Supporting Information

Stereoselective Synthesis of Organosulfur Compounds Incorporating N-Aromatic Heterocyclic Motifs and Quaternary Carbon Centers via a Sulfa-Michael Triggered Tandem Reaction

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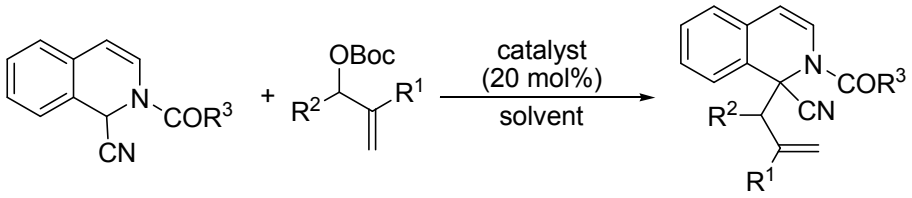
Table of Contents

I. General Information

All reactions were carried out under inert atmospheric condition unless otherwise noted, and solvents were dried according to established procedures. Reactions were monitored by thin layer chromatography (TLC) visualizing with ultraviolet light (UV), and $KMnO_4$; column chromatography purifications were carried out using silica gel. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a 300 or 500 MHz spectrometer in $CDCl_3$, and carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on 75 or 125 MHz spectrometer in $CDCl_3$ unless otherwise noted. Chemical shifts for protons are reported in parts per million downfield from tetramethylsilane (TMS) and are referenced to residual protium in the NMR solvent ($CHCl_3$ = δ 7.26 ppm). Chemical shifts for carbon are reported in parts per million downfield from tetramethylsilane (TMS) and are referenced to the carbon resonances of the solvent residual peak ($CDCl_3$ = δ 77.16 ppm). NMR data are presented as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constant in Hertz (Hz), integration. Mass spectra were recorded on the Bruker MicrOTOF Q II. Melting points were measured on a melting point apparatus and were uncorrected. The enantiomeric excesses of products were determined by chiral phase HPLC analysis.

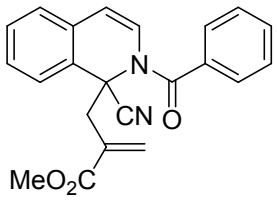
II. General Procedure and Experimental Details of Allylic Alkylation Reaction of MBH Adducts with compound S-1[4]

Morita-Baylis-Hillman Carbonates **S-2** were prepared according to the literature procedure.[1] Compounds **S-1** were prepared by the literature procedure.[2, 3]



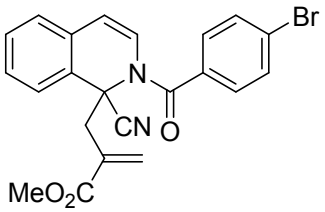
S-1 **S-2** **1**

A mixture of compound **S-1**, MBH carbonate **S-2** (1.3 eqv.) and DABCO (20%) were dissolved in CH_3CN at 30 ℃. The reaction was monitored by TLC. Upon completion, the reaction mixture was concentrated *in vacuo*. The crude product was purified directly by flash chromatography (silica gel, EtOAc/Petroleum ether (60-90 ℃)). Single isomer can be got by recrystallization or flash chromatography.



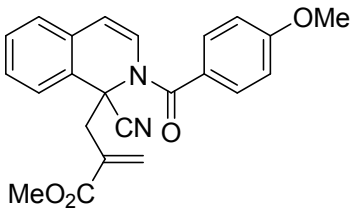
1aa

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (d, *J* = 7.4 Hz, 2H), 7.59 (d, *J* = 7.6 Hz, 1H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.34 – 7.28 (m, 2H), 7.08 (d, *J* = 7.3 Hz, 1H), 6.44 (d, *J* = 7.9 Hz, 1H), 6.31 (s, 1H), 5.74 (d, *J* = 7.9 Hz, 1H), 5.67 (s, 1H), 3.65 (d, *J* = 13.1 Hz, 1H), 3.46 (s, 3H), 3.14 (d, *J* = 13.1 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.71, 166.80, 133.60, 133.29, 132.19, 131.87, 129.79, 129.68, 129.56, 128.85, 127.93, 127.74, 127.18, 126.87, 125.25, 117.41, 107.48, 61.05, 52.10, 38.77. HRMS (m/z) calcd for $C_{22}H_{19}N_2O_3$ $[M+H]^+$: 359.1390, found: 359.1393.



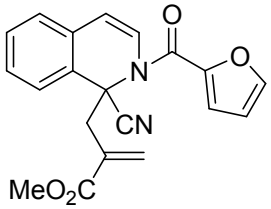
1ab

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 – 7.58 (m, 3H), 7.53 (d, *J* = 8.1 Hz, 2H), 7.35 – 7.27 (m, 2H), 7.09 (d, *J* = 7.1 Hz, 1H), 6.38 (d, *J* = 7.8 Hz, 1H), 6.29 (s, 1H), 5.77 (d, *J* = 7.8 Hz, 1H), 5.62 (s, 1H), 3.64 (d, *J* = 13.1 Hz, 1H), 3.46 (s, 3H), 3.09 (d, *J* = 13.1 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.71, 166.76, 133.44, 132.14, 131.86, 131.18, 129.84, 129.34, 128.08, 127.68, 127.08, 126.96, 126.38, 125.35, 117.28, 108.01, 61.05, 52.09, 38.90. HRMS (m/z) calcd for $C_{22}H_{18}BrN_2O_3$ $[M+H]^+$: 437.0495, found: 437.0487. Mp: 58 – 60 ℃.



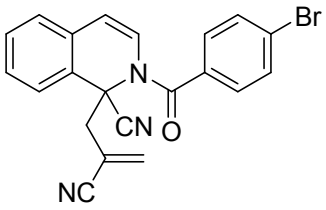
1ac

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.7 Hz, 2H), 7.56 (d, *J* = 7.7 Hz, 1H), 7.32 (t, *J* = 7.1 Hz, 1H), 7.28 – 7.25 (m, 1H), 7.09 (d, *J* = 7.4 Hz, 1H), 6.95 (d, *J* = 8.8 Hz, 2H), 6.50 (d, *J* = 7.9 Hz, 1H), 6.32 (s, 1H), 5.78 (d, *J* = 7.9 Hz, 1H), 5.71 (s, 1H), 3.87 (s, 3H), 3.60 (d, *J* = 13.0 Hz, 1H), 3.43 (s, 3H), 3.16 (d, *J* = 13.1 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.08, 166.63, 162.72, 133.55, 131.93, 131.64, 129.58, 129.55, 127.61, 127.59, 127.15, 127.00, 125.01, 124.97, 117.22, 113.92, 107.09, 61.11, 55.52, 51.88, 38.14. HRMS (m/z) calcd for $C_{23}H_{21}N_2O_4$ $[M+H]^+$: 389.1496, found: 389.1502. Mp: 115 – 117 ℃



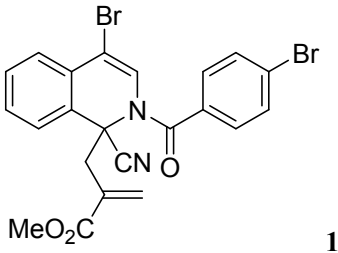
1ad

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62 (dd, *J* = 1.7, 0.8 Hz, 1H), 7.54 – 7.51 (m, 1H), 7.34 – 7.30 (m, 2H), 7.25 (td, *J* = 7.6, 1.6 Hz, 1H), 7.20 – 7.19 (m, 1H), 7.10 (dd, *J* = 7.3, 1.5 Hz, 1H), 6.88 (d, *J* = 7.9 Hz, 1H), 6.57 (dd, *J* = 3.5, 1.7 Hz, 1H), 6.31 (s, 1H), 5.90 (d, *J* = 7.9 Hz, 1H), 5.67 (s, 1H), 3.59 (d, *J* = 13.1 Hz, 1H), 3.42 (s, 3H), 3.14 (d, *J* = 13.1 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.48, 158.11, 146.35, 145.71, 133.32, 131.77, 129.63, 129.27, 127.61, 127.38, 126.84, 125.60, 125.10, 120.03, 116.86, 112.06, 108.14, 60.95, 51.88, 38.44. HRMS (m/z) calcd for $C_{20}H_{17}N_2O_4$ $[M+H]^+$: 349.1183, found: 349.1179.



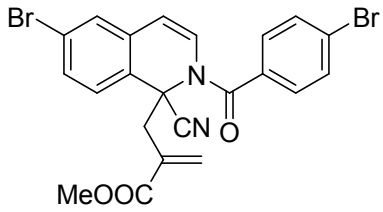
1ah

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70 – 7.67 (m, 1H), 7.65 – 7.61 (m, 2H), 7.56 – 7.52 (m, 2H), 7.44 – 7.37 (m, 2H), 7.15 – 7.12 (m, 1H), 6.50 (d, *J* = 8.0 Hz, 1H), 6.01 (s, 1H), 5.79 (d, *J* = 7.9 Hz, 1H), 5.74 (s, 1H), 3.55 (d, *J* = 13.8 Hz, 1H), 3.02 (d, *J* = 14.1 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.09, 137.73, 132.29, 131.72, 131.12, 130.59, 129.19, 128.87, 127.23, 127.09, 126.86, 126.45, 125.84, 118.05, 116.85, 115.44, 107.90, 59.95, 42.79. HRMS (m/z) calcd for $C_{21}H_{15}BrN_3O$ $[M+H]^+$: 404.0393, found: 404.0384. Mp: 173 – 175 ℃.



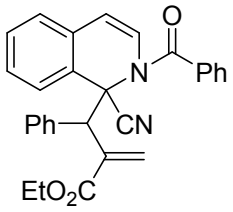
1ai

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.3 Hz, 3H), 7.62 (d, *J* = 7.8 Hz, 3H), 7.54 (d, *J* = 8.4 Hz, 1H), 7.51 (d, *J* = 7.7 Hz, 1H), 7.45 (t, *J* = 7.5 Hz, 1H), 7.39 (t, *J* = 7.5 Hz, 1H), 6.70 (s,1H), 6.29 (s, 1H), 5.56 (s, 1H), 3.67 (d, *J* = 13.2 Hz, 1H), 3.48 (s, 3H), 3.08 (d, *J* = 13.2 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.84, 166.52, 133.02, 132.25, 131.67, 131.27, 131.12, 130.05, 129.33, 128.75, 127.80, 127.42, 126.89, 126.74, 125.43, 116.77, 102.91, 61.13, 52.03, 39.44. HRMS (m/z) calcd for $C_{22}H_{17}Br_2N_2O_3$ $[M+H]^+$: 514.9600, found: 514.9603. Mp: 124 – 126 ℃.



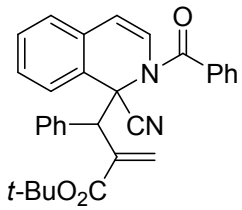
1aj

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.3 Hz, 2H), 7.51 (d, *J* = 8.3 Hz, 2H), 7.44 – 7.39 (m, 2H), 7.23 (s, 1H), 6.44 (d, *J* = 7.9 Hz, 1H), 6.32 (s, 1H), 5.71 (d, *J* = 7.9 Hz, 1H), 5.68 (s, 1H), 3.60 (d, *J* = 13.1 Hz, 1H), 3.50 (s, 3H), 3.08 (d, *J* = 13.2 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.71, 166.67, 133.19, 132.26, 132.18, 131.76, 131.40, 131.20, 130.70, 128.71, 127.95, 127.70, 127.26, 126.44, 123.99, 116.87, 106.67, 60.82, 52.22, 38.70. HRMS (m/z) calcd for $C_{22}H_{17}Br_2N_2O_3$ $[M+H]^+$: 514.9600, found: 514.9598. Mp: 166 – 168 ℃.



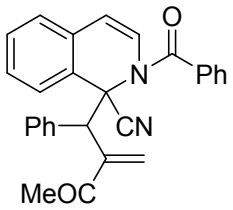
1ca

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 －7.46 (m, 3H), 7.42 －7.39 (m, 2H), 7.25 (t, *J* = 7.4 Hz, 1H), 7.17 －7.10 (m, 5H), 7.02 －7.46 (m, 3H), 6.85 (s, 1H), 6.76 (s, 1H), 6.35 (d, *J* = 7.7 Hz, 1H), 6.01 (d, *J* = 7.7 Hz, 1H), 5.17 (s, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 1.28 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.09, 167.24, 137.07, 135.65, 134.11, 131.64, 130.34, 129.49, 129.16, 129.08, 128.66, 128.32, 128.07, 128.03, 127.93, 127.26, 126.93, 125.01, 116.68, 109.80, 62.91, 61.47, 48.60, 14.32. HRMS (m/z) calcd for $C_{29}H_{25}N_2O_3$ $[M+H]^+$: 449.1860, found: 449.1867. Mp: 127 – 129℃.



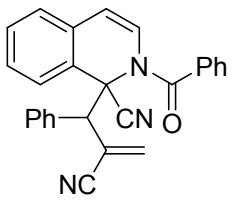
1da

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50 – 7.49 (m, 1H), 7.48 – 7.47 (m, 2H), 7.43 (s, 1H), 7.42 – 7.40 (m, 1H), 7.27 (td, *J* = 7.4, 1.2 Hz, 1H), 7.16 – 7.11 (m, 3H), 7.09 – 7.06 (m, 2H), 7.03 – 6.97 (m, 3H), 6.82 (s, 1H), 6.70 (s, 1H), 6.34 (d, *J* = 7.7 Hz, 1H), 6.00 (d, *J* = 7.7 Hz, 1H), 5.16 (s, 1H), 1.43 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.04, 166.34, 138.18, 135.97, 134.25, 131.57, 130.36, 129.78, 129.52, 129.24, 129.04, 128.68, 128.39, 128.19, 128.01, 127.87, 127.28, 126.93, 125.02, 116.74, 109.82, 81.56, 63.06, 48.29, 28.21. HRMS (m/z) calcd for $C_{31}H_{29}N_2O_3$ $[M+H]^+$: 477.2173, found: 477.2169. Mp: 156 -158 ℃.



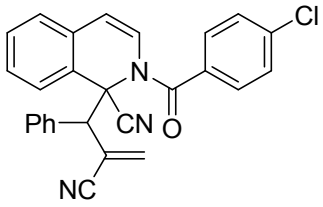
1ea

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51－7.46 (m, 3H), 7.42 －7.39 (m, 2H), 7.19 (t, *J* = 7.4 Hz, 1H), 7.13 – 7.07 (m, 7H), 7.04 (s, 1H), 6.92 (t, *J* = 7.6 Hz, 1H), 6.61 (s, 1H), 6.35 (d, *J* = 7.7 Hz, 1H), 6.08 (d, *J* = 7.7 Hz, 1H), 5.31 (s, 1H), 2.44 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.41, 169.27, 145.54, 136.35, 133.94, 131.89, 130.79, 130.18, 129.32, 129.04, 128.70, 128.21, 128.19, 127.92, 127.80, 127.21, 127.18, 124.91, 116.87, 109.82, 63.36, 45.67, 26.24. HRMS (m/z) calcd for $C_{28}H_{23}N_2O_2$ $[M+H]^+$: 419.1754, found: 419.1750. Mp: 143 -145 ℃.



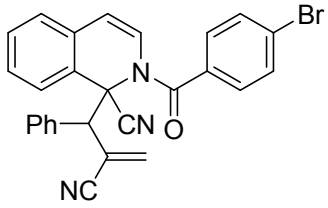
1fa

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 – 7.49 (dd, *J* = 16.7, 7.4 Hz, 6H), 7.46 – 7.40 (m, 7H), 7.37 (d, *J* = 4.5 Hz, 1H), 7.36 – 7.33 (m, 2H), 7.24 – 7.19 (m, 3H), 7.18 – 7.13 (m, 7H), 7.07 (d, *J* = 7.5 Hz, 2H), 6.44 (d, *J* = 7.9 Hz, 1H), 6.37 (s, 1H), 6.27 (s, 1H), 6.13 (d, *J* = 7.9 Hz, 1H), 5.97 (s, 1H), 5.91 (d, *J* = 7.9 Hz, 1H), 5.87 (s, 1H), 5.52 (d, *J* = 7.9 Hz, 1H), 4.84 (s, 1H), 4.72 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.77, 169.39, 137.99, 137.68, 133.17, 133.12, 133.09, 132.38, 132.06, 131.93, 130.60, 130.45, 130.42, 130.06, 129.93, 129.50, 129.47, 129.18, 129.08, 128.93, 128.88, 128.84, 128.76, 128.71, 128.50, 128.41, 127.93, 127.36, 127.08, 126.27, 125.39, 125.32, 125.23, 124.69, 120.80, 120.14, 118.14, 118.05, 116.37, 116.21, 109.10, 107.84, 63.75, 63.72, 56.03, 54.87. HRMS (m/z) calcd for $C_{27}H_{20}N_3O$ $[M+H]^+$: 402.1601, found: 402.1602.



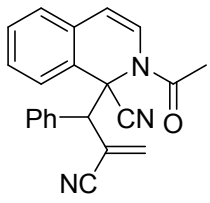
1fb

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.5 Hz, 2H), 7.47 (d, *J* = 7.8 Hz, 1H), 7.43 (d, *J* = 7.6 Hz, 2H), 7.40 – 7.37 (m, 1H), 7.26 (s, 2H), 7.16 – 7.14 (m, 4H), 7.07 (d, *J* = 6.9 Hz, 1H), 6.42 (s, 1H), 6.31 (s, 1H), 6.09 (d, *J* = 7.4 Hz, 1H), 5.53 (d, *J* = 7.4 Hz, 1H), 4.73 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.70, 138.48, 137.85, 132.30, 131.47, 130.70, 130.48, 130.05, 129.30, 129.09, 128.98, 128.81, 128.43, 128.17, 125.87, 125.35, 125.19, 120.60, 118.04, 116.24, 108.30, 63.87, 54.78. HRMS (m/z) calcd for $C_{27}H_{19}ClN_3O$ $[M+H]^+$: 436.1211, found: 436.1212. Mp: 151 – 153 ℃.



