Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting Information

Intermolecular Dearomative C2-Arylation of N-Ac Indoles Activated by $FeCl_3$

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Table of Contents

I. General Information

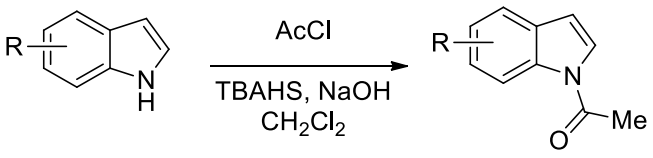
Unless otherwise stated, all reactions were carried out under air atmosphere. Dichloromethane was distilled under argon over CaH_2. Unless otherwise noted, all reagent-grade chemicals and other solvents were obtained from commercial suppliers and were used as received. Reactions were monitored with analytical thin-layer chromatography (TLC) on silica gel 60 F254 plates and visualized under UV (254 nm) and/or by staining with vanillin (1%) + sulfuric acid (5%) in EtOH or $KMnO_4$ solution followed by heating. Flash chromatography were performed on silica gel (Chromagel Si60ACC [70-200 µm]) as stationary phase. ^{1}H NMR spectra were recorded on Bruker AC250 (250 MHz), Bruker DRX300 (300 MHz), Bruker AM360 (360 MHz), Bruker 400 (400 MHz) instruments; chemical shifts (δ) are given in parts per million with respect to the residual protonated solvent (δ = 7.26 ppm for $CDCl_3$, 2.50 ppm for DMSO-d^6), which served as an internal standard. ^{13}C NMR spectra were recorded on Bruker AC250 (62 MHz), DRX300 (75 MHz), AM360 (90 MHz) and Bruker 400 (100 MHz) instruments; chemical shifts are expressed with respect to the deuterated solvent (δ = 77.16 ppm for $CDCl_3$, 39.52 ppm for DMSO-d^6). Coupling constant(s) in hertz (Hz) were measured from one-dimensional spectra and multiplicities were abbreviated as following: br (broad), s (singlet), d (doublet), t (triplet), q (quadruplet), m (multiplet). Melting points were measured with a Reichert Austria microscope. Infrared spectra were recorded as neat on a Bruker Vertex 70 with ATR-GE spectrometer and some of compounds recorded as thin films on NaCl plates. High resolution mass spectra (HRMS) were recorded using Electrospray Ionization (ESI) method with a Bruker Daltonics MicrOTOF-Q instrument.

II. Procedures and characterizations data of compounds

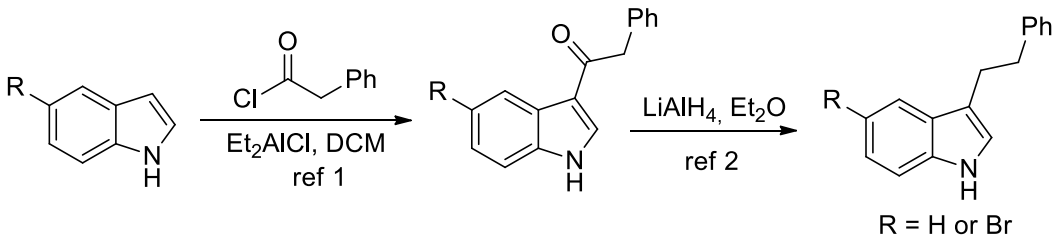
General procedure for the synthesis of N-Ac indoles

Commercially available N-H indoles were transformed into N-Ac indoles according to the procedure described in:

A. Coste, M. Toumi, K. Wright, V. Razafimahaléo, F. Couty, J. Marot, G. Evano *Org. Lett.* 2008, **10**, 3841-3844.



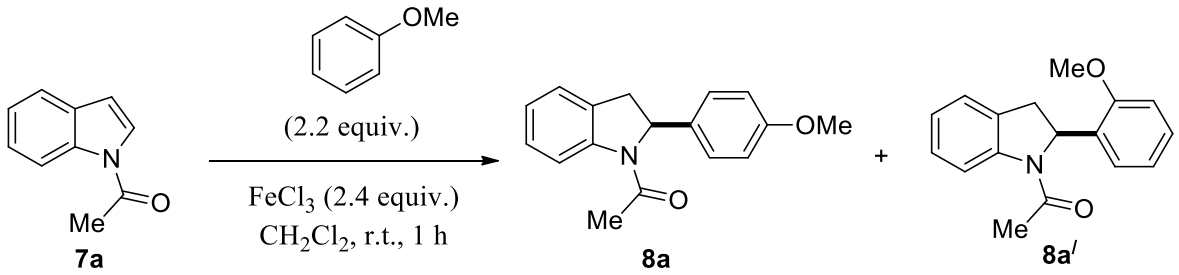
The N-H precursors of N-Ac indoles **13a,b** were prepared according to:



1. D. Bardiot, G. Carlens, K. Dallmeier, S. Kaptein, M. McNaughton, A. Marchand, J. Neyts, W. Smets, *PCT Int. Appl*. **2013**, *WO 2013045516 A1 20130404*.
2. T. Tomoo, T. Nakatsuka, T. Katayama, Y. Hayashi, Y. Fujieda, M. Terakawa, K. Nagahira, *J.Med.Chem.* **2014**, *57*, 7244−7262.

General procedure I for the 2-hydroarylation of N-Ac indole derivatives:

To a solution of the N-acetyl indole derivative **7** (1 eq.) in CH_2Cl_2 (0.5M), was successively added arene (2.2 equiv) **5** and $FeCl_3$ (2.2 equiv). After 1 hr at RT, the consumption of the starting indole **7** was checked by TLC (20% AcOEt/Petroleum ether; if indole **7** is not completely consumed, $FeCl_3$ (0.2 -0.4 equiv) were added and the mixture was stirred for an additional 1 hr after which a TLC control was done). The reaction was then quenched with a saturated NaCl aqueous solution and diluted with AcOEt. The organic and aqueous phases were separated. The aqueous phase was then extracted twice with AcOEt. The combined organic phases were then dried over Na_2SO_4, filtered and concentrated under vacuum. The crude oil was then purified by flash column chromatography or PTLC (20% to 50% AcOEt/ Petroleum ether).



8a was obtained from 1-Acetylindole **7a** (80 mg, 0.502 mmol) following above general procedure using anisole **5a** as electron-rich arene. Flash column chromatography purification (Cyclohexane/EtOAc : 9/1 to 8/2) led to *N*-Acetyl-2-(4-methoxyphenyl)indoline **8a** as colorless oil (42 mg, 0.157 mmol, **32%**) and *N*-Acetyl-2-(2-methoxyphenyl)indoline **8a′** as a white solid (52 mg, 0.195 mmol, **39%**) along with an inseparable mixture (1/3) of **8a** and **8a′** respectively (21 mg, 0.078 mmol, **15%**).

***N*-Acetyl-2-(4-methoxyphenyl)indoline (8a):**

R_f : 0.14 (Cyclohexane/EtOAc : 8/2)

^{1}H NMR (360 MHz, $CDCl_3$) δ (ppm) : 2.04 (s, 3H), 2.94 (dd, *J* = 16.1, 1.8 Hz, 1H), 3.76 (s, 3H), 3.79-3.71 (m, 1H), 5.32 (d, *J* = 10.0 Hz, 1H), 6.82 (d, *J* = 8.4 Hz, 2H), 7.14-7.02 (m, 4H), 7.26 (t, *J* = 7.7 Hz, 1H), 8.31 (d, *J* = 7.9 Hz, 1H).

^{13}C NMR (90 MHz, $CDCl_3$) δ (ppm) : 24.3, 39.2, 55.4, 63.2, 114.5, 117.1, 124.1, 125.0, 126.3, 126.3, 127.8, 127.8, 129.4, 135.4, 143.4, 159.2, 169.7.

IR (NaCl), ν (cm^{-1}) : 3002, 2955, 2836, 1660, 1611, 1598, 1512, 1480, 1394, 1248, 1177, 755

HRMS (ESI^+) : calculated: 290.1151 ($[C_{17}H_{17}NNaO_2]^+$;$[M+Na]^+$); found: 290.1149

***N*-Acetyl-2-(2-methoxyphenyl)indoline (8a$'$) :**

M.p. : 107-109 °C

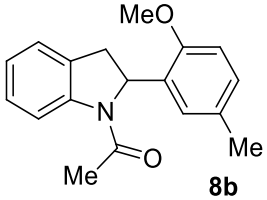
R_f : 0.22 (Cyclohexane/EtOAc : 8/2)

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) : 2.01 (s, 3H)), 2.86 (dd, *J* = 16.2, 1.9 Hz, 1H), 3.75 (dd, *J* = 16.2, 10.0 Hz, 1H), 3.92 (s, 3H), 5.73 (dd, *J* = 10.0, 1.9 Hz, 1H), 6.83 (t, *J* = 7.3 Hz, 1H), 6.91 (d, *J* = 8.2 Hz, 1H), 6.97 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.02 (td, *J* = 7.3, 1.0 Hz, 1H), 7.11-7.08 (m, 1H), 7.28-7.21 (m, 2H), 8.33 (d, *J* = 8.2 Hz, 1H).

^{13}C NMR (75.5 MHz, $CDCl_3$) δ (ppm) : 23.8, 37.8, 55.5, 58.2, 110.5, 117.2, 121.1, 124.0, 125.0, 125.1, 127.6, 128.7, 130.1, 131.0, 143.4, 155.6, 169.7.

IR (NaCl), ν (cm^{-1}) : 3005, 2936, 2837, 1662, 1599, 1481, 1462, 1396, 1243, 1107, 1027, 753

HRMS (ESI^+) : calculated: 290.1151 ($[C_{17}H_{17}NNaO_2]^+$;$[M+Na]^+$); found: 290.1145



8b

***N*-Acetyl-2-(2-methoxy-5-methylphenyl)indoline (8b):**

Compounds 8b (246.6 mg, 86%) was obtained from 4-Me anisole **5b** (275 mg, 2.25 mmol), N-Ac indole **7a** (162.7 mg, 1.02 mmol) and $FeCl_3$ (396 mg, 2.44 mmol) in 2 mL of CH_2Cl_2.

Melting point: 72 – 80 °C.

R_f: 0.35 (EtOAc/pet. ether 20:80).

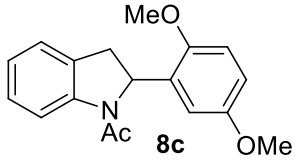
^{1}H-NMR (250 MHz, $CDCl_3$) δ (ppm) : 2.04(s, 3H), 2.17 (s, 3H), 2.88 (dd, *J* = 16.2, 2.2 Hz, 1H), 3.77 (dd, *J* = 16.2, 10.2 Hz, 1H), 3.89 (s, 3H), 5.72 (dd, *J* = 10.2, 2.2 Hz, 1H), 6.77 (d, J = 1.7 Hz, 1H), 6.82 (d, *J* = 8.2 Hz, 1H), 7.02-7.13 (m, 3H), 7.25-7.31 (m, 1H), 8.37 (d, *J* = 8 Hz, 1H).

^{13}C NMR (90 MHz, $CDCl_3$) δ (ppm) : 20.7, 23.8, 37.8, 55.5, 58.0, 110.5, 117.1, 123.9, 124.9, 125.4, 127.5, 128.9, 130.2, 130.3, 130.7, 143.4, 153.5, 169.7.

IR (ATR), ν (cm^{-1}) : 2951, 1655 , 1484, 1397, 1246, 1034, 760

HRMS (ESI^+): calculated ($C_{18}H_{20}NO_2^+$): 282.1489 [M + H^+]; found: 282.1488.

calculated ($C_{18}H_{19}NNaO_2^+$): 304.1308 [M + Na^+]; found: 304.1305.



8c

1-(2-(2,5-dimethoxyphenyl)indolin-1-yl)ethan-1-one (8c) :

Compounds 8c (180.4 mg, 59%) was obtained from 1,4-dimethoxy benzene **5c** (305 mg, 2.20 mmol), N-Ac indole **7a** (163.0 mg, 1.02 mmol) and $FeCl_3$ (389.3 mg, 2.4 mmol) in 2 mL of CH_2Cl_2.

melting point: 67 – 69 °C.

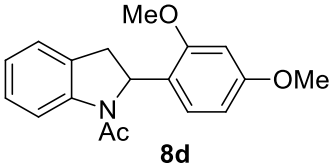
R_f: 0.25 (EtOAc/pet. ether 20:80).

^{1}H-NMR (360 MHz, $CDCl_3$) δ (ppm) : 2.04 (s, 3H), 2.87 (d, *J* = 16.2 Hz, 1H), 3.63 (s, 3H), 3.75 (dd, *J* = 16.2, 10.1 Hz, 1H), 3.86 (s, 3H), 5.70 (d, *J* = 10.1 Hz, 1H), 6.58 (d, *J* = 2.1 Hz, 1H), 6.74 (dd, *J* = 8.6, 2.5 Hz, 1H), 6.83 (d, *J* = 8.6 Hz, 1H), 7.02 (t, *J* = 7.5 Hz, 1H), 7.10 (d, *J* = 6.8 Hz, 1H), 7.24 (t, *J* = 7.5 Hz, 1H), 8.33 (d, *J* = 7.9 Hz, 1H).

^{13}C-NMR (90 MHz, $CDCl_3$) δ (ppm) : 23.7, 37.7, 55.5, 55.9, 58.0, 111.4, 111.8, 112.2, 117.1, 123.9, 124.9, 127.6, 129.9, 132.1, 143.2, 149.7, 153.9, 169.5.

IR (ATR), ν (cm^{-1}) : 2948, 1652, 1485, 1397, 1244, 1034, 837.

HRMS (ESI^+): calculated ($C_{18}H_{19}NNaO_3^+$): 320.1257 [M + Na^+]; found: 320.1257.



8d

1-(2-(2,4-dimethoxyphenyl)indolin-1-yl)ethanone (8d) :

Compounds 8d (286.1 mg, 48%) was obtained from 1,3-dimethoxy benzene **5d** (609.1 mg, 4.4 mmol), N-Ac indole **7a** (319.0 mg, 2.00 mmol) and $FeCl_3$ (778.4 mg, 4.8 mmol) in 3 mL of CH_2Cl_2.

melting point: 76 – 78 °C.

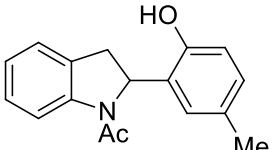
R_f: 0.31 (EtOAc/pet. ether 20:80).

^{1}H-NMR (360 MHz, $CDCl_3$) δ (ppm) : 2.04 (s, 3H), 2.85 (dd, *J* = 15.8, 1.4 Hz, 1H), 3.72 (dd, *J* = 15.8, 10.1 Hz, 1H), 3.77 (s, 3H), 3.89 (s, 3H), 5.66 (dd, *J* = 9.4, 1.8 Hz, 1H), 6.35 (dd, *J* = 8.6, 2.1 Hz, 1H), 6.50 (d, *J* = 2.1 Hz, 1H), 7.03 (t, *J* = 7.2 Hz, 1H), 7.11 (d, *J* = 7.2 Hz, 1H), 7.26 (t, *J* = 7.9 Hz, 1H), 8.33 (d, *J* = 8.2 Hz, 1H).

^{13}C-NMR (75 MHz, $CDCl_3$) δ (ppm) : 23.6, 37.9, 55.3, 55.4, 57.9, 98.7, 104.2, 116.9, 123.3, 123.8, 124.9, 125.5, 127.4, 130.1, 143.3, 156.6, 160.3, 169.6.

IR (ATR), ν (cm^{-1}) : 1653, 1615, 1584, 1502, 1481, 1402, 1214, 1161, 1030, 759.

HRMS (ESI^+): calculated ($C_{18}H_{19}NNaO_3^+$): 320.1257 [M + Na^+]; found: 320.1259.



8e

1-(2-(2-hydroxy-5-methylphenyl)indolin-1-yl)ethanone (8e) :

M: 267.33 g/mol.

Compounds 8e (122.9 mg, 46% ; off-white solid) was obtained from *p*-cresol **5e** (276 mg, 2.5 mmol), N-Ac indole **7a** (160.8 mg, 1.01 mmol) and $FeCl_3$ (389.3 mg, 2.4 mmol) in 2 mL of CH_2Cl_2.

melting point: 91 – 100 °C.

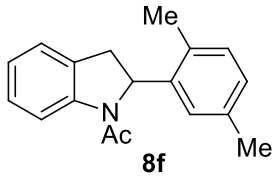
R_f: 0.29 (EtOAc/pet. ether 20:80).

^{1}H-NMR (250 MHz, acetone-d^6 δ (ppm) : 1.99 (s, 3H), 2.10 (s, 3H), 2.90 (d, *J* = 16.5 Hz, 1H), 3.78 (dd, *J* = 16.5, 10 Hz, 1H), 5.84 (d, *J* = 9.7 Hz, 1H), 6.69 (s, 1H), 6.84-6.95 (m, 2H), 7.03 (d, t, *J* = 7.1 Hz, 1H) 7.16-7.27 (m, 2H), 8.30 (d, *J* = 8 Hz, 1H), 8.82 (s, 1H).

^{13}C-NMR (62 MHz, acetone-d^6 δ (ppm) : 19.8, 22.8, 37.5, 57.9, 115.4, 116.4, 123.5, 124.9, 127.1, 128.7, 128.8, 129.6, 130.4, 143.9, 151.3, 168.8.

IR (ATR), ν (cm^{-1}) : 3113, 1623, 1484, 1411, 1267, 753, 734.

HRMS (ESI^+): calculated ($C_{17}H_{17}NNaO_2^+$): 290.1151 [M + Na^+]; found: 290.1146.



8f

1-(2-(2,5-dimethylphenyl)indolin-1-yl)ethanone (8f) :

Compounds 8f (142.5 mg, 54% ; colourless solid) was obtained from *p*-xylene **5f** (233 mg, 2.2 mmol), N-Ac indole **7a** (159.2 mg, 1.00 mmol) and $FeCl_3$ (389.3 mg, 2.4 mmol) in 2 mL of CH_2Cl_2.

melting point: 77-80 °C.

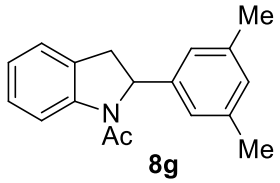
R_f: 0.53 (EtOAc/pet. ether 20:80).

^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) : 1.99 (s, 3H), 2.19 (s, 3H), 2.38 (s, 3H), 2.87 (dd, *J* = 15.9, 2.1 Hz, 1H), 3.82 (dd, *J* = 15.9, 10.2 Hz, 1H), 5.53 (dd, *J* = 10.2, 2.4 Hz, 1H), 6.80 (s, 1H), 6.98 (d, *J* = 7.5 Hz, 1H), 704-7.14 (m, 3H), 7.30 (t, *J* = 7.5 Hz, 1H), 8.38 (d, *J* = 7.8 Hz, 1H).

^{13}C-NMR (75 MHz, $CDCl_3$) δ (ppm) : 19.0, 21.3, 23.9, 37.7, 60.5, 117.2, 124.2, 124.4, 125.1, 127.9, 128.3, 129.3, 130.3, 130.9, 136.6, 141.0, 143.6, 169.7.

IR (ATR), ν (cm^{-1}) : 2946, 1653, 1499, 1397, 1276, 1245, 1034, 837.

HRMS (ESI$^+$): calculated ($C_{18}H_{19}NNaO^+$): 288.1359 [M + Na$^+$]; found: 288.1360.



8g

1-(2-(3,5-dimethylphenyl)indolin-1-yl)ethanone (8g) :

Compounds 8g (157.5 mg, 60% ; brown solid) was obtained from *m*-xylene **5g** (233.2 mg, 2.2 mmol), N-Ac indole **7a** (160.0 mg, 1.00 mmol) and $FeCl_3$ (388.7 mg, 2.4 mmol) in 2 mL of CH_2Cl_2.

melting point: 39-45 °C.

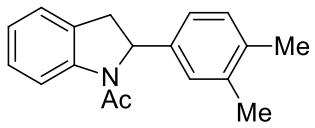
R_f: 0.26 (EtOAc/pet. ether 20:80).

^{1}H-NMR (360 MHz, $CDCl_3$) δ (ppm) : 1.97 (s, 3H), 2.27 (s, 3H), 2.38 (s, 3H), 2.83 (dd, *J* = 15.8, 1.4 Hz, 1H), 3.79 (dd, *J* = 15.8, 10.0 Hz, 1H), 5.51 (dd, *J* = 10.0, 2.1 Hz, 1H), 6.87 (s, 2H), 7.01-7.11 (m, 3H), 7.27 (t, *J* = 7.5 Hz, 1H), 8.35 (d, *J* = 8.2 Hz, 1H).

^{1}H-NMR (62 MHz, $CDCl_3$) δ (ppm) : 19.3, 20.9, 23.8, 37.7, 60.4, 117.0, 123.9, 124.1, 125.0, 127.5, 127.8, 129.3, 131.7, 133.2, 137.2, 138.2, 143.5, 169.6.

IR (ATR), ν (cm^{-1}) : 2918, 1659, 1481, 1396, 1277, 1033, 761.

HRMS (ESI$^+$): calculated ($C_{18}H_{20}NO^+$): 266.1539 [M + H$^+$]; found: 266.1537.



8h

1-(2-(3,4-dimethylphenyl)indolin-1-yl)ethanone (8h):

Compounds 8h (52.9 mg, 47% ; yellow foam) was obtained from *o*-xylene **5h** (155 µL, 1.28 mmol), N-Ac indole **7a** (68.0 mg, 0.427 mmol) and $FeCl_3$ (180.3 mg, 1.11 mmol) in 0.6 mL of CH_2Cl_2.

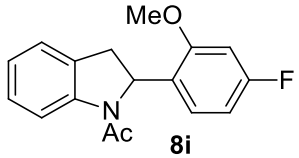
R_f: 0.45 (EtOAc/pet. ether 20:80).

^{1}H-NMR (360 MHz, $CDCl_3$) δ (ppm) : 2.06 (s, 3H), 2.22 (s, 3H), 2.24 (s, 3H), 2.97 (dd, *J* = 15.7, 2.1 Hz, 1H), 3.78 (dd, *J* = 15.7, 10.3 Hz, 1H), 5.34 (dd, *J* = 10.3, 2.4, 1H), 6.89-6.94 (m, 2H), 7.04-7.15 (m, 3H), 7.28 (t, *J* = 8.0 Hz, 1H), 8.35 (d, *J* = 8.0 Hz, 1H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ [ppm] = 19.4, 19.9, 24.2, 39.1, 63.4, 117.0, 122.4, 124.0, 124.9, 126.1, 127.7, 129.3, 130.3, 136.1, 137.4, 140.7, 143.4, 169.7.

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 2920, 1662, 1598, 1480, 1461, 1395, 1276.

HRMS (ESI^+): calculated ($C_{18}H_{19}NNaO^+$): 288.1359 [M + Na^+]; found: 288.1354.



8i

1-(2-(4-fluoro-2-methoxyphenyl)indolin-1-yl)ethanone (8i) :

Compounds 8i (172.1 mg, 57% ; off-white solid) was obtained from 1-fluoro-3-methoxybenzene **5i** (296 mg, 2.35 mmol), N-Ac indole **7a** (170 mg, 1.06 mmol) and $FeCl_3$ (412 mg, 2.54 mmol) in 2 mL of CH_2Cl_2.

melting point: 59-65 °C.

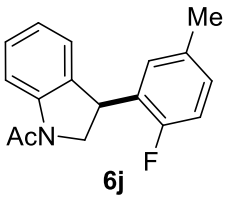
R_f: 0.26 (EtOAc/pet. ether 20:80).

^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) : 2.00 (s, 3H), 2.82 (d, *J* = 16.2 Hz, 1H), 3.72 (dd, *J* = 16.2, 10.2 Hz, 1H), 3.88 (s, 3H), 5.65 (d, *J* = 9.3 Hz, 1H), 6.51 (td, *J* = 8.1, 2.1 Hz, 1H), 6.64 (dd, *J* = 10.5, 2.1 Hz, 1H), 6.87-6.92 (m, 1H), 6.99-7.11 (m, 2H), 7.22-7.27 (m, 1H), 8.31 (d, *J* = 7.8 Hz, 1H).

^{1}H-NMR (75 MHz, $CDCl_3$) δ (ppm) : 23.7, 37.8, 55.8, 57.8, 99.0 (d, *J* = 26 Hz), 107.1 (d, *J* = 26 Hz), 117.0, 124.0, 124.9, 125.9 (d, *J* = 10 Hz), 126.6, 127.6, 129.8, 143.2, 156.7 (d, *J* = 10 Hz), 163.0 (d, *J* = 251 Hz), 169.4.

IR (ATR), ν (cm^{-1}) : 1661, 1480, 1396, 1279, 1033, 833, 762.

HRMS (ESI^+): calculated ($C_{17}H_{17}FNO_2^+$): 286.1238 [M + H^+]; found: 286.1234.



6j

1-(3-(2-fluoro-5-methylphenyl)indolin-1-yl)ethanone (6j) :

Compounds **6j** (62.1 mg, 23% ; brown solid) was obtained from 1-fluoro-4-methylbenzene **5j** (242 mg, 2.2 mmol), N-Ac indole **7a** (159.1 mg, 1.00 mmol) and $FeCl_3$ (389.3 mg, 2.54 mmol) in 2 mL of CH_2Cl_2.

melting point: 70-75 °C.

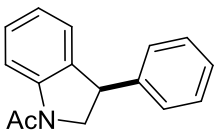
R_f: 0.27 (EtOAc/pet. ether 20:80).

^{1}H-NMR (360 MHz, $CDCl_3$) δ (ppm): 2.22 (s, 3H), 2.24 (s, 3H), 3.93 (dd, *J* = 10.4, 6.4 Hz, 1H), 4.47 (t, *J* = 10.4 Hz, 1H), 4.92 (dd, *J* = 10.4, 6.4 Hz, 1H), 6.81 (dd, *J* = 7.5, 1.4 Hz, 1H), 6.95-7.05 (m, 4H), 7.26-7.30 (m, 1H), 8.38 (d, *J* = 7.8 Hz, 1H).

^{13}C-NMR (90 MHz, $CDCl_3$) δ (ppm): 20.8, 24.3, 39.2, 56.8, 115.2 (d, *J* = 21 Hz), 117.1, 124.0, 125.1, 128.3, 129.2, 129.3, 129.4, 132.9, 134.2, 143.2, 158.9 (d, J= 244 Hz), 168.7.

IR (ATR), ν (cm^{-1}) : 1662, 1597, 1479, 1400, 830, 768.

HRMS (ESI^+): calculated ($C_{17}H_{17}FNO^+$): 270.1289 [M + H^+]; found: 270.1292.



6k

1-(3-phenylindolin-1-yl)ethanone (6k):

Compounds **6k** (65.8 mg, 27% ; brown solid) was obtained from benzene **5k** (178 mg, 2.28 mmol), N-Ac indole **7a** (165 mg, 1.03 mmol) and $FeCl_3$ (400 mg, 2.46 mmol) in 2 mL of CH_2Cl_2.

melting point: 52-58 °C.

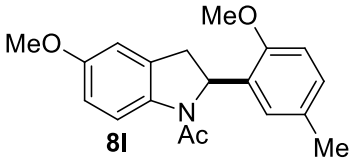
R_f: 0.22 (EtOAc/pet. ether 20:80).

^{1}H-NMR (360 MHz, $CDCl_3$) δ (ppm): 2.22 (s, 3H), 3.94 (dd, *J* = 10.4, 6.8 Hz, 1H), 4.45 (t, *J* = 10.4 Hz, 1H), 4.62 (dd, *J* = 10.4, 6.8 Hz, 1H), 6.97-7.04 (m, 2H), 7.20 (d, *J* = 7.2 Hz, 2H), 7.24-7.37 (m, 4H), 8.32 (d, *J* = 8.2 Hz, 1H).

^{13}C-NMR (90 MHz, $CDCl_3$) δ (ppm): 24.2, 26.5, 58.0, 116.9, 123.9, 125.0, 127.3, 127.8, 128.2, 128.9, 134.5, 142.9, 143.1, 168.6.

IR (ATR), ν (cm^{-1}) : 1654, 1598, 1480, 1402, 1285, 761, 703.

HRMS (ESI^+): calculated ($C_{16}H_{16}NO^+$): 238.1226 [M + H^+]; found: 238.1227.



8l

1-(5-methoxy-2-(2-methoxy-5-methylphenyl)indolin-1-yl)ethan-1-one (8l) :

Compound **8l** (208.6 mg, 67% ; yellow-brown solid) was obtained from 4-Me anisole **5b** (268.8 mg, 2.2 mmol), 5-Methoxy N-Ac indole **7b** (189.3 mg, 1.00 mmol) and $FeCl_3$ (389.3 mg, 2.4 mmol) in 2 mL of CH_2Cl_2.

Melting point: 68-75 °C.

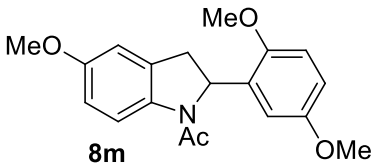
R_f: 0.24 (EtOAc/pet. ether 20:80).

^{1}H-NMR (250 MHz, $CDCl_3$) δ (ppm): 1.99 (s, 3H), 2.15 (s, 3H), 2.81 (dd, *J* = 16.2, 1.2 Hz, 1H), 3.72 (dd, *J* = 16.2, 10.0 Hz, 1H), 3.75 (s, 3H), 3.86 (s, 3H), 5.68 (dd, *J* = 10, 2 Hz, 1H), 6.66 (s, 1H), 6.75 – 6.81 (m, 3H), 7.01 (dd, *J* = 8.5, 1.2 Hz, 1H), 8.26 (d, *J* = 8.7 Hz, 1H).

^{13}C-NMR (62.5 MHz, $CDCl_3$) δ (ppm): 20.7, 23.6, 37.9, 55.5, 55.6, 58.3, 110.4, 111.1, 112.0, 117.7, 125.5, 128.9, 130.3, 130.7, 131.8, 137.2, 153.5, 156.6, 169.0.

IR (ATR), ν (cm^{-1}) : 2950, 1651, 1485, 1397, 1245, 1034, 837, 809.

HRMS (ESI^+): calculated ($C_{19}H_{21}NNaO_3^+$): 334.1414 [M + Na^+]; found: 334.1406.



8m

1-(2-(2,5-dimethoxyphenyl)-5-methoxyindolin-1-yl)ethan-1-one (8m) :

Compound **8m** (115.6 mg, 35% ; pale-white solid) was obtained from 1,4dimethoxybenzene **5c** (305 mg, 2.2 mmol), 5-Methoxy N-Ac indole **7b** (189.2 mg, 1.00 mmol) and $FeCl_3$ (389.3 mg, 2.4 mmol) in 2 mL of CH_2Cl_2.

melting point: 72-78 °C.

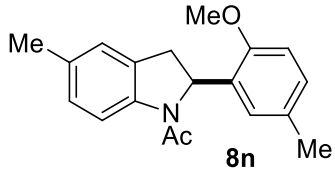
R_f: 0.12 (EtOAc/pet. ether 20:80).

