Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

C–H Carboxylation of heteroarenes with ambient CO_2

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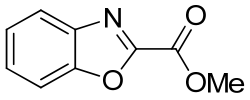
Contents

General remarks:

Reactions were carried out on a 1.00 mmol scale under a N_2 atmosphere using pre-dried glassware. The following starting materials were synthesized according to previously described methods: 5-methyl-benzo[*d*]oxazole (**1b**),[1] 5-chloro-benzo[*d*]oxazole (**1c**),[1] 2-(4-methylphenyl)-1,3,4-oxadiazole(**6a**),[2] and 2-phenyl-1,3,4-oxadiazole (**6b**).[2] Other chemicals were obtained from commercial sources, and were used without further purification. DMF was dried over CaH_2 for 8 h, degassed and distilled under reduced pressure. Yields refer to isolated compounds, estimated to be > 95% pure as determined by ^{1}H-NMR analysis. Flash chromatography: Merck silica gel 60 (230-400 mesh). NMR: Spectra were recorded on Varian-NMR *Mercury 300*, *Unity 300* and Varian-NMR *Inova 500* in the solvent indicated; chemical shifts (δ) are given in ppm.

Representative Procedure: Direct Carboxylation of Heteroaromatic C–H bonds Using CO_2

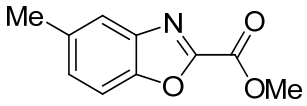
Methylbenzo[*d*]oxazole-2-carboxylate (3a): A mixture of benzo[*d*]oxazole (**1a**) (118 mg, 0.99 mmol), KO*t*-Bu (135 mg, 1.20 mmol) and DMF (5.0 mL) was degassed in a Schlenk-tube. The Schlenk-tube was then flushed with CO_2 *via* a balloon and CO_2 was bubbled through the reaction mixture for 10–20 minutes. After removal of the balloon, the reaction was heated to 100 °C for 18 h. It was then cooled to 65 °C, methyl iodide (**2a**) (3.00 equiv) was added and the reaction mixture was stirred at 65 °C for 2 h. At ambient temperature, the reaction mixture was diluted with H_2O (25 mL) and Et_2O (25 mL). The aqueous layer was extracted with Et_2O (3 x 25 mL) and the combined organic layers were dried over Na_2SO_4. Purification by column chromatography (*n*-pentane/Et_2O = 20/1 → 10/1 → 7/1 → 5/1) yielded **3a** (141 mg, 80%) as a colorless solid.



3a

m.p. = 102–104 °C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.88 (ddd, J = 7.7, 1.5, 0.7 Hz, 1H), 7.66 (m, 1H), 7.53 (m, 1H), 7.45 (m, 1H), 4.09 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 156.8 (C_q), 152.5, (C_q), 150.8 (C_q), 140.4 (C_q), 128.2 (CH), 125.8 (CH), 122.1 (CH), 111.7 (CH), 53.6 (CH_3). IR (neat): 2956, 1742, 1538, 1440, 1306, 1106, 744, 626 cm^{-1}. MS (EI) *m/z* (relative intensity) 177 ([M^+] 100), 119 (24), 104 (45), 64 (69), 43 (99). HR-MS (EI) *m/z* calcd for $C_9H_7NO_3$ 177.0426, found 177.0427.

The analytical data are in accordance with those reported in the literature. [2,3]



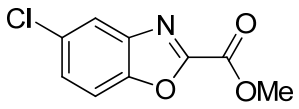
3b

Methyl-5-methylbenzo[*d*]oxazole-2-carboxylate (3b): The representative procedure was followed using 5-methyl-benzo[*d*]oxazole (**1b**) (134 mg, 1.00 mmol) and KO*t*-Bu (135 mg, 1.20 mmol). Purification by column chromatography (*n*-pentane/Et_2O = 20/1 → 10/1 → 8/1 → 5/1) yielded **3b** (129 mg, 66%) as a brown solid.

m.p. = 99–101 °C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.64 (dd, J = 1.6, 0.8 Hz, 1H), 7.52 (d, J = 8.5 Hz, 1H), 7.32 (m, 1H), 4.07 (s, 3H), 2.49 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 156.9 (C_q), 152.5 (C_q), 149.2 (C_q), 140.7 (C_q), 135.9 (C_q), 129.6 (CH), 121.6 (CH), 111.1 (CH), 53.6 (CH_3), 21.5 (CH_3). IR (neat):

3020, 1746, 1554, 1435, 1301, 1110, 807, 631, 433 cm^{-1}. MS (EI) *m/z* (relative intensity) 191 (100 [M^+]), 146 (65), 118 (62), 104 (41), 77 (74), 51 (48). HR-MS (EI) *m/z* calcd for $C_{10}H_9NO_3$ 191.0582, found 191.0591.

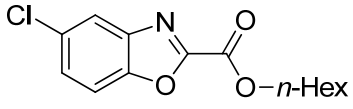
The analytical data are in accordance with those reported in the literature.[2,3]



3c

Methyl-6-chlorobenzo[*d*]oxazole-2-carboxylate (3c): The representative procedure was followed using 5-chlorobenzo[*d*]oxazole (**1c**) (154 mg, 1.00 mmol), and KO*t*-Bu (135 mg, 1.20 mmol). Purification by column chromatography (*n*-pentane/Et_2O = 20/1 → 10/1 → 7/1 → 6/1) yielded **3c** (133 mg, 63%) as a colorless solid.
m.p. = 122–124°C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.86 (d, J = 2.1 Hz, 1H), 7.59 (d, J = 8.9, 1H), 7.49 (dd, J = 8.9, 2.1 Hz, 1H), 4.09 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 156.5 (C_q), 153.6 (C_q), 149.4 (C_q), 141.4 (C_q), 131.5 (C_q), 128.8 (CH), 121.9 (CH), 112.6 (CH), 53.8 (CH_3). IR (neat): 3098, 2961, 1738, 1544, 1431, 1300, 1155, 812, 701 cm^{-1}. MS (EI) *m/z* (relative intensity) 211 ([M^+] 100), 167 (32), 124 (67), 104 (50), 98 (41), 63 (64). HR-MS (EI) *m/z* calcd for $C_9H_6ClNO_3$ 211.0036, found 211.0035.

The analytical data are in accordance with those reported in the literature.[2,3]

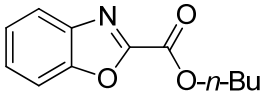


3d

***n*-Hexyl-5-chlorobenzo[*d*]oxazole-2-carboxylate (3d):** The representative procedure was followed using 5-chloro-benzo[*d*]oxazole (**1c**) (153 mg, 1.00 mmol), KO*t*-Bu (135 mg, 1.20 mmol) and *n*-hexyl iodide (**2b**) (3.00 equiv) . Purification by column chromatography (*n*-pentane/Et_2O = 40/1 → 20/1) yielded **3d** (255 mg, 91%) as a pale yellow solid.

m.p. = 48–50 °C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.86 (d, J = 2.0 Hz, 1H), 7.59 (d, J = 8.8 Hz, 1H), 7.48 (dd, J = 8.8, 2.0 Hz, 1H), 4.48 (t, J = 6.8 Hz, 2H), 1.84 (dq, J = 8.4, 6.8 Hz, 2H), 1.53 – 1.22 (m, 6H), 0.93 – 0.86 (m, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 156.2 (C_q), 153.9 (C_q), 149.4 (C_q), 141.5 (C_q), 131.4 (C_q), 128.6 (CH), 121.8 (CH), 112.5 (CH), 67.5 (CH_2), 31.3 (CH_2), 28.4 (CH_2), 25.4 (CH_2), 22.5 (CH_2), 14.0 (CH_3). IR (neat): 3100, 2928, 1738, 1541, 1303, 1154, 919, 813, 637 cm^{-1}. MS (EI) *m/z* (relative intensity) 281 ([M^+] 23), 236 (11), 194 (30), 180 (74), 153 (100), 43 (80). HR-MS (EI) *m/z* calcd for $C_{14}H_{16}ClNO_3$ 281.0819, found 281.0813.

The analytical data are in accordance with those reported in the literature.[4]



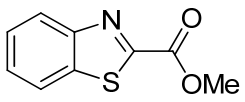
3e

***n*-Butyl-benzo[*d*]oxazole-2-carboxylate (3e):** The repre-sentative procedure was followed using benzo[*d*]oxazole (**1a**) (119 mg, 1.00 mmol), KO*t*-Bu (135 mg, 1.20 mmol) and *n*-butyl iodide (**2c**) (3.00 equiv). Purification by column chromatography (*n*-pentane/Et_2O = 20/1 → 10/1 → 7/1) yielded **3e** (139 mg, 64%) as a colorless oil.

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.89 (m, 1H), 7.66 (ddd, J = 8.3, 8.3, 0.9 Hz, 1H), 7.51 (m, 1H), 7.44 (ddd, J = 7.6, 7.6, 1.3 Hz, 1H), 4.49 (t, J = 6.8 Hz, 2H), 1.91 – 1.74 (m, 2H),

1.59 – 1.37 (m, 2H), 0.98 (t, J = 7.4 Hz, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 156.6 (C_q), 152.8 (C_q), 150.9 (C_q), 140.5 (C_q), 128.1 (CH), 125.7 (CH), 122.1 (CH), 111.7 (CH), 67.0 (CH_2), 30.5 (CH_2), 19.0 (CH_2), 13.6 (CH_3). IR (neat): 2960, 2874, 1739, 1545, 1292, 1138, 842, 744, 429 cm^{-1}. MS (EI) *m/z* (relative intensity) 219 (32 [M^+]), 174 (11), 160 (17), 146 (56), 119 (100), 91 (42). HR-MS (EI) *m/z* calcd for $C_{12}H_{13}NO_3$ 219.0895, found 219.0892.