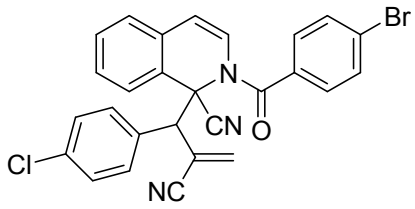
1fc

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 – 7.58 (m, 2H), 7.47 (d, *J* = 7.9 Hz, 1H), 7.45 – 7.43 (m, 2H), 7.39 (td, *J* = 7.5, 1.0 Hz, 1H), 7.28 – 7.25 (m, 2H), 7.18 – 7.15 (m, 2H), 7.14 – 7.12 (m, 2H), 7.08 (d, *J* = 7.4 Hz, 1H), 6.42 (s, 1H), 6.31 (s, 1H), 6.08 (d, *J* = 7.8 Hz, 1H), 5.53 (d, *J* = 7.8 Hz, 1H), 4.72 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.98, 138.06, 132.42, 132.24, 132.08, 130.96, 130.66, 130.21, 129.44, 129.16, 128.97, 128.61, 128.35, 127.09, 125.98, 125.53, 125.32, 120.72, 118.20, 116.41, 108.51, 64.01, 54.93. HRMS (m/z) calcd for $C_{27}H_{19}BrN_3O$ $[M+H]^+$: 480.0706, found: 480.0699. Mp: 169-171 ℃.



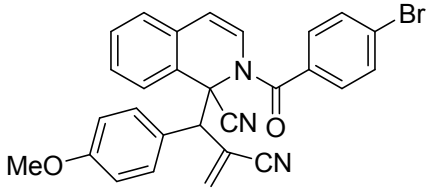
1fd

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50 (d, *J* = 7.8 Hz, 1H), 7.37 (td, *J* = 7.5, 1.2 Hz, 1H), 7.30 – 7.23 (m, 2H), 7.19 – 7.24 (m, 2H), 7.06 – 6.99 (m, 3H), 6.44 (s, 1H), 6.30 (s, 1H), 6.19 (d, *J* = 8.0 Hz, 1H), 5.52 (d, *J* = 8.0 Hz, 1H), 4.61 (s, 0H), 2.26 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.41, 138.47, 132.36, 130.64, 130.24, 129.45, 129.10, 129.03, 128.50, 128.25, 125.39, 125.13, 124.08, 120.42, 118.09, 116.83, 108.54, 63.04, 55.04, 23.10. HRMS (m/z) calcd for $C_{22}H_{18}N_3O$ $[M+H]^+$: 340.1444, found: 340.1435. Mp: 141 – 143 ℃



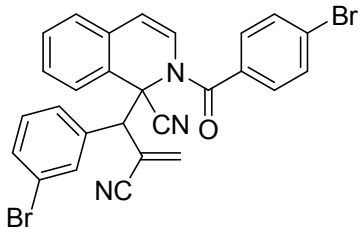
1fe

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.2 Hz, 2H), 7.50 (d, *J* = 7.8 Hz, 1H), 7.45 (d, *J* = 8.2 Hz, 2H), 7.42 (t, *J* = 7.5 Hz, 1H), 7.31 (t, *J* = 7.6 Hz, 1H), 7.15 (d, *J* = 8.3 Hz, 2H), 7.09 (d, *J* = 7.7 Hz, 1H), 7.06 (d, *J* = 8.3 Hz, 2H), 6.42 (s, 1H), 6.33 (s, 1H), 6.11 (d, *J* = 7.8 Hz, 1H), 5.54 (d, *J* = 7.8 Hz, 1H), 4.74 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.03, 138.36, 135.49, 132.33, 131.88, 131.48, 131.01, 130.98, 130.91, 129.43, 129.00, 128.81, 128.60, 127.34, 126.10, 125.67, 124.97, 120.31, 117.96, 116.22, 108.51, 63.99, 54.38. HRMS (m/z) calcd for $C_{27}H_{18}BrClN_3O$ $[M+H]^+$: 514.0316, found: 514.0309. Mp: 174 – 176 ℃.



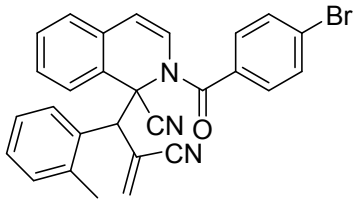
1ff

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.4 Hz, 2H), 7.48 (d, *J* = 7.9 Hz, 1H), 7.44 (d, *J* = 8.4 Hz, 2H), 7.39 (t, *J* = 7.4 Hz, 1H), 7.30 – 7.26 (m, 1H), 7.08 (d, *J* = 7.4 Hz, 1H), 7.04 (d, *J* = 8.7 Hz, 2H), 6.69 (d, *J* = 8.8 Hz, 2H), 6.39 (s, 1H), 6.29 (s, 1H), 6.09 (d, *J* = 7.8 Hz, 1H), 5.54 (d, *J* = 7.9 Hz, 1H), 4.68 (s, 1H), 3.74 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.94, 160.23, 137.72, 132.22, 132.11, 131.34, 130.95, 130.62, 129.42, 128.99, 128.36, 127.05, 126.03, 125.50, 125.39, 124.22, 123.59, 120.95, 120.15, 118.26, 116.52, 113.91, 108.44, 64.04, 55.39, 54.23. HRMS (m/z) calcd for $C_{28}H_{21}BrN_3O_2$ $[M+H]^+$: 510.0812, found: 510.0802. Mp: 144 – 146 ℃.



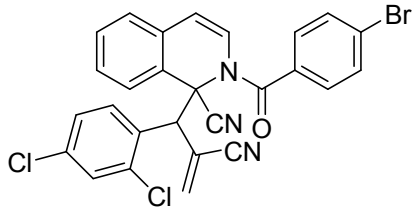
1fg

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.63 – 7.59 (m, 2H), 7.53 (d, *J* = 8.1 Hz, 1H), 7.47 – 7.42 (m, 4H), 7.33 (td, *J* = 7.8, 1.4 Hz, 1H), 7.23 – 7.20 (m, 1H), 7.12 – 7.05 (m, 3H), 6.45 (s, 1H), 6.35 (s, 1H), 6.06 (d, *J* = 7.9 Hz, 1H), 5.51 (d, *J* = 7.9 Hz, 1H), 4.74 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.07, 138.66, 134.56, 133.54, 132.30, 132.23, 131.88, 130.98, 130.85, 130.04, 129.46, 128.92, 128.54, 128.44, 127.18, 125.95, 125.68, 124.67, 122.38, 119.92, 117.79, 116.13, 108.35, 63.95, 54.50. HRMS (m/z) calcd for $C_{27}H_{18}Br_2N_3O$ $[M+H]^+$: 557.9811, found: 557.9809. Mp: 93 – 95 ℃.



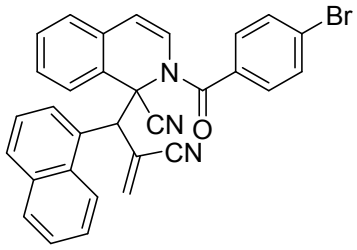
1fh

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 – 7.74 (m, 1H), 7.59 (d, *J* = 8.4 Hz, 2H), 7.43 (d, *J* = 8.4 Hz, 2H), 7.36 – 7.33 (m, 2H), 7.18 – 7.14 (m, 3H), 7.08 (d, *J* = 7.4 Hz, 1H), 6.96 – 6.94 (m, 1H), 6.33 (d, *J* = 7.8 Hz, 1H), 6.28 (s, 1H), 6.24 (s, 1H), 5.79 (d, *J* = 7.8 Hz, 1H), 4.97 (s, 1H), 1.86 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.93, 137.73, 136.80, 132.22, 132.09, 131.18, 130.87, 130.73, 130.44, 129.42, 129.36, 128.86, 128.76, 128.16, 127.20, 126.29, 126.21, 126.14, 125.35, 121.51, 118.31, 116.55, 108.92, 63.49, 48.58, 19.41. HRMS (m/z) calcd for $C_{28}H_{21}BrN_3O$ $[M+H]^+$: 494.0863, found: 494.0862. Mp: 97 – 99 ℃.



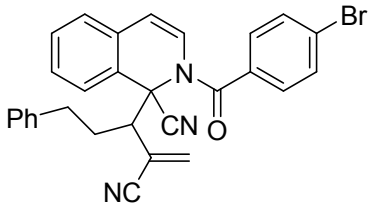
1fi

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.3 Hz, 2H), 7.59 (d, *J* = 7.9 Hz, 1H), 7.49 (d, *J* = 8.3 Hz, 2H), 7.42 (t, *J* = 7.4 Hz, 1H), 7.35 (t, *J* = 7.6 Hz, 1H), 7.28 (d, *J* = 8.7 Hz, 1H), 7.22 (d, *J* = 1.9 Hz, 1H), 7.07 (dd, *J* = 8.7, 2.0 Hz, 1H), 7.05 (d, *J* = 7.4 Hz, 1H), 6.44 (s, 1H), 6.37 (s, 1H), 6.27 (d, *J* = 7.8 Hz, 1H), 5.55 (d, *J* = 7.8 Hz, 1H), 5.49 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.87, 139.31, 136.40, 135.68, 132.28, 131.81, 131.54, 131.23, 130.99, 130.10, 129.62, 128.82, 128.63, 128.58, 127.34, 127.00, 126.01, 125.68, 124.83, 119.83, 117.65, 116.06, 108.54, 63.75, 48.79. HRMS (m/z) calcd for $C_{27}H_{17}BrCl_2N_3O$ $[M+H]^+$: 547.9927, found: 547.9932. Mp: 135 – 137 ℃.



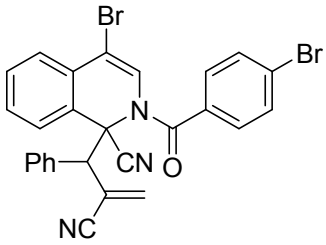
1fj

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.5 Hz, 1H), 7.77 – 7.75 (m, 2H), 7.68 (d, *J* = 7.7 Hz, 1H), 7.51 (d, *J* = 8.4 Hz, 2H), 7.48 – 7.45 (m, 1H), 7.43 – 7.40 (m, 2H), 7.36 (td, *J* = 7.5, 1.1 Hz, 1H), 7.32 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.29 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 7.8 Hz, 1H), 7.00 – 6.96 (m, 1H), 6.63 (s, 1H), 6.42 (d, *J* = 8.5 Hz, 1H), 5.94 (s, 1H), 5.66 (d, *J* = 7.8 Hz, 1H), 5.25 (d, *J* = 7.9 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.23, 139.44, 133.90, 132.68, 132.11, 131.99, 130.89, 130.83, 130.15, 129.64, 129.45, 129.13, 128.48, 128.23, 127.72, 126.97, 126.94, 126.01, 125.83, 125.54, 125.03, 124.71, 121.35, 120.81, 118.26, 116.74, 108.04, 64.68, 47.60. HRMS (m/z) calcd for $C_{31}H_{21}BrN_3O$ $[M+H]^+$: 530.0863, found: 530.0868. Mp: 100 – 102 ℃.



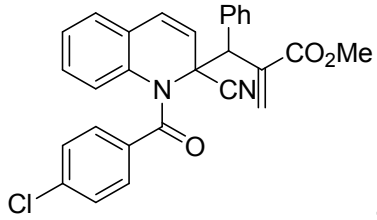
1fk

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 – 7.71 (m, 1H), 7.59 (d, *J* = 8.2 Hz, 2H), 7.43 – 7.41 (m, 2H), 7.39 (d, *J* = 8.3 Hz, 2H), 7.22 – 7.16 (m, 3H), 7.12 – 7.11 (m, 1H), 6.94 (d, *J* = 7.1 Hz, 2H), 6.45 (d, *J* = 7.8 Hz, 1H), 6.28 (s, 1H), 6.05 (s, 1H), 5.79 (d, *J* = 7.8 Hz, 1H), 3.24 (dd, *J* = 11.5, 2.4 Hz, 1H), 2.72 – 2.67 (m, 1H), 2.30 – 2.24 (m, 1H), 2.11 – 1.99 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.53, 140.01, 137.55, 132.21, 131.99, 130.97, 130.48, 129.24, 128.76, 128.67, 128.36, 127.03, 126.98, 126.54, 125.83, 125.77, 121.00, 117.25, 115.90, 108.93, 63.39, 50.10, 32.88, 28.52. HRMS (m/z) calcd for $C_{29}H_{23}BrN_3O$[M+H]$^+$: 508.1019, found: 508.1013. Mp: 184 – 186 ℃



1fl

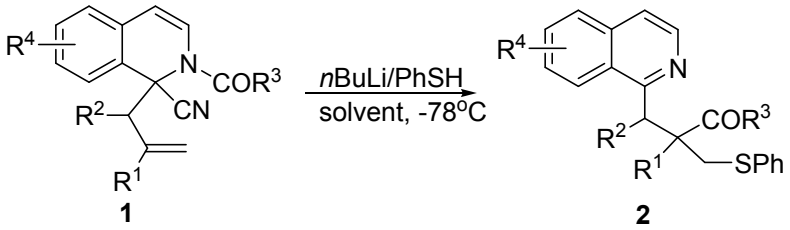
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.4 Hz, 2H), 7.60 (d, *J* = 7.9 Hz, 1H), 7.55 – 7.50 (m, 2H), 7.47 (d, *J* = 8.4 Hz, 2H), 7.44 – 7.41 (m, 1H), 7.29 – 7.26 (m, 1H), 7.21 (t, *J* = 7.6 Hz, 2H), 7.11 (d, *J* = 7.5 Hz, 2H), 6.46 (s, 1H), 6.35 (s, 1H), 6.24 (s, 1H), 4.79 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.28, 138.94, 132.50, 132.13, 131.31, 131.21, 131.07, 129.83, 129.80, 129.46, 129.16, 129.05, 128.90, 127.78, 126.55, 125.94, 125.14, 119.99, 117.95, 116.22, 103.86, 64.53, 55.58. HRMS (m/z) calcd for $C_{27}H_{18}Br_2N_3O$ [M+H]$^+$: 557.9811, found: 557.9818. Mp:154 – 156 ℃.



4b

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (d, *J* = 6.3 Hz, 2H), 7.38 – 7.33 (m, 3H), 7.23 – 7.14 (m, 5H), 7.08 (t, *J* = 7.4 Hz, 1H), 6.92 (t, *J* = 7.7 Hz, 1H), 6.77 (d, *J* = 9.6 Hz, 1H), 6.62 (s, 1H), 6.54 (s, 1H), 6.30 (d, *J* = 8.1 Hz, 1H), 6.23 (d, *J* = 9.6 Hz, 1H), 4.92 (s, 1H), 3.59 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.45, 166.91, 137.69, 136.87, 136.26, 135.11, 133.22, 131.16, 129.95, 128.73, 128.67, 128.57, 128.54, 128.43, 127.30, 126.99, 126.97, 126.53, 125.84, 125.14, 117.66, 60.39, 52.52, 48.76. HRMS (m/z) calcd for $C_{28}H_{22}ClN_2O_3$ [M+H]$^+$: 469.1313, found: 469.1307. Mp: 146– 148 ℃

III. General Procedure and Experimental Details of Sulfa-Michael Triggered Tandem Reaction



1 **2**

Procedure A

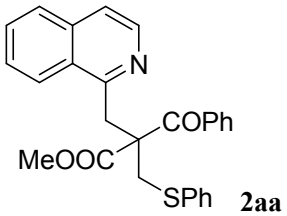
To a solution of thiophenol (0.26 mmol) in THF (1 mL) was added butyllithium (1.6 M in hexanes, 0.24 mmol) at -78 °C. After stirring 20 min, a solution of substrate **1** (0.2 mmol) in THF (1 mL) was added slowly. The resulting mixture was stirred at this temperature to completion and monitored by TLC, then quenched with saturated ammonium chloride solution at the same temperature. H_2O (10 mL) was added and the mixture was extracted with ethyl acetate (10 mL×3). The combined organic layer was washed with brine (10 mL) and dried with anhydrous $NaSO_4$. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography on silica gel to give the desired products.

Procedure B

To a solution of thiophenol (0.26 mmol) in THF (1 mL) was added butyllithium (1.6 M in hexanes, 0.24 mmol) at 0 °C. After stirring 20 min, the solution of lithium thiolate was added slowly to a solution of substrate **1** (0.2 mmol) in THF (1 mL) at -78 °C. The rest of procedure is similar to the general procedure A.

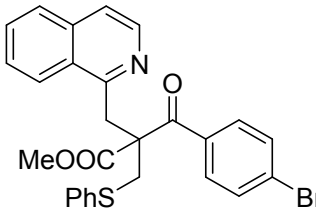
Procedure C

To a solution of thiophenol (0.26 mmol) in CH_2Cl_2 (1 mL) was added *n*-butyllithium (1.6 M in hexanes, 0.24 mmol) at -78 °C, and lithium thiophenolate was precipitated as white solid. After stirring 20 min, a solution of substrate **1** (0.2 mmol) in CH_2Cl_2 (1 mL) was added slowly. The rest of procedure is similar to the general procedure A.



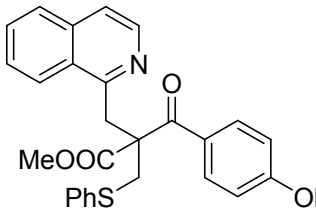
2aa

Following the general procedure A, the residue was purified by column chromatography (EtOAc/Petroleum = 1/10) to afford product as colorless oil (83 mg, 94 %). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.26 (d, *J* = 5.6 Hz, 1H), 8.10 (d, *J* = 7.7 Hz, 1H), 7.79 – 7.76 (m, 2H), 7.70 (d, *J* = 8.1 Hz, 1H), 7.61 – 7.56 (m, 1H), 7.51 – 7.45 (m, 1H), 7.41 – 7.28 (m, 4H), 7.19 – 7.15 (m, 2H), 7.00 – 6.88 (m, 3H), 4.45 (d, *J* = 17.5 Hz, 1H), 4.27 (d, *J* = 17.5 Hz, 1H), 4.14 (d, *J* = 14.0 Hz, 1H), 3.91 (d, *J* = 14.0 Hz, 1H), 3.58 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.25, 171.89, 156.04, 140.81, 138.22, 136.02, 135.59, 131.76, 130.62, 130.00, 128.71, 128.36, 128.18, 127.44, 127.39, 127.24, 126.43, 125.02, 119.77, 62.13, 52.91, 38.50, 36.12. HRMS (m/z) calcd for $C_{27}H_{24}NO_3S$ $[M+H]^+$: 442.1471, found: 442.1477.



