Supporting Information

Mechanistic Pathways in Amide Activation: Flexible Synthesis of Oxazoles and Imidazoles

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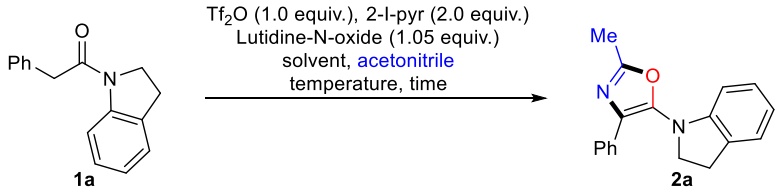
1. General Information

Unless otherwise stated, all glassware was flame-dried before use and all reactions were performed under an atmosphere of argon. All solvents were distilled from appropriate drying agents prior to use. Triflic anhydride was distilled over P_4O_{10} prior to use. All other reagents were used as received from commercial suppliers unless otherwise stated. Reaction progress was monitored by thin layer chromatography (TLC) performed on aluminium plates coated with silica gel F_{254} with 0.2 mm thickness. Chromatograms were visualized by fluorescence quenching with UV light at 254 nm or by staining using potassium permanganate. Flash column chromatography was performed using silica gel 60 (230-400 mesh, Merck and co.). Neat infra-red spectra were recorded using a Perkin-Elmer Spectrum 100 FT-IR spectrometer. Wavenumbers ($\boldsymbol{\nu_{max}}$) are reported in cm^{-1}. Mass spectra were obtained using a Finnigan MAT 8200 or (70 eV) or an Agilent 5973 (70 eV) spectrometer, using electrospray ionization (ESI). All ^1H NMR and ^{13}C NMR spectra were recorded using a Bruker AV-400 or AV-600 spectrometer at 300K. Chemical shifts were given in parts per million (ppm, δ), referenced to the solvent peak of $CDCl_3$, defined at δ = 7.26 ppm (^1H NMR) and δ = 77.16 (^{13}C NMR). Coupling constants are quoted in Hz (*J*). ^1H NMR and ^{13}C splitting patterns were designated as singlet (s), doublet (d), triplet (t), quartet (q), sextet (sext), septet (sept). Splitting patterns that could not be interpreted or easily visualized were designated as multiplet (m) or broad (br).

2. Optimization

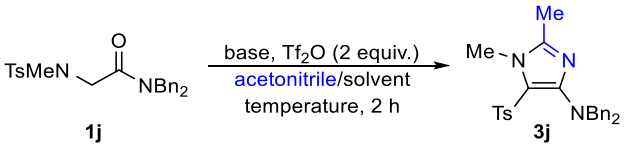
2.1. Oxazole



Entry	Solvent	Nitrile [equiv.]	T	t	Yield[a]
1	MeCN (0.02M)	solvent	110°C	2h	63%
2	MeCN (0.02M)	solvent	rt	12h	27%
3	DCM (0.02M)	20	rt	12h	14%
4	DCM (0.1M)	20	40°C	2h	14%
5	DCM (0.1M)	40	40°C	2h	26%
6	MeCN (0.1M)	solvent	80°C	2h	64% (59%[b])

Reaction conditions: **1a** (0.2 mmol), base (2 equiv.), MS 3Å, solvent, triflic anhydride (1.0 equiv.) for 15 min at 0 °C, then lutidine-*N*-oxide (1.05 equiv.) added and stirred at 80 °C for 2 h. [a]NMR yield using 1,3,5-trimethoxybenzene as internal standard. [b]Isolated yield.

2.2. Imidazole

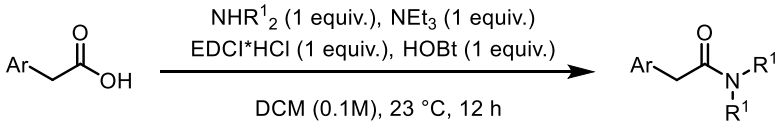


Entry	Base	T	Solvent	Yield[a]
1[b]	2-I-pyr	0 to 80 °C	MeCN (0.02M)	12%
2	2-I-pyr	0 to 23 °C	MeCN (0.05M)	14%
3	2-Cl-pyr	0 to 23 °C	MeCN (0.05M)	23%
4	2-F-pyr	0 to 23 °C	MeCN (0.05M)	37%
5	2-NO_2-pyr	0 to 23 °C	MeCN (0.05M)	44%
6	2-NO_2-pyr	–20 to 23 °C[c]	MeCN (0.05M)	22%
7	2-NO_2-pyr	0 to 40 °C	MeCN (0.05M)	27%
8	2-NO_2-pyr	0 to 23 °C	DCM (0.2M)[d]	37%
9	2-NO_2-pyr	0 to 23 °C	DCE (0.2M)[d]	30%
10	2-NO_2-pyr	0 to 23 °C	PhMe (0.05M)[d]	22%

Reaction conditions: **1j** (0.2 mmol), base (2 equiv.), MS 3Å, solvent, triflic anhydride (2 equiv.) for 2 h. [a]NMR yield using 1,3,5-trimethoxybenzene as internal standard. [b]With 2,6-lutidine *N*-oxide (1.05 equiv.). [c]Reaction time 14 h. [d]With 20 equiv. of nitrile. 2-I-pyr = 2-iodopyridine; 2-Cl-pyr = 2-chloropyridine; 2-F-pyr = 2-fluoropyridine; 2-NO_2-pyr = 2-nitropyridine.

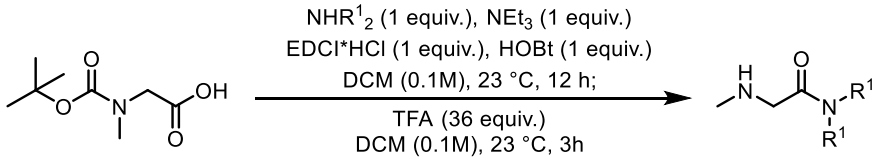
3. Substrates

3.1. General Procedure A (1a–d)

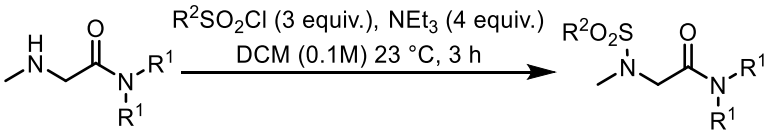


To a solution of the amine (1.00 equiv.), triethylamine (1.00 equiv.), hydroxybenzotriazole (HOBt, 1.00 equiv.) and 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDCI*HCl, 1.00 equiv.) in dichloromethane (0.1 M), the corresponding carboxylic acid was added and the resulting solution was stirred at ambient temperature overnight (14 h). After this time, the organic solution was extracted sequentially with 0.5 M aqueous hydrochloric acid, saturated aqueous sodium bicarbonate and saturated aqueous sodium chloride. The washed solution was dried over anhydrous sodium sulfate, filtered and concentrated under reduced pressure. The resulting crude material was purified by flash column chromatography on silica gel (heptane/ethyl acetate) to afford the desired compound.

3.2. General Procedure B (1j–m)



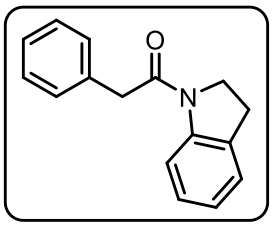
To a solution of *N*-Boc-sarcosine (1.00 equiv.) in anhydrous DCM (0.1M), 1-hydroxybenzotriazole hydrate (HOBt, 1.00 equiv.), 1-ethyl-3-(3-dimethyl aminopropyl) carbodiimide (EDCI*HCl, 1.00 equiv.) and triethylamine (1.00 equiv.) were added and stirred until complete dissolution. After this, the secondary amine was added and the solution was stirred for 12 h at 23 °C. The reaction was worked up by the addition of an aqueous solution of HCl (0.5M) in a ratio 4:1 with respect to the solvent. The organic phase was then washed with a saturated aqueous solution of $NaHCO_3$ in a 4:1 ratio with respect to the solvent and then with brine. The washed solution was dried over anhydrous Na_2SO_4, filtered and the filtrate was concentrated under reduced pressure. The crude residue was dissolved in DCM (0.1M) and trifluoroacetic acid (36.0 equiv.) was added. The resulting solution was stirred for 3 h at 23 °C. After this time, the acid was quenched by the dropwise addition of a saturated aqueous solution of $NaHCO_3$. The organic phase was then separated and washed with brine, dried over anhydrous Na_2SO_4, filtered and the filtrate was concentrated under reduced pressure. The crude residue was used in the next steps without further purification.



To a solution of the amide (1.00 equiv.) in DCM (0.1M), triethylamine (4.00 equiv.) was added, followed by the corresponding sulfonyl chloride (R^2SO_2Cl) (3.00 equiv.). The mixture was stirred until complete dissolution and then stirred for 3 h at 23 °C. Excess sulfonyl chloride was quenched by the addition of a saturated aqueous solution of $NaHCO_3$ in a 4:1 ratio with respect to the solvent. The organic phase was separated and subsequently washed with brine. The organic phase was then dried over anhydrous Na_2SO_4, filtered and the filtrate was concentrated under reduced pressure. The product was purified by flash column chromatography on silica gel (heptane/ethyl acetate) to afford the desired product.

3.3. Characterization of Substrates

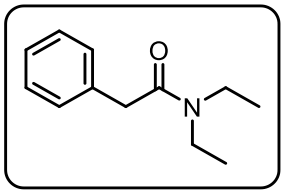
1-(Indolin-1-yl)-2-phenylethan-1-one (1a)



Synthesized following general procedure A. All spectroscopic data were in good accordance with the data reported in the literature.[1]

^{1}H-NMR included below.

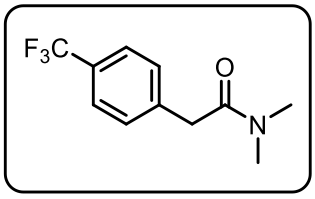
***N,N*-Diethyl-2-phenylacetamide (1b)**



Synthesized following general procedure A. All spectroscopic data were in good accordance with the data reported in the literature.[2]

^{1}H-NMR included below.

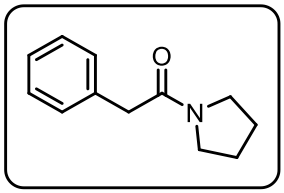
***N,N*-Dimethyl-2-(4-(trifluoromethyl)phenyl)acetamide (1c)**



Synthesized following general procedure A. All spectroscopic data were in good accordance with the data reported in the literature.[3]

^{1}H-NMR included below.

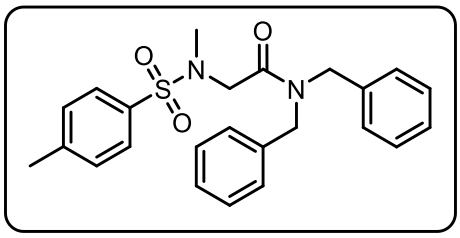
2-Phenyl-1-(pyrrolidin-1-yl)ethan-1-one (1d)



Synthesized following general procedure A. All spectroscopic data were in good accordance with the data reported in the literature.[4]

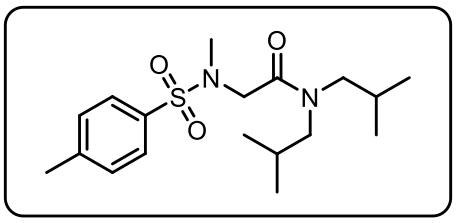
^{1}H-NMR included below.

