Supporting Information

Phosphine-Catalyzed [3+2] Annulation of β-Sulfonamido-Substituted Enones with *trans*-α-Cyano-α,β-Unsaturated Ketones for the Synthesis of Highly Substituted Pyrrolidines

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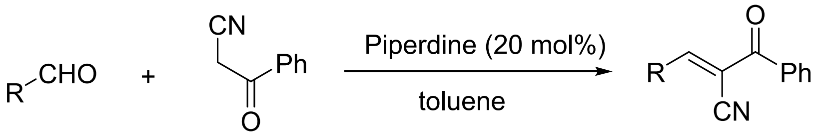
General Information

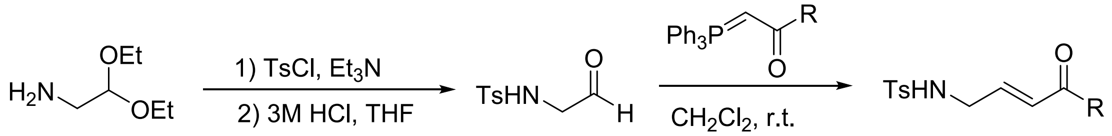
All reactions were performed under Ar atmospheres in oven-dried glassware with magnetic stirring. Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. All solvents were purified and dried according to standard methods prior to use. Organic solutions were concentrated under reduced pressure on a rotary evaporator or an oil pump. Reactions were monitored through thin layer chromatography (TLC) on silica gel-precoated glass plates. Chromatograms were visualized by fluorescence quenching with UV light at 254 nm. Flash column chromatography was performed using Qingdao Haiyang flash silica gel (200–300 mesh). ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ using a 400 or 500 MHz NMR instrument (referenced internally to Me_4Si). ^{1}H NMR data are reported as follows: chemical shift, multiplicity (s = singlet; d = doublet; q = quartet; m = multiplet; br = broad), coupling constant (Hz), and integral. Data for ^{13}C NMR spectra are reported in terms of chemical shift. Melting points were determined by an X-4 digital micro melting point apparatus. Accurate mass measurements were performed using an Agilent instrument with the ESI-MS technique. X-ray crystallographic data were collected using a Gemini E Rigaku.

General Procedure for Synthesis of *trans*-α-Cyano-α,β-Unsaturated Ketones 1[1]and β-Sulfonamido-Substituted Enones 2[2] .



1a - 1p

The corresponding aldehyde (1 mmol) and piperidine (2 mol %, 0.02 mmol, 2 μL) was added to the solution of benzyolacetonitril (1mmol, 145 mg), 4Å MS (10 mg) in toluene (7.5 mL) under argon atmosphere. The reaction mixture was heated at 80°C for 8 hours. The concentrated mixture was purified by silica gel column chromatography (4-6% EA in Hexane) to give the products **1a**-**1p**.



2a—2n

To a stirred solution of aminoacetaldehyde diethyl acetal (7.26 mL, 50.0 mmol) and anhydrous Et_3N (14.0 mL, 100 mmol) in CH_2Cl_2 (100 mL) was added dropwise a solution of *p*-toluenesulfonyl chloride (10.5 g, 55.0 mmol) in CH_2Cl_2 (100 mL) over 30 min at 0 ºC. After 2 h the reaction mixture was diluted with water (200 mL). The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (100 mL). The organic extracts were combined, washed with 1 M aq. HCl (50 mL), water (100 mL), and saturated aq. $NaHCO_3$ (100 mL), dried over Na_2SO_4, and concentrated *in vacuo*. Purification of the residue by silica gel column chromatography (petroleum ether/EtOAc 4:1) afforded the tosylamino acetaldehyde diethyl acetal as a white solid. To a solution of the sulfonamide (5.0 mmol) in THF (50 mL) was added 3 M aq. HCl (15 mL) at room temperature, and the reaction mixture was stirred for 24 h at room temperature. The reaction mixture was then diluted with EtOAc (50 mL) and washed with brine (50 mL). The organic portion was then dried over Na_2SO_4 and concentrated *in vacuo* to afford the corresponding tosylamino acetaldehyde which was used without further purification. Wittig reagent (5.0 mmol, 1 equiv) was added to a solution of tosylamino acetaldehyde (5.0 mmol, 1 equiv) in CH_2Cl_2 (30 mL) in round bottom flask. The solution was stirred at r.t. for 30 h. After concentration under reduced pressure, the residue was purified by flash chromatography (petroleum ether/EtOAc 3:1) to afford products **2a**-**2n**.

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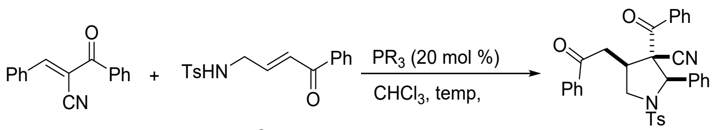
1. Pan, S. C., Nath, U. *Eur. J. Org. Chem.* **2017**, *43*, 6457.

2. Zhao, B.; Du, D. *Asian J. Org. Chem.* **2015**, *4*, 1120.

General Procedure for [3+2] Annulation of β-Sulfonamido-Substituted Enones and *trans*-α-Cyano-α,β-Unsaturated Ketones

Under argon atmosphere, to a mixture of unsaturated ketones **1** (0.12 mmol), β-sulfonamido-substituted enones **2** (0.1 mmol) and catalyst PMe_3 (20 mol %, 0.02 mmol) in a Schlenk tube, 5 mL of $CHCl_3$ was added at room temperature. The resulting mixture was stirred until the starting material was completely consumed (monitored by TLC) and then was concentrated to dryness. The residue was purified through flash column chromatography (EtOAc / PE) to afford the corresponding cycloaddition products **3**.

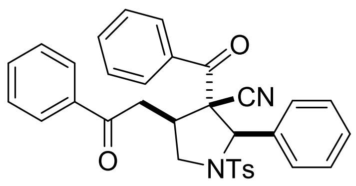
Screening Reaction Conditions for [3+2] Annulation



Entry	PR_3	Temperature/°C	*t*/h	Additive	Con./mol/L^{-1}	yield(%)^b	dr^c
1	PMe_3	25	72	PhCOOH	0.02	35	-
2	PMe_3	25	72	Et_3N	0.02	NR	-
3	PMe_3	25	72	Na_2CO_3	0.02	76	13:1
4	PMe_3	-20	72	-	0.02	NR	3:1
5	PMe_3	0	72	-	0.02	Trace	3:1
6	PMe_3	40	24	-	0.02	83	8:1

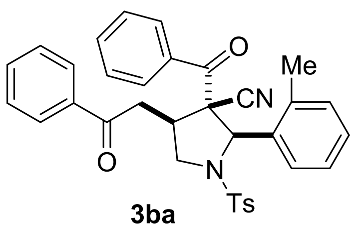
^{a}Unless otherwise indicated, all reactions were carried out at room temperature using 0.12 mmol of **1aa** and 0.1 mmol of **2aa** in a solvent containing 20 mol % of the catalyst. ^{b}Isolated yield. ^{c}Determined by ^{1}H NMR.

Characterization Data of the Products 3



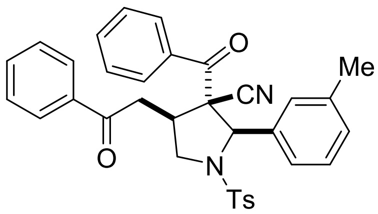
3aa

White solid, 86% yield, 14:1 dr. Purified by flash chromatography (12% EtOAc/PE). mp = 166-167 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 – 7.72 (m, 2H), 7.62 (d, *J* = 8.2 Hz, 2H), 7.48 (t, *J* = 7.4 Hz, 1H), 7.44 – 7.34 (m, 3H), 7.34 – 7.23 (m, 9H), 7.19 – 7.16 (m, 2H), 4.91 (s, 1H), 4.34 (dd, *J* = 11.8, 7.4 Hz, 1H), 3.60 – 3.46 (m, 1H), 3.28 – 3.19 (m, 1H), 3.18 – 3.14 (m, 1H), 3.04 (dd, *J* = 17.5, 4.6 Hz, 1H), 2.39 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 194.9, 190.3, 143.4, 134.8, 134.6, 134.1, 132.8, 132.7, 132.4, 128.9, 128.4, 128.3, 127.7, 127.5, 127.2, 127.1, 127.0, 126.9, 116.0, 70.8, 63.8, 52.0, 41.6, 37.0, 20.6; HRMS (ESI) calcd for $C_{33}H_{29}N_2O_4S^+$ $[M+H]^+$ 549.1848, found 549.1849.



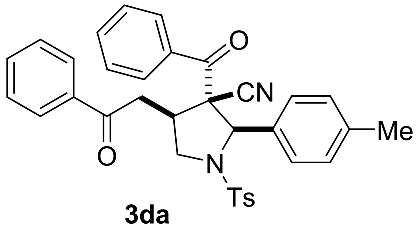
3ba

White solid, 75% yield, 10.5:1 dr. Purified by flash chromatography (12% EtOAc/PE). mp = 179-180 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.77 (m, 2H), 7.76 – 7.68 (m, 1H), 7.63 – 7.53 (m, 2H), 7.53 – 7.46 (m, 1H), 7.45 – 7.35 (m, 3H), 7.33 – 7.29 (m, 2H), 7.28 – 7.23 (m, 3H), 7.22 – 7.13 (m, 3H), 6.99 – 6.89 (m, 1H), 5.24 (s, 1H), 4.38 (dd, J = 11.5, 7.0 Hz, 1H), 3.51 (t, J = 11.1 Hz, 1H), 3.45 – 3.28 (m, 1H), 3.21 – 3.12 (m, 1H), 3.10 – 3.00 (m, 1H), 2.38 (s, 3H), 1.86 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 196.1, 191.1, 144.3, 136.0, 135.9, 134.6, 134.2, 134.1, 134.0, 133.8, 130.4, 129.9, 129.3, 129.0, 128.9, 128.8, 128.3, 128.1, 127.9, 126.6, 117.2, 66.5, 64.2, 52.6, 42.9, 38.0, 21.7, 19.4. HRMS (ESI) calcd for $C_{34}H_{31}N_2O_4S^+$ $[M+H]^+$ 563.2005, found 563.2007.



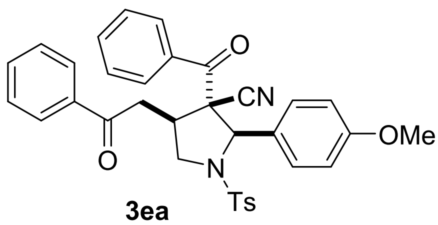
3ca

White solid, 77% yield, 12.5:1 dr. Purified by flash chromatography (12% EtOAc/PE). mp = 176-177 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (dd, *J* = 8.3, 1.1 Hz, 2H), 7.61 (d, *J* = 8.3 Hz, 2H), 7.52 – 7.46 (m, 1H), 7.45 – 7.39 (m, 1H), 7.34 (ddd, *J* = 12.1, 9.6, 4.6 Hz, 4H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.21 – 7.13 (m, 3H), 7.12 – 6.98 (m, 3H), 4.89 (s, 1H), 4.36 (dd, *J* = 11.8, 7.4 Hz, 1H), 3.59 – 3.43 (m, 1H), 3.24 (tdd, *J* = 10.9, 7.5, 4.6 Hz, 1H), 3.14 (dd, *J* = 17.5, 9.1 Hz, 1H), 3.03 (dd, *J* = 17.5, 4.6 Hz, 1H), 2.39 (s, 3H), 2.19 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 194.9, 190.5, 143.3, 137.1, 134.8, 134.4, 134.2, 132.8, 129.1, 128.9, 128.6, 128.4, 127.7, 127.6, 127.4, 127.2, 127.0, 126.9, 126.3, 124.1, 116.0, 70.7, 63.9, 51.9, 41.6, 36.9, 20.6, 20.4. HRMS (ESI) calcd for $C_{34}H_{31}N_2O_4S^+$ $[M+H]^+$ 563.2005, found 563.2008.



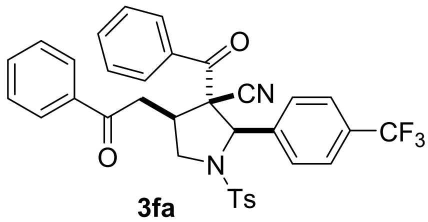
3da

White solid, 78% yield, 10.5:1 dr. Purified by flash chromatography (12% EtOAc/PE). mp = 177-178 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (dd, *J* = 8.3, 1.1 Hz, 2H), 7.63 (d, *J* = 8.2 Hz, 2H), 7.51 – 7.47 (m, 1H), 7.41 (dd, *J* = 10.6, 4.3 Hz, 1H), 7.38 – 7.27 (m, 6H), 7.20 (ddd, *J* = 7.5, 6.0, 4.1 Hz, 4H), 7.08 (d, *J* = 7.8 Hz, 2H), 4.87 (s, 1H), 4.31 (dd, *J* = 11.8, 7.3 Hz, 1H), 3.53 (dd, *J* = 11.6, 10.7 Hz, 1H), 3.22 (tdd, *J* = 10.3, 8.1, 4.3 Hz, 1H), 3.14 (t, *J* = 8.7 Hz, 1H), 3.03 (dd, *J* = 17.3, 4.3 Hz, 1H), 2.40 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 194.9, 190.5, 143.3, 138.2, 134.8, 134.2, 132.8, 132.7, 132.4, 131.6, 128.9, 128.4, 128.2, 127.7, 127.2, 127.0, 126.9, 126.9, 116.1, 70.6, 63.9, 52.0, 41.5, 37.0, 20.6, 20.3. HRMS (ESI) calcd for $C_{34}H_{31}N_2O_4S^+$ $[M+H]^+$ 563.2005, found 563.2008.



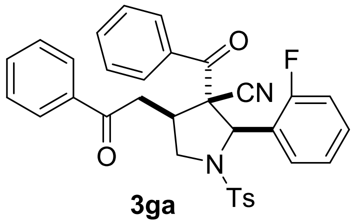
3ea

White solid, 80% yield, 14:1 dr. Purified by flash chromatography (12% EtOAc/PE). mp = 127-128 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.3 Hz, 2H), 7.60 (d, *J* = 8.2 Hz, 2H), 7.49 (t, *J* = 7.4 Hz, 1H), 7.42 (t, *J* = 7.4 Hz, 1H), 7.39 – 7.32 (m, 4H), 7.30 – 7.27 (m, 2H), 7.26 – 7.18 (m, 4H), 6.84 – 6.74 (m, 2H), 4.83 (s, 1H), 4.32 (dd, *J* = 11.8, 7.5 Hz, 1H), 3.75 (s, 3H), 3.56 – 3.49 (m, 1H), 3.28 – 3.20 (m, 1H), 3.18 – 3.10 (m, 1H), 3.07 – 3.00 (m, 1H), 2.40 (s, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 195.0, 190.5, 159.3, 143.3, 134.8, 134.2, 132.8, 132.7, 132.4, 128.9, 128.3, 128.4, 127.7, 127.2, 127.0, 126.9, 126.4, 116.2, 112.9, 70.5, 63.9, 54.3, 51.9, 41.3, 37.1, 20.6. HRMS (ESI) calcd for $C_{34}H_{31}N_2O_5S^+$ $[M+H]^+$ 579.1954., found 579.1958.



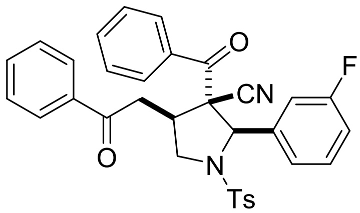
3fa

White solid, 66% yield, 10.5:1 dr. Purified by flash chromatography (12% EtOAc/PE). mp = 138-139 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 – 7.71 (m, 2H), 7.65 – 7.59 (m, 2H), 7.52 – 7.47 (m, 3H), 7.46 – 7.40 (m, 3H), 7.40 – 7.32 (m, 4H), 7.32 – 7.27 (m, 2H), 7.22 – 7.17 (m, 2H), 5.04 (s, 1H), 4.47 – 4.24 (m, 1H), 3.62 – 3.45 (m, 1H), 3.25 – 3.12 (m, 2H), 3.12 – 3.03 (m, 1H), 2.40 (s, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 194.7, 189.7, 143.7, 138.8, 134.7, 134.0, 133.2, 132.8, 132.1, 130.5, 130.2, 129.1, 128.8, 128.3, 128.1, 127.8, 127.7, 127.5, 127.4, 127.0, 126.5, 124.5, 123.9, 121.7, 115.7, 69.9, 63.4, 52.0, 42.0, 36.9, 20.6. HRMS (ESI) calcd for $C_{34}H_{28}F_3N_2O_4S^+$ $[M+H]^+$ 616.1644, found 616.1648.



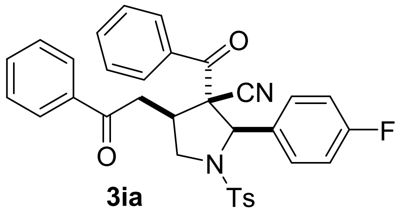
3ga

White solid, 72% yield, 9.5:1 dr. Purified by flash chromatography (12% EtOAc/PE). mp = 163-164 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.79 (m, 1H), 7.79 – 7.68 (m, 4H), 7.53 – 7.39 (m, 5H), 7.39 – 7.33 (m, 4H), 7.32 – 7.26 (m, 1H), 7.24 – 7.17 (m, 2H), 6.92 – 6.77 (m, 1H), 5.33 (s, 1H), 4.29 (dd, *J* = 12.0, 6.4 Hz, 1H), 3.58 – 3.43 (m, 1H), 3.21 – 2.95 (m, 3H), 2.41 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.9, 190.4, 161.3, 158.8, 144.7, 135.8, 134.8, 134.0, 133.8, 132.8, 130.9, 130.8, 130.2, 129.2, 128.8, 128.4, 128.1, 124.8, 124.2, 124.0, 116.9, 63.8, 52.9, 43.3, 37.9, 29.7, 21.8. HRMS (ESI) calcd for $C_{33}H_{28}FN_2O_4S^+$ $[M+H]^+$ 567.1754, found 567.1756.



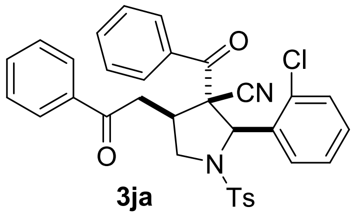
3ha

White solid, 74% yield, 6:1 dr. Purified by flash chromatography (12% EtOAc/PE). mp = 134-135 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.5 Hz, 2H), 7.64 (d, *J* = 8.2 Hz, 2H), 7.46 (dd, *J* = 18.0, 7.4 Hz, 2H), 7.43 – 7.39 (m, 2H), 7.38 – 7.27 (m, 4H), 7.22 (t, *J* = 7.9 Hz, 3H), 7.09 – 6.97 (m, 3H), 4.98 (s, 1H), 4.32 (dd, *J* = 11.8, 6.8 Hz, 1H), 3.52 (dd, *J* = 13.1, 9.1 Hz, 1H), 3.17 (dt, *J* = 17.1, 6.4 Hz, 2H), 3.06 (t, *J* = 10.7 Hz, 1H), 2.40 (s, 3H).^{13}C NMR (126 MHz, CDCl3) δ 194.8, 190.1, 162.6, 160.6, 143.6, 137.4, 134.7, 134.1, 132.9 (d, J = 31.2 Hz), 132.2, 129.0, 128.3, 127.8, 127.4, 127.0, 126.9, 122.6, 122.6, 115.4 (d, J = 21.1 Hz), 114.1 (d, J = 22.8 Hz), 70.0, 63.6, 52.0, 41.9, 36.9, 20.7. HRMS (ESI) calcd for $C_{33}H_{28}FN_2O_4S^+$ $[M+H]^+$ 567.1754, found 567.1760.



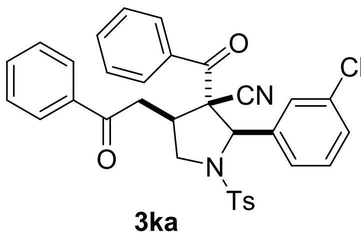
3ia

White solid, 76% yield, 5:1 dr. Purified by flash chromatography (12% EtOAc/PE). mp = 134-135 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.4 Hz, 2H), 7.62 (d, *J* = 8.3 Hz, 2H), 7.49 (t, *J* = 7.4 Hz, 1H), 7.45 – 7.41 (m, 2H), 7.36 (dt, *J* = 4.3, 3.4 Hz, 4H), 7.30 (d, *J* = 8.1 Hz, 3H), 7.21 (dd, *J* = 17.1, 9.0 Hz, 2H), 6.96 (t, *J* = 8.5 Hz, 2H), 4.91 (s, 1H), 4.33 (dd, *J* = 11.8, 7.2 Hz, 1H), 3.57 – 3.48 (m, 1H), 3.25 – 3.19 (m, 1H), 3.18 – 3.12 (m, 1H), 3.05 (dd, *J* = 17.1, 4.2 Hz, 1H), 2.41 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 194.8, 190.1, 163.2, 161.2, 143.6, 134.7, 134.1, 132.9 (d, J = 26.8 Hz), 132.2, 129.0, 128.9, 128.3, 127.7, 127.4, 126.9 (d, J = 11.1 Hz), 115.9, 114.7, 114.5, 70.1, 51.9, 41.6, 37.0, 28.7, 20.7. HRMS (ESI) calcd for $C_{33}H_{28}FN_2O_4S^+$ $[M+H]^+$ 567.1754, found 567.1760.



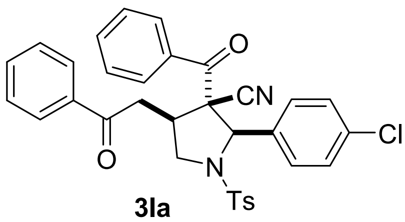
3ja

White solid, 74% yield, 8:1 dr. Purified by flash chromatography (12% EtOAc/PE). mp = 201-202 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.90 (m, 1H), 7.82 – 7.73 (m, 4H), 7.59 – 7.45 (m, 2H), 7.45 – 7.38 (m, 4H), 7.38 – 7.34 (m, 3H), 7.32 – 7.26 (m, 1H), 7.23 – 7.17 (m, 3H), 5.46 (s, 1H), 4.37 – 4.14 (m, 1H), 3.65 – 3.44 (m, 1H), 3.21 – 3.10 (m, 2H), 3.09 – 2.99 (m, 1H), 2.42 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 194.9, 189.1, 143.7, 134.8, 133.6, 133.5, 133.1, 132.8, 132.4, 131.4, 129.4, 129.3, 129.1, 128.3, 128.2, 127.8, 127.3, 127.0, 126.9, 126.5, 115.9, 65.5, 62.5, 51.8, 42.1, 36.9, 20.7. HRMS (ESI) calcd for $C_{33}H_{28}ClN_2O_4S^+$ $[M+H]^+$ 583.1458, found 583.1454.



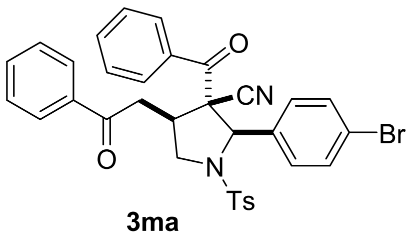
3ka

White solid, 76 % yield, 10:1 dr. Purified by flash chromatography (12% EtOAc/PE). mp = 198-199 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 – 7.72 (m, 2H), 7.66 – 7.59 (m, 2H), 7.59 – 7.47 (m, 1H), 7.47 – 7.39 (m, 4H), 7.36 (m, 2H), 7.30 (m, 2H), 7.28 – 7.19 (m, 5H), 4.97 (s, 1H), 4.34 (dd, J = 11.7, 7.1 Hz, 1H), 3.58 – 3.44 (m, 1H), 3.24 – 3.12 (m, 2H), 3.06 (M, 1H), 2.40 (s, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 194.8, 189.9, 143.6, 134.7, 133.7, 133.5, 133.1, 132.8, 132.4, 129.0, 128.8, 128.5, 128.3, 128.0, 127.8, 127.5, 127.1, 127.0, 126.9, 126.4, 115.7, 69.8, 63.6, 51.9, 41.9, 36.9, 20.7. HRMS (ESI) calcd for $C_{33}H_{28}ClN_2O_4S^+$ [M+H]$^+$ 583.1458, found 583.1457.



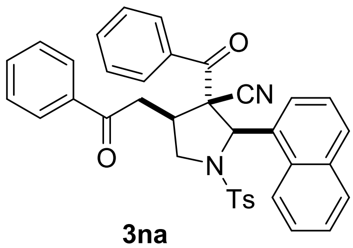
3la

White solid, 82 % yield, 5:1 dr. Purified by flash chromatography (12% EtOAc/PE). mp = 200-201 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, J = 7.4 Hz, 2H), 7.62 (d, J = 8.1 Hz, 2H), 7.47 (ddd, J = 11.9, 11.1, 5.6 Hz, 3H), 7.42 – 7.37 (m, 4H), 7.37 – 7.29 (m, 4H), 7.25 (s, 2H), 7.23 – 7.18 (m, 1H), 4.93 (d, J = 6.2 Hz, 1H), 4.36 – 4.26 (m, 1H), 3.52 (t, J = 11.1 Hz, 1H), 3.23 – 3.12 (m, 2H), 3.05 (dd, J = 16.5, 3.6 Hz, 1H), 2.41 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 194.8, 190.0, 143.6, 134.7, 133.8, 133.3, 133.1, 132.8, 132.2, 129.0, 128.8, 128.6, 128.3, 128.0, 127.8, 127.6, 127.4, 127.0, 126.9, 126.4, 115.9, 70.0, 63.6, 52.0, 41.8, 36.9, 20.7. HRMS (ESI) calcd for $C_{33}H_{28}ClN_2O_4S^+$ [M+H]$^+$ 583.1458, found 583.1454.



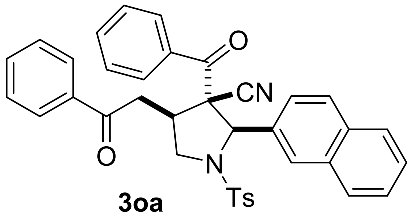
3ma

White solid, 85% yield, 6:1 dr. Purified by flash chromatography (12% EtOAc/PE). mp = 100-101 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.4 Hz, 2H), 7.62 (d, *J* = 8.2 Hz, 2H), 7.49 (t, *J* = 7.4 Hz, 1H), 7.45 (dd, *J* = 9.5, 4.4 Hz, 1H), 7.39 (t, *J* = 7.0 Hz, 4H), 7.36 – 7.33 (m, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.26 – 7.17 (m, 4H), 4.93 (d, *J* = 6.2 Hz, 1H), 4.35 – 4.28 (m, 1H), 3.52 (dd, *J* = 14.1, 8.1 Hz, 1H), 3.24 – 3.09 (m, 2H), 3.09 – 2.98 (m, 1H), 2.41 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 194.8, 190.0, 143.6, 134.7, 133.8, 133.3, 132.8, 132.2, 129.0, 128.8, 128.6, 128.3, 128.0, 127.8, 127.4, 127.0, 126.9, 126.4, 115.8, 70.0, 63.5, 52.0, 41.8, 36.9, 20.7. HRMS (ESI) calcd for $C_{33}H_{28}BrN_2O_4S^+$ $[M+H]^+$ 627.0953, found 627.0952.



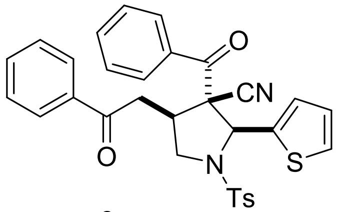
3na

White solid, 81% yield, 14:1 dr. Purified by flash chromatography (12% EtOAc/PE). mp = 163-164 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 – 7.73 (m, 4H), 7.64 – 7.60 (m, 3H), 7.52 – 7.46 (m, 2H), 7.45 – 7.30 (m, 8H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.07 (t, *J* = 7.9 Hz, 2H), 5.13 (s, 1H), 4.41 (dd, *J* = 11.8, 7.4 Hz, 1H), 3.66 – 3.53 (m, 1H), 3.35 – 3.25 (m, 1H), 3.19 (dd, *J* = 17.6, 9.1 Hz, 1H), 3.08 (dd, *J* = 17.6, 4.7 Hz, 1H), 2.35 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 196.0, 192.1, 144.5, 135.9, 134.7, 133.8, 133.5, 133.2, 131.9, 130.8, 130.0, 129.7, 129.2, 129.0, 128.8, 128.2, 128.1, 128.0, 127.2, 126.7, 125.7, 125.5, 121.6, 117.1, 66.2, 65.0, 53.1, 43.9, 38.1, 21.7. HRMS (ESI) calcd for $C_{37}H_{31}N_2O_4S^+$ $[M+H]^+$ 599.2005, found 599.2005.



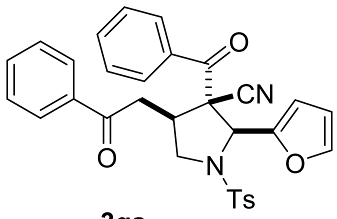
3oa

White solid, 80% yield, 8:1 dr. Purified by flash chromatography (12% EtOAc/PE). mp = 161-162 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 7.3 Hz, 1H), 7.86 – 7.73 (m, 4H), 7.66 (d, *J* = 7.9 Hz, 2H), 7.57 (t, *J* = 7.7 Hz, 1H), 7.49 (t, *J* = 7.4 Hz, 1H), 7.37 (dd, *J* = 16.4, 8.5 Hz, 3H), 7.31 (d, *J* = 7.9 Hz, 2H), 7.27 – 7.20 (m, 2H), 7.18 – 7.09 (m, 3H), 7.00 – 6.90 (m, 2H), 5.93 (s, 1H), 4.40 (dd, *J* = 11.8, 7.0 Hz, 1H), 3.62 (t, *J* = 11.0 Hz, 1H), 3.41 – 3.28 (m, 1H), 3.27 – 3.15 (m, 1H), 3.12 – 3.02 (m, 1H), 2.41 (s, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 194.9, 190.4, 143.4, 134.8, 134.1, 132.8, 132.7, 132.6, 132.0, 131.8, 128.9, 128.3, 127.8, 127.4, 127.2, 127.0, 126.9, 126.7, 126.6, 125.4, 124.2, 116.0, 70.8, 63.8, 52.0, 41.8, 37.0, 20.6. HRMS (ESI) calcd for $C_{37}H_{31}N_2O_4S^+$ [M+H]$^+$ 599.2005, found 599.2002.



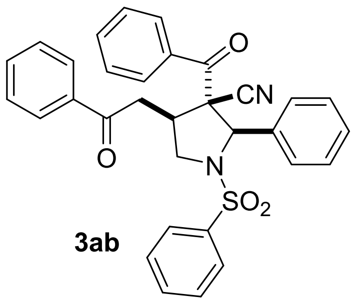
3pa

White solid, 78% yield, 7:1 dr. Purified by flash chromatography (12% EtOAc/PE). mp = 135-136 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (dd, *J* = 8.3, 1.1 Hz, 2H), 7.66 – 7.54 (m, 4H), 7.48 (ddd, *J* = 13.8, 10.6, 4.3 Hz, 3H), 7.37 (dd, *J* = 10.7, 4.8 Hz, 2H), 7.28 (ddd, *J* = 6.0, 5.4, 4.4 Hz, 4H), 7.04 (d, *J* = 3.4 Hz, 1H), 6.92 (dd, *J* = 5.1, 3.6 Hz, 1H), 5.34 (s, 1H), 4.22 – 4.06 (m, 1H), 3.50 (dd, *J* = 11.6, 9.3 Hz, 1H), 3.34 – 3.23 (m, 2H), 3.16 (t, *J* = 8.2 Hz, 1H), 2.39 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.2, 190.5, 162.3, 159.7, 143.4, 134.5, 134.3, 132.8, 132.4, 129.6, 128.9, 128.3, 128.3, 127.5, 127.2, 126.9, 123.6, 115.9, 115.7, 70.9, 63.7, 52.0, 41.8, 41.7, 20.7. HRMS (ESI) calcd for $C_{31}H_{27}N_2O_4S_2^+$ [M+H]$^+$ 555.1412, found 555.1411.



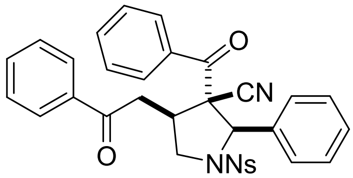
3qa

White solid, 80% yield, 14:1 dr. Purified by flash chromatography (12% EtOAc/PE). mp = 123-125 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 – 7.80 (m, 2H), 7.79 – 7.70 (m, 2H), 7.55 – 7.46 (m, 4H), 7.41 – 7.32 (m, 4H), 7.30 (s, 1H), 7.20 – 7.15 (m, 2H), 6.50 (s, 1H), 6.35 (d, *J* = 1.7 Hz, 1H), 5.25 (s, 1H), 4.07 – 3.92 (m, 1H), 3.57 – 3.46 (m, 1H), 3.45 – 3.36 (m, 2H), 3.36 – 3.28 (m, 1H), 2.35 (s, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 195.4, 188.4, 148.1, 143.1, 142.4, 135.0, 133.3, 132.7, 132.6, 132.4, 128.8, 128.6, 127.9, 127.8, 127.7, 127.6, 127.1, 127.0, 126.6, 126.2, 115.3, 110.2, 109.9, 62.4, 60.0, 51.5, 39.7, 38.1, 20.6. HRMS (ESI) calcd for $C_{31}H_{27}N_2O_5S^+$ $[M+H]^+$ 539.16461, found 539.1646.



