

Supplementary Information

Decarboxylative acylation of indolines with α -keto acids under palladium catalysis: a facile strategy for the synthesis of 7-substituted indoles

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General methods

Commercially available reagents were used without additional purification, unless otherwise stated. Sealed tubes ($13 \times 100 \text{ mm}^2$) 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 60F₂₅₄ (Merck). For flash column chromatography, E. Merck Kieselgel 60 (230–400 mesh) was used. Nuclear magnetic resonance spectra (¹H and ¹³C NMR) were recorded on a Bruker Unity 300, 400, 500 and 700 MHz spectrometer for CDCl₃ and CD₃OD 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*-acylindolines (1a–c**, **1e–p**, **1r** and **1s**)**

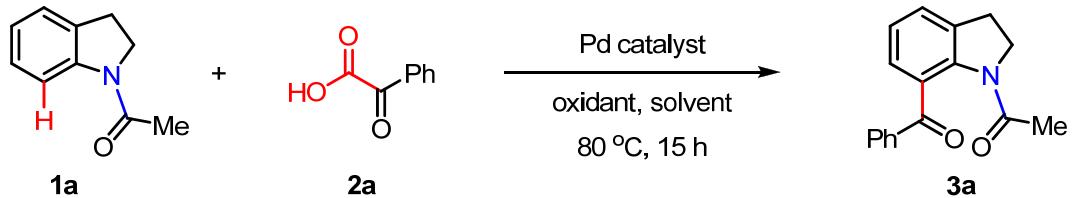
To a stirred solution of indoline (8.4 mmol) and triethyl amine (25.2 mmol) in CH₂Cl₂ (10 mL) was added a solution of acyl chloride (12.6 mmol) in CH₂Cl₂ (7 mL) at 0°C. The reaction mixture was stirred for 15 min at this temperature and further stirred for 2.5 hours at room temperature. The resulting mixture was partitioned between CH₂Cl₂ and H₂O. The organic layer was dried over Na₂SO₄ and concentrated in vacuo. The residue was purified by flash column chromatography (silica gel, *n*-hexanes/EtOAc = 10:1) to afford the corresponding *N*-acyl compounds.¹

General procedure for the synthesis of *N*-benzoylcarbazole (1q**)**

To a stirred solution of 9*H*-carbazole (1.00 g, 5.99 mmol) in DMF (30 mL) was added NaH (0.48g, 11.98 mmol, 60% dispersion in mineral oil) at 0 °C. The solution was stirred for 30 min at 0°C. To a resulting mixture was added dropwise a solution of benzoyl chloride (1.04 mL, 8.99 mmol) at 0°C. The reaction mixture was stirred at this temperature for 10 min and further stirred for 2.5 hours at room temperature. The reaction mixture was quenched and partitioned between EtOAc and H₂O. The organic layer was dried over Na₂SO₄ and concentrated in vacuo. The residue was purified by flash column chromatography (silica gel, *n*-hexanes/EtOAc = 15:1) to afford **1q**.

(1) (a) G. Yang, P. Lindovska, D. Zhu, J. Kim, P. Wang, R.-Y. Tang, M. Movassaghi and J.-Q. Yu, *J. Am. Chem. Soc.*, 2014, **136**, 10807; (b) K. G. Liu, J. R. Lo and A. J. Robichaud, *Tetrahedron*, 2010, **66**, 573.

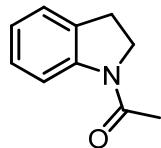
Selected optimization of the reaction conditions



| entry | catalyst (mol %) | oxidant (equiv.) | solvent | yield (%) |
|-----------|--------------------------------|---|-------------|-----------|
| 1 | Pd(OAc) ₂ (10) | (NH ₄) ₂ S ₂ O ₈ (2) | DCE | 47 |
| 2 | Pd(OAc) ₂ (10) | K ₂ S ₂ O ₈ (2) | DCE | 32 |
| 3 | Pd(OAc) ₂ (10) | Na ₂ S ₂ O ₈ (2) | DCE | 35 |
| 4 | Pd(OAc) ₂ (10) | Ag ₂ O (2) | DCE | trace |
| 5 | Pd(OAc) ₂ (10) | oxone (2) | DCE | 12 |
| 6 | Pd(OAc) ₂ (10) | (NH ₄) ₂ S ₂ O ₈ (2) | diglyme | 34 |
| 7 | Pd(OAc) ₂ (10) | (NH ₄) ₂ S ₂ O ₈ (2) | 1,4-dioxane | 38 |
| 8 | Pd(OAc) ₂ (10) | (NH ₄) ₂ S ₂ O ₈ (2) | THF | 30 |
| 9 | Pd(OAc) ₂ (10) | (NH ₄) ₂ S ₂ O ₈ (2) | toluene | 10 |
| 10 | Pd(OAc) ₂ (10) | (NH ₄) ₂ S ₂ O ₈ (2) | DMF | trace |
| 11 | PdCl ₂ (10) | (NH ₄) ₂ S ₂ O ₈ (2) | DCE | N.R. |
| 12 | Pd(OTf) ₂ (10) | (NH ₄) ₂ S ₂ O ₈ (2) | DCE | 45 |
| 13 | Pd(TFA) ₂ (10) | (NH ₄) ₂ S ₂ O ₈ (2) | DCE | 68 |
| 14 | Pd(TFA)₂ (5) | (NH₄)₂S₂O₈ (2) | DCE | 65 |
| 15 | Pd(TFA) ₂ (2.5) | (NH ₄) ₂ S ₂ O ₈ (2) | DCE | 48 |
| 16 | Pd(TFA) ₂ (5) | (NH ₄) ₂ S ₂ O ₈ (3) | DCE | 56 |
| 17 | Pd(TFA) ₂ (5) | (NH ₄) ₂ S ₂ O ₈ (1.5) | DCE | 54 |

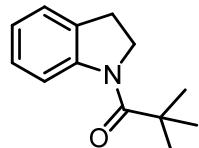
Characterization data for *N*-acylindolines (**1a–c** and **1e–s**)

1-(Indolin-1-yl)ethanone (1a)



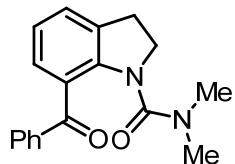
¹H NMR (700 MHz, CDCl₃) δ 8.20 (d, *J* = 8.0 Hz, 1H), 7.20–7.16 (m, 2H), 7.01–6.99 (m, 1H), 4.05 (t, *J* = 8.4 Hz, 2H), 3.20 (t, *J* = 8.4 Hz, 2H), 2.22 (s, 3H); ¹³C NMR (175 MHz, CDCl₃) δ 168.7, 142.9, 131.0, 127.5, 124.5, 123.5, 117.0, 48.7, 28.0, 24.2.

1-(Indolin-1-yl)-2,2-dimethylpropan-1-one (1b)



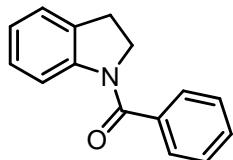
¹H NMR (500 MHz, CDCl₃) δ 8.23 (d, *J* = 8.5 Hz, 1H), 7.26–7.17 (m, 2H), 7.02 (t, *J* = 7.0 Hz, 1H), 4.23 (t, *J* = 8.1 Hz, 2H), 3.14 (t, *J* = 8.1 Hz, 2H), 1.38 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 176.5, 144.7, 130.7, 127.3, 124.2, 123.6, 118.4, 49.4, 40.2, 29.3, 27.7.

7-Benzoyl-*N,N*-dimethylindoline-1-carboxamide (1c)



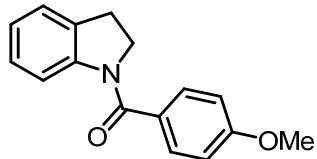
¹H NMR (700 MHz, CDCl₃) δ 7.19 (d, *J* = 7.2 Hz, 1H), 7.16–7.14 (m, 1H), 6.96 (d, *J* = 7.9 Hz, 1H), 6.91–6.89 (m, 1H), 3.92 (t, *J* = 8.2 Hz, 2H), 3.05 (t, *J* = 8.2 Hz, 2H), 2.96 (s, 6H); ¹³C NMR (175 MHz, CDCl₃) δ 160.3, 144.3, 131.4, 127.0, 124.8, 121.3, 113.3, 50.3, 38.1, 28.1.

Indolin-1-yl(phenyl)methanone (1e)



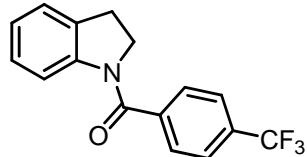
^1H NMR (700 MHz, CD₃OD) δ 7.57–7.50 (m, 6H), 7.27 (d, $J = 7.8$ Hz, 1H), 7.08 (br s, 2H), 4.06 (br s, 2H), 3.14 (t, $J = 8.0$ Hz, 2H); ^{13}C NMR (175 MHz, CD₃OD) δ 171.3, 143.8, 138.4, 134.4, 131.7, 129.9, 128.1, 126.2, 125.8, 118.8, 52.4, 29.2.

Indolin-1-yl(4-methoxyphenyl)methanone (1f)



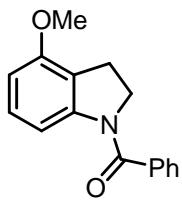
^1H NMR (700 MHz, CD₃OD) δ 8.10 (d, $J = 9.0$ Hz, 1H), 7.56 (d, $J = 8.4$ Hz, 2H), 7.26 (d, $J = 7.4$ Hz, 1H), 7.10 (d, $J = 8.9$ Hz, 1H), 7.05–7.03 (m, 3H), 4.12 (t, $J = 8.1$ Hz, 2H), 3.88 (s, 3H), 3.13 (t, $J = 8.1$ Hz, 2H); ^{13}C NMR (175 MHz, CD₃OD) δ 171.2, 166.6, 143.9, 133.9, 130.4, 128.1, 126.2, 125.5, 122.3, 115.6, 115.1, 56.1, 52.3, 29.1.

Indolin-1-yl(4-(trifluoromethyl)phenyl)methanone (1g)



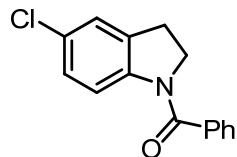
^1H NMR (700 MHz, CD₃OD) δ 8.18 (br s, 1H), 7.85–7.79 (m, 4H), 7.29 (t, $J = 7.9$ Hz, 2H), 7.12 (br s, 1H), 4.03 (br s, 2H), 3.17 (t, $J = 7.9$ Hz, 2H); ^{13}C NMR (175 MHz, CD₃OD) δ 169.6, 143.7, 142.2, 134.3, 133.3, 128.8, 128.3, 126.9, 126.5, 126.2, 118.8, 52.3, 29.4.

(4-Methoxyindolin-1-yl)(phenyl)methanone (1h)



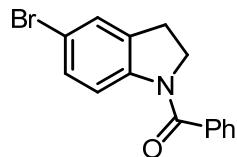
¹H NMR (700 MHz, CD₃OD) δ 7.56–7.50 (m, 6H), 7.19 (br s, 1H), 6.72 (br s, 1H), 4.07 (br s, 2H), 3.85 (s, 3H), 3.04 (t, *J* = 8.1 Hz, 2H); ¹³C NMR (175 MHz, CD₃OD) δ 171.3, 157.6, 144.9, 138.4, 131.7, 129.9, 129.7, 128.1, 121.4, 111.7, 108.1, 56.1, 52.8, 26.2.

(5-Chloroindolin-1-yl)(phenyl)methanone (1i)



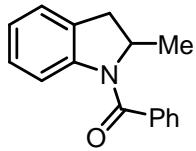
¹H NMR (700 MHz, CD₃OD) δ 7.59–7.51 (m, 6H), 7.29 (s, 1H), 7.21 (br s, 1H), 4.10 (br s, 2H), 3.15 (t, *J* = 8.2 Hz, 2H); ¹³C NMR (175 MHz, CD₃OD) δ 171.3, 142.7, 138.1, 136.8, 131.8, 130.5, 129.9, 129.2, 128.1, 126.3, 119.6, 52.6, 29.1.

(5-Bromoindolin-1-yl)(phenyl)methanone (1j)



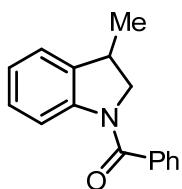
¹H NMR (700 MHz, CD₃OD) δ 7.59–7.51 (m, 6H), 7.43 (s, 1H), 7.34 (br s, 1H), 4.09 (br s, 2H), 3.15 (t, *J* = 8.2 Hz, 2H); ¹³C NMR (175 MHz, CD₃OD) δ 171.3, 138.1, 137.1, 134.0, 131.8, 131.1, 130.8, 129.9, 129.3, 128.1, 117.9, 52.5, 29.0.

(2-Methylindolin-1-yl)(phenyl)methanone (1k)



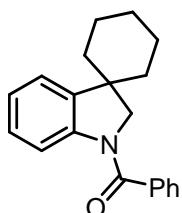
¹H NMR (700 MHz, CD₃OD) δ 7.57–7.50 (m, 5H), 7.28 (d, *J* = 8.3 Hz, 1H), 7.05 (br s, 2H), 4.74 (br s, 1H), 3.49–3.46 (m, 1H), 2.69 (d, *J* = 15.6 Hz, 1H), 1.19 (s, 3H); ¹³C NMR (175 MHz, CD₃OD) δ 171.3, 142.4, 138.3, 133.9, 130.8, 129.5, 128.2, 128.1, 126.8, 125.6, 118.2, 58.7, 36.7, 21.1.

(3-Methylindolin-1-yl)(phenyl)methanone (1l)



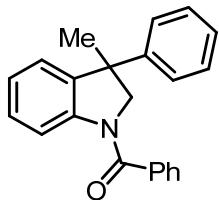
¹H NMR (700 MHz, CD₃OD) δ 7.58–7.51 (m, 6H), 7.28 (d, *J* = 7.4 Hz, 2H), 7.12 (br s, 1H), 4.23 (br s, 1H), 3.63 (br s, 1H), 3.46 (t, *J* = 7.1 Hz, 1H), 1.32 (s, 3H); ¹³C NMR (175 MHz, CD₃OD) δ 171.2, 143.2, 139.5, 138.3, 131.7, 129.9, 128.3, 128.2, 126.0, 125.1, 118.7, 60.4, 36.4, 19.8.

Phenyl(spiro[cyclohexane-1,3'-indoline]-1'-yl)methanone (1m)



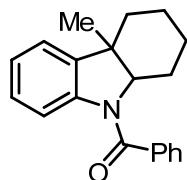
¹H NMR (700 MHz, CD₃OD) δ 7.58–7.54 (m, 6H), 7.27 (d, *J* = 8.2 Hz, 2H), 7.11 (br s, 1H), 3.92 (br s, 2H), 1.69 (br s, 8H), 1.35 (s, 2H); ¹³C NMR (175 MHz, CD₃OD) δ 171.3, 143.4, 142.6, 138.3, 131.8, 130.1, 128.6, 128.2, 126.1, 123.9, 118.9, 62.5, 37.7, 26.5, 24.2.

(3-Methyl-3-phenylindolin-1-yl)(phenyl)methanone (1n)



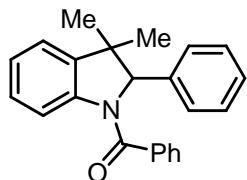
¹H NMR (700 MHz, CD₃OD) δ 8.03 (s, 1H), 7.41–7.35 (m, 5H), 7.18–7.02 (m, 8H), 4.07–3.99 (m, 2H), 1.63 (s, 3H); ¹³C NMR (175 MHz, CD₃OD) δ 161.1, 137.6, 133.3, 132.4, 127.8, 121.9, 120.0, 119.7, 118.9, 118.2, 117.9, 117.5, 116.3, 115.5, 109.1, 23.2, 20.9, 16.5.

(4a-Methyl-2,3,4,4a-tetrahydro-1*H*-carbazol-9(*9aH*)-yl(phenyl)methanone (1o)



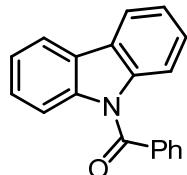
¹H NMR (700 MHz, CD₃OD) δ 7.58–7.52 (m, 6H), 7.25 (d, *J* = 8.8 Hz, 1H), 7.13 (br s, 2H), 2.35 (d, *J* = 15.1 Hz, 1H), 1.61–1.54 (m, 4H), 1.27 (s, 3H), 1.15–1.12 (m, 3H); ¹³C NMR (175 MHz, CD₃OD) δ 171.6, 142.0, 141.5, 138.1, 131.7, 130.1, 128.3, 128.2, 126.1, 123.3, 119.4, 70.6, 33.4, 31.1, 30.1, 23.9, 23.3.

(3,3-Dimethyl-2-phenylindolin-1-yl)(phenyl)methanone (1p)



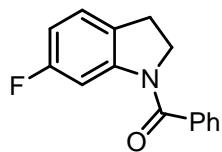
¹H NMR (700 MHz, CD₃OD) δ 7.45–7.34 (m, 5H), 7.23–7.19 (m, 7H), 6.82 (br s, 2H), 5.01 (s, 1H), 1.48 (s, 3H), 0.92 (s, 3H); ¹³C NMR (175 MHz, CD₃OD) δ 170.9, 141.7, 140.9, 140.8, 139.6, 136.7, 129.8, 128.1, 127.9, 127.4, 127.3, 126.3, 124.9, 122.6, 116.5, 78.1, 31.1, 21.4.

(9H-Carbazol-9-yl)(phenyl)methanone (1q)



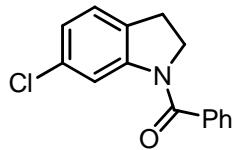
¹H NMR (700 MHz, CD₃OD) δ 7.94 (d, *J* = 7.7 Hz, 2H), 7.60–7.58 (m, 1H), 7.55 (dd, *J* = 7.0, 1.5 Hz, 2H), 7.46 (t, *J* = 7.5 Hz, 2H), 7.31 (d, *J* = 8.3 Hz, 2H), 7.23 (td, *J* = 7.7, 0.9 Hz, 2H), 7.18 (dt, *J* = 7.7, 1.3 Hz, 2H); ¹³C NMR (175 MHz, CD₃OD) δ 171.3, 140.5, 137.3, 133.7, 130.3, 130.1, 127.9, 127.5, 124.8, 121.1, 116.8.

(6-Fluoroindolin-1-yl)(phenyl)methanone (1r)



¹H NMR (700 MHz, CD₃OD) δ 7.59–7.51 (m, 6H), 7.23 (dt, *J* = 8.0, 1.3 Hz, 1H), 6.80 (br s, 1H), 4.11 (br s, 2H), 3.11 (t, *J* = 8.2 Hz, 2H); ¹³C NMR (175 MHz, CD₃OD) δ 171.4, 163.4 (d, *J*_{C-F} = 238.1 Hz), 145.1, 138.0, 131.8, 129.9, 129.4, 128.1, 126.8 (d, *J*_{C-F} = 30.8 Hz), 111.8 (d, *J*_{C-F} = 21.7 Hz), 106.4, 53.2, 28.5.

(6-Chloroindolin-1-yl)(phenyl)methanone (1s)



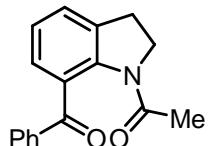
¹H NMR (700 MHz, CD₃OD) δ 7.61–7.52 (m, 6H), 7.24 (d, *J* = 8.0 Hz, 1H), 7.08 (br s, 1H), 4.11 (br s, 2H), 3.13 (t, *J* = 8.3 Hz, 2H); ¹³C NMR (175 MHz, CD₃OD) δ 171.5, 145.1, 138.0, 133.6, 133.2, 131.9, 129.9, 128.1, 127.1, 125.4, 118.7, 52.5, 28.7.

Typical procedure for C7-acylation of indolines (3a–c**, **3e–s** and **4b–m**)**

To an oven-dried sealed tube charged with *N*-acetylindoline (**1a**) (32.2 mg, 0.2 mmol, 100 mol %), Pd(TFA)₂ (3.3 mg, 0.01 mmol, 5 mol %) and (NH₄)₂S₂O₈ (91.2 mg, 0.4 mmol, 200 mol %) in DCE (1 mL) was added phenylglyoxylic acid (**2a**) (45 mg, 0.3 mmol, 150 mol %). The reaction mixture was allowed to stir at 80 °C for 15 h, and cooled to room temperature. The reaction mixture was diluted with EtOAc (3 mL) and concentrated in vacuo. The residue was purified by flash column chromatography (*n*-hexanes/EtOAc = 3:1) to afford 34.5 mg of **3a** in 65% yield.

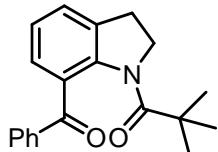
Characterization data for products (3a–c, 3e–s and 4b–m)

1-(7-Benzoylindolin-1-yl)ethanone (3a)



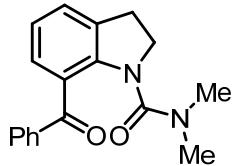
¹H NMR (700 MHz, CDCl₃) δ 7.83 (d, *J* = 7.8 Hz, 2H), 7.45–7.43 (m, 1H), 7.35 (t, *J* = 7.9 Hz, 2H), 7.25 (d, *J* = 7.4 Hz, 1H), 7.08 (d, *J* = 7.5 Hz, 1H), 7.01 (t, *J* = 7.4 Hz, 1H), 4.07 (t, *J* = 8.1 Hz, 2H), 3.15 (t, *J* = 8.1 Hz, 2H), 2.00 (s, 3H); ¹³C NMR (175 MHz, CDCl₃) δ 194.1, 167.7, 138.8, 137.4, 133.5, 132.2, 129.9, 128.8, 128.1, 127.1, 126.3, 123.8, 49.4, 28.9, 23.3; IR (KBr) ν 3054, 2928, 1660, 1597, 1446, 1433, 1394, 1324, 1273, 1169, 1006, 926, 735 cm⁻¹; HRMS (EI) calcd for C₁₇H₁₅NO₂ [M]⁺ 265.1103, found 265.1103.

1-(7-Benzoylindolin-1-yl)-2,2-dimethylpropan-1-one (3b)



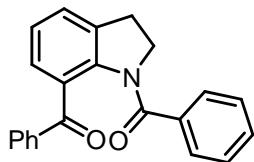
¹H NMR (300 MHz, CDCl₃) δ 7.77–7.73 (m, 2H), 7.53–7.47 (m, 1H), 7.43–7.39 (m, 4H), 7.18 (t, *J* = 7.5 Hz, 1H), 4.20 (t, *J* = 7.7 Hz, 2H), 3.15 (t, *J* = 7.4 Hz, 2H); ¹³C NMR (175 MHz, CDCl₃) δ 193.6, 176.7, 141.4, 137.9, 133.0, 131.9, 129.3, 128.7, 127.9, 126.7, 124.5, 50.2, 39.2, 30.2, 27.4; IR (KBr) ν 3055, 2967, 1664, 1634, 1587, 1476, 1447, 1432, 1399, 1358, 1322, 1278, 1205, 1097, 989, 739 cm⁻¹; HRMS (EI) calcd for C₂₀H₂₁NO₂ [M]⁺ 307.1572, found 307.1581.

7-Benzoyl-N,N-dimethylindoline-1-carboxamide (3c)



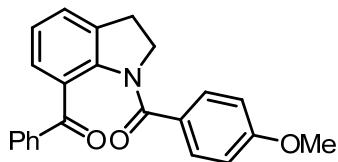
¹H NMR (700 MHz, CDCl₃) δ 7.68 (d, *J* = 8.1 Hz, 2H), 7.42–7.41 (m, 1H), 7.32 (t, *J* = 8.0 Hz, 2H), 7.26–7.23 (m, 2H), 6.93 (t, *J* = 7.4 Hz, 1H), 3.83 (t, *J* = 8.2 Hz, 2H), 3.08 (t, *J* = 8.3 Hz, 2H), 2.56 (s, 6H); ¹³C NMR (175 MHz, CDCl₃) δ 195.4, 161.2, 143.8, 137.8, 132.9, 132.0, 130.0, 129.6, 128.5, 128.3, 127.9, 127.3, 126.3, 122.1, 51.5, 37.2, 29.3; IR (KBr) ν 3049, 2926, 1658, 1598, 1447, 1381, 1268, 1225, 1166, 985, 733 cm⁻¹; HRMS (EI) calcd for C₁₈H₁₈N₂O₂ [M]⁺ 294.1368, found 294.1367.

Indoline-1,7-diylbis(phenylmethanone) (3e)



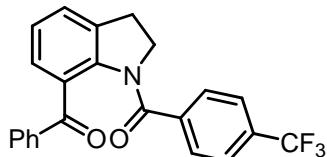
¹H NMR (700 MHz, CDCl₃) δ 7.80 (d, *J* = 7.4 Hz, 2H), 7.43 (tt, *J* = 7.3, 1.2 Hz, 1H), 7.34–7.32 (m, 6H), 7.28–7.25 (m, 3H), 7.11 (t, *J* = 7.5 Hz, 1H), 4.03 (t, *J* = 7.9 Hz, 2H), 3.05 (t, *J* = 7.9 Hz, 2H); ¹³C NMR (175 MHz, CDCl₃) δ 194.3, 169.5, 140.2, 137.2, 135.5, 134.3, 133.6, 132.3, 131.0, 129.9, 128.9, 128.2, 128.1, 127.8, 127.1, 124.5, 52.6, 29.5; IR (KBr) ν 3055, 1659, 1638, 1575, 1446, 1431, 1383, 1352, 1325, 1264, 1071, 983, 735, 694 cm⁻¹; HRMS (EI) calcd for C₂₂H₁₇NO₂ [M]⁺ 327.1259, found 327.1254.

(7-Benzoylindolin-1-yl)(4-methoxyphenyl)methanone (3f)



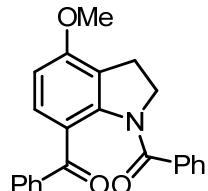
¹H NMR (700 MHz, CDCl₃) δ 7.89 (d, *J* = 7.2 Hz, 2H), 7.52–7.49 (m, 1H), 7.43–7.40 (m, 5H), 7.35 (d, *J* = 7.2 Hz, 1H), 7.18 (t, *J* = 7.5 Hz, 1H), 6.84 (d, *J* = 8.7 Hz, 2H), 4.16 (t, *J* = 7.9 Hz, 2H), 3.82 (s, 3H), 3.14 (t, *J* = 7.9 Hz, 2H); ¹³C NMR (175 MHz, CDCl₃) δ 194.4, 169.4, 161.8, 140.6, 137.1, 134.2, 132.3, 130.0, 129.9, 128.7, 128.0, 127.8, 127.6, 127.1, 124.3, 113.5, 55.3, 52.9, 29.5; IR (KBr) ν 3055, 2934, 1664, 1643, 1604, 1511, 1446, 1375, 1327, 1251, 1171, 1027, 842, 733 cm⁻¹; HRMS (EI) calcd for C₂₃H₁₉NO₃ [M]⁺ 357.1365, found 357.1359.

(7-Benzoylindolin-1-yl)(4-trifluoromethylphenyl)methanone (3g)



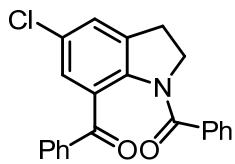
¹H NMR (700 MHz, CDCl₃) δ 7.78 (d, *J* = 7.0 Hz, 2H), 7.51 (d, *J* = 7.8 Hz, 2H), 7.44–7.42 (m, 3H), 7.34–7.32 (m, 3H), 7.27 (d, *J* = 7.6 Hz, 1H), 7.12 (t, *J* = 7.6 Hz, 1H), 3.98 (t, *J* = 7.7 Hz, 2H), 3.06 (t, *J* = 7.9 Hz, 2H); ¹³C NMR (175 MHz, CDCl₃) δ 194.3, 168.0, 139.8, 139.0, 137.1, 134.3, 132.6 (q, *J*_{C-F} = 32.1 Hz), 132.4, 129.9, 128.9, 128.2, 128.1, 127.9, 127.2, 125.4 (q, *J*_{C-F} = 3.8 Hz), 124.9, 123.6 (q, *J*_{C-F} = 270.8 Hz), 52.4, 29.5; IR (KBr) ν 3057, 2928, 1717, 1657, 1596, 1448, 1408, 1385, 1320, 1266, 1169, 1127, 1065, 1017, 736 cm⁻¹; HRMS (EI) calcd for C₂₃H₁₆F₃NO₂ [M]⁺ 395.1133, found 395.1126.

(4-Methoxyindoline-1,7-diyl)bis(phenylmethanone) (3h)



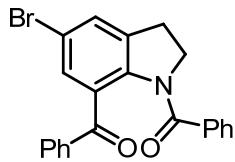
¹H NMR (300 MHz, CDCl₃) δ 7.85 (d, *J* = 7.4 Hz, 2H), 7.48–7.32 (m, 9H), 6.71 (d, *J* = 8.4 Hz, 1H), 4.09 (t, *J* = 7.7 Hz, 2H), 3.91 (s, 3H), 3.03 (t, *J* = 7.6 Hz, 2H); ¹³C NMR (175 MHz, CDCl₃) δ 194.0, 169.7, 157.9, 142.2, 137.8, 135.6, 132.1, 130.9, 130.4, 129.8, 128.2, 127.9, 127.8, 122.4, 121.3, 106.4, 55.6, 53.0, 29.7; IR (KBr) ν 3067, 2923, 1660, 1642, 1600, 1443, 1418, 1377, 1334, 1270, 1098, 1052, 994, 833, 708, 693 cm⁻¹; HRMS (EI) calcd for C₂₃H₁₉NO₃ [M]⁺ 357.1365, found 357.1367.

(5-Chloroindoline-1,7-diyl)bis(phenylmethanone) (3i)



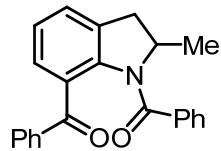
¹H NMR (300 MHz, CDCl₃) δ 7.87 (d, *J* = 6.9 Hz, 2H), 7.53–7.50 (m, 1H), 7.45–7.31 (m, 9H), 4.12 (t, *J* = 7.8 Hz, 2H), 3.12 (t, *J* = 8.0 Hz, 2H); ¹³C NMR (175 MHz, CDCl₃) δ 192.9, 169.4, 138.9, 136.6, 136.3, 135.1, 132.7, 131.2, 129.9, 129.7, 128.3, 128.2, 127.8, 127.5, 127.1, 52.7, 29.3; IR (KBr) ν 3054, 2921, 1717, 1662, 1596, 1579, 1448, 1419, 1365, 1322, 1266, 1209, 1172, 1013, 882, 736 cm⁻¹; HRMS (EI) calcd for C₂₂H₁₆ClNO₂ [M]⁺ 361.0870, found 361.0862.

(5-Bromoindoline-1,7-diyl)bis(phenylmethanone) (3j)



¹H NMR (300 MHz, CDCl₃) δ 7.87 (d, *J* = 7.4 Hz, 2H), 7.52–7.34 (m, 10H), 4.11 (t, *J* = 7.6 Hz, 2H), 3.13 (t, *J* = 7.6 Hz, 2H); ¹³C NMR (175 MHz, CDCl₃) δ 192.8, 169.4, 139.4, 136.7, 136.6, 135.1, 132.7, 131.2, 130.3, 130.1, 129.9, 128.3, 128.2, 127.8, 117.1, 52.7, 29.3; IR (KBr) ν 3063, 2917, 2666, 1689, 1664, 1600, 1579, 1448, 1415, 1365, 1319, 1267, 1069, 875, 708 cm⁻¹; HRMS (EI) calcd for C₂₂H₁₆BrNO₂ [M]⁺ 405.0364, found 405.0374.

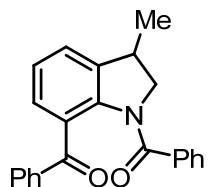
(2-Methylindoline-1,7-diyl)bis(phenylmethanone) (3k)



¹H NMR (300 MHz, CDCl₃) δ 7.77 (d, *J* = 7.3 Hz, 2H), 7.55–7.22 (m, 9H), 7.12–7.09 (m, 2H), 4.28 (t, *J* = 6.5 Hz, 1H), 3.41–3.34 (m, 1H), 2.62 (d, *J* = 15.5 Hz, 1H), 1.35 (d, *J* = 6.4 Hz, 3H); ¹³C NMR (175 MHz, CDCl₃) δ 194.1, 169.8, 138.9, 135.9, 133.5, 132.2, 130.2, 129.8, 129.5, 128.3, 128.2, 128.1, 127.9, 126.7, 125.2, 58.9, 37.1, 21.1; IR (KBr) ν 3060, 2960, 2924, 1664, 1646, 1444, 1371, 1344, 1324, 1267, 1210, 1150, 1072, 994, 859, 734 cm⁻¹; HRMS (EI)

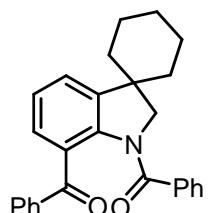
calcd for C₂₃H₁₉NO₂ [M]⁺ 341.1416, found 341.1413.

(3-Methylindoline-1,7-diyl)bis(phenylmethanone) (3l)



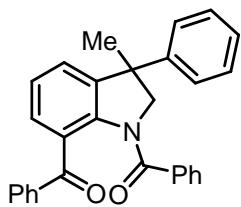
¹H NMR (300 MHz, CDCl₃) δ 7.89 (d, *J* = 6.9 Hz, 2H), 7.49 (d, *J* = 6.4 Hz, 1H), 7.43–7.36 (m, 9H), 7.22 (t, *J* = 7.3 Hz, 1H), 4.20 (t, *J* = 8.9 Hz, 1H), 3.69 (t, *J* = 7.8 Hz, 1H), 3.48–3.41 (m, 1H), 1.33 (d, *J* = 6.5 Hz, 3H); ¹³C NMR (175 MHz, CDCl₃) δ 194.4, 169.3, 139.8, 139.3, 137.2, 135.5, 132.3, 130.9, 129.9, 128.8, 128.3, 128.1, 127.9, 127.8, 125.8, 124.7, 60.4, 36.2, 18.4; IR (KBr) ν 3055, 2963, 2927, 1717, 1664, 1598, 1439, 1379, 1328, 1271, 1172, 1024, 965, 706 cm⁻¹; HRMS (EI) calcd for C₂₃H₁₉NO₂ [M]⁺ 341.1416, found 341.1419.

Spiro[cyclohexane-1,3'-indoline]-1',7'-diylbis(phenylmethanone) (3m)



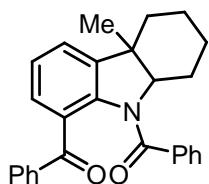
¹H NMR (300 MHz, CDCl₃) δ 7.88 (d, *J* = 7.5 Hz, 2H), 7.52–7.47 (m, 1H), 7.43–7.31 (m, 9H), 7.21 (t, *J* = 7.5 Hz, 1H), 3.89 (s, 2H), 1.71–1.63 (m, 6H), 1.28–1.15 (m, 4H); ¹³C NMR (175 MHz, CDCl₃) δ 194.4, 169.6, 143.3, 139.3, 137.2, 135.6, 132.3, 130.8, 130.0, 128.8, 128.3, 128.2, 128.1, 127.6, 124.8, 124.7, 62.2, 45.7, 35.7, 25.3, 22.9; IR (KBr) ν 3054, 2923, 1649, 1598, 1434, 1378, 1342, 1322, 1265, 1248, 1210, 1024, 963, 735, 708, 689 cm⁻¹; HRMS (EI) calcd for C₂₇H₂₅NO₂ [M]⁺ 395.1885, found 395.1882.

(3-Methyl-3-phenylindoline-1,7-diyl)bis(phenylmethanone) (3n)



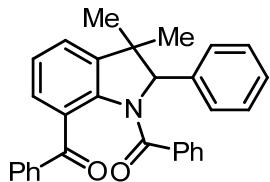
¹H NMR (700 MHz, CDCl₃) δ 7.94 (d, *J* = 7.9 Hz, 2H), 7.52–7.41 (m, 4H), 7.37–7.29 (m, 7H), 7.28–7.20 (m, 5H), 4.22 (d, *J* = 10.7 Hz, 1H), 4.05 (d, *J* = 10.7 Hz, 1H), 1.72 (s, 3H); ¹³C NMR (175 MHz, CDCl₃) δ 194.4, 169.4, 144.9, 142.7, 139.8, 137.2, 135.3, 132.4, 130.9, 130.1, 129.1, 128.6, 128.4, 128.3, 128.1, 127.6, 126.9, 126.5, 126.4, 125.1, 68.5, 49.2, 22.7; IR (KBr) ν 3053, 2968, 2873, 1718, 1659, 1598, 1436, 1370, 1322, 1264, 1154, 1067, 1027, 732 cm⁻¹; HRMS (EI) calcd for C₂₉H₂₃NO₂ [M]⁺ 417.1729, found 417.1720.

(4a-Methyl-2,3,4,4a-tetrahydro-1*H*-carbazole-8,9(9a*H*)-diylbis(phenylmethanone) (3o)



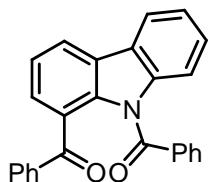
¹H NMR (300 MHz, CDCl₃) δ 7.81 (d, *J* = 7.5 Hz, 2H), 7.51–7.47 (m, 2H), 7.42–7.27 (m, 7H), 7.15 (d, *J* = 8.0 Hz, 2H), 3.62 (s, 1H), 2.32 (d, *J* = 13.8 Hz, 1H), 2.13–2.08 (m, 1H), 1.66–1.50 (m, 4H), 1.23–1.14 (m, 2H), 1.09 (s, 3H); ¹³C NMR (175 MHz, CDCl₃) δ 194.4, 170.1, 141.7, 138.8, 137.6, 136.4, 132.1, 130.5, 130.2, 129.8, 128.4, 128.1, 127.9, 126.4, 125.5, 124.4, 45.4, 32.6, 29.7, 29.6, 29.3, 23.2, 22.1; IR (KBr) ν 3060, 2928, 2857, 1739, 1666, 1598, 1445, 1432, 1370, 1330, 1304, 1274, 1149, 1072, 736, 700 cm⁻¹; HRMS (EI) calcd for C₂₇H₂₅NO₂ [M]⁺ 395.1885, found 395.1882.

(3,3-Dimethyl-2-phenylindoline-1,7-diyl)bis(phenylmethanone) (3p)



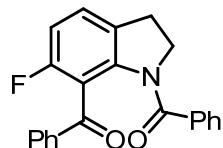
¹H NMR (300 MHz, CDCl₃) δ 8.04 (d, *J* = 7.5 Hz, 2H), 7.56–7.51 (m, 1H), 7.44 (t, *J* = 8.0 Hz, 2H), 7.39–7.31 (m, 5H), 7.27–7.23 (m, 3H), 7.21–7.16 (m, 5H), 4.77 (s, 1H), 1.38 (s, 3H), 0.99 (s, 3H); ¹³C NMR (175 MHz, CDCl₃) δ 194.7, 170.2, 142.7, 139.8, 139.3, 136.8, 135.5, 132.5, 130.6, 130.4, 128.5, 128.2, 128.1, 127.9, 127.8, 127.7, 127.5, 127.1, 124.9, 124.8, 46.7, 31.3, 22.3; IR (KBr) ν 3057, 2961, 1651, 1599, 1437, 1372, 1327, 1266, 1154, 1073, 923, 735, 700 cm⁻¹; HRMS (EI) calcd for C₃₀H₂₅NO₂ [M]⁺ 431.1885, found 431.1887.

(9H-Carbazole-1,9-diyl)bis(phenylmethanone) (3q)



¹H NMR (300 MHz, CDCl₃) δ 8.24 (d, *J* = 7.6 Hz, 1H), 8.09 (d, *J* = 7.5 Hz, 1H), 7.81 (dd, *J* = 8.1, 1.2 Hz, 2H), 7.70 (dd, *J* = 8.1, 1.2 Hz, 2H), 7.54–7.47 (m, 4H), 7.45–7.35 (m, 6H), 6.99 (d, *J* = 8.1 Hz, 1H); ¹³C NMR (175 MHz, CDCl₃) δ 195.3, 170.5, 139.8, 137.2, 136.9, 134.8, 133.2, 132.8, 130.6, 130.2, 130.1, 128.8, 128.4, 128.1, 127.3, 127.1, 126.7, 124.9, 122.8, 122.4, 120.1, 113.8; IR (KBr) ν 3058, 2930, 1786, 1675, 1598, 1477, 1443, 1325, 1299, 1211, 1175, 1154, 1070, 860, 786, 754, 704 cm⁻¹; HRMS (EI) calcd for C₂₆H₁₇NO₂ [M]⁺ 375.1259, found 375.1254.

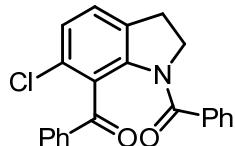
(6-Fluoroindoline-1,7-diyl)bis(phenylmethanone) (3r)



¹H NMR (300 MHz, CDCl₃) δ 7.97 (d, *J* = 7.3 Hz, 2H), 7.54–7.28 (m, 9H), 6.88 (t, *J* = 8.3 Hz, 1H), 4.14 (t, *J* = 7.8 Hz, 2H), 3.08 (t, *J* = 7.8 Hz, 2H); ¹³C NMR (175 MHz, CDCl₃) δ 190.5, 169.2, 159.2 (d, *J*_{C-F} = 244.0 Hz), 141.5 (d, *J*_{C-F} = 63.5 Hz), 137.8, 135.3, 132.7, 131.1, 129.7 (d, *J*_{C-F} = 2.5 Hz), 129.4, 128.3, 128.2, 127.9, 126.7 (d, *J*_{C-F} = 9.6 Hz), 118.0 (d, *J*_{C-F} = 20.9 Hz), 111.7 (d, *J*_{C-F} = 23.8 Hz), 53.5, 29.0; IR (KBr) ν 2924, 2851, 1714, 1684, 1650, 1598, 1493,

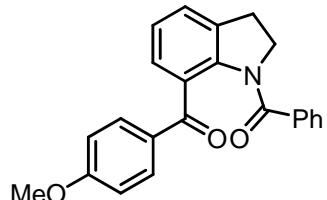
1463, 1448, 1384, 1318, 1264, 1170, 1099, 1005, 886, 732 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{22}\text{H}_{16}\text{FNO}_2$ [M]⁺ 345.1165, found 345.1170.

(6-Chloroindoline-1,7-diyl)bis(phenylmethanone) (3s)



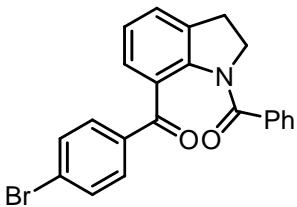
¹H NMR (300 MHz, CDCl_3) δ 7.94 (d, $J = 7.2$ Hz, 2H), 7.56–7.26 (m, 9H), 7.18 (d, $J = 7.2$ Hz, 1H), 4.09 (t, $J = 7.9$ Hz, 2H), 3.09 (t, $J = 7.9$ Hz, 2H); ¹³C NMR (175 MHz, CDCl_3) δ 192.0, 169.1, 141.5, 137.7, 135.3, 133.1, 132.5, 131.1, 130.5, 129.5, 128.3, 128.2, 127.8, 127.6, 126.4, 126.2, 53.2, 29.3; IR (KBr) ν 2950, 2660, 2550, 1679, 1600, 1495, 1419, 1322, 1286, 1179, 1071, 930, 702 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{22}\text{H}_{16}\text{ClNO}_2$ [M]⁺ 361.0870, found 361.0866.