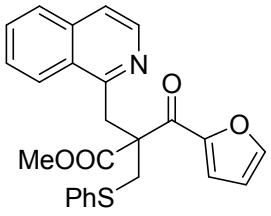
2ab

Following the general procedure A, the residue was purified by column chromatography (EtOAc/Petroleum = 1/10) to afford product as white solid (99 mg, 95 %). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21 (d, *J* = 5.6 Hz, 1H), 8.08 (d, *J* = 8.4 Hz, 1H), 7.71 (d, *J* = 8.2 Hz, 1H), 7.63 (d, *J* = 8.2 Hz, 2H), 7.60 (d, *J* = 7.9 Hz, 1H), 7.51 (t, *J* = 7.5 Hz, 1H), 7.43 (d, *J* = 8.4 Hz, 2H), 7.41 (d, *J* = 6.0 Hz, 1H), 7.16 (d, *J* = 7.7 Hz, 2H), 6.98 (t, *J* = 7.5 Hz, 2H), 6.91 (t, *J* = 7.2 Hz, 1H), 4.43 (d, *J* = 17.5 Hz, 1H), 4.21 (d, *J* = 17.5 Hz, 1H), 4.09 (d, *J* = 14.1 Hz, 1H), 3.82 (d, *J* = 14.1 Hz, 1H), 3.54 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.28, 171.69, 155.68, 140.59, 136.98, 135.98, 135.32, 131.60, 130.65, 130.11, 129.74, 128.74, 127.41, 127.35, 127.32, 126.61, 126.53, 124.90, 119.92, 62.09, 53.02, 38.50, 36.15. HRMS (m/z) calcd for $C_{27}H_{23}BrNO_3S$ $[M+H]^+$: 520.0577, found: 520.0578. Mp: 104 – 106 ℃



2ac

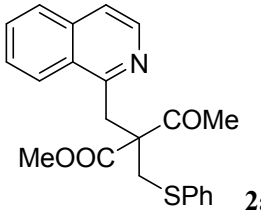
Following the general procedure A, the residue was purified by column chromatography (EtOAc/Petroleum = 1/15) to afford product as white solid (69 mg, 73 %). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.27 (d, *J* = 5.7 Hz, 1H), 8.14 – 8.11 (m, 1H), 7.84 – 7.79 (m, 2H), 7.70 (d, *J* = 7.7 Hz, 1H), 7.61 – 7.56 (m, 1H), 7.50 – 7.44 (m, 1H), 7.40 (d, *J* = 5.7 Hz, 1H), 7.17 – 7.13 (m, 2H), 7.00 – 6.90 (m, 3H), 6.82 – 6.77 (m, 2H), 4.39 (d, *J* = 17.1 Hz, 1H), 4.26 (d, *J* = 17.1 Hz, 1H), 4.04 (d, *J* = 13.9 Hz, 1H), 3.89 (d, *J* = 13.9 Hz, 1H), 3.77 (s, 3H), 3.52 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 194.73, 172.22, 162.49, 156.15, 140.86, 135.86, 135.49, 130.41, 130.38, 130.11, 129.79, 128.50, 127.39, 127.22, 127.02, 126.20, 124.90, 119.55, 113.53, 61.66, 55.36, 52.68, 38.33, 36.05. HRMS (m/z) calcd for $C_{28}H_{26}NO_4S$ $[M+H]^+$: 472.1577, found: 472.1575. Mp: 98 – 100 ℃



2ad

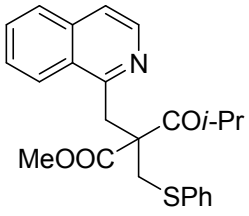
Following the general procedure A, the residue was purified by column chromatography (EtOAc/Petroleum = 1/15) to afford product as colorless oil (78 mg, 90 %). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.31 (d, *J* = 5.7 Hz, 1H), 8.18 (d, *J* = 8.5 Hz, 1H), 7.74 (d, *J* = 8.1 Hz, 1H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 1H), 7.44 (d, *J* = 6.4 Hz, 2H), 7.20 (d, *J* = 7.5 Hz, 2H), 7.17 (d, *J*

= 3.5 Hz, 1H), 7.02 (t, *J* = 7.5 Hz, 2H), 6.96 (t, *J* = 7.3 Hz, 1H), 6.40 (dd, *J* = 3.4, 1.3 Hz, 1H), 4.37 (d, *J* = 16.4 Hz, 1H), 4.28 (d, *J* = 16.4 Hz, 1H), 3.94 – 3.87 (m, 2H), 3.47 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 184.06, 171.33, 156.51, 151.72, 145.87, 141.32, 136.13, 135.52, 130.83, 129.99, 128.67, 127.70, 127.42, 127.20, 126.51, 125.13, 119.73, 117.93, 112.37, 61.46, 52.69, 37.59, 35.21. HRMS (m/z) calcd for $C_{25}H_{22}NO_4S$ $[M+H]^+$: 432.1264, found: 432.1258.



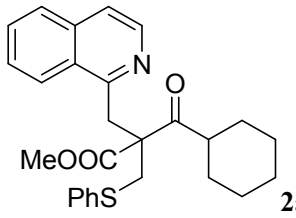
2ae

Following the general procedure A, the residue was purified by column chromatography (EtOAc/Petroleum = 1/10) to afford product as colorless oil (71 mg, 94 %). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.25 (d, *J* = 5.7 Hz, 1H), 8.09 (d, *J* = 8.4 Hz, 1H), 7.74 (d, *J* = 8.1 Hz, 1H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.53 (t, *J* = 7.7 Hz, 1H), 7.43 (d, *J* = 5.7 Hz, 1H), 7.16 (d, *J* = 7.4 Hz, 2H), 6.97 (t, *J* = 7.6 Hz, 2H), 6.89 (t, *J* = 7.3 Hz, 1H), 4.20 (d, *J* = 17.7 Hz, 1H), 4.12 (d, *J* = 17.7 Hz, 1H), 3.98 (d, *J* = 13.9 Hz, 1H), 3.79 (d, *J* = 13.9 Hz, 1H), 3.58 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 203.53, 171.33, 156.23, 140.78, 135.97, 135.54, 130.51, 130.08, 128.73, 127.36, 127.33, 127.29, 126.44, 124.91, 119.68, 63.90, 52.80, 37.26, 35.43, 27.06. HRMS (m/z) calcd for $C_{22}H_{22}NO_3S$ $[M+H]^+$: 380.1315, found: 380.1307.



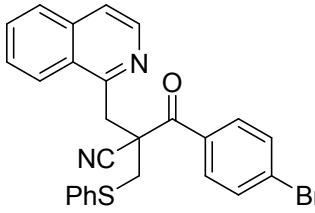
2af

Following the general procedure A, the residue was purified by column chromatography (EtOAc/Petroleum = 1/10) to afford product as colorless oil (67 mg, 82 %). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24 (d, *J* = 5.6 Hz, 1H), 8.07 (d, *J* = 8.4 Hz, 1H), 7.73 (d, *J* = 8.1 Hz, 1H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.53 (t, *J* = 7.5 Hz, 1H), 7.42 (d, *J* = 5.6 Hz, 1H), 7.12 (d, *J* = 7.6 Hz, 2H), 6.91 (t, *J* = 7.5 Hz, 2H), 6.83 (t, *J* = 7.2 Hz, 1H), 4.22 – 4.15 (m, 2H), 4.09 (d, *J* = 13.9 Hz, 1H), 3.86 (d, *J* = 13.9 Hz, 1H), 3.58 (s, 3H), 3.21 – 3.13 (m, 1H), 1.10 (d, *J* = 6.7 Hz, 3H), 1.07 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 210.12, 171.53, 156.32, 140.76, 135.93, 135.73, 130.16, 130.06, 128.67, 127.34, 127.32, 127.28, 126.20, 124.94, 119.66, 63.44, 52.56, 37.23, 36.87, 35.49, 20.49, 20.43. HRMS (m/z) calcd for $C_{24}H_{26}NO_3S$ $[M+H]^+$: 408.1628, found: 408.1626.



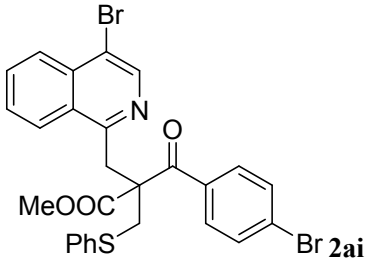
2ag

Following the general procedure A, the residue was purified by column chromatography (EtOAc/Petroleum = 1/10) to afford product as colorless oil (54 mg, 60 %). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.23 (d, *J* = 5.7 Hz, 1H), 8.07 (d, *J* = 8.4 Hz, 1H), 7.72 (d, *J* = 8.1 Hz, 1H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.53 – 7.50 (m, 1H), 7.41 (d, *J* = 5.7 Hz, 1H), 7.11 – 7.09 (m, 2H), 6.91 – 6.88 (m, 2H), 6.83 – 6.79 (m, 1H), 4.19 (d, *J* = 18.2 Hz, 1H), 4.15 (d, *J* = 18.3 Hz, 1H), 4.07 (d, *J* = 13.9 Hz, 1H), 3.86 (d, *J* = 13.9 Hz, 1H), 3.57 (s, 3H), 2.89 (tt, *J* = 11.5, 3.1 Hz, 1H), 1.79 – 1.63 (m, 5H), 1.44 – 1.37 (m, 2H), 1.27 – 1.12 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 208.86, 171.53, 156.39, 140.79, 135.91, 135.75, 130.09, 129.99, 128.62, 127.31, 127.21, 126.12, 124.95, 119.58, 63.39, 52.50, 47.29, 37.16, 35.42, 30.40, 30.22, 25.98, 25.93, 25.83. HRMS (m/z) calcd for $C_{27}H_{30}NO_3S$ $[M+H]^+$: 448.1941, found: 448.1935.



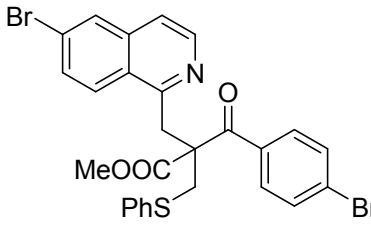
2ah

Following the general procedure C (but the temperature was increased to -30 ℃ slowly), the residue was purified by column chromatography (EtOAc/Petroleum = 1/10) to afford product as lightyellow oil (58 mg, 60 %). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 (d, *J* = 5.7 Hz, 1H), 8.02 (d, *J* = 8.4 Hz, 2H), 7.89 (d, *J* = 8.4 Hz, 1H), 7.79 (d, *J* = 8.1 Hz, 1H), 7.67 (t, *J* = 7.5 Hz, 1H), 7.63 (d, *J* = 8.6 Hz, 2H), 7.59 (t, *J* = 7.6 Hz, 1H), 7.48 – 7.47 (m, 3H), 7.31 – 7.28 (m, 2H), 7.27 – 7.24 (m, 1H), 4.30 (d, *J* = 16.9 Hz, 1H), 4.19 (d, *J* = 16.9 Hz, 1H), 3.77 (d, *J* = 13.5 Hz, 1H), 3.65 (d, *J* = 13.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 194.86, 153.56, 140.25, 136.64, 136.12, 134.95, 131.63, 131.56, 131.03, 130.52, 129.48, 127.84, 127.82, 127.71, 127.47, 126.71, 124.22, 121.35, 120.52, 51.51, 43.35, 43.08. HRMS (m/z) calcd for $C_{26}H_{20}BrN_2OS$ $[M+H]^+$: 487.0474, found: 487.0478.



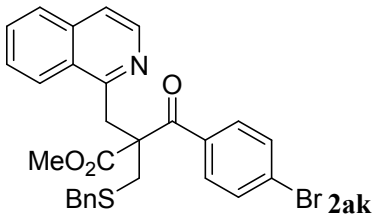
2ai

Following the general procedure A, the residue was purified by column chromatography (EtOAc/Petroleum = 1/10) to afford product as white solid (113 mg, 94 %). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.40 (s, 1H), 8.07 (t, *J* = 7.7 Hz, 2H), 7.72 (t, *J* = 7.8 Hz, 1H), 7.63 (d, *J* = 8.6 Hz, 2H), 7.57 (t, *J* = 7.7 Hz, 1H), 7.46 (d, *J* = 8.6 Hz, 2H), 7.13 (d, *J* = 7.7 Hz, 2H), 6.94 (t, *J* = 7.5 Hz, 2H), 6.88 (t, *J* = 7.3 Hz, 1H), 4.37 (d, *J* = 17.6 Hz, 1H), 4.16 (d, *J* = 17.6 Hz, 1H), 4.06 (d, *J* = 14.2 Hz, 1H), 3.81 (d, *J* = 14.2 Hz, 1H), 3.56 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.07, 171.54, 155.41, 142.25, 136.71, 135.10, 134.66, 131.72, 131.38, 130.70, 129.75, 128.74, 128.57, 128.28, 126.87, 126.78, 126.57, 125.33, 118.77, 62.09, 53.12, 38.45, 36.01. HRMS (m/z) calcd for $C_{27}H_{22}Br_2NO_3S$ $[M+H]^+$: 597.9682, found: 597.9681. Mp: 151 – 153 ℃.



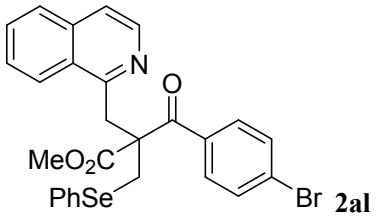
2aj

Following the general procedure A, the residue was purified by column chromatography (EtOAc/Petroleum = 1/10) to afford product as white solid (114 mg, 95 %). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22 (d, *J* = 5.7 Hz, 1H), 7.92 (d, *J* = 9.0 Hz, 1H), 7.86 (d, *J* = 1.5 Hz, 1H), 7.63 (d, *J* = 8.5 Hz, 2H), 7.55 (dd, *J* = 9.0, 1.7 Hz, 1H), 7.44 (d, *J* = 8.6 Hz, 2H), 7.30 (d, *J* = 5.6 Hz, 1H), 7.14 (d, *J* = 7.4 Hz, 2H), 6.97 (t, *J* = 7.4 Hz, 2H), 6.92 (t, *J* = 7.2 Hz, 1H), 4.37 (d, *J* = 17.4 Hz, 1H), 4.17 (d, *J* = 17.4 Hz, 1H), 4.05 (d, *J* = 14.2 Hz, 1H), 3.79 (d, *J* = 14.2 Hz, 1H), 3.55 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.04, 171.53, 156.07, 141.69, 137.13, 136.76, 135.14, 131.64, 130.77, 130.62, 129.72, 129.44, 128.76, 126.75, 126.67, 126.56, 125.70, 124.84, 118.83, 62.12, 53.06, 38.39, 36.08. HRMS (m/z) calcd for $C_{27}H_{22}Br_2NO_3S$ $[M+H]^+$: 597.9682, found: 597.9680. Mp: 92 – 94℃



2ak

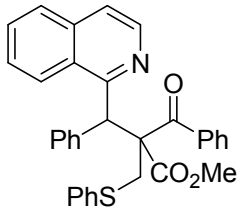
Following the general procedure B, the residue was purified by column chromatography (EtOAc/Petroleum = 1/10) to afford product as white solid (87 mg, 82 %). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.25 (d, *J* = 8.4 Hz, 1H), 8.22 (d, *J* = 5.7 Hz, 1H), 7.77 (d, *J* = 8.1 Hz, 1H), 7.67 – 7.63 (m, 3H), 7.59 (t, *J* = 7.6 Hz, 1H), 7.46 – 7.43 (m, 3H), 7.12 – 7.05 (m, 3H), 6.96 – 6.94 (m, 2H), 4.35 (d, *J* = 17.0 Hz, 1H), 4.18 (d, *J* = 17.0 Hz, 1H), 3.67 (s, 3H), 3.51 (d, *J* = 13.2 Hz, 1H), 3.46 (d, *J* = 13.8 Hz, 1H), 3.43 (d, *J* = 13.9 Hz, 1H), 3.24 (d, *J* = 13.3 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.06, 172.10, 156.01, 140.86, 137.67, 136.64, 136.17, 131.67, 130.19, 129.82, 128.82, 128.45, 127.56, 127.48, 127.06, 126.86, 125.02, 119.88, 61.91, 53.11, 37.46, 36.30, 35.07. HRMS (m/z) calcd for $C_{28}H_{25}BrNO_3S$ $[M+H]^+$: 534.0733, found: 534.0736. Mp: 95 – 97 ℃.



2al

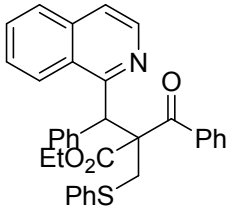
Following the general procedure C (but the temperature was increased to -20 ℃ slowly), the residue was purified by column chromatography (EtOAc/Petroleum = 1/10) to afford product as colorless oil (83 mg, 73 %). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21 (d, *J* = 5.7 Hz, 1H), 8.03 (d, *J* = 8.4 Hz, 1H), 7.72 (d, *J* = 8.1 Hz, 1H), 7.63 – 7.60 (m, 3H), 7.51 (t, *J* = 7.6 Hz, 1H), 7.43 – 7.40 (m,

3H), 7.26 – 7.24 (m, 2H), 6.93 – 6.89 (m, 3H), 4.39 (d, *J* = 17.4 Hz, 1H), 4.21 (d, *J* = 17.4 Hz, 1H), 4.04 (d, *J* = 13.3 Hz, 1H), 3.76 (d, *J* = 13.3 Hz, 1H), 3.52 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.56, 171.82, 155.70, 140.61, 136.97, 135.97, 133.24, 131.56, 130.06, 129.85, 129.47, 128.83, 127.42, 127.32, 127.03, 126.59, 124.85, 119.86, 62.24, 52.92, 37.24, 32.85. HRMS (m/z) calcd for $C_{27}H_{23}BrNO_3Se$ $[M+H]^+$: 568.0021, found: 568.0023.