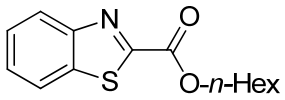
The analytical data are in accordance with those reported in the literature.[5]



3f

Methyl-benzo[*d*]thiazole-2-carboxylate (3f): The representative procedure was followed using benzo[*d*]thiazole (**1d**) (138 mg, 1.00 mmol), and KO*t*-Bu (135 mg, 1.20 mmol). Purification by column chromatography (*n*-pentane/Et_2O = 20/1 → 10/1 → 7/1 → 5/1) yielded **3f** (131 mg, 66%) as a yellow solid. m.p. = 92–94 °C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.24 (m, 1H), 7.97 (m, 1H), 7.55 (m, 2H), 4.08 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 161.1 (C_q), 158.0 (C_q), 153.1 (C_q), 136.8 (C_q), 127.6 (CH), 127.1 (CH), 125.5 (CH), 122.1 (CH), 53.6 (CH_3). IR (neat): 2952, 1711, 1494, 1287, 1096, 923, 766, 731, 432 cm^{-1}. MS (EI) *m/z* (relative intensity) 193 ([M^+] 59), 162 (19), 135 (100), 108 (26), 90 (22), 69 (23). HR-MS (EI) *m/z* calcd for $C_9H_7NO_2S$ 193.0197, found 193.0199.

The analytical data are in accordance with those reported in the literature.[2]



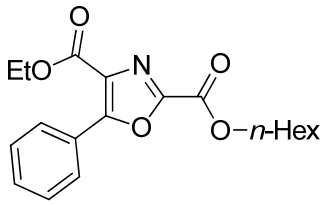
3g

***n*-Hexyl-benzo[*d*]thiazole-2-carboxylate (3g):** The representative procedure was followed using benzo[*d*]thiazole (**1d**) (139 mg, 1.03 mmol), KO*t*-Bu (135 mg, 1.20 mmol) and *n*-hexyl iodide (**2b**) (3.00 equiv). Purification by column chromatography (*n*-pentane/Et_2O = 20/1) yielded **3g** (168 mg, 62%) as a yellow solid.

m.p. = 38–40 °C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.26 (m, 1H), 8.98 (m, 1H), 7.63 – 7.49 (m, 2H), 4.48 (t, J = 6.9 Hz, 2H), 1.94 – 1.75 (m, 2H), 1.55 – 1.25 (m, 6H), 0.94 – 0.87 (m, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 160.6 (C_q), 158.4 (C_q), 153.2 (C_q), 136.7 (C_q), 127.5 (CH), 127.0 (CH), 125.5 (CH), 122.0 (CH), 67.2 (CH_2), 31.4 (CH_2), 28.5 (CH_2), 25.5 (CH_2), 22.5 (CH_2), 14.0 (CH_3). IR (neat): 3058, 2918, 1728, 1496, 1254, 1099, 865, 765, 583 cm^{-1}. MS (EI) *m/z* (relative intensity) 263 (10 [M^+]), 219 (30), 180 (33), 162 (82), 135 (100), 90 (11), 43 (29). HR-MS (EI) *m/z* calcd for $C_{14}H_{17}NO_2S$ 263.0980, found 263.0988.

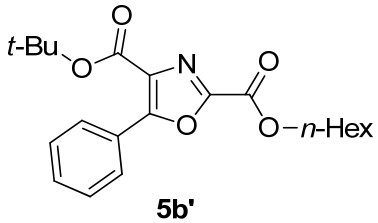
Synthesis of 2-*n*-Hexyl-4-ethyl-5-phenyloxazole-2,4-dicarboxylate (5b) and 2-*n*-Hexyl-4-*tert*-butyl-5-phenyloxazole-2,4-dicarboxylate (5b')

The representative procedure was followed using ethyl 5-phenyloxazole-4-carboxylate (**4a**) (213 mg, 0.98 mmol), KO*t*-Bu (135 mg, 1.20 mmol) and *n*-hexyl iodide (**2b**) (3.00 equiv). Purification by column chromatography (*n*-pentane/Et_2O = 10/1 → 7/1 → 5/1) yielded **5b** (222 mg, 65%) and **5b'** (11 mg, 3%) as yellow oils.



5b

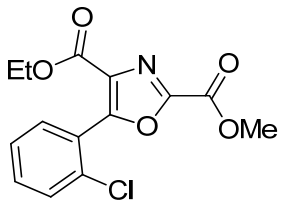
2-*n*-Hexyl-4-ethyl-5-phenyloxazole-2,4-dicarboxylate (5b): ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.19 – 8.06 (m, 2H), 7.56 – 7.44 (m, 3H), 4.53 – 4.34 (m, 4H), 1.81 (dq, J = 8.2, 6.9 Hz, 2H), 1.51 – 1.22 (m, 9H), 0.95 – 0.84 (m, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 161.4 (C_q), 157.4 (C_q), 155.4 (C_q), 150.0 (C_q), 131.3 (CH), 128.9 (CH), 128.6 (C_q), 128.5 (CH), 125.9 (C_q), 67.1 (CH_2), 61.8 (CH_2), 31.3 (CH_2), 28.4 (CH_2), 25.4 (CH_2), 22.5 (CH_2), 14.2 (CH_3), 14.0 (CH_3). IR (neat): 2931, 2859, 1721, 1549, 1334, 1171, 1093, 763, 690 cm^{-1}. MS (EI) *m/z* (relative intensity) 345 ([M$^+$] 23), 300 (18), 244 (45), 189 (28), 105 (100), 43 (99). HR-MS (EI) *m/z* calcd for $C_{19}H_{23}NO_5$ 345.1576, found 345.1577.



5b'

2-*n*-Hexyl-4-*tert*-butyl-5-phenyloxazole-2,4-dicarboxylate (5b'): ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.06 – 7.98 (m, 2H), 7.53 – 7.44 (m, 3H), 4.42 (t, J = 6.9 Hz, 2H), 1.88 – 1.74 (m, 2H), 1.58 (s, 9H), 1.51 – 1.24 (m, 6H), 0.95 – 0.83 (m, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 160.5 (C_q), 156.6 (C_q), 155.5 (C_q), 150.0 (C_q), 131.0 (CH), 129.9 (C_q), 129.0 (CH), 128.4 (CH), 126.3 (C_q), 83.1 (CH_2), 67.0 (C_q), 31.4 (CH_2), 28.4 (CH_2), 28.1 (CH_3), 25.4 (CH_2), 22.5 (CH_2), 14.0 (CH_3). IR (neat): 2931, 1716, 1547, 1367, 1236, 1160, 1094, 844, 690 cm^{-1}. MS (EI) *m/z* (relative intensity) 373 ([M$^+$] 46), 317 (80), 273 (56), 216

(100), 105 (61), 43 (45). HR-MS (EI) *m/z* calcd for $C_{21}H_{27}NO_5$ 373.1889, found 373.1880.



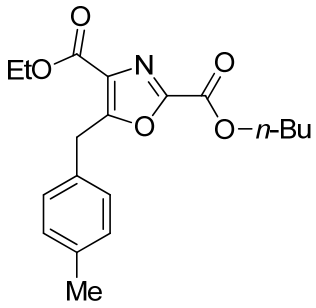
5c

4-Ethyl-2-methyl-5-(2-chlorophenyl)oxazole-2,4-dicarboxylate (5c): The representative procedure was followed using ethyl 5-(2-chlorophenyl)oxazole-4-carboxylate (**4b**) (259 mg, 1.03 mmol), and KO*t*-Bu (135 mg, 1.20 mmol). Purification by column chromatography (*n*-pentane/Et_2O = 10/1 → 5/1 → 3/1 → 2/1) yielded **5c** (164 mg, 52%) as an off-white solid.
m.p. = 83–85 °C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.56 – 7.52 (m, 2H), 7.47 (ddd, J = 7.6, 7.6, 1.7 Hz, 1H), 7.39 (ddd, J = 7.3, 7.3, 1.7 Hz, 1H), 4.32 (q, J = 7.1 Hz, 2H), 4.03 (s, 3H), 1.26 (t, J = 7.1 Hz, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 160.3 (C_q), 155.6 (C_q), 155.0 (C_q), 151.1 (C_q), 134.4 (C_q), 132.2 (CH), 132.1 (CH), 131.5 (C_q), 130.0 (CH), 126.5 (CH), 125.7 (C_q), 61.6 (CH_2), 53.5 (CH_3), 14.0 (CH_3). IR (neat): 2991, 1738, 1721, 1551, 1339, 1194, 1028, 753, 653 cm^{-1}. MS (EI) *m/z* (relative intensity) 274 (96), 246 (100), 214 (77), 139 (49), 59 (21). HR-MS (EI) *m/z* calcd for $C_{14}H_{12}ClNO_5$ 309.0404, found 309.0410.

Synthesis of 2-*n*-Butyl-4-ethyl-5-(4-methylbenzyl)oxazole-2,4-dicarboxylate (5d) and 2-Butyl-4-ethyl-5-(1-(4-methyl-phenyl)pentyl)oxazole-2,4-dicarboxylate (5d')

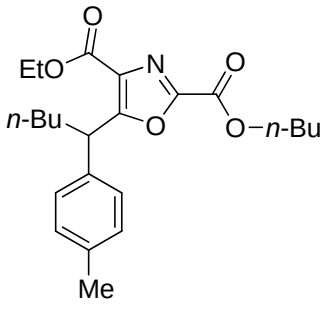
The representative procedure was followed using ethyl 5-(4-methylbenzyl)oxazole-4-carboxylate (**4c**) (242 mg, 0.99 mmol), KO*t*-Bu (135 mg, 1.20 mmol) and *n*-butyl iodide (**2c**)

(3.00 equiv). Purification by column chromatography (*n*-pentane/Et_2O = 10/1 → 7/1 → 5/1) yielded **5d** (174 mg, 51%) and **5d'** (25 mg, 6%) as yellow oils.



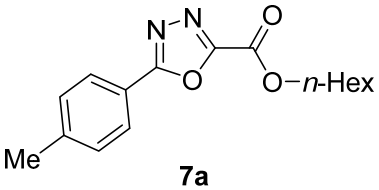
5d

2-*n*-Butyl-4-ethyl-5-(4-methylbenzyl)oxazole-2,4-dicarboxylate (5d): ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.21 (d, J = 8.0 Hz, 2H), 7.11 (d, J = 8.0 Hz, 2H), 4.49 – 4.33 (m, 6H), 2.31 (s, 3H), 1.82 – 1.68 (m, 2H), 1.49 – 1.33 (m, 5H), 0.94 (t, J = 7.4 Hz, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 161.3 (C_q), 160.6 (C_q), 155.4 (C_q), 150.5 (C_q), 137.0 (C_q), 132.1 (C_q), 129.5 (CH), 129.2 (C_q), 128.7 (CH), 66.7 (CH_2), 61.5 (CH_2), 31.8 (CH_2), 30.4 (CH_2), 21.0 (CH_3), 18.9 (CH_2), 14.3 (CH_3), 13.6 (CH_3). IR (neat): 2906, 2874, 1737, 1549, 1249, 1154, 1067, 791, 655 cm^{-1}. MS (EI) *m/z* (relative intensity) 345 ([M^+] 27), 299 (15), 243 (100), 199 (79), 105 (33), 41 (25). HR-MS (EI) *m/z* calcd for $C_{19}H_{23}NO_5$ 345.1567, found 345.1572.



