

Supporting Information

Cascade Radical Cyclization of *N*-Propargyl Indoles: Substituents Dictate Stereoselective Formation of *N*-Fused Indolines v/s Indoles

Santosh J. Gharpure,* Yogesh G. Shelke

Department of Chemistry, Indian Institute of Technology Bombay, Powai, Mumbai – 400076, India

E-mail: sjgharpure@iitb.ac.in

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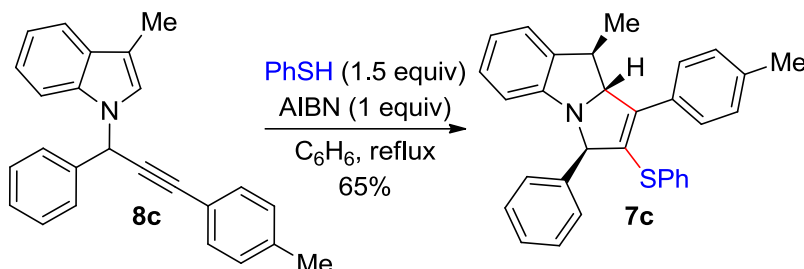
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General

IR spectra were recorded on Nicolet 6700 spectrophotometer. ^1H and ^{13}C NMR spectra were recorded on Bruker Avance 400 and 500 spectrophotometer. The chemical shifts (δ , ppm) and coupling constants (Hz) are reported in the standard fashion with reference to residual CHCl_3 at (7.26 ppm for ^1H) and the central line (77.16 ppm for ^{13}C) of CDCl_3 . In the ^{13}C NMR spectra, the nature of the carbons (C, CH, CH_2 or CH_3) was determined by recording the DEPT-135 experiment, and are given in parentheses. NOE spectrum was recorded in Bruker Avance 400 spectrophotometer. Analytical thin-layer chromatography (TLC) were performed on glass plates (7.5×2.5 and 9×5.0 cm) coated with Merck or Acme's silica gel G containing 13% calcium sulphate as binder or on pre-coated 0.2 mm thick Merck 60 F₂₄₅ silica plates and various combinations of ethyl acetate and hexanes were used as eluent. Visualization of spots was accomplished by either exposure to iodine vapour or KMnO_4 stain. Acme's silica gel (100-200 mesh) was used for column chromatography (approximately 15-20 g per 1 g of the crude product). Melting points are recorded using Buchi melting point apparatus in capillary tubes and are uncorrected. All small-scale dry reactions were carried out using standard syringe septum technique. Low temperature reactions were conducted in jullabo. Dry THF, ether, benzene were obtained by distillation over sodium-benzophenone ketyl. Dry dichloromethane and dry DMF, dry acetonitrile were prepared by distilling over calcium hydride. PhSH, Bu_3SnH and AIBN were obtained from Aldrich. AIBN was recrystallize from methanol before using. All the commercial reagents were used as such without further purification.

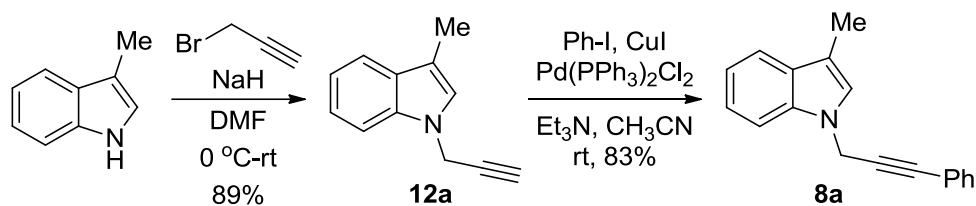
Experimental and Characterization of Compounds

Representative experimental procedure for cascade radical cyclization



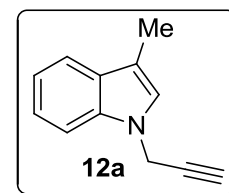
To a magnetically stirred solution of the propargyl indole derivative **8c** (350 mg, 1.04 mmol) and AIBN (28 mg, 0.17 mmol) in dry benzene (30 mL) was added a thiophenol (160 μ L, 1.56 mmol). The reaction mixture was refluxed and AIBN (143 mg, 0.87 mmol) was added in portion wise after interval of 0.5 hr under nitrogen atmosphere. The reaction mixture was reflux till the completion of reaction (TLC control). Solvent was evaporated under reduced pressure and purification of the residue on a silica gel column chromatography using EtOAc/Pet ether as eluent, furnished the *N*-fused indoline **7c** (301 mg, 65%) as a white solid.

Preparation of primary *N*-Propargyl indoles (**8a**)



3-methyl-1-(prop-2-yn-1-yl)-1H-indole (12a):

Sodium hydride (1.8 gm, 45.472 mmol) was added to a cooled (0 °C) solution of 3-methyl indole (4.0 gm, 30.495 mmol) in dry DMF (60 mL) and allowed to stir for 0.5 hr at 0 °C. Then propargyl bromide (4 mL, 45.472 mmol) was added dropwise to the reaction mixture at 0 °C. Resulting solution was stirred at room temperature until disappearance of starting material (TLC control). Reaction mixture was diluted with saturated NH₄Cl solution and extracted with EtOAc (3×10 mL). The organic layer was washed with brine and dried (Na₂SO₄) and evaporated under reduced pressure. The



crude product was subjected to the purification by silica gel column chromatography using EtOAc/Pet ether as eluent, furnished the product **12a** (4.6 mg, 89%) as yellowish sticky liquid.

Physical appearance: yellowish sticky liquid.

R_f: 0.8 (1:9, EtOAc: Pet ether).

IR (neat): 3250, 3021, 2915, 2857, 1590, 1457, 1345, 1238, 1103, 742, 698 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ 7.60 (d, *J* = 8.0 Hz, 1H), 7.38 (d, *J* = 8.0 Hz, 1H), 7.27 (t, *J* = 8.0 Hz, 1H), 7.16 (t, *J* = 8.0 Hz, 1H), 6.99 (s, 1H), 4.83 (d, *J* = 2.4 Hz, 2H), 2.38 (t, *J* = 2.4 Hz, 1H), 2.36 (s, 3H).

¹³C NMR (100 MHz, CDCl₃, DEPT): δ 136.3 (C), 129.3 (C), 125.0 (CH), 122.0 (CH), 119.4 (CH), 119.3 (CH), 111.5 (C), 109.3 (CH), 78.3 (C), 73.2 (CH), 35.6 (CH₂), 9.7 (CH₃).

HRMS (ESI, M+H⁺): m/z calcd. for C₁₂H₁₂N, 170.1891 found 170.1890.

3-methyl-1-(3-phenylprop-2-yn-1-yl)-1H-indole (8a):

To a magnetically stirred solution of terminal alkyne **12a** (1.0 gm, 5.909 mmol) in dry CH₃CN (10 mL) and Et₃N (2.4 mL) was added iodobenzene (793 μL, 7.091 mmol), Pd(PPh₃)₂Cl₂ (207 mg, 5mol%) and CuI (4 mg, 1 mol%) under nitrogen atmosphere at room temperature. The reaction mixture was stirred overnight at room temperature. Then reaction mixture was evaporated to dryness under reduced pressure. Purification of crude residue on a silica gel column chromatography using EtOAc/Pet ether as eluent, furnished product **8a** (1.22 gm, 83%) as a yellowish sticky liquid.

Physical appearance: yellowish sticky liquid.

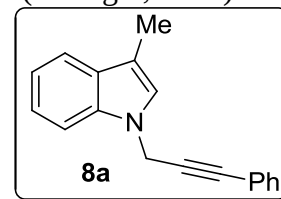
R_f: 0.8 (1:9, EtOAc: Pet ether).

IR (neat): 3029, 2900, 2112, 1530, 1457, 1205, 1103, 787 cm⁻¹.

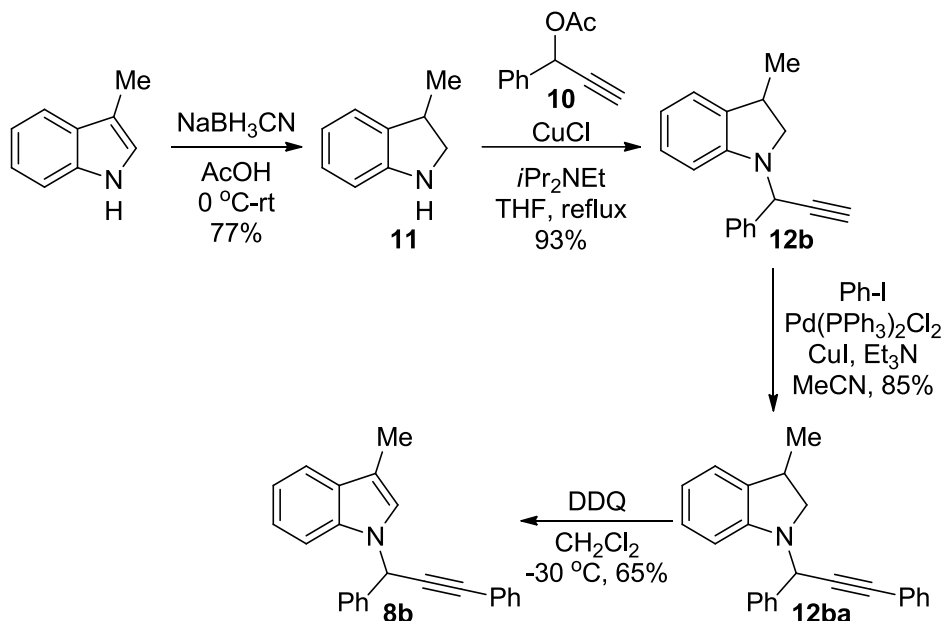
¹H NMR (400 MHz, CDCl₃): δ 7.61 (d, *J* = 8.0 Hz, 1H), 7.45-7.40 (m, 3H), 7.30-7.25 (m, 4H), 7.16 (t, *J* = 8.0 Hz, 1H), 7.07 (s, 1H), 5.06 (s, 2H), 2.36 (s, 3H).

¹³C NMR (100 MHz, CDCl₃, DEPT): δ 136.3 (C), 131.9 (2×CH), 129.3 (C), 128.7 (CH), 128.4 (2×CH), 125.1 (CH), 122.6 (C), 121.9 (CH), 119.3 (CH), 119.2 (CH), 111.2 (C), 109.4 (CH), 85.0 (C), 83.6 (C), 36.5 (CH₂), 10.0 (CH₃).

HRMS (ESI, M+K⁺): m/z calcd. for C₁₈H₁₅KN, 284.0836 found 284.0836.



Preparation of secondary *N*-propargyl indoles (**8b**)



3-methylindoline (**11**):

To a cooled solution of 3-methyl indole (1 gm, 7.625 mmol) in glacial acetic acid (15 mL) sodium cyanoborohydride (1.1 gm, 19.064 mmol) was added in portionwise. Reaction mixture was allowed to room temperature and stirred until completion of starting material. The reaction mixture was quenched with 2M NaOH and PH of solution was adjusted to neutral. The aqueous layer was extracted with EtOAc (3 x 10 mL). The combined organic extracts was dried (Na_2SO_4). Organic solvent was evaporated under reduced pressure and purification of residue on a silica gel column chromatography using EtOAc/Pet ether as eluent, furnished the 3-methyl indoline **11** (782 mg, 77%) as a colorless oil.

Physical appearance: colorless oil.

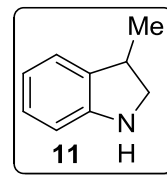
R_f: 0.4 (1:9, EtOAc: Pet ether).

IR (neat): 3378, 2960, 2868, 1609, 1487, 1464, 1240, 745 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ 7.16-7.00 (m, 2H), 6.77 (t, $J = 7.4$ Hz, 1H), 6.67 (d, $J = 7.7$ Hz, 1H), 3.81-3.62 (m, 2H), 3.49-3.30 (m, 1H), 3.13 (t, $J = 8.6$ Hz, 1H), 1.35 (dd, $J = 6.8$ Hz, $J = 1.5$ Hz, 3H)

^{13}C NMR (100 MHz, CDCl_3 , DEPT): δ 151.2 (C), 134.4 (C), 127.4 (CH), 123.4 (CH), 118.8 (CH), 109.6 (CH), 55.5 (CH_2), 36.7 (CH), 18.7 (CH_3).

HRMS (ESI, $\text{M}+\text{Na}^+$): m/z calcd. for $\text{C}_6\text{H}_{11}\text{NaN}$ 156.0791 and found 156.0790.



3-methyl-1-(1-phenylprop-2-yn-1-yl)indoline (12b):

A solution of 3-methyl indoline **11** (600 mg, 4.505 mmol) in THF (20 ml) was charged with CuCl (45 mg, 0.4505 mmol). The suspension was stirred for 5 min at room temperature, after which Hunig's base (863 μ L, 4.955 mmol) was added dropwise. The resulting suspension was allowed to stir for 5 min and solution of propargylic acetate **10** (941 mg, 5.406 mmol) in THF (5 ml) was added over the period of 2 min. The suspension was heated at reflux until the completion of starting material. The reaction mixture was filtered through a pad of celite and wash with EtOAc. Organic solvent was evaporated under reduced pressure and purification of residue on a silica gel column chromatography using EtOAc/Pet ether as eluent, furnished the terminal alkyne **12b** (1.04 gm, 93%) as a colorless oil.

Physical appearance: colorless oil.

R_f: 0.6 (1:9, EtOAc: Pet ether).

IR (neat): 3010, 2950, 2120, 1590, 1498, 1340, 1115, 768 cm^{-1} .

¹H NMR (400 MHz, CDCl₃, major isomer): δ 7.69 (d, J = 8.0 Hz, 2H), 7.45-7.40 (m, 3H), 7.15-7.10 (m, 2H), 6.83 (t, J = 8.0 Hz, 1H), 6.72 (d, J = 8.0 Hz, 1H), 5.67 (s, 1H), 3.25-3.20 (m, 2H), 2.43 (brs, 1H), 2.95-2.90 (m, 1H), 1.35 (d, J = 6.4 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃, DEPT, major isomer): δ 150.7 (C), 137.4 (C), 135.7 (C), 128.6 (2 $\times$ CH), 128.0 (2 $\times$ CH), 127.8 (CH), 127.4 (CH), 123.2 (CH), 119.2 (CH), 108.5 (CH), 79.4 (C), 74.8 (CH), 56.8 (CH₂), 52.8 (CH), 34.9 (CH), 17.7 (CH₃).

HRMS (ESI, M+H⁺): m/z calcd. for C₁₈H₁₈N 248.1440 and found 248.1435.

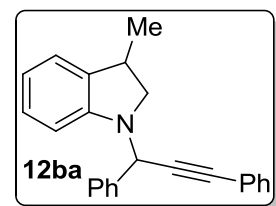
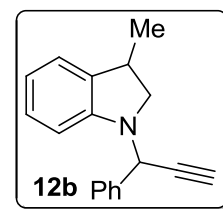
1-(1,3-diphenylprop-2-yn-1-yl)-3-methylindoline (12ba):

To a magnetically stirred solution of terminal alkyne **12b** (850 mg, 3.437 mmol) in dry CH₃CN (20 mL) and Et₃N (1.437 mL, 10.310 mmol) was added iodobenzene (462 μ L, 4.124 mmol), Pd(PPh₃)₂Cl₂ (122 mg, 0.172 mmol) and CuI (7 mg, 0.034 mmol) under nitrogen atmosphere at room temperature. The reaction mixture was stirred overnight at room temperature. Solvent was evaporated under reduced pressure and purification of residue on a silica gel column chromatography using EtOAc/Pet ether as eluent, furnished the internal alkyne **12ba** (945 mg, 85%) as a yellowish oil.

Physical appearance: yellowish oil.

R_f: 0.6 (1:9, EtOAc: Pet ether).

IR (neat): 2930, 4650, 1430, 1120, 780 cm^{-1} .



¹H NMR (500 MHz, CDCl₃, major isomer): δ 7.74 (t, *J* = 6.5 Hz, 2H), 7.45-7.32 (m, 4H), 7.30-7.28 (m, 5H), 7.17 (t, *J* = 6.5 Hz, 1H), 6.82 (t, *J* = 6.5 Hz, 1H), 6.80-6.75 (m, 1H), 5.87 (s, 1H), 3.40-3.25 (m, 2H), 3.07-3.01 (m, 1H), 1.36 (d, *J* = 6.0 Hz, 3H).

¹³C NMR (125 MHz, CDCl₃, DEPT, major isomer): δ 150.9 (C), 138.2 (C), 135.7 (C), 132.0 (CH), 128.6 (2×CH), 128.3 (3×CH), 128.1 (2×CH), 127.9 (2×CH), 127.4 (CH), 123.2 (C), 123.0 (CH), 119.0 (CH), 108.6 (CH), 87.0 (C), 85.4 (C), 57.0 (CH₂), 53.4 (CH), 35.0 (CH), 18.0 (CH₃).

HRMS (ESI, M+Na⁺): *m/z* calcd. for C₂₄H₂₁NaN 346.1571 and found 346.1572.

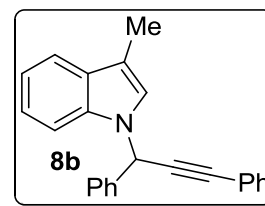
1-(1,3-diphenylprop-2-yn-1-yl)-3-methyl-1H-indole (8b):

Internal alkyne **12ba** (650 mg, 2.010 mmol) was dissolved in dry CH₂Cl₂ (20 ml) and cooled to -30 °C. To the reaction mixture DDQ (684 mg, 3.014 mmol) was added in one portion and allowed to stir for 20 min at the same temperature. Then crude material was passed through a pad of celite and diluted with EtOAc and washed sequentially with 10% aq. NaHCO₃ (2x10 ml), water (2x 10 ml) and brine 10 ml. The combined organic extracts was dried (Na₂SO₄). Organic solvent was evaporated under reduced pressure and purification of residue on a silica gel column chromatography using EtOAc-Pet ether as eluent, furnished the propargyl indole **8b** (420 mg, 65%) as a yellowish oil.

Physical appearance: yellowish oil.

R_f: 0.6 (1:9, EtOAc: Pet ether).

IR (neat): 3020, 2940, 1580, 1460, 1210, 764 cm⁻¹.



¹H NMR (500 MHz, CDCl₃): δ 7.67 (d, *J* = 7.5 Hz, 1H), 7.56 (d, *J* = 7.5 Hz, 2H), 7.50-7.45 (m, 3H), 7.40-7.35 (m, 6H), 7.27 (t, *J* = 7.5 Hz, 1H), 7.21-7.19 (m, 2H), 6.65 (s, 1H), 2.42 (s, 3H).

¹³C NMR (125 MHz, CDCl₃, DEPT): δ 138.6 (C), 136.1 (C), 132.0 (CH), 129.5 (C), 128.9 (2×CH), 128.8 (CH), 128.4 (2×CH), 128.3 (CH), 126.9 (2×CH), 124.1 (CH), 122.4 (C), 121.9 (CH), 119.3 (CH), 119.2 (CH), 111.6 (C), 109.9 (CH), 86.9 (C), 85.9 (C), 52.1 (CH), 9.9 (CH₃).

HRMS (ESI, M+Na⁺): *m/z* calcd. for C₂₄H₁₉NaN 344.1420 and found 344.1417.

(9R,9aR)-9-methyl-1-phenyl-2-(phenylthio)-9,9a-dihydro-3H-pyrrolo[1,2-a]indole (7a):

To a magnetically stirred solution of the alkyne derivative **8a** (100 mg, 0.407 mmol) and AIBN (11 mg, 0.067 mmol) in dry benzene (18 mL) was added a thiophenol (63 μL, 0.611 mmol). The reaction mixture was refluxed and AIBN (55 mg, 0.340 mmol) was added in portion wise after interval of 0.5 hr under nitrogen atmosphere. The reaction mixture was reflux till the completion of reaction (TLC control). Solvent was evaporated under reduced pressure and purification of the residue on a

silica gel column chromatography using EtOAc/Pet ether as eluent, furnished the *N*-fused indoline **7a** (58 mg, 40%) as a yellow sticky liquid.

Physical appearance: yellow sticky liquid.

R_f: 0.5 (1:9, EtOAc: Pet ether).

IR (neat): 2980, 1588, 1450, 1130, 788 cm⁻¹.

¹H NMR (500 MHz, CDCl₃): δ 7.45-7.40 (m, 4H), 7.35-7.25 (m, 6H), 7.14 (t, *J* = 8.0 Hz, 1H), 7.04 (d, *J* = 8.0 Hz, 1H), 6.87 (t, *J* = 8.0 Hz, 1H), 6.67 (d, *J* = 8.0 Hz, 1H), 4.97 (q, *J* = 3.5 Hz, 1H), 4.12 (dd, *J* = 15.0, 3.5 Hz, 1H), 3.99 (dd, *J* = 15.0, 3.5 Hz, 1H), 3.33 (qd, *J* = 7.5, 3.5 Hz, 1H), 1.38 (d, *J* = 7.5 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃, DEPT): δ 153.1 (C), 141.9 (C), 135.5 (C), 134.1 (C), 132.9 (C), 131.4 (2×CH), 129.2 (2×CH), 128.6 (2×CH), 128.0 (C), 127.9 (2×CH), 127.8 (CH), 127.5 (CH), 127.3 (CH), 124.3 (CH), 121.2 (CH), 112.4 (CH), 82.6 (CH), 63.9 (CH₂), 40.7 (CH), 22.7 (CH₃).

HRMS (ESI, M+H⁺): *m/z* calcd. for C₂₄H₂₂NS 356.1470 and found 356.1472.

(3*R*,9*R*,9*aR*)-9-methyl-1,3-diphenyl-2-(phenylthio)-9,9*a*-dihydro-3*H*-pyrrolo[1,2-*a*]indole (7b):

To a magnetically stirred solution of the alkyne derivative **8b** (164 mg, 0.510 mmol) and AIBN (14 mg, 0.085 mmol) in dry benzene (18 mL) was added a thiophenol (78 μL, 0.765 mmol). The reaction mixture was refluxed and AIBN (70 mg, 0.425 mmol) was added in portion wise after interval of 0.5 hr under nitrogen atmosphere. The reaction mixture was reflux till the completion of reaction (TLC control). Solvent was evaporated under reduced pressure and purification of the residue on a silica gel column chromatography using EtOAc/Pet ether as eluent, furnished the *N*-fused indoline **7b** (150 mg, 68%) as a white solid.

Physical appearance: white solid.

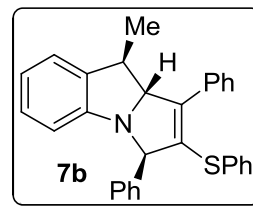
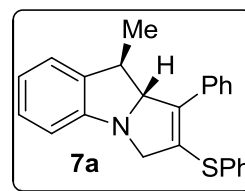
M.P.: 152-154 °C.

R_f: 0.4 (1:9, EtOAc: Pet ether).

IR (neat): 3056, 2867, 1602, 1479, 1469, 1308, 1216, 753 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ 7.59 (dd, *J* = 8.0, 1.2 Hz, 2H), 7.42 (t, *J* = 8.0 Hz, 2H), 7.35-7.25 (m, 6H), 7.20-7.15 (m, 4H), 7.09 (d, *J* = 8.0 Hz, 1H), 7.05 (dd, *J* = 8.0, 1.2 Hz, 2H), 6.91 (td, *J* = 8.0, 1.2 Hz, 1H), 6.76 (d, *J* = 8.0 Hz, 1H), 5.17 (t, *J* = 3.6 Hz, 1H), 5.09 (d, *J* = 3.6 Hz, 1H), 3.43 (qd, *J* = 6.8, 3.6 Hz, 1H), 1.40 (d, *J* = 6.8 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃, DEPT): δ 153.2 (C), 145.0 (C), 141.4 (C), 135.1 (C), 134.0 (C), 133.5 (C), 130.6 (C), 130.3 (2×CH), 129.0 (2×CH), 128.6 (4×CH), 128.2 (CH), 128.0 (2×CH), 127.9



(CH), 127.7 (CH), 127.6 (2×CH), 126.8 (CH), 124.3 (CH), 121.3 (CH), 112.1 (CH), 81.9 (CH), 78.0 (CH), 40.8 (CH), 22.6 (CH₃).

HRMS (ESI, M+H⁺): m/z calcd. for C₃₀H₂₆NS 432.1780, found 432.1780.

(3R,9R,9aR)-9-methyl-3-phenyl-2-(phenylthio)-1-(p-tolyl)-9,9a-dihydro-3H-pyrrolo[1,2-a]indole (7c):

Reaction of the alkyne **8c** (100 mg, 0.298 mmol) with thiophenol (46 μL, 0.447 mmol) and AIBN (49 mg, 0.298 mmol) in benzene (10 mL) as described for *N*-fused indoline **7a** followed by purification of the residue on a silica gel column chromatography using ethyl acetate-Pet ether as eluent, furnished the *N*-fused indoline derivative **7c** (86 mg, 65%) as a white solid.

Physical appearance: white solid.

M.P.: 158-160 °C.

R_f: 0.5 (1:9, EtOAc: Pet ether).

IR (neat): 2958, 2928, 1601, 1461, 1234, 1044, 802 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ 7.47 (d, *J* = 8.0 Hz, 2H), 7.35-7.20 (m, 8H), 7.15-7.10 (m, 3H), 7.07 (d, *J* = 8.0 Hz, 1H), 7.02 (dd, *J* = 8.0, 1.6 Hz, 2H), 6.89 (td, *J* = 8.0, 1.2 Hz, 1H), 6.75 (d, *J* = 8.0 Hz, 1H), 5.14 (t, *J* = 3.6 Hz, 1H), 5.08 (d, *J* = 3.6 Hz, 1H), 3.42 (q, *J* = 7.6, 3.6 Hz, 1H), 2.38 (s, 3H), 1.39 (d, *J* = 7.6 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 153.2 (C), 145.3 (C), 141.4 (C), 138.2 (C), 135.2 (C), 133.8 (C), 131.0 (C), 130.1 (2×CH), 129.6 (C), 129.4 (2×CH), 129.0 (2×CH), 128.6 (2×CH), 128.0 (2×CH), 127.9 (CH), 127.7 (CH), 127.6 (2×CH), 126.7 (CH), 124.4 (CH), 121.4 (CH), 112.2 (CH), 81.9 (CH), 78.1 (CH), 40.8 (CH), 22.6 (CH₃), 21.5 (CH₃).

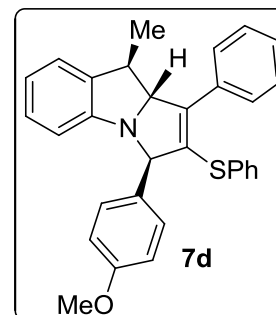
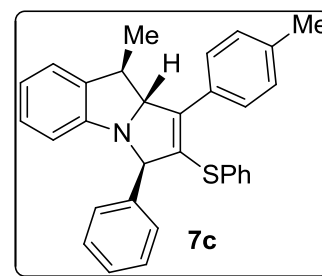
HRMS (ESI, M+H⁺): m/z calcd. for C₃₁H₂₈NS 446.1937, found 446.1935.

(3R,9R,9aR)-3-(4-methoxyphenyl)-9-methyl-1-phenyl-2-(phenylthio)-9,9a-dihydro-3H-pyrrolo[1,2-a]indole (7d):

Reaction of the alkyne **8d** (110 mg, 0.313 mmol) with thiophenol (48 μL, 0.469 mmol) and AIBN (52 mg, 0.313 mmol) in benzene (12 mL) as described for *N*-fused indoline **7a** followed by purification of the residue on a silica gel column chromatography using ethyl acetate-Pet ether as eluent, furnished the *N*-fused indoline derivative **7d** (80 mg, 55%) as a white solid.

Physical appearance: white solid.

M.P.: 164-166 °C.



R_f: 0.3 (1:9, EtOAc: Pet ether).

IR (neat): 2950, 2920, 1619, 1450, 1250, 1044, 1031, 802 cm⁻¹.

¹H NMR (500 MHz, CDCl₃): δ 7.56 (dd, *J* = 9.0, 1.5 Hz, 2H), 7.40 (t, *J* = 9.0 Hz, 2H), 7.32 (td, *J* = 9.0, 0.8 Hz, 1H), 7.15-7.10 (m, 6H), 7.06 (d, *J* = 7.0 Hz, 1H), 7.02 (dt, *J* = 7.0, 0.8 Hz, 2H), 6.88 (t, *J* = 7.0 Hz, 1H), 6.84 (d, *J* = 7.0 Hz, 2H), 6.73 (d, *J* = 7.0 Hz, 1H), 5.12 (t, *J* = 3.5 Hz, 1H), 5.04 (d, *J* = 3.5 Hz, 1H), 3.80 (s, 3H), 3.39 (qd, *J* = 7.0, 3.5 Hz, 1H), 1.37 (d, *J* = 7.0 Hz, 3H).

¹³C NMR (125 MHz, CDCl₃, DEPT): δ 159.2 (C), 144.7 (C), 135.2 (C), 134.1 (C), 133.6 (C), 133.5 (C), 130.8 (C), 130.4 (2×CH), 129.0 (CH), 128.7 (2×CH), 128.6 (2×CH), 128.2 (2×CH), 128.1 (2×CH), 128.15 (C), 128.0 (CH), 126.8 (CH), 124.4 (CH), 121.3 (CH), 114.1 (2×CH), 112.2 (CH), 81.7 (CH), 77.5 (CH), 55.4 (CH₃), 40.8 (CH), 22.6 (CH₃).

HRMS (ESI, M+H⁺): *m/z* calcd. for C₃₁H₂₈NOS 462.1890, found 462.1894.

1-(4-((3*R*,9*R*,9*aR*)-9-methyl-3-phenyl-2-(phenylthio)-9,9*a*-dihydro-3*H*-pyrrolo[1,2-*a*]indol-1-yl)phenyl)ethanone (7e):

Reaction of the alkyne **8e** (70 mg, 0.193 mmol) with thiophenol (30 μL, 0.289 mmol) and AIBN (31 mg, 0.193 mmol) in benzene (5 mL) as described for *N*-fused indoline **7a** followed by purification of the residue on a silica gel column using ethyl acetate–pet ether as eluent, furnished the *N*-fused indoline derivative **7e** (75 mg, 82%) as a sticky liquid.

Physical appearance: sticky liquid.

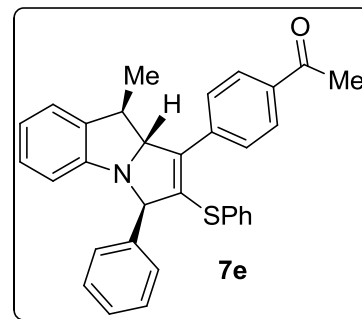
R_f: 0.2 (1:9, EtOAc: Pet ether).

IR (neat): 3054, 2959, 2925, 1683, 1601, 1478, 1356, 1267, 843, 768 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ 8.01 (d, *J* = 8.8 Hz, 2H), 7.69 (d, *J* = 8.8 Hz, 2H), 7.35-7.30 (m, 3H), 7.25-7.20 (m, 2H), 7.20-7.15 (m, 4H), 7.08 (d, *J* = 7.6 Hz, 1H), 7.04 (dd, *J* = 7.6, 0.8 Hz, 2H), 6.91 (td, *J* = 7.6, 0.8 Hz, 1H), 6.76 (d, *J* = 7.6 Hz, 1H), 5.19 (t, *J* = 3.2 Hz, 1H), 5.12 (d, *J* = 3.2 Hz, 1H), 3.37 (qd, *J* = 6.8, 3.2 Hz, 1H), 2.63 (s, 3H), 1.39 (d, *J* = 6.8 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃, DEPT): δ 197.5 (C), 152.9 (C), 142.5 (C), 140.8 (C), 139.1 (C), 136.3 (C), 134.9 (C), 133.8 (C), 132.5 (C), 131.1 (2×CH), 129.1 (2×CH), 128.7 (2×CH), 128.6 (2×CH), 128.2 (2×CH), 128.0 (CH), 127.8 (CH), 127.5 (CH), 127.4 (CH), 124.4 (2×CH), 121.5 (CH), 112.2 (CH), 81.8 (CH), 78.2 (CH), 40.8 (CH), 25.3 (CH₃), 22.6 (CH₃).

HRMS (ESI, M+Na⁺): *m/z* calcd. for C₃₂H₂₇NaNOS 496.1720, found 496.1718.



(3*R*,9*R*,9*aR*)-9-methyl-3-phenyl-2-(phenylthio)-1-(thiophen-2-yl)-9,9*a*-dihydro-3*H*-pyrrolo[1,2-*a*]indole (7*f*):

Reaction of the alkyne **8f** (90 mg, 0.275 mmol) with thiophenol (42 μ L, 0.413 mmol) and AIBN (45.0 mg, 0.275 mmol) in benzene (8 mL) as described for *N*-fused indoline **7a** followed by purification of the residue on a silica gel column chromatography using ethyl acetate-Pet ether as eluent, furnished the *N*-fused indoline derivative **7f** (94 mg, 78%) as a white solid.

Physical appearance: White solid.

M.P.: 152-154 $^{\circ}$ C.

R_f: 0.4 (1:9, EtOAc: Pet ether).

IR (neat): 3067, 2918, 2861, 1602, 1581, 1479, 1344, 1288, 1024, 752, 697 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ 7.42 (d, J = 6.4 Hz, 1H), 7.40-7.30 (m, 4H), 7.27 (dd, J = 6.4, 1.6 Hz, 2H), 7.20-7.15 (m, 6H), 7.07 (dt, J = 7.0, 0.8 Hz, 2H), 6.94 (t, J = 7.0 Hz, 1H), 6.78 (d, J = 7.0 Hz, 1H), 5.15 (t, J = 3.2 Hz, 1H), 5.11 (d, J = 3.2 Hz, 1H), 3.83 (qd, J = 7.0, 3.2 Hz, 1H), 1.61 (d, J = 7.0 Hz, 3H).

^{13}C NMR (125 MHz, CDCl_3 , DEPT): δ 153.0 (C), 141.5 (C), 137.9 (C), 135.8 (C), 134.9 (C), 132.9 (C), 130.6 (2 $\times$ CH), 129.5 (C), 129.0 (2 $\times$ CH), 128.6 (2 $\times$ CH), 127.9 (CH), 127.7 (CH), 127.5 (2 $\times$ CH), 127.3 (CH), 127.1 (CH), 126.9 (CH), 126.8 (CH), 124.2 (CH), 121.4 (CH), 112.1 (CH), 82.0 (CH), 78.6 (CH), 41.5 (CH), 23.0 (CH_3).

HRMS (ESI, $\text{M}+\text{Na}^+$): m/z calcd. for $\text{C}_{28}\text{H}_{23}\text{NaNS}_2$ 460.1175, found 460.1172.

(3*R*,9*aR*)-1,3-diphenyl-2-(phenylthio)-9,9*a*-dihydro-3*H*-pyrrolo[1,2-*a*]indole (7*g*):

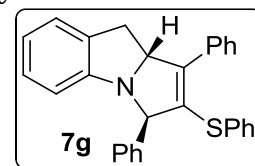
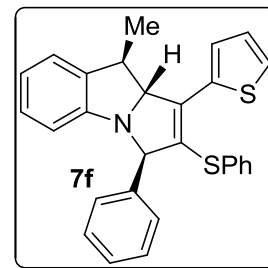
Reaction of the alkyne **8g** (100 mg, 0.325 mmol) with thiophenol (50 μ L, 0.488 mmol) and AIBN (53.0 mg, 0.325 mmol) in benzene (10 mL) as described for *N*-fused indoline **7a** followed by purification of the residue on a silica gel column chromatography using ethyl acetate-Pet ether as eluent, furnished the *N*-fused indoline derivative **7g** (88 mg, 65%) as a sticky solid.

Physical appearance: sticky solid.

R_f: 0.6 (1:9, EtOAc: Pet ether).

IR (neat): 2950, 1585, 1420, 1140, 989, 760 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ 7.61 (dd, J = 7.6, 1.2 Hz, 2H), 7.41 (t, J = 7.6 Hz, 2H), 7.35-7.30 (m, 6H), 7.20-7.15 (m, 4H), 7.10 (d, J = 7.6 Hz, 1H), 7.04 (dd, J = 7.6, 1.2 Hz, 2H), 6.89 (t, J = 7.6



Hz, 1H), 6.77 (d, $J = 7.6$ Hz, 1H), 5.60 (dt, $J = 10.0, 3.6$ Hz, 1H), 5.14 (d, $J = 3.6$ Hz, 1H), 3.31 (dd, $J = 16.4, 10.0$ Hz, 1H), 3.16 (dd, $J = 16.4, 3.6$ Hz, 1H).

^{13}C NMR (100 MHz, CDCl_3 , DEPT): δ 153.8 (C), 145.0 (C), 141.2 (C), 133.8 (C), 133.5 (C), 130.6 (C), 130.3 (2 $\times$ CH), 129.2 (C), 129.0 (2 $\times$ CH), 128.7 (2 $\times$ CH), 128.6 (2 $\times$ CH), 128.2 (CH), 128.1 (2 $\times$ CH), 127.7 (CH), 127.6 (CH), 127.5 (2 $\times$ CH), 126.8 (CH), 125.1 (CH), 121.2 (CH), 112.0 (CH), 78.0 (CH), 73.3 (CH), 33.7 (CH_2).

HRMS (ESI, $\text{M}+\text{H}^+$): m/z calcd. for $\text{C}_{29}\text{H}_{24}\text{NS}$ 418.6132 and found 418.6132.

(3*R*,9*R*,9*aR*)-9-cyclohexyl-1,3-diphenyl-2-(phenylthio)-9,9*a*-dihydro-3*H*-pyrrolo[1,2-*a*]indole (7*h*):

Reaction of the alkyne **8h** (100 mg, 0.257 mmol) with thiophenol (40 μL , 0.386 mmol) and AIBN (42.0 mg, 0.257 mmol) in benzene (10 mL) as described for synthesis of *N*-fused indoline **7a** followed by purification of the residue on a silica gel column chromatography using ethyl acetate-Pet ether as eluent, furnished the *N*-fused indoline derivative **7h** (100 mg, 78%) as a white solid.

Physical appearance: white solid.

M.P.: 164-166 $^\circ\text{C}$

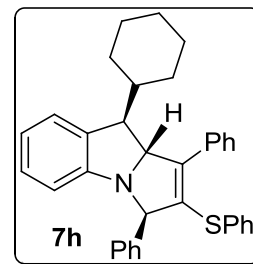
R_f: 0.6 (1:9, EtOAc: Pet ether).

IR (neat): 3010, 2985, 2945, 1600, 1420, 1275, 1020, 785 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ 7.42 (dd, $J = 8.0, 1.6$ Hz, 2H), 7.38 (t, $J = 8.0$ Hz, 2H), 7.35-7.30 (m, 6H), 7.20-7.10 (m, 5H), 6.95 (dd, $J = 8.0, 1.2$ Hz, 2H), 6.90 (td, $J = 8.0, 0.8$ Hz, 1H), 6.79 (d, $J = 8.0$ Hz, 1H), 5.18 (t, $J = 2.4$ Hz, 1H), 5.09 (d, $J = 2.4$ Hz, 1H), 3.18 (dd, $J = 6.0, 2.4$ Hz, 1H), 1.75-1.55 (m, 6H), 1.20-1.10 (m, 4H), 1.00-0.90 (m, 1H).

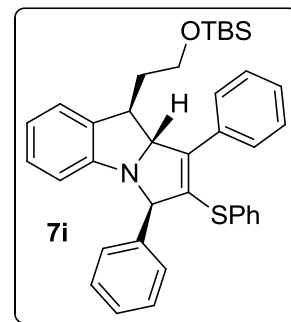
^{13}C NMR (100 MHz, CDCl_3 , DEPT): δ 154.6 (C), 147.3 (C), 141.1 (C), 134.2 (C), 134.1 (C), 131.8 (C), 130.7 (C), 129.6 (2 $\times$ CH_2), 129.0 (2 $\times$ CH_2), 128.6 (2 $\times$ CH_2), 128.5 (2 $\times$ CH_2), 128.2 (2 $\times$ CH_2), 128.1 (CH), 127.8 (CH), 127.7 (2 $\times$ CH_2), 127.6 (CH), 126.5 (CH), 125.8 (CH), 120.9 (CH), 112.0 (CH), 77.9 (CH), 77.4 (CH), 50.8 (CH), 43.9 (CH), 30.1 (CH_2), 30.0 (CH_2), 26.7 (CH_2), 26.6 (CH_2), 26.5 (CH_2).

HRMS (ESI, $\text{M}+\text{H}^+$): m/z calcd. for $\text{C}_{35}\text{H}_{34}\text{NS}$ 500.2436 and found 500.2436.



(3*R*,9*R*,9*aR*)-9-(2-((*tert*-butyldimethylsilyl)oxy)ethyl)-1,3-diphenyl-2-(phenylthio)-9,9*a*-dihydro-3*H*-pyrrolo[1,2-*a*]indole (7i):

Reaction of the alkyne **8i** (175 mg, 0.376 mmol) with thiophenol (58 μ L, 0.564 mmol) and AIBN (62 mg, 0.376 mmol) in benzene (15 mL) as described for *N*-fused indoline **7a** followed by purification of the residue on a silica gel column using ethyl acetate–pet ether as eluent, furnished the *N*-fused indoline derivative **7i** (162 mg, 75%) as a sticky solid.



Physical appearance: sticky solid.

R_f: 0.4 (1:9, EtOAc: Pet ether).

IR (neat): 3010, 2945, 1590, 1485, 1310, 1020, 780 cm^{-1} .

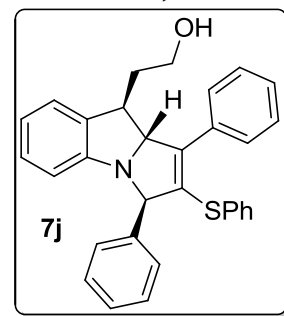
¹H NMR (400 MHz, CDCl₃): δ 7.57 (d, *J* = 7.6 Hz, 2H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.35–7.30 (m, 6H), 7.20–7.15 (m, 5H), 7.02 (dd, *J* = 7.6, 1.2 Hz, 2H), 6.93 (t, *J* = 7.6 Hz, 1H), 6.83 (t, *J* = 7.6 Hz, 1H), 5.33 (t, *J* = 2.8 Hz, 1H), 5.13 (d, *J* = 2.8 Hz, 1H), 3.75 (brt, *J* = 5.6 Hz, 2H), 3.52 (td, *J* = 6.8, 2.8 Hz, 1H), 2.05–1.85 (m, 2H), 0.89 (s, 9H), 0.07 (s, 3H), 0.04 (s, 3H).

¹³C NMR (100 MHz, CDCl₃, DEPT): δ 153.8 (C), 146.0 (C), 141.0 (C), 134.0 (C), 133.8 (C), 133.2 (C), 130.6 (C), 130.0 (2 $\times$ CH), 129.0 (2 $\times$ CH), 128.6 (2 $\times$ CH), 128.5 (2 $\times$ CH), 128.1 (CH), 128.0 (2 $\times$ CH), 127.9 (CH), 127.6 (2 $\times$ CH), 126.7 (CH), 125.2 (CH), 121.2 (CH), 112.2 (CH), 80.1 (CH), 77.7 (CH), 60.9 (CH₂), 42.5 (CH), 39.7 (CH₂), 26.0 (3 $\times$ CH₃), 18.3 (C), -5.1 (CH₃), -5.2 (CH₃).

HRMS (ESI, M+H⁺): *m/z* calcd. for C₃₇H₄₂NOSSi 576.2760, found 576.2762.

2-((3*R*,9*R*,9*aR*)-1,3-diphenyl-2-(phenylthio)-9,9*a*-dihydro-3*H*-pyrrolo[1,2-*a*]indol-9-yl)ethanol (7j):

Reaction of the alkyne **8j** (70 mg, 0.199 mmol) with thiophenol (31 μ L, 0.298 mmol) and AIBN (33.0 mg, 0.199 mmol) in benzene (8 mL) as described for *N*-fused indoline **7a** followed by purification of the residue on a silica gel column using ethyl acetate–pet ether as eluent, furnished the *N*-fused indoline derivative **7j** (64 mg, 70%) as a sticky solid.



Physical appearance: sticky solid.

R_f: 0.4 (2:8, EtOAc: Pet ether).

IR (neat): 3320, 2980, 1580, 1478, 1234, 1150, 790 cm^{-1} .