(1-Benzoylindolin-7-yl)(4-methoxyphenyl)methanone (4b)



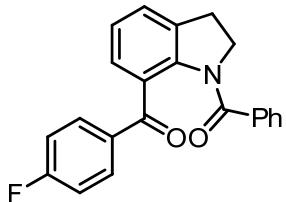
¹H NMR (700 MHz, CDCl_3) δ 7.80 (d, $J = 8.1$ Hz, 2H), 7.39 (d, $J = 7.2$ Hz, 2H), 7.32–7.29 (m, 2H), 7.27–7.23 (m, 3H), 7.08 (t, $J = 7.5$ Hz, 1H), 6.82 (d, $J = 7.1$ Hz, 2H), 4.04 (t, $J = 7.8$ Hz, 2H), 3.76 (s, 3H), 3.04 (t, $J = 7.9$ Hz, 2H); ¹³C NMR (175 MHz, CDCl_3) δ 193.2, 169.4, 163.1, 140.1, 135.6, 134.4, 132.2, 130.9, 130.1, 129.2, 128.2, 128.1, 127.7, 126.7, 124.4, 113.4, 55.4, 52.7, 29.5; IR (KBr) ν 2924, 2840, 1658, 1636, 1598, 1573, 1508, 1432, 1379, 1330, 1253, 1143, 1081, 1026, 998, 884, 732 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{23}\text{H}_{19}\text{NO}_3$ [M]⁺ 357.1365, found 357.1364.

(1-Benzoylindolin-7-yl)(4-bromophenyl)methanone (4c)



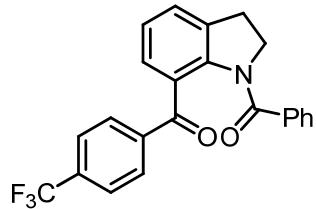
¹H NMR (700 MHz, CDCl₃) δ 7.78 (d, *J* = 8.3 Hz, 2H), 7.57 (d, *J* = 8.5 Hz, 2H), 7.46–7.42 (m, 4H), 7.38 (t, *J* = 7.3 Hz, 2H), 7.33 (d, *J* = 7.6 Hz, 1H), 7.21 (t, *J* = 7.6 Hz, 1H), 4.14 (t, *J* = 7.9 Hz, 2H), 3.15 (t, *J* = 7.9 Hz, 2H); ¹³C NMR (175 MHz, CDCl₃) δ 193.3, 169.5, 140.1, 136.1, 135.3, 134.4, 131.5, 131.3, 131.1, 128.5, 128.4, 127.8, 127.5, 127.4, 127.2, 124.6, 52.7, 29.5; IR (KBr) ν 3054, 2924, 1642, 1583, 1447, 1431, 1381, 1350, 1327, 1278, 1205, 1063, 989, 883, 788, 751 cm⁻¹; HRMS (EI) calcd for C₂₂H₁₆BrNO₂ [M]⁺ 405.0364, found 405.0364.

(1-Benzoylindolin-7-yl)(4-fluorophenyl)methanone (4d)



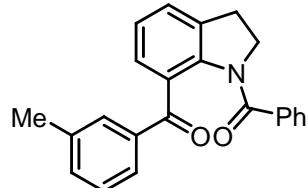
¹H NMR (700 MHz, CDCl₃) δ 7.95–7.93 (m, 2H), 7.47–7.41 (m, 4H), 7.38–7.33 (m, 3H), 7.20 (t, *J* = 7.5 Hz, 1H), 7.15–7.09 (m, 2H), 4.13 (t, *J* = 7.9 Hz, 2H), 3.15 (t, *J* = 7.8 Hz, 2H); ¹³C NMR (175 MHz, CDCl₃) δ 192.9, 169.5, 165.3 (d, *J*_{C-F} = 252.4 Hz), 140.1, 135.4, 134.4, 133.6, 132.5 (d, *J*_{C-F} = 8.9 Hz), 131.1, 128.6, 128.3, 127.8, 127.5, 127.1, 124.6, 115.1 (d, *J*_{C-F} = 22.1 Hz), 52.7, 29.5; IR (KBr) ν 3060, 2923, 1665, 1596, 1504, 1447, 1430, 1379, 1327, 1287, 1224, 1151, 1093, 1006, 847, 757, 734 cm⁻¹; HRMS (EI) calcd for C₂₂H₁₆FNO₂ [M]⁺ 345.1165, found 345.1165.

(1-Benzoylindolin-7-yl)(4-trifluoromethyl)phenyl)methanone (4e)



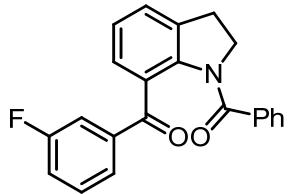
¹H NMR (700 MHz, CDCl₃) δ 7.90 (d, *J* = 8.1 Hz, 2H), 7.58 (d, *J* = 8.1 Hz, 2H), 7.36–7.32 (m, 2H), 7.30–7.24 (m, 5H), 7.13 (t, *J* = 7.5 Hz, 1H), 4.02 (t, *J* = 7.9 Hz, 2H), 3.06 (t, *J* = 7.9 Hz, 2H); ¹³C NMR (175 MHz, CDCl₃) δ 193.1, 169.7, 140.3, 140.1, 135.2, 134.4, 133.5 (q, *J*_{C-F} = 31.8 Hz), 131.2, 130.2, 128.3, 128.1, 127.6, 127.5, 127.4, 125.1 (q, *J*_{C-F} = 2.3 Hz), 124.8, 123.8 (q, *J*_{C-F} = 270.7 Hz), 52.6, 29.5; IR (KBr) ν 3049, 2941, 1658, 1639, 1586, 1447, 1432, 1381, 1350, 1319, 1287, 1205, 1166, 1131, 1107, 1060, 990, 851, 761, 748, 693 cm⁻¹; HRMS (EI) calcd for C₂₃H₁₆F₃NO₂ [M]⁺ 395.1133, found 395.1130.

(1-Benzoylindolin-7-yl)(*m*-tolyl)methanone (4f)



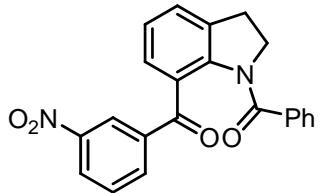
¹H NMR (700 MHz, CDCl₃) δ 7.78 (s, 1H), 7.70 (d, *J* = 7.0 Hz, 1H), 7.48 (d, *J* = 7.0 Hz, 2H), 7.43–7.41 (m, 2H), 7.38–7.33 (m, 5H), 7.20 (t, *J* = 7.6 Hz, 1H), 4.14 (t, *J* = 7.9 Hz, 2H), 3.16 (t, *J* = 7.9 Hz, 2H), 2.39 (s, 3H); ¹³C NMR (175 MHz, CDCl₃) δ 194.5, 169.5, 140.2, 137.8, 137.1, 135.6, 134.3, 133.2, 130.9, 130.4, 129.1, 128.2, 127.9, 127.8, 127.4, 126.9, 124.4, 52.7, 29.5, 21.3; IR (KBr) ν 3054, 2919, 2857, 1655, 1641, 1599, 1583, 1448, 1432, 1384, 1352, 1328, 1279, 1136, 1024, 875, 792, 749, 709 cm⁻¹; HRMS (EI) calcd for C₂₃H₁₉NO₂ [M]⁺ 341.1416, found 341.1412.

(1-Benzoylindolin-7-yl)(3-fluorophenyl)methanone (4g)



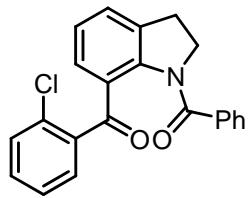
¹H NMR (700 MHz, CDCl₃) δ 7.85 (d, *J* = 7.7 Hz, 1H), 7.70 (d, *J* = 7.6 Hz, 1H), 7.61 (d, *J* = 9.2 Hz, 1H), 7.47–7.34 (m, 7H), 7.23–7.20 (m, 2H), 4.14 (t, *J* = 7.9 Hz, 2H), 3.15 (t, *J* = 7.9 Hz, 2H); ¹³C NMR (175 MHz, CDCl₃) δ 192.8, 169.5, 162.5 (d, *J*_{C-F} = 245.2 Hz), 140.1, 139.3 (d, *J*_{C-F} = 6.0 Hz), 135.4, 134.4, 131.1, 129.7 (d, *J*_{C-F} = 7.5 Hz), 128.3, 128.2, 127.8, 127.6, 127.3, 125.7 (d, *J*_{C-F} = 2.6 Hz), 124.7, 119.3 (d, *J*_{C-F} = 21.0 Hz), 116.6 (d, *J*_{C-F} = 22.2 Hz), 52.7, 29.5; IR (KBr) ν 3066, 2922, 1722, 1660, 1639, 1585, 1445, 1431, 1385, 1352, 1326, 1292, 1266, 1218, 1127, 1073, 998, 808, 784, 746, 710 cm⁻¹; HRMS (EI) calcd for C₂₂H₁₆FNO₂ [M]⁺ 345.1165, found 345.1165.

(1-Benzoylindolin-7-yl)(3-nitrophenyl)methanone (4h)



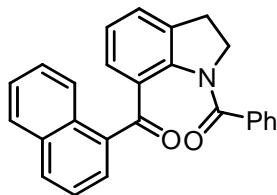
¹H NMR (700 MHz, CDCl₃) δ 8.67 (s, 1H), 8.36–8.33 (m, 2H), 7.62 (t, *J* = 7.9 Hz, 1H), 7.49 (dd, *J* = 7.4, 1.1 Hz, 1H), 7.44–7.40 (m, 3H), 7.38–7.34 (m, 3H), 7.27 (q, *J* = 7.9 Hz, 1H), 4.18 (t, *J* = 7.9 Hz, 2H), 3.20 (t, *J* = 7.9 Hz, 2H); ¹³C NMR (175 MHz, CDCl₃) δ 191.4, 169.5, 148.0, 139.9, 138.6, 135.5, 135.1, 134.5, 131.2, 129.4, 128.4, 127.8, 127.6, 127.5, 127.4, 126.6, 125.1, 124.6, 52.7, 29.5; IR (KBr) ν 3077, 2940, 1653, 1638, 1527, 1448, 1432, 1381, 1345, 1325, 1272, 1204, 1155, 1079, 1010, 907, 820, 739, 699 cm⁻¹; HRMS (EI) calcd for C₂₂H₁₆N₂O₄ [M]⁺ 372.1110, found 372.1115.

(1-Benzoylindolin-7-yl)(2-chlorophenyl)methanone (4i)



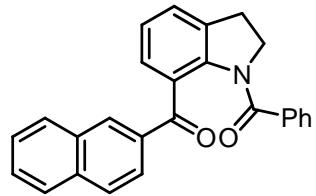
¹H NMR (700 MHz, CDCl₃) δ 7.75 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.47–7.34 (m, 9H), 7.25 (td, *J* = 8.1, 1.1 Hz, 1H), 7.20 (t, *J* = 7.6 Hz, 1H), 4.12 (t, *J* = 7.8 Hz, 2H), 3.12 (t, *J* = 7.8 Hz, 2H); ¹³C NMR (175 MHz, CDCl₃) δ 192.9, 170.2, 140.8, 137.0, 135.4, 134.7, 132.9, 132.4, 131.7, 131.2, 130.2, 129.5, 128.3, 128.2, 128.1, 128.0, 126.3, 124.8, 53.1, 29.5; IR (KBr) ν 3062, 2899, 1682, 1644, 1584, 1467, 1428, 1376, 1329, 1287, 1252, 1174, 1062, 998, 882, 788 cm⁻¹; HRMS (EI) calcd for C₂₂H₁₆ClNO₂ [M]⁺ 361.0870, found 361.0865.

(7-(1-Naphthoyl)indolin-1-yl)(phenyl)methanone (4j)



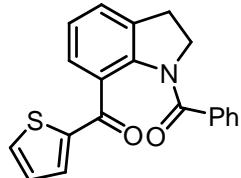
¹H NMR (700 MHz, CDCl₃) δ 8.69 (d, *J* = 8.5 Hz, 1H), 7.98 (d, *J* = 8.2 Hz, 1H), 7.90 (d, *J* = 7.0 Hz, 1H), 7.86 (d, *J* = 7.5 Hz, 1H), 7.54–7.40 (m, 3H), 7.34–7.32 (m, 3H), 7.15 (t, *J* = 7.6 Hz, 1H), 4.14 (t, *J* = 7.9 Hz, 2H), 3.15 (t, *J* = 7.9 Hz, 2H); ¹³C NMR (175 MHz, CDCl₃) δ 196.1, 169.9, 140.9, 135.5, 134.7, 134.5, 133.8, 132.4, 131.5, 131.1, 130.2, 130.1, 128.7, 128.2, 128.1, 128.0, 127.5, 127.4, 126.3, 126.1, 124.4, 124.1, 52.8, 29.5; IR (KBr) ν 3060, 2940, 1720, 1640, 1594, 1575, 1509, 1443, 1429, 1377, 1345, 1324, 1277, 1245, 1198, 1080, 1051, 955, 889, 773, 751, 703 cm⁻¹; HRMS (EI) calcd for C₂₆H₁₉NO₂ [M]⁺ 377.1416, found 377.1416.

(7-(2-Naphthoyl)indolin-1-yl)(phenyl)methanone (4k)



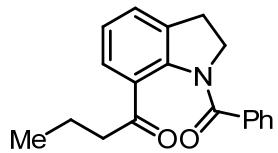
¹H NMR (700 MHz, CDCl₃) δ 8.39 (s, 1H), 8.06 (d, *J* = 8.4 Hz, 1H), 7.92 (d, *J* = 7.9 Hz, 1H), 7.87 (m, 2H), 7.59 (dt, *J* = 7.4, 1.2 Hz, 1H), 7.53 (dt, *J* = 7.4, 1.1 Hz, 1H), 7.47–7.43 (m, 2H), 7.38–7.37 (m, 3H), 7.28–7.23 (m, 3H), 4.16 (t, *J* = 7.9 Hz, 2H), 3.19 (t, *J* = 7.8 Hz, 2H); ¹³C NMR (175 MHz, CDCl₃) δ 194.3, 169.5, 140.3, 135.4, 134.5, 134.4, 132.4, 131.6, 130.9, 129.4, 129.1, 128.2, 128.1, 127.9, 127.8, 127.7, 127.1, 126.3, 125.8, 124.5, 52.7, 29.6; IR (KBr) ν 3053, 2921, 1722, 1653, 1629, 1591, 1446, 1433, 1378, 1326, 1284, 1118, 1024, 898, 759, 730 cm⁻¹; HRMS (EI) calcd for C₂₆H₁₉NO₂ [M]⁺ 377.1416, found 377.1414.

(1-Benzoylindolin-7-yl)(thiophen-2-yl)methanone (4l)



¹H NMR (700 MHz, CDCl₃) δ 7.55 (dd, *J* = 5.2, 1.3 Hz, 2H), 7.46 (d, *J* = 7.2 Hz, 2H), 7.38 (d, *J* = 7.7 Hz, 1H), 7.35–7.28 (m, 4H), 7.10 (t, *J* = 7.5 Hz, 1H), 7.04 (t, *J* = 4.7 Hz, 1H), 4.08 (t, *J* = 7.9 Hz, 2H), 3.05 (t, *J* = 7.9 Hz, 2H); ¹³C NMR (175 MHz, CDCl₃) δ 186.5, 169.3, 144.1, 139.8, 135.6, 134.6, 133.7, 133.6, 131.1, 128.9, 128.3, 128.1, 127.6, 127.5, 127.1, 124.4, 52.7, 29.5; IR (KBr) ν 3049, 2923, 2856, 1730, 1638, 1621, 1519, 1447, 1429, 1413, 1385, 1352, 1326, 1292, 1204, 1080, 1051, 965, 792, 723, 700 cm⁻¹; HRMS (EI) calcd for C₂₀H₁₅NO₂S [M]⁺ 333.0823, found 333.0826.

1-(1-Benzoylindolin-7-yl)butan-1-one (4m)

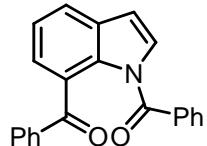


¹H NMR (300 MHz, CDCl₃) δ 7.66 (d, *J* = 8.4 Hz, 2H), 7.50–7.42 (m, 3H), 7.38 (d, *J* = 7.6 Hz, 1H), 7.34 (dd, *J* = 7.4, 0.9 Hz, 1H), 7.16 (t, *J* = 7.5 Hz, 1H), 4.16 (t, *J* = 7.9 Hz, 2H), 3.09 (t, *J* = 7.9 Hz, 2H), 2.87 (t, *J* = 7.4 Hz, 2H), 1.80–1.68 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H); ¹³C NMR (175 MHz, CDCl₃) δ 202.6, 169.8, 138.9, 135.8, 134.5, 131.5, 131.1, 128.5, 128.1, 126.8, 125.6, 124.8, 52.7, 42.6, 29.4, 17.5, 13.9; IR (KBr) ν 2927, 1692, 1647, 1574, 1491, 1445, 1373, 1322, 1250, 1114, 1073, 1026, 876, 790 cm⁻¹; HRMS (EI) calcd for C₁₉H₁₉NO₂ [M]⁺ 293.1416, found 293.1412.

One-pot scale-up experiment and characterization of **5a**

To an oven-dried sealed tube charged with *N*-benzoylindoline (**1e**) (0.5 g, 2.2 mmol, 100 mol %), Pd(TFA)₂ (36.5 mg, 0.11 mmol, 5 mol %), and (NH₄)₂S₂O₈ (1.03 g, 4.4 mmol, 200 mol %) in DCE (10 mL) was added phenylglyoxylic acid (**2a**) (0.49 g, 3.3 mmol, 150 mol%). The reaction mixture was allowed to stir at 80 °C for 30 h, and cooled to room temperature. DDQ (2.49 g, 11.0 mmol, 500 mol %) was added to the reaction mixture and the reaction mixture was stirred at 120 °C for 18 h. The reaction mixture was diluted with EtOAc (30 mL) and washed with water. The aqueous layer was extracted with EtOAc (3 × 30 mL). The combined organic layer was dried over Mg₂SO₄ and concentrated in vacuo. The residue was purified by flash column chromatography (*n*-hexanes/EtOAc = 5:1) to afford 0.44 g of **5a** in 62% yield.

(1*H*-Indole-1,7-diyl)bis(phenylmethanone) (**5a**)

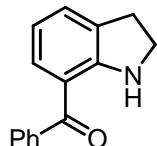


¹H NMR (700 MHz, CDCl₃) δ 7.84 (dd, *J* = 8.1, 1.1 Hz, 2H), 7.68 (dd, *J* = 7.7, 1.2 Hz, 1H), 7.63 (dd, *J* = 8.1, 1.1 Hz, 2H), 7.46–7.41 (m, 2H), 7.35–7.31 (m, 5H), 7.27 (t, *J* = 7.6 Hz, 1H), 7.17 (d, *J* = 3.7 Hz, 1H), 6.59 (d, *J* = 3.7 Hz, 1H); ¹³C NMR (175 MHz, CDCl₃) δ 194.9, 168.1, 137.5, 133.1, 132.8, 132.7, 132.4, 132.1, 130.1, 129.8, 129.2, 128.6, 128.2, 127.4, 125.5, 123.7, 123.1, 108.0; IR (KBr) ν 3057, 2923, 2851, 1692, 1664, 1597, 1542, 1448, 1413, 1321, 1270, 1198, 1178, 1067, 1021, 888, 872, 787 cm⁻¹; HRMS (EI) calcd for C₂₂H₁₅NO₂ [M]⁺ 325.1103, found 325.1102.

General procedure and characterization for the deprotection of *N*-benzoylindoline **3e**

To a stirred solution of indoline-1,7-diylbis(phenylmethanone) (**3e**) (68.7 mg, 0.21 mmol) in EtOH (4 mL) was added saturated solution of KOH (3 mL) at room temperature. The reaction mixture was allowed to stir for 12 h at 100 °C. The reaction mixture was diluted with EtOAc (10 mL) and washed with water. The aqueous layer was extracted with EtOAc (3 × 10 mL). The combined organic layer was dried over Mg₂SO₄ and concentrated in vacuo. The residue was purified by flash column chromatography (*n*-hexanes/EtOAc = 10:1) to afford 37.9 mg of free-(NH)-indoline **5b** in 81% yield.

Indolin-7-yl(phenyl)methanone (**5b**)

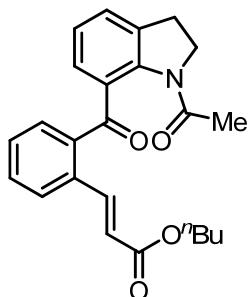


¹H NMR (300 MHz, CDCl₃) δ 7.66 (dd, *J* = 7.8, 1.3 Hz, 2H), 7.52–7.46 (m, 3H), 7.29–7.26 (m, 1H), 7.20 (dd, *J* = 6.9, 1.2 Hz, 2H), 6.49 (t, *J* = 6.9 Hz, 1H), 3.82 (t, *J* = 8.4 Hz, 2H), 3.12 (t, *J* = 8.7 Hz, 2H); ¹³C NMR (175 MHz, CDCl₃) δ 197.4, 155.5, 139.7, 131.4, 130.8, 130.7, 128.8, 128.1, 115.1, 114.9, 46.7, 28.1; IR (KBr) ν 3392, 3060, 2928, 2890, 1620, 1569, 1507, 1470, 1390, 1306, 1226, 1198, 1008, 735, 702 cm⁻¹; HRMS (EI) calcd for C₁₅H₁₃NO [M]⁺ 223.0997, found 223.1003.

General procedure for the olefination of C7-acylated indoline **3a**

To an oven-dried sealed tube charged with 1-(7-benzoylindolin-1-yl)ethanone (**3a**) (52.9 mg, 0.2 mmol, 100 mol %), $[\text{Ru}(p\text{-cymene})_2\text{Cl}_2]$ (3.1 mg, 0.005 mmol, 2.5 mol %), AgSbF_6 (6.8 mg, 0.02 mmol, 10 mol%) and $\text{Cu}(\text{OAc})_2$ (9.0 mg, 0.05 mmol, 25 mol %) in DCE (1 mL) was added *n*-butyl acrylate (51.2 mg, 0.4 mmol, 200 mol %). The reaction mixture was allowed to stir for 12 h at 110 °C. The reaction mixture was diluted with EtOAc (10 mL) and washed with water. The aqueous layer was extracted with EtOAc (3×10 mL). The combined organic layer was dried over Mg_2SO_4 and concentrated in vacuo. The residue was purified by flash column chromatography (*n*-hexanes/EtOAc = 2:1) to afford desired product **5c** (35.2 mg, 45% yield) and starting material **3a** (20.1 mg, 38% recovered yield).

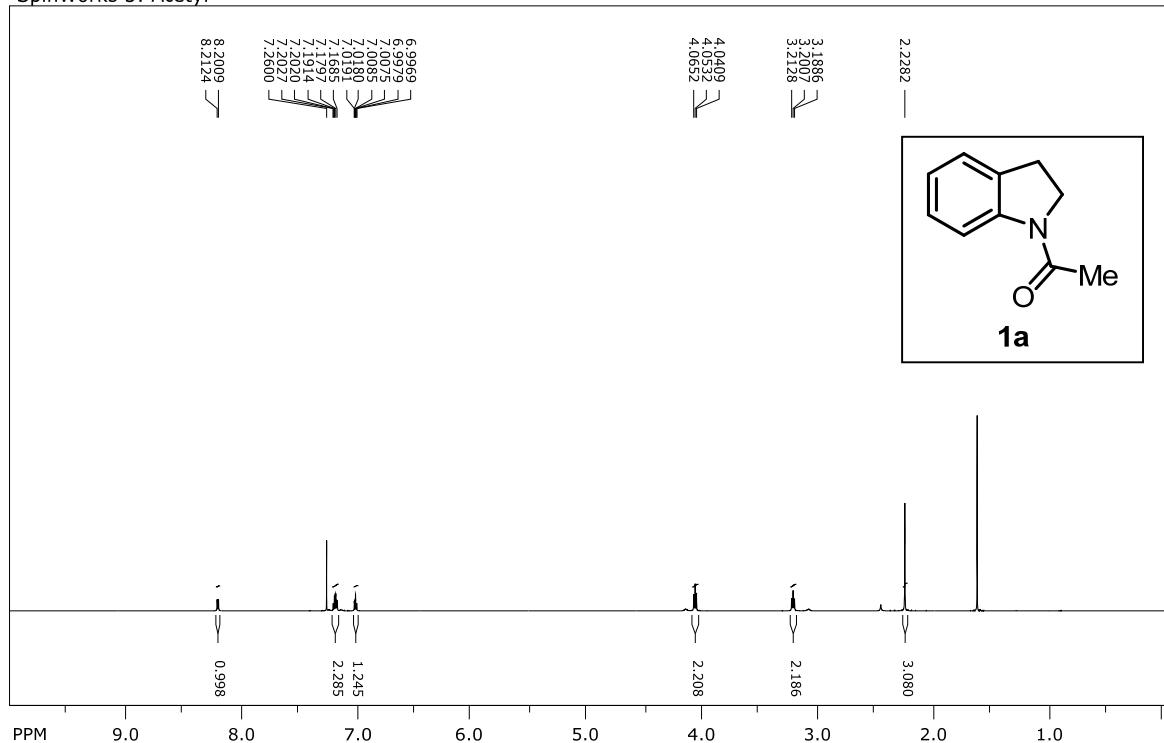
(*E*)-Butyl 3-(2-(1-acetylindoline-7-carbonyl)phenyl)acrylate (**5c**)



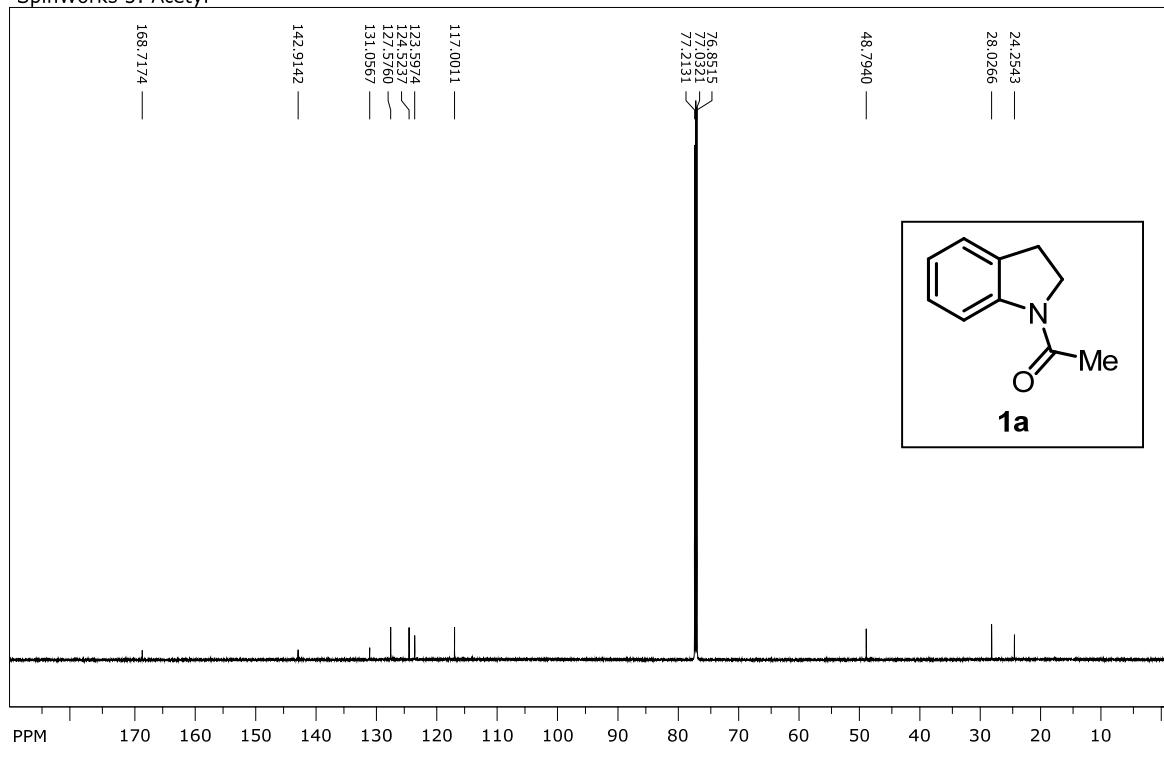
^1H NMR (500 MHz, CDCl_3) δ 8.28 (d, $J = 15.9$ Hz, 1H), 7.67–7.62 (m, 2H), 7.49 (t, $J = 7.5$ Hz, 1H), 7.38–7.34 (m, 2H), 7.13–7.06 (m, 2H), 6.30 (d, $J = 15.9$ Hz, 1H), 4.16–4.13 (m, 4H) 3.21 (t, $J = 8.0$ Hz, 2H), 2.08 (s, 3H), 1.66–1.58 (m, 2H), 1.42–1.39 (m, 2H), 0.94 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 194.7, 167.9, 166.7, 144.2, 139.3, 137.4, 136.4, 133.8, 131.7, 131.5, 129.7, 128.7, 127.6, 127.1, 125.7, 124.1, 120.3, 64.2, 49.6, 30.7, 28.9, 23.2, 19.1, 13.7; IR (KBr) ν 3054, 2924, 1642, 1583, 1447, 1431, 1381, 1350, 1327, 1278, 1205, 1063, 989, 883, 788, 751 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{24}\text{H}_{25}\text{NO}_4$ [M^+] 391.1784, found 391.1781.

¹H and ¹³C NMR spectra of all compounds

SpinWorks 3: Acetyl

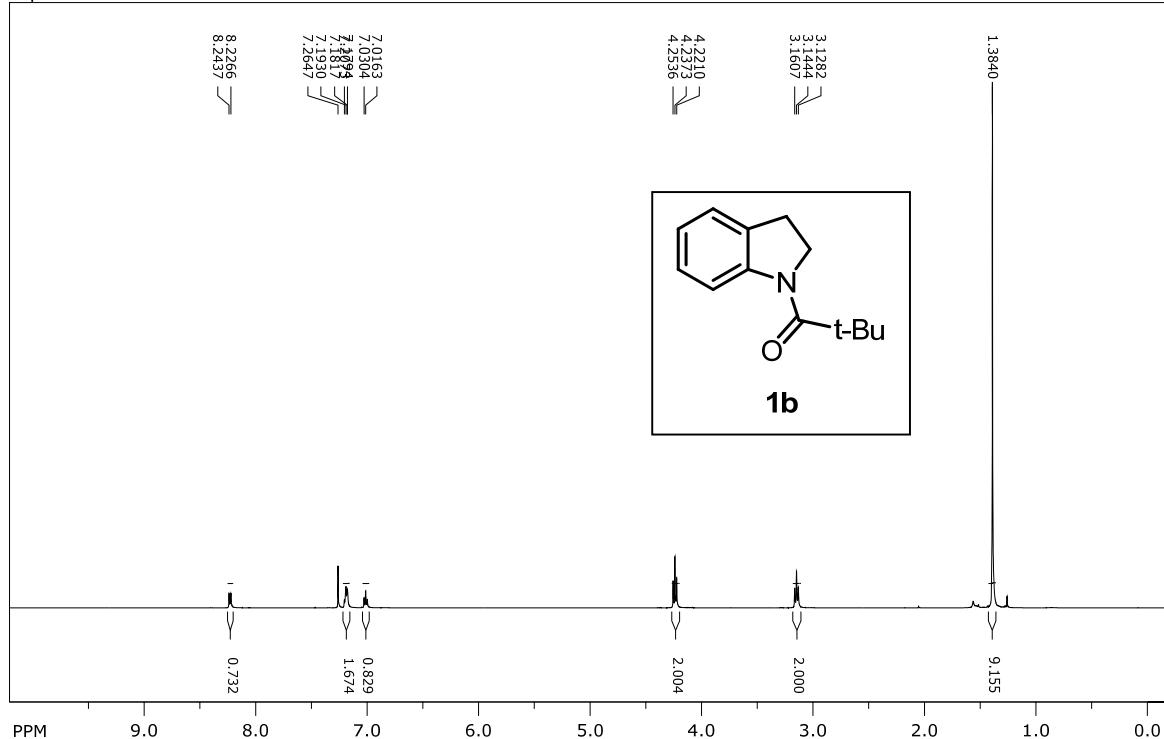


SpinWorks 3: Acetyl

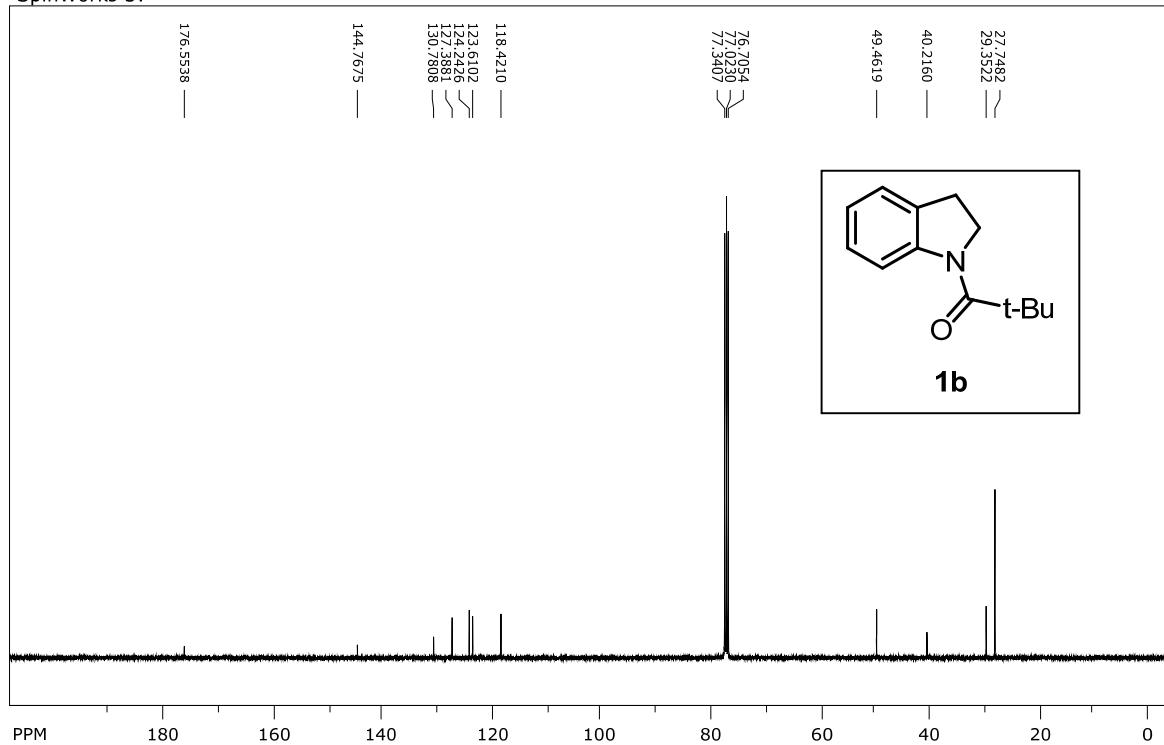


S30

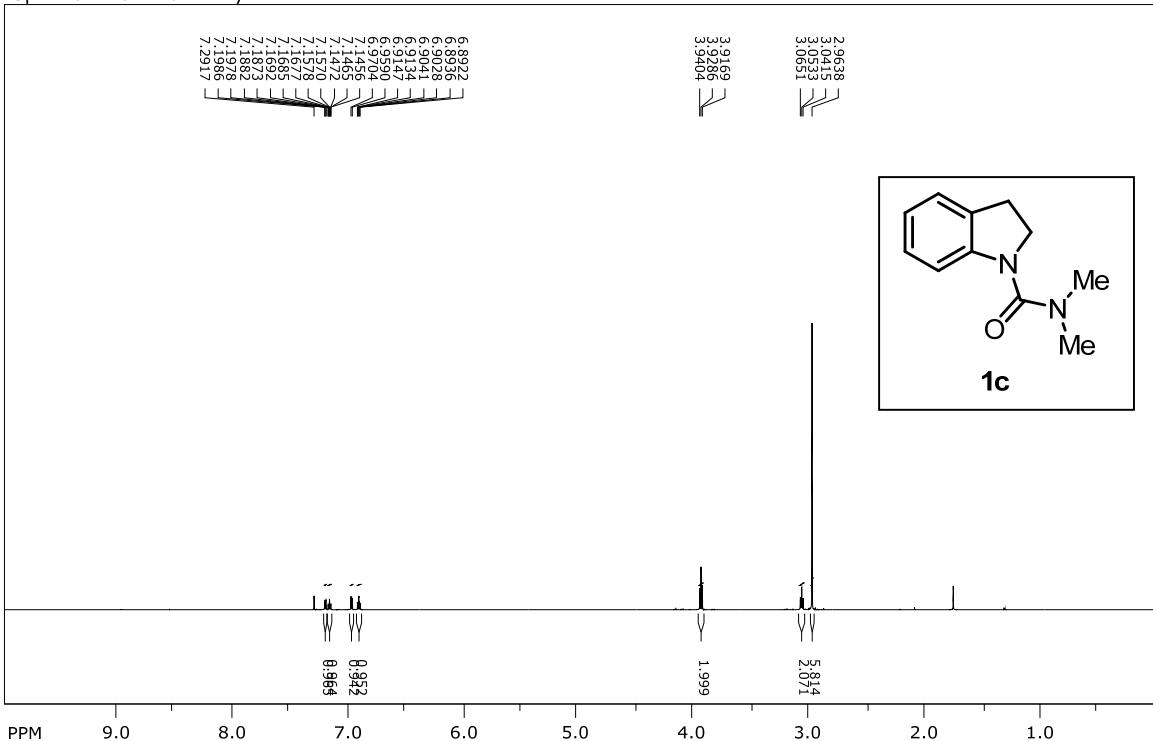
SpinWorks 3: PIV



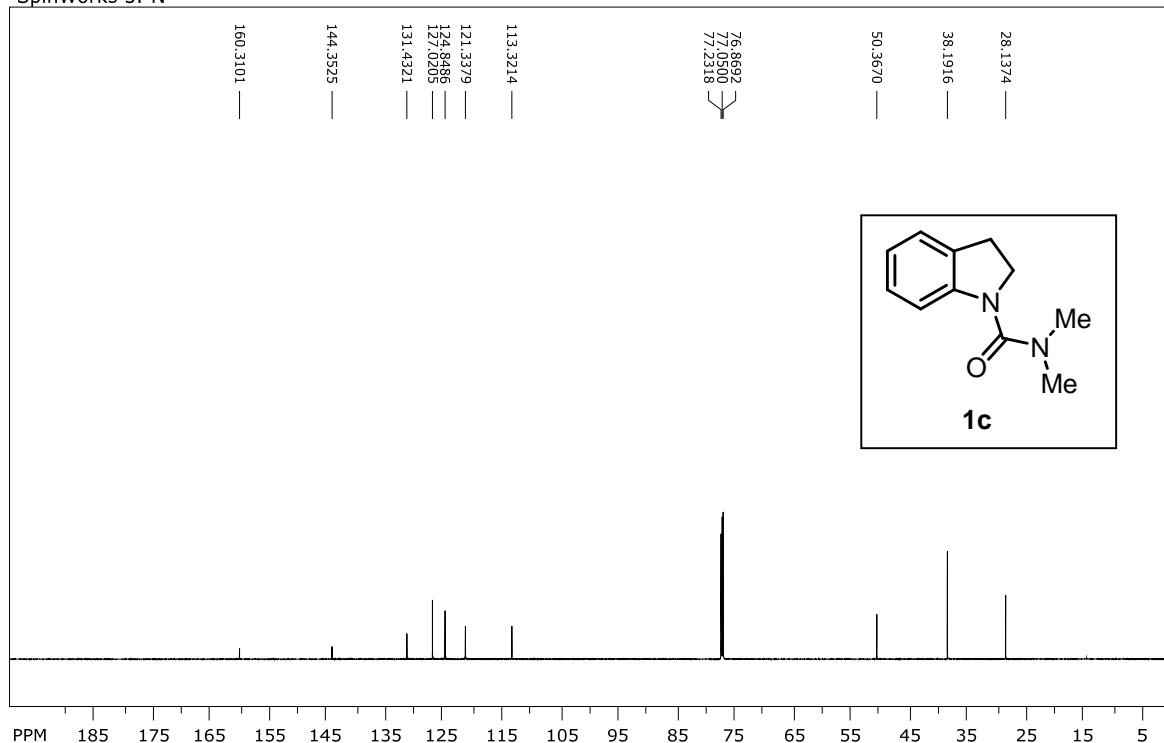
SpinWorks 3:

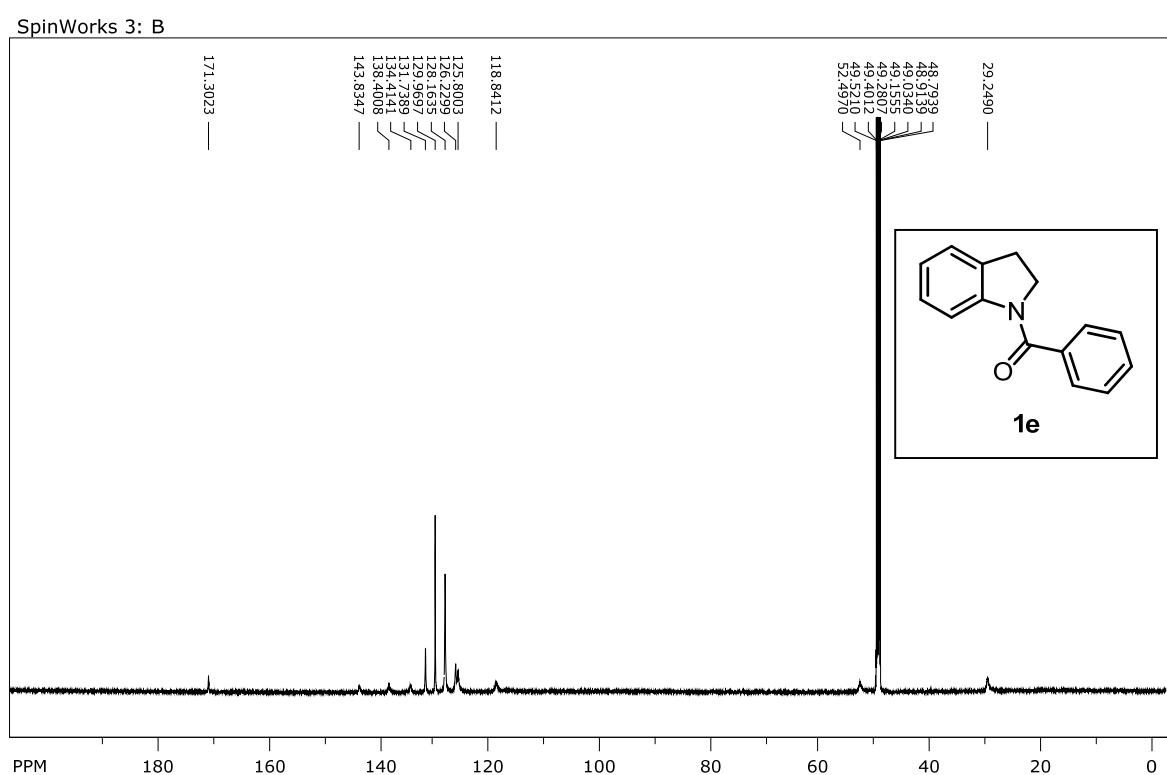
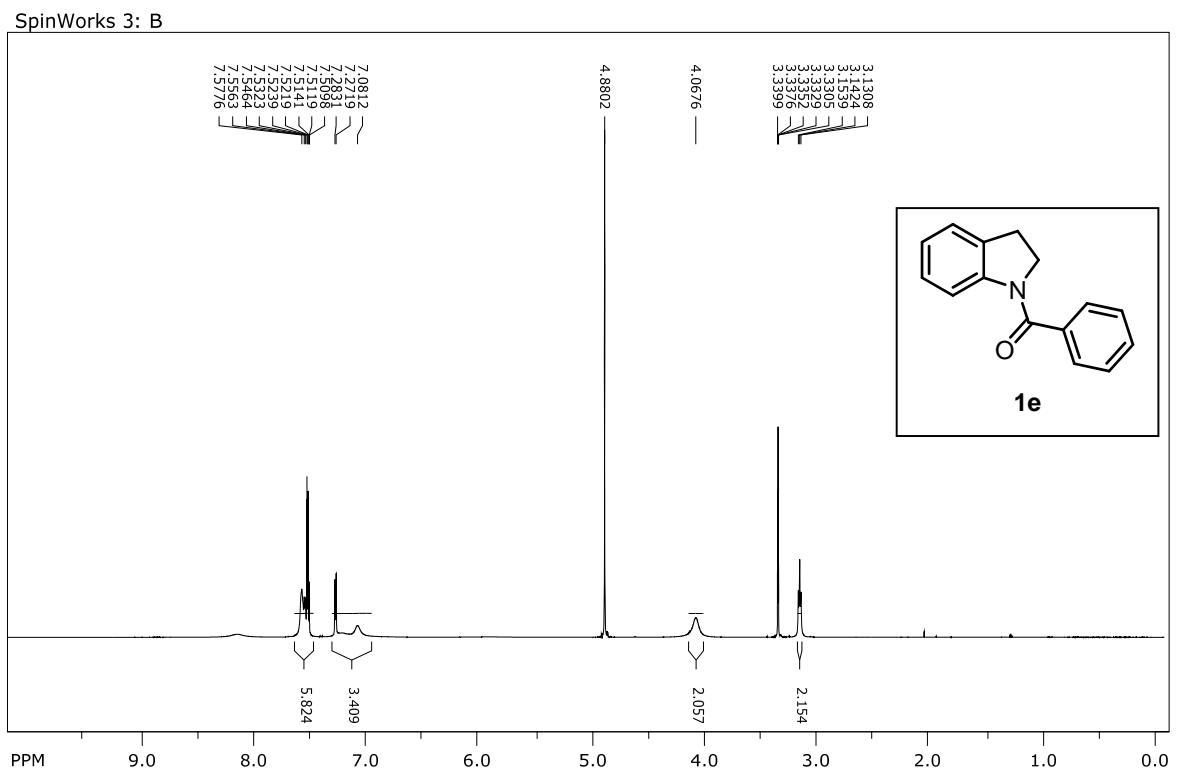


