SUPPORTING INFORMATION

$B(C_6F_5)_3$-Catalyzed Direct C3 Alkylation of Indoles and Oxindoles

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Table of Contents

1. General information

Unless stated otherwise, all reactions were performed using oven-dried vials sealed with an aluminium crimped cap and were stirred with Teflon-coated magnetic stirrer bars. Dry tetrahydrofuran (THF), toluene, hexanes and diethyl ether were obtained after passing these previously degassed solvents through activated alumina columns (Mbraun, SPS-800). Xylenes, 1,2-dichloroethane (DCE) were dried over Na/benzophenone and CaH_2 respectively. All other solvents and commercial reagents were used as supplied without further purification unless stated otherwise.

Unless stated otherwise, a nitrogen-filled glove box (MBraun) was used to manipulate reagents including the storage of starting materials, catalysts and preparation of reactions. Dry solvents were degassed and stored in an ampoule fitted with a Teflon valve under nitrogen atmosphere to use in the glove box.

Room temperature (rt) refers to 20−25 °C. Temperatures of 0 °C was obtained using ice/water. All reactions involving heating were carried out using DrySyn blocks and a contact thermometer. *In vacuo* refers to the use of a rotary evaporator under reduced pressure.

Analytical thin layer chromatography was carried out using aluminium plates coated with silica (Kieselgel 60 F_{254} silica) and visualization was achieved using ultraviolet light (254 nm), followed by staining with iodine or 1% aqueous $KMnO_4$ solution. Flash chromatography used Kieselgel 60 silica in the solvent system stated.

Melting points were recorded on a Gallenkamp melting point apparatus, and corrected by linear interpolation of melting point standards benzophenone (47–49 ˚C), and benzoic acid (121–123 ˚C).

Infrared spectra were recorded on a Shimadzu IRAffinity-1 Fourier Transform ATIR spectrometer as thin films using a Pike MIRacle ATR accessory. Characteristic peaks are quoted (ν_{max} / cm^{-1}).

^{1}H, $^{13}C\{^{1}H\}$, $^{19}F\{^{1}H\}$ NMR spectra were obtained on either a Bruker Avance 400 (400 MHz ^{1}H, 101 MHz ^{13}C, 376 MHz ^{19}F) or a Bruker Avance 500 (500 MHz ^{1}H, 126 MHz ^{13}C, 471 MHz ^{19}F) spectrometer at rt in the solvent stated. Chemical shifts are reported in parts per million (ppm) relative to the residual solvent signal. All coupling constants, *J*, are quoted in Hz. Multiplicities are reported with the following symbols: s = singlet, d = doublet, t = triplet, q = quartet, hept = heptet, m = multiplet and multiples thereof. The abbreviation Ph to denote phenyl, br to denote broad.

Mass spectra were obtained from a Micromass Quattro LC Spectrometer (electrospray). High resolution mass spectrometry (HRMS, *m/z*) data was acquired at Cardiff University on a Micromass LCT spectrometer or at the University of Leicester on a Waters Acquity XEVO Q ToF spectrometer (electrospray).

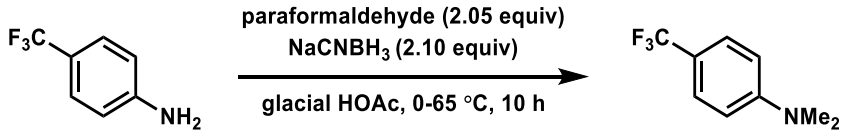
Tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) was bought from Acros Organics and sublimed at 120 °C under reduced pressure (high vacuum) before use in the glove box. Tris(pentafluorophenyl)borane ($B(C_6F_5)_3$), used in the in situ drying procedure was purchased from Alfa Aesar and used without further

purification. Tris(2,4,6-trifluorophenyl)borane ($B(2,4,6\text{-}F_3C_6H_2)_3$) and tris(2,6-difluorophenyl)borane ($B(2,6\text{-}F_2C_6H_3)_3$) were prepared as described in literature.[1]

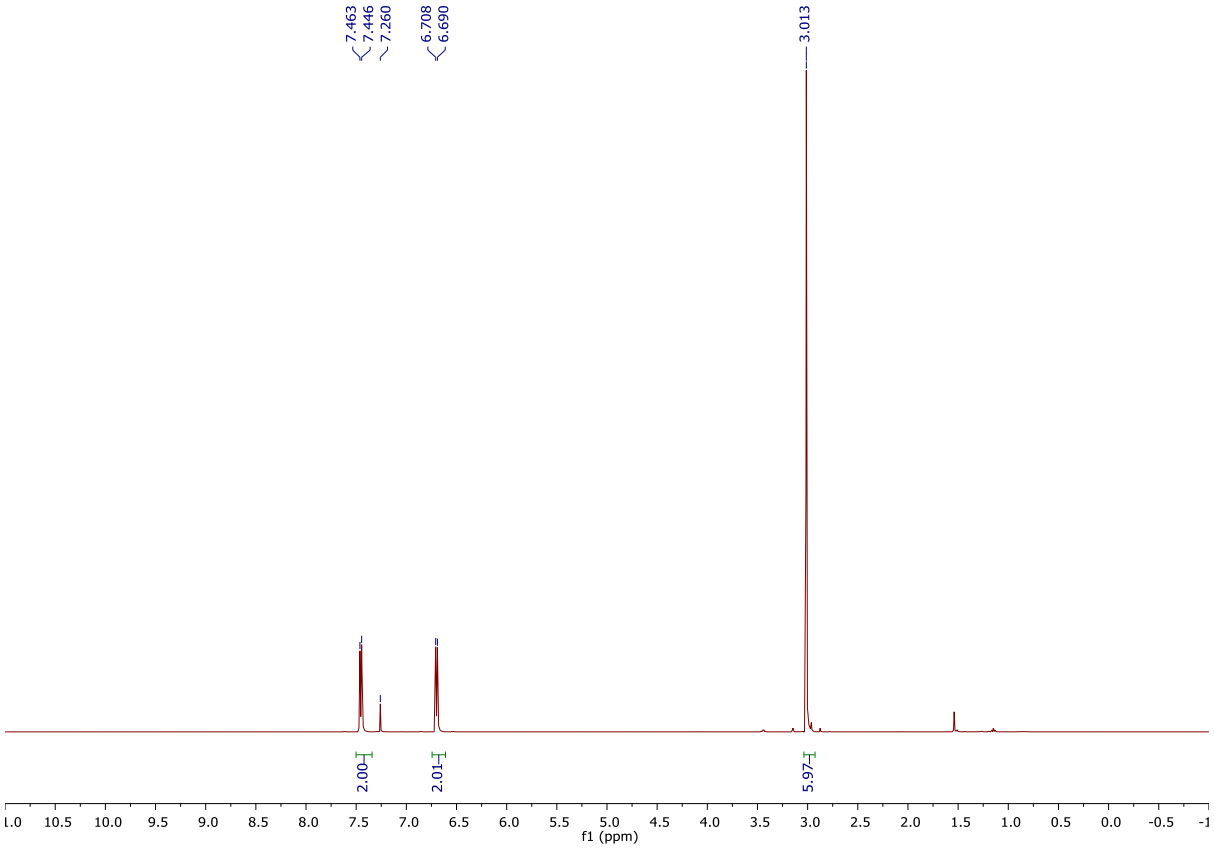
2. Experimental and characterization data

2.1. Synthesis of alkylating agents

N,N-Dimethyl-4-(trifluoromethyl)aniline S3



A 100 mL round-bottomed flask equipped with a magnetic stirrer bar was charged with 4-(trifluoromethyl)aniline (2.42 g, 15.0 mmol), paraformaldehyde (0.92 g, 30.8 mmol) and glacial acetic acid (23 mL). The mixture was cooled in an ice bath and sodium cyanoborohydride (1.98 g, 31.5 mmol) was added. The resultant mixture was stirred at 0 °C for 30 min. Then ice bath was removed, and the mixture was heated to 65 °C. This was stirred at that temperature for 10 h. The hot reaction mixture was poured over 5 M aqueous sodium hydroxide solution (80 mL) and then diluted with hexanes (60 mL). The organic layer was separated and the aqueous phase was washed with hexanes (2 × 30 mL). The organics were combined, washed with brine, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Purification by flash silica chromatography (eluent = 1% EtOAc in hexanes, 40 × 180 mm silica) gave the title compound **S3** as a white crystalline solid (1.78 g, 9.41 mmol, 63%); mp 68–70 °C (Lit. 68–69 °C);[2] R_f = 0.32 (eluent = 2% EtOAc in hexanes); ν_{max} / cm^{-1} (film) 1616, 1537, 1370, 1323, 1231, 1196, 1155, 1094, 1063, 941, 816, 723, 579, 511, 480; ^1H NMR (500 MHz, $CDCl_3$) δ_H: 3.01 (6H, s), 6.70 (2H, d, *J* 8.5), 7.45 (2H, d, *J* 8.5); ^{19}F NMR (376 MHz, $CDCl_3$) δ_F: -60.8; ^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 40.3, 111.3, 117.7 (q, *J* 32.6), 125.3 (q, *J* 270.1), 126.5 (q, *J* 3.8), 152.4; HRMS (ES^+) calculated for $[C_9H_{11}NF_3]^+$ $(M+H)^+$ m/z: 190.0844, found 190.0846 (+1.1 ppm).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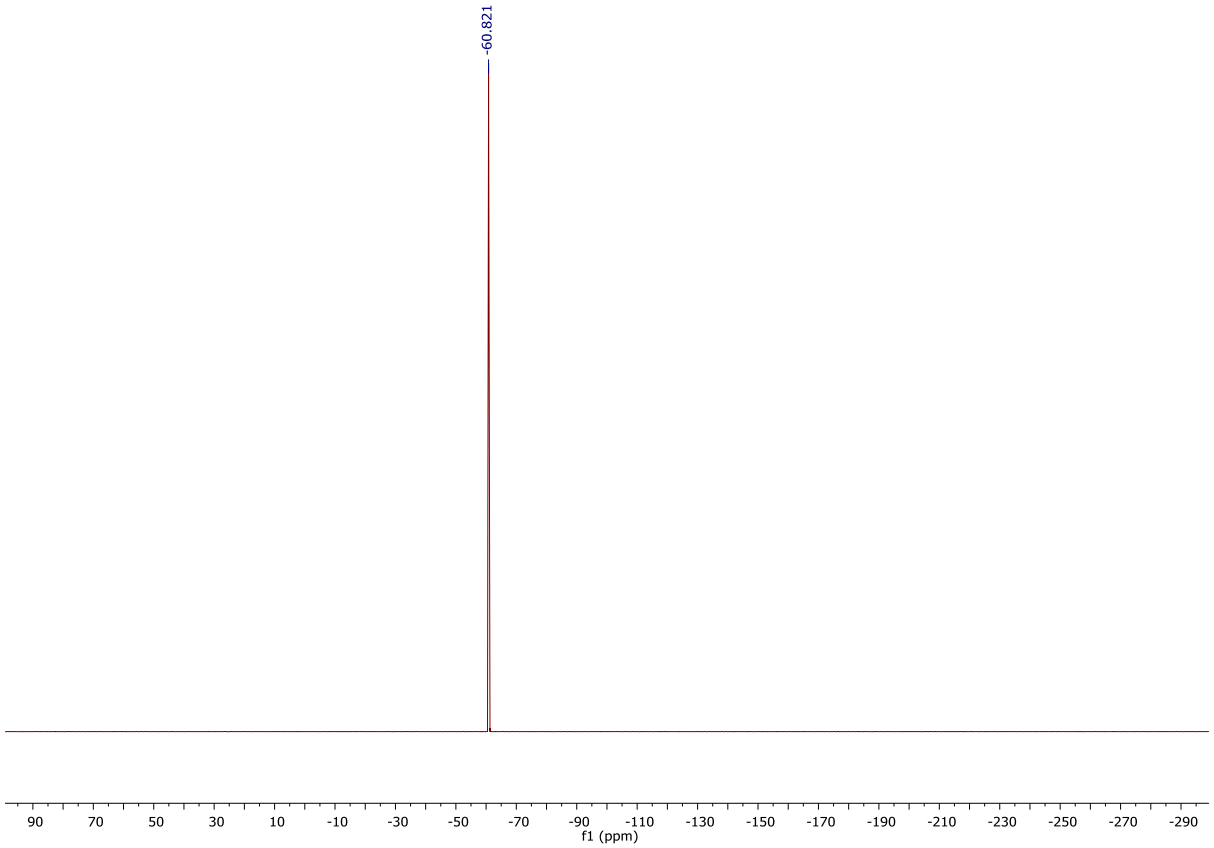
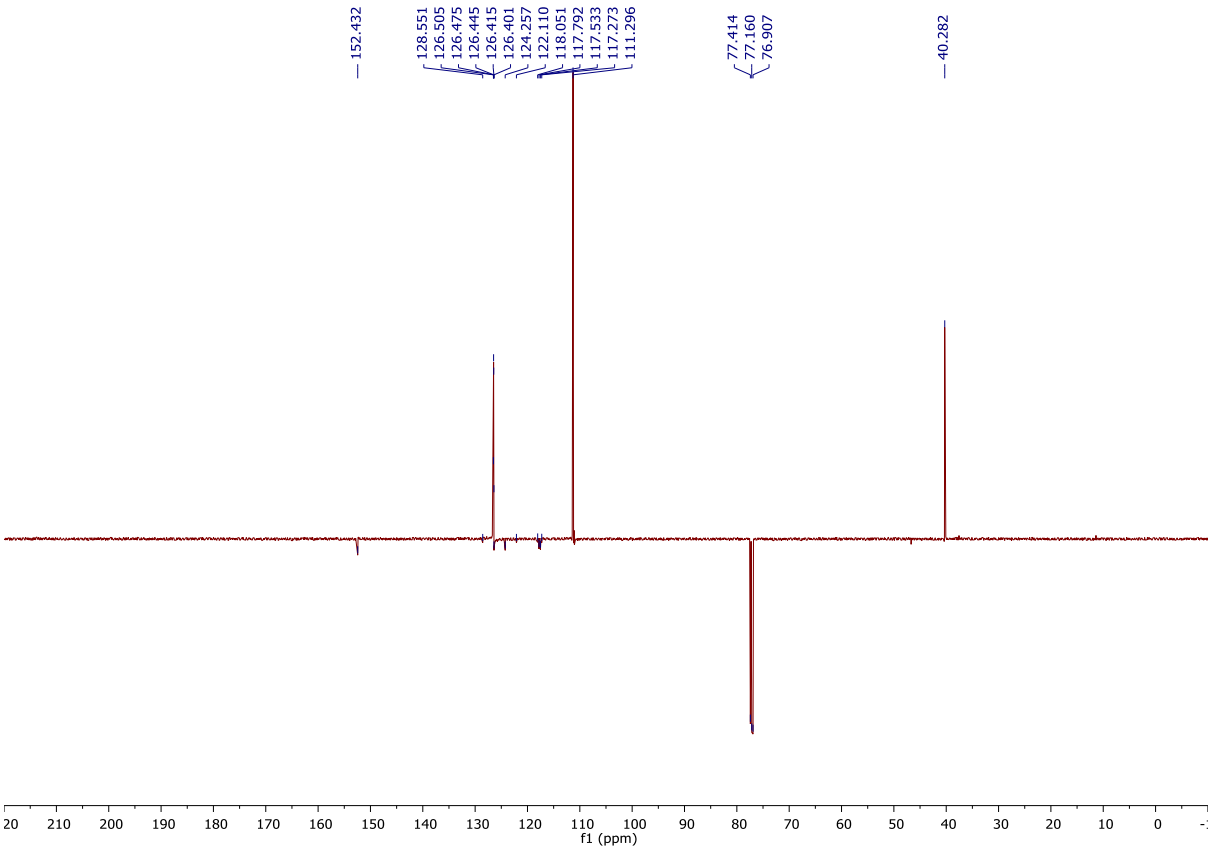
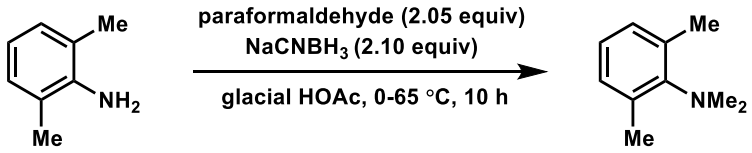
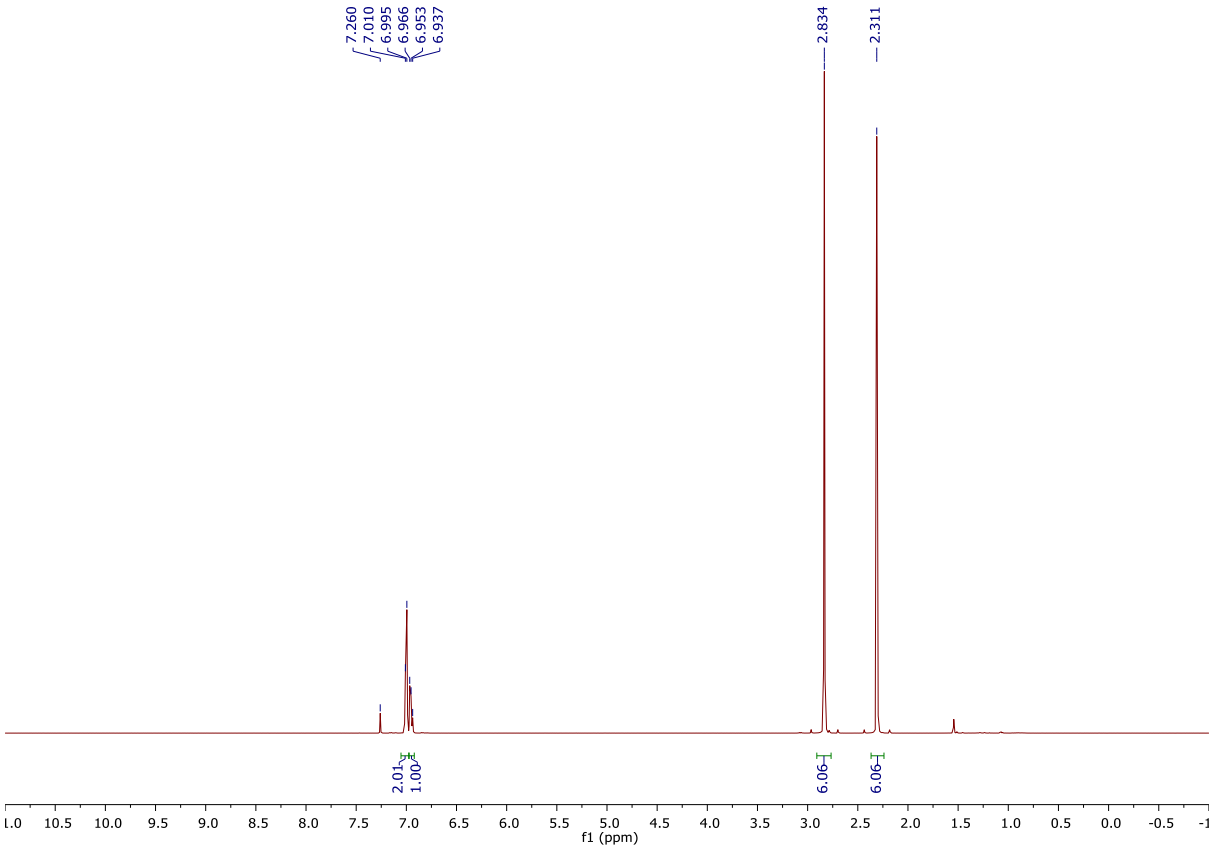

-60.821
f1 (ppm)



N,N,2,6-Tetramethylaniline 3



A 100 mL round-bottomed flask equipped with a magnetic stirrer bar was charged with 2,6-dimethylaniline (1.82 g, 15.0 mmol), paraformaldehyde (0.92 g, 30.8 mmol) and glacial acetic acid (23 mL). The mixture was cooled in an ice bath and sodium cyanoborohydride (1.98 g, 31.5 mmol) was added. The resultant mixture was stirred at 0 °C for 30 min. Then ice bath was removed, and the mixture was heated to 65 °C. This was stirred at that temperature for 10 h. The hot reaction mixture was poured over 5 M aqueous sodium hydroxide solution (80 mL) and then diluted with hexanes (60 mL). The organic layer was separated and the aqueous phase was washed with hexanes (2 × 30 mL). The organics were combined, washed with brine, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Purification by flash silica chromatography (eluent = pet. ether, 40 × 150 mm silica) gave the title compound **3** as a colorless oil (1.9 g, 12.7 mmol, 85%); R_f = 0.58 (eluent = pet. ether); ν_{max} / cm^{-1} (film) 2959, 2914, 2781, 1476, 1373, 1319, 1215, 1150, 1090, 1057, 953, 764, 573, 500; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 2.31 (6H, s), 2.83 (6H, s), 6.92–6.98 (1H, m), 7.00 (2H, d, *J* 7.3); ^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 19.3, 42.6, 124.8, 128.9, 137.3, 149.8; HRMS (AP$^+$) calculated for $[C_{10}H_{16}N]^+$ $(M+H)^+$ m/z: 150.1283, found 150.1279 (-2.7 ppm).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7.010
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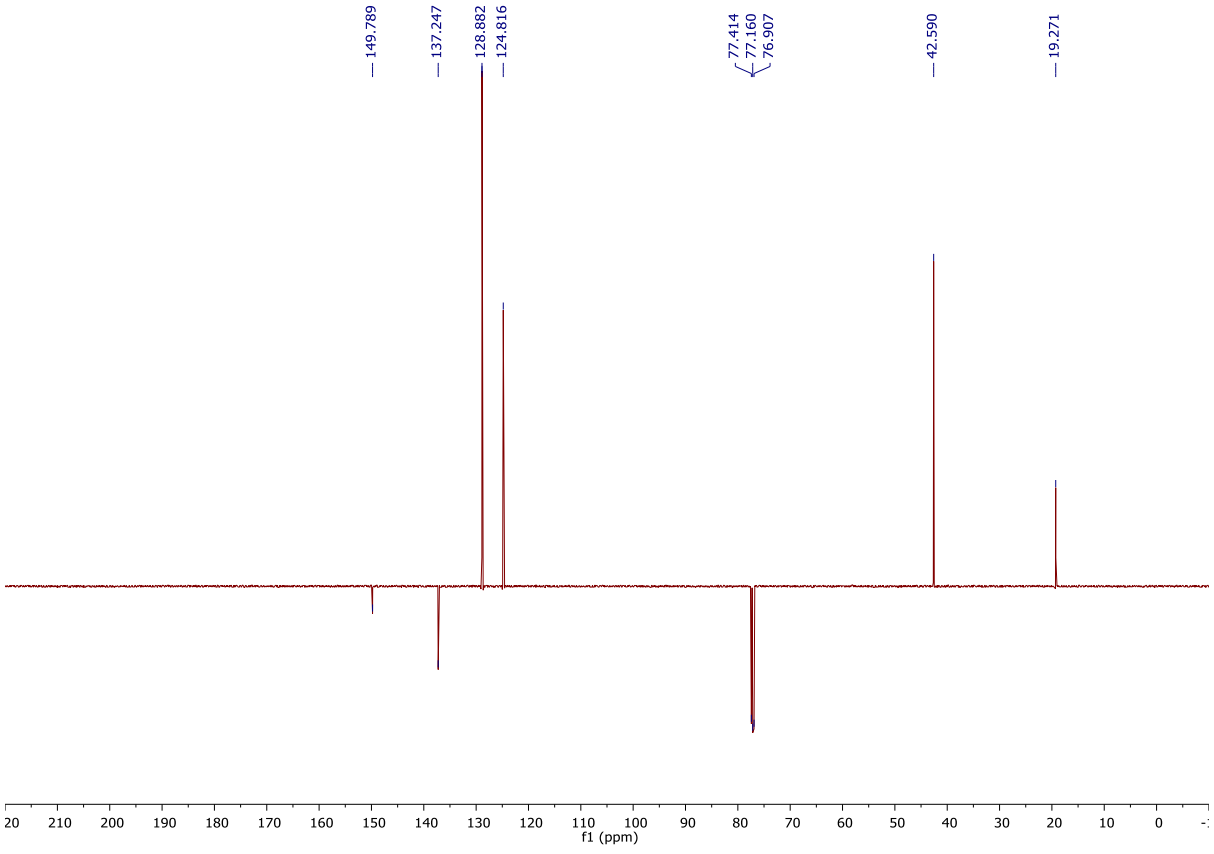
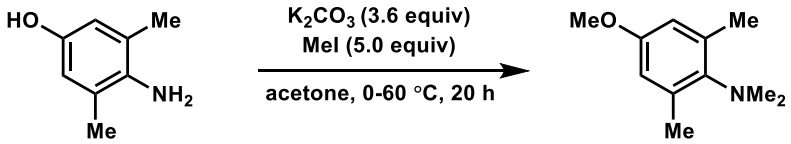
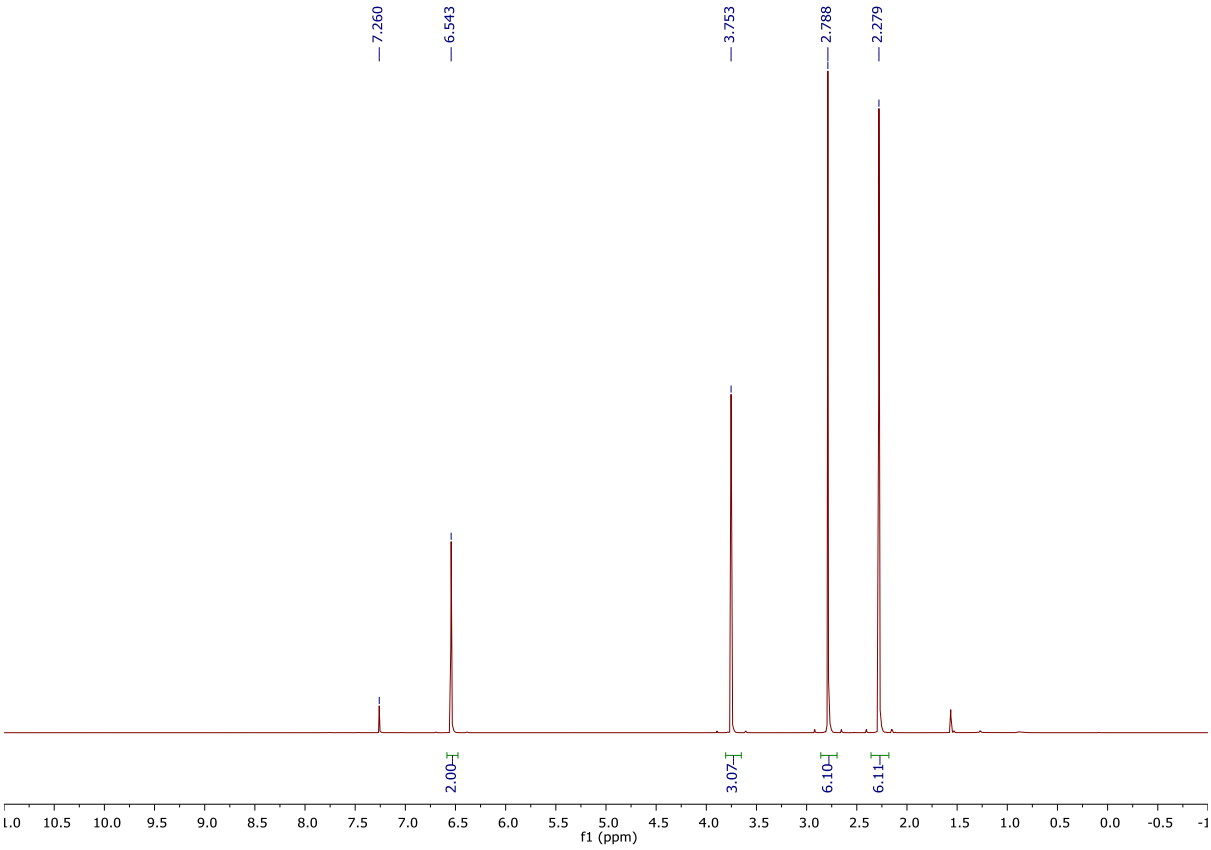
1.00
6.06
6.06
f1 (ppm)

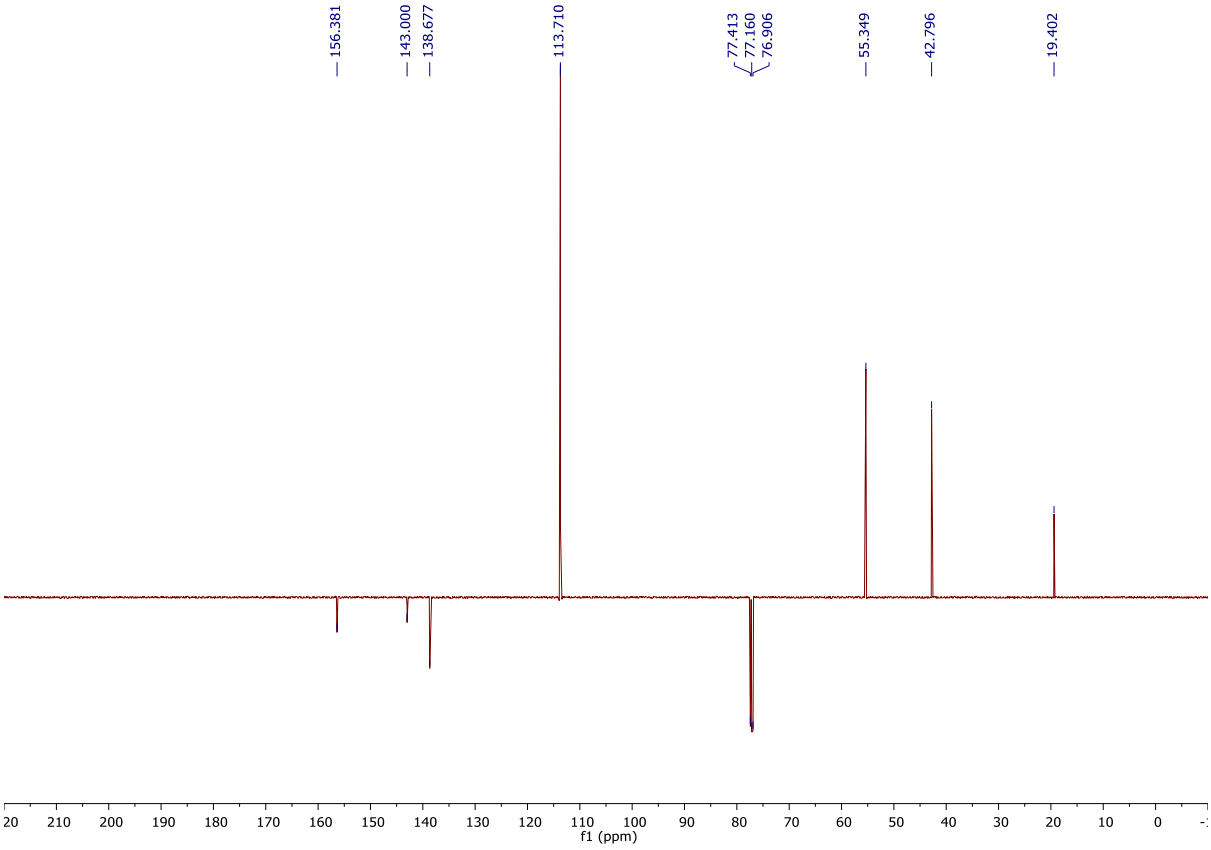

149.789
137.247
128.882
124.816
77.414
77.160
76.907
42.590
19.271
f1 (ppm)

4-Methoxy-N,N,2,6-tetramethylaniline S6

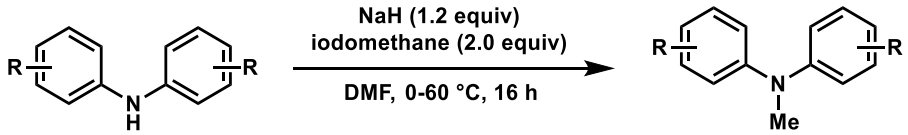


A 20 mL vial equipped with a magnetic stirrer bar was charged with 4-Amino-3,5-dimethylphenol (1.00 g, 7.30 mmol) and acetone (14 mL). The mixture was cooled in an ice bath and K_2CO_3 (3.60 g, 26.3 mmol) was added. Then ice bath was removed and the resultant mixture was stirred at rt for 10 min. Again, the mixture was cooled in the ice bath and MeI (2.3 mL, 36.5 mmol) was added. The reaction mixture in the vial was sealed and stirred at 60 °C for 20 h. Then the reaction mixture was cooled, filtered and acetone was removed *in vacuo*. The reaction mixture was diluted with EtOAc (50 mL) and water (30 mL). The organic layer was separated, washed with brine, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Purification by flash silica chromatography (eluent = 1% EtOAc in hexanes, 30 × 150 mm silica) gave the title compound **S6** as a colorless oil (0.97 g, 5.41 mmol, 74%); R_f = 0.63 (eluent = 5% EtOAc in hexanes); ν_{max} / cm^{-1} (film) 2913, 2833, 2778, 1603, 1489, 1300, 1192, 1163, 1063, 961, 928, 855, 833, 681, 617, 571, 463; ^1H NMR (500 MHz, $CDCl_3$) δ_H: 2.28 (6H, s), 2.79 (6H, s), 3.75 (3H, s), 6.54 (2H, s); ^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 19.4, 42.8, 55.4, 113.7, 138.7, 143.0, 156.4; HRMS (ES^+) calculated for $[C_{11}H_{18}NO]^+$ $(M+H)^+$ m/z: 180.1388, found 180.1395 (+3.9 ppm).



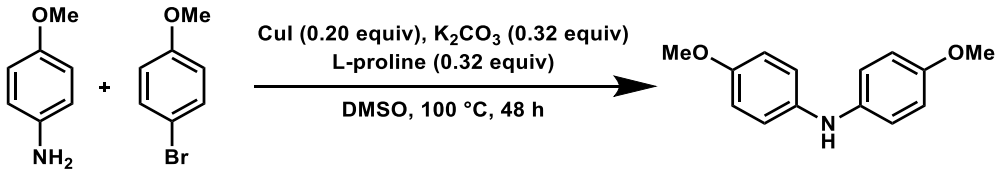


General procedure 1: N-methylation of diarylamines

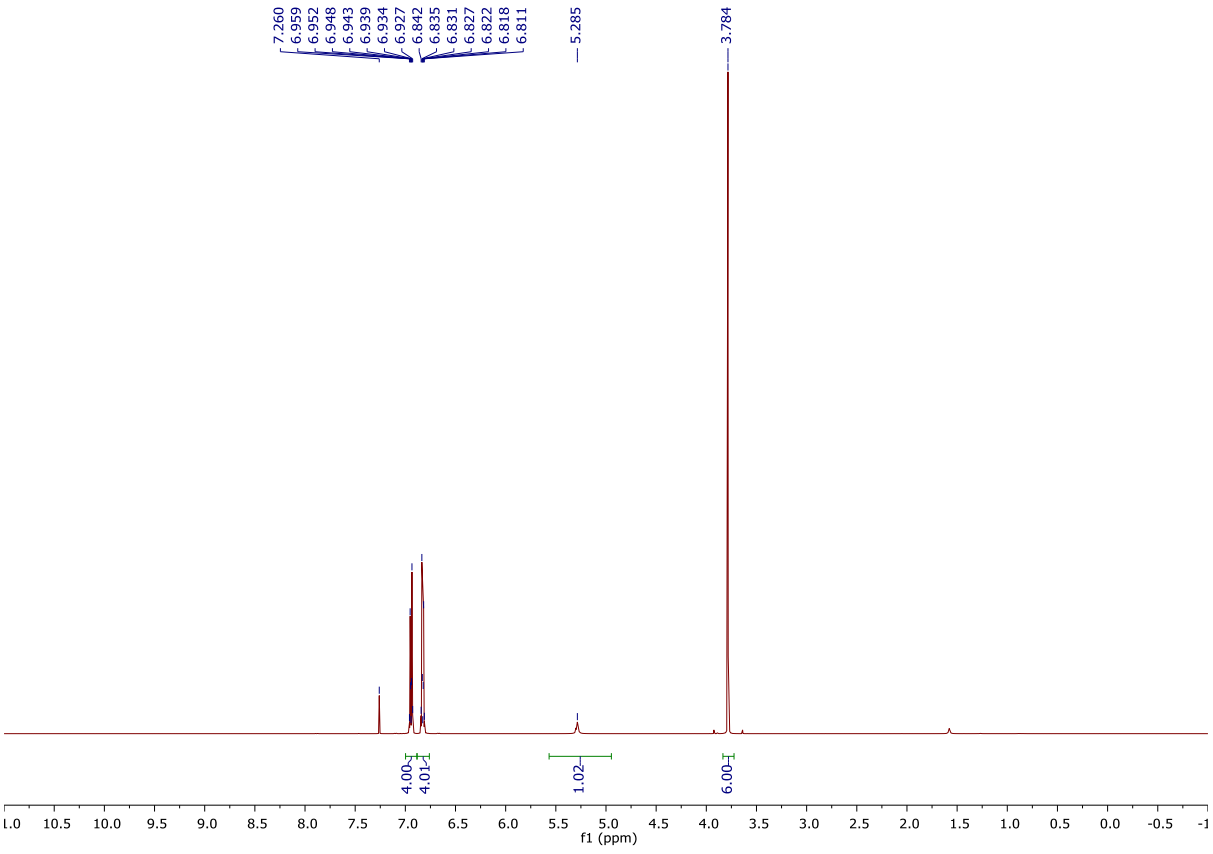


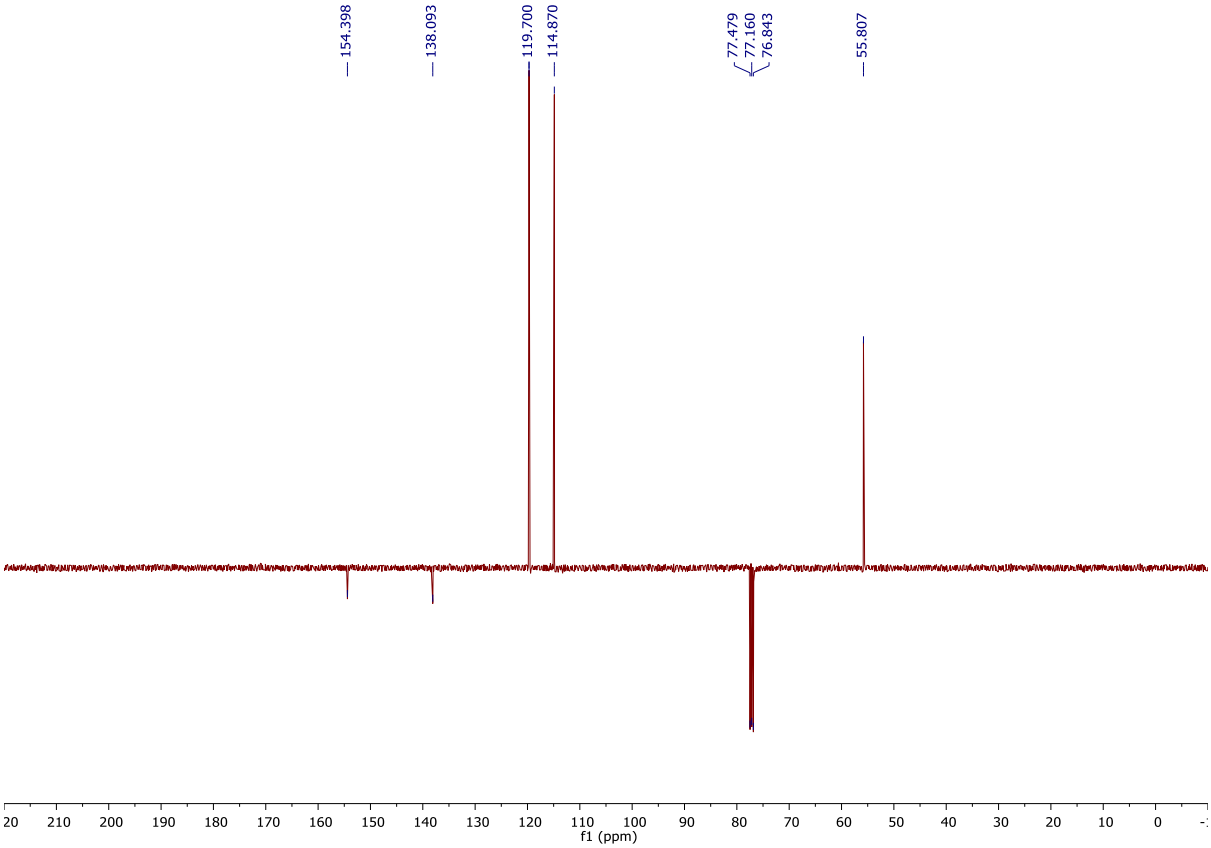
A sealed tube equipped with a magnetic stirrer bar was charged with diarylamine (1.0 equiv) and DMF (3 mL/mmol) and sealed with rubber septum under a nitrogen atmosphere. The mixture was cooled in an ice bath and NaH (60% in mineral oil) (1.2 equiv) was added. Then ice bath was removed and the resultant mixture was stirred at rt for 30 min. Again, the mixture was cooled in the ice bath and iodomethane (2.0 equiv) was added. Then the ice bath was removed and the reaction mixture was allowed to warm and stirred at rt for 1 h under nitrogen atmosphere. Then the reaction mixture in the sealed tube was sealed and stirred at 60 °C for 16 h. Then the reaction mixture was cooled to 0 °C. Water and EtOAc was added to the reaction mixture. The organic layer was separated, washed with brine (× 5–6), dried over $MgSO_4$, filtered, and concentrated *in vacuo*.

Bis(4-methoxyphenyl)amine

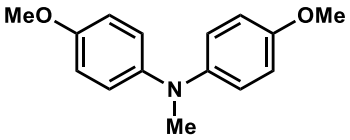


4-Aminoanisole (21.4 g, 200 mmol), 4-bromoanisole (20 mL, 30.0 g, 160 mmol), copper iodide (7.6 g, 40 mmol), potassium carbonate (8.9 g, 64 mmol) and L-proline (7.4 g, 64 mmol) were added to DMSO (250 mL) under N_2. The reaction mixture was stirred at 100 °C for 48 h, then quenched with water (250 mL) and extracted with diethyl ether (3 × 200 mL). The organics were combined, washed with brine, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Purification by flash silica chromatography (eluent = 10% EtOAc in hexanes, 70 × 180 mm silica) gave the title compound as a brown solid (15.0 g, 66 mmol, 41%); mp 106–109 °C (Lit. 100–104 °C);[3] R_f = 0.5 (eluent = 20% EtOAc in hexanes); ν_{max} / cm^{-1} (film) 2839, 1510, 1493, 1466, 1439, 1300, 1250, 1217, 1079, 1030, 816, 762, 706, 540, 523, 511, 419; ^1H NMR (500 MHz, $CDCl_3$) δ_H: 3.78 (6H, s), 5.29 (1H, br s), 6.76–6.88 (4H, m), 6.88–7.00 (4H, m); ^{13}C NMR (101 MHz, $CDCl_3$) δ_C: 55.8, 114.9, 119.7, 138.1, 154.4; HRMS (AP^+) calculated for $[C_{14}H_{16}NO_2]^+$ $(M+H)^+$ m/z: 230.1181, found 230.1185 (+1.7 ppm).

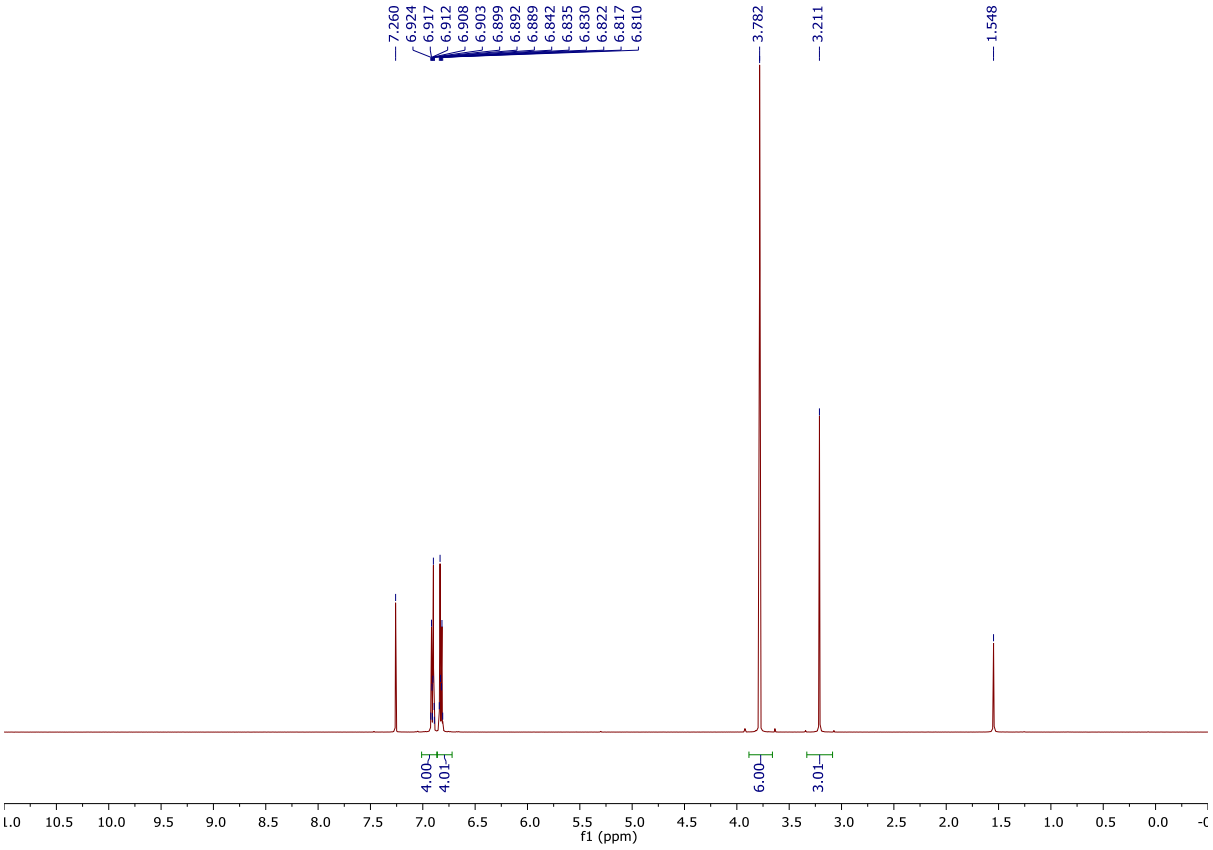




4-Methoxy-N-(4-methoxyphenyl)-N-methylaniline 4a



The title compound was prepared according to general procedure 1 using bis(4-methoxyphenyl)amine (3.06 g, 13.4 mmol). Purification by flash silica chromatography (eluent = 2% EtOAc in hexanes, 40 × 180 mm silica) gave the title compound **4a** as an off-white solid (2.64 g, 10.8 mmol, 81%); mp 96–98 °C (Lit. 99–99.5 °C);[4] R_f = 0.57 (eluent = 10% EtOAc in hexanes); ν_{max} / cm^{-1} (film) 2953, 2835, 1508, 1464, 1439, 1331, 1281, 1231, 1182, 1076, 1028, 824, 766, 556, 530; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 3.21 (3H, s), 3.78 (6H, s), 6.79–6.86 (4H, m), 6.87–6.94 (4H, m); ^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 41.2, 55.8, 114.7, 121.7, 143.8, 154.5; HRMS (ES$^+$) calculated for $[C_{15}H_{18}NO_2]^+$ $(M+H)^+$ m/z: 244.1338, found 244.1329 (-3.7 ppm).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6.903
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6.892
6.889
6.842
6.835
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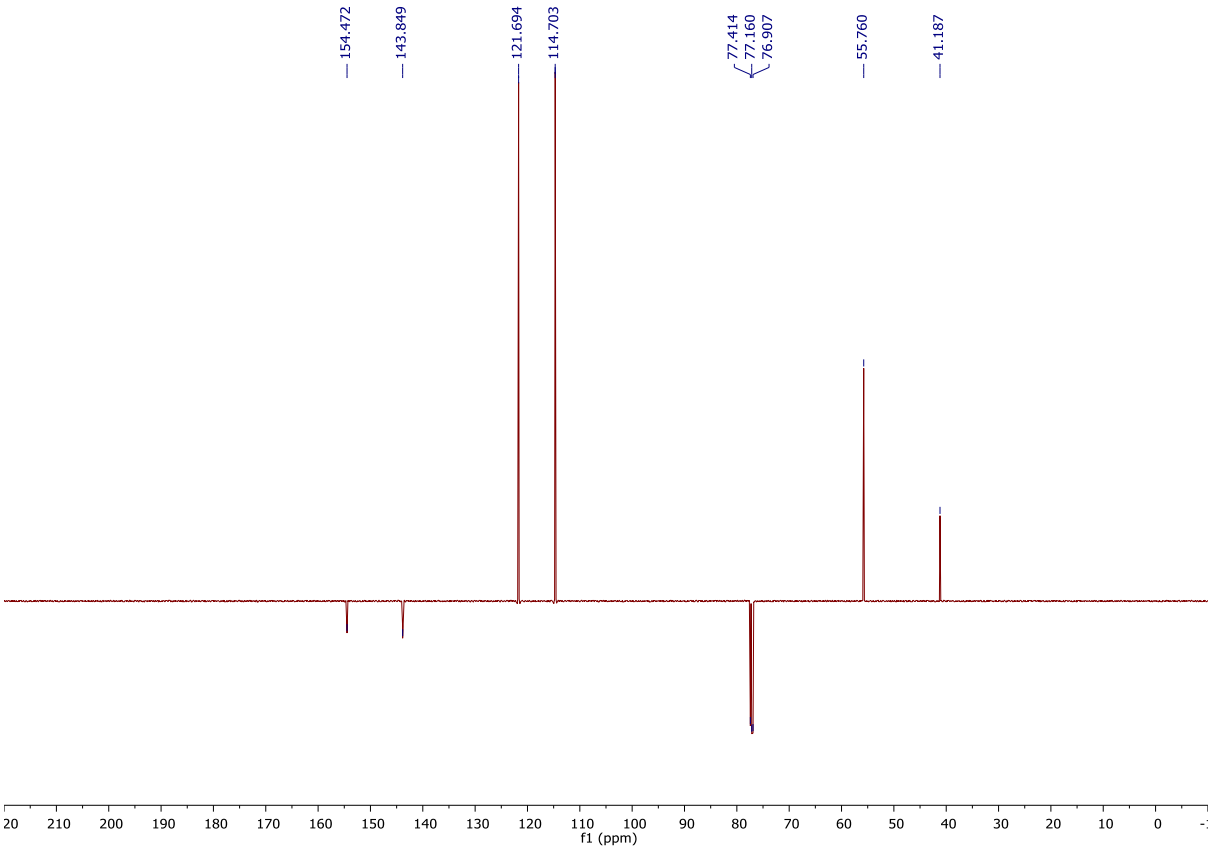
4.00
4.01
6.00
3.01
f1 (ppm)


154.472
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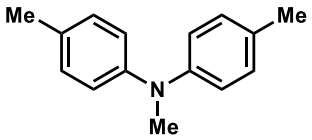
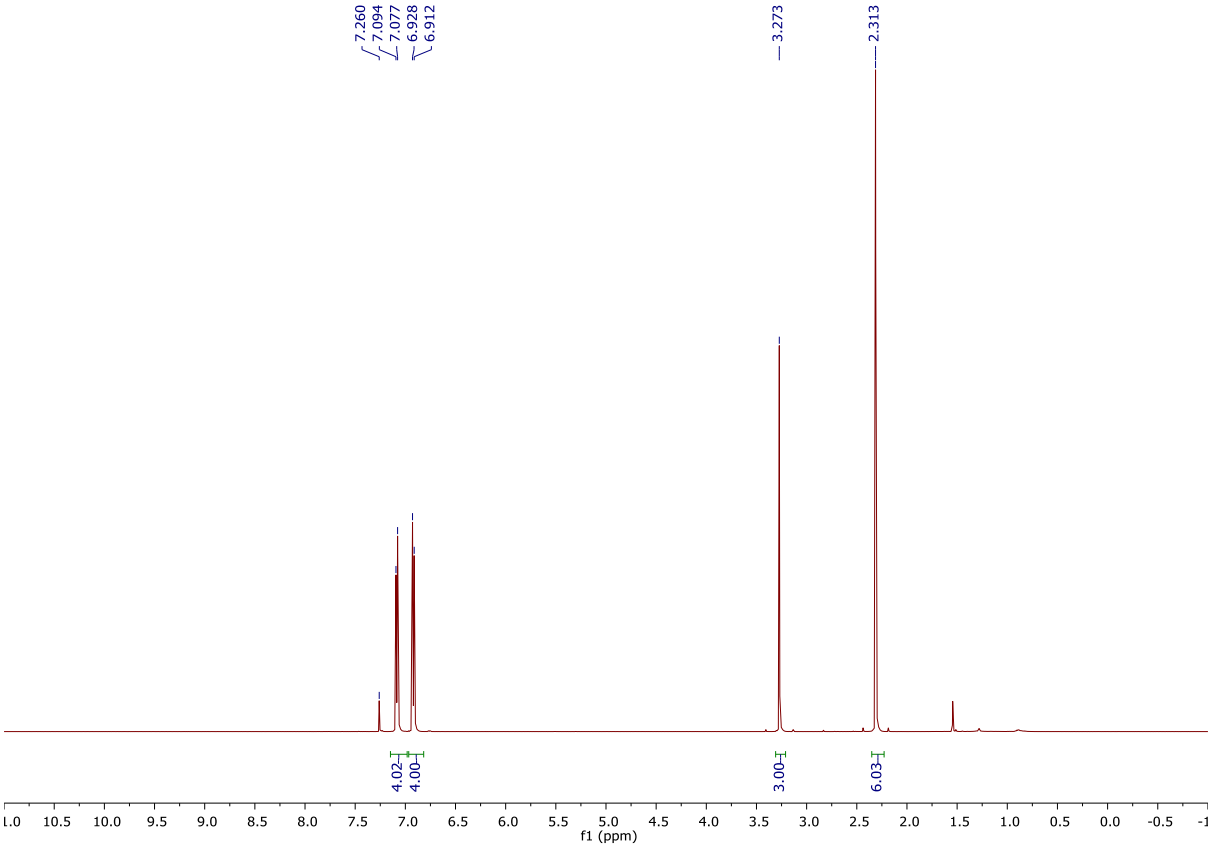
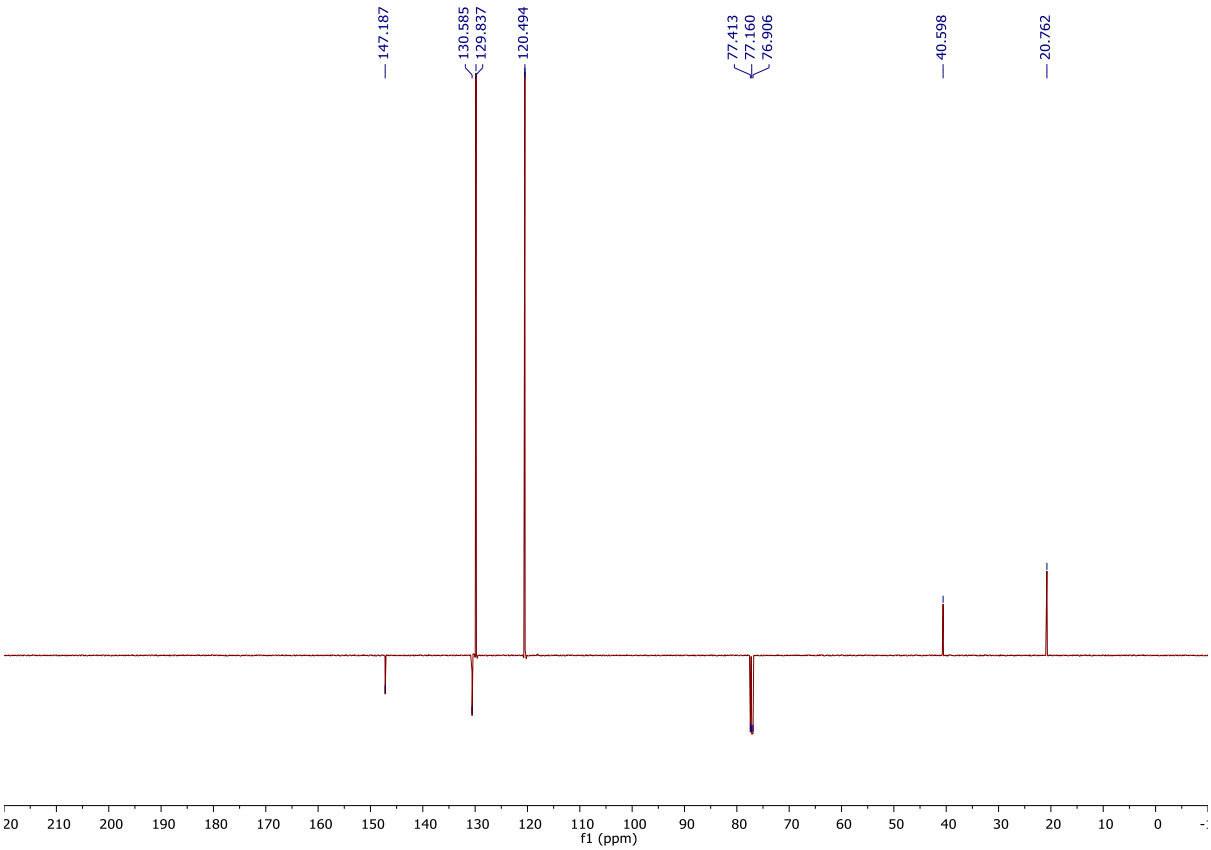
f1 (ppm)

N,4-Dimethyl-N-(*p*-tolyl)aniline S7

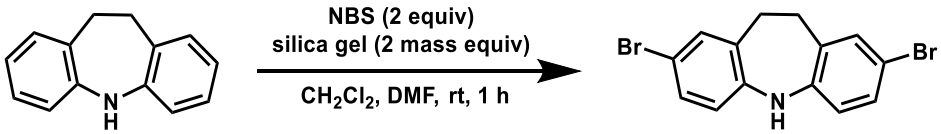


The title compound was prepared according to general procedure 1 using di-*p*-tolylamine (4.00 g, 20.3 mmol). Purification by flash silica chromatography (eluent = 1-2% EtOAc in hexanes, 40 × 180 mm silica) gave the title compound **S7** as colorless oil (3.92 g, 18.6 mmol, 91%); R_f = 0.67 (eluent = 5% EtOAc in hexanes); ν_{max} / cm^{-1} (film) 3024, 2918, 2860, 2806, 1609, 1570, 1506, 1333, 1252, 1123, 1107, 1072, 870, 804, 721, 561, 534, 507, 459, 417; ^1H NMR (500 MHz, $CDCl_3$) δ_H: 2.31 (6H, s), 3.27 (3H, s), 6.92 (4H, d, *J* 8.3), 7.09 (4H, d, *J* 8.3); ^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 20.8, 40.6, 120.5, 129.8, 130.6, 147.2; HRMS (ES^+) calculated for $[C_{15}H_{18}N]^+$ $(M+H)^+$ m/z: 212.1439, found 212.1434 (-2.4 ppm).

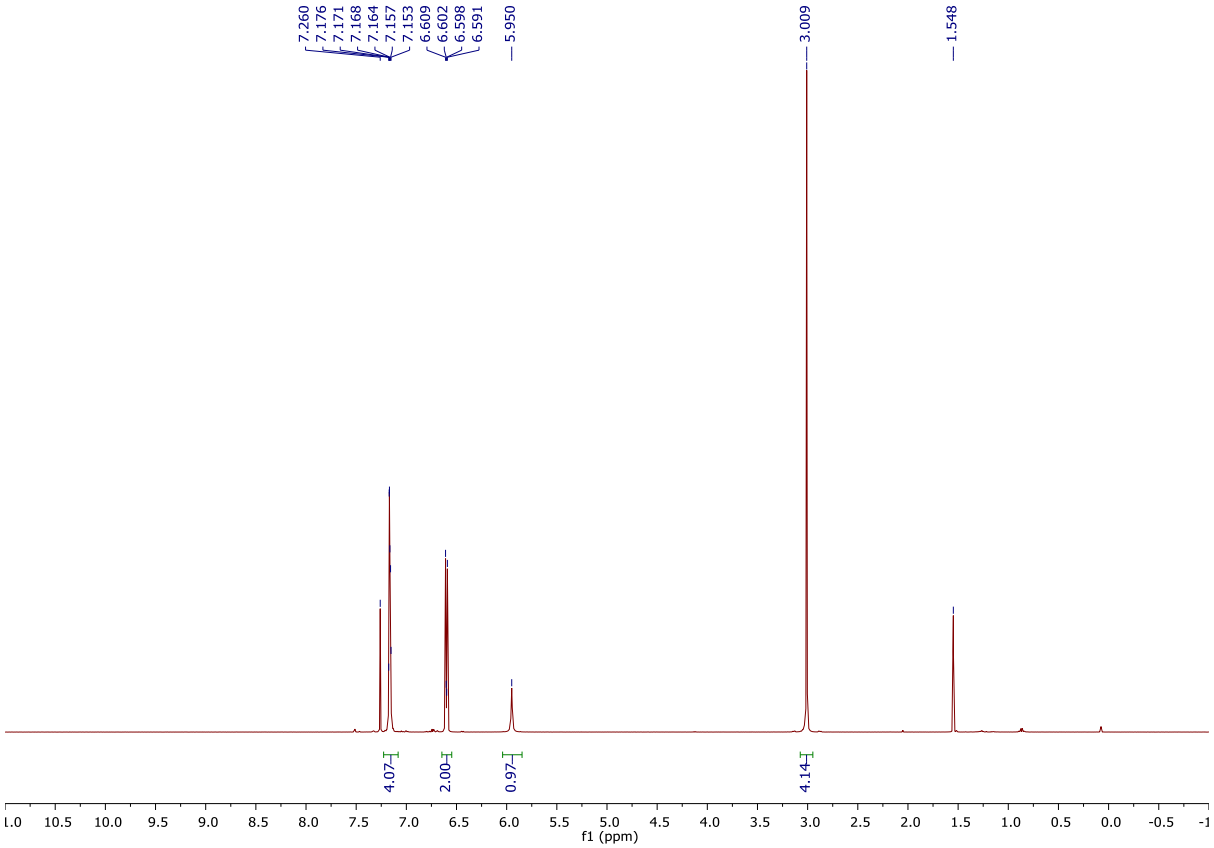




2,8-Dibromo-10,11-dihydro-5H-dibenzo[*b*,*f*]azepine



Iminodibenzyl (10.0 g, 51.2 mmol) was added to a stirred mixture of silica gel (20.0 g) in CH_2Cl_2 (150 mL). After stirring for 5 min, N-bromosuccinimide (18.3 g, 102 mmol) dissolved in CH_2Cl_2 : DMF (250 : 150 mL) was added dropwise and stirred for 1 h at room temperature. Reaction mixture was filtered and washed with CH_2Cl_2. Purification by flash silica chromatography (eluent = 2–5% EtOAc in hexanes, 50 × 180 mm silica) gave the title compound as an off-white solid (16.8 g, 47.8 mmol, 94%); mp 179–182 °C (Lit. 177–178 °C);[5] R_f = 0.67 (eluent = 20% EtOAc in hexanes); ν_{max} / cm^{-1} (film) 3404, 1607, 1570, 1518, 1485, 1437, 1397, 1341, 1325, 1244, 1136, 1125, 1090, 891, 878, 801, 503, 482, 442; ^1H NMR (500 MHz, $CDCl_3$) δ_H: 3.01 (4H, s), 5.95 (1H, br s), 6.55–6.65 (2H, m), 7.08–7.23 (4H, m); ^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 34.5, 111.9, 119.7, 129.8, 130.6, 133.3, 141.2; HRMS $(ES)^+$ calculated for $[C_{14}H_{12}NBr_2]^+$ $(M+H)^+$ m/z: 351.9337, found 351.9344 (+2.0 ppm).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7.157
7.153
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1.548
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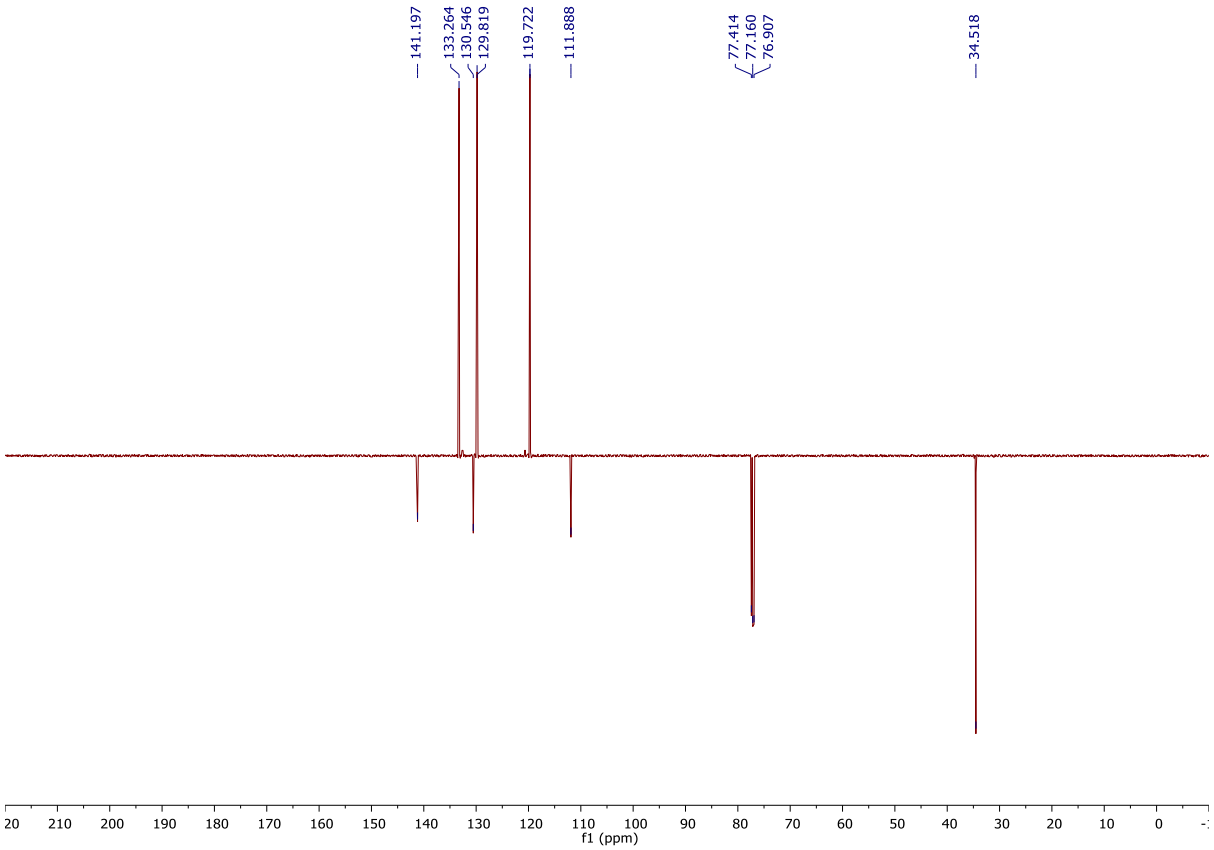
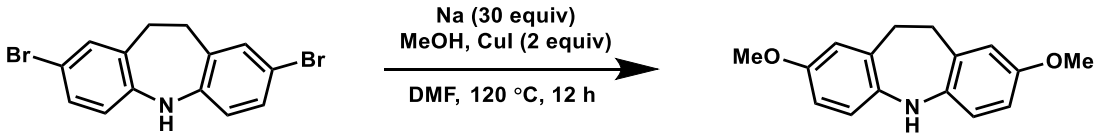
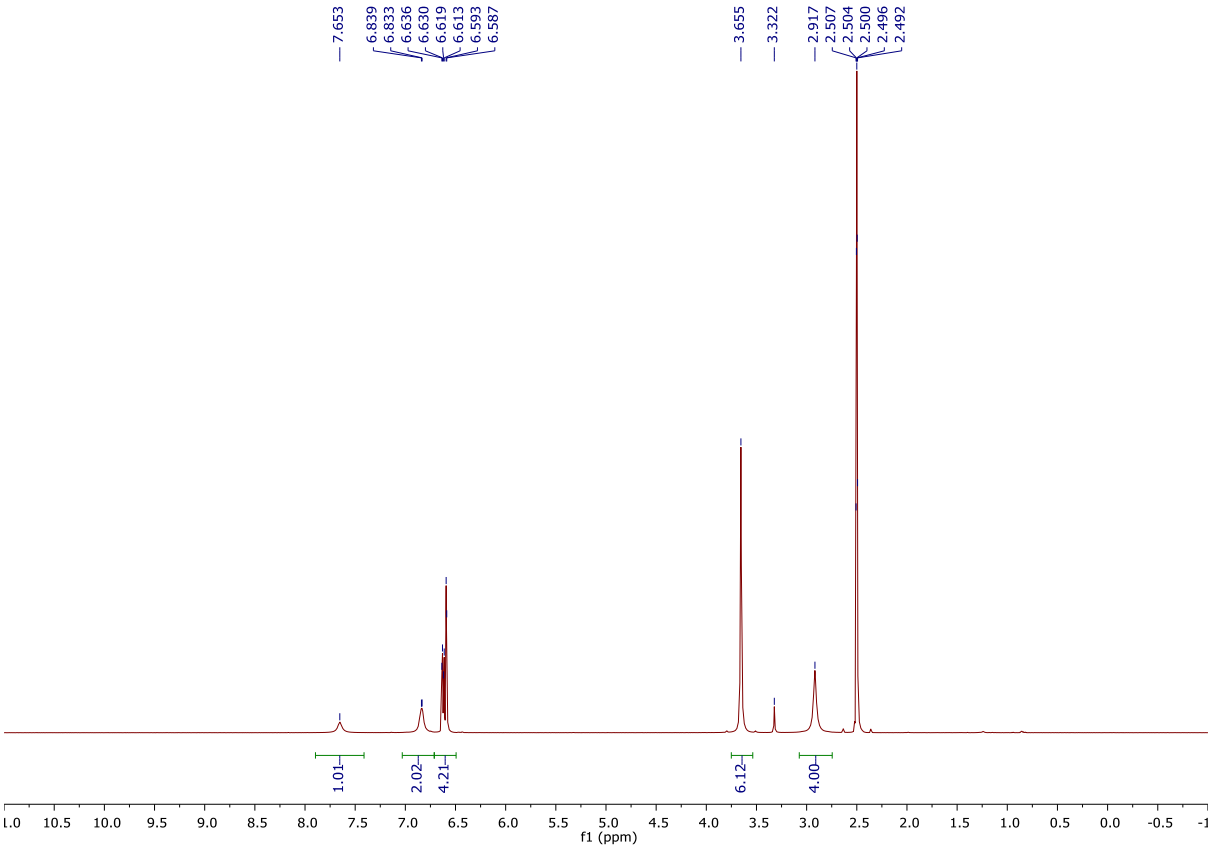
2.00
0.97
4.14
f1 (ppm)

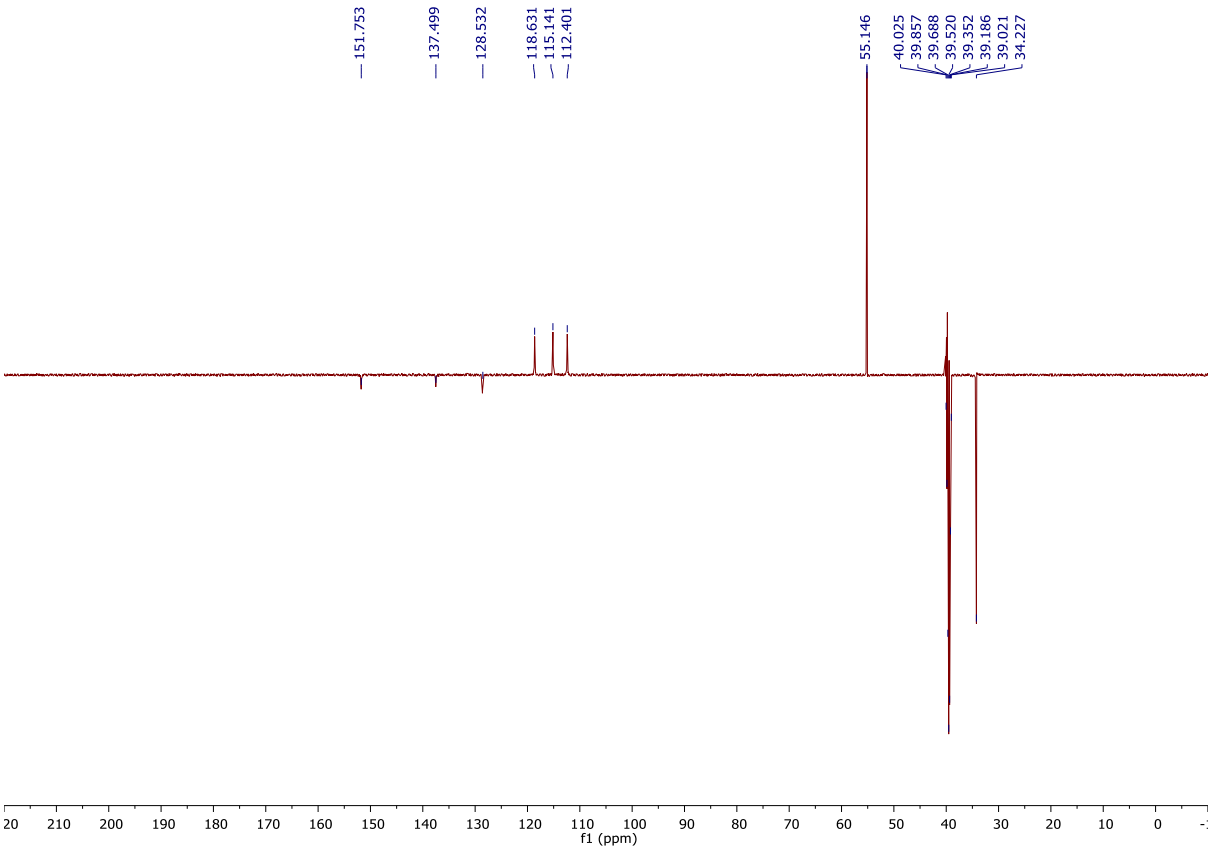

141.197
133.264
130.546
129.819
119.722
111.888
77.414
77.160
76.907
34.518
f1 (ppm)

2,8-Dimethoxy-10,11-dihydro-5H-dibenzo[*b*,*f*]azepine

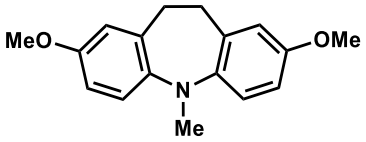


Na (35.0 g, 1.52 mol) was dissolved in dry MeOH (400 mL) under N_2 at 0 °C, and then 2,8-dibromo-10,11-dihydro-5H-dibenzo[*b*,*f*]azepine (17.9 g, 51.0 mmol), CuI (19.4 g, 102 mmol) and DMF (200 mL) were added at room temperature and stirred at 120 °C for 12 h. After cooling to room temperature, the mixture was filtered through Celite with EtOAc, and evaporated and cold water added. The precipitate was filtered and washed thoroughly with cold water to obtain the crude brown solid. The solid was dissolved in CH_2Cl_2 and passed through short silica plug (70 × 100 mm silica) and eluted with CH_2Cl_2 to obtain the title compound as an off-white solid (12.1 g, 47.2 mmol, 93%); mp 130–133 °C; R_f = 0.40 (eluent = 10% EtOAc in hexanes); ν_{max} / cm^{-1} (film) 3387, 2943, 2911, 1501, 1433, 1250, 1221, 1194, 1163, 1032, 986, 910, 853, 826, 808, 727, 704, 569, 490; ^{1}H NMR (500 MHz, DMSO-d_6) δ_H: 2.92 (4H, s), 3.66 (6H, s), 6.49–6.71 (4H, m), 6.71–7.03 (2H, m), 7.65 (1H, br s); ^{13}C NMR (126 MHz, DMSO-d_6) δ_C: 34.2, 55.2, 112.4, 115.1, 118.6, 128.5, 137.5, 151.8; HRMS (ES)$^+$ calculated for $[C_{16}H_{18}NO_2]^+$ $(M+H)^+$ m/z: 256.1338, found 256.1344 (+2.3 ppm).

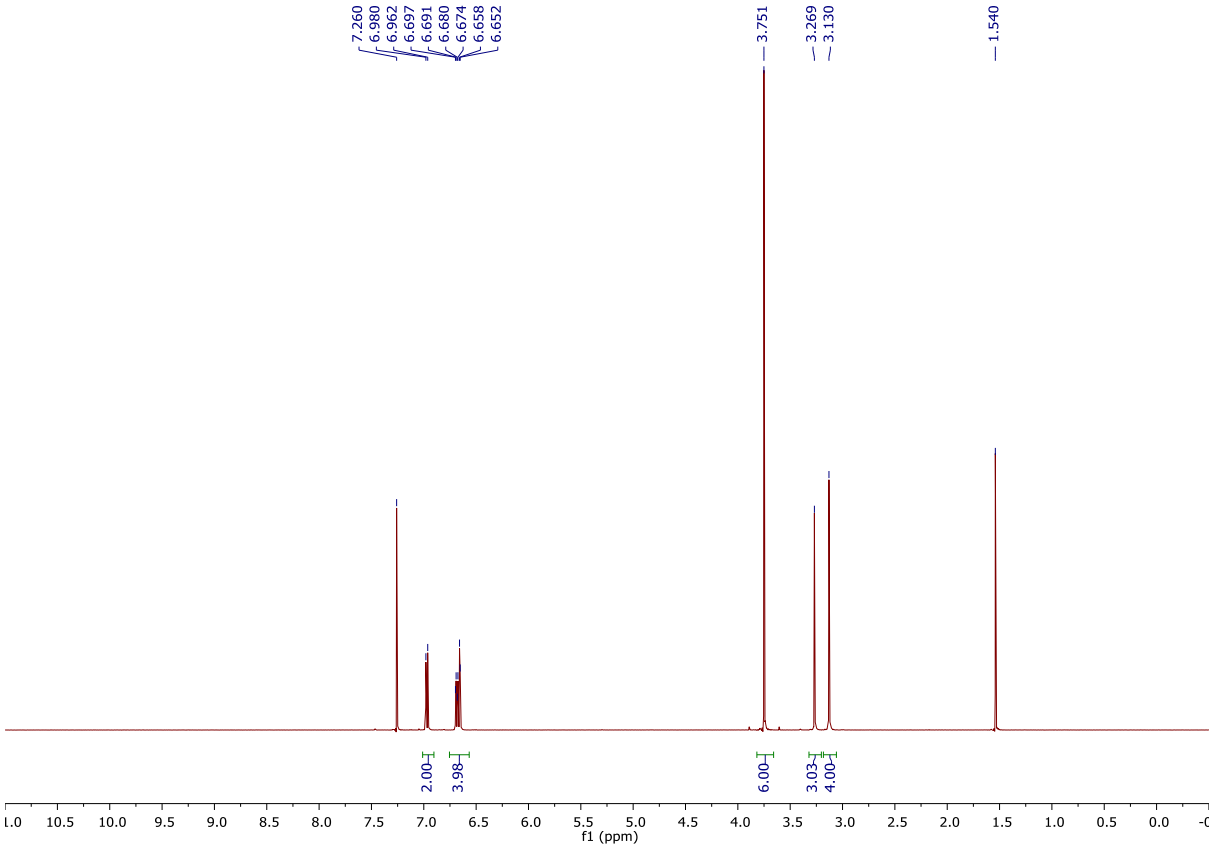


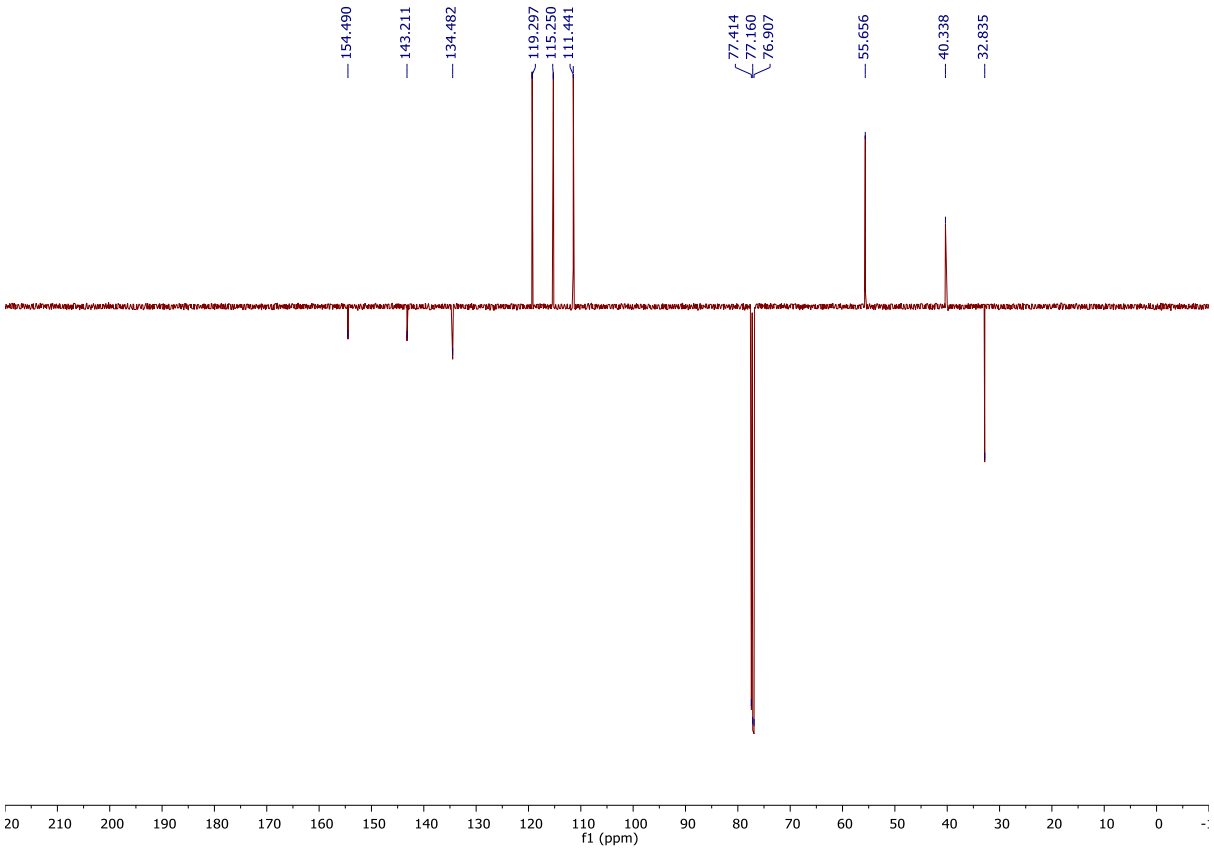


2,8-Dimethoxy-5-methyl-10,11-dihydro-5H-dibenzo[*b*,*f*]azepine 6a

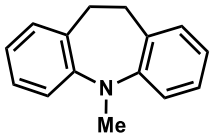


The title compound was prepared according to general procedure 1 using 2,8-dimethoxy-10,11-dihydro-5H-dibenzo[*b*,*f*]azepine (2.74 g, 10.7 mmol). Purification by flash silica chromatography (eluent = 1-2% EtOAc in hexanes, 40 × 180 mm silica) gave the title compound **6a** as a white crystalline solid (2.67 g, 9.93 mmol, 93%); mp 141–144 °C; R_f = 0.52 (eluent = 10% EtOAc in hexanes); ν_{max} / cm^{-1} (film) 2963, 2914, 1605, 1584, 1491, 1479, 1466, 1445, 1427, 1225, 1213, 1155, 1144, 1047, 1030, 880, 849, 814, 721, 704, 606, 544, 500; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 3.13 (4H, s), 3.27 (3H, s), 3.75 (6H, s), 6.57–6.75 (4H, m), 6.97 (2H, d, *J* 8.7); ^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 32.8, 40.3, 55.7, 111.4, 115.3, 119.3, 134.5, 143.2, 154.5; HRMS (ES)$^+$ calculated for $[C_{17}H_{20}NO_2]^+$ $(M+H)^+$ m/z: 270.1494, found 270.1502 (+3.0 ppm).

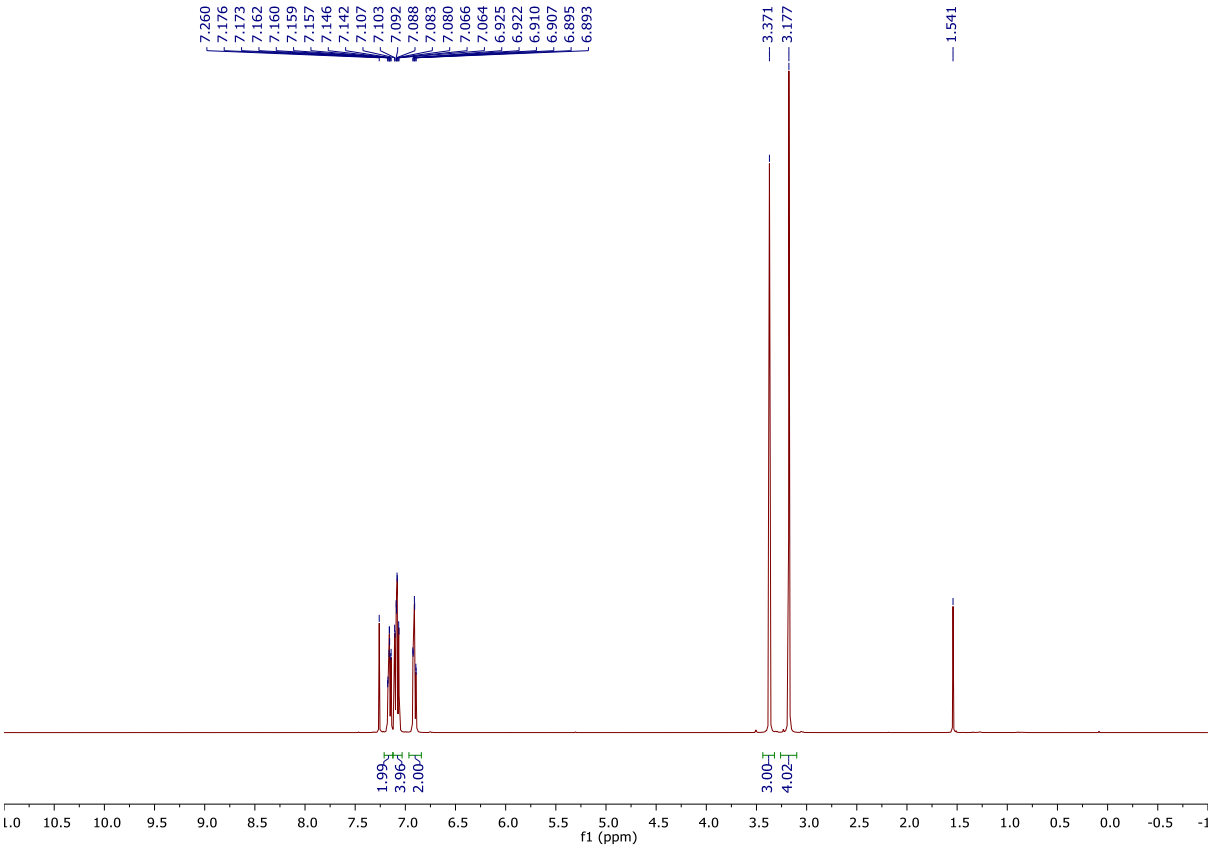

7.260
6.980
6.962
6.697
6.691
6.680
6.674
6.658
6.652
3.751
3.269
3.130
1.540
2.00
3.98
6.00
3.03
4.00
f1 (ppm)

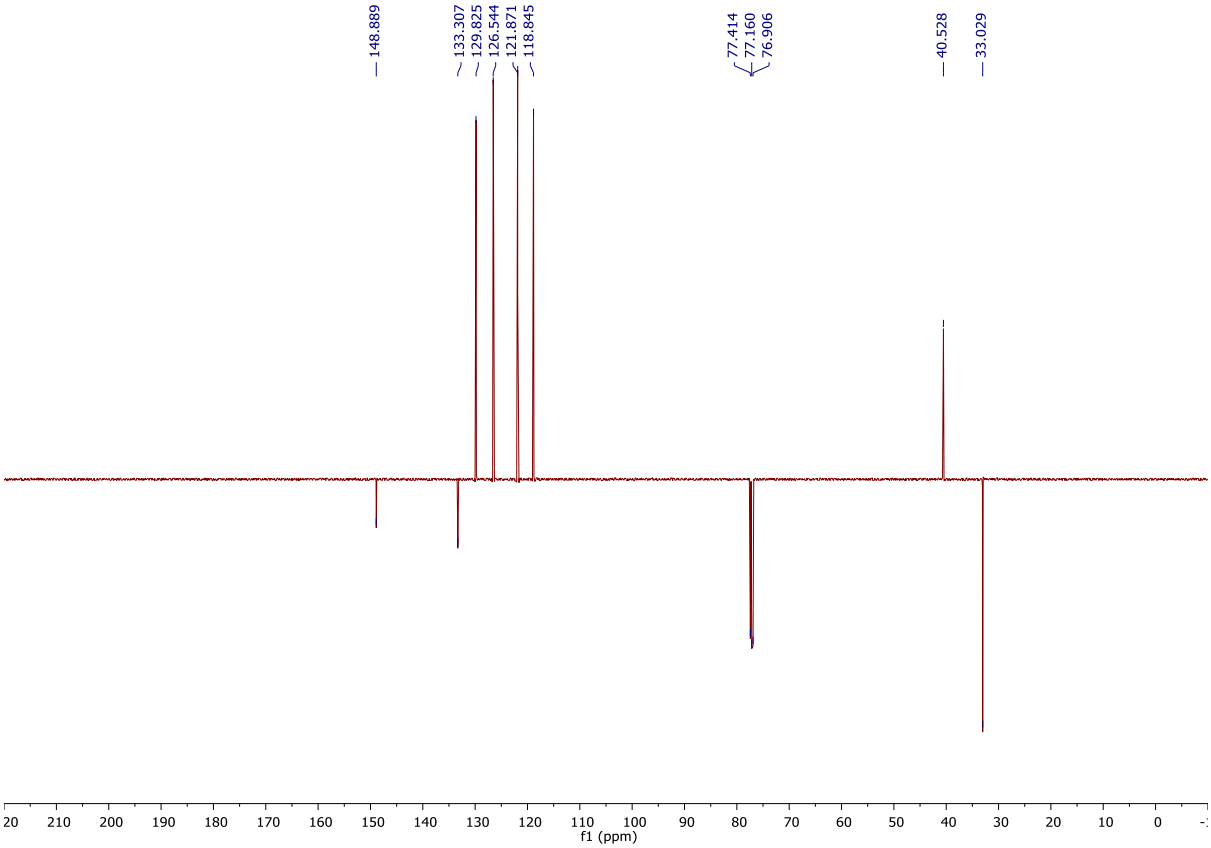

154.490
143.211
134.482
119.297
115.250
111.441
77.414
77.160
76.907
55.656
40.338
32.835
f1 (ppm)

5-Methyl-10,11-dihydro-5H-dibenzo[*b*,*f*]azepine 7

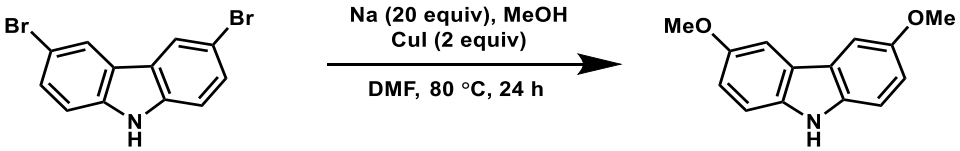


The title compound was prepared according to general procedure 1 using iminodibenzyl (5.0 g, 25.6 mmol). Purification by flash silica chromatography (eluent = 1–2% EtOAc in hexanes, 40 × 180 mm silica) gave the title compound **7** as white solid (4.4 g, 21.2 mmol, 83%); mp 109–111 °C (Lit. 106–107 °C);[6] R_f = 0.48 (eluent = 5% EtOAc in hexanes); ν_{max} / cm^{-1} (film) 2909, 1591, 1570, 1474, 1447, 1325, 1263, 1233, 1128, 1107, 1053, 934, 916, 847, 762, 739, 712, 598, 583, 502, 446; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 3.18 (4H, s), 3.37 (3H, s), 6.91 (2H, td, *J* 7.3, 1.3), 7.06–7.11 (4H, m), 7.14–7.18 (2H, m); ^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 33.0, 40.5, 118.9, 121.9, 126.5, 129.8, 133.3, 148.9; HRMS (AP^+) calculated for $[C_{15}H_{16}N]^+$ $(M+H)^+$ m/z: 210.1283, found 210.1286 (+1.4 ppm).

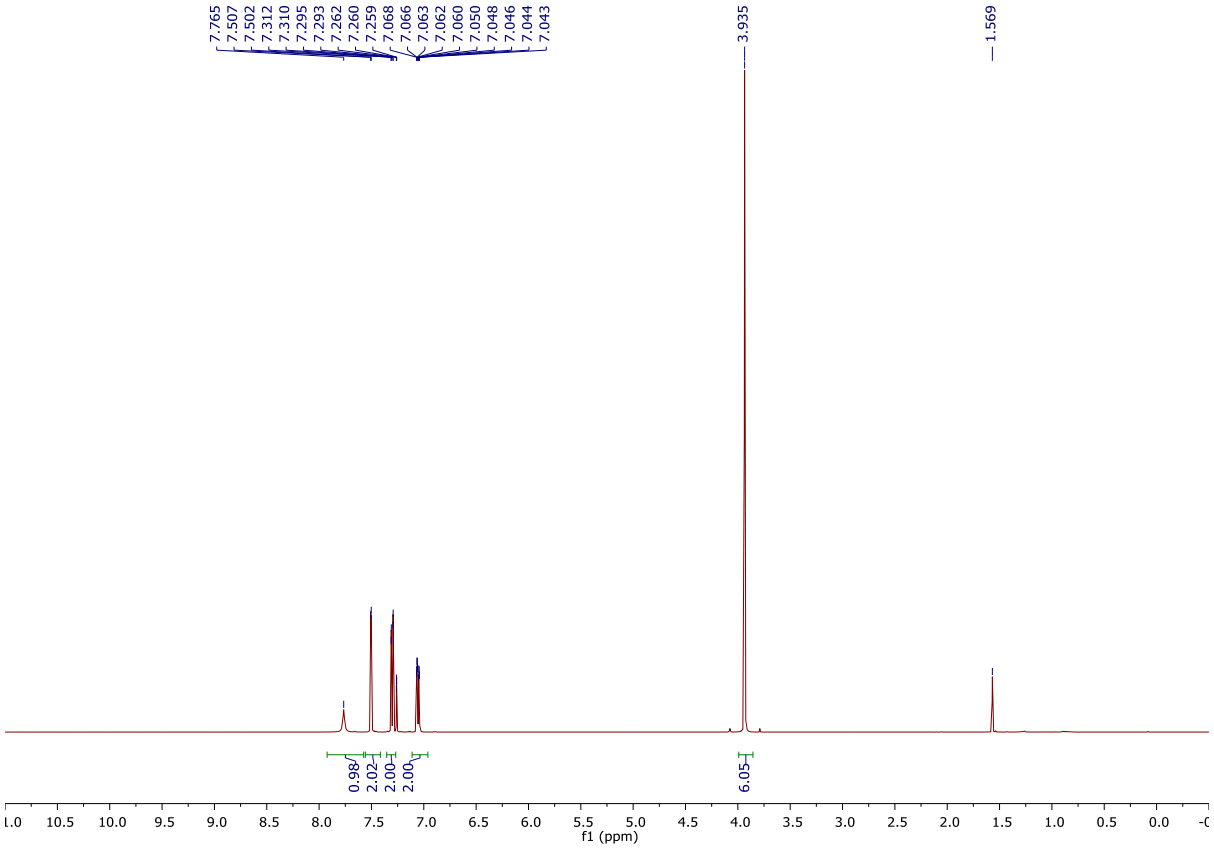


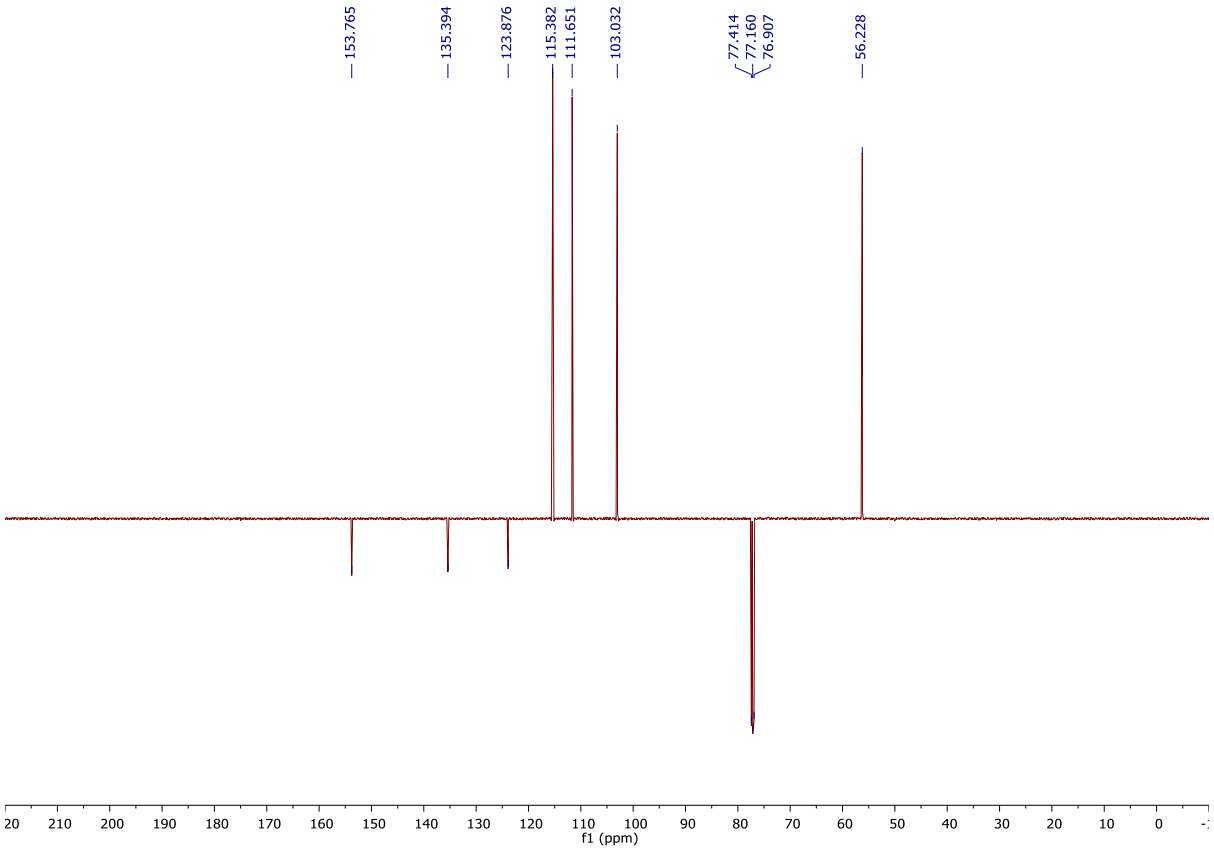


3,6-Dimethoxy-9H-carbazole

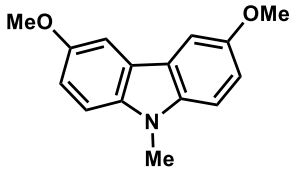


Na (3.54 g, 154 mmol) was dissolved in dry MeOH (42 mL) under N_2 at 0 °C, and then 3,6-dibromo-9H-carbazole (2.50 g, 7.7 mmol), CuI (2.93 g, 15.4 mmol) and DMF (84 mL) were added at room temperature and stirred at 80 °C for 24 h. After cooling to room temperature, the mixture was filtered through Celite, and evaporated. Water (60 mL) and EtOAc (100 mL) was added to the reaction mixture. The organic layer was separated, washed with brine (5 × 50 mL), dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Purification by flash silica chromatography (eluent = 10% EtOAc in pet. ether, 40 × 150 mm silica) gave the title compound as a white solid (1.51 g, 6.64 mmol, 86%); mp 110–112 °C (Lit. 105–107 °C);[7] R_f = 0.2 (eluent = 10% EtOAc in pet. ether); ν_{max} / cm^{-1} (film) 3431, 3408, 3374, 2996, 2940, 2903, 2830, 1611, 1574, 1495, 1462, 1429, 1335, 1302, 1265, 1200, 1153, 1024, 828, 808, 777, 594, 482, 442, 422; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 3.94 (6H, s), 7.06 (2H, ddd, *J* 8.7, 2.9, 0.9), 7.30 (2H, dd, *J* 8.8, 1.0), 7.50 (2H, d, *J* 2.5), 7.77 (1H, br s); ^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 56.2, 103.0, 111.7, 115.4, 123.9, 135.4, 153.8; HRMS (ES^+) calculated for $[C_{14}H_{14}NO_2]^+$ $(M+H)^+$ m/z: 228.1025, found 228.1027 (+0.9 ppm).

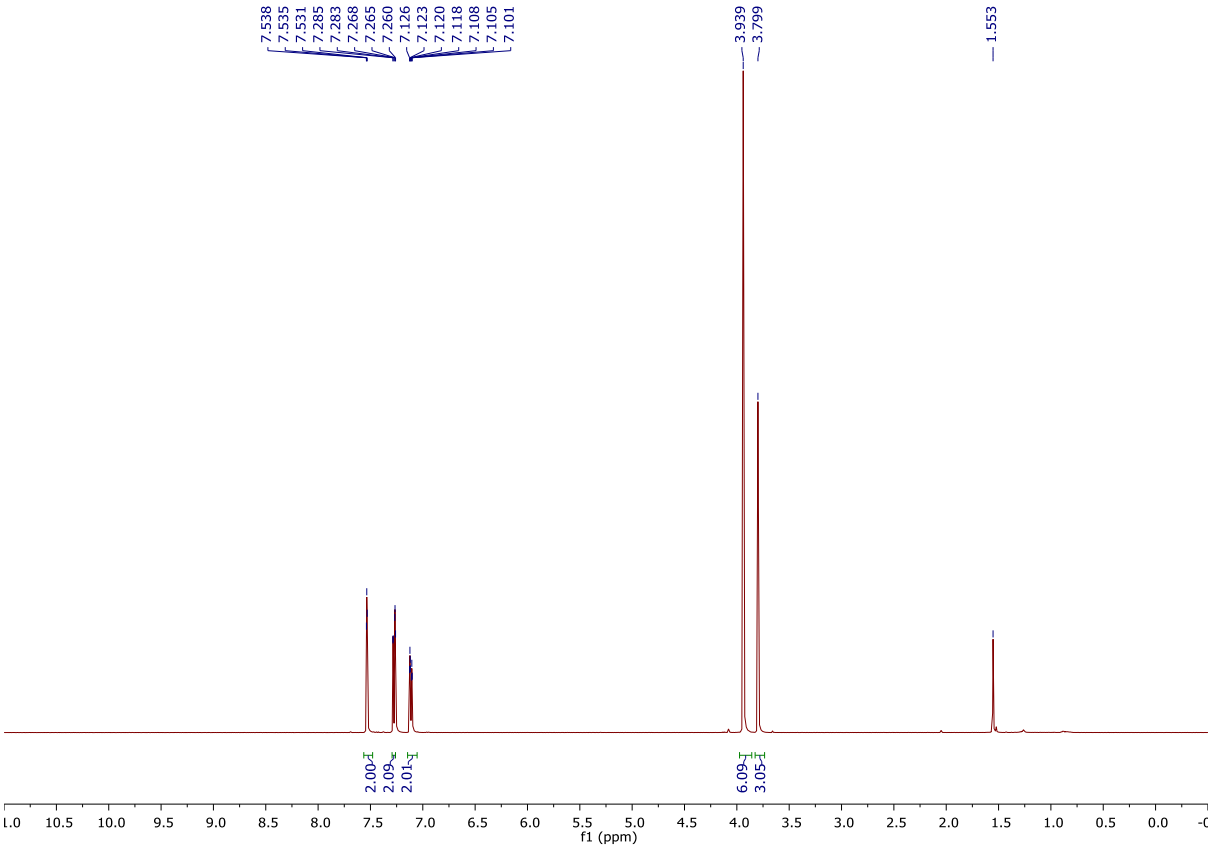

7.765
7.507
7.502
7.312
7.310
7.295
7.293
7.262
7.260
7.259
7.068
7.066
7.063
7.062
7.060
7.050
7.048
7.046
7.044
7.043
3.935
1.569
0.98
2.02
2.00
2.00
6.05
f1 (ppm)

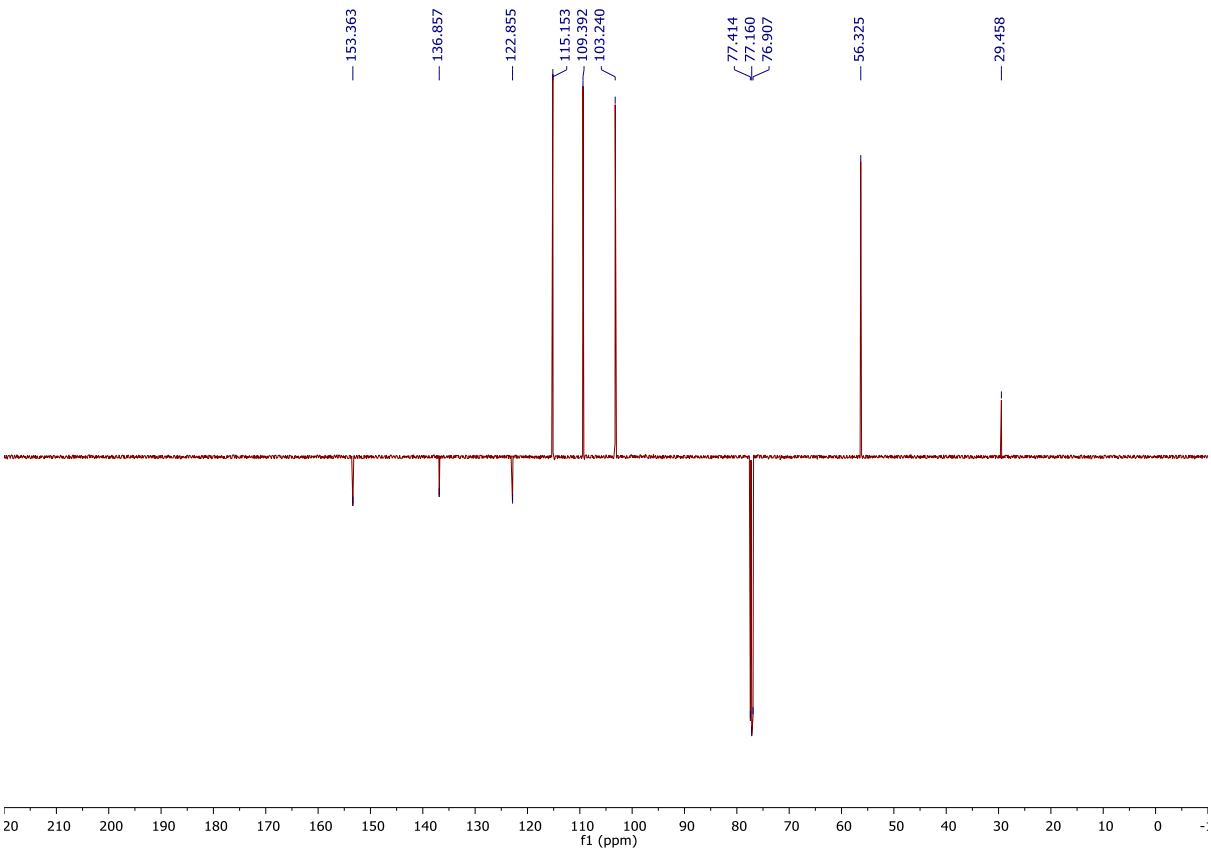

153.765
135.394
123.876
115.382
111.651
103.032
77.414
77.160
76.907
56.228
f1 (ppm)

3,6-Dimethoxy-9-methyl-9H-carbazole S8

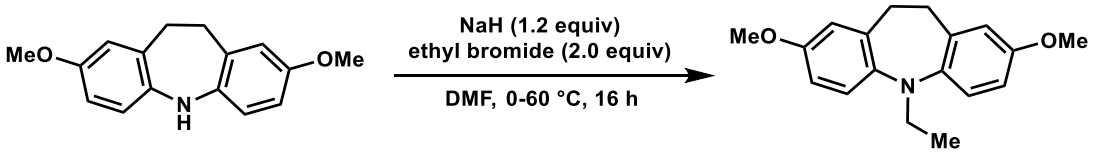


The title compound was prepared according to general procedure 1 using 3,6-dimethoxy-9H-carbazole (1.44 g, 6.31 mmol). Purification by flash silica chromatography (eluent = 10% EtOAc in hexanes, 30 × 180 mm silica) gave the title compound **S8** as a white crystalline solid (1.49 g, 6.17 mmol, 98%); mp 186–188 °C; R_f = 0.38 (eluent = 10% EtOAc in hexanes); ν_{max} / cm^{-1} (film) 2970, 2936, 2830, 1603, 1574, 1483, 1422, 1329, 1304, 1267, 1211, 1200, 1155, 1059, 1022, 835, 806, 775, 650, 586, 556, 482, 424; ^1H NMR (500 MHz, $CDCl_3$) δ_H: 3.80 (3H, s), 3.94 (6H, s), 7.05–7.15 (2H, m), 7.28 (2H, dd, *J* 8.7, 1.2), 7.53 (2H, t, *J* 1.8); ^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 29.5, 56.3, 103.2, 109.4, 115.2, 122.9, 136.9, 153.4; HRMS (ES)$^+$ calculated for $[C_{15}H_{16}NO_2]^+$ $(M+H)^+$ m/z: 242.1181, found 242.1184 (+1.2 ppm).

