

Supporting Information

For

O-Acylation Triggered γ -Umpolung Functionalization of Electron-poor Alkenyl Sulfoxides for the Synthesis of 3-Allyl Indoles

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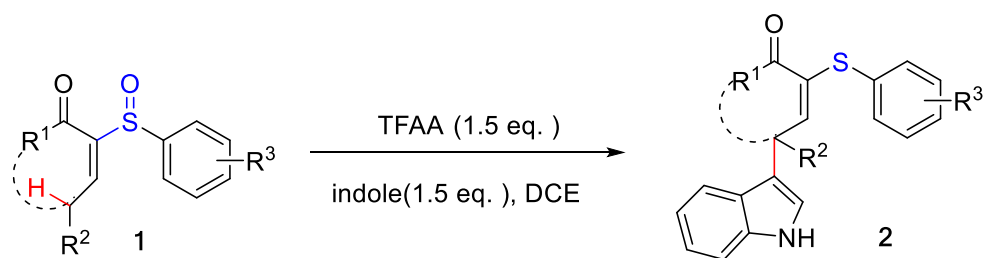
1. General Experimental Methods

Unless otherwise noted, all the operation and reaction processes are carried out in the air environment, and the chemical reagents are from Energy Chemical, Bidepharm or Adamas. The reagents are directly used in the experiment process and have not been further purified. Thin layer chromatography was carried out on a silica gelplates and the color was developed by UV lamp 254. Column chromatography is performed on silica gel, NMR spectra were measured on a Bruker magnetic resonance spectrometer (^1H at 400 MHz, ^{13}C at 101 MHz and ^{19}F at 376 MHz). Chemical shifts are reported in ppm. CDCl_3 were used as a solvent and an internal standard, respectively. HRMS data were obtained on a VG ZAB-
HS mass spectrometer, Brucker Apex IV FTMS spectrometer.

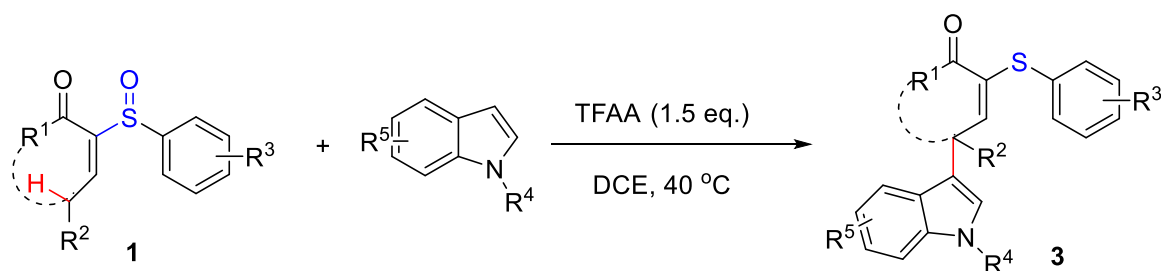
2. Typical Procedure for the Preparation of 1

Alkenyl sulfoxides **1** were prepared according to the known procedures.¹

General Procedure for the syntheses of 2 and 3



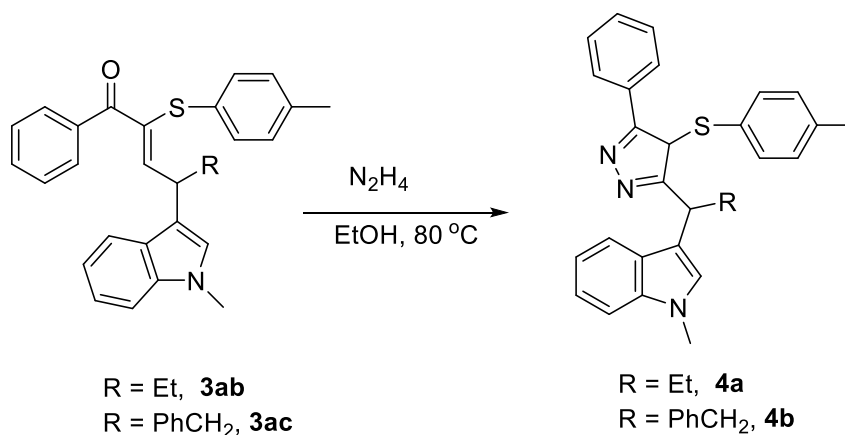
To a solution of **1** (0.3 mmol) and indole (0.45 mmol, 1.5 equiv.) in DCE (1 mL) was added TFAA (0.45 mmol, 1.5 equiv.) at 40 °C. The resulting solution was stirred and monitored by TLC. After completion, the reaction was quenched with water, extracted with DCM and dried over anhydrous Na₂SO₄. After removal of solvent, the residue left was purified by flash column chromatography with silica gel (eluent: petroleum ether/ethyl acetate = 5:1) to give desired product **2**.



To a solution of **1** (0.3 mmol) and N-Methylindole (0.45 mmol, 1.5 equiv.) in DCE (1 mL) was added TFAA (0.45 mmol, 1.5 equiv.) at 40 °C. The resulting solution was stirred and monitored by TLC. After completion,

the reaction was quenched with water, extracted with DCM and dried over anhydrous Na_2SO_4 . After removal of solvent, the residue left was purified by flash column chromatography with silica gel (eluent: petroleum ether/ethyl acetate = 5:1) to give desired product **3**.

General Procedure for the syntheses of **4**

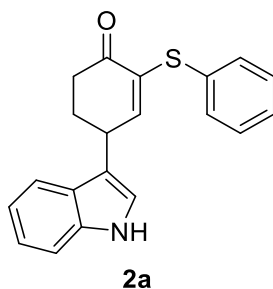


To a solution of **3ab** or **3ac** (1 mmol) in EtOH (10 mL) was added and N_2H_4 (5 mmol, 5 equiv.) at 80 °C. The resulting solution was stirred and monitored by TLC. After completion, the reaction was quenched with water, extracted with EtOAc and dried over anhydrous Na_2SO_4 . After removal of solvent, the residue left was purified by flash column chromatography with silica gel (eluent: petroleum ether/ethyl acetate = 8:1) to give desired product **4a** or **4b**.

3. Reference.

1. L. Jiang, L. Gao, X. Li, T. Shao, J. Yao, M. Miao and H. Zhou, *Synthesis*, 2024, **56**, 47.

4. The spectroscopic data of compounds



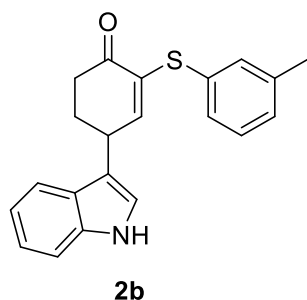
4-(1*H*-indol-3-yl)-2-(phenylthio)cyclohex-2-en-1-one (2a): Pure **2a** was prepared with general procedure and isolated through a silica gel flash column (PE:EtOAc = 5:1) as yellow solid (77 mg, 80% yield); mp 164-166 °C

¹H NMR (400 MHz, CDCl₃) δ 9.13 (s, 1H), 7.61 (d, *J* = 7.7 Hz, 1H), 7.44 (d, *J* = 8.1 Hz, 1H), 7.28 – 7.24 (m, 1H), 7.18 (d, *J* = 7.9 Hz, 2H), 7.15 (s, 1H), 7.09 – 7.06 (m, 2H), 7.05 (s, 1H), 6.96 – 6.93 (m, 1H), 6.18 (dd, *J* = 10.1, 2.4 Hz, 1H), 4.51 – 4.46 (m, 1H), 2.59 – 2.53 (m, 2H), 2.34 (dd, *J* = 13.0, 4.9 Hz, 1H), 2.22 – 2.16 (m, 1H);

¹³C NMR (101 MHz, CDCl₃) δ 199.4, 150.8, 144.1, 139.0, 135.9, 130.6, 129.9, 128.9, 125.4, 124.8, 123.0, 121.2, 119.4, 111.4, 99.6, 37.0, 34.5, 30.0;

IR (neat): 1632, 1598, 852cm⁻¹;

HRMS (ESI-TOF) ([M+H]⁺) Calcd For C₂₀H₁₈NOS⁺: 320.1104; Found: 320.1107.



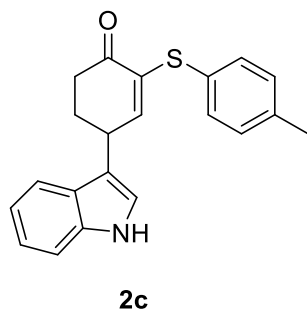
4-(1*H*-indol-3-yl)-2-(*m*-tolylthio)cyclohex-2-en-1-one (2b): Pure **2b** was prepared with general procedure and isolated through a silica gel flash column (PE:EtOAc = 5:1) as yellow solid (85 mg, 85% yield); mp 197-199 °C

¹H NMR (400 MHz, CDCl₃) δ 9.02 (s, 1H), 7.61 (d, J = 7.7 Hz, 1H), 7.43 (d, J = 8.0 Hz, 1H), 7.25 (s, 1H), 7.16 (d, J = 7.1 Hz, 1H), 7.04 (t, J = 7.6 Hz, 1H), 6.94 (d, J = 8.1 Hz, 2H), 6.88 (d, J = 7.2 Hz, 1H), 6.78 (d, J = 7.6 Hz, 1H), 6.18 (d, J = 10.1 Hz, 1H), 4.50 – 4.45 (m, 1H), 2.58 – 2.53 (m, 2H), 2.33 (dt, J = 9.8, 5.5 Hz, 1H), 2.24 (s, 3H), 2.21 – 2.15 (m, 1H);

¹³C NMR (101 MHz, CDCl₃) δ 199.3, 150.7, 144.1, 138.7, 138.6, 135.8, 130.7, 130.0, 128.8, 126.0, 125.8, 123.0, 122.4, 121.1, 119.5, 111.4, 99.7, 37.0, 34.6, 30.0, 21.4;

IR (neat): 2916, 1593, 875cm⁻¹;

HRMS (ESI-TOF) ([M+H]⁺) Calcd For C₂₁H₂₀NOS⁺: 334.1260; Found: 334.1264.



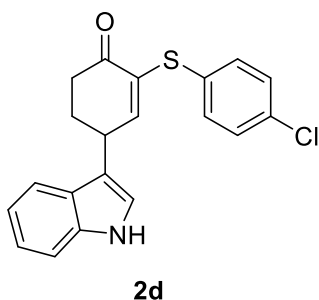
4-(1*H*-indol-3-yl)-2-(*p*-tolylthio)cyclohex-2-en-1-one (2c): Pure **2c** was prepared with general procedure and isolated through a silica gel flash column (PE:EtOAc = 5:1) as yellow solid (91 mg, 91% yield); mp 199-200 °C

¹H NMR (400 MHz, CDCl₃) δ 9.05 (s, 1H), 7.63 (d, J = 7.6 Hz, 1H), 7.44 (d, J = 8.0 Hz, 1H), 7.25 (d, J = 7.2 Hz, 1H), 7.18 (t, J = 7.4 Hz, 1H), 6.97 (d, J = 8.5 Hz, 5H), 6.22 – 6.17 (m, 1H), 4.50 (dd, J = 6.6, 2.7 Hz, 1H), 2.60 – 2.54 (m, 2H), 2.35 (dd, J = 12.6, 5.1 Hz, 1H), 2.27 (s, 3H), 2.20 (dd, J = 8.5, 4.8 Hz, 1H);

¹³C NMR (101 MHz, CDCl₃) δ 199.5, 150.9, 144.0, 135.9, 135.3, 134.6, 130.6, 129.9, 129.6, 125.6, 123.0, 121.1, 119.4, 111.4, 100.1, 37.0, 34.6, 30.0, 20.9;

IR (neat): 3037, 1632, 851cm⁻¹;

HRMS (ESI-TOF) ([M+H]⁺) Calcd For C₂₁H₂₀NOS⁺: 334.1260; Found: 334.1265.