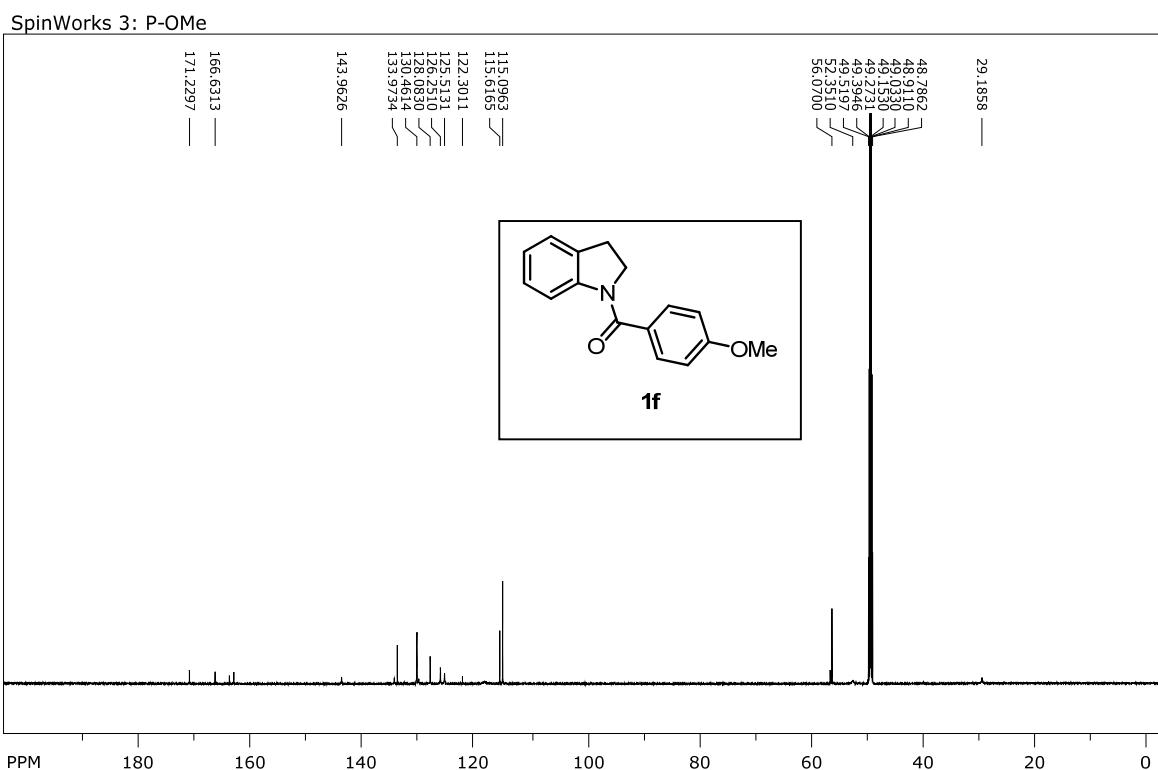
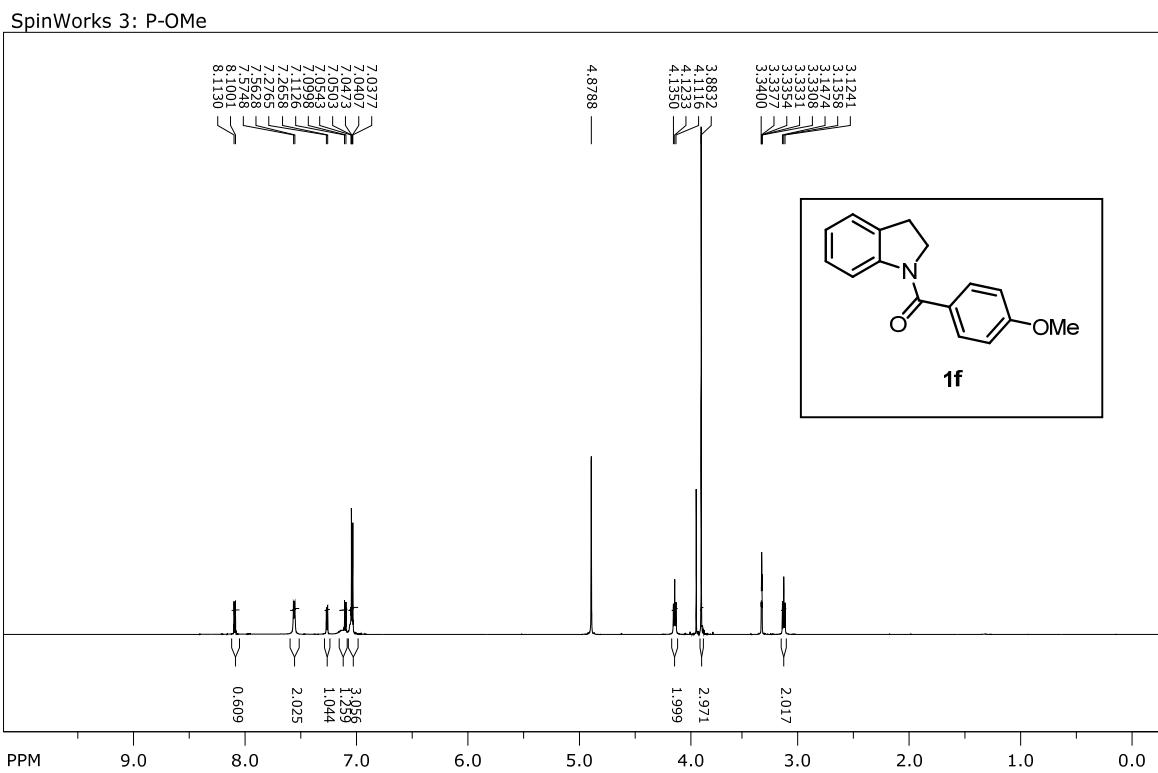
SpinWorks 3: N-dimethyl



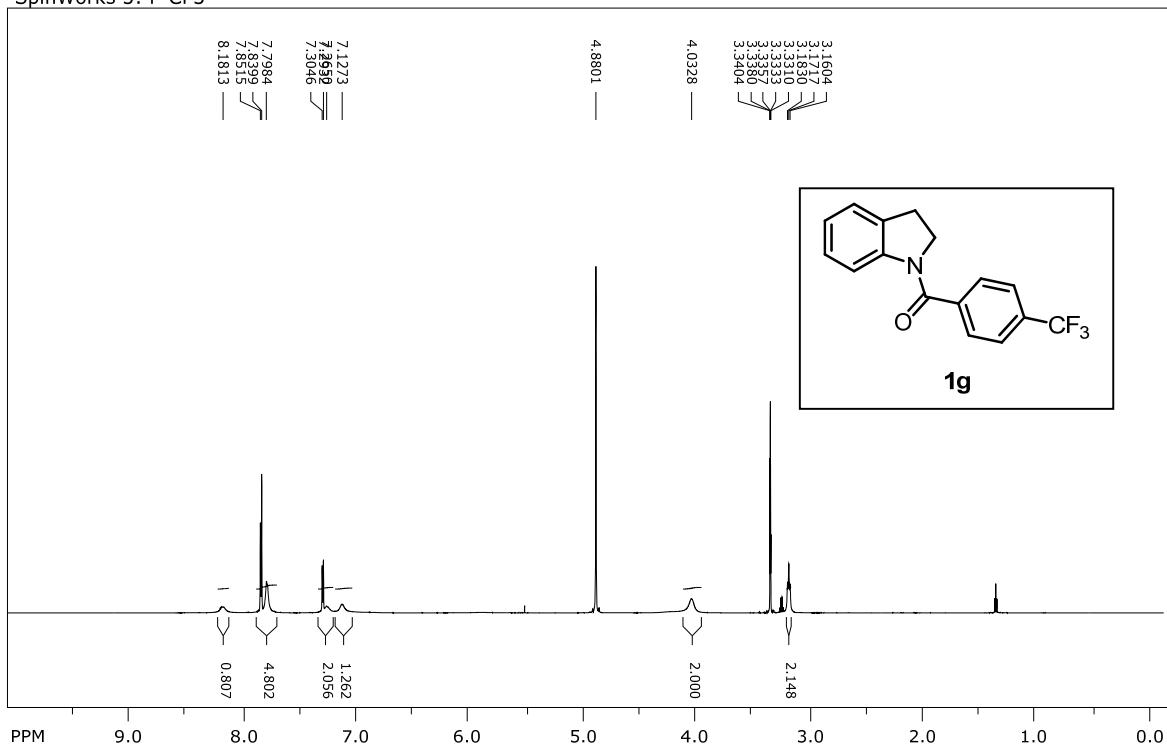
SpinWorks 3: N



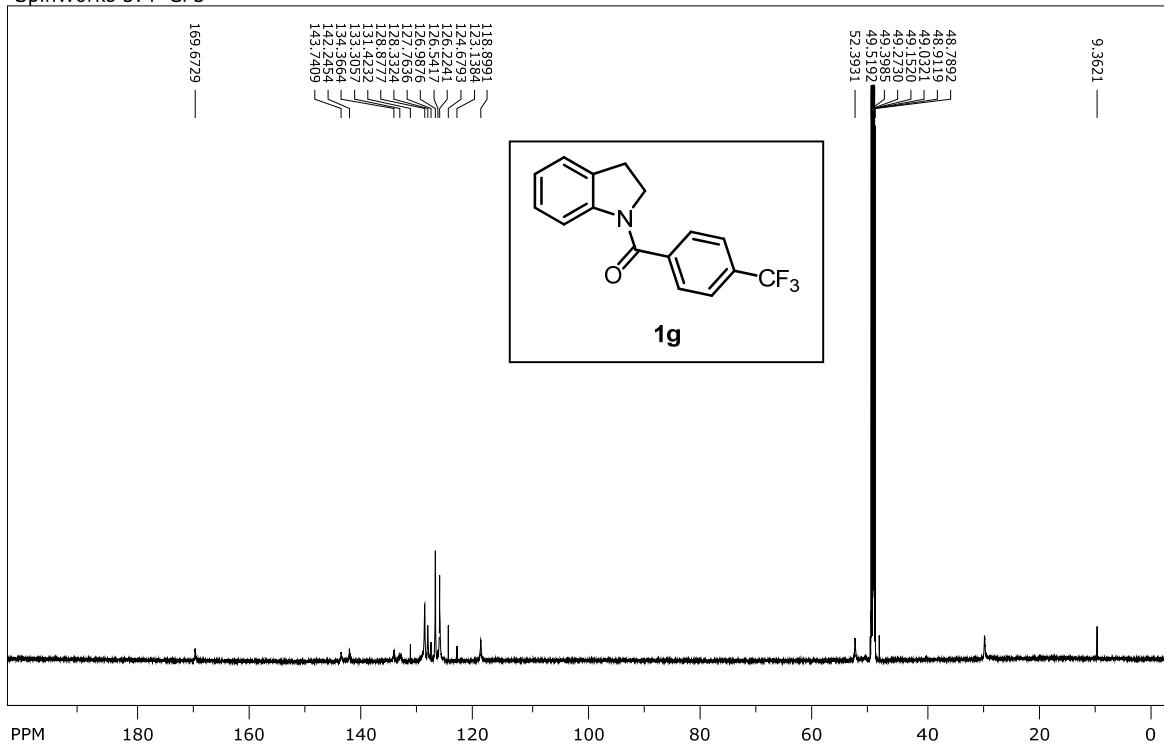




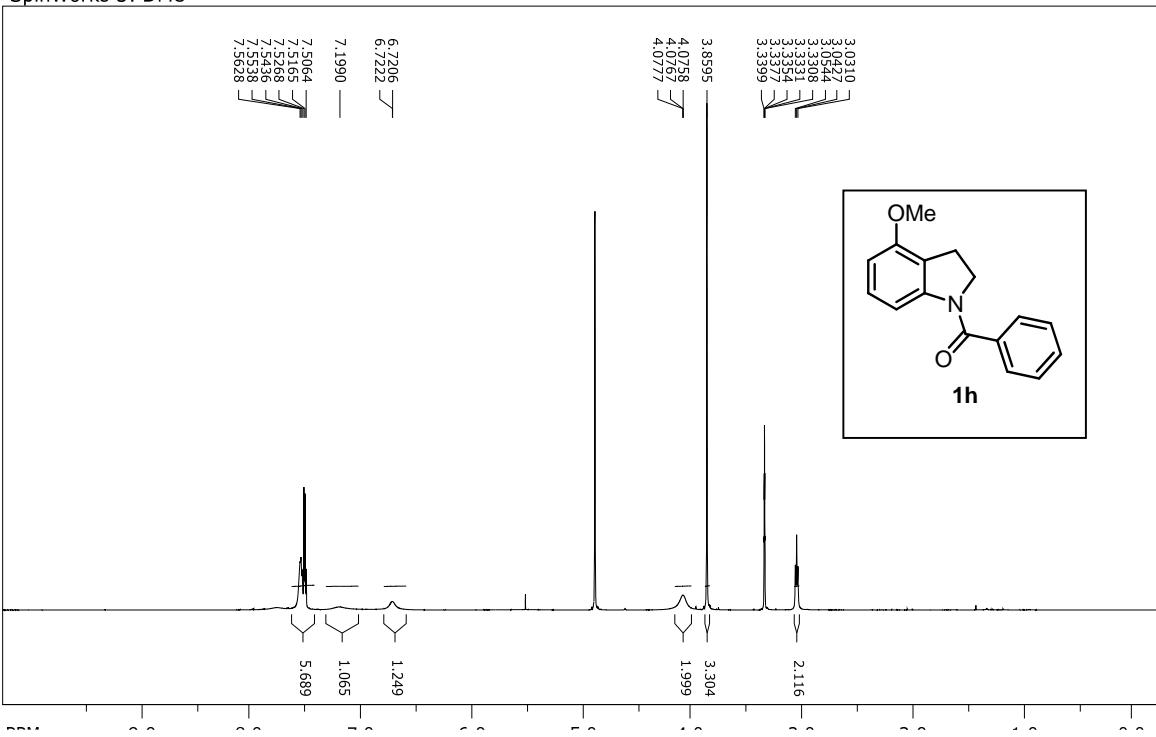
SpinWorks 3: P-CF₃



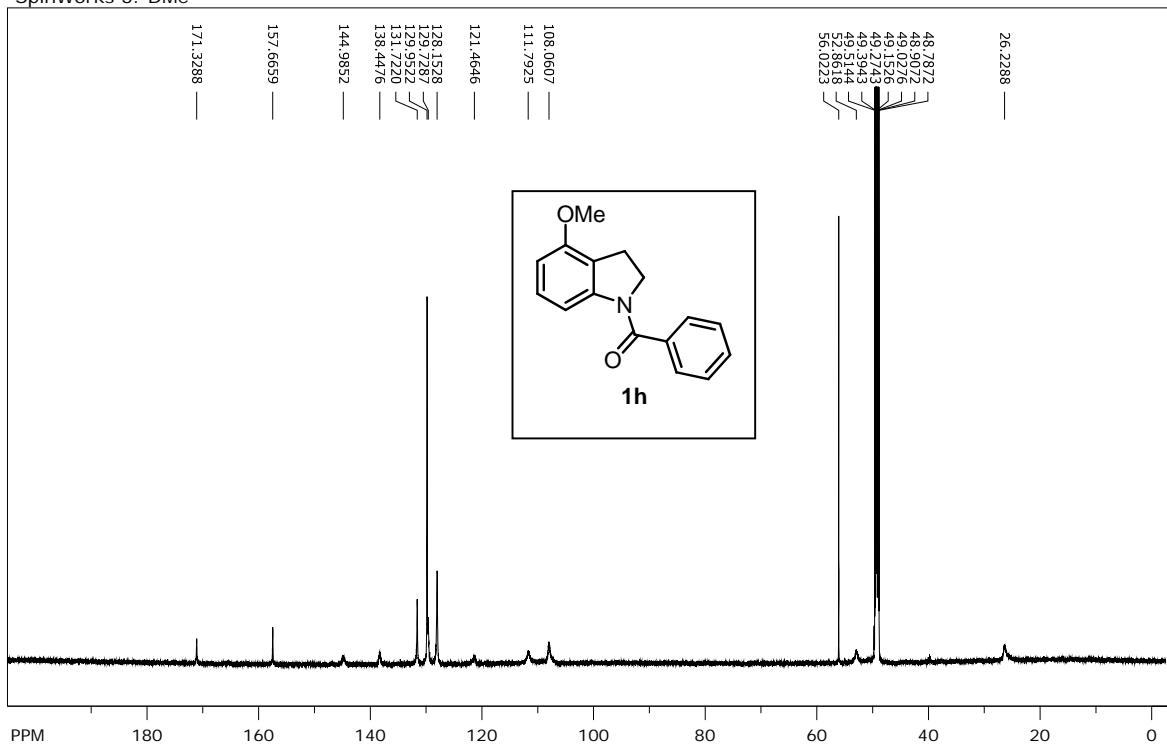
SpinWorks 3: P-CF₃

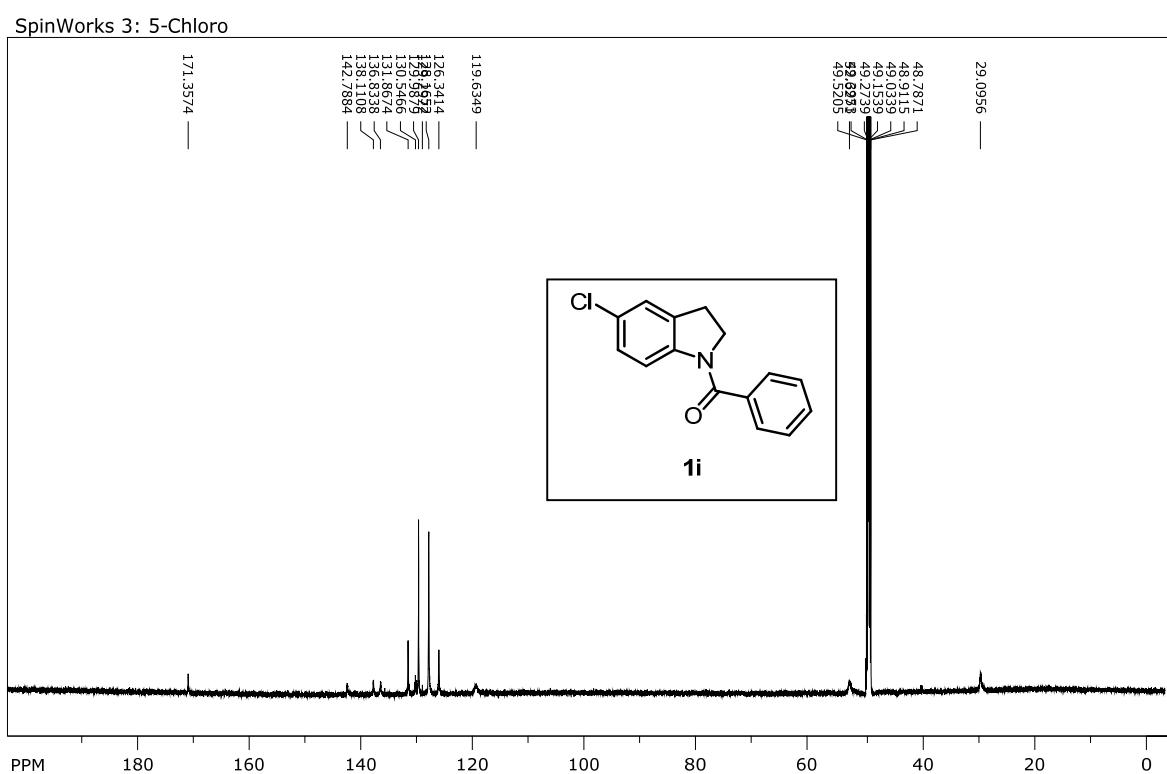
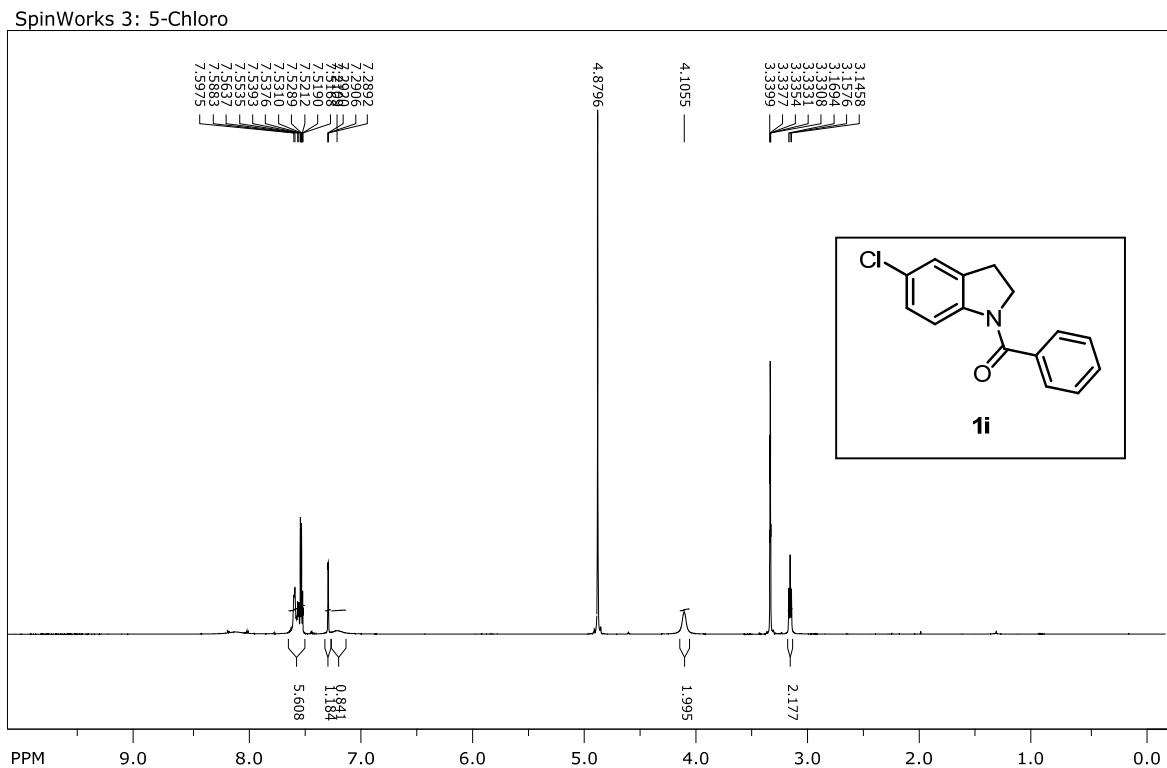


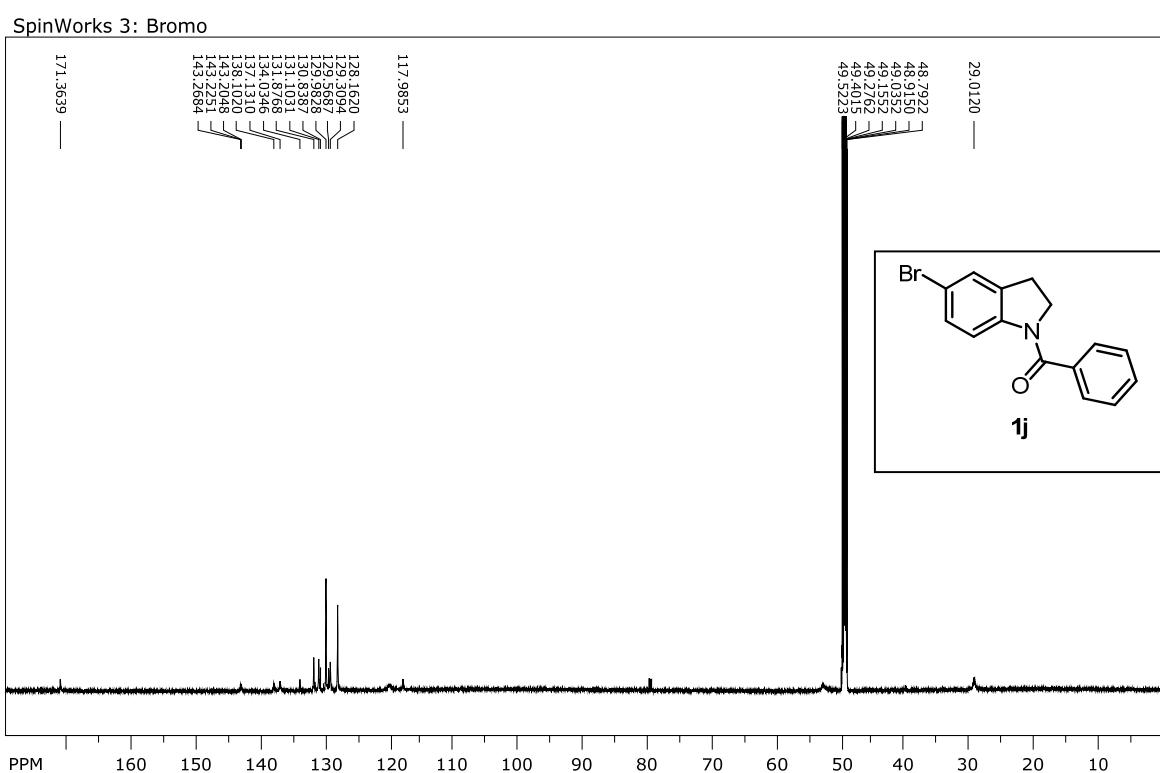
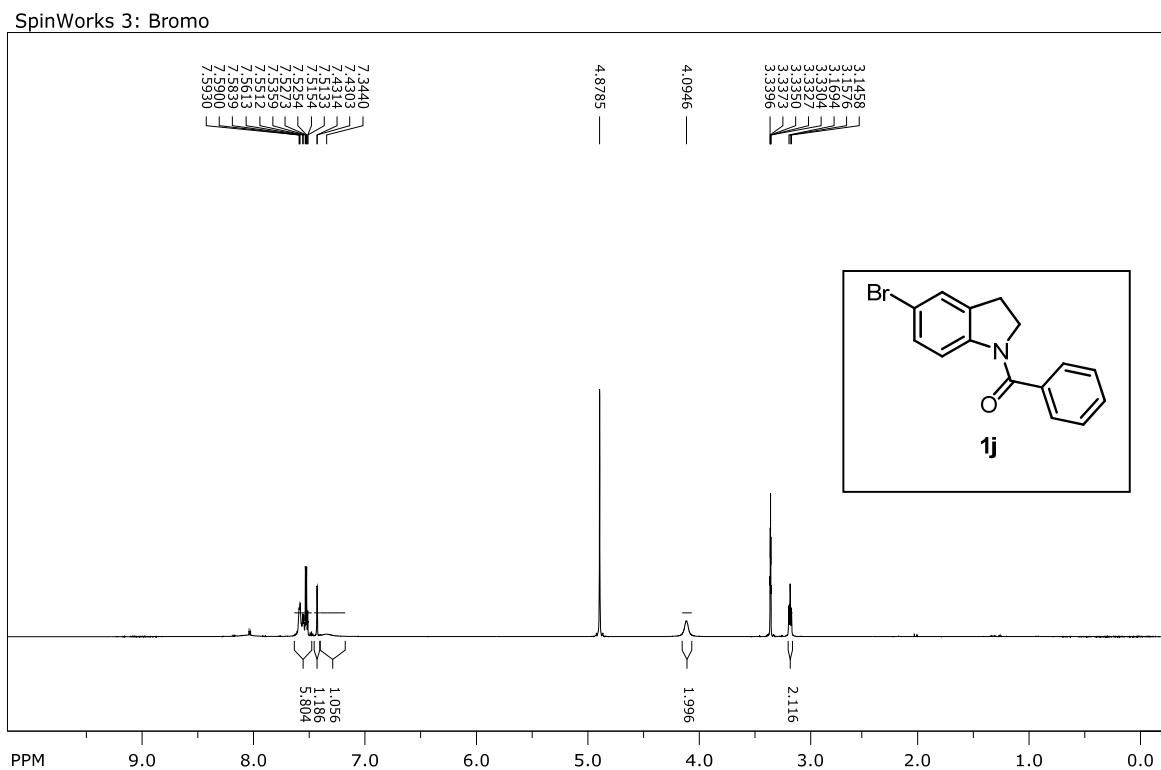
SpinWorks 3: DMe

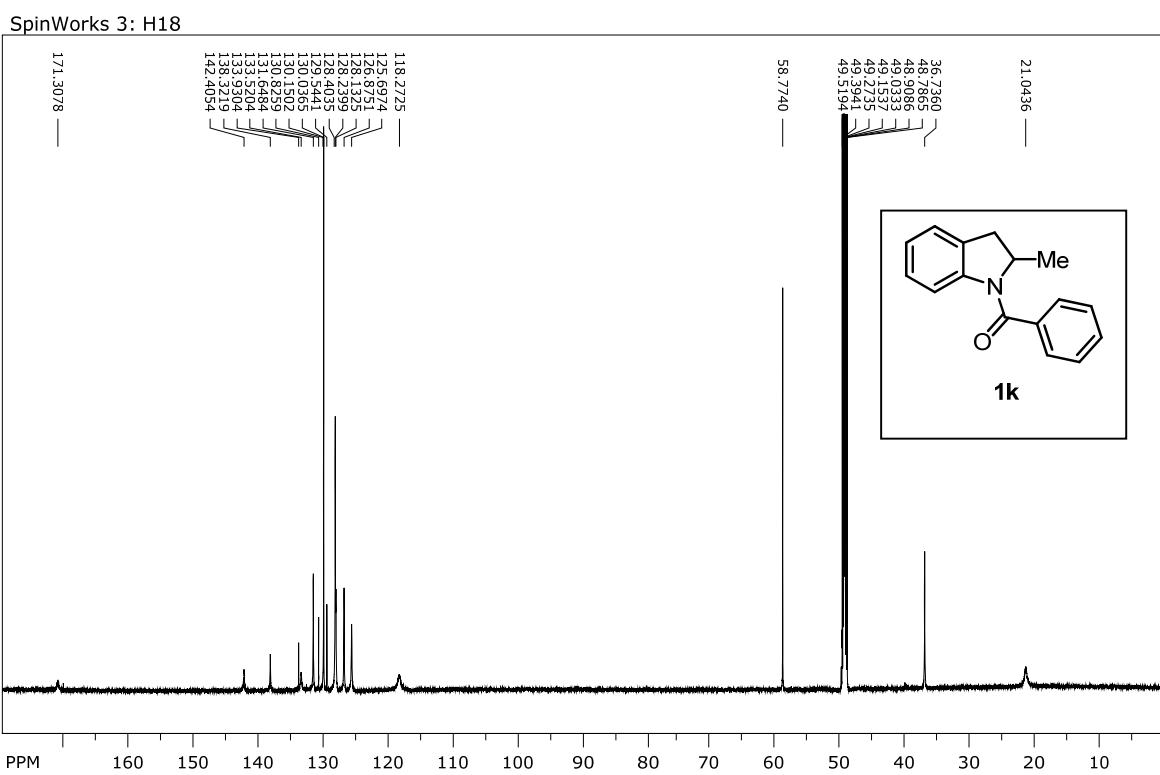
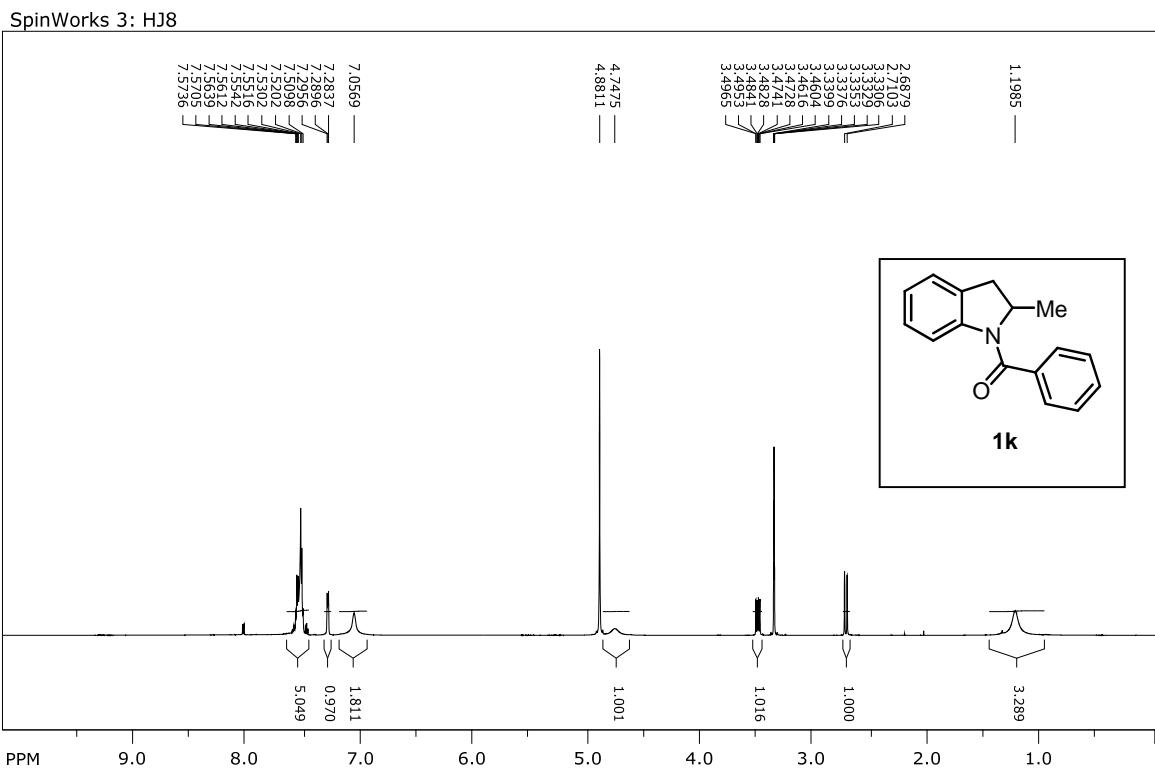


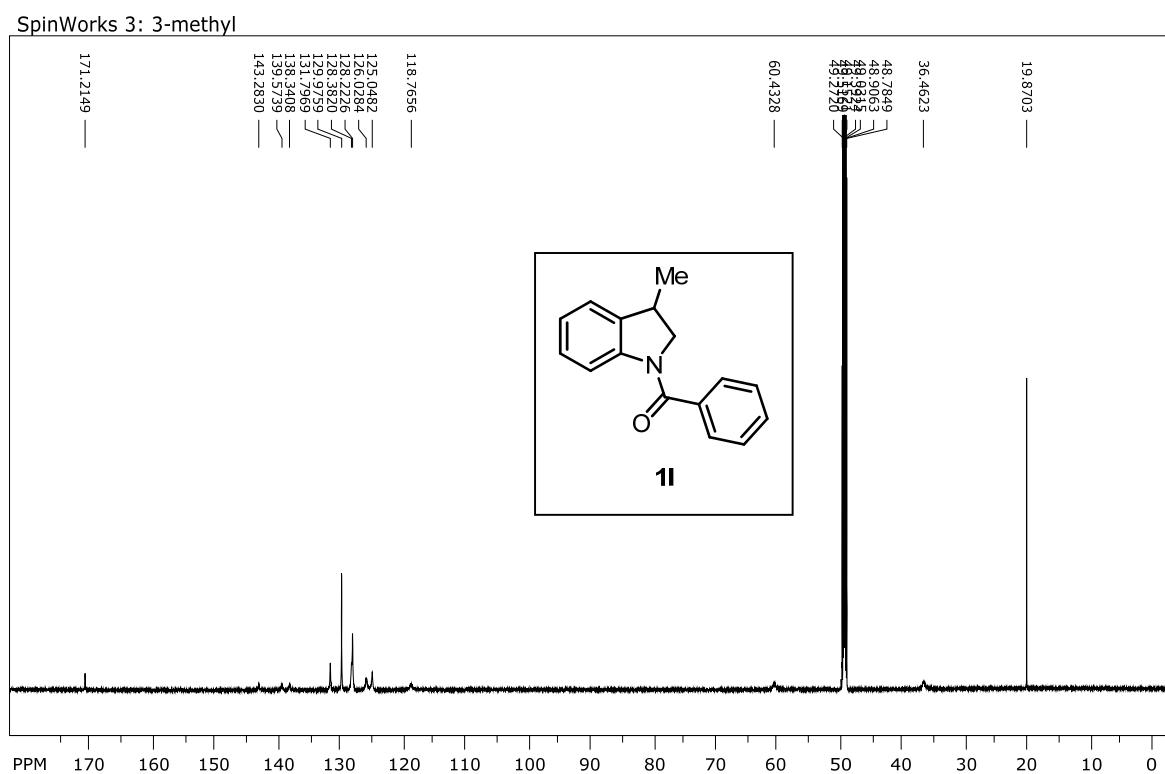
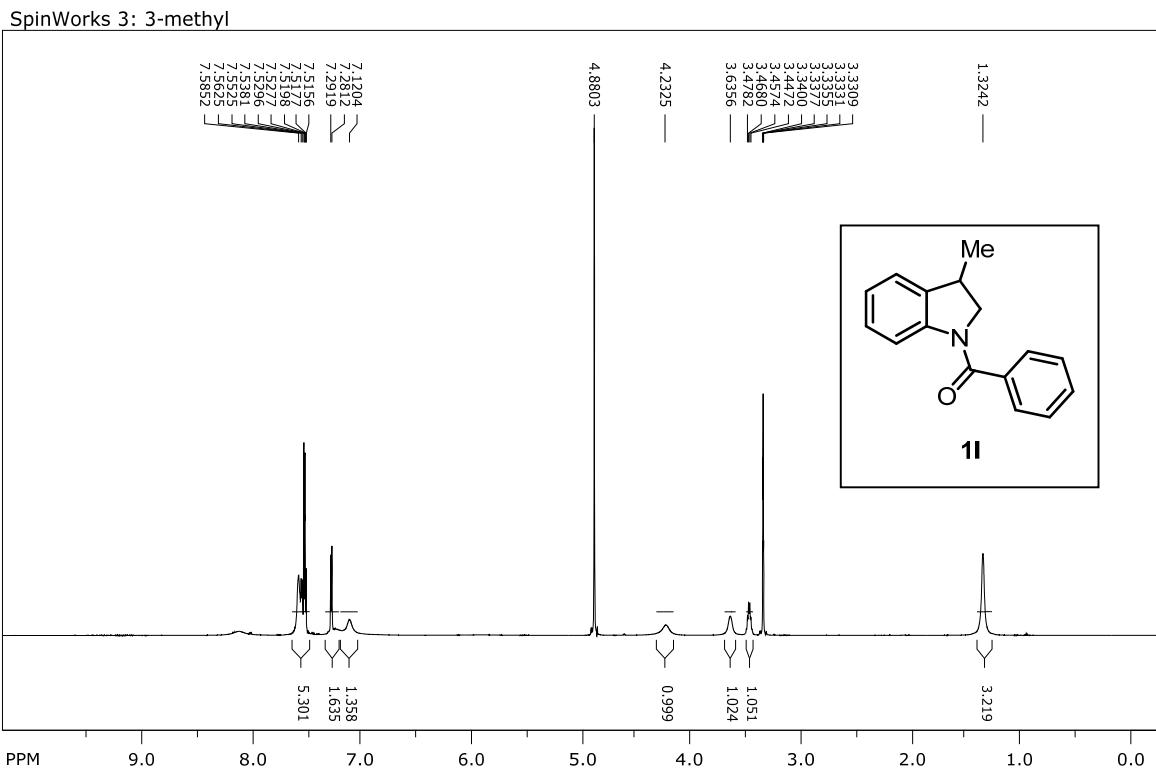
SpinWorks 3: DMe