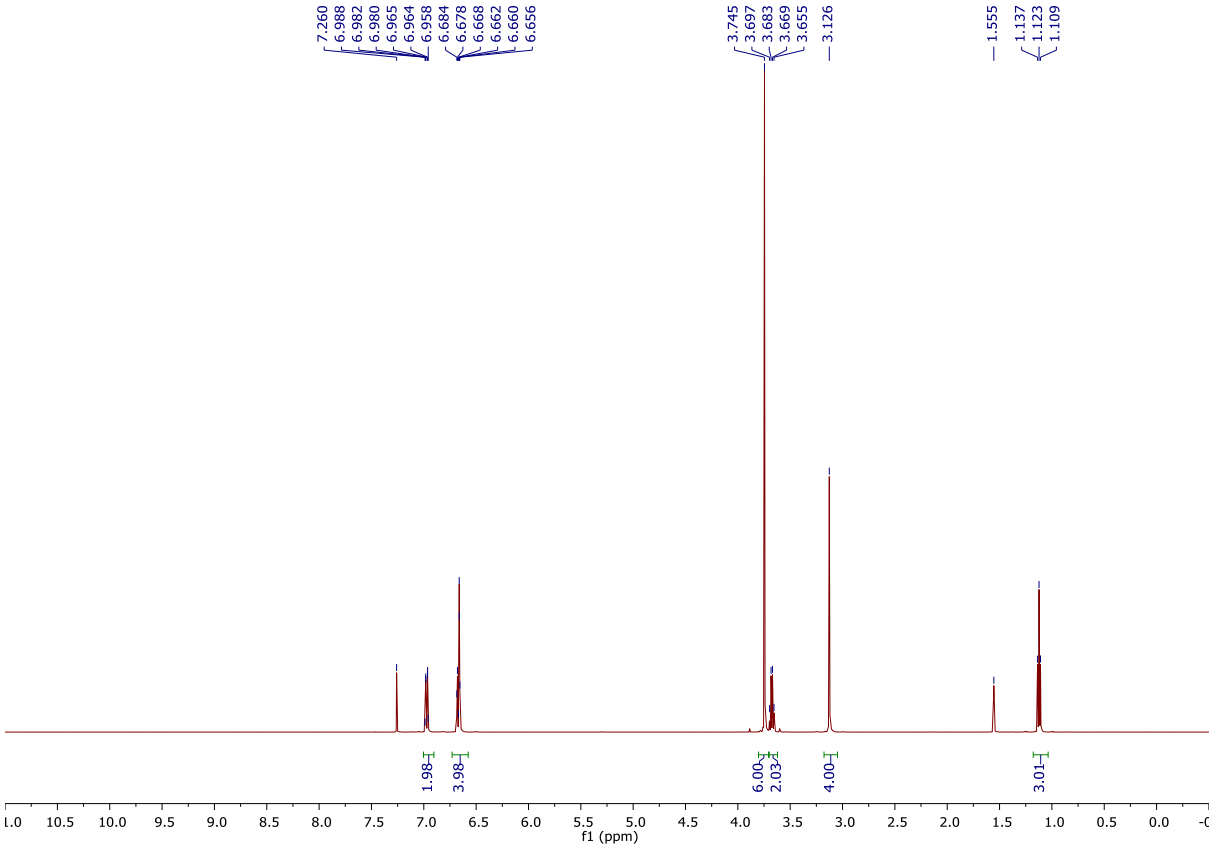


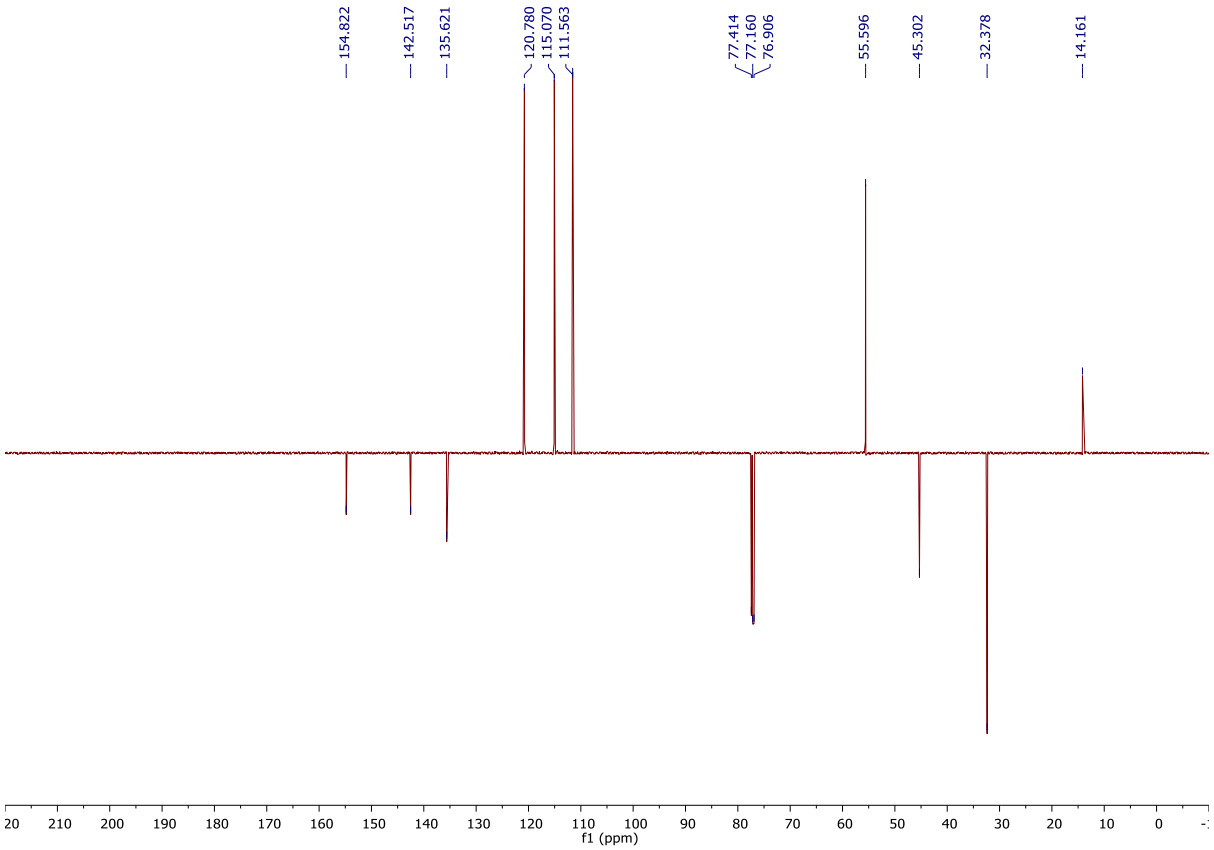


5-Ethyl-2,8-dimethoxy-10,11-dihydro-5H-dibenzo[*b*,*f*]azepine 6b

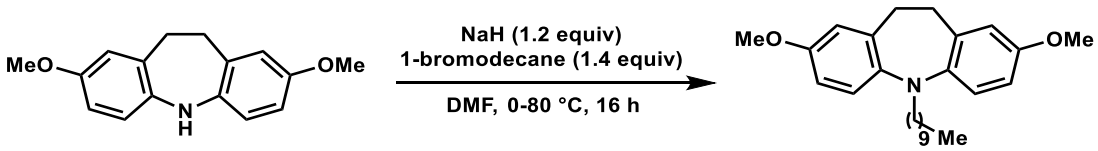


A sealed tube equipped with a magnetic stirrer bar was charged with 2,8-dimethoxy-10,11-dihydro-5H-dibenzo[*b*,*f*]azepine (1.5 g, 5.88 mmol) and DMF (18 mL). The mixture was cooled in an ice bath and NaH (60% in mineral oil) (283 mg, 7.08 mmol) was added. Then ice bath was removed and the resultant mixture was stirred at rt for 30 min. Again, the mixture was cooled in the ice bath and ethyl bromide (0.87 mL, 11.8 mmol) was added. After removing rubber septa, the reaction mixture in the sealed tube was sealed with a screw tight cap and stirred at 60 °C for 16 h. Then the reaction mixture was cooled. Water (50 mL) and EtOAc (100 mL) was added to the reaction mixture. The organic layer was separated, washed with brine (5 × 50 mL), dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Purification by flash silica chromatography (eluent = 1–2% EtOAc in hexanes, 30 × 180 mm silica) gave the title compound **6b** as a white solid (934 mg, 3.30 mmol, 56%) along with recovery of the starting material (601 mg, 2.35 mmol, 40%); mp 79–81 °C; R_f = 0.39 (eluent = 5% EtOAc in hexanes); ν_{max} / cm^{-1} (film) 2976, 2830, 1605, 1491, 1468, 1427, 1316, 1267, 1252, 1217, 1153, 1047, 1030, 988, 883, 858, 808, 797, 720, 702, 608, 571, 550, 532, 491, 446, 432; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 1.12 (3H, t, *J* 7.0), 3.13 (4H, s), 3.68 (2H, q, *J* 7.0), 3.75 (6H, s), 6.58–6.73 (4H, m), 6.97 (2H, dd, *J* 8.2, 0.8); ^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 14.2, 32.4, 45.3, 55.6, 111.6, 115.1, 120.8, 135.6, 142.5, 154.8; HRMS (AP)$^+$ calculated for $[C_{18}H_{22}NO_2]^+$ $(M+H)^+$ m/z: 284.1651, found 284.1657 (+2.1 ppm).

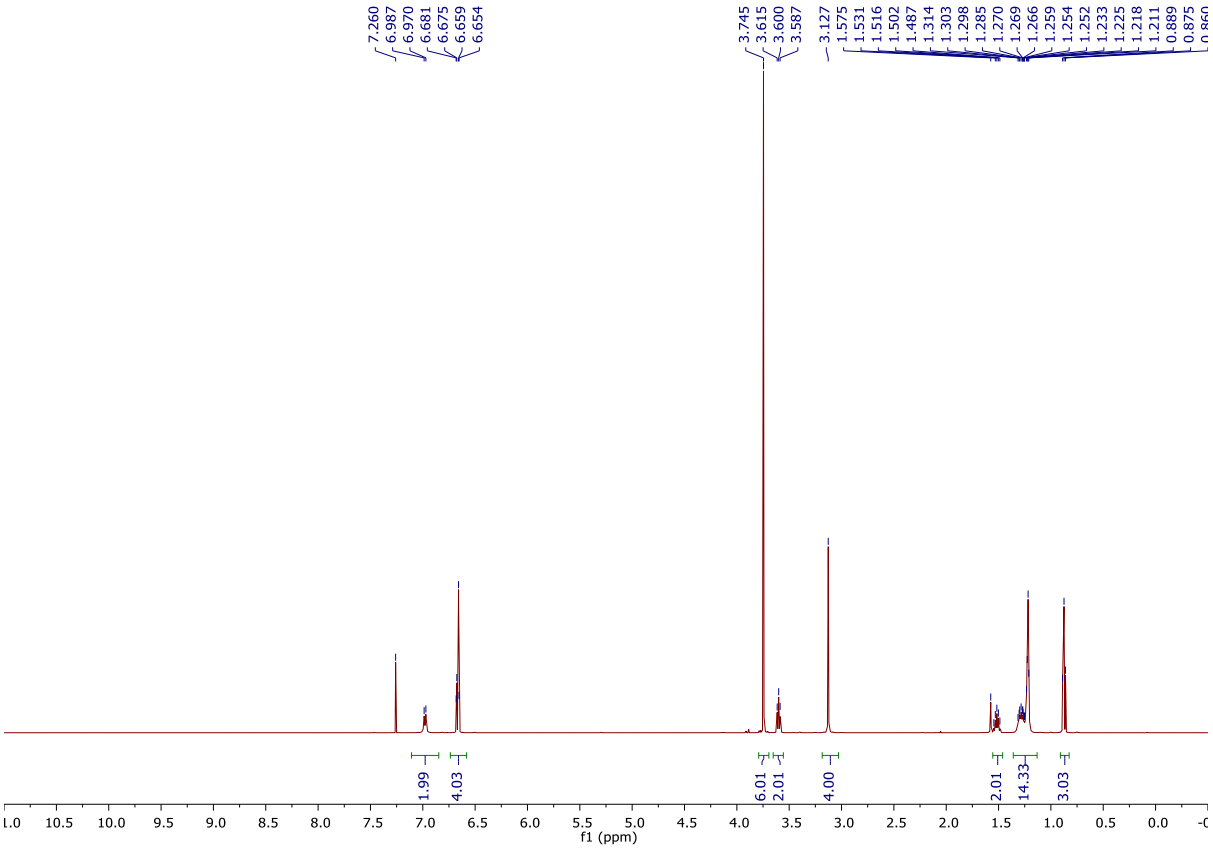

7.260
6.988
6.982
6.980
6.965
6.964
6.958
6.684
6.678
6.668
6.662
6.660
6.656
3.745
3.697
3.683
3.669
3.655
3.126
1.555
1.137
1.123
1.109
1.98
3.98
6.00
2.03
4.00
3.01
f1 (ppm)

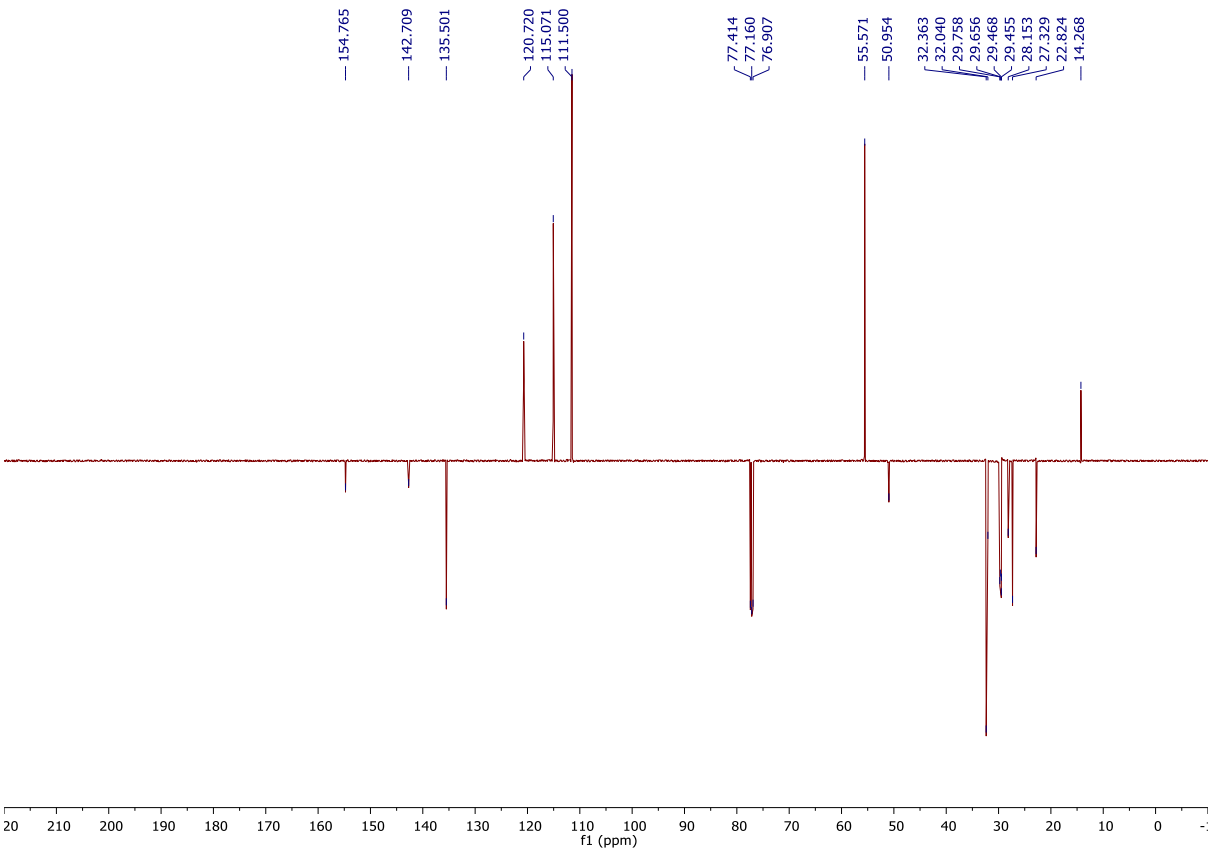

154.822
142.517
135.621
120.780
115.070
111.563
77.414
77.160
76.906
55.596
45.302
32.378
14.161
f1 (ppm)

5-Decyl-2,8-dimethoxy-10,11-dihydro-5H-dibenzo[*b*,*f*]azepine 6c

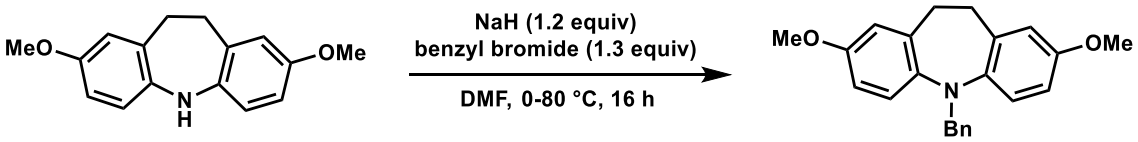


A sealed tube equipped with a magnetic stirrer bar was charged with 2,8-dimethoxy-10,11-dihydro-5H-dibenzo[*b*,*f*]azepine (1.5 g, 5.88 mmol) and DMF (18 mL). The mixture was cooled in an ice bath and NaH (60% in mineral oil) (283 mg, 7.08 mmol) was added. Then ice bath was removed and the resultant mixture was stirred at rt for 30 min. Again, the mixture was cooled in the ice bath and 1-bromodecane (1.7 mL, 8.26 mmol) was added. After removing rubber septa, the reaction mixture in the sealed tube was sealed with a screw tight cap and stirred at 80 °C for 16 h. Then the reaction mixture was cooled. Water (50 mL) and EtOAc (100 mL) was added to the reaction mixture. The organic layer was separated, washed with brine (5 × 50 mL), dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Purification by flash silica chromatography (eluent = 0.75–1% EtOAc in hexanes, 40 x 180 mm silica) gave the title compound **6c** as a yellow oil (813 mg, 2.06 mmol, 35%) along with recovery of the starting material (858 mg, 3.36 mmol, 57%); R_f = 0.44 (eluent = 5% EtOAc in hexanes); ν_{max} / cm^{-1} (film) 2922, 2851, 1607, 1491, 1464, 1277, 1248, 1215, 1155, 1136, 1049, 909, 868, 808, 756, 731, 613, 567; ^1H NMR (500 MHz, $CDCl_3$) δ_H: 0.87 (3H, t, *J* 7.0), 1.13–1.36 (14H, m), 1.46–1.56 (2H, m), 3.13 (4H, s), 3.60 (2H, t, *J* 7.0), 3.75 (6H, s), 6.65–6.68 (4H, m), 6.98 (2H, d, *J* 8.4); ^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 14.3, 22.8, 27.3, 28.2, 29.5, 29.5, 29.7, 29.8, 32.0, 32.4, 51.0, 55.6, 111.5, 115.1, 120.7, 135.5, 142.7, 154.8; HRMS $(ES)^+$ calculated for $[C_{26}H_{38}NO_2]^+$ $(M+H)^+$ m/z: 396.2903, found 396.2904 (+0.3 ppm).



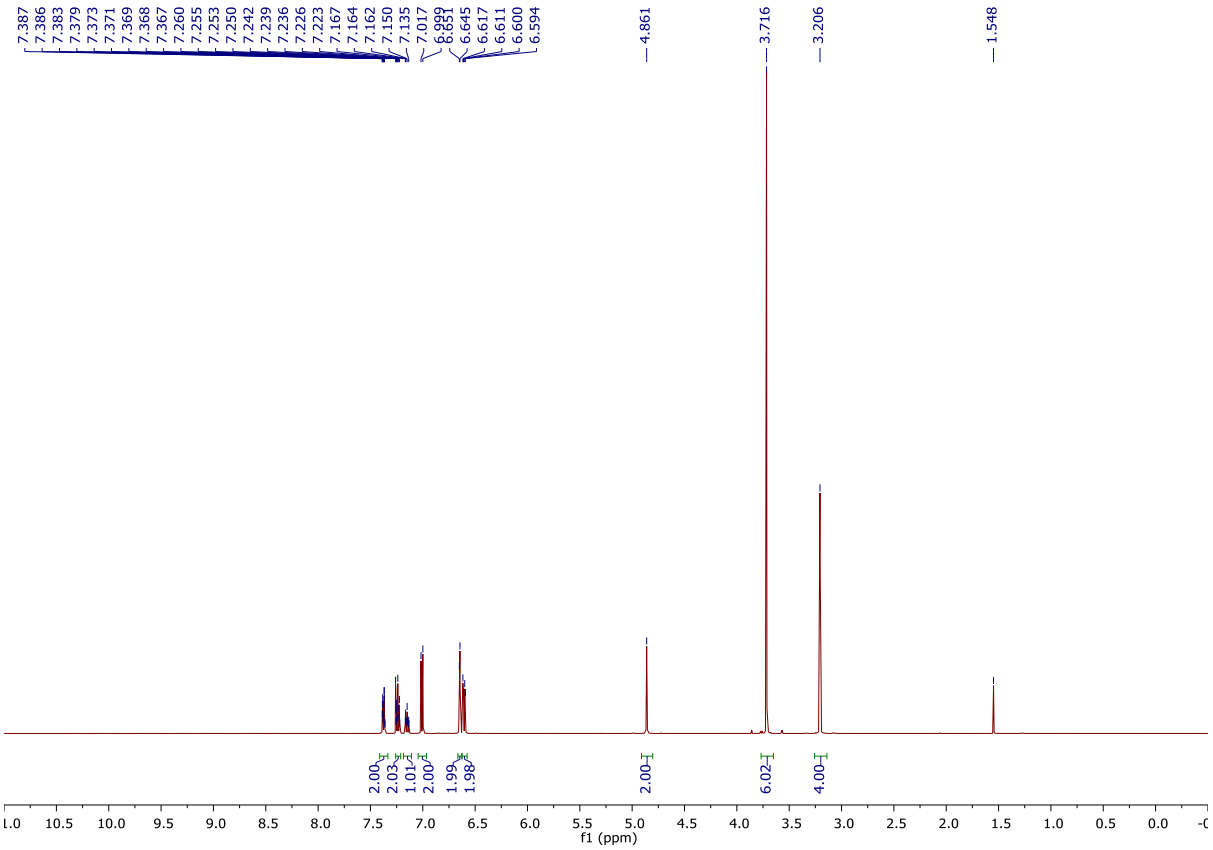


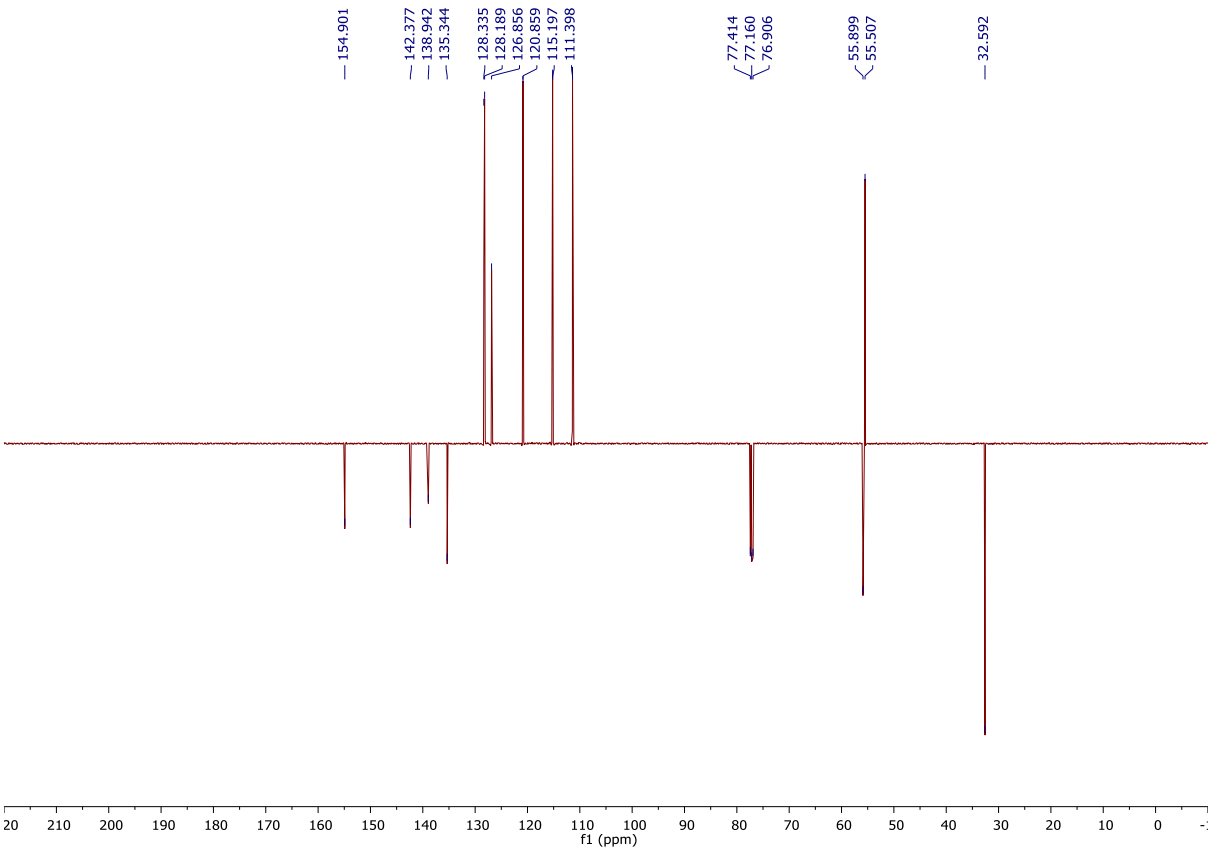
5-Benzyl-2,8-dimethoxy-10,11-dihydro-5H-dibenzo[*b*,*f*]azepine 6d



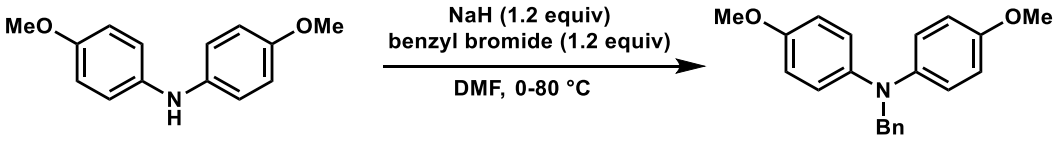
A sealed tube equipped with a magnetic stirrer bar was charged with 2,8-dimethoxy-10,11-dihydro-5H-dibenzo[*b*,*f*]azepine (1.5 g, 5.88 mmol) and DMF (18 mL). The mixture was cooled in an ice bath and NaH (60% in mineral oil) (283 mg, 7.08 mmol) was added. Then ice bath was removed and the resultant mixture was stirred at rt for 30 min. Again, the mixture was cooled in the ice bath and benzyl bromide (0.91 mL, 7.67 mmol) was added. After removing rubber septa, the reaction mixture in the sealed tube was sealed with a screw tight cap and stirred at 80 °C for 16 h. Then the reaction mixture was cooled. Water (50 mL) and EtOAc (100 mL) was added to the reaction mixture. The organic layer was separated, washed with brine (5 × 50 mL), dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Purification by flash silica chromatography (eluent = 1–2% EtOAc in hexanes, 30 × 180 mm silica) gave the title compound **6d** as a white solid (1.90 g, 5.51 mmol, 94%); mp 109–111 °C; R_f = 0.35 (eluent = 5% EtOAc in hexanes); ν_{max} / cm^{-1} (film) 2902, 2832, 1605, 1576, 1491, 1466, 1422, 1279, 1234, 1207, 1163, 1128, 1065, 1042, 1024, 1011, 901, 862, 802, 741, 696, 613, 556, 507, 469, 444; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 3.21 (4H, s), 3.72 (6H, s), 4.86 (2H, s), 6.61 (2H, dd, *J* 8.8, 3.0), 6.65 (2H, d, *J* 3.0), 7.01 (2H, d, *J* 8.8), 7.11–7.18 (1H, m), 7.21–7.26 (2H, m), 7.33–7.41 (2H, m); ^{13}C NMR (126 MHz,

$CDCl_3$) δ_C: 32.6, 55.5, 55.9, 111.4, 115.2, 120.9, 126.9, 128.2, 128.3, 135.3, 138.9, 142.4, 154.9; HRMS $(ES)^+$ calculated for $[C_{23}H_{24}NO_2]^+$ $(M+H)^+$ m/z: 346.1807, found 346.1802 (-1.4 ppm).

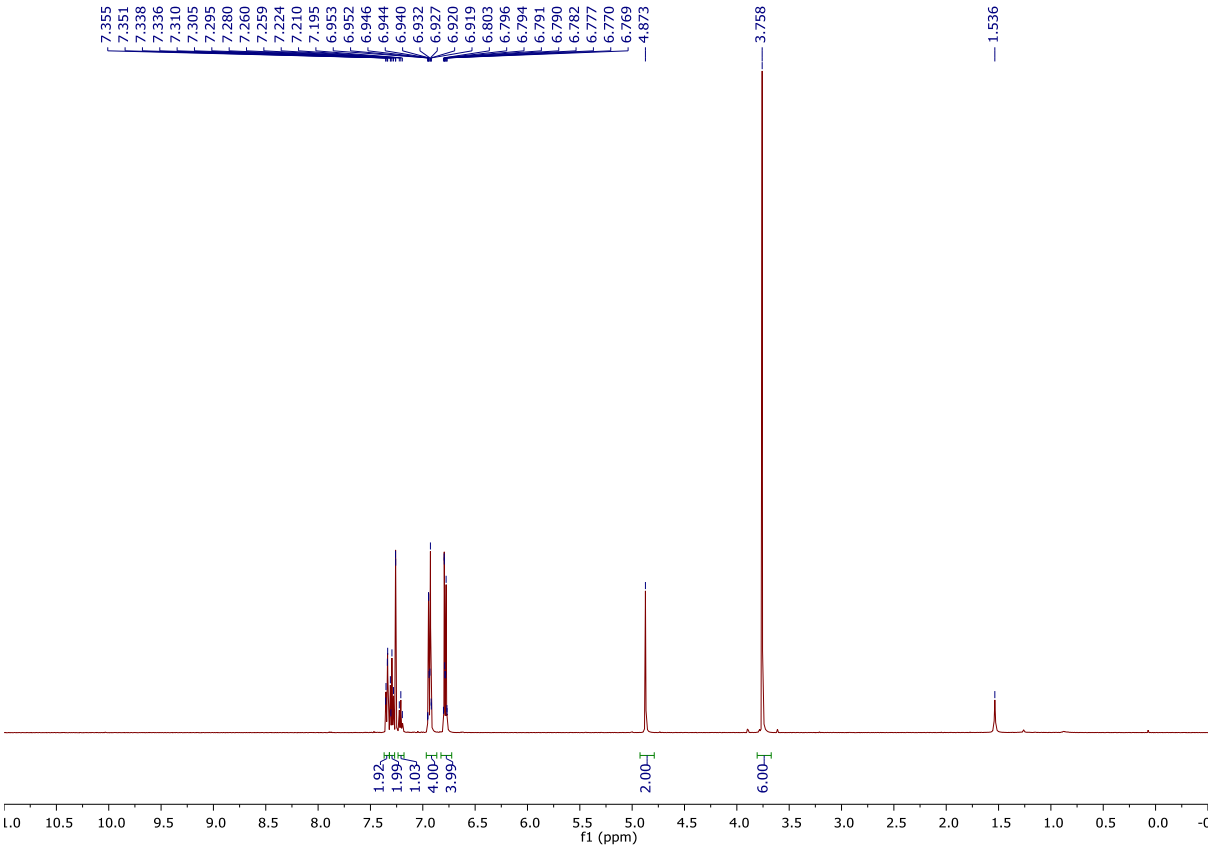


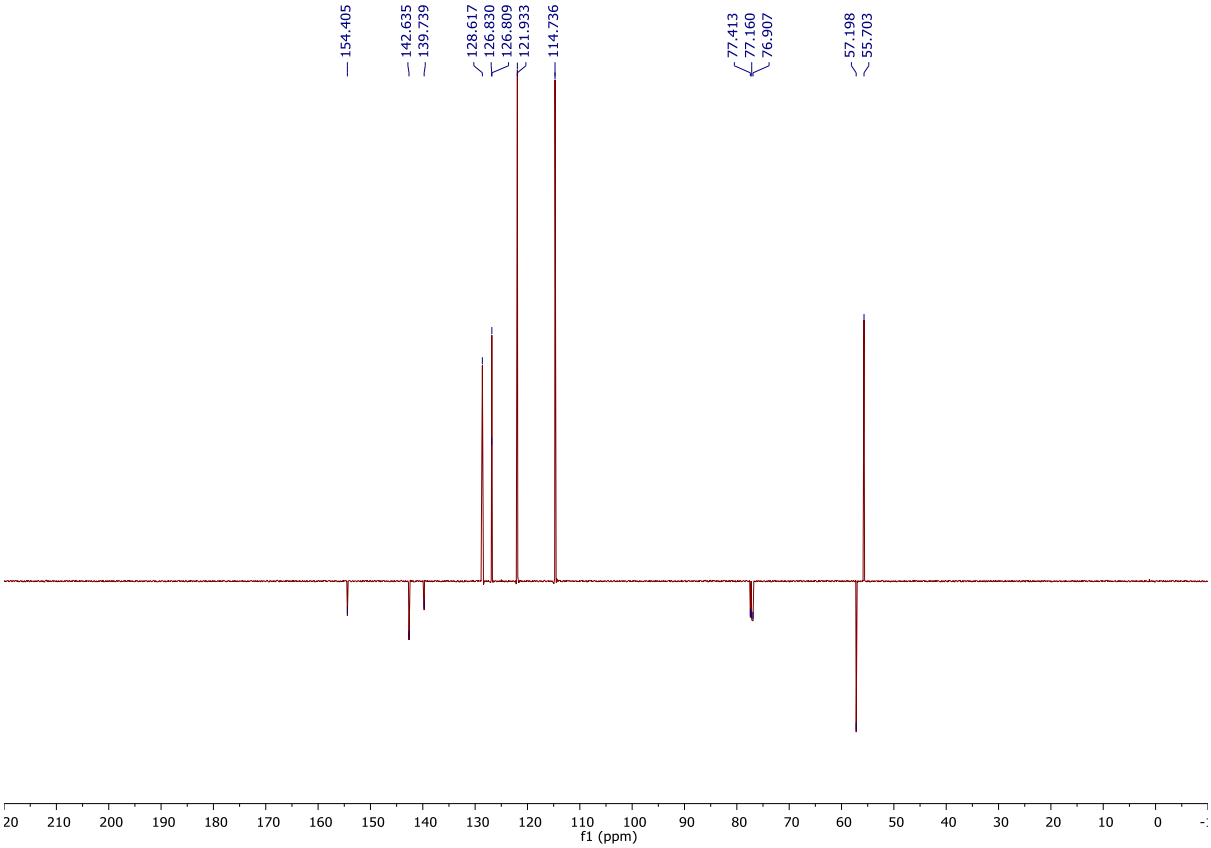


N-Benzyl-4-methoxy-N-(4-methoxyphenyl)aniline 4b

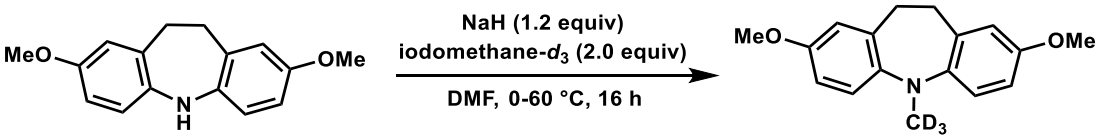


A sealed tube equipped with a magnetic stirrer bar was charged with bis(4-methoxyphenyl)amine (3.0 g, 13.1 mmol) and DMF (40 mL). The mixture was cooled in an ice bath and NaH (60% in mineral oil) (628 mg, 15.7 mmol) was added. Then ice bath was removed and the resultant mixture was stirred at rt for 30 min. Again, the mixture was cooled in the ice bath and benzyl bromide (1.9 mL, 15.7 mmol) was added. After removing rubber septa, the reaction mixture in the sealed tube was sealed with a screw tight cap and stirred at 80 °C for 4 h. Then the reaction mixture was cooled. Water (70 mL) and EtOAc (120 mL) was added to the reaction mixture. The organic layer was separated, washed with brine (5 × 50 mL), dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Purification by flash silica chromatography (eluent = 2% EtOAc in hexanes, 40 × 180 mm silica) gave the title compound **4b** as a yellow oil (2.4 g, 7.52 mmol, 57%); R_f = 0.55 (eluent = 10% EtOAc in hexanes); ν_{max} / cm^{-1} (film) 2953, 2835, 1499, 1454, 1439, 1237, 1219, 1177, 1030, 1015, 822, 766, 723, 696, 602, 571, 546, 521, 459, 457; ^1H NMR (500 MHz, $CDCl_3$) δ_H: 3.76 (6H, s), 4.87 (2H, s), 6.72–6.83 (4H, m), 6.87–6.97 (4H, m), 7.21 (1H, t, *J* 7.3), 7.29 (2H, t, *J* 7.6), 7.35 (2H, dd, *J* 8.0, 1.5); ^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 55.7, 57.2, 114.7, 121.9, 126.8, 126.8, 128.6, 139.7, 142.6, 154.4; HRMS $(AP)^+$ calculated for $[C_{21}H_{22}NO_2]^+$ $(M+H)^+$ m/z: 320.1651, found 320.1657 (+1.9 ppm).

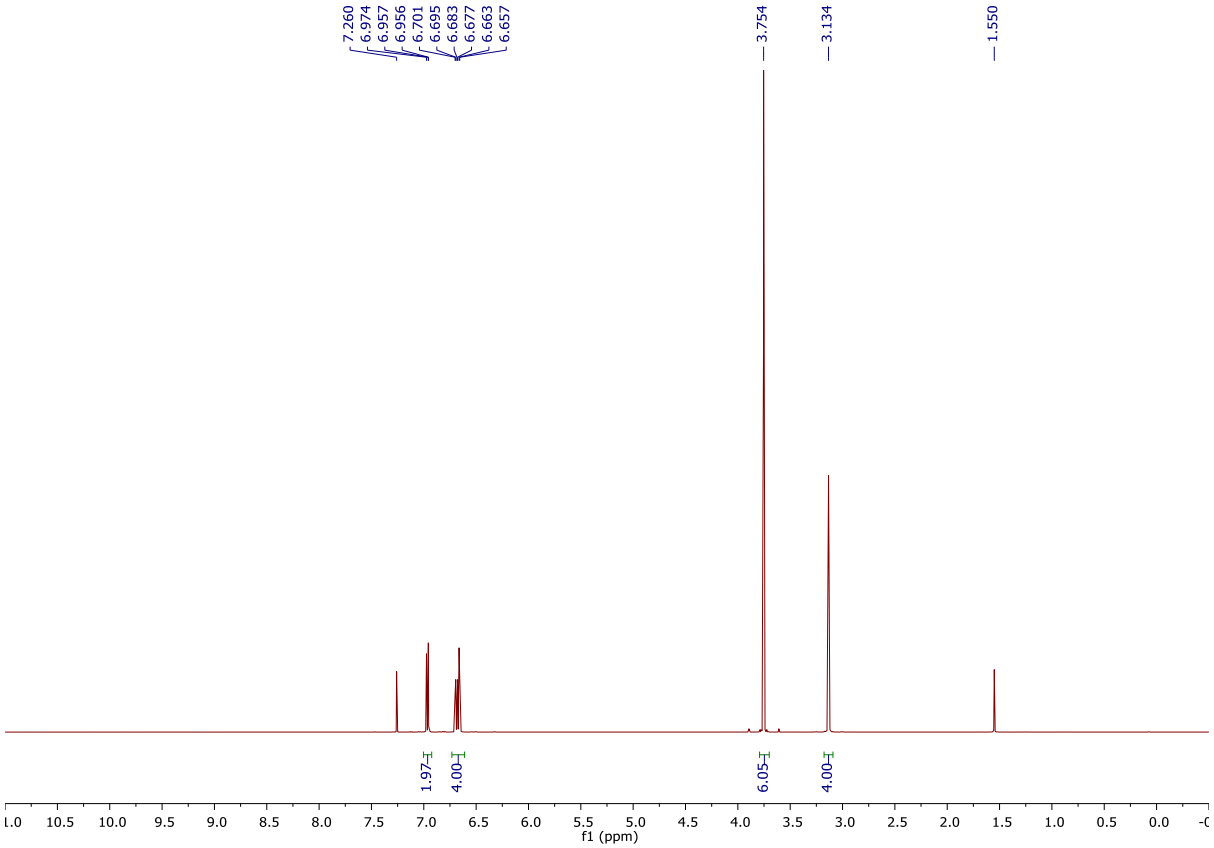


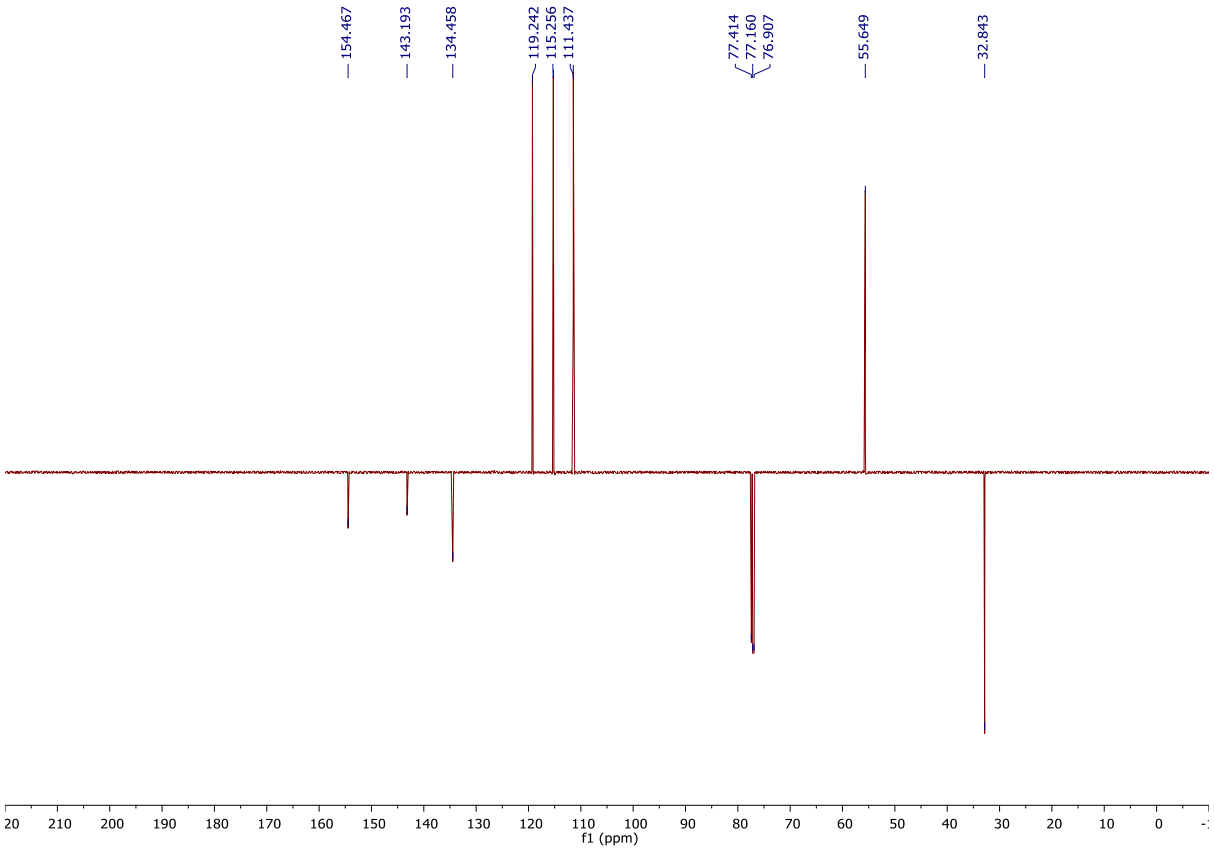


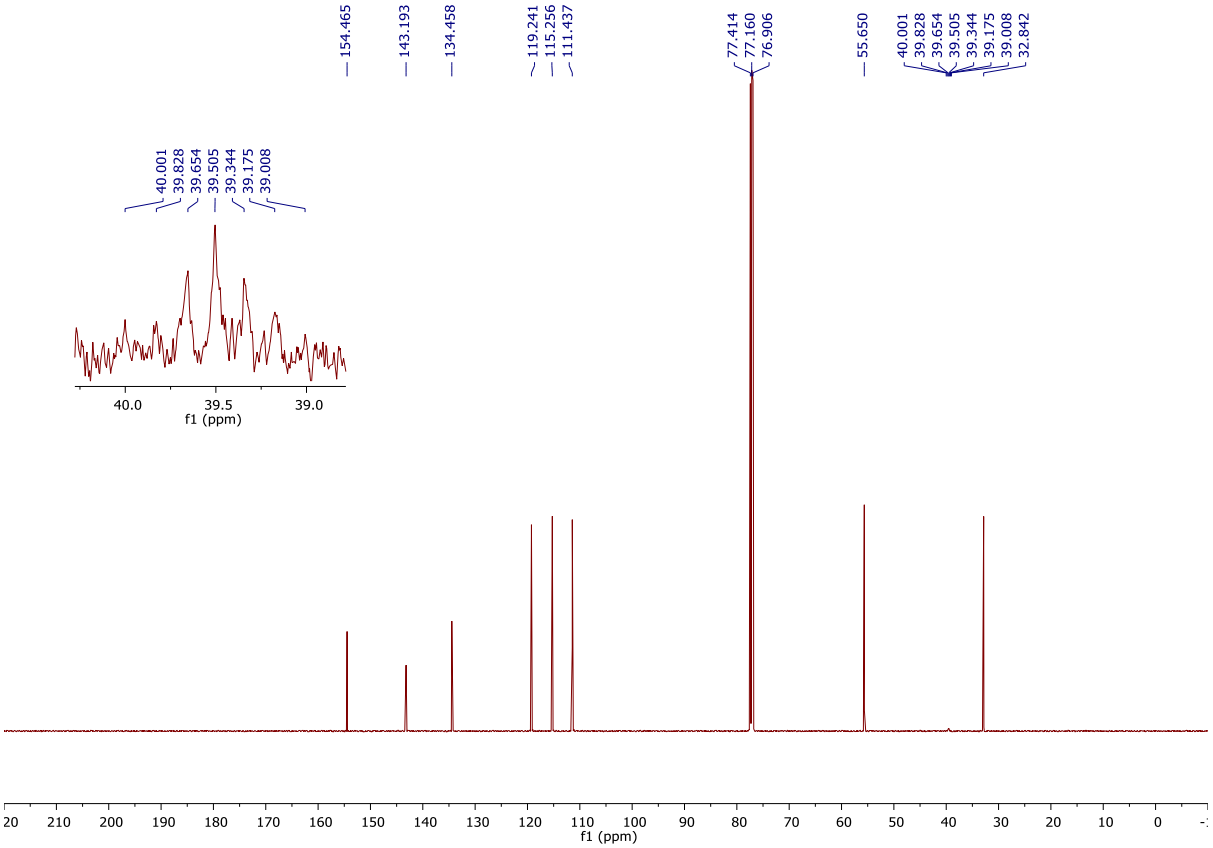
2,8-Dimethoxy-5-(methyl-d_3)-10,11-dihydro-5H-dibenzo[*b*,*f*]azepine 6a-d_3



The title compound was prepared according to general procedure 1 using 2,8-dimethoxy-10,11-dihydro-5H-dibenzo[*b*,*f*]azepine (1.50 g, 5.88 mmol) and iodomethane-d_3 (0.74 mL, 11.8 mmol). Purification by flash silica chromatography (eluent = 1-2% EtOAc in hexanes, 30 × 180 mm silica) gave the title compound **6a-d_3** as a white solid (1.50 g, 5.50 mmol, 94%, >99% D); mp 134–137 °C; R_f = 0.39 (eluent = 5% EtOAc in hexanes); ν_{max} / cm^{-1} (film) 2914, 2832, 2234, 2199, 2064, 1607, 1584, 1491, 1466, 1429, 1410, 1294, 1258, 1223, 1150, 1051, 1034, 878, 849, 806, 764, 720, 704, 606, 548, 534, 500; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 3.13 (4H, s), 3.75 (6H, s), 6.61–6.73 (4H, m), 6.92–7.00 (2H, m); ^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 32.8, 39.5 (hept, *J* 20.9), 55.7, 111.4, 115.3, 119.2, 134.5, 143.2, 154.5; HRMS (AP)$^+$ calculated for $[C_{17}{}^1H_{17}{}^2H_3NO_2]^+$ (M+H)$^+$ m/z: 273.1682, found 273.1675 (-2.6 ppm).

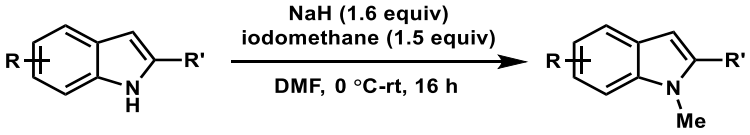

7.260
6.974
6.957
6.956
6.701
6.695
6.683
6.677
6.663
6.657
3.754
3.134
1.550
1.97
4.00
6.05
4.00
f1 (ppm)


154.467
143.193
134.458
119.242
115.256
111.437
77.414
77.160
76.907
55.649
32.843
f1 (ppm)



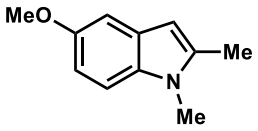
2.2. Synthesis of the indole substrates

General procedure 2: N-methylation of indoles

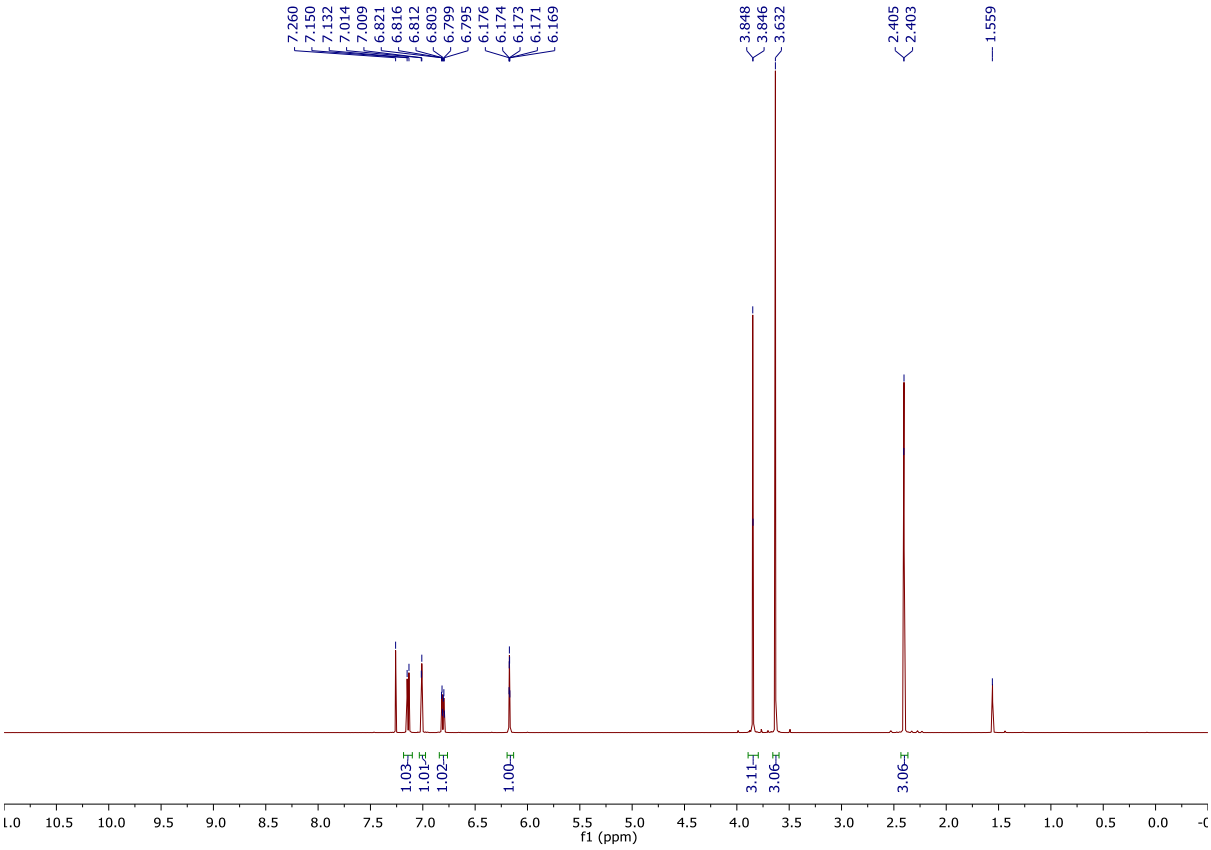


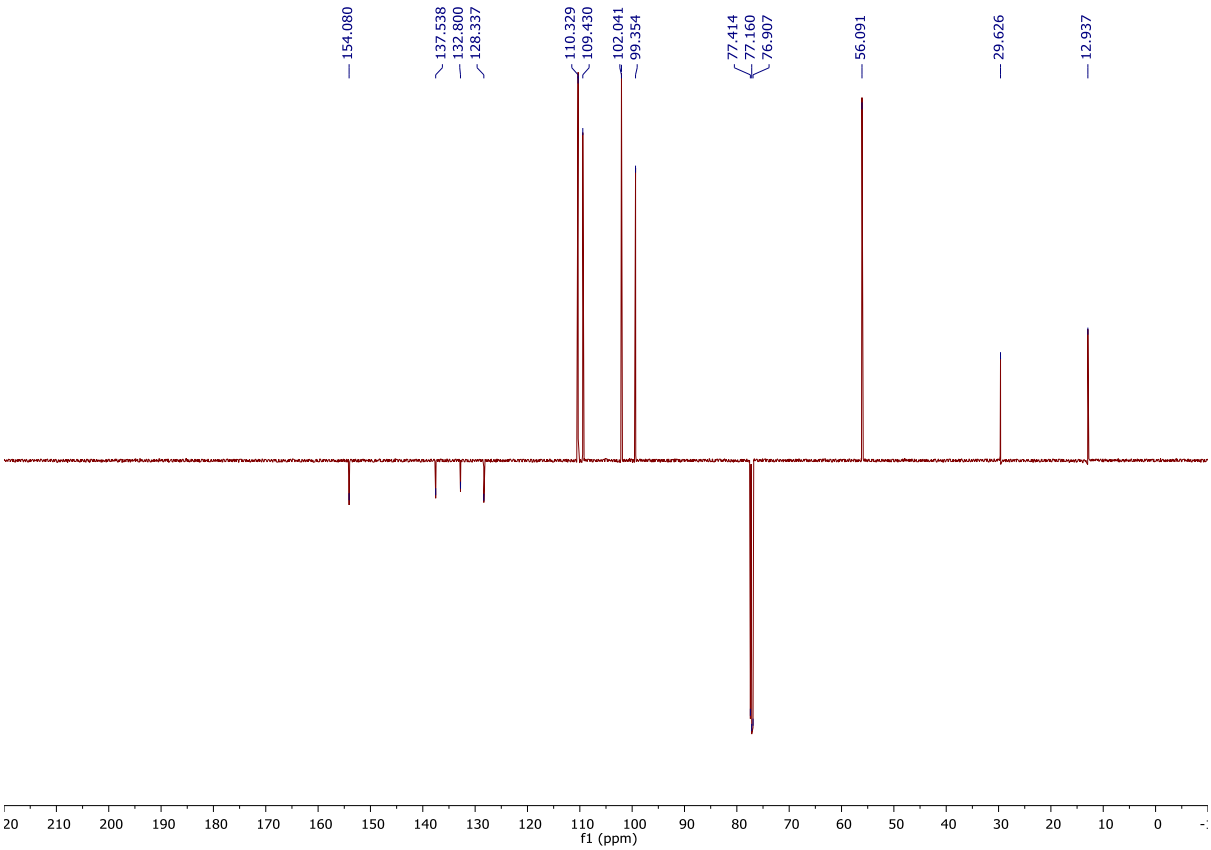
An oven-dried round-bottomed flask equipped with a magnetic stirrer bar was charged with indole derivative (1.0 equiv) and DMF (4 mL/mmol) and sealed with rubber septum under nitrogen atmosphere. The mixture was cooled in an ice bath and NaH (60% in mineral oil) (1.6 equiv) was added. Then ice bath was removed and the resultant mixture was stirred at rt for 30 min. Again, the mixture was cooled in the ice bath and iodomethane (1.5 equiv) was added. Then ice bath was removed and the reaction mixture was allowed to warm and stirred at rt for 16 h under the nitrogen atmosphere. Then the reaction mixture was cooled to 0 °C. Water and EtOAc were added to the reaction mixture. The organic layer was separated, washed with brine (× 5–6), dried over $MgSO_4$, filtered, and concentrated *in vacuo*.

5-Methoxy-1,2-dimethyl-1H-indole 1c

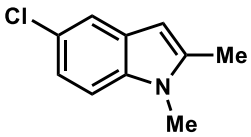


The title compound was prepared according to general procedure 2 using 5-methoxy-2-methyl-1H-indole (484 mg, 3.00 mmol). Purification by flash silica chromatography (eluent = 1–2% EtOAc in hexanes, 25 × 160 mm silica) gave the title compound **1c** as an off-white solid (517 mg, 2.95 mmol, 98%); mp 76–77 °C (Lit. 73–74 °C);[8] R_f = 0.38 (eluent = 5% EtOAc in hexanes); ν_{max} / cm^{-1} (film) 2909, 1614, 1580, 1543, 1489, 1451, 1431, 1397, 1343, 1290, 1242, 1211, 1157, 1138, 1099, 1030, 943, 878, 845, 824, 797, 775, 756, 729, 698, 654, 604, 557; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 2.40 (3H, d, *J* 1.0), 3.63 (3H, s), 3.85 (3H, d, *J* 1.0), 6.17–6.18 (1H, m), 6.80–6.82 (1H, m), 7.01 (1H, d, *J* 2.4), 7.14 (1H, d, *J* 8.8); ^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 12.9, 29.6, 56.1, 99.4, 102.0, 109.4, 110.3, 128.3, 132.8, 137.5, 154.1; HRMS (AP)$^+$ calculated for $[C_{11}H_{14}NO]^+$ $(M+H)^+$ m/z: 176.1075, found 176.1074 (-0.6 ppm).

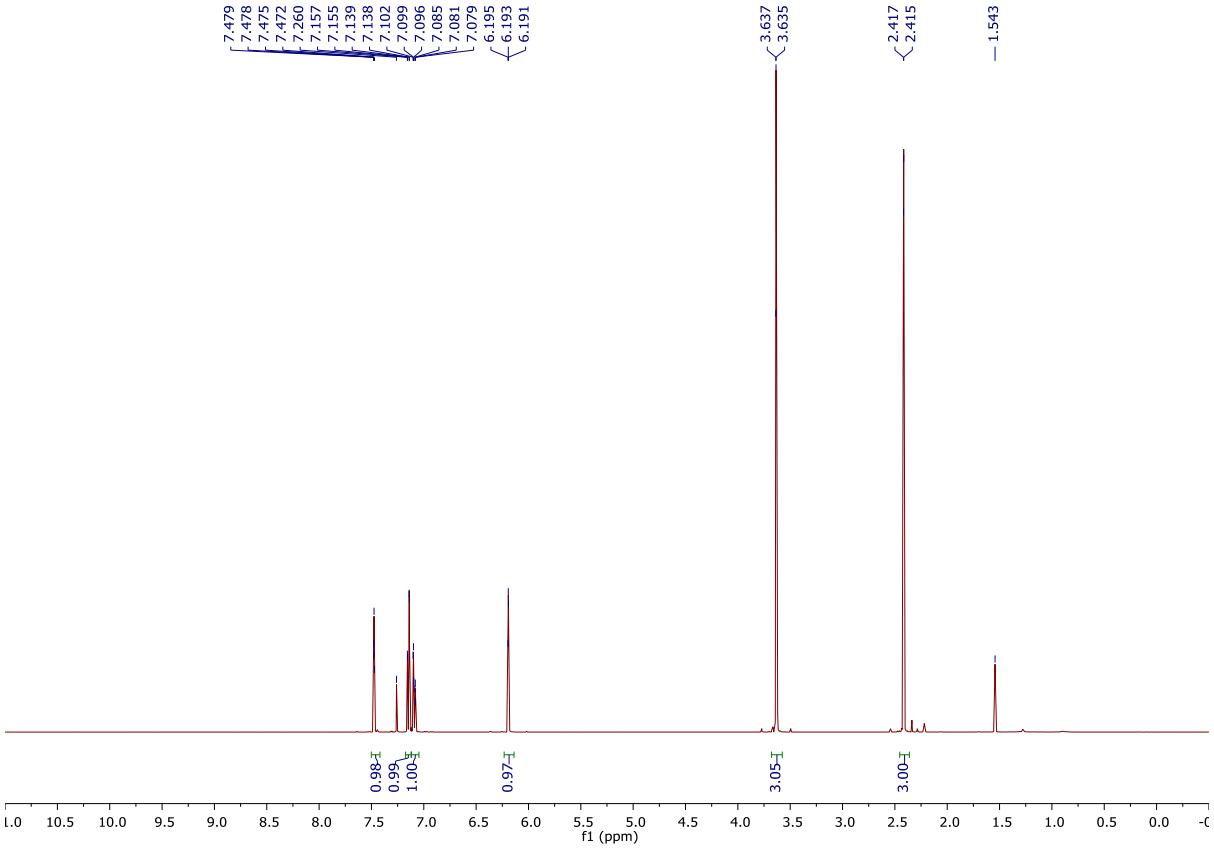


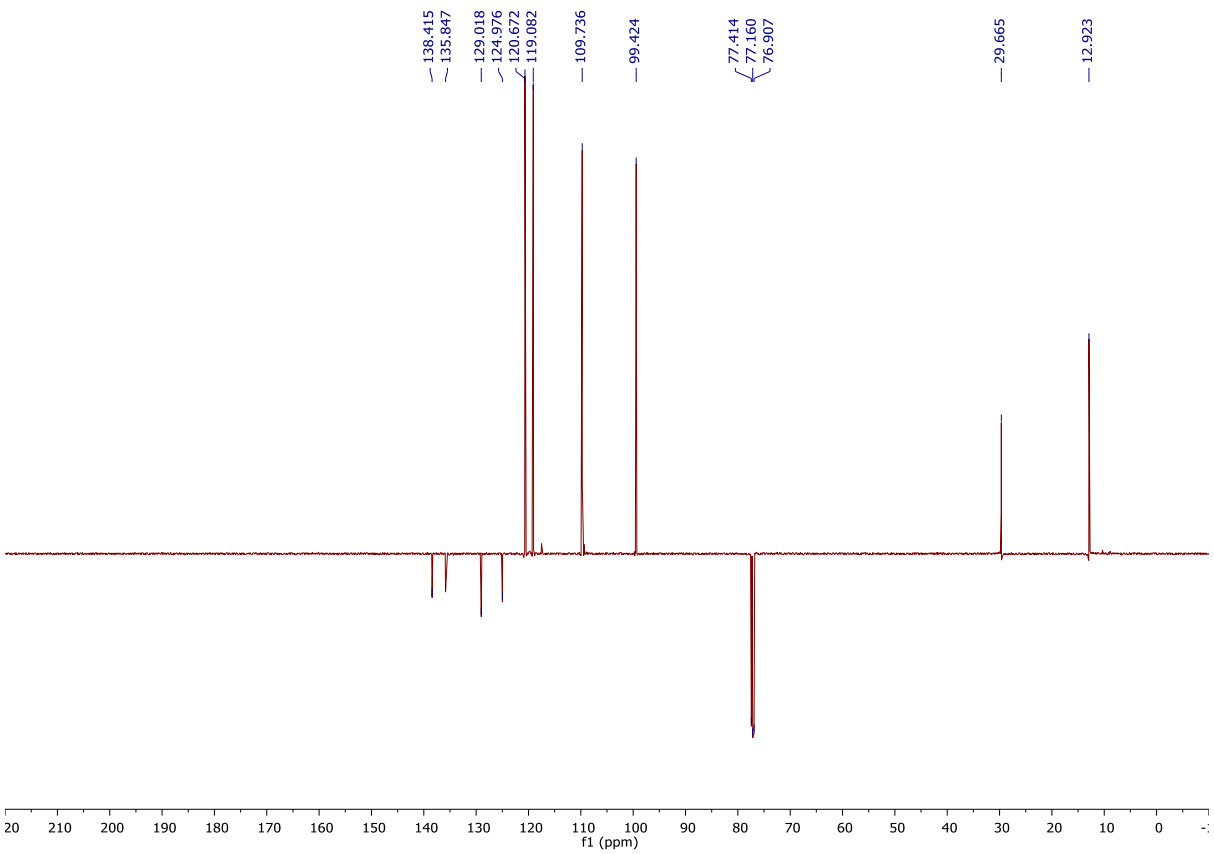


5-Chloro-1,2-dimethyl-1H-indole 1d

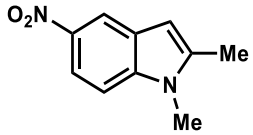


The title compound was prepared according to general procedure 2 using 5-chloro-2-methyl-1H-indole (497 mg, 3.0 mmol). Purification by flash silica chromatography (eluent = 1–2% EtOAc in hexanes, 25 × 160 mm silica) gave the title compound **1d** as a yellow solid (501 mg, 2.79 mmol, 93%); mp 66–68 °C (Lit. 56–58 °C);[9] R_f = 0.47 (eluent = 5% EtOAc in hexanes); ν_{max} / cm^{-1} (film) 2911, 1844, 1607, 1566, 1549, 1472, 1439, 1429, 1393, 1381, 1327, 1271, 1233, 1180, 1142, 1101, 1061, 912, 862, 791, 747, 625, 584, 544; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 2.42 (3H, d, *J* 0.9), 3.64 (3H, d, *J* 0.9), 6.14–6.23 (1H, m), 7.08–7.10 (1H, m), 7.15 (1H, dd, *J* 8.6, 0.7), 7.42–7.50 (1H, m); ^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 12.9, 29.7, 99.4, 109.7, 119.1, 120.7, 125.0, 129.0, 135.9, 138.4; HRMS (AP)$^+$ calculated for $[C_{10}H_{11}N^{35}Cl]^+$ $(M+H)^+$ m/z: 180.0580, found 180.0574 (-3.3 ppm).

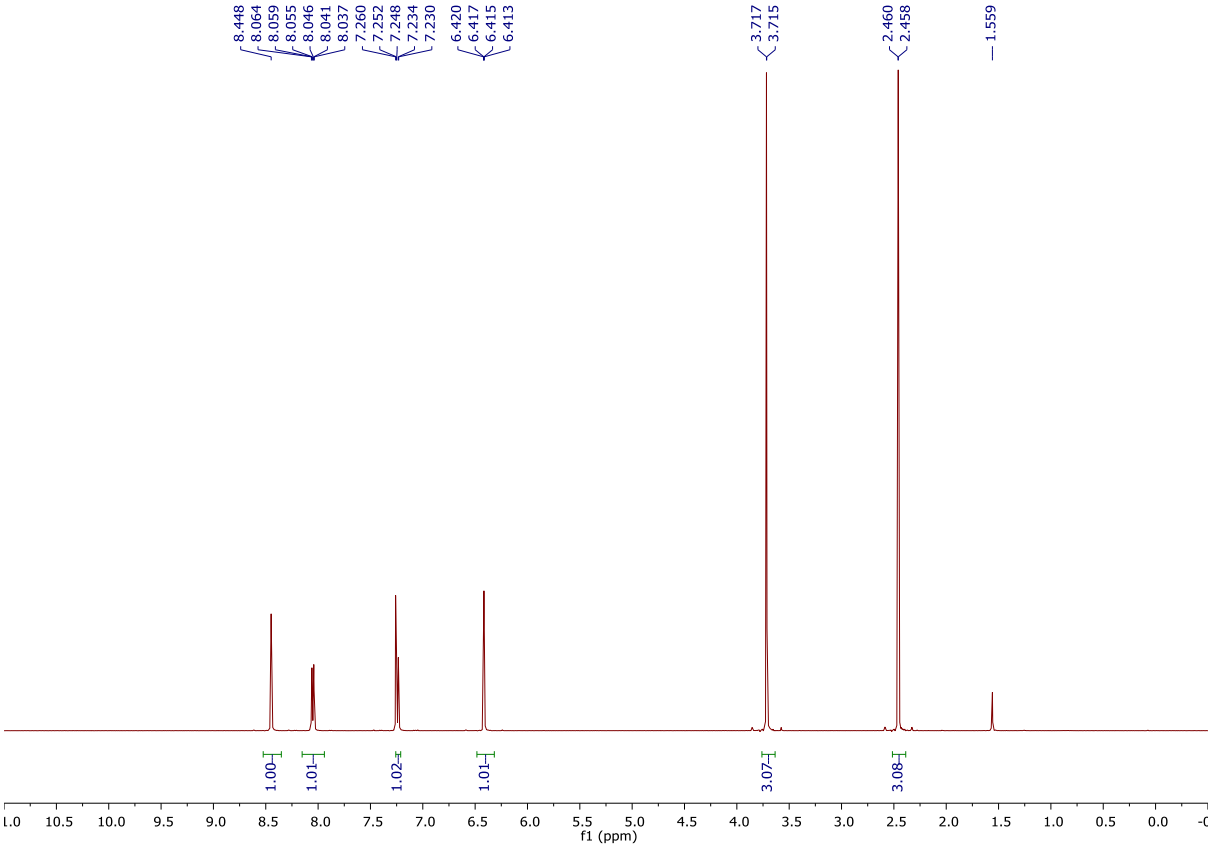

7.479
7.478
7.475
7.472
7.260
7.157
7.155
7.139
7.138
7.102
7.099
7.096
7.085
7.081
7.079
6.195
6.193
6.191
3.637
3.635
2.417
2.415
1.543
0.98
0.99
1.00
0.97
3.05
3.00
f1 (ppm)

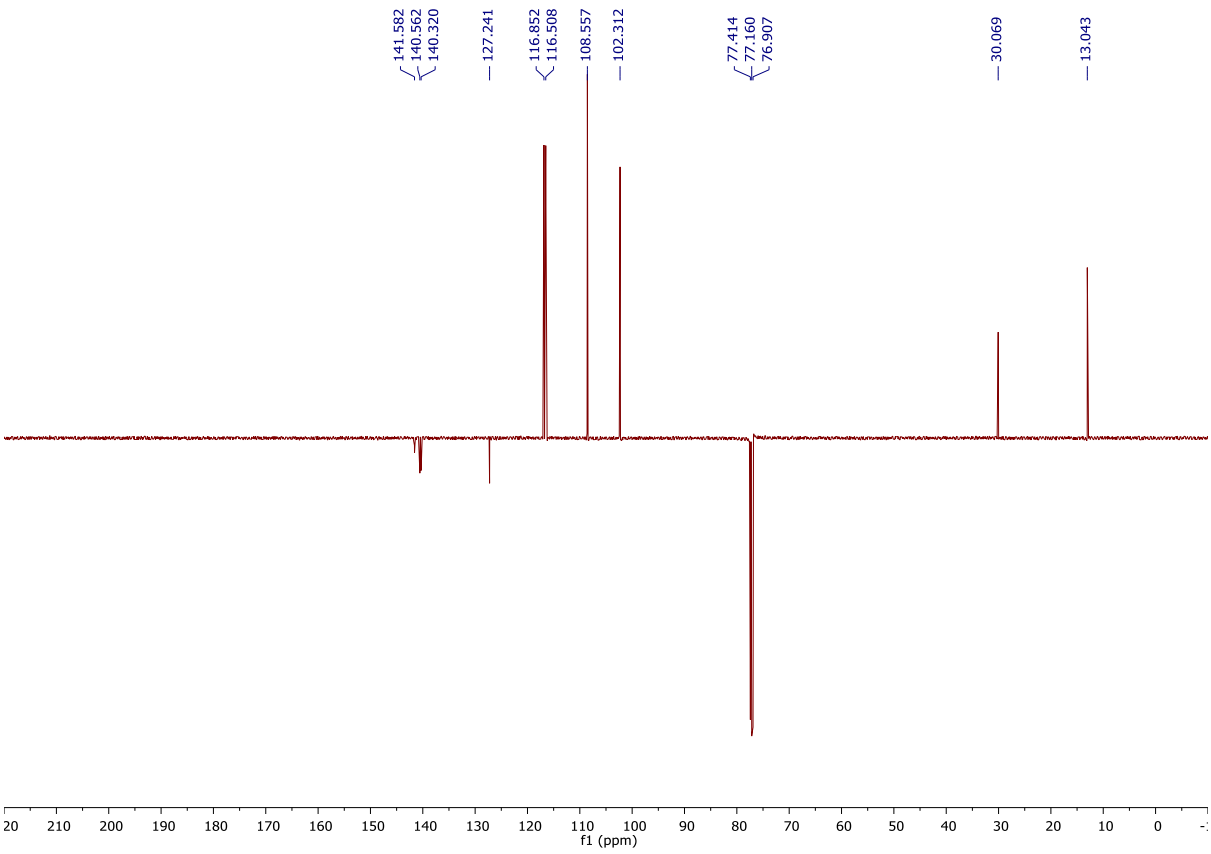

138.415
135.847
129.018
124.976
120.672
119.082
109.736
99.424
77.414
77.160
76.907
29.665
12.923
f1 (ppm)

1,2-Dimethyl-5-nitro-1H-indole 1e

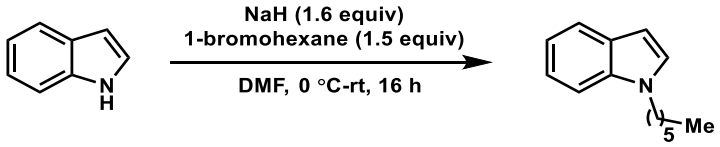


The title compound was prepared according to general procedure 2 using 2-methyl-5-nitro-1H-indole (529 mg, 3.0 mmol). Purification by flash silica chromatography (eluent = 20% EtOAc in hexanes, 25 × 160 mm silica) gave the title compound **1e** as a yellow solid (562 mg, 2.95 mmol, 98%); mp 128–130 °C (Lit. 128–129 °C);[10] R_f = 0.31 (eluent = 20% EtOAc in hexanes); ν_{max} / cm^{-1} (film) 1613, 1557, 1514, 1481, 1474, 1454, 1397, 1350, 1314, 1234, 1182, 1146, 1065, 899, 824, 806, 774, 748, 737, 669, 615, 559, 432; ^1H NMR (500 MHz, $CDCl_3$) δ_H: 2.46 (3H, d, *J* 1.0), 3.72 (3H, d, *J* 1.2), 6.42 (1H, q, *J* 1.0), 7.24 (1H, dd, *J* 9.0, 1.7), 8.05 (1H, dt, *J* 9.0, 2.3), 8.45 (1H, s); ^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 13.0, 30.1, 102.3, 108.6, 116.5, 116.9, 127.2, 140.3, 140.6, 141.6; HRMS $(AP)^+$ calculated for $[C_{10}H_{11}N_2O_2]^+$ $(M+H)^+$ m/z: 191.0821, found 191.0820 (-0.5 ppm).

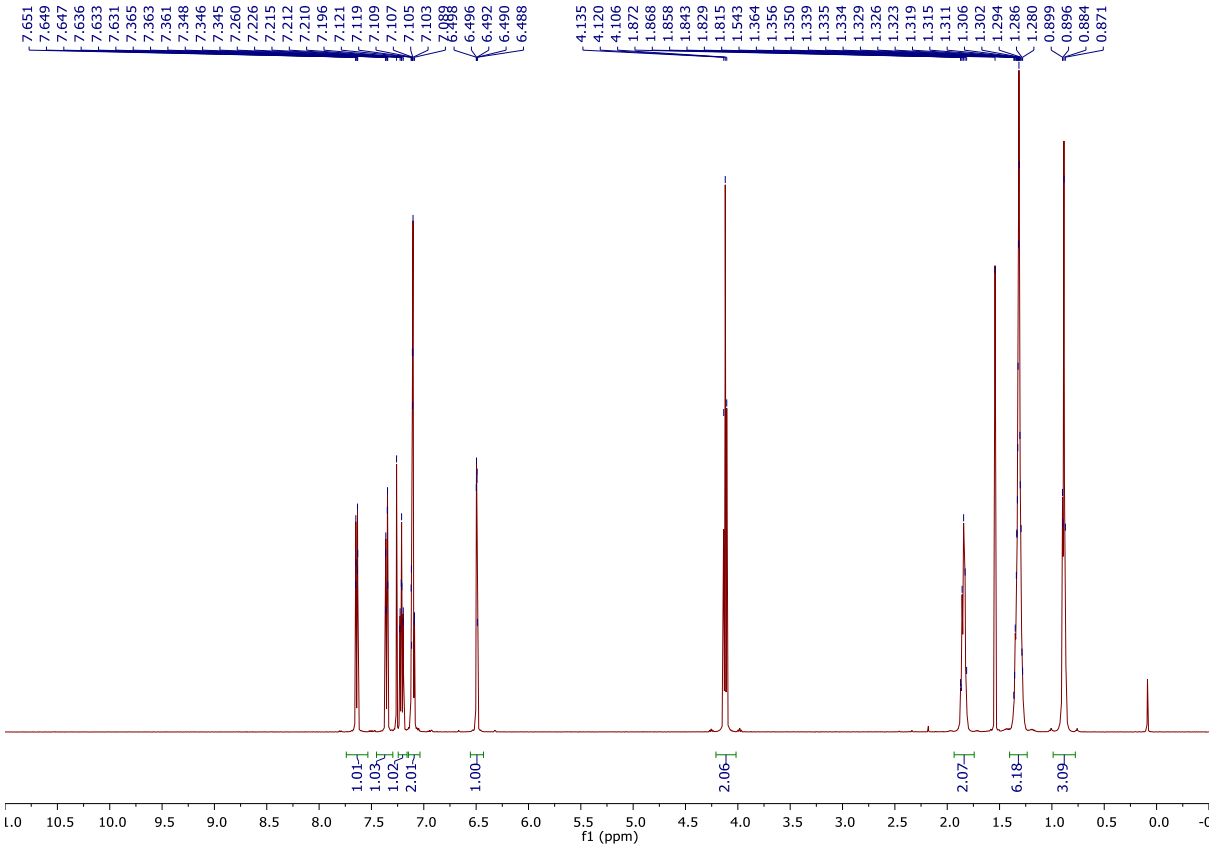




1-Hexyl-1H-indole 1g



An oven-dried round-bottomed flask equipped with a magnetic stirrer bar was charged with indole (586 mg, 5.0 mmol) and DMF (15 mL) and sealed with rubber septum under nitrogen atmosphere. The mixture was cooled in an ice bath and NaH (60% in mineral oil) (320 mg, 8.0 mmol) was added. Then ice bath was removed and the resultant mixture was stirred at rt for 30 min. Again, the mixture was cooled in the ice bath and 1-bromohexane (1.1 mL, 7.5 mmol) was added. Then ice bath was removed and the reaction mixture was allowed to warm and stirred at rt for 16 h under the nitrogen atmosphere. Then the reaction mixture was cooled to 0 °C. Water (40 mL) and EtOAc (60 mL) was added to the reaction mixture. The organic layer was separated, washed with brine (6 × 30 mL), dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Purification by flash silica chromatography (eluent = 1% EtOAc in hexanes, 30 × 160 mm silica) gave the title compound **1g** as a light yellow oil (962 mg, 4.78 mmol, 96%); R_f = 0.64 (eluent = 2% EtOAc in hexanes); ν_{max} / cm^{-1} (film) 3055, 2955, 2928, 2857, 1510, 1462, 1314, 1238, 1180, 1113, 1013, 883, 762, 735, 712, 571, 465, 424; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 0.78–0.99 (3H, m), 1.24–1.40 (6H, m), 1.74–1.93 (2H, m), 4.12 (2H, t, *J* 7.2), 6.49 (1H, dd, *J* 3.1, 1.0), 7.04–7.15 (2H, m), 7.21 (1H, ddd, *J* 8.2, 7.0, 1.2), 7.35 (1H, dt, *J* 8.2, 1.0), 7.64 (1H, dt, *J* 7.9, 1.1); ^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 14.2, 22.7, 26.8, 30.4, 31.6, 46.6, 100.9, 109.5, 119.3, 121.1, 121.4, 127.9, 128.7, 136.1; HRMS (AP)$^+$ calculated for $[C_{14}H_{20}N]^+$ $(M+H)^+$ m/z: 202.1596, found 202.1600 (+2.0 ppm).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7.631
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7.348
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7.226
7.215
7.212
7.210
7.196
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1.334
1.329
1.326
1.323
1.319
1.315
1.311
1.306
1.302
1.294
1.286
1.280
0.899
0.896
0.884
0.871
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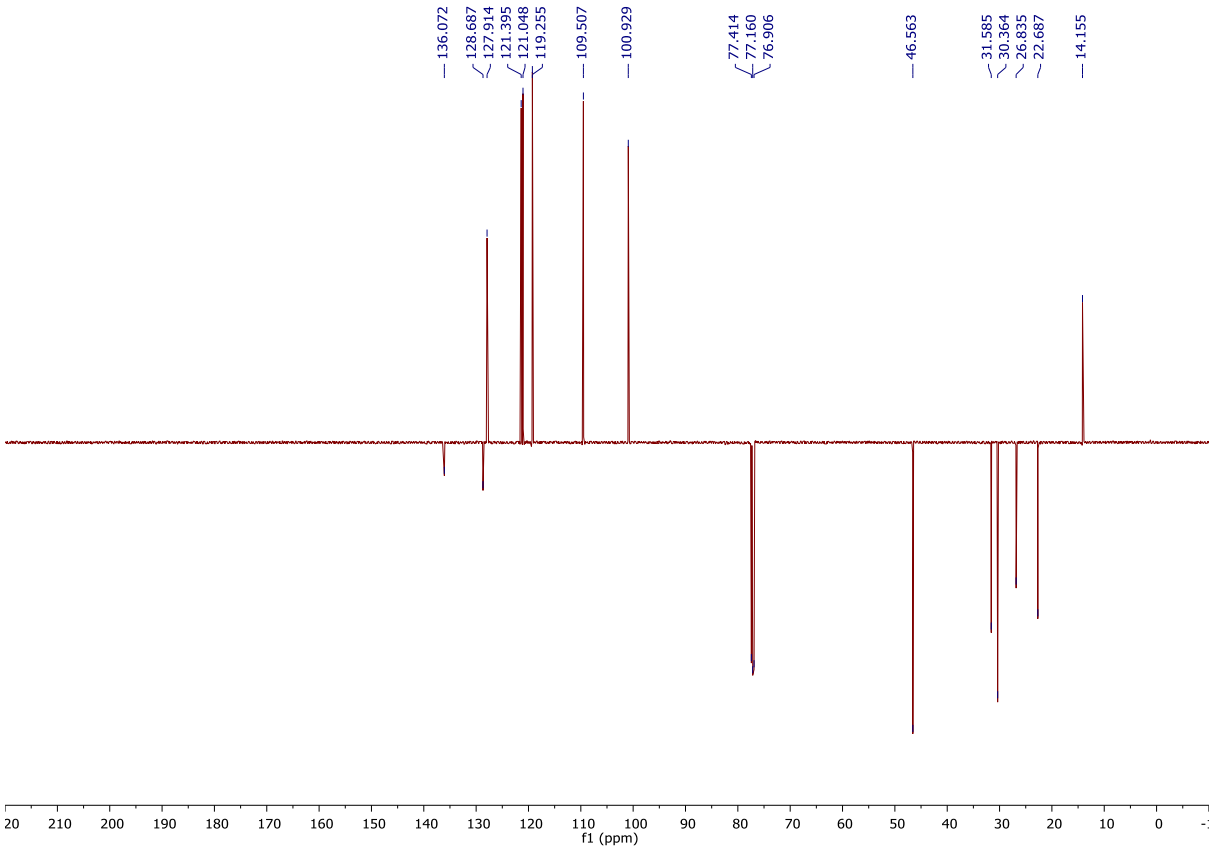
1.03
1.02
2.01
1.00
2.06
2.07
6.18
3.09
f1 (ppm)


136.072
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121.048
119.255
109.507
100.929
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77.160
76.906
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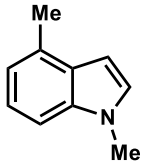
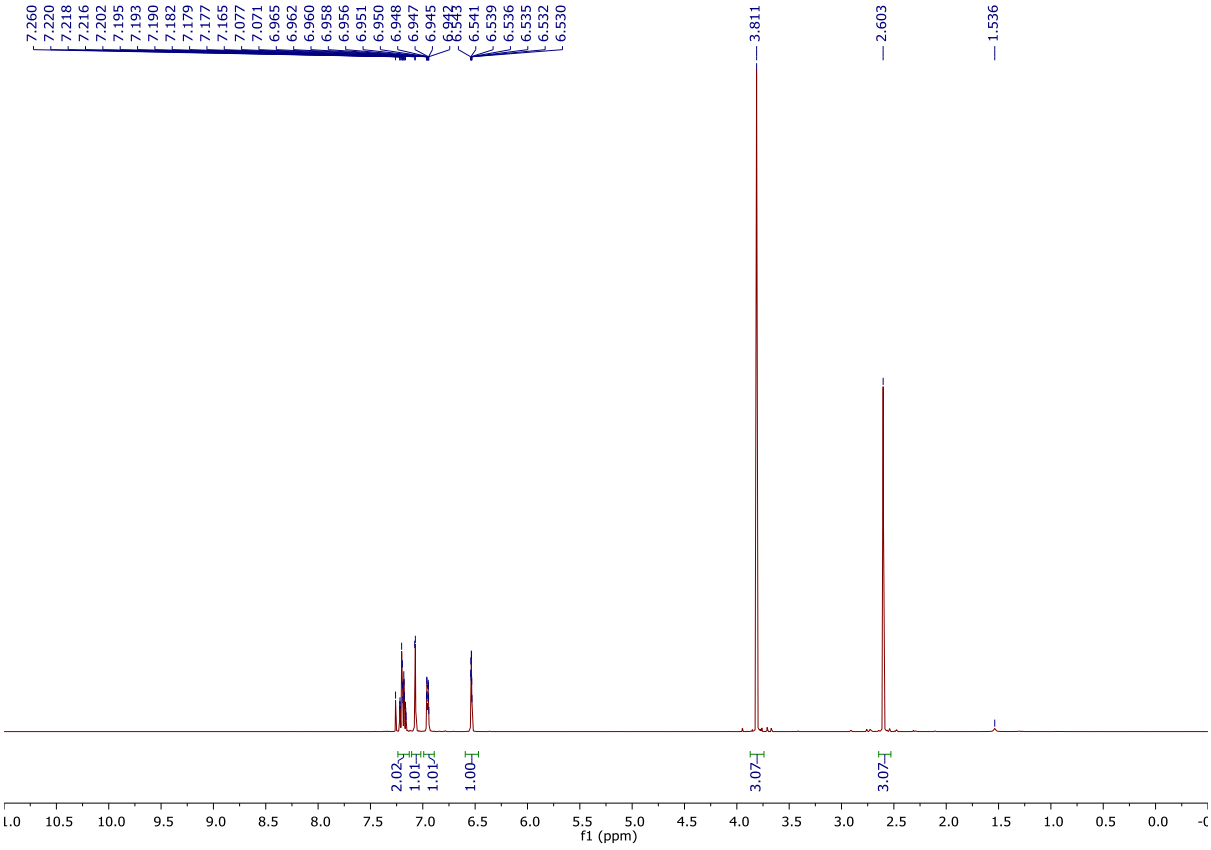
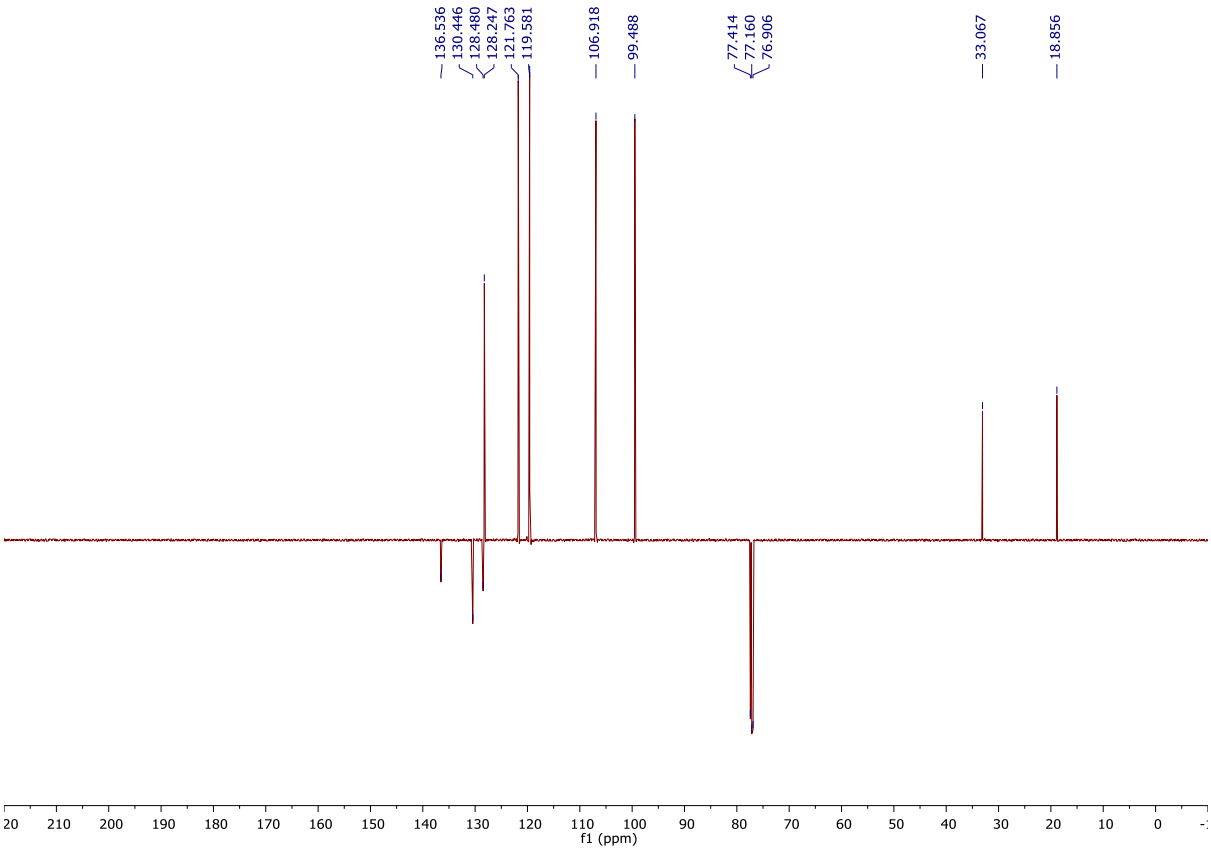
31.585
30.364
26.835
22.687
14.155
f1 (ppm)

1,4-Dimethyl-1H-indole 1i

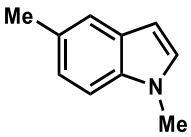


The title compound was prepared according to general procedure 2 using 4-methyl-1H-indole (394 mg, 3.0 mmol). Purification by flash silica chromatography (eluent = 0.5–1% EtOAc in hexanes, 25 × 160 mm silica) gave the title compound **1i** as a light yellow oil (380 mg, 2.62 mmol, 87%); R_f = 0.34 (eluent = 1% EtOAc in hexanes); ν_{max} / cm^{-1} (film) 1586, 1514, 1495, 1458, 1416, 1335, 1294, 1242, 1153, 1084, 939, 743, 710, 673, 550, 503; ^1H NMR (500 MHz, $CDCl_3$) δ_H: 2.60 (3H, s), 3.81 (3H, s), 6.53–6.54 (1H, m), 6.92–6.98 (1H, m), 7.07 (1H, d, *J* 3.1), 7.14–7.24 (2H, m); ^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 18.9, 33.1, 99.5, 106.9, 119.6, 121.8, 128.3, 128.5, 130.5, 136.5; HRMS $(AP)^+$ calculated for $[C_{10}H_{12}N]^+$ $(M+H)^+$ m/z: 146.0970, found 146.0963 (-4.8 ppm).

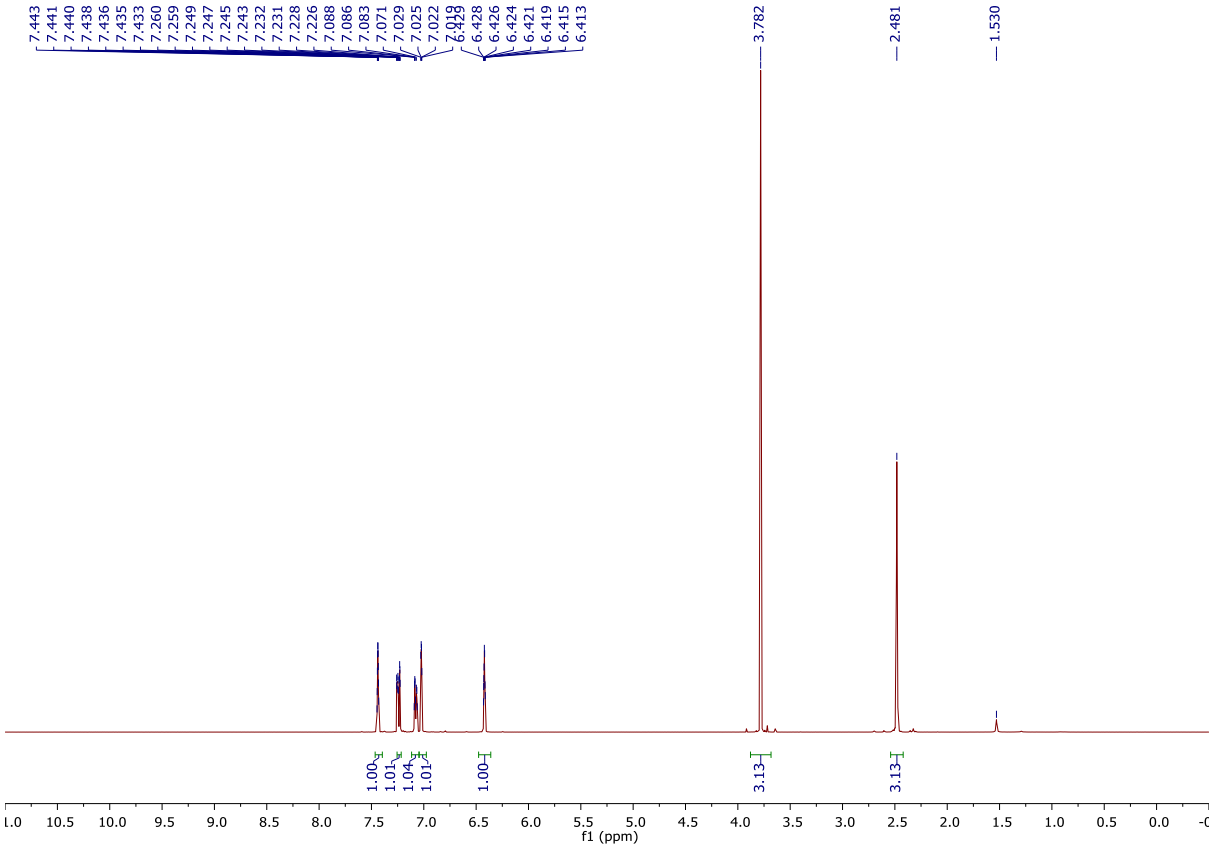


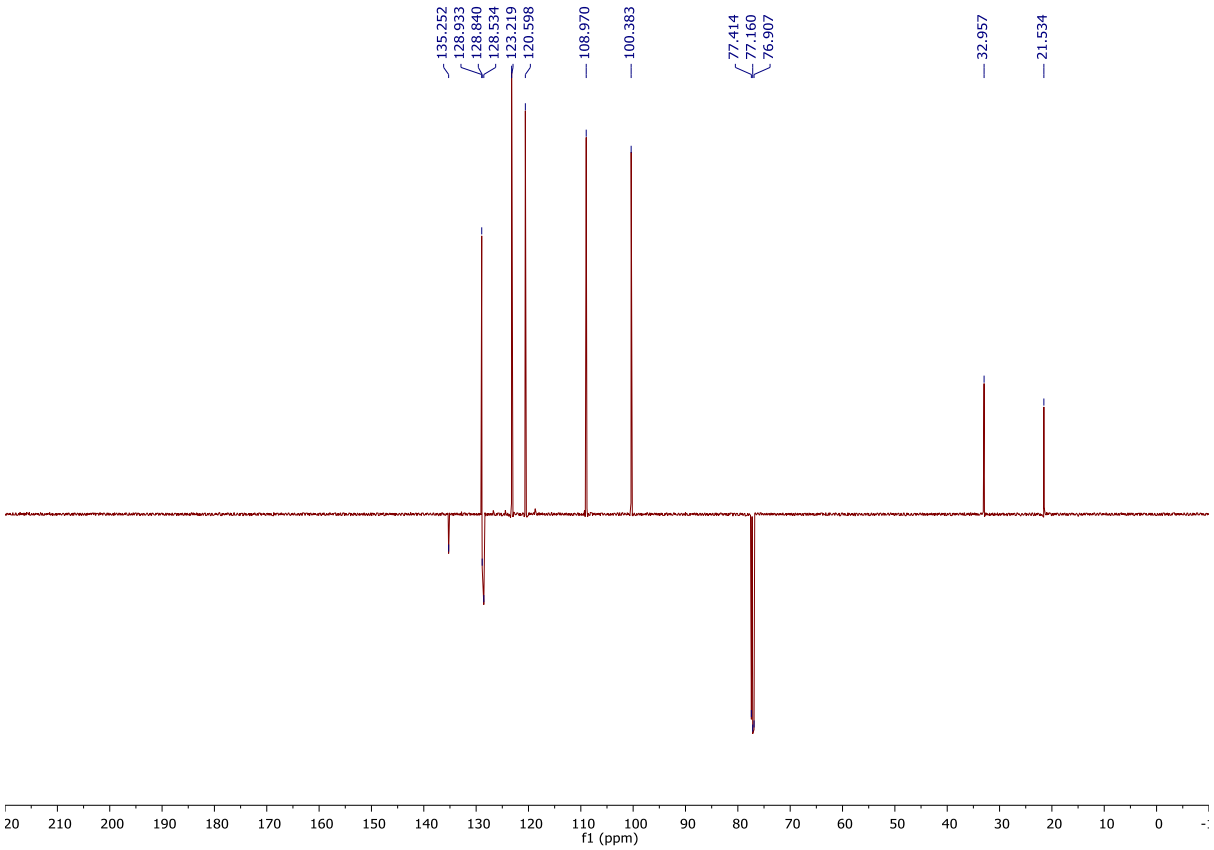


1,5-Dimethyl-1H-indole 1j

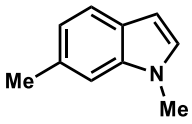


The title compound was prepared according to general procedure 2 using 5-methyl-1H-indole (394 mg, 3.0 mmol). Purification by flash silica chromatography (eluent = 0.5–1% EtOAc in hexanes, 25 × 160 mm silica) gave the title compound **1j** as a light yellow oil (416 mg, 2.86 mmol, 96%); R_f = 0.38 (eluent = 1% EtOAc in hexanes); ν_{max} / cm^{-1} (film) 2909, 1568, 1510, 1495, 1422, 1331, 1294, 1242, 1155, 1103, 1078, 1011, 868, 789, 756, 712, 662, 598, 473, 424; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 2.48 (3H, s), 3.78 (3H, s), 6.41–6.43 (1H, m), 7.02 (1H, dd, *J* 3.1, 1.8), 7.04–7.12 (1H, m), 7.22–7.26 (1H, m), 7.43–7.45 (1H, m); ^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 21.5, 33.0, 100.4, 109.0, 120.6, 123.2, 128.5, 128.8, 128.9, 135.3; HRMS $(EI)^+$ calculated for $[C_{10}H_{11}N]^+$ $(M)^+$ m/z: 145.0891, found 145.0896 (+3.4 ppm).