2-((4-chlorophenyl)thio)-4-(1*H*-indol-3-yl)cyclohex-2-en-1-one (2d):

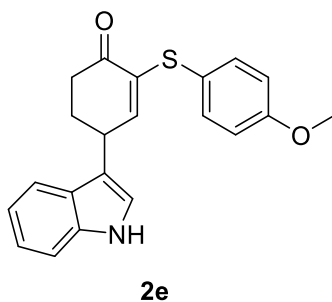
Pure **2d** was prepared with general procedure and isolated through a silica gel flash column (PE:EtOAc = 5:1) as yellow solid (80 mg, 76% yield); mp 186-188 °C

¹H NMR (400 MHz, CDCl₃) δ 9.11 (s, 1H), 7.57 (d, *J* = 7.9 Hz, 1H), 7.45 (d, *J* = 8.1 Hz, 1H), 7.27 (t, *J* = 6.4 Hz, 1H), 7.18 (t, *J* = 7.4 Hz, 1H), 7.13 (d, *J* = 8.4 Hz, 2H), 6.95 (dd, *J* = 16.4, 5.7 Hz, 3H), 6.20 (d, *J* = 10.0 Hz, 1H), 4.49 – 4.43 (m, 1H), 2.57 (q, *J* = 5.0, 4.5 Hz, 2H), 2.34 (dd, *J* = 12.9, 5.4 Hz, 1H), 2.24 – 2.15 (m, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 199.2, 150.4, 144.2, 137.6, 135.9, 130.8, 130.6, 129.6, 128.9, 126.6, 123.2, 121.3, 119.3, 111.5, 99.2, 37.0, 34.5, 30.1;

IR (neat): 1632, 1587, 851cm⁻¹;

HRMS (ESI-TOF) ([M+H]⁺) Calcd For C₂₀H₁₇NOS⁺: 354.0714; Found: 354.0715.



4-(1*H*-indol-3-yl)-2-((4-methoxyphenyl)thio)cyclohex-2-en-1-one (2e):

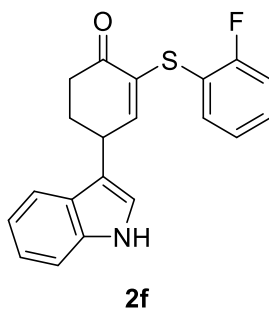
Pure **2e** was prepared with general procedure and isolated through a silica gel flash column (PE:EtOAc = 5:1) as yellow solid (98 mg, 94% yield); mp 149-151 °C

¹H NMR (400 MHz, CDCl₃) δ 9.04 (s, 1H), 7.65 (d, J = 7.6 Hz, 1H), 7.42 (d, J = 7.8 Hz, 1H), 7.24 (d, J = 8.1 Hz, 1H), 7.18 (t, J = 6.8 Hz, 1H), 7.09 – 7.03 (m, 2H), 6.94 (d, J = 9.9 Hz, 1H), 6.78 – 6.72 (m, 2H), 6.18 (d, J = 10.0 Hz, 1H), 4.52 (dd, J = 6.0, 2.7 Hz, 1H), 3.74 (s, 3H), 2.58 (s, 2H), 2.36 – 2.30 (m, 1H), 2.23 – 2.14 (m, 1H);

¹³C NMR (101 MHz, CDCl₃) δ 199.3, 157.7, 150.8, 143.7, 135.8, 130.6, 129.9, 129.5, 127.8, 122.9, 121.1, 119.4, 114.6, 111.4, 101.2, 55.4, 37.1, 34.6, 30.0;

IR (neat): 3045, 1632, 824cm⁻¹;

HRMS (ESI-TOF) ([M+H]⁺) Calcd For C₂₁H₂₀NO₂S⁺: 350.1209; Found: 350.1212.



2-((2-fluorophenyl)thio)-4-(1*H*-indol-3-yl)cyclohex-2-en-1-one (2f):

Pure **2f** was prepared with general procedure and isolated through a silica gel flash column (PE:EtOAc = 5:1) as yellow solid (85 mg, 84% yield); mp 184-186 °C

¹H NMR (400 MHz, CDCl₃) δ 9.21 (s, 1H), 7.62 (d, *J* = 7.8 Hz, 1H), 7.45 (d, *J* = 8.0 Hz, 1H), 7.28 – 7.25 (m, 1H), 7.19 (t, *J* = 7.4 Hz, 1H), 7.05 (d, *J* = 7.2 Hz, 2H), 6.95 (d, *J* = 10.2 Hz, 1H), 6.88 (t, *J* = 7.0 Hz, 1H), 6.73 (t, *J* = 7.7 Hz, 1H), 6.23 – 6.17 (m, 1H), 4.52 (dd, *J* = 7.0, 4.4 Hz, 1H), 2.61 – 2.56 (m, 2H), 2.36 (dd, *J* = 13.1, 5.2 Hz, 1H), 2.20 (dd, *J* = 12.9, 8.4 Hz, 1H);

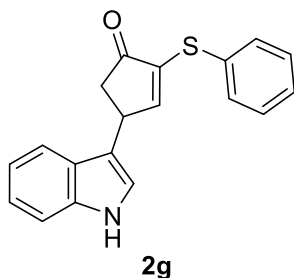
¹³C NMR (101 MHz, CDCl₃) δ 199.4, 159.1 (d, *J* = 242 Hz), 150.6, 144.5, 136.0, 130.7, 129.8, 127.5, 126.4 (d, *J* = 7 Hz), 126.1 (d, *J* = 17 Hz), 124.5 (d, *J* = 4 Hz), 123.1, 121.2, 119.3, 115.3 (d, *J* = 20 Hz), 111.5, 97.5, 37.0, 34.5, 30.0;

¹⁹F NMR (376 MHz, CDCl₃) δ -113.68;

IR (neat): 1632, 1590, 784cm⁻¹;

HRMS (ESI-TOF) ([M+H]⁺) Calcd For C₂₀H₁₇FNOS⁺: 338.1009; Found:

338.1016.



4-(1*H*-indol-3-yl)-2-(phenylthio)cyclopent-2-en-1-one (2g): Pure **2g**

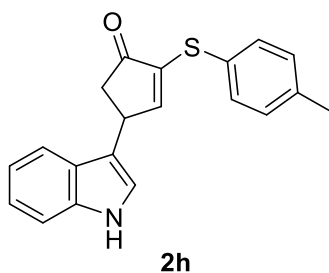
was prepared with general procedure and isolated through a silica gel flash column (PE:EtOAc = 5:1) as green solid (53 mg, 58% yield); mp 132-134 °C

¹H NMR (400 MHz, CDCl₃) δ 9.00 (s, 1H), 7.67 – 7.58 (m, 2H), 7.39 (d, J = 8.0 Hz, 1H), 7.26 – 7.22 (m, 1H), 7.17 (t, J = 7.2 Hz, 3H), 7.06 (d, J = 7.7 Hz, 3H), 6.38 – 6.32 (m, 1H), 4.96 – 4.91 (m, 1H), 2.86 (dd, J = 19.2, 7.1 Hz, 1H), 2.46 (d, J = 19.2 Hz, 1H);

¹³C NMR (101 MHz, CDCl₃) δ 210.1, 165.6, 142.1, 139.1, 136.2, 134.5, 130.0, 128.9, 125.6, 125.5, 124.9, 123.1, 121.1, 119.4, 111.5, 100.4, 41.5, 38.7;

IR (neat): 3048, 1632, 823cm⁻¹;

HRMS (ESI-TOF) ([M+H]⁺) Calcd For C₁₉H₁₆NOS⁺: 306.0947; Found: 306.0951.



4-(1*H*-indol-3-yl)-2-(*p*-tolylthio)cyclopent-2-en-1-one (2h): Pure **2h**

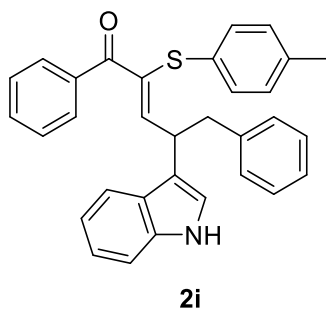
was prepared with general procedure and isolated through a silica gel flash column (PE:EtOAc = 5:1) as green solid (62 mg, 65% yield); mp 147-148 °C

¹H NMR (400 MHz, CDCl₃) δ 8.97 (s, 1H), 7.63 (t, *J* = 6.9 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 1H), 7.23 (d, *J* = 6.9 Hz, 1H), 7.16 (t, *J* = 7.4 Hz, 1H), 6.98 (s, 4H), 6.34 (d, *J* = 4.5 Hz, 1H), 4.97 – 4.91 (m, 1H), 2.86 (dd, *J* = 19.3, 7.1 Hz, 1H), 2.46 (d, *J* = 19.7 Hz, 1H), 2.26 (s, 3H);

¹³C NMR (101 MHz, CDCl₃) δ 209.5, 165.0, 141.9, 136.0, 135.3, 134.8, 134.7, 130.0, 129.6, 125.9, 123.1, 121.1, 119.5, 111.3, 101.1, 41.5, 38.7, 20.9;

IR (neat): 3046, 1632, 829cm⁻¹;

HRMS (ESI-TOF) ([M+H]⁺) Calcd For C₂₀H₁₈NOS⁺: 320.1104; Found: 320.1108.



(Z)-4-(1*H*-indol-3-yl)-1,5-diphenyl-2-(*p*-tolylthio)pent-2-en-1-one (2i):

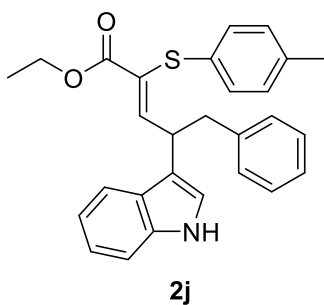
Pure **2i** was prepared with general procedure and isolated through a silica gel flash column (PE:EtOAc = 5:1) as yellow oil (99 mg, 70% yield);

¹H NMR (400 MHz, CDCl₃) δ 9.37 (s, 1H), 7.75 (d, J = 7.4 Hz, 2H), 7.59 – 7.53 (m, 2H), 7.42 – 7.31 (m, 4H), 7.22 – 7.16 (m, 2H), 7.14 (d, J = 5.2 Hz, 4H), 7.06 (d, J = 7.0 Hz, 2H), 6.89 (s, 3H), 6.78 (d, J = 15.2 Hz, 1H), 4.71 (q, J = 7.4 Hz, 1H), 3.21 (t, J = 6.7 Hz, 2H), 2.18 (s, 3H);

¹³C NMR (101 MHz, CDCl₃) δ 190.9, 148.0, 143.4, 138.1, 137.2, 136.0, 135.2, 134.4, 133.2, 129.9, 129.5, 129.0, 128.6, 128.6, 128.5, 126.8, 126.6, 126.0, 122.7, 120.8, 119.4, 111.3, 100.8, 42.1, 40.5, 20.8;

IR (neat): 1632, 1564, 874cm⁻¹;

HRMS (ESI-TOF) ([M+H]⁺) Calcd For C₃₂H₂₈NOS⁺: 474.1886; Found: 474.1886.



ethyl (Z)-4-(1H-indol-3-yl)-5-phenyl-2-(p-tolylthio)pent-2-enoate (2j):

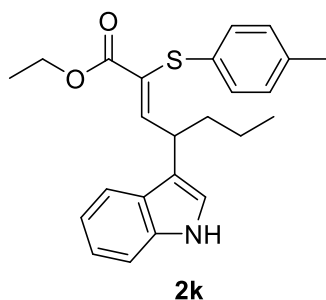
Pure **2j** was prepared with general procedure and isolated through a silica gel flash column (PE:EtOAc = 5:1) as yellow oil (95 mg, 72% yield);

¹H NMR (400 MHz, CDCl₃) δ 8.05 (s, 1H), 7.74 (d, J = 7.9 Hz, 1H), 7.37 (d, J = 9.3 Hz, 1H), 7.29 (s, 1H), 7.23 (s, 1H), 7.14 (d, J = 4.6 Hz, 4H), 7.00 (d, J = 3.3 Hz, 2H), 6.96 (d, J = 8.0 Hz, 2H), 6.80 (d, J = 8.0 Hz, 2H), 5.76 (d, J = 16.7 Hz, 1H), 4.35 (d, J = 7.0 Hz, 1H), 4.13 (d, J = 7.1 Hz, 2H), 3.30 (dd, J = 7.5, 3.5 Hz, 2H), 2.27 (s, 3H), 1.24 (t, J = 7.1 Hz, 3H);

¹³C NMR (101 MHz, CDCl₃) δ 166.7, 150.1, 139.5, 137.2, 136.2, 132.4, 129.9, 129.1, 128.2, 127.9, 126.2, 126.1, 124.2, 123.2, 121.3, 121.2, 120.3, 119.9, 111.2, 60.2, 42.4, 40.1, 20.9, 14.2;

IR (neat): 3053, 1632, 804cm⁻¹;

HRMS (ESI-TOF) ([M+H]⁺) Calcd For C₂₈H₂₈NO₂S⁺: 442.1835; Found: 442.1835.