¹H NMR (400 MHz, CDCl₃): δ 7.50 (dd, *J* = 6.8, 1.2 Hz, 2H), 7.41 (td, *J* = 6.8, 1.2 Hz, 2H), 7.35–7.25 (m, 6H), 7.20–7.10 (m, 4H), 7.09 (d, *J* = 7.6

Hz, 1H), 7.00-6.95 (m, 2H), 6.94 (td, $J = 7.6, 0.8$ Hz, 1H), 6.83 (d, $J = 7.6$ Hz, 1H), 5.28 (t, $J = 2.8$ Hz, 1H), 5.11 (d, $J = 2.8$ Hz, 1H), 3.70-3.55 (m, 2H), 3.53 (td, $J = 6.0, 2.8$ Hz, 1H), 2.05-1.90 (m, 2H).

^{13}C NMR (100 MHz, CDCl_3 , DEPT): δ 153.6 (C), 145.4 (C), 140.6 (C), 134.0 (C), 133.5 (C), 132.5 (C), 131.0 (C), 130.2 (2 $\times$ CH), 129.0 (2 $\times$ CH), 128.8 (2 $\times$ CH), 128.7 (2 $\times$ CH), 128.3 (CH), 128.2 (CH), 128.0 (2 $\times$ CH), 127.8 (CH), 127.6 (2 $\times$ CH), 126.8 (CH), 125.1 (CH), 121.8 (CH), 112.6 (CH), 80.0 (CH), 77.6 (CH), 60.3 (CH_2), 42.4 (CH), 39.0 (CH_2).

HRMS (ESI, $\text{M}+\text{Na}^+$): m/z calcd. for $\text{C}_{31}\text{H}_{27}\text{NaNOS}$ 484.1720, found 484.1728.

2-((3*R*,9*R*,9*aR*)-3-phenyl-2-(phenylthio)-1-(thiophen-2-yl)-9,9*a*-dihydro-3*H*-pyrrolo[1,2-*a*]indol-9-yl)ethanol (7k):

Reaction of the alkyne **8k** (80 mg, 0.224 mmol) with thiophenol (34 μL , 0.335 mmol) and AIBN (36.0 mg, 0.224 mmol) in benzene (10 mL) as described for *N*-fused indoline **7a** followed by purification of the residue on a silica gel column using ethyl acetate–pet ether as eluent, furnished the *N*-fused indoline derivative **7k** (75 mg, 72%) as a sticky solid.

Physical appearance: sticky solid.

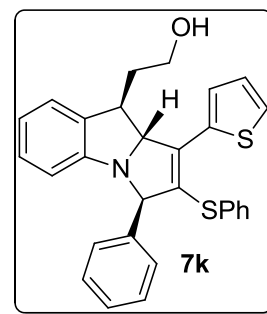
R_f : 0.4 (2:8, EtOAc: Pet ether).

IR (neat): 3310, 2980, 1595, 1400, 1234, 1132, 1044, 815, 784 cm^{-1} .

^1H NMR (500 MHz, CDCl_3): δ 7.38 (dd, $J = 5.5, 1.0$ Hz, 1H), 7.35 (dd, $J = 5.5, 1.0$ Hz, 1H), 7.30-7.25 (m, 3H), 7.25-7.20 (m, 2H), 7.20-7.15 (m, 2H), 7.15-7.10 (m, 4H), 6.98 (dd, $J = 7.0, 1.0$ Hz, 2H), 6.93 (td, $J = 7.0, 1.0$ Hz, 1H), 6.81 (d, $J = 7.0$ Hz, 1H), 5.24 (t, $J = 2.5$ Hz, 1H), 5.08 (d, $J = 2.5$ Hz, 1H), 3.96 (td, $J = 6.0, 2.5$ Hz, 1H), 3.76 (ddd, $J = 15.0, 12.5, 6.5$ Hz, 1H), 3.73 (ddd, $J = 15.0, 11.0, 6.0$ Hz, 1H), 2.15-2.10 (m, 2H).

^{13}C NMR (125 MHz, CDCl_3 , DEPT): δ 153.4 (C), 140.7 (C), 137.8 (C), 135.5 (2 $\times$ CH), 133.0 (C), 132.3 (C), 130.6 (C), 129.9 (C), 129.1 (2 $\times$ CH), 128.7 (2 $\times$ CH), 128.2 (CH), 127.8 (CH), 127.5 (CH), 127.4 (2 $\times$ CH), 127.2 (CH), 127.0 (CH), 126.8 (CH), 125.0 (CH), 121.8 (CH), 112.5 (CH), 80.2 (CH), 78.1 (CH), 60.2 (CH_2), 43.1 (CH), 39.1 (CH_2).

HRMS (ESI, $\text{M}+\text{Na}^+$): m/z calcd. for $\text{C}_{29}\text{H}_{25}\text{NaNOS}_2$ 490.1280, found 490.1284.



(3*R*,9*R*,9*aR*)-2-((4-methoxyphenyl)thio)-9-methyl-1,3-diphenyl-9,9*a*-dihydro-3*H*-pyrrolo[1,2-*a*]indole (7l):

Reaction of the alkyne **8b** (65 mg, 0.202 mmol) with 4-methoxy thiophenol (38.0 μ L, 0.303 mmol) and AIBN (34.0 mg, 0.202 mmol) in benzene (5 mL) as described for *N*-fused indoline **7a** followed by purification of the residue on a silica gel column using ethyl acetate–pet ether as eluent, furnished the *N*-fused indoline derivative **7l** (71 mg, 76%) as a sticky solid.

Physical appearance: sticky solid.

R_f: 0.4 (1:9, EtOAc: Pet ether).

IR (neat): 2950, 1598, 145, 1258, 1020, 968, 778 cm^{-1} .

¹H NMR (400 MHz, CDCl₃): δ 7.62 (d, J = 7.6 Hz, 2H), 7.45 (t, J = 7.6 Hz, 2H), 7.35–7.25 (m, 4H), 7.21 (dd, J = 8.0, 1.6 Hz, 2H), 7.15 (t, J = 8.0 Hz, 1H), 7.07 (d, J = 7.6 Hz, 1H), 6.97 (d, J = 6.8 Hz, 2H), 6.89 (t, J = 7.6 Hz, 1H), 6.76 (d, J = 8.0 Hz, 1H), 6.67 (d, J = 6.8 Hz, 2H), 5.14 (t, J = 3.6 Hz, 1H), 5.00 (d, J = 3.6 Hz, 1H), 3.79 (s, 3H), 3.41 (qd, J = 7.2, 3.6 Hz, 1H), 1.37 (d, J = 7.2 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃, DEPT): δ 159.5 (C), 153.0 (C), 141.1 (C), 140.6 (C), 135.3 (C), 134.3 (C), 134.2 (2 $\times$ CH), 132.4 (C), 128.7 (4 $\times$ CH), 128.1 (2 $\times$ CH), 127.9 (2 $\times$ CH), 127.7 (3 $\times$ CH), 124.4 (CH), 122.6 (C), 121.4 (CH), 114.5 (2 $\times$ CH), 112.2 (CH), 81.9 (CH), 78.5 (CH), 55.5 (CH₃), 40.7 (CH), 22.6 (CH₃).

HRMS (ESI, M+Na⁺): m/z calcd. for C₃₁H₂₇NaNOS 484.1715, found 484.1710.

(3*R*,9*R*,9*aR*)-9-methyl-2-(naphthalen-2-ylthio)-1,3-diphenyl-9,9*a*-dihydro-3*H*-pyrrolo[1,2-*a*]indole (7m):

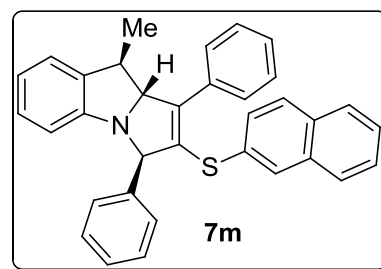
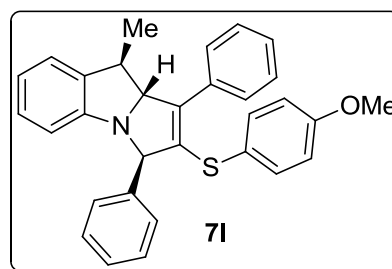
Reaction of the alkyne **8b** (70 mg, 0.218 mmol) with 2-naphthalenethiol (52 mg, 0.327 mmol) and AIBN (36.0 mg, 0.218 mmol) in benzene (5 mL) as described for *N*-fused indoline **7a** followed by purification of the residue on a silica gel column using ethyl acetate–pet ether as eluent, furnished the *N*-fused indoline derivative **7m** (84 mg, 80%) as a sticky solid.

Physical appearance: sticky solid.

R_f: 0.4 (1:9, EtOAc: Pet ether).

IR (neat): 3010, 2910, 1610, 1598, 1478, 1354, 1120, 866 cm^{-1} .

¹H NMR (400 MHz, CDCl₃): δ 7.79–7.77 (m, 1H), 7.66 (d, J = 8.4 Hz, 1H), 7.60 (d, J = 8.0 Hz, 2H), 7.45–7.40 (m, 4H), 7.35–



7.30 (m, 8H), 7.20-7.15 (m, 3H), 6.99 (t, $J = 8.0$ Hz, 1H), 6.78 (d, $J = 8.0$ Hz, 1H), 5.22 (brs, 2H), 3.47 (brq, $J = 7.2$ Hz, 1H), 1.43 (d, $J = 7.2$ Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3 , DEPT): δ 153.1 (C), 146.8 (C), 141.0 (C), 135.1 (C), 133.9 (C), 133.8 (C), 132.0 (C), 131.4 (C), 129.9 (C), 128.7 (4 $\times$ CH), 128.6 (CH), 128.4 (CH), 128.1 (CH), 128.0 (2 $\times$ CH), 127.8 (CH), 127.7 (CH), 127.6 (2 $\times$ CH), 127.5 (CH), 127.4 (CH), 127.3 (CH), 126.6 (CH), 126.0 (CH), 124.5 (CH), 121.6 (CH), 112.4 (CH), 81.8 (CH), 78.0 (CH), 40.7 (CH), 22.8 (CH_3).

HRMS (ESI, $\text{M}+\text{Na}^+$): m/z calcd. for $\text{C}_{34}\text{H}_{27}\text{NaNS}$ 504.1670, found 504.1676.

3,3,9-trimethyl-1-phenyl-2-(phenylthio)-3H-pyrrolo[1,2-a]indole (6a):

Reaction of the alkyne **13a** (90 mg, 0.329 mmol) with thiophenol (51 μL , 0.494 mmol) and AIBN (54 mg, 0.329 mmol) in benzene (10 mL) as described for *N*-fused indoline **7a** followed by purification of the residue on a silica gel column using ethyl acetate–pet ether as eluent, furnished the pyrrolo[1,2-*a*]indole derivative **6a** (107 mg, 85%) as a white solid.

Physical appearance: White solid.

M.P.: 170-172 $^\circ\text{C}$

R_f: 0.5 (1:9, EtOAc: Pet ether).

IR (neat): 3061, 2979, 1581, 1474, 1339, 1163, 1022, 761, 740 cm^{-1} .

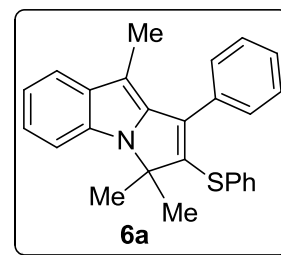
^1H NMR (400 MHz, CDCl_3): δ 7.64 (d, $J = 8.0$ Hz, 1H), 7.56 (dd, $J = 8.0, 0.8$ Hz, 2H), 7.45-7.40 (m, 4H), 7.30-7.25 (m, 2H), 7.21 (d, $J = 8.0$ Hz, 1H), 7.17 (t, $J = 8.0$ Hz, 2H), 7.15-7.10 (m, 2H), 2.15 (s, 3H), 1.65 (s, 6 H).

^{13}C NMR (100 MHz, CDCl_3 , DEPT): δ 143.5 (C), 139.6 (C), 139.0 (C), 136.5 (C), 133.6 (C), 133.3 (C), 132.9 (C), 129.5 (2 $\times$ CH), 128.9 (2 $\times$ CH), 128.5 (2 $\times$ CH), 128.2 (CH), 128.1 (2 $\times$ CH), 126.2 (CH), 122.0 (CH), 120.2 (CH), 118.7 (CH), 109.4 (CH), 102.9 (C), 68.3 (C), 25.9 (2 $\times$ CH_3), 9.1 (CH_3).

HRMS (ESI, $\text{M}+\text{Na}^+$): m/z calcd. for $\text{C}_{26}\text{H}_{23}\text{NaNS}$ 404.1460, found 404.1458.

3,3,9-trimethyl-2-(phenylthio)-1-(p-tolyl)-3H-pyrrolo[1,2-a]indole (6b):

Reaction of the alkyne **13b** (136 mg, 0.474 mmol) with thiophenol (73 μL , 0.711 mmol) and AIBN (78 mg, 0.474 mmol) in benzene (15 mL) as described for *N*-fused indoline **7a** followed by



purification of the residue on a silica gel column using ethyl acetate–pet ether as eluent, furnished the pyrrolo[1,2-a]indole derivative **6b** (150 mg, 80%) as a white solid.

Physical appearance: White solid.

M.P.: 174-176 °C.

R_f: 0.6 (1:9, EtOAc: Pet ether).

IR (neat): 2920, 1610, 1478, 1450, 1044, 1031, 815, 750 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ 7.65 (d, *J* = 7.6 Hz, 1H), 7.48 (dd, *J* = 7.6, 1.6 Hz, 2H), 7.43 (d, *J* = 7.6 Hz, 1H), 7.30-7.25 (m, 5H), 7.19 (t, *J* = 8.0 Hz, 2H), 7.15-7.10 (m, 2H), 2.41 (s, 3H), 2.19 (s, 3H), 1.64 (s, 6H).

¹³C NMR (100 MHz, CDCl₃, DEPT): δ 144.0 (C), 139.6 (C), 138.5 (C), 138.2 (C), 136.8 (C), 133.6 (C), 133.3 (C), 129.8 (C), 129.4 (2×CH), 129.0 (2×CH), 128.9 (2×CH), 128.3 (2×CH), 126.0 (CH), 122.0 (CH), 120.2 (CH), 118.7 (CH), 109.7 (CH), 103.0 (C), 68.3 (C), 26.0 (2×CH₃), 21.6 (CH₃), 9.21 (CH₃).

HRMS (ESI, M+Na⁺): *m/z* calcd. for C₂₇H₂₅NaNS 418.1623, found 275.148.1620.

1-(4-methoxyphenyl)-3,3,9-trimethyl-2-(phenylthio)-3H-pyrrolo[1,2-a]indole (6c):

Reaction of the alkyne **13c** (120 mg, 0.396 mmol) with thiophenol (61 μL, 0.593 mmol) and AIBN (65 mg, 0.396 mmol) in benzene (12 mL) as described for *N*-fused indoline **7a** followed by purification of the residue on a silica gel column using ethyl acetate–pet ether as eluent, furnished the pyrrolo[1,2-a]indole derivative **6c** (127 mg, 78%) as a white solid.

Physical appearance: White solid.

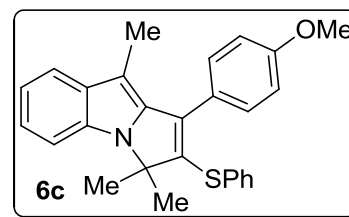
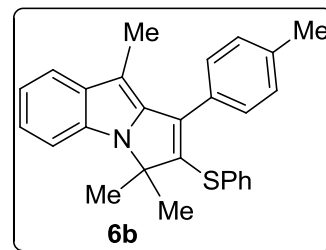
M.P.: 176-178 °C.

R_f: 0.4 (1:9, EtOAc: Pet ether).

IR (neat): 3061, 2983, 2932, 1617, 1573, 1476, 1439, 1363, 1239, 1036, 770 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ 7.62 (d, *J* = 8.0 Hz, 1H), 7.50 (dd, *J* = 8.0, 1.6 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 1H), 7.23 (t, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 1H), 7.16 (t, *J* = 8.0 Hz, 2H), 7.10-7.05 (m, 2H), 6.93 (dd, *J* = 8.0, 1.6 Hz, 2H), 3.84 (s, 3H), 2.17 (s, 3H), 1.61 (s, 6H).

¹³C NMR (100 MHz, CDCl₃, DEPT): δ 159.9 (C), 143.6 (C), 139.7 (C), 137.9 (C), 136.9 (C), 133.6 (C), 133.3 (C), 130.8 (2×CH), 128.9 (2×CH), 128.1 (2×CH), 126.0 (CH), 125.0 (C), 122.0 (CH), 120.2 (CH), 118.7 (CH), 113.7 (2×CH), 109.4 (CH), 102.9 (C), 68.2 (C), 55.4 (CH₃), 25.9 (2×CH₃), 9.3 (CH₃).



HRMS (ESI, M+Na⁺): m/z calcd. for C₂₇H₂₅NaNOS 434.1560 and found 434.1560.

1-(3,5-dimethylphenyl)-3,3,9-trimethyl-2-(phenylthio)-3H-pyrrolo[1,2-a]indole (6d):

Reaction of the alkyne **13d** (100 mg, 0.331 mmol) with thiophenol (51 μ L, 0.496 mmol) and AIBN (54 mg, 0.331 mmol) in benzene (10 mL) as described for *N*-fused indoline **7a** followed by purification of the residue on a silica gel column using ethyl acetate–pet ether as eluent, furnished the pyrrolo[1,2-a]indole derivative **6d** (115 mg, 85%) as a white sticky solid.

Physical appearance: White sticky solid.

R_f: 0.6 (1:9, EtOAc: Pet ether).

IR (neat): 2900, 1690, 1480, 1390, 1200, 1120, 1044, 1035, 815, 774 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ 7.65 (d, *J* = 8.0 Hz, 1H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.25–7.15 (m, 5H), 7.13 (td, *J* = 8.0, 2.4 Hz, 2H), 7.02 (s, 1H), 2.35 (s, 6H), 2.17 (s, 3H), 1.65 (s, 6H).

¹³C NMR (100 MHz, CDCl₃, DEPT): δ 143.5 (C), 139.8 (C), 138.7 (C), 137.5 (2 $\times$ C), 136.6 (C), 133.6 (C), 133.3 (C), 132.6 (C), 130.1 (CH), 128.8 (CH), 128.7 (2 $\times$ CH), 127.2 (2 $\times$ CH), 126.1 (CH), 121.9 (CH), 120.2 (CH), 118.6 (CH), 109.3 (CH), 102.8 (C), 68.2 (C), 26.0 (2 $\times$ CH₃), 21.5 (2 $\times$ CH₃), 9.1 (CH₃).

HRMS (ESI, M+H⁺): m/z calcd. for C₂₈H₂₈NS 419.1952, found 419.1955.

1-(4-(3,3,9-trimethyl-2-(phenylthio)-3H-pyrrolo[1,2-a]indol-1-yl)phenyl)ethanone (6e):

Reaction of the alkyne **13e** (120 mg, 0.381 mmol) with thiophenol (58 μ L, 0.572 mmol) and AIBN (62 mg, 0.381 mmol) in benzene (12 mL) as described for *N*-fused indoline **7a** followed by purification of the residue on a silica gel column using ethyl acetate–hexanes as eluent, furnished pyrrolo[1,2-a]indole derivative **6e** (142 mg, 88%) as a yellow solid.

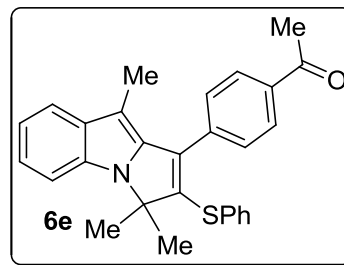
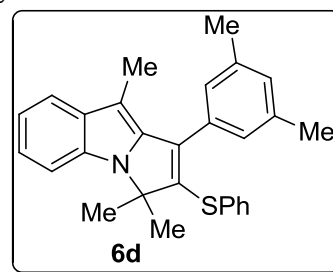
Physical appearance: yellow solid.

M.P.: 178–180 °C.

R_f: 0.4 (1:9, EtOAc: Pet ether).

IR (neat): 2928, 2863, 1686, 1608, 1457, 1340, 1266, 958, 741 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ 8.00 (d, *J* = 8.4 Hz, 2H), 7.66 (d, *J* = 8.4 Hz, 2H), 7.64 (d, *J* = 8.4 Hz, 1H), 7.43 (d, *J* = 8.4 Hz, 1H), 7.25–7.20 (m, 3H), 7.20–7.10 (m, 4H), 2.64 (s, 3H), 2.13 (s, 3H), 1.67 (s, 6H).

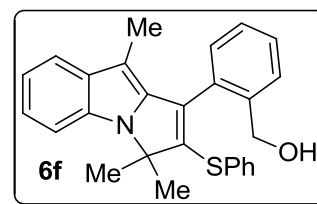


¹³C NMR (125 MHz, CDCl₃, DEPT): δ 197.8 (C), 142.0 (C), 140.4 (C), 139.0 (C), 138.0 (C), 137.0 (C), 135.8 (C), 133.6 (C), 133.2 (C), 129.8 (2×CH), 129.0 (2×CH), 128.7 (2×CH), 128.2 (2×CH), 126.5 (CH), 122.2 (CH), 120.3 (CH), 119.0 (CH), 109.4 (CH), 103.0 (C), 68.4 (C), 26.8 (CH₃), 25.9 (2×CH₃), 9.2 (CH₃).

HRMS (ESI, M+Na⁺): m/z calcd. for C₂₈H₂₅NaNOS 446.1550, found 446.1556.

(2-(3,3,9-trimethyl-2-(phenylthio)-3H-pyrrolo[1,2-a]indol-1-yl)phenyl)methanol (6f):

Reaction of the alkyne **13f** (100 mg, 0.330 mmol) with thiophenol (50 μL, 0.494 mmol) and AIBN (54 mg, 0.330 mmol) in benzene (10 mL) as described for *N*-fused indoline **7a** followed by purification of the residue on a silica gel column using ethyl acetate–pet ether as eluent, furnished the pyrrolo[1,2-*a*]indole derivative **6f** (102 mg, 75%) as a sticky solid.



Physical appearance: sticky solid.

R_f: 0.5 (2:8, EtOAc: Pet ether).

IR (neat): 3340, 2985, 2910, 1590, 1456, 1230, 1050, 765 cm⁻¹.

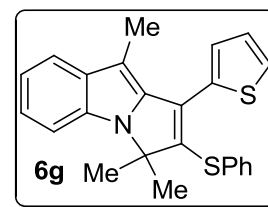
¹H NMR (400 MHz, CDCl₃): δ 7.55 (t, *J* = 8.0 Hz, 2H), 7.41 (t, *J* = 8.0 Hz, 1H), 7.40 (td, *J* = 8.0, 1.6 Hz, 1H), 7.28 (td, *J* = 8.0, 0.8 Hz, 1H), 7.25–7.20 (m, 4H), 7.15–7.05 (m, 4H), 4.57 (AB, *J* = 13.2 Hz, 1H), 4.52 (AB, *J* = 13.2 Hz, 1H), 1.87 (s, 3H), 1.73 (s, 3H), 1.68 (s, 3H).

¹³C NMR (100 MHz, CDCl₃, DEPT): δ 142.2 (C), 140.0 (C), 139.7 (C), 139.4 (C), 134.6 (C), 133.6 (C), 133.1 (C), 131.4 (C), 130.9 (2×CH), 129.6 (CH), 128.9 (2×CH), 128.8 (CH), 128.0 (CH), 127.7 (CH), 127.1 (CH), 122.0 (CH), 120.2 (CH), 118.8 (CH), 109.3 (CH), 102.6 (C), 68.1 (C), 63.2 (CH₂), 26.2 (CH₃), 25.6 (CH₃), 8.1 (CH₃).

HRMS (ESI, M+Na⁺): m/z calcd. for C₂₇H₂₅NaNOS 434.1549 and found 434.1551.

3,3,9-trimethyl-2-(phenylthio)-1-(thiophen-2-yl)-3H-pyrrolo[1,2-a]indole (6g):

Reaction of the alkyne **13g** (120 mg, 0.429 mmol) with thiophenol (66 μL, 0.643 mmol) and AIBN (71 mg, 0.429 mmol) in benzene (12 mL) as described for *N*-fused indoline **7a** followed by purification of the residue on a silica gel column using ethyl acetate–pet ether as eluent, furnished the pyrrolo[1,2-*a*]indole derivative **6g** (143 mg, 86%) as a white solid.



Physical appearance: White solid.

M.P.: 154–156 °C.

R_f: 0.5 (1:9, EtOAc: Pet ether).

IR (neat): 2900, 2896, 1580, 1478, 1400, 1234, 1044, 1031, 965, 815, 689 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ 7.70 (d, *J* = 8.0 Hz, 1H), 7.45-7.40 (m, 3H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.25-7.20 (m, 3H), 7.20-7.10 (m, 3H), 2.40 (s, 3H), 1.67 (s, 6H).

¹³C NMR (100 MHz, CDCl₃, DEPT): δ 139.4 (C), 138.9 (C), 137.2 (C), 136.5 (C), 133.6 (C), 133.4 (C), 132.9 (C), 129.5 (CH), 129.0 (2×CH), 128.0 (2×CH), 127.1 (CH), 126.8 (CH), 126.2 (CH), 122.2 (CH), 120.3 (CH), 118.9 (CH), 109.5 (CH), 103.3 (C), 68.2 (C), 25.8 (2×CH₃), 9.8 (CH₃).

HRMS (ESI, M+Na⁺): *m/z* calcd. for C₂₄H₂₁NaNS₂ 410.1020, found 410.1024.

9'-methyl-1'-phenyl-2'-(phenylthio)spiro[cyclopentane-1,3'-pyrrolo[1,2-*a*]indole] (6h):

Reaction of the alkyne **13h** (90 mg, 0.300 mmol) with thiophenol (46 μL, 0.450 mmol) and AIBN (50 mg, 0.300 mmol) in benzene (10 mL) as described for *N*-fused indoline **7a** followed by purification of the residue on a silica gel column using ethyl acetate–pet ether as eluent, furnished the pyrrolo[1,2-*a*]indole derivative **6h** (100 mg, 82%) as a white solid.

Physical appearance: White solid.

M.P.: 156-158 °C.

R_f: 0.6 (1:9, EtOAc: Pet ether).

IR (neat): 2930, 1620, 1478, 1460, 1234, 1150, 1044, 875, 790 cm⁻¹.

¹H NMR (500 MHz, CDCl₃): δ 7.64 (d, *J* = 7.5 Hz, 1H), 7.56 (dd, *J* = 7.5, 1.5 Hz, 2H), 7.40-7.35 (m, 4H), 7.25-7.20 (m, 3H), 7.16 (t, *J* = 7.5 Hz, 2H), 7.15-7.10 (m, 2H), 7.10-7.05 (m, 2H), 2.30-2.25 (m, 2H), 2.20-2.15 (m, 4H), 2.14 (s, 3H).

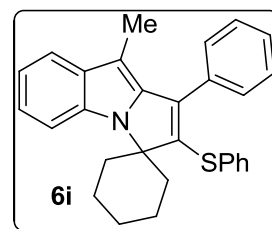
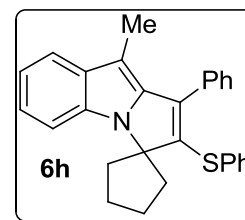
¹³C NMR (125 MHz, CDCl₃, DEPT): δ 143.0 (C), 140.2 (C), 138.8 (C), 136.8 (C), 133.5 (C), 132.9 (C), 132.8 (C), 129.5 (2×CH), 128.9 (2×CH), 128.5 (CH), 128.2 (2×CH), 127.8 (2×CH), 126.0 (CH), 121.9 (CH), 120.3 (CH), 118.7 (CH), 109.4 (CH), 102.9 (C), 77.2 (C), 37.7 (2×CH₂), 27.6 (2×CH₂), 9.1 (CH₃).

HRMS (ESI, M+Na⁺): *m/z* calcd. for C₂₈H₂₅NaNS 430.1625, found 430.1620.

9'-methyl-1'-phenyl-2'-(phenylthio)spiro[cyclohexane-1,3'-pyrrolo[1,2-*a*]indole] (6i):

Reaction of the alkyne **13i** (120 mg, 0.383 mmol) with thiophenol (59 μL, 0.575 mmol) and AIBN (63 mg, 0.383 mmol) in benzene (12 mL) as described for *N*-fused indoline **7a** followed by purification of the residue on a silica gel column using ethyl acetate–Pet ether (1:9) as eluent, furnished the pyrrolo[1,2-*a*]indole derivative **6i** (121 mg, 75%) as a white solid.

Physical appearance: white solid.



M.P.: 162-164 °C.

R_f: 0.6 (1:9, EtOAc: Pet ether).

IR (neat): 3054, 2931, 2864, 1581, 1475, 1450, 1335, 1243, 1077, 753, 739 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ 7.66 (d, *J* = 8.0 Hz, 1H), 7.60 (d, *J* = 8.0 Hz, 1H), 7.50-7.45 (m, 2H), 7.40-7.35 (m, 3H), 7.26 (td, *J* = 8.0, 1.6 Hz, 1H), 7.20-7.15 (m, 5H), 7.08 (tt, *J* = 8.0, 1.6 Hz, 1H), 2.39 (ddd, *J* = 13.2, 13.2, 4.0 Hz, 2H), 2.30-2.20 (m, 2H), 2.11 (s, 3H), 2.00-1.90 (m, 6H).

¹³C NMR (100 MHz, CDCl₃, DEPT): δ 144.4 (C), 139.7 (C), 138.7 (C), 137.3 (C), 133.6 (C), 133.2 (C), 133.0 (C), 129.5 (2×CH), 128.9 (2×CH), 128.3 (CH), 128.1 (2×CH), 127.3 (2×CH), 125.6 (CH), 121.8 (CH), 120.2 (CH), 118.7 (CH), 110.3 (CH), 102.7 (C), 69.9 (C), 36.0 (2×CH₂), 25.3 (CH₂), 22.6 (2×CH₂), 8.9 (CH₃).

HRMS (ESI, M+Na⁺): *m/z* calcd. for C₂₉H₂₇NaNS 444.1772, found 444.1778.

9'-methyl-1'-phenyl-2'-(phenylthio)spiro[cycloheptane-1,3'-pyrrolo[1,2-a]indole] (6j):

Reaction of the alkyne **13j** (110 mg, 0.336 mmol) with thiophenol (51 μL, 0.504 mmol) and AIBN (55 mg, 0.336 mmol) in benzene (12 mL) as described for *N*-fused indoline **7a** followed by purification of the residue on a silica gel column using ethyl acetate–pet ether as eluent, furnished the pyrrolo[1,2-*a*]indole derivative **6j** (105 mg, 72%) as a white solid.

Physical appearance: White solid.

M.P.: 168-170 °C.

R_f: 0.5 (1:9, EtOAc: Pet ether).

IR (neat): 2930, 2910, 1610, 1400, 1394, 1234, 1140, 1044, 985, 765 cm⁻¹.

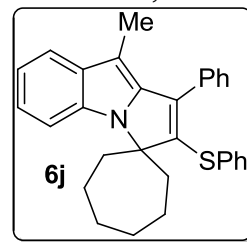
¹H NMR (400 MHz, CDCl₃): δ 7.70 (d, *J* = 8.4 Hz, 1H), 7.63 (d, *J* = 8.4 Hz, 1H), 7.50 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.40-7.35 (m, 3H), 7.25-7.20 (m, 3H), 7.15-7.10 (m, 4H), 2.35-2.30 (m, 2H), 2.20-2.15 (m, 2H), 2.10 (s, 3H), 2.00-1.95 (m, 4H), 1.85-1.75 (m, 4H).

¹³C NMR (100 MHz, CDCl₃, DEPT): δ 143.1 (C), 140.6 (C), 140.0 (C), 136.9 (C), 133.8 (C), 133.5 (C), 133.0 (C), 129.5 (2×CH), 128.8 (2×CH), 128.3 (CH), 128.1 (2×CH), 128.0 (2×CH), 125.8 (CH), 121.9 (CH), 120.2 (CH), 118.6 (CH), 111.0 (CH), 102.9 (C), 75.2 (C), 39.2 (2×CH₂), 32.3 (2×CH₂), 25.0 (2×CH₂), 9.0 (CH₃).

HRMS (ESI, M+Na⁺): *m/z* calcd. for C₃₀H₂₉NaNS 458.1936 and found 458.1938.

3,3-Dimethyl-1-phenyl-2-(phenylthio)-3H-pyrrolo[1,2-*a*]indole (6k):

Reaction of the alkyne **13k** (120 mg, 0.463 mmol) with thiophenol (71 μL, 0.694 mmol) and AIBN (76 mg, 0.463 mmol) in benzene (12 mL) as described for *N*-fused indoline **7a** followed by



purification of the residue on a silica gel column using ethyl acetate–pet ether as eluent, furnished the pyrrolo[1,2-a]indole derivative **6k** (122 mg, 72%) as a white solid.

Physical appearance: white solid.

M.P.: 142-144 °C.

R_f: 0.5 (1:9, EtOAc: Pet ether).

IR (neat): 3055, 2937, 2931, 1581, 1476, 1451, 1362, 1183, 1013, 741 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ 7.90 (d, *J* = 8.0 Hz, 2H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.49 (d, *J* = 8.0 Hz, 1H), 7.40-7.35 (m, 2H), 7.30-7.20 (m, 6H), 7.12 (d, *J* = 8.0 Hz, 2H), 6.50 (s, 1H), 1.68 (s, 6H).

¹³C NMR (100 MHz, CDCl₃, DEPT): δ 143.6 (C), 141.2 (C), 138.6 (C), 136.0 (C), 134.0 (C), 132.6 (2×C), 129.1 (2×CH), 129.0 (2×CH), 128.8 (2×CH), 128.5 (2×CH), 128.2 (CH), 126.2 (CH), 122.3 (CH), 121.8 (CH), 119.5 (CH), 109.7 (CH), 93.4 (CH), 69.2 (C), 25.7 (2×CH₃).

HRMS (ESI, M+Na⁺): *m/z* calcd. for C₂₅H₂₁NaNS 390.1380, found 390.1382.

9-Cyclohexyl-3,3-dimethyl-1-phenyl-2-(phenylthio)-3H-pyrrolo[1,2-a]indole (6l):

Reaction of the alkyne **13l** (100 mg, 0.293 mmol) with thiophenol (45 μL, 0.440 mmol) and AIBN (48 mg, 0.293 mmol) in benzene (10 mL) as described for *N*-fused indoline **7a** followed by purification of the residue on a silica gel column using ethyl acetate–hexanes as eluent, furnished the pyrrolo[1,2-a]indole derivative **6l** (115 mg, 87%) as a white solid.

Physical appearance: white solid.

M.P.: 152-154 °C.

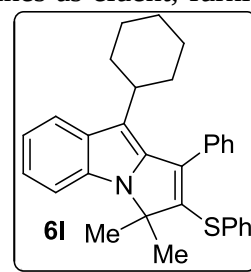
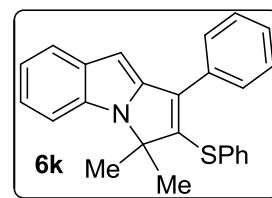
R_f: 0.6 (1:9, EtOAc: Pet ether).

IR (neat): 2950, 2910, 1600, 1495, 1310, 1205, 1158, 988, 850, 744 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ 7.86 (d, *J* = 8.0 Hz, 1H), 7.50-7.45 (m, 2H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.41 (dd, *J* = 8.0, 2.0 Hz, 3H), 7.30-7.20 (m, 2H), 7.20-7.15 (m, 3H), 7.10 (tt, *J* = 8.0, 2.0 Hz, 1H), 7.06 (td, *J* = 8.0, 0.8 Hz, 1H), 2.50 (tt, *J* = 8.0, 3.6 Hz, 1H), 1.90-1.80 (m, 2H), 1.75-1.60 (m, 5H), 1.65 (s, 6H), 1.30-1.20 (m, 1H), 1.05-0.95 (m, 2H).

¹³C NMR (100 MHz, CDCl₃, DEPT): δ 144.0 (C), 139.4 (C), 138.8 (C), 136.5 (C), 134.2 (C), 133.4 (C), 131.2 (C), 129.2 (2×CH), 128.9 (2×CH), 128.7 (2×CH), 128.5 (2×CH), 128.1 (CH), 126.2 (CH), 122.7 (CH), 121.5 (CH), 118.2 (CH), 114.1 (C), 109.7 (CH), 68.2 (C), 35.7 (CH), 33.4 (2×CH₂), 27.3 (2×CH₂), 26.3 (CH₂), 25.8 (2×CH₃).

HRMS (ESI, M+Na⁺): *m/z* calcd. for C₃₁H₃₁NaNS 472.2095, found 472.2090.



7-Methoxy-3,3-dimethyl-1-phenyl-2-(phenylthio)-3H-pyrrolo[1,2-a]indole (6m):

Reaction of the alkyne **13m** (120 mg, 0.415 mmol) with thiophenol (63 μ L, 0.622 mmol) and AIBN (68 mg, 0.415 mmol) in benzene (12 mL) as described for *N*-fused indoline **7a** followed by purification of the residue on a silica gel column using ethyl acetate–pet ether as eluent, furnished the pyrrolo[1,2-a]indole derivative **6m** (116 mg, 70%) as a white solid.

Physical appearance: White solid.

M.P.: 168-170 °C

R_f: 0.3 (1:9, EtOAc: Pet ether).

IR (neat): 2950, 2860, 1590, 1470, 1210, 1150, 780 cm^{-1} .

¹H NMR (400 MHz, CDCl₃): δ 7.85 (dd, J = 7.6, 2.0 Hz, 2H), 7.45-7.35 (m, 5H), 7.26 (dd, J = 7.6, 1.6 Hz, 2H), 7.18 (t, J = 7.6 Hz, 3H), 7.11 (t, J = 7.6 Hz, 1H), 6.89 (dd, J = 7.6, 2.0 Hz, 1H), 3.87 (s, 3H), 1.64 (s, 6H).

¹³C NMR (100 MHz, CDCl₃, DEPT): δ 154.1 (C), 144.2 (C), 141.4 (C), 138.2 (C), 136.1 (C), 133.0 (C), 132.6 (C), 129.5 (C), 129.0 (2 $\times$ CH), 128.9 (2 $\times$ CH), 128.8 (2 $\times$ CH), 128.5 (2 $\times$ CH), 128.1 (CH), 126.2 (CH), 112.2 (CH), 110.3 (CH), 103.9 (CH), 93.1 (CH), 69.2 (C), 56.0 (CH₃), 25.9 (2 $\times$ CH₃).

HRMS (ESI, M+H⁺): m/z calcd. for C₂₆H₂₄NOS 398.1573 and found 398.1578.

2-(3,3-Dimethyl-1-phenyl-2-(phenylthio)-3H-pyrrolo[1,2-a]indol-9-yl)ethanol (6n):

Reaction of the alkyne **13n** (130 mg, 0.428 mmol) with thiophenol (65 μ L, 0.642 mmol) and AIBN (70 mg, 0.428 mmol) in benzene (12 mL) as described for *N*-fused indoline **7a** followed by purification of the residue on a silica gel column using ethyl acetate–hexanes as eluent, furnished the pyrrolo[1,2-a]indole derivative **6n** (148 mg, 84%) as a sticky solid.

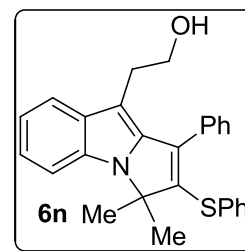
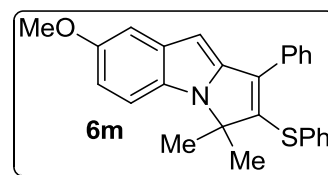
Physical appearance: sticky solid.

R_f: 0.3 (2:8, EtOAc: Pet ether).

IR (neat): 3290, 2980, 1596, 1485, 1020, 948, 860, 685 cm^{-1} .

¹H NMR (400 MHz, CDCl₃): δ 7.68 (d, J = 8.0 Hz, 1H), 7.49 (dd, J = 8.0, 1.2 Hz, 2H), 7.44 (d, J = 8.0 Hz, 1H), 7.43-7.40 (m, 3H), 7.25-7.20 (m, 3H), 7.20-7.10 (m, 4H), 3.59 (t, J = 7.6 Hz, 2H), 2.82 (t, J = 7.6 Hz, 2H), 1.66 (s, 6H).

¹³C NMR (100 MHz, CDCl₃, DEPT): δ 142.7 (C), 140.9 (C), 140.7 (C), 135.8 (C), 133.7 (C), 132.9 (C), 132.8 (C), 129.3 (2 $\times$ CH), 129.1 (2 $\times$ CH), 128.9 (2 $\times$ CH), 128.7 (CH), 128.4 (2 $\times$ CH), 126.5



(CH), 122.1 (CH), 120.4 (CH), 119.1 (CH), 109.6 (CH), 103.3 (C), 68.4 (C), 63.5 (CH₂), 27.5 (CH₂), 25.8 (2×CH₃).

HRMS (ESI, M+Na⁺): m/z calcd. for C₂₇H₂₅NaNOS 434.1548, found 434.1548.

(3*S*,9*R*,9*aR*)-9-methyl-1,3-diphenyl-9,9*a*-dihydro-3*H*-pyrrolo[1,2-*a*]indole (16):

Freshly prepared Raney Ni (approx. 1 gm) was added to the solution of vinyl sulfide **7b** (150 mg, 0.348 mmol) in dry ethanol (8 mL). Reaction mixture was refluxed until completion of starting material. Reaction mixture was filtered through a pad of celite and washed with ethyl acetate. Organic layer was evaporated under reduced pressure. Purification of the residue on a silica gel column using ethyl acetate–pet ether as eluent, furnished the indoline derivative **16** (73 mg, 65%) as a colorless liquid.

Physical appearance: colorless liquid.

R_f: 0.5 (1:9, EtOAc: Pet ether).

IR (neat): 3034, 2960, 2931, 1601, 1480, 1261, 1076, 798, 754 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ 7.50 (dd, *J* = 8.0, 1.2 Hz, 2H), 7.45–7.35 (m, 6H), 7.35–7.30 (m, 2H), 7.17 (t, *J* = 8.0 Hz, 1H), 7.08 (d, *J* = 8.0 Hz, 1H), 6.89 (dd, *J* = 8.0, 1.2 Hz, 2H), 6.15 (t, *J* = 2.4 Hz, 1H), 5.25 (t, *J* = 2.4 Hz, 1H), 5.09 (brq, *J* = 2.4 Hz, 1H), 3.50 (qd, *J* = 6.8, 2.4 Hz, 1H), 1.54 (d, *J* = 6.8 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃, DEPT): δ 154.2 (C), 143.3 (C), 143.0 (C), 135.6 (C), 134.2 (C), 128.9 (2×CH), 128.8 (CH), 128.0 (2×CH), 127.9 (CH), 127.4 (2×CH), 126.8 (CH), 126.7 (3×CH), 124.3 (CH), 121.2 (CH), 112.2 (CH), 79.8 (CH), 77.4 (CH), 40.8 (CH), 22.9 (CH₃).

HRMS (ESI, M+Na⁺): m/z calcd. for C₂₄H₂₁NaN 346.1570 and found 346.1570.

3,3,9-trimethyl-1-phenyl-3*H*-pyrrolo[1,2-*a*]indole (17a):

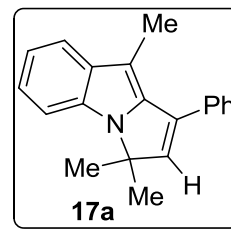
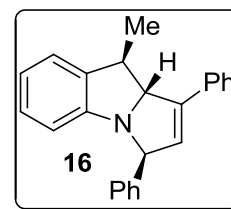
Reaction of the alkyne **13a** (100 mg, 0.365 mmol) with thiophenol (112 μL, 1.10 mmol) and AIBN (60 mg, 0.365 mmol) in benzene (8 mL) as described for *N*-fused indoline **7a** followed by purification of the residue on a silica gel column using ethyl acetate–pet ether as eluent, furnished the pyrrolo[1,2-*a*]indole derivative **17a** (55 mg, 55%) as a white solid.

Physical appearance: white solid.

M.P.: 124–126 °C.

R_f: 0.6 (1:9, EtOAc: Pet ether).

IR (neat): 3052, 1599, 1483, 1350, 1025, 768 cm⁻¹.



¹H NMR (400 MHz, CDCl₃): δ 7.70-7.66 (m, 3H), 7.52-7.45 (m, 4H), 7.26 (t, *J* = 7.6 Hz, 1H), 7.17 (t, *J* = 7.6 Hz, 1H), 6.40 (s, 1H), 2.36 (s, 3H), 1.71 (s, 6H).