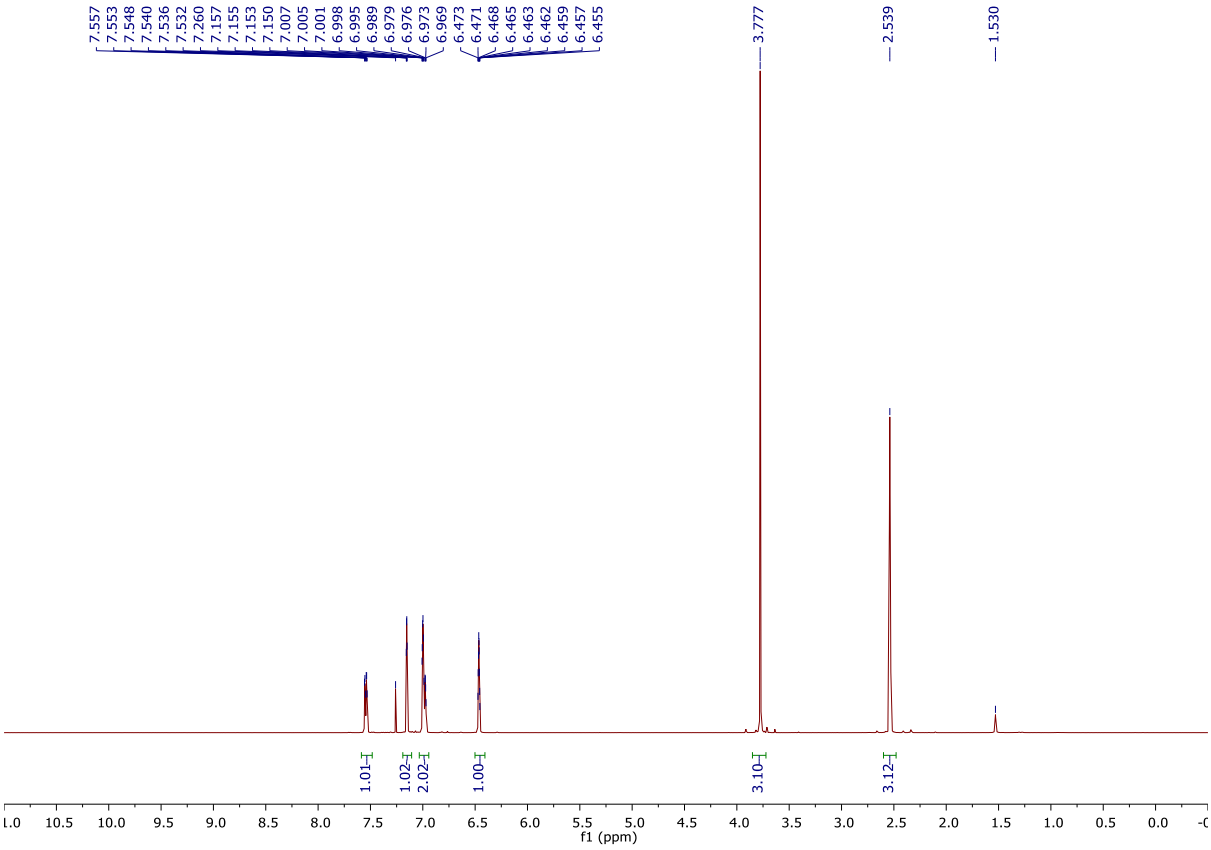

7.443
7.441
7.440
7.438
7.436
7.435
7.433
7.260
7.259
7.249
7.247
7.245
7.243
7.232
7.231
7.228
7.226
7.088
7.086
7.083
7.071
7.029
7.025
7.022
6.428
6.426
6.424
6.421
6.419
6.415
6.413
3.782
2.481
1.530
1.00
1.01
1.04
1.01
1.00
3.13
3.13
f1 (ppm)

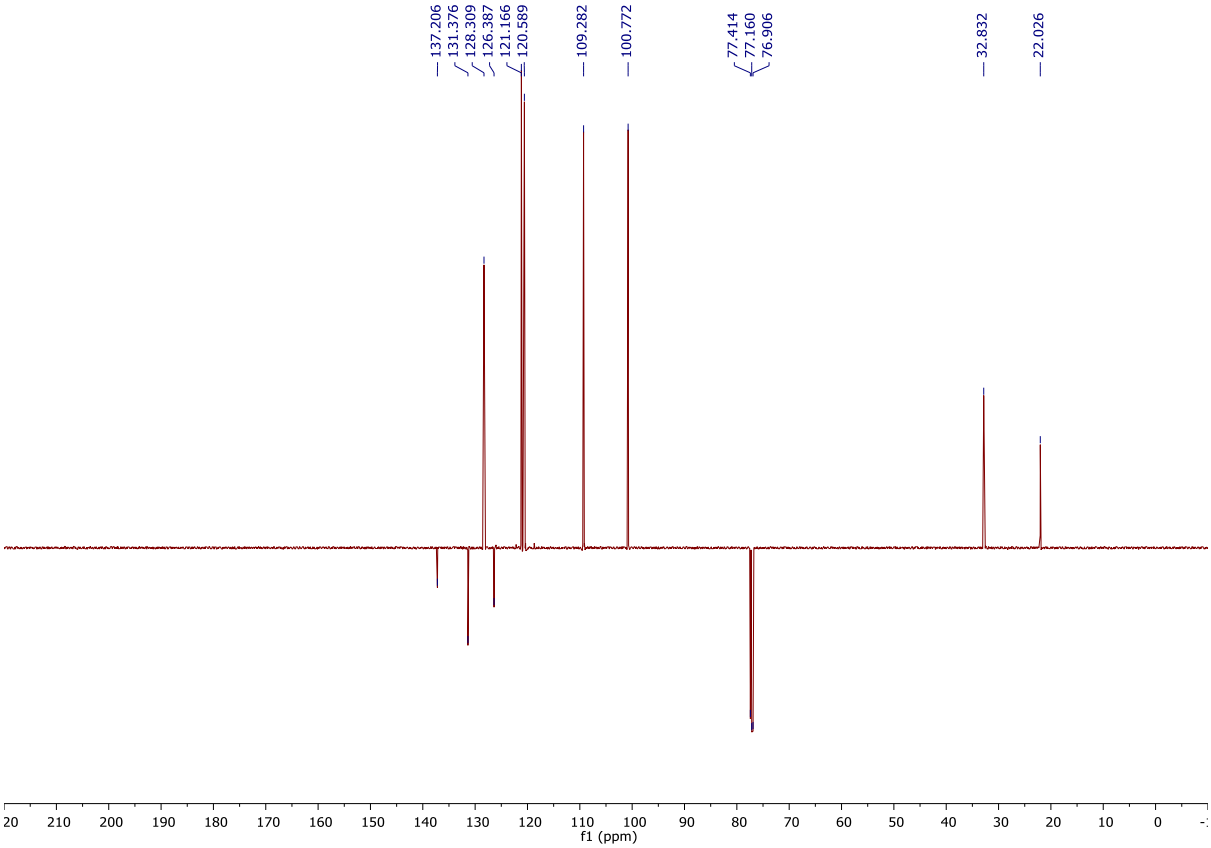

135.252
128.933
128.840
128.534
123.219
120.598
108.970
100.383
77.414
77.160
76.907
32.957
21.534
f1 (ppm)

1,6-Dimethyl-1H-indole 1k



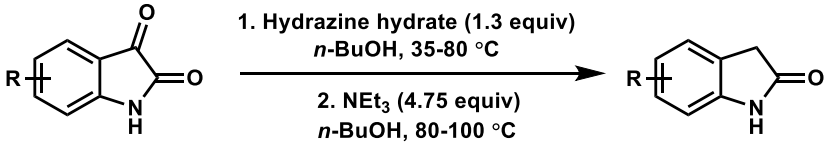
The title compound was prepared according to general procedure 2 using 6-methyl-1H-indole (394 mg, 3.0 mmol). Purification by flash silica chromatography (eluent = 2% EtOAc in hexanes, 25 × 160 mm silica) gave the title compound **1k** as a light yellow oil (397 mg, 2.73 mmol, 91%); R_f = 0.33 (eluent = 2% EtOAc in hexanes); ν_{max} / cm^{-1} (film) 2914, 1622, 1510, 1470, 1443, 1418, 1339, 1325, 1310, 1242, 1198, 1094, 1076, 932, 847, 797, 750, 710, 679, 600, 563, 505, 428; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 2.54 (3H, s), 3.78 (3H, s), 6.46–6.47 (1H, m), 6.94–7.03 (2H, m), 7.11–7.19 (1H, m), 7.54 (1H, dt, *J* 8.1, 2.1); ^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 22.0, 32.8, 100.8, 109.3, 120.6, 121.2, 126.4, 128.3, 131.4, 137.2; HRMS (EI)$^+$ calculated for $[C_{10}H_{11}N]^+$ $(M)^+$ m/z: 145.0891, found 145.0891 (+0.0 ppm).





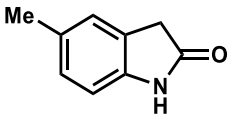
2.3. Synthesis of the oxindole substrates

General procedure 3: reduction of isatins to oxindoles



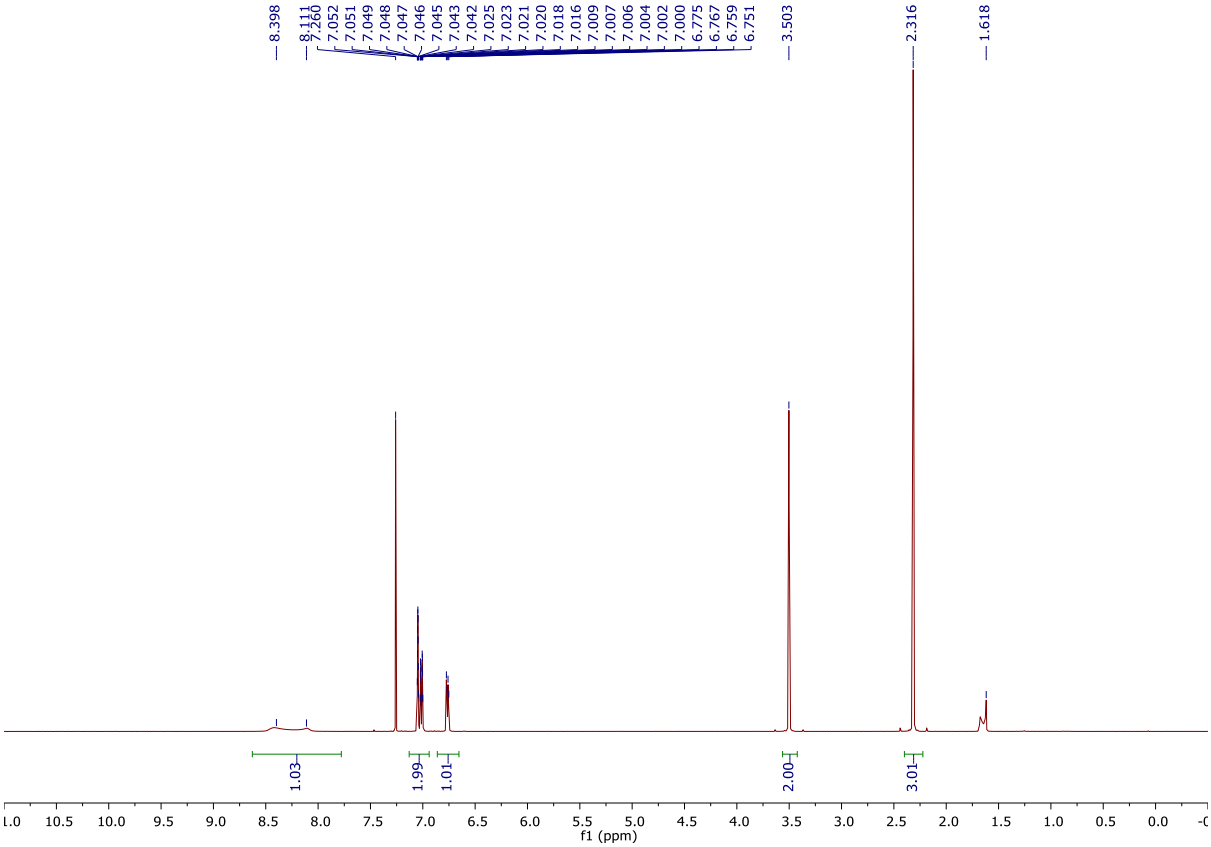
A round-bottomed flask equipped with a magnetic stirrer bar was charged with isatin derivative (1.0 equiv) and *n*-butyl alcohol (6 mL/mmol). Hydrazine hydrate 80% in water (1.3 equiv) was slowly added for 30 minutes at 35 °C and it was allowed to react for 4 h at 80 °C. Then triethylamine (4.75 equiv) was slowly added at the same temperature, while stirring and was allowed to react for 11 h at 100 °C. It was then cooled and concentrated *in vacuo* to remove the volatiles.

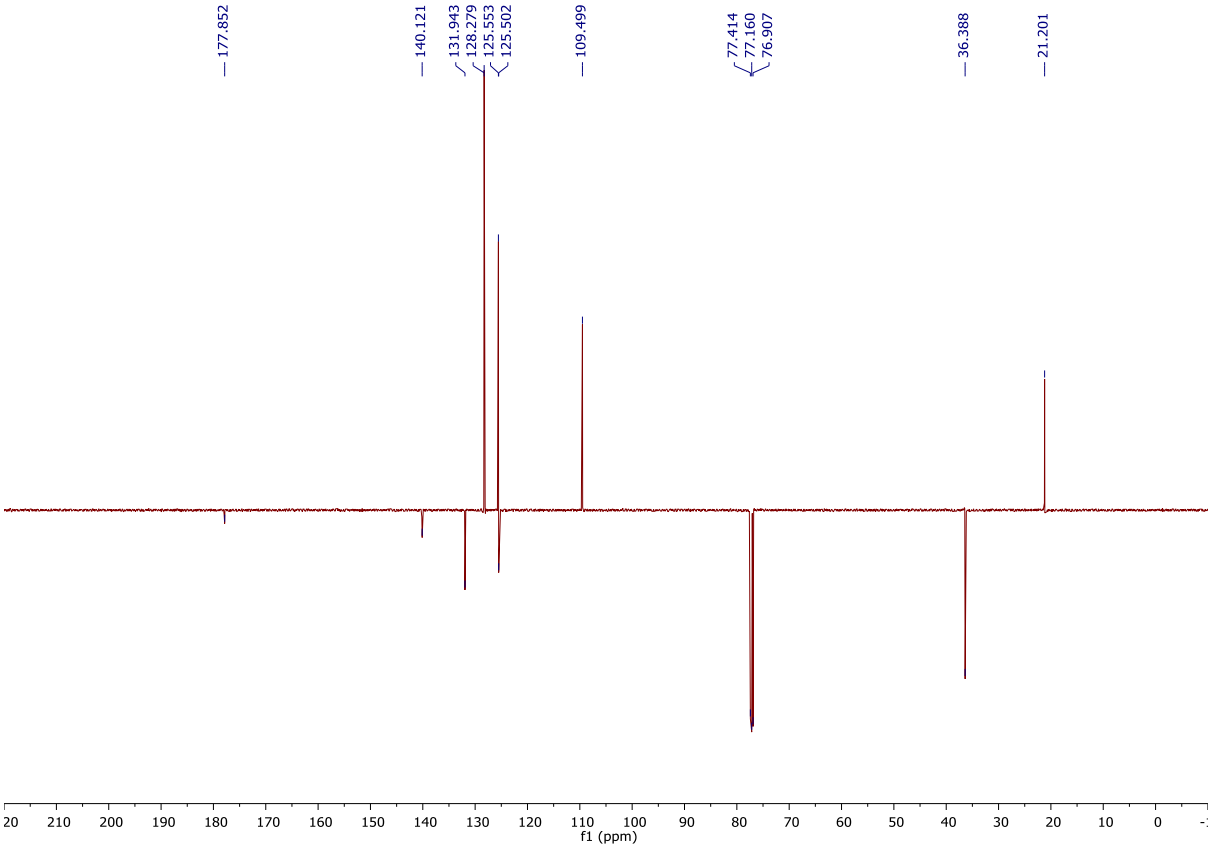
5-Methylindolin-2-one



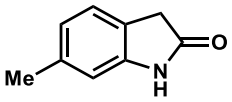
The title compound was prepared according to general procedure 3 using 5-methylindoline-2,3-dione (806 mg, 5.0 mmol). Purification by flash silica chromatography (eluent = 25% EtOAc in cyclohexane, 30 × 180 mm silica) gave the title compound as a yellow solid (643 mg, 4.37 mmol, 87%); mp 180–182 °C (Lit. 172–174 °C);[11] R_f = 0.21 (eluent = 30% EtOAc in cyclohexane); ν_{max} / cm^{-1} (film) 3150, 2860,

1694, 1620, 1487, 1422, 1383, 1317, 1248, 1215, 1200, 1128, 951, 932, 887, 851, 818, 772, 712, 669, 588, 552; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 2.32 (3H, s), 3.50 (2H, s), 6.76 (1H, dd, *J* 7.9, 3.7), 6.94–7.13 (2H, m), 7.76–8.85 (1H, m); ^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 21.2, 36.4, 109.5, 125.5, 125.6, 128.3, 131.9, 140.1, 177.9; HRMS (AP)$^+$ calculated for $[C_9H_{10}NO]^+$ $(M+H)^+$ m/z: 148.0762, found 148.0765 (+2.0 ppm).

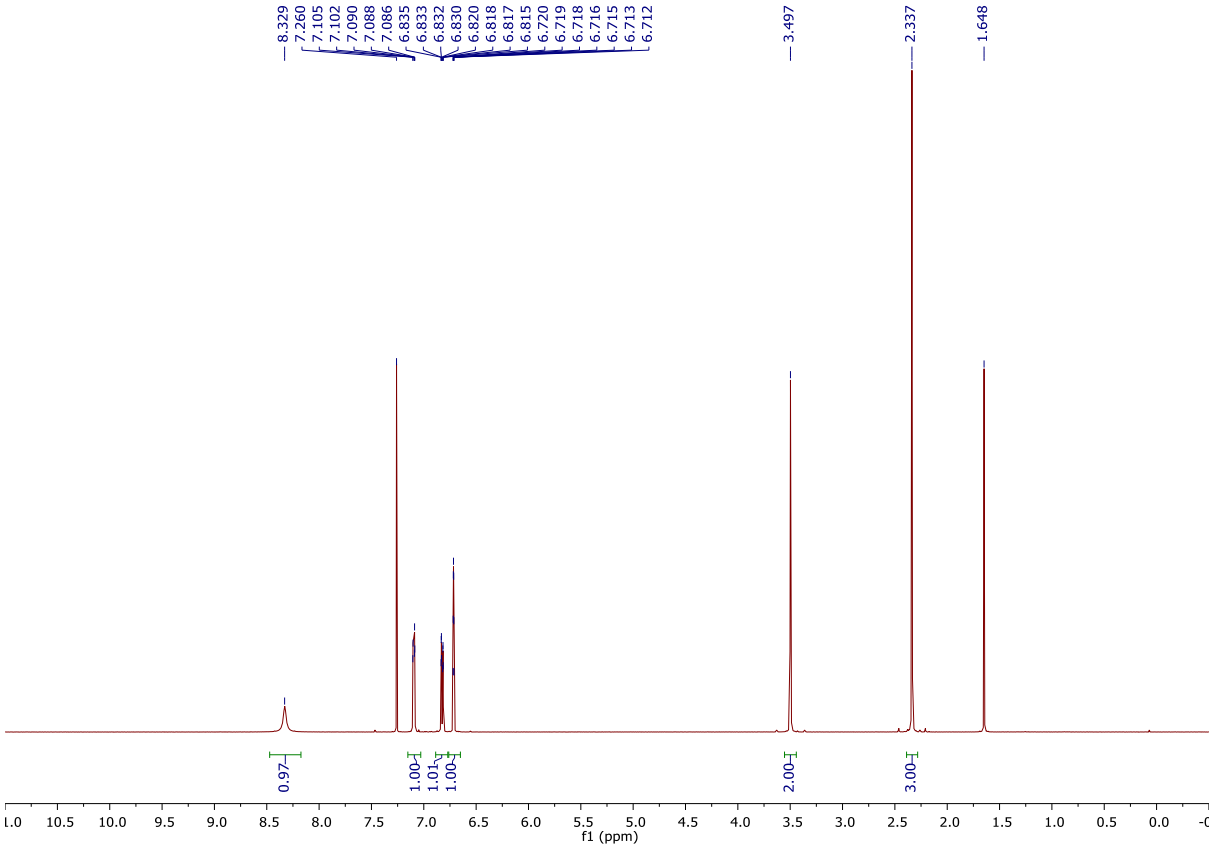


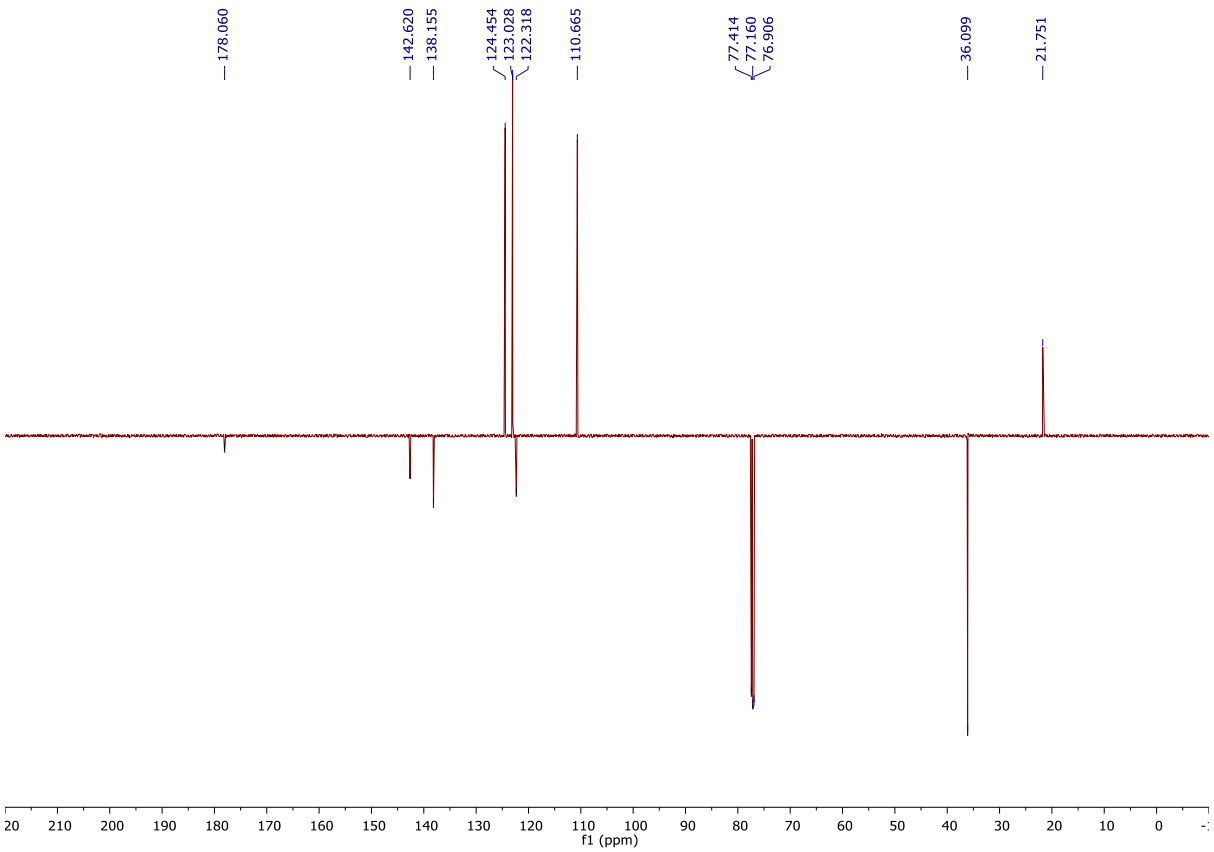


6-Methylindolin-2-one

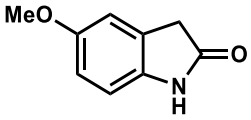


The title compound was prepared according to general procedure 3 using 6-methylindoline-2,3-dione (806 mg, 5.0 mmol). Purification by flash silica chromatography (eluent = 20% EtOAc in hexanes, 30 × 180 mm silica) gave the title compound as a yellow solid (615 mg, 4.18 mmol, 84%); mp 185–187 °C (Lit. 188–190 °C);[12] R_f = 0.67 (eluent = 50% EtOAc in hexanes); ν_{max} / cm^{-1} (film) 3069, 1714, 1670, 1628, 1591, 1506, 1466, 1385, 1337, 1310, 1250, 1202, 1140, 1115, 957, 862, 818, 797, 764, 689, 596, 565, 538, 449, 421; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 2.34 (3H, s), 3.50 (2H, s), 6.65–6.76 (1H, m), 6.82 (1H, ddd, *J* 7.5, 1.6, 0.8), 7.03–7.15 (1H, m), 8.33 (1H, br s); ^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 21.8, 36.1, 110.7, 122.3, 123.0, 124.5, 138.2, 142.6, 178.1; HRMS (AP)$^+$ calculated for $[C_9H_{10}NO]^+$ $(M+H)^+$ m/z: 148.0762, found 148.0755 (-4.7 ppm).

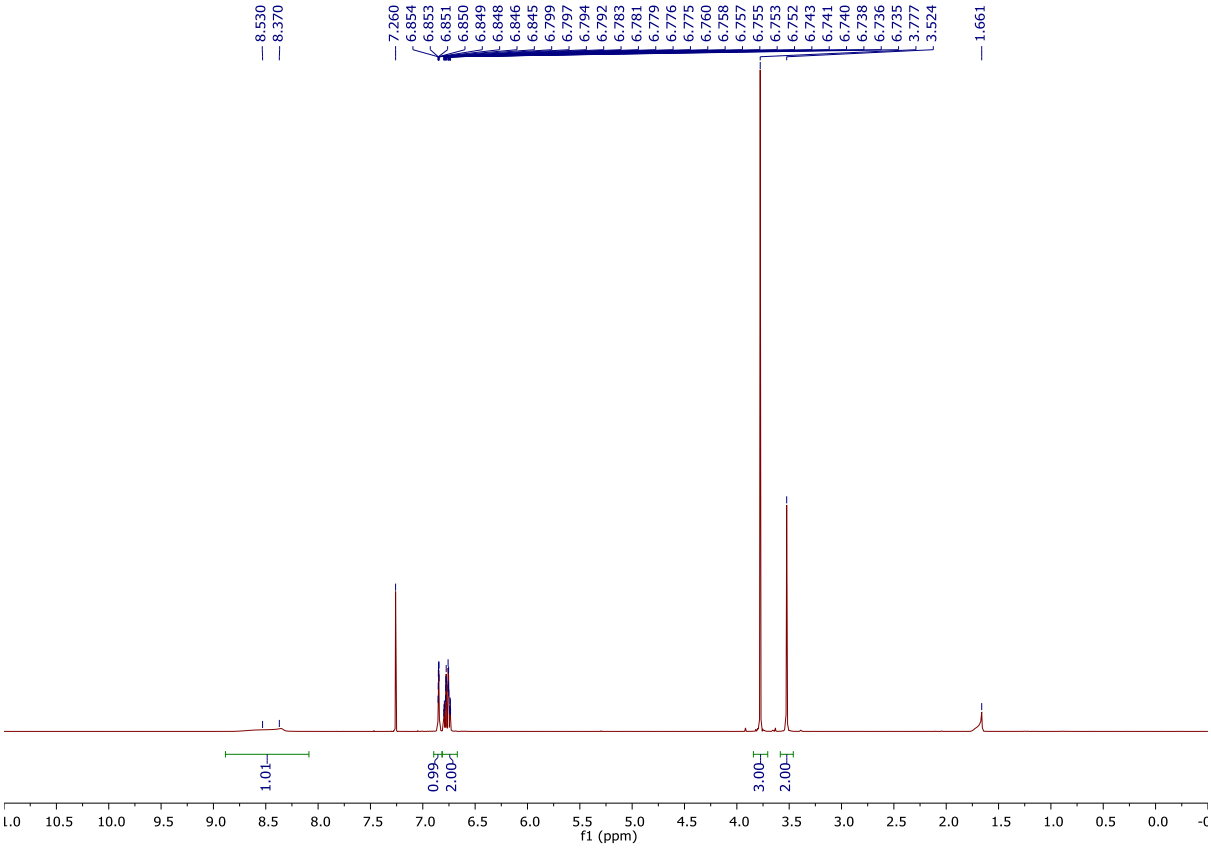

8.329
7.260
7.105
7.102
7.090
7.088
7.086
6.835
6.833
6.832
6.830
6.820
6.818
6.817
6.815
6.720
6.719
6.718
6.716
6.715
6.713
6.712
3.497
2.337
1.648
0.97
1.00
1.01
1.00
2.00
3.00
f1 (ppm)

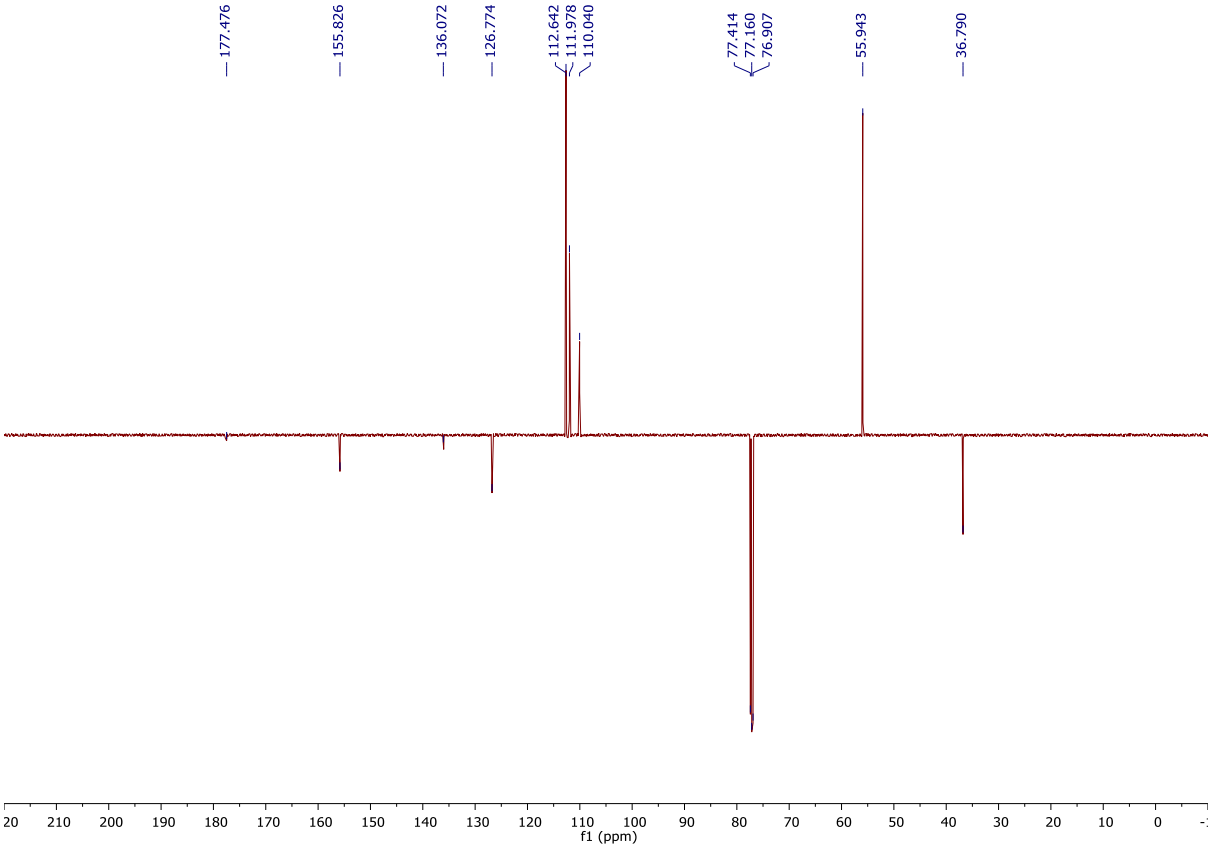

178.060
142.620
138.155
124.454
123.028
122.318
110.665
77.414
77.160
76.906
36.099
21.751
f1 (ppm)

5-Methoxyindolin-2-one

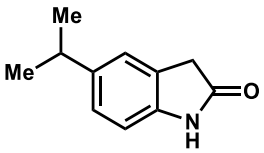


The title compound was prepared according to general procedure 3 using 5-methoxyindoline-2,3-dione (886 mg, 5.0 mmol). Purification by flash silica chromatography (eluent = 40% EtOAc in hexanes, 30 × 180 mm silica) gave the title compound as an off-white solid (629 mg, 3.86 mmol, 77%); mp 151–153 °C (Lit. 148–151 °C);[13] R_f = 0.28 (eluent = 50% EtOAc in hexanes); ν_{max} / cm^{-1} (film) 3154, 3048, 1682, 1636, 1605, 1487, 1466, 1427, 1387, 1316, 1279, 1225, 1198, 1184, 1138, 1115, 1034, 945, 930, 887, 874, 851, 791, 775, 735, 712, 671, 608, 552; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 3.52 (2H, s), 3.78 (3H, s), 6.67–6.81 (2H, m), 6.82–6.90 (1H, m), 8.07–8.87 (1H, m); ^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 36.8, 55.9, 110.0, 112.0, 112.6, 126.8, 136.1, 155.8, 177.5; HRMS (EI)$^+$ calculated for $[C_9H_9NO_2]^+$ $(M)^+$ m/z: 163.0633, found 163.0631 (-1.2 ppm).

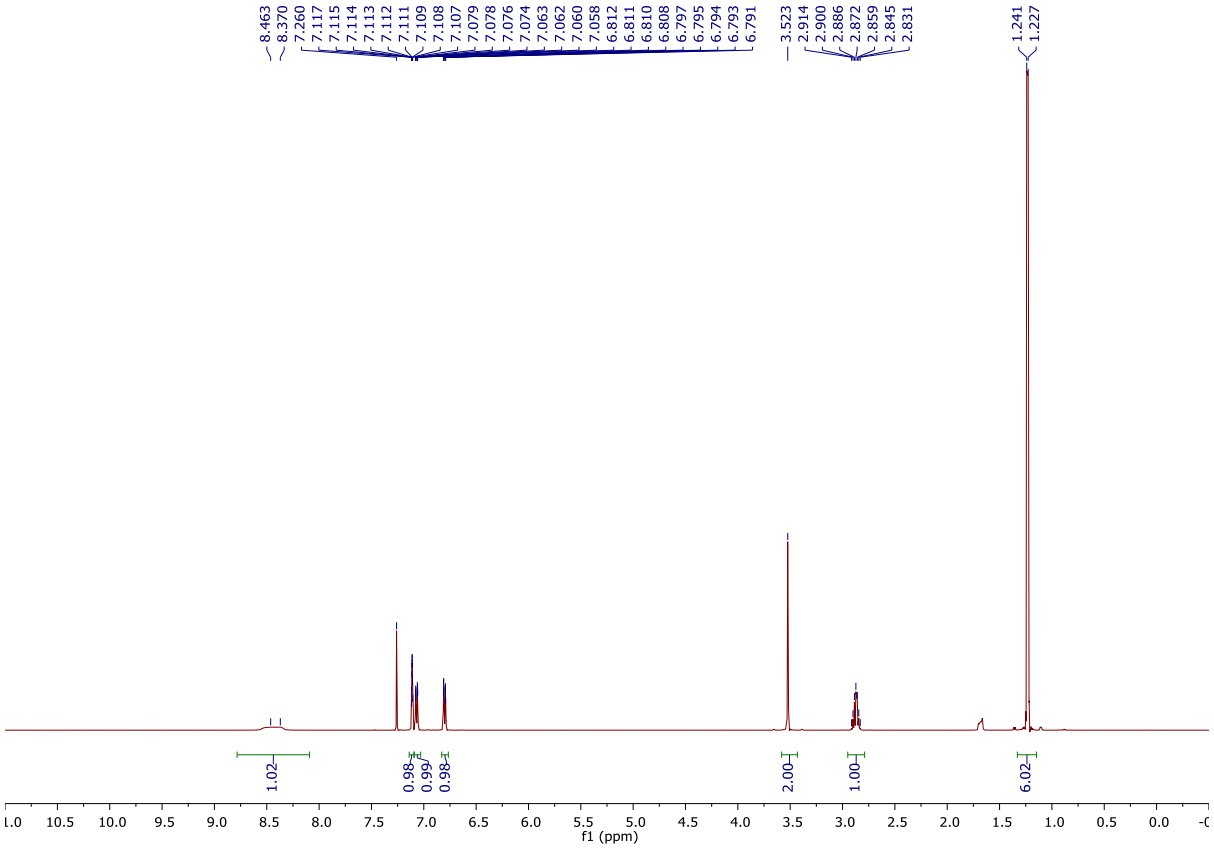


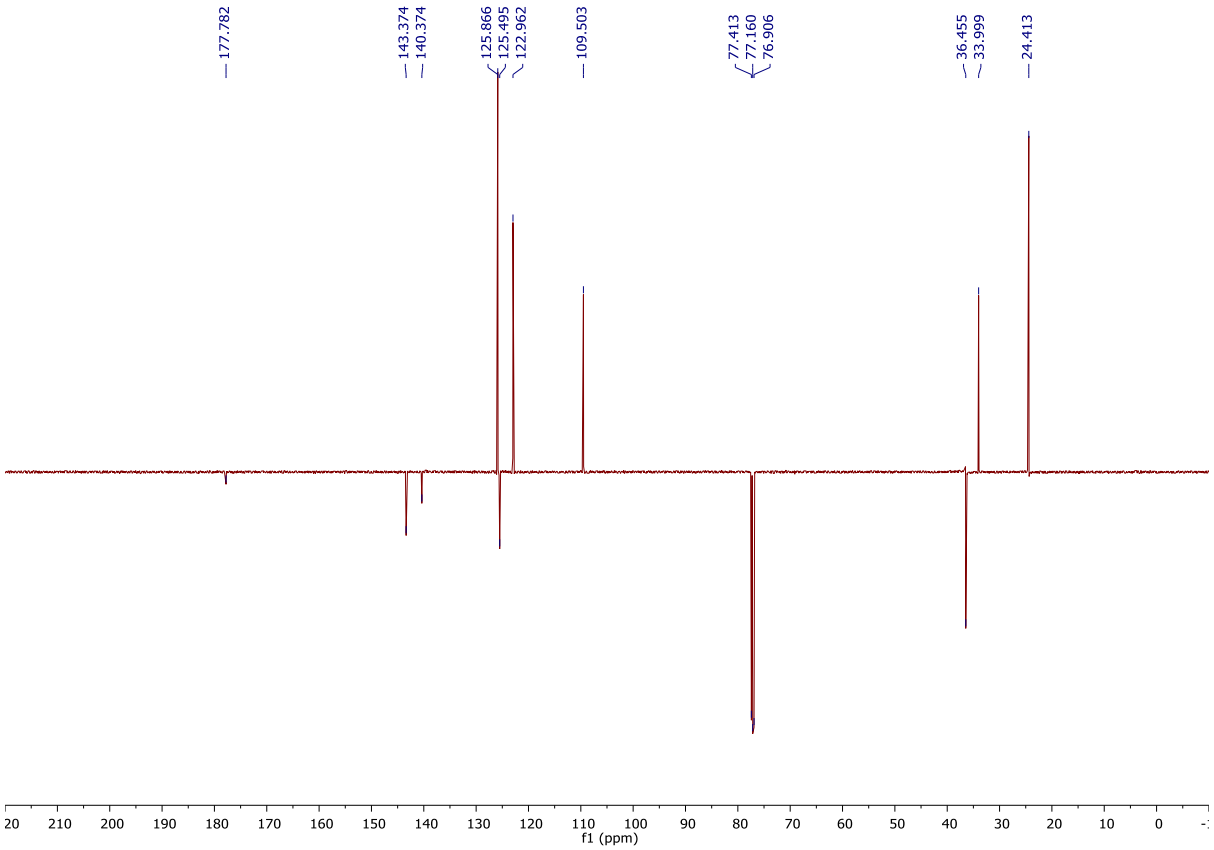


5-Isopropylindolin-2-one

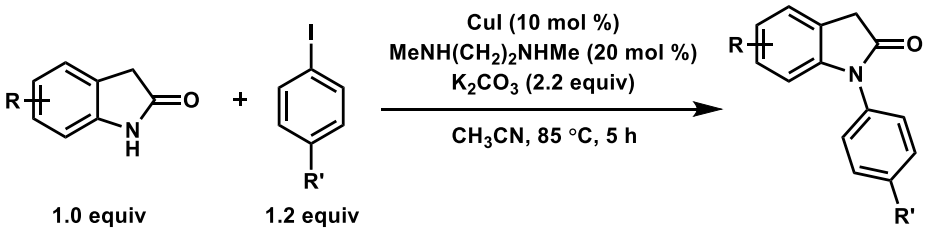


The title compound was prepared according to general procedure 3 using 5-isopropylindoline-2,3-dione (946 mg, 5.0 mmol). Purification by flash silica chromatography (eluent = 25% EtOAc in hexanes, 30 × 180 mm silica) gave the title compound as a yellow solid (763 mg, 4.03 mmol, 81%); mp 118–120 °C; R_f = 0.53 (eluent = 50% EtOAc in hexanes); ν_{max} / cm^{-1} (film) 3156, 2957, 2872, 1701, 1622, 1485, 1458, 1420, 1381, 1364, 1337, 1310, 1231, 1200, 1161, 1117, 1099, 1057, 936, 901, 866, 820, 795, 727, 710, 665, 615, 594, 575, 552, 513; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 1.23 (6H, d, *J* 6.9), 2.87 (1H, hept, *J* 6.9), 3.52 (2H, s), 6.77–6.83 (1H, m), 7.07 (1H, ddd, *J* 7.9, 1.8, 0.8), 7.09–7.14 (1H, m), 8.07–8.78 (1H, m); ^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 24.4, 34.0, 36.5, 109.5, 123.0, 125.5, 125.9, 140.4, 143.4, 177.8; HRMS $(ES)^+$ calculated for $[C_{11}H_{14}NO]^+$ $(M+H)^+$ m/z: 176.1075, found 176.1077 (+1.1 ppm).


8.463
8.370
7.260
7.117
7.115
7.114
7.113
7.112
7.111
7.109
7.108
7.107
7.079
7.078
7.076
7.074
7.063
7.062
7.060
7.058
6.812
6.811
6.810
6.808
6.797
6.795
6.794
6.793
6.791
3.523
2.914
2.900
2.886
2.872
2.859
2.845
2.831
1.241
1.227
1.02
0.98
0.99
0.98
2.00
1.00
6.02
f1 (ppm)

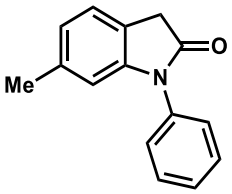

177.782
143.374
140.374
125.866
125.495
122.962
109.503
77.413
77.160
76.906
36.455
33.999
24.413
f1 (ppm)

General procedure 4: N-arylation of oxindoles

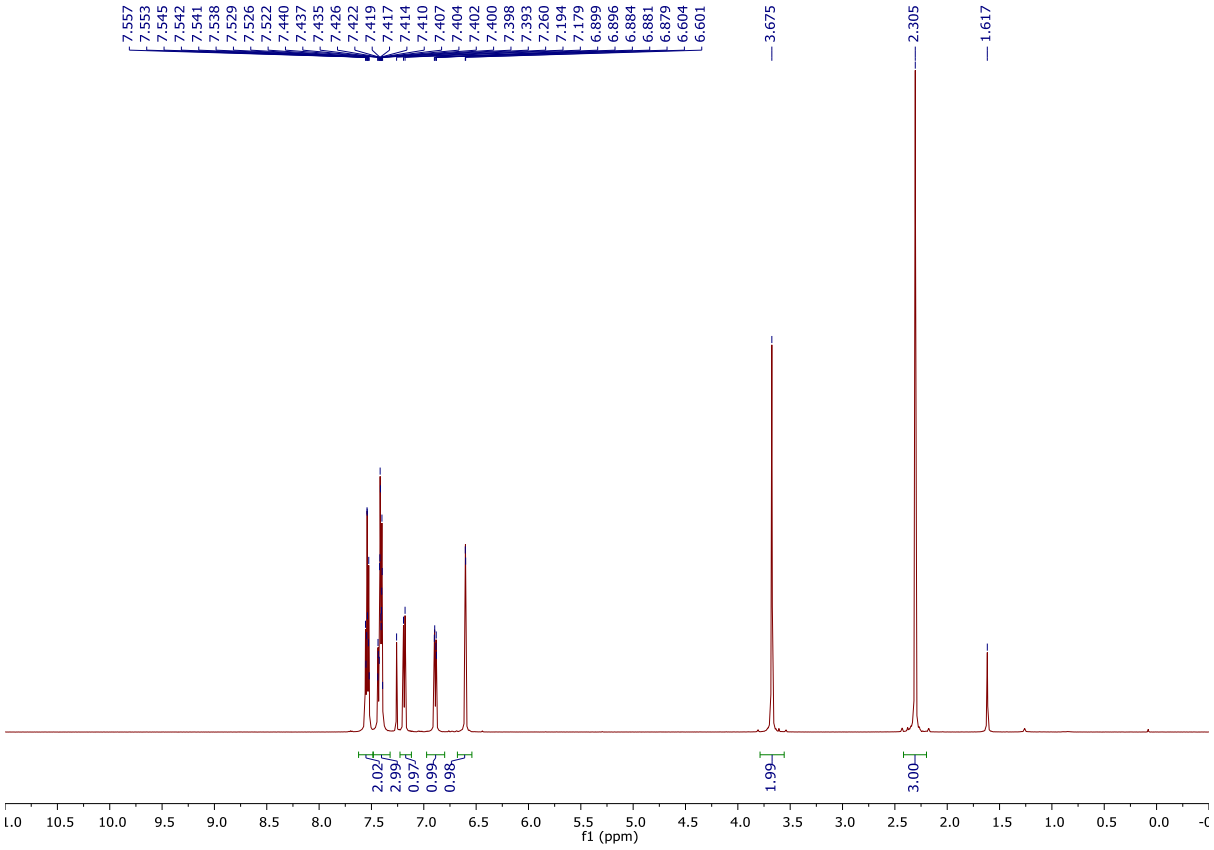


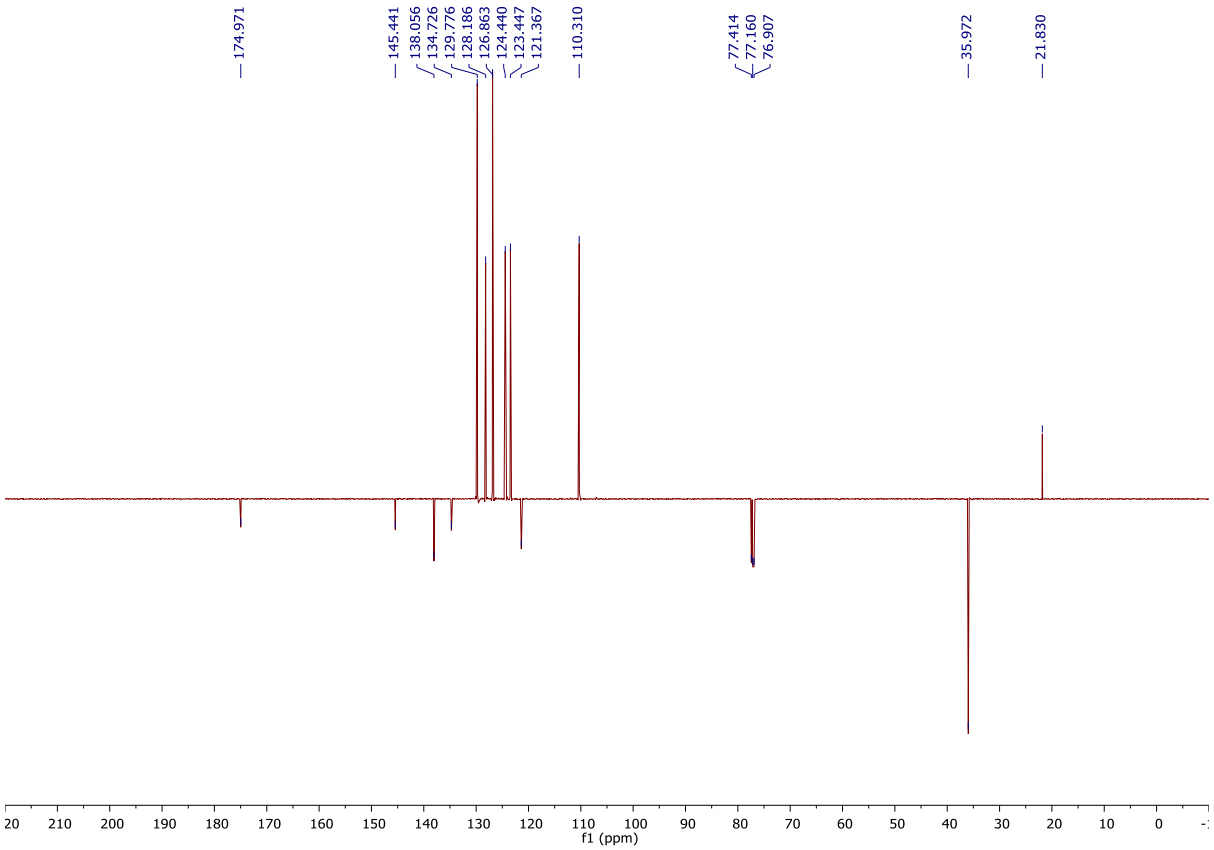
An oven dried vial was charged with oxindole derivative (1.0 equiv), iodoarene (1.2 equiv) and acetonitrile (3 mL/mmol) under a nitrogen atmosphere. The mixture was purged with N_2 for 15 min at 40 °C. Thereafter potassium carbonate (2.2 equiv), copper (I) iodide (10 mol %), and N,N'-dimethylethylenediamine (20 mol %) were added and sealed under nitrogen blanket. Then the reaction mixture was stirred for 5 h at 85 °C. The reaction mixture was then cooled to room temperature and HCl (1 M, 10 mL/mmol) was added. Then reaction mixture was extracted with EtOAc (3 × 15 mL/mmol). The combined organic layer was washed with brine (2 × 10 mL/mmol), dried over $MgSO_4$, filtered, and concentrated *in vacuo*.

6-Methyl-1-phenylindolin-2-one 8b

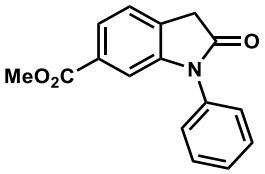


The title compound was prepared according to general procedure 4 using 6-methylindolin-2-one (571 mg, 3.88 mmol) and iodobenzene (520 µL, 4.66 mmol). Purification by flash silica chromatography (eluent = 15% EtOAc in hexanes, 30 × 180 mm silica) gave the title compound **8b** as a yellow solid (639 mg, 2.86 mmol, 74%); mp 119–121 °C; R_f = 0.43 (eluent = 20% EtOAc in hexanes); ν_{max} / cm^{-1} (film) 3042, 1711, 1622, 1609, 1589, 1506, 1493, 1456, 1433, 1371, 1314, 1285, 1242, 1192, 1163, 1148, 1109, 1074, 1024, 953, 926, 847, 802, 764, 694, 667, 596, 496, 428; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 2.31 (3H, s), 3.68 (2H, s), 6.60 (1H, d, *J* 1.5), 6.89 (1H, dd, *J* 7.4, 1.4), 7.19 (1H, d, *J* 7.5), 7.32–7.49 (3H, m), 7.54 (2H, tt, *J* 8.1, 2.0); ^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 21.8, 36.0, 110.3, 121.4, 123.5, 124.4, 126.9, 128.2, 129.8, 134.7, 138.1, 145.4, 175.0; HRMS $(AP)^+$ calculated for $[C_{15}H_{14}NO]^+$ $(M+H)^+$ m/z: 224.1075, found 224.1082 (+3.1 ppm).

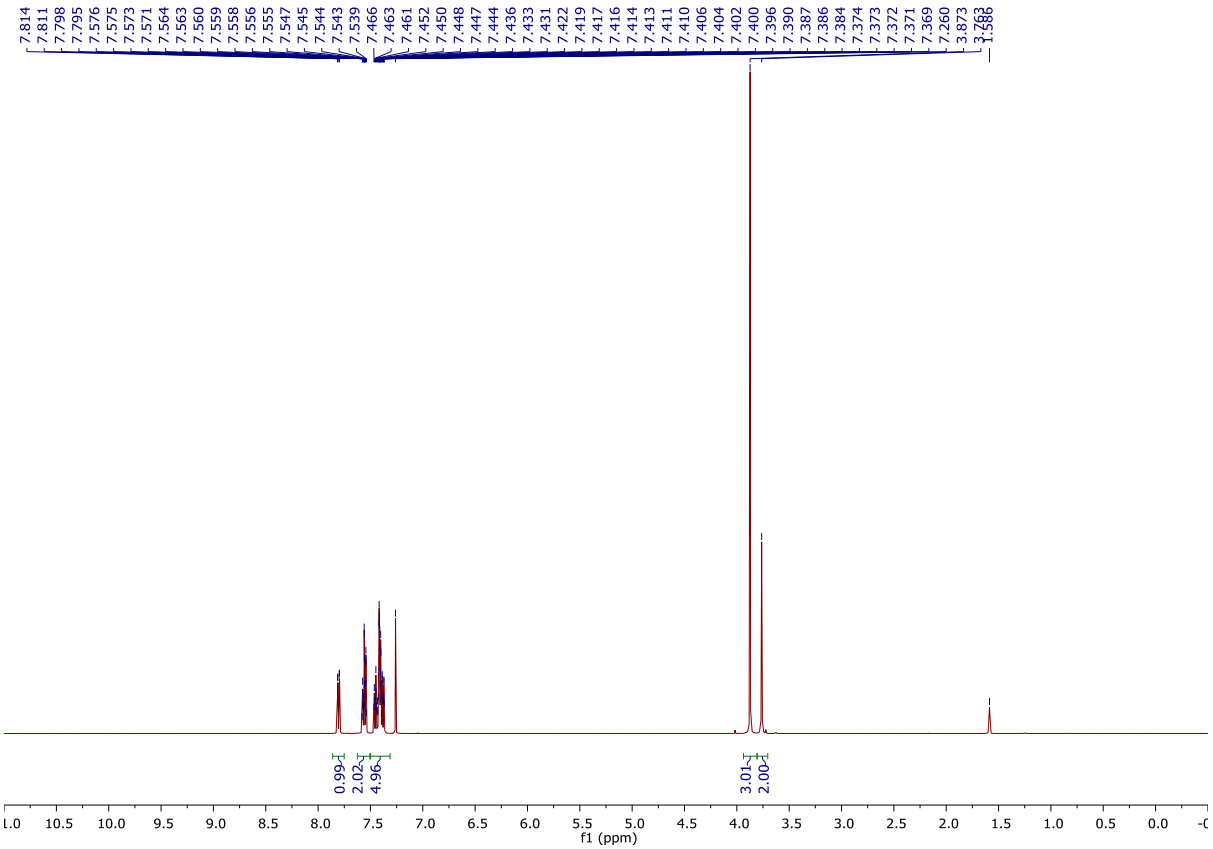

7.557
7.553
7.545
7.542
7.541
7.538
7.529
7.526
7.522
7.440
7.437
7.435
7.426
7.422
7.419
7.417
7.414
7.410
7.407
7.404
7.402
7.400
7.398
7.393
7.260
7.194
7.179
6.899
6.896
6.884
6.881
6.879
6.604
6.601
3.675
2.305
1.617
2.02
2.99
0.97
0.99
0.98
1.99
3.00
f1 (ppm)

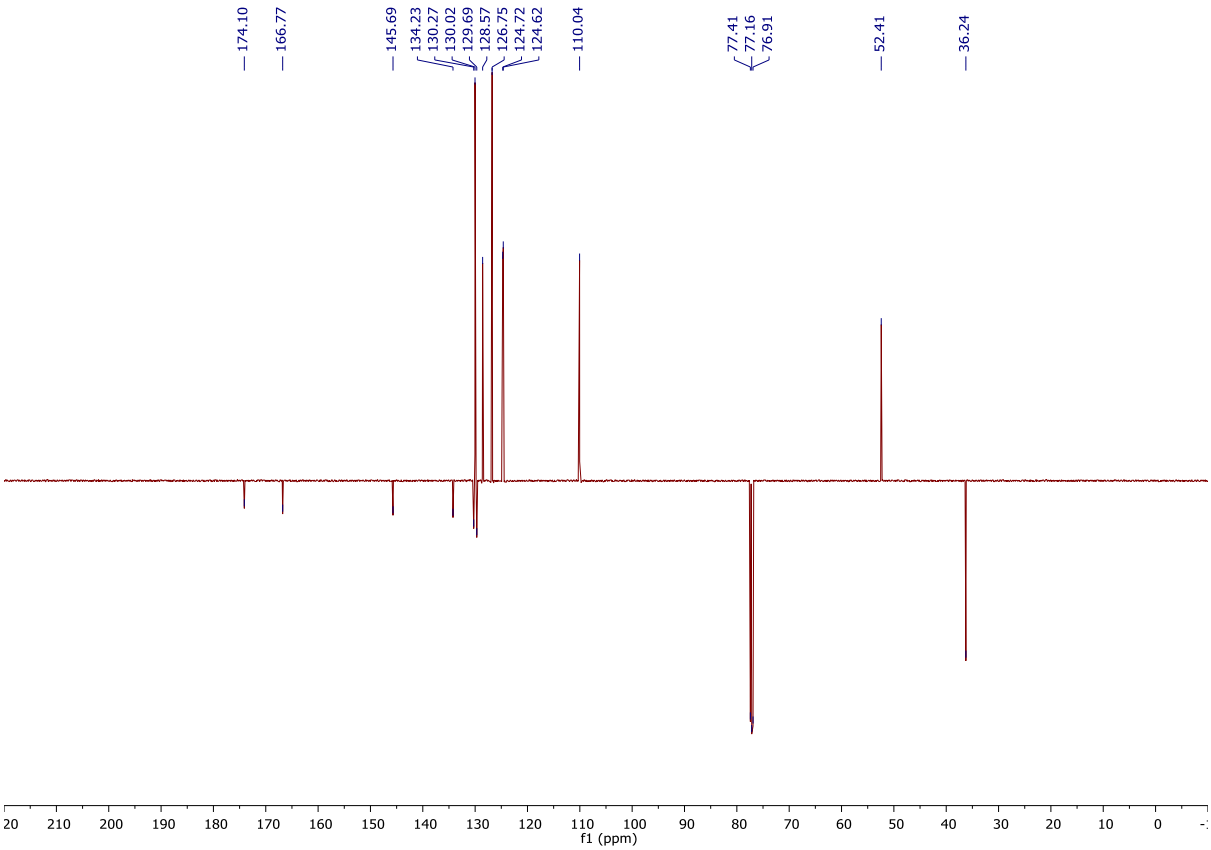

174.971
145.441
138.056
134.726
129.776
128.186
126.863
124.440
123.447
121.367
110.310
77.414
77.160
76.907
35.972
21.830
f1 (ppm)

Methyl 2-oxo-1-phenylindoline-6-carboxylate 8c

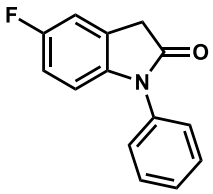


The title compound was prepared according to general procedure 4 using methyl 2-oxoindoline-6-carboxylate (574 mg, 3.0 mmol) and iodobenzene (403 µL, 3.6 mmol). Purification by flash silica chromatography (eluent = 10–15% EtOAc in hexanes, 30 × 180 mm silica) gave the title compound **8c** as an off-white solid (685 mg, 2.56 mmol, 85%); mp 194–198 °C; R_f = 0.17 (eluent = 20% EtOAc in hexanes); ν_{max} / cm^{-1} (film) 1711, 1620, 1586, 1503, 1441, 1371, 1279, 1250, 1188, 1167, 1090, 1007, 968, 949, 922, 882, 855, 804, 752, 691, 667, 654, 602, 486; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 3.76 (2H, s), 3.87 (3H, s), 7.31–7.50 (5H, m), 7.51–7.63 (2H, m), 7.80 (1H, dd, *J* 7.7, 1.5); ^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 36.2, 52.4, 110.0, 124.6, 124.7, 126.8, 128.6, 129.7, 130.0, 130.3, 134.2, 145.7, 166.8, 174.1; HRMS (ES)$^+$ calculated for $[C_{16}H_{14}NO_3]^+$ $(M+H)^+$ m/z: 268.0974, found 268.0985 (+4.1 ppm).

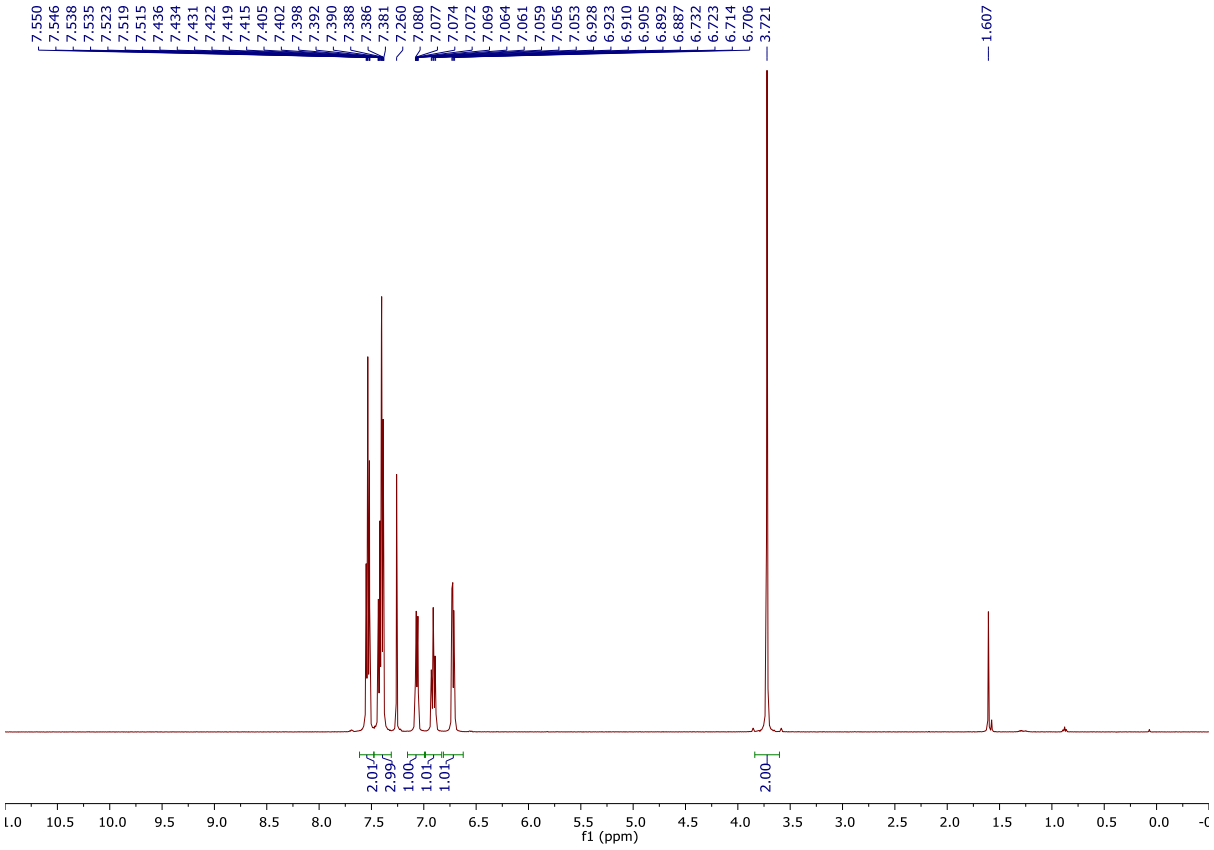




5-Fluoro-1-phenylindolin-2-one 8d



The title compound was prepared according to general procedure 4 using 5-fluoroindolin-2-one (756 mg, 5.0 mmol) and iodobenzene (670 µL, 6.0 mmol). Purification by flash silica chromatography (eluent = 10–15% EtOAc in hexanes, 30 × 180 mm silica) gave the title compound **8d** as an off-white solid (911 mg, 4.0 mmol, 80%); mp 132–134 °C; R_f = 0.31 (eluent = 20% EtOAc in hexanes); ν_{max} / cm^{-1} (film) 1709, 1618, 1593, 1501, 1481, 1449, 1387, 1360, 1327, 1258, 1227, 1173, 1130, 1098, 1076, 1024, 941, 926, 860, 847, 814, 754, 694, 671, 600, 586, 530, 502, 451, 426; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 3.72 (2H, s), 6.72 (1H, dd, *J* 8.7, 4.3), 6.91 (1H, td, *J* 8.9, 2.7), 7.07 (1H, ddt, *J* 7.9, 2.6, 1.2), 7.31–7.48 (3H, m), 7.54 (2H, dd, *J* 8.6, 7.0); ^{19}F NMR (471 MHz, $CDCl_3$) δ_F: -120.5; ^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 36.4 (d, *J* 1.6), 110.0 (d, *J* 8.2), 112.7 (d, *J* 25.0), 114.2 (d, *J* 23.4), 125.9 (d, *J* 8.8), 126.7, 128.4, 129.9, 134.6, 141.3 (d, *J* 1.9), 159.4 (d, *J* 241.2), 174.1; HRMS (ES)$^+$ calculated for $[C_{14}H_{11}NOF]^+$ $(M+H)^+$ m/z: 228.0825, found 228.0829 (+1.8 ppm).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7.546
7.538
7.535
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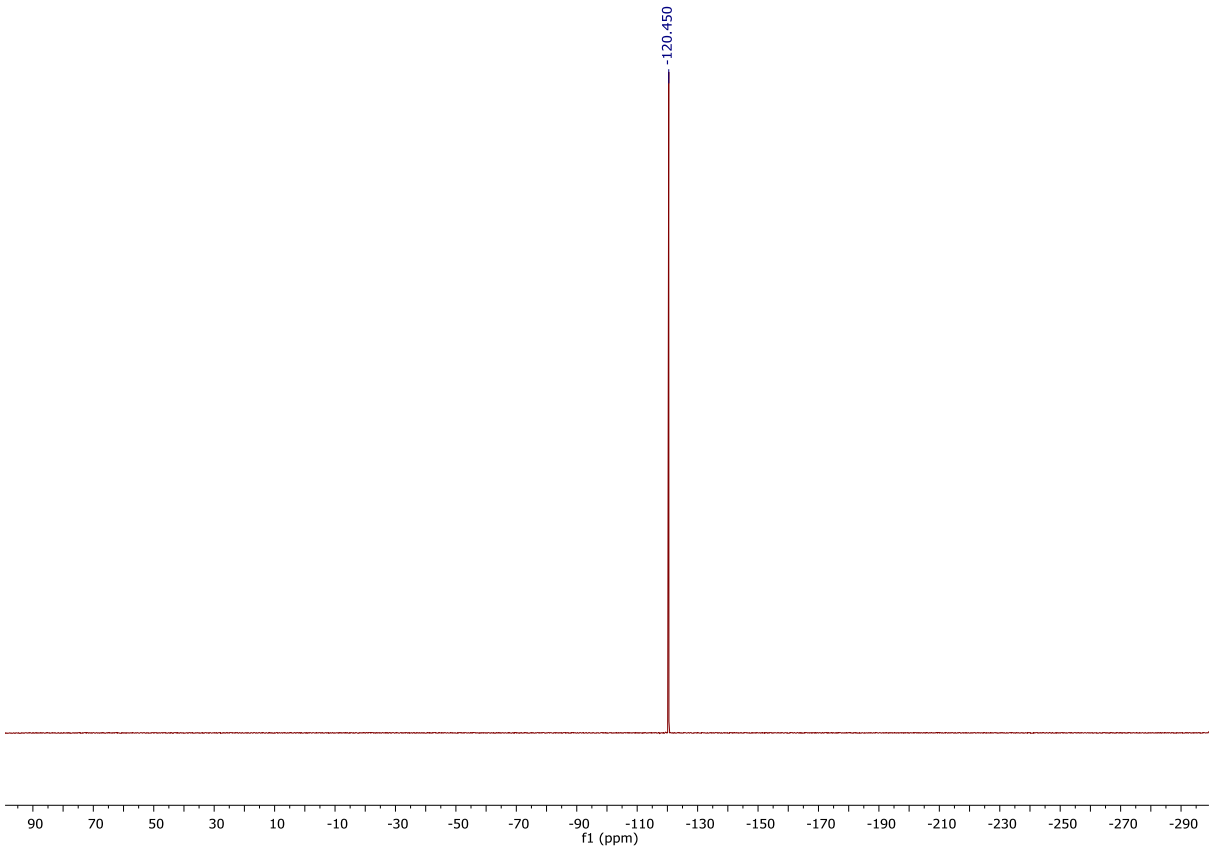
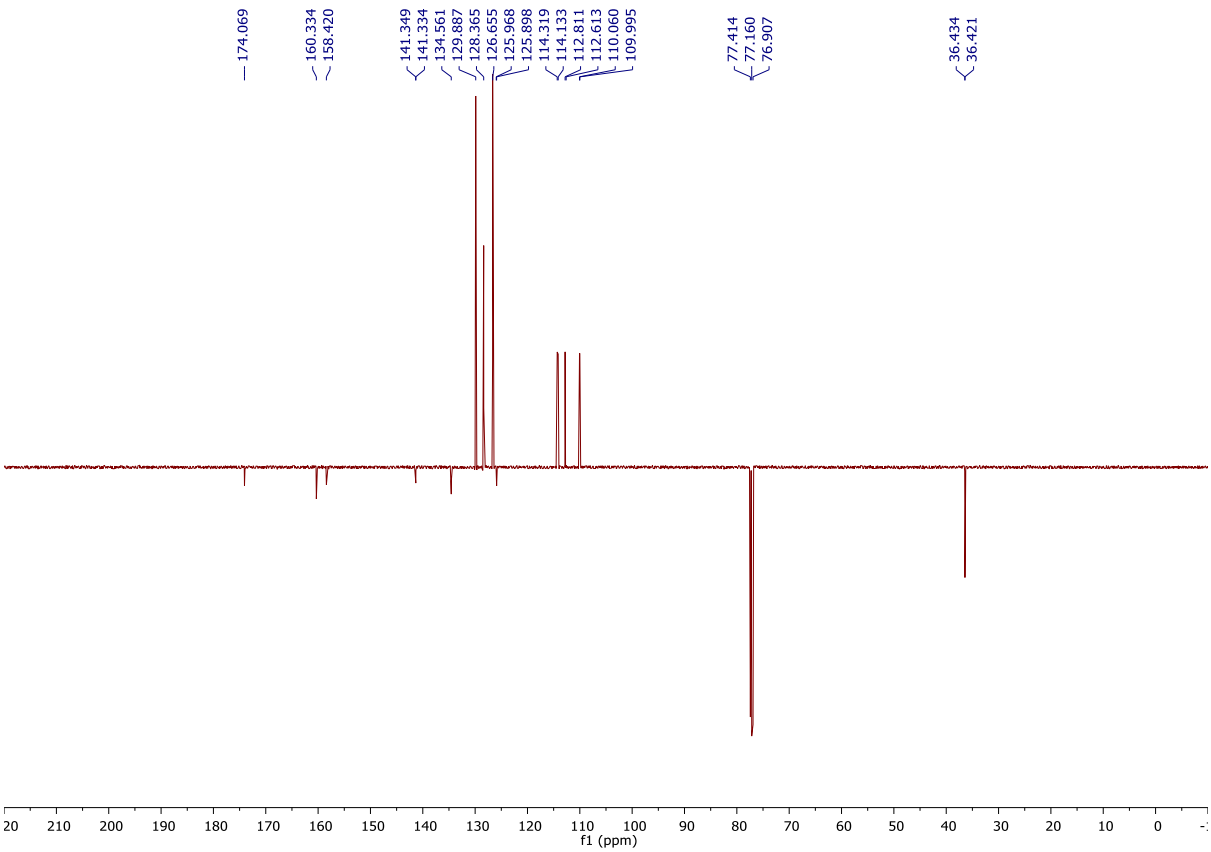
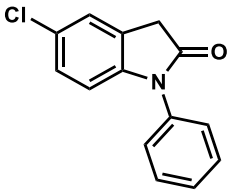
7.519
7.515
7.436
7.434
7.431
7.422
7.419
7.415
7.405
7.402
7.398
7.392
7.390
7.388
7.386
7.381
7.260
7.080
7.077
7.074
7.072
7.069
7.064
7.061
7.059
7.056
7.053
6.928
6.923
6.910
6.905
6.892
6.887
6.732
6.723
6.714
6.706
3.721
1.607
2.01
2.99
1.00
1.01
1.01
2.00
f1 (ppm)

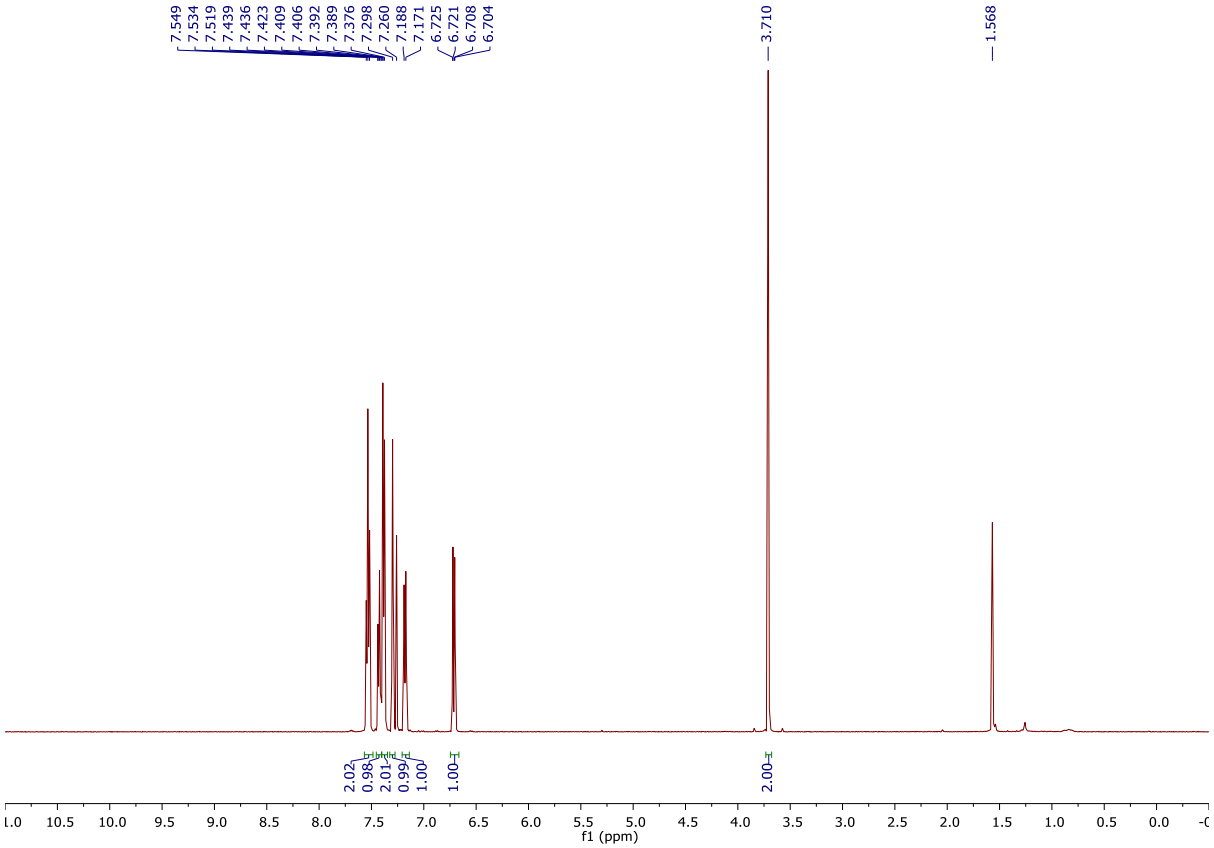

-120.450
f1 (ppm)



5-Chloro-1-phenylindolin-2-one 8e



The title compound was prepared according to general procedure 4 using 5-chloroindolin-2-one (838 mg, 5.0 mmol) and iodobenzene (670 µL, 6.0 mmol). Purification by flash silica chromatography (eluent = 15% EtOAc in hexanes, 30 × 180 mm silica) gave the title compound **8e** as a white solid (883 mg, 3.6 mmol, 72%); mp 151–153 °C; R_f = 0.33 (eluent = 20% EtOAc in hexanes); ν_{max} / cm^{-1} (film) 1711, 1611, 1501, 1476, 1456, 1431, 1387, 1358, 1325, 1306, 1269, 1242, 1196, 1169, 1117, 1069, 934, 880, 849, 839, 829, 750, 731, 712, 691, 671, 654, 598, 548, 523, 496; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 3.71 (2H, s), 6.71 (1H, dd, *J* 8.5, 2.2), 7.18 (1H, d, *J* 8.5), 7.30 (1H, s), 7.35–7.40 (2H, m), 7.40–7.45 (1H, m), 7.53 (2H, t, *J* 7.6); ^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 36.1, 110.4, 125.1, 126.0, 126.6, 127.9, 128.3, 128.5, 129.9, 134.3, 143.9, 173.9; HRMS (ES)$^+$ calculated for $[C_{14}H_{11}NOCl]^+$ $(M+H)^+$ m/z: 244.0529, found 244.0535 (+2.5 ppm).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7.423
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7.406
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7.389
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7.260
7.188
7.171
6.725
6.721
6.708
6.704
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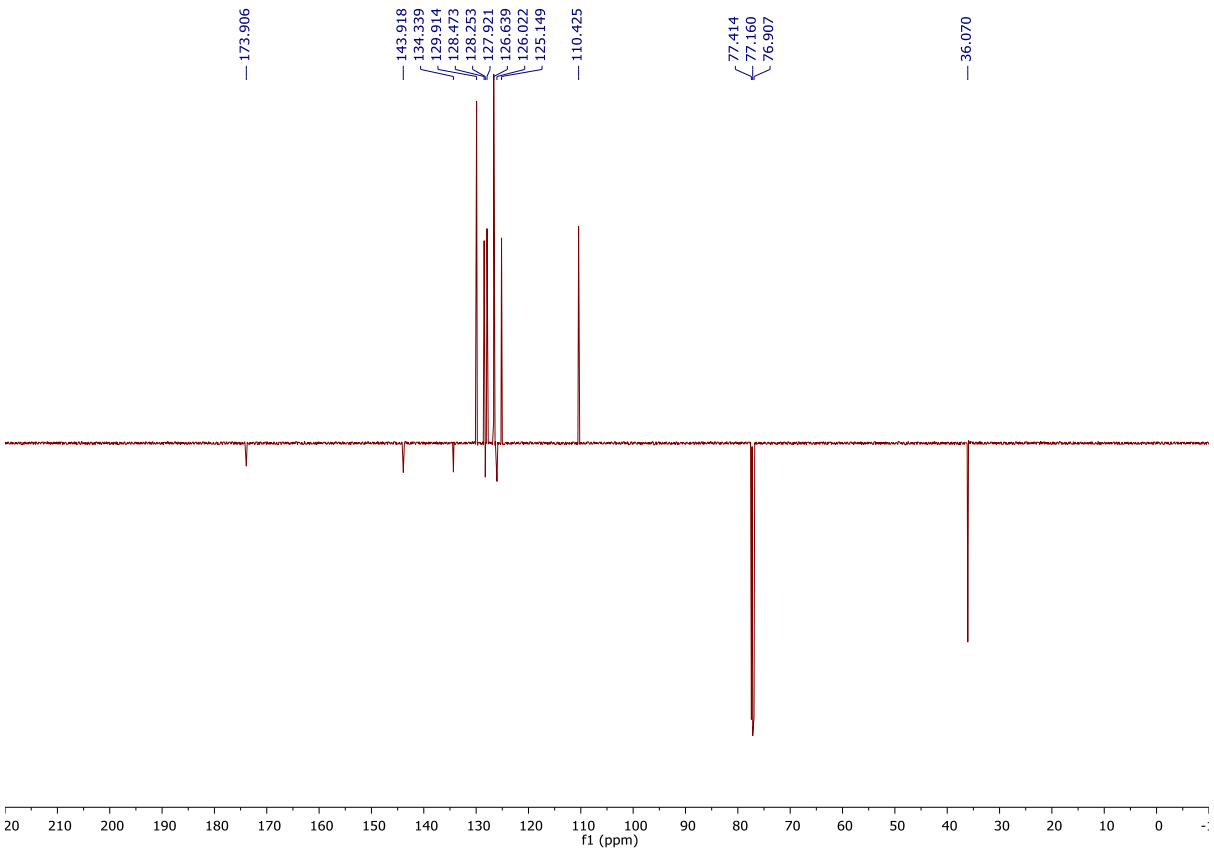
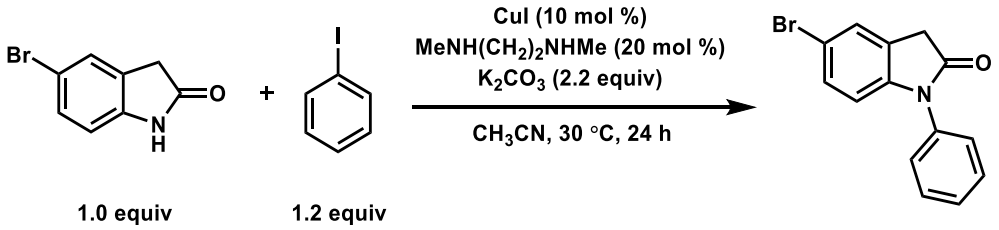
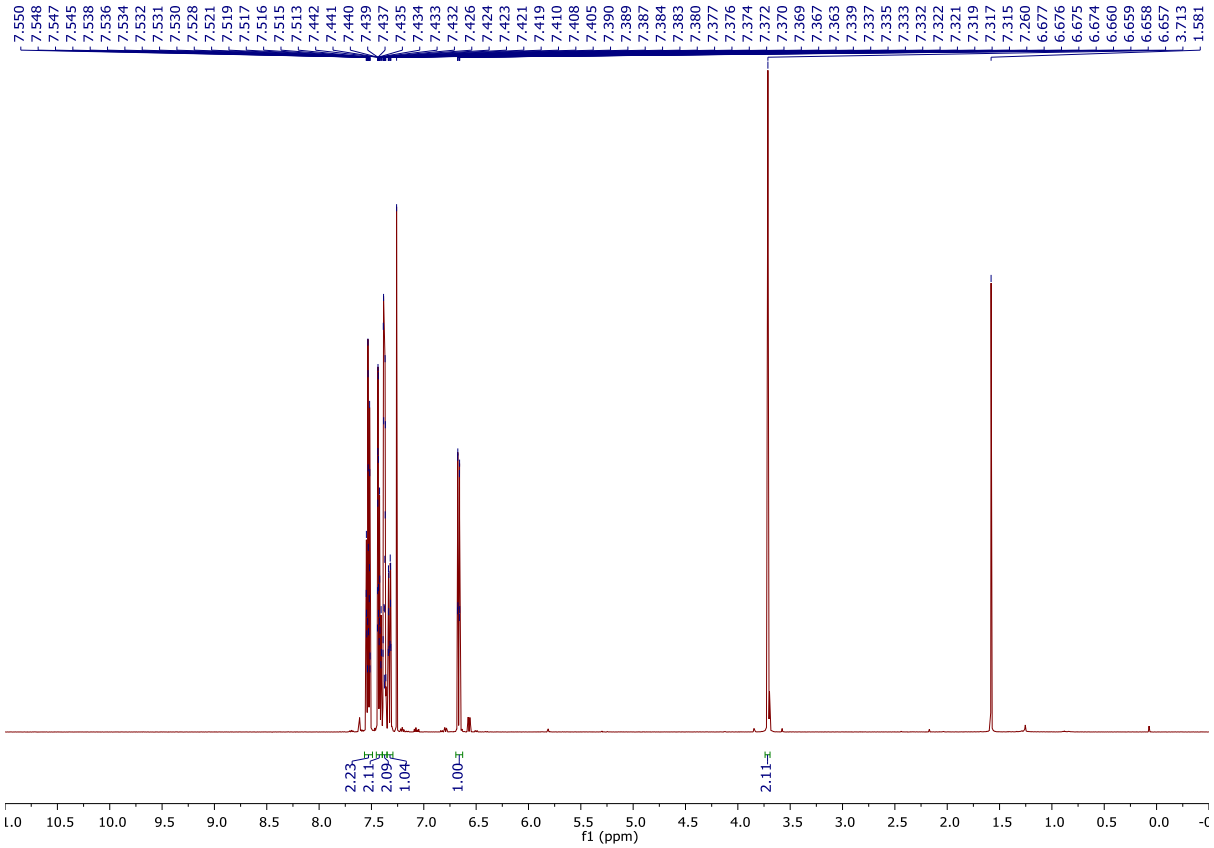
0.98
2.01
0.99
1.00
1.00
2.00
f1 (ppm)


173.906
143.918
134.339
129.914
128.473
128.253
127.921
126.639
126.022
125.149
110.425
77.414
77.160
76.907
36.070
f1 (ppm)

5-Bromo-1-phenylindolin-2-one 8f



An oven dried round-bottomed flask was charged with 5-bromoindolin-2-one (1.06 g, 5.0 mmol), iodobenzene (0.67 mL, 6.0 mmol) and acetonitrile (35 mL) under a nitrogen atmosphere. The mixture was purged with N_2 for 15 min at 30 °C. Thereafter potassium carbonate (1.52 g, 11.0 mmol), copper (I) iodide (95 mg, 0.5 mmol), and N,N'-dimethylethylenediamine (108 µL, 1.0 mmol) were added and stirred for 24 h at 30 °C under nitrogen atmosphere. The reaction mixture was then cooled to room temperature and 50 mL HCl (1 M) was added. Then reaction mixture was extracted with EtOAc (50 mL × 3). The combined organic layer was washed with brine (2 × 50 mL), dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Purification by flash silica chromatography (eluent = 10% EtOAc in hexanes, 30 × 180 mm silica) gave the title compound **8f** as an off-white solid (544 mg, 1.89 mmol, 38%); mp 166–168 °C (Lit. 162 °C);[14] R_f = 0.45 (eluent = 20% EtOAc in hexanes); ν_{max} / cm^{-1} (film) 1705, 1605, 1499, 1474, 1454, 1427, 1385, 1356, 1325, 1306, 1271, 1242, 1198, 1167, 1117, 1061, 932, 839, 826, 748, 690, 667, 598, 532, 519, 494; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 3.71 (2H, s), 6.63–6.69 (1H, m), 7.33 (1H, ddt, *J* 8.4, 1.9, 0.9), 7.35–7.40 (2H, m), 7.40–7.45 (2H, m), 7.49–7.57 (2H, m); ^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 36.0, 110.9, 115.5, 126.4, 126.6, 127.9, 128.5, 129.9, 130.8, 134.3, 144.4, 173.8; HRMS $(ES)^+$ calculated for $[C_{14}H_{11}NOBr]^+$ $(M+H)^+$ m/z: 288.0024, found 288.0022 (-0.7 ppm).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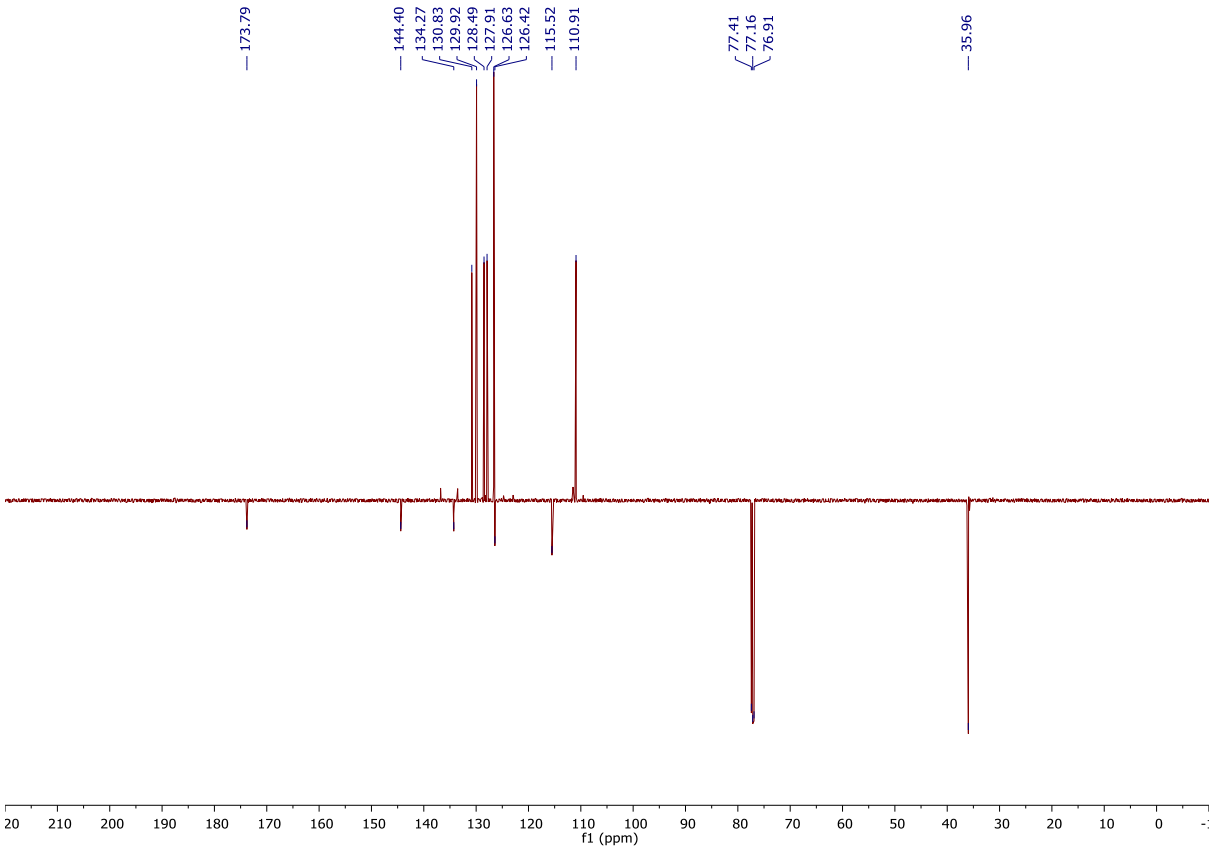
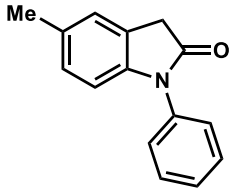
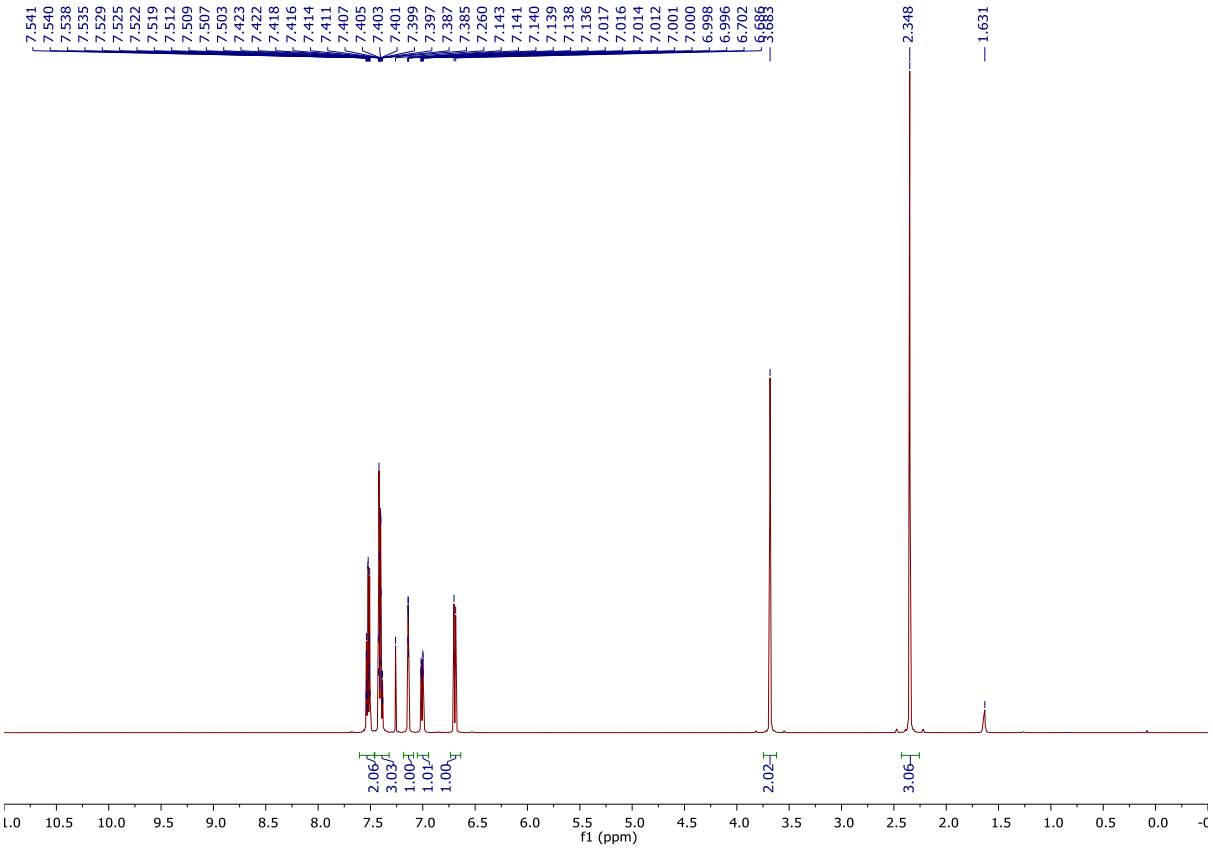
1.04
1.00
2.11
f1 (ppm)

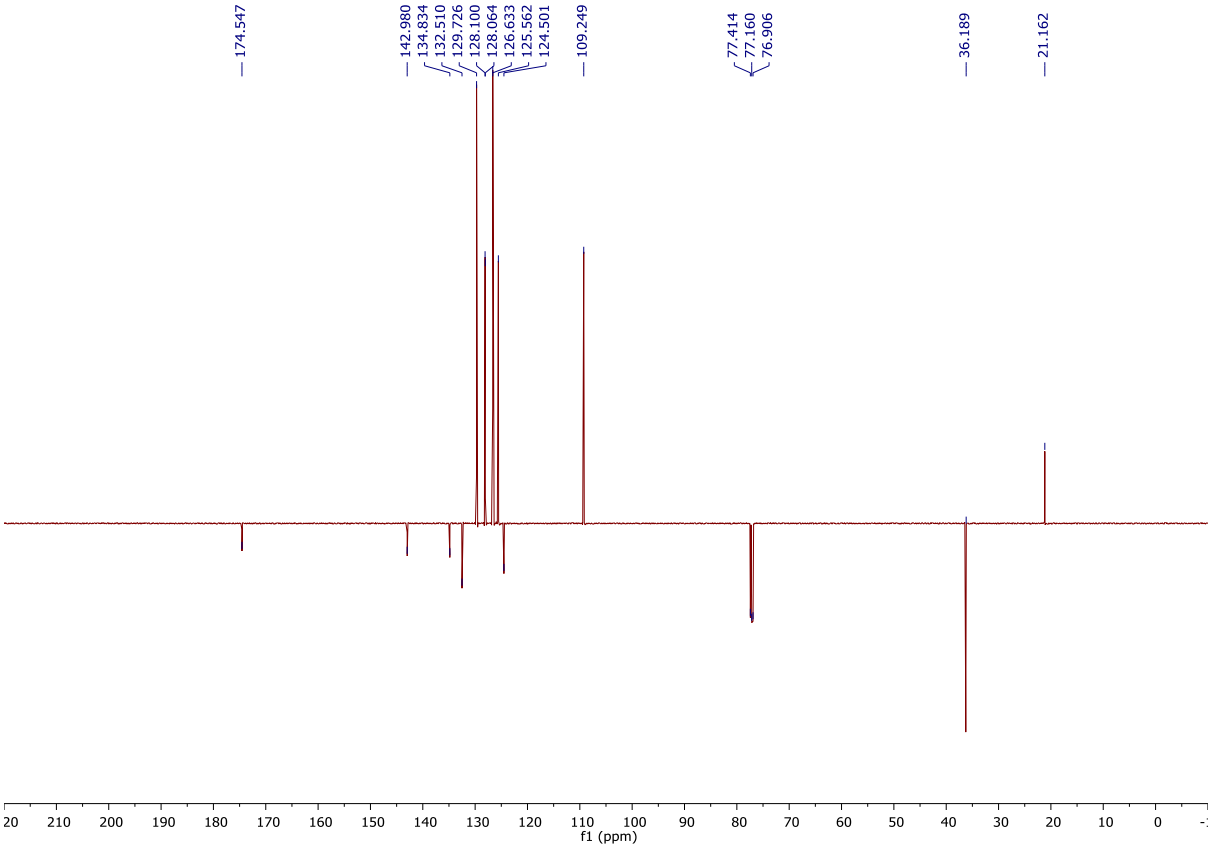

173.79
144.40
134.27
130.83
129.92
128.49
127.91
126.63
126.42
115.52
110.91
77.41
77.16
76.91
35.96
f1 (ppm)

5-Methyl-1-phenylindolin-2-one 8g

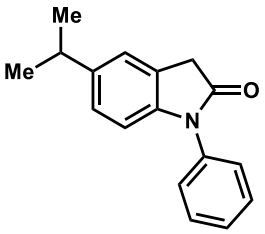


The title compound was prepared according to general procedure 4 using 5-methylindolin-2-one (599 mg, 4.07 mmol) and iodobenzene (550 µL, 4.89 mmol). Purification by flash silica chromatography (eluent = 15% EtOAc in hexanes, 30 × 180 mm silica) gave the title compound **8g** as a yellow solid (577 mg, 2.58 mmol, 64%); mp 120–123 °C; R_f = 0.44 (eluent = 20% EtOAc in hexanes); ν_{max} / cm^{-1} (film) 3059, 2914, 1709, 1613, 1593, 1501, 1487, 1451, 1362, 1323, 1290, 1252, 1215, 1202, 1179, 1163, 1117, 1071, 945, 808, 754, 696, 669, 600, 583, 519, 498, 449, 417; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 2.35 (3H, s), 3.68 (2H, s), 6.69 (1H, d, *J* 8.0), 7.01 (1H, ddd, *J* 8.0, 1.8, 0.9), 7.09–7.18 (1H, m), 7.32–7.46 (3H, m), 7.46–7.61 (2H, m); ^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 21.2, 36.2, 109.3, 124.5, 125.6, 126.6, 128.1, 128.1, 129.7, 132.5, 134.8, 143.0, 174.6; HRMS $(EI)^+$ calculated for $[C_{15}H_{13}NO]^+$ $(M)^+$ m/z: 223.0997, found 223.1000 (+1.3 ppm).

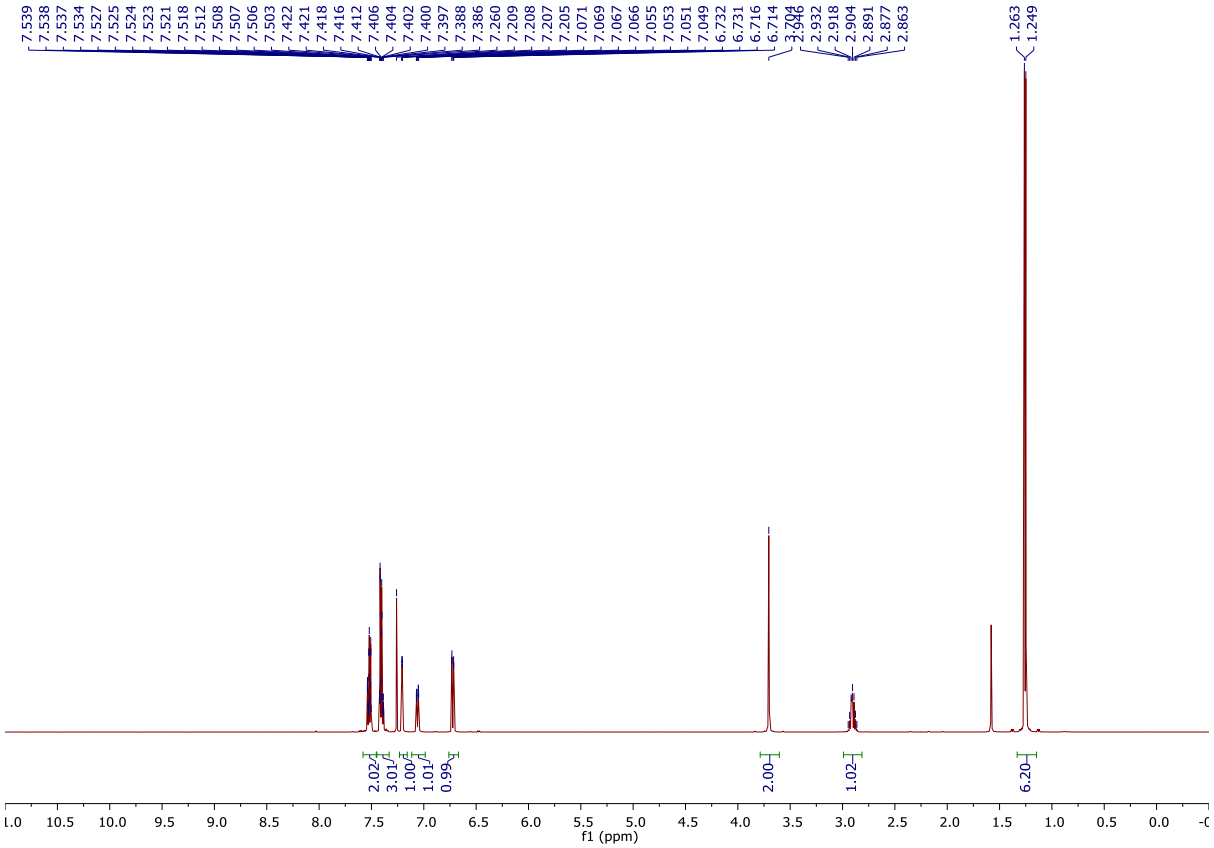




5-Isopropyl-1-phenylindolin-2-one 8h



The title compound was prepared according to general procedure 4 using 5-isopropylindolin-2-one (604 mg, 3.45 mmol) and iodobenzene (460 µL, 4.14 mmol). Purification by flash silica chromatography (eluent = 15% EtOAc in hexanes, 30 × 180 mm silica) gave the title compound **8h** as an off-white solid (343 mg, 1.37 mmol, 40%); mp 86–89 °C; R_f = 0.36 (eluent = 20% EtOAc in hexanes); ν_{max} / cm^{-1} (film) 2959, 1711, 1618, 1593, 1487, 1460, 1371, 1346, 1323, 1310, 1252, 1202, 1184, 1163, 1126, 1072, 951, 882, 818, 760, 694, 669, 600, 548, 498, 440, 424; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 1.26 (6H, d, *J* 6.9), 2.90 (1H, hept, *J* 6.9), 3.70 (2H, s), 6.67–6.76 (1H, m), 7.06 (1H, ddd, *J* 8.1, 1.8, 0.8), 7.21 (1H, dd, *J* 1.2, 0.6), 7.33–7.45 (3H, m), 7.45–7.58 (2H, m); ^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 24.4, 34.0, 36.4, 109.3, 122.9, 124.5, 125.7, 126.7, 128.1, 129.7, 134.9, 143.3, 143.9, 174.7; HRMS $(AP)^+$ calculated for $[C_{17}H_{18}NO]^+$ $(M+H)^+$ m/z: 252.1388, found 252.1395 (+2.8 ppm).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2.918
2.904
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2.877
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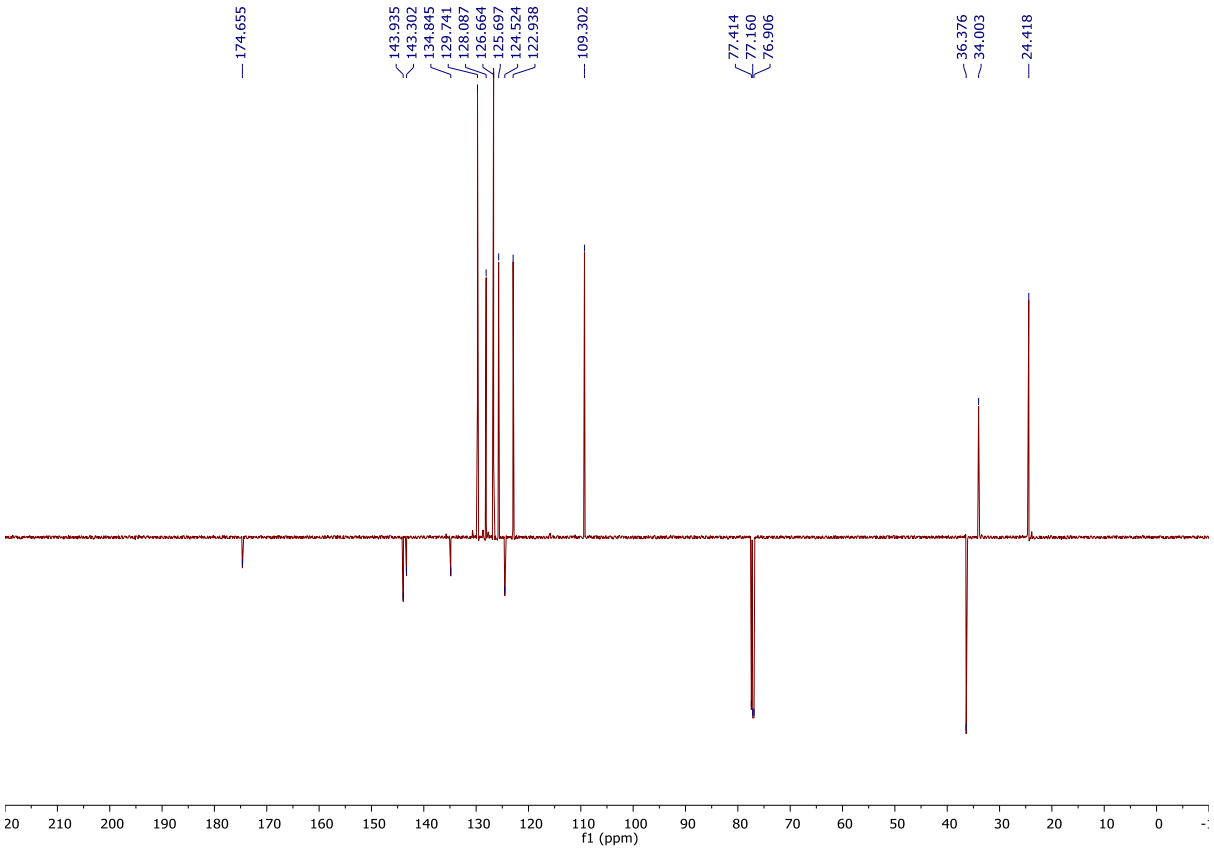
1.02
6.20
f1 (ppm)


174.655
143.935
143.302
134.845
129.741
128.087
126.664
125.697
124.524
122.938
109.302
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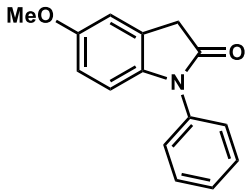
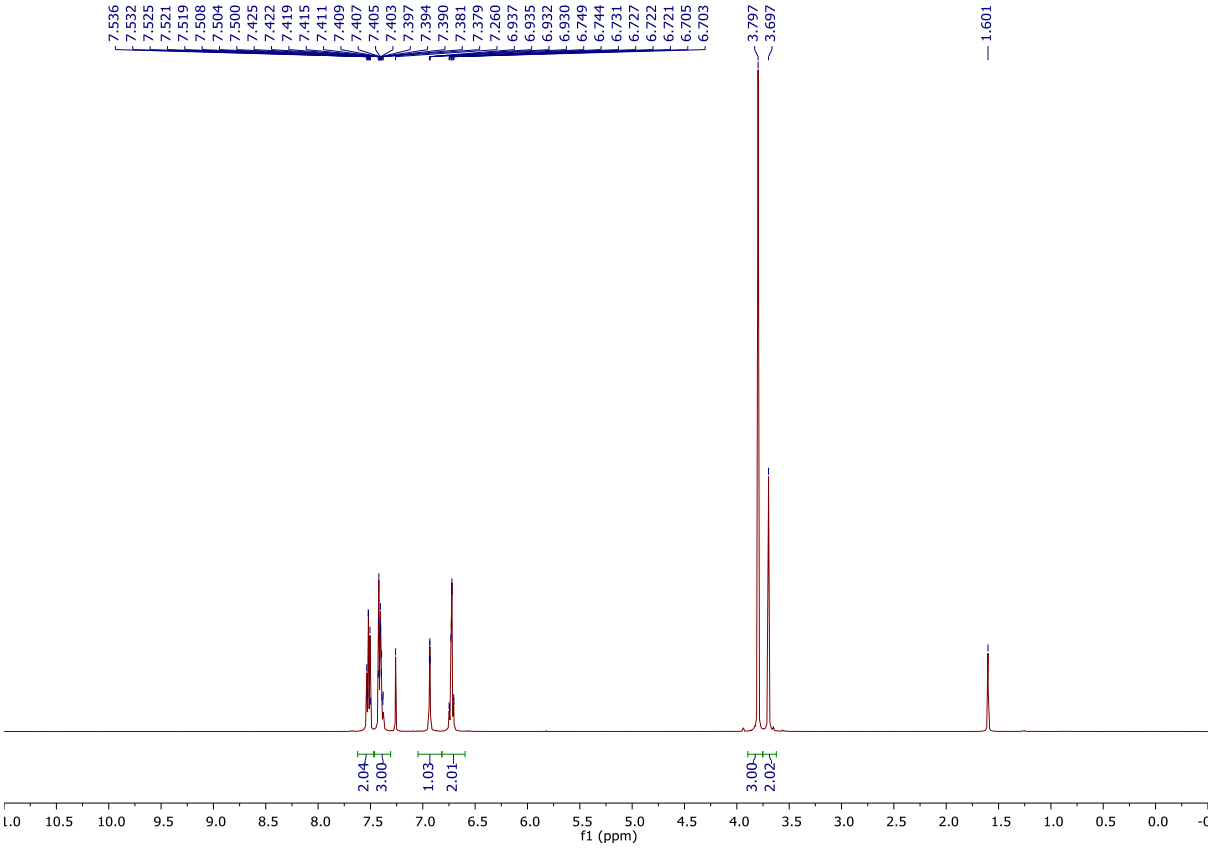
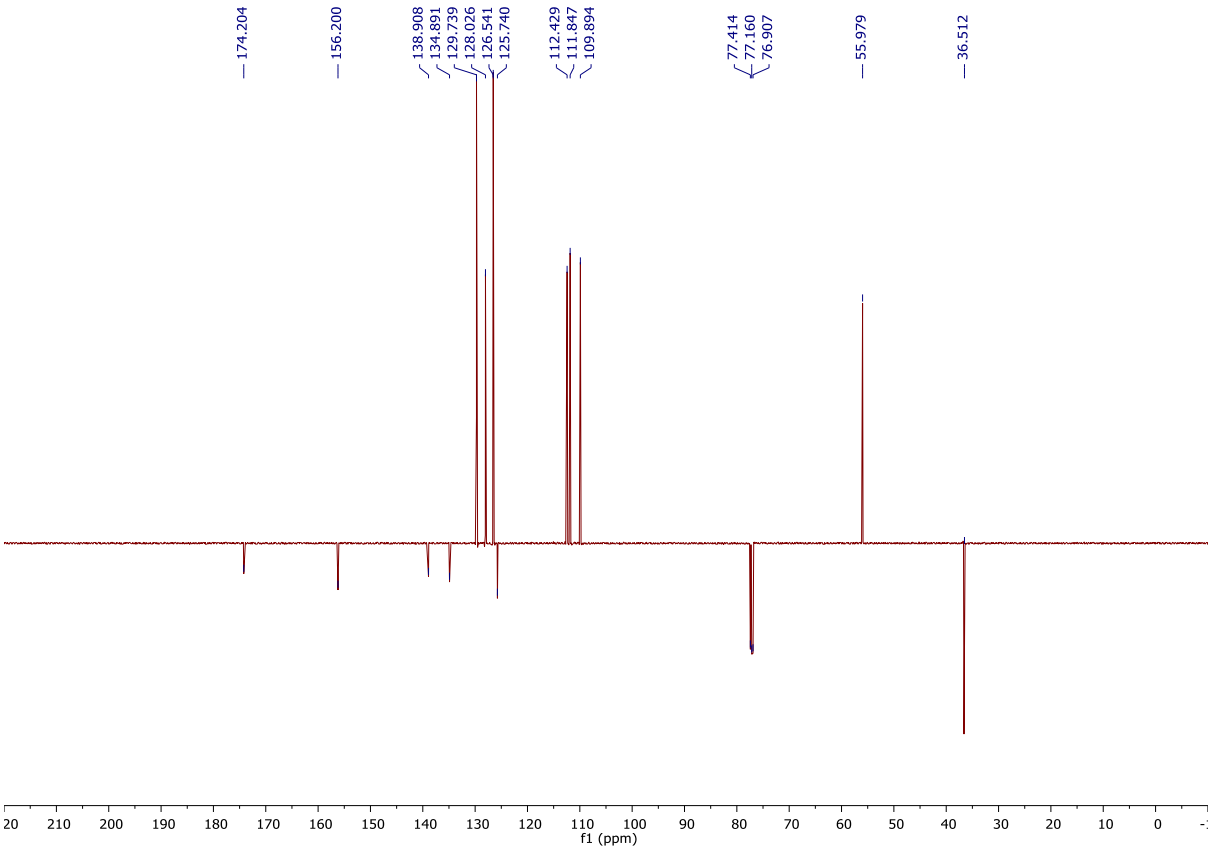
77.160
76.906
36.376
34.003
24.418
f1 (ppm)

5-Methoxy-1-phenylindolin-2-one 8i

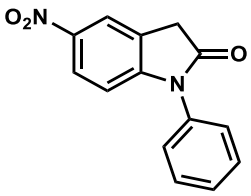


The title compound was prepared according to general procedure 4 using 5-methoxyindolin-2-one (586 mg, 3.6 mmol) and iodobenzene (480 µL, 4.3 mmol). Purification by flash silica chromatography (eluent = 15% EtOAc in hexanes, 30 × 180 mm silica) gave the title compound **8i** as an off-white solid (371 mg, 1.55 mmol, 43%); mp 115–118 °C; R_f = 0.23 (eluent = 20% EtOAc in hexanes); ν_{max} / cm^{-1} (film) 2957, 1707, 1595, 1501, 1483, 1451, 1437, 1362, 1337, 1285, 1231, 1179, 1142, 1032, 976, 939, 903, 868, 810, 754, 694, 669, 615, 584, 498, 436; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 3.70 (2H, s), 3.80 (3H, s), 6.60–6.82 (2H, m), 6.82–7.05 (1H, m), 7.31–7.47 (3H, m), 7.46–7.62 (2H, m); ^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 36.5, 56.0, 109.9, 111.9, 112.4, 125.7, 126.5, 128.0, 129.7, 134.9, 138.9, 156.2, 174.2; HRMS $(AP)^+$ calculated for $[C_{15}H_{14}NO_2]^+$ $(M+H)^+$ m/z: 240.1025, found 240.1033 (+3.3 ppm).

