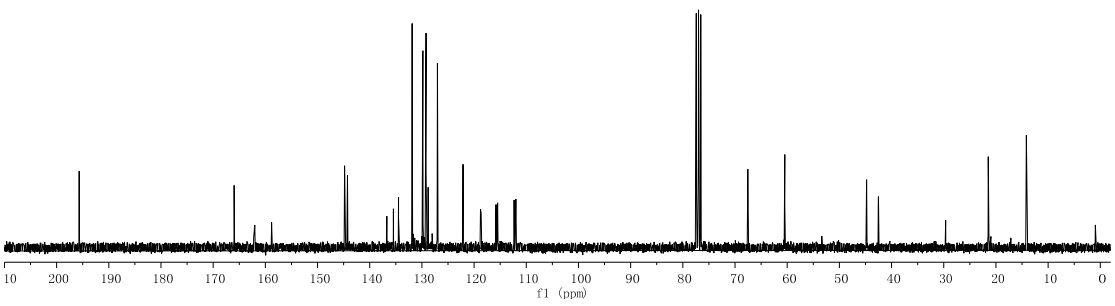

1.00
3.39
1.08
2.91
1.04
1.00
0.84
2.00
1.07
1.02
2.88
1.11
3.28
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

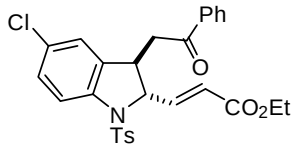

220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Br
F
O
N
Ts
CO2Et

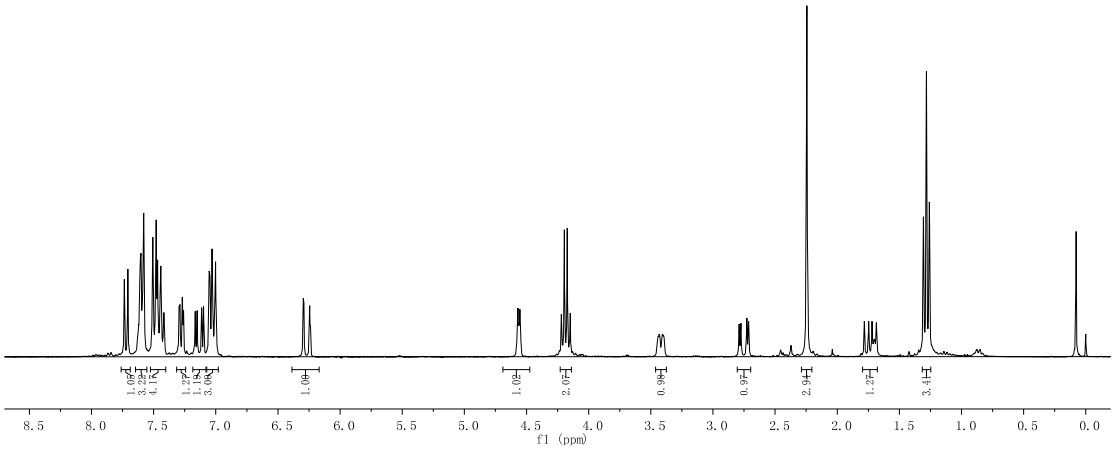
8qa

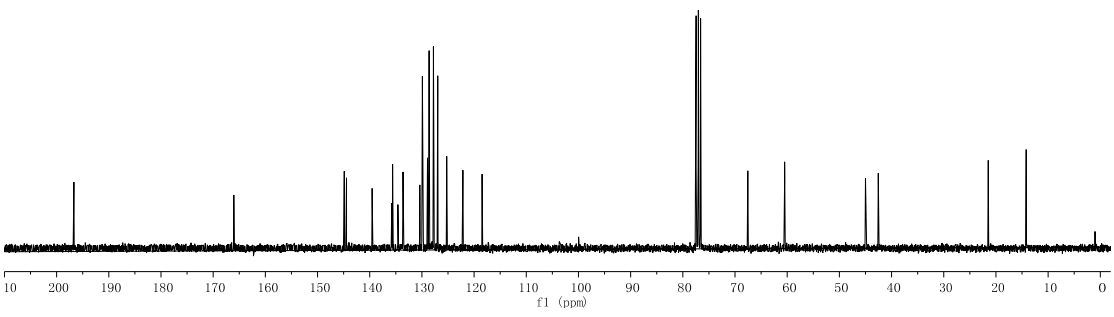

1.47
2.25
4.18
1.19
3.00
1.15
1.00
0.98
2.24
1.04
1.08
3.00
1.06
3.48
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