5d'

2-*n*-Butyl-4-ethyl-5-{1-(4-methylphenyl)pentyl}oxazole-2,4-dicarboxylate (5d'): ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.29 (d, J = 8.1 Hz, 2H), 7.12 (d, J = 7.9 Hz, 2H), 4.89 (t, J = 8.0 Hz, 1H), 4.49 – 4.32 (m, 4H), 2.30 (s, 3H), 2.22 – 1.97 (m, 2H), 1.83 – 1.70 (m, 2H), 1.52 – 1.13 (m, 9H), 0.96 (t, J = 7.4 Hz, 3H), 0.85 (t, J = 7.1 Hz, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 163.7 (C_q), 161.4 (C_q), 155.4 (C_q), 150.3 (C_q), 137.0 (C_q), 136.8 (C_q), 129.4 (CH), 128.6 (C_q), 127.9 (CH), 66.6 (CH_2), 61.4 (CH_2), 42.2 (CH), 33.6 (CH_2), 30.4 (CH_2), 29.7 (CH_2), 22.3 (CH_2), 21.0 (CH_3), 19.0 (CH_2), 14.3 (CH_3), 13.8 (CH_3), 13.6 (CH_3). IR (neat): 2958, 2872, 1738, 1549, 1375, 1156, 1060, 655 cm^{-1}. MS (EI) m/z (relative intensity) 401 ([M^+] 53), 355 (100), 312 (82), 256 (98), 212 (49), 105 (38). HR-MS (EI) m/z calcd for $C_{23}H_{31}NO_5$ 401.2202, found 401.2192.

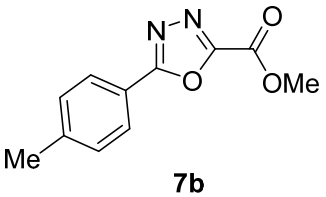


7a

***n*-Hexyl-5-(4-methylphenyl)-1,3,4-oxadiazole-2-carboxylate (7a):** The representative procedure was followed using 2-(4-methylphenyl)-1,3,4-oxadiazole (**6a**) (160 mg, 1.00 mmol), KO*t*-Bu (135 mg, 1.20 mmol) and *n*-hexyl iodide (**2b**) (3.00 equiv). Purification by column chromatography (*n*-pentane/Et_2O = 20/1 → 15/1 → 10/1 → 8/1) yielded **7a** (146 mg, 51%) as a brown oil.

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.04 (d, J = 8.2 Hz, 2H), 7.34 (d, J = 8.2 Hz, 2H), 4.47 (t, J = 6.8 Hz, 2H), 2.44 (s, 3H), 1.91 – 1.75 (m, 2H), 1.54 – 1.23 (m, 6H), 0.97 – 0.81 (m, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 166.6 (C_q), 156.2 (C_q), 154.6 (C_q), 143.6 (C_q), 129.9 (CH), 127.6 (CH), 120.0 (C_q), 67.5 (CH_2), 31.3 (CH_2), 28.4 (CH_2), 25.4 (CH_2), 22.5 (CH_2), 21.70 (CH_3), 14.0 (CH_3). IR (neat): 2928, 2859, 1743, 1492, 1272, 1170,

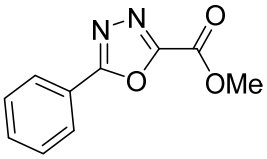
1090, 825, 732 cm^{-1}. MS (EI) *m/z* (relative intensity) 288 (13 [M^+]), 244 (16), 187 (69), 159 (100), 117 (73), 91 (57), 43 (59). HR-MS (EI) *m/z* calcd for $C_{16}H_{20}N_2O_3$ 288.1474, found 288.1471.



7b

Methyl-5-(4-methylphenyl)-1,3,4-oxadiazole-2-carboxylate (7b): The representative procedure was followed using 2-(4-methylphenyl)-1,3,4-oxadiazole (**6a**) (160 mg, 1.00 mmol), and KO*t*-Bu (135 mg, 1.20 mmol). Purification by column chromatography (*n*-pentane/Et_2O = 10/1 → 5/1 → 4/1 → 3/1) yielded **7b** (121 mg, 56%) as a colorless solid.

m.p. = 118–120 °C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.04 (d, J = 8.2 Hz, 2H), 7.34 (d, J = 8.0 Hz, 2H), 4.08 (s, 3H), 2.44 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 166.7 (C_q), 156.1 (C_q), 154.9 (C_q), 143.7 (C_q), 129.9 (CH), 127.6 (CH), 119.9 (C_q), 53.7 (CH_3), 21.7 (CH_3). IR (neat): 2956, 2854, 1741, 1529, 1447, 1202, 1163, 819, 728 cm^{-1}. MS (EI) *m/z* (relative intensity) 218 ([M^+] 81), 159 (100), 131 (21), 117 (54), 91 (56), 65 (18). HR-MS (EI) *m/z* calcd for $C_{11}H_{10}N_2O_3$ 218.0691, found 218.0693.



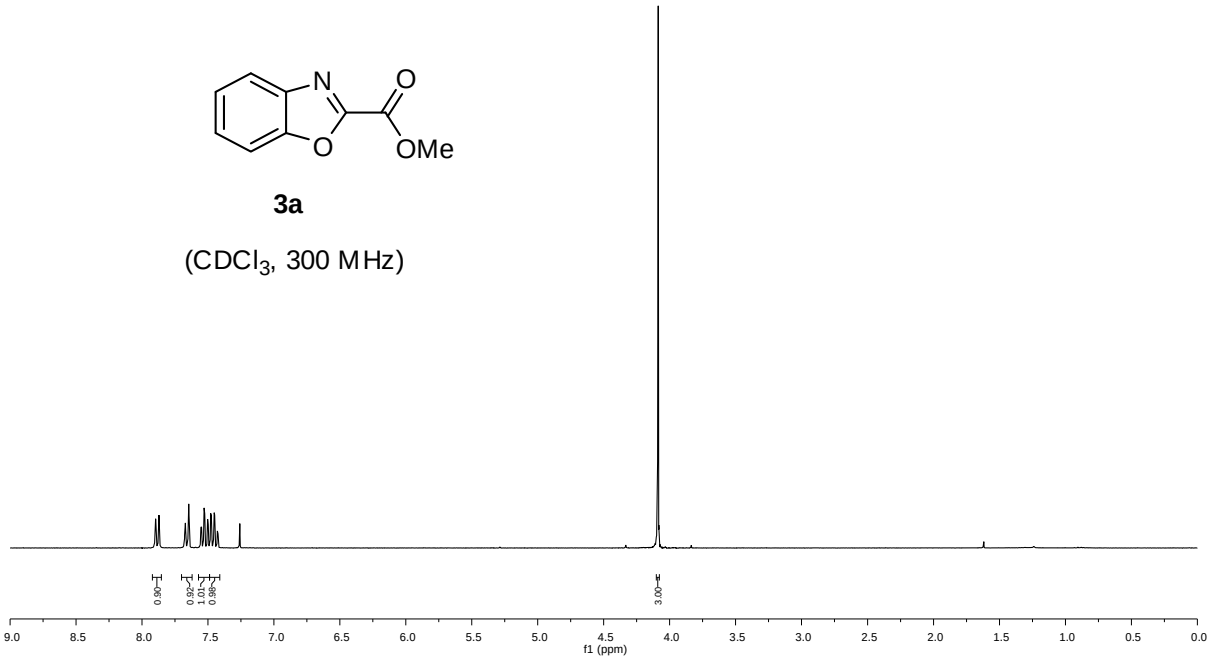
7c

Methyl-5-phenyl-1,3,4-oxadiazole-2-carboxylate (7c): The representative procedure was followed using 2-phenyl-1,3,4-oxadiazole (**6b**) (149 mg, 1.00 mmol), and KO*t*-Bu (135 mg, 1.20 mmol). Purification by column chromatography

(*n*-pentane/Et_2O = 10/1 → 5/1 → 4/1) yielded **7c** (89 mg, 43%) as a colorless solid.