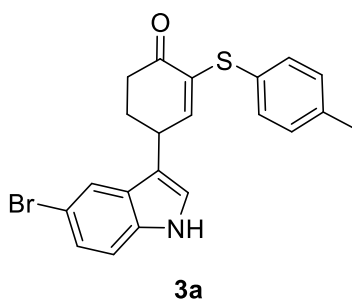
ethyl (Z)-4-(1H-indol-3-yl)-2-(p-tolylthio)hept-2-enoate (2k): Pure **2k** was prepared with general procedure and isolated through a silica gel flash column (PE:EtOAc = 8:1) as yellow oil (74 mg, 63% yield);

¹H NMR (400 MHz, CDCl₃) δ 8.22 (s, 1H), 7.67 (d, J = 8.0 Hz, 1H), 7.34 – 7.29 (m, 2H), 7.22 (d, J = 7.2 Hz, 1H), 7.12 (t, J = 7.5 Hz, 1H), 7.03 (s, 4H), 5.76 (dd, J = 15.7, 1.4 Hz, 1H), 4.14 (d, J = 7.2 Hz, 2H), 4.07 – 4.02 (m, 1H), 2.29 (s, 3H), 2.02 – 1.94 (m, 2H), 1.30 (d, J = 8.6 Hz, 2H), 1.25 (s, 3H), 0.87 (t, J = 7.3 Hz, 3H);

¹³C NMR (101 MHz, CDCl₃) δ 167.0, 151.2, 137.2, 136.1, 132.9, 129.9, 127.6, 126.3, 123.5, 123.2, 122.4, 121.9, 120.6, 120.3, 119.8, 111.2, 60.2, 40.1, 35.9, 21.0, 21.0, 14.2, 13.9;

IR (neat): 3028, 1632, 805cm⁻¹;

HRMS (ESI-TOF) ([M+H]⁺) Calcd For C₂₄H₂₈NO₂S⁺: 394.1835; Found: 394.1842.



4-(5-bromo-1*H*-indol-3-yl)-2-(*p*-tolylthio)cyclohex-2-en-1-one (3a):

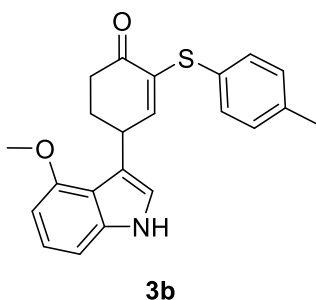
Pure **3a** was prepared with general procedure and isolated through a silica gel flash column (PE:EtOAc = 5:1) as yellow oil (69 mg, 56% yield);

¹H NMR (400 MHz, CDCl₃) δ 8.93 (s, 1H), 7.74 (s, 1H), 7.35 – 7.28 (m, 2H), 7.00 (d, *J* = 7.9 Hz, 2H), 6.92 (d, *J* = 8.3 Hz, 3H), 6.19 (d, *J* = 10.0 Hz, 1H), 4.49 – 4.43 (m, 1H), 2.55 (t, *J* = 5.3 Hz, 2H), 2.33 (dd, *J* = 13.6, 5.3 Hz, 1H), 2.27 (s, 3H), 2.16 (dd, *J* = 13.9, 7.8 Hz, 1H);

¹³C NMR (101 MHz, CDCl₃) δ 199.3, 150.4, 145.2, 134.9, 134.8, 134.5, 131.8, 130.7, 129.8, 125.9, 125.6, 122.0, 114.6, 112.9, 100.0, 37.0, 34.5, 29.9, 20.9;

IR (neat): 3023, 1633, 830⁻¹;

HRMS (ESI-TOF) ([M+H]⁺) Calcd For C₂₁H₁₉BrNOS⁺: 412.0365; Found: 412.0358.



4-(4-methoxy-1*H*-indol-3-yl)-2-(*p*-tolylthio)cyclohex-2-en-1-one (3b):

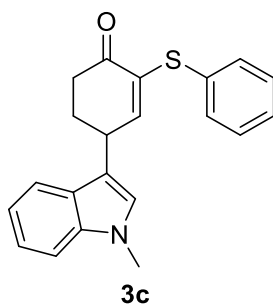
Pure **3b** was prepared with general procedure and isolated through a silica gel flash column (PE:EtOAc = 5:1) as yellow oil (62 mg, 57% yield);

¹H NMR (400 MHz, CDCl₃) δ 9.03 (s, 1H), 7.14 (t, J = 7.9 Hz, 1H), 7.02 (d, J = 11.2 Hz, 5H), 6.91 (d, J = 9.9 Hz, 1H), 6.56 (d, J = 7.7 Hz, 1H), 6.13 (d, J = 10.1 Hz, 1H), 4.51 (d, J = 10.7 Hz, 1H), 3.73 (s, 3H), 2.55 – 2.50 (m, 2H), 2.33 – 2.28 (m, 1H), 2.26 (s, 3H), 2.17 – 2.10 (m, 1H);

¹³C NMR (101 MHz, CDCl₃) δ 199.4, 154.4, 151.1, 142.9, 137.5, 137.0, 134.2, 130.5, 129.3, 125.9, 123.6, 119.3, 104.7, 101.9, 99.2, 55.7, 37.1, 34.3, 30.1, 20.9;

IR (neat): 3022, 1577, 830cm⁻¹;

HRMS (ESI-TOF) ([M+H]⁺) Calcd For C₂₂H₂₂NO₂S⁺: 364.1366; Found: 364.1369.



4-(1-methyl-1H-indol-3-yl)-2-(phenylthio)cyclohex-2-en-1-one (3c):

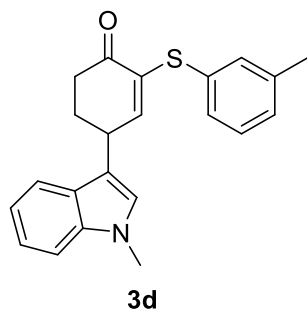
Pure **3c** was prepared with general procedure and isolated through a silica gel flash column (PE:EtOAc = 5:1) as yellow oil (71 mg, 71% yield);

¹H NMR (400 MHz, CDCl₃) δ 7.62 (d, J = 7.8 Hz, 1H), 7.39 (d, J = 8.2 Hz, 1H), 7.31 (d, J = 7.0 Hz, 1H), 7.16 (t, J = 8.7 Hz, 3H), 7.04 (d, J = 17.7 Hz, 4H), 6.18 (dd, J = 10.1, 3.1 Hz, 1H), 4.65 – 4.60 (m, 1H), 3.83 (s, 3H), 2.58 (dd, J = 12.7, 4.8 Hz, 2H), 2.33 (dd, J = 12.1, 5.8 Hz, 1H), 2.20 (dd, J = 13.9, 3.8 Hz, 1H);

¹³C NMR (101 MHz, CDCl₃) δ 198.2, 151.6, 145.3, 139.3, 137.6, 129.9, 129.3, 128.9, 125.3, 124.8, 122.9, 121.1, 119.6, 109.5, 99.5, 38.0, 35.2, 31.5, 30.1;

IR (neat): 1654, 1579, 741cm⁻¹;

HRMS (ESI-TOF) ([M+H]⁺) calcd for C₂₁H₂₀NOS⁺: 334.1260; found: 334.1268.



4-(1-methyl-1*H*-indol-3-yl)-2-(*m*-tolylthio)cyclohex-2-en-1-one (3d):

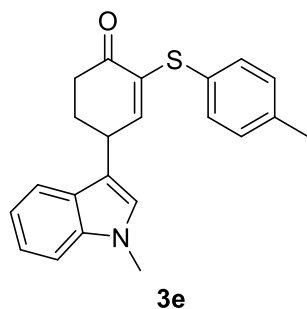
Pure **3d** was prepared with general procedure and isolated through a silica gel flash column (PE:EtOAc = 5:1) as yellow oil (78 mg, 75% yield);

¹H NMR (400 MHz, CDCl₃) δ 7.60 (d, *J* = 7.7 Hz, 1H), 7.37 (d, *J* = 7.9 Hz, 1H), 7.30 (d, *J* = 6.9 Hz, 1H), 7.17 (t, *J* = 7.4 Hz, 1H), 7.00 (d, *J* = 13.9 Hz, 2H), 6.91 (s, 1H), 6.86 (d, *J* = 7.3 Hz, 1H), 6.73 (d, *J* = 7.5 Hz, 1H), 6.18 (d, *J* = 10.4 Hz, 1H), 4.65 – 4.59 (m, 1H), 3.81 (s, 3H), 2.60 – 2.51 (m, 2H), 2.32 (dd, *J* = 12.4, 6.3 Hz, 1H), 2.23 (s, 3H), 2.18 (d, *J* = 4.8 Hz, 1H);

¹³C NMR (101 MHz, CDCl₃) δ 198.2, 151.6, 145.2, 139.0, 138.6, 129.9, 129.4, 128.7, 125.9, 125.7, 122.8, 122.3, 121.0, 119.6, 109.4, 99.6, 38.0, 35.2, 31.5, 30.1, 21.4;

IR (neat): 3050, 1591, 744cm⁻¹;

HRMS (ESI-TOF) ([M+H]⁺) Calcd For C₂₂H₂₂NOS⁺: 348.1417; Found: 348.1422.



4-(1-methyl-1*H*-indol-3-yl)-2-(*p*-tolylthio)cyclohex-2-en-1-one (3e):

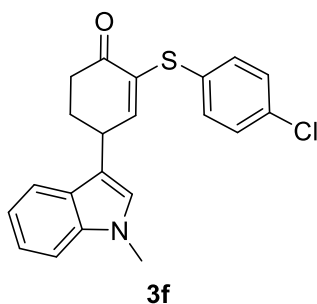
Pure **3e** was prepared with general procedure and isolated through a silica gel flash column (PE:EtOAc = 5:1) as yellow oil (83 mg, 80% yield);

¹H NMR (400 MHz, CDCl₃) δ 7.60 (d, *J* = 8.3 Hz, 1H), 7.36 (d, *J* = 7.9 Hz, 1H), 7.29 (d, *J* = 7.5 Hz, 1H), 7.19 – 7.14 (m, 1H), 6.94 (dt, *J* = 20.7, 10.5 Hz, 5H), 6.16 (d, *J* = 9.6 Hz, 1H), 4.67 – 4.58 (m, 1H), 3.84 – 3.77 (m, 3H), 2.64 – 2.54 (m, 2H), 2.37 – 2.28 (m, 1H), 2.23 (s, 3H), 2.21 – 2.15 (m, 1H);

¹³C NMR (101 MHz, CDCl₃) δ 198.2, 151.7, 145.1, 137.5, 135.6, 134.6, 129.9, 129.6, 129.3, 125.5, 122.8, 121.0, 119.6, 109.4, 100.0, 38.0, 35.1, 31.4, 30.1, 20.9;

IR (neat): 3041, 1591, 744cm⁻¹;

HRMS (ESI-TOF) ([M+H]⁺) Calcd For C₂₂H₂₂NOS⁺: 348.1417; Found: 348.1421.



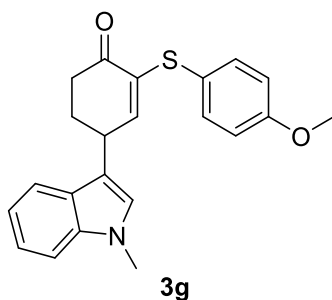
2-((4-chlorophenyl)thio)-4-(1-methyl-1*H*-indol-3-yl)cyclohex-2-en-1-one (3f): Pure **3f** was prepared with general procedure and isolated through a silica gel flash column (PE:EtOAc = 5:1) as yellow oil (73 mg, 66% yield);

¹H NMR (400 MHz, CDCl₃) δ 7.56 (d, *J* = 7.8 Hz, 1H), 7.38 (d, *J* = 8.2 Hz, 1H), 7.31 (t, *J* = 7.6 Hz, 1H), 7.18 (t, *J* = 7.4 Hz, 1H), 7.10 (d, *J* = 6.9 Hz, 2H), 6.96 (d, *J* = 12.3 Hz, 1H), 6.91 (d, *J* = 6.8 Hz, 2H), 6.17 (dd, *J* = 10.3, 3.1 Hz, 1H), 4.57 (dd, *J* = 7.6, 3.8 Hz, 1H), 3.82 (d, *J* = 1.7 Hz, 3H), 2.58 (d, *J* = 18.2 Hz, 2H), 2.35 – 2.24 (m, 1H), 2.18 (d, *J* = 13.5 Hz, 1H);

¹³C NMR (101 MHz, CDCl₃) δ 198.0, 151.3, 145.3, 137.9, 137.6, 130.5, 130.0, 129.1, 128.9, 126.5, 123.0, 121.3, 119.4, 109.5, 99.0, 38.0, 35.1, 31.5, 30.1;

IR (neat): 3052, 1682, 745, cm⁻¹;

HRMS (ESI-TOF) ([M+H]⁺) Calcd For C₂₁H₁₉ClNOS⁺: 368.0870; Found: 368.0874.