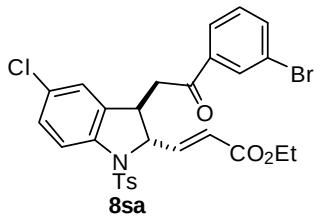

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Cl
Ph
O
CO2Et
N
Ts

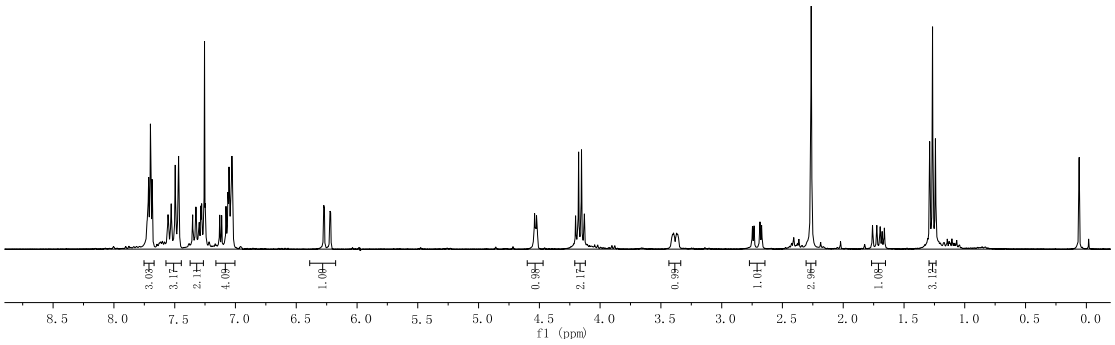
8ra

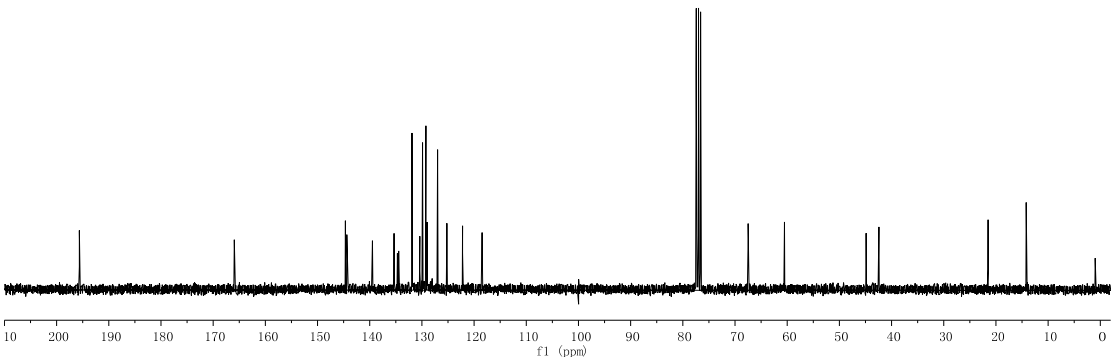

8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Cl
Br
O
CO2Et
N
Ts

8sa


3.03
3.17
2.11
4.09
1.00
0.98
2.17
0.89
1.01
2.96
1.09
3.12
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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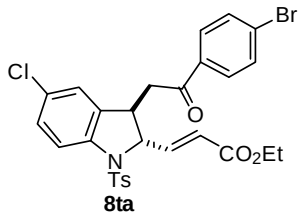
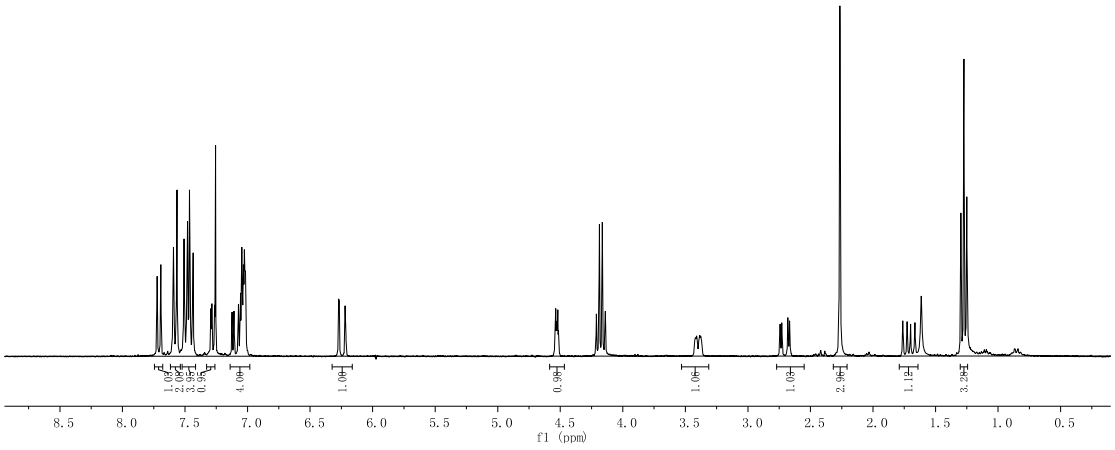
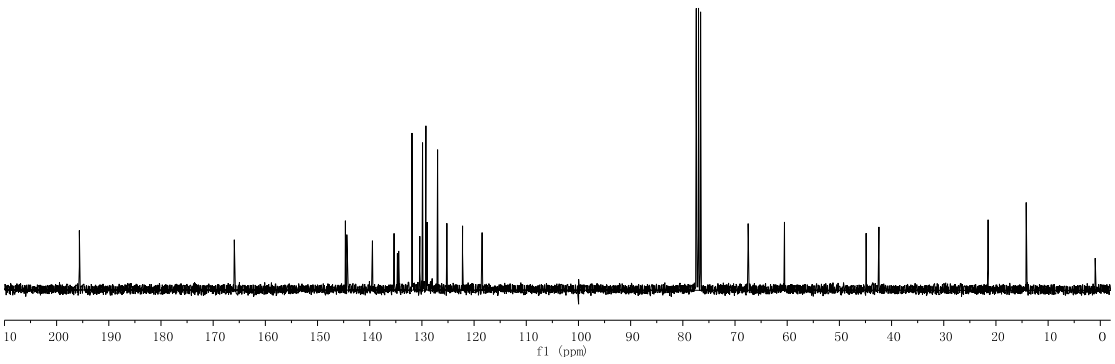
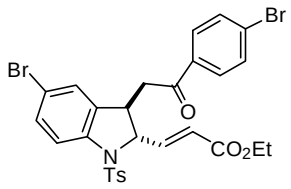
f1 (ppm)