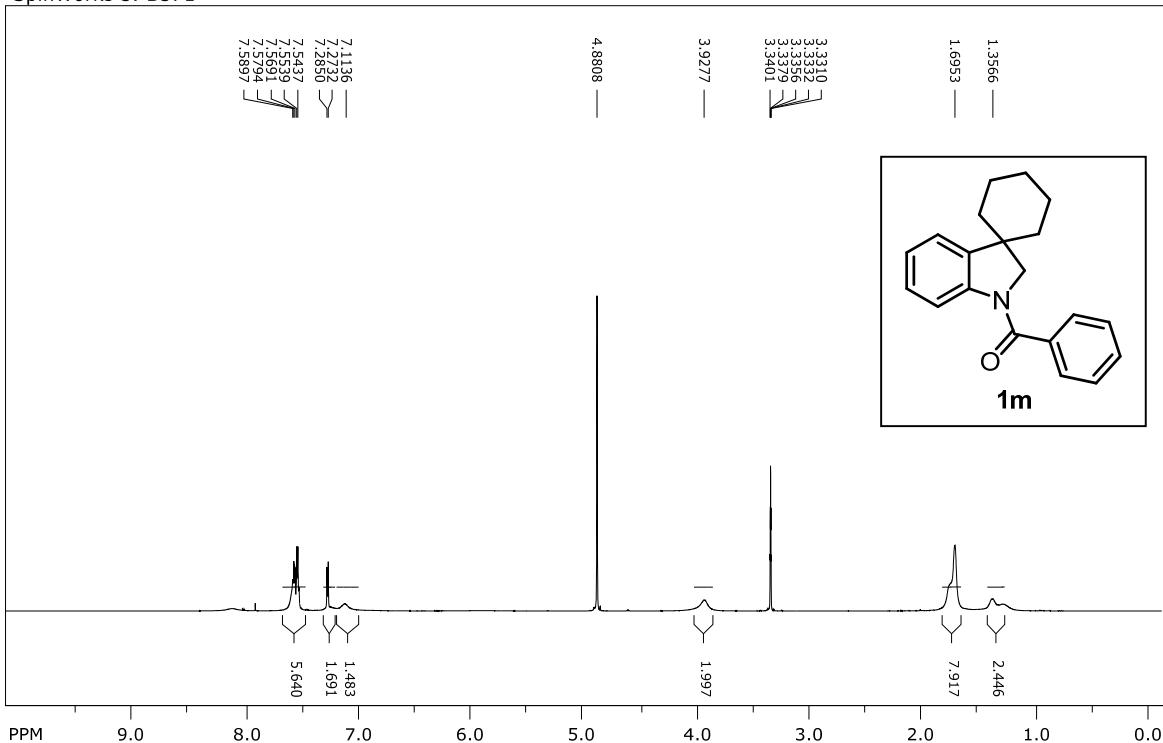




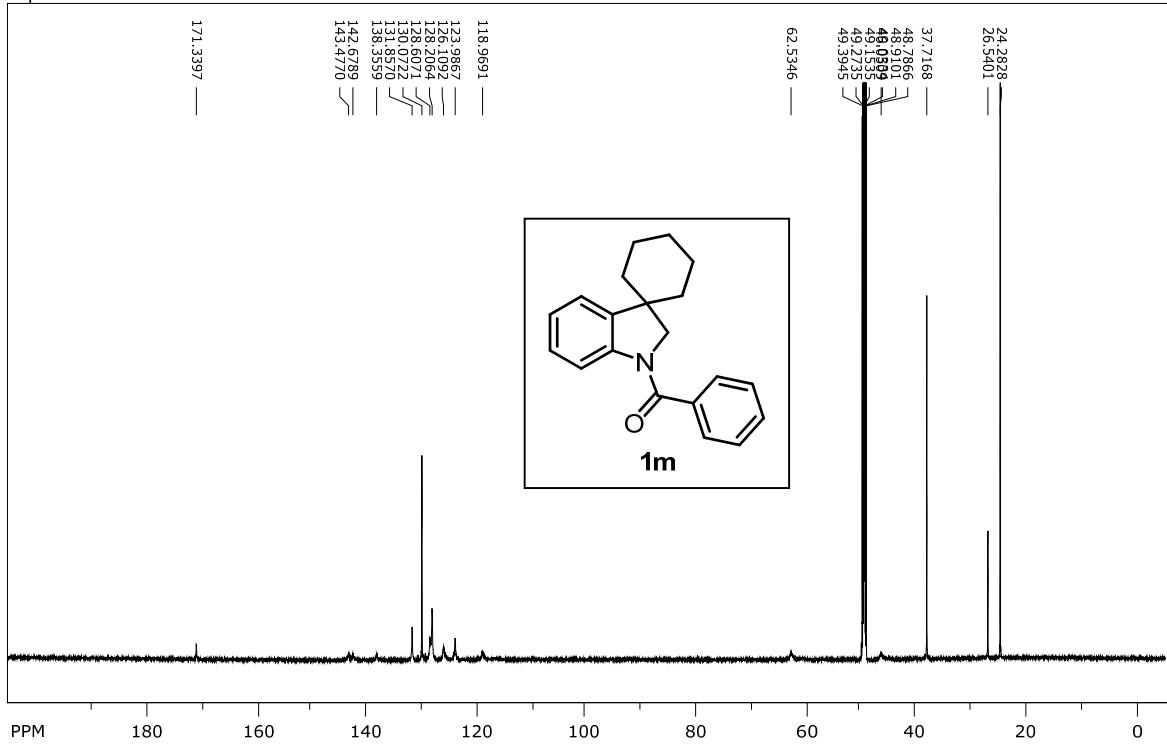




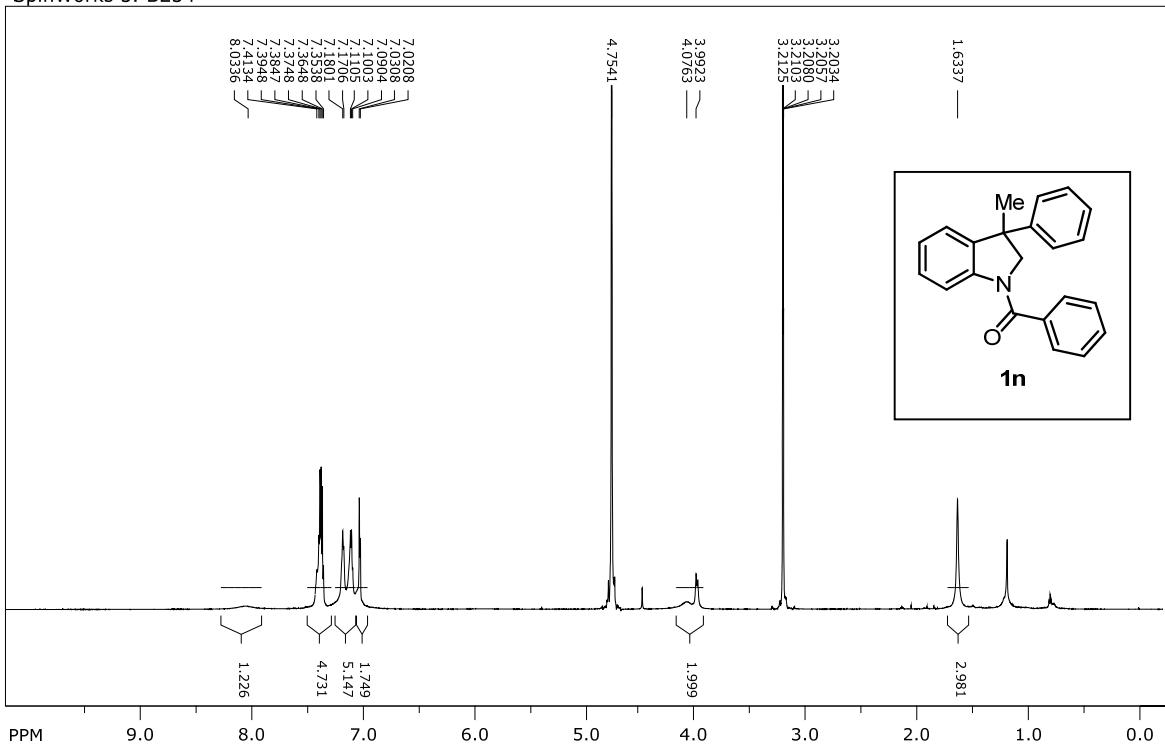
SpinWorks 3: B371



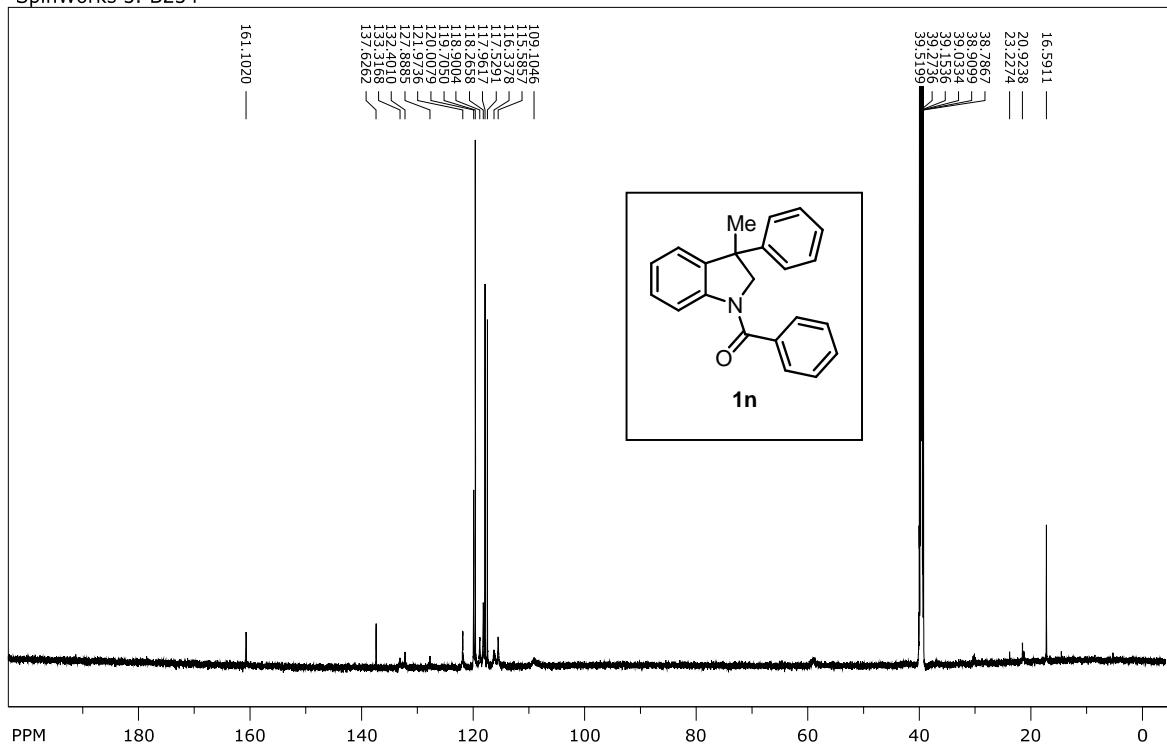
SpinWorks 3: B371

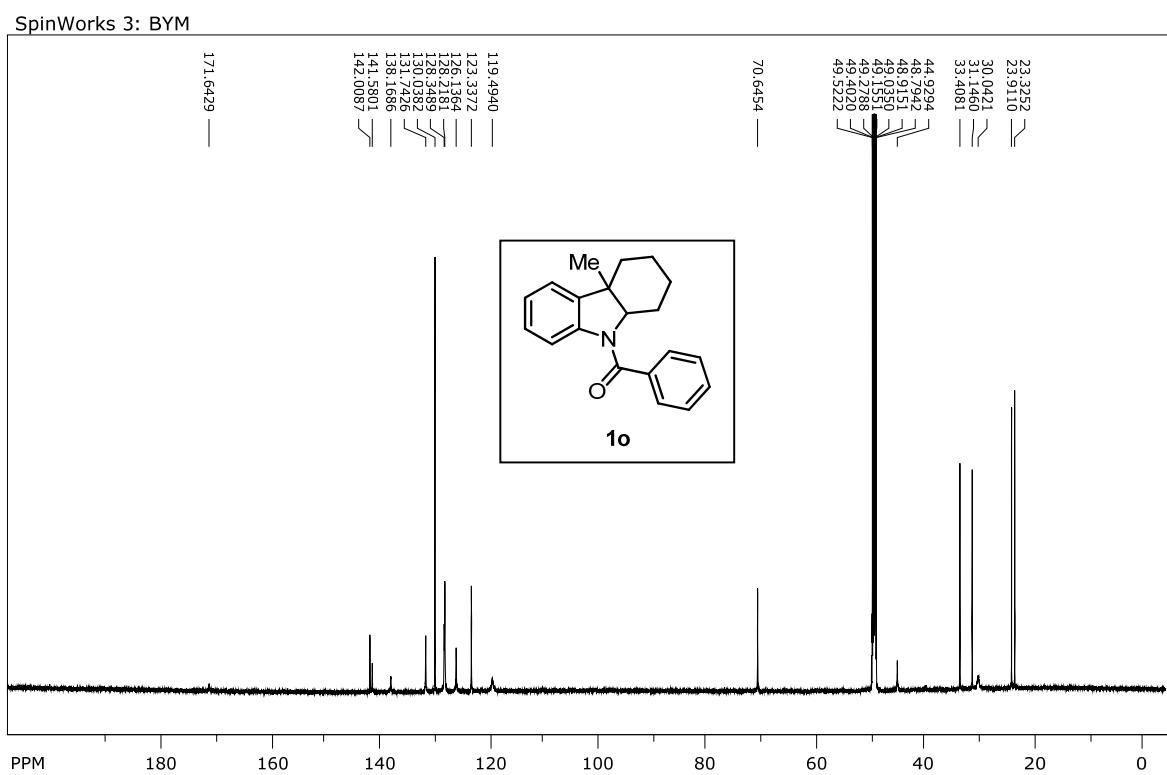
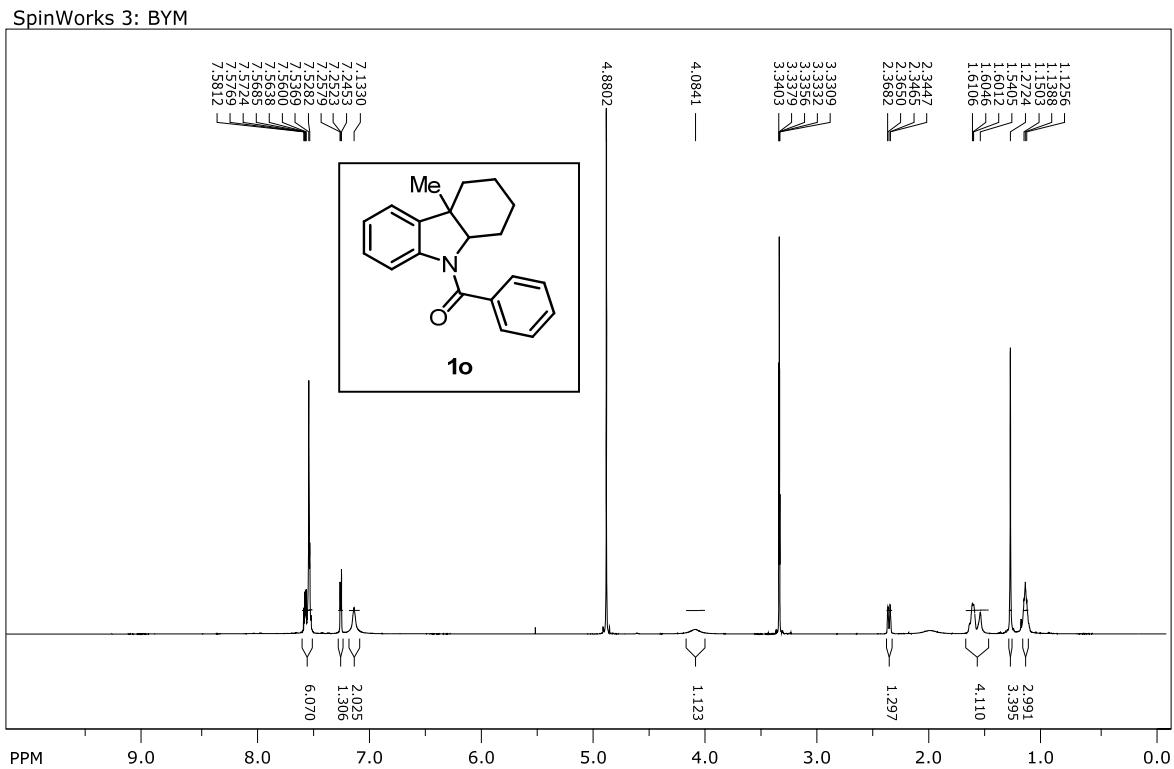


SpinWorks 3: B234

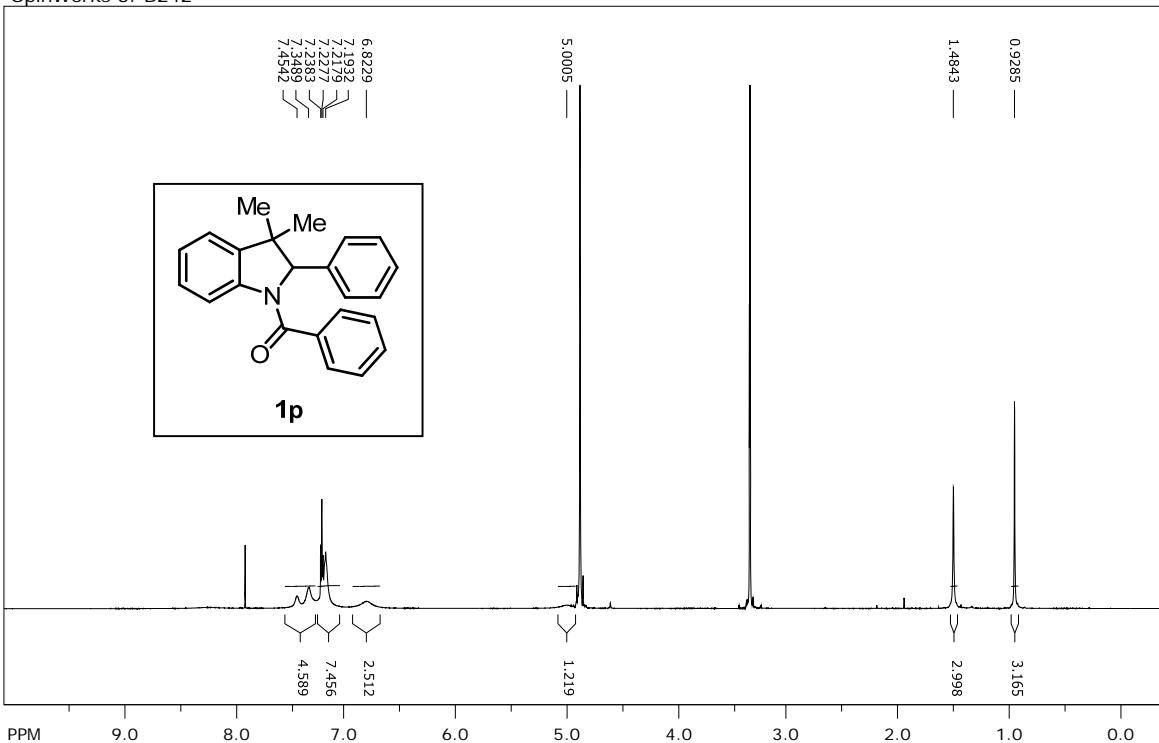


SpinWorks 3: B234

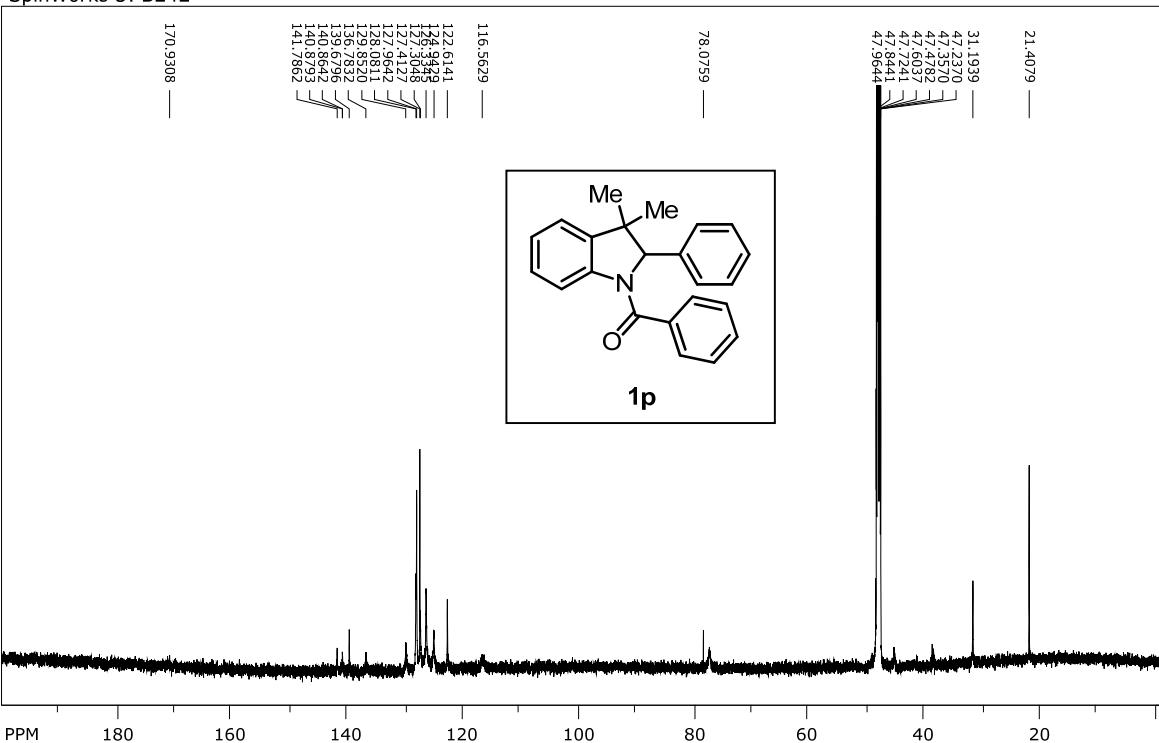


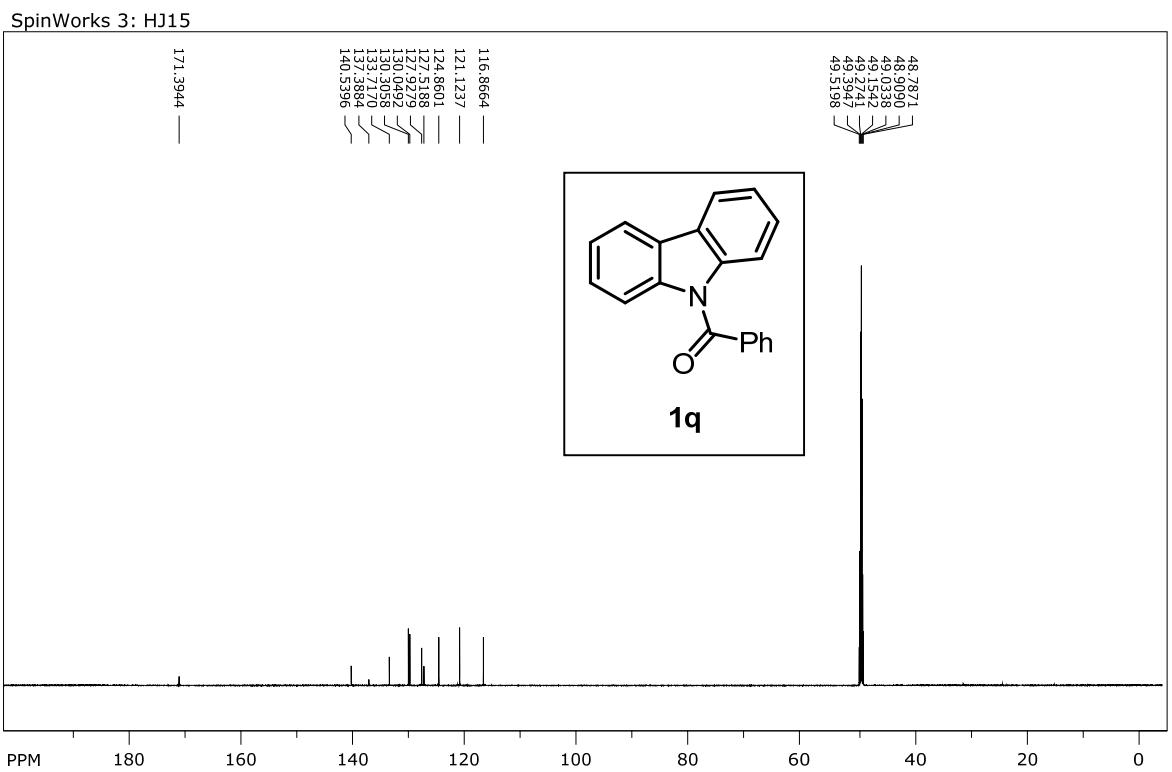
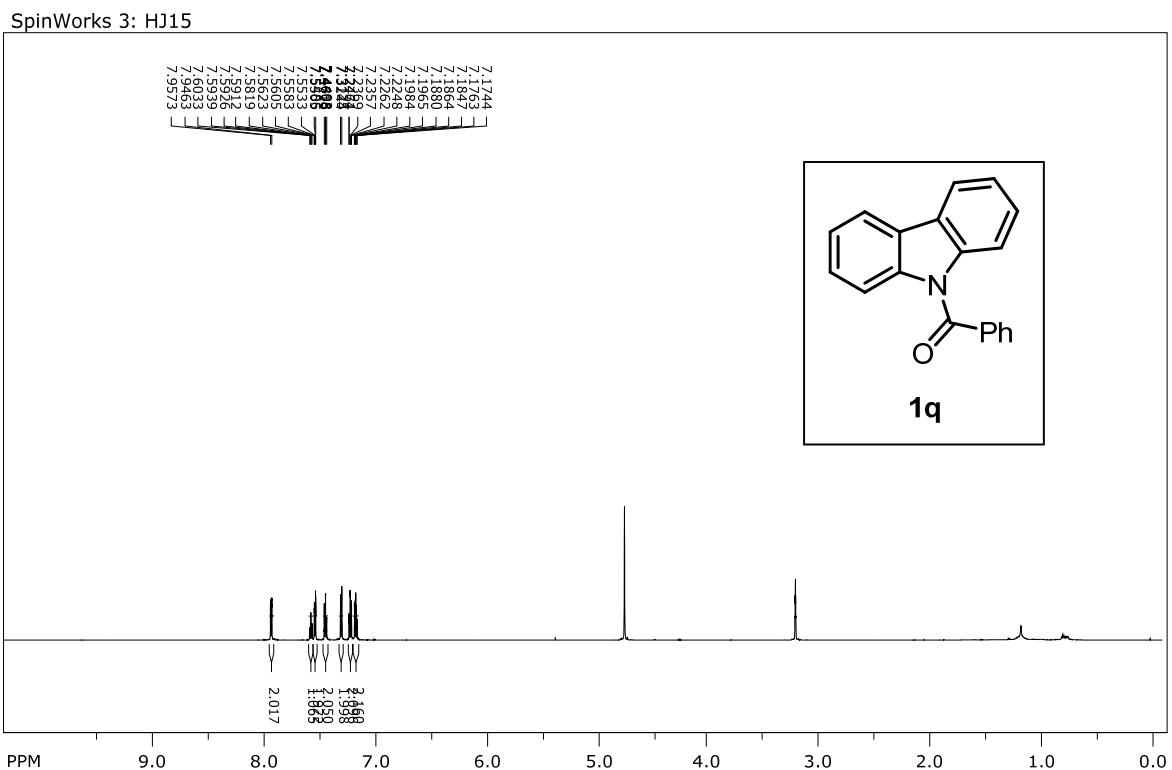


SpinWorks 3: B242

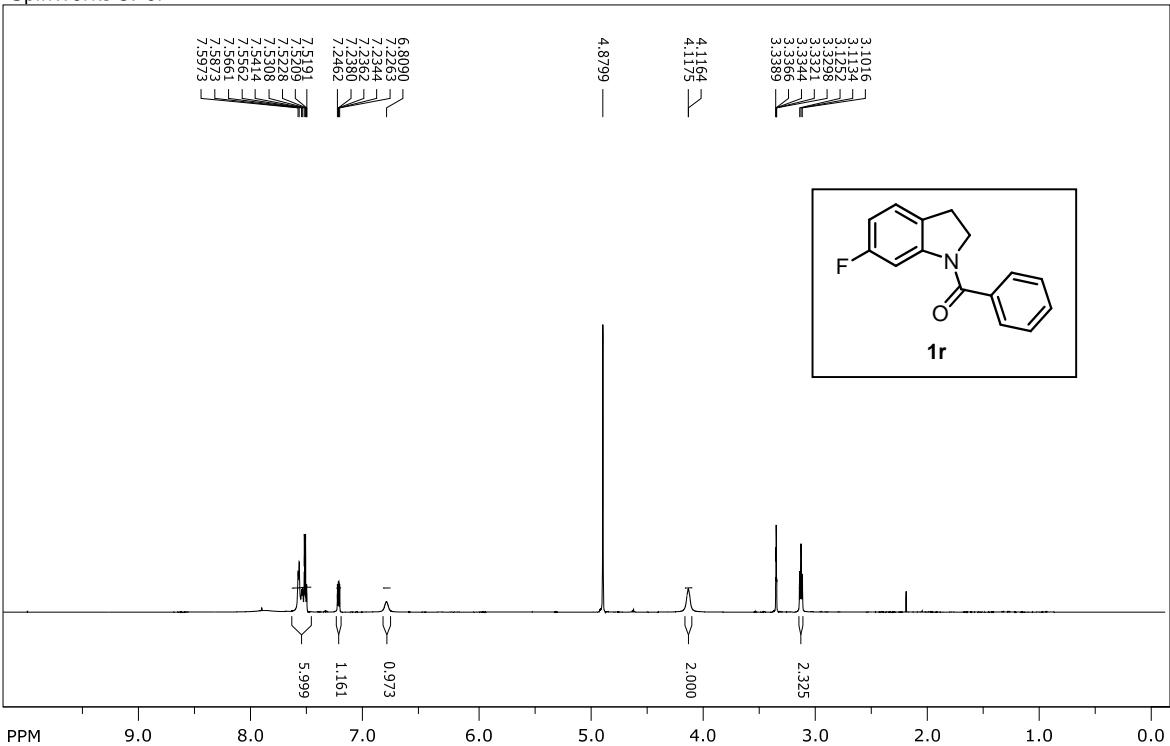


SpinWorks 3: B242

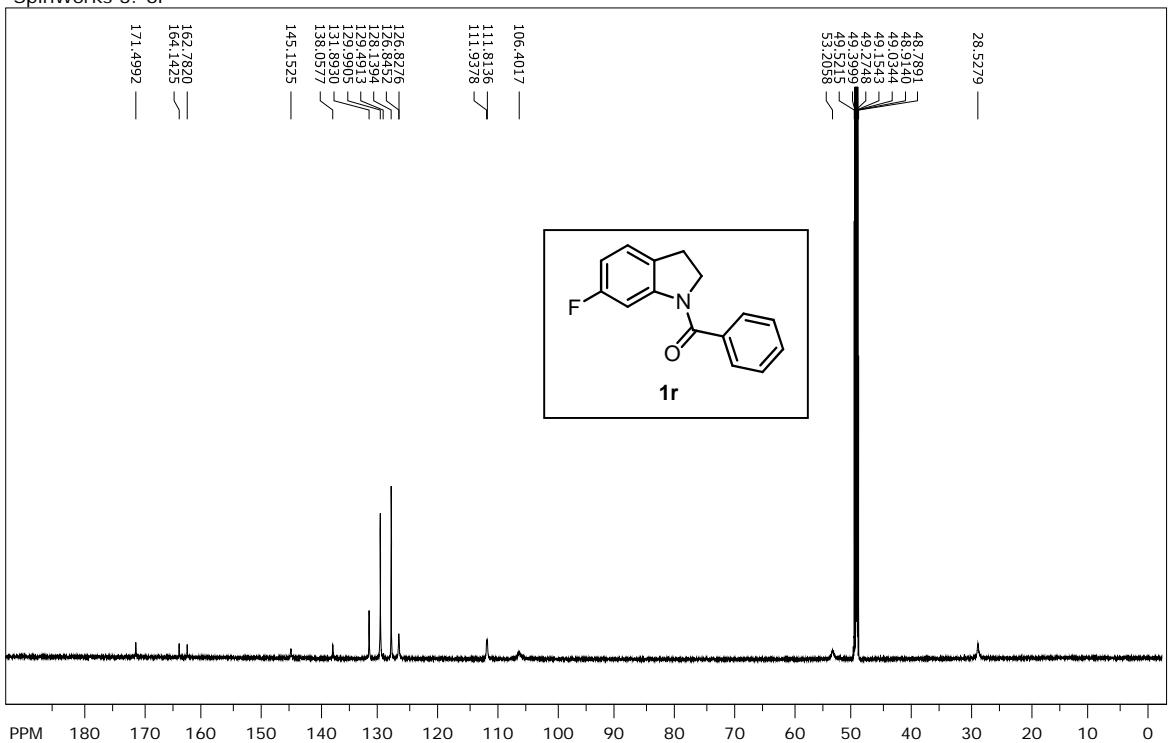


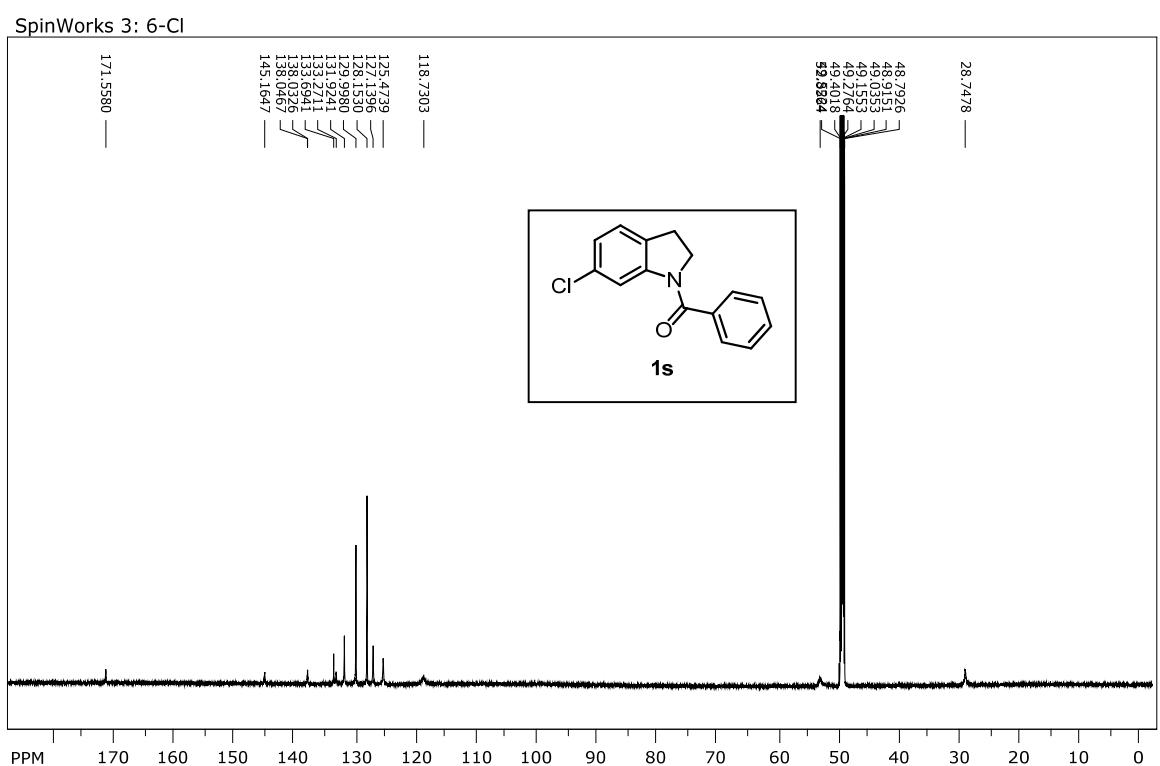
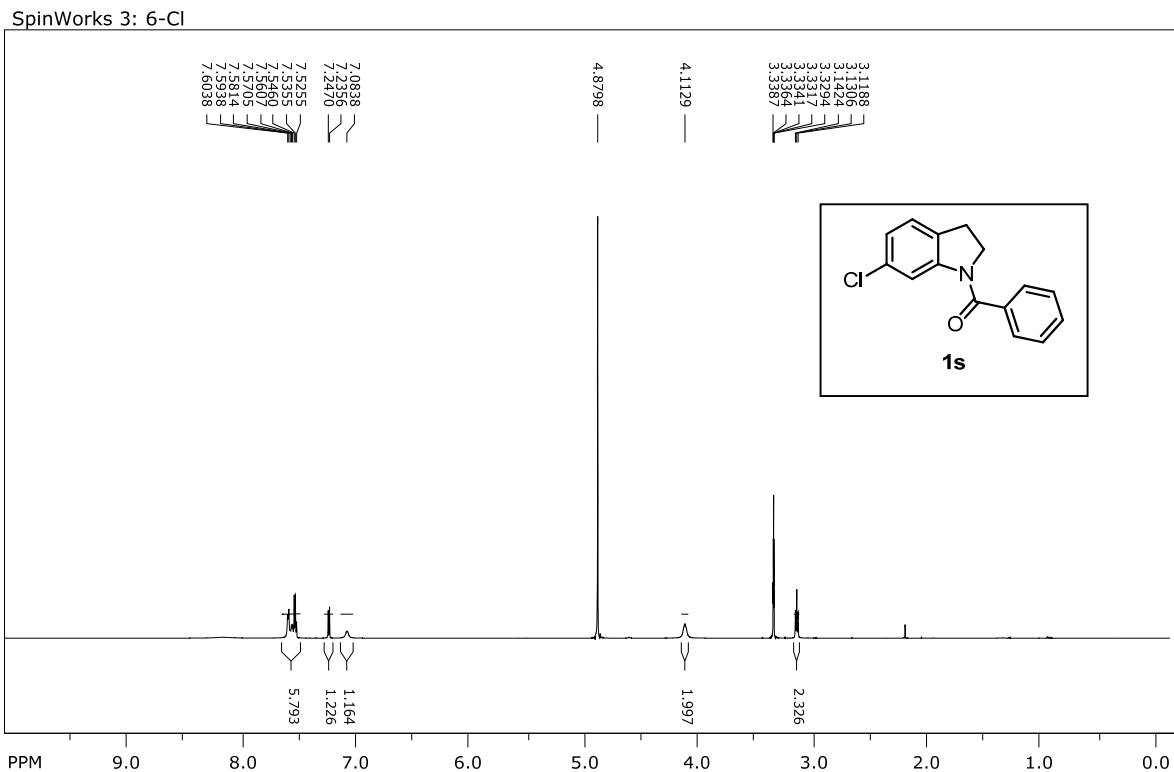


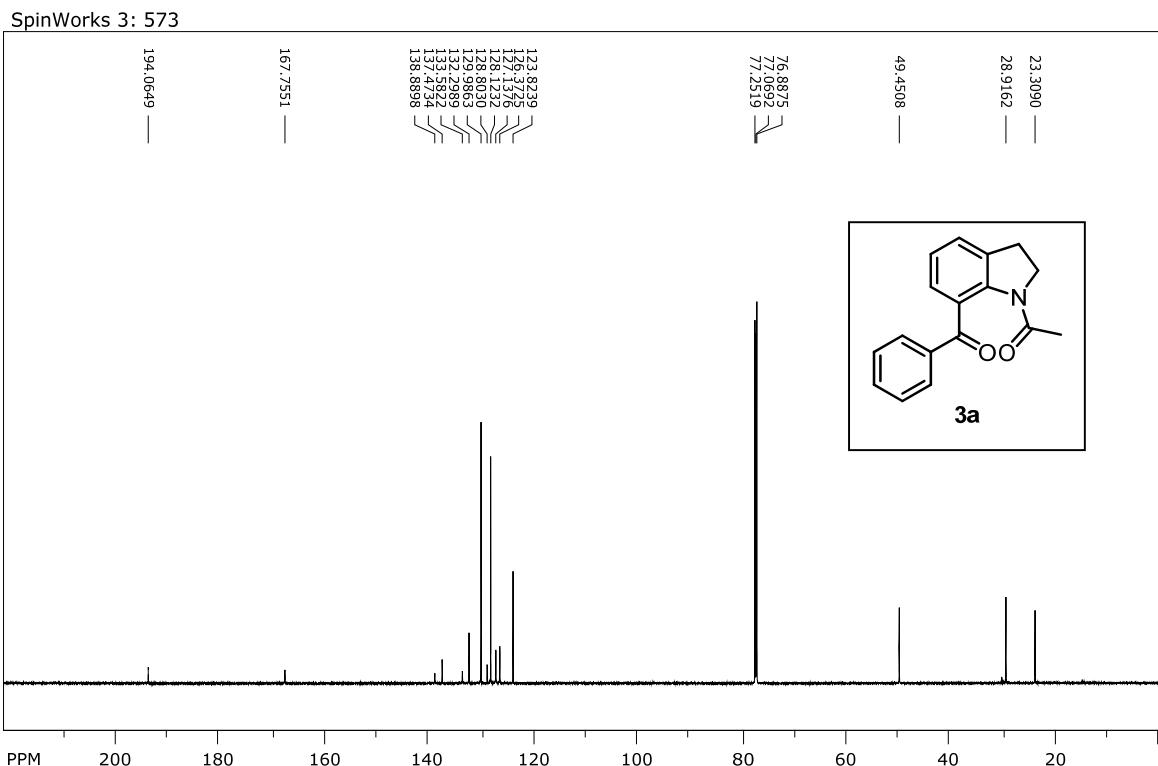
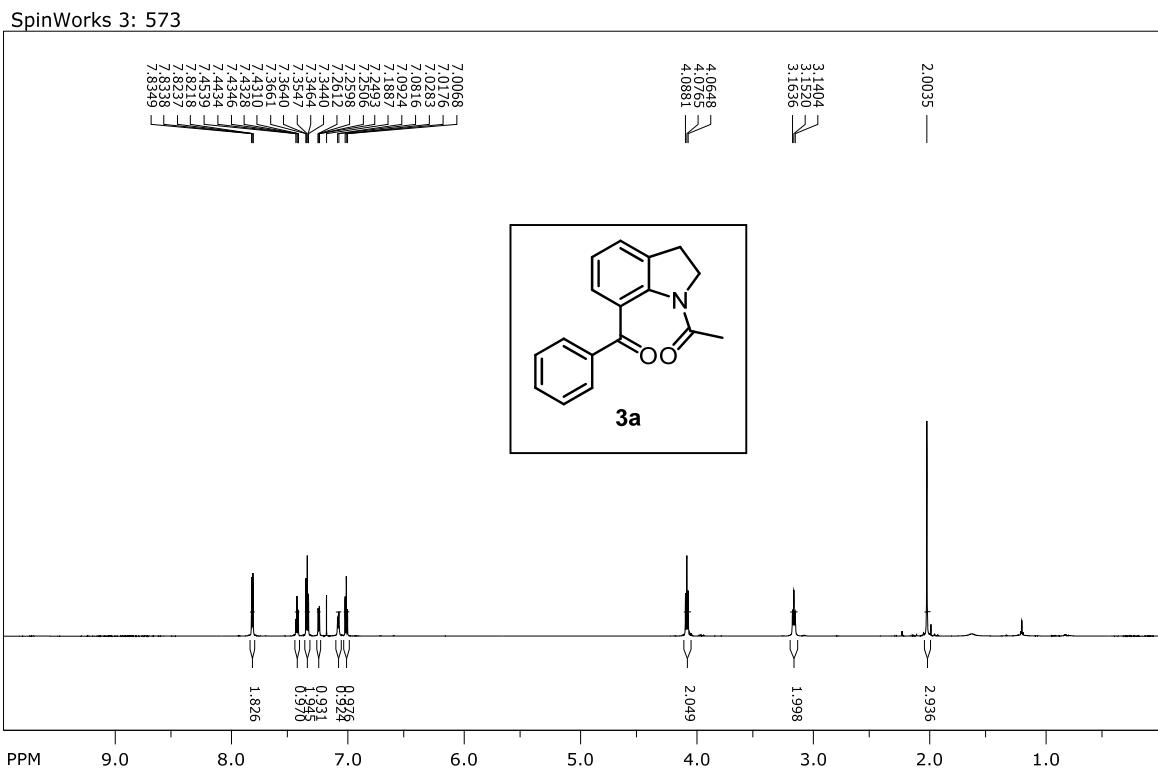
SpinWorks 3: 6F