2ba

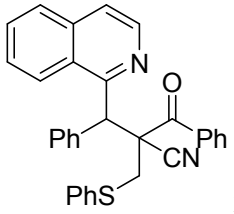
Following the general procedure B, but mixed solvent (THF/CH_3CN = 3/1) was used, the residue was purified by column Chromatography (EtOAc/Petroleum /Et_3N= 1/40/1) to afford product as an unseparated white solid (81 mg, 78 %, **2ba**/**2ba'** = 3.7/1 (dr)). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.42 (d, *J* = 5.7 Hz, 2H of **2ba'**), 8.19 (d, *J* = 8.4 Hz, 1H of **2ba**), 8.16 (d, *J* = 5.5 Hz, 3H), 7.74 – 7.72 (m, 1H of **2ba'**), 7.67 (d, *J* = 8.0 Hz, 1H of **2ba**), 7.61 (d, *J* = 7.6 Hz, 2H of **2ba'**), 7.58 – 7.55 (m, 4H), 7.52 (d, *J* = 7.7 Hz, 2H of **2ba'**), 7.49 – 7.46 (m, 2H), 7.42 (d, *J* = 7.0 Hz, 4H), 7.30 (d, *J* = 7.4 Hz, 1H of **2ba'**), 7.28 – 7.22 (m, 6H), 7.18 – 7.14 (m, 5H), 7.13 – 7.08 (m, 3H), 7.02 – 6.98 (m, 3H of **2ba'**), 6.94 (dd, *J* = 7.2, 2.2 Hz, 2H of **2ba'**), 6.36 (s, 1H of **2ba'**), 6.29 (s, 1H of **2ba**), 4.00 (d, *J* = 13.5 Hz, 1H of **2ba'**), 3.96 (d, *J* = 13.5 Hz, 1H of **2ba'**), 3.91 (d, *J* = 13.4 Hz, 1H of **2ba**), 3.85 (d, *J* = 13.4 Hz, 1H of **2ba**), 3.47 (s, 3H of **2ba'**), 3.17 (s, 3H of **2ba**). ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.52, 196.54, 172.74, 172.18, 159.96, 159.92, 140.52, 139.94, 139.52, 138.14, 137.36, 136.89, 136.73, 136.61, 131.69, 131.61, 131.06, 130.33, 129.92, 129.76, 128.83, 128.60, 128.39, 128.05, 128.00, 127.96, 127.69, 127.65, 127.61, 127.57, 127.48, 127.37, 127.07, 126.56, 126.40, 126.30, 125.45, 125.18, 120.43, 119.96, 66.70, 66.21, 52.76, 52.16, 51.75, 50.36, 41.11, 40.57. HRMS (m/z) calcd for $C_{33}H_{28}NO_3S$ $[M+H]^+$: 518.1784, found: 518.1790



2ca

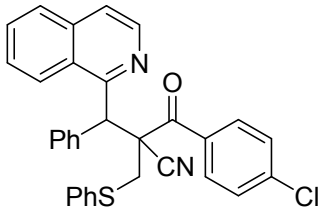
Following the general procedure B, but mixed solvent (THF/CH_3CN = 3/1) was used, the residue was purified by column chromatography (EtOAc/Petroleum /Et_3N= 1/40/1) to afford product as an unseparated white solid (81 mg, 76 %, **2ca**/**2ca'** = 3.3/1 (dr)). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.43 (d, *J* = 5.7 Hz, 1H of **2ca'**), 8.41 – 8.39 (m, 1H of **2ca'**), 8.21 (d, *J* = 8.4 Hz, 1H of **2ca**), 8.18 (d, *J* = 5.7 Hz, 1H of **2ca**), 7.67 – 7.65 (m, 2H), 7.60 – 7.56 (m, 4H), 7.52 (t, *J* = 7.1 Hz, 1H), 7.48 – 7.43 (m, 7H), 7.29 – 7.25 (m, 4H), 7.24 – 7.19 (m, 6H), 7.18 – 7.13 (m, 7H), 7.12 – 7.07 (m, 3H), 7.00 – 6.97 (m, 2H of **2ca'**), 6.93 – 6.91 (m, 2H of **2ca'**), 6.43 (s, 1H of **2ca'**), 6.28 (s, 1H of **2ca**), 4.16 (d, *J* = 13.5 Hz, 1H of **2ca'**), 4.08 (d, *J* = 13.5 Hz, 1H of **2ca'**), 3.93 – 3.83 (m, 4H), 3.73 (dq, *J* = 10.7, 7.1 Hz, 1H of **2ca**), 3.65 – 3.54 (m, 1H of **2ca**), 0.72 (t, *J* = 7.1 Hz, 3H of **2ca'**), 0.56 (t, *J* = 7.2 Hz, 3H of **2ca**). ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.83, 196.58, 172.25, 171.50, 160.20,

160.00, 143.45, 140.54, 139.92, 139.79, 138.19, 137.64, 137.41, 136.67, 136.62, 131.72, 131.65, 130.92, 130.19, 130.15, 129.92, 128.82, 128.79, 128.52, 128.42, 128.00, 127.92, 127.57, 127.35, 127.12, 126.57, 126.32, 126.12, 125.48, 125.41, 125.22, 120.42, 119.93, 66.82, 61.54, 61.41, 52.76, 50.04, 41.24, 40.21, 13.43, 13.19. HRMS (m/z) calcd for $C_{34}H_{30}NO_3S$ $[M+H]^+$: 532.1941, found: 532.1944.



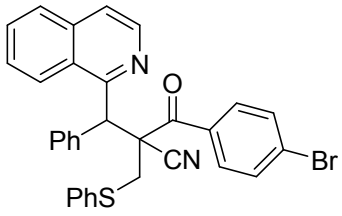
2fa

Following the general procedure C, the residue was purified by column chromatography (EtOAc/Petroleum = 1/15) to afford product as light yellow solid (61 mg, 63 %). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24 (d, *J* = 5.3 Hz, 1H), 8.13 (d, *J* = 7.3 Hz, 2H), 7.85 (d, *J* = 8.3 Hz, 1H), 7.72 (d, *J* = 7.9 Hz, 1H), 7.53 (s, 1H), 7.48 (d, *J* = 5.4 Hz, 1H), 7.45 – 7.44 (m, 3H), 7.37 (d, *J* = 7.5 Hz, 1H), 7.33 – 7.31 (m, 3H), 7.25 – 7.24 (d, *J* = 6.6 Hz, 2H), 7.19 – 7.17 (m, 3H), 5.94 (s, 1H), 3.67 (d, *J* = 12.8 Hz, 1H), 3.60 (d, *J* = 12.8 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.09, 157.42, 139.90, 138.33, 137.46, 136.84, 134.85, 132.41, 130.83, 130.66, 130.04, 129.72, 129.18, 129.08, 128.62, 128.13, 127.66, 127.53, 127.30, 126.47, 125.39, 121.01, 120.90, 56.69, 56.23, 42.37. HRMS (m/z) calcd for $C_{32}H_{25}N_2OS$ $[M+H]^+$: 485.1680, found: 485.1681. Mp: 143 – 145 ℃.



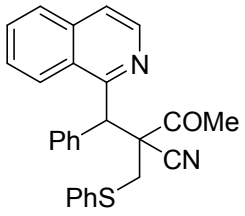
2fb

Following the general procedure C, the residue was purified by column chromatography (EtOAc/Petroleum = 1/15) to afford product as white solid (78 mg, 75 %). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21 (d, *J* = 5.7 Hz, 1H), 8.09 (d, *J* = 8.3 Hz, 2H), 7.82 (d, *J* = 8.5 Hz, 1H), 7.73 (d, *J* = 8.2 Hz, 1H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.50 (d, *J* = 5.7 Hz, 1H), 7.43 – 7.39 (m, 4H), 7.37 – 7.30 (m, 4H), 7.24 – 7.16 (m, 5H), 5.88 (s, 1H), 3.68 (d, *J* = 13.0 Hz, 1H), 3.55 (d, *J* = 13.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 195.31, 157.26, 139.74, 138.79, 137.36, 136.90, 136.86, 134.69, 131.33, 130.82, 130.68, 130.16, 129.24, 129.16, 128.74, 128.43, 127.71, 127.64, 127.41, 126.49, 126.47, 125.40, 121.09, 120.92, 57.42, 56.39, 42.60. HRMS (m/z) calcd for $C_{32}H_{24}ClN_2OS$ $[M+H]^+$: 519.1292, found: 519.1290. Mp: 178 – 180℃.



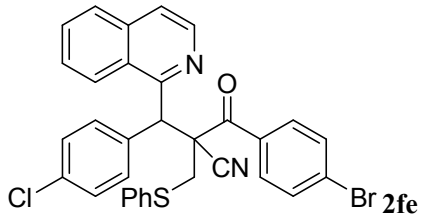
2fc

Following the general procedure C, the residue was purified by column chromatography (EtOAc/Petroleum = 1/15) to afford product as white solid (93 mg, 82 %). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.20 (d, *J* = 5.1 Hz, 1H), 8.01 (d, *J* = 7.8 Hz, 2H), 7.81 (d, *J* = 8.2 Hz, 1H), 7.73 (d, *J* = 7.9 Hz, 1H), 7.58 (d, *J* = 7.9 Hz, 2H), 7.55 – 7.52 (m, 1H), 7.50 (d, *J* = 5.0 Hz, 1H), 7.42 (d, *J* = 5.8 Hz, 2H), 7.38 – 7.32 (m, 4H), 7.25 – 7.23 (m, 3H), 7.19 (d, *J* = 7.2 Hz, 2H), 5.88 (s, 1H), 3.68 (d, *J* = 12.9 Hz, 1H), 3.55 (d, *J* = 12.9 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 195.53, 157.22, 139.71, 137.34, 137.30, 136.88, 134.66, 131.41, 131.40, 130.80, 130.66, 130.15, 129.24, 129.15, 128.73, 127.70, 127.63, 127.48, 127.41, 126.44, 125.39, 121.10, 120.88, 57.45, 56.39, 42.58. HRMS (m/z) calcd for $C_{32}H_{24}BrN_2OS$ $[M+H]^+$: 563.0787, found: 563.0771. Mp: 201 – 203 ℃.



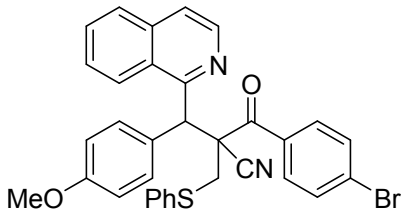
2fd

Following the general procedure C, the residue was purified by column chromatography (EtOAc/Petroleum = 1/15) to afford product as white solid (71 mg, 84 %). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.46 (d, *J* = 5.7 Hz, 1H), 7.76 (dd, *J* = 16.9, 8.4 Hz, 2H), 7.56 (d, *J* = 5.7 Hz, 1H), 7.53 (t, *J* = 7.6 Hz, 1H), 7.37 – 7.34 (m, 4H), 7.33 – 7.30 (m, 3H), 7.29 – 7.26 (m, 2H), 7.25 – 7.20 (m, 2H), 5.53 (s, 1H), 3.47 (d, *J* = 12.8 Hz, 1H), 3.39 (d, *J* = 12.8 Hz, 1H), 2.79 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 203.20, 157.40, 139.98, 137.61, 136.86, 134.86, 130.73, 130.28, 130.07, 129.31, 129.17, 128.59, 127.69, 127.55, 127.45, 126.36, 125.29, 121.11, 120.68, 57.46, 56.74, 41.65, 31.78. HRMS (m/z) calcd for $C_{27}H_{22}Br_2NO_3S$ $[M+H]^+$: 423.1526, found: 423.1531. Mp: 178 – 180 ℃.



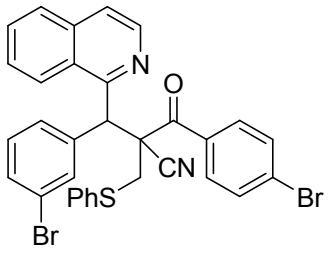
2fe

Following the general procedure C, the residue was purified by column chromatography (EtOAc/Petroleum = 1/15) to afford product as white solid (85 mg, 71 %). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21 (d, *J* = 5.7 Hz, 1H), 7.99 (d, *J* = 8.4 Hz, 2H), 7.78 – 7.74 (m, 2H), 7.59 – 7.55 (m, 3H), 7.51 (d, *J* = 5.6 Hz, 1H), 7.40 (t, *J* = 7.7 Hz, 1H), 7.36 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 8.3 Hz, 2H), 7.25 – 7.20 (dd, *J* = 18.4, 6.6 Hz, 5H), 5.89 (s, 1H), 3.63 (d, *J* = 13.0 Hz, 1H), 3.53 (d, *J* = 12.9 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 195.00, 156.78, 139.79, 137.03, 136.91, 135.83, 134.86, 134.38, 131.87, 131.47, 131.34, 131.00, 130.29, 129.43, 129.31, 127.83, 127.81, 127.66, 127.61, 126.29, 125.14, 121.26, 120.75, 56.31, 56.15, 42.45. HRMS (m/z) calcd for $C_{32}H_{23}BrClN_2OS$ $[M+H]^+$: 597.0398, found: 597.0404. Mp: 195 -197 ℃.



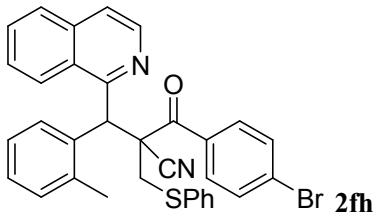
2ff

Following the general procedure C, the residue was purified by column chromatography (EtOAc/Petroleum = 1/15) to afford product as white solid (88 mg, 75 %). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.18 (d, *J* = 5.7 Hz, 1H), 8.01 (d, *J* = 8.6 Hz, 2H), 7.83 (d, *J* = 8.6 Hz, 1H), 7.72 (d, *J* = 8.2 Hz, 1H), 7.58 (d, *J* = 8.6 Hz, 2H), 7.53 (t, *J* = 7.6 Hz, 1H), 7.48 (d, *J* = 5.7 Hz, 1H), 7.37 (t, *J* = 7.7 Hz, 1H), 7.33 (d, *J* = 8.5 Hz, 2H), 7.24 (d, *J* = 6.8 Hz, 2H), 7.22 – 7.15 (m, 3H), 6.85 (d, *J* = 8.7 Hz, 2H), 5.83 (s, 1H), 3.75 (s, 3H), 3.68 (d, *J* = 12.9 Hz, 1H), 3.56 (d, *J* = 12.9 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 195.66, 159.80, 157.46, 139.66, 137.38, 136.88, 134.73, 131.73, 131.38, 130.80, 130.12, 129.32, 129.24, 127.68, 127.59, 127.43, 127.39, 126.44, 125.48, 121.02, 114.56, 56.90, 56.60, 55.40, 42.60. HRMS (m/z) calcd for $C_{33}H_{26}BrN_2O_2S$ $[M+H]^+$: 593.0893, found: 593.0895. Mp: 178 – 180℃.



2fg

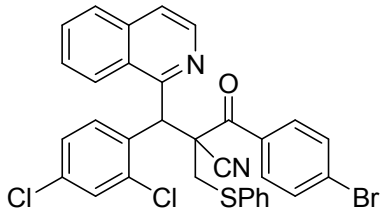
Following the general procedure C, the residue was purified by column chromatography (EtOAc/Petroleum = 1/15) to afford product as white solid (84 mg, 65 %). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22 (d, *J* = 5.6 Hz, 1H), 7.99 (d, *J* = 8.2 Hz, 2H), 7.80 (d, *J* = 8.5 Hz, 1H), 7.76 (d, *J* = 8.2 Hz, 1H), 7.67 (s, 1H), 7.59 – 7.57 (d, *J* = 8.1 Hz, 3H), 7.52 (d, *J* = 5.6 Hz, 1H), 7.46 – 7.42 (m, 2H), 7.31 (d, *J* = 7.6 Hz, 1H), 7.28 – 7.24 (m, 3H), 7.23 – 7.17 (m, 3H), 5.88 (s, 1H), 3.62 (d, *J* = 13.0 Hz, 1H), 3.55 (d, *J* = 13.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 194.86, 156.60, 139.88, 139.58, 136.94, 134.32, 133.36, 131.99, 131.48, 131.34, 131.15, 130.71, 130.33, 129.35, 129.28, 127.91, 127.85, 127.70, 127.67, 126.36, 125.09, 123.13, 121.31, 120.61, 56.17, 56.15, 42.44. HRMS (m/z) calcd for $C_{32}H_{23}Br_2N_2OS$ $[M+H]^+$: 640.9892, found: 640.9891. Mp: 199 - 201℃.



2fh

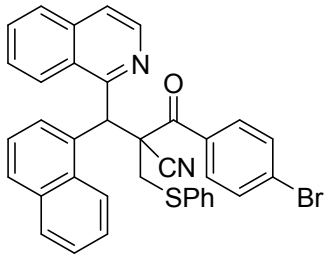
Following the general procedure C, the residue was purified by column chromatography (EtOAc/Petroleum = 1/15) to afford product as white solid (80 mg, 65 %). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (d, *J* = 5.8 Hz, 1H), 8.12 (d, *J* = 8.5 Hz, 2H), 7.72 (d, *J* = 8.2 Hz, 1H), 7.60 (d, *J* = 8.6 Hz, 2H), 7.57 – 7.51 (m, 2H), 7.48 (d, *J* = 5.7 Hz, 1H), 7.37 – 7.51 (m, 2H), 7.22 – 7.15 (m,

6H), 7.07 – 7.04 (m, 1H), 6.08 (s, 1H), 3.82 (d, *J* = 12.5 Hz, 1H), 3.40 (d, *J* = 12.3 Hz, 1H), 2.87 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.50, 157.80, 139.40, 137.85, 136.94, 136.07, 135.80, 134.98, 131.71, 131.50, 131.29, 130.15, 130.06, 129.24, 128.58, 127.80, 127.73, 127.33, 127.17, 127.08, 126.27, 124.80, 121.12, 120.96, 58.51, 54.31, 42.09, 21.09. HRMS (m/z) calcd for $C_{33}H_{26}BrN_2OS$ $[M+H]^+$: 577.0944, found: 577.0946. Mp: 148 – 150℃.