Br
Cl
O
CO2Et
N
Ts

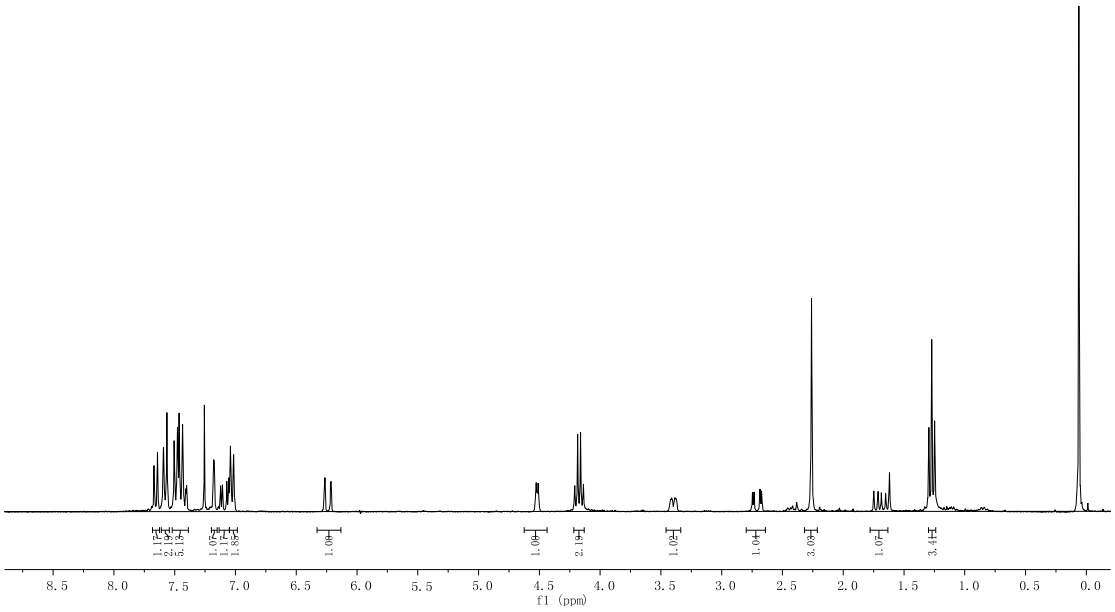
8ta

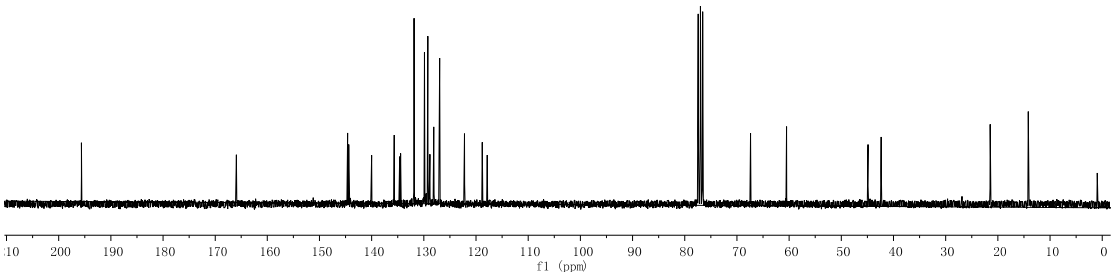

1.00
2.05
3.05
0.55
4.04
1.04
0.99
1.04
1.04
2.06
1.14
3.28
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

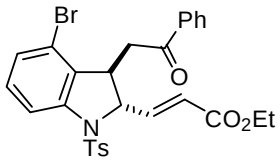

10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Br
Br
O
N
Ts
CO2Et

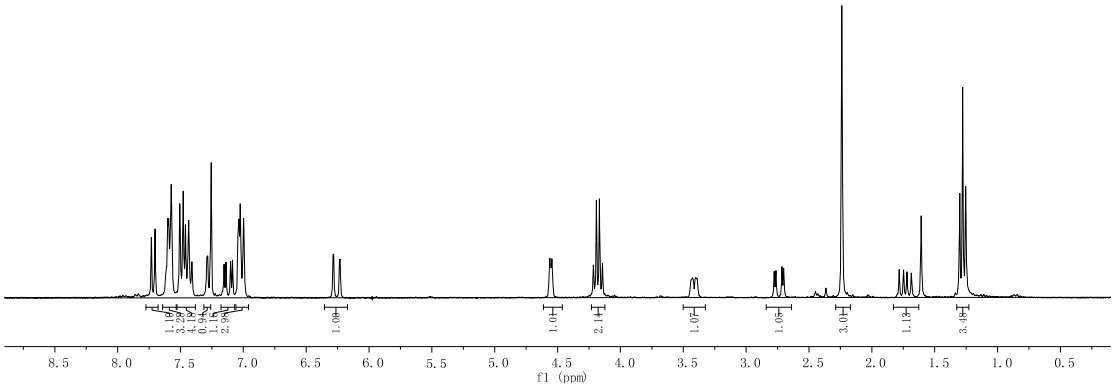
8ua

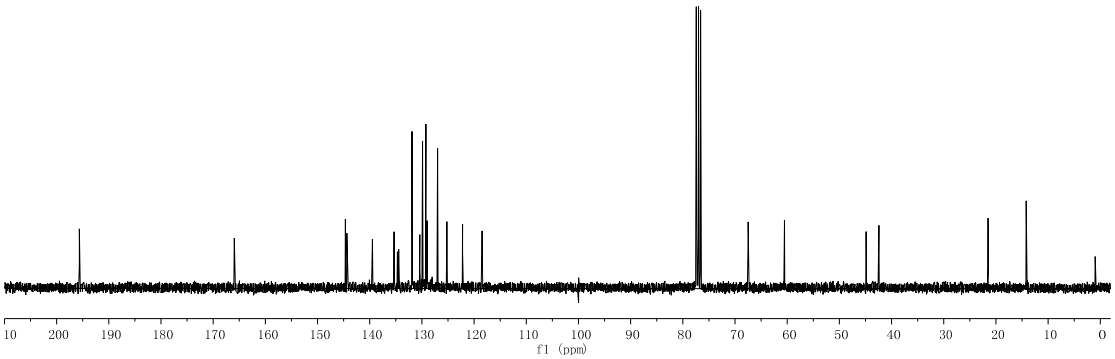

1.12
2.00
3.13
1.05
1.07
1.85
1.00
1.00
2.19
1.02
1.04
3.03
1.07
3.41
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