^{1}H-NMR (360 MHz, $CDCl_3$) δ (ppm) : 1.98 (s, 3H), 2.80 (dd, *J* = 16.2, 1.8 Hz, 1H), 3.61 (s, 3H), 3.70 (dd, *J* = 16.4, 10.0 Hz, 1H), 3.73 (s, 3H), 3.83 (s, 3H), 5.66 (dd, *J* = 9.9, 1.8 Hz, 1H), 6.54 (d, *J* = 2.8 Hz, 1H), 6.64 (d, *J* = 2.2 Hz, 1H), 6.73 (td, *J* = 9, 2.8 Hz, 2H), 6.81 (d, *J* = 8.6 Hz, 1H), 8.21 (d, *J* = 9 Hz, 1H).

^{13}C-NMR (90 MHz, $CDCl_3$) δ (ppm) : 23.5, 37.9, 55.6, 55.9, 58.3, 111.1, 111.3, 111.9, 112.1, 112.2, 117.7, 131.6, 132.1, 137.1, 149.7, 153.9, 156.6, 168.8.

IR (ATR), ν (cm^{-1}) : 2837, 1654, 1487, 1398, 1276, 1220, 1028, 717.

HRMS (ESI^+): calculated ($C_{19}H_{22}NO_4^+$): 328.1543 [M + H^+]; found: 328.1534.



8n

1-(2-(2-methoxy-5-methylphenyl)-5-methylindolin-1-yl)ethan-1-one (8n):

Compound **8n** (218.3 mg, 74% ; off-white solid) was obtained from 4-Me anisole **5b** (271.6 mg, 2.2 mmol), 5-Methyl N-Ac indole **7c** (173 mg, 1.00 mmol) and $FeCl_3$ (389.3 mg, 2.4 mmol) in 2 mL of CH_2Cl_2.

melting point: 67-72 °C.

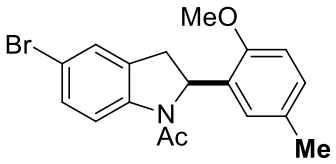
R_f: 0.47 (EtOAc/pet. ether 20:80).

^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) : 2.00 (s, 3H), 2.15 (s, 3H), 2.30 (s, 3H), 2.82 (d, *J* = 16.2 Hz, 1H), 3.71 (dd, 16.2, 10.2 Hz, 1H), 3.87 (s, 3H), 5.69 (d, *J* = 9.9 Hz, 1H), 6.76 (s, 1H), 6.80 (d, *J* = 8.4 Hz, 1H), 6.91 (s, 1H), 7.00-7.07 (m, 2H), 8.22 (d, *J* = 8.4 Hz, 1H).

^{13}C-NMR (75 MHz, $CDCl_3$) δ (ppm) : 20.7, 21.1, 23.8, 37.9, 55.6, 58.2, 110.5, 116.9, 125.5, 125.6, 128.0, 128.9, 130.2, 130.3, 130.9, 133.6, 141.2, 153.5, 169.4.

IR (ATR), ν (cm^{-1}) : 1652, 1486, 1398, 1276, 1245, 1034, 809, 753.

HRMS (ESI^+): calculated ($C_{19}H_{21}NNaO_2^+$): 318.1465 [M + Na^+]; found: 318.1458.



8o

1-(5-bromo-2-(2-methoxy-5-methylphenyl)indolin-1-yl)ethan-1-one (8o) :

Compound **8o** (298.8 mg, 83% ; light yellow solid) was obtained from 4-Me-anisole **5b** (270.3 mg, 2.2 mmol), 5-Bromo N-Ac indole **7d** (238.6 mg, 1.00 mmol) and $FeCl_3$ (350 mg, 2.2 mmol) in 2 mL of CH_2Cl_2.

melting point: 47 – 55 °C.

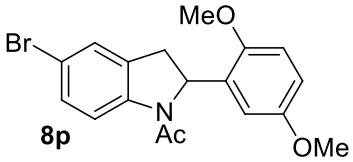
R_f: 0.42 (EtOAc/pet. ether 20:80).

^{1}H-NMR (250 MHz, $CDCl_3$) δ (ppm) : 2.00 (s, 3H), 2.16 (s, 3H), 2.83 (dd, *J* = 16.5, 2 Hz, 1H), 3.71 (dd, *J* = 16.5, 10 Hz, 1H), 3.86 (s, 3H), 5.69 (dd, *J* = 10, 2.2 Hz, 1H), 6.70 (d, *J* = 1.5 Hz, 1H), 6.80 (d, *J* = 8.5 Hz, 1H), 7.02 (dd, *J* = 8.2, 1.5 Hz, 1H), 7.20 (s, 1H), 7.35 (dd, *J* = 8.5, 1.7 Hz, 1H), 8.22 (d, *J* = 8.7 Hz, 1H).

^{13}C-NMR (62.5 MHz, $CDCl_3$) δ (ppm) : 20.7, 23.7, 37.6, 55.6, 58.3, 110.6, 116.3, 118.5, 125.3, 127.9, 129.2, 130.2, 130.4, 132.6, 142.6, 153.5, 169.8.

IR (ATR), ν (cm^{-1}) : 1652, 1485, 1398, 1245, 1034, 837, 809.

HRMS (ESI^+): calculated ($C_{18}H_{18}BrNNaO_2^+$): 382.0413 [M + Na^+]; found: 382.0400.



8p

1-(5-bromo-2-(2,5-dimethoxyphenyl)indolin-1-yl)ethan-1-one (8p) :

Compound **8p** (203 mg, 54% ; off-white solid) was obtained from 1,4dimethoxybenzene **5c** (305 mg, 2.2 mmol), 5-Bromo N-Ac indole **7d** (238.2 mg, 1.00 mmol) and $FeCl_3$ (389.3 mg, 2.4 mmol) in 2 mL of CH_2Cl_2.

melting point: 73-79 °C.

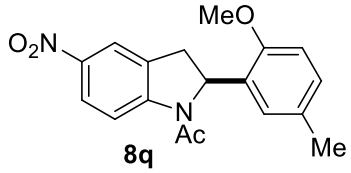
R_f: 0.29 (EtOAc/pet. ether 20:80).

^{1}H-NMR (250 MHz, $CDCl_3$) δ (ppm) : 2.01 (s, 3H), 2.83 (dd, *J* = 16.5, 1.4 Hz, 1H), 3.64 (s, 3H), 3.71 (dd, *J* = 16.5, 10.2 Hz, 1H), 3.84 (s, 3H), 5.68 (dd, *J* = 10.0, 1.9 Hz, 1H), 6.50 (d, *J* = 2.9 Hz, 1H), 6.74 (dd, *J* = 8.9, 2.9 Hz, 1H), 6.83 (d, *J* = 8.9 Hz, 1H), 7.19 (s, 1H), 7.33 (dd, *J* = 8.6, 1.9 Hz, 1H), 8.18 (d, *J* = 8.6 Hz, 1H).

^{13}C-NMR (62.5 MHz, $CDCl_3$) δ (ppm) : 23.7, 37.5, 55.7, 55.9, 58.4, 111.5, 111.9, 112.5, 116.4, 118.5, 127.9, 130.5, 131.7, 132.5, 142.5, 149.7, 154, 169.6.

IR (ATR), ν (cm^{-1}) : 1662, 1495, 1471, 1387, 1218, 1054, 826.

HRMS (ESI^+): calculated ($C_{18}H_{19}BrNO_3^+$): 376.0543 [M + H^+]; found: 376.0547.



8q

1-(2-(2-methoxy-5-methylphenyl)-5-nitroindolin-1-yl)ethanone (8q):

Compound **8q** (129.9 mg, 40% ; light brown solid) was obtained from 4-Me anisole **5b** (268.8 mg, 2.2 mmol), 5-Nitro N-Ac indole **7e** (204.8 mg, 1.00 mmol) and $FeCl_3$ (389 mg, 2.4 mmol) in 2 mL of CH_2Cl_2.

melting point: 88 – 97 °C.

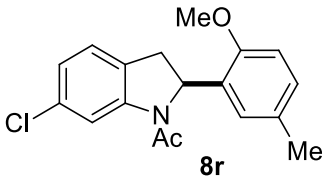
R_f: 0.63 (EtOAc/pet. ether 20:80).

^{1}H-NMR (250 MHz, $CDCl_3$) δ (ppm) : 2.05 (s, 3H), 2.16 (s, 3H), 2.95 (dd, *J* = 16.7, 2.2 Hz, 1H), 3.77 (dd, *J* = 16.7, 10.2 Hz, 1H), 3.86 (s, 3H), 5.81 (dd, *J* = 10.5, 2.2 Hz, 1H), 6.65 (d, *J* = 2 Hz, 1H), 6.82 (d, *J* = 8 Hz, 1H), 7.05 (dd, *J* = 8.5, 2 Hz, 1H), 7.97 (s, 1H), 8.19 (dd, *J* = 9, 2.2 Hz, 1H), 8.43 (d, *J* = 8.7 Hz, 1H).

^{13}C-NMR (62.5 MHz, $CDCl_3$) δ (ppm) : 20.7, 23.9, 37.3, 55.7, 59.2, 110.9, 116.4, 120.8, 124.8, 125.3, 129.6, 130.6, 131.7, 144.0, 148.9, 153.5, 170.6.

IR (ATR), ν (cm^{-1}) : 1674, 1654, 1599, 1500, 1485, 1395, 1334, 1246, 1034, 810, 754.

HRMS (ESI^+): calculated ($C_{18}H_{18}N_2NaO_4^+$): 349.1159 [M + Na^+]; found: 349.1156.



8r

1-(6-chloro-2-(2-methoxy-5-methylphenyl)indolin-1-yl)ethan-1-one (8r) :

Compound **8r** (174.2 mg, 55% ; (off-white solid) was obtained from 4-Me anisole **5b** (268.8 mg, 2.2 mmol), 6-Chloro N-Ac indole **7f** (193.6 mg, 1.00 mmol) and $FeCl_3$ (389 mg, 2.4 mmol) in 2 mL of CH_2Cl_2.

melting point: 61-70 °C.

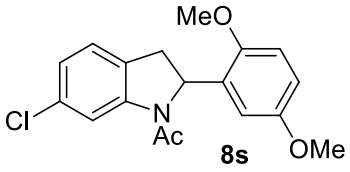
R_f: 0.25 (EtOAc/pet. ether 20:80).

^{1}H-NMR (360 MHz, $CDCl_3$) δ (ppm) : 2.00 (s, 3H), 2.17 (s, 3H), 2.82 (dd, *J* = 16.2, 2.2 Hz, 1H), 3.68 (dd, 16.5, 10.0 Hz, 1H), 3.86 (s, 1H), 5.72 (dd, *J* = 10.0, 2.1 Hz, 1H), 6.71 (s, 1H), 6.80 (d, *J* = 8.2 Hz, 1H), 6.99-7.04 (m, 3H), 8.38 (s, 1H).

^{13}C-NMR (90 MHz, $CDCl_3$) δ (ppm) : 20.7, 23.8, 37.4, 55.6, 58.7, 110.6, 117.4, 123.9, 125.3, 125.6, 128.7, 129.2, 130.3, 130.4, 133.1, 144.4, 153.5, 169.9.

IR (ATR), ν (cm^{-1}) : 1649, 1483, 1395, 1274, 1242, 1219, 1032, 836, 808.

HRMS (ESI^+): calculated ($C_{18}H_{18}ClNNaO_2^+$): 338.0918 [M + Na^+]; found: 338.0907.



8s

1-(6-chloro-2-(2,5-dimethoxyphenyl)indolin-1-yl)ethan-1-one (8s) :

Compound **8s** (205.5 mg, 62% ; off-white solid) was obtained from 1,4dimethoxybenzene **5c** (306.8 mg, 2.2 mmol), 6-Chloro N-Ac indole **7f** (193.8 mg, 1.00 mmol) and $FeCl_3$ (389.3 mg, 2.4 mmol) in 2 mL of CH_2Cl_2.

melting point: 64-65 °C.

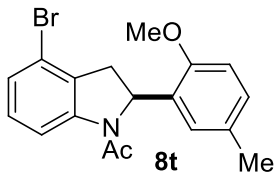
R_f: 0.43 (EtOAc/pet. ether 20:80).

^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) : 2.00 (s, 3H), 2.82 (d, *J* = 16.5 Hz, 1H), 3.63 (s, 3H), 3.67 (dd, *J* = 16.2, 9.9 Hz, 1H), 3.84 (s, 3H), 5.70 (d, *J* = 9.6 Hz, 1H), 6.51 (d, 2.7 Hz, 1H), 6.74 (dd, *J* = 9, 3 Hz, 1H), 6.83 (d, *J* = 8.7 Hz, 1H), 6.97 (s, 2H), 8.34 (s, 1H).

^{13}C-NMR (75 MHz, $CDCl_3$) δ (ppm) : 23.7, 37.4, 55.7, 55.9, 58.7, 111.5, 111.9, 112.4, 117.4, 123.9, 125.6, 128.5, 131.8, 133.2, 144.4, 149.7, 154.0, 169.7.

IR (ATR), ν (cm^{-1}) : 1650, 1497, 1275, 1244, 1033, 836, 808.

HRMS (ESI^+): calculated ($C_{18}H_{19}ClNO_3$): 332.1048 [M + H^+]; found: 332.1050.



8t

1-(4-bromo-2-(2-methoxy-5-methylphenyl)indolin-1-yl)ethanone (8t) :

Compound **8t** (308.4 mg, 86% ; (off-white solid) was obtained from 4-Me anisole **5b** (268.5 mg, 2.2 mmol), 4-Bromo N-Ac indole **7h** (239.5 mg, 1.00 mmol) and $FeCl_3$ (389.3 mg, 2.4 mmol) in 2 mL of CH_2Cl_2.

melting point: 70-78 °C.

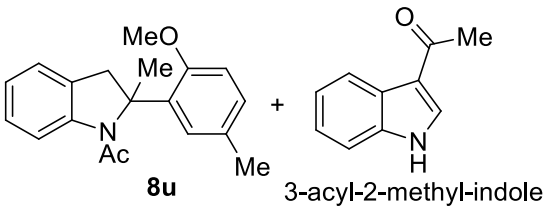
R_f: 0.42 (EtOAc/pet. ether 20:80).

^{1}H-NMR (360 MHz, **$CDCl_3$) δ (ppm) :** 2.01 (s, 3H), 2.17 (s, 3H), 2.87 (dd, *J* = 16.9, 2.4 Hz, 1H), 3.64 – 3.72 (dd, *J* = 16.9, 10.3 Hz, 1H), 3.87 (s, 3H), 5.72 (dd, *J* = 10.1, 2.1 Hz, 1H), 6.75 (s, 1H), 6.81 (d, *J* = 8.3 Hz, 1H), 7.03 (d, *J* = 7.9 Hz, 1H), 7.11 – 7.15 (m, 1H), 7.17 (dd, *J* = 8.0, 1.2 Hz, 1H), 8.30 (d, *J* = 7.5 Hz, 1H).

^{13}C-NMR (90 MHz, **$CDCl_3$) δ (ppm) :** 20.7, 23.8, 39.3, 55.6, 57.6, 110.6, 115.8, 119.5, 125.3, 126.7, 129.2, 129.3, 130.3, 130.8, 144.3, 153.4, 170.0.

IR (ATR), ν (cm^{-1}) : 1672, 1499, 1446, 1377, 1246, 780, 767, 707.

HRMS (ESI^+): calculated ($C_{18}H_{19}BrNaO_2^+$): 360.0594 [M + H^+]; found: 360.0612.



Compound **8u** (41 mg, 30**%** ; colorless oil) was obtained from 4-Me anisole **5b** (268.5 mg, 2.2 mmol), 1-Acetyl-2-methylindole **7i** (80 mg, 0.461 mmol) and $FeCl_3$ (180 mg, 1.1 mmol) in 1 mL of CH_2Cl_2 (along with 3-Acetyl-2-methylindole as a white solid; 22 mg, 28%).

1-(2-(2-methoxy-5-methylphenyl)-2-methylindolin-1-yl)ethanone (8u) :

R_f : 0.26 (EtOAc/Cyclohexane 20:80).

^{1}H NMR (360 MHz, $CDCl_3$) δ (ppm) : 1.73 (s, 3H), 1.88 (s, 3H), 2.32 (s, 3H), 3.06 (d, *J* = 14.5 Hz, 1H), 3.59 (s, 3H), 3.59 (d, *J* = 14.5 Hz, 1H), 6.81 (d, *J* = 8.0 Hz, 1H), 7.05-7.00 (m, 1H), 7.15-7.08 (m, 2H), 7.17 (d, *J* = 1.8 Hz, 1H), 7.25-7.19 (m, 1H), 8.38 (d, *J* = 8.0 Hz, 1H).

^{13}C NMR (90 MHz, $CDCl_3$) δ (ppm) : 20.9, 24.6, 27.1, 47.4, 55.9, 67.1, 112.2, 118.4, 123.4, 123.9, 127.4, 127.5, 129.6, 129.6, 129.8, 132.7, 143.5, 155.5, 169.7.

IR (NaCl), ν (cm^{-1}) : 2935, 2834, 1649, 1598, 1498, 1481, 1461, 1379, 1250, 1140, 1028, 754

HRMS (ESI^+) : calculated: 318.1465 ($[C_{19}H_{21}NNaO_2]^+$;$[M+Na]^+$); found: 318.1456

3-Acetyl-2-methylindole :

melting point: 155-160 °C

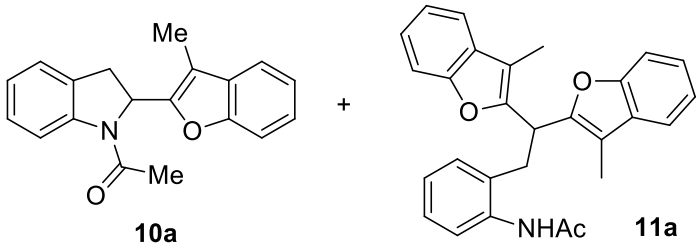
R_f: 0.26 (EtOAc/Cyclohexane 30:70)

^{1}H NMR (300 MHz, DMSO-d^6) δ (ppm) : 2.51 (s, 3H), 2.67 (s, 3H), 7.16-7.10 (m, 2H), 7.39-7.33 (m, 1H), 8.04-7.98 (m, 1H), 11.83 (br, 1H).

^{13}C NMR (75.5 MHz, DMSO-d^6) δ (ppm) : 15.0, 30.9, 111.1, 113.5, 120.6, 121.2, 121.7, 126.9, 134.7, 144.1, 193.0.

IR (NaCl), ν (cm^{-1}) : 3169, 3102, 2918, 1610, 1578, 1486, 1458, 1415, 1192, 1027, 969, 738

HRMS (ESI^+) : calculated: 174.0913 ($[C_{11}H_{12}NO]^+$;$[M+H]^+$); found: 174.0908



1-(2-(3-methylbenzofuran-2-yl)indolin-1-yl)ethanone (10a) :

Compounds **10a** (40 mg, 14% ;gummy) and **11a** (349.4 mg, 83% ; yellow solid) were obtained from 3-methylbenzofuran **9a** (290.2 mg, 2.2 mmol), N-Ac indole **7a** (159.4 mg, 1.00 mmol) and $FeCl_3$ (389 mg, 2.4 mmol) in 2 mL of CH_2Cl_2.

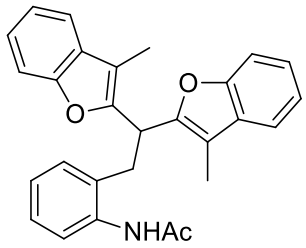
R_f: 0.25 (EtOAc/pet. ether 20:80).

^{1}H-NMR (250 MHz, **$CDCl_3$) δ (ppm) :** 2.21 (s, 3H), 2.45 (br s, 3H), 3.11 (d, *J* = 15.7 Hz, 1H), 3.76 (dd, *J* = 15.7, 10.3 Hz, 1H), 5.67 (d, *J* = 10.3 Hz, 1H), 6.91-6.93 (m, 2H), 7.04-7.32 (m, 5H), 8.28 (d, *J* = 7.5 Hz, 1H).

^{13}C-NMR (75 MHz, **$CDCl_3$) δ (ppm) :** 23.9, 39.3, 60.0, 117.3, 123.7, 124.1, 124.4, 124.9, 126.7, 127.8, 129.0, 146.2, 169.1.

IR (ATR), ν (cm^{-1}) : 2902, 1655, 1477, 1398, 1277, 1238, 752, 731.

HRMS (ESI^+): calculated ($C_{19}H_{18}NO_2^+$): 292.1332 [M + H^+]; found: 292.1342.



N-(2-(2,2-bis(3-methylbenzofuran-2-yl)ethyl)phenyl)acetamide (11a) :

Melting point: 49-56°C.

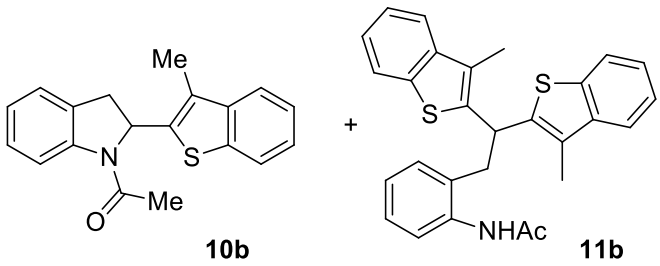
R_f: 0.07 (EtOAc/pet. ether 20:80).

^{1}H-NMR (360 MHz, $CDCl_3$) δ (ppm) : 2.00 (s, 6H), 2.03 (s, 3H), 3.57 (d, *J* = 7.5, 2H), 4.64 (t, *J* = 7.5 Hz, 1H), 7.00 (br, 1H), 7.10 (t, *J* = 7.9 Hz, 1H), 7.18-7.32 (m, 6H), 7.44 (d, *J* = 7.2 Hz, 2H), 7.51 (d, *J* = 7.9 Hz, 2H),7.59 (d, *J* = 7.5 Hz, 1H).

^{13}C NMR (90 MHz, $CDCl_3$) δ (ppm) : 7.7, 24.1, 33.4, 37.9, 111.1, 111.7, 119.4, 122.6, 124.1, 124.9, 125.9, 127.5, 130.0, 130.4, 131.6, 135.6, 150.9, 153.9, 168.8.

IR (ATR), ν (cm^{-1}) : 3244, 1689, 1454, 1181, 1043, 744.

HRMS (ESI$^+$): calculated ($C_{28}H_{25}NNaO_3^+$): 446.1727 [M + Na^+]; found: 446.1748.



Compounds **10b** (21.9 mg, 14% ;yellow gum) and **11b** (129 mg, 56%, yellow gum) were obtained from 3-methylbenzothiophen **9b** (133 μL, 1.018 mmol), N-Ac indole **7a** (81.0 mg, 0.509 mmol) and $FeCl_3$ (214.8 mg, 1.32 mmol) in 0.6 mL of CH_2Cl_2.

1-(2-(3-methylbenzo[b]thiophen-2-yl)indolin-1-yl)ethanone (10b) :

R_f: 0.65 (EtOAc/pet. ether 30:70).

^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) : 2.16 (s, 3H), 2.49 (s, 3H), 3.11 (d, *J* = 15.8 Hz, 1H), 3.84 (dd, *J* = 15.8, 9.5 Hz, 1H), 5.84 (d, *J* = 9.5 Hz, 1H), 7.06-7.41 (m, 5H), 7.65-7.70 (m, 2H), 8.31 (d, *J* = 7.5 Hz, 1H).

^{13}C-NMR (90 MHz, **$CDCl_3$**) **δ (ppm) :** 11.9, 23.9, 38.4, 58.6, 117.4, 121.6, 122.5, 124.2, 124.3, 124.6, 124.8, 128.0, 128.8, 137.9, 140.2, 169.1.

HRMS (ESI$^+$): calculated ($C_{19}H_{17}NNaOS^+$): 330.0923 [M + Na^+]; found: 330.0924.

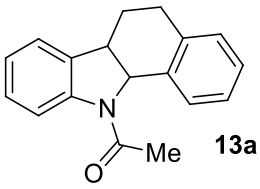
N-(2-(2,2-bis(3-methylbenzo[b]thiophen-2-yl)ethyl)phenyl)acetamide (11b) :

R_f: 0.40 (EtOAc/pet. ether 30:70).

^{1}H-NMR (250 MHz, **$CDCl_3$**) **δ (ppm) :** 1.78 (s, 3H), 2.02 (s, 6H), 3.52 (d, *J* = 7.5 Hz, 2H), 5.07 (t, *J* = 7.5 Hz, 1H), 6.43 (br, 1H), 7.15-7.44 (m, 7H), 7.56-7.63 (m, 3H), 7.81-7.85 (m, 2H)

^{13}C-NMR (90 MHz, **$CDCl_3$**) **δ (ppm) :** 11.4, 23.6, 39.7, 41.4, 121.9, 122.4, 124.4, 124.5, 124.7, 125.7, 127.5, 128.9, 130.9, 131.2, 136.0, 138.0, 140.1, 140.3, 168 .6.

HRMS (ESI$^+$): calculated ($C_{28}H_{25}NOS_2Na^+$): 478.127 [M + Na^+]; found: 478.1269.



13a

1-(6,6a-dihydro-5H-benzo[a]carbazol-11(11aH)-yl)ethanone (13a):

Compound **13a** (172.0 mg, 48%; yellow gummy) was obtained from **12a** (355 mg, 1.35 mmol), and $FeCl_3$ (525.2 mg, 3.2 mmol) in 27 mL of CH_2Cl_2 (0.05M).

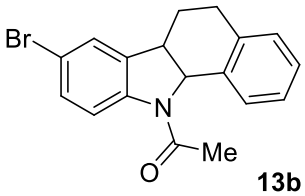
R_f: 0.25 (EtOAc/pet. ether 20:80).

^{1}H-NMR (400 MHz, DMSO-d^6, 365 K) δ (ppm) : 1.92-1.96 (m, 1H), 2.33-2.39 (m, 1H), 2.36 (s, 3H),, 2.62-2.66 (m, 2H), 3.96-4.01 (m, 1H), 5.71 (d, *J* = 8.6 Hz, 1H), 7.02-7.08 (m, 2H), 7.11-7.18 (m, 3H), 7.23 (d, *J* = 8.0 Hz, 1H), 7.41 (d, *J* = 7.7 Hz, 1H), 7.56 (d, *J* = 7.7 Hz, 1H).

^{13}C-NMR (100 MHz, DMSO-d^6, 365K) δ (ppm) : 22.7, 23.3, 25.4, 38.8, 60.7, 116.6, 123.1, 123.3, 125.7, 126.3, 126.4, 126.8, 127.1, 135.1, 135.6, 138.1, 141.8, 168.1.

IR (ATR), ν (cm^{-1}) : 1653, 1480, 1388, 1268, 1244, 751.

HRMS (ESI$^+$): calculated ($C_{18}H_{17}NNaO^+$): 286.1208 [M + Na^+]; found: 286.1205.



13b

1-(8-bromo-6,6a-dihydro-5H-benzo[a]carbazol-11(11aH)-yl)ethanone (13b) :

Compound **13b** (140.0 mg, 41%; yellow solid) was obtained from **12b** (343 mg, 1 mmol), and $FeCl_3$ (390 mg, 2.4 mmol) in 20 mL of CH_2Cl_2 (0.05M).

Melting point: 95-102 °C.

R_f: 0.23 (EtOAc/pet. ether 20:80).

^{1}H-NMR (400 MHz, DMSO, 360 K) δ (ppm) : 1.87-1.91 (m, 1H), 2.36 (s, 3H), 2.36-2.40 (m, 1H), 2.63-2.67 (m, 2H), 4.02-4.05 (m, 1H), 5.69 (d, *J* = 8.0 Hz, 1H), 7.10 (d, J = 7.5 Hz, 1H), 7.13-7.20 (m, 2H), 7.29-7.36 (m, 2H), 7.40 (s, 1H), 7.56 (d, *J* = 7.5 Hz, 1H).

