Supplementary Information

Rh-catalyzed oxidative C-C bond formation and C-N bond cleavage: direct access to C2-olefinated free (NH)-indoles and pyrroles

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General methods

Commercially available reagents were used without additional purification, unless otherwise stated. Sealed tubes (13 × 100 mm^2) were purchased from Fischer Scientific and dried in oven for overnight and cooled at room temperature prior to use. Thin layer chromatography was carried out using plates coated with Kieselgel $60F_{254}$ (Merck). For flash column chromatography, E. Merck Kieselgel 60 (230–400 mesh) was used. Nuclear magnetic resonance spectra (^1H and ^{13}C NMR) were recorded on a Bruker Unity 700 MHz spectrometer for $CDCl_3$ and DMSO-d_6 solution and chemical shifts are reported as parts per million (ppm). Resonance patterns are reported with the notations s (singlet), d (doublet), t (triplet), q (quartet), and m (multiplet). In addition, the notation br is used to indicate a broad signal. Coupling constants (*J*) are reported in hertz (Hz). IR spectra were recorded on a Varian 2000 Infrared spectrophotometer and are reported as cm^{-1}. High-resolution mass spectra (HRMS) were recorded on a JEOL JMS-600 spectrometer.

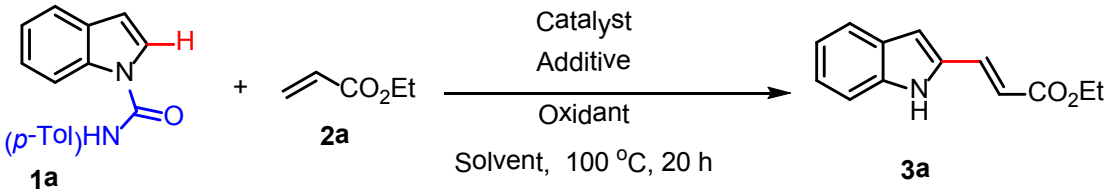
General procedure for the synthesis of *N*-*p*-tolyl-1*H*-indole-1-carboxamide and *N*-*p*-tolyl-1*H*-indole-1-carboxamide (1a, 1f–1r and 5a)

To a stirred suspension of indole or pyrrole (1.0 equiv.) in dry DMF (30 mL) was added NaH (60% dispersion in mineral oil, 2.0 equiv.) at 0 ^{o}C under N_2 atmosphere. The reaction mixture was then stirred at room temperature for 3 h and *p*-tolyl isocyanate (1.5 equiv.) was added dropwise. The reaction mixture was then stirred at room temperature for overnight. The reaction mixture was washed with H_2O and extracted with EtOAc (50 mL). The organic layer was then washed with an aqueous solution of 1 N HCl (50 mL). The organic layer was dried over Mg_2SO_4 and concentrated in vacuo. The residue was purified by flash column chromatography.

Typical procedure for the synthesis of alkenylated product (3a, 3f–3p, 4b–4l, and 6a–c)

To an oven-dried sealed tube charged with *N*-*p*-tolyl-1*H*-indole-1-carboxamide (**1a**) (37.5 mg, 0.15 mmol, 100 mol%), $[RhCp^*Cl_2]_2$ (2.3 mg, 0.0037 mmol, 2.5 mol %), $AgSbF_6$ (5.2 mg, 0.015 mmol, 10 mol %), and $Cu(OAc)_2{\cdot}H_2O$ (60 mg, 0.3 mmol, 200 mol %) was added ethyl acrylate (**2a**) (32 μL, 0.3 mmol, 200 mol %) and *t*-amyl alcohol (1 mL). The reaction mixture was allowed to stir for 20 h at 100 ^{o}C. The reaction mixture was diluted with EtOAc (10 mL) and concentrated in vacuo. The residue was purified by flash column chromatography (*n*-hexanes/EtOAc = 25:1) to afford the alkenylated product **3a** (25.1 mg) in 78% yield.

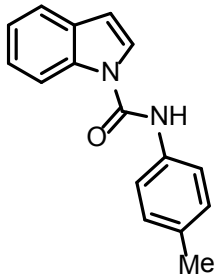
Selected optimization for the reaction conditions



entry	catalyst (mol %)	oxidant (equiv)	additive (mol %)	solvent	yield (%) of **3a**
1	$[RhCp^*Cl_2]_2$ (2.5)	$Cu(OAc)_2 \cdot H_2O$ (2)	$AgSbF_6$ (10)	DCE	62
2	$[RhCp^*Cl_2]_2$ (2.5)	$Cu(OAc)_2$ (2)	$AgSbF_6$ (10)	DCE	60
3	$[RhCp^*Cl_2]_2$ (2.5)	Ag_2CO_3 (2)	$AgSbF_6$ (10)	DCE	15
4	$[RhCp^*Cl_2]_2$ (2.5)	AgOAc (2)	$AgSbF_6$ (10)	DCE	trace
5	$[RhCp^*Cl_2]_2$ (2.5)	$Cu(OAc)_2 \cdot H_2O$ (2)	$AgSbF_6$ (10)	THF	55
6	$[RhCp^*Cl_2]_2$ (2.5)	$Cu(OAc)_2 \cdot H_2O$ (2)	$AgSbF_6$ (10)	CH_3CN	37
7	$[RhCp^*Cl_2]_2$ (2.5)	$Cu(OAc)_2 \cdot H_2O$ (2)	$AgSbF_6$ (10)	dioxane	48
8	$[RhCp^*Cl_2]_2$ (2.5)	$Cu(OAc)_2 \cdot H_2O$ (2)	$AgSbF_6$ (10)	t-BuOH	70
9	**$[RhCp^*Cl_2]_2$ (2.5)**	**$Cu(OAc)_2 \cdot H_2O$ (2)**	**$AgSbF_6$ (10)**	**t-AmOH**	**78**
10	$[RhCp^*Cl_2]_2$ (2.5)		$AgSbF_6$ (10)	t-AmOH	trace
11	$[RhCp^*Cl_2]_2$ (2.5)	$Cu(OAc)_2 \cdot H_2O$ (2)		t-AmOH	65
12	$[RhCp^*Cl_2]_2$ (2.5)	$Cu(OAc)_2 \cdot H_2O$ (0.2)	$AgSbF_6$ (10)	t-AmOH	10
13	$[RhCp^*Cl_2]_2$ (5)	$Cu(OAc)_2 \cdot H_2O$ (2)	$AgSbF_6$ (20)	t-AmOH	80

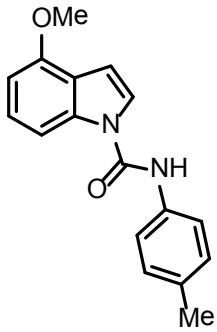
Characterization data for starting materials (1a, 1f–1r and 5a)

N-*p*-Tolyl-1H-indole-1-carboxamide (1a)



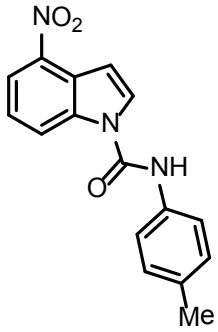
^{1}H NMR (700 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.3 Hz, 1H), 7.68 (d, *J* = 7.7 Hz, 1H), 7.61–7.59 (m, 1H), 7.47–7.44 (m, 2H), 7.41–7.38 (m, 1H), 7.35 (br s, 1H), 7.32–7.30 (m, 1H), 7.25–7.22 (m, 2H), 6.73–6.71 (m, 1H), 2.40 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 149.9, 135.3, 134.8, 134.5, 130.5, 129.9, 124.6, 124.3, 122.7, 121.6, 120.8, 114.2, 107.7, 21.0; IR (KBr) υ 3247, 3148, 3050, 2858, 1672, 1596, 1529, 1448, 1330, 1251, 1202, 1086, 1013, 812, 741 cm^{-1}; HRMS (EI) calcd for $C_{16}H_{14}N_2O$ $[M]^+$ 250.1106, found 250.1107.

4-Methoxy-*N*-*p*-tolyl-1H-indole-1-carboxamide (1f)



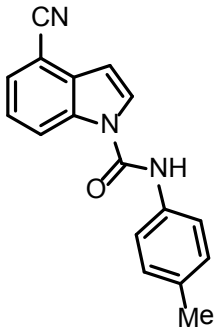
^{1}H NMR (700 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.4 Hz, 1H), 7.41 (d, *J* = 3.5 Hz, 1H), 7.36 (d, *J* = 8.4 Hz, 2H), 7.33 (br s, 1H), 7.22 (d, *J* = 8.3 Hz, 1H), 7.13 (d, *J* = 8.0 Hz, 2H), 6.74 (d, *J* = 3.6 Hz, 1H), 6.64 (d, *J* = 7.8 Hz, 1H), 3.92 (s, 3H), 2.30 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 153.5, 149.9, 136.4, 134.7, 134.6, 129.9, 125.6, 122.9, 120.9, 120.7, 107.1, 104.7, 102.9, 55.6, 21.0; IR (KBr) υ 3317, 3121, 3036, 2937, 1677, 1588, 1517, 1490, 1432, 1327, 1260, 1221, 1065, 1023, 808, 739 cm^{-1}; HRMS (EI) calcd for $C_{17}H_{16}N_2O_2$ $[M]^+$ 280.1212, found 280.1209.

4-Nitro-*N*-*p*-tolyl-1H-indole-1-carboxamide (1g)



^{1}H NMR (700 MHz, $CDCl_3$) δ 8.59 (d, *J* = 8.2 Hz, 1H), 8.21 (d, *J* = 8.0 Hz, 1H), 7.69 (d, *J* = 3.6 Hz, 1H), 7.46 (d, *J* = 3.5 Hz, 1H), 7.43 (t, *J* = 8.1 Hz, 1H), 7.39 (d, *J* = 8.3 Hz, 2H), 7.25 (br s, 1H), 7.20 (d, *J* = 8.1 Hz, 2H), 2.35 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 149.1, 140.8, 137.6, 135.5, 133.9, 130.1, 127.2, 124.5, 124.1, 121.6, 121.0, 119.9, 107.5, 21.1; IR (KBr) υ 3413, 3291, 3126, 3027, 2917, 1715, 1687, 1597, 1530, 1406, 1325, 1194, 1112, 875, 740 cm^{-1}; HRMS (EI) calcd for $C_{16}H_{13}N_3O_3$ $[M]^+$ 295.0957, found 295.0960.

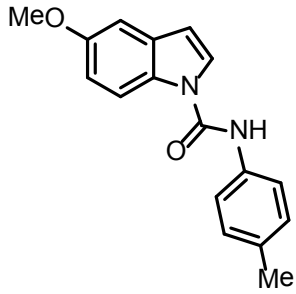
4-Cyano-*N*-*p*-tolyl-1H-indole-1-carboxamide (1h)



^{1}H NMR (700 MHz, $CDCl_3$) δ 8.45 (d, *J* = 8.4 Hz, 1H), 7.65 (d, *J* = 3.6 Hz, 1H), 7.58 (d, *J* = 7.5 Hz, 1H), 7.40–7.38 (m, 3H), 7.22–7.19 (m, 3H), 6.91 (d, *J* = 3.6 Hz, 1H), 2.35 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 149.1, 135.4, 134.0, 131.7, 130.1, 128.2, 127.6, 126.0, 124.6, 121.0, 119.7, 118.0, 106.3, 104.2, 21.1; IR (KBr) υ 3298, 3120, 3020, 2918, 1685, 1596,

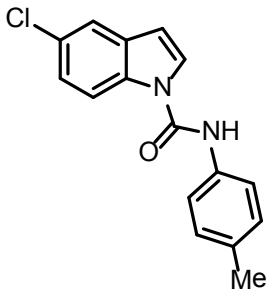
1520, 1411, 1320, 1180, 870, 740 cm^{-1}; HRMS (EI) calcd for $C_{17}H_{13}N_3O$ $[M]^+$ 275.1059, found 275.1054.

5-Methoxy-*N*-*p*-tolyl-1H-indole-1-carboxamide (1i)



^{1}H NMR (700 MHz, $CDCl_3$) δ 7.99 (d, *J* = 9.0 Hz, 1H), 7.50 (d, *J* = 3.5 Hz, 1H), 7.39 (d, *J* = 8.4 Hz, 2H), 7.18–7.17 (m, 3H), 7.06 (d, *J* = 2.4 Hz, 1H), 6.95 (dd, *J* = 8.9, 2.4 Hz, 1H), 6.59 (d, *J* = 3.5 Hz, 1H), 3.85 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 156.0, 149.7, 134.7, 134.6, 131.3, 130.2, 130.0, 124.7, 120.7, 115.0, 113.7, 107.7, 103.8, 55.8, 21.0; IR (KBr) υ 3413, 3291, 3126, 3027, 2917, 1715, 1687, 1597, 1530, 1406, 1325, 1194, 1112, 875, 740 cm^{-1}; HRMS (EI) calcd for $C_{17}H_{16}N_2O_2$ $[M]^+$ 280.1212, found 280.1212.

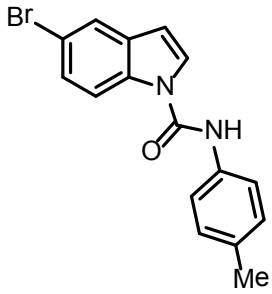
5-Chloro-*N*-*p*-tolyl-1H-indole-1-carboxamide (1j)



^{1}H NMR (700 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.8 Hz, 1H), 7.57 (d, *J* = 2.0 Hz, 1H), 7.51 (d, *J* = 3.6 Hz, 1H), 7.37 (d, *J* = 8.4 Hz, 2H), 7.28 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.18–7.17 (m, 3H), 6.61 (d, *J* = 3.5 Hz, 1H), 2.33 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 149.5, 135.0, 134.3, 134.0, 131.4, 130.0, 128.5, 125.0, 124.9, 121.0, 120.9, 115.6, 107.3, 21.1; IR (KBr) υ 3288, 3181, 3027,

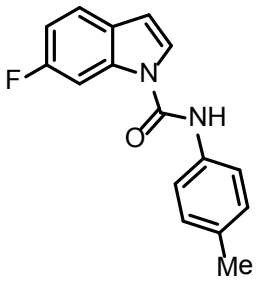
2917, 1669, 1595, 1527, 1447, 1333, 1266, 1249, 1200, 1022, 802 cm^{-1}; HRMS (EI) calcd for $C_{16}H_{13}ClN_2O$ $[M]^+$ 284.0716, found 284.0712.