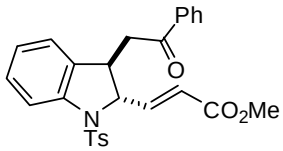

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Br
Ph
O
CO2Et
N
Ts

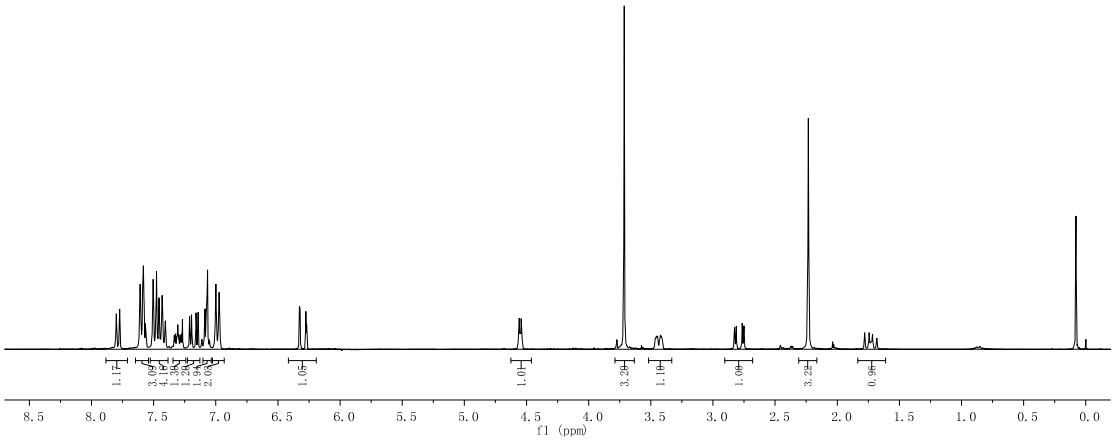
8va

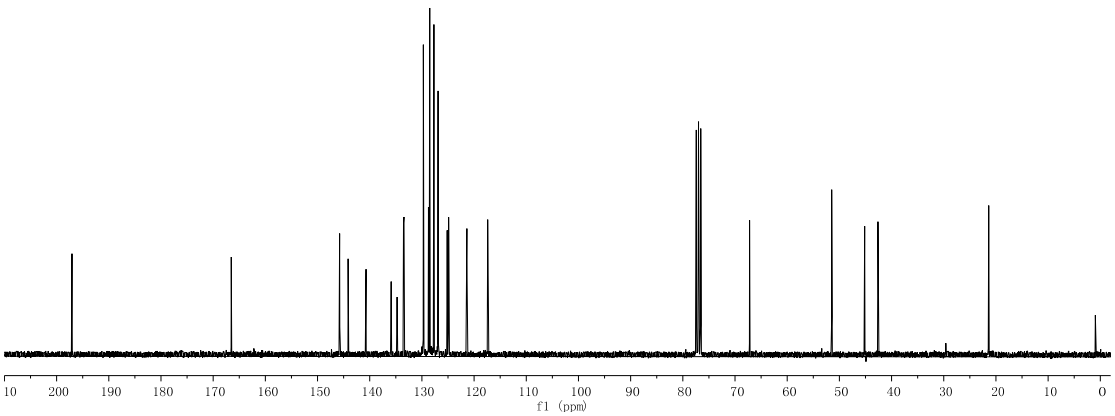

8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

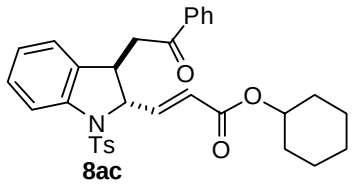

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



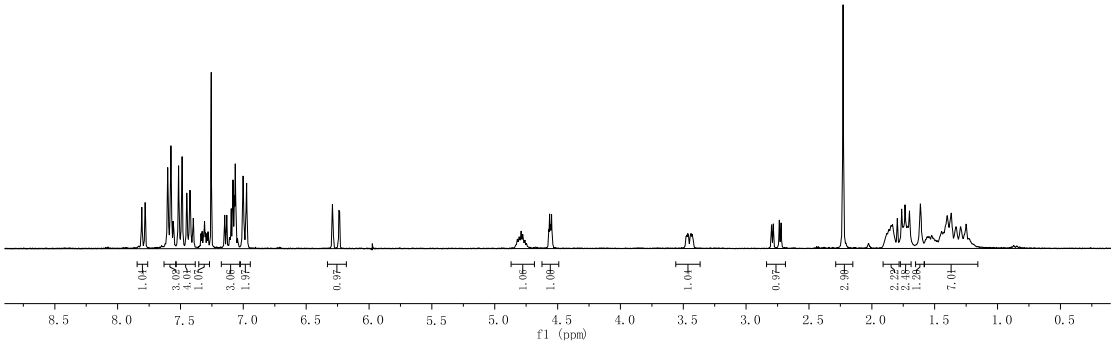
8ab

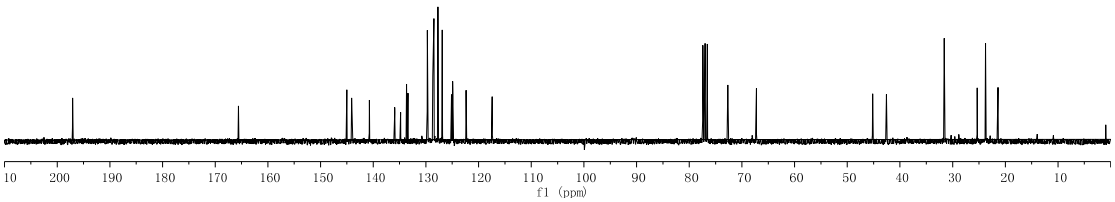





Ph
O
O
N
Ts
O

8ac


1.04
3.02
4.01
1.05
3.00
1.97
0.97
1.06
1.00
1.04
0.97
2.90
2.29
2.19
1.38
7.01
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
f1 (ppm)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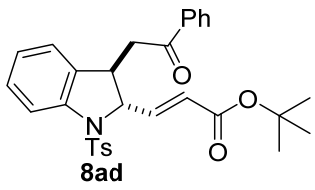
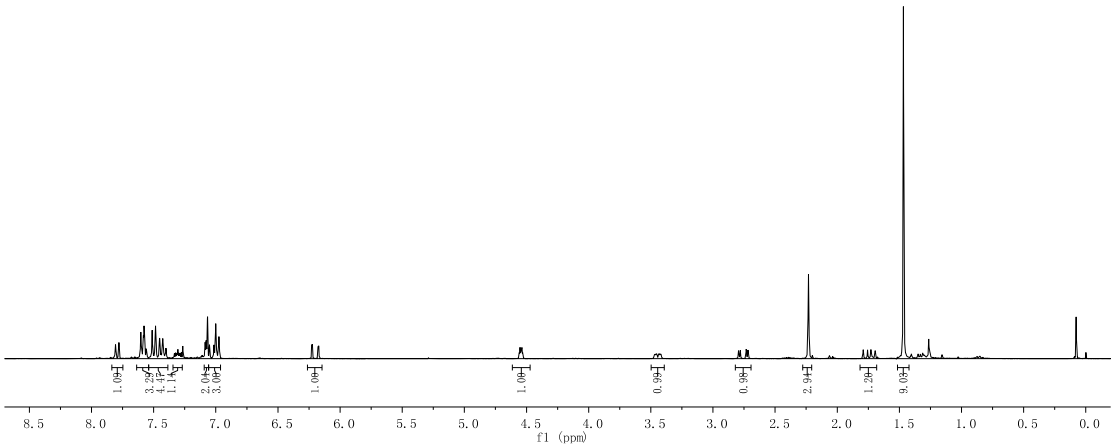
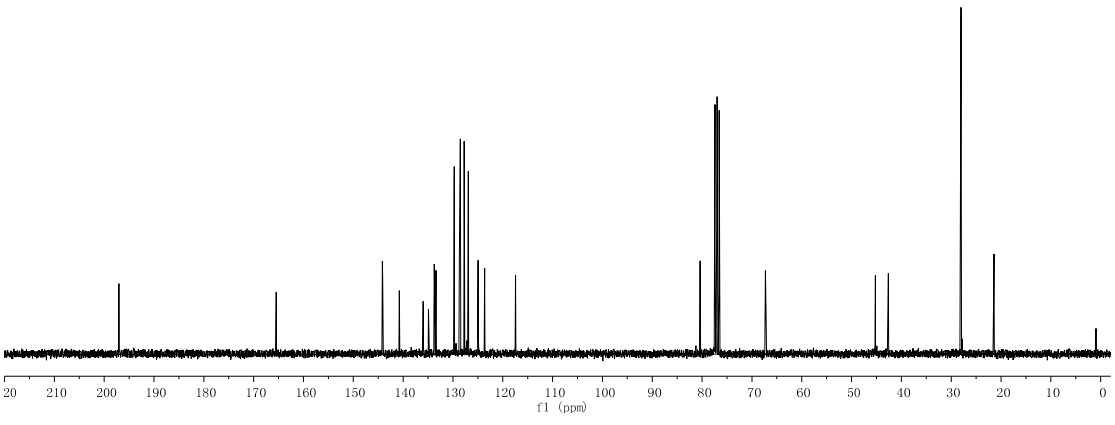
f1 (ppm)


Ph
O
O
O
N
Ts

8ad


1.00
3.21
4.11
1.15
2.04
3.00
1.00
1.00
0.96
0.98
2.91
1.39
9.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

X-Ray Crystallography Data

Crystallographic data for **8aa** has been deposited with the Cambridge Crystallographic Data Centre as deposition number CCDC 995194 and 995195. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

X-Ray Crystallography Data of **8aa**

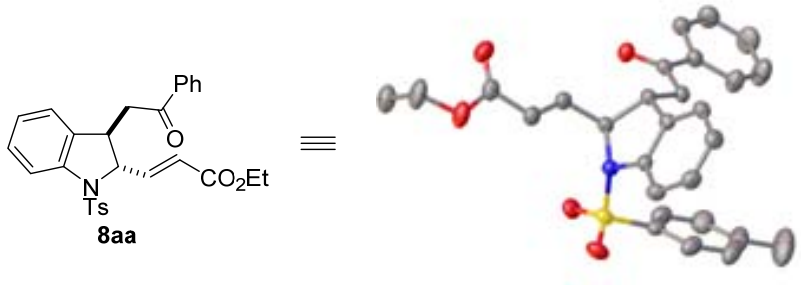


Table 1. Crystal data and structure refinement for **8aa**.

Identification code	**8aa**
Empirical formula	$C_{28}H_{27}NO_5S$
Formula weight	489.57
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P2(1)/n
Unit cell dimensions	a = 10.290(3) Å alpha = 90 °. b = 16.124(4) Å beta = 106.600(3) °. c = 15.403(4) Å gamma = 90 °.
Volume	2449.1(12) $Å^3$
Z, Calculated density	4, 1.328 Mg/m^3
Absorption coefficient	0.172 mm^{-1}
F(000)	1032
Crystal size	0.39 x 0.34 x 0.30 mm
Theta range for data collection	2.42 to 27.50 °.
Limiting indices	-13<=h<=12, -20<=k<=20, -19<=l<=19