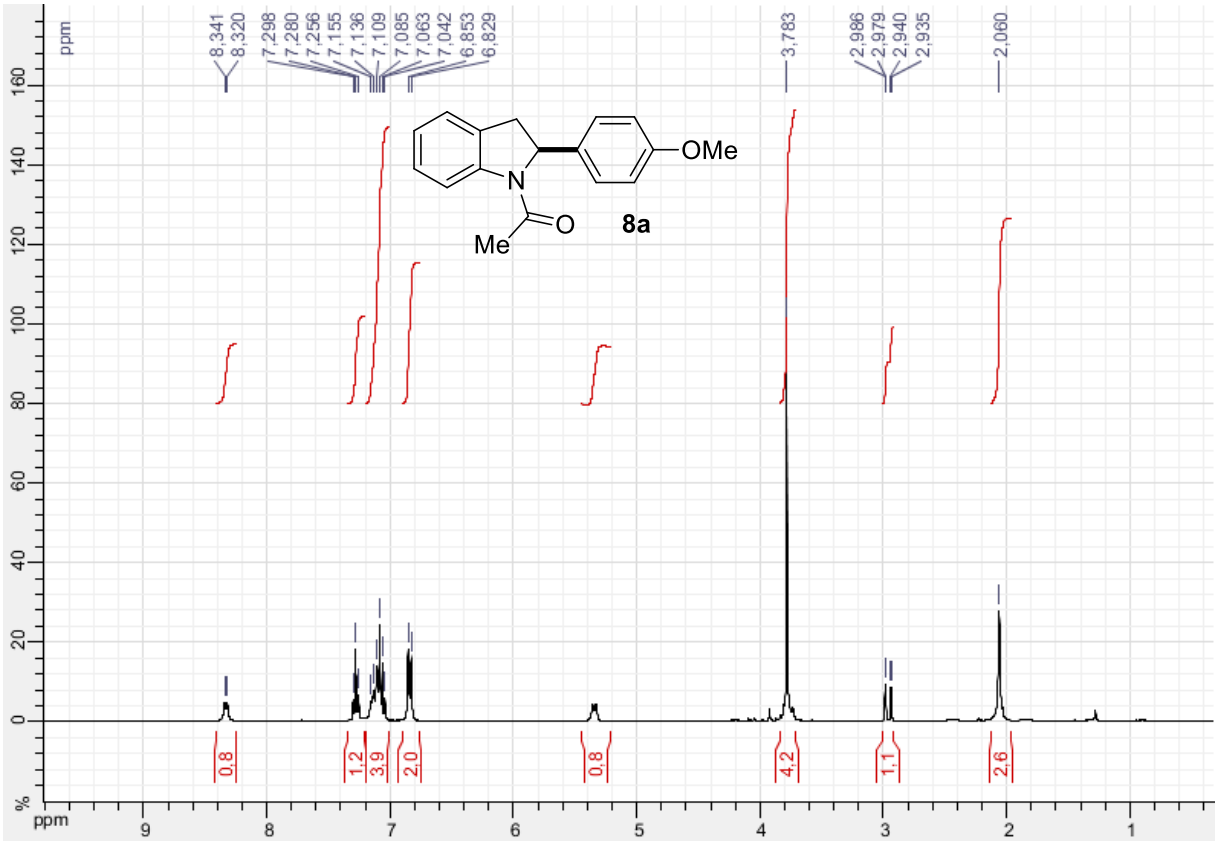
^{13}C-NMR (100 MHz, DMSO, 360 K) δ (ppm) : 22.7, 23.2, 25.5, 38.8, 60.9, 115.2, 118.4, 125.8, 126.2, 126.3, 126.5, 127.2, 129.2, 134.6, 138.1, 138.6, 141.2, 168.2

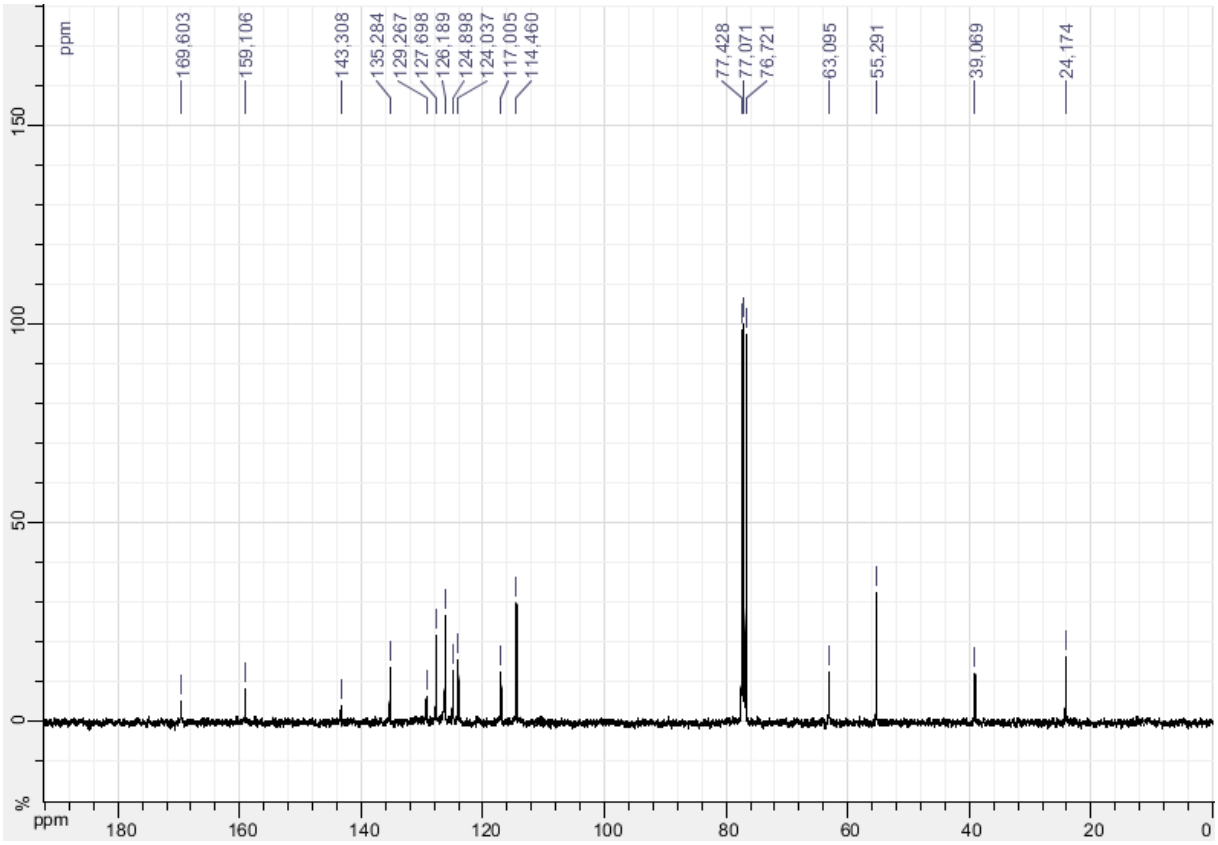
IR (ATR), ν (cm^{-1}) : 1650, 1491, 1383, 1257, 831, 793.

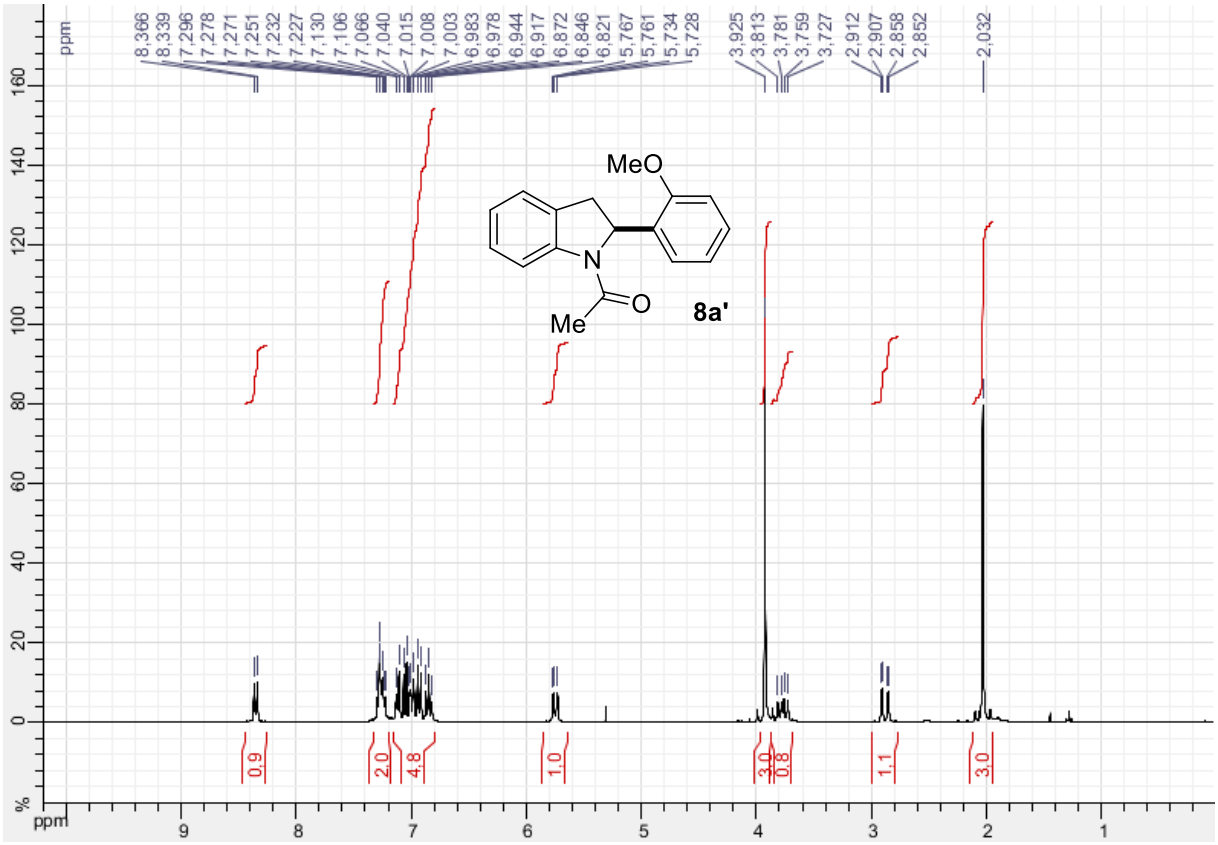
HRMS (ESI^{+}): calculated ($C_{18}H_{17}BrNO^{+}$)$^{+}$: 344.0473 [M + H $^{+}$]; found: 344.0461.

III 1H NMR and 13C NMR spectra

Recorded in $CDCl_3$ unless otherwise noted



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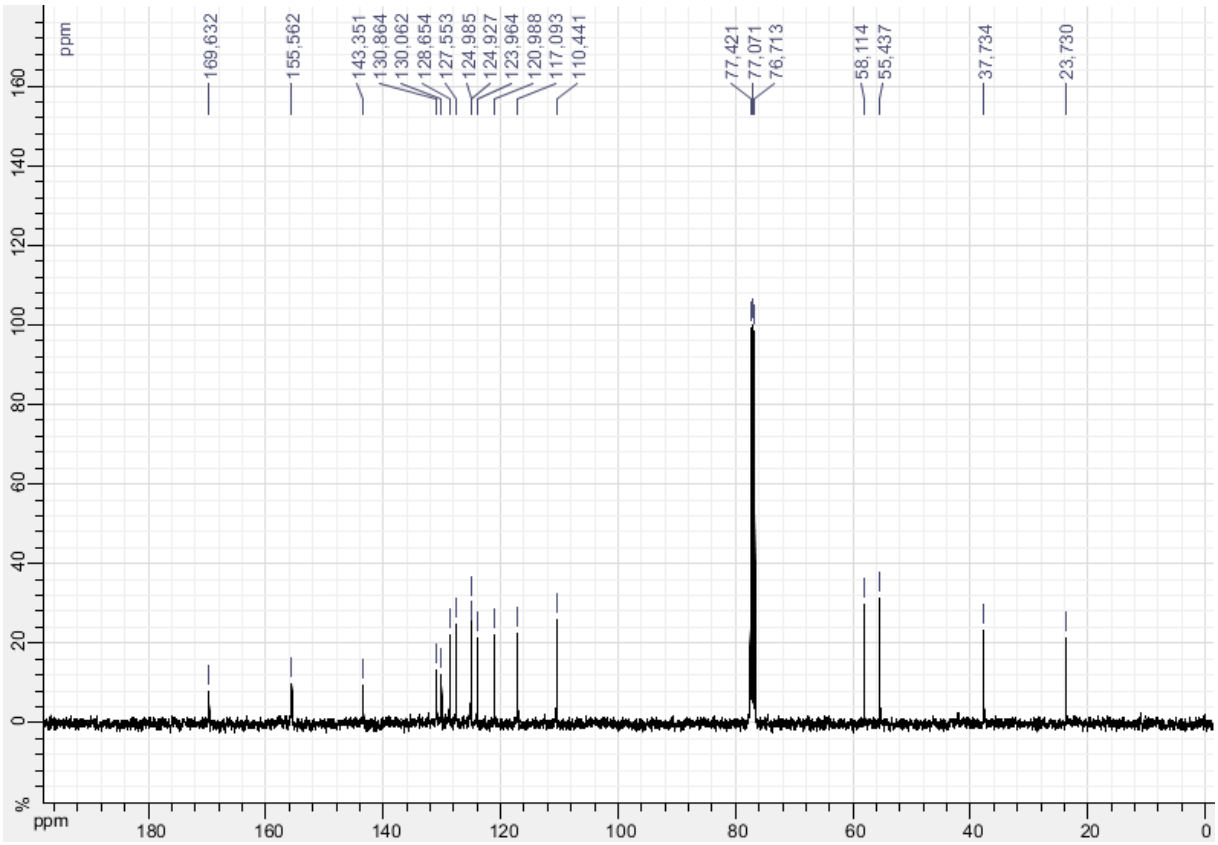
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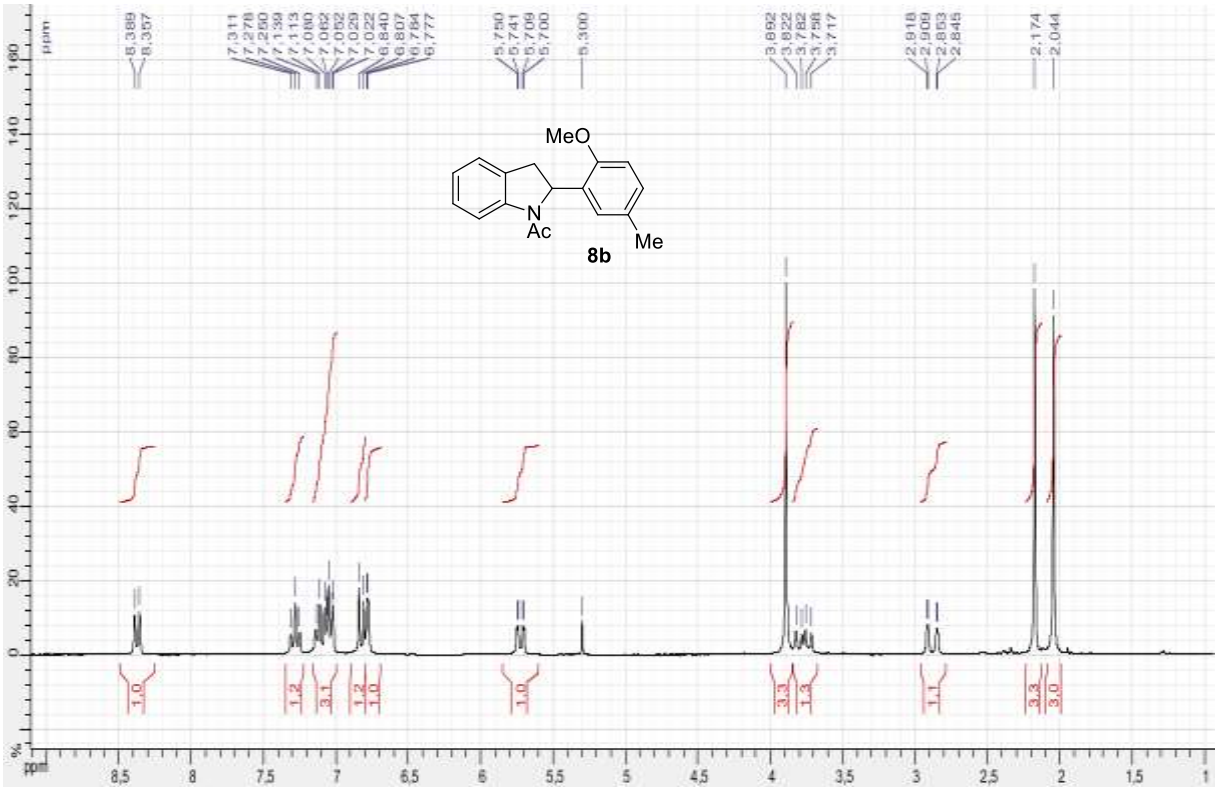
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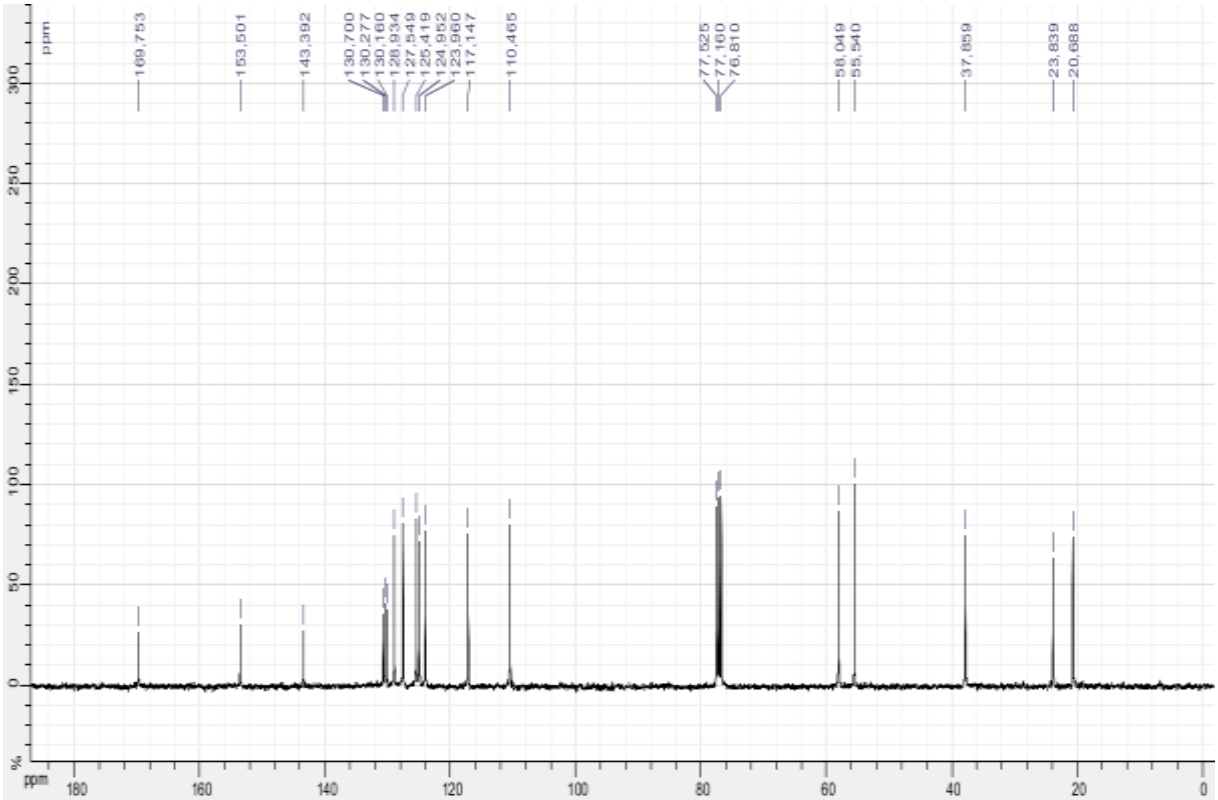