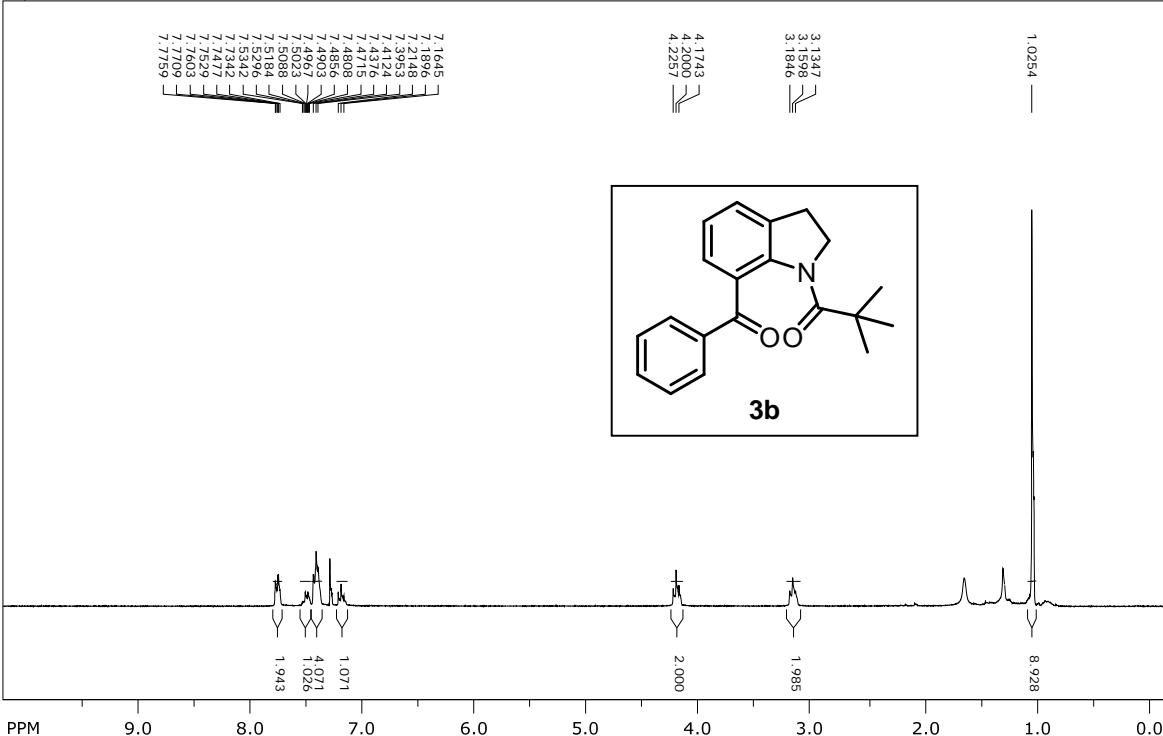
SpinWorks 3: 6F



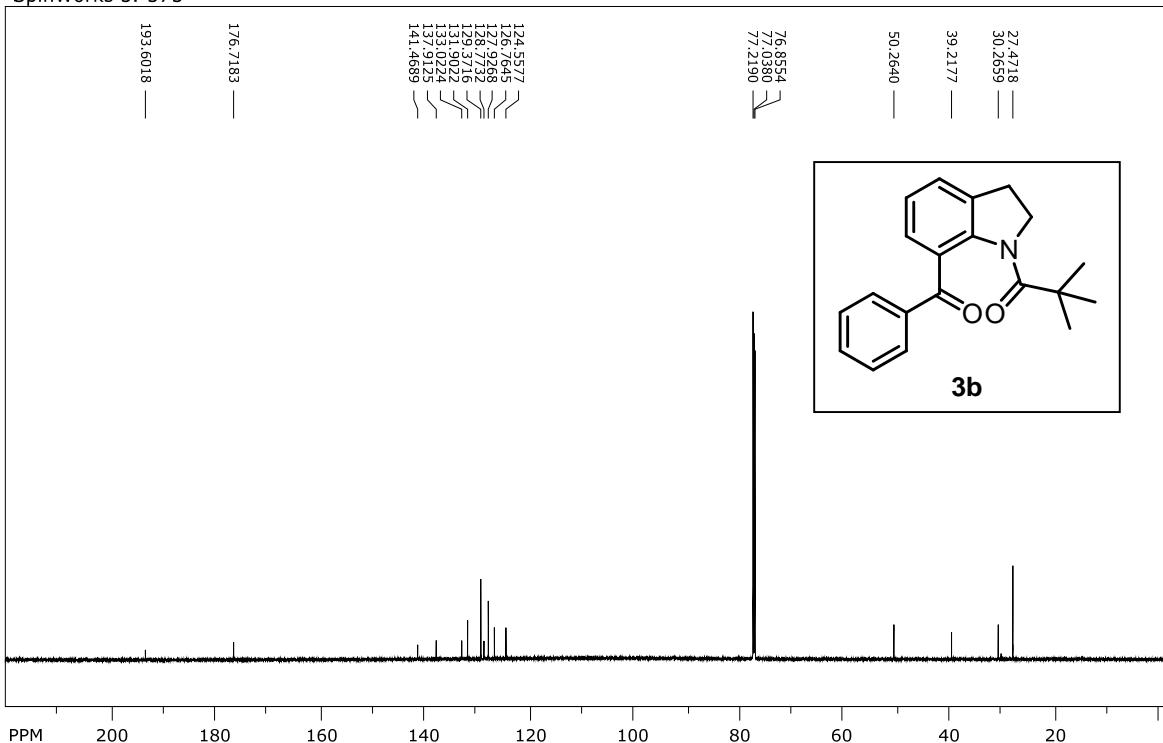




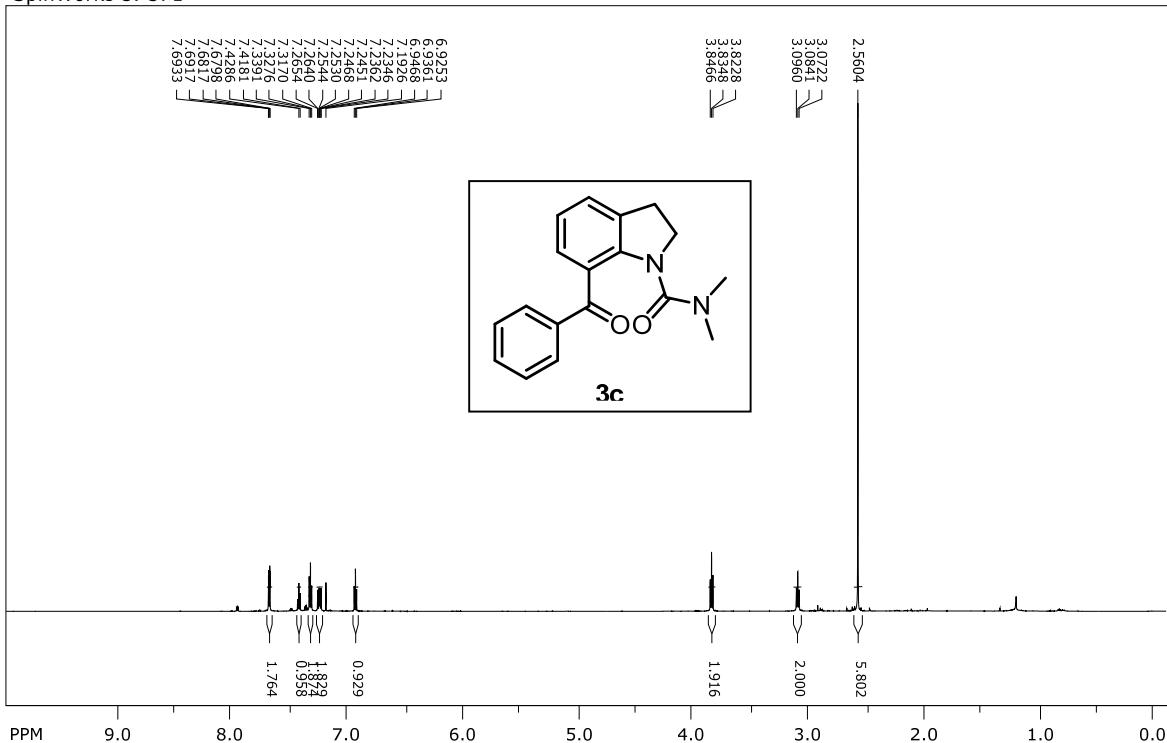
SpinWorks 3: MY575



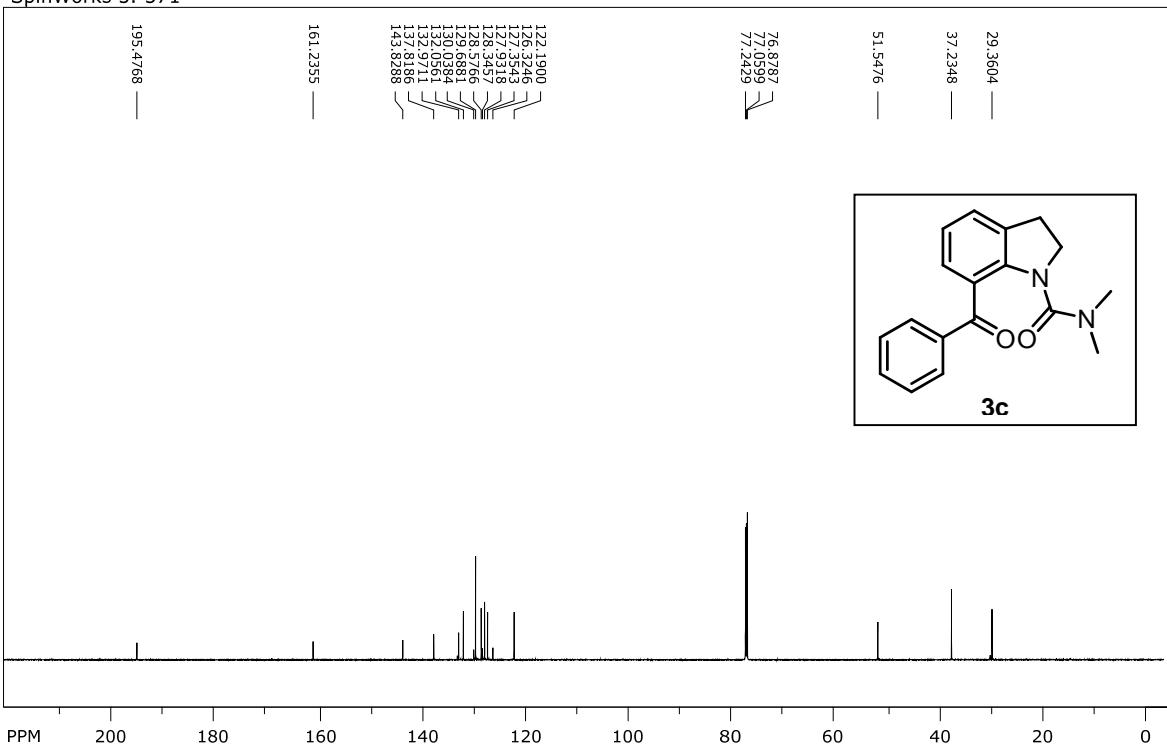
SpinWorks 3: 575



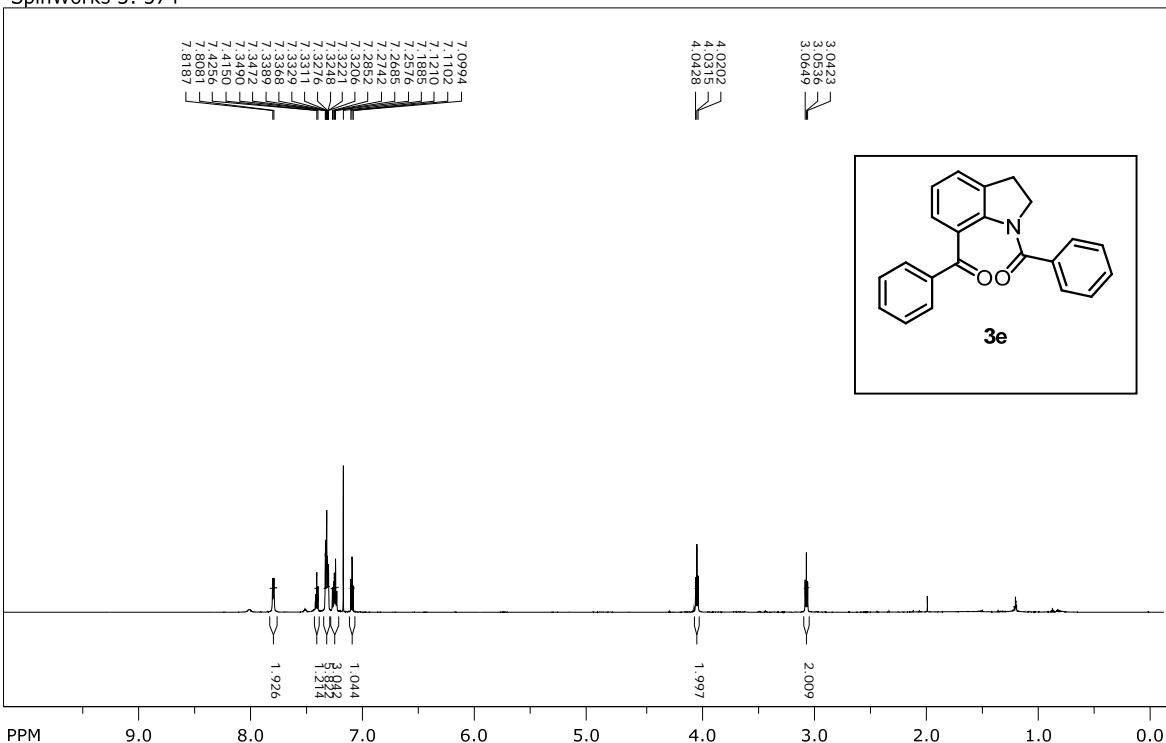
SpinWorks 3: 571



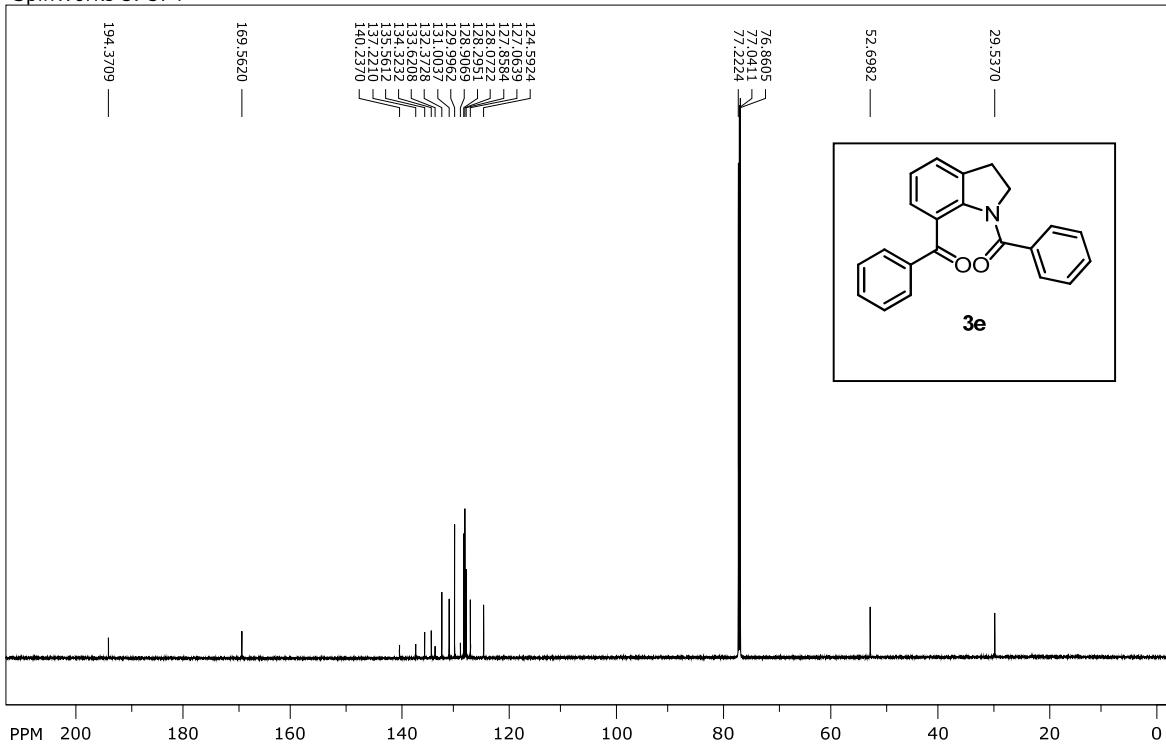
SpinWorks 3: 571



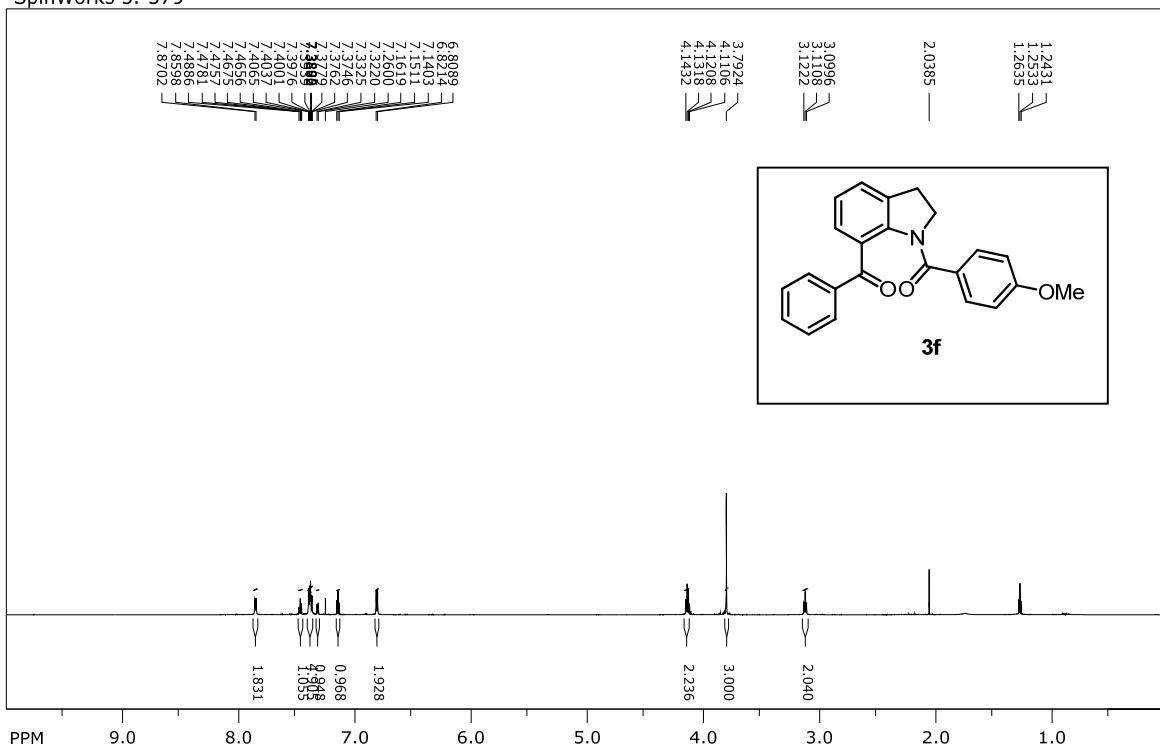
SpinWorks 3: 574



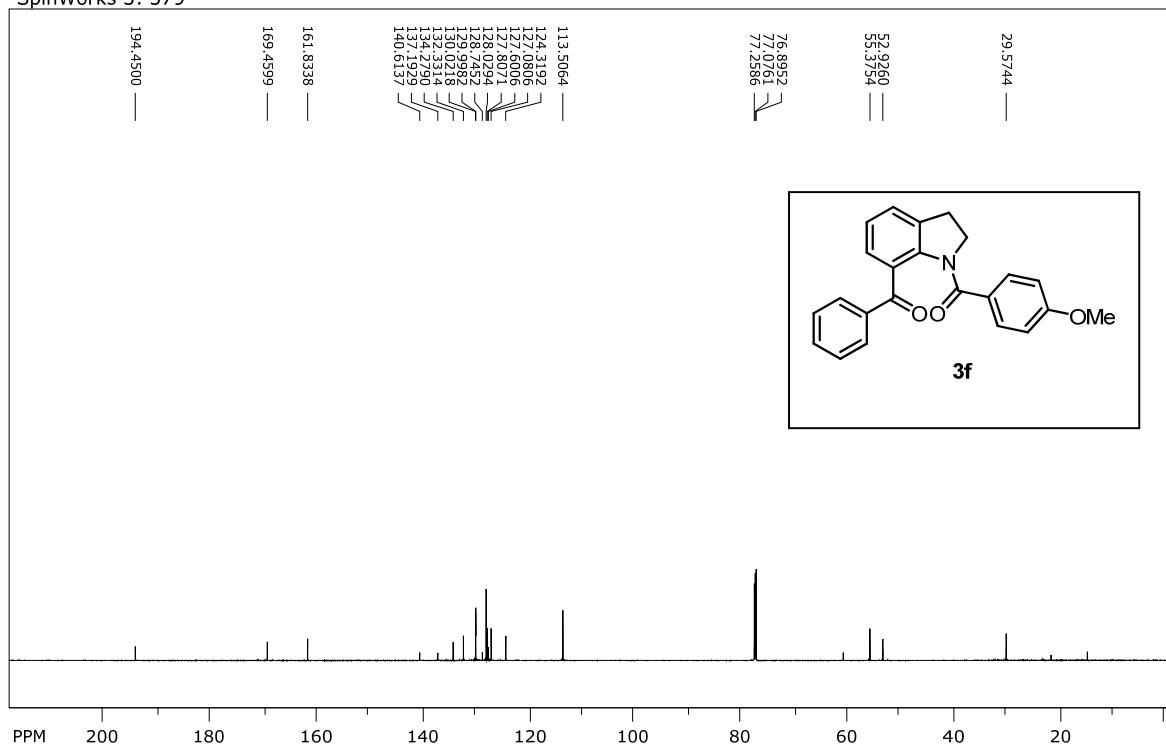
SpinWorks 3: 574



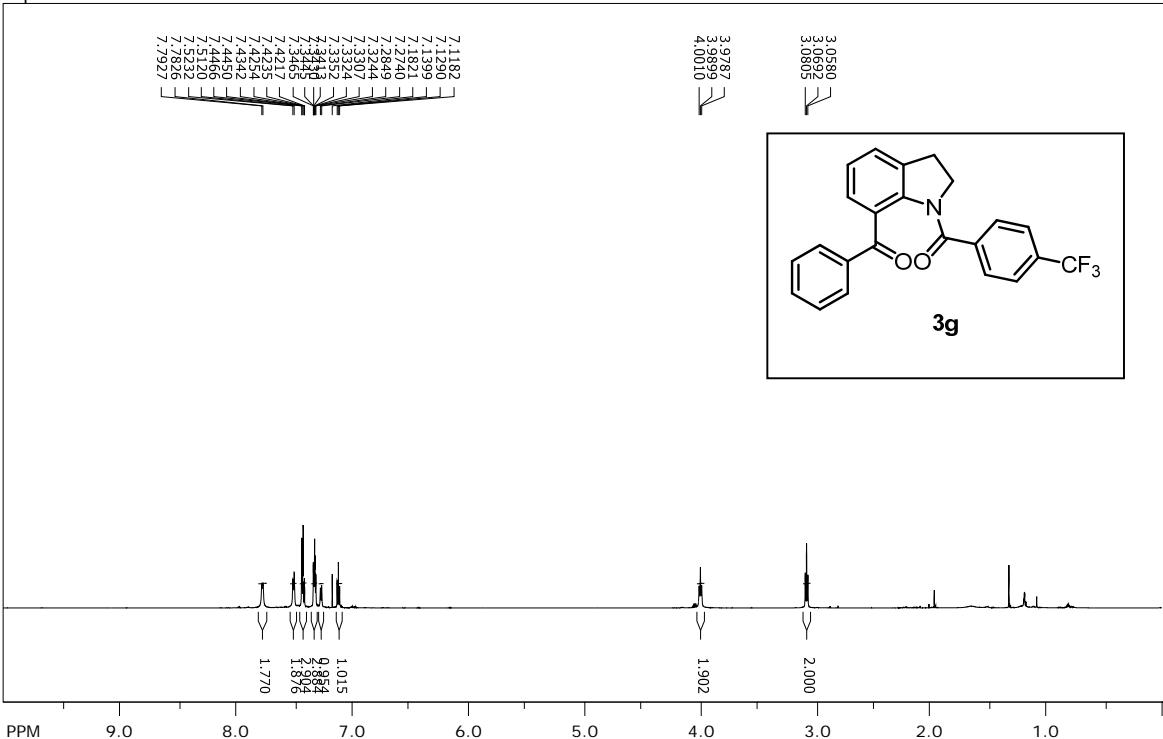
SpinWorks 3: 579



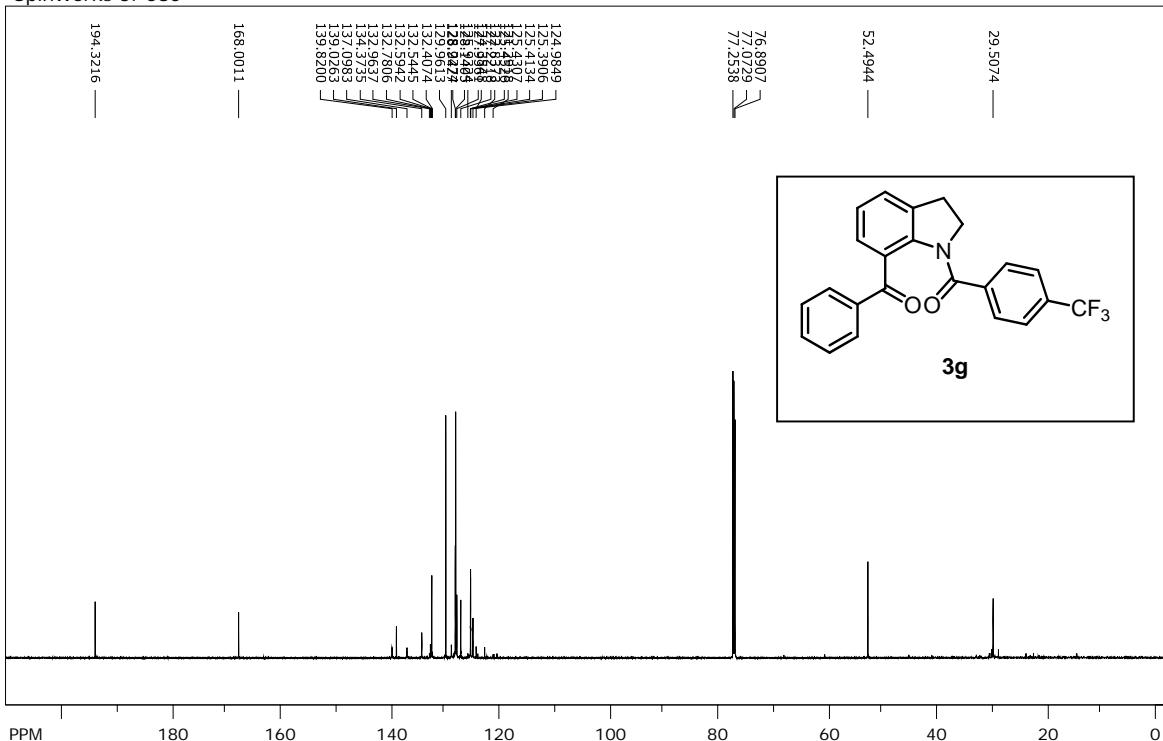
SpinWorks 3: 579



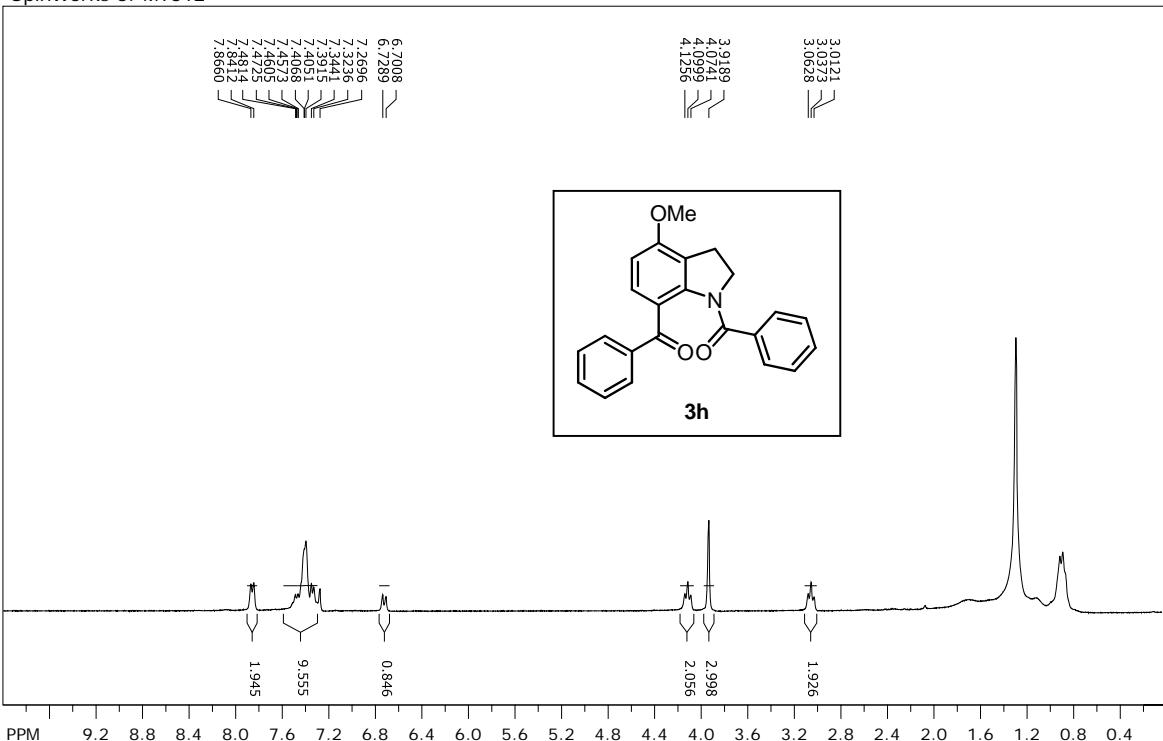
SpinWorks 3: 580



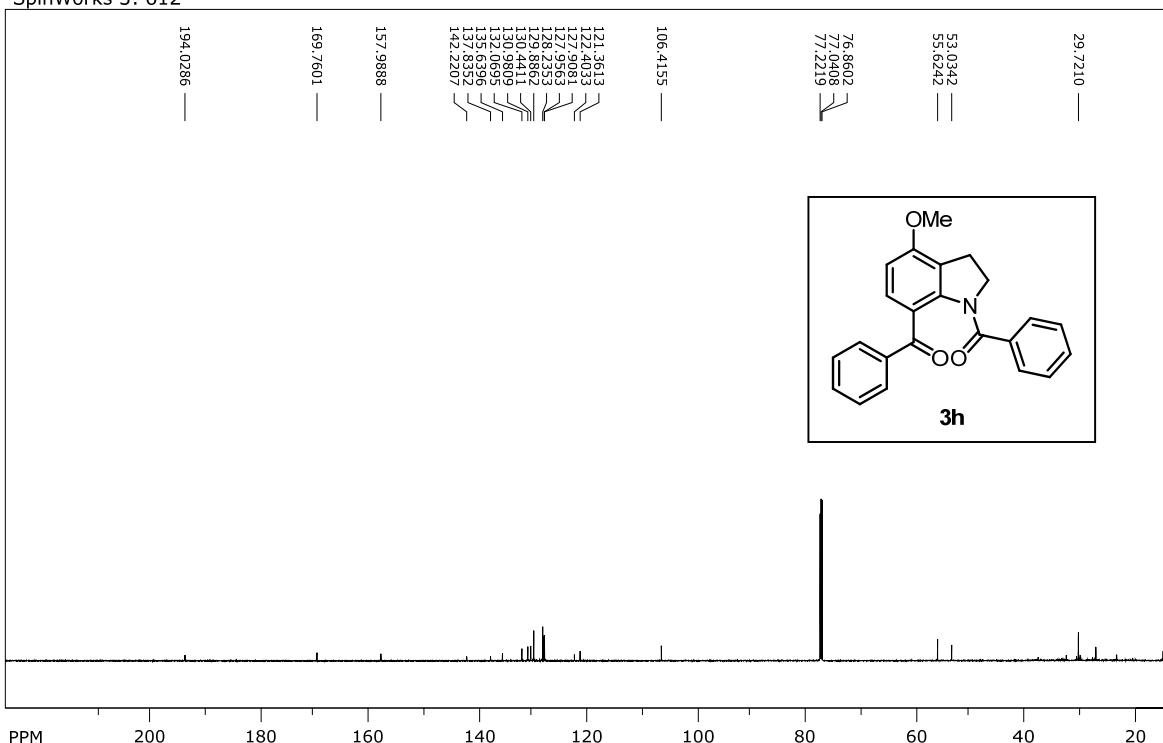
SpinWorks 3: 580



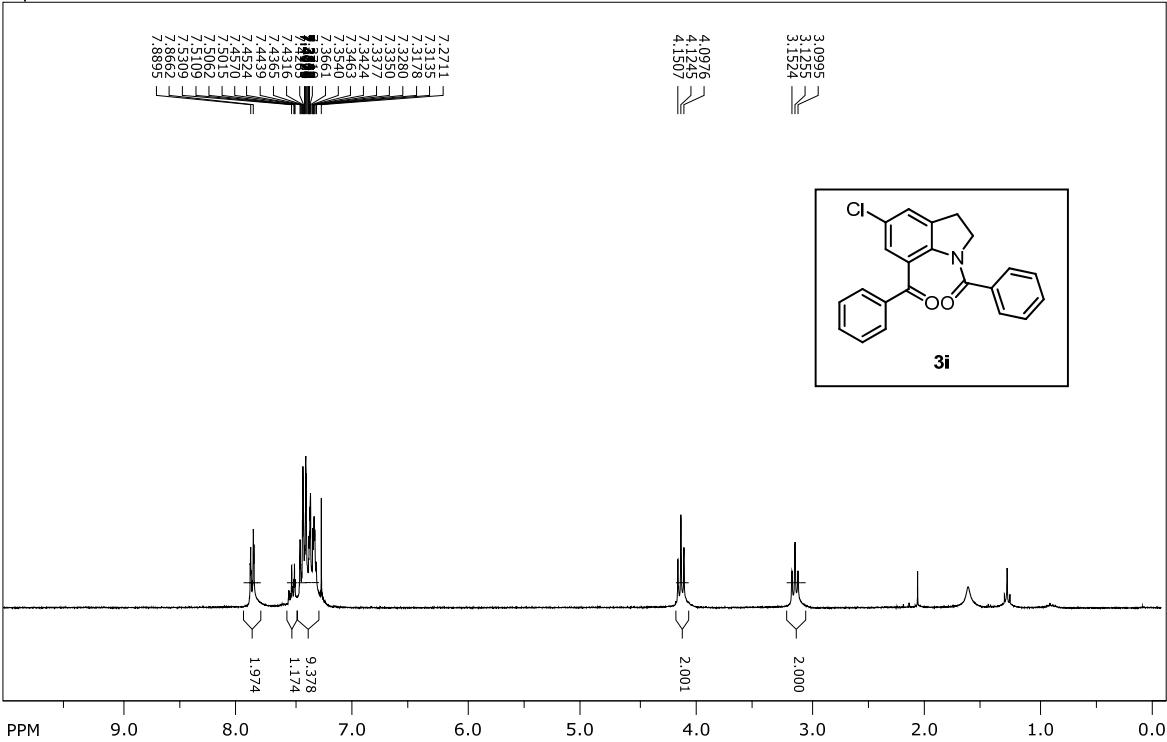
SpinWorks 3: MY612



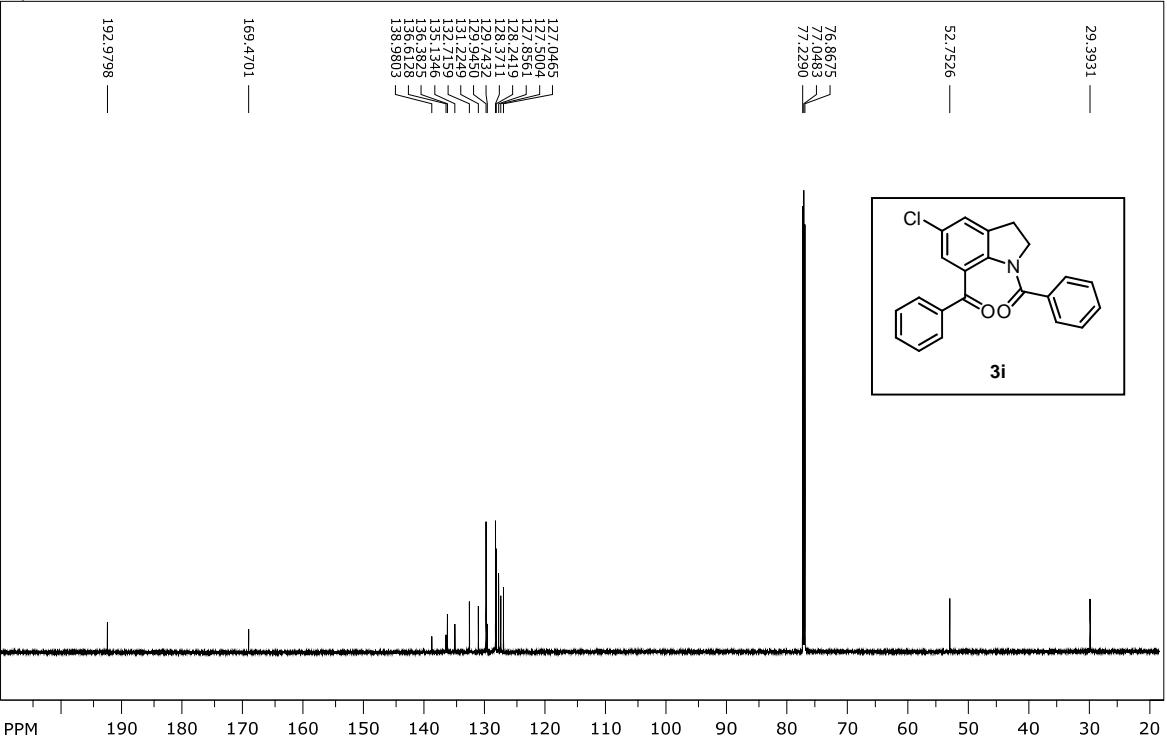
SpinWorks 3: 612



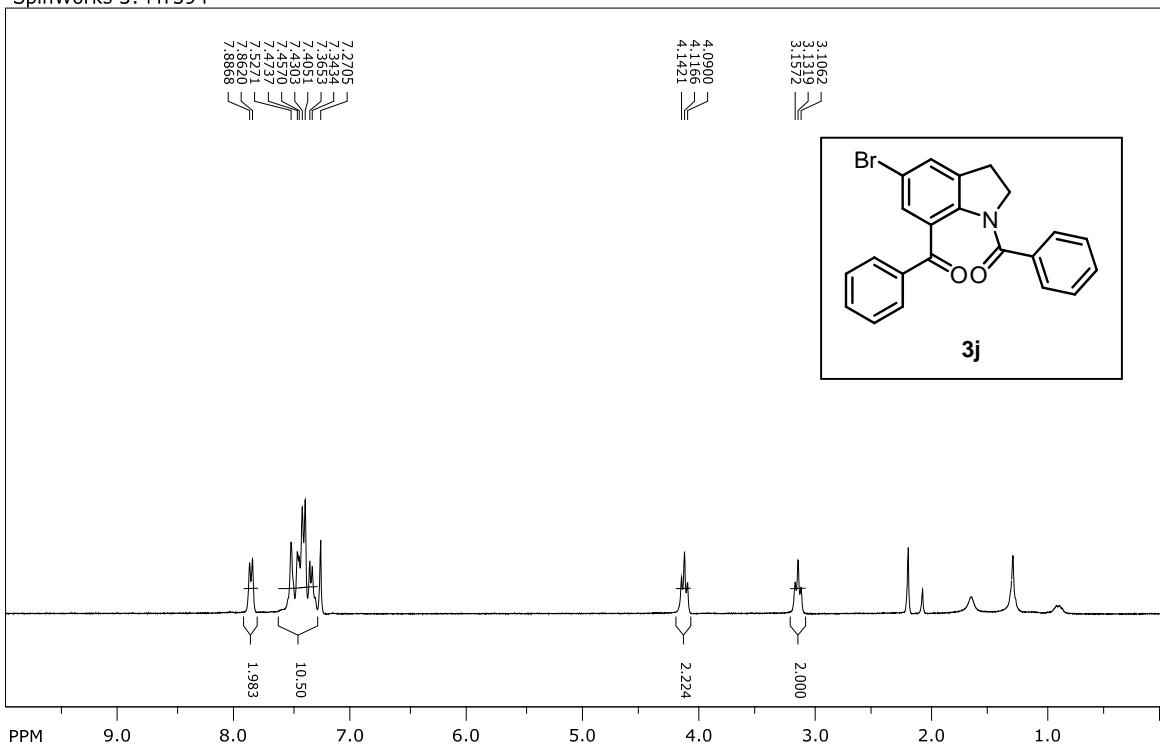
SpinWorks 3: MY601



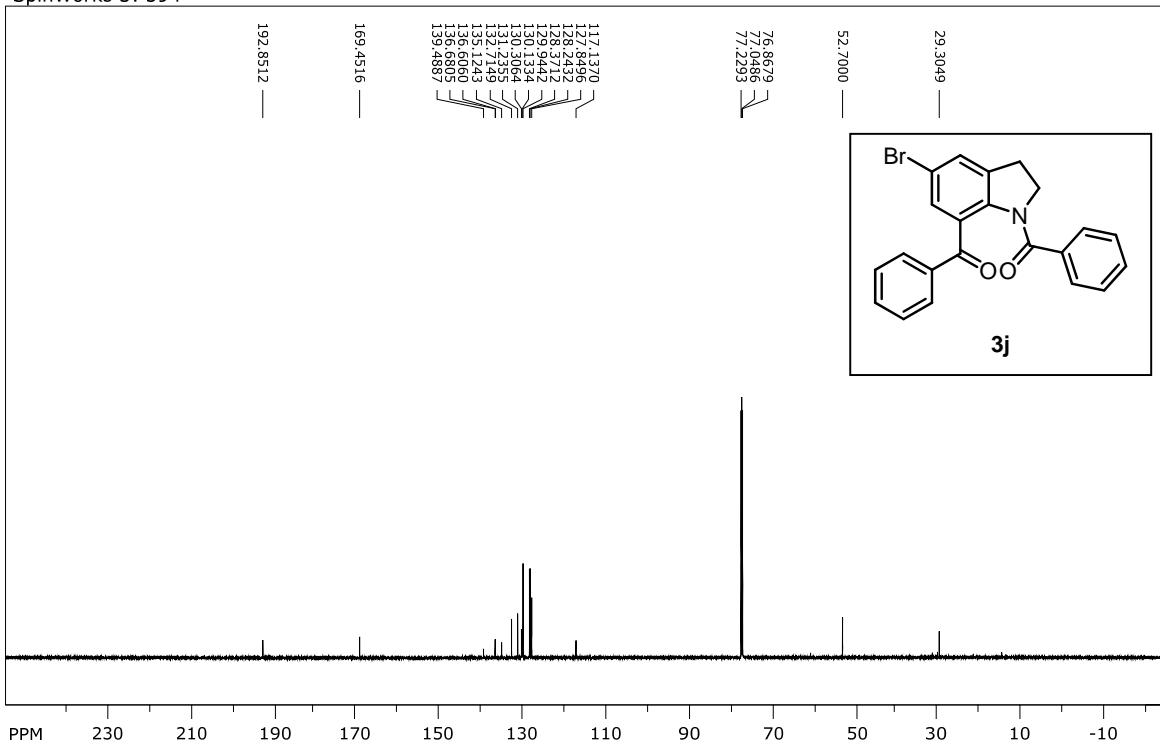
SpinWorks 3: 601



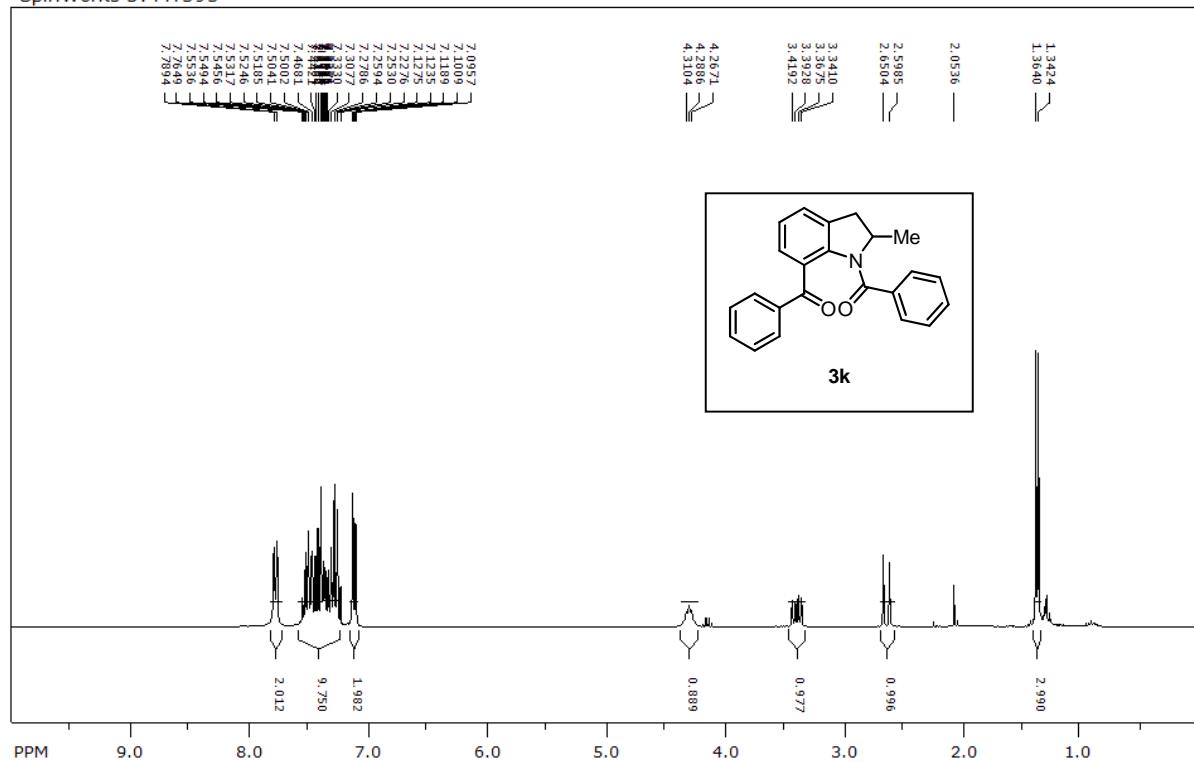