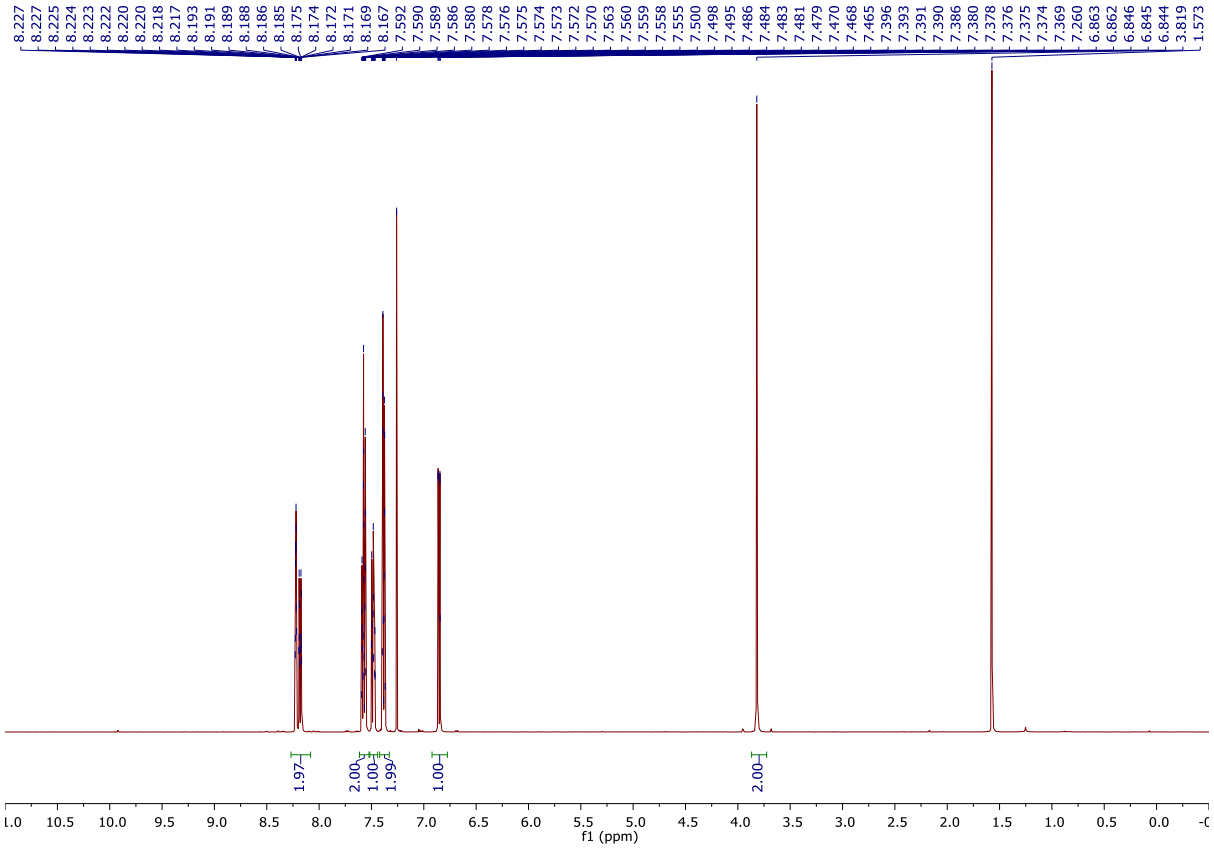




5-Nitro-1-phenylindolin-2-one 8j



The title compound was prepared according to general procedure 4 using 5-nitroindolin-2-one (534 mg, 3.0 mmol) and iodobenzene (403 µL, 3.6 mmol). Purification by flash silica chromatography (eluent = 10–15% EtOAc in hexanes, 30 × 180 mm silica) gave the title compound **8j** as an off-white solid (343 mg, 1.35 mmol, 45%); mp 209–212 °C; R_f = 0.22 (eluent = 20% EtOAc in hexanes); ν_{max} / cm^{-1} (film) 1717, 1616, 1501, 1478, 1335, 1273, 1238, 1202, 1159, 1117, 1067, 937, 910, 876, 849, 831, 745, 691, 667, 650, 602, 546, 490; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 3.82 (2H, s), 6.85 (1H, dd, *J* 8.7, 0.5), 7.33–7.42 (2H, m), 7.44–7.52 (1H, m), 7.52–7.61 (2H, m), 8.08–8.27 (2H, m); ^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 35.7, 109.1, 120.7, 125.0, 125.3, 126.7, 129.2, 130.2, 133.6, 143.7, 150.8, 174.1; HRMS $(ES)^-$ calculated for $[C_{14}H_9N_2O_3]^-$ $(M\text{-}H)^-$ m/z: 253.0613, found 253.0614 (+0.4 ppm).


8.227
8.227
8.225
8.224
8.223
8.222
8.220
8.220
8.218
8.217
8.193
8.191
8.189
8.188
8.186
8.185
8.175
8.174
8.172
8.171
8.169
8.167
7.592
7.590
7.589
7.586
7.580
7.578
7.576
7.575
7.574
7.573
7.572
7.570
7.563
7.560
7.559
7.558
7.555
7.500
7.498
7.495
7.486
7.484
7.483
7.481
7.479
7.470
7.468
7.465
7.396
7.393
7.391
7.390
7.386
7.380
7.378
7.376
7.375
7.374
7.369
7.260
6.863
6.862
6.846
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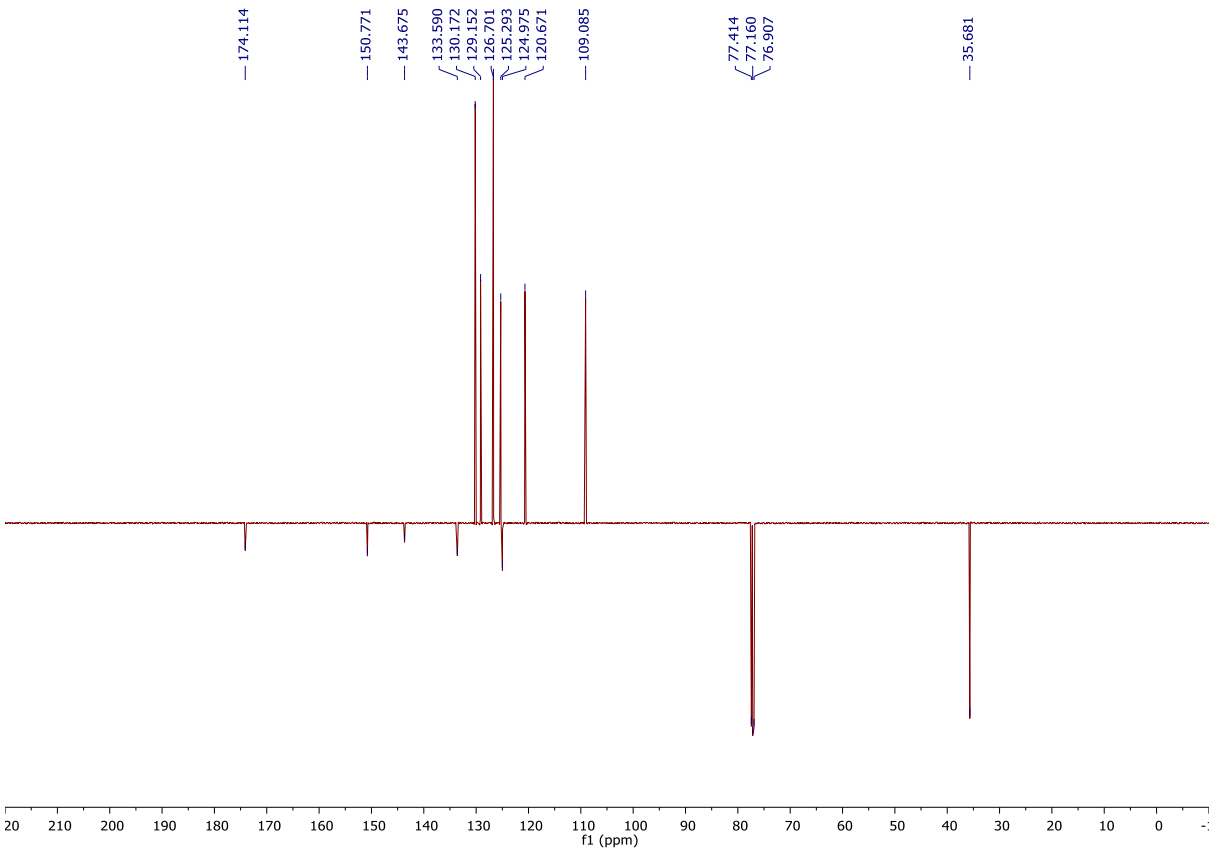
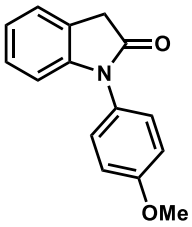
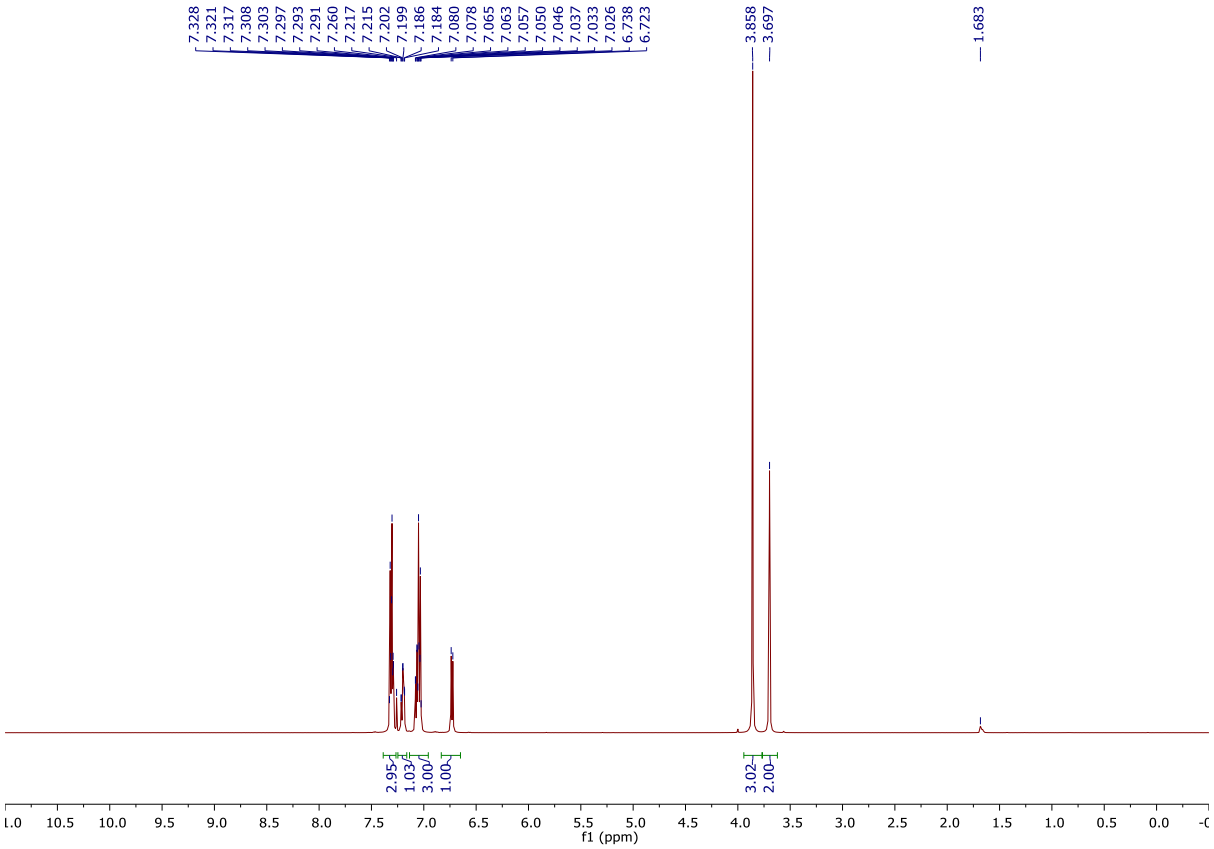
1.97
2.00
1.00
1.99
1.00
2.00
f1 (ppm)

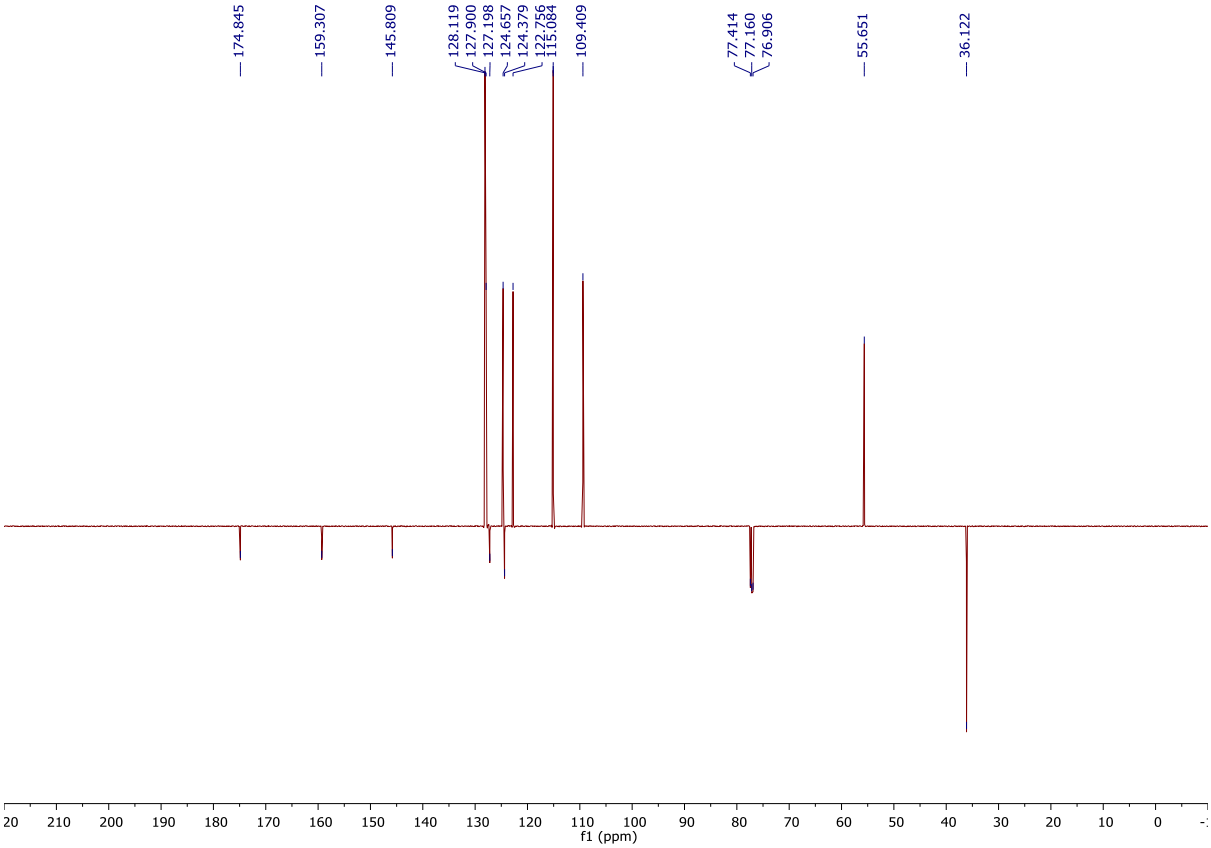

174.114
150.771
143.675
133.590
130.172
129.152
126.701
125.293
124.975
120.671
109.085
77.414
77.160
76.907
35.681
f1 (ppm)

1-(4-Methoxyphenyl)indolin-2-one 8k

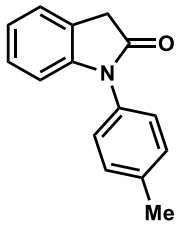


The title compound was prepared according to general procedure 4 using 2-oxindole (666 mg, 5.0 mmol) and 4-iodoanisole (1.40 g, 6.0 mmol). Purification by flash silica chromatography (eluent = 15–20% EtOAc in hexanes, 30 × 180 mm silica) gave the title compound **8k** as an orange crystalline solid (1.12 g, 4.68 mmol, 94%); mp 138–140 °C (Lit. 131–132 °C);[15] R_f = 0.20 (eluent = 20% EtOAc in hexanes); ν_{max} / cm^{-1} (film) 2957, 2916, 2832, 1701, 1611, 1508, 1485, 1462, 1443, 1375, 1327, 1296, 1242, 1175, 1161, 1103, 1030, 951, 822, 762, 721, 694, 637, 573, 517, 496; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 3.70 (2H, s), 3.86 (3H, s), 6.73 (1H, d, *J* 7.8), 7.01–7.10 (3H, m), 7.20 (1H, td, *J* 7.7, 1.3), 7.28–7.35 (3H, m); ^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 36.1, 55.7, 109.4, 115.1, 122.8, 124.4, 124.7, 127.2, 127.9, 128.1, 145.8, 159.3, 174.9; HRMS (ASAP)$^+$ calculated for $[C_{15}H_{14}NO_2]^+$ $(M+H)^+$ m/z: 240.1025, found 240.1025 (+0.0 ppm).

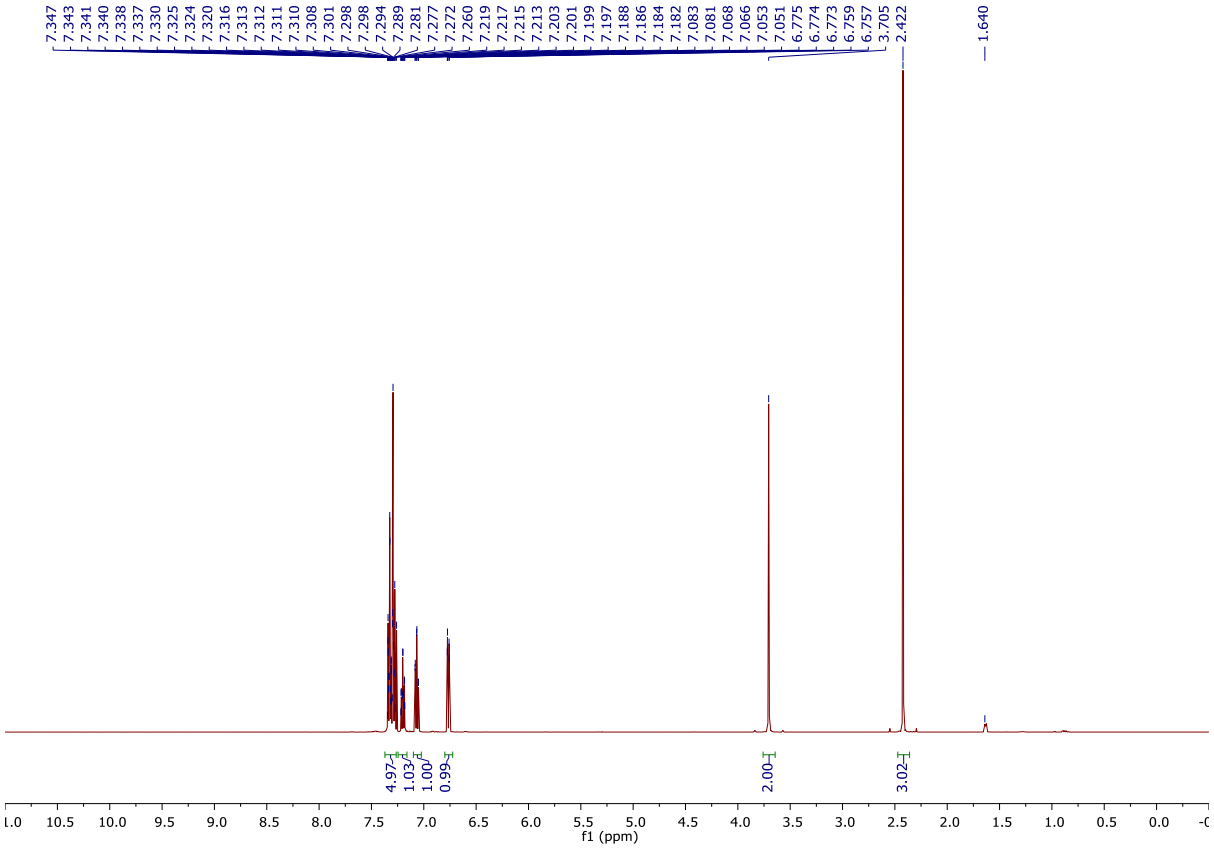


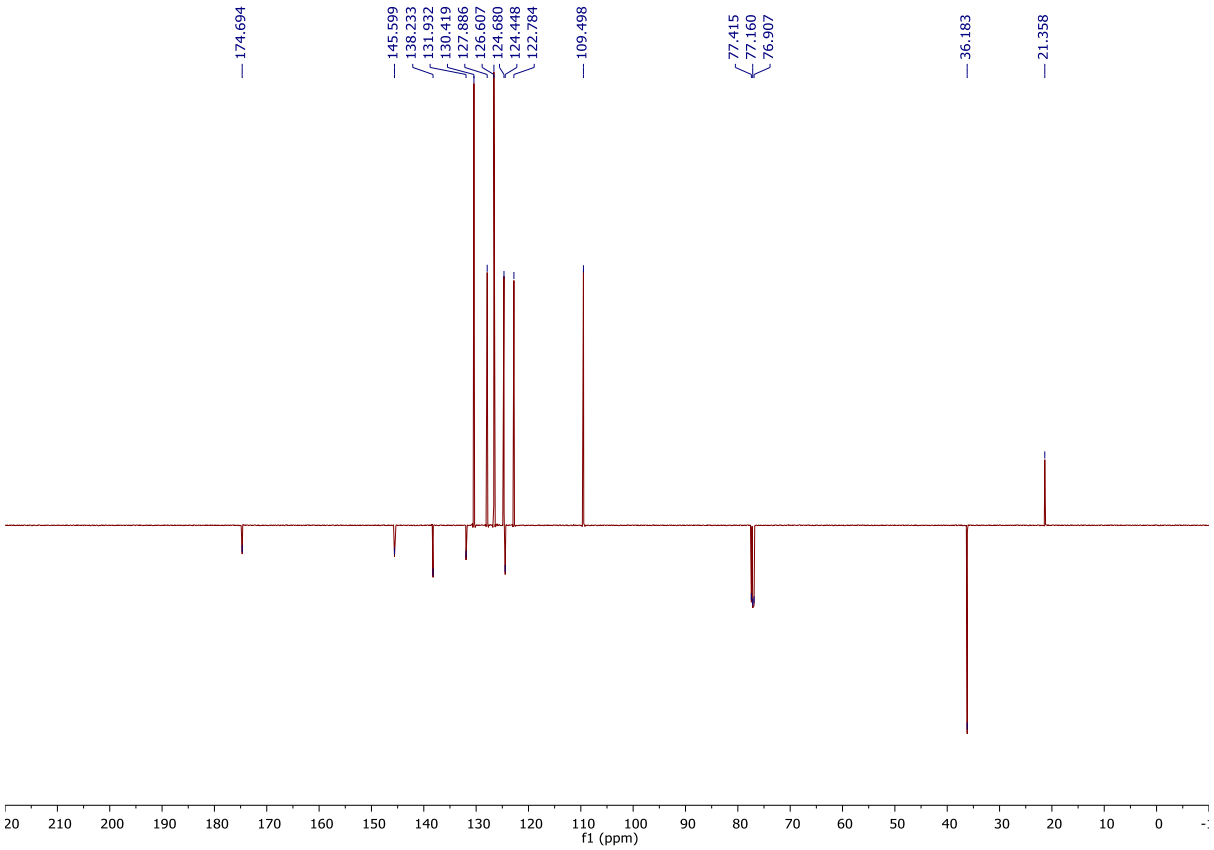


1-(*p*-Tolyl)indolin-2-one 8l

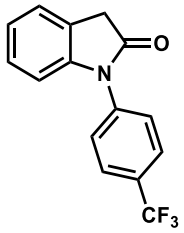


The title compound was prepared according to general procedure 4 using 2-oxindole (666 mg, 5.0 mmol) and 4-iodotoluene (1.31 g, 6.0 mmol). Purification by flash silica chromatography (eluent = 10–15% EtOAc in hexanes, 30 × 180 mm silica) gave the title compound **8l** as a yellow solid (952 mg, 4.26 mmol, 85%); mp 91–93 °C (Lit. 90–92 °C);[16] R_f = 0.35 (eluent = 20% EtOAc in hexanes); ν_{max} / cm^{-1} (film) 1707, 1607, 1514, 1481, 1458, 1373, 1321, 1298, 1240, 1202, 1167, 1144, 1096, 1022, 941, 856, 808, 747, 712, 692, 635, 596, 565, 503, 486; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 2.42 (3H, s), 3.71 (2H, s), 6.72–6.80 (1H, m), 7.07 (1H, td, *J* 7.5, 1.1), 7.16–7.25 (1H, m), 7.26–7.37 (5H, m); ^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 21.4, 36.2, 109.5, 122.8, 124.5, 124.7, 126.6, 127.9, 130.4, 131.9, 138.2, 145.6, 174.7; HRMS (ASAP)$^+$ calculated for $[C_{15}H_{14}NO]^+$ $(M+H)^+$ m/z: 224.1075, found 224.1075 (+0.0 ppm).

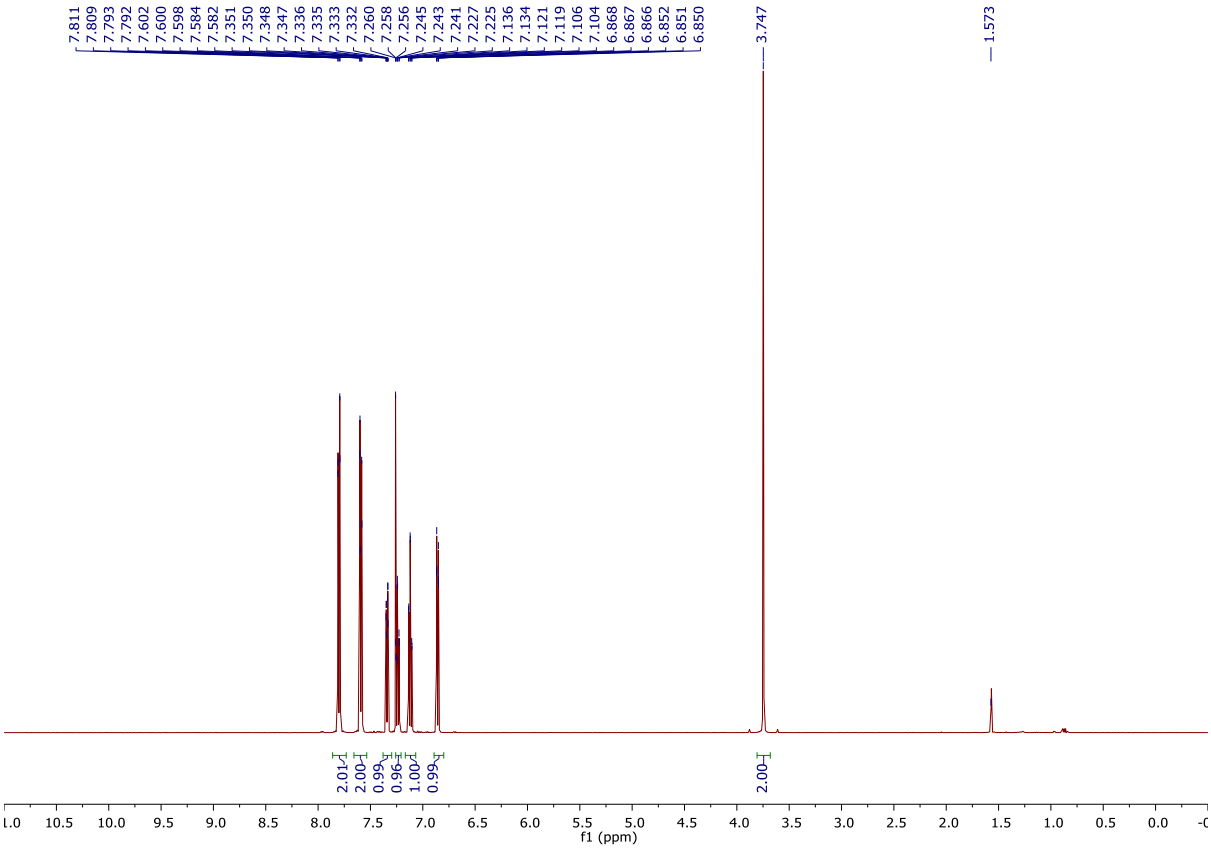

7.347
7.343
7.341
7.340
7.338
7.337
7.330
7.325
7.324
7.320
7.316
7.313
7.312
7.311
7.310
7.308
7.301
7.298
7.298
7.294
7.289
7.281
7.277
7.272
7.260
7.219
7.217
7.215
7.213
7.203
7.201
7.199
7.197
7.188
7.186
7.184
7.182
7.083
7.081
7.068
7.066
7.053
7.051
6.775
6.774
6.773
6.759
6.757
3.705
2.422
1.640
4.97
1.03
1.00
0.99
2.00
3.02
f1 (ppm)

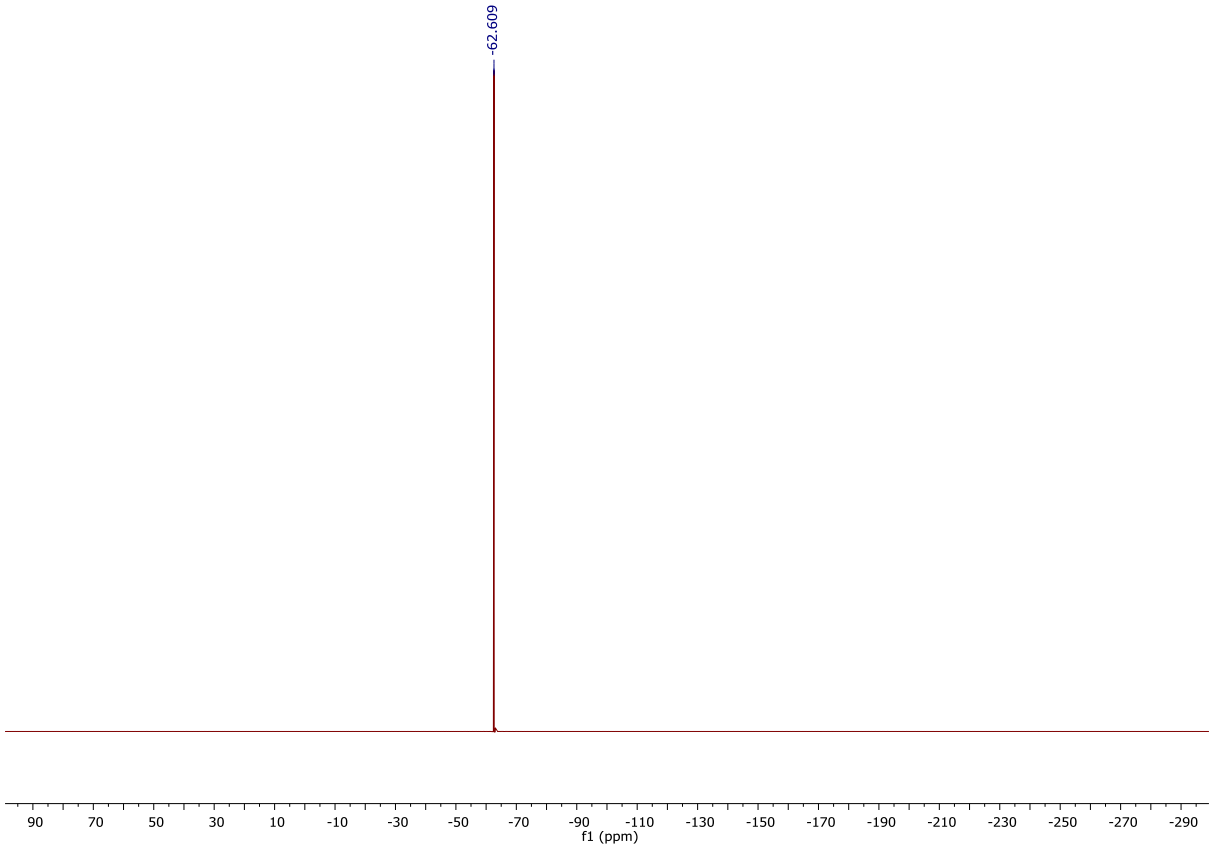

174.694
145.599
138.233
131.932
130.419
127.886
126.607
124.680
124.448
122.784
109.498
77.415
77.160
76.907
36.183
21.358
f1 (ppm)

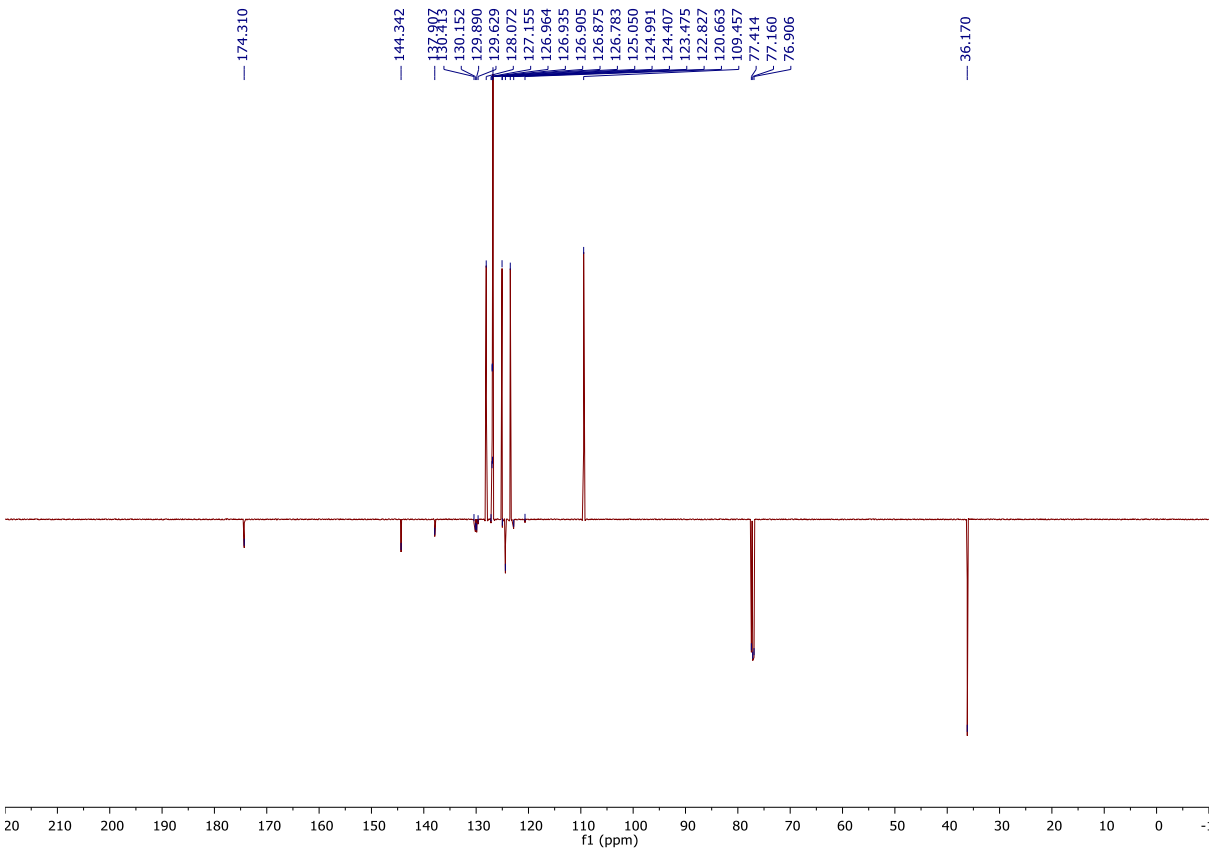
1-(4-(Trifluoromethyl)phenyl)indolin-2-one 8m



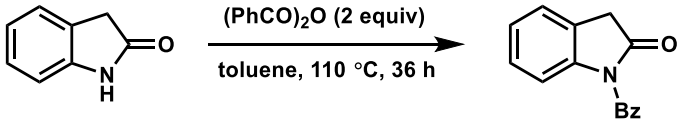
The title compound was prepared according to general procedure 4 using 2-oxindole (666 mg, 5.0 mmol) and 1-iodo-4-(trifluoromethyl)benzene (0.88 mL, 6.0 mmol). Purification by flash silica chromatography (eluent = 10–15% EtOAc in hexanes, 30 × 180 mm silica) gave the title compound **8m** as an off-white solid (1.24 g, 4.47 mmol, 90%); mp 134–136 °C (Lit. 125 °C);[15] R_f = 0.38 (eluent = 20% EtOAc in hexanes); ν_{max} / cm^{-1} (film) 1709, 1611, 1522, 1483, 1460, 1414, 1395, 1368, 1321, 1238, 1202, 1167, 1117, 1107, 1065, 1015, 947, 943, 849, 824, 748, 712, 671, 613, 581, 492, 434, 419; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 3.75 (2H, s), 6.86 (1H, dt, *J* 7.9, 0.7), 7.12 (1H, td, *J* 7.5, 1.0), 7.24 (1H, td, *J* 7.8, 1.0), 7.34 (1H, ddd, *J* 7.4, 1.3, 0.7), 7.54–7.66 (2H, m), 7.73–7.86 (2H, m); ^{19}F NMR (471 MHz, $CDCl_3$) δ_F: -62.6; ^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 36.2, 109.5, 123.5, 123.9 (q, *J* 272.7), 124.4, 125.1, 126.8, 126.9 (q, *J* 3.78), 128.1, 130.0 (q, *J* 33.0), 137.9, 144.3, 174.3; HRMS (ES)$^+$ calculated for $[C_{15}H_{11}NOF_3]^+$ $(M+H)^+$ m/z: 278.0793, found 278.0804 (+4.0 ppm).



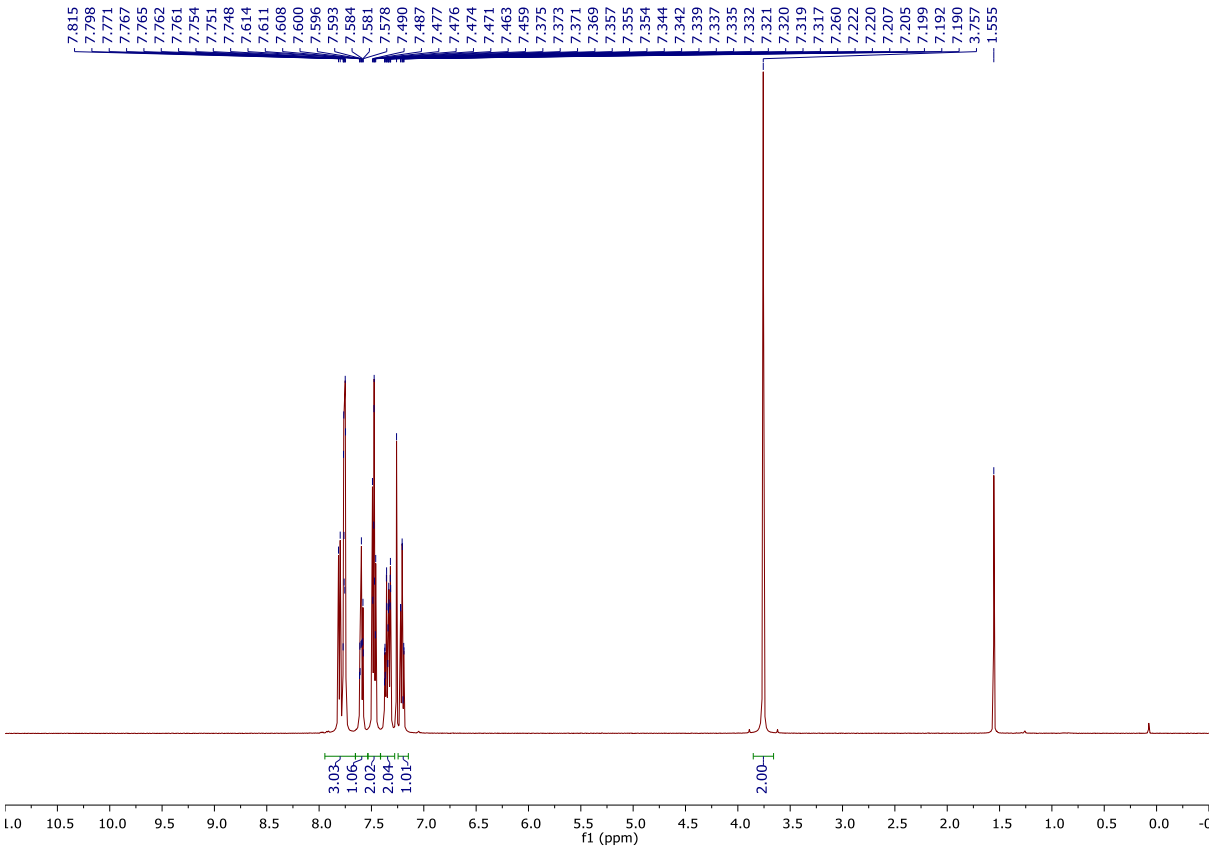

-62.609
90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230 -250 -270 -290
f1 (ppm)

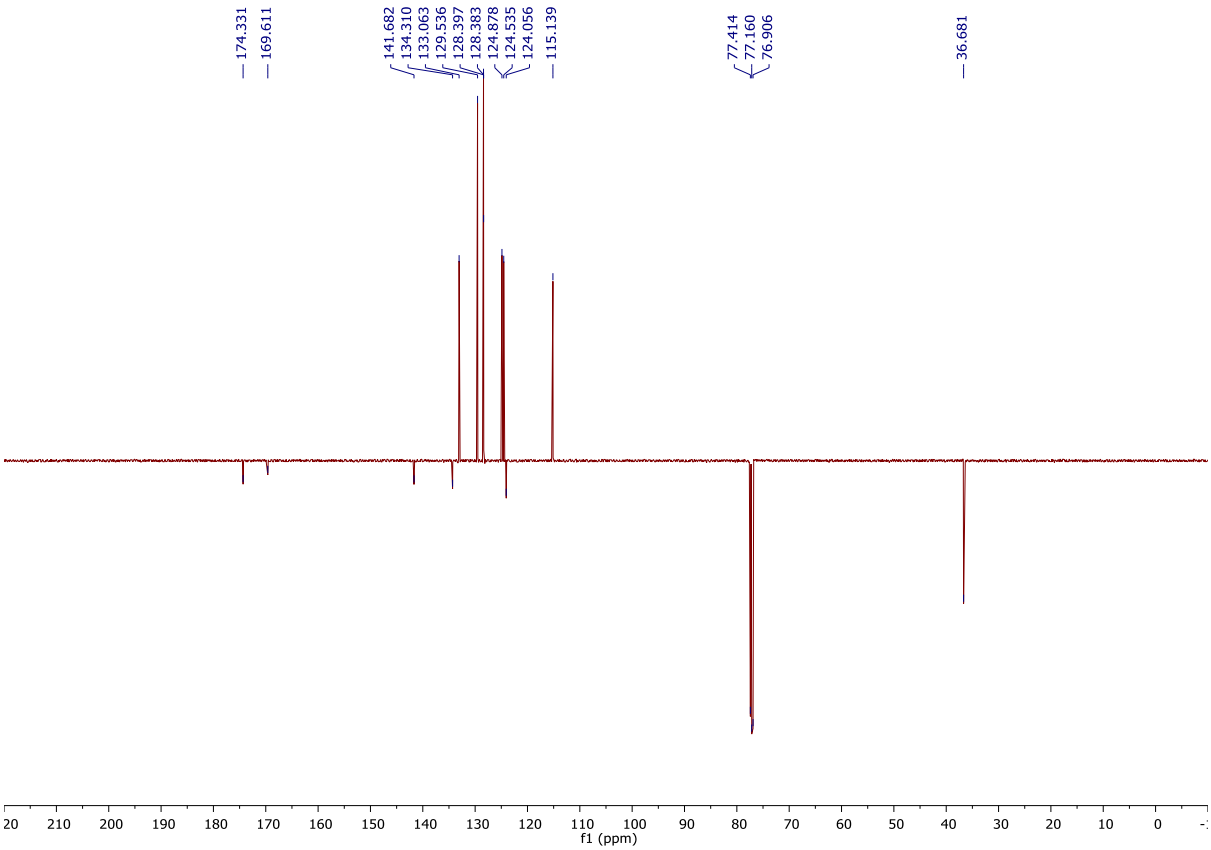

174.310
144.342
137.907
137.413
130.152
129.890
129.629
128.072
127.155
126.964
126.935
126.905
126.875
126.783
125.050
124.991
124.407
123.475
122.827
120.663
109.457
77.414
77.160
76.906
36.170
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

1-Benzoylindolin-2-one 8o

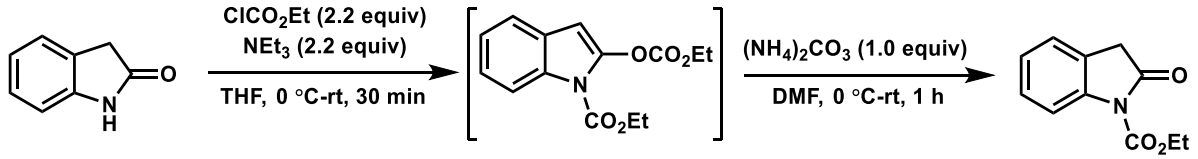


A 20 mL vial was charged with 2-oxindole (0.67 g, 5.0 mmol), benzoic anhydride (2.26 g, 10 mmol) and toluene (2 mL) and was left to react at 110 °C for 24 h and then 130 °C for 12 h. It was then cooled. Toluene was evaporated *in vacuo*. Purification by flash silica chromatography (eluent = 8% EtOAc in hexanes, 25 × 180 mm silica) gave the title compound **8o** as an off-white solid (0.76 g, 3.2 mmol, 64%); mp 143–145 °C (lit. 134–136 °C);[17] R_f = 0.21 (eluent = 10% EtOAc in hexanes); ν_{max} / cm^{-1} (film) 1753, 1678, 1479, 1462, 1346, 1292, 1246, 1198, 1150, 1082, 1069, 870, 785, 756, 723, 700, 658, 631, 517, 419; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 3.76 (2H, s), 7.21 (1H, td, *J* 7.5, 1.1), 7.28–7.41 (2H, m), 7.41–7.54 (2H, m), 7.53–7.65 (1H, m), 7.65–7.95 (3H, m); ^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 36.7, 115.1, 124.1, 124.5, 124.9, 128.4, 128.4, 129.5, 133.1, 134.3, 141.7, 169.6, 174.3; HRMS (ES)$^+$ calculated for $[C_{15}H_{11}NO_2{}^{23}Na]^+$ $(M+Na)^+$ m/z: 260.0687, found 260.0688 (+0.4 ppm).



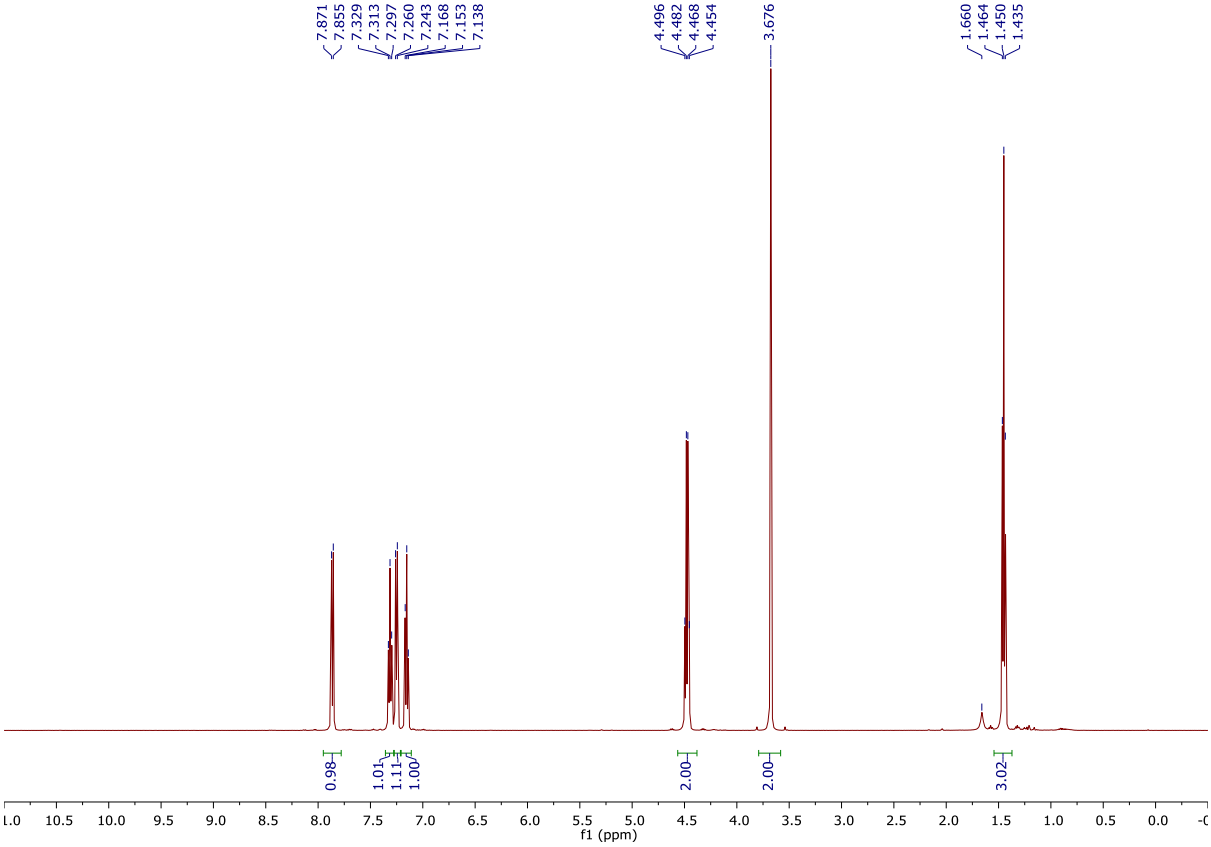


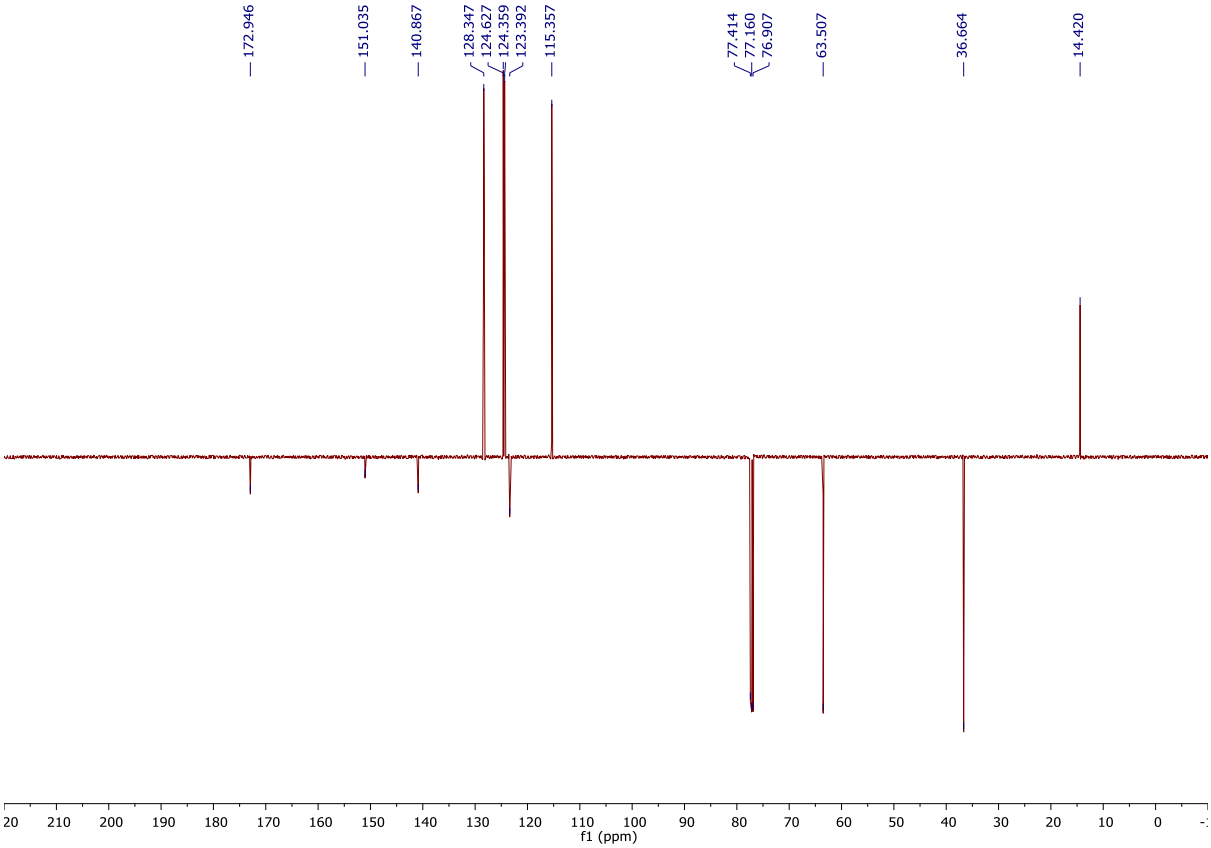
Ethyl 2-oxoindoline-1-carboxylate 8p



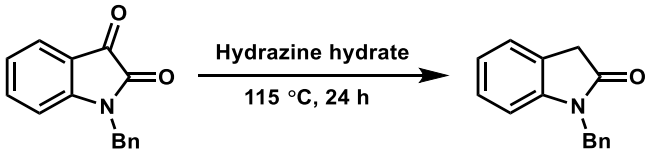
To a solution of 2-oxindole (1.33 g, 10 mmol) and Et_3N (3.1 mL, 22 mmol) in THF (36 mL), was added $ClCO_2Et$ (2.1 mL, 22 mmol) dropwise. The reaction temperature was kept below 30 °C during the addition. After stirring for 30 min at room temperature, the solvent was evaporated. Water (50 mL) was added to the residue and the mixture was extracted with Et_2O (3 × 70 mL). The combined organic layer was washed with brine (2 × 50 mL), dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was then dissolved in DMF (20 mL). Finely powdered $(NH_4)_2CO_3$ (963 mg, 10 mmol) was added to the mixture at 0–5 °C. The mixture was stirred for 1 h at room temperature then poured into ice-water. The aqueous layer was extracted with Et_2O (3 × 70 mL). The combined organics were washed with brine (5 × 50 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo*. Purification by flash silica chromatography (eluent = 10% EtOAc in hexanes, 30 × 180 mm silica) gave the title compound **8p** as an off-white crystalline solid (1.12 g, 5.46 mmol, 55%); mp 81–83 °C (lit. 80–81 °C);[18] R_f = 0.37 (eluent = 20% EtOAc in hexanes); ν_{max} / cm^{-1} (film) 3370, 2978, 1765, 1722, 1483, 1466, 1397, 1373, 1343, 1281, 1252, 1236, 1206, 1153, 1086, 1055, 1018, 961, 866, 752, 712, 677, 623, 513, 484, 436, 421; ^1H NMR (500 MHz, $CDCl_3$) δ_H: 1.45 (3H, t, *J* 7.1), 3.68 (2H, s), 4.48 (2H, q, *J* 7.1), 7.15 (1H, t, *J* 7.5), 7.25 (1H, d, *J* 8.4,), 7.31 (1H, t, *J* 7.8), 7.86 (1H, d, *J* 8.2); ^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 14.4,

36.7, 63.5, 115.4, 123.4, 124.4, 124.6, 128.3, 140.9, 151.0, 173.0; HRMS (AP)$^+$ calculated for $[C_{11}H_{12}NO_3]^+$ $(M+H)^+$ m/z: 206.0817, found 206.0811 (-2.9 ppm).

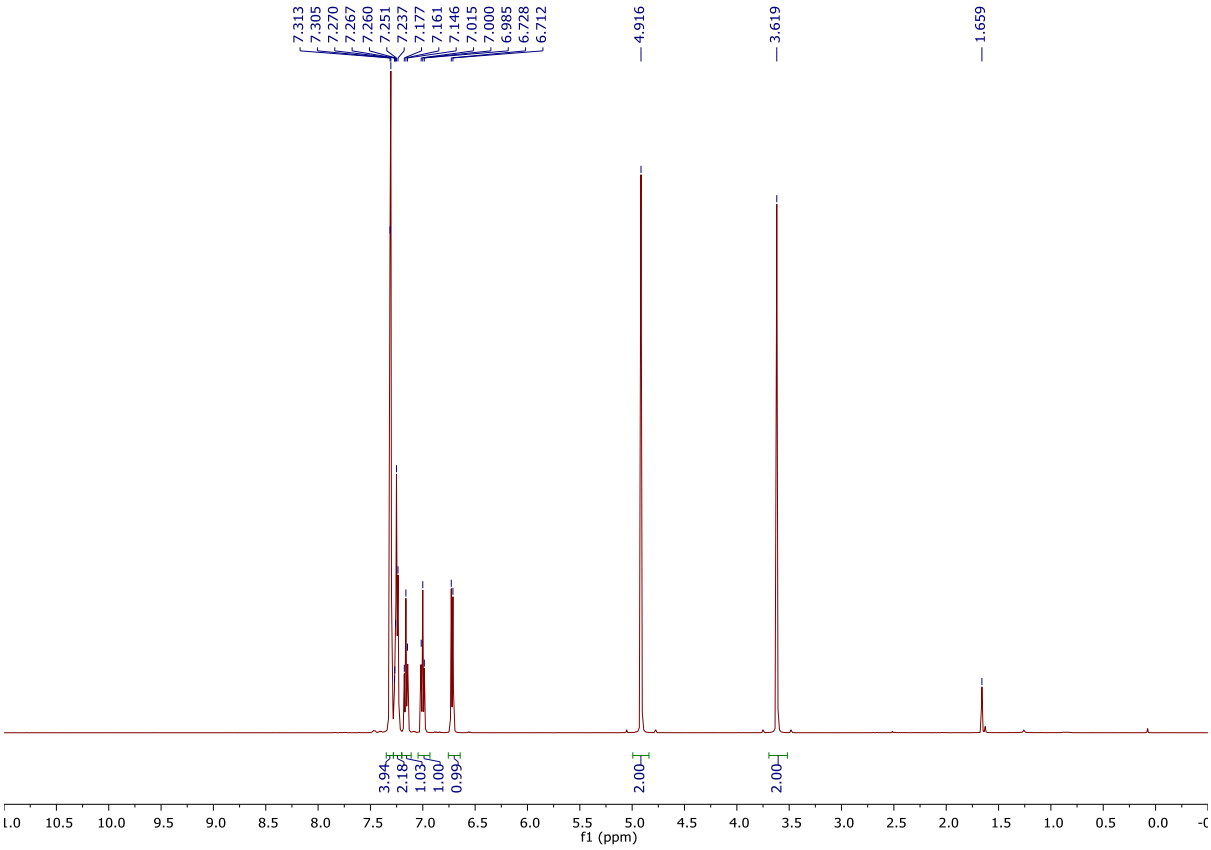


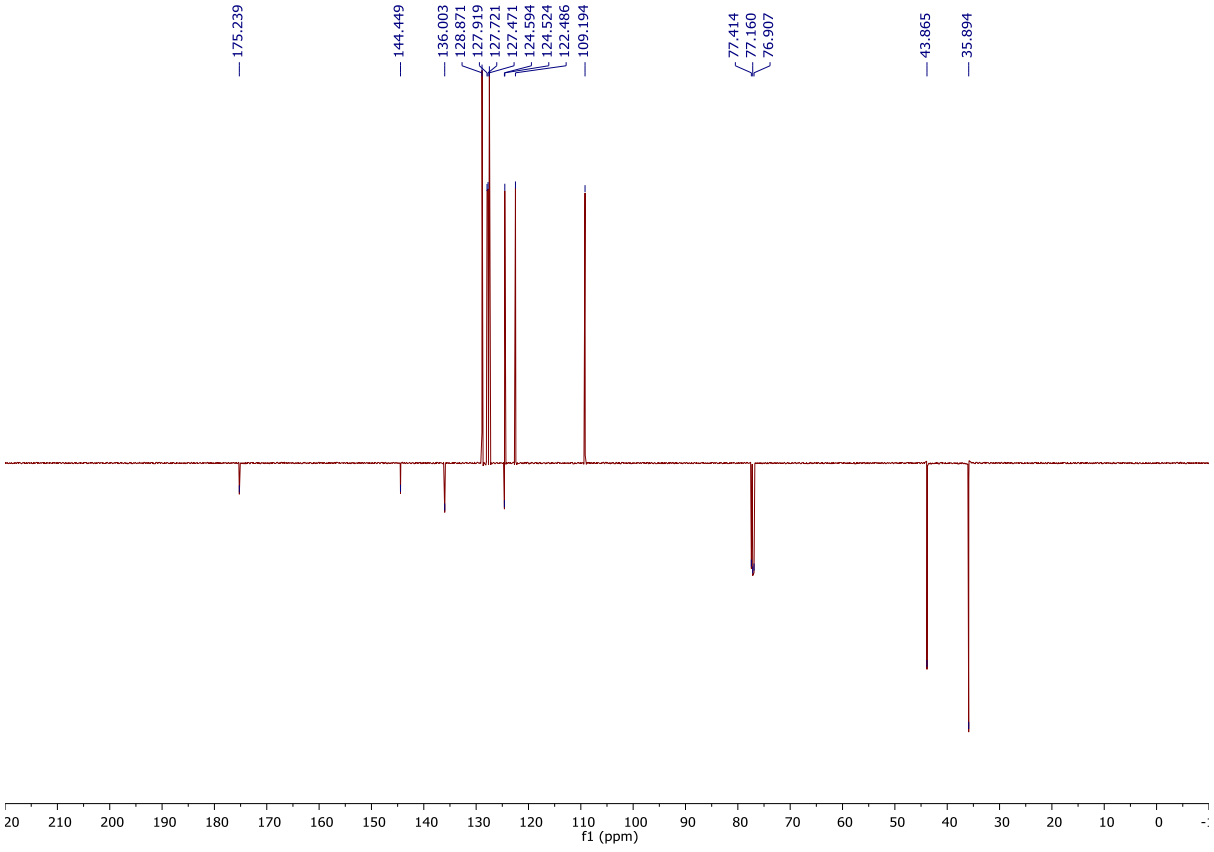


1-Benzylindolin-2-one 8q



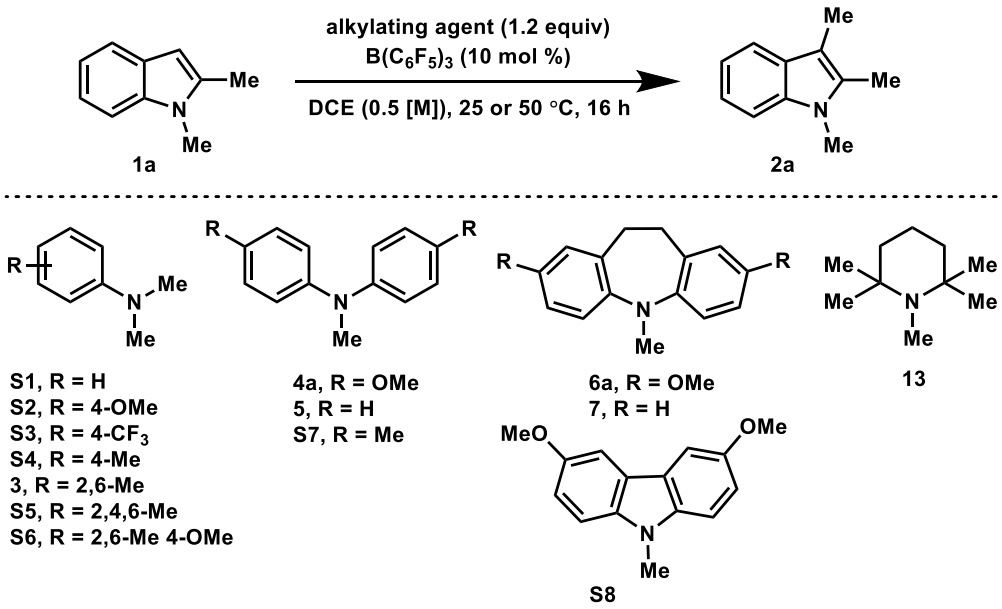
A 250 mL round-bottomed flask was charged with N-benzyl isatin (4.75 g, 20.0 mmol) and hydrazine hydrate 50–60 % in H_2O (60 mL), and was left to react at 115 °C for 24 h. It was then cooled followed by the addition of EtOAc (150 mL). The organic layer was collected and the aqueous phase was washed with EtOAc (2 × 75 mL). The organics were combined, dried over $MgSO_4$, filtered and concentrated *in vacuo*. Purification by flash silica chromatography (eluent = 15% EtOAc in hexanes, 40 × 180 mm silica) gave the title compound **8q** as an off-white solid (4.02 g, 18.0 mmol, 90%); mp 78–80 °C (Lit. 76–77 °C);[19] R_f = 0.35 (eluent = 20% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 3.62 (2H, s), 4.92 (2H, s), 6.72 (1H, d, *J* 7.9), 7.00 (1H, t, *J* 7.5), 7.16 (1H, t, *J* 7.8), 7.25 (2H, t, *J* 5.8), 7.28–7.35 (4H, m); ^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 35.9, 43.9, 109.2, 122.5, 124.5, 124.6, 127.5, 127.7, 127.9, 128.9, 136.0, 144.5, 175.2. Spectroscopic data in accordance with that stated in the literature.[20]




175.239
144.449
136.003
128.871
127.919
127.721
127.471
124.594
124.524
122.486
109.194
77.414
77.160
76.907
43.865
35.894
f1 (ppm)

2.4. Optimization studies

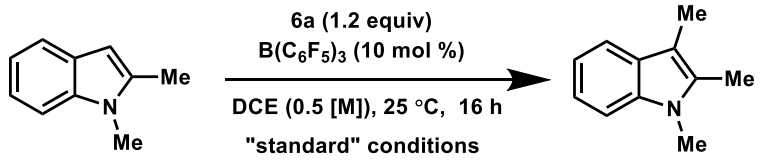
Table S1. Screening of methylating agents for C3 methylation of 1,2-dimethylindole (**1a**)



Entry[a]	Alkylating Agents and Temperature	Yield[b] [%]
1	**S1**, 50 °C	14
2	**S2**, 50 °C	15
3	**S3**, 50 °C	8
4	**S4**, 50 °C	14
5	**3**, 50 °C	>99
6	**S5**, 50 °C	86
7	**S6**, 50 °C	71
8	**4a**, 50 °C	>99
9	**5**, 50 °C	>99
10	**S7**, 50 °C	>99
11	**6a**, 50 °C	>99
12	**7**, 50 °C	>99
13	**S8**, 50 °C	0
14	**13**, 50 °C	0
15	**3**, 25 °C	49
16	**4a**, 25 °C	>99
17	**5**, 25 °C	31
18	**S7**, 25 °C	>99
19	**6a**, 25 °C	>99
20	**7**, 25 °C	70

[a] Reactions were performed using 0.2 mmol of 1,2-dimethylindole in its 0.5 [M] solution of DCE. [b] Yields were determined by ^{1}H NMR analysis of the crude reaction mixture with 1,3,5-trimethoxybenzene as the internal standard.

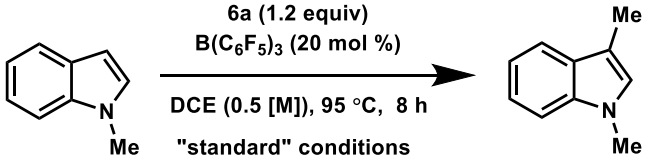
Table S2. Optimization of the C3 methylation of 1,2-disubstituted indole derivatives



Entry[a]	Variation from "standard" conditions	Yield[b] [%]
1	none	>99
2	24 h	>99
3	8 h	>99
4	4 h	70
5	$B(C_6F_5)_3$ (5 mol %), 24 h	82
6	$B(C_6F_5)_3$ (2.5 mol %), 24 h	51

[a] Reactions were performed using 0.2 mmol of 1,2-dimethylindole in its 0.5 [M] solution of DCE. [b] Yields were determined by ^{1}H NMR analysis of the crude reaction mixture with 1,3,5-trimethoxybenzene as the internal standard.

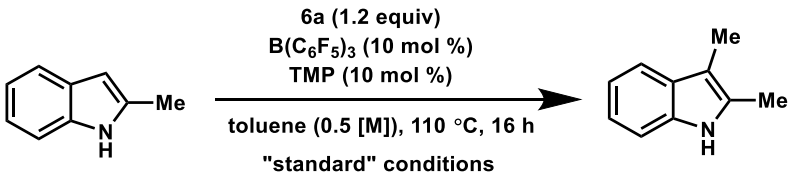
Table S3. Optimization for the C3 methylation of N-alkyl indoles



Entry[a]	Variation from "standard" conditions	Yield[b] [%]
1	none	72 (no SM)
2	1 h	52
3	2 h	66
4	4 h	72 (4 % SM)
5	16 h	68
6	24 h	64
7	**6a** (2.0 equiv), 24 h	68
8	**4a** (1.2 equiv), $B(C_6F_5)_3$ (10 mol %), 50 °C, 24 h	11
9	**7** (1.2 equiv), $B(C_6F_5)_3$ (10 mol %), 50 °C, 24 h	5
10	**6a** (1.2 equiv), $B(C_6F_5)_3$ (10 mol %), 50 °C, 24 h	10
11	**4a** (1.2 equiv), $B(C_6F_5)_3$ (10 mol %), 150 °C in xylenes, 24 h	36
12	**S7** (1.2 equiv), $B(C_6F_5)_3$ (10 mol %), 150 °C in xylenes, 24 h	26
13	**6a** (1.2 equiv), $B(C_6F_5)_3$ (10 mol %), 150 °C in xylenes, 24 h	45
14	**6a** (1.2 equiv), $B(C_6F_5)_3$ (10 mol %), 110 °C in toluene, 24 h	40
15	**6a** (1.2 equiv), $B(C_6F_5)_3$ (10 mol %), 85 °C, 24 h	48
16	**6a** (1.2 equiv), $B(C_6F_5)_3$ (10 mol %), 24 h	53
17	**6a** (1.5 equiv), $B(C_6F_5)_3$ (10 mol %), 24 h	55
18	**6a** (2.0 equiv), $B(C_6F_5)_3$ (10 mol %), 24 h	65
19	**6a** (1.2 equiv), 2,4,6-$B(C_6H_2F_3)_3$ (10 mol %), 85 °C, 24 h	0

[a] Reactions were performed using 0.2 mmol of N-methylindole in its 0.5 [M] solution of desired solvent. [b] Yields were determined by ^{1}H NMR analysis of the crude reaction mixture with 1,3,5-trimethoxybenzene as the internal standard.

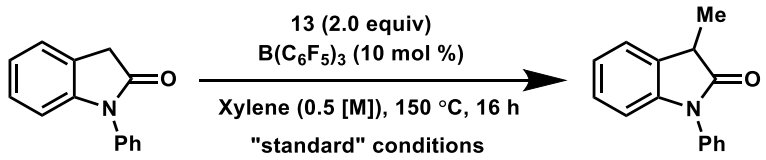
Table S4. Optimization for the C3 methylation of NH-indoles



Entry[a]	Variation from "standard" conditions	Yield[b] [%]
1	none	>99
2	24 h	>99
3	8 h	>99
4	4 h	>99
5	2 h	91
6	1 h	63
7	$B(C_6F_5)_3$ (5 mol %)	45
8	$B(C_6F_5)_3$ (2.5 mol %)	14
9	**4a**, 24 h	96
10	**4a**, no TMP, 24 h	10
11	**4a**, no TMP, 2,6-Lutidine (10 mol %), 24 h	38
12	**4a**, no TMP, 2,4,6-Collidine (10 mol %), 24 h	91
13	**4a**, no TMP, **13** (10 mol %), 24 h	96
14	**4a**, 50 °C in DCE, 24 h	4
15	**4a**, 85 °C in DCE, 24 h	84
16	**4a**, 150 °C in xylenes, 24 h	99
17	**S7**, 85 °C in DCE, 24 h	35
18	**6a**, 85 °C in DCE, 24 h	89

[a] Reactions were performed using 0.2 mmol of 2-methylindole in its 0.5 [M] solution of desired solvent. [b] Yields were determined by ^{1}H NMR analysis of the crude reaction mixture with 1,3,5-trimethoxybenzene as the internal standard.

Table S5. Optimization for the C3 methylation of *N*R oxindoles

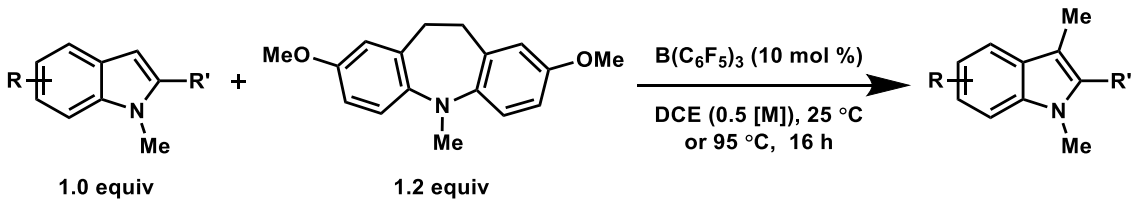


Entry[a]	Variation from "standard" conditions	Yield[b] [%]
1	none	92
2	8 h	69
3	24 h	91
4	140 °C	85
5	110 °C in toluene	19
6	85 °C in DCE	0
7	40 °C in CH_2Cl_2	0
6	no catalyst	0
7	$B(C_6F_5)_3$ (5 mol %)	48
8	$B(2,6\text{-}F_2C_6H_3)_3$ (10 mol %)	7
9	$B(2,4,6\text{-}F_3C_6H_2)_3$ (10 mol %)	17
10	$B(C_6F_5)_3$ (5 mol %) + $B(2,6\text{-}F_2C_6H_3)_3$ (5 mol %)	46
11	$B(C_6F_5)_3$ (5 mol %) + $B(2,4,6\text{-}F_3C_6H_2)_3$ (5 mol %)	35
12	xylenes (0.25 [M])	76
13	xylenes (1.00 [M])	82
14	no **13**	0
15	1.1 equiv of **13**	61
16	1.5 equiv of **13**	80
17	2.5 equiv of **13**	92
17	no **13**, **5** (2.0 equiv)	0
18	no **13**, **4a** (2.0 equiv)	0
19	no **13**, **7** (2.0 equiv)	0
20	no **13**, **6a** (2.0 equiv)	0
21	no **13**, **4a** (2.0 equiv), TMP (10 mol %)	29

[a] Reactions were performed using 0.2 mmol of 1-phenylindolin-2-one in its 0.5 [M] solution of desired solvent. [b] Yields were determined by ^{1}H NMR analysis of the crude reaction mixture with 1,3,5-trimethoxybenzene as the internal standard.

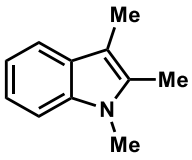
2.5. Substrate scope in the $B(C_6F_5)_3$-catalyzed alkylation

General procedure 5: C3 methylation of 1,2-disubstituted indole derivatives

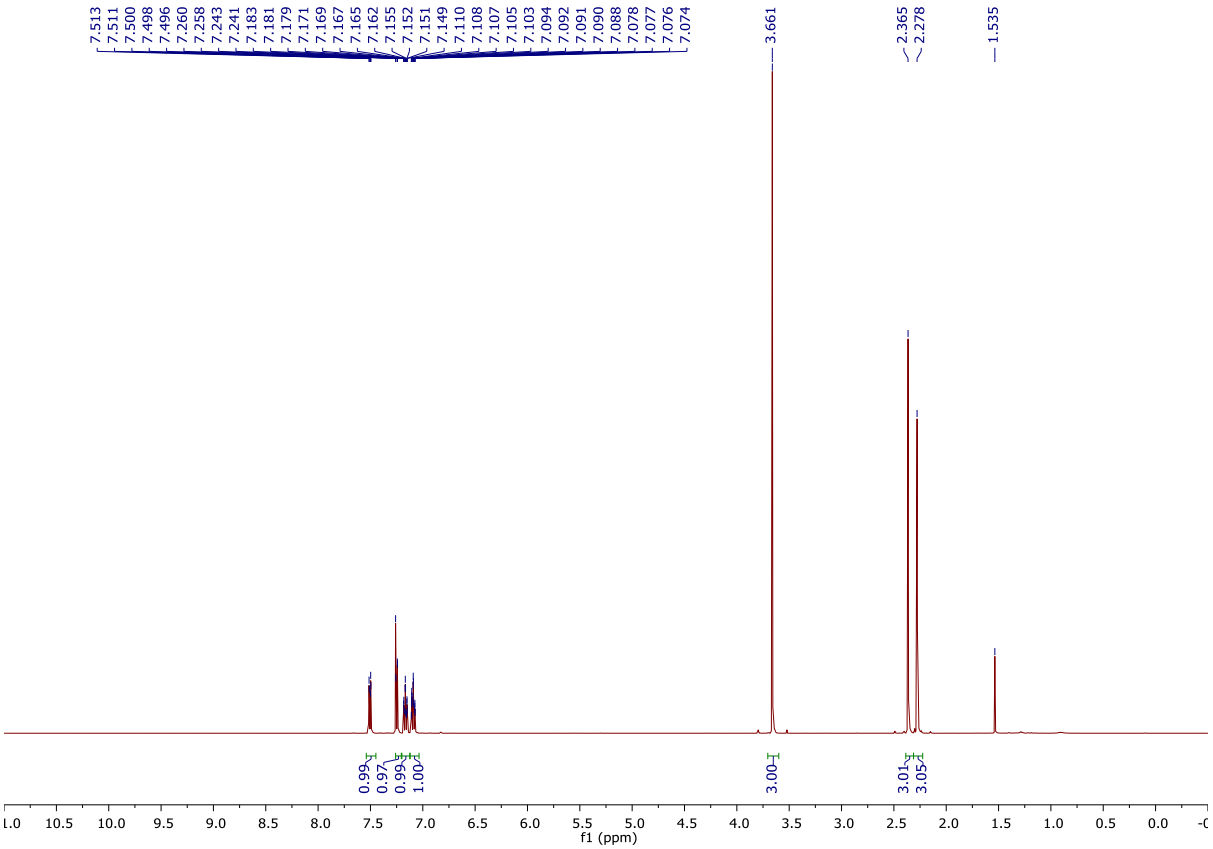


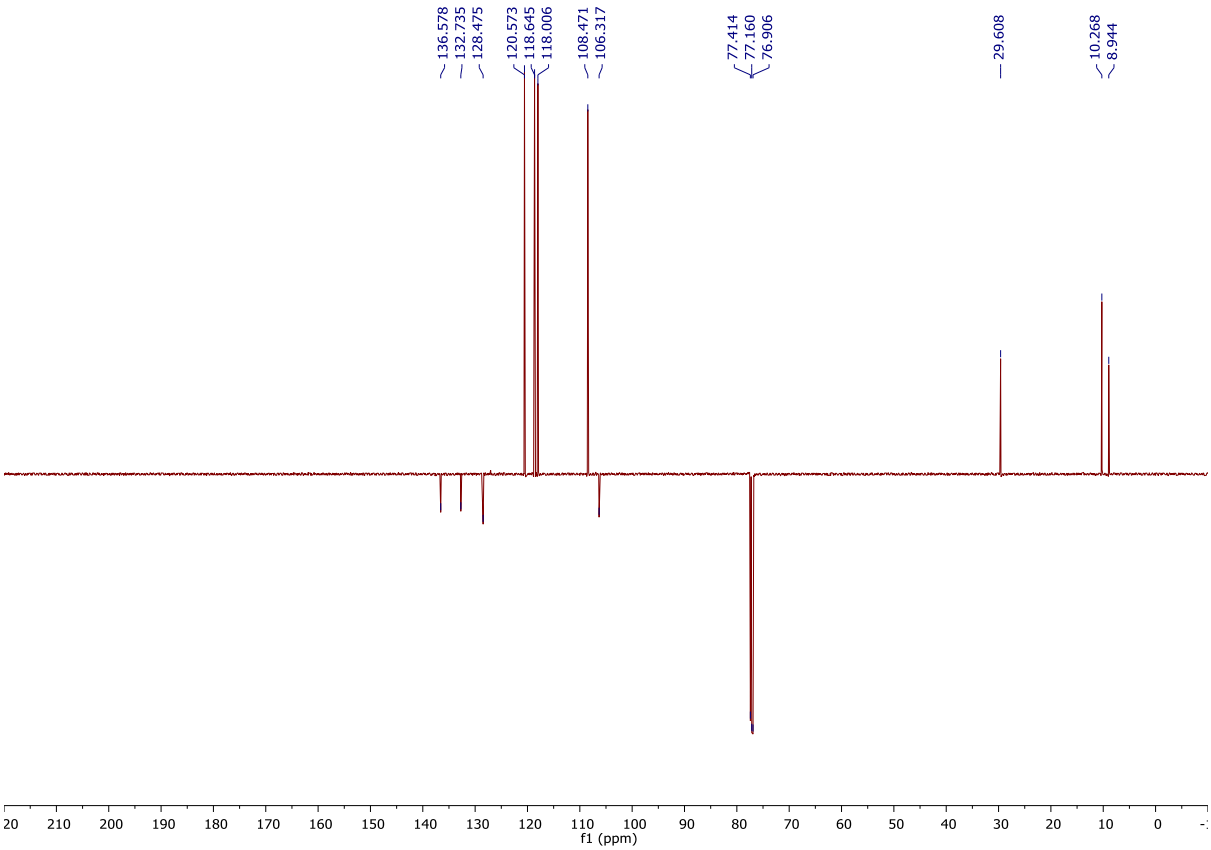
In a nitrogen-filled glove box, a 10 mL vial equipped with a magnetic stirrer bar was charged with the 1,2-disubstituted indole derivative (0.5 mmol), **6a** (161 mg, 0.6 mmol), $B(C_6F_5)_3$ (25.6 mg, 0.05 mmol) and DCE (1.0 mL). The vial was sealed with an aluminium crimped cap and was left to stir at 25 °C or 95 °C for 16 h. The reaction mixture was then directly purified by silica gel chromatography.

1,2,3-Trimethyl-1H-indole 2a

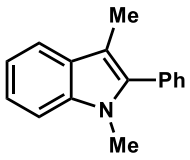


The title compound was prepared according to general procedure 5 using 1,2-dimethylindole **1a** (72.6 mg, 0.5 mmol) at 25 °C. Purification by flash silica chromatography (eluent = 0.3–0.5% EtOAc in hexanes, 20 × 180 mm silica) gave the title compound **2a** as a light red oil (76.4 mg, 0.48 mmol, 96%); R_f = 0.47 (eluent = 2% EtOAc in hexanes); ν_{max} / cm^{-1} (film) 2913, 1472, 1408, 1368, 1325, 1246, 1190, 1150, 1128, 1011, 953, 916, 849, 787, 731, 569, 546, 432; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 2.28 (3H, s), 2.36 (3H, s), 3.66 (3H, s), 7.04–712 (1H, m), 7.12–7.20 (1H, m), 7.21–7.26 (1H, m), 7.50 (1H, dd, *J* 7.8, 1.0); ^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 8.9, 10.3, 29.6, 106.3, 108.5, 118.0, 118.7, 120.6, 128.5, 132.7, 136.6; HRMS (AP)$^+$ calculated for $[C_{11}H_{14}N]^+$ $(M+H)^+$ m/z: 160.1126, found 160.1126 (+0.0 ppm).

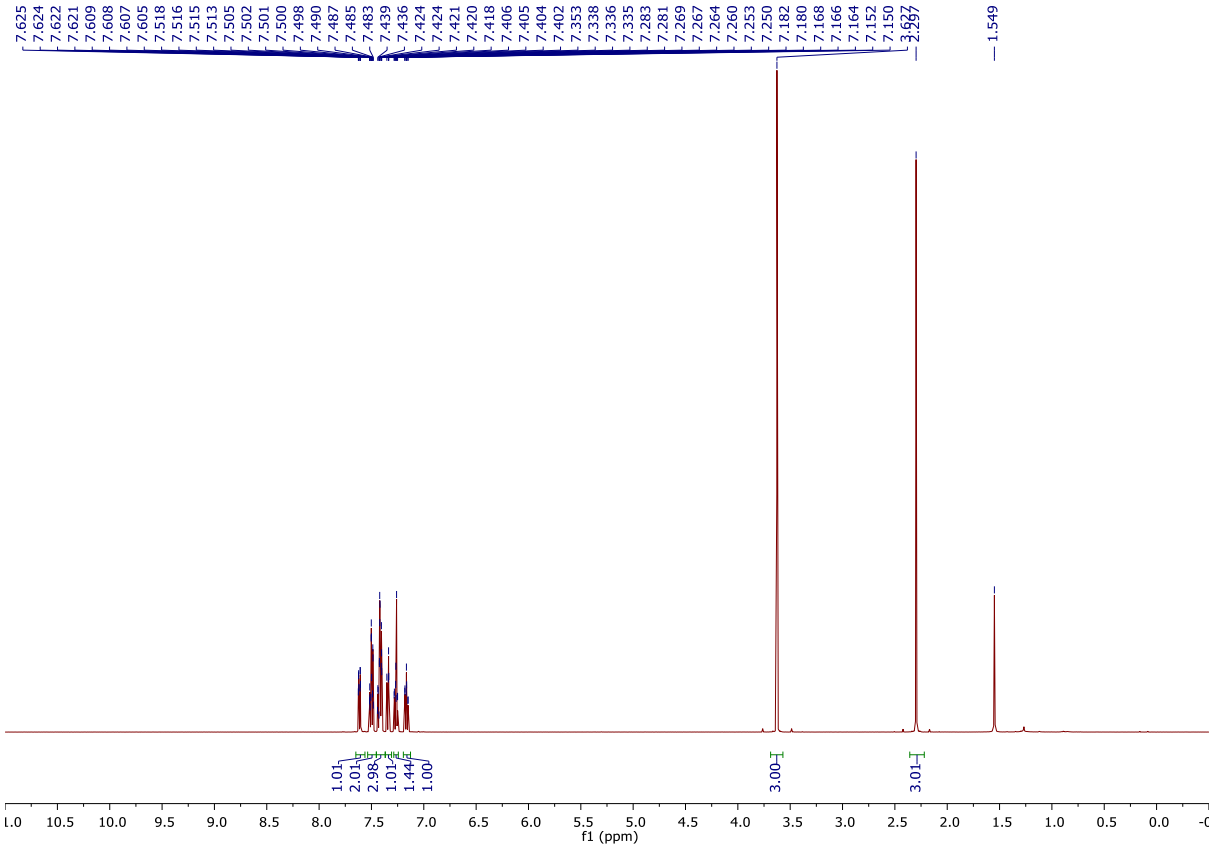




1,3-Dimethyl-2-phenyl-1H-indole 2b



The title compound was prepared according to general procedure 5 using 1-methyl-2-phenyl-1H-indole **1b** (104 mg, 0.50 mmol) at 95 °C. Purification by flash silica chromatography (eluent = 0.4% EtOAc in hexanes, 20 × 180 mm silica) gave the title compound **2b** as a colorless viscous oil (109 mg, 0.49 mmol, 98%); R_f = 0.56 (eluent = 5% EtOAc in hexanes); ν_{max} / cm^{-1} (film) 3046, 2932, 1605, 1468, 1354, 1327, 1236, 1155, 1128, 1067, 1017, 1005, 924, 845, 820, 806, 760, 739, 700, 611, 554, 490, 451; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 2.30 (3H, s), 3.63 (3H, s), 7.13–7.20 (1H, m), 7.24–7.29 (1H, m), 7.31–7.37 (1H, m), 7.37–7.45 (3H, m), 7.45–7.54 (2H, m), 7.62 (1H, ddd, *J* 7.8, 1.2, 0.7); ^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 9.5, 31.1, 108.7, 109.4, 118.9, 119.2, 121.9, 127.9, 128.5, 128.6, 130.8, 132.3, 137.3, 137.8; HRMS $(EI)^+$ calculated for $[C_{16}H_{15}N]^+$ $(M)^+$ m/z: 221.1204, found 221.1209 (+2.3 ppm).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7.622
7.621
7.609
7.608
7.607
7.605
7.518
7.516
7.515
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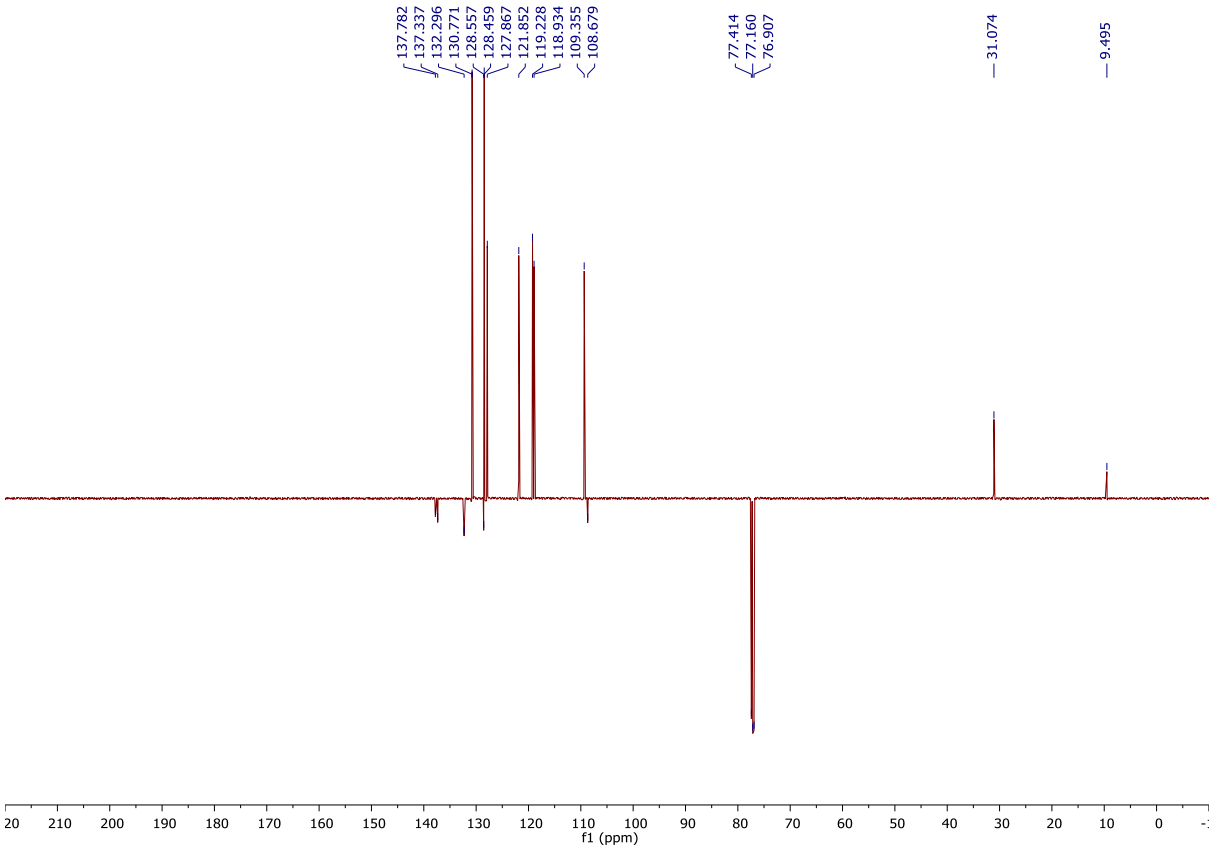
7.505
7.502
7.501
7.500
7.498
7.490
7.487
7.485
7.483
7.439
7.436
7.424
7.424
7.421
7.420
7.418
7.406
7.405
7.404
7.402
7.353
7.338
7.336
7.335
7.283
7.281
7.269
7.267
7.264
7.260
7.253
7.250
7.182
7.180
7.168
7.166
7.164
7.152
7.150
3.627
2.257
1.549
1.01
2.01
2.98
1.01
1.44
1.00
3.00
3.01
f1 (ppm)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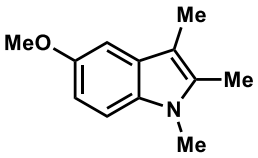
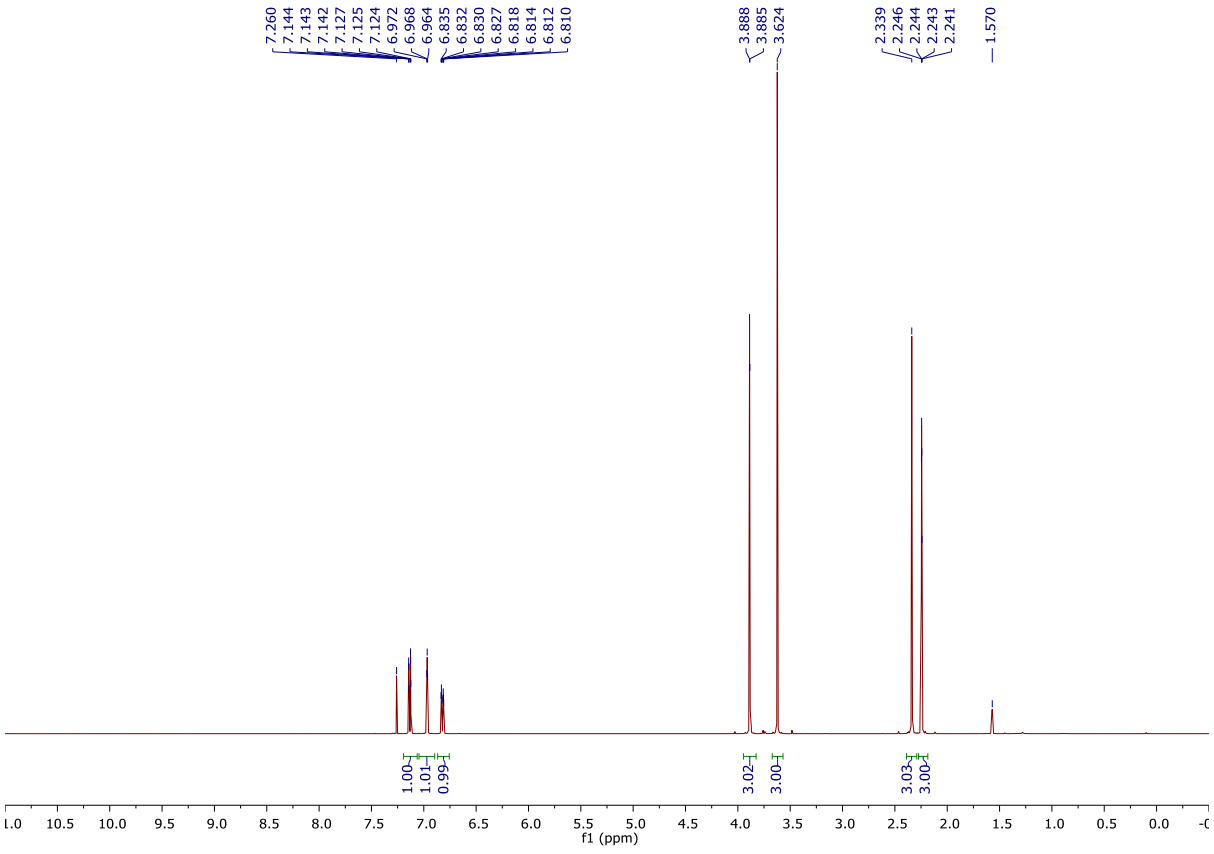
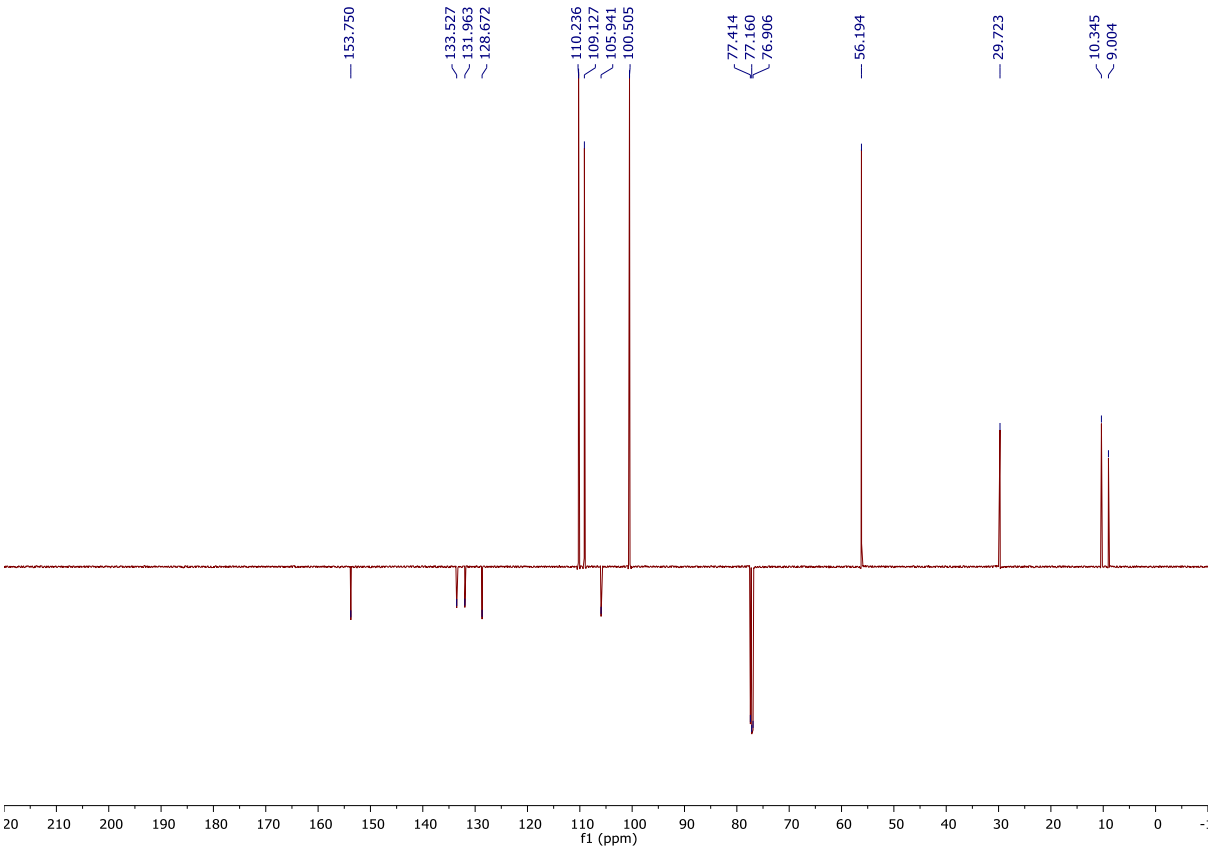
137.337
132.296
130.771
128.557
128.459
127.867
121.852
119.228
118.934
109.355
108.679
77.414
77.160
76.907
31.074
9.495
f1 (ppm)

5-Methoxy-1,2,3-trimethyl-1H-indole 2c

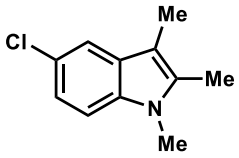


The title compound was prepared according to general procedure 5 using 5-methoxy-1,2-dimethyl-1H-indole **1c** (87.6 mg, 0.5 mmol) at 25 °C. Purification by flash silica chromatography (eluent = 0.3–0.5% EtOAc in hexanes, 20 × 180 mm silica) gave the title compound **2c** as an off-white solid (84.2 mg, 0.45 mmol, 89%); mp 102–104 °C (Lit. 93–95 °C);[21] R_f = 0.44 (eluent = 5% EtOAc in hexanes); ν_{max} / cm^{-1} (film) 2928, 1620, 1584, 1489, 1460, 1437, 1414, 1370, 1292, 1248, 1229, 1188, 1157, 1044, 897, 822, 787, 700, 638, 600, 550; ^1H NMR (500 MHz, $CDCl_3$) δ_H: 2.24 (3H, dd, *J* 1.4, 0.8), 2.34 (3H, s), 3.62 (3H, s), 3.89 (3H, d, *J* 1.3), 6.82 (1H, ddd, *J* 8.7, 2.5, 1.5), 6.97 (1H, t, *J* 1.9), 7.06–7.19 (1H, m); ^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 9.0, 10.3, 29.7, 56.2, 100.5, 105.9, 109.1, 110.2, 128.7, 132.0, 133.5, 153.8; HRMS $(EI)^+$ calculated for $[C_{12}H_{15}NO]^+$ $(M)^+$ m/z: 189.1154, found 189.1156 (+1.1 ppm).