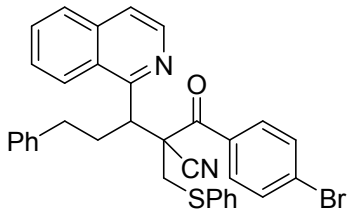
2fi

Following the general procedure C, the residue was purified by column chromatography (EtOAc/Petroleum = 1/15) to afford product as white solid (90 mg, 71 %). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.17 (d, *J* = 5.7 Hz, 1H), 8.08 (d, *J* = 8.5 Hz, 2H), 7.75 (t, *J* = 9.1 Hz, 2H), 7.59 (d, *J* = 8.8 Hz, 4H), 7.50 (d, *J* = 5.7 Hz, 1H), 7.49 – 7.46 (m, 1H), 7.24 (d, *J* = 7.1 Hz, 1H), 7.23 – 7.14 (m, 5H), 7.11 (dd, *J* = 8.5, 1.7 Hz, 1H), 6.41 (s, 1H), 4.01 (d, *J* = 12.8 Hz, 1H), 3.41 (d, *J* = 12.7 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 195.81, 156.81, 139.79, 137.50, 136.87, 135.44, 135.10, 134.71, 133.66, 133.64, 131.67, 131.33, 130.55, 130.13, 129.81, 129.25, 128.35, 128.30, 127.83, 127.68, 127.25, 126.08, 124.45, 121.44, 120.68, 57.88, 53.04, 42.35. HRMS (m/z) calcd for $C_{32}H_{22}BrCl_2N_2OS$ $[M+H]^+$: 631.0008, found: 631.0002. Mp: 194 - 196℃.



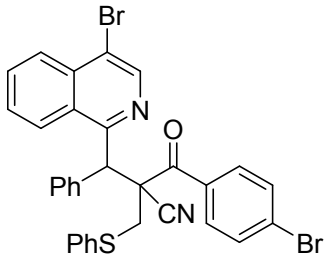
2fj

Following the general procedure C, the residue was purified by column chromatography (EtOAc/Petroleum = 1/15) to afford product as white solid (86 mg, 70 %). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.78 (d, *J* = 8.6 Hz, 1H), 8.19 (d, *J* = 5.7 Hz, 1H), 8.13 (d, *J* = 8.5 Hz, 2H), 7.99 (d, *J* = 8.1 Hz, 1H), 7.82 (t, *J* = 9.0 Hz, 2H), 7.70 (d, *J* = 8.2 Hz, 1H), 7.66 – 7.63 (m, 1H), 7.61 (d, *J* = 8.6 Hz, 2H), 7.56 (d, *J* = 8.6 Hz, 1H), 7.51 (d, *J* = 5.7 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 1H), 7.41 (d, *J* = 7.1 Hz, 1H), 7.34 (t, *J* = 7.7 Hz, 1H), 7.17 – 7.14 (m, 1H), 7.11 – 7.10 (m, 2H), 7.01 – 7.00 (m, 2H), 6.80 (s, 1H), 3.79 (d, *J* = 12.8 Hz, 1H), 3.17 (d, *J* = 12.8 Hz, 1H), 3.17 (d, *J* = 12.8 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.41, 158.05, 139.52, 137.76, 136.82, 134.81, 134.14, 133.40, 132.18, 131.70, 131.32, 130.49, 130.20, 130.13, 129.75, 129.41, 129.10, 127.81, 127.70, 127.46, 126.97, 126.41, 126.22, 126.01, 124.85, 122.44, 121.11, 120.97, 58.69, 52.20, 42.58. HRMS (m/z) calcd for $C_{36}H_{26}BrN_2OS$ $[M+H]^+$: 613.0944, found: 613.0951. Mp: 175 – 177℃.



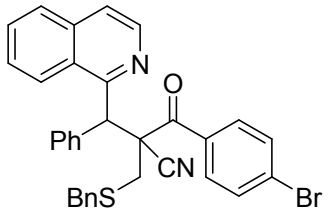
2fk

Following the general procedure C (but temperature was -50 ℃), the residue was purified by column chromatography (EtOAc/Petroleum = 1/20) to afford product as white solid (76 mg, 64 %). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.46 (d, *J* = 5.5 Hz, 1H), 7.94 (d, *J* = 8.5 Hz, 1H), 7.77 (d, *J* = 8.1 Hz, 1H), 7.66 (t, *J* = 7.4 Hz, 1H), 7.59 (t, *J* = 7.6 Hz, 1H), 7.51 – 7.49 (m, 3H), 7.39 – 7.37 (m, 4H), 7.26 – 7.23 (m, 2H), 7.21 – 7.13 (m, 4H), 6.92 (d, *J* = 7.1 Hz, 2H), 4.36 (dd, *J* = 10.7, 2.4 Hz, 1H), 3.93 (d, *J* = 13.1 Hz, 1H), 3.87 (d, *J* = 13.1 Hz, 1H), 2.81 – 2.73 (m, 1H), 2.42 – 2.36 (m, 1H), 2.34 – 2.37 (m, 1H), 2.25 – 2.19 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 195.17, 158.64, 141.96, 140.66, 136.43, 135.58, 135.03, 131.47, 131.36, 130.68, 130.43, 129.30, 128.59, 128.50, 128.21, 127.95, 127.85, 127.74, 127.66, 126.39, 124.65, 120.82, 120.21, 58.39, 46.85, 42.82, 33.64, 33.31. HRMS (m/z) calcd for $C_{34}H_{28}BrN_2OS$ $[M+H]^+$: 591.1100, found: 591.1099. Mp: 184 – 186 ℃.



2fl

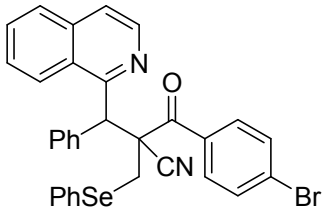
Following the general procedure C, the residue was purified by column chromatography (EtOAc/Petroleum = 1/15) to afford product as white solid (94 mg, 74 %). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.43 (s, 1H), 8.12 (d, *J* = 8.4 Hz, 1H), 7.99 (d, *J* = 8.1 Hz, 2H), 7.86 (d, *J* = 8.4 Hz, 1H), 7.68 (t, *J* = 7.5 Hz, 1H), 7.59 (d, *J* = 8.1 Hz, 2H), 7.46 (t, *J* = 7.6 Hz, 1H), 7.41 (d, *J* = 6.3 Hz, 2H), 7.35 – 7.33 (m, 3H), 7.22 – 7.18 (m, 5H), 5.86 (s, 1H), 5.29 (s, 1H), 3.64 (d, *J* = 13.1 Hz, 1H), 3.55 (d, *J* = 13.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 195.06, 157.10, 141.52, 136.93, 136.86, 135.57, 134.46, 131.58, 131.46, 131.34, 130.99, 130.62, 129.28, 128.92, 128.62, 127.89, 127.74, 127.55, 127.15, 125.84, 120.67, 119.99, 56.62, 56.19, 42.55. HRMS (m/z) calcd for $C_{32}H_{23}Br_2N_2OS$ $[M+H]^+$: 640.9892, found: 640.9898. Mp: 264 – 266 ℃.



2fm

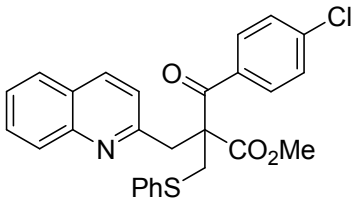
Following the general procedure C, the residue was purified by column chromatography (EtOAc/Petroleum = 1/20) to afford product as white solid (78 mg, 68 %). ^{1}H NMR (300 MHz, $cdcl_3$) δ 8.17 (d, *J* = 5.7 Hz, 1H), 8.15 – 8.12 (m, 2H), 7.74 (t, *J* = 7.9 Hz, 2H), 7.67 – 7.63 (m, 2H), 7.55 – 7.49 (m, 2H), 7.37 – 7.33 (m, 1H), 7.31 (s, 5H), 7.23 – 7.20 (m, 3H), 7.07 – 7.03 (m, 2H),

5.70 (s, 1H), 3.76 (d, J = 13.3 Hz, 1H), 3.61 (d, J = 13.3 Hz, 1H), 3.13 (d, J = 13.6 Hz, 1H), 3.03 (d, J = 13.6 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.75, 157.16, 139.66, 137.77, 137.47, 137.12, 136.86, 131.46, 131.37, 130.66, 130.13, 129.36, 129.06, 128.79, 128.57, 127.67, 127.59, 127.40, 126.38, 125.41, 121.53, 121.09, 58.30, 56.66, 38.22, 37.36. HRMS (m/z) calcd for $C_{33}H_{26}BrN_2OS$ $[M+H]^+$: 577.0944, found: 577.0945. Mp: 163 – 165 ℃.



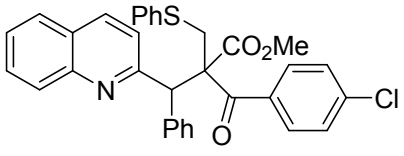
2fn

Following the general procedure C, the residue was purified by column chromatography (EtOAc/Petroleum = 1/15) to afford product as light yellow solid (82 mg, 68%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21 (d, J = 5.7 Hz, 1H), 8.02 (d, J = 8.5 Hz, 2H), 7.82 (d, J = 8.5 Hz, 1H), 7.73 (d, J = 8.2 Hz, 1H), 7.58 (d, J = 8.5 Hz, 2H), 7.54 (t, J = 7.5 Hz, 1H), 7.50 (d, J = 5.7 Hz, 1H), 7.43 (d, J = 6.4 Hz, 2H), 7.38 – 7.35 (m, 3H), 7.35 – 7.30 (m, 3H), 7.22 – 7.17 (m, 3H), 5.88 (s, 1H), 3.56 – 3.50 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 195.50, 157.35, 139.73, 137.39, 137.08, 136.89, 133.37, 131.48, 131.44, 130.65, 130.16, 129.40, 129.12, 128.72, 127.92, 127.70, 127.63, 127.56, 126.47, 125.43, 121.09, 57.88, 56.24, 34.69. HRMS (m/z) calcd for $C_{32}H_{24}BrN_2OSe$ $[M+H]^+$: 611.0232, found: 611.0239. Mp: 184 – 186 ℃.



5a

Following the general procedure A, the residue was purified by column chromatography (EtOAc/Petroleum = 1/15) to afford product as white solid (91 mg, 96%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (d, J = 8.4 Hz, 1H), 7.84 (d, J = 8.4 Hz, 1H), 7.77 (d, J = 8.7 Hz, 2H), 7.71 (d, J = 8.1 Hz, 1H), 7.65 – 7.61 (m, 1H), 7.45 (t, J = 7.5 Hz, 1H), 7.32 (d, J = 8.6 Hz, 2H), 7.28 – 7.26 (m, 2H), 7.16 – 7.09 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 194.74, 171.72, 156.75, 147.56, 138.71, 136.38, 135.42, 131.03, 129.85, 129.57, 128.95, 128.90, 128.87, 127.64, 126.87, 126.32, 122.41, 62.22, 52.97, 40.43, 38.23. HRMS (m/z) calcd for $C_{27}H_{23}ClNO_3S$ $[M+H]^+$: 476.1082 found: 476.1083. Mp: 117 – 119 ℃.

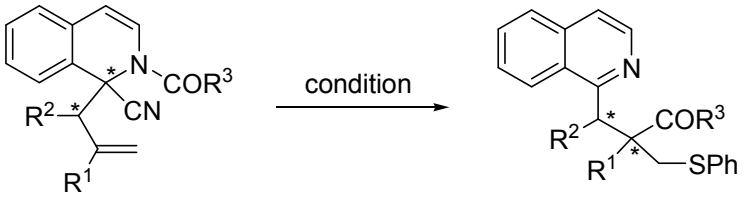


5b

Following the general procedure B, but mixed solvent (THF/CH_3CN = 3/1) was used, the residue was purified by column chromatography (EtOAc/Petroleum /Et_3N= 1/20/1) to afford product as an unseparated white solid (91 mg, 96 %, **5b**/**5b'** = 1.7/1(dr)). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (d, J = 5.3 Hz, 1H of **5b'**), 7.98 (d, J = 5.2 Hz, 1H of **5b'**), 7.95 (d, J = 8.5 Hz, 1H of **5b**), 7.71 (d, J =

8.5 Hz, 1H of **5b'**), 7.69 (d, *J* = 8.2 Hz, 1H of **5b**), 7.66 – 7.65(m, 2H), 7.62 (d, *J* = 8.1 Hz, 1H of **5b'**), 7.57 – 7.48 (m, 8H), 7.46 – 7.41 (m, 2H), 7.37 (d, *J* = 8.6 Hz, 2H of **5b**), 7.31 (d, *J* = 8.5 Hz, 2H of **5b'**), 7.24 – 7.23 (m, 5H), 7.20 – 7.14 (m, 6H), 7.11 (d, *J* = 7.6 Hz, 1H of **5b**), 7.09 (d, *J* = 8.6 Hz, 2H of **5b**), 7.04 – 7.03 (m, 2H), 7.00 – 6.98 (m, 2H of **5b'**), 5.55 (s, 1H of **5b'**), 5.50 (s, 1H of **5b**), 3.86 (d, *J* = 13.6 Hz, 1H of **5b'**), 3.81 (dd, *J* = 13.5, 7.3 Hz, 2H), 3.73 (d, *J* = 13.5 Hz, 1H of **5b**), 3.47 (s, 3H of **5b'**), 3.16 (s, 3H of **5b**). ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.40, 194.95, 172.61, 171.95, 160.71, 160.62, 147.15, 146.51, 138.33, 138.05, 137.77, 137.62, 136.95, 136.73, 136.34, 136.09, 135.93, 135.91, 135.90, 131.82, 131.73, 130.64, 130.52, 130.21, 130.14, 129.45, 129.30, 129.15, 128.89, 128.75, 128.52, 128.35, 128.12, 128.02, 127.94, 127.77, 127.72, 127.69, 127.66, 126.91, 126.85, 126.63, 126.55, 126.35, 126.18, 123.87, 123.02, 66.06, 57.41, 56.05, 52.37, 51.81, 41.43, 40.44. HRMS (m/z) calcd for $C_{33}H_{27}ClNO_3S$ $[M+H]^+$: 552.1395, found: 552.1400.

IV. Asymmetric Transformation



1 **2**

Condition:

a) **1ab**-*ent* (95% ee)/*n*BuLi/PhSH = 1/1.2 /1.3, DCM/CH_3CN = 3/1, -78°C, 6 h;

b) **1fc**-*ent* (99% ee, dr >19/1)/*n*BuLi/PhSH = 1/1.2/1.3, DCM, -78°C, 6 h;

2ab-*ent* (R^1 = CO_2Me, R^2 = H, R^3 = *p*-BrC_6H_5): 94% yield, 91% ee;

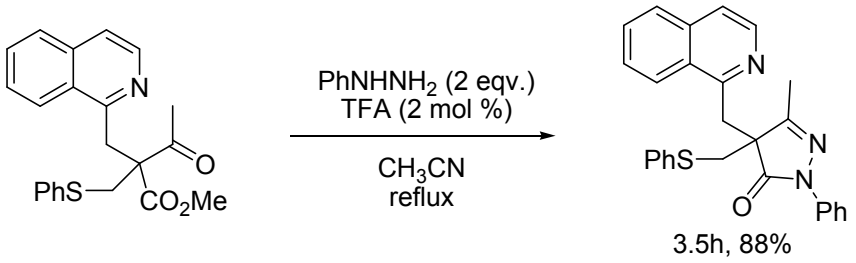
2fc-*ent* (R^1 = CN, R^2 = Ph, R^3 = *p*-BrC_6H_4): 75% yield, 99% ee, dr >19/1;

According to the literature procedure,[4] quinidine (10 mol%) was used. After recrystalization from DCM/ Petroleum ether, compound **1ab**-*ent* was obtained in 95 % ee (AD-H column, n-Hexane/i-PrOH = 80/20, flow rate 0.5 ml/min, λ = 254 nm, t_R = 42.5 min (minor), t_R = 54.0 min (major)), $[\alpha]_D^{25}$ = -287 (c = 0.92, $CHCl_3$); compound **1fc**-*ent* was obtained in 99 % ee (AD-H column, n-Hexane/i-PrOH = 80/20, flow rate 0.5 ml/min, λ = 254 nm, t_R = 24.5 min (major), t_R = 46.0 min (minor)), $[\alpha]_D^{25}$ = +293 (c = 0.64, $CHCl_3$).

Following the general procedure C, substrate **1ab**-*ent* (95% ee) and the mixture solvent (DCM/CH_3CN = 3/1) was used. The desired product **2ab**-*ent* was obtained in 94% yield with 91% ee (AD-H column, n-Hexane/i-PrOH = 80/20, flow rate 0.5 ml/min, λ = 254 nm, t_R = 31.0 min (minor), t_R = 35.0 min (major)), $[\alpha]_D^{25}$ = -15 (c = 0.92, $CHCl_3$).

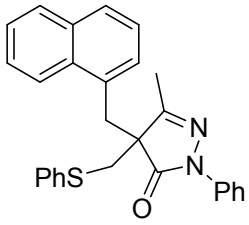
Following the general procedure C, substrate **1fc**-*ent* (99% ee, dr > 19/1) was used. The desired product **2fc**-*ent* was obtained in 75% yield with dr > 19/1 and 99% ee (AD-H column, n-Hexane/i-PrOH = 80/20, flow rate 0.5 ml/min, λ = 254 nm, t_R = 92.3 min (major), t_R = 130.9 min (minor)), $[\alpha]_D^{25}$ = -392 (c = 0.25, $CHCl_3$).