SpinWorks 3: MY594



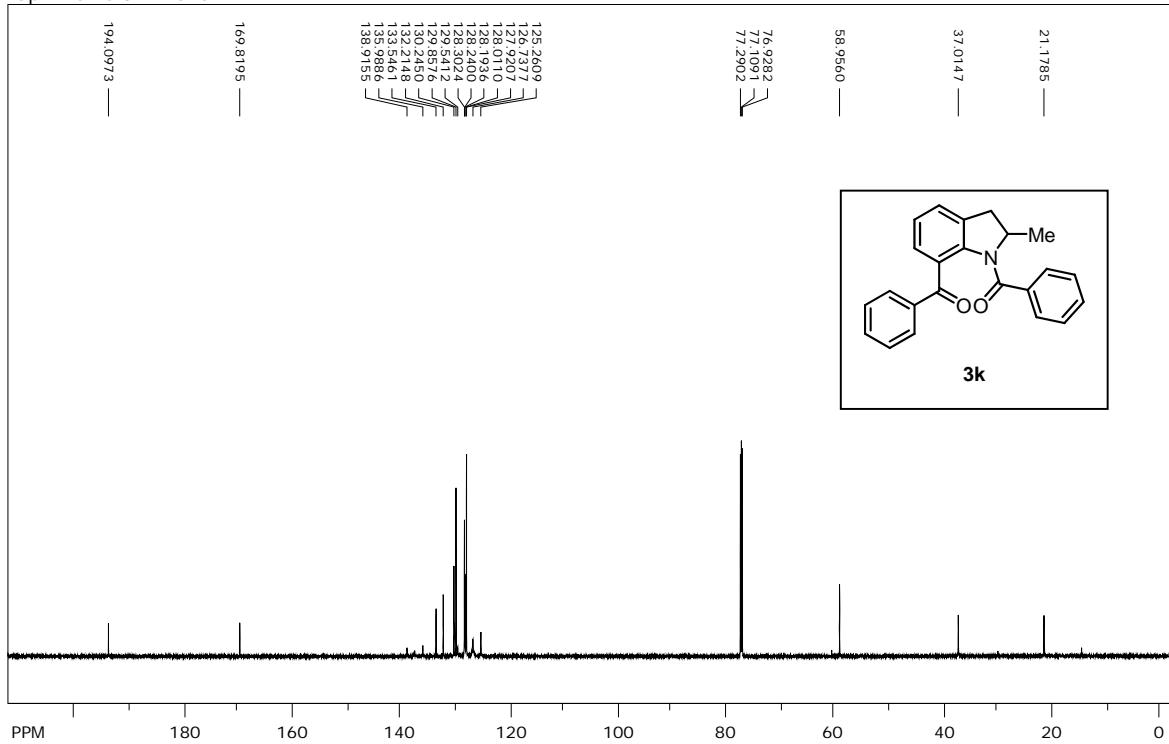
SpinWorks 3: 594



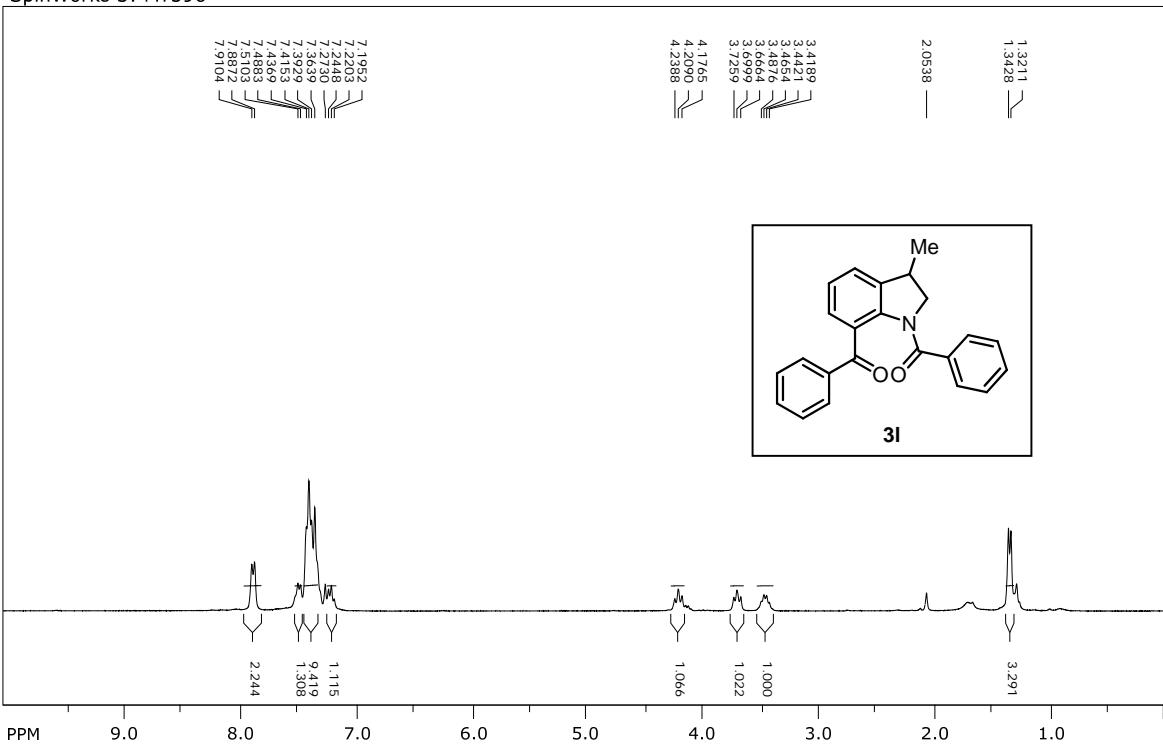
SpinWorks 3: MY595



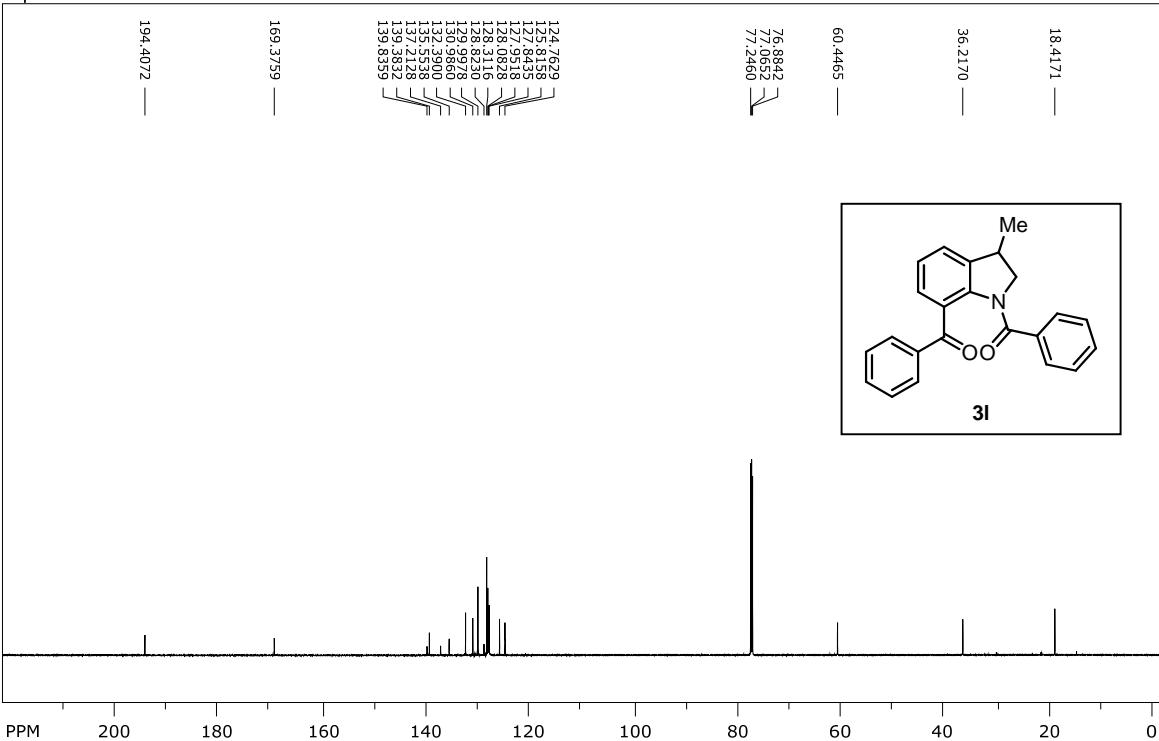
SpinWorks 3: YM595



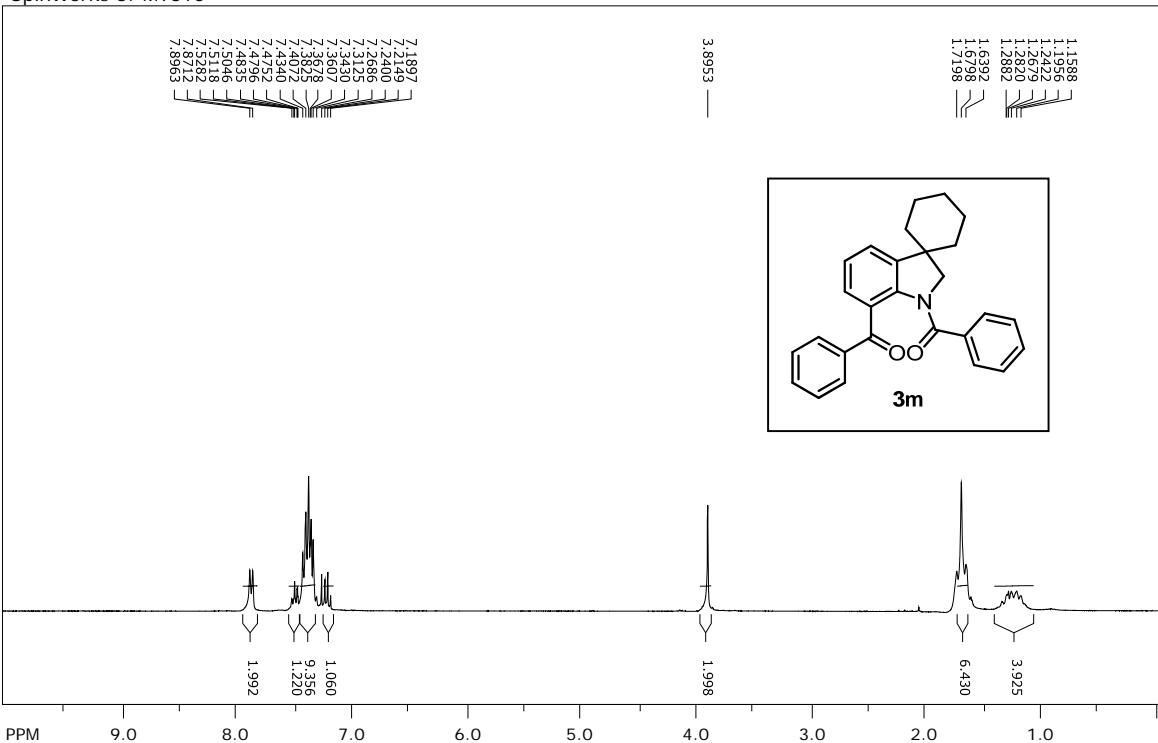
SpinWorks 3: MY596



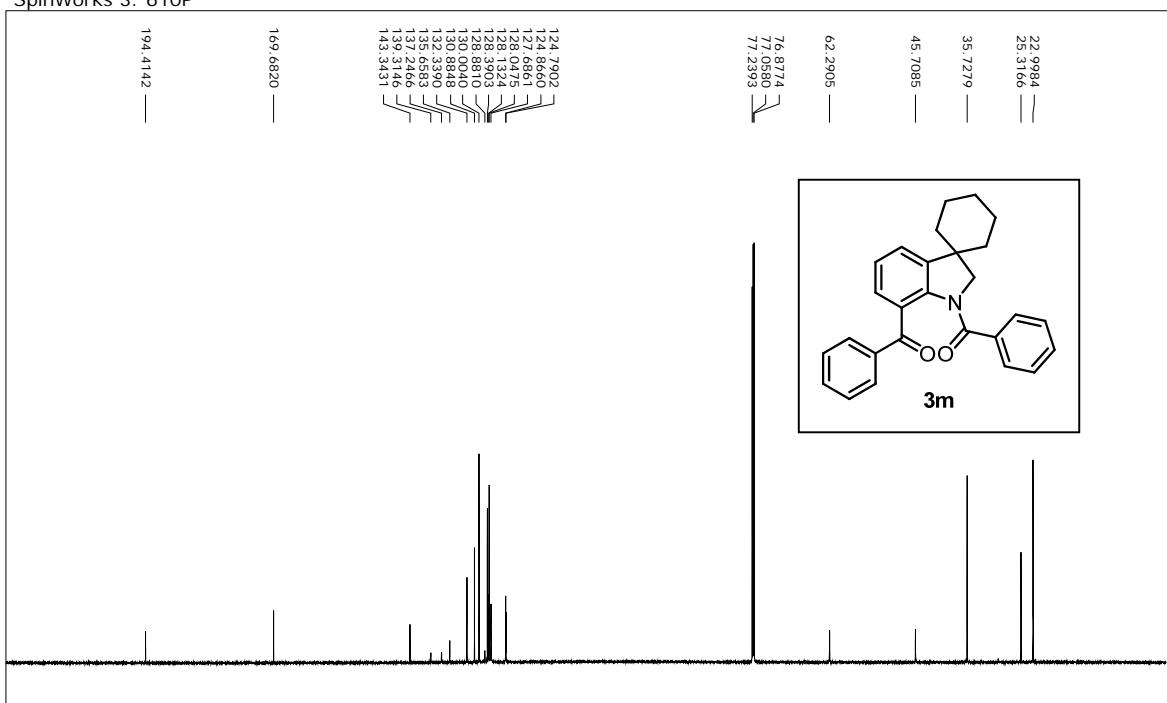
SpinWorks 3: 596



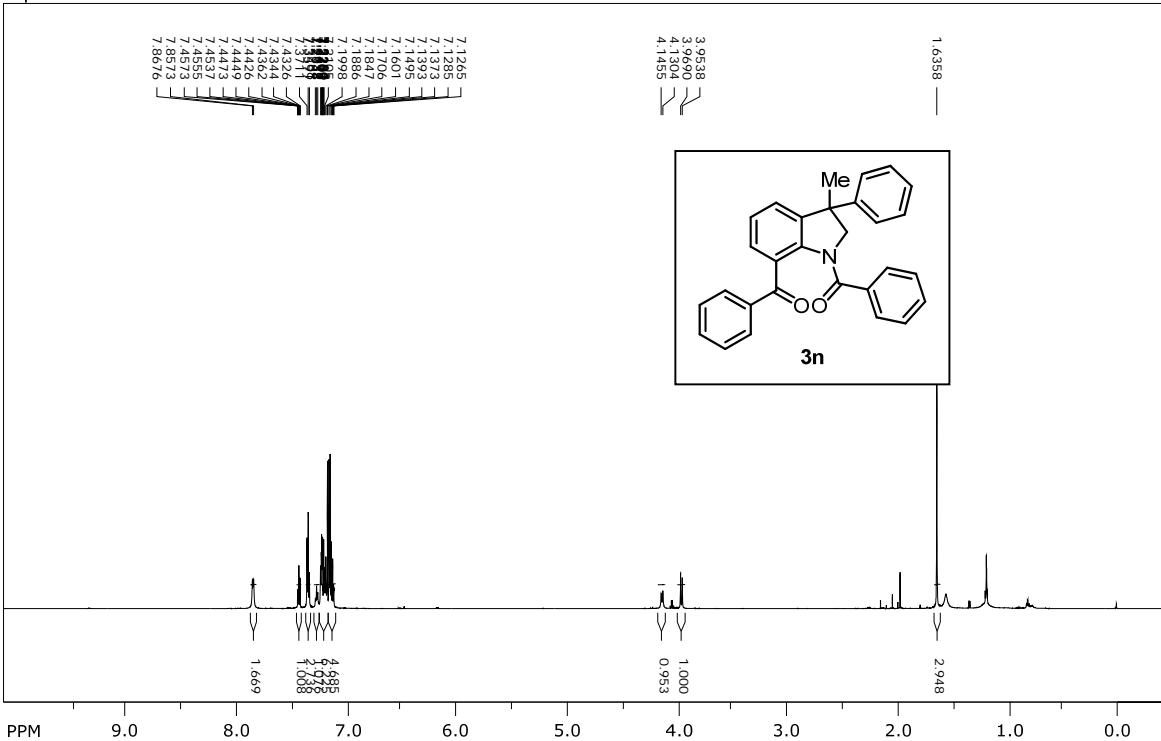
SpinWorks 3: MY610



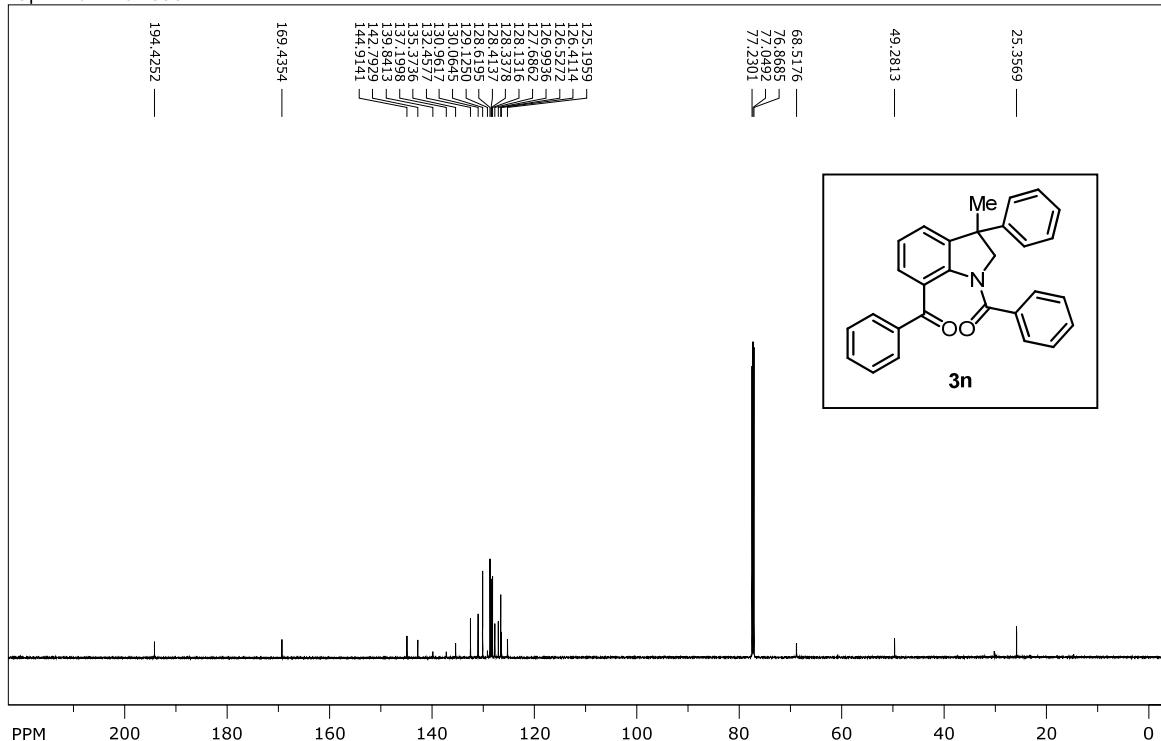
SpinWorks 3: 610P



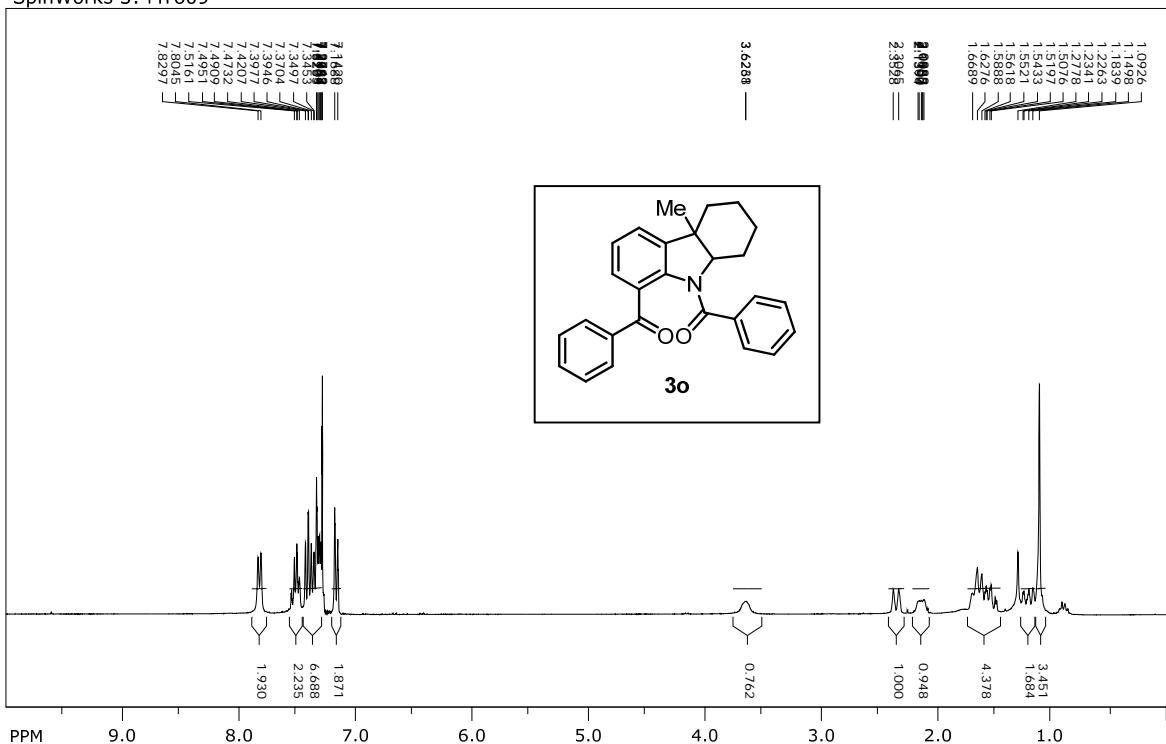
SpinWorks 3: 599



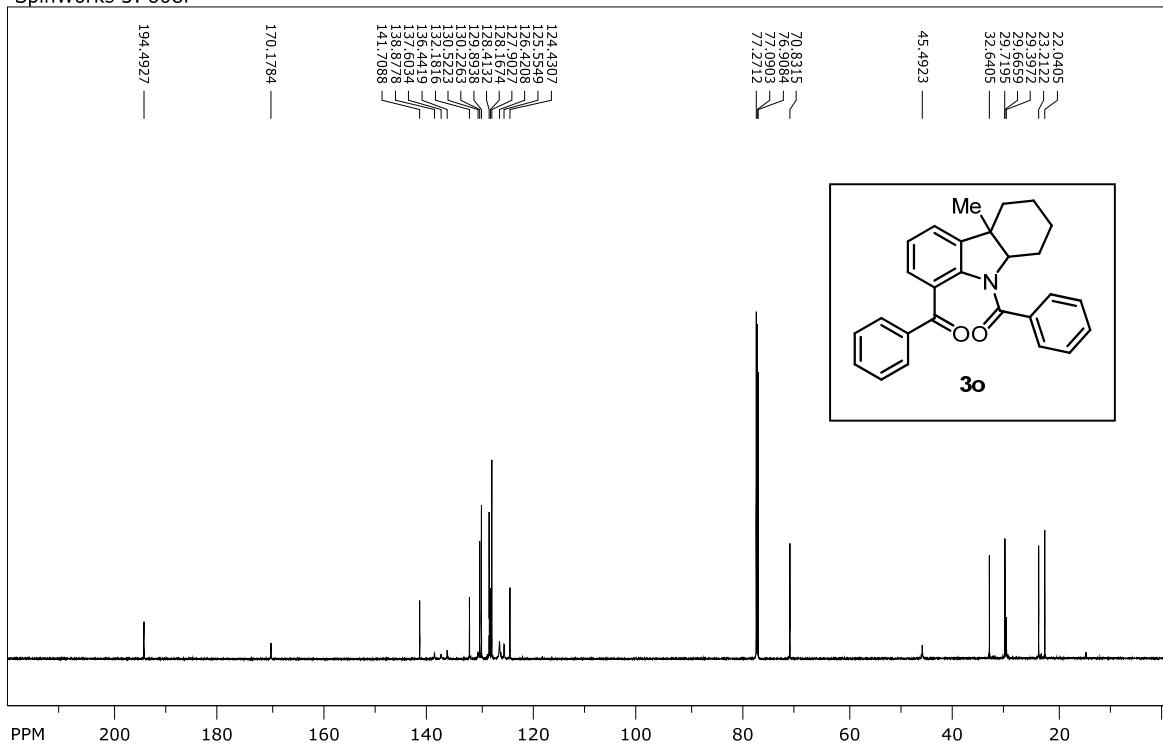
SpinWorks 3: 599



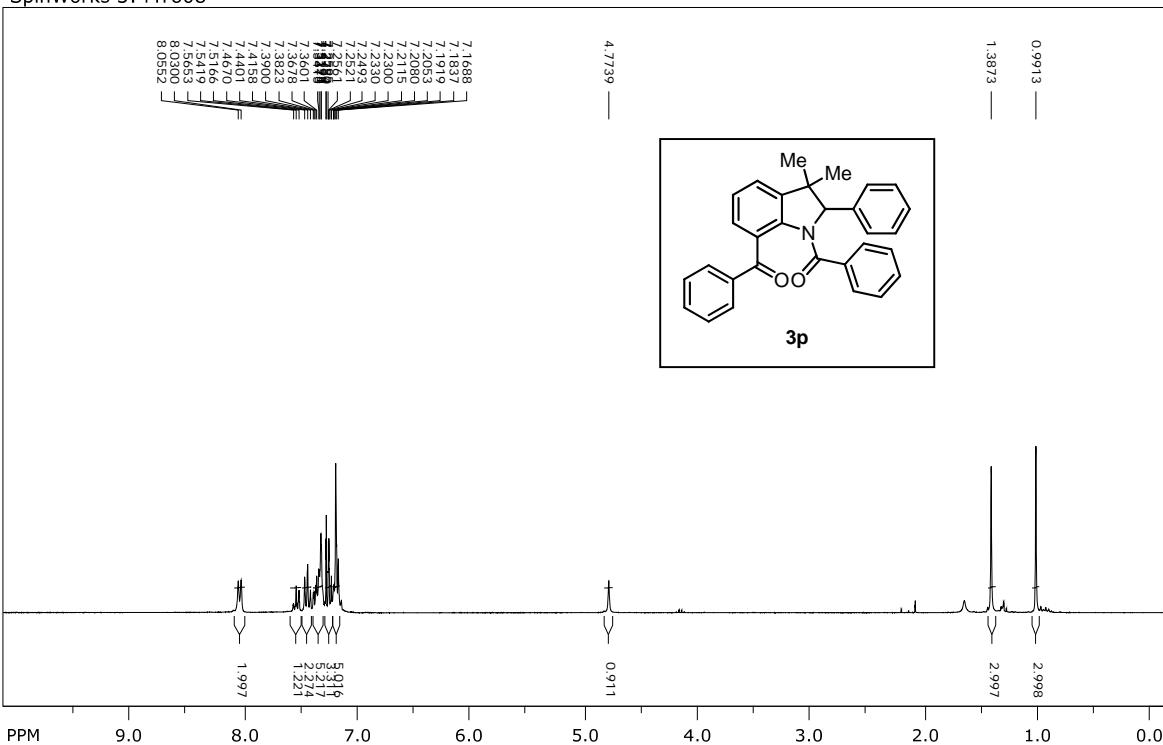
SpinWorks 3: MY609



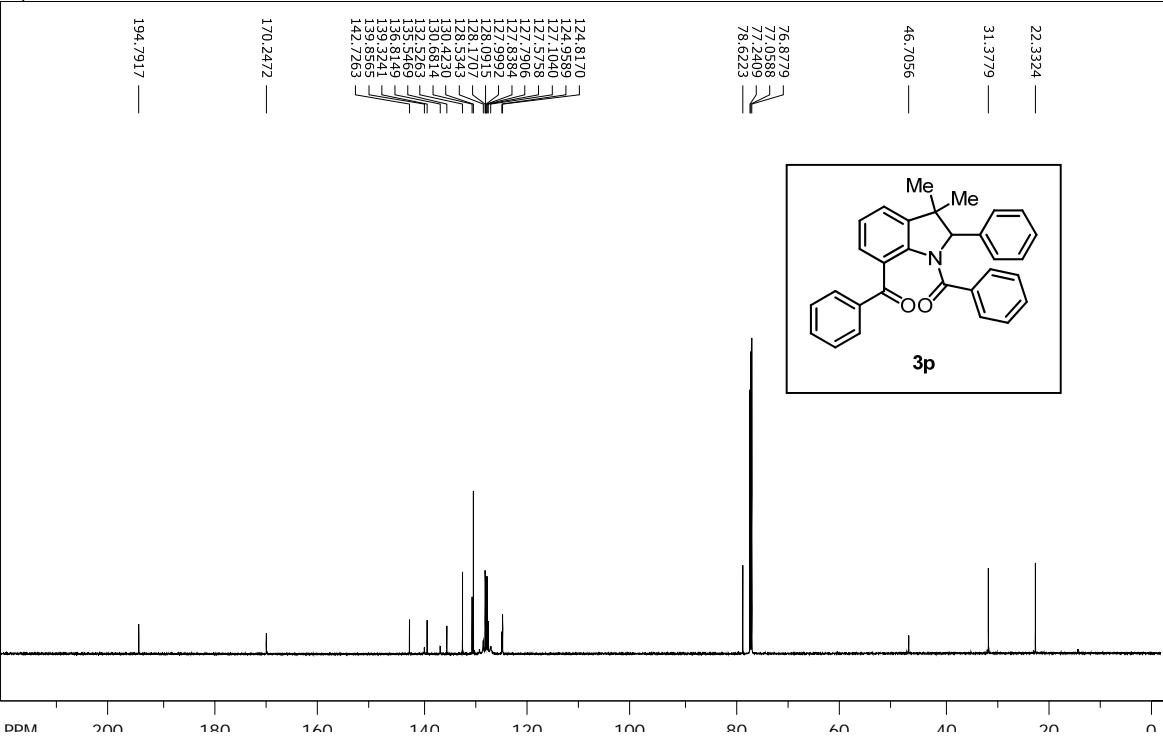
SpinWorks 3: 608P



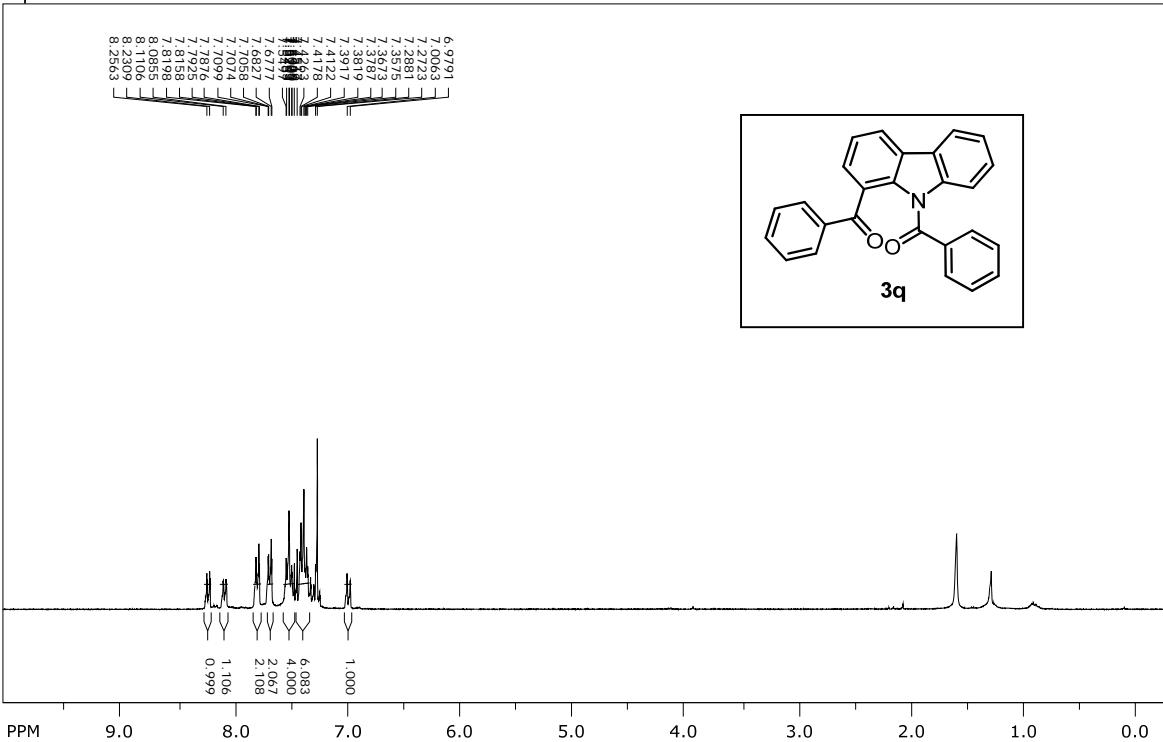
SpinWorks 3: MY608



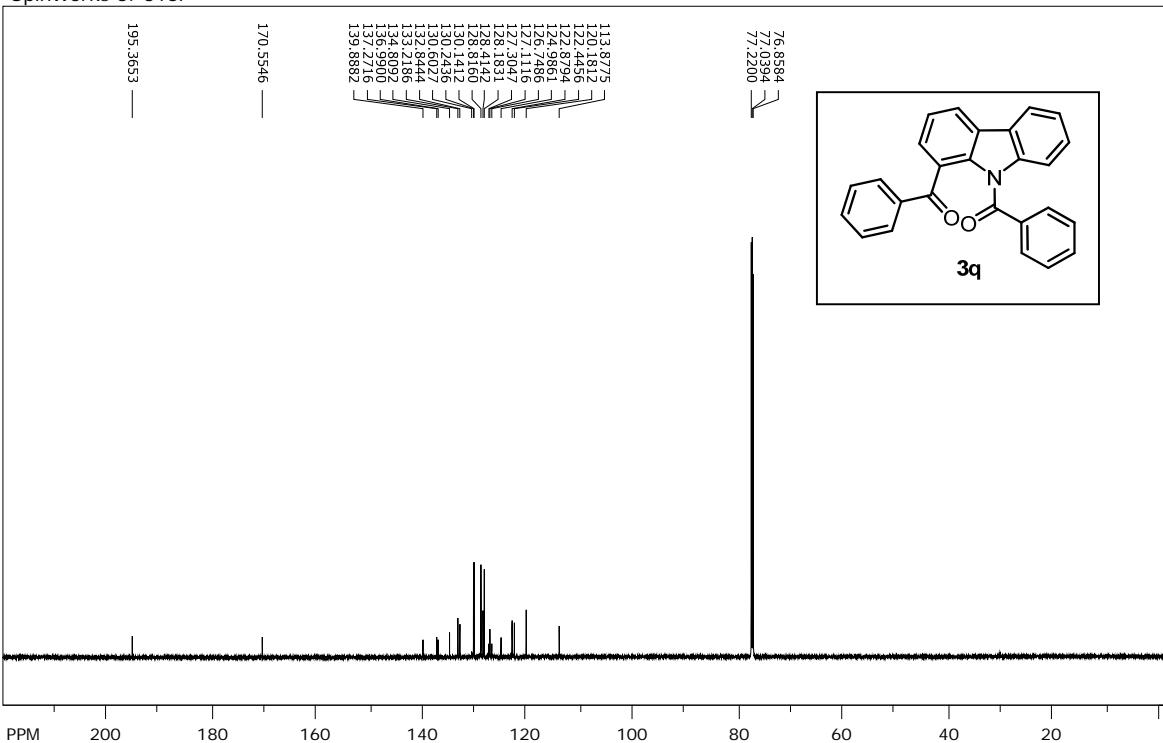
SpinWorks 3: 609P



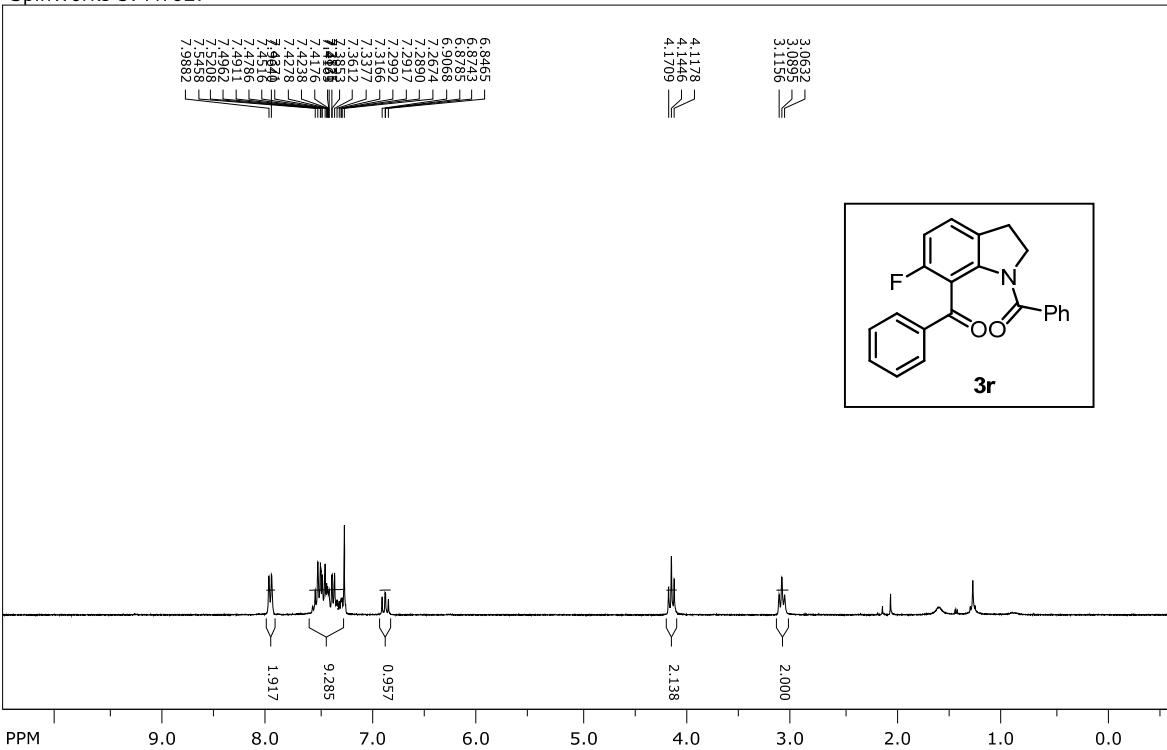
SpinWorks 3: MY616



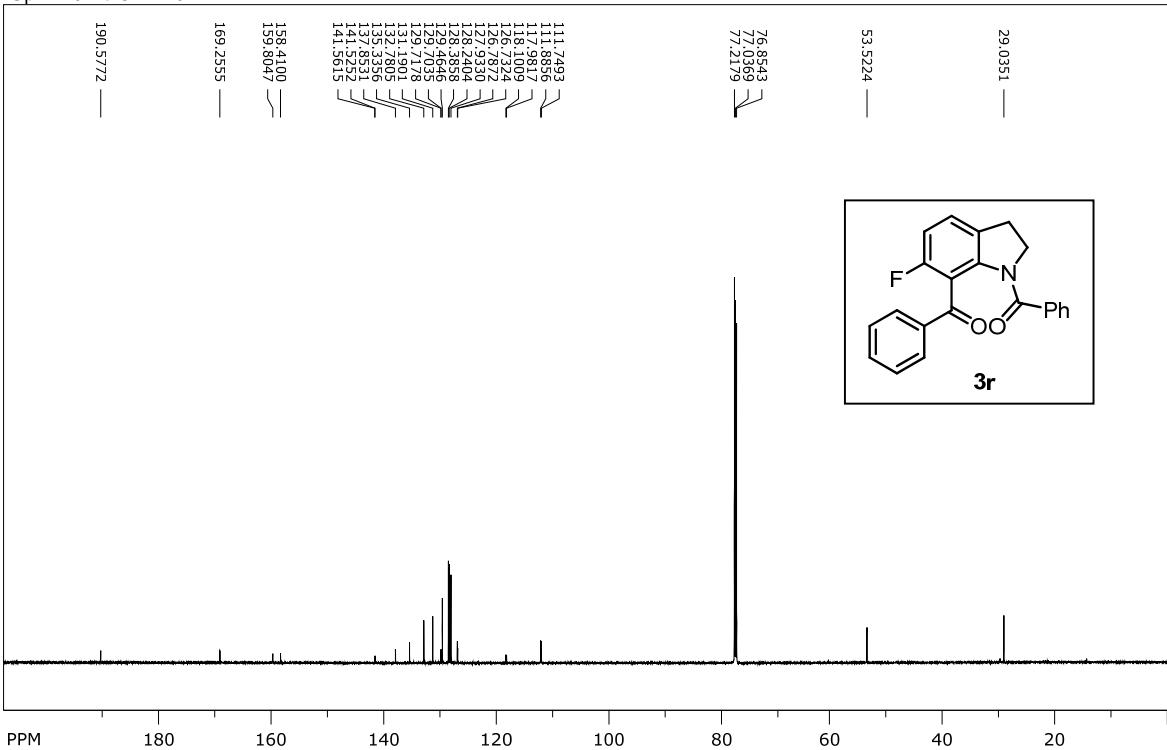
SpinWorks 3: 616P



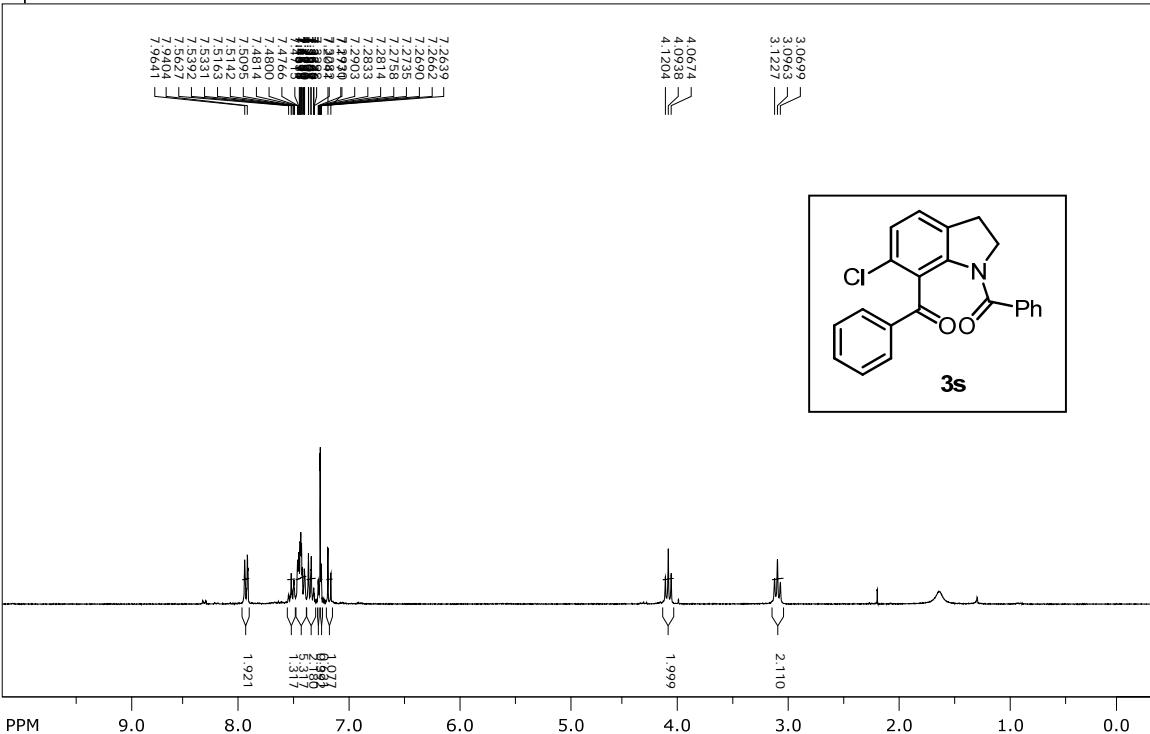