5-Bromo-*N*-*p*-tolyl-1H-indole-1-carboxamide (1k)



^{1}H NMR (700 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.7 Hz, 1H), 7.72 (s, 1H), 7.48 (d, *J* = 3.5 Hz, 1H), 7.40 (dd, *J* = 8.7, 1.8 Hz, 1H), 7.36 (d, *J* = 8.3 Hz, 2H), 7.22 (br s, 1H), 7.16 (d, *J* = 8.2 Hz, 2H), 6.58 (d, *J* = 3.5 Hz, 1H), 2.32 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 149.5, 135.1, 134.4, 134.32, 134.30, 132.0, 130.0, 127.5, 124.9, 124.0, 120.9, 116.1, 116.0, 107.2, 21.1; IR (KBr) υ 3295, 3114, 3038, 2920, 1675, 1598, 1517, 1445, 1406, 1328, 1266, 1197, 1023, 804, 740 cm^{-1}; HRMS (EI) calcd for $C_{16}H_{13}BrN_2O$ $[M]^+$ 328.0211, found 328.0211.

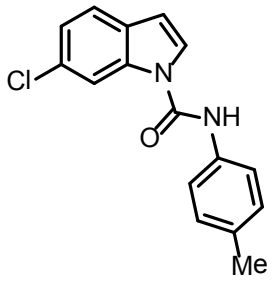
6-Fluoro-*N*-*p*-tolyl-1H-indole-1-carboxamide (1l)



^{1}H NMR (700 MHz, $CDCl_3$) δ 7.92 (dd, *J* = 10.2, 2.2 Hz, 1H), 7.51 (dd, *J* = 8.6, 5.3 Hz, 1H), 7.45 (d, *J* = 3.6 Hz, 1H), 7.38 (d, *J* = 8.3 Hz, 2H), 7.18–7.16 (m, 3H), 6.99 (dt, *J* = 8.7, 2.2 Hz, 1H), 6.64 (d, *J* = 3.5 Hz, 1H), 2.33 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 161.2 (d, $J_{C\text{-}F}$ = 239.1 Hz), 149.6, 135.8, 135.0, 134.6, 130.0, 126.5, 123.9 (d, $J_{C\text{-}F}$ = 4.0 Hz), 122.0 (d, $J_{C\text{-}F}$ = 9.4 Hz), 120.9, 111.3 (d, $J_{C\text{-}F}$ = 24.2 Hz), 107.9, 102.1 (d, $J_{C\text{-}F}$ = 28.4 Hz), 21.1; IR (KBr) υ 3293,

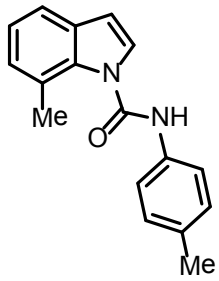
3120, 3034, 2923, 1671, 1596, 1521, 1477, 1440, 1332, 1257, 1210, 1114, 943, 800 cm^{-1}; HRMS (EI) calcd for $C_{16}H_{13}FN_2O$ $[M]^+$ 268.1012, found 268.1016.

6-Chloro-*N*-*p*-tolyl-1H-indole-1-carboxamide (1m)



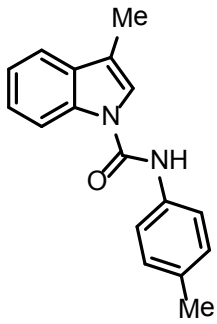
^1H NMR (700 MHz, $CDCl_3$) δ 8.19 (s, 1H), 7.49–7.44 (m, 2H), 7.37–7.34 (m, 2H), 7.27–7.20 (m, 2H), 7.19–7.14 (m, 2H), 6.62–6.60 (m, 1H), 2.32 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 149.5, 135.9, 135.1, 134.2, 130.7, 129.9, 128.7, 124.3, 123.4, 122.0, 120.9, 115.0, 107.8, 21.1; IR (KBr) υ 3273, 3113, 3032, 2920, 1672, 1597, 1517, 1434, 1328, 1249, 1200, 1122, 805 cm^{-1}; HRMS (EI) calcd for $C_{16}H_{13}ClN_2O$ $[M]^+$ 284.0716, found 284.0714.

7-Methyl-*N*-*p*-tolyl-1H-indole-1-carboxamide (1n)



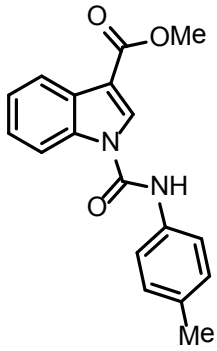
^1H NMR (700 MHz, $CDCl_3$) δ 7.46 (d, J = 7.7 Hz, 1H), 7.41–7.38 (m, 3H), 7.23 (br s, 1H), 7.17–7.15 (m, 3H), 7.10 (d, J = 7.2 Hz, 1H), 6.59 (s, 1H), 2.51 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 150.0, 134.8, 134.6, 134.5, 131.4, 130.0, 127.2, 127.0, 123.8, 122.9, 119.9, 119.2, 106.9, 21.0, 20.6; IR (KBr) υ 3273, 3126, 3046, 2921, 1681, 1600, 1520, 1407, 1321, 1206, 1078 cm^{-1}; HRMS (EI) calcd for $C_{17}H_{16}N_2O$ $[M]^+$ 264.1263, found 264.1267.

3-Methyl-*N*-*p*-tolyl-1H-indole-1-carboxamide (1o)



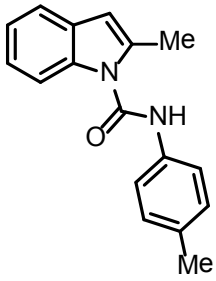
^{1}H NMR (700 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.2 Hz, 1H), 7.54 (d, *J* = 7.7 Hz, 1H), 7.38 (d, *J* = 6.7 Hz, 2H), 7.33 (t, *J* = 7.7 Hz, 1H), 7.28–7.24 (m, 2H), 7.21–7.16 (m, 3H), 2.32 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 149.6, 135.5, 134.6, 134.3, 131.1, 129.7, 124.5, 122.2, 120.9, 120.5, 119.3, 117.0, 114.2, 20.8, 9.6; IR (KBr) υ 3215, 3104, 3030, 2918, 1658, 1594, 1520, 1447, 1345, 1252, 1215, 1085, 737 cm^{-1}; HRMS (EI) calcd for $C_{17}H_{16}N_2O$ $[M]^+$ 264.1263, found 264.1265.

Methyl 1-(*p*-tolylcarbamoyl)-1H-indole-3-carboxylate (1p)



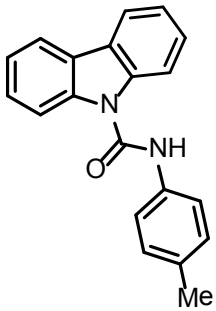
^{1}H NMR (700 MHz, $CDCl_3$) δ 8.25 (s, 1H), 8.13 (d, *J* = 8.2 Hz, 1H), 8.06 (d, *J* = 8.1 Hz, 1H), 7.69 (s, 1H), 7.43 (d, *J* = 8.3 Hz, 2H), 7.37–7.31 (m, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 3.89 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 165.0, 149.0, 135.7, 135.3, 134.1, 130.6, 130.0, 127.4, 125.4, 124.1, 122.1, 120.8, 114.3, 112.2, 51.8, 21.1; IR (KBr) υ 3304, 3132, 3054, 2921, 1681, 1600, 1517, 1449, 1316, 1194, 1112, 735 cm^{-1}; HRMS (EI) calcd for $C_{18}H_{16}N_2O_3$ $[M]^+$ 308.1161, found 308.1161.

2-Methyl-*N*-*p*-tolyl-1H-indole-1-carboxamide (1q)



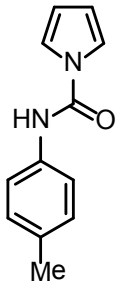
^{1}H NMR (700 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.6 Hz, 1H), 7.49 (d, *J* = 8.0 Hz, 1H), 7.42 (m, 3H), 7.21–7.15 (m, 4H), 6.33 (s, 1H), 2.58 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 149.8, 137.4, 135.5, 134.7, 134.6, 130.0, 129.6, 122.9, 122.2, 120.6, 120.0, 111.8, 106.3, 21.0, 15.0; IR (KBr) υ 3247, 3149, 2858, 1672, 1596, 1529, 1448, 1330, 1251, 1087, 1013, 814 cm^{-1}; HRMS (EI) calcd for $C_{17}H_{16}N_2O$ $[M]^+$ 264.1263, found 264.1260.

***N*-*p*-Tolyl-9H-carbazole-9-carboxamide (1r)**



^{1}H NMR (700 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.9 Hz, 4H), 7.49–7.45 (m, 4H), 7.43 (br s, 1H), 7.36–7.34 (m, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 2.35 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 150.3, 138.4, 134.7, 134.6, 130.0, 127.3, 125.4, 122.8, 120.5, 120.3, 113.7, 21.1; IR (KBr) υ 3216, 3104, 3029, 2917, 1658, 1594, 1520, 1448, 1346, 1251, 1214, 1084 cm^{-1}; HRMS (EI) calcd for $C_{20}H_{16}N_2O$ $[M]^+$ 300.1263, found 300.1264.

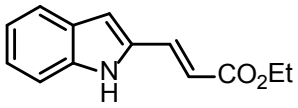
***N*-*p*-Tolyl-1H-pyrrole-1-carboxamide (5a)**



^{1}H NMR (700 MHz, $CDCl_3$) δ 7.35 (d, J = 8.4 Hz, 2H), 7.27–7.24 (m, 2H), 7.21 (br s, 1H), 7.15 (d, J = 8.1 Hz, 2H), 6.31–6.30 (m, 2H), 2.32 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 148.7, 134.9, 134.3, 129.9, 120.8, 118.7, 112.6, 21.0; IR (KBr) υ 3243, 3146, 2860, 1672, 1597, 1449, 1331, 1250, 1086, 1013, 814 cm^{-1}; HRMS (EI) calcd for $C_{12}H_{12}N_2O$ $[M]^+$ 200.0950, found 200.0948.

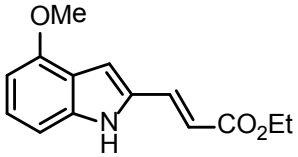
Characterization data for products (3a, 3f–3p, 4b–4l and 6a–c)

(*E*)-Ethyl 3-(1*H*-indol-2-yl)acrylate (3a)



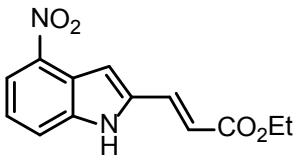
^{1}H NMR (700 MHz, $CDCl_3$) δ 8.60 (br s, 1H), 7.68 (d, *J* = 16.0 Hz, 1H), 7.60 (d, *J* = 7.8 Hz, 1H), 7.34 (d, *J* = 8.1 Hz, 1H), 7.25–7.23 (m, 1H), 7.10 (t, *J* = 7.8 Hz, 1H), 6.79 (s, 1H), 6.25 (d, *J* = 16.0 Hz, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 1.33 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 167.0, 137.7, 134.4, 133.3, 128.3, 124.6, 121.5, 120.5, 115.5, 111.1, 108.9, 60.6, 14.3; IR (KBr) υ 3312, 2981, 1682, 1627, 1611, 1580, 1424, 1368, 1278, 1237, 1178, 1124, 1040, 963, 928, 861, 798 cm^{-1}; HRMS (EI) calcd for $C_{13}H_{13}NO_2$ $[M]^+$ 215.0946, found 215.0944.

(*E*)-Ethyl 3-(4-methoxy-1*H*-indol-2-yl)acrylate (3f)



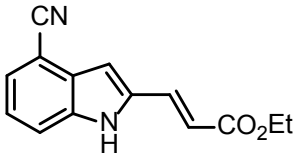
^{1}H NMR (700 MHz, DMSO-d_6) δ 7.60 (d, *J* = 15.9 Hz, 1H), 7.11 (t, *J* = 7.9 Hz, 1H), 6.96 (d, *J* = 8.2 Hz, 1H), 6.91 (s,1H), 6.50–6.48 (m, 2H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.86 (s, 3H), 1.25 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (175 MHz, DMSO-d_6) δ 166.4, 153.3, 139.3, 134.7, 132.3, 125.2, 118.8, 114.8, 106.1, 104.6, 99.4, 59.8, 54.9, 14.2; IR (KBr) υ 3311, 2924, 1683, 1608, 1587, 1511, 1462, 1365, 1315, 1249, 1161, 1133, 1095, 1033, 972, 769 cm^{-1}; HRMS (EI) calcd for $C_{14}H_{15}NO_3$ $[M]^+$ 245.1052, found 245.1049.

(*E*)-Ethyl 3-(4-nitro-1*H*-indol-2-yl)acrylate (3g)



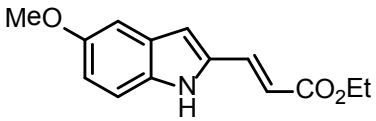
^{1}H NMR (700 MHz, DMSO-d_6) δ 12.40 (br s, 1H), 8.07 (d, J = 7.9 Hz, 1H), 7.87 (d, J = 7.9 Hz, 1H), 7.73 (d, J = 16.1 Hz, 1H), 7.48 (s, 1H), 7.40 (t, J = 7.9 Hz, 1H), 6.73 (d, J = 16.1 Hz, 1H), 4.22 (q, J = 7.1 Hz, 2H), 1.27 (t, J = 7.0 Hz, 3H); ^{13}C NMR (175 MHz, DMSO-d_6) δ 165.8, 139.7, 139.6, 138.0, 133.6, 122.8, 121.3, 119.3, 119.1, 117.6, 106.7, 60.2, 14.1; IR (KBr) υ 3299, 2981, 2927, 1988, 1689, 1638, 1507, 1488, 1343, 1325, 1276, 1237, 1179, 1136, 1036, 991, 795 cm^{-1}; HRMS (EI) calcd for $C_{13}H_{12}N_2O_4$ $[M]^+$ 260.0797, found 260.0789.