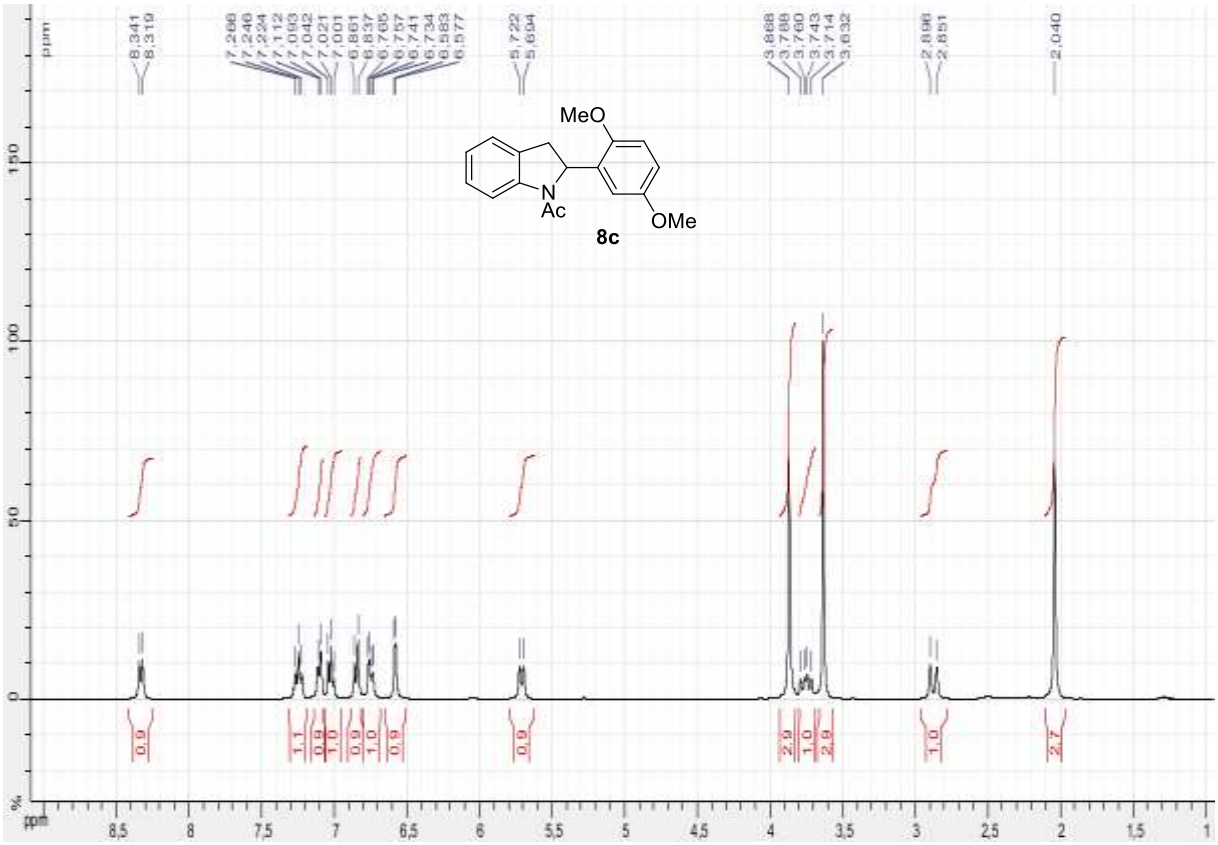
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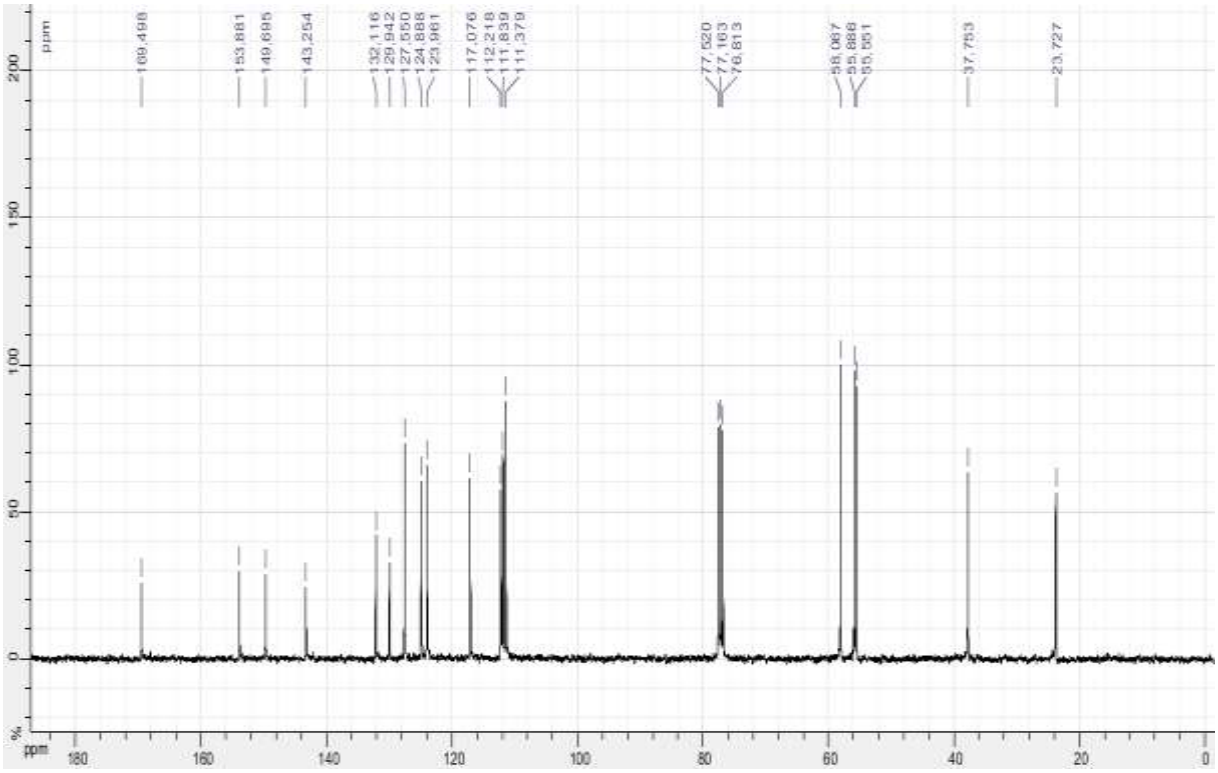
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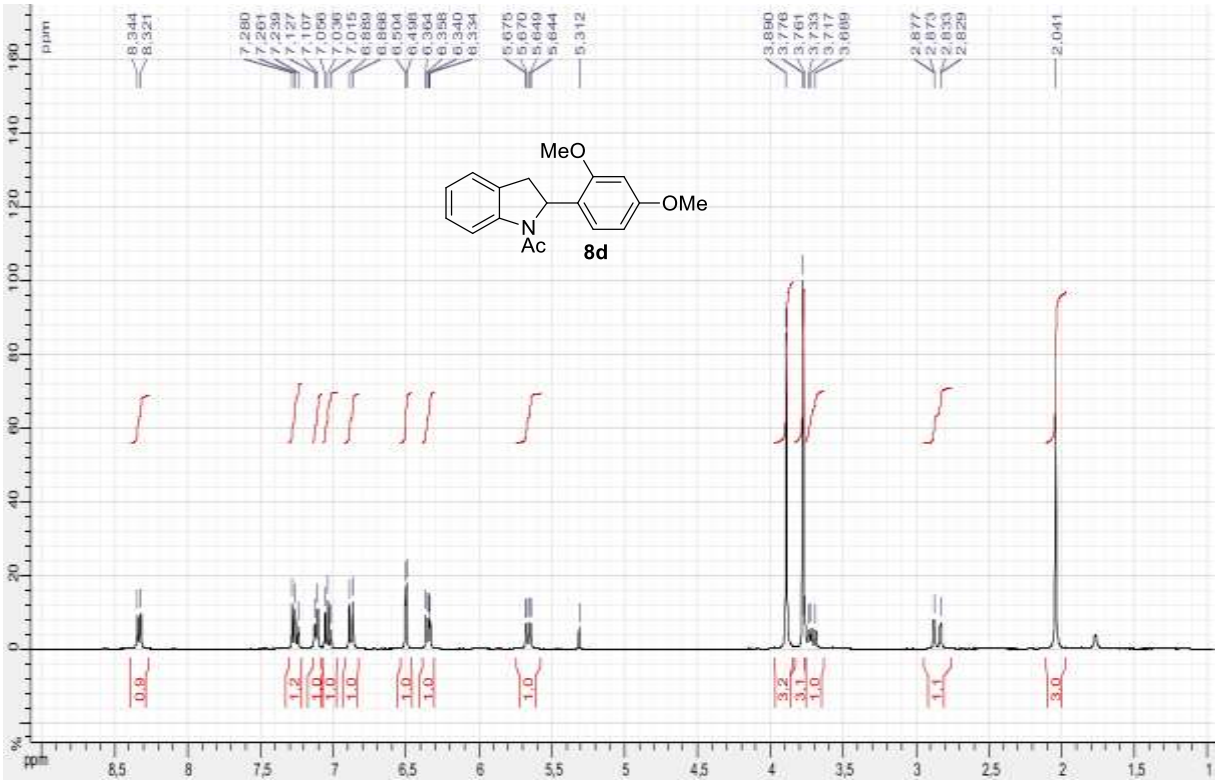
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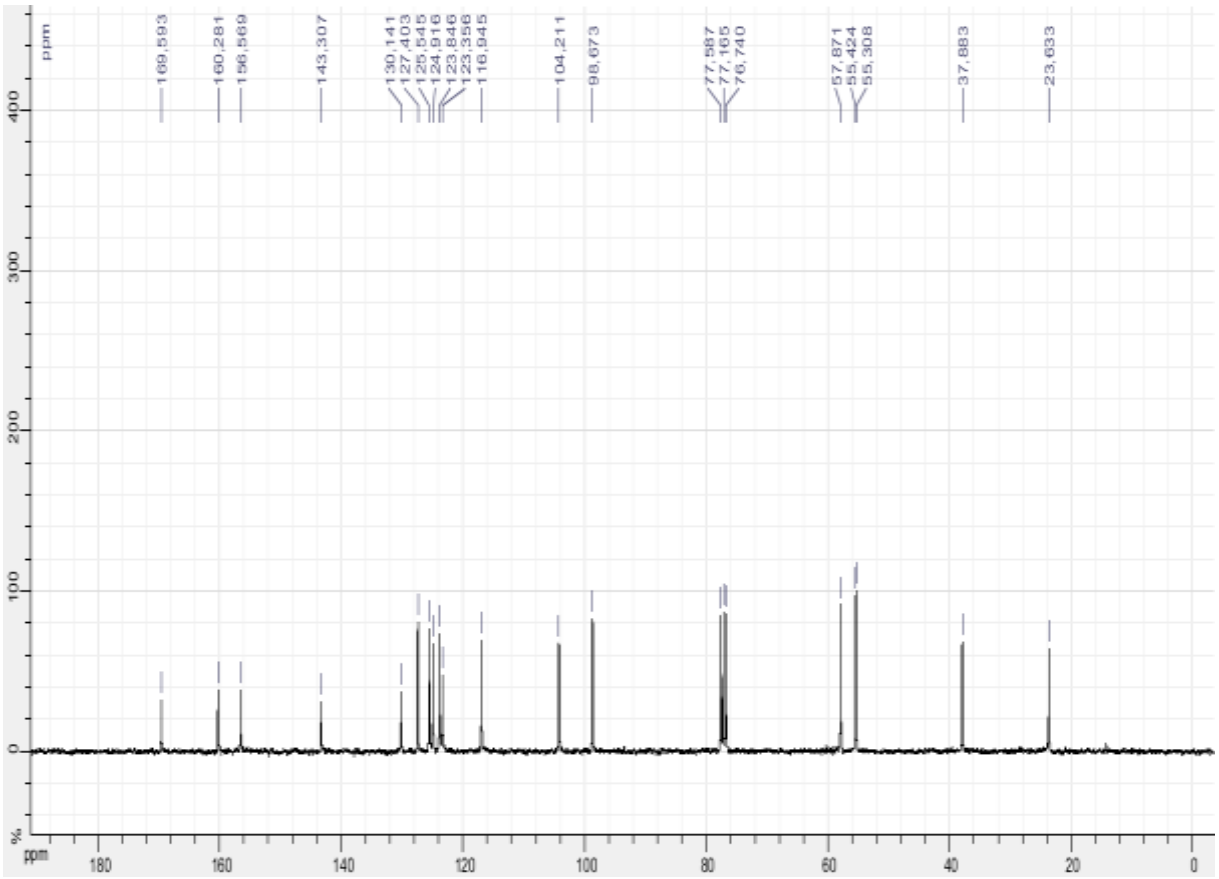
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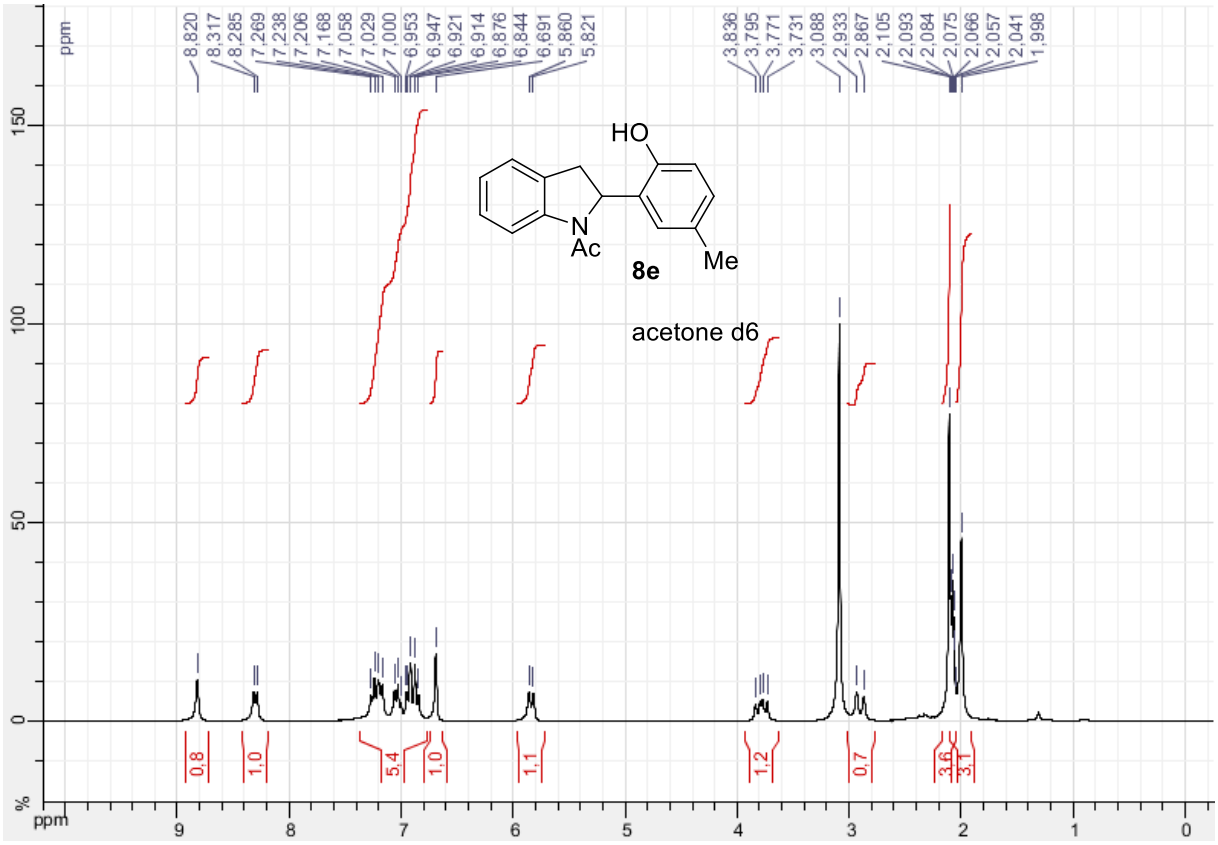
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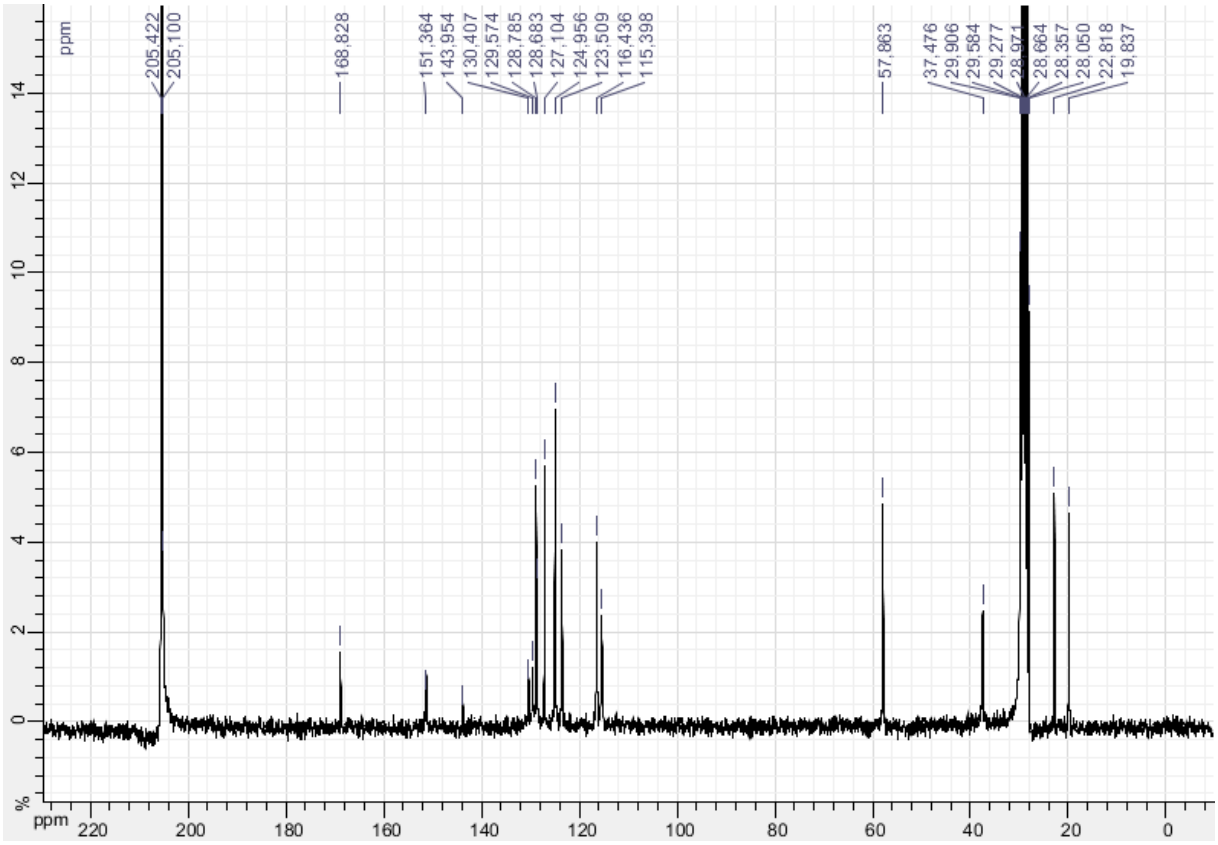
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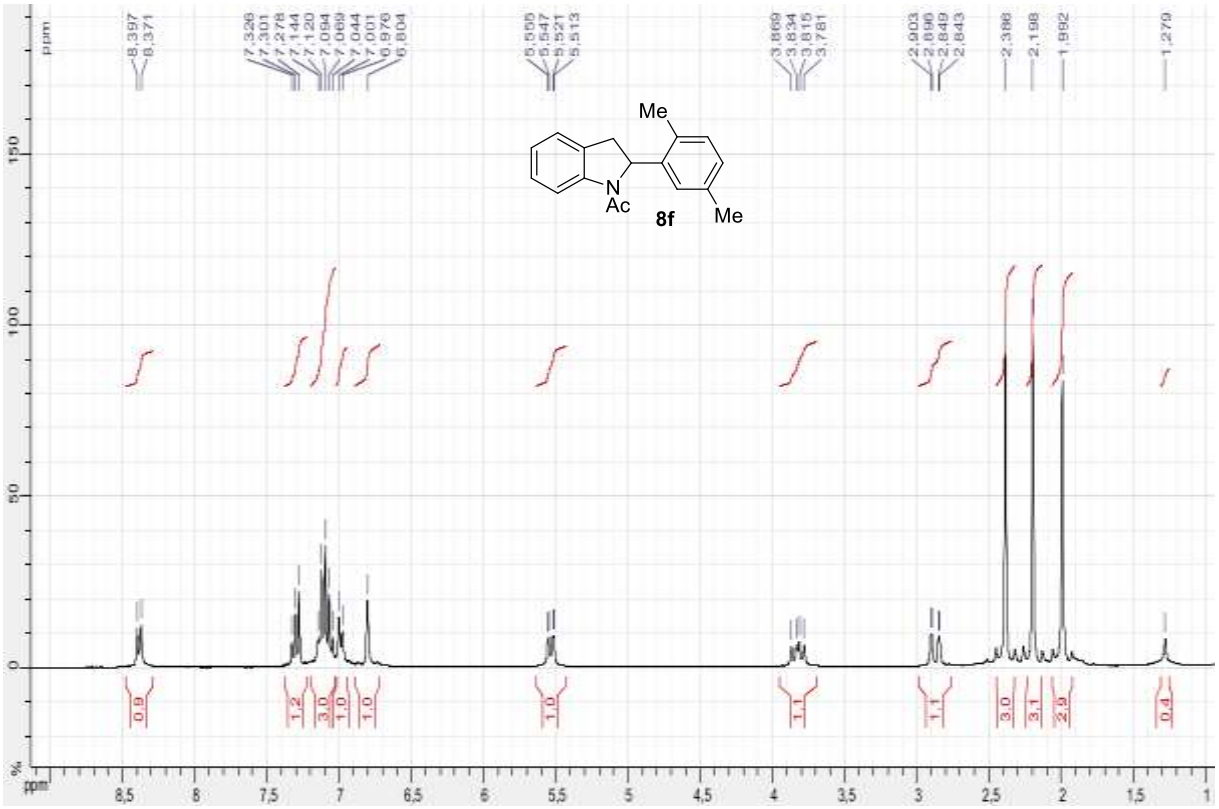
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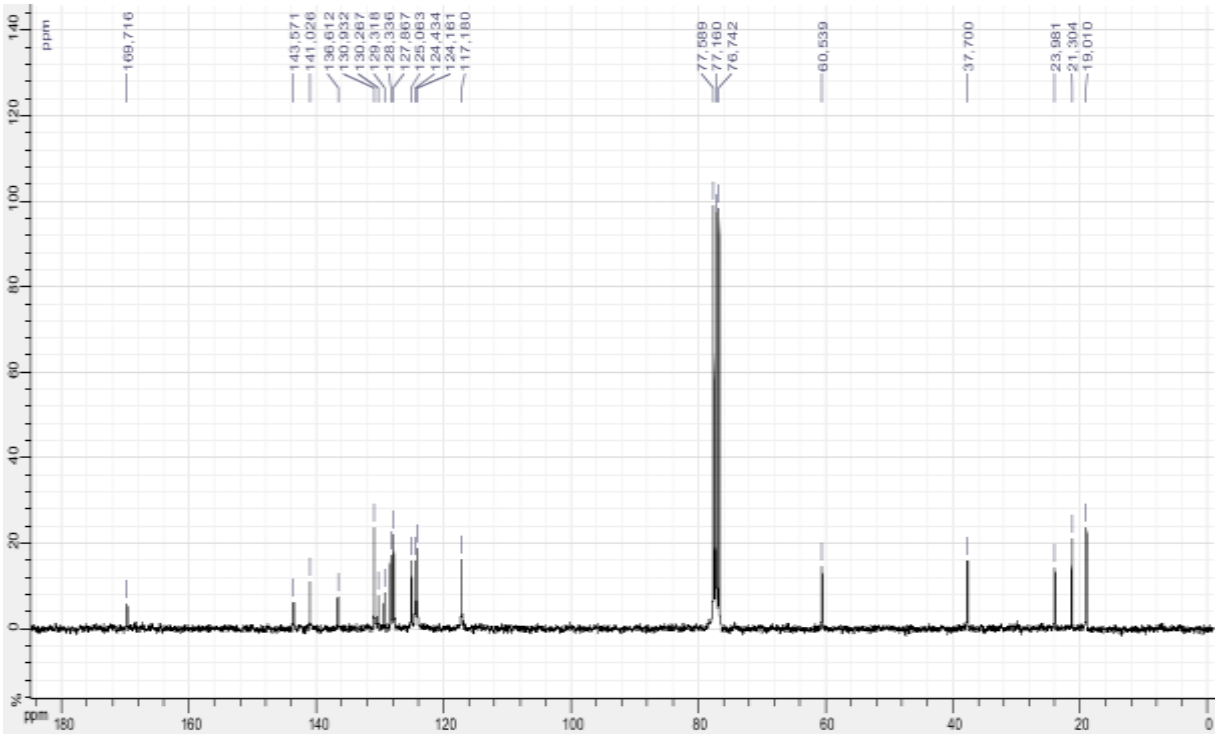
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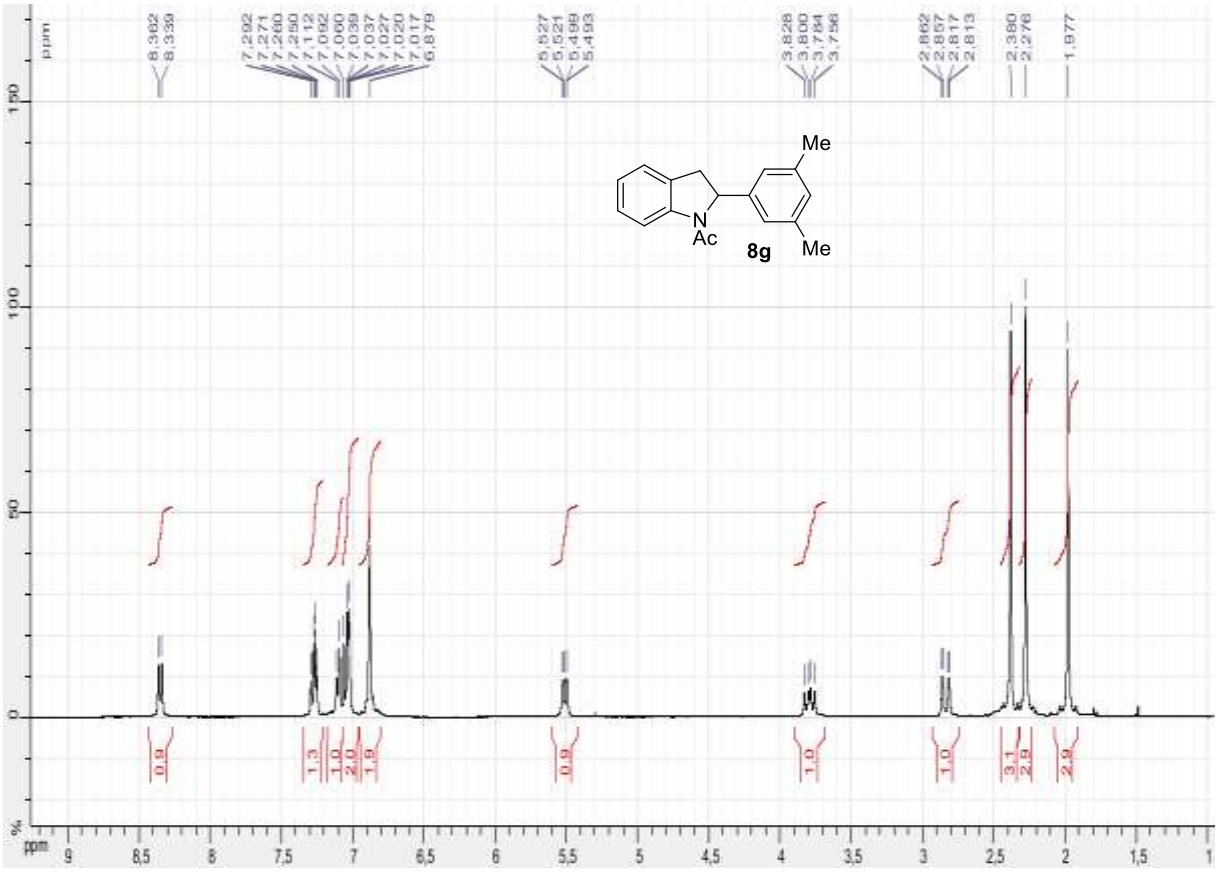
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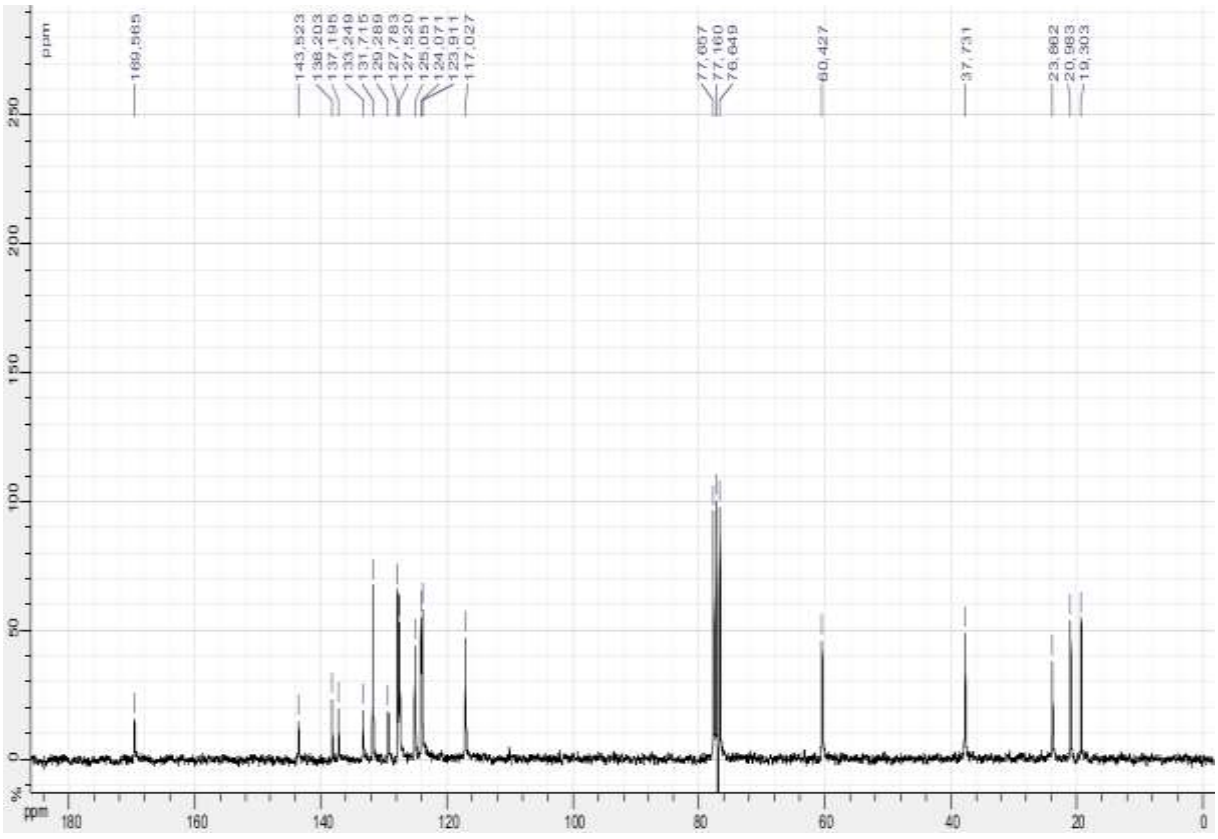
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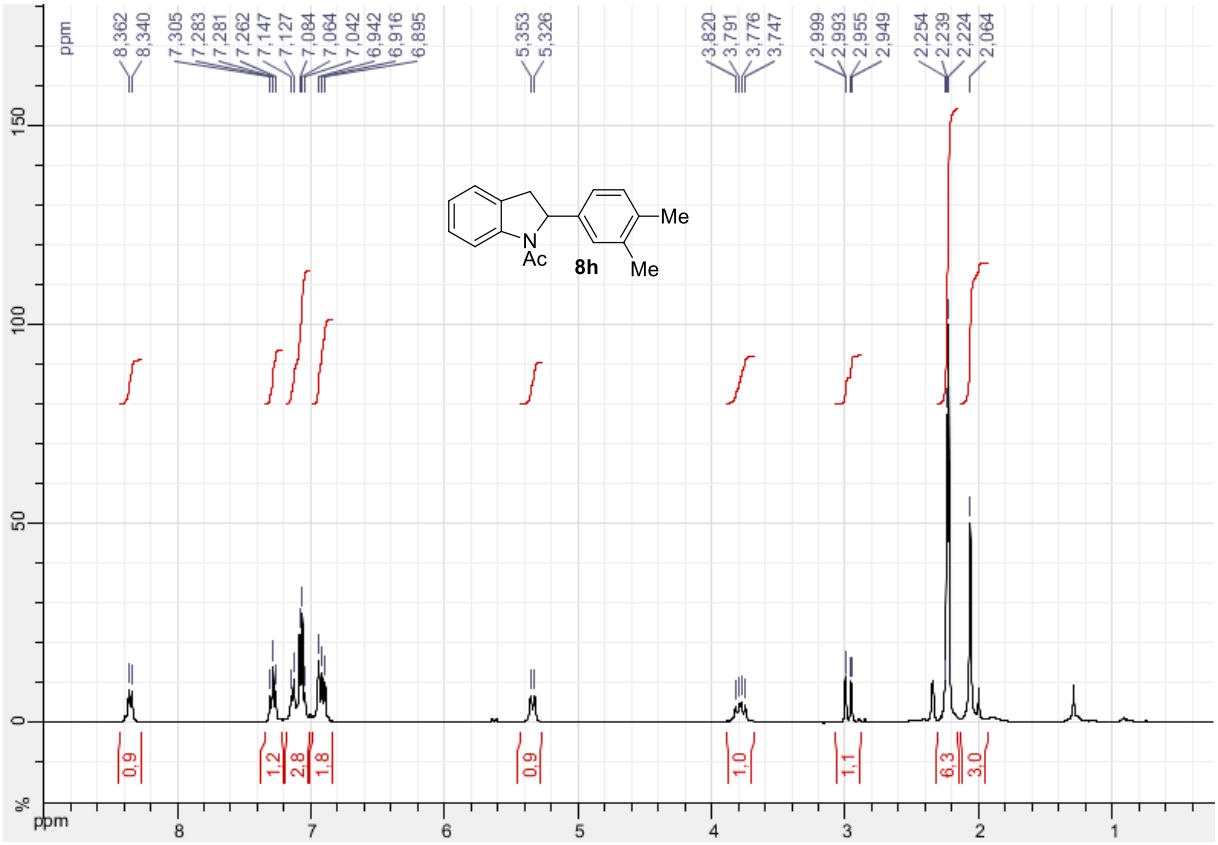
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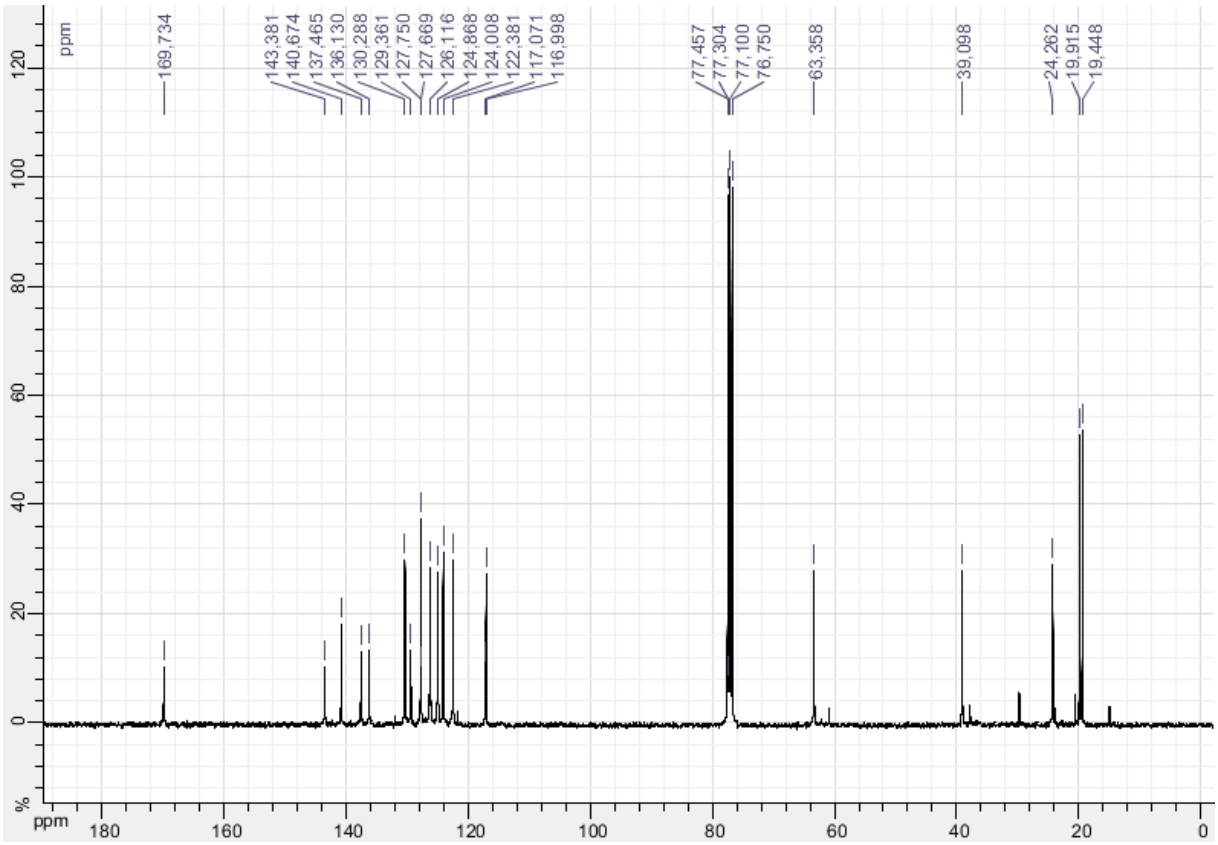
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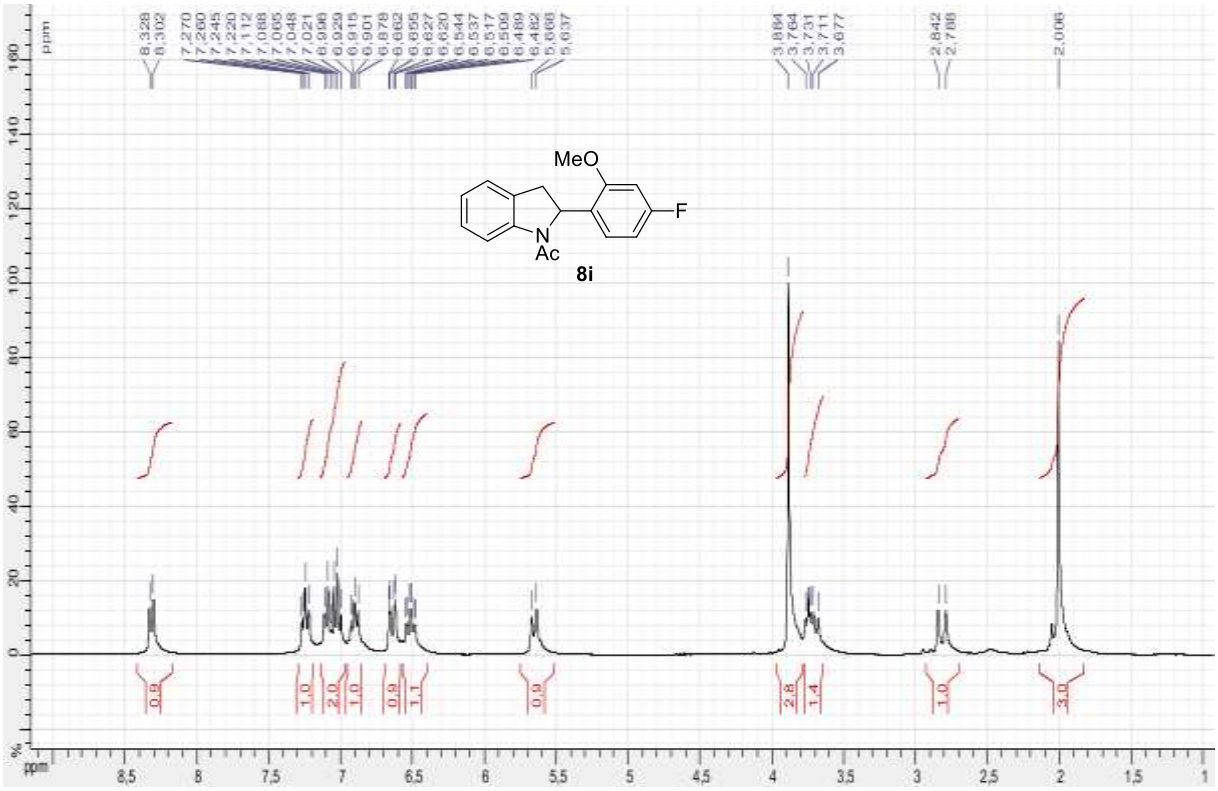
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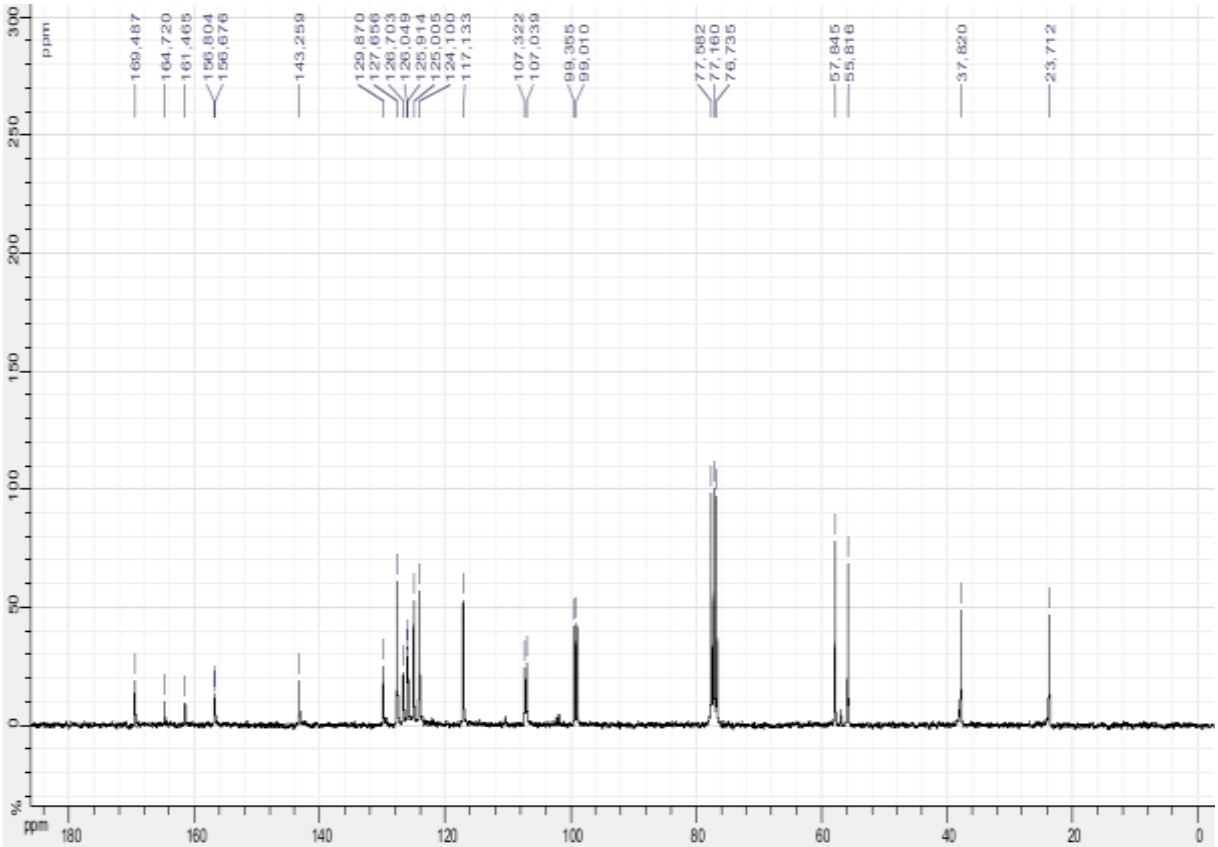
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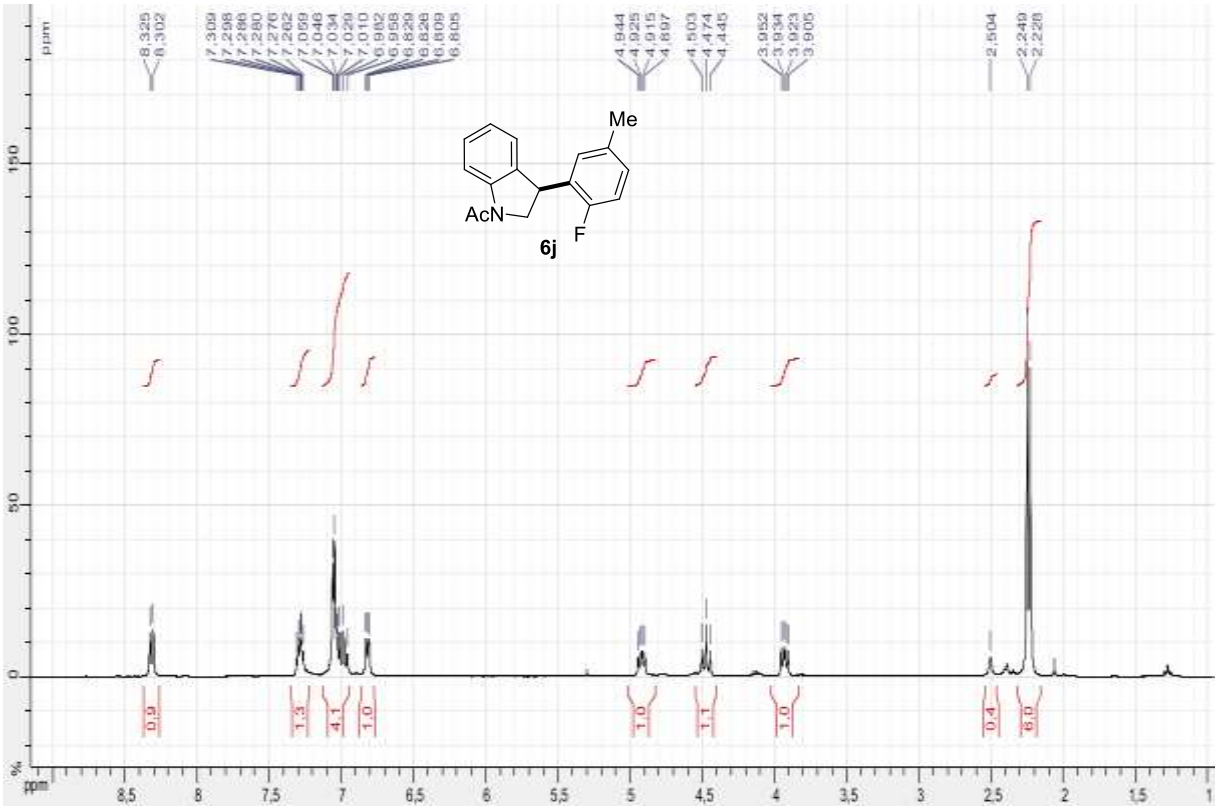
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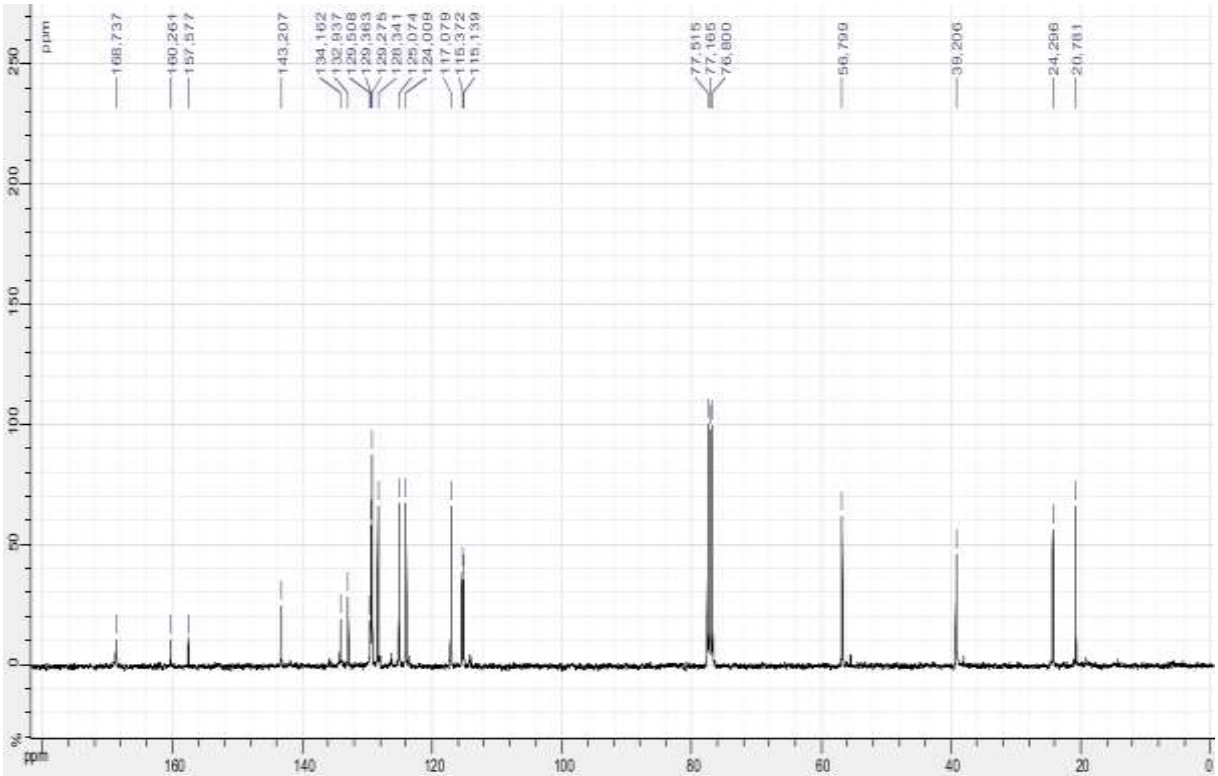
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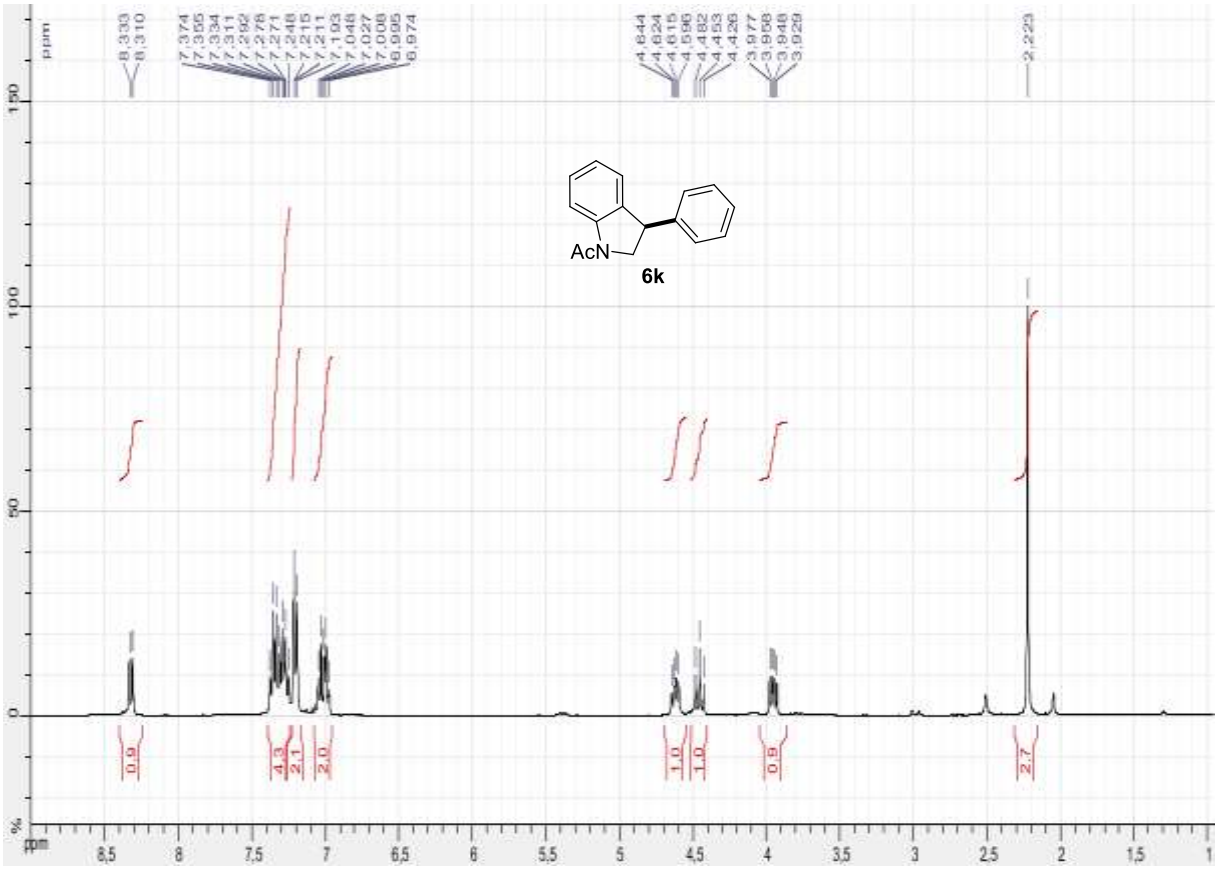
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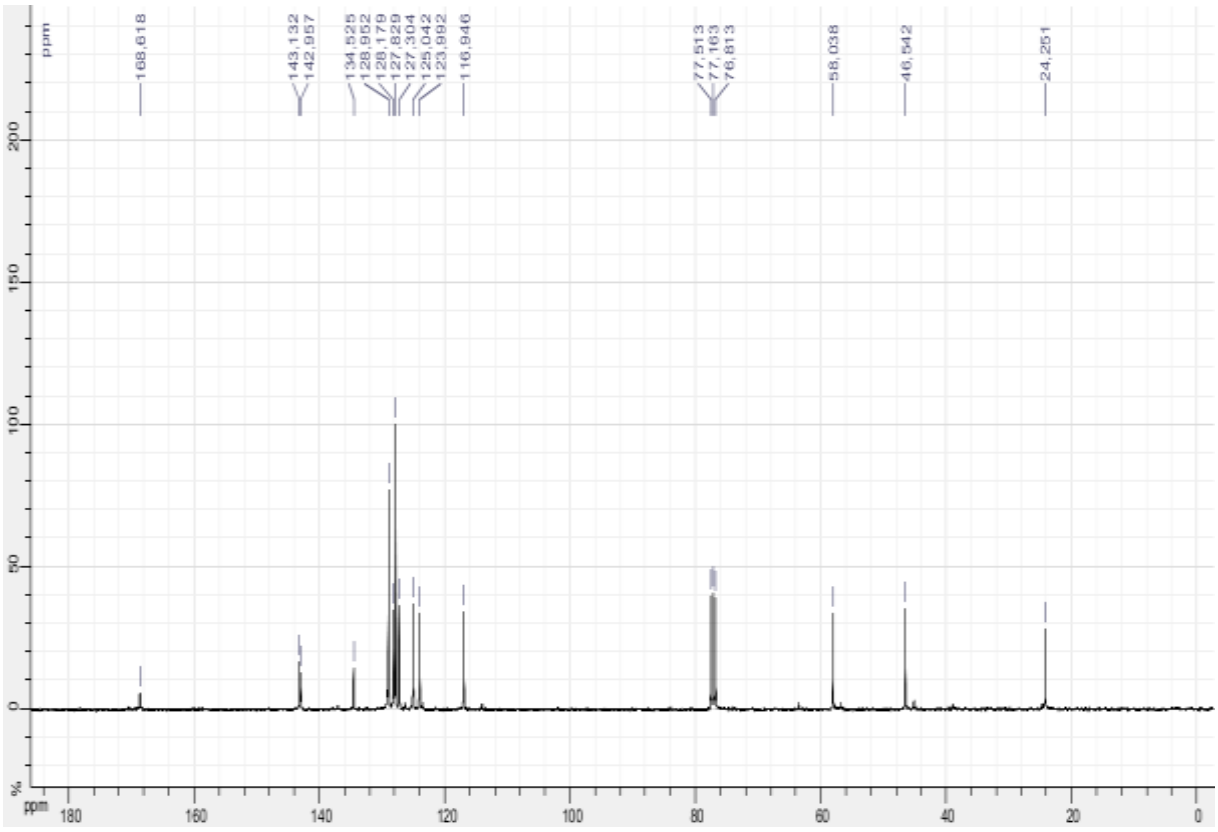
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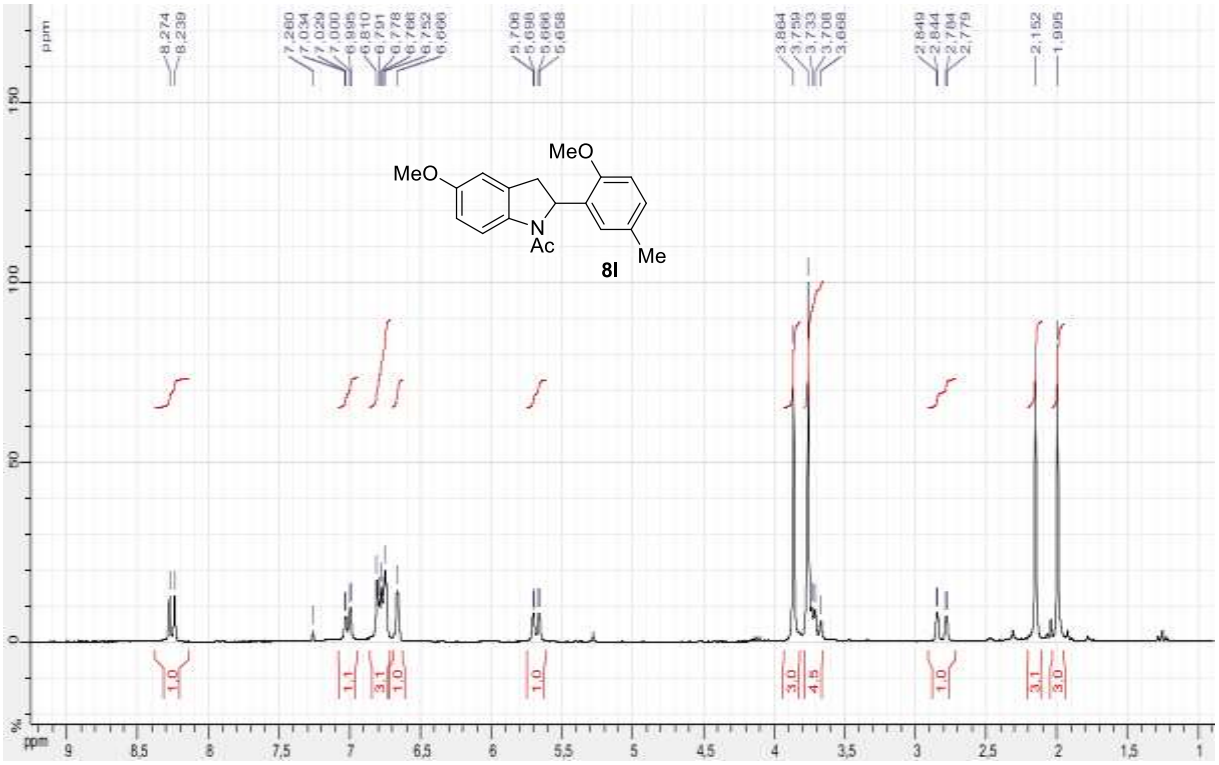
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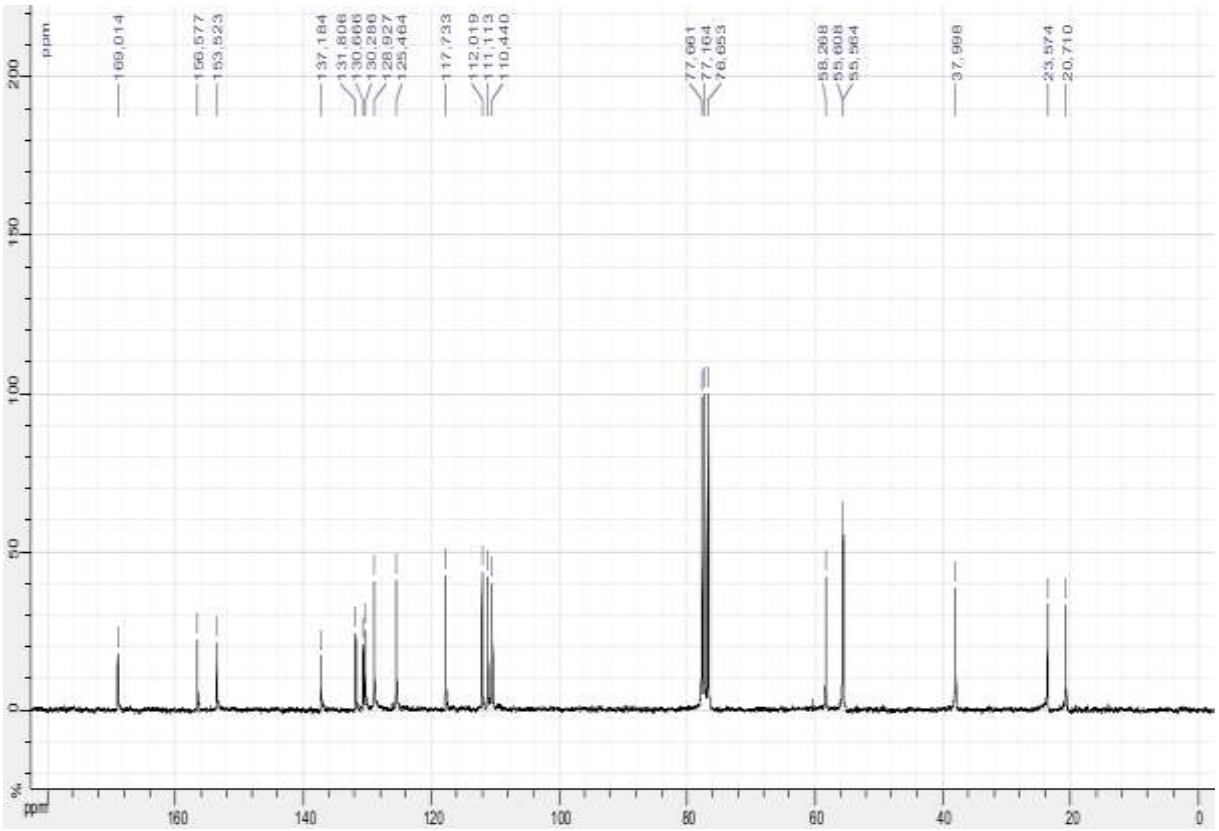
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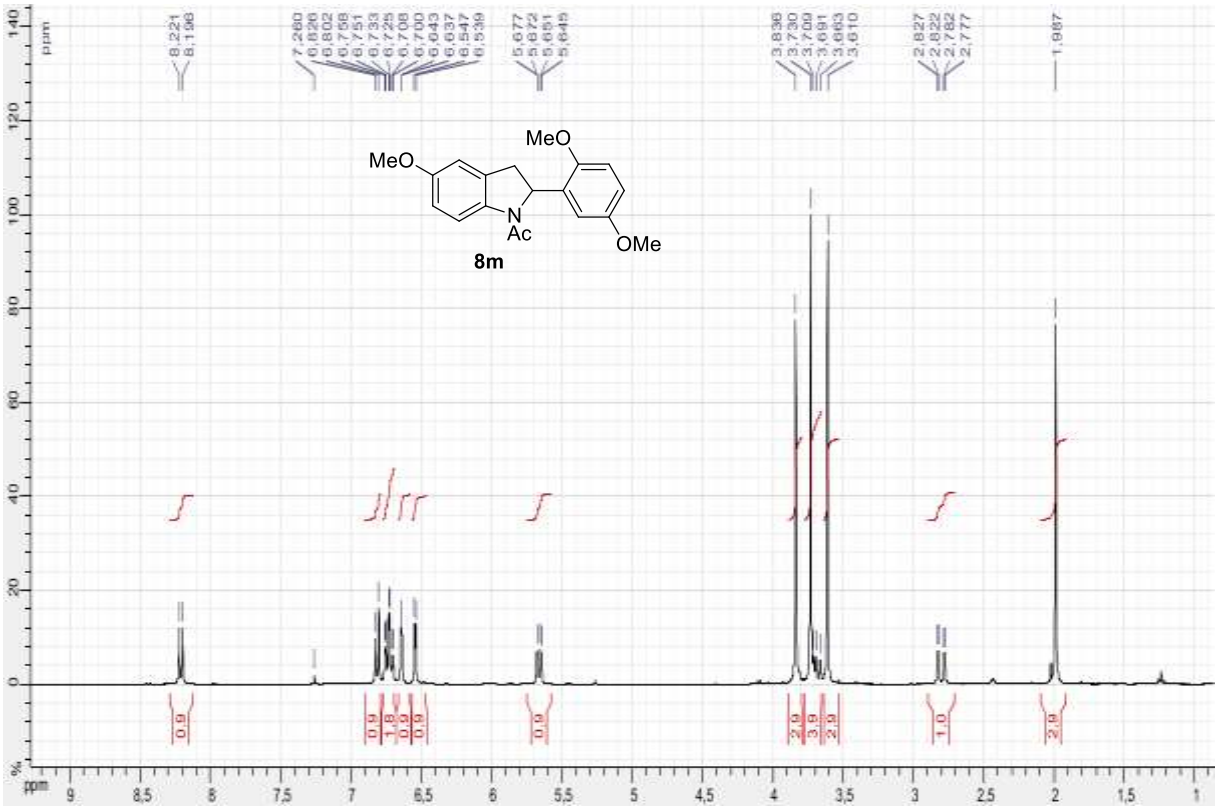
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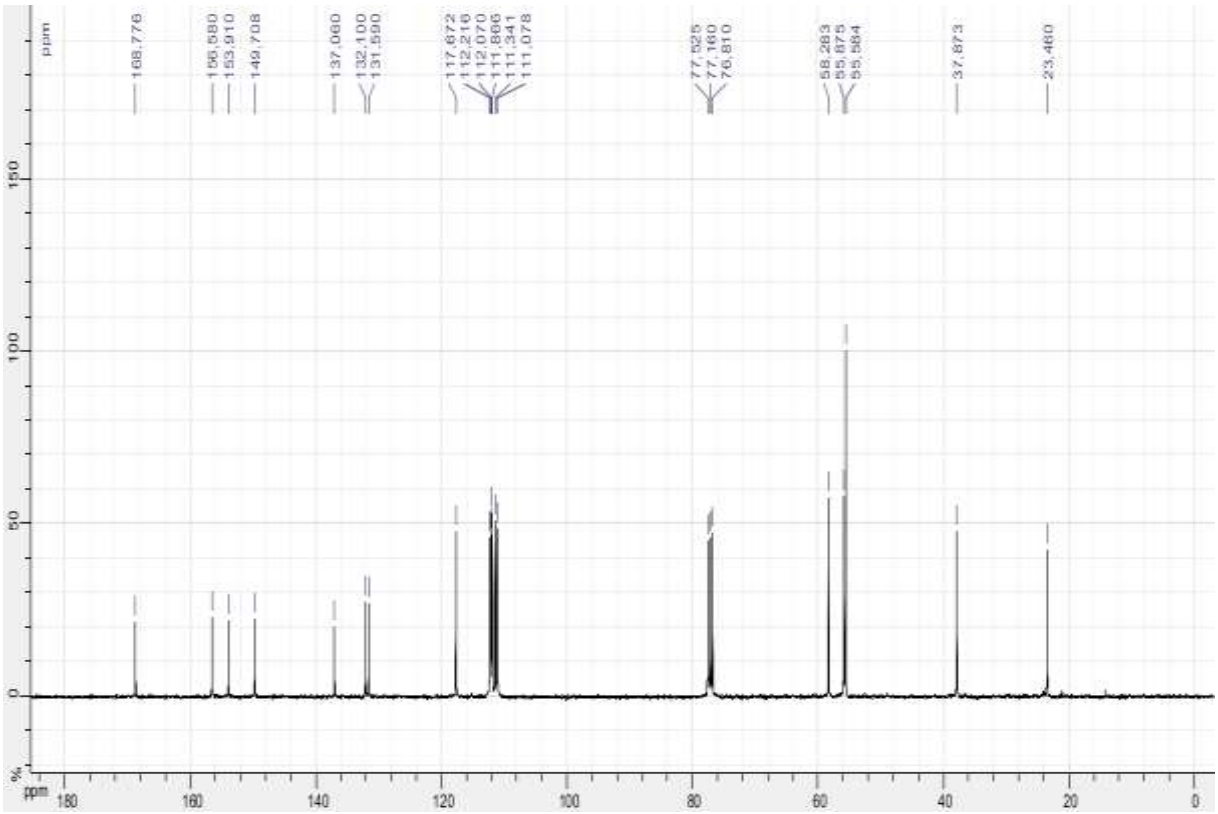