SpinWorks 3: MY627



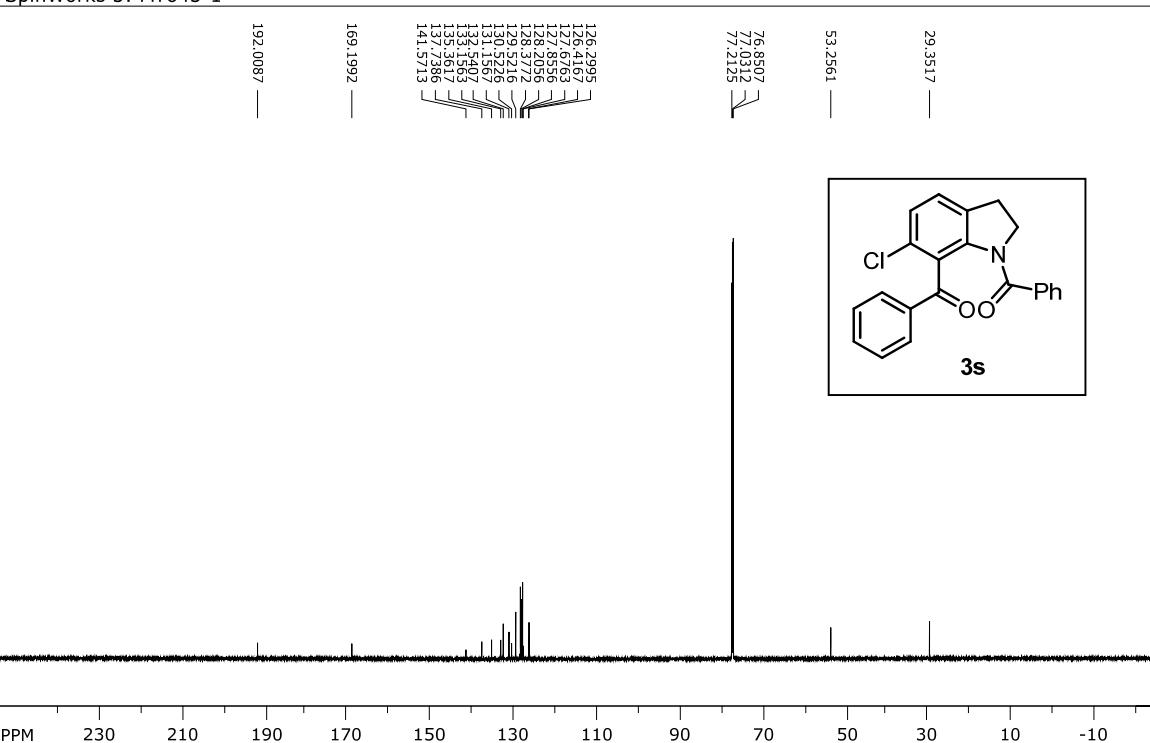
SpinWorks 3: MY627P



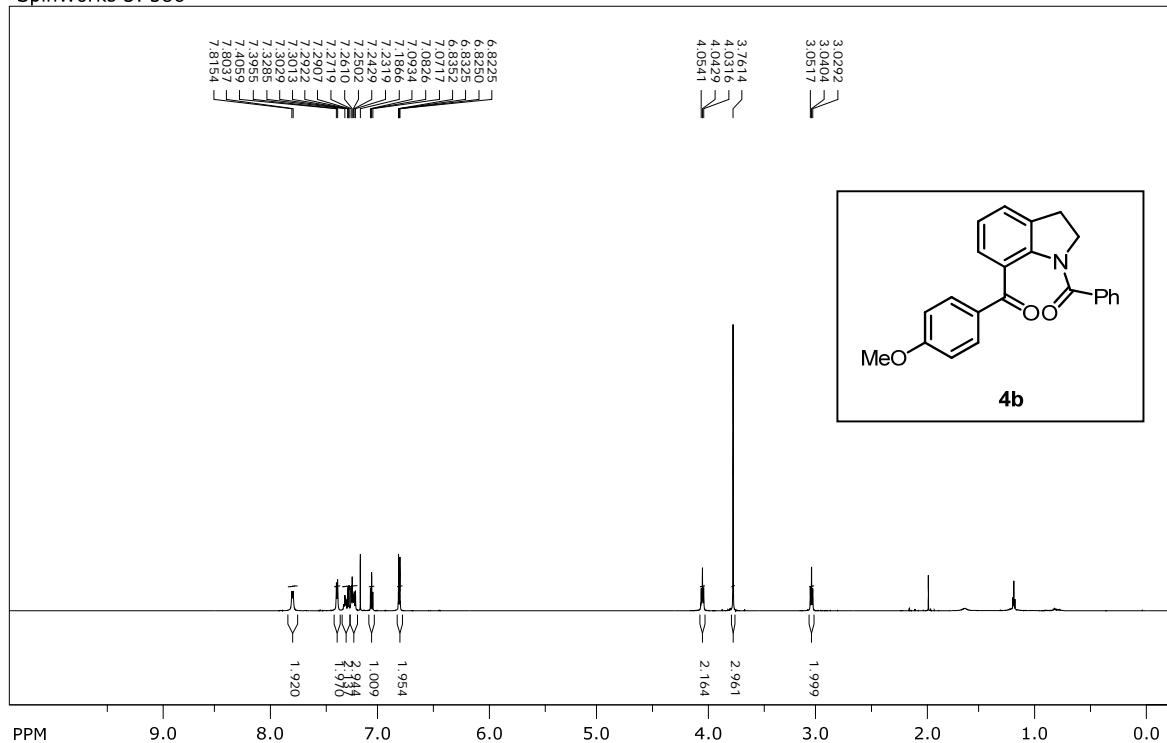
SpinWorks 3: MY643-1



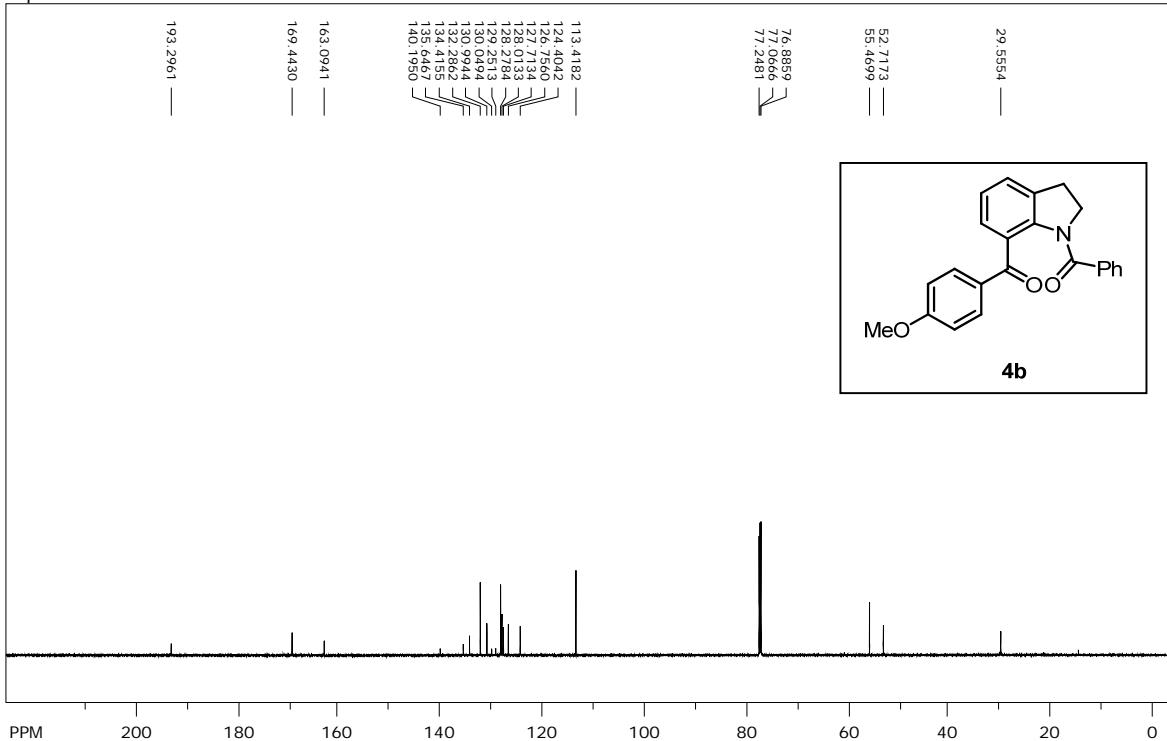
SpinWorks 3: MY643-1



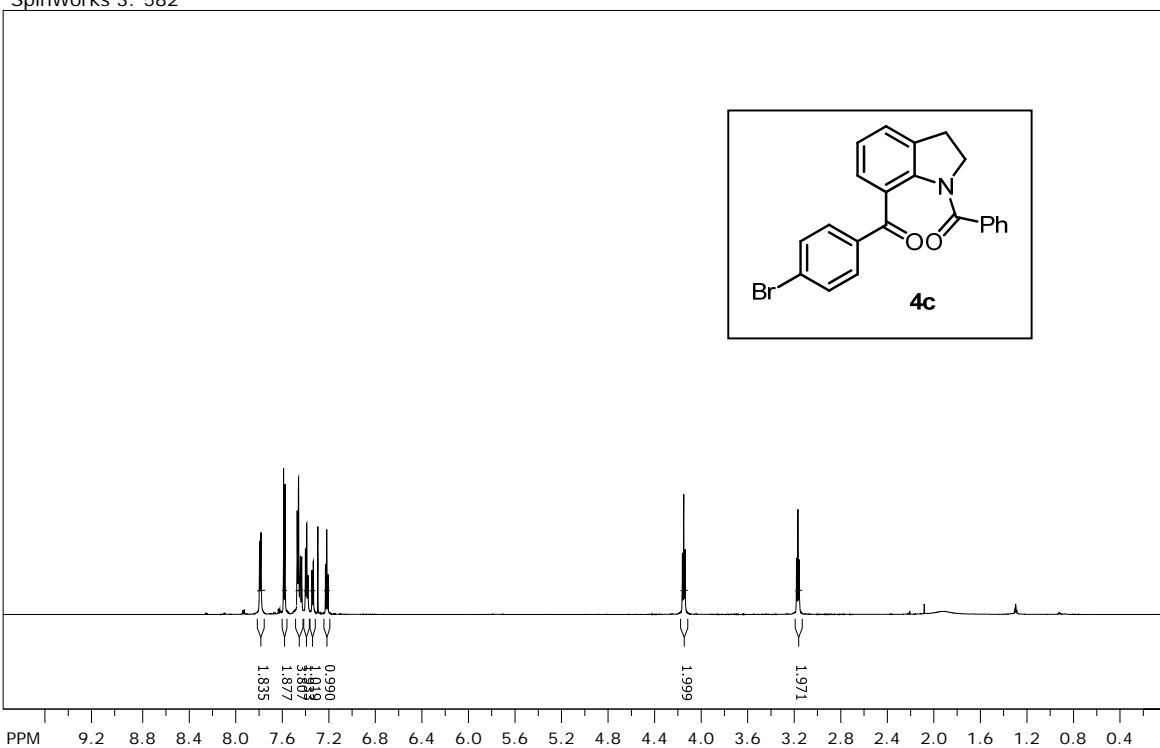
SpinWorks 3: 586



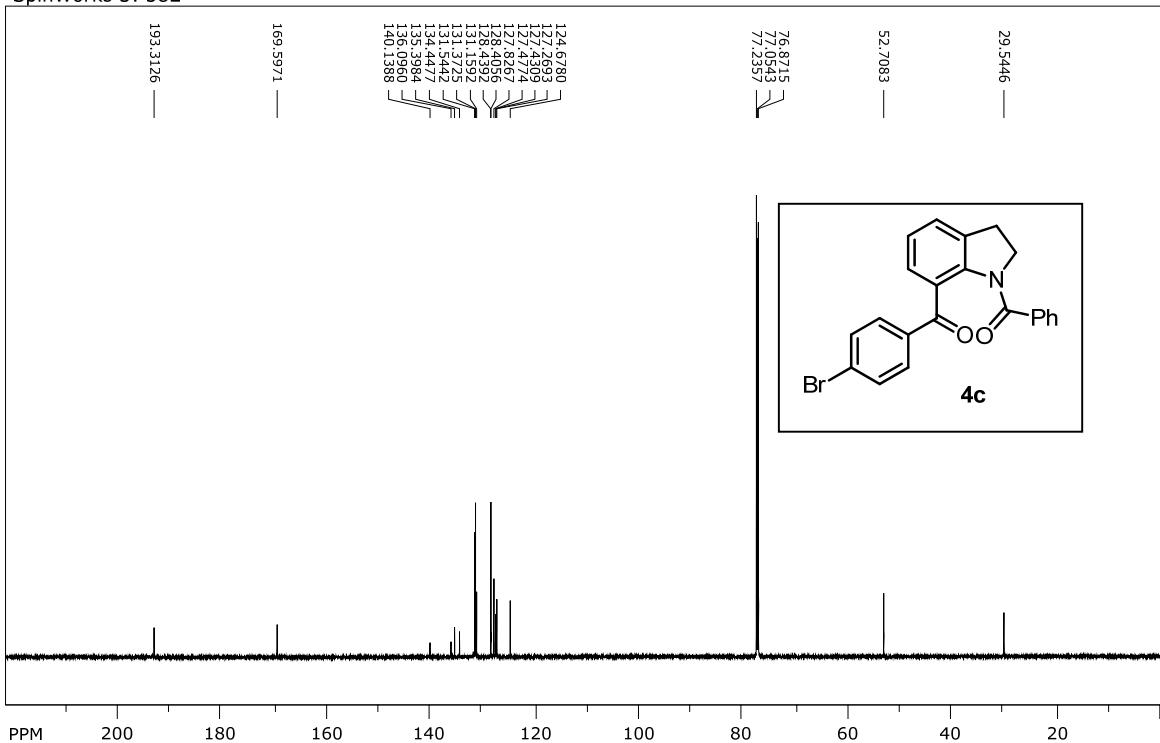
SpinWorks 3: 586



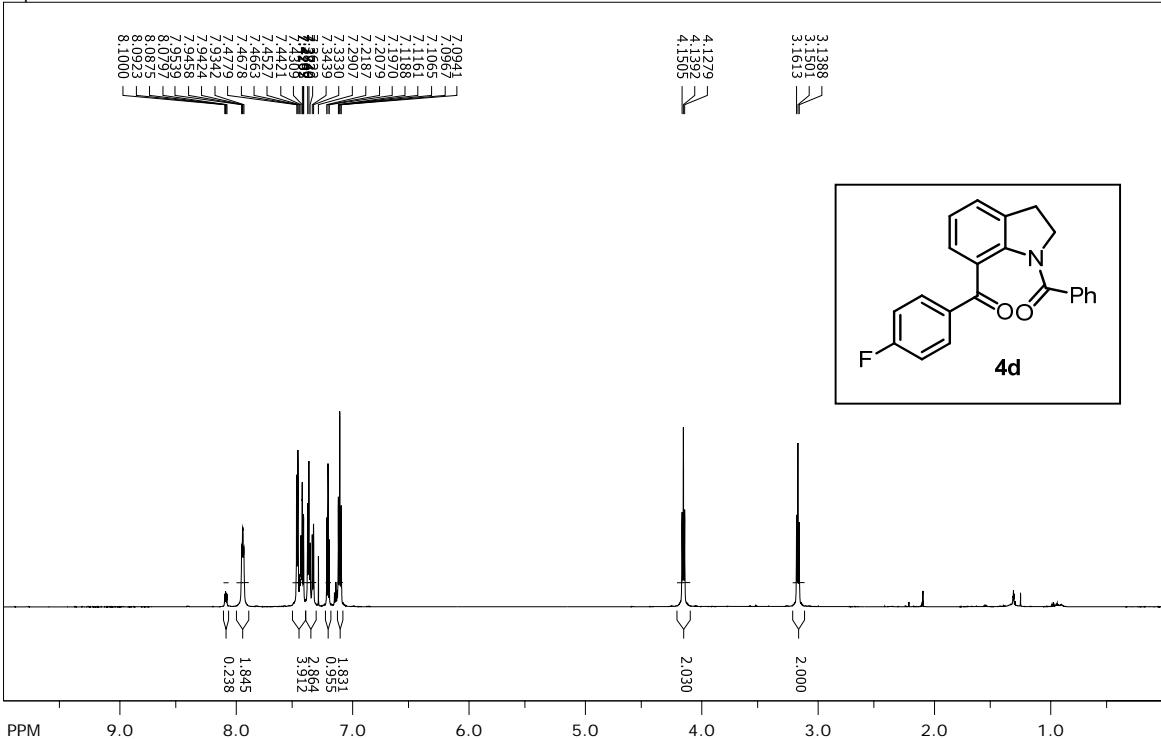
SpinWorks 3: 582



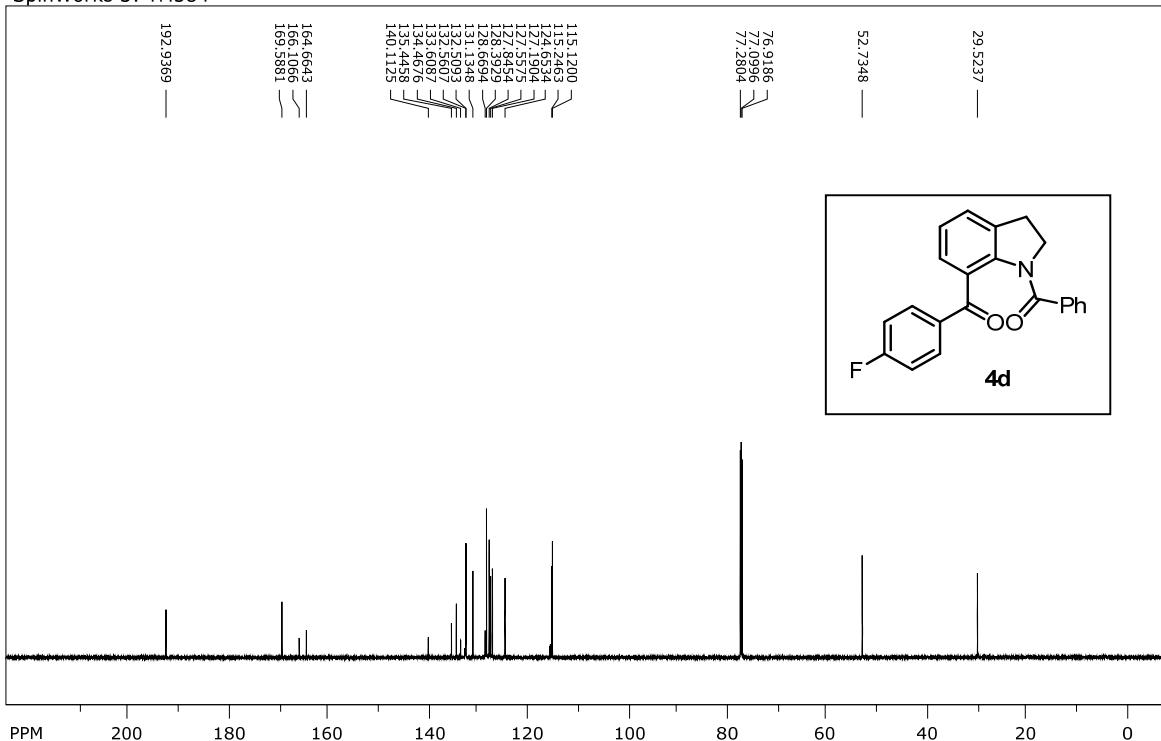
SpinWorks 3: 582



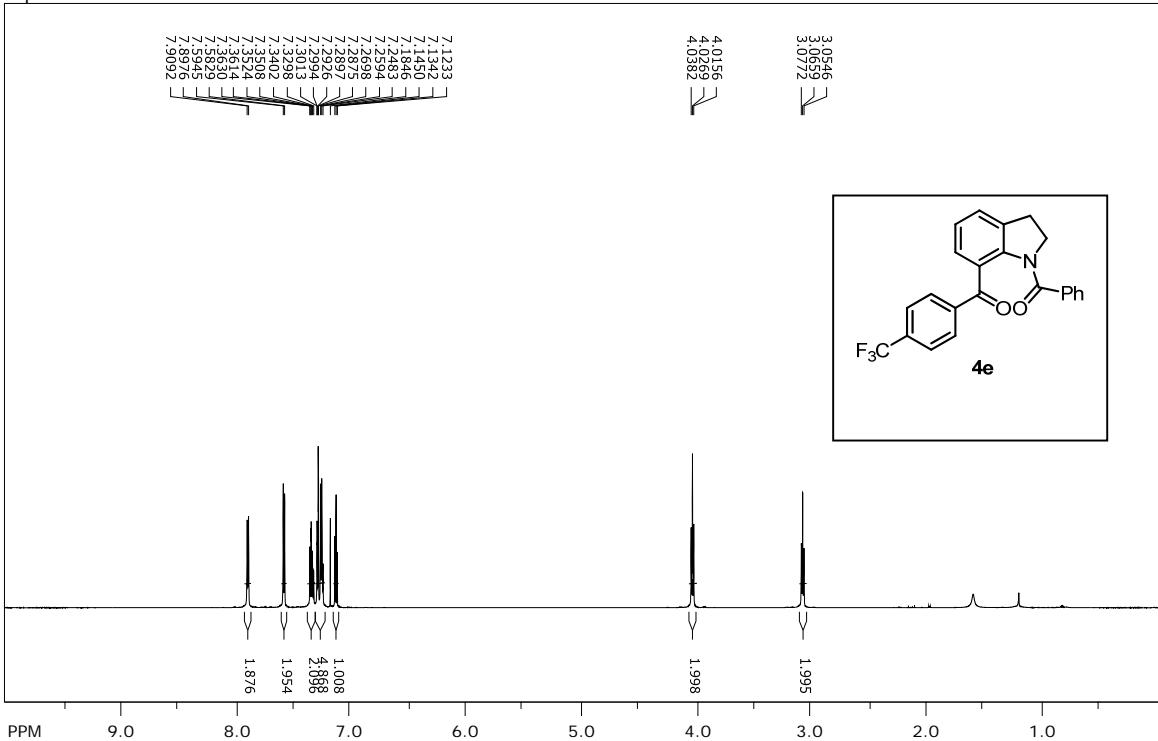
SpinWorks 3: 584



SpinWorks 3: YM584

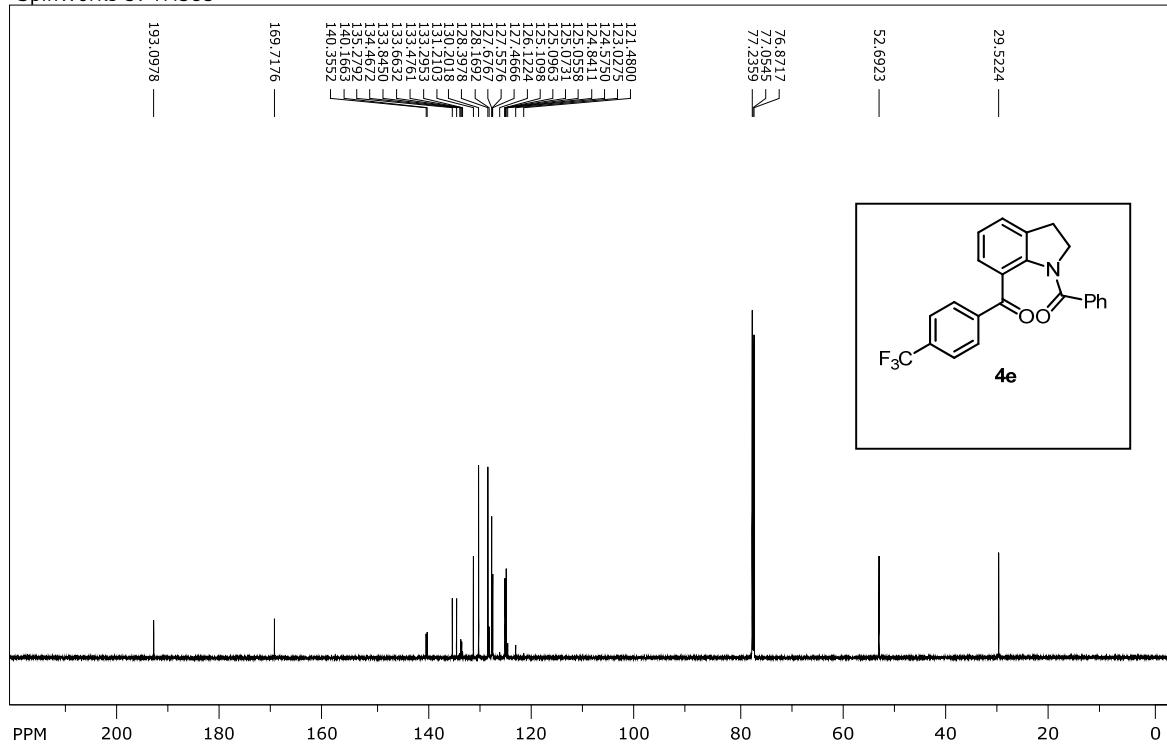


SpinWorks 3: 585

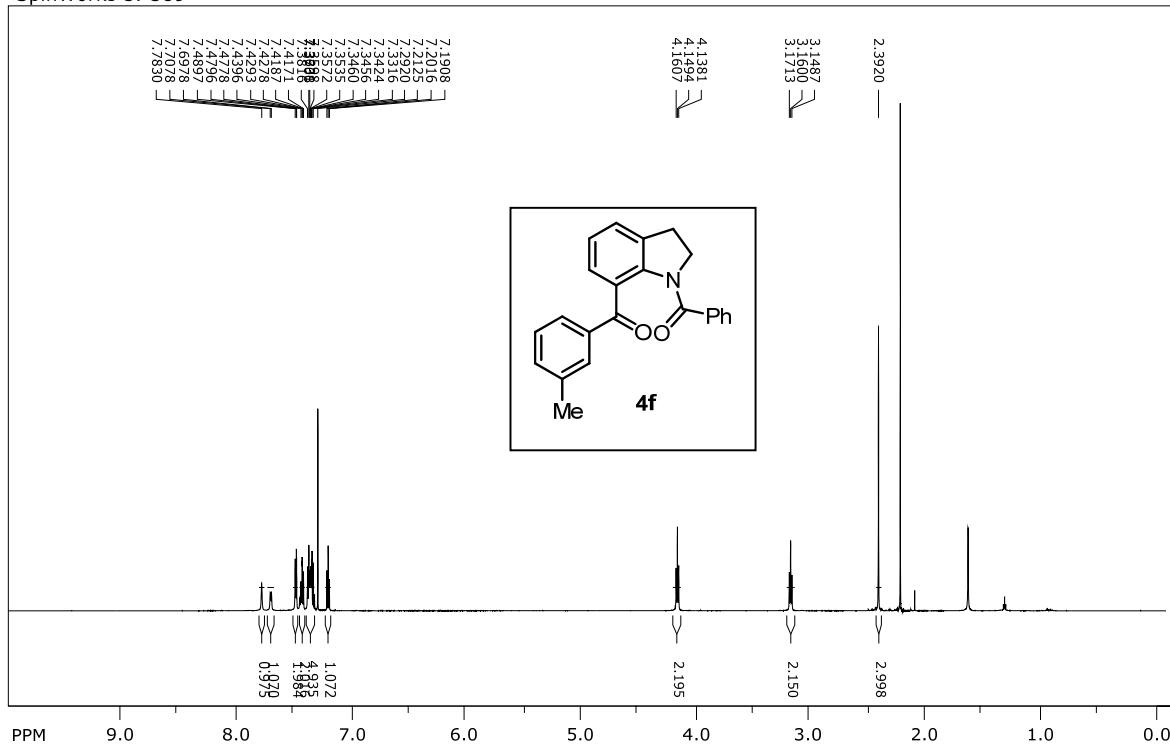


4e

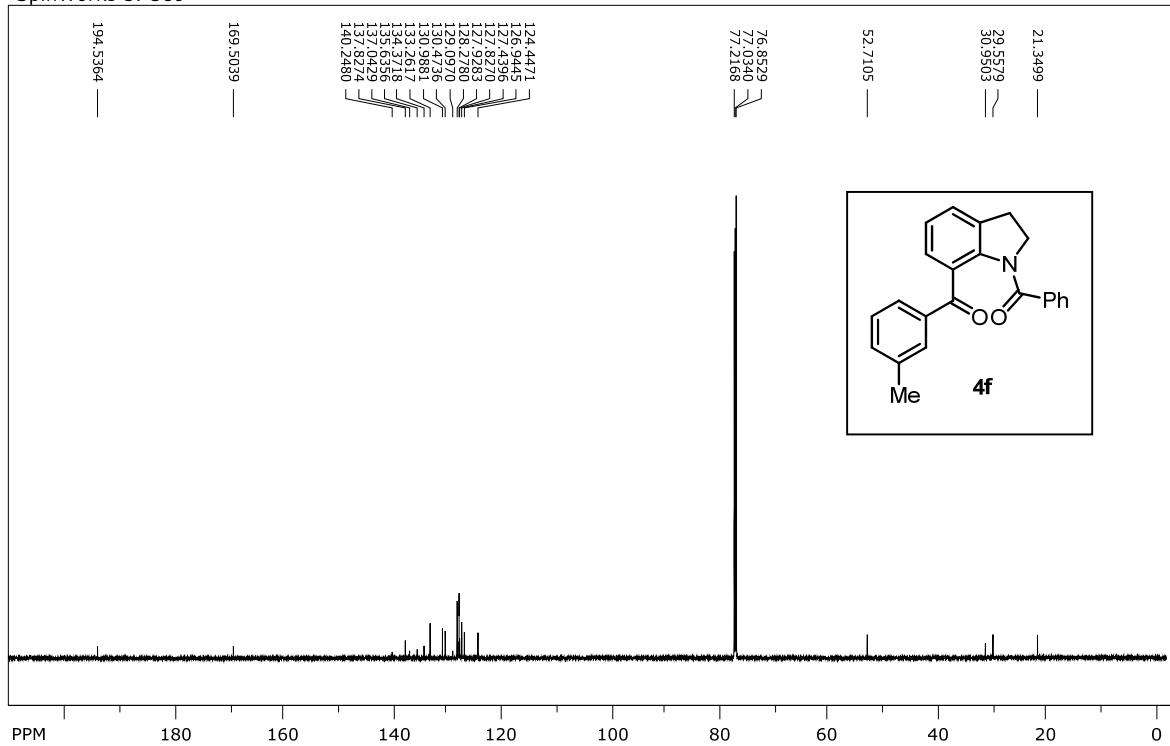
SpinWorks 3: YM585



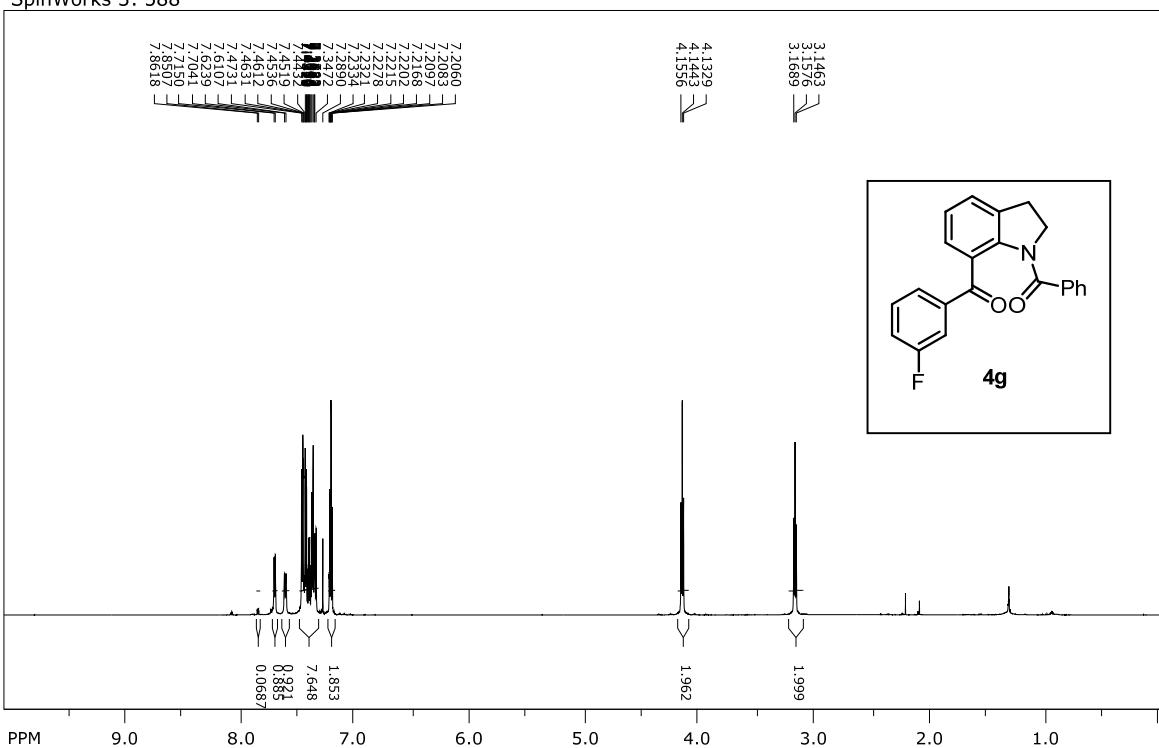
SpinWorks 3: 589



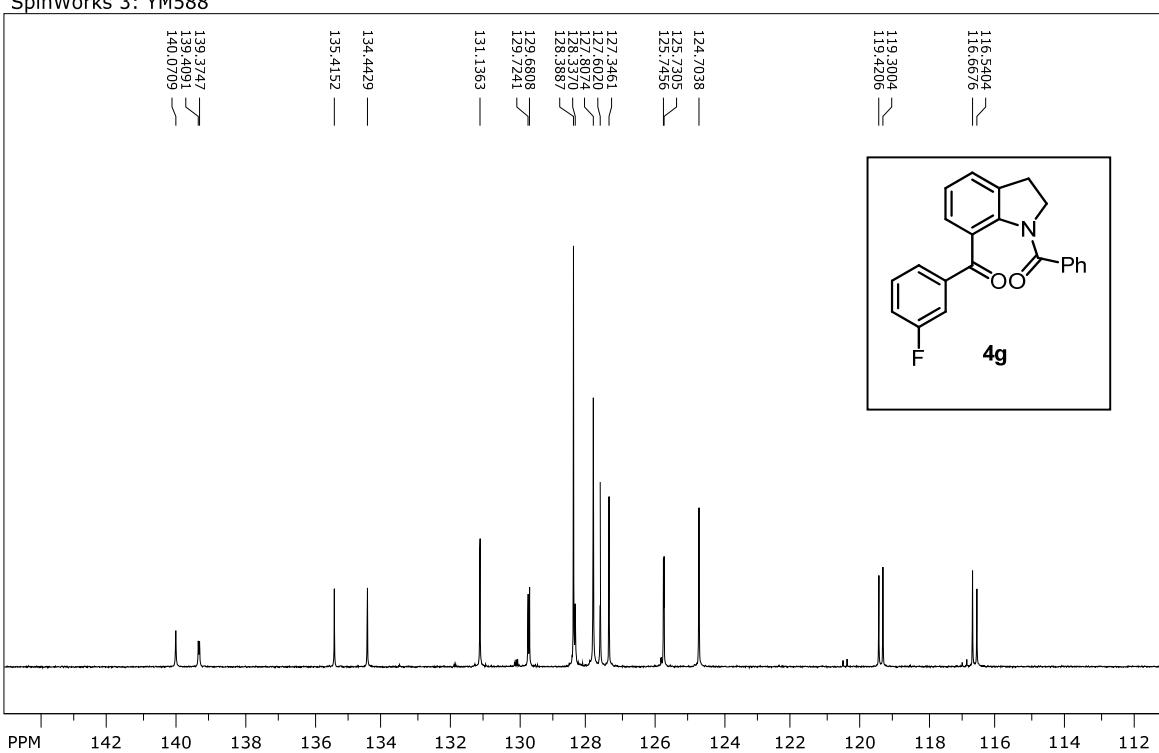
SpinWorks 3: 589



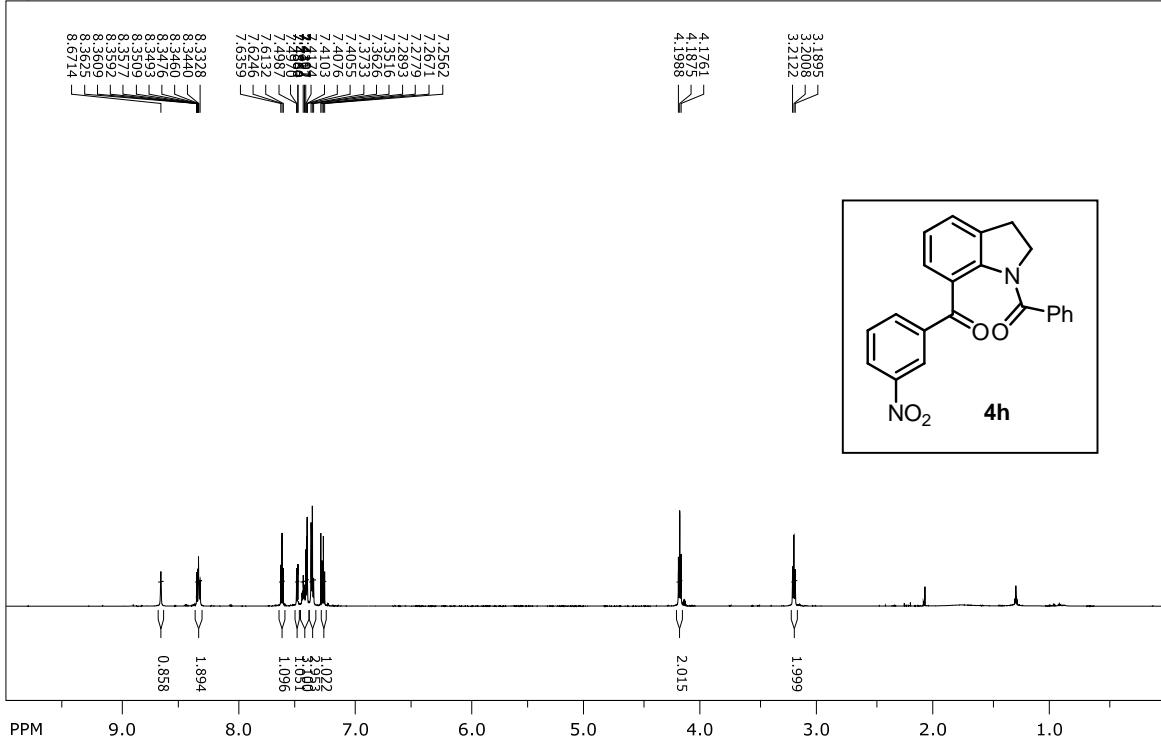
SpinWorks 3: 588



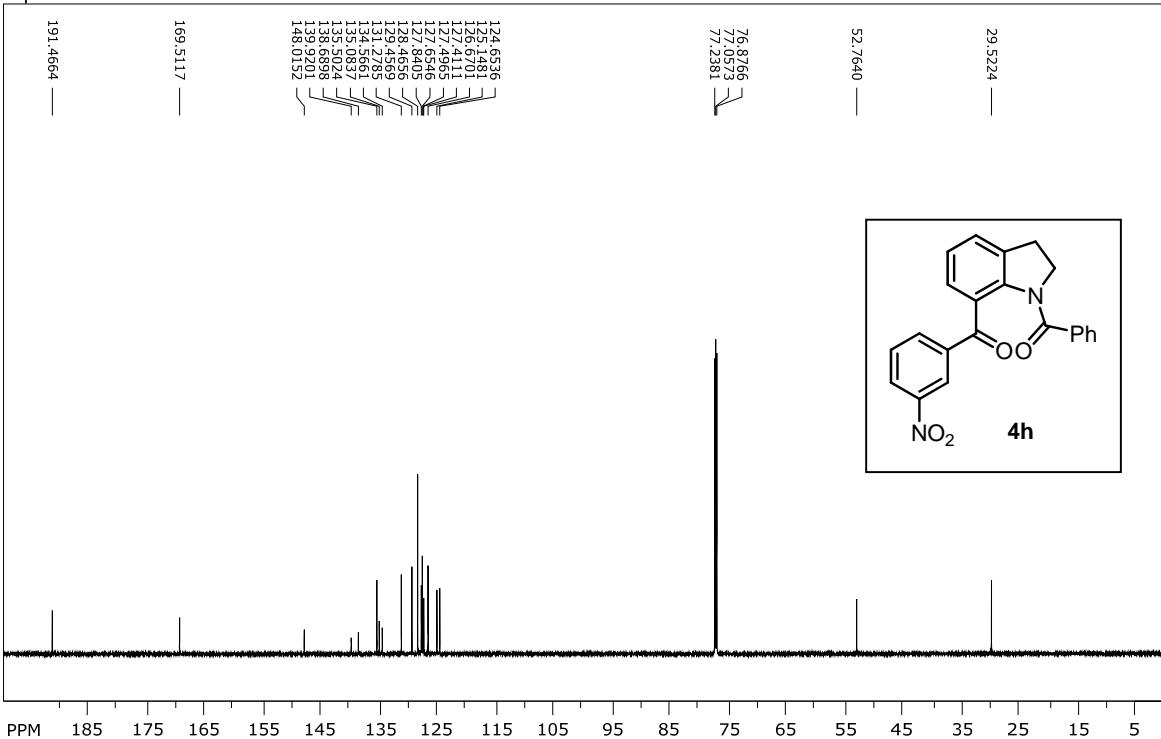
SpinWorks 3: YM588