***N,N*-Dibenzyl-2-((*N*,4-dimethylphenyl)sulfonamido)acetamide (1j)**



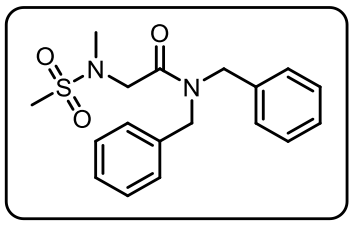
Synthesized following general procedure B; colorless solid; 862 mg (69% yield). **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.68–7.64 (m, 2H), 7.42–7.28 (m, 8H), 7.21–7.16 (m, 2H), 4.58 (app d, *J* = 3.6 Hz, 4H), 3.97 (s, 2H), 2.85 (s, 3H), 2.43 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 167.8, 143.9, 136.9, 136.2, 134.1, 129.8 (2C), 129.2 (2C), 128.8 (2C), 128.4 (2C), 128.0, 127.9 (2C), 127.8, 127.8 (2C), 52.4, 49.8, 48.8, 35.8, 21.7; **IR (neat) ν_{max}:** 3030, 1664, 1599, 1495, 1451, 1423, 1340, 1307, 1216, 1163, 1121, 1089 700; **HRMS (ESI^+):** exact mass calculated for $[M+Na]^+$ ($C_{24}H_{26}N_2O_3SNa$) requires *m*/*z* 445.1556, found *m*/*z* 445.1556.

2-((*N*,4-Dimethylphenyl)sulfonamido)-*N,N*-diisobutylacetamide (1k)



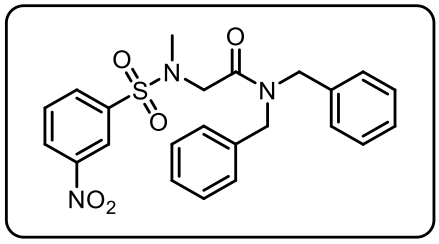
Synthesized following general procedure B; light-yellow oil, 348 mg (33% yield). **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.69–7.65 (m, 2H), 7.33–7.29 (m, 2H), 3.89 (s, 2H), 3.25 (d, *J* = 7.6 Hz, 2H), 3.16 (d, *J* = 7.6 Hz, 2H), 2.79 (s, 3H), 2.42 (s, 3H), 2.02–1.90 (m, 2H), 0.96 (d, *J* = 6.7 Hz, 6H), 0.86 (d, *J* = 6.7 Hz, 6H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 167.5, 143.8, 134.0, 129.8 (2C), 127.8 (2C), 54.7, 53.1, 52.7, 35.6, 27.8, 26.4, 21.7, 20.3, 20.1; **IR (neat) ν_{max}:** 2959, 2930, 1647, 1454, 1338, 1162, 1021, 921, 759, 690; **HRMS (ESI^+):** exact mass calculated for $[M+Na]^+$ ($C_{18}H_{30}N_2O_3SNa$) requires *m*/*z* 377.1869, found *m*/*z* 377.1861.

***N,N*-Dibenzyl-2-(*N*-methylmethylsulfonamido)acetamide (1l)**



Synthesized following general procedure B; colorless oil, 576 mg (64% yield). **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.41–7.30 (m, 6H), 7.21–7.13 (m, 4H), 4.61 (s, 2H), 4.40 (s, 2H), 4.23 (s, 2H), 3.08 (s, 3H), 3.02 (s, 3H); **^{13}C-NMR (150 MHz, $CDCl_3$):** δ 169.3, 137.3, 136.4, 130.1 (2C), 129.7 (2C), 129.1 (2C), 128.9, 128.6, 127.1 (2C), 52.4, 50.2, 49.8, 39.4, 36.4; **IR (neat) ν_{max}:** 2923, 1657, 1495, 1468, 1324, 1218, 1156, 1139, 1002, 786, 736, 700; **HRMS (ESI^+):** exact mass calculated for $[M+Na]^+$ ($C_{18}H_{22}N_2O_3SNa$) requires *m*/*z* 369.1243, found *m*/*z* 369.1249.

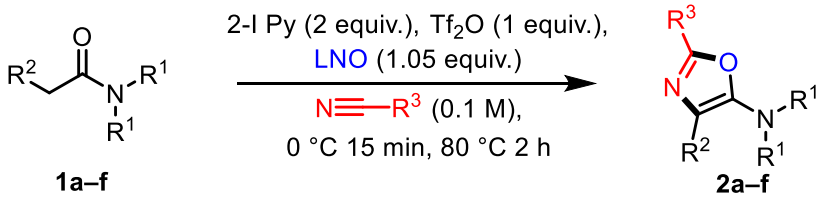
***N,N*-Dibenzyl-2-((*N*-methyl-3-nitrophenyl)sulfonamido)acetamide (1m)**



Synthesized following general procedure B; yellow solid, 112 mg (44% yield). **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 8.13–8.08 (m, 1H), 7.70–7.65 (m, 2H), 7.62–7.58 (m, 1H), 7.41–7.29 (m, 6H), 7.18–7.16 (m, 4H), 4.56 (s, 2H), 4.44 (s, 2H), 4.28 (s, 2H), 3.08 (s, 3H); **^{13}C-NMR (150 MHz, $CDCl_3$):** δ 168.5, 143.3, 137.5, 136.6, 134.2, 133.6, 132.5, 131.9, 130.0, 129.5, 129.2, 128.8, 128.5, 127.3, 124.9, 52.4, 50.2, 49.8, 37.1; **IR (neat) ν_{max}:** 3359, 3193, 2956, 2921, 2850, 1659, 1632, 1543, 1352; **HRMS (ESI^+):** exact mass calculated for $[M+Na]^+$ ($C_{23}H_{23}N_3O_5SNa$) requires *m*/*z* 476.1251, found *m*/*z* 476.1248.

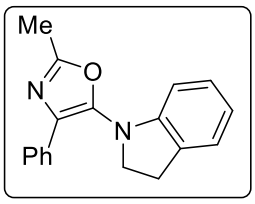
4. Products

4.1. Oxazoles



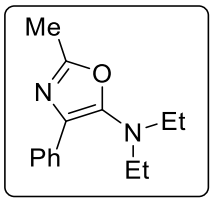
To a stirred solution of amide **1** (1.00 equiv., 0.200 mmol) and 2-iodopyridine (2.00 equiv., 0.400 mmol, 42.5 µl) in the corresponding nitrile (2 mL, 0.1M) was added triflic anhydride (1.00 equiv., 0.200 mmol, 34 µl) at 0°C under an atmosphere of argon. After 15 min, lutidine-*N*-oxide (1.05 equiv., 0.210 mmol, 23.5 µl) was added and the reaction mixture was heated at 80 °C for another 2 h. After cooling to room temperature, the reaction mixture was quenched by the addition of saturated aqueous solution of $NaHCO_3$ (10 mL), extracted with DCM (2 × 10 mL), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude residue was purified by flash column chromatography on silica gel using (heptane/ethyl acetate) to afford the desired products **2**.

5-(Indolin-1-yl)-2-methyl-4-phenyloxazole (2a)



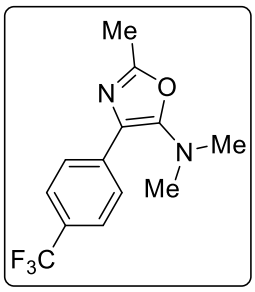
Reddish solid, 23 mg (59% yield); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.74–7.71 (m, 2H), 7.26 (t, *J* = 7.7 Hz, 2H), 7.18–7.10 (m, 2H), 6.93 (t, *J* = 7.5 Hz, 1H), 6.73 (t, *J* = 7.4 Hz, 1H), 6.27 (d, *J* = 7.8 Hz, 1H), 3.84 (t, *J* = 8.6 Hz, 2H), 3.15 (t, *J* = 8.7 Hz, 2H), 2.07 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 157.7, 147.8, 143.3, 131.2, 129.4, 128.4 (2C), 127.5, 127.2, 126.1 (2C), 125.0, 120.1 (2C), 109.2, 52.2, 28.7, 14.4; **IR (neat) ν_{max}:** 3055, 2984, 1733, 1648, 1484, 1374, 1265, 1046, 736, 705, 631; **HRMS (ESI$^+$):** exact mass calculated for $[M+H]^+$ ($C_{18}H_{16}N_2O$) requires *m*/*z* 277.1341, found *m*/*z* 277.1329.

***N,N*-Diethyl-2-methyl-4-phenyloxazol-5-amine (2b)**



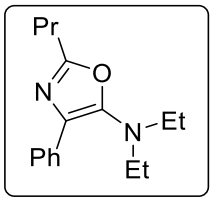
Yellowish oil, 21 mg (44% yield); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.95 (d, *J* = 8.6 Hz, 2H), 7.28 (t, *J* = 7.8 Hz, 2H), 7.14 (t, *J* = 7.2 Hz, 1H), 2.99 (q, *J* = 7.2 Hz, 4H), 2.34 (s, 3H), 0.98 (t, *J* = 7.2 Hz, 6H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 156.8, 149.7, 143.3, 132.2, 128.2 (2C), 126.6, 125.8 (2C), 47.6 (2C), 14.5, 13.0 (2C); **IR (neat) ν_{max}:**2972, 1705, 1634, 1589, 1447, 1344, 1257, 1219, 1147, 1043, 957, 715, 694; **HRMS (ESI$^+$):** exact mass calculated for $[M+H]^+$ ($C_{14}H_{18}N_2O$) requires *m*/*z* 231.1497, found *m*/*z* 231.1485.

***N,N*,2-Trimethyl-4-(4-(trifluoromethyl)phenyl)oxazol-5-amine (2c)**



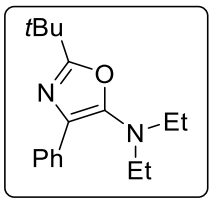
Colorless oil, 21 mg (39% yield); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.99 (d, *J* = 8.4 Hz, 2H), 7.63 (d, *J* = 8.6 Hz, 2H), 2.82 (s, 6H), 2.44 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 155.6, 153.5, 136.0, 125.7 (4C), 125.2 (2C), 121.3, 42.3 (2C), 14.2; **^{19}F-NMR (700 MHz, $CDCl_3$):** δ –62.32; **HRMS (ESI^+):** exact mass calculated for $[M+H]^+$ ($C_{13}H_{13}N_2OF_3$) requires *m*/*z* 271.1058, found *m*/*z* 271.1045.

***N,N*-Diethyl-4-phenyl-2-propyloxazol-5-amine (2d)**



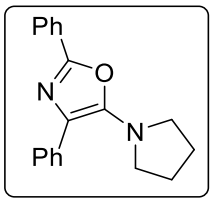
Yellowish oil, 17 mg (33% yield); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.96 (d, *J* = 8.2 Hz, 2H), 7.28 (t, *J* = 7.9 Hz, 2H), 7.14 (t, *J* = 7.2 Hz, 1H), 3.00 (q, *J* = 7.2 Hz, 4H), 2.62 (t, *J* = 7.5 Hz, 2H), 1.78–1.67 (m, 2H), 0.97 (t, *J* = 7.0 Hz, 6H), 0.93 (t, *J* = 7.3 Hz, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 160.3, 149.5, 132.4, 128.1 (2C), 127.3, 126.6, 125.8 (2C), 47.6 (2C), 30.7, 20.7, 13.7, 13.0 (2C); **IR (neat) ν_{max}:** 3057, 2969, 2873, 1737, 1603, 1497, 1342, 1290, 1218, 1181, 1090, 1046, 982, 738, 698; **HRMS (ESI^+):** exact mass calculated for $[M+H]^+$ ($C_{16}H_{22}N_2O$) requires *m*/*z* 259.1810, found *m*/*z* 259.1800.