2-((4-methoxyphenyl)thio)-4-(1-methyl-1*H*-indol-3-yl)cyclohex-2-en-

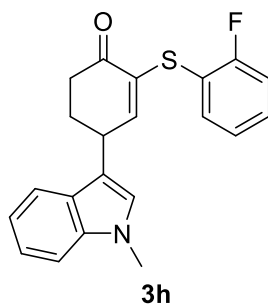
1-one (3g): Pure **3g** was prepared with general procedure and isolated through a silica gel flash column (PE:EtOAc = 5:1) as yellow oil (93 mg, 85% yield);

¹H NMR (400 MHz, CDCl₃) δ 7.65 (d, J = 7.9 Hz, 1H), 7.36 (s, 1H), 7.32 – 7.27 (m, 1H), 7.19 (t, J = 7.6 Hz, 1H), 7.01 (dt, J = 9.3, 2.1 Hz, 3H), 6.73 (dd, J = 8.7, 1.7 Hz, 2H), 6.20 (dd, J = 10.2, 3.0 Hz, 1H), 4.72 – 4.61 (m, 1H), 3.81 (d, J = 1.7 Hz, 3H), 3.73 (d, J = 1.6 Hz, 3H), 2.60 (dd, J = 12.4, 4.9 Hz, 2H), 2.31 (dd, J = 12.5, 6.3 Hz, 1H), 2.18 (d, J = 11.9 Hz, 1H);

¹³C NMR (101 MHz, CDCl₃) δ 198.3, 157.6, 151.8, 144.8, 137.5, 129.9, 129.8, 129.4, 127.6, 122.8, 121.0, 119.6, 114.6, 109.4, 101.1, 55.3, 38.0, 35.2, 31.4, 30.1;

IR (neat): 2934, 1592, 1030cm⁻¹;

HRMS (ESI-TOF) ([M+H]⁺) Calcd For C₂₂H₂₂NO₂S⁺: 364.1366; Found: 364.1371.



2-((2-fluorophenyl)thio)-4-(1-methyl-1*H*-indol-3-yl)cyclohex-2-en-1-

one (3h): Pure **3h** was prepared with general procedure and isolated through a silica gel flash column (PE:EtOAc = 5:1) as yellow oil (60 mg, 57% yield);

¹H NMR (400 MHz, CDCl₃) δ 7.60 (d, J = 7.6 Hz, 1H), 7.38 (d, J = 8.1 Hz, 1H), 7.31 (t, J = 7.6 Hz, 1H), 7.18 (t, J = 7.4 Hz, 1H), 7.04 (s, 1H), 7.03 – 6.96 (m, 2H), 6.85 (t, J = 7.2 Hz, 1H), 6.67 (t, J = 7.8 Hz, 1H), 6.19 (d, J = 10.1 Hz, 1H), 4.70 – 4.64 (m, 1H), 3.82 (s, 3H), 2.60 (dd, J = 11.5, 5.0 Hz, 2H), 2.33 (dd, J = 12.1, 6.9 Hz, 1H), 2.20 (dd, J = 13.3, 3.2 Hz, 1H);

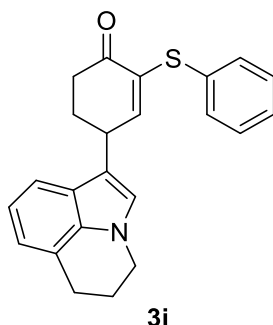
¹³C NMR (101 MHz, CDCl₃) δ 198.2, 158.8 (d, J =243 Hz), 151.6, 145.6, 137.7, 130.1, 129.2, 127.5 (d, J =2 Hz), 126.4 (d, J =8 Hz), 124.4(d, J =3 Hz), 123.0, 121.2, 119.5, 115.3 (d, J =21 Hz), 109.4, 97.5, 38.0, 35.2, 31.5, 30.1;

¹⁹F NMR (376 MHz, CDCl₃) δ -113.72;

IR (neat): 2891, 1632, 873cm⁻¹;

HRMS (ESI-TOF) ([M+H]⁺) Calcd For C₂₁H₁₉FNOS⁺: 352.1166; Found:

352.1172.



4-(5,6-dihydro-4H-pyrrolo[3,2,1-ij]quinolin-1-yl)-2-

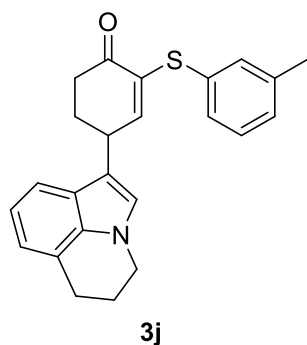
(phenylthio)cyclohex-2-en-1-one (3i): Pure **3i** was prepared with general procedure and isolated through a silica gel flash column (PE:EtOAc = 8:1) as yellow oil (66 mg, 61% yield);

¹H NMR (400 MHz, CDCl₃) δ 7.39 (d, J = 7.8 Hz, 1H), 7.17 (d, J = 7.2 Hz, 1H), 7.14 (s, 1H), 7.08 – 6.99 (m, 5H), 6.96 (s, 1H), 6.20 – 6.14 (m, 1H), 4.59 – 4.53 (m, 1H), 4.15 (dt, J = 11.9, 5.4 Hz, 2H), 3.05 – 3.00 (m, 2H), 2.57 (dd, J = 12.4, 3.8 Hz, 2H), 2.29 (d, J = 5.7 Hz, 2H), 2.27 – 2.15 (m, 2H);

¹³C NMR (101 MHz, CDCl₃) δ 198.3, 151.4, 144.1, 139.5, 134.6, 130.0, 128.8, 127.6, 125.4, 124.7, 122.0, 121.1, 120.0, 116.9, 98.7, 43.8, 37.9, 34.9, 30.0, 24.5, 22.9;

IR (neat): 3051, 1632, 780cm⁻¹;

HRMS (ESI-TOF) ([M+H]⁺) Calcd For C₂₃H₂₂NOS⁺: 360.1417; Found: 360.1421.



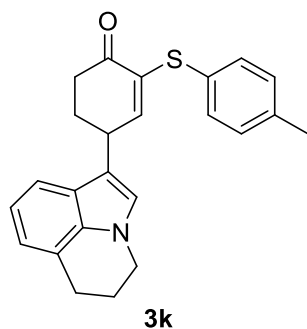
4-(5,6-dihydro-4H-pyrrolo[3,2,1-*ij*]quinolin-1-yl)-2-(*m*-tolylthio)cyclohex-2-en-1-one (3j): Pure **3j** was prepared with general procedure and isolated through a silica gel flash column (PE:EtOAc = 8:1) as yellow oil (71 mg, 63% yield);

¹H NMR (400 MHz, CDCl₃) δ 7.40 (d, *J* = 7.8 Hz, 1H), 7.06 (dd, *J* = 16.7, 8.5 Hz, 2H), 7.00 (d, *J* = 6.1 Hz, 1H), 6.96 (s, 2H), 6.87 (d, *J* = 7.2 Hz, 1H), 6.77 (d, *J* = 7.8 Hz, 1H), 6.17 (d, *J* = 10.2 Hz, 1H), 4.57 (dd, *J* = 7.6, 1.7 Hz, 1H), 4.15 (dt, *J* = 12.2, 5.8 Hz, 2H), 3.03 (s, 2H), 2.62 – 2.54 (m, 2H), 2.33 (d, *J* = 12.9 Hz, 1H), 2.30 – 2.27 (m, 2H), 2.25 (s, 3H), 2.21 (d, *J* = 12.2 Hz, 1H);

¹³C NMR (101 MHz, CDCl₃) δ 198.3, 151.5, 144.0, 139.3, 138.5, 134.6, 130.0, 128.7, 127.7, 126.0, 125.7, 122.4, 121.9, 121.1, 119.9, 116.9, 98.8, 43.8, 38.0, 34.9, 30.0, 24.6, 22.9, 21.4;

IR (neat): 3047, 1632, 779cm⁻¹;

HRMS (ESI-TOF) ([M+H]⁺) Calcd For C₂₄H₂₄NOS⁺: 374.1573; Found: 374.1572.



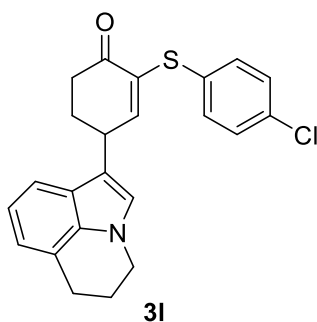
4-(5,6-dihydro-4H-pyrrolo[3,2,1-*ij*]quinolin-1-yl)-2-(*p*-tolylthio)cyclohex-2-en-1-one (3k): Pure **3k** was prepared with general procedure and isolated through a silica gel flash column (PE:EtOAc = 8:1) as yellow oil (84 mg, 75% yield);

¹H NMR (400 MHz, CDCl₃) δ 7.40 (d, J = 7.9 Hz, 1H), 7.07 (t, J = 7.5 Hz, 1H), 7.00 – 6.94 (m, 6H), 6.17 (d, J = 10.0 Hz, 1H), 4.61 – 4.55 (m, 1H), 4.15 (dq, J = 11.7, 6.1 Hz, 2H), 3.03 (t, J = 5.7 Hz, 2H), 2.61 – 2.50 (m, 2H), 2.34 – 2.30 (m, 1H), 2.28 (s, 2H), 2.25 (s, 3H), 2.20 (d, J = 11.6 Hz, 1H);

¹³C NMR (101 MHz, CDCl₃) δ 198.3, 151.5, 143.9, 135.8, 134.6, 134.5, 130.0, 129.6, 127.7, 125.6, 121.9, 121.0, 120.0, 116.9, 99.3, 43.8, 38.0, 34.9, 30.0, 24.6, 22.9, 20.9;

IR (neat): 1632, 1577, 805cm⁻¹;

HRMS (ESI-TOF) ([M+H]⁺) Calcd For C₂₄H₂₄NOS⁺: 374.1573; Found: 374.1572.



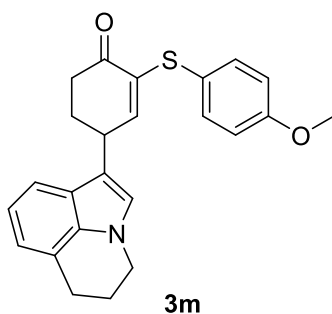
2-((4-chlorophenyl)thio)-4-(5,6-dihydro-4H-pyrrolo[3,2,1-*ij*]quinolin-1-yl)cyclohex-2-en-1-one (3l): Pure **3l** was prepared with general procedure and isolated through a silica gel flash column (PE:EtOAc = 8:1) as yellow oil (71 mg, 60% yield);

¹H NMR (400 MHz, CDCl₃) δ 7.36 (d, *J* = 7.8 Hz, 1H), 7.12 (d, *J* = 8.6 Hz, 2H), 7.08 (d, *J* = 7.7 Hz, 1H), 7.00 (d, *J* = 7.1 Hz, 1H), 6.97 (s, 2H), 6.95 (s, 1H), 6.20 – 6.15 (m, 1H), 4.56 – 4.50 (m, 1H), 4.16 (dt, *J* = 11.6, 5.7 Hz, 2H), 3.04 (t, *J* = 5.9 Hz, 2H), 2.58 (dd, *J* = 13.3, 4.7 Hz, 2H), 2.31 (s, 1H), 2.29 (d, *J* = 5.5 Hz, 2H), 2.19 (d, *J* = 12.5 Hz, 1H);

¹³C NMR (101 MHz, CDCl₃) δ 198.1, 151.1, 144.1, 138.2, 134.6, 130.4, 130.1, 128.9, 127.4, 126.6, 122.1, 121.3, 120.1, 116.7, 98.2, 43.8, 37.9, 34.8, 30.0, 24.5, 22.9;

IR (neat): 1632, 1577, 816cm⁻¹;

HRMS (ESI-TOF) ([M+H]⁺) Calcd For C₂₃H₂₁ClNOS⁺: 394.1027; Found: 394.1028.