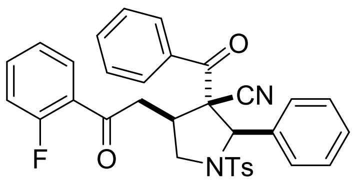
3ab

White solid, 84% yield, 10:1 dr. Purified by flash chromatography (12% EtOAc/PE). mp = 157-158 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 – 7.68 (m, 4H), 7.63 – 7.54 (m, 1H), 7.53 – 7.46 (m, 3H), 7.41 (t, *J* = 7.5 Hz, 1H), 7.36 (t, *J* = 7.8 Hz, 2H), 7.29 (m, 7.7 Hz, 7H), 7.18 (t, *J* = 7.9 Hz, 2H), 4.95 (s, 1H), 4.38 (dd, *J* = 11.8, 7.4 Hz, 1H), 3.60 – 3.47 (m, 1H), 3.29 – 3.20 (m, 1H), 3.19 – 3.12 (m, 1H), 3.04 (dd, *J* = 17.5, 4.4 Hz, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ 194.8, 190.2, 135.4, 134.7, 134.4, 134.0, 132.9, 132.8, 132.5, 128.4, 128.3, 128.0, 127.7, 127.6, 127.3, 127.0, 126.8, 116.0, 70.7, 63.7, 51.9, 41.7, 36.9. HRMS (ESI) calcd for $C_{32}H_{27}N_2O_4S^+$ $[M+H]^+$ 535.1692, found 535.1692.



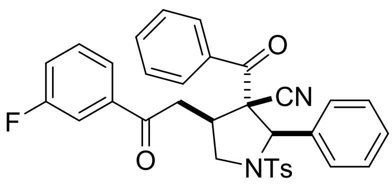
3ac

White solid, 81% yield, 4.5:1 dr. Purified by flash chromatography (12% EtOAc/PE). mp = 125-126 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 – 8.22 (m, 2H), 8.05 – 7.96 (m, 1H), 7.87 – 7.76 (m, 3H), 7.75 – 7.57 (m, 1H), 7.54 – 7.41 (m, 2H), 7.40 – 7.27 (m, 5H), 7.27 – 7.16 (m, 5H), 5.03 (s, 1H), 4.47 (dd, *J* = 11.6, 7.2 Hz, 1H), 3.56 (t, *J* = 11.2 Hz, 1H), 3.41 – 3.27 (m, 1H), 3.26 – 2.84 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.8, 190.9, 150.4, 143.0, 135.7, 134.8, 134.7, 134.2, 134.0, 129.8, 129.5, 129.0, 128.9, 128.7, 128.5, 128.2, 128.1, 124.4, 116.9, 71.5, 64.4, 52.9, 43.0, 37.9. HRMS (ESI) calcd for $C_{32}H_{26}N_3O_6S^+$ $[M+H]^+$ 580.1542, found 580.1541.



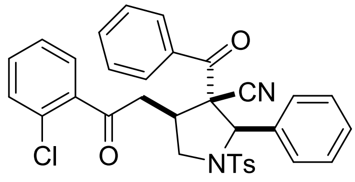
3ad

White solid, 77% yield, 8:1 dr. Purified by flash chromatography (12% EtOAc/PE). mp = 163-164 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (t, *J* = 7.7, 1.7 Hz, 1H), 7.63 (d, *J* = 8.2 Hz, 2H), 7.50 – 7.37 (m, 3H), 7.35 – 7.27 (m, 8H), 7.21 – 7.13 (m, 3H), 7.01 (t, *J* = 7.8, 6.1 Hz, 1H), 4.95 (s, 1H), 4.33 (dd, *J* = 11.8, 7.0 Hz, 1H), 3.61 – 3.49 (m, 1H), 3.28 – 3.15 (m, 2H), 3.12 – 3.01 (m, 1H), 2.40 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 194.5, 190.4, 143.7, 143.4, 134.6, 134.1, 132.8, 132.31, 132.28, 129.0, 128.4, 128.3, 127.9, 127.5, 127.2, 127.1, 127.0, 126.9, 116.0, 70.8, 63.8, 52.0, 41.7, 36.8, 20.7. HRMS (ESI) calcd for $C_{33}H_{28}FN_2O_4S^+$ $[M+H]^+$ 567.1754, found 567.1760.



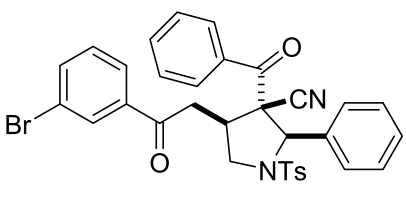
3ae

White solid, 79% yield, 9:1 dr. Purified by flash chromatography (12% EtOAc/PE). mp = 134-135 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (td, J = 7.7, 1.8 Hz, 1H), 7.62 (t, J = 7.9 Hz, 2H), 7.49 – 7.38 (m, 3H), 7.35 – 7.26 (m, 8H), 7.20 – 7.13 (m, 3H), 7.02 (dt, J = 7.8, 6.2 Hz, 1H), 4.95 (s, 1H), 4.37 – 4.30 (m, 1H), 3.58 – 3.49 (m, 1H), 3.28 – 3.12 (m, 2H), 3.11 – 2.96 (m, 1H), 2.40 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.2, 190.5, 162.3, 159.7, 143.5, 134.5, 134.2, 133.0, 132.8, 132.3, 129.6, 128.9, 128.3, 127.9, 127.5, 127.2, 127.0, 126.9, 126.6, 123.4, 115.9, 70.9, 63.7, 52.0, 41.8, 41.6, 20.7. HRMS (ESI) calcd for $C_{33}H_{28}FN_2O_4S^+$ $[M+H]^+$ 567.1754, found 567.1760.



3af

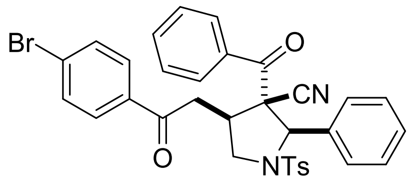
White solid, 82% yield, 8:1 dr. Purified by flash chromatography (12% EtOAc/PE). mp = 136-137 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (t, J = 10.2 Hz, 2H), 7.47 – 7.37 (m, 2H), 7.33 – 7.26 (m, 11H), 7.24 – 7.20 (m, 1H), 7.18 (t, J = 7.9 Hz, 2H), 4.92 (s, 1H), 4.31 (dd, J = 11.7, 6.5 Hz, 1H), 3.63 – 3.49 (m, 1H), 3.25 – 3.19 (m, 1H), 3.18 – 3.16 (m, 1H), 3.06 – 2.98 (m, 1H), 2.41 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.1, 190.3, 143.4, 136.9, 134.5, 134.1, 132.9, 132.3, 131.4, 130.0, 129.7, 129.0, 128.4, 128.3, 128.1, 127.6, 127.2, 127.0, 126.9, 126.1, 115.9, 70.8, 63.6, 51.8, 41.7, 41.1, 20.7. HRMS (ESI) calcd for $C_{33}H_{28}ClN_2O_4S^+$ $[M+H]^+$ 583.1458, found 583.1454.



3ag

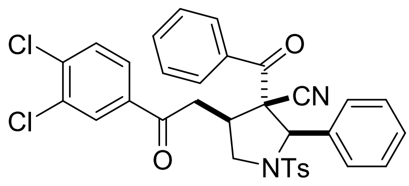
White solid, 74% yield, 9:1 dr. Purified by flash chromatography (12% EtOAc/PE). mp = 125-126 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.72 – 7.66 (m, 1H), 7.65 – 7.58 (m, 3H), 7.47 – 7.37 (m, 2H), 7.32 – 7.28 (m, 7H), 7.27 – 7.23 (m, 2H), 7.20 – 7.15 (m, 2H), 4.87 (s, 1H), 4.33 (dd, J = 11.7, 7.4 Hz, 1H), 3.52 (t, J = 11.3 Hz, 1H), 3.30 – 3.16 (m, 1H), 3.15 – 3.05 (m, 1H), 3.04 – 2.94 (m, 1H), 2.40 (s, 3H). ^{13}C

NMR (101 MHz, $CDCl_3$) δ 195.5, 191.4, 146.5, 144.4, 139.6, 135.6, 135.2, 134.5, 133.9, 133.4, 130.0, 129.4, 129.0, 128.7, 128.6, 128.5, 128.3, 128.1, 128.0, 127.3, 117.1, 71.9, 64.9, 53.1, 42.7, 38.1, 21.7. HRMS (ESI) calcd for $C_{33}H_{28}BrN_2O_4S^+$ $[M+H]^+$ 627.0953, found 627.0952.



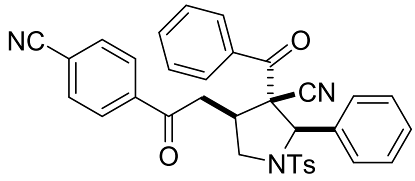
3ah

White solid, 85% yield, 8:1 dr. Purified by flash chromatography (12% EtOAc/PE). mp = 99-100 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.83 (m, 1H), 7.64 – 7.62 (m, 1H), 7.59 – 7.50 (m, 4H), 7.42 – 7.36 (m, 3H), 7.34 – 7.32 (m, 3H), 7.31 – 7.28 (m, 4H), 7.22 – 7.15 (m, 2H), 4.91 (s, 1H), 4.35 (dd, J = 11.8, 7.3 Hz, 1H), 3.65 – 3.46 (m, 1H), 3.32 – 3.22 (m, 1H), 3.22 – 3.12 (m, 1H), 3.12 – 3.02 (m, 1H), 2.39 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.7, 191.2, 144.5, 137.5, 136.6, 135.5, 135.0, 134.0, 133.4, 131.1, 130.4, 129.5, 128.6, 128.3, 128.1, 127.9, 126.6, 123.2, 117.0, 71.9, 64.6, 52.9, 42.4, 38.1, 21.7. HRMS (ESI) calcd for $C_{33}H_{28}BrN_2O_4S^+$ $[M+H]^+$ 627.0953, found 627.0951.



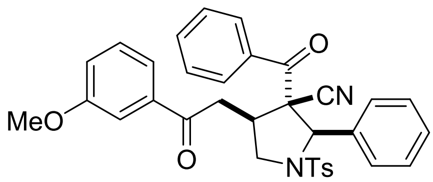
3ai

White solid, 74% yield, 10:1 dr. Purified by flash chromatography (12% EtOAc/PE). mp = 190-191 °C;^1H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.79 (m, 1H), 7.64 – 7.53 (m, 3H), 7.51 – 7.37 (m, 3H), 7.35 – 7.23 (m, 8H), 7.22 – 7.15 (m, 2H), 4.86 (s, 1H), 4.32 (dd, J = 11.7, 7.5 Hz, 1H), 3.52 (t, J = 11.3 Hz, 1H), 3.31 – 3.17 (m, 1H), 3.13 – 3.03 (m, 1H), 3.03 – 2.94 (m, 1H), 2.40 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 193.9, 191.1, 144.5, 138.5, 135.4, 135.3, 134.9, 134.1, 133.6, 133.4, 130.9, 130.03, 129.99, 129.5, 128.6, 128.3, 128.1, 127.9, 127.4, 127.1, 117.0, 71.8, 64.6, 52.8, 42.3, 38.1, 21.7. HRMS (ESI) calcd for $C_{33}H_{27}Cl_2N_2O_4S^+$ [M+H]$^+$ 617.1069, found 617.1066.



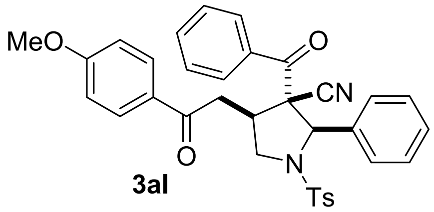
3aj

White solid, 86% yield, 11:1 dr. Purified by flash chromatography (12% EtOAc/PE). mp = 100-101 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.79 (m, 2H), 7.72 – 7.63 (m, 2H), 7.62 – 7.55 (m, 2H), 7.46 – 7.38 (m, 1H), 7.35 – 7.23 (m, 9H), 7.21 – 7.14 (m, 2H), 4.86 (s, 1H), 4.35 (dd, *J* = 11.6, 7.5 Hz, 1H), 3.52 (t, *J* = 11.2 Hz, 1H), 3.34 – 3.23 (m, 1H), 3.20 – 3.10 (m, 1H), 3.09 – 2.99 (m, 1H), 2.40 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.8, 191.0, 144.5, 138.6, 135.3, 134.8, 134.1, 133.5, 132.6, 130.0, 129.54, 129.51, 128.6, 128.5, 128.3, 128.1, 127.9, 117.7, 117.1, 117.0, 71.7, 64.5, 52.7, 42.2, 38.4, 21.7. HRMS (ESI) calcd for $C_{34}H_{28}N_3O_4S^+$ [M+H]$^+$ 574.1801, found 574.1805.



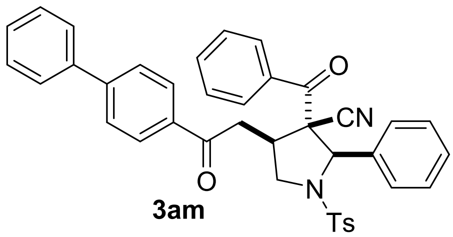
3ak

White solid, 79% yield, 10:1 dr. Purified by flash chromatography (12% EtOAc/PE). mp = 127-128 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.56 (m, 2H), 7.46 – 7.38 (m, 2H), 7.34 – 7.30 (m, 4H), 7.30 – 7.26 (m, 6H), 7.25 – 7.20 (m, 1H), 7.20 – 7.13 (m, 2H), 7.06 – 6.98 (m, 1H), 4.89 (s, 1H), 4.33 (dd, *J* = 11.8, 7.4 Hz, 1H), 3.75 (s, 3H), 3.53 (t, *J* = 11.2 Hz, 1H), 3.29 – 3.17 (m, 1H), 3.16 – 3.07 (m, 1H), 3.06 – 2.96 (m, 1H), 2.39 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.9, 191.4, 159.9, 144.4, 137.1, 135.6 135.1, 133.9, 133.4, 130.0, 129.8, 129.7, 129.4, 128.6, 128.3, 128.1, 127.9, 120.7, 120.3, 117.0, 112.2, 71.8, 64.8, 55.5, 53.0, 42.7, 38.1, 21.7. HRMS (ESI) calcd for $C_{34}H_{31}N_2O_5S^+$ [M+H]$^+$ 579.1954, found 579.1954.



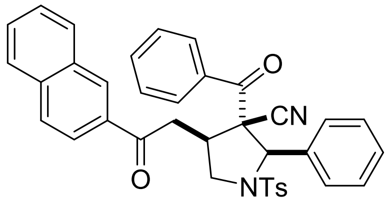
3al

White solid, 80% yield, 8.5:1 dr. Purified by flash chromatography (12 % EtOAc/PE). mp = 127-128 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (dd, *J* = 20.5, 8.2 Hz, 4H), 7.46 – 7.37 (m, 2H), 7.33 – 7.29 (m, 5H), 7.28 (s, 2H), 7.16 (dt, *J* = 11.3, 7.0 Hz, 5H), 4.91 (s, 1H), 4.32 (dd, *J* = 11.8, 7.4 Hz, 1H), 3.53 (t, *J* = 11.3 Hz, 1H), 3.27 – 3.17 (m, 1H), 3.12 (dd, *J* = 17.4, 9.1 Hz, 1H), 3.00 (dd, *J* = 17.4, 4.6 Hz, 1H), 2.39 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.9, 191.4, 159.9, 144.4, 137.1, 135.6, 135.1, 133.9, 133.4, 130.0, 129.8, 129.4, 128.6, 128.3, 128.1, 127.9, 120.7, 120.3, 117.1, 112.2, 71.8, 64.8, 55.5, 42.7, 38.1, 21.7. HRMS (ESI) calcd for $C_{34}H_{31}N_2O_5S^+$ $[M+H]^+$ 579.1954, found 579.1954.



3am

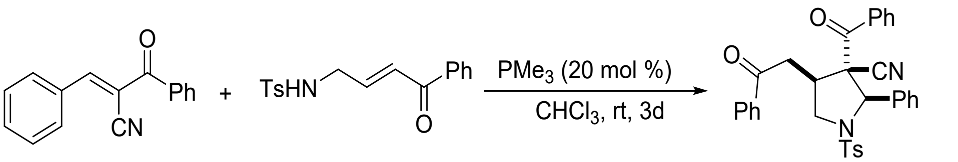
White solid, 86% yield, 12.5:1 dr. Purified by flash chromatography (12% EtOAc/PE). mp = 160-162 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 – 7.81 (m, 2H), 7.66 – 7.60 (m, 2H), 7.59 – 7.55 (m, 2H), 7.55 – 7.50 (m, 2H), 7.45 – 7.42 (m, 1H), 7.41 – 7.36 (m, 3H), 7.35 – 7.28 (m, 9H), 7.20 – 7.16 (m, 2H), 4.92 (s, 1H), 4.35 (dd, *J* = 11.8, 7.4 Hz, 1H), 3.59 – 3.50 (m, 1H), 3.30 – 3.22 (m, 1H), 3.22 – 3.12 (m, 1H), 3.11 – 3.02 (m, 1H), 2.39 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 194.5, 190.4, 145.4, 143.4, 138.5, 134.6, 134.2, 133.5, 132.9, 132.4, 129.0, 128.38, 128.36, 128.1, 128.0, 127.63, 127.56, 127.5, 127.4, 127.3, 127.0, 126.9, 126.3, 126.2, 116.0, 70.8, 63.8, 52.0, 41.7, 37.0, 20.7. HRMS (ESI) calcd for $C_{39}H_{33}N_2O_4S^+$ $[M+H]^+$ 625.2156, found 625.2159.



3an

White solid, 81% yield, 8:1 dr. Purified by flash chromatography (12% EtOAc/PE). mp = 162-163 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.26 (s, 1H), 7.86 – 7.82 (m, 2H), 7.78 (dd, J = 8.5, 3.5 Hz, 2H), 7.63 (d, J = 8.2 Hz, 2H), 7.52 (dd, J = 11.0, 3.9 Hz, 1H), 7.47 (dd, J = 11.4, 4.2 Hz, 1H), 7.41 (dd, J = 12.0, 4.4 Hz, 1H), 7.35 – 7.30 (m, 5H), 7.28 (t, J = 6.9 Hz, 4H), 7.18 (d, J = 7.7 Hz, 2H), 4.91 (s, 1H), 4.37 (dd, J = 11.8, 6.9 Hz, 1H), 3.64 – 3.53 (m, 1H), 3.29 (ddd, J = 22.5, 12.7, 6.4 Hz, 2H), 3.18 (t, J = 10.6 Hz, 1H), 2.36 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 194.8, 190.3, 143.4, 134.8, 134.6, 134.1, 132.9, 132.3, 132.1, 131.3, 128.99, 128.95, 128.6, 128.4, 127.95, 127.87, 127.7, 127.6, 127.3, 127.0, 126.9, 126.8, 126.0, 122.4, 116.1, 70.9, 63.8, 52.0, 41.8, 37.0, 20.6. HRMS (ESI) calcd for $C_{37}H_{31}N_2O_4S^+$ $[M+H]^+$ 599.2005, found 599.2002.

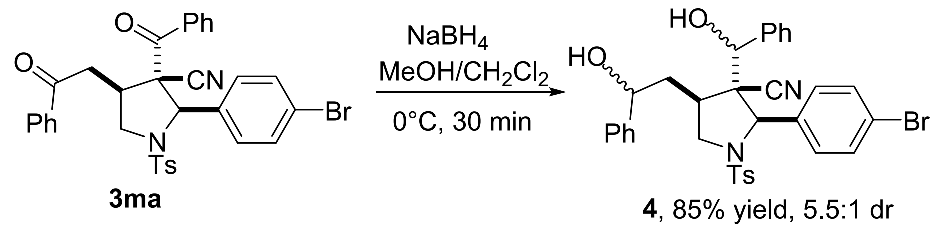
The reaction on the gram-scale of the product



1a (0.699g, 3.0mmol) **2a** (0.788g, 2.5mmol) **3aa** 1.11g, 81% yield, 13:1 dr

Under argon atmosphere, to a mixture of unsaturated ketones **1** (3.0 mmol), β-sulfonamido-substituted enones **2** (2.5 mmol) and catalyst PMe_3 (20 mol %, 0.5 mmol) in a Schlenk tube, 125 mL of $CHCl_3$ was added at room temperature. The resulting mixture was stirred until the starting material was completely consumed (monitored by TLC) and then was concentrated to dryness. The residue was purified through flash column chromatography (EtOAc/PE) to afford the corresponding cycloaddition products **3**.

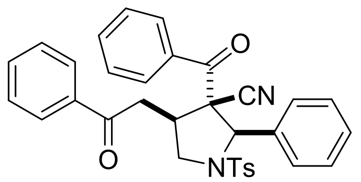
The reaction on further transformation of the product 3am



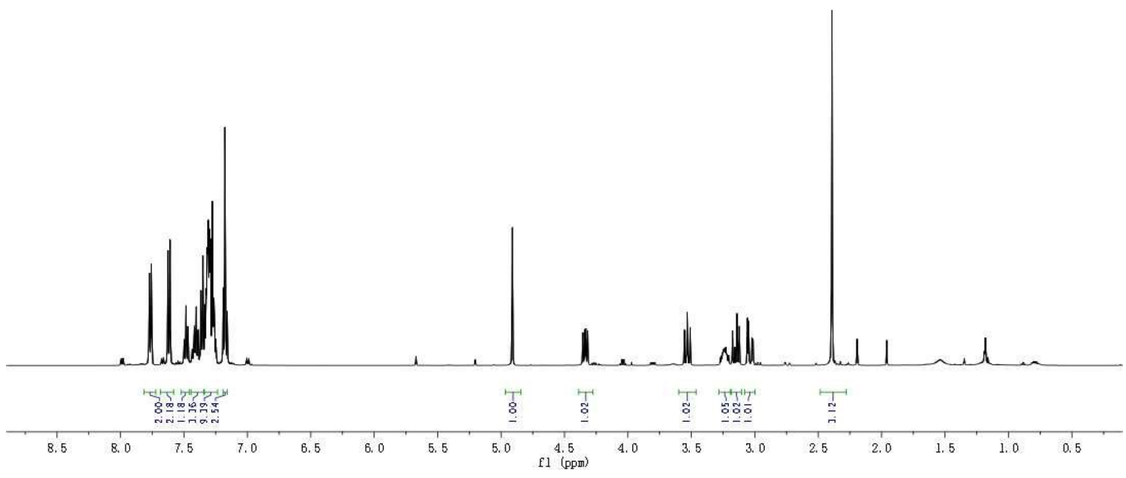
$NaBH_4$ (0.3 mmol, 12 mg) was added in portions to a solution of **3a** (0.1 mmol, 62.6 mg) in MeOH (1 mL) at 0 °C. The mixture was stirred at 0 °C until the reaction was completed as monitored by TLC (30 min). When **3ma** was consumed, H_2O (3 mL) was added to the reaction tube. The aqueous phase was extracted with DCM. The combined organic layers were dried over Na_2SO_4, filtered and concentrated in vacuo. Then the residue was purified by column chromatography to afford compound **7** as a White solid (53.6 mg, 85% yield).

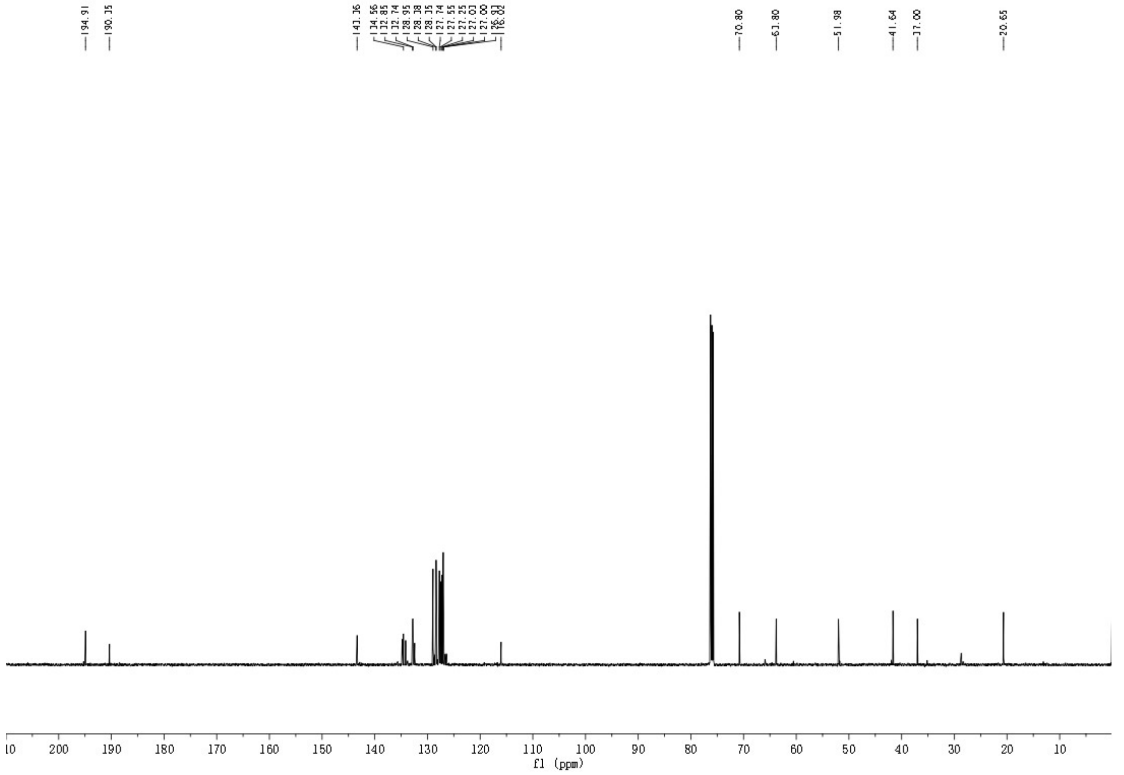
White solid, 85% yield, 5.5:1 dr. Purified by flash chromatography (25% EtOAc/PE). mp = 202-203 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 – 7.34 (m, 2H), 7.33 – 7.14 (m, 9H), 7.13 – 7.05 (m, 5H), 7.01 – 6.85 (m, 2H), 4.94 (s, 1H), 4.40 (d, J = 4.7 Hz, 1H), 4.26 (s, 1H), 4.16 – 3.99 (m, 1H), 3.36 – 3.15 (m, 1H), 3.00 (s, 1H), 2.34 (s, 3H), 2.19 – 2.09 (m, 1H), 2.09 – 1.99 (m, 1H), 1.60 – 1.41 (m, 1H), 1.32 – 1.20 (m, 1H).^{13}C NMR (126 MHz, $CDCl_3$) δ 142.9, 142.2, 136.6, 136.1, 134.4, 130.3, 130.2, 128.8, 128.6, 128.4, 128.3, 127.9, 127.7, 127.6, 126.9, 126.5, 126.4, 124.5, 121.2, 116.3, 76.3, 76.0, 75.8, 75.7, 71.1, 67.1, 60.5, 59.4, 52.4, 39.6, 37.2, 20.6. HRMS (ESI) calcd for $C_{33}H_{31}BrN_2O_4SNa^+$ $[M+Na]^+$ 653.1093, found 653.1096.