2-(*tert*-Butyl)-*N,N*-diethyl-4-phenyloxazol-5-amine (2e)



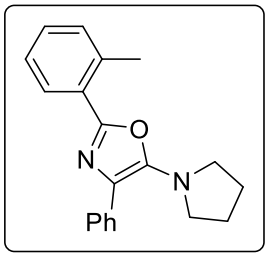
Colorless oil, 31 mg (57% yield); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.96 (d, *J* = 8.2 Hz, 2H), 7.27 (t, *J* = 7.9 Hz, 2H), 7.13 (t, *J* = 7.2 Hz, 1H), 3.00 (q, *J* = 7.2 Hz, 4H), 1.31 (s, 9H), 0.97 (t, *J* = 7.2 Hz, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 166.1, 149.3, 132.7, 131.3, 128.1 (2C), 126.4, 125.9 (2C), 47.5 (2C), 33.9, 28.3 (3C), 13.0 (2C); **IR (neat) ν_{max}:** 2972, 2932, 1640, 1604, 1449, 1378, 1087, 978; **HRMS (ESI^+):** exact mass calculated for $[M+H]^+$ ($C_{17}H_{24}N_2O$) requires *m*/*z* 273.1967, found *m*/*z* 273.1963.

2,4-Diphenyl-5-(pyrrolidin-1-yl)oxazole (2f)



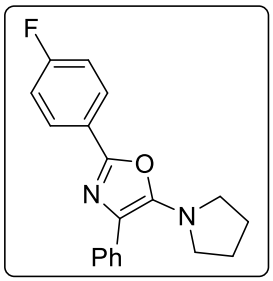
Yellowish oil, 35 mg (60% yield); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.91 (d, *J* = 7.9 Hz, 2H), 7.66 (d, *J* = 8.2 Hz, 2H), 7.37–7.25 (m, 5H), 7.15 (t, *J* = 7.2 Hz, 1H), 3.31–3.25 (m, 4H), 1.94–1.88 (m, 4H); **^{13}C-NMR (175 MHz, $CDCl_3$):** δ 153.0, 150.6, 133.0, 129.0, 128.6 (2C), 128.1 (2C), 127.0 (2C), 126.0, 125.3 (2C), 119.7, 50.1 (2C), 25.4 (2C); **IR (neat) ν_{max}:** 2967, 2932, 2872, 1638, 1583, 1497, 1378, 1341, 1289, 1150, 1068, 1043, 1023, 981, 958, 716, 695; **HRMS (ESI$^+$):** exact mass calculated for $[M+H]^+$ ($C_{19}H_{18}N_2O$) requires *m*/*z* 291.1497, found *m*/*z* 291.1491.

4-Phenyl-5-(pyrrolidin-1-yl)-2-(o-tolyl)oxazole (2g)



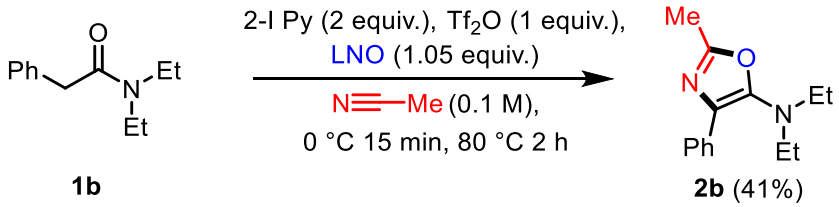
colorless oil, 27 mg (44% yield); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.98–7.92 (m, 1H), 7.79–7.74 (m, 2H), 7.43–7.36 (m, 2H), 7.28–7.26 (m, 2H), 7.26–7.19 (m, 2H), 3.39–3.32 (m, 4H), 2.74 (s, 3H), 2.02–1.95 (m, 4H); **^{13}C-NMR (175 MHz, $CDCl_3$):** δ 153.7, 150.5, 136.7, 133.4, 131.6, 128.9, 128.2 (2C), 128.0, 127.1, 126.9 (2C), 126.1, 125.9, 119.7, 50.4 (2C), 25.6 (2C), 22.2; **IR (neat) ν_{max}:** 2968, 2925, 2872, 1613, 1498, 1447, 1420, 1039, 768, 724, 700; **HRMS (ESI$^+$):** exact mass calculated for $[M+H]^+$ ($C_{20}H_{21}N_2O$) requires *m*/*z* 305.1648, found *m*/*z* 305.1643.

2-(4-Fluorophenyl)-4-phenyl-5-(pyrrolidin-1-yl)oxazole (2h)



orange oil, 33.1 mg (53% yield); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 8.01–7.94 (m, 2H), 7.75–7.69 (m, 2H), 7.42–7.36 (m, 2H), 7.26–7.21 (m, 1H), 7.15–7.08 (m, 2H), 3.38–3.3 (m, 4H), 2.02–1.95 (m, 4H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 163.4 (d, *J* = 249.5 Hz), 152.5, 150.8, 133.1, 128.3 (2C), 127.4 (d, *J* = 8.4 Hz, 2C), 127.1 (2C), 126.3, 124.6 (d, *J* = 3.2 Hz), 119.8, 115.8 (d, *J* = 22.2 Hz, 2C), 50.3 (2C), 25.6 (2C); **^{19}F-NMR (659 MHz, $CDCl_3$)**: –111.64; (**IR (neat) ν_{max}:** 2954, 2924, 2872, 2853, 1611, 1501, 1446, 1412, 1231, 1155; **HRMS (ESI$^+$):** exact mass calculated for $[M+H]^+$ ($C_{19}H_{18}FN_2O$) requires *m*/*z* 309.1398, found *m*/*z* 309.1389.

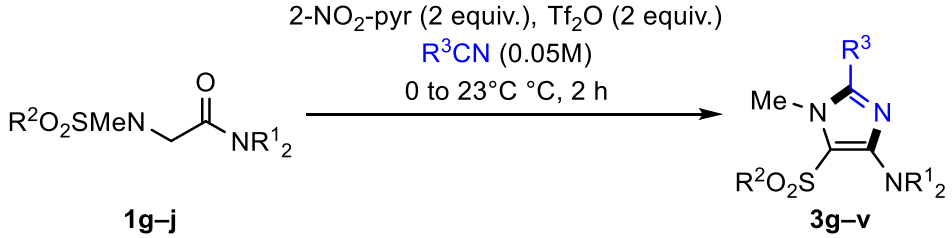
4.2. 1.5 mmol Experiment



1b **2b** (41%)

To a stirred solution of amide **1b** (1.0 equiv., 1.5 mmol, 287 mg) and 2-iodopyridine (2.0 equiv., 3.0 mmol, 319 µl) in acetonitrile (15 mL, 0.1M) was added triflic anhydride (1.0 equiv., 1.65 mmol, 466 µl) at 0°C under an atmosphere of argon. After 15 min, lutidine-*N*-oxide (1.05 equiv., 1.58 mmol, 194 µl) was added and the reaction mixture was heated at 80 °C for another 2 h. After cooling to room temperature, the reaction mixture was quenched by the addition of saturated aqueous solution of $NaHCO_3$ (10 mL), extracted with DCM (2 × 10 mL), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude residue was purified by flash column chromatography on silica gel using (heptane/ethyl acetate: 10/1) to afford the desired products **2b** as yellowish oil in 41 % yield (141 mg).

4.3. Imidazoles

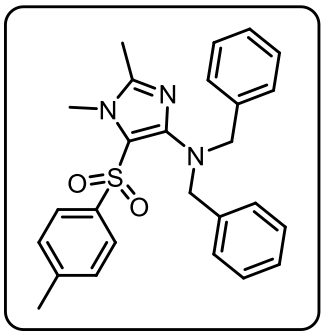


1g–j **3g–v**

To a cooled (0 °C) solution of the corresponding amide (1.00 equiv.) and 2-nitropyridine (2.00 equiv.) in the appropriate nitrile (0.05M) over activated molecular sieves (3Å), triflic anhydride (2.00 equiv.) was added. The resulting mixture was allowed to stir at 0 °C for 15 min, after which the cooling bath was removed and the reaction mixture was stirred at 23 °C for 2 h. After this time, the mixture was filtered over celite and the molecular sieves were washed with DCM. The resulting filtrate was washed with a saturated aqueous solution of $NaHCO_3$ (4:1 with respect to the solvent) and then with brine. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and the filtrate was concentrated under reduced pressure. The resulting crude product was purified by flash column chromatography on silica gel (heptane/ethyl acetate) to afford the desired compound.

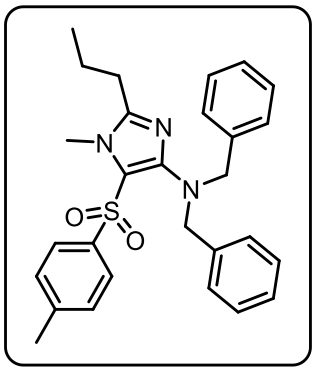
For nitriles solid at 0 °C, DCM was added to the reaction mixture. The corresponding ratios are given below.

***N,N*-Dibenzyl-1,2-dimethyl-5-tosyl-*1H*-imidazol-4-amine (3j)**



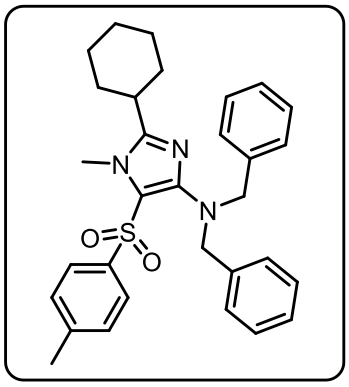
colorless solid, 39.1 mg (44% yield); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.61–7.57 (m, 2H), 7.30–7.19 (m, 10H), 7.18–7.14 (m, 2H), 4.48 (s, 4H), 3.55 (s, 3H), 2.38 (s, 3H), 2.29 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 156.5, 147.2, 143.5, 140.7, 139.1 (2C), 129.7 (2C), 128.7 (4C), 128.3 (4C), 126.9 (2C), 126.5 (2C), 111.5, 56.6 (2C), 32.8, 21.6, 13.8; **IR (neat) ν_{max}:** 3027, 1597, 1520, 1452, 1406, 1365, 1318, 1152, 1134, 1078, 832, 699; **HRMS (ESI^+):** exact mass calculated for $[M+H]^+$ ($C_{26}H_{28}N_3O_2S$) requires *m/z* 446.1897, found *m/z* 446.1901.

***N,N*-Dibenzyl-1-methyl-2-propyl-5-tosyl-*1H*-imidazol-4-amine (3k)**



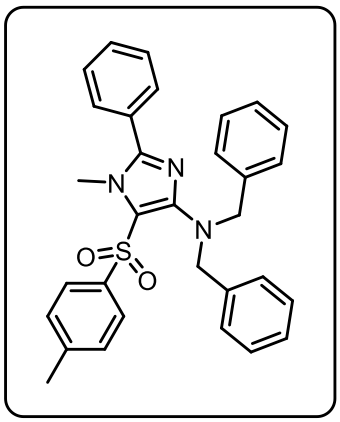
light-yellow oil, 41.5 mg (44% yield); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.56–7.54 (m, 2H), 7.31–7.15 (m, 12H), 4.48 (s, 4H), 3.54 (s, 3H), 2.55 (t, *J* = 7.4 Hz, 2H), 2.38 (s, 3H), 1.67 (app sext, *J* = 7.6 Hz, 2H), 0.89 (t, *J* = 7.4 Hz, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 156.7, 150.7, 143.4, 140.7, 139.2 (2C), 129.7 (2C), 128.8 (4C), 128.2 (4C), 126.9 (2C), 126.5 (2C), 111.4, 56.8 (2C), 32.4, 29.1, 21.6, 21.1, 13.7; **IR (neat) ν_{max}:** 3358, 3062, 3029, 2959, 2926, 2855, 1721, 1658, 1607, 1524, 1494, 1452, 1395; **HRMS (ESI$^+$):** exact mass calculated for $[M+H]^+$ ($C_{28}H_{32}N_3O_2S$) requires *m*/*z* 474.2210, found *m*/*z* 474.2217.