¹³C NMR (100 MHz, CDCl₃, DEPT): δ 140.6 (C), 140.3 (CH), 136.4 (C), 134.3 (C), 133.9 (C), 133.0 (C), 128.5 (2×CH), 128.3 (3×CH), 121.4 (CH), 119.8 (CH), 118.3 (CH), 109.1 (CH), 101.0 (C), 64.0 (C), 25.6 (2×CH₃), 9.5 (CH₃).

HRMS (ESI, M+H⁺): *m/z* calcd. for C₂₀H₂₀N 274.1580 and found 274.1584.

3,3,9-Trimethyl-1-(thiophen-2-yl)-3H-pyrrolo[1,2-a]indole (17g):

Reaction of the alkyne **13g** (120 mg, 0.429 mmol) with thiophenol (131 μL, 1.287 mmol) and AIBN (70 mg, 0.429 mmol) in benzene (10 mL) as described for *N*-fused indoline **7a** followed by purification of the residue on a silica gel column using ethyl acetate–pet ether as eluent, furnished the pyrrolo[1,2-a]indole derivative **17g** (84 mg, 70%) as a sticky solid.

Physical appearance: sticky solid.

R_f: 0.6 (1:9, EtOAc: Pet ether).

IR (neat): 2980, 1560, 1489, 1050, 896, 788 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ 7.67 (d, *J* = 8.0 Hz, 1H), 7.45-7.40 (m, 2H), 7.35 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.24 (td, *J* = 8.0, 1.2 Hz, 1H), 7.15-7.10 (m, 2H), 6.43 (s, 1H), 2.49 (s, 3H), 1.67 (s, 6H).

¹³C NMR (100 MHz, CDCl₃, DEPT): δ 140.5 (CH), 139.7 (C), 135.8 (C), 133.8 (C), 132.9 (C), 129.4 (C), 127.6 (CH), 126.9 (CH), 125.2 (CH), 121.6 (CH), 119.9 (CH), 118.4 (CH), 109.1 (CH), 101.3 (C), 63.8 (C), 25.6 (2×CH₃), 9.7 (CH₃).

HRMS (ESI, M+Na⁺): *m/z* calcd. for C₁₈H₁₇NaNS 302.0970 and found 302.0972.

3,3-dimethyl-1-phenyl-3H-pyrrolo[1,2-a]indole (17k):

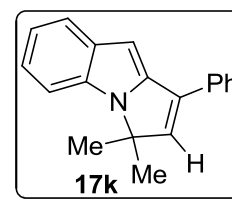
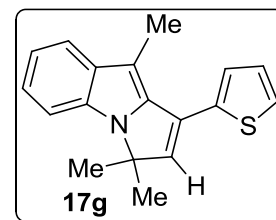
Reaction of the alkyne **13k** (100 mg, 0.385 mmol) with thiophenol (118 μL, 1.155 mmol) and AIBN (63 mg, 0.385 mmol) in benzene (10 mL) as described for *N*-fused indoline **7a** followed by purification of the residue on a silica gel column using ethyl acetate–pet ether as eluent, furnished the pyrrolo[1,2-a]indole derivative **17k** (63 mg, 63%) as a white solid.

Physical appearance: white solid.

M.P.: 122-124 °C.

R_f: 0.6 (1:9, EtOAc: Pet ether).

IR (neat): 3020, 1595, 1488, 1320, 1055, 788 cm⁻¹.



¹H NMR (400 MHz, CDCl₃): δ 7.82 (dd, *J* = 7.6, 1.6 Hz, 2H), 7.73 (d, *J* = 7.6 Hz, 1H), 7.50-7.45 (m, 3H), 7.41 (tt, *J* = 7.6, 2.0 Hz, 1H), 7.23 (td, *J* = 7.6, 1.2 Hz, 1H), 7.13 (td, *J* = 7.6, 1.2 Hz, 1H), 6.66 (s, 1H), 6.58 (s, 1H), 1.71 (s, 6H).

¹³C NMR (100 MHz, CDCl₃, DEPT): δ 144.1 (C), 139.1 (CH), 134.1 (C), 133.3 (C), 133.2 (C), 133.1 (C), 128.9 (CH), 128.6 (CH), 126.8 (CH), 121.9 (CH), 121.3 (CH), 119.0 (CH), 109.4 (CH), 92.4 (CH), 64.7 (C), 25.4 (2×CH₃).

HRMS (ESI, M+H⁺): *m/z* calcd. for C₁₉H₁₈N 260.1441 and found 260.1442.

(1*R*,2*S*)-3,3,9-trimethyl-1-phenyl-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indol-2-ol (18a):

Solution of indole **17a** (70 mg, 0.256 mmol) in anhydrous THF (6 mL) was cooled to 0 °C under a nitrogen atmosphere, and 1.0 M solution of BH₃·THF (4.609 mL, 4.609 mmol) was added. The reaction mixture was stirred at room temperature overnight. The reaction mixture was then cooled to 0 °C and treated with 15% aqueous sodium hydroxide (0.35 mL) and 30% hydrogen peroxide (0.50 mL). This mixture was stirred at room temperature for 2 h and extracted with EtOAc. The organic layer was washed with water and brine, dried over MgSO₄ and concentrated under reduced pressure. Purification of the residue on a silica gel column using ethyl acetate–pet ether as eluent, furnished the indoline derivative **18a** (52 mg, 70%) as a colorless liquid.

Physical appearance: colorless liquid.

R_f: 0.3 (1:9, EtOAc: Pet ether).

IR (neat): 3280, 3052, 2952, 1598, 1480, 1320, 1275, 998, 750 cm⁻¹.

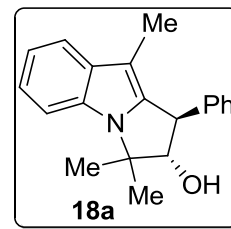
¹H NMR (400 MHz, CDCl₃): δ 7.56 (d, *J* = 8.0 Hz, 1H), 7.49 (d, *J* = 8.0 Hz, 1H), 7.45-7.35 (m, 5H), 7.19 (td, *J* = 8.0, 1.2 Hz, 1H), 7.13 (td, *J* = 8.0, 1.2 Hz, 1H), 4.22 (d, *J* = 8.4 Hz, 1H), 4.19 (d, *J* = 8.4 Hz, 1H), 1.92 (s, 3H), 1.87 (s, 3H), 1.46 (s, 3H).

¹³C NMR (100 MHz, CDCl₃, DEPT): δ 139.9 (C), 136.5 (C), 132.7 (C), 131.8 (C), 128.9 (2×CH), 128.4 (2×CH), 127.4 (CH), 120.7 (CH), 118.9 (CH), 118.6 (CH), 109.6 (CH), 103.1 (C), 90.3 (CH), 62.2 (C), 50.5 (CH), 26.2 (CH₃), 20.3 (CH₃), 8.4 (CH₃).

HRMS (ESI, M+Na⁺): *m/z* calcd. for C₂₀H₂₁NaNO 314.1521 and found 314.1520.

(1*R*,2*S*,3*R*,9*R*,9*aR*)-9-methyl-1,3-diphenyl-2,3,9,9*a*-tetrahydro-1*H*-pyrrolo[1,2-*a*]indol-2-ol (19):

Solution of indoline **16** (60 mg, 0.186 mmol) in anhydrous THF (6 mL) was cooled to 0 °C under a nitrogen atmosphere, and 1.0 M solution of BH₃·THF (3.34 mL, 3.34 mmol) was added. The reaction mixture was stirred at room temperature overnight. The reaction mixture was then cooled to 0 °C and treated with 15% aqueous sodium hydroxide (0.25 mL) and 30% hydrogen peroxide



(0.50 mL). This mixture was stirred at room temperature for 2 h and extracted with EtOAc. The organic layer was washed with water and brine, dried over MgSO_4 and concentrated under reduced pressure. Purification of the residue on a silica gel column using ethyl acetate–pet ether as eluent, furnished the indoline derivative **19** (46 mg, 72%) as a colorless liquid.

Physical appearance: colorless liquid.

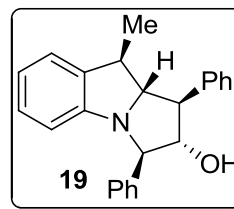
R_f: 0.2 (1:9, EtOAc: Pet ether).

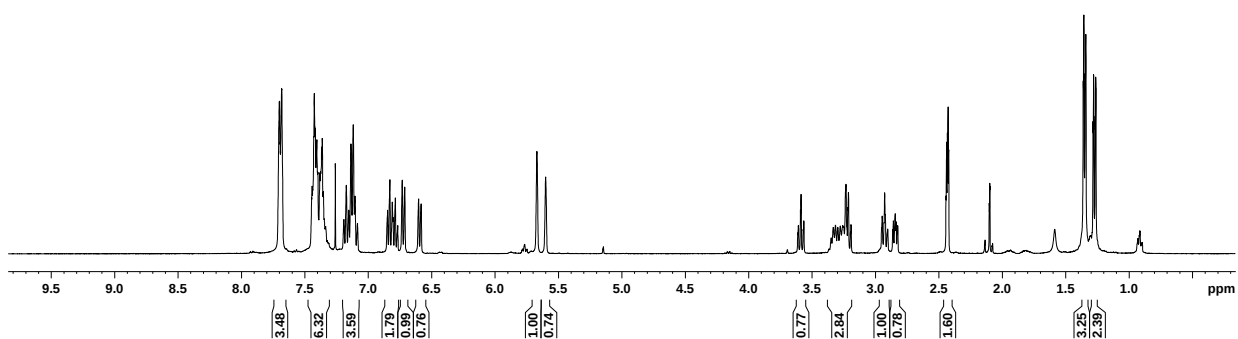
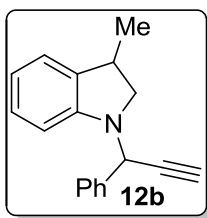
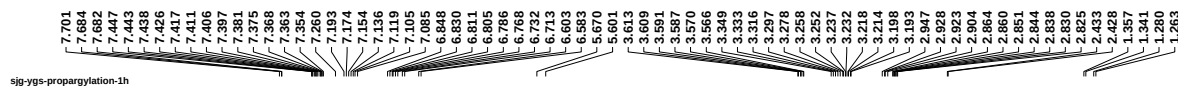
IR (neat): 3250, 3010, 2952, 2910, 1610, 1490, 1320, 1015, 778 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ 7.64 (d, J = 7.2 Hz, 2H), 7.43 (t, J = 7.2 Hz, 2H), 7.40–7.35 (m, 3H), 7.30 (brd, J = 7.2 Hz, 3H), 7.12 (d, J = 7.2 Hz, 1H), 7.06 (t, J = 7.2 Hz, 1H), 6.82 (t, J = 7.2 Hz, 1H), 6.42 (d, J = 7.2 Hz, 1H), 4.34 (ddd, J = 10.8, 8.0, 3.6 Hz, 1H), 4.24 (d, J = 8.0 Hz, 1H), 4.01 (dd, J = 10.8, 3.6 Hz, 1H), 3.39 (qd, J = 8.0, 3.6 Hz, 1H), 3.03 (t, J = 10.8 Hz, 1H), 2.01 (brd, J = 3.6 Hz, 1H), 1.25 (d, J = 7.6 Hz, 3H).

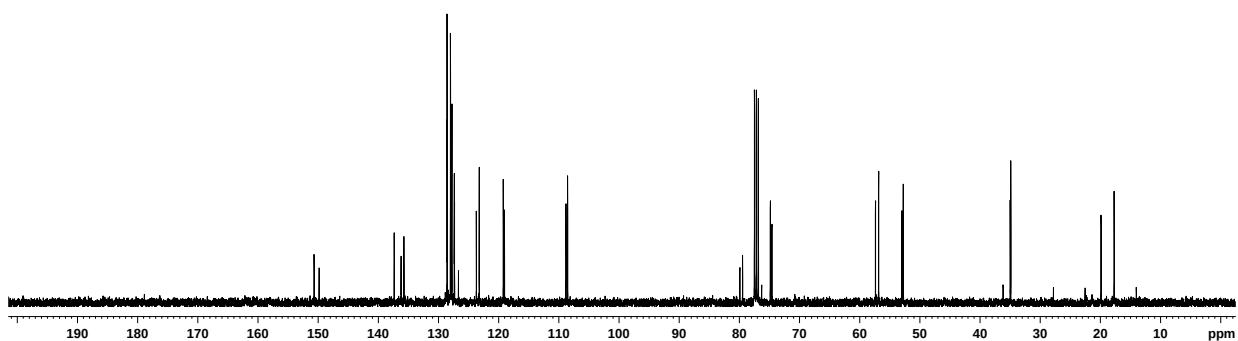
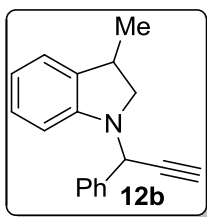
^{13}C NMR (100 MHz, CDCl_3 , DEPT): δ 137.5 (C), 135.0 (C), 129.8 (C), 129.1 (2 $\times$ CH), 128.8 (2 $\times$ CH), 128.2 (CH), 128.1 (2 $\times$ CH), 127.6 (2 $\times$ CH), 126.6 (CH), 124.3 (CH), 120.8 (C), 120.2 (CH), 115.4 (CH), 110.8 (CH), 86.4 (CH), 76.5 (CH), 74.1 (CH), 58.1 (CH), 40.7 (CH), 22.3 (CH_3).

HRMS (ESI, $\text{M}+\text{H}^+$): m/z calcd. for $\text{C}_{24}\text{H}_{24}\text{NO}$ 342.1860 and found 342.1864.





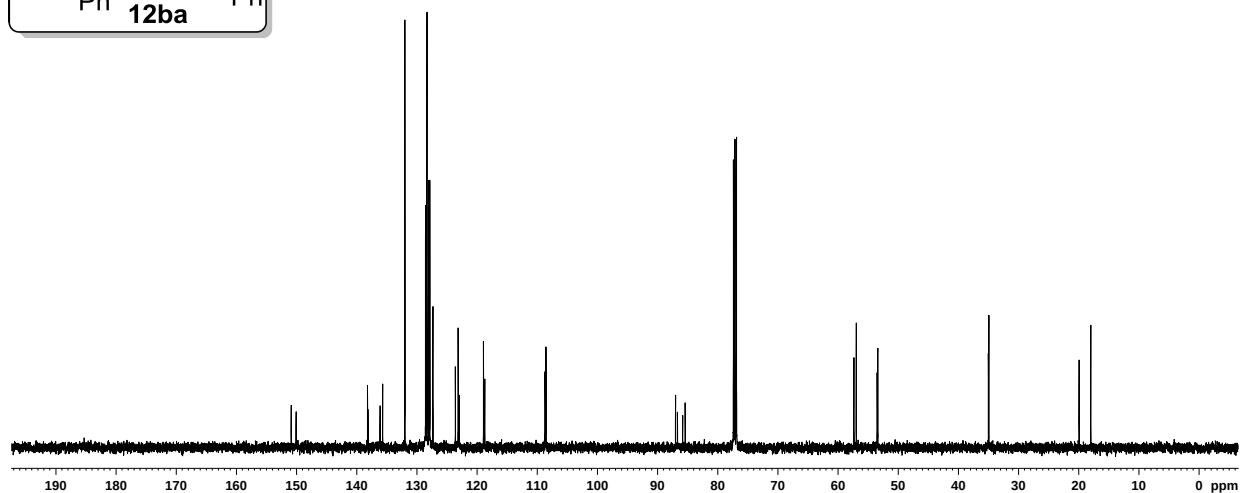
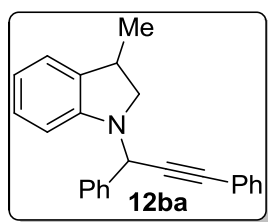
13C NMR spectrum (100 MHz, CDCl₃) of compound 12b.

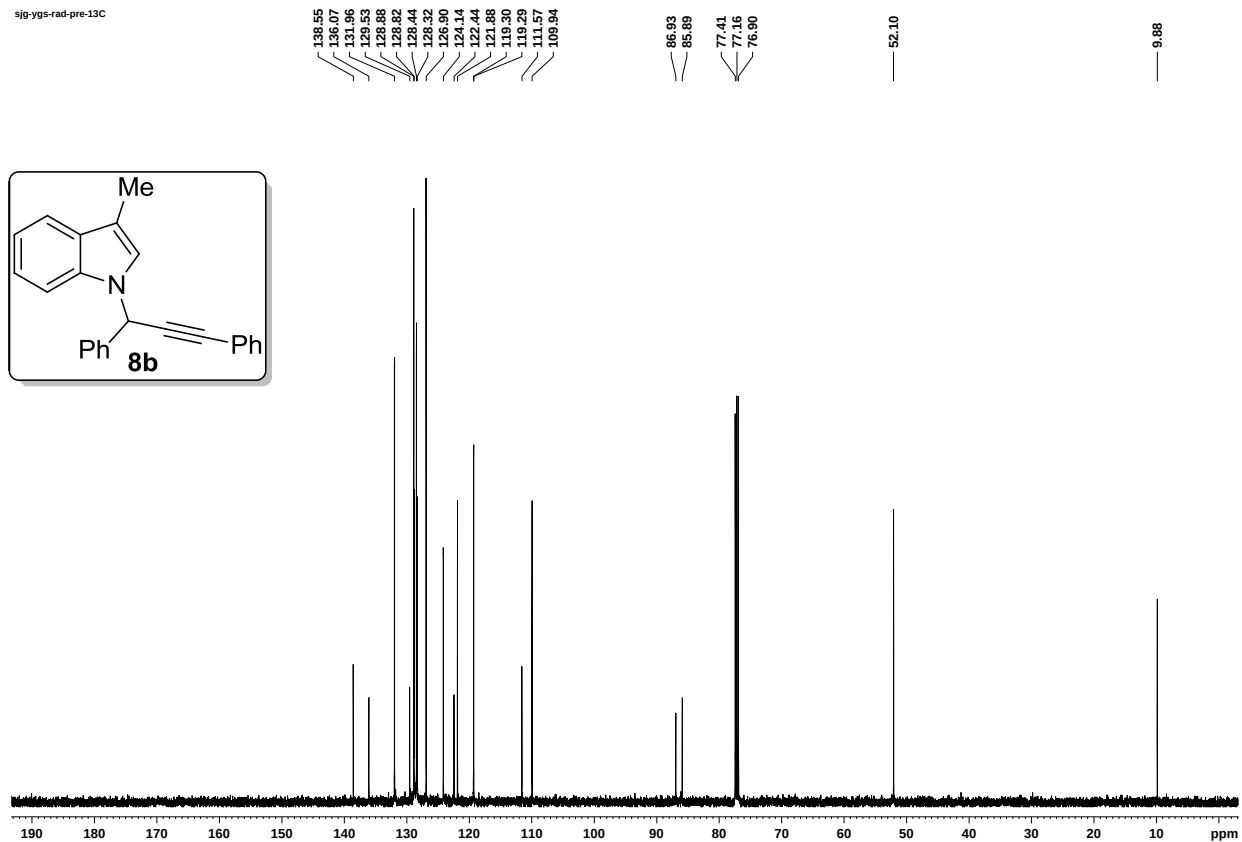
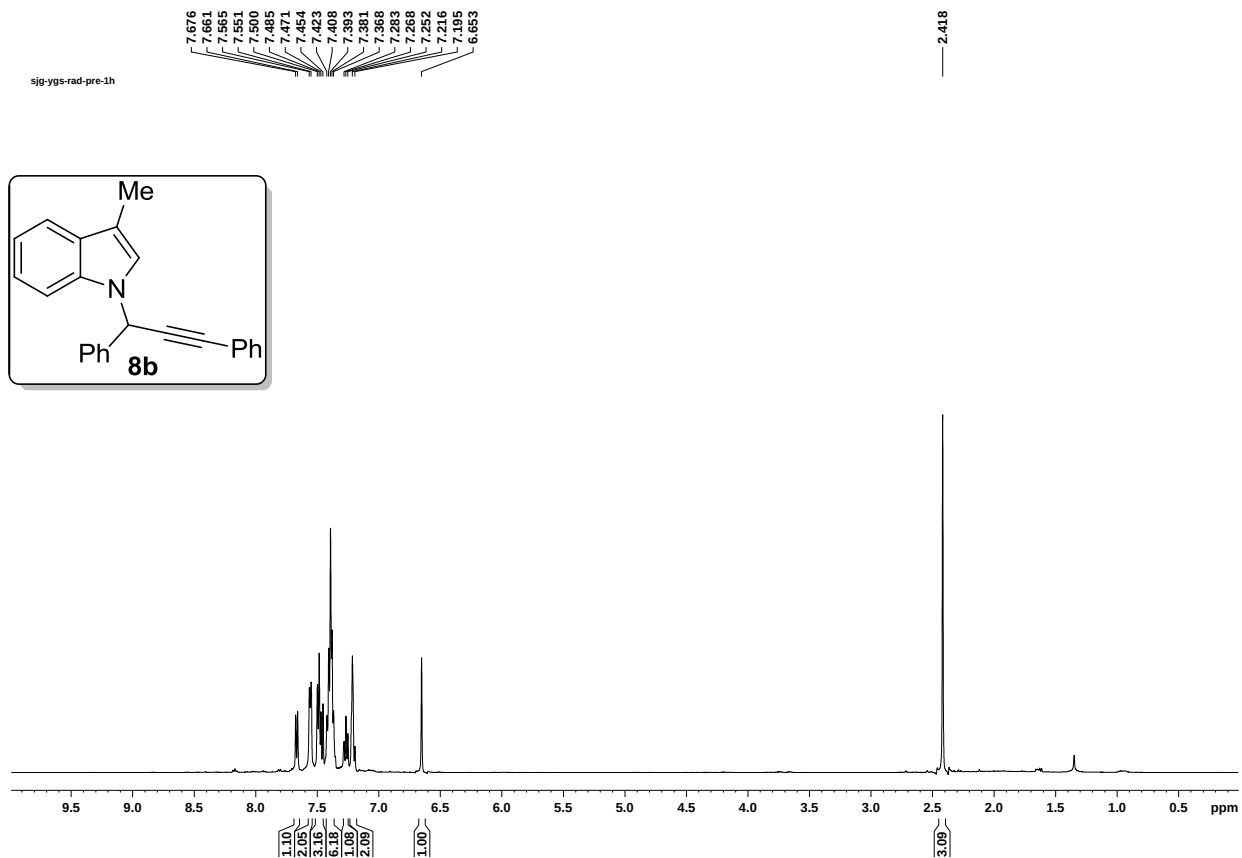


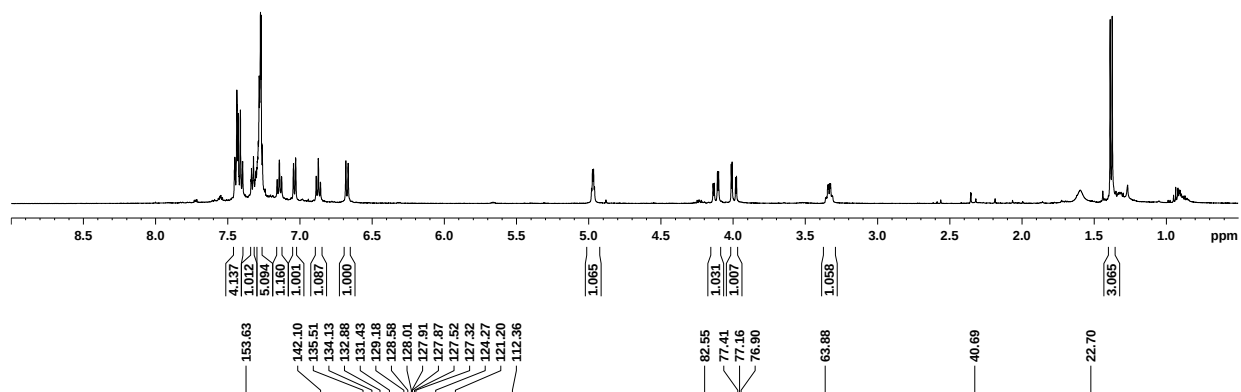
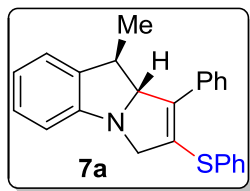
SJG-YGS-10-123-1H



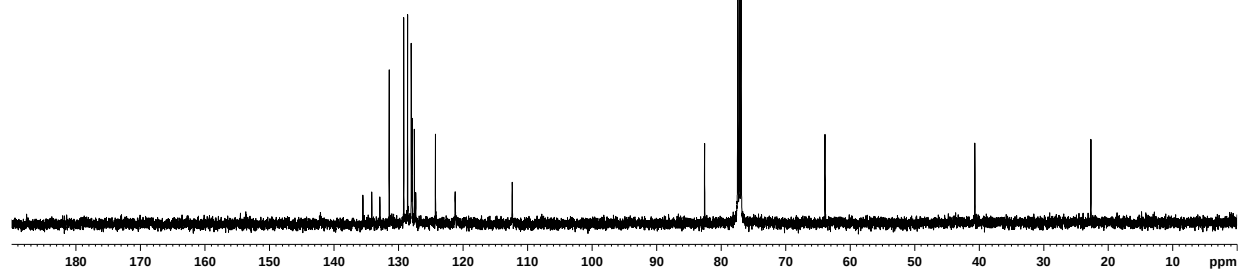
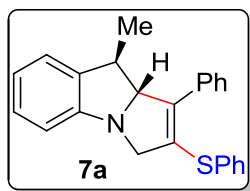
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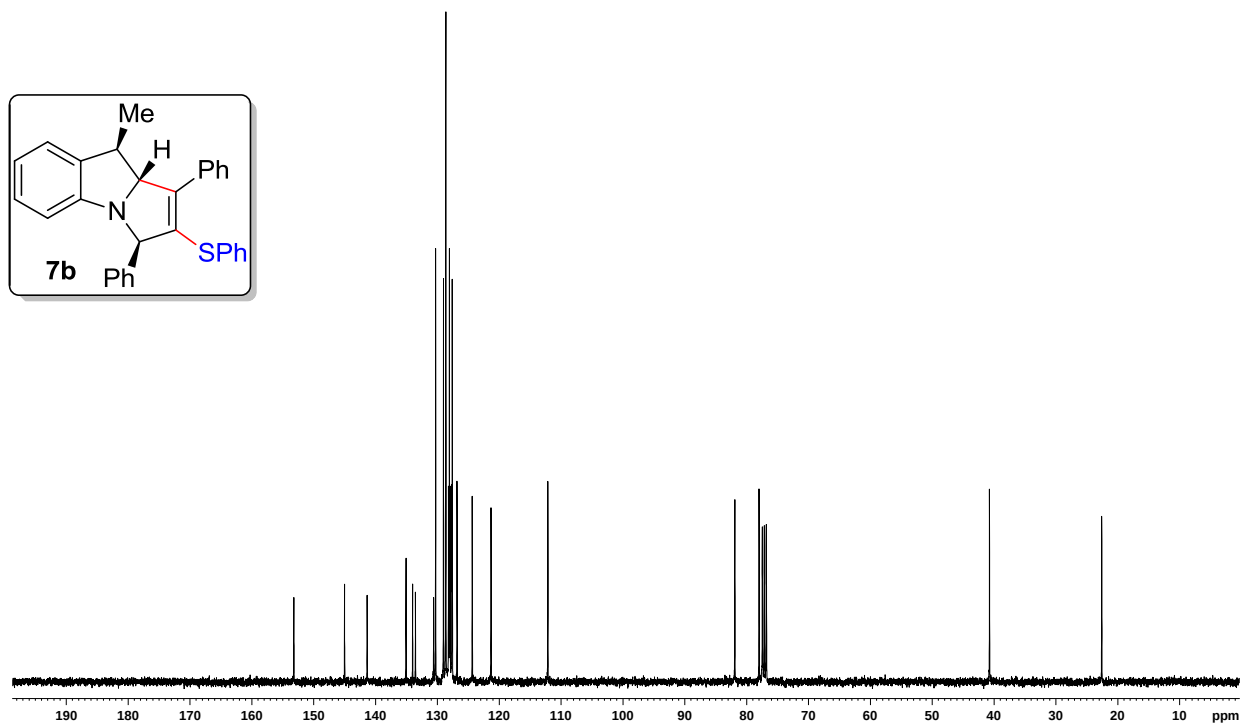
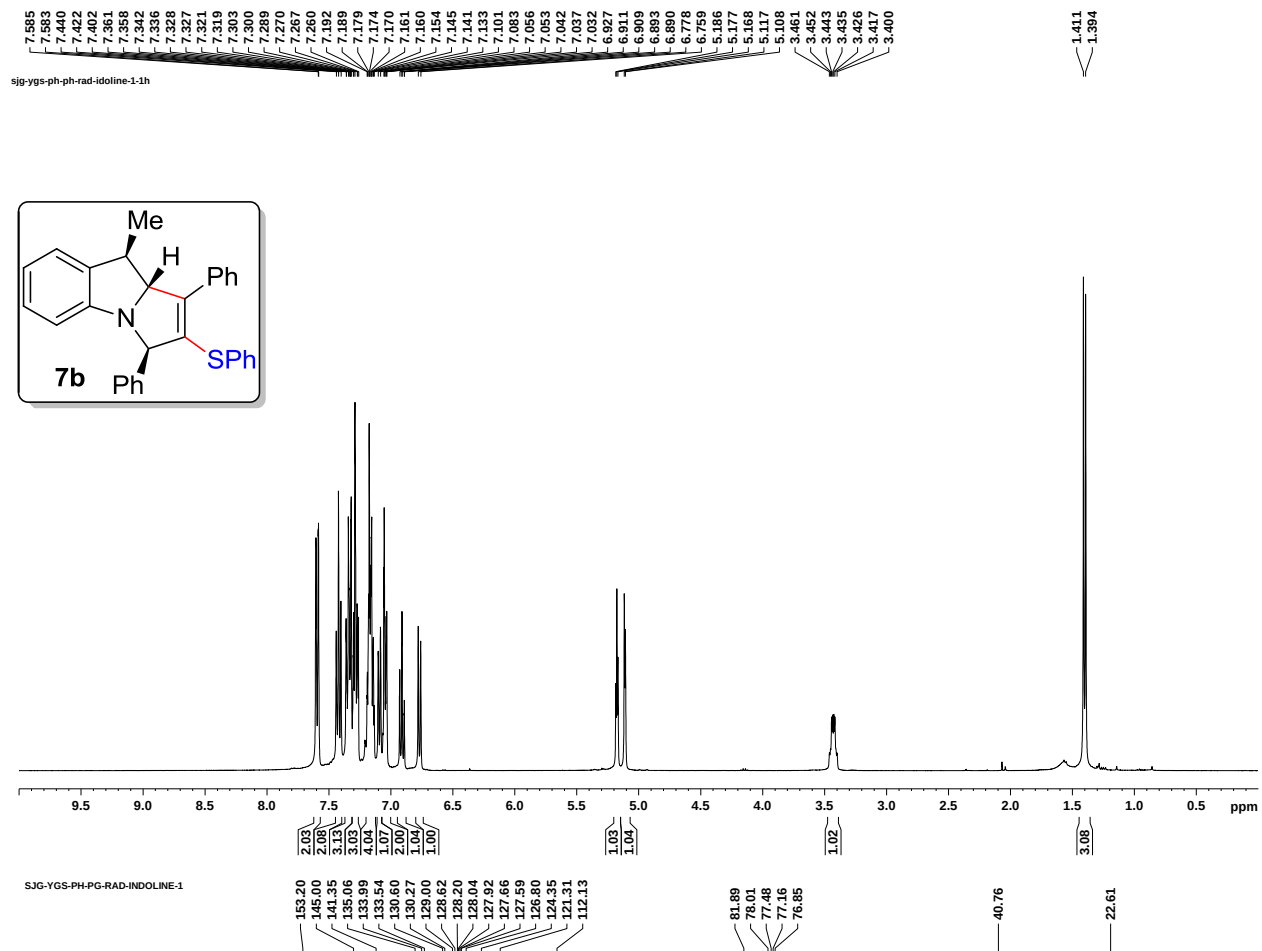




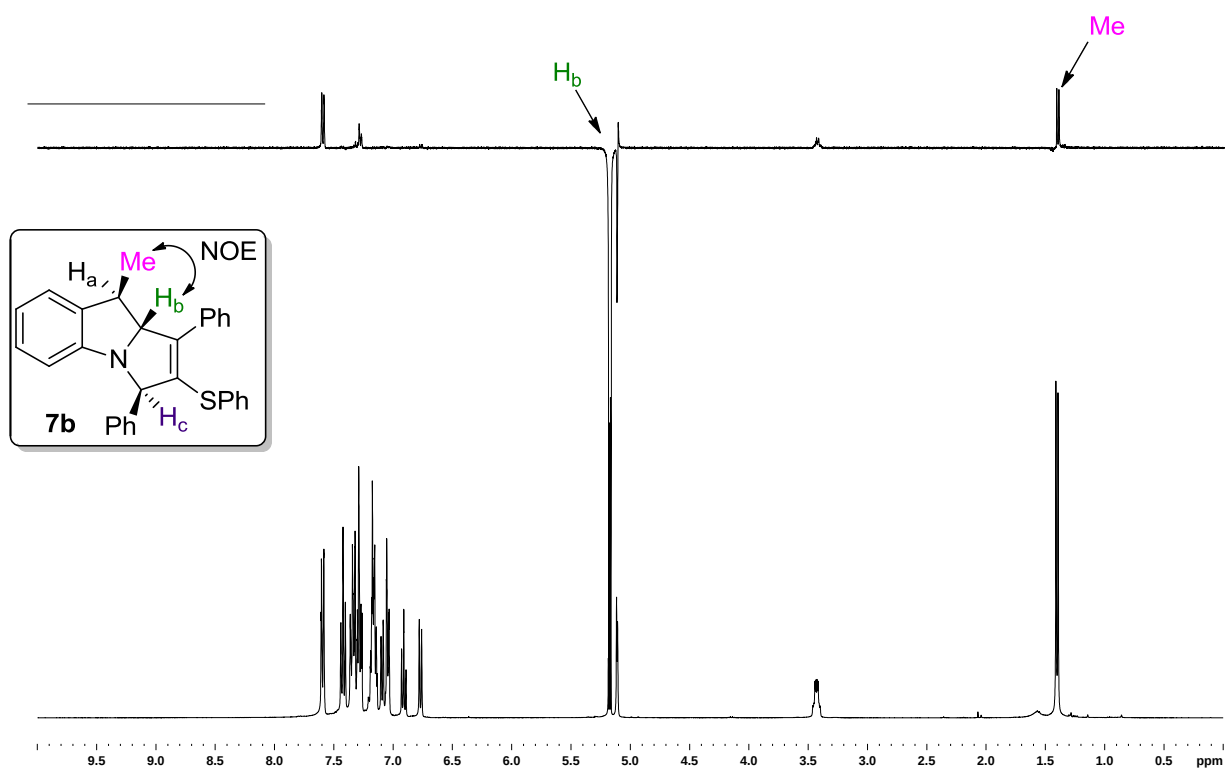


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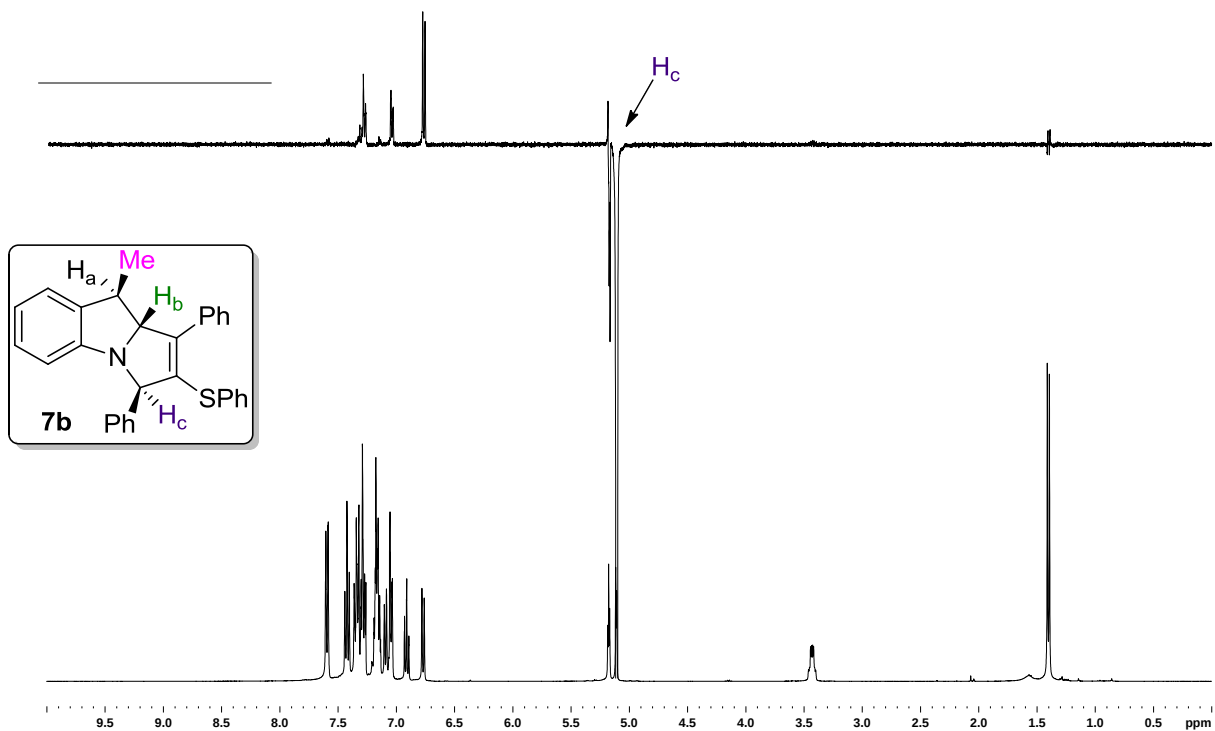




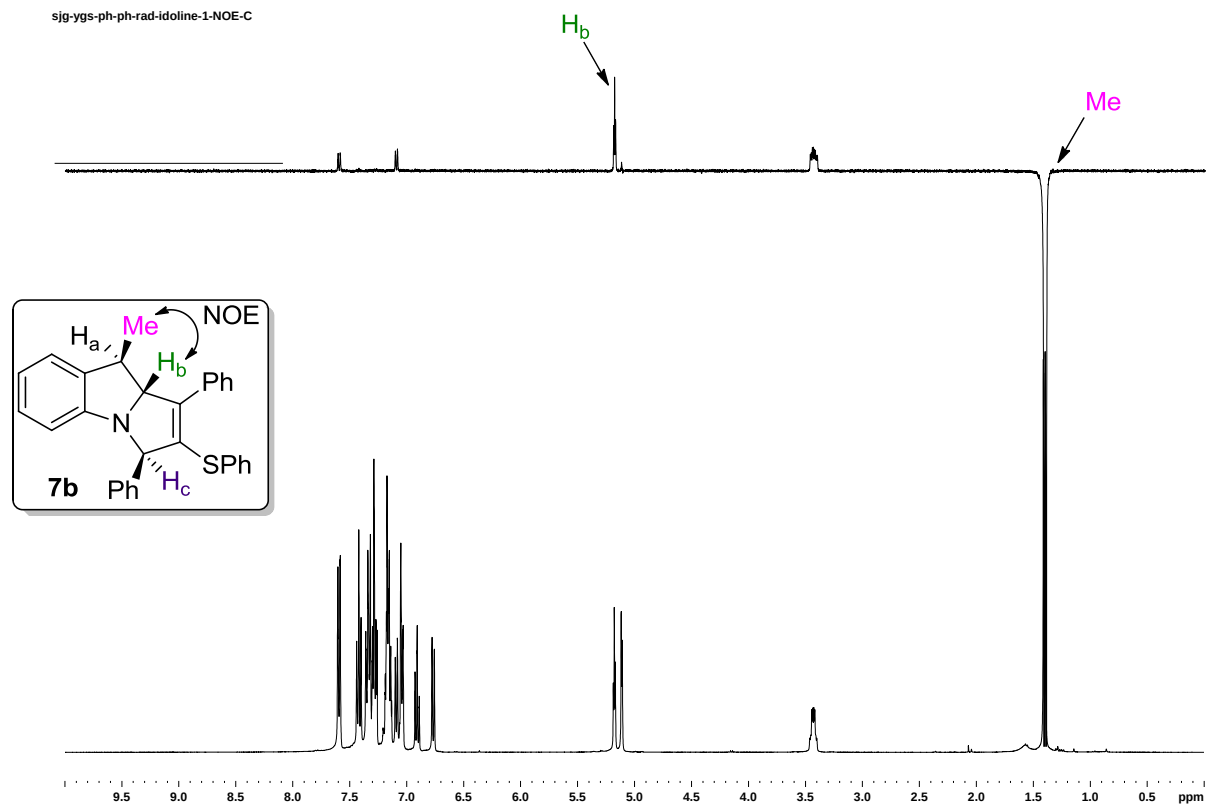
sjg-ygs-ph-ph-rad-idoline-1-NOE-A



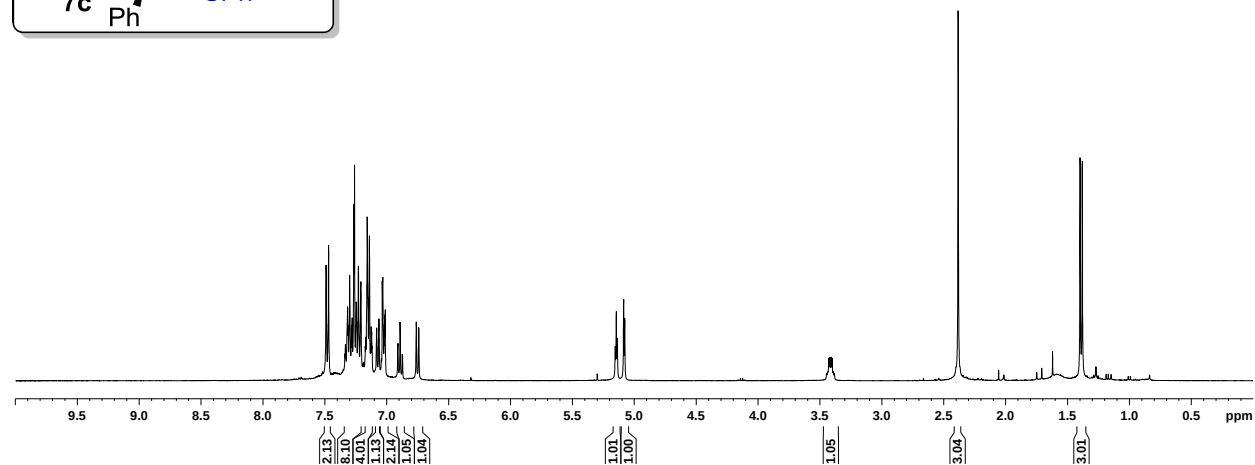
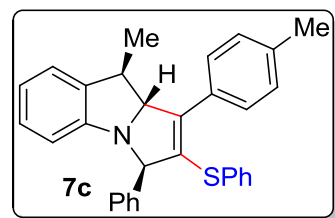
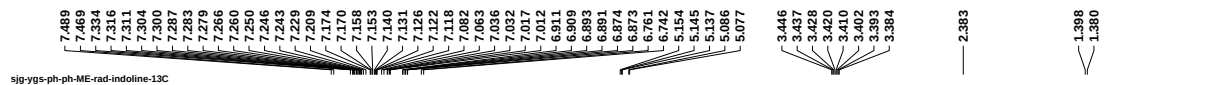
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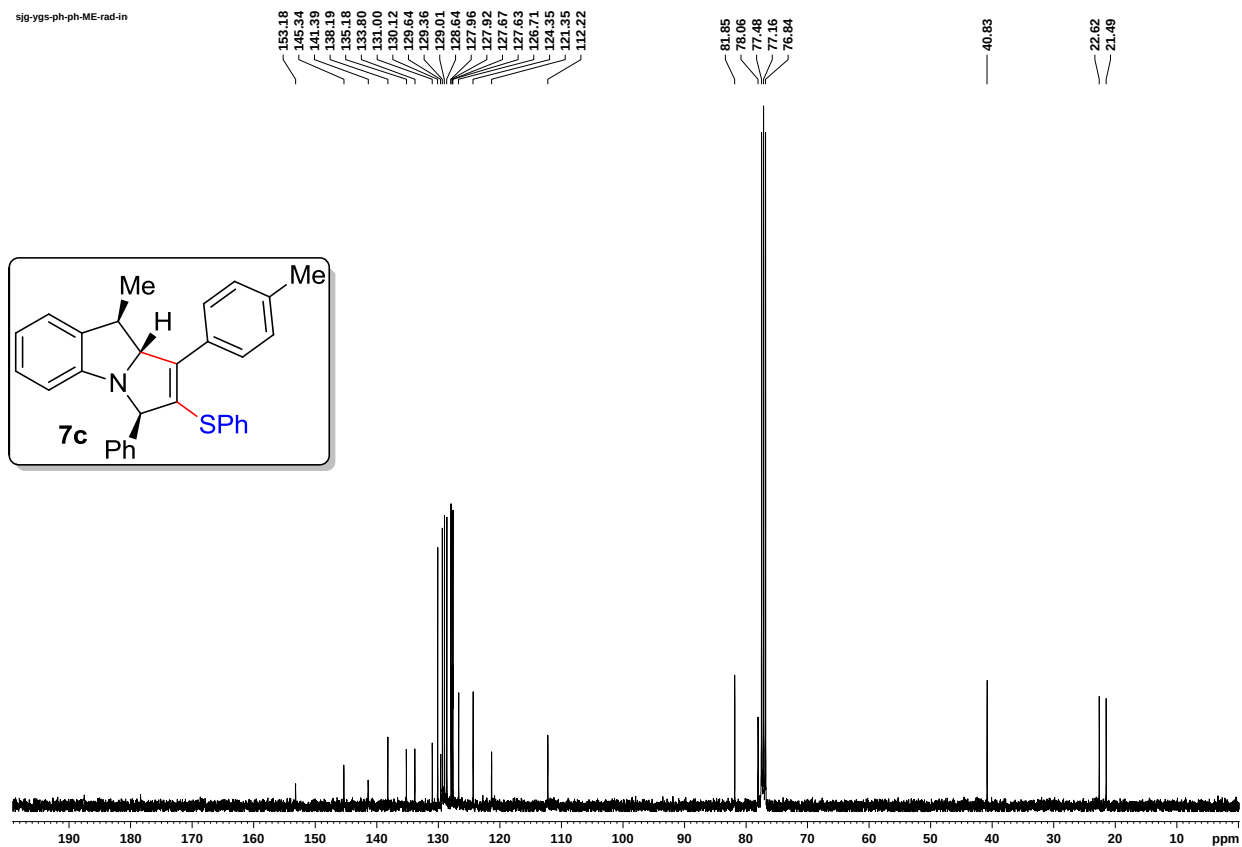
sjg-ygs-ph-ph-rad-idoline-1-NOE-C