V. Synthetic transformation



2ae **6**

The reaction of substrate **2ae** (0.1 mmol) with phenylhydrazine (2 eqv.) was carried out with 2 mol % TFA in acetonitrile at 80 ℃. [5] After the resulting mixture was stirred at this temperature to completion, the solvent was removed under reduced pressure and the residue was purified by flash column chromatography on silica gel to give the product in 88% yield.



6

Following the procedure mentioned, the residue was purified by column Chromatography (EtOAc/Petroleum = 1/10) to afford product as colorless oil (38 mg, 88 %). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.13 (d, *J* = 5.7 Hz, 1H), 8.07 (d, *J* = 8.4 Hz, 1H), 7.78 – 7.71 (m, 3H), 7.64 – 7.53 (m, 2H), 7.45 – 7.42 (m, 2H), 7.40 (d, *J* = 5.8 Hz, 1H), 7.38 – 7.33 (m, 2H), 7.29 – 7.21 (m, 3H), 7.17 – 7.12 (m, 1H), 3.93 (d, *J* = 16.2 Hz, 1H), 3.76 (d, *J* = 16.2 Hz, 1H), 3.54 (d, *J* = 13.1 Hz, 1H), 3.46 (d, *J* = 13.1 Hz, 1H), 1.93 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.76, 161.26, 154.69, 141.59, 138.49, 136.10, 135.20, 131.67, 130.12, 129.21, 128.83, 127.57, 127.49, 127.43, 126.67, 124.96, 124.55, 120.21, 119.53, 58.40, 40.88, 38.44, 15.02. HRMS (m/z) calcd for $C_{27}H_{24}N_3OS$ $[M+H]^+$: 438.1635, found: 438.1639.

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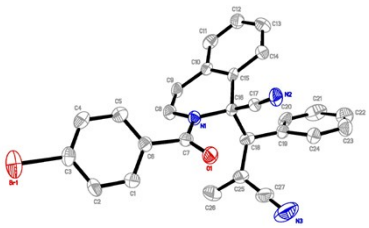
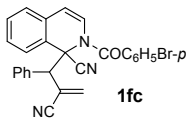
VI. Crystal Data and Structure Refinement for Compound 1fc and 2fa

1)





CCDC 1049135

Table 1. Crystal data and structure refinement for 1fc

Identification code	1fc
Empirical formula	C27 H18 Br N3 O
Formula weight	480.35
Temperature	296(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P 21
Unit cell dimensions	a = 8.1413(16) A alpha = 90 deg. b = 13.747(3) A beta = 108.05(3) deg. c = 10.606(2) A gamma = 90 deg.
Volume	1128.6(4) A^3
Z, Calculated density	2, 1.414 Mg/m^3
Absorption coefficient	1.845 mm^-1
F(000)	488
Crystal size	0.17 x 0.15 x 0.14 mm
Theta range for data collection	3.02 to 27.48 deg.
Limiting indices	-10<=h<=10, -16<=k<=17, -13<=l<=13
Reflections collected / unique	10791 / 4949 [R(int) = 0.0952]

Completeness to theta = 27.48	98.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7783 and 0.7420
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4949 / 1 / 289
Goodness-of-fit on F^2	0.972
Final R indices [I>2sigma(I)]	R1 = 0.0668, wR2 = 0.1175
R indices (all data)	R1 = 0.1771, wR2 = 0.1519
Absolute structure parameter	0.046(15)
Largest diff. peak and hole	0.250 and -0.286 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for 7Q76. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Br(1)	-1123(1)	-3215(1)	8629(1)	104(1)
C(1)	1280(10)	-583(5)	8997(6)	57(2)
C(2)	429(11)	-1366(5)	9241(7)	63(2)
C(3)	83(10)	-2127(4)	8347(7)	55(2)
C(4)	599(10)	-2079(5)	7232(6)	59(2)
C(5)	1480(9)	-1273(5)	7003(6)	53(2)
C(6)	1848(9)	-513(4)	7887(5)	46(2)
C(7)	2661(9)	420(4)	7650(5)	47(2)
C(8)	5104(10)	-476(4)	7314(6)	52(2)
C(9)	6268(10)	-547(4)	6684(6)	51(2)
C(10)	6402(9)	172(4)	5733(5)	44(2)
C(11)	7338(10)	13(5)	4832(7)	57(2)
C(12)	7330(10)	687(5)	3885(6)	61(2)
C(13)	6399(10)	1519(5)	3792(6)	66(2)

C(14)	5485(8)	1726(6)	4666(5)	53(2)
C(15)	5524(8)	1035(4)	5649(5)	39(2)
C(16)	4708(8)	1266(4)	6749(5)	40(2)
C(17)	3287(10)	1969(4)	6199(5)	45(2)
C(18)	6191(8)	1722(6)	7964(5)	47(2)
C(19)	7001(10)	2610(4)	7623(6)	45(2)
C(20)	8612(11)	2535(5)	7476(6)	61(2)
C(21)	9396(12)	3340(8)	7134(8)	88(3)
C(22)	8561(13)	4206(7)	6926(7)	79(2)
C(23)	6986(13)	4307(6)	7064(7)	70(2)
C(24)	6179(10)	3522(4)	7413(6)	52(2)
C(25)	5698(10)	1781(7)	9234(6)	65(2)
C(26)	6129(14)	1042(7)	10126(7)	104(4)
C(27)	4802(14)	2579(7)	9495(7)	80(3)
N(1)	4038(7)	369(3)	7151(4)	43(1)
N(2)	2313(9)	2539(4)	5651(5)	60(2)
N(3)	4089(13)	3258(6)	9735(8)	130(4)
O(1)	2113(7)	1180(3)	7894(4)	63(1)

Table 3. Bond lengths [A] and angles [deg] for 7Q76.

Br(1)-C(3)	1.863(7)
C(1)-C(2)	1.348(9)
C(1)-C(6)	1.395(8)
C(1)-H(1)	0.9300
C(2)-C(3)	1.381(9)
C(2)-H(2)	0.9300
C(3)-C(4)	1.374(8)
C(4)-C(5)	1.382(9)
C(4)-H(4)	0.9300
C(5)-C(6)	1.374(8)
C(5)-H(5)	0.9300
C(6)-C(7)	1.500(8)
C(7)-O(1)	1.195(6)
C(7)-N(1)	1.382(8)
C(8)-C(9)	1.321(9)
C(8)-N(1)	1.428(8)
C(8)-H(8)	0.9300
C(9)-C(10)	1.440(8)
C(9)-H(9)	0.9300
C(10)-C(15)	1.374(8)
C(10)-C(11)	1.412(8)
C(11)-C(12)	1.365(9)

C(11)-H(11)	0.9300
C(12)-C(13)	1.359(9)
C(12)-H(12)	0.9300
C(13)-C(14)	1.386(8)
C(13)-H(13)	0.9300
C(14)-C(15)	1.403(8)
C(14)-H(14)	0.9300
C(15)-C(16)	1.543(8)
C(16)-N(1)	1.464(7)
C(16)-C(17)	1.482(9)
C(16)-C(18)	1.596(8)
C(17)-N(2)	1.138(8)
C(18)-C(19)	1.485(9)
C(18)-C(25)	1.522(8)
C(18)-H(18)	0.9800
C(19)-C(20)	1.371(10)
C(19)-C(24)	1.407(9)
C(20)-C(21)	1.382(11)
C(20)-H(20)	0.9300
C(21)-C(22)	1.354(11)
C(21)-H(21)	0.9300
C(22)-C(23)	1.342(11)
C(22)-H(22)	0.9300
C(23)-C(24)	1.372(9)
C(23)-H(23)	0.9300
C(24)-H(24)	0.9300
C(25)-C(26)	1.358(11)
C(25)-C(27)	1.392(13)
C(26)-H(26A)	0.9300
C(26)-H(26B)	0.9300
C(27)-N(3)	1.169(11)

C(2)-C(1)-C(6)	122.8(6)
C(2)-C(1)-H(1)	118.6
C(6)-C(1)-H(1)	118.6
C(1)-C(2)-C(3)	118.8(6)
C(1)-C(2)-H(2)	120.6
C(3)-C(2)-H(2)	120.6
C(4)-C(3)-C(2)	120.2(6)
C(4)-C(3)-Br(1)	119.6(5)
C(2)-C(3)-Br(1)	120.2(5)
C(3)-C(4)-C(5)	120.2(6)
C(3)-C(4)-H(4)	119.9
C(5)-C(4)-H(4)	119.9

C(6)-C(5)-C(4)	120.4(6)
C(6)-C(5)-H(5)	119.8
C(4)-C(5)-H(5)	119.8
C(5)-C(6)-C(1)	117.7(6)
C(5)-C(6)-C(7)	123.4(5)
C(1)-C(6)-C(7)	118.6(5)
O(1)-C(7)-N(1)	122.0(6)
O(1)-C(7)-C(6)	119.8(6)
N(1)-C(7)-C(6)	118.2(5)
C(9)-C(8)-N(1)	120.2(6)
C(9)-C(8)-H(8)	119.9
N(1)-C(8)-H(8)	119.9
C(8)-C(9)-C(10)	121.7(6)
C(8)-C(9)-H(9)	119.2
C(10)-C(9)-H(9)	119.2
C(15)-C(10)-C(11)	117.9(5)
C(15)-C(10)-C(9)	119.2(6)
C(11)-C(10)-C(9)	122.8(6)
C(12)-C(11)-C(10)	120.9(6)
C(12)-C(11)-H(11)	119.6
C(10)-C(11)-H(11)	119.6
C(13)-C(12)-C(11)	120.0(6)
C(13)-C(12)-H(12)	120.0
C(11)-C(12)-H(12)	120.0
C(12)-C(13)-C(14)	121.8(6)
C(12)-C(13)-H(13)	119.1
C(14)-C(13)-H(13)	119.1
C(13)-C(14)-C(15)	117.7(7)
C(13)-C(14)-H(14)	121.2
C(15)-C(14)-H(14)	121.2
C(10)-C(15)-C(14)	121.7(5)
C(10)-C(15)-C(16)	117.7(5)
C(14)-C(15)-C(16)	120.4(5)
N(1)-C(16)-C(17)	110.4(5)
N(1)-C(16)-C(15)	109.5(4)
C(17)-C(16)-C(15)	107.6(4)
N(1)-C(16)-C(18)	110.6(5)
C(17)-C(16)-C(18)	111.4(5)
C(15)-C(16)-C(18)	107.2(5)
N(2)-C(17)-C(16)	170.4(6)
C(19)-C(18)-C(25)	115.5(6)
C(19)-C(18)-C(16)	114.1(5)
C(25)-C(18)-C(16)	113.3(5)
C(19)-C(18)-H(18)	104.1

C(25)-C(18)-H(18)	104.1
C(16)-C(18)-H(18)	104.1
C(20)-C(19)-C(24)	118.3(6)
C(20)-C(19)-C(18)	118.6(6)
C(24)-C(19)-C(18)	123.1(6)
C(19)-C(20)-C(21)	120.4(7)
C(19)-C(20)-H(20)	119.8
C(21)-C(20)-H(20)	119.8
C(22)-C(21)-C(20)	119.8(8)
C(22)-C(21)-H(21)	120.1
C(20)-C(21)-H(21)	120.1
C(23)-C(22)-C(21)	121.5(8)
C(23)-C(22)-H(22)	119.3
C(21)-C(22)-H(22)	119.3
C(22)-C(23)-C(24)	120.0(8)
C(22)-C(23)-H(23)	120.0
C(24)-C(23)-H(23)	120.0
C(23)-C(24)-C(19)	120.0(7)
C(23)-C(24)-H(24)	120.0
C(19)-C(24)-H(24)	120.0
C(26)-C(25)-C(27)	119.3(6)
C(26)-C(25)-C(18)	119.6(8)
C(27)-C(25)-C(18)	121.1(7)
C(25)-C(26)-H(26A)	120.0
C(25)-C(26)-H(26B)	120.0
H(26A)-C(26)-H(26B)	120.0
N(3)-C(27)-C(25)	178.3(11)
C(7)-N(1)-C(8)	122.0(5)
C(7)-N(1)-C(16)	119.2(5)
C(8)-N(1)-C(16)	116.9(6)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for 7Q76.

The anisotropic displacement factor exponent takes the form:

-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Br(1)	97(1)	77(1)	143(1)	17(1)	41(1)	-27(1)

C(1)	73(6)	51(4)	48(4)	0(3)	22(4)	0(4)
C(2)	83(6)	48(4)	62(4)	17(3)	30(4)	-1(4)
C(3)	48(5)	37(4)	76(4)	6(3)	16(4)	2(3)
C(4)	55(6)	52(4)	62(4)	-13(3)	8(4)	-5(4)
C(5)	51(5)	54(4)	53(4)	-4(3)	15(3)	2(4)
C(6)	52(5)	38(3)	44(3)	6(3)	8(3)	7(3)
C(7)	60(6)	37(4)	44(3)	2(3)	18(3)	11(3)
C(8)	60(5)	37(3)	54(4)	6(3)	12(4)	11(3)
C(9)	61(6)	28(3)	62(4)	3(3)	18(4)	9(3)
C(10)	47(5)	37(4)	46(3)	-6(3)	12(3)	-3(3)
C(11)	45(5)	58(4)	69(4)	-18(3)	21(4)	-1(4)
C(12)	77(7)	54(4)	66(5)	-6(3)	44(4)	-5(4)
C(13)	73(6)	76(7)	55(4)	10(3)	29(4)	-1(4)
C(14)	63(5)	46(3)	47(3)	5(3)	14(3)	4(4)
C(15)	43(5)	26(3)	48(3)	-5(2)	13(3)	1(3)
C(16)	49(5)	32(3)	37(3)	0(2)	10(3)	1(3)
C(17)	60(5)	37(4)	40(3)	2(3)	20(3)	1(4)
C(18)	43(4)	53(4)	42(3)	-9(3)	9(3)	8(4)
C(19)	44(5)	40(4)	53(4)	-1(3)	16(3)	4(3)
C(20)	66(6)	47(4)	75(5)	-14(3)	31(4)	3(4)
C(21)	46(6)	132(9)	96(6)	-38(6)	39(5)	-7(6)
C(22)	78(8)	87(6)	81(5)	-9(4)	39(5)	-31(6)
C(23)	73(7)	56(5)	78(5)	5(4)	20(5)	-12(5)
C(24)	44(5)	50(4)	64(4)	-2(3)	20(4)	-2(4)
C(25)	86(6)	63(4)	44(4)	-12(4)	16(3)	-16(6)
C(26)	160(11)	98(6)	41(4)	6(4)	14(5)	-21(7)
C(27)	107(9)	82(6)	68(5)	-26(5)	53(5)	-36(6)
N(1)	49(4)	34(3)	47(3)	4(2)	18(3)	6(3)
N(2)	74(5)	38(3)	65(3)	10(3)	16(3)	7(3)
N(3)	164(10)	119(7)	146(8)	-70(6)	105(8)	-43(7)
O(1)	84(4)	43(3)	72(3)	2(2)	41(3)	14(3)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for 7Q76.

	x	y	z	U(eq)
H(1)	1497	-67	9594	68
H(2)	80	-1393	9997	75
H(4)	353	-2591	6628	71
H(5)	1827	-1246	6247	63
H(8)	4978	-978	7865	62
H(9)	7020	-1075	6860	61
H(11)	7969	-558	4885	68
H(12)	7962	576	3303	73
H(13)	6373	1961	3123	79
H(14)	4867	2303	4604	63
H(18)	7115	1235	8161	56
H(20)	9180	1939	7608	73
H(21)	10494	3288	7046	105
H(22)	9091	4742	6682	94
H(23)	6441	4910	6923	84
H(24)	5089	3593	7510	63
H(26A)	5826	1073	10902	125
H(26B)	6728	505	9962	125

Table 6. Torsion angles [deg] for 7Q76.