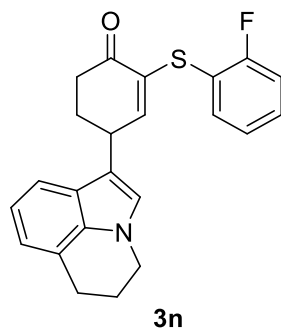
4-(5,6-dihydro-4H-pyrrolo[3,2,1-ij]quinolin-1-yl)-2-((4-methoxyphenyl)thio)cyclohex-2-en-1-one (3m): Pure **3m** was prepared with general procedure and isolated through a silica gel flash column (PE:EtOAc = 8:1) as yellow oil (88 mg, 75% yield);

¹H NMR (400 MHz, CDCl₃) δ 7.43 (d, J = 7.9 Hz, 1H), 7.09 (d, J = 7.2 Hz, 1H), 7.05 (d, J = 8.9 Hz, 2H), 6.98 (d, J = 7.6 Hz, 2H), 6.74 (d, J = 8.0 Hz, 2H), 6.18 (d, J = 10.0 Hz, 1H), 4.64 – 4.57 (m, 1H), 4.13 (tt, J = 12.1, 6.4 Hz, 2H), 3.73 (s, 3H), 3.01 (t, J = 5.5 Hz, 2H), 2.61 – 2.51 (m, 2H), 2.28 (s, 1H), 2.26 (d, J = 5.5 Hz, 2H), 2.18 (d, J = 10.9 Hz, 1H);

¹³C NMR (101 MHz, CDCl₃) δ 198.3, 157.6, 151.6, 143.6, 134.5, 130.0, 127.8, 127.7, 121.9, 121.0, 119.9, 116.8, 114.6, 100.4, 55.3, 43.8, 38.0, 34.9, 30.0, 24.6, 22.9;

IR (neat): 3038, 1632, 828cm⁻¹;

HRMS (ESI-TOF) ([M+H]⁺) Calcd For C₂₄H₂₄NO₂S⁺: 390.1522; Found: 390.1525.



4-(5,6-dihydro-4H-pyrrolo[3,2,1-*ij*]quinolin-1-yl)-2-((2-fluorophenyl)thio)cyclohex-2-en-1-one (3n): Pure **3n** was prepared with general procedure and isolated through a silica gel flash column (PE:EtOAc = 8:1) as yellow oil (62 mg, 55% yield);

¹H NMR (400 MHz, CDCl₃) δ 7.40 (d, J = 7.9 Hz, 1H), 7.09 (t, J = 7.5 Hz, 1H), 7.07 – 7.04 (m, 1H), 7.04 – 6.99 (m, 2H), 6.97 (d, J = 10.3 Hz, 1H), 6.87 (t, J = 7.3 Hz, 1H), 6.74 (t, J = 7.7 Hz, 1H), 6.22 – 6.16 (m, 1H), 4.65 – 4.59 (m, 1H), 4.17 (dq, J = 15.5, 5.9 Hz, 2H), 3.03 (t, J = 5.8 Hz, 2H), 2.60 (dd, J = 10.8, 4.7 Hz, 2H), 2.30 (s, 1H), 2.28 (d, J = 5.4 Hz, 2H), 2.21 (dd, J = 13.0, 3.7 Hz, 1H);

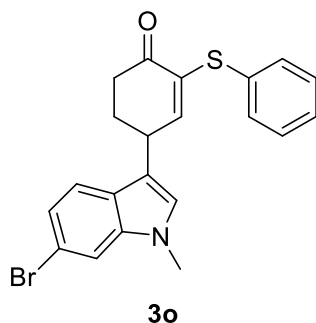
¹³C NMR (101 MHz, CDCl₃) δ 198.2, 159.1 (d, J = 242 Hz), 151.1, 144.4, 134.7, 130.2, 127.6, 127.6, 126.5 (d, J = 17 Hz), 126.4 (d, J = 7 Hz), 124.4 (d, J = 3 Hz), 122.0, 121.2, 120.1, 116.8, 115.2 (d, J = 21 Hz), 96.7, 44.0, 37.9, 34.8, 29.9, 24.5, 22.9;

¹⁹F NMR (376 MHz, CDCl₃) δ -113.81;

IR (neat): 1633, 1467, 830cm⁻¹;

HRMS (ESI-TOF) ([M+H]⁺) Calcd For C₂₃H₂₁FNOS⁺: 378.1322; Found:

378.1324.



4-(6-bromo-1-methyl-1H-indol-3-yl)-2-(phenylthio)cyclohex-2-en-1-

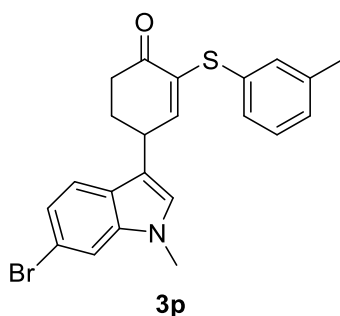
one (3o): Pure **3o** was prepared with general procedure and isolated through a silica gel flash column (PE:EtOAc = 5:1) as yellow oil (72 mg, 58% yield);

¹H NMR (400 MHz, CDCl₃) δ 7.52 (s, 1H), 7.44 (d, J = 8.4 Hz, 1H), 7.26 (d, J = 8.0 Hz, 1H), 7.15 (t, J = 7.5 Hz, 2H), 7.06 (t, J = 7.3 Hz, 1H), 6.98 (s, 2H), 6.96 (s, 1H), 6.17 (dd, J = 10.0, 2.5 Hz, 1H), 4.61 – 4.55 (m, 1H), 3.78 (s, 3H), 2.56 (dd, J = 13.3, 4.6 Hz, 2H), 2.30 (dq, J = 12.6, 7.6 Hz, 1H), 2.18 (d, J = 12.9 Hz, 1H);

¹³C NMR (101 MHz, CDCl₃) δ 197.9, 150.9, 145.8, 138.7, 138.3, 130.1, 128.9, 128.2, 125.4, 125.0, 124.4, 120.8, 116.4, 112.6, 100.2, 37.9, 35.2, 31.6, 30.0;

IR (neat): 3023, 1632, 828cm⁻¹;

HRMS (ESI-TOF) ([M+H]⁺) Calcd For C₂₁H₁₉BrNOS⁺: 412.0365; Found: 412.0367.



4-(6-bromo-1-methyl-1*H*-indol-3-yl)-2-(*m*-tolylthio)cyclohex-2-en-1-

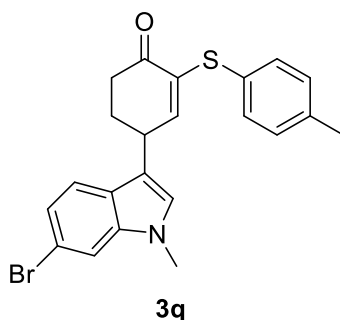
one (3p): Pure **3p** was prepared with general procedure and isolated through a silica gel flash column (PE:EtOAc = 5:1) as yellow oil (77 mg, 60% yield);

¹H NMR (400 MHz, CDCl₃) δ 7.52 (s, 1H), 7.44 (d, *J* = 8.4 Hz, 1H), 7.26 – 7.24 (m, 1H), 7.01 (d, *J* = 7.9 Hz, 1H), 6.97 (d, *J* = 10.1 Hz, 1H), 6.87 (s, 2H), 6.70 (d, *J* = 7.7 Hz, 1H), 6.20 – 6.15 (m, 1H), 4.61 – 4.54 (m, 1H), 3.78 (s, 3H), 2.61 – 2.53 (m, 2H), 2.30 (dd, *J* = 12.3, 5.2 Hz, 1H), 2.23 (s, 3H), 2.18 (d, *J* = 13.4 Hz, 1H);

¹³C NMR (101 MHz, CDCl₃) δ 197.9, 151.0, 145.8, 138.7, 138.5, 138.3, 130.1, 128.8, 128.3, 126.0, 124.3, 122.4, 120.9, 116.4, 112.6, 100.3, 37.9, 35.2, 31.6, 30.0, 21.4;

IR (neat): 3050, 1632, 829 cm⁻¹;

HRMS (ESI-TOF) ([M+H]⁺) Calcd For C₂₂H₂₁BrNOS⁺: 426.0522; Found: 426.0519.



4-(6-bromo-1-methyl-1H-indol-3-yl)-2-(p-tolylthio)cyclohex-2-en-1-

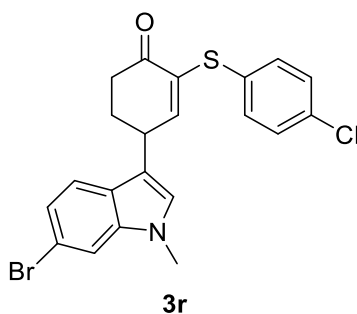
one (3q): Pure **3q** was prepared with general procedure and isolated through a silica gel flash column (PE:EtOAc = 5:1) as light yellow oil (83 mg, 65% yield);

¹H NMR (400 MHz, CDCl₃) δ 7.51 (s, 1H), 7.44 (d, J = 9.0 Hz, 1H), 7.25 (s, 1H), 6.98 (s, 1H), 6.96 (s, 2H), 6.88 (d, J = 7.4 Hz, 2H), 6.17 (d, J = 10.1 Hz, 1H), 4.62 – 4.56 (m, 1H), 3.76 (s, 3H), 2.61 – 2.52 (m, 2H), 2.29 (dd, J = 12.5, 5.5 Hz, 1H), 2.24 (s, 3H), 2.18 (d, J = 12.5 Hz, 1H);

¹³C NMR (101 MHz, CDCl₃) δ 198.0, 151.1, 145.7, 138.3, 135.1, 134.9, 130.0, 129.7, 128.2, 125.6, 124.3, 120.9, 116.4, 112.6, 100.8, 37.9, 35.2, 31.6, 30.0, 20.9;

IR (neat): 3024, 1632, 823cm⁻¹;

HRMS (ESI-TOF) ([M+H]⁺) Calcd For C₂₂H₂₁BrNOS⁺: 426.0522; Found: 426.0521.



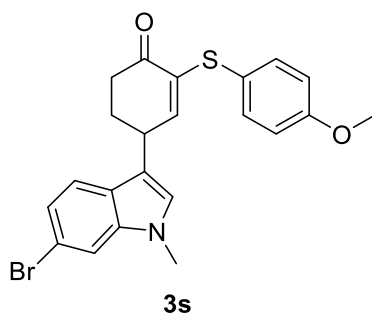
4-(6-bromo-1-methyl-1*H*-indol-3-yl)-2-((4-chlorophenyl)thio)cyclohex-2-en-1-one (3r): Pure **3r** was prepared with general procedure and isolated through a silica gel flash column (PE:EtOAc = 5:1) as yellow oil (68 mg, 51% yield);

¹H NMR (400 MHz, CDCl₃) δ 7.53 (s, 1H), 7.39 (d, *J* = 8.3 Hz, 1H), 7.25 (s, 1H), 7.11 (d, *J* = 7.2 Hz, 2H), 6.94 (d, *J* = 10.3 Hz, 1H), 6.88 (d, *J* = 7.2 Hz, 2H), 6.17 (d, *J* = 9.8 Hz, 1H), 4.56 – 4.50 (m, 1H), 3.78 (s, 3H), 2.61 – 2.53 (m, 2H), 2.31 (td, *J* = 12.7, 4.4 Hz, 1H), 2.18 (d, *J* = 12.7 Hz, 1H);

¹³C NMR (101 MHz, CDCl₃) δ 197.8, 150.6, 146.0, 138.4, 137.4, 130.8, 130.2, 129.0, 128.0, 126.5, 124.5, 120.6, 116.6, 112.7, 99.7, 37.9, 35.1, 31.6, 30.0;

IR (neat): 3023, 1632, 824cm⁻¹;

HRMS (ESI-TOF) ([M+H]⁺) Calcd For C₂₁H₁₈BrClNOS⁺: 445.9976; Found: 445.9974.



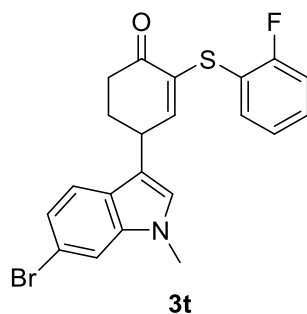
4-(6-bromo-1-methyl-1H-indol-3-yl)-2-((4-methoxyphenyl)thio)cyclohex-2-en-1-one (3s): Pure **3s** was prepared with general procedure and isolated through a silica gel flash column (PE:EtOAc = 5:1) as yellow oil (90 mg, 68% yield);

¹H NMR (400 MHz, CDCl₃) δ 7.50 (s, 1H), 7.47 (d, J = 8.4 Hz, 1H), 7.26 – 7.23 (m, 1H), 6.98 (s, 1H), 6.96 (s, 2H), 6.72 (d, J = 8.8 Hz, 2H), 6.18 (dd, J = 10.2, 2.7 Hz, 1H), 4.65 – 4.58 (m, 1H), 3.74 (s, 3H), 3.72 (s, 3H), 2.57 (dd, J = 13.3, 4.1 Hz, 2H), 2.27 (dt, J = 12.5, 6.2 Hz, 1H), 2.15 (d, J = 14.6 Hz, 1H);

¹³C NMR (101 MHz, CDCl₃) δ 197.9, 157.8, 151.1, 145.4, 138.2, 130.0, 129.2, 128.2, 127.8, 124.2, 120.8, 116.3, 114.7, 112.5, 101.9, 55.3, 37.9, 35.2, 31.5, 30.0;

IR (neat): 1632, 1577, 874cm⁻¹;

HRMS (ESI-TOF) ([M+H]⁺) Calcd For C₂₂H₂₁BrNO₂S⁺: 442.0471; Found: 442.0474.