***N,N*-dibenzyl-2-cyclohexyl-1-methyl-5-tosyl-*1H*-imidazol-4-amine (3l)**



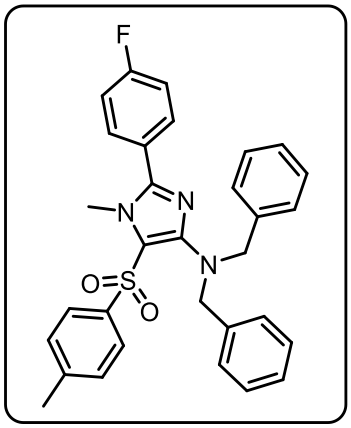
10% v/v DCM were added to the reaction mixture; yellow oil, 39.3 mg (38% yield); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.52–7.47 (m, 2H), 7.36–7.32 (m, 4H), 7.29–7.25 (m, 3H), 7.25–7.18 (m, 3H), 7.15–7.11 (m, 2H), 4.48 (s, 4H), 3.52 (s, 3H), 2.52 (tt, *J* = 11.4, 3.6 Hz, 1H), 2.38 (s, 3H), 1.89–1.80 (m, 2H), 1.80–1.70 (m, 3H), 1.69–1.57 (m, 2H), 1.37–1.28 (m, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 156.8, 154.1, 143.2, 140.8, 139.4 (2C), 129.7 (2C), 129.1 (4C), 128.1 (4C), 126.8 (2C), 126.4 (2C), 110.9, 56.9 (2C), 36.1, 31.9, 31.0 (2C), 26.1 (2C), 25.8, 21.6; **IR (neat) ν_{max}:** 3511, 3452, 3359, 2923, 2851, 1657, 1632, 1522, 1494, 1467, 1451, 1421, 1373; **HRMS (ESI$^+$):** exact mass calculated for $[M+H]^+$ ($C_{31}H_{36}N_3O_2S$) requires *m*/*z* 514.2523, found *m*/*z* 514.2524.

***N,N*-Dibenzyl-1-methyl-2-phenyl-5-tosyl-*1H*-imidazol-4-amine (3m)**



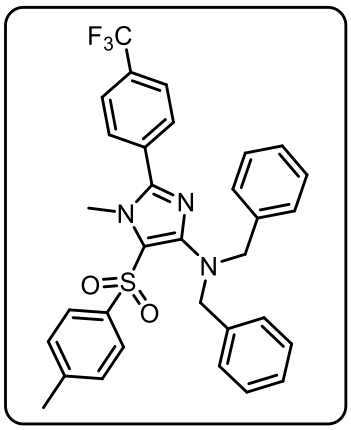
yellow solid, 64.2 mg (63% yield); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.65–7.61 (m, 2H), 7.53–7.48 (m, 2H), 7.48–7.43 (m, 3H), 7.36–7.32 (m, 4H), 7.31–7.27 (m, 3H), 7.27–7.20 (m, 3H), 7.20–7.16 (m, 2H), 4.54 (s, 4H), 3.66 (s, 3H), 2.39 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 156.9, 149.3, 143.7, 140.5, 139.1 (2C), 130.0, 129.8 (2C), 129.7 (2C), 129.4, 128.9 (4C), 128.8 (2C), 128.3 (4C), 127.0 (2C), 126.7 (2C), 113.3, 56.7 (2C), 34.7, 21.7; **IR (neat) ν_{max}:** 3367, 3061, 3030, 2924, 2851, 1745, 1712, 1684, 1615, 1493, 1032, 1011; **HRMS (ESI^+):** exact mass calculated for $[M+H]^+$ ($C_{31}H_{30}N_3O_2S$) requires *m*/*z* 508.2053, found *m*/*z* 508.2060.

***N,N*-dibenzyl-2-(4-fluorophenyl)-1-methyl-5-tosyl-*1H*-imidazol-4-amine (3n)**



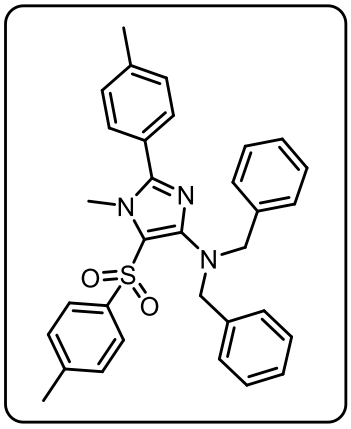
55% v/v DCM were added to the reaction mixture; yellow oil, 53.5 mg (51% yield); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.65–7.60 (m, 2H), 7.51–7.46 (m, 2H), 7.34–7.29 (m, 4H), 7.29–7.25 (m, 3H), 7.25–7.10 (m, 7H), 4.51 (s, 4H), 3.63 (s, 3H), 2.38 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 163.7 (d, *J* = 250 Hz), 156.8, 148.3, 143.8, 140.5, 139.0 (2C), 131.7 (d, *J* = 8.7 Hz, 2C), 129.9 (2C), 128.9 (4C), 128.3 (4C), 127.0 (2C), 126.7 (2C), 125.5 (d, *J* = 3.5 Hz), 116.0 (d, *J* = 11.0 Hz, 2C), 113.4, 56.7 (2C), 34.7, 21.7; **IR (neat) ν_{max}:** 3362, 3198, 2921, 2851, 1658, 1632, 1467, 736, 703; **HRMS (ESI^+):** exact mass calculated for $[M+H]^+$ ($C_{31}H_{29}FN_3O_2S$) requires *m*/*z* 526.1959, found *m*/*z* 526.1957.

***N,N*-dibenzyl-1-methyl-5-tosyl-2-(4-(trifluoromethyl)phenyl)-*1H*-imidazol-4-amine (3o)**



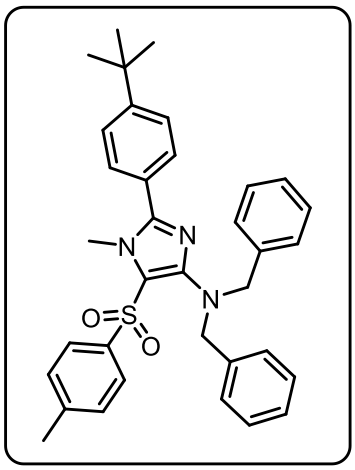
70% v/v DCM were added to the reaction mixture; yellow oil, 25.1 mg (22% yield); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.75–7.70 (m, 2H), 7.67–7.63 (m, 4H), 7.36–7.18 (m, 12H), 4.53 (s, 4H), 3.69 (s, 3H), 2.30 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 156.7, 147.5, 143.9, 140.3, 139.0 (2C), 134.0 (q, *J* = 5.7 Hz), 132.9, 130.1, 129.9, 128.9 (4C), 128.7 (q, *J* = 38.1 Hz, 2C), 128.3 (4C), 127.1 (2C), 126.7 (2C), 125.7 (q, *J* = 3.7 Hz, 2C), 121.2 (q, *J* = 262.2 Hz), 114.2, 56.8 (2C), 34.8, 21.7; **^{19}F-NMR (659 MHz, $CDCl_3$):** δ –62.90; **IR (neat) ν_{max}:** 3361, 2921, 2851, 1658, 1632, 1520, 1466, 1454, 1412, 1323, 1266, 1159, 1131; **HRMS (ESI^+):** exact mass calculated for $[M+H]^+$ ($C_{32}H_{29}F_3N_3O_2S$) requires *m*/*z* 576.1927, found *m*/*z* 576.1922.

***N,N*-Dibenzyl-1-methyl-2-(*p*-tolyl)-5-tosyl-*1H*-imidazol-4-amine (3p)**



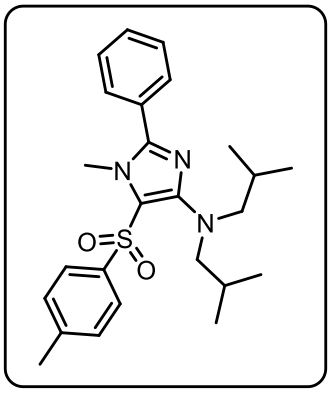
70% v/v DCM were added to the reaction mixture; light-yellow oil, 60.5 mg (58% yield); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.64–7.59 (m, 2H), 7.41–7.37 (m, 2H), 7.35–7.31 (m, 4H), 7.29–7.14 (m, 10H), 4.53 (s, 4H), 3.63 (s, 3H), 2.38 (s, 3H), 2.38 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 156.9, 149.5, 143.6, 140.6, 140.1, 139.1 (2C), 129.8 (2C), 129.5 (2C), 129.4 (2C), 128.9 (4C), 128.2 (4C), 126.9 (2C), 126.6 (2C), 126.4, 113.0, 56.7 (2C), 34.7, 21.7, 21.5; **IR (neat) ν_{max}:** 3360, 2921, 2851, 1658, 1632, 1614, 1452, 1365, 1158, 700, 683; **HRMS (ESI^+):** exact mass calculated for $[M+H]^+$ ($C_{32}H_{32}N_3O_2S$) requires *m*/*z* 522.2210, found *m*/*z* 522.2208.

***N,N*-Dibenzyl-2-(4-(tert-butyl)phenyl)-1-methyl-5-tosyl-*1H*-imidazol-4-amine (3q)**



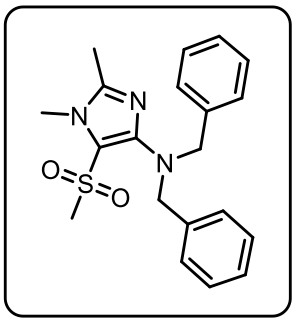
10% v/v DCM were added to the reaction mixture; yellow oil, 49.5 mg (44% yield); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.65–7.60 (m, 2H), 7.47–7.44 (m, 3H), 7.35–7.31 (m, 4H), 7.30–7.21 (m, 7H), 7.19–7.16 (m, 2H), 4.54 (s, 4H), 3.66 (s, 3H), 2.39 (s, 3H), 1.33 (s, 9H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 157.0, 153.3, 149.5, 143.6, 140.7, 139.2 (2C), 129.8 (2C), 129.4 (2C), 128.9 (4C), 128.2 (4C), 126.9 (2C), 126.6 (2C), 126.5, 125.8 (2C), 112.9, 56.7 (2C), 35.0, 34.7, 31.3 (3C), 21.9; **IR (neat) ν_{max}:** 3359, 2922, 2852, 1659, 1632, 1467, 1422, 1265, 736, 703; **HRMS (ESI$^+$):** exact mass calculated for $[M+H]^+$ ($C_{35}H_{38}N_3O_2S$) requires *m/z* 564.2679, found *m/z* 564.2673.