(*E*)-Ethyl 3-(4-cyano-1*H*-indol-2-yl)acrylate (3h)



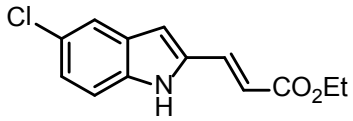
^{1}H NMR (700 MHz, $CDCl_3$) δ 8.93 (br s, 1H), 7.68 (d, J = 16.0 Hz, 1H), 7.58 (dt, J = 8.3, 0.8 Hz, 1H), 7.46 (dd, J = 7.3, 0.8 Hz, 1H), 7.28–7.26 (m, 1H), 6.99 (s, 1H), 6.38 (d, J = 16.0 Hz, 1H), 4.30 (q, J = 7.1 Hz, 2H), 1.34 (t, J = 7.1 Hz, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 166.4, 137.1, 135.6, 133.3, 129.5, 126.1, 123.8, 118.5, 118.1, 115.8, 106.2, 103.8, 60.9, 14.2; IR (KBr) υ 3307, 2980, 2217, 1690, 1633, 1520, 1432, 1367, 1345, 1276, 1176, 1141, 1032, 968, 859, 780 cm^{-1}; HRMS (EI) calcd for $C_{14}H_{12}N_2O_2$ $[M]^+$ 240.0899, found 240.0894.

(*E*)-Ethyl 3-(5-methoxy-1*H*-indol-2-yl)acrylate (3i)



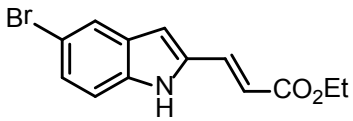
^{1}H NMR (700 MHz, $CDCl_3$) δ 8.58 (br s, 1H), 7.64 (d, J = 15.9 Hz, 1H), 7.22 (d, J = 8.8 Hz, 1H), 7.01 (s, 1H), 6.91 (d, J = 8.8 Hz, 1H), 6.72 (s, 1H), 6.23 (d, J = 15.9 Hz, 1H), 4.26 (q, J = 7.1 Hz, 2H), 3.82 (s, 3H), 1.32 (t, J = 7.0 Hz, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 167.1, 155.5, 134.4, 133.9, 133.0, 128.7, 115.5, 115.1, 112.0, 108.3, 102.1, 60.6, 55.6, 14.3; IR (KBr) υ 3332, 2934, 1686, 1619, 1520, 1454, 1368, 1264, 1162, 1122, 1030, 970, 839, 972 cm^{-1}; HRMS (EI) calcd for $C_{14}H_{15}NO_3$ $[M]^+$ 245.1052, found 245.1053.

(*E*)-Ethyl 3-(5-chloro-1*H*-indol-2-yl)acrylate (3j)



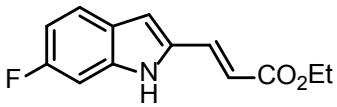
^{1}H NMR (700 MHz, DMSO-d_6) δ 11.76 (br s, 1H), 7.63–7.61 (m, 2H), 7.38 (d, *J* = 8.6 Hz, 1H), 7.18 (dd, *J* = 8.6, 2.1 Hz, 1H), 6.88 (s, 1H), 6.57 (d, *J* = 15.9 Hz, 1H), 4.19 (q, *J* = 7.0 Hz, 2H), 1.26 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (175 MHz, DMSO-d_6) δ 166.1, 136.3, 135.2, 134.3, 128.8, 124.2, 123.8, 120.1, 116.7, 113.0, 107.5, 60.0, 14.2; IR (KBr) υ 3329, 2923, 2852, 1690, 1628, 1613, 1519, 1467, 1310, 1272, 1187, 1126, 1030, 967, 864, 795 cm^{-1}; HRMS (EI) calcd for $C_{13}H_{12}ClNO_2$ $[M]^+$ 249.0557, found 249.0542.

(*E*)-Ethyl 3-(5-bromo-1*H*-indol-2-yl)acrylate (3k)



^{1}H NMR (700 MHz, DMSO-d_6) δ 11.77 (s, 1H), 7.76 (d, *J* = 1.8 Hz, 1H), 7.62 (d, *J* = 15.9 Hz, 1H), 7.34 (d, *J* = 8.6 Hz, 1H), 7.21 (dd, *J* = 8.6, 1.9 Hz, 1H), 6.88 (s, 1H), 6.57 (d, *J* = 15.9 Hz, 1H), 4.19 (q, *J* = 7.0 Hz, 2H), 1.26 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (175 MHz, DMSO-d_6) δ 166.1, 136.5, 135.0, 134.2, 129.6, 126.2, 123.1, 116.7, 113.4, 112.1, 107.4, 60.0, 14.1; IR (KBr) υ 3312, 2924, 1686, 1624, 1569, 1416, 1310, 1281, 1182, 1125, 1030, 967, 854, 794 cm^{-1}; HRMS (EI) calcd for $C_{13}H_{12}BrNO_2$ $[M]^+$ 293.0051, found 293.0052.

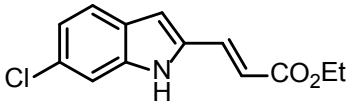
(*E*)-Ethyl 3-(6-fluoro-1*H*-indol-2-yl)acrylate (3l)



^{1}H NMR (700 MHz, $CDCl_3$) δ 8.84 (br s, 1H), 7.64 (d, *J* = 15.9 Hz, 1H), 7.51–7.49 (m, 1H), 7.02 (d, *J* = 9.3 Hz, 1H), 6.86 (t, *J* = 9.5 Hz, 1H), 6.75 (s, 1H), 6.25 (d, *J* = 15.9 Hz, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 1.33 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 167.1, 161.2

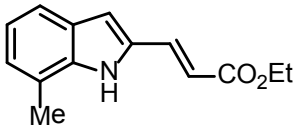
(d, $J_{C\text{-}F}$ = 240.8 Hz), 138.0 (d, $J_{C\text{-}F}$ = 12.3 Hz), 134.1, 133.9 (d, $J_{C\text{-}F}$ = 3.0 Hz), 124.9, 122.5 (d, $J_{C\text{-}F}$ = 10.4 Hz), 115.2, 109.7 (d, $J_{C\text{-}F}$ = 24.6 Hz), 108.9, 97.4 (d, $J_{C\text{-}F}$ = 26.8 Hz), 60.7, 14.3; IR (KBr) υ 3313, 2923, 1685, 1613, 1503, 1446, 1366, 1264, 1235, 1137, 1104, 1037, 970, 812, 730 cm^{-1}; HRMS (EI) calcd for $C_{13}H_{12}FNO_2$ $[M]^+$ 233.0852, found 233.0845.

(*E*)-Ethyl 3-(6-chloro-1*H*-indol-2-yl)acrylate (3m)



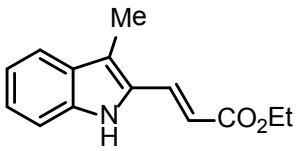
^{1}H NMR (700 MHz, $CDCl_3$) δ 8.76 (br s, 1H), 7.64 (d, *J* = 16.0 Hz, 1H), 7.49 (d, *J* = 8.4 Hz, 1H), 7.33 (s, 1H), 7.06 (dd, *J* = 8.4, 1.7 Hz, 1H), 6.75 (s, 1H), 6.27 (d, *J* = 16.0 Hz, 1H), 4.28 (q, *J* = 7.0 Hz, 2H), 1.34 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 167.2, 138.3, 134.3, 134.2, 130.5, 127.1, 122.5, 121.6, 116.3, 111.2, 108.8, 61.0, 14.5; IR (KBr) υ 3319, 2923, 1683, 1607, 1573, 1444, 1367, 1281, 1131, 1041, 966, 922, 816 cm^{-1}; HRMS (EI) calcd for $C_{13}H_{12}ClNO_2$ $[M]^+$ 249.0557, found 249.0554.

(*E*)-Ethyl 3-(7-methyl-1*H*-indol-2-yl)acrylate (3n)



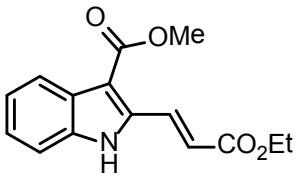
^{1}H NMR (700 MHz, $CDCl_3$) δ 8.39 (br s, 1H), 7.68 (d, *J* = 16.0 Hz, 1H), 7.45 (d, *J* = 7.6 Hz, 1H), 7.05–7.01 (m, 2H), 6.80 (s, 1H), 6.30 (d, *J* = 16.0 Hz, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 2.50 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 167.2, 137.6, 134.7, 133.3, 128.2, 125.2, 121.0, 120.6, 119.4, 115.5, 109.7, 60.8, 16.8, 14.5; IR (KBr) υ 3339, 2924, 2854, 1692, 1632, 1516, 1461, 1369, 1264, 1178, 1041, 972, 806, 735 cm^{-1}; HRMS (EI) calcd for $C_{14}H_{15}NO_2$ $[M]^+$ 229.1103, found 229.1099.

(*E*)-Ethyl 3-(3-methyl-1*H*-indol-2-yl)acrylate (3o)



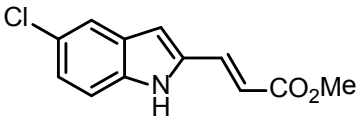
^{1}H NMR (700 MHz, $CDCl_3$) δ 8.15 (br s, 1H), 7.80 (d, *J* = 15.9 Hz, 1H), 7.56 (d, *J* = 7.9 Hz, 1H), 7.29 (d, *J* = 8.1 Hz, 1H), 7.26–7.24 (m, 1H), 7.09 (t, *J* = 7.9 Hz, 1H), 6.11 (d, *J* = 15.9 Hz, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 2.41 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 167.2, 137.3, 132.1, 129.9, 129.0, 125.0, 119.9, 119.8, 118.7, 113.7, 110.9, 60.5, 14.3, 8.9; IR (KBr) υ 3323, 2978, 2924, 1682, 1611, 1531, 1456, 1367, 1294, 1236, 1184, 1040, 960, 851, 739 cm^{-1}; HRMS (EI) calcd for $C_{14}H_{15}NO_2$ $[M]^+$ 229.1103, found 229.1102.

(*E*)-Methyl 2-(3-ethoxy-3-oxoprop-1-enyl)-1*H*-indole-3-carboxylate (3p)



^{1}H NMR (700 MHz, $CDCl_3$) δ 9.26 (br s, 1H), 8.56 (d, *J* = 16.5 Hz, 1H), 8.16 (d, *J* = 8.1 Hz, 1H), 7.38 (d, *J* = 8.1 Hz, 1H), 7.30 (t, *J* = 7.0 Hz, 1H), 7.24–7.22 (m, 1H), 6.47 (d, *J* = 16.3 Hz, 1H), 4.31 (q, *J* = 7.1 Hz, 2H), 3.96 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 166.7, 165.6, 137.5, 136.5, 133.4, 127.4, 125.5, 122.8, 122.6, 120.1, 111.4, 109.8, 61.3, 51.6, 14.5; IR (KBr) υ 3295, 2924, 1684, 1516, 1498, 1447, 1368, 1279, 1182, 1080, 1042, 983, 866, 788 cm^{-1}; HRMS (EI) calcd for $C_{15}H_{15}NO_4$ $[M]^+$ 273.1001, found 273.1010.

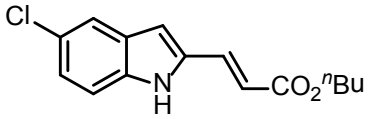
(*E*)-Methyl 3-(5-chloro-1*H*-indol-2-yl)acrylate (4b)



^{1}H NMR (700 MHz, DMSO-d_6) δ 11.78 (br s, 1H), 7.65–7.62 (m, 2H), 7.39 (d, *J* = 8.6 Hz, 1H), 7.17 (dd, *J* = 8.6, 1.9 Hz, 1H), 6.89 (s, 1H), 6.57 (d, *J* = 16.0 Hz, 1H), 3.73 (s, 3H); ^{13}C NMR (175 MHz, DMSO-d_6) δ 166.4, 136.1, 134.9, 134.3, 128.6, 124.0, 123.6, 119.9, 116.0,

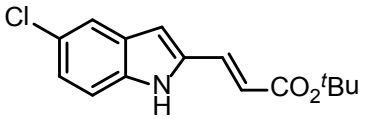
112.8, 107.5, 51.3; IR (KBr) υ 3340, 1693, 1630, 1514, 1436, 1369, 1293, 1273, 1129, 1034, 973, 913, 859, 785 cm^{-1}; HRMS (EI) calcd for $C_{12}H_{10}ClNO_2$ $[M]^+$ 235.0400, found 235.0398.

(*E*)-Butyl 3-(5-chloro-1*H*-indol-2-yl)acrylate (4c)



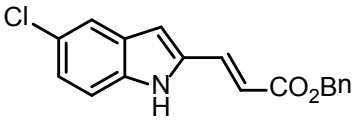
^{1}H NMR (700 MHz, DMSO-d_6) δ 11.77 (br s, 1H), 7.63–7.61 (m, 2H), 7.38 (d, *J* = 8.6 Hz, 1H), 7.18 (dd, *J* = 8.6, 2.1 Hz, 1H), 6.89 (s, 1H), 6.57 (d, *J* = 16.0 Hz, 1H), 4.15 (t, *J* = 6.5 Hz, 2H), 1.64–1.61 (m, 2H), 1.39–1.36 (m, 2H), 0.92 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (175 MHz, DMSO-d_6) δ 165.9,136.1, 135.0, 134.1, 128.6, 124.0, 123.5, 119.0, 116.4, 112.8, 107.3, 63.5, 30.0, 18.4, 13.3; IR (KBr) υ 3348, 2939, 2030, 1693, 1631, 1449, 1418, 1309, 1275, 1177, 1129, 1025, 915, 795 cm^{-1}; HRMS (EI) calcd for $C_{15}H_{16}ClNO_2$ $[M]^+$ 277.0870, found 277.0876.