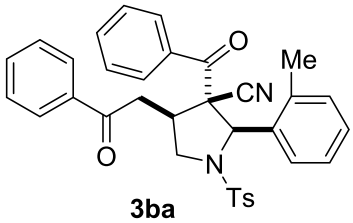
^{1}H and ^{13}C NMR Spectra



3aa







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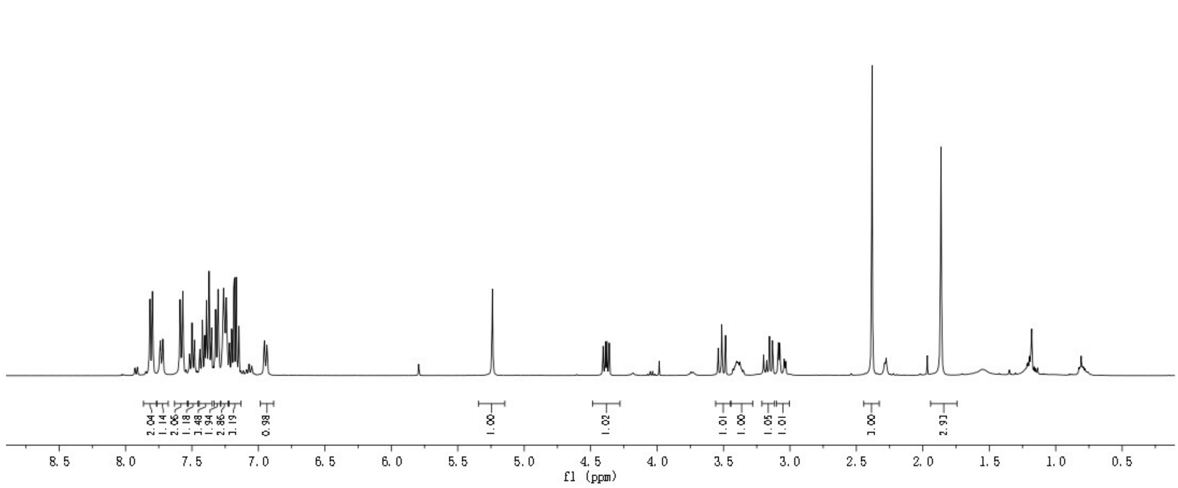
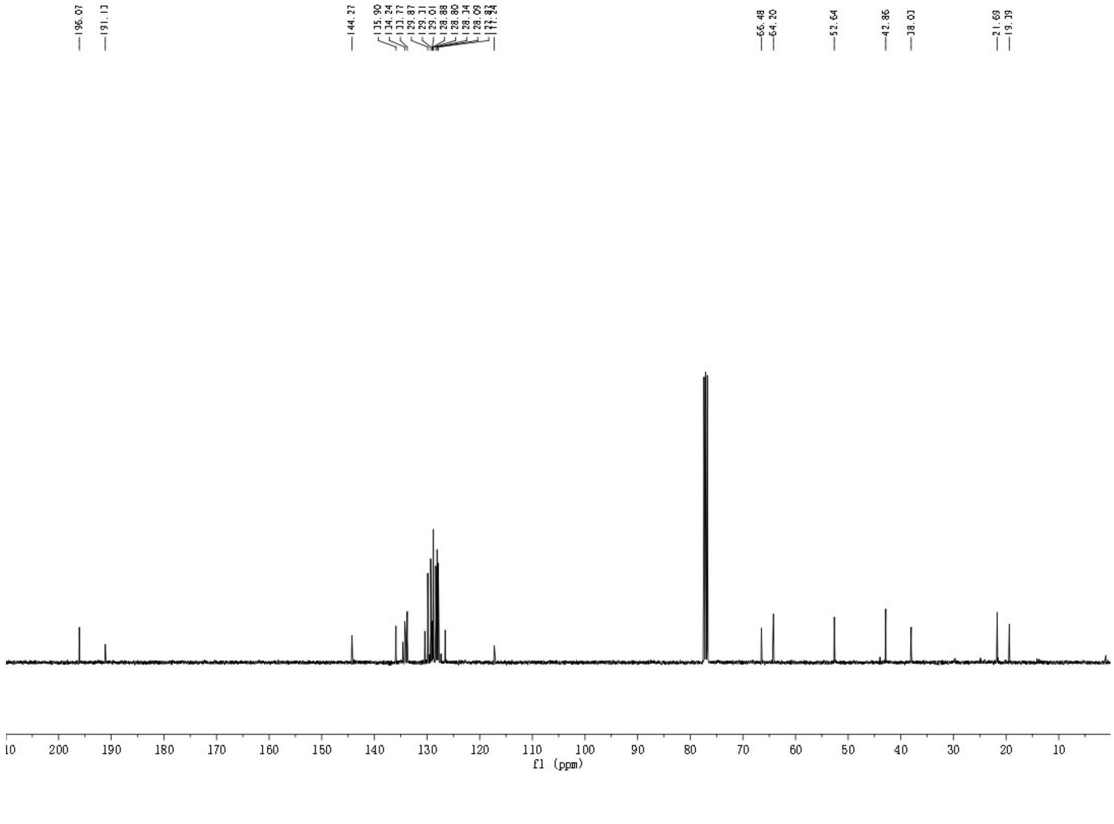
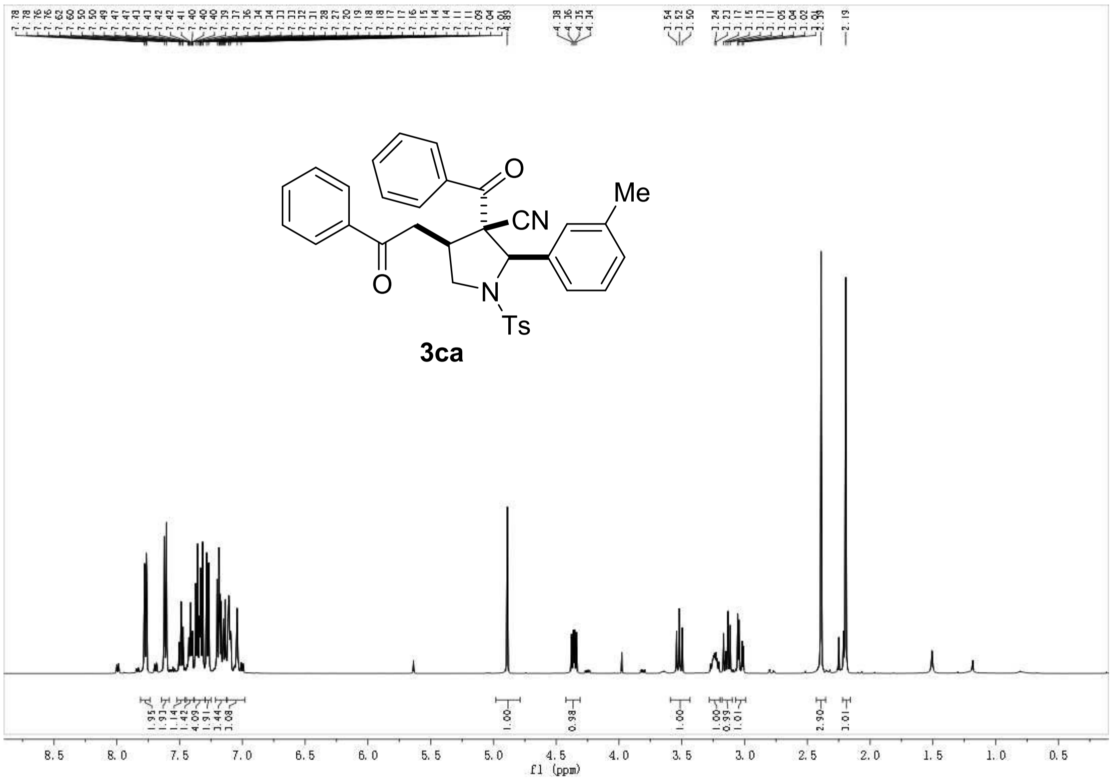
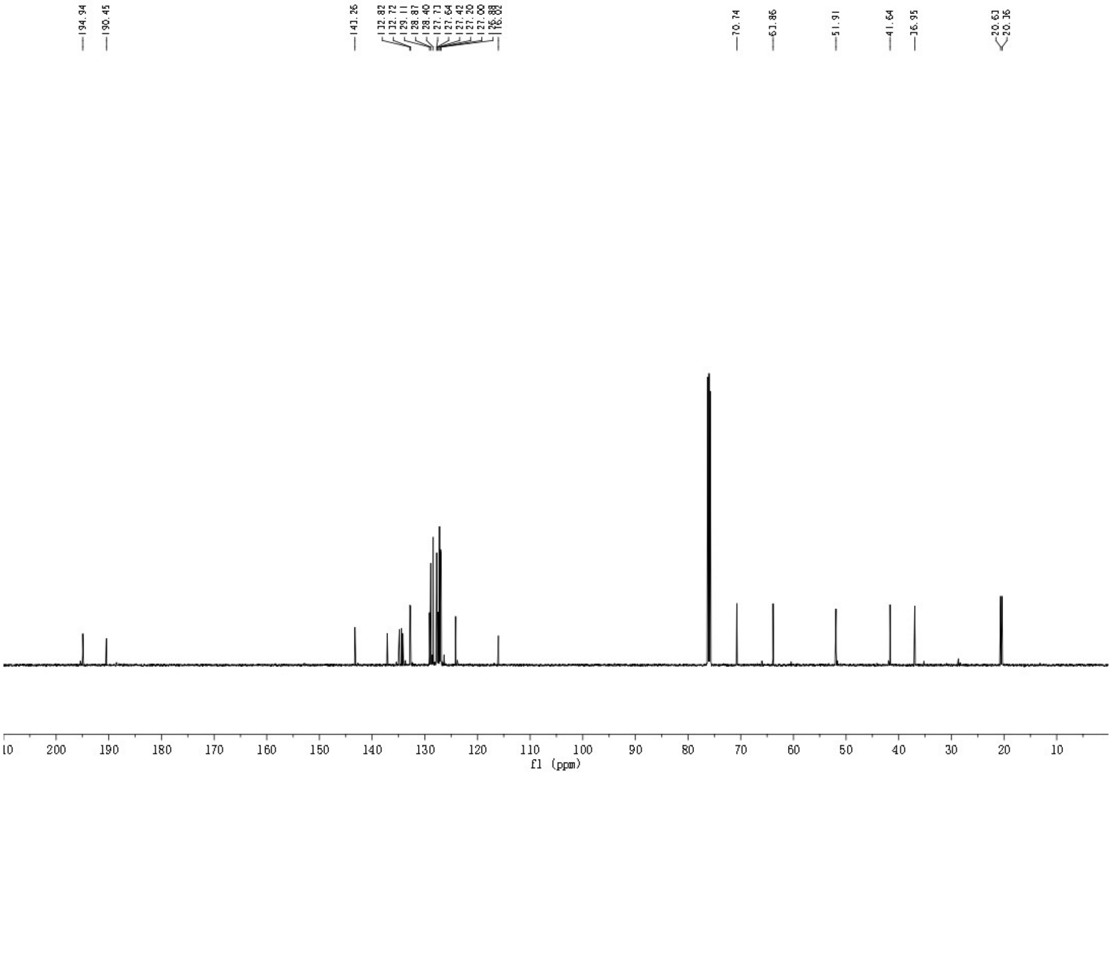
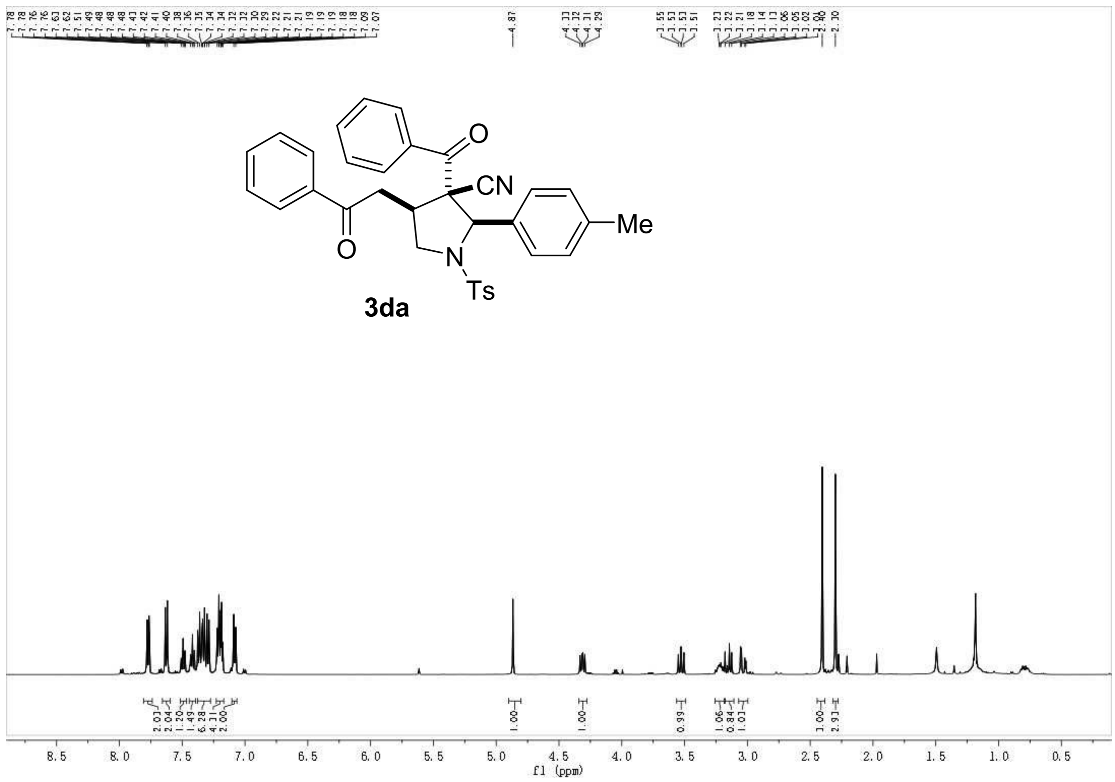


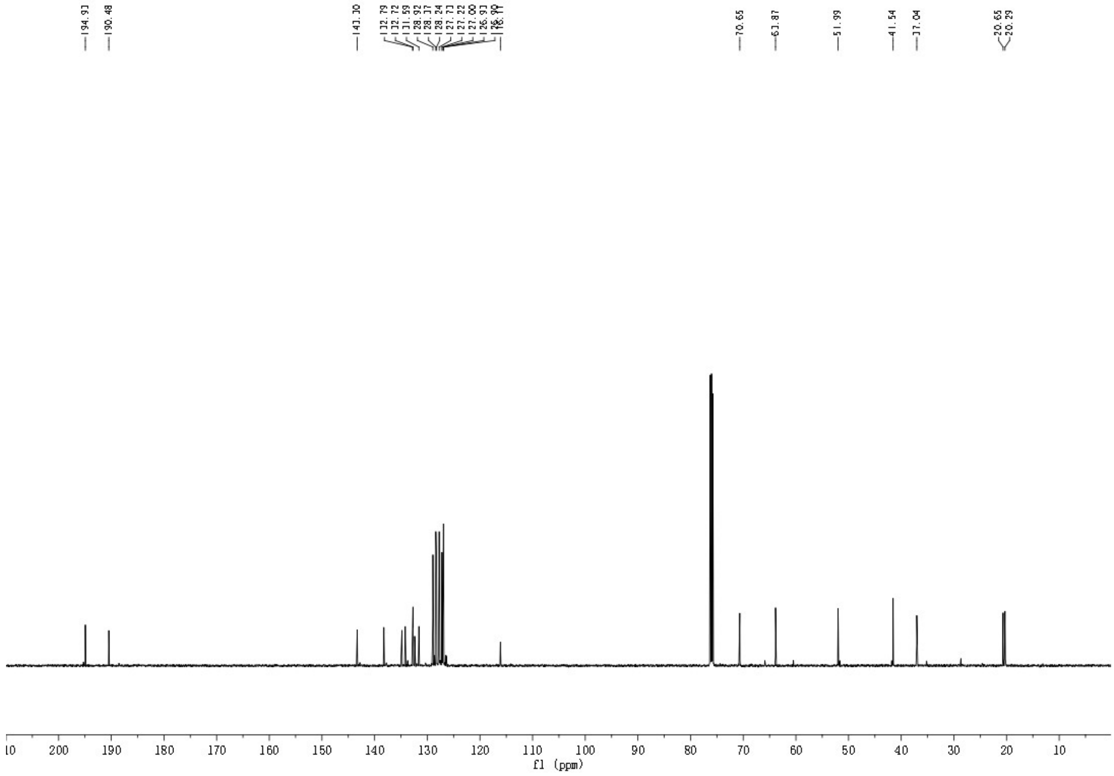



Me
CN
Ts
3ca
f1 (ppm)

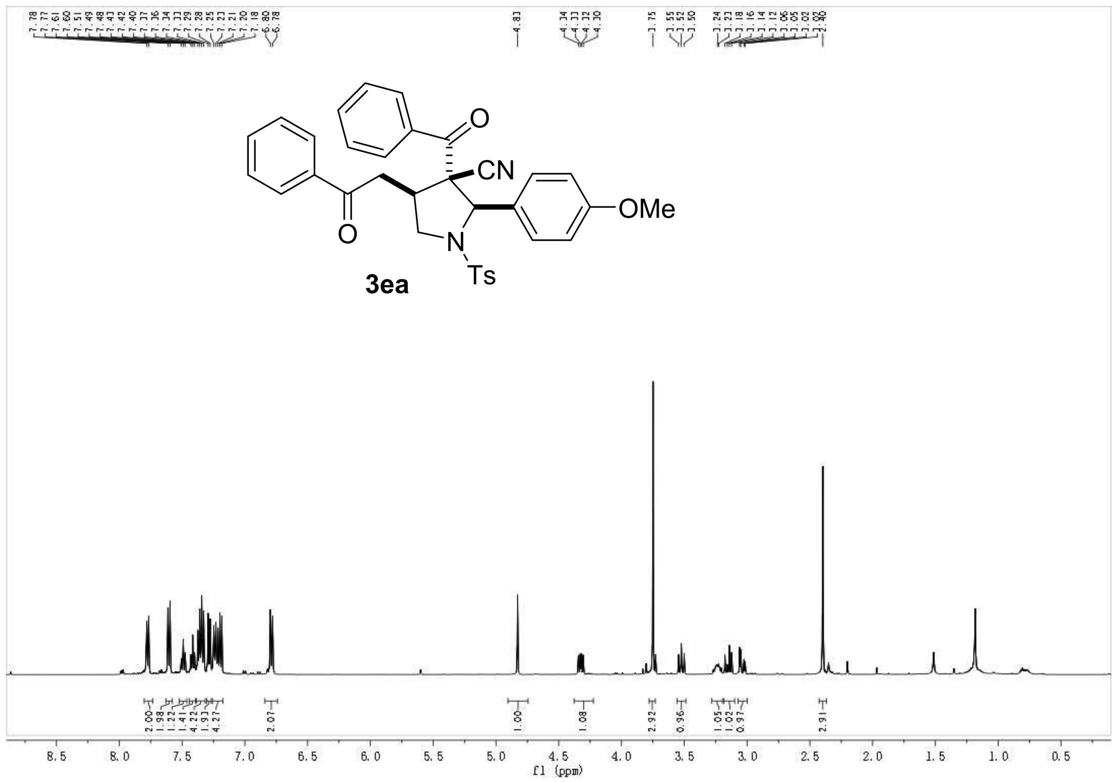

f1 (ppm)

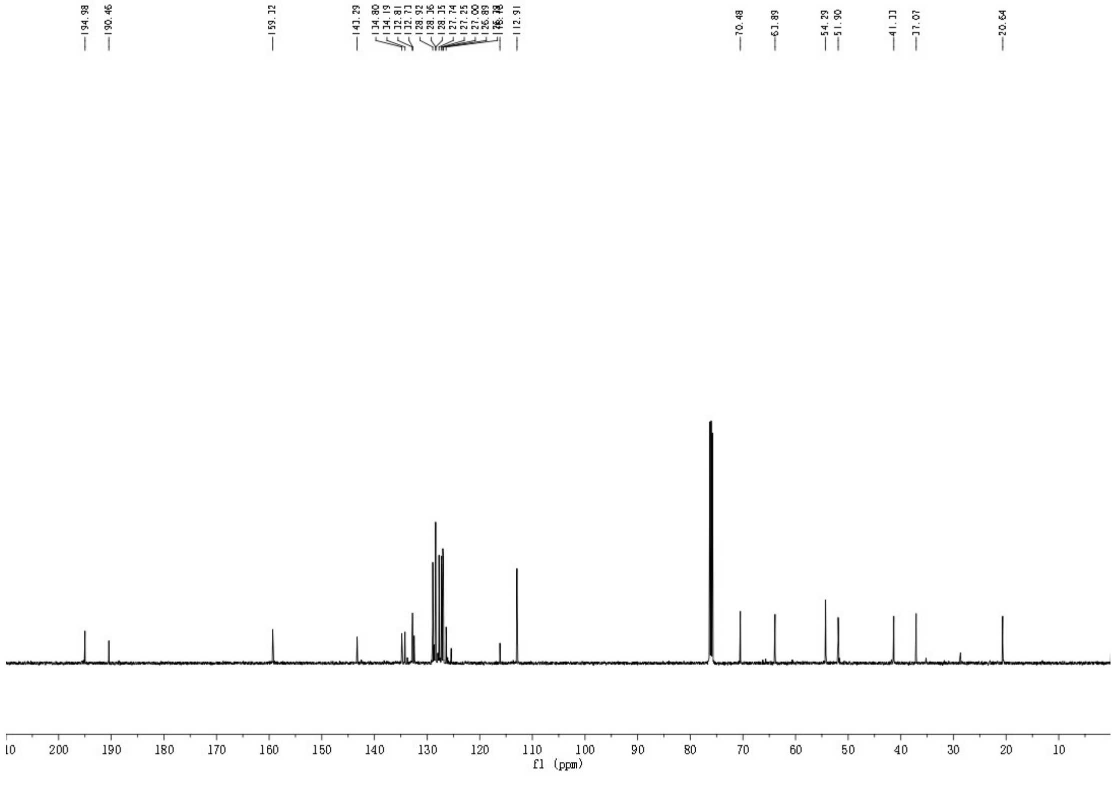


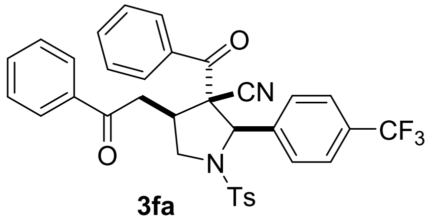
3da
CN
Me
Ts
O
N
f1 (ppm)



f1 (ppm)







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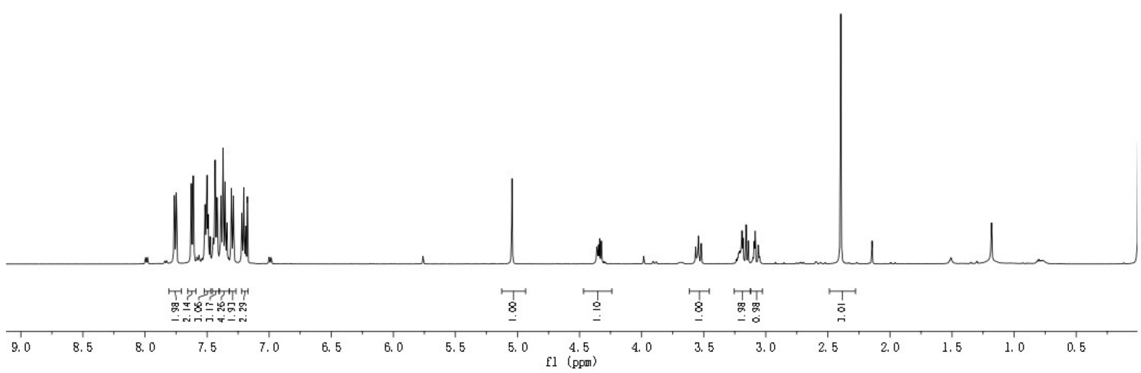
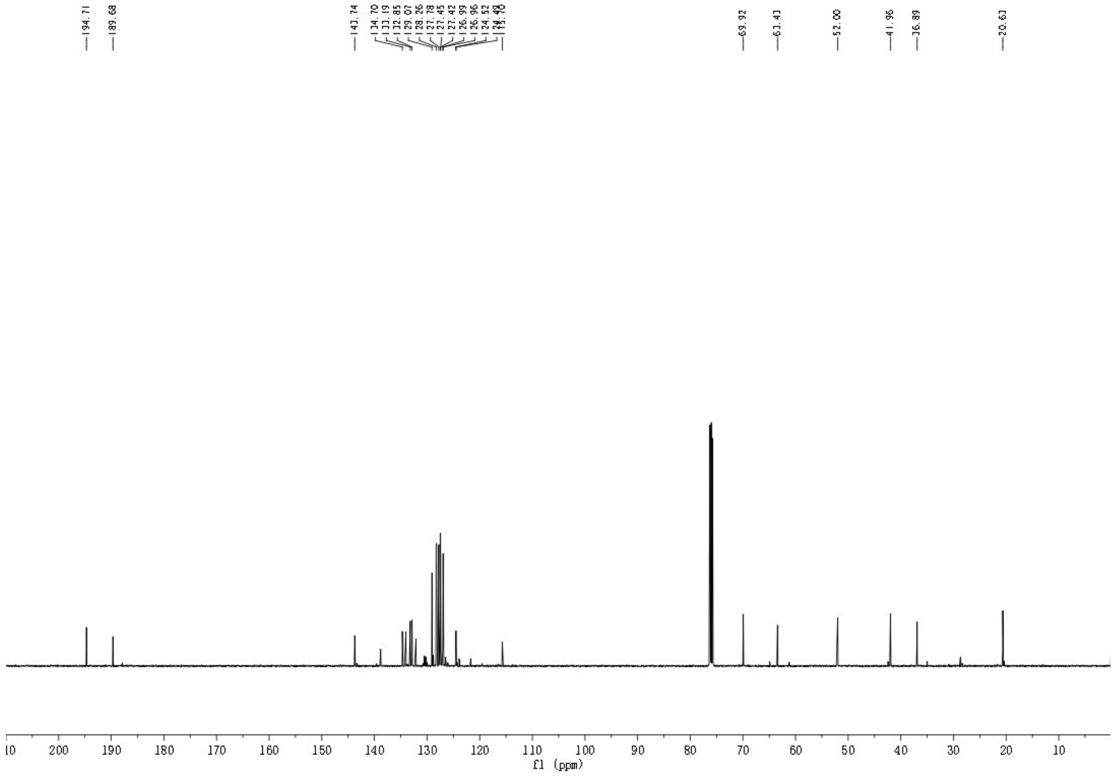
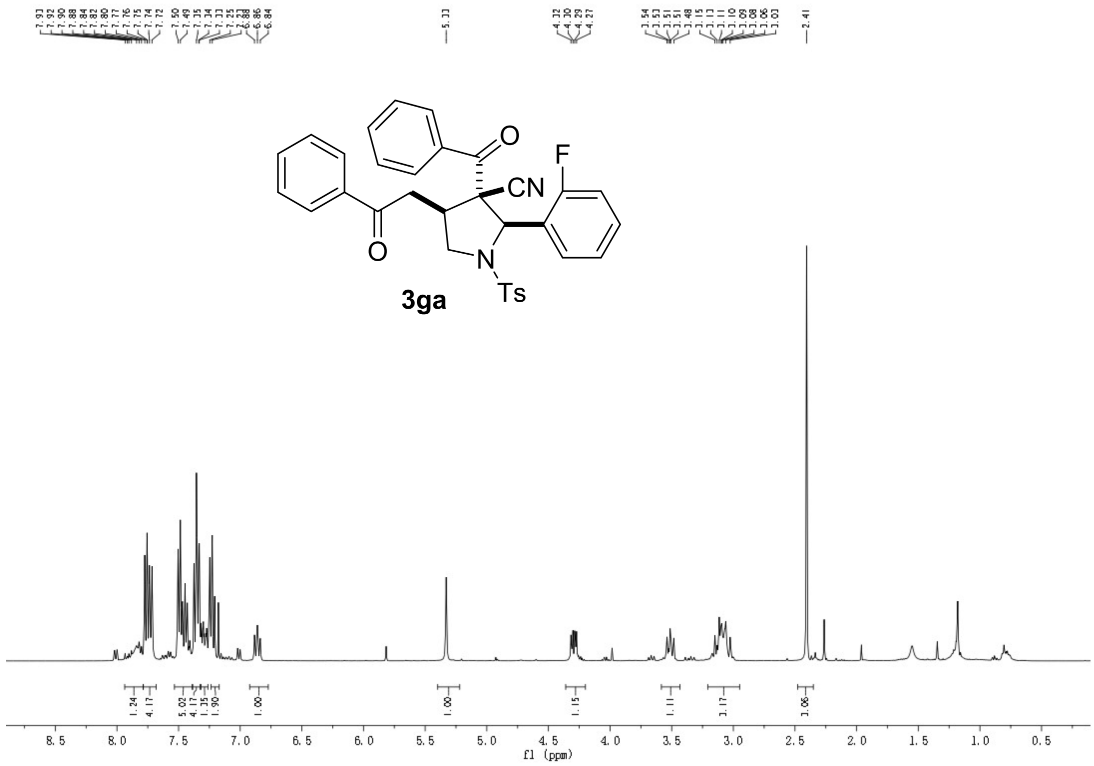
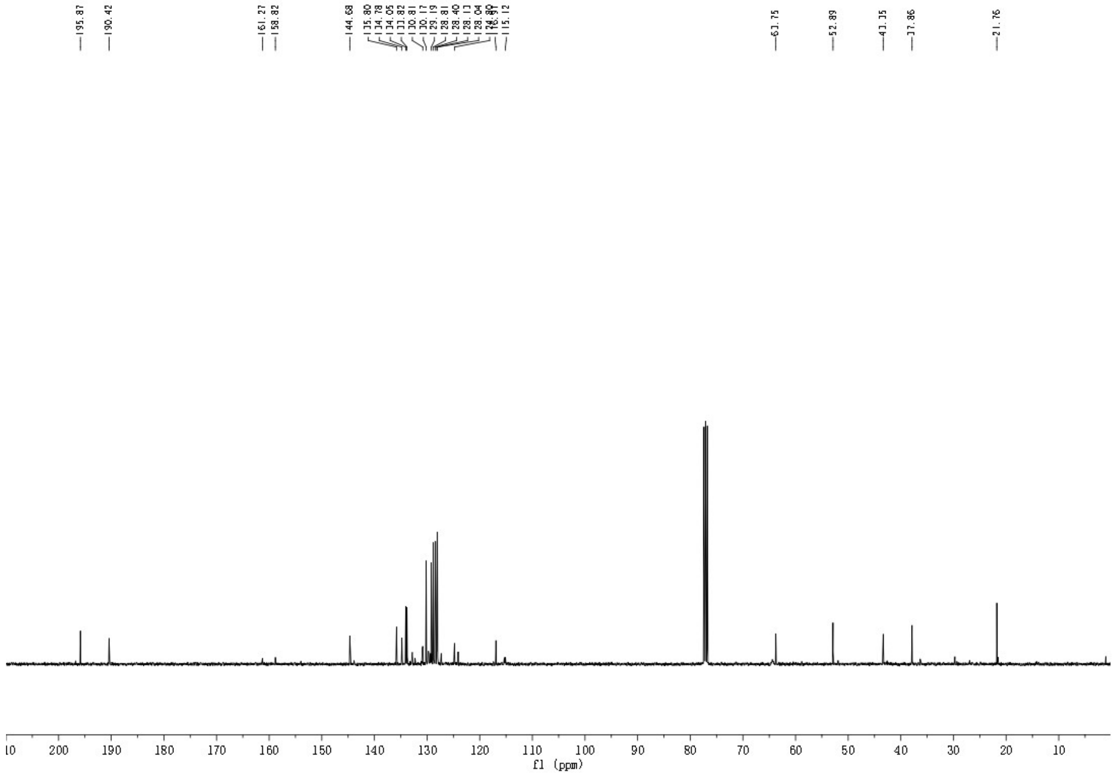





3ga
CN
F
N
Ts
O
O
f1 (ppm)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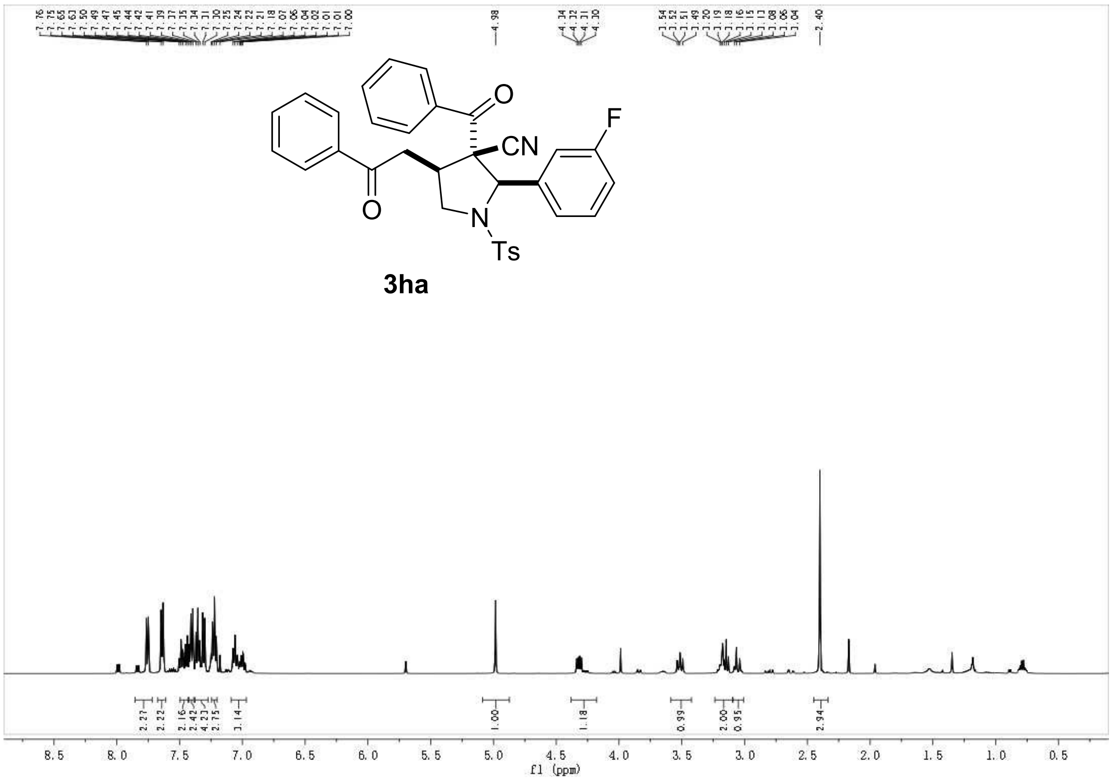
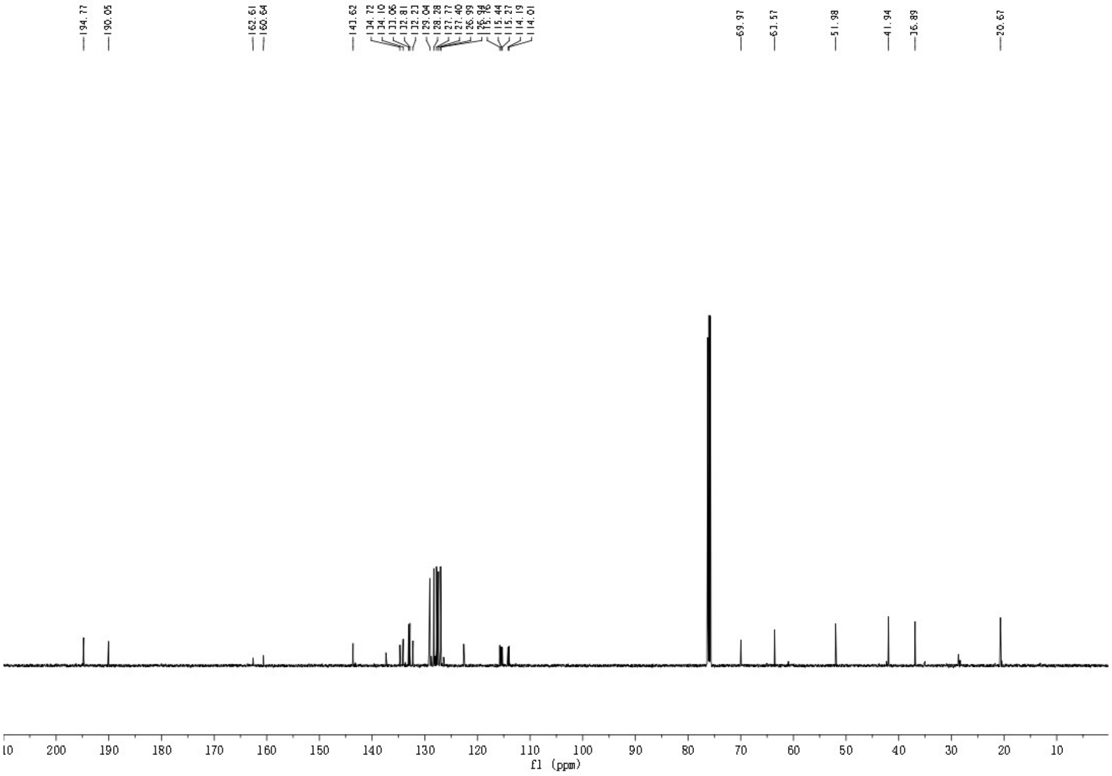
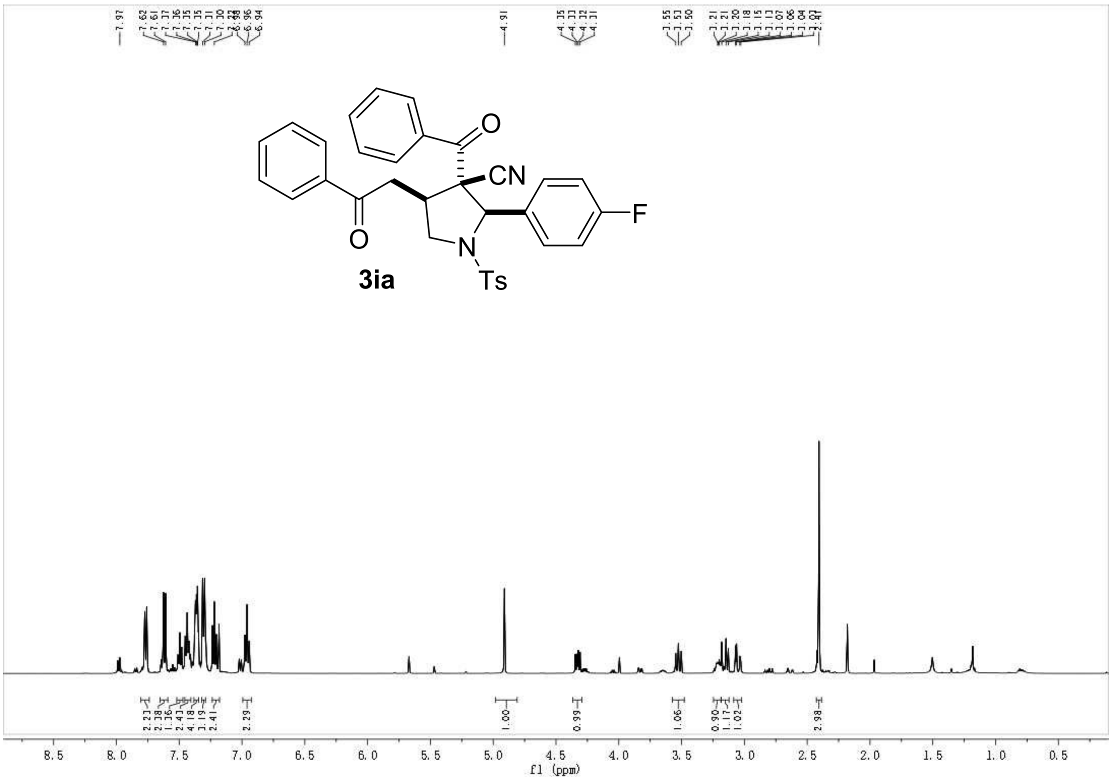
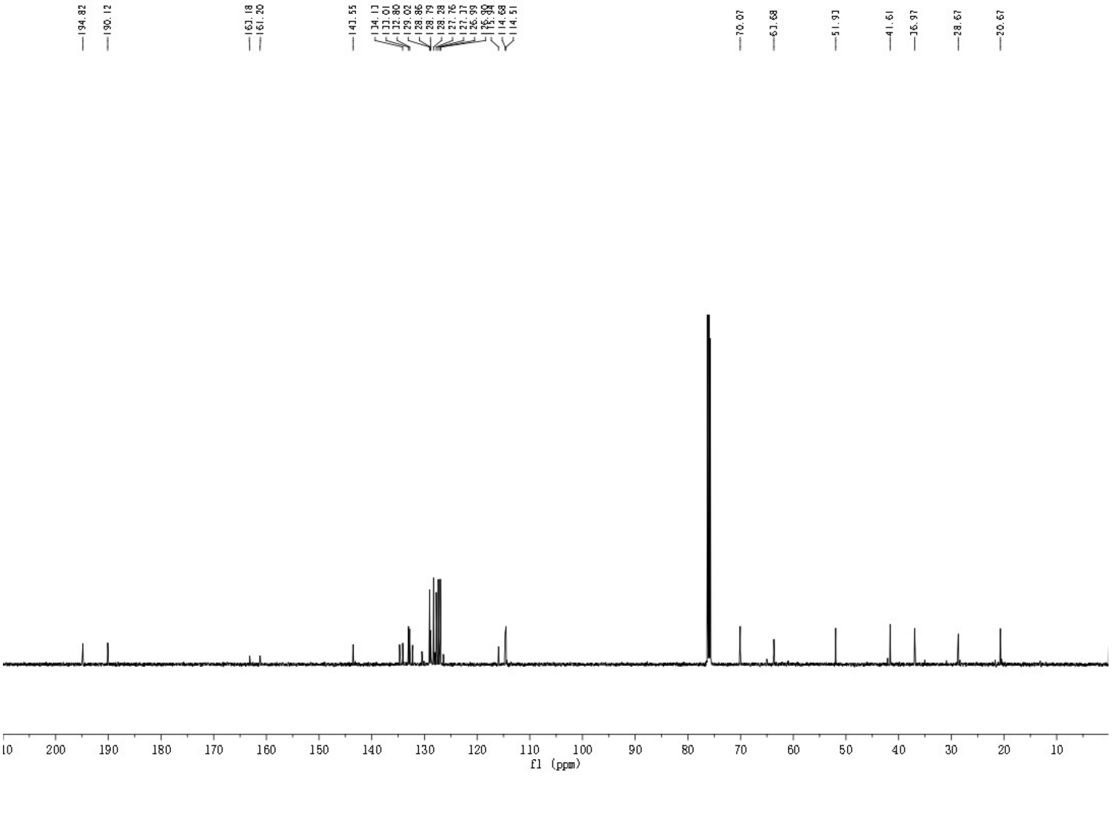