***N,N*-Di*iso*butyl-1-methyl-2-phenyl-5-tosyl-*1H*-imidazol-4-amine (3r)**



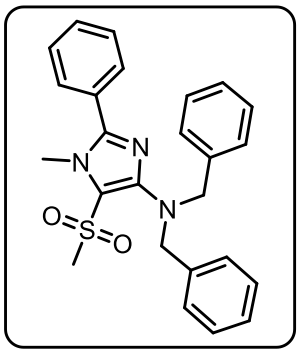
colorless oil, 44.8 mg (51% yield); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.76–7.72 (m, 2H), 7.55–7.51 (m, 2H), 7.46–7.42 (m, 4H), 7.29–7.26 (m, 2H), 3.67 (s, 3H), 3.27 (d, *J* = 7.3 Hz, 4H), 2.41 (s, 3H), 1.91 (sept, *J* = 6.7 Hz, 2H), 0.81 (d, *J* = 6.7 Hz, 12H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 158.6, 150.1, 143.3, 141.5, 132.9, 129.9, 129.8 (2C), 129.7 (2C), 128.7 (2C), 125.3 (2C), 108.8, 59.8 (2C), 35.0, 27.0 (2C), 21.6, 20.4 (4C); **IR (neat) ν_{max}**: 3360, 2959, 1649, 1460, 1263, 1164, 918, 747; **HRMS (ESI$^+$):** exact mass calculated for $[M+H]^+$ ($C_{25}H_{34}N_3O_2S$) requires *m/z* 440.2366, found *m/z* 440.2374.

***N,N*-Dibenzyl-1,2-dimethyl-5-(methylsulfonyl)-*1H*-imidazol-4-amine (3s)**



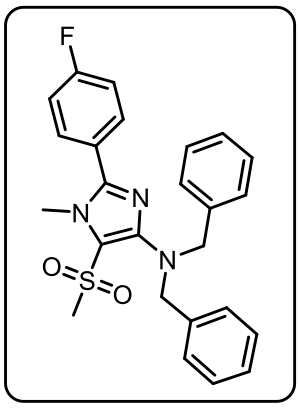
colorless oil, 36.8 mg (47% yield); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.29–7.22 (m, 8H), 7.22–7.16 (m, 2H), 4.37 (s, 4H), 3.66 (s, 3H), 2.86 (s, 3H), 2.35 (s, 3H); **^{13}C-NMR (150 MHz, $CDCl_3$):** δ 154.9, 146.9, 138.8 (2C), 128.8 (4C), 128.4 (4C), 127.1 (2C), 113.8, 56.5 (2C), 44.9, 33.0, 13.8; **IR (neat) ν_{max}**: 2921, 2851, 1520, 1494, 1452, 1406, 1362, 1305, 1149, 1121, 950, 760, 741, 699; **HRMS (ESI^+):** exact mass calculated for $[M+H]^+$ ($C_{20}H_{23}N_3O_2SNa$) requires *m*/*z* 392.1403, found *m*/*z* 392.1408.

***N,N*-Dibenzyl-1-methyl-5-(methylsulfonyl)-2-phenyl-*1H*-imidazol-4-amine (3t)**



yellow oil, 39.7 mg (46% yield); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.59–7.55 (m,2), 7.53–7.47 (m, 3H),7.36–7.19 (m, 10H), 4.46 (s, 4H), 3.80 (s, 3H), 2.99 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 155.3, 149.2, 138.9 (2C), 130.0, 129.7 (2C), 129.3, 129.0 (4C), 128.9 (2C), 128.4 (4C), 127.2 (2C), 115.6, 56.7 (2C), 44.9, 34.9; **IR (neat) ν_{max}**: 2956, 2923, 2853, 1520, 1494, 1467, 1453, 1398, 1365, 1312, 1266, 1155, 951, 735, 700; **HRMS (ESI^+):** exact mass calculated for $[M+H]^+$ ($C_{25}H_{26}N_3O_2S$) requires *m*/*z* 432.1740, found *m*/*z* 432.1740.

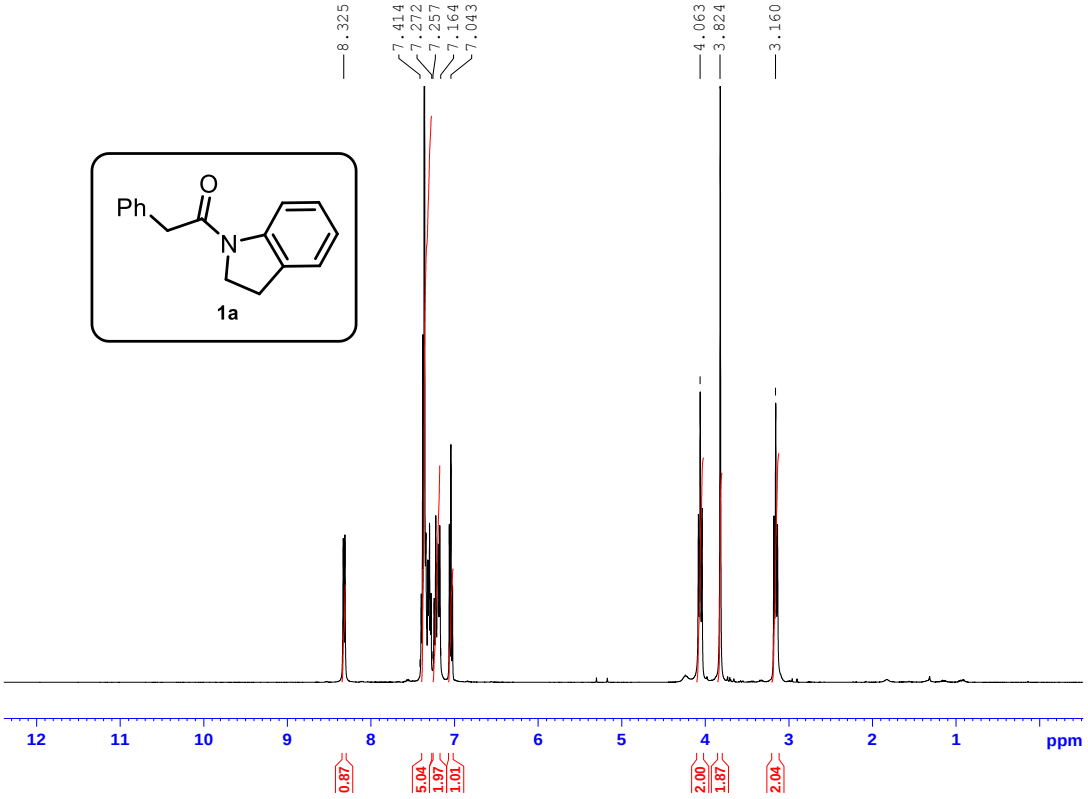
***N,N*-Dibenzyl-2-(4-fluorophenyl)-1-methyl-5-(methylsulfonyl)-*1H*-imidazol-4-amine (3u)**

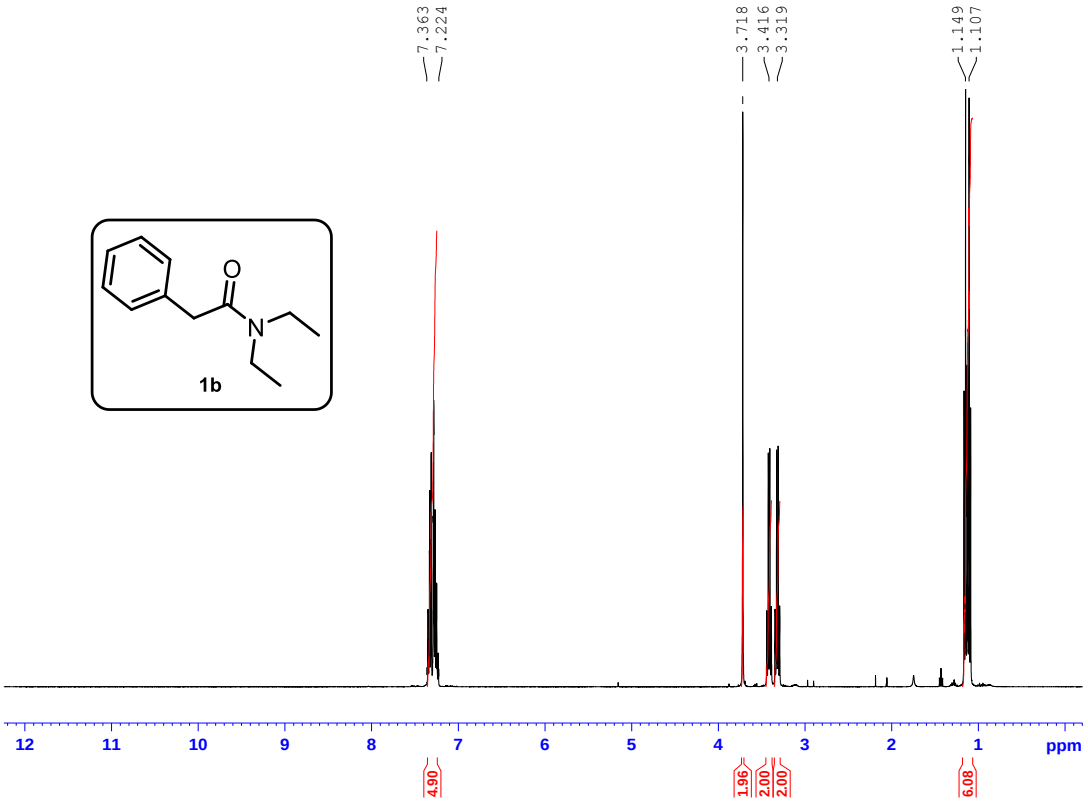


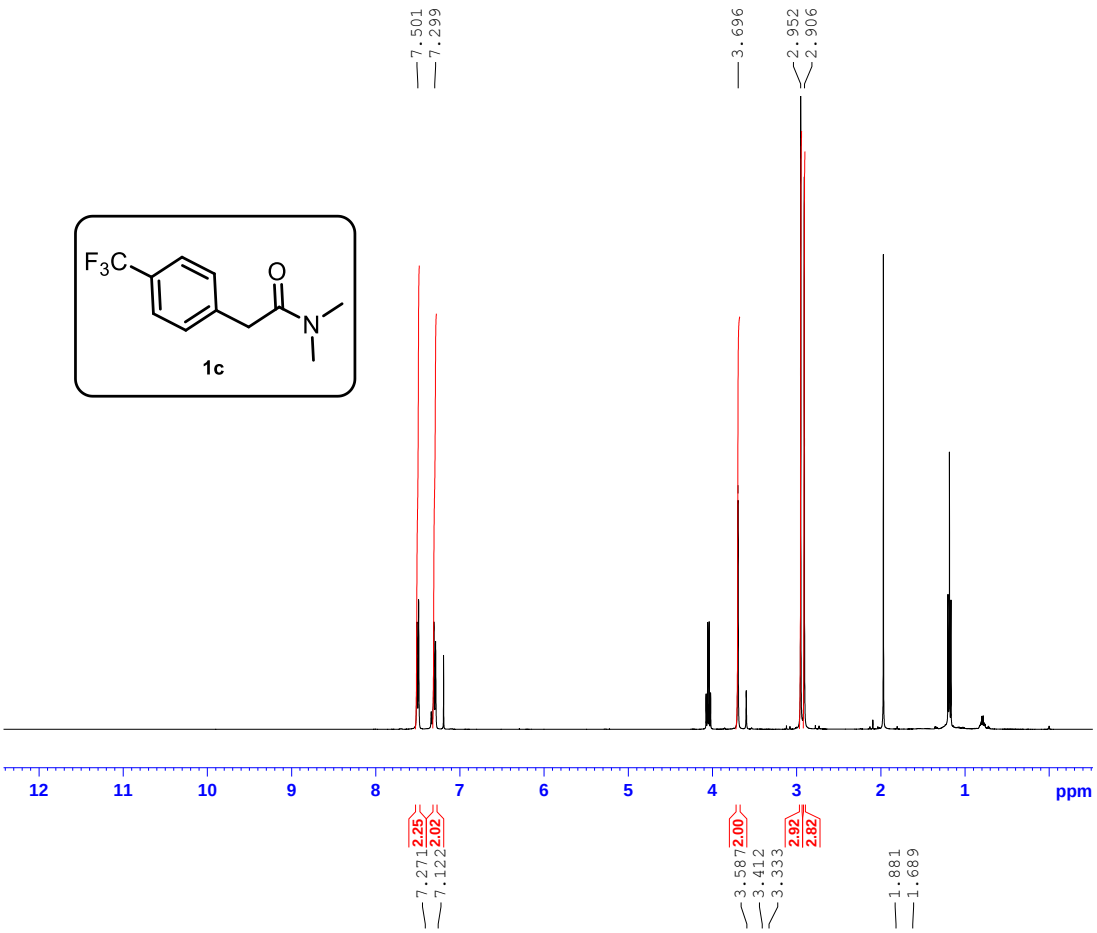
yellow oil, 47.2 mg (50% yield); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.60–7.53 (m,2), 7.35–7.17 (m, 12H), 4.45 (s, 4H), 3.78 (s, 3H), 3.00 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 163.8 (d, *J* = 250.0 Hz), 155.2, 148.2, 138.8 (2C), 131.8 (d, *J* = 8.2 Hz, 2C), 129.0 (4C), 128.4 (4C), 127.2 (2C), 125.5 (d, *J* = 3.5 Hz), 116.1 (d, *J* = 21.9 Hz, 2C), 115.5, 56.6 (2C), 45.0, 34.9; **IR (neat) ν_{max}**: 2920, 2851, 1526, 1458, 1376, 1314, 1263, 1230, 1156, 1121, 952, 844, 742, 702; **HRMS (ESI^+):** exact mass calculated for $[M+H]^+$ ($C_{25}H_{24}FN_3O_2SNa$) requires *m*/*z* 472.1465, found *m*/*z* 472.1471.