(*E*)-*tert*-Butyl 3-(5-chloro-1*H*-indol-2-yl)acrylate (4d)



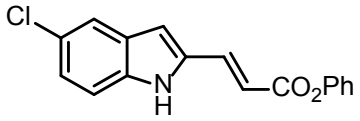
^{1}H NMR (700 MHz, $CDCl_3$) δ 8.68 (br s, 1H), 7.55–7.52 (m, 2H), 7.26 (d, *J* = 8.6 Hz, 1H), 7.17 (dd, *J* = 8.6, 1.9 Hz, 1H), 6.69 (s, 1H), 6.23 (d, *J* = 16.0 Hz, 1H), 1.54 (s, 9H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 166.1, 135.9, 134.8, 133.0, 129.4, 126.0, 124.6, 120.6, 118.5, 112.0, 107.4, 80.9, 28.2; IR (KBr) υ 3318, 2978, 2930, 1681, 1629, 1515, 1475, 1366, 1286, 1156, 1127, 1063, 965, 918, 854, 794 cm^{-1}; HRMS (EI) calcd for $C_{15}H_{16}ClNO_2$ $[M]^+$ 277.0870, found 277.0868.

(*E*)-Benzyl 3-(5-chloro-1*H*-indol-2-yl)acrylate (4e)



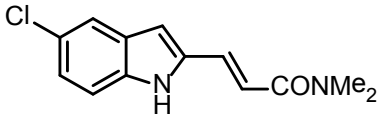
^{1}H NMR (700 MHz, $CDCl_3$) δ 8.47 (br s, 1H), 7.67 (d, *J* = 16.0 Hz, 1H), 7.55 (d, *J* = 1.8 Hz, 1H), 7.40–7.32 (m, 5H), 7.25–7.24 (m, 1H), 7.18 (dd, *J* = 8.6, 2.0 Hz, 1H), 6.72 (s, 1H), 6.29 (d, *J* = 16.0 Hz, 1H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 166.7, 136.2, 136.0, 134.7, 134.6, 129.5, 128.8, 128.5, 128.4, 126.5, 125.2, 121.0, 116.3, 112.4, 108.4, 66.8; IR (KBr) υ 3325, 2923, 1684, 1630, 1516, 1450, 1373, 1270, 1164, 1125, 1059, 1006, 966, 915, 852, 793 cm^{-1}; HRMS (EI) calcd for $C_{18}H_{14}ClNO_2$ $[M]^+$ 311.0713, found 311.0712.

(*E*)-Phenyl 3-(5-chloro-1*H*-indol-2-yl)acrylate (4f)



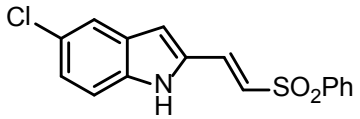
^{1}H NMR (700 MHz, $CDCl_3$) δ 8.53 (br s, 1H), 7.83 (d, *J* = 15.9 Hz, 1H), 7.58 (s, 1H), 7.41–7.39 (m, 2H), 7.26–7.24 (m, 1H), 7.19–7.15 (m, 3H), 6.81 (s, 1H), 6.43 (d, *J* = 15.9 Hz, 1H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 165.4, 150.9, 136.4, 135.9, 134.5, 129.7, 129.5, 126.6, 126.1, 125.4, 121.8, 121.1, 115.6, 112.5, 108.9; IR (KBr) υ 3350, 2922, 2853, 2029, 1702, 1631, 1591, 1520, 1491, 1415, 1364, 1305, 1275, 1193, 1139, 1064, 970, 857, 796 cm^{-1}; HRMS (EI) calcd for $C_{17}H_{12}ClNO_2$ $[M]^+$ 297.0557, found 297.0560.

(*E*)-3-(5-Chloro-1*H*-indol-2-yl)-*N*,*N*-dimethylacrylamide (4g)



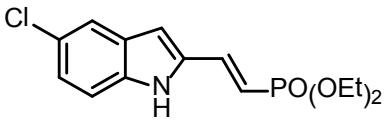
^{1}H NMR (700 MHz, DMSO-d_6) δ 11.67 (br s, 1H), 7.59 (d, *J* = 1.9 Hz, 1H), 7.44 (d, *J* = 15.3 Hz, 1H), 7.38 (d, *J* = 8.6 Hz, 1H), 7.20 (d, *J* = 15.4 Hz, 1H), 7.15 (dd, *J* = 8.6, 2.1 Hz, 1H), 6.78 (s, 1H), 3.16 (s, 3H), 2.94 (s, 3H); ^{13}C NMR (175 MHz, DMSO-d_6) δ 165.0, 136.2, 135.7, 130.8, 128.8, 123.7, 122.8, 119.5, 117.1, 112.5, 105.6, 36.5, 35.0; IR (KBr) υ 3254, 2924, 1624, 1590, 1422, 1398, 1311, 1249, 1151, 1125, 1059, 983, 913, 858, 786 cm^{-1}; HRMS (EI) calcd for $C_{13}H_{13}ClNO_2$ $[M]^+$ 248.0716, found 248.0711.

(*E*)-5-Chloro-2-(2-(phenylsulfonyl)vinyl)-1*H*-indole (4h)



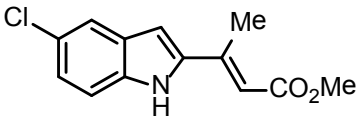
^{1}H NMR (700 MHz, $CDCl_3$) δ 8.92 (br s, 1H), 7.91 (d, *J* = 8.4 Hz, 2H), 7.65 (d, *J* = 15.3 Hz, 1H), 7.60–7.58 (m, 1H), 7.54–7.50 (m, 3H), 7.20 (d, *J* = 8.6 Hz, 1H), 7.16 (dd, *J* = 8.6, 1.9 Hz, 1H), 6.82 (d, *J* = 15.4 Hz, 1H), 6.77 (s, 1H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 140.5, 136.4, 133.5, 132.3, 132.2, 129.4, 128.9, 127.4, 126.4, 125.5, 124.8, 120.9, 112.5, 109.6; IR (KBr) υ 3341, 2921, 2852, 1607, 1511, 1445, 1313, 1283, 1141, 1082, 962, 915, 832, 787 cm^{-1}; HRMS (EI) calcd for $C_{16}H_{12}ClNO_2S$ $[M]^+$ 317.0277, found 317.0273.

(*E*)-Diethyl 2-(5-chloro-1*H*-indol-2-yl)vinylphosphonate (4i)



^{1}H NMR (700 MHz, $CDCl_3$) δ 10.86 (br s, 1H), 7.54 (d, *J* = 1.9 Hz, 1H), 7.41 (dd, *J* = 22.4, 17.4 Hz, 1H), 7.30 (d, *J* = 8.6 Hz, 1H), 6.64 (s, 1H), 6.38 (t, *J* = 17.8 Hz, 1H), 4.15–4.10 (m, 4H), 1.33 (t, *J* = 7.0 Hz, 6H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 138.6 (d, $J_{C\text{-}P}$ = 5.7 Hz), 136.3, 135.5 (d, $J_{C\text{-}P}$ = 25.7 Hz), 129.0, 125.5, 124.2, 120.4, 112.5, 111.0 (d, $J_{C\text{-}P}$ = 193.6 Hz), 106.0, 62.3, 62.2, 16.4, 16.3; IR (KBr) υ 3180, 2978, 2030, 1610, 1574, 1443, 1420, 1316, 1214, 1132, 1045, 1021, 960, 855, 792 cm^{-1}; HRMS (EI) calcd for $C_{14}H_{17}ClNO_3P$ $[M]^+$ 313.0635, found 313.0642.

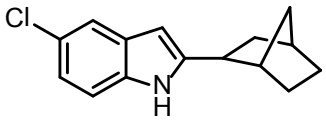
(*E*)-Methyl 3-(5-chloro-1*H*-indol-2-yl)but-2-enoate (4j)



^{1}H NMR (700 MHz, $CDCl_3$) δ 8.33 (br s, 1H), 7.55 (d, *J* = 7.9 Hz, 1H), 7.24 (d, *J* = 7.7 Hz, 1H), 7.17 (dd, *J* = 8.6, 1.9 Hz, 1H), 6.78 (s, 1H), 6.15 (s, 1H), 3.75 (s, 3H), 2.59 (s, 3H); ^{13}C

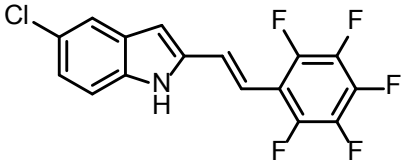
NMR (175 MHz, $CDCl_3$) δ 167.0, 145.2, 139.1, 135.4, 129.4, 126.1, 124.5, 120.6, 113.0, 112.1, 104.8, 51.3, 16.0; IR (KBr) υ 3337, 2927, 2856, 2030, 1714, 1672, 1604, 1517, 1437, 1315, 1283, 1199, 1154, 1060, 912, 858, 793 cm^{-1}; HRMS (EI) calcd for $C_{13}H_{12}ClNO_2$ $[M]^+$ 249.0557, found 249.0554.

2-Bicyclo[2.2.1]heptan-2-yl-5-chloro-1*H*-indole (4k)



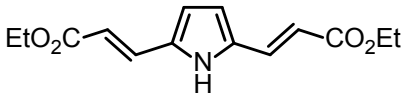
^1H NMR (700 MHz, $CDCl_3$) δ 7.85 (br s, 1H), 7.45 (d, J = 2.0 Hz, 1H), 7.16 (d, J = 8.4 Hz, 1H), 7.04 (dd, J = 8.4, 1.9 Hz, 1H), 6.13 (s, 1H), 2.78 (t, J = 6.7 Hz, 1H), 2.42–2.36 (m, 2H), 1.75–1.73 (m, 2H), 1.63–1.56 (m, 2H), 1.48–1.45 (m, 1H), 1.34–1.32 (m, 1H), 1.28–1.25 (m, 1H), 1.20–1.19 (m, 1H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 146.4, 134.2, 129.6, 125.0, 121.1, 119.2, 111.1, 97.9, 42.6, 41.2, 37.3, 36.3, 36.2, 29.7, 28.8; IR (KBr) υ 3415, 2950, 2869, 1708, 1575, 1539, 1459, 1408, 1305, 1204, 1150, 1058, 913, 863, 781 cm^{-1}; HRMS (EI) calcd for $C_{15}H_{16}ClN$ $[M]^+$ 245.0971, found 245.0977.

(*E*)-5-Chloro-2-(perfluorostyryl)-1*H*-indole (4l)



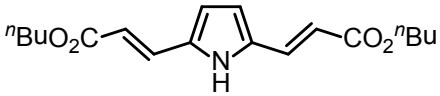
^1H NMR (700 MHz, $CDCl_3$) δ 8.28 (br s, 1H), 7.54 (d, J = 1.9 Hz, 1H), 7.40 (d, J = 16.8 Hz, 1H), 7.26 (d, J = 8.6 Hz, 1H), 7.16 (dd, J = 8.6, 2.0 Hz, 1H), 6.76 (d, J = 16.8 Hz, 1H), 6.64 (s, 1H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 144.7 (d, $J_{C\text{-}F}$ = 247.1 Hz), 137.8 (d, $J_{C\text{-}F}$ = 248.2 Hz), 136.5, 136.3 (d, $J_{C\text{-}F}$ = 240.4 Hz), 135.6, 129.6, 129.4, 126.6, 126.1, 124.0, 120.4, 111.8, 111.5, 105.3; IR (KBr) υ 3460, 2924, 2029, 1962, 1493, 1415, 1308, 1226, 1151, 1006, 955, 868, 792 cm^{-1}; HRMS (EI) calcd for $C_{16}H_7ClF_5N$ $[M]^+$ 343.0187, found 343.0175.

(2*E*,2'*E*)-Diethyl 3,3'-(1*H*-pyrrole-2,5-diyl)diacrylate (6a)



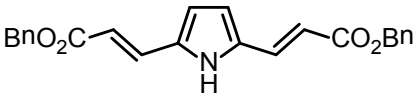
^{1}H NMR (700 MHz, $CDCl_3$) δ 9.88 (br s, 1H), 7.52 (d, *J* = 15.9 Hz, 2H), 6.53 (d, *J* = 2.3 Hz, 2H), 6.35 (d, *J* = 15.9 Hz, 2H), 4.27 (q, *J* = 7.1 Hz, 4H), 1.31 (t, *J* = 7.0 Hz, 6H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 167.8, 133.6, 132.4, 116.1, 114.4, 60.9, 14.5; IR (KBr) υ 3329, 2923, 2853, 1708, 1682, 1622, 1546, 1366, 1271, 1168, 1047, 1035, 965, 862, 788 cm^{-1}; HRMS (EI) calcd for $C_{14}H_{17}NO_4$ $[M]^+$ 263.1158, found 263.1164.

(2*E*,2'*E*)-Dibutyl 3,3'-(1*H*-pyrrole-2,5-diyl)diacrylate (6b)



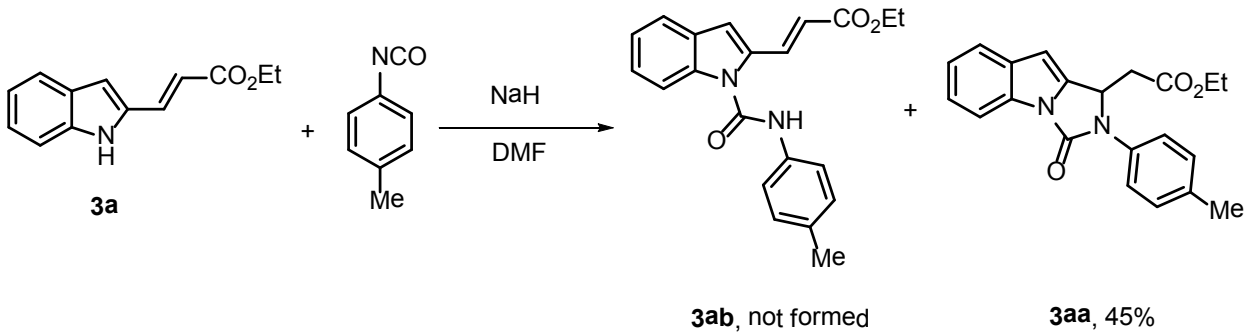
^{1}H NMR (700 MHz, $CDCl_3$) δ 10.28 (br s, 1H), 7.52 (d, *J* = 15.9 Hz, 2H), 6.53 (d, *J* = 2.3 Hz, 2H), 6.40 (d, *J* = 15.9 Hz, 2H), 4.21 (t, *J* = 6.5 Hz, 4H), 1.67–1.63 (m, 4H), 1.43–1.34 (m, 4H), 0.93 (t, *J* = 7.3 Hz, 6H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 168.0, 133.7, 132.5, 116.1, 114.3, 64.9, 31.0, 19.4, 13.9; IR (KBr) υ 3333, 2954, 1704, 1678, 1619, 1545, 1463, 1385, 1276, 1162, 1062, 1001, 965, 864, 785 cm^{-1}; HRMS (EI) calcd for $C_{18}H_{25}NO_4$ $[M]^+$ 319.1784, found 319.1780.