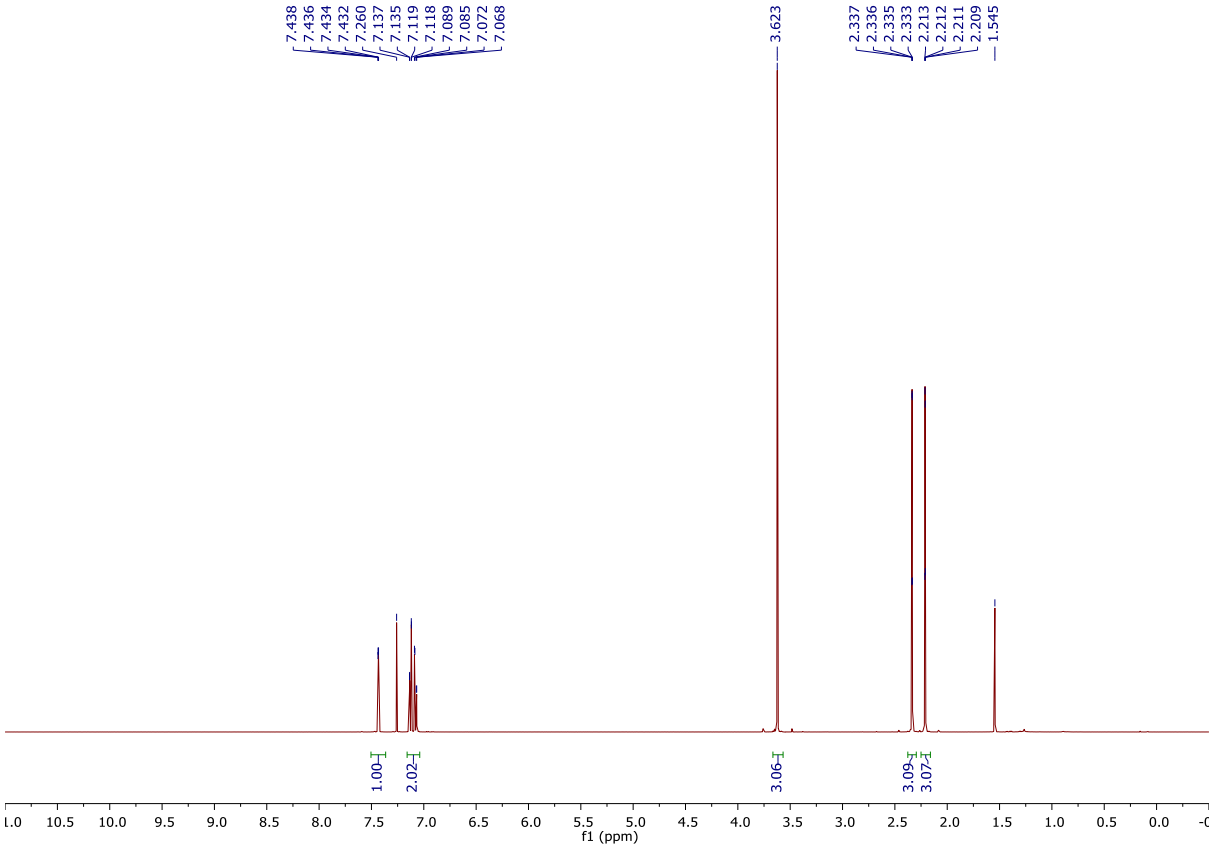




5-Chloro-1,2,3-trimethyl-1H-indole 2d



The title compound was prepared according to general procedure 5 using 5-chloro-1,2-dimethyl-1H-indole **1d** (89.8 mg, 0.50 mmol) at 95 °C. Purification by flash silica chromatography (eluent = 0.3–0.4% EtOAc in hexanes, 20 × 180 mm silica) gave the title compound **2d** as a brown oil (96.1 mg, 0.50 mmol, 99%); R_f = 0.53 (eluent = 5% EtOAc in hexanes); ν_{max} / cm^{-1} (film) 2914, 2859, 1854, 1717, 1572, 1474, 1431, 1408, 1366, 1344, 1277, 1242, 1188, 1136, 1069, 1038, 953, 860, 820, 797, 637, 586, 532, 428; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 2.21 (3H, q, *J* 0.7), 2.34 (3H, q, *J* 0.7), 3.62 (3H, s), 7.04–7.16 (2H, m), 7.43 (1H, dd, *J* 2.0, 0.6); ^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 8.9, 10.4, 29.8, 106.2, 109.4, 117.5, 120.6, 124.4, 129.5, 134.3, 135.0; HRMS (EI)$^+$ calculated for $[C_{11}H_{12}NCl]^+$ $(M)^+$ m/z: 193.0658, found 193.0656 (-1.0 ppm).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7.436
7.434
7.432
7.260
7.137
7.135
7.119
7.118
7.089
7.085
7.072
7.068
3.623
2.337
2.336
2.335
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2.213
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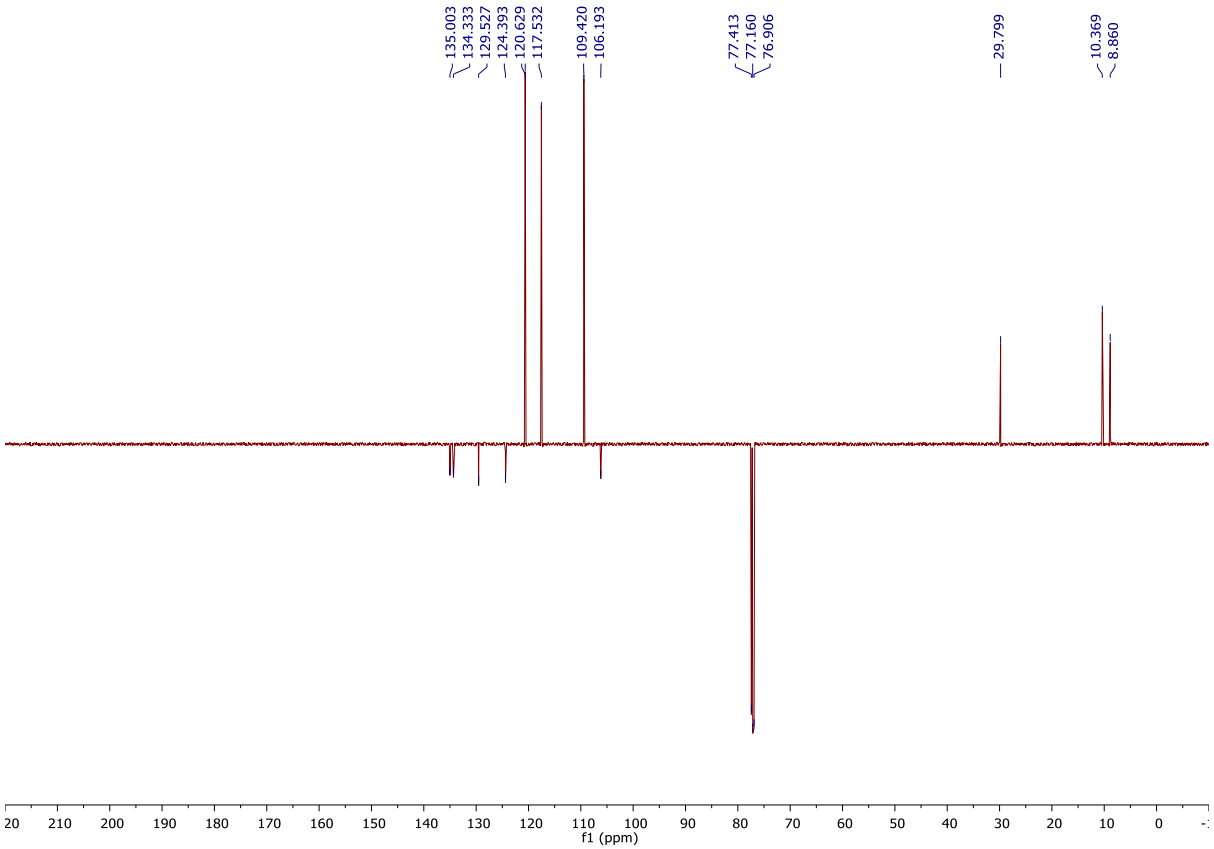
1.00
2.02
3.06
3.09
3.07
f1 (ppm)


135.003
134.333
129.527
124.393
120.629
117.532
109.420
106.193
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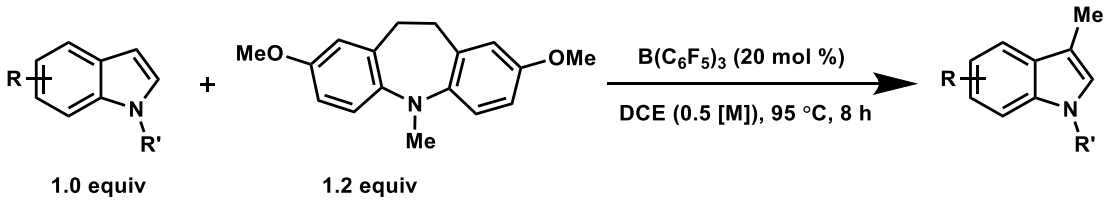
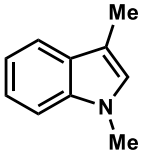
77.160
76.906
29.799
10.369
8.860
f1 (ppm)

General procedure 6: C3 methylation of N-substituted indole derivatives

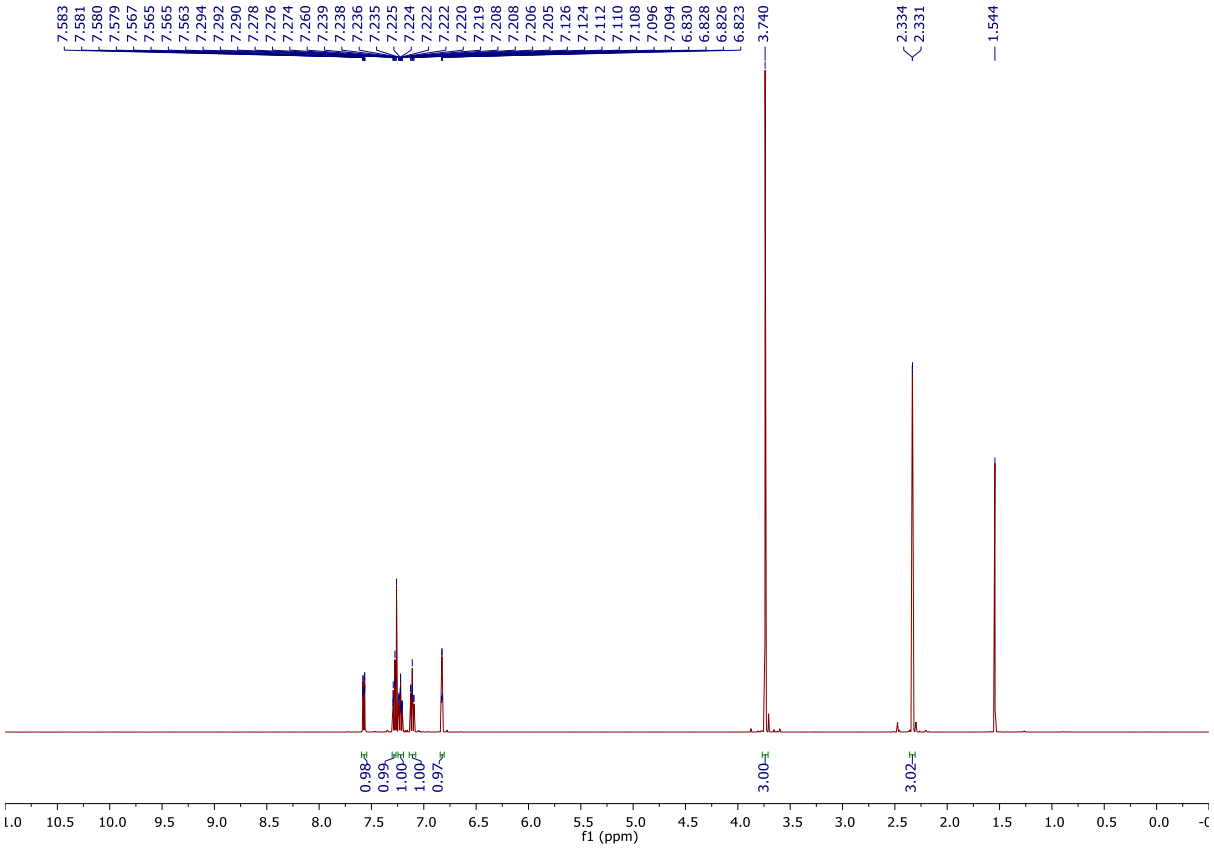


In a nitrogen-filled glove box, a 10 mL vial equipped with a magnetic stirrer bar was charged with the N-substituted indole derivative (0.5 mmol), **13** (161 mg, 0.6 mmol), $B(C_6F_5)_3$ (51.2 mg, 0.10 mmol) and DCE (1.0 mL). The vial was sealed with an aluminium crimped cap and was left to stir at 95 °C for 8 h. The reaction mixture was then directly purified using silica gel chromatography.

1,3-Dimethyl-1H-indole 2f



The title compound was prepared according to general procedure 6 using 1-methyl-1H-indole **1f** (65.6 mg, 0.50 mmol). Purification by flash silica chromatography (eluent = 0.3–0.4% EtOAc in hexanes, 20 × 180 mm silica) gave the title compound **2f** as a colorless oil (54.2 mg, 0.37 mmol, 75%); R_f = 0.38 (eluent = 1% EtOAc in hexanes); ν_{max} / cm^{-1} (film) 3053, 2914, 1616, 1560, 1483, 1470, 1424, 1385, 1366, 1323, 1246, 1204, 1157, 1125, 1065, 1011, 982, 920, 839, 789, 733, 608, 596, 548, 426; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 2.33 (3H, d, *J* 1.1), 3.74 (3H, s), 6.83 (1H, q, *J* 1.1), 7.11 (1H, ddd, *J* 7.9, 6.9, 1.1), 7.19–7.25 (1H, m), 7.28 (1H, dt, *J* 8.2, 1.0), 7.54–7.60 (1H, m); ^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 9.7, 32.6, 109.1, 110.2, 118.6, 119.1, 121.5, 126.6, 128.8, 137.1; HRMS $(ES)^+$ calculated for $[C_{10}H_{12}N]^+$ $(M+H)^+$ m/z: 146.0970, found 146.0970 (+0.0 ppm).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7.579
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7.565
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7.563
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7.292
7.290
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7.276
7.274
7.260
7.239
7.238
7.236
7.235
7.225
7.224
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7.208
7.208
7.206
7.205
7.126
7.124
7.112
7.110
7.108
7.096
7.094
6.830
6.828
6.826
6.823
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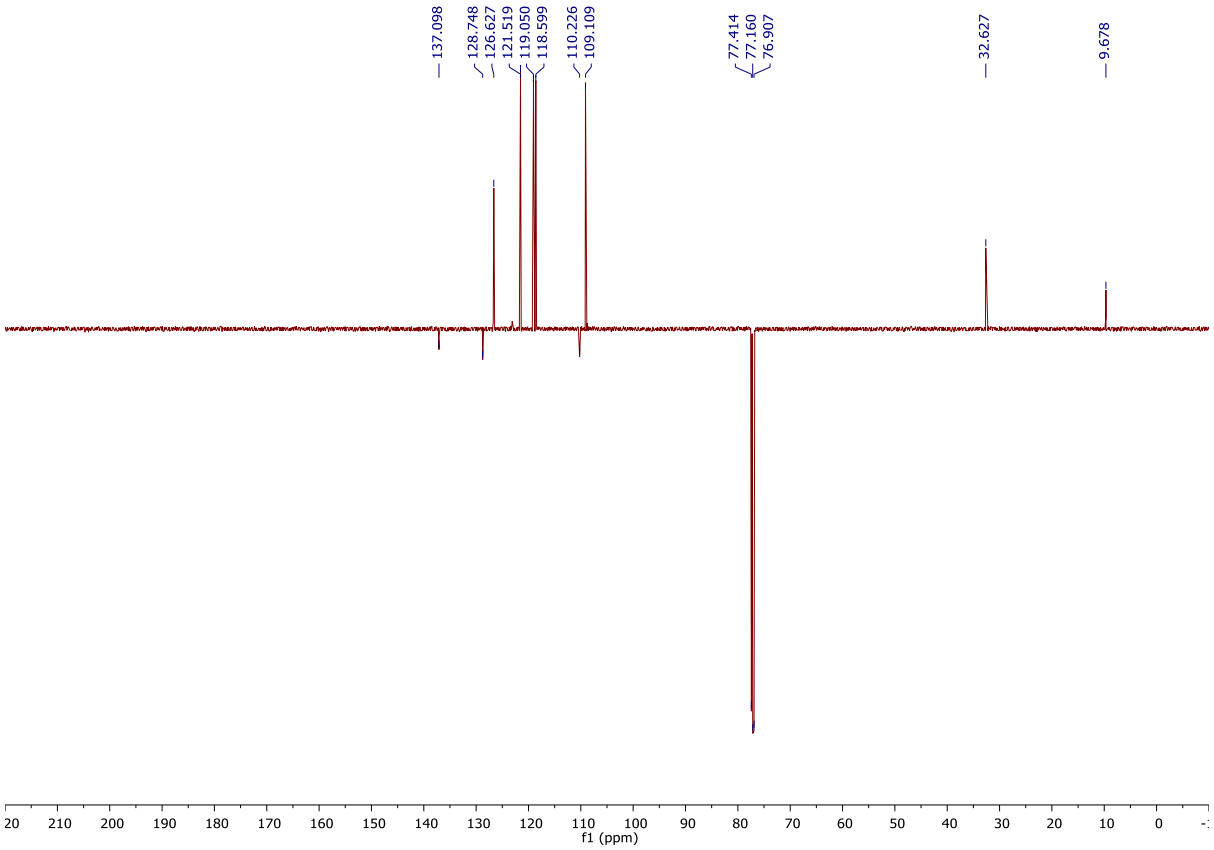
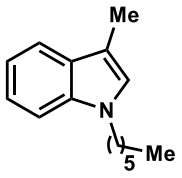
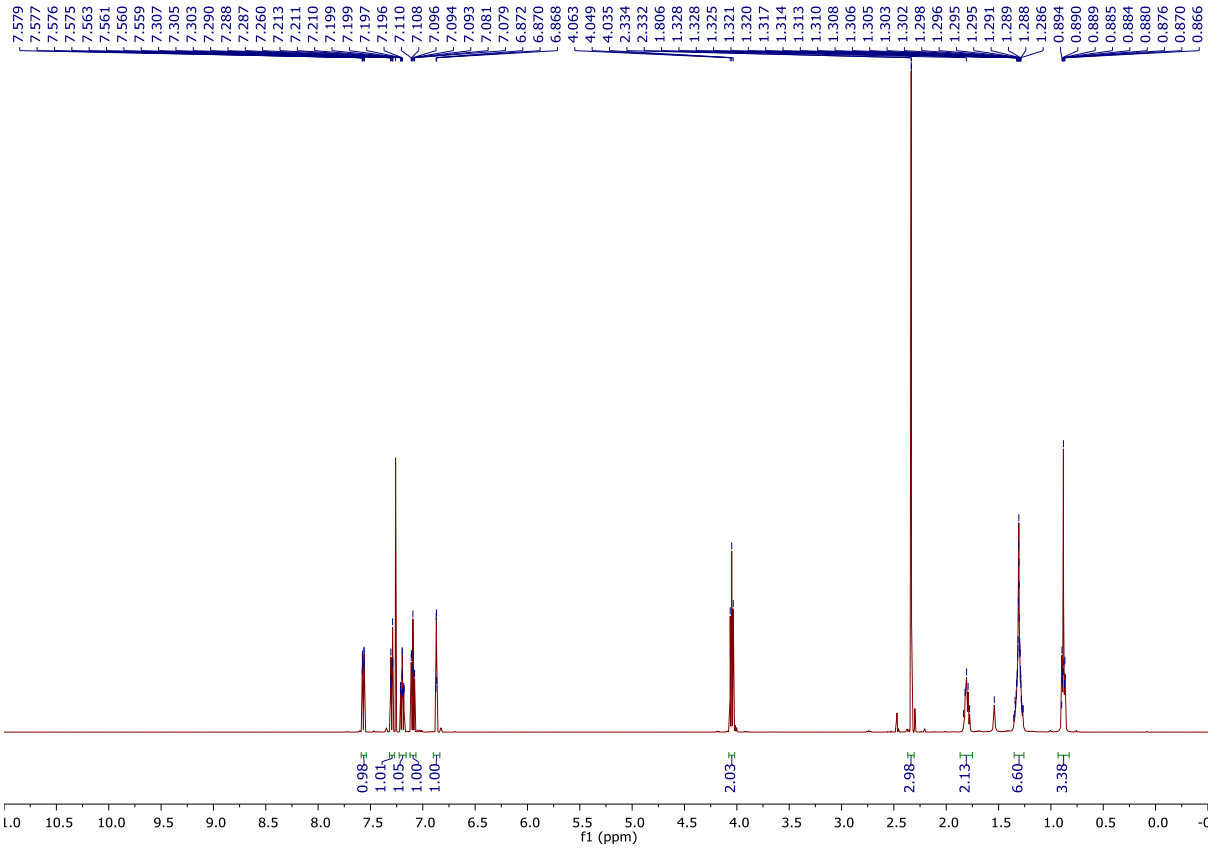
2.331
1.544
0.98
0.99
1.00
1.00
0.97
3.00
3.02
f1 (ppm)

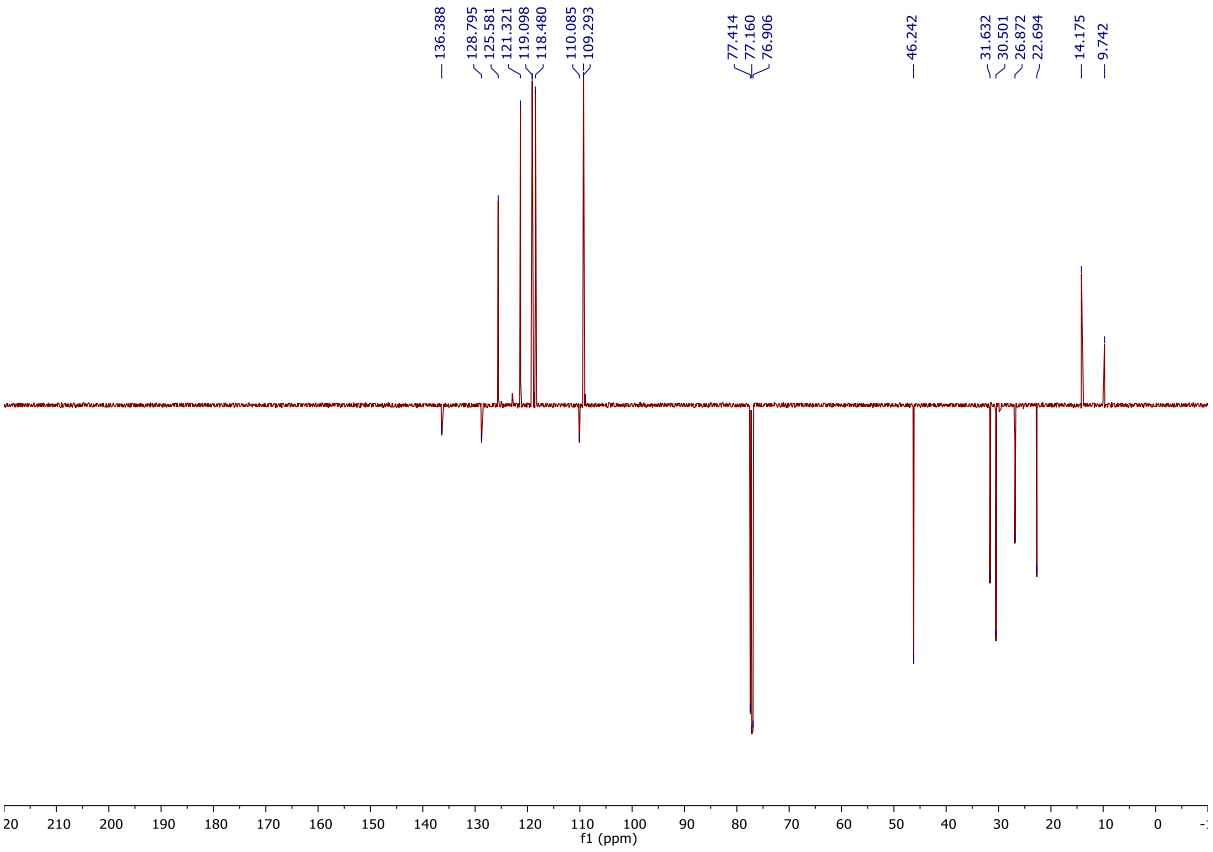

137.098
128.748
126.627
121.519
119.050
118.599
110.226
109.109
77.414
77.160
76.907
32.627
9.678
f1 (ppm)

1-Hexyl-3-methyl-1H-indole 2g

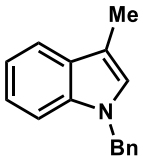


The title compound was prepared according to general procedure 6 using 1-hexyl-1H-indole **1g** (101 mg, 0.50 mmol). Purification by flash silica chromatography (eluent = 0.2–0.3% EtOAc in hexanes, 20 × 180 mm silica) gave the title compound **2g** as a light yellow oil (78.3 mg, 0.36 mmol, 73%); R_f = 0.63 (eluent = 1% EtOAc in hexanes); ν_{max} / cm^{-1} (film) 3053, 2953, 2926, 2857, 1559, 1466, 1362, 1331, 1240, 1202, 1180, 1126, 1092, 1013, 785, 733, 654, 598, 540, 426; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 0.83–0.93 (3H, m), 1.26–1.35 (6H, m), 1.75–1.87 (2H, m), 2.33 (3H, d, *J* 1.1), 4.02–4.08 (2H, t, *J* 7.2), 6.87 (1H, q, *J* 1.1), 7.09 (1H, ddd, *J* 7.9, 7.0, 1.0), 7.16–7.23 (1H, m), 7.30 (1H, dt, *J* 8.2, 0.9), 7.57 (1H, ddd, *J* 7.9, 1.2, 0.8); ^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 9.7, 14.2, 22.7, 26.9, 30.5, 31.6, 46.2, 109.3, 110.1, 118.5, 119.1, 121.3, 125.6, 128.8, 136.4; HRMS (ES)$^+$ calculated for $[C_{15}H_{22}N]^+$ $(M+H)^+$ m/z: 216.1752, found 216.1758 (+2.8 ppm).

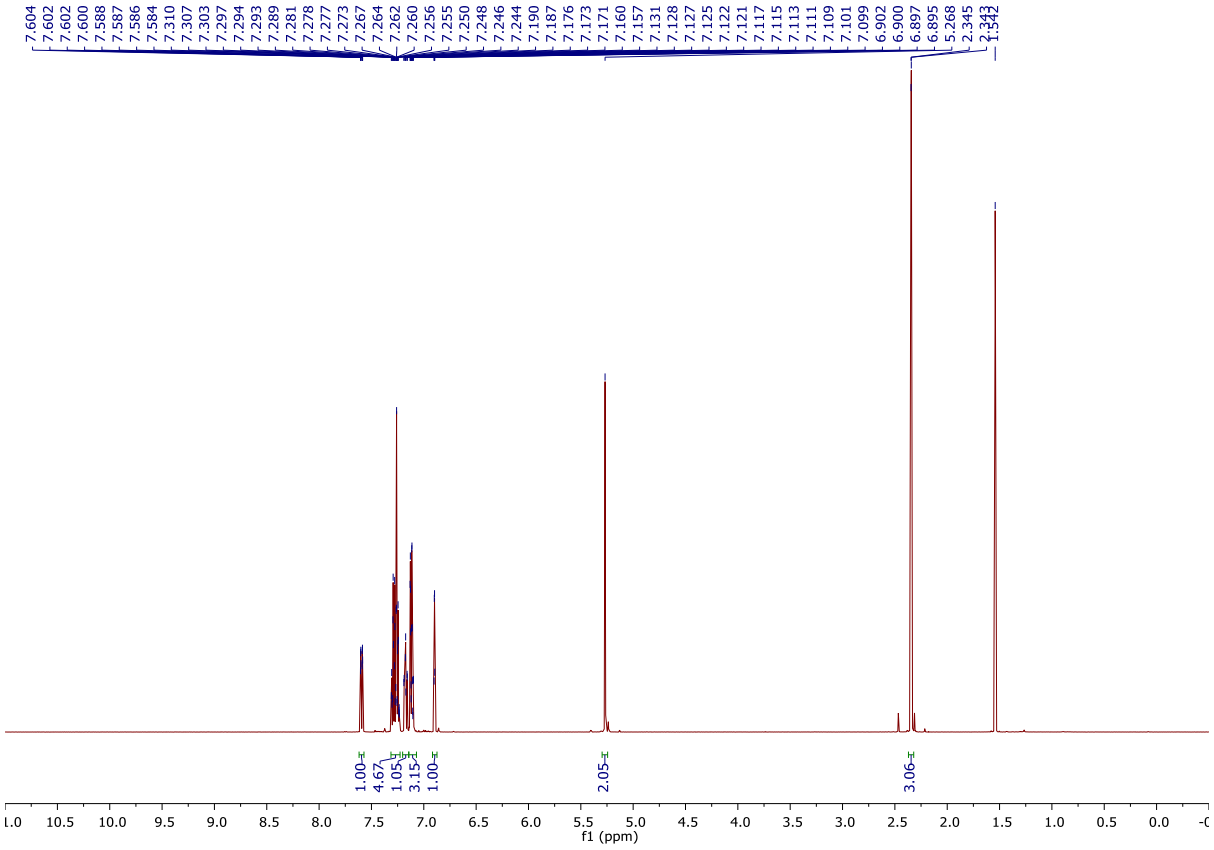


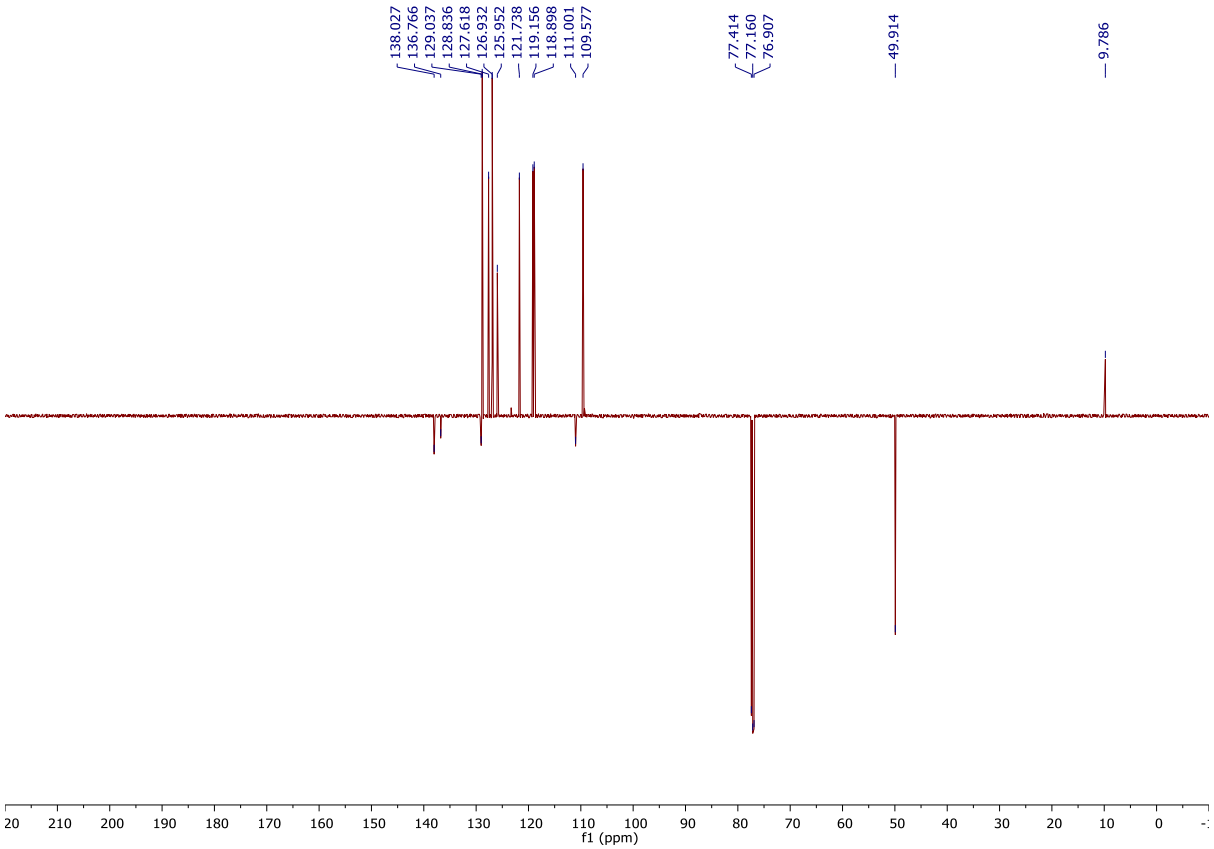


1-Benzyl-3-methyl-1H-indole 2h

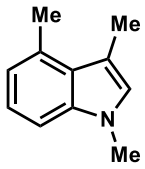


The title compound was prepared according to general procedure 6 using 1-benzyl-1H-indole **1h** (104 mg, 0.50 mmol). Purification by flash silica chromatography (eluent = 0.3–0.4% EtOAc in hexanes, 20 × 180 mm silica) gave the title compound **2h** as a light red semi-solid (87.6 mg, 0.40 mmol, 79%); R_f = 0.43 (eluent = 1% EtOAc in hexanes); ν_{max} / cm^{-1} (film) 3030, 2913, 1613, 1584, 1495, 1481, 1466, 1452, 1439, 1387, 1358, 1329, 1302, 1258, 1202, 1179, 1111, 1072, 1028, 1010, 984, 961, 922, 797, 789, 758, 731, 694, 669, 453, 426; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 2.34 (3H, d, *J* 1.1), 5.27 (2H, s), 6.90 (1H, q, *J* 1.1), 7.07–7.14 (3H, m), 7.17 (1H, ddd, *J* 8.2, 7.0, 1.3), 7.23–7.31 (4H, m), 7.59 (1H, ddd, *J* 7.8, 1.3, 0.8).; ^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 9.8, 49.9, 109.6, 111.0, 118.9, 119.2, 121.7, 126.0, 126.9, 127.6, 128.8, 129.0, 136.8, 138.0.; HRMS $(EI)^+$ calculated for $[C_{16}H_{15}N]^+$ $(M)^+$ m/z: 221.1204, found 221.1207 (+1.4 ppm).

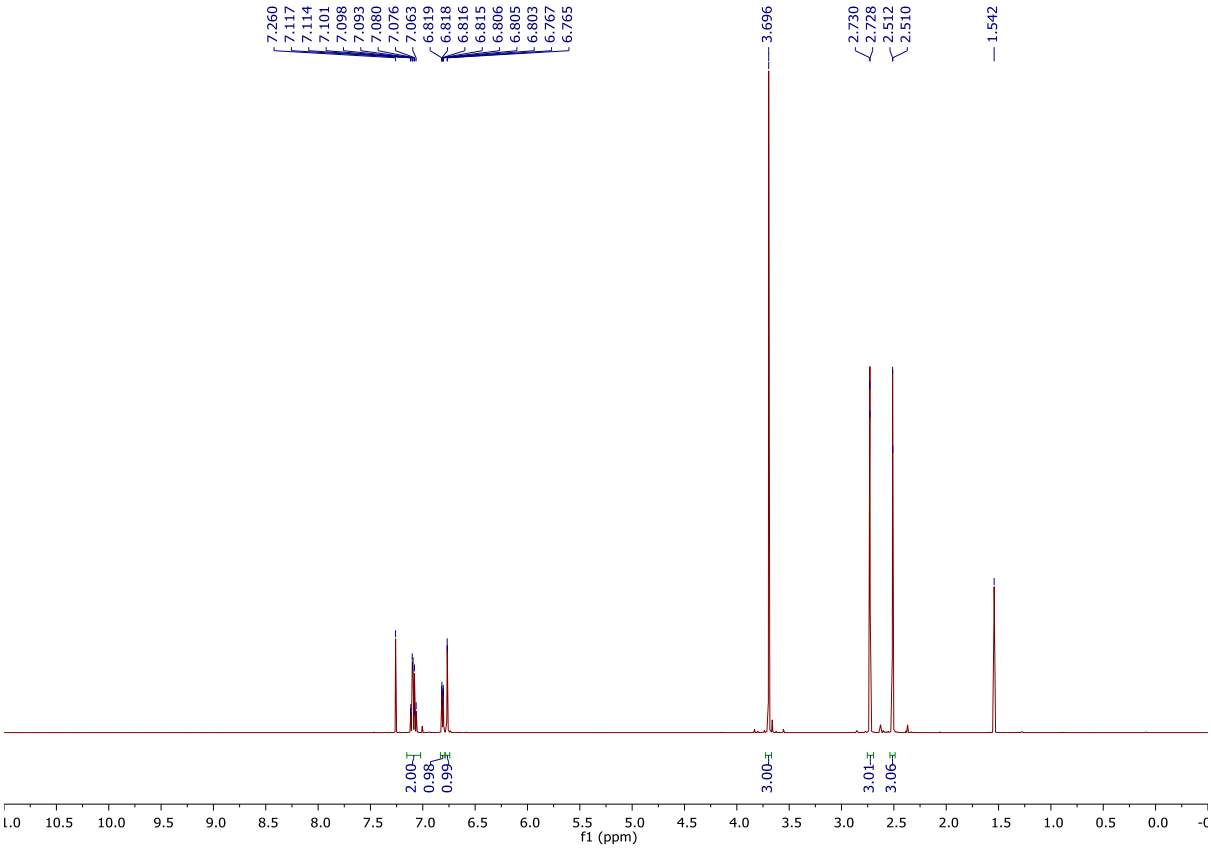

7.604
7.602
7.602
7.600
7.588
7.587
7.586
7.584
7.310
7.307
7.303
7.297
7.294
7.293
7.289
7.281
7.278
7.277
7.273
7.267
7.264
7.262
7.260
7.256
7.255
7.250
7.248
7.246
7.244
7.190
7.187
7.176
7.173
7.171
7.160
7.157
7.131
7.128
7.127
7.125
7.122
7.121
7.117
7.115
7.113
7.111
7.109
7.101
7.099
6.902
6.900
6.897
6.895
5.268
2.345
2.343
1.542
1.00
4.67
1.05
3.15
1.00
2.05
3.06
f1 (ppm)

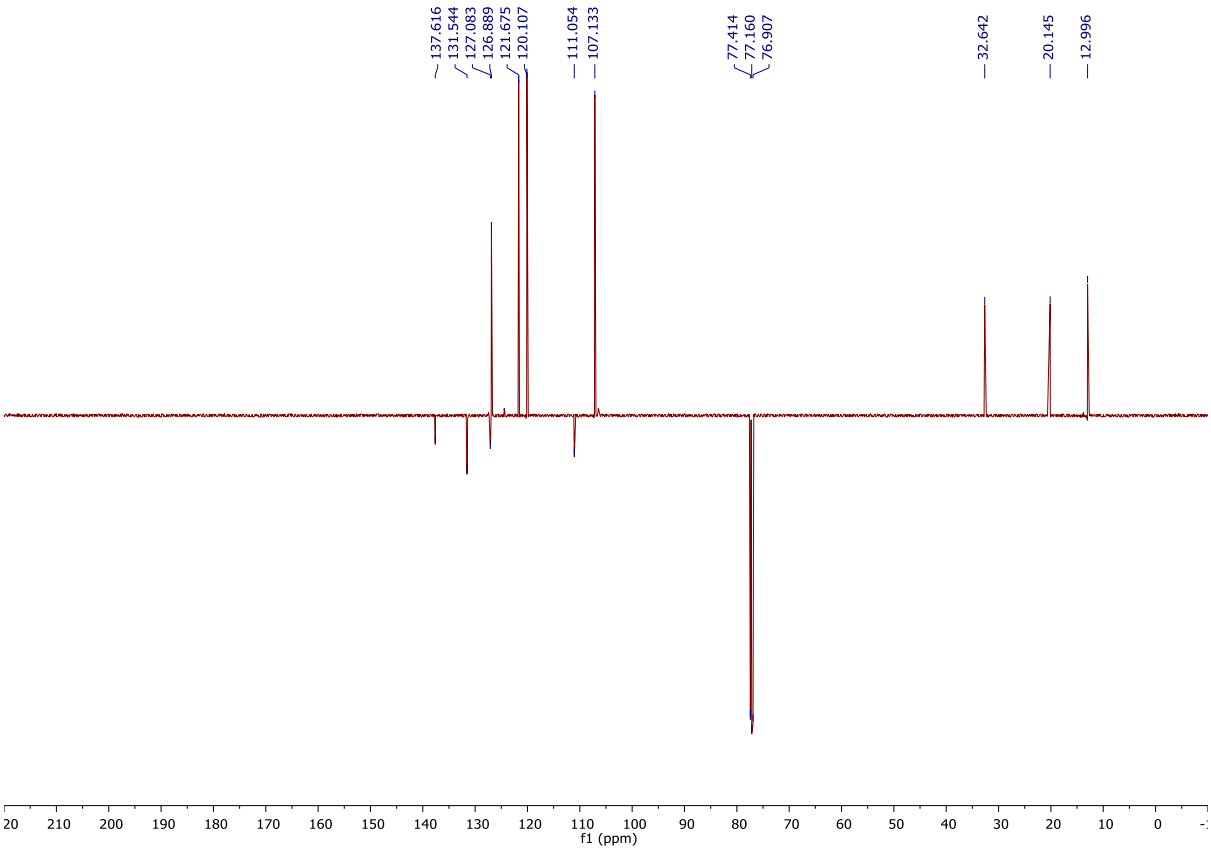

138.027
136.766
129.037
128.836
127.618
126.932
125.952
121.738
119.156
118.898
111.001
109.577
77.414
77.160
76.907
49.914
9.786
f1 (ppm)

1,3,4-Trimethyl-1H-indole 2i

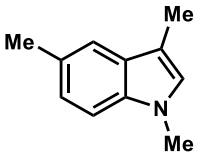


The title compound was prepared according to general procedure 6 using 1,4-dimethyl-1H-indole **1i** (72.6 mg, 0.50 mmol). Purification by flash silica chromatography (eluent = 0.4% EtOAc in hexanes, 20 × 180 mm silica) gave the title compound **2i** as an off-white solid (65.6 mg, 0.41 mmol, 82%); mp 54–56 °C; R_f = 0.36 (eluent = 1% EtOAc in hexanes); ν_{max} / cm^{-1} (film) 3042, 2953, 2918, 1607, 1551, 1535, 1497, 1452, 1416, 1366, 1335, 1312, 1250, 1202, 1157, 1057, 984, 910, 766, 737, 669, 602, 569; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 2.51 (3H, d, *J* 1.1), 2.73 (3H, d, *J* 0.9), 3.70 (3H, s), 6.74–6.79 (1H, m), 6.79–6.83 (1H, m), 7.02–7.15 (2H, m); ^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 13.0, 20.2, 32.6, 107.1, 111.1, 120.1, 121.7, 126.9, 127.1, 131.5, 137.6; HRMS (EI)$^+$ calculated for $[C_{11}H_{13}N]^+$ $(M)^+$ m/z: 159.1048, found 159.1051 (+1.9 ppm).

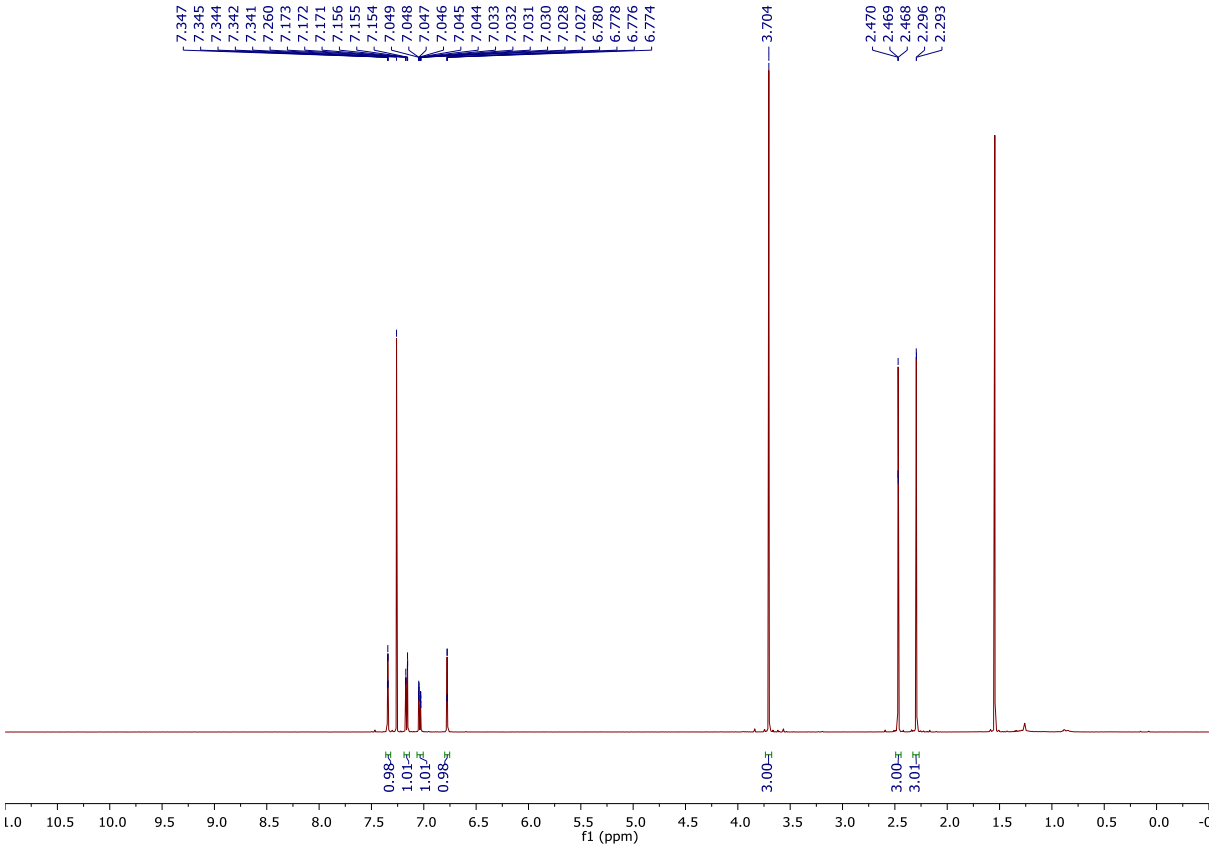


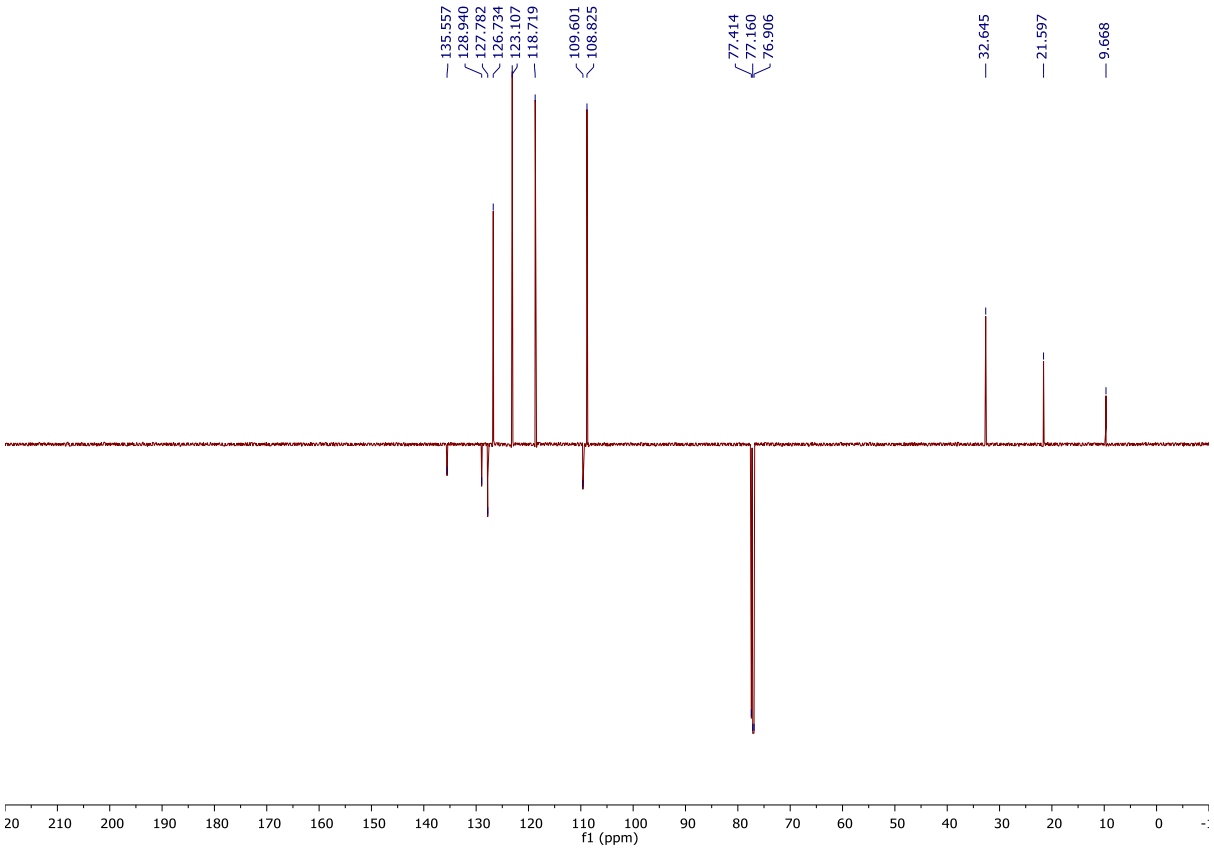


1,3,5-Trimethyl-1H-indole 2j

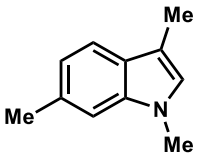


The title compound was prepared according to general procedure 6 using 1,5-dimethyl-1H-indole **1j** (72.6 mg, 0.50 mmol). Purification by flash silica chromatography (eluent = 0.5% EtOAc in hexanes, 20 × 180 mm silica) gave the title compound **2j** as a colorless oil (57.4 mg, 0.36 mmol, 72%); R_f = 0.46 (eluent = 1% EtOAc in hexanes); ν_{max} / cm^{-1} (film) 2914, 2859, 1578, 1493, 1458, 1424, 1387, 1366, 1296, 1250, 1209, 1190, 1148, 1057, 980, 883, 866, 781, 610, 561, 424; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 2.29 (3H, d, *J* 1.1), 2.44–2.49 (3H, m), 3.70 (3H, s), 6.78 (1H, q, *J* 1.1), 7.04 (1H, ddt, *J* 8.3, 1.7, 0.5), 7.16 (1H, dt, *J* 8.2, 0.4), 7.34 (1H, dt, *J* 1.6, 0.8); ^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 9.7, 21.6, 32.6, 108.8, 109.6, 118.7, 123.1, 126.7, 127.8, 128.9, 135.6; HRMS (EI)$^+$ calculated for $[C_{11}H_{13}N]^+$ $(M)^+$ m/z: 159.1048, found 159.1050 (+1.3 ppm).

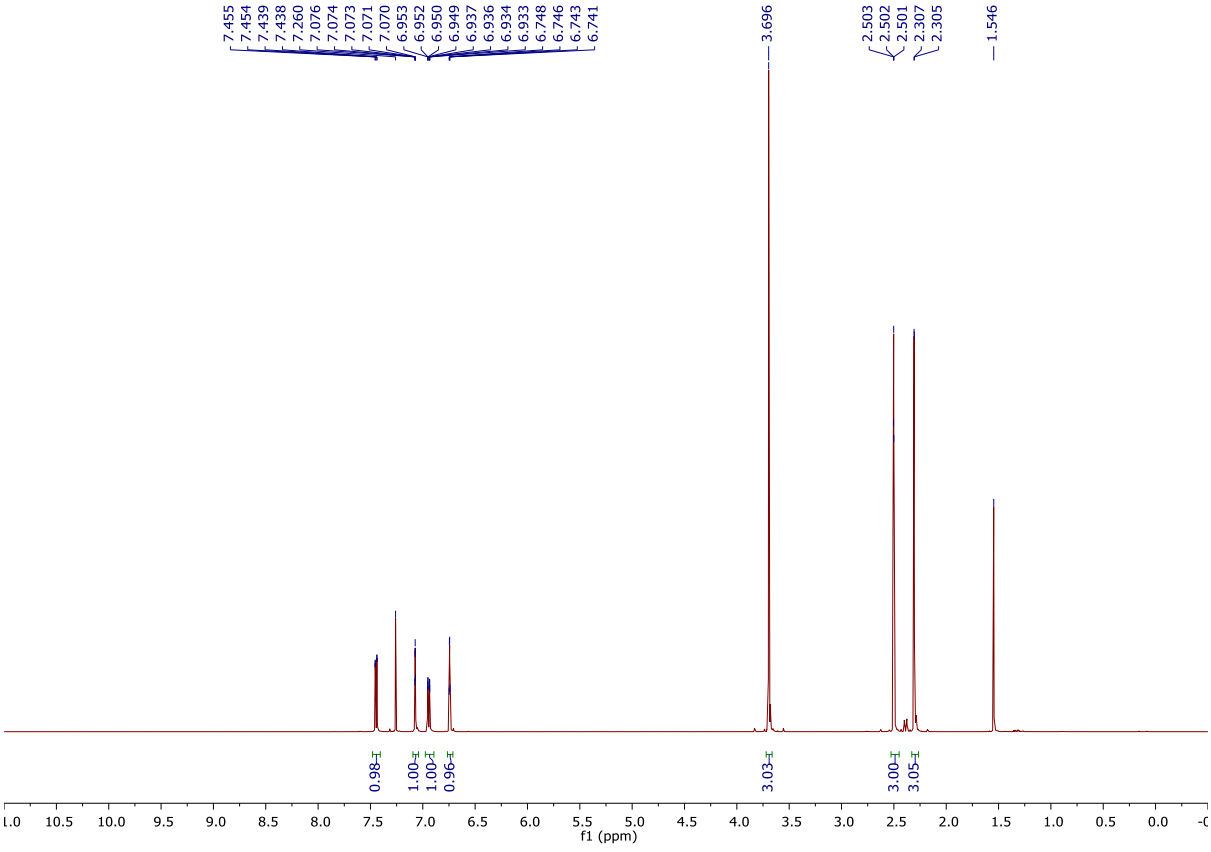

7.347
7.345
7.344
7.342
7.341
7.260
7.173
7.172
7.171
7.156
7.155
7.154
7.049
7.048
7.047
7.046
7.045
7.044
7.033
7.032
7.031
7.030
7.028
7.027
6.780
6.778
6.776
6.774
3.704
2.470
2.469
2.468
2.296
2.293
0.98
1.01
1.01
0.98
3.00
3.00
3.01
f1 (ppm)

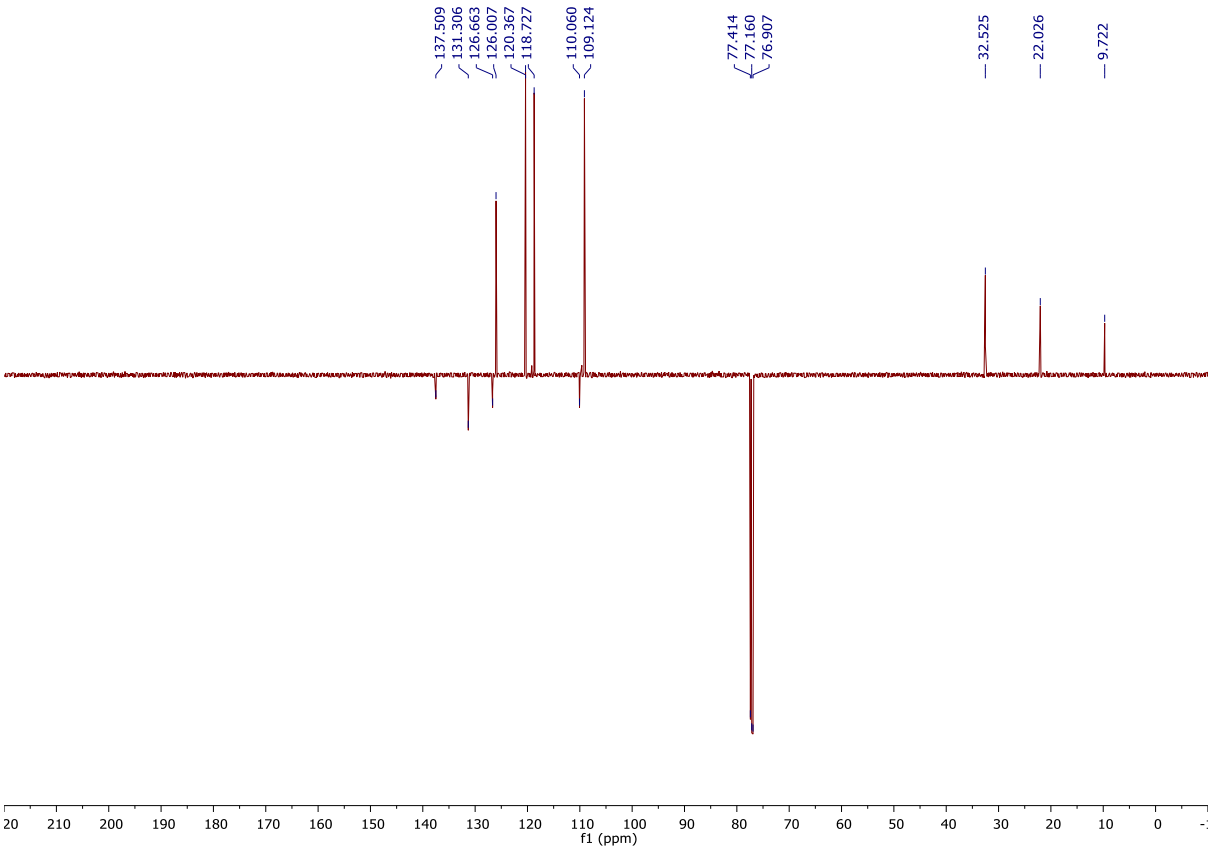

135.557
128.940
127.782
126.734
123.107
118.719
109.601
108.825
77.414
77.160
76.906
32.645
21.597
9.668
f1 (ppm)

1,3,6-Trimethyl-1H-indole 2k

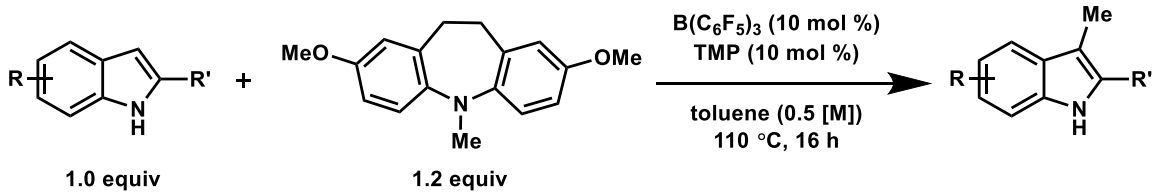


The title compound was prepared according to general procedure 6 using 1,6-dimethyl-1H-indole **1k** (72.6 mg, 0.50 mmol). Purification by flash silica chromatography (eluent = 0.5% EtOAc in hexanes, 20 × 180 mm silica) gave the title compound **2k** as a colorless oil (59.4 mg, 0.37 mmol, 75%); R_f = 0.35 (eluent = 1% EtOAc in hexanes); ν_{max} / cm^{-1} (film) 2914, 2859, 1624, 1557, 1476, 1445, 1387, 1366, 1327, 1248, 1182, 1142, 1119, 1063, 843, 797, 691, 600, 590, 573, 428; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 2.31 (3H, d, *J* 1.1), 2.45–2.53 (3H, m), 3.70 (3H, s), 6.74 (1H, q, *J* 1.1), 6.94 (1H, ddd, *J* 8.0, 1.4, 0.6), 7.07 (1H, dt, *J* 1.5, 0.8), 7.45 (1H, dd, *J* 8.0, 0.7); ^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 9.7, 22.0, 32.5, 109.1, 110.1, 118.7, 120.4, 126.0, 126.7, 131.3, 137.5; HRMS (EI)$^+$ calculated for $[C_{11}H_{13}N]^+$ $(M)^+$ m/z: 159.1048, found 159.1047 (-0.6 ppm).





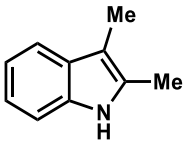
General procedure 7: C3 methylation of NH-indole derivatives



1.0 equiv **1.2 equiv**

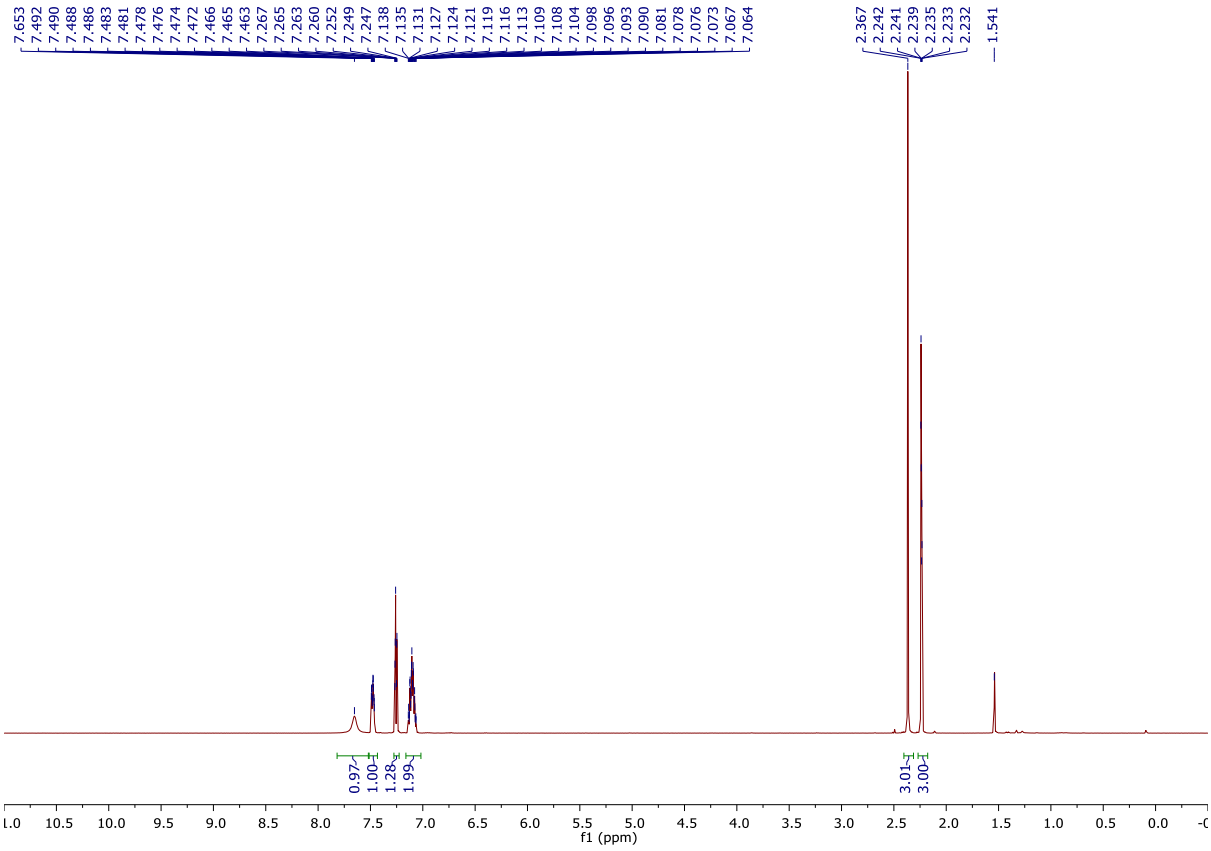
In a nitrogen-filled glove box, a 10 mL vial equipped with a magnetic stirrer bar was charged with the NH-indole derivative (0.5 mmol), **6a** (161 mg, 0.6 mmol), 2,2,6,6-tetramethylpiperidine (TMP) (8.4 µL, 0.05 mmol), $B(C_6F_5)_3$ (25.6 mg, 0.05 mmol) and toluene (1.0 mL). The vial was sealed with an aluminium crimped cap and was left to stir at 110 °C for 16 h. The reaction mixture was then directly purified using silica gel chromatography.

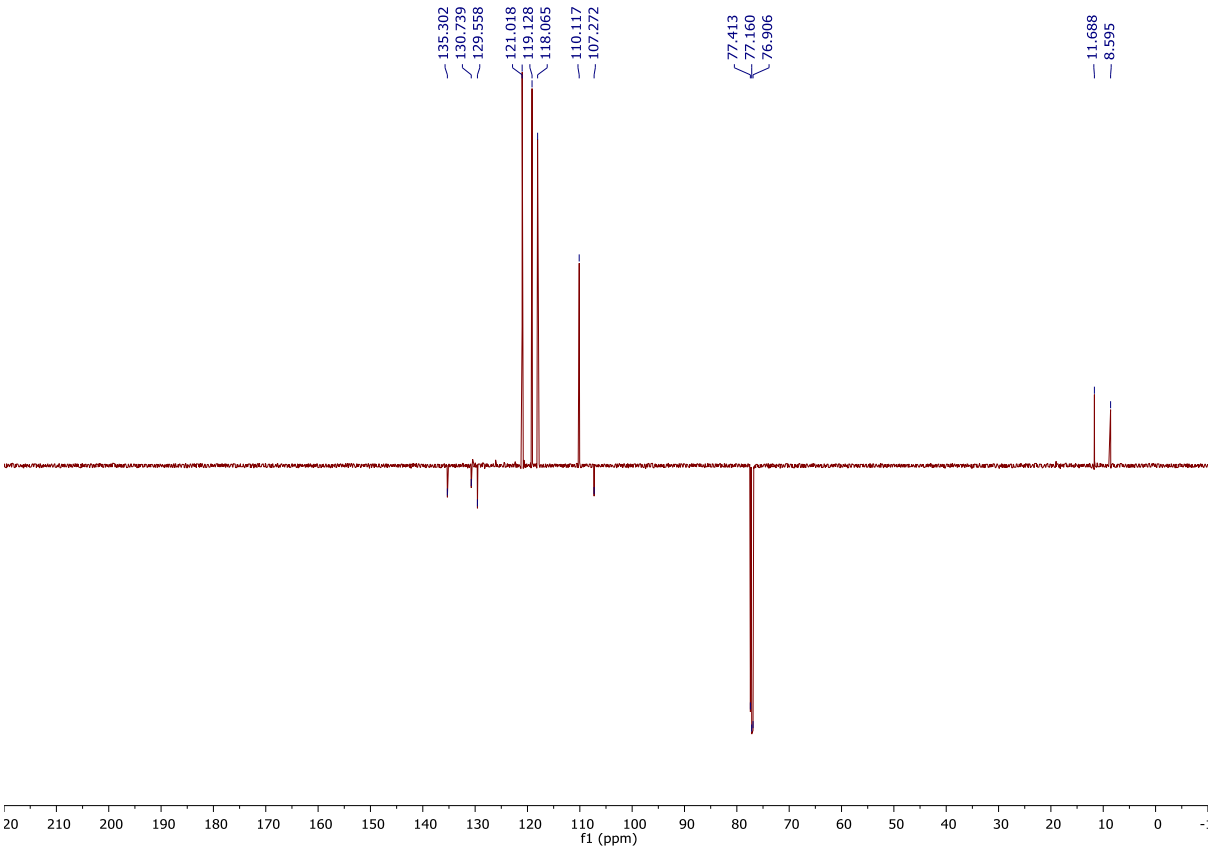
2,3-Dimethyl-1H-indole 2l



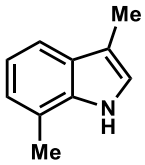
The title compound was prepared according to general procedure 7 using 2-methyl-1H-indole **1l** (65.6 mg, 0.50 mmol). Purification by flash silica chromatography (eluent = 0.5% EtOAc in hexanes, 25 × 180

mm silica) gave the title compound **2l** as an off-white solid (70.4 mg, 0.49 mmol, 97%); mp 98–100 °C (Lit. 104–106 °C);[22] R_f = 0.23 (eluent = 5% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 2.18–2.27 (3H, m), 2.37 (3H, s), 7.02–7.16 (2H, m), 7.23–7.28 (1H, m), 7.43–7.51 (1H, m), 7.65 (1H, br s).; ^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 8.6, 11.7, 107.3, 110.1, 118.1, 119.1, 121.0, 129.6, 130.7, 135.3. Spectroscopic data in accordance with that stated in the literature.[22]

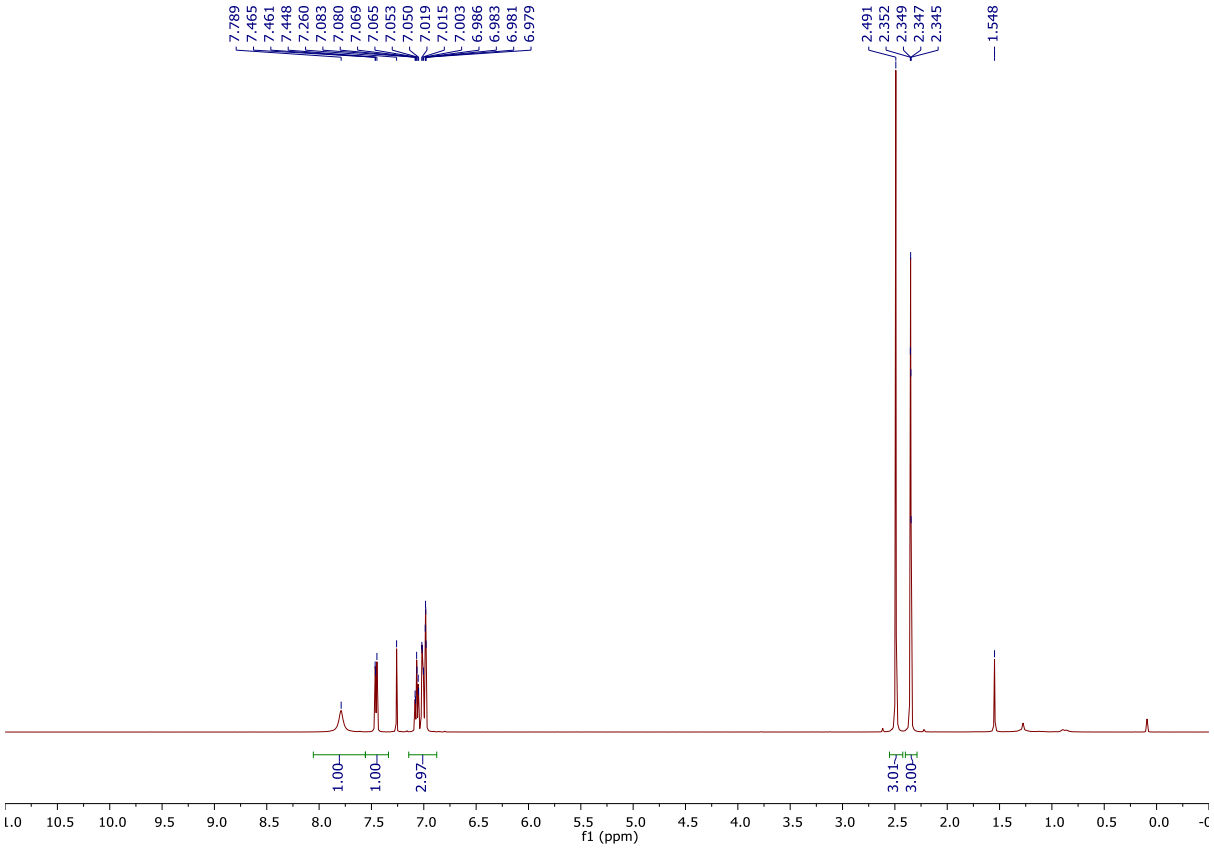




3,7-Dimethyl-1H-indole 2m



The title compound was prepared according to general procedure 7 using 7-methyl-1H-indole **1m** (65.6 mg, 0.50 mmol). Purification by flash silica chromatography (eluent = 0.3% EtOAc in cyclohexane, 25 × 180 mm silica) gave the title compound **2m** as an off-white solid (61.4 mg, 0.42 mmol, 85%); mp 61–63 °C (Lit. 57.3–59.1 °C);[23] R_f = 0.24 (eluent = 5% EtOAc in cyclohexane); ν_{max} / cm^{-1} (film) 3387, 2916, 1894, 1825, 1757, 1614, 1452, 1429, 1354, 1333, 1225, 1169, 1086, 1063, 1036, 1011, 974, 932, 856, 804, 777, 747, 583, 525, 517, 482; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 2.29–2.40 (3H, m), 2.49 (3H, s), 6.88–7.14 (3H, m), 7.34–7.56 (1H, m), 7.79 (1H, br s); ^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 10.0, 16.7, 112.4, 116.7, 119.5, 120.2, 121.4, 122.5, 128.0, 136.0; HRMS (EI)$^+$ calculated for $[C_{10}H_{11}N]^+$ $(M)^+$ m/z: 145.0891, found 145.0886 (-3.4 ppm).


7.789
7.465
7.461
7.448
7.260
7.083
7.080
7.069
7.065
7.053
7.050
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7.015
7.003
6.986
6.983
6.981
6.979
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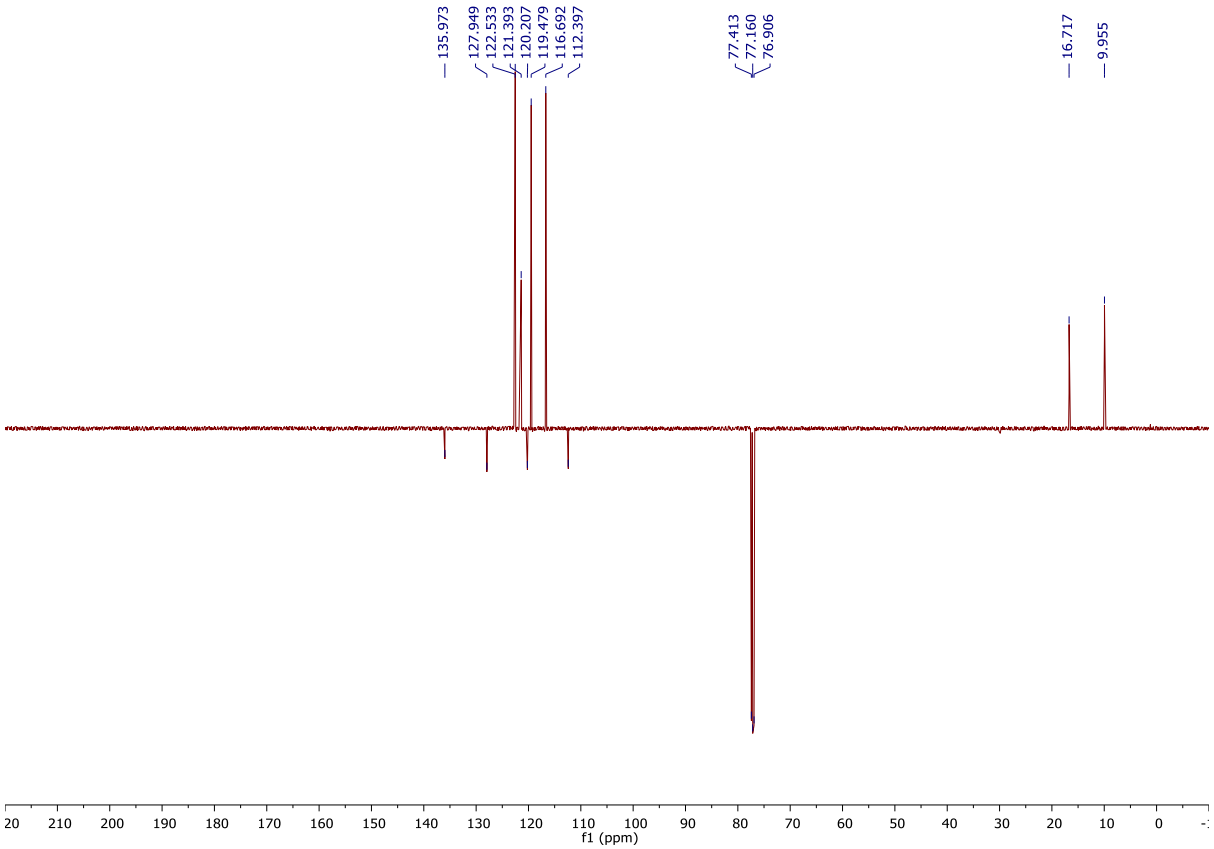
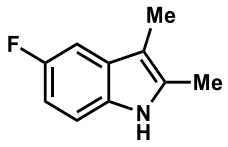
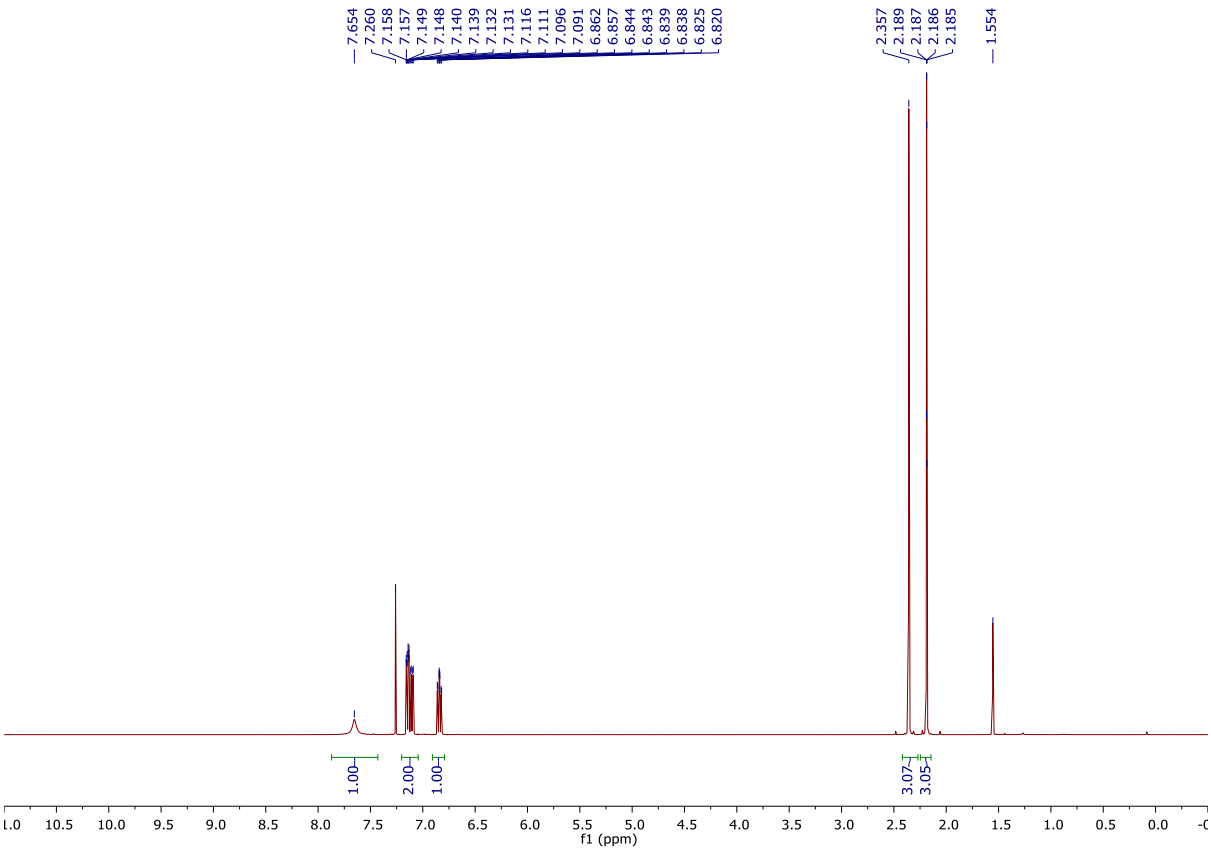
1.00
1.00
2.97
3.01
3.00
f1 (ppm)

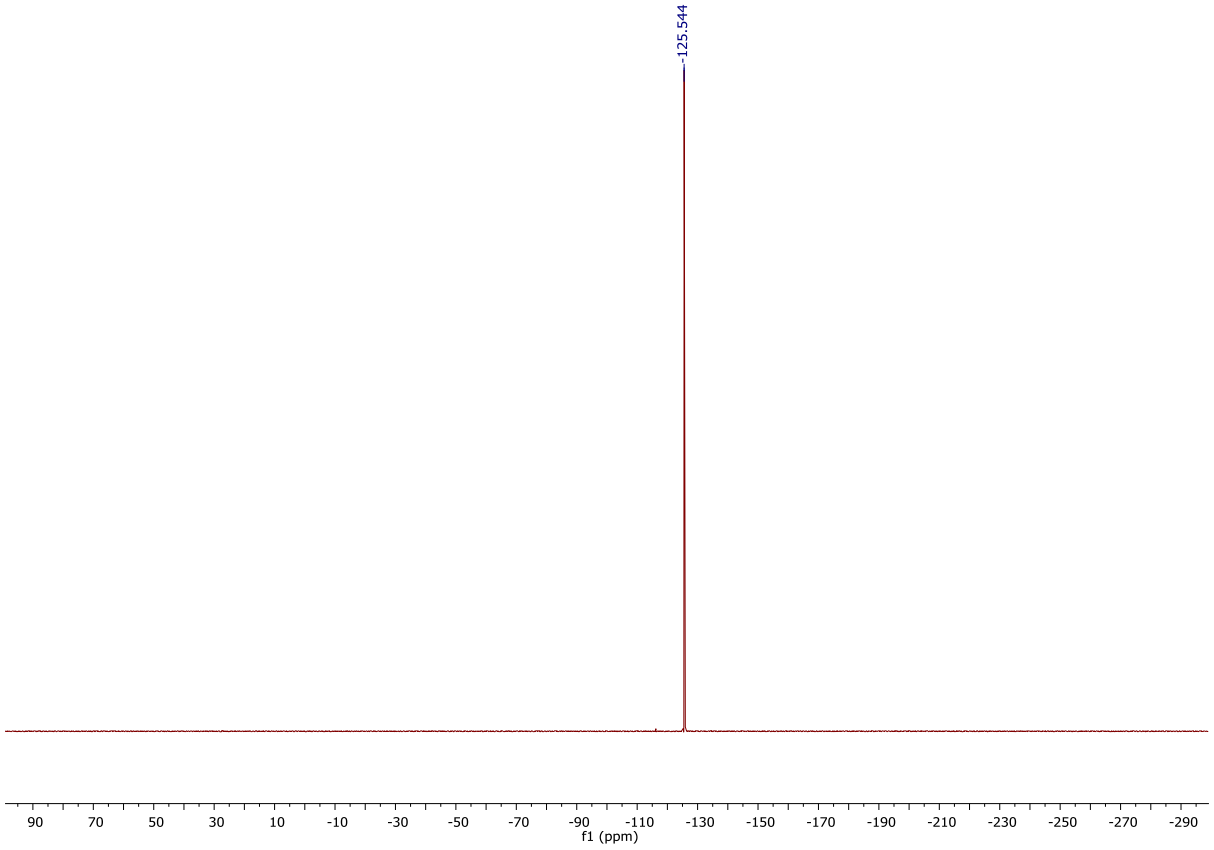

135.973
127.949
122.533
121.393
120.207
119.479
116.692
112.397
77.413
77.160
76.906
16.717
9.955
f1 (ppm)

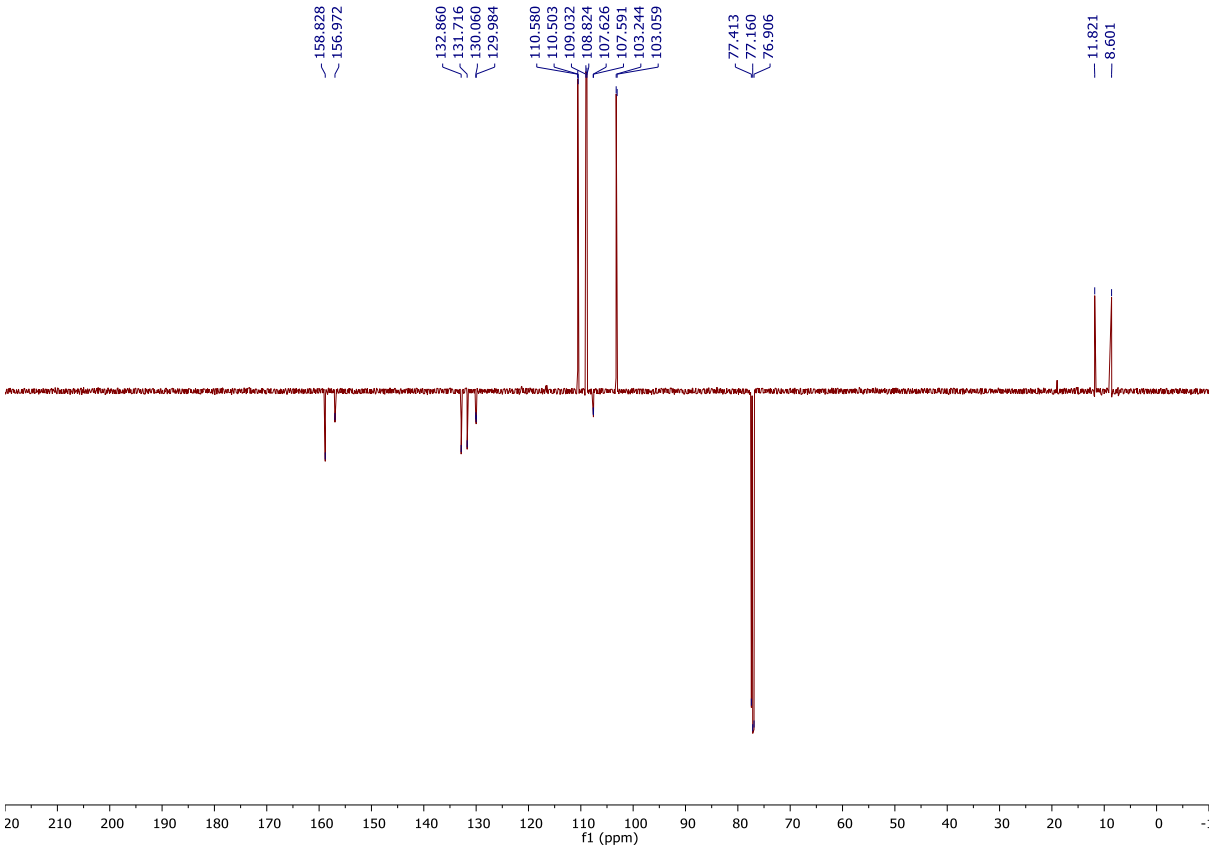
5-Fluoro-2,3-dimethyl-1H-indole 2o



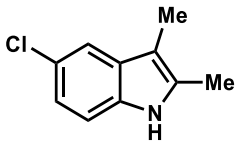
The title compound was prepared according to general procedure 7 using 5-fluoro-2-methyl-1H-indole **1o** (74.6 mg, 0.50 mmol). Purification by flash silica chromatography (eluent = 0.5% EtOAc in hexanes, 25 × 180 mm silica) gave the title compound **2o** as an off-white solid (71.4 mg, 0.44 mmol, 88%); mp 108–110 °C (Lit. 98–99 °C);[24] R_f = 0.16 (eluent = 5% EtOAc in hexanes); ν_{max} / cm^{-1} (film) 3401, 3370, 2916, 2864, 1587, 1578, 1485, 1458, 1437, 1391, 1354, 1310, 1290, 1234, 1179, 1169, 1128, 1111, 1049, 1017, 943, 839, 791, 739, 702, 633, 598, 561, 505, 475, 432; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 2.15–2.25 (3H, m), 2.36 (3H, s), 6.84 (1H, ddd, *J* 9.4, 8.7, 2.5), 7.04–7.20 (2H, m), 7.65 (1H, br s); ^{19}F NMR (376 MHz, $CDCl_3$) δ_F: -125.5; ^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 8.6, 11.8, 103.2 (d, *J* 23.3), 107.6 (d, *J* 4.4), 108.9 (d, *J* 26.2), 110.5 (d *J* 9.7), 130.0 (d, *J* 9.6), 131.7, 132.9, 157.9 (d, *J* 233.9); HRMS (ASAP)$^+$ calculated for $[C_{10}H_{11}NF]^+$ (M+H)$^+$ m/z: 164.0876, found 164.0870 (-3.7 ppm).



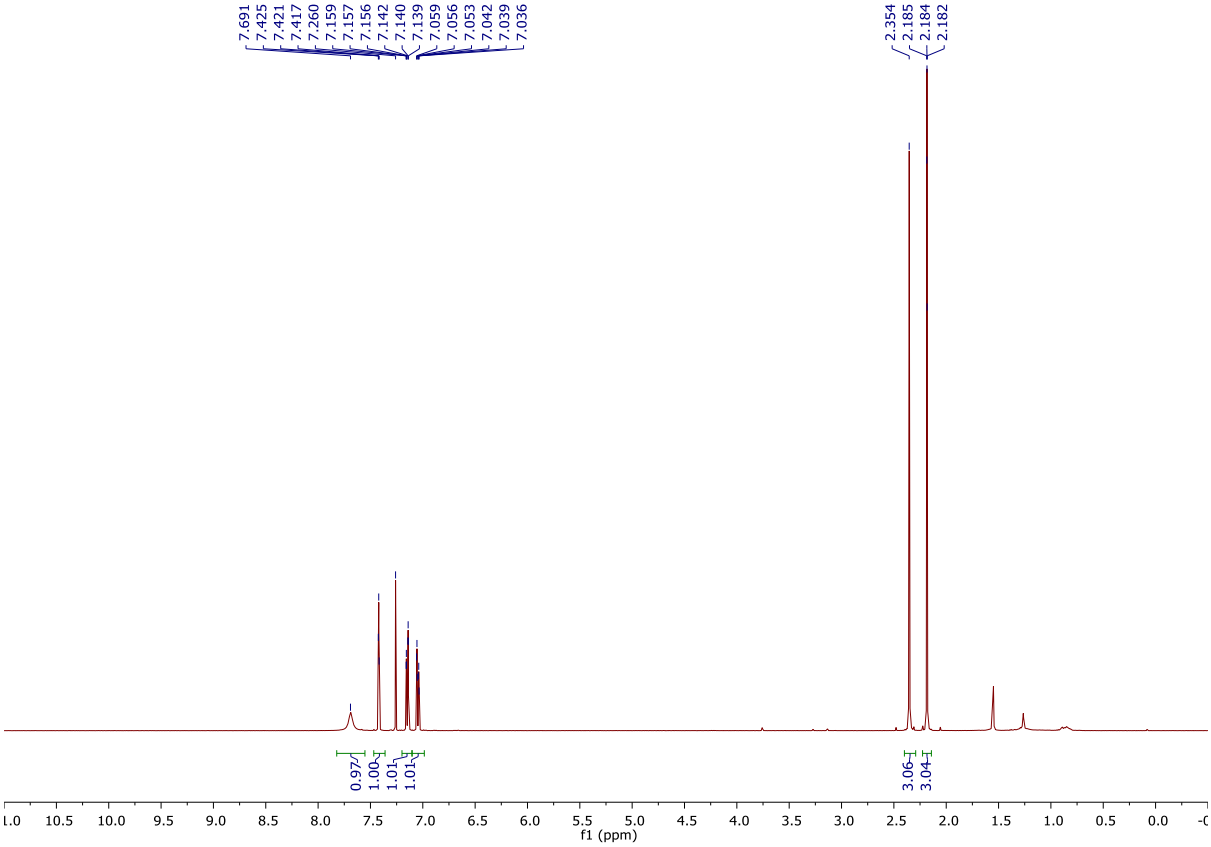

-125.544
90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230 -250 -270 -290
f1 (ppm)

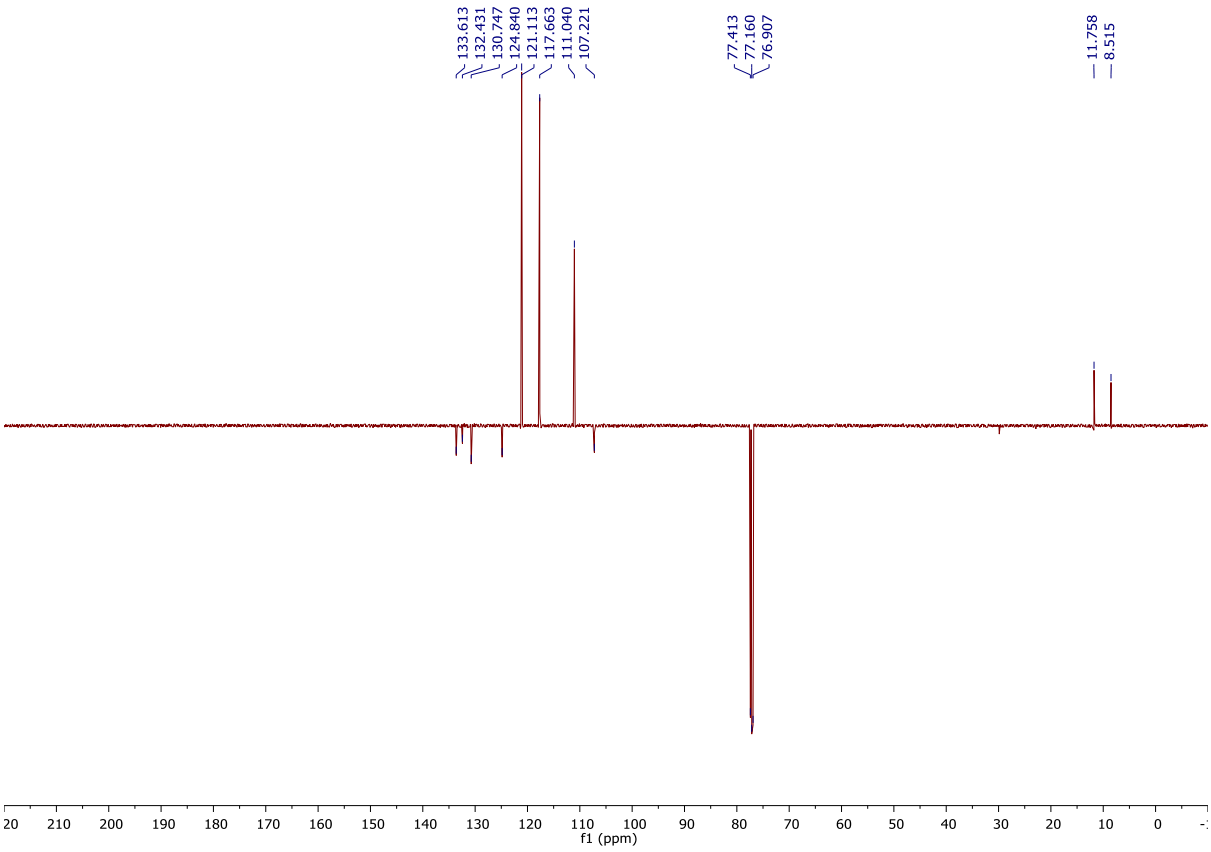

158.828
156.972
132.860
131.716
130.060
129.984
110.580
110.503
109.032
108.824
107.626
107.591
103.244
103.059
77.413
77.160
76.906
11.821
8.601
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

5-Chloro-2,3-dimethyl-1H-indole 2p

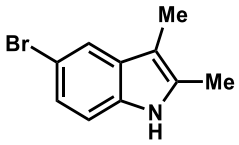


The title compound was prepared according to general procedure 7 using 5-chloro-2-methyl-1H-indole **1p** (82.8 mg, 0.50 mmol). Purification by flash silica chromatography (eluent = 0.75% EtOAc in cyclohexane, 25 × 180 mm silica) gave the title compound **2p** as a white solid (88.3 mg, 0.49 mmol, 98%); mp 146–148 °C (Lit. 144 °C);[25] R_f = 0.21 (eluent = 5% EtOAc in cyclohexane); ν_{max} / cm^{-1} (film) 3397, 2918, 2853, 1846, 1721, 1576, 1470, 1431, 1387, 1302, 1277, 1238, 1074, 1049, 1003, 963, 905, 864, 801, 758, 745, 677, 638, 594, 540, 496, 426; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 2.14–2.23 (3H, m), 2.35 (3H, s), 7.05 (1H, dt, *J* 8.5, 1.6), 7.10–7.20 (1H, m), 7.42 (1H, t, *J* 1.8), 7.69 (1H, br s); ^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 8.5, 11.8, 107.2, 111.0, 117.7, 121.1, 124.8, 130.8, 132.4, 133.6; HRMS (EI)$^+$ calculated for $[C_{10}H_{10}NCl]^+$ $(M)^+$ m/z: 179.0502, found 179.0497 (-2.8 ppm).

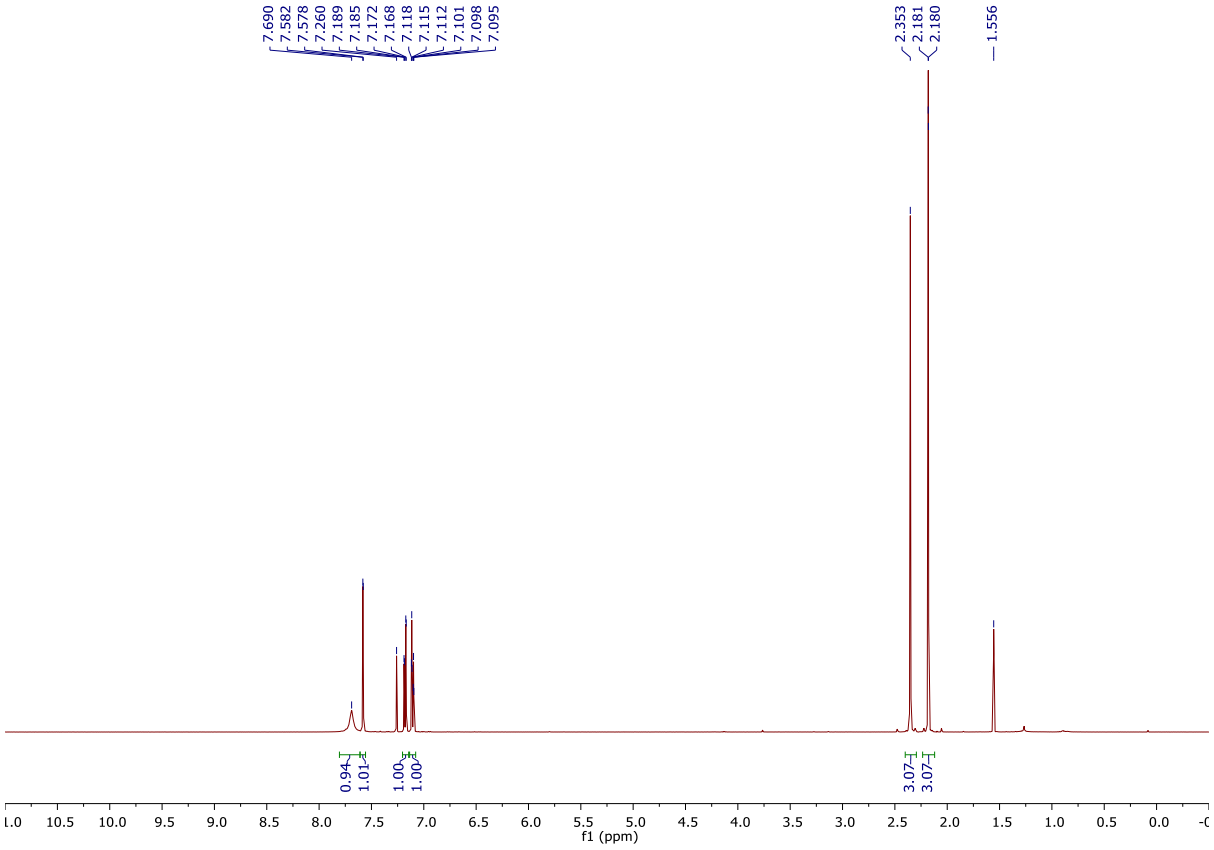


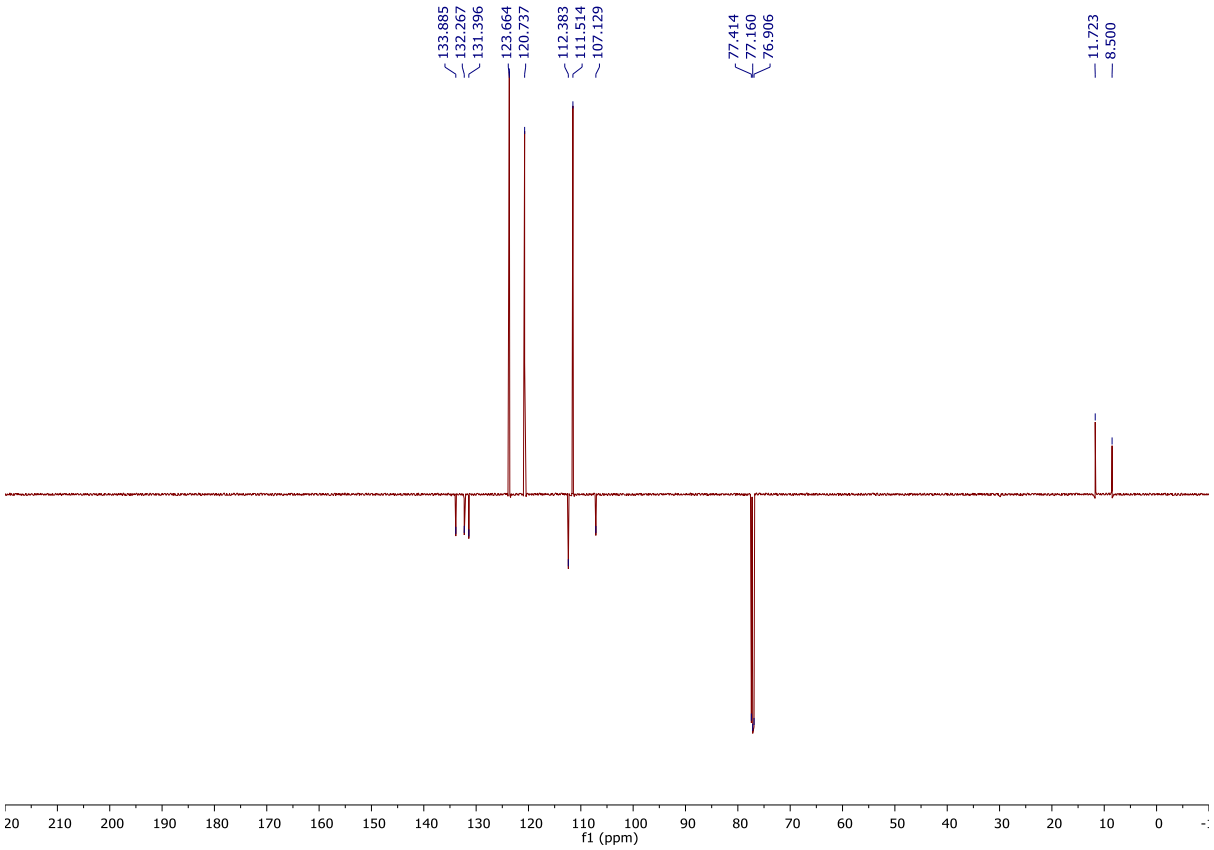


5-Bromo-2,3-dimethyl-1H-indole 2q

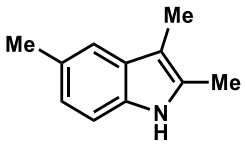


The title compound was prepared according to general procedure 7 using 5-bromo-2-methyl-1H-indole **1q** (105 mg, 0.50 mmol). Purification by flash silica chromatography (eluent = 1% EtOAc in cyclohexane, 25 × 180 mm silica) gave the title compound **2q** as a white solid (106 mg, 0.47 mmol, 94%); mp 146–147 °C (Lit. 138 °C);[25] R_f = 0.19 (eluent = 5% EtOAc in cyclohexane); ν_{max} / cm^{-1} (film) 3404, 1570, 1466, 1427, 1304, 1240, 1045, 1003, 961, 901, 860, 799, 741, 669, 638, 584, 494; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 2.12–2.24 (3H, m), 2.35 (3H, s), 7.06–7.15 (1H, m), 7.18 (1H, dd, *J* 8.5, 1.9), 7.58 (1H, d, *J* 1.9), 7.69 (1H, br s); ^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 8.5, 11.7, 107.1, 111.5, 112.4, 120.7, 123.7, 131.4, 132.3, 133.9; HRMS (ES)$^+$ calculated for $[C_{10}H_9NBr]^+$ $(M-H)^+$ m/z: 221.9918, found 221.9929 (+5.0 ppm).

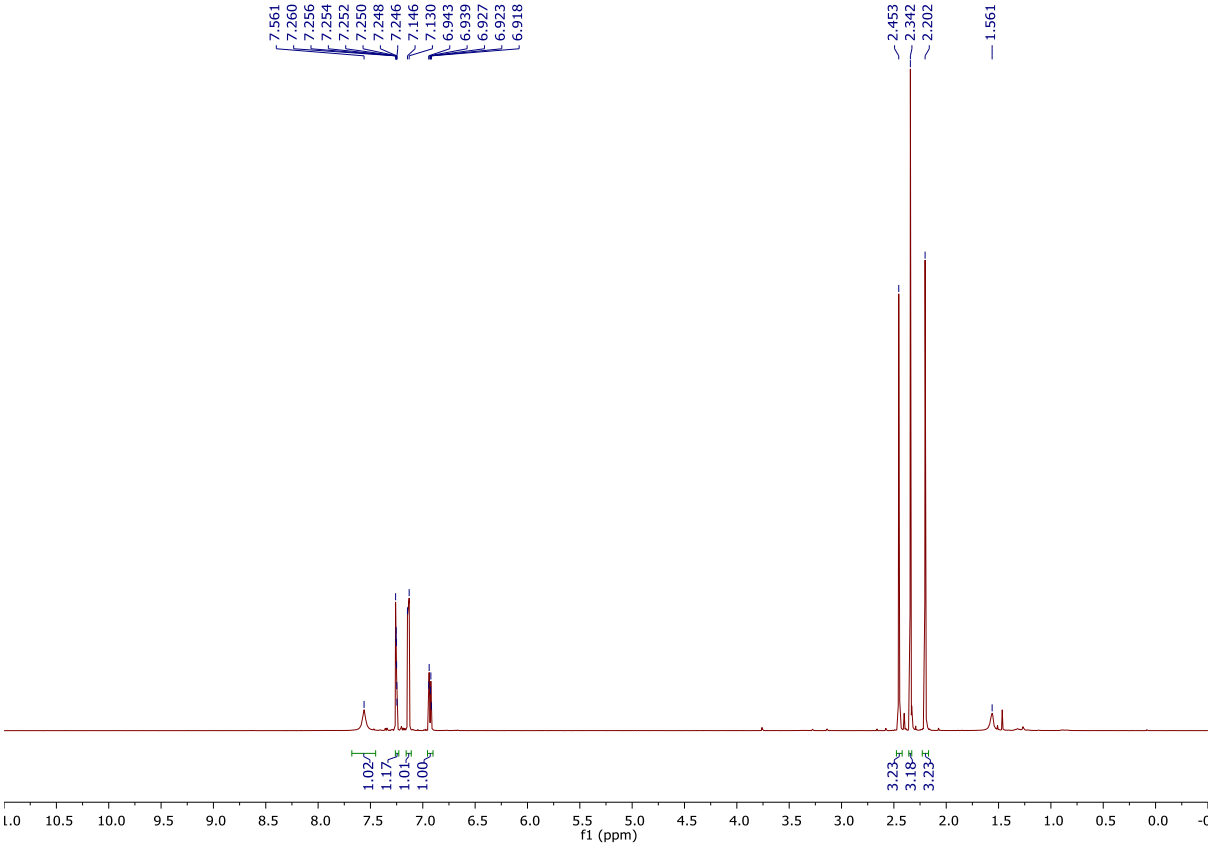

7.690
7.582
7.578
7.260
7.189
7.185
7.172
7.168
7.118
7.115
7.112
7.101
7.098
7.095
2.353
2.181
2.180
1.556
0.94
1.01
1.00
1.00
3.07
3.07
f1 (ppm)

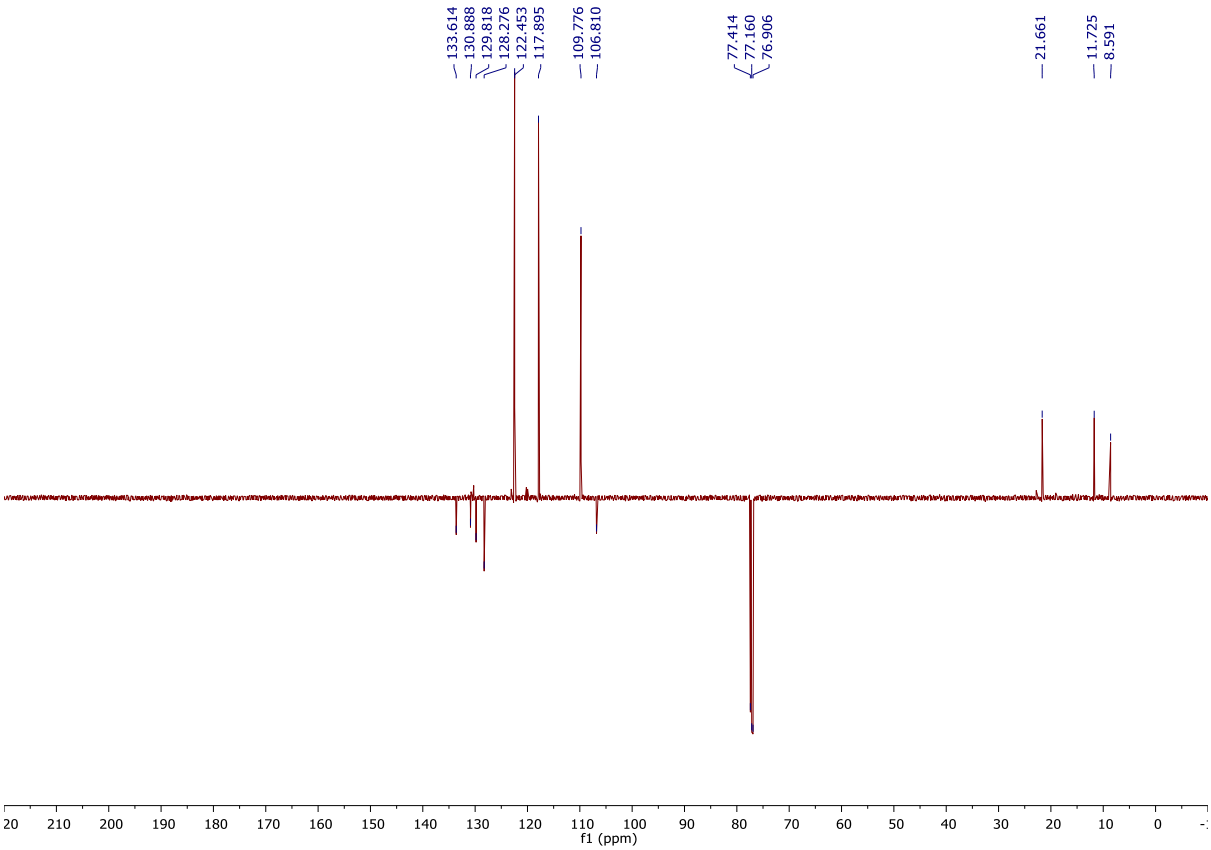

133.885
132.267
131.396
123.664
120.737
112.383
111.514
107.129
77.414
77.160
76.906
11.723
8.500
f1 (ppm)

2,3,5-Trimethyl-1H-indole 2r

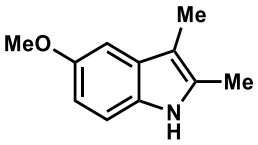


The title compound was prepared according to general procedure 7 using 2,5-dimethyl-1H-indole **1r** (72.6 mg, 0.50 mmol). Purification by flash silica chromatography (eluent = 0.4% EtOAc in hexanes, 25 × 180 mm silica) gave the title compound **2r** as an off-white solid (71.4 mg, 0.45 mmol, 90%); mp 120–123 °C (Lit. 118–120 °C);[26] R_f = 0.36 (eluent = 5% EtOAc in hexanes); ν_{max} / cm^{-1} (film) 3389, 2911, 2857, 1593, 1481, 1456, 1433, 1302, 1242, 1198, 1126, 1038, 934, 872, 789, 638, 590; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 2.20 (3H, s), 2.34 (3H, s), 2.45 (3H, s), 6.93 (1H, dd, *J* 8.1, 1.8), 7.14 (1H, d, *J* 8.1), 7.23–7.26 (1H, m), 7.56 (1H, br s); ^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 8.6, 11.7, 21.7, 106.8, 109.8, 117.9, 122.5, 128.3, 129.8, 130.9, 133.6; HRMS $(AP)^+$ calculated for $[C_{11}H_{14}N]^+$ $(M+H)^+$ m/z: 160.1126, found 160.1122 (-2.5 ppm).