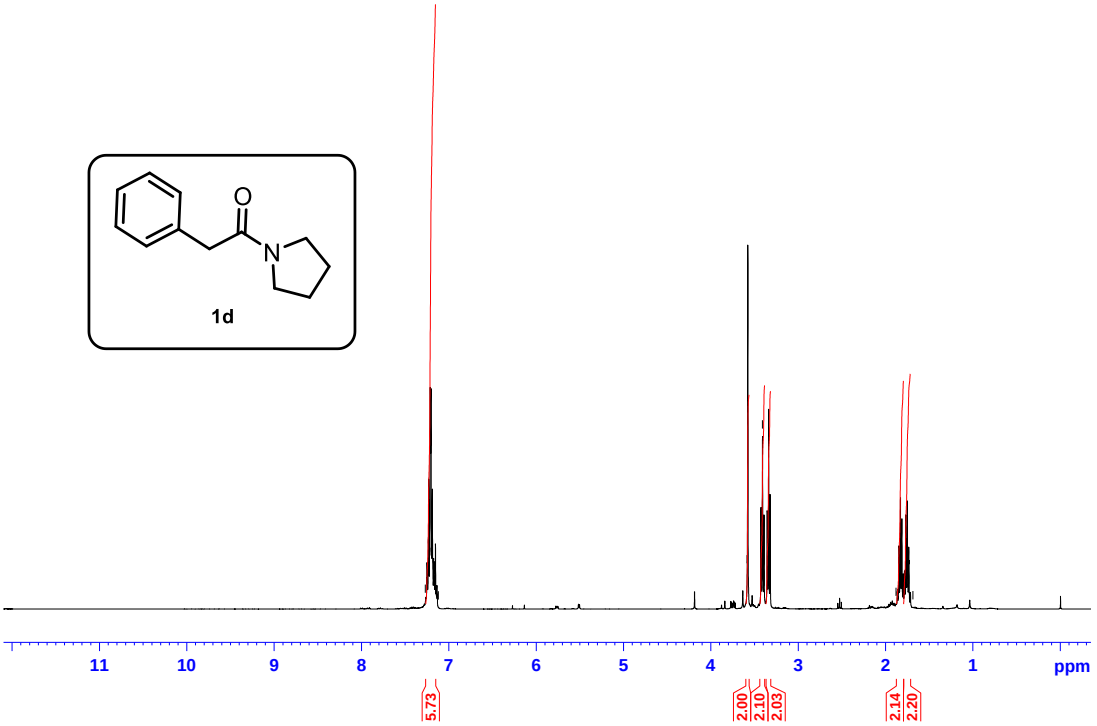
5. NMR Spectra

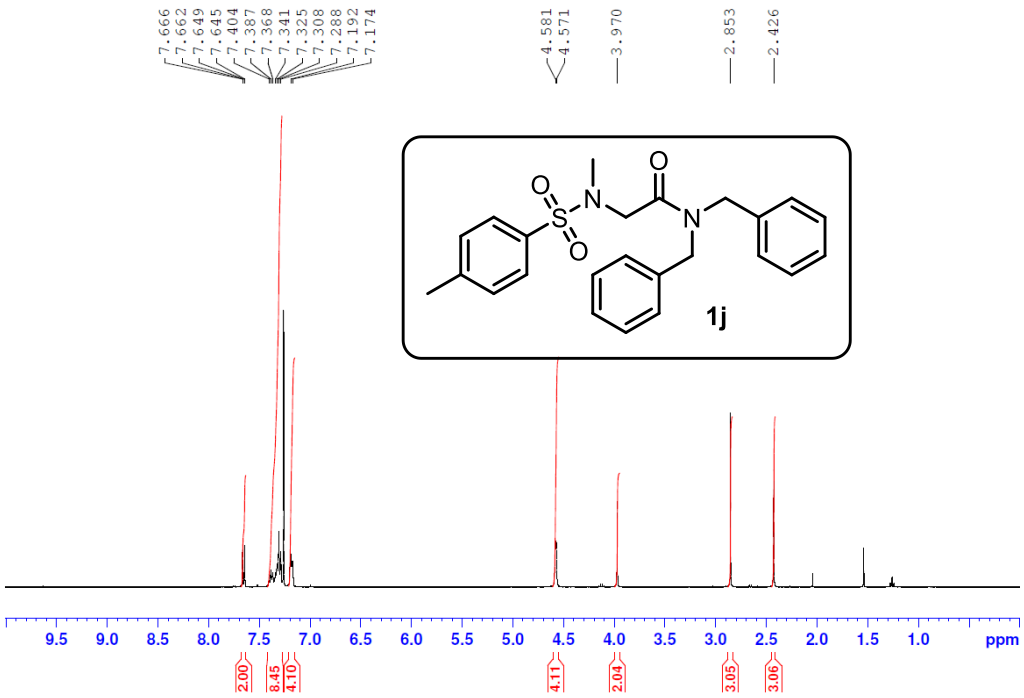
5.1. Substrates

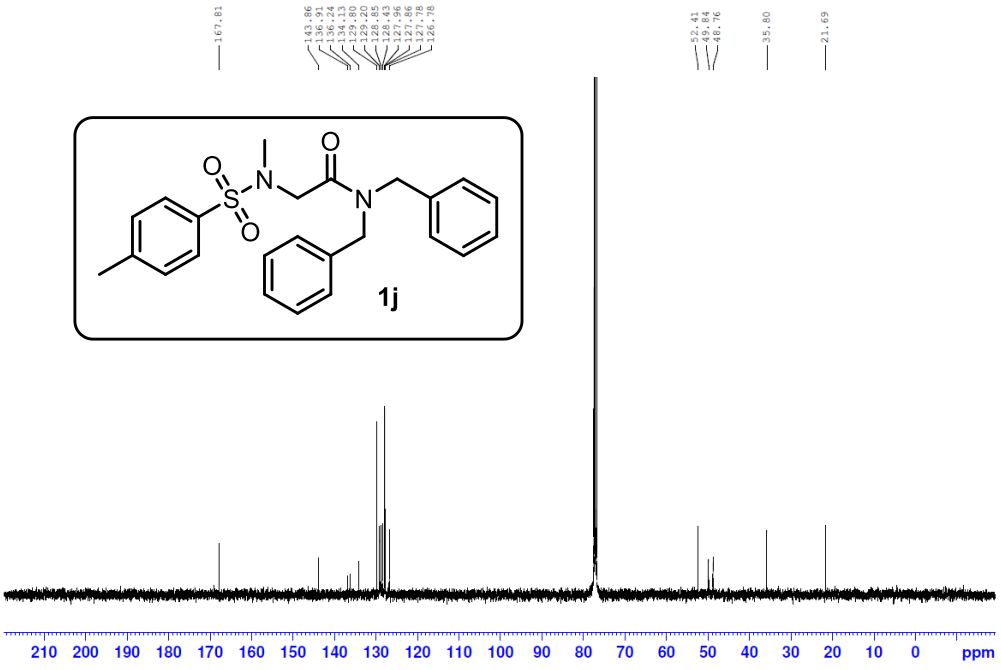


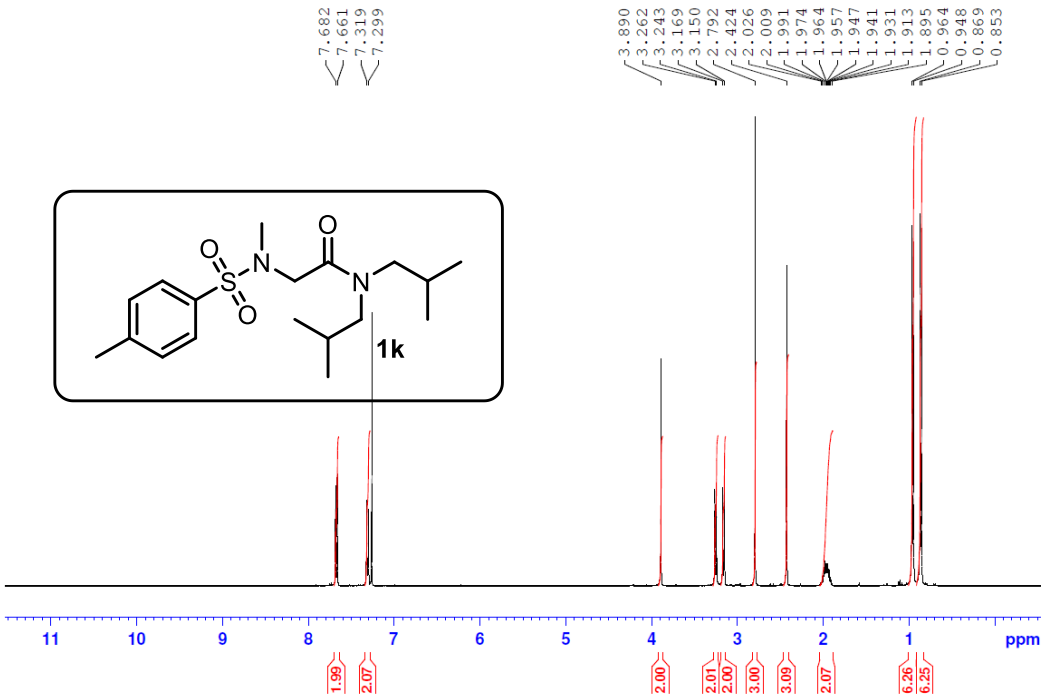


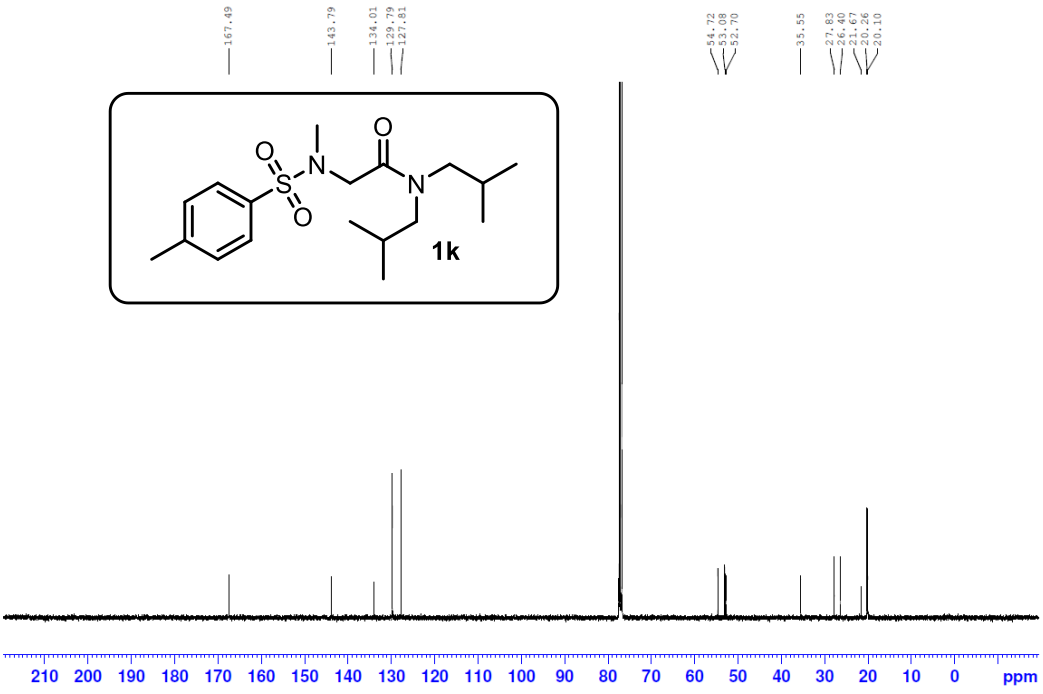

7.501
7.299
3.696
2.952
2.906
F3C
O
N
1c
12
11
10
9
8
7
6
5
4
3
2
1
ppm
2.25
2.02
2.00
2.92
2.82
7.271
7.122
3.587
3.412
3.333
1.881
1.689

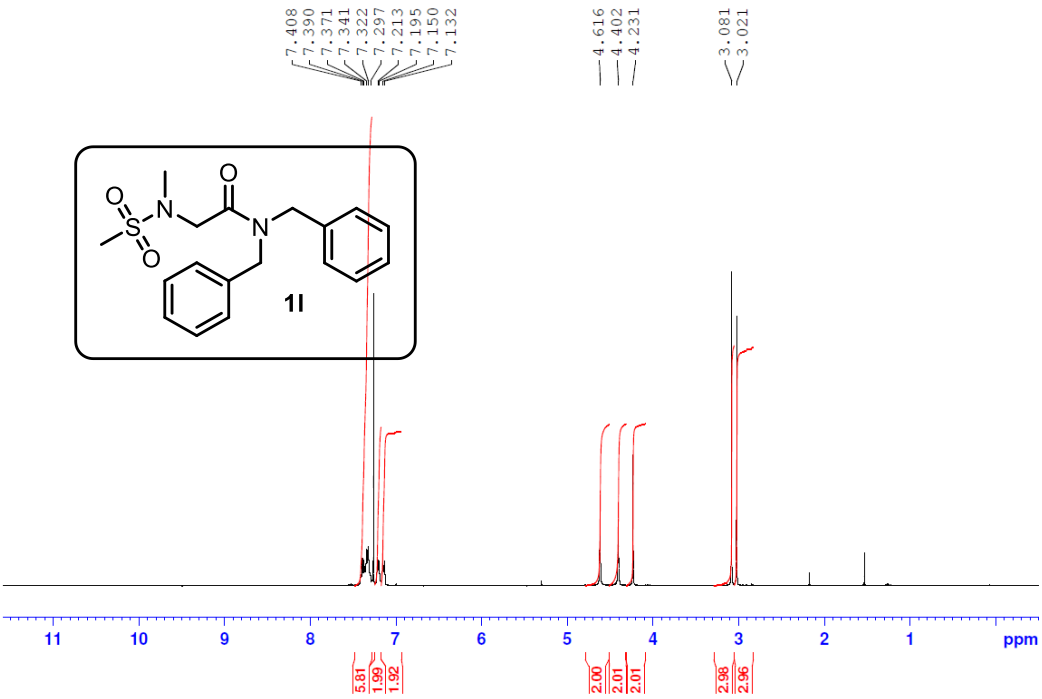

O
N
1d
11
10
9
8
7
6
5
4
3
2
1
ppm
5.73
2.00
2.10
2.03
2.14
2.20

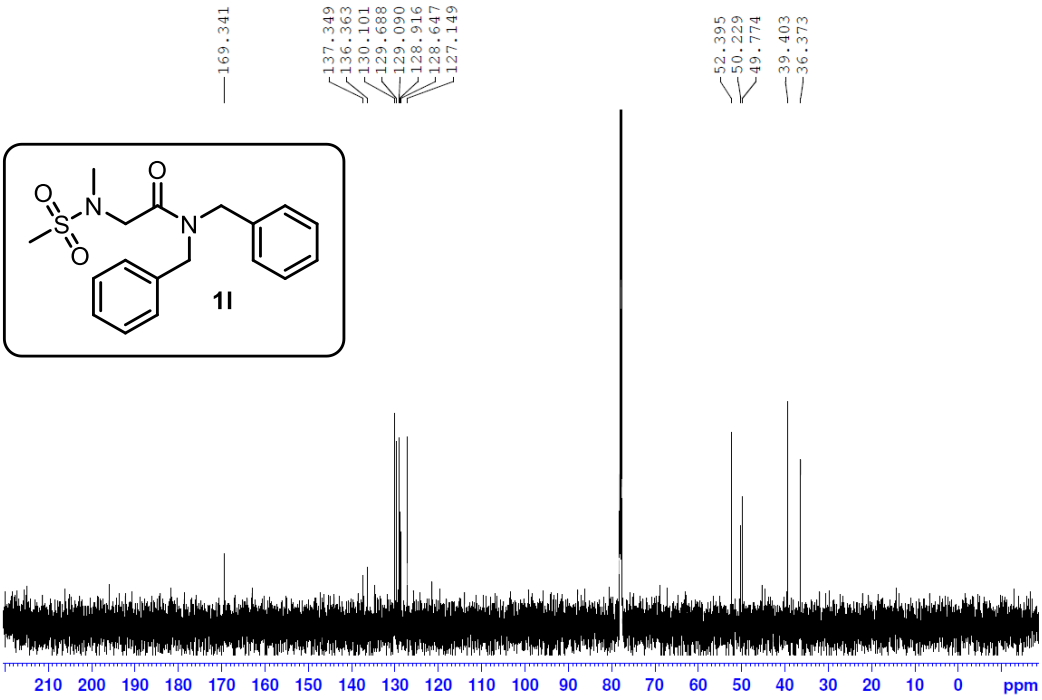

7.666
7.662
7.649
7.645
7.404
7.387
7.368
7.341
7.325
7.308
7.288
7.192
7.174
4.581