O
CN
F
O
N
Ts
3ha
f1 (ppm)


f1 (ppm)



3ia
CN
O
O
N
Ts
F
f1 (ppm)



194.82
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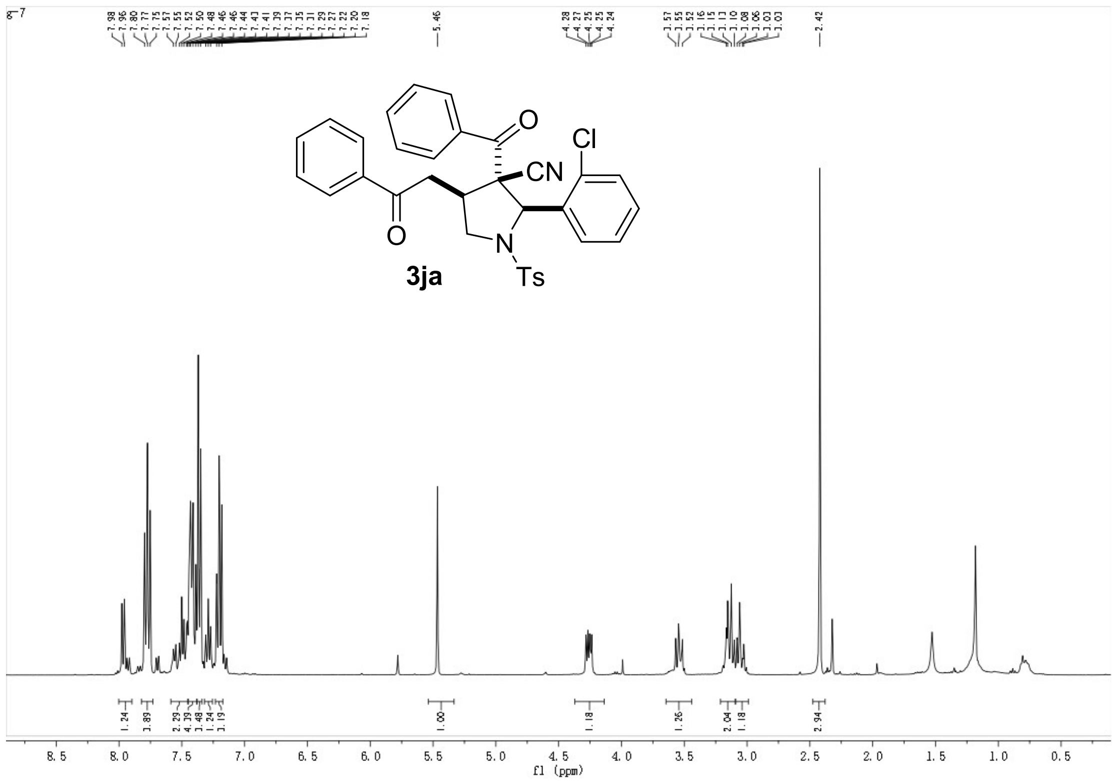
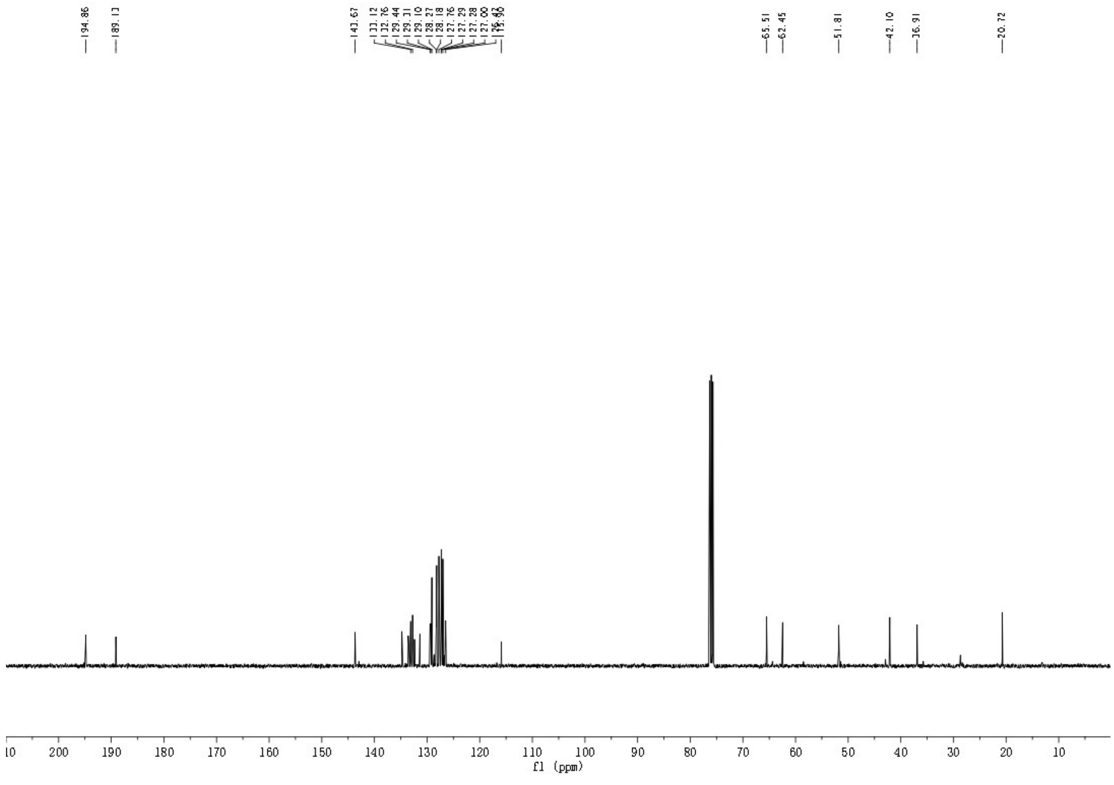
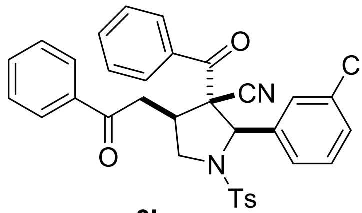
70.07
63.68
51.93
41.61
36.97
28.67
20.67
f1 (ppm)



3ja
Cl
CN
O
N
Ts
f1 (ppm)



f1 (ppm)



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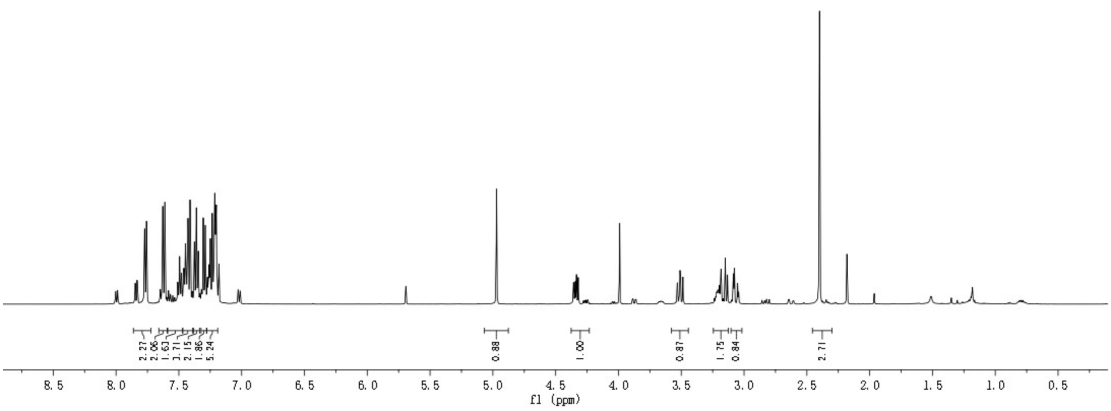
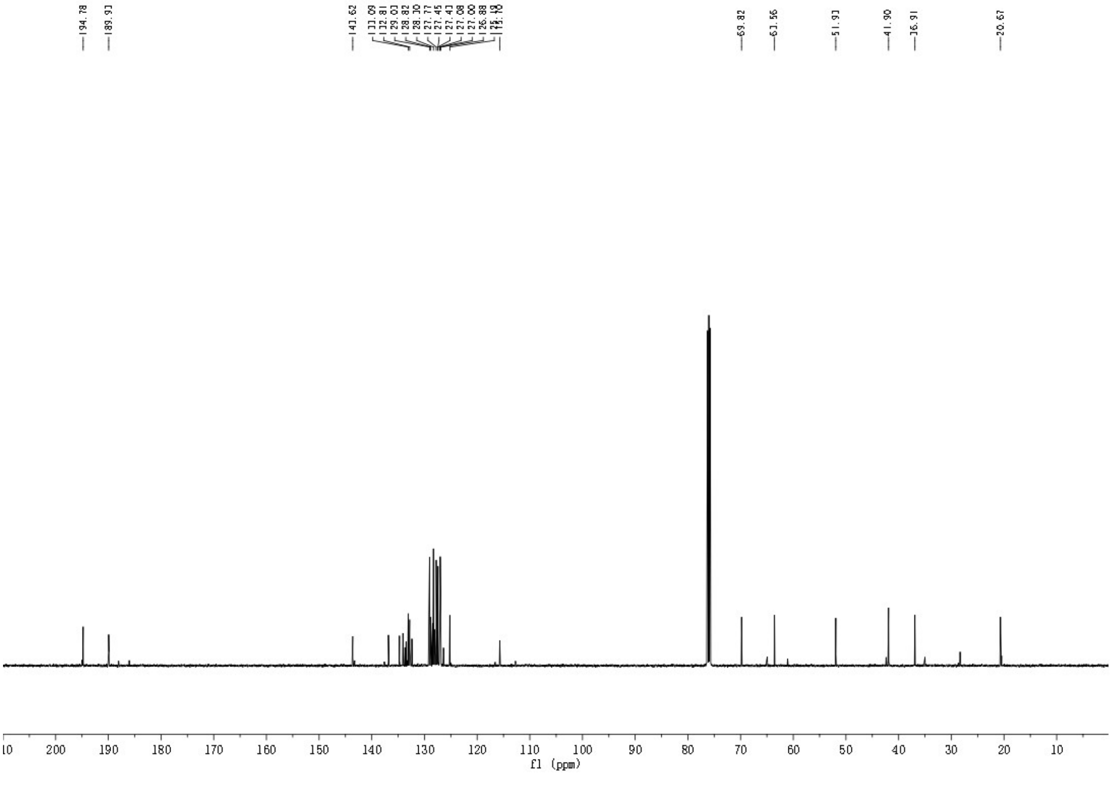
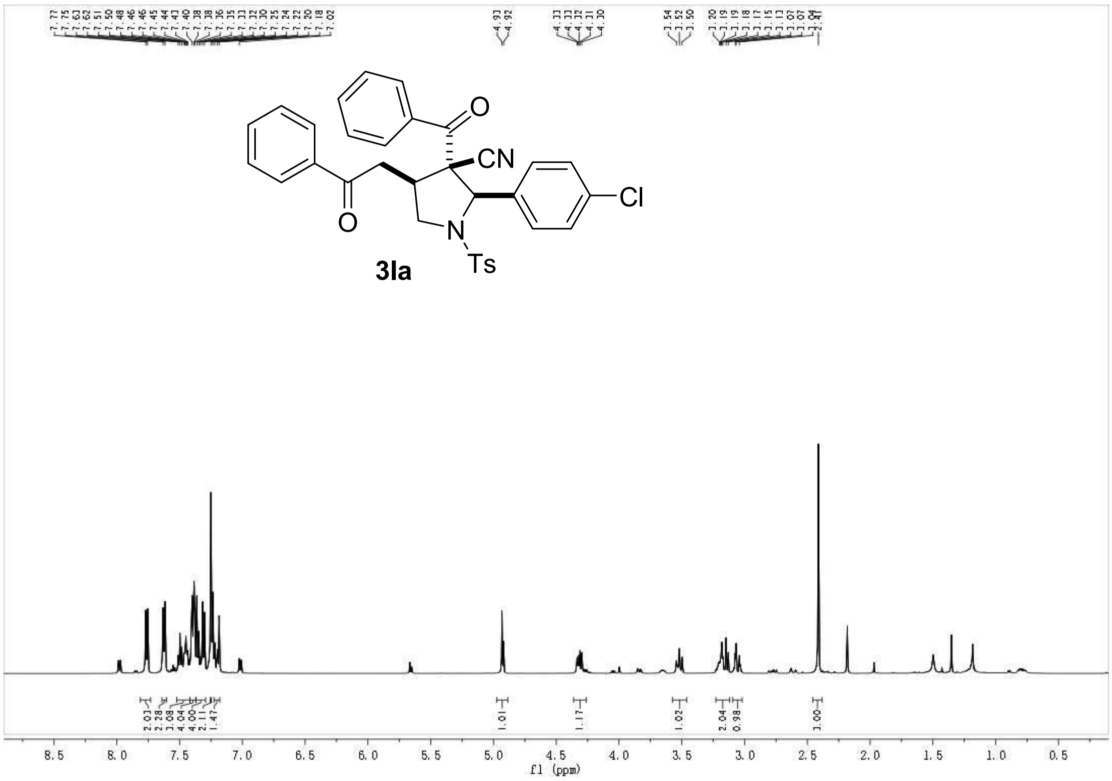
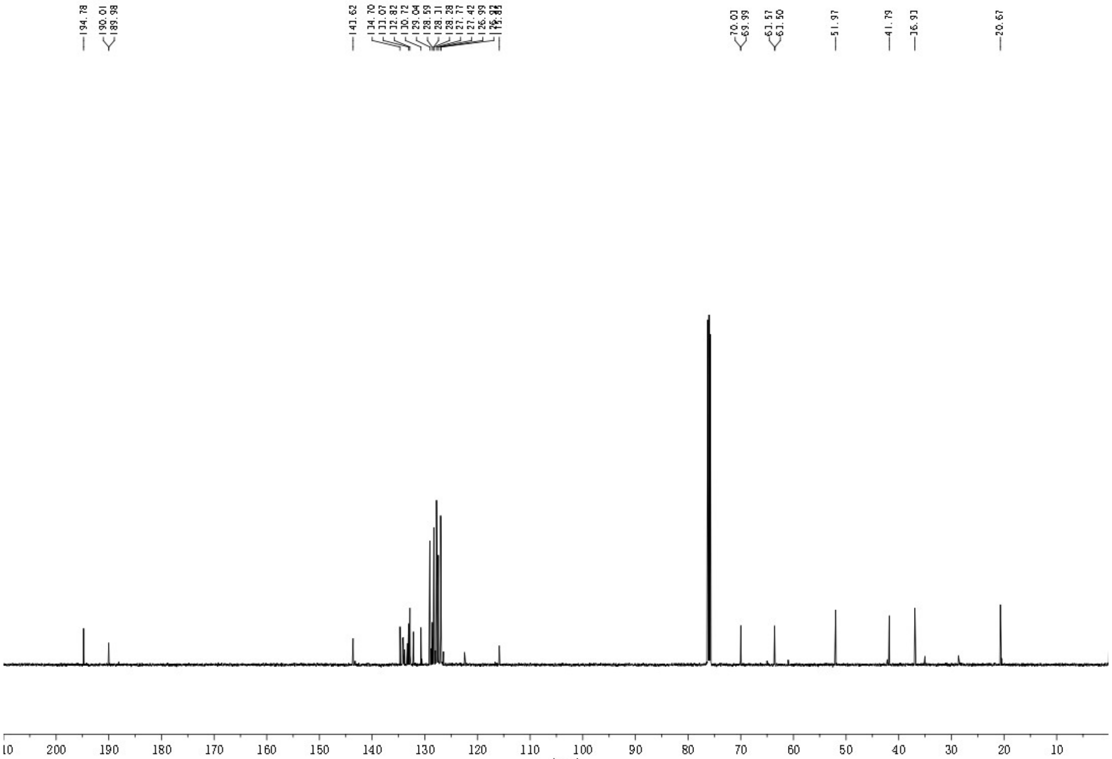
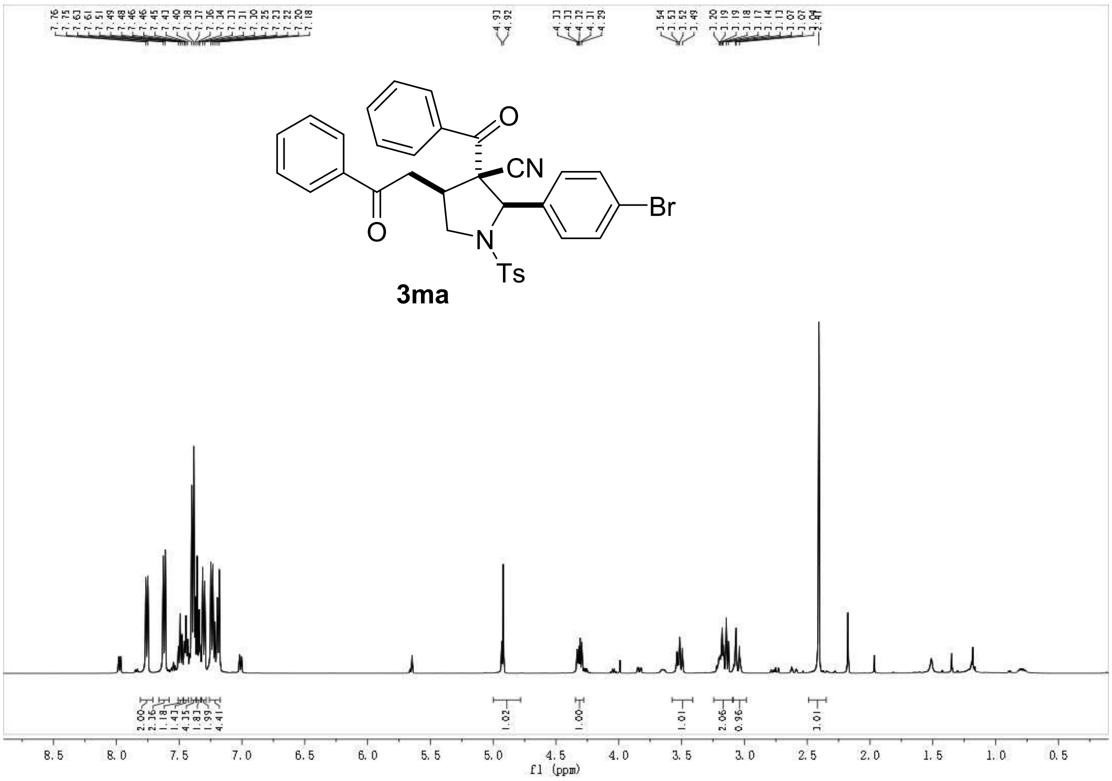
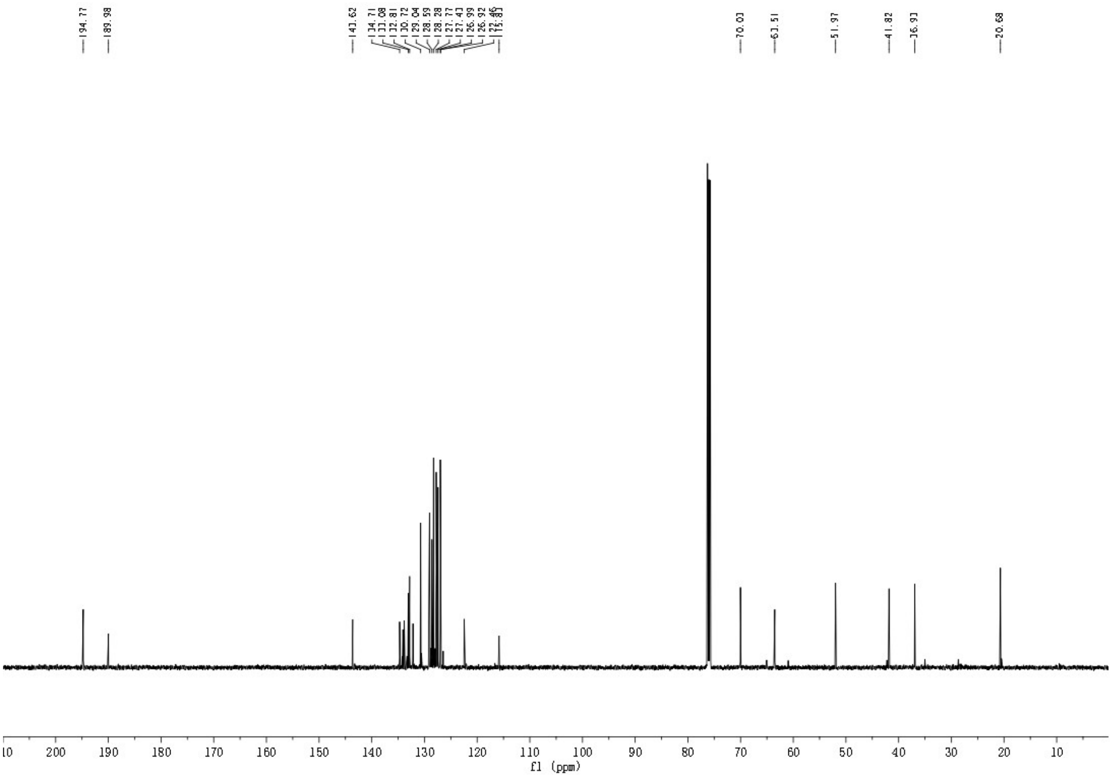









O
CN
Br
O
N
Ts
3ma
f1 (ppm)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189.98
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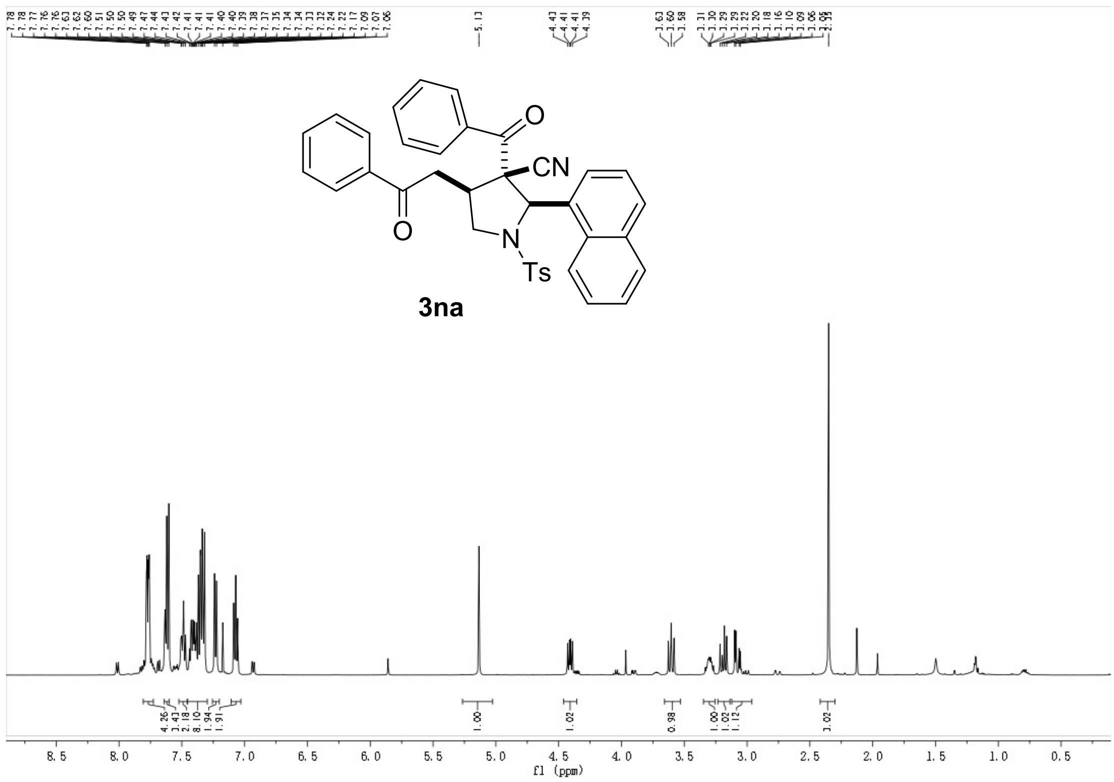
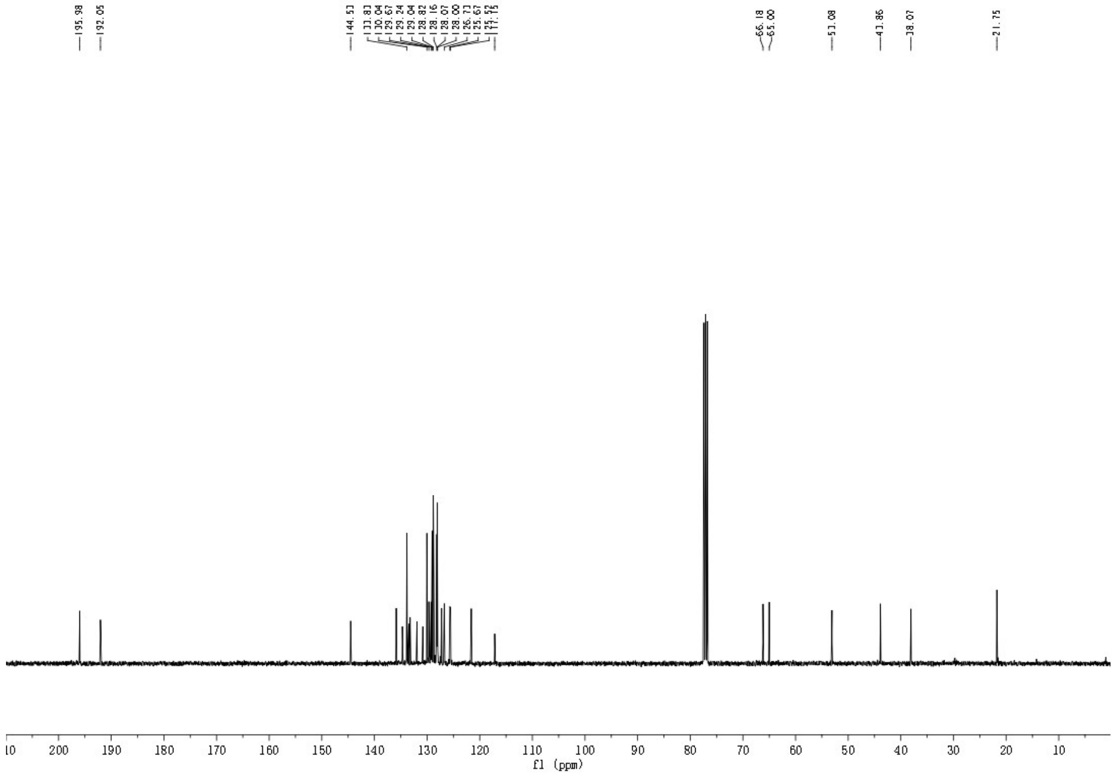
63.51
51.97
41.82
36.93
20.68
f1 (ppm)



CN
O
O
N
Ts
3na
f1 (ppm)