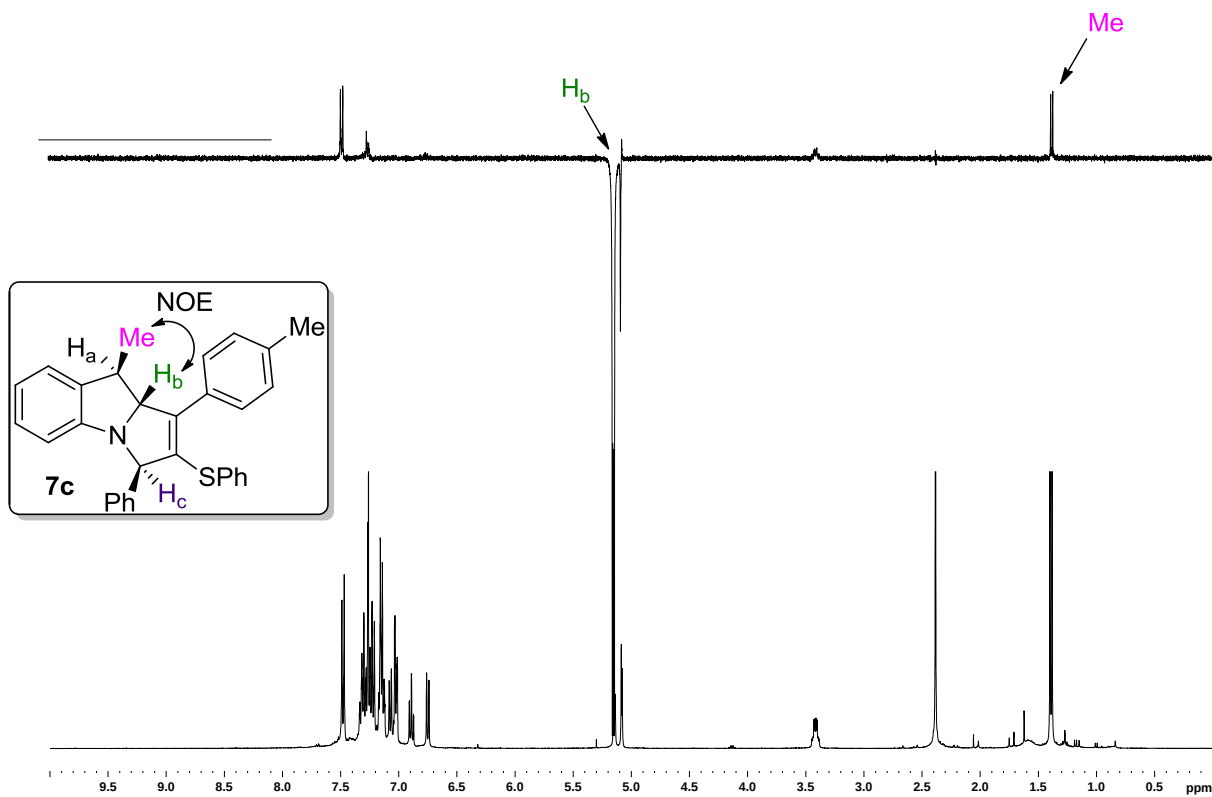
NOE enhancement = 5%



sig-ygs-ph-ph-ME-rad-in

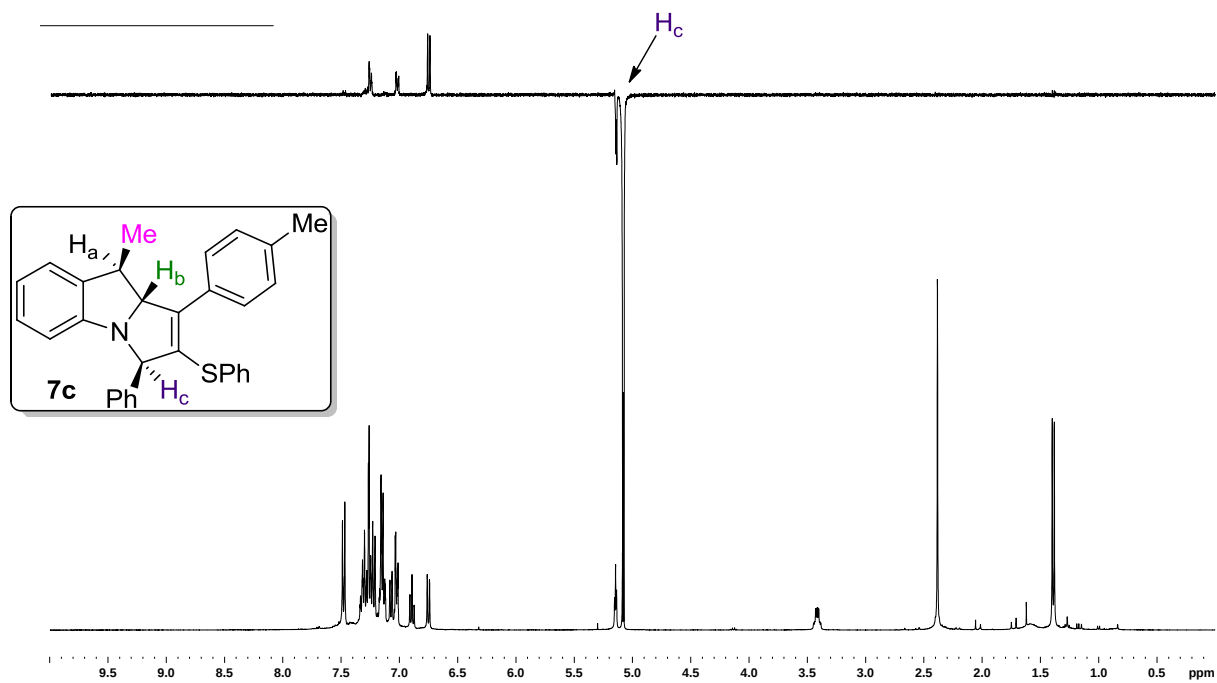


sig-ygs-ph-ph-ME-rad-indoline-noe-a

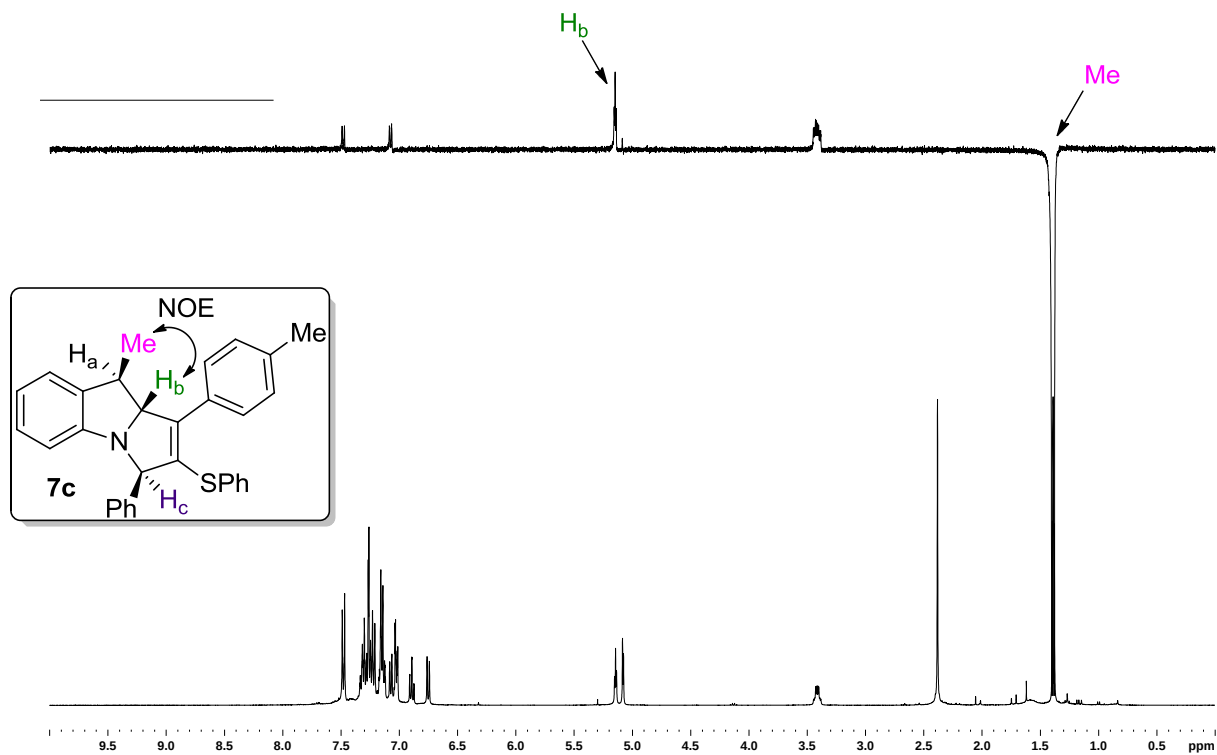


NOE enhancement = 4%

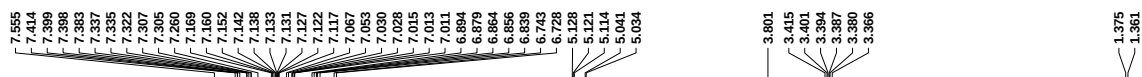
sjg-ygs-ph-ph-ME-rad-indoline-noe-b



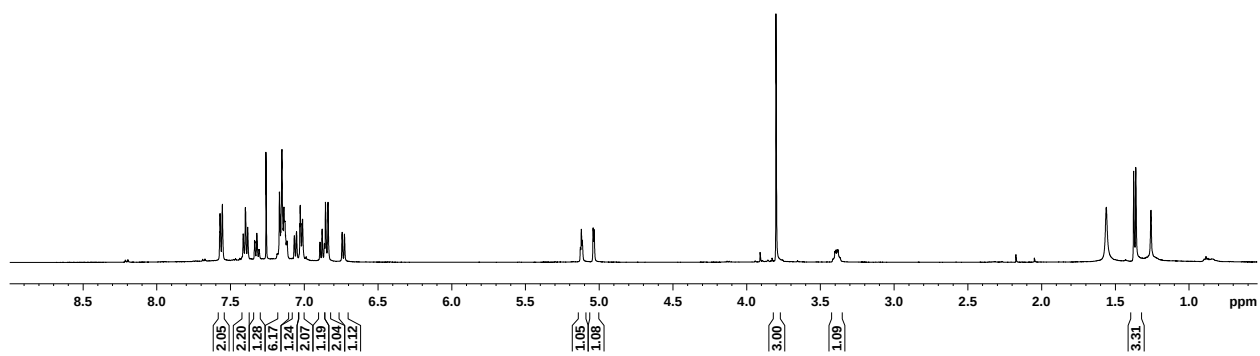
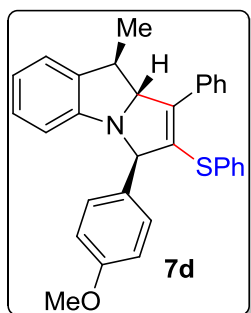
sjg-ygs-ph-ph-ME-rad-indoline-noe-c



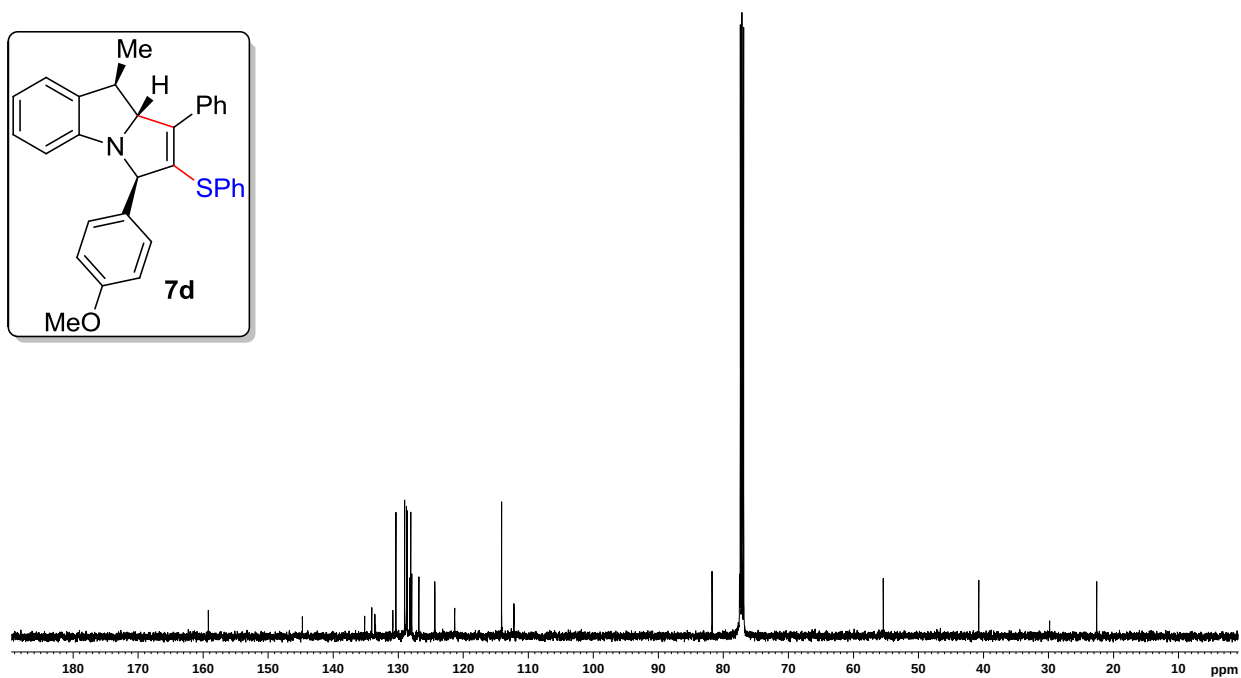
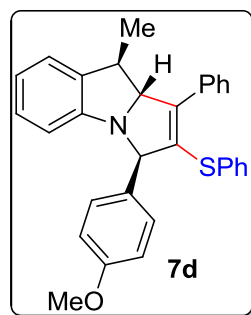
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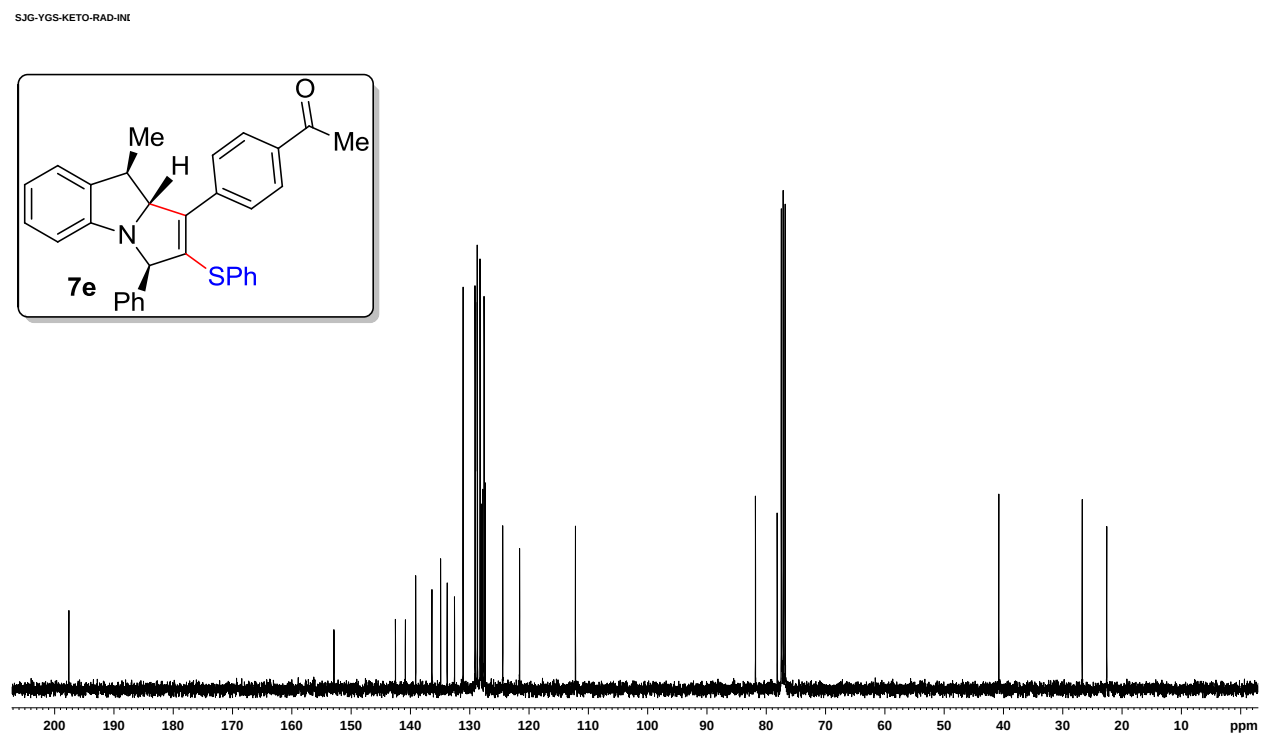
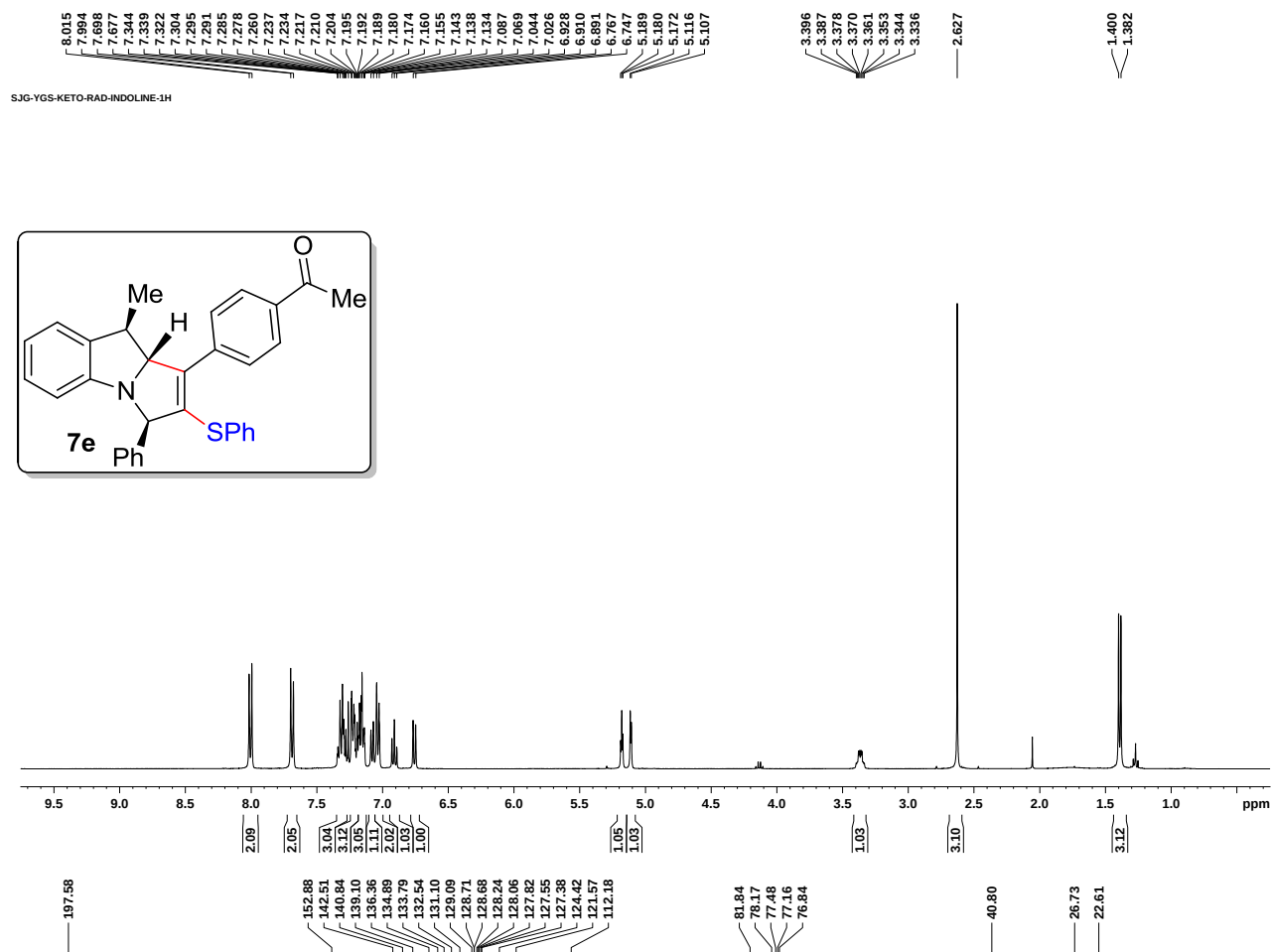


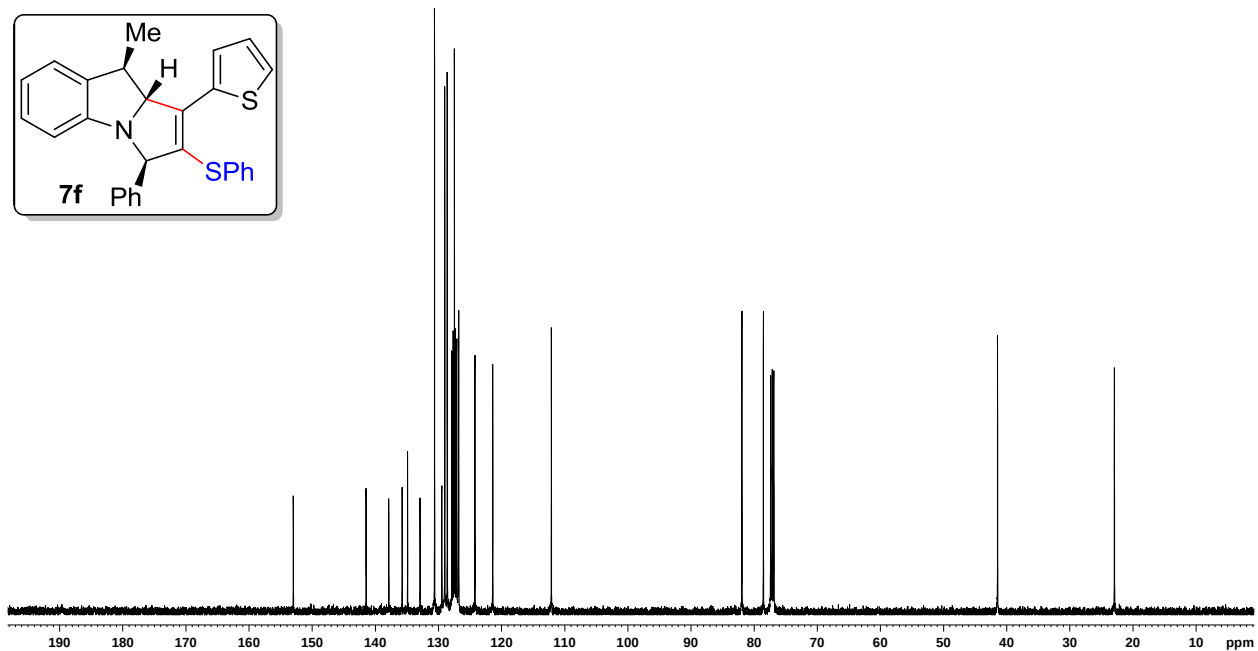
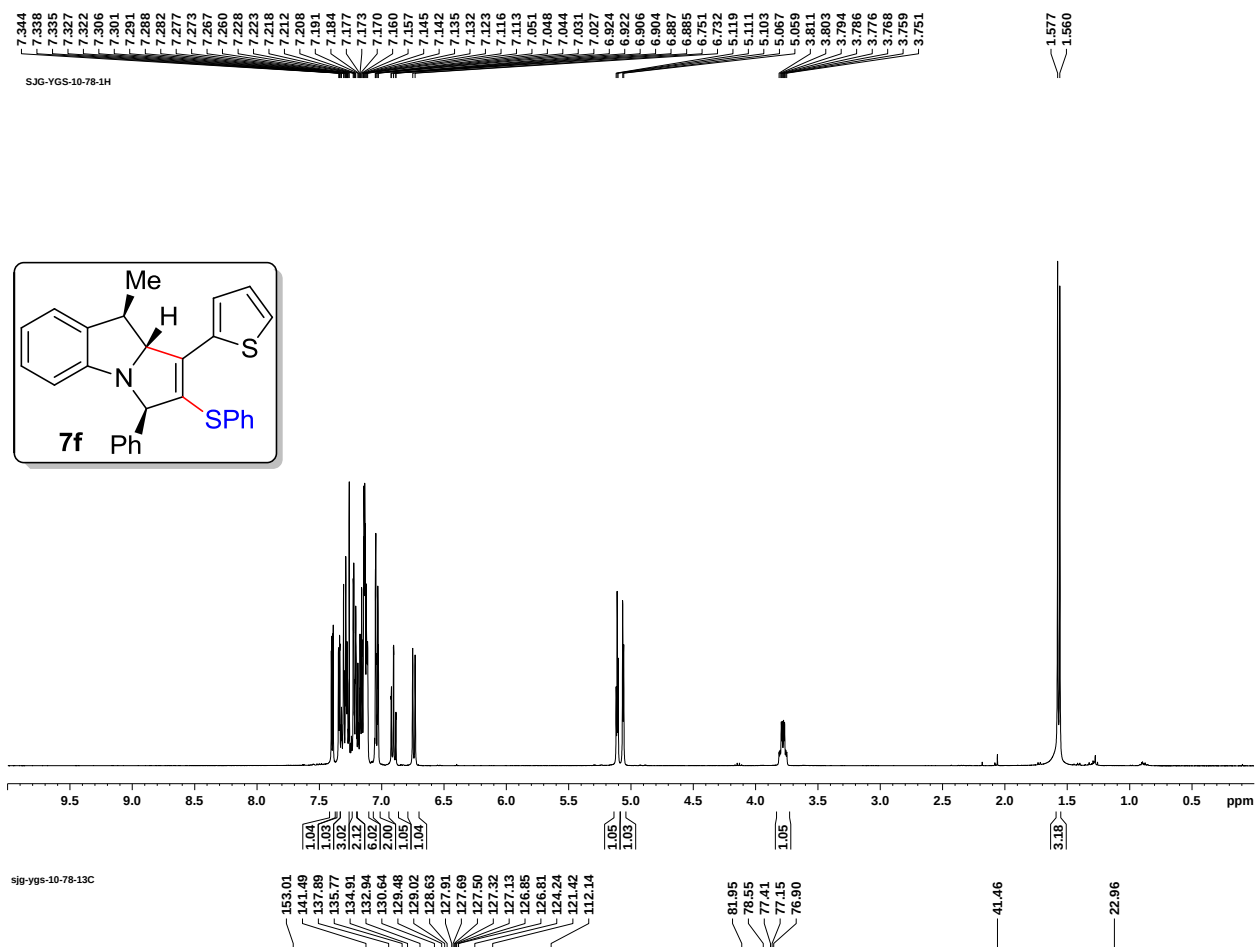
sjg-ygs-10-79-01-1h



sjg-ygs-10-79-01-13C

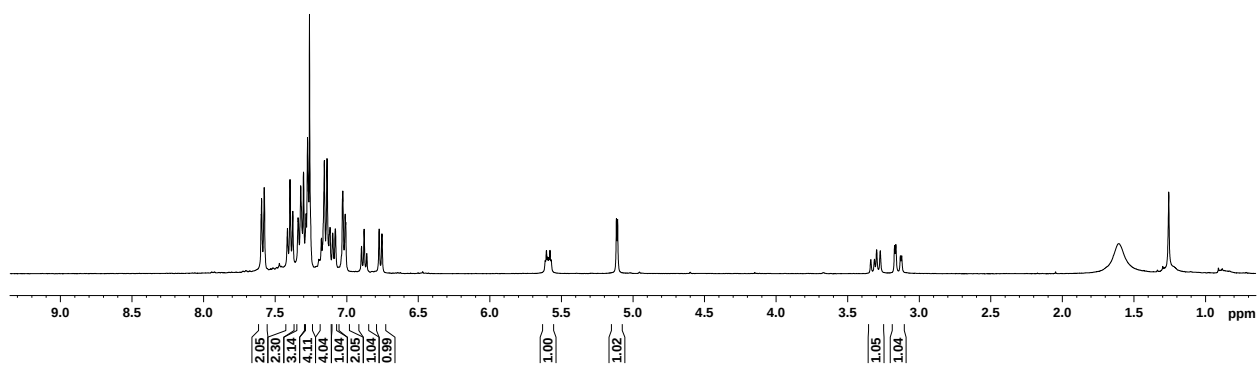
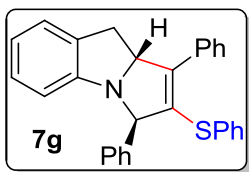




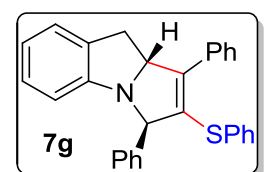
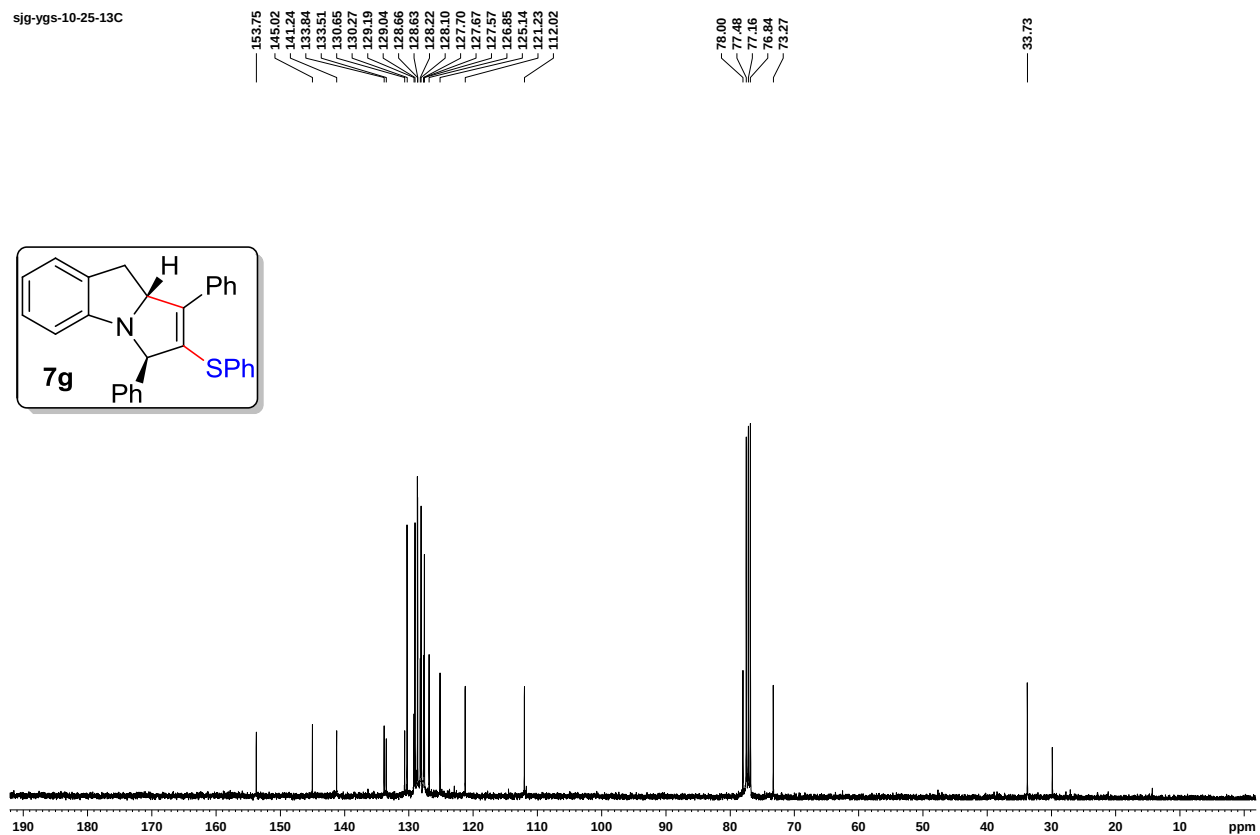


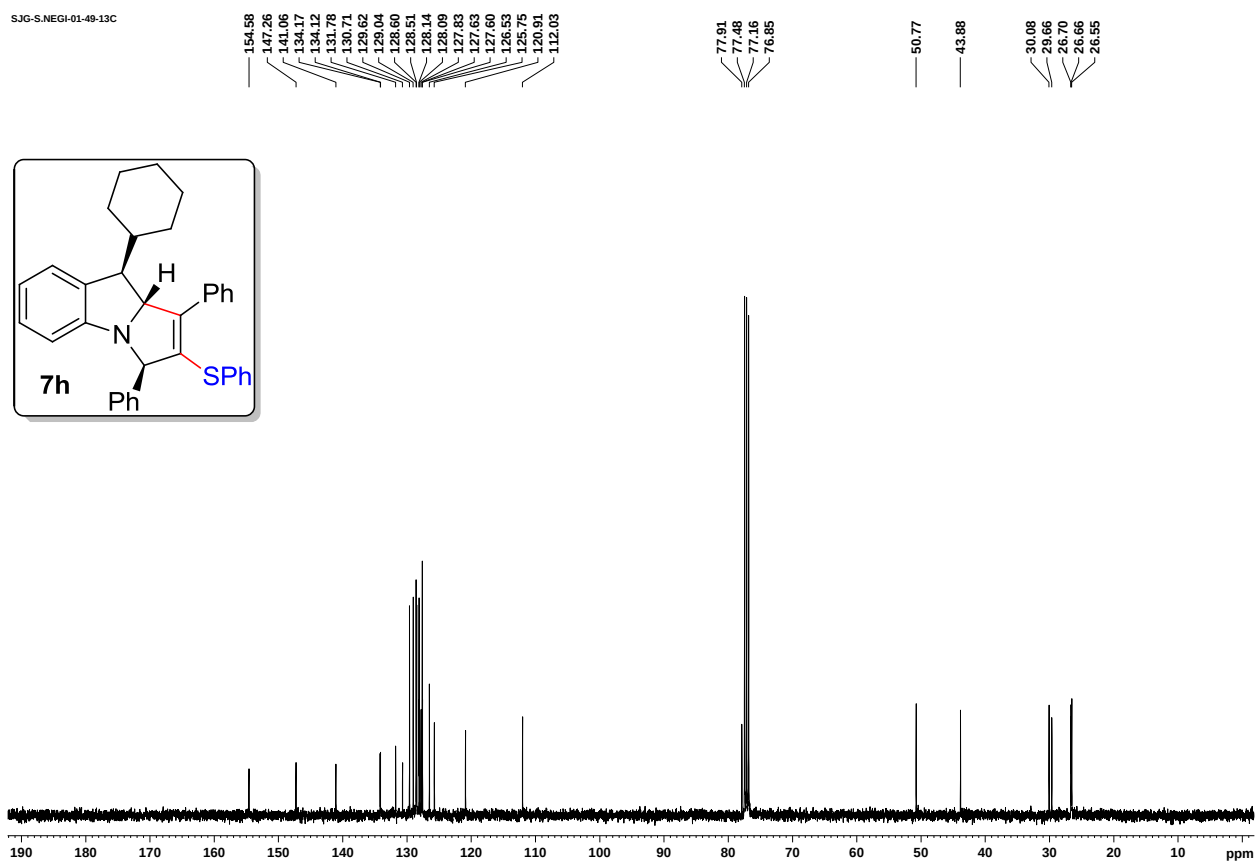
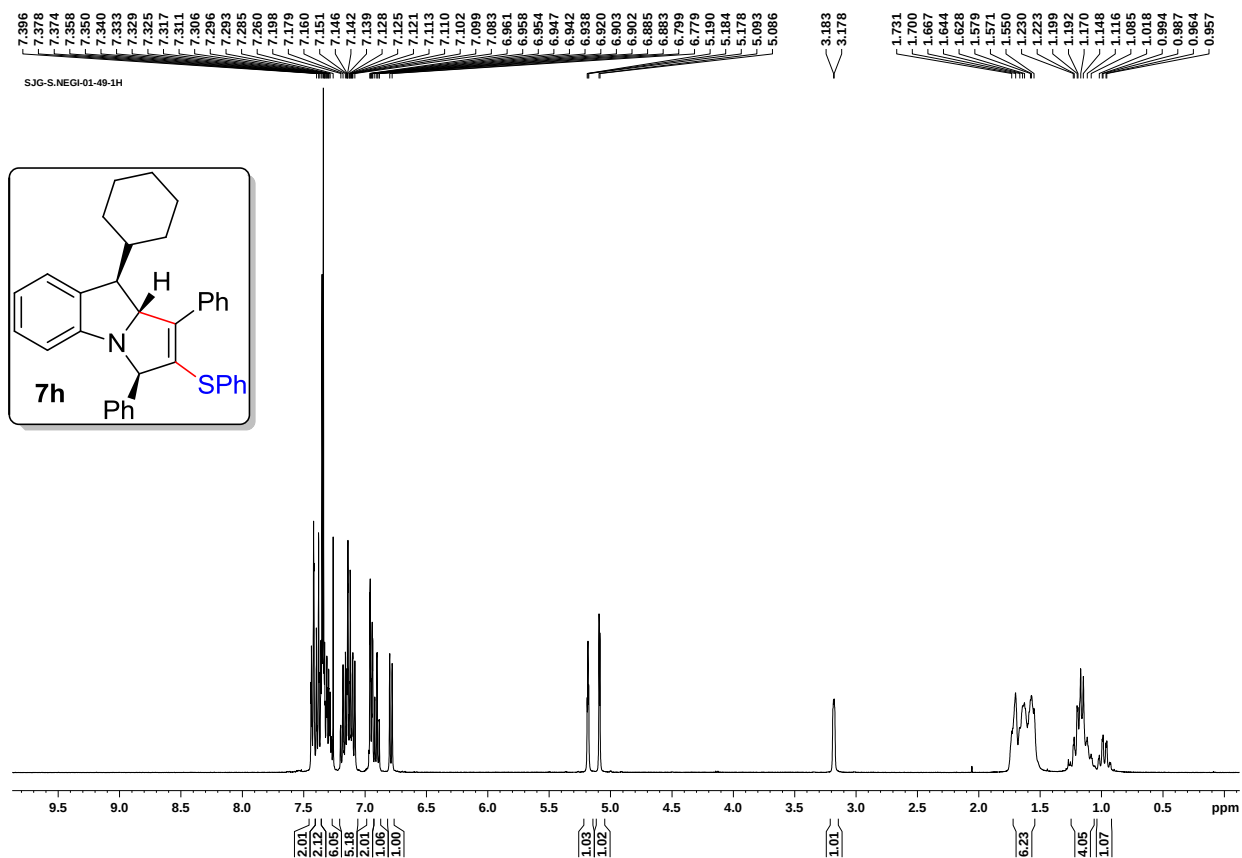


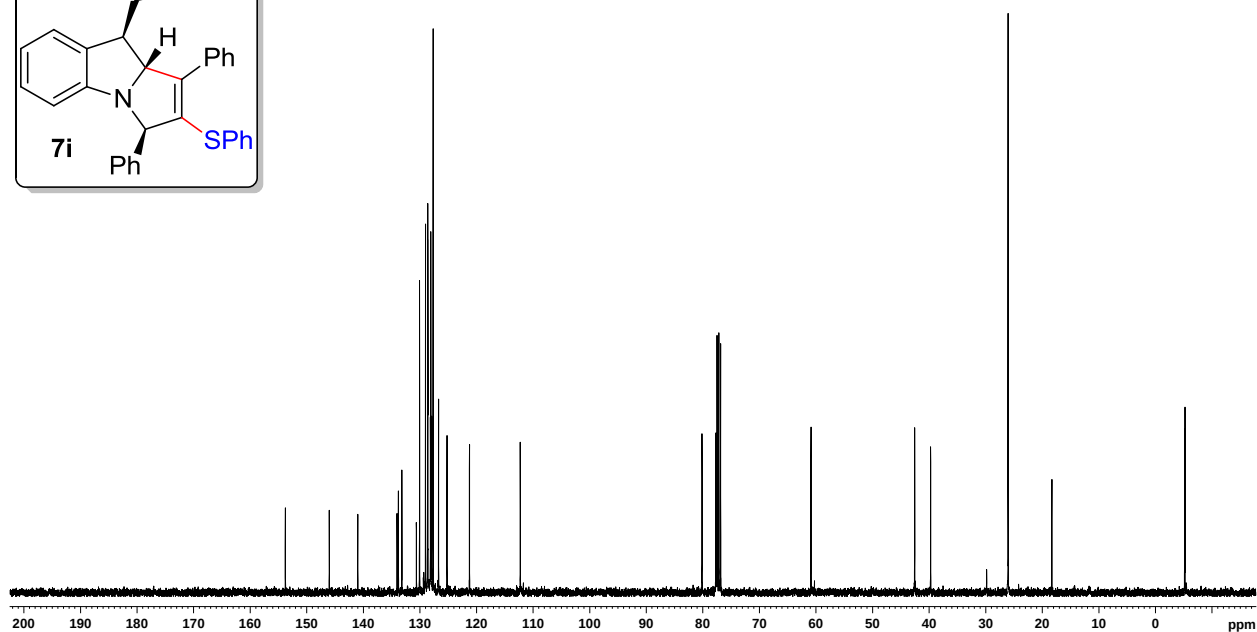
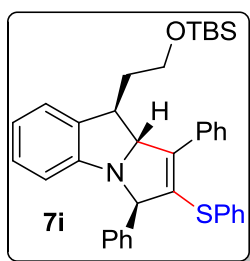
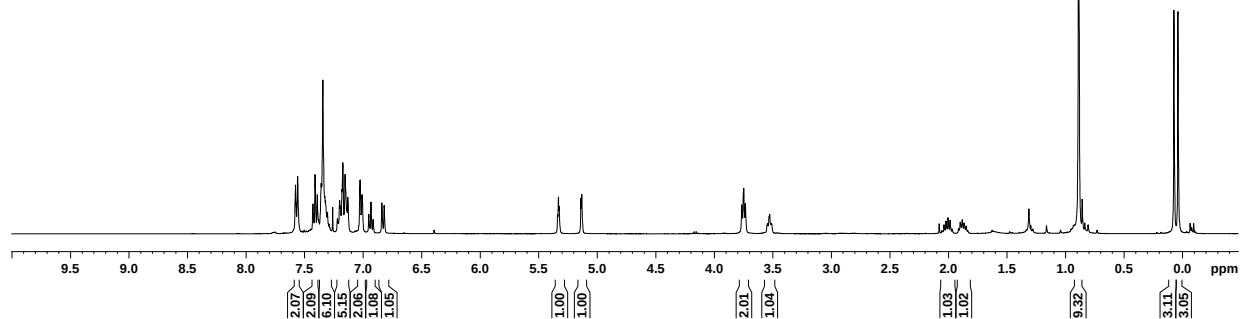
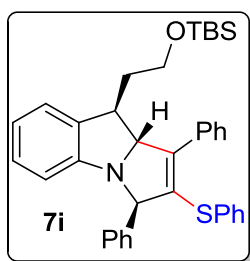
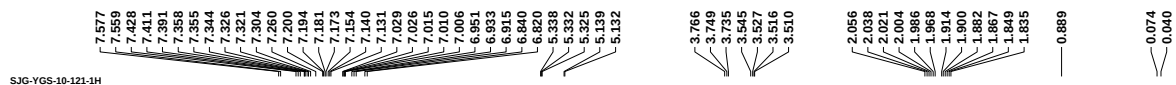
sjg-ygs-wo-me-indolie