(2*E*,2'*E*)-Benzyl 3,3'-(1*H*-pyrrole-2,5-diyl)diacrylate (6c)



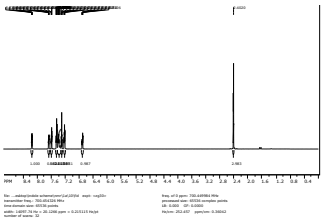
^{1}H NMR (700 MHz, $CDCl_3$) δ 9.88 (br s, 1H), 7.54 (d, *J* = 15.9 Hz, 2H), 7.40–7.25 (m, 10H), 6.53 (d, *J* = 2.1 Hz, 2H), 6.40 (d, *J* = 15.9 Hz, 2H), 5.23–5.19 (m, 4H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 167.5, 136.1, 134.0, 132.5, 128.7, 128.5, 128.4, 116.4, 114.1, 66.7; IR (KBr) υ 3335, 2927, 1960, 1686, 1620, 1544, 1455, 1414, 1377, 1260, 1154, 1008, 971, 854, 784 cm^{-1}; HRMS (EI) calcd for $C_{24}H_{21}NO_4$ $[M]^+$ 387.1471, found 387.1473.

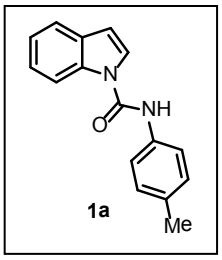
Ethyl 2-(3-oxo-2-p-tolyl-2,3-dihydro-1H-imidazo[1,5-a]indol-1-yl)acetate (3aa)

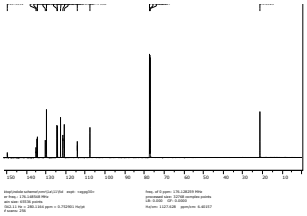


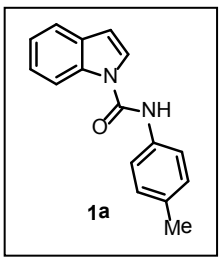
To a stirred suspension of **3a** (120 mg, 0.56 mmol) in dry DMF (2 mL) was added NaH (60% dispersion in mineral oil, 2.0 equiv.) at 0 ^{o}C under N_2 atmosphere. The reaction mixture was then stirred at room temperature for 3 h and *p*-tolyl isocyanate (1.5 equiv.) was added dropwise. The reaction mixture was then stirred at room temperature for overnight. The reaction mixture was washed with H_2O and extracted with EtOAc (10 mL). The organic layer was then washed with an aqueous solution of 1 N HCl (10 mL). The organic layer was dried over Mg_2SO_4 and concentrated in vacuo. The residue was purified by flash column chromatography.

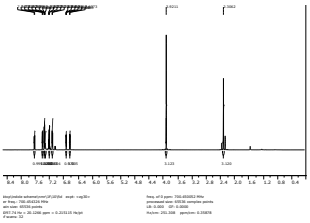
^{1}H NMR (700 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.0 Hz, 1H), 7.58 (d, *J* = 7.8 Hz, 1H), 7.37 (d, *J* = 8.4 Hz, 2H), 7.30 (t, *J* = 8.1 Hz, 1H), 7.25–7.23 (m, 3H), 6.43 (s, 1H), 5.59–5.57 (m, 1H), 4.14–4.11 (m, 2H), 3.00 (dd, *J* = 16.4, 4.1 Hz, 1H), 2.58 (dd, *J* = 15.1, 9.3 Hz, 1H), 2.35 (s, 3H), 1.97 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 169.9, 150.1, 137.2, 136.1, 133.4, 133.1, 130.7, 130.2, 123.6, 123.5, 123.0, 121.3, 112.9, 98.8, 61.2, 53.9, 38.0, 21.1, 14.2; IR (KBr) υ 3332, 2924, 1962, 1680, 1610, 1540, 1457, 1414, 1377, 1240, 1144, 1008, 971, 854, 784 cm^{-1}; HRMS (EI) calcd for $C_{21}H_{20}N_2O_3$ $[M]^+$ 348.1474, found 348.1472.

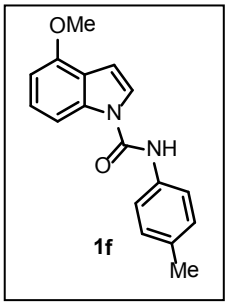


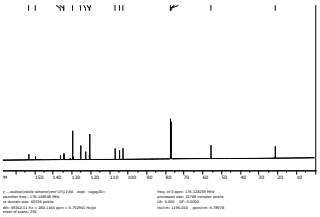

N
NH
O
1a
Me

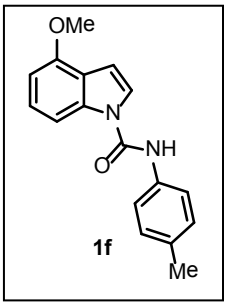


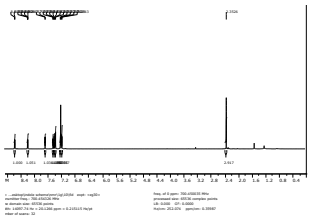

N
NH
O
1a
Me

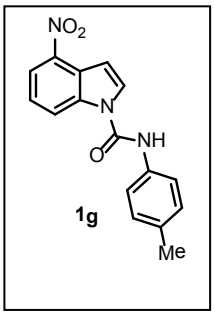


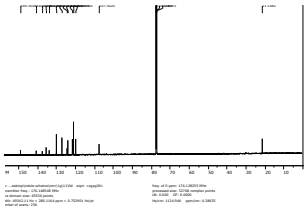

OMe
N
NH
O
1f
Me

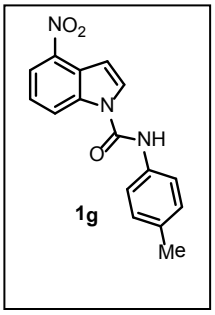


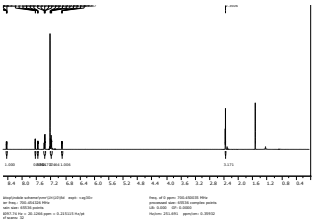

OMe
N
NH
O
1f
Me

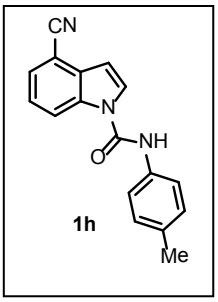











CN
N
NH
O
1h
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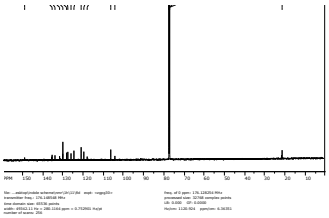

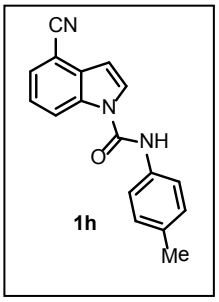
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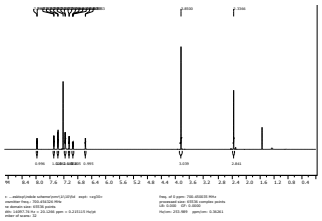

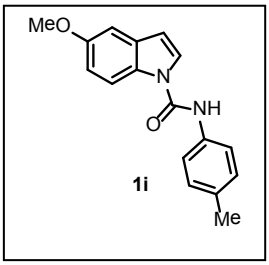

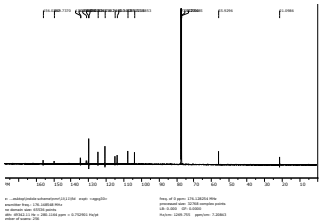

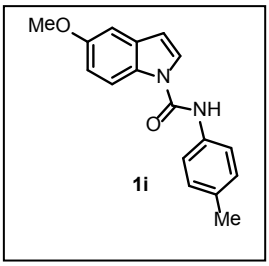

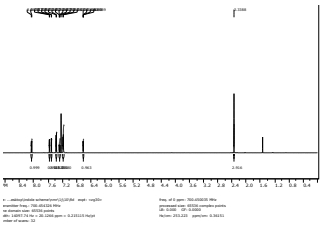

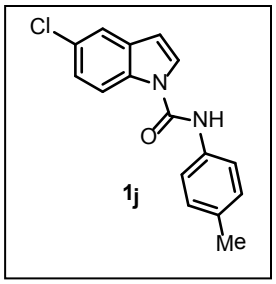

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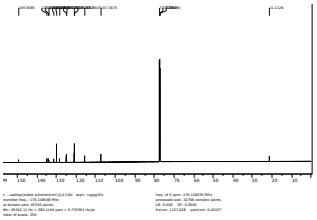

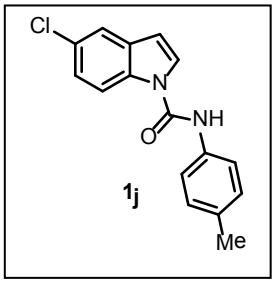

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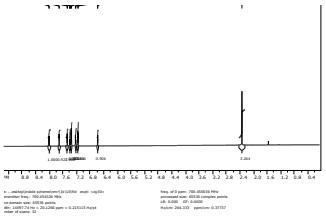

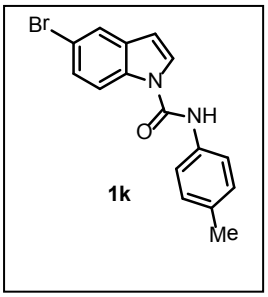
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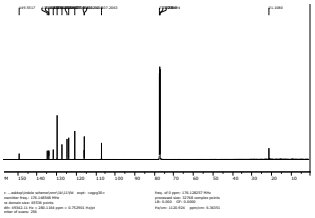

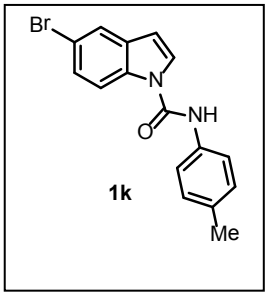
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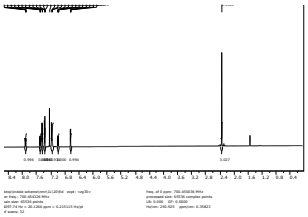

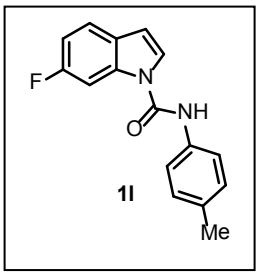
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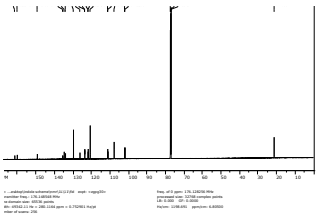

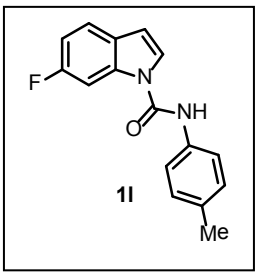
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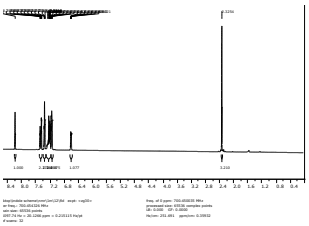

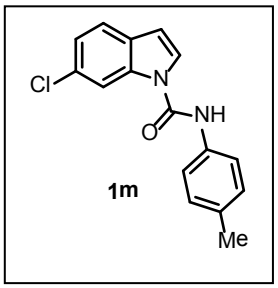
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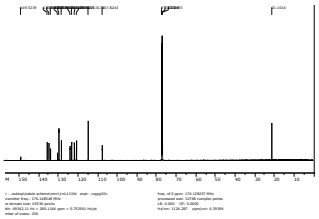

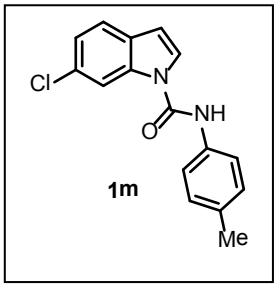
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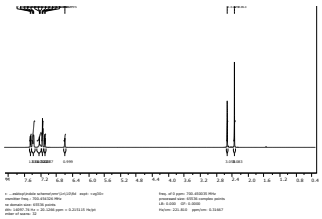

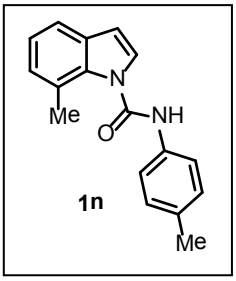
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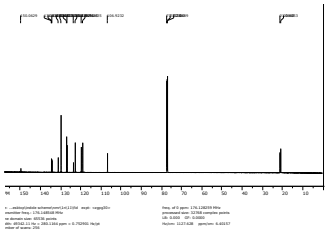

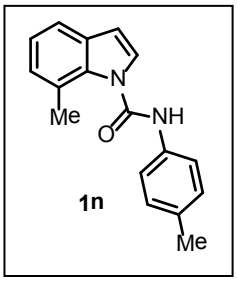
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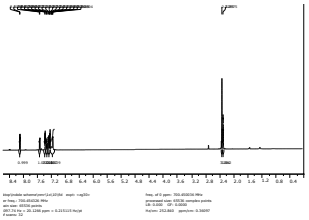

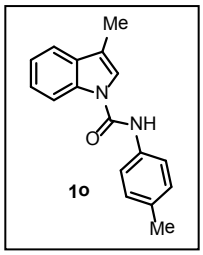
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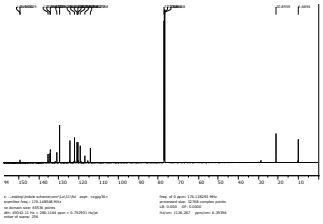

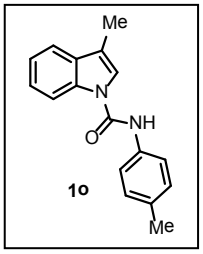
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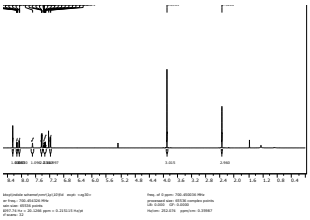