4.571
3.970
2.853
2.426
1j
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
2.00
8.45
4.10
4.11
2.04
3.05
3.06

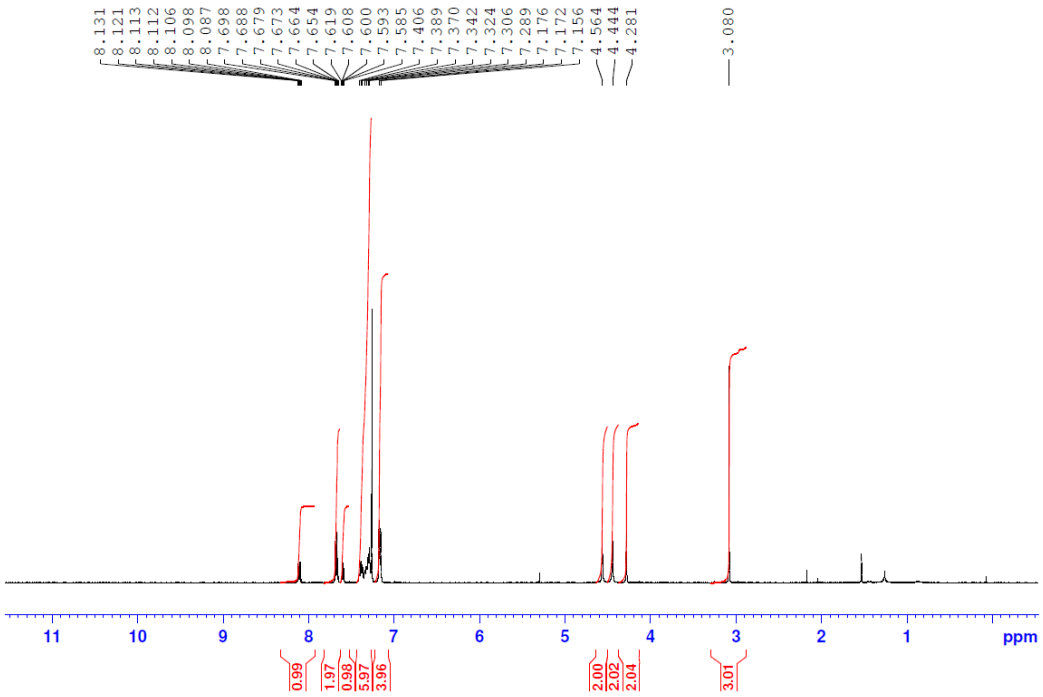

167.81
143.86
136.91
136.24
134.13
129.80
129.20
128.85
128.43
127.96
127.86
127.78
126.78
52.41
49.84
46.76
35.80
21.69
1j
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

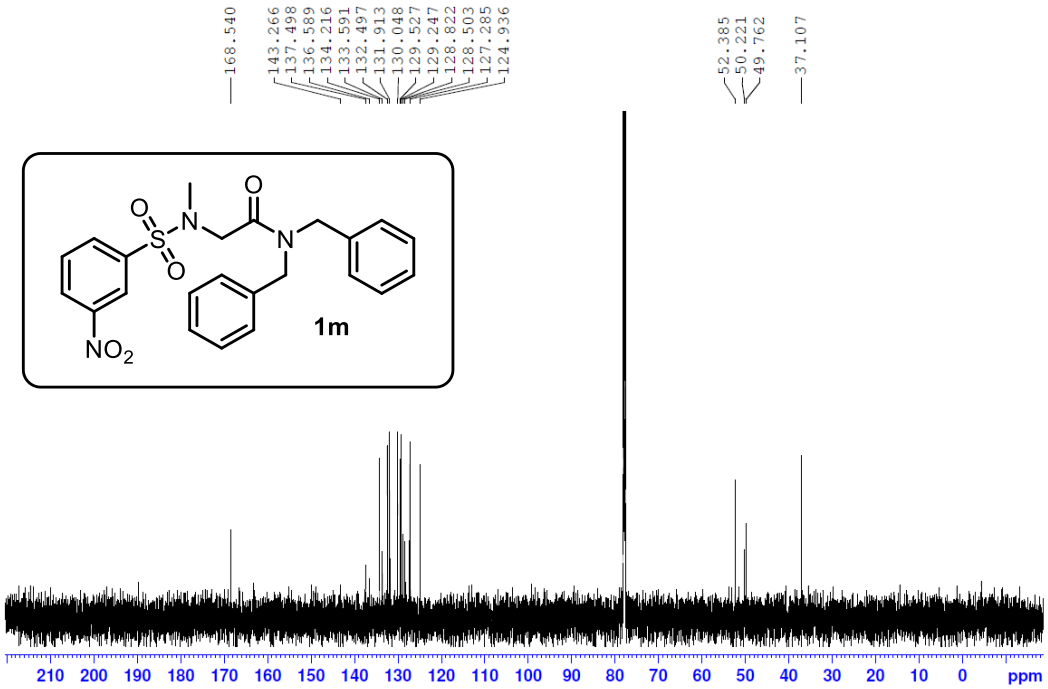

7.682
7.661
7.319
7.299
3.890
3.262
3.243
3.169
3.150
2.792
2.424
2.026
2.009
1.991
1.974
1.964
1.957
1.947
1.941
1.931
1.913
1.895
0.964
0.948
0.869
0.853
1k
11
10
9
8
7
6
5
4
3
2
1
ppm
1.99
2.07
2.00
2.01
2.00
3.00
3.09
2.07
6.26
6.25