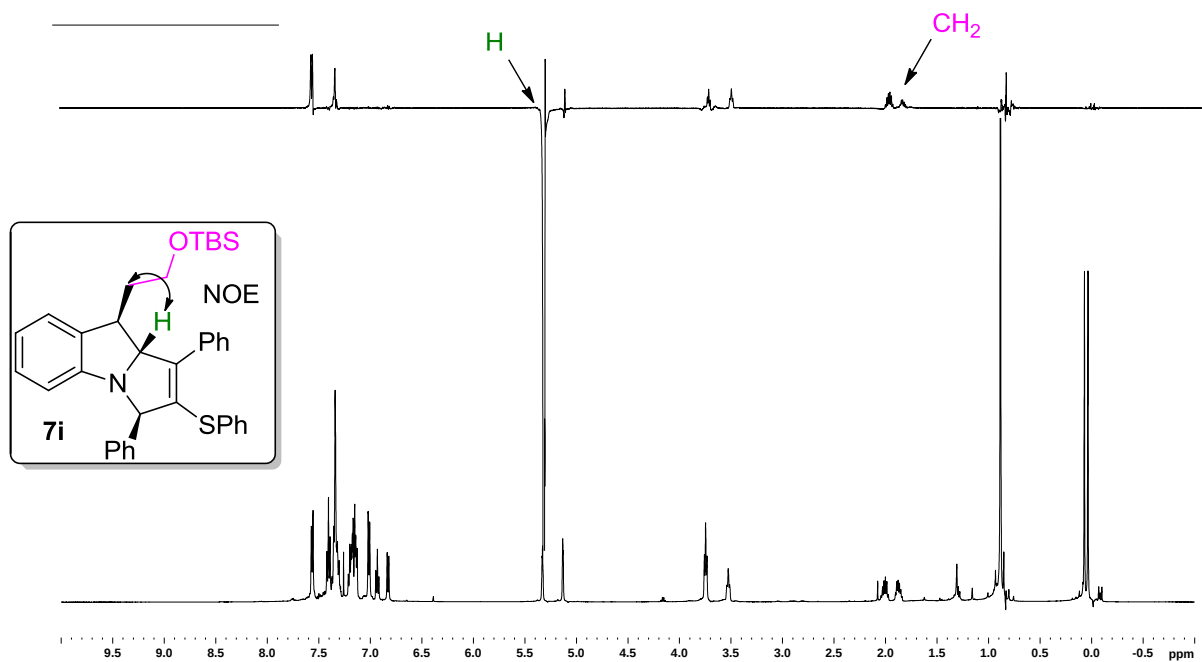
sjg-ygs-10-25-13C





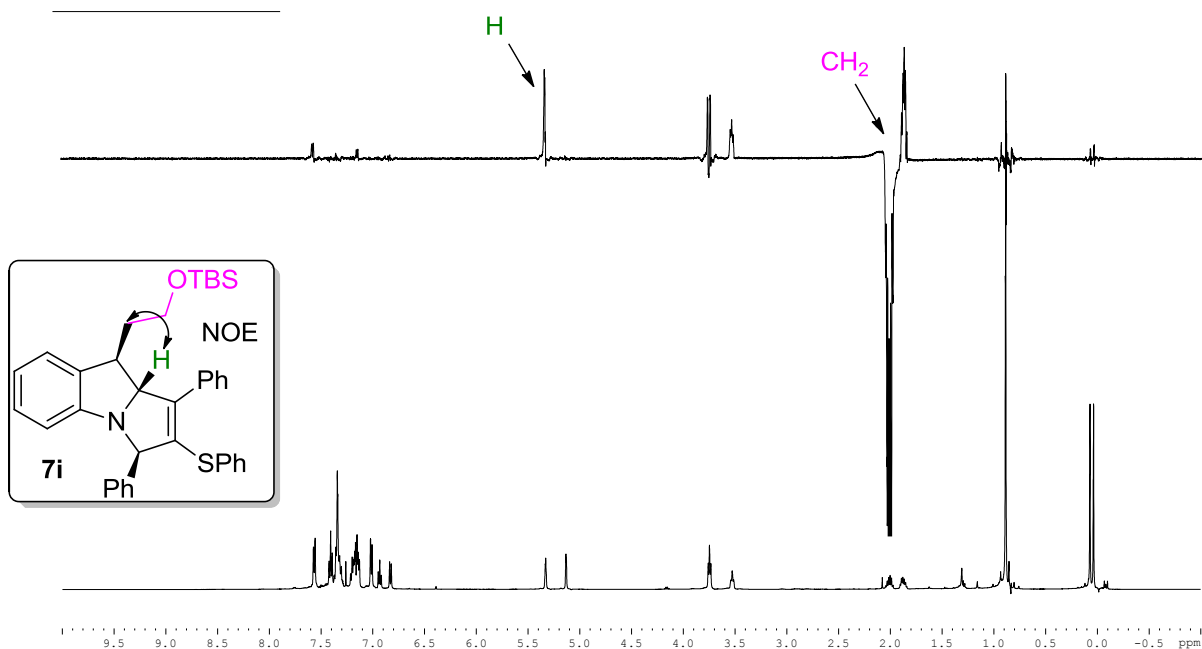


SJG-YGS-10-121-NOE-A

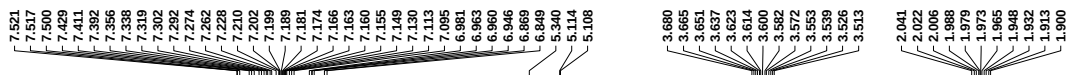


NOE enhancement = 4%

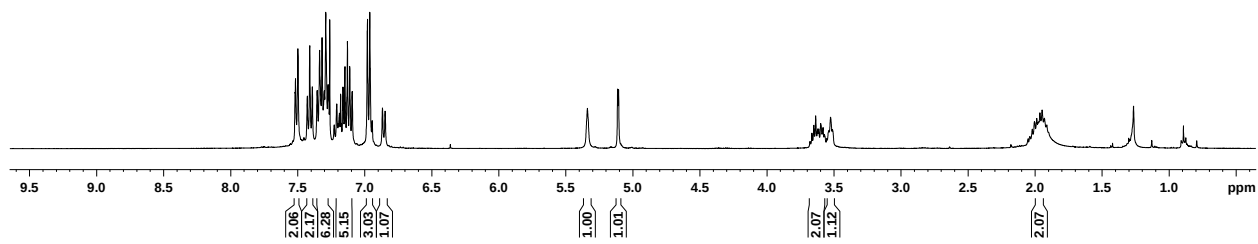
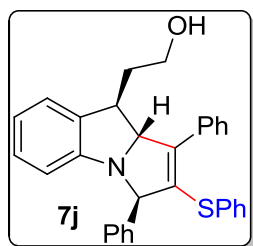
SJG-YGS-10-121-NOE-D



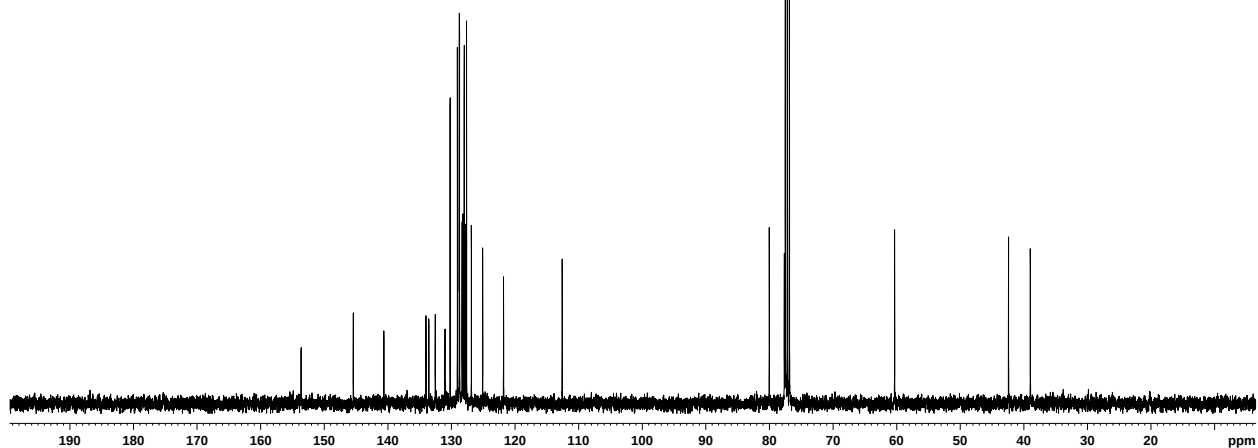
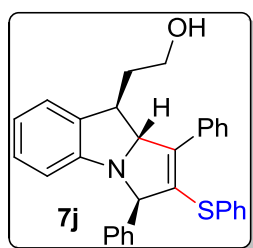
NOE enhancement = 4%

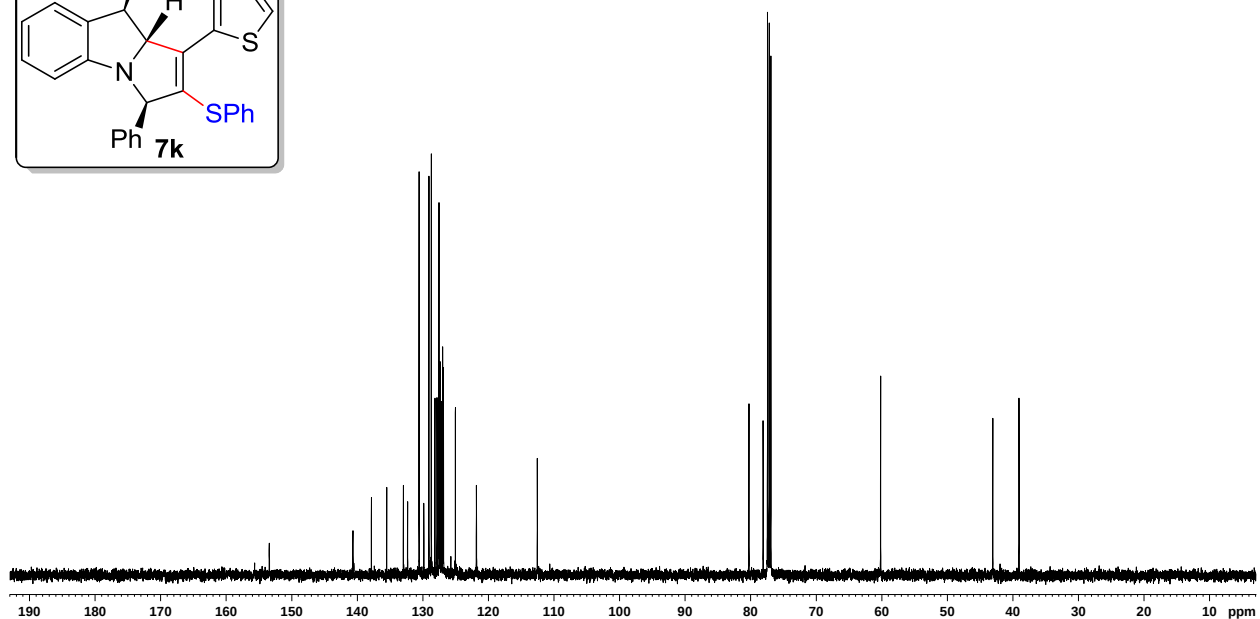
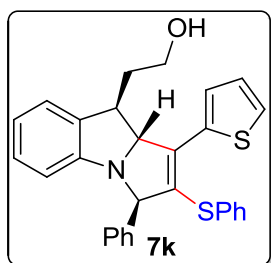
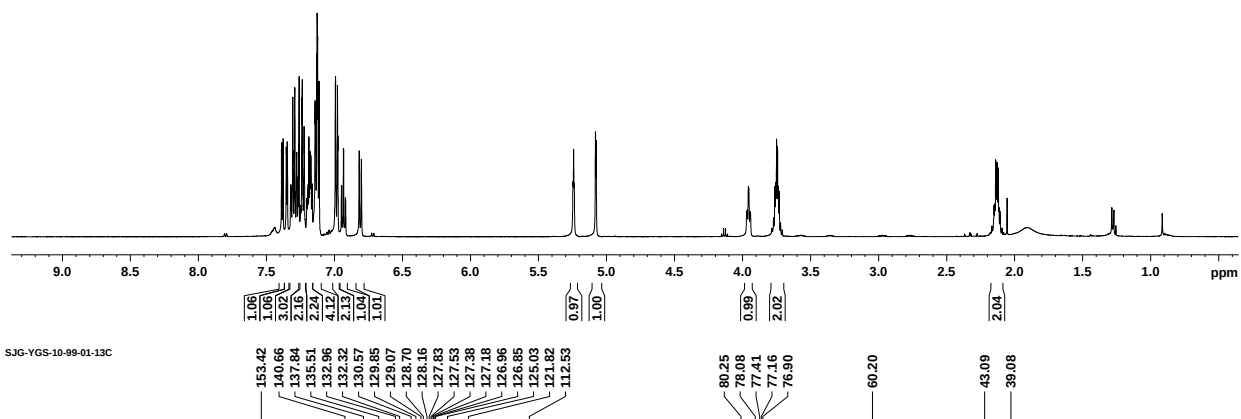
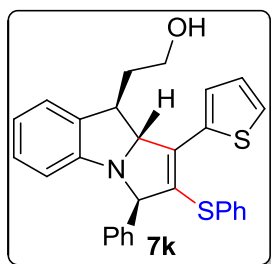
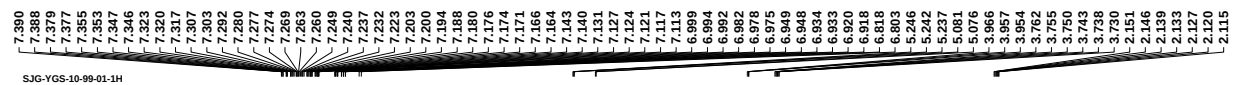


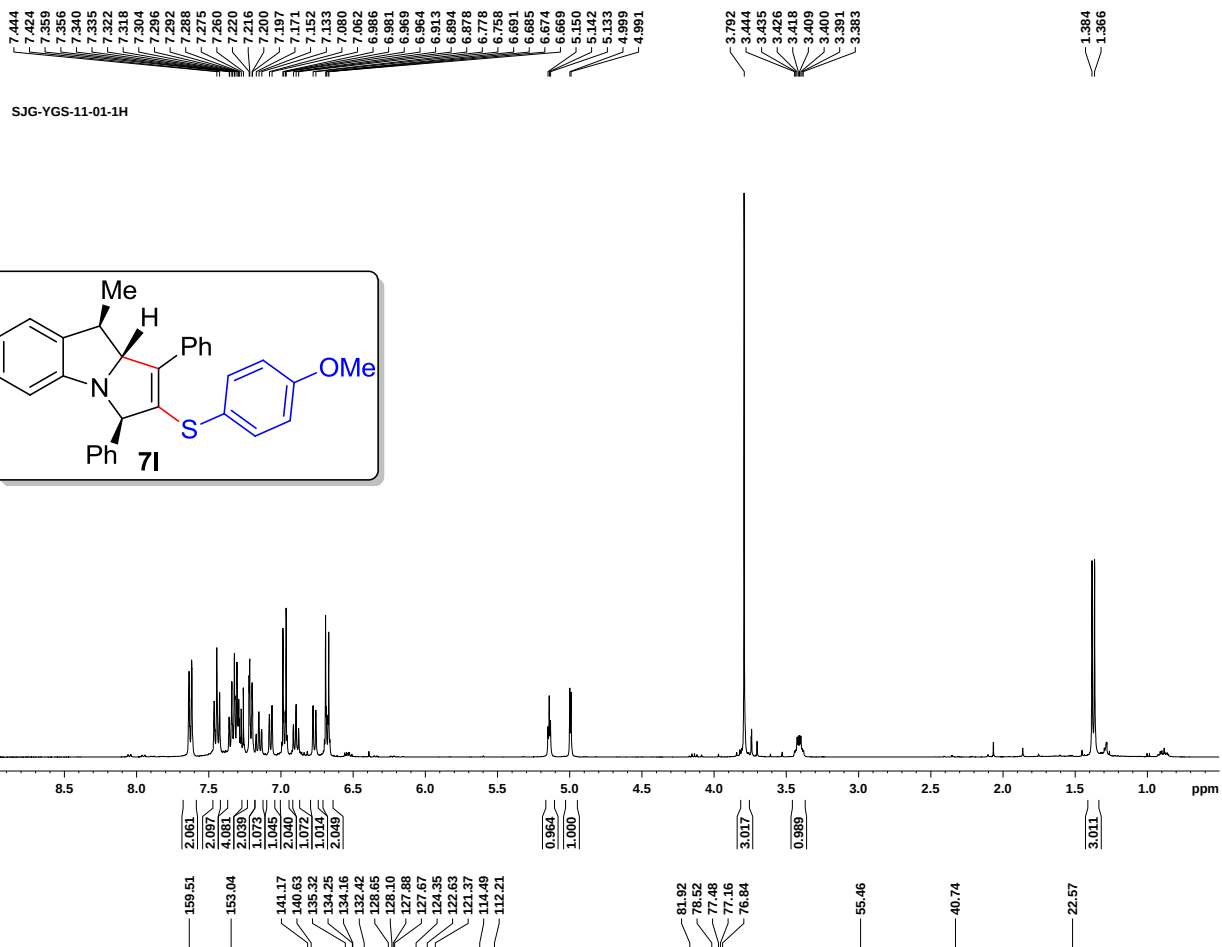
SJG-YGS-OH-RAD-INE



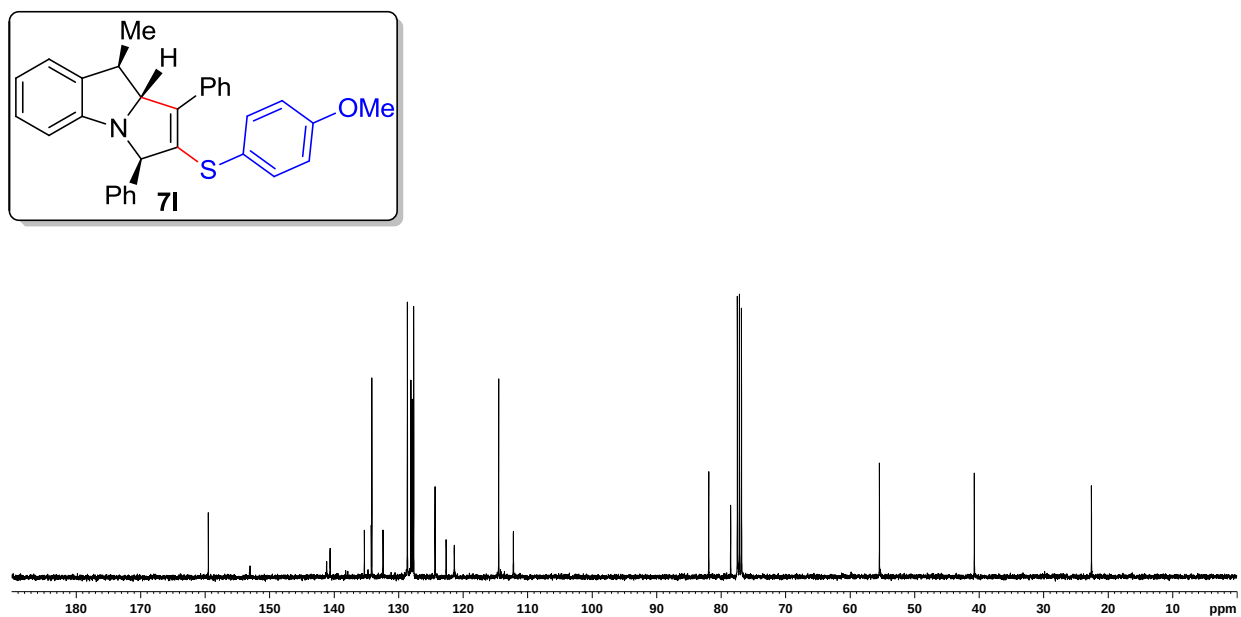
SJG-YGS-10-102-13C







SJG-YGS-11-01-13C



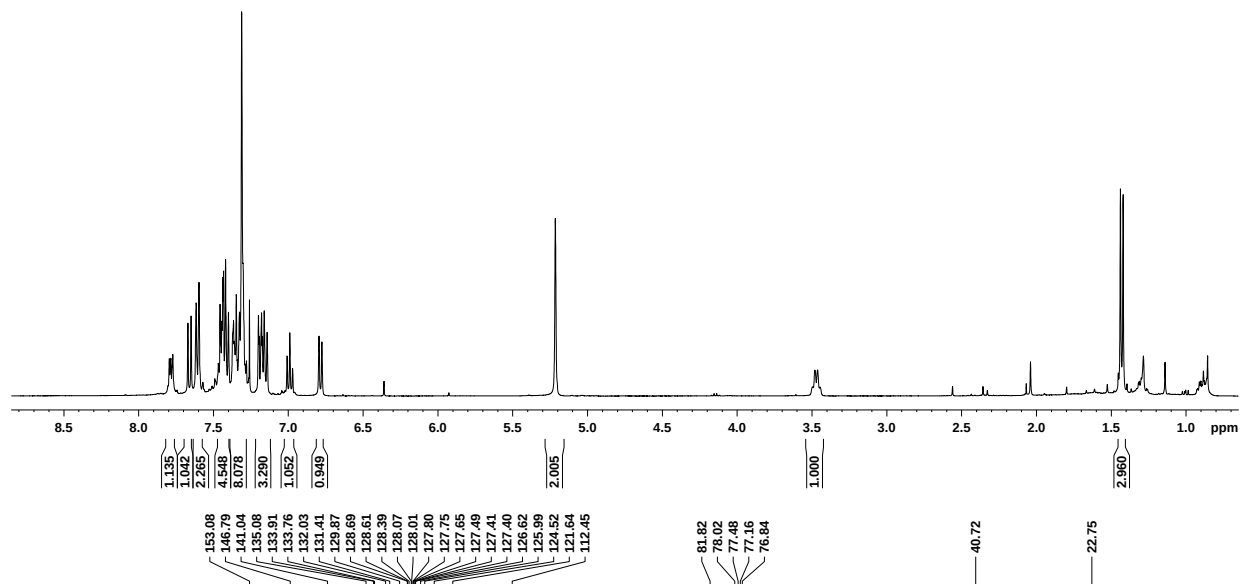
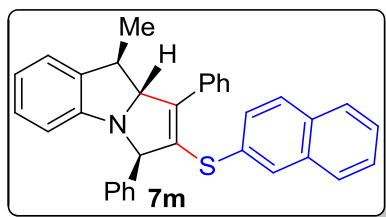


5.216

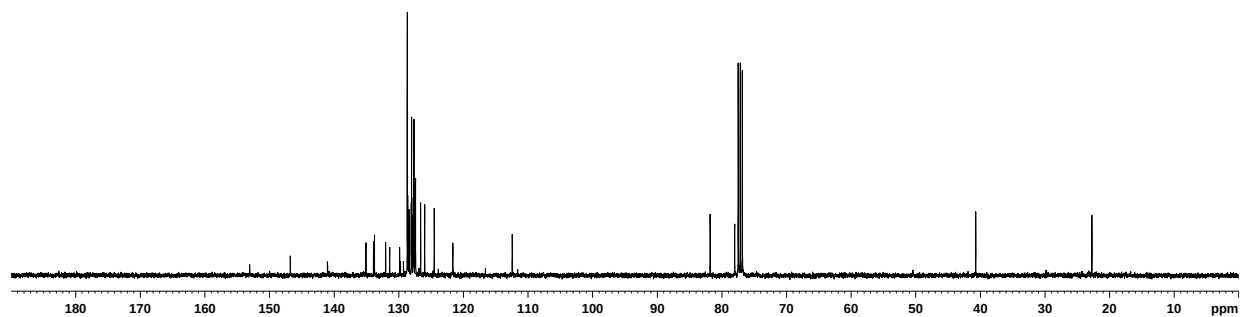
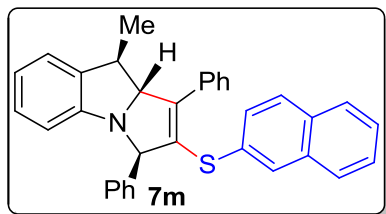
3.497
3.481
3.463
3.446

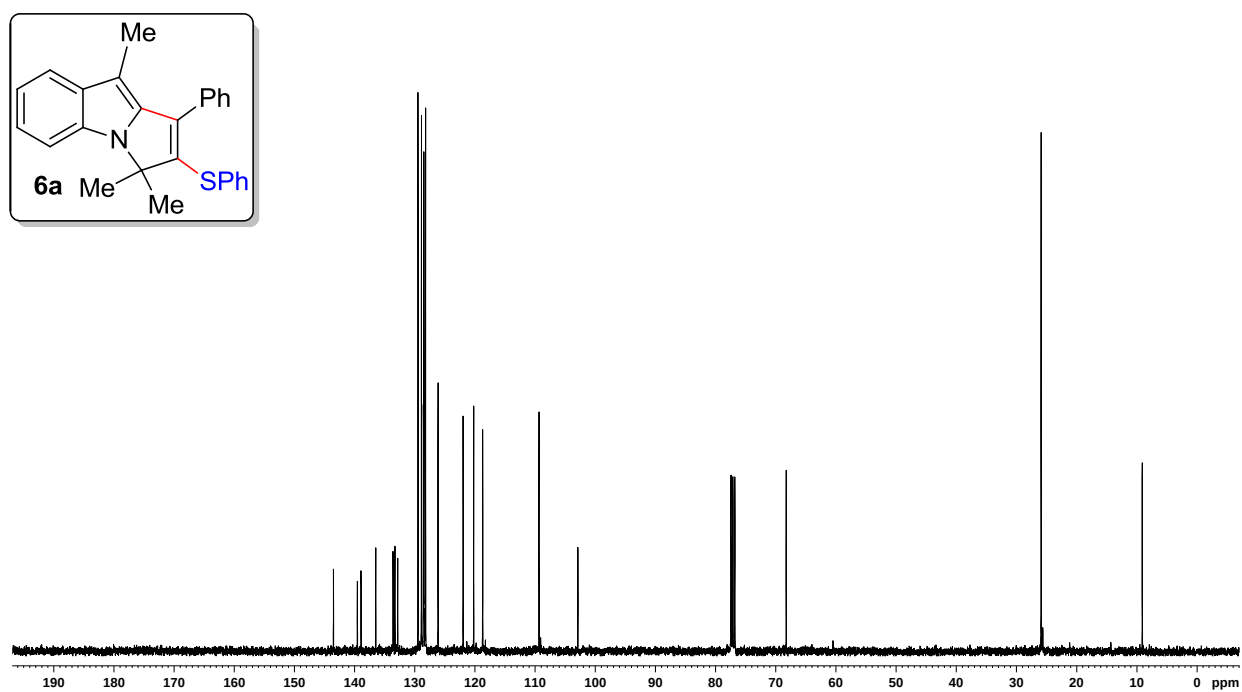
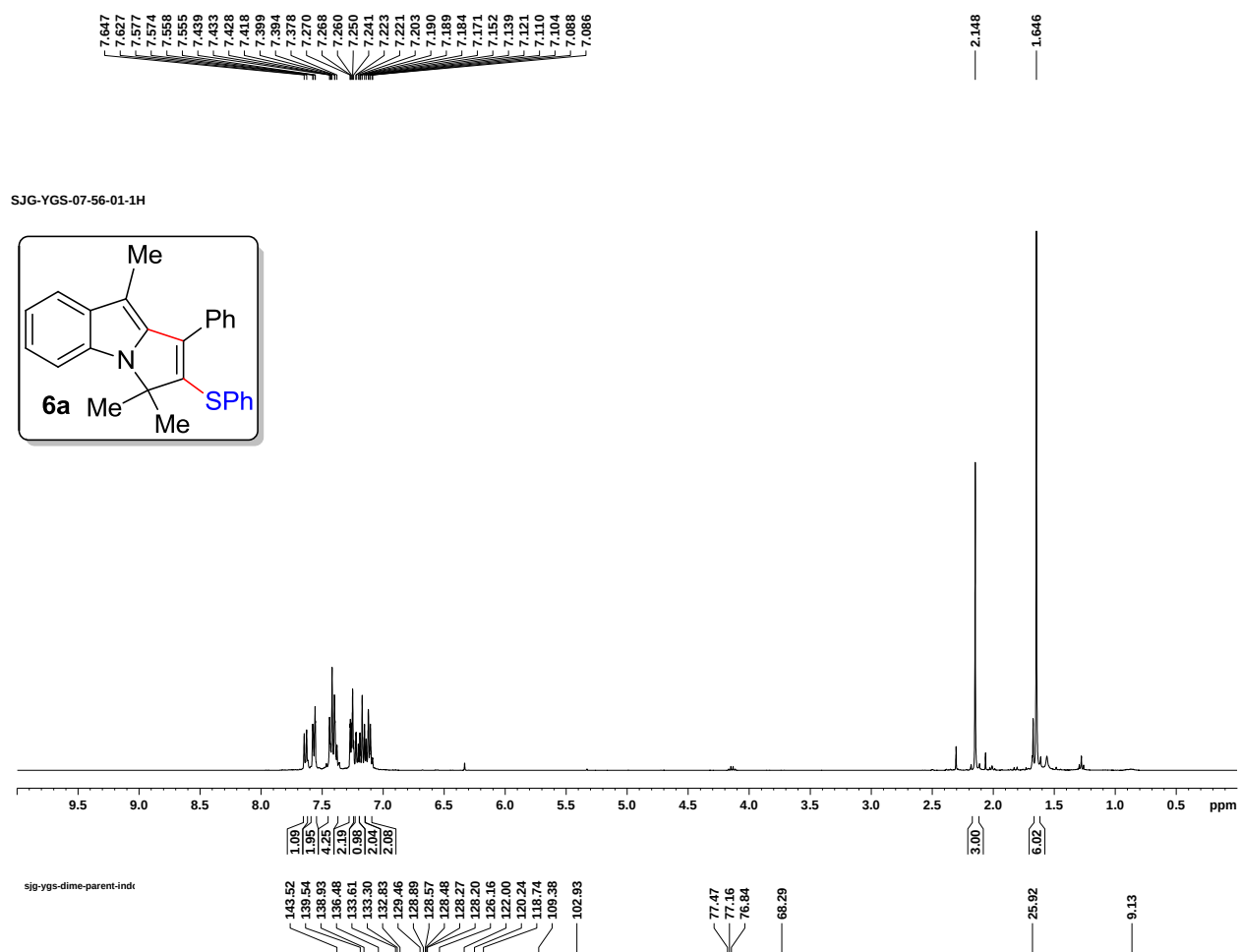
1.439
1.421

SJG-YGS-11-02-1H

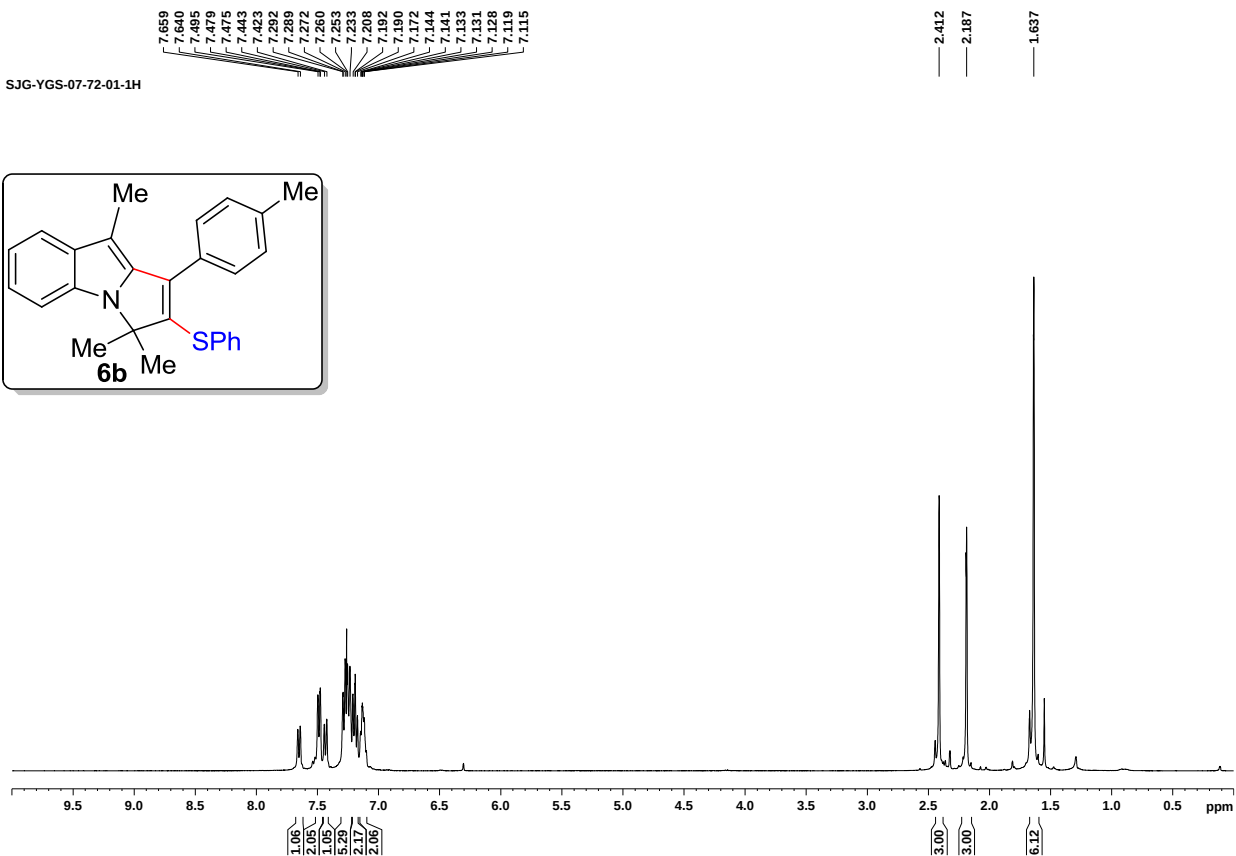
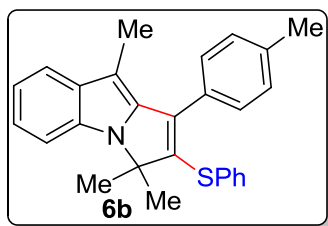


SJG-YGS-11-02-13C

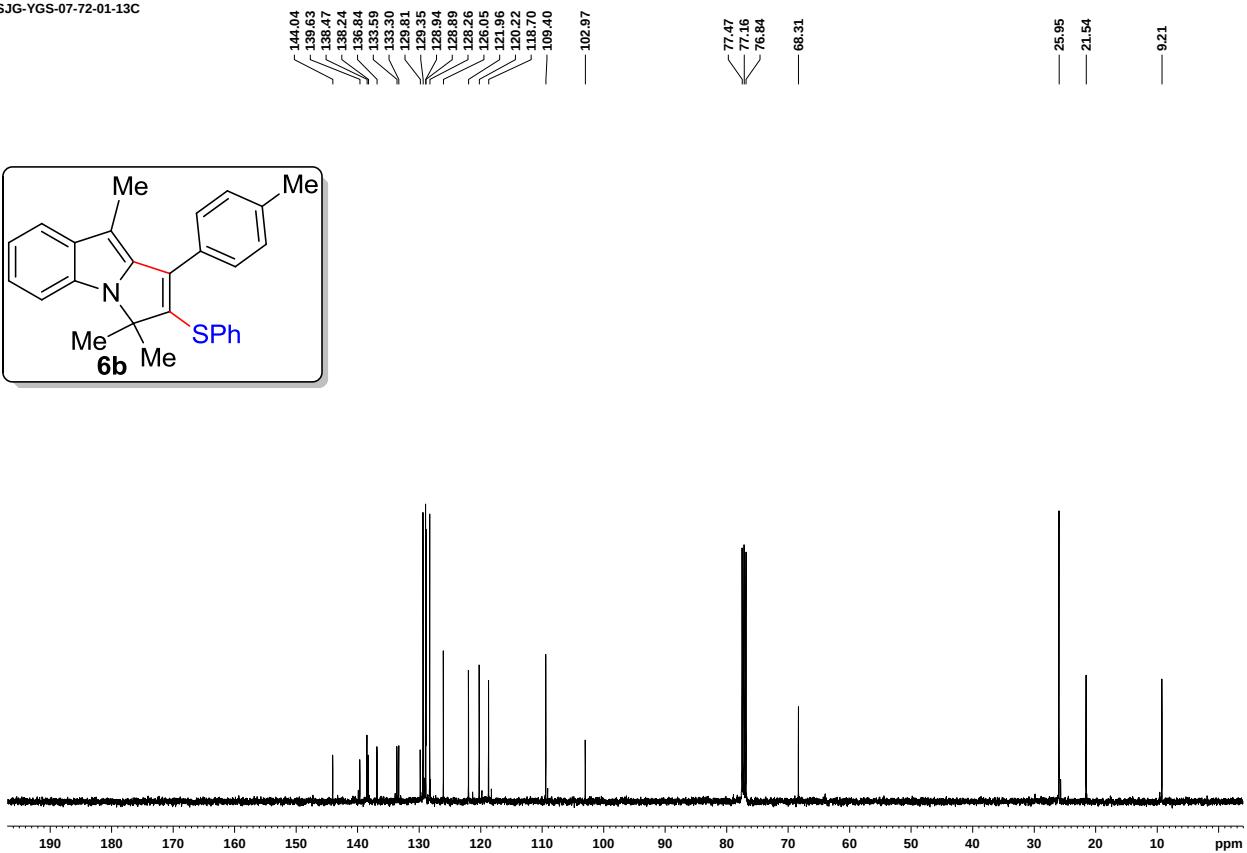
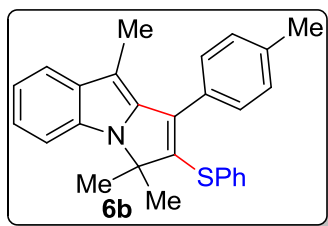




SJG-YGS-07-72-01-1H



SJG-YGS-07-72-01-13C



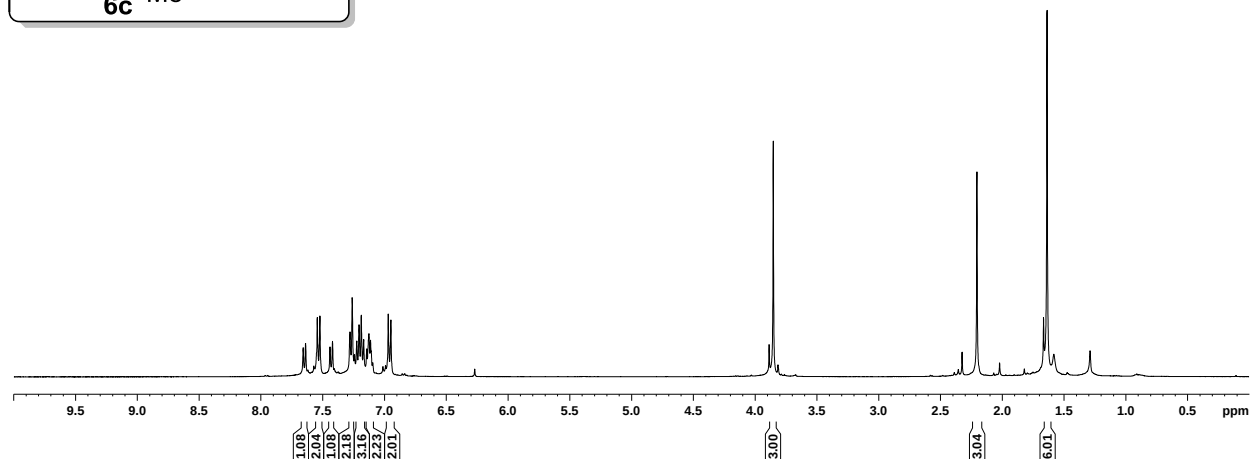
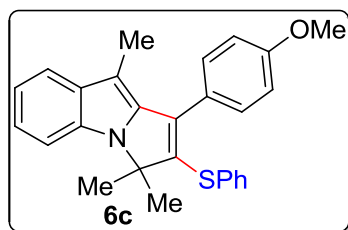
SJG-YGS-OME-INDOLE-1H

7.657
7.638
7.543
7.522
7.440
7.420
7.278
7.261
7.242
7.223
7.205
7.187
7.168
7.143
7.125
7.112
7.107
7.084
6.969
6.947

3.893

2.204

1.637



SJG-YGS-OME-INDOLE-1

159.88

143.55
139.70
137.88
136.86
133.62
133.33
130.80
128.91
128.15
126.03
125.01
121.96
120.21
118.71
113.66
109.41
102.91

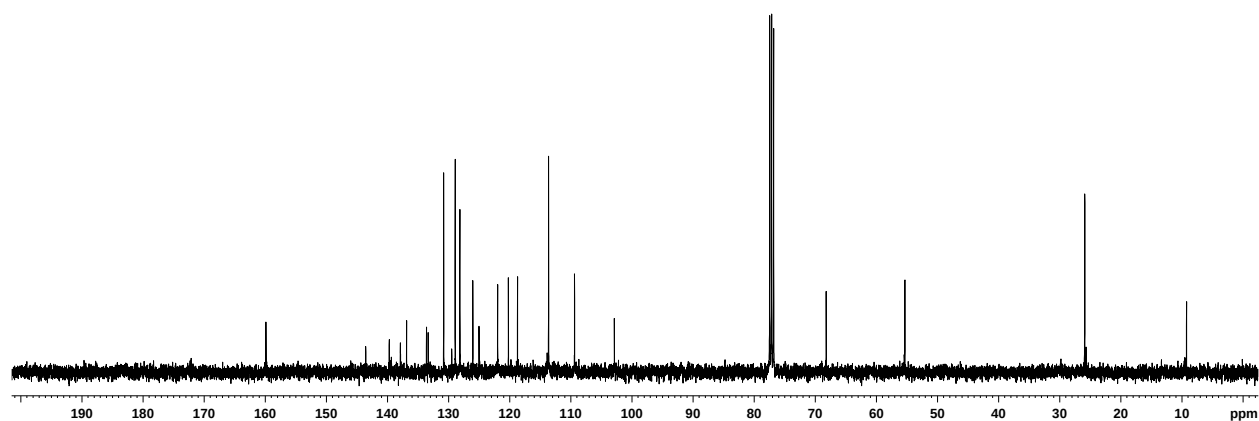
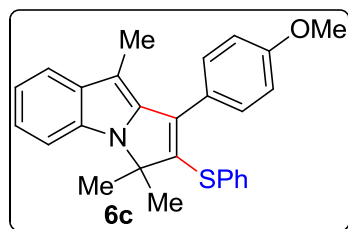
77.47
77.16
76.84