Reflections collected / unique	17780 / 5581 [R(int) = 0.0435]
Completeness to theta = 27.50	99.3%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.0000 and 0.6712
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5581 / 0 / 318
Goodness-of-fit on F^2	1.200
Final R indices [I>2sigma(I)]	R1 = 0.0601, wR2 = 0.1316
R indices (all data)	R1 = 0.0644, wR2 = 0.1343
Largest diff. peak and hole	0.248 and -0.381 e. $Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **8aa**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
S(1)	1486(1)	2534(1)	6168(1)	32(1)
O(1)	1346(2)	3166(1)	5498(1)	44(1)
O(2)	1329(2)	1680(1)	5906(1)	41(1)
O(3)	3969(2)	684(1)	8963(1)	34(1)
O(4)	6887(2)	667(1)	6697(1)	51(1)
O(5)	6240(2)	1388(1)	5391(1)	46(1)
N(1)	3037(2)	2613(1)	6857(1)	28(1)
C(1)	3616(2)	1908(1)	7472(1)	28(1)
C(2)	4145(2)	2296(1)	8438(1)	27(1)
C(3)	4134(2)	3215(1)	8239(1)	26(1)
C(4)	4649(2)	3868(1)	8820(1)	31(1)
C(5)	4478(2)	4671(1)	8486(1)	35(1)
C(6)	3824(2)	4817(1)	7579(1)	36(1)
C(7)	3320(2)	4169(1)	6983(1)	33(1)
C(8)	3472(2)	3373(1)	7334(1)	26(1)
C(9)	371(2)	2758(1)	6810(1)	32(1)
C(10)	-194(2)	2105(1)	7171(2)	40(1)
C(11)	-1019(2)	2278(2)	7716(2)	50(1)
C(12)	-1286(2)	3094(2)	7904(2)	55(1)
C(13)	-733(2)	3731(2)	7526(2)	54(1)
C(14)	96(2)	3573(1)	6982(2)	43(1)
C(15)	-2200(4)	3279(3)	8492(3)	91(1)
C(16)	3267(2)	2078(1)	9055(1)	28(1)
C(17)	3334(2)	1165(1)	9295(1)	28(1)
C(18)	2607(2)	864(1)	9949(1)	31(1)
C(19)	1665(2)	1349(1)	10209(2)	43(1)
C(20)	1012(3)	1038(2)	10808(2)	56(1)
C(21)	1302(3)	246(2)	11154(2)	56(1)
C(22)	2247(3)	-237(2)	10908(2)	46(1)
C(23)	2894(2)	69(1)	10303(1)	35(1)
C(24)	4725(2)	1486(1)	7186(1)	31(1)
C(25)	5097(2)	1659(1)	6454(1)	34(1)
C(26)	6174(2)	1180(1)	6222(2)	37(1)
C(27)	7214(3)	936(2)	5051(2)	55(1)
C(28)	6670(3)	131(2)	4643(2)	54(1)