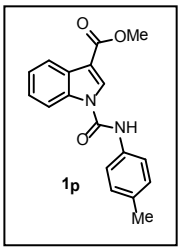
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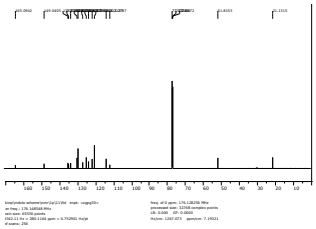

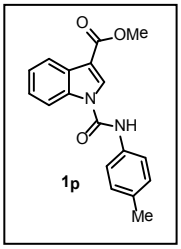
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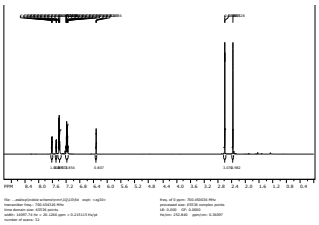

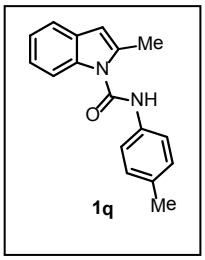

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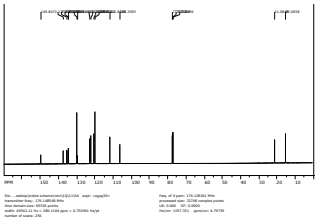

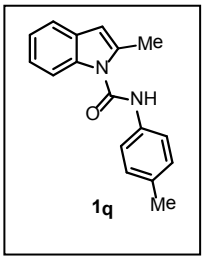

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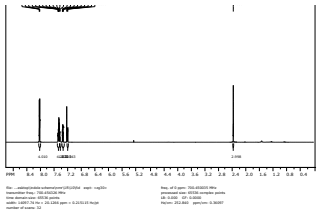

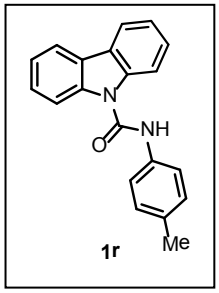

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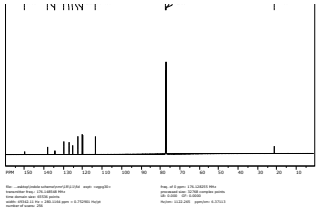

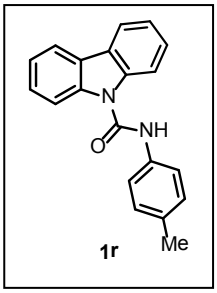

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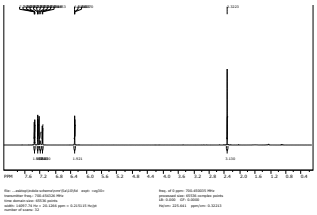

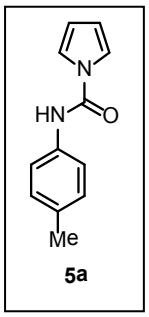

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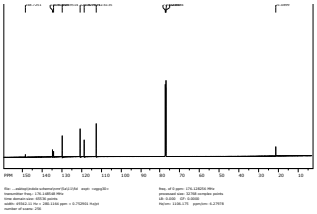

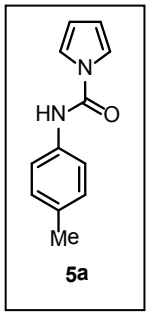

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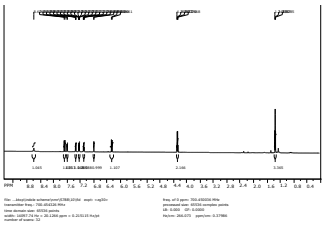

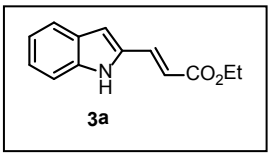

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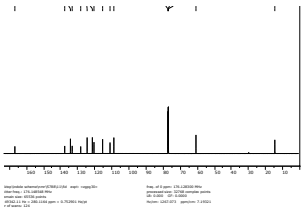

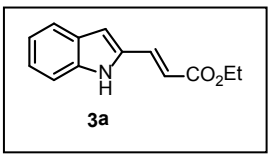

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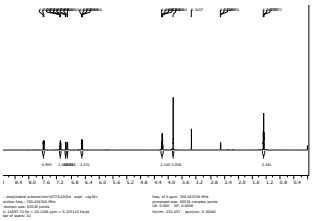

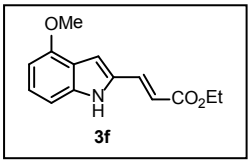

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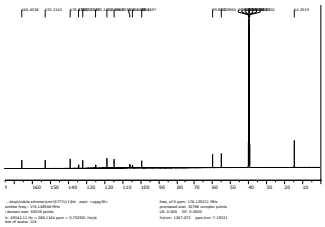

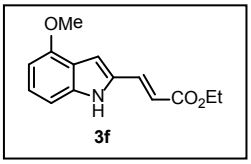

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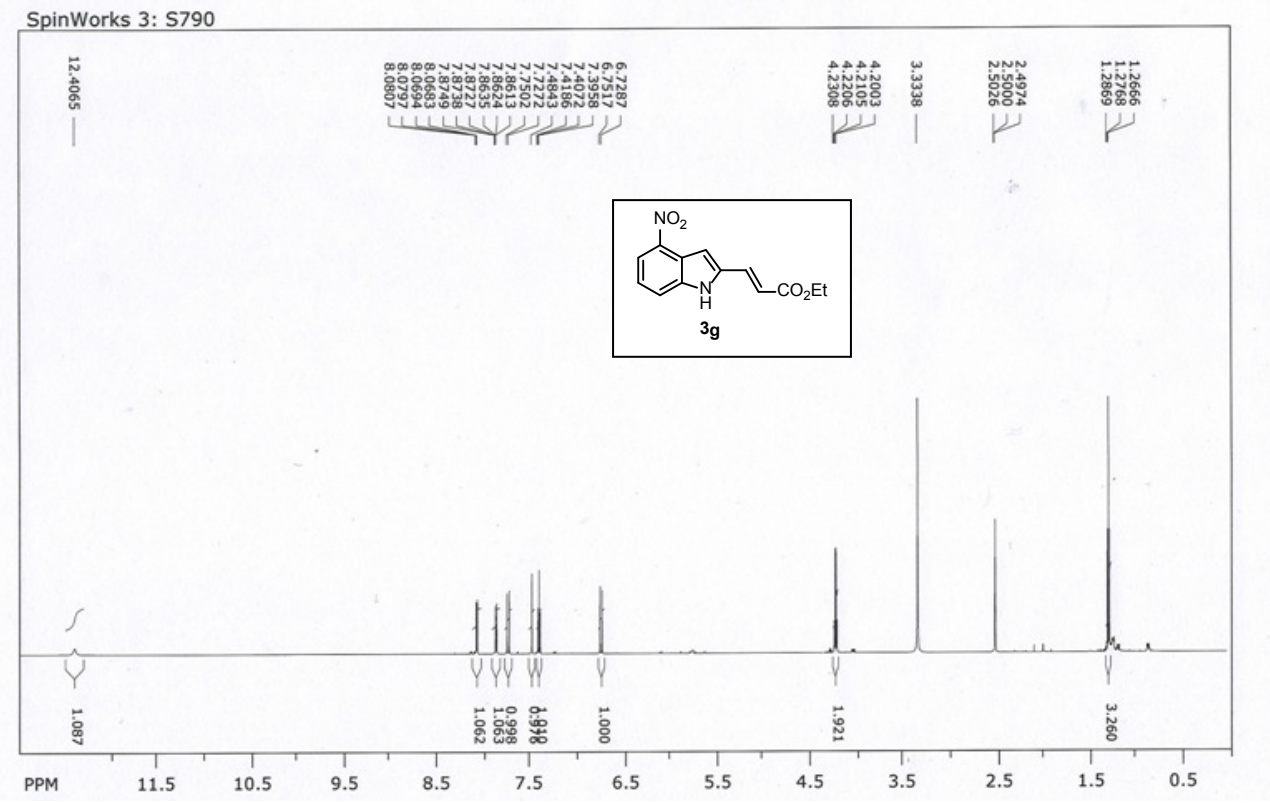
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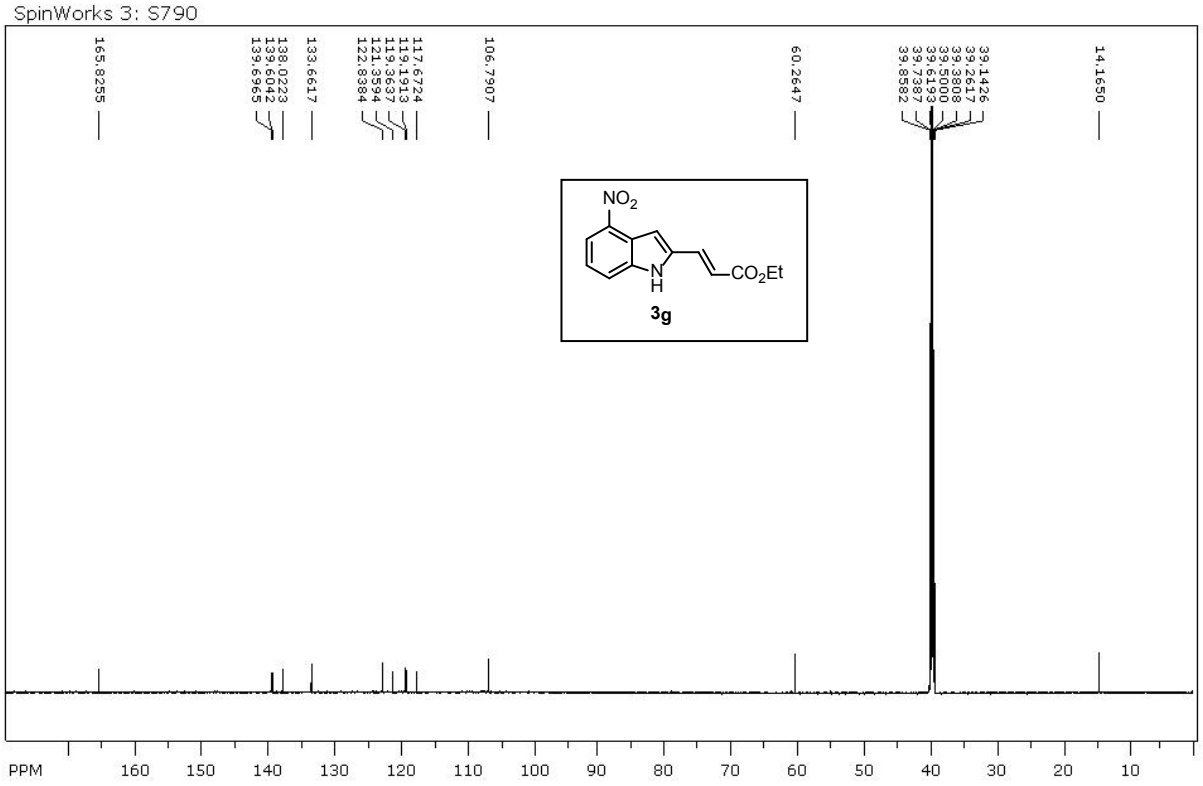
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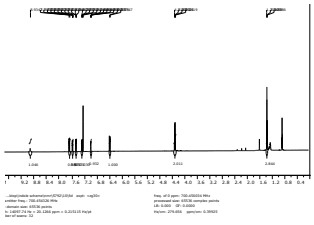

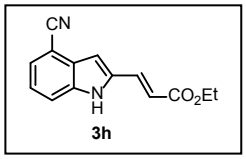

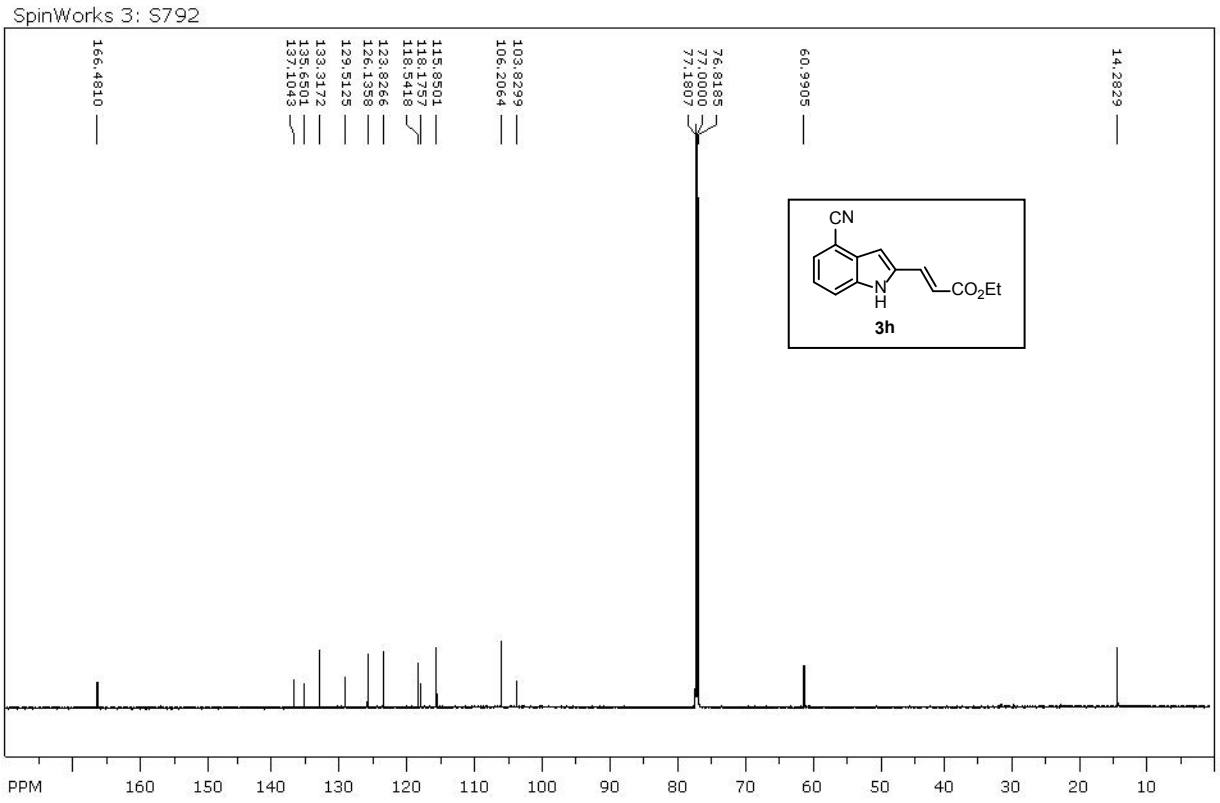

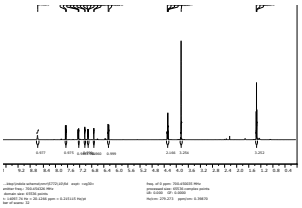

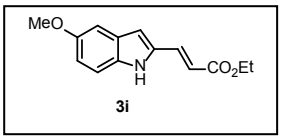

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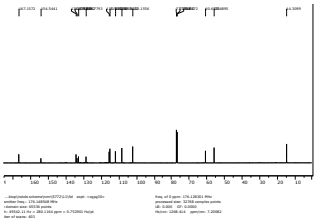