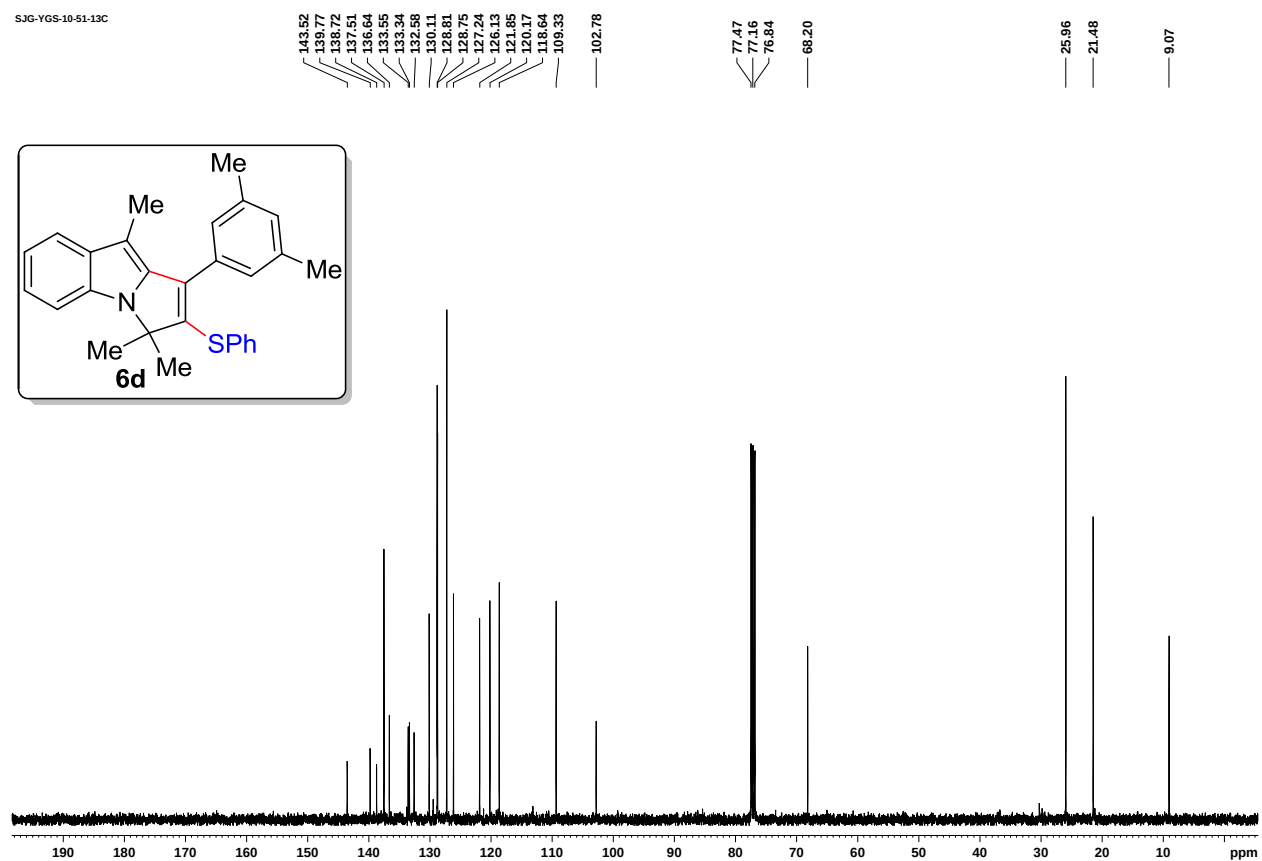
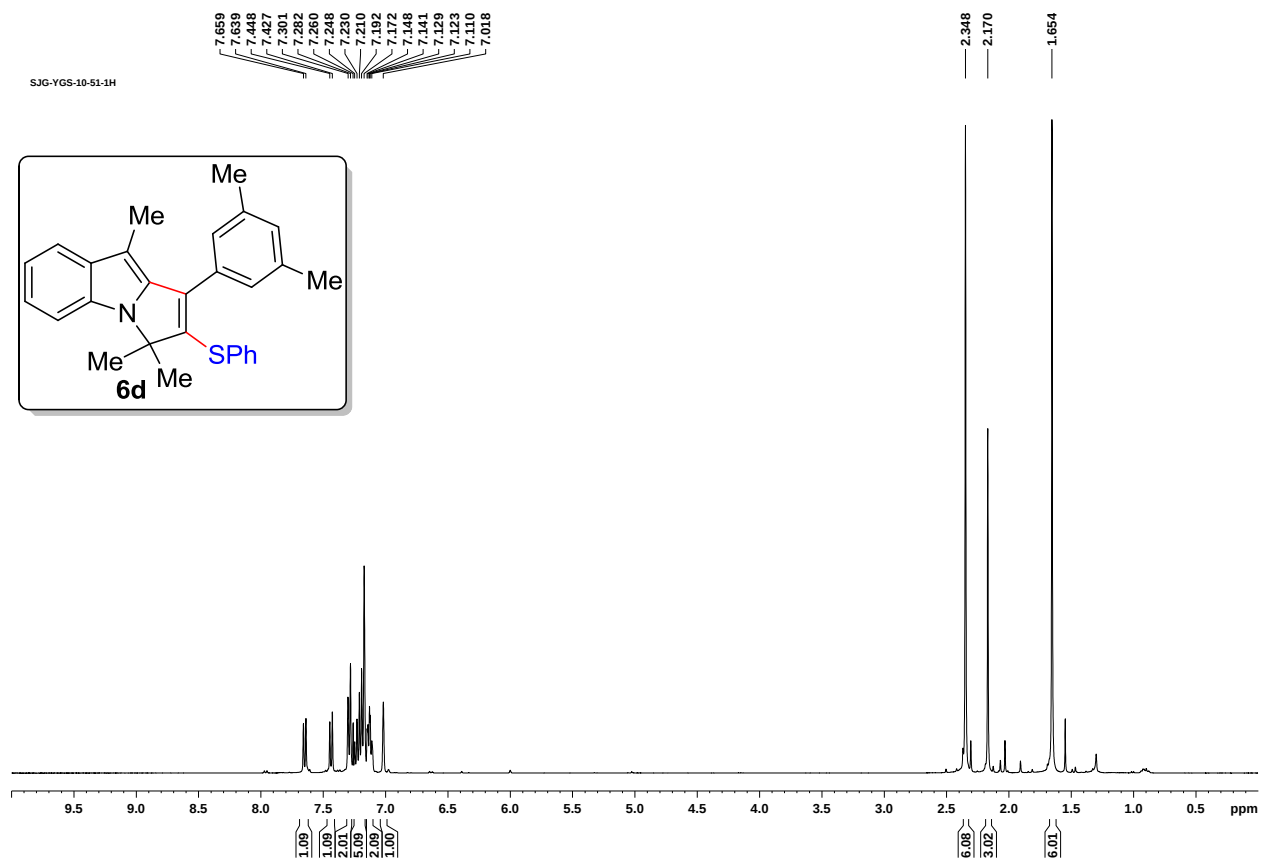
68.24

55.36

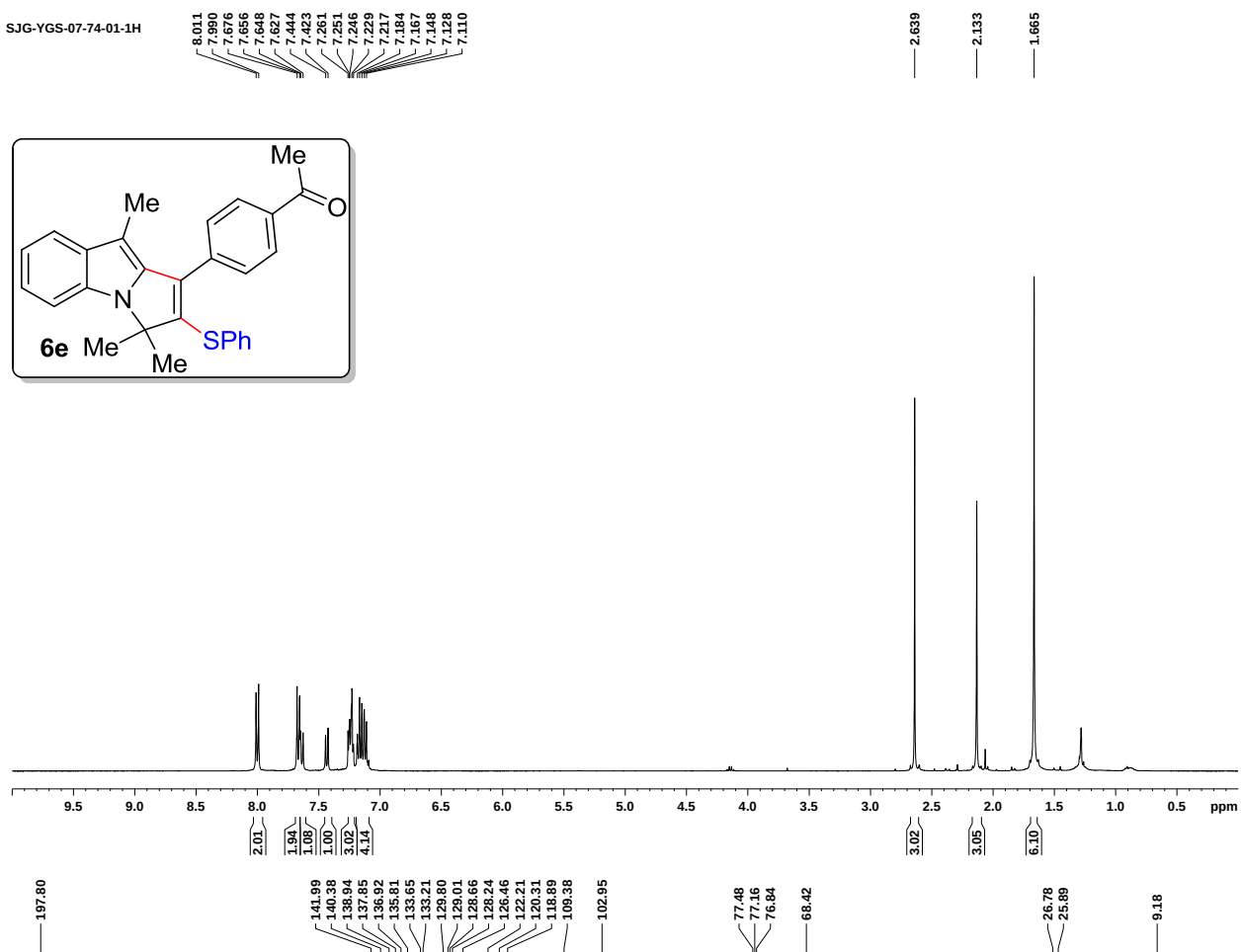
25.92

9.27

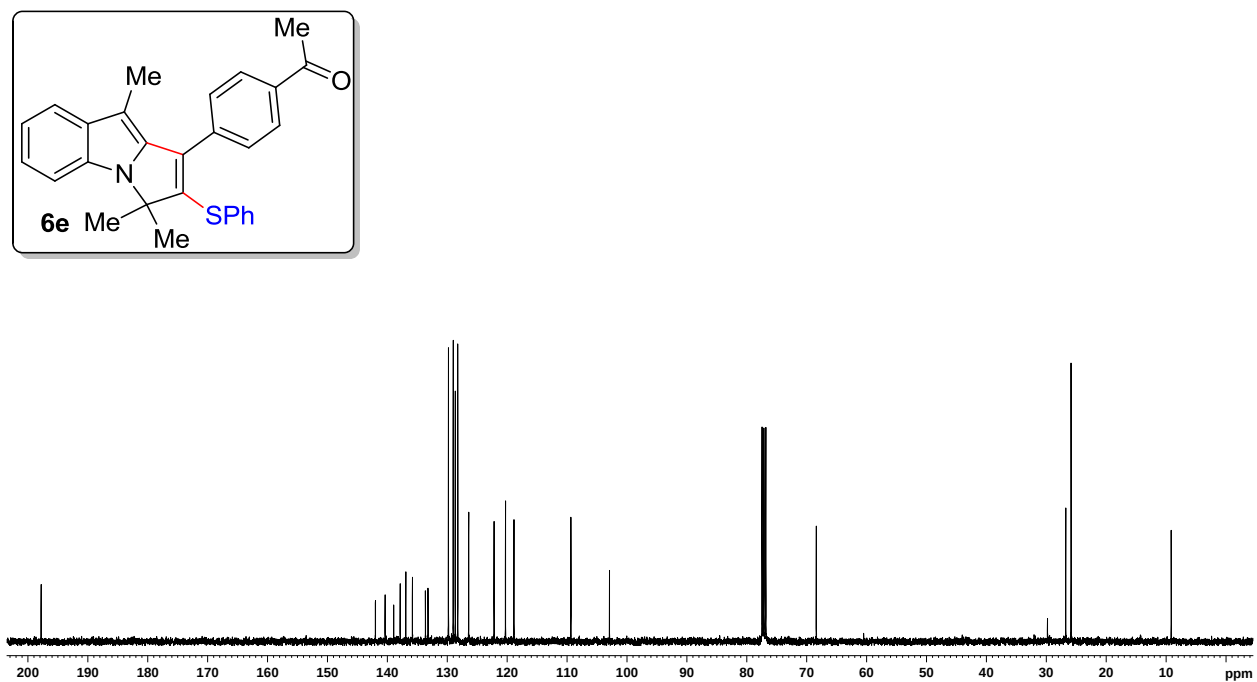


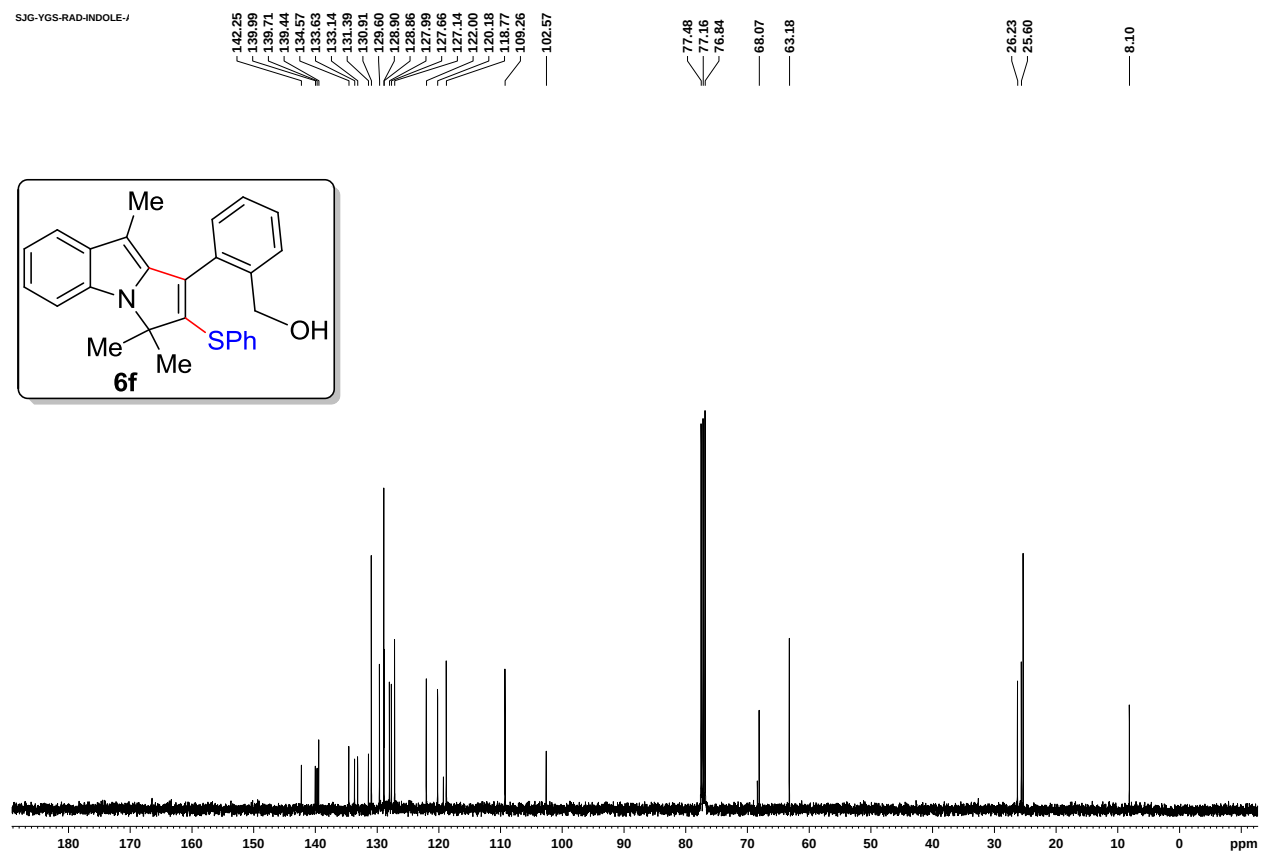
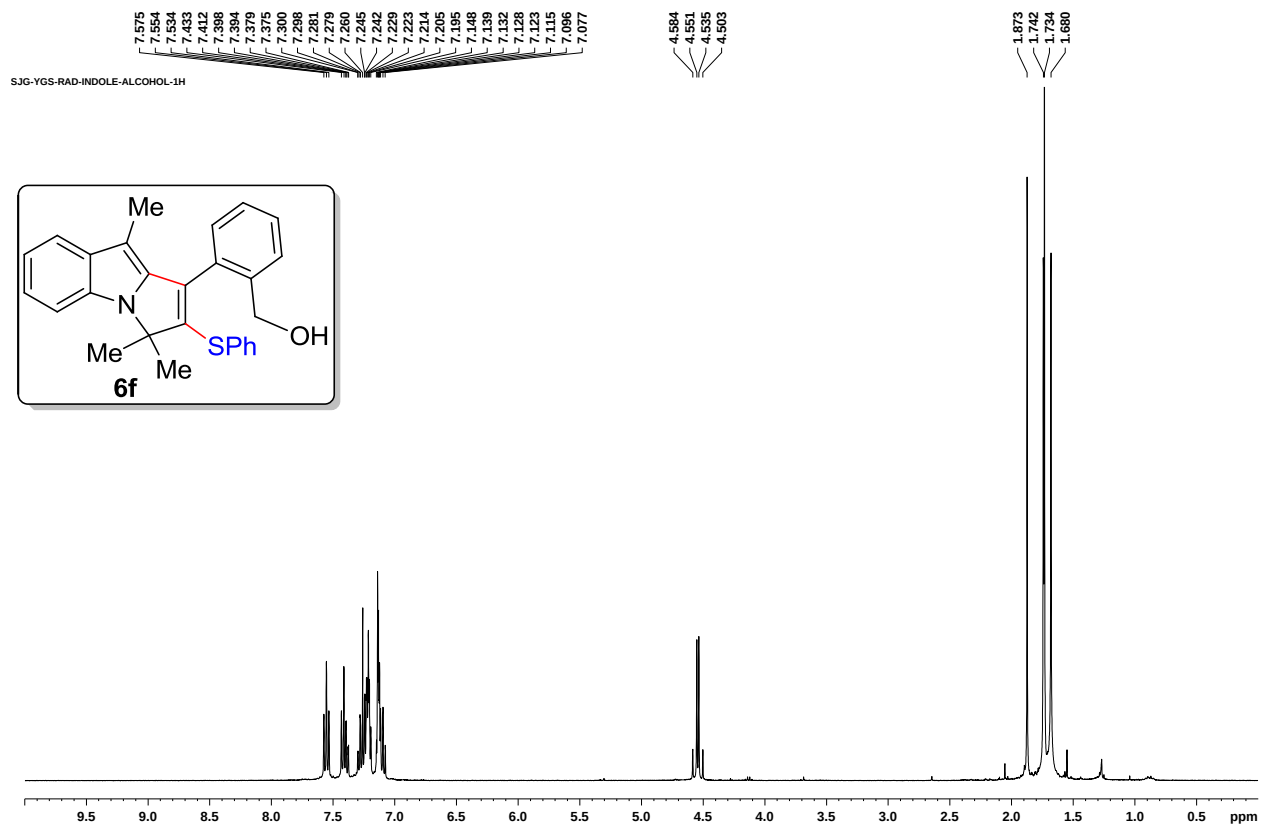


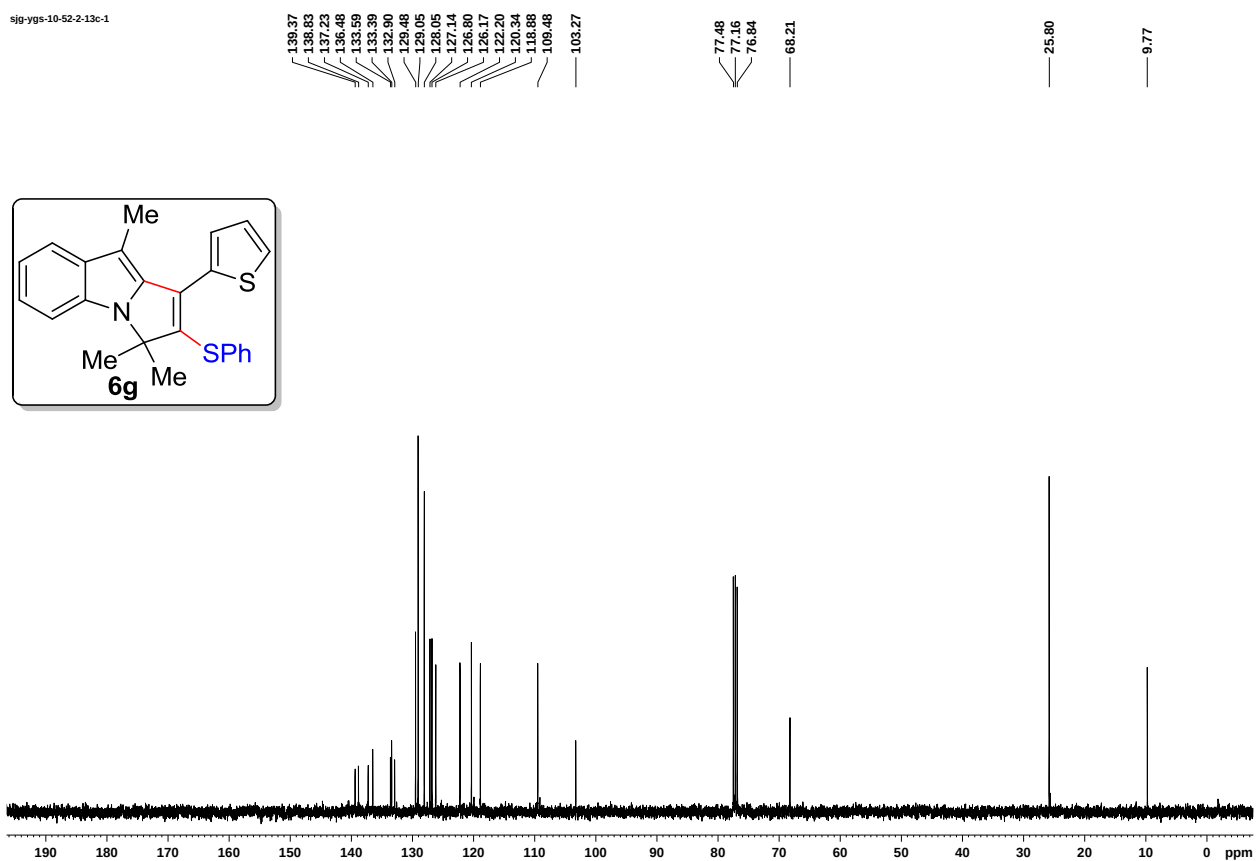
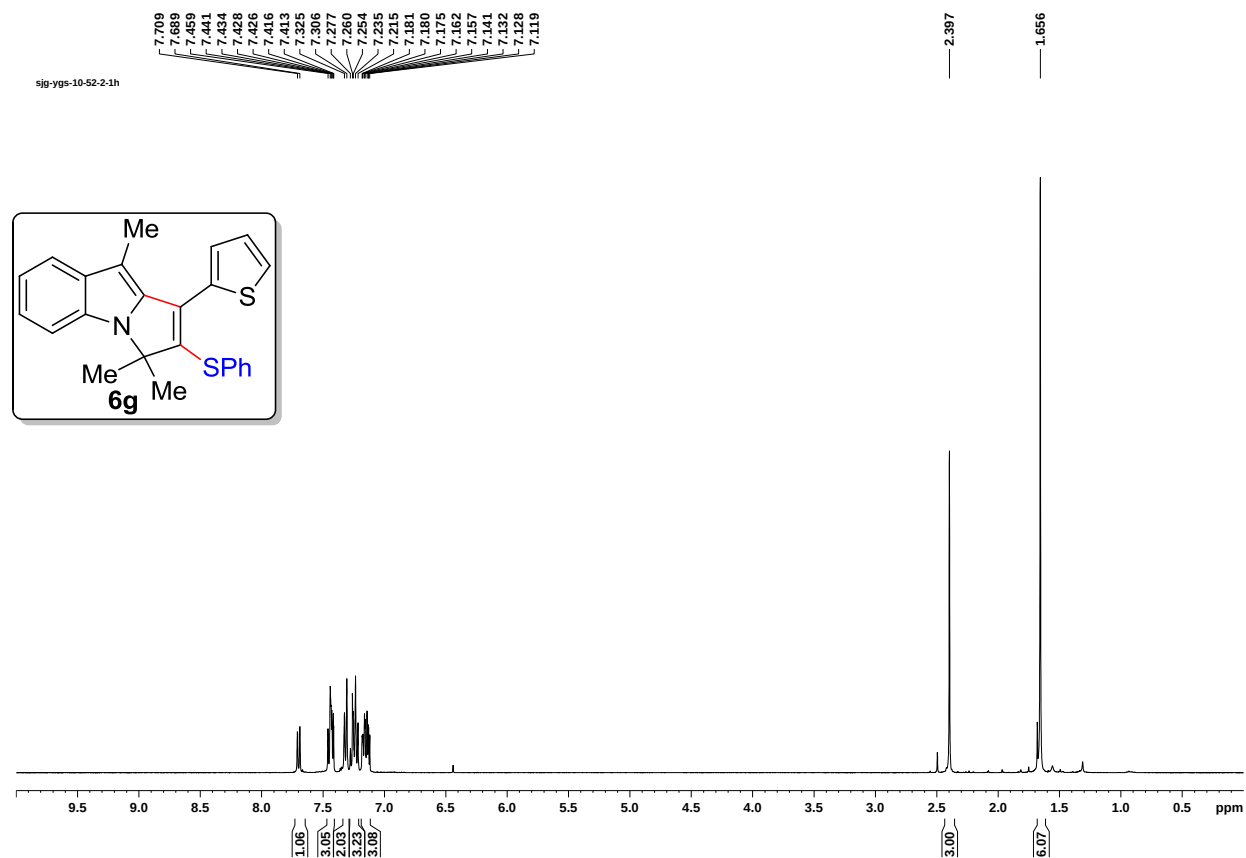
SJG-YGS-07-74-01-1H

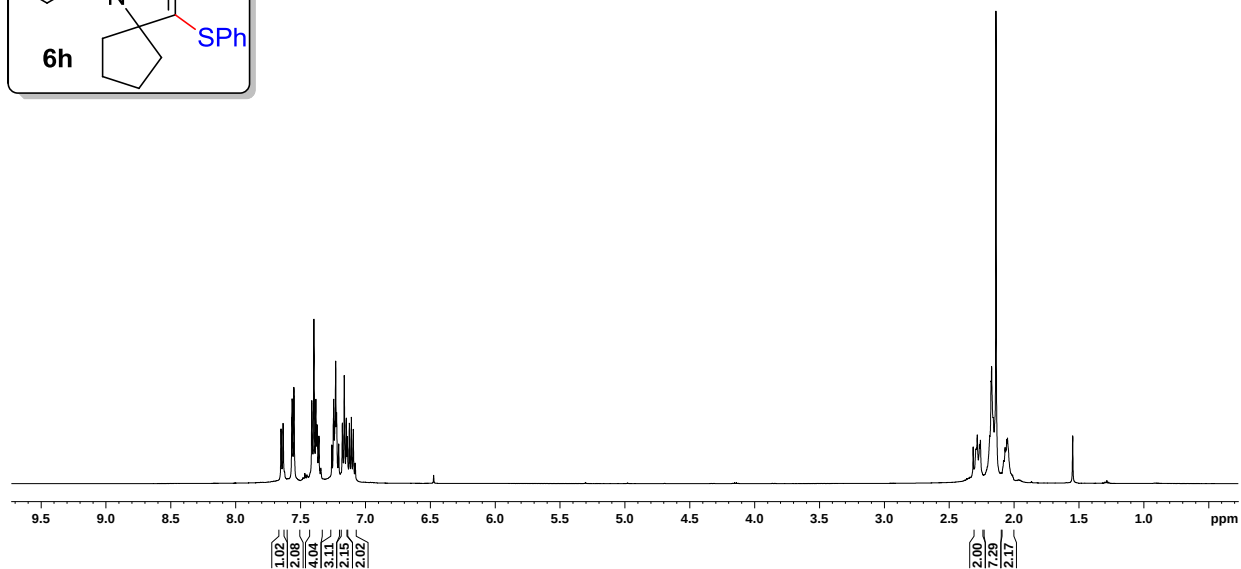
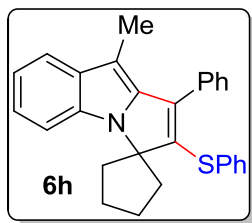
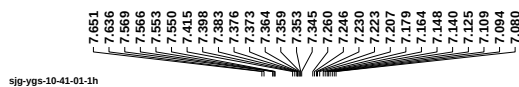


SJG-YGS-07-74-01-13C

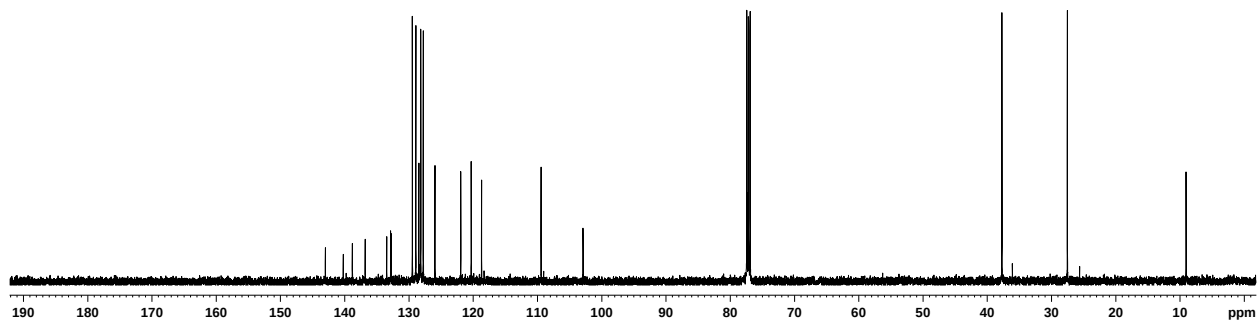
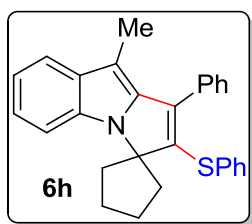






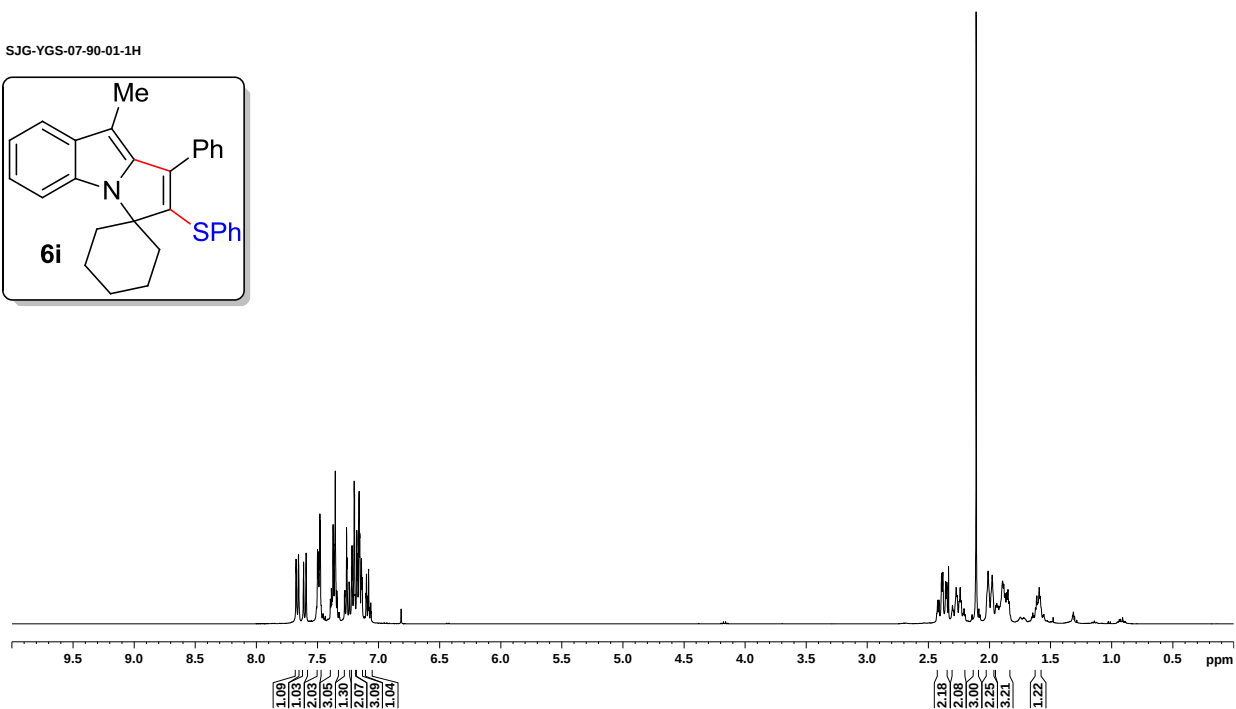
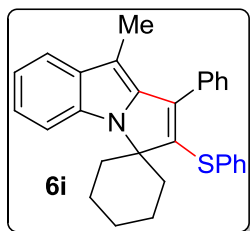


sig-ygs-10-41-01-13C

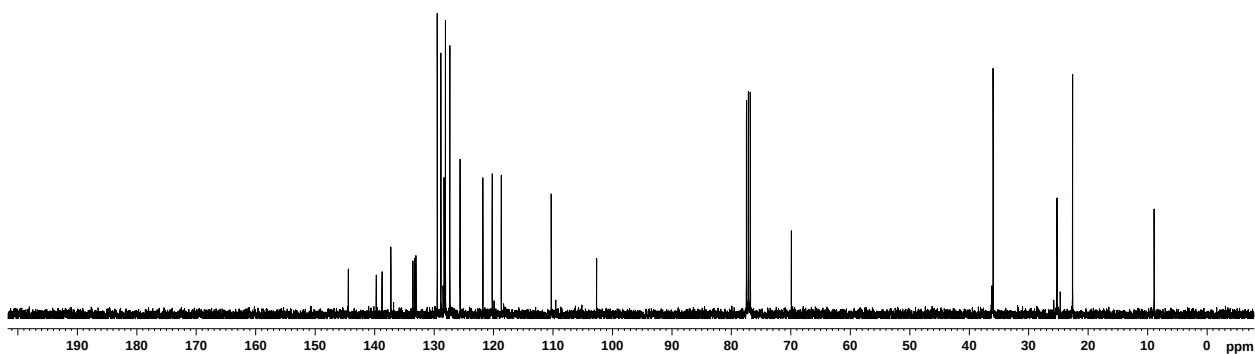
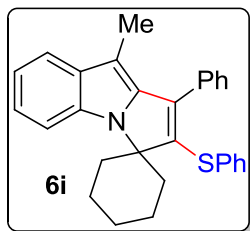




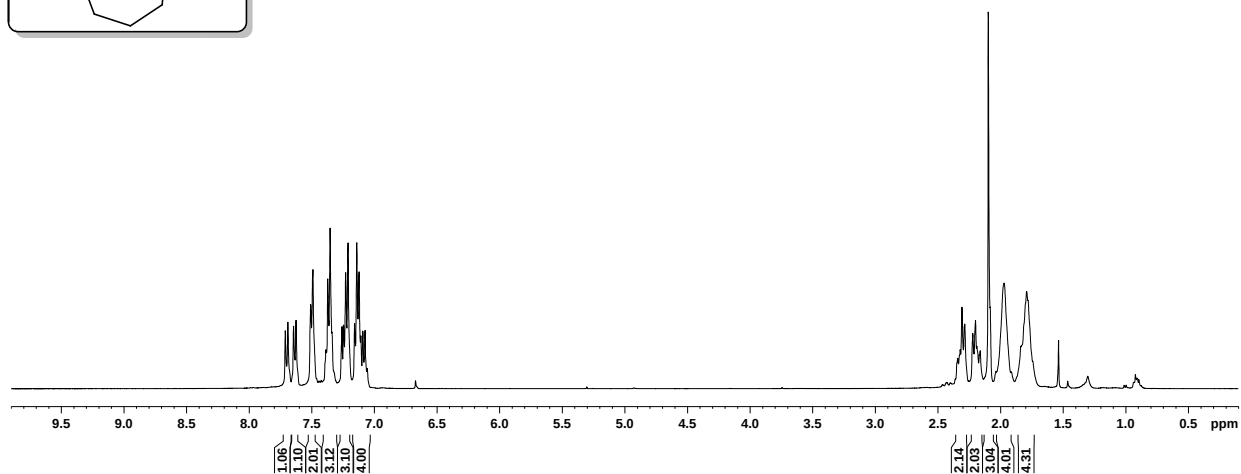
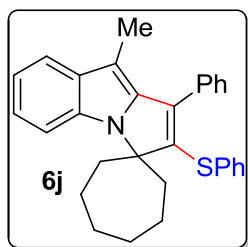
SJG-YGS-07-90-01-1H



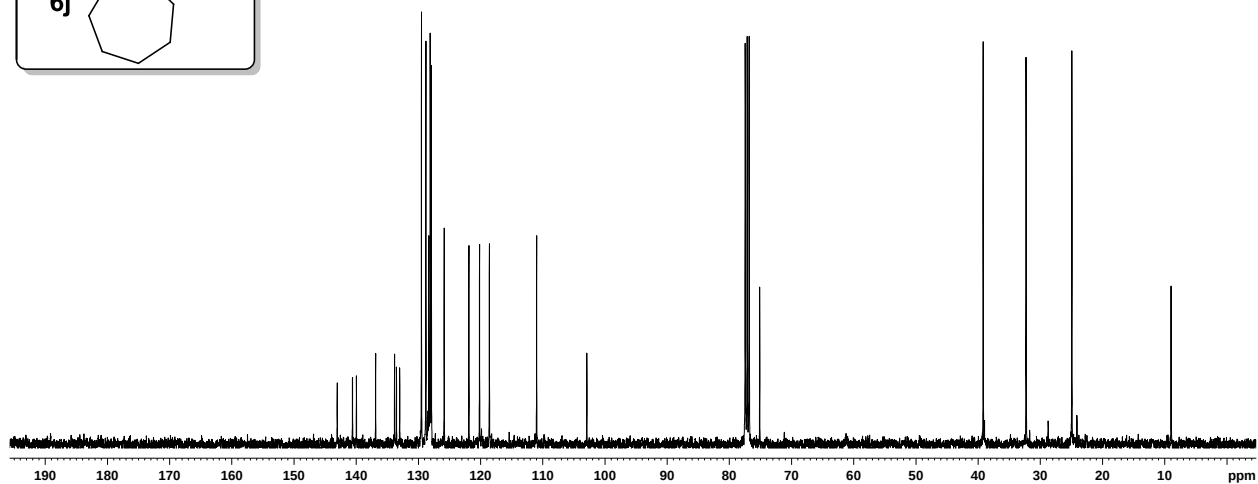
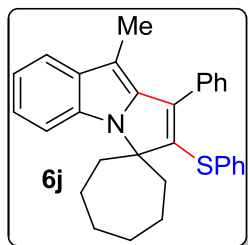
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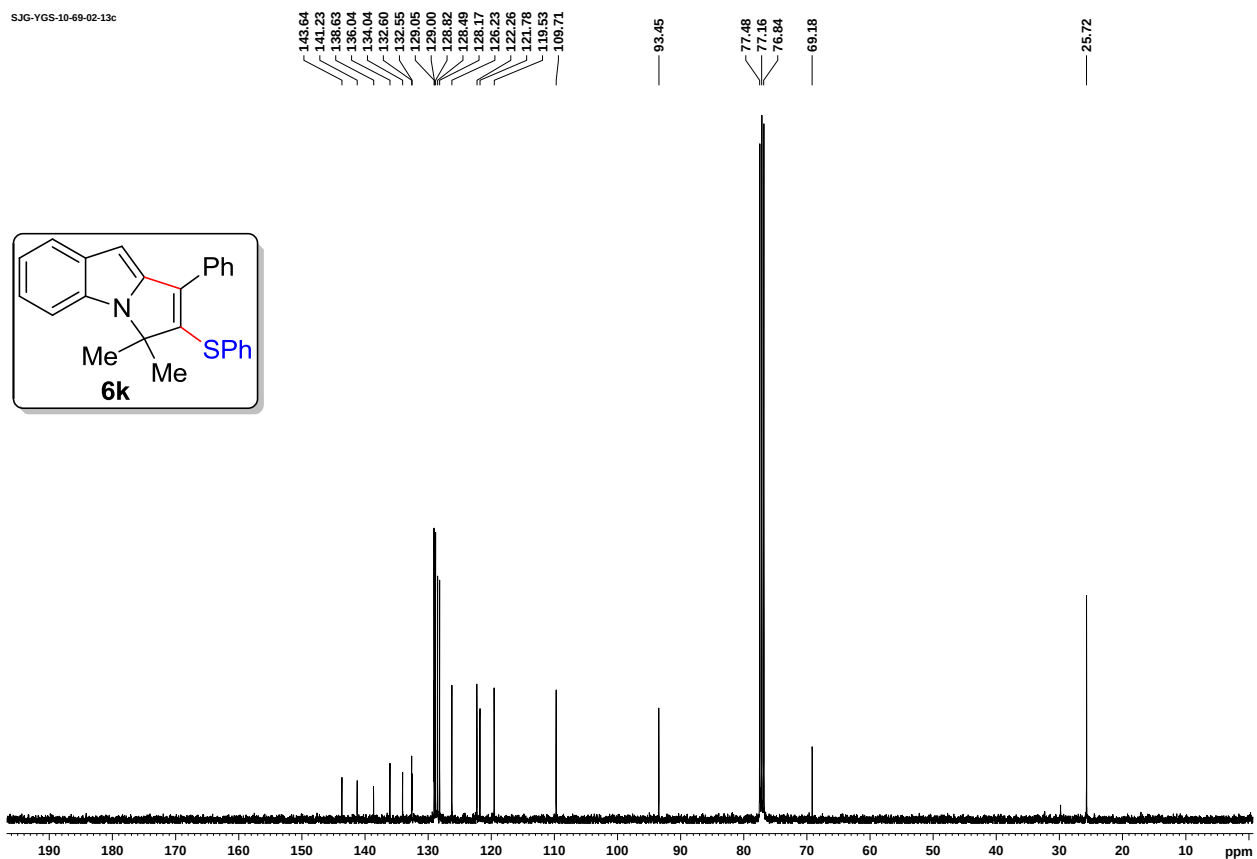
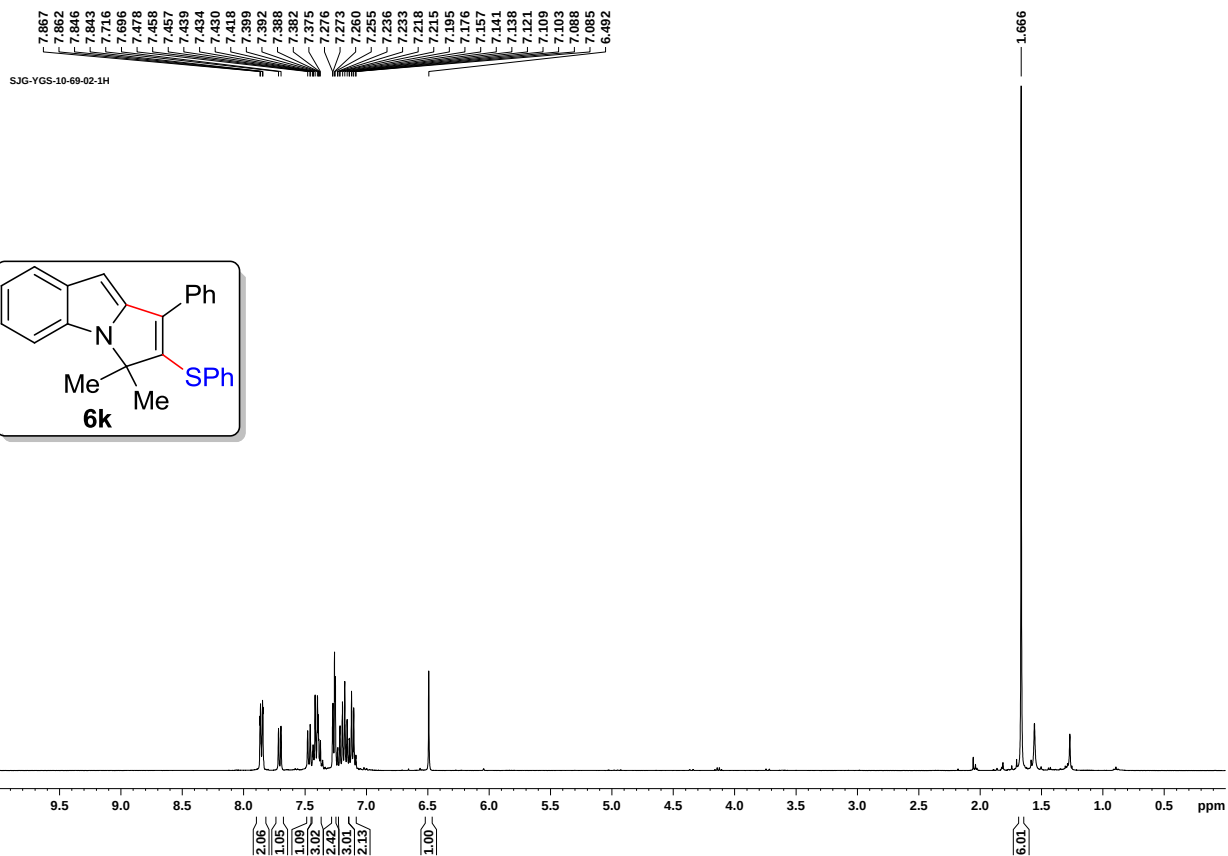