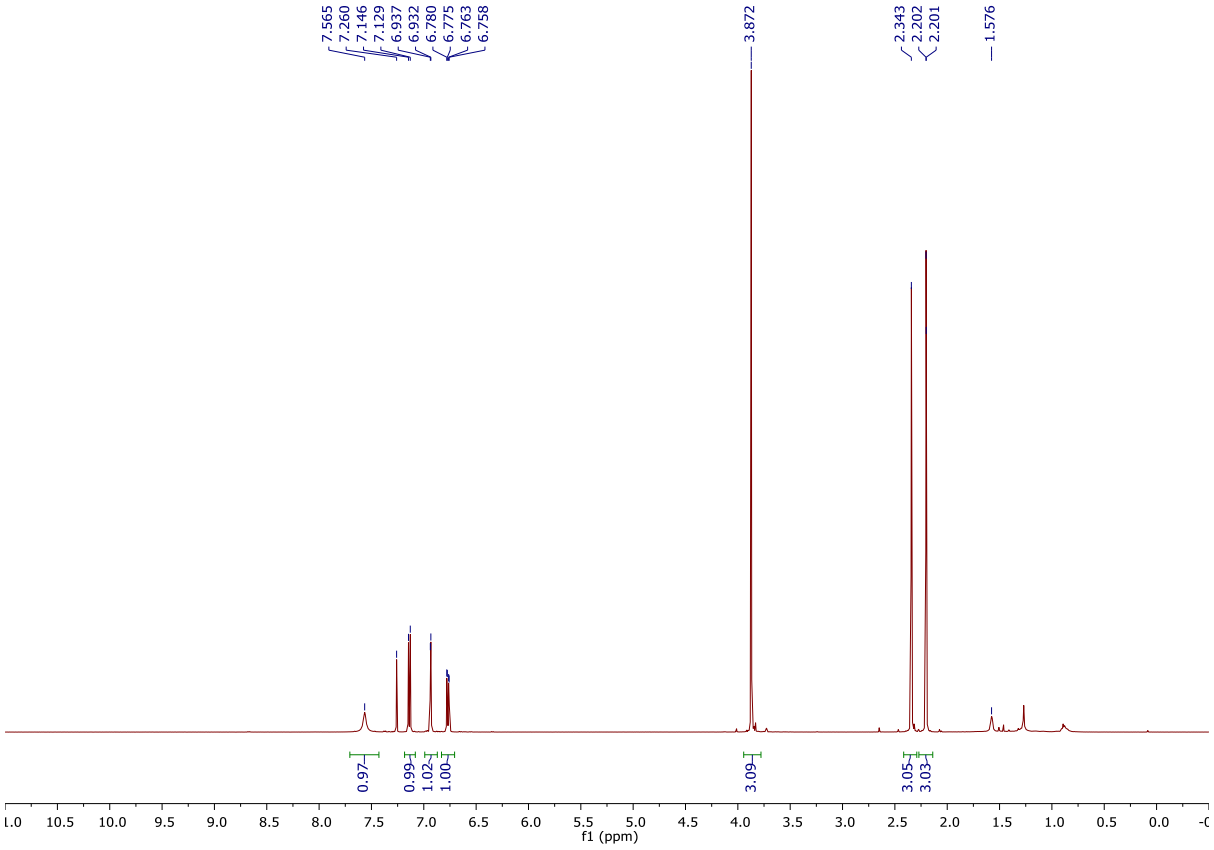


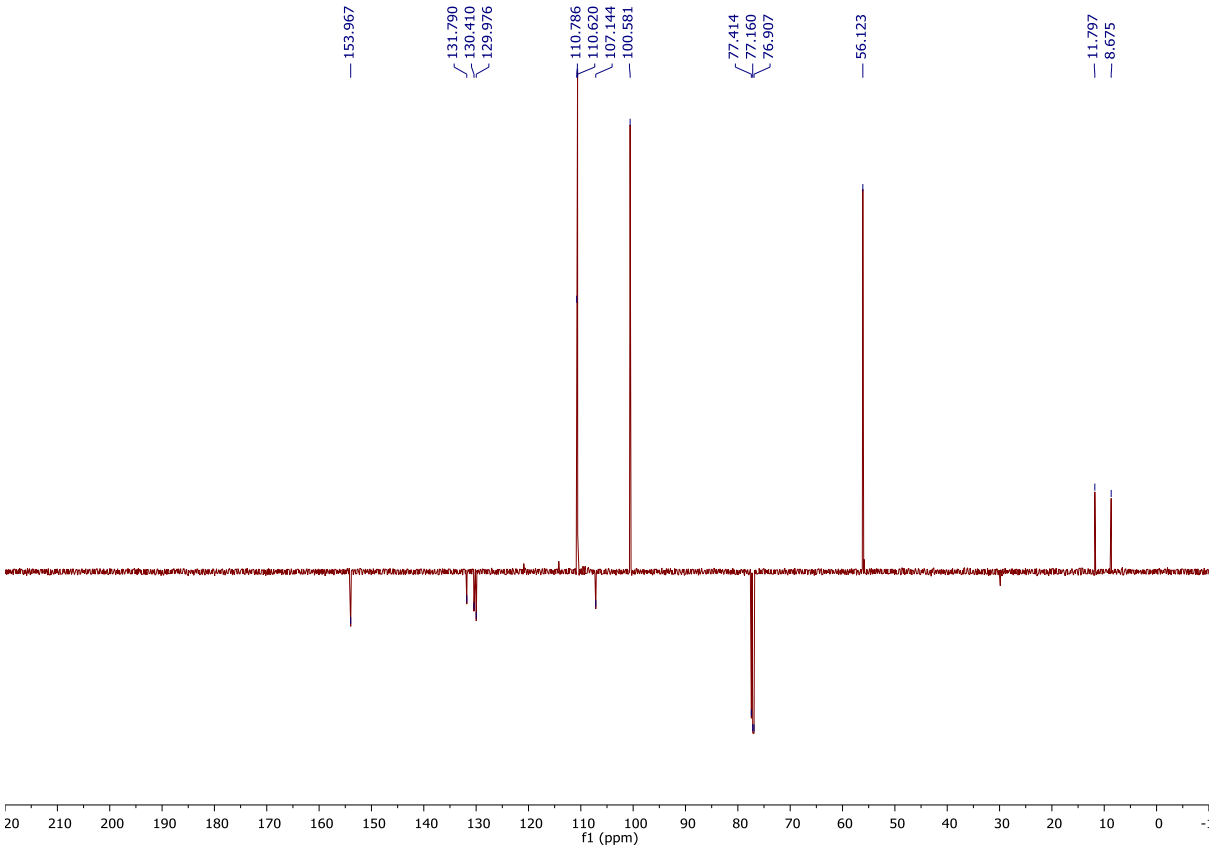


5-Methoxy-2,3-dimethyl-1H-indole 2s

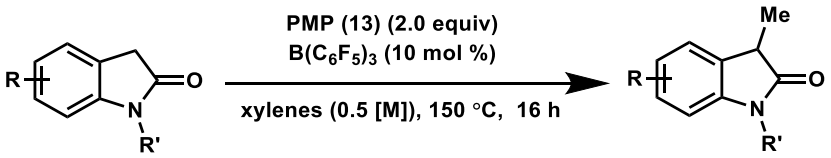


The title compound was prepared according to general procedure 7 using 5-methoxy-2-methyl-1H-indole **2s** (80.6 mg, 0.50 mmol). Purification by flash silica chromatography (eluent = 0.5–1% EtOAc in hexanes, 25 × 180 mm silica) gave the title compound **2s** as a white solid (77.6 mg, 0.44 mmol, 89%); mp 111–113 °C (Lit. 109–112 °C);[26] R_f = 0.15 (eluent = 5% EtOAc in hexanes); ν_{max} / cm^{-1} (film) 3374, 2914, 1589, 1479, 1451, 1425, 1292, 1240, 1215, 1177, 1134, 1115, 1055, 1026, 930, 847, 829, 700, 631, 611, 557, 509, 430, 419; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 2.14–2.27 (3H, m), 2.34 (3H, s), 3.87 (3H, s), 6.77 (1H, dd, *J* 8.7, 2.4), 6.93 (1H, d, *J* 2.4), 7.14 (1H, d, *J* 8.6), 7.56 (1H, br s); ^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 8.7, 11.8, 56.1, 100.6, 107.1, 110.6, 110.8, 130.0, 130.4, 131.8, 154.0; HRMS $(AP)^+$ calculated for $[C_{11}H_{14}NO]^+$ $(M+H)^+$ m/z: 176.1075, found 176.1080 (+2.8 ppm).


7.565
7.260
7.146
7.129
6.937
6.932
6.780
6.775
6.763
6.758
3.872
2.343
2.202
2.201
1.576
0.97
0.99
1.02
1.00
3.09
3.05
3.03
f1 (ppm)

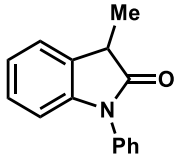

153.967
131.790
130.410
129.976
110.786
110.620
107.144
100.581
77.414
77.160
76.907
56.123
11.797
8.675
f1 (ppm)

General procedure 8: C3 methylation of oxindole derivatives

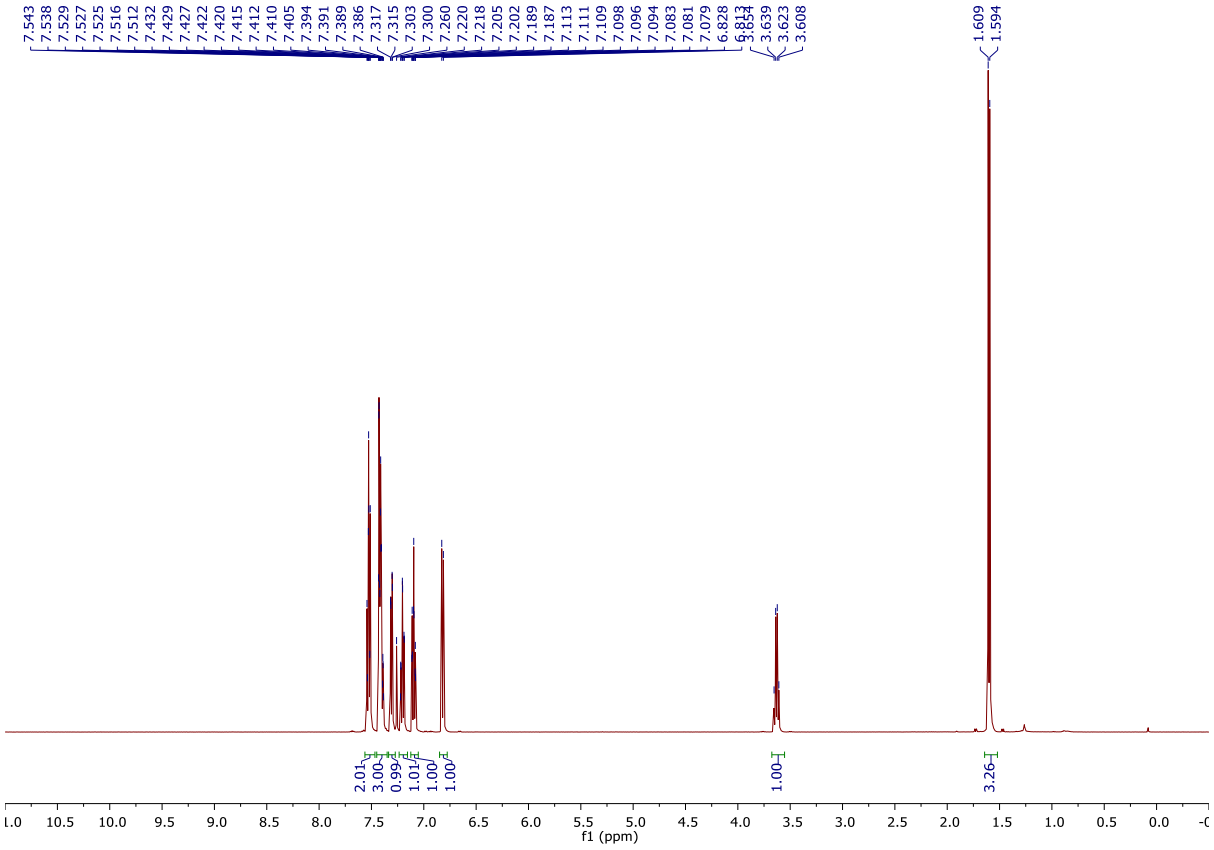


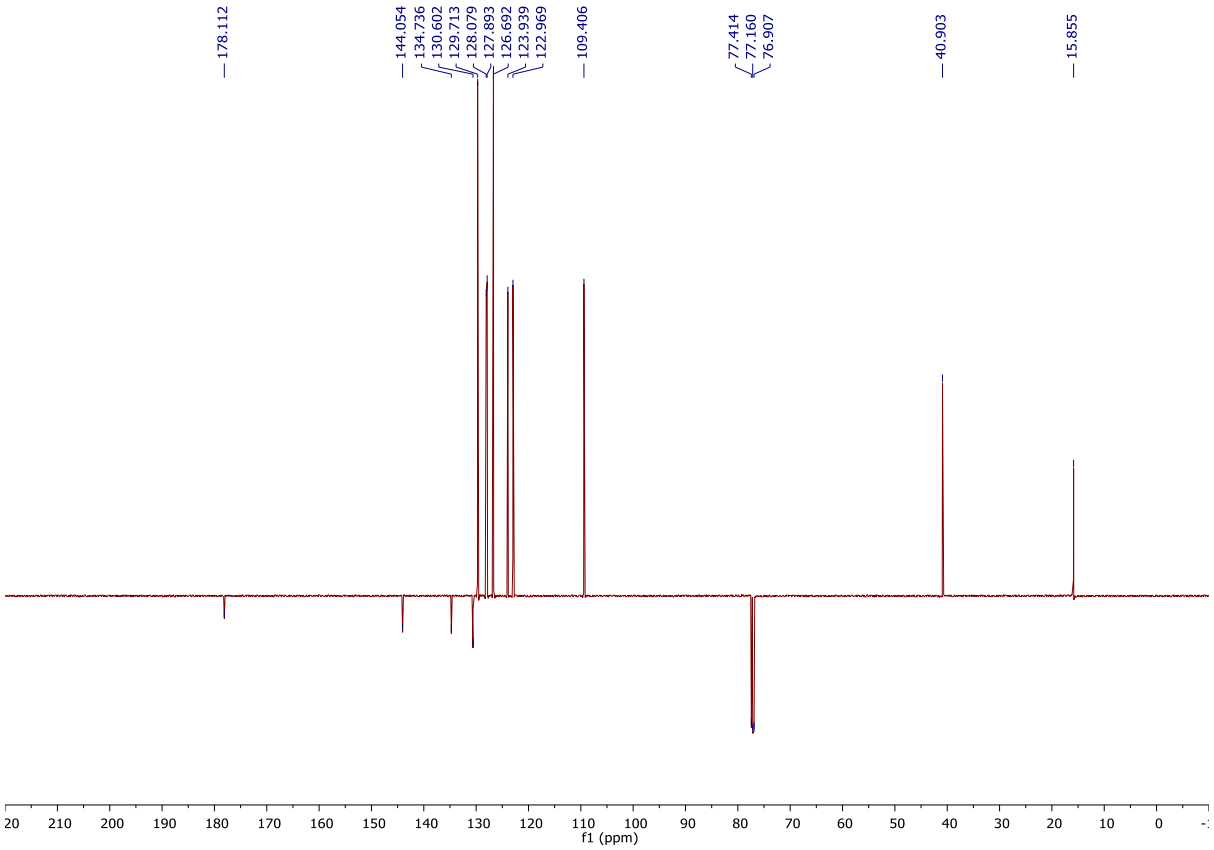
In a nitrogen-filled glove box, a 10 mL vial equipped with a magnetic stirrer bar was charged with the oxindole derivative (0.5 mmol), 1,2,2,6,6-pentamethylpiperidine (**13**, PMP) (181 µL, 1.0 mmol), $B(C_6F_5)_3$ (25.6 mg, 0.05 mmol) and xylenes (1.0 mL). The vial was sealed with an aluminium crimped cap and was left to stir at 150 °C for 16 h. The reaction mixture was then directly purified by silica gel chromatography.

3-Methyl-1-phenylindolin-2-one 9a

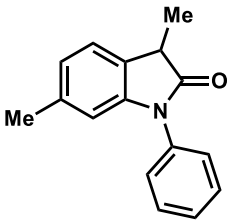


The title compound was prepared according to general procedure 8 using 1-phenylindolin-2-one **8a** (105 mg, 0.50 mmol). Purification by flash silica chromatography (eluent = 5% EtOAc in hexanes, 20 × 180 mm silica) gave the title compound **9a** as a colorless gummy oil (101 mg, 0.45 mmol, 90%); R_f = 0.25 (eluent = 10% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 1.60 (3H, d, *J* 7.6), 3.63 (1H, q, *J* 7.6), 6.82 (1H, d, *J* 7.8), 7.02–7.13 (1H, m), 7.20 (1H, td, *J* 7.7, 1.2), 7.31 (1H, dd, *J* 7.4, 1.2), 7.34–7.46 (3H, m), 7.46–7.58 (2H, m); ^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 15.9, 40.9, 109.4, 123.0, 123.9, 126.7, 127.9, 128.1, 129.7, 130.6, 134.7, 144.1, 178.1. Spectroscopic data in accordance with that stated in the literature.[27]

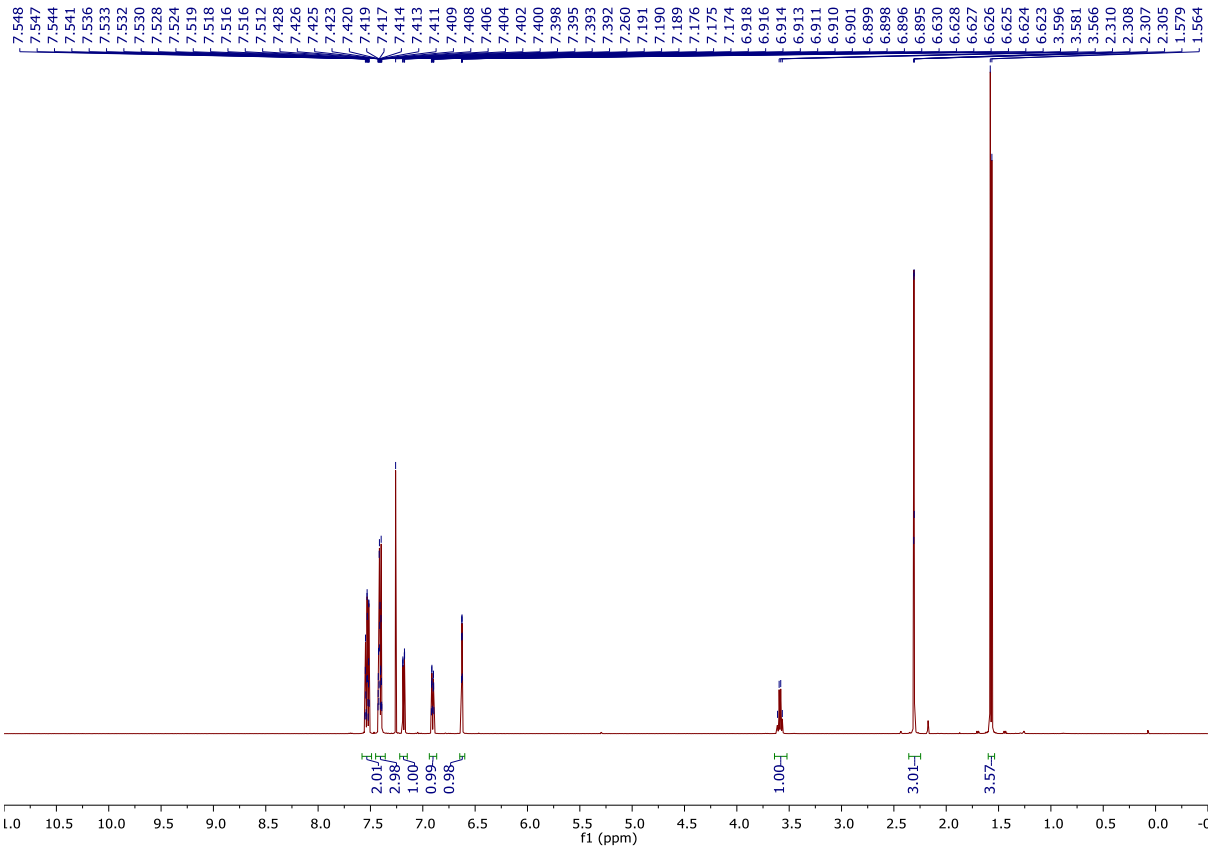

7.543
7.538
7.529
7.527
7.525
7.516
7.512
7.432
7.429
7.427
7.422
7.420
7.415
7.412
7.410
7.405
7.394
7.391
7.389
7.386
7.317
7.315
7.303
7.300
7.260
7.220
7.218
7.205
7.202
7.189
7.187
7.113
7.111
7.109
7.098
7.096
7.094
7.083
7.081
7.079
6.828
3.639
3.623
3.608
1.609
1.594
2.01
3.00
0.99
1.01
1.00
1.00
1.00
3.26
f1 (ppm)

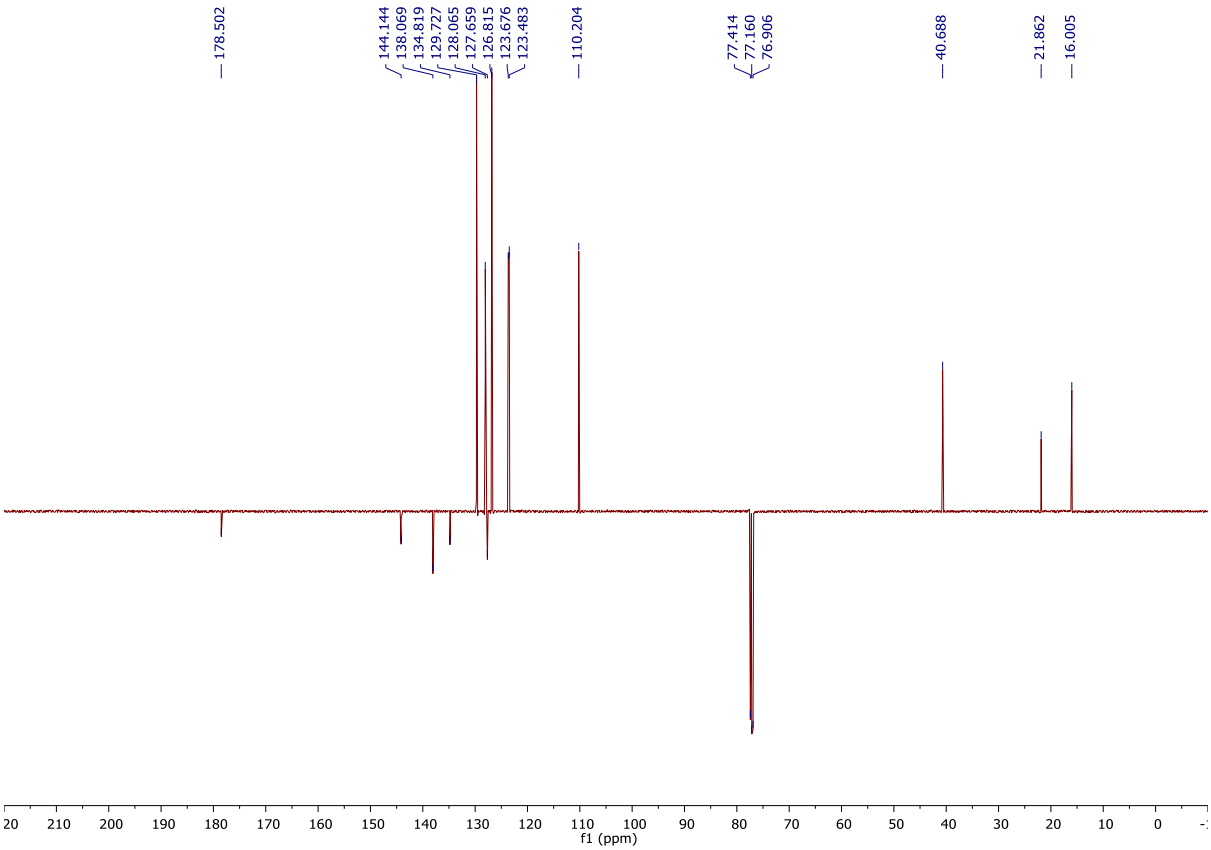

178.112
144.054
134.736
130.602
129.713
128.079
127.893
126.692
123.939
122.969
109.406
77.414
77.160
76.907
40.903
15.855
f1 (ppm)

3,6-Dimethyl-1-phenylindolin-2-one 9b

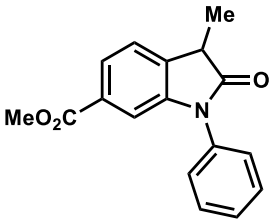


The title compound was prepared according to general procedure 8 using 6-methyl-1-phenylindolin-2-one **8b** (112 mg, 0.50 mmol). Purification by flash silica chromatography (eluent = 5% EtOAc in cyclohexane, 20 × 180 mm silica) gave the title compound **9b** as an off-white solid (70.8 mg, 0.30 mmol, 60%); mp 68–70 °C; R_f = 0.36 (eluent = 10% EtOAc in cyclohexane); ν_{max} / cm^{-1} (film) 3028, 2920, 1719, 1611, 1591, 1505, 1489, 1433, 1377, 1289, 1234, 1194, 1167, 1117, 1009, 889, 856, 804, 764, 729, 692, 646, 598, 554, 503, 463, 446; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 1.57 (3H, d, *J* 7.6), 2.25–2.36 (3H, m), 3.59 (1H, q, *J* 7.6), 6.60–6.65 (1H, m), 6.87–6.94 (1H, m), 7.15–7.22 (1H, m), 7.36–7.45 (3H, m), 7.49–7.58 (2H, m); ^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 16.0, 21.9, 40.7, 110.2, 123.5, 123.7, 126.8, 127.7, 128.1, 129.7, 134.8, 138.1, 144.1, 178.5; HRMS $(AP)^+$ calculated for $[C_{16}H_{16}NO]^+$ $(M+H)^+$ m/z: 238.1232, found 238.1237 (+2.1 ppm).

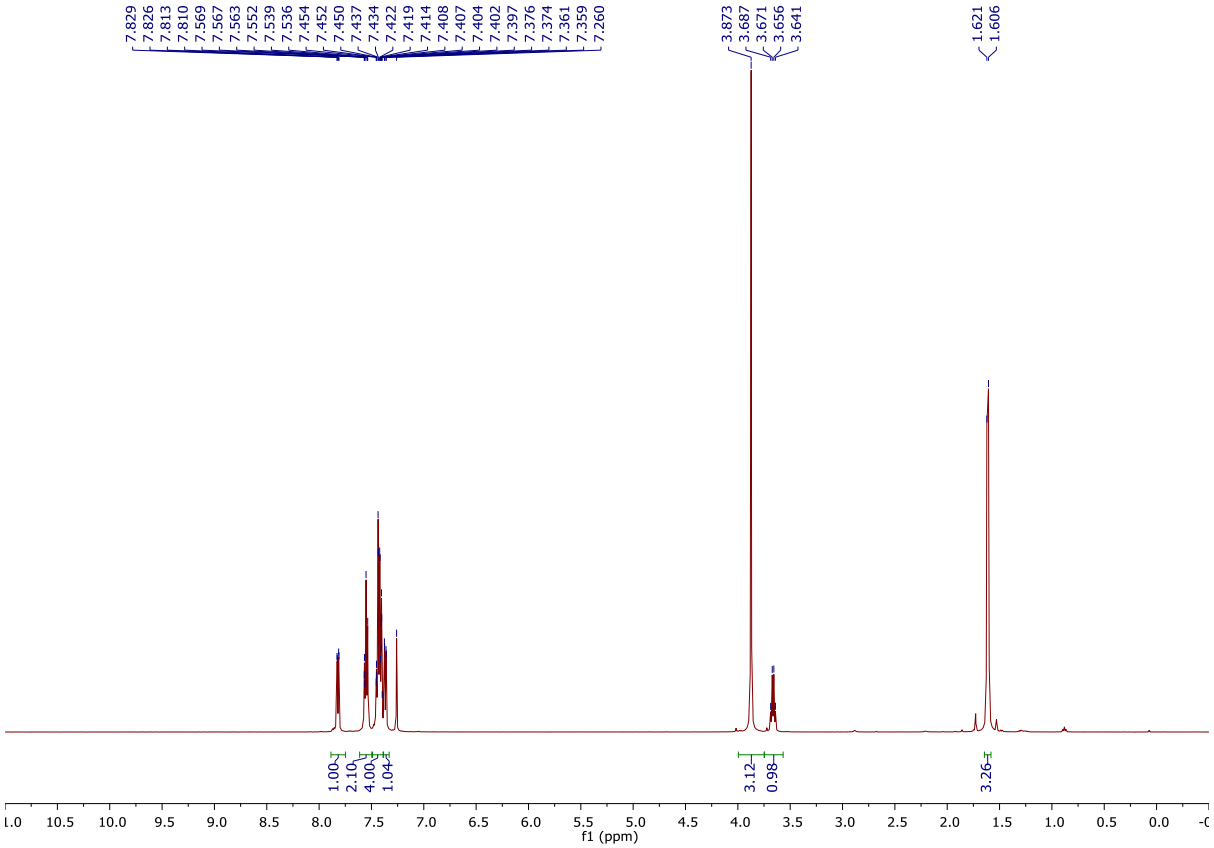




Methyl 3-methyl-2-oxo-1-phenylindoline-6-carboxylate 9c



The title compound was prepared according to general procedure 8 using methyl 2-oxo-1-phenylindoline-6-carboxylate **8c** (134 mg, 0.50 mmol). Purification by flash silica chromatography (eluent = 10% EtOAc in hexanes, 20 × 180 mm silica) gave the title compound **9c** as an off-white solid (114 mg, 0.41 mmol, 81%); mp 145–148 °C; R_f = 0.36 (eluent = 20% EtOAc in hexanes); ν_{max} / cm^{-1} (film) 1711, 1614, 1589, 1501, 1431, 1371, 1331, 1289, 1248, 1190, 1171, 1088, 999, 957, 876, 843, 791, 762, 727, 710, 691, 642, 598, 527, 503, 455; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 1.61 (3H, d, *J* 7.6), 3.66 (1H, q, *J* 7.6), 3.87 (3H, s), 7.33–7.39 (1H, m), 7.38–7.50 (4H, m), 7.55 (2H, *t*, J7.8), 7.82 (1H, dd, *J* 7.7, 1.5); ^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 15.6, 41.0, 52.4, 110.0, 123.8, 124.8, 126.7, 128.4, 130.0, 130.2, 134.3, 135.7, 144.4, 166.8, 177.7; HRMS $(ES)^+$ calculated for $[C_{17}H_{16}NO_3]^+$ $(M+H)^+$ m/z: 282.1130, found 282.1141 (+3.9 ppm).


7.829
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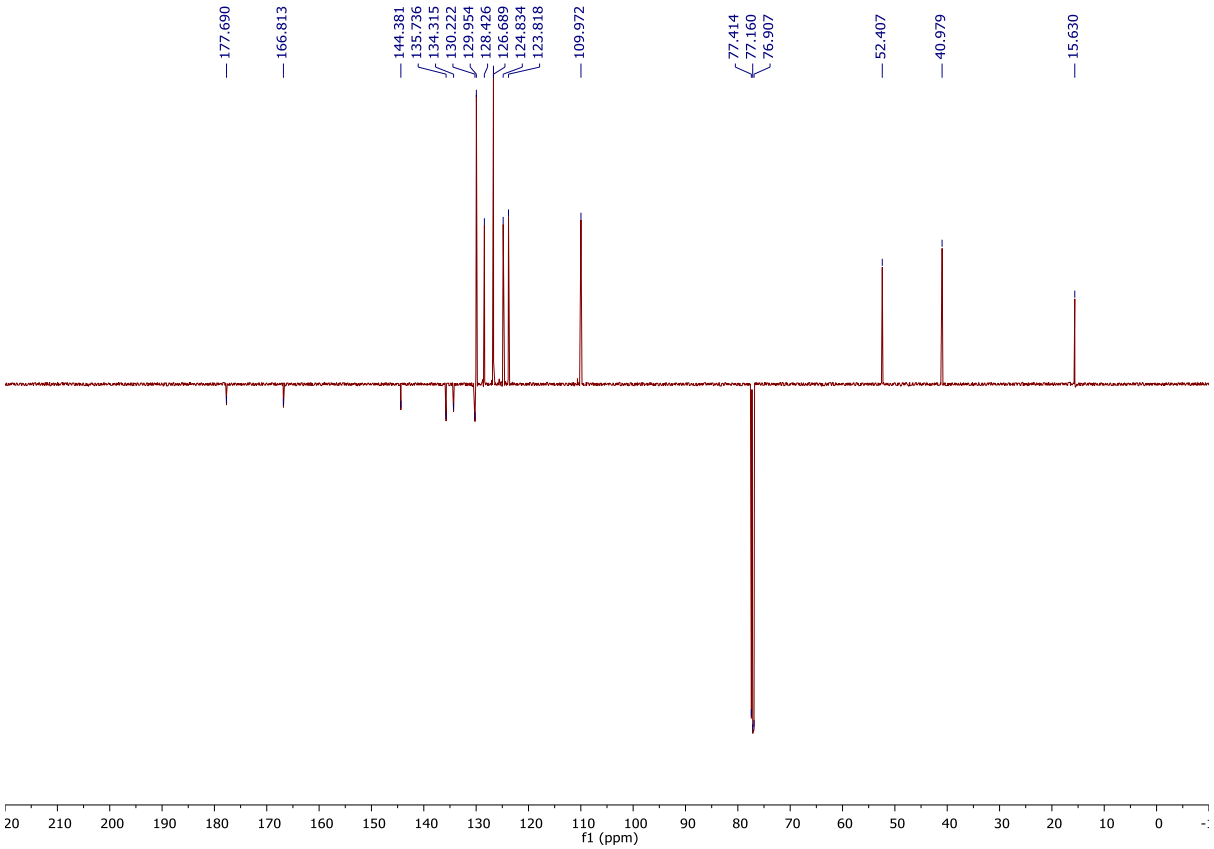
7.810
7.569
7.567
7.563
7.552
7.539
7.536
7.454
7.452
7.450
7.437
7.434
7.422
7.419
7.414
7.408
7.407
7.404
7.402
7.397
7.376
7.374
7.361
7.359
7.260
3.873
3.687
3.671
3.656
3.641
1.621
1.606
1.00
2.10
4.00
1.04
3.12
0.98
3.26
f1 (ppm)


177.690
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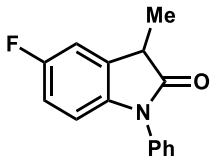
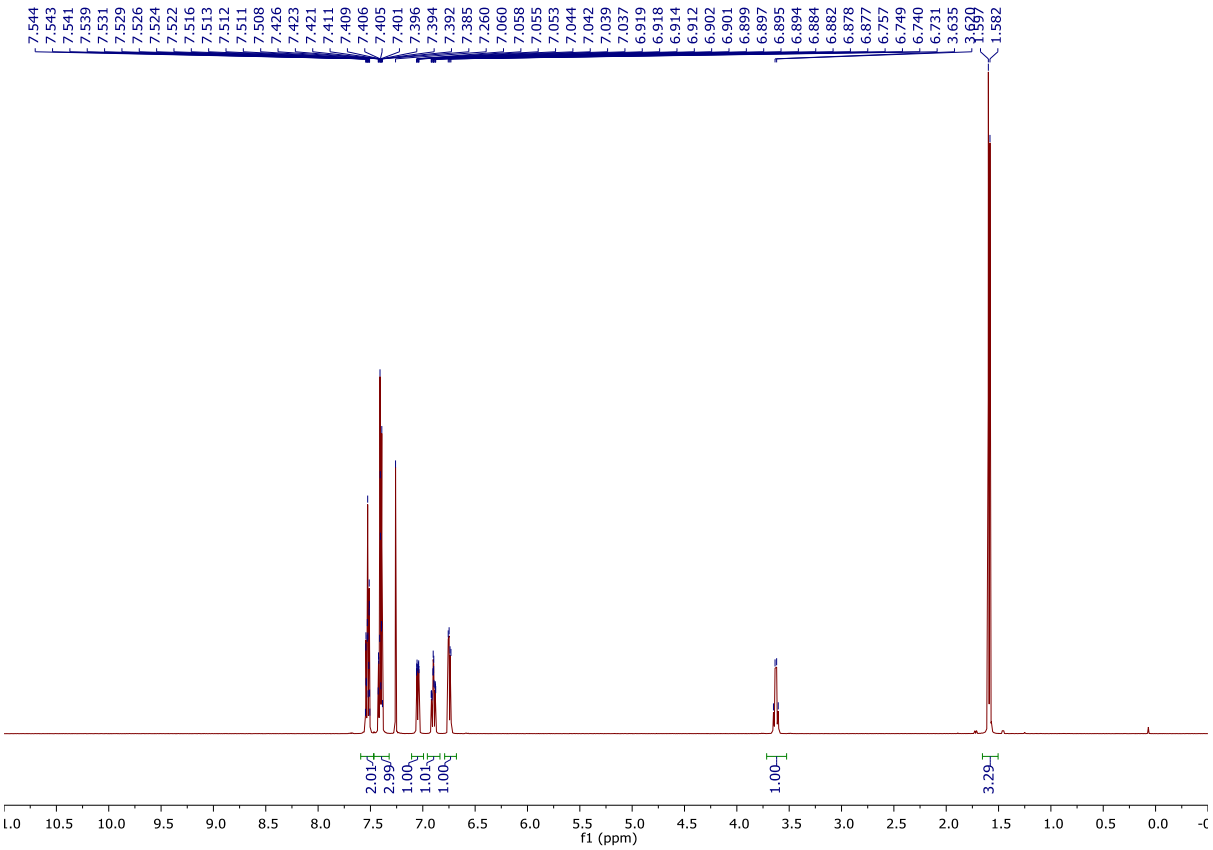
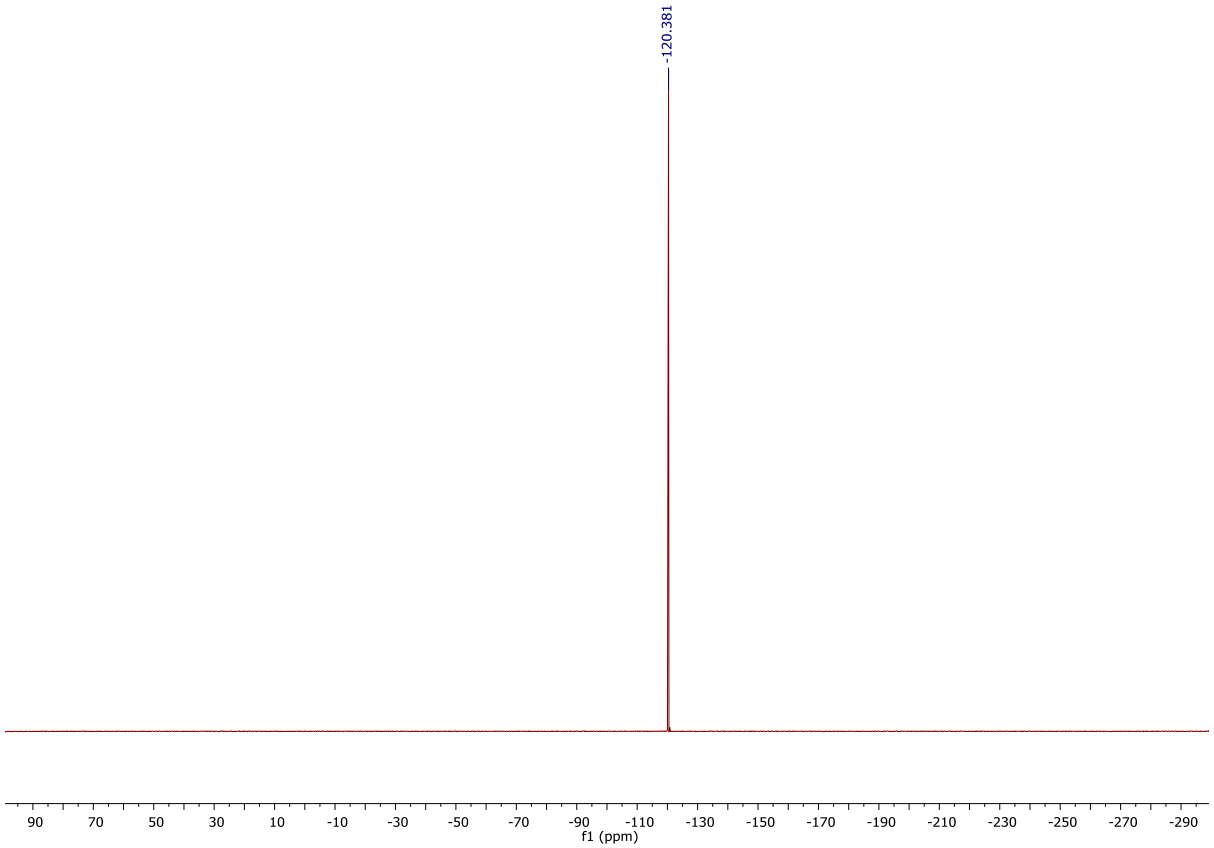
134.315
130.222
129.954
128.426
126.689
124.834
123.818
109.972
77.414
77.160
76.907
52.407
40.979
15.630
f1 (ppm)

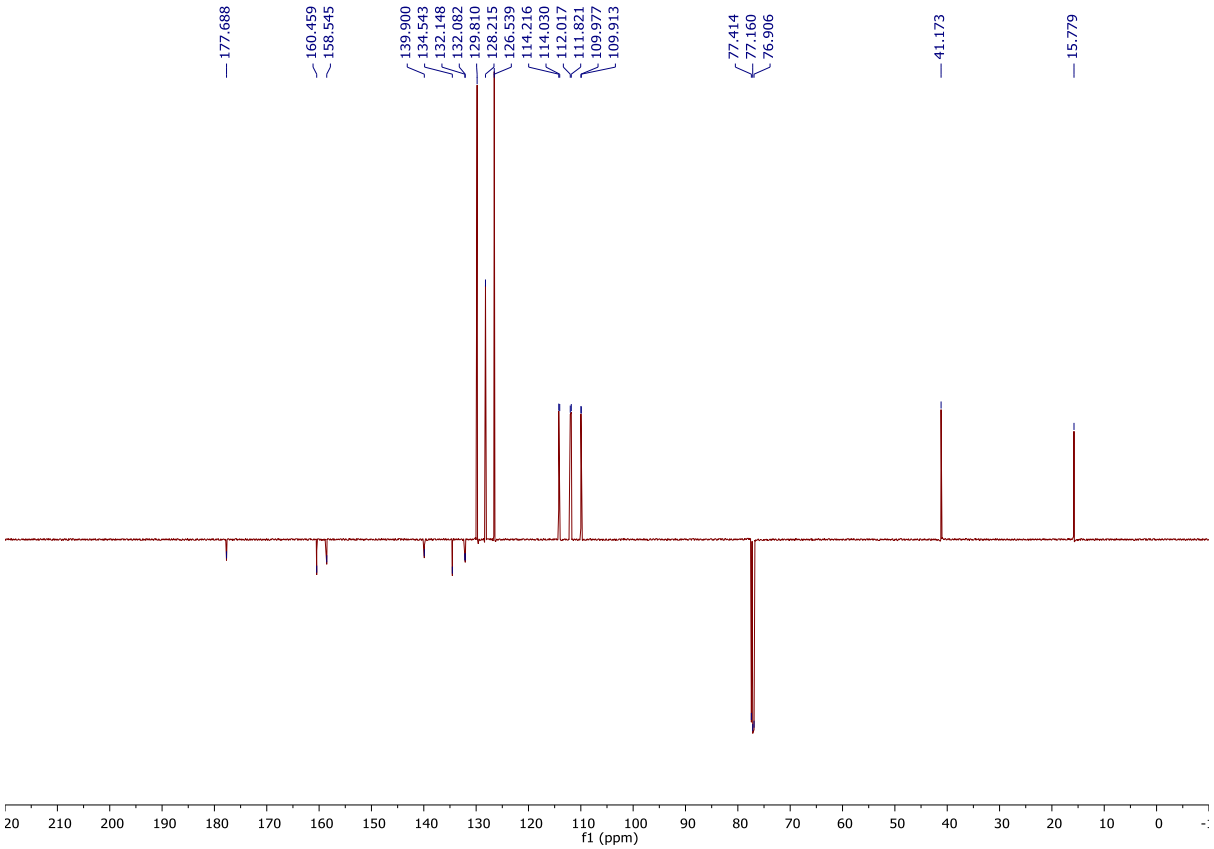
5-Fluoro-3-methyl-1-phenylindolin-2-one 9d



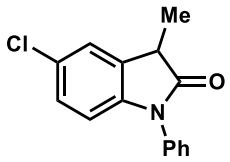
The title compound was prepared according to general procedure 8 using 5-fluoro-1-phenylindolin-2-one **8d** (114 mg, 0.50 mmol). Purification by flash silica chromatography (eluent = 4% EtOAc in hexanes, 20 × 180 mm silica; 2% NEt_3 in hexanes was used to neutralize the silica before doing column) gave the title compound **9d** as a yellow solid (87.1 mg, 0.36 mmol, 72%); mp 95–97 °C; R_f = 0.21 (eluent = 10% EtOAc in hexanes); ν_{max} / cm^{-1} (film) 3296, 2924, 1709, 1611, 1476, 1441, 1366, 1335, 1265, 1240, 1169, 1134, 1076, 1026, 926, 878, 858, 820, 756, 731, 691, 635, 596, 567, 503, 451; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 1.59 (3H, d, *J* 7.6), 3.63 (1H, q, *J* 7.6), 6.74 (1H, dd, *J* 8.6, 4.3), 6.84–6.96 (1H, m), 7.05 (1H, ddd, *J* 7.9, 2.6, 1.2), 7.32–7.47 (3H, m), 7.47–7.59 (2H, m); ^{19}F NMR (471 MHz, $CDCl_3$) δ_F: -120.4; ^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 15.8, 41.2, 110.0 (d, *J* 8.1), 111.9 (d, *J* 24.7), 114.1 (d, *J* 23.4), 126.5, 128.2, 129.8, 132.1 (d, *J* 8.3), 134.5, 139.9, 159.5 (d, *J* 241.2), 177.7; HRMS (ES)$^+$ calculated for $[C_{15}H_{13}NOF]^+$ $(M+H)^+$ m/z: 242.0981, found 242.0986 (+2.1 ppm).



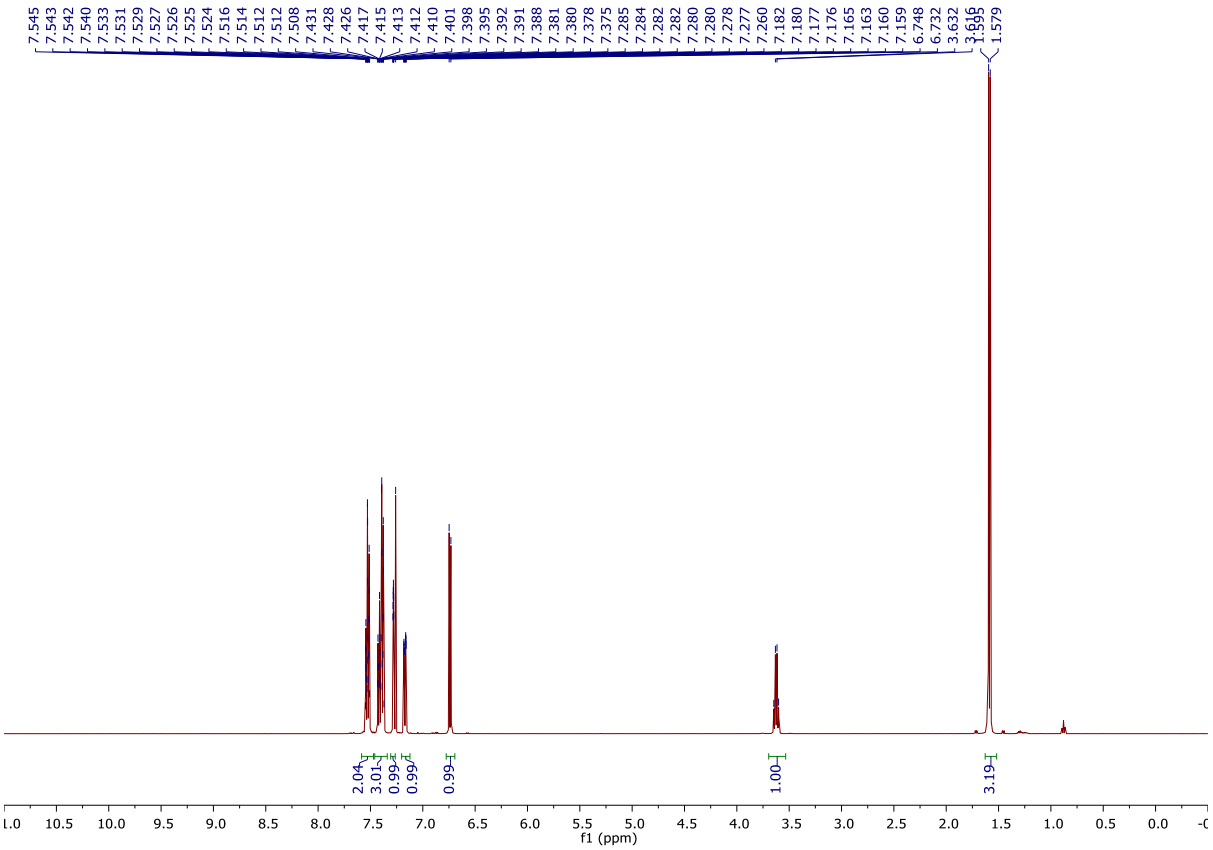

-120.381
90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230 -250 -270 -290
f1 (ppm)

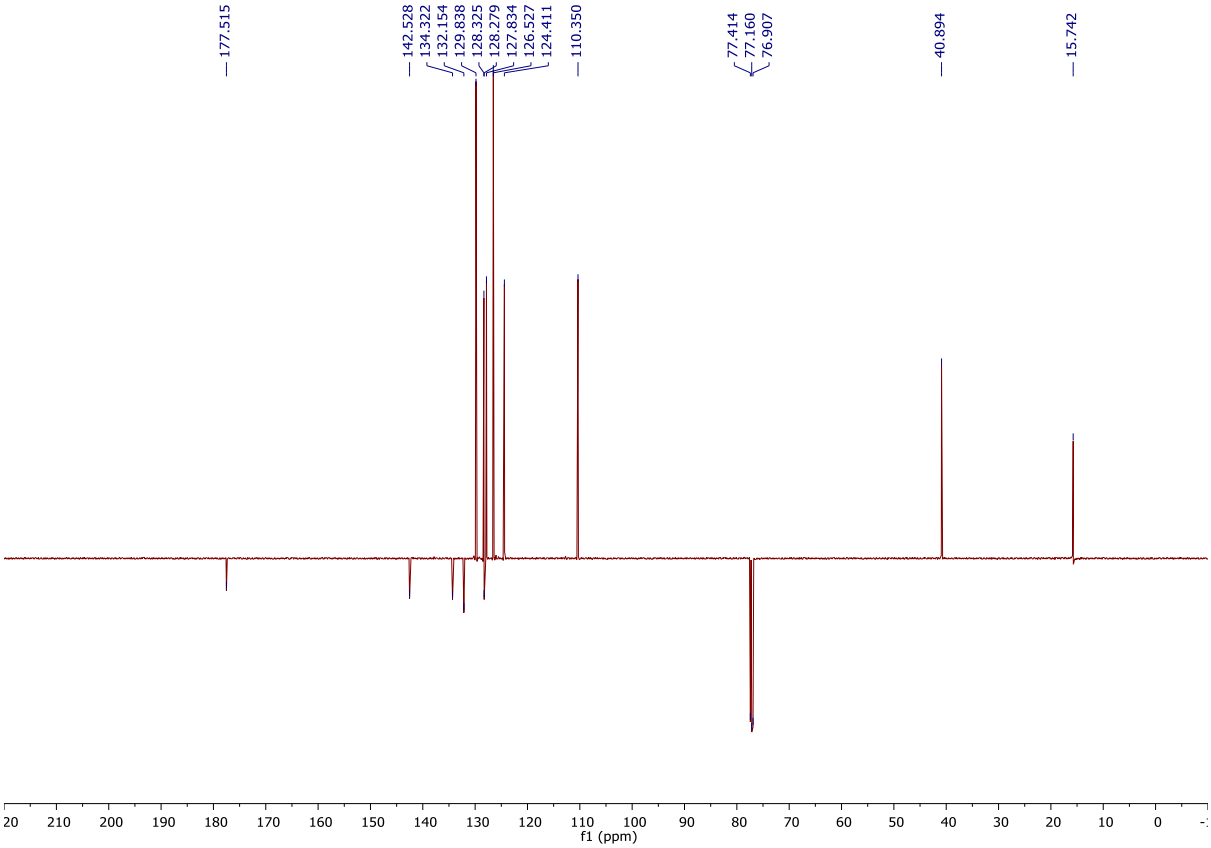

177.688
160.459
158.545
139.900
134.543
132.148
132.082
129.810
128.215
126.539
114.216
114.030
112.017
111.821
109.977
109.913
77.414
77.160
76.906
41.173
15.779
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

5-Chloro-3-methyl-1-phenylindolin-2-one 9e

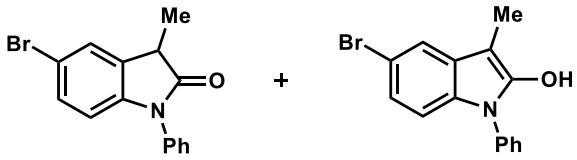


The title compound was prepared according to general procedure 8 using 5-chloro-1-phenylindolin-2-one **8e** (122 mg, 0.50 mmol). Purification by flash silica chromatography (eluent = 5% EtOAc in hexanes, 20 × 180 mm silica; 2% NEt_3 in hexanes was used to neutralize the silica before doing column) gave the title compound **9e** as a yellow solid (106 mg, 0.41 mmol, 82%); mp 107–109 °C (Lit. 106–107 °C);[28] R_f = 0.25 (eluent = 10% EtOAc in hexanes); ν_{max} / cm^{-1} (film) 2934, 1709, 1601, 1491, 1472, 1425, 1364, 1325, 1308, 1265, 1207, 1157, 1119, 1061, 1026, 893, 868, 826, 768, 752, 712, 694, 662, 635, 584, 567, 546, 500, 451; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 1.59 (3H, d, *J* 7.6), 3.62 (1H, q, *J* 7.6), 6.74 (1H, d, *J* 8.4), 7.17 (1H, ddd, *J* 8.4, 2.2, 0.8), 7.28 (1H, ddd, *J* 2.1, 1.2, 0.4), 7.34–7.46 (3H, m), 7.47–7.58 (2H, m); ^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 15.7, 40.9, 110.4, 124.4, 126.5, 127.8, 128.3, 128.3, 129.8, 132.2, 134.3, 142.5, 177.5; HRMS $(ES)^+$ calculated for $[C_{15}H_{13}NOCl]^+$ $(M+H)^+$ m/z: 258.0686, found 258.0689 (+1.2 ppm).





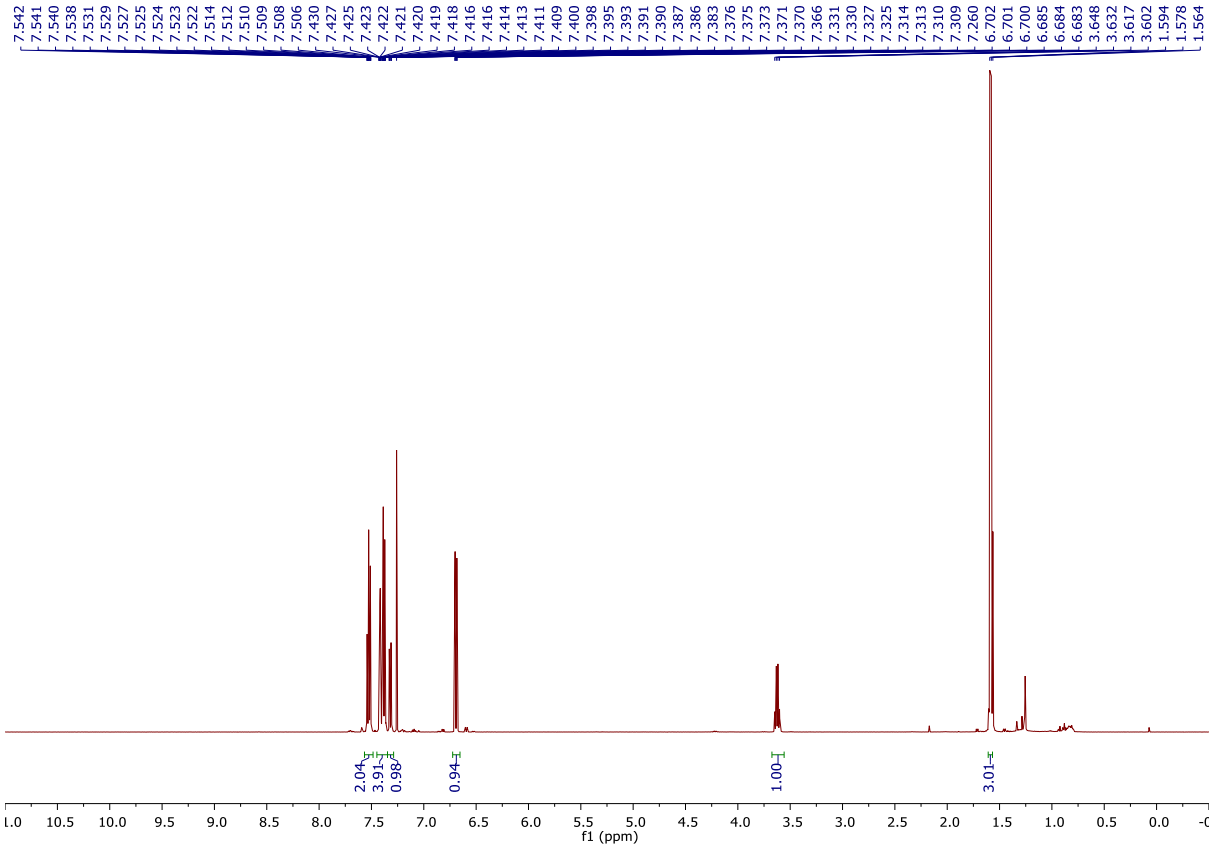
5-Bromo-3-methyl-1-phenylindolin-2-one 9f and 5-Bromo-3-methyl-1-phenyl-1H-indol-2-ol 9f'

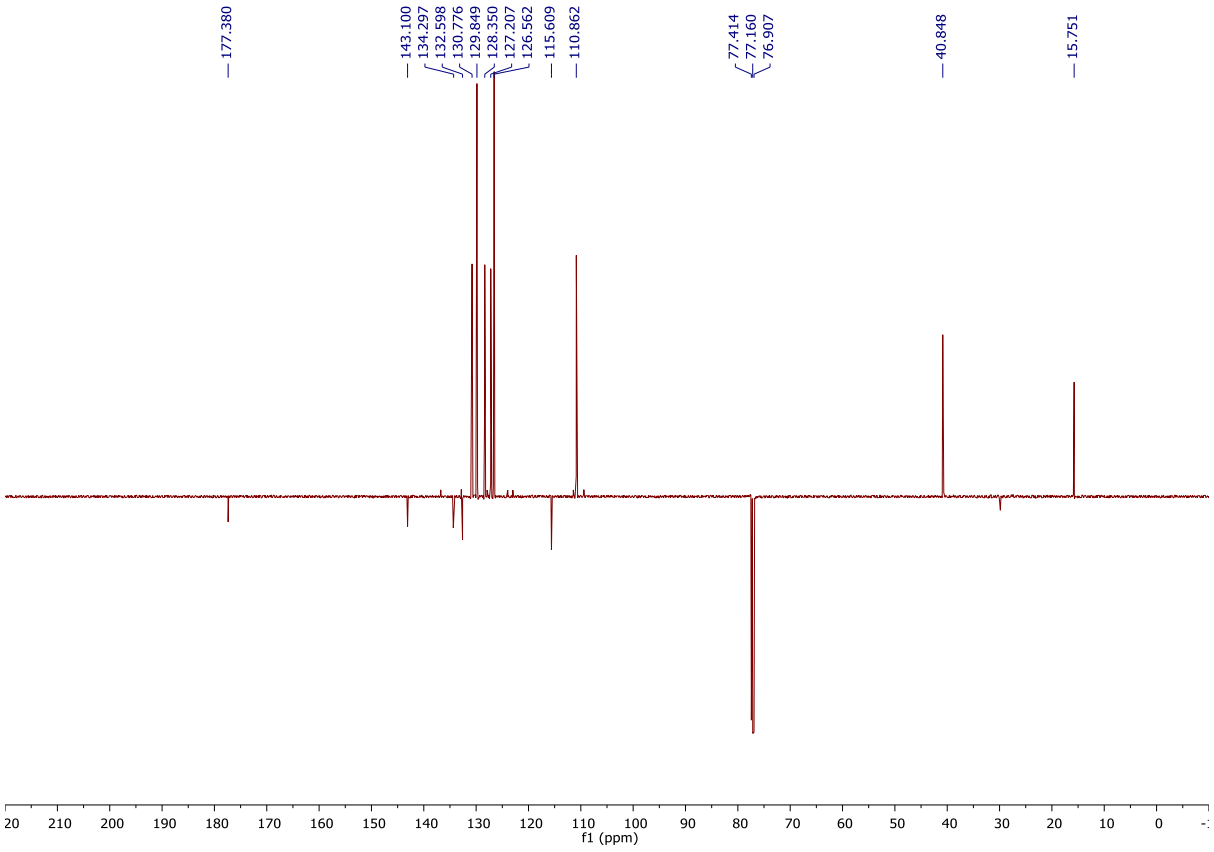


9f **9f'**

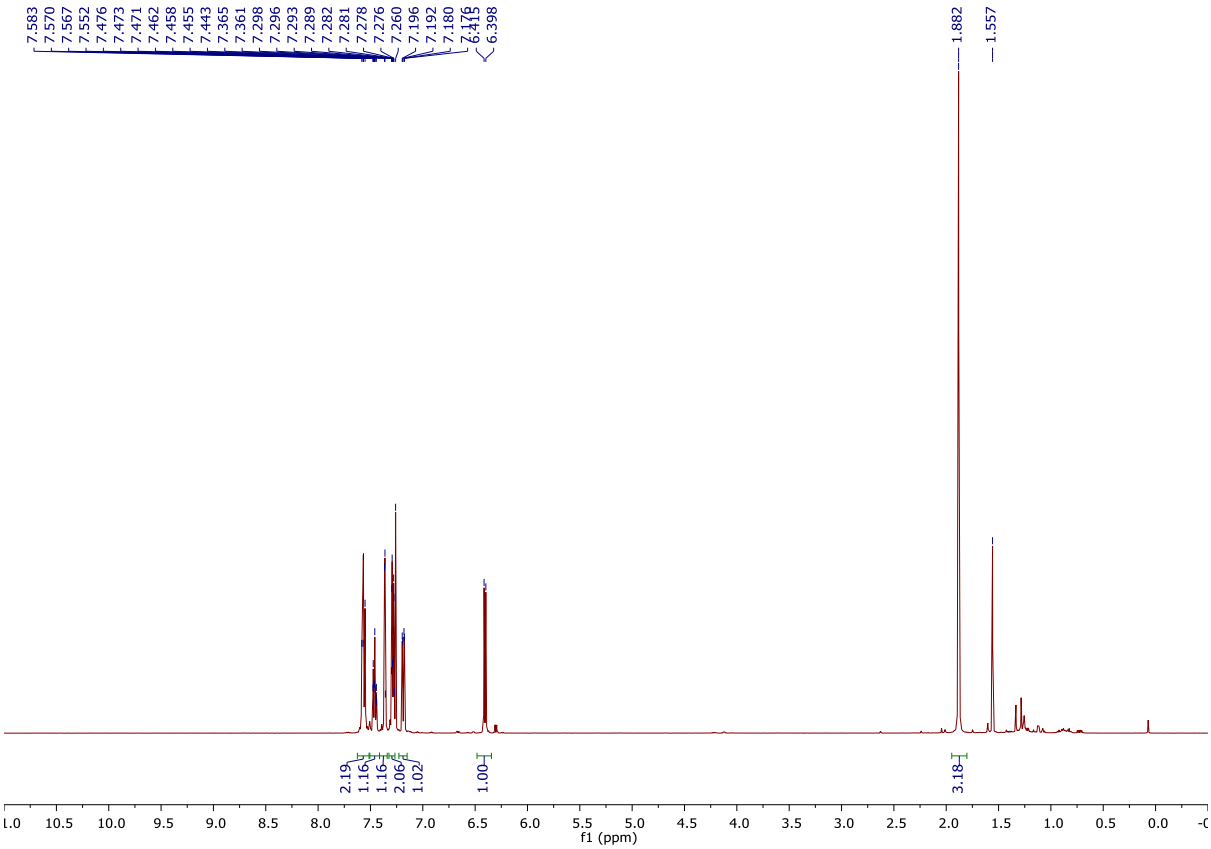
The title compounds were prepared according to general procedure 8 using 5-bromo-1-phenylindolin-2-one **8f** (144 mg, 0.50 mmol). Purification by flash silica chromatography (eluent = 3–5% EtOAc in cyclohexane, 20 × 180 mm silica) gave the title compounds **9f** as an off-white solid (89.7 mg, 0.30 mmol, 59%) and **9f'** as a light yellow solid (34.9 mg, 0.12 mmol, 23%);

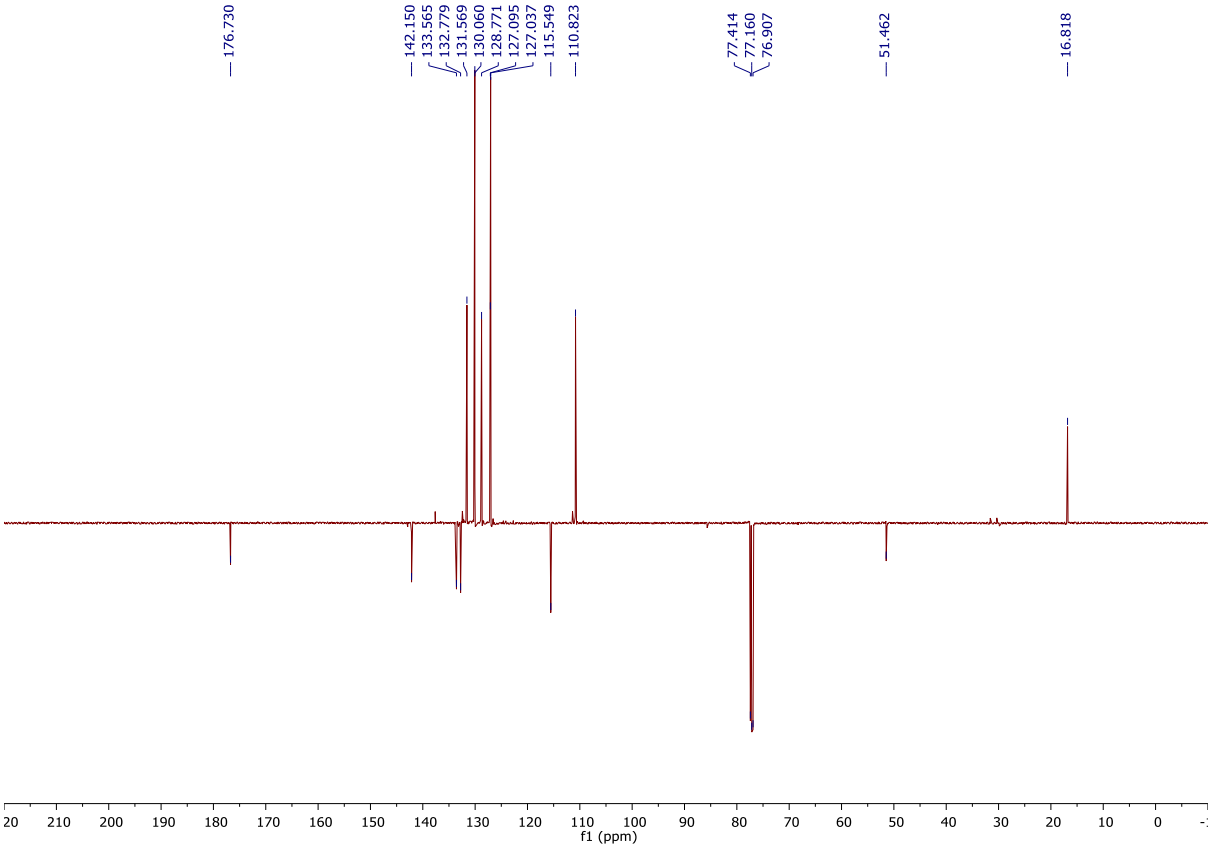
9f: mp 113–116 °C (Lit. 112–115 °C);[29] R_f = 0.19 (eluent = 5% EtOAc in cyclohexane); ν_{max} / cm^{-1} (film) 1711, 1601, 1499, 1468, 1454, 1418, 1362, 1325, 1308, 1267, 1204, 1157, 1119, 1076, 1055, 1026, 870, 822, 748, 692, 635, 586, 556, 529, 500, 449; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 1.59 (3H, d, *J* 7.6), 3.63 (1H, q, *J* 7.6), 6.69 (1H, d, *J* 8.4), 7.32 (1H, ddd, *J* 8.4, 2.0, 0.8), 7.35–7.45 (4H, m), 7.49–7.56 (2H, m); ^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 15.8, 40.8, 110.9, 115.6, 126.6, 127.2, 128.3, 129.8, 130.8, 132.6, 134.3, 143.1, 177.4; HRMS (ES)$^+$ calculated for $[C_{15}H_{13}NOBr]^+$ $(M+H)^+$ m/z: 302.0181, found 302.0179 (-0.7 ppm).


7.542
7.541
7.540
7.538
7.531
7.529
7.527
7.525
7.524
7.523
7.522
7.514
7.512
7.510
7.509
7.508
7.506
7.430
7.427
7.425
7.423
7.422
7.421
7.420
7.419
7.418
7.416
7.416
7.414
7.413
7.411
7.409
7.400
7.398
7.395
7.393
7.391
7.390
7.387
7.386
7.383
7.376
7.375
7.373
7.371
7.370
7.366
7.331
7.330
7.327
7.325
7.314
7.313
7.310
7.309
7.260
6.702
6.701
6.700
6.685
6.684
6.683
3.648
3.632
3.617
3.602
1.594
1.578
1.564
2.04
3.91
0.98
0.94
1.00
3.01
f1 (ppm)

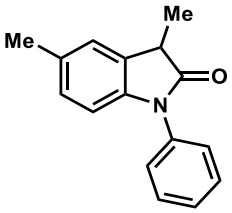

177.380
143.100
134.297
132.598
130.776
129.849
128.350
127.207
126.562
115.609
110.862
77.414
77.160
76.907
40.848
15.751
f1 (ppm)

9f': mp 242–245 °C; R_f = 0.28 (eluent = 5% EtOAc in cyclohexane); ν_{max} / cm^{-1} (film) 2976, 1709, 1599, 1497, 1476, 1464, 1416, 1360, 1321, 1304, 1267, 1234, 1182, 1138, 1072, 964, 905, 883, 835, 797, 748, 706, 689, 664, 650, 615, 584, 534, 502, 476, 428; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 1.88 (3H, s), 6.41 (1H, d, *J* 8.4), 7.19 (1H, dd, *J* 8.4, 2.0), 7.27–7.32 (2H, m), 7.36 (1H, d, *J* 2.0), 7.41–7.51 (1H, m), 7.57 (2H, dd, *J* 8.6, 7.0); ^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 16.8, 51.5, 110.8, 115.6, 127.0, 127.1, 128.8, 130.1, 131.6, 132.8, 133.6, 142.2, 176.7; HRMS (AP)$^+$ calculated for $[C_{15}H_{11}NOBr]^+$ (M-H)$^+$ m/z: 300.0024, found 300.0025 (+0.3 ppm).

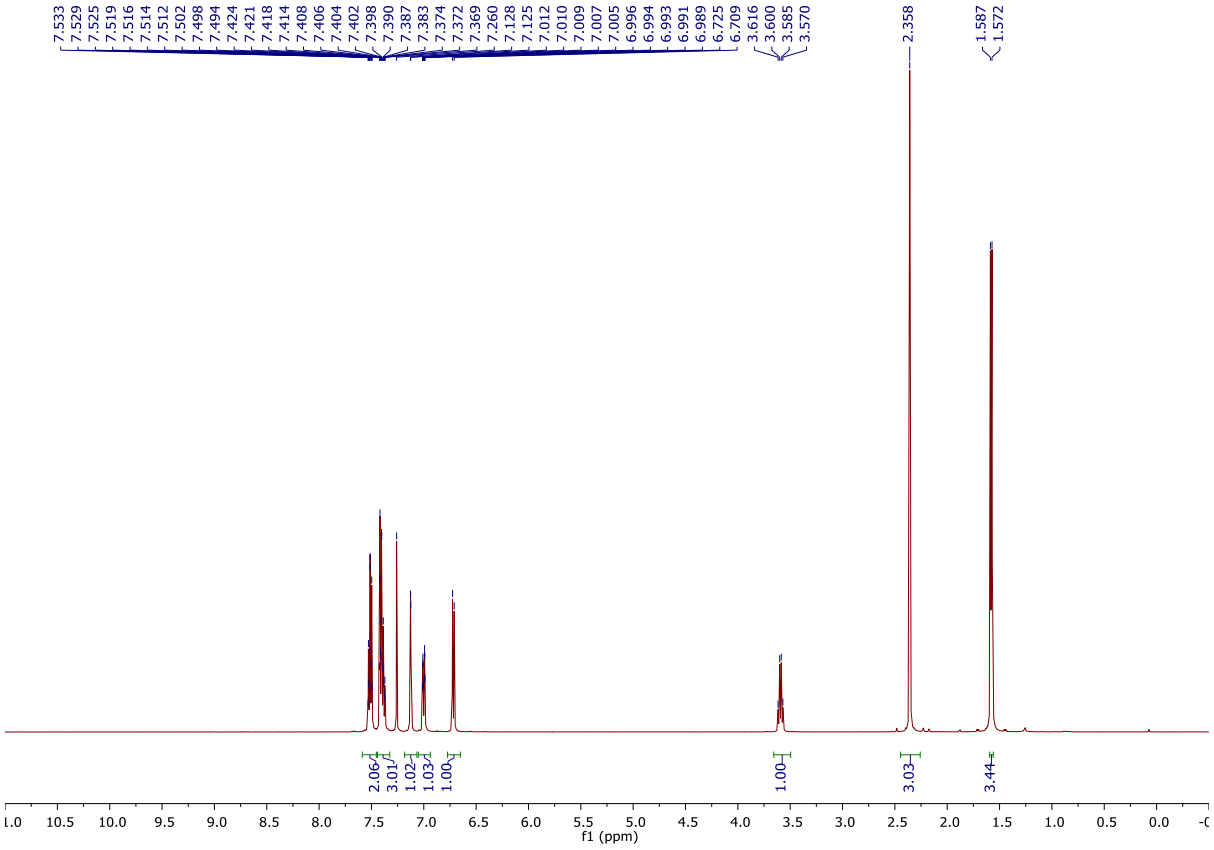




3,5-Dimethyl-1-phenylindolin-2-one 9g



The title compound was prepared according to general procedure 8 using 5-methyl-1-phenylindolin-2-one **8g** (112 mg, 0.50 mmol). Purification by flash silica chromatography (eluent = 5% EtOAc in cyclohexane, 20 × 180 mm silica) gave the title compound **9g** as an off-white solid (77.7 mg, 0.33 mmol, 66%); mp 98–100 °C; R_f = 0.33 (eluent = 10% EtOAc in cyclohexane); ν_{max} / cm^{-1} (film) 2967, 2928, 2866, 1713, 1616, 1597, 1497, 1485, 1454, 1360, 1323, 1285, 1238, 1202, 1180, 1136, 1074, 806, 768, 729, 694, 640, 602, 502, 449; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 1.58 (3H, d, *J* 7.6), 2.36 (3H, s), 3.59 (1H, q, *J* 7.6), 6.72 (1H, d, *J* 8.0), 7.00 (1H, ddt, *J* 7.9, 1.8, 0.9), 7.13 (1H, d, *J* 1.6), 7.33–7.45 (3H, m), 7.44–7.59 (2H, m); ^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 15.9, 21.2, 41.0, 109.2, 124.8, 126.6, 127.9, 128.1, 129.7, 130.7, 132.6, 134.9, 141.7, 178.1; HRMS $(AP)^+$ calculated for $[C_{16}H_{16}NO]^+$ $(M+H)^+$ m/z: 238.1232, found 238.1239 (+2.9 ppm).


7.533
7.529
7.525
7.519
7.516
7.514
7.512
7.502
7.498
7.494
7.424
7.421
7.418
7.414
7.408
7.406
7.404
7.402
7.398
7.390
7.387
7.383
7.374
7.372
7.369
7.260
7.128
7.125
7.012
7.010
7.009
7.007
7.005
6.996
6.994
6.993
6.991
6.989
6.725
6.709
3.616
3.600
3.585
3.570
2.358
1.587
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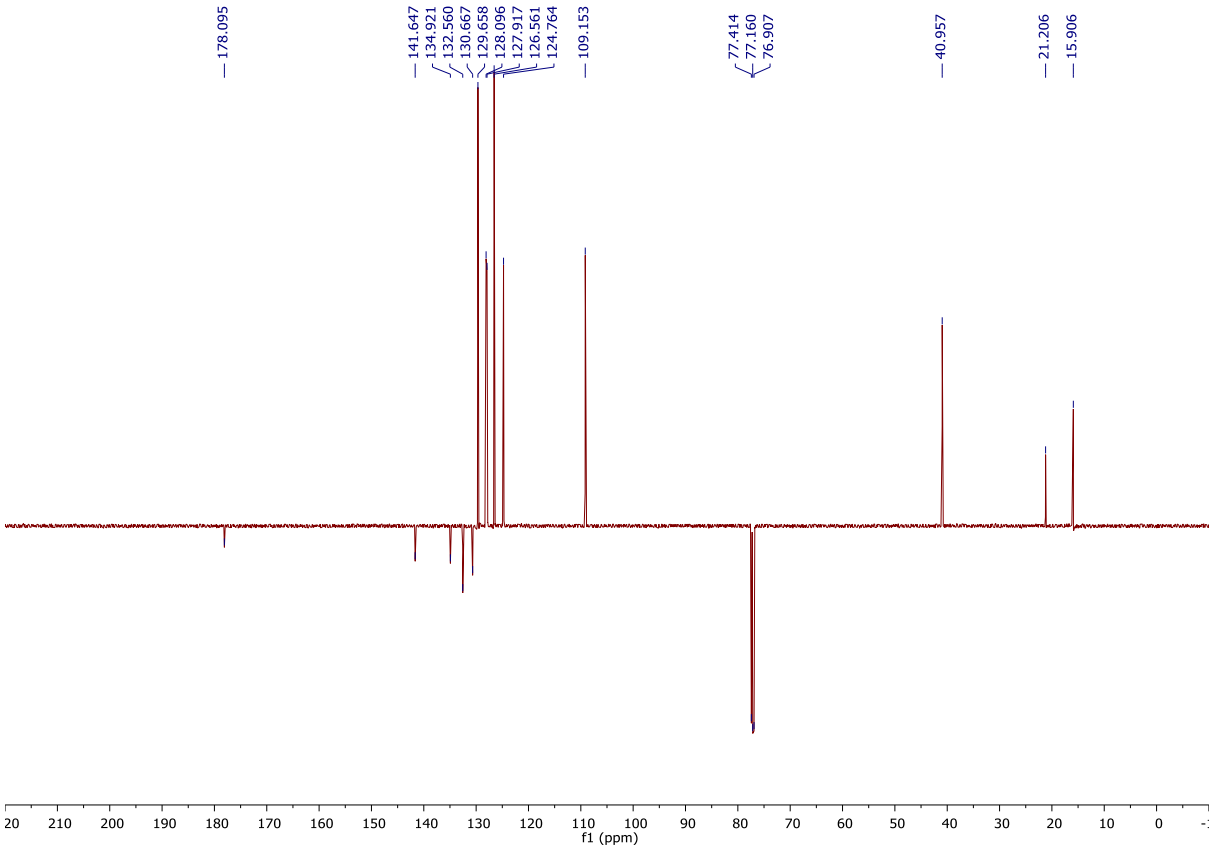
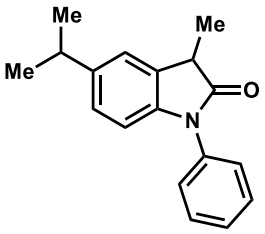
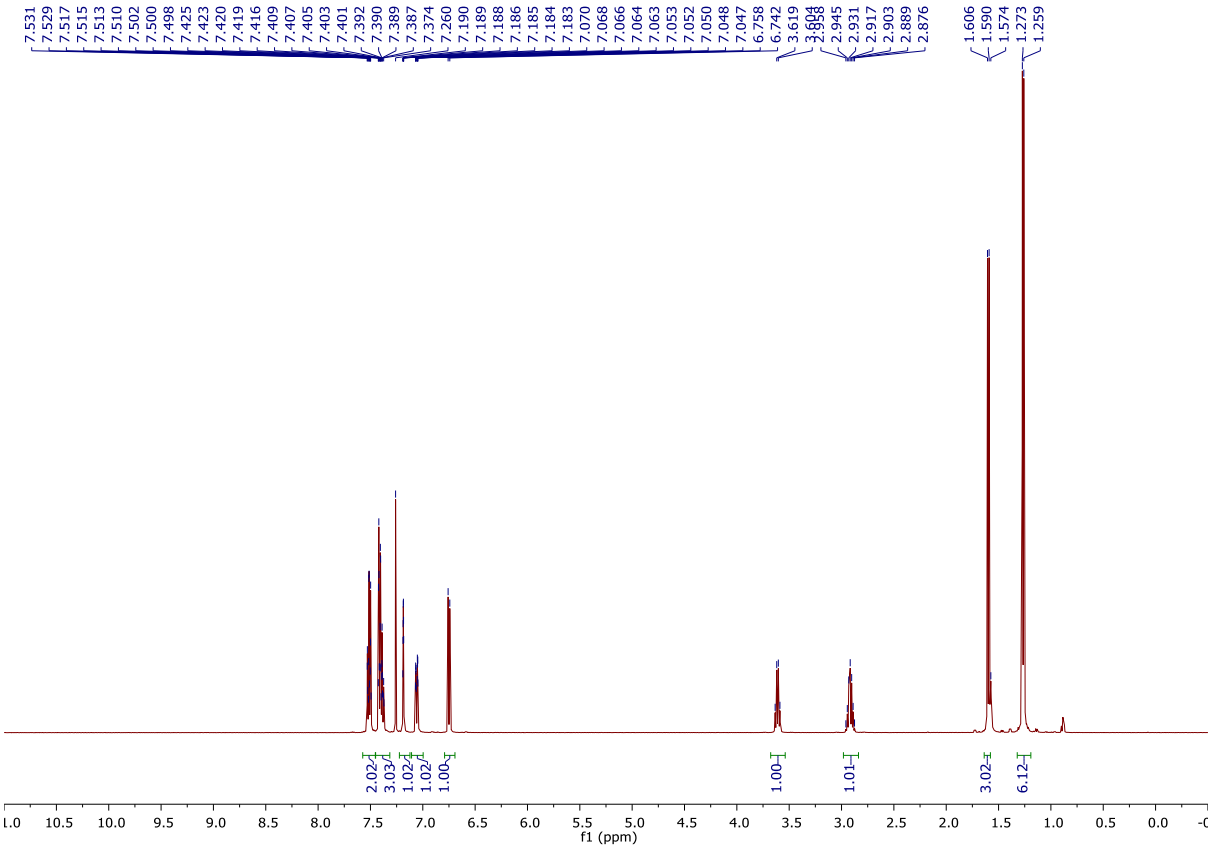
2.06
3.01
1.02
1.03
1.00
1.00
3.03
3.44
f1 (ppm)

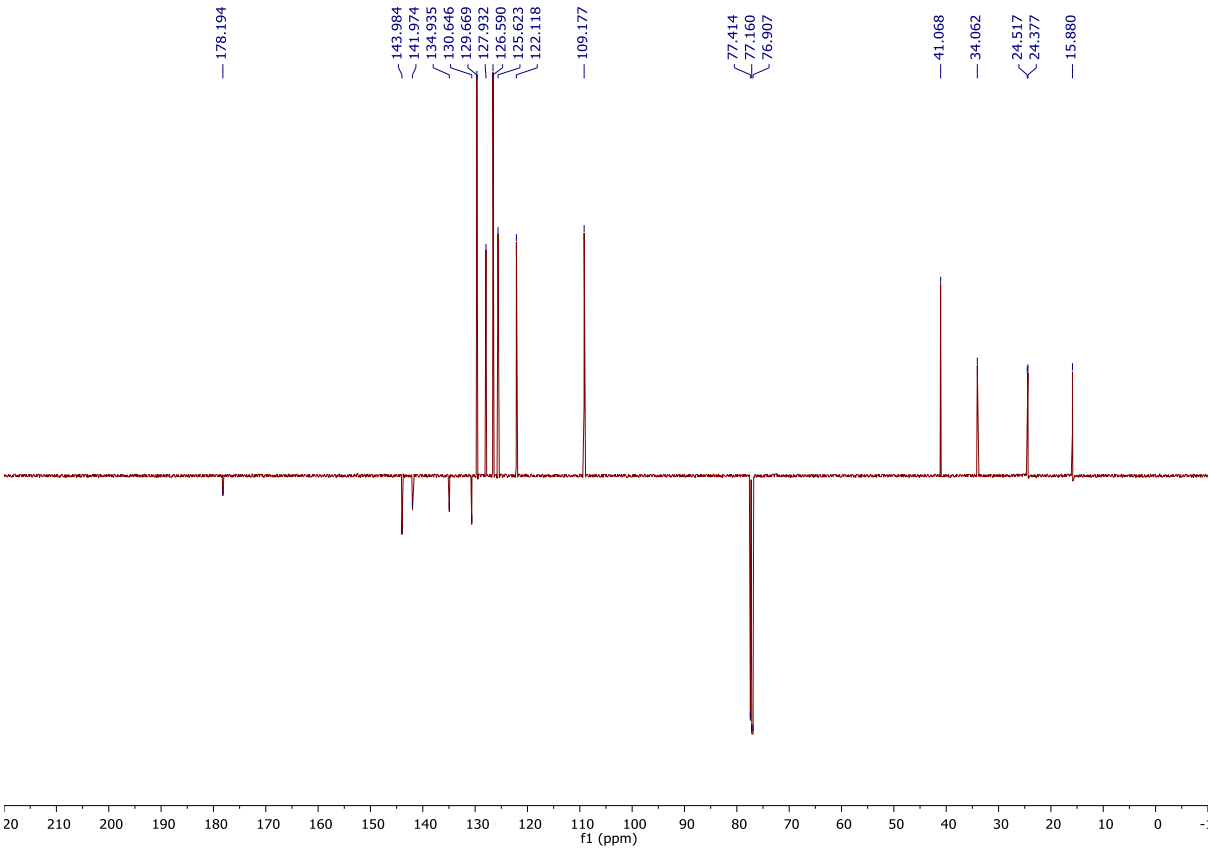

178.095
141.647
134.921
132.560
130.667
129.658
128.096
127.917
126.561
124.764
109.153
77.414
77.160
76.907
40.957
21.206
15.906
f1 (ppm)

5-Isopropyl-3-methyl-1-phenylindolin-2-one 9h

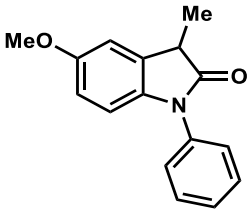


The title compound was prepared according to general procedure 8 using 5-isopropyl-1-phenylindolin-2-one **8h** (126 mg, 0.50 mmol). Purification by flash silica chromatography (eluent = 4% EtOAc in cyclohexane, 20 × 180 mm silica) gave the title compound **9h** as a light green solid (107 mg, 0.40 mmol, 81%); mp 69–72 °C; R_f = 0.36 (eluent = 10% EtOAc in cyclohexane); ν_{max} / cm^{-1} (film) 2959, 1709, 1613, 1597, 1501, 1485, 1460, 1375, 1327, 1242, 1206, 1163, 1134, 1030, 918, 814, 758, 741, 720, 692, 646, 623, 604, 573, 507, 463; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 1.27 (6H, d, *J* 6.8), 1.60 (3H, d, *J* 7.6), 2.92 (1H, hept, *J* 6.8), 3.61 (1H, q, *J* 7.6), 6.75 (1H, d, *J* 8.1), 6.99–7.11 (1H, m), 7.12–7.22 (1H, m), 7.31–7.45 (3H, m), 7.45–7.57 (2H, m); ^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 15.9, 24.4, 24.5, 34.1, 41.1, 109.2, 122.1, 125.6, 126.6, 127.9, 129.7, 130.7, 134.9, 142.0, 144.0, 178.2; HRMS $(AP)^+$ calculated for $[C_{18}H_{20}NO]^+$ $(M+H)^+$ m/z: 266.1545, found 266.1550 (+1.9 ppm).

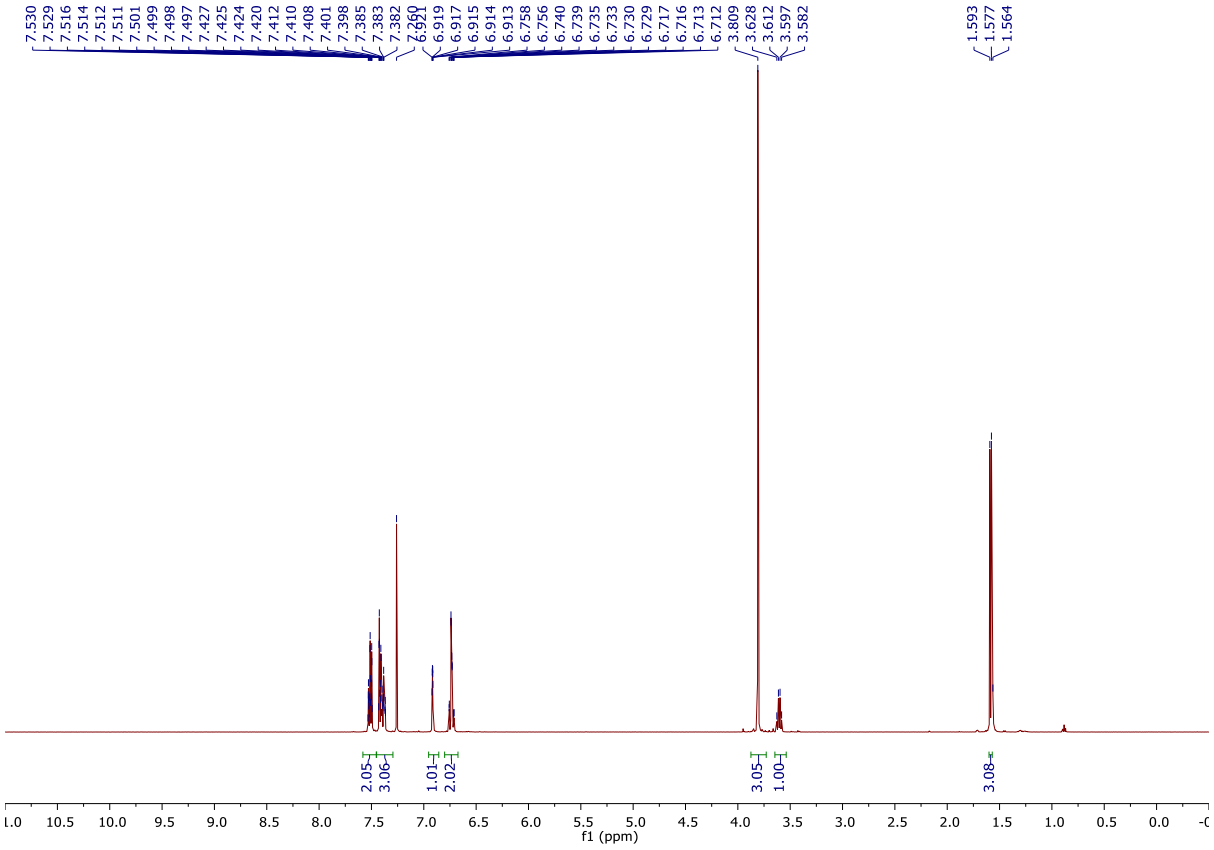


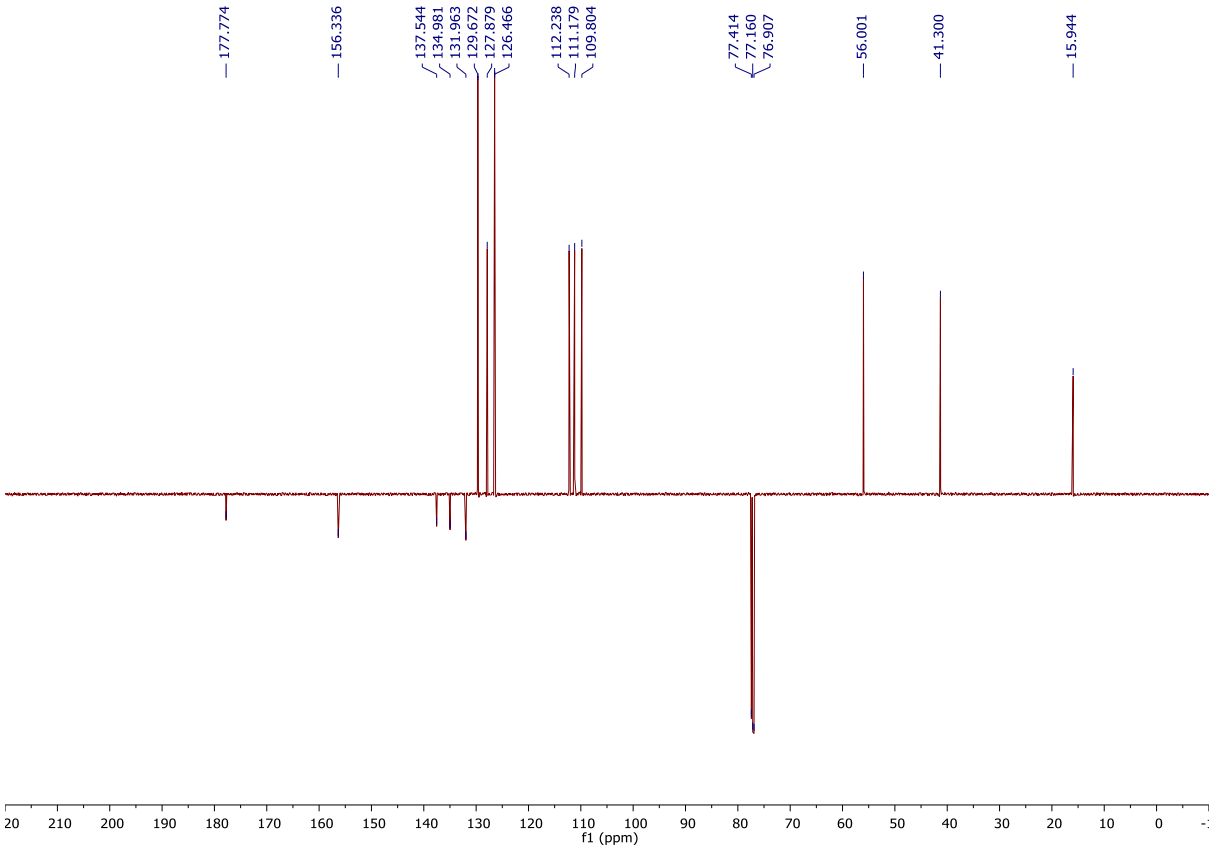


5-Methoxy-3-methyl-1-phenylindolin-2-one 9i



The title compound was prepared according to general procedure 8 using 5-methoxy-1-phenylindolin-2-one **8i** (120 mg, 0.50 mmol). Purification by flash silica chromatography (eluent = 10% EtOAc in cyclohexane, 20 × 180 mm silica) gave the title compound **9i** as a light green solid (94.5 mg, 0.37 mmol, 75%); mp 101–103 °C (Lit. 100–102 °C);[29] R_f = 0.19 (eluent = 10% EtOAc in cyclohexane); ν_{max} / cm^{-1} (film) 2963, 2934, 2837, 1701, 1601, 1483, 1456, 1435, 1362, 1300, 1258, 1202, 1179, 1152, 1028, 872, 812, 760, 696, 638, 613, 567, 513, 455; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 1.59 (3H, d, *J* 7.6), 3.60 (1H, q, *J* 7.6), 3.81 (3H, s), 6.67–6.80 (2H, m), 6.86–6.95 (1H, m), 7.29–7.45 (3H, m), 7.45–7.58 (2H, m); ^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 15.9, 41.3, 56.0, 109.8, 111.2, 112.2, 126.5, 127.9, 129.7, 132.0, 135.0, 137.5, 156.3, 177.8; HRMS (ES)$^+$ calculated for $[C_{16}H_{16}NO_2]^+$ $(M+H)^+$ m/z: 254.1181, found 254.1186 (+2.0 ppm).


7.530
7.529
7.516
7.514
7.512
7.511
7.501
7.499
7.498
7.497
7.427
7.425
7.424
7.420
7.412
7.410
7.408
7.401
7.398
7.385
7.383
7.382
7.260
6.921
6.919
6.917
6.915
6.914
6.913
6.758
6.756
6.740
6.739
6.735
6.733
6.730
6.729
6.717
6.716
6.713
6.712
3.809
3.628
3.612
3.597
3.582
1.593
1.577
1.564
2.05
3.06
1.01
2.02
3.05
1.00
3.08
f1 (ppm)


177.774
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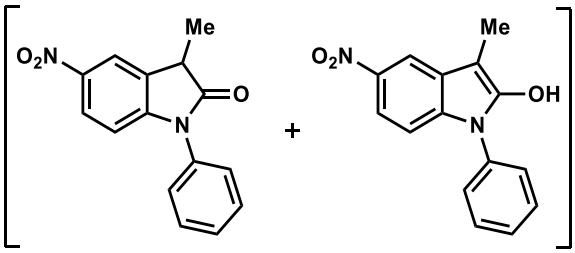
134.981
131.963
129.672
127.879
126.466
112.238
111.179
109.804
77.414
77.160
76.907
56.001
41.300
15.944
f1 (ppm)

3-Methyl-5-nitro-1-phenylindolin-2-one and 3-methyl-5-nitro-1-phenyl-1H-indol-2-ol 9j and 9j'



The mixture of title compounds was prepared according to general procedure 8 using 5-nitro-1-phenylindolin-2-one **8j** (127 mg, 0.50 mmol). Purification by flash silica chromatography (eluent = 10% EtOAc in hexanes, 20 × 180 mm silica) gave an off-white solid (55.4 mg, 0.21 mmol, 41%) as an inseparable mixture of tautomers **9j** and **9j'** in 38:62 ratio; R_f = 0.39 (eluent = 20% EtOAc in hexanes);

ν_{max} / cm^{-1} (film) 1719, 1611, 1595, 1491, 1479, 1373, 1327, 1269, 1227, 1206, 1161, 1090, 1057, 1003, 909, 822, 747, 714, 691, 635, 592, 557, 507, 451;

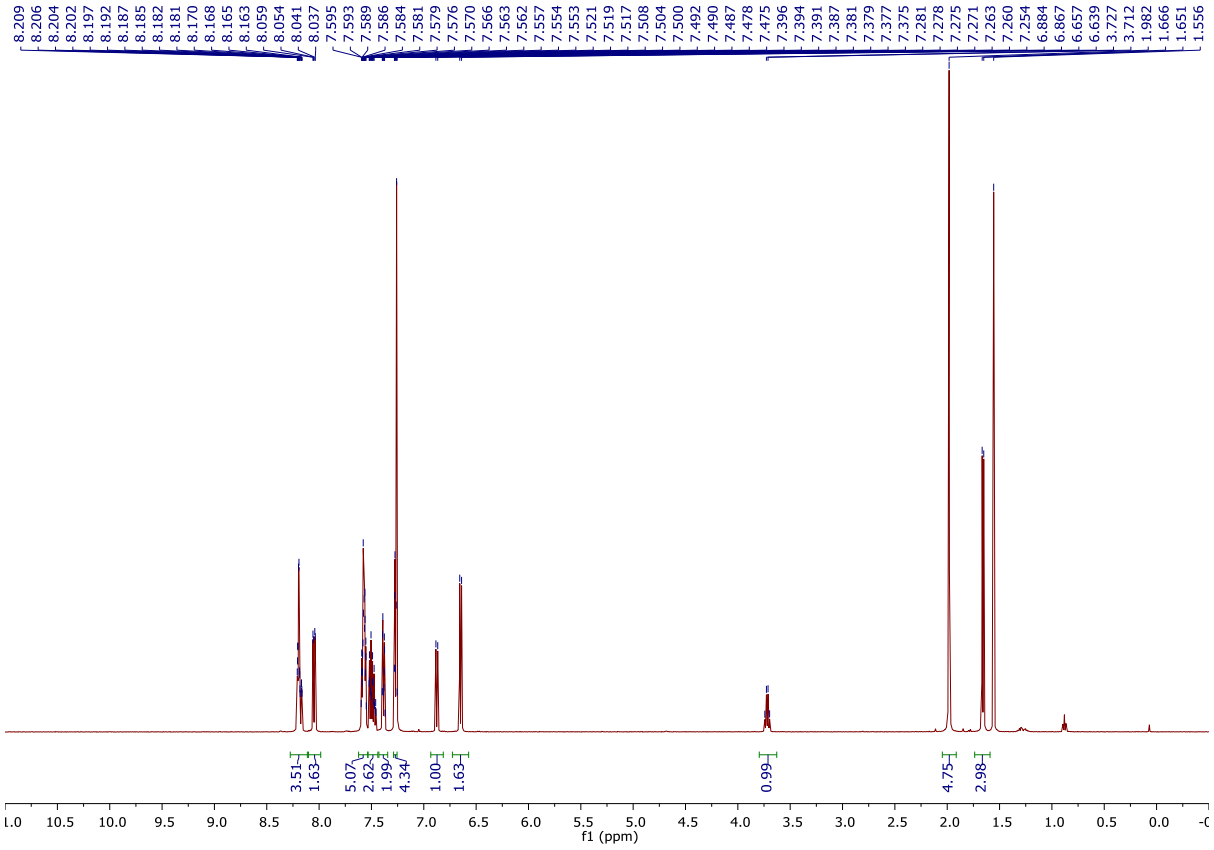
Selected data for 3-methyl-5-nitro-1-phenylindolin-2-one **9j**

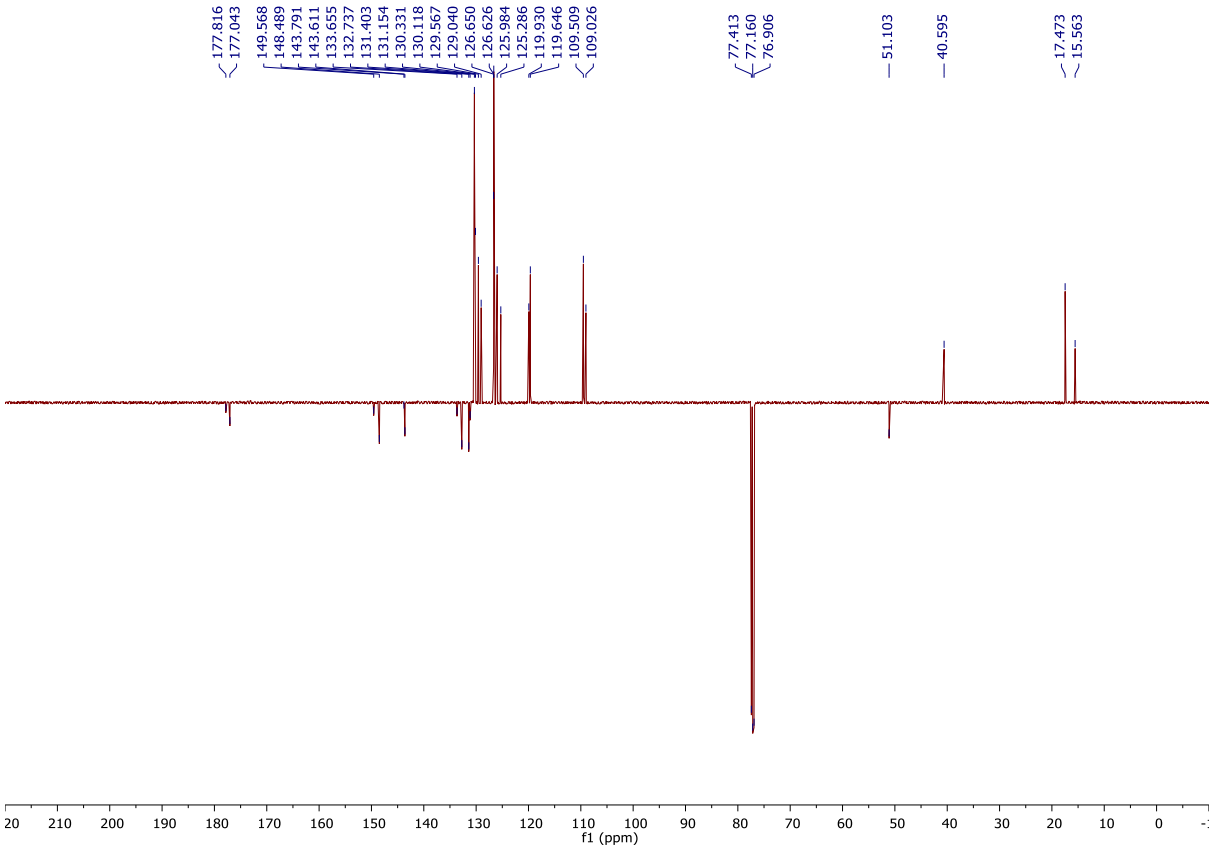
^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 1.66 (3H, d, *J* 7.6), 3.72 (1H, q, *J* 7.6), 6.88 (1H, d, *J* 8.7), 7.26–7.29 (1H, m), 7.34–7.43 (2H, m), 7.44–7.53 (1H, m), 7.54–7.62 (1H, m), 8.11–8.28 (2H, m); ^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 15.6, 40.6, 109.0, 119.6, 125.3, 126.7, 129.0, 130.1, 131.2, 133.7, 143.8, 149.6, 177.8;

Selected data for 3-methyl-5-nitro-1-phenyl-1H-indol-2-ol **9j'**

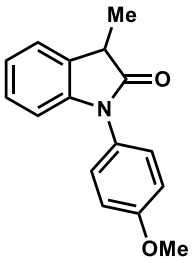
^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 1.98 (3H, s), 6.65 (1H, d, *J* 8.7), 7.26–7.29 (1H, m), 7.44–7.53 (1H, m), 7.54–7.62 (3H, m), 8.05 (1H, dd, *J* 8.7, 2.3), 8.11–8.28 (1H, m); ^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 17.5, 51.1, 109.5, 119.7, 126.0, 126.6, 129.6, 130.3, 131.4, 132.7, 143.6, 148.5, 177.0;

HRMS $(ES)^-$ calculated for $[C_{15}H_{11}N_2O_3]^-$ $(M-H)^-$ m/z: 267.0770, found 267.0782 (+4.5 ppm).