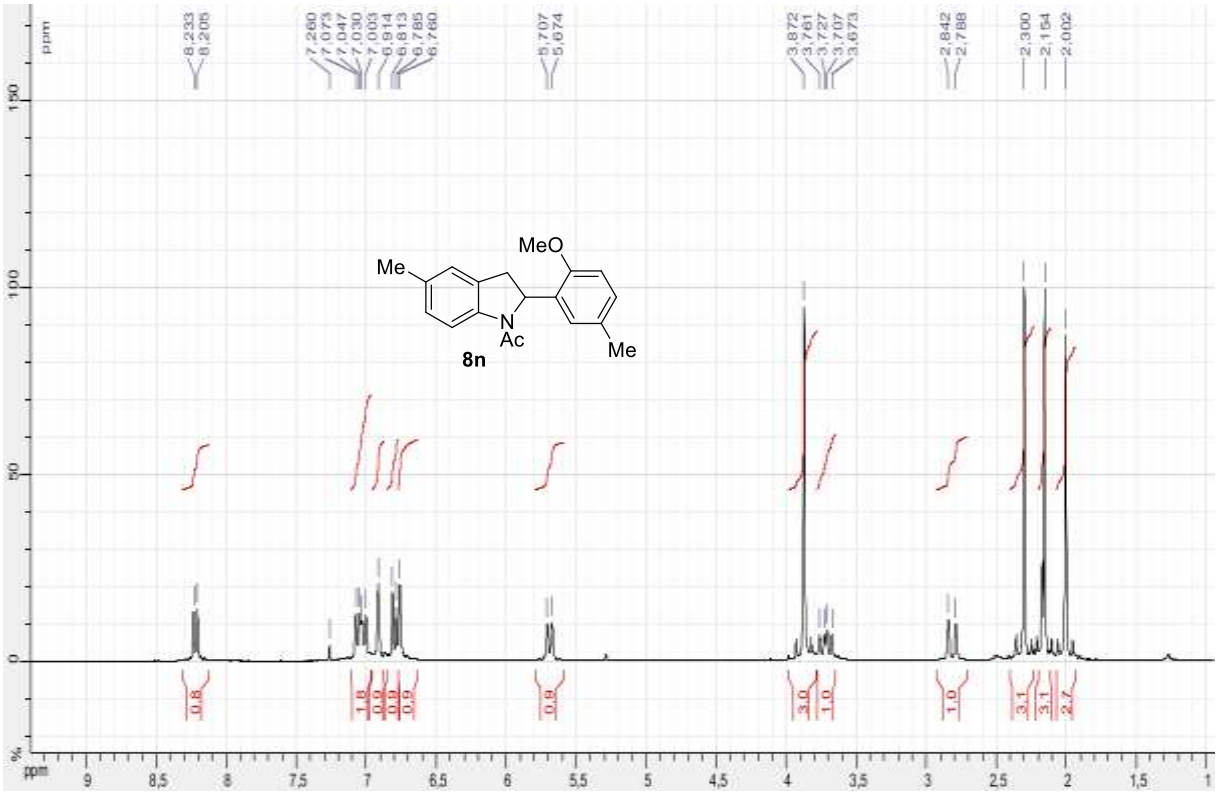
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2.154
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Me
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Ac
Me
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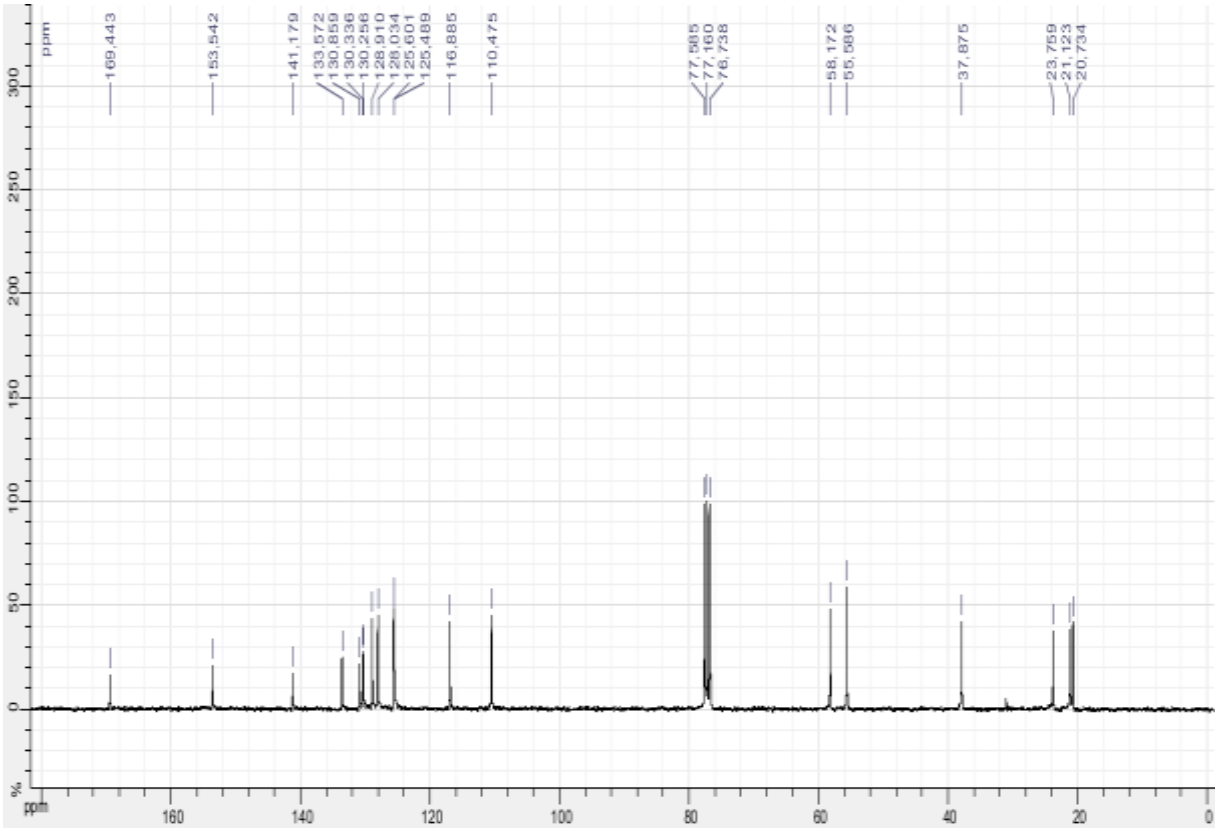
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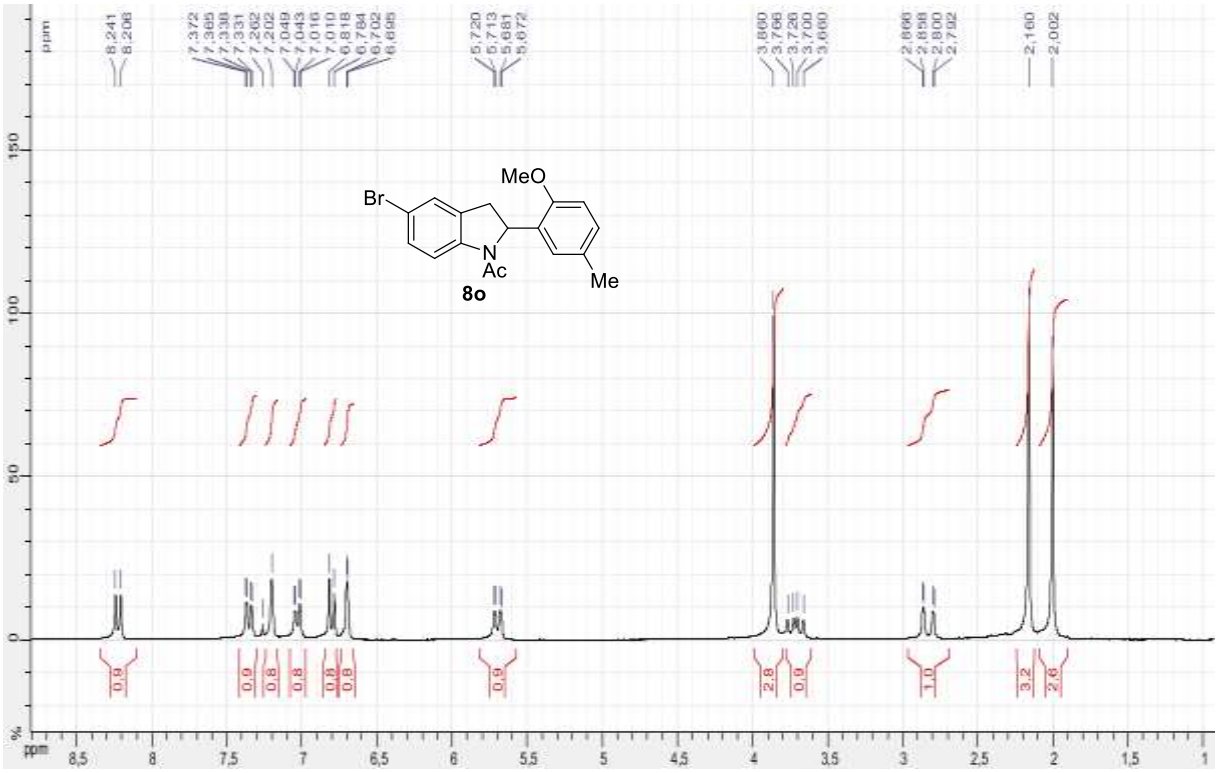
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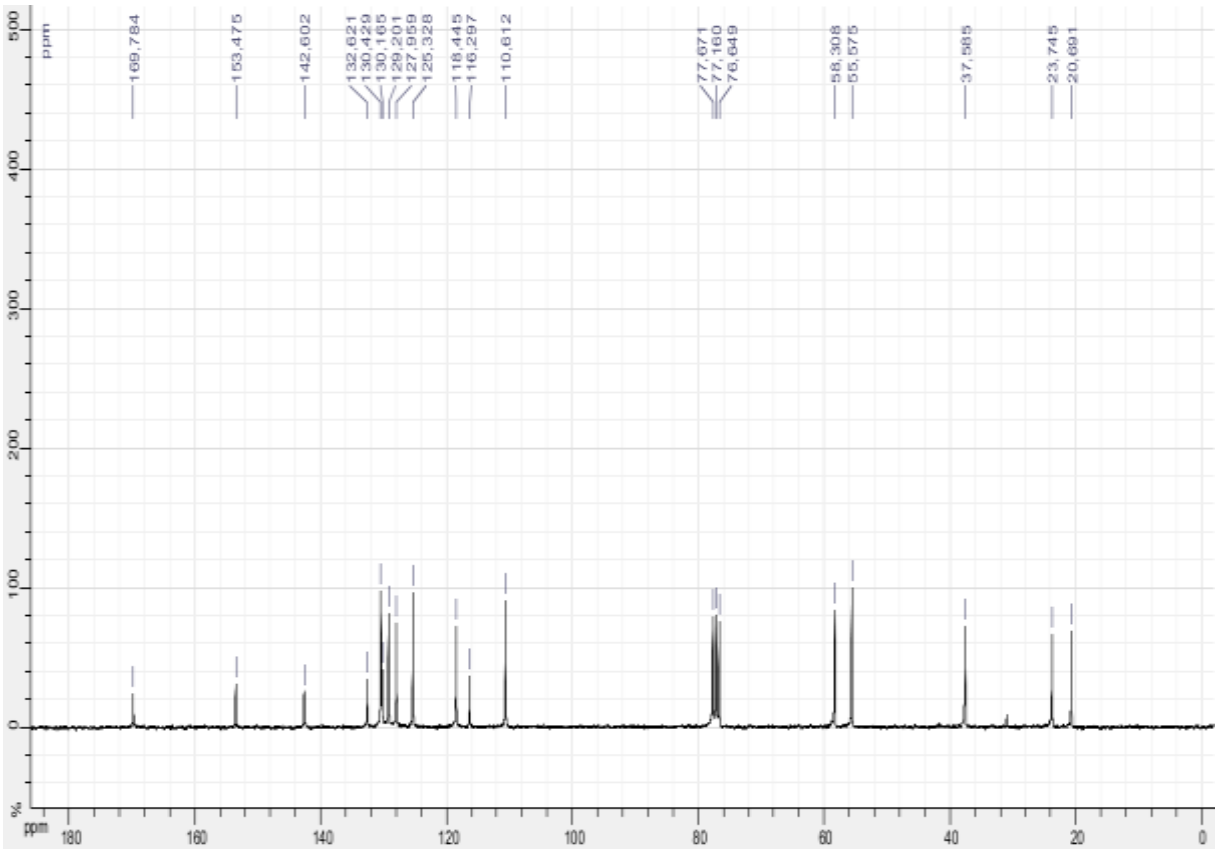
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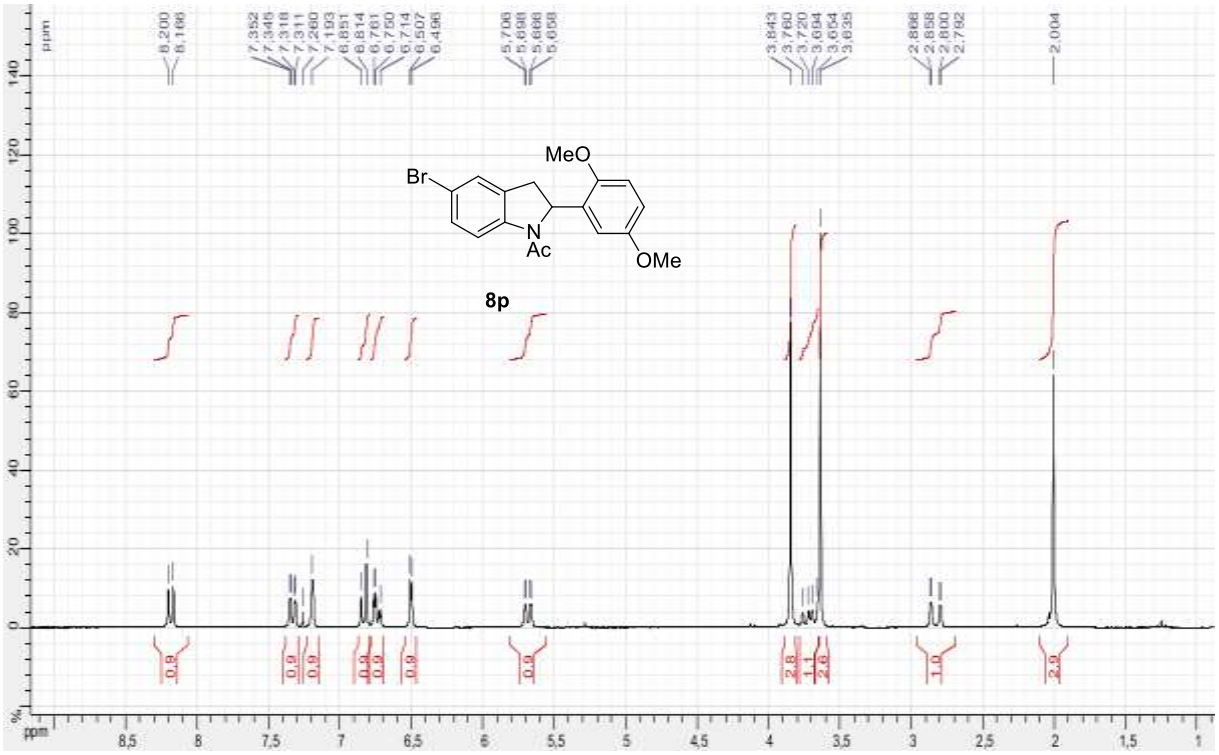
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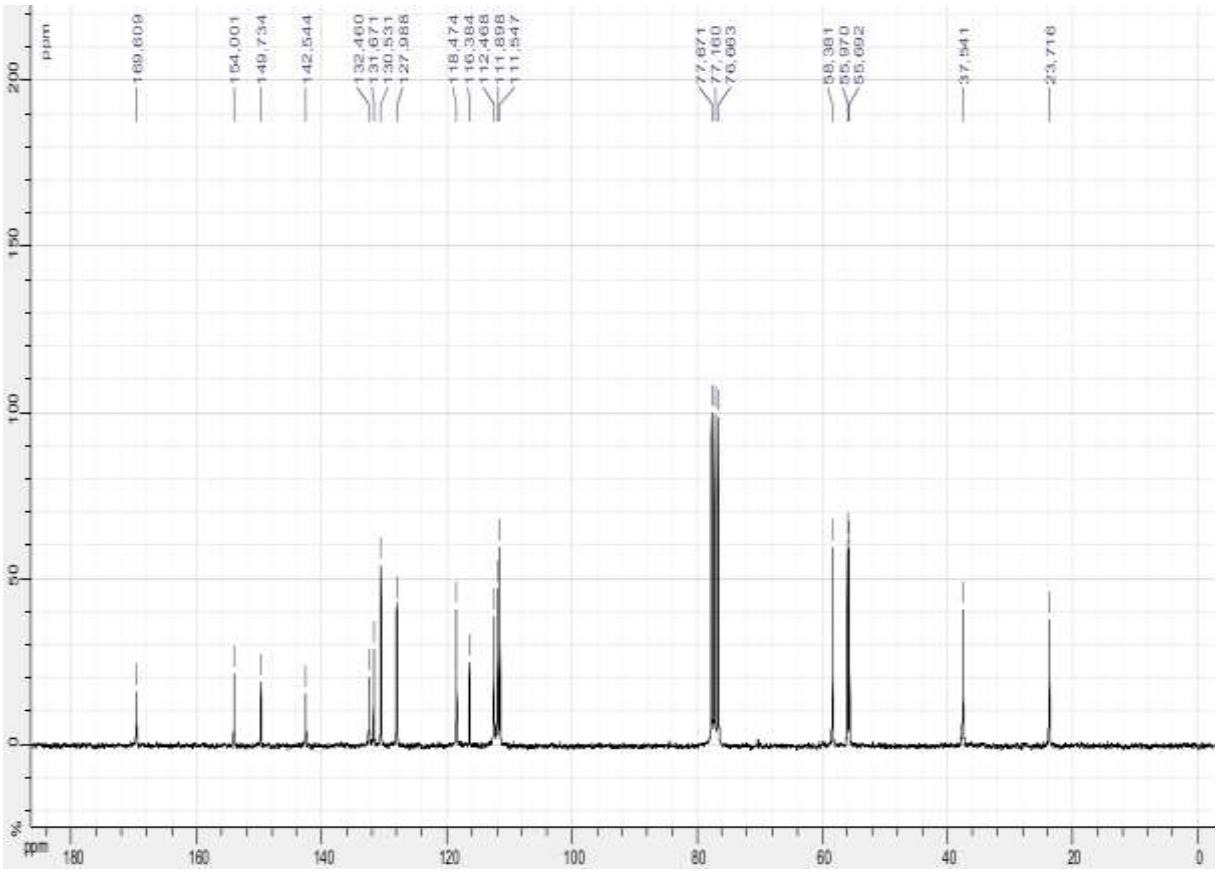
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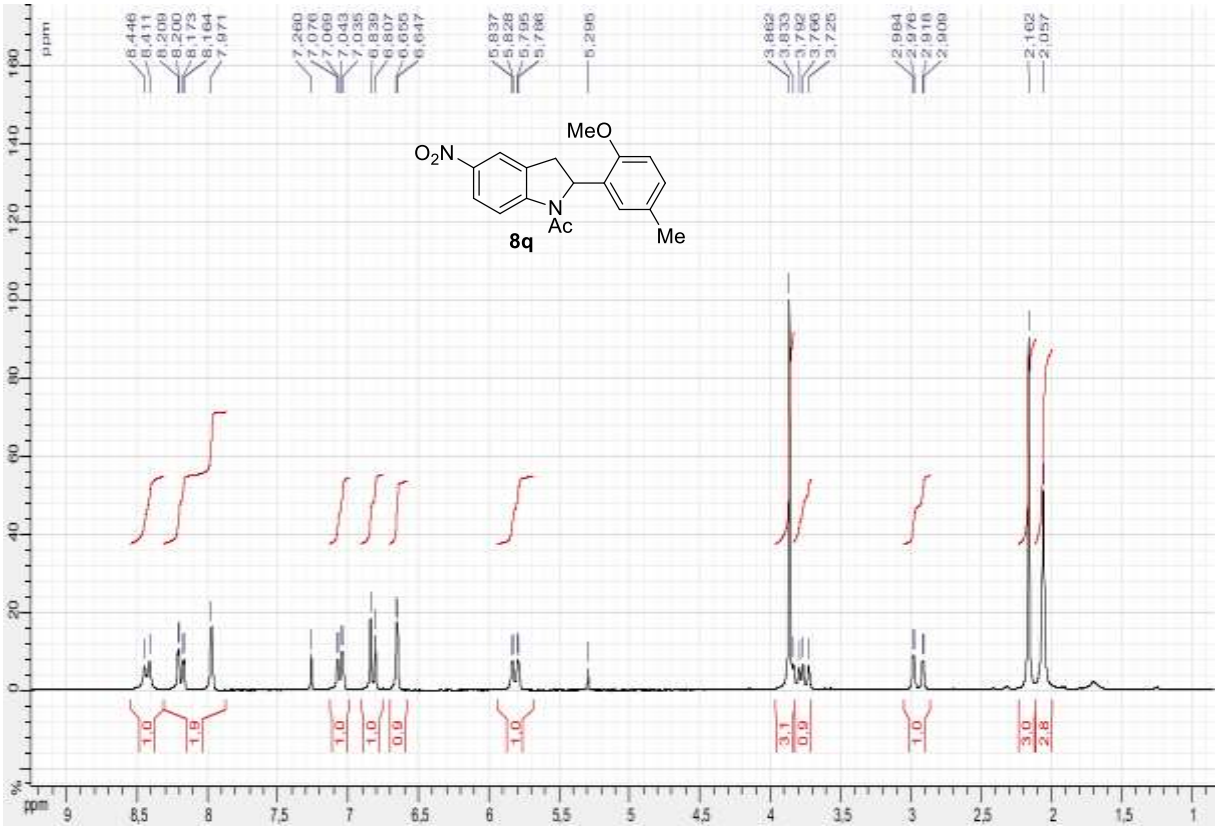
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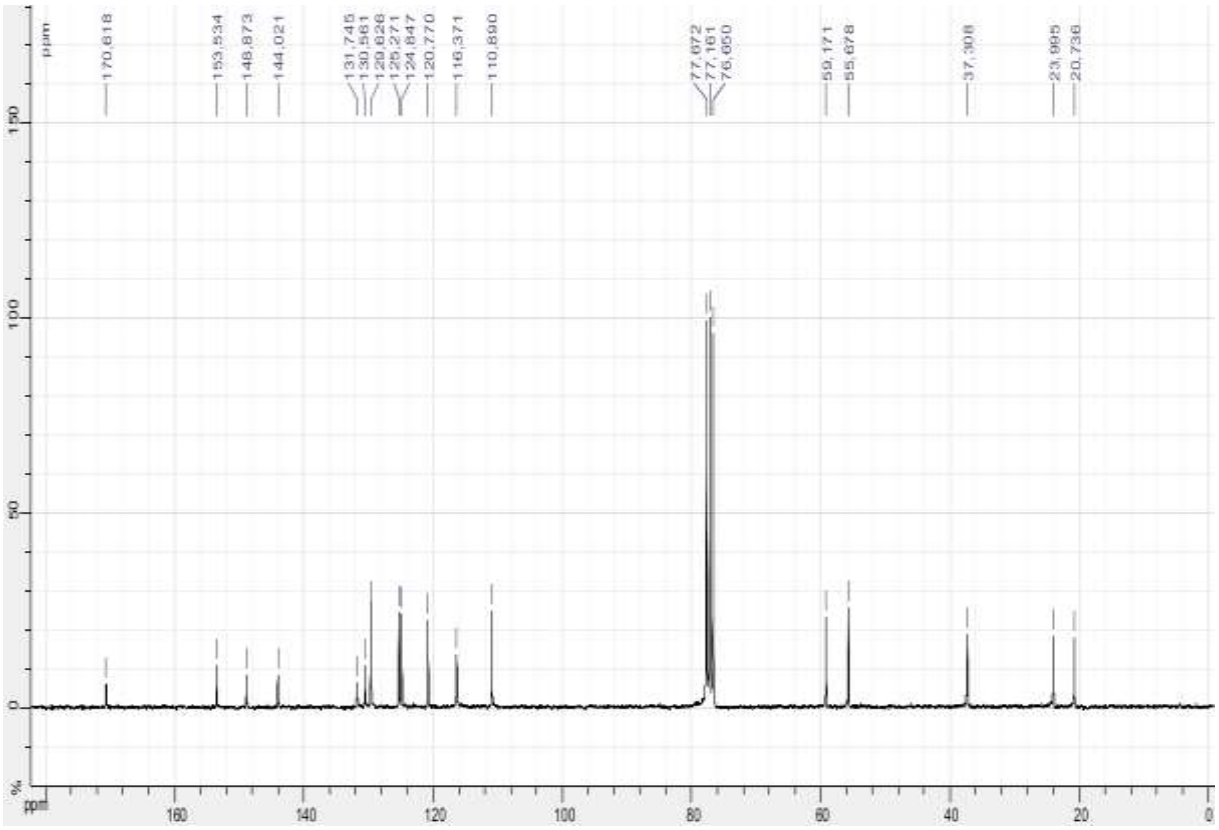
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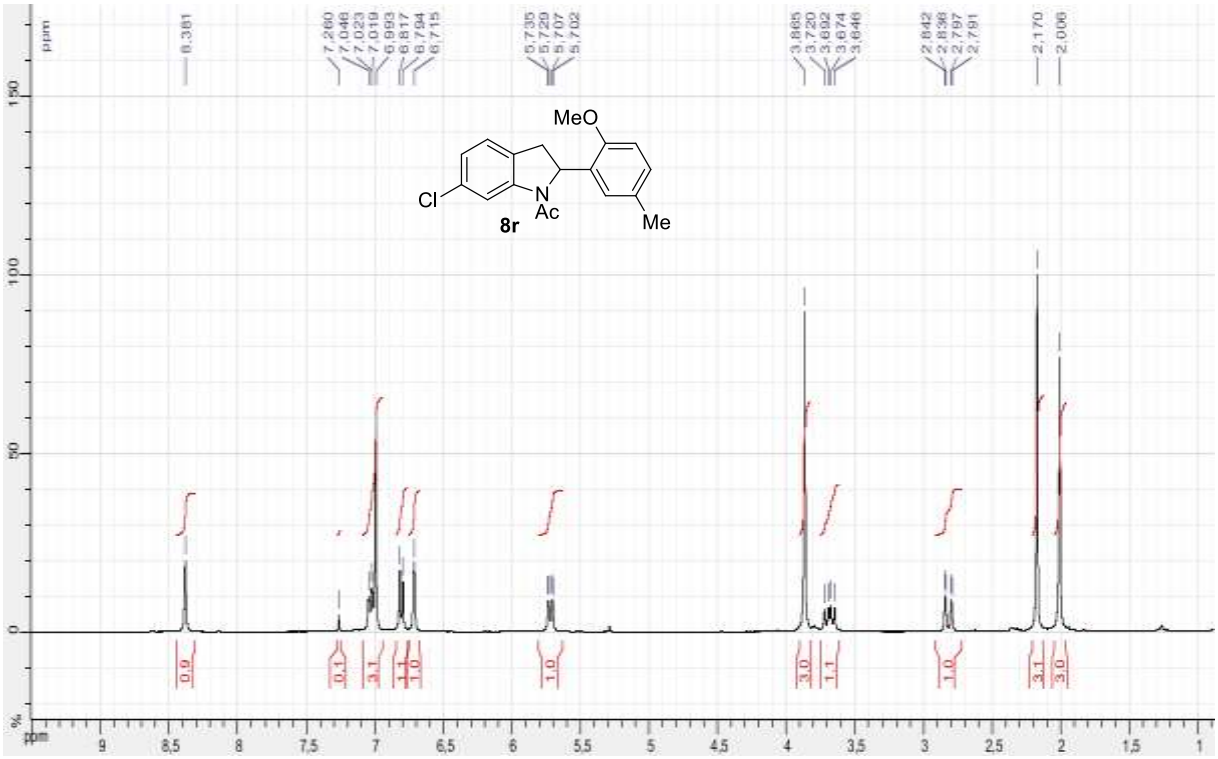
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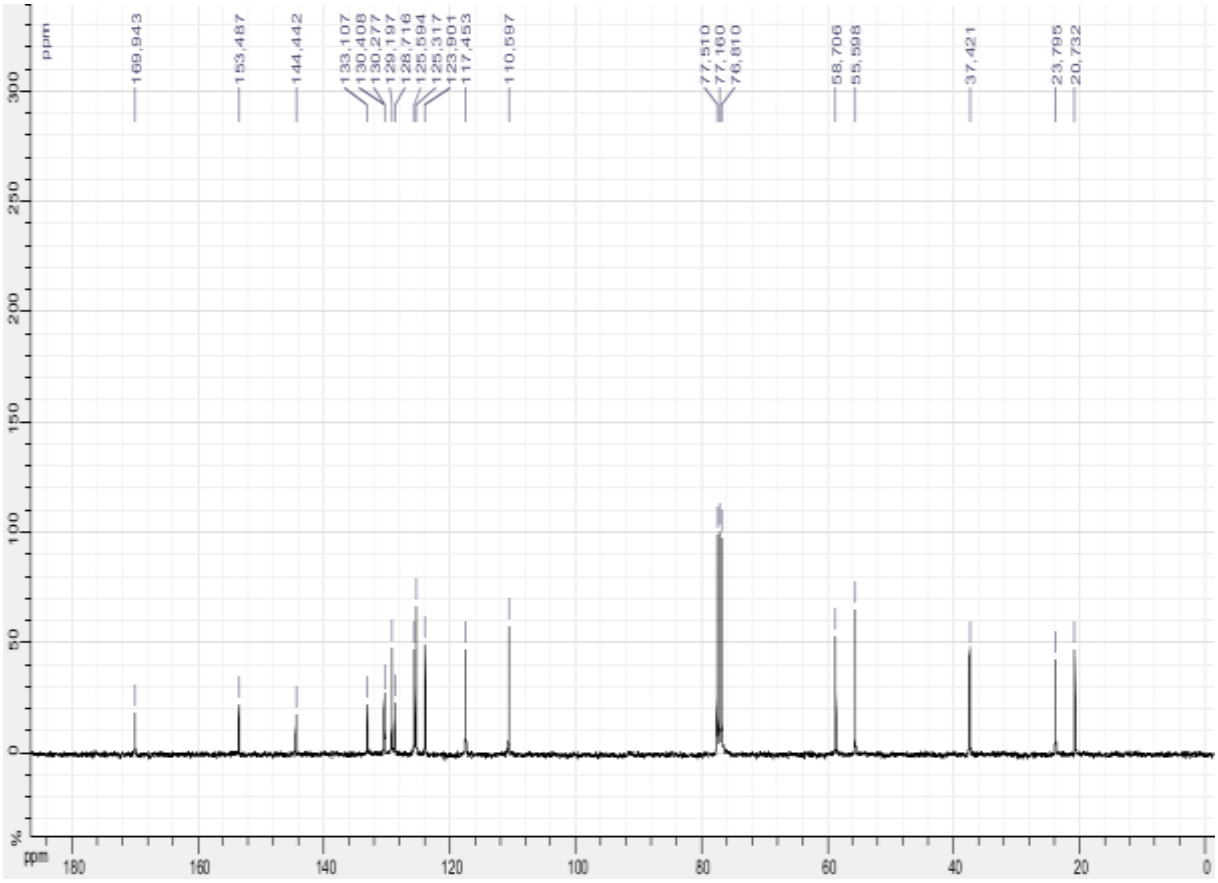
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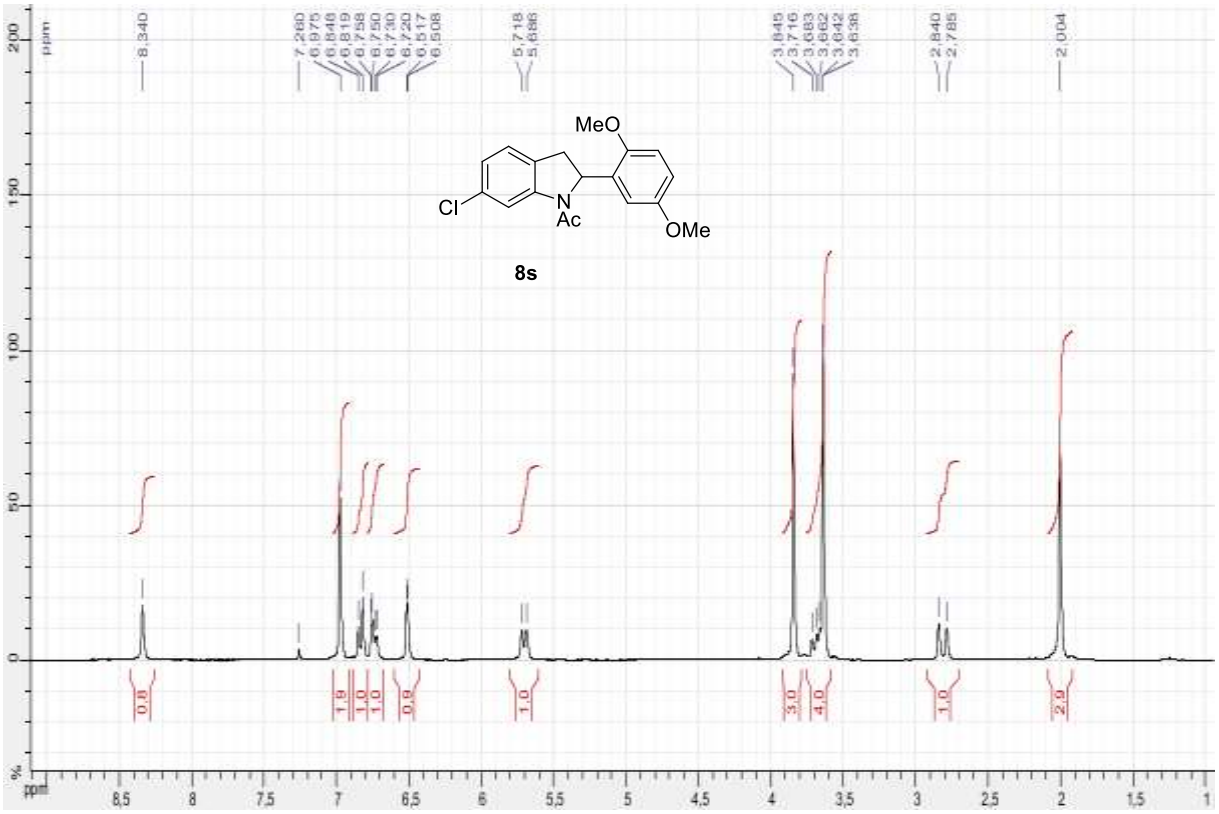