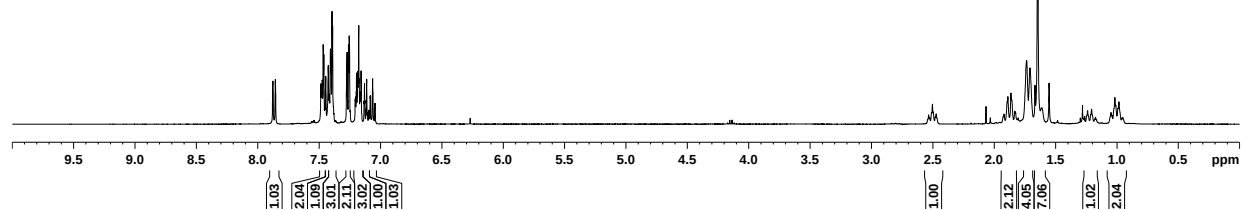
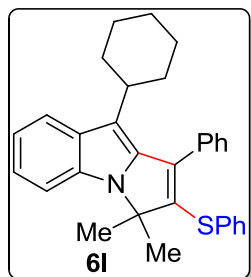
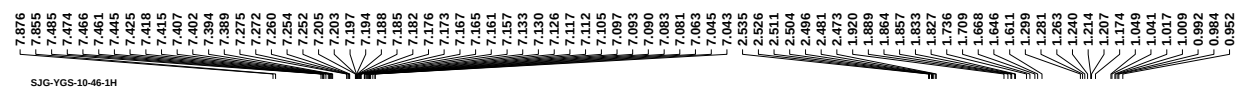
sjg-ygs-10-42-01-1h



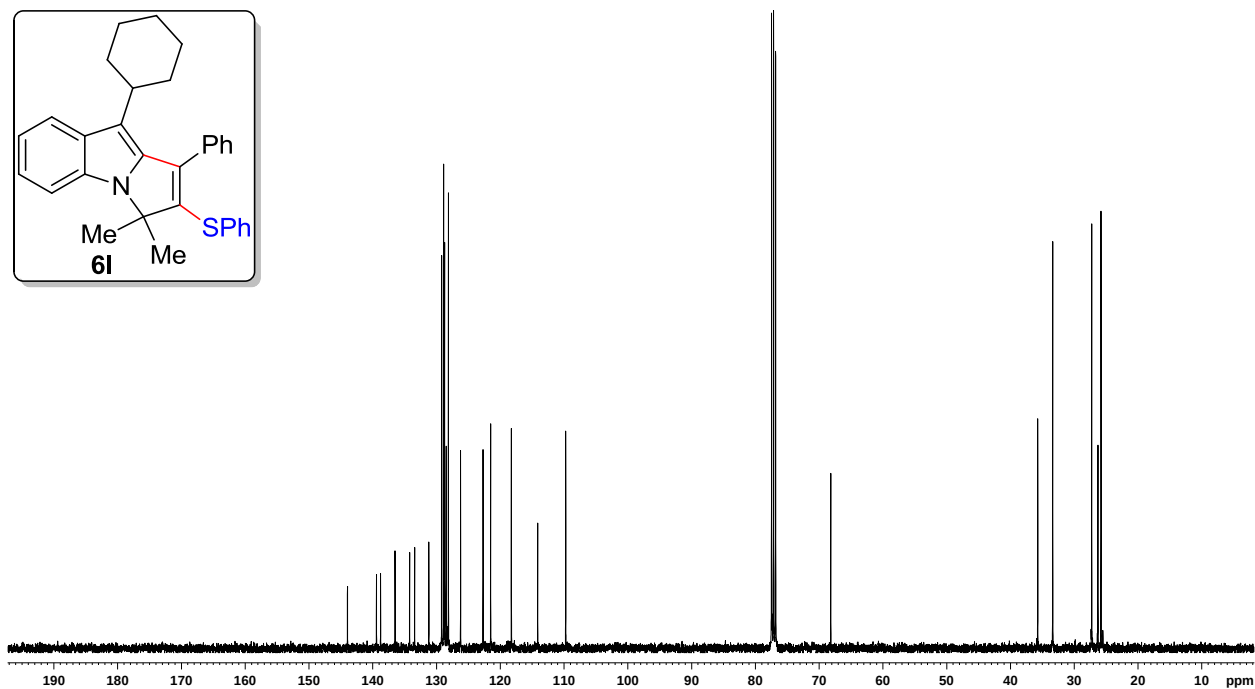
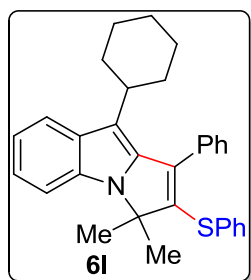
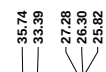
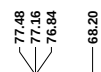
sjg-ygs-10-42-01-13c

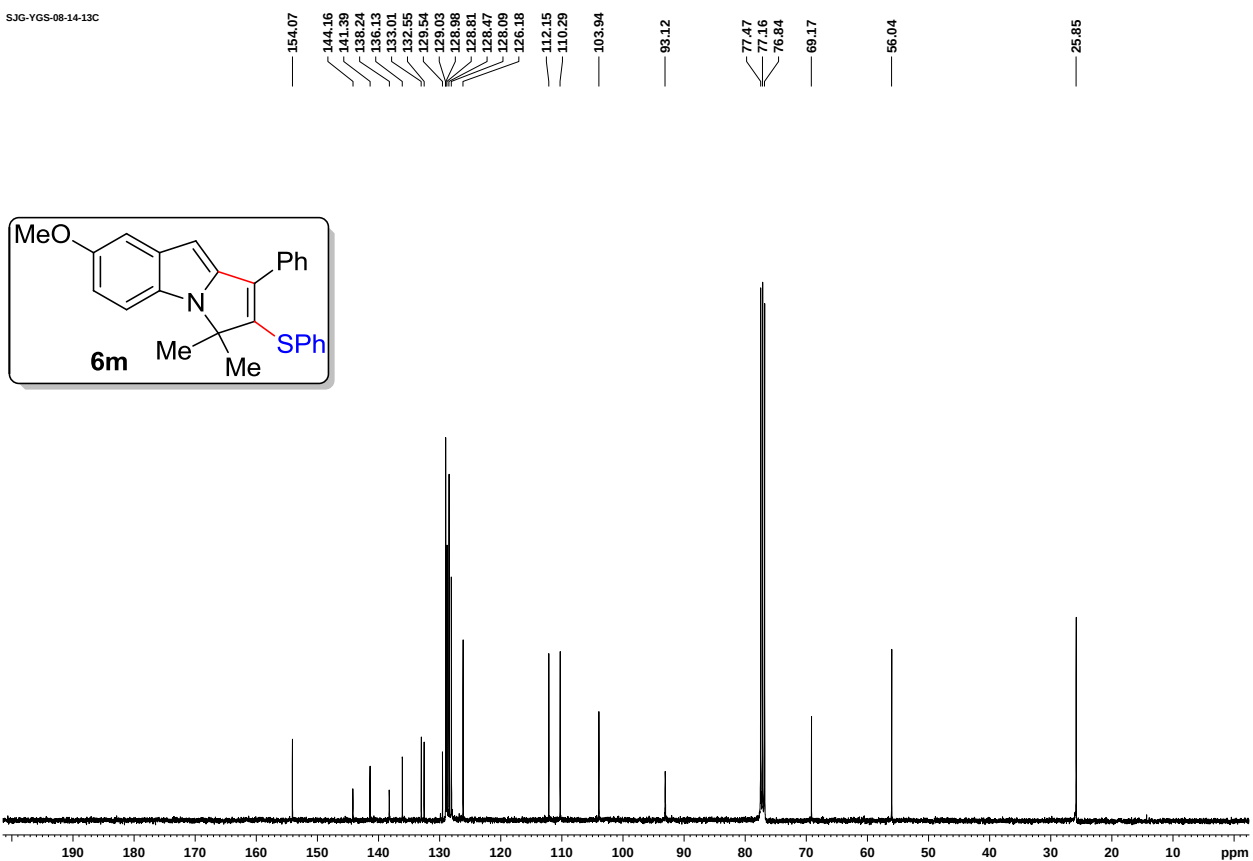
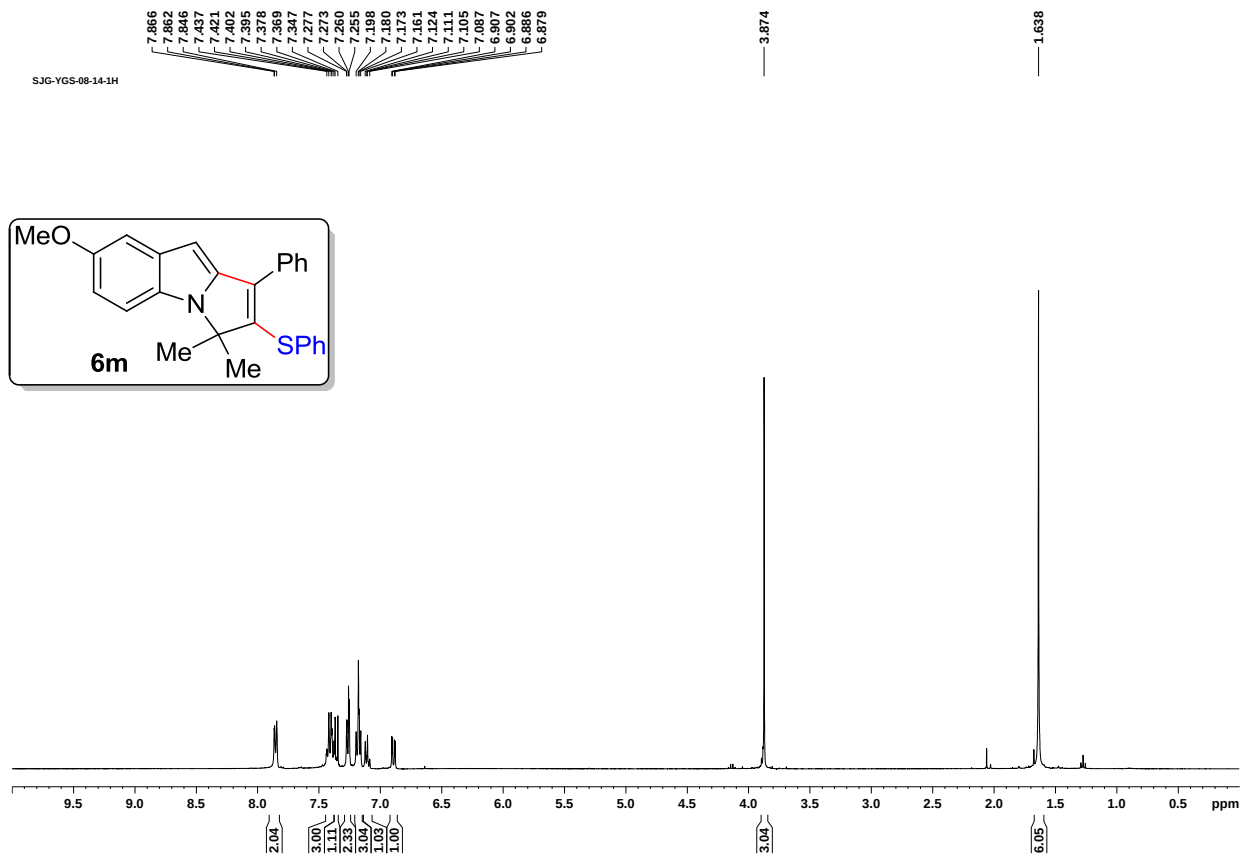


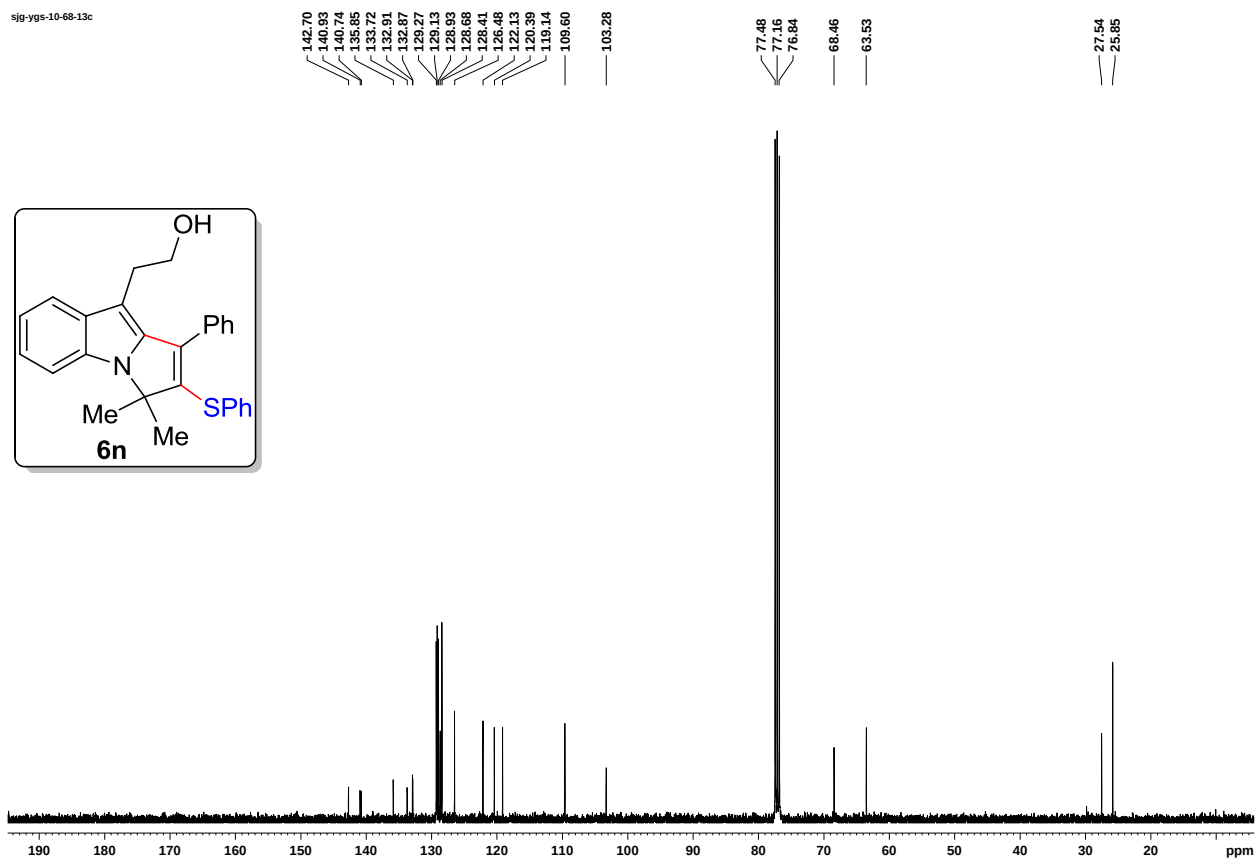
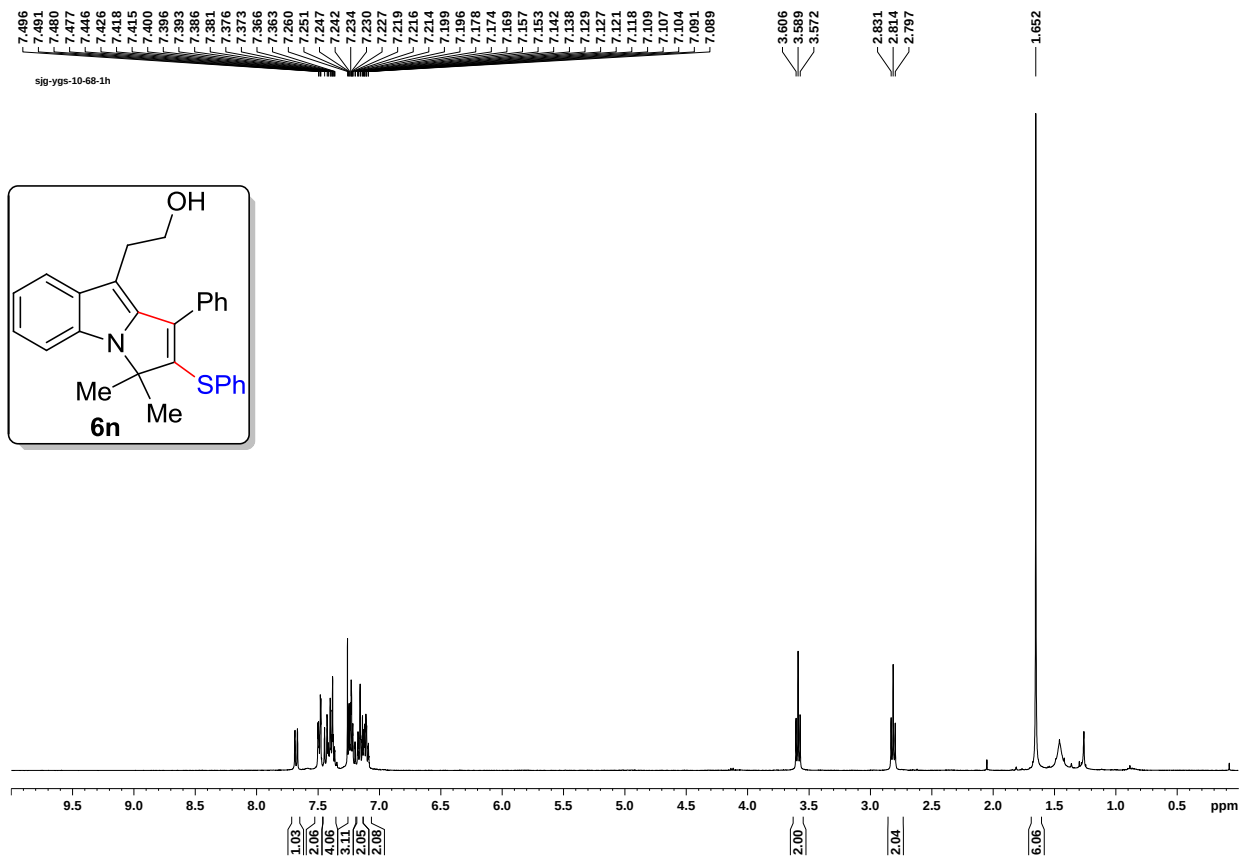


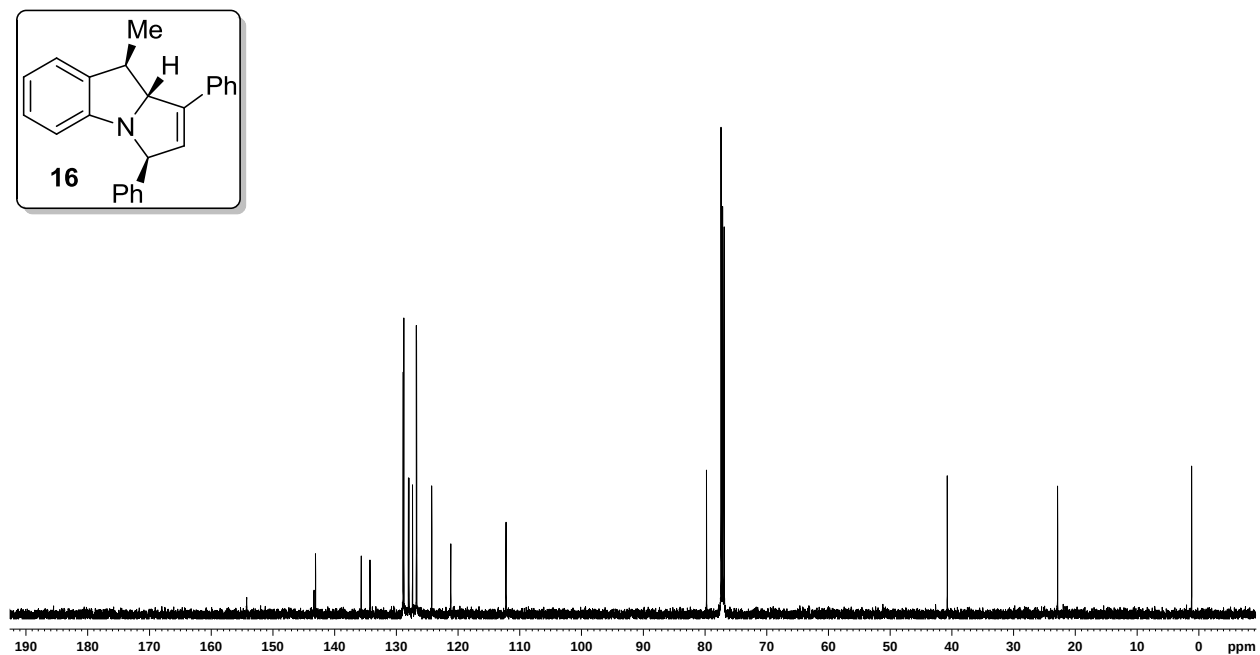
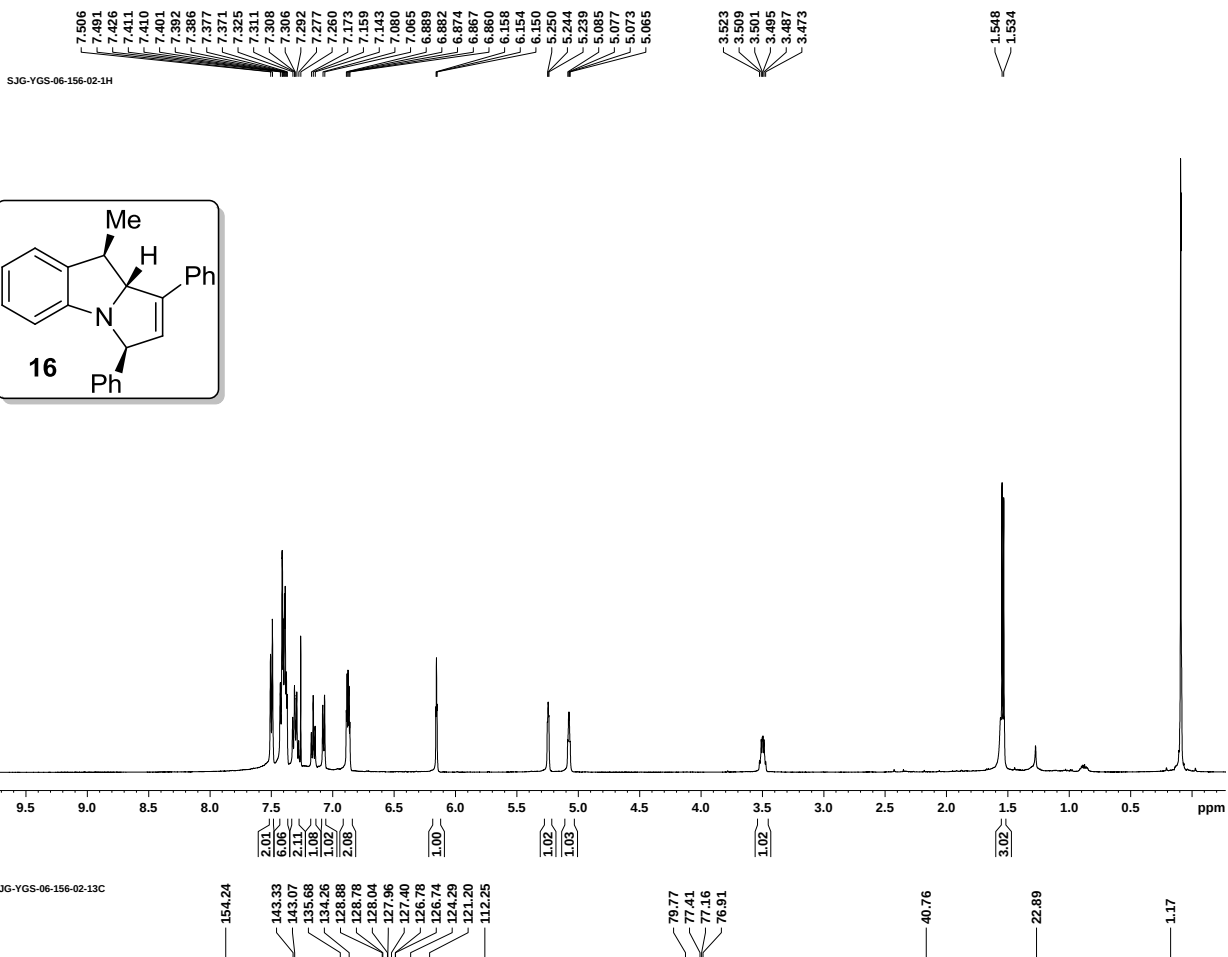


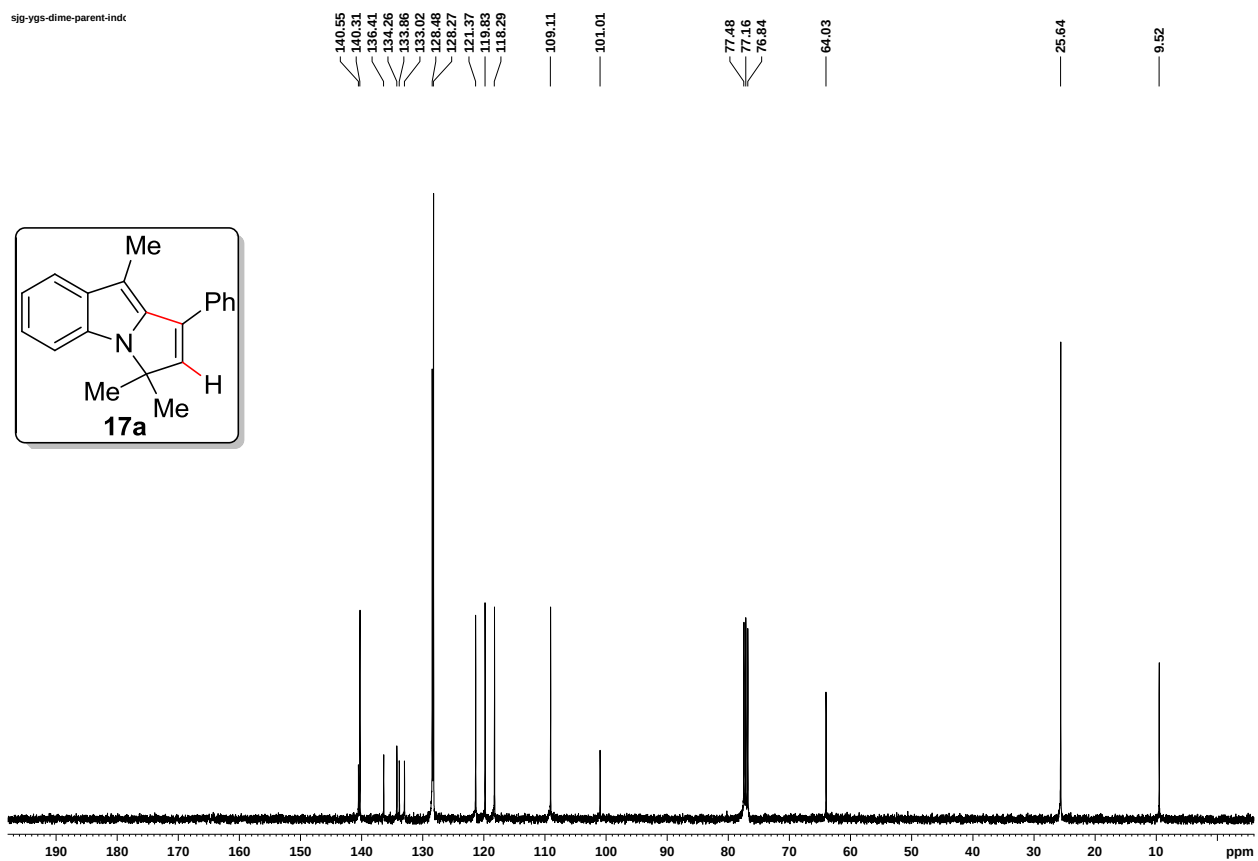
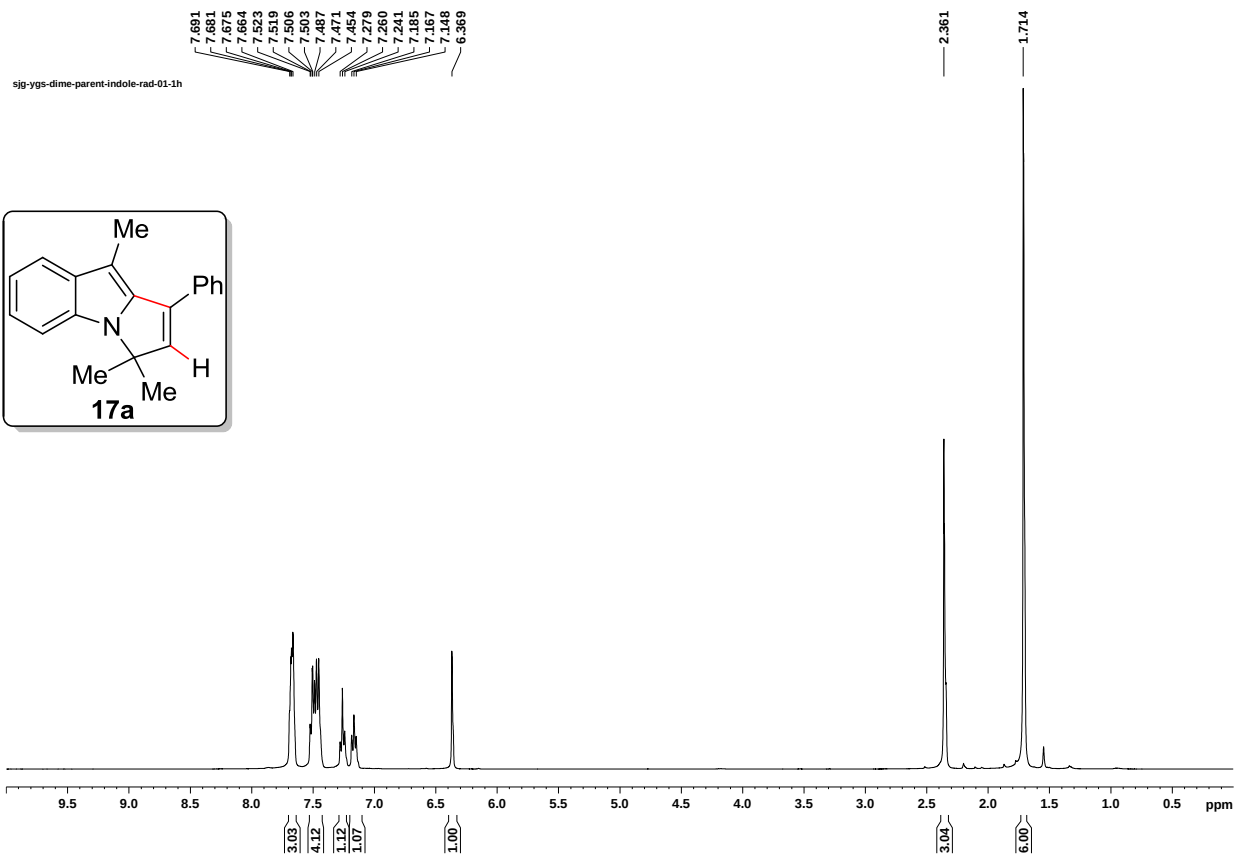
SJG-YGS-10-46-13C

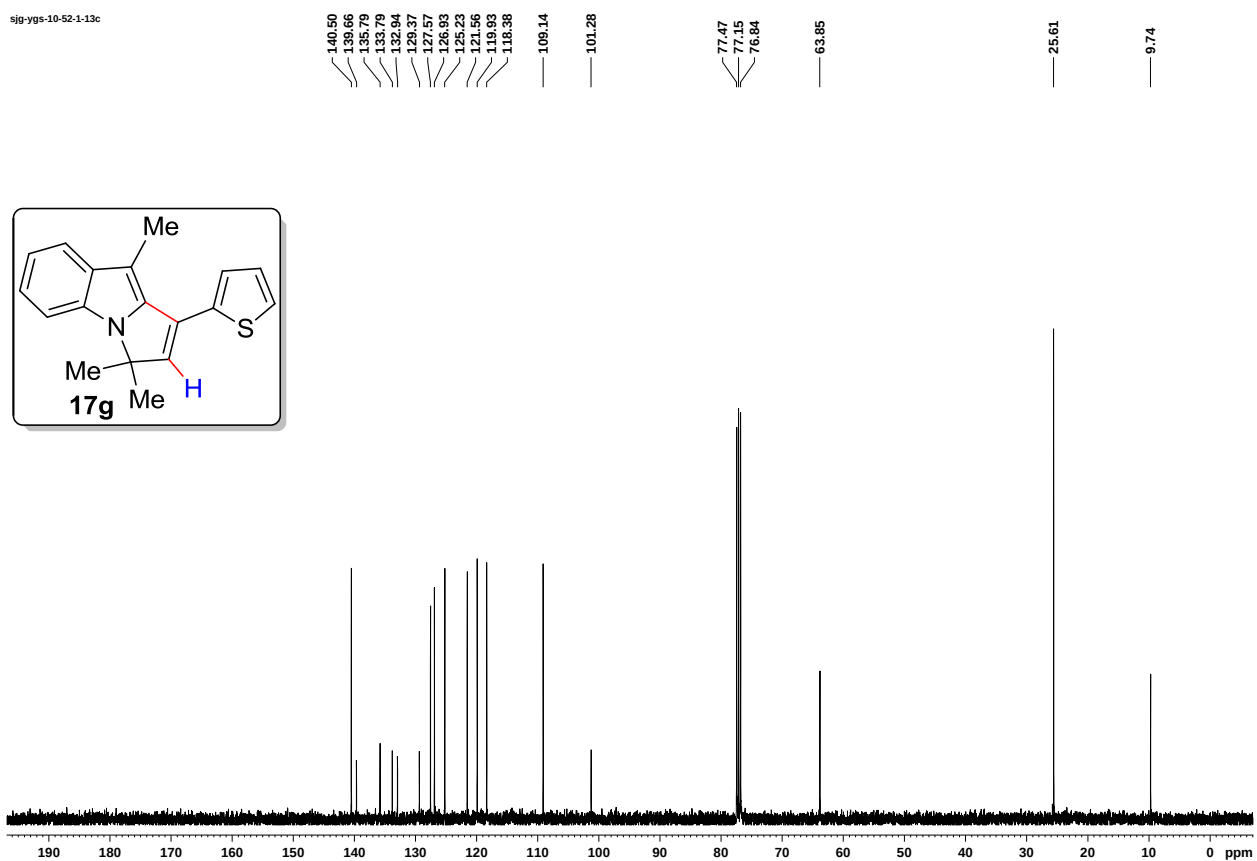
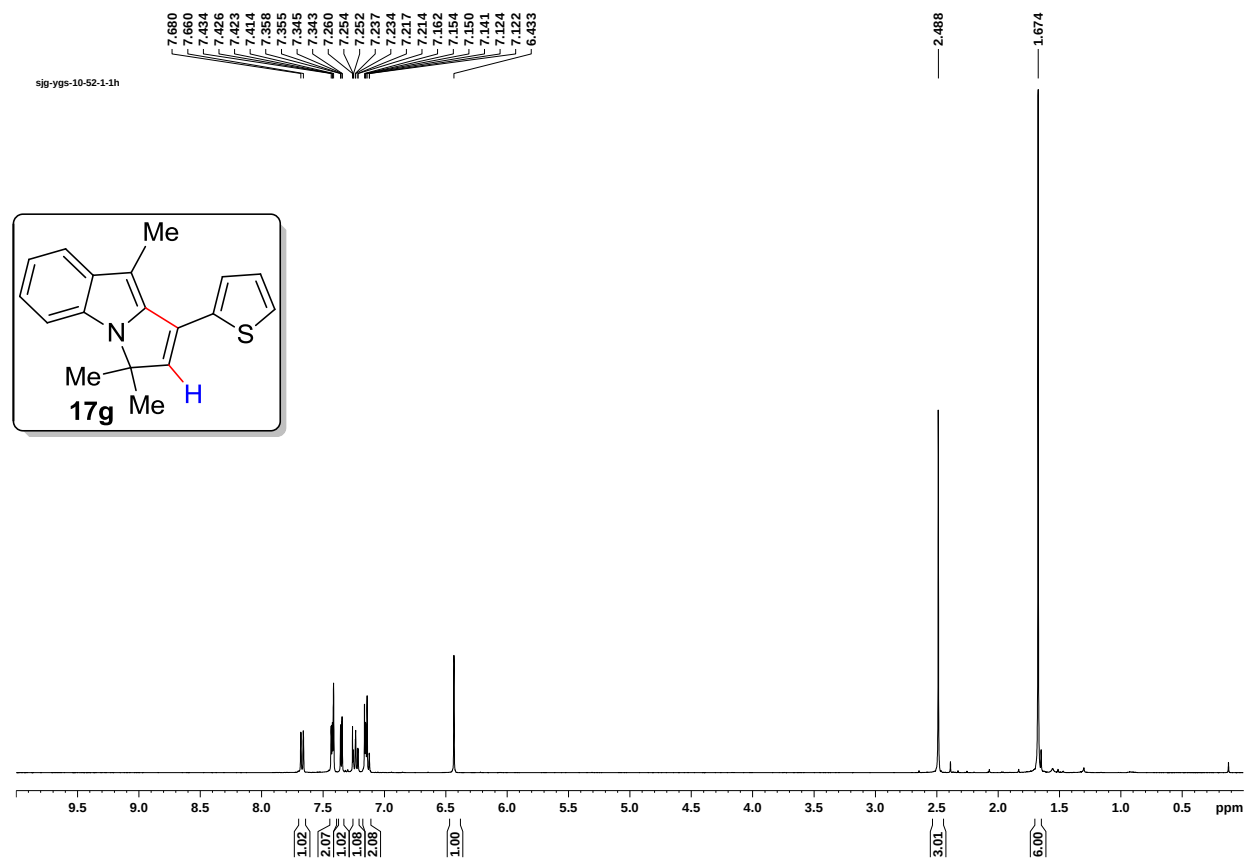


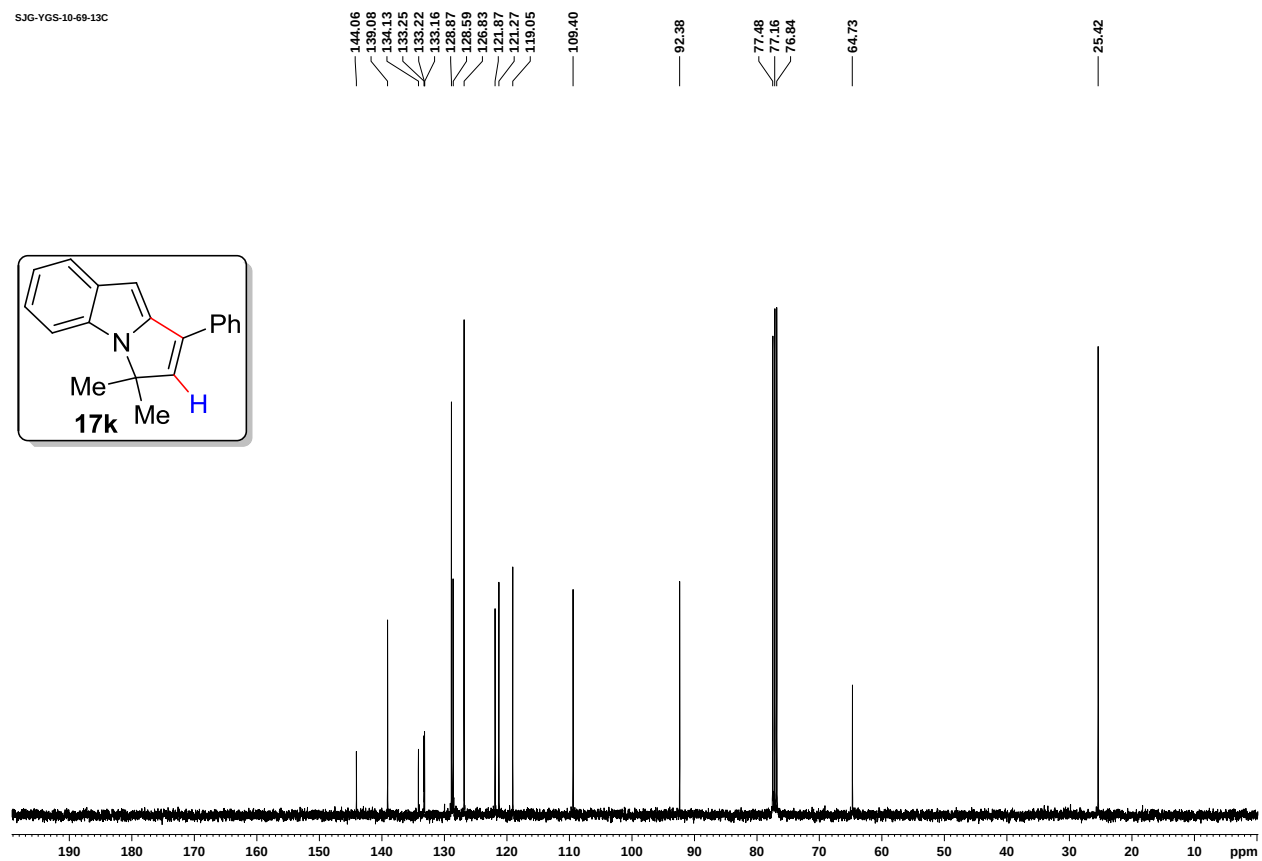
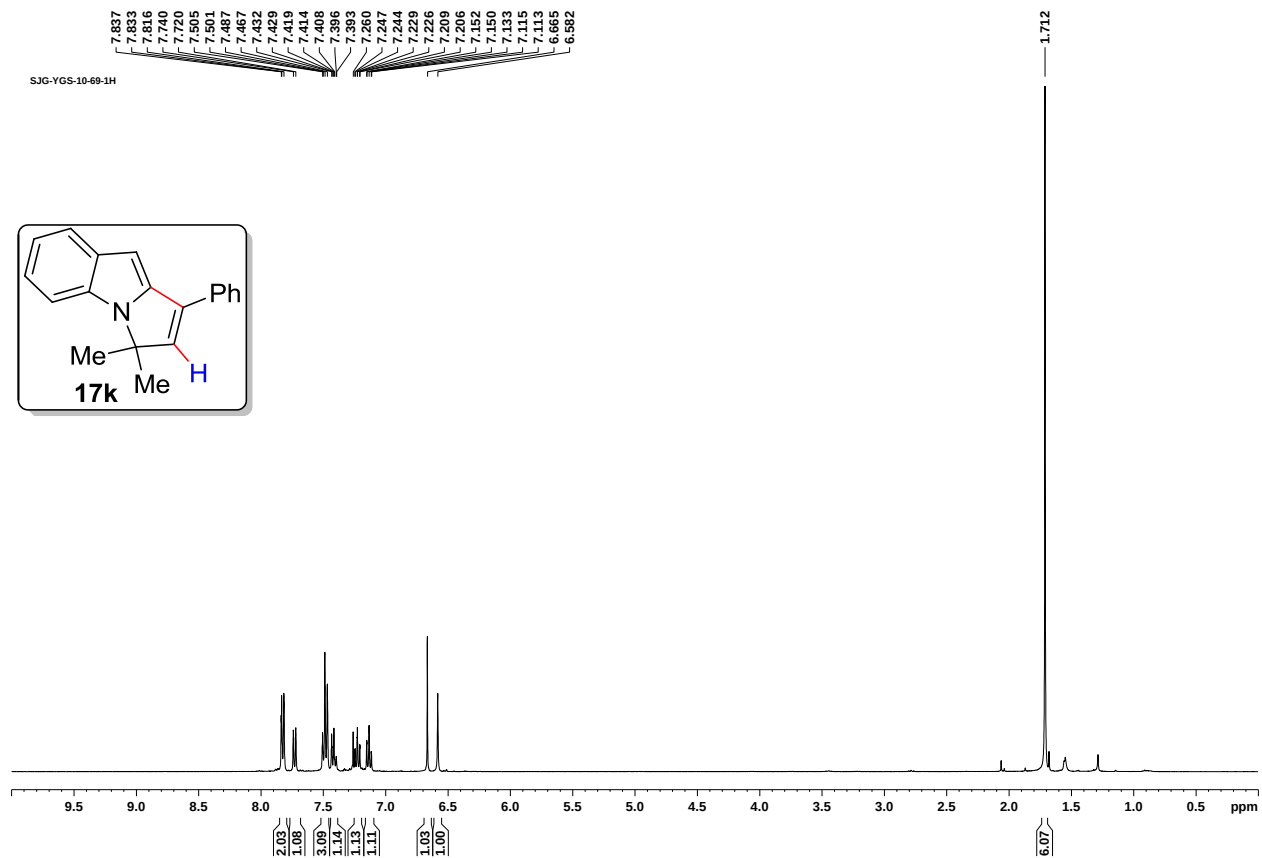