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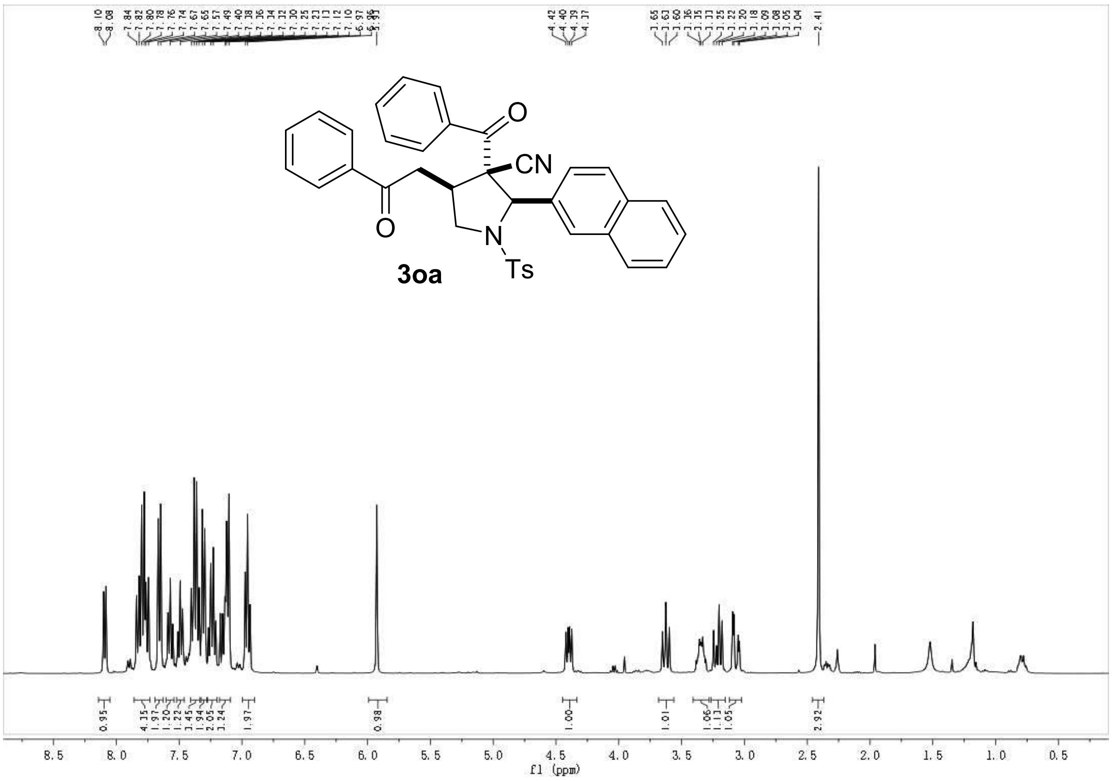
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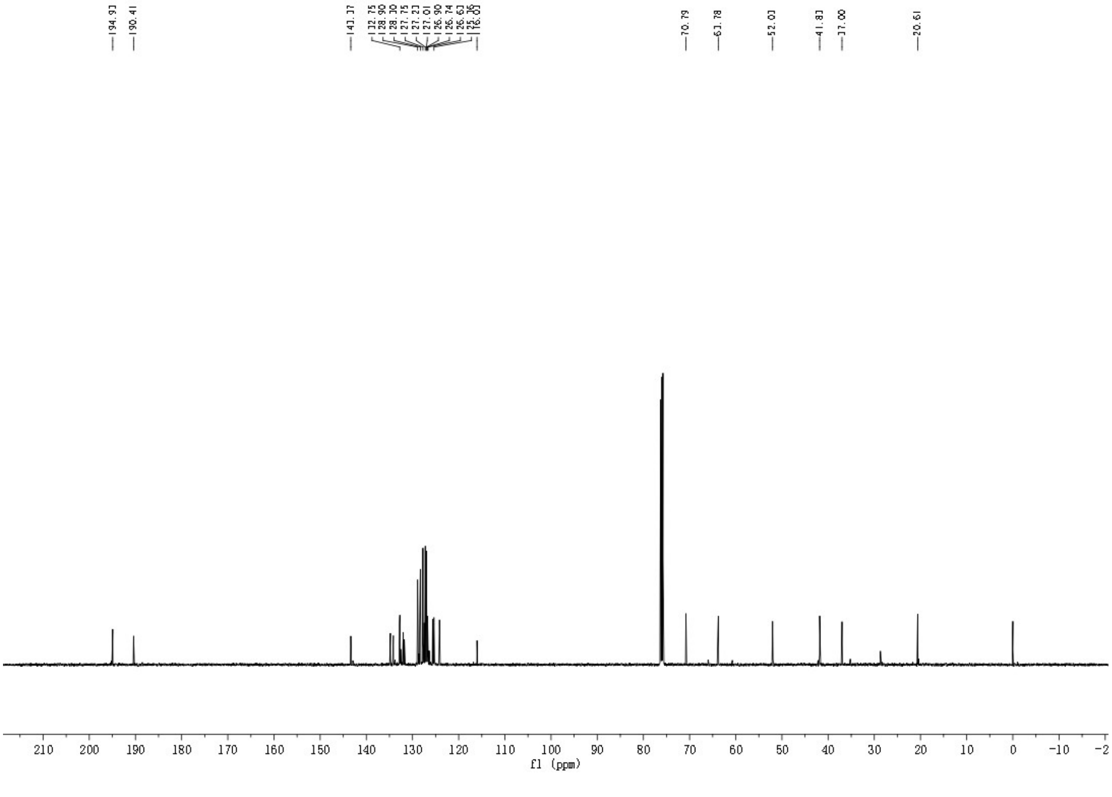
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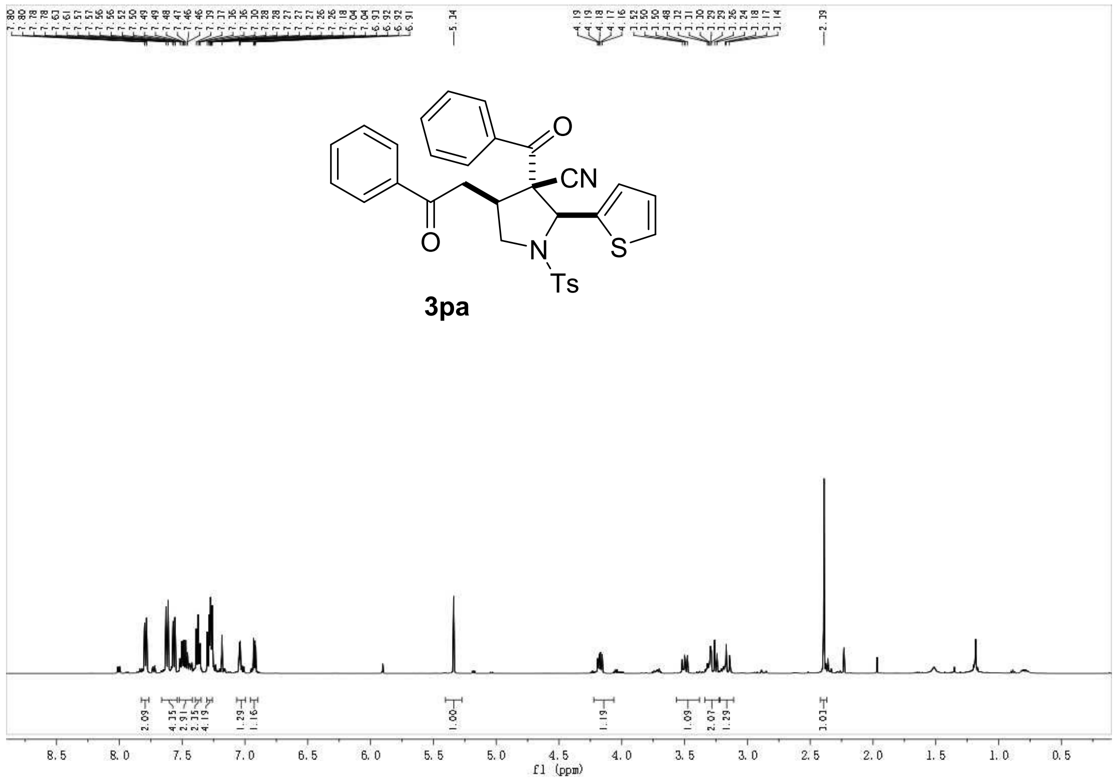
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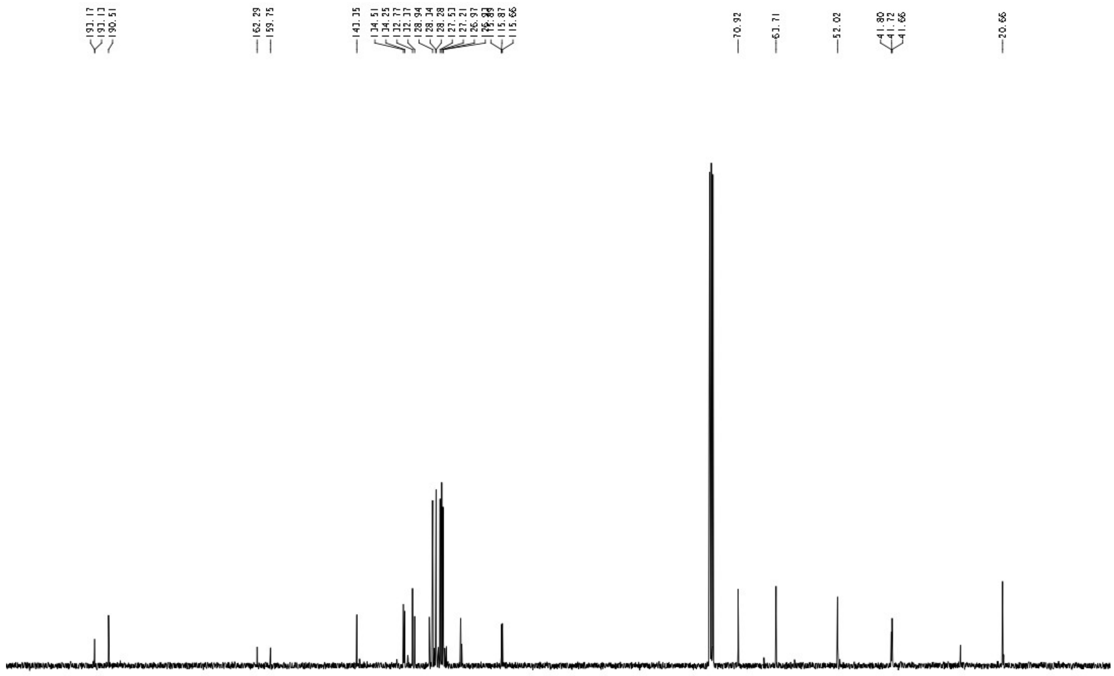
O
O
N
S
Ts
3pa
f1 (ppm)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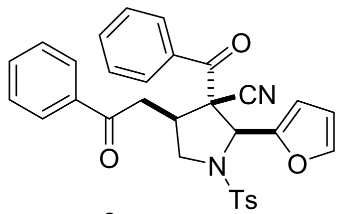

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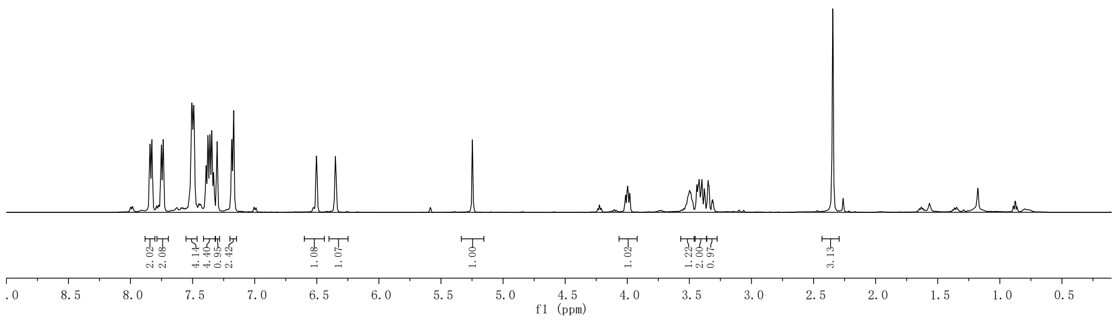

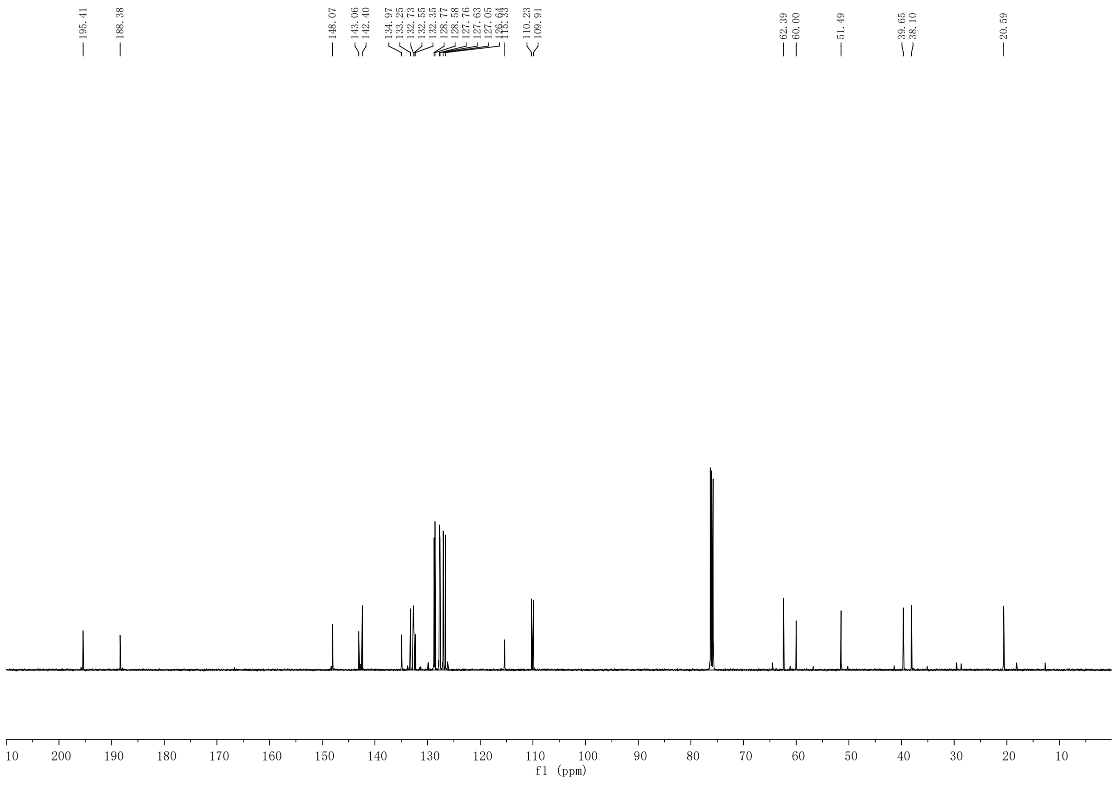

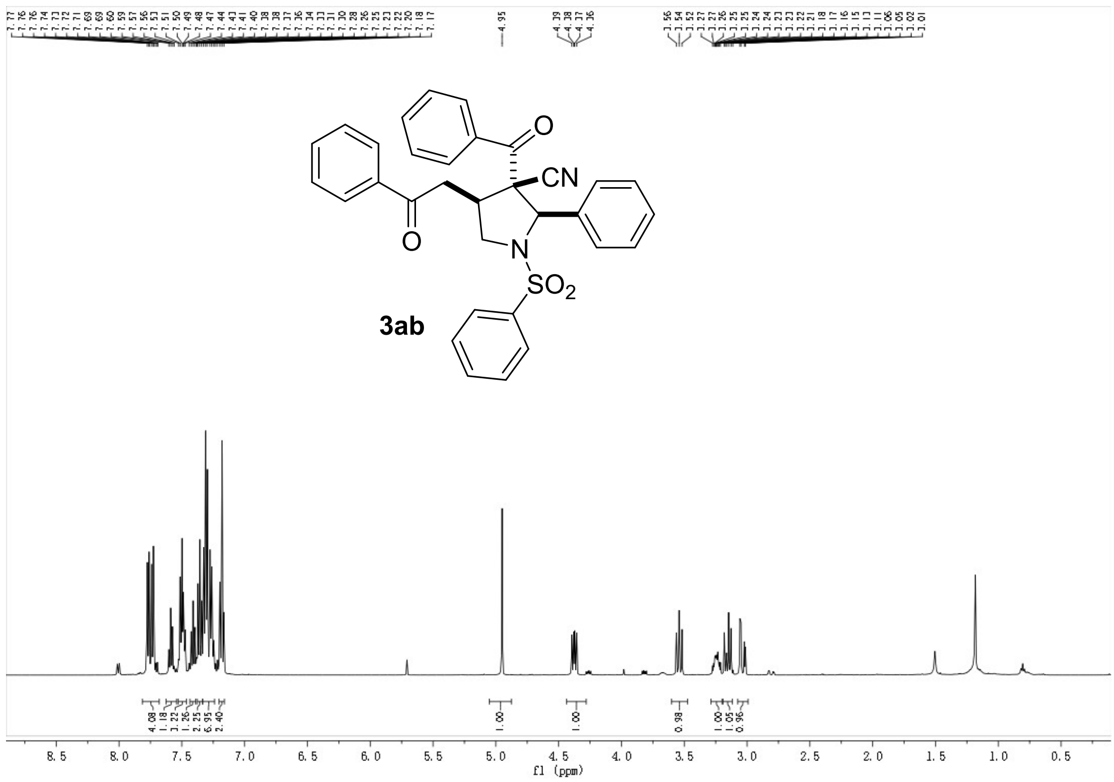
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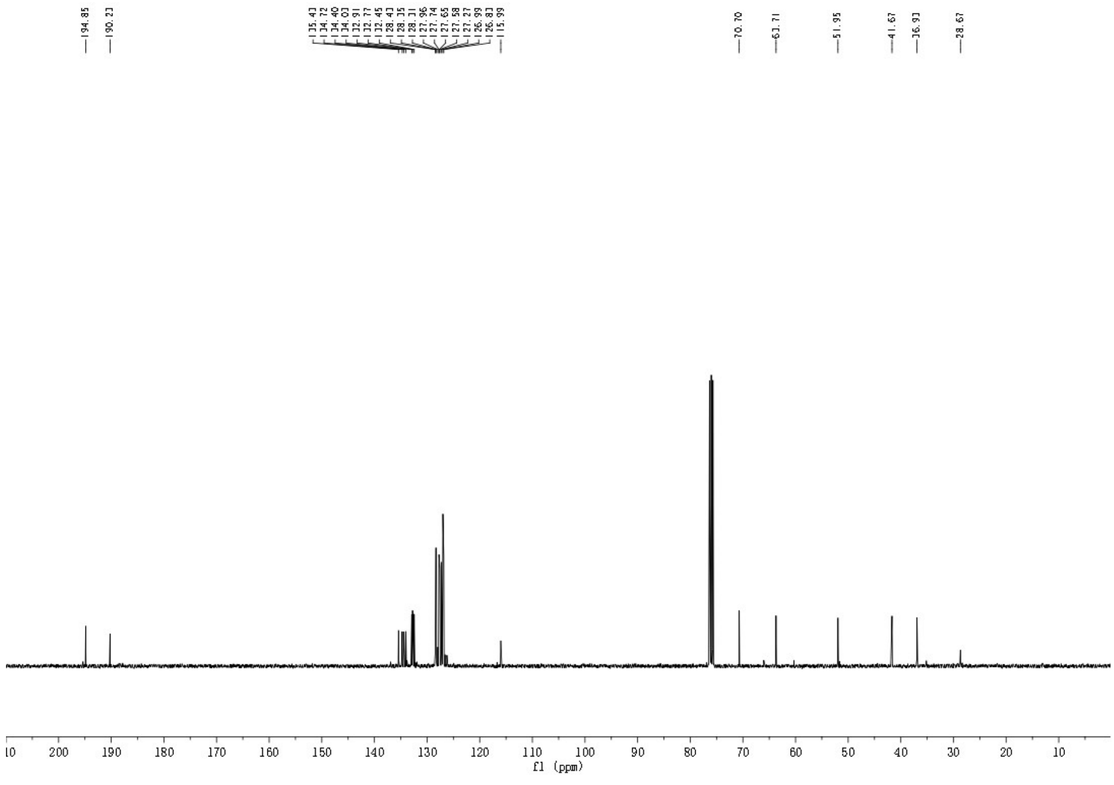
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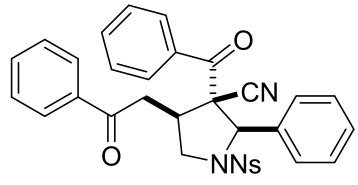
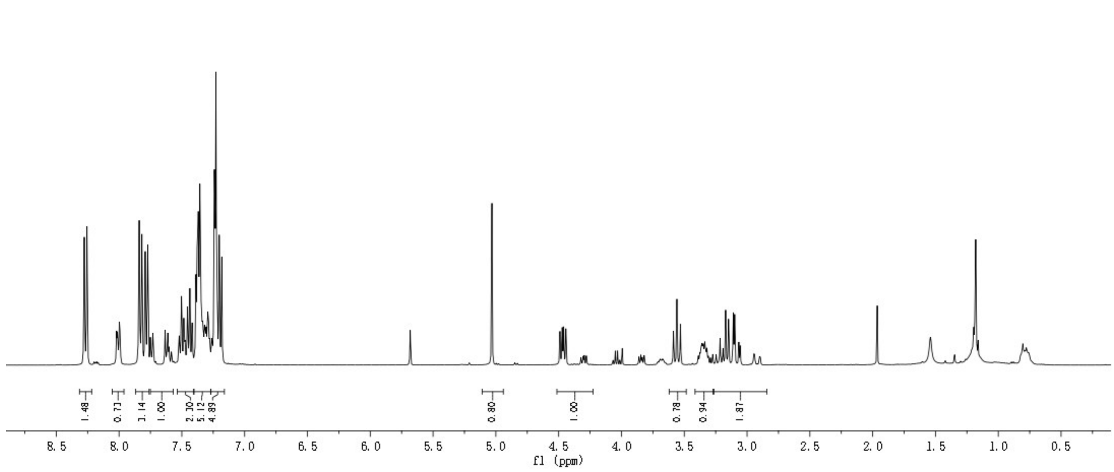
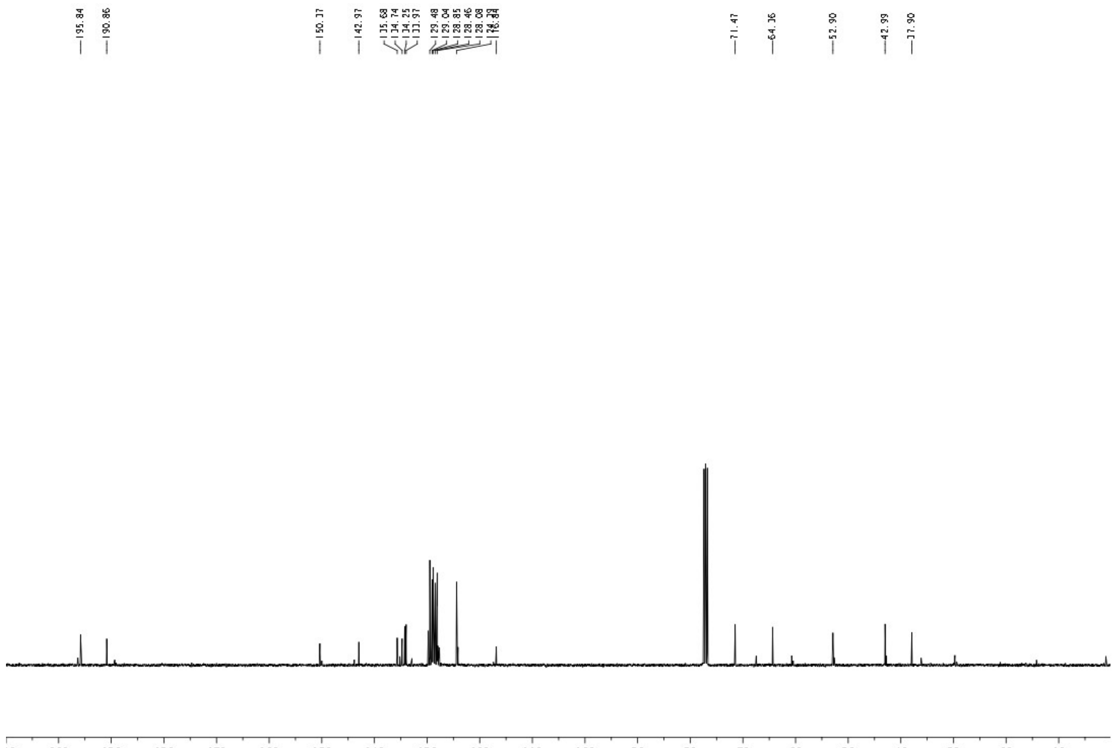
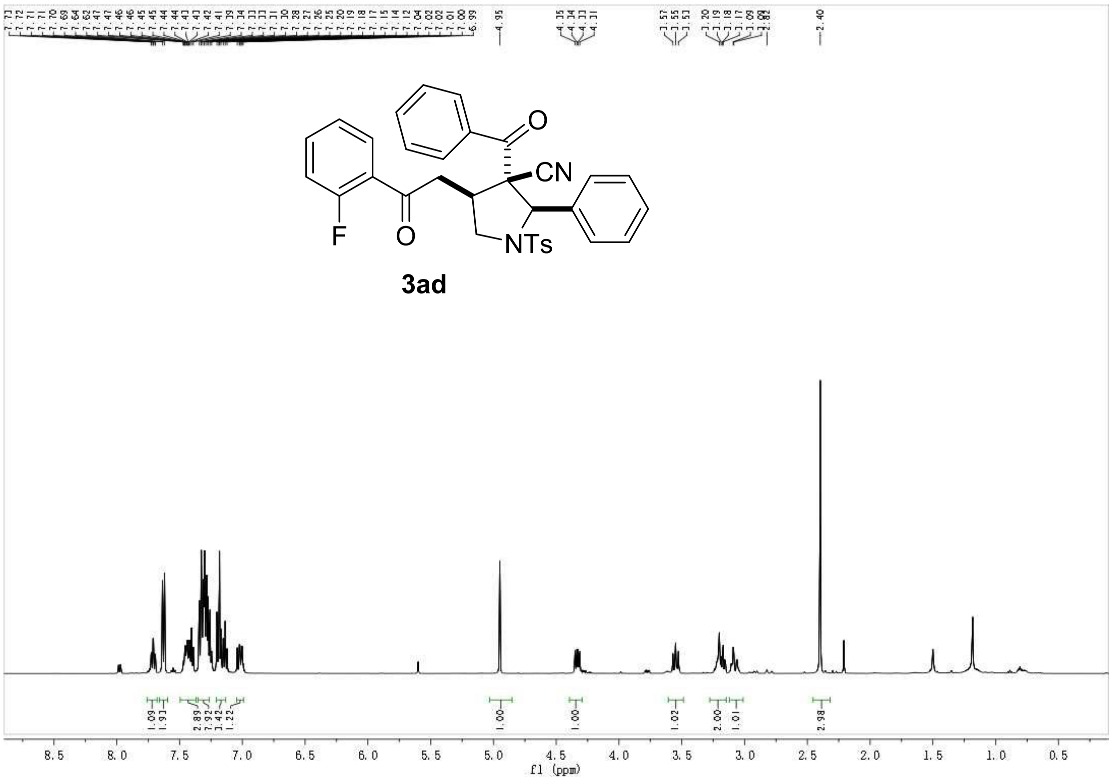
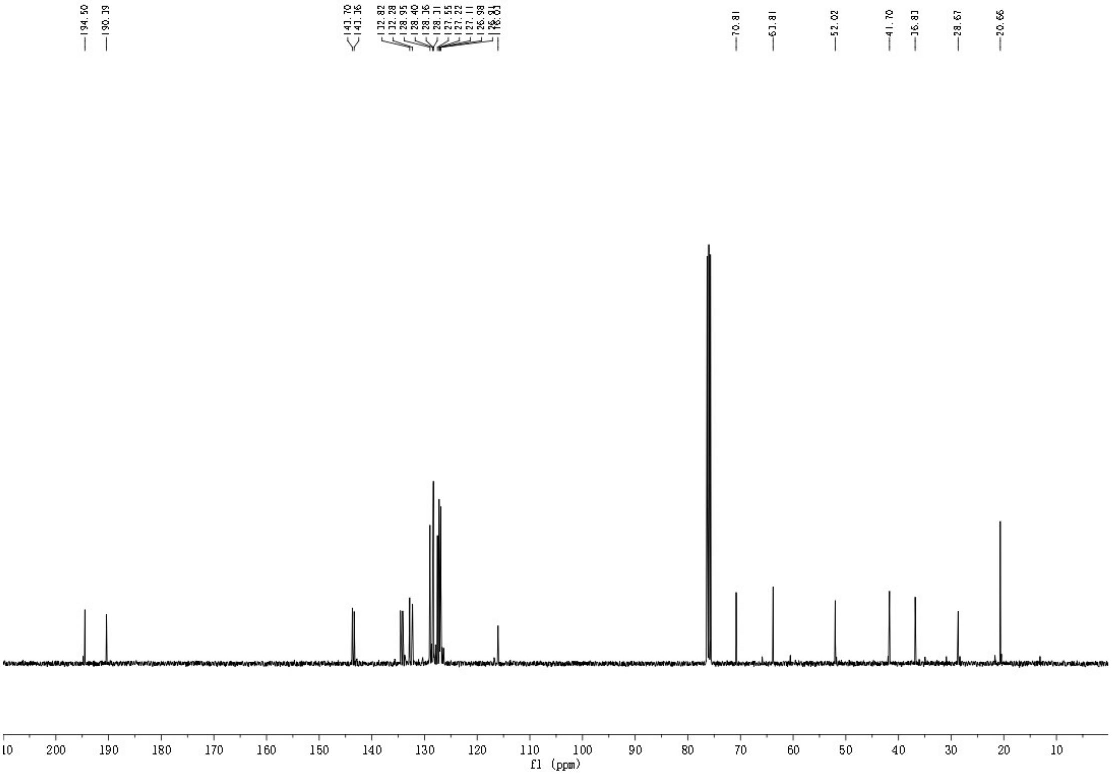