C(6)-C(1)-C(2)-C(3)	-0.8(11)
C(1)-C(2)-C(3)-C(4)	-0.2(11)
C(1)-C(2)-C(3)-Br(1)	-178.9(6)
C(2)-C(3)-C(4)-C(5)	0.6(10)
Br(1)-C(3)-C(4)-C(5)	179.4(5)
C(3)-C(4)-C(5)-C(6)	-0.1(10)
C(4)-C(5)-C(6)-C(1)	-0.9(9)
C(4)-C(5)-C(6)-C(7)	-174.5(6)
C(2)-C(1)-C(6)-C(5)	1.4(10)
C(2)-C(1)-C(6)-C(7)	175.3(7)
C(5)-C(6)-C(7)-O(1)	136.1(7)
C(1)-C(6)-C(7)-O(1)	-37.5(9)

C(5)-C(6)-C(7)-N(1)	-43.9(9)
C(1)-C(6)-C(7)-N(1)	142.5(6)
N(1)-C(8)-C(9)-C(10)	-5.6(10)
C(8)-C(9)-C(10)-C(15)	11.9(10)
C(8)-C(9)-C(10)-C(11)	-165.1(6)
C(15)-C(10)-C(11)-C(12)	-1.8(9)
C(9)-C(10)-C(11)-C(12)	175.3(7)
C(10)-C(11)-C(12)-C(13)	-0.6(11)
C(11)-C(12)-C(13)-C(14)	2.1(12)
C(12)-C(13)-C(14)-C(15)	-1.1(11)
C(11)-C(10)-C(15)-C(14)	2.8(9)
C(9)-C(10)-C(15)-C(14)	-174.4(6)
C(11)-C(10)-C(15)-C(16)	-172.0(5)
C(9)-C(10)-C(15)-C(16)	10.9(9)
C(13)-C(14)-C(15)-C(10)	-1.4(10)
C(13)-C(14)-C(15)-C(16)	173.2(6)
C(10)-C(15)-C(16)-N(1)	-36.8(8)
C(14)-C(15)-C(16)-N(1)	148.4(6)
C(10)-C(15)-C(16)-C(17)	-156.8(6)
C(14)-C(15)-C(16)-C(17)	28.4(8)
C(10)-C(15)-C(16)-C(18)	83.3(6)
C(14)-C(15)-C(16)-C(18)	-91.5(7)
N(1)-C(16)-C(17)-N(2)	-141(4)
C(15)-C(16)-C(17)-N(2)	-22(4)
C(18)-C(16)-C(17)-N(2)	96(4)
N(1)-C(16)-C(18)-C(19)	177.2(5)
C(17)-C(16)-C(18)-C(19)	-59.7(6)
C(15)-C(16)-C(18)-C(19)	57.8(6)
N(1)-C(16)-C(18)-C(25)	-47.9(8)
C(17)-C(16)-C(18)-C(25)	75.2(7)
C(15)-C(16)-C(18)-C(25)	-167.3(6)
C(25)-C(18)-C(19)-C(20)	122.1(7)
C(16)-C(18)-C(19)-C(20)	-104.0(7)
C(25)-C(18)-C(19)-C(24)	-59.3(8)
C(16)-C(18)-C(19)-C(24)	74.5(7)
C(24)-C(19)-C(20)-C(21)	0.1(10)
C(18)-C(19)-C(20)-C(21)	178.7(6)
C(19)-C(20)-C(21)-C(22)	-0.8(11)
C(20)-C(21)-C(22)-C(23)	1.0(13)
C(21)-C(22)-C(23)-C(24)	-0.5(12)
C(22)-C(23)-C(24)-C(19)	-0.2(11)
C(20)-C(19)-C(24)-C(23)	0.3(10)
C(18)-C(19)-C(24)-C(23)	-178.2(6)
C(19)-C(18)-C(25)-C(26)	-132.8(8)

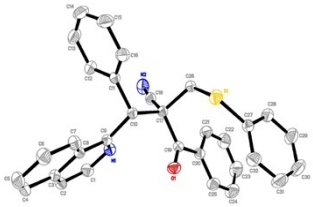
C(16)-C(18)-C(25)-C(26)	92.9(8)
C(19)-C(18)-C(25)-C(27)	47.5(9)
C(16)-C(18)-C(25)-C(27)	-86.7(8)
C(26)-C(25)-C(27)-N(3)	81(29)
C(18)-C(25)-C(27)-N(3)	-99(29)
O(1)-C(7)-N(1)-C(8)	156.1(6)
C(6)-C(7)-N(1)-C(8)	-23.9(8)
O(1)-C(7)-N(1)-C(16)	-7.9(9)
C(6)-C(7)-N(1)-C(16)	172.1(5)
C(9)-C(8)-N(1)-C(7)	171.5(6)
C(9)-C(8)-N(1)-C(16)	-24.1(8)
C(17)-C(16)-N(1)-C(7)	-33.8(7)
C(15)-C(16)-N(1)-C(7)	-152.1(5)
C(18)-C(16)-N(1)-C(7)	89.9(7)
C(17)-C(16)-N(1)-C(8)	161.3(5)
C(15)-C(16)-N(1)-C(8)	43.0(7)
C(18)-C(16)-N(1)-C(8)	-74.9(6)

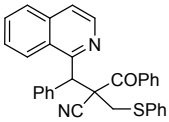
Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for 7Q76 [A and deg.].

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

2)





2fa

CCDC 1049136

able 1. Crystal data and structure refinement for 2fa.

Identification code	2fa
Empirical formula	C32 H24 N2 O S
Formula weight	484.59
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	Triclinic, P -1
Unit cell dimensions	a = 9.4724(19) A alpha = 104.00(3) deg. b = 12.292(3) A beta = 109.97(3) deg. c = 12.563(3) A gamma = 102.72(3) deg.
Volume	1258.3(4) A^3
Z, Calculated density	2, 1.279 Mg/m^3
Absorption coefficient	0.157 mm^-1
F(000)	508
Crystal size	0.13 x 0.12 x 0.10 mm
Theta range for data collection	2.99 to 27.48 deg.
Limiting indices	-11<=h<=12, -15<=k<=15, -16<=l<=16
Reflections collected / unique	12455 / 5714 [R(int) = 0.0392]
Completeness to theta = 27.48	99.1 %

Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9845 and 0.9799
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5714 / 0 / 325
Goodness-of-fit on F^2	1.031
Final R indices [I>2sigma(I)]	R1 = 0.0548, wR2 = 0.1578
R indices (all data)	R1 = 0.0856, wR2 = 0.1836
Largest diff. peak and hole	0.339 and -0.296 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for 9Q74C. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
C(1)	6378(3)	771(2)	1502(2)	47(1)
C(2)	5937(3)	-80(2)	1946(2)	48(1)
C(3)	4955(2)	46(2)	2569(2)	42(1)
C(4)	4432(3)	-798(2)	3065(2)	54(1)
C(5)	3492(3)	-632(3)	3653(3)	62(1)
C(6)	3023(3)	375(2)	3783(2)	54(1)
C(7)	3494(3)	1208(2)	3315(2)	46(1)
C(8)	4466(2)	1063(2)	2686(2)	38(1)
C(9)	4981(2)	1882(2)	2148(2)	36(1)
C(10)	4383(2)	2936(2)	2160(2)	34(1)
C(11)	2598(2)	2514(2)	1338(2)	37(1)
C(12)	1941(3)	1603(2)	228(2)	51(1)
C(13)	321(3)	1216(3)	-492(3)	66(1)
C(14)	-660(3)	1727(3)	-107(3)	69(1)
C(15)	-25(3)	2625(3)	985(3)	65(1)
C(16)	1597(3)	3014(2)	1701(2)	49(1)
C(17)	5395(2)	3886(2)	1840(2)	34(1)
C(18)	5097(3)	3390(2)	556(2)	43(1)

C(19)	7179(2)	4278(2)	2728(2)	35(1)
C(20)	8487(2)	4940(2)	2481(2)	39(1)
C(21)	8260(3)	5246(2)	1452(2)	52(1)
C(22)	9554(3)	5868(3)	1316(3)	66(1)
C(23)	11072(3)	6197(3)	2193(3)	70(1)
C(24)	11304(3)	5943(3)	3237(3)	65(1)
C(25)	10022(3)	5305(2)	3376(2)	48(1)
C(26)	4870(2)	5013(2)	1961(2)	42(1)
C(27)	7220(3)	6825(2)	4087(2)	41(1)
C(28)	7736(3)	7561(2)	3521(2)	50(1)
C(29)	9288(3)	8323(3)	4055(3)	66(1)
C(30)	10316(3)	8374(3)	5154(3)	74(1)
C(31)	9817(3)	7645(3)	5724(3)	72(1)
C(32)	8268(3)	6861(3)	5184(2)	54(1)
N(1)	5910(2)	1752(2)	1595(2)	42(1)
N(2)	4770(3)	3061(2)	-455(2)	63(1)
O(1)	7473(2)	4097(2)	3672(1)	45(1)
S(1)	5212(1)	5875(1)	3466(1)	49(1)

Table 3. Bond lengths [A] and angles [deg] for 9Q74C.

C(1)-C(2)	1.352(4)
C(1)-N(1)	1.366(3)
C(1)-H(1)	0.9300
C(2)-C(3)	1.415(3)
C(2)-H(2)	0.9300
C(3)-C(4)	1.418(3)
C(3)-C(8)	1.418(3)
C(4)-C(5)	1.354(4)
C(4)-H(4)	0.9300
C(5)-C(6)	1.396(4)
C(5)-H(5)	0.9300
C(6)-C(7)	1.365(3)
C(6)-H(6)	0.9300
C(7)-C(8)	1.416(3)
C(7)-H(7)	0.9300
C(8)-C(9)	1.430(3)
C(9)-N(1)	1.307(3)
C(9)-C(10)	1.523(3)
C(10)-C(11)	1.534(3)
C(10)-C(17)	1.562(3)
C(10)-H(10)	0.9800

C(11)-C(16)	1.378(3)
C(11)-C(12)	1.390(3)
C(12)-C(13)	1.386(4)
C(12)-H(12)	0.9300
C(13)-C(14)	1.381(5)
C(13)-H(13)	0.9300
C(14)-C(15)	1.369(5)
C(14)-H(14)	0.9300
C(15)-C(16)	1.387(3)
C(15)-H(15)	0.9300
C(16)-H(16)	0.9300
C(17)-C(18)	1.480(3)
C(17)-C(19)	1.558(3)
C(17)-C(26)	1.564(3)
C(18)-N(2)	1.140(3)
C(19)-O(1)	1.210(2)
C(19)-C(20)	1.493(3)
C(20)-C(25)	1.390(3)
C(20)-C(21)	1.393(3)
C(21)-C(22)	1.382(3)
C(21)-H(21)	0.9300
C(22)-C(23)	1.376(4)
C(22)-H(22)	0.9300
C(23)-C(24)	1.377(4)
C(23)-H(23)	0.9300
C(24)-C(25)	1.382(3)
C(24)-H(24)	0.9300
C(25)-H(25)	0.9300
C(26)-S(1)	1.806(3)
C(26)-H(26A)	0.9700
C(26)-H(26B)	0.9700
C(27)-C(32)	1.380(3)
C(27)-C(28)	1.384(3)
C(27)-S(1)	1.777(2)
C(28)-C(29)	1.380(3)
C(28)-H(28)	0.9300
C(29)-C(30)	1.368(4)
C(29)-H(29)	0.9300
C(30)-C(31)	1.376(5)
C(30)-H(30)	0.9300
C(31)-C(32)	1.387(4)
C(31)-H(31)	0.9300
C(32)-H(32)	0.9300

C(2)-C(1)-N(1)	124.1(2)
C(2)-C(1)-H(1)	118.0
N(1)-C(1)-H(1)	118.0
C(1)-C(2)-C(3)	119.0(2)
C(1)-C(2)-H(2)	120.5
C(3)-C(2)-H(2)	120.5
C(2)-C(3)-C(4)	123.1(2)
C(2)-C(3)-C(8)	117.9(2)
C(4)-C(3)-C(8)	119.0(2)
C(5)-C(4)-C(3)	120.6(3)
C(5)-C(4)-H(4)	119.7
C(3)-C(4)-H(4)	119.7
C(4)-C(5)-C(6)	120.7(2)
C(4)-C(5)-H(5)	119.7
C(6)-C(5)-H(5)	119.7
C(7)-C(6)-C(5)	120.7(3)
C(7)-C(6)-H(6)	119.6
C(5)-C(6)-H(6)	119.6
C(6)-C(7)-C(8)	120.4(2)
C(6)-C(7)-H(7)	119.8
C(8)-C(7)-H(7)	119.8
C(7)-C(8)-C(3)	118.7(2)
C(7)-C(8)-C(9)	123.8(2)
C(3)-C(8)-C(9)	117.6(2)
N(1)-C(9)-C(8)	123.1(2)
N(1)-C(9)-C(10)	117.10(19)
C(8)-C(9)-C(10)	119.74(19)
C(9)-C(10)-C(11)	110.60(17)
C(9)-C(10)-C(17)	111.61(17)
C(11)-C(10)-C(17)	112.58(17)
C(9)-C(10)-H(10)	107.2
C(11)-C(10)-H(10)	107.2
C(17)-C(10)-H(10)	107.2
C(16)-C(11)-C(12)	118.2(2)
C(16)-C(11)-C(10)	120.5(2)
C(12)-C(11)-C(10)	121.2(2)
C(13)-C(12)-C(11)	120.5(3)
C(13)-C(12)-H(12)	119.8
C(11)-C(12)-H(12)	119.8
C(14)-C(13)-C(12)	120.2(3)
C(14)-C(13)-H(13)	119.9
C(12)-C(13)-H(13)	119.9
C(15)-C(14)-C(13)	119.8(2)
C(15)-C(14)-H(14)	120.1

C(13)-C(14)-H(14)	120.1
C(14)-C(15)-C(16)	119.8(3)
C(14)-C(15)-H(15)	120.1
C(16)-C(15)-H(15)	120.1
C(11)-C(16)-C(15)	121.4(3)
C(11)-C(16)-H(16)	119.3
C(15)-C(16)-H(16)	119.3
C(18)-C(17)-C(19)	113.54(18)
C(18)-C(17)-C(10)	109.02(17)
C(19)-C(17)-C(10)	109.16(16)
C(18)-C(17)-C(26)	105.70(18)
C(19)-C(17)-C(26)	108.05(16)
C(10)-C(17)-C(26)	111.36(18)
N(2)-C(18)-C(17)	173.8(3)
O(1)-C(19)-C(20)	120.44(19)
O(1)-C(19)-C(17)	117.45(19)
C(20)-C(19)-C(17)	121.94(18)
C(25)-C(20)-C(21)	118.8(2)
C(25)-C(20)-C(19)	116.5(2)
C(21)-C(20)-C(19)	124.6(2)
C(22)-C(21)-C(20)	120.0(2)
C(22)-C(21)-H(21)	120.0
C(20)-C(21)-H(21)	120.0
C(23)-C(22)-C(21)	120.6(3)
C(23)-C(22)-H(22)	119.7
C(21)-C(22)-H(22)	119.7
C(22)-C(23)-C(24)	119.8(3)
C(22)-C(23)-H(23)	120.1
C(24)-C(23)-H(23)	120.1
C(23)-C(24)-C(25)	120.1(3)
C(23)-C(24)-H(24)	120.0
C(25)-C(24)-H(24)	120.0
C(24)-C(25)-C(20)	120.6(3)
C(24)-C(25)-H(25)	119.7
C(20)-C(25)-H(25)	119.7
C(17)-C(26)-S(1)	116.11(15)
C(17)-C(26)-H(26A)	108.3
S(1)-C(26)-H(26A)	108.3
C(17)-C(26)-H(26B)	108.3
S(1)-C(26)-H(26B)	108.3
H(26A)-C(26)-H(26B)	107.4
C(32)-C(27)-C(28)	119.5(2)
C(32)-C(27)-S(1)	118.9(2)
C(28)-C(27)-S(1)	121.61(17)

C(29)-C(28)-C(27)	120.0(2)
C(29)-C(28)-H(28)	120.0
C(27)-C(28)-H(28)	120.0
C(30)-C(29)-C(28)	120.5(3)
C(30)-C(29)-H(29)	119.8
C(28)-C(29)-H(29)	119.8
C(29)-C(30)-C(31)	120.1(3)
C(29)-C(30)-H(30)	120.0
C(31)-C(30)-H(30)	120.0
C(30)-C(31)-C(32)	119.9(3)
C(30)-C(31)-H(31)	120.1
C(32)-C(31)-H(31)	120.1
C(27)-C(32)-C(31)	120.1(3)
C(27)-C(32)-H(32)	119.9
C(31)-C(32)-H(32)	119.9
C(9)-N(1)-C(1)	118.3(2)
C(27)-S(1)-C(26)	103.57(11)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for 9Q74C.

The anisotropic displacement factor exponent takes the form:

-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
C(1)	52(1)	45(1)	46(1)	12(1)	22(1)	21(1)
C(2)	51(1)	38(1)	51(1)	14(1)	14(1)	19(1)
C(3)	42(1)	33(1)	40(1)	13(1)	7(1)	7(1)
C(4)	62(2)	37(1)	58(2)	24(1)	15(1)	13(1)
C(5)	69(2)	51(2)	64(2)	34(1)	23(1)	6(1)
C(6)	58(2)	56(2)	52(1)	27(1)	27(1)	10(1)
C(7)	48(1)	42(1)	49(1)	21(1)	21(1)	13(1)
C(8)	34(1)	33(1)	36(1)	14(1)	7(1)	5(1)
C(9)	35(1)	31(1)	36(1)	12(1)	10(1)	6(1)
C(10)	35(1)	30(1)	34(1)	13(1)	12(1)	7(1)
C(11)	35(1)	32(1)	41(1)	19(1)	11(1)	8(1)
C(12)	43(1)	41(1)	51(1)	11(1)	10(1)	4(1)
C(13)	56(2)	53(2)	56(2)	14(1)	2(1)	-5(1)
C(14)	34(1)	75(2)	81(2)	41(2)	5(1)	4(1)

C(15)	41(1)	79(2)	84(2)	46(2)	24(1)	22(1)
C(16)	44(1)	50(1)	55(1)	25(1)	19(1)	14(1)
C(17)	36(1)	30(1)	33(1)	14(1)	10(1)	7(1)
C(18)	48(1)	34(1)	39(1)	16(1)	12(1)	5(1)
C(19)	37(1)	31(1)	35(1)	12(1)	12(1)	12(1)
C(20)	37(1)	36(1)	46(1)	14(1)	17(1)	12(1)
C(21)	46(1)	53(2)	55(1)	27(1)	18(1)	8(1)
C(22)	71(2)	62(2)	72(2)	32(2)	39(2)	10(1)
C(23)	54(2)	62(2)	92(2)	22(2)	43(2)	5(1)
C(24)	38(1)	68(2)	79(2)	16(2)	24(1)	11(1)
C(25)	39(1)	52(2)	53(1)	15(1)	20(1)	17(1)
C(26)	36(1)	32(1)	48(1)	17(1)	7(1)	7(1)
C(27)	41(1)	35(1)	42(1)	8(1)	15(1)	14(1)
C(28)	49(1)	42(1)	48(1)	15(1)	12(1)	9(1)
C(29)	57(2)	52(2)	70(2)	16(1)	19(1)	-2(1)
C(30)	47(2)	66(2)	70(2)	-2(2)	7(1)	0(1)
C(31)	61(2)	76(2)	48(1)	2(1)	1(1)	24(2)
C(32)	61(2)	57(2)	42(1)	14(1)	18(1)	22(1)
N(1)	44(1)	40(1)	44(1)	16(1)	19(1)	14(1)
N(2)	86(2)	47(1)	38(1)	17(1)	16(1)	6(1)
O(1)	42(1)	50(1)	38(1)	20(1)	10(1)	11(1)
S(1)	42(1)	43(1)	61(1)	12(1)	24(1)	12(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for 9Q74C.

	x	y	z	U(eq)
H(1)	7041	683	1110	56
H(2)	6275	-738	1844	58
H(4)	4737	-1472	2987	65
H(5)	3156	-1194	3972	75
H(6)	2383	479	4193	65
H(7)	3174	1875	3410	55
H(10)	4515	3314	2985	41
H(12)	2593	1249	-33	61
H(13)	-106	611	-1237	79
H(14)	-1748	1462	-589	82
H(15)	-681	2973	1247	77
H(16)	2019	3626	2440	59

H(21)	7237	5031	857	63
H(22)	9396	6066	625	79
H(23)	11940	6590	2082	83
H(24)	12323	6201	3849	78
H(25)	10189	5118	4073	58
H(26A)	3741	4764	1450	50
H(26B)	5428	5528	1653	50
H(28)	7037	7542	2782	60
H(29)	9637	8804	3666	80
H(30)	11353	8902	5517	89
H(31)	10517	7679	6470	86
H(32)	7935	6358	5561	65

Table 6. Torsion angles [deg] for 9Q74C.