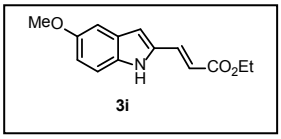

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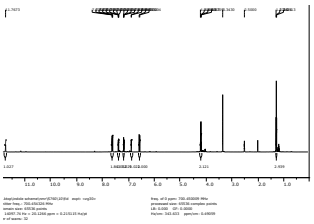

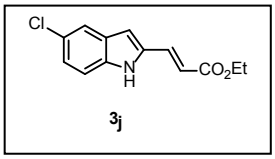

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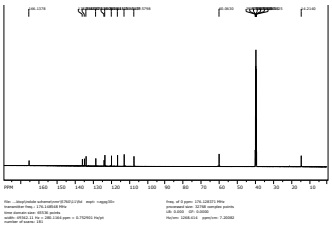

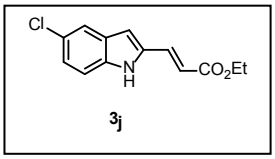

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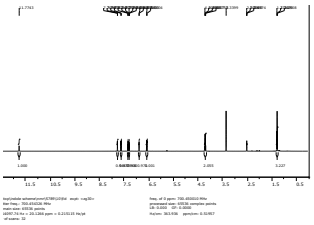

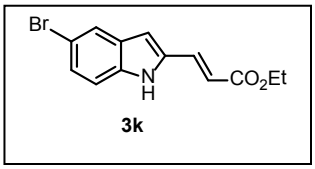

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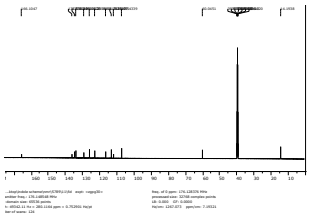

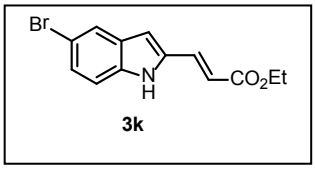

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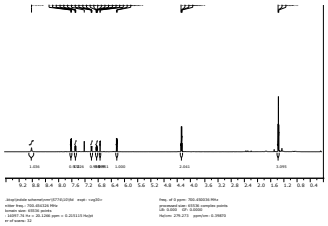

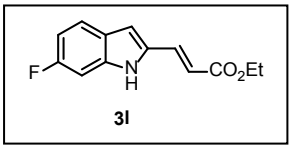

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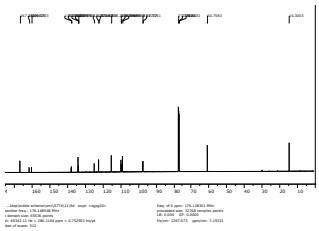

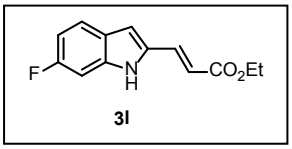

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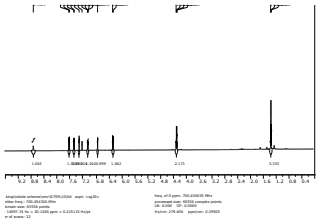

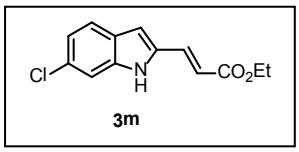

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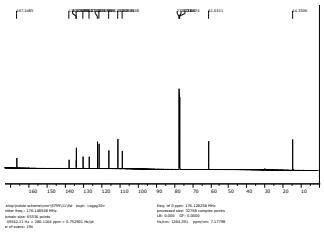

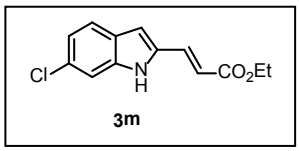

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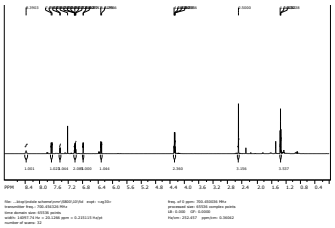

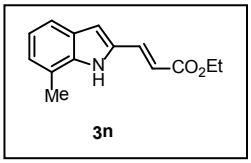

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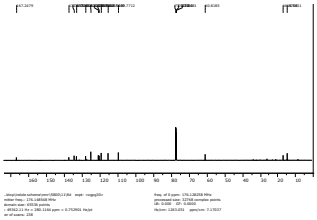

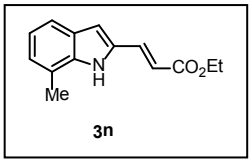

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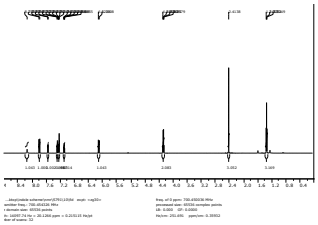

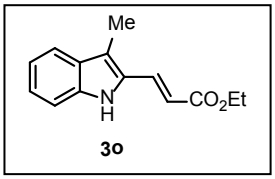

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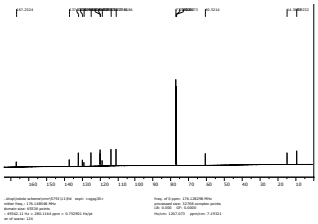

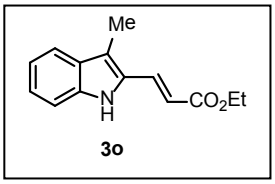

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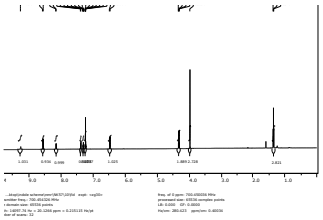

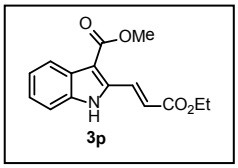

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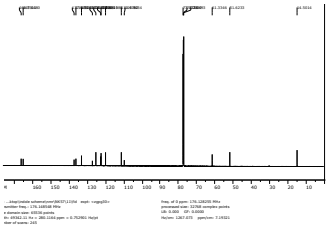

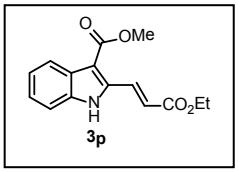

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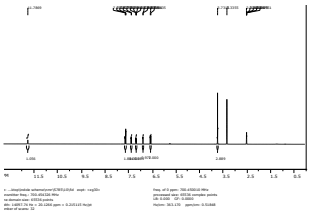

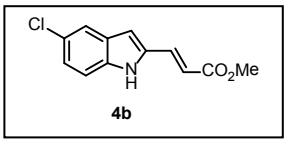

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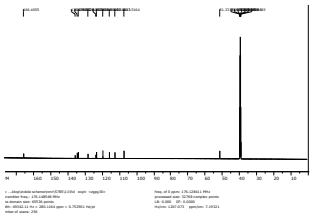

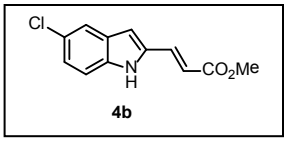

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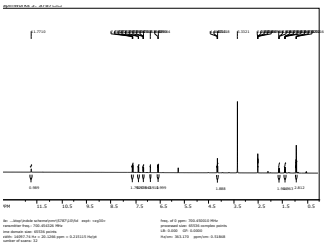

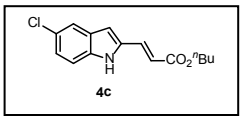

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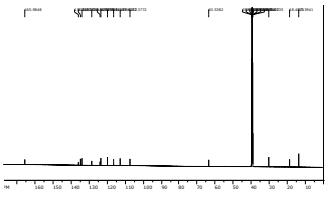

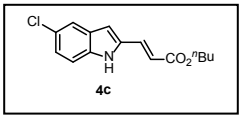

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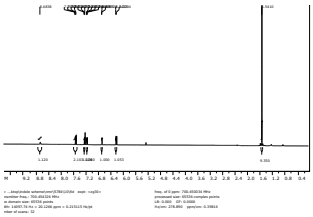

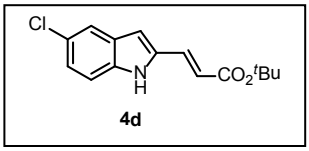

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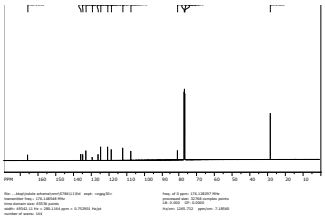

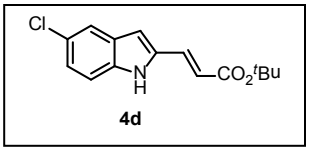

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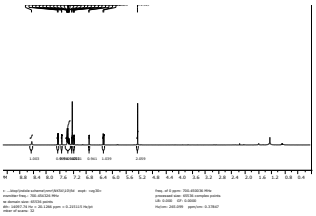

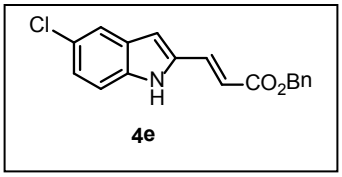

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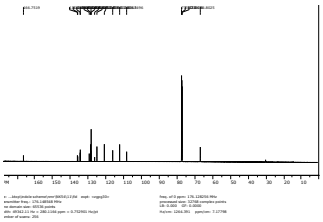

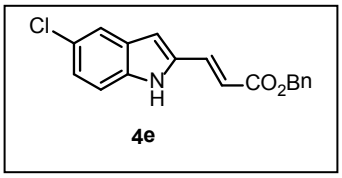

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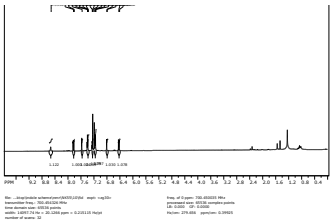

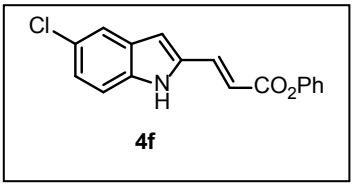

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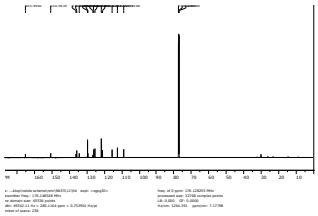

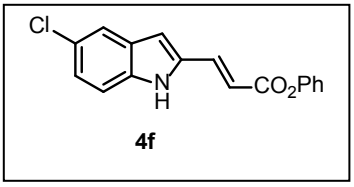

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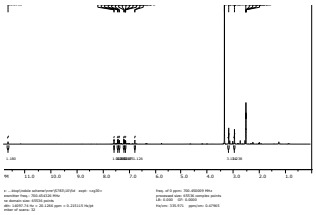

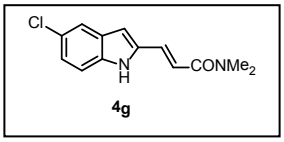

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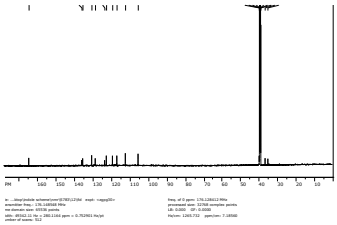

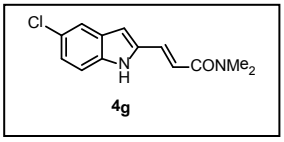

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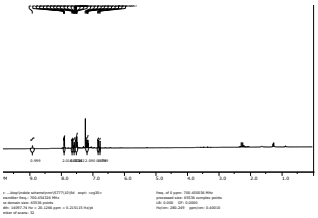

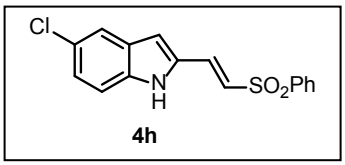

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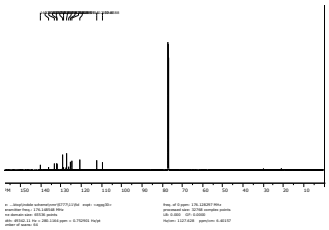

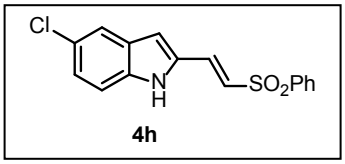

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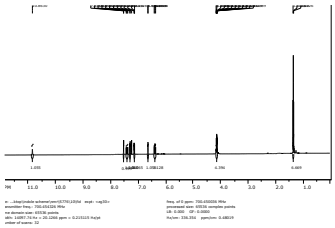

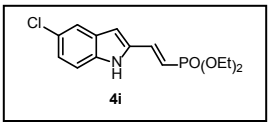

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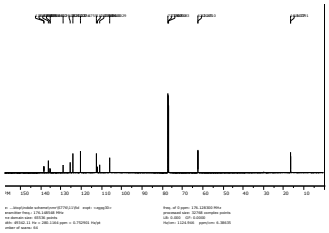