4-(6-bromo-1-methyl-1*H*-indol-3-yl)-2-((2-fluorophenyl)sulfinyl)cyclohex-2-en-1-one (3t): Pure **3t** was prepared with general procedure and isolated through a silica gel flash column (PE:EtOAc = 5:1) as yellow oil (62 mg, 48% yield);

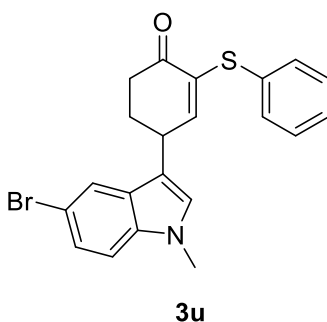
¹H NMR (400 MHz, CDCl₃) δ 7.53 (s, 1H), 7.44 (d, *J* = 8.4 Hz, 1H), 7.27 (d, *J* = 4.2 Hz, 1H), 7.05 (dd, *J* = 14.7, 7.8 Hz, 2H), 6.97 (d, *J* = 10.3 Hz, 1H), 6.86 (d, *J* = 7.1 Hz, 1H), 6.65 (t, *J* = 7.7 Hz, 1H), 6.21 – 6.17 (m, 1H), 4.66 – 4.61 (m, 1H), 3.79 (s, 3H), 2.59 (dd, *J* = 10.9, 3.8 Hz, 2H), 2.31 (dd, *J* = 12.2, 6.4 Hz, 1H), 2.20 (d, *J* = 11.9 Hz, 1H);

¹³C NMR (101 MHz, CDCl₃) δ 197.8, 169.4 (d, *J* = 243 Hz), 150.7, 146.2, 138.4, 130.2, 128.1, 127.6 (d, *J* = 3 Hz), 126.7 (d, *J* = 10 Hz), 125.9 (d, *J* = 17 Hz), 124.5, 124.5, 124.4, 120.7, 116.5, 115.4 (d, *J* = 21 Hz), 112.7, 98.2, 37.9, 35.1, 31.7, 29.9;

¹⁹F NMR (376 MHz, CDCl₃) δ -113.40;

IR (neat): 3023, 1632, 807cm⁻¹;

HRMS (ESI-TOF) ([M+H]⁺) Calcd For C₂₁H₁₈BrFNOS⁺: 430.0271; Found: 430.0275.



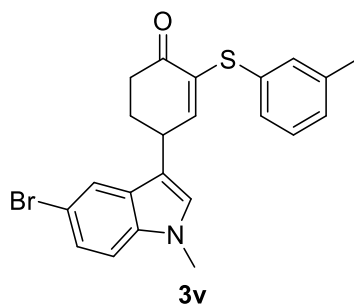
4-(5-bromo-1-methyl-1*H*-indol-3-yl)-2-(phenylthio)cyclohex-2-en-1-one (3u): Pure **3u** was prepared with general procedure and isolated through a silica gel flash column (PE:EtOAc = 5:1) as yellow oil (64 mg, 52% yield);

¹H NMR (400 MHz, CDCl₃) δ 7.72 (s, 1H), 7.36 (d, J = 8.6 Hz, 1H), 7.22 (d, J = 8.5 Hz, 1H), 7.16 (t, J = 7.4 Hz, 2H), 7.06 (t, J = 6.9 Hz, 1H), 6.97 (d, J = 7.2 Hz, 3H), 6.19 – 6.14 (m, 1H), 4.61 – 4.55 (m, 1H), 3.79 (s, 3H), 2.61 – 2.52 (m, 2H), 2.33 – 2.25 (m, 1H), 2.17 (d, J = 13.0 Hz, 1H);

¹³C NMR (101 MHz, CDCl₃) δ 197.9, 150.9, 146.4, 138.7, 136.3, 131.1, 130.1, 128.9, 125.8, 125.3, 125.0, 122.0, 114.7, 111.0, 99.4, 37.9, 35.1, 31.6, 29.9;

IR (neat): 3023, 1632, 830cm⁻¹;

HRMS (ESI-TOF) ([M+H]⁺) Calcd For C₂₁H₁₉BrNOS⁺: 412.0365; Found: 412.0363.



4-(5-bromo-1-methyl-1H-indol-3-yl)-2-(m-tolylthio)cyclohex-2-en-1-

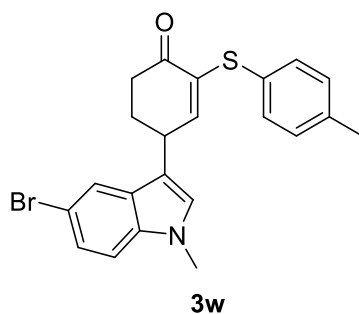
one (3v): Pure **3v** was prepared with general procedure and isolated through a silica gel flash column (PE:EtOAc = 5:1) as yellow oil (70 mg, 55% yield);

¹H NMR (400 MHz, CDCl₃) δ 7.73 (s, 1H), 7.36 (d, J = 8.7 Hz, 1H), 7.22 (d, J = 8.7 Hz, 1H), 7.03 (t, J = 7.6 Hz, 1H), 6.96 (d, J = 10.0 Hz, 1H), 6.88 (d, J = 7.6 Hz, 2H), 6.69 (d, J = 7.8 Hz, 1H), 6.17 (dd, J = 10.0, 2.6 Hz, 1H), 4.61 – 4.55 (m, 1H), 3.79 (s, 3H), 2.56 (dd, J = 13.4, 4.6 Hz, 2H), 2.30 (dd, J = 11.9, 5.5 Hz, 1H), 2.24 (s, 3H), 2.18 (d, J = 12.1 Hz, 1H);

¹³C NMR (101 MHz, CDCl₃) δ 198.0, 151.0, 146.4, 138.7, 138.5, 136.3, 131.2, 130.1, 128.8, 126.0, 125.9, 125.8, 122.3, 122.1, 114.6, 110.9, 99.5, 37.9, 35.2, 31.6, 29.9, 21.4;

IR (neat): 2828, 1682, 778cm⁻¹;

HRMS (ESI-TOF) ([M+H]⁺) Calcd For C₂₂H₂₁BrNOS⁺: 426.0522; Found: 426.0521.



4-(5-bromo-1-methyl-1*H*-indol-3-yl)-2-(*p*-tolylthio)cyclohex-2-en-1-

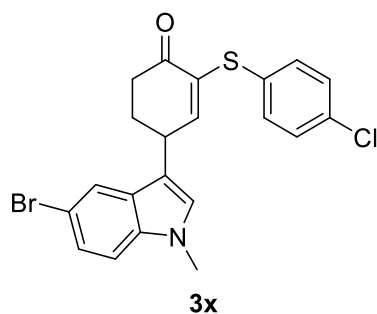
one (3w): Pure **3w** was prepared with general procedure and isolated through a silica gel flash column (PE:EtOAc = 5:1) as yellow oil (83 mg, 65% yield);

¹H NMR (400 MHz, CDCl₃) δ 7.73 (s, 1H), 7.35 (d, J = 8.6 Hz, 1H), 7.21 (d, J = 8.6 Hz, 1H), 6.99 (s, 1H), 6.96 (d, J = 5.1 Hz, 2H), 6.88 (d, J = 7.4 Hz, 2H), 6.17 (d, J = 10.1 Hz, 1H), 4.59 (dd, J = 7.1, 2.4 Hz, 1H), 3.78 (s, 3H), 2.56 (dd, J = 13.4, 4.2 Hz, 2H), 2.32 (dd, J = 12.7, 5.2 Hz, 1H), 2.25 (s, 3H), 2.18 (d, J = 12.3 Hz, 1H);

¹³C NMR (101 MHz, CDCl₃) δ 198.0, 151.0, 146.3, 136.2, 135.1, 134.9, 131.2, 130.0, 129.7, 125.7, 125.5, 122.0, 114.6, 110.9, 99.9, 37.9, 35.1, 31.6, 30.0, 20.9;

IR (neat): 2927, 1632, 872cm⁻¹;

HRMS (ESI-TOF) ([M+H]⁺) Calcd For C₂₂H₂₁BrNOS⁺: 426.0522; Found: 426.0524.



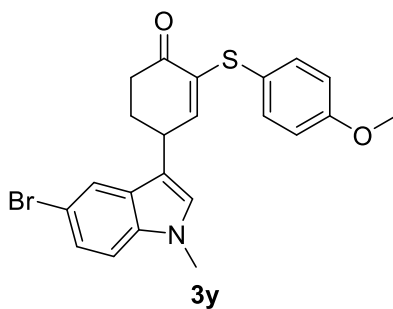
4-(5-bromo-1-methyl-1*H*-indol-3-yl)-2-((4-chlorophenyl)thio)cyclohex-2-en-1-one (3x): Pure **3x** was prepared with general procedure and isolated through a silica gel flash column (PE:EtOAc = 5:1) as yellow oil (68 mg, 51% yield);

¹H NMR (400 MHz, CDCl₃) δ 7.68 (s, 1H), 7.37 (d, *J* = 8.7 Hz, 1H), 7.23 (d, *J* = 8.8 Hz, 1H), 7.12 (d, *J* = 8.5 Hz, 2H), 6.93 (d, *J* = 10.1 Hz, 1H), 6.88 (d, *J* = 8.5 Hz, 2H), 6.17 (dd, *J* = 10.0, 2.6 Hz, 1H), 4.57 – 4.51 (m, 1H), 3.80 (s, 3H), 2.57 (dd, *J* = 18.8, 5.3 Hz, 2H), 2.30 (dt, *J* = 12.1, 6.7 Hz, 1H), 2.17 (d, *J* = 12.5 Hz, 1H);

¹³C NMR (101 MHz, CDCl₃) δ 197.8, 150.6, 146.5, 137.4, 136.3, 130.9, 130.8, 130.2, 129.0, 126.5, 126.0, 121.8, 114.8, 111.1, 98.8, 37.9, 35.1, 31.6, 30.0;

IR (neat): 2911, 1646, 874cm⁻¹;

HRMS (ESI-TOF) ([M+H]⁺) Calcd For C₂₁H₁₈BrClNOS⁺: 445.9976; Found: 445.9977.



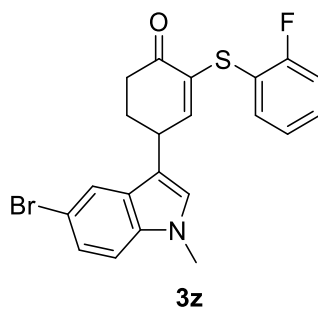
4-(5-bromo-1-methyl-1*H*-indol-3-yl)-2-((4-methoxyphenyl)thio)cyclohex-2-en-1-one (3y): Pure **3y** was prepared with general procedure and isolated through a silica gel flash column (PE:EtOAc = 5:1) as yellow oil (82 mg, 62% yield);

¹H NMR (400 MHz, CDCl₃) δ 7.76 (s, 1H), 7.34 (d, *J* = 8.1 Hz, 1H), 7.20 (d, *J* = 8.6 Hz, 1H), 6.96 (d, *J* = 8.6 Hz, 3H), 6.73 (d, *J* = 8.5 Hz, 2H), 6.18 (d, *J* = 10.1 Hz, 1H), 4.62 (dd, *J* = 8.6, 2.2 Hz, 1H), 3.76 (s, 3H), 3.72 (s, 3H), 2.61 – 2.55 (m, 2H), 2.27 (dd, *J* = 12.2, 5.2 Hz, 1H), 2.14 (d, *J* = 14.1 Hz, 1H);

¹³C NMR (101 MHz, CDCl₃) δ 198.0, 157.8, 151.1, 146.0, 136.1, 131.2, 130.0, 129.2, 127.7, 125.7, 122.0, 114.7, 114.5, 110.9, 101.0, 55.3, 37.9, 35.1, 31.6, 29.9;

IR (neat): 3023, 1492, 825cm⁻¹;

HRMS (ESI-TOF) ([M+H]⁺) Calcd For C₂₂H₂₁BrNO₂S⁺: 442.0471; Found: 442.0474.