Table 3. Bond lengths [Å] and angles [°] for **8aa**.

S(1)-O(1)	1.4282(16)
S(1)-O(2)	1.4303(15)
S(1)-N(1)	1.6496(17)
S(1)-C(9)	1.753(2)
O(3)-C(17)	1.217(2)
O(4)-C(26)	1.204(3)
O(5)-C(26)	1.344(3)
O(5)-C(27)	1.452(3)
N(1)-C(8)	1.433(2)
N(1)-C(1)	1.491(2)
C(1)-C(24)	1.498(3)
C(1)-C(2)	1.561(2)
C(1)-H(1)	1.0000
C(2)-C(3)	1.513(3)
C(2)-C(16)	1.527(3)
C(2)-H(2)	1.0000
C(3)-C(4)	1.386(3)
C(3)-C(8)	1.390(3)
C(4)-C(5)	1.387(3)
C(4)-H(4)	0.9500
C(5)-C(6)	1.386(3)
C(5)-H(5)	0.9500
C(6)-C(7)	1.390(3)
C(6)-H(6)	0.9500
C(7)-C(8)	1.384(3)
C(7)-H(7)	0.9500
C(9)-C(14)	1.385(3)
C(9)-C(10)	1.394(3)
C(10)-C(11)	1.382(3)
C(10)-H(10)	0.9500
C(11)-C(12)	1.391(4)
C(11)-H(11)	0.9500
C(12)-C(13)	1.382(4)
C(12)-C(15)	1.510(4)
C(13)-C(14)	1.379(3)
C(13)-H(13)	0.9500
C(14)-H(14)	0.9500
C(15)-H(15A)	0.9800
C(15)-H(15B)	0.9800
C(15)-H(15C)	0.9800
C(16)-C(17)	1.516(3)
C(16)-H(16A)	0.9900
C(16)-H(16B)	0.9900

C(17)-C(18)	1.497(3)
C(18)-C(19)	1.389(3)
C(18)-C(23)	1.392(3)
C(19)-C(20)	1.382(3)
C(20)-C(21)	1.382(4)
C(20)-H(20)	0.9500
C(21)-C(22)	1.381(4)
C(21)-H(21)	0.9500
C(22)-C(23)	1.382(3)
C(22)-H(22)	0.9500
C(23)-H(23)	0.9500
C(24)-C(25)	1.321(3)
C(24)-H(24)	0.9500
C(25)-C(26)	1.475(3)
C(25)-H(25)	0.9500
C(27)-C(28)	1.481(3)
C(27)-H(27A)	0.9900
C(27)-H(27B)	0.9900
C(28)-H(28A)	0.9800
C(28)-H(28B)	0.9800
C(28)-H(28C)	0.9800
O(1)-S(1)-O(2)	120.14(9)
O(1)-S(1)-N(1)	106.79(9)
O(2)-S(1)-N(1)	105.50(9)
O(1)-S(1)-C(9)	108.24(10)
O(2)-S(1)-C(9)	108.58(10)
N(1)-S(1)-C(9)	106.87(9)
C(26)-O(5)-C(27)	116.52(19)
C(8)-N(1)-C(1)	108.46(14)
C(8)-N(1)-S(1)	119.94(12)
C(1)-N(1)-S(1)	119.17(13)
N(1)-C(1)-C(24)	111.03(15)
N(1)-C(1)-C(2)	105.54(14)
C(24)-C(1)-C(2)	112.01(15)
N(1)-C(1)-H(1)	109.4
C(24)-C(1)-H(1)	109.4
C(2)-C(1)-H(1)	109.4
C(3)-C(2)-C(16)	112.26(15)
C(3)-C(2)-C(1)	102.64(14)
C(16)-C(2)-C(1)	113.17(15)
C(3)-C(2)-H(2)	109.5
C(16)-C(2)-H(2)	109.5
C(1)-C(2)-H(2)	109.5
C(4)-C(3)-C(8)	119.74(18)
C(4)-C(3)-C(2)	129.38(17)

C(8)-C(3)-C(2)	110.87(16)
C(3)-C(4)-C(5)	119.04(18)
C(3)-C(4)-H(4)	120.5
C(5)-C(4)-H(4)	120.5
C(6)-C(5)-C(4)	120.41(19)
C(6)-C(5)-H(5)	119.8
C(4)-C(5)-H(5)	119.8
C(5)-C(6)-C(7)	121.35(19)
C(5)-C(6)-H(6)	119.3
C(7)-C(6)-H(6)	119.3
C(8)-C(7)-C(6)	117.38(18)
C(8)-C(7)-H(7)	121.3
C(6)-C(7)-H(7)	121.3
C(7)-C(8)-C(3)	122.04(18)
C(7)-C(8)-N(1)	127.52(17)
C(3)-C(8)-N(1)	110.42(16)
C(14)-C(9)-S(1)	120.43(17)
C(10)-C(9)-S(1)	118.96(16)
C(11)-C(10)-C(9)	119.3(2)
C(11)-C(10)-H(10)	120.4
C(10)-C(11)-C(12)	120.6(2)
C(10)-C(11)-H(11)	119.7
C(12)-C(11)-H(11)	119.7
C(13)-C(12)-C(11)	119.1(2)
C(13)-C(12)-C(15)	120.5(3)
C(11)-C(12)-C(15)	120.4(3)
C(14)-C(13)-C(12)	121.3(2)
C(14)-C(13)-H(13)	119.3
C(12)-C(13)-H(13)	119.3
C(13)-C(14)-C(9)	119.1(2)
C(13)-C(14)-H(14)	120.4
C(9)-C(14)-H(14)	120.4
C(12)-C(15)-H(15A)	109.5
C(12)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	109.5
C(12)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5
C(17)-C(16)-C(2)	112.42(15)
C(17)-C(16)-H(16A)	109.1
C(2)-C(16)-H(16A)	109.1
C(17)-C(16)-H(16B)	109.1
C(2)-C(16)-H(16B)	109.1
H(16A)-C(16)-H(16B)	107.9