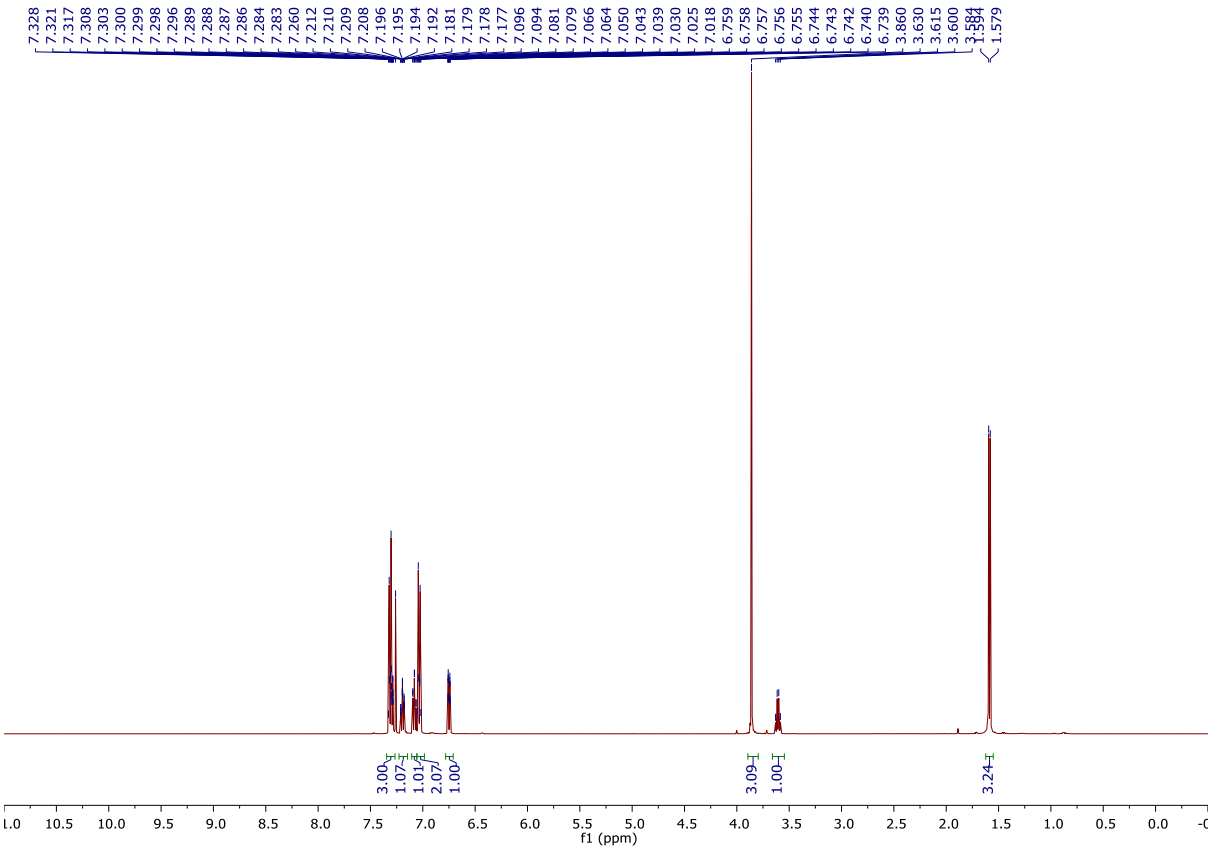

8.209
8.206
8.204
8.202
8.197
8.192
8.187
8.185
8.182
8.181
8.170
8.168
8.165
8.163
8.059
8.054
8.041
8.037
7.595
7.593
7.589
7.586
7.584
7.581
7.579
7.576
7.570
7.566
7.563
7.562
7.557
7.554
7.553
7.521
7.519
7.517
7.508
7.504
7.500
7.492
7.490
7.487
7.478
7.475
7.396
7.394
7.391
7.387
7.381
7.379
7.377
7.375
7.281
7.278
7.275
7.271
7.263
7.260
7.254
6.884
6.867
6.657
6.639
3.727
3.712
1.982
1.666
1.651
1.556
3.51
1.63
5.07
2.62
1.99
4.34
1.00
1.63
0.99
4.75
2.98
f1 (ppm)

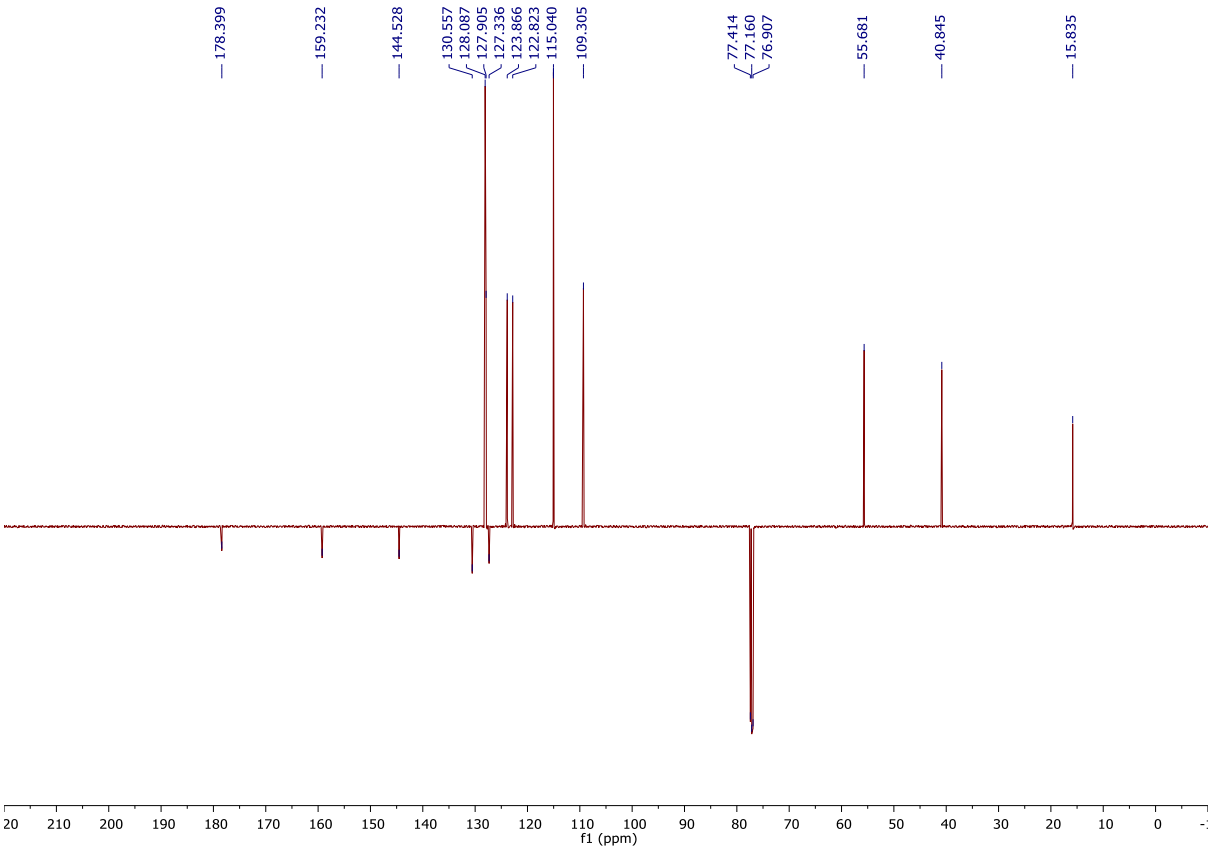

177.816
177.043
149.568
148.489
143.791
143.611
133.655
132.737
131.403
131.154
130.331
130.118
129.567
129.040
126.650
126.626
125.984
125.286
119.930
119.646
109.509
109.026
77.413
77.160
76.906
51.103
40.595
17.473
15.563
f1 (ppm)

1-(4-Methoxyphenyl)-3-methylindolin-2-one 9k

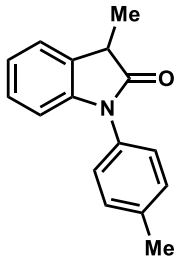


The title compound was prepared according to general procedure 8 using 1-(4-methoxyphenyl)indolin-2-one **8k** (120 mg, 0.50 mmol). Purification by flash silica chromatography (eluent = 10% EtOAc in hexanes, 20 × 180 mm silica) gave the title compound **9k** as an off-white solid (88.5 mg, 0.35 mmol, 70%); mp 86–88 °C; R_f = 0.32 (eluent = 20% EtOAc in hexanes); ν_{max} / cm^{-1} (film) 2976, 1717, 1611, 1514, 1485, 1458, 1375, 1329, 1294, 1250, 1233, 1209, 1165, 1094, 1022, 826, 747, 602, 575, 552, 525, 494, 449; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 1.59 (3H, d, *J* 7.6), 3.61 (1H, q, *J* 7.6), 3.86 (3H, s), 6.71–6.78 (1H, m), 6.98–7.06 (2H, m), 7.08 (1H, td, *J* 7.5, 1.0), 7.19 (1H, tdd, *J* 7.8, 1.3, 0.8), 7.27–7.35 (3H, m); ^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 15.8, 40.9, 55.7, 109.3, 115.0, 122.8, 123.9, 127.3, 127.9, 128.1, 130.6, 144.5, 159.2, 178.4; HRMS (ASAP)$^+$ calculated for $[C_{16}H_{16}NO_2]^+$ $(M+H)^+$ m/z: 254.1181, found 254.1175 (-2.4 ppm).

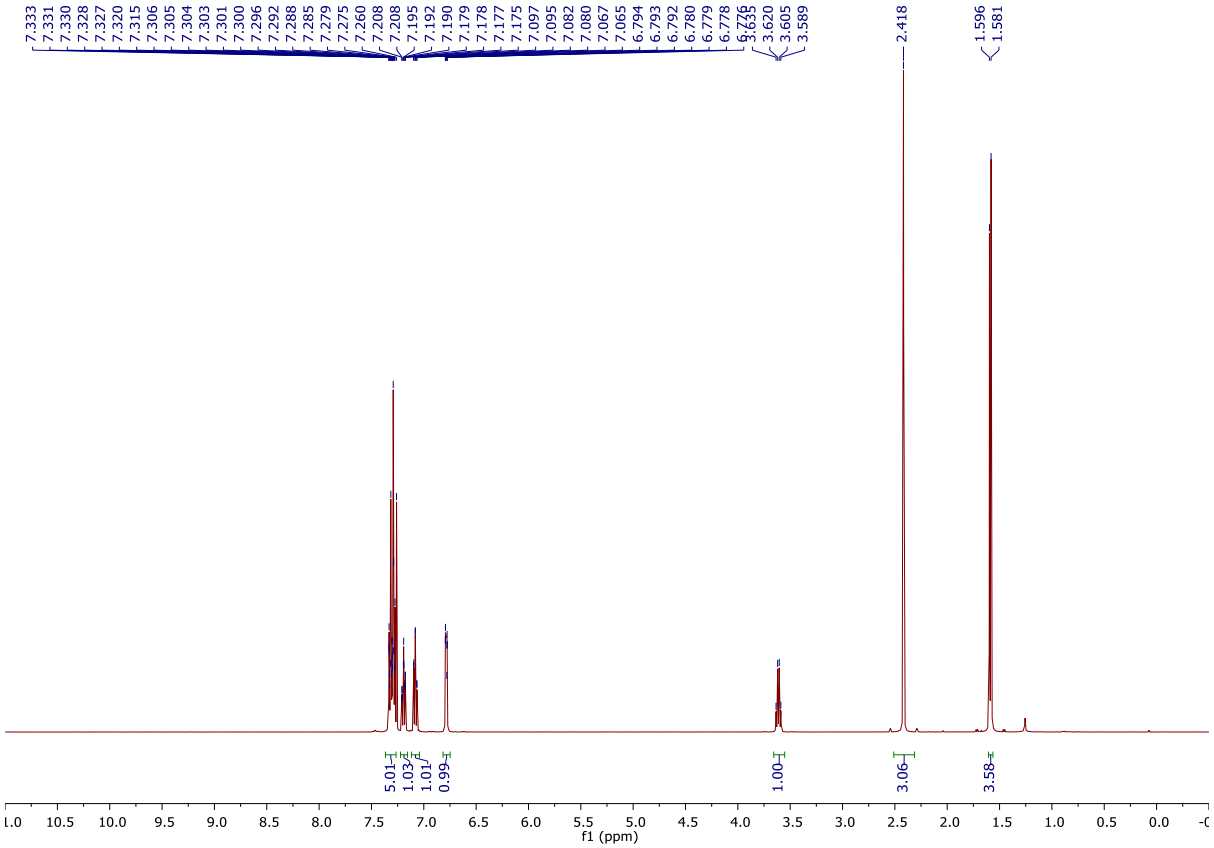


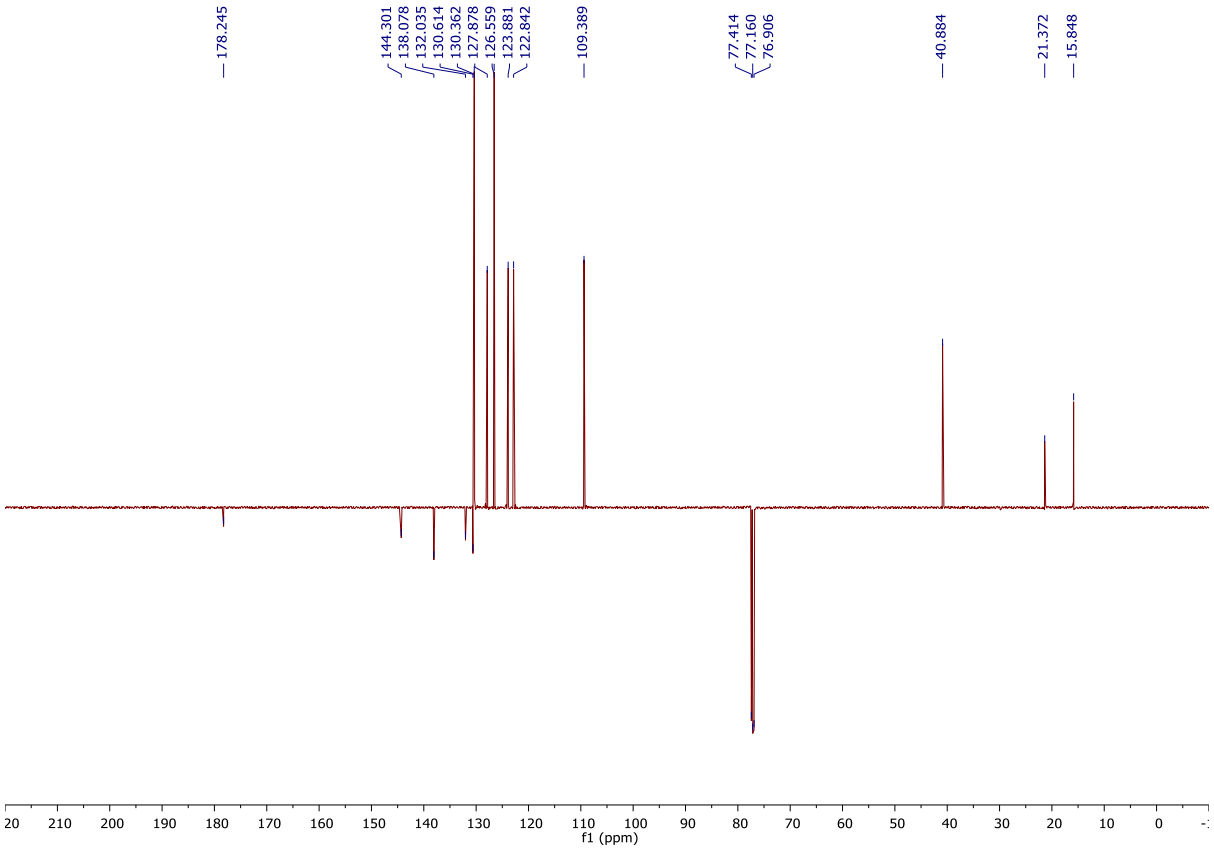


3-Methyl-1-(*p*-tolyl)indolin-2-one 9l

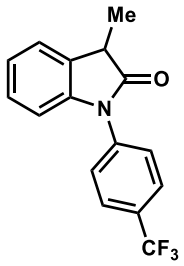


The title compound was prepared according to general procedure 8 using 1-(*p*-tolyl)indolin-2-one **8l** (112 mg, 0.50 mmol). Purification by flash silica chromatography (eluent = 10% EtOAc in hexanes, 20 × 180 mm silica) gave the title compound **9l** as an off-white solid (90.1 mg, 0.40 mmol, 81%); mp 99–102 °C; R_f = 0.27 (eluent = 10% EtOAc in hexanes); ν_{max} / cm^{-1} (film) 2980, 1711, 1607, 1512, 1483, 1462, 1370, 1331, 1296, 1231, 1209, 1171, 1098, 812, 750, 727, 691, 617, 596, 548, 505, 490, 453; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 1.59 (3H, d, *J* 7.6), 2.42 (3H, s), 3.61 (1H, q, *J* 7.6), 6.75–6.82 (1H, m), 7.08 (1H, td, *J* 7.5, 1.1), 7.16–7.22 (1H, m), 7.26–7.37 (5H, m); ^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 15.9, 21.4, 40.9, 109.4, 122.8, 123.9, 126.6, 127.9, 130.4, 130.6, 132.0, 138.1, 144.3, 178.2; HRMS (ASAP)$^+$ calculated for $[C_{16}H_{16}NO]^+$ $(M+H)^+$ m/z: 238.1232, found 238.1236 (+1.7 ppm).

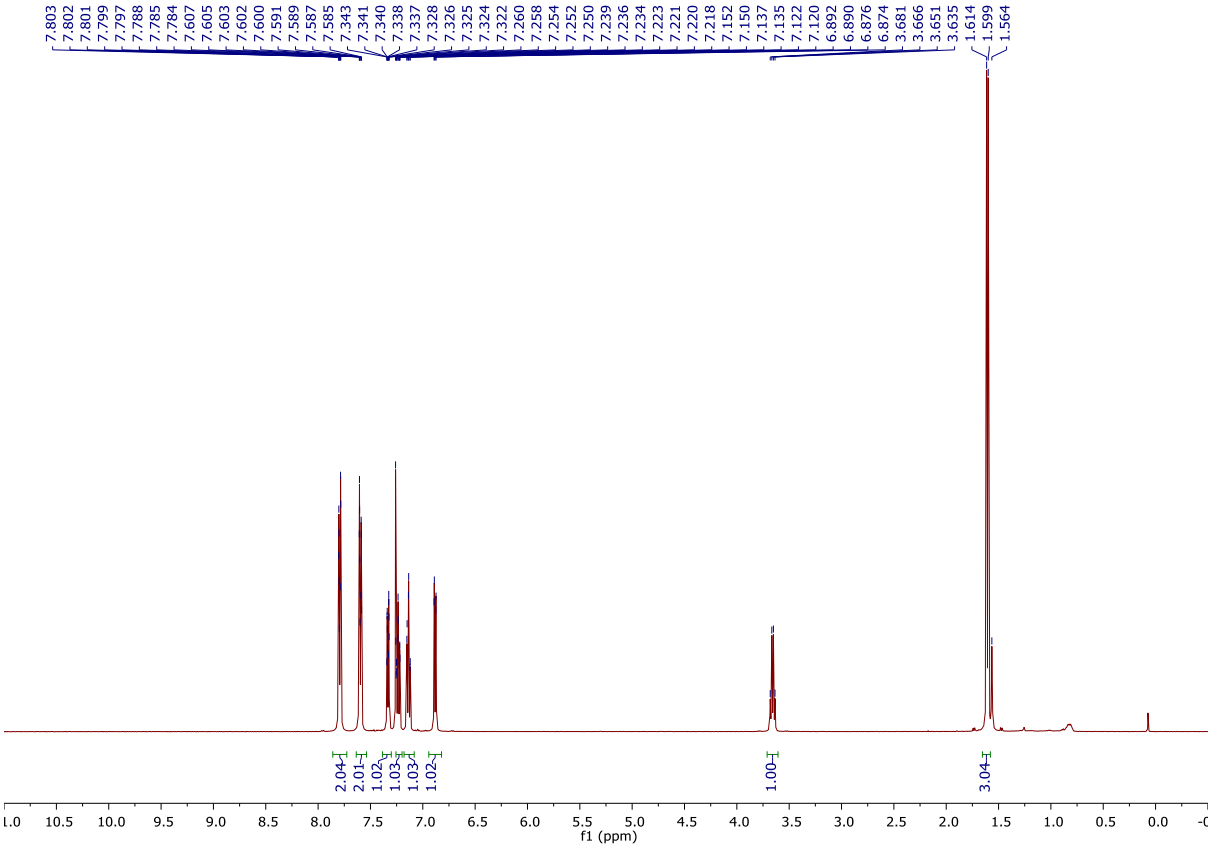

7.333
7.331
7.330
7.328
7.327
7.320
7.315
7.306
7.305
7.304
7.303
7.301
7.300
7.296
7.292
7.288
7.285
7.279
7.275
7.260
7.208
7.208
7.195
7.192
7.190
7.179
7.178
7.177
7.175
7.097
7.095
7.082
7.080
7.067
7.065
6.794
6.793
6.792
6.780
6.779
6.778
3.635
3.620
3.605
3.589
2.418
1.596
1.581
5.01
1.03
1.01
0.99
1.00
3.06
3.58
f1 (ppm)

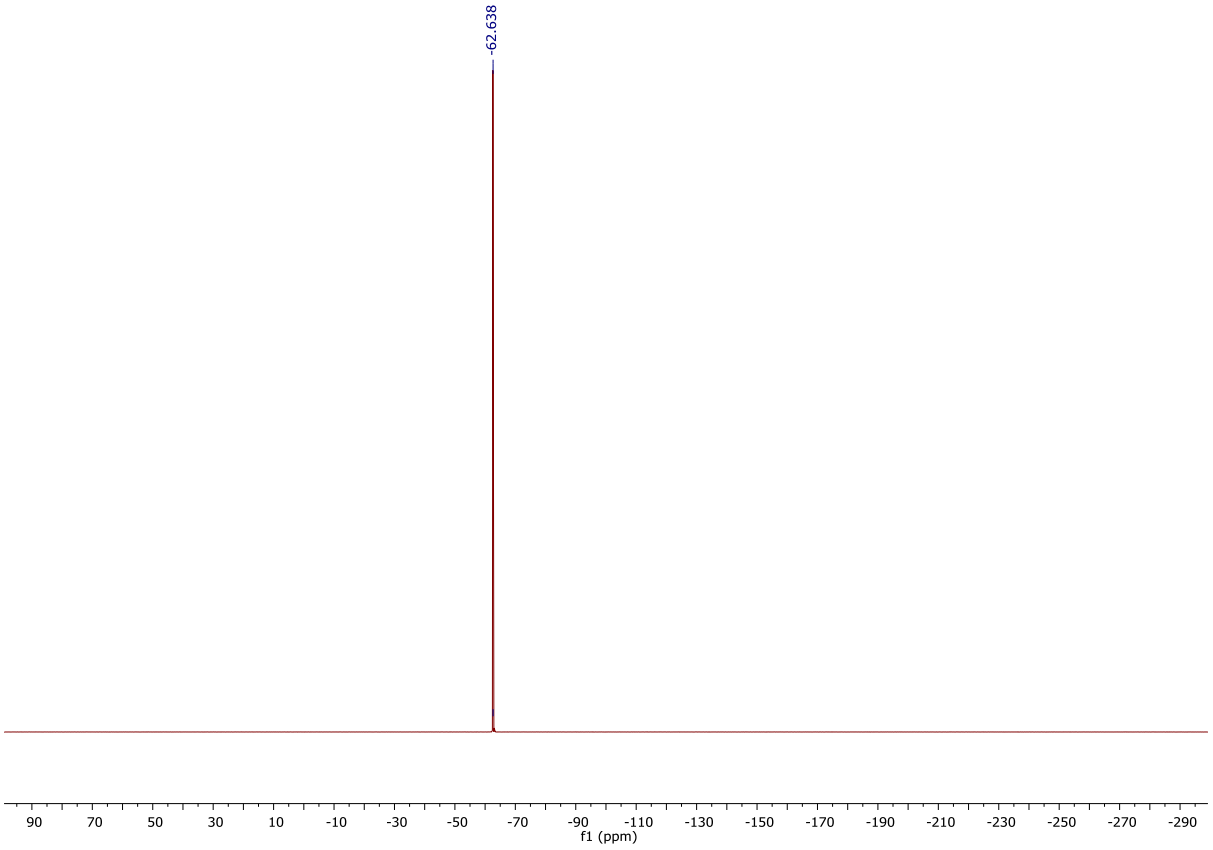

178.245
144.301
138.078
132.035
130.614
130.362
127.878
126.559
123.881
122.842
109.389
77.414
77.160
76.906
40.884
21.372
15.848
f1 (ppm)

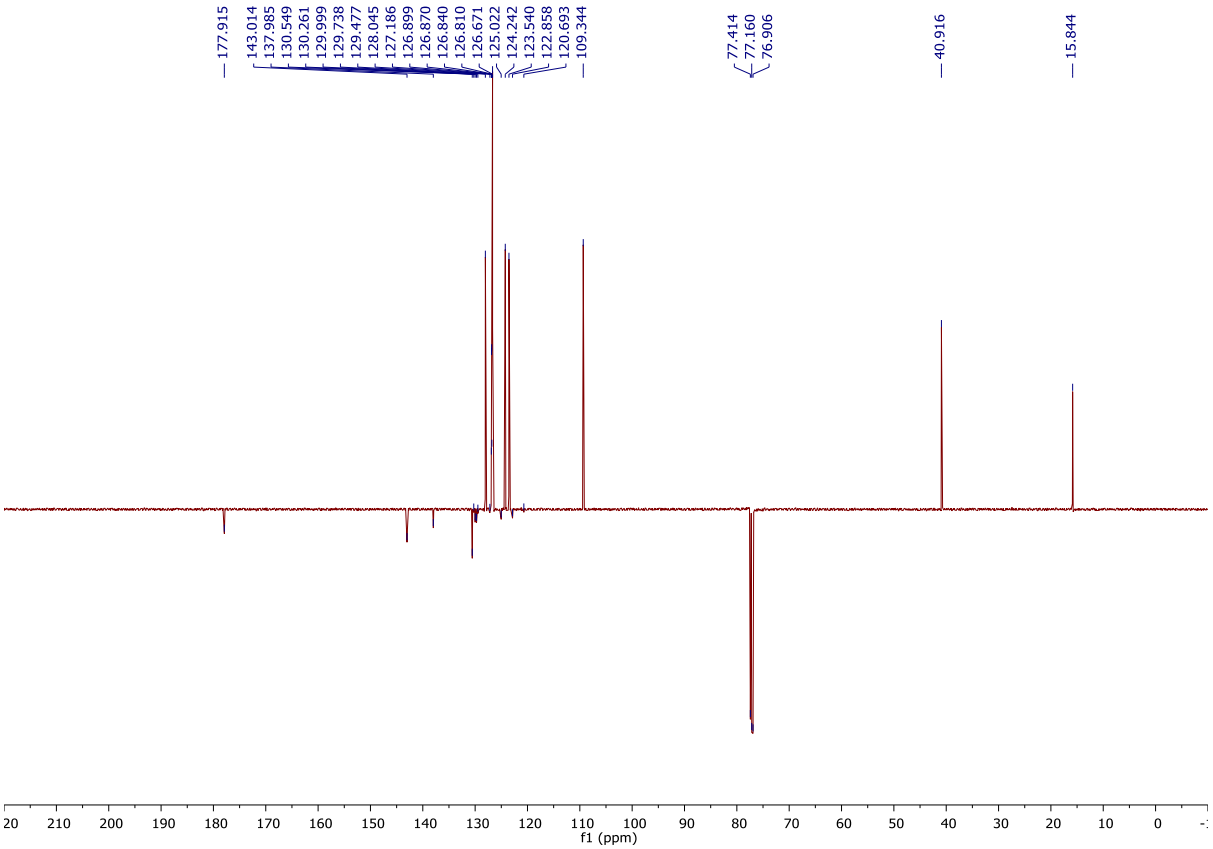
3-Methyl-1-(4-(trifluoromethyl)phenyl)indolin-2-one 9m



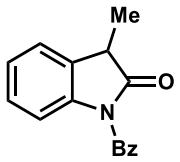
The title compound was prepared according to general procedure 8 using 1-(4-(trifluoromethyl)phenyl)indolin-2-one **8m** (139 mg, 0.50 mmol). Purification by flash silica chromatography (eluent = 4% EtOAc in hexanes, 20 × 180 mm silica) gave the title compound **9m** as a light yellow solid (133 mg, 0.46 mmol, 91%); mp 95–97 °C; R_f = 0.29 (eluent = 10% EtOAc in hexanes); ν_{max} / cm^{-1} (film) 2957, 2918, 1711, 1611, 1526, 1485, 1458, 1416, 1375, 1323, 1229, 1209, 1165, 1105, 1063, 1017, 835, 748, 698, 658, 619, 594, 490, 459, 432; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 1.61 (3H, d, *J* 7.6), 3.66 (1H, q, *J* 7.6), 6.88 (1H, dd, *J* 7.9, 1.1), 7.14 (1H, td, *J* 7.5, 1.1), 7.20–7.26 (1H, m), 7.30–7.39 (1H, m), 7.54–7.64 (2H, m), 7.73–7.86 (2H, m); ^{19}F NMR (471 MHz, $CDCl_3$) δ_F: -62.6; ^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 15.8, 40.9, 109.3, 123.5, 123.9 (q, *J* 272.7), 124.2, 126.7, 126.9 (q, *J* 3.8), 128.1, 129.9 (q, *J* 32.9), 130.6, 138.0, 143.0, 177.9; HRMS (ES)$^+$ calculated for $[C_{16}H_{13}NOF_3]^+$ (M+H)$^+$ m/z: 292.0949, found 292.0961 (+4.1 ppm).



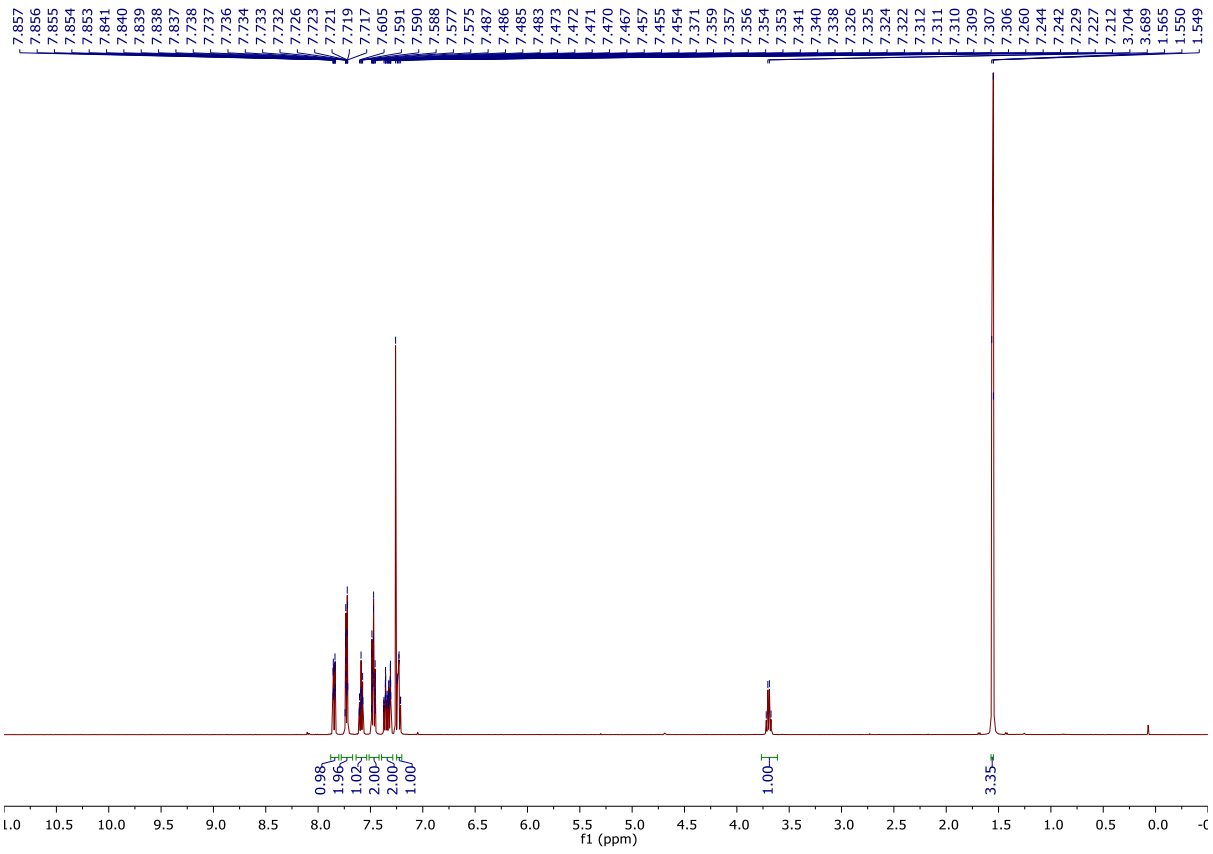

-62.638
90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230 -250 -270 -290
f1 (ppm)

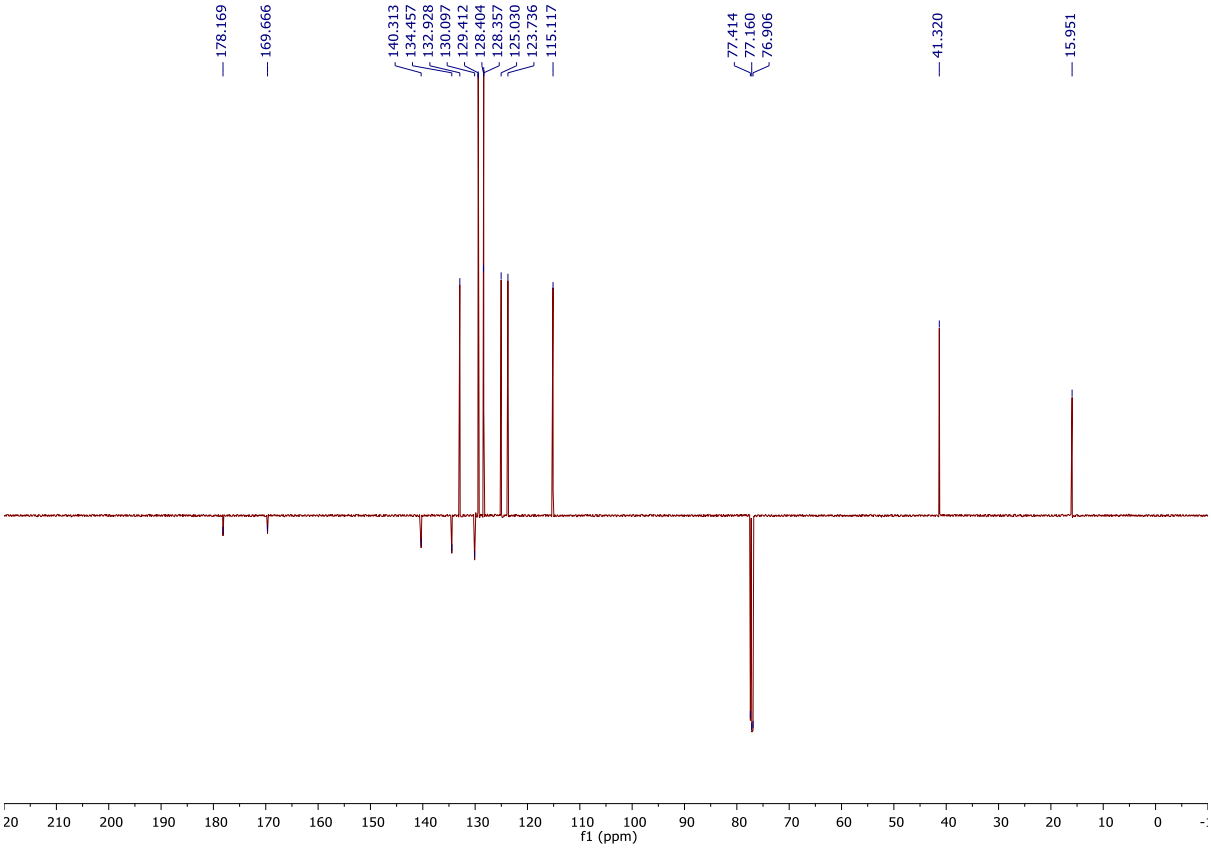

177.915
143.014
137.985
130.549
130.261
129.999
129.738
129.477
128.045
127.186
126.899
126.870
126.840
126.810
126.671
125.022
124.242
123.540
122.858
120.693
109.344
77.414
77.160
76.906
40.916
15.844
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

1-Benzoyl-3-methylindolin-2-one 9o

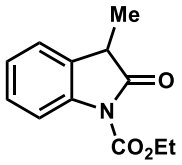


The title compound was prepared according to general procedure 8 using 1-benzoylindolin-2-one **8o** (119 mg, 0.50 mmol). Purification by flash silica chromatography (eluent = 5% EtOAc in hexanes, 20 × 180 mm silica) gave the title compound **9o** as a white solid (32.3 mg, 0.13 mmol, 26%); mp 115–117 °C; R_f = 0.38 (eluent = 10% EtOAc in hexanes); ν_{max} / cm^{-1} (film) 2980, 1746, 1686, 1479, 1450, 1348, 1288, 1200, 1163, 1088, 1063, 1018, 939, 868, 789, 752, 714, 691, 656, 627, 598, 556, 453; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 1.56 (3H, d, *J* 7.6), 3.70 (1H, q, *J* 7.6), 7.23 (1H, td, *J* 7.5, 1.0), 7.29–7.39 (2H, m), 7.42–7.51 (2H, m), 7.59 (1H, ddt, *J* 8.0, 7.0, 1.3), 7.67–7.78 (2H, m), 7.80–7.88 (1H, m); ^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 16.0, 41.3, 115.1, 123.7, 125.0, 128.4, 128.4, 129.4, 130.1, 132.9, 134.5, 140.3, 169.7, 178.2; HRMS (ES)$^+$ calculated for $[C_{16}H_{13}NO_2{}^{23}Na]^+$ (M+Na)$^+$ m/z: 274.0844, found 274.0845 (+0.4 ppm).

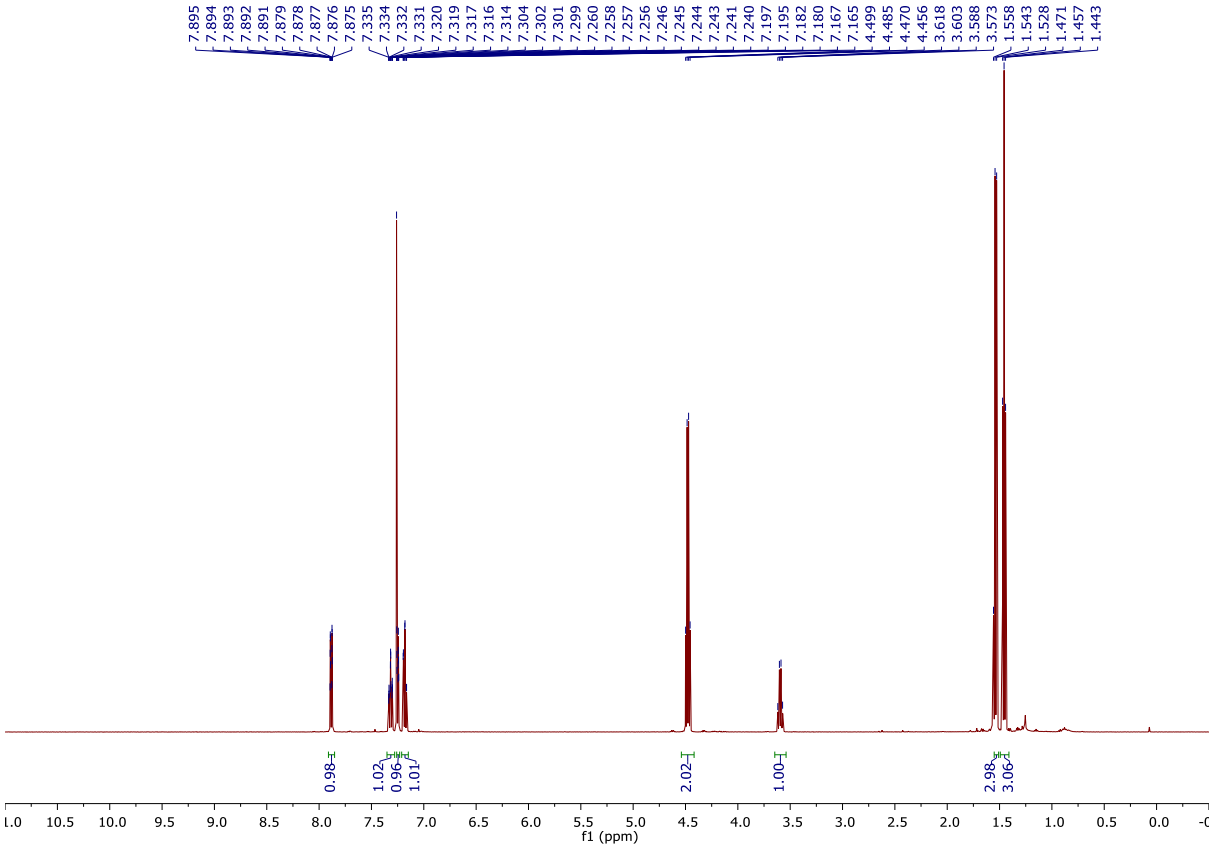


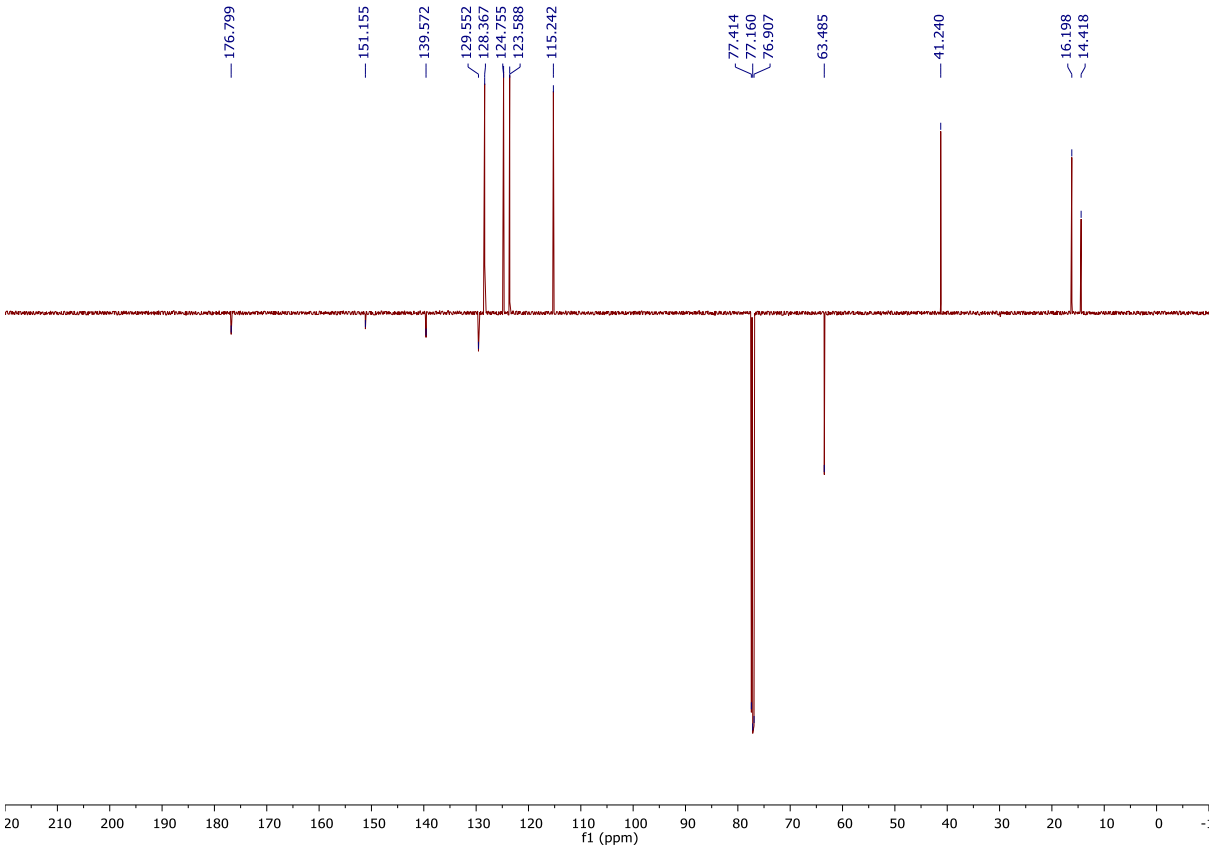


Ethyl 3-methyl-2-oxoindoline-1-carboxylate 9p

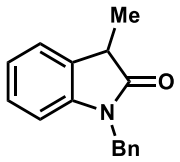


The title compound was prepared according to general procedure 8 using ethyl 2-oxoindoline-1-carboxylate **8p** (103 mg, 0.50 mmol). Purification by flash silica chromatography (eluent = 4% EtOAc in hexanes, 20 × 180 mm silica) gave the title compound **9p** as an off-white solid (32 mg, 0.15 mmol, 29%); mp 75–77 °C (Lit. 75–76 °C);[30] R_f = 0.54 (eluent = 10% EtOAc in hexanes); ν_{max} / cm^{-1} (film) 2976, 1759, 1728, 1715, 1611, 1481, 1468, 1395, 1375, 1344, 1314, 1281, 1236, 1206, 1157, 1117, 1094, 1065, 1044, 1024, 941, 860, 760, 741, 725, 677, 625, 571, 542, 498, 453, 430; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 1.46 (3H, t, *J* 7.1), 1.54 (3H, d, *J* 7.6), 3.60 (1H, q, *J* 7.6), 4.48 (2H, q, *J* 7.1), 7.18 (1H, td, *J* 7.5, 1.0), 7.23–7.26 (1H, m), 7.28–7.35 (1H, m), 7.85–7.91 (1 H, m); ^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 14.4, 16.2, 41.2, 63.5, 115.2, 123.6, 124.8, 128.4, 129.6, 139.6, 151.2, 176.8; HRMS $(ES)^+$ calculated for $[C_{12}H_{13}NO_3{}^{23}Na]^+$ $(M+Na)^+$: m/z 242.0793, found 242.0792 (-0.4 ppm).

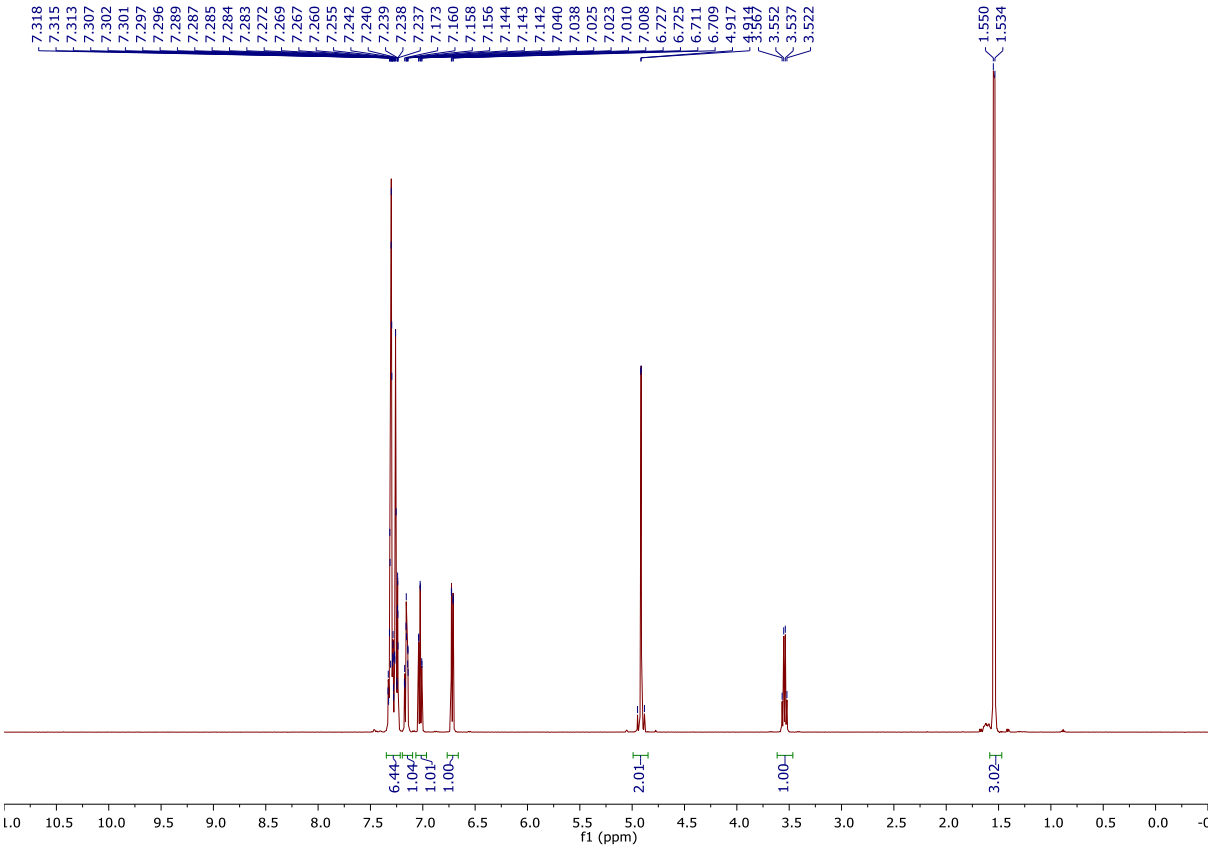

7.895
7.894
7.893
7.892
7.891
7.879
7.878
7.877
7.876
7.875
7.335
7.334
7.332
7.331
7.320
7.319
7.317
7.316
7.314
7.304
7.302
7.301
7.299
7.260
7.258
7.257
7.256
7.246
7.245
7.244
7.243
7.241
7.240
7.197
7.195
7.182
7.180
7.167
7.165
4.499
4.485
4.470
4.456
3.618
3.603
3.588
3.573
1.558
1.543
1.528
1.471
1.457
1.443
0.98
1.02
0.96
1.01
2.02
1.00
2.98
3.06
f1 (ppm)

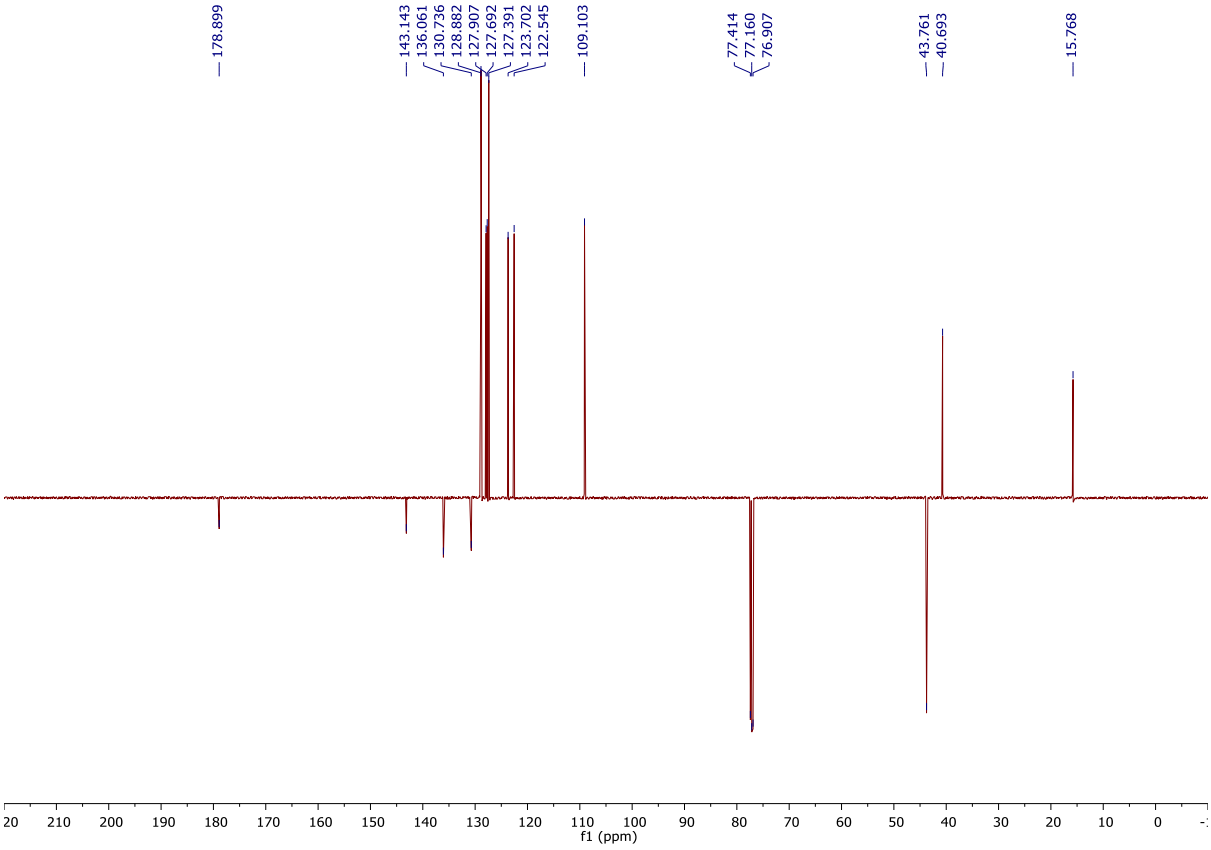

176.799
151.155
139.572
129.552
128.367
124.755
123.588
115.242
77.414
77.160
76.907
63.485
41.240
16.198
14.418
f1 (ppm)

1-Benzyl-3-methylindolin-2-one 9q

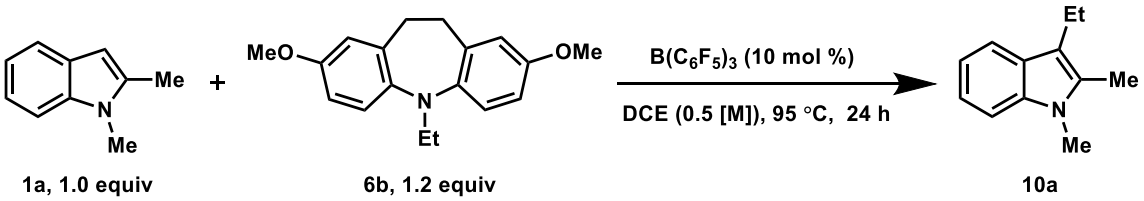


The title compound was prepared according to general procedure 8 using 1-benzylindolin-2-one **8q** (117 mg, 0.50 mmol). Purification by flash silica chromatography (eluent = 7.5% EtOAc in hexanes, 20 × 180 mm silica) gave the title compound **9q** as an off-white solid (85.2 mg, 0.36 mmol, 72%); mp 123–125 °C (Lit. 119–120 °C);[31] R_f = 0.24 (eluent = 10% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 1.54 (3H, d, *J* 7.6), 3.54 (1H, q, *J* 7.6), 4.85–4.99 (2H, m), 6.72 (1H, dd, *J* 7.8, 0.9), 7.02 (1H, td, *J* 7.5, 1.0), 7.10–7.20 (1H, m), 7.22–7.35 (6H, m); ^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 15.8, 40.7, 43.8, 109.1, 122.6, 123.7, 127.4, 127.7, 127.9, 128.9, 130.7, 136.1, 143.1, 178.9. Spectroscopic data in accordance with that stated in the literature.[31]



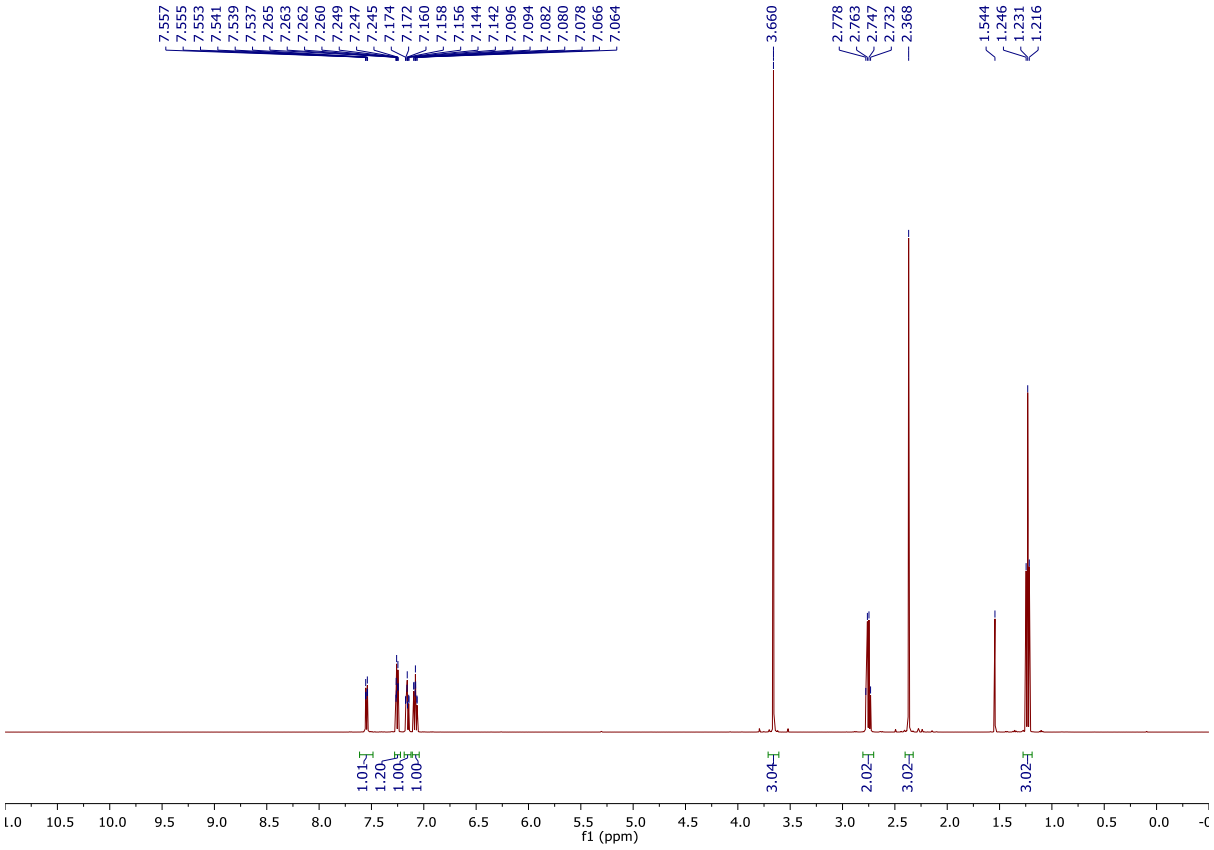


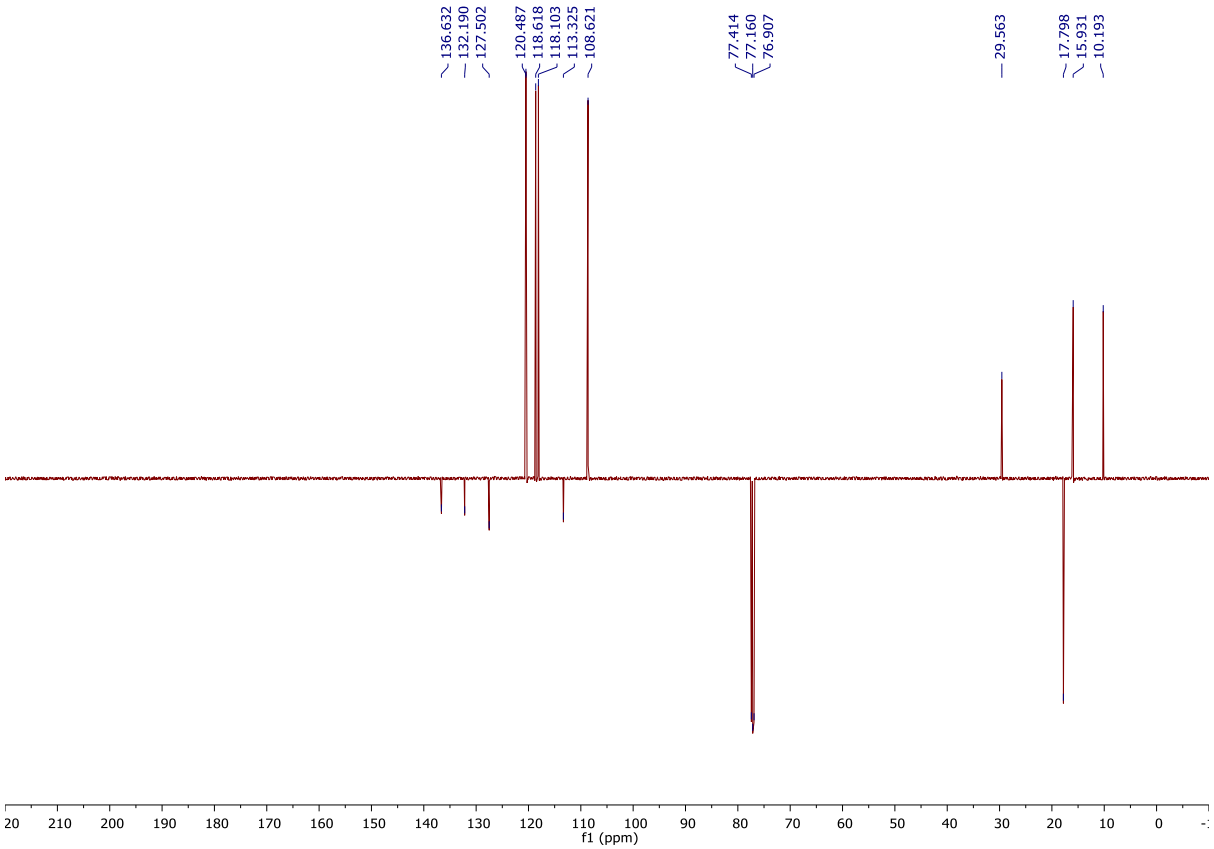
3-Ethyl-1,2-dimethyl-1H-indole 10a



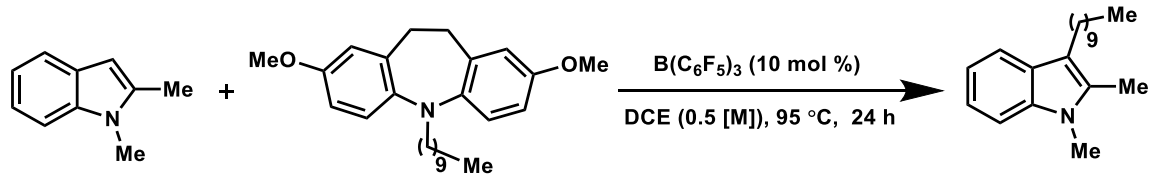
1a, 1.0 equiv **6b, 1.2 equiv** **10a**

In a nitrogen-filled glove box, a 10 mL vial equipped with a magnetic stirrer bar was charged with the 1,2-dimethylindole **1a** (29.0 mg, 0.2 mmol), 5-ethyl-2,8-dimethoxy-10,11-dihydro-5H-dibenzo[*b*,*f*]azepine **6b** (68.0 mg, 0.24 mmol), $B(C_6F_5)_3$ (10.2 mg, 0.02 mmol) and DCE (0.4 mL). The vial was sealed with an aluminium crimped cap and was left to stir at 95 °C for 24 h. The reaction mixture was then directly loaded into the column for purification. Purification by flash silica chromatography (eluent = 0.4% EtOAc in hexanes, 20 × 180 mm silica) gave the title compound **10a** as a light red oil (33.7 mg, 0.20 mmol, 97%); R_f = 0.28 (eluent = 2% EtOAc in hexanes); ν_{max} / cm^{-1} (film) 3051, 2959, 2926, 2855, 1614, 1570, 1472, 1408, 1370, 1330, 1269, 1240, 1186, 1128, 1067, 1013, 936, 843, 733, 569, 550, 432; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 1.23 (3H, *t*, *J* 7.6), 2.37 (3H, s), 2.75 (2H, q, *J* 7.6), 3.66 (3H, s), 7.04–7.11 (1H, m), 7.12–7.19 (1H, m), 7.22–7.28 (1H, m), 7.55 (1H, dt, *J* 7.7, 1.0); ^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 10.2, 15.9, 17.8, 29.6, 108.6, 113.3, 118.1, 118.6, 120.5, 127.5, 132.2, 136.6; HRMS $(ES)^+$ calculated for $[C_{12}H_{16}N]^+$ $(M+H)^+$ m/z: 174.1283, found 174.1280 (-1.7 ppm).


7.557
7.555
7.553
7.541
7.539
7.537
7.265
7.263
7.262
7.260
7.249
7.247
7.245
7.174
7.172
7.160
7.158
7.156
7.144
7.142
7.096
7.094
7.082
7.080
7.078
7.066
7.064
3.660
2.778
2.763
2.747
2.732
2.368
1.544
1.246
1.231
1.216
1.01
1.20
1.00
1.00
3.04
2.02
3.02
3.02
f1 (ppm)

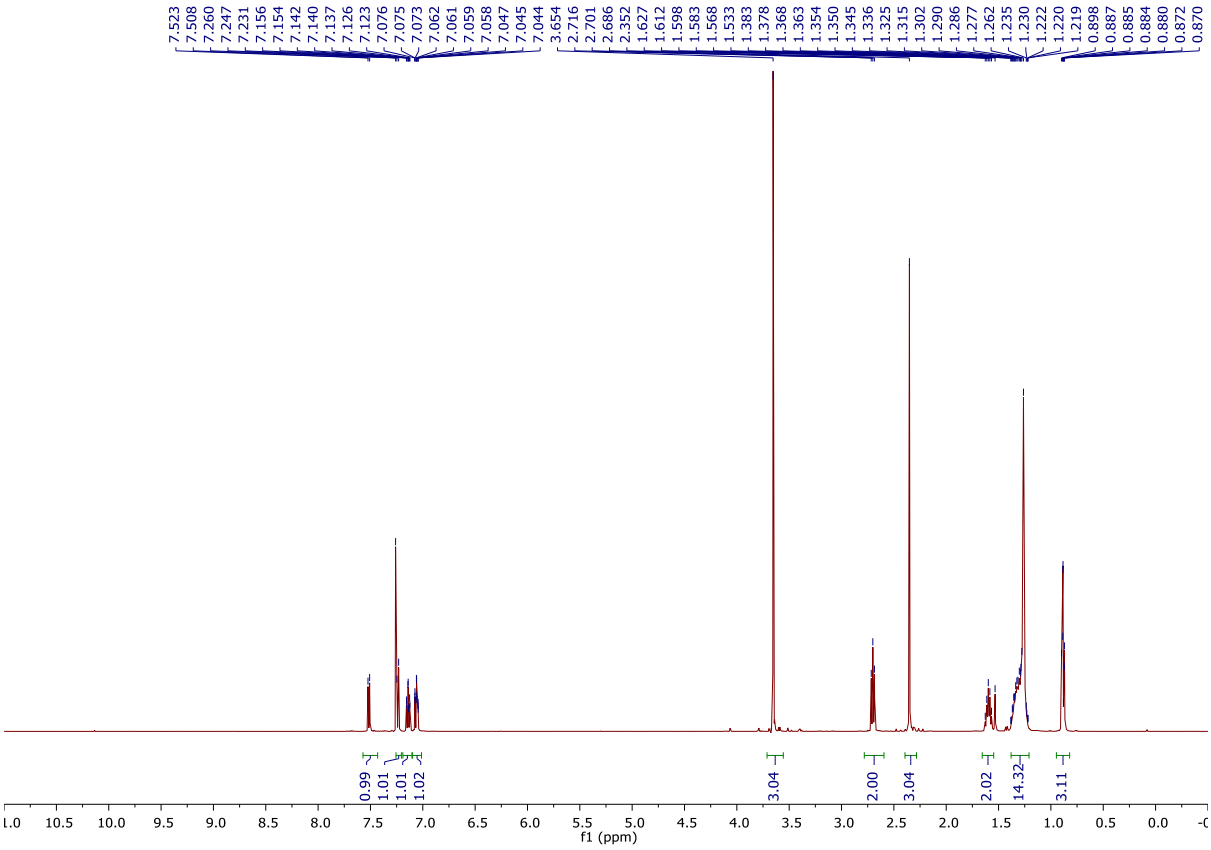

136.632
132.190
127.502
120.487
118.618
118.103
113.325
108.621
77.414
77.160
76.907
29.563
17.798
15.931
10.193
f1 (ppm)

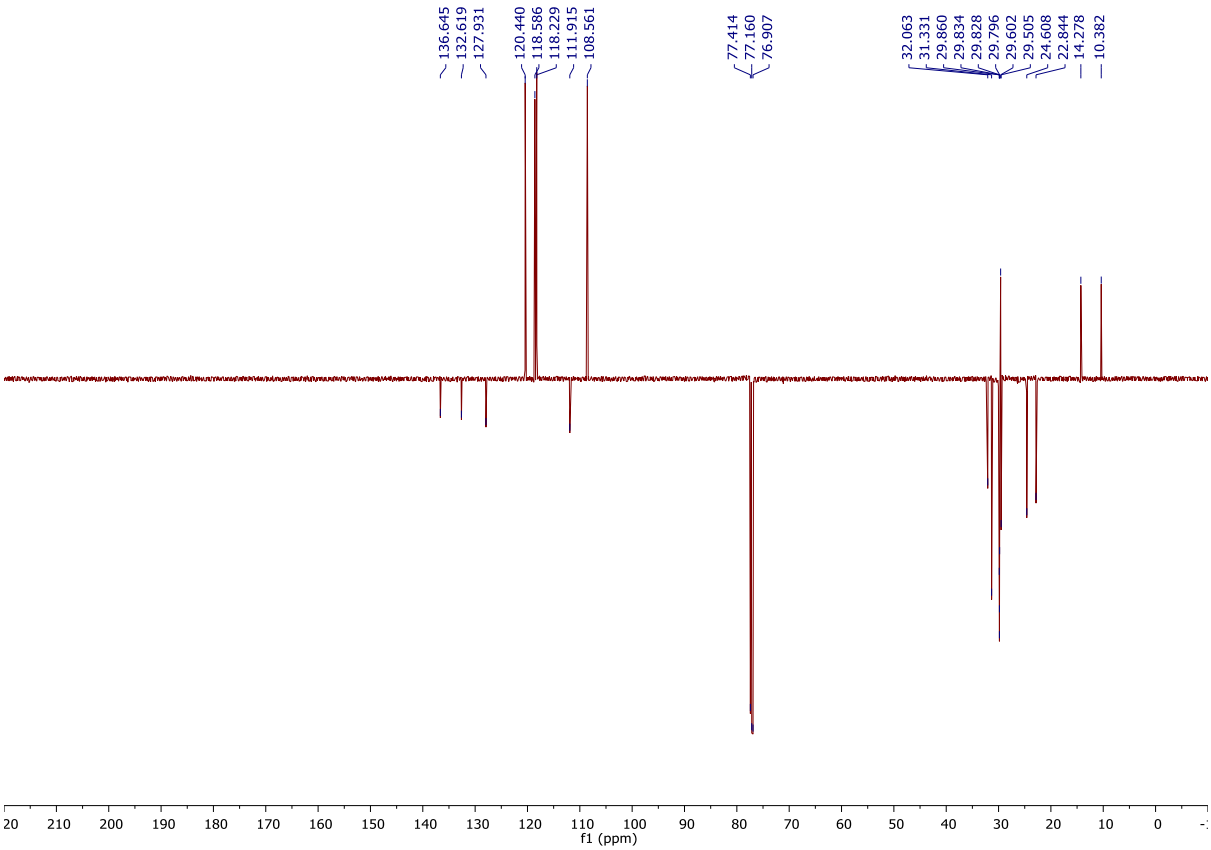
3-Decyl-1,2-dimethyl-1H-indole 11a



1a, 1.0 equiv **6c, 1.2 equiv** **11a**

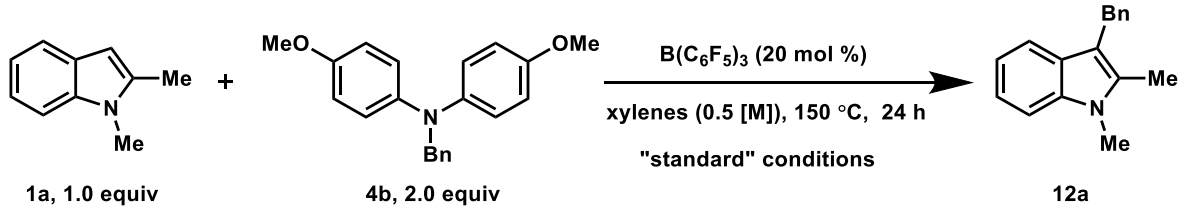
In a nitrogen-filled glove box, a 10 mL vial equipped with a magnetic stirrer bar was charged with the 1,2-dimethylindole **1a** (29.0 mg, 0.2 mmol), 5-decyl-2,8-dimethoxy-10,11-dihydro-5H-dibenzo[*b*,*f*]azepine **6c** (94.9 mg, 0.24 mmol), $B(C_6F_5)_3$ (10.2 mg, 0.02 mmol) and DCE (0.4 mL). The vial was sealed with an aluminium crimped cap and was left to stir at 95 °C for 24 h. The reaction mixture was then directly loaded into the column for purification. Purification by flash silica chromatography (eluent = 0.3% EtOAc in hexanes, 20 × 180 mm silica) gave the title compound **11a** as a light red oil (52.1 mg, 0.18 mmol, 91%); R_f = 0.35 (eluent = 2% EtOAc in hexanes); ν_{max} / cm^{-1} (film) 2920, 2851, 1614, 1568, 1472, 1439, 1410, 1370, 1331, 1244, 1188, 1015, 910, 802, 733, 559, 432; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 0.82–0.95 (3H, m), 1.21–1.38 (14H, m), 1.55–1.66 (2H, m), 2.35 (3H, s), 2.70 (2H, t, *J* 7.6), 3.65 (3H, s), 7.01–7.10 (1H, m), 7.10–7.19 (1H, m), 7.24 (1H, d, *J* 8.1), 7.52 (1H, d, *J* 7.8); ^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 10.4, 14.3, 22.8, 24.6, 29.5, 29.6, 29.8, 29.8, 29.8, 29.9, 31.3, 32.1, 108.6, 111.9, 118.2, 118.6, 120.4, 127.9, 132.6, 136.7; HRMS (ES)$^+$ calculated for $[C_{20}H_{32}N]^+$ $(M+H)^+$ m/z: 286.2535, found 286.2535 (+0.0 ppm).





3-Benzyl-1,2-dimethyl-1H-indole 12a

Table S6. Optimization for the C3 benzylation of 1,2-dimethylindole



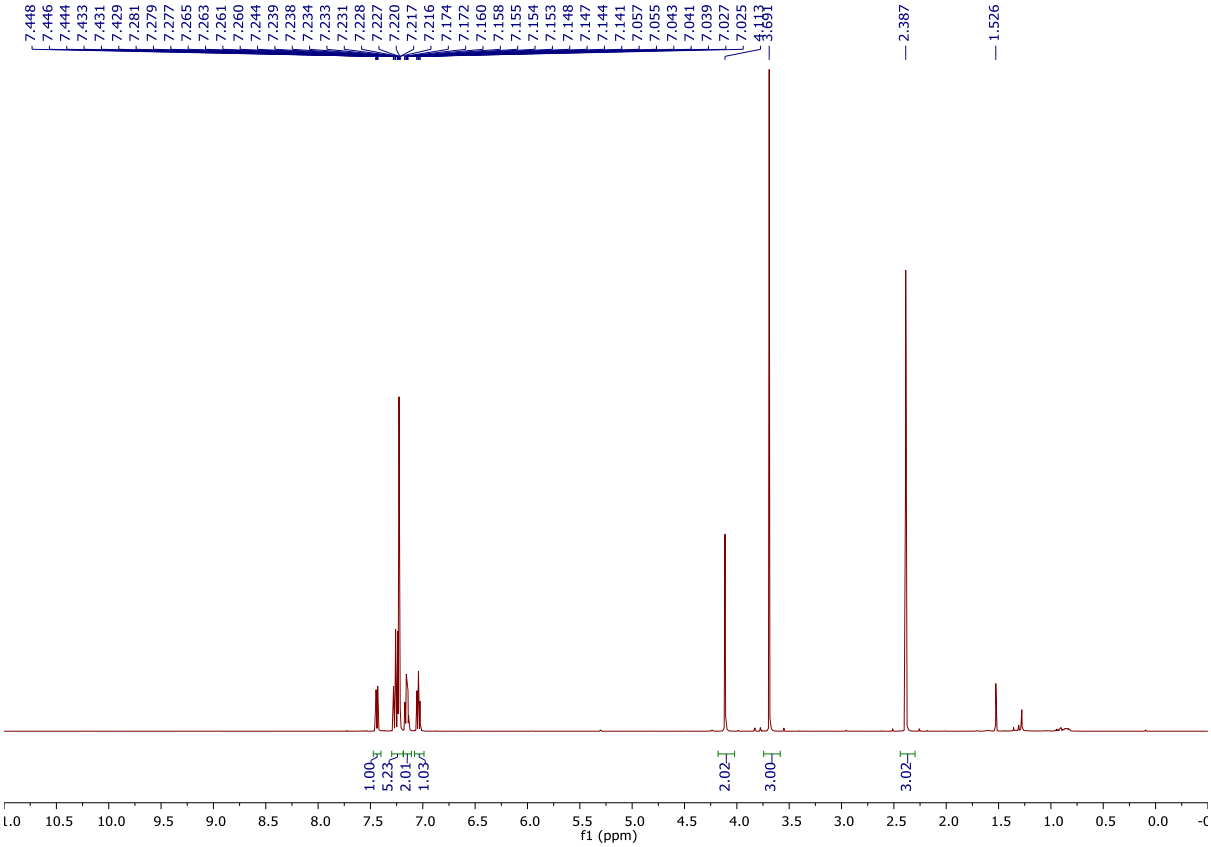
1a, 1.0 equiv | 4b, 2.0 equiv | 12a

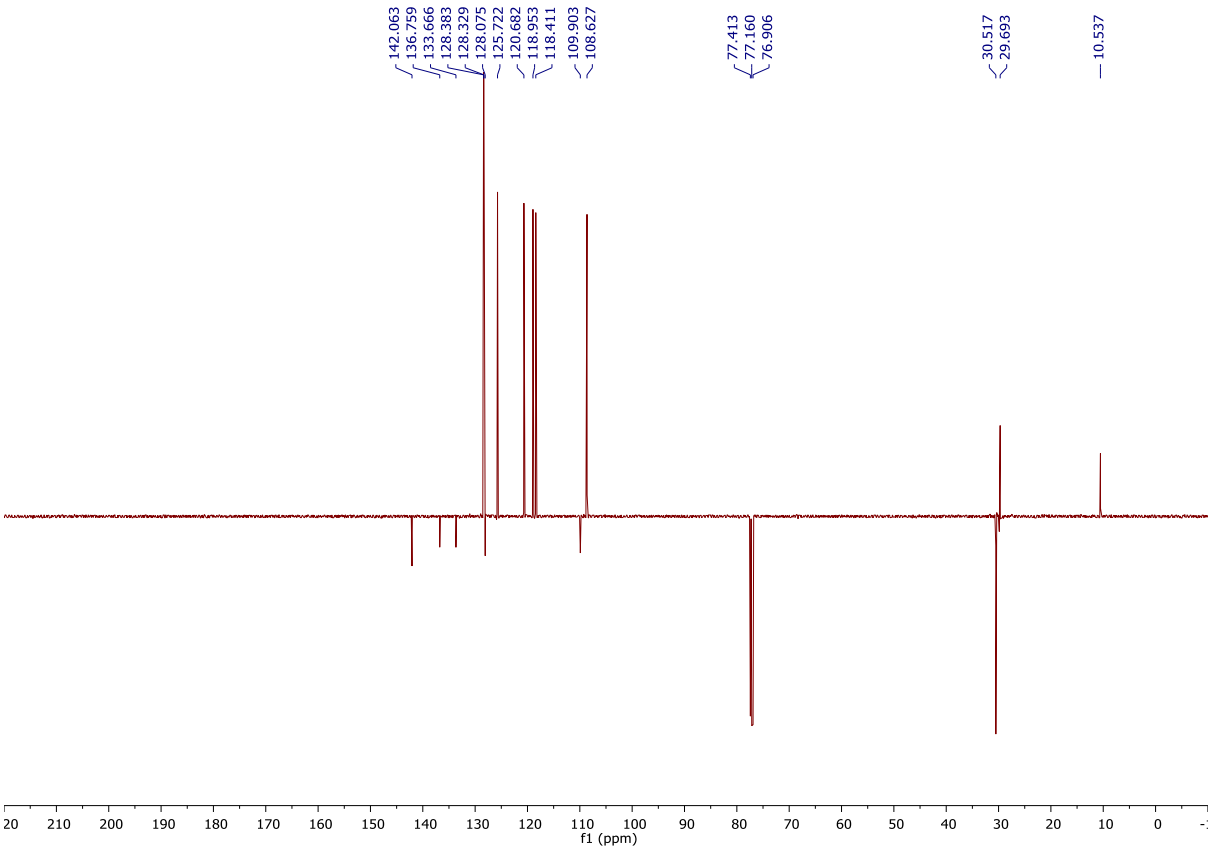
Entry[a]	Variation from "standard" conditions	Yield[b] [%]
1	none	~90[c]
2	**4b** (1.2 equiv)	~82[c]
3	**4b** (1.2 equiv), BCF (10 mol %)	~57[c]
4	**6d** (1.2 equiv), BCF (10 mol %)	47
5	**6d** (1.2 equiv), BCF (10 mol %), DCE, 25 °C, 16 h	0
6	**6d** (1.2 equiv), BCF (10 mol %), DCE, 95 °C, 16 h	43

[a] Reactions were performed using 0.2 mmol of 1,2-dimethylindole in its 0.5 [M] solution of desired solvent. [b] Yields were determined by ^{1}H NMR analysis of the crude reaction mixture with 1,3,5-trimethylbenzene as the internal standard. [c] For reactions with **4b**, internal standard peak slightly overlapped with other peaks, so approximate NMR yields are reported.

In a nitrogen-filled glove box, a 10 mL vial equipped with a magnetic stirrer bar was charged with the 1,2-dimethylindole **1a** (29.0 mg, 0.2 mmol), N-benzyl-4-methoxy-N-(4-methoxyphenyl)aniline **4b** (128 mg, 0.4 mmol), $B(C_6F_5)_3$ (20.5 mg, 0.04 mmol) and xylenes (0.4 mL). The vial was sealed with an aluminium crimped cap and was left to stir at 150 °C for 24 h. The reaction mixture was then directly

loaded into the column for purification. Purification by flash silica chromatography (eluent = 0.6% EtOAc in hexanes, 20 × 180 mm silica) gave the title compound **12a** as a light yellow gummy oil (44.7 mg, 0.19 mmol, 95%); R_f = 0.29 (eluent = 2% EtOAc in hexanes); ν_{max} / cm^{-1} (film) 3024, 2909, 1601, 1566, 1493, 1472, 1452, 1431, 1408, 1368, 1329, 1248, 1198, 1179, 1128, 1053, 1017, 934, 843, 804, 733, 700, 596, 554, 457, 434; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 2.39 (3H, s), 3.69 (3H, s), 4.11 (2H, s), 7.04 (1H, ddd, *J* 8.0, 7.0, 1.0), 7.10–7.19 (2H, m), 7.19–7.29 (5H, m), 7.44 (1H, dt, *J* 7.9, 0.9); ^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 10.5, 29.7, 30.5, 108.6, 109.9, 118.4, 119.0, 120.7, 125.7, 128.1, 128.3, 128.4, 133.7, 136.8, 142.1m; HRMS (AP)$^+$ calculated for $[C_{17}H_{18}N]^+$ $(M+H)^+$ m/z: 236.1439, found 236.1436 (-1.3 ppm).





2.6. The use of $H_2O{\cdot}B(C_6F_5)_3$ in the borane-catalyzed alkylation of indoles and oxindoles

General procedure 9: C3 methylation and benzylation of indoles and oxindoles

The following procedure was used to prepare active $B(C_6F_5)_3$ after forming $H_2O{\cdot}B(C_6F_5)_3$ as a result of weighing commercially received $B(C_6F_5)_3$ on an open bench.

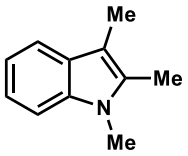
An oven-dried J. Youngs flask equipped with a stir bar was cooled under vacuum and charged with N_2 gas. $B(C_6F_5)_3$ (10.2 mg, 0.02 mmol) as received from the supplier was added to the J. Youngs flask and the atmosphere cycled three times *via* vacuum-N_2 backfills. Using standard syringe-septa techniques, desired anhydrous solvent (0.15 mL, used as received, no further drying was required) was added. The mixture was stirred and Et_3SiH (6.4 µL, 0.04 mmol) was added. Effervescence was observed and ceased within 15 seconds. The mixture was stirred for 10 minutes.

We found it convenient to prepare larger batches of active $B(C_6F_5)_3$ solutions the same day as its intended use by simply scaling up the above procedure and then removing desired aliquots and dosing into reactions vessels using standard syringe-septa techniques.

Indole **1** or oxindole **8** (0.20 mmol) and alkylating agent (0.24 mmol) were weighed into a vial and sealed with a septa. The atmosphere in the vial was cycled three times *via* vacuum-N_2 backfills and the indole/amine mixture was subsequently dissolved in the reaction solvent (0.2 mL). The solution was transferred to the J. Youngs flask containing active $B(C_6F_5)_3$ using standard syringe-septa techniques. The vial was washed with the reaction solvent (0.15 mL) and the washings were transferred to the reaction flask. The J. Youngs flask was sealed and the mixture was stirred for the stated time at the

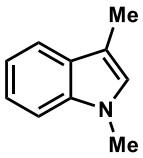
stated temperature. Saturated $NaHCO_3$ (1.5 mL) was added and the mixture vigorously stirred. The aqueous phase was separated and extracted with CH_2Cl_2 (3 × 2 mL). The combined organic phases were dried over $MgSO_4$ and the volatiles removed *in vacuo*. An NMR spectroscopic yield was obtained using $MeNO_2$ as an internal standard.

1,2,3-Trimethyl-1H-indole 2a



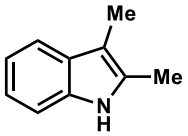
Following general procedure 9, using 1,2-dimethyl indole **1a** (29.0 mg, 0.20 mmol), amine **6a** (64.6 mg, 0.24 mmol), $B(C_6F_5)_3$ (10.2 mg, 0.02 mmol, 10 mol %), Et_3SiH (6.4 µL, 0.04 mmol), DCE (0.5 mL), 16 h at 25 °C, gave the title compound **2a** (81% spectroscopic yield).

1,3-Dimethyl-1H-indole 2f



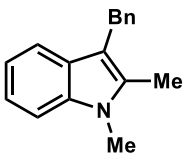
Following general procedure 9, using 1-methyl-1H-indole **1f** (26.2 mg, 0.20 mmol), amine **6a** (64.6 mg, 0.24 mmol), $B(C_6F_5)_3$ (20.5 mg, 0.04 mmol, 20 mol %), Et_3SiH (12.8 µL, 0.08 mmol), DCE (0.5 mL), 8 h at 95 °C, gave the title compound **2f** (65% spectroscopic yield).

2,3-Dimethyl-1H-indole 2l



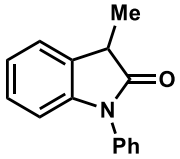
Following general procedure 9, 2-methyl-1H-indole **1l** (26.2 mg, 0.20 mmol), amine **6a** (64.6 mg, 0.24 mmol), TMP (3.4 µL, 0.02 mmol, 10 mol %) added after the indole/amine mixture, $B(C_6F_5)_3$ (10.2 mg, 0.02 mmol, 10 mol %), Et_3SiH (6.4 µL, 0.04 mmol), toluene (0.5 mL), 16 h at 110 °C, gave the title compound **2l** (75% spectroscopic yield).

3-Benzyl-1,2-dimethyl-1H-indole 12a



Following general procedure 9, 1,2-dimethylindole **1a** (72.6 mg, 0.50 mmol), amine **4b** (192 mg, 0.60 mmol), $B(C_6F_5)_3$ (51.2 mg, 0.10 mmol, 20 mol %), Et_3SiH (31.9 µL, 0.20 mmol), *p*-xylene (1.2 mL), 16 h at 150 °C, gave the title compound **12a** (63% spectroscopic yield).

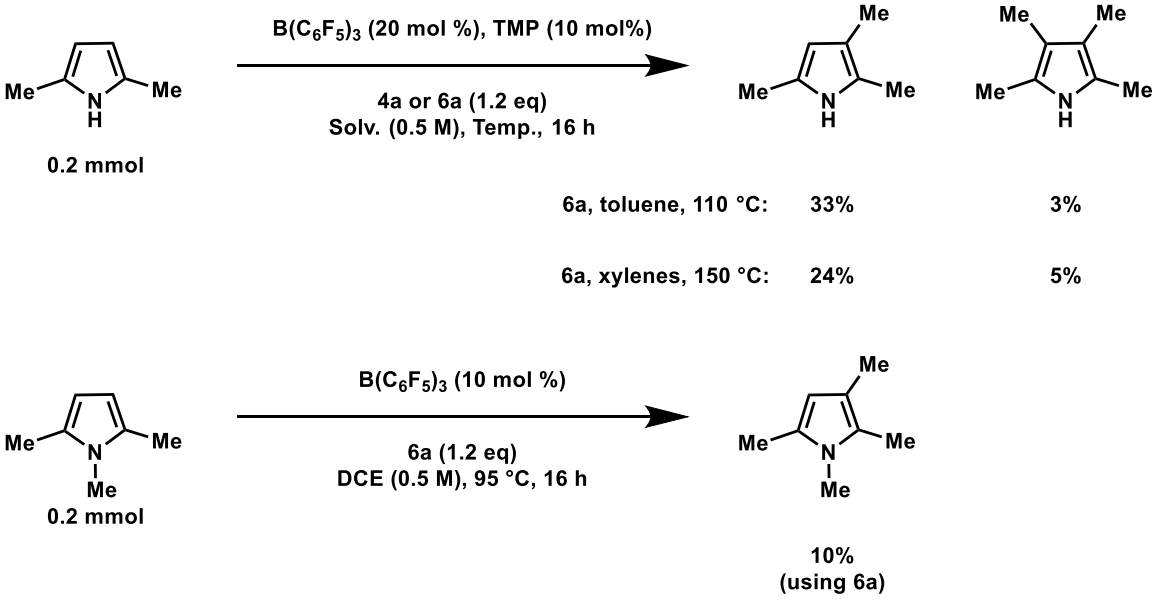
3-Methyl-1-phenylindolin-2-one 9a



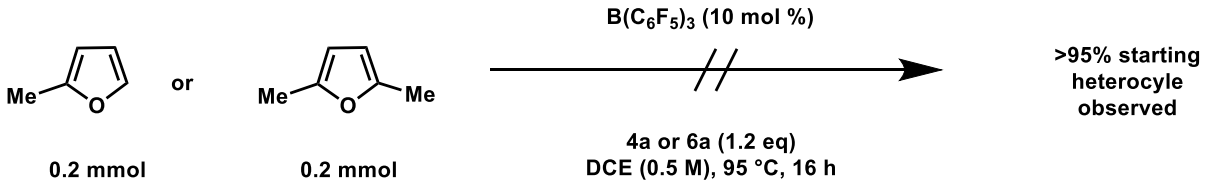
Following general procedure 9, 1-phenylindolin-2-one **8a** (105 mg, 0.50 mmol), PMP **13** (181 µL, 1.0 mmol), $B(C_6F_5)_3$ (25.6 mg, 0.05 mmol, 10 mol %), Et_3SiH (16.0 µL, 0.10 mmol), *p*-xylene (1.2 mL), 16 h at 150 °C, gave the title compound **9a** (42% spectroscopic yield). Following a modified general procedure 9, using 1-phenylindolin-2-one **8a** (42 mg, 0.20 mmol), PMP **13** (72 µL, 1.0 mmol), $B(C_6F_5)_3$ (10.2 mg, 0.02 mmol, 10 mol %), Et_3SiH (6.4 µL, 0.04 mmol), *p*-xylene (0.5 mL), 16 h at 150 °C, and removing the $O(SiEt_3)_2$ by-product from the $B(C_6F_5)_3$ solution by applying dynamic vacuum (aprox. 1 mbar) for 3 h at 60 °C prior to adding the oxindole and PMP, gave **9a** (64% spectroscopic yield). Following a modified general procedure 9, using 1-phenylindolin-2-one **8a** (42 mg, 0.20 mmol), PMP **13** (72 µL, 1.0 mmol), $B(C_6F_5)_3$ (20.4 mg, 0.04 mmol, 10 mol %), Et_3SiH (13 µL, 0.08 mmol), *p*-xylene (0.5 mL), 16 h at 150 °C, and removing the $O(SiEt_3)_2$ by-product from the $B(C_6F_5)_3$ solution by applying dynamic vacuum (aprox. 1 mbar) for 3 h at 60 °C prior to adding the oxindole and PMP, gave **9a** (80% spectroscopic yield).

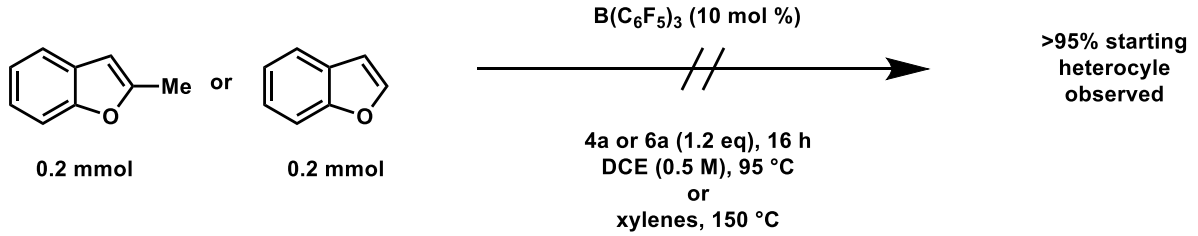
2.7. Attempted $B(C_6F_5)_3$-catalyzed alkylation of other electron rich heterocycles

Pyrroles:

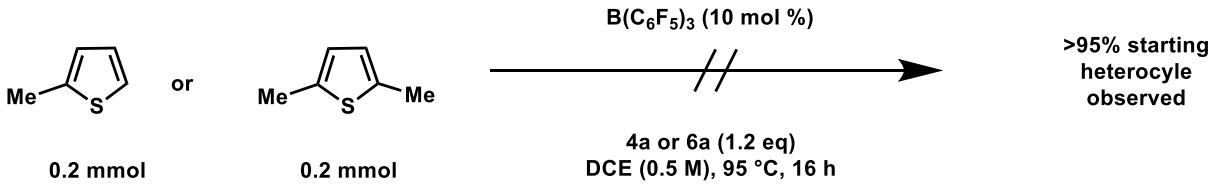


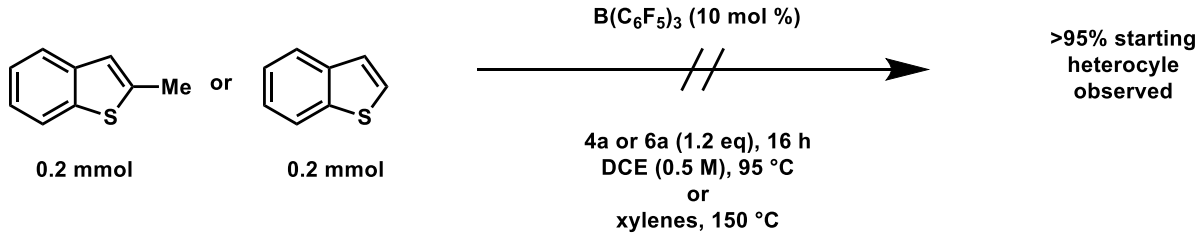
Furans and benzofurans:



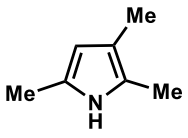


Thiophenes and benzothiophenes



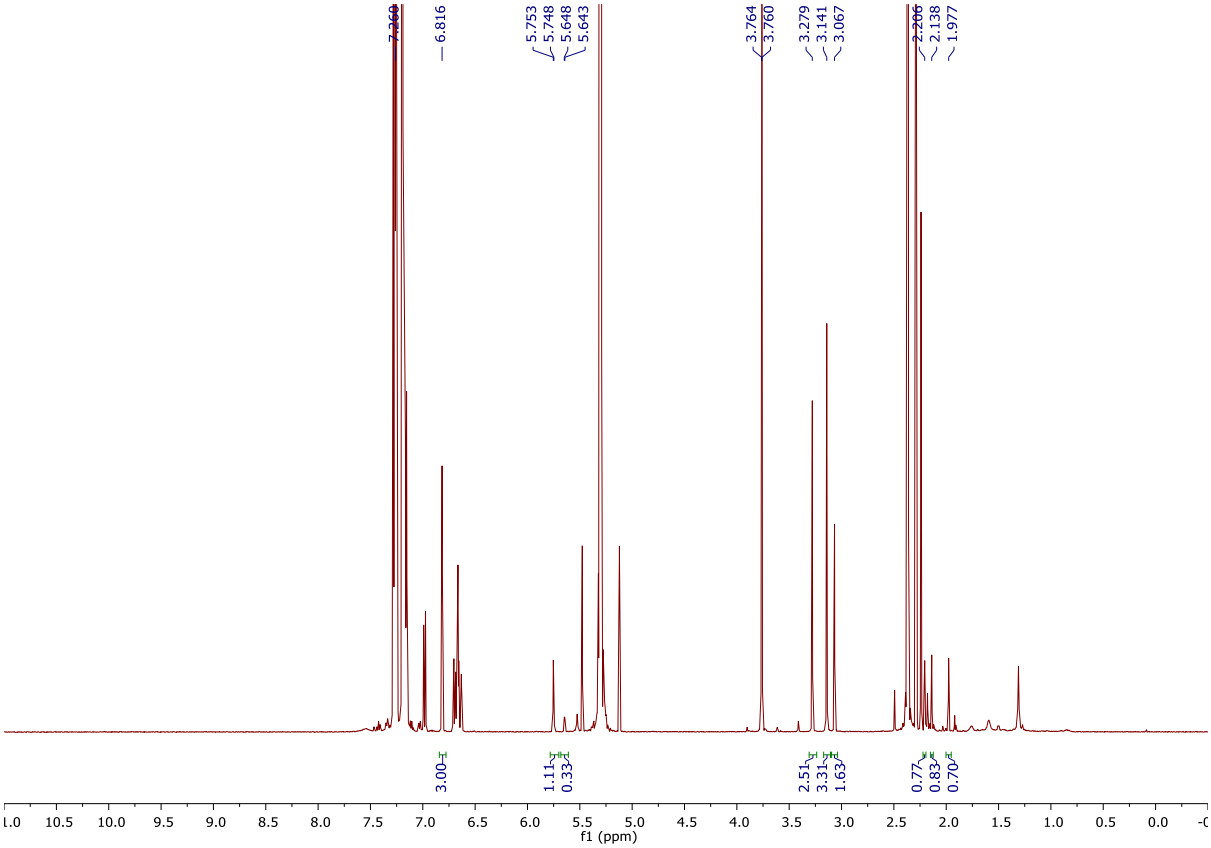


2,3,5-Trimethyl-1H-pyrrole



In a nitrogen-filled glove box, a 10 mL vial equipped with a magnetic stirrer bar was charged with the 2,5-dimethyl-1H-pyrrole (19.0 mg, 0.2 mmol), **6a** (64.6 mg, 0.24 mmol), 2,2,6,6-tetramethylpiperidine (TMP) (3.4 µL, 0.02 mmol), $B(C_6F_5)_3$ (20.5 mg, 0.04 mmol) and toluene (0.4 mL). The vial was sealed with an aluminium crimped cap and was left to stir at 110 °C for 16 h. The title compound was obtained in 33% yield (determined by ^1H NMR analysis of the crude reaction mixture with 1,3,5-trimethylbenzene as the internal standard). Spectroscopic data of the product in the crude reaction mixture in accordance with that stated in the literature.[32]

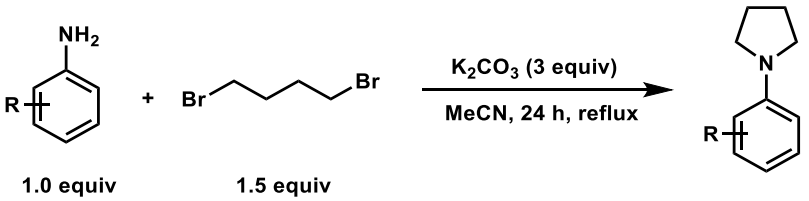
Following is the ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of the crude reaction mixture with 1,3,5-trimethylbenzene as the internal standard.



Reported Spectroscopic data of 2,3,5-trimethyl-1H-pyrrole: ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 5.64 (d, 1H, *J* 2.4 Hz, CH), 2.21 (s, 3H, CH_3), 2.14 (s, 3H, CH_3), 1.97 (s, 3H, CH_3).[32]

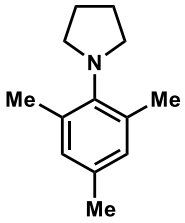
2.8. Synthesis of pyrrolidines 14a–d

General procedure 10: N-heterocyclisation of aryl amines



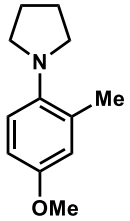
Aniline derivative (1 equiv), K_2CO_3 (3 equiv), 1,4-dibromobutane (1.5 equiv) and MeCN (1.5 mL/mmol) were successively added to a round-bottom flask equipped with a magnetic stir bar. The suspension was stirred under reflux for 24 h after which time sat. $NaHCO_3$ (4 mL/mmol) and EtOAc (4 mL/mmol) were added. The phases were separated, and the aqueous phase was extracted with EtOAc (4 mL/mmol × 3). The combined organic phases were washed with water (8 mL/mmol), brine (8 mL/mmol) and dried over $MgSO_4$. After filtration, the volatiles were removed *in vacuo* and the crude product was purified *via* flash column chromatography on silica gel to obtain the pure pyrrolidine (**14a**–**d**).