4-(5-bromo-1-methyl-1*H*-indol-3-yl)-2-((2-fluorophenyl)thio)cyclohex-2-en-1-one (3z): Pure **3z** was prepared with general procedure and isolated through a silica gel flash column (PE:EtOAc = 5:1) as yellow oil (59 mg, 46% yield);

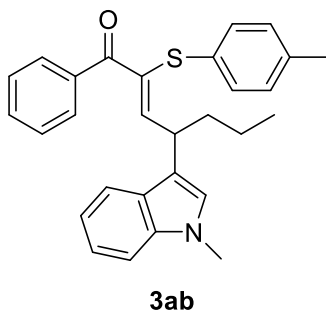
¹H NMR (400 MHz, CDCl₃) δ 7.71 (s, 1H), 7.35 (d, *J* = 8.7 Hz, 1H), 7.22 (d, *J* = 8.7 Hz, 1H), 7.04 (dd, *J* = 14.5, 7.9 Hz, 2H), 6.95 (d, *J* = 10.1 Hz, 1H), 6.87 (t, *J* = 7.4 Hz, 1H), 6.63 (t, *J* = 7.7 Hz, 1H), 6.18 (dd, *J* = 10.4, 2.2 Hz, 1H), 4.66 – 4.61 (m, 1H), 3.79 (s, 3H), 2.58 (dd, *J* = 11.7, 5.1 Hz, 2H), 2.30 (dd, *J* = 12.4, 6.5 Hz, 1H), 2.18 (d, *J* = 11.4 Hz, 1H);

¹³C NMR (101 MHz, CDCl₃) δ 197.8, 159.2 (d, *J* = 243 Hz), 150.6, 146.8, 136.4, 131.0, 130.3, 127.4 (d, *J* = 3 Hz), 126.7 (d, *J* = 7 Hz), 125.9, 125.8, 125.7, 124.6 (d, *J* = 4 Hz), 121.9, 115.4 (d, *J* = 20 Hz), 114.7, 111.1, 97.3, 97.3, 37.9, 35.1, 31.2, 29.9;

¹⁹F NMR (376 MHz, CDCl₃) δ -113.47;

IR (neat): 1683, 1633, 791 cm⁻¹;

HRMS (ESI-TOF) ([M+H]⁺) Calcd For C₂₁H₁₈BrFNOS⁺: 430.0271; Found: 430.0269.



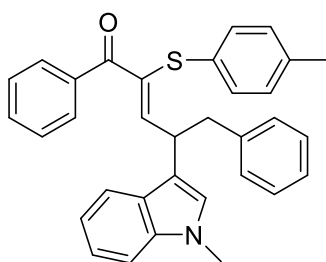
(Z)-4-(1-methyl-1*H*-indol-3-yl)-1-phenyl-2-(*p*-tolylthio)hept-2-en-1-one (3ab): Pure **3ab** was prepared with general procedure and isolated through a silica gel flash column (PE:EtOAc = 8:1) as yellow solid (86 mg, 65% yield); mp 198-201 °C

¹H NMR (400 MHz, CDCl₃) δ 7.79 (t, J = 6.8 Hz, 3H), 7.52 – 7.31 (m, 6H), 7.17 (t, J = 7.1 Hz, 1H), 7.00 (d, J = 7.9 Hz, 2H), 6.91 (d, J = 8.1 Hz, 2H), 6.80 (d, J = 15.3 Hz, 1H), 4.30 (q, J = 7.3 Hz, 1H), 3.75 (s, 3H), 2.24 (s, 3H), 2.08 (dt, J = 12.8, 6.7 Hz, 2H), 1.33 (dd, J = 12.7, 5.9 Hz, 2H), 0.91 (t, J = 7.3 Hz, 3H);

¹³C NMR (101 MHz, CDCl₃) δ 191.0, 151.9, 138.5, 138.0, 135.5, 133.5, 132.5, 129.9, 128.5, 128.4, 126.2, 125.4, 125.4, 125.2, 123.2, 123.2, 120.6, 119.5, 110.1, 41.4, 36.4, 30.2, 21.1, 20.9, 14.0;

IR (neat): 1668, 1597, 804cm⁻¹;

HRMS (ESI-TOF) ([M+H]⁺) Calcd For C₂₉H₃₀NOS⁺: 440.2043; Found: 440.2044.



3ac

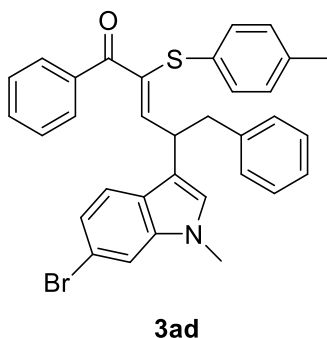
(Z)-4-(1-methyl-1H-indol-3-yl)-1,5-diphenyl-2-(p-tolylthio)pent-2-en-1-one (3ac): Pure **3ac** was prepared with general procedure and isolated through a silica gel flash column (PE:EtOAc = 8:1) as yellow oil (98 mg, 67% yield);

¹H NMR (400 MHz, CDCl₃) δ 7.85 (d, J = 7.8 Hz, 1H), 7.71 (d, J = 7.6 Hz, 2H), 7.52 – 7.46 (m, 2H), 7.35 (q, J = 8.5, 8.0 Hz, 5H), 7.21 (s, 1H), 7.17 (s, 1H), 7.16 (s, 1H), 7.07 (d, J = 6.4 Hz, 2H), 6.93 (d, J = 7.6 Hz, 2H), 6.74 (s, 1H), 6.71 (d, J = 7.0 Hz, 1H), 4.57 (q, J = 7.1 Hz, 1H), 3.65 (s, 3H), 3.37 (dd, J = 15.8, 7.8 Hz, 2H), 2.22 (s, 3H);

¹³C NMR (101 MHz, CDCl₃) δ 190.9, 150.4, 139.6, 138.5, 137.9, 135.5, 133.1, 132.5, 129.9, 129.1, 128.5, 128.3, 128.3, 126.4, 126.1, 125.9, 125.9, 125.3, 123.1, 122.3, 120.6, 119.6, 110.1, 43.8, 40.8, 30.2, 30.2, 20.9;

IR (neat): 1632, 1349, 918cm⁻¹;

HRMS (ESI-TOF) ([M+H]⁺) Calcd For C₃₃H₃₀NOS⁺: 488.2043; Found: 488.2046.



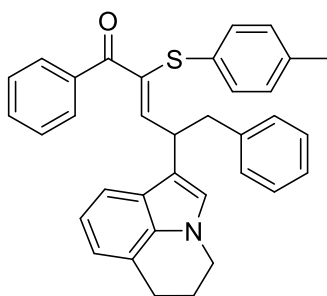
(Z)-4-(6-bromo-1-methyl-1H-indol-3-yl)-1,5-diphenyl-2-(p-tolylthio)pent-2-en-1-one (3ad): Pure **3ad** was prepared with general procedure and isolated through a silica gel flash column (PE:EtOAc = 8:1) as yellow solid (95 mg, 56% yield); mp 188-191 °C

¹H NMR (400 MHz, CDCl₃) δ 7.71 (d, J = 7.5 Hz, 2H), 7.66 (d, J = 8.5 Hz, 1H), 7.50 (s, 2H), 7.46 – 7.41 (m, 1H), 7.39 (d, J = 7.5 Hz, 2H), 7.28 (s, 1H), 7.25 (d, J = 2.6 Hz, 1H), 7.16 (s, 1H), 7.14 (s, 2H), 7.03 (s, 1H), 7.02 (s, 1H), 6.92 (d, J = 8.0 Hz, 2H), 6.73 (s, 1H), 6.66 (s, 2H), 4.56 – 4.51 (m, 1H), 3.58 (s, 3H), 3.32 (dd, J = 15.8, 7.8 Hz, 2H), 2.21 (s, 3H);

¹³C NMR (101 MHz, CDCl₃) δ 190.7, 150.1, 139.3, 139.2, 137.7, 135.8, 132.6, 132.5, 130.0, 128.5, 128.4, 128.3, 127.1, 126.6, 126.2, 125.8, 124.1, 122.9, 122.3, 121.7, 117.1, 113.1, 43.6, 40.6, 30.36, 20.9;

IR (neat): 3024, 1632, 803cm⁻¹;

HRMS (ESI-TOF) ([M+H]⁺) Calcd For C₃₃H₂₉BrNOS⁺: 566.1148; Found: 566.1151.



3ae

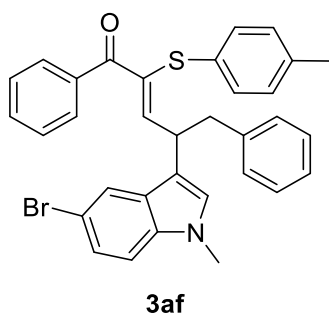
(Z)-4-(5,6-dihydro-4H-pyrrolo[3,2,1-*ij*]quinolin-1-yl)-1,5-diphenyl-2-(*p*-tolylthio)pent-2-en-1-one (3ae): Pure **3ae** was prepared with general procedure and isolated through a silica gel flash column (PE:EtOAc = 15:1) as yellow oil (94 mg, 61% yield);

¹H NMR (400 MHz, CDCl₃) δ 7.70 (d, *J* = 7.9 Hz, 2H), 7.64 (d, *J* = 8.0 Hz, 1H), 7.51 – 7.47 (m, 1H), 7.46 – 7.39 (m, 1H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.17 (d, *J* = 7.1 Hz, 2H), 7.15 – 7.13 (m, 1H), 7.09 (d, *J* = 6.6 Hz, 2H), 7.06 (s, 1H), 6.99 (d, *J* = 7.1 Hz, 1H), 6.91 (d, *J* = 7.9 Hz, 2H), 6.72 (d, *J* = 6.9 Hz, 2H), 6.69 (s, 1H), 4.51 (q, *J* = 7.5 Hz, 1H), 3.93 (tt, *J* = 13.0, 6.8 Hz, 2H), 3.34 (tt, *J* = 13.1, 6.4 Hz, 2H), 2.96 (t, *J* = 5.2 Hz, 2H), 2.21 (s, 3H), 2.16 – 2.09 (m, 2H);

¹³C NMR (101 MHz, CDCl₃) δ 191.0, 150.6, 139.7, 137.9, 136.0, 135.5, 133.1, 132.5, 129.9, 129.2, 128.5, 128.3, 128.3, 126.5, 126.1, 125.7, 123.9, 123.4, 122.2, 121.6, 119.9, 119.8, 118.0, 43.6, 42.1, 40.9, 25.1, 22.7, 20.9;

IR (neat): 1632, 1560, 829cm⁻¹;

HRMS (ESI-TOF) ([M+H]⁺) Calcd For C₃₅H₃₂NOS⁺: 514.2199; Found: 514.2201.



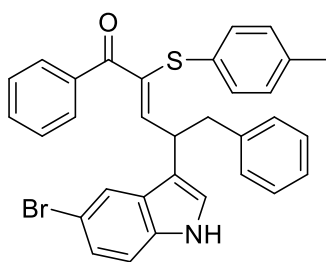
(Z)-4-(5-bromo-1-methyl-1H-indol-3-yl)-1,5-diphenyl-2-(p-tolylthio)pent-2-en-1-one (3af): Pure **3af** was prepared with general procedure and isolated through a silica gel flash column (PE:EtOAc = 8:1) as yellow solid (86 mg, 51% yield); mp 188-191 °C

¹H NMR (400 MHz, CDCl₃) δ 7.93 (d, J = 1.5 Hz, 1H), 7.73 (d, J = 7.2 Hz, 2H), 7.51 (t, J = 7.4 Hz, 1H), 7.39 (t, J = 7.6 Hz, 5H), 7.22 – 7.17 (m, 2H), 7.16 (s, 2H), 7.07 – 7.04 (m, 2H), 6.93 (d, J = 8.0 Hz, 2H), 6.70 – 6.68 (m, 2H), 4.55 – 4.50 (m, 1H), 3.61 (s, 3H), 3.37 – 3.27 (m, 2H), 2.21 (s, 3H);

¹³C NMR (101 MHz, CDCl₃) δ 190.9, 149.8, 139.3, 137.8, 137.0, 135.9, 132.7, 132.4, 130.0, 129.1, 128.4, 128.3, 127.7, 126.8, 126.6, 126.3, 126.1, 126.0, 122.8, 121.5, 113.0, 111.6, 43.6, 40.6, 30.4, 20.9;

IR (neat): 3023, 1632, 829cm⁻¹;

HRMS (ESI-TOF) ([M+H]⁺) Calcd For C₃₃H₂₉BrNOS⁺: 566.1148; Found: 566.1138.