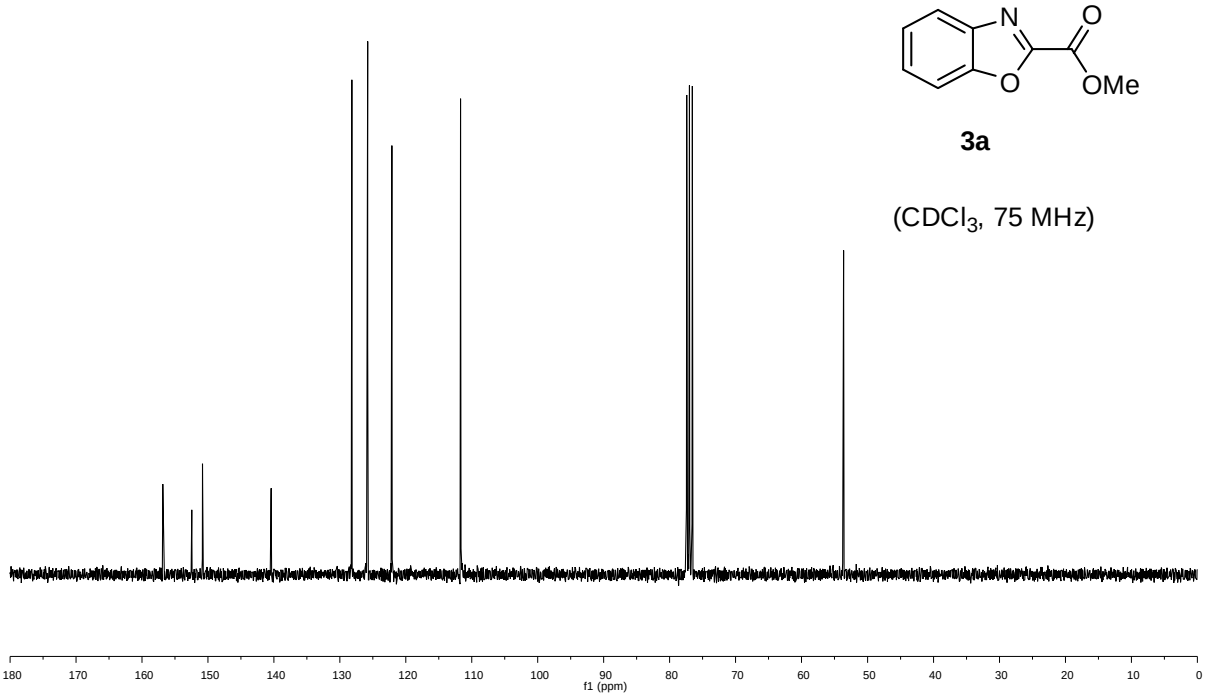
m.p. = 118–119 °C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.20 - 8.13 (m, 2H), 7.65 - 7.50 (m, 3H), 4.09 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 166.5 (C_q), 156.3 (C_q), 154.8 (C_q), 132.9 (CH), 129.2 (CH), 127.6 (CH), 122.7 (C_q), 53.8 (CH_3). IR (neat): 2963, 1737, 1539, 1378, 1204, 1094, 811, 710, 642 cm^{-1}. MS (EI) *m/z* (relative intensity) 204 ([M^+] 44), 145 (100) 103 (20), 77 (64), 43 (17). HR-MS (EI) *m/z* calcd for $C_{10}H_8N_2O_3$ 204.0535, found 204.0537.

The analytical data are in accordance with those reported in the literature.[6]



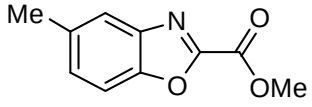
3a

($CDCl_3$, 300 MHz)



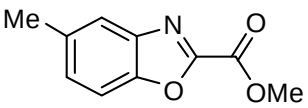
3a

($CDCl_3$, 75 MHz)



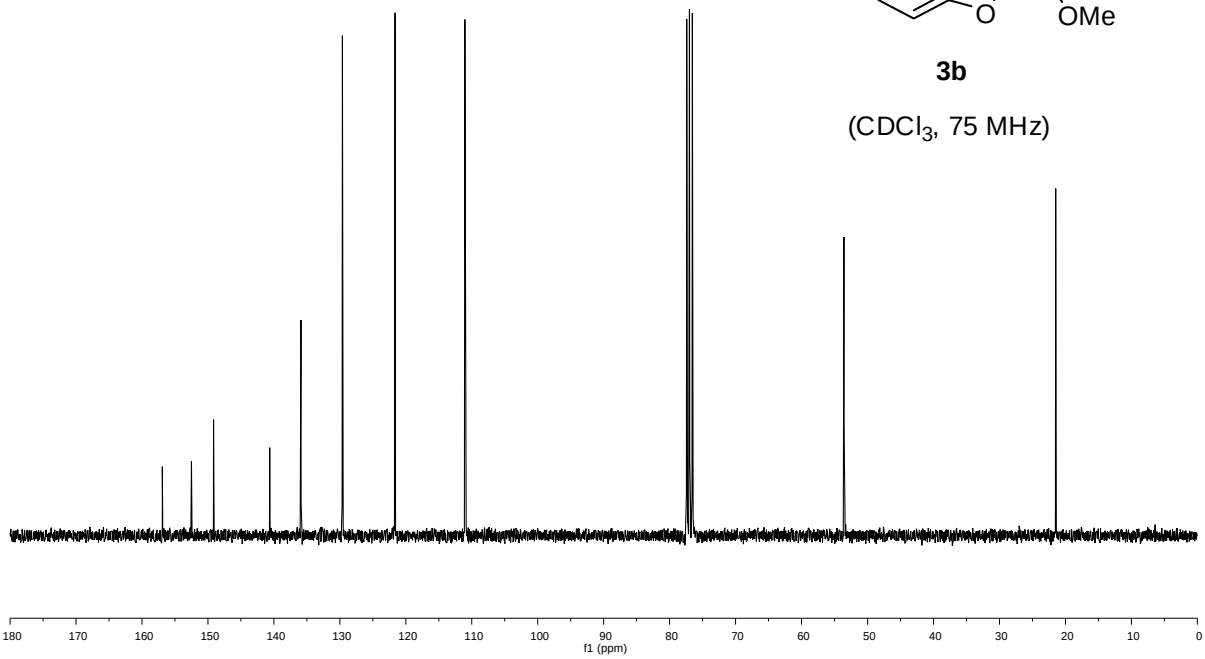
3b

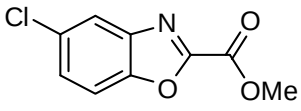
($CDCl_3$, 300 MHz)



3b

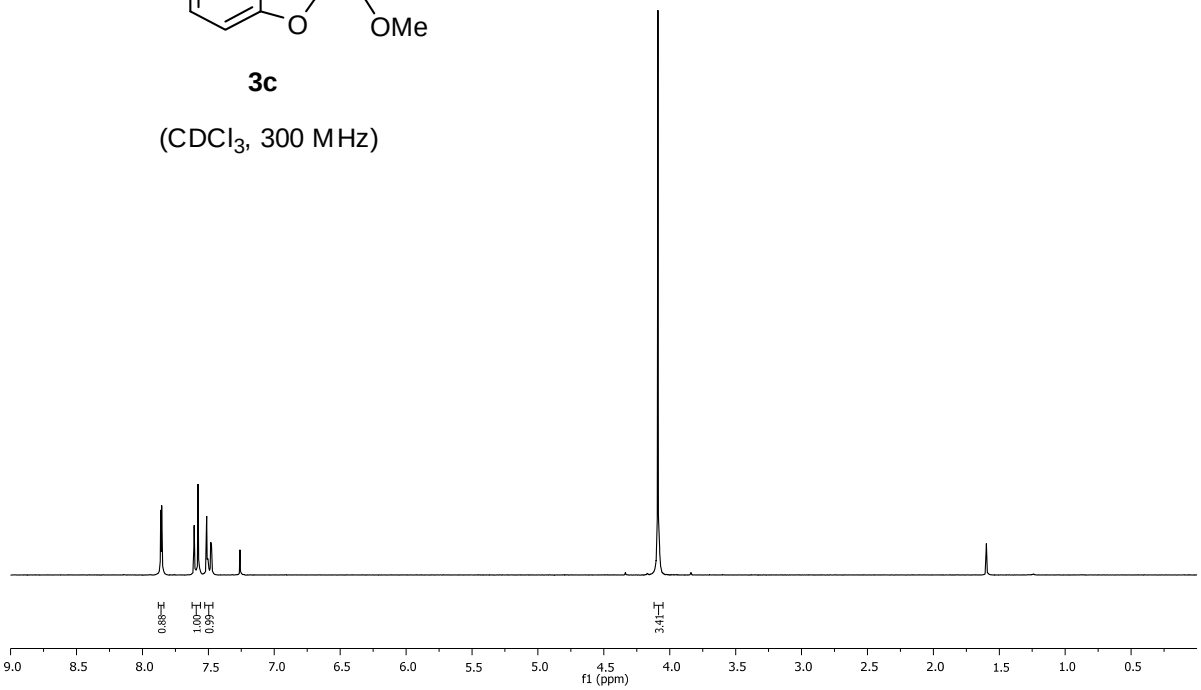
($CDCl_3$, 75 MHz)

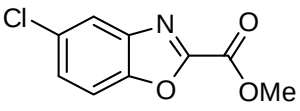




3c

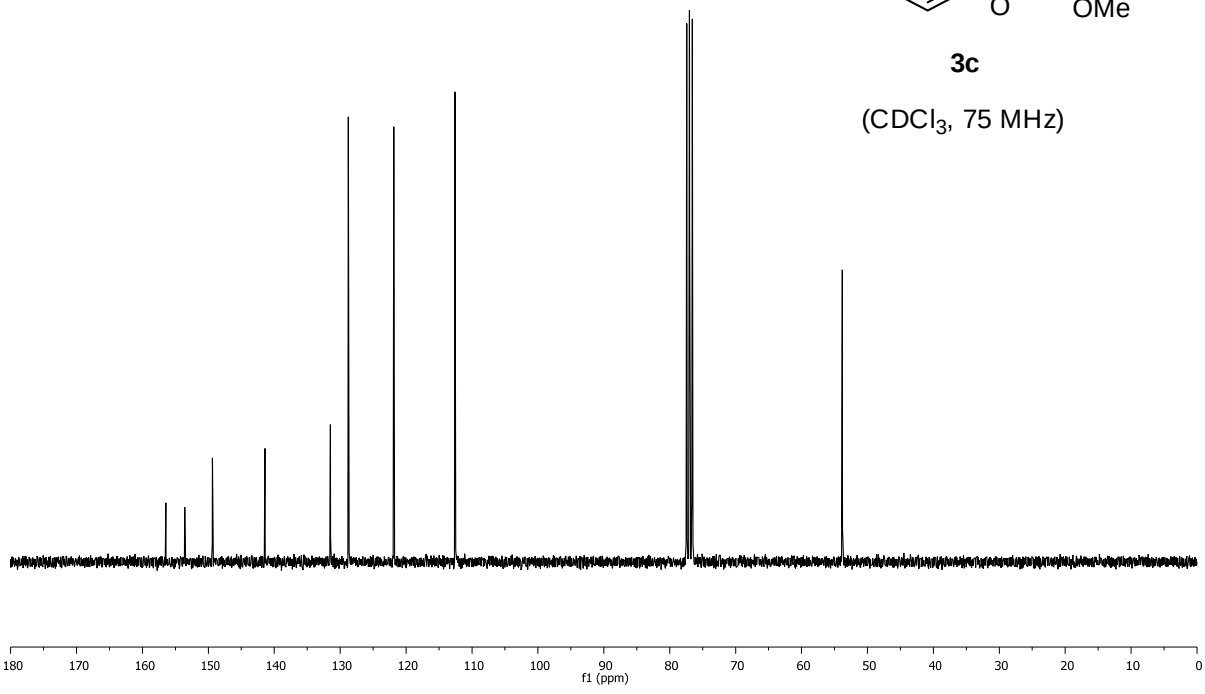
($CDCl_3$, 300 MHz)

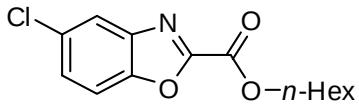




3c

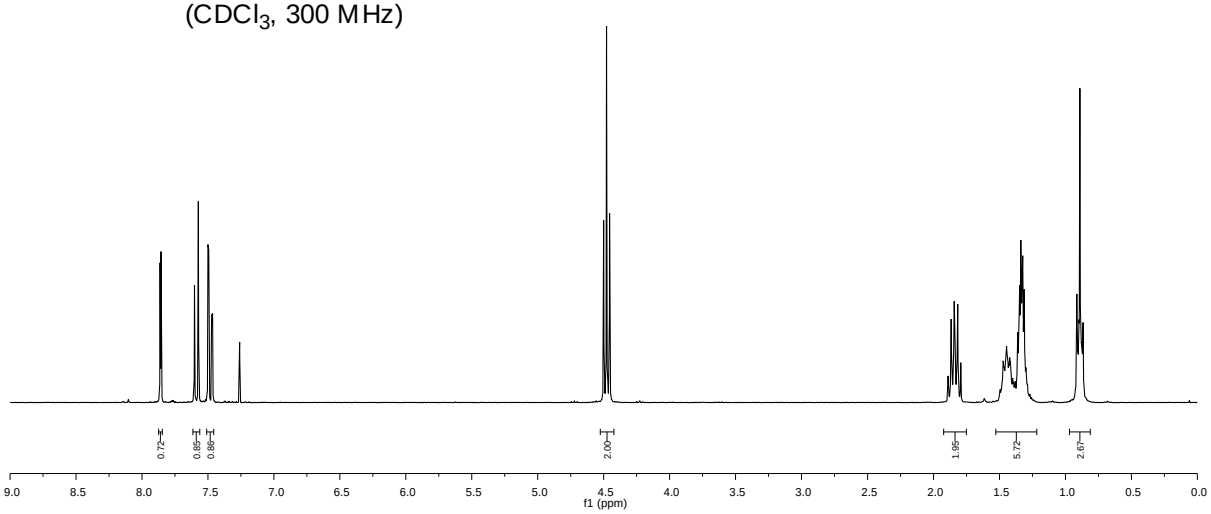
($CDCl_3$, 75 MHz)

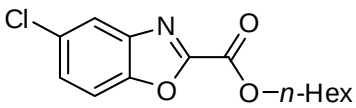




3d

($CDCl_3$, 300 MHz)





3d

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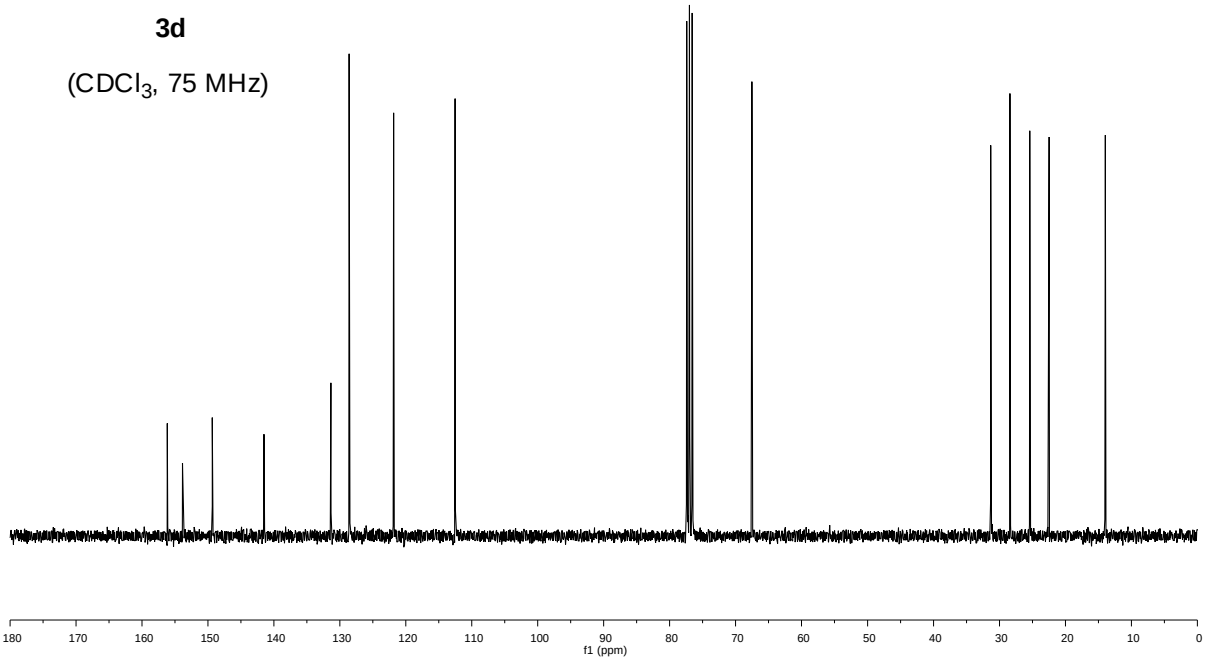

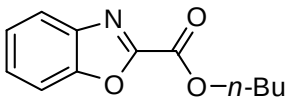

3e

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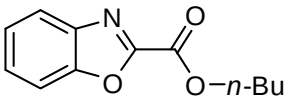
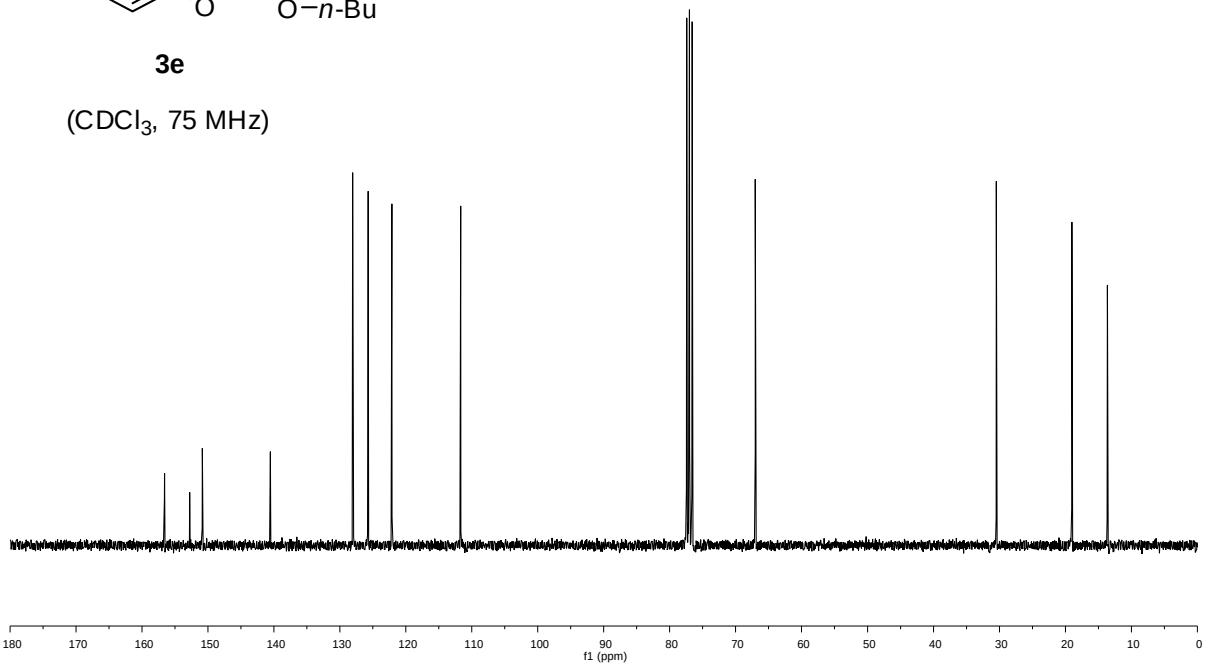
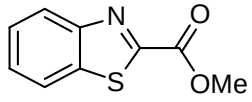


3e

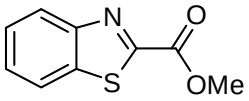
($CDCl_3$, 75 MHz)





3f

($CDCl_3$, 300 MHz)



3f

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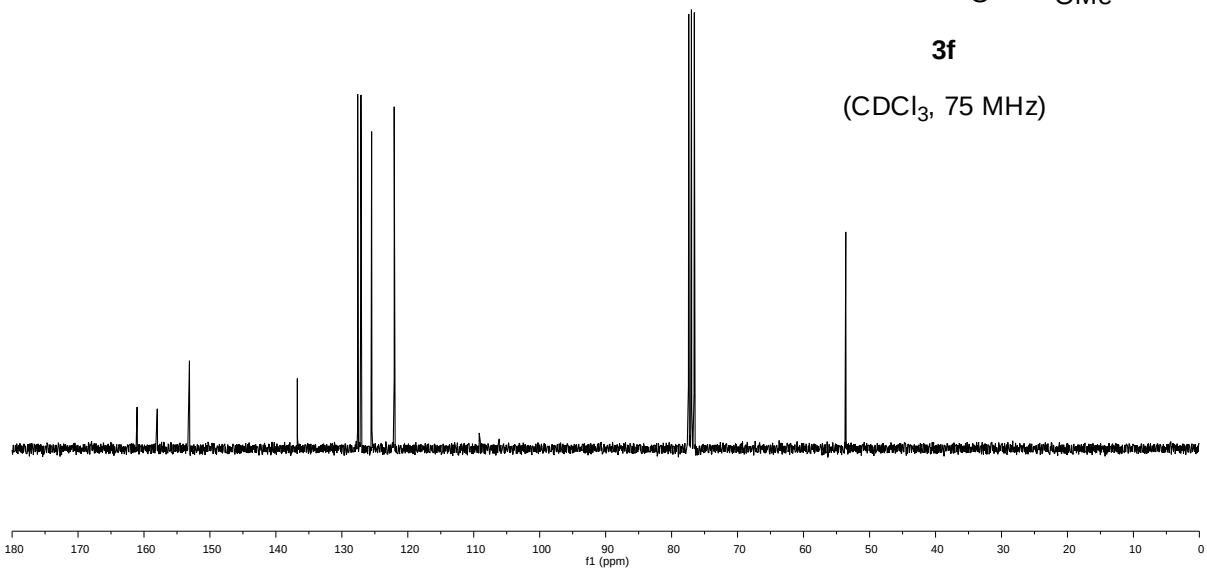
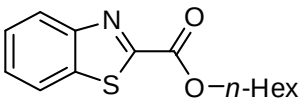
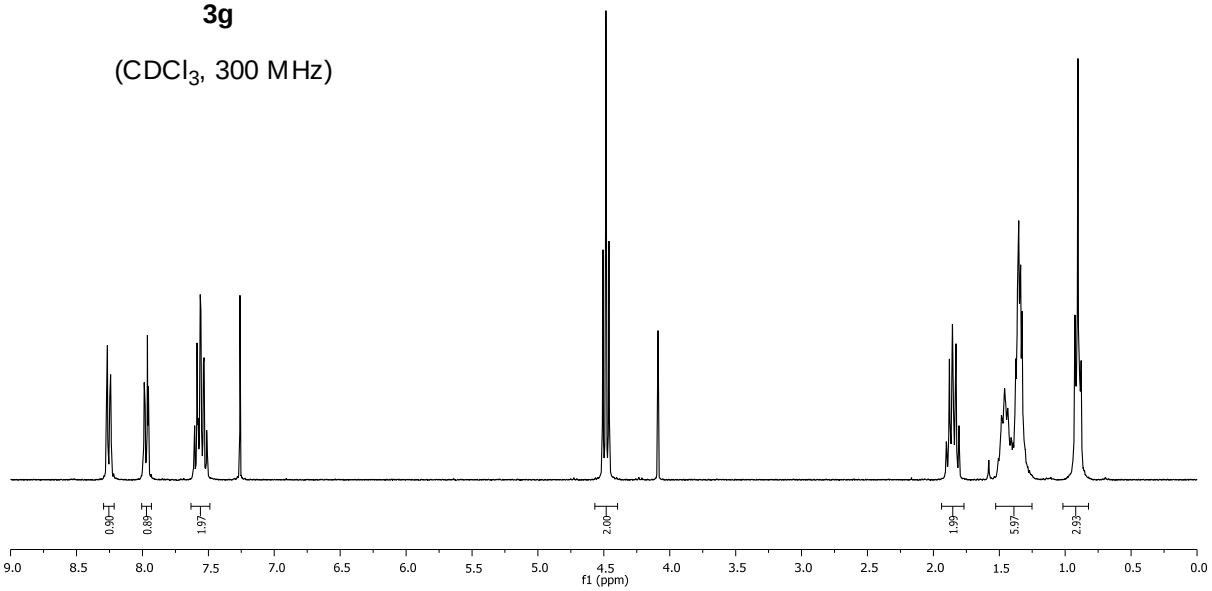
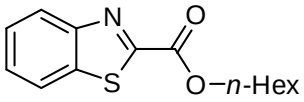




3g

($CDCl_3$, 300 MHz)





3g

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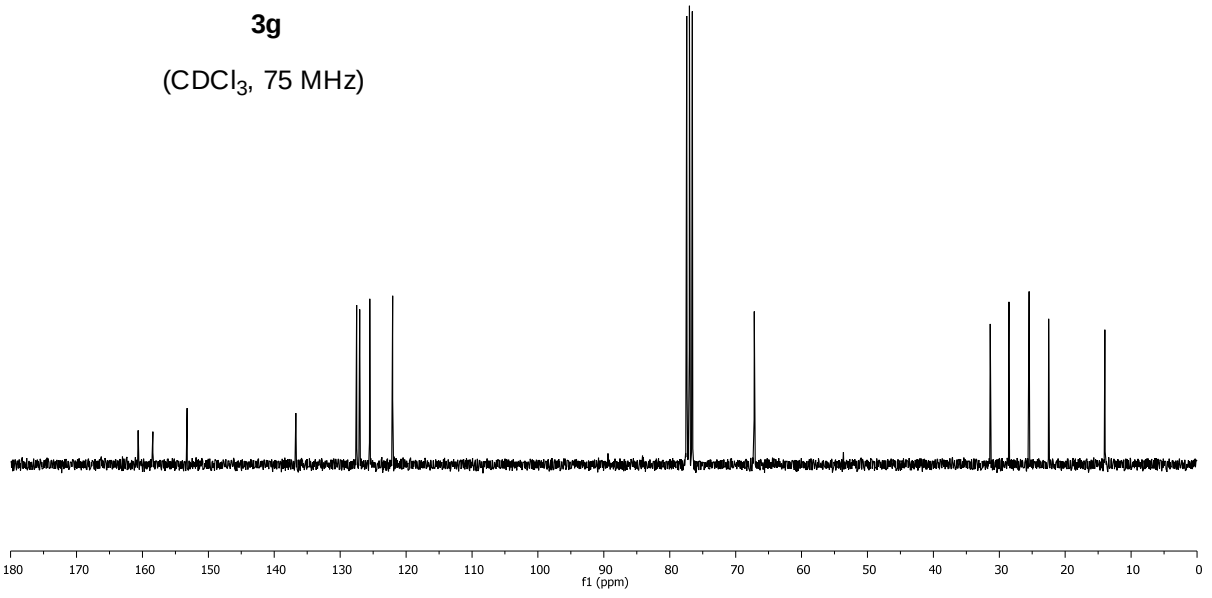
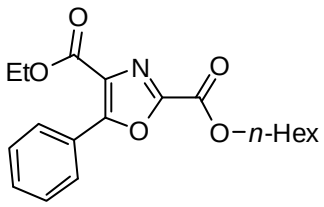
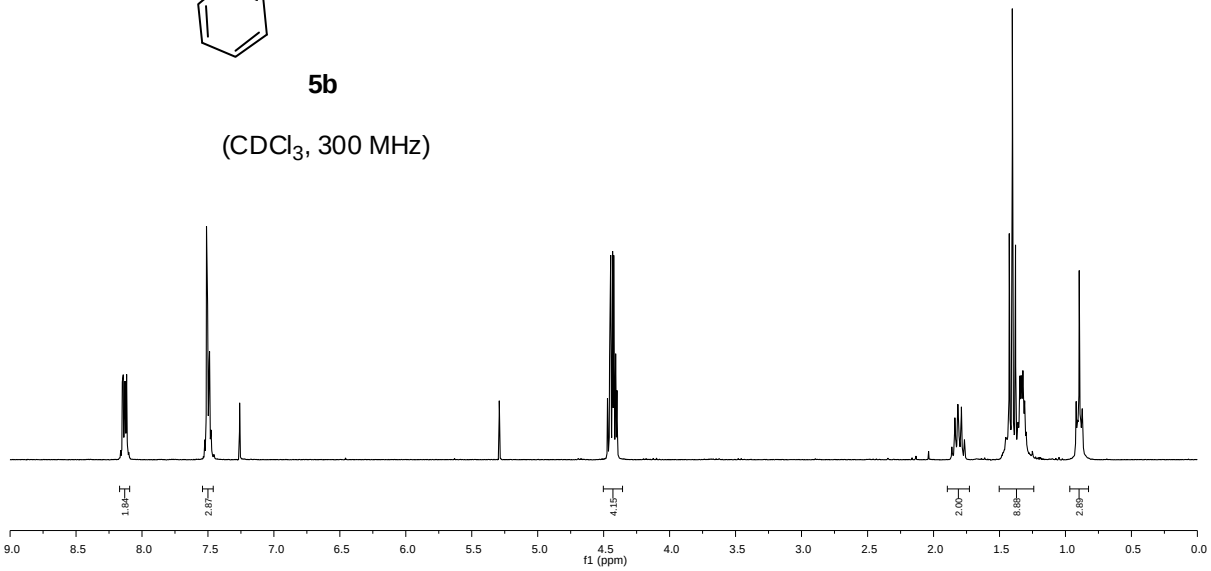
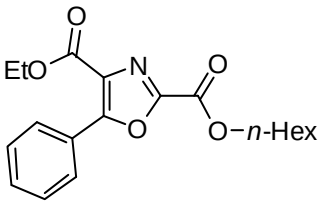




5b

($CDCl_3$, 300 MHz)





5b

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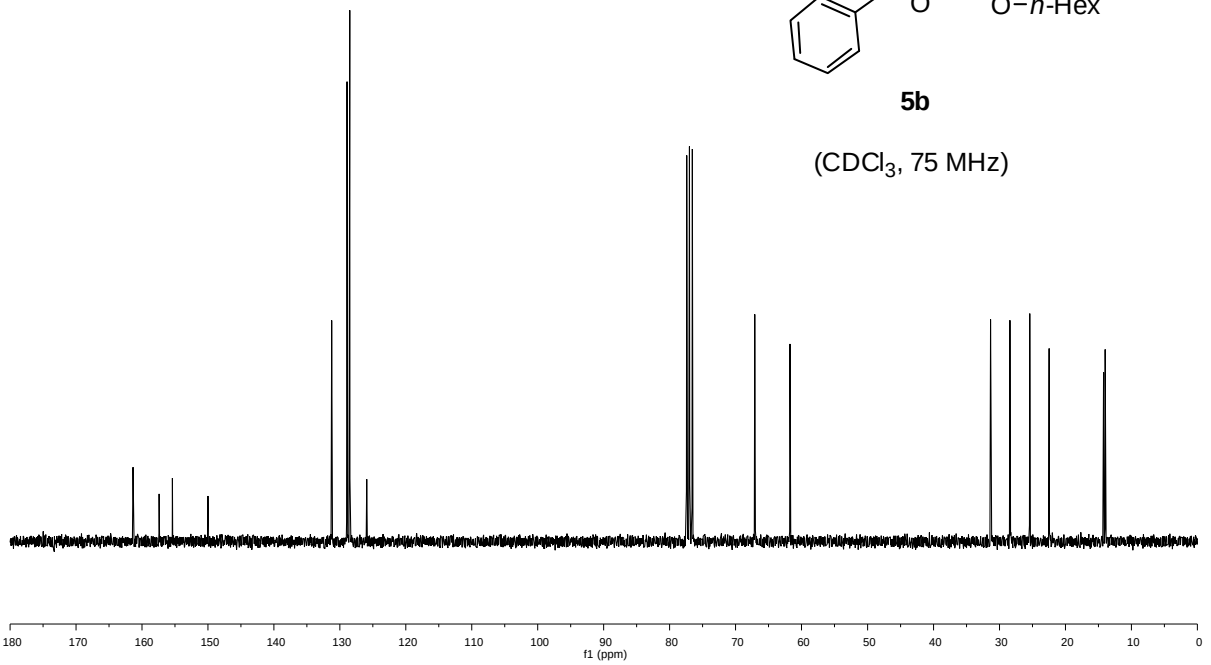

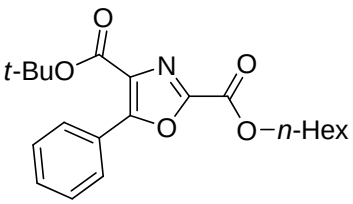

5b'

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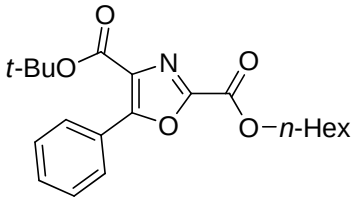

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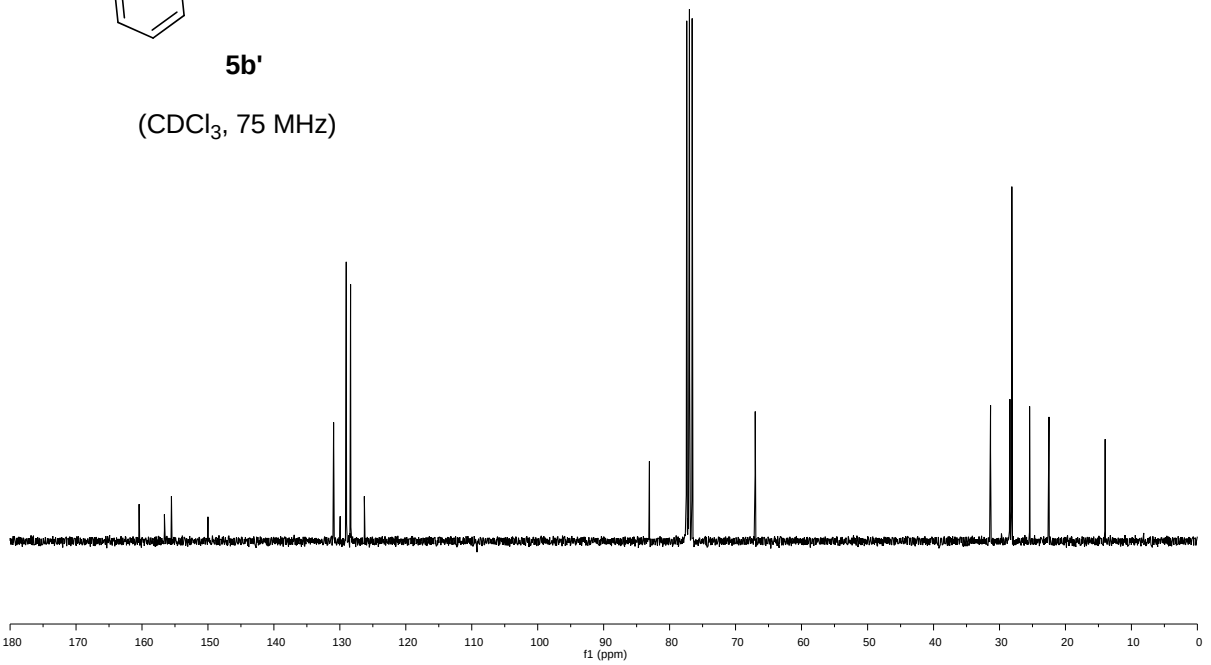
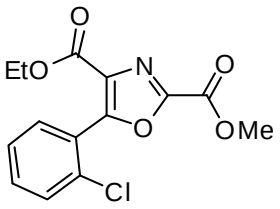
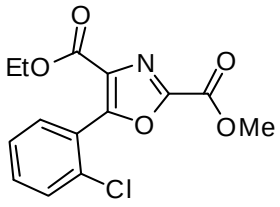




5c

($CDCl_3$, 300 MHz)



5c

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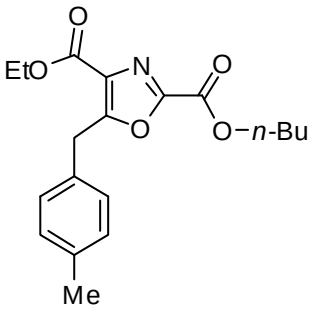
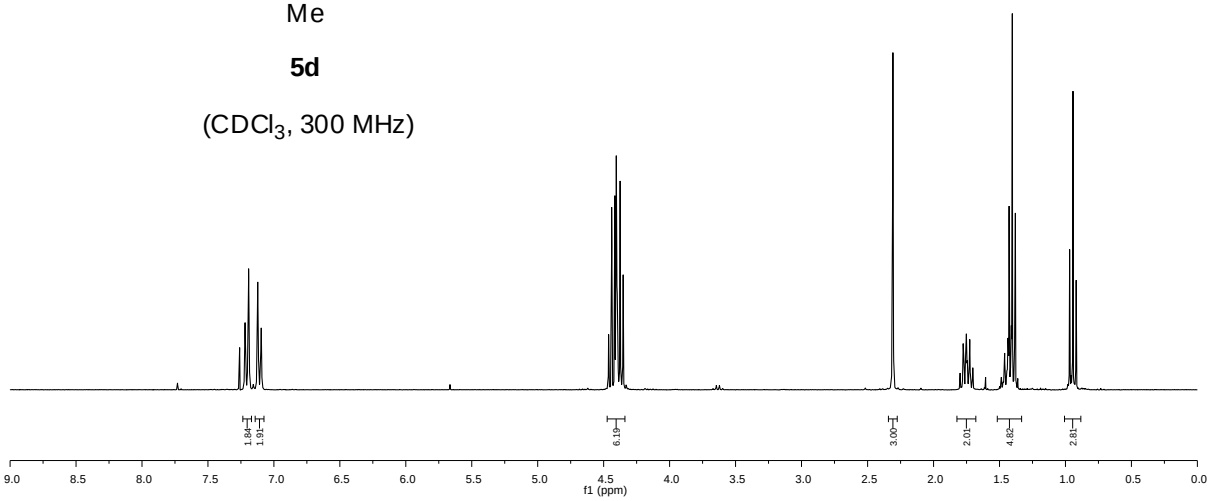
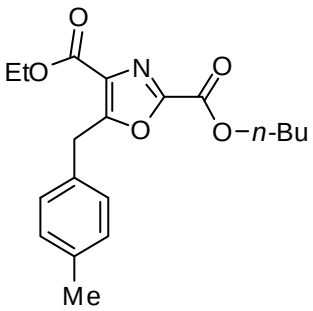


5d

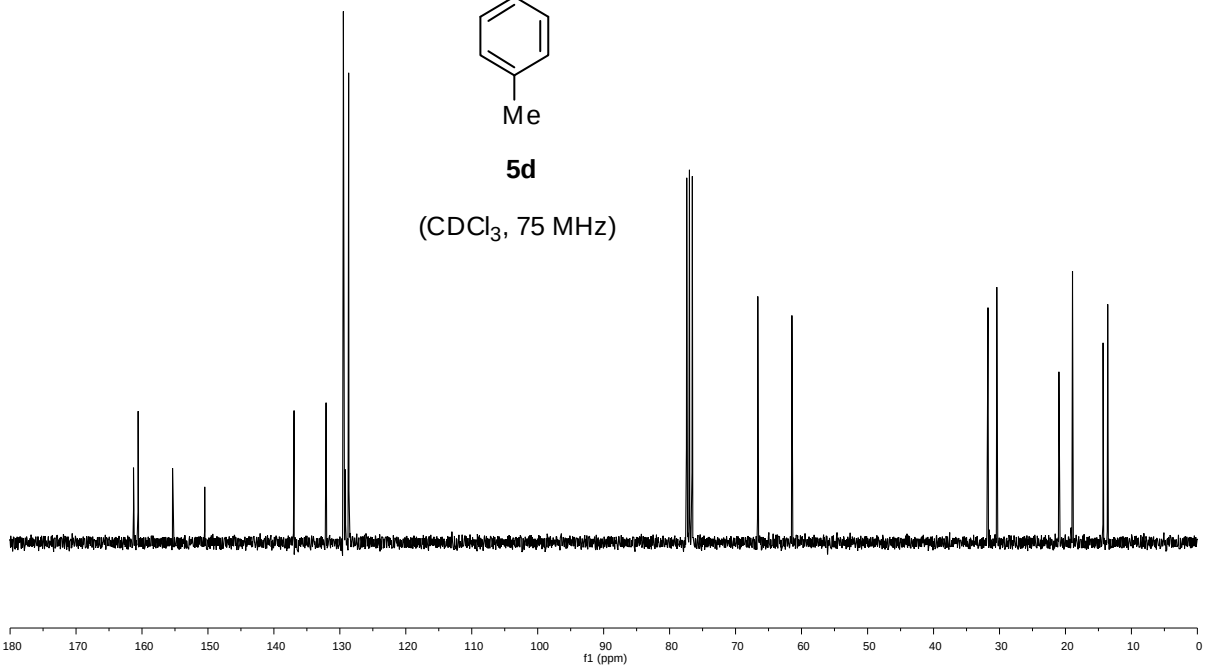
($CDCl_3$, 300 MHz)

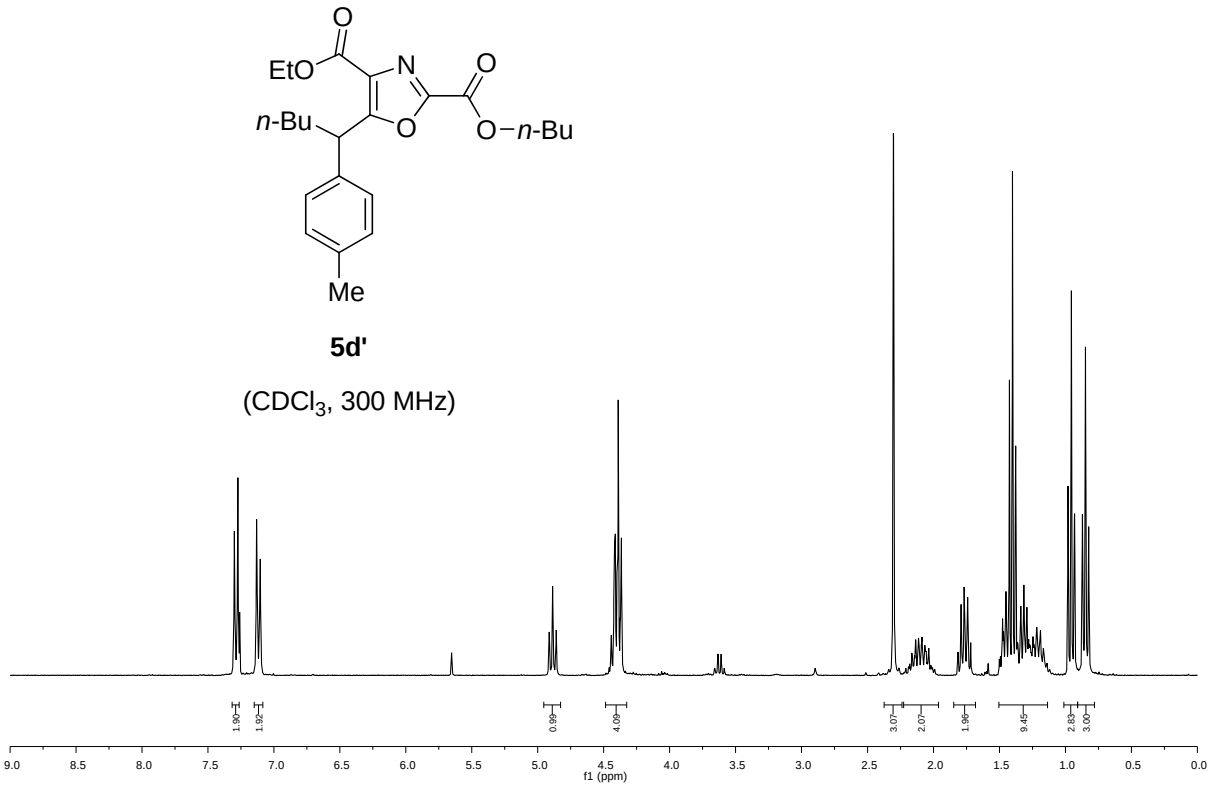




5d

($CDCl_3$, 75 MHz)





5d'

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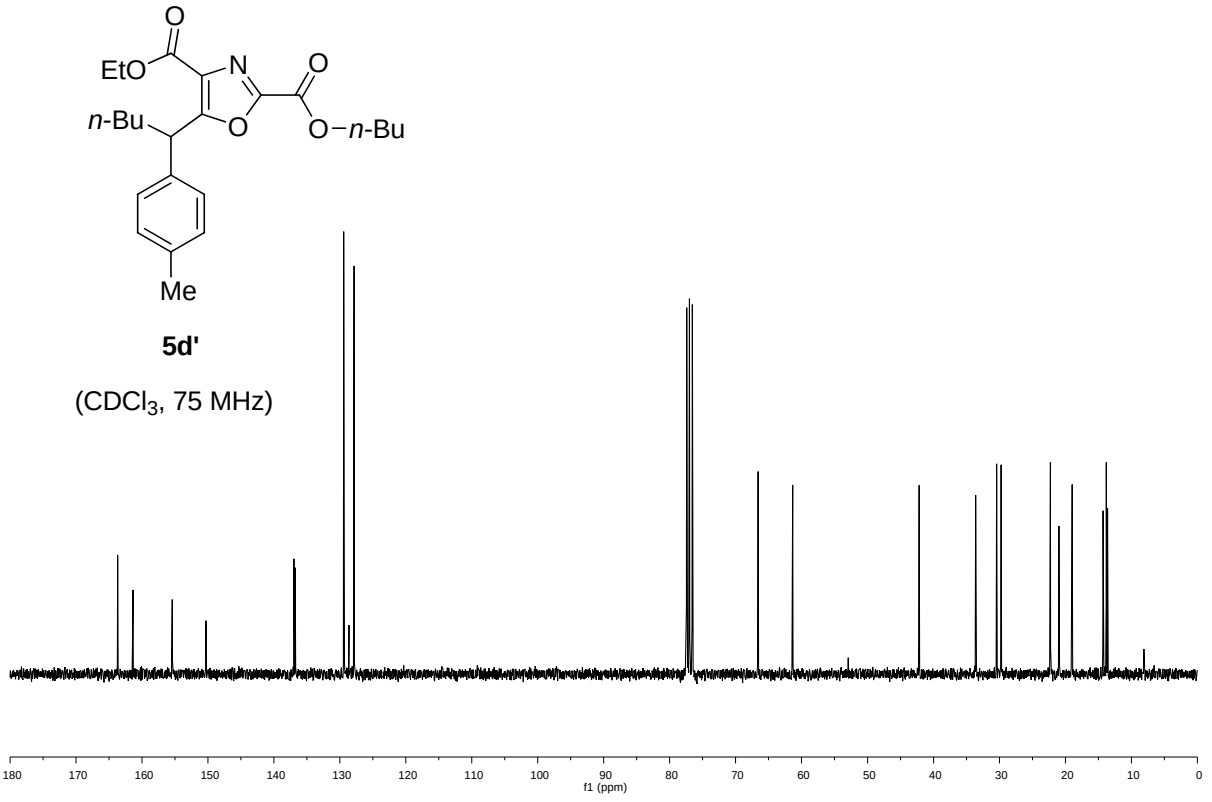

5d'

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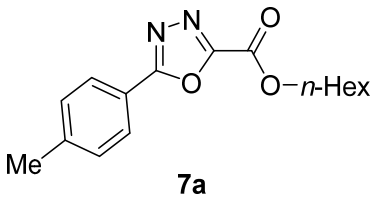
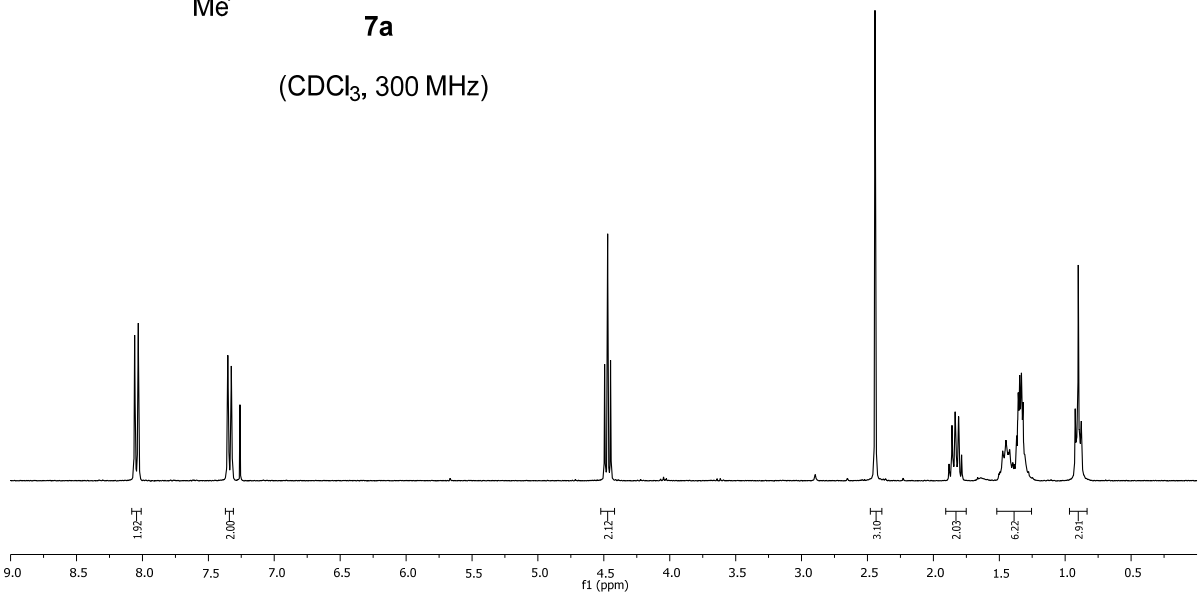
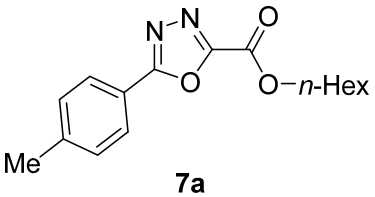


7a

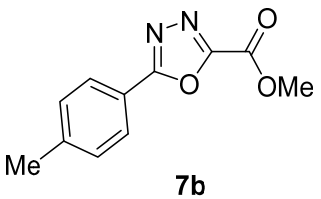
($CDCl_3$, 300 MHz)





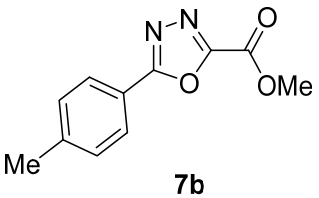
7a

($CDCl_3$, 75 MHz)



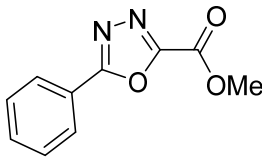
7b

($CDCl_3$, 300 MHz)



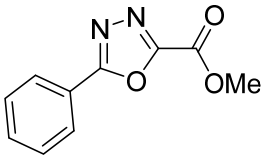
7b

($CDCl_3$, 75 MHz)



7c

($CDCl_3$, 300 MHz)



7c

($CDCl_3$, 75 MHz)

References

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