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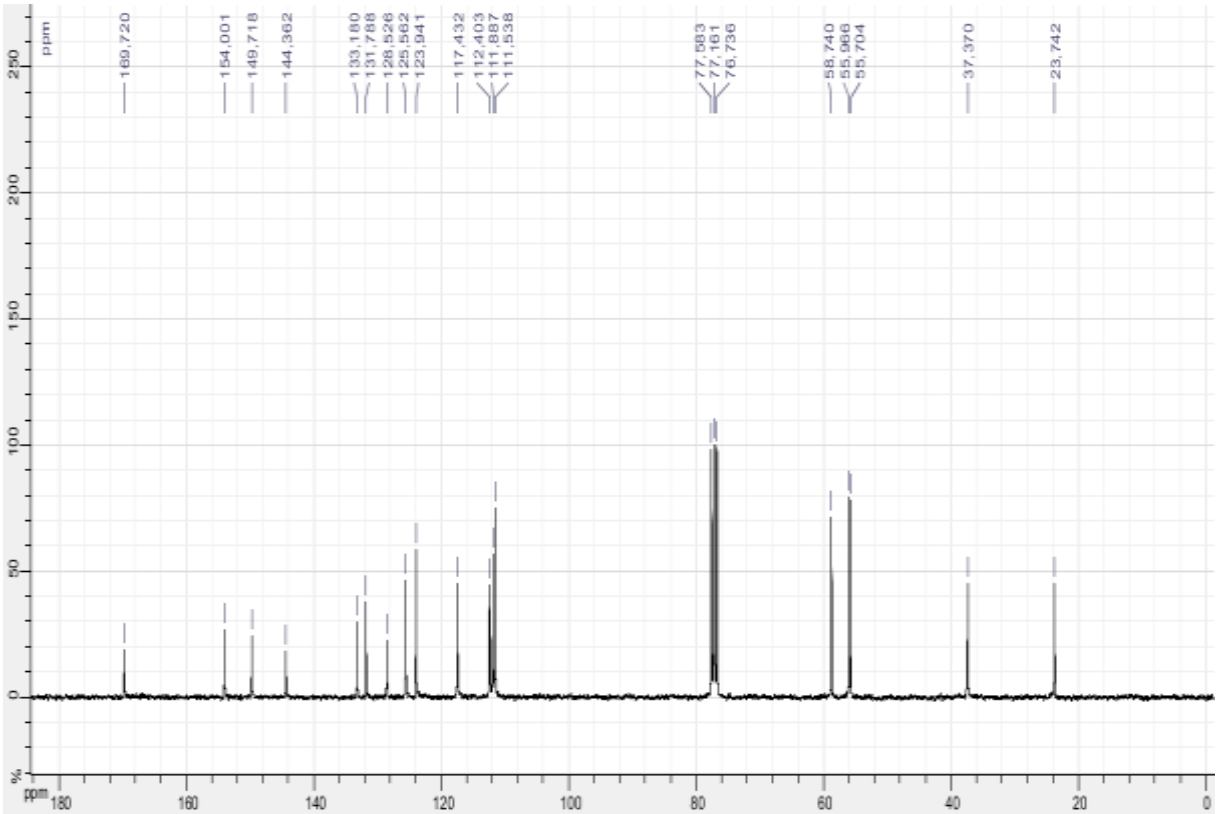
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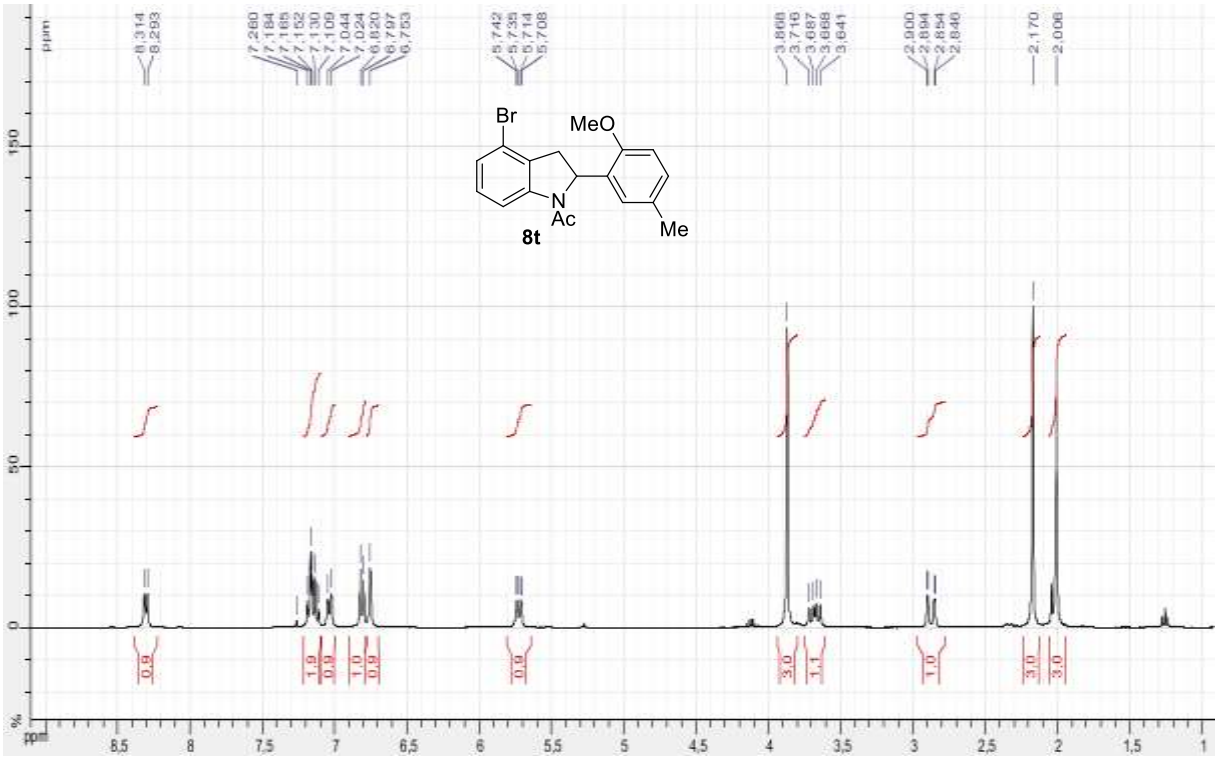
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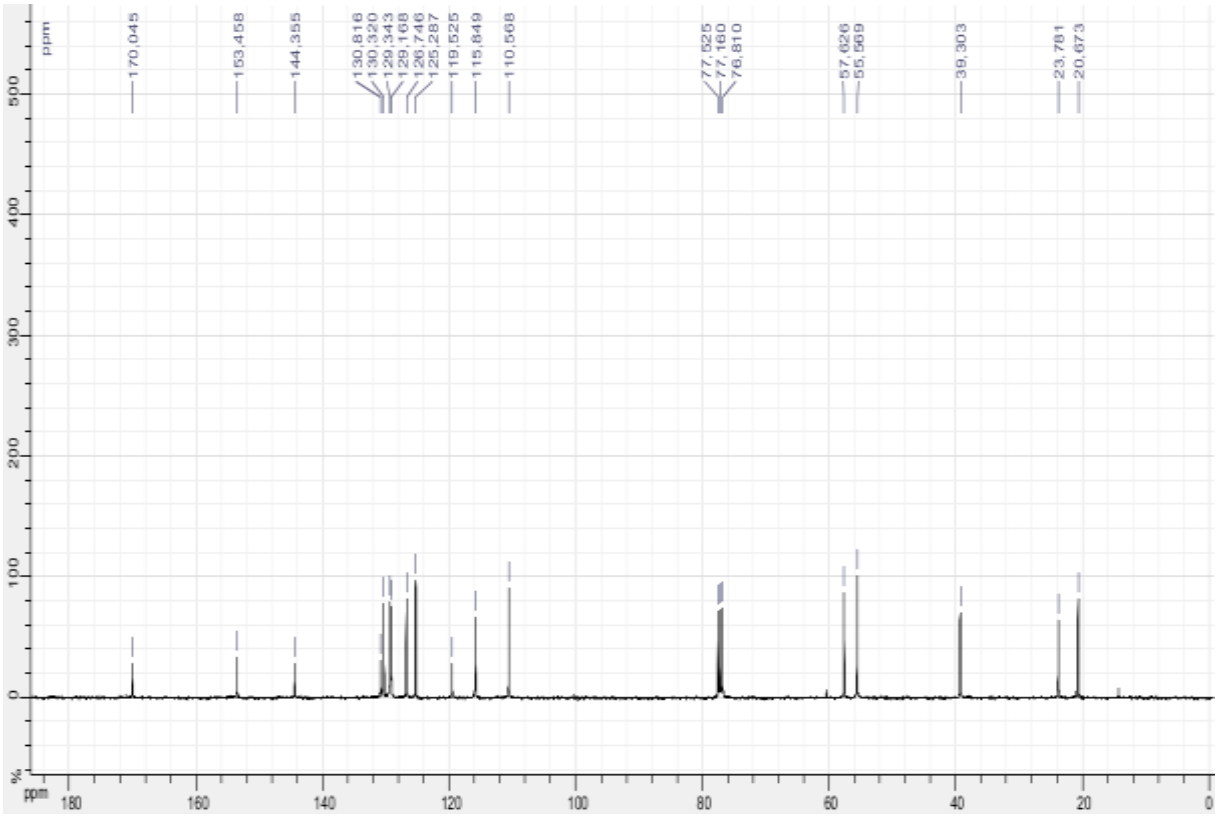
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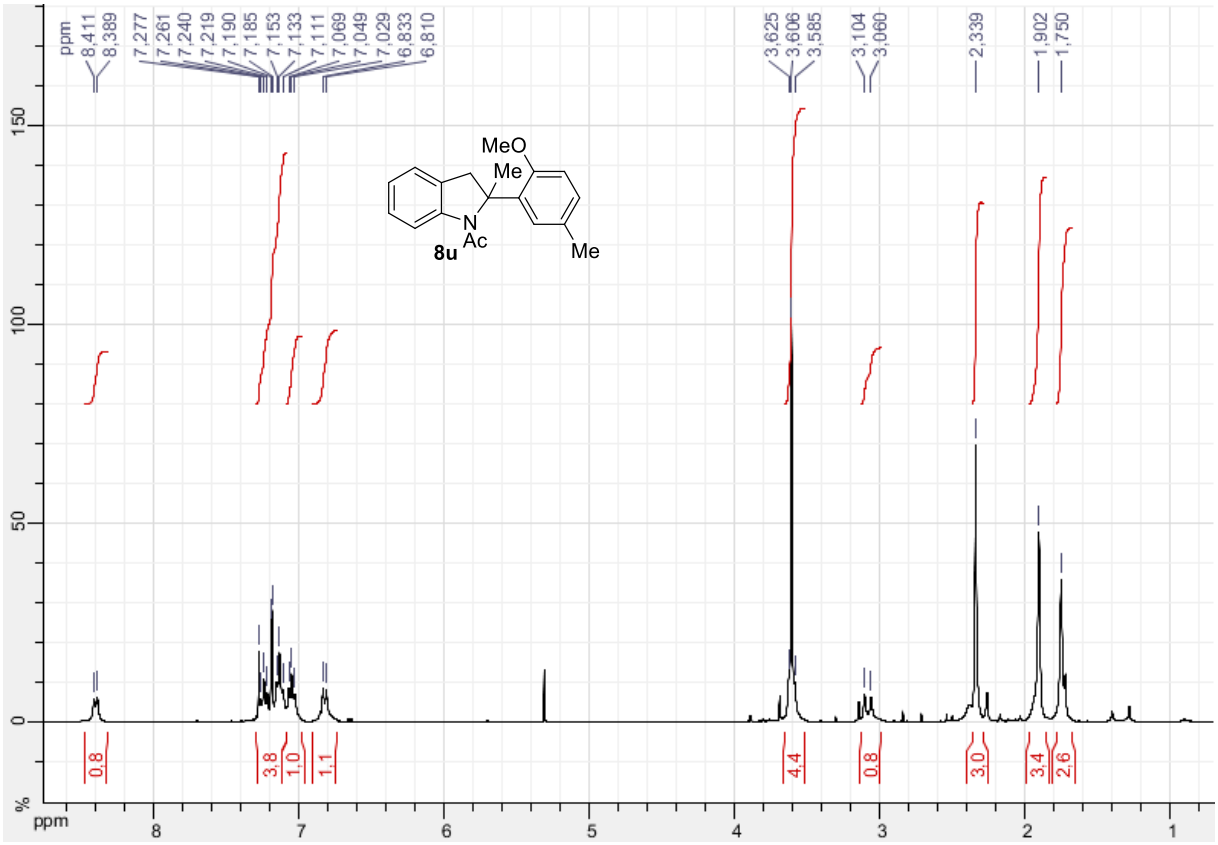
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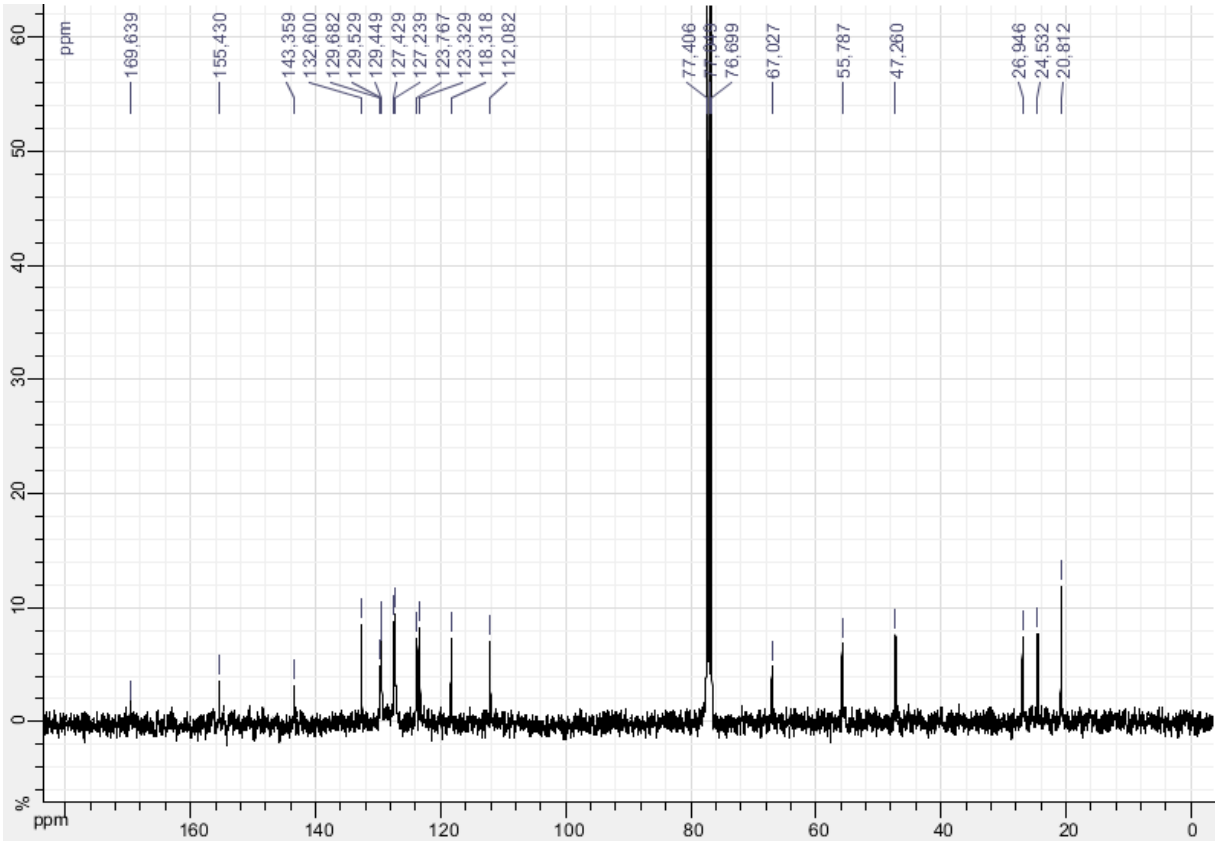
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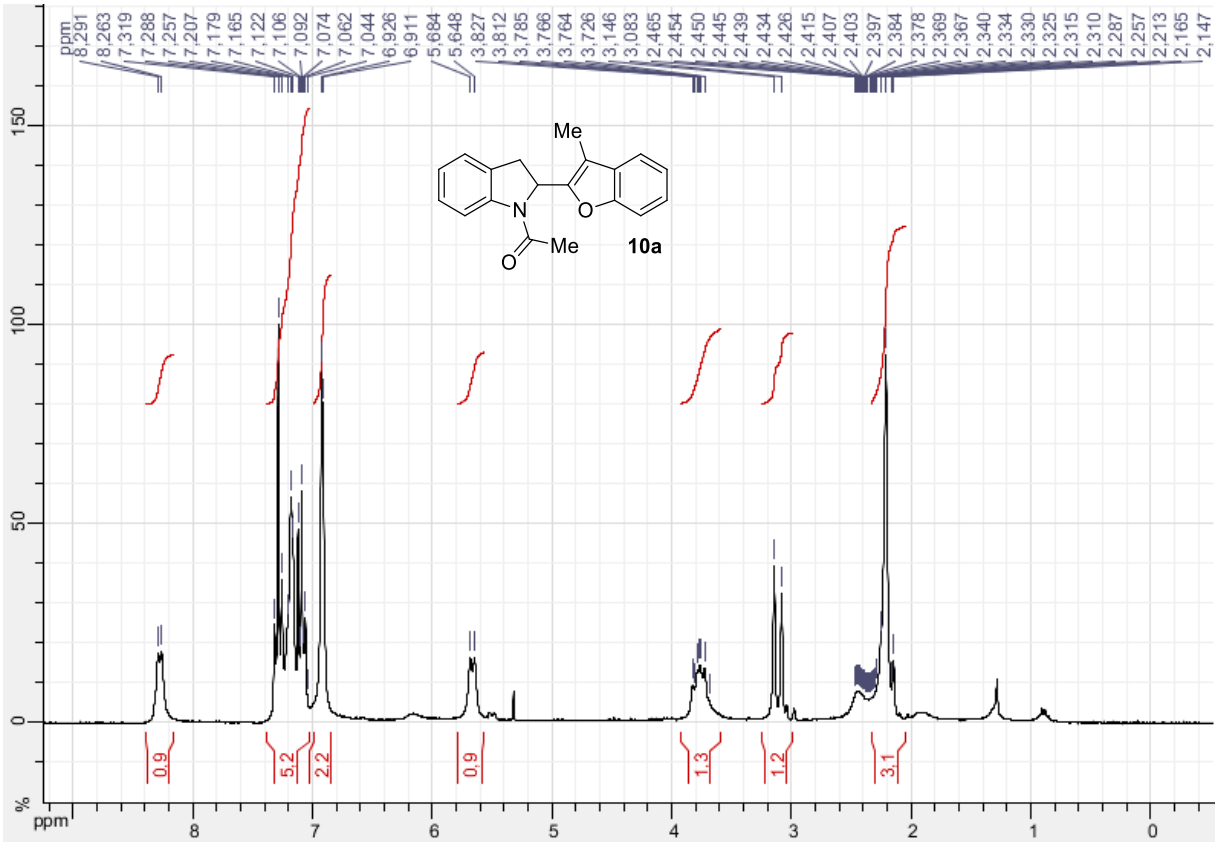
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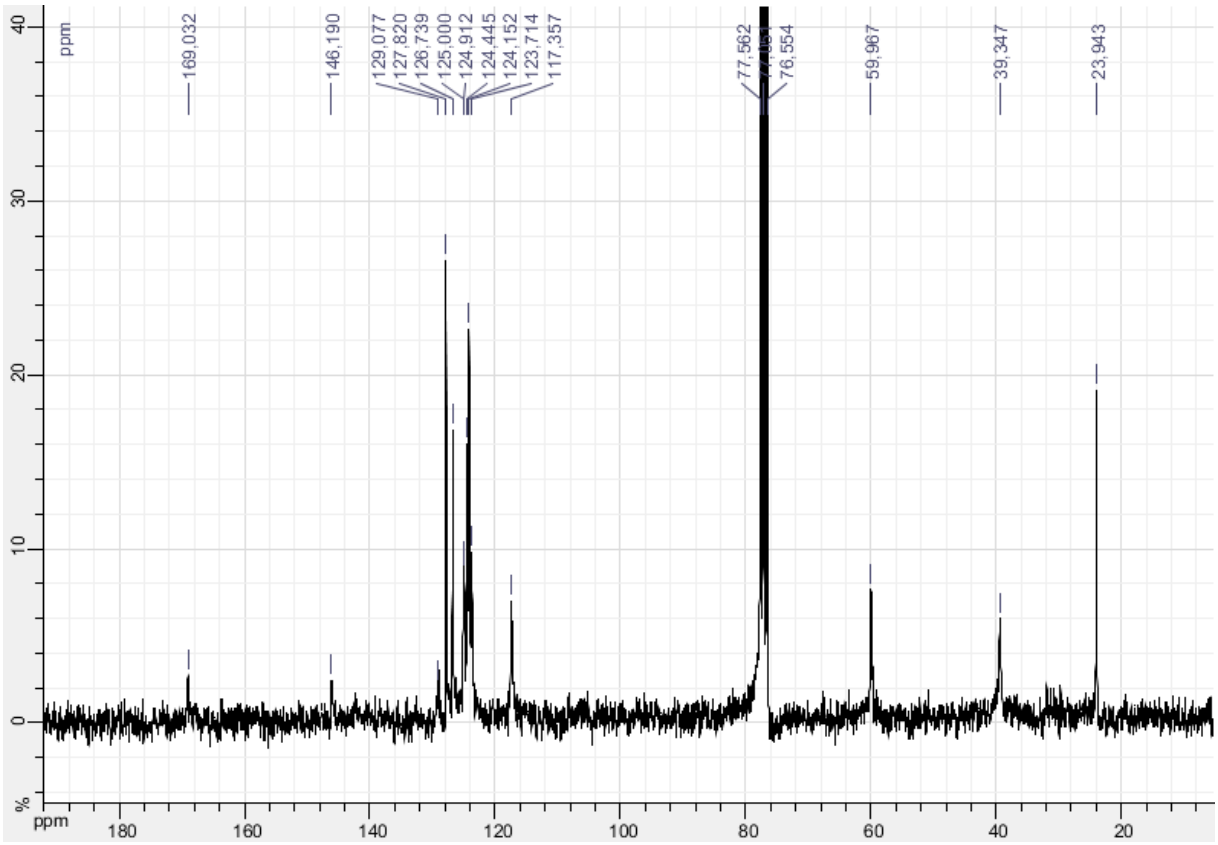
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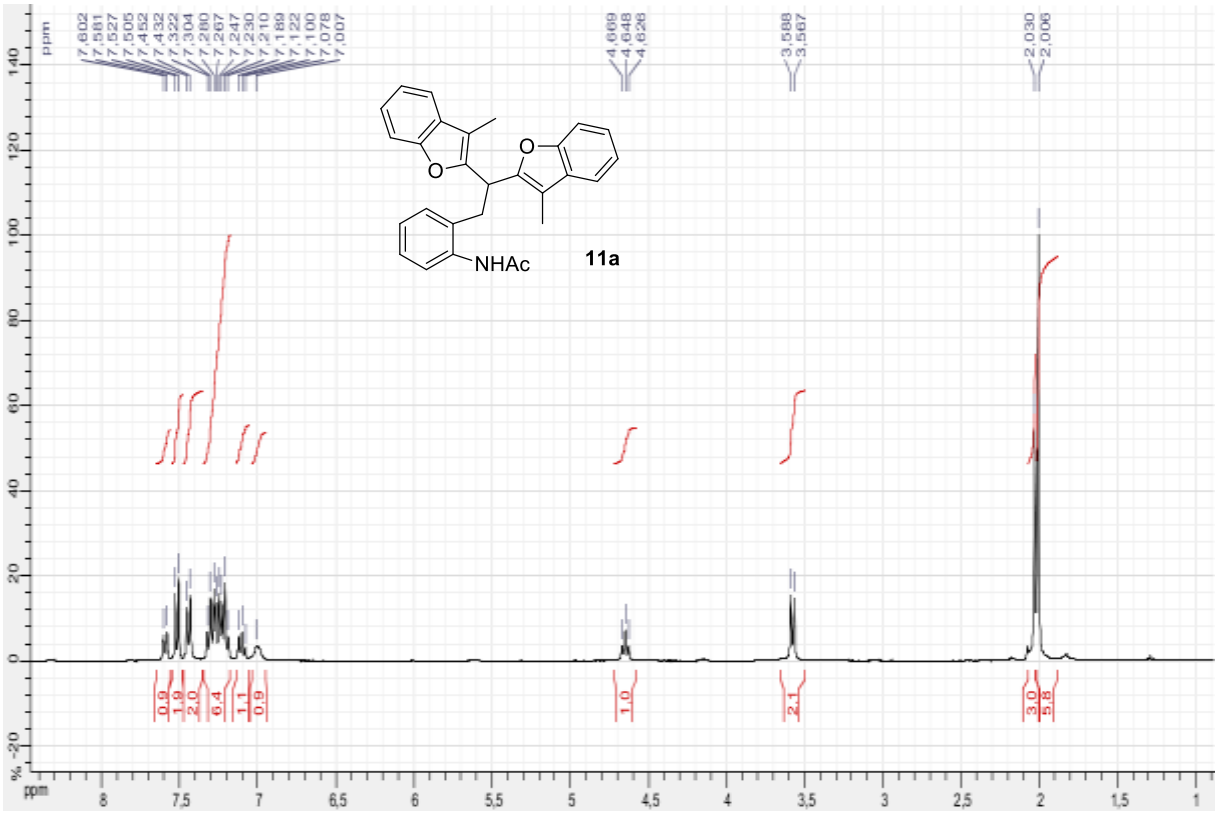
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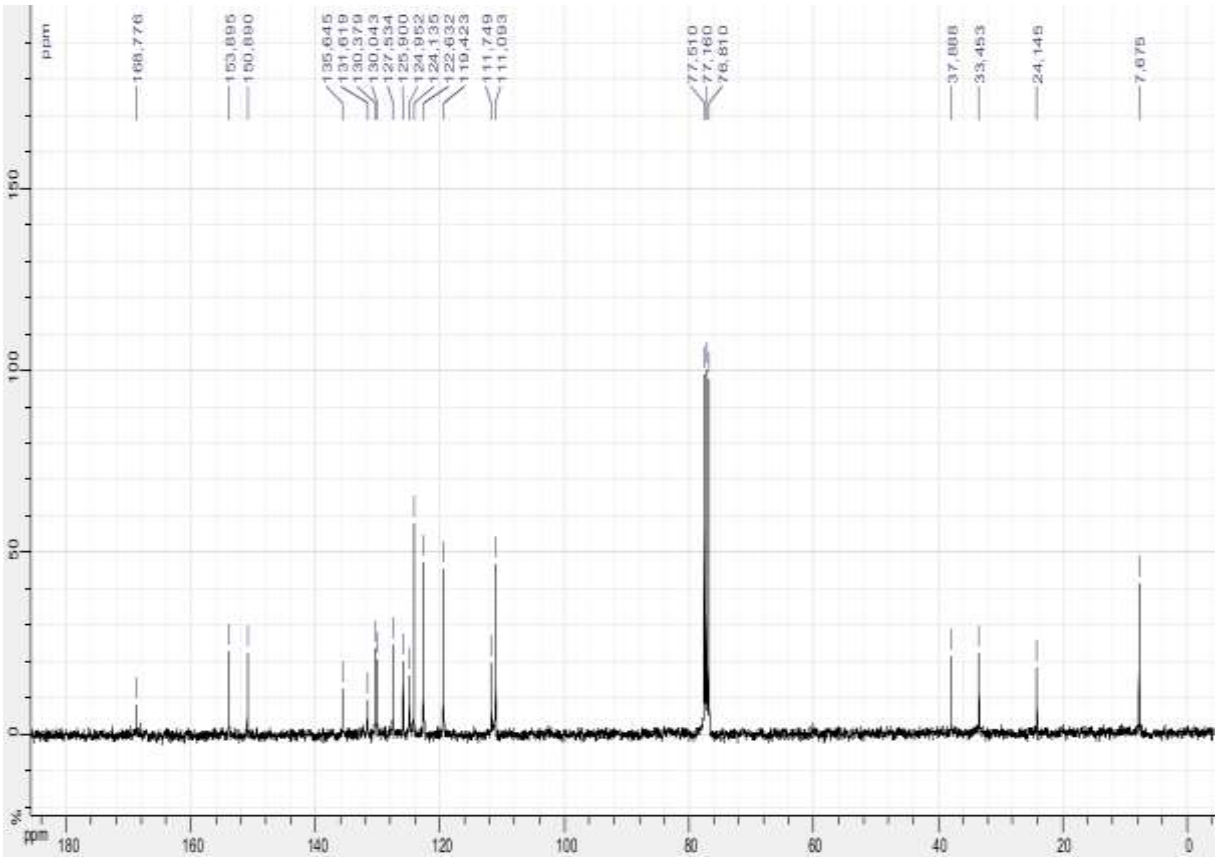
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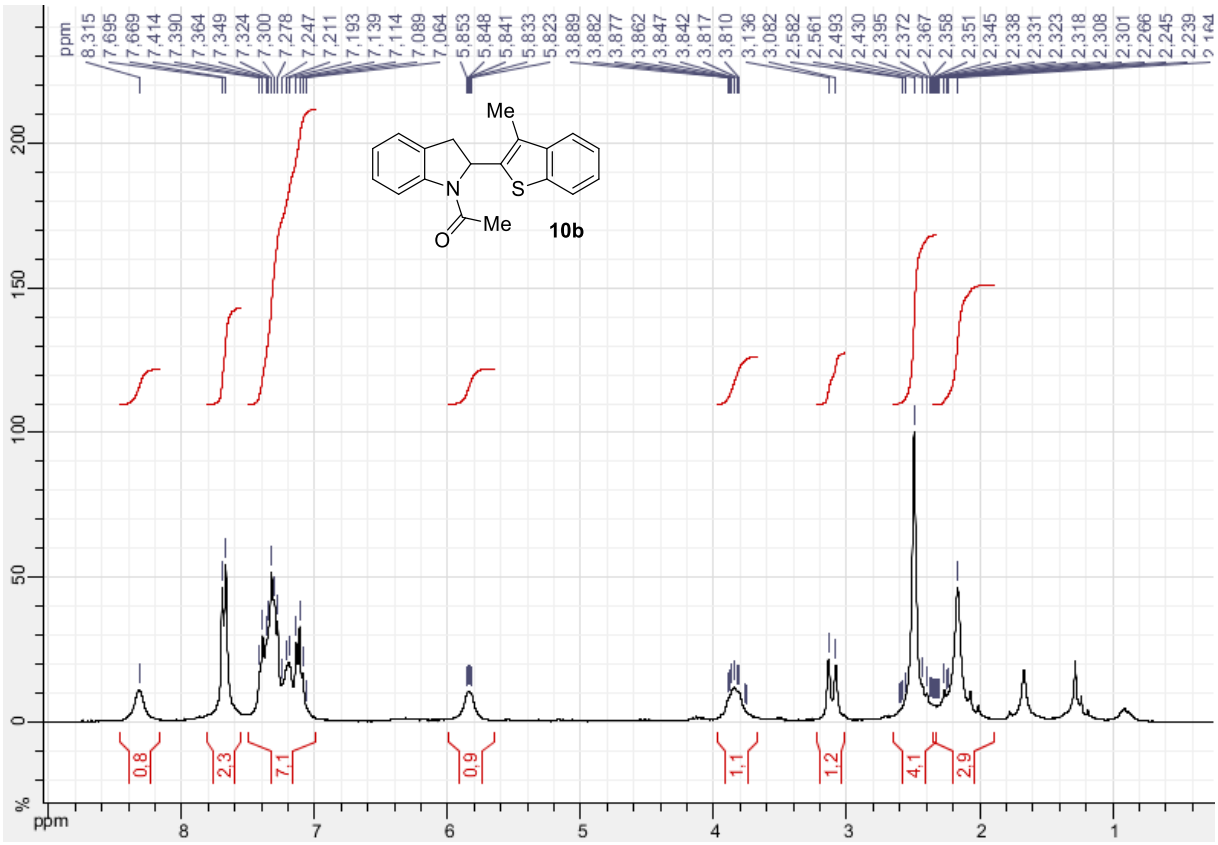
7.675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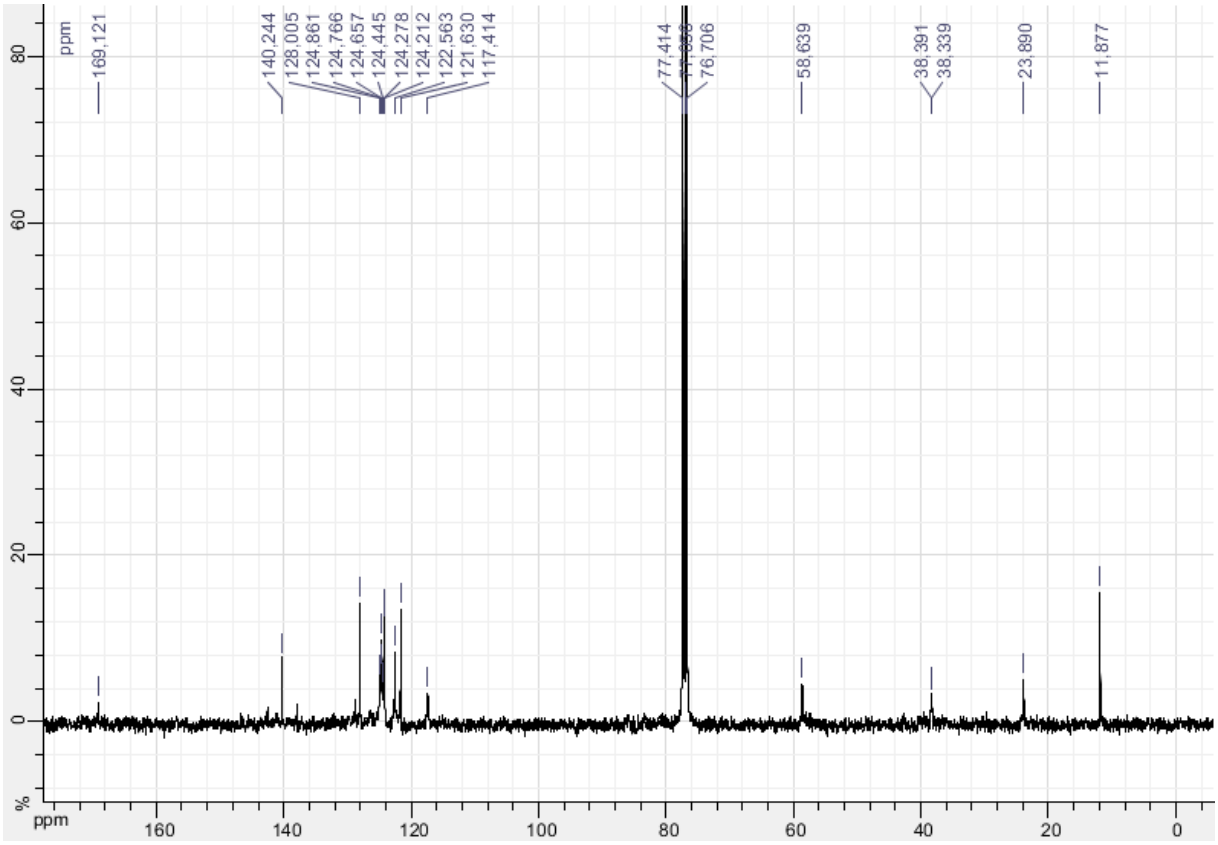
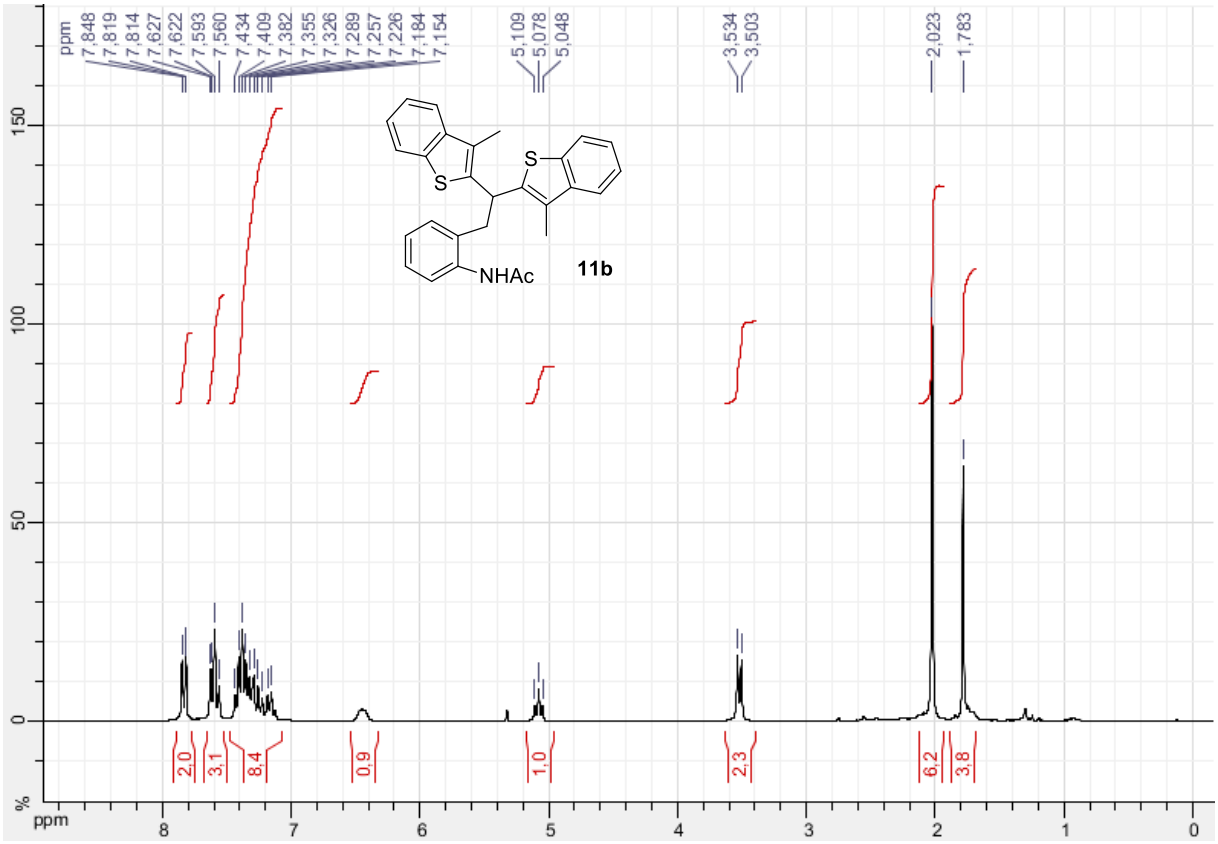
S
Me
O
10b