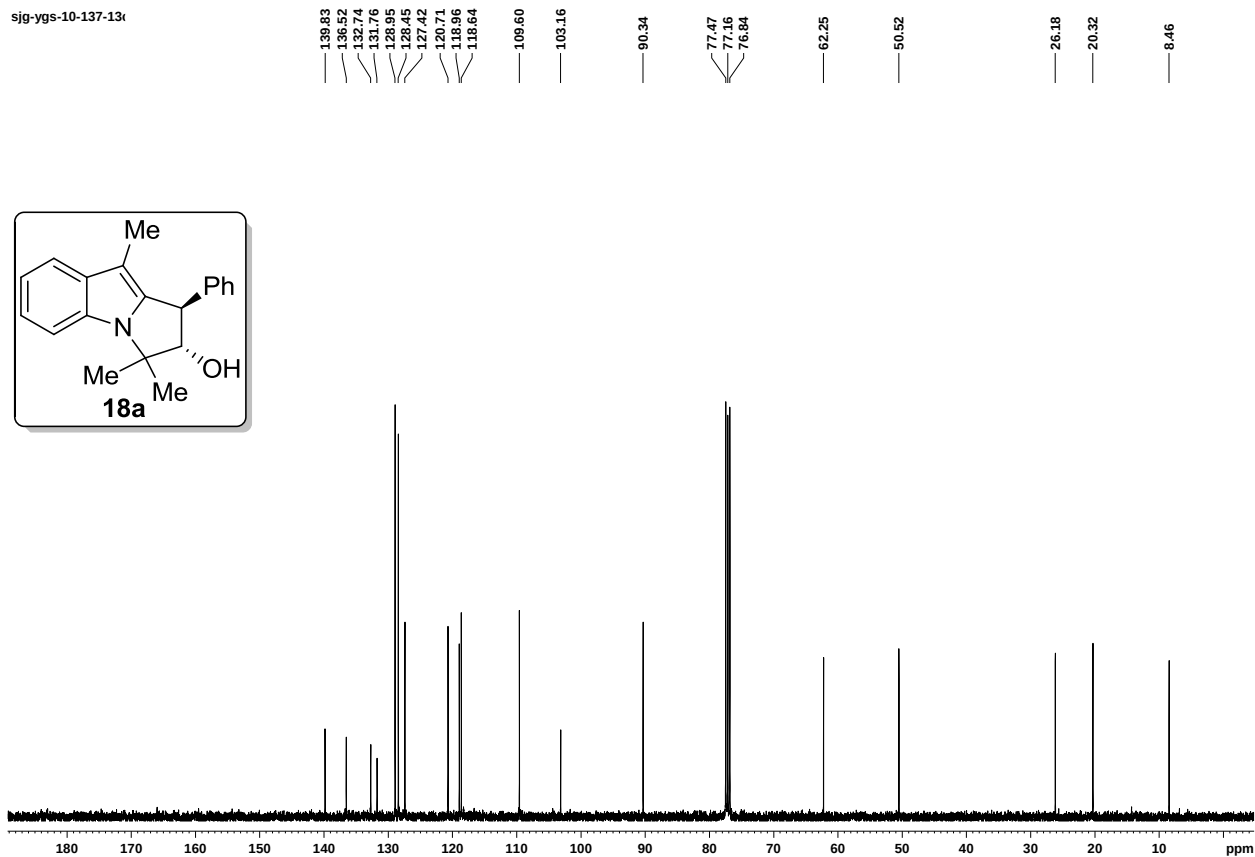
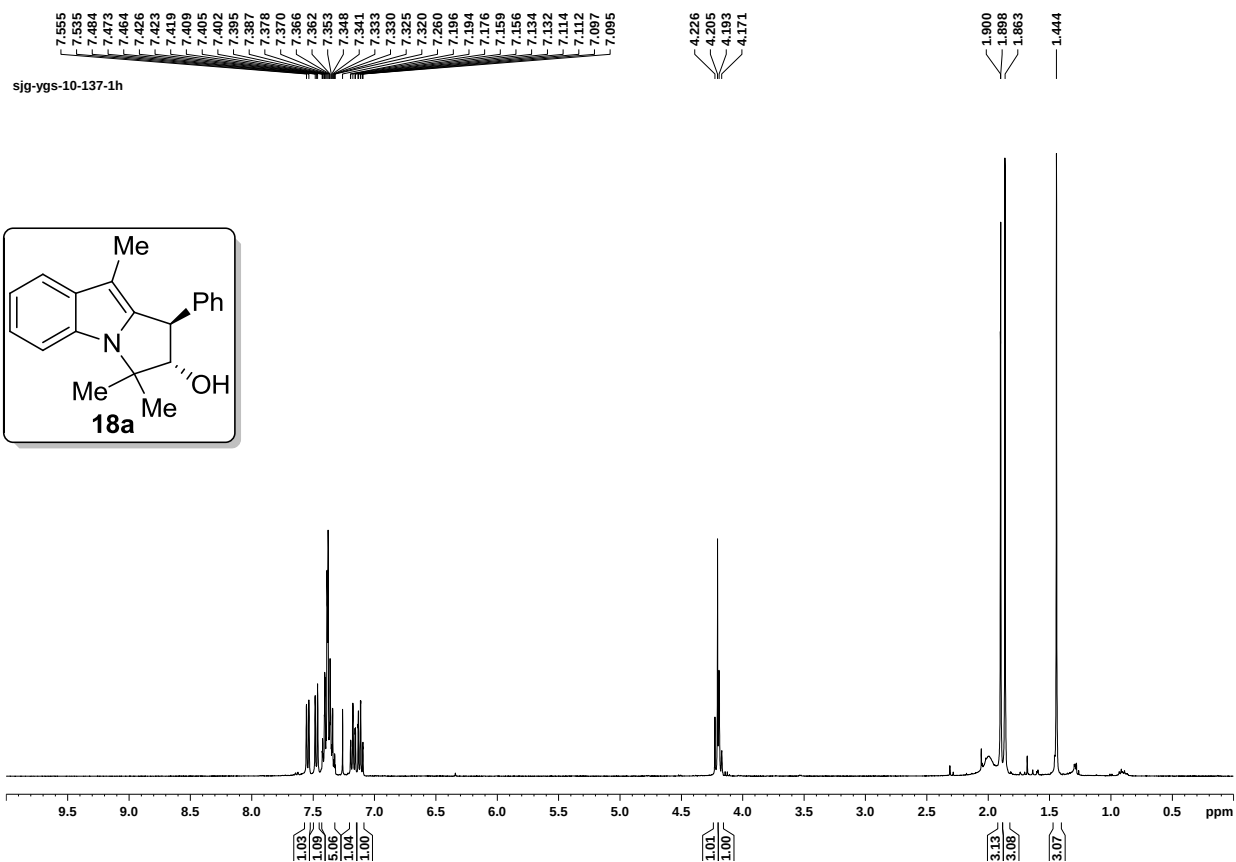


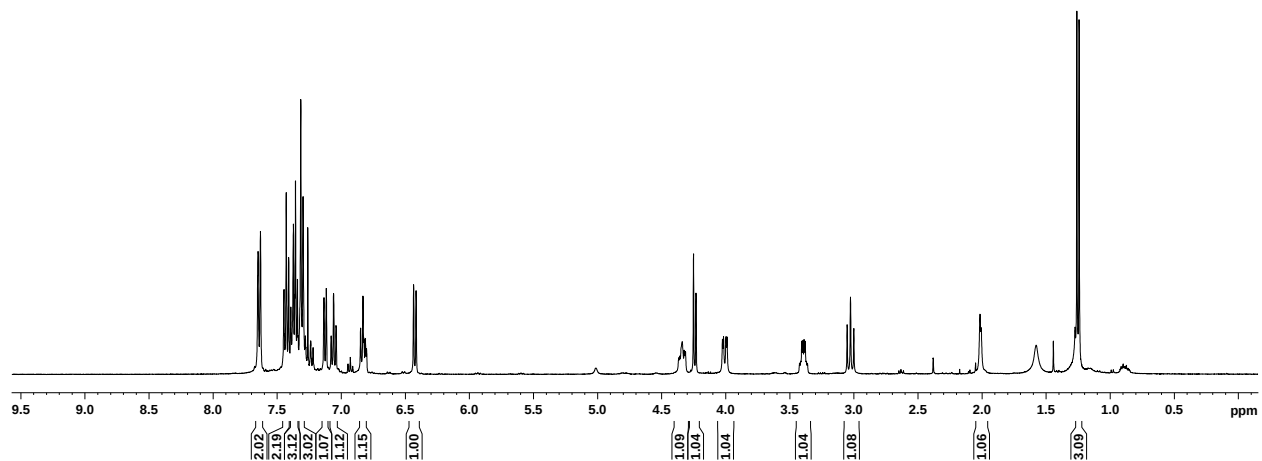
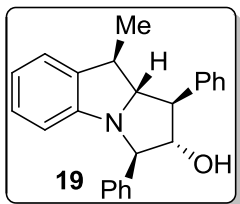
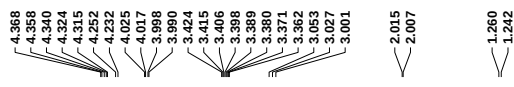
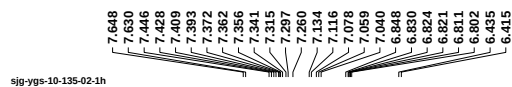




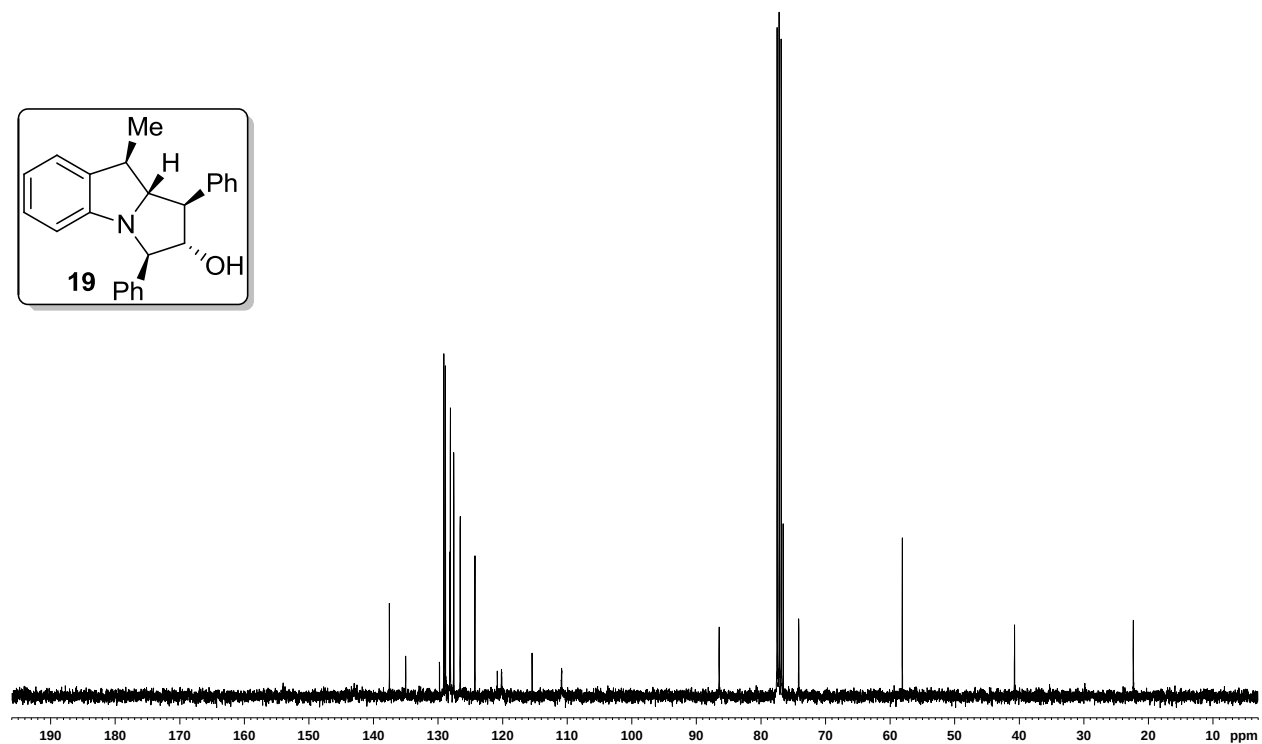
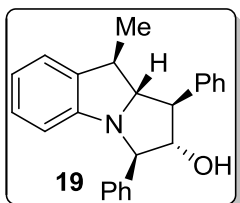




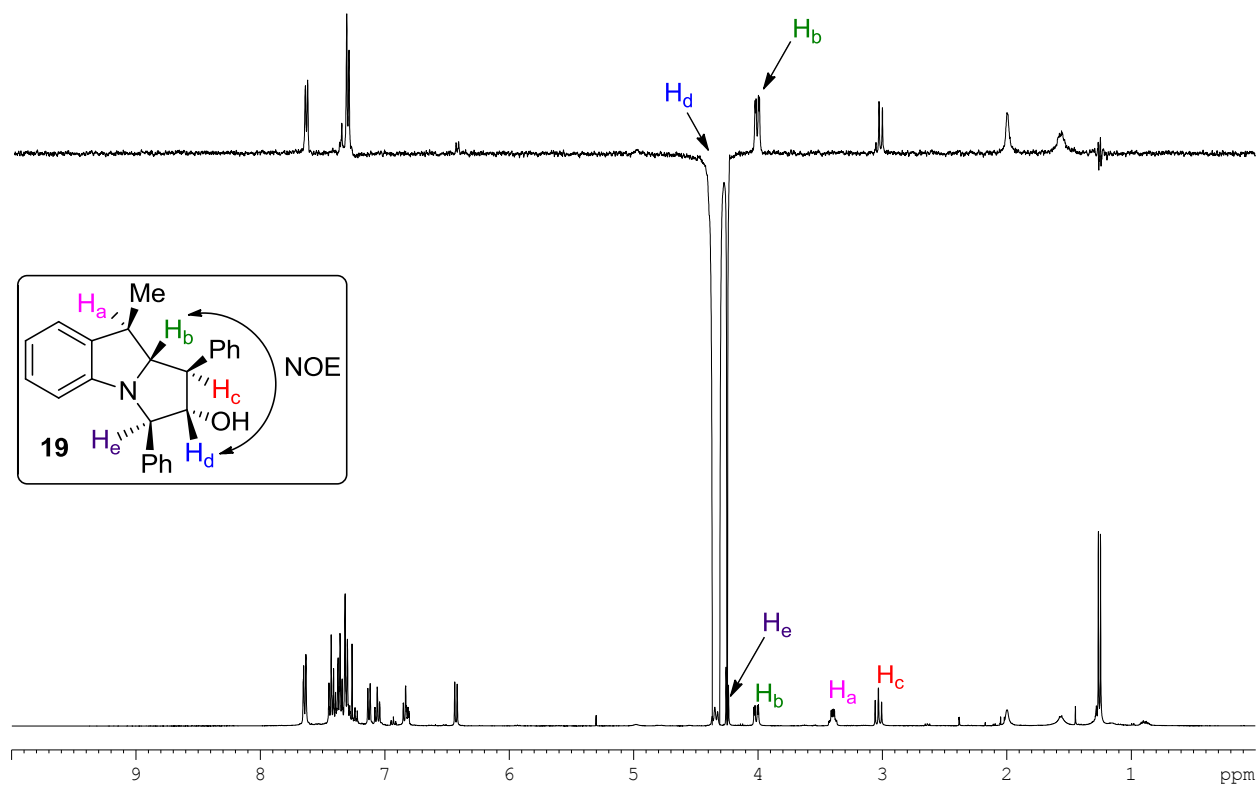




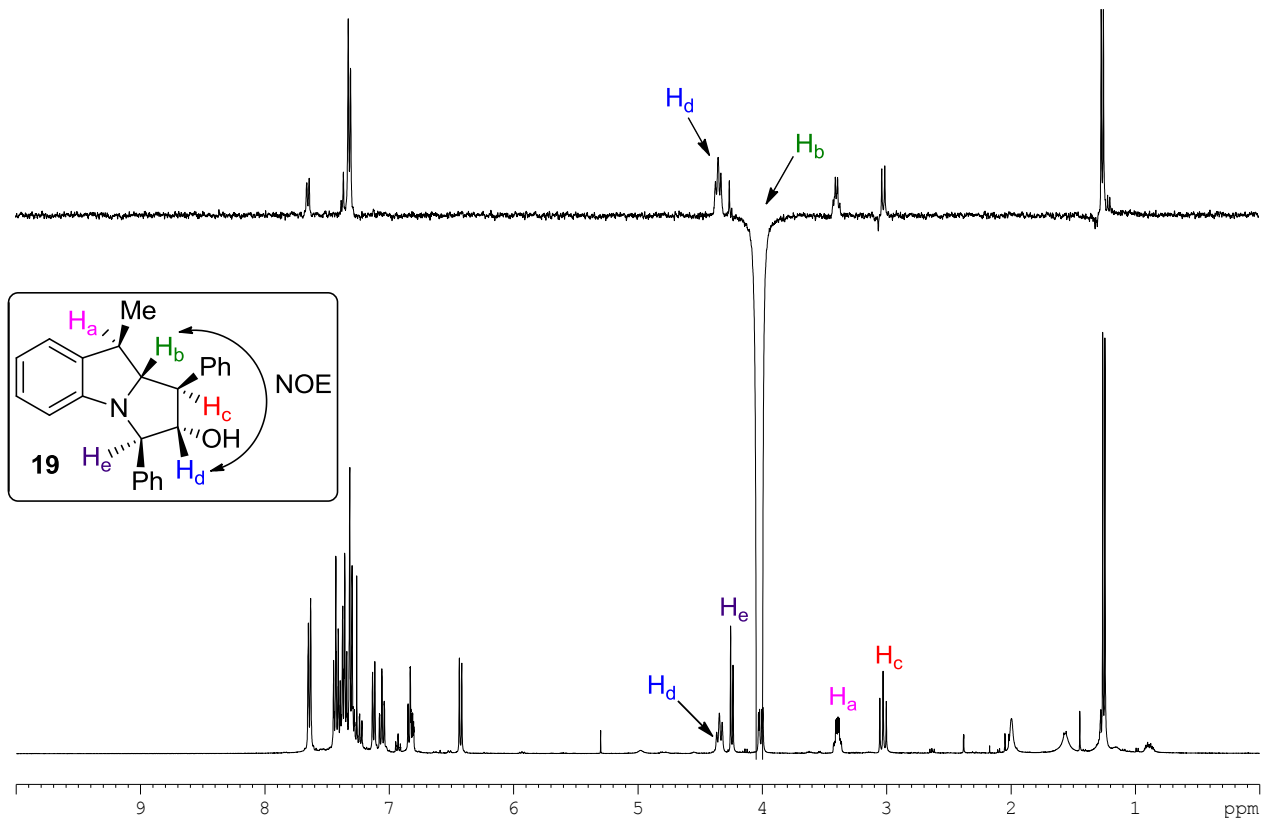
sig-yys-10-135-02-13c



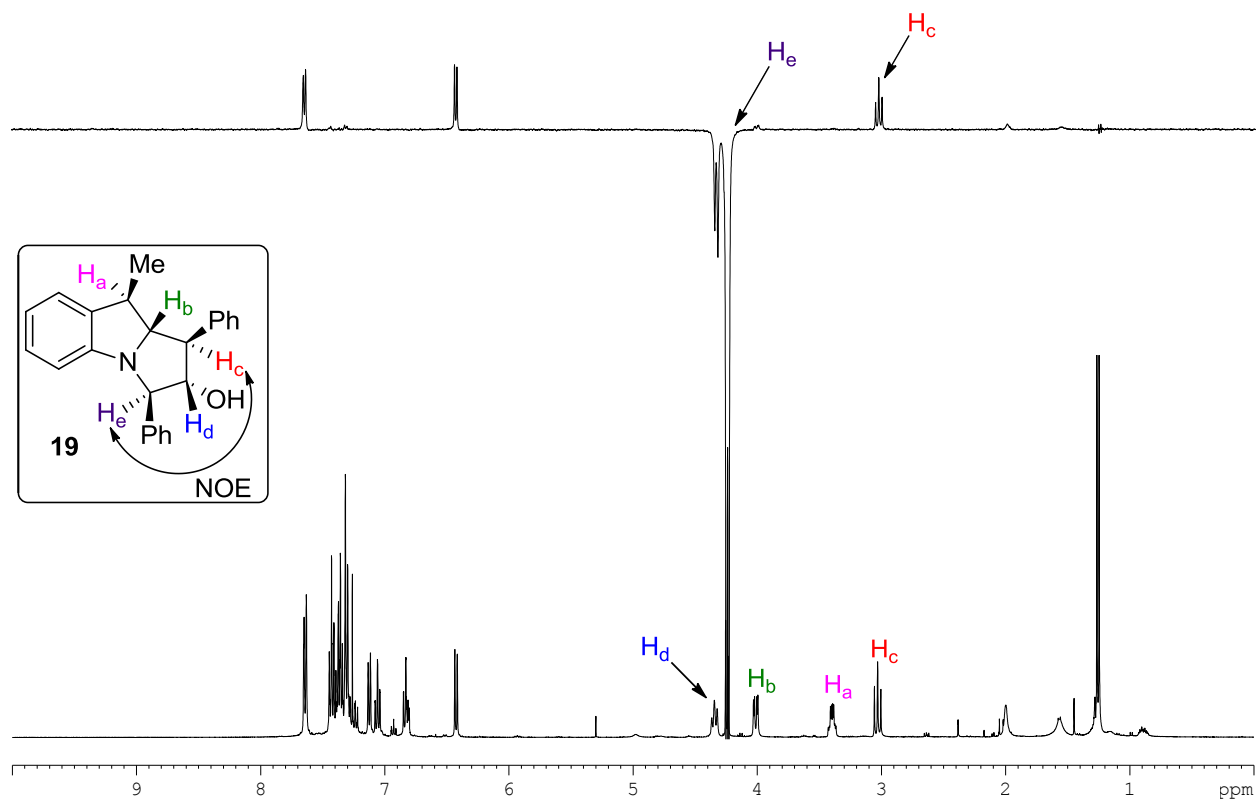
sjg-ygs-10-135-02-noe-a



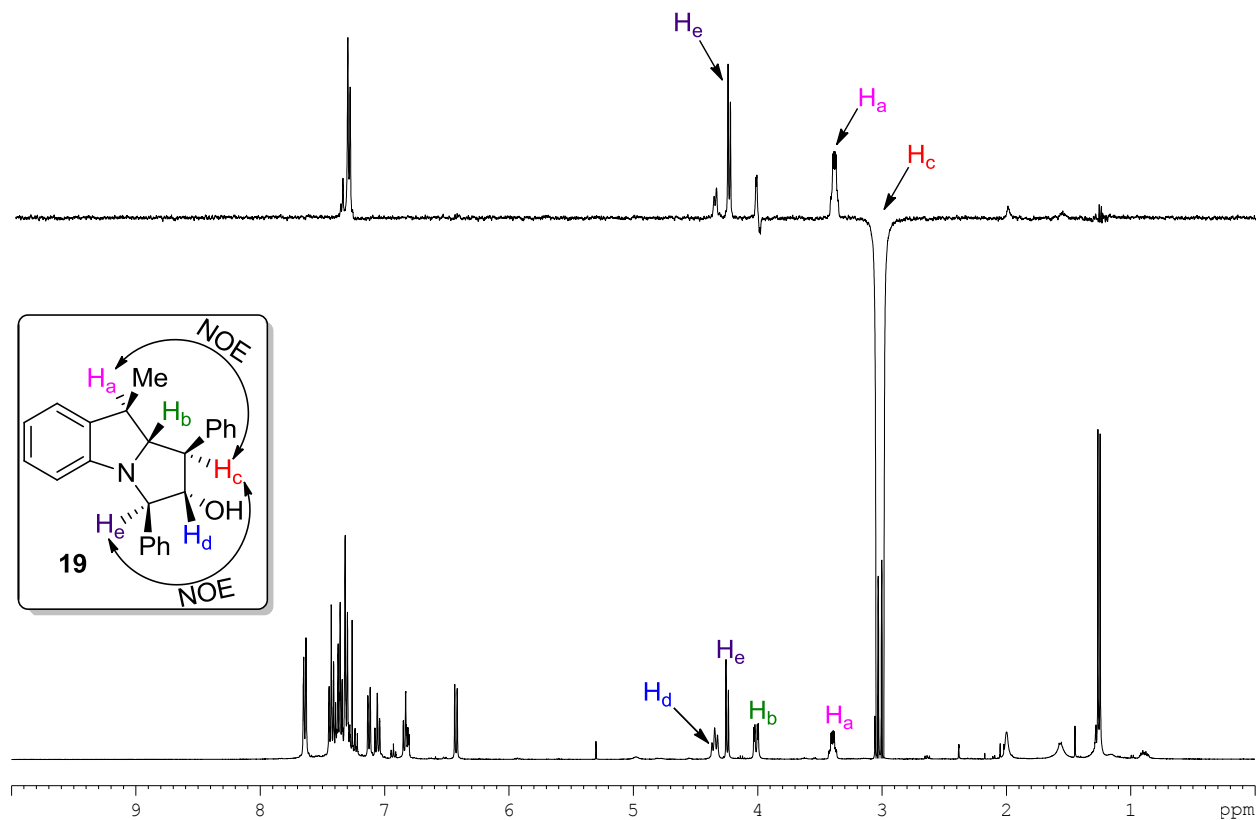
sjg-ygs-10-135-02-noe-c

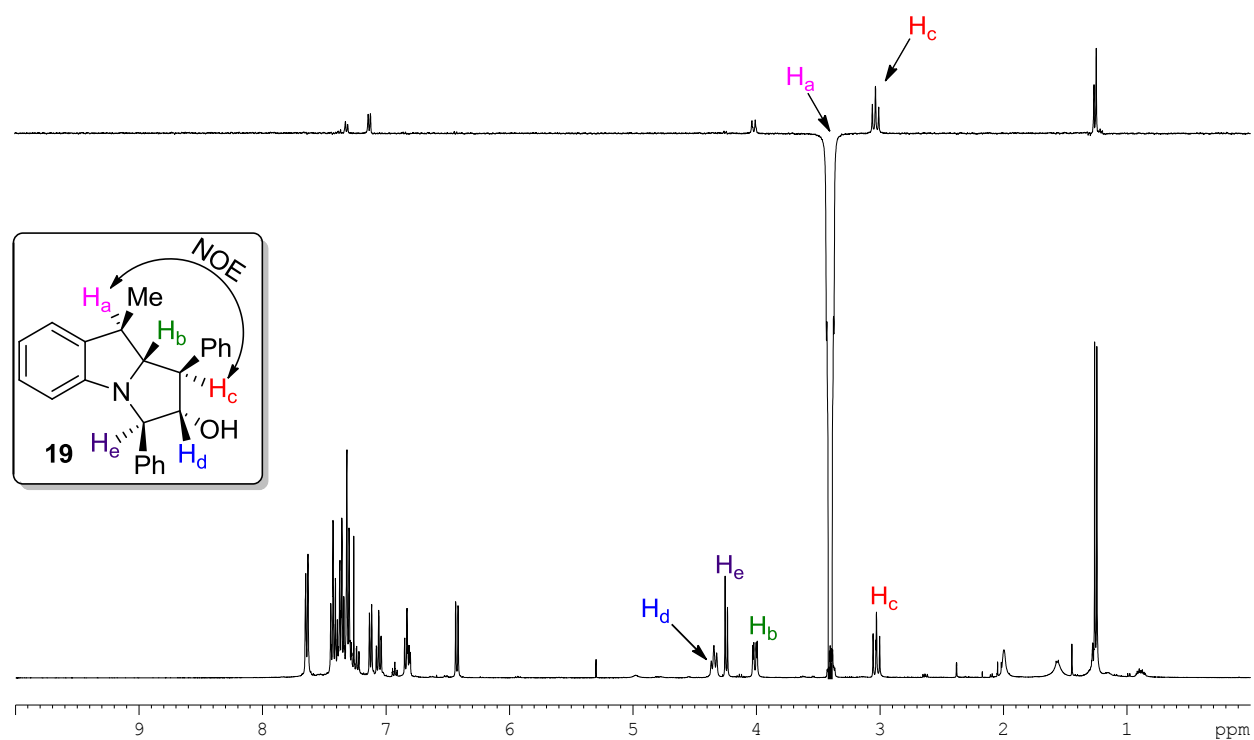


sjg-ygs-10-135-02-noe-b



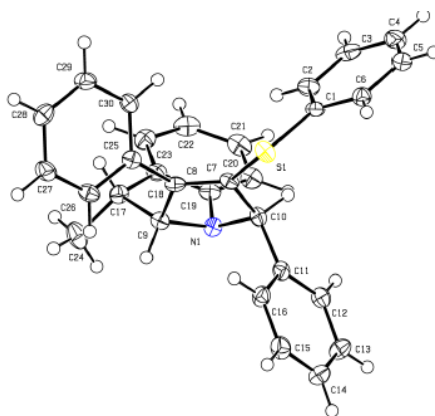
sjg-ygs-10-135-02-noe-e





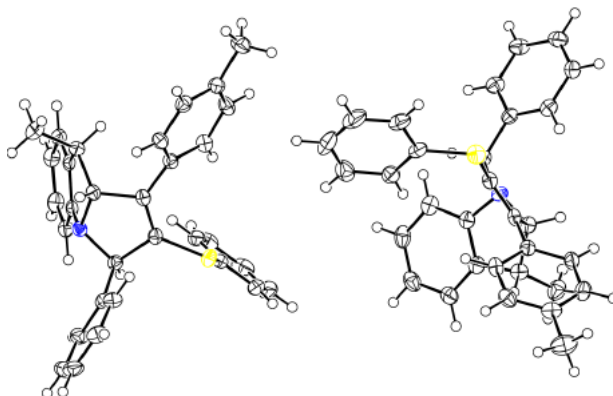
X-Ray crystallographic analysis:

Crystal data and structure refinement for 7b



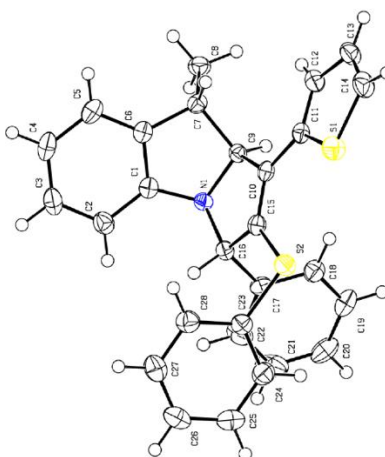
Identification code	7b		
Solvent	CH ₂ Cl ₂		
CCDC	1555451		
Bond precision:	C-C = 0.0056 Å	Wavelength= 0.71070	
Cell:	a= 9.264(6)	b= 11.632(7)	c= 10.797(7)
	alpha= 90	beta= 91.753(1)	gamma= 90
Temperature:	100 K		
	Calculated	Reported	
Volume	1162.9(13)	1162.9(13)	
Space group	P 21	P 1 21 1	
Hall group	P 2yb	P 2yb	
Moiety formula	C30 H25 N S	C30 H25 N S	
Sum formula	C30 H25 N S	C30 H25 N S	
Mr	431.57	431.57	
Dx, g cm-3	1.232	1.232	
Z	2	2	
Mu (mm-1)	0.157	0.157	
F000	456.0	456.0	
F000'	456.40		
h,k,l max	11,13,12	11,13,12	
Nref	4077[2149]	3943	
Tmin,Tmax	0.961,0.997	0.963,984	
Tmin'	0.950		
Correction method=	NUMERICAL		
Data completeness =	0.97	Theta(max)= 24.991	
R(reflections) =	0.0508(3442)	wR2(reflections)=	
		0.0833(3943)	
S = 1.056			
	Npar =289		

Crystal data and structure refinement for 7c



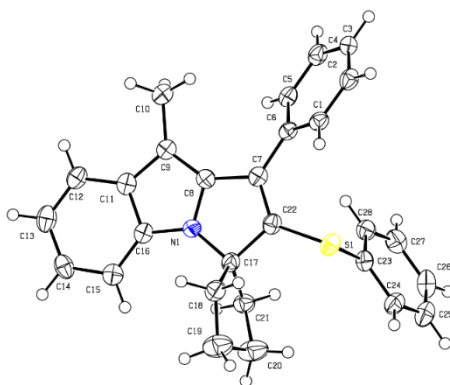
Identification code	7c		
Solvent	CH ₂ Cl ₂		
CCDC	1555453		
Bond precision:	C-C = 0.0046 Å	Wavelength= 0.71073	
Cell:	a= 11.1368 (3)	b= 11.7379 (3)	c= 18.6478 (5)
	alpha= 90	beta= 92.278 (3)	gamma= 90
Temperature:	100 K		
	Calculated	Reported	
Volume	2435.76 (11)	2435.76 (11)	
Space group	P 21	P 1 21 1	
Hall group	P 2yb	P 2yb	
Moiety formula	C31 H27 N S	C31 H27 N S	
Sum formula	C31 H27 N S	C31 H27 N S	
Mr	445.60	178.24	
Dx, g cm-3	1.215	1.215	
Z	4	10	
Mu (mm-1)	0.152	0.152	
F000	944.0	944.0	
F000'	944.81		
h,k,l max	13,13,22	13,13,22	
Nref	8569[4517]	8375	
Tmin,Tmax	0.970,0.979	0.728, 1.000	
Tmin'	0.964		
Correction method=	MULTI-SCAN		
Data completeness =	0.98	Theta(max)= 24.995	
R(reflections) =	0.0378 (7752)	wR2(reflections)= 0.0884 (8375)	
S = 1.023			
	Npar = 599		

Crystal data and structure refinement for 7f



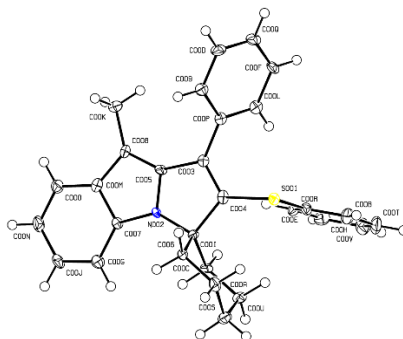
Identification code	7f		
Solvent	EtOAc		
CCDC	1555457		
Bond precision:	C-C = 0.0032 Å	Wavelength= 0.71073	
Cell:	a= 11.9061(5)	b= 20.9485(8)	c= 9.3642(5)
	alpha= 90	beta= 105.939(5)	gamma= 90
Temperature:	150 K		
	Calculated	Reported	
Volume	2245.78(18)	2245.78(18)	
Space group	P 21/c	P 1 21/c 1	
Hall group	-P 2ybc	-P 2ybc	
Moiety formula	C28 H23 N S2	C28 H23 N S2	
Sum formula	C28 H23 N S2	C28 H23 N S2	
Mr	437.59	437.59	
Dx, g cm-3	1.294	1.294	
Z	4	4	
Mu (mm-1)	0.253	0.253	
F000	920.0	920.0	
F000'	921.27		
h,k,l max	14,24,11	14,24,11	
Nref	3948	3897	
Tmin,Tmax	0.964,0.985	0.720,1.000	
Tmin'	0.922		
Correction method=	NUMERICAL		
Data completeness =	0.987	Theta(max)= 24.994	
R(reflections) =	0.0430(3331)	wR2(reflections)=	
		0.1221(3897)	
S = 1.130			
	Npar = 281		

Crystal data and structure refinement for 6h



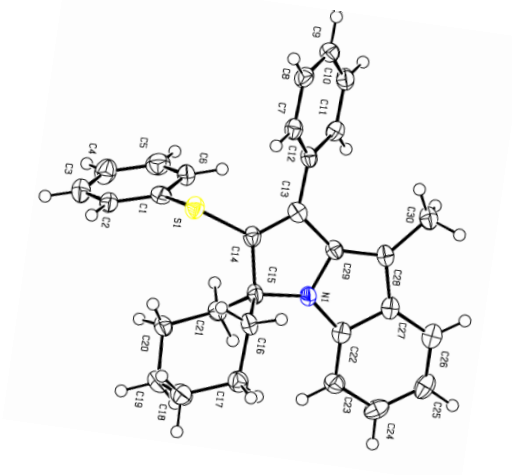
Identification code	6h		
Solvent	CH ₂ Cl ₂		
CCDC	1555452		
Bond precision:	C-C = 0.0045 Å	Wavelength= 0.71073	
Cell:	a= 10.419(11)	b= 10.521(12)	c= 14.721(16)
	alpha= 90	beta= 90	gamma= 90
Temperature:	150 K		
	Calculated	Reported	
Volume	4175.4(4)	4175.4(4)	
Space group	P b c a	P b c a	
Hall group	-P 2ac 2ab	-P 2ac 2ab	
Moiety formula	C ₂₈ H ₂₅ N S	C ₂₈ H ₂₅ N S	
Sum formula	C ₂₈ H ₂₅ N S	C ₂₈ H ₂₅ N S	
Mr	407.55	407.55	
Dx, g cm-3	1.297	1.297	
Z	8	8	
Mu (mm-1)	0.170	0.170	
F000	1728.0	1728.0	
F000'	1729.55		
h,k,l max	18,12,29	18,12,29	
Nref	3675	3651	
Tmin,Tmax	0.958,0.989	0.688,1.000	
Tmin'	0.942		
Correction method=	NUMERICAL		
Data completeness =	0.993	Theta(max)= 24.997	
R(reflections) =	0.0626(2571)	wR2(reflections)=	
		0.1723(3651)	
S = 1.037			
	Npar = 272		

Crystal data and structure refinement for 6i



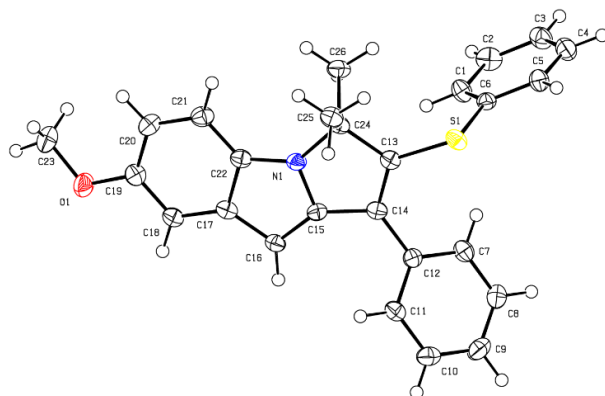
Identification code	6i		
Solvent	CH ₂ Cl ₂		
CCDC	1555455		
Bond precision:	C-C = 0.0076 Å	Wavelength= 0.71073	
Cell:	a= 5.8422(7)	b= 10.5157(13)	c= 18.784(2)
	alpha= 83.484(10)	beta= 85.789(10)	gamma= 75.971(10)
Temperature:	150 K		
	Calculated	Reported	
Volume	1116.9(2)	1117.0(2)	
Space group	P-1	P-1	
Hall group	-P1	-P1	
Moiety formula	C ₂₉ H ₂₇ N S	C ₂₉ H ₂₇ N S	
Sum formula	C ₂₉ H ₂₇ N S	C ₂₉ H ₂₇ N S	
Mr	421.58	421.57	
Dx, g cm-3	1.254	1.253	
Z	2	2	
Mu (mm-1)	0.162	0.162	
F000	448.0	448.0	
F000'	448.39		
h,k,l max	6, 12, 22	6, 12, 22	
Nref	3922	3918	
Tmin,Tmax	0.986, 0.992	0.478, 1.000	
Tmin'	0.974		
Correction method=	NUMERICAL		
Data completeness =	0.999	Theta(max)= 24.999	
R(reflections) =	0.0984(2581)	wR2(reflections)= 0.2778(3918)	
S = 1.071			
	Npar = 281		

Crystal data and structure refinement for 6j



Identification code		6j	
Solvent		CH ₂ Cl ₂	
CCDC		1555456	
Bond precision:	C-C = 0.0048 Å	Wavelength= 0.71073	
Cell:	a= 13.5883(12)	b= 15.4922(13)	c= 10.9888(9)
	alpha= 90	beta= 99.499(8)	gamma= 90
Temperature:	150 K		
	Calculated	Reported	
Volume	2281.6(3)	2281.6(3)	
Space group	P 21/c	P 1 21/c 1	
Hall group	-P 2ybc	-P 2ybc	
Moiety formula	C ₃₀ H ₂₉ N S	C ₃₀ H ₂₉ N S	
Sum formula	C ₃₀ H ₂₉ N S	C ₃₀ H ₂₉ N S	
Mr	435.60	435.60	
Dx, g cm ⁻³	1.268	1.268	
Z	4	4	
Mu (mm ⁻¹)	0.160	0.160	
F ₀₀₀	928.0	928.0	
F ₀₀₀ [']	928.79		
h,k,l max	16,18,13	16,18,13	
Nref	4015	4001	
Tmin,Tmax	0.979,0.994	0.891,1.000	
Tmin [']	0.979		
Correction method=	NUMERICAL		
Data completeness =	0.997	Theta(max)= 25.000	
R(reflections) =	0.0632(2554)	wR2(reflections)=	
		0.1676(4001)	
S = 1.042			
	Npar =290		

Crystal data and structure refinement for 6m



Identification code

Solvent

CCDC

Bond precision:

Cell:

Temperature:

6m

CH₂Cl₂

1555454

Wavelength= 0.71073

b= 30.2371(16)

beta= 97.641(5)

c= 6.1071(4)

gamma= 90

C-C = 0.0035 Å

a= 10.8730(6)

alpha= 90

150 K

Volume

Space group

Hall group

Moiety formula

Sum formula

Mr

Dx, g cm⁻³

Z

Mu (mm⁻¹)

F000

F000'

h,k,l max

Nref

Tmin,Tmax

Tmin'

Correction method=

Data completeness =

R(reflections) =

S = 1.065

Calculated

1990.0(2)

P 21/c

-P 2ybc

C₂₆ H₂₃ N O S

C₂₆ H₂₃ N O S

397.51

1.327

4

0.180

840.0

840.80

12,35,7

3499

0.968,0.982

0.962

NUMERICAL

0.999

0.0547(2796)

Npar =265

Reported

1989.99(19)

P 1 21/c 1

-P 2ybc

C₂₆ H₂₃ N O S

C₂₆ H₂₃ N O S

397.51

1.327

4

0.180

840.0

840.80

12,35,7

3497

0.462,1.000

Theta(max)= 24.997

wR2(reflections)=

0.1408(3497)