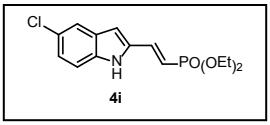

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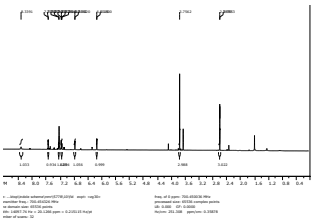

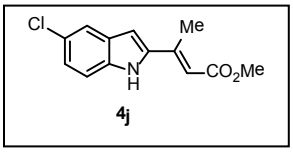

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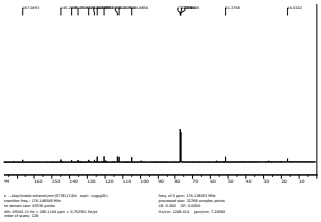

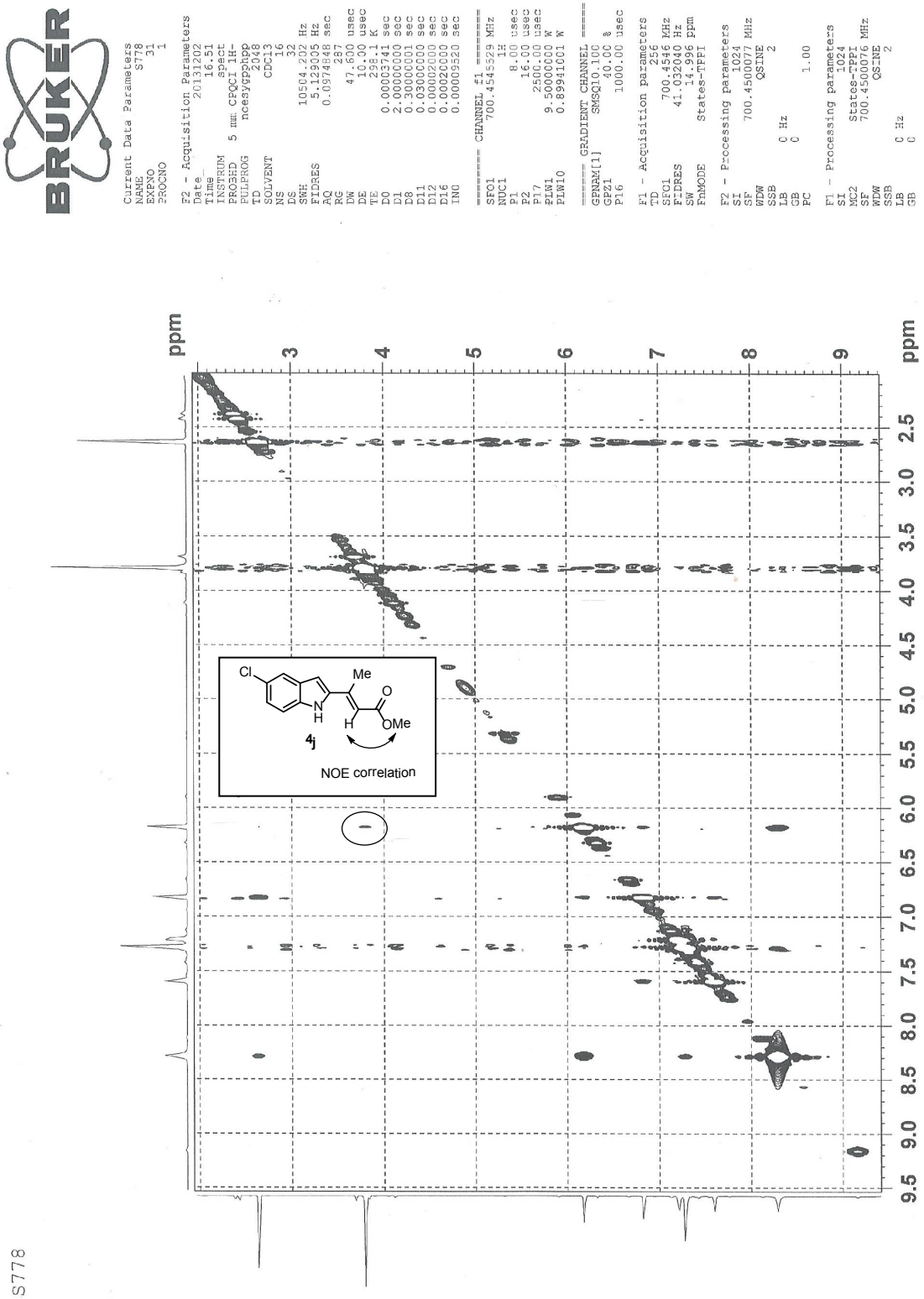
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PROCNO 1
F2 - Acquisition Parameters
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Time 16.51
INSTRUM spect
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PULPROG ncesygpphpp
TD 2048
SOLVENT CDCl3
NS 16
DS 32
SWH 10504.202 Hz
FIDRES 5.129005 Hz
AQ 0.0974848 sec
RG 287
DW 47.600 usec
DE 10.00 usec
TE 298.1 K
D0 0.00003741 sec
D1 2.00000000 sec
D8 0.30000001 sec
D11 0.03000000 sec
D12 0.00002000 sec
D16 0.00020000 sec
IN0 0.00009520 sec
======== CHANNEL f1 ========
SFO1 700.4545529 MHz
NUC1 1H
P1 8.00 usec
P2 16.00 usec
P17 2500.00 usec
PLW1 9.50000000 W
PLW10 0.89941001 W
====== GRADIENT CHANNEL =====
GPNAM[1] SMSQ10.100
GPZ1 40.00 %
P16 1000.00 usec
F1 - Acquisition parameters
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SFO1 700.4546 MHz
FIDRES 41.032040 Hz
SW 14.996 ppm
FnMODE States-TPPI
F2 - Processing parameters
SI 1024
SF 700.4500077 MHz
WDW QSINE
SSB 2
LB 0 Hz
GB 0
PC 1.00
F1 - Processing parameters
SI 1024
MC2 States-TPPI
SF 700.4500076 MHz
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ppm
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Me
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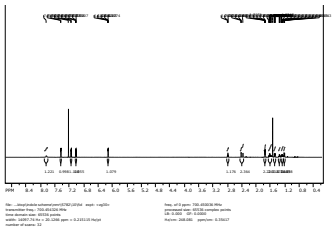
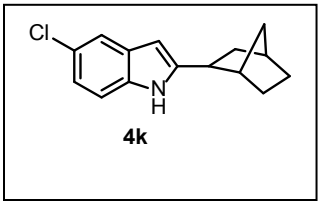
S778





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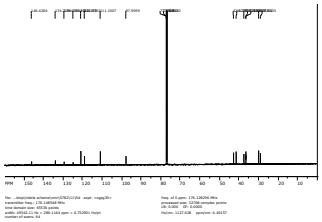

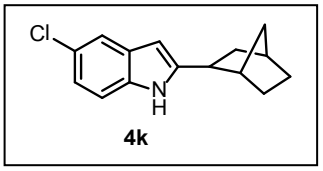

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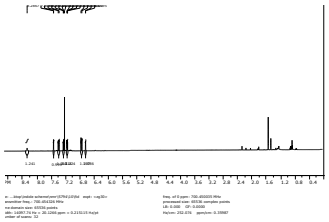

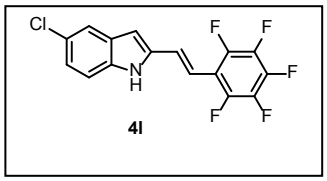

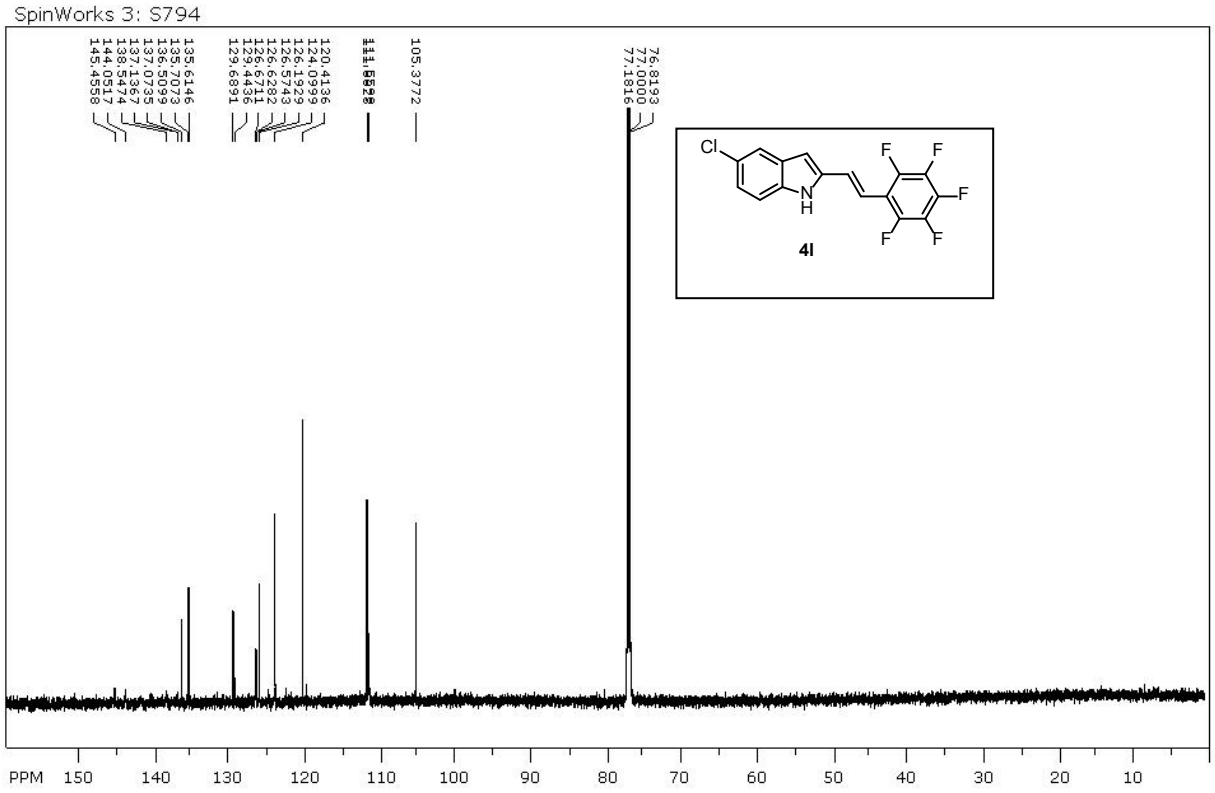

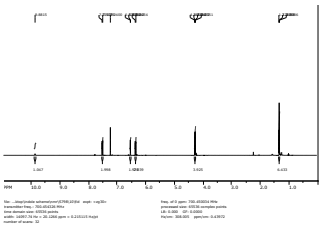

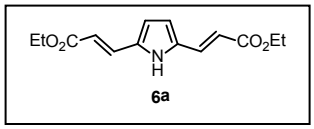

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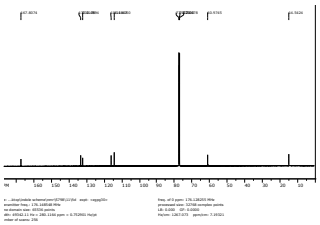

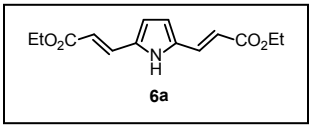

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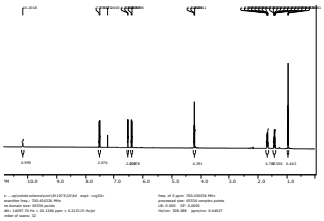

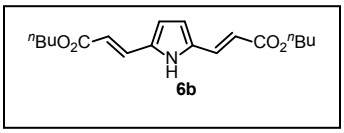

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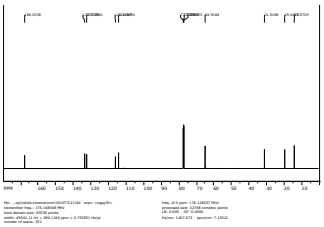

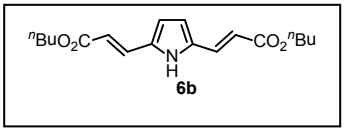

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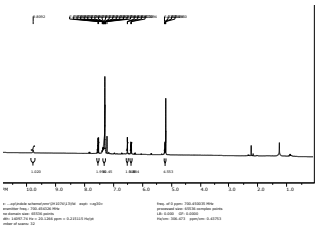

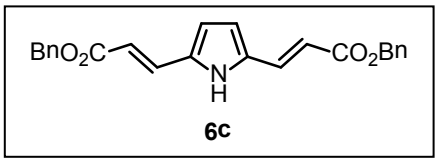

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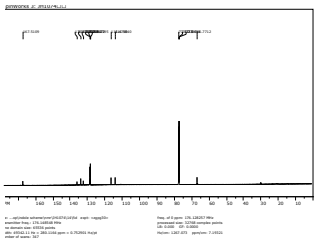

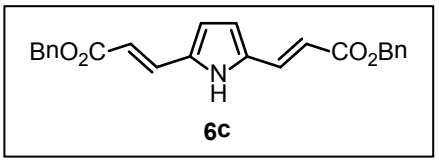

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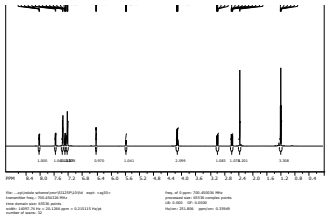

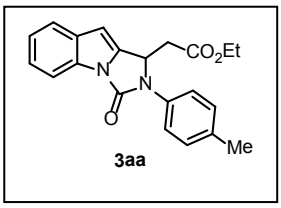

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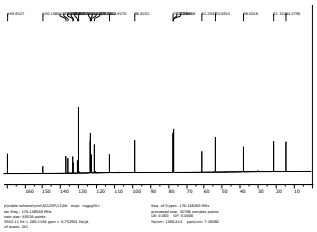

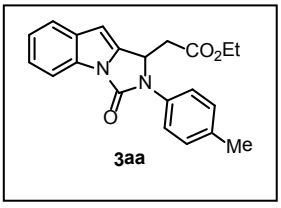

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