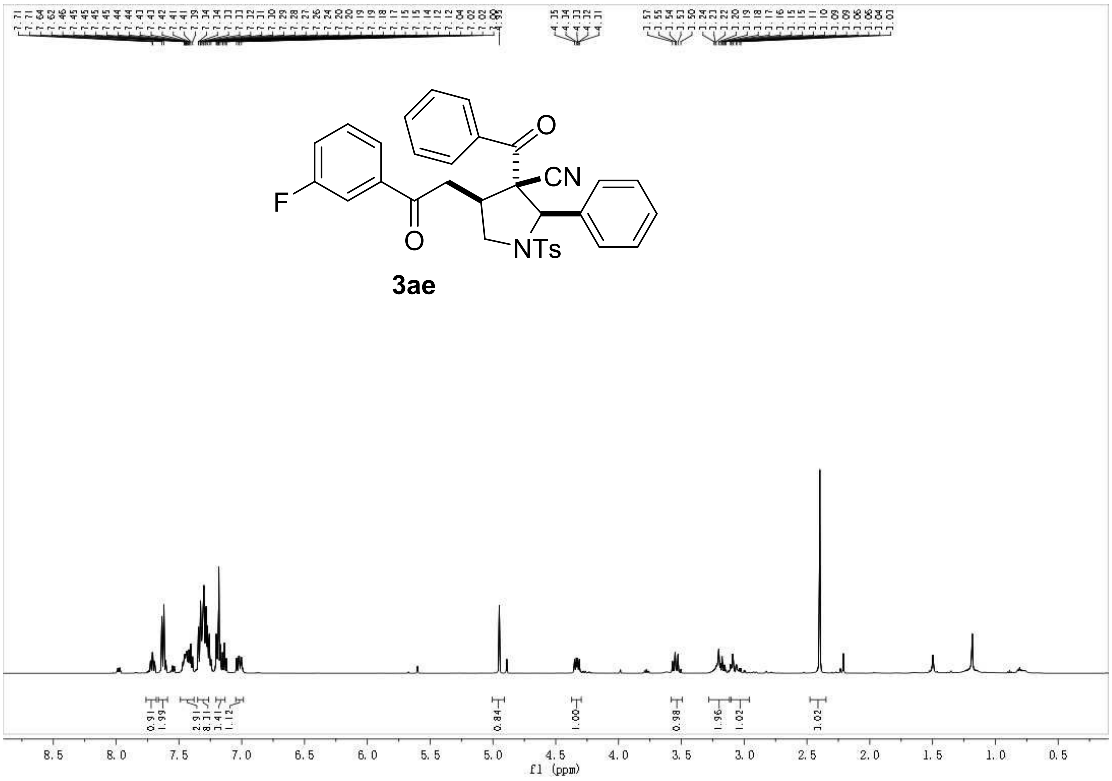
3ac

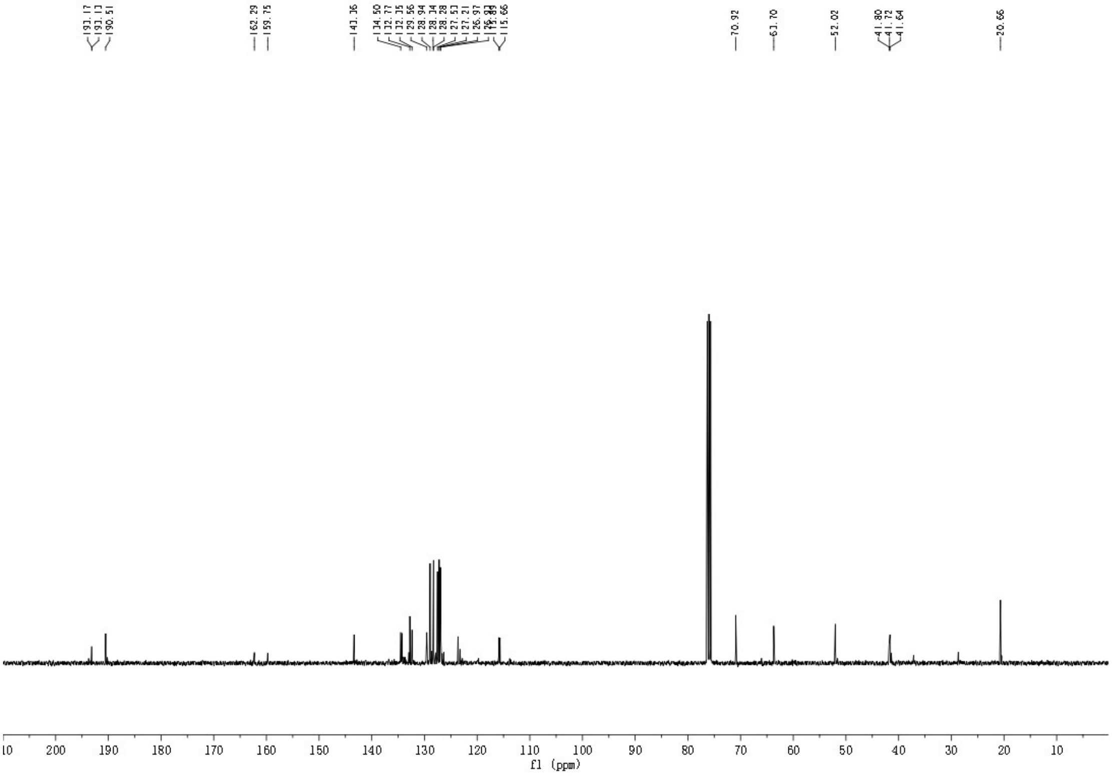


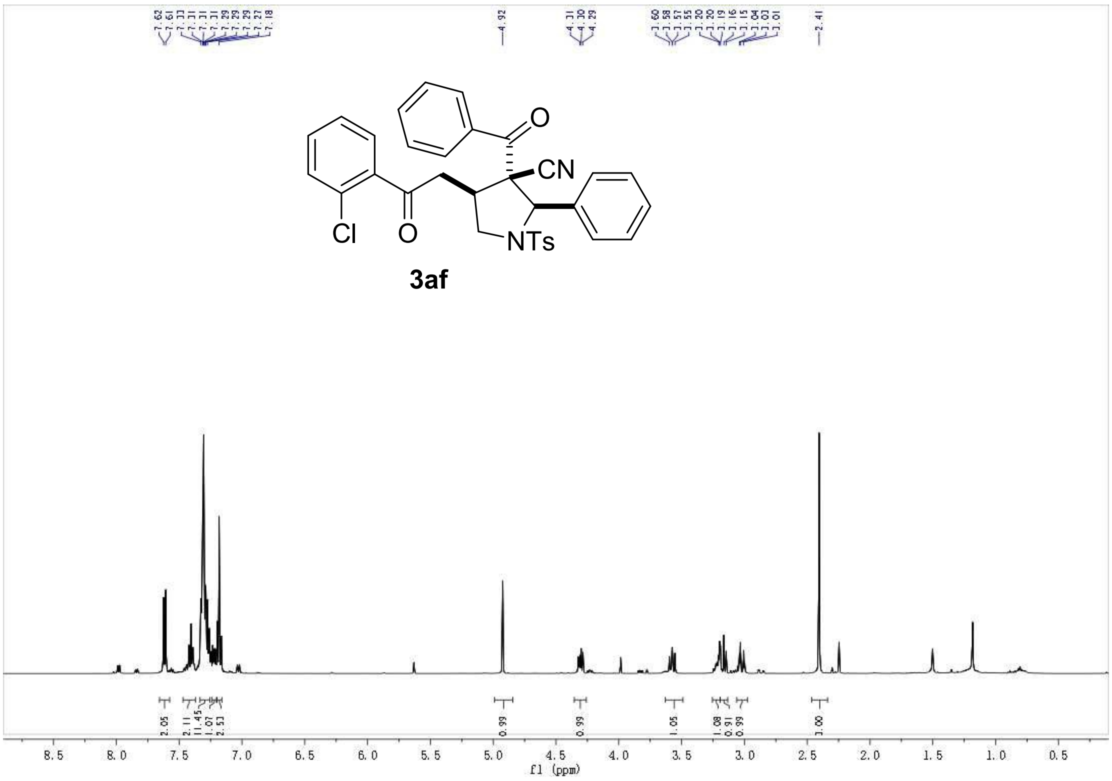


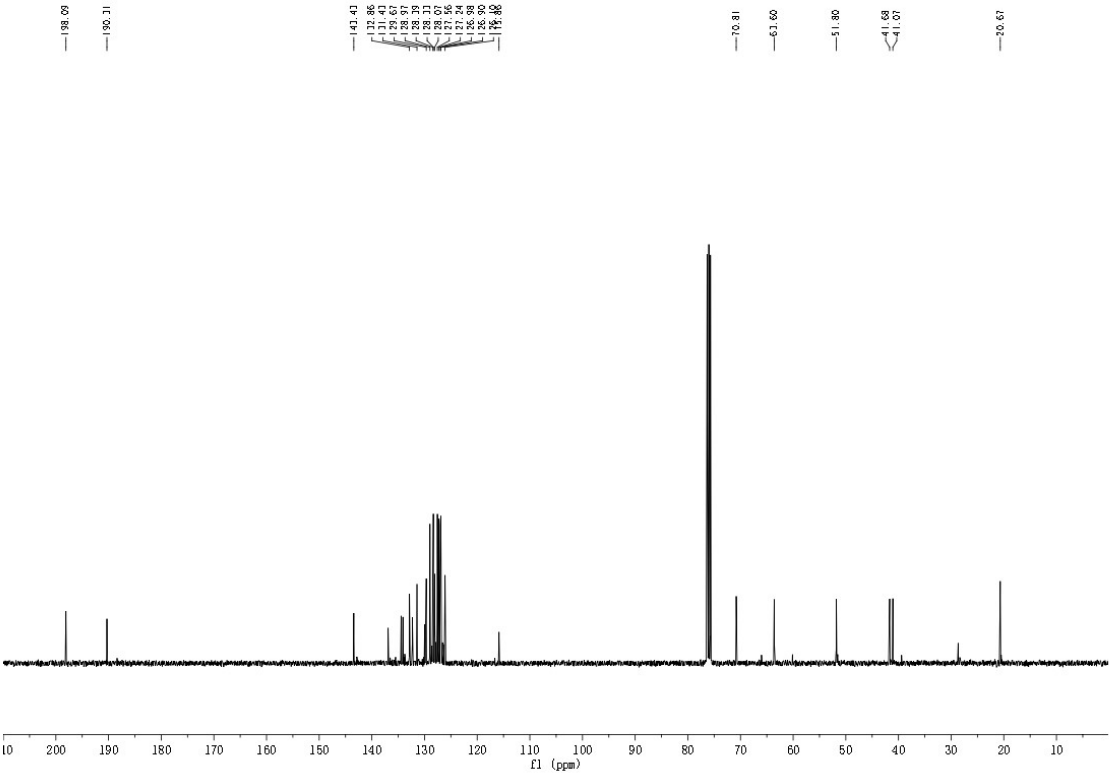

O
CN
F
O
NTs
3ad
f1 (ppm)

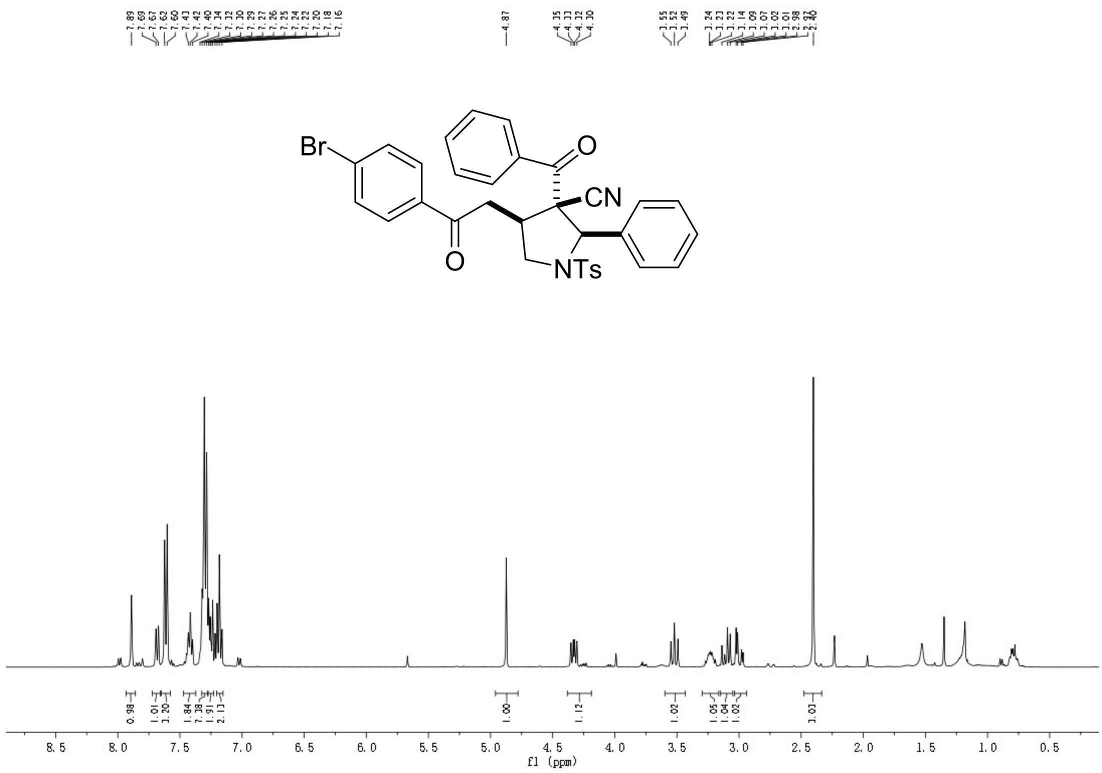

f1 (ppm)

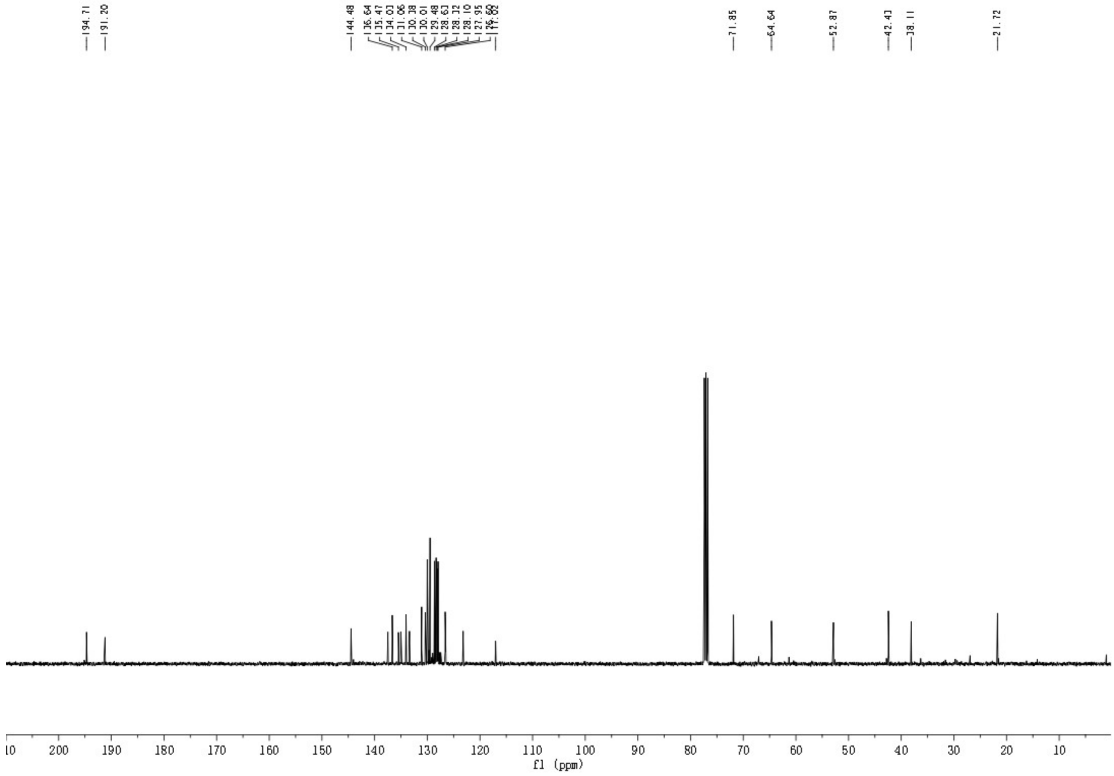


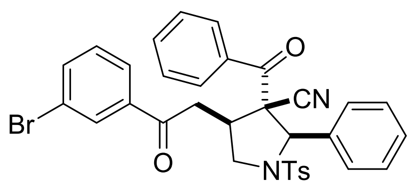



O
CN
Cl
O
NTs
3af
f1 (ppm)

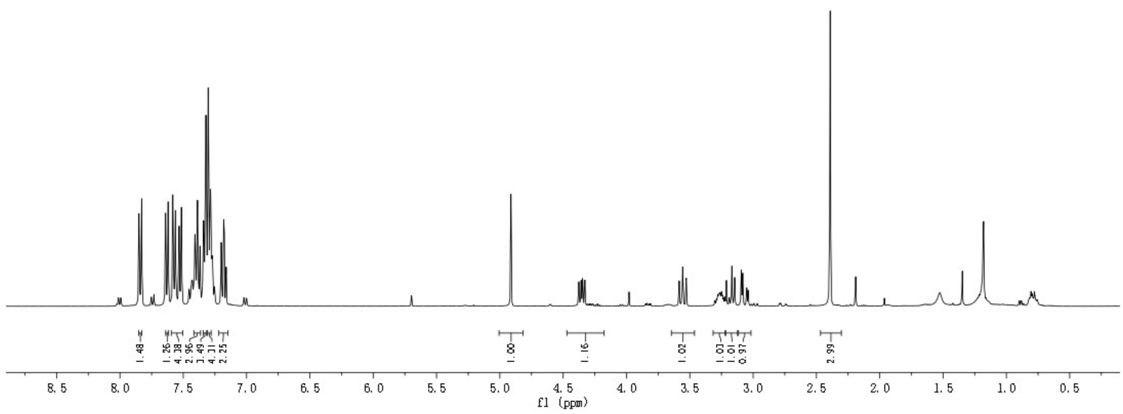

f1 (ppm)

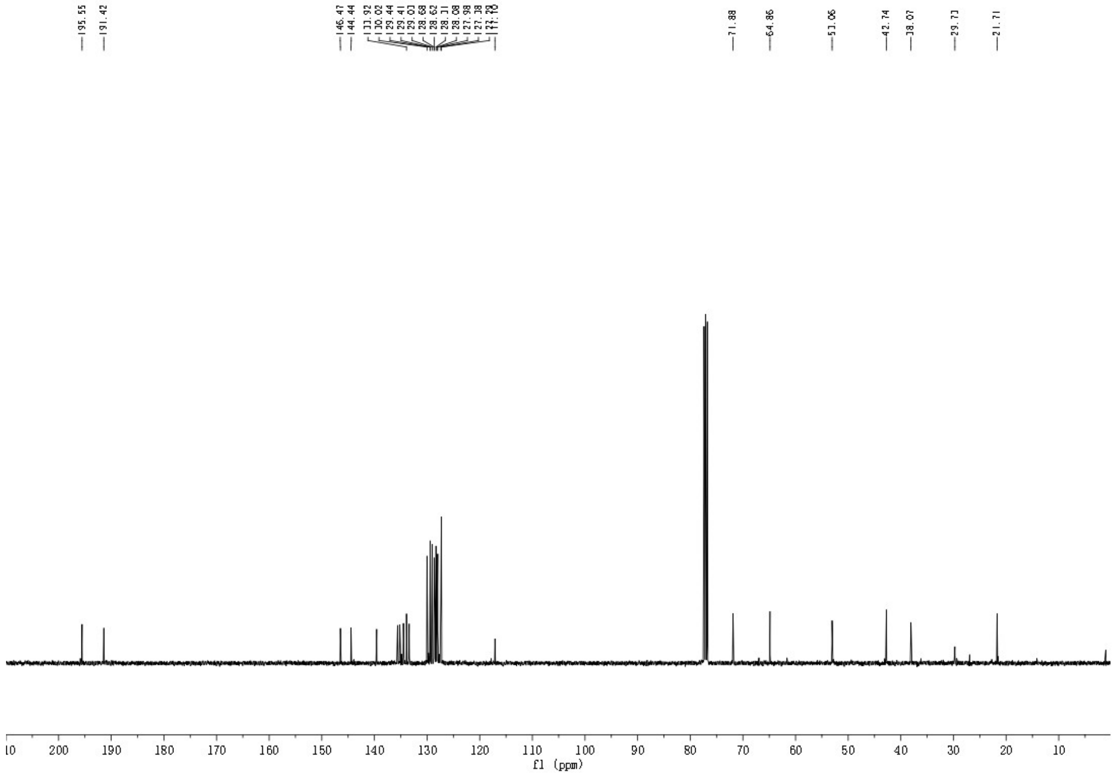

Br
O
CN
O
NTs
f1 (ppm)

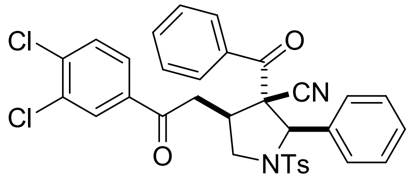

f1 (ppm)