1-(2,4,6-Trimethylphenyl)pyrrolidine 14a



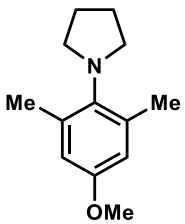
Following general procedure 10, the reaction of 2,4,6-trimethylaniline (2.00 g, 14.8 mmol) and 1,4-dibromobutane (2.65 mL, 22.2 mmol) gave, after purification by flash column chromatography on silica gel (eluent = 5% EtOAc in pet. ether), the title compound **14a** as an orange oil (1.53 g, 8.1 mmol, 55%); R_f = 0.6 (eluent = 5% EtOAc in pet. ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 1.99 (4H, AA'BB', m), 2.25 (6H, s), 2.28 (3H, s), 3.19 (4H, AA'BB', m), 6.88 (2H, s); ^{13}C NMR (101 MHz, $CDCl_3$) δ_C: 18.6 (CH_3), 20.8 (CH_3), 26.6 (CH_2), 50.2 (CH_2), 129.3 (CH), 134.5 (C), 138.2 (C), 142.8 (C-N). Spectroscopic data in accordance with that stated in the literature.[33]

1-(4-Methoxy-2-methylphenyl)pyrrolidine 14b



Following general procedure 10, the reaction of 4-methoxy-2-methylaniline (0.47 mL, 3.64 mmol) and 1,4-dibromobutane (0.65 mL, 5.47 mmol) gave, after purification by flash column chromatography on silica gel (eluent = 5% EtOAc in pet. ether), the title compound **14b** as an orange oil (420 mg, 2.2 mmol, 60%); R_f = 0.4 (eluent = 5% EtOAc in pet. ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 1.92 (4H, AA'BB', m), 2.31 (3H, s), 3.05–3.08 (4H, m), 3.77 (3H, s), 6.69 (1H, dd, *J* 8.6, 3.1), 6.80 (1H, d, *J* 3.1), 6.91 (1H, d, *J* 8.6); ^{13}C NMR (101 MHz, $CDCl_3$) δ_C: 19.8 (CH_3), 24.5 (CH_2), 51.6 (CH_2), 55.5 (OCH_3), 110.8 (CH), 117.3 (CH), 117.5 (CH), 132.0 (C), 143.1 (C-N), 154.2 (C). Spectroscopic data in accordance with that stated in the literature.[34]

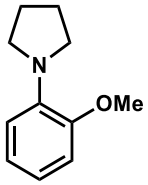
1-(4-Methoxy-2,6-dimethylphenyl)pyrrolidine 14c



Following general procedure 10, the reaction of 4-methoxy-2,6-dimethylaniline (700 mg, 4.63 mmol) and 1,4-dibromobutane (0.83 mL, 6.94 mmol) gave, after purification by flash column chromatography on silica gel (eluent = 10% EtOAc in pet. ether), the title compound **14c** as a brown oil (368 mg, 1.79

mmol, 39%); R_f = 0.6 (eluent = 10% EtOAc in pet. ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 1.97 (4H, AA'BB', m), 2.23 (6H, s), 3.15 (4H, AA'BB', m), 3.76 (3H, s), 6.60 (2H, s); ^{13}C NMR (101 MHz, $CDCl_3$) δ_C: 18.8 (CH_3), 26.6 (CH_2), 50.3 (CH_2), 55.2 (OCH_3), 113.5 (CH), 138.5 (C),139.7 (C-N), 156.5 (C). Spectroscopic data in accordance with that stated in the literature.[33]

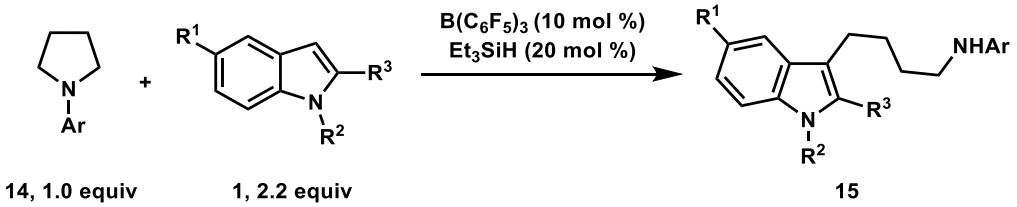
1-(2-Methoxyphenyl)pyrrolidine 14d



Following general procedure 10, the reaction of *o*-anisidine (1 g, 8.12 mmol) and 1,4-dibromobutane (0.97 mL, 8.11 mmol) gave, after purification by flash column chromatography on silica gel (eluent = 10% EtOAc in pet. ether), the title compound **14d** as a brown oil (550 mg, 3.1 mmol, 38%); R_f = 0.5 (eluent = 10% EtOAc in pet. ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 1.94 (4H, AA'BB', m), 3.30 (4H, AA'BB', m), 3.85 (3H, s), 6.79–6.94 (4H, m); ^{13}C NMR (101 MHz, $CDCl_3$) δ_C: 24.7 (CH_2) 50.5 (CH_2), 55.6 (OCH_3), 111.7 (CH), 117.5 (CH), 119.6 (CH),121.1 (CH), 140.0 (C), 150.5 (C-N). Spectroscopic data in accordance with that stated in the literature.[35]

2.9. $B(C_6F_5)_3$-catalyzed alkylation-ring opening cascade

General procedure 11: Synthesis of 4-(3-indolyl)butylamines



14, 1.0 equiv **1, 2.2 equiv** **15**

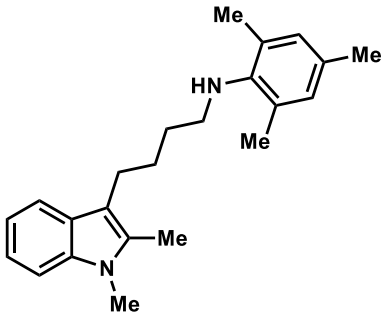
The following procedure was used to prepare active $B(C_6F_5)_3$ after forming $H_2O{\cdot}B(C_6F_5)_3$ as a result of weighing commercially received $B(C_6F_5)_3$ on an open bench. Anhydrous solvents were purchased (Sigma-Aldrich) and used as received without further purification.

An oven-dried J. Youngs flask equipped with a stir bar was cooled under vacuum and charged with N_2 gas. $B(C_6F_5)_3$ (10.2 mg, 0.02 mmol) as received from the supplier was added to the J. Youngs flask and the atmosphere cycled three times *via* vacuum-N_2 backfills. Using standard syringe-septa techniques, desired anhydrous solvent (0.15 mL) was added. The mixture was stirred and Et_3SiH (6.4 µL, 0.04 mmol) was added. Effervescence was observed and ceased within 15 seconds. The mixture was stirred for 10 min.

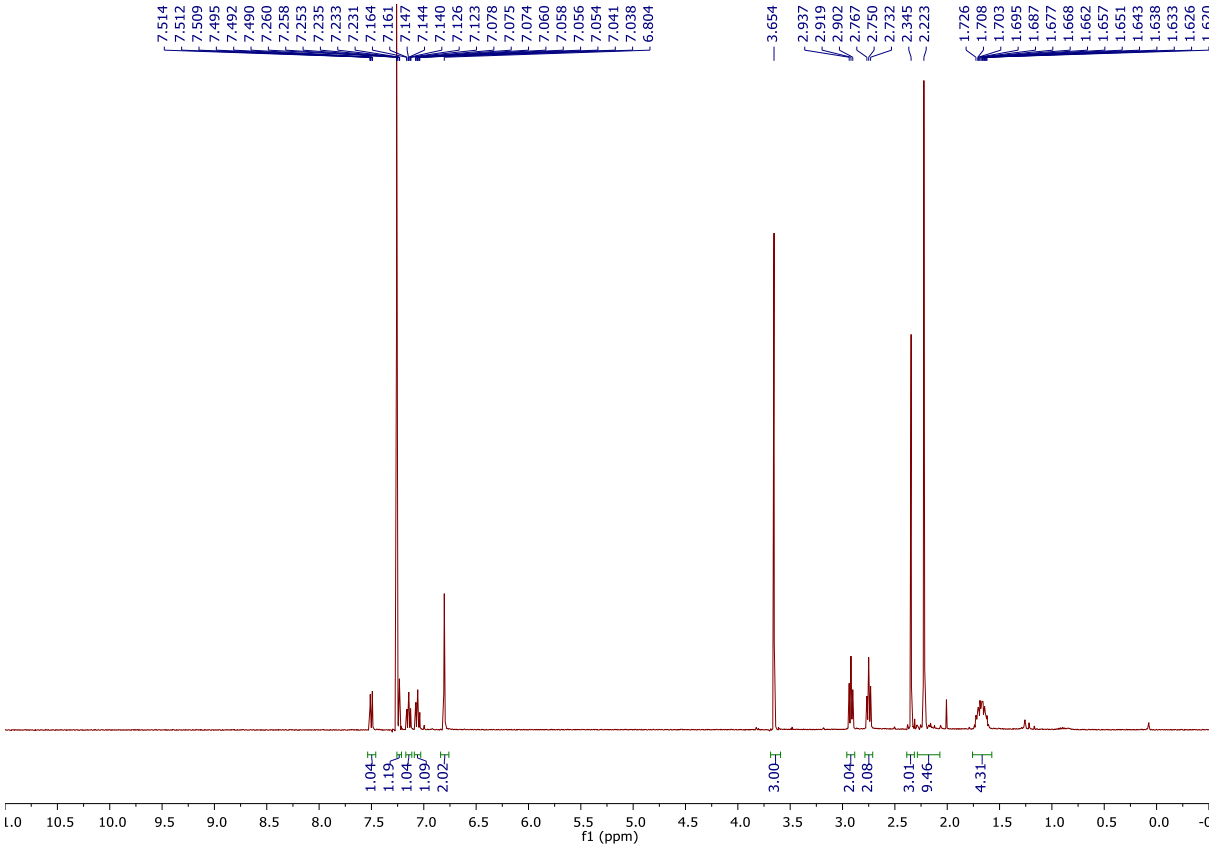
We found it convenient to prepare larger batches of active $B(C_6F_5)_3$ solutions the same day as its intended use by simply scaling up the above procedure and then removing desired aliquots and dosing into reactions vessels using standard syringe-septa techniques.

Indole **1** (0.44 mmol) and pyrrolidine **14** (0.20 mmol) were weighed into a vial and sealed with a septa. The atmosphere in the vial was cycled three times *via* vacuum-N_2 backfills and the indole/amine mixture was subsequently dissolved in the reaction solvent (0.2 mL). The solution was transferred to the J. Youngs flask containing active $B(C_6F_5)_3$ using standard syringe-septa techniques. The vial was washed with the reaction solvent (0.15 mL) and the washings were transferred to the reaction flask. The J. Youngs flask was sealed and the mixture was stirred for the stated time at the stated temperature. After cooling, sat. $NaHCO_3$ (1.5 mL) was added and the mixture was vigorously stirred. The aqueous phase was separated and extracted with CH_2Cl_2 (3 × 2mL). The combined organic phases were dried over $MgSO_4$ and the volatiles removed *in vacuo*. An NMR spectroscopic yield was obtained using $MeNO_2$ as an internal standard. The crude material was purified *via* flash column chromatography on silica gel to obtain the pure alkylated indole **15**.

***N*-(4-(1,2-Dimethyl-1H-indol-3-yl)butyl)-2,4,6-trimethylaniline 15a**



Following general procedure 11, using pyrrolidine **14a** (37.8 mg, 0.2 mmol), 1,2-dimethylindole **1a** (63.9 mg, 0.44 mmol), $B(C_6F_5)_3$ (10.2 mg, 0.02 mmol, 10 mol %), Et_3SiH (6.4 µL, 0.04 mmol) at 110 °C for 22 h in 1,2-$Cl_2C_6H_4$ gave compound **15a** (66% spectroscopic yield). Purification by flash silica chromatography (eluent = 60% CH_2Cl_2 in pet. ether or 10% EtOAc in pet. ether) gave the title compound **15a** as a dark yellow film (35 mg, 0.10 mmol, 52%); R_f = 0.2 (eluent = 5% EtOAc in pet. ether); ν_{max} / cm^{-1} (film) 3409, 2919, 2852, 1472, 1439, 1370, 1330, 1302, 1189, 1013, 853, 736; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 1.57–1.76 (4H, m), 2.21 (1H, br s), 2.22 (9H, s), 2.34 (3H, s), 2.75 (2H, t, *J* 7.1), 2.92 (2H, t, *J* 6.8), 3.65 (3H, s), 6.80 (2H, s), 7.06 (1H, ddd, *J* 8.0, 7.1, 1.0), 7.14 (1H, ddd, *J* 8.1, 6.9, 1.2), 7.21–7.26 (1H, s), 7.50 (1H, dt, *J* 7.8, 0.9); ^{13}C NMR (101 MHz, $CDCl_3$) δ_C: 10.4 (CH_3), 18.5 (CH_3), 20.7 (CH_3), 24.5 (CH_2), 28.9 (CH_2), 29.6 (CH_2), 31.3 (NCH_3), 49.1 (CH_2), 108.6 (C), 111.4 (CH), 118.2 (CH), 118.7 (CH), 120.6 (CH), 127.9 (C), 129.5 (C), 129.8 (CH), 131.2 (C), 132.8 (C), 136.7 (C), 143.9 (C-N); HRMS $(ESI)^+$ calculated for $[C_{23}H_{31}N_2]^+$ $(M+H)^+$ m/z: 335.2487, found 335.2487 (+0.0 ppm).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7.258
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7.235
7.233
7.231
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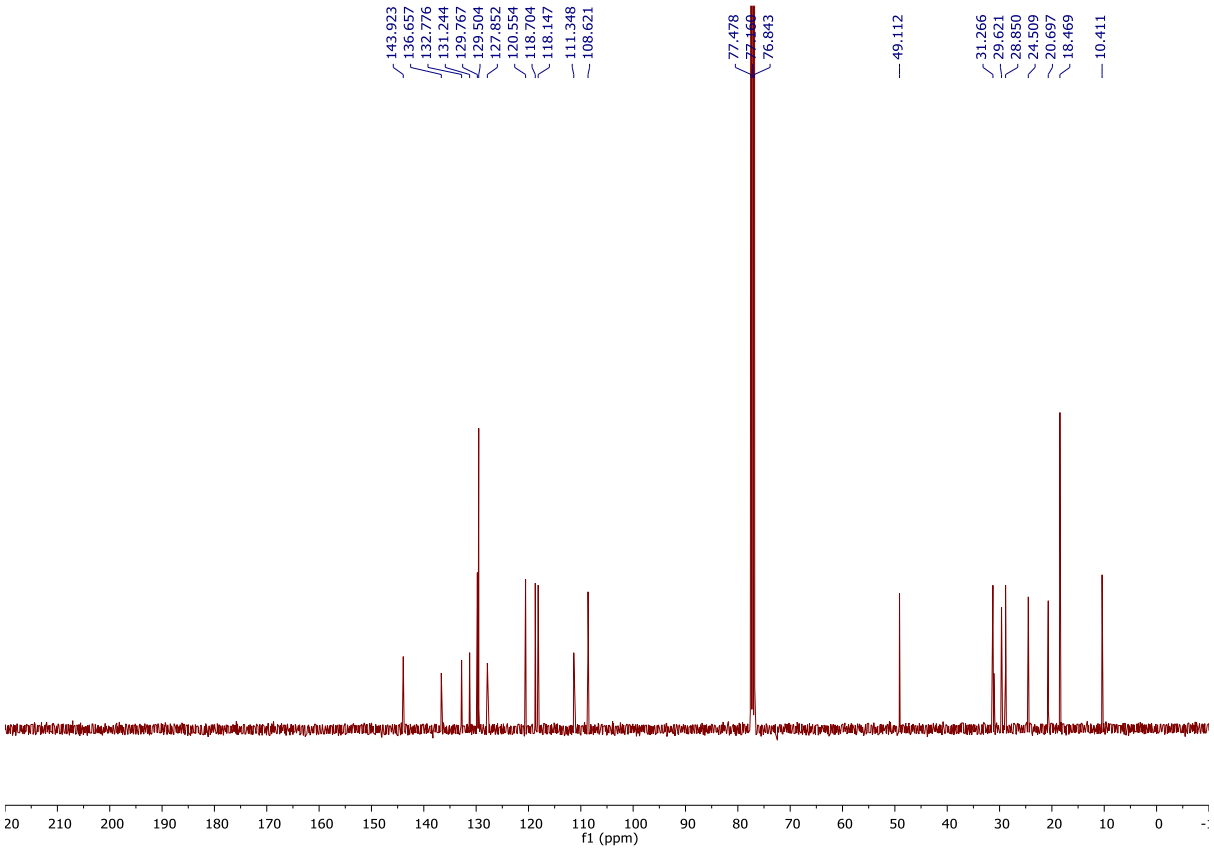
7.161
7.147
7.144
7.140
7.126
7.123
7.078
7.075
7.074
7.060
7.058
7.056
7.054
7.041
7.038
6.804
3.654
2.937
2.919
2.902
2.767
2.750
2.732
2.345
2.223
1.726
1.708
1.703
1.695
1.687
1.677
1.668
1.662
1.657
1.651
1.643
1.638
1.633
1.626
1.04
1.19
1.04
1.09
2.02
3.00
2.04
2.08
3.01
9.46
4.31
f1 (ppm)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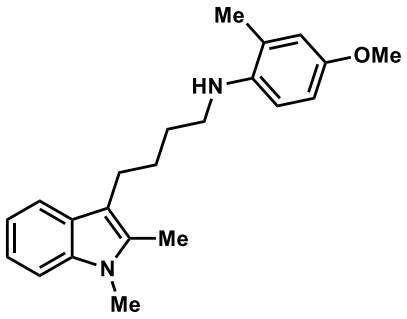
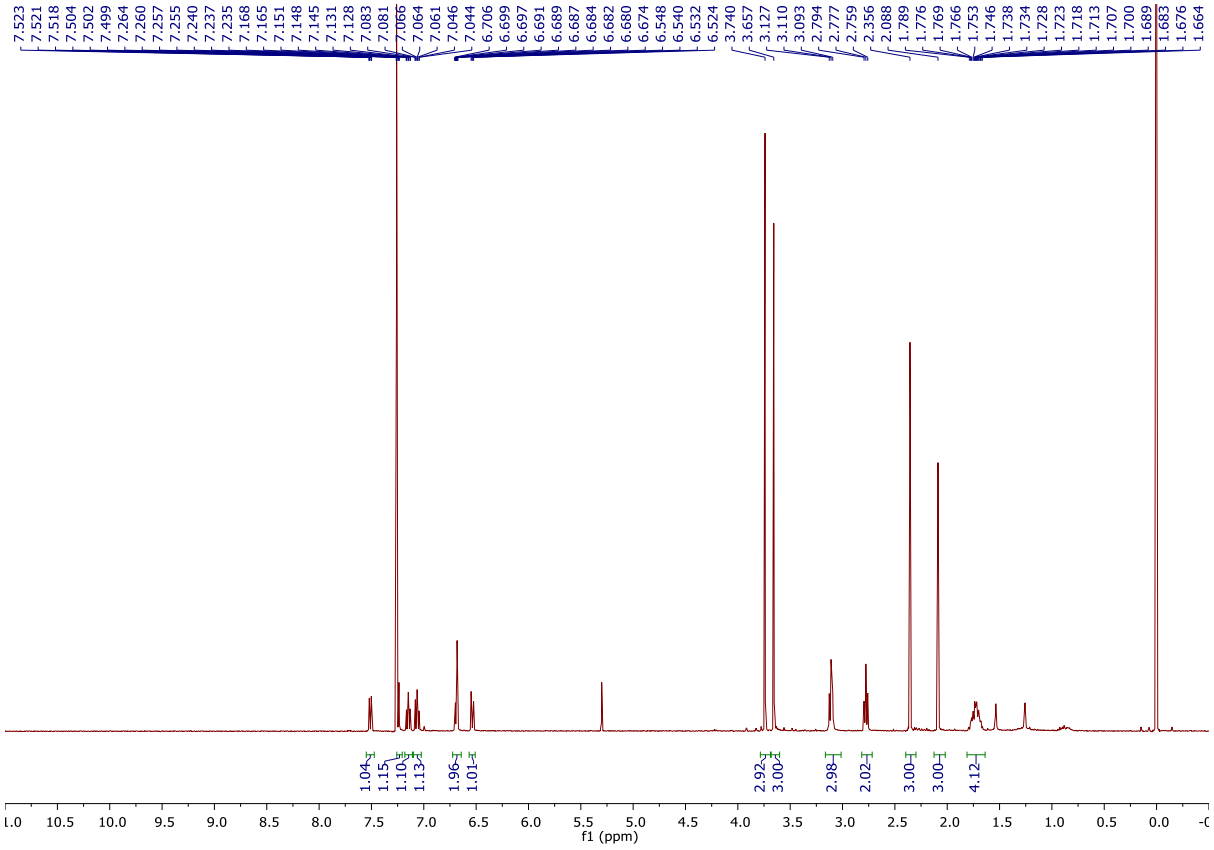
129.504
127.852
120.554
118.704
118.147
111.348
108.621
77.478
77.160
76.843
49.112
31.266
29.621
28.850
24.509
20.697
18.469
10.411
f1 (ppm)

***N*-(4-(1,2-Dimethyl-1H-indol-3-yl)butyl)-4-methoxy-2-methylaniline 15b**



Following general procedure 11, using pyrrolidine **14b** (35.4 mg, 0.20 mmol), 1,2-dimethylindole **1a** (63.9 mg, 0.44 mmol), $B(C_6F_5)_3$ (10.2 mg, 0.02 mmol, 10 mol %), Et_3SiH (6.4 µL, 0.04 mmol), at 110 °C for 22 h in 1,2-$Cl_2C_6H_4$ gave compound **15b** (72% spectroscopic yield). Purification by flash silica chromatography (eluent = 5% EtOAc in pet. ether) gave the title compound **15b** as a brown film (32 mg, 0.09 mmol, 46%); R_f = 0.1 (eluent = 5% EtOAc in pet. ether); ν_{max} / cm^{-1} (film) 3410, 2927, 2851, 1508, 1471, 1369, 1330, 1286, 1225, 1189, 1159, 1129, 1013, 924, 863, 798, 737; ^{1}NMR (400 MHz, $CDCl_3$) δ_H: 1.64–1.81 (4H, m), 2.09 (3H, s), 2.36 (3H, s), 2.78 (2H, t, *J* 7.0), 3.08 (1H, br s), 3.11 (2H, t, *J* 6.7), 3.66 (3H, s), 3.74 (3H, s), 6.51–6.57 (1H, m), 6.64–6.72 (2H, m), 7.06 (1H, ddd, *J* 8.0, 7.0, 1.1), 7.15 (1H, ddd, *J* 8.2, 7.0, 1.2), 7.21–7.27 (1H, m), 7.51 (1H, dt, *J* 7.8, 1.0); ^{13}C NMR (101 MHz, $CDCl_3$) δ_C: 10.4 (CH_3), 17.8 (CH_3), 24.4 (CH_2), 28.7 (CH_2), 29.6 (CH_2), 29.6 (NCH_3), 44.9 (CH_2), 55.9 (OCH_3), 108.6 (C), 111.0 (CH), 111.2 (CH), 111.7 (CH), 117.0 (CH), 118.1 (CH), 118.7 (CH), 120.6 (CH), 123.8 (C), 127.8 (C), 132.8 (C), 136.7 (C), 140.9 (C), 151.6 (C); HRMS $(ESI)^+$ calculated for $[C_{22}H_{29}N_2O]^+$ $(M+H)^+$ m/z: 337.2280, found 337.2285 (+1.5 ppm).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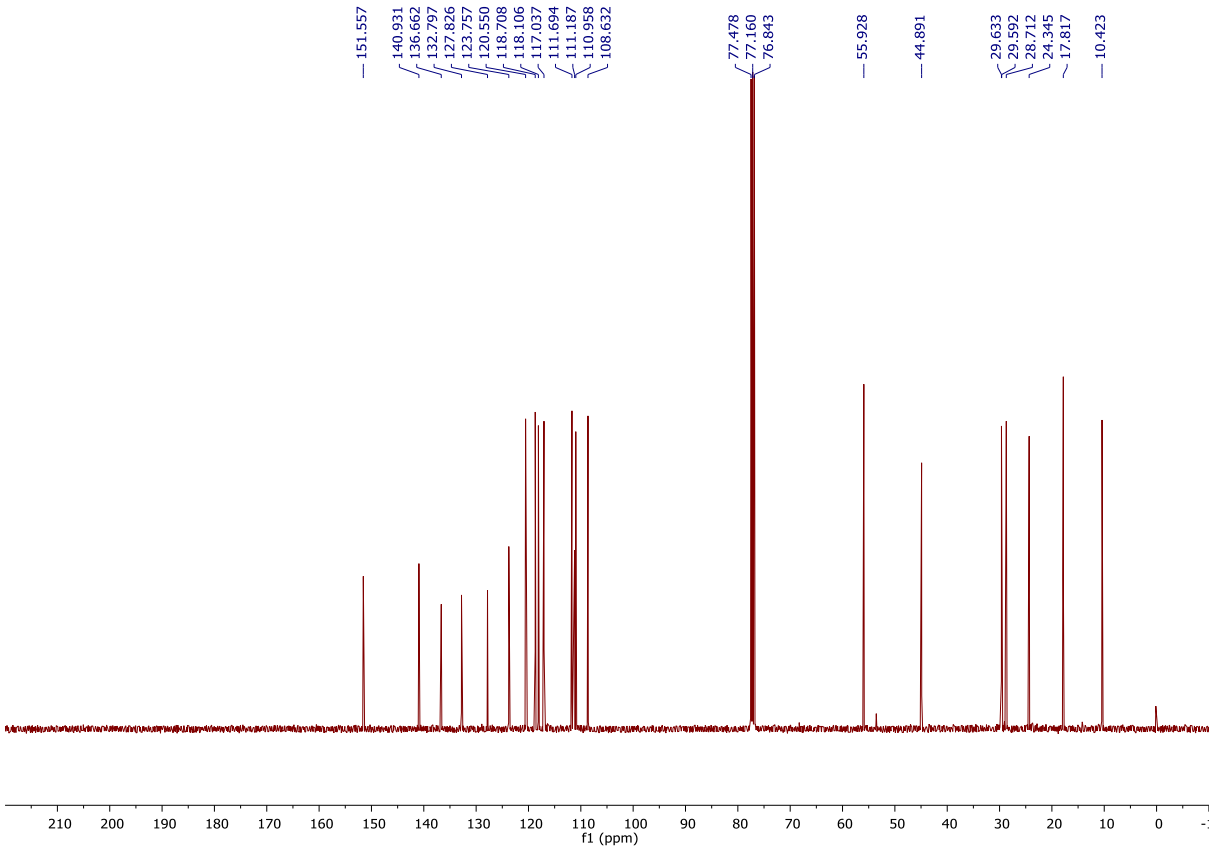
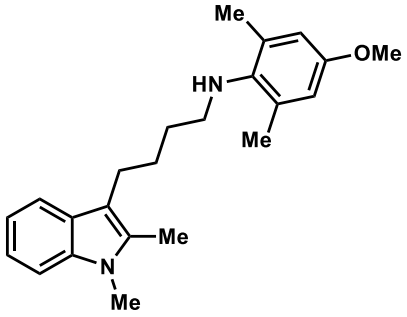
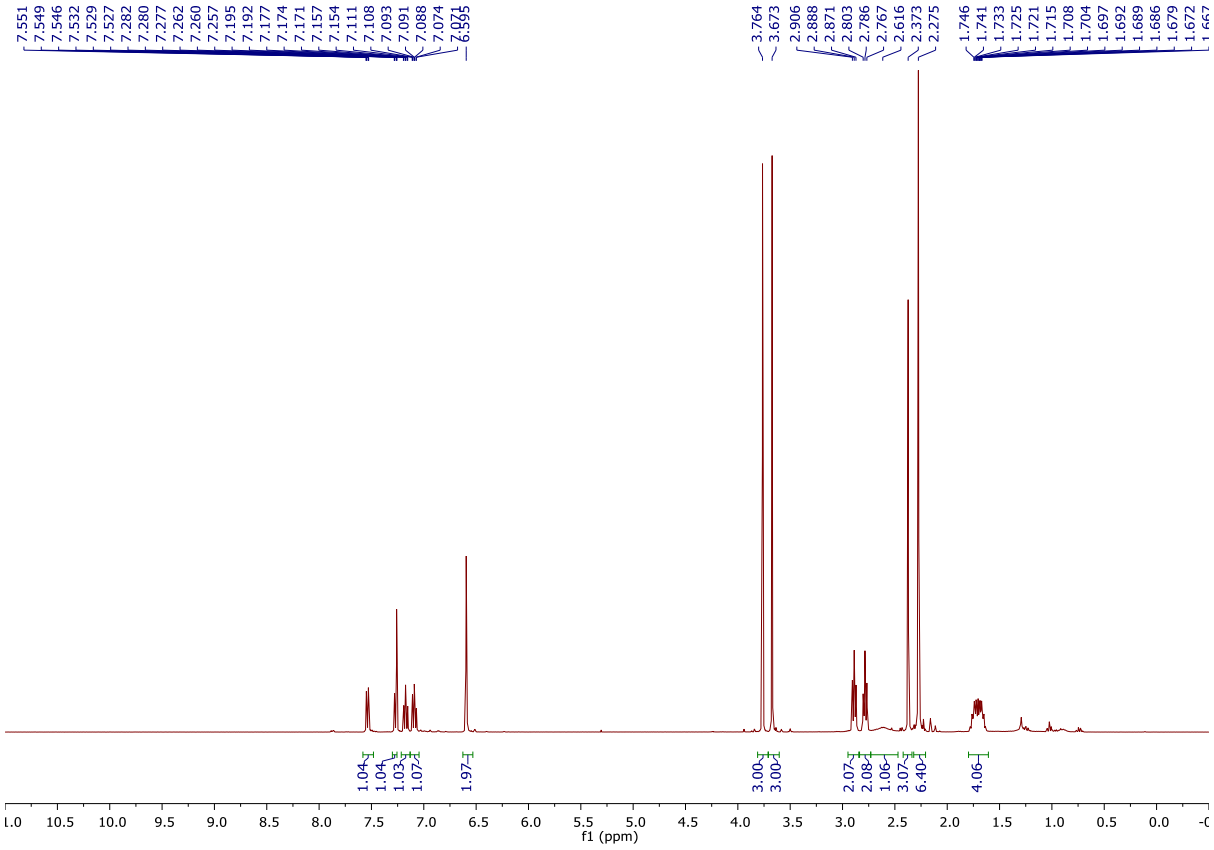
1.04 1.15 1.10 1.13 1.96 1.01 2.92 3.00 2.98 2.02 3.00 3.00 4.12
f1 (ppm)


151.557 140.931 136.662 132.797 127.826 123.757 120.550 118.708 118.106 117.037 111.694 111.187 110.958 108.632 77.478 77.160 76.843 55.928 44.891 29.633 29.592 28.712 24.345 17.817 10.423
f1 (ppm)

***N*-(4-(1,2-Dimethyl-1H-indol-3-yl)butyl)-4-methoxy-2,6-dimethylaniline 15c**



Following general procedure 11, using pyrrolidine **14c** (41.1 mg, 0.20 mmol), 1,2-dimethylindole **1a** (63.9 mg, 0.44 mmol), $B(C_6F_5)_3$ (10.2 mg, 0.02 mmol, 10 mol %), Et_3SiH (6.4 µL, 0.04 mmol) at 110 °C for 22 h in 1,2-$Cl_2C_6H_4$ gave compound **15c** (60% spectroscopic yield). Purification by flash silica chromatography (eluent = 60% CH_2Cl_2 in pet. ether or 10% EtOAc in pet. ether) gave the title compound **15c** as an orange film (31 mg, 0.09 mmol, 45%); R_f = 0.2 (eluent = 5% EtOAc in pet. ether); ν_{max} / cm^{-1} (film) 3375, 2933, 1602, 1471, 1369, 1317, 1217, 1191, 1150, 1065, 1014, 907, 855, 729, 647; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 1.61–1.80 (4H, m), 2.27 (6H, s), 2.37 (3H, s), 2.62 (1H, br s), 2.79 (2H, t, *J* 7.1), 2.89 (2H, t, *J* 6.8), 3.67 (3H, s), 3.76 (3H, s), 6.60 (2H, s), 7.09 (1H, ddd, *J* 7.9, 6.9, 1.1), 7.17 (1H, ddd, *J* 8.2, 7.0, 1.2), 7.26–7.30 (1H, m), 7.54 (1H, dt, *J* 7.8, 1.0); ^{13}C NMR (101 MHz, $CDCl_3$) δ_C: 10.4 (CH_3), 18.7 (CH_3), 24.5 (CH_2), 28.9 (CH_2), 29.6 (CH_2), 31.2 (NCH_3), 49.5 (CH_2), 55.5 (OCH_3), 108.6 (C), 111.4 (CH), 114.0 (CH), 118.2 (CH), 118.7 (CH), 120.6 (CH), 127.9 (C), 131.9 (C), 132.8 (C), 136.7 (C), 139.8 (C), 154.8 (C); HRMS $(ESI)^+$ calculated for $[C_{23}H_{31}N_2O]^+$ $(M+H)^+$ m/z: 351.2436, found 351.2439 (+0.9 ppm).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3.07
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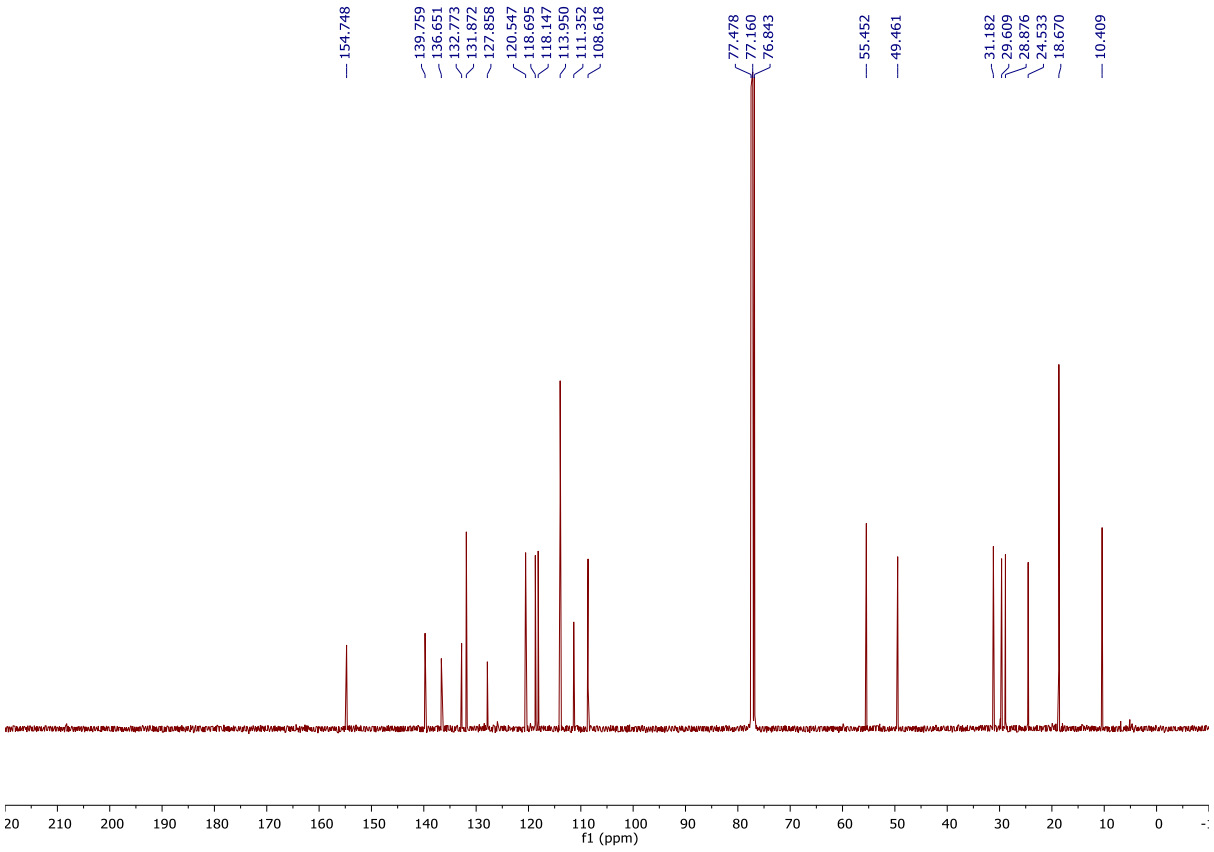
4.06
f1 (ppm)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77.160
76.843
55.452
49.461
31.182
29.609
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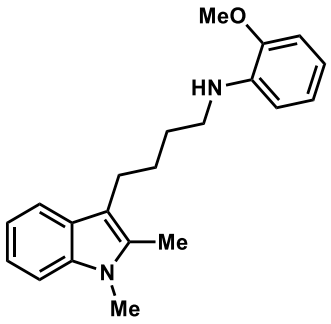
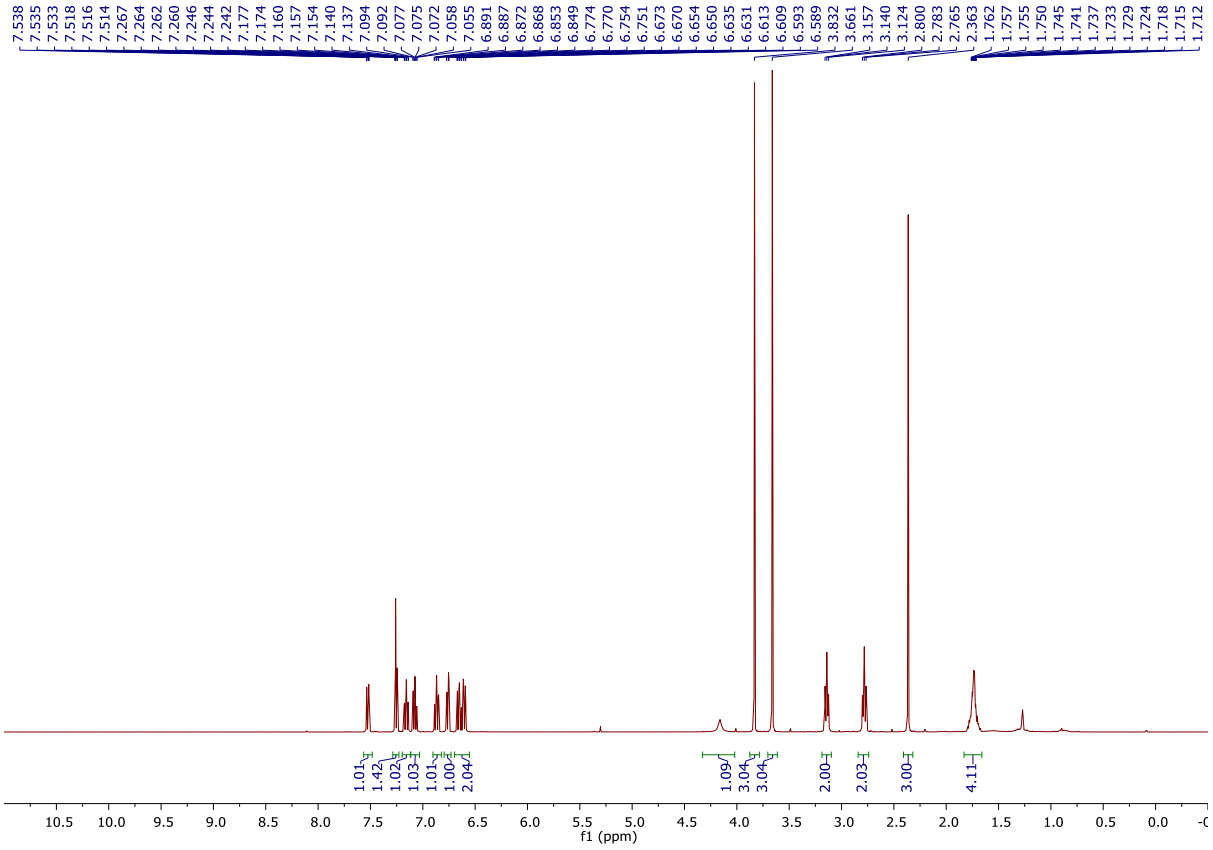
18.670
10.409
f1 (ppm)

N-(4-(1,2-Dimethyl-1H-indol-3-yl)butyl)-2-methoxyaniline 15d



Following general procedure 11, using pyrrolidine **14d** (35.4 mg, 0.20 mmol), 1,2-dimethylindole **1a** (63.9 mg, 0.44 mmol), $B(C_6F_5)_3$ (10.2 mg, 0.02 mmol, 10 mol %), Et_3SiH (6.4 µL, 0.04) at 110 °C for 22 h in 1,2-$Cl_2C_6H_4$ gave compound **15d** (55% spectroscopic yield). Purification by flash silica chromatography (eluent = 60% CH_2Cl_2 in pet. ether or 10% EtOAc in pet. ether) gave the title compound **15d** as an orange film (25 mg, 0.08 mmol, 39%); R_f = 0.1 (eluent = 5% EtOAc in pet. ether); ν_{max} / cm^{-1} (film) 3421, 2930, 2853, 1601, 1512, 1472, 1456, 1370, 1330, 1246, 1221, 1177, 1151, 1126, 1049, 1028; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H: 1.66–1.83 (4H, m), 2.36 (3H, s), 2.78 (2H, t, *J* 7.0), 3.14 (2H, t, *J* 6.7), 3.66 (3H, s), 3.83 (3H, s), 4.16 (1H, br s), 6.55–6.70 (2H, m), 6.76 (1H, dd, *J* 7.9, 1.4), 6.87 (1H, td, *J* 7.6, 1.4), 7.07 (1H, ddd, *J* 8.0, 7.0, 1.1), 7.16 (1H, ddd, *J* 8.2, 7.0, 1.2), 7.23–7.29 (1H, m), 7.53 (1H, dt, *J* 7.7, 1.0); ^{13}C NMR (101 MHz, $CDCl_3$) δ_C: 10.5 (CH_3), 24.4 (CH_2), 28.8 (CH_2), 29.5 (CH_2), 29.6 (NCH_3), 43.9 (CH_2), 55.5 (OCH_3), 108.6 (C), 109.5 (CH), 109.9 (CH), 111.3 (CH), 116.2 (CH), 118.2 (CH), 118.7 (CH), 120.5 (CH), 121.4 (CH), 127.9 (C), 132.8 (C), 136.7 (C), 138.7 (C), 146.9 (C); HRMS $(ESI)^+$ calculated for $[C_{21}H_{28}N_2O]^+$ $(M+H)^+$ m/z: 323.2123, found 323.2122 (-0.3 ppm).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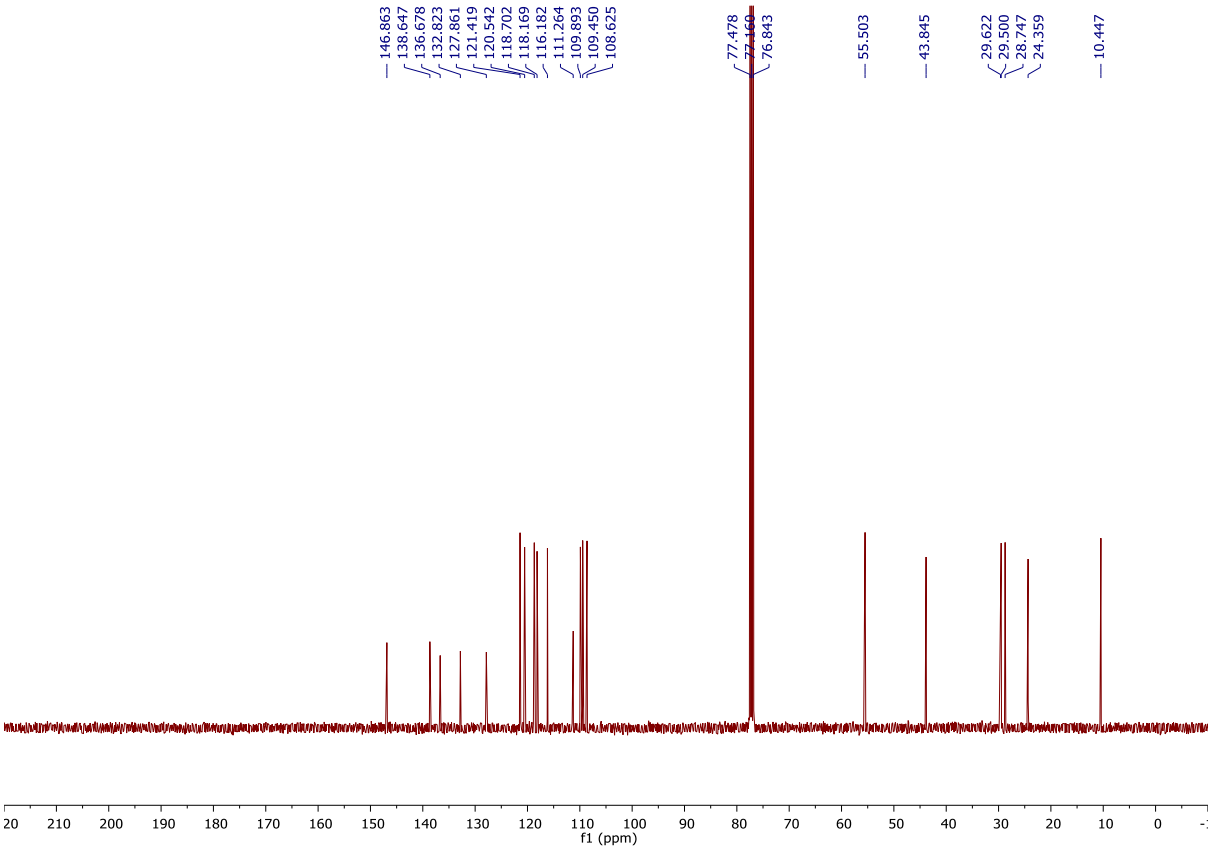
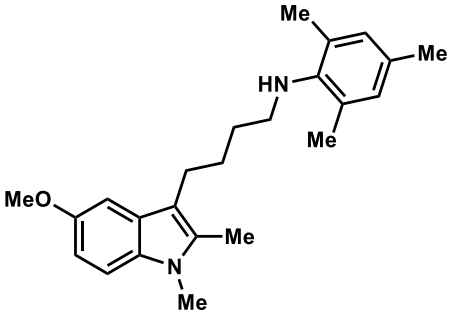
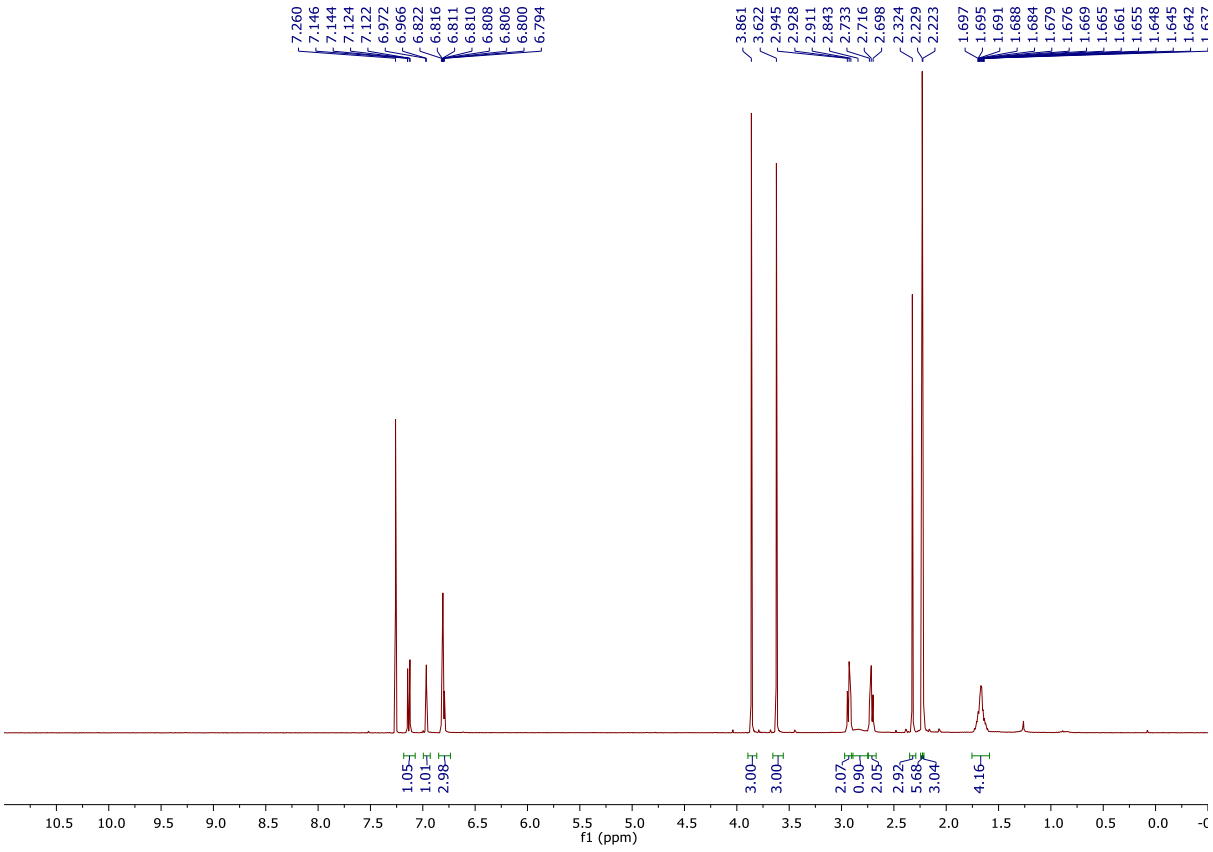
7.075
7.072
7.058
7.055
6.891
6.887
6.872
6.868
6.853
6.849
6.774
6.770
6.754
6.751
6.673
6.670
6.654
6.650
6.635
6.631
6.613
6.609
6.593
6.589
3.832
3.661
3.157
3.140
3.124
2.800
2.783
2.765
2.363
1.762
1.757
1.755
1.750
1.745
1.741
1.737
1.733
1.729
1.724
1.718
1.715
1.712
1.01
1.42
1.02
1.03
1.01
1.00
2.04
1.09
3.04
3.04
2.00
2.03
3.00
4.11
f1 (ppm)

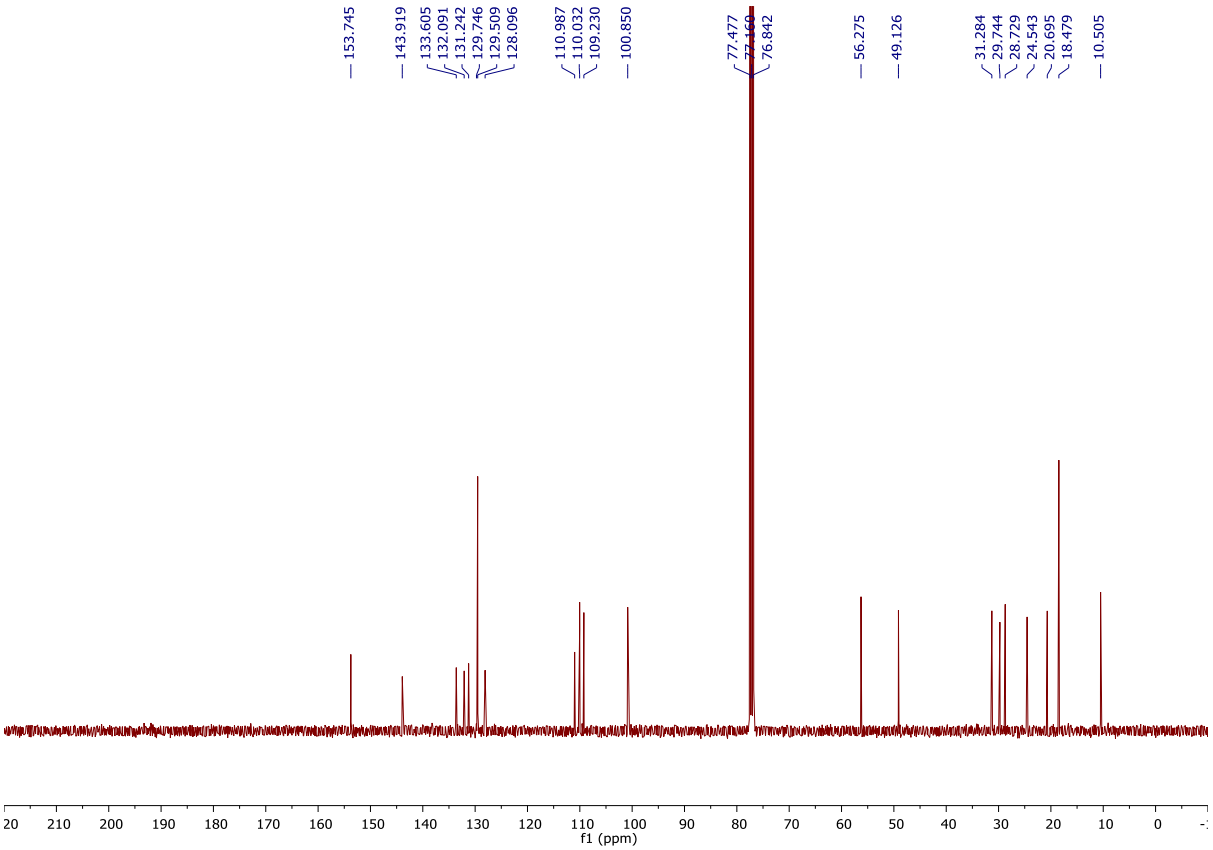

146.863
138.647
136.678
132.823
127.861
121.419
120.542
118.702
118.169
116.182
111.264
109.893
109.450
108.625
77.478
77.160
76.843
55.503
43.845
29.622
29.500
28.747
24.359
10.447
f1 (ppm)

N-(4-(5-Methoxy-1,2-dimethyl-1H-indol-3-yl)butyl)-2,4,6-trimethylaniline 15e

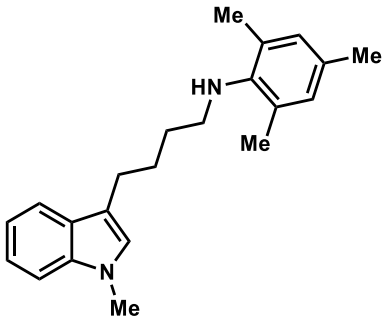


Following general procedure 11, using pyrrolidine **14a** (37.8 mg, 0.20 mmol), 5-methoxy-1,2-dimethyl indole **1c** (77.0 mg, 0.44 mmol), $B(C_6F_5)_3$ (10.2 mg, 0.02 mmol, 10 mol %), Et_3SiH (6.4 µL, 0.04 mmol), at 60 °C for 22 h in toluene gave compound **15e** (55% spectroscopic yield). Purification by flash silica chromatography (eluent = 60% CH_2Cl_2 in pet. ether or 10% EtOAc in pet. ether) gave the title compound **15e** as a brown film (31 mg, 0.09 mmol, 42%); R_f = 0.1 (eluent = 5% EtOAc in pet. ether); ν_{max} / cm^{-1} (film) 3375, 2922, 2852, 1675, 1619, 1582, 1486, 1457, 1411, 1375, 1229, 1150, 1029, 852, 793, 736, 699; ^1H NMR (400 MHz, $CDCl_3$) δ_H: 1.59–1.75 (4H, m), 2.22 (3H, s), 2.23 (6H, s), 2.32 (3H, s), 2.72 (2H, t, *J* 7.0), 2.84 (1H, br s), 2.93 (2H, t, *J* 6.8), 3.62 (3H, s), 3.86 (3H, s), 6.74–6.85 (3H, m), 6.97 (1H, d, *J* 2.4), 7.13 (1H, dd, *J* 8.8, 0.5); ^{13}C NMR (101 MHz, $CDCl_3$) δ_C: 10.5 (CH_3), 18.5 (CH_3), 20.7 (CH_3), 24.5 (CH_2), 28.7 (CH_2), 29.7 (CH_2), 31.3 (NCH_3), 49.1 (CH_2), 56.3 (OCH_3), 100.9 (CH), 109.2 (C), 110.0 (CH), 111.0 (CH), 128.1 (C), 129.5 (C), 129.8 (CH), 131.2 (C), 132.1 (C), 133.6 (C), 143.9 (CN), 153.8 (C); HRMS $(ESI)^+$ calculated for $[C_{24}H_{33}N_2O]^+$ $(M+H)^+$ m/z: 365.2593, found 365.2596 (+0.8 ppm).



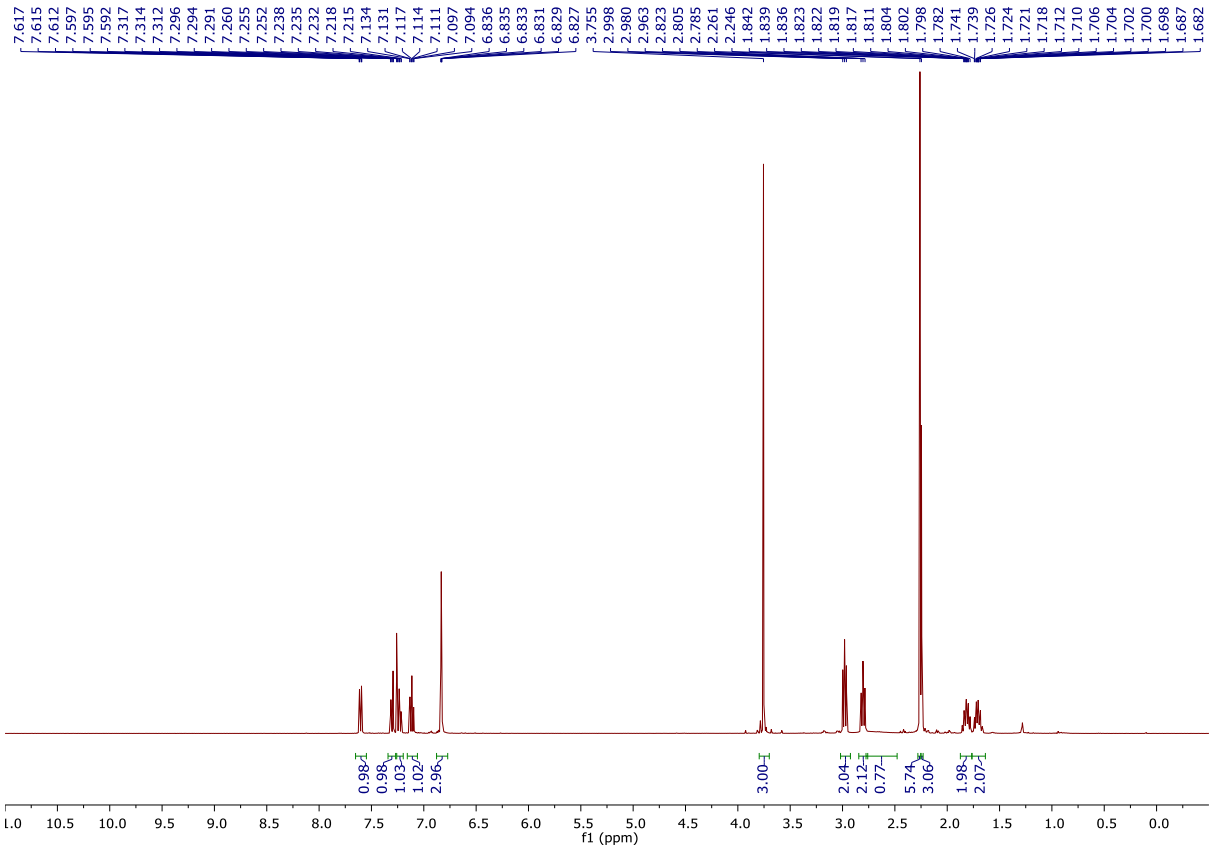


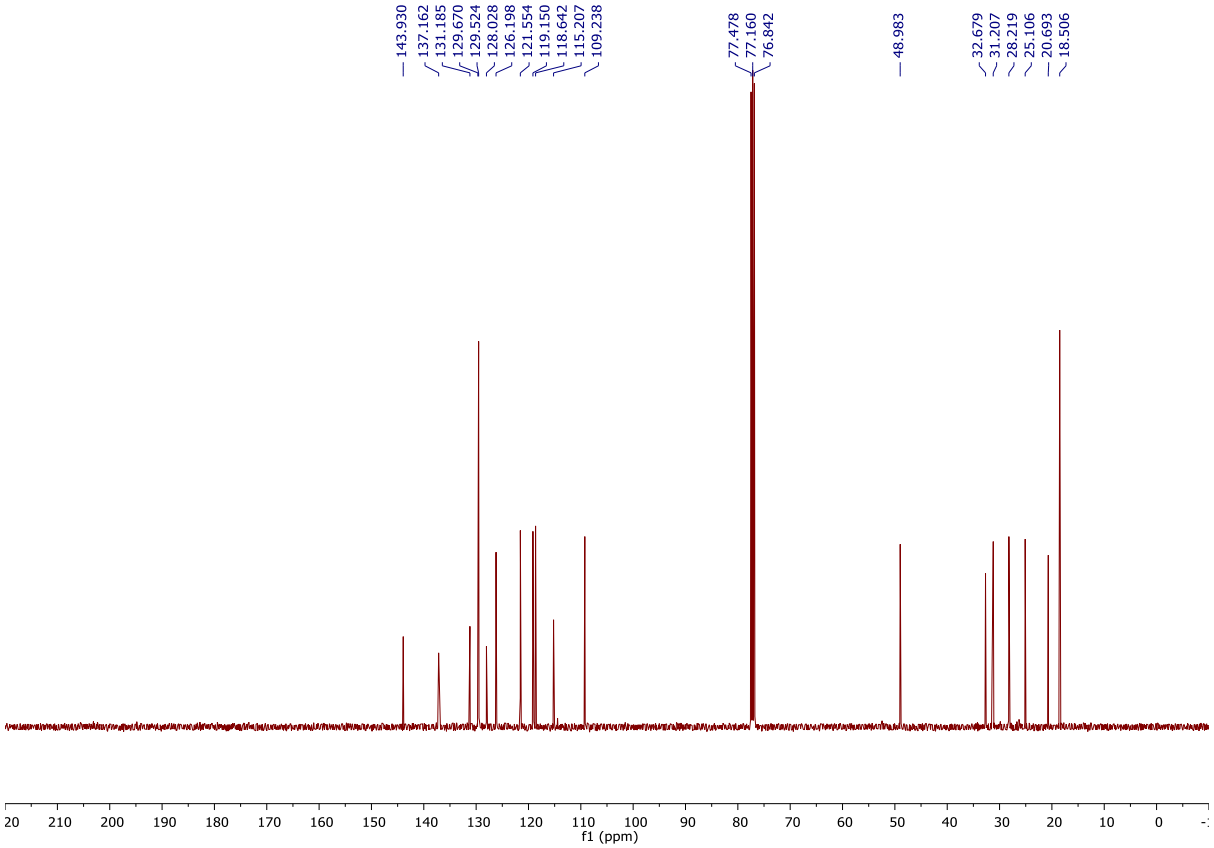
2,4,6-Trimethyl-N-(4-(1-methyl-1H-indol-3-yl)butyl)aniline 15f



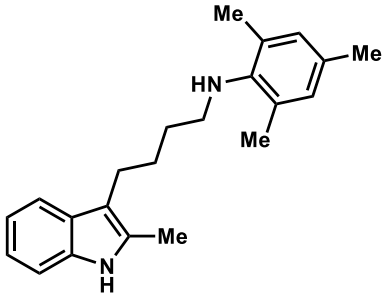
Following general procedure 11, using pyrrolidine **14a** (37.8 mg, 0.20 mmol), 1-methyl-1H-indole **1f** (57.7 mg, 0.44 mmol), $B(C_6F_5)_3$ (10.2 mg, 0.02 mmol, 10 mol %), Et_3SiH (6.4 µL, 0.04 mmol) at 110 °C for 22 h in 1,2-$Cl_2C_6H_4$ gave compound **15f** (75% spectroscopic yield). Purification by flash silica chromatography (eluent = 60% CH_2Cl_2 in pet. ether or 10% EtOAc in pet. ether) gave the title compound **15f** as a yellow film (41 mg, 0.13 mmol, 64%); R_f = 0.2 (eluent = 5% EtOAc in pet. ether); ν_{max} / cm^{-1} (film) 3387, 2925, 2853, 1614, 1483, 1374, 1324, 1232, 1153, 1128, 1011, 854, 737; ^1H NMR (400 MHz, $CDCl_3$) δ_H: 1.64–1.77 (2H, m), 1.76–1.87 (2H, m), 2.25 (3H, s), 2.26 (6H, s), 2.64 (1H, br s), 2.80 (2H, t, *J* 7.7), 2.98 (2H, t, *J* 7.0), 3.76 (3H, s), 6.77–6.88 (3H, m), 7.11 (1H, ddd, *J* 8.0, 6.9, 1.1), 7.23 (1H, ddd, *J* 8.0, 6.9, 1.1), 7.30 (1H, dt, *J* 8.2, 1.0), 7.60 (1H, dt, *J* 7.9, 1.0); ^{13}C NMR (101 MHz, $CDCl_3$) δ_C: 18.5 (CH_3), 20.7 (CH_3), 25.1 (CH_2), 28.2 (CH_2), 31.2 (NCH_3), 32.7 (CH_2), 49.0 (CH_2), 109.2 (CH), 115.2 (C),118.6 (CH), 119.2 (CH), 121.6 (CH), 126.2 (CH), 128.0 (C), 129.5 (C), 129.7 (CH), 131.2 (C),

137.2 (C), 143.9 (C-N); HRMS (ESI)$^+$ calculated for $[C_{22}H_{29}N_2]^+$ $(M+H)^+$ m/z: 321.2331, found 321.2335 (+1.3 ppm).

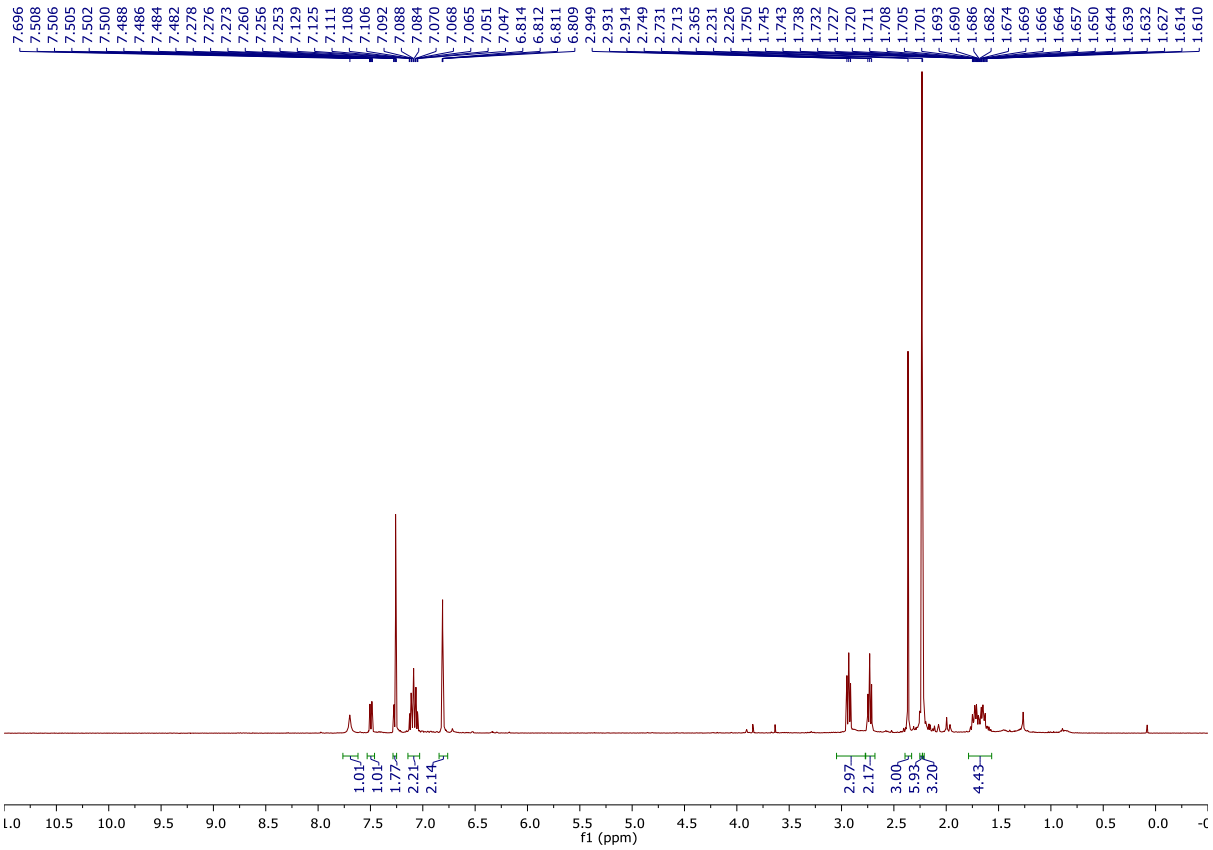


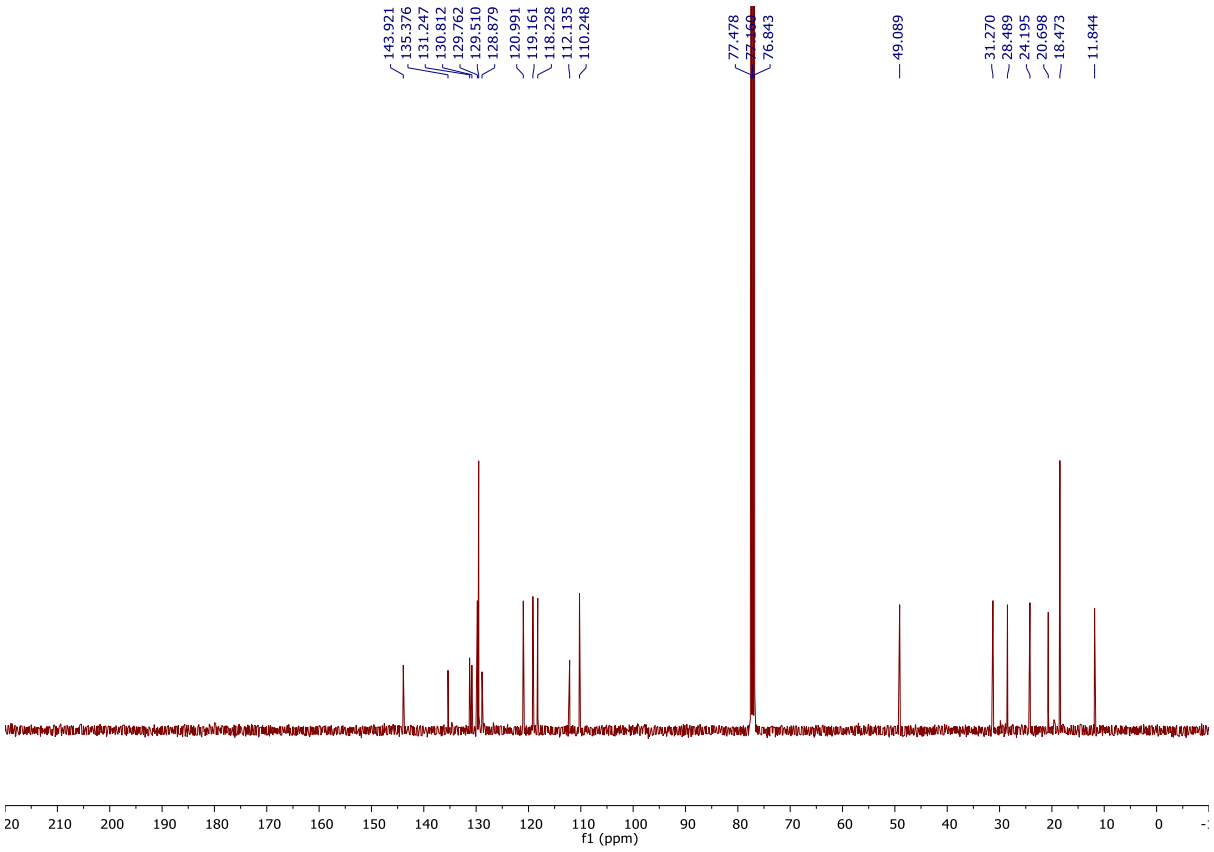


2,4,6-Trimethyl-N-(4-(2-methyl-1H-indol-3-yl)butyl)aniline 15g



Following general procedure 11, with pyrrolidine **14a** (37.8 mg, 0.20 mmol) and 2-methyl-1H-indole **1l** (57.7 mg, 0.44 mmol), $B(C_6F_5)_3$ (10.2 mg, 0.02 mmol, 10 mol %), Et_3SiH (6.4 µL, 0.04 mmol) at 110 °C for 22 h in toluene gave compound **15g** (40% spectroscopic yield). Purification by flash silica chromatography (eluent = 60% CH_2Cl_2 in pet. ether or 10% EtOAc in pet. ether) gave the title compound **15g** as a yellow film (15 mg, 0.05 mmol, 22%); R_f = 0.1 (eluent = 5% EtOAc in pet. ether); ν_{max} / cm^{-1} (film) 3403, 2920, 2852, 1587, 1483, 1460, 1373, 1297, 1264, 1231, 1153, 1011, 854, 735, 702; ^1H NMR (400 MHz, $CDCl_3$) δ_H: 1.57–1.79 (4H, m), 2.23 (3H, s), 2.23 (6H, s), 2.37 (3H, s), 2.73 (2H, t, *J* 7.2), 2.89 (1H, br s), 2.93 (2H, t, *J* 7.0), 6.76–6.85 (2H, m), 7.03–7.14 (2H, m), 7.25–7.29 (1H, m), 7.46–7.53 (1H, m), 7.70 (1H, br s); ^{13}C NMR (101 MHz, $CDCl_3$) δ_C: 11.8 (CH_3), 18.5 (CH_3), 20.7 (CH_3), 24.2 (CH_2), 28.5 (CH_2), 31.3 (CH_2), 49.1 (CH_2), 110.3 (C), 112.1 (CH), 118.2 (CH), 119.2 (CH), 121.0 (CH), 128.9 (C), 129.5 (C), 129.8 (CH), 130.8 (C), 131.3 (C), 135.4 (C),143.9 (C-N); HRMS $(ESI)^+$ calculated for $[C_{22}H_{29}N_2]^+$ $(M+H)^+$ m/z: 321.2331, found 321.2336 (+1.6 ppm).

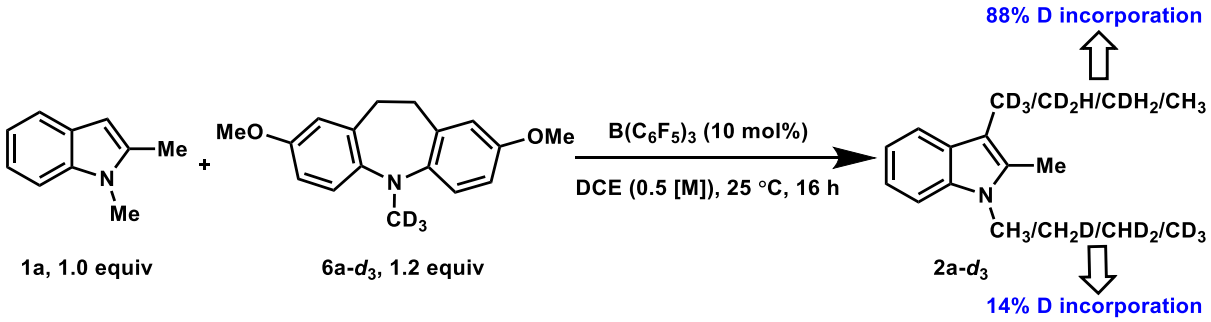



143.921
135.376
131.247
130.812
129.762
129.510
128.879
120.991
119.161
118.228
112.135
110.248
77.478
77.160
76.843
49.089
31.270
28.489
24.195
20.698
18.473
11.844
f1 (ppm)

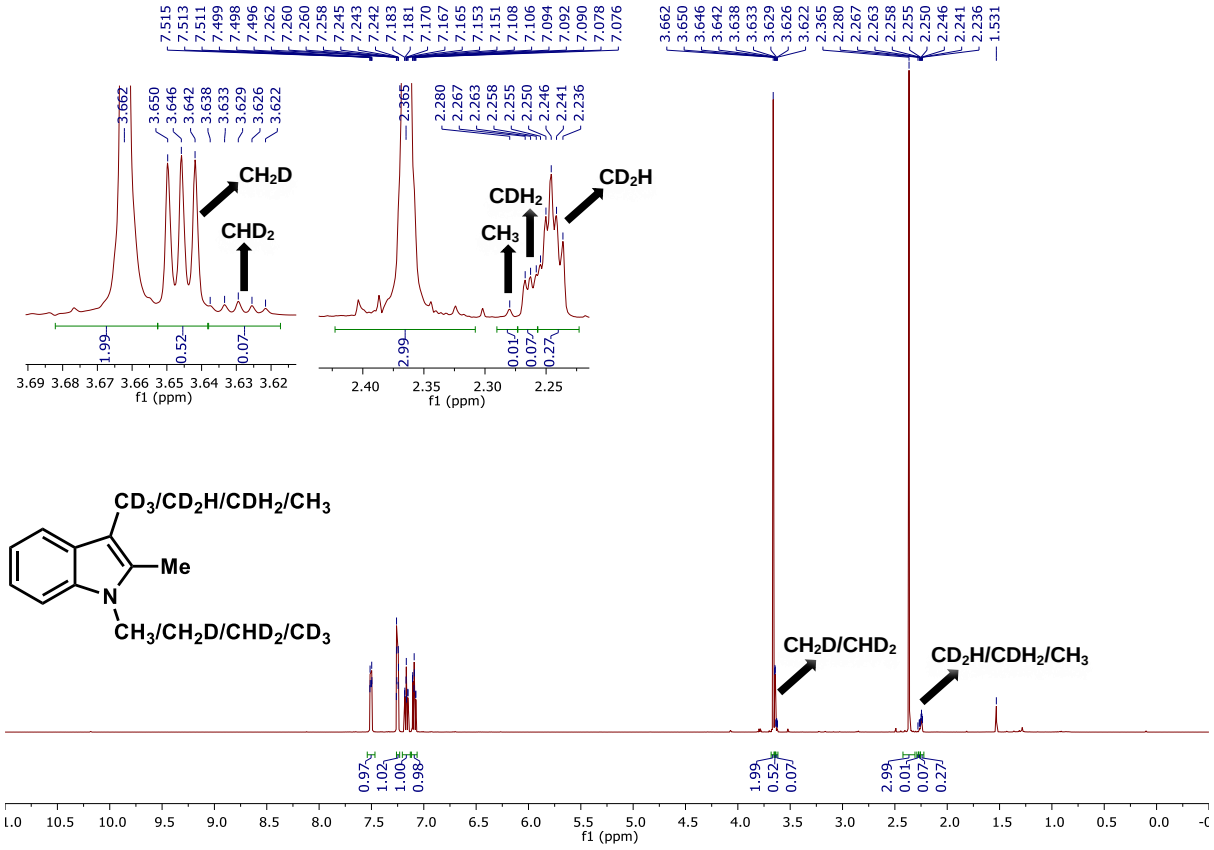
2.10. Mechanistic studies

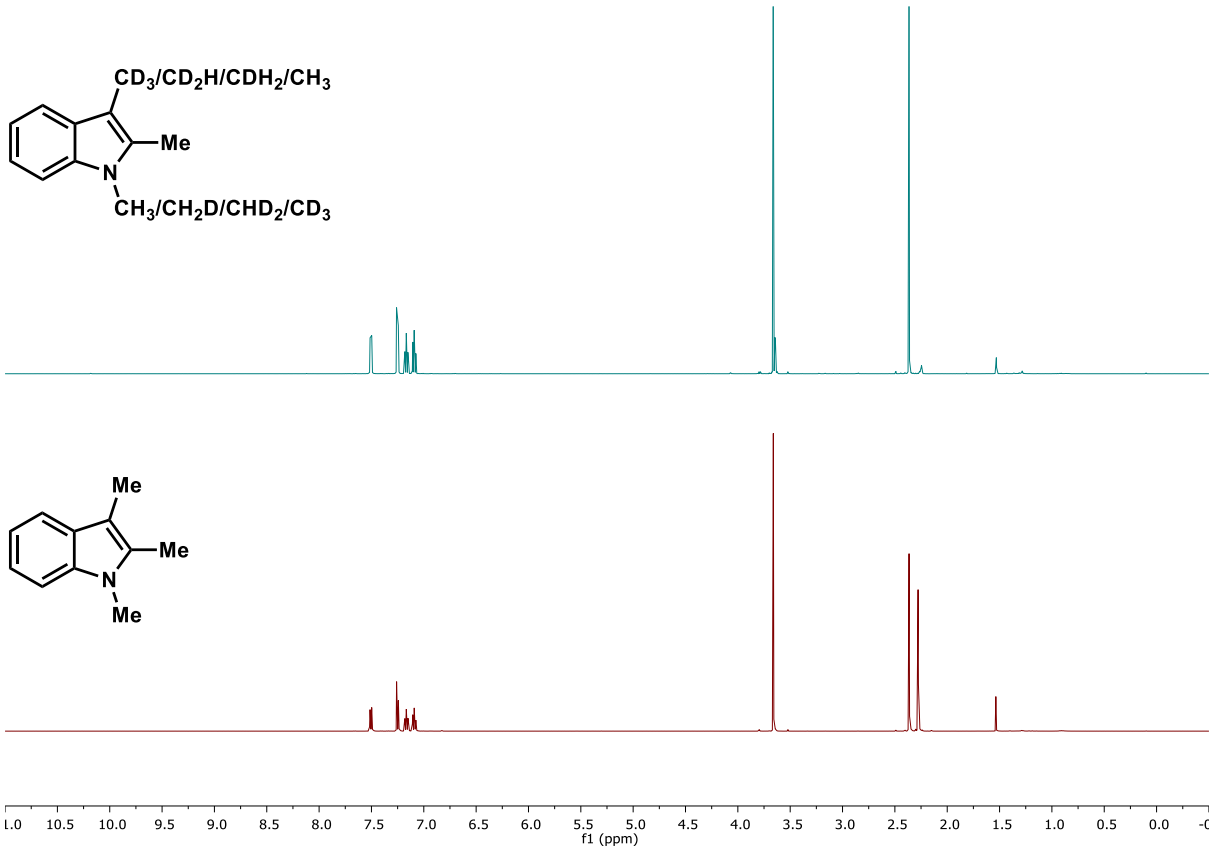
Mechanistic experiments employing 2,8-dimethoxy-5-(methyl-d_3)-10,11-dihydro-5H-dibenzo[*b*,*f*]azepine (6a-d_3) as alkylating agent

1,2-Dimethyl-3-(methyl-d_3)-1H-indole 2a-d_3

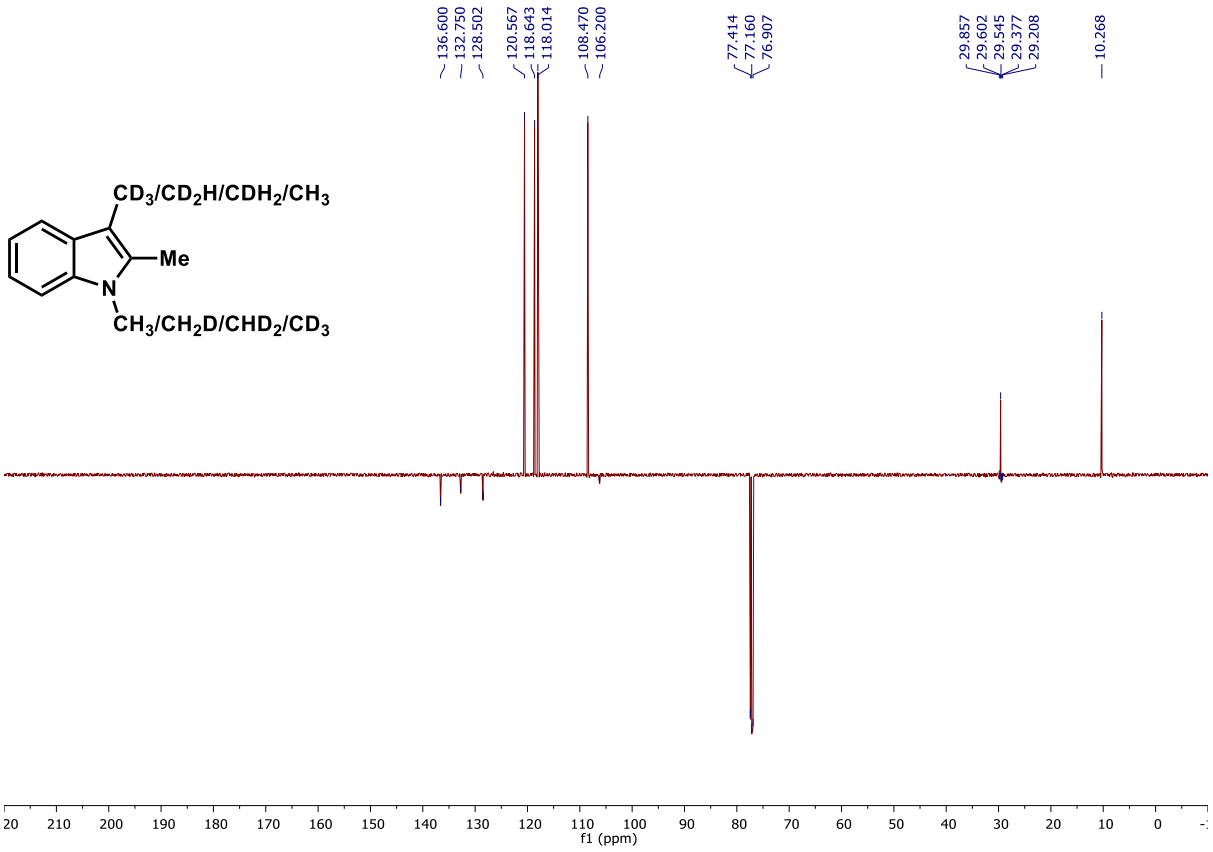


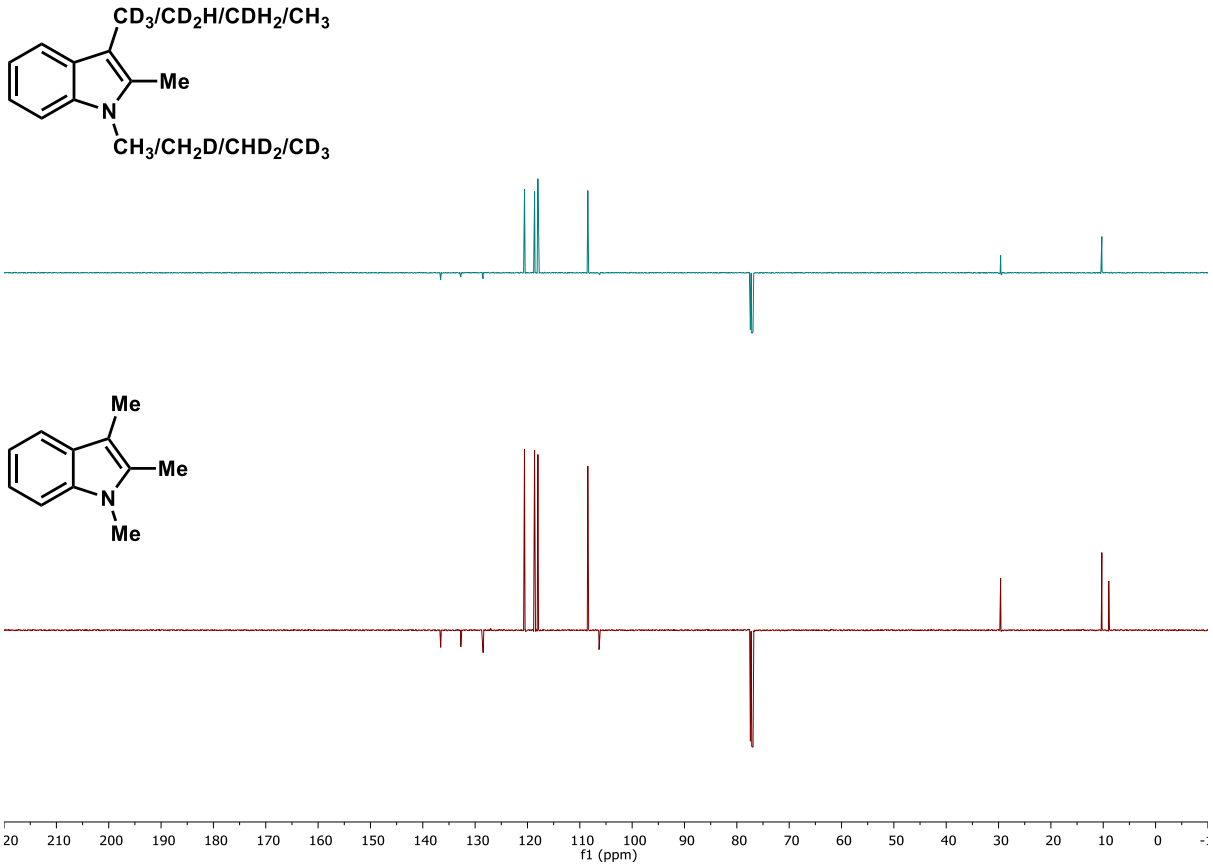
In a nitrogen-filled glove box, a 10 mL vial equipped with a magnetic stirrer bar was charged with the 1,2-dimethylindole **1a** (29.0 mg, 0.2 mmol), 2,8-dimethoxy-5-(methyl-d_3)-10,11-dihydro-5H-dibenzo[*b*,*f*]azepine **6a-d_3** (65.4 mg, 0.24 mmol, >99% D), $B(C_6F_5)_3$ (10.2 mg, 0.02 mmol) and DCE (0.4 mL). The vial was sealed with an aluminium crimped cap and was left to stir at 25 °C for 16 h. The reaction mixture was then directly loaded into the column for purification. Purification by flash silica chromatography (eluent = 0.3–0.5% EtOAc in hexanes, 20 × 180 mm silica) gave the title compound **2a-d_3** as a light red oil (31.0 mg, 0.19 mmol, 96%); R_f = 0.31 (eluent = 2% EtOAc in hexanes); ν_{max} / cm^{-1} (film) 3051, 2913, 1614, 1566, 1472, 1443, 1410, 1370, 1325, 1248, 1194, 1150, 1128, 1011, 914, 731, 557, 525, 432; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 2.25 (0.27H, p, *J* 2.5), 2.26 (0.07H, t, *J* 2.3), 2.28 (0.01H, s), 2.37 (s, 3H), 3.63 (0.07H, p, *J* 2.0), 3.65 (0.52H, t, *J* 2.0), 3.66 (1.99H, s), 7.09 (1H, ddd, *J* 7.9, 7.0, 1.1), 7.17 (1H, ddd, *J* 8.2, 7.0, 1.2), 7.23–7.26 (1H, m), 7.51 (1H, dt, *J* 7.8, 0.9); ^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 10.3, 29.4 (hept, *J* 26.9), 29.6, 106.2, 108.5, 118.0, 118.6, 120.6, 128.5, 132.8, 136.6; HRMS $(AP)^+$ calculated for $[C_{11}{}^1H_{11}{}^2H_3N]^+$ $(M+H)^+$ m/z: 163.1315, found 163.1312 (-1.8 ppm).


CD3/CD2H/CDH2/CH3
Me
N
CH3/CH2D/CHD2/CD3
CH2D/CHD2
CD2H/CDH2/CH3
f1 (ppm)


CD3/CD2H/CDH2/CH3
Me
N
CH3/CH2D/CHD2/CD3
f1 (ppm)

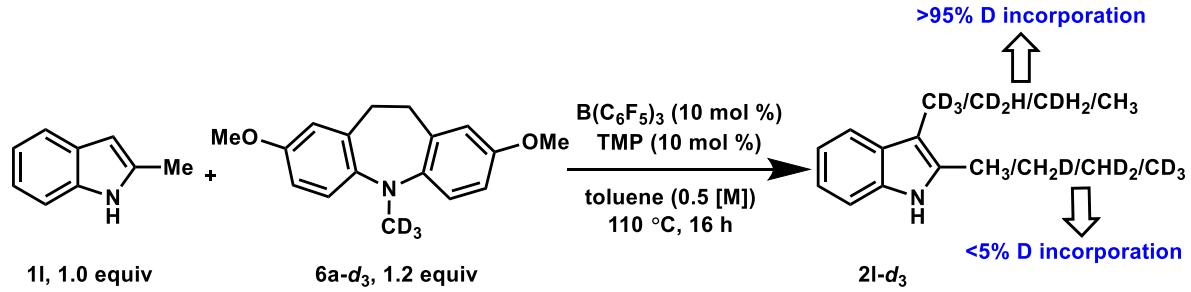
Me
Me
N
Me
f1 (ppm)


136.600
132.750
128.502
120.567
118.643
118.014
108.470
106.200
77.414
77.160
76.907
29.857
29.602
29.545
29.377
29.208
10.268
CD3/CD2H/CDH2/CH3
Me
N
CH3/CH2D/CHD2/CD3
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

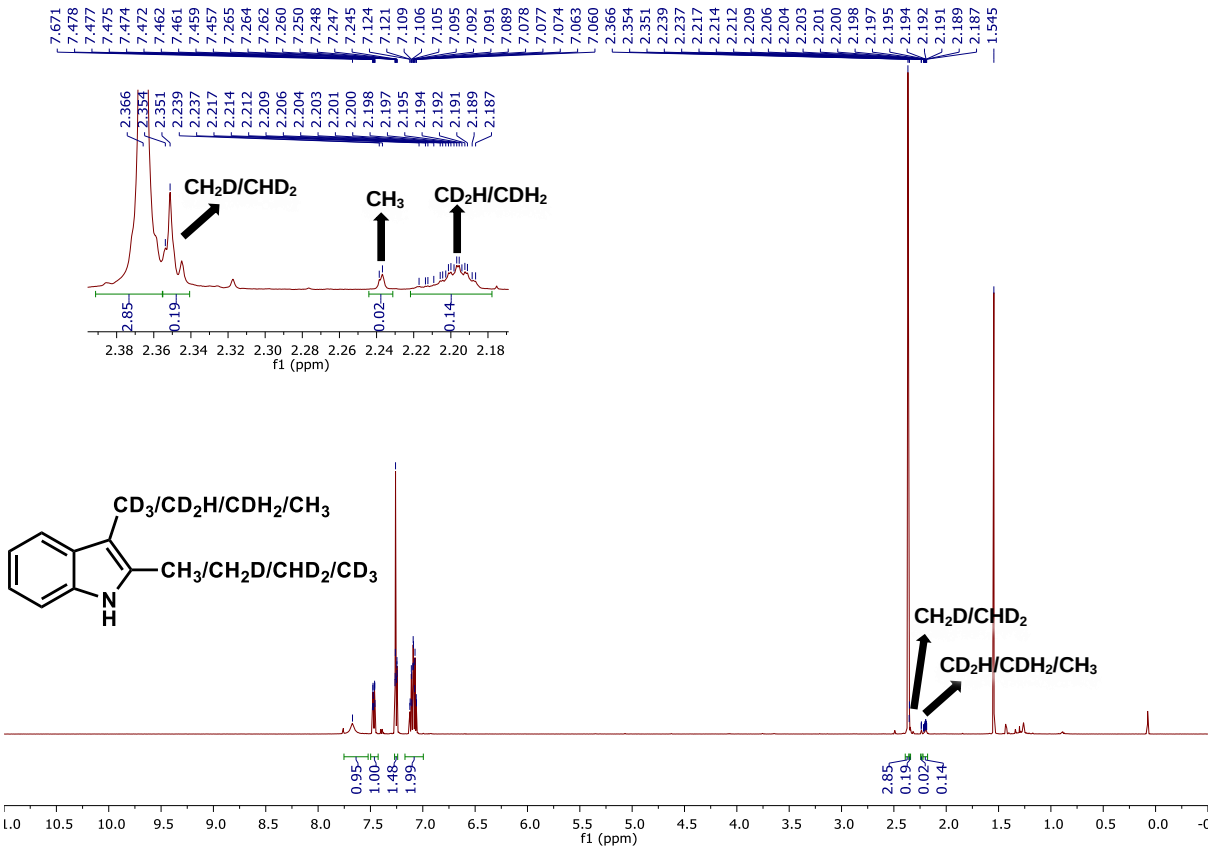

CD3/CD2H/CDH2/CH3
Me
N
CH3/CH2D/CHD2/CD3
Me
Me
N
Me
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

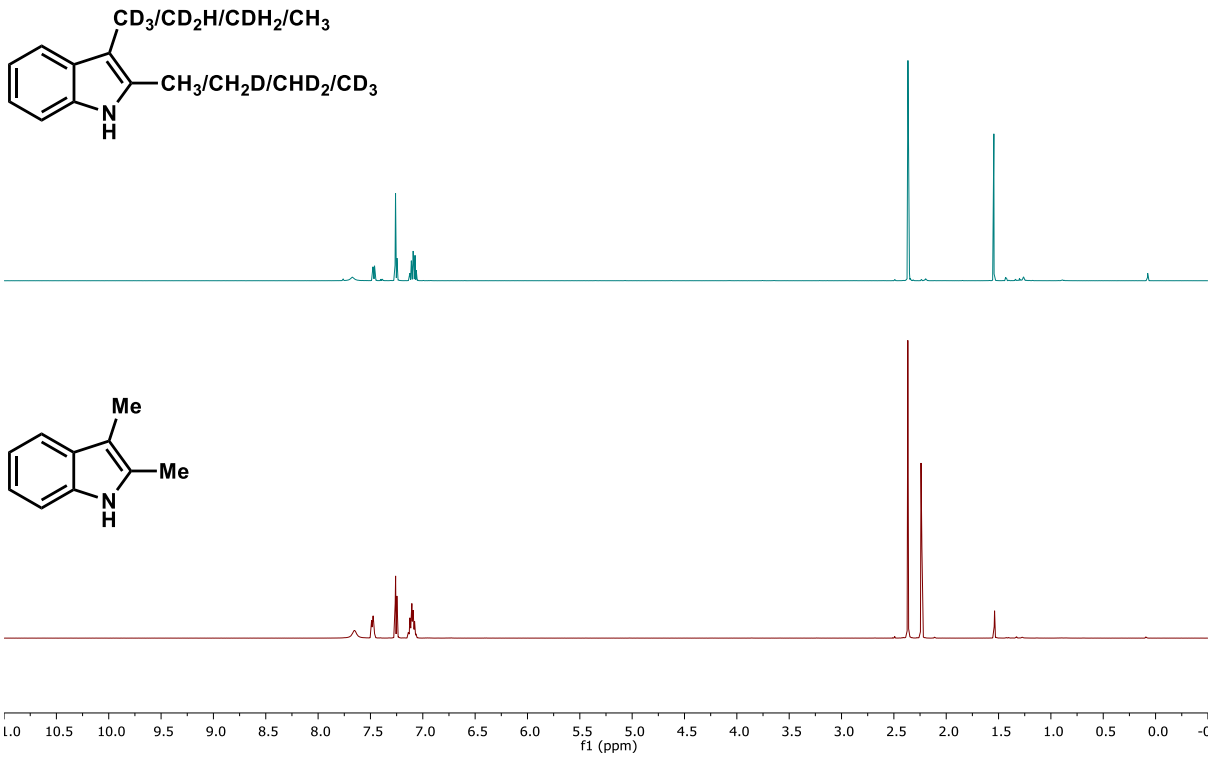
Deuterium incorporation equation: % D incorporation = {(3 - total integral of peaks CH_3 or CH_2D or CHD_2)/3}*100

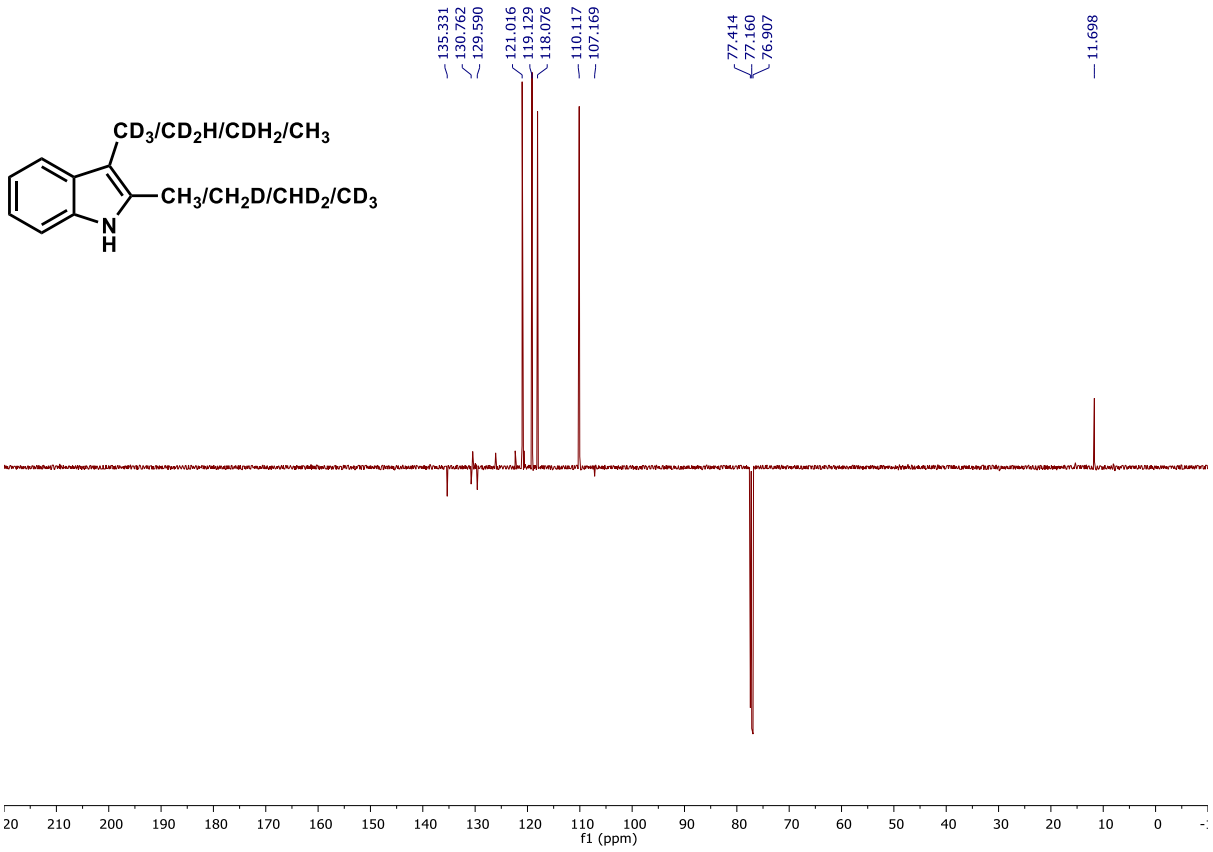
2-Methyl-3-(methyl-*d*$_3$)-1H-indole 2l-*d*$_3$

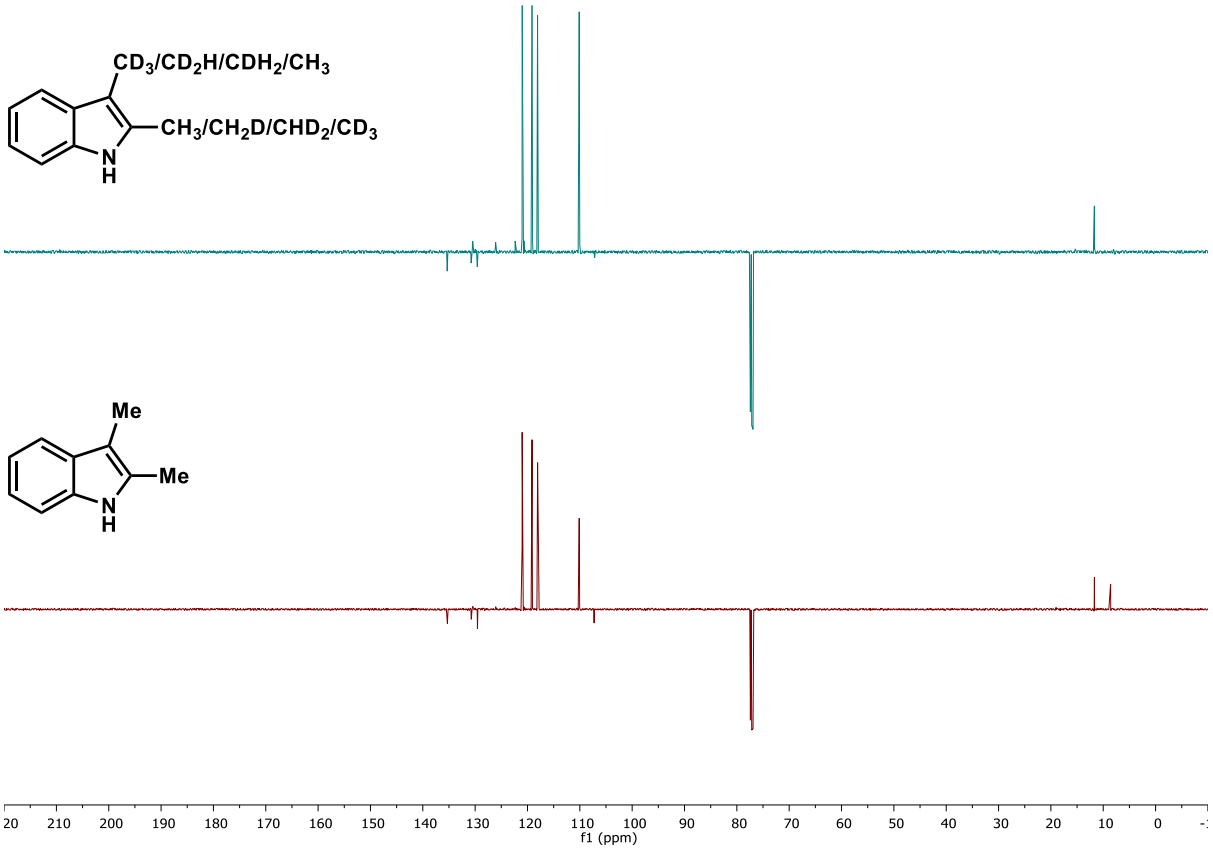


In a nitrogen-filled glove box, a 10 mL vial equipped with a magnetic stirrer bar was charged with the 2-methylindole **1l** (26.2 mg, 0.2 mmol), 2,8-dimethoxy-5-(methyl-*d*$_3$)-10,11-dihydro-5H-dibenzo[*b*,*f*]azepine **2l-*d*$_3$** (65.4 mg, 0.24 mmol, >99% D), 2,2,6,6-tetramethylpiperidine (TMP) (3.4 µL, 0.02 mmol), $B(C_6F_5)_3$ (10.2 mg, 0.02 mmol) and toluene (0.4 mL). The vial was sealed with an aluminium crimped cap and was left to stir at 110 °C for 16 h. The reaction mixture was then directly loaded into the column for purification. Purification by flash silica chromatography (eluent = 0.4–0.6% EtOAc in hexanes, 20 × 180 mm silica) gave the title compound **2l-*d*$_3$** as an off-white solid (29.1 mg, 0.20 mmol, 98%); mp 90–92 °C; R_f = 0.28 (eluent = 5% EtOAc in hexanes); ν_{max} / cm^{-1} (film) 3391, 3053, 2914, 1618, 1460, 1431, 1389, 1333, 1300, 1244, 1167, 1111, 1047, 999, 912, 735, 619, 579, 484, 430; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 2.18–2.22 (0.14H, m), 2.24 (0.02H, d, *J* 1.0), 2.35–2.36 (0.15H, m), 2.37 (2.85H, s), 6.99–7.17 (2H, m), 7.24–7.27 (1H, m), 7.43–7.50 (1H, m), 7.67 (1H, br s); ^{13}C NMR (126 MHz, $CDCl_3$) δ_C: 11.7, 107.2, 110.1, 118.1, 119.1, 121.0, 129.6, 130.8, 135.3; HRMS $(AP)^+$ calculated for $[C_{10}{}^1H_9{}^2H_3N]^+$ $(M+H)^+$ m/z: 149.1158, found 149.1153 (-3.4 ppm).


CD3/CD2H/CDH2/CH3
CH3/CH2D/CHD2/CD3
CH2D/CHD2
CD2H/CDH2/CH3
CH3
CD2H/CDH2
f1 (ppm)


CD3/CD2H/CDH2/CH3
CH3/CH2D/CHD2/CD3
Me
Me
f1 (ppm)


135.331
130.762
129.590
121.016
119.129
118.076
110.117
107.169
77.414
77.160
76.907
11.698
CD3/CD2H/CDH2/CH3
CH3/CH2D/CHD2/CD3
N
H
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


CD3/CD2H/CDH2/CH3
CH3/CH2D/CHD2/CD3
N
H
Me
Me
N
H
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

3. References

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