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7,257
7,226
7,184
7,154
5,109
5,078
5,048
3,534
3,503
2,023
1,783
S
S
NHAc
11b
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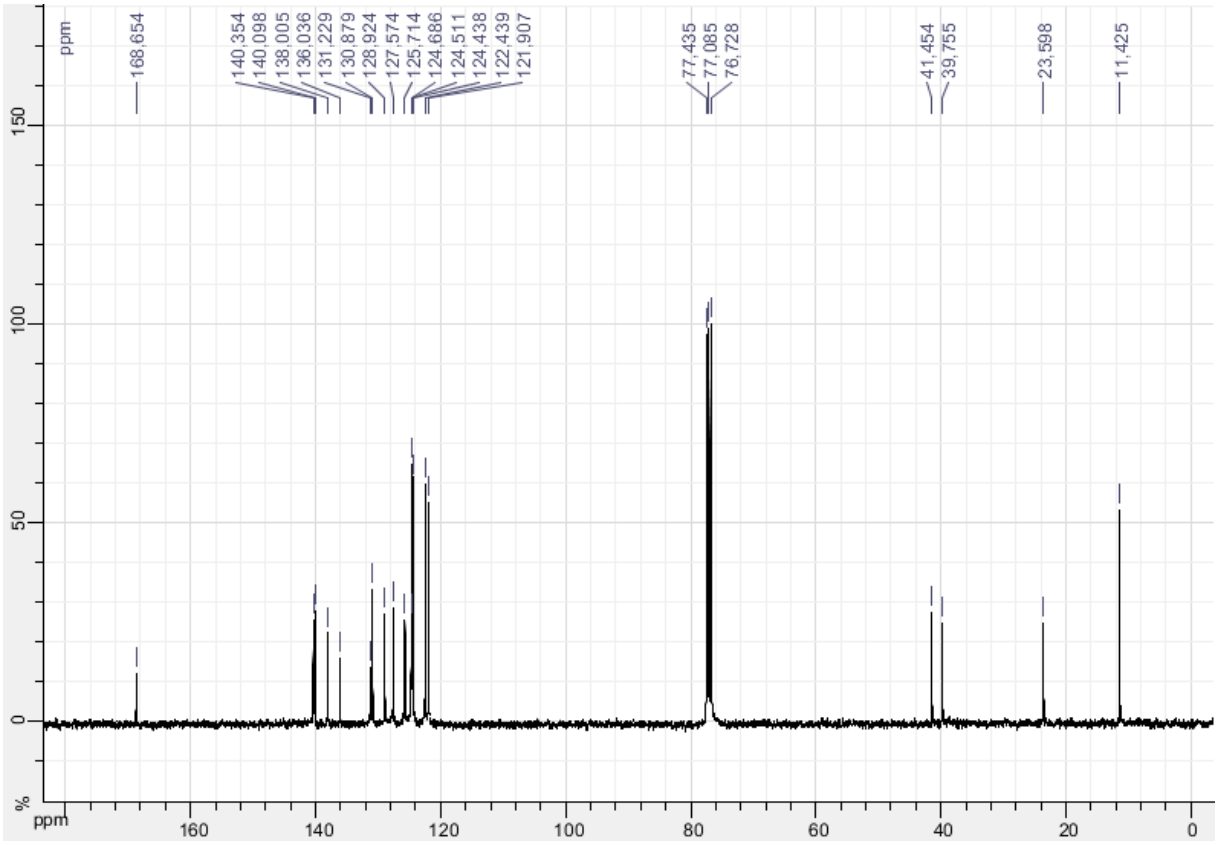
8,4
0,9
1,0
2,3
6,2
3,8
%
ppm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138,005
136,036
131,229
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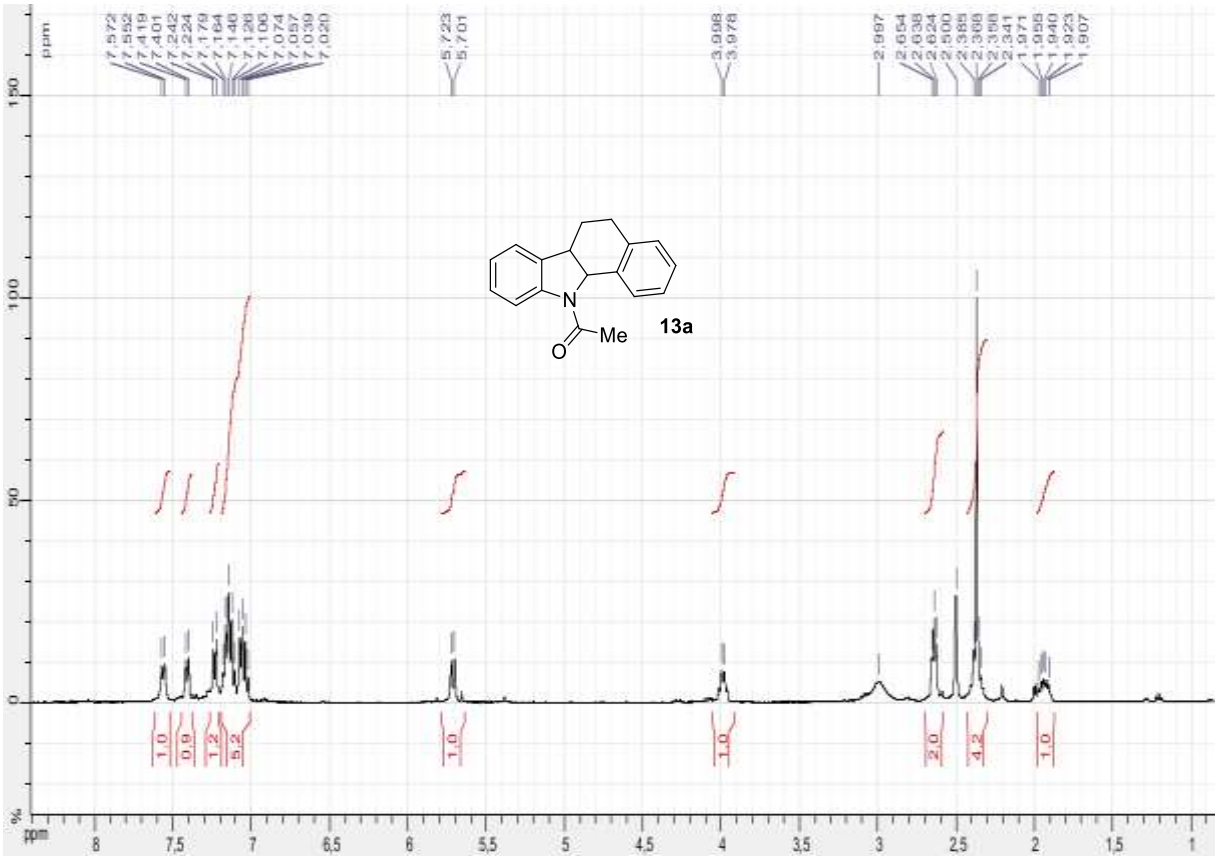
%
ppm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7.039
7.020
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5.701
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2.997
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2.638
2.624
2.500
2.389
2.368
2.358
2.341
1.971
1.958
1.940
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N
O
Me
13a
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0.9
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1.0
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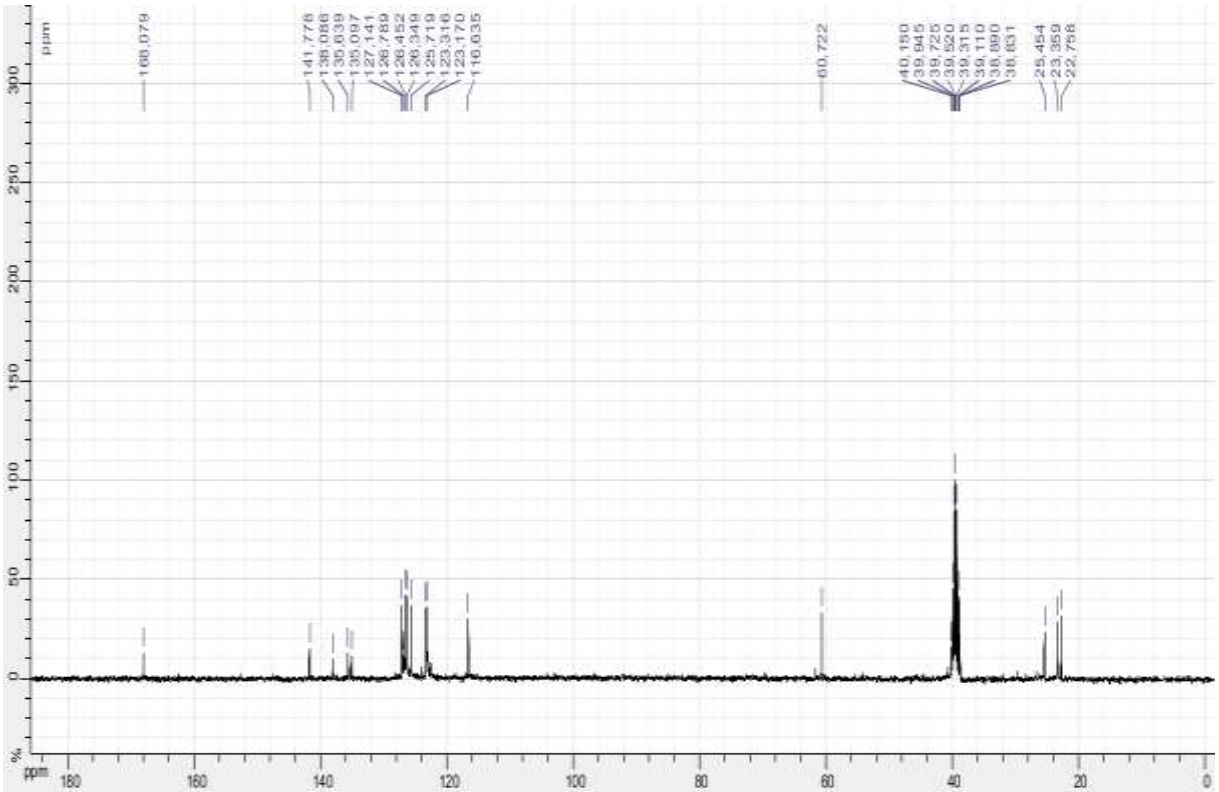
4.2
1.0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141.776
138.086
135.039
135.097
127.141
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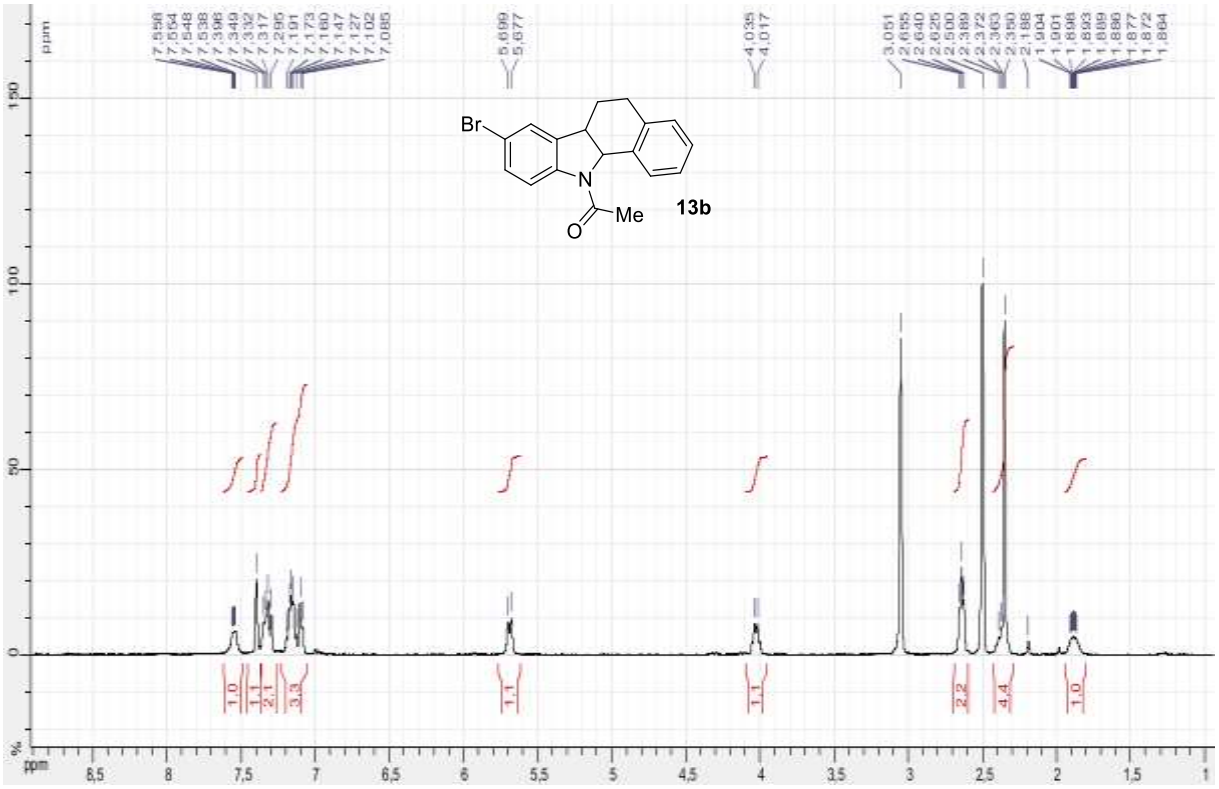
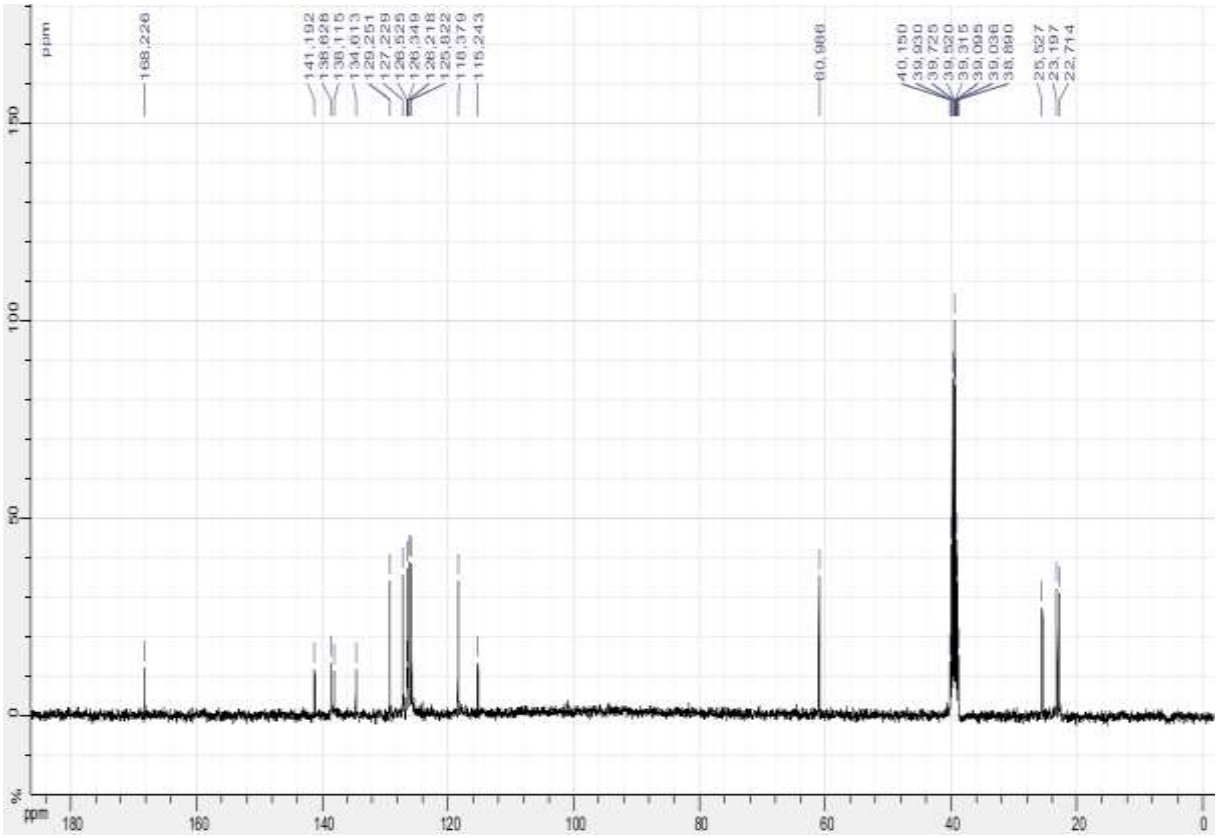
38.890
38.631
25.454
23.359
22.798