O(3)-C(17)-C(18)	120.59(18)
O(3)-C(17)-C(16)	120.56(17)
C(19)-C(18)-C(23)	119.58(18)
C(19)-C(18)-C(17)	122.40(18)
C(23)-C(18)-C(17)	118.02(18)
C(20)-C(19)-C(18)	120.0(2)
C(20)-C(19)-H(19)	120.0
C(18)-C(19)-H(19)	120.0
C(19)-C(20)-C(21)	120.0(2)
C(19)-C(20)-H(20)	120.0
C(21)-C(20)-H(20)	120.0
C(22)-C(21)-C(20)	120.4(2)
C(22)-C(21)-H(21)	119.8
C(20)-C(21)-H(21)	119.8
C(21)-C(22)-C(23)	119.8(2)
C(21)-C(22)-H(22)	120.1
C(23)-C(22)-H(22)	120.1
C(22)-C(23)-C(18)	120.2(2)
C(22)-C(23)-H(23)	119.9
C(18)-C(23)-H(23)	119.9
C(25)-C(24)-C(1)	125.90(18)
C(25)-C(24)-H(24)	117.0
C(1)-C(24)-H(24)	117.0
C(24)-C(25)-C(26)	121.16(19)
C(24)-C(25)-H(25)	119.4
C(26)-C(25)-H(25)	119.4
O(4)-C(26)-O(5)	124.2(2)
O(4)-C(26)-C(25)	125.6(2)
O(5)-C(26)-C(25)	110.24(19)
O(5)-C(27)-C(28)	112.2(2)
O(5)-C(27)-H(27A)	109.2
C(28)-C(27)-H(27A)	109.2
O(5)-C(27)-H(27B)	109.2
C(28)-C(27)-H(27B)	109.2
H(27A)-C(27)-H(27B)	107.9
C(27)-C(28)-H(28A)	109.5
C(27)-C(28)-H(28B)	109.5
H(28A)-C(28)-H(28B)	109.5
C(27)-C(28)-H(28C)	109.5
H(28A)-C(28)-H(28C)	109.5
H(28B)-C(28)-H(28C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($A^2 \times 10^3$) for **8aa**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U11	U22	U33	U23	U13	U12
S(1)	36(1)	32(1)	24(1)	-3(1)	1(1)	2(1)
O(1)	52(1)	45(1)	28(1)	6(1)	0(1)	1(1)
O(2)	47(1)	36(1)	35(1)	-11(1)	3(1)	1(1)
O(3)	40(1)	30(1)	35(1)	-1(1)	15(1)	4(1)
O(4)	50(1)	51(1)	54(1)	-3(1)	16(1)	18(1)
O(5)	58(1)	37(1)	56(1)	-2(1)	38(1)	2(1)
N(1)	31(1)	27(1)	25(1)	1(1)	6(1)	4(1)
C(1)	32(1)	26(1)	25(1)	1(1)	8(1)	3(1)
C(2)	27(1)	29(1)	24(1)	0(1)	7(1)	1(1)
C(3)	24(1)	28(1)	28(1)	1(1)	10(1)	-1(1)
C(4)	32(1)	34(1)	27(1)	-2(1)	7(1)	-2(1)
C(5)	36(1)	30(1)	38(1)	-5(1)	9(1)	-5(1)
C(6)	37(1)	27(1)	43(1)	4(1)	11(1)	-1(1)
C(7)	33(1)	32(1)	32(1)	5(1)	8(1)	1(1)
C(8)	26(1)	26(1)	27(1)	-2(1)	8(1)	0(1)
C(9)	27(1)	32(1)	34(1)	-4(1)	1(1)	2(1)
C(10)	36(1)	32(1)	48(1)	-2(1)	7(1)	0(1)
C(11)	39(1)	54(2)	60(2)	-3(1)	17(1)	-9(1)
C(12)	36(1)	65(2)	68(2)	-24(1)	20(1)	-7(1)
C(13)	38(1)	45(1)	80(2)	-24(1)	17(1)	1(1)
C(14)	36(1)	32(1)	57(1)	-5(1)	7(1)	2(1)
C(15)	67(2)	105(3)	122(3)	-46(2)	59(2)	-20(2)
C(16)	32(1)	29(1)	25(1)	-1(1)	9(1)	1(1)
C(17)	29(1)	30(1)	24(1)	-1(1)	5(1)	0(1)
C(18)	35(1)	29(1)	29(1)	1(1)	11(1)	-1(1)
C(19)	52(1)	35(1)	49(1)	6(1)	27(1)	6(1)
C(20)	67(2)	49(1)	70(2)	9(1)	46(2)	10(1)
C(21)	68(2)	54(2)	60(2)	14(1)	41(1)	-1(1)
C(22)	57(1)	39(1)	44(1)	11(1)	20(1)	2(1)
C(23)	40(1)	33(1)	31(1)	2(1)	10(1)	2(1)
C(24)	36(1)	25(1)	32(1)	-1(1)	9(1)	3(1)
C(25)	41(1)	27(1)	36(1)	0(1)	14(1)	5(1)
C(26)	40(1)	30(1)	44(1)	-6(1)	17(1)	-2(1)
C(27)	61(2)	45(1)	77(2)	-12(1)	48(1)	-4(1)
C(28)	66(2)	46(1)	62(2)	-9(1)	36(1)	0(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for **8aa**.