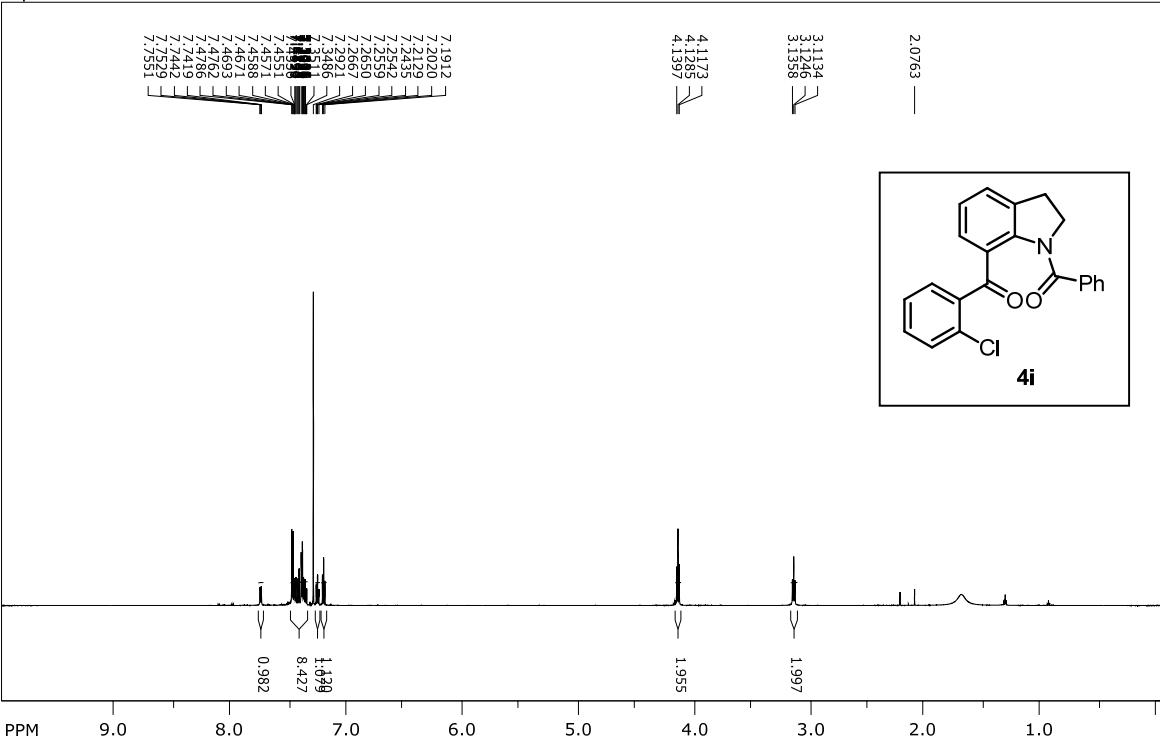
SpinWorks 3: 587



SpinWorks 3: YM587

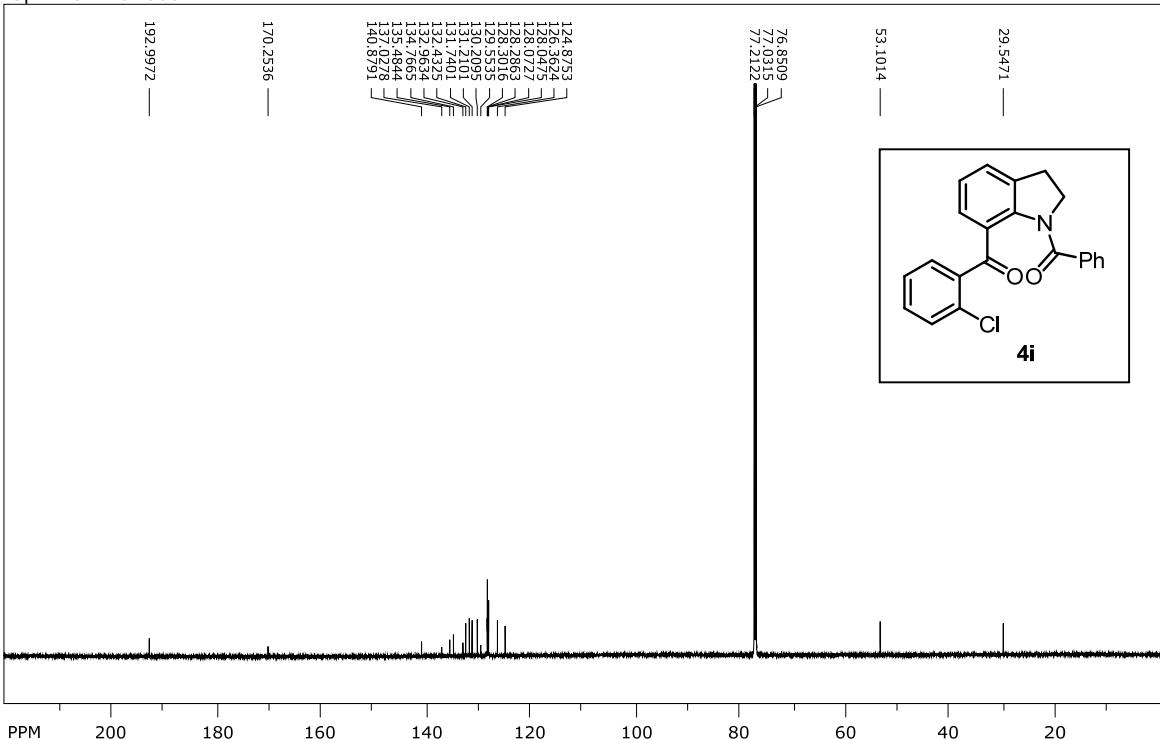


SpinWorks 3: 583



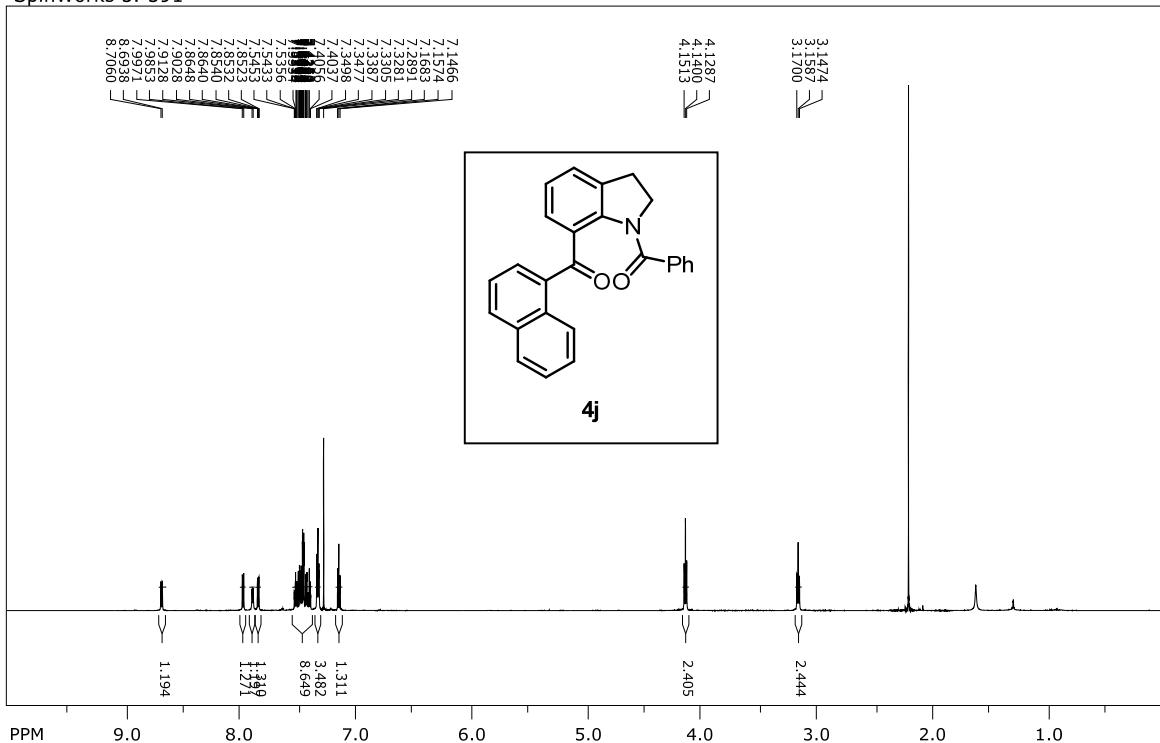
4i

SpinWorks 3: 583

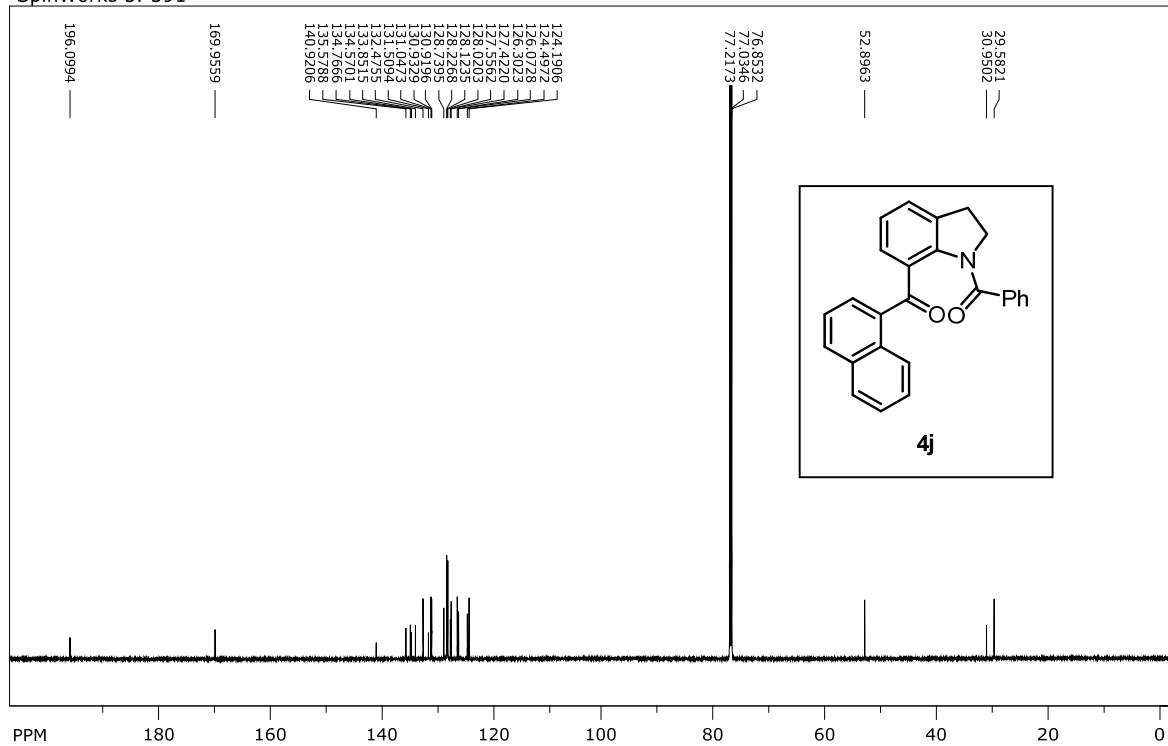


4i

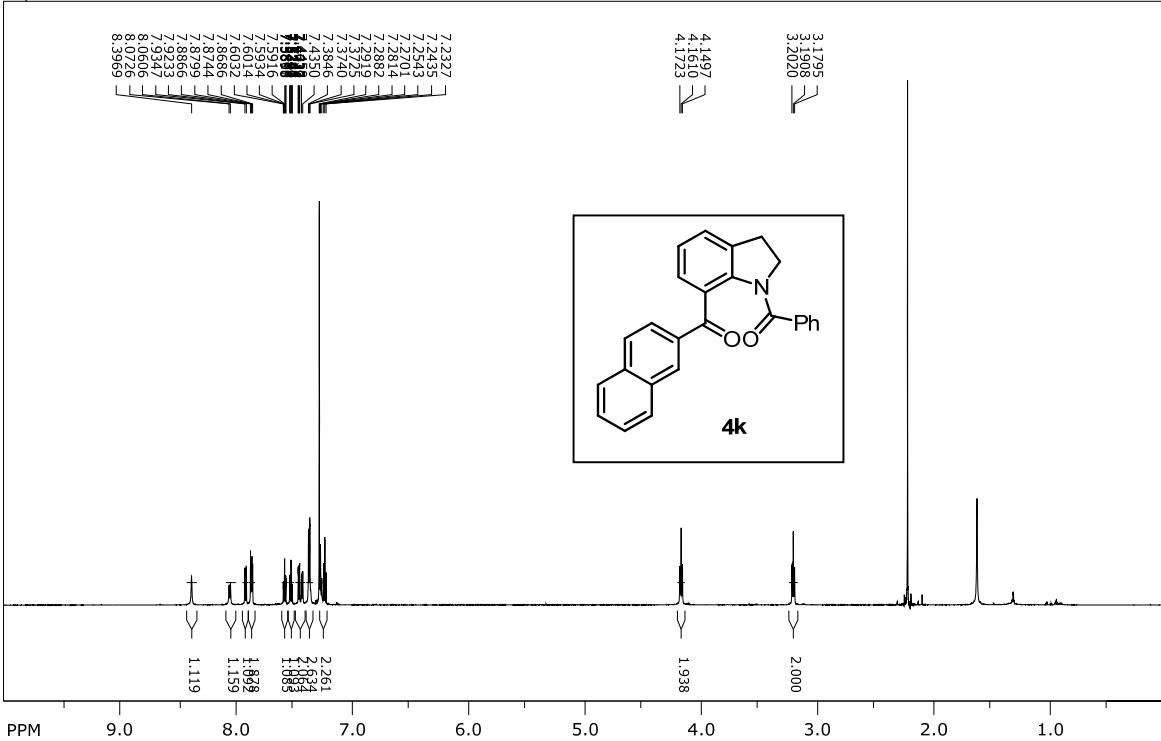
SpinWorks 3: 591



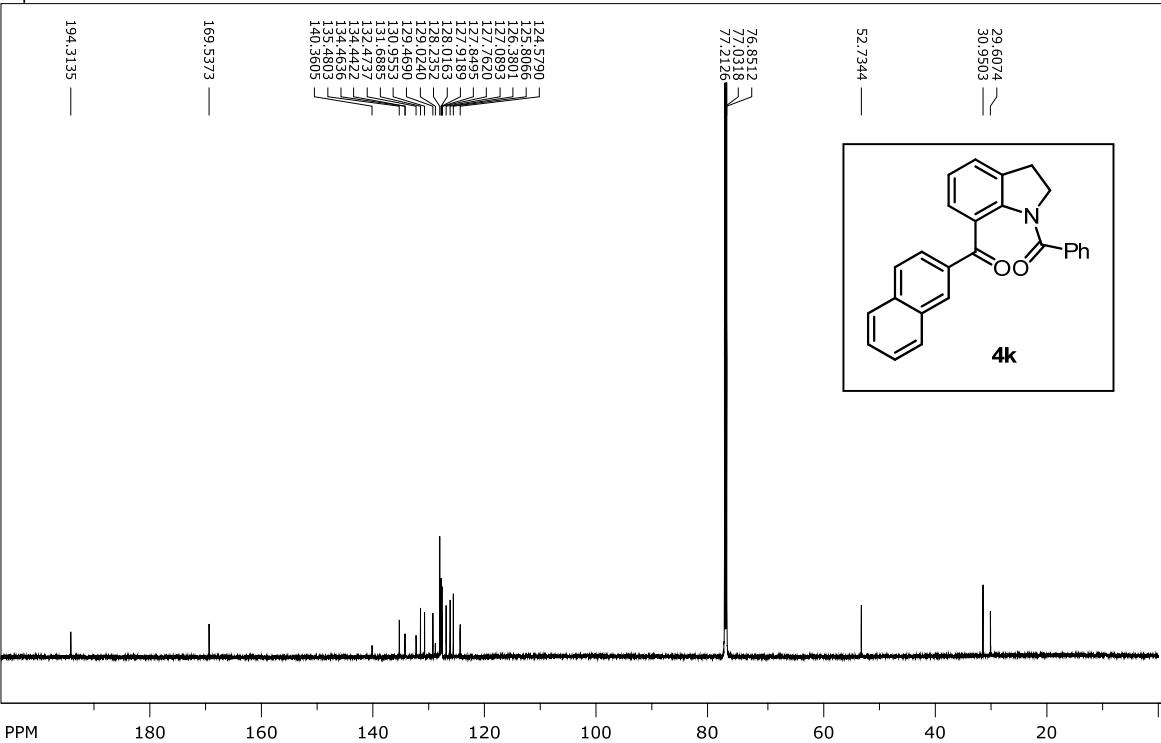
SpinWorks 3: 591



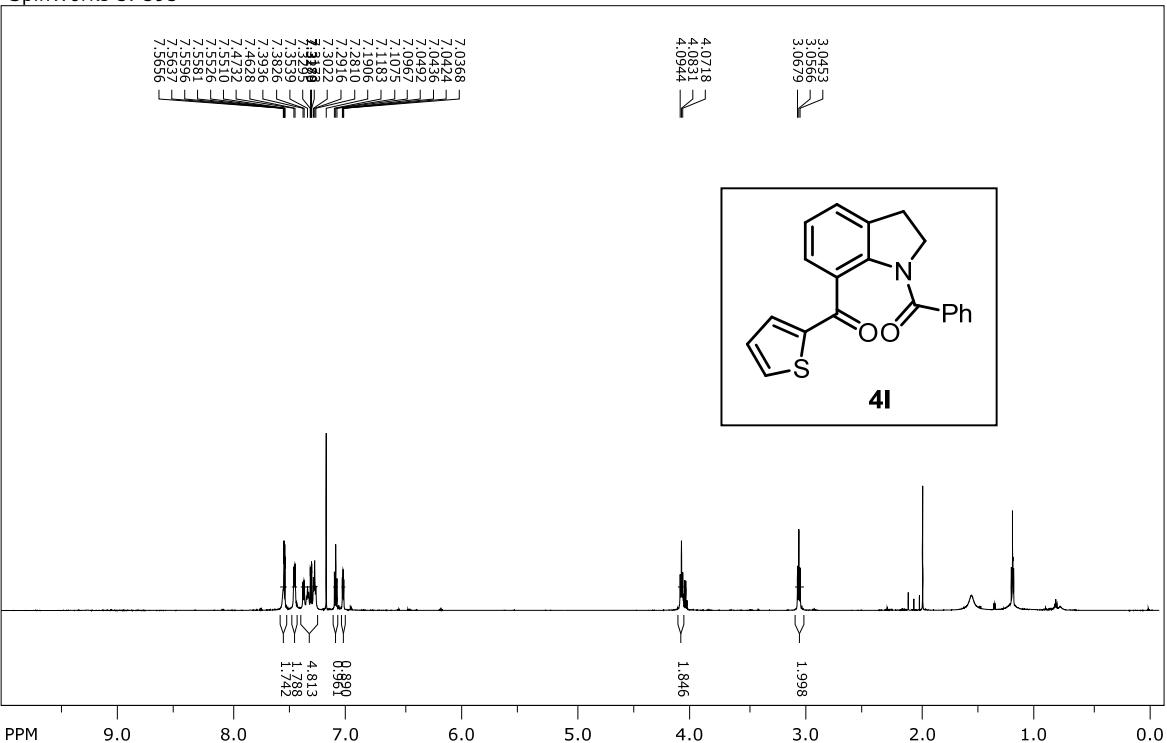
SpinWorks 3: 592



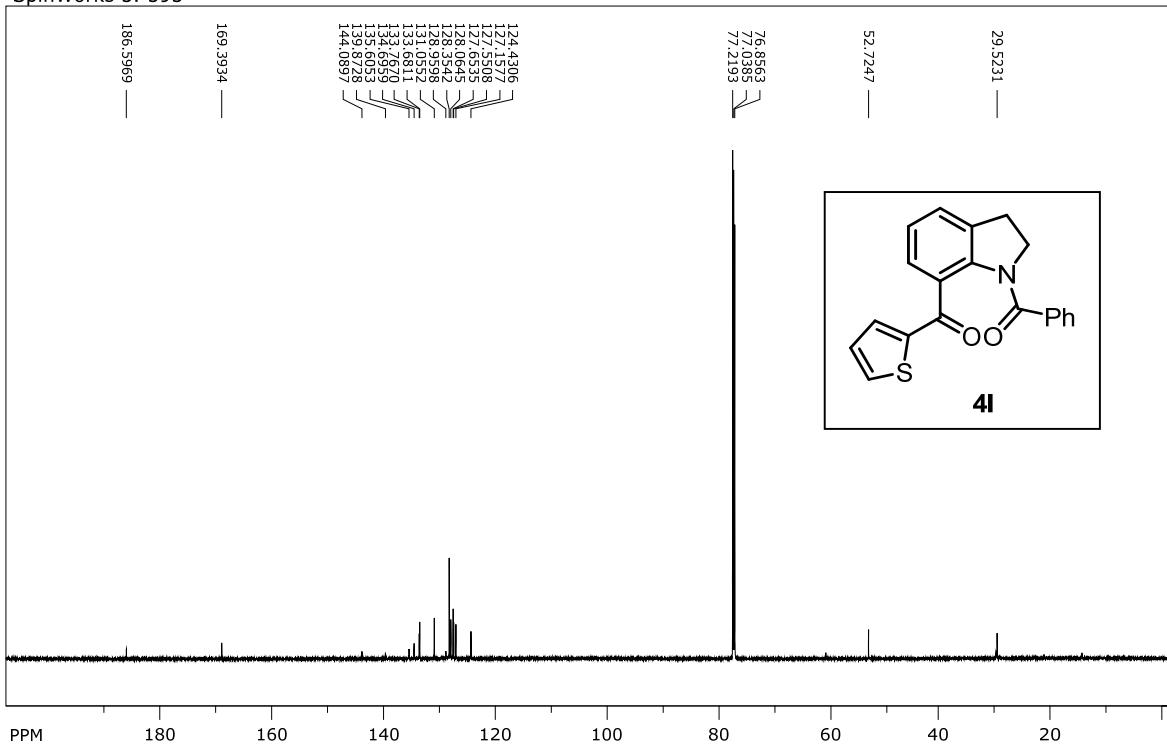
SpinWorks 3: 592



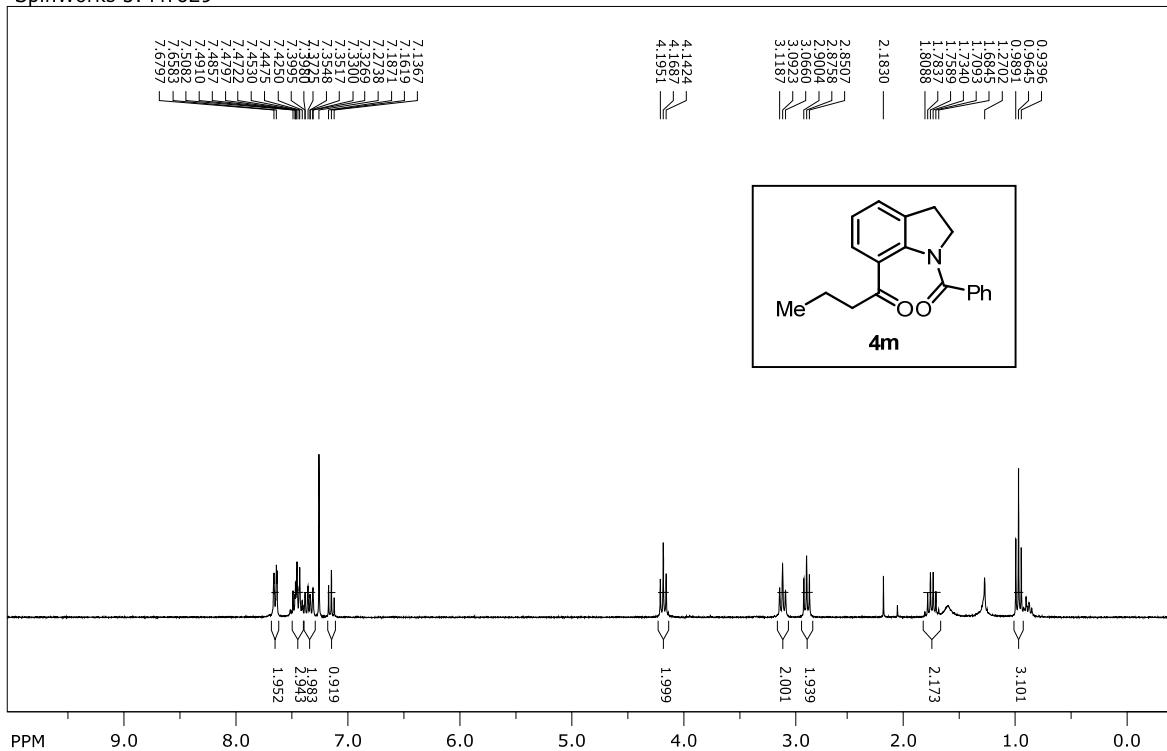
SpinWorks 3: 593



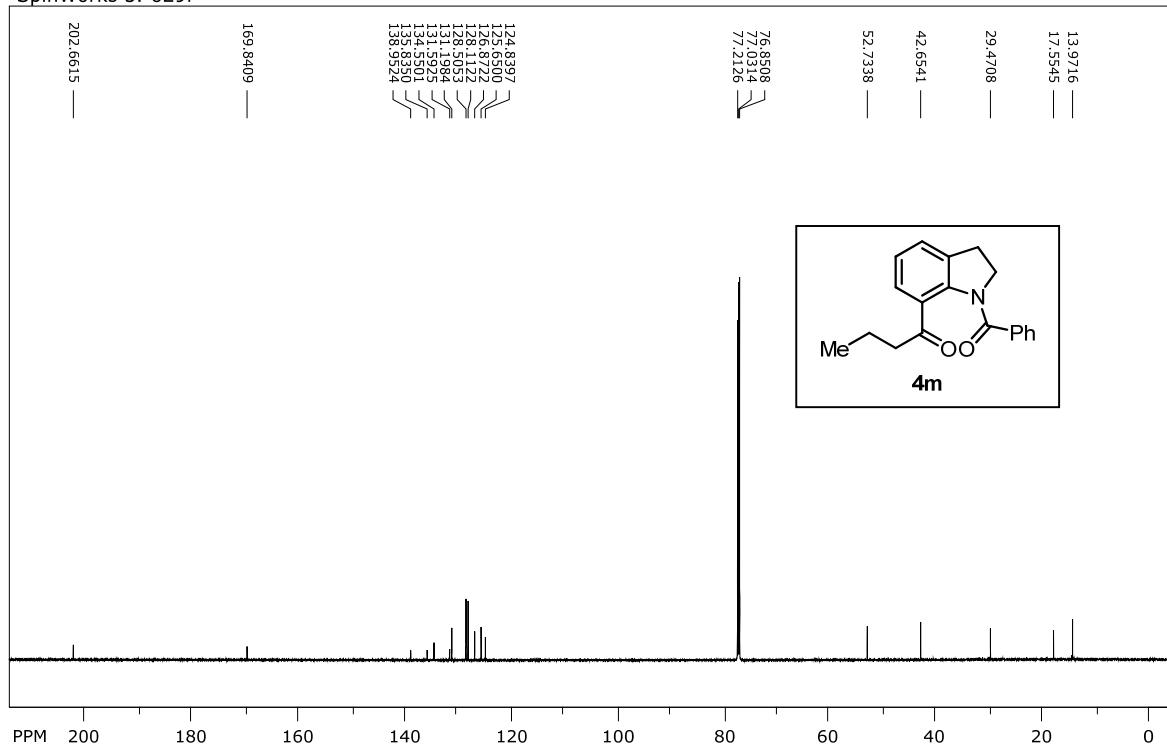
SpinWorks 3: 593



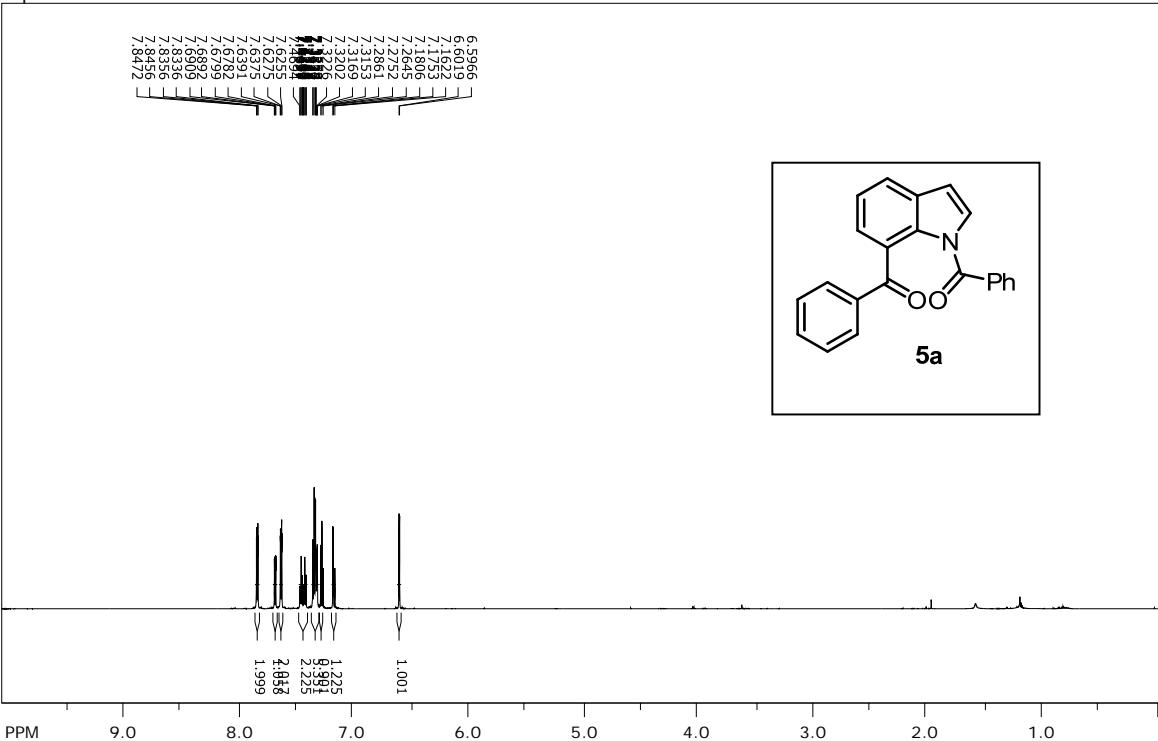
SpinWorks 3: MY629



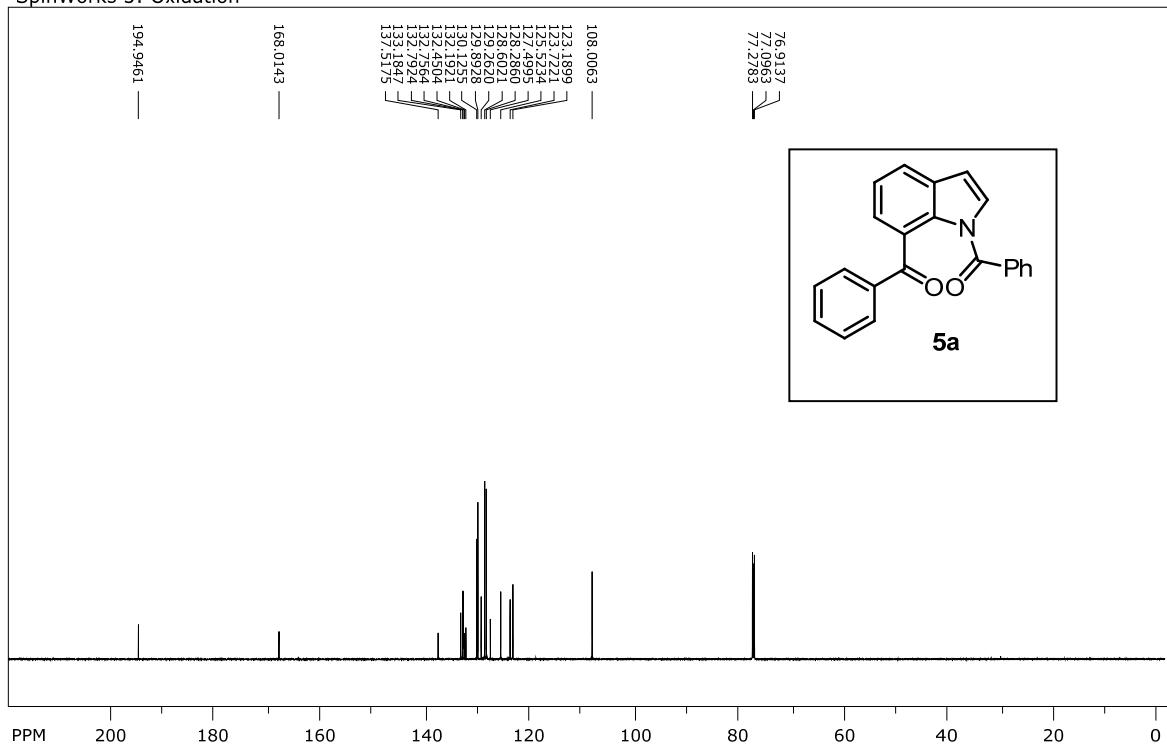
SpinWorks 3: 629P



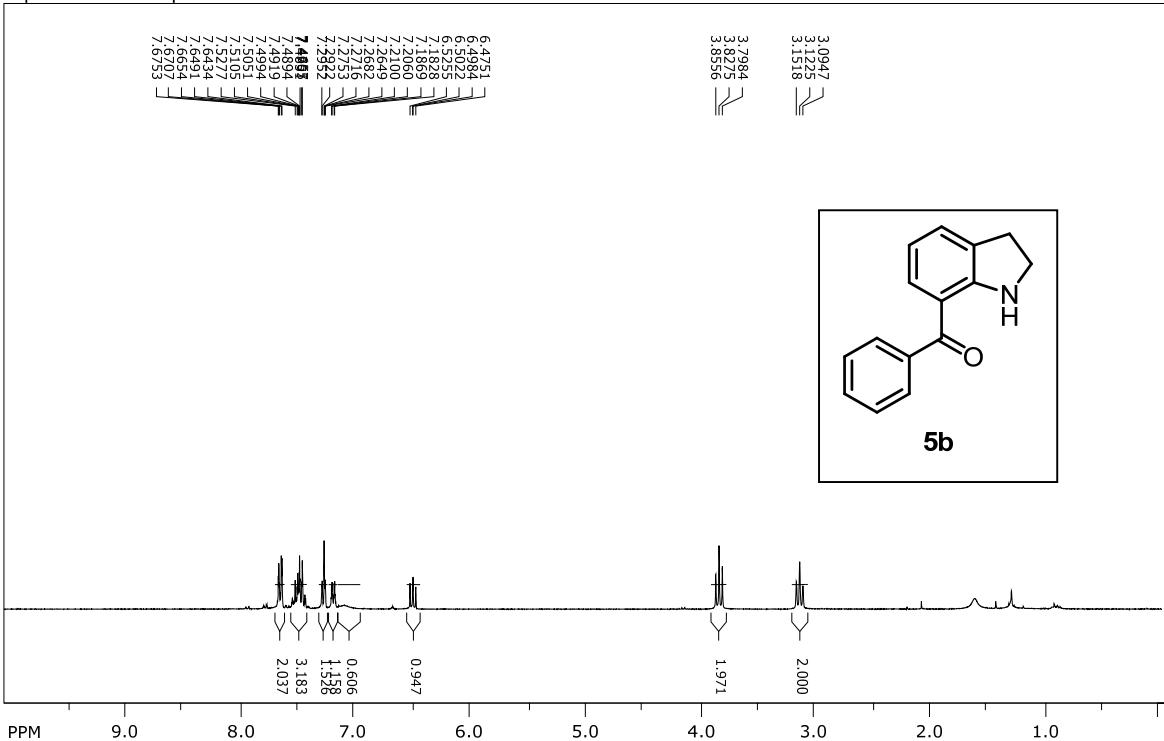
SpinWorks 3: Oxidation



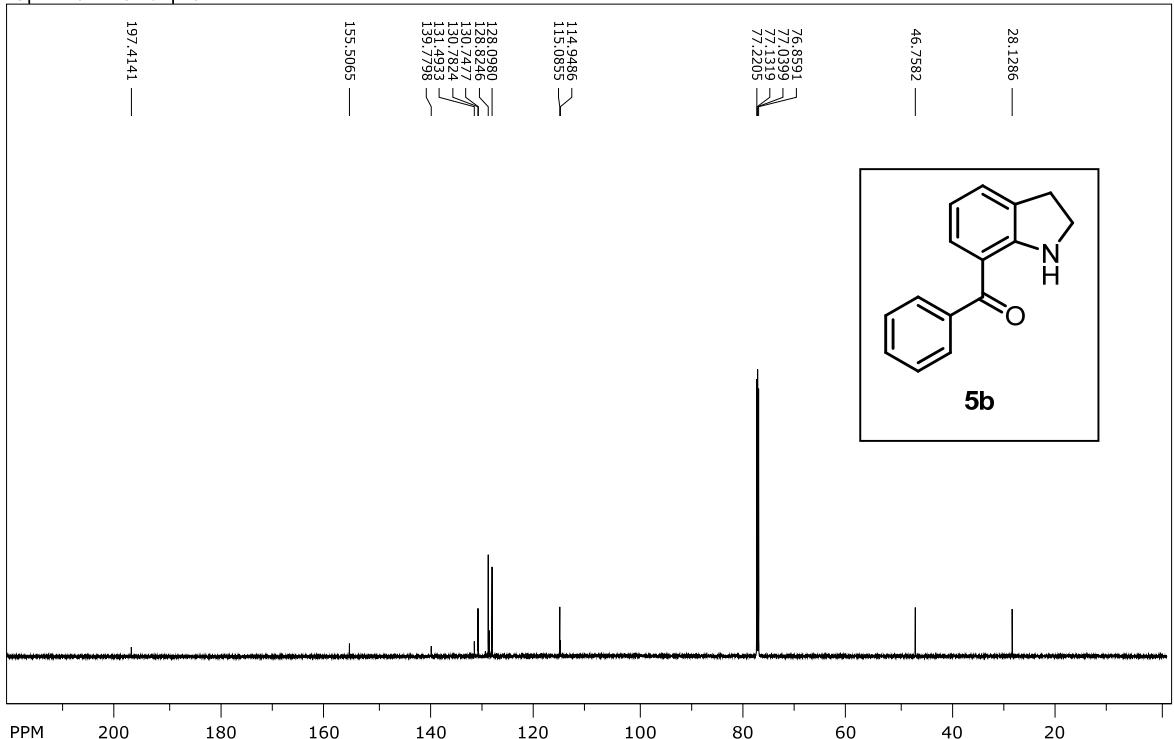
SpinWorks 3: Oxidation



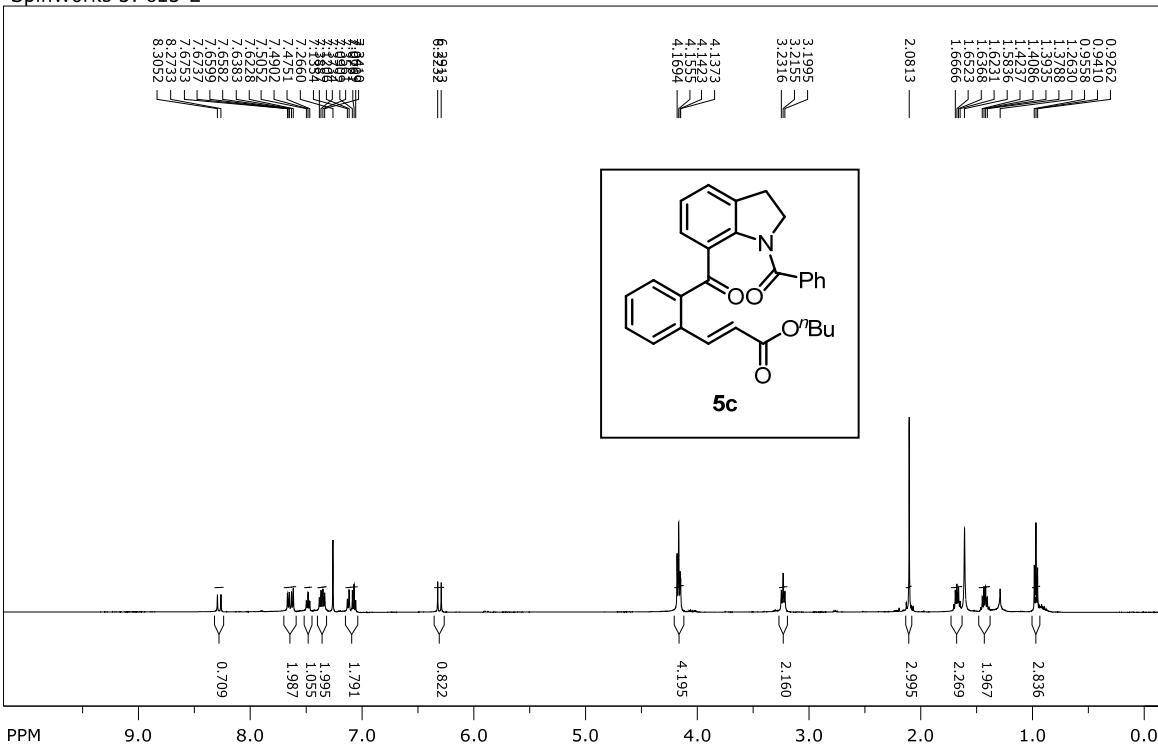
SpinWorks 3: Deprotect



SpinWorks 3: deprotect



SpinWorks 3: 623-2



SpinWorks 3:

