SUPPORTING INFORMATION

Metal- and Base-free Selective Amidations of Organoboronic Acids with Dioxazolones and Isocyanates

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1. MATERIALS AND GENERAL METHODS

1.1. Glassware, Solvents and Reagents

All manipulations were performed with oven-dried (130 °C for a minimum of 12 h) glassware under air or an atmosphere of nitrogen, unless otherwise stated.

All anhydrous solvents were commercially supplied. Reagents were purchased from commercial sources and used as received.

1.2. Chromatography and Instrumentation

Thin layer chromatography (TLC) was performed using Kepunuo Kieselgel 60 GF254 fluorescent treated silica, which was visualized under UV light, or by staining with aqueous basic potassium permanganate followed by heating.

Flash column chromatography (FCC) was carried out using Liang Chen Guiyuan silica gel (300-400 mesh).

NMR spectra were recorded, using Bruker 400 MHz for ^{1}H, ^{13}C and ^{19}F acquisitions. All NMR spectra were recorder at 25 °C unless otherwise stated. Chemical shifts (δ) are reported in parts per million (ppm) and referenced to $CDCl_3$ (^{1}H: 7.26 ppm; ^{13}C: 77.16 ppm) or d_6-DMSO (^{1}H: 2.50 ppm; ^{13}C: 39.5 ppm). Coupling constants (J) are given in Hertz (Hz) and refer to apparent multiplicities (s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, hex = hextet, h = heptet, m = multiplet, brs = broad signal, dd = doublet of doublets, etc.). The ^{1}H NMR spectra are reported as follows: chemical shift (multiplicity, coupling constants, number of protons).

IR spectra were recorded were recorded on Bruker INVENIO. Selected absorption maxima (ν_{max}) are reported in wavenumbers (cm^{-1}).

High resolution mass spectra (HRMS) were recorded on a Bruker Daltonics MicrOTOF II by Electrospray Ionisation (ESI).

Melting point (M. p.): Stuart melting point apparatus X-4, Ruihongcheng Scientific, values are uncorrected.

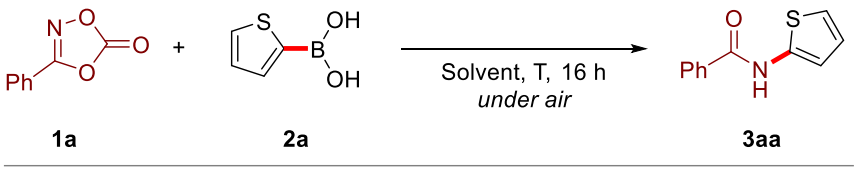
1.3. Naming of Compounds

Compound names are those generated by ChemDraw Professional 20.0 software (PerkinElmer), following the IUPAC nomenclature.

2. EXPERIMENTAL DATA

2.1. Reaction Optimizations

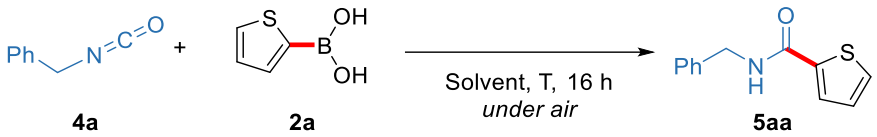
Table S1: Optimization studies for the coupling reaction of 3-phenyl-1,4,2-dioxazol-5-one[1] (1a) and 2-thiopheneboronic acid (2a).[a]



Entry	**2**	Solvent	T / °C	**3aa** (%)[b]
1	**2a**	CH_3CN	120	56
2	**2a**	DCE	120	trace
3	**2a**	DMAc	120	n.d.
4	**2a**	1,4-dioxane	120	n.d.
5	**2a**	DCE:CH_3CN (1:1)	120	76
6[c]	**2a**	DCE:CH_3CN (1:1)	120	54
7[c]	**2a**	DCE:CH_3CN (1:1)	130	41
8	**2b**	DCE:CH_3CN (1:1)	120	38
9	**2c**	DCE:CH_3CN (1:1)	120	n.d.
10	**2d**	DCE:CH_3CN (1:1)	120	n.d.
11	**2a**	DCE:CH_3CN (1:1)	100	23
12[d]	**2a**	DCE:CH_3CN (1:1)	120	73

[a] Reaction conditions: **1a** (0.25 mmol), **2** (0.75 mmol), and solvent (2.0 mL) under air for 16 hours; [b] Isolated yields; [c] 1.0 mL solvent was used. [d] The reaction was performed in dark. n.d. = not detected. DCE = Dichloroethane; DMAc = Dimethylacetamide.

Table S2: Optimization studies for the coupling reaction of benzylisocyanate (4a) and 2-thiopheneboronic acid (2a).[a]



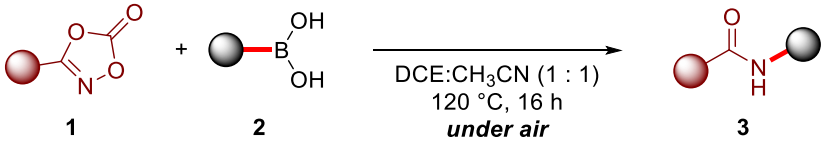
4a 2a 5aa

Entry	Solvent	Tempt. / °C	Time	**5aa** (%)[b]
1	DCE	120	16 h	85
2	DMAc	120	16 h	Trace
3	$PhCH_3$	120	16 h	57
4	1,4-dioxane	120	16 h	49
5	THF	120	16 h	38
6	DME	120	16 h	50
7	CH_3CN	120	16 h	39
8	/	120	16 h	47
9	DCE	100	16 h	58
10	DCE	130	16 h	91

[a] Reaction conditions: **4a** (0.75 mmol, 3.0 equiv.), **2a** (0.25 mmol, 1.0 equiv.), and DCE (1.0 mL), air, 16 h; [b] Isolated yield.

2.2. General Procedures

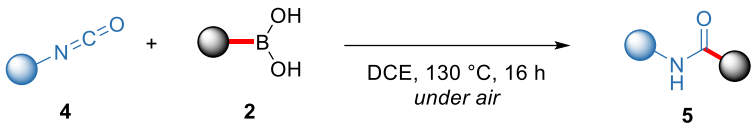
2.2.1. General Procedure A: Reactions of dioxazolones 1 with boronic acids 2



1 2 3

To a 10 mL vial equipped with a magnetic stir bar was added dioxazolone (**1**) (0.25 mmol, 1.0 equiv.), boronic acid (**2**) (0.75 mmol, 3.0 equiv.), and DCE/CH_3CN (1:1, 2.0 mL). Under air, the vial was sealed with a septum and allowed to stir at 120 °C for 16 hours. After the reaction, the mixture was cooled to room temperature and diluted with DCM (2.0 mL) and transferred into a 25 mL round flask, and concentrated under reduced pressure. The residue was purified by flash column chromatography to afford the coupled product **3**.

2.2.2. General Procedure B: Reactions of isocyanate 4 with boronic acids 2

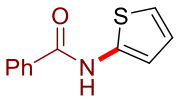


4 2 5

To a 10 mL vial equipped with a magnetic stir bar was added isocyanate (**4**) (0.75 mmol, 3.0 equiv.), boronic acid (**2**) (0.25 mmol, 1.0 equiv.), and DCE (1.0 mL). Under air, the vial was sealed with a septum and allowed to stir at 130 °C for 16 hours. After the reaction, the mixture was cooled to room temperature and diluted with DCM (2.0 mL) and transferred into a 25 mL round flask, and concentrated under reduced pressure. The residue was purified by flash column chromatography to afford the coupled product **5**.

2.3. Characterization Data

***N*-(Thiophen-2-yl)benzamide (3aa)**



3aa

Prepared following **General Procedure A**, using 3-phenyl-1,4,2-dioxazol-5-one (**1a**) (40.8 mg, 0.25 mmol, 1.0 equiv.), 2-thiopheneboronic acid (**2a**) (96.0 mg, 0.75 mmol, 3.0 equiv.), and DCE/CH_3CN (1:1, 2.0 mL). Purification by flash column chromatography (Petroleum ether / EtOAc: 5 / 1) gave the title compound **3aa** (38.6 mg, 76%) as a white solid.

TLC: R_f = 0.55 (Petroleum ether / EtOAc: 5 / 1, $KMnO_4$ stain).

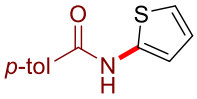
NMR Spectroscopy (*see spectra*):

^{1}H NMR (400 MHz, d_6-DMSO): δ_H 11.56 (s, 1H), 8.05 – 7.96 (m, 2H), 7.65 – 7.51 (m, 3H), 7.07 – 6.84 (m, 3H) ppm;

^{13}C NMR (101 MHz, d_6-DMSO): δ_C 163.2, 140.0, 133.1, 131.9, 128.5, 127.6, 124.1, 117.4, 112.1 ppm.

All recorded spectroscopic data matched those previously reported in the literature.[2]

4-Methyl-*N*-(thiophen-2-yl)benzamide (3ba)



3ba

Prepared following **General Procedure A**, using 3-(*p*-tolyl)-1,4,2-dioxazol-5-one (**1b**) (44.3 mg, 0.25 mmol, 1.0 equiv.), 2-thiopheneboronic acid (**2a**) (96.0 mg, 0.75 mmol, 3.0 equiv.), and DCE/CH_3CN (1:1, 2.0 mL). Purification by flash column chromatography (Petroleum ether / EtOAc: 5 / 1) gave the title compound **3ba** (46.3 mg, 83%) as a white solid.

TLC: R_f = 0.28 (Petroleum ether / EtOAc: 5 / 1, $KMnO_4$ stain).

M. p.: 208 – 210 °C.

NMR Spectroscopy (*see spectra*):

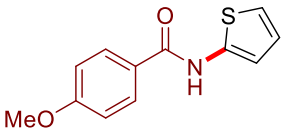
^{1}H NMR (400 MHz, d_6-DMSO): δ_H 11.46 (s, 1H), 7.97 – 7.86 (m, 2H), 7.35 (d, J = 8.0 Hz, 2H), 6.99 (dd, J = 5.2, 1.6 Hz, 1H), 6.95 – 6.87 (m, 2H), 2.38 (s, 3H) ppm;

^{13}C NMR (101 MHz, d_6-DMSO): δ_C 163.1, 142.0, 140.1, 130.3, 129.1, 127.6, 124.0, 117.3, 111.9, 21.1 ppm.

IR (film): ν_{max} 3454, 3217, 3038, 1627, 1577, 1497, 1349, 1320, 898, 831, 808, 736, 684 cm^{-1}.

HRMS (ESI^+): m/z calculated for $C_{12}H_{12}NOS$ $[M+H]^+$, 218.0634; found, 218.0640.

4-Methoxy-*N*-(thiophen-2-yl)benzamide (3ca)



3ca

Prepared following **General Procedure A**, using 3-(4-methoxyphenyl)-1,4,2-dioxazol-5-one (**1c**) (48.3 mg, 0.25 mmol, 1.0 equiv.), 2-thiopheneboronic acid (**2a**) (96.0 mg, 0.75 mmol, 3.0 equiv.),

and DCE/CH_3CN (1:1, 2.0 mL). Purification by flash column chromatography (Petroleum ether / EtOAc: 5 / 1) gave the title compound **3ca** (37.6 mg, 64%) as a white solid.

TLC: R_f = 0.14 (Petroleum ether / EtOAc: 5 / 1, $KMnO_4$ stain).

M. p.: 174.5 – 176.9 °C.

NMR Spectroscopy (*see spectra*):

^{1}H NMR (400 MHz, d_6-DMSO): δ_H 11.39 (s, 1H), 7.99 (d, J = 8.3 Hz, 2H), 7.08 (d, J = 8.8 Hz, 2H), 7.03 – 6.84 (m, 3H), 3.84 (s, 3H) ppm;

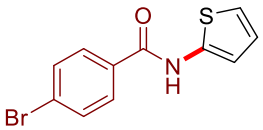
^{13}C NMR (101 MHz, d_6-DMSO): δ_C 162.7, 162.1, 140.2, 129.6, 125.2, 124.0, 117.2, 113.8, 111.7, 55.5 ppm.

M. p.: 174.5 – 176.9 °C.

IR (film): ν_{max} 3443, 1627, 1609, 1572, 1517, 1351, 1320, 1255, 1173, 1036, 842, 809, 739, 685 cm^{-1}.

HRMS (ESI^+): m/z calculated for $C_{12}H_{12}NO_2S$ $[M+H]^+$, 234.0583; found, 234.0587.

4-Bromo-*N*-(thiophen-2-yl)benzamide (3da)



3da

Prepared following **General Procedure A**, using 3-(4-bromophenyl)-1,4,2-dioxazol-5-one (**1d**) (60.5 mg, 0.25 mmol, 1.0 equiv.), 2-thiopheneboronic acid (**2a**) (96.0 mg, 0.75 mmol, 3.0 equiv.), and DCE/CH_3CN (1:1, 2.0 mL). Purification by flash column chromatography (Petroleum ether / EtOAc: 5 / 1) gave the title compound **3da** (54.2 mg, 77%) as a brown solid.

TLC: R_f = 0.30 (Petroleum ether / EtOAc: 5 / 1, $KMnO_4$ stain).

M. p.: 231 – 233 °C.

NMR Spectroscopy (*see spectra*):

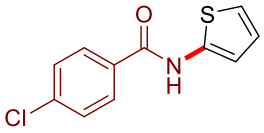
^{1}H NMR (400 MHz, d_6-DMSO): δ_H 11.62 (s, 1H), 7.95 (d, J = 8.2 Hz, 2H), 7.76 (d, J = 8.2 Hz, 2H), 7.17 – 6.81 (m, 3H) ppm;

^{13}C NMR (101 MHz, d_6-DMSO): δ_C 162.2, 139.8, 132.2, 131.6, 129.7, 125.8, 124.1, 117.6, 112.3 ppm.

IR (film): ν_{max} 3222, 3038, 1628, 1589, 1507, 1482, 1353, 1321, 1068, 1010, 836, 807, 737, 691 cm^{-1}.

HRMS (ESI^+): m/z calculated for $C_{11}H_9BrNOS$ $[M+H]^+$, 281.9583; found, 281.9590.

4-Chloro-*N*-(thiophen-2-yl)benzamide (3ea)



3ea

Prepared following **General Procedure A**, using 3-(4-chlorophenyl)-1,4,2-dioxazol-5-one (**1e**) (49.4 mg, 0.25 mmol, 1.0 equiv.), 2-thiopheneboronic acid (**2a**) (96.0 mg, 0.75 mmol, 3.0 equiv.), and DCE/CH_3CN (1:1, 2.0 mL). Purification by flash column chromatography (Petroleum ether / EtOAc: 5 / 1) gave the title compound **3ea** (43.0 mg, 72%) as a brown solid.

TLC: R_f = 0.26 (Petroleum ether / EtOAc: 5 / 1, $KMnO_4$ stain).

M. p.: 243 – 244 °C.

NMR Spectroscopy (*see spectra*):

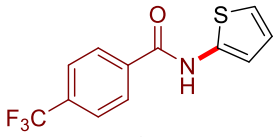
^{1}H NMR (400 MHz, d_6-DMSO): δ_H 11.62 (s, 1H), 8.02 (d, J = 8.2 Hz, 2H), 7.62 (d, J = 8.2 Hz, 2H), 7.18 – 6.78 (m, 3H) ppm;

^{13}C NMR (101 MHz, d_6-DMSO): δ_C 162.1, 139.8, 136.8, 131.8, 129.6, 128.7, 124.1, 117.6, 112.3 ppm.

IR (film): ν_{max} 3222, 3039, 1636, 1577, 1559, 1483, 1348, 1322, 1090, 1012, 897, 840, 807, 692, 678 cm^{-1}.

HRMS (ESI^+): m/z calculated for $C_{11}H_9ClNOS$ $[M+H]^+$, 238.0088; found, 238.0095.

***N*-(Thiophen-2-yl)-4-(trifluoromethyl)benzamide (3fa)**



3fa

Prepared following **General Procedure A**, using 3-[4-(trifluoromethyl)phenyl]-1,4,2-dioxazol-5-one (**1f**) (57.8 mg, 0.25 mmol, 1.0 equiv.), 2-thiopheneboronic acid (**2a**) (96.0 mg, 0.75 mmol, 3.0 equiv.), and DCE/CH_3CN (1:1, 2.0 mL). Purification by flash column chromatography (Petroleum ether / EtOAc: 5 / 1) gave the title compound **3fa** (37.0 mg, 55%) as a white solid.

TLC: R_f = 0.33 (Petroleum ether / EtOAc: 5 / 1, $KMnO_4$ stain).

M. p.: 201 – 203 °C.

NMR Spectroscopy (*see spectra*):

^{1}H NMR (400 MHz, d_6-DMSO): δ_H 11.79 (s, 1H), 8.19 (d, J = 8.0 Hz, 2H), 7.94 (d, J = 8.1 Hz, 2H), 7.05 (d, J = 5.3 Hz, 1H), 6.99 – 6.89 (m, 2H) ppm;

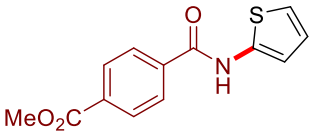
^{13}C NMR (101 MHz, d_6-DMSO): δ_C 162.0, 139.6, 136.9, 131.6 (q, $^2J_{C\text{-}F}$ = 31.8 Hz), 128.6, 125.6 (q, $^3J_{C\text{-}F}$ = 3.8 Hz), 124.2, 123.9 (q, $^1J_{C\text{-}F}$ = 272.4 Hz), 117.9, 112.7 ppm;

^{19}F NMR (376 MHz, d_6-DMSO): δ_F -61.35 ppm.

IR (film): ν_{max} 3327, 1651, 1600, 1531, 1420, 1407, 1331, 1184, 1156, 1112, 1063, 833, 753, 728 cm^{-1}.

HRMS (ESI^+): m/z calculated for $C_{12}H_9F_3NOS$ $[M+H]^+$, 272.0351; found, 272.0359.

Methyl 4-(thiophen-2-ylcarbamoyl)benzoate (3ga)



3ga

Prepared following **General Procedure A**, using methyl 4-(5-oxo-1,4,2-dioxazol-3-yl)benzoate (**1g**) (55.3 mg, 0.25 mmol, 1.0 equiv.), 2-thiopheneboronic acid (**2a**) (96.0 mg, 0.75 mmol, 3.0 equiv.), and

DCE/CH_3CN (1:1, 2.0 mL). Purification by flash column chromatography (Petroleum ether / EtOAc: 5 / 1) gave the title compound **3ga** (30.0 mg, 46%) as a brown solid.

TLC: R_f = 0.14 (Petroleum ether / EtOAc: 5 / 1, $KMnO_4$ stain).

M. p.: 167 – 169 °C.

NMR Spectroscopy (*see spectra*):

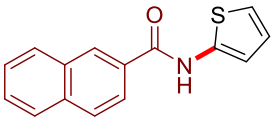
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 9.03 (s, 1H), 8.13 – 8.05 (m, 2H), 7.98 – 7.87 (m, 2H), 7.01 – 6.83 (m, 3H), 3.94 (s, 3H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 166.3, 163.2, 139.0, 137.2, 133.3, 130.1, 127.4, 124.3, 118.9, 113.2, 52.7 ppm.

IR (film): ν_{max} 3333, 3119, 2949, 1720, 1699, 1662, 1555, 1445, 1351, 1284, 1126, 825, 698, 643 cm^{-1}.

HRMS (ESI^+): m/z calculated for $C_{13}H_{12}NO_3S$ $[M+H]^+$, 262.0532; found, 262.0540.

***N*-(Thiophen-2-yl)-2-naphthamide (3ha)**



3ha

Prepared following **General Procedure A**, using 3-(naphthalen-2-yl)-1,4,2-dioxazol-5-one (**1h**) (53.3 mg, 0.25 mmol, 1.0 equiv.), 2-thiopheneboronic acid (**2a**) (96.0 mg, 0.75 mmol, 3.0 equiv.), and DCE/CH_3CN (1:1, 2.0 mL). Purification by flash column chromatography (Petroleum ether / EtOAc: 5 / 1) gave the title compound **3ha** (52.8 mg, 83%) as a black solid.

TLC: R_f = 0.26 (Petroleum ether / EtOAc: 5 / 1, $KMnO_4$ stain).

M. p.: 179 – 180 °C.

NMR Spectroscopy (*see spectra*):

^{1}H NMR (400 MHz, d_6-DMSO): δ_H 11.77 (s, 1H), 8.65 (s, 1H), 8.25 – 7.92 (m, 4H), 7.71 – 7.56 (m, 2H), 7.16 – 6.86 (m, 3H) ppm;

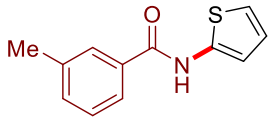
^{13}C NMR (101 MHz, d_6-DMSO): δ_C 163.2, 140.1, 134.4, 132.1, 130.5, 129.0, 128.2, 128.1, 128.0,

127.7, 127.0, 124.2, 124.1, 117.4, 112.2 ppm.

IR (film): ν_{max} 3455, 3230, 3118, 3051, 1634, 1570, 1513, 1498, 1439, 908, 837, 814, 776, 762 cm^{-1}.

HRMS (ESI^+): m/z calculated for $C_{15}H_{12}NOS$ $[M+H]^+$, 254.0634; found, 254.0639.

3-Methyl-*N*-(thiophen-2-yl)benzamide (3ia)



3ia

Prepared following **General Procedure A**, using 3-(*m*-tolyl)-1,4,2-dioxazol-5-one (**1i**) (44.3 mg, 0.25 mmol, 1.0 equiv.), 2-thiopheneboronic acid (**2a**) (96.0 mg, 0.75 mmol, 3.0 equiv.), and DCE/CH_3CN (1:1, 2.0 mL). Purification by flash column chromatography (Petroleum ether / EtOAc: 5 / 1) gave the title compound **3ia** (40.7 mg, 75%) as a light yellow solid.

TLC: R_f = 0.31 (Petroleum ether / EtOAc: 5 / 1, $KMnO_4$ stain).

M. p.: 122 – 123 °C.

NMR Spectroscopy (*see spectra*):

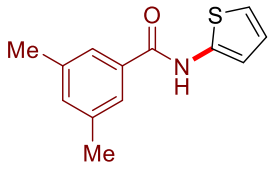
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.76 (s, 1H), 7.70 (s, 1H), 7.68 – 7.63 (m, 1H), 7.39 – 7.32 (m, 2H), 6.95 – 6.86 (m, 2H), 6.81 (dd, *J* = 3.8, 1.4 Hz, 1H), 2.40 (s, 3H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 164.2, 139.4, 138.9, 133.2, 133.1, 128.8, 128.0, 124.2, 124.1, 118.4, 112.4, 21.5 ppm.

IR (film): ν_{max} 3301, 3217, 3043, 1630, 1566, 1508, 1351, 1312, 1080, 853, 819, 802, 729, 679 cm^{-1}.

HRMS (ESI^+): m/z calculated for $C_{12}H_{12}NOS$ $[M+H]^+$, 218.0634; found, 218.0638.

3,5-Dimethyl-*N*-(thiophen-2-yl)benzamide (3ja)



3ja

Prepared following **General Procedure A**, using 3-(3,5-dimethylphenyl)-1,4,2-dioxazol-5-one (**1j**) (47.8 mg, 0.25 mmol, 1.0 equiv.), 2-thiopheneboronic acid (**2a**) (96.0 mg, 0.75 mmol, 3.0 equiv.), and DCE/CH_3CN (1:1, 2.0 mL). Purification by flash column chromatography (Petroleum ether / EtOAc: 5 / 1) gave the title compound **3ja** (41.3 mg, 71%) as a white solid.

TLC: R_f = 0.34 (Petroleum ether / EtOAc: 5 / 1, $KMnO_4$ stain).

M. p.: 185 – 186 °C.

NMR Spectroscopy (*see spectra*):

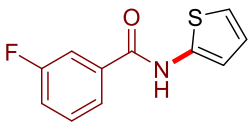
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.98 (s, 1H), 7.47 (s, 2H), 7.13 (s, 1H), 6.93 – 6.82 (m, 3H), 2.32 (s, 6H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 164.5, 139.5, 138.6, 133.9, 133.1, 125.0, 124.1, 118.3, 112.4, 21.3 ppm.

IR (film): ν_{max} 3455, 3232, 3054, 1633, 1596, 1562, 1507, 1352, 1328, 866, 852, 802, 738, 689 cm^{-1}.

HRMS (ESI^+): m/z calculated for $C_{13}H_{14}NOS$ $[M+H]^+$, 232.0791; found, 232.0796.

3-Fluoro-*N*-(thiophen-2-yl)benzamide (3ka)



3ka

Prepared following **General Procedure A**, using 3-(3-fluorophenyl)-1,4,2-dioxazol-5-one (**1k**) (45.3 mg, 0.25 mmol, 1.0 equiv.), 2-thiopheneboronic acid (**2a**) (96.0 mg, 0.75 mmol, 3.0 equiv.), and DCE/CH_3CN

(1:1, 2.0 mL). Purification by flash column chromatography (Petroleum ether / EtOAc: 5 / 1) gave the title compound **3ka** (42.1 mg, 76%) as a white solid.

TLC: R_f = 0.28 (Petroleum ether / EtOAc: 5 / 1, $KMnO_4$ stain).

NMR Spectroscopy (*see spectra*):

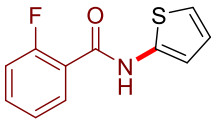
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 9.25 (s, 1H), 7.74 – 7.50 (m, 2H), 7.38 (td, *J* = 7.8, 5.4 Hz, 1H), 7.23 – 7.14 (m, 1H), 6.96 – 6.82 (m, 3H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 163.2 (d, $^4J_{C\text{-}F}$ = 2.3 Hz), 162.8 (d, $^1J_{C\text{-}F}$ = 248.5 Hz), 138.9, 135.4 (d, $^3J_{C\text{-}F}$ = 7.0 Hz), 130.6 (d, $^3J_{C\text{-}F}$ = 8.0 Hz), 124.3, 122.8 (d, $^4J_{C\text{-}F}$ = 3.2 Hz), 119.3 (d, $^2J_{C\text{-}F}$ = 21.1 Hz), 118.8, 114.7 (d, $^2J_{C\text{-}F}$ = 23.2 Hz), 113.4 ppm;

^{19}F NMR (376 MHz, $CDCl_3$): δ_F -111.01 ppm.

All recorded spectroscopic data matched those previously reported in the literature.[3]

2-Fluoro-*N*-(thiophen-2-yl)benzamide (3la)



3la

Prepared following **General Procedure A**, using 3-(2-fluorophenyl)-1,4,2-dioxazol-5-one (**1l**) (45.3 mg, 0.25 mmol, 1.0 equiv.), 2-thiopheneboronic acid (**2a**) (96.0 mg, 0.75 mmol, 3.0 equiv.), and DCE/CH_3CN (1:1, 2.0 mL). Purification by flash column chromatography (Petroleum ether / EtOAc: 5 / 1) gave the title compound **3la** (30.0 mg, 54%) as a white solid.

TLC: R_f = 0.32 (Petroleum ether / EtOAc: 5 / 1, $KMnO_4$ stain).

M. p.: 107 – 110 °C.

NMR Spectroscopy (*see spectra*):

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 9.17 (s, 1H), 8.21 (t, *J* = 7.9 Hz, 1H), 7.54 (tdd, *J* = 7.6, 5.2, 1.8 Hz, 1H), 7.32 (t, *J* = 7.6 Hz, 1H), 7.19 (dd, *J* = 12.4, 8.2 Hz, 1H), 6.99 – 6.87 (m, 2H), 6.80 (dd, *J* = 3.7, 1.4 Hz, 1H) ppm;

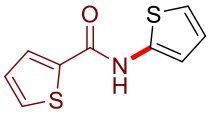
^{13}C NMR (101 MHz, $CDCl_3$): δ_C 160.6 (d, $^1J_{C\text{-}F}$ = 246.8 Hz), 159.6 (d, $^3J_{C\text{-}F}$ = 3.4 Hz), 138.8, 134.3 (d, $^3J_{C\text{-}F}$ = 9.7 Hz), 132.5 (d, $^4J_{C\text{-}F}$ = 1.8 Hz), 125.4 (d, $^3J_{C\text{-}F}$ = 3.2 Hz), 124.1, 119.7 (d, $^2J_{C\text{-}F}$ = 10.6 Hz), 118.7, 116.3 (d, $^2J_{C\text{-}F}$ = 25.0 Hz), 112.7 ppm;

^{19}F NMR (376 MHz, $CDCl_3$): δ_F -113.01 ppm.

IR (film): ν_{max} 3250, 3111, 1633, 1613, 1563, 1508, 1446, 1353, 1321, 902, 812, 780, 752, 690 cm^{-1}.

HRMS (ESI^+): m/z calculated for $C_{11}H_9FNOS$ $[M+H]^+$, 222.0383; found, 222.0389.

***N*-(Tiophen-2-yl)thiophene-2-carboxamide (3ma)**



3ma

Prepared following **General Procedure A**, using 3-(thiophen-2-yl)-1,4,2-dioxazol-5-one (**1m**) (42.3 mg, 0.25 mmol, 1.0 equiv.), 2-thiopheneboronic acid (**2a**) (96.0 mg, 0.75 mmol, 3.0 equiv.), and DCE/CH_3CN (1:1, 2.0 mL). Purification by flash column chromatography (Petroleum ether / EtOAc: 5 / 1) gave the title compound **3ma** (46.3 mg, 89%) as a brown solid.

TLC: R_f = 0.17 (Petroleum ether / EtOAc: 5 / 1, $KMnO_4$ stain).

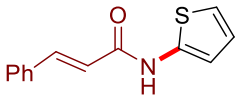
NMR Spectroscopy (*see spectra*):

^{1}H NMR (400 MHz, d_6-DMSO): δ_H 11.55 (s, 1H), 8.05 – 7.96 (m, 1H), 7.92 – 7.83 (m, 1H), 7.28 – 7.18 (m, 1H), 7.01 (dd, *J* = 4.8, 2.3 Hz, 1H), 6.95 – 6.86 (m, 2H) ppm;

^{13}C NMR (101 MHz, d_6-DMSO): δ_C 158.0, 139.6, 138.2, 132.3, 129.3, 128.3, 124.2, 117.6, 112.1 ppm.

All recorded spectroscopic data matched those previously reported in the literature.[4]

***N*-(Thiophen-2-yl)cinnamamide (3na)**



3na

Prepared following **General Procedure A**, using (*E*)-3-styryl-1,4,2-dioxazol-5-one (**1n**) (47.3 mg, 0.25 mmol, 1.0 equiv.), 2-thiopheneboronic acid (**2a**) (96.0 mg, 0.75 mmol, 3.0 equiv.), and DCE/CH_3CN (1:1, 2.0 mL). Purification by flash column chromatography (Petroleum ether / EtOAc: 5 / 1) gave the title compound **3na** (34.3 mg, 60%) as a bright yellow solid.

TLC: R_f = 0.17 (Petroleum ether / EtOAc: 5 / 1, $KMnO_4$ stain).

M. p.: 137 – 139 °C.

NMR Spectroscopy (*see spectra*):

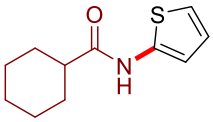
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 9.72 (s, 1H), 7.77 (d, *J* = 15.6 Hz, 1H), 7.41 – 7.36 (m, 2H), 7.32 – 7.23 (m, 3H), 6.91 – 6.85 (m, 3H), 6.79 (d, *J* = 15.6 Hz, 1H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 163.2, 143.1, 139.3, 134.5, 130.2, 128.9, 128.2, 124.3, 119.5, 118.6, 112.8 ppm.

IR (film): ν_{max} 3314, 1657, 1619, 1558, 1499, 1445, 1254, 1166, 983, 856, 812, 772, 708, 678, cm^{-1}.

HRMS (ESI^+): m/z calculated for $C_{13}H_{12}NOS$ $[M+H]^+$, 230.0634; found, 230.0641.

***N*-(Thiophen-2-yl)cyclohexanecarboxamide (3oa)**



3oa

Prepared following **General Procedure A**, using 3-cyclohexyl-1,4,2-dioxazol-5-one (**1o**) (43.0 mg, 0.25 mmol, 1.0 equiv.), 2-thiopheneboronic acid (**2a**) (96.0 mg, 0.75 mmol, 3.0 equiv.), and DCE/CH_3CN (1:1, 2.0 mL). Purification by flash column chromatography (Petroleum ether / EtOAc: 5 / 1) gave the title compound **3oa** (12.1 mg, 23%) as a brown solid.

TLC: R_f = 0.30 (Petroleum ether / EtOAc: 5 / 1, $KMnO_4$ stain).

M. p.: 199 – 200 °C.

NMR Spectroscopy (*see spectra*):

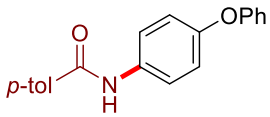
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.02 (s, 1H), 6.89 – 6.79 (m, 2H), 6.63 (d, J = 3.6 Hz, 1H), 2.28 (tt, J = 11.8, 3.6 Hz, 1H), 2.03 – 1.90 (m, 2H), 1.88 – 1.78 (m, 2H), 1.71 – 1.50 (m, 4H), 1.37 – 1.18 (m, 2H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 172.7, 139.2, 123.9, 118.0, 111.4, 45.4, 29.7, 25.7, 25.7 ppm.

IR (film): ν_{max} 3443, 2850, 1645, 1577, 1507, 1445, 1396, 1272, 1080, 956, 893, 845, 806, 683 cm^{-1}.

HRMS (ESI^+): m/z calculated for $C_{11}H_{16}NOS$ $[M+H]^+$, 210.0947; found, 210.0952.

4-Methyl-*N*-(4-phenoxyphenyl)benzamide (3bb)



3bb

Prepared following **General Procedure A**, using 3-(*p*-tolyl)-1,4,2-dioxazol-5-one (**1b**) (44.3 mg, 0.25 mmol, 1.0 equiv.), 4-phenoxyphenyl boronic acid (**2b**) (160.5 mg, 0.75 mmol, 3.0 equiv.), and CH_3CN (2.0 mL) at 140 °C. Purification by flash column chromatography (Petroleum ether / EtOAc: 5 / 1) gave the title compound **3bb** (55.3 mg, 73%) as a white solid.

TLC: R_f = 0.31 (Petroleum ether / EtOAc: 5 / 1, $KMnO_4$ stain).

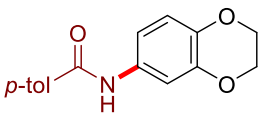
NMR Spectroscopy (*see spectra*):

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.97 (s, 1H), 7.76 (d, J = 7.9 Hz, 2H), 7.64 – 7.56 (m, 2H), 7.37 – 7.30 (m, 2H), 7.26 (d, J = 8.0 Hz, 2H), 7.09 (m, 1H), 7.04 – 6.97 (m, 4H), 2.41 (s, 3H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 165.9, 157.6, 153.7, 142.5, 133.6, 132.0, 129.9, 129.5, 127.2, 123.2, 122.2, 119.8, 118.6, 21.6 ppm.

All recorded spectroscopic data matched those previously reported in the literature.[5]

***N*-(2,3-Dihydrobenzo[*b*][1,4]dioxin-6-yl)-4-methylbenzamide (3bc)**



3bc

Prepared following **General Procedure A**, using 3-(p-tolyl)-1,4,2-dioxazol-5-one (**1b**) (44.3 mg, 0.25 mmol, 1.0 equiv.), 1,4-benzodioxane-6-boronic acid (**2c**) (135.0 mg, 0.75 mmol, 3.0 equiv.), and CH_3CN (2.0 mL) at 140 °C. Purification by flash column chromatography (Petroleum ether / EtOAc: 5 / 1) gave the title compound **3bc** (33.2 mg, 49%) as a white solid.

TLC: R_f = 0.16 (Petroleum ether / EtOAc: 5 / 1, $KMnO_4$ stain).

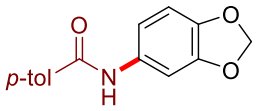
NMR Spectroscopy (*see spectra*):

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.73 (d, *J* = 7.8 Hz, 3H), 7.25 (d, *J* = 8.7 Hz, 3H), 7.01 (dd, *J* = 8.6, 2.5 Hz, 1H), 6.83 (d, *J* = 8.6 Hz, 1H), 4.25 (s, 4H), 2.41 (s, 3H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 165.7, 143.6, 142.3, 140.6, 132.2, 131.8, 129.5, 127.1, 117.3, 114.0, 110.2, 64.6, 64.4, 21.6 ppm.

All recorded spectroscopic data matched those previously reported in the literature.[6]

***N*-(Benzo[*d*][1,3]dioxol-5-yl)-4-methylbenzamide (3bd)**



3bd

Prepared following **General Procedure A**, using 3-(*p*-tolyl)-1,4,2-dioxazol-5-one (**1b**) (44.3 mg, 0.25 mmol, 1.0 equiv.), 3,4-methylenedioxyphenylboronic acid (**2d**) (124.5 mg, 0.75 mmol, 3.0 equiv.), and DCE/CH_3CN (1:1, 2.0 mL). Purification by flash column chromatography (Petroleum ether / EtOAc: 5 / 1) gave the title compound **3bd** (38.3 mg, 60%) as a white solid.

TLC: R_f = 0.24 (Petroleum ether / EtOAc: 5 / 1, $KMnO_4$ stain).

M. p.: 164 – 165 °C.

NMR Spectroscopy (*see spectra*):

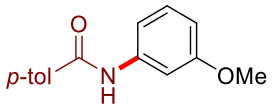
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.91 (s, 1H), 7.73 (d, *J* = 8.0 Hz, 2H), 7.33 (s, 1H), 7.23 (d, *J* = 7.9 Hz, 2H), 6.90 (d, *J* = 8.1 Hz, 1H), 6.74 (d, *J* = 8.3 Hz, 1H), 5.95 (s, 2H), 2.40 (s, 3H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 165.8, 147.9, 144.5, 142.4, 132.4, 132.1, 129.5, 127.1, 113.7, 108.2, 103.4, 101.4, 21.6 ppm.

IR (film): ν_{max} 3446, 3269, 2885, 1644, 1539, 1503, 1491, 1448, 1343, 1246, 1196, 1040, 933, 857, 812 cm^{-1}.

HRMS (ESI^+): m/z calculated for $C_{15}H_{14}NO_3$ $[M+H]^+$, 256.0968; found, 256.0973.

***N*-(3-Methoxyphenyl)-4-methylbenzamide (3be)**



3be

Prepared following **General Procedure A**, using 3-(*p*-tolyl)-1,4,2-dioxazol-5-one (**1b**) (44.3 mg, 0.25 mmol, 1.0 equiv.), 3-methoxyphenylboronic acid (**2e**) (114.0 mg, 0.75 mmol, 3.0 equiv.), and CH_3CN (2.0 mL) at 140 °C. Purification by flash column chromatography (Petroleum ether / EtOAc: 5 / 1) gave the title compound **3be** (41.3 mg, 68%) as a white solid.

TLC: R_f = 0.27 (Petroleum ether / EtOAc: 5 / 1, $KMnO_4$ stain).

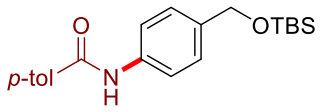
NMR Spectroscopy (*see spectra*):

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.92 (s, 1H), 7.75 (d, *J* = 8.2 Hz, 2H), 7.44 (t, *J* = 2.2 Hz, 1H), 7.29 – 7.21 (m, 3H), 7.09 (dd, *J* = 8.0, 2.0 Hz, 1H), 6.69 (dd, *J* = 8.2, 2.5 Hz, 1H), 3.81 (s, 3H), 2.41 (s, 3H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 165.9, 160.3, 142.5, 139.4, 132.2, 129.8, 129.6, 127.1, 112.4, 110.6, 105.8, 55.4, 21.6 ppm.

All recorded spectroscopic data matched those previously reported in the literature.[7]

***N*-{4-{[(*tert*-Butyldimethylsilyl)oxy]methyl}phenyl}-4-methylbenzamide (3bf)**



3bf

Prepared following **General Procedure A**, using 3-(*p*-tolyl)-1,4,2-dioxazol-5-one (**1b**) (44.3 mg, 0.25 mmol, 1.0 equiv.), {4-{[(1,1-dimethylethyl)dimethylsilyl]oxy}methyl}phenylboronic acid (**2f**) (200.0 mg, 0.75 mmol, 3.0 equiv.), and CH_3CN (2.0 mL) at 140 °C. Purification by flash column chromatography (Petroleum ether / EtOAc: 10 / 1) gave the title compound **3bf** (38.9 mg, 44%) as a white solid.

TLC: R_f = 0.47 (Petroleum ether / EtOAc: 5 / 1, $KMnO_4$ stain).

M. p.: 103 – 104 °C.

NMR Spectroscopy (*see spectra*):

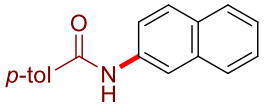
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.82 (s, 1H), 7.76 (d, *J* = 8.1 Hz, 2H), 7.60 (d, *J* = 8.4 Hz, 2H), 7.30 (dd, *J* = 16.2, 8.1 Hz, 4H), 4.72 (s, 2H), 2.42 (s, 3H), 0.94 (s, 9H), 0.10 (s, 6H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 165.7, 142.5, 137.7, 136.9, 132.3, 129.6, 127.1, 127.0, 120.1, 64.8, 26.1, 21.7, 18.6, -5.1 ppm;

IR (film): ν_{max} 3363, 2854, 1660, 1632, 1597, 1412, 1382, 1362, 1252, 1065, 1048, 839, 774, 716 cm^{-1}.

HRMS (ESI^+): m/z calculated for $C_{21}H_{30}NO_2Si$ $[M+H]^+$, 356.2040; found, 356.2045.

4-Methyl-*N*-(naphthalen-2-yl)benzamide (3bg)



3bg

Prepared following **General Procedure A**, using 3-(p-tolyl)-1,4,2-dioxazol-5-one (**1b**) (44.3 mg, 0.25 mmol, 1.0 equiv.), 2-naphthaleneboronic acid (**1g**) (129.0 mg, 0.75 mmol, 3.0 equiv.), and CH_3CN (2.0 mL) at 140 °C. Purification by flash column chromatography (Petroleum ether / EtOAc: 10 / 1) gave the title compound **3bg** (44.0 mg, 67%) as a white solid.

TLC: R_f = 0.33 (Petroleum ether / EtOAc: 5 / 1, $KMnO_4$ stain).

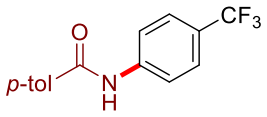
NMR Spectroscopy (*see spectra*):

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.33 (s, 1H), 8.17 (s, 1H), 7.87 – 7.72 (m, 5H), 7.60 (d, *J* = 8.7 Hz, 1H), 7.51 – 7.37 (m, 2H), 7.24 (s, 2H), 2.41 (s, 3H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 166.1, 142.5, 135.6, 134.0, 132.1, 130.8, 129.5, 128.9, 127.8, 127.7, 127.2, 126.6, 125.2, 120.3, 117.2, 21.6 ppm.

All recorded spectroscopic data matched those previously reported in the literature.[8]

4-Methyl-*N*-[4-(trifluoromethyl)phenyl]benzamide (3bh)



3bh

Prepared following **General Procedure A**, using 3-(p-tolyl)-1,4,2-dioxazol-5-one (**1b**) (44.3 mg, 0.25 mmol, 1.0 equiv.), 4-trifluoromethylphenylboronic acid (**2h**) (142.4 mg, 0.75 mmol, 3.0 equiv.), and DCE/CH_3CN (1:1, 2.0 mL). Purification by flash column chromatography (Petroleum ether / EtOAc: 5 / 1) gave the title compound **3bh** (39.6 mg, 57%) as a white solid.

TLC: R_f = 0.41 (Petroleum ether / EtOAc: 5 / 1, $KMnO_4$ stain).

NMR Spectroscopy (*see spectra*):

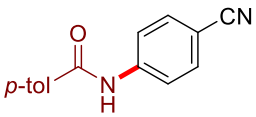
^{1}H NMR (400 MHz, d_6-DMSO): δ_H 10.50 (s, 1H), 8.02 (d, *J* = 8.5 Hz, 2H), 7.96 – 7.87 (m, 2H), 7.71 (d, *J* = 8.6 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 2.39 (s, 3H) ppm;

^{13}C NMR (101 MHz, d_6-DMSO): δ_C 165.8, 142.9, 142.0, 131.6, 129.0, 127.9, 125.9 (q, $^3J_{C\text{-}F}$ = 3.8 Hz), 123.5 (d, $^2J_{C\text{-}F}$ = 31.9 Hz), 124.4 (d, $^1J_{C\text{-}F}$ = 271.3 Hz), 120.1, 21.0 ppm;

^{19}F NMR (376 MHz, d_6-DMSO): δ_F -60.31 ppm.

All recorded spectroscopic data matched those previously reported in the literature.[9]

***N*-(4-Cyanophenyl)-4-methylbenzamide (3bi)**



3bi

Prepared following **General Procedure A**, using 3-(*p*-tolyl)-1,4,2-dioxazol-5-one (**1b**) (44.3 mg, 0.25 mmol, 1.0 equiv.), 4-cyanophenylboronic acid (**2i**) (110.2 mg, 0.75 mmol, 3.0 equiv.), and DCE/CH_3CN (1:1, 2.0 mL). Purification by flash column chromatography (Petroleum ether / EtOAc: 5 / 1) gave the title compound **3bi** (23.4 mg, 40%) as a light yellow solid.

TLC: R_f = 0.15 (Petroleum ether / EtOAc: 5 / 1, $KMnO_4$ stain).

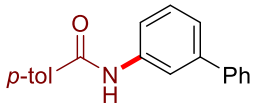
NMR Spectroscopy (*see spectra*):

^{1}H NMR (400 MHz, d_6-DMSO): δ_H 10.56 (s, 1H), 7.99 (d, *J* = 8.4 Hz, 2H), 7.88 (d, *J* = 7.9 Hz, 2H), 7.81 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 7.8 Hz, 2H), 2.39 (s, 3H) ppm;

^{13}C NMR (101 MHz, d_6-DMSO): δ_C 166.0, 143.6, 142.2, 133.1, 131.5, 129.0, 127.9, 120.1, 119.1, 105.2, 21.0 ppm.

All recorded spectroscopic data matched those previously reported in the literature.[10]

***jN*-([1,1'-Biphenyl]-3-yl)-4-methylbenzamide (3bj)**



3bj

Prepared following **General Procedure A**, using 3-(*p*-tolyl)-1,4,2-dioxazol-5-one (**1b**) (44.3 mg, 0.25 mmol, 1.0 equiv.), 3-biphenylboronic acid (**2j**) (148.5 mg, 0.75 mmol, 3.0 equiv.), and CH_3CN (2.0 mL) at 140 °C. Purification by flash column chromatography (Petroleum ether / EtOAc: 10 / 1) gave the title compound **3bj** (50.5 mg, 70%) as a white solid.

TLC: R_f = 0.58 (Petroleum ether / EtOAc: 5 / 1, $KMnO_4$ stain).

M. p.: 122 – 123 °C.

NMR Spectroscopy (*see spectra*):

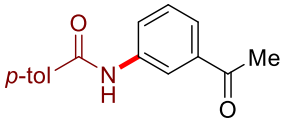
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.14 (s, 1H), 7.90 (s, 1H), 7.79 (d, *J* = 8.1 Hz, 2H), 7.65 (dt, *J* = 7.6, 1.9 Hz, 1H), 7.62 – 7.57 (m, 2H), 7.47 – 7.31 (m, 5H), 7.24 (d, *J* = 7.9 Hz, 2H), 2.41 (s, 3H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 166.0, 142.5, 142.2, 140.7, 138.6, 132.1, 129.5, 129.5, 128.8, 127.6, 127.3, 127.2, 123.3, 119.3, 119.2, 21.6 ppm.

IR (film): ν_{max} 3450, 2831, 1603, 1363, 1079, 894, 769, 700 cm^{-1}.

HRMS (ESI^+): m/z calculated for $C_{20}H_{18}NO$ $[M+H]^+$, 288.1383; found, 288.1382.

***jN*-(3-Acetylphenyl)-4-methylbenzamide (3bk)**



3bk

Prepared following **General Procedure A**, using 3-(*p*-tolyl)-1,4,2-dioxazol-5-one (**1b**) (44.3 mg, 0.25 mmol, 1.0 equiv.), 3-acetylphenylboronic acid (**2k**) (123.0 mg, 0.75 mmol, 3.0 equiv.), and CH_3CN (2.0 mL) at 140 °C. Purification by flash column chromatography (Petroleum ether / EtOAc: 5 / 1) gave the title compound **3bk** (62.1 mg, 98%) as a white solid.

TLC: R_f = 0.18 (Petroleum ether / EtOAc: 5 / 1, $KMnO_4$ stain).

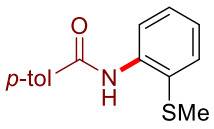
NMR Spectroscopy (*see spectra*):

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.26 (s, 1H), 8.16 (t, *J* = 1.9 Hz, 1H), 8.07 (d, *J* = 8.0 Hz, 1H), 7.80 (d, *J* = 7.9 Hz, 2H), 7.71 (dt, *J* = 7.7, 1.2 Hz, 1H), 7.46 (t, *J* = 7.9 Hz, 1H), 7.28 (d, *J* = 7.8 Hz, 2H), 2.60 (s, 3H), 2.42 (s, 3H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 198.3, 166.1, 142.8, 138.8, 137.8, 131.8, 129.6, 129.5, 127.3, 125.0, 124.4, 119.8, 26.8, 21.7 ppm.

All recorded spectroscopic data matched those previously reported in the literature.[11]

4-Methyl-*N*-[2-(methylthio)phenyl]benzamide (3bl)



3bl

Prepared following **General Procedure A**, using 3-(*p*-tolyl)-1,4,2-dioxazol-5-one (**1b**) (44.3 mg, 0.25 mmol, 1.0 equiv.), 2-methylthiophenylboronic acid (**1l**) (126.0 mg, 0.75 mmol, 3.0 equiv.), and DCE/CH_3CN (1:1, 2.0 mL). Purification by flash column chromatography (Petroleum ether / EtOAc: 10 / 1) gave the title compound **3bl** (25.8 mg, 40%) as a white solid.

TLC: R_f = 0.58 (Petroleum ether / EtOAc: 5 / 1, $KMnO_4$ stain).

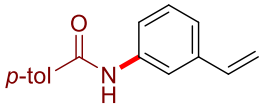
NMR Spectroscopy (*see spectra*):

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 9.23 (s, 1H), 8.54 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.86 (d, *J* = 8.1 Hz, 2H), 7.41 – 7.29 (m, 3H), 7.10 (td, *J* = 7.6, 1.4 Hz, 1H), 2.44 (s, 3H), 2.41 (s, 3H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 165.3, 142.7, 138.9, 133.6, 132.2, 129.7, 129.4, 127.2, 125.4, 124.4, 120.5, 21.7, 19.4 ppm.

All recorded spectroscopic data matched those previously reported in the literature.[12]

4-Methyl-*N*-(3-vinylphenyl)benzamide (3bm)



3bm

Prepared following **General Procedure A**, using 3-(*p*-tolyl)-1,4,2-dioxazol-5-one (**1b**) (44.3 mg, 0.25 mmol, 1.0 equiv.), 4-Vinylphenylboronic acid (**2m**) (111.0 mg, 0.75 mmol, 3.0 equiv.), and CH_3CN (2.0 mL) at 140 °C. Purification by flash column chromatography (Petroleum ether / EtOAc: 5 / 1) gave the title compound **3bm** (43.1 mg, 73%) as a white solid.

TLC: R_f = 0.33 (Petroleum ether / EtOAc: 5 / 1, $KMnO_4$ stain).

M. p.: 120 – 121 °C.

NMR Spectroscopy (*see spectra*):

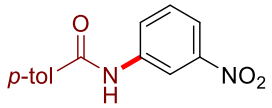
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.04 (s, 1H), 7.86 – 7.66 (m, 3H), 7.54 (dd, *J* = 7.9, 2.2 Hz, 1H), 7.33 – 7.17 (m, 4H), 6.69 (dd, *J* = 17.6, 10.8 Hz, 1H), 5.77 (d, *J* = 17.6 Hz, 1H), 5.27 (d, *J* = 10.9 Hz, 1H), 2.41 (s, 3H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 166.0, 142.5, 138.6, 138.4, 136.6, 132.1, 129.5, 129.2, 127.2, 122.4, 119.8, 118.1, 114.6, 21.6 ppm.

IR (film): ν_{max} 3458, 2928, 2831, 1608, 1549, 1515, 1466, 1364, 1869, 804, 776 cm^{-1}.

HRMS (ESI^+): m/z calculated for $C_{16}H_{16}NO$ $[M+H]^+$, 238.1226; found, 238.1224.

4-Methyl-*N*-(3-nitrophenyl)benzamide (3bn)



3bn

Prepared following **General Procedure A**, using 3-(*p*-tolyl)-1,4,2-dioxazol-5-one (**1b**) (44.3 mg, 0.25 mmol, 1.0 equiv.), 3-nitrophenylboronic acid (**2n**) (125.2 mg, 0.75 mmol, 3.0 equiv.), and DCE/CH_3CN (1:1, 2.0 mL). Purification by flash column chromatography (Petroleum ether / EtOAc: 10 / 1) gave the title compound **3ba** (17.9 mg, 28%) as a white solid.

TLC: R_f = 0.34 (Petroleum ether / EtOAc: 5 / 1, $KMnO_4$ stain).

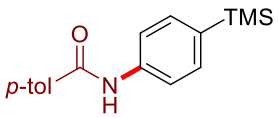
NMR Spectroscopy (*see spectra*):

^{1}H NMR (400 MHz, d_6-DMSO): δ_H 10.62 (s, 1H), 8.81 (s, 1H), 8.20 (d, *J* = 8.1 Hz, 1H), 7.96 (d, *J* = 8.2 Hz, 1H), 7.91 (d, *J* = 7.8 Hz, 2H), 7.65 (t, *J* = 8.2 Hz, 1H), 7.37 (d, *J* = 7.8 Hz, 2H), 2.40 (s, 3H) ppm;

^{13}C NMR (101 MHz, d_6-DMSO): δ_C 165.8, 147.9, 142.2, 140.5, 131.3, 130.0, 129.0, 127.8, 126.1, 118.0, 114.3, 21.1 ppm.

All recorded spectroscopic data matched those previously reported in the literature.[13]

4-Methyl-*N*-[4-(trimethylsilyl)phenyl]benzamide (3bo)



3bo

Prepared following **General Procedure A**, using 3-(*p*-tolyl)-1,4,2-dioxazol-5-one (**1b**) (44.3 mg, 0.25 mmol, 1.0 equiv.), 4-(trimethylsilyl)phenylboronic acid (**2o**) (145.6 mg, 0.75 mmol, 3.0 equiv.), and DCE/CH_3CN (1:1, 2.0 mL). Purification by flash column chromatography (Petroleum ether / EtOAc: 5 / 1) gave the title compound **3bo** (21.9 mg, 31%) as a white solid.

TLC: R_f = 0.51 (Petroleum ether / EtOAc: 5 / 1, $KMnO_4$ stain).

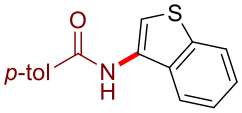
NMR Spectroscopy (*see spectra*):

^{1}H NMR (400 MHz, d_6-DMSO): δ_H 10.17 (s, 1H), 7.93 – 7.83 (m, 2H), 7.83 – 7.72 (m, 2H), 7.53 – 7.43 (m, 2H), 7.33 (d, J = 8.0 Hz, 2H), 2.38 (s, 3H), 0.24 (s, 9H) ppm;

^{13}C NMR (101 MHz, d_6-DMSO): δ_C 165.3, 141.6, 139.9, 134.2, 133.6, 132.0, 128.9, 127.7, 119.6, 21.0, -1.0 ppm.

All recorded spectroscopic data matched those previously reported in the literature.[14]

***N*-(Benzo[*b*]thiophen-3-yl)-4-methylbenzamide (3bp)**



3bp

Prepared following **General Procedure A**, using 3-(*p*-tolyl)-1,4,2-dioxazol-5-one (**1b**) (44.3 mg, 0.25 mmol, 1.0 equiv.), benzothiophene-3-boronic acid (**2p**) (133.5 mg, 0.75 mmol, 3.0 equiv.), and DCE/CH_3CN (1:1, 2.0 mL). Purification by flash column chromatography (Petroleum ether / EtOAc: 5 / 1) gave the title compound **3bp** (48.7 mg, 73%) as a white solid.

TLC: R_f = 0.40 (Petroleum ether / EtOAc: 5 / 1, $KMnO_4$ stain).

M. p.: 154 – 155 °C.

NMR Spectroscopy (*see spectra*):

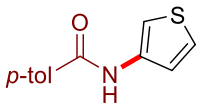
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.29 (s, 1H), 8.06 (s, 1H), 7.87 – 7.82 (m, 1H), 7.79 (d, *J* = 7.9 Hz, 2H), 7.69 – 7.61 (m, 1H), 7.42 – 7.34 (m, 2H), 7.26 (d, *J* = 7.9 Hz, 2H), 2.40 (s, 3H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 165.5, 142.7, 138.1, 132.8, 131.5, 129.6, 128.6, 127.2, 125.0, 124.1, 123.4, 118.9, 113.0, 21.6 ppm.

IR (film): ν_{max} 3273, 1646, 1612, 1547, 1509, 1456, 1434, 1299, 1185, 1079, 1021, 749, 729, 690 cm^{-1}.

HRMS (ESI^+): m/z calculated for $C_{16}H_{14}NOS$ $[M+H]^+$, 268.0791; found, 268.0796.

4-Methyl-*N*-(thiophen-3-yl)benzamide (3bq)



3bq

Prepared following **General Procedure B**, using 3-(*p*-tolyl)-1,4,2-dioxazol-5-one (**1b**) (44.3 mg, 0.25 mmol, 1.0 equiv.), 3-thiopheneboronic acid (**2q**) (96.0 mg, 0.75 mmol, 3.0 equiv.), and DCE/CH_3CN (1:1, 2.0 mL). Purification by flash column chromatography (Petroleum ether / EtOAc: 5 / 1) gave the title compound **3bq** (53.2 mg, 98%) as a light yellow solid.

TLC: R_f = 0.40 (Petroleum ether / EtOAc: 5 / 1, $KMnO_4$ stain).

M. p.: 187 – 188 °C.

NMR Spectroscopy (*see spectra*):

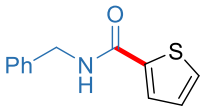
^{1}H NMR (400 MHz, d_6-DMSO): δ_H 10.61 (s, 1H), 7.88 (d, *J* = 7.9 Hz, 2H), 7.74 (s, 1H), 7.51 – 7.43 (m, 1H), 7.39 – 7.25 (m, 3H), 2.38 (s, 3H) ppm;

^{13}C NMR (101 MHz, d_6-DMSO): δ_C 164.3, 141.6, 137.1, 131.5, 129.0, 127.6, 124.4, 122.1, 109.3, 21.0 ppm.

IR (film): ν_{max} 3250, 1634, 1585, 1531, 1407, 1390, 1370, 1351, 1303, 1290, 842, 830, 773, 735 cm^{-1}.

HRMS (ESI^+): m/z calculated for $C_{12}H_{12}NOS$ $[M+H]^+$, 218.0634; found, 218.0634.

***N*-Benzylthiophene-2-carboxamide (5aa)**



5aa

Prepared following **General Procedure B**, using thiophene-2-boronic acid (**2a**) (32.0 mg, 0.25 mmol, 1.0 equiv.), benzylisocyanate (**4a**) (99.9 mg, 0.75 mmol, 3.0 equiv.), and DCE (1.0 mL). Purification by flash column chromatography (DCM: 100%) gave the title compound **5aa** (49.4 mg, 91%) as a white solid.

Gram-scale reaction was conducted following **General Procedure B**, using thiophene-2-boronic acid (**2a**) (1.28 g, 10 mmol, 1.0 equiv.), benzylisocyanate (**4a**) (4.0 g, 30 mmol, 3.0 equiv.), and DCE (10.0 mL). Purification by flash column chromatography (DCM: 100%) gave the title compound **5aa** (1.33 g, 61%) as a white solid.

TLC: R_f = 0.35 (DCM: 100%, $KMnO_4$ stain).

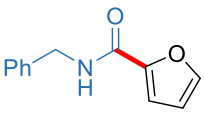
NMR Spectroscopy (*see spectra*):

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.51 (dd, *J* = 3.7, 1.1 Hz, 1H), 7.48 (dd, *J* = 5.0, 1.2 Hz, 1H), 7.39 – 7.27 (m, 5H), 7.07 (dd, *J* = 5.0, 3.7 Hz, 1H), 6.30 (s, 1H), 4.62 (d, *J* = 5.8 Hz, 2H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 161.9, 138.9, 138.2, 130.2, 128.9, 128.3, 128.1, 127.8, 127.8, 44.2 ppm.

All recorded spectroscopic data matched those previously reported in the literature.[1]

***N*-Benzylfuran-2-carboxamide (5ab)**



5ab

Prepared following **General Procedure B**, using 2-furanboronic acid (**2b**) (28.0 mg, 0.25 mmol, 1.0 equiv.), benzylisocyanate (**4a**) (99.9 mg, 0.75 mmol, 3.0 equiv.), and DCE (1.0 mL). Purification by flash

column chromatography (DCM / EtOAc: 40 / 1) gave the title compound **5ab** (34.2 mg, 68%) as a white solid.

TLC: R_f = 0.42 (DCM / EtOAc: 20 / 1, $KMnO_4$ stain).

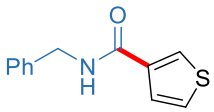
NMR Spectroscopy (*see spectra*):

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.43 – 7.40 (m, 1H), 7.37 – 7.33 (m, 4H), 7.33 – 7.27 (m, 1H), 7.15 (d, *J* = 3.5 Hz, 1H), 6.65 (brs, 1H), 6.50 (dd, *J* = 3.5, 1.8 Hz, 1H), 4.62 (d, *J* = 5.9 Hz, 2H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 158.4, 148.0, 144.0, 138.1, 128.9, 128.1, 127.8, 114.5, 112.3, 43.3 ppm.

All recorded spectroscopic data matched those previously reported in the literature.[1]

***N*-Benzylthiophene-3-carboxamide (5ac)**



5ac

Prepared following **General Procedure B**, using 3-thiopheneboronic acid (**2c**) (32.0 mg, 0.25 mmol, 1.0 equiv.), benzylisocyanate (**4a**) (99.9 mg, 0.75 mmol, 3.0 equiv.), and DCE (1.0 mL). Purification by flash column chromatography (DCM / EtOAc: 40 / 1) gave the title compound **5ac** (25.5 mg, 47%) as a white solid.

TLC: R_f = 0.43 (DCM / EtOAc: 20 / 1, $KMnO_4$ stain).

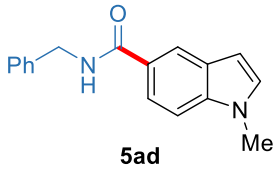
NMR Spectroscopy (*see spectra*):

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.88 (dd, *J* = 3.0, 1.4 Hz, 1H), 7.43 – 7.29 (m, 7H), 6.28 (s, 1H), 4.62 (d, *J* = 5.7 Hz, 2H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 163.1, 138.3, 137.4, 128.9, 128.5, 128.0, 127.7, 126.6, 126.2, 43.9 ppm.

All recorded spectroscopic data matched those previously reported in the literature.[15]

***N*-Benzyl-1-methyl-*1H*-indole-5-carboxamide (5ad)**



5ad

Prepared following **General Procedure B**, using *N*-methylindole-5-boronic acid (**2d**) (43.7 mg, 0.25 mmol, 1.0 equiv.), benzylisocyanate (**4a**) (99.9 mg, 0.75 mmol, 3.0 equiv.), and DCE (1.0 mL). Purification by flash column chromatography (DCM / EtOAc: 40 / 1) gave the title compound **5ad** (33.6 mg, 51%) as a pink solid.

TLC: R_f = 0.47 (DCM/EtOAc: 20 / 1, $KMnO_4$ stain).

M. p.: 127 – 129 °C.

NMR Spectroscopy (*see spectra*):

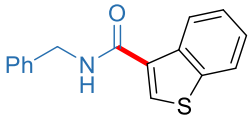
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.11 (s, 1H), 7.71 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.43 – 7.26 (m, 6H), 7.10 (d, *J* = 3.2 Hz, 1H), 6.59 – 6.47 (m, 2H), 4.68 (d, *J* = 5.6 Hz, 2H), 3.80 (s, 3H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 168.6, 138.8, 138.4, 130.4, 128.8, 128.1, 128.0, 127.6, 125.8, 120.8, 120.5, 109.2, 102.3, 44.2, 33.1 ppm.

IR (film): ν_{max} 3362, 3056, 2936, 1792, 1633, 1524, 1483, 1454, 1341, 1296, 1272, 753, 730, 699 cm^{-1}.

HRMS (ESI^+): m/z calculated for $C_{17}H_{17}N_2O$ $[M+H]^+$, 265.1335; found, 265.1345.

***N*-Benzylbenzo[*b*]thiophene-3-carboxamide (5ae)**



5ae

Prepared following **General Procedure B**, using benzo[*b*]thiophen-6-ylboronic acid (**2e**) (44.5 mg, 0.25 mmol, 1.0 equiv.), benzylisocyanate (**4a**) (99.9 mg, 0.75 mmol, 3.0 equiv.), and DCE (1.0 mL).

Purification by flash column chromatography (DCM: 100%) gave the title compound **5ae** (54.4 mg, 81%) as a white solid.

TLC: R_f = 0.42 (DCM: 100%, $KMnO_4$ stain).

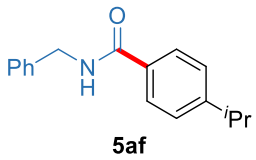
NMR Spectroscopy (*see spectra*):

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.43 – 8.36 (m, 1H), 7.90 – 7.82 (m, 2H), 7.49 – 7.23 (m, 7H), 6.47 (s, 1H), 4.66 (d, *J* = 5.7 Hz, 2H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 164.0, 140.3, 138.2, 136.9, 132.0, 129.3, 128.9, 128.0, 127.8, 125.3, 125.3, 124.5, 122.7, 44.0 ppm.

All recorded spectroscopic data matched those previously reported in the literature.[16]

***N* -Benzyl-4-isopropylbenzamide (5af)**



5af

Prepared following **General Procedure B**, using 4-isopropylbenzeneboronic acid (**2f**) (41.0 mg, 0.25 mmol, 1.0 equiv.), benzylisocyanate (**4a**) (99.9 mg, 0.75 mmol, 3.0 equiv.), and DCE (1.0 mL). Purification by flash column chromatography (DCM / EtOAc: 40 / 1) gave the title compound **5af** (28.5 mg, 45%) as a white solid.

TLC: R_f = 0.41 (DCM / EtOAc: 20 / 1, $KMnO_4$ stain).

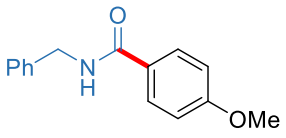
NMR Spectroscopy (*see spectra*):

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.78 – 7.66 (m, 2H), 7.38 – 7.26 (m, 7H), 6.36 (s, 1H), 4.65 (d, *J* = 5.7 Hz, 2H), 2.95 (m, 1H), 1.25 (d, *J* = 6.9 Hz, 6H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 167.4, 153.0, 138.4, 132.0, 128.9, 128.1, 127.7, 127.2, 126.8, 44.2, 34.2, 23.9 ppm.

All recorded spectroscopic data matched those previously reported in the literature.[17]

***N*-Benzyl-4-methoxybenzamide (5ag)**



5ag

Prepared following **General Procedure B**, using 4-methoxyphenylboronic acid (**2g**) (38.0 mg, 0.25 mmol, 1.0 equiv.), benzylisocyanate (**4a**) (99.9 mg, 0.75 mmol, 3.0 equiv.), and DCE (1.0 mL). Purification by flash column chromatography (DCM / EtOAc: 40 / 1) gave the title compound **5ag** (46.7 mg, 77%) as a white solid.

TLC: R_f = 0.52 (DCM / EtOAc: 20 / 1, $KMnO_4$ stain).

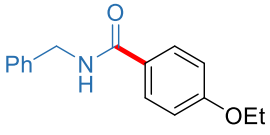
NMR Spectroscopy (*see spectra*):

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.83 – 7.70 (m, 2H), 7.38 – 7.26 (m, 5H), 6.97 – 6.84 (m, 2H), 6.42 (s, 1H), 4.62 (d, *J* = 5.7 Hz, 2H), 3.84 (s, 3H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 167.0, 162.3, 138.5, 128.9, 128.9, 128.0, 127.7, 126.8, 113.9, 55.5, 44.2 ppm.

All recorded spectroscopic data matched those previously reported in the literature.[1]

***N*-Benzyl-4-ethoxybenzamide (5ah)**



5ah

Prepared following **General Procedure B**, using 4-ethoxybenzeneboronic acid (**2h**) (41.5 mg, 0.25 mmol, 1.0 equiv.), benzylisocyanate (**4a**) (99.9 mg, 0.75 mmol, 3.0 equiv.), and DCE (1.0 mL). Purification by flash column chromatography (DCM / EtOAc: 40 / 1) gave the title compound **5ah** (41.2 mg, 65%) as a white solid.

TLC: R_f = 0.50 (DCM / EtOAc: 20 / 1, $KMnO_4$ stain).

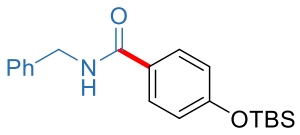
NMR Spectroscopy (*see spectra*):

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.79 – 7.71 (m, 2H), 7.36 – 7.26 (m, 5H), 6.94 – 6.83 (m, 2H), 6.47 (s, 1H), 4.61 (d, *J* = 5.7 Hz, 2H), 4.06 (q, *J* = 7.0 Hz, 2H), 1.42 (t, *J* = 7.0 Hz, 3H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 167.0, 161.7, 138.6, 128.9, 128.8, 128.0, 127.6, 126.5, 114.3, 63.8, 44.1, 14.8 ppm.

All recorded spectroscopic data matched those previously reported in the literature.[18]

***N*-Benzyl-4-[(*tert*-butyldimethylsilyl)oxy]benzamide (5ai)**



5ai

Prepared following **General Procedure B**, using 4-(*tert*-butyldimethylsilyloxy)phenylboronic acid (**2i**) (63.0 mg, 0.25 mmol, 1.0 equiv.), benzylisocyanate (**4a**) (99.9 mg, 0.75 mmol, 3.0 equiv.), and DCE (1.0 mL). Purification by flash column chromatography (DCM / EtOAc: 40 / 1) gave the title compound **5ai** (52.7 mg, 62%) as a white solid.

TLC: R_f = 0.52 (DCM / EtOAc: 20 / 1, $KMnO_4$ stain).

M. p.: 105 – 107 °C.

NMR Spectroscopy (*see spectra*):

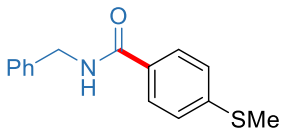
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.75 – 7.66 (m, 2H), 7.37 – 7.24 (m, 5H), 6.88 – 6.80 (m, 2H), 6.55 (s, 1H), 4.60 (d, *J* = 5.7 Hz, 2H), 0.98 (s, 9H), 0.21 (s, 6H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 167.1, 158.9, 138.6, 128.9, 128.8, 128.0, 127.6, 127.4, 120.1, 44.1, 25.7, 18.3, -4.3 ppm.

IR (film): ν_{max} 3313, 2928, 1630, 1605, 1556, 1503, 1249, 1175, 908, 859, 836, 777, 717, 694 cm^{-1}.

HRMS (ESI^+): m/z calculated for $C_{20}H_{28}NO_2Si$ $[M+H]^+$, 342.1883; found, 342.1887.

***N*-Benzyl-4-(methylthio)benzamide (5aj)**



5aj

Prepared following **General Procedure B**, using 4-(methylthiophenyl)boronic acid (**2j**) (42.0 mg, 0.25 mmol, 1.0 equiv.), benzylisocyanate (**4a**) (99.9 mg, 0.75 mmol, 3.0 equiv.), and DCE (1.0 mL). Purification by flash column chromatography (DCM / EtOAc: 40 / 1) gave the title compound **5aj** (33.8 mg, 53%) as a white solid.

TLC: R_f = 0.65 (DCM / EtOAc: 20 / 1, $KMnO_4$ stain).

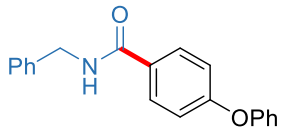
NMR Spectroscopy (*see spectra*):

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.74 – 7.66 (m, 2H), 7.37 – 7.25 (m, 5H), 7.25 – 7.20 (m, 2H), 6.57 (s, 1H), 4.61 (d, J = 5.7 Hz, 2H), 2.49 (s, 3H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 167.0, 143.6, 138.4, 130.5, 128.9, 128.0, 127.7, 127.5, 125.5, 44.2, 15.1 ppm.

All recorded spectroscopic data matched those previously reported in the literature.[19]

***N*-Benzyl-4-phenoxybenzamide (5ak)**



5ak

Prepared following **General Procedure B**, using 4-phenoxyphenyl boronic acid (**2k**) (53.5 mg, 0.25 mmol, 1.0 equiv.), benzylisocyanate (**4a**) (99.9 mg, 0.75 mmol, 3.0 equiv.), and DCE (1.0 mL). Purification by flash column chromatography (DCM / EtOAc: 40 / 1) gave the title compound **5ak** (31.5 mg, 42%) as a white solid.

TLC: R_f = 0.69 (DCM / EtOAc: 20 / 1, $KMnO_4$ stain).

M. p.: 176 – 177 °C.

NMR Spectroscopy (*see spectra*):

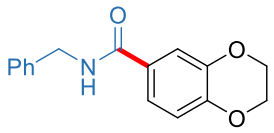
^{1}H NMR (400 MHz, d_6-DMSO): δ_H 9.02 (s, 1H), 7.98 – 7.91 (m, 2H), 7.50 – 7.38 (m, 2H), 7.36 – 7.17 (m, 6H), 7.12 – 6.99 (m, 4H), 4.48 (d, J = 6.0 Hz, 2H) ppm;

^{13}C NMR (101 MHz, d_6-DMSO): δ_C 165.4, 159.4, 155.6, 139.8, 130.2, 129.5, 129.0, 128.3, 127.2, 126.7, 124.3, 119.5, 117.4, 42.6 ppm.

IR (film): ν_{max} 3422, 1629, 1586, 1556, 1484, 1236, 1195, 1172, 868, 854, 753, 728, 694 cm^{-1}.

HRMS (ESI$^+$): m/z calculated for $C_{20}H_{18}NO_2$ $[M+H]^+$ 304.1332; found, 304.1339.

***N*-Benzyl-2,3-dihydrobenzo[*b*][1,4]dioxine-6-carboxamide (5al)**



5al

Prepared following **General Procedure B,** using 1,4-benzodioxane-6-boronic acid (**2l**) (45.0 mg, 0.25 mmol, 1.0 equiv.), benzylisocyanate (**4a**) (99.9 mg, 0.75 mmol, 3.0 equiv.), and DCE (1.0 mL). Purification by flash column chromatography (DCM / EtOAc: 40 / 1) gave the title compound **5al** (39.7 mg, 59%) as a white solid.

TLC: R_f = 0.38 (DCM / EtOAc: 20 / 1, $KMnO_4$ stain).

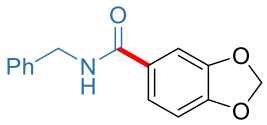
NMR Spectroscopy (*see spectra*):

^{1}H NMR (400 MHz, d_6-DMSO): δ_H 8.89 (s, 1H), 7.49 – 7.39 (m, 2H), 7.37 – 7.15 (m, 5H), 6.92 (d, J = 8.3 Hz, 1H), 4.45 (d, J = 5.9 Hz, 2H), 4.28 (s, 4H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 166.8, 146.6, 143.5, 138.5, 128.8, 128.0, 127.8, 127.6, 120.5, 117.3, 116.7, 64.6, 64.3, 44.2 ppm.

All recorded spectroscopic data matched those previously reported in the literature.[20]

***N*-benzylbenzo[*d*][1,3]dioxole-5-carboxamide (5am)**



5am

Prepared following **General Procedure B**, using 1,3-benzodioxol-5-ylboronic acid (**2m**) (41.5 mg, 0.25 mmol, 1.0 equiv.), benzylisocyanate (**4a**) (99.9 mg, 0.75 mmol, 3.0 equiv.), and DCE (1.0 mL). Purification by flash column chromatography (DCM / EtOAc: 40 / 1) gave the title compound **5am** (48.3 mg, 76%) as a white solid.

TLC: R_f = 0.56 (DCM / EtOAc: 20 / 1, $KMnO_4$ stain).

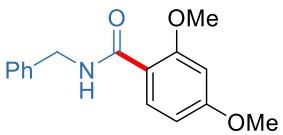
NMR Spectroscopy (*see spectra*):

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.37 – 7.26 (m, 7H), 6.78 (d, J = 8.0 Hz, 1H), 6.56 (d, J = 4.3 Hz, 1H), 5.99 (s, 2H), 4.58 (d, J = 5.7 Hz, 2H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 166.8, 150.4, 148.0, 138.4, 128.8, 128.7, 127.9, 127.6, 121.7, 108.1, 107.8, 101.8, 44.2 ppm.

All recorded spectroscopic data matched those previously reported in the literature.[21]

***N*-Benzyl-2,4-dimethoxybenzamide (5an)**



5an

Prepared following **General Procedure B**, using 2,4-dimethoxyphenylboronic acid (**2n**) (45.5 mg, 0.25 mmol, 1.0 equiv.), benzylisocyanate (**4a**) (99.9 mg, 0.75 mmol, 3.0 equiv.), and DCE (1.0 mL). Purification by flash column chromatography (DCM / EtOAc: 40 / 1) gave the title compound **5an** (44.2 mg, 70%) as a white solid.

TLC: R_f = 0.49 (DCM / EtOAc: 20 / 1, $KMnO_4$ stain).

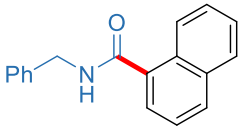
NMR Spectroscopy (*see spectra*):

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.23 (d, *J* = 8.8 Hz, 1H), 8.10 (s, 1H), 7.41 – 7.22 (m, 5H), 6.61 (dd, *J* = 8.8, 2.3 Hz, 1H), 6.47 (d, *J* = 2.3 Hz, 1H), 4.67 (d, *J* = 5.7 Hz, 2H), 3.88 (s, 3H), 3.84 (s, 3H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 165.3, 163.5, 158.9, 139.2, 134.2, 128.7, 127.6, 127.3, 114.5, 105.3, 98.7, 56.0, 55.6, 43.7 ppm.

All recorded spectroscopic data matched those previously reported in the literature.[22]

***N*-Benzyl-1-naphthamide (5ao)**



5ao

Prepared following **General Procedure B**, using 1-naphthylboronic acid (**2o**) (43.0 mg, 0.25 mmol, 1.0 equiv.), benzylisocyanate (**4a**) (99.9 mg, 0.75 mmol, 3.0 equiv.), and DCE (1.0 mL). Purification by flash column chromatography (DCM: 100%) gave the title compound **5ao** (26.8 mg, 41%) as a pink solid.

TLC: R_f = 0.35 (DCM: 100%, $KMnO_4$ stain).

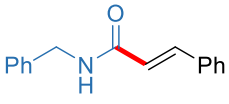
NMR Spectroscopy (*see spectra*):

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.35 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.95 – 7.82 (m, 2H), 7.64 – 7.50 (m, 3H), 7.46 – 7.28 (m, 6H), 6.33 (s, 1H), 4.72 (d, *J* = 5.8 Hz, 2H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 169.5, 138.2, 134.4, 133.8, 130.8, 130.3, 129.0, 128.4, 128.0, 127.8, 127.3, 126.6, 125.5, 125.0, 124.8, 44.2 ppm.

All recorded spectroscopic data matched those previously reported in the literature.[23]

***N*-Benzylcinnamamide (5ap)**



5ap

Prepared following **General Procedure B**, using (*E*)-styrylboronic acid (**2p**) (37.0 mg, 0.25 mmol, 1.0 equiv.), benzylisocyanate (**4a**) (99.9 mg, 0.75 mmol, 3.0 equiv.), and DCE (1.0 mL). Purification by flash column chromatography (DCM / EtOAc: 40 / 1) gave the title compound **5ap** (19.0 mg, 32%) as a white solid.

TLC: R_f = 0.46 (DCM / EtOAc: 20 / 1, $KMnO_4$ stain).

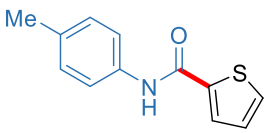
NMR Spectroscopy (*see spectra*):

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.68 (d, *J* = 15.6 Hz, 1H), 7.55 – 7.47 (m, 2H), 7.43 – 7.26 (m, 8H), 6.41 (d, *J* = 15.6 Hz, 1H), 5.94 (s, 1H), 4.58 (d, *J* = 5.8 Hz, 2H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 165.9, 141.5, 138.3, 134.9, 129.8, 128.9, 128.9, 128.0, 127.9, 127.7, 120.6, 44.0 ppm.

All recorded spectroscopic data matched those previously reported in the literature.[1]

***N*-(*p*-Tolyl)thiophene-2-carboxamide (5ba)**



5ba

Prepared following **General Procedure B**, using 2-thiopheneboronic acid (**2a**) (32.0 mg, 0.25 mmol, 1.0 equiv.), *p*-tolyl isocyanate (**4b**) (99.9 mg, 0.75 mmol, 3.0 equiv.), and DCE (1.0 mL). Purification by flash column chromatography (Petroleum ether / DCM: 2 / 3) gave the title compound **5ba** (42.9 mg, 79%) as a white solid.

TLC: R_f = 0.29 (Petroleum ether / DCM: 2 / 3, $KMnO_4$ stain).

NMR Spectroscopy (*see spectra*):

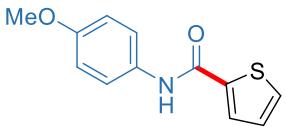
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.71 (s, 1H), 7.61 (dd, *J* = 3.7, 1.1 Hz, 1H), 7.53 (dd, *J* = 5.0, 1.2 Hz, 1H), 7.51 – 7.46 (m, 2H), 7.15 (d, *J* = 8.1 Hz, 2H), 7.11 (dd, *J* = 5.0, 3.7 Hz, 1H), 2.33 (s, 3H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 160.0, 139.5, 135.1, 134.5, 130.7, 129.7, 128.5, 127.9, 120.5, 21.0

ppm.

All recorded spectroscopic data matched those previously reported in the literature.[24]

***N*-(4-Methoxyphenyl)thiophene-2-carboxamide (5ca)**



5ca

Prepared following **General Procedure B**, using 2-thiopheneboronic acid (**2a**) (32.0 mg, 0.25 mmol, 1.0 equiv.), 4-methoxyphenyl isocyanate (**4c**) (97.2 mg, 0.75 mmol, 3.0 equiv.), and DCE (1.0 mL). Purification by flash column chromatography (Petroleum ether / DCM / EtOAc: 4 / 2 / 1) gave the title compound **5ca** (41.6 mg, 71%) as a brown powder.

TLC: R_f = 0.42 (Petroleum ether / DCM / EtOAc: 4 / 2 / 1, $KMnO_4$ stain).

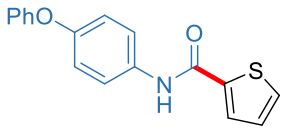
NMR Spectroscopy (*see spectra*):

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.79 (s, 1H), 7.61 (dd, *J* = 3.7, 1.2 Hz, 1H), 7.53 – 7.47 (m, 3H), 7.09 (dd, *J* = 5.0, 3.7 Hz, 1H), 6.90 – 6.84 (m, 2H), 3.80 (s, 3H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 160.1, 156.8, 139.4, 130.7, 130.6, 128.5, 127.9, 122.4, 114.3, 55.6 ppm.

All recorded spectroscopic data matched those previously reported in the literature.[25]

***N*-(4-Phenoxyphenyl)thiophene-2-carboxamide (5da)**



5da

Prepared following **General Procedure B**, using 2-thiopheneboronic acid (**2a**) (32.0 mg, 0.25 mmol, 1.0 equiv.), 4-phenoxyphenyl isocyanate (**4d**) (158.4 mg, 0.75 mmol, 3.0 equiv.), and

DCE (1.0 mL). Purification by flash column chromatography (Petroleum ether / DCM / EtOAc: 8 / 4 / 1) gave the title compound **5da** (72.3 mg, 98%) as a white solid.

TLC: R_f = 0.40 (Petroleum ether / DCM / EtOAc: 8 / 4 / 1, $KMnO_4$ stain).

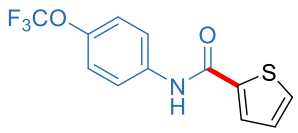
NMR Spectroscopy (*see spectra*):

^{1}H NMR (400 MHz, d_6-DMSO): δ_H 10.27 (s, 1H), 8.02 (dd, J = 3.8, 1.2 Hz, 1H), 7.84 (dd, J = 5.0, 1.1 Hz, 1H), 7.79 – 7.71 (m, 2H), 7.42 – 7.33 (m, 2H), 7.22 (dd, J = 5.0, 3.7 Hz, 1H), 7.15 – 7.08 (m, 1H), 7.07 – 6.95 (m, 4H). ppm;

^{13}C NMR (101 MHz, d_6-DMSO): δ_C 159.7, 157.2, 152.3, 140.0, 134.5, 131.7, 130.0, 129.0, 128.0, 123.1, 122.1, 119.2, 118.0 ppm.

All recorded spectroscopic data matched those previously reported in the literature.[26]

***N*-[4-(Trifluoromethoxy)phenyl]thiophene-2-carboxamide (5ea)**



5ea

Prepared following **General Procedure B**, using 2-thiopheneboronic acid (**2a**) (32.0 mg, 0.25 mmol, 1.0 equiv.), 4-(trifluoromethoxy)phenyl isocyanate (**4e**) (152.3 mg, 0.75 mmol, 3.0 equiv.), and DCE (1.0 mL). Purification by flash column chromatography (Petroleum ether / DCM: 1 / 1) gave the title compound **5ea** (62.8 mg, 88%) as a white solid.

TLC: R_f = 0.65 (Petroleum ether / DCM: 2 / 3, $KMnO_4$ stain).

M. p.: 138 – 139 °C.

NMR Spectroscopy (*see spectra*):

^{1}H NMR (400 MHz, d_6-DMSO): δ_H 10.4 (s, 1H), 8.0 (dd, J = 3.8, 1.2 Hz, 1H), 7.9 – 7.8 (m, 3H), 7.4 (d, J = 8.3 Hz, 2H), 7.2 (dd, J = 5.0, 3.8 Hz, 1H) ppm;

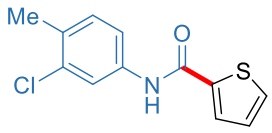
^{13}C NMR (101 MHz, d_6-DMSO): δ_C 160.0, 143.9 (q, $^3J_{C\text{-}F}$ = 2.2 Hz), 139.6, 138.0, 132.1, 129.4, 128.1, 121.7, 121.5, 120.2 (q, $^1J_{C\text{-}F}$ = 255.6 Hz) ppm;

^{19}F NMR (376 MHz, d_6-DMSO): δ_F -57.11 ppm.

IR (film): ν_{max} 3425, 2934, 2832, 2718, 1593, 1360, 1032, 776, 607, 516 cm^{-1}.

HRMS (ESI^+): m/z calculated for $C_{12}H_9F_3NO_2S$ $[M+H]^+$, 288.0301; found, 288.0295.

***N*-(3-Chloro-4-methylphenyl)thiophene-2-carboxamide (5fa)**



5fa

Prepared following **General Procedure B**, using 2-thiopheneboronic acid (**2a**) (32.0 mg, 0.25 mmol, 1.0 equiv.), 3-chloro-4-methylphenyl isocyanate (**4f**) (125.7 mg, 0.75 mmol, 3.0 equiv.), and DCE (1.0 mL). Purification by flash column chromatography (Petroleum ether / DCM / EtOAc: 8 / 4 / 1) gave the title compound **5fa** (57.3 mg, 91%) as a white solid.

TLC: R_f = 0.40 (Petroleum ether / DCM / EtOAc: 8 / 4 / 1, $KMnO_4$ stain).

M. p.: 135 – 136 °C.

NMR Spectroscopy (*see spectra*):

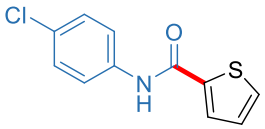
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.79 (s, 1H), 7.68 (d, J = 2.2 Hz, 1H), 7.62 (d, J = 3.8 Hz, 1H), 7.54 (d, J = 5.0 Hz, 1H), 7.38 (dd, J = 8.3, 2.3 Hz, 1H), 7.17 (d, J = 8.3 Hz, 1H), 7.13 – 7.07 (m, 1H), 2.33 (s, 3H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 160.1, 139.1, 136.4, 134.7, 132.4, 131.2, 131.1, 128.7, 128.0, 121.0, 118.7, 19.6 ppm.

IR (film): ν_{max} 3305, 3206, 1635, 1588, 1513, 1446, 1422, 1310, 1258, 1048, 926, 839, 812, 708 cm^{-1}.

HRMS (ESI^+): m/z calculated for $C_{12}H_{11}ClNOS$ $[M+H]^+$, 252.0244; found, 252.0252.

***N*-(4-Chlorophenyl)thiophene-2-carboxamide (5ga)**



5ga

Prepared following **General Procedure B**, using 2-thiopheneboronic acid (**2a**) (32.0 mg, 0.25 mmol, 1.0 equiv.), 4-chlorophenyl isocyanate (**5g**) (115.2 mg, 0.75 mmol, 3.0 equiv.), and DCE (1.0 mL). Purification by flash column chromatography (Petroleum ether / DCM: 1 / 1) gave the title compound **5ga** (47.0 mg, 79%) as a white solid.

TLC: R_f = 0.35 (Petroleum ether / DCM: 1 / 2, $KMnO_4$ stain).

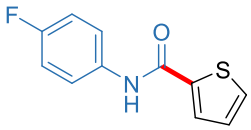
NMR Spectroscopy (*see spectra*):

^{1}H NMR (400 MHz, d_6-DMSO): δ_H 10.35 (s, 1H), 8.03 (d, J = 3.8 Hz, 1H), 7.87 (d, J = 5.0 Hz, 1H), 7.78 (d, J = 8.5 Hz, 2H), 7.41 (d, J = 8.5 Hz, 2H), 7.23 (m, 1H) ppm;

^{13}C NMR (101 MHz, d_6-DMSO): δ_C 160.4, 140.2, 138.2, 132.6, 129.8, 129.1, 128.6, 127.9, 122.3 ppm.

All recorded spectroscopic data matched those previously reported in the literature.[27]

***N*-(4-Fluorophenyl)thiophene-2-carboxamide (5ha)**



5ha

Prepared following **General Procedure B**, using 2-thiopheneboronic acid (**2a**) (32.0 mg, 0.25 mmol, 1.0 equiv.), 4-fluorophenyl isocyanate (**4h**) (102.8 mg, 0.75 mmol, 3.0 equiv.), and DCE (1.0 mL). Purification by flash column chromatography (Petroleum ether / DCM / EtOAc: 6 / 3 / 1) gave the title compound **5ha** (38.2 mg, 69%) as a white solid.

TLC: R_f = 0.31 (Petroleum ether / DCM / EtOAc: 6 / 3 / 1, $KMnO_4$ stain).

NMR Spectroscopy (*see spectra*):

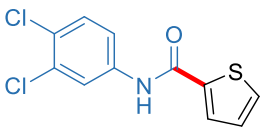
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.10 (s, 1H), 7.65 (dd, J = 3.8, 1.2 Hz, 1H), 7.59 – 7.48 (m, 3H), 7.07 (dd, J = 5.0, 3.7 Hz, 1H), 7.04 – 6.94 (m, 2H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 160.3, 159.7 (d, $^{1}J_{C\text{-}F}$ = 245.4 Hz), 139.1, 133.7 (d, $^{4}J_{C\text{-}F}$ = 3.0 Hz), 131.0, 128.7, 128.0, 122.5 (d, $^{3}J_{C\text{-}F}$ = 8.1 Hz), 115.8 (d, $^{2}J_{C\text{-}F}$ = 23.2 Hz) ppm;

^{19}F NMR (376 MHz, $CDCl_3$): δ_F -117.43 ppm.

All recorded spectroscopic data matched those previously reported in the literature.[28]

***N*-(3,4-Dichlorophenyl)thiophene-2-carboxamide (5ia)**



5ia

Prepared following **General Procedure B**, using 2-thiopheneboronic acid (**2a**) (32.0 mg, 0.25 mmol, 1.0 equiv.), 3,4-dichlorophenylisocyanate (**4i**) (141.0 mg, 0.75 mmol, 3.0 equiv.), and DCE (1.0 mL). Purification by flash column chromatography (Petroleum ether / DCM: 1 / 1) gave the title compound **5ia** (60.3 mg, 89%) as a white solid.

TLC: R_f = 0.26 (Petroleum ether / DCM: 1 / 1, $KMnO_4$ stain).

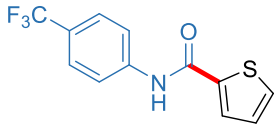
NMR Spectroscopy (*see spectra*):

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.88 (s, 1H), 7.83 (d, J = 2.5 Hz, 1H), 7.64 (dd, J = 3.8, 1.2 Hz, 1H), 7.57 (dd, J = 5.0, 1.2 Hz, 1H), 7.48 – 7.35 (m, 2H), 7.12 (dd, J = 5.0, 3.7 Hz, 1H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 160.2, 138.6, 137.2, 133.0, 131.6, 130.7, 129.1, 128.1, 128.0, 122.1, 119.6 ppm.

All recorded spectroscopic data matched those previously reported in the literature.[29]

***N*-[4-(Trifluoromethyl)phenyl]thiophene-2-carboxamide (5ja)**



5ja

Prepared following **General Procedure B**, using 2-thiopheneboronic acid (**2a**) (32.0 mg, 0.25 mmol, 1.0 equiv.), 4-(trifluoromethyl)phenylisocyanate (**4j**) (140.3 mg, 0.75 mmol, 3.0 equiv.), and DCE (1.0 mL). Purification by flash column chromatography (Petroleum ether / DCM: 1 / 1) gave the title compound **5ja** (60.3 mg, 89%) as a white solid.

TLC: R_f = 0.39 (Petroleum ether / DCM: 1 / 1, $KMnO_4$ stain).

NMR Spectroscopy (*see spectra*):

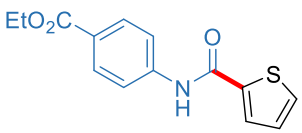
^{1}H NMR (400 MHz, d_6-DMSO): δ_H 10.54 (s, 1H), 8.08 (dd, J = 3.8, 1.2 Hz, 1H), 7.98 (d, J = 8.5 Hz, 2H), 7.89 (dd, J = 5.0, 1.1 Hz, 1H), 7.71 (d, J = 8.6 Hz, 2H), 7.24 (dd, J = 5.0, 3.8 Hz, 1H) ppm;

^{13}C NMR (101 MHz, d_6-DMSO): δ_C 160.3, 142.5, 139.4, 132.5, 129.8, 128.2, 126.0 (q, $^{3}J_{C\text{-}F}$ = 3.8 Hz), 124.4 (q, $^{1}J_{C\text{-}F}$ = 272.0 Hz), 123.7 (q, $^{2}J_{C\text{-}F}$ = 32.0 Hz), 120.1 ppm.

^{19}F NMR (376 MHz, d_6-DMSO): δ_F -60.43 ppm.

All recorded spectroscopic data matched those previously reported in the literature.[30]

Ethyl 4-(thiophene-2-carboxamido)benzoate (5ka)



5ka

Prepared following **General Procedure B**, using 2-thiopheneboronic acid (**2a**) (32.0 mg, 0.25 mmol, 1.0 equiv.), ethyl 4-isocyanatobenzoate (**4k**) (143.4 mg, 0.75 mmol, 3.0 equiv.), and DCE (1.0 mL). Purification by flash column chromatography (Petroleum ether / DCM: 1 / 5) gave the title compound **5ka** (67.4 mg, 98%) as a white solid.

TLC: R_f = 0.21 (Petroleum ether / DCM: 1 / 5, $KMnO_4$ stain).

M. p.: 183 – 185 °C.

NMR Spectroscopy (*see spectra*):

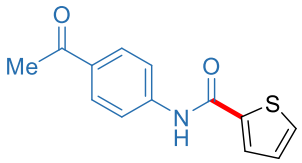
^{1}H NMR (400 MHz, d_6-DMSO): δ_H 10.51 (s, 1H), 8.08 (dd, J = 3.9, 1.2 Hz, 1H), 8.03 – 7.80 (m, 5H), 7.24 (dd, J = 5.0, 3.8 Hz, 1H), 4.29 (q, J = 7.1 Hz, 2H), 1.32 (t, J = 7.1 Hz, 3H) ppm;

^{13}C NMR (101 MHz, d_6-DMSO): δ_C 165.3, 160.2, 143.2, 139.5, 132.5, 130.1, 129.7, 128.1, 124.6, 119.5, 60.4, 14.2 ppm.

IR (film): ν_{max} 3361, 3091, 1667, 1594, 1529, 1473, 1418, 1310, 1286, 1250, 866, 794, 771, 730 cm^{-1}.

HRMS (ESI^+): m/z calculated for $C_{14}H_{14}NO_3S$ $[M+H]^+$, 276.0689; found, 276.0692.

***N*-(4-Acetylphenyl)thiophene-2-carboxamide (5la)**



5la

Prepared following **General Procedure B**, using 2-thiopheneboronic acid (**2a**) (32.0 mg, 0.25 mmol, 1.0 equiv.), 4-acetylphenyl isocyanate (**4l**) (120.9 mg, 0.75 mmol, 3.0 equiv.), and DCE (1.0 mL). Purification by flash column chromatography (DCM / EtOAc: 20 / 1) gave the title compound **5la** (39.9 mg, 65%) as a white solid.

TLC: R_f = 0.40 (DCM / EtOAc: 20 / 1, $KMnO_4$ stain).

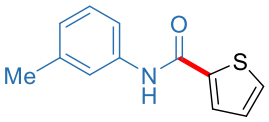
NMR Spectroscopy (*see spectra*):

^{1}H NMR (400 MHz, d_6-DMSO): δ_H 10.46 (s, 1H), 8.03 (dd, J = 3.8, 1.1 Hz, 1H), 7.96 – 7.82 (m, 5H), 7.20 (dd, J = 5.0, 3.8 Hz, 1H), 2.54 (s, 3H) ppm;

^{13}C NMR (101 MHz, d_6-DMSO): δ_C 196.6, 160.2, 143.2, 139.5, 132.5, 132.0, 129.7, 129.3, 128.2, 119.4, 26.4 ppm.

All recorded spectroscopic data matched those previously reported in the literature.[31]

***N*-(*m*-Tolyl)thiophene-2-carboxamide (5ma)**



5ma

Prepared following **General Procedure B**, using 2-thiopheneboronic acid (**2a**) (32.0 mg, 0.25 mmol, 1.0 equiv.), *m*-tolyl isocyanate (**4m**) (100.0 mg, 0.75 mmol, 3.0 equiv.), and DCE (1.0 mL). Purification by flash column chromatography (Petroleum ether / DCM / EtOAc: 8 / 4 / 1) gave the title compound **5ma** (28.3 mg, 52%) as a white solid.

TLC: R_f = 0.30 (Petroleum ether / DCM / EtOAc: 8 / 4 / 1, $KMnO_4$ stain).

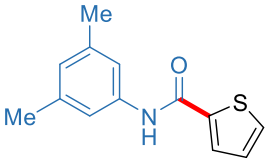
NMR Spectroscopy (*see spectra*):

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.93 (s, 1H), 7.64 (dd, *J* = 3.7, 1.1 Hz, 1H), 7.51 (dd, *J* = 5.0, 1.2 Hz, 1H), 7.47 (s, 1H), 7.40 (d, *J* = 7.9 Hz, 1H), 7.21 (t, *J* = 7.8 Hz, 1H), 7.08 (dd, *J* = 5.0, 3.7 Hz, 1H), 6.94 (d, *J* = 7.5 Hz, 1H), 2.32 (s, 3H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 160.2, 139.5, 139.1, 137.6, 130.8, 129.0, 128.6, 127.9, 125.5, 121.1, 117.6, 21.6 ppm.

All recorded spectroscopic data matched those previously reported in the literature.[32]

***N*-(3,5-Dimethylphenyl)thiophene-2-carboxamide (5na)**



5na

Prepared following **General Procedure B**, using 2-thiopheneboronic acid (**2a**) (32.0 mg, 0.25 mmol, 1.0 equiv.), 3,5-dimethylphenyl isocyanate (**4n**) (105.6 mg, 0.75 mmol, 3.0 equiv.), and DCE (1.0 mL). Purification by flash column chromatography (Petroleum ether / DCM: 1 / 1) gave the title compound **5na** (52.2 mg, 90%) as a white solid.

TLC: R_f = 0.28 (Petroleum ether / DCM: 1 / 1, $KMnO_4$ stain).

M. p.: 136 – 137 °C.

NMR Spectroscopy (*see spectra*):

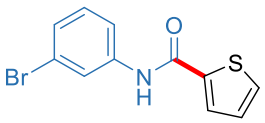
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.94 (s, 1H), 7.65 (dd, *J* = 3.7, 1.2 Hz, 1H), 7.50 (dd, *J* = 5.0, 1.2 Hz, 1H), 7.24 (s, 2H), 7.07 (dd, *J* = 5.0, 3.7 Hz, 1H), 6.76 (s, 1H), 2.27 (s, 6H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 160.2, 139.6, 138.8, 137.5, 130.7, 128.5, 127.9, 126.4, 118.3, 21.4 ppm.

IR (film): ν_{max} 3290, 2914, 1635, 1535, 1353, 1294, 1248, 1174, 851, 829, 726, 714, 689, 614 cm^{-1}.

HRMS (ESI^+): m/z calculated for $C_{13}H_{14}NOS$ $[M+H]^+$, 232.0790; found, 232.0798.

***N*-(3-Bromophenyl)thiophene-2-carboxamide (5oa)**



5oa

Prepared following **General Procedure B**, using 2-thiopheneboronic acid (**2a**) (32.0 mg, 0.25 mmol, 1.0 equiv.), 3-bromophenyl isocyanate (**4o**) (148.5 mg, 0.75 mmol, 3.0 equiv.), and DCE (1.0 mL). Purification by flash column chromatography (Petroleum ether / DCM / EtOAc: 8 / 4 / 1) gave the title compound **5oa** (63.5 mg, 90%) as a white solid.

TLC: R_f = 0.32 (Petroleum ether / DCM / EtOAc: 8 / 4 / 1, $KMnO_4$ stain).

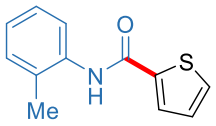
NMR Spectroscopy (*see spectra*):

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.86 (s, 1H), 7.77 (s, 1H), 7.63 (dd, *J* = 3.8, 1.2 Hz, 1H), 7.56 (dd, *J* = 5.0, 1.1 Hz, 1H), 7.53 (d, *J* = 8.2 Hz, 1H), 7.27 – 7.19 (m, 2H), 7.12 (dd, *J* = 5.0, 3.7 Hz, 1H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 160.1, 138.9, 138.9, 131.4, 130.5, 128.9, 128.1, 127.7, 123.3, 122.8, 118.8 ppm.

All recorded spectroscopic data matched those previously reported in the literature.[33]

_N_-(_o_-Tolyl)thiophene-2-carboxamide (5pa)



5pa

Prepared following **General Procedure B**, using 2-thiopheneboronic acid (**2a**) (32.0 mg, 0.25 mmol, 1.0 equiv.), *o*-tolyl isocyanate (**4p**) (100.0 mg, 0.75 mmol, 3.0 equiv.), and DCE (1.0 mL). Purification by flash column chromatography (Petroleum ether / DCM / EtOAc: 8 / 4 / 1) gave the title compound **5pa** (41.8 mg, 77%) as a white solid.

TLC: R_f = 0.37 (Petroleum ether / DCM / EtOAc: 8 / 4 / 1, $KMnO_4$ stain).

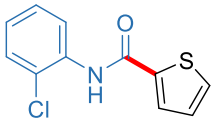
NMR Spectroscopy (*see spectra*):

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.85 (d, *J* = 8.0 Hz, 1H), 7.63 (d, *J* = 3.7 Hz, 2H), 7.54 (dd, *J* = 5.0, 1.2 Hz, 1H), 7.27 – 7.20 (m, 2H), 7.16 – 7.08 (m, 2H), 2.32 (s, 3H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 160.1, 139.2, 135.5, 130.7, 130.7, 129.6, 128.7, 128.0, 127.0, 125.7, 123.5, 17.9 ppm.

All recorded spectroscopic data matched those previously reported in the literature.[34]

_N_-(2-Chlorophenyl)thiophene-2-carboxamide (5qa)



5qa

Prepared following **General Procedure B**, using 2-thiopheneboronic acid (**2a**) (32.0 mg, 0.25 mmol, 1.0 equiv.), 2-chlorophenyl isocyanate (**4q**) (115.2 mg, 0.75 mmol, 3.0 equiv.), and DCE (1.0 mL).

Purification by flash column chromatography (Petroleum ether / DCM: 1 / 1) gave the title compound **5qa** (52.1 mg, 88%) as a white solid.

TLC: R_f = 0.30 (Petroleum ether / DCM: 1 / 1, $KMnO_4$ stain).

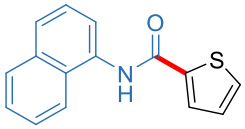
NMR Spectroscopy (*see spectra*):

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.48 (dd, *J* = 8.3, 1.6 Hz, 1H), 8.31 (s, 1H), 7.66 (dd, *J* = 3.8, 1.2 Hz, 1H), 7.58 (dd, *J* = 5.0, 1.2 Hz, 1H), 7.40 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.31 (td, *J* = 7.9, 1.5 Hz, 1H), 7.15 (dd, *J* = 5.0, 3.8 Hz, 1H), 7.07 (td, *J* = 7.7, 1.6 Hz, 1H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 159.8, 139.2, 134.6, 131.4, 129.1, 128.8, 128.1, 128.0, 124.9, 122.9, 121.6 ppm.

All recorded spectroscopic data matched those previously reported in the literature.[35]

***N*-(Naphthalen-1-yl)thiophene-2-carboxamide (5ra)**



5ra

Prepared following **General Procedure B**, using 2-thiopheneboronic acid (**2a**) (32.0 mg, 0.25 mmol, 1.0 equiv.), 1-naphthyl isocyanate (**4r**) (126.9 mg, 0.75 mmol, 3.0 equiv.), and DCE (1.0 mL). Purification by flash column chromatography (Petroleum ether / DCM: 1 / 2) gave the title compound **5ra** (42.2 mg, 67%) as a pink solid.

TLC: R_f = 0.28 (Petroleum ether / DCM: 1 / 2, $KMnO_4$ stain).

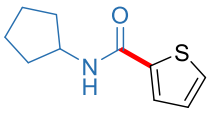
NMR Spectroscopy (*see spectra*):

^{1}H NMR (400 MHz, d_6-DMSO): δ_H 10.48 (s, 1H), 8.15 (dd, *J* = 3.8, 1.2 Hz, 1H), 7.98 (dd, *J* = 6.3, 3.3 Hz, 2H), 7.91 – 7.85 (m, 2H), 7.61 – 7.52 (m, 4H), 7.27 (dd, *J* = 5.0, 3.7 Hz, 1H) ppm;

^{13}C NMR (101 MHz, d_6-DMSO): δ_C 160.7, 139.7, 133.8, 133.2, 131.7, 129.3, 129.2, 128.2, 128.1, 126.5, 126.2, 126.1, 125.6, 124.1, 123.3 ppm.

All recorded spectroscopic data matched those previously reported in the literature.[36]

***N*-Cyclopentylthiophene-2-carboxamide (5sa)**



5sa

Prepared following **General Procedure B**, using 2-thiopheneboronic acid (**2a**) (32.0 mg, 0.25 mmol, 1.0 equiv.), cyclopentyl isocyanate (**4s**) (83.4 mg, 0.75 mmol, 3.0 equiv.), and DCE (1.0 mL). Purification by flash column chromatography (DCM: 100%) gave the title compound **5sa** (47.8 mg, 98%) as a white solid.

TLC: R_f = 0.41 (DCM: 100%, $KMnO_4$ stain).

M. p.: 178 – 180 °C.

NMR Spectroscopy (*see spectra*):

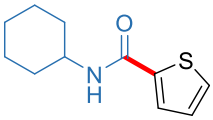
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.48 (d, *J* = 3.7 Hz, 1H), 7.43 (d, *J* = 5.0 Hz, 1H), 7.04 (dd, *J* = 5.0, 3.8 Hz, 1H), 6.02 (s, 1H), 4.35 (q, *J* = 7.1 Hz, 1H), 2.15 – 1.98 (m, 2H), 1.77 – 1.57 (m, 4H), 1.53 – 1.42 (m, 2H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 161.7, 139.5, 129.7, 127.9, 127.6, 51.9, 33.3, 23.9 ppm.

IR (film): ν_{max} 3103, 2960, 2864, 1612, 1421, 1362, 1317, 1290, 1245, 1187, 935, 860, 777, 731 cm^{-1}.

HRMS (ESI^+): m/z calculated for $C_{10}H_{14}NOS$ $[M+H]^+$, 196.0791; found, 196.0797.

***N*-Cyclohexylthiophene-2-carboxamide (5ta)**



5ta

Prepared following **General Procedure B**, using 2-thiopheneboronic acid (**2a**) (32.0 mg, 0.25 mmol, 1.0 equiv.), cyclohexyl isocyanate (**4t**) (148.5 mg, 0.75 mmol, 3.0 equiv.), and DCE (1.0 mL). Purification

by flash column chromatography (Petroleum ether / EtOAc: 4 / 1) gave the title compound **5ta** (50.5 mg, 97%) as a white solid.

TLC: R_f = 0.52 (Petroleum ether / EtOAc: 2 / 1, $KMnO_4$ stain).

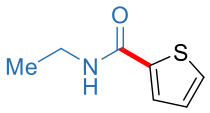
NMR Spectroscopy (*see spectra*):

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.49 (dd, *J* = 3.7, 1.2 Hz, 1H), 7.43 (dd, *J* = 5.0, 1.2 Hz, 1H), 7.03 (dd, *J* = 5.0, 3.7 Hz, 1H), 6.14 – 5.94 (m, 1H), 3.99 – 3.85 (m, 1H), 2.05 – 1.95 (m, 2H), 1.78 – 1.67 (m, 2H), 1.67 – 1.56 (m, 1H), 1.47 – 1.29 (m, 2H), 1.29 – 1.08 (m, 3H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 161.1, 139.6, 129.7, 127.8, 127.6, 48.9, 33.3, 25.6, 25.0 ppm.

All recorded spectroscopic data matched those previously reported in the literature.[37]

***N*-Ethylthiophene-2-carboxamide (5ua)**



5ua

Prepared following **General Procedure B**, using 2-thiopheneboronic acid (**2a**) (32.0 mg, 0.25 mmol, 1.0 equiv.), ethyl isocyanate (**4u**) (53.3 mg, 0.75 mmol, 3.0 equiv.), and DCE (1.0 mL). Purification by flash column chromatography (DCM / EtOAc: 40 / 1) gave the title compound **5ua** (29.3 mg, 76%) as a white solid.

TLC: R_f = 0.40 (DCM / EtOAc: 20 / 1, $KMnO_4$ stain).

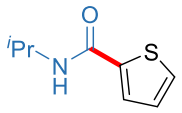
NMR Spectroscopy (*see spectra*):

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.51 (dd, *J* = 3.8, 1.2 Hz, 1H), 7.44 (dd, *J* = 5.0, 1.1 Hz, 1H), 7.05 (dd, *J* = 5.0, 3.7 Hz, 1H), 6.21 (s, 1H), 3.46 (qd, *J* = 7.2, 5.6 Hz, 2H), 1.23 (t, *J* = 7.3 Hz, 3H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 162.0, 139.3, 129.8, 127.9, 127.7, 35.0, 15.0 ppm.

All recorded spectroscopic data matched those previously reported in the literature.[38]

***N*-Isopropylthiophene-2-carboxamide (5va)**



5va

Prepared following **General Procedure B**, using 2-thiopheneboronic acid (**2a**) (32.0 mg, 0.25 mmol, 1.0 equiv.), isopropyl isocyanate (**4v**) (63.8 mg, 0.75 mmol, 3.0 equiv.), and DCE (1.0 mL). Purification by flash column chromatography (DCM: 100%) gave the title compound **5va** (36.2 mg, 86%) as a white solid.

TLC: R_f = 0.46 (DCM: 100%, $KMnO_4$ stain).

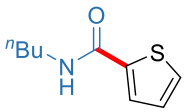
NMR Spectroscopy (*see spectra*):

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.52 (dd, *J* = 3.6, 1.7 Hz, 1H), 7.45 (dd, *J* = 5.1, 1.8 Hz, 1H), 7.06 (dd, *J* = 5.0, 3.7 Hz, 1H), 6.04 (s, 1H), 4.34 – 4.19 (m, 1H), 1.26 (d, *J* = 6.6 Hz, 6H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 161.2, 139.6, 129.7, 127.8, 127.6, 42.1, 22.9 ppm.

All recorded spectroscopic data matched those previously reported in the literature.[39]

***N*-Butylthiophene-2-carboxamide (5wa)**



5wa

Prepared following **General Procedure B**, using 2-thiopheneboronic acid (**2a**) (32.0 mg, 0.25 mmol, 1.0 equiv.), butyl isocyanate (**4w**) (74.3 mg, 0.75 mmol, 3.0 equiv.), and DCE (1.0 mL). Purification by flash column chromatography (DCM / EtOAc: 40 / 1) gave the title compound **5wa** (42.7 mg, 93%) as a white solid.

TLC: R_f = 0.48 (DCM / EtOAc: 20 / 1, $KMnO_4$ stain).

NMR Spectroscopy (*see spectra*):

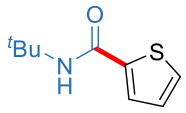
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.52 (dd, *J* = 3.7, 1.2 Hz, 1H), 7.43 (dd, *J* = 5.0, 1.2 Hz, 1H), 7.04 (dd, *J* = 5.0, 3.7 Hz, 1H), 6.33 (brs, 1H), 3.40 (td, *J* = 7.2, 5.8 Hz, 2H), 1.62 – 1.51 (m, 2H), 1.43 –

1.31 (m, 2H), 0.92 (t, J = 7.4 Hz, 3H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 162.1, 139.4, 129.7, 127.9, 127.6, 39.9, 31.8, 20.2, 13.9 ppm.

All recorded spectroscopic data matched those previously reported in the literature.[40]

***N*-(*tert*-Butyl)thiophene-2-carboxamide (5xa)**



5xa

Prepared following **General Procedure B**, using 2-thiopheneboronic acid (**2a**) (32.0 mg, 0.25 mmol, 1.0 equiv.), *tert*-butylisocyanate (**4x**) (74.3 mg, 0.75 mmol, 3.0 equiv.), and DCE (1.0 mL). Purification by flash column chromatography (DCM: 100%) gave the title compound **5xa** (32.1 mg, 70%) as a white solid.

TLC: R_f = 0.56 (DCM: 100%, $KMnO_4$ stain).

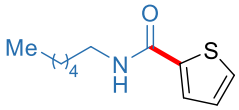
NMR Spectroscopy (*see spectra*):

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.45 – 7.37 (m, 2H), 7.03 (dd, J = 4.8, 3.9 Hz, 1H), 5.92 – 5.70 (brs, 1H), 1.45 (s, 9H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 161.4, 140.6, 129.5, 127.6, 127.5, 52.1, 29.0 ppm.

All recorded spectroscopic data matched those previously reported in the literature.[41]

***N*-Hexylthiophene-2-carboxamide (5ya)**



5ya

Prepared following **General Procedure B**, using 2-thiopheneboronic acid (**2a**) (32.0 mg, 0.25 mmol, 1.0 equiv.), hexyl isocyanate (**4y**) (95.4 mg, 0.75 mmol, 3.0 equiv.), and DCE (1.0 mL). Purification by flash

column chromatography (Petroleum ether / EtOAc: 4 / 1) gave the title compound **5ya** (49.7 mg, 94%) as a white solid.

TLC: R_f = 0.55 (Petroleum ether / EtOAc: 2 / 1, $KMnO_4$ stain).

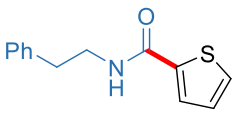
NMR Spectroscopy (*see spectra*):

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.52 (dd, *J* = 3.7, 1.2 Hz, 1H), 7.43 (dd, *J* = 5.0, 1.2 Hz, 1H), 7.04 (dd, *J* = 5.0, 3.7 Hz, 1H), 6.34 (s, 1H), 3.39 (td, *J* = 7.3, 5.8 Hz, 2H), 1.58 (ddd, *J* = 14.8, 8.1, 6.5 Hz, 2H), 1.36 – 1.25 (m, 6H), 0.94 – 0.81 (m, 3H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 162.1, 139.4, 129.7, 127.9, 127.6, 40.2, 31.6, 29.7, 26.7, 22.6, 14.1 ppm.

All recorded spectroscopic data matched those previously reported in the literature.[42]

***N*-Phenethylthiophene-2-carboxamide (5za)**



5za

Prepared following **General Procedure B**, using 2-thiopheneboronic acid (**2a**) (32.0 mg, 0.25 mmol, 1.0 equiv.), phenethyl isocyanate (**4z**) (110.4 mg, 0.75 mmol, 3.0 equiv.), and DCE (1.0 mL). Purification by flash column chromatography (DCM: 100%) gave the title compound **5za** (53.2 mg, 92%) as a white solid.

TLC: R_f = 0.45 (DCM: 100%, $KMnO_4$ stain).

NMR Spectroscopy (*see spectra*):

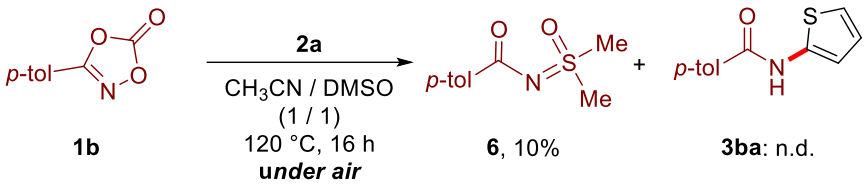
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.44 (d, *J* = 4.4 Hz, 2H), 7.35 – 7.27 (m, 2H), 7.27 – 7.18 (m, 3H), 7.08 – 7.00 (m, 1H), 6.31 (s, 1H), 3.73 – 3.60 (m, 2H), 2.91 (t, *J* = 7.1 Hz, 2H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 162.0, 139.2, 138.9, 129.9, 128.9, 128.8, 128.0, 127.7, 126.7, 41.3, 35.8 ppm.

All recorded spectroscopic data matched those previously reported in the literature.[43]

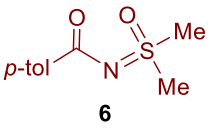
3. MECHANISTIC STUDIES

3.1. Additional experiment



To a 10 mL vial equipped with a magnetic stir bar was added 3-(*p*-tolyl)-1,4,2-dioxazol-5-one (**1b**) (44.3 mg, 0.25 mmol, 1.0 equiv.), 2-thiopheneboronic acid (**2a**) (96.0 mg, 0.75 mmol, 3.0 equiv.), and CH_3CN/DMSO (1:1, 2.0 mL). Under air, the vial was sealed with a septum and allowed to stir at 120 °C for 16 hours. After the reaction, the mixture was diluted with DCM (2.0 mL) and transferred into a 25 mL round flask, and concentrated under reduced pressure. The residue was purified by flash column chromatography (Petroleum ether / EtOAc: 1 / 2) gave the title compound **6** (5.3 mg, 10%) as a white solid, and the product **3ba** was not observed.

***N* -(Dimethyl(oxo)-λ^6-sulfaneylidene)-4-methylbenzamide (6)**



6

TLC: R_f = 0.28 (Petroleum ether / EtOAc: 1 / 2, $KMnO_4$ stain).

NMR Spectroscopy (*see spectra*):

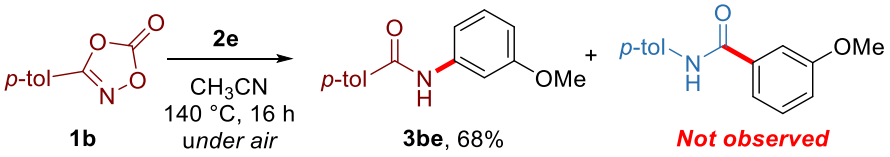
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.01 (d, *J* = 7.8 Hz, 2H), 7.20 (d, *J* = 7.8 Hz, 2H), 3.38 (s, 6H), 2.39 (s, 3H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 174.3, 142.8, 132.8, 129.4, 128.9, 41.9, 21.7 ppm.

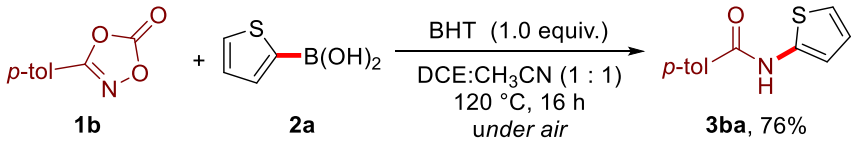
All recorded spectroscopic data matched those previously reported in the literature.[44]

3.2. Control experiment

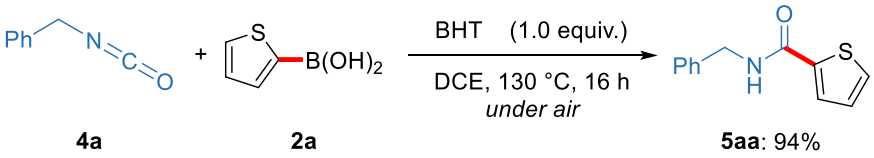
Following **General Procedure A**, using 3-(*p*-tolyl)-1,4,2-dioxazol-5-one (**1b**) (44.3 mg, 0.25 mmol, 1.0 equiv.), 3-methoxyphenylboronic acid (**2e**) (114.0 mg, 0.75 mmol, 3.0 equiv.), and CH_3CN (2.0 mL) at 140 °C. Purification by flash column chromatography (Petroleum ether / EtOAc: 5 / 1) gave the title compound **3be** (41.3 mg, 68%) as a sole product.



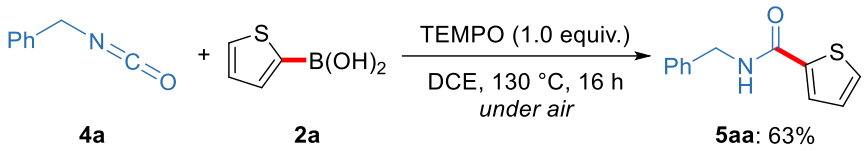
3.3. Radical trap experiments



Following **General Procedure A**, using 3-(*p*-tolyl)-1,4,2-dioxazol-5-one (**1b**) (44.3 mg, 0.25 mmol, 1.0 equiv.), 2-thiopheneboronic acid (**2a**) (96.0 mg, 0.75 mmol, 3.0 equiv.), butylated Hydroxytoluene (BHT) (55.1 mg, 1.0 equiv.), and DCE/CH_3CN (1:1, 2.0 mL) at 120 °C for 16 hours. Purification by flash column chromatography (Petroleum ether / EtOAc: 5 / 1) gave the title compound **3ba** (41.3 mg, 76%) as a sole product.



Prepared following **General Procedure B**, using thiophene-2-boronic acid (**2a**) (32.0 mg, 0.25 mmol, 1.0 equiv.), benzylisocyanate (**4a**) (99.9 mg, 0.75 mmol, 3.0 equiv.), butylated Hydroxytoluene (BHT) (55.1 mg, 1.0 equiv.), and DCE (1.0 mL). Purification by flash column chromatography (DCM: 100%) gave the title compound **5aa** (51.1 mg, 94%) as a white solid.

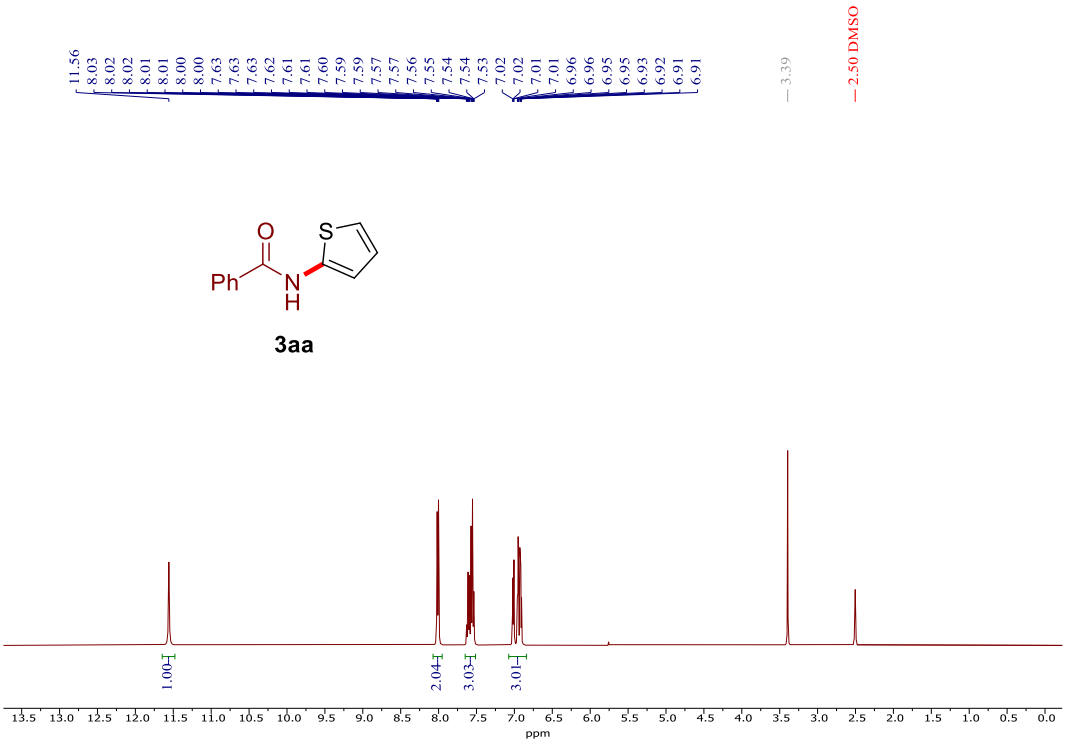


4a **2a** **5aa**: 63%

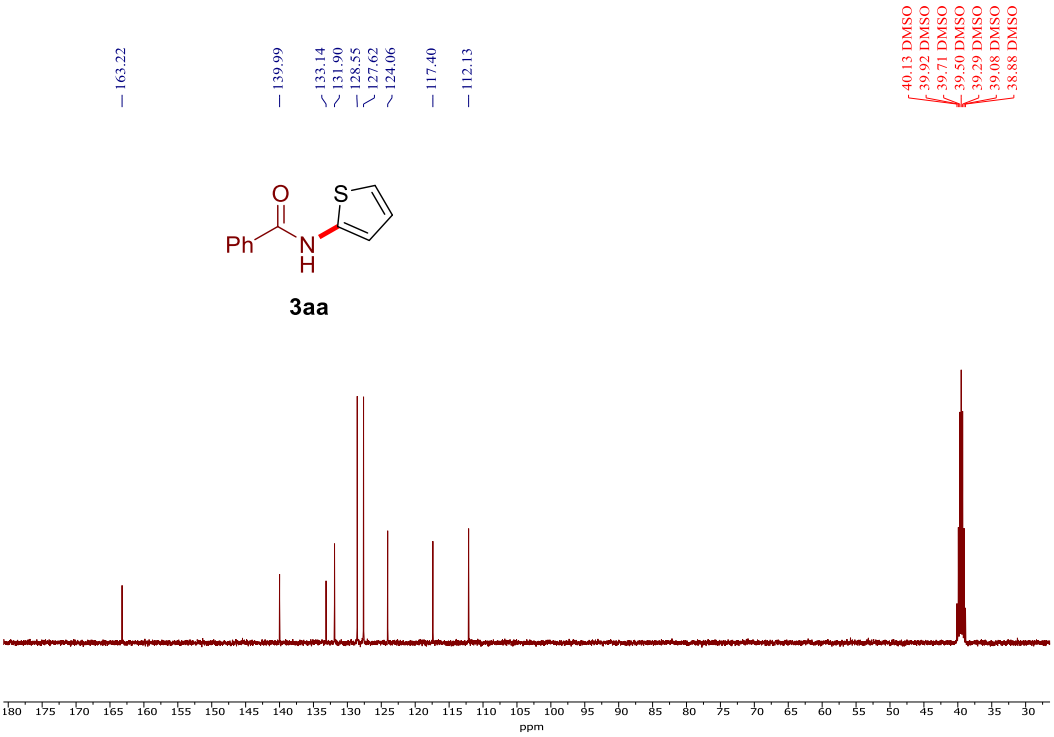
Prepared following **General Procedure B**, using thiophene-2-boronic acid (**2a**) (32.0 mg, 0.25 mmol, 1.0 equiv.), benzylisocyanate (**4a**) (99.9 mg, 0.75 mmol, 3.0 equiv.), 2,2,6,6-tetramethylpiperidinooxy (TEMPO) (39.1 mg, 1.0 equiv.), and DCE (1.0 mL). Purification by flash column chromatography (DCM: 100%) gave the title compound **5aa** (34.2 mg, 63%) as a white solid.

4. SPECTROSCOPIC DATA

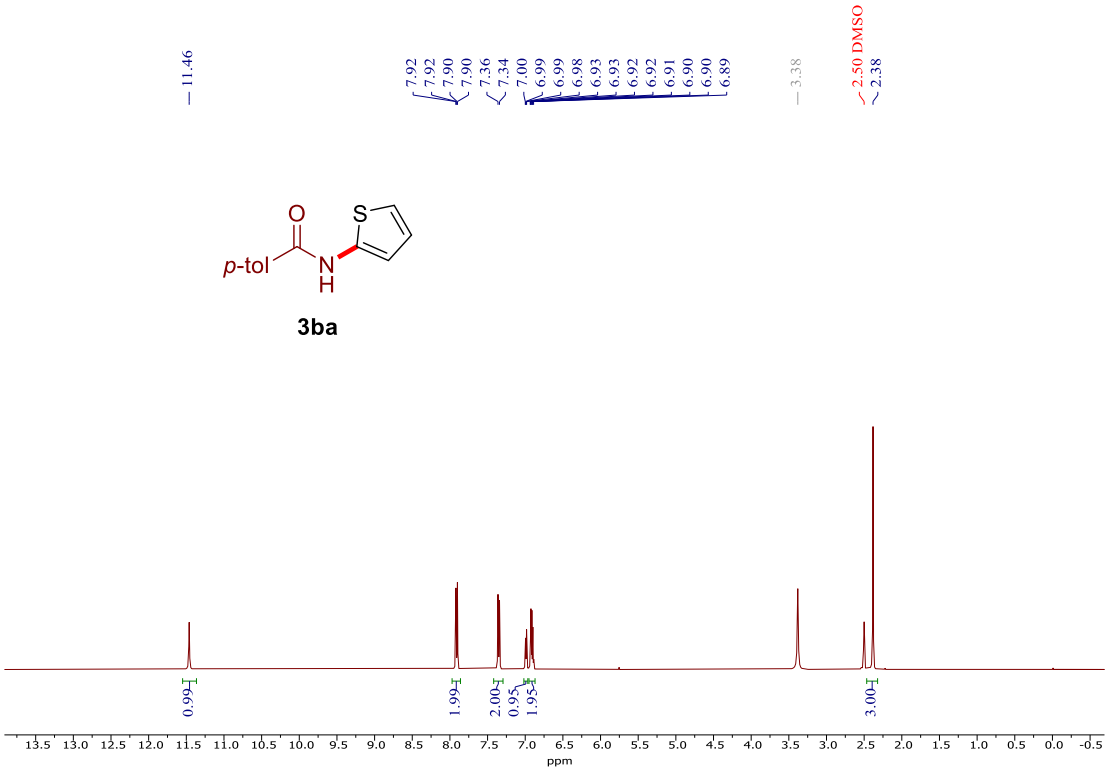
^{1}H NMR (400 MHz, d_6-DMSO) of **3aa** (*see procedure*)



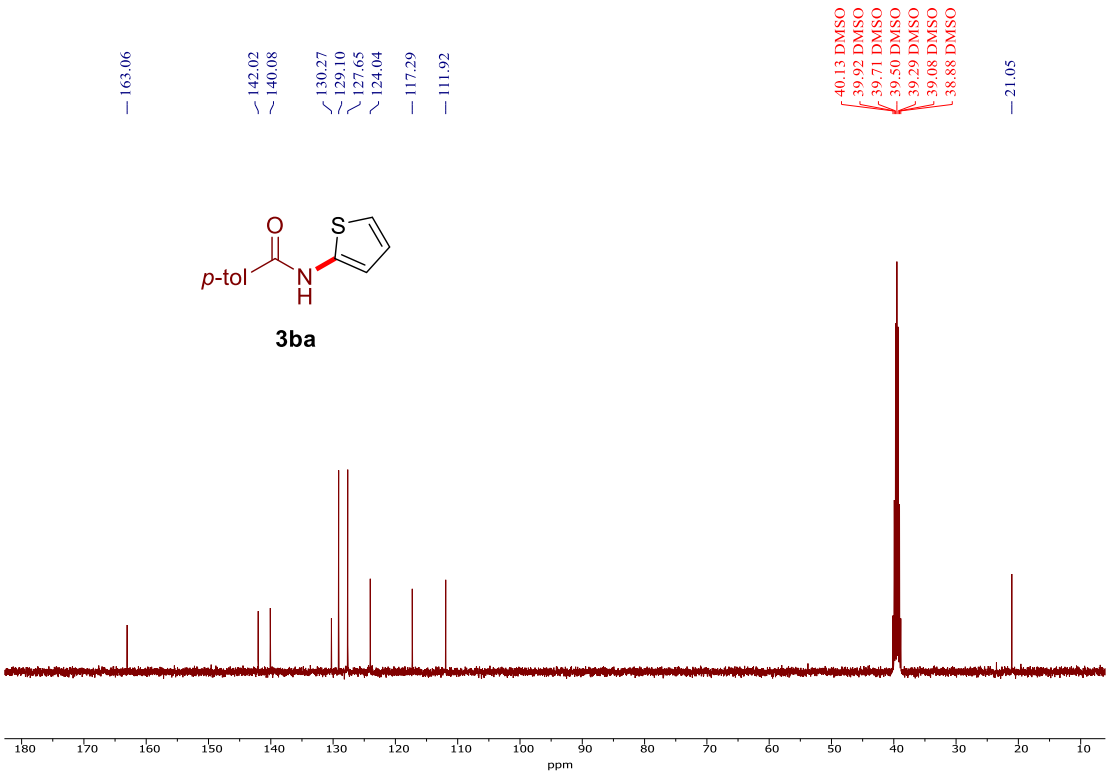
^{13}C NMR (101 MHz, d_6-DMSO) of **3aa**



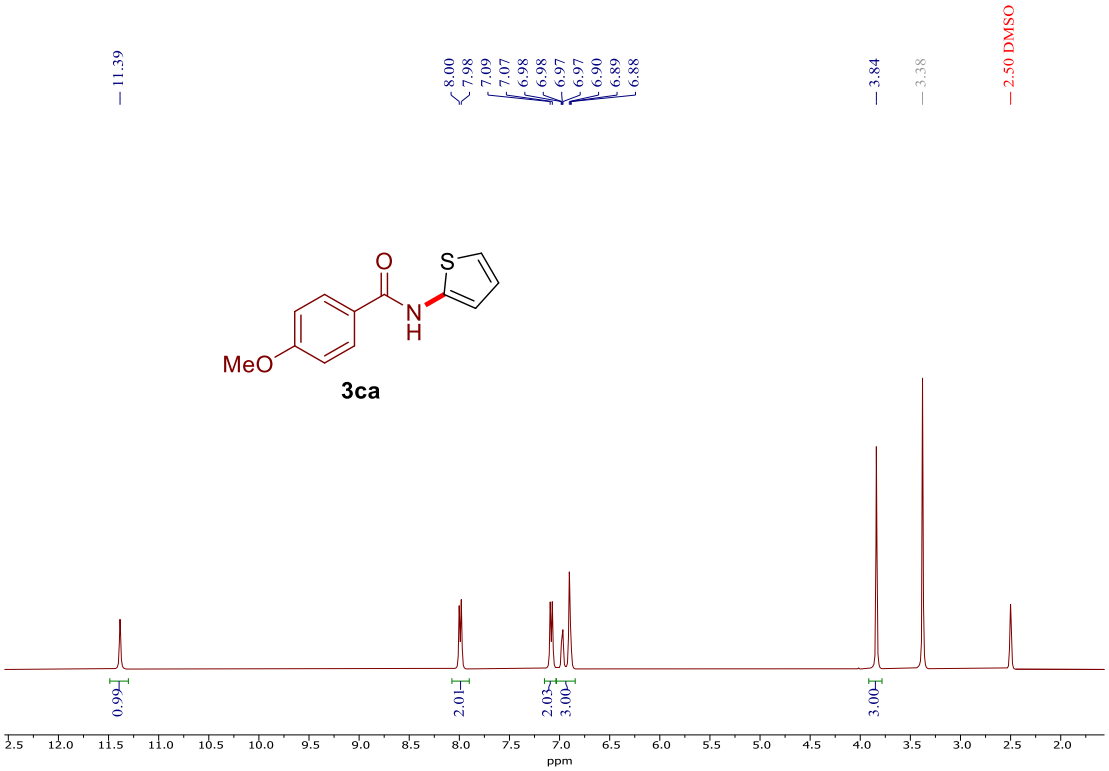
^{1}H NMR (400 MHz, d_6-DMSO) of **3ba** (*see procedure*)



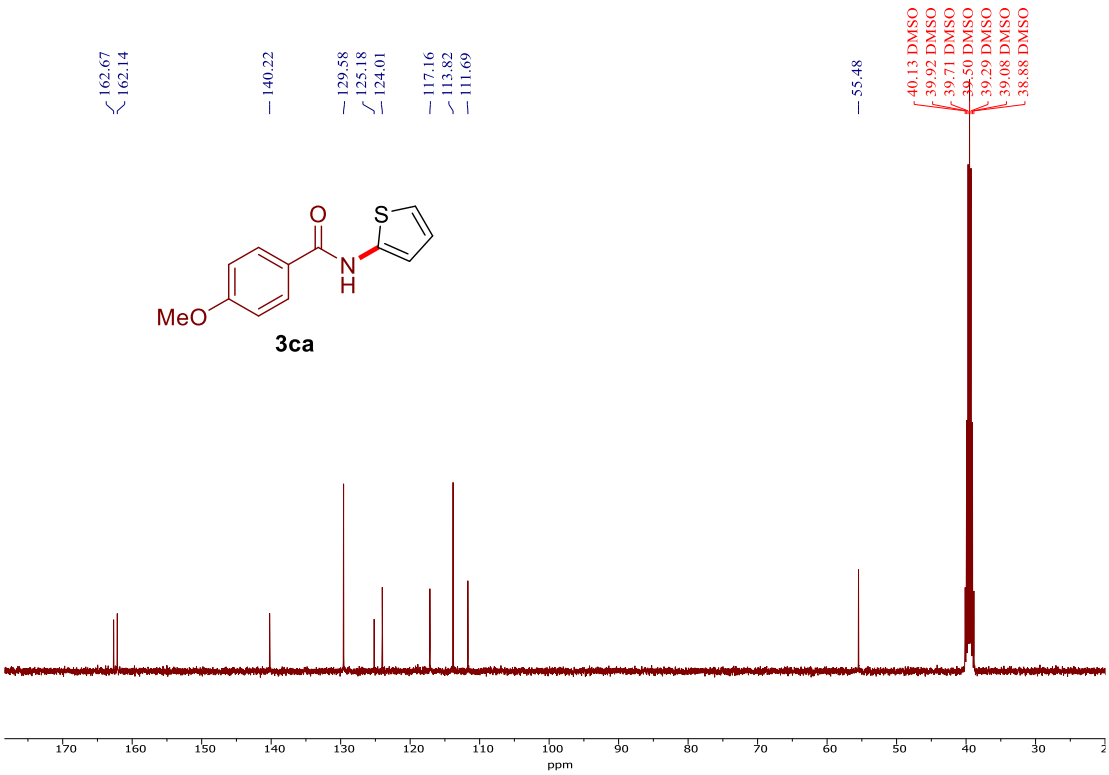
^{13}C NMR (101 MHz, d_6-DMSO) of **3ba**



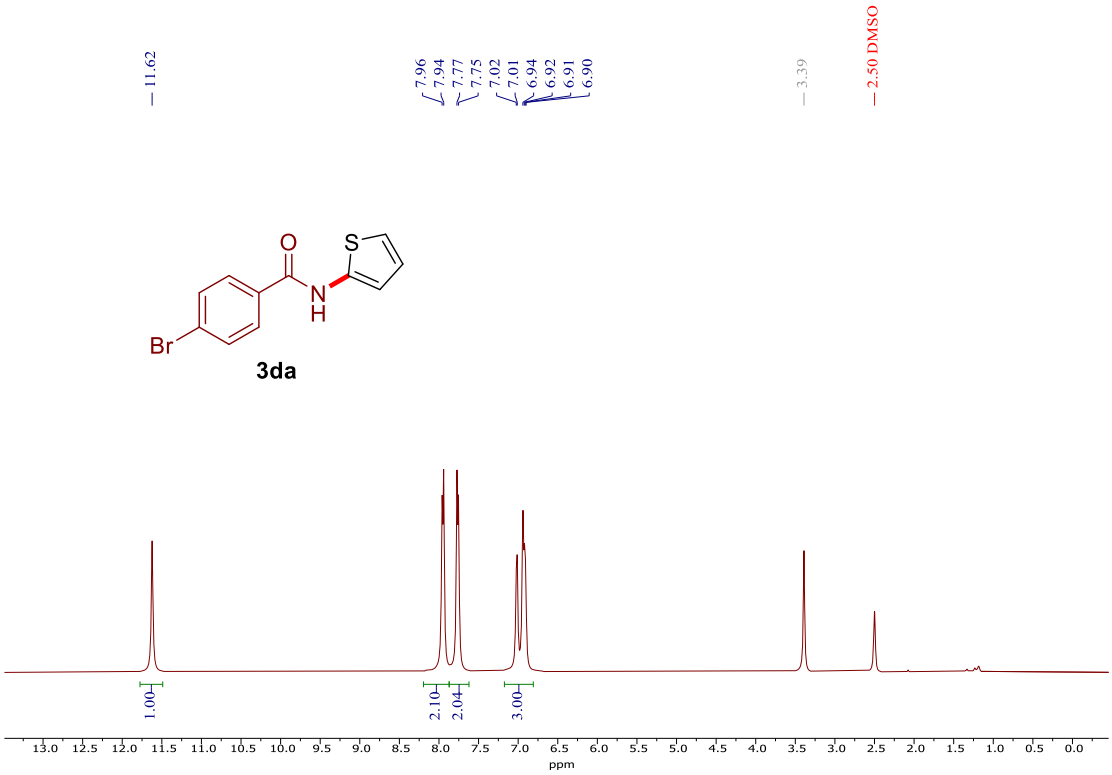
[1]H NMR (400 MHz, d_6-DMSO) of **3ca** (*see procedure*)



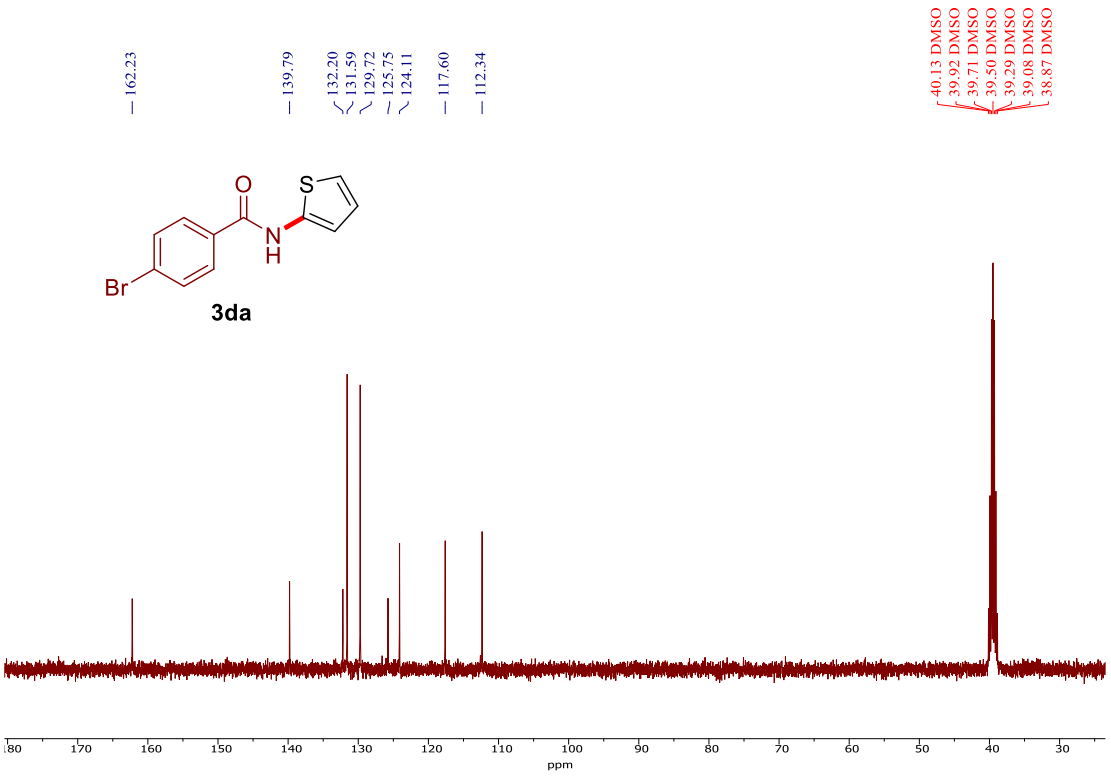
[13]C NMR (101 MHz, d_6-DMSO) of **3ca**



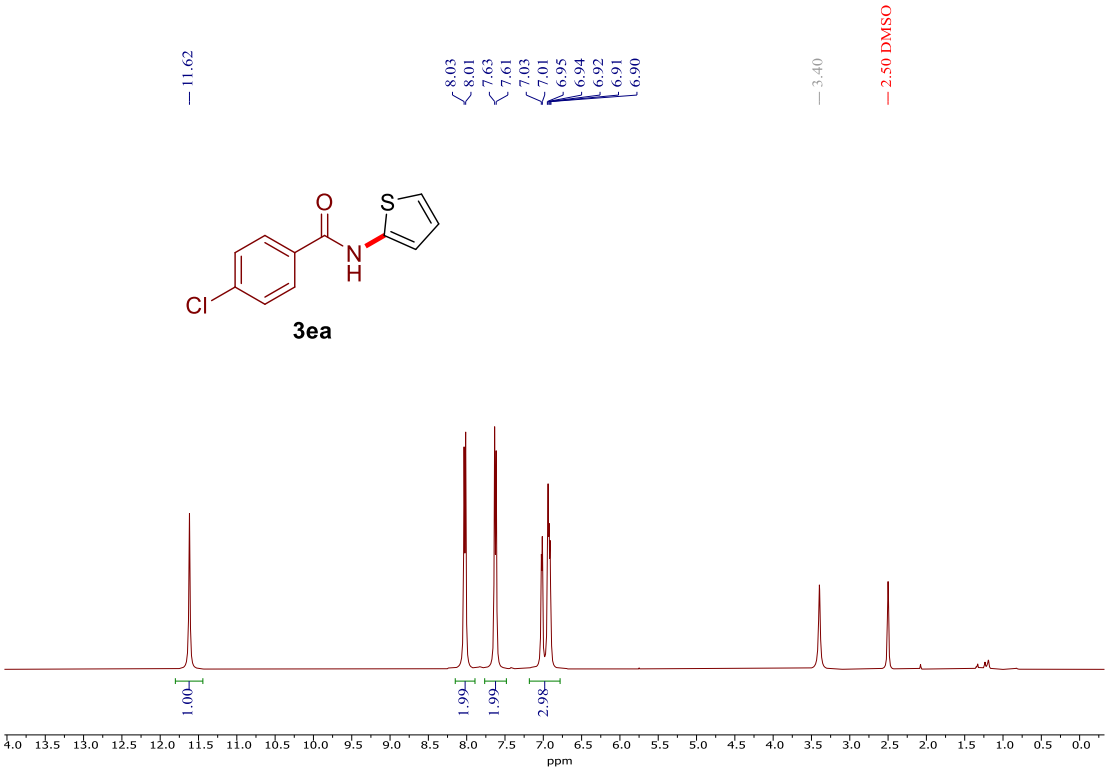
^{1}H NMR (400 MHz, d_6-DMSO) of **3da** (*see procedure*)



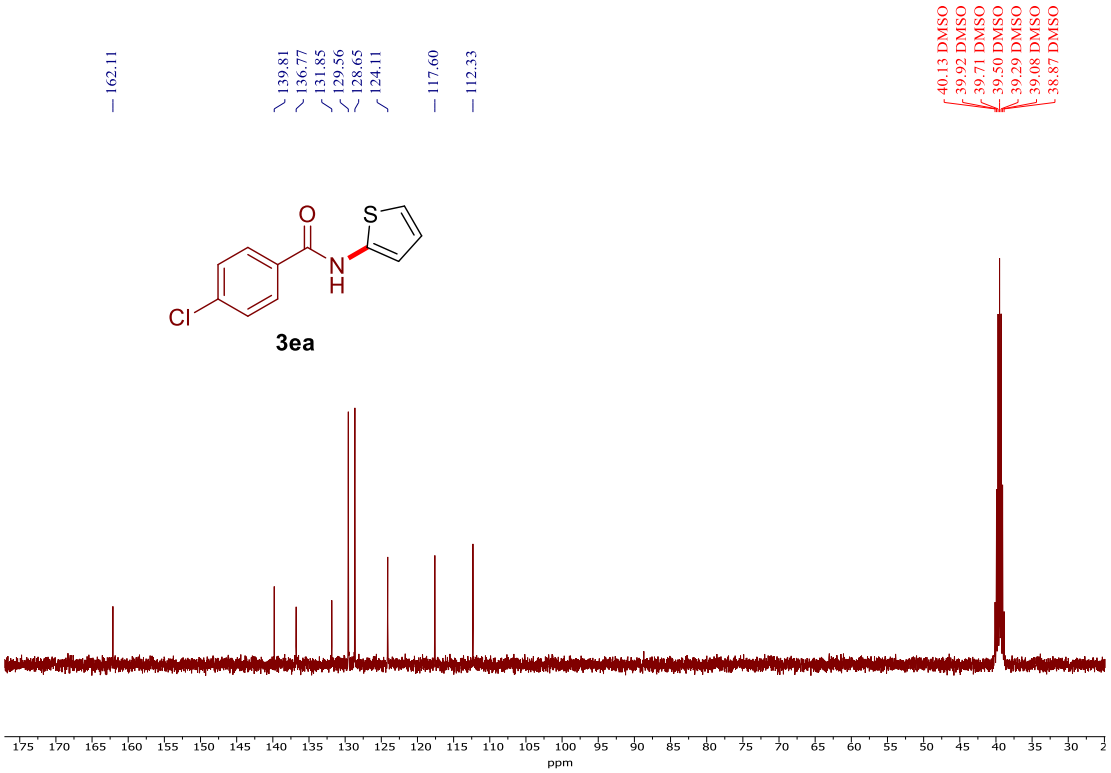
^{13}C NMR (101 MHz, d_6-DMSO) of 3da



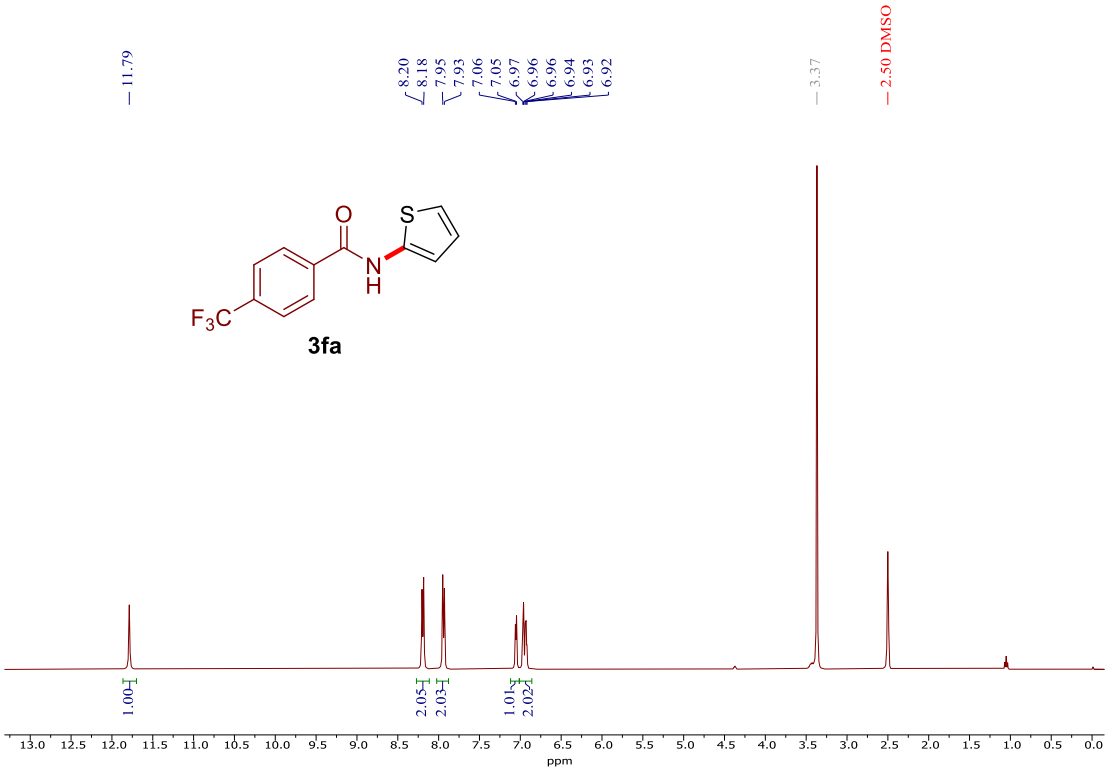
^{1}H NMR (400 MHz, d_6-DMSO) of **3ea** (*see procedure*)



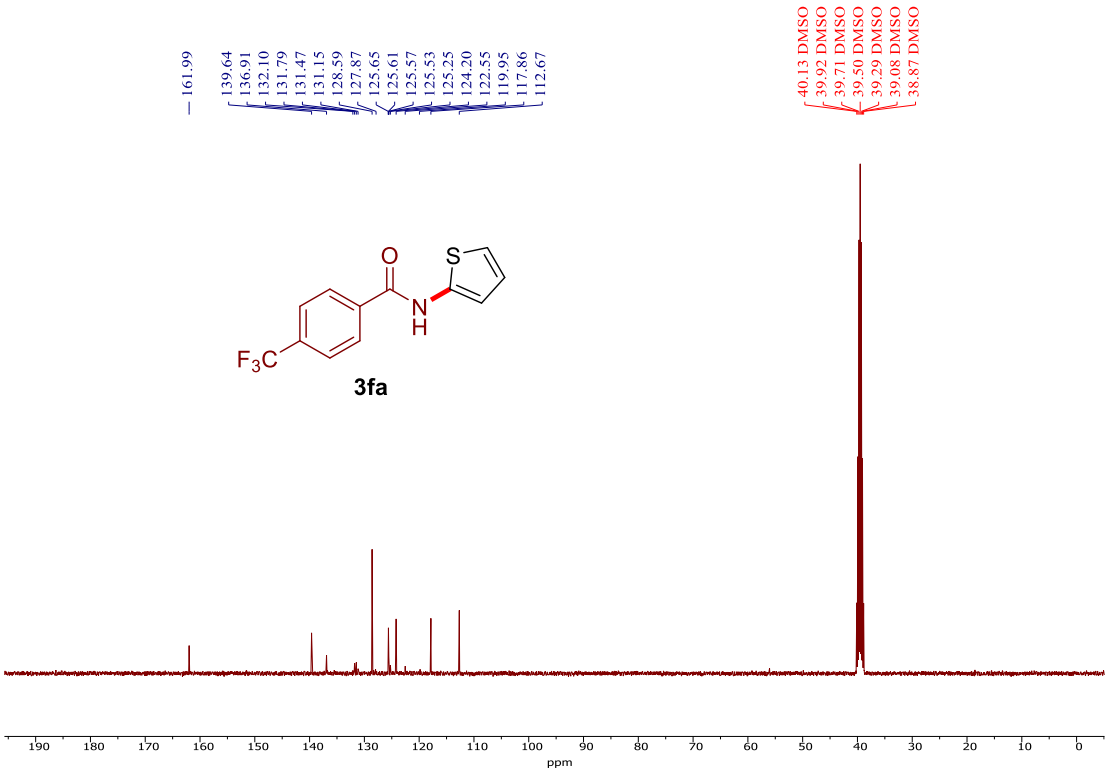
^{13}C NMR (101 MHz, d_6-DMSO) of **3ea**



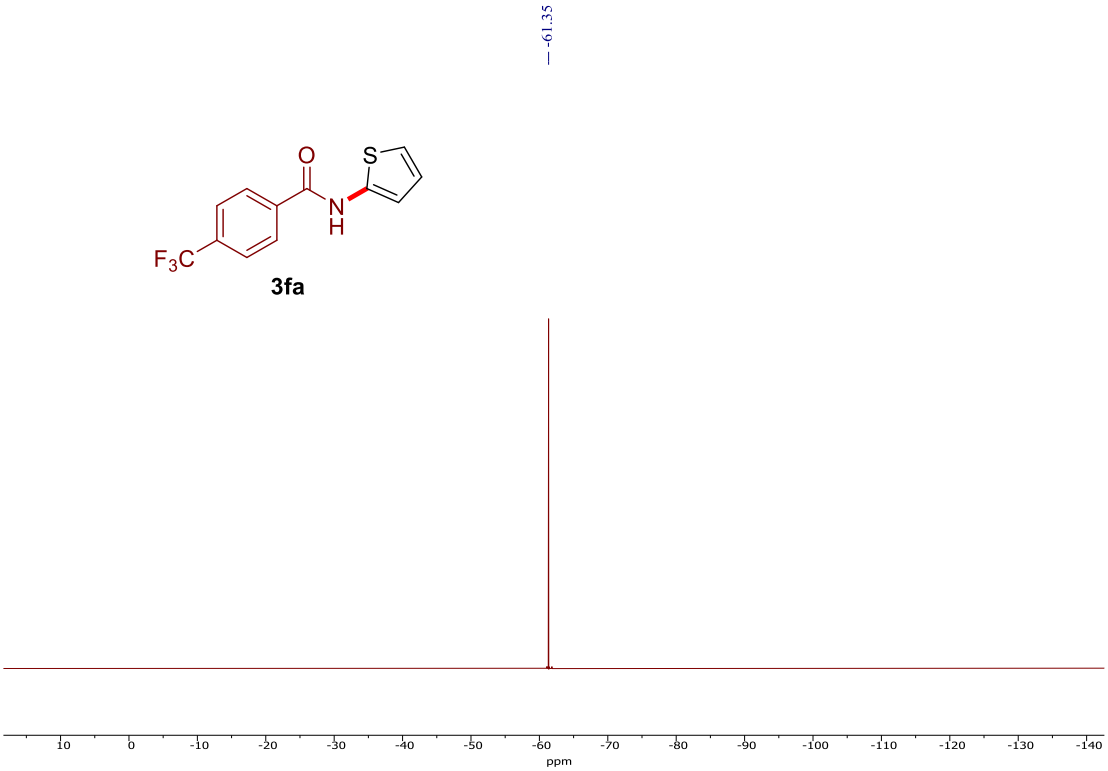
^{1}H NMR (400 MHz, d_6-DMSO) of **3fa** (*see procedure*)



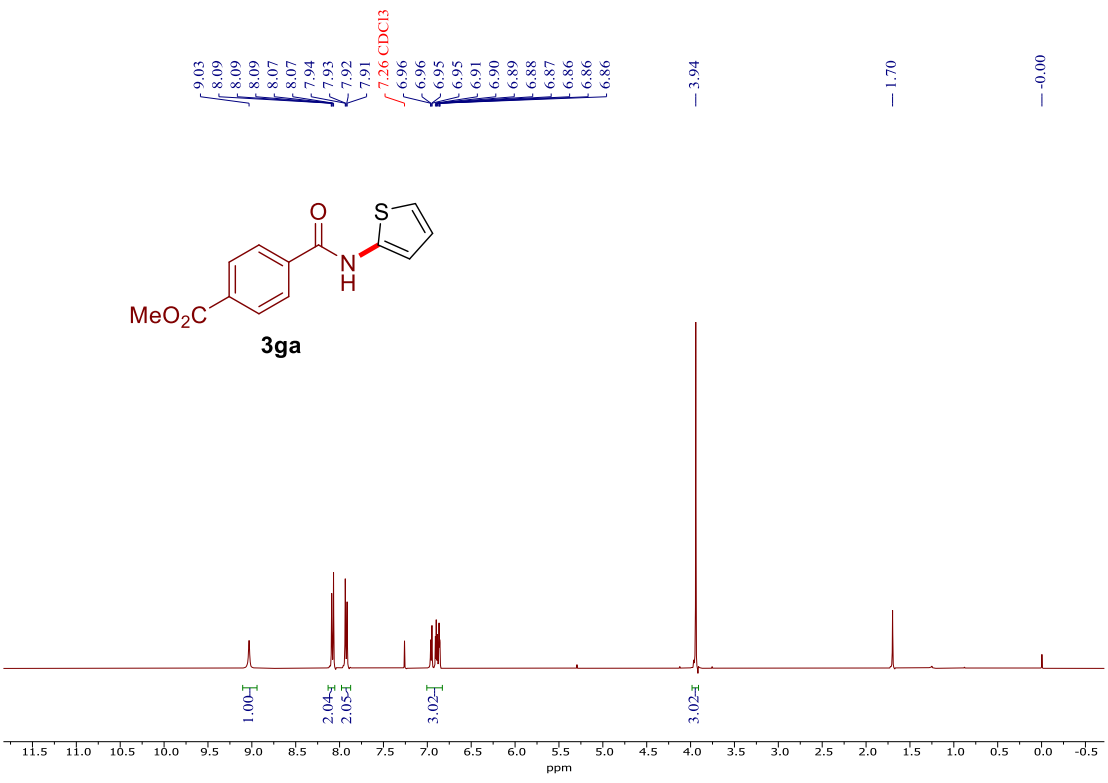
^{13}C NMR (101 MHz, d_6-DMSO) of **3fa**



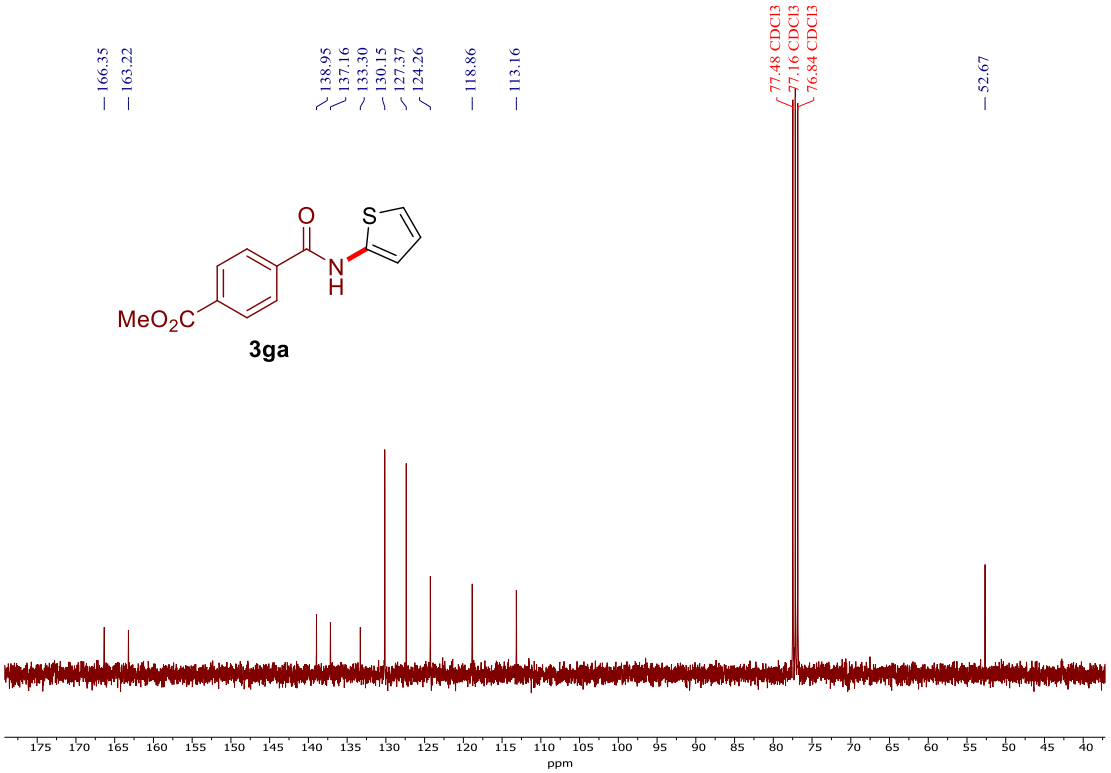
^{19}F NMR (376 MHz, d_6-DMSO) of **3fa**



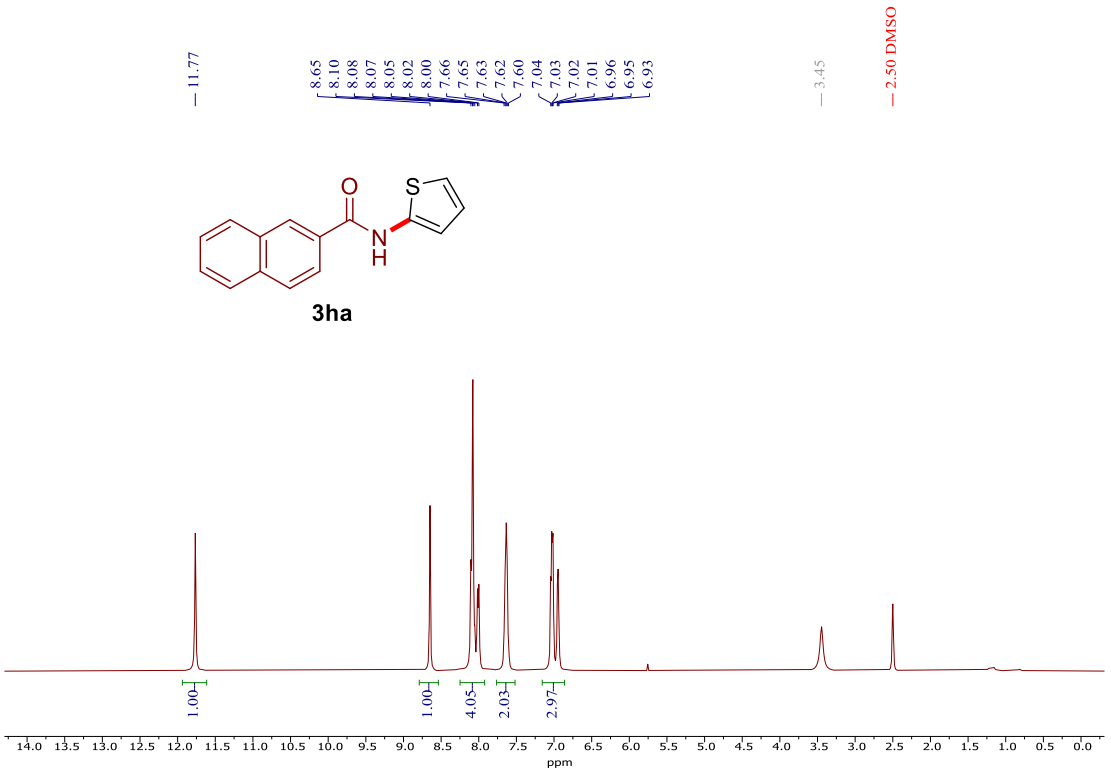
^{1}H NMR (400 MHz, $CDCl_3$) of **3ga** (*see procedure*)



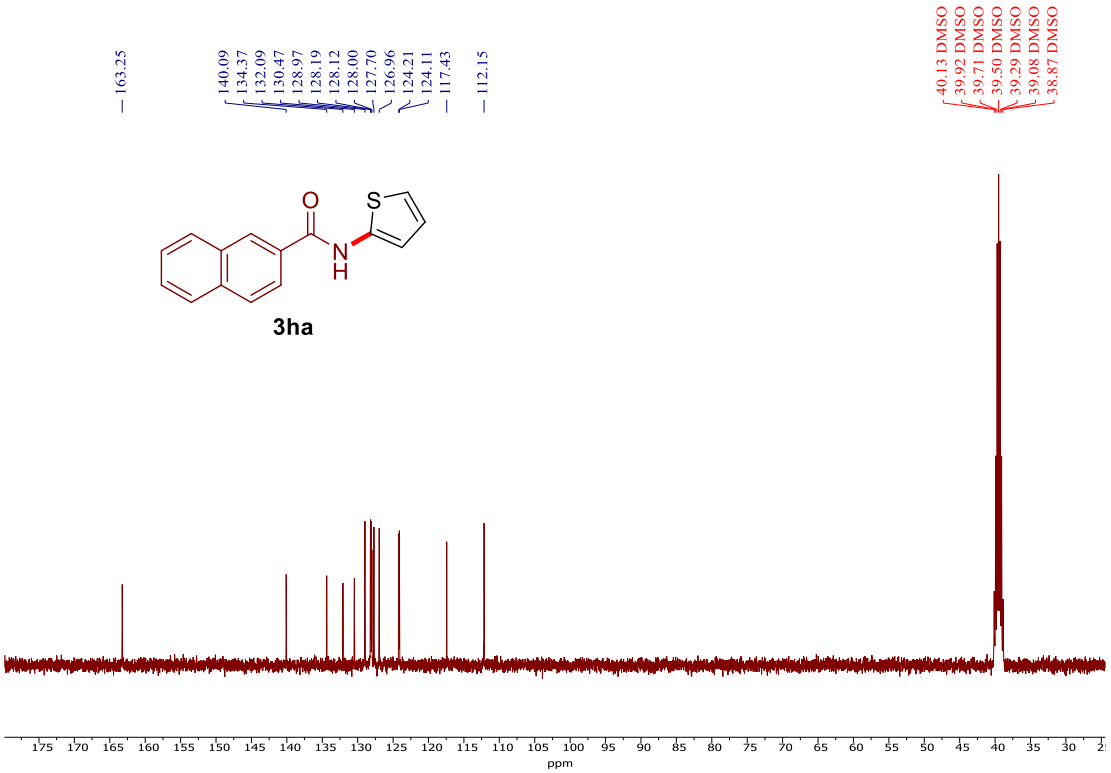
^{13}C NMR (101 MHz, $CDCl_3$) of **3ga**



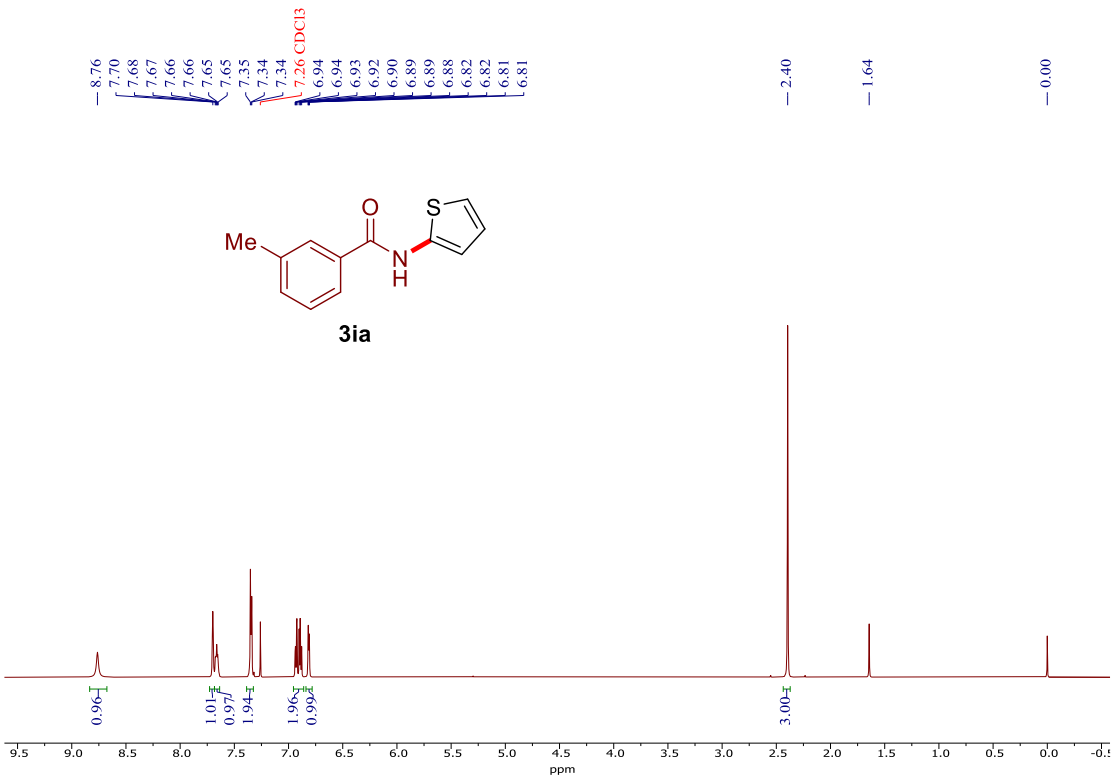
^{1}H NMR (400 MHz, d_6-DMSO) of **3ha** (*see procedure*)



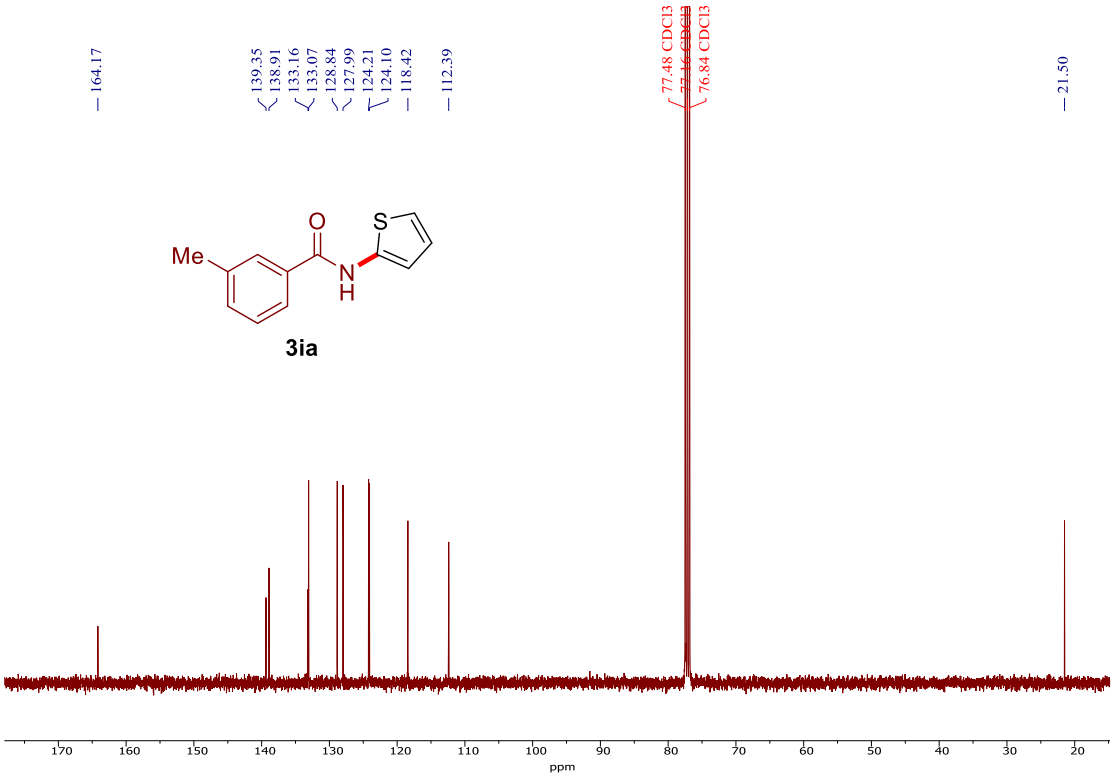
^{13}C NMR (101 MHz, d_6-DMSO) of **3ha**



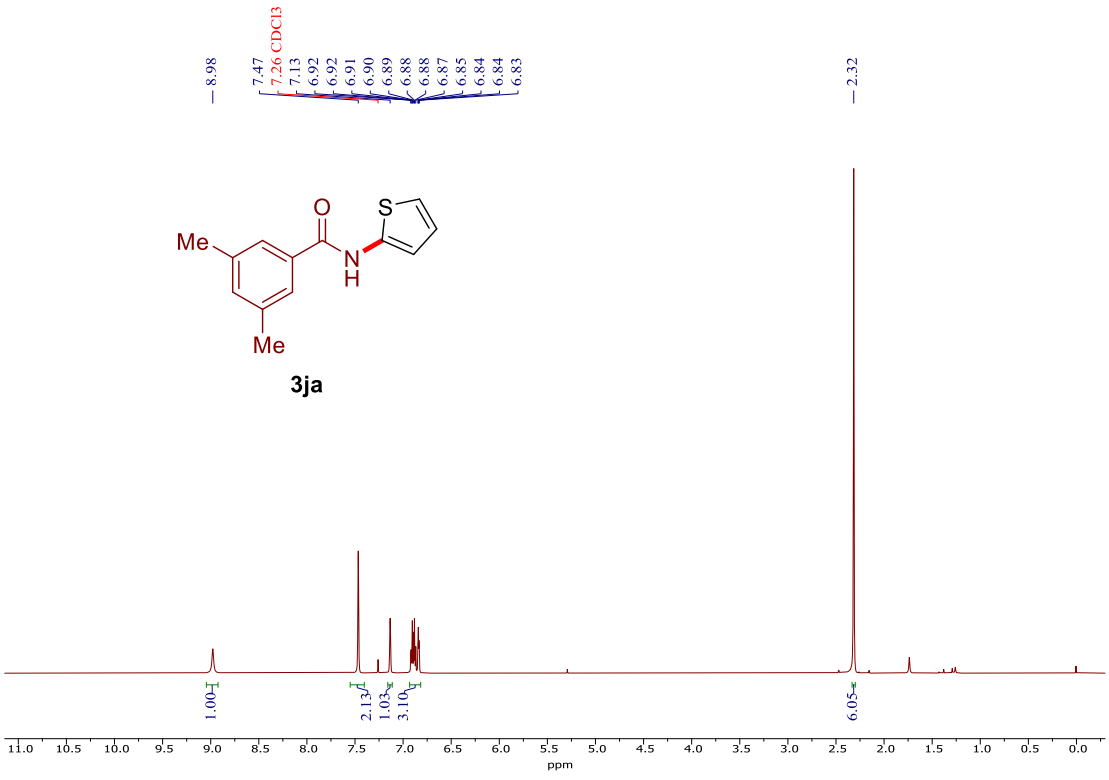
^{1}H NMR (400 MHz, $CDCl_3$) of **3ia** (*see procedure*)



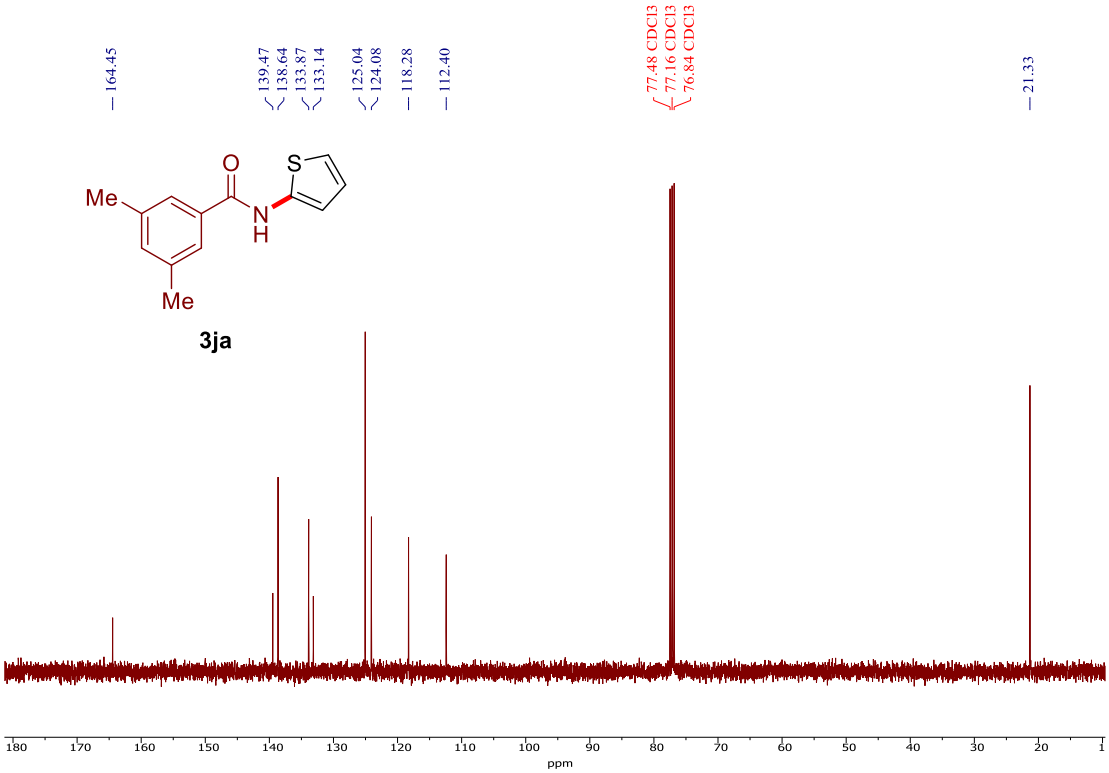
^{13}C NMR (101 MHz, $CDCl_3$) of **3ia**



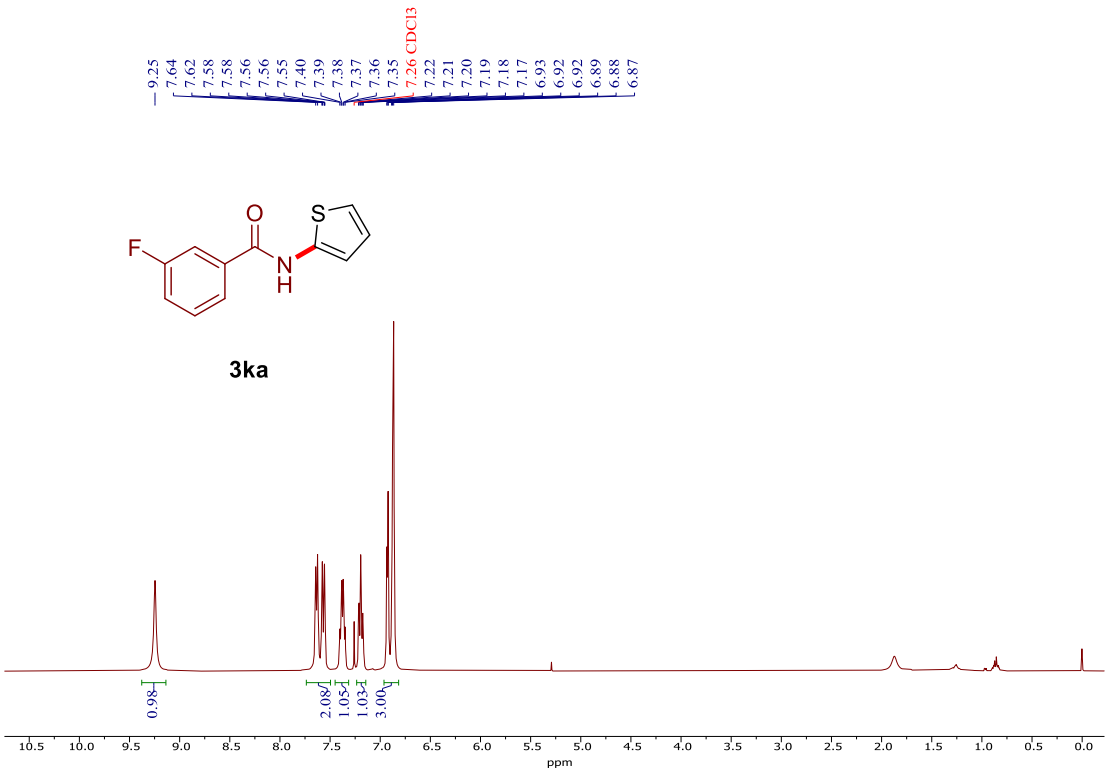
^{1}H NMR (400 MHz, $CDCl_3$) of **3ja** (*see procedure*)



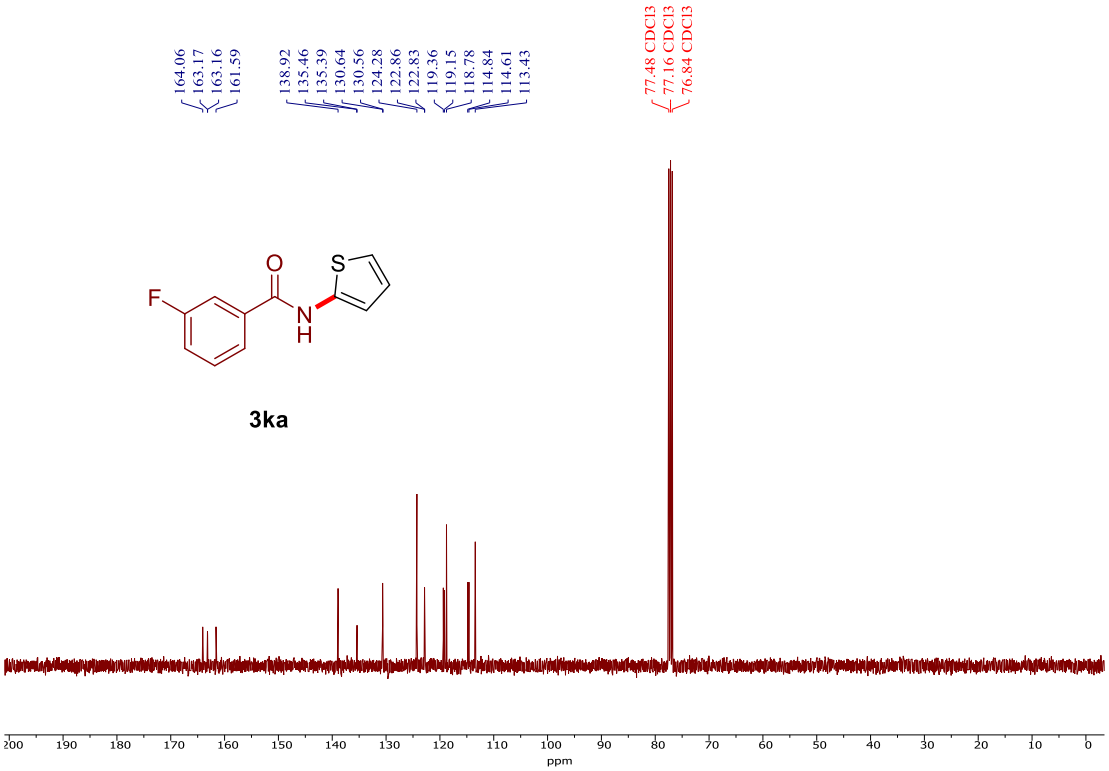
^{13}C NMR (101 MHz, $CDCl_3$) of **3ja**



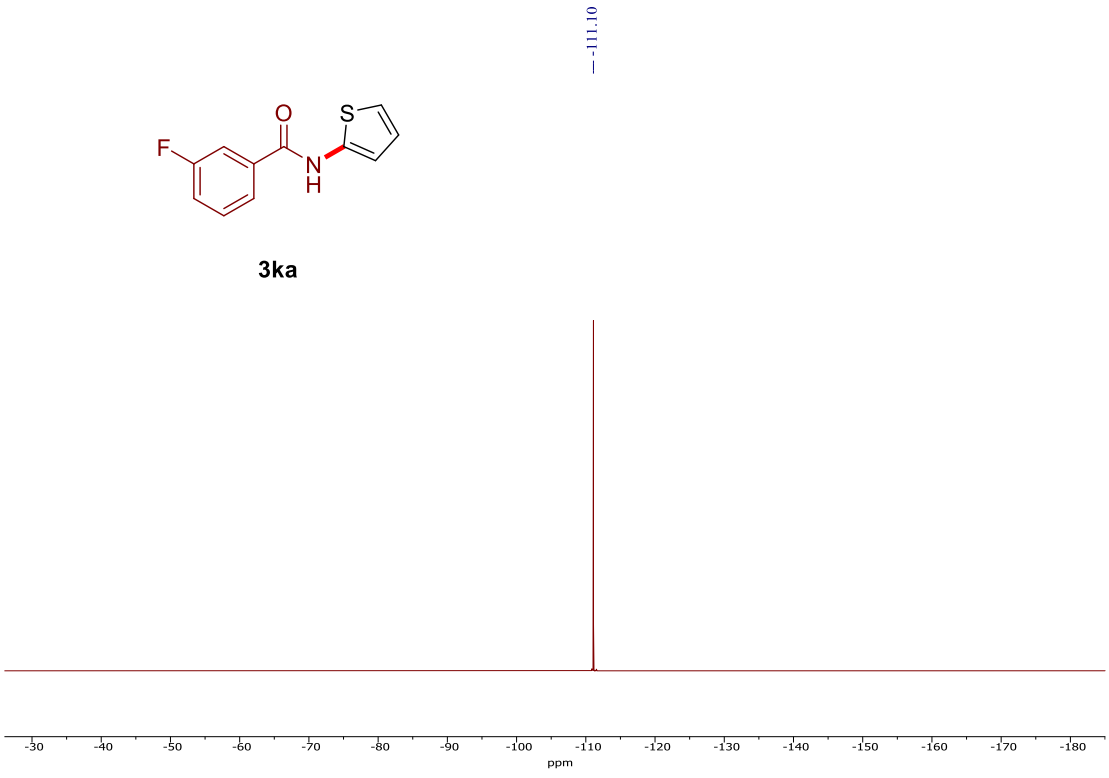
^{1}H NMR (400 MHz, $CDCl_3$) of **3ka** (*see procedure*)



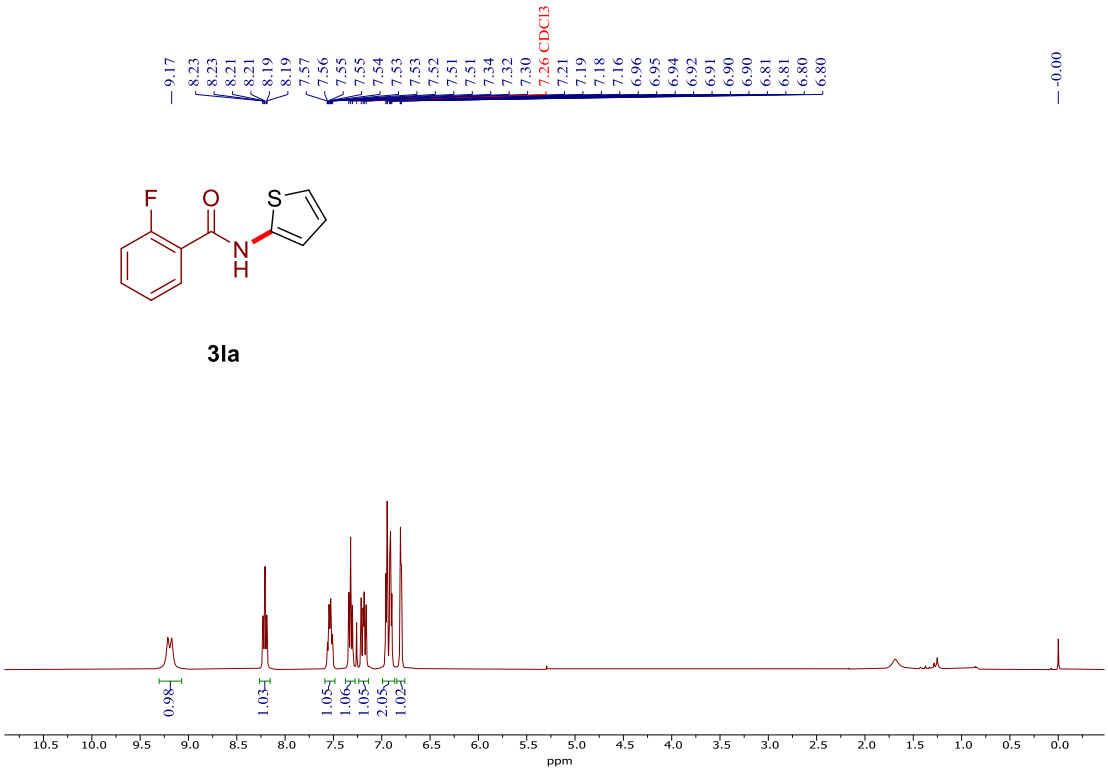
^{13}C NMR (101 MHz, $CDCl_3$) of **3ka**



^{19}F NMR (376 MHz, $CDCl_3$) of **3ka**

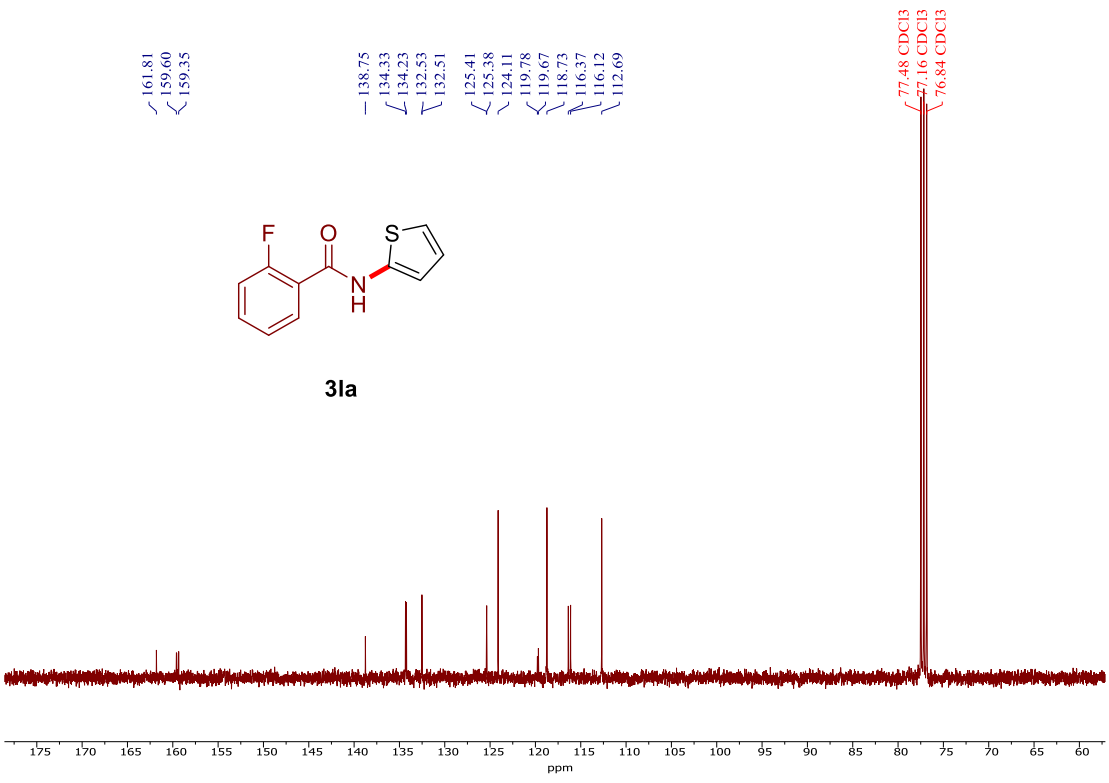


^{1}H NMR (400 MHz, $CDCl_3$) of **3la** (*see procedure*)



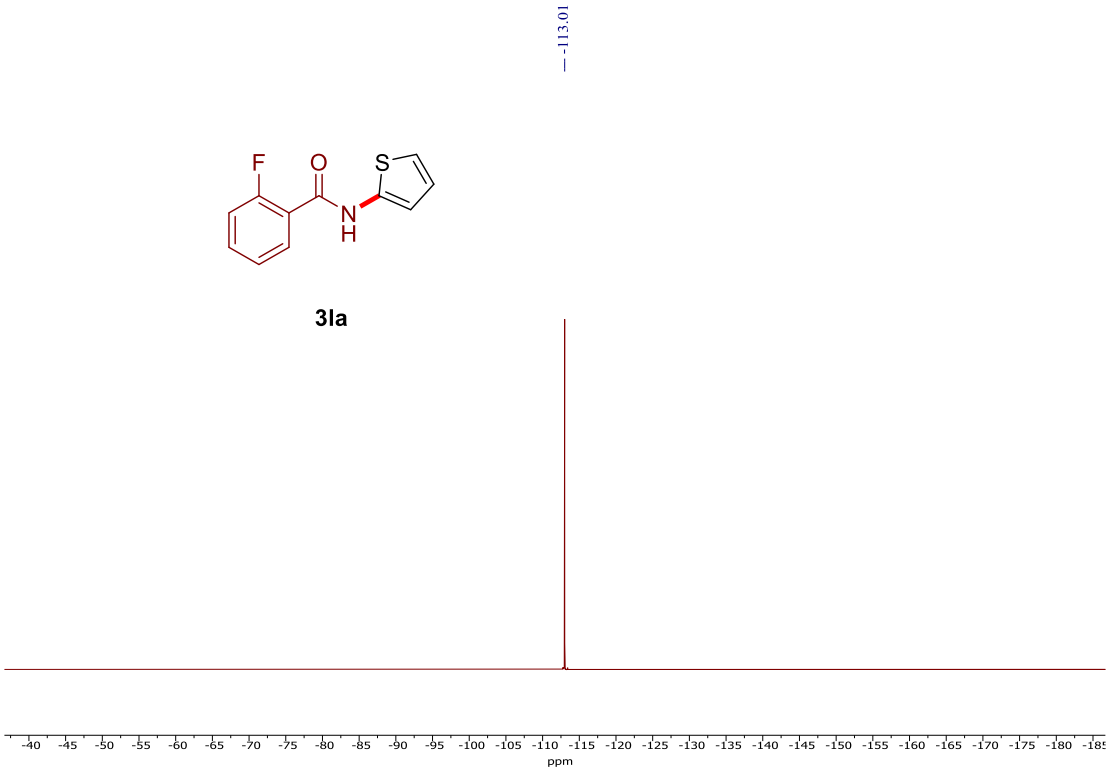
3la

^{13}C NMR (101 MHz, $CDCl_3$) of **3la**

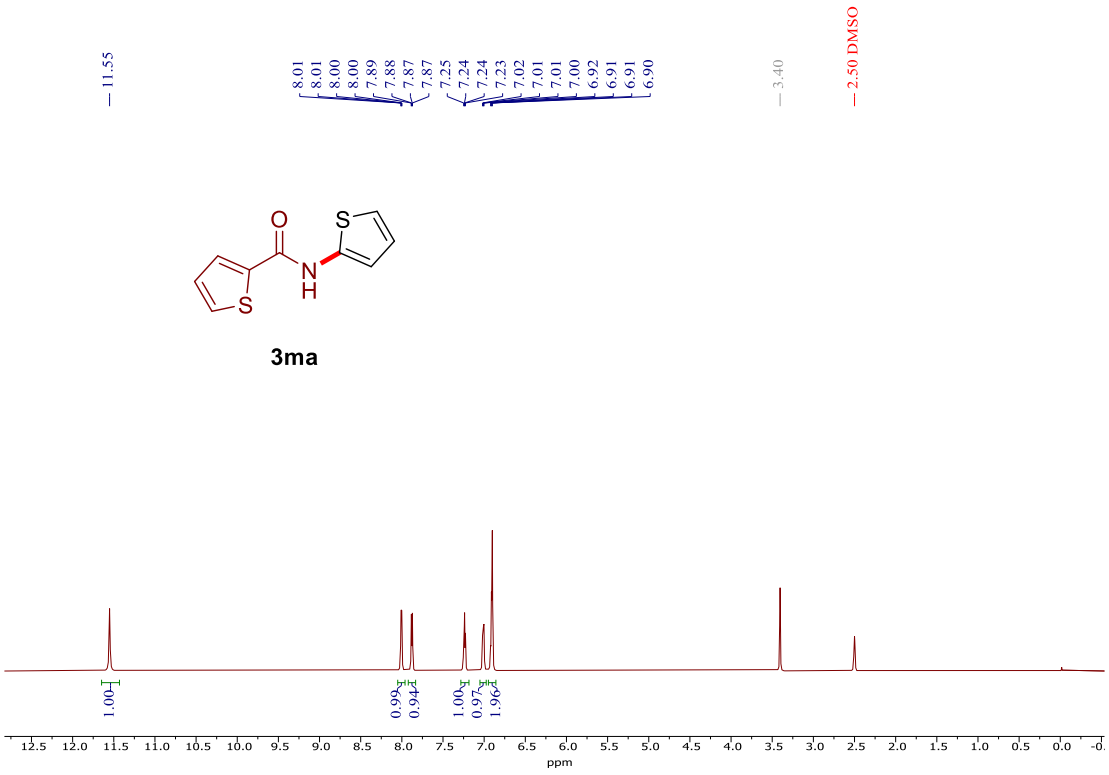


3la

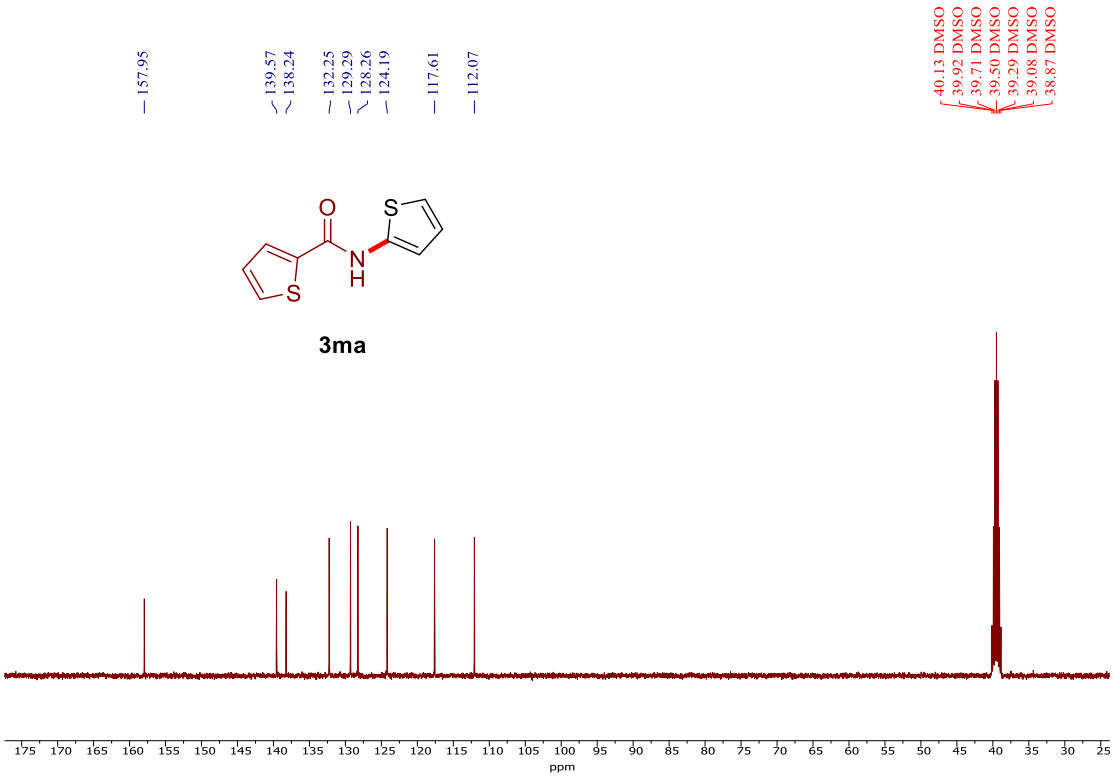
^{19}F NMR (376 MHz, $CDCl_3$) of **3la**



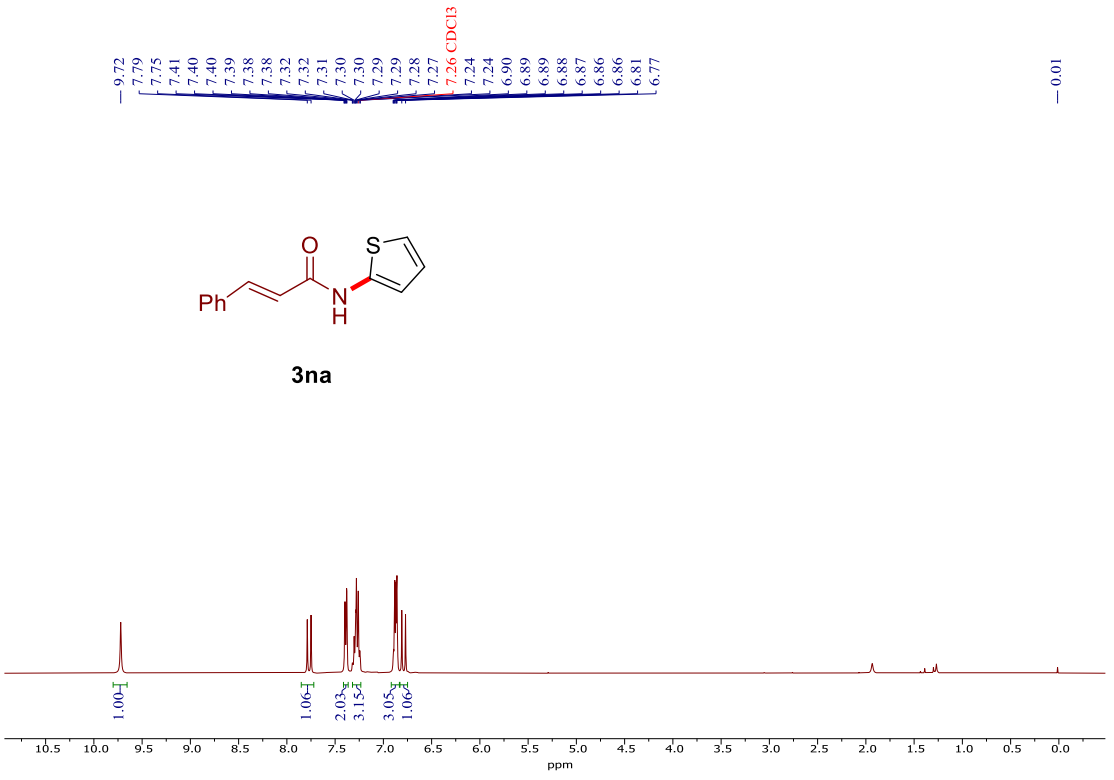
^{1}H NMR (400 MHz, d_6-DMSO) of **3ma** (*see procedure*)



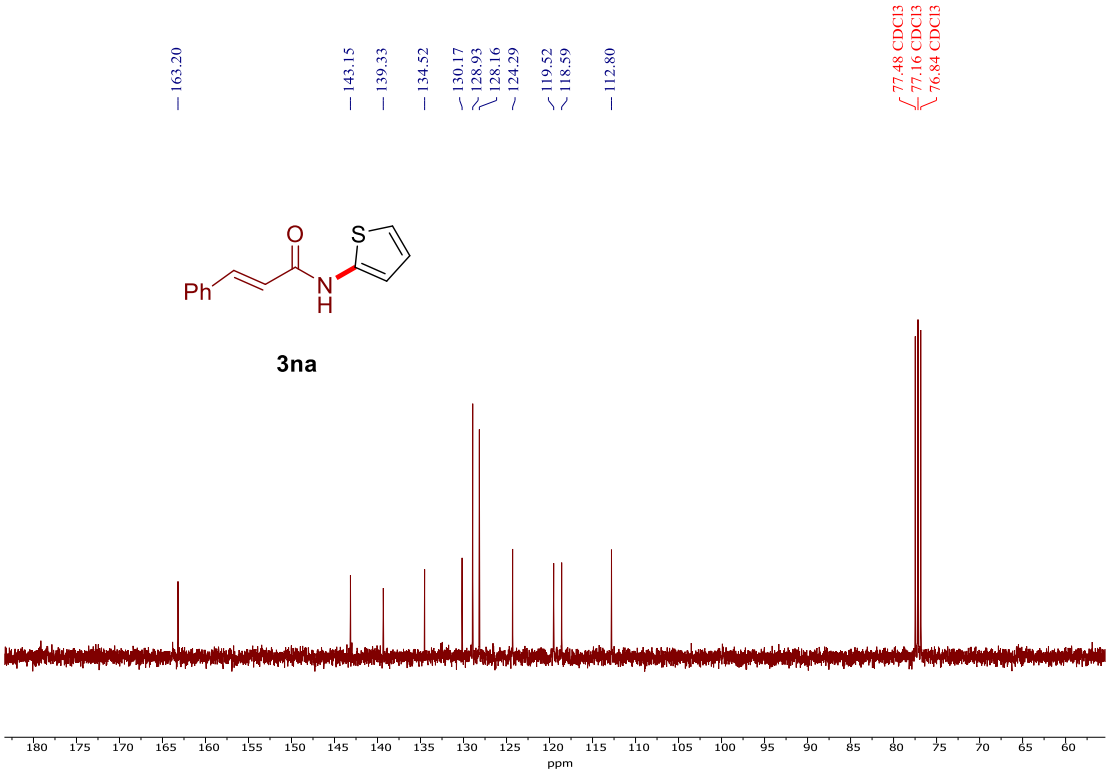
^{13}C NMR (101 MHz, d_6-DMSO) of **3ma**



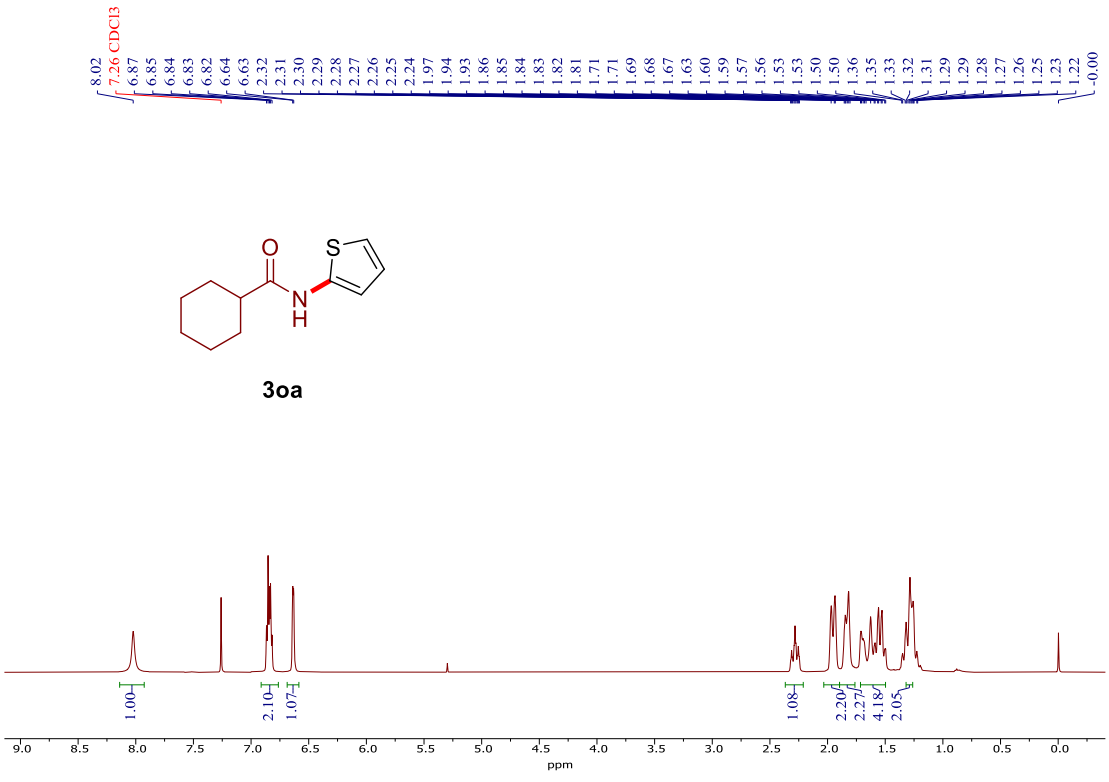
^{1}H NMR (400 MHz, $CDCl_3$) of **3na** (*see procedure*)



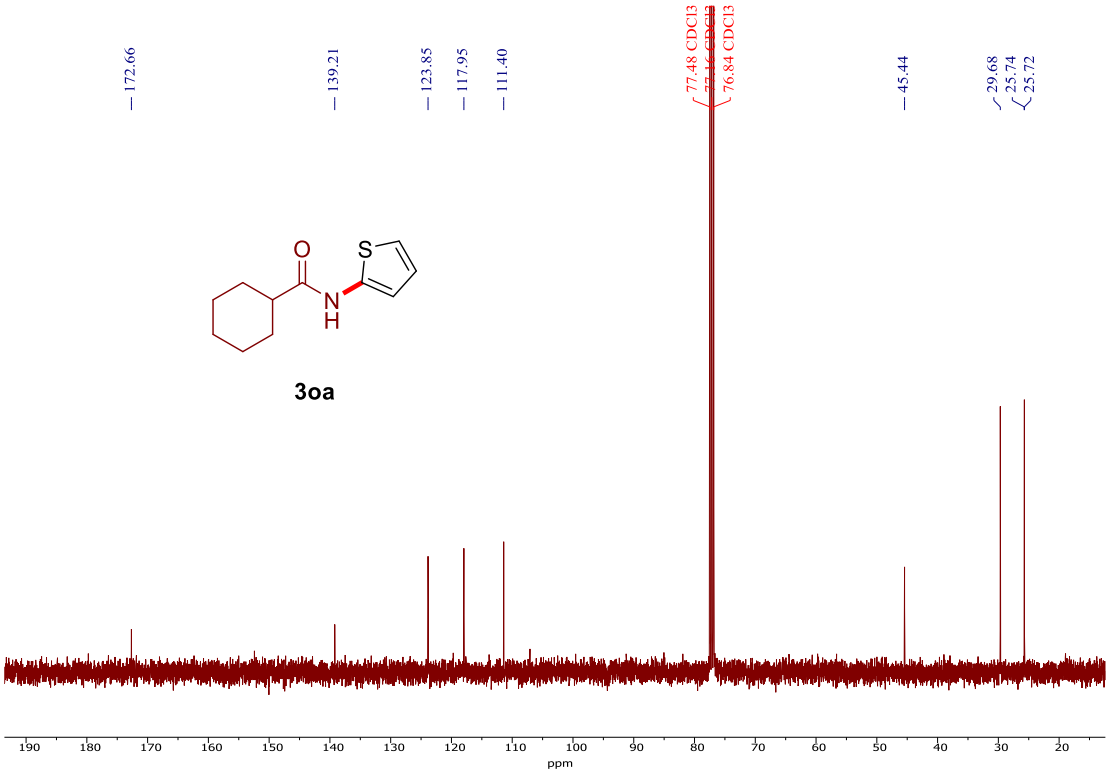
^{13}C NMR (101 MHz, $CDCl_3$) of **3na**



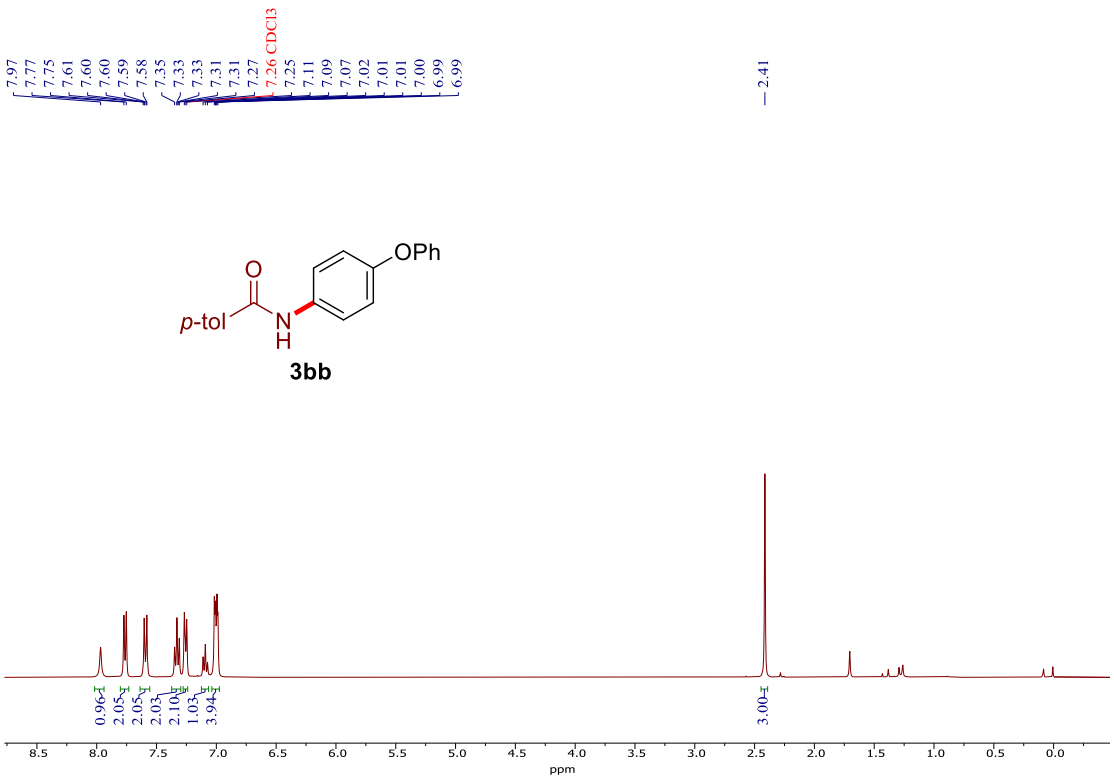
^{1}H NMR (400 MHz, $CDCl_3$) of **3oa** (*see procedure*)



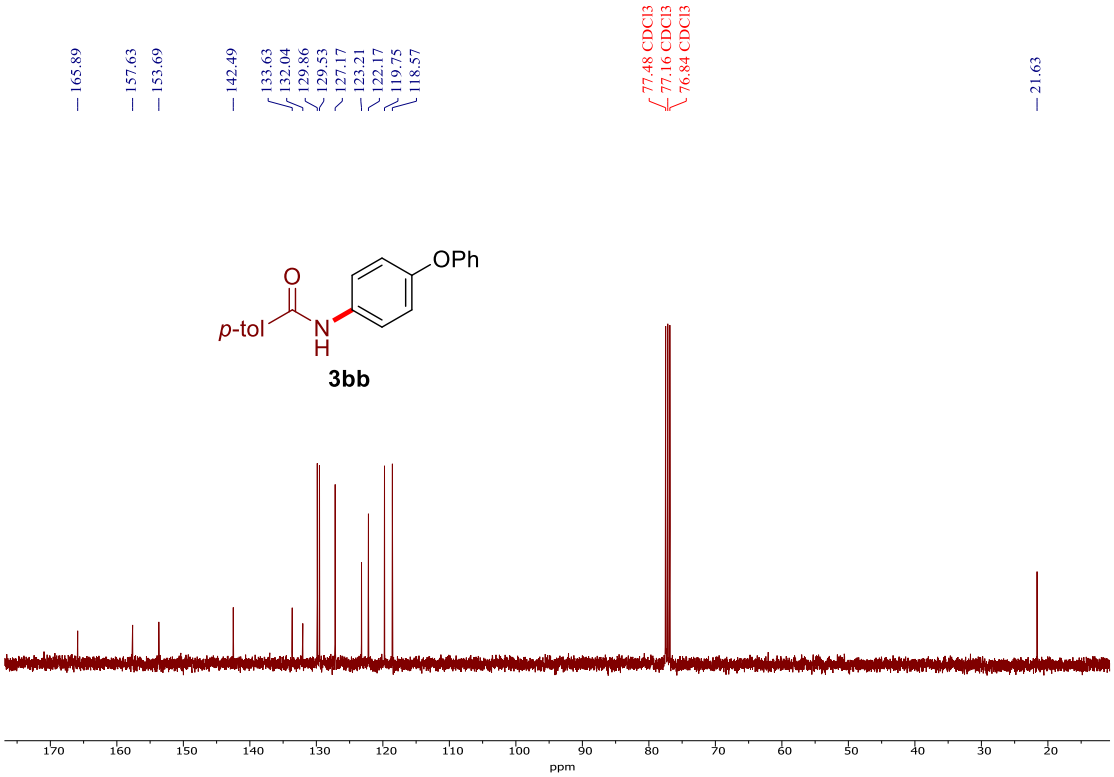
^{13}C NMR (101 MHz, $CDCl_3$) of **3oa**



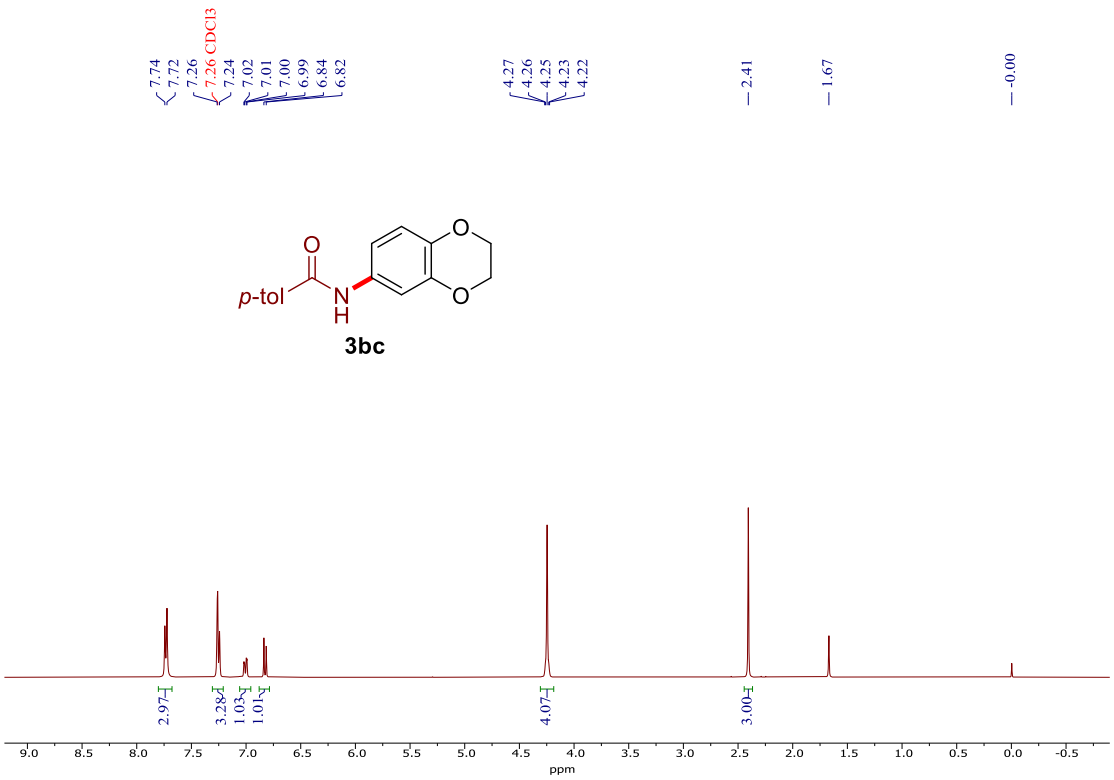
^{1}H NMR (400 MHz, $CDCl_3$) of **3bb** (*see procedure*)



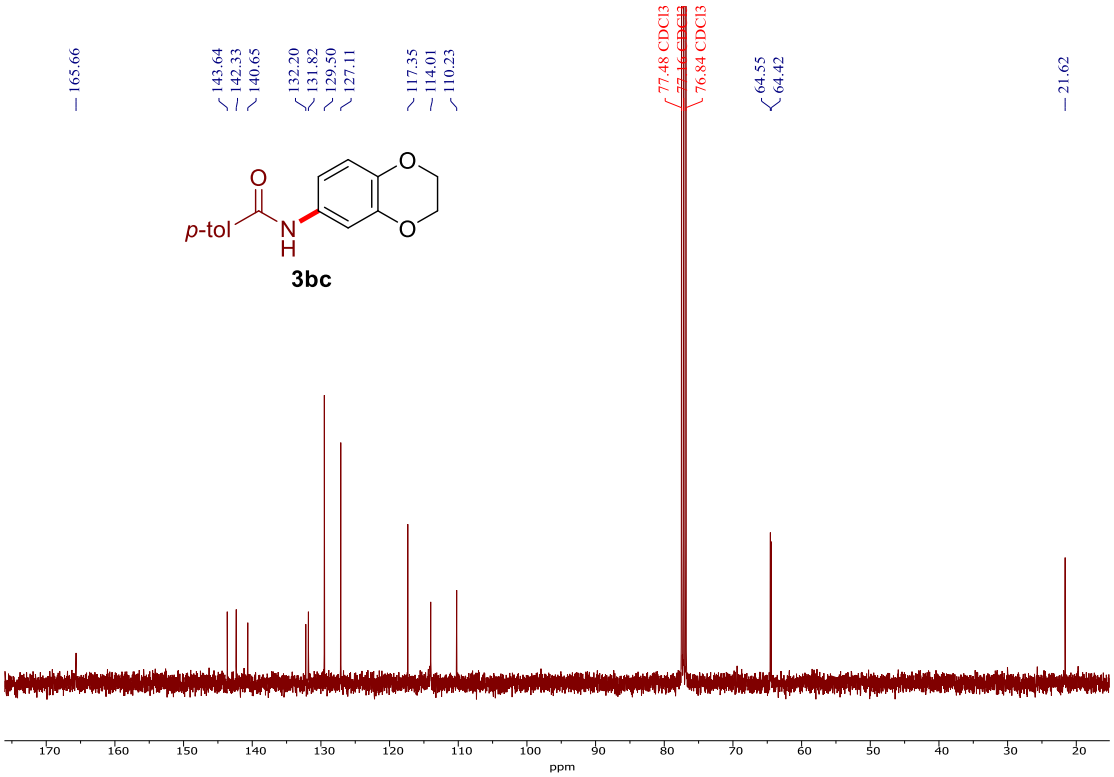
^{13}C NMR (101 MHz, $CDCl_3$) of **3bb**



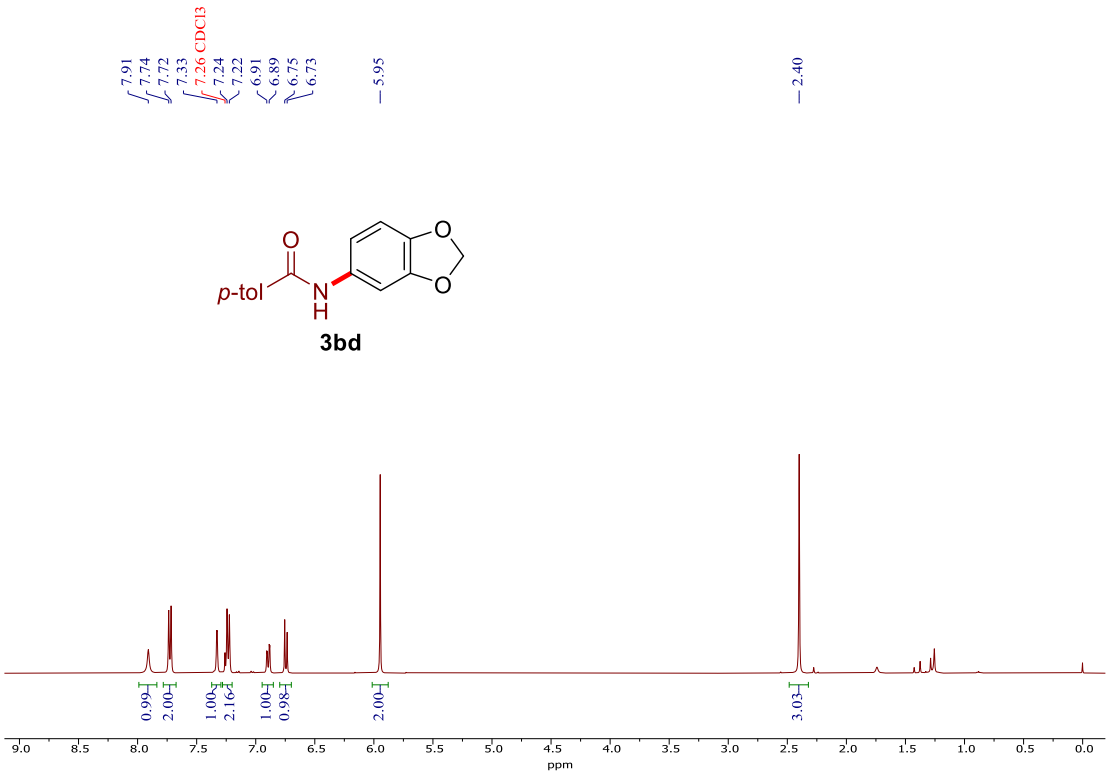
^{1}H NMR (400 MHz, $CDCl_3$) of **3bc** (*see procedure*)



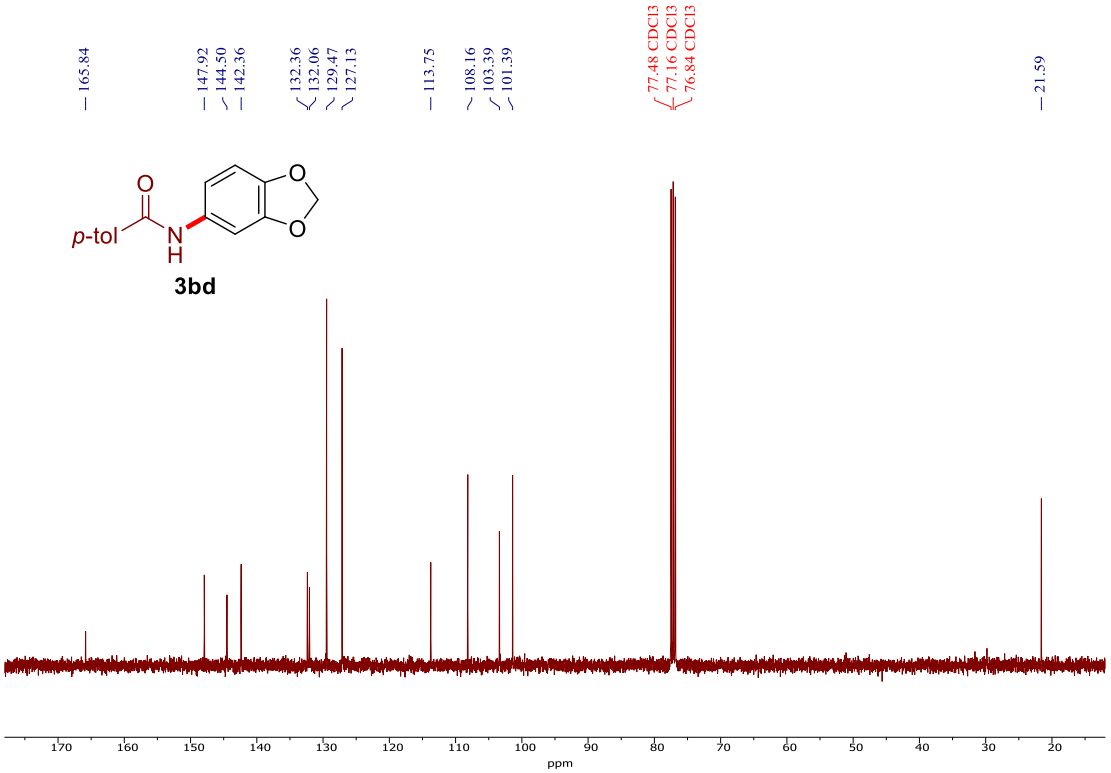
^{13}C NMR (101 MHz, $CDCl_3$) of **3bc**



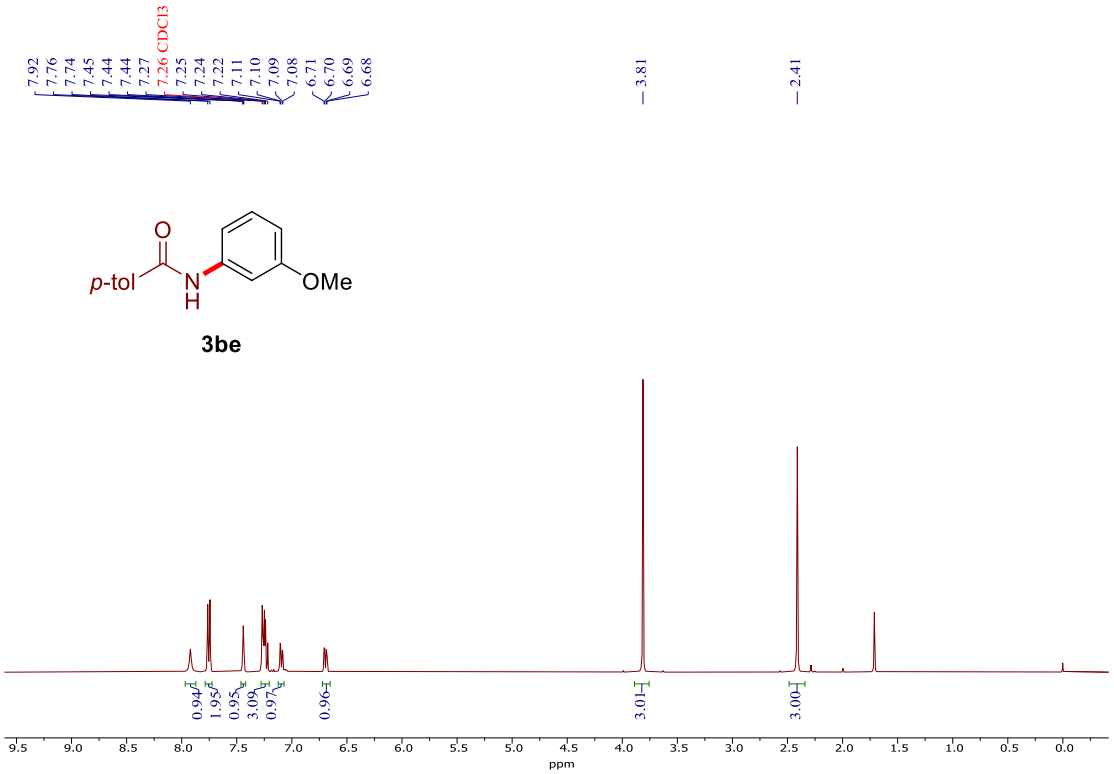
^{1}H NMR (400 MHz, $CDCl_3$) of **3bd** (*see procedure*)



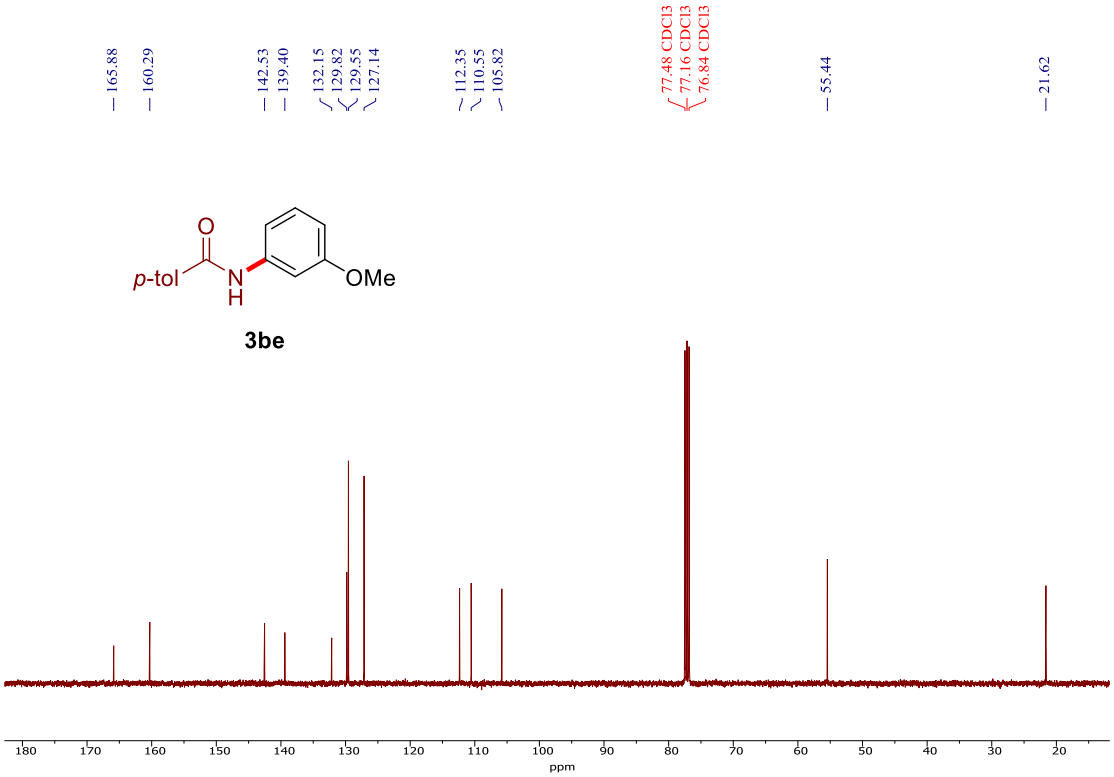
^{13}C NMR (101 MHz, $CDCl_3$) of **3bd**



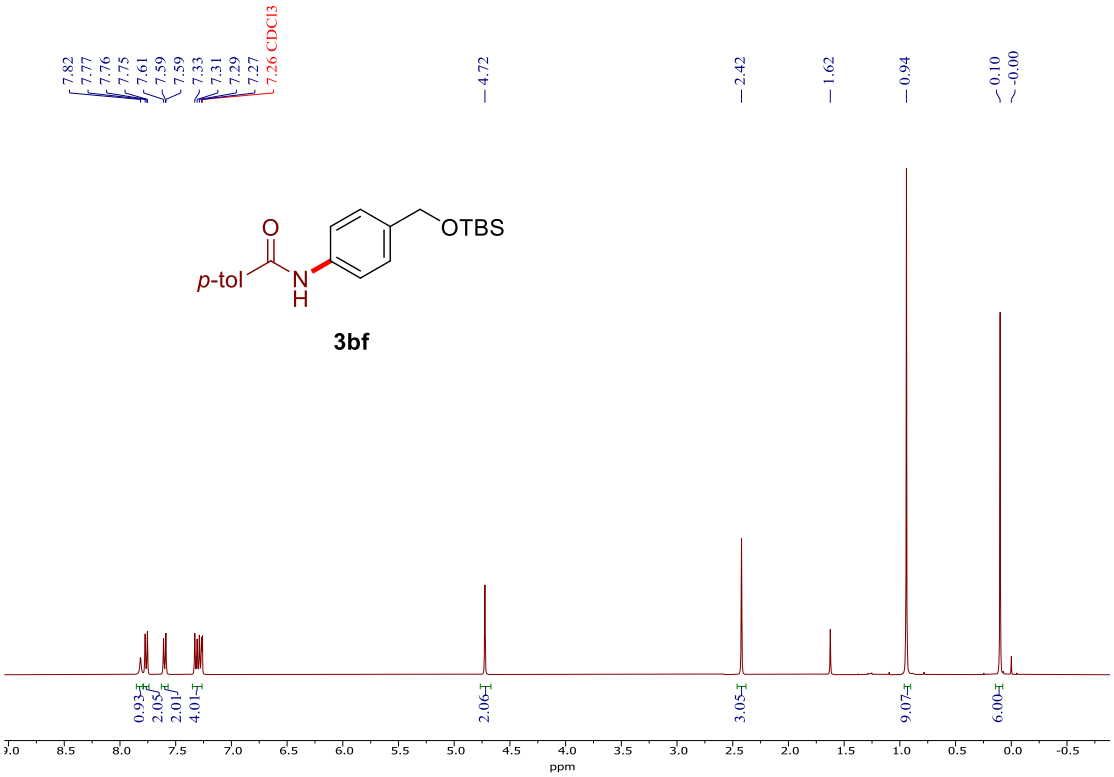
^{1}H NMR (400 MHz, $CDCl_3$) of **3be** (*see procedure*)



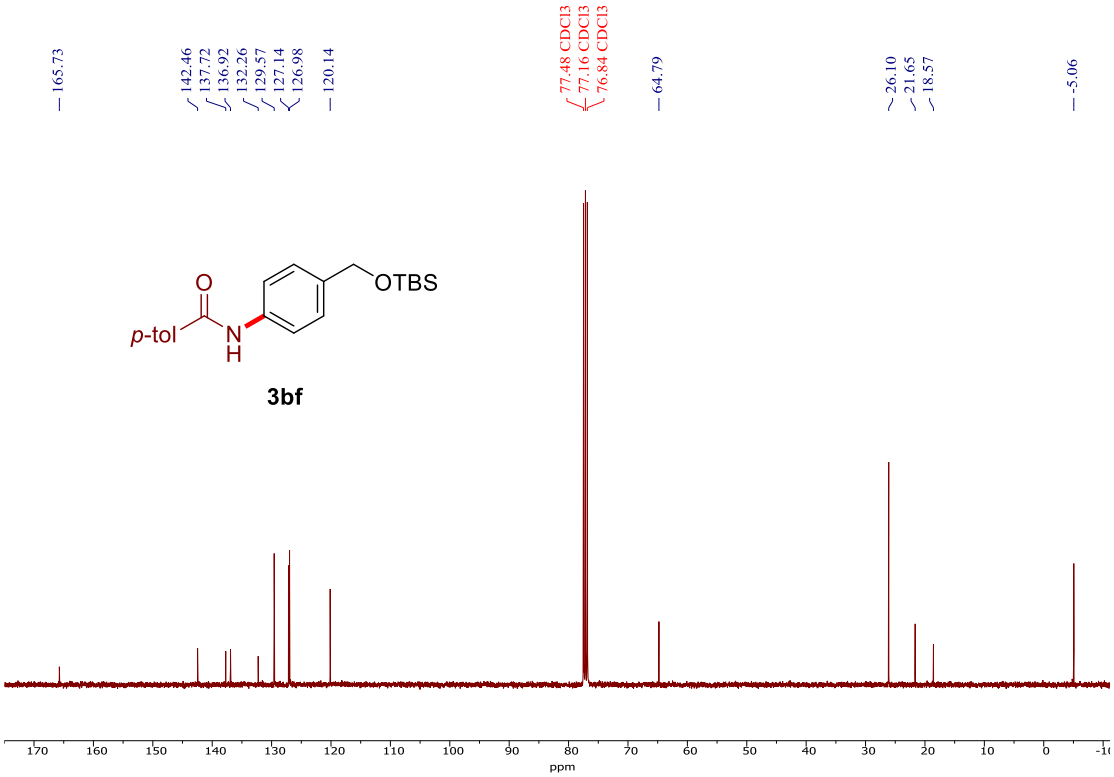
^{13}C NMR (101 MHz, $CDCl_3$) of **3be**



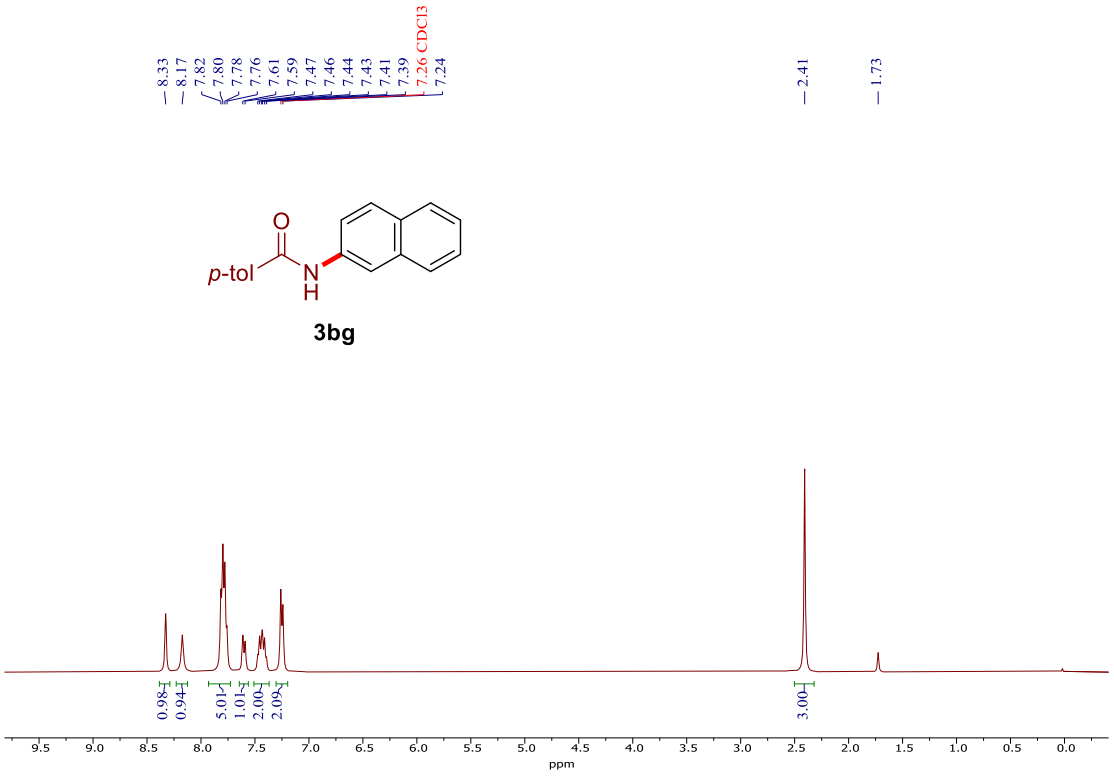
^{1}H NMR (400 MHz, $CDCl_3$) of **3bf** (*see procedure*)



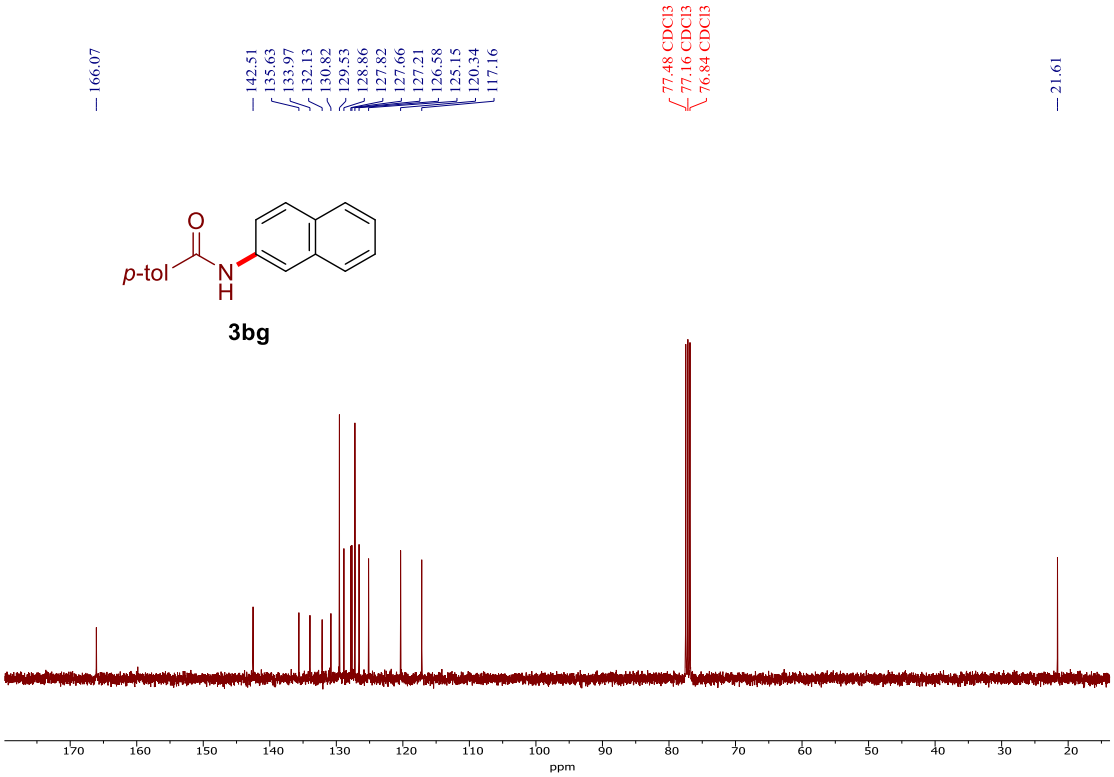
^{13}C NMR (101 MHz, $CDCl_3$) of **3bf**



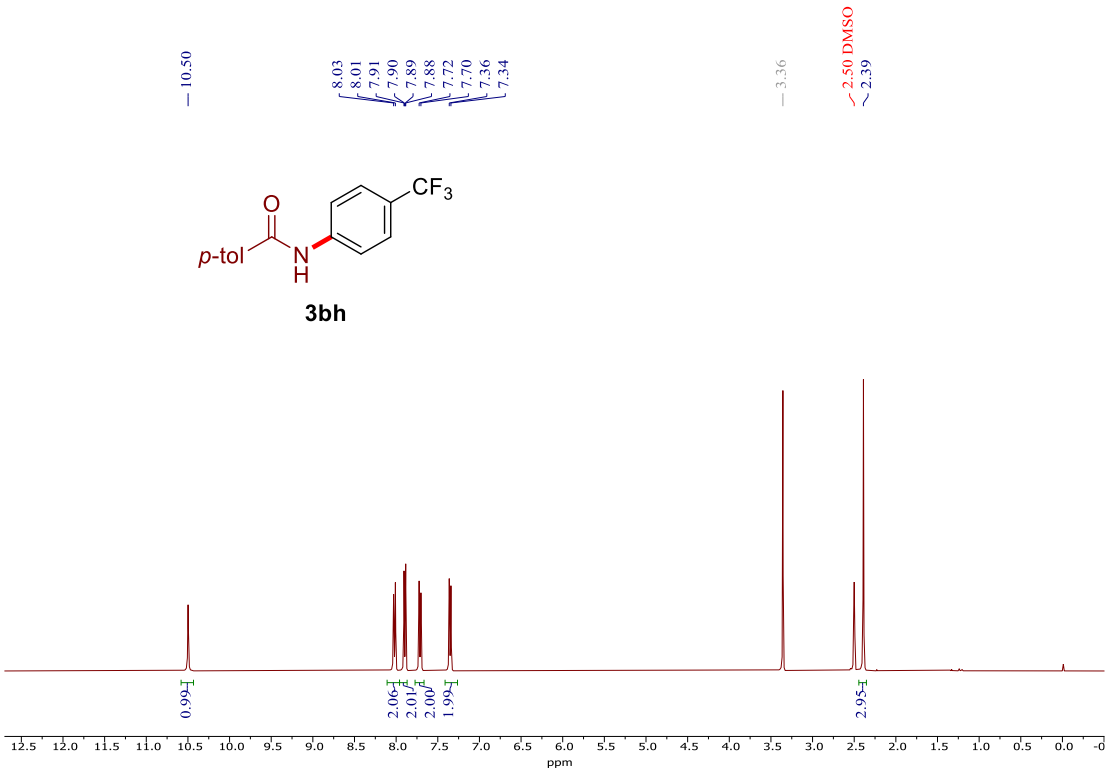
^{1}H NMR (400 MHz, $CDCl_3$) of **3bg** (*see procedure*)



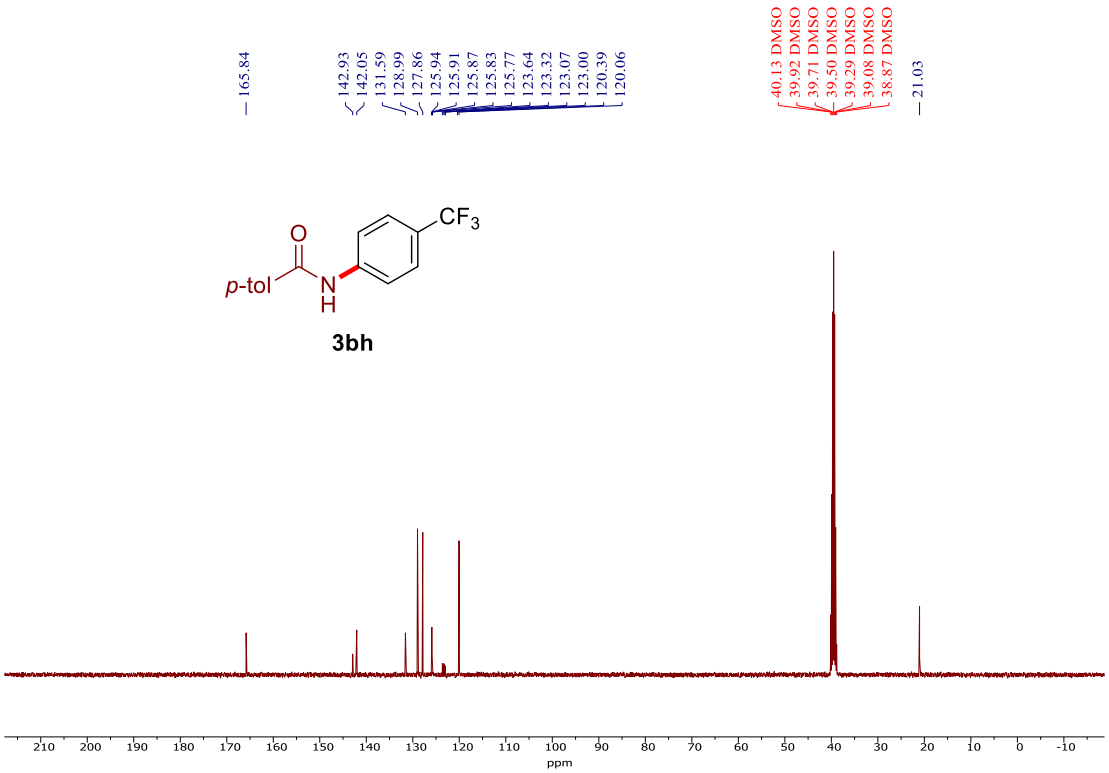
^{13}C NMR (101 MHz, $CDCl_3$) of **3bg**



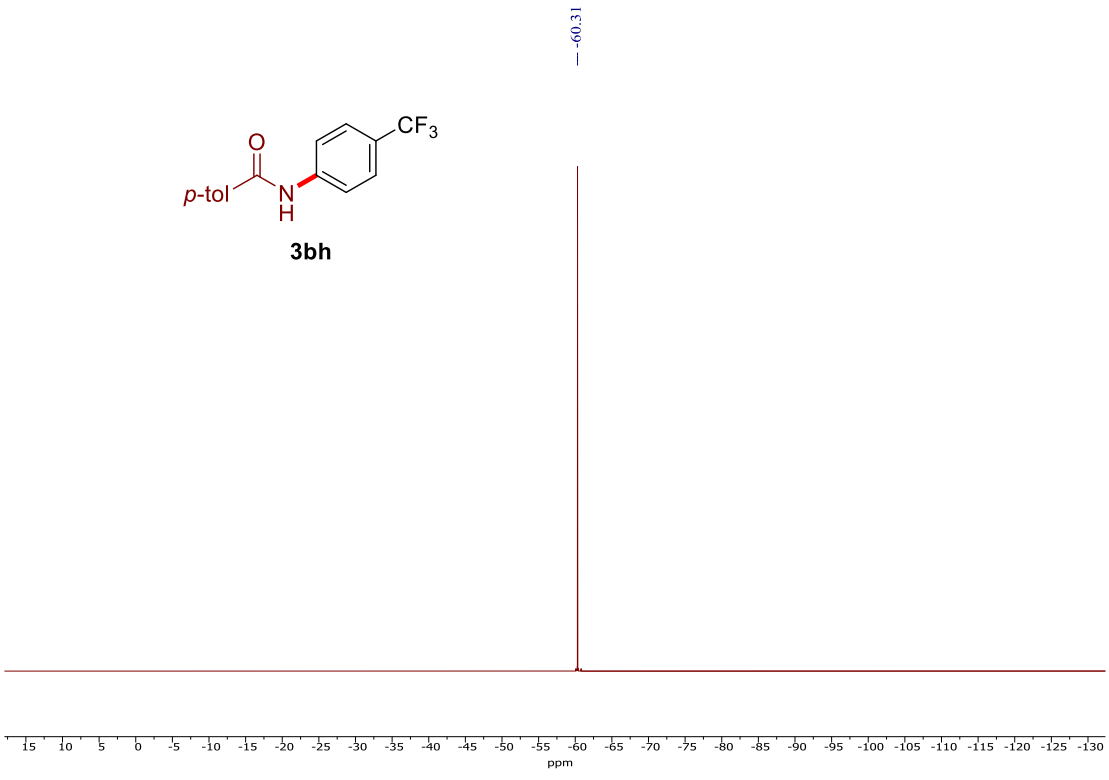
^{1}H NMR (400 MHz, d_6-DMSO) of **3bh** (*see procedure*)



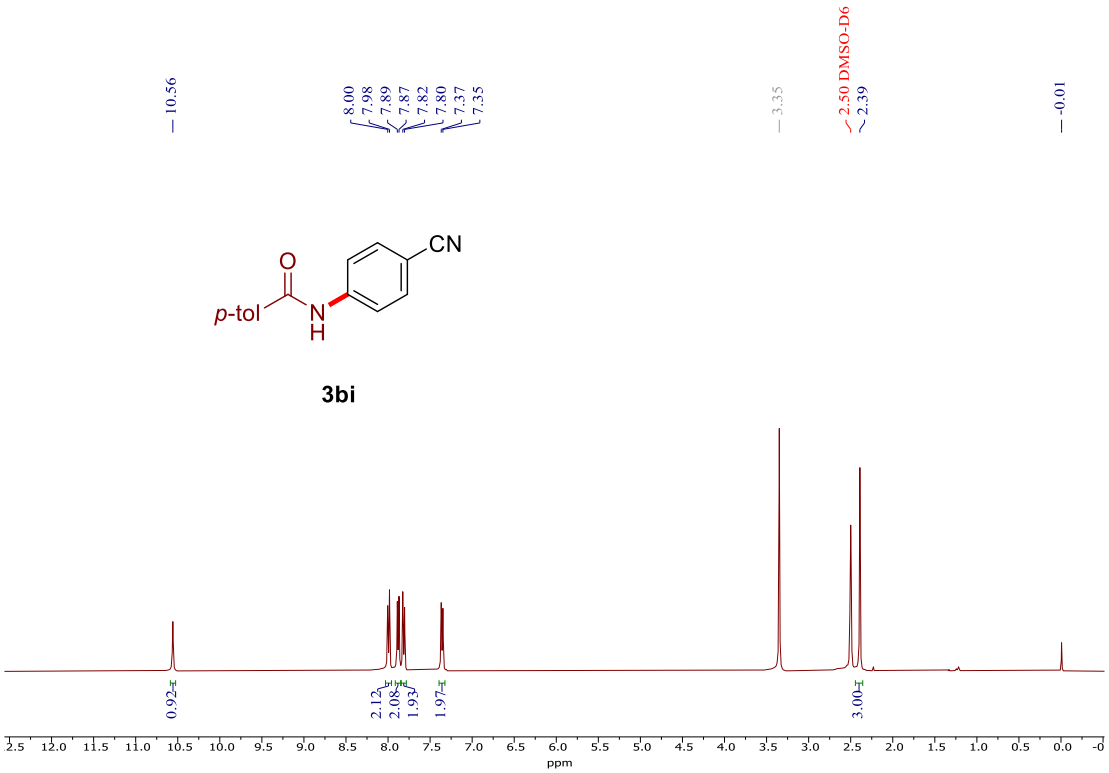
^{13}C NMR (101 MHz, d_6-DMSO) of **3bh**



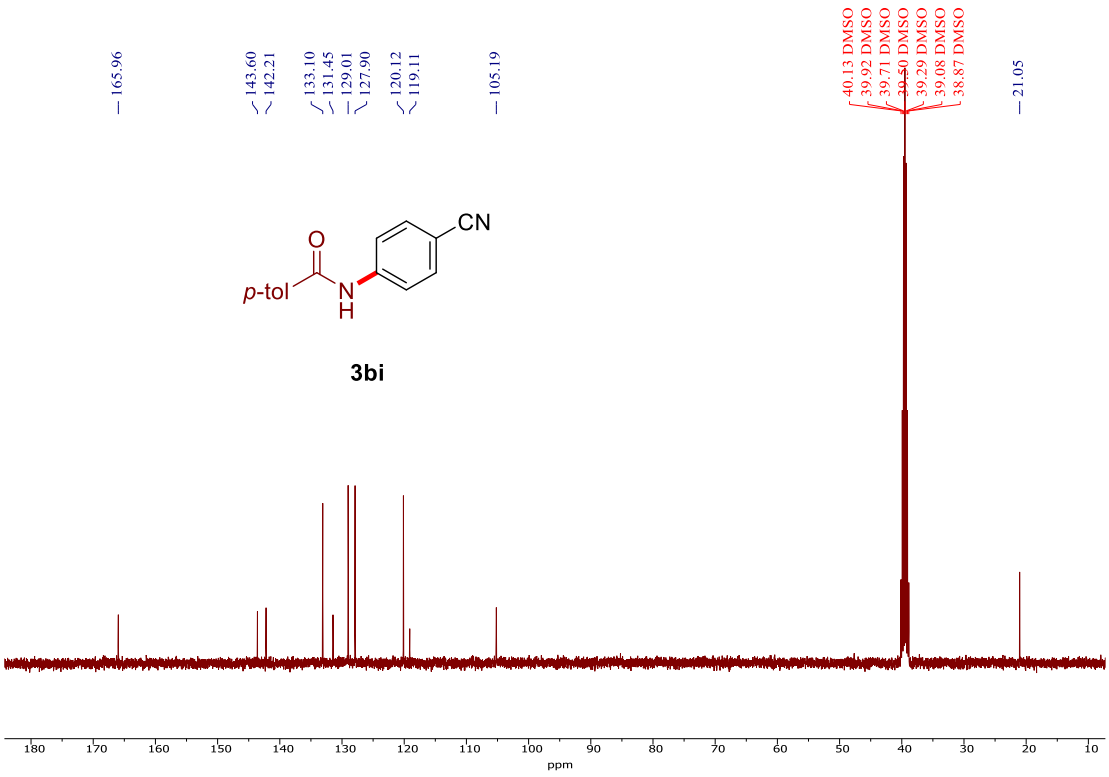
^{19}F NMR (376 MHz, d_6-DMSO) of **3bh**



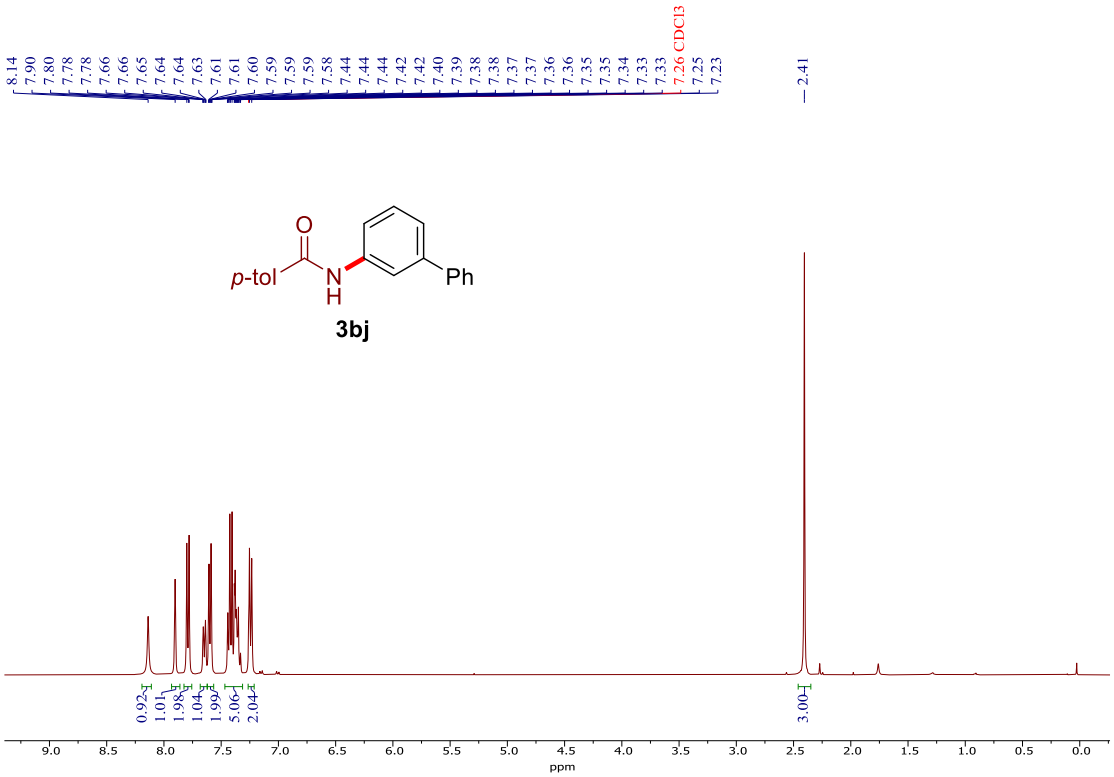
^{1}H NMR (400 MHz, d_6-DMSO) of **3bi** (*see procedure*)



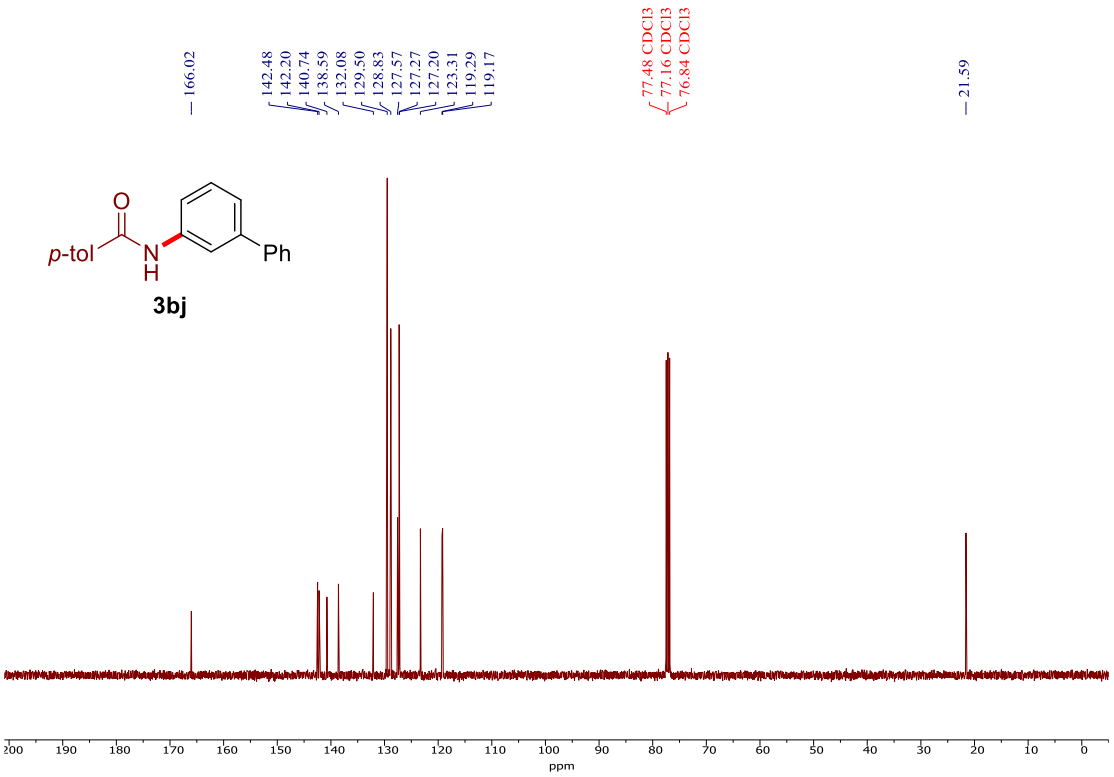
^{13}C NMR (101 MHz, d_6-DMSO) of **3bi**



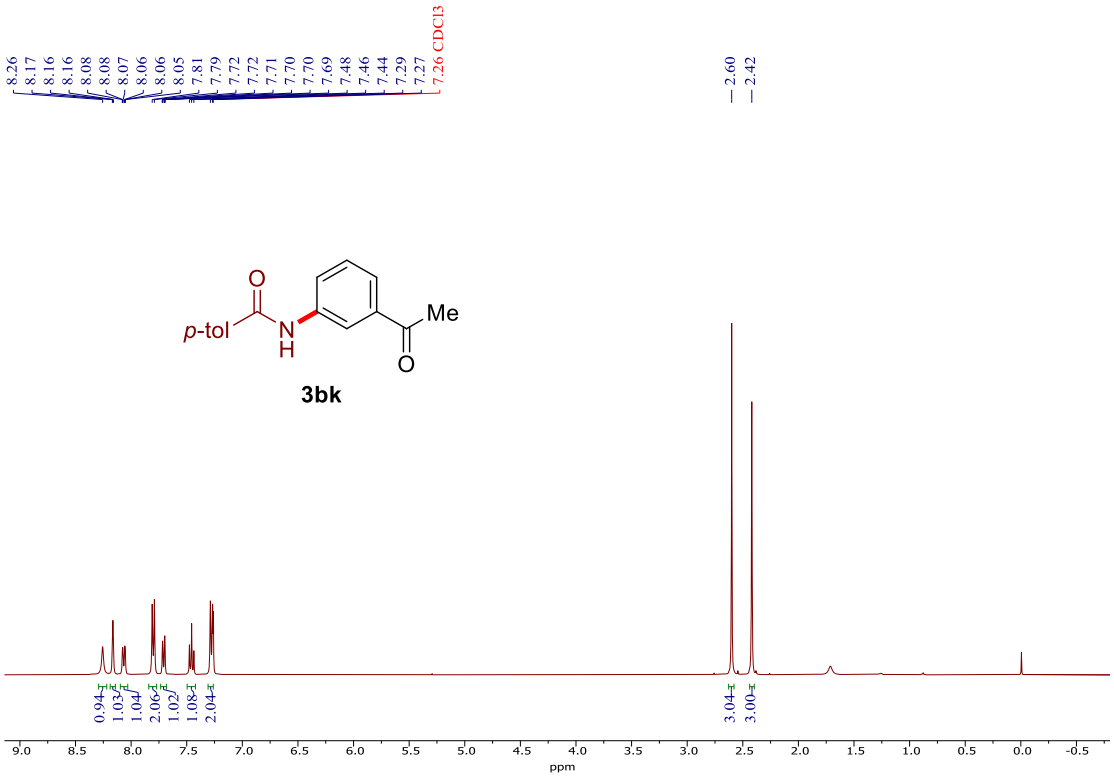
^{1}H NMR (400 MHz, $CDCl_3$) of **3bj** (*see procedure*)



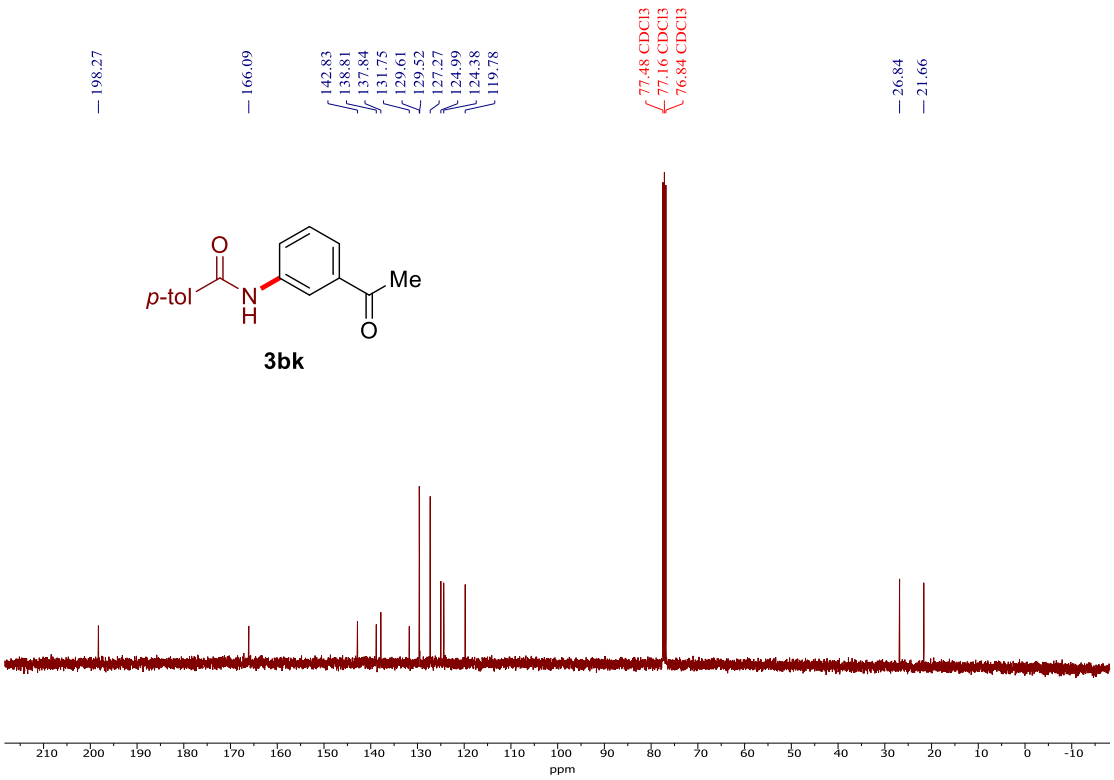
^{13}C NMR (101 MHz, $CDCl_3$) of **3bj**



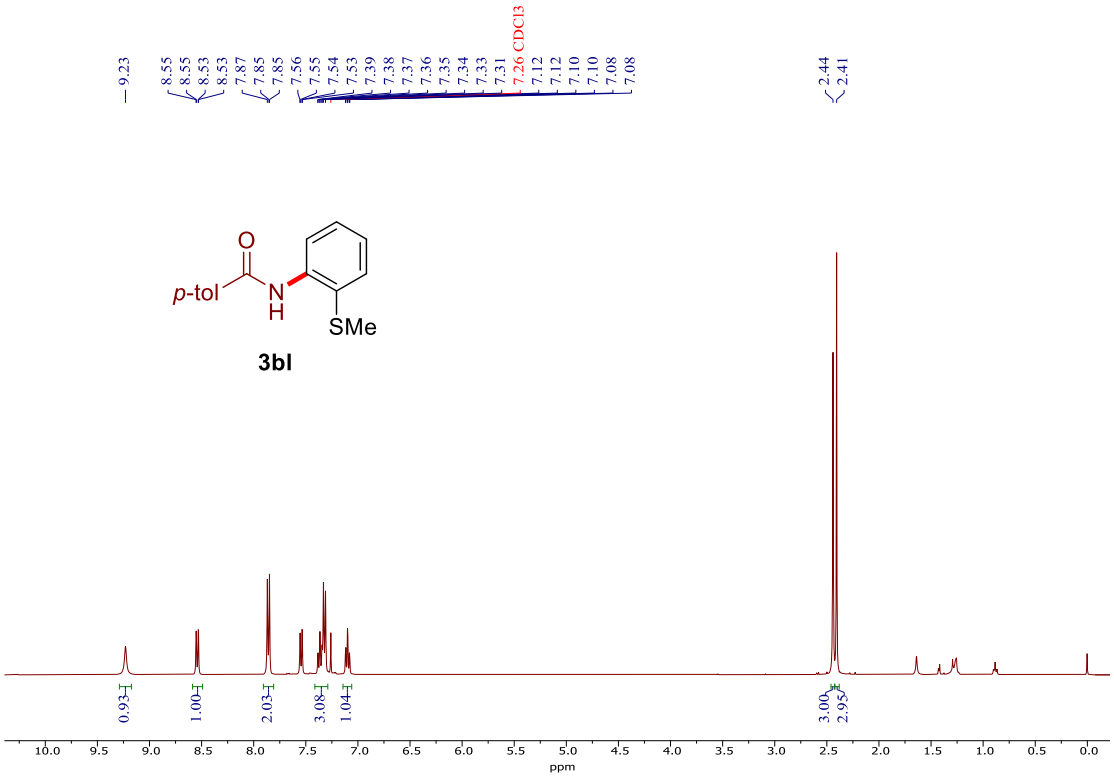
^{1}H NMR (400 MHz, $CDCl_3$) of **3bk** (*see procedure*)



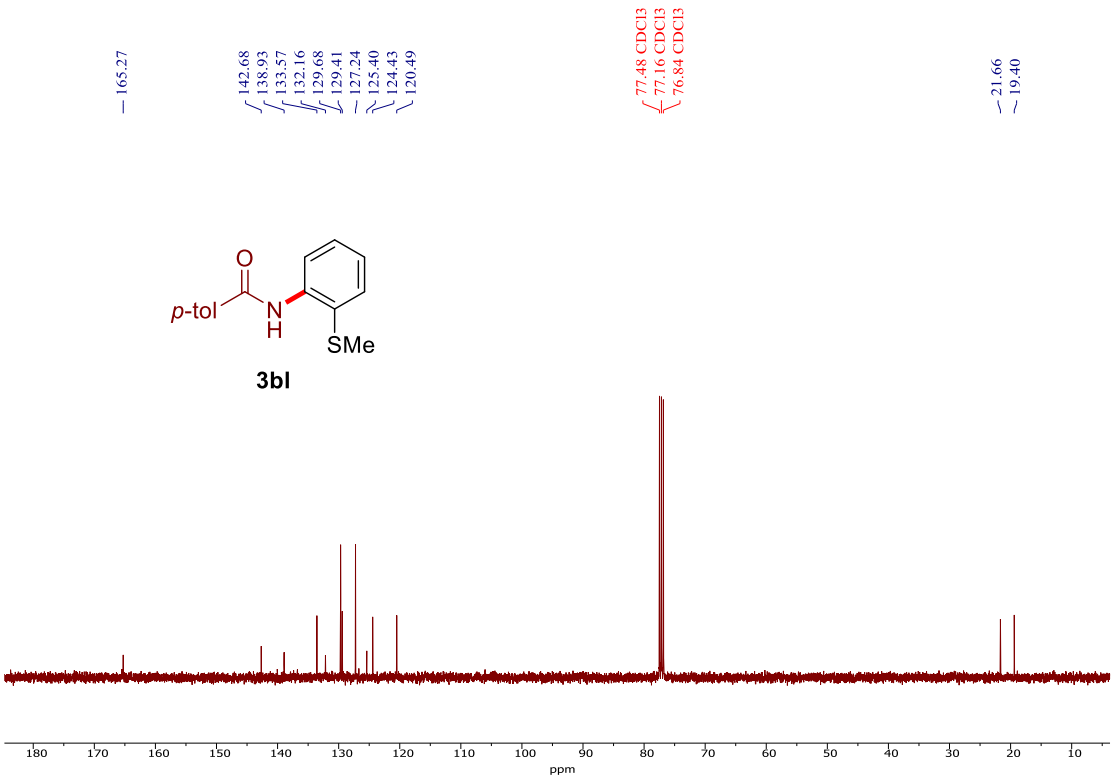
^{13}C NMR (101 MHz, $CDCl_3$) of **3bk**



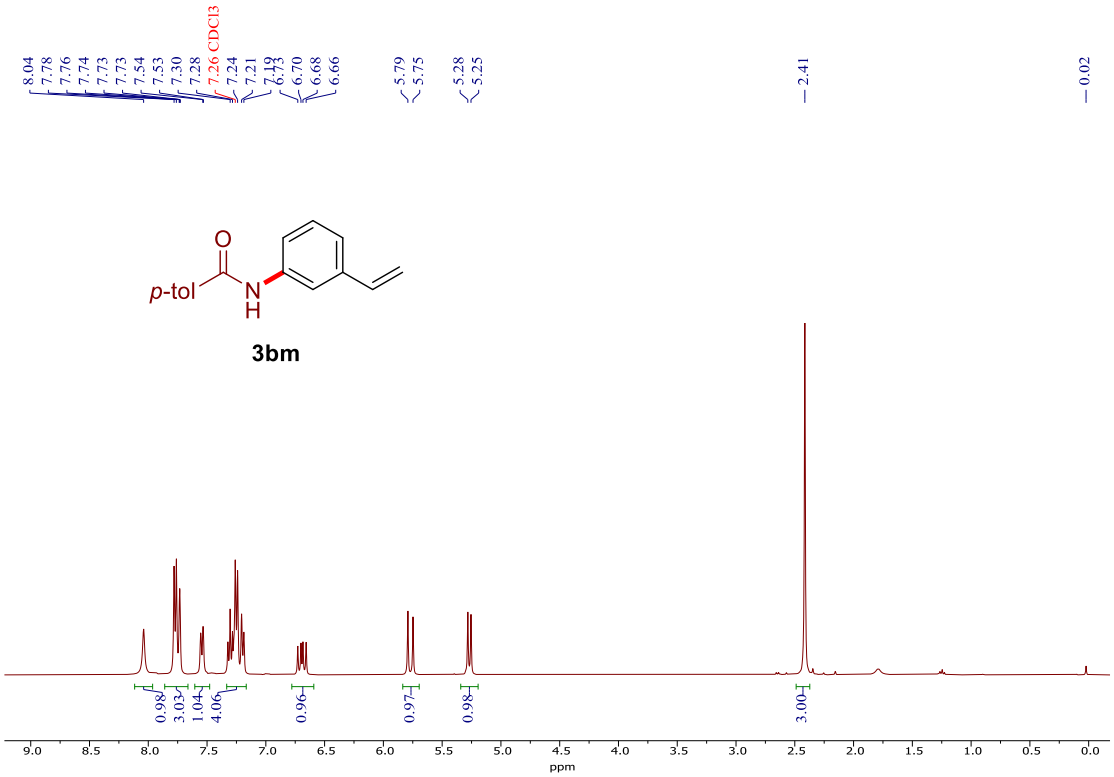
^{1}H NMR (400 MHz, $CDCl_3$) of **3bl** (*see procedure*)



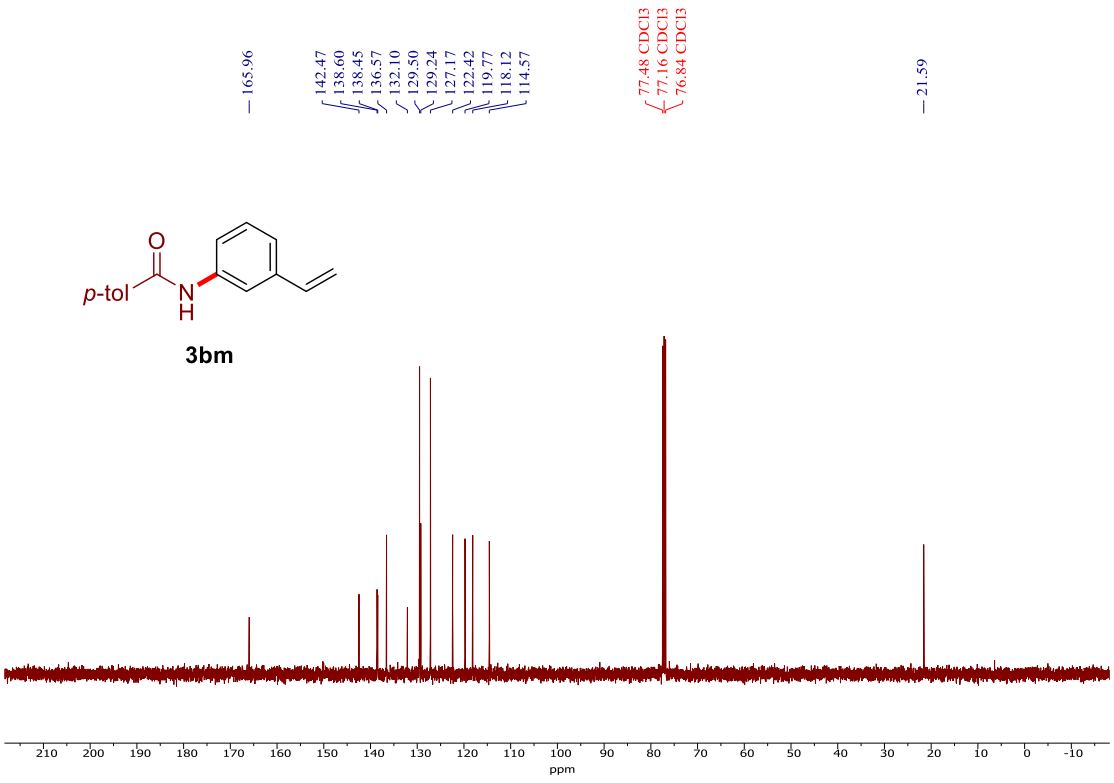
^{13}C NMR (101 MHz, $CDCl_3$) of **3bl**



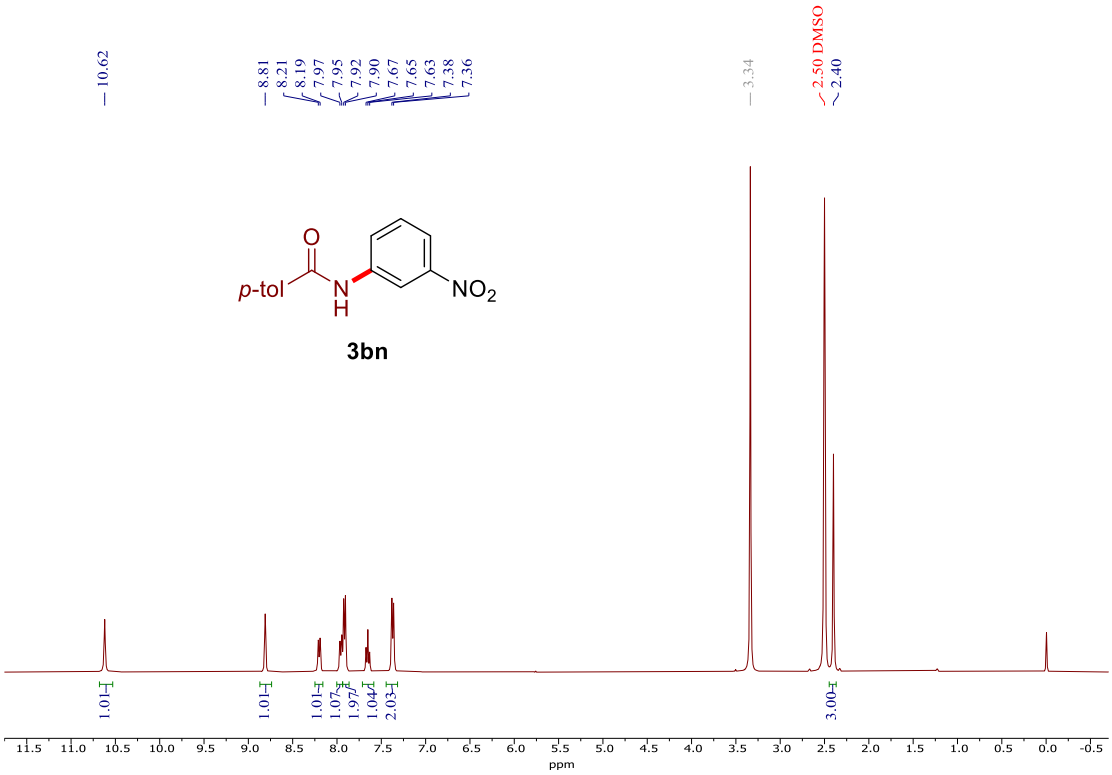
^{1}H NMR (400 MHz, $CDCl_3$) of **3bm** (*see procedure*)



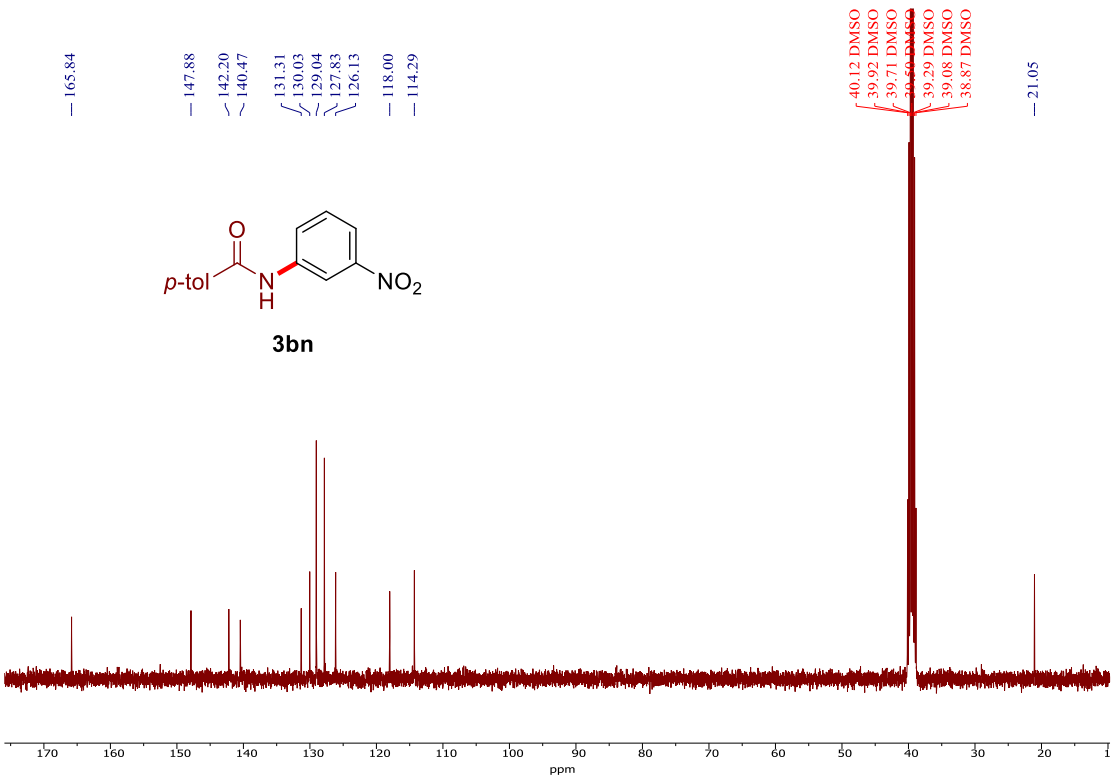
^{13}C NMR (101 MHz, $CDCl_3$) of **3bm**



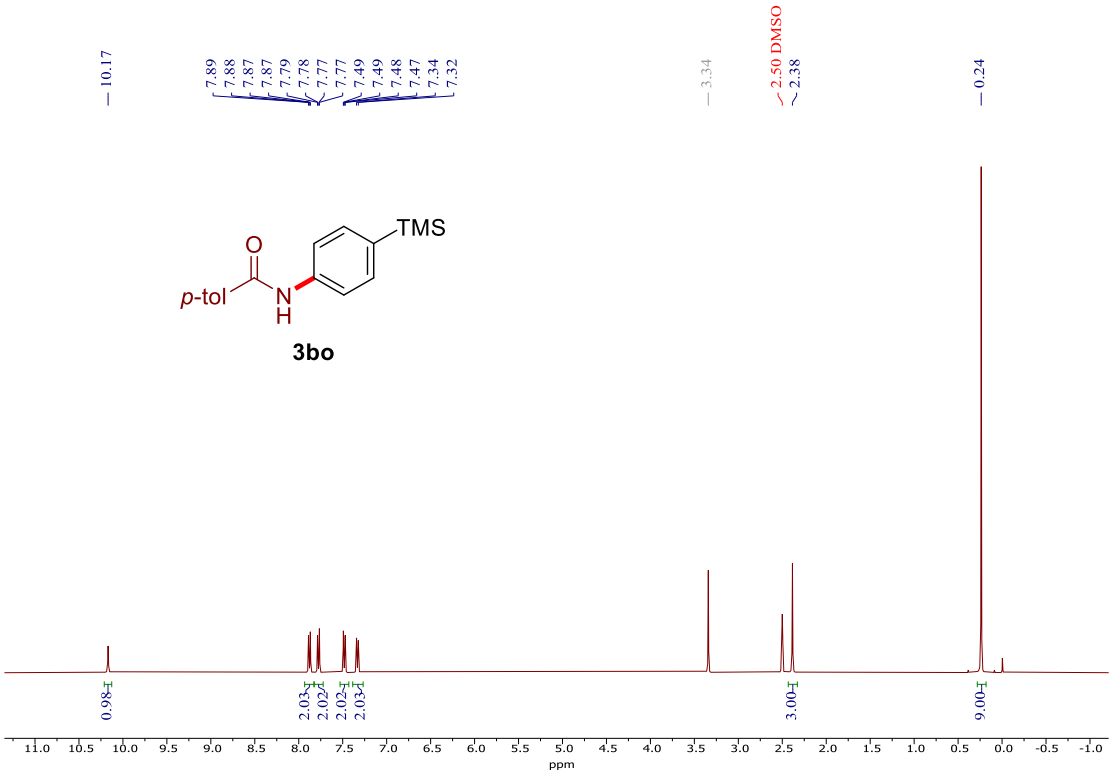
^{1}H NMR (400 MHz, d_6-DMSO) of **3bn** (*see procedure*)



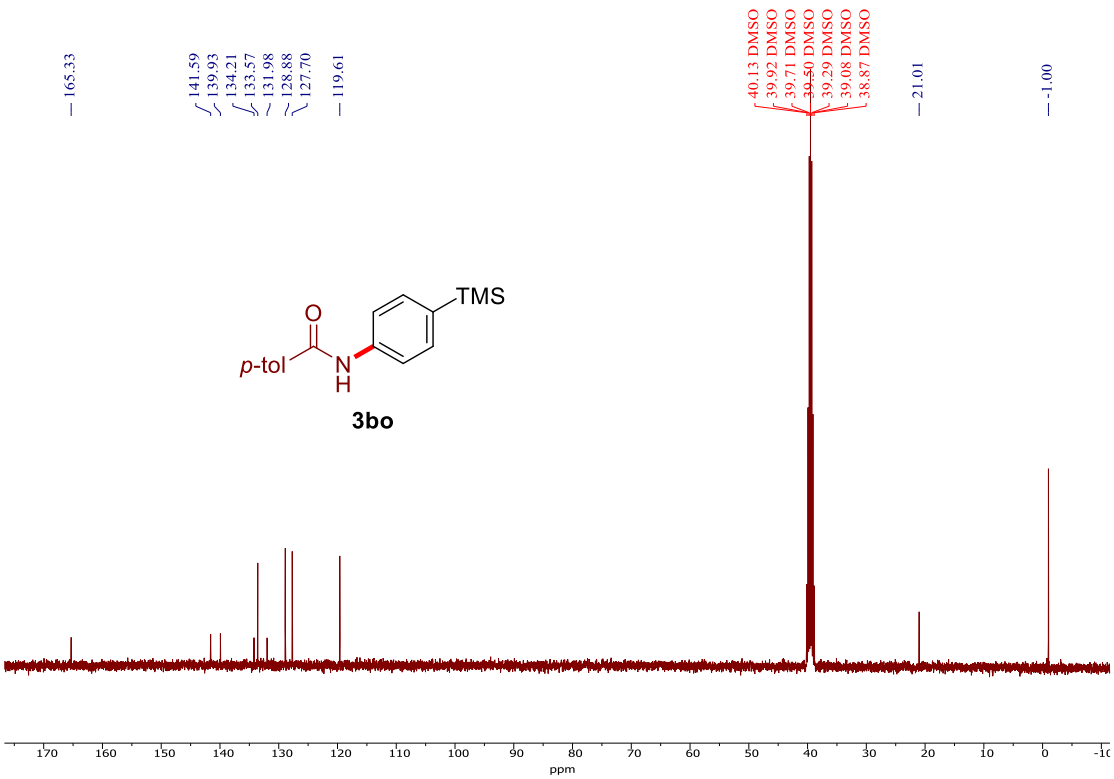
^{13}C NMR (101 MHz, d_6-DMSO) of **3bn**



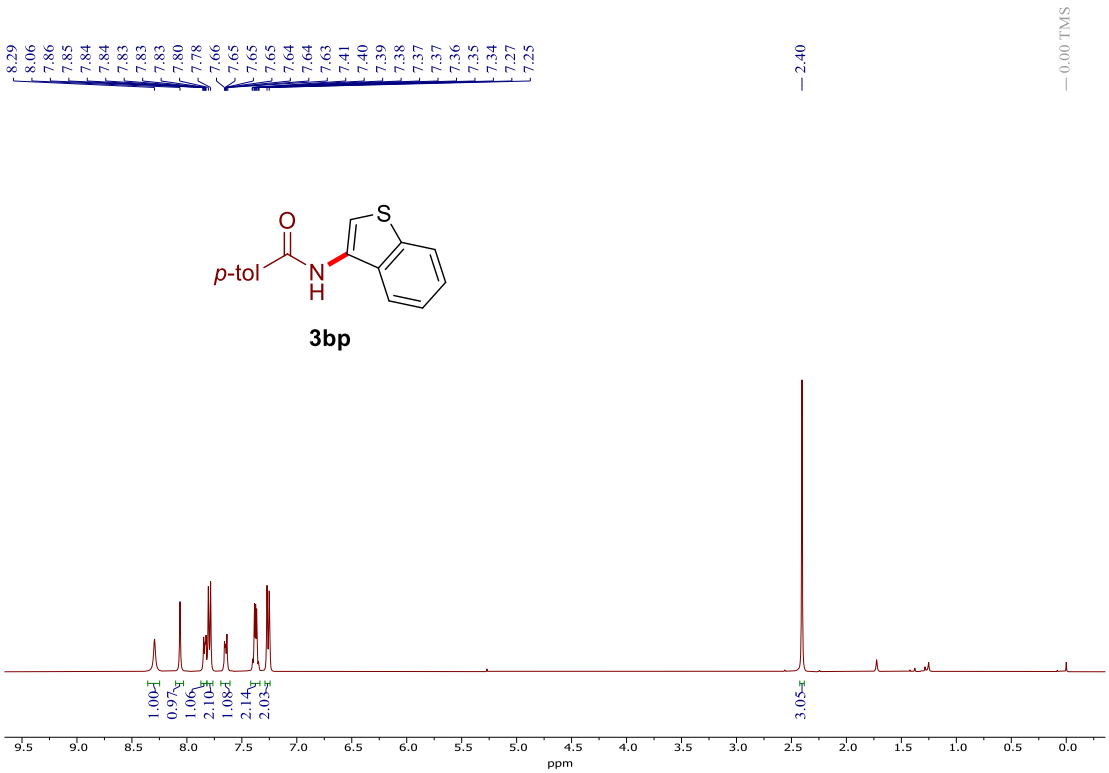
^{1}H NMR (400 MHz, d_6-DMSO) of **3bo** (*see procedure*)



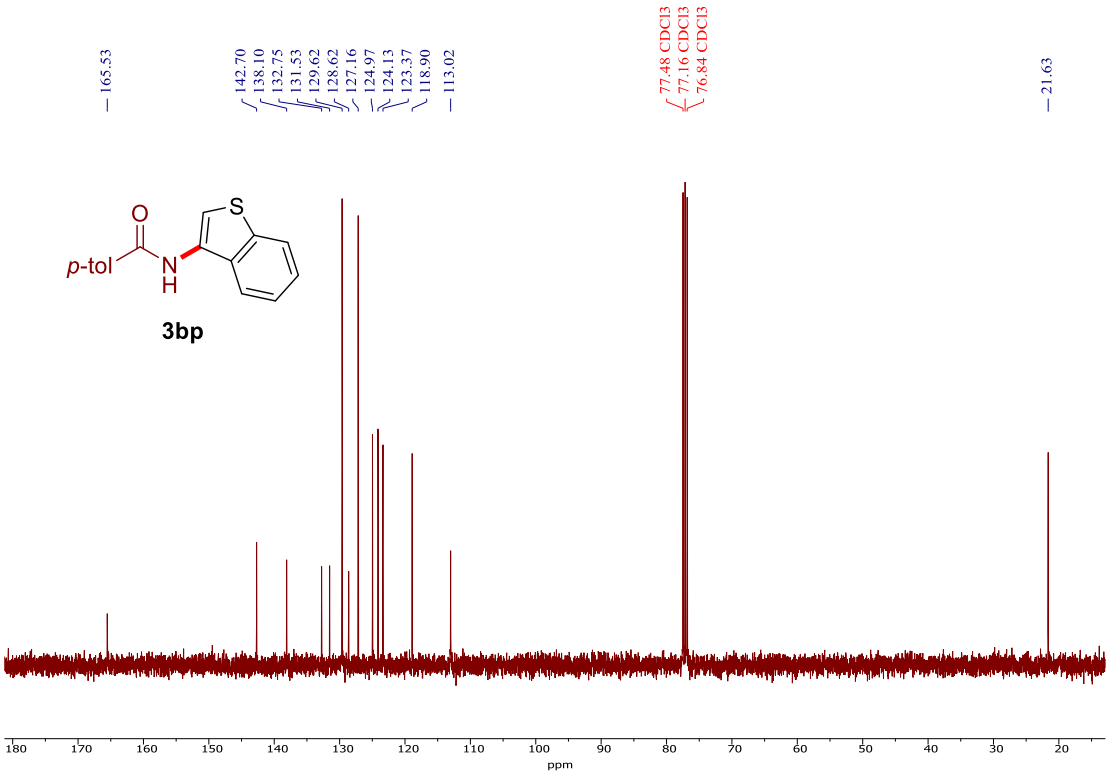
^{13}C NMR (101 MHz, $CDCl_3$) of **3bo**



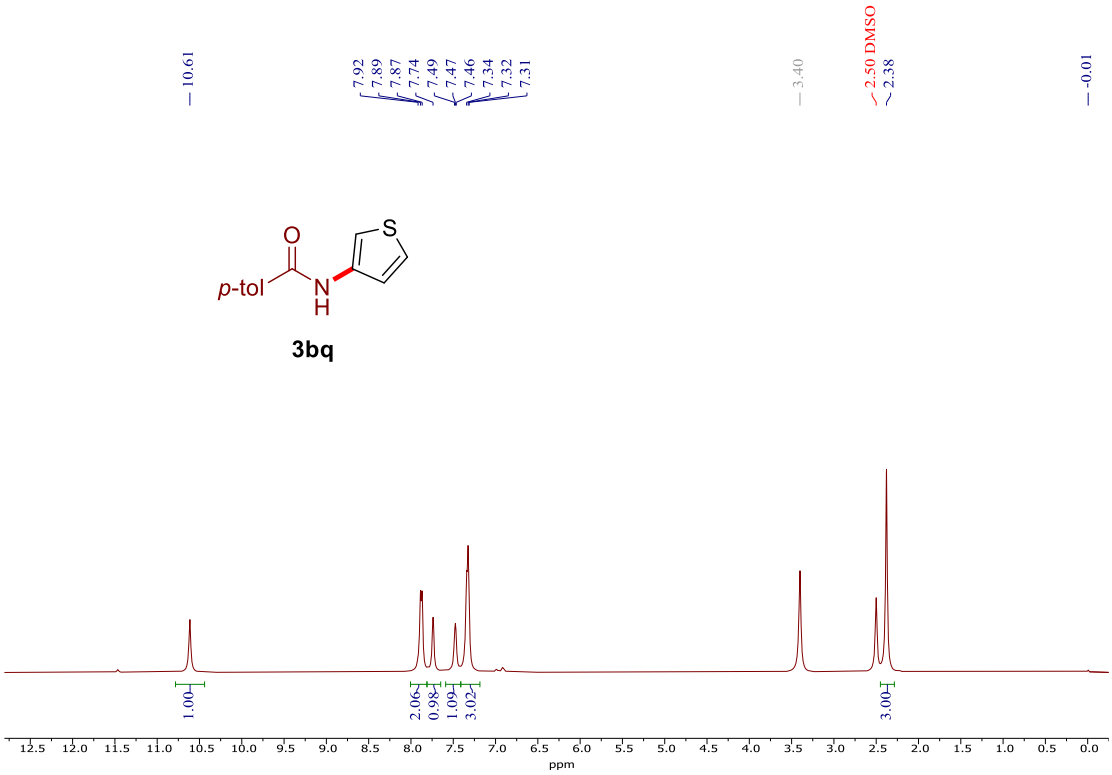
^{1}H NMR (400 MHz, $CDCl_3$) of **3bp** (*see procedure*)



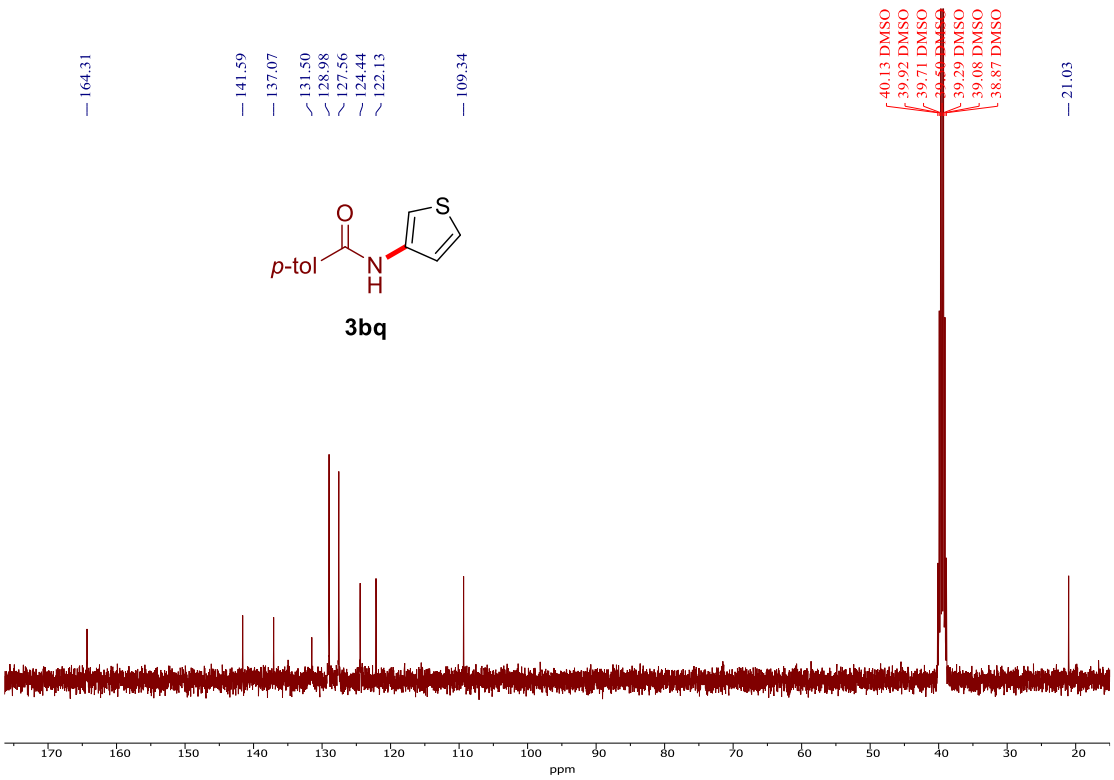
^{13}C NMR (101 MHz, $CDCl_3$) of **3bp**



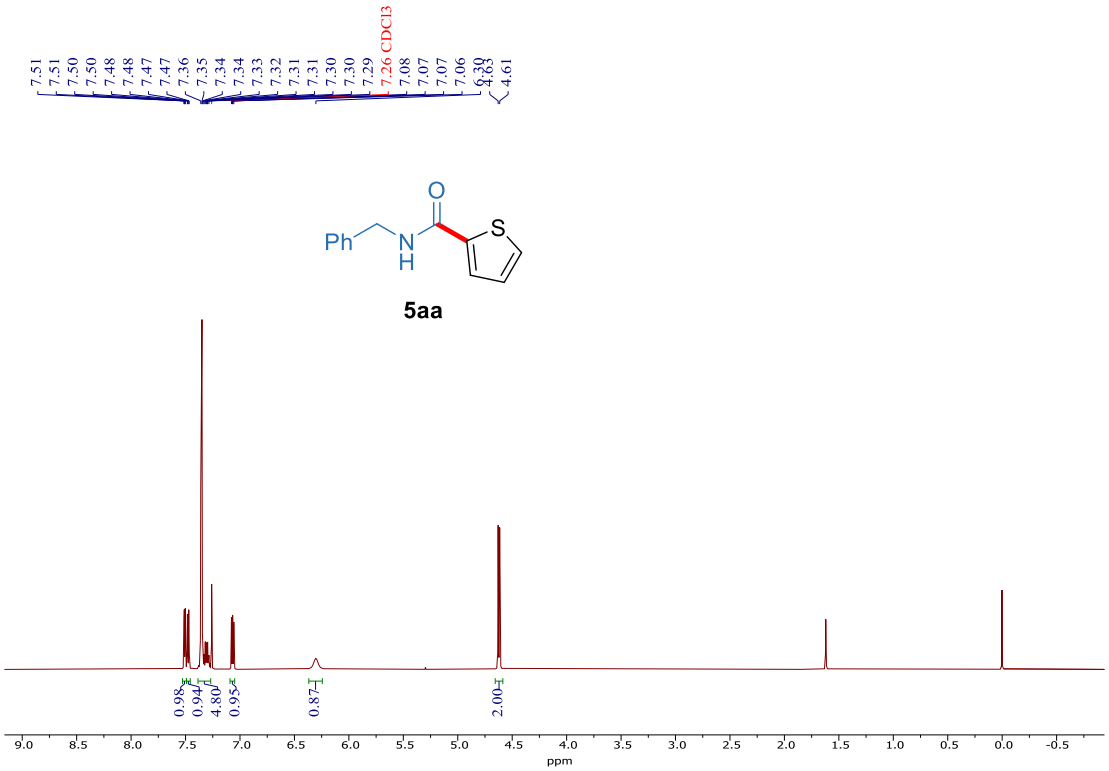
^{1}H NMR (400 MHz, d_6-DMSO) of **3bq** (*see procedure*)



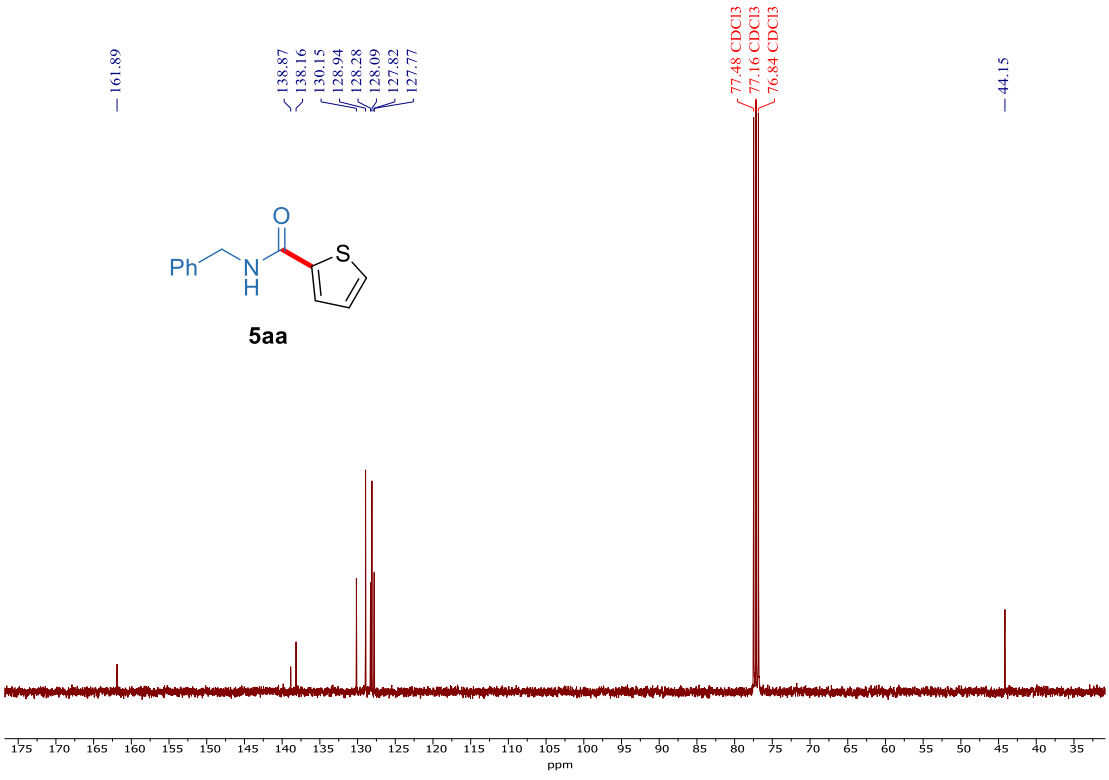
^{13}C NMR (101 MHz, d_6-DMSO) of **3bq**



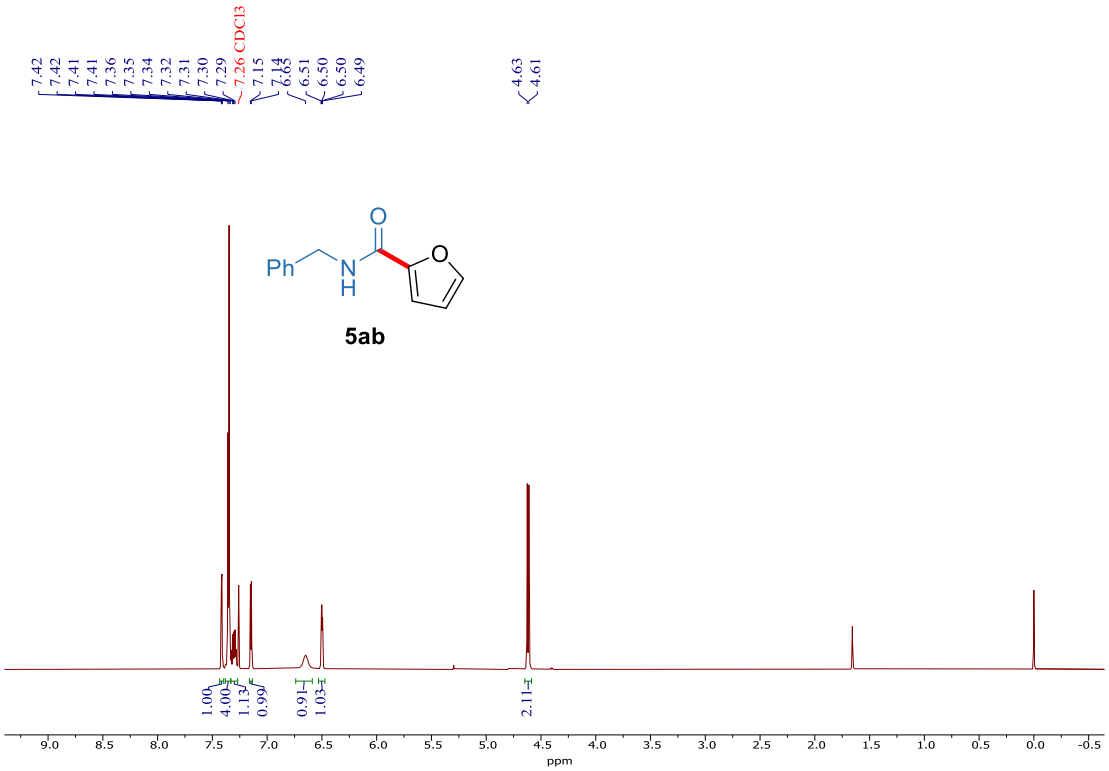
^{1}H NMR (400 MHz, $CDCl_3$) of **5aa** (*see procedure*)



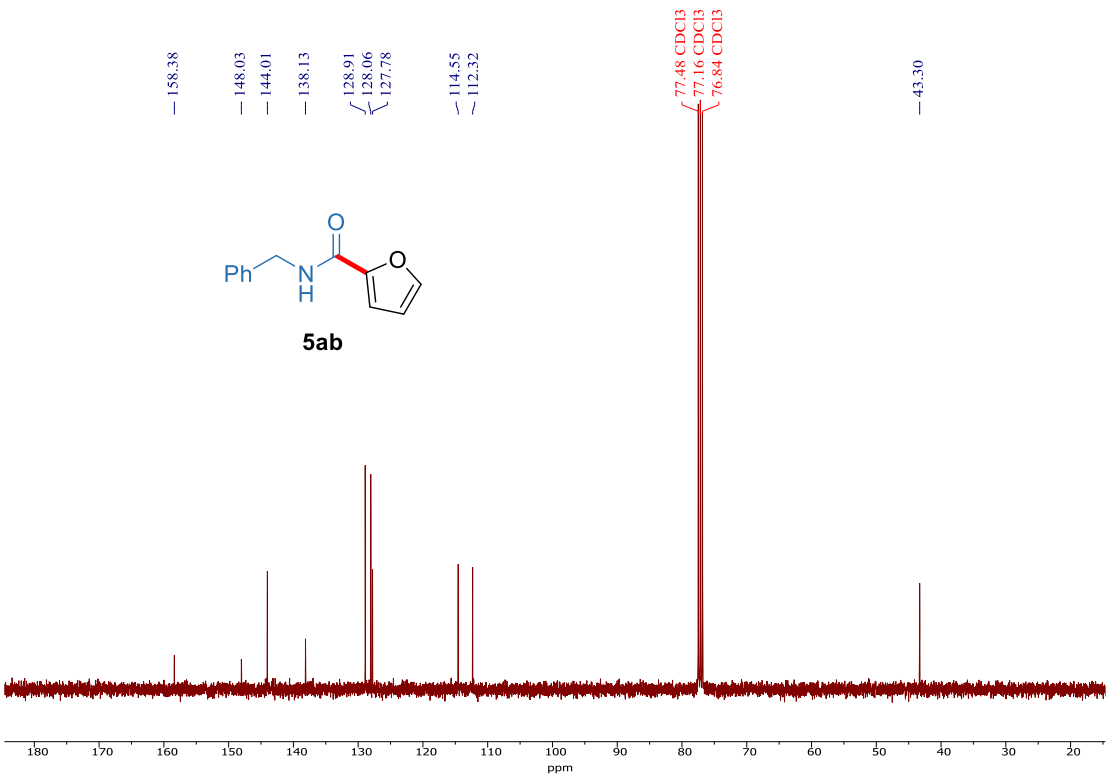
^{13}C NMR (101 MHz, $CDCl_3$) of **5aa**



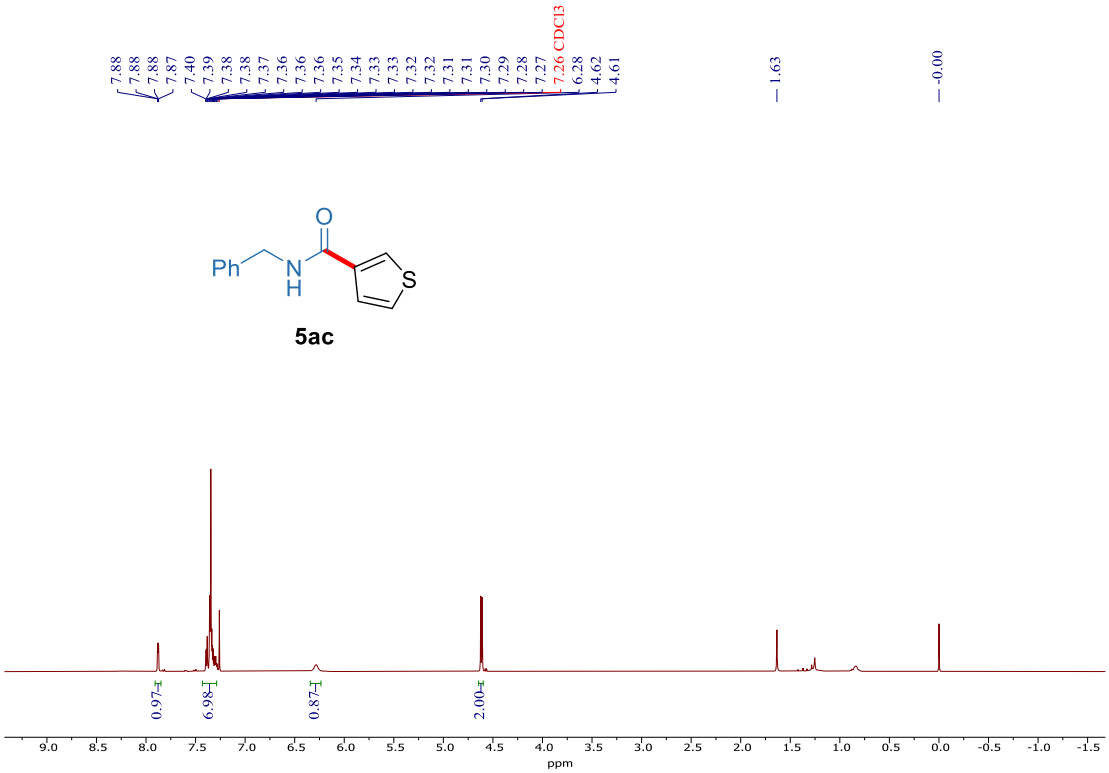
^{1}H NMR (400 MHz, $CDCl_3$) of **5ab** (*see procedure*)



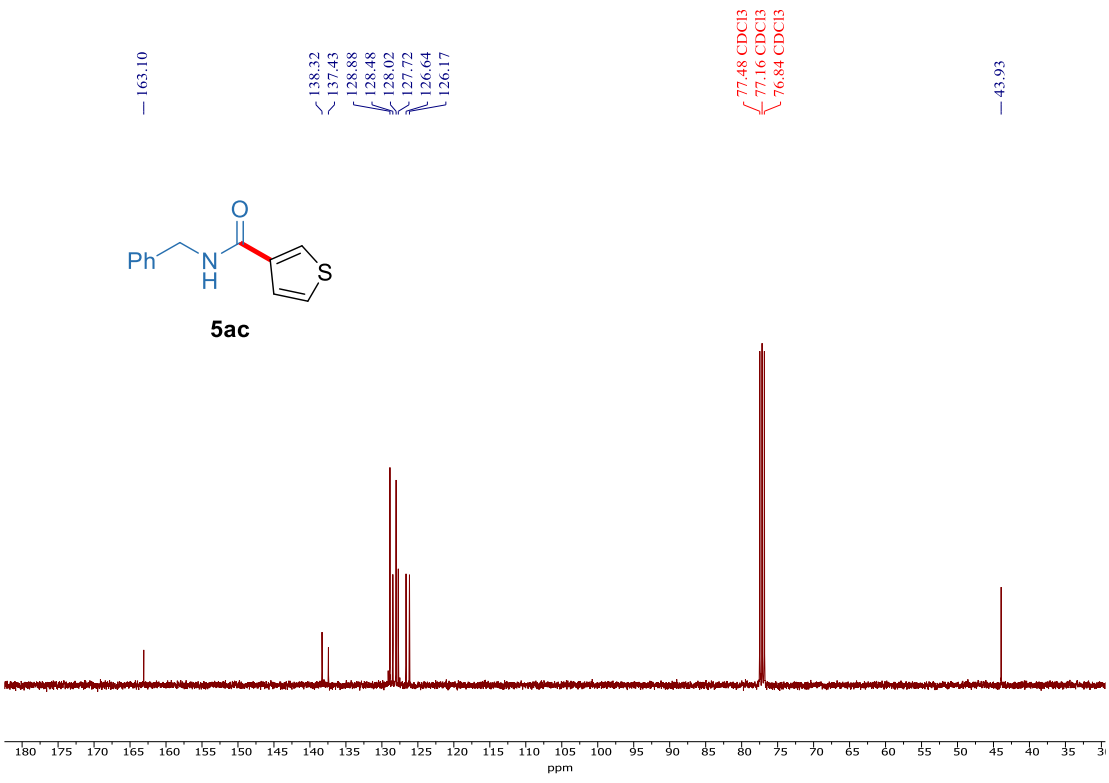
^{13}C NMR (101 MHz, $CDCl_3$) of **5ab**



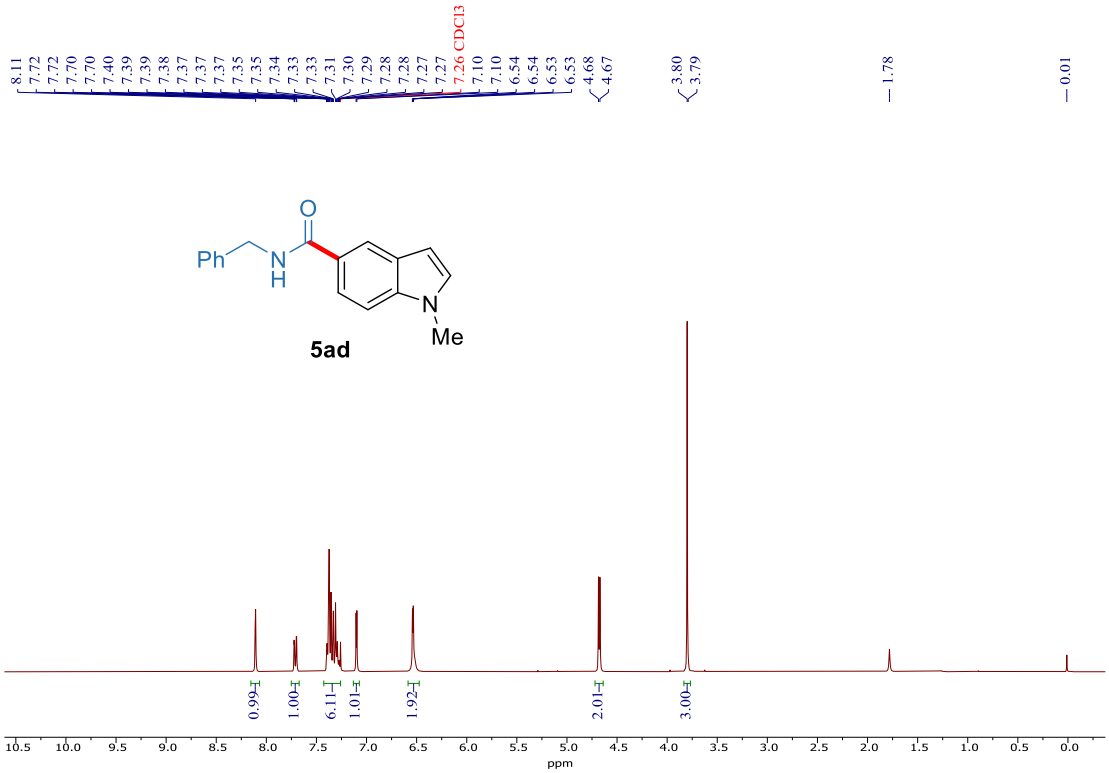
^{1}H NMR (400 MHz, $CDCl_3$) of **5ac** (*see procedure*)



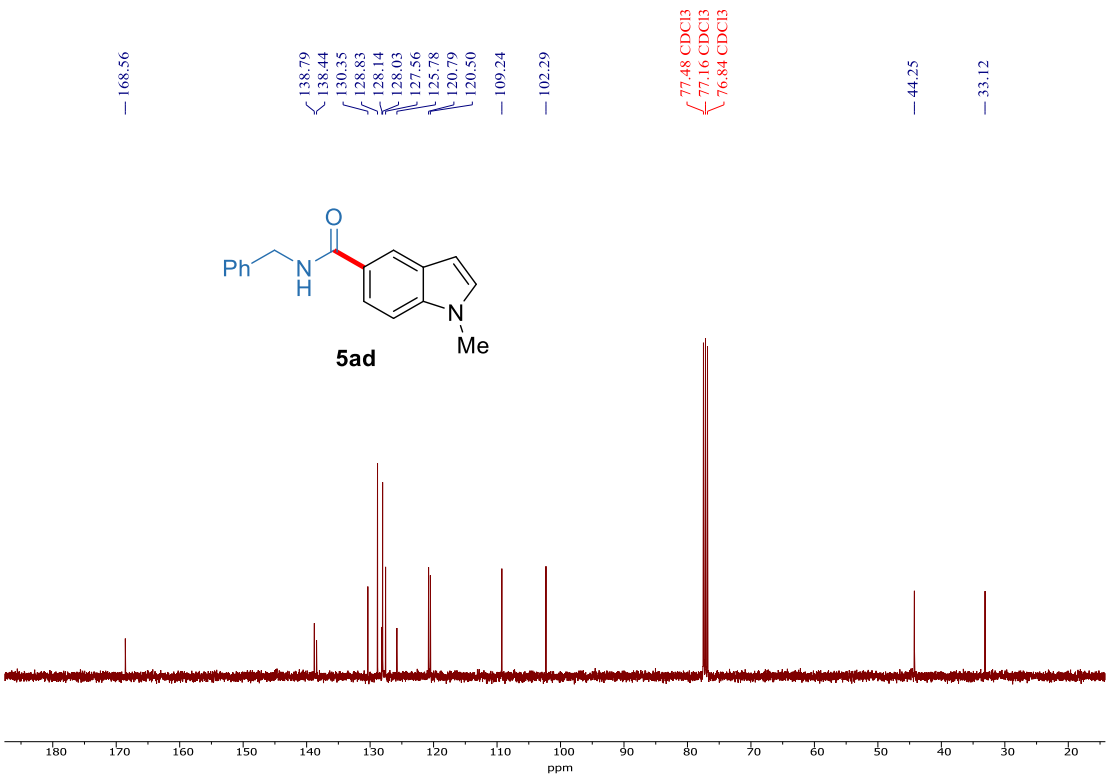
^{13}C NMR (101 MHz, $CDCl_3$) of **5ac**



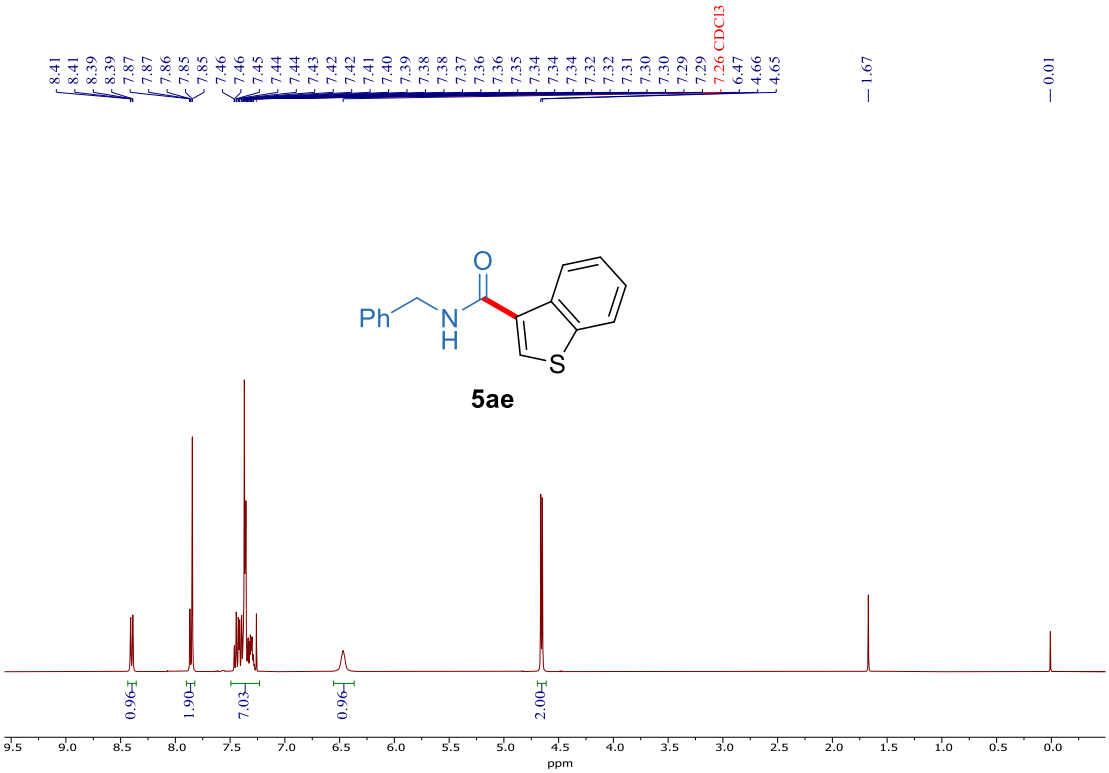
^{1}H NMR (400 MHz, $CDCl_3$) of **5ad** (*see procedure*)



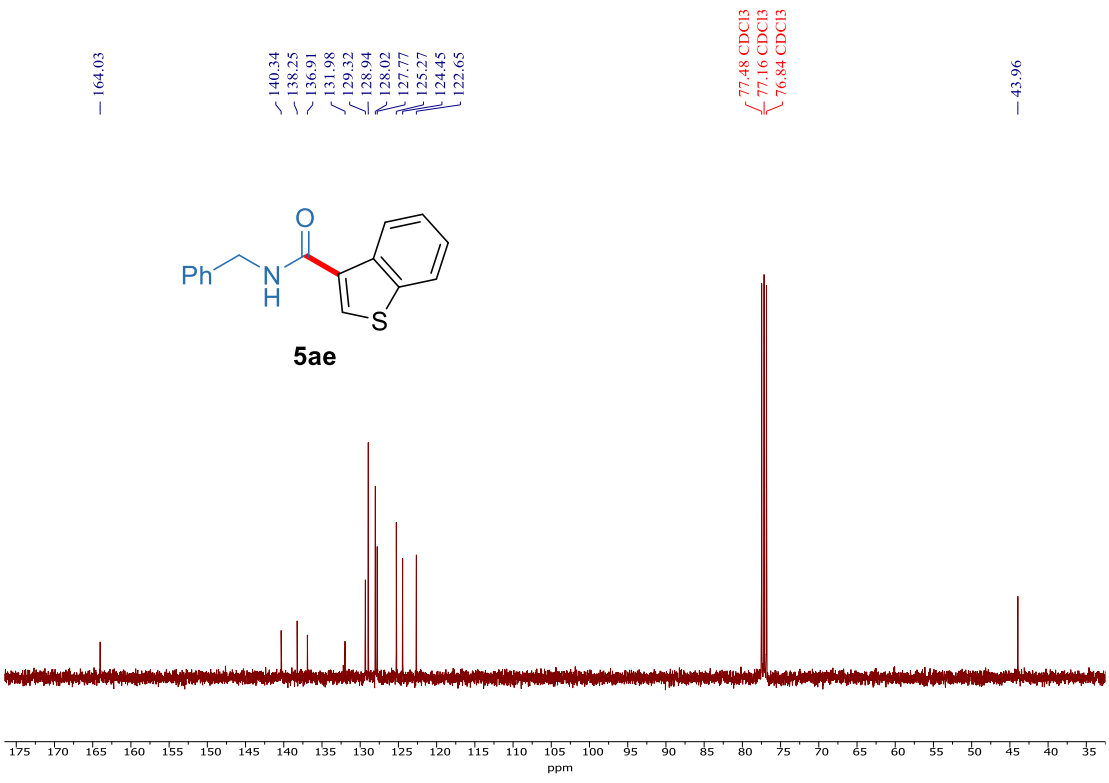
^{13}C NMR (101 MHz, $CDCl_3$) of **5ad**



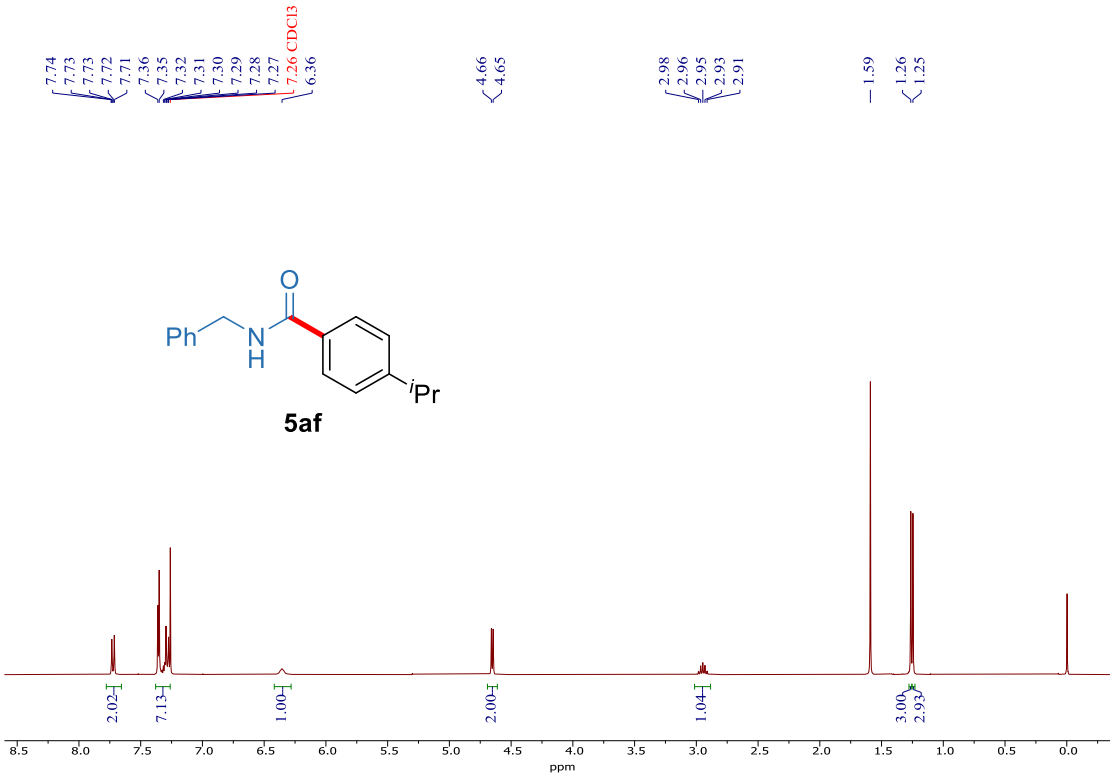
^{1}H NMR (400 MHz, $CDCl_3$) of **5ae** (*see procedure*)



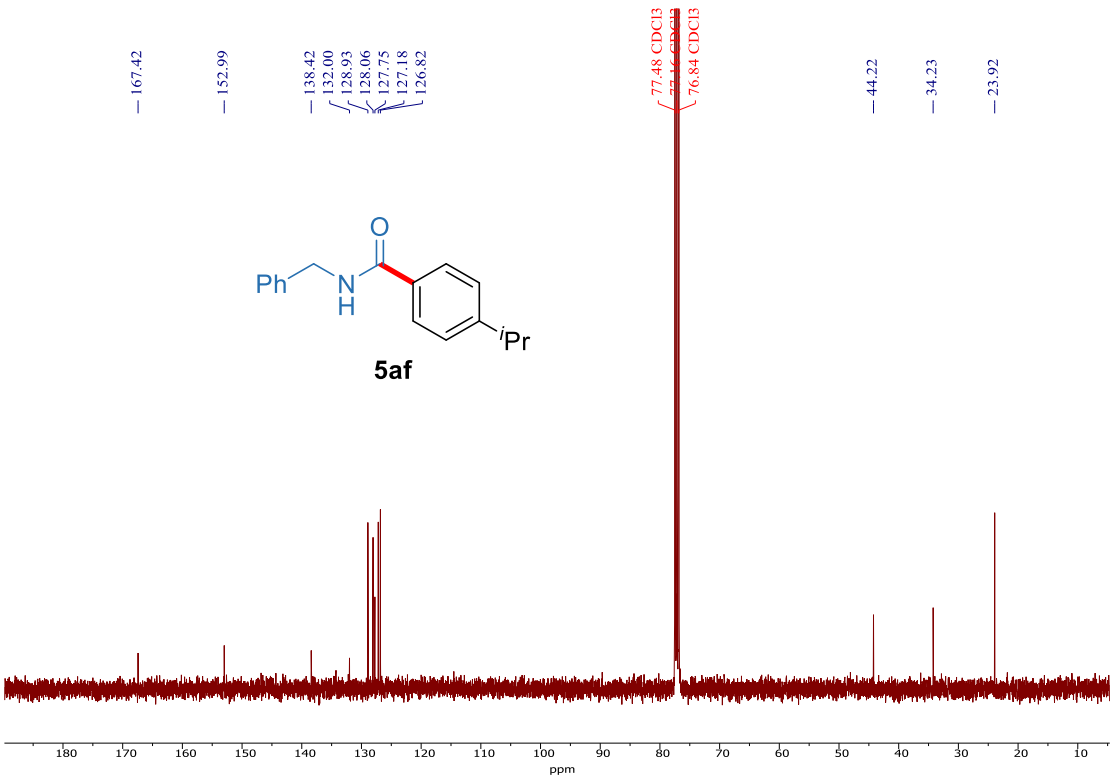
^{13}C NMR (101 MHz, $CDCl_3$) of **5ae**



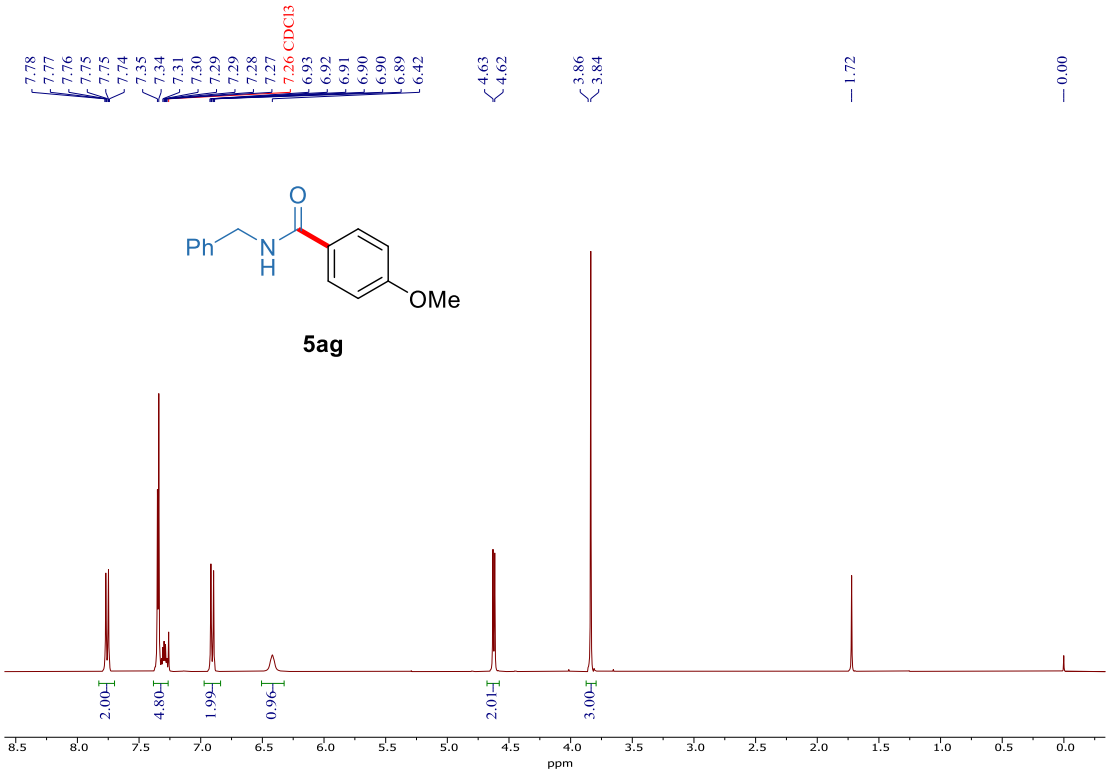
^{1}H NMR (400 MHz, $CDCl_3$) of **5af** (*see procedure*)



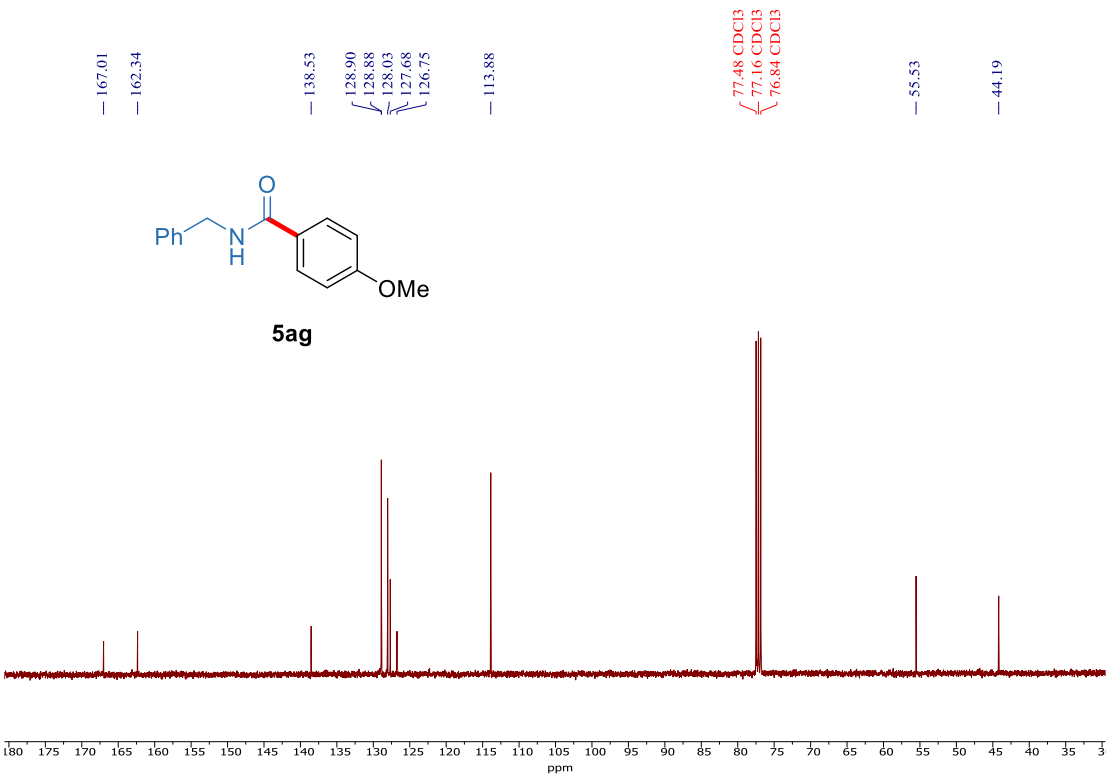
^{13}C NMR (101 MHz, $CDCl_3$) of **5af**



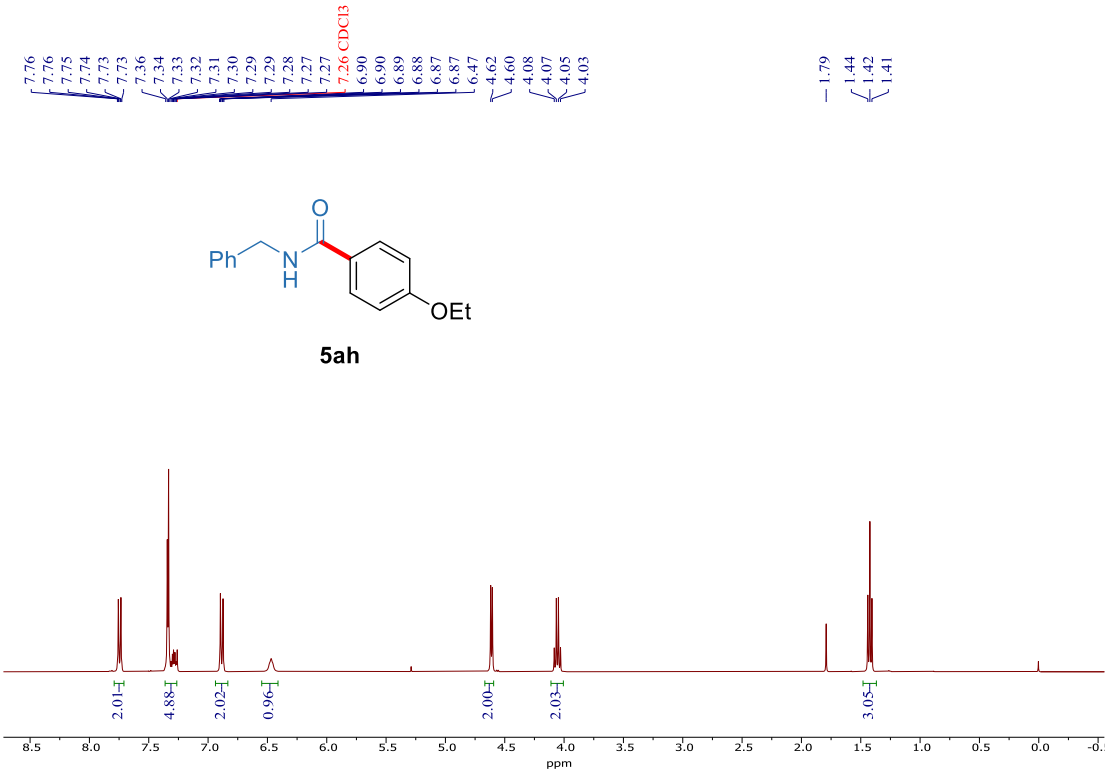
^{1}H NMR (400 MHz, $CDCl_3$) of **5ag** (*see procedure*)



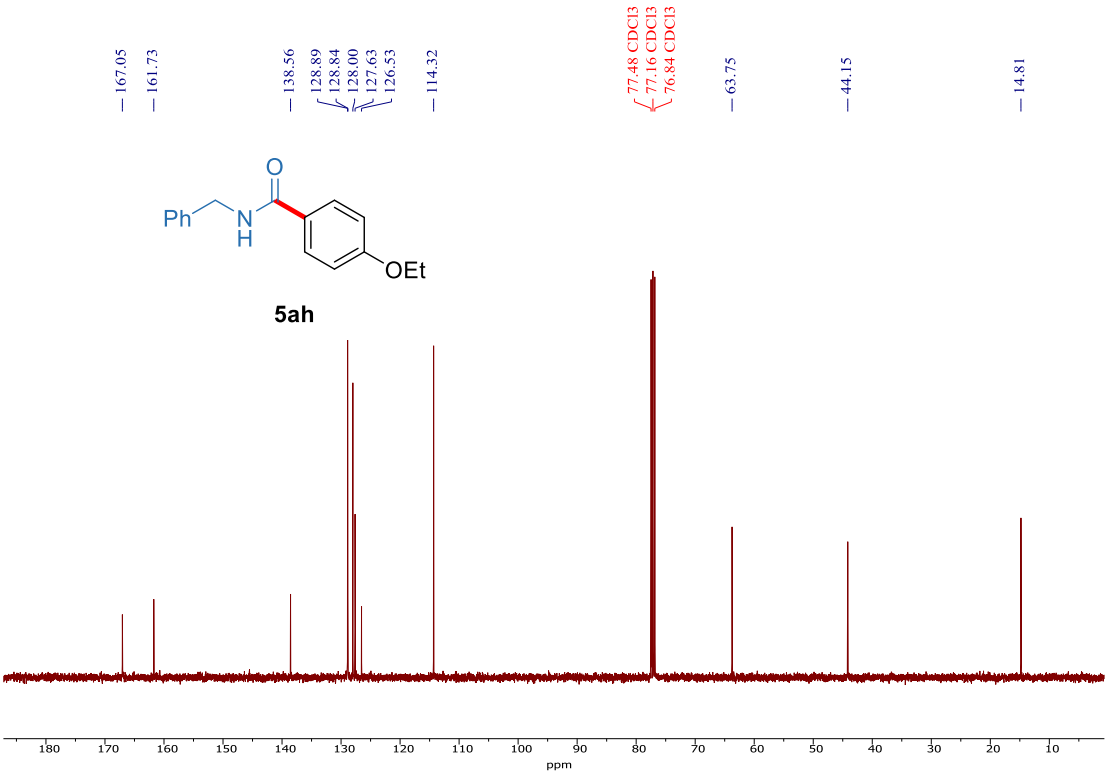
^{13}C NMR (101 MHz, $CDCl_3$) of **5ag**



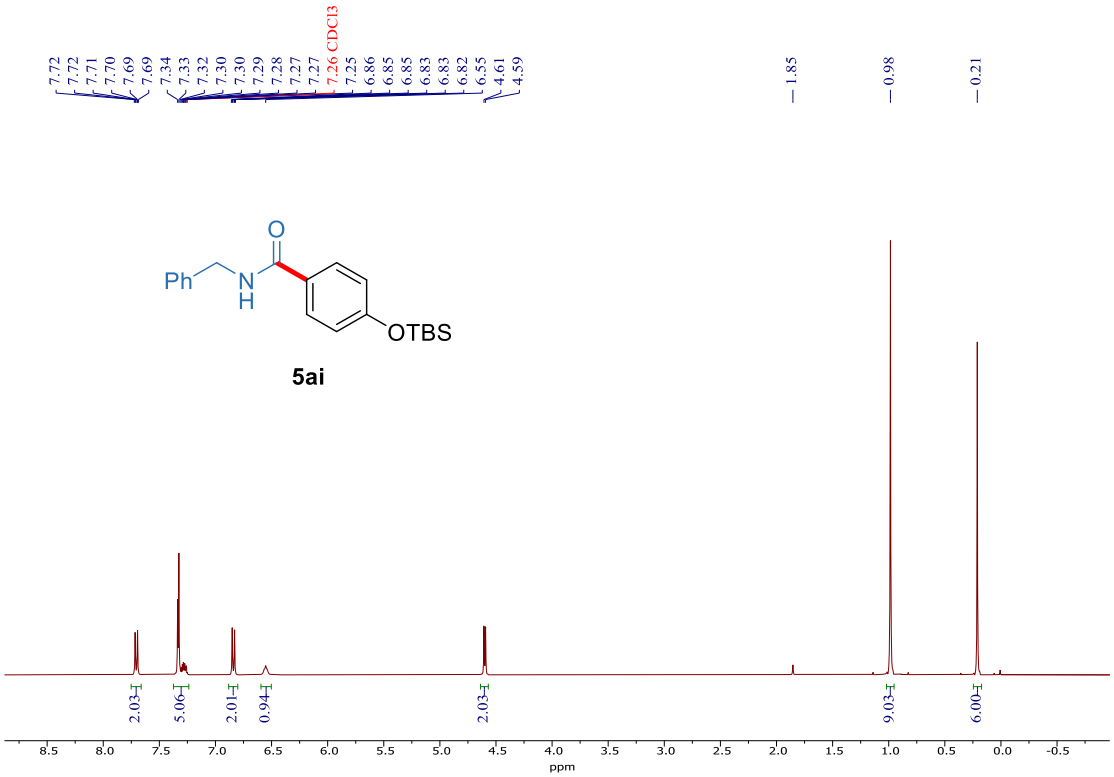
^{1}H NMR (400 MHz, $CDCl_3$) of **5ah** (*see procedure*)



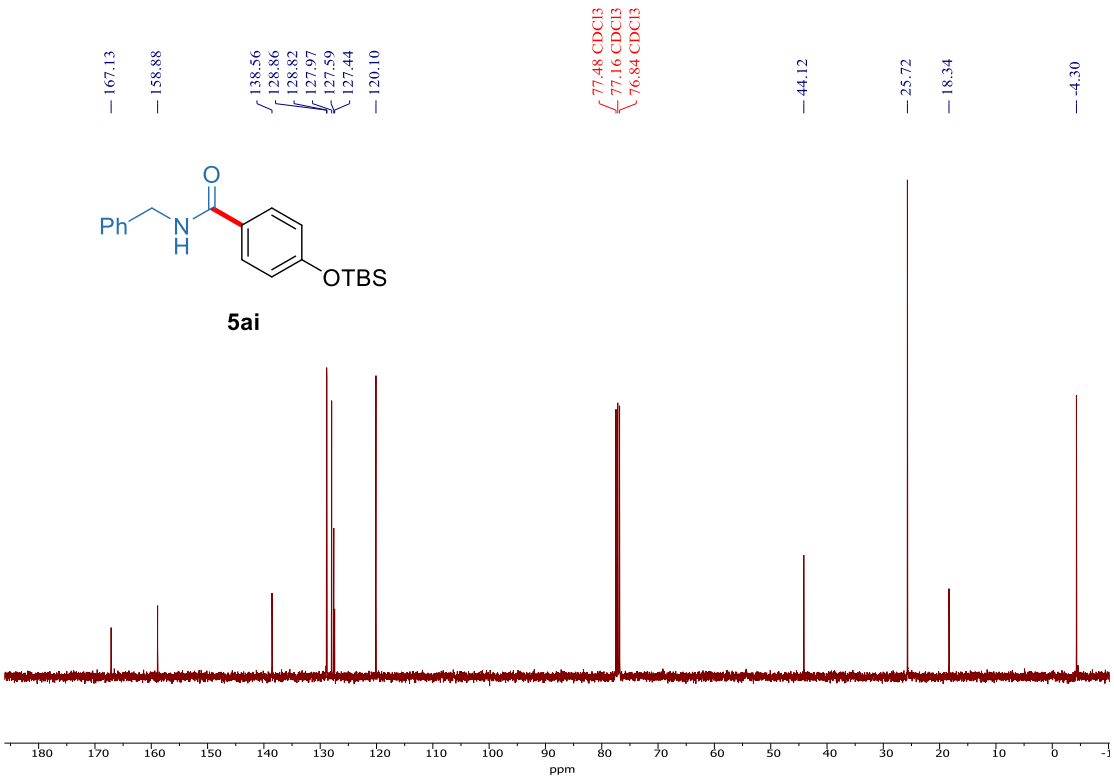
^{13}C NMR (101 MHz, $CDCl_3$) of **5ah**



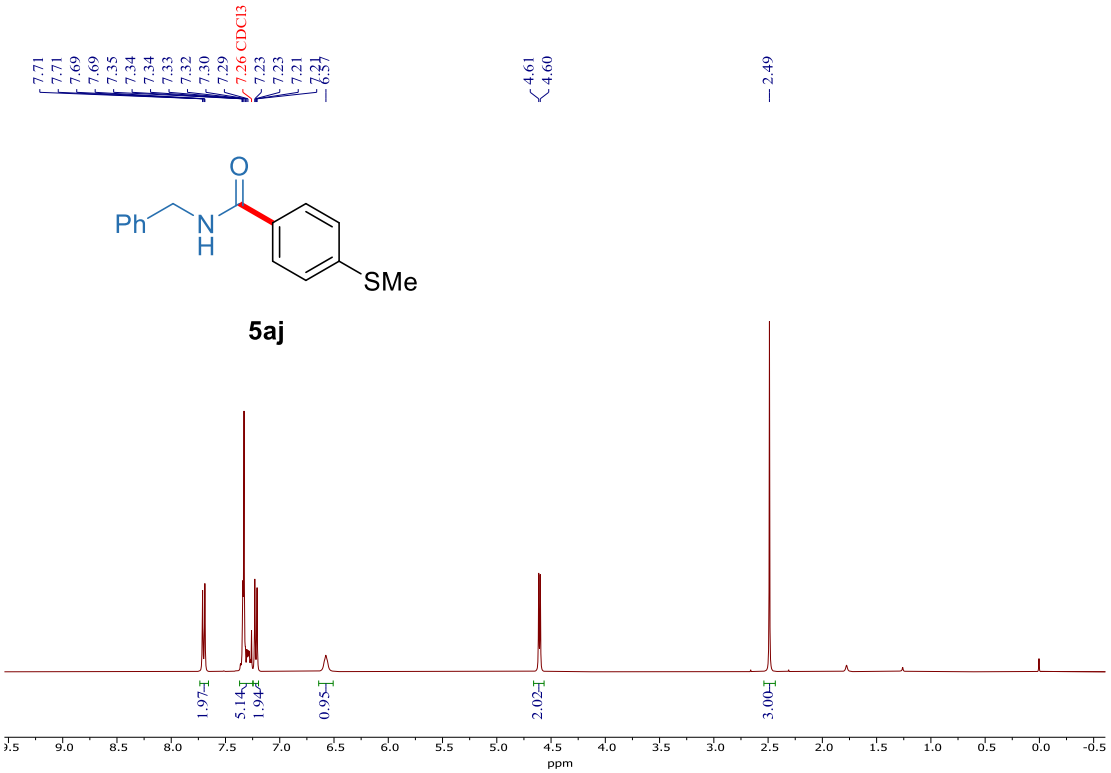
^{1}H NMR (400 MHz, $CDCl_3$) of **5ai** (*see procedure*)



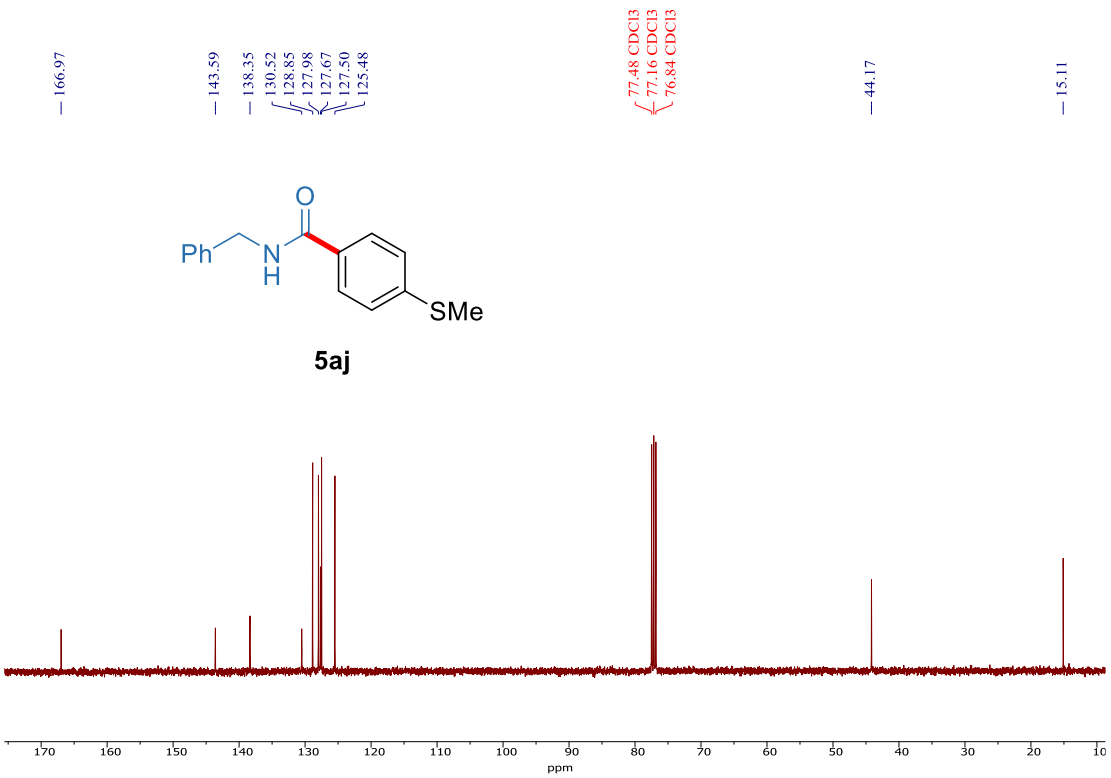
^{13}C NMR (101 MHz, $CDCl_3$) of **5ai**



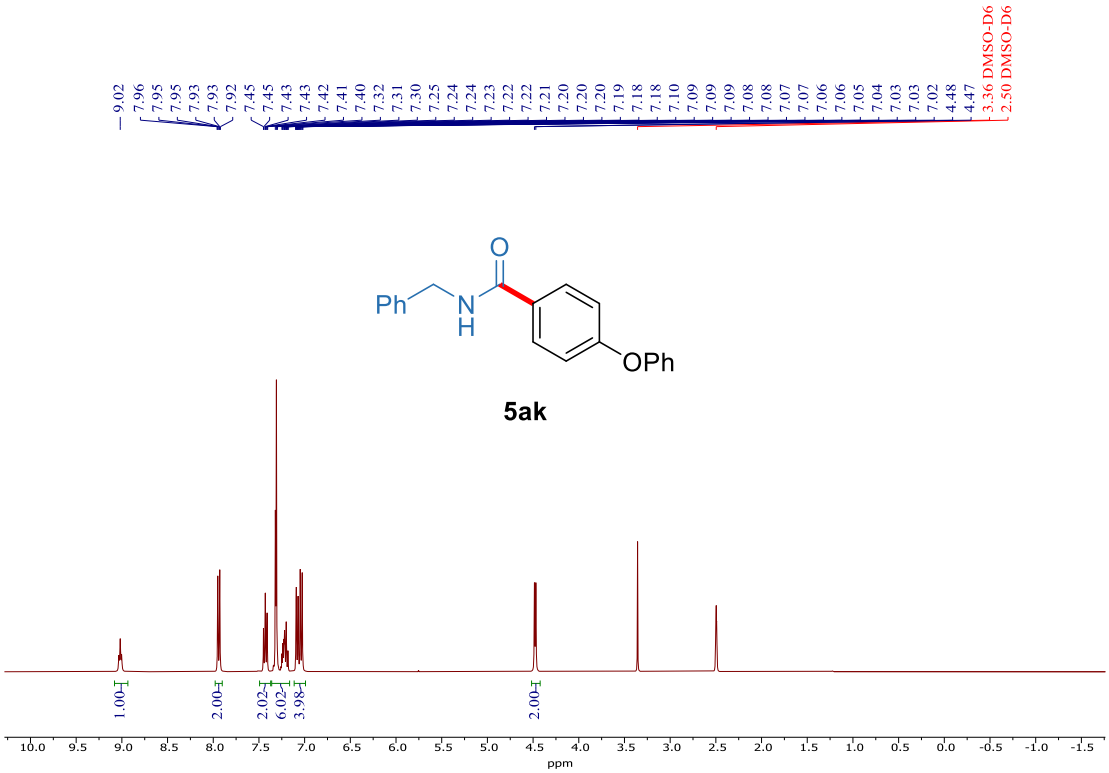
^{1}H NMR (400 MHz, $CDCl_3$) of **5aj** (*see procedure*)



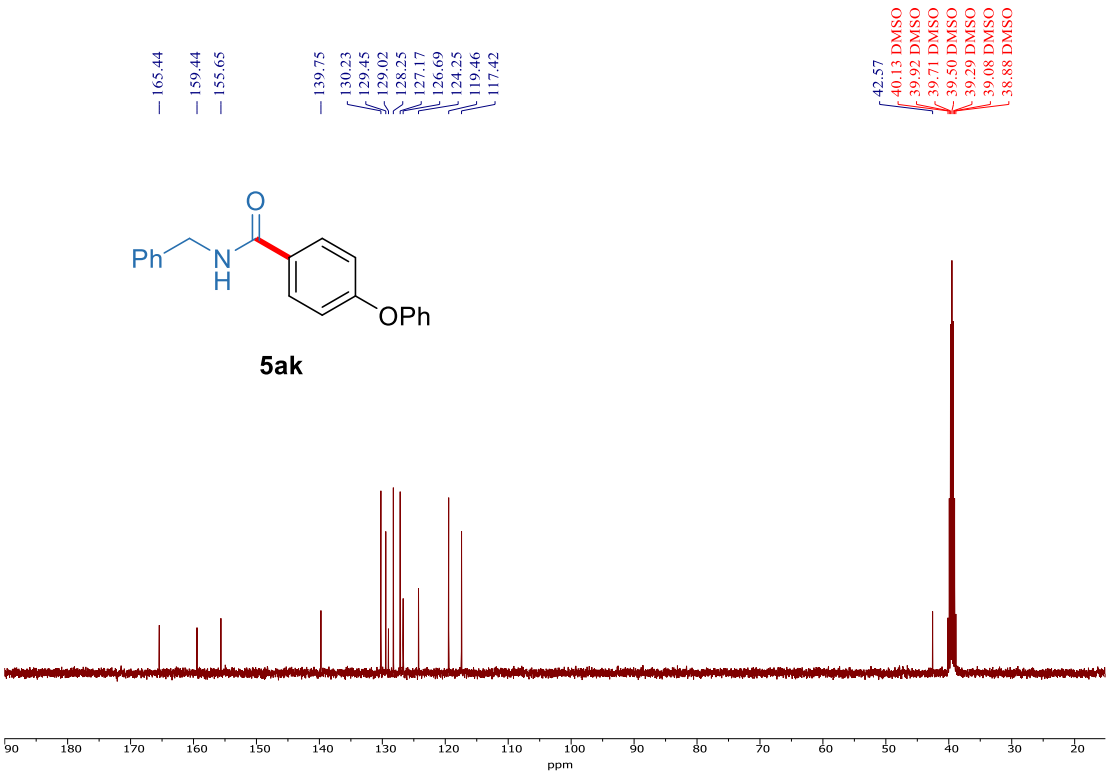
^{13}C NMR (101 MHz, $CDCl_3$) of **5aj**



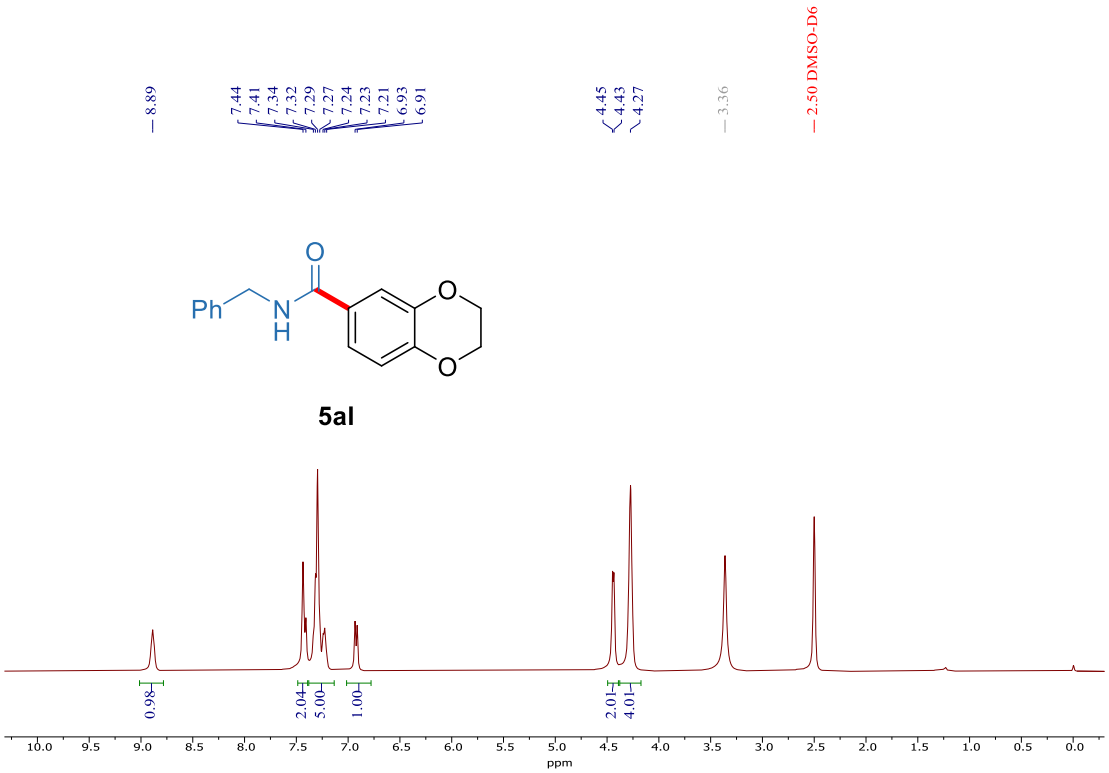
^{1}H NMR (400 MHz, d_6-DMSO) of **5ak** (*see procedure*)



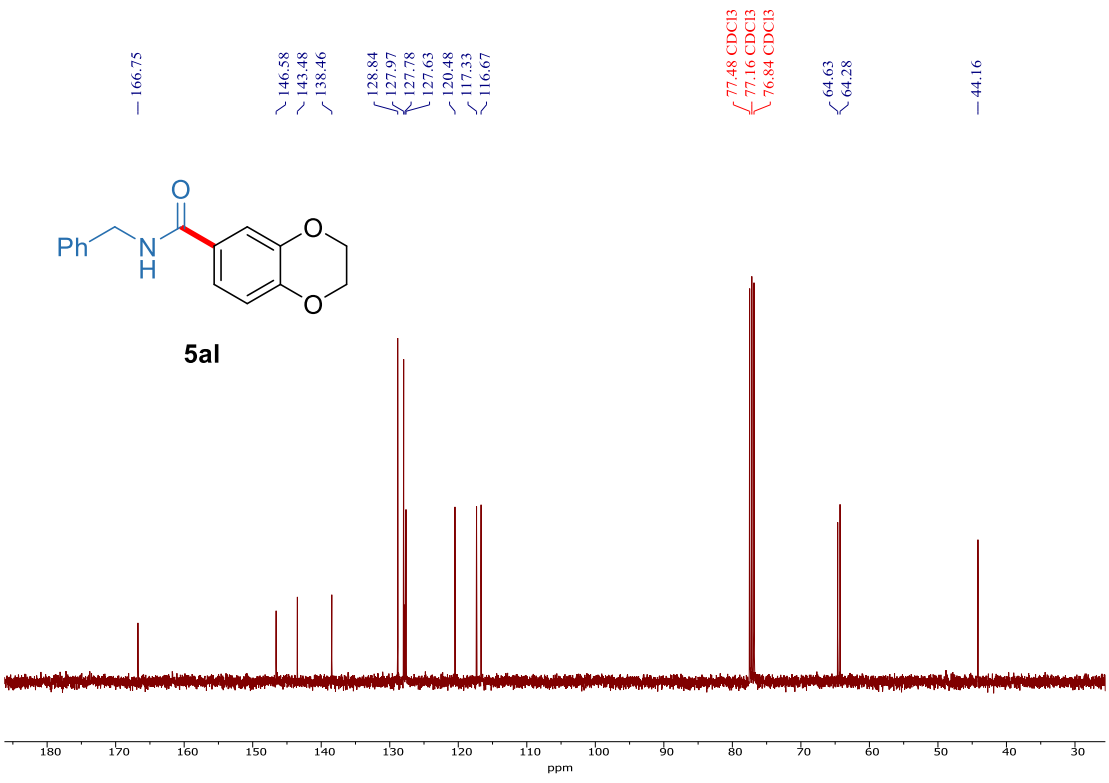
^{13}C NMR (101 MHz, d_6-DMSO) of **5ak**



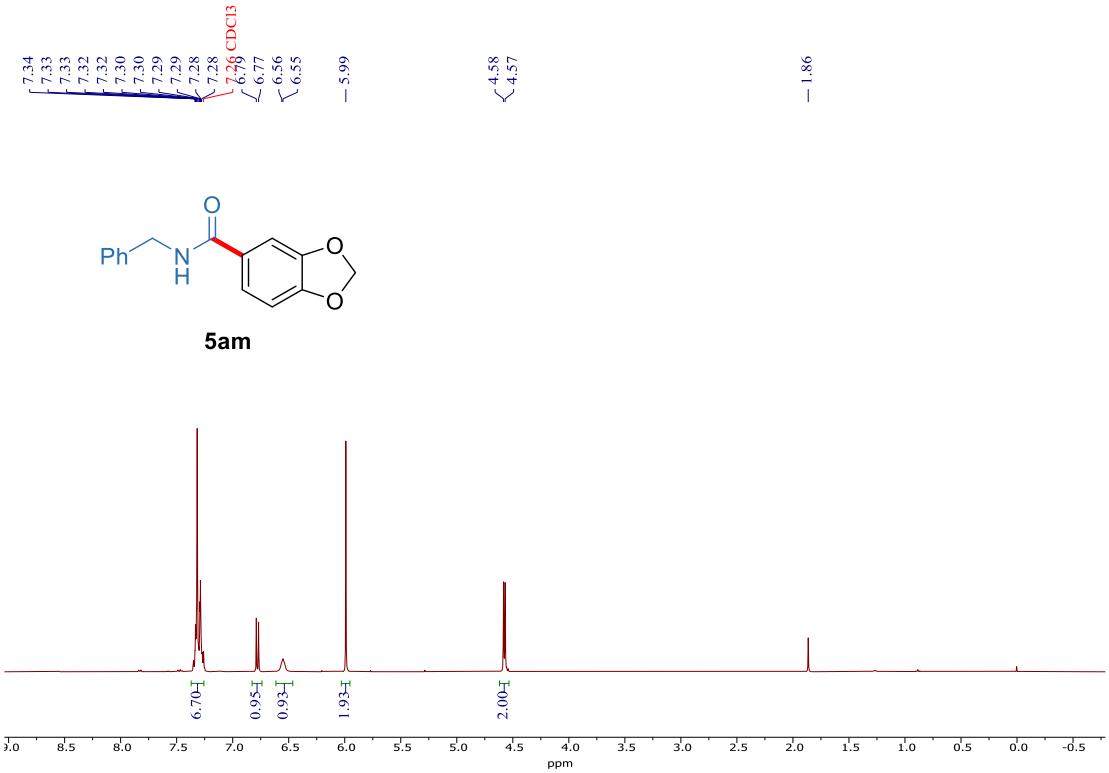
^{1}H NMR (400 MHz, d_6-DMSO) of **5al** (*see procedure*)



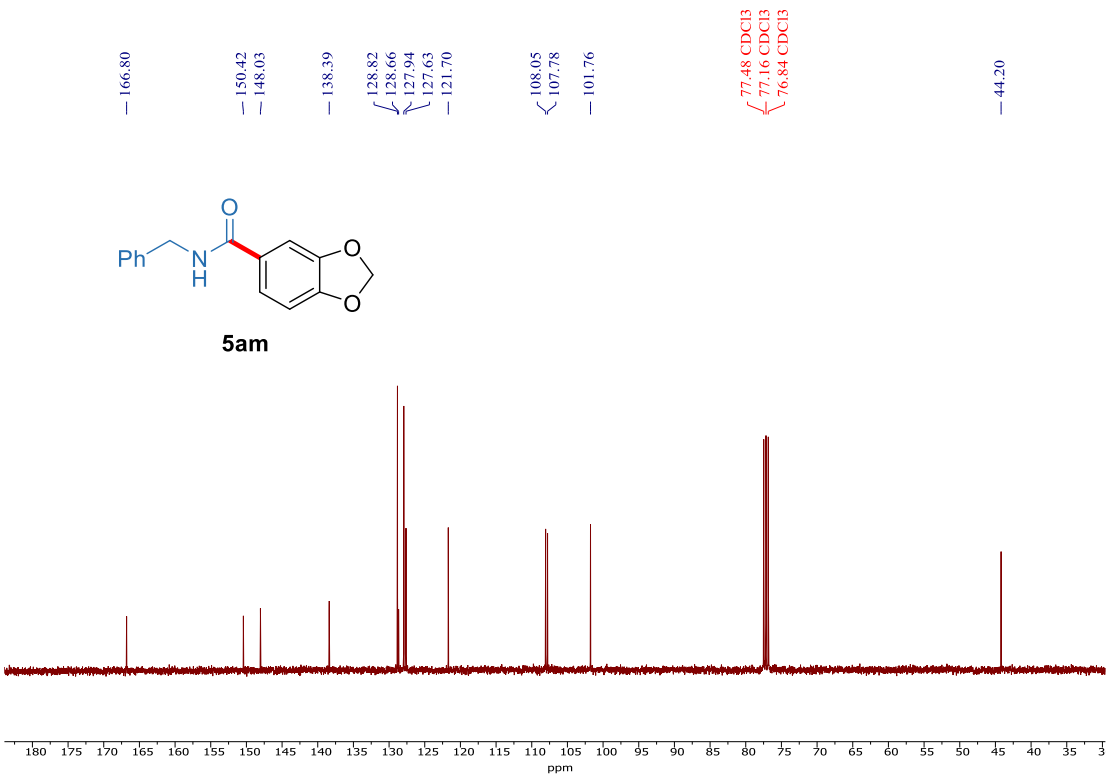
^{13}C NMR (101 MHz, $CDCl_3$) of **5al**



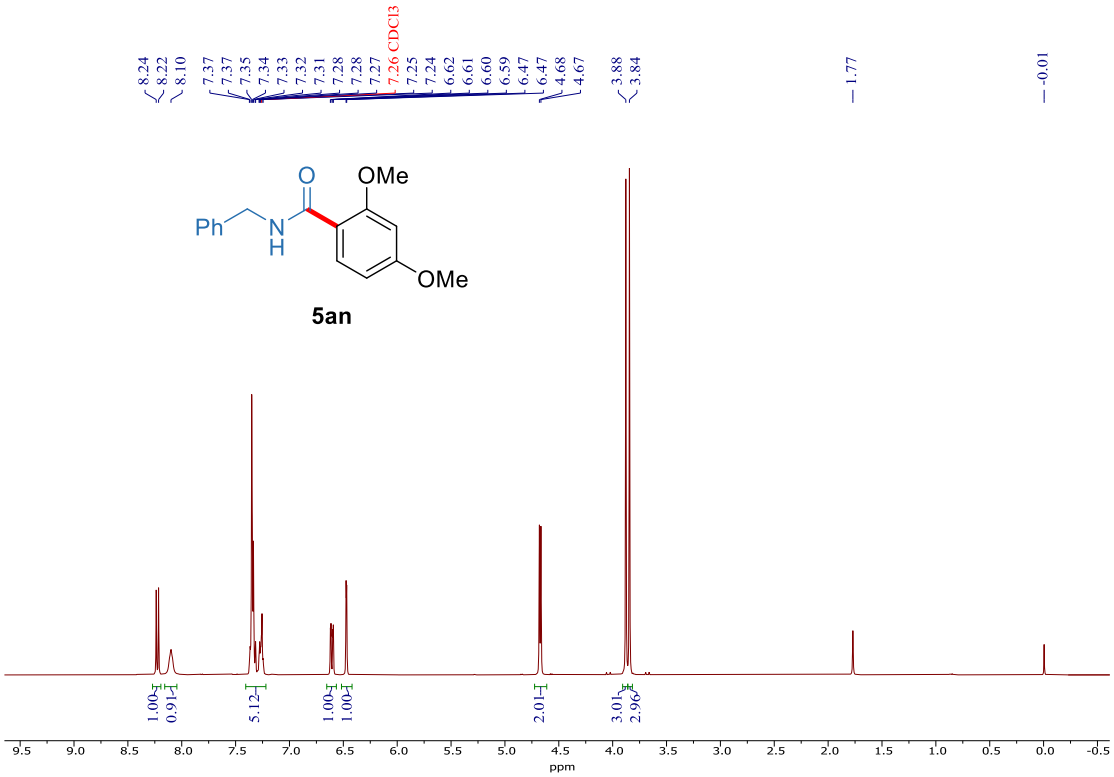
^{1}H NMR (400 MHz, $CDCl_3$) of **5am** (*see procedure*)



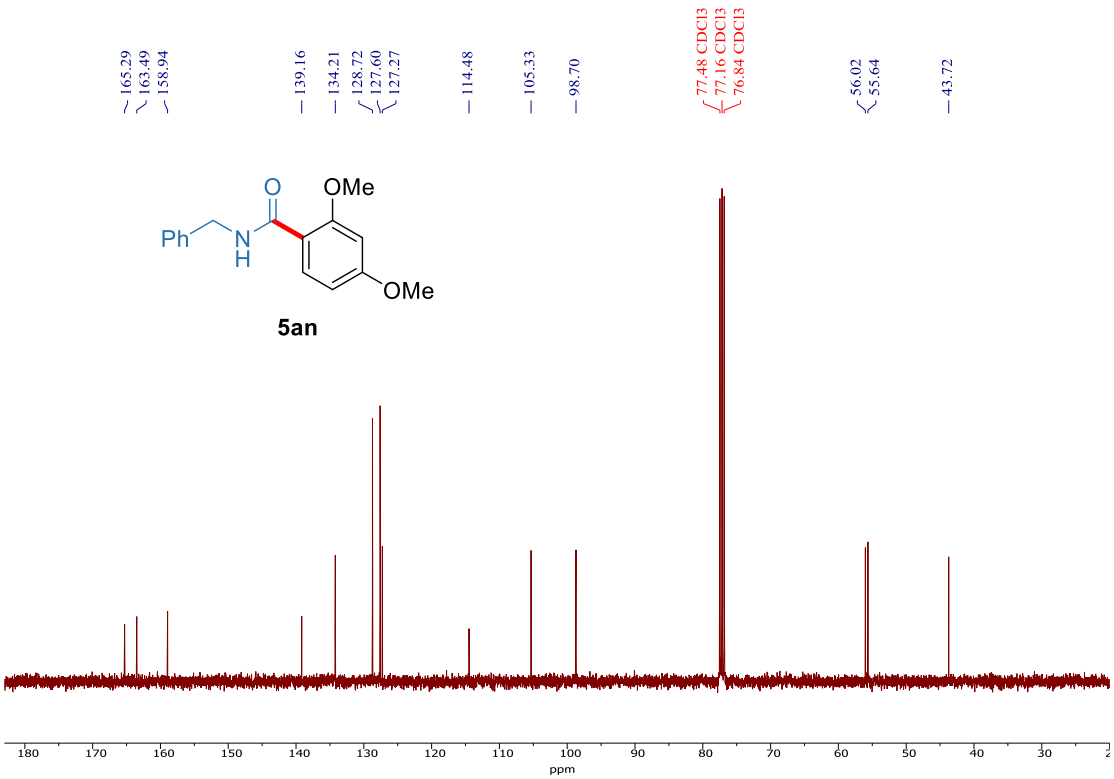
^{13}C NMR (101 MHz, $CDCl_3$) of **5am**



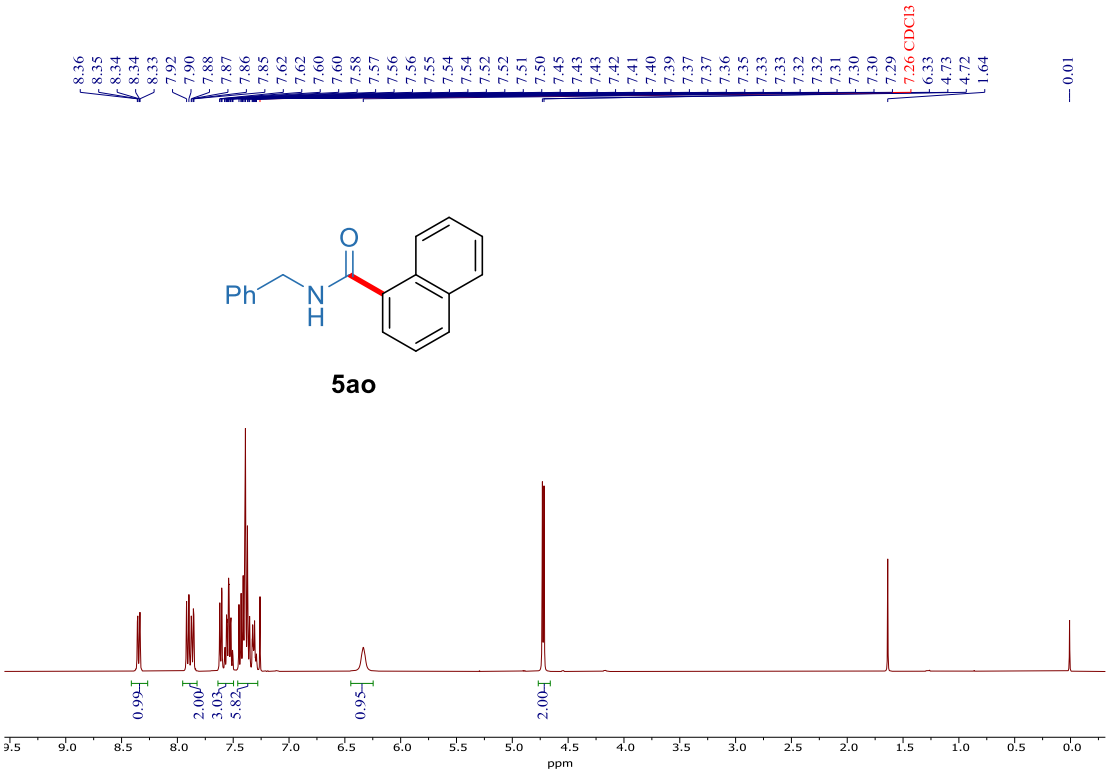
^{1}H NMR (400 MHz, $CDCl_3$) of **5an** (*see procedure*)



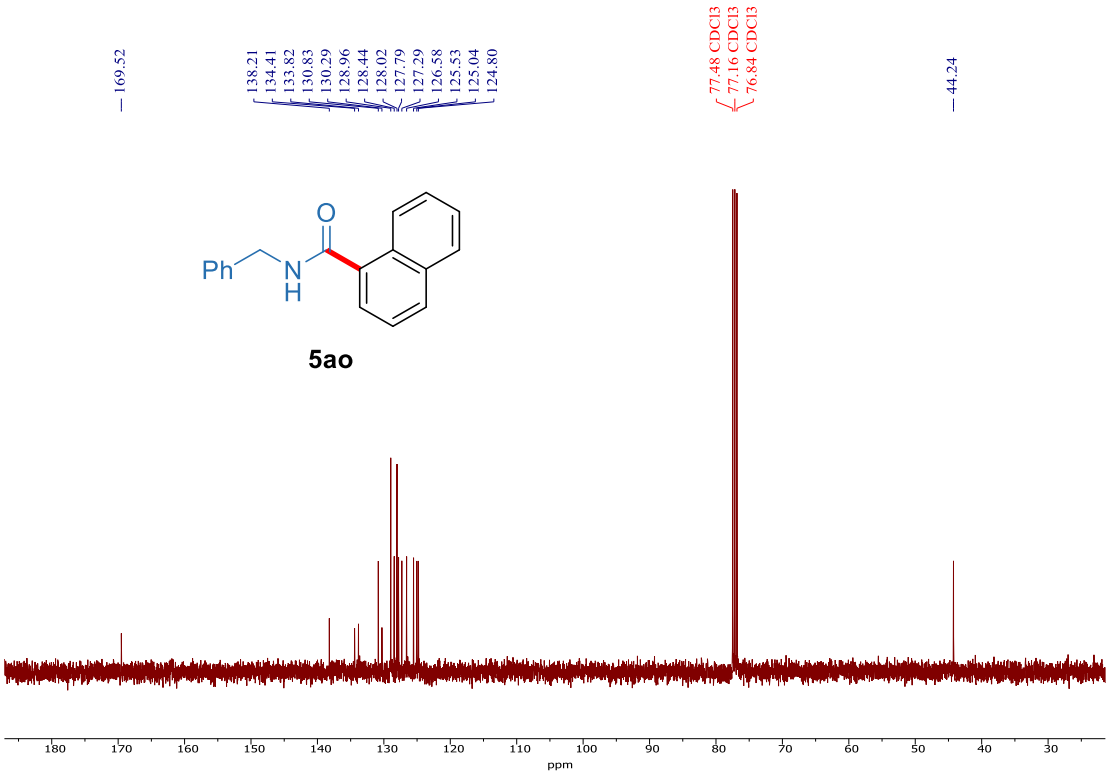
^{13}C NMR (101 MHz, $CDCl_3$) of **5an**



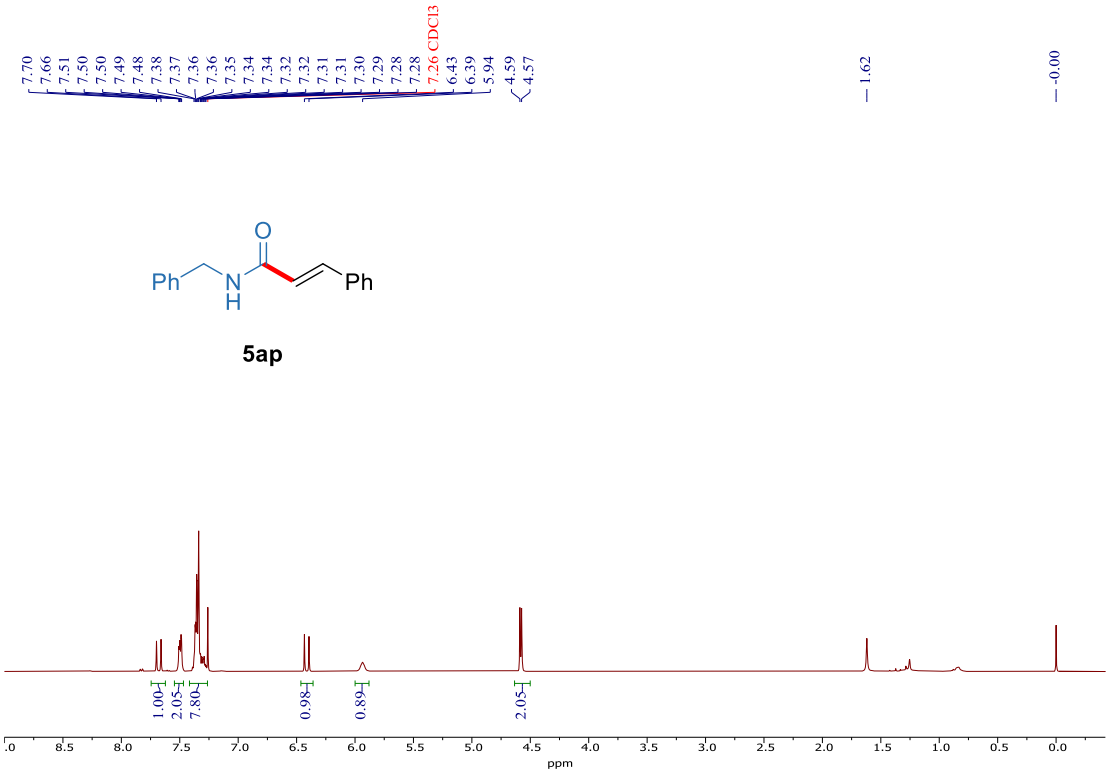
^{1}H NMR (400 MHz, $CDCl_3$) of **5ao** (*see procedure*)



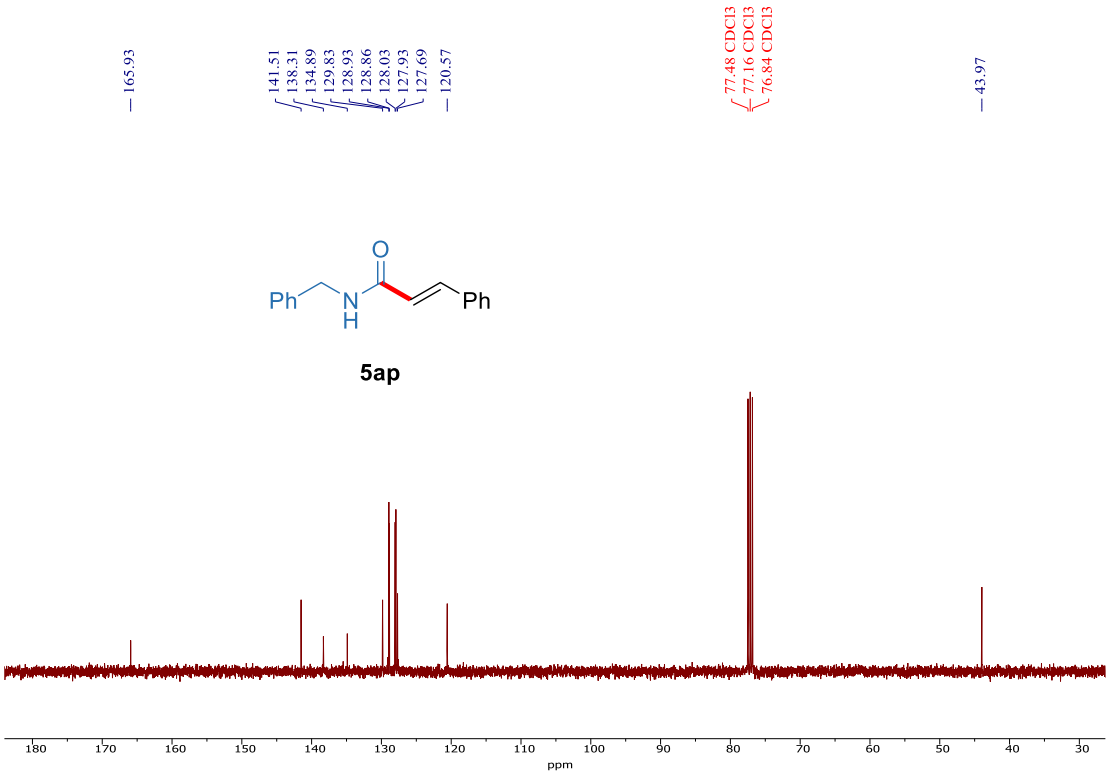
^{13}C NMR (101 MHz, $CDCl_3$) of **5ao**



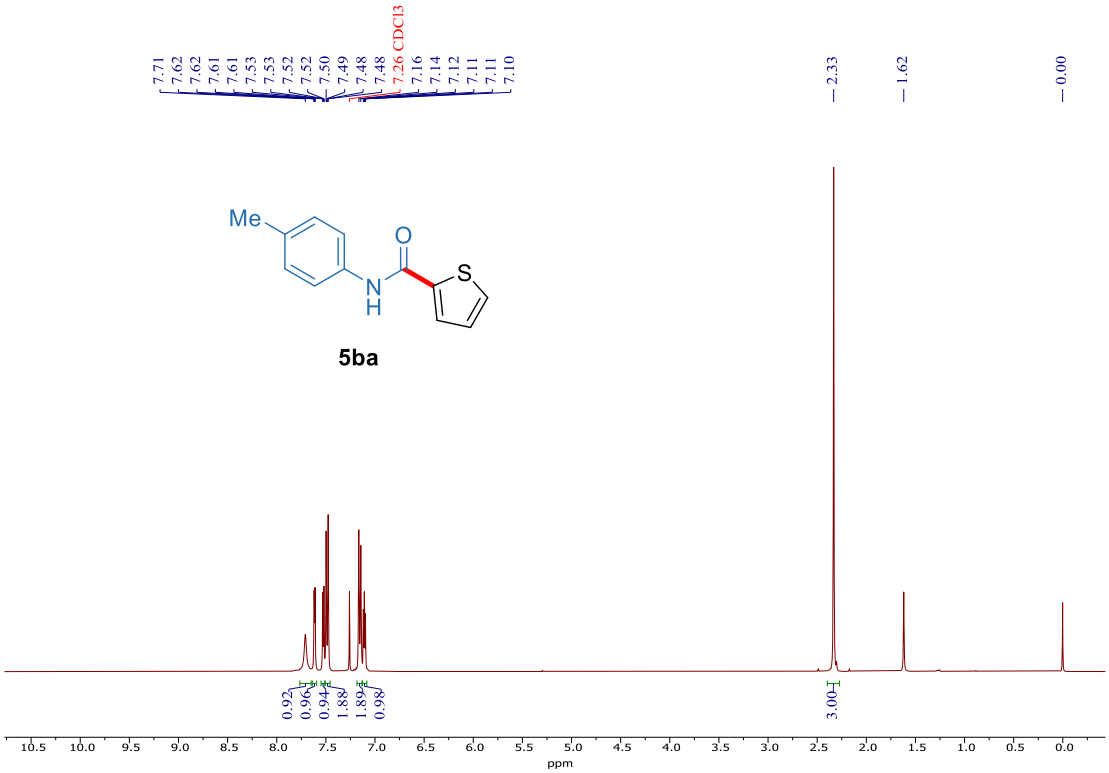
^{1}H NMR (400 MHz, $CDCl_3$) of **5ap** (*see procedure*)



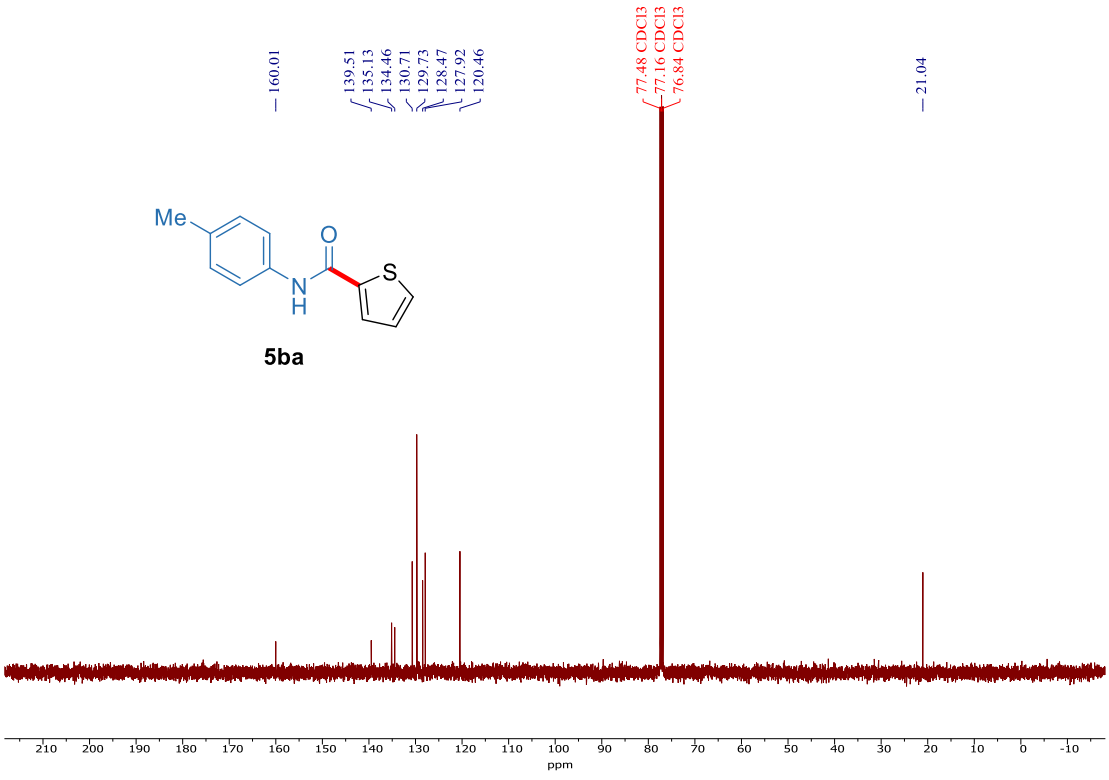
^{13}C NMR (101 MHz, $CDCl_3$) of **5ap**



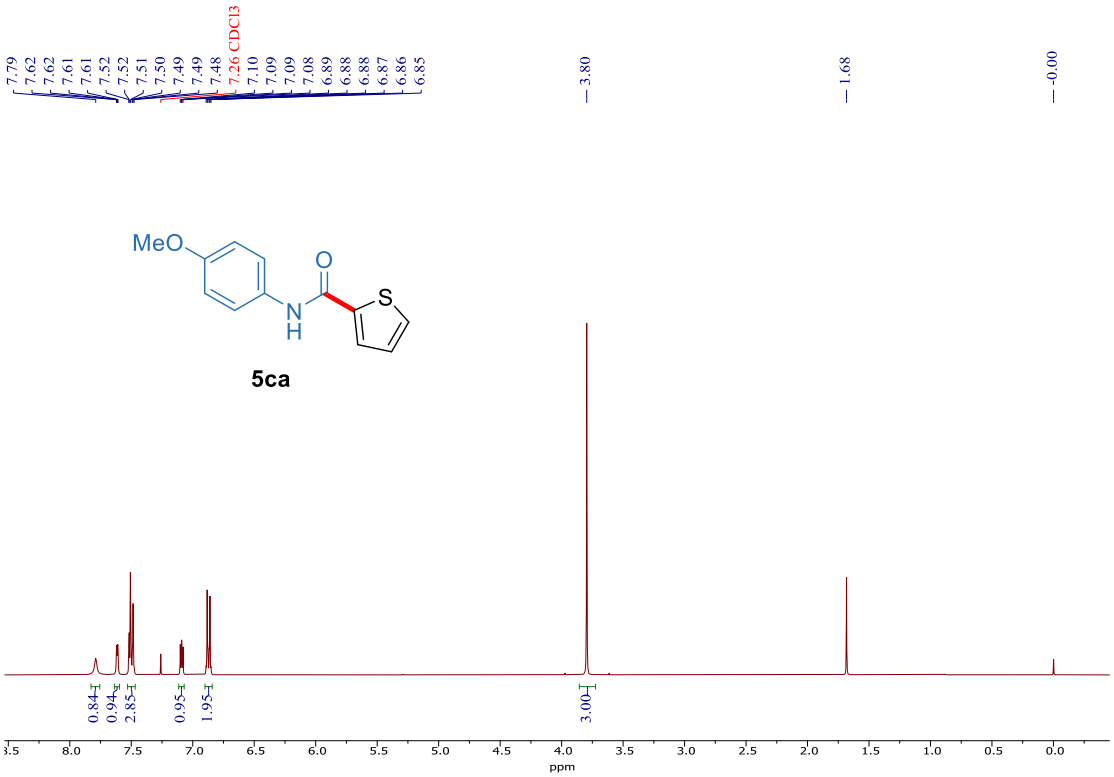
^{1}H NMR (400 MHz, $CDCl_3$) of **5ba** (*see procedure*)



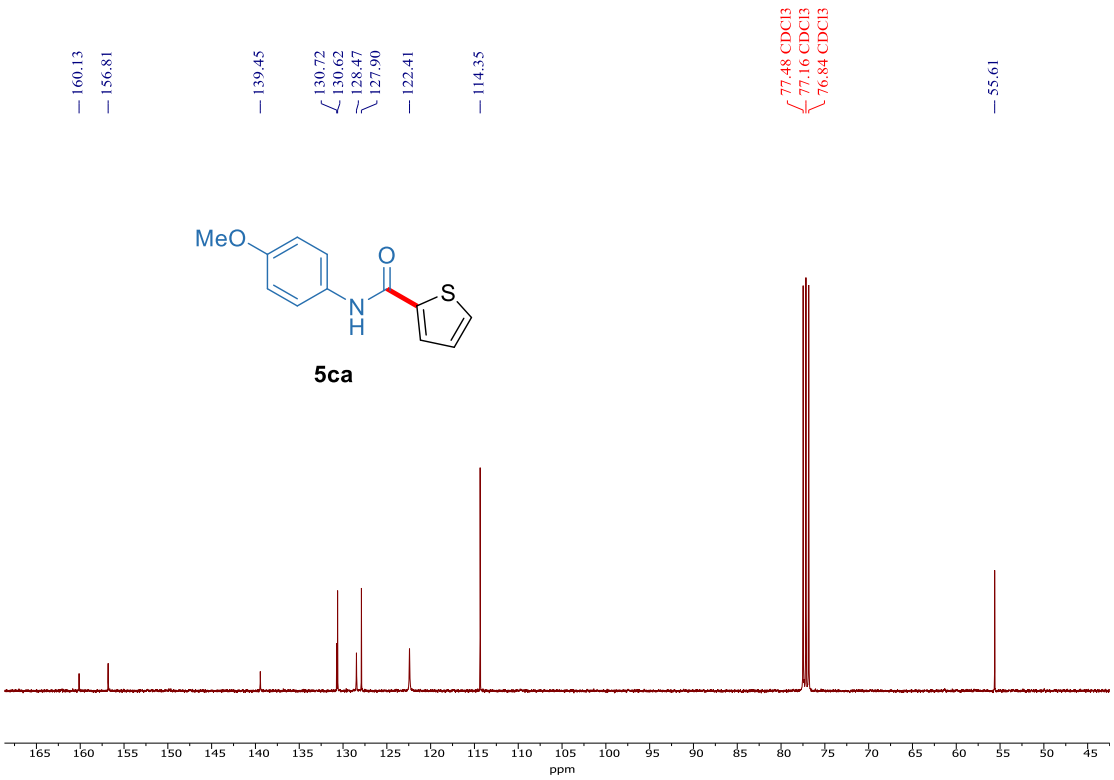
^{13}C NMR (101 MHz, $CDCl_3$) of **5ba**



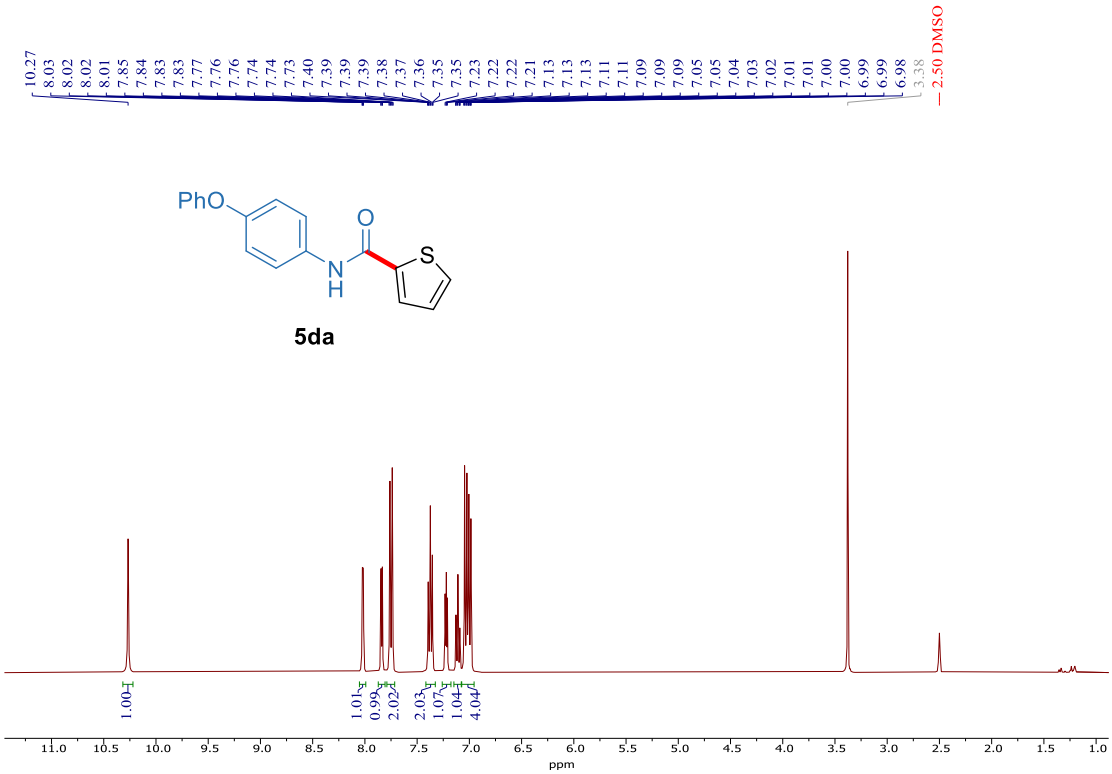
^{1}H NMR (400 MHz, $CDCl_3$) of **5ca** (*see procedure*)



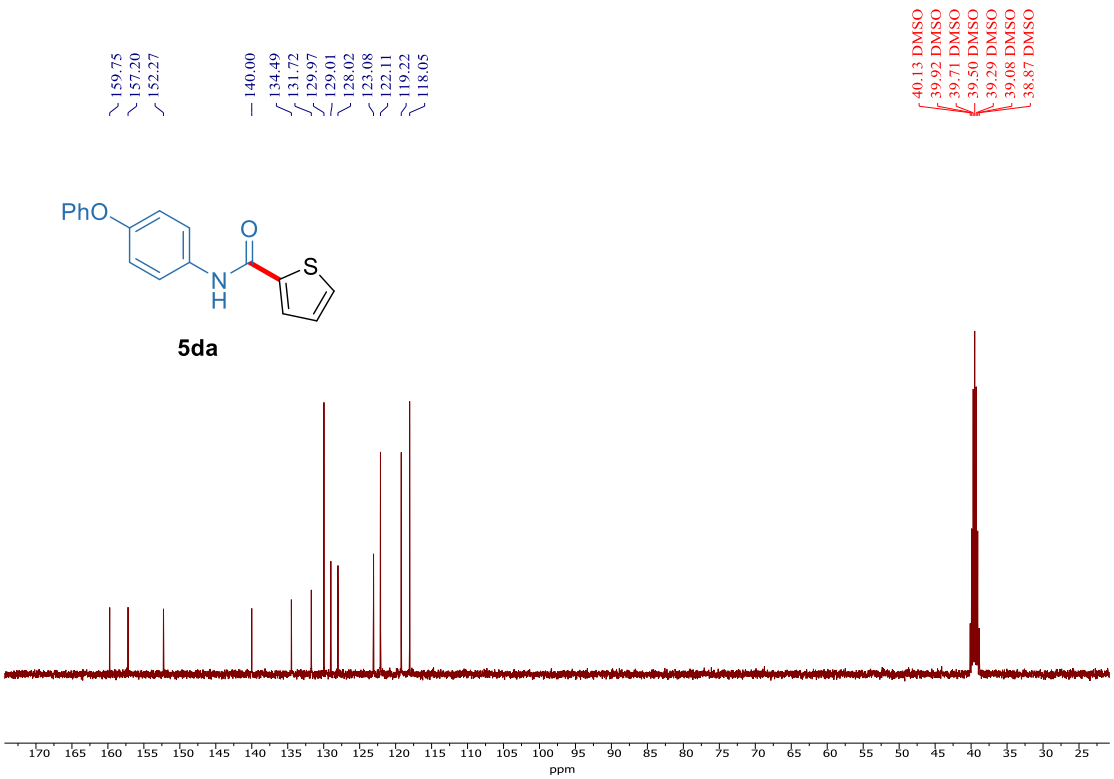
^{13}C NMR (101 MHz, $CDCl_3$) of **5ca**



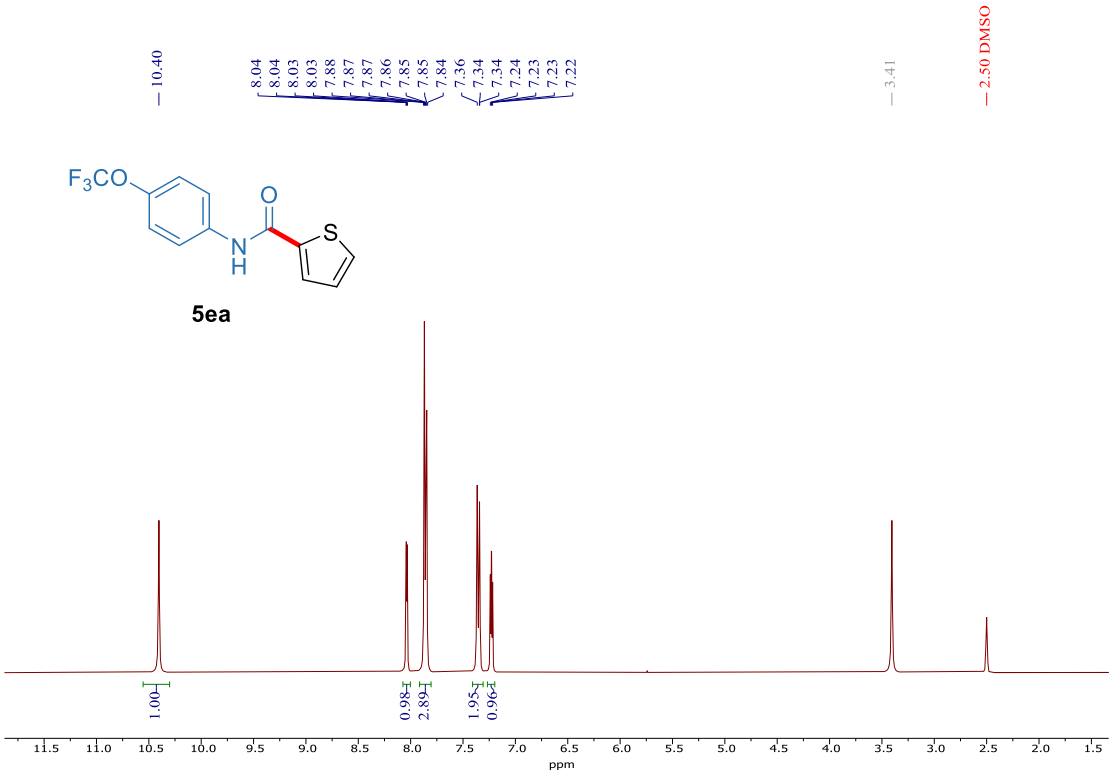
^{1}H NMR (400 MHz, d_6-DMSO) of **5da** (*see procedure*)



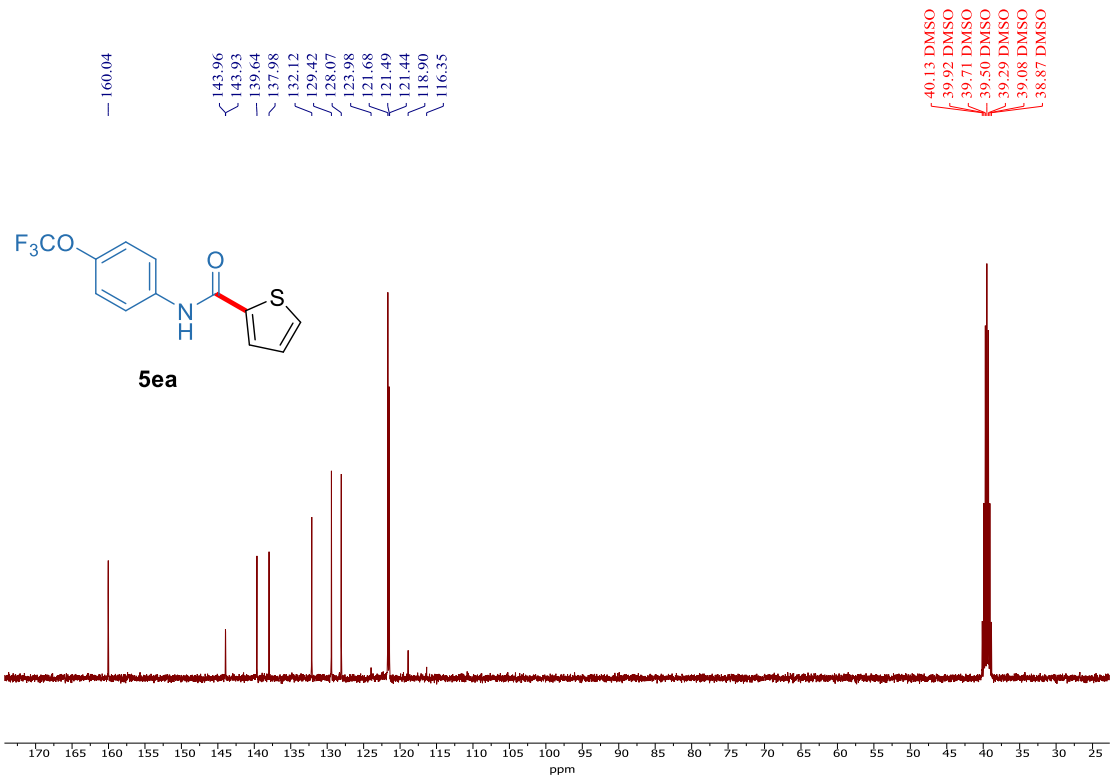
^{13}C NMR (101 MHz, d_6-DMSO) of **5da**



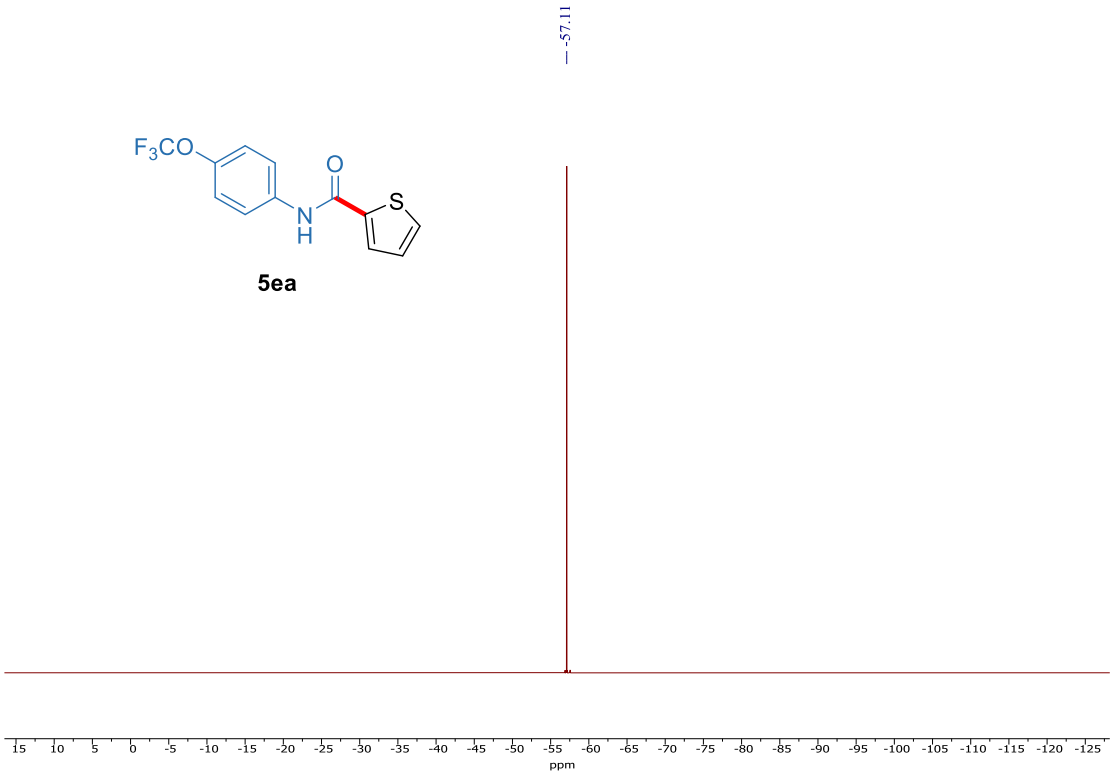
^{1}H NMR (400 MHz, d_6-DMSO) of **5ea** (*see procedure*)



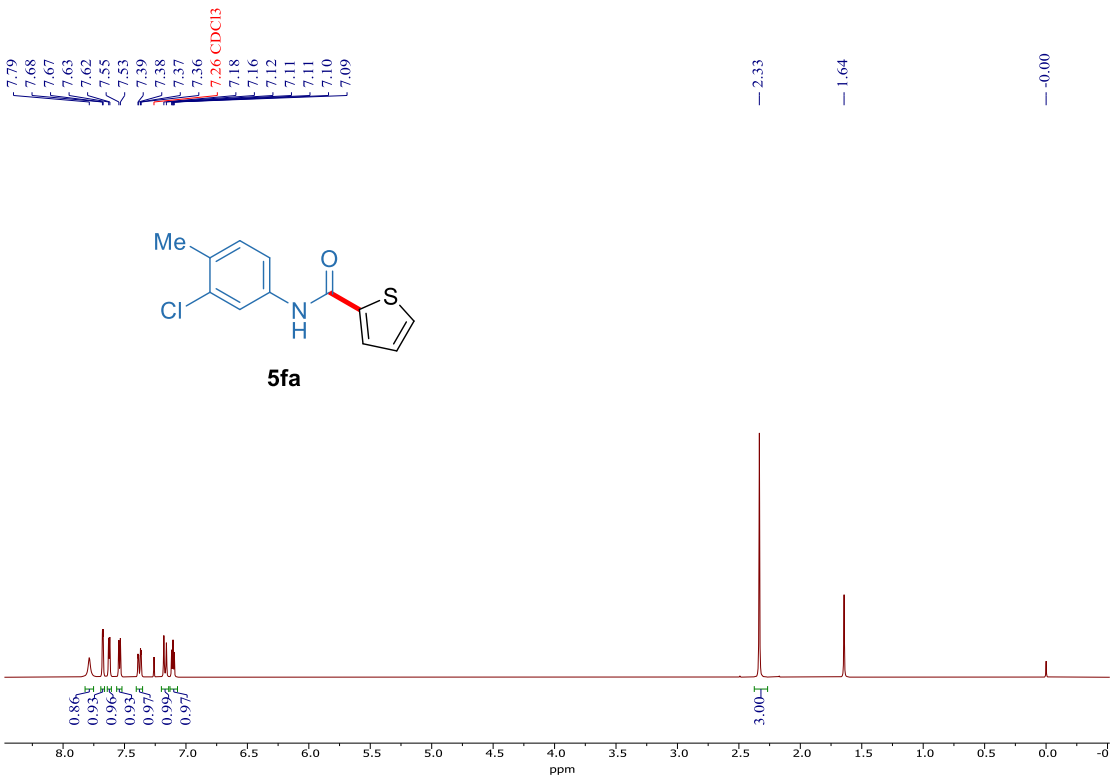
^{13}C NMR (101 MHz, d_6-DMSO) of **5ea**



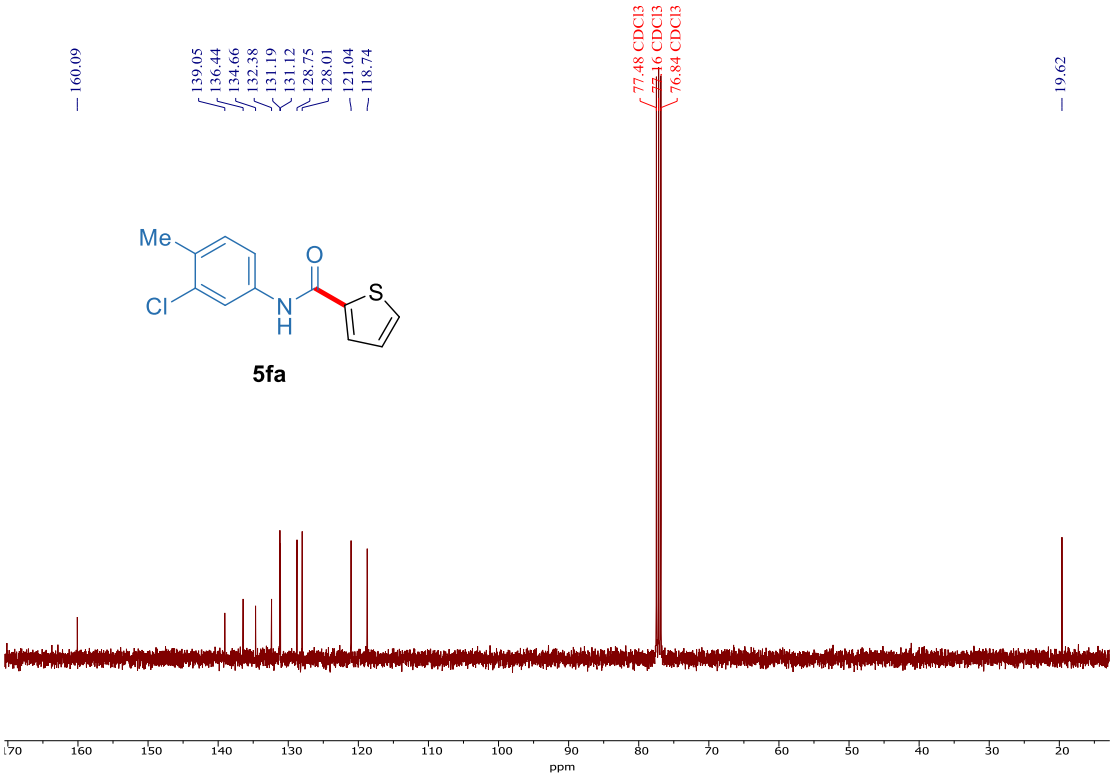
^{19}F NMR (376 MHz, d_6-DMSO) of **5ea**



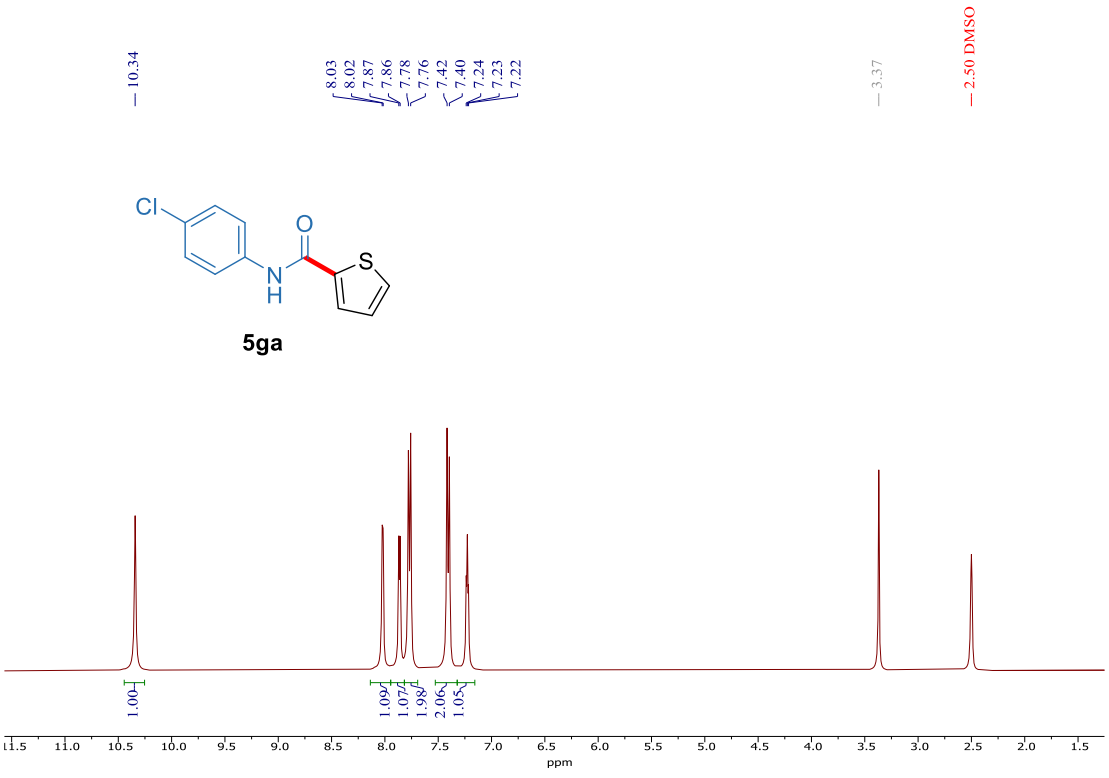
^{1}H NMR (400 MHz, $CDCl_3$) of **5fa** (*see procedure*)



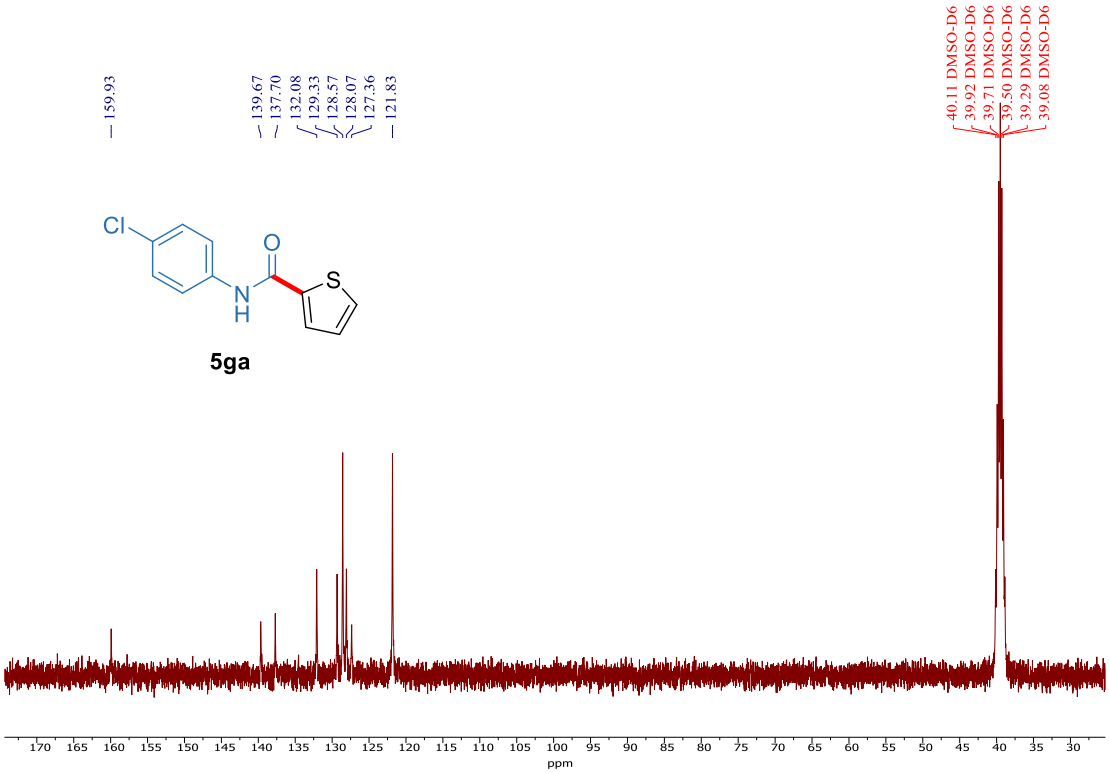
^{13}C NMR (101 MHz, $CDCl_3$) of **5fa**



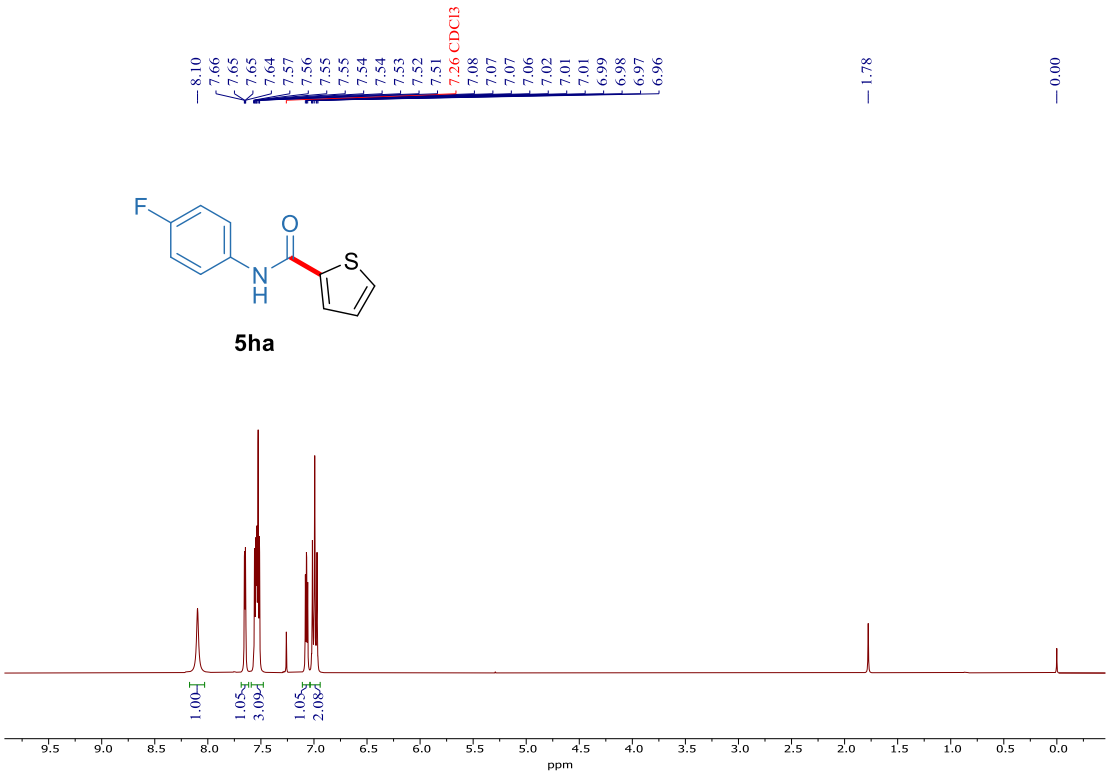
^{1}H NMR (400 MHz, d_6-DMSO) of **5ga** (*see procedure*)



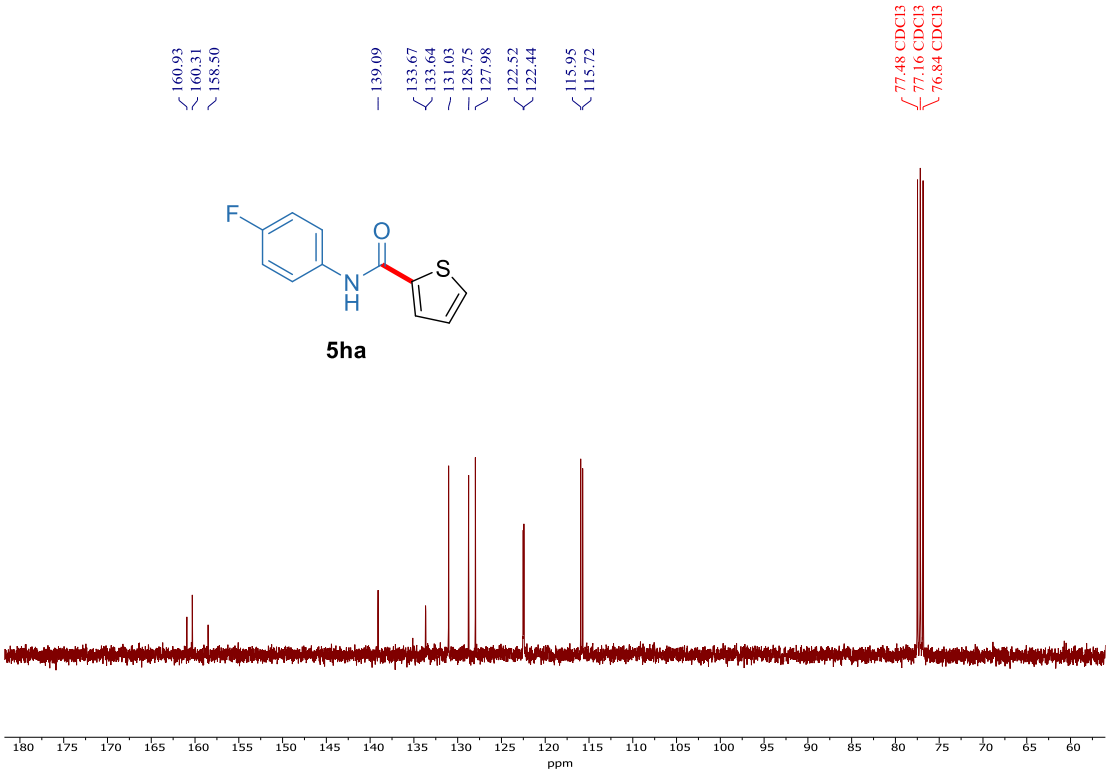
^{13}C NMR (101 MHz, d_6-DMSO) of **5ga**



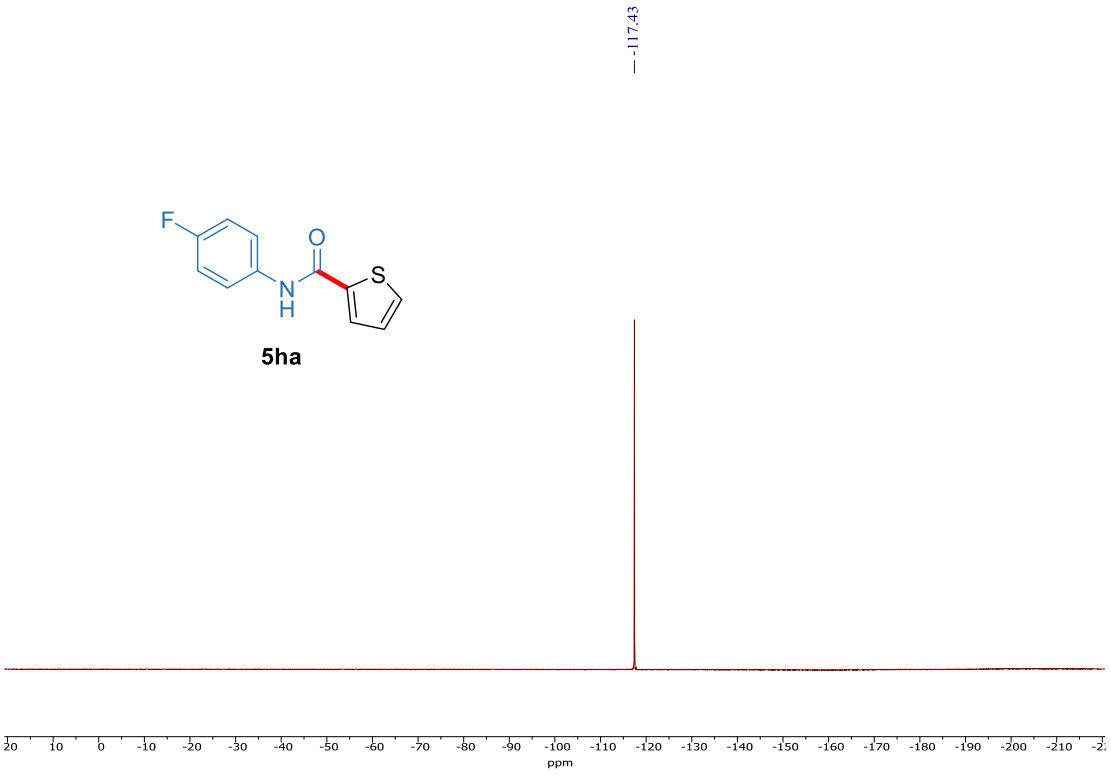
^{1}H NMR (400 MHz, $CDCl_3$) of **5ha** (*see procedure*)



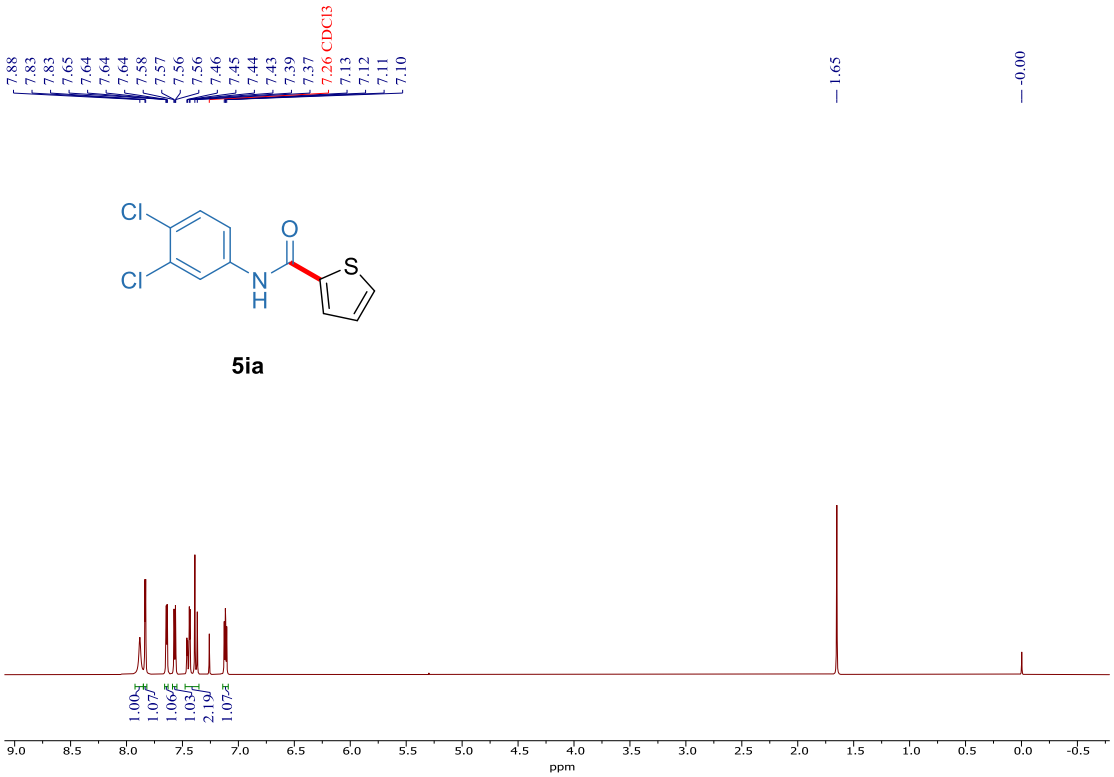
^{13}C NMR (101 MHz, $CDCl_3$) of **5ha**



^{19}F NMR (376 MHz, $CDCl_3$) of **5ha**

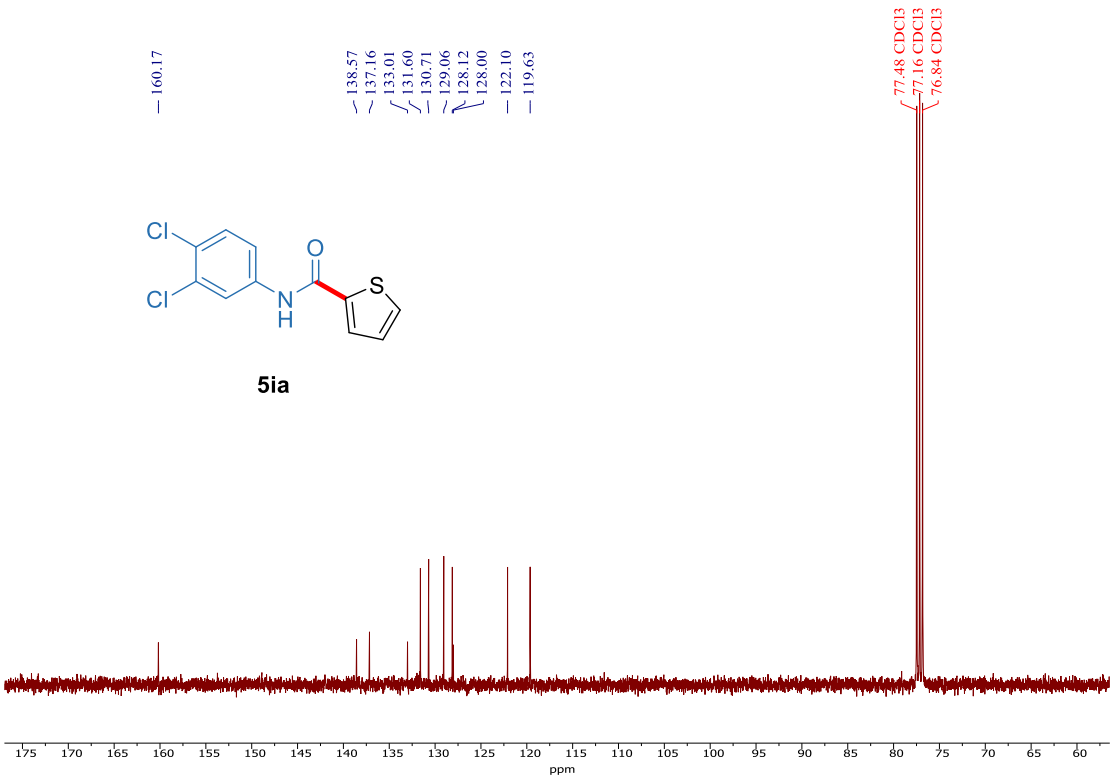


^{1}H NMR (400 MHz, $CDCl_3$) of **5ia** (*see procedure*)



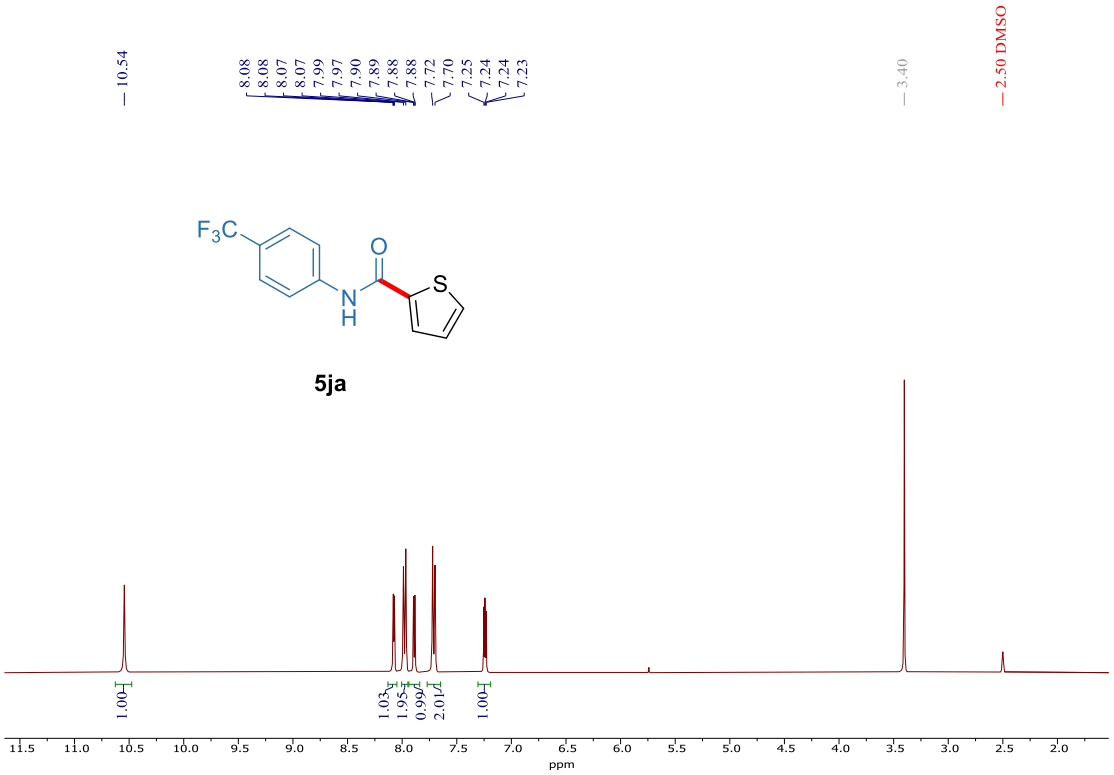
5ia

^{13}C NMR (101 MHz, $CDCl_3$) of **5ia**

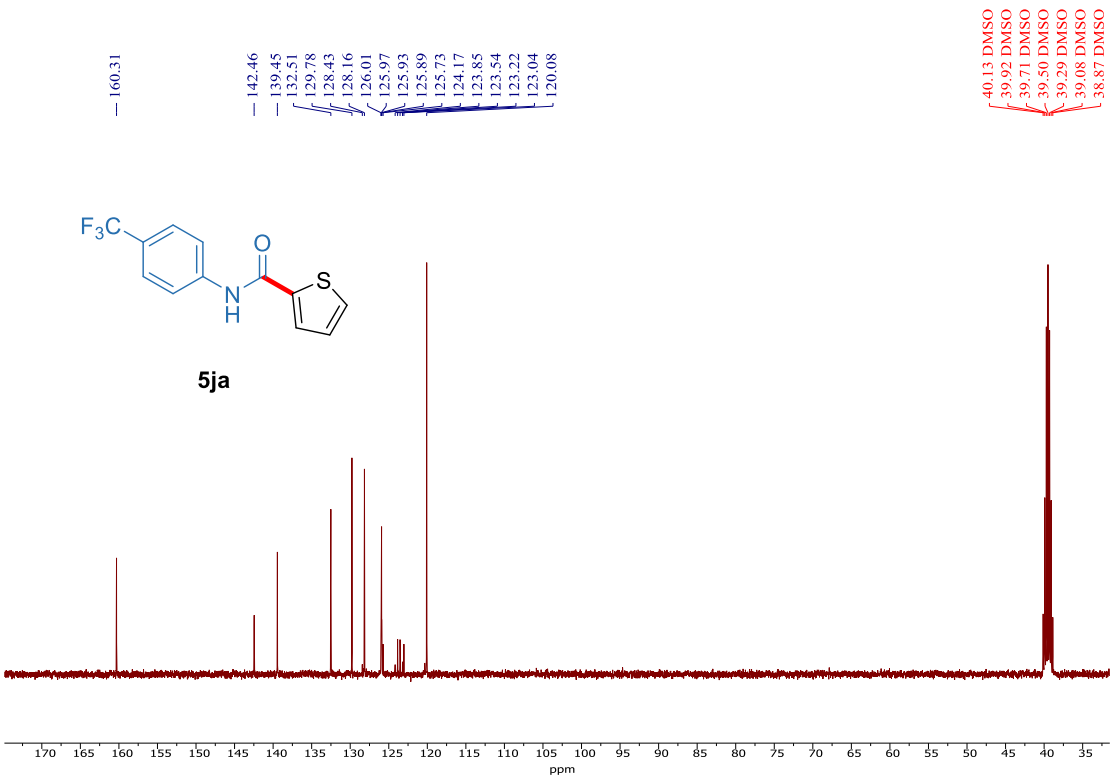


5ia

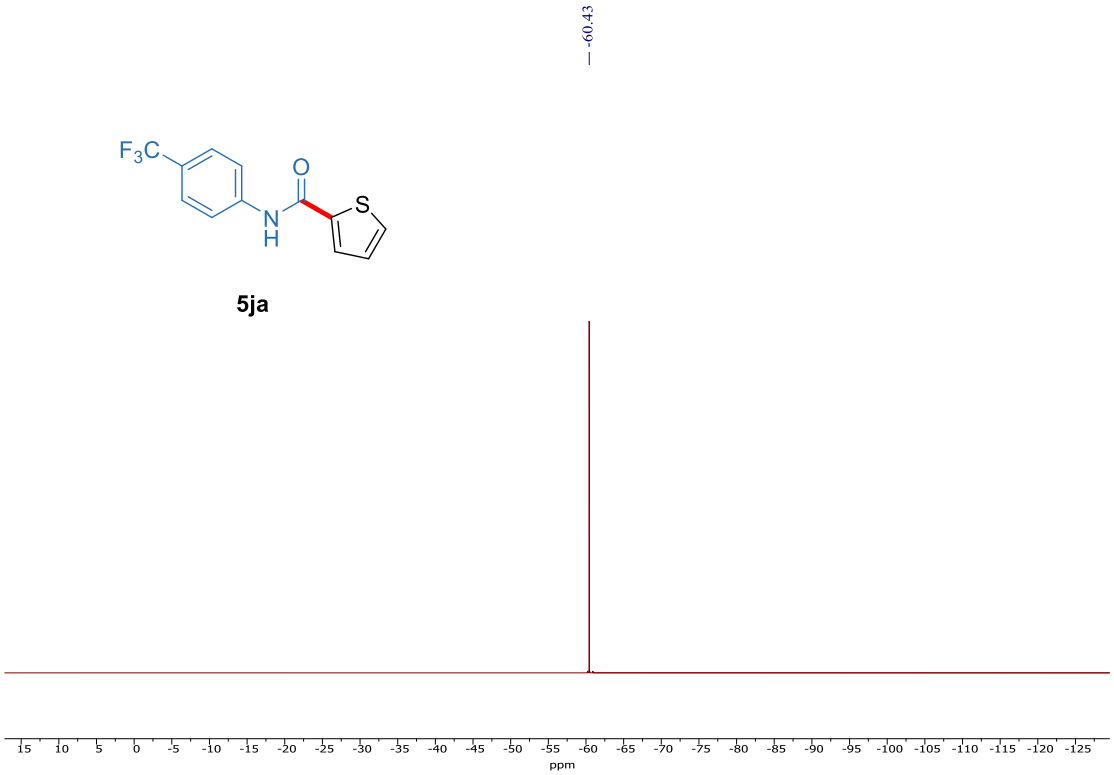
^{1}H NMR (400 MHz, d_6-DMSO) of **5ja** (*see procedure*)



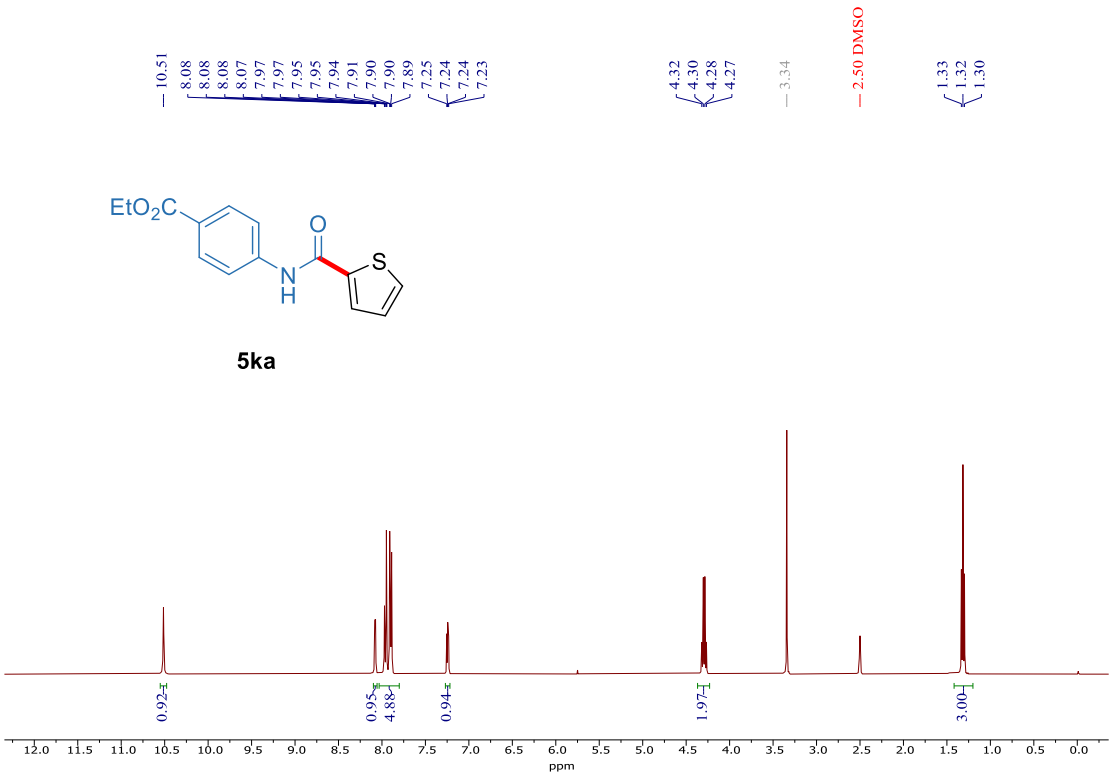
^{13}C NMR (101 MHz, d_6-DMSO) of **5ja**



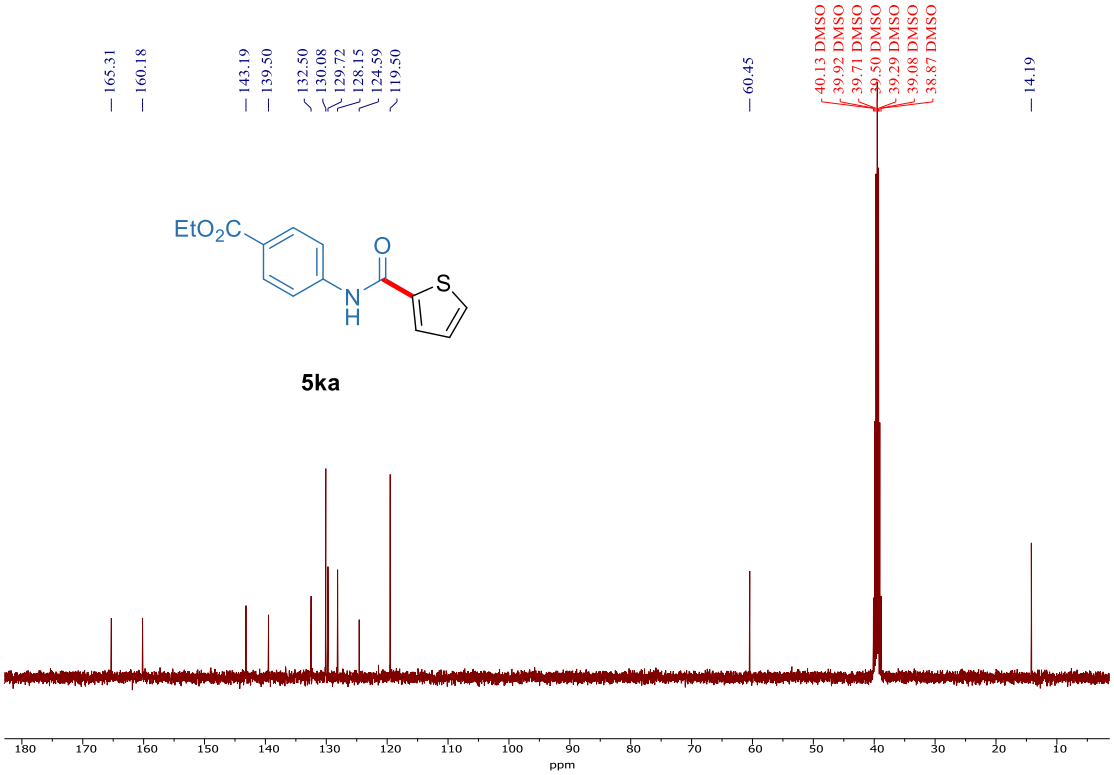
^{19}F NMR (376 MHz, d_6-DMSO) of **5ja**



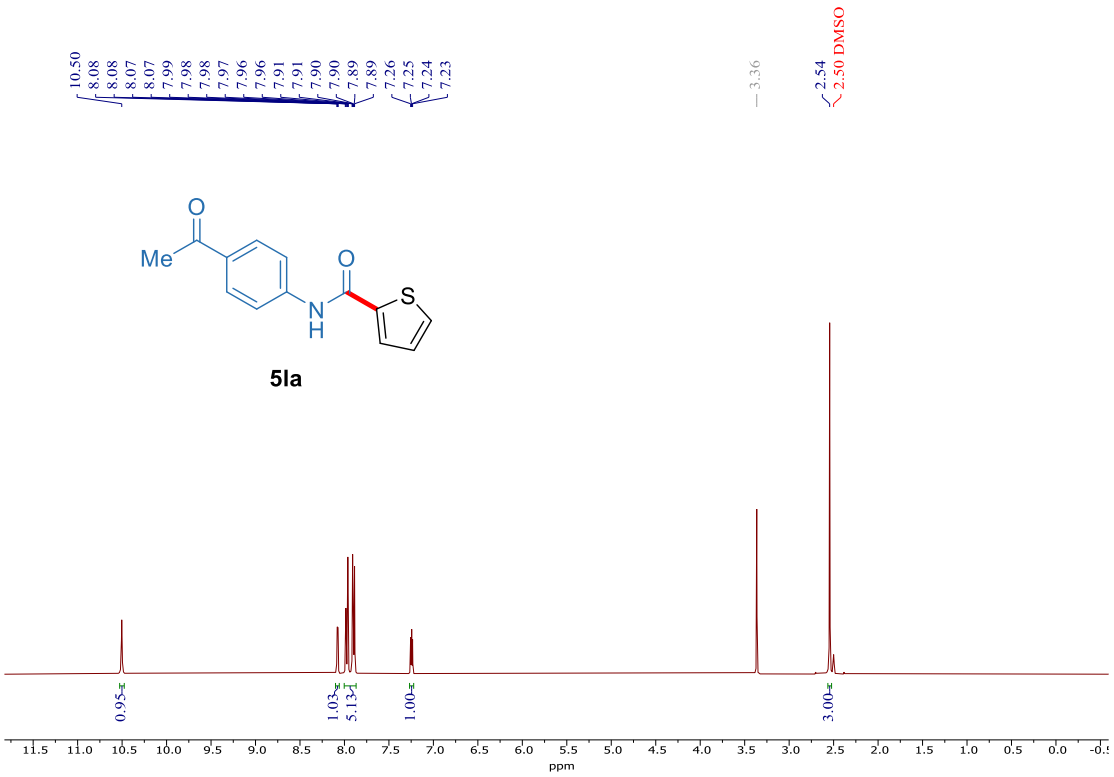
^{1}H NMR (400 MHz, d_6-DMSO) of **5ka** (*see procedure*)



^{13}C NMR (101 MHz, d_6-DMSO) of **5ka**



^{1}H NMR (400 MHz, d_6-DMSO) of **5la** (*see procedure*)



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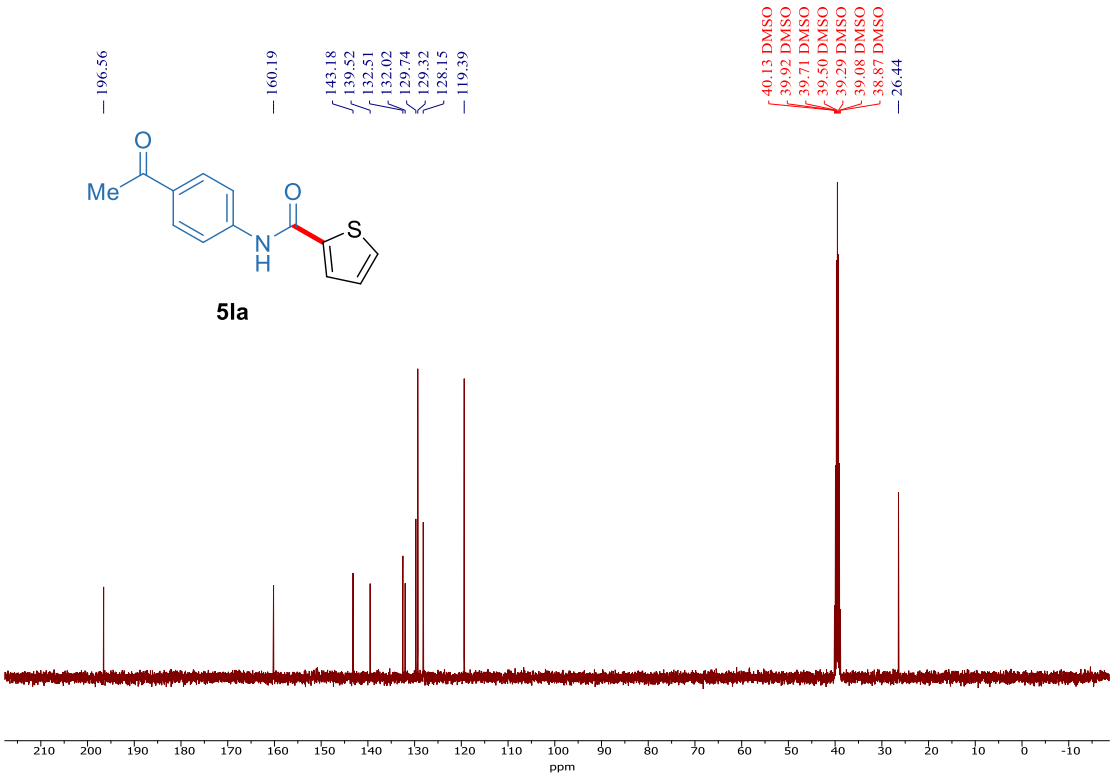
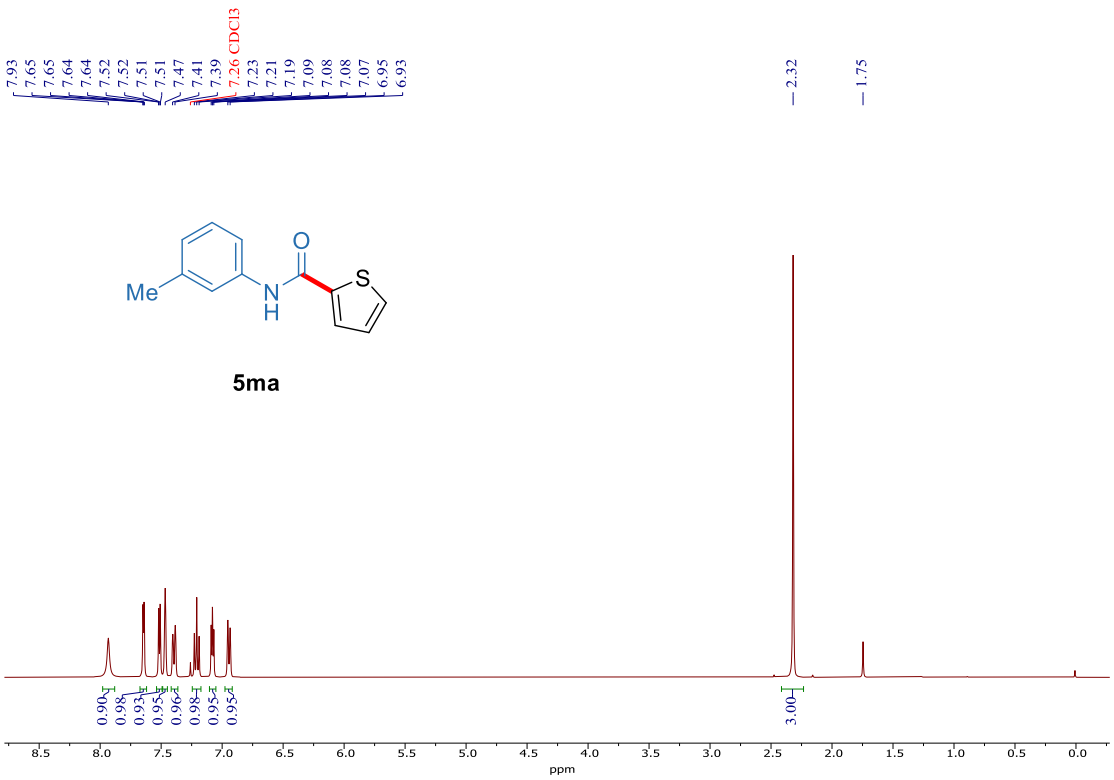
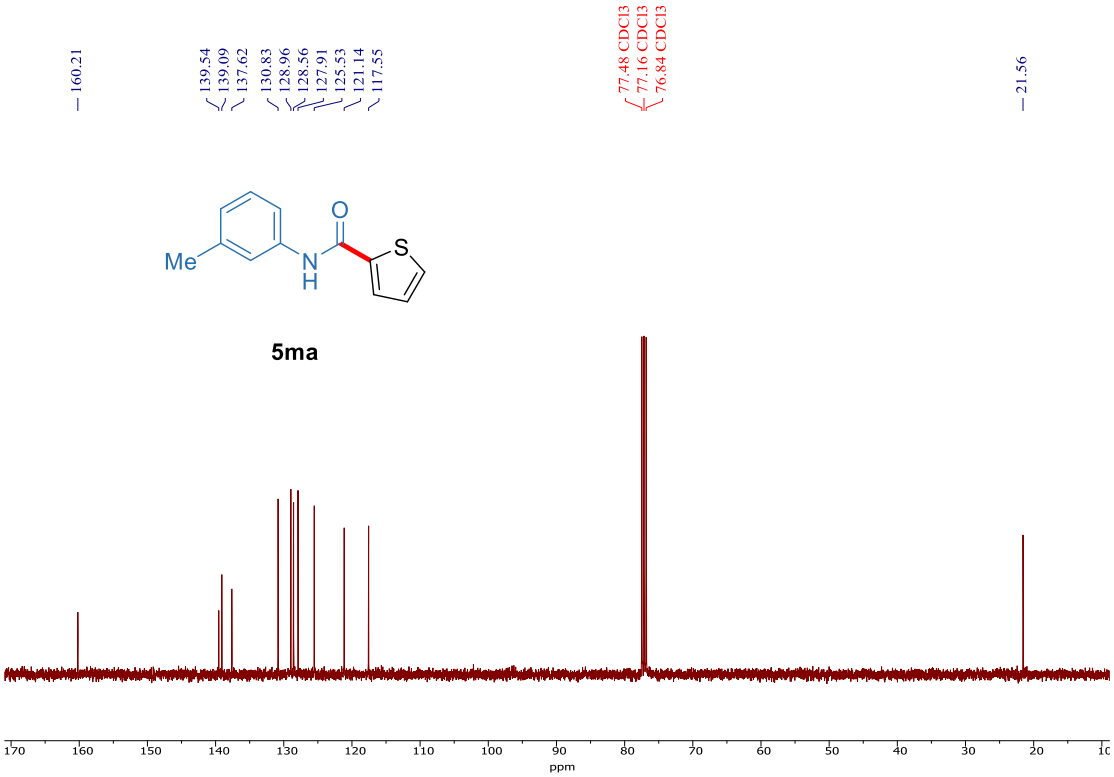


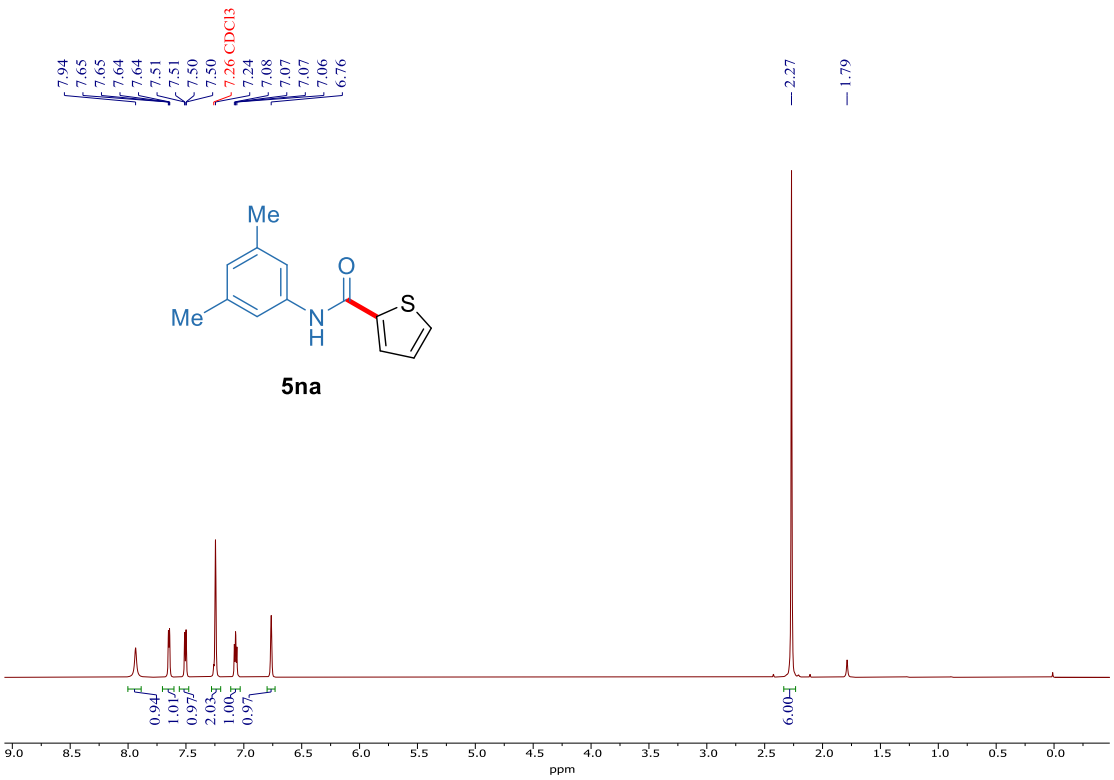
^{1}H NMR (400 MHz, $CDCl_3$) of **5ma** (*see procedure*)



^{13}C NMR (101 MHz, $CDCl_3$) of **5ma**



^{1}H NMR (400 MHz, $CDCl_3$) of **5na** (*see procedure*)



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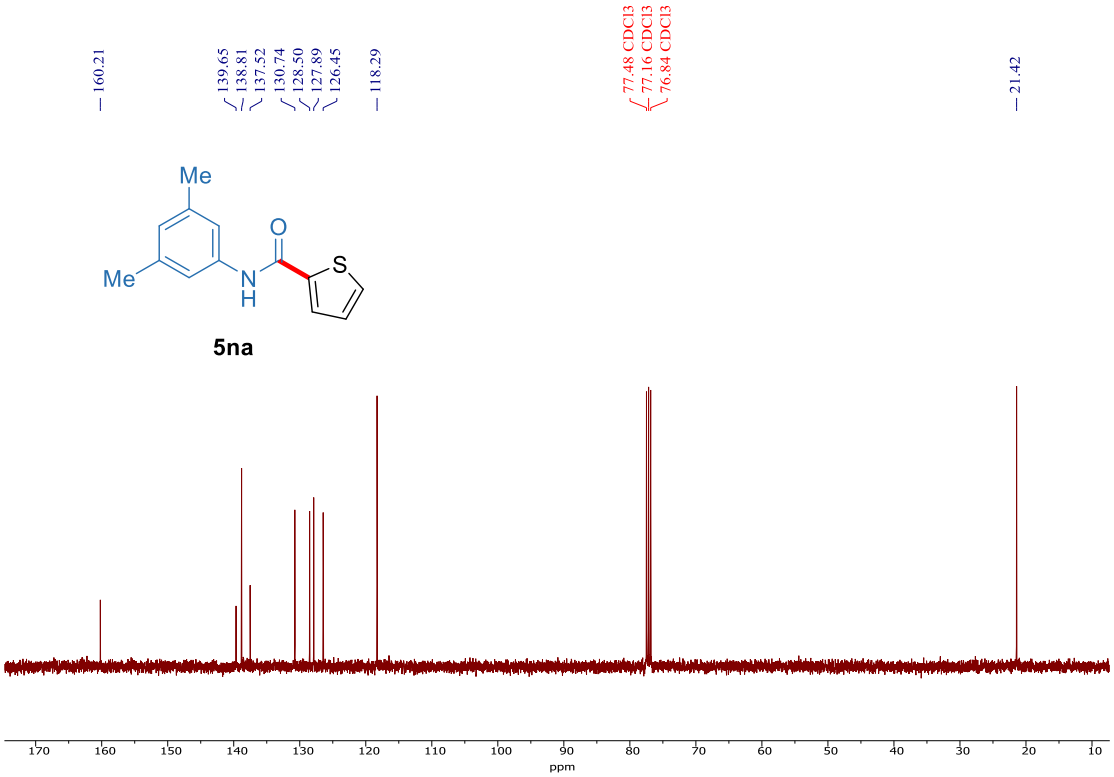
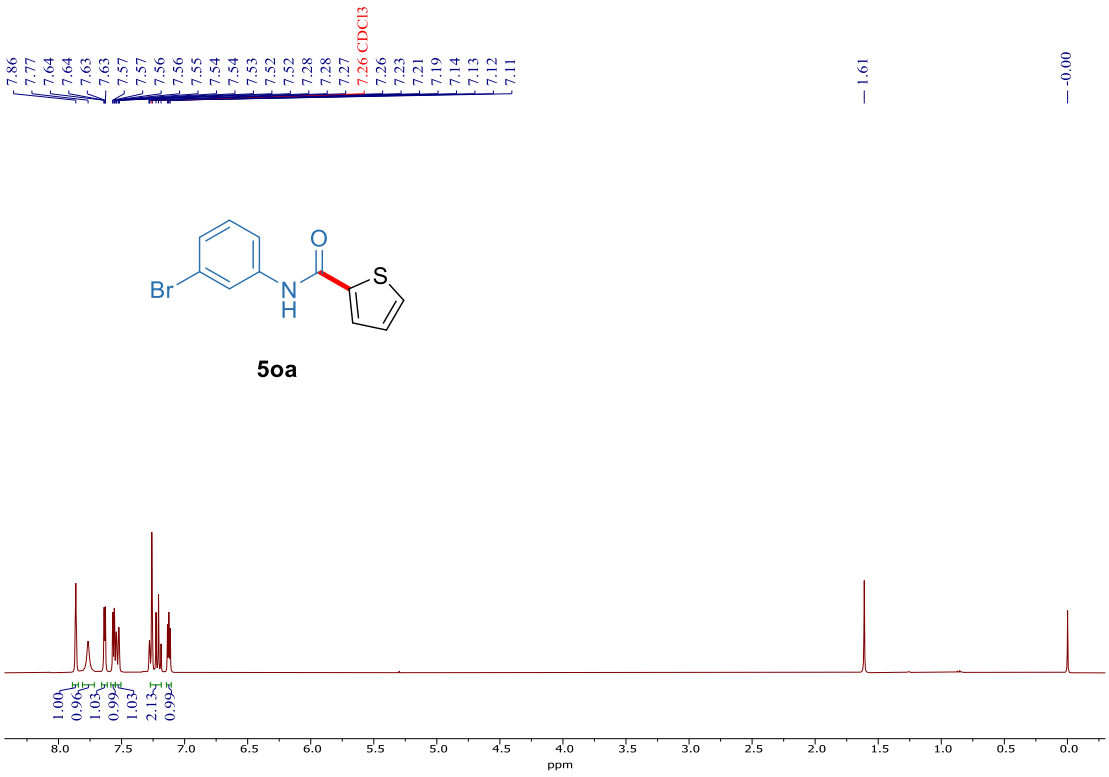


^{1}H NMR (400 MHz, $CDCl_3$) of **5oa** (*see procedure*)



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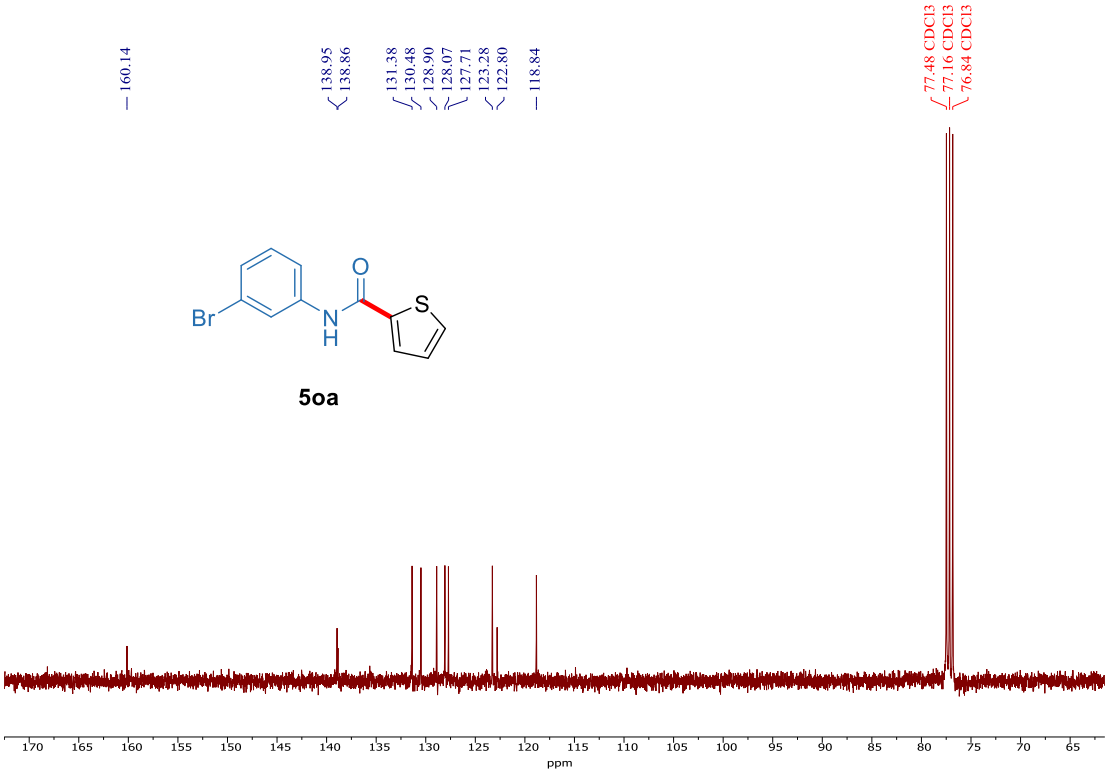
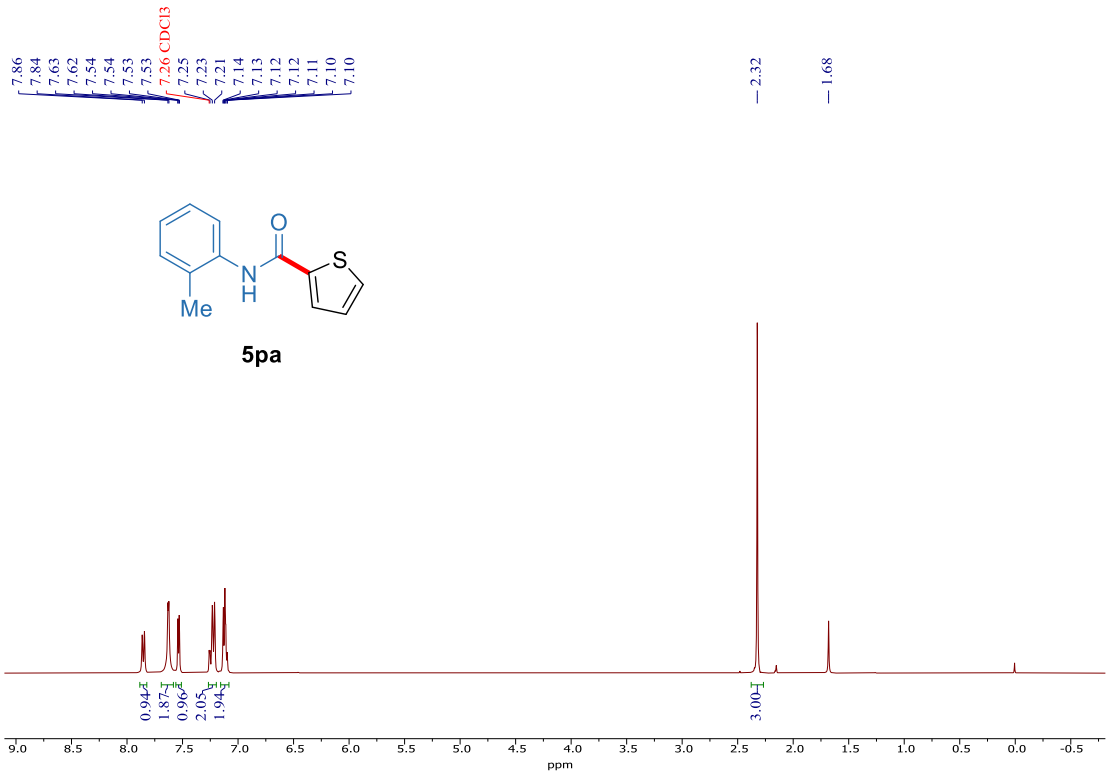


^{1}H NMR (400 MHz, $CDCl_3$) of **5pa** (*see procedure*)



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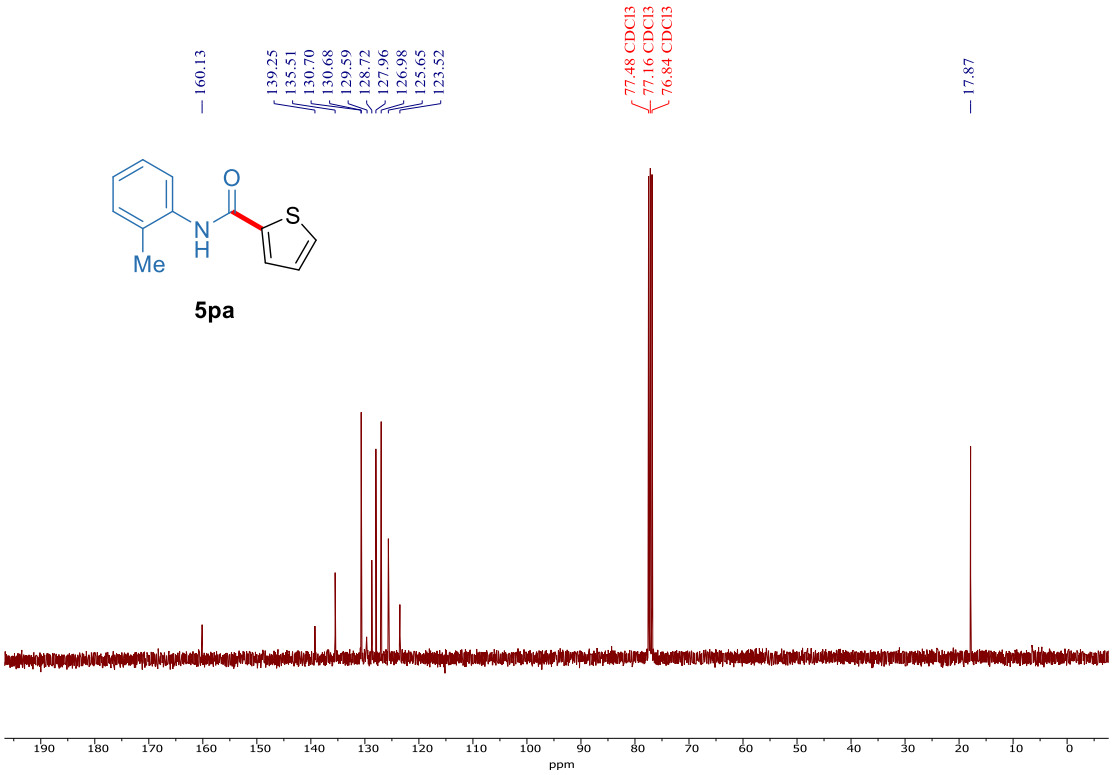

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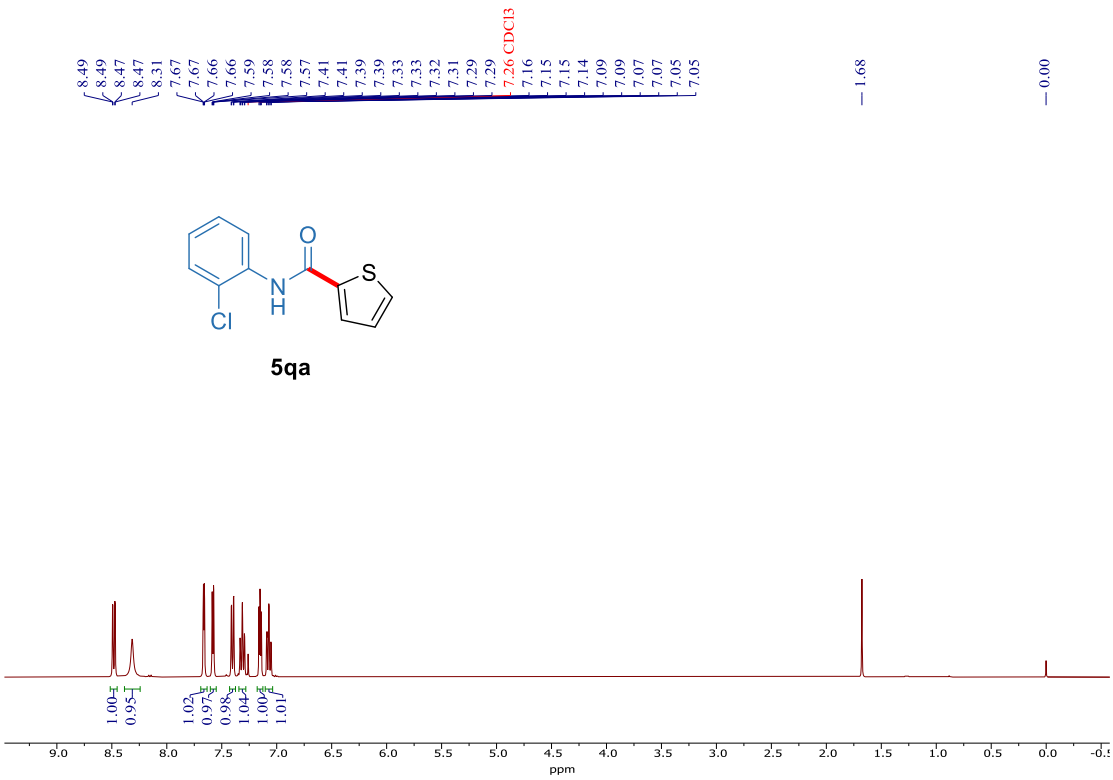

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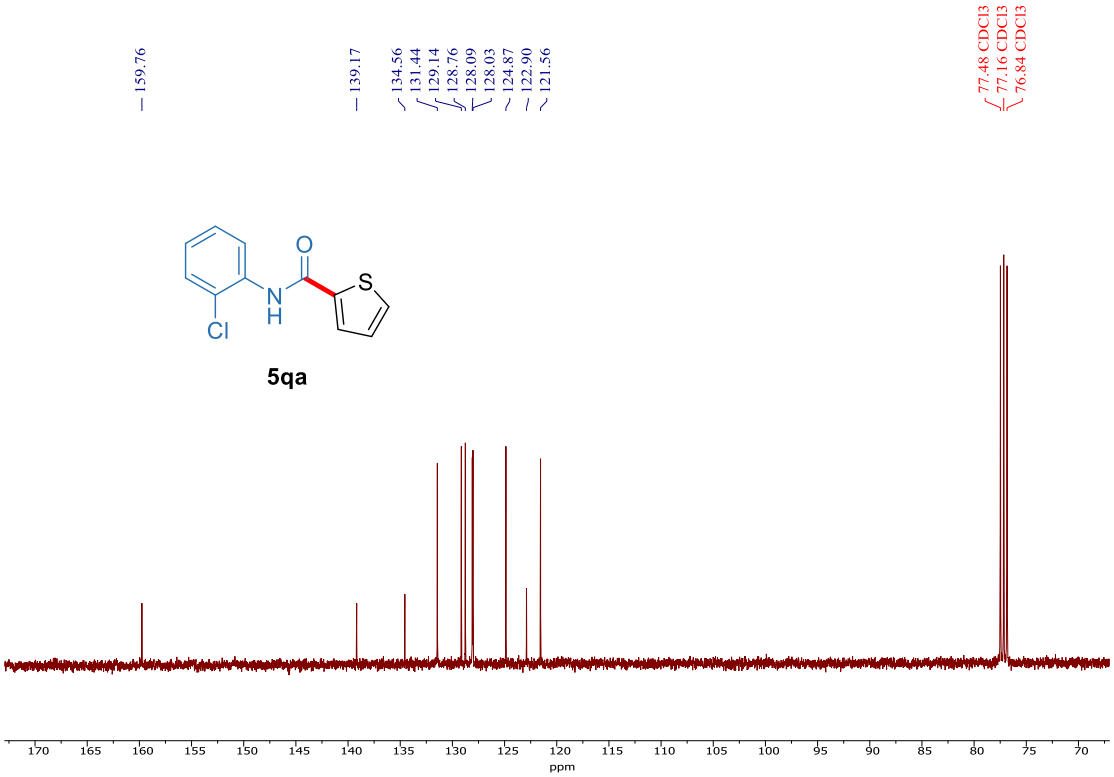

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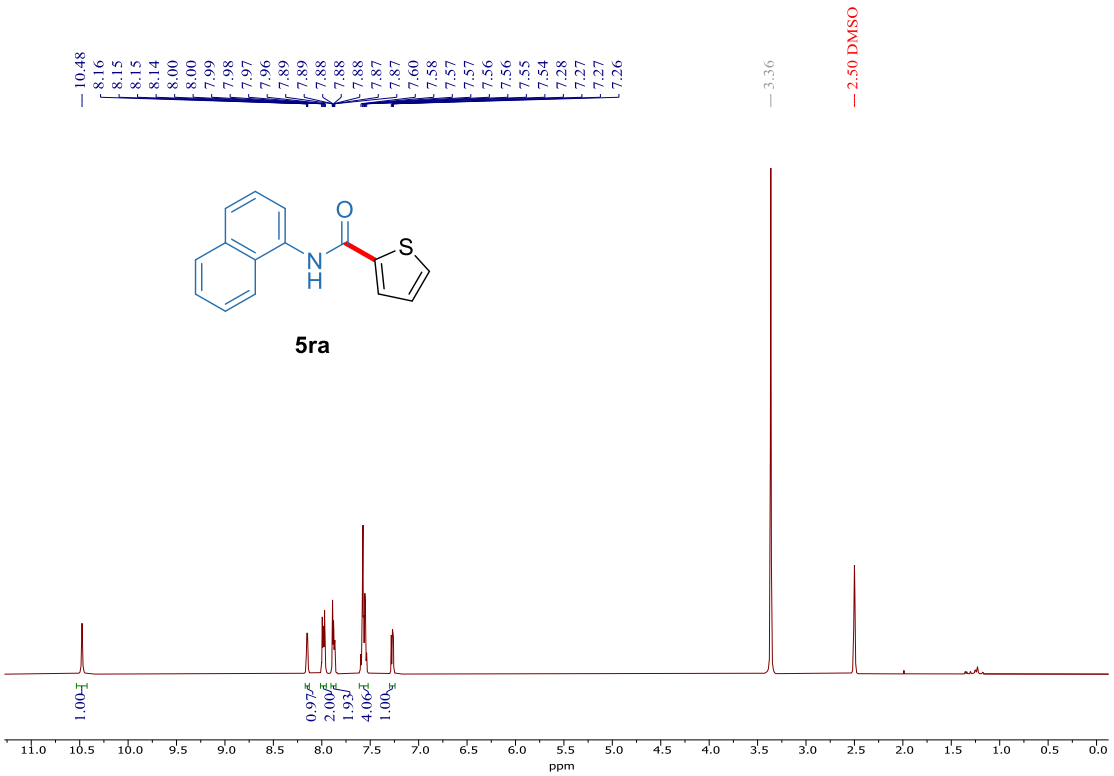
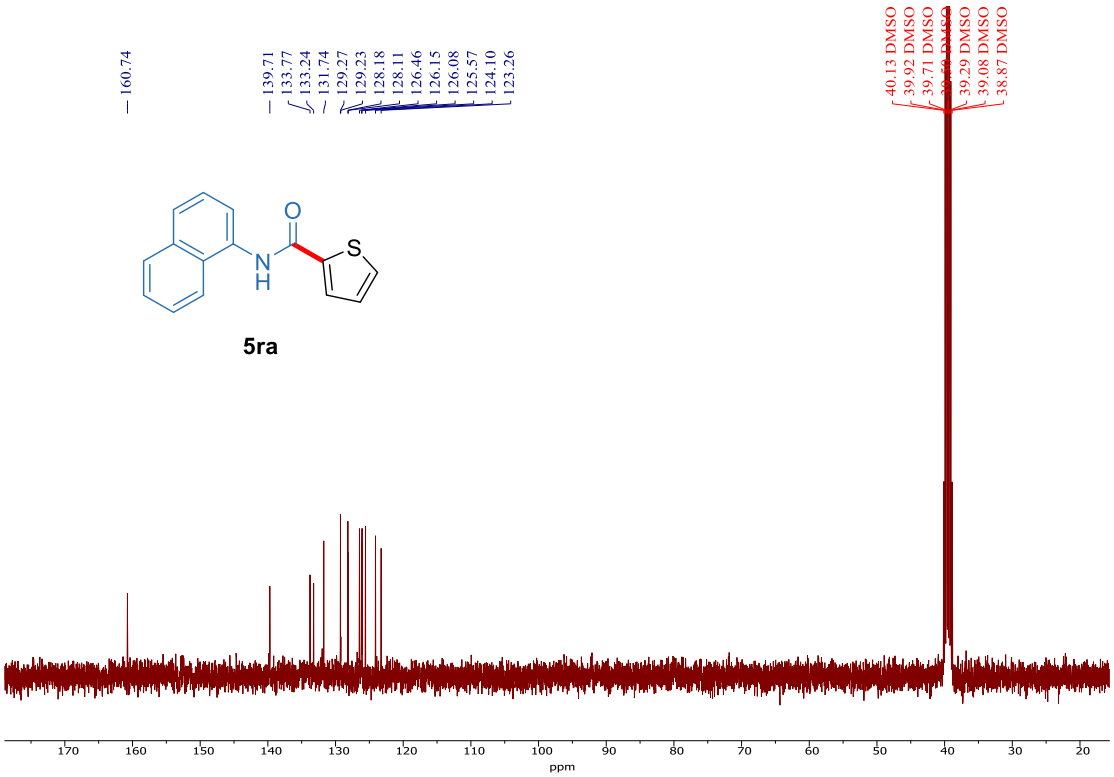


^{13}C NMR (101 MHz, d_6-DMSO) of **5ra**



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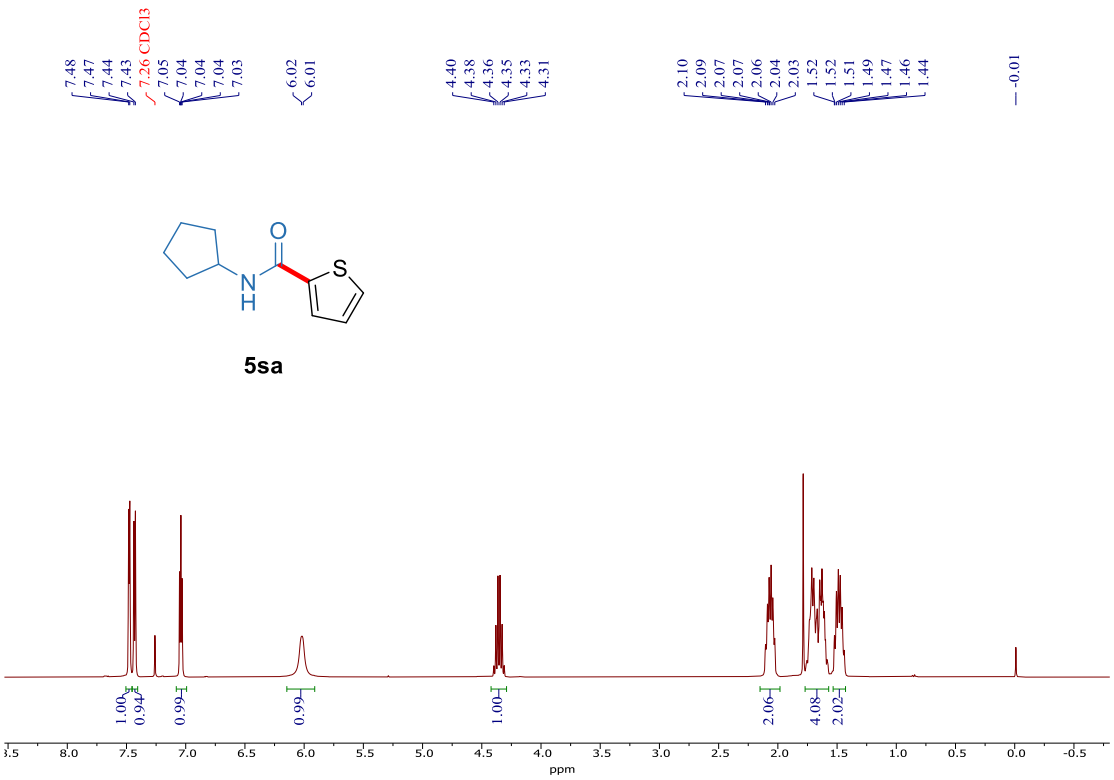

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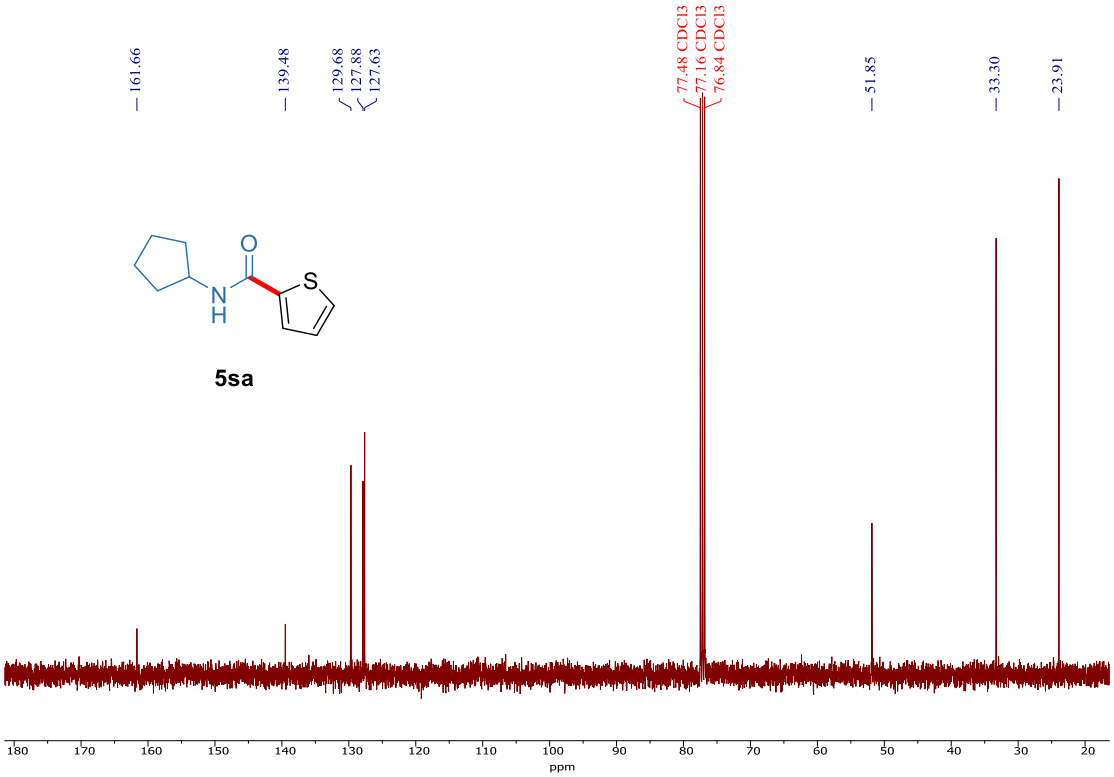

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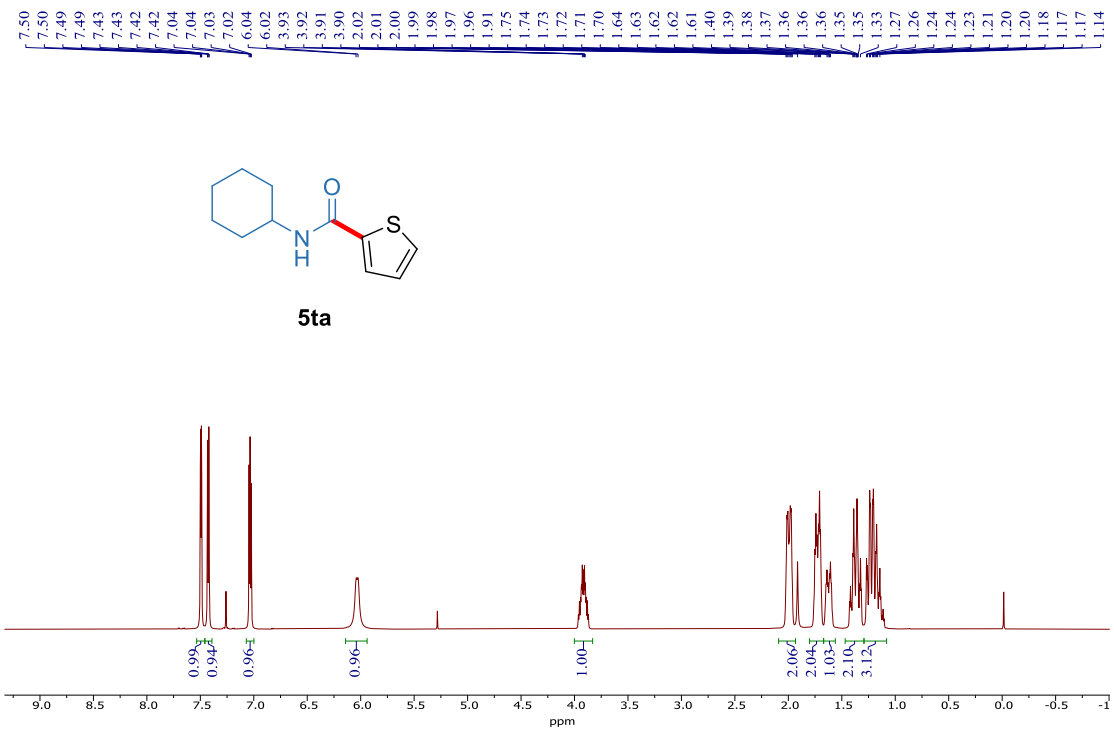

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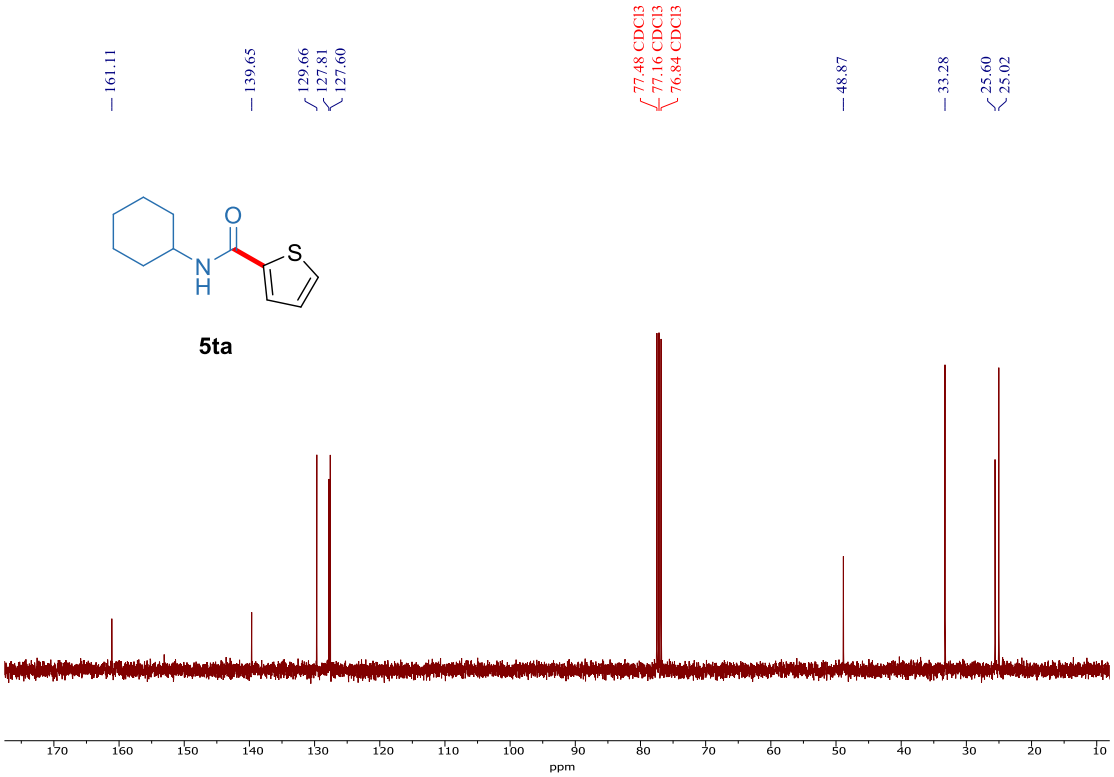

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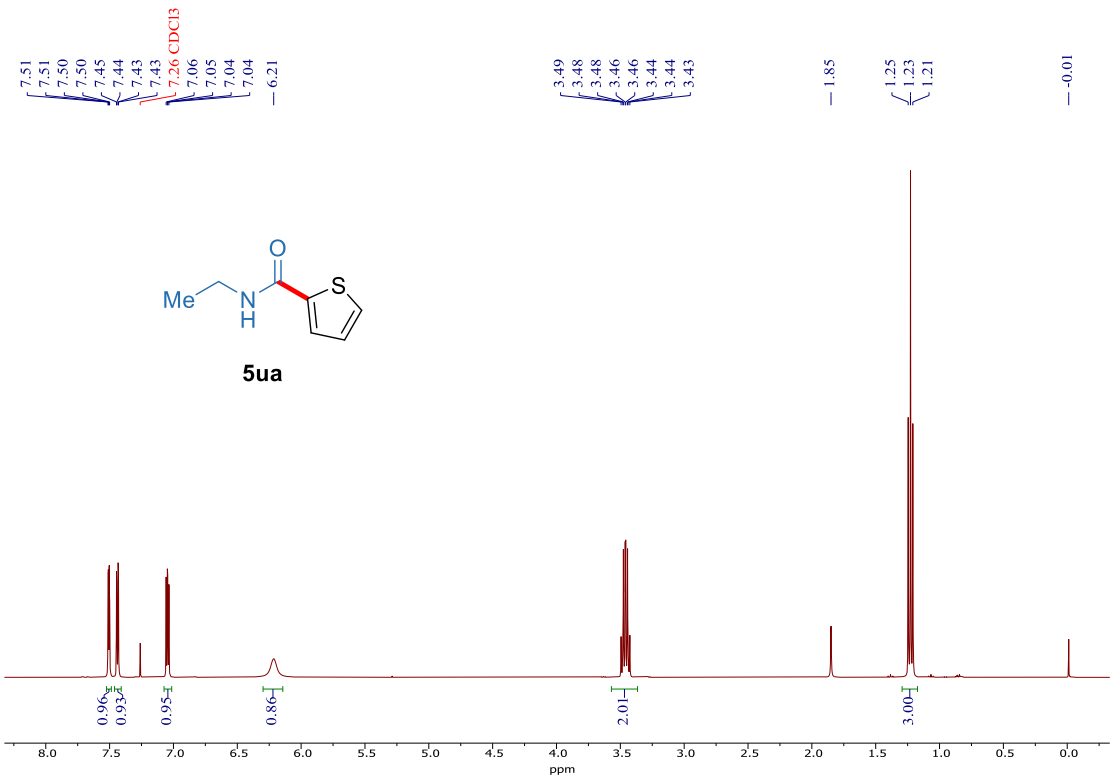
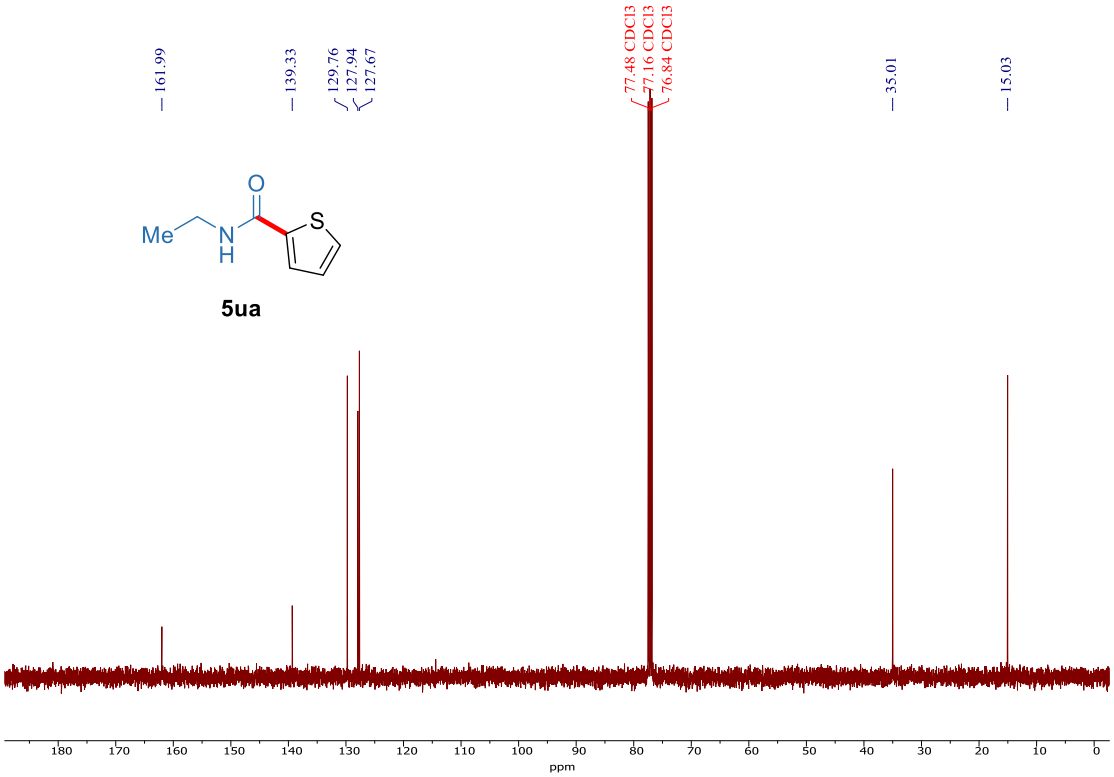
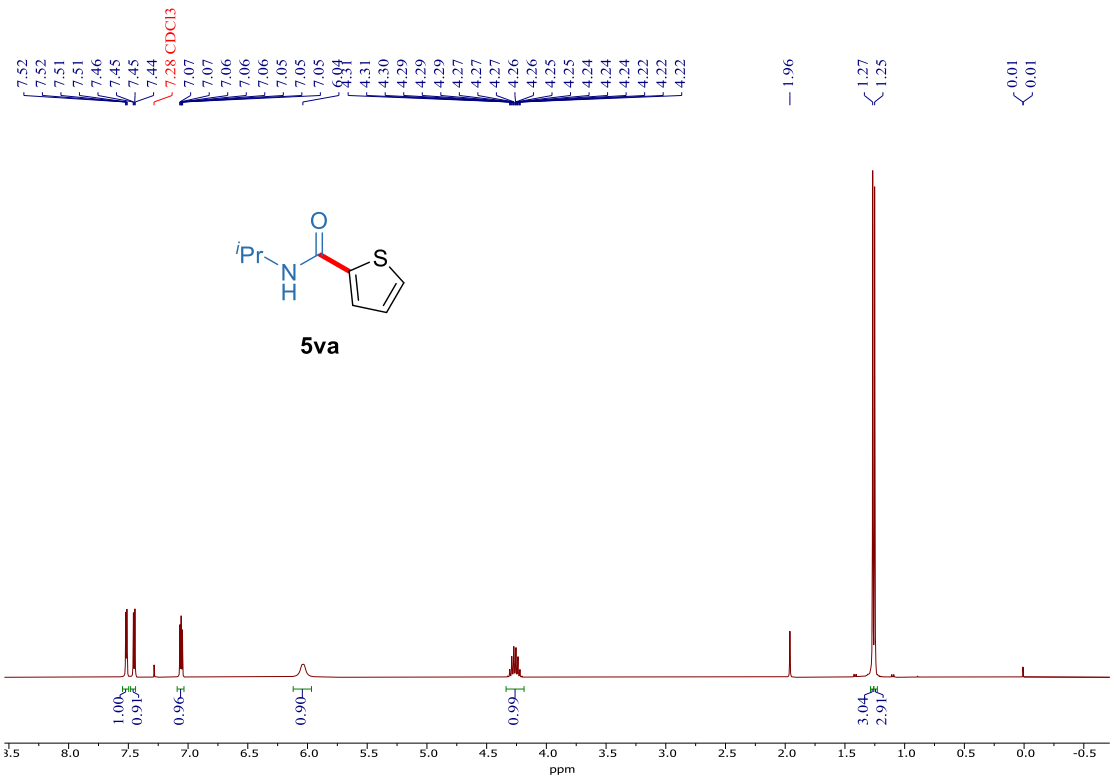


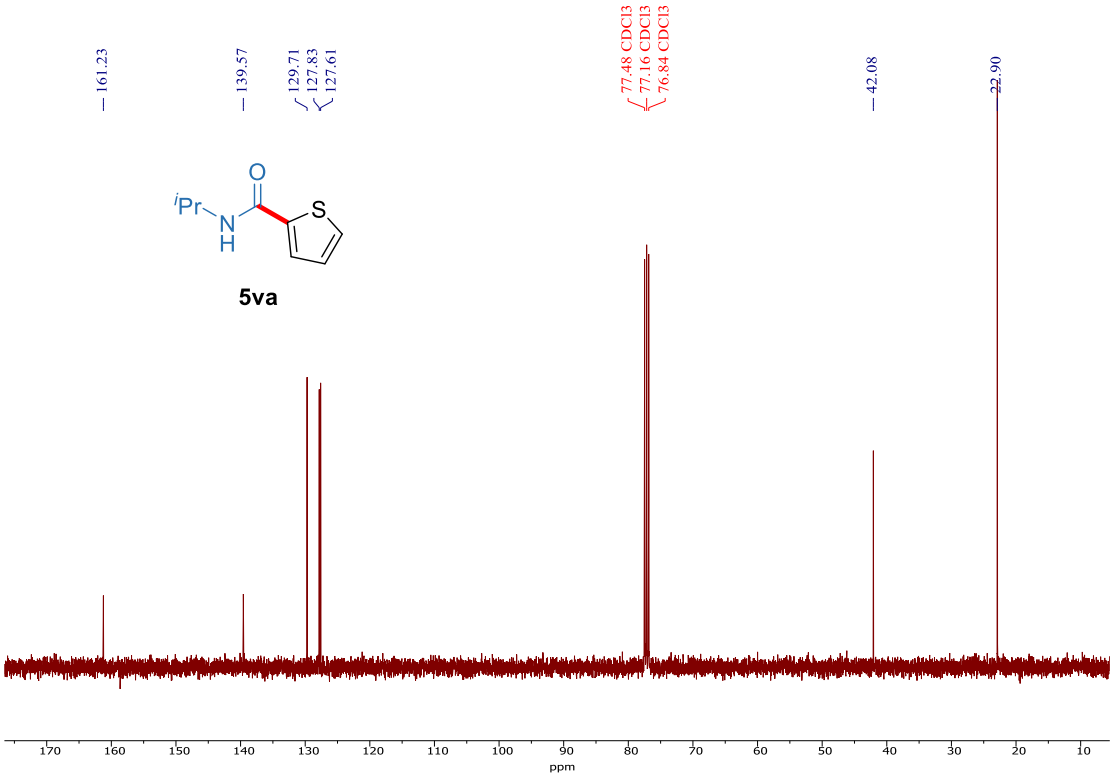
^{13}C NMR (101 MHz, $CDCl_3$) of **5ua**



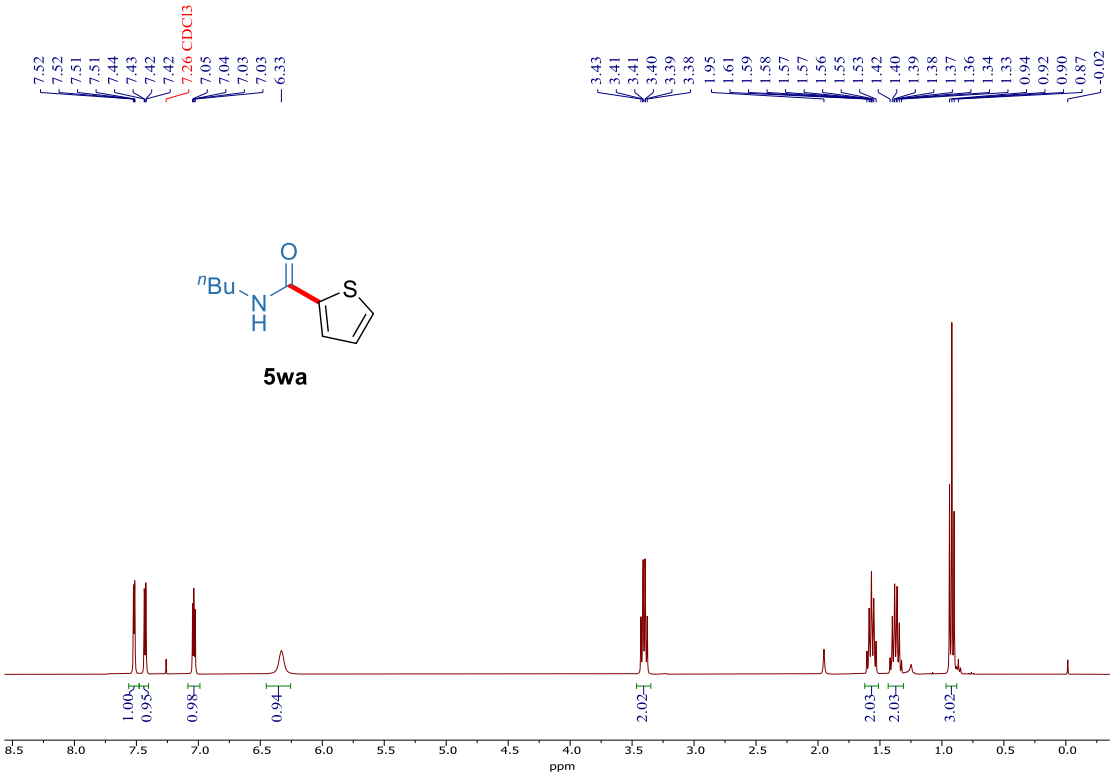
^{1}H NMR (400 MHz, $CDCl_3$) of **5va** (*see procedure*)



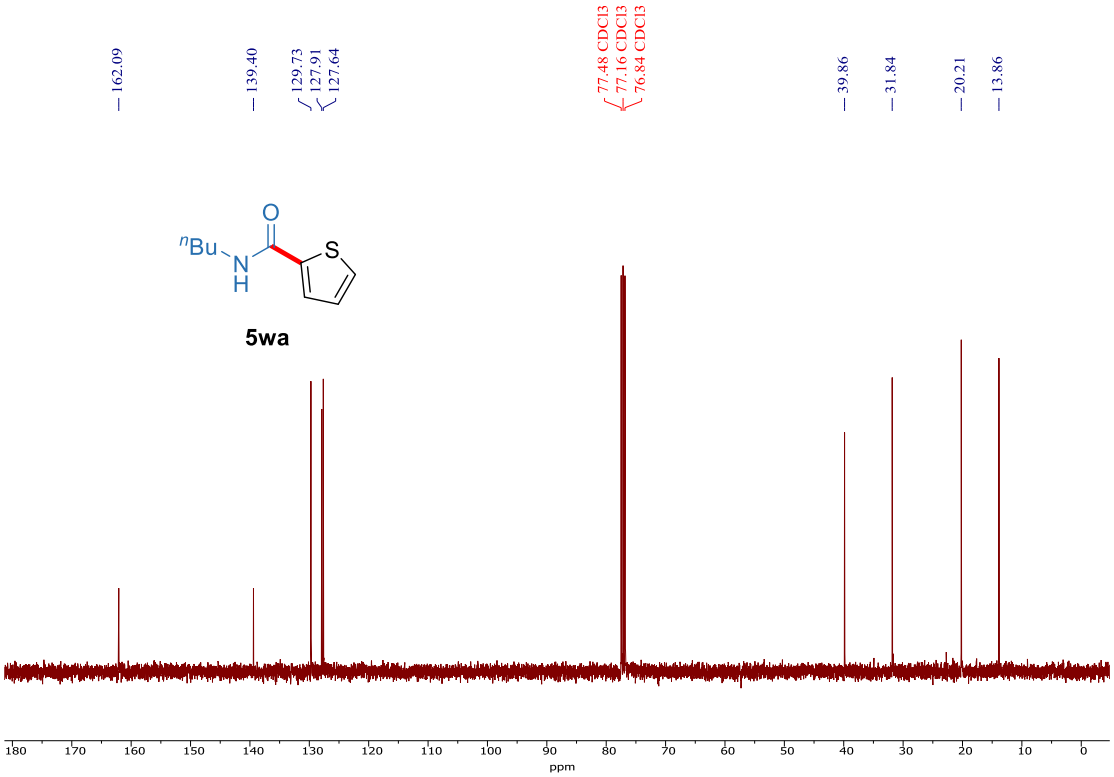
^{13}C NMR (101 MHz, $CDCl_3$) of **5va**



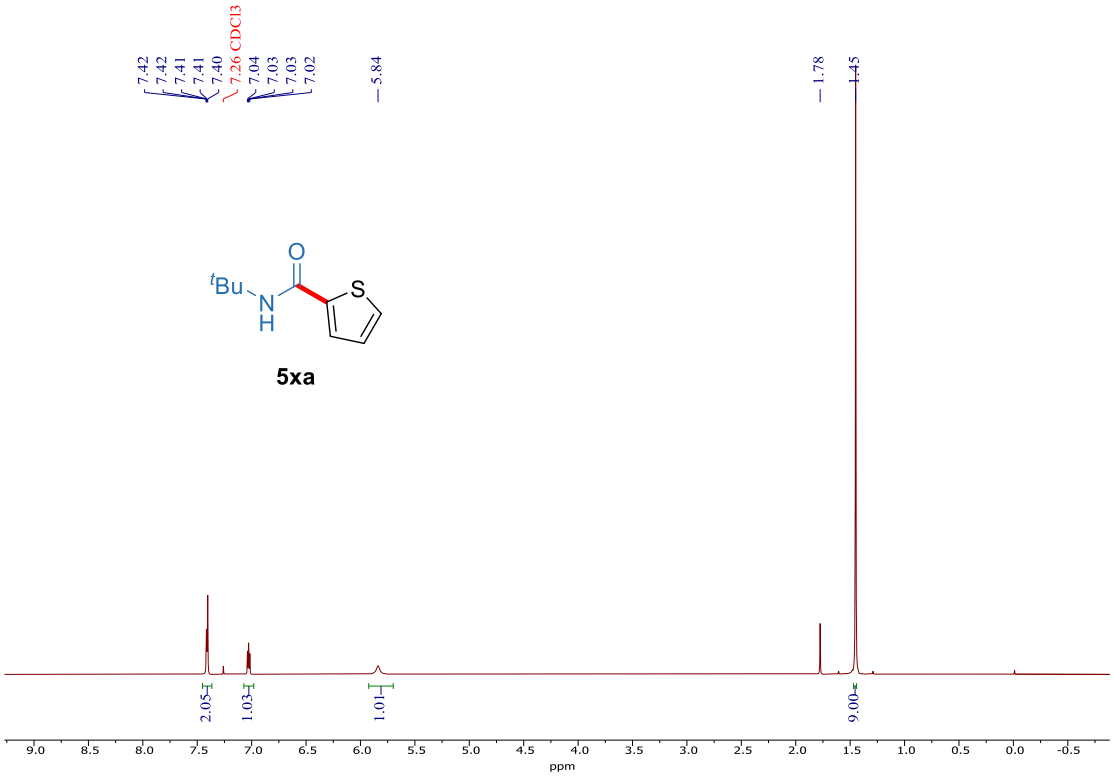
^{1}H NMR (400 MHz, $CDCl_3$) of **5wa** (*see procedure*)



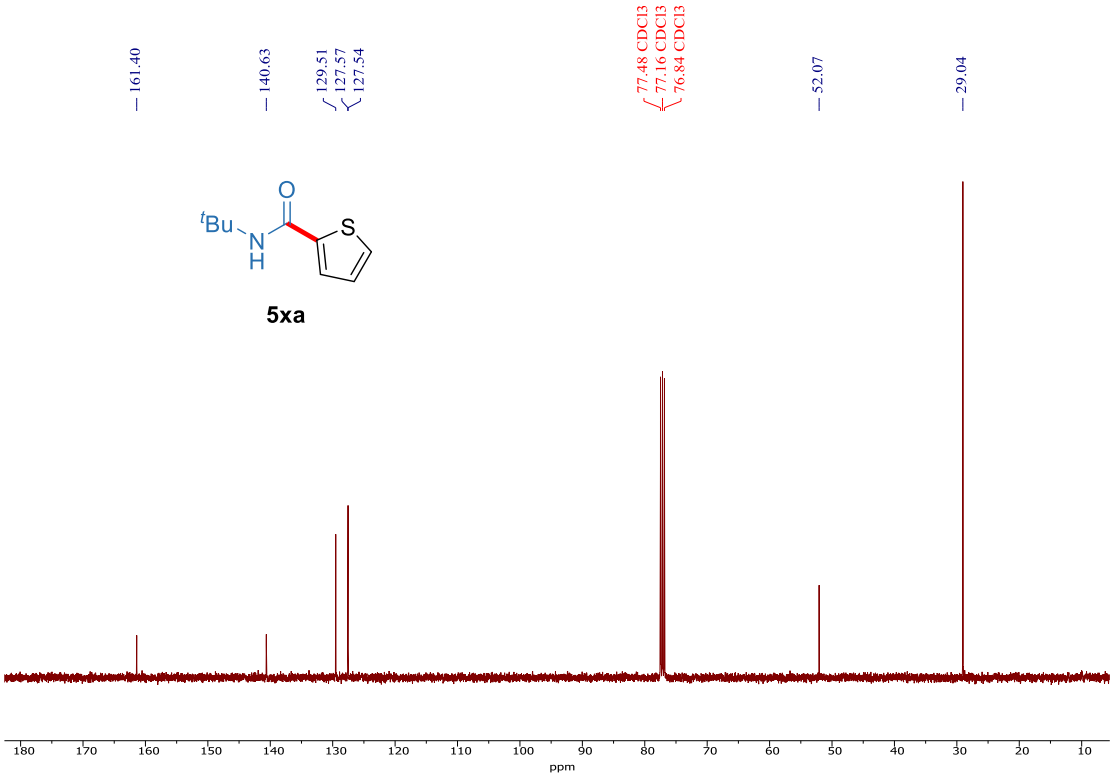
^{13}C NMR (101 MHz, $CDCl_3$) of **5wa**



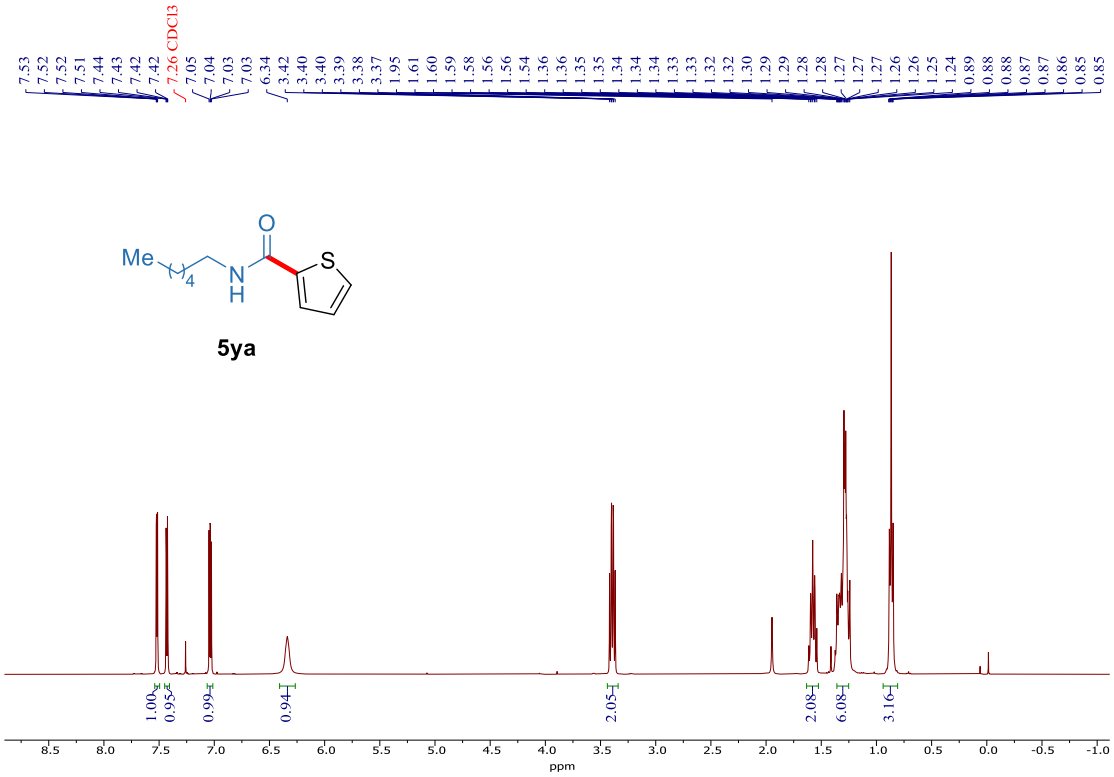
^{1}H NMR (400 MHz, $CDCl_3$) of **5xa** (*see procedure*)



^{13}C NMR (101 MHz, $CDCl_3$) of **5xa**



^{1}H NMR (400 MHz, $CDCl_3$) of **5ya** (*see procedure*)



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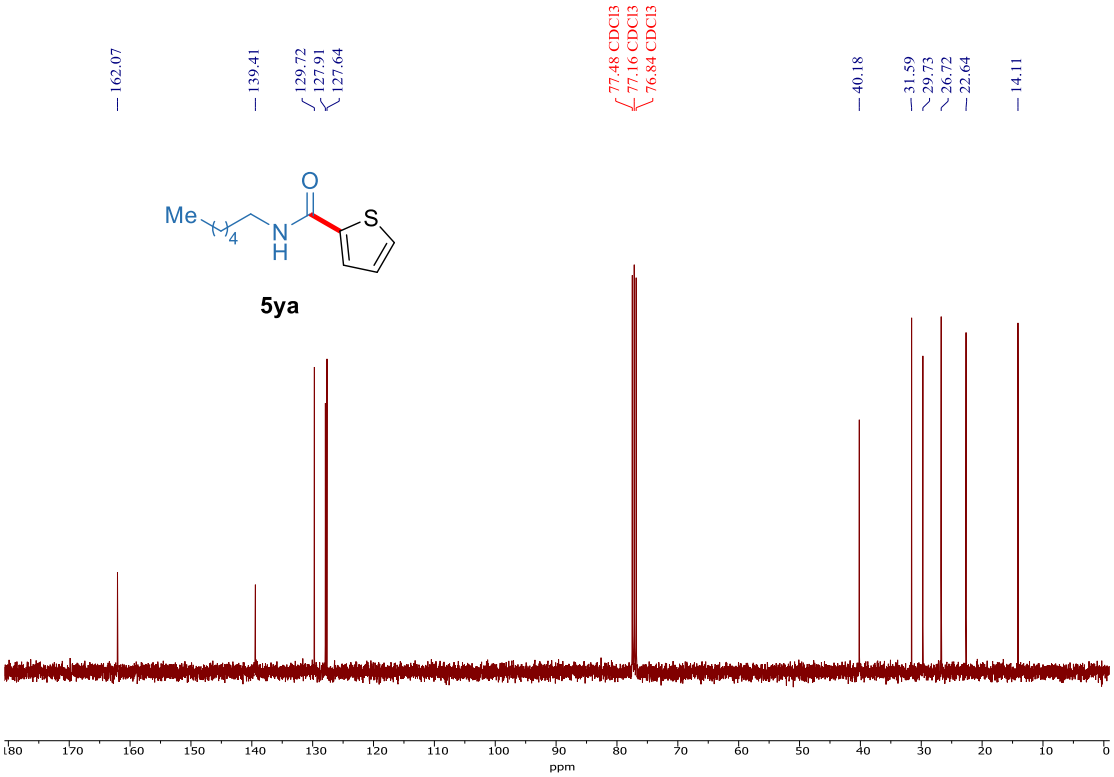
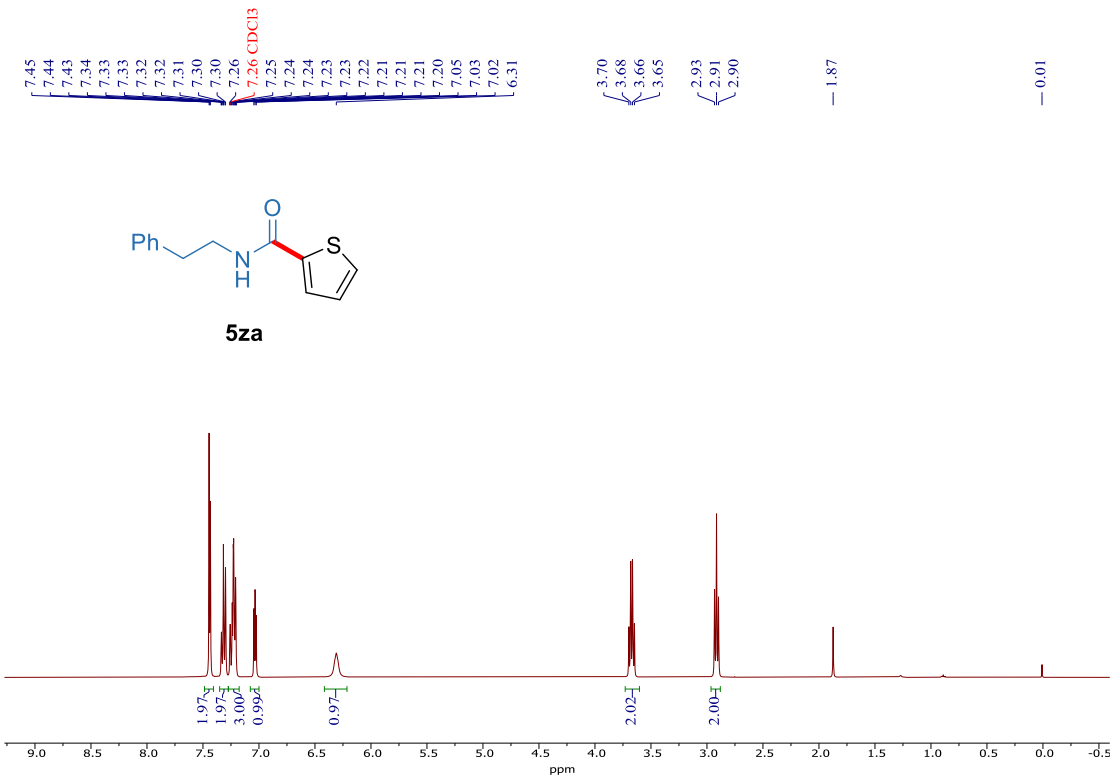


^{1}H NMR (400 MHz, $CDCl_3$) of **5za** (*see procedure*)



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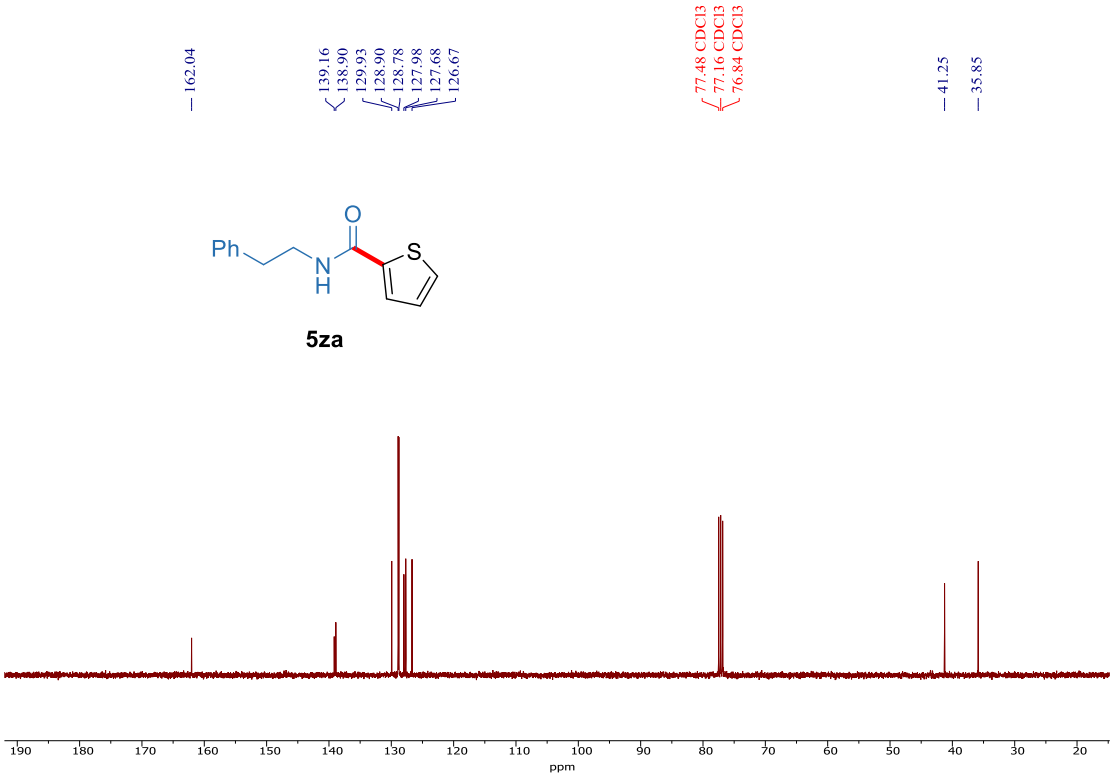
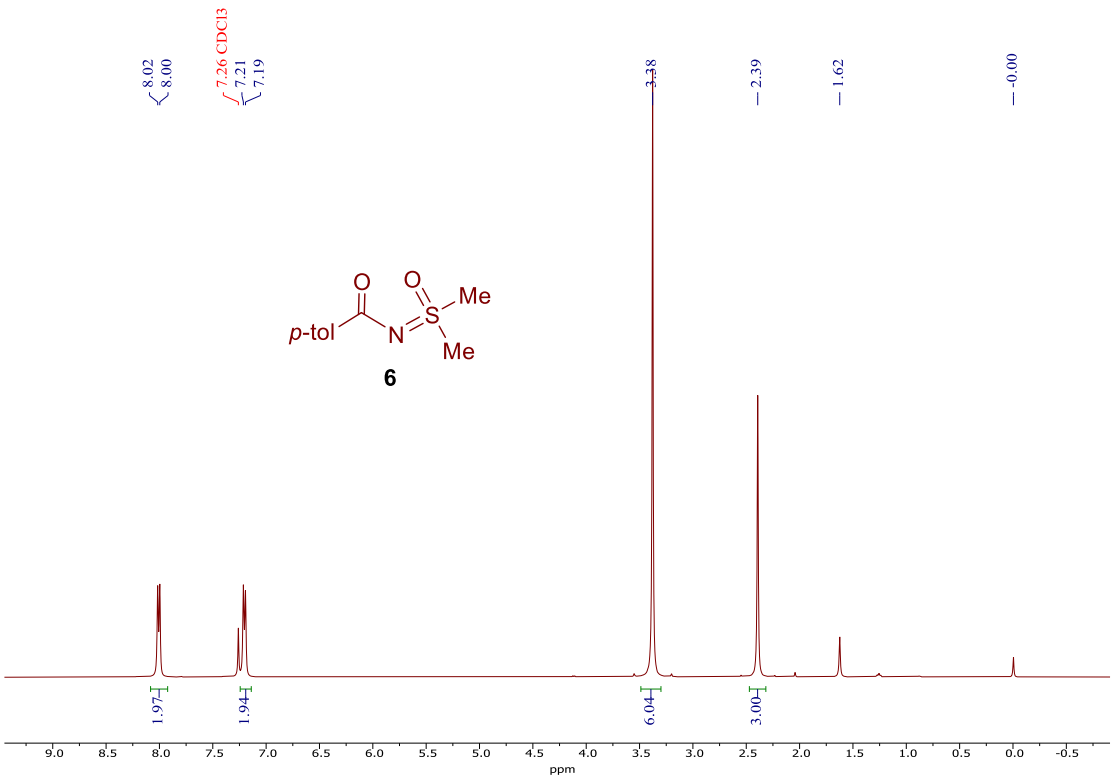
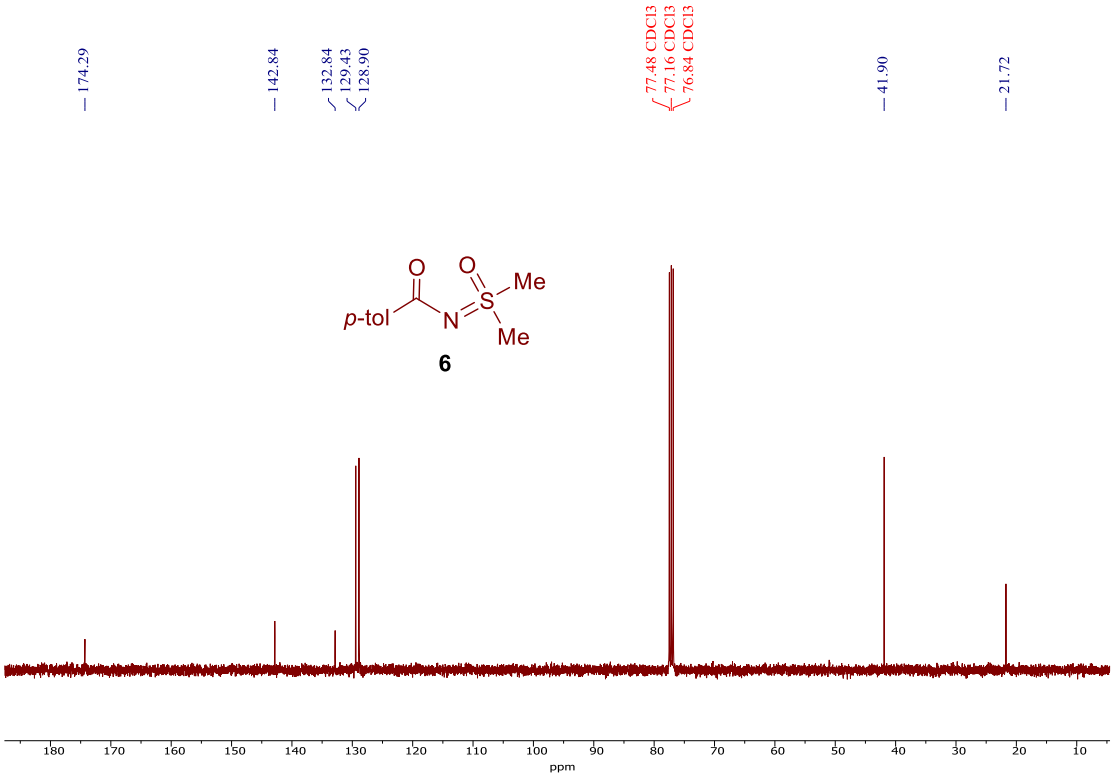


^{1}H NMR (400 MHz, $CDCl_3$) of **6** (*see procedure*)



^{13}C NMR (101 MHz, $CDCl_3$) of **6**



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