	x	y	z	U(eq)
H(1)	2883	1499	7465	33
H(2)	5098	2109	8727	32
H(4)	5113	3767	9439	38
H(5)	4811	5125	8881	42
H(6)	3719	5371	7360	43
H(7)	2888	4269	6359	39
H(10)	-14	1547	7045	48
H(11)	-1407	1835	7965	60
H(13)	-927	4289	7642	65
H(14)	473	4017	6728	51
H(15A)	-2918	2859	8386	137
H(15B)	-2608	3828	8340	137
H(15C)	-1668	3268	9130	137
H(16A)	3570	2409	9618	34
H(16B)	2314	2230	8747	34
H(19)	1470	1894	9974	51
H(20)	364	1368	10983	67
H(21)	847	33	11563	67
H(22)	2452	-777	11155	55
H(23)	3537	-265	10127	41
H(24)	5202	1055	7566	37
H(25)	4665	2099	6070	41
H(27A)	8044	837	5555	66
H(28A)	5821	223	4165	82
H(28B)	6498	-230	5110	82
H(28C)	7331	-134	4383	82

Table 6. Torsion angles [°] for **8aa**.

O(1)-S(1)-N(1)-C(8)	58.64(16)
O(2)-S(1)-N(1)-C(8)	-172.47(14)
C(9)-S(1)-N(1)-C(8)	-57.03(16)
O(1)-S(1)-N(1)-C(1)	-163.64(13)

O(2)-S(1)-N(1)-C(1)	-34.74(16)
C(9)-S(1)-N(1)-C(1)	80.69(15)
C(8)-N(1)-C(1)-C(24)	-107.95(17)
S(1)-N(1)-C(1)-C(24)	109.97(16)
C(8)-N(1)-C(1)-C(2)	13.63(19)
S(1)-N(1)-C(1)-C(2)	-128.45(14)
N(1)-C(1)-C(2)-C(3)	-13.83(18)
C(24)-C(1)-C(2)-C(3)	107.11(17)
N(1)-C(1)-C(2)-C(16)	107.39(17)
C(24)-C(1)-C(2)-C(16)	-131.67(17)
C(16)-C(2)-C(3)-C(4)	66.8(2)
C(1)-C(2)-C(3)-C(4)	-171.39(19)
C(16)-C(2)-C(3)-C(8)	-112.02(18)
C(1)-C(2)-C(3)-C(8)	9.82(19)
C(8)-C(3)-C(4)-C(5)	0.8(3)
C(2)-C(3)-C(4)-C(5)	-177.91(19)
C(3)-C(4)-C(5)-C(6)	-1.3(3)
C(4)-C(5)-C(6)-C(7)	0.2(3)
C(5)-C(6)-C(7)-C(8)	1.2(3)
C(6)-C(7)-C(8)-C(3)	-1.7(3)
C(6)-C(7)-C(8)-N(1)	179.89(18)
C(4)-C(3)-C(8)-C(7)	0.7(3)
C(2)-C(3)-C(8)-C(7)	179.66(17)
C(4)-C(3)-C(8)-N(1)	179.37(16)
C(2)-C(3)-C(8)-N(1)	-1.7(2)
C(1)-N(1)-C(8)-C(7)	170.73(19)
S(1)-N(1)-C(8)-C(7)	-47.5(3)
C(1)-N(1)-C(8)-C(3)	-7.8(2)
S(1)-N(1)-C(8)-C(3)	133.93(14)
O(1)-S(1)-C(9)-C(14)	-33.8(2)
O(2)-S(1)-C(9)-C(14)	-165.74(17)
N(1)-S(1)-C(9)-C(14)	80.90(18)
O(1)-S(1)-C(9)-C(10)	148.56(16)
O(2)-S(1)-C(9)-C(10)	16.62(19)
N(1)-S(1)-C(9)-C(10)	-96.74(17)
C(14)-C(9)-C(10)-C(11)	-0.9(3)
S(1)-C(9)-C(10)-C(11)	176.71(17)
C(9)-C(10)-C(11)-C(12)	0.0(4)

C(10)-C(11)-C(12)-C(13)	1.1(4)
C(10)-C(11)-C(12)-C(15)	179.4(3)
C(11)-C(12)-C(13)-C(14)	-1.2(4)
C(15)-C(12)-C(13)-C(14)	-179.5(3)
C(12)-C(13)-C(14)-C(9)	0.3(4)
C(10)-C(9)-C(14)-C(13)	0.8(3)
S(1)-C(9)-C(14)-C(13)	-176.83(18)
C(3)-C(2)-C(16)-C(17)	-176.99(15)
C(1)-C(2)-C(16)-C(17)	67.4(2)
C(2)-C(16)-C(17)-O(3)	-4.3(3)
C(2)-C(16)-C(17)-C(18)	175.65(16)
O(3)-C(17)-C(18)-C(19)	-167.2(2)
C(16)-C(17)-C(18)-C(19)	12.8(3)
O(3)-C(17)-C(18)-C(23)	12.7(3)
C(23)-C(18)-C(19)-C(20)	-0.6(4)
C(17)-C(18)-C(19)-C(20)	179.3(2)
C(18)-C(19)-C(20)-C(21)	0.4(4)
C(19)-C(20)-C(21)-C(22)	0.4(5)
C(20)-C(21)-C(22)-C(23)	-0.9(4)
C(21)-C(22)-C(23)-C(18)	0.8(4)
C(19)-C(18)-C(23)-C(22)	0.0(3)
C(17)-C(18)-C(23)-C(22)	-179.9(2)
N(1)-C(1)-C(24)-C(25)	-4.7(3)
C(2)-C(1)-C(24)-C(25)	-122.4(2)
C(1)-C(24)-C(25)-C(26)	-177.77(19)
C(27)-O(5)-C(26)-O(4)	2.0(3)
C(27)-O(5)-C(26)-C(25)	-177.09(18)
C(24)-C(25)-C(26)-O(4)	-7.9(4)
C(24)-C(25)-C(26)-O(5)	171.18(19)
C(26)-O(5)-C(27)-C(28)	83.2(3)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for **8aa** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)