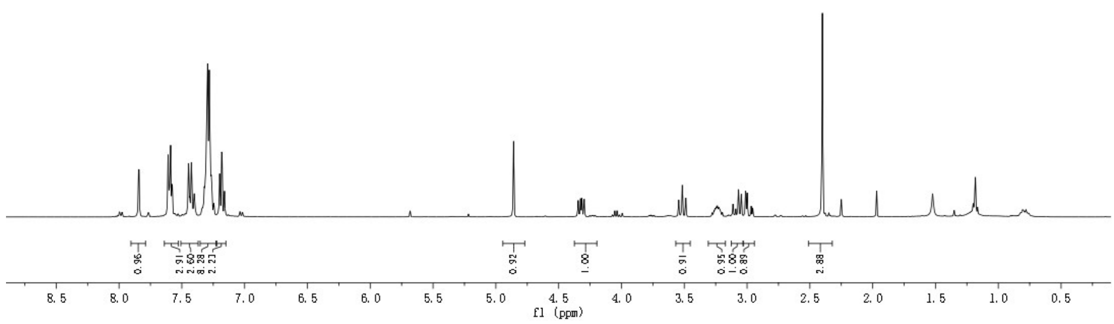
3ag

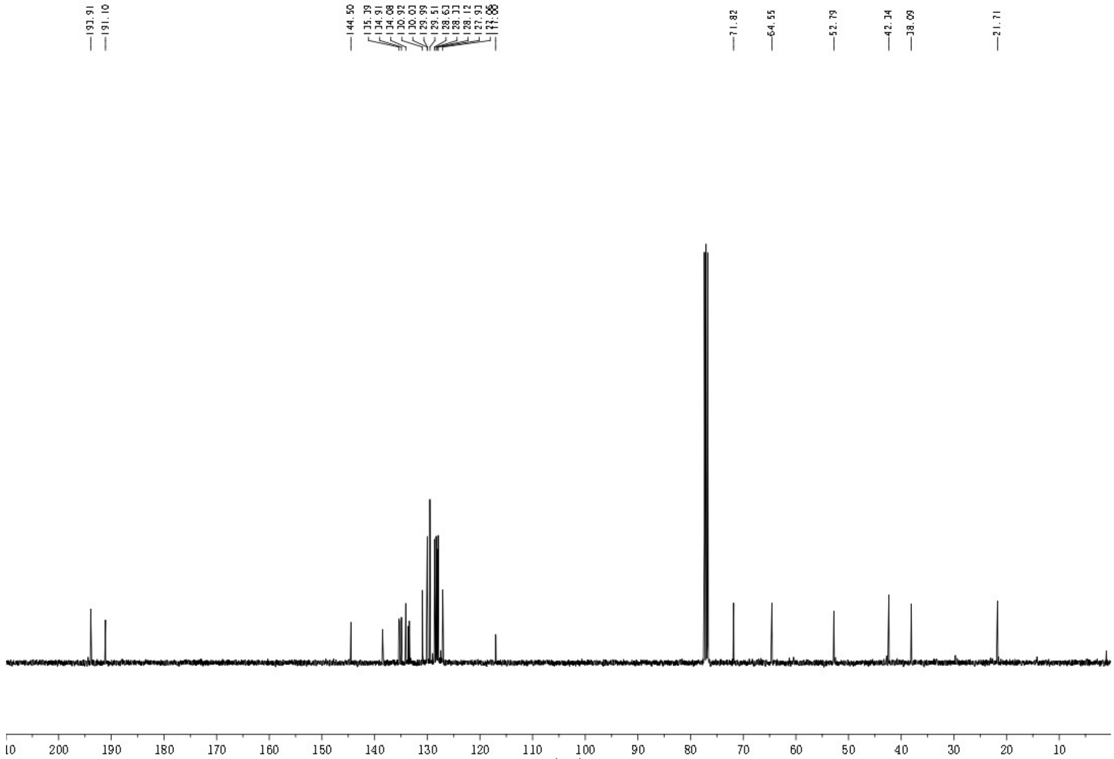


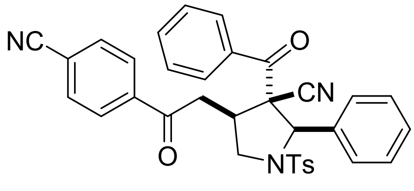




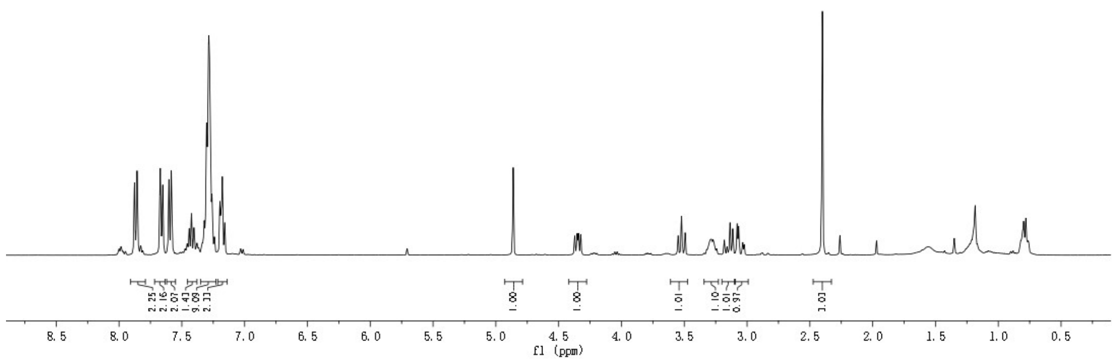
3ai

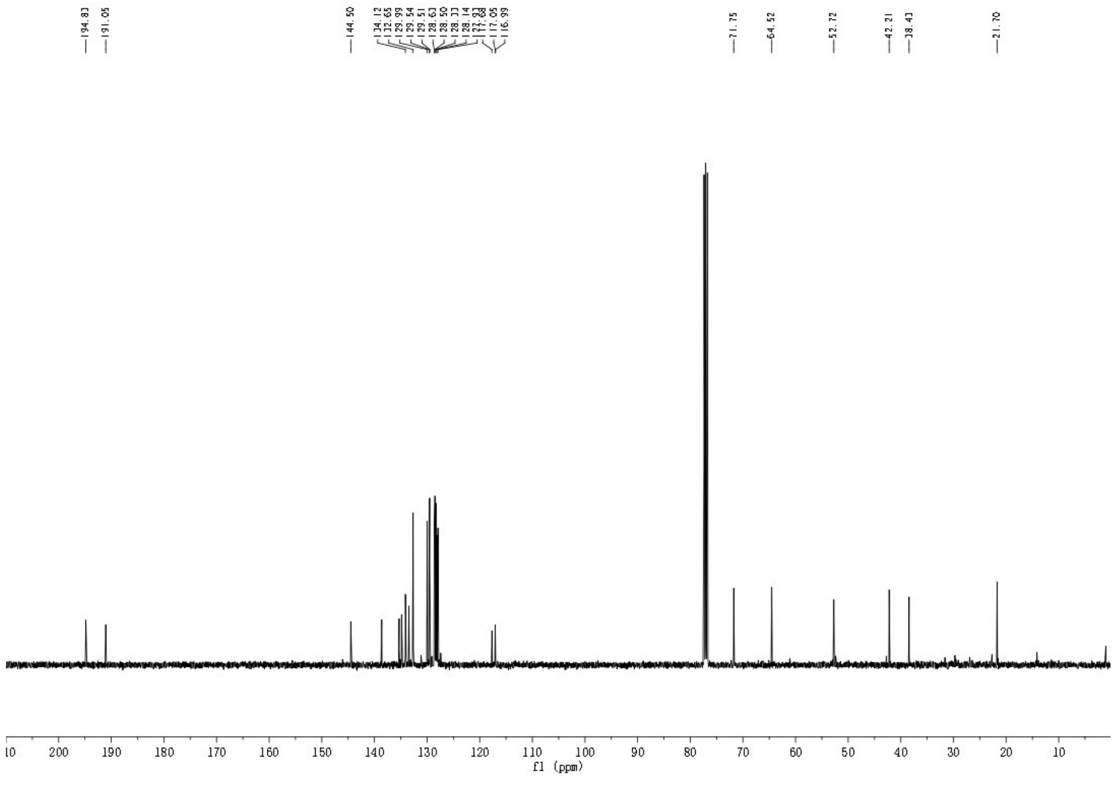


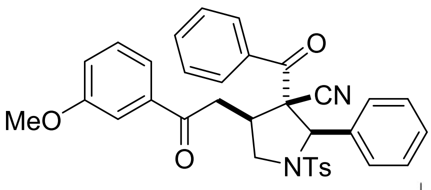




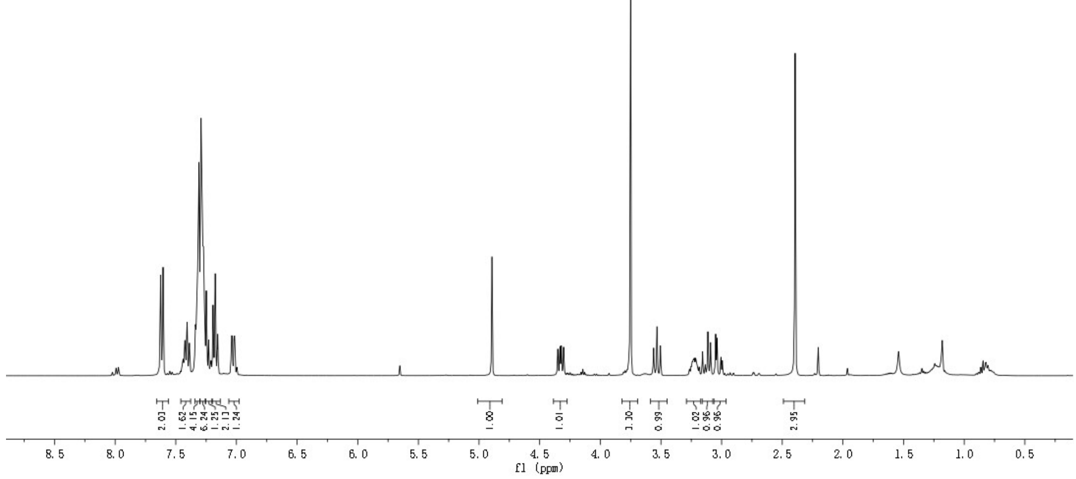
3aj

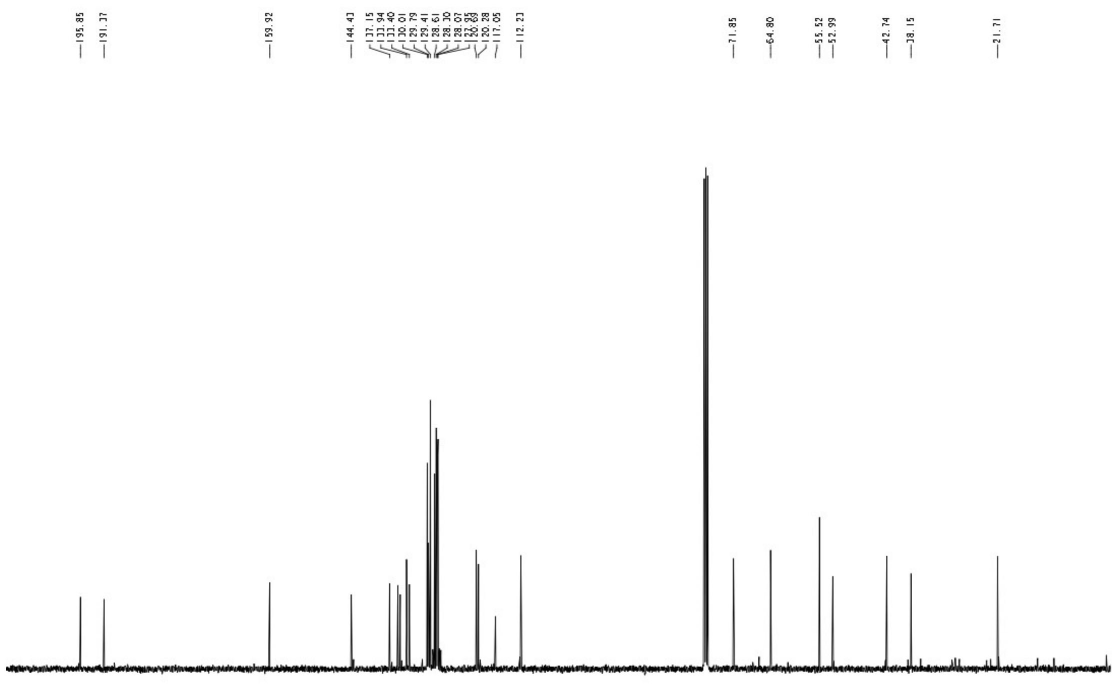


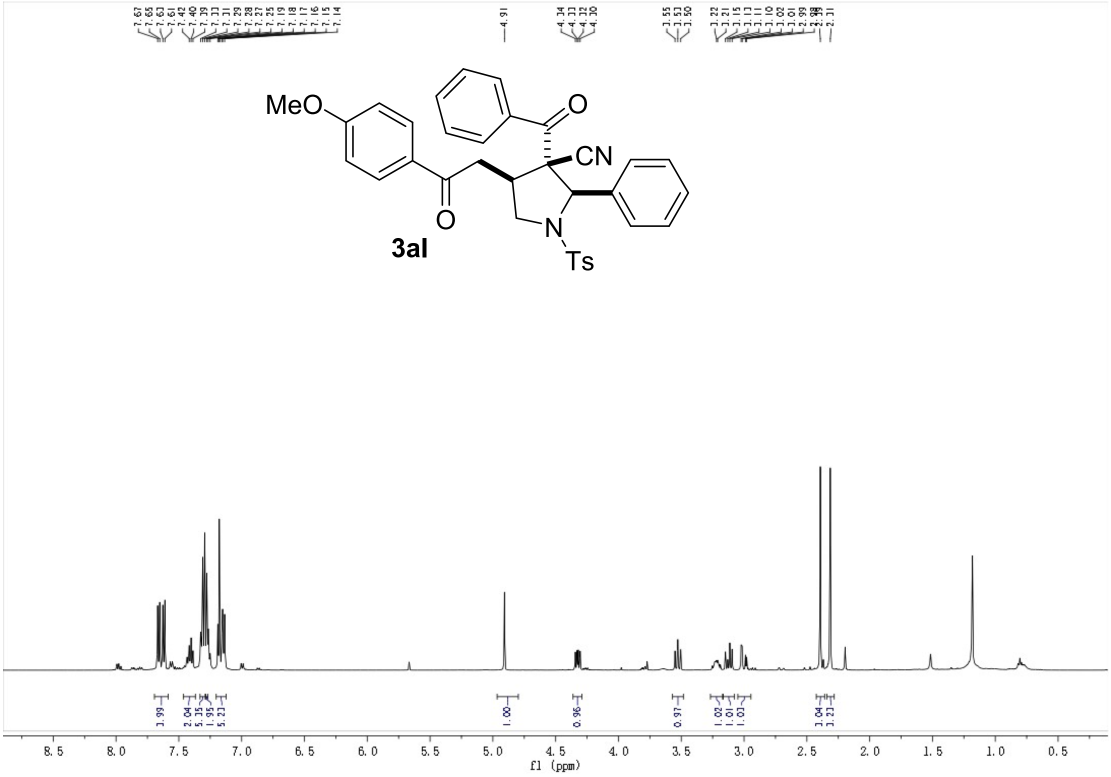


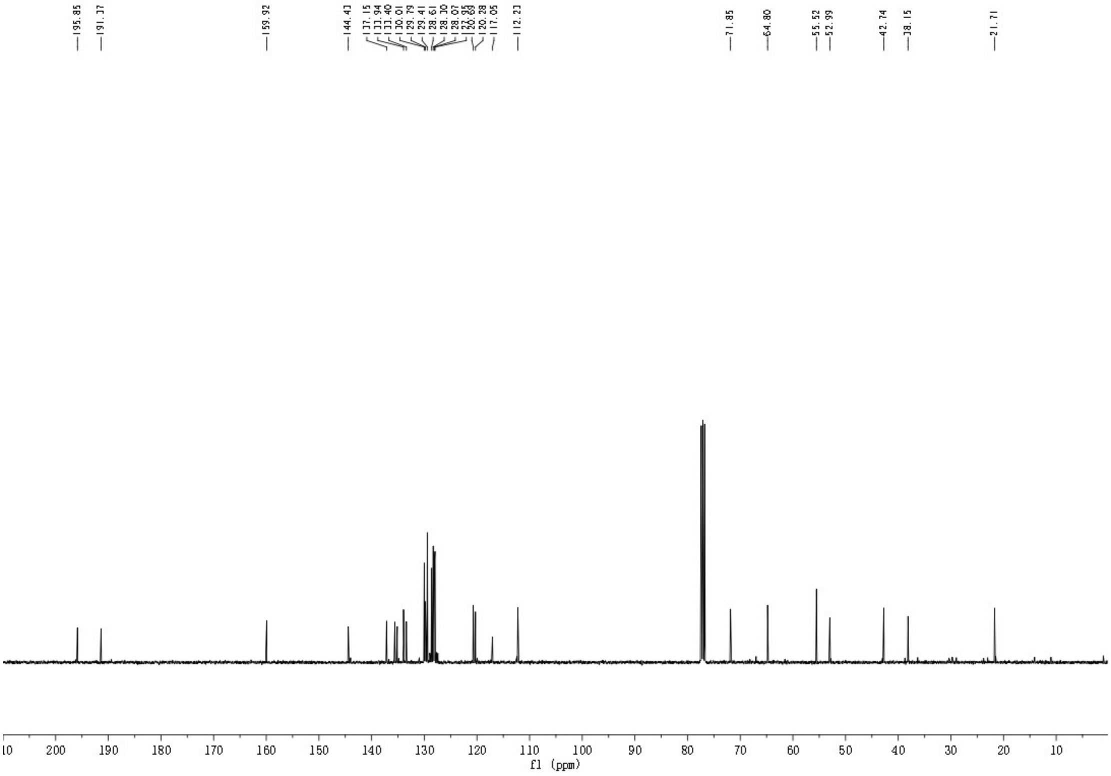


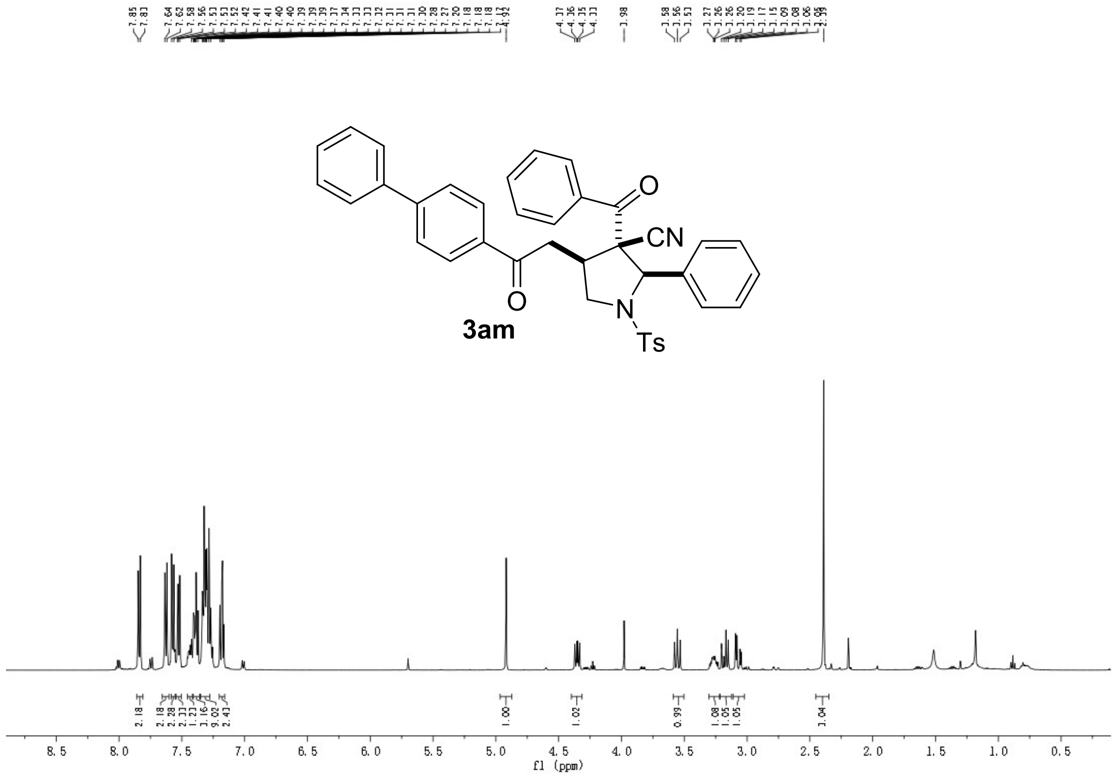
3ak

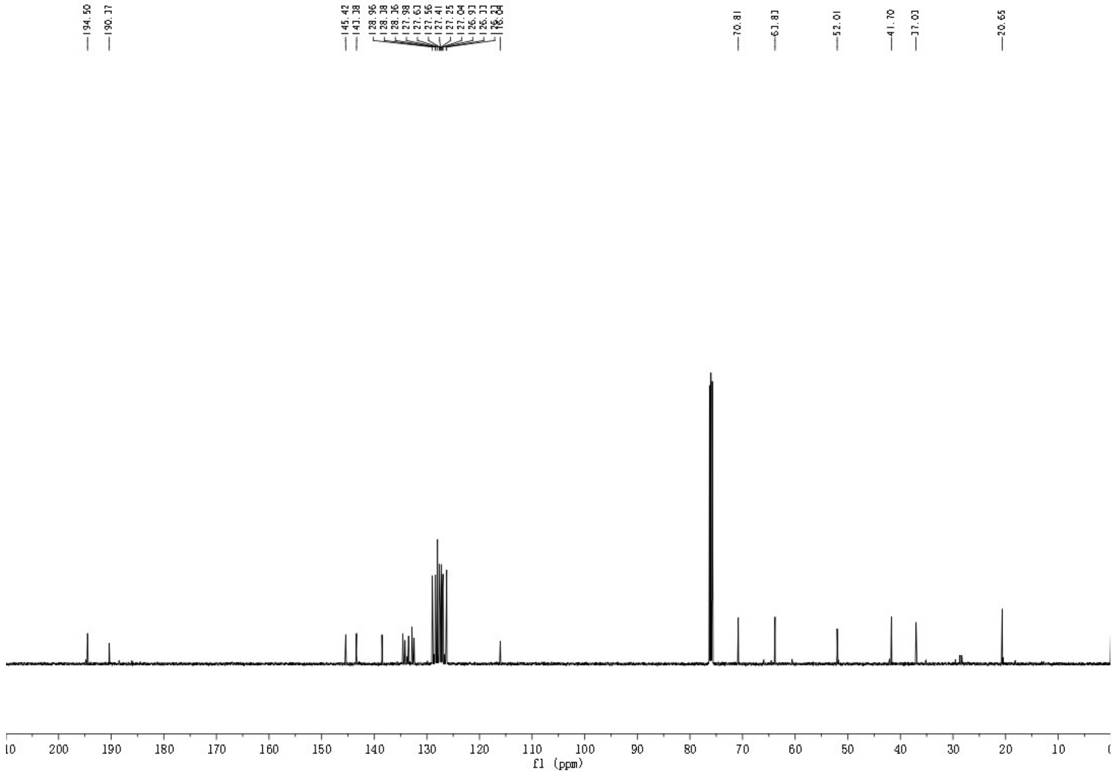


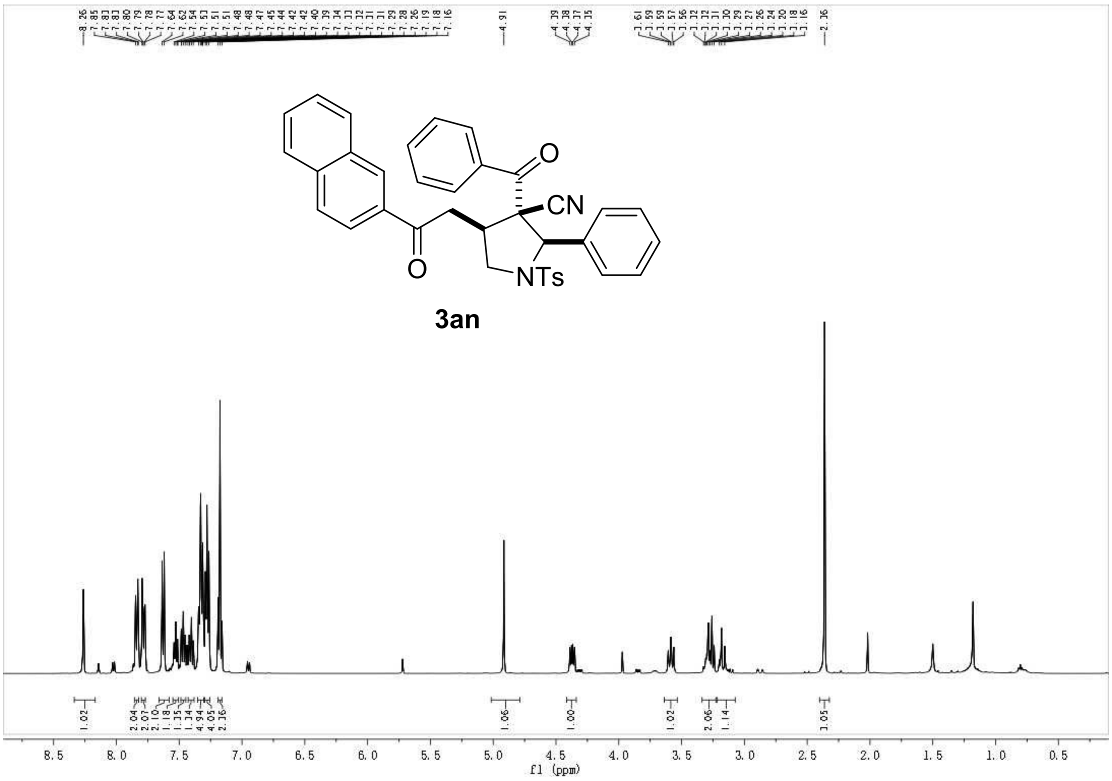



MeO
O
O
CN
N
Ts
3al
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

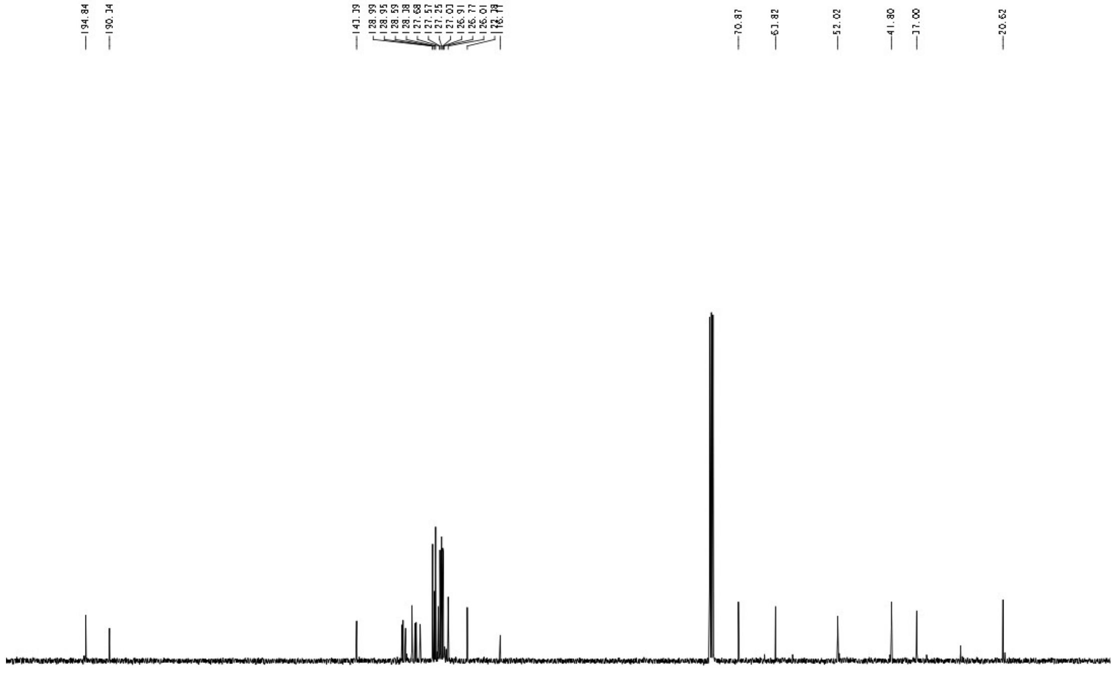

195.85
191.37
159.92
144.43
112.23
71.85
64.80
55.52
52.99
42.74
38.15
21.71
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

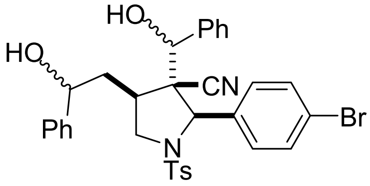

3am
CN
O
N
Ts
f1 (ppm)


f1 (ppm)

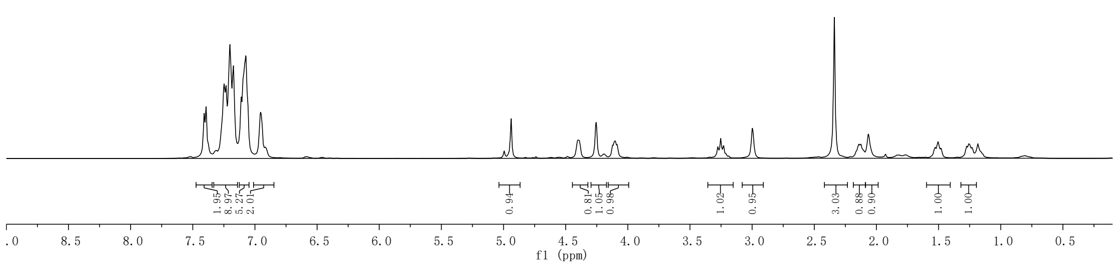


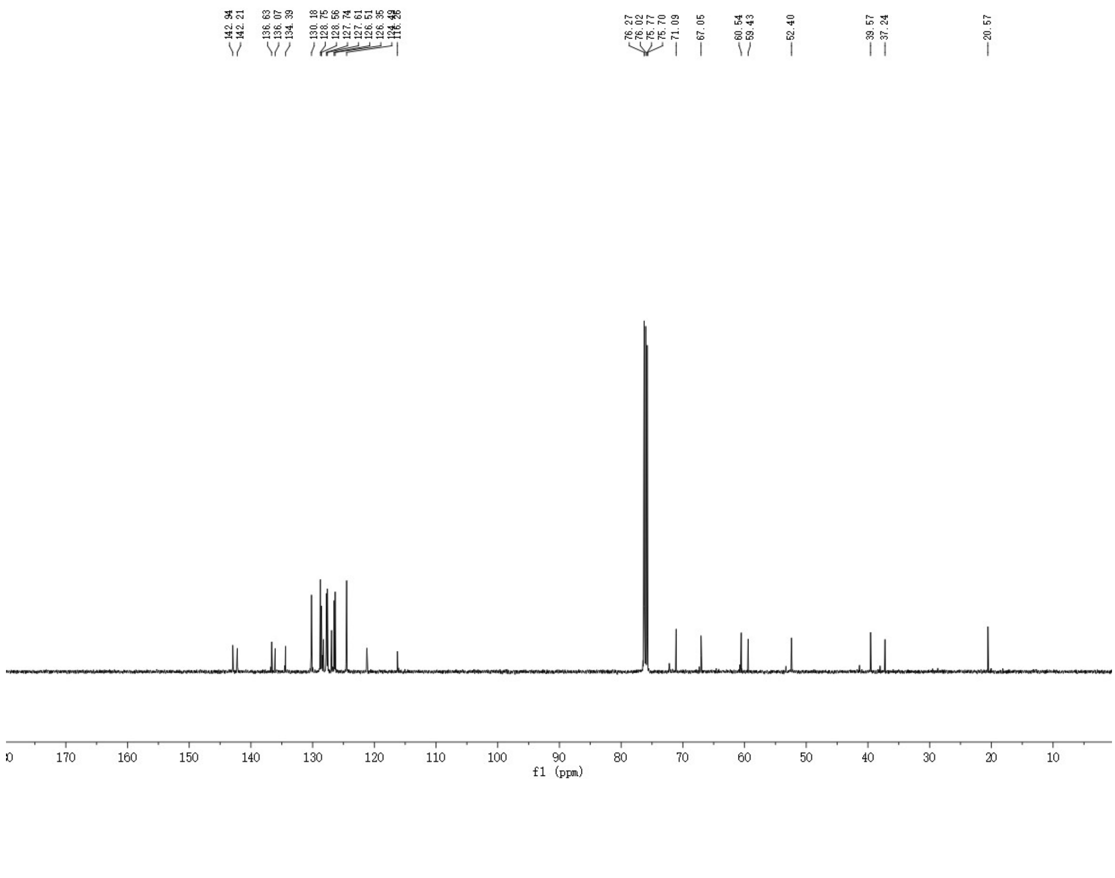
3an




HO
Ph
HO
CN
Br
Ph
N
Ts

4


7.41
7.39
7.31
7.25
7.23
7.20
7.17
7.11
7.09
7.07
6.95
6.92
4.94
4.40
4.39
4.26
4.12
4.11
4.10
4.09
3.28
3.25
3.23
3.21
3.00
2.34
2.14
2.13
2.06
1.53
1.50
1.48
1.27
1.26
1.23
1.18
1.95
8.97
5.27
2.01
0.94
0.81
1.05
0.98
1.02
0.95
3.03
0.88
0.90
1.00
1.00
f1 (ppm)


142.94
142.21
136.63
136.07
134.39
130.18
128.75
128.56
127.74
127.61
126.51
126.35
76.27
76.02
75.77
75.70
71.09
67.05
60.54
59.43
52.40
39.57
37.24
20.57
f1 (ppm)

X-Ray Crystallographic Data of 3aa

Crystallographic data for **3aa** have been deposited with the Cam-bridge Crystallographic Data Centre as deposition number CCDC 2081095. 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.

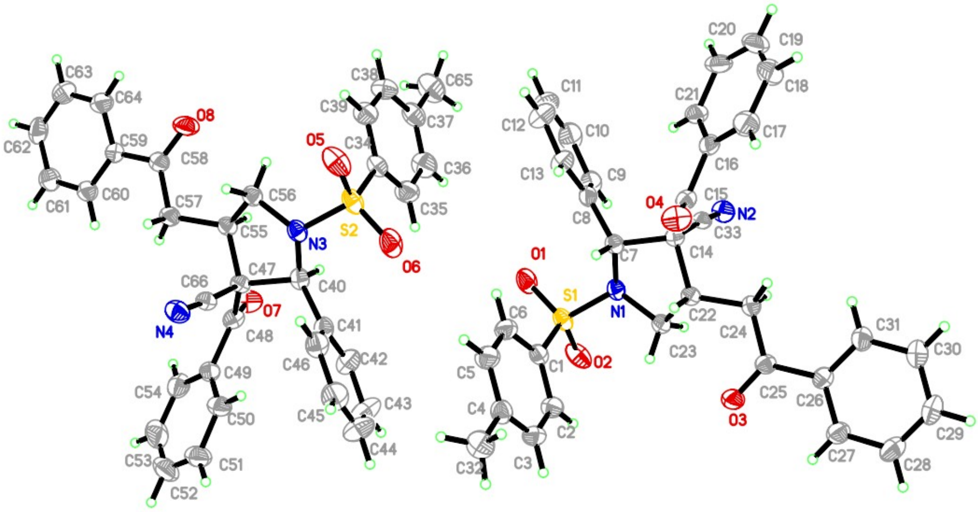


Table 1. Crystal data and structure refinement for 3aa.

Identification code	**3aa**	
Empirical formula	$C_{66} H_{56} N_4 O_8 S_2$	
Formula weight	1097.26	
Temperature	293(2) K	
Wavelength	1.54184 A	
Crystal system, space group	Monoclinic, P2(1)	
Unit cell dimensions	a/Å= 9.7583(3)	α/° = 90
	b/Å = 21.2841(7)	β/°= 92.287(2)
	c/Å = 13.5807(4)	γ/°= 90
Volume/Å^3	2818.42(15)	
Z, Calculated density g/cm^3	2, 1.293	
Absorption coefficient/mm^{-1}	1.351	
F(000)	1152	

Crystal size/mm^3	0.120 × 0.120 × 0.110
Theta range for data collection/°	3.257 to 67.236 .
Limiting indices	-11<=h<=8, -21<=k<=25, -16<=l<=16
Reflections collected / unique	10591 / 7300 [R(int) = 0.0221]
Completeness to theta = 67.236	99.8 %
Max. and min. transmission	1.00000 and 0.73560
Data / restraints / parameters	7300 / 1 / 724
Goodness-of-fit on F^2	1.056
Final R indices [I>2σ(I)]	R_1 = 0.0378, wR_2 = 0.0993
R indices (all data)	R_1 = 0.0438, w_{R2} = 0.1100
Absolute structure parameter	0.026(12)
Extinction coefficient	0.0040(2)
Largest diff. peak and hole/ e.Å^{-3}	0.217 and -0.299

Table 2. Atomic coordinates (×10^4) and equivalent isotropic displacement parameters (Å^2×10^3) for 3aa. $U_{(eq)}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	*x*	*y*	*z*	U(eq)
S(1)	8373(1)	1936(1)	2858(1)	49(1)
S(2)	4619(1)	-130(1)	5343(1)	53(1)
N(1)	8871(3)	1586(2)	1853(2)	42(1)
N(2)	11598(3)	979(2)	443(3)	53(1)
N(3)	4030(3)	176(2)	6349(2)	44(1)
N(4)	1078(3)	714(2)	7647(3)	57(1)
O(1)	8625(3)	1510(2)	3650(2)	66(1)
O(2)	9006(3)	2541(2)	2867(2)	65(1)
O(3)	7593(4)	2611(2)	-774(2)	64(1)
O(4)	7097(3)	298(2)	-162(2)	62(1)
O(5)	3950(3)	-722(2)	5226(2)	71(1)
O(6)	4490(3)	337(2)	4591(2)	74(1)
O(7)	5441(3)	1436(2)	8543(2)	67(1)
O(8)	4953(4)	-924(2)	9000(2)	77(1)
C(1)	6589(4)	2044(2)	2714(3)	44(1)
C(2)	6067(4)	2605(2)	2344(3)	51(1)
C(3)	4673(4)	2672(2)	2204(3)	56(1)
C(4)	3782(4)	2193(2)	2423(3)	55(1)
C(5)	4332(5)	1645(2)	2817(4)	65(1)
C(6)	5709(4)	1566(2)	2962(3)	58(1)
C(7)	8510(3)	925(2)	1651(3)	40(1)

C(8)	9133(4)	438(2)	2338(3)	47(1)
C(9)	10456(4)	489(3)	2753(3)	58(1)
C(10)	10982(5)	-16(3)	3305(4)	83(2)
C(11)	10212(8)	-548(3)	3440(4)	96(2)
C(12)	8943(8)	-588(3)	3042(4)	90(2)
C(13)	8384(5)	-102(2)	2499(3)	66(1)
C(14)	8941(3)	866(2)	564(3)	37(1)
C(15)	8311(4)	278(2)	47(3)	43(1)
C(16)	9169(4)	-266(2)	-209(3)	49(1)
C(17)	8805(7)	-595(2)	-1074(4)	77(2)
C(18)	9603(9)	-1095(3)	-1345(5)	97(2)
C(19)	10703(7)	-1285(3)	-766(5)	91(2)
C(20)	11044(5)	-984(2)	99(5)	71(1)
C(21)	10287(4)	-467(2)	371(3)	55(1)
C(22)	8316(3)	1484(2)	132(2)	38(1)
C(23)	8739(4)	1961(2)	932(2)	43(1)
C(24)	8727(4)	1634(2)	-907(3)	44(1)
C(25)	8058(4)	2221(2)	-1319(3)	43(1)
C(26)	8026(4)	2323(2)	-2407(3)	44(1)
C(27)	7559(5)	2897(2)	-2763(3)	57(1)
C(28)	7506(5)	3017(3)	-3768(3)	67(1)
C(29)	7919(5)	2569(3)	-4416(3)	72(2)
C(30)	8391(5)	1997(3)	-4075(3)	70(1)
C(31)	8435(4)	1876(3)	-3067(3)	57(1)
C(32)	2262(4)	2269(3)	2255(4)	73(1)
C(33)	10446(4)	905(2)	501(3)	39(1)
C(34)	6376(4)	-284(2)	5567(3)	48(1)
C(35)	7319(4)	190(2)	5445(4)	66(1)
C(36)	8688(5)	65(3)	5626(4)	75(2)
C(37)	9148(4)	-516(3)	5925(4)	62(1)
C(38)	8188(5)	-980(2)	6046(4)	63(1)
C(39)	6808(4)	-871(2)	5872(3)	58(1)
C(40)	4302(3)	841(2)	6613(3)	43(1)
C(41)	3703(4)	1333(2)	5930(3)	50(1)
C(42)	4396(5)	1894(3)	5861(4)	70(1)
C(43)	3819(8)	2391(3)	5353(5)	100(2)
C(44)	2562(8)	2328(4)	4908(5)	99(2)
C(45)	1867(6)	1771(3)	4946(4)	83(2)
C(46)	2431(4)	1269(3)	5457(3)	59(1)
C(47)	3742(3)	854(2)	7675(2)	37(1)
C(48)	4258(4)	1433(2)	8262(3)	46(1)
C(49)	3305(4)	1964(2)	8494(3)	49(1)
C(50)	2319(4)	2178(2)	7821(3)	55(1)
C(51)	1508(5)	2687(2)	8043(5)	74(1)

C(52)	1669(6)	2962(3)	8966(5)	91(2)
C(53)	2608(8)	2738(3)	9626(5)	92(2)
C(54)	3470(6)	2245(2)	9404(3)	68(1)
C(55)	4350(3)	234(2)	8091(3)	40(1)
C(56)	4089(4)	-222(2)	7255(2)	44(1)
C(57)	3833(4)	58(2)	9097(3)	50(1)
C(58)	4511(4)	-518(2)	9529(3)	51(1)
C(59)	4627(4)	-592(2)	10625(3)	46(1)
C(60)	4302(4)	-120(2)	11275(3)	54(1)
C(61)	4470(5)	-218(3)	12274(3)	66(1)
C(62)	4947(5)	-784(3)	12638(3)	70(1)
C(63)	5252(5)	-1253(3)	11992(4)	74(1)
C(64)	5074(5)	-1160(2)	10997(3)	66(1)
C(65)	10640(5)	-647(3)	6136(4)	89(2)
C(66)	2235(4)	796(2)	7646(3)	40(1)

Table 3. Bond lengths for 3aa.

Atom Atom Length/Å; Atom Atom Length/Å; Atom Atom Length/Å

S(1)-O(1):1.420(3); S(1)-O(2):1.427(3); S(1)-N(1): 1.646(3); S(1)-C(1): 1.760(4); S(2)-O(5):1.425(4); S(2)-O(6): 1.426(4); S(2)-N(3): 1.639(3); S(2)-C(34):1.760(4); N(1)-C(7):1.474(5); N(1)-C(23):1.485(5); N(2)-C(33):1.141(5); N(3)-C(40):1.480(5); N(3)-C(56):1.495(5); N(4)-C(66):1.142(5); O(3)-C(25):1.212(5); O(4)-C(15):1.207(4); O(7)-C(48):1.201(5); O(8)-C(58):1.214(5); C(1)-C(6):1.383(6); C(1)-C(2):1.384(6); C(2)-C(3):1.373(6); C(2)-H(2):0.9300; C(3)-C(4) :1.381(6); C(3)-H(3):0.9300; C(4)-C(5):1.383(6) ; C(4)-C(32):1.500(6) ; C(5)-C(6) :1.360(6) C(5)-H(5):0.9300; C(6)-H(6):0.9300; C(7)-C(8):1.506(5); C(7)-C(14):1.557(5); C(7)-H(7) :0.9800; C(8)-C(13):1.383(6); C(8)-C(9):1.393(5); C(9)-C(10):1.397(7); C(9)-H(9):0.9300; C(10)-C(11): 1.375(9); C(10)-H(10): 0.9300; C(11)-C(12):1.334(9); C(11)-H(11):0.9300 ; C(12)-C(13):1.371(8); C(12)-H(12):0.9300; C(13)-H(13):0.9300 ; C(14)-C(33):1.476(5) ; C(14)-C(15):1.550(5); C(14)-C(22): 1.554(5) ; C(15)-C(16):1.480(6) ; C(16)-C(21):1.387(6) ; C(16)-C(17):1.401(6); C(17)-C(18): 1.377(8) ; C(17)-H(17): 0.9300 ; C(18)-C(19): 1.367(9) ; C(18)-H(18):0.9300; C(19)-C(20):1.367(8) ; C(19)-

H(19):0.9300 ; C(20)-C(21): 1.384(6) ; C(20)-H(20):0.9300; C(21)-H(21):0.9300 ; C(22)-C(24):1.517(5) ; C(22)-C(23):1.532(5) ; C(22)-H(22): 0.9800 ; C(23)-H(23A):0.9700 ; C(23)-H(23B):0.9700 ; C(24)-C(25):1.507(5) ; C(24)-H(24A):0.9700; C(24)-H(24B):0.9700 ; C(25)-C(26):1.493(5) ; C(26)-C(31):1.377(6) ; C(26)-C(27):1.384(6) ; C(27)-C(28):1.387(6) ; C(27)-H(27):0.9300 ; C(28)-C(29):1.369(7) ; C(28)-H(28):0.9300 ; C(29)-C(30):1.376(7) ; C(29)-H(29):0.9300 ; C(30)-C(31):1.391(6) ; C(30)-H(30):0.9300 ; C(31)-H(31):0.9300 ; C(32)-H(32A):0.9600 ; C(32)-H(32B):0.9600 ; C(32)-H(32C):0.9600 ; C(34)-C(39):1.378(6) ; C(34)-C(35):1.379(6) ; C(35)-C(36):1.374(6) ; C(35)-H(35):0.9300 ; C(36)-C(37):1.371(7) ; C(36)-H(36):0.9300 ; C(37)-C(38):1.376(7) ; C(37)-C(65):1.499(6) ; C(38)-C(39):1.377(6) ; C(38)-H(38): 0.9300 ; C(39)-H(39):0.9300 ; C(40)-C(41):1.501(5) ; C(40)-C(47):1.563(5) ; C(40)-H(40):0.9800 ; C(41)-C(42):1.377(7) ; C(41)-C(46): 1.382(5) ; C(42)-C(43):1.372(7) ; C(42)-H(42): 0.9300 ; C(43)-C(44):1.353(9) ; C(43)-H(43): 0.9300 ; C(44)-C(45):1.368(9) ; C(44)-H(44): 0.9300 ; C(45)-C(46): 1.377(7) ; C(45)-H(45):0.9300 ; C(46)-H(46):0.9300 ; C(47)-C(66): 1.475(5) ; C(47)-C(48):1.542(5) ; C(47)-C(55): 1.546(5) ; C(48)-C(49):1.505(6) ; C(49)-C(54):1.377(6) ; C(49)-C(50):1.377(6) ; C(50)-C(51);1.381(6) ; C(50)-H(50):0.9300 ; C(51)-C(52) :1.386(8) ; C(51)-H(51) :0.9300 ; C(52)-C(53) :1.344(9) ; C(52)-H(52) :0.9300 ; C(53)-C(54) :1.386(8) ; C(53)-H(53) : 0.9300 ; C(54)-H(54) : 0.9300 ; C(55)-C(56) :1.508(5) ; C(55)-C(57) :1.522(5) ; C(55)-H(55) :0.9800 ; C(56)-H(56A):0.9700 ; C(56)-H(56B) :0.9700 ; C(57)-C(58) :1.500(6) ; C(57)-H(57A) :0.9700 ; C(57)-H(57B) :0.9700 ; C(58)-C(59) :1.496(5) ; C(59)-C(64) :1.376(6) ; C(59)-C(60):1.382(6) ; C(60)-C(61):1.375(6) ; C(60)-H(60):0.9300 ; C(61)-C(62):1.377(7) ; C(61)-H(61):0.9300 ; C(63)-C(64):1.370(6) ; C(63)-H(63):0.9300 ; C(64)-H(64):0.9300 ; C(65)-H(65A):0.9600 ; C(65)-H(65B):0.9600 ; C(65)-H(65C): 0.9600

Table 4. Bond angles for 3aa.