Br
N
O
Me
13b



IV X-Ray Crystal data

The single crystal X-ray diffraction data of the compounds **8b** and **13b** were collected by using a Kappa X8 APEX II Bruker diffractometer with graphite-monochromated $Mo_{K\alpha}$ radiation (ƛ = 0.71073 Å). X-ray diffraction data of compound **11b** was collected by using a Kappa VENTURE PHOTON 100 Bruker diffractometer with IμS microfocus graphite-monochromated $Mo_{K\alpha}$ radiation (ƛ = 0.71073 Å). Crystals were mounted on a CryoLoop (Hampton Research) with Paratone-N (Hampton Research) as cryoprotectant and then flashfrozen in a nitrogen-gas stream at 100 K. The temperature of the crystal was maintained at the selected value (100 K) by means of a 700 series Cryostream cooling device to within an accuracy of ±1 K. The data were corrected for Lorentz polarization, and absorption effects. The structures were solved by direct methods using SIR-97[1] and refined against F^2 by full-matrix least-squares techniques using SHELXL-2014[2] with anisotropic displacement parameters for all non-hydrogen atoms. All calculations were performed by using the Crystal Structure crystallographic software package WINGX [3].

The crystal data collection and refinement parameters are given in Table S1.

CCDC 1450298-1450300 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/Community/Requestastructure.

Compound	**8b**	**11b**	**13b**
	CCDC 1450298	CCDC 1450300	CCDC 1450299
Empirical Formula	C_{18} H_{19} N O_2	C_{18} H_{16} Br N O	C_{28} H_{25} N O_3
M_r	281.34	342.23	423.49
Crystal size, mm^3	0.31 x 0.28 x 0.11	0.29 x 0.25 x 0.21	0.12 x 0.09 x0.03
Crystal system	orthorhombic	triclinic	monoclinic
Space group	*P b c a*	*P -1*	*P 2_1/n*
a, Å	9.5809(4)	7.9573(3)	7.7189(4)
b, Å	13.6588(6)	9.6303(3)	9.7482(5)
c, Å	22.8484(9)	10.5963(3)	29.5931(14)
α, °	90	68.1470(10)	90
β, °	90	75.128(2)	94.235(2)
γ, °	90	69.3120(10)	90
Cell volume, $Å^3$	2990.0(2)	697.70(4)	2220.66(19)
Z	8	2	4
T, K	100(1)	100(1)	100(1)
F_{000}	1200	348	896
μ, mm^{-1}	0.081	2.944	0.082
θ range, °	1.783 – 33.440	2.093 - 30.685	2.200 - 31.318
Reflection collected	47 102	13 259	76 548
Reflections unique	5 808	4 228	7 273
R_{int}	0.0307	0.0362	0.0335
GOF	1.068	1.039	1.070
Refl. obs. (I>2σ(I))	4 969	3 719	6 212
Parameters / restraints	193 / 0	191 / 0	292 / 0
wR_2 (all data)	0.1351	0.0694	0.1247
R value (I>2σ(I))	0.0446	0.0285	0.0490
Largest diff. peak and hole (e-.$Å^{-3}$)	-0.264 ; 0.489	-0.616; 0.677	- -0.268 ; 0.430

Table S1. Crystallographic data and structure refinement details for the compounds **8b**, **11b** and **13b**.

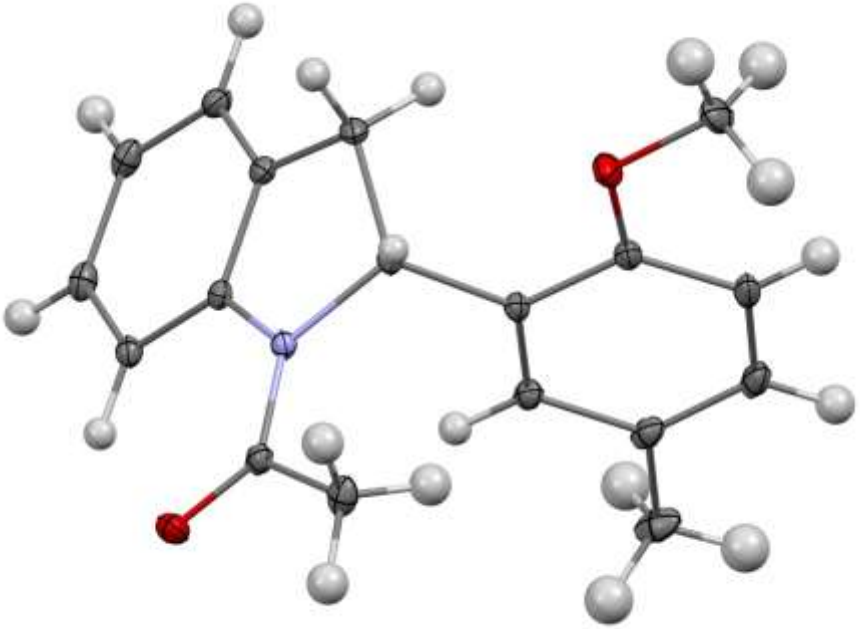


Figure S1. CSD Mercury[4] ellipsoid view of the structure of compound **8b**. Ellipsoids are drawn at the 30% probability level.

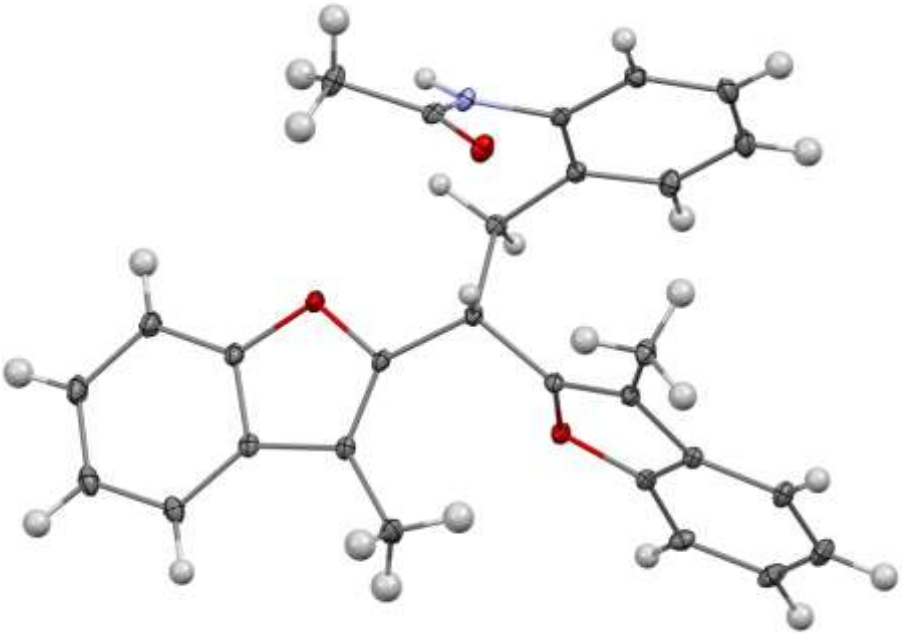


Figure S2. CSD Mercury ellipsoid view of the structure of compound **11b**. Ellipsoids are drawn at the 30% probability level.

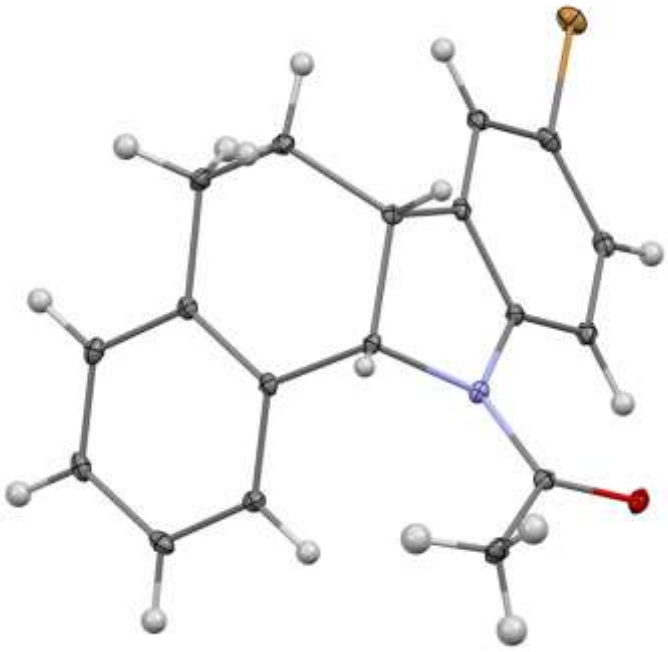


Figure S3. CSD Mercury ellipsoid view of the structure of compound **13b**. Ellipsoids are drawn at the 30% probability level.

1. A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori and R. Spagna, *J. Appl. Crystallogr.*, 1999, **32**, 115-119.

2. G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, **64**, 112-122.

3. L. J. Farrugia, *J. Appl. Crystallogr.*, 1999, **32**, 837-838.

4. C. F. Macrae, P. R. Edgington, P. McCabe, E. Pidcock, G. P. Shields, R. Taylor, Towler and van der Streek, *J. Appl. Crystallogr.*, 2006, **39**, 453-457.