N(1)-C(1)-C(2)-C(3)	-1.3(4)
C(1)-C(2)-C(3)-C(4)	180.0(2)
C(1)-C(2)-C(3)-C(8)	0.6(3)
C(2)-C(3)-C(4)-C(5)	180.0(2)
C(8)-C(3)-C(4)-C(5)	-0.6(3)
C(3)-C(4)-C(5)-C(6)	-0.2(4)
C(4)-C(5)-C(6)-C(7)	0.4(4)
C(5)-C(6)-C(7)-C(8)	0.1(4)
C(6)-C(7)-C(8)-C(3)	-0.8(3)
C(6)-C(7)-C(8)-C(9)	178.6(2)
C(2)-C(3)-C(8)-C(7)	-179.48(19)
C(4)-C(3)-C(8)-C(7)	1.1(3)
C(2)-C(3)-C(8)-C(9)	1.0(3)
C(4)-C(3)-C(8)-C(9)	-178.42(18)
C(7)-C(8)-C(9)-N(1)	178.3(2)
C(3)-C(8)-C(9)-N(1)	-2.2(3)
C(7)-C(8)-C(9)-C(10)	-4.3(3)
C(3)-C(8)-C(9)-C(10)	175.12(17)
N(1)-C(9)-C(10)-C(11)	109.0(2)
C(8)-C(9)-C(10)-C(11)	-68.5(2)
N(1)-C(9)-C(10)-C(17)	-17.2(3)
C(8)-C(9)-C(10)-C(17)	165.31(17)
C(9)-C(10)-C(11)-C(16)	138.1(2)
C(17)-C(10)-C(11)-C(16)	-96.3(2)
C(9)-C(10)-C(11)-C(12)	-40.3(3)
C(17)-C(10)-C(11)-C(12)	85.3(3)
C(16)-C(11)-C(12)-C(13)	0.3(4)

C(10)-C(11)-C(12)-C(13)	178.7(2)
C(11)-C(12)-C(13)-C(14)	-0.7(4)
C(12)-C(13)-C(14)-C(15)	0.6(5)
C(13)-C(14)-C(15)-C(16)	-0.2(4)
C(12)-C(11)-C(16)-C(15)	0.1(4)
C(10)-C(11)-C(16)-C(15)	-178.3(2)
C(14)-C(15)-C(16)-C(11)	-0.2(4)
C(9)-C(10)-C(17)-C(18)	68.7(2)
C(11)-C(10)-C(17)-C(18)	-56.4(2)
C(9)-C(10)-C(17)-C(19)	-55.9(2)
C(11)-C(10)-C(17)-C(19)	179.04(17)
C(9)-C(10)-C(17)-C(26)	-175.11(16)
C(11)-C(10)-C(17)-C(26)	59.8(2)
C(19)-C(17)-C(18)-N(2)	-142(2)
C(10)-C(17)-C(18)-N(2)	97(2)
C(26)-C(17)-C(18)-N(2)	-23(2)
C(18)-C(17)-C(19)-O(1)	-141.9(2)
C(10)-C(17)-C(19)-O(1)	-20.1(3)
C(26)-C(17)-C(19)-O(1)	101.2(2)
C(18)-C(17)-C(19)-C(20)	42.8(3)
C(10)-C(17)-C(19)-C(20)	164.62(19)
C(26)-C(17)-C(19)-C(20)	-74.1(2)
O(1)-C(19)-C(20)-C(25)	1.0(3)
C(17)-C(19)-C(20)-C(25)	176.2(2)
O(1)-C(19)-C(20)-C(21)	-176.5(2)
C(17)-C(19)-C(20)-C(21)	-1.4(4)
C(25)-C(20)-C(21)-C(22)	2.0(4)
C(19)-C(20)-C(21)-C(22)	179.5(2)
C(20)-C(21)-C(22)-C(23)	-0.4(5)
C(21)-C(22)-C(23)-C(24)	-2.4(5)
C(22)-C(23)-C(24)-C(25)	3.4(5)
C(23)-C(24)-C(25)-C(20)	-1.7(4)
C(21)-C(20)-C(25)-C(24)	-1.0(4)
C(19)-C(20)-C(25)-C(24)	-178.7(2)
C(18)-C(17)-C(26)-S(1)	-176.20(14)
C(19)-C(17)-C(26)-S(1)	-54.3(2)
C(10)-C(17)-C(26)-S(1)	65.5(2)
C(32)-C(27)-C(28)-C(29)	0.0(4)
S(1)-C(27)-C(28)-C(29)	177.3(2)
C(27)-C(28)-C(29)-C(30)	-1.3(5)
C(28)-C(29)-C(30)-C(31)	1.4(5)
C(29)-C(30)-C(31)-C(32)	-0.2(5)
C(28)-C(27)-C(32)-C(31)	1.2(4)
S(1)-C(27)-C(32)-C(31)	-176.2(2)

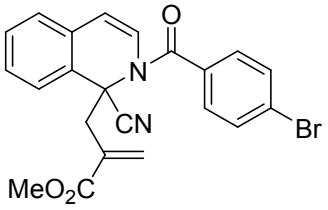
C(30)-C(31)-C(32)-C(27)	-1.1(4)
C(8)-C(9)-N(1)-C(1)	1.7(3)
C(10)-C(9)-N(1)-C(1)	-175.76(17)
C(2)-C(1)-N(1)-C(9)	0.1(3)
C(32)-C(27)-S(1)-C(26)	-127.5(2)
C(28)-C(27)-S(1)-C(26)	55.2(2)
C(17)-C(26)-S(1)-C(27)	84.84(17)

Symmetry transformations used to generate equivalent atoms:

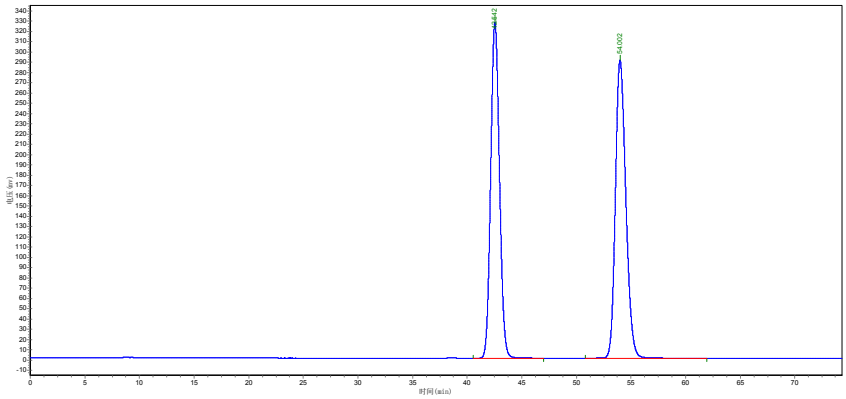
Table 7. Hydrogen bonds for 9Q74C [A and deg.].

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

VII. HPLC and NMR Spectra

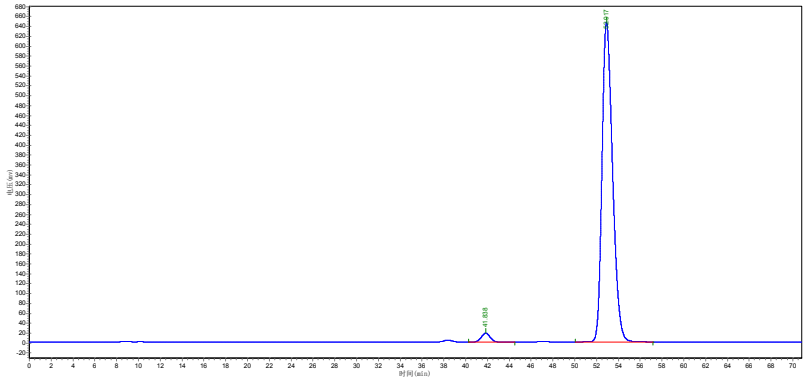


1ab-*ent*



Result Table

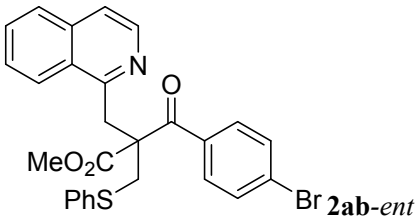
Peak#	Ret. Time/min	Height/μV	Area/μV·s	Area %
1	42.542	327031.906	18273390.000	48.6350
2	54.002	290286.281	19299100.000	51.3650
total		617318.188	37572490.000	100.0000



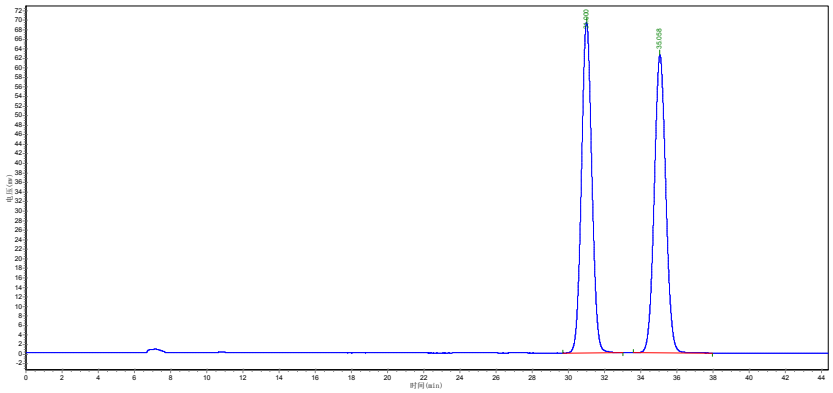
Result Table

Peak#	Ret. Time/min	Height/μV	Area/μV·s	Area %
1	41.838	17886.000	996998.500	2.2353
2	52.917	646481.188	43606000.000	97.7647
total		664367.188	44602998.500	100.0000

95% ee. The ee of the **1ab**-*ent* was determined by HPLC using an AD-H column (n-Hexane/i-PrOH = 80/20, flow rate 0.5 ml/min, λ = 254 nm, t_R = 42.5 min (minor), t_R = 54.0 min (major))

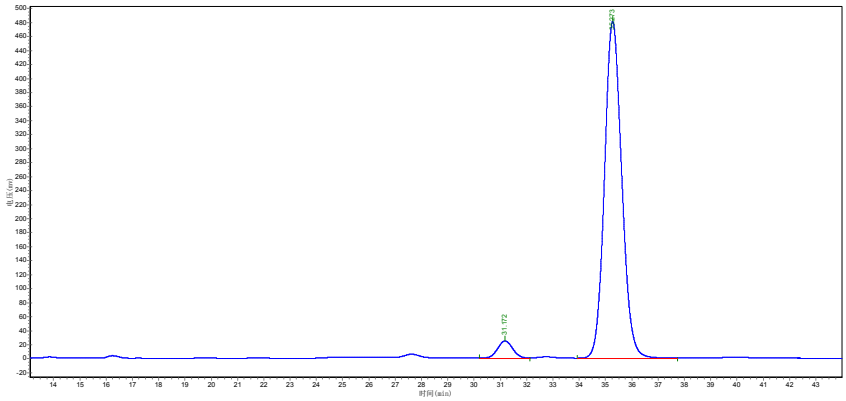


2ab-*ent*



Result Table

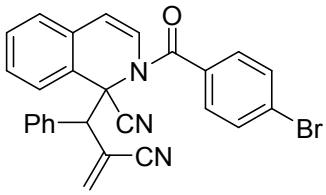
Peak#	Ret. Time/min	Height/μV	Area/μV·s	Area %
1	31.000	69254.625	2758778.750	49.9985
2	35.058	62492.371	2758945.000	50.0015
total		131746.996	5517723.750	100.0000



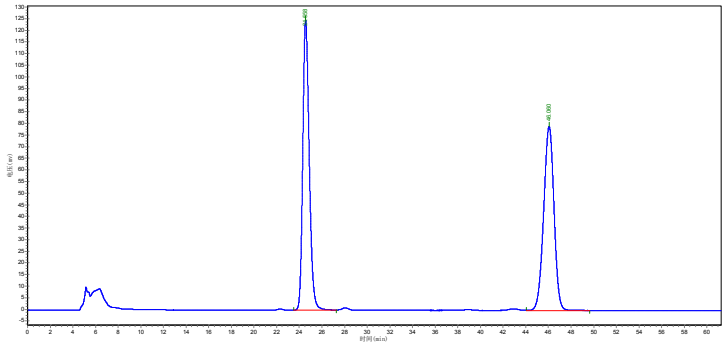
Result Table

Peak#	Ret. Time/min	Height/μV	Area/μV·s	Area %
1	31.172	24675.303	1013106.750	4.4084
2	35.237	480948.375	21968308.000	95.5916
total		505623.678	22981414.750	100.0000

91% ee. The ee of the **2ab**-*ent* was determined by HPLC using an AD-H column (n-Hexane/i-PrOH = 80/20, flow rate 0.5 ml/min, λ = 254 nm, t_R = 31.0 min (minor), t_R = 35.0 min (major))

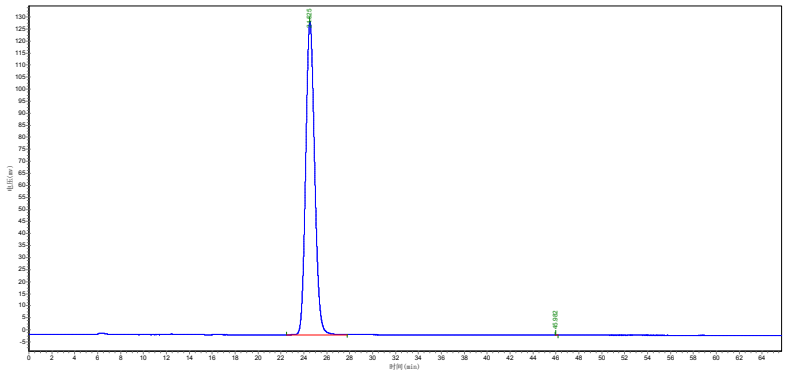


1fc-*ent*



Result Table

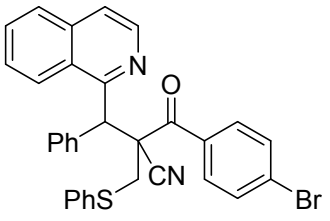
Peak#	Ret. Time/min	Height/μV	Area/μV·s	Area %
1	24.558	124563.992	4956660.000	49.7149
2	46.060	79129.180	5013513.500	50.2851
total		203693.172	9970173.500	100.0000



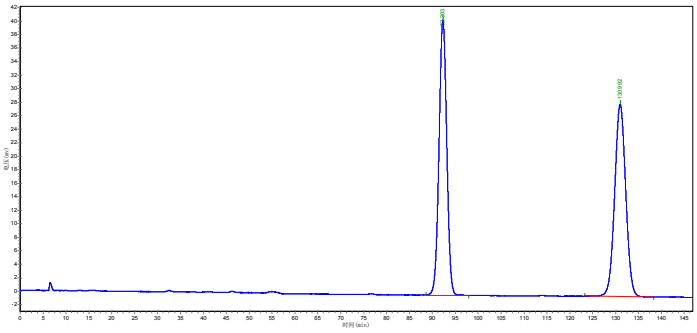
Result Table

Peak#	Ret. Time/min	Height/μV	Area/μV·s	Area %
1	24.525	130083.750	7070335.000	99.9993
2	45.982	5.160	52.800	0.0007
total				100.0000

99% ee. The ee of the **1fc**-*ent* was determined by HPLC using an AD-H column (n-Hexane/i-PrOH = 80/20, flow rate 0.5 ml/min, λ = 254 nm, t_R = 24.5 min (major), t_R = 46.0 min (minor))

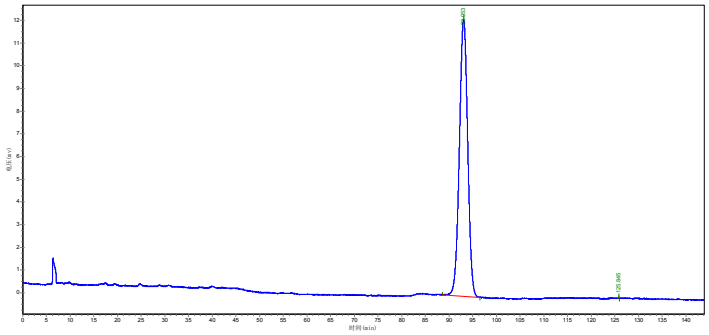


2fc-*ent*



Result Table

Peak#	Ret. Time/min	Height/μV	Area/μV·s	Area %
1	92.303	40731.676	481.4642.000	50.1762
2	130.992	28471.148	4780824.000	49.8238
total		69202.824	9596466.000	100.0000



Result Table

Peak#	Ret. Time/min	Height/μV	Area/μV·s	Area %
1	93.053	12196.705	1487380.250	99.9912
2	125.845	36.407	130.350	0.0088
total		12233.112	1487510.600	100.0000

99% ee. The ee of the **2fc**-*ent* was determined by HPLC using an AD-H column (n-Hexane/i-PrOH = 80/20, flow rate 0.5 ml/min, λ = 254 nm, t_R = 92.3 min (major), t_R = 130.9 min (minor))