Atom Atom Atom Angle/° ;	**Atom Atom Atom Angle/°;**
O(1)-S(1)-O(2):120.5(2);	O(1)-S(1)-N(1):106.92(18) ;
O(2)-S(1)-N(1):105.86(18)	O(1)-S(1)-C(1):107.95(19);
O(2)-S(1)-C(1):107.97(19);	N(1)-S(1)-C(1):106.90(16)
O(5)-S(2)-O(6):120.6(2);	O(5)-S(2)-N(3):105.70(19) ;
O(6)-S(2)-N(3):107.21(19)	O(5)-S(2)-C(34):107.1(2);
O(6)-S(2)-C(34):108.1(2);	N(3)-S(2)-C(34):107.54(16)
C(7)-N(1)-C(23):110.2(3) ;	C(7)-N(1)-S(1):120.6(2) ;
C(23)-N(1)-S(1):115.9(3)	C(40)-N(3)-C(56):110.0(3);
C(40)-N(3)-S(2:121.1(3) ;	C(56)-N(3)-S(2):117.2(3)
C(6)-C(1)-C(2):120.0(3) ;	C(6)-C(1)-S(1):119.9(3) ;
C(2)-C(1)-S(1):120.1(3)	C(3)-C(2)-C(1):119.2(4) ;
C(3)-C(2)-H(2):120.4;	C(1)-C(2)-H(2):120.4;
C(2)-C(3)-C(4): 121.5(4) ;	C(2)-C(3)-H(3):119.3;
C(4)-C(3)-H(3):119.3;	C(3)-C(4)-C(5):117.9(4) ;
C(3)-C(4)-C(32):121.0(4);	C(5)-C(4)-C(32):121.1(4) ;
C(6)-C(5)-C(4):121.8(4) ;	C(6)-C(5)-H(5):119.1 ;
C(4)-C(5)-H(5):119.1	C(5)-C(6)-C(1):119.5(4);
C(5)-C(6)-H(6):120.2;	C(1)-C(6)-H(6):120.2;
N(1)-C(7)-C(8):117.1(3);	N(1)-C(7)-C(14):100.4(3);
C(8)-C(7)-C(14):114.5(3);	N(1)-C(7)-H(7):108.1 ;
C(8)-C(7)-H(7):108.1	C(14)-C(7)-H(7):108.1;
C(13)-C(8)-C(9):119.2(4) ;	C(13)-C(8)-C(7):117.8(4) ;
C(9)-C(8)-C(7):122.8(4)	C(8)-C(9)-C(10):118.2(5);
C(8)-C(9)-H(9):120.9;	C(10)-C(9)-H(9):120.9;
C(11)-C(10)-C(9):121.0(5);	C(11)-C(10)-H(10):119.5;
C(9)-C(10)-H(10):119.5;	C(12)-C(11)-C(10):120.1(5);
C(12)-C(11)-H(11):120.0;	C(10)-C(11)-H(11):120.0;
C(11)-C(12)-C(13):120.9(6);	C(11)-C(12)-H(12):119.6;

C(13)-C(12)-H(12):119.6;	C(12)-C(13)-C(8):120.7(5);
C(12)-C(13)-H(13):119.7;	C(8)-C(13)-H(13):119.7;
C(33)-C(14)-C(15):113.4(3);	C(33)-C(14)-C(22):107.9(3);
C(15)-C(14)-C(22):111.7(3)	C(33)-C(14)-C(7):110.9(3);
C(15)-C(14)-C(7):112.1(3);	C(22)-C(14)-C(7):100.0(3);
O(4)-C(15)-C(16):122.1(4);	O(4)-C(15)-C(14):116.6(3) ;
C(16)-C(15)-C(14):121.4(3);	C(21)-C(16)-C(17):119.4(5);
C(21)-C(16)-C(15):123.2(4);	C(17)-C(16)-C(15):117.4(4)
C(18)-C(17)-C(16):118.9(6);	C(18)-C(17)-H(17):120.6;
C(16)-C(17)-H(17):120.6 ;	C(19)-C(18)-C(17):120.9(5);
C(19)-C(18)-H(18):119.5 ;	C(17)-C(18)-H(18):119.5 ;
C(18)-C(19)-C(20):121.0(5);	C(18)-C(19)-H(19):119.5;
C(20)-C(19)-H(19):119.5;	C(19)-C(20)-C(21):119.2(5);
C(19)-C(20)-H(20):120.4;	C(21)-C(20)-H(20):120.4;
C(20)-C(21)-C(16):120.6(5);	C(20)-C(21)-H(21):119.7;
C(16)-C(21)-H(21):119.7 ;	C(24)-C(22)-C(23):116.6(3);
C(24)-C(22)-C(14):114.4(3);	C(23)-C(22)-C(14):101.7(3)
C(24)-C(22)-H(22):107.9;	C(23)-C(22)-H(22):107.9;
C(14)-C(22)-H(22):107.9;	N(1)-C(23)-C(22):104.6(3);
N(1)-C(23)-H(23A):110.8;	C(22)-C(23)-H(23A):110.8 ;
N(1)-C(23)-H(23B):110.8;	C(22)-C(23)-H(23B):110.8;
H(23A)-C(23)-H(23B):108.9 ;	C(25)-C(24)-C(22):113.1(3);
C(25)-C(24)-H(24A):109.0;	C(22)-C(24)-H(24A):109.0 ;
C(25)-C(24)-H(24B):109.0;	C(22)-C(24)-H(24B):109.0;
H(24A)-C(24)-H(24B):107.8 ;	O(3)-C(25)-C(26):120.7(4);
O(3)-C(25)-C(24):120.6(3);	C(26)-C(25)-C(24):118.7(3);
C(31)-C(26)-C(27):118.8(4);	C(31)-C(26)-C(25):123.3(4);
C(27)-C(26)-C(25):117.9(4);	C(26)-C(27)-C(28):120.4(4);
C(26)-C(27)-H(27):119.8;	C(28)-C(27)-H(27):119.8;
C(29)-C(28)-C(27):120.3(5);	C(29)-C(28)-H(28):119.9;

C(27)-C(28)-H(28):119.9; C(28)-C(29)-C(30):120.2(4) ;

C(28)-C(29)-H(29) :119.9 ; C(30)-C(29)-H(29):119.9 ;

C(29)-C(30)-C(31):119.4(5); C(29)-C(30)-H(30):120.3;

C(31)-C(30)-H(30):120.3; C(26)-C(31)-C(30):121.0(5);

C(26)-C(31)-H(31):119.5; C(30)-C(31)-H(31):119.5 ;

C(4)-C(32)-H(32A):109.5; C(4)-C(32)-H(32B):109.5;

H(32A)-C(32)-H(32B):109.5; C(4)-C(32)-H(32C):109.5;

H(32A)-C(32)-H(32C):109.5; H(32B)-C(32)-H(32C):109.5 ;

N(2)-C(33)-C(14):175.3(4); C(39)-C(34)-C(35):120.1(4);

C(39)-C(34)-S(2):120.3(3); C(35)-C(34)-S(2):119.6(3);

C(36)-C(35)-C(34):119.1(5); C(36)-C(35)-H(35):120.5 ;

C(34)-C(35)-H(35):120.5; C(37)-C(36)-C(35):122.1(5);

C(37)-C(36)-H(36):118.9 ; C(35)-C(36)-H(36):118.9 ; C(36)-C(37)-C(38):117.8(4) ; C(36)-C(37)-C(65):122.0(5);

C(38)-C(37)-C(65):120.3(5) ; C(37)-C(38)-C(39):121.6(5); C(37)-C(38)-H(38):119.2; C(39)-C(38)-H(38):119.2 ; C(38)-C(39)-C(34):119.3(4); C(38)-C(39)-H(39):120.4;

C(34)-C(39)-H(39):120.4; N(3)-C(40)-C(41):117.1(3) ; N(3)-C(40)-C(47):100.1(3) ; C(41)-C(40)-C(47):114.5(3) ; N(3)-C(40)-H(40):108.2 ; C(41)-C(40)-H(40):108.2 ;

C(47)-C(40)-H(40):108.2; C(42)-C(41)-C(46):119.2(5); C(42)-C(41)-C(40):117.8(4); C(46)-C(41)-C(40):122.6(4); C(43)-C(42)-C(41):120.7(5) ; C(43)-C(42)-H(42):119.6 ;

C(41)-C(42)-H(42):119.6; C(44)-C(43)-C(42):119.6(6) ; C(44)-C(43)-H(43):120.2 ; C(42)-C(43)-H(43):120.2 ; C(43)-C(44)-C(45):120.7(6) ; C(43)-C(44)-H(44):119.6 ;

C(45)-C(44)-H(44):119.6 ; C(44)-C(45)-C(46): 120.2(5) ; C(44)-C(45)-H(45):119.9; C(46)-C(45)-H(45):119.9 ; C(45)-C(46)-C(41):119.4(5) ; C(45)-C(46)-H(46):120.3 ;

C(41)-C(46)-H(46):120.3 ; C(66)-C(47)-C(48):112.7(3) ; C(66)-C(47)-

C(55):107.8(3); C(48)-C(47)-C(55):112.4(3) ; C(66)-C(47)-C(40):111.0(3) ; C(48)-C(47)-C(40):111.9(3) ;

C(55)-C(47)-C(40):100.3(3) ; O(7)-C(48)-C(49):121.6(4) ; O(7)-C(48)-C(47):117.3(4) ; C(49)-C(48)-C(47):121.1(3) ; C(54)-C(49)-C(50):120.4(4) ; C(54)-C(49)-C(48):117.6(4) ;

C(50)-C(49)-C(48):122.1(4) ; C(49)-C(50)-C(51): 120.4(5) ; C(49)-C(50)-H(50): 119.8 ; C(51)-C(50)-H(50):119.8; C(50)-C(51)-C(52):118.9(5) ; C(50)-C(51)-H(51):120.6 ;

C(52)-C(51)-H(51):120.6 ; C(53)-C(52)-C(51):120.2(5) ; C(53)-C(52)-H(52):119.9 ; C(52)-C(53)-C(54):121.8(6); C(52)-C(53)-H(53):119.1; C(54)-C(53)-H(53):119.1 ;

C(49)-C(54)-C(53):118.3(5) ; C(49)-C(54)-H(54):120.9 ; C(53)-C(54)-H(54):120.9 ; C(56)-C(55)-C(57):117.7(3) ; C(56)-C(55)-C(47):102.9(3) ; C(57)-C(55)-C(47):113.7(3) ;

C(56)-C(55)-H(55:107.3 ; C(57)-C(55)-H(55):107.3 ; C(47)-C(55)-H(55):107.3 ; N(3)-C(56)-C(55):104.7(3) ; N(3)-C(56)-H(56A):110.8 ; C(55)-C(56)-H(56A):110.8 ;

N(3)-C(56)-H(56B):110.8 ; C(55)-C(56)-H(56B):110.8 ; H(56A)-C(56)-H(56B):108.9; C(58)-C(57)-C(55):113.3(3) ; C(58)-C(57)-H(57A):108.9 ; C(55)-C(57)-H(57A):108.9 ;

C(58)-C(57)-H(57B):108.9 ; C(55)-C(57)-H(57B):108.9 ; H(57A)-C(57)-H(57B):107.7 ; O(8)-C(58)-C(59):119.9(4) ; O(8)-C(58)-C(57):120.8(4) ; C(59)-C(58)-C(57):119.3(4) ;

C(64)-C(59)-C(60):118.7(4) ; C(64)-C(59)-C(58):117.9(4) ; C(60)-C(59)-C(58):123.3(4) ; C(61)-C(60)-C(59):120.0(4) ; C(61)-C(60)-H(60):120.0 ; C(59)-C(60)-H(60):120.0 ;

C(60)-C(61)-C(62):120.8(5) ; C(60)-C(61)-H(61): 119.6 ; C(62)-C(61)-H(61):119.6 ; C(63)-C(62)-C(61):119.1(4) ; C(63)-C(62)-H(62):120.4 ; C(61)-C(62)-H(62): 120.4 ;

C(64)-C(63)-C(62):120.3(5) ; C(64)-C(63)-H(63):119.9 ; C(62)-C(63)-

H(63):119.9 ; C(63)-C(64)-C(59):121.1(5) ; C(63)-C(64)-H(64):119.5 ; C(59)-C(64)-H(64):119.5 ;

C(37)-C(65)-H(65A):109.5 ; C(37)-C(65)-H(65B): 109.5 ; H(65A)-C(65)-H(65B):109.5 ; C(37)-C(65)-H(65C):109.5 ; H(65A)-C(65)-H(65C):109.5 ; H(65B)-C(65)-H(65C):109.5 ;

N(4)-C(66)-C(47):175.7(4)

Symmetry transformations used to generate equivalent atoms:

Table 5. Anisotropic displacement parameters (Å^2 ×10^3) for 3aa. The anisotropic displacement factor exponent takes the form: $-2\pi^2$ [$h^2 a^{*2}$ U11 + ... + 2 h k a* b* U_{12}]

Atom	U11	U22	U33	U23	U13	U12
S(1)	40(1)	66(1)	39(1)	-14(1)	-2(1)	8(1)
S(2)	47(1)	72(1)	39(1)	-15(1)	-2(1)	6(1)
N(1)	40(2)	51(2)	34(2)	-4(2)	2(1)	2(2)
N(2)	41(2)	52(2)	68(2)	-1(2)	6(2)	-4(2)
N(3)	43(2)	55(2)	36(2)	-6(2)	0(1)	5(2)
N(4)	45(2)	56(2)	70(2)	-6(2)	3(2)	4(2)
O(1)	67(2)	96(3)	34(1)	-5(2)	-3(1)	26(2)
O(2)	47(2)	73(2)	76(2)	-36(2)	-1(1)	-3(2)
O(3)	97(2)	48(2)	45(2)	-5(1)	-1(2)	20(2)
O(4)	52(2)	58(2)	76(2)	-5(2)	-18(1)	-9(1)
O(5)	51(2)	86(3)	75(2)	-40(2)	-2(2)	-6(2)
O(6)	77(2)	108(3)	36(1)	-2(2)	-1(1)	25(2)
O(7)	57(2)	58(2)	85(2)	-8(2)	-28(2)	-2(2)
O(8)	134(3)	51(2)	48(2)	-5(2)	9(2)	33(2)
C(1)	41(2)	50(2)	41(2)	-4(2)	4(1)	4(2)
C(2)	44(2)	44(2)	65(2)	0(2)	7(2)	-4(2)
C(3)	54(2)	51(3)	64(3)	9(2)	4(2)	13(2)
C(4)	47(2)	63(3)	56(2)	1(2)	8(2)	0(2)
C(5)	54(2)	52(3)	92(3)	12(3)	19(2)	-3(2)
C(6)	51(2)	53(3)	69(3)	15(2)	11(2)	9(2)
C(7)	32(2)	46(2)	40(2)	-2(2)	2(1)	2(2)
C(8)	50(2)	55(2)	35(2)	4(2)	7(2)	9(2)
C(9)	51(2)	78(3)	46(2)	3(2)	-1(2)	16(2)
C(10)	72(3)	120(6)	57(3)	16(3)	-4(2)	36(4)
C(11)	133(6)	87(5)	69(3)	30(3)	12(4)	48(4)
C(12)	121(5)	66(4)	83(4)	26(3)	16(4)	6(4)
C(13)	79(3)	60(3)	59(3)	14(2)	6(2)	0(3)
C(14)	34(2)	37(2)	39(2)	0(2)	-1(1)	0(2)

C(15)	49(2)	40(2)	39(2)	4(2)	-3(2)	-3(2)
C(16)	67(2)	37(2)	44(2)	1(2)	8(2)	-7(2)
C(17)	118(4)	50(3)	61(3)	-11(3)	2(3)	-13(3)
C(18)	170(7)	52(3)	72(4)	-22(3)	30(4)	-12(4)
C(19)	123(5)	37(3)	118(5)	-6(3)	62(4)	2(3)
C(20)	68(3)	35(2)	110(4)	11(3)	29(3)	7(2)
C(21)	62(2)	37(2)	68(3)	3(2)	13(2)	-1(2)
C(22)	36(2)	38(2)	38(2)	-2(2)	1(1)	1(2)
C(23)	49(2)	39(2)	42(2)	-4(2)	4(2)	0(2)
C(24)	50(2)	45(2)	38(2)	-2(2)	2(2)	4(2)
C(25)	48(2)	38(2)	43(2)	-2(2)	-3(2)	-1(2)
C(26)	43(2)	46(2)	42(2)	2(2)	-3(2)	-3(2)
C(27)	71(3)	50(3)	50(2)	3(2)	-6(2)	6(2)
C(28)	81(3)	63(3)	58(3)	17(2)	-11(2)	3(3)
C(29)	87(3)	86(4)	42(2)	14(3)	2(2)	-4(3)
C(30)	84(3)	78(4)	47(2)	3(3)	11(2)	5(3)
C(31)	62(2)	66(3)	43(2)	3(2)	4(2)	7(2)
C(32)	44(2)	90(4)	85(3)	6(3)	-1(2)	3(2)
C(33)	45(2)	32(2)	40(2)	-2(2)	1(1)	4(2)
C(34)	45(2)	53(3)	47(2)	-13(2)	5(2)	2(2)
C(35)	56(2)	54(3)	89(3)	3(3)	14(2)	2(2)
C(36)	53(2)	70(4)	104(4)	-8(3)	18(2)	-14(3)
C(37)	45(2)	72(3)	69(3)	-17(3)	3(2)	1(2)
C(38)	57(2)	52(3)	80(3)	-5(2)	-5(2)	8(2)
C(39)	52(2)	49(3)	74(3)	-12(2)	4(2)	-10(2)
C(40)	33(2)	55(2)	40(2)	0(2)	-2(1)	0(2)
C(41)	49(2)	63(3)	40(2)	2(2)	3(2)	2(2)
C(42)	72(3)	69(3)	68(3)	19(3)	1(2)	-5(3)
C(43)	136(6)	72(4)	91(4)	37(4)	-9(4)	-5(4)
C(44)	121(5)	86(5)	90(4)	38(4)	-6(4)	28(4)
C(45)	77(3)	115(5)	56(3)	14(3)	-9(2)	29(3)
C(46)	52(2)	80(3)	47(2)	5(2)	-4(2)	6(2)
C(47)	37(2)	40(2)	34(2)	-3(2)	-4(1)	5(2)
C(48)	51(2)	44(2)	44(2)	2(2)	-7(2)	-3(2)
C(49)	58(2)	36(2)	54(2)	-6(2)	9(2)	-5(2)
C(50)	52(2)	42(2)	72(3)	-6(2)	3(2)	2(2)
C(51)	62(3)	47(3)	115(4)	2(3)	17(3)	4(2)
C(52)	87(4)	55(3)	134(6)	-19(4)	51(4)	4(3)
C(53)	133(5)	65(4)	81(4)	-28(3)	46(4)	-15(4)
C(54)	96(4)	52(3)	58(3)	-6(2)	12(2)	-15(3)
C(55)	38(2)	43(2)	39(2)	-2(2)	-3(1)	6(2)
C(56)	46(2)	46(2)	41(2)	-3(2)	1(2)	3(2)
C(57)	60(2)	47(2)	42(2)	-1(2)	4(2)	10(2)
C(58)	62(2)	44(2)	47(2)	-3(2)	7(2)	6(2)

C(59)	47(2)	46(2)	47(2)	3(2)	8(2)	1(2)
C(60)	66(2)	52(3)	46(2)	0(2)	6(2)	9(2)
C(61)	85(3)	66(3)	46(2)	-6(2)	8(2)	3(3)
C(62)	75(3)	92(4)	43(2)	14(3)	9(2)	-1(3)
C(63)	86(3)	71(3)	63(3)	22(3)	4(2)	16(3)
C(64)	90(3)	51(3)	59(3)	6(2)	9(2)	15(3)
C(65)	48(2)	111(5)	109(4)	-19(4)	3(3)	2(3)
C(66)	42(2)	37(2)	41(2)	-4(2)	-2(1)	4(2)

Table 5. Hydrogen coordinates (Å×10^4) and isotropic displacement parameters (Å^2 ×10^3) for 3aa.

Atom	x	y	z	U(eq)
H(2)	6653	2932	2192	61
H(3)	4322	3049	1956	67
H(5)	3745	1322	2987	78
H(6)	6055	1192	3226	69
H(7)	7510	885	1660	47
H(9)	10976	849	2664	70
H(10)	11866	7	3585	99
H(11)	10576	-881	3809	115
H(12)	8430	-950	3135	107
H(13)	7493	-135	2235	79
H(17)	8037	-478	-1458	92
H(18)	9390	-1306	-1931	117
H(19)	11227	-1624	-963	110
H(20)	11775	-1125	500	85
H(21)	10531	-251	948	66
H(22)	7316	1444	123	45
H(23A)	9605	2159	788	52
H(23B)	8046	2285	986	52
H(24A)	9715	1683	-909	53
H(24B)	8480	1282	-1333	53
H(27)	7280	3204	-2327	69
H(28)	7188	3403	-4002	81
H(29)	7881	2652	-5089	86
H(30)	8678	1693	-4514	83
H(31)	8744	1488	-2836	69
H(32A)	2048	2705	2159	110
H(32B)	1802	2115	2819	110
H(32C)	1964	2035	1682	110
H(35)	7033	588	5244	79
H(36)	9322	385	5543	90
H(38)	8478	-1377	6251	76

H(39)	6175	-1191	5958	70
H(40)	5297	902	6665	51
H(42)	5264	1936	6162	84
H(43)	4291	2769	5314	120
H(44)	2165	2667	4573	119
H(45)	1011	1731	4626	100
H(46)	1961	889	5482	71
H(50)	2199	1979	7215	66
H(51)	865	2842	7582	89
H(52)	1125	3303	9128	109
H(53)	2682	2919	10249	110
H(54)	4143	2108	9858	82
H(55)	5345	291	8168	48
H(56A)	4824	-528	7230	53
H(56B)	3229	-443	7329	53
H(57A)	3992	407	9545	60
H(57B)	2852	-13	9037	60
H(60)	3970	263	11038	65
H(61)	4260	103	12708	79
H(62)	5060	-847	13314	84
H(63)	5581	-1637	12230	88
H(64)	5257	-1487	10567	80
H(65A)	11181	-328	5839	134
H(65B)	10870	-1050	5870	134
H(65C)	10825	-648	6836	134

Table 6. Torsion angles for 3aa.

A B C D	Angle/°
O(1)-S(1)-N(1)-C(7)	44.7(3)
O(2)-S(1)-N(1)-C(7)	174.4(3)
C(1)-S(1)-N(1)-C(7)	-70.7(3)
O(1)-S(1)-N(1)-C(23)	-178.1(3)
O(2)-S(1)-N(1)-C(23)	-48.4(3)
C(1)-S(1)-N(1)-C(23)	66.5(3)
O(5)-S(2)-N(3)-C(40)	-168.9(3)
O(6)-S(2)-N(3)-C(40)	-39.1(3)
C(34)-S(2)-N(3)-C(40)	77.0(3)
O(5)-S(2)-N(3)-C(56)	51.6(3)
O(6)-S(2)-N(3)-C(56)	-178.5(3)
C(34)-S(2)-N(3)-C(56)	-62.5(3)
O(1)-S(1)-C(1)-C(6)	-29.5(4)
O(2)-S(1)-C(1)-C(6)	-161.3(3)
N(1)-S(1)-C(1)-C(6)	85.2(4)
O(1)-S(1)-C(1)-C(2)	151.2(3)
O(2)-S(1)-C(1)-C(2)	19.4(4)
N(1)-S(1)-C(1)-C(2)	-94.1(3)
C(6)-C(1)-C(2)-C(3)	-1.7(6)
S(1)-C(1)-C(2)-C(3)	177.7(3)
C(1)-C(2)-C(3)-C(4)	-0.1(7)
C(2)-C(3)-C(4)-C(5)	1.8(7)
C(2)-C(3)-C(4)-C(32)	-179.3(4)
C(3)-C(4)-C(5)-C(6)	-1.9(7)
C(32)-C(4)-C(5)-C(6)	179.2(5)
C(4)-C(5)-C(6)-C(1)	0.2(7)
C(2)-C(1)-C(6)-C(5)	1.6(6)
S(1)-C(1)-C(6)-C(5)	-177.7(4)
C(23)-N(1)-C(7)-C(8)	154.4(3)
S(1)-N(1)-C(7)-C(8)	-66.2(4)
C(23)-N(1)-C(7)-C(14)	29.9(3)
S(1)-N(1)-C(7)-C(14)	169.2(2)
N(1)-C(7)-C(8)-C(13)	149.0(4)
C(14)-C(7)-C(8)-C(13)	-93.8(4)
N(1)-C(7)-C(8)-C(9)	-35.8(5)
C(14)-C(7)-C(8)-C(9)	81.3(5)
C(13)-C(8)-C(9)-C(10)	1.0(6)
C(7)-C(8)-C(9)-C(10)	-174.1(4)
C(8)-C(9)-C(10)-C(11)	-0.3(8)
C(9)-C(10)-C(11)-C(12)	-0.1(9)
C(10)-C(11)-C(12)-C(13)	-0.2(10)

C(11)-C(12)-C(13)-C(8)	0.9(9)
C(9)-C(8)-C(13)-C(12)	-1.3(7)
C(7)-C(8)-C(13)-C(12)	174.0(4)
N(1)-C(7)-C(14)-C(33)	68.4(3)
C(8)-C(7)-C(14)-C(33)	-58.0(4)
N(1)-C(7)-C(14)-C(15)	-163.7(3)
C(8)-C(7)-C(14)-C(15)	70.0(4)
N(1)-C(7)-C(14)-C(22)	-45.2(3)
C(8)-C(7)-C(14)-C(22)	-171.6(3)
C(33)-C(14)-C(15)-O(4)	-160.8(3)
C(22)-C(14)-C(15)-O(4)	-38.7(5)
C(7)-C(14)-C(15)-O(4)	72.6(4)
C(33)-C(14)-C(15)-C(16)	16.9(5)
C(22)-C(14)-C(15)-C(16)	139.0(3)
C(7)-C(14)-C(15)-C(16)	-109.7(4)
O(4)-C(15)-C(16)-C(21)	-147.0(4)
C(14)-C(15)-C(16)-C(21)	35.4(6)
O(4)-C(15)-C(16)-C(17)	31.9(6)
C(14)-C(15)-C(16)-C(17)	-145.7(4)
C(21)-C(16)-C(17)-C(18)	-2.6(7)
C(15)-C(16)-C(17)-C(18)	178.4(4)
C(16)-C(17)-C(18)-C(19)	2.5(9)
C(17)-C(18)-C(19)-C(20)	-0.1(9)
C(18)-C(19)-C(20)-C(21)	-2.2(8)
C(19)-C(20)-C(21)-C(16)	2.0(7)
C(17)-C(16)-C(21)-C(20)	0.4(7)
C(15)-C(16)-C(21)-C(20)	179.3(4)
C(33)-C(14)-C(22)-C(24)	55.4(4)
C(15)-C(14)-C(22)-C(24)	-69.9(4)
C(7)-C(14)-C(22)-C(24)	171.3(3)
C(33)-C(14)-C(22)-C(23)	-71.3(3)
C(15)-C(14)-C(22)-C(23)	163.5(3)
C(7)-C(14)-C(22)-C(23)	44.7(3)
C(7)-N(1)-C(23)-C(22)	-1.9(4)
S(1)-N(1)-C(23)-C(22)	-143.3(2)
C(24)-C(22)-C(23)-N(1)	-152.3(3)
C(14)-C(22)-C(23)-N(1)	-27.1(3)
C(23)-C(22)-C(24)-C(25)	-63.9(4)
C(14)-C(22)-C(24)-C(25)	177.6(3)
C(22)-C(24)-C(25)-O(3)	20.1(5)
C(22)-C(24)-C(25)-C(26)	-162.1(3)
O(3)-C(25)-C(26)-C(31)	-174.5(4)
C(24)-C(25)-C(26)-C(31)	7.7(6)
O(3)-C(25)-C(26)-C(27)	5.4(6)

C(24)-C(25)-C(26)-C(27)	-172.4(4)
C(31)-C(26)-C(27)-C(28)	0.0(6)
C(25)-C(26)-C(27)-C(28)	-179.9(4)
C(26)-C(27)-C(28)-C(29)	-0.2(7)
C(27)-C(28)-C(29)-C(30)	0.0(8)
C(28)-C(29)-C(30)-C(31)	0.5(8)
C(27)-C(26)-C(31)-C(30)	0.4(6)
C(25)-C(26)-C(31)-C(30)	-179.7(4)
C(29)-C(30)-C(31)-C(26)	-0.7(7)
O(5)-S(2)-C(34)-C(39)	-18.2(4)
O(6)-S(2)-C(34)-C(39)	-149.5(3)
N(3)-S(2)-C(34)-C(39)	95.0(4)
O(5)-S(2)-C(34)-C(35)	162.5(4)
O(6)-S(2)-C(34)-C(35)	31.1(4)
N(3)-S(2)-C(34)-C(35)	-84.3(4)
C(39)-C(34)-C(35)-C(36)	0.4(7)
S(2)-C(34)-C(35)-C(36)	179.8(4)
C(34)-C(35)-C(36)-C(37)	0.0(8)
C(35)-C(36)-C(37)-C(38)	-0.3(8)
C(35)-C(36)-C(37)-C(65)	-179.0(5)
C(36)-C(37)-C(38)-C(39)	0.3(8)
C(65)-C(37)-C(38)-C(39)	179.0(5)
C(37)-C(38)-C(39)-C(34)	0.0(7)
C(35)-C(34)-C(39)-C(38)	-0.4(7)
S(2)-C(34)-C(39)-C(38)	-179.7(3)
C(56)-N(3)-C(40)-C(41)	-153.7(3)
S(2)-N(3)-C(40)-C(41)	64.2(4)
C(56)-N(3)-C(40)-C(47)	-29.4(3)
S(2)-N(3)-C(40)-C(47)	-171.4(2)
N(3)-C(40)-C(41)-C(42)	-150.1(4)
C(47)-C(40)-C(41)-C(42)	93.2(4)
N(3)-C(40)-C(41)-C(46)	36.7(5)
C(47)-C(40)-C(41)-C(46)	-80.0(5)
C(46)-C(41)-C(42)-C(43)	1.9(8)
C(40)-C(41)-C(42)-C(43)	-171.5(5)
C(41)-C(42)-C(43)-C(44)	-0.5(10)
C(42)-C(43)-C(44)-C(45)	-1.1(11)
C(43)-C(44)-C(45)-C(46)	1.3(10)
C(44)-C(45)-C(46)-C(41)	0.1(8)
C(42)-C(41)-C(46)-C(45)	-1.6(7)
C(40)-C(41)-C(46)-C(45)	171.4(4)
N(3)-C(40)-C(47)-C(66)	-69.8(3)
C(41)-C(40)-C(47)-C(66)	56.4(4)
N(3)-C(40)-C(47)-C(48)	163.4(3)

C(41)-C(40)-C(47)-C(48)	-70.5(4)
N(3)-C(40)-C(47)-C(55)	44.1(3)
C(41)-C(40)-C(47)-C(55)	170.2(3)
C(66)-C(47)-C(48)-O(7)	161.3(4)
C(55)-C(47)-C(48)-O(7)	39.2(5)
C(40)-C(47)-C(48)-O(7)	-72.7(4)
C(66)-C(47)-C(48)-C(49)	-17.2(5)
C(55)-C(47)-C(48)-C(49)	-139.3(3)
C(40)-C(47)-C(48)-C(49)	108.7(4)
O(7)-C(48)-C(49)-C(54)	-36.6(6)
C(47)-C(48)-C(49)-C(54)	141.8(4)
O(7)-C(48)-C(49)-C(50)	141.9(5)
C(47)-C(48)-C(49)-C(50)	-39.6(6)
C(54)-C(49)-C(50)-C(51)	1.6(7)
C(48)-C(49)-C(50)-C(51)	-176.8(4)
C(49)-C(50)-C(51)-C(52)	-2.4(7)
C(50)-C(51)-C(52)-C(53)	0.5(8)
C(51)-C(52)-C(53)-C(54)	2.2(9)
C(50)-C(49)-C(54)-C(53)	1.0(7)
C(48)-C(49)-C(54)-C(53)	179.5(4)
C(52)-C(53)-C(54)-C(49)	-2.9(8)
C(66)-C(47)-C(55)-C(56)	72.4(3)
C(48)-C(47)-C(55)-C(56)	-162.9(3)
C(40)-C(47)-C(55)-C(56)	-43.8(3)
C(66)-C(47)-C(55)-C(57)	-56.1(4)
C(48)-C(47)-C(55)-C(57)	68.7(4)
C(40)-C(47)-C(55)-C(57)	-172.3(3)
C(40)-N(3)-C(56)-C(55)	2.3(4)
S(2)-N(3)-C(56)-C(55)	146.0(2)
C(57)-C(55)-C(56)-N(3)	152.3(3)
C(47)-C(55)-C(56)-N(3)	26.3(3)
C(56)-C(55)-C(57)-C(58)	64.0(4)
C(47)-C(55)-C(57)-C(58)	-175.5(3)
C(55)-C(57)-C(58)-O(8)	-28.1(6)
C(55)-C(57)-C(58)-C(59)	152.5(4)
O(8)-C(58)-C(59)-C(64)	-8.5(7)
C(57)-C(58)-C(59)-C(64)	170.9(4)
O(8)-C(58)-C(59)-C(60)	171.9(4)
C(57)-C(58)-C(59)-C(60)	-8.6(6)
C(64)-C(59)-C(60)-C(61)	2.1(7)
C(58)-C(59)-C(60)-C(61)	-178.3(4)
C(59)-C(60)-C(61)-C(62)	-0.7(7)
C(60)-C(61)-C(62)-C(63)	-0.1(8)
C(61)-C(62)-C(63)-C(64)	-0.5(8)

C(62)-C(63)-C(64)-C(59)	2.0(8)
C(60)-C(59)-C(64)-C(63)	-2.8(7)
C(58)-C(59)-C(64)-C(63)	177.6(5)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for 3aa [Å and°].

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