3ag

(Z)-4-(5-bromo-1*H*-indol-3-yl)-1,5-diphenyl-2-(*p*-tolylthio)pent-2-en-

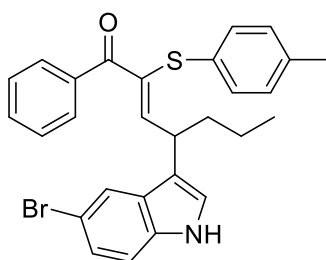
1-one (3ag): Pure **3ag** was prepared with general procedure and isolated through a silica gel flash column (PE:EtOAc = 8:1) as light yellow oil (116 mg, 70% yield);

¹H NMR (400 MHz, CDCl₃) δ 9.89 (s, 1H), 7.77 (d, J = 7.0 Hz, 2H), 7.71 (s, 1H), 7.58 (d, J = 7.3 Hz, 1H), 7.44 (d, J = 5.6 Hz, 3H), 7.26 – 7.23 (m, 1H), 7.13 (s, 4H), 7.04 (s, 2H), 6.89 (d, J = 7.7 Hz, 4H), 6.81 (d, J = 15.8 Hz, 1H), 4.70 (d, J = 7.3 Hz, 1H), 3.20 (d, J = 7.2 Hz, 2H), 2.19 (s, 3H);

¹³C NMR (101 MHz, CDCl₃) δ 191.2, 148.1, 144.8, 137.8, 137.1, 134.8, 134.8, 134.7, 133.5, 131.8, 129.6, 128.9, 128.7, 128.7, 128.5, 126.9, 126.7, 125.9, 125.6, 121.9, 114.2, 112.8, 100.4, 42.2, 40.5, 20.8;

IR (neat): 3023, 1491, 803cm⁻¹;

HRMS (ESI-TOF) ([M+H]⁺) Calcd For C₃₂H₂₇BrNOS⁺: 552.0991; Found: 552.0997.



3ah

(Z)-4-(5-bromo-1H-indol-3-yl)-1-phenyl-2-(p-tolylthio)hept-2-en-1-

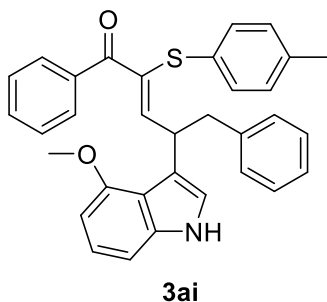
one (3ah): Pure **3ah** was prepared with general procedure and isolated through a silica gel flash column (PE:EtOAc = 8:1) as yellow oil (98 mg, 65% yield);

¹H NMR (400 MHz, CDCl₃) δ 9.67 (s, 1H), 7.79 (d, J = 8.0 Hz, 3H), 7.58 (s, 1H), 7.43 (t, J = 7.7 Hz, 3H), 7.33 – 7.27 (m, 2H), 7.17 (d, J = 8.5 Hz, 1H), 6.94 (s, 3H), 6.84 (d, J = 15.2 Hz, 1H), 4.36 (d, J = 7.7 Hz, 1H), 2.18 (s, 3H), 1.86 (d, J = 6.9 Hz, 2H), 1.27 (t, J = 7.4 Hz, 2H), 0.84 (s, 3H);

¹³C NMR (101 MHz, CDCl₃) δ 191.1, 149.1, 145.6, 137.2, 135.0, 134.7, 134.6, 133.4, 131.9, 129.6, 128.7, 128.6, 126.1, 125.8, 125.5, 121.8, 114.2, 112.8, 100.2, 40.0, 36.0, 20.8, 20.6, 13.7;

IR (neat): 3023, 1632, 801cm⁻¹;

HRMS (ESI-TOF) ([M+H]⁺) Calcd For C₂₈H₂₇BrNOS⁺: 504.0991; Found: 504.0984.



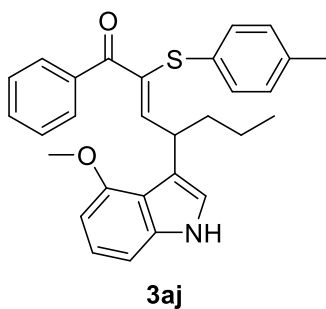
(Z)-4-(4-methoxy-1*H*-indol-3-yl)-1,5-diphenyl-2-(*p*-tolylthio)pent-2-en-1-one (3ai): Pure **3ai** was prepared with general procedure and isolated through a silica gel flash column (PE:EtOAc = 8:1) as yellow solid (91 mg, 60% yield); mp 175-177 °C

¹H NMR (400 MHz, CDCl₃) δ 9.35 (s, 1H), 7.74 (d, J = 7.7 Hz, 2H), 7.54 (s, 1H), 7.40 (t, J = 7.7 Hz, 3H), 7.13 (s, 3H), 7.08 (d, J = 8.9 Hz, 3H), 6.95 – 6.93 (m, 3H), 6.89 (d, J = 7.8 Hz, 2H), 6.76 (d, J = 15.4 Hz, 1H), 6.53 (d, J = 7.8 Hz, 1H), 4.77 (d, J = 7.4 Hz, 1H), 3.72 (s, 3H), 3.18 (t, J = 6.7 Hz, 2H), 2.19 (s, 3H);

¹³C NMR (101 MHz, CDCl₃) δ 190.9, 154.4, 148.4, 142.3, 138.1, 137.7, 137.3, 137.0, 134.0, 133.2, 129.2, 129.0, 128.6, 128.6, 128.5, 126.8, 126.5, 126.2, 123.3, 119.3, 104.7, 101.6, 55.6, 41.5, 40.4, 20.9;

IR (neat): 2831, 1585, 779cm⁻¹;

HRMS (ESI-TOF) ([M+H]⁺) Calcd For C₃₃H₃₀NO₂S⁺: 504.1992; Found: 504.1992.



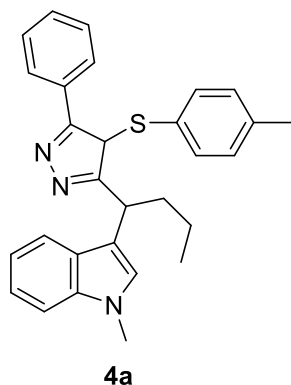
(Z)-4-(4-methoxy-1*H*-indol-3-yl)-1-phenyl-2-(*p*-tolylthio)hept-2-en-1-one (3aj): Pure **3aj** was prepared with general procedure and isolated through a silica gel flash column (PE:EtOAc = 8:1) as yellow oil (76 mg, 56% yield);

¹H NMR (400 MHz, CDCl₃) δ 9.25 (s, 1H), 7.77 (d, *J* = 7.8 Hz, 2H), 7.54 (t, *J* = 7.3 Hz, 1H), 7.40 (t, *J* = 7.6 Hz, 2H), 7.25 (d, *J* = 7.5 Hz, 1H), 7.10 (s, 1H), 7.03 (d, *J* = 8.0 Hz, 2H), 6.97 (d, *J* = 8.1 Hz, 1H), 6.93 (d, *J* = 7.8 Hz, 2H), 6.80 (d, *J* = 15.3 Hz, 1H), 6.55 (d, *J* = 7.8 Hz, 1H), 4.46 – 4.40 (m, 1H), 3.74 (s, 3H), 2.19 (s, 3H), 1.84 (d, *J* = 7.6 Hz, 2H), 1.29 – 1.25 (m, 2H), 0.84 (t, *J* = 7.3 Hz, 3H);

¹³C NMR (101 MHz, CDCl₃) δ 191.0, 154.3, 149.7, 143.0, 137.7, 137.4, 137.3, 133.9, 133.0, 129.2, 128.6, 128.6, 126.1, 126.0, 123.2, 119.4, 104.6, 101.6, 99.8, 55.7, 39.4, 36.0, 20.8, 20.5, 13.8;

IR (neat): 2826, 1592, 784cm⁻¹;

HRMS (ESI-TOF) ([M+H]⁺) Calcd For C₂₉H₃₀NO₂S⁺: 456.1992; Found: 456.1994.



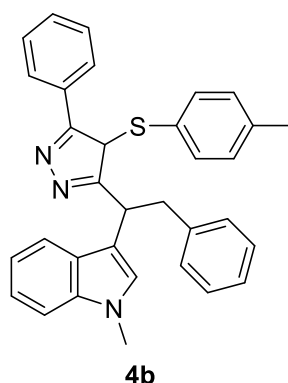
1-methyl-3-(2-phenyl-1-(5-phenyl-4-(*p*-tolylthio)-4*H*-pyrazol-3-yl)ethyl)-1*H*-indole (4a): Pure **4a** was prepared with general procedure for the further transformations and isolated through a silica gel flash column (PE:EtOAc = 8:1) as yellow oil (384 mg, 85% yield);

¹H NMR (400 MHz, CDCl₃) δ 7.65 (dt, *J* = 17.0, 8.0 Hz, 4.7H), 7.38 – 7.32 (m, 3H), 7.30 – 7.24 (m, 3H), 7.20 (t, *J* = 7.2 Hz, 2H), 7.08 (d, *J* = 11.0 Hz, 4H), 7.02 (d, *J* = 6.9 Hz, 1.7H), 6.92 – 6.84 (m, 3H), 6.46 (s, 1H), 4.94 (t, *J* = 4.5 Hz, 1H), 4.69 (t, *J* = 7.3 Hz, 0.6H), 3.75 (s, 3H), 3.68 (s, 2H), 2.41 (s, 1H), 2.41 (s, 0.6H), 2.26 (s, 3H), 2.26 (s, 2H), 1.62 – 1.56 (m, 2H), 1.56 – 1.51 (m, 1.2H), 1.45 – 1.51 (m, 2H), 1.38 – 1.45 (m, 1.2H), 0.88 (t, *J* = 7.5 Hz 3H), 0.78 (t, *J* = 7.3 Hz, 2)

¹³C NMR (101 MHz, CDCl₃) δ 138.5, 137.1, 136.8, 135.8, 133.5, 130.1, 128.6, 127.9, 127.6, 127.6, 127.5, 127.0, 126.2, 126.0, 125.5, 125.3, 123.2, 122.6, 121.6, 121.3, 120.5, 119.7, 119.5, 119.3, 118.8, 118.6, 117.4, 116.7, 110.0, 109.1, 100.6, 74.3, 48.3, 36.0, 35.5, 34.8, 33.7, 32.8, 32.7, 31.4, 30.2, 29.7, 28.7, 22.8, 22.4, 21.0, 20.9, 14.6, 14.1, 13.9;

IR (neat): 3032, 1632, 807 cm^{-1} ;

HRMS (ESI-TOF) ($[\text{M}+\text{H}]^+$) Calcd For $\text{C}_{29}\text{H}_{30}\text{N}_3\text{S}^+$: 452.2153; Found: 452.2162.



1-methyl-3-(1-(5-phenyl-4-(p-tolylthio)-4H-pyrazol-3-yl)butyl)-1H-

indole (4b): Pure **4b** was prepared with general procedure for the further transformations and isolated through a silica gel flash column (PE:EtOAc = 8:1) as yellow oil (399 mg, 80% yield);

^1H NMR (400 MHz, CDCl_3) δ 7.78 (d, J = 8.0 Hz, 1H), 7.69 (d, J = 8.0 Hz, 2H), 7.34 (dd, J = 16.9, 8.0 Hz, 6H), 7.15 (d, J = 5.0 Hz, 3H), 7.07 – 7.04 (m, 2H), 6.95 (d, J = 7.9 Hz, 2H), 6.69 (d, J = 8.0 Hz, 2H), 6.48 (s, 1H), 5.06 (t, J = 8.5 Hz, 1H), 3.75 – 3.70 (m, 1H), 3.63 (s, 3H), 3.61 – 3.54 (m, 2H), 2.26 (s, 3H);

^{13}C NMR (101 MHz, CDCl_3) δ 139.7, 138.5, 135.7, 133.1, 132.6, 130.0, 129.1, 128.6, 128.2, 127.7, 126.6, 126.2, 125.6, 125.4, 124.4, 123.1, 121.7, 120.7, 119.8, 110.0, 101.2, 63.0, 40.3, 38.2, 14.2;

IR (neat): 3046, 1461, 739 cm^{-1} ;

HRMS (ESI-TOF) ($[\text{M}+\text{Na}]^+$) Calcd For $\text{C}_{33}\text{H}_{29}\text{N}_3\text{NaS}^+$: 522.1974;

Found: 522.1994.

5. Characterization data