167.49
143.79
134.01
129.79
127.81
54.72
53.08
52.70
35.55
27.83
26.40
21.67
20.26
20.10
1k
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

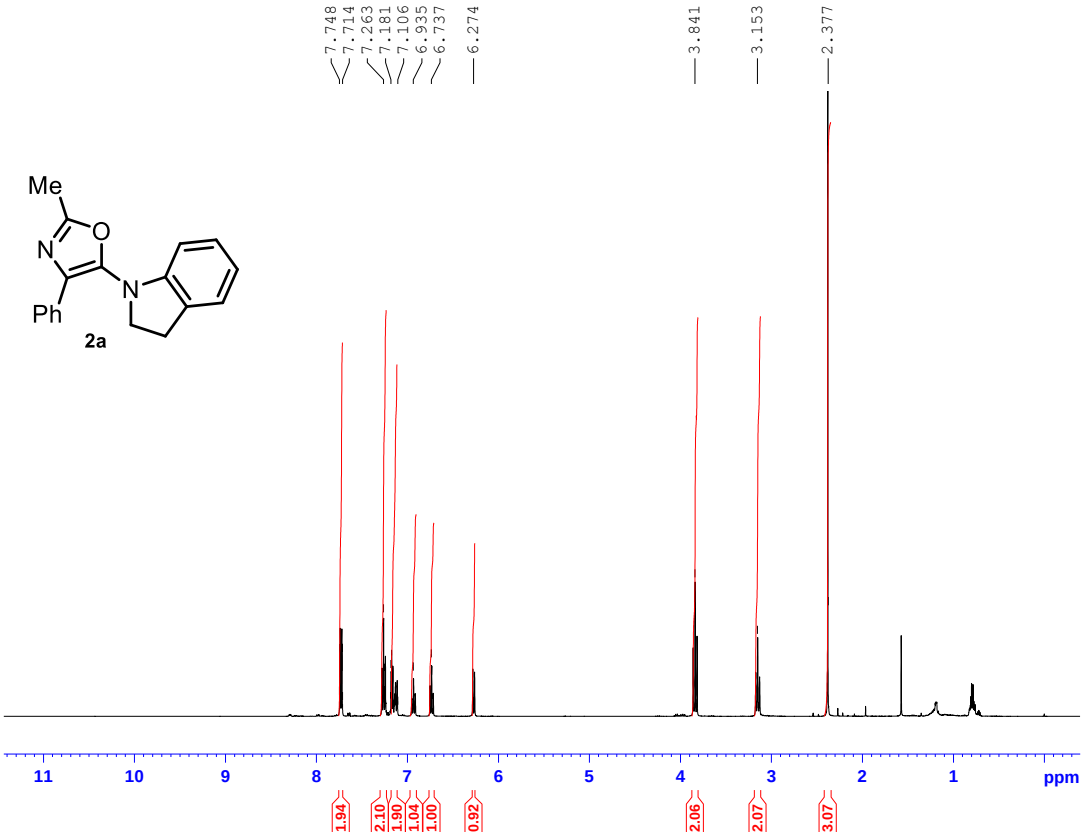

7.408
7.390
7.371
7.341
7.322
7.297
7.213
7.195
7.150
7.132
4.616
4.402
4.231
3.081
3.021
1l
11
10
9
8
7
6
5
4
3
2
1
ppm
5.81
1.99
1.92
2.00
2.01
2.01
2.98
2.96

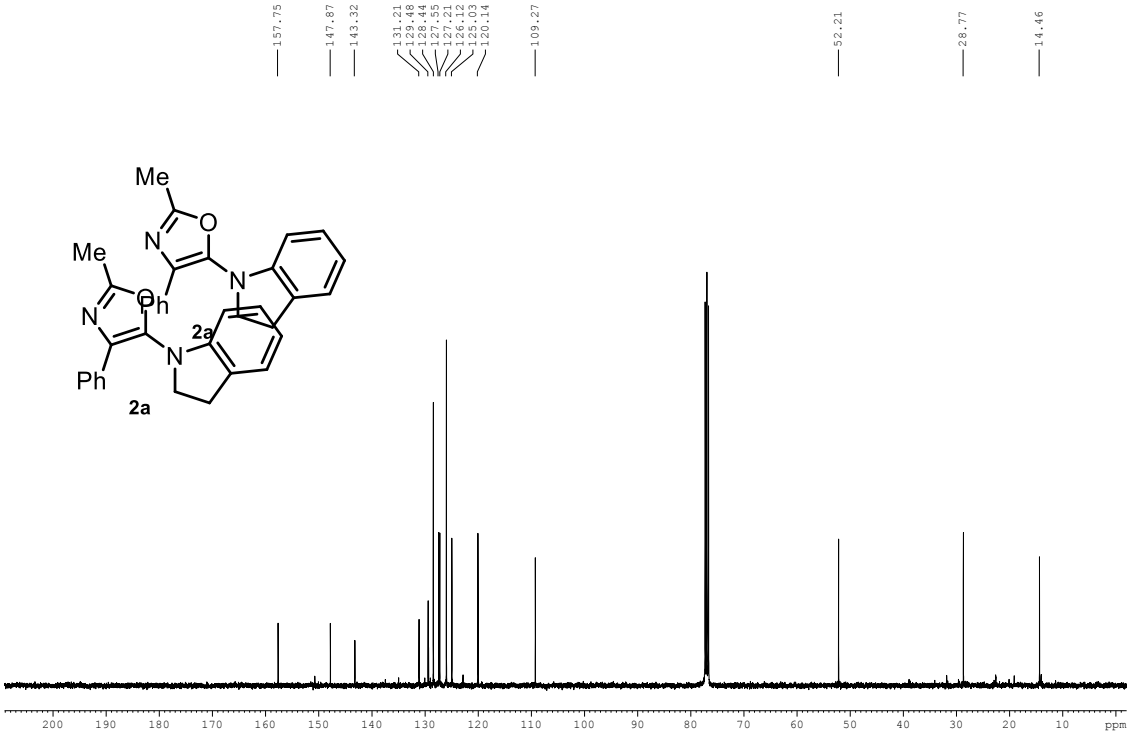

169.341
137.349
136.363
130.101
129.688
129.090
128.916
128.647
127.149
52.395
50.229
49.774
39.403
36.373
1l
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

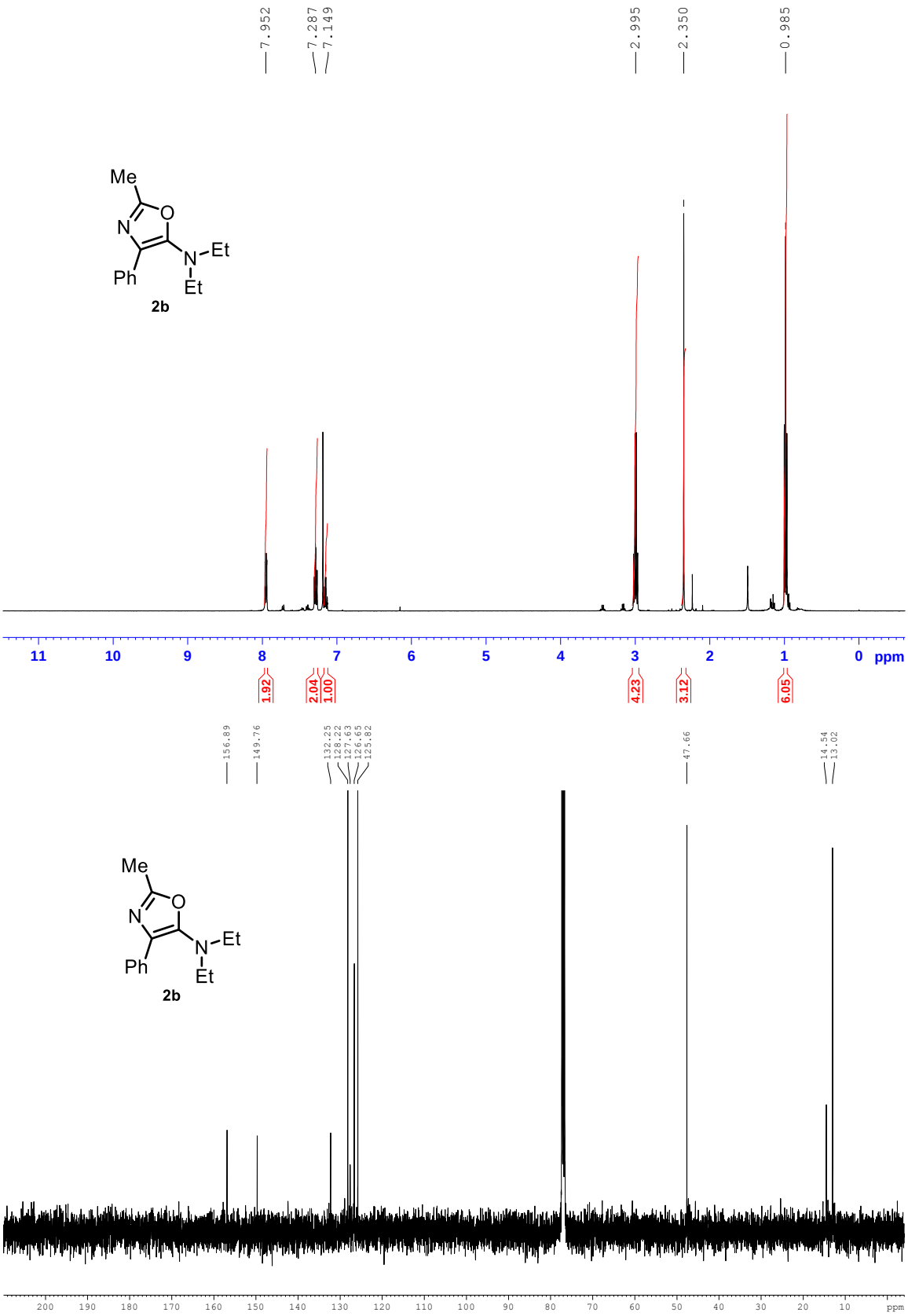

8.131
8.121
8.113
8.112
8.106
8.098
8.087
7.698
7.688
7.679
7.673
7.664
7.654
7.619
7.608
7.600
7.593
7.585
7.406
7.389
7.370
7.342
7.324
7.306
7.289
7.176
7.172
7.156
4.564
4.444
4.281
3.080
11 10 9 8 7 6 5 4 3 2 1 ppm
0.99 1.97 0.98 5.97 3.96 2.00 2.02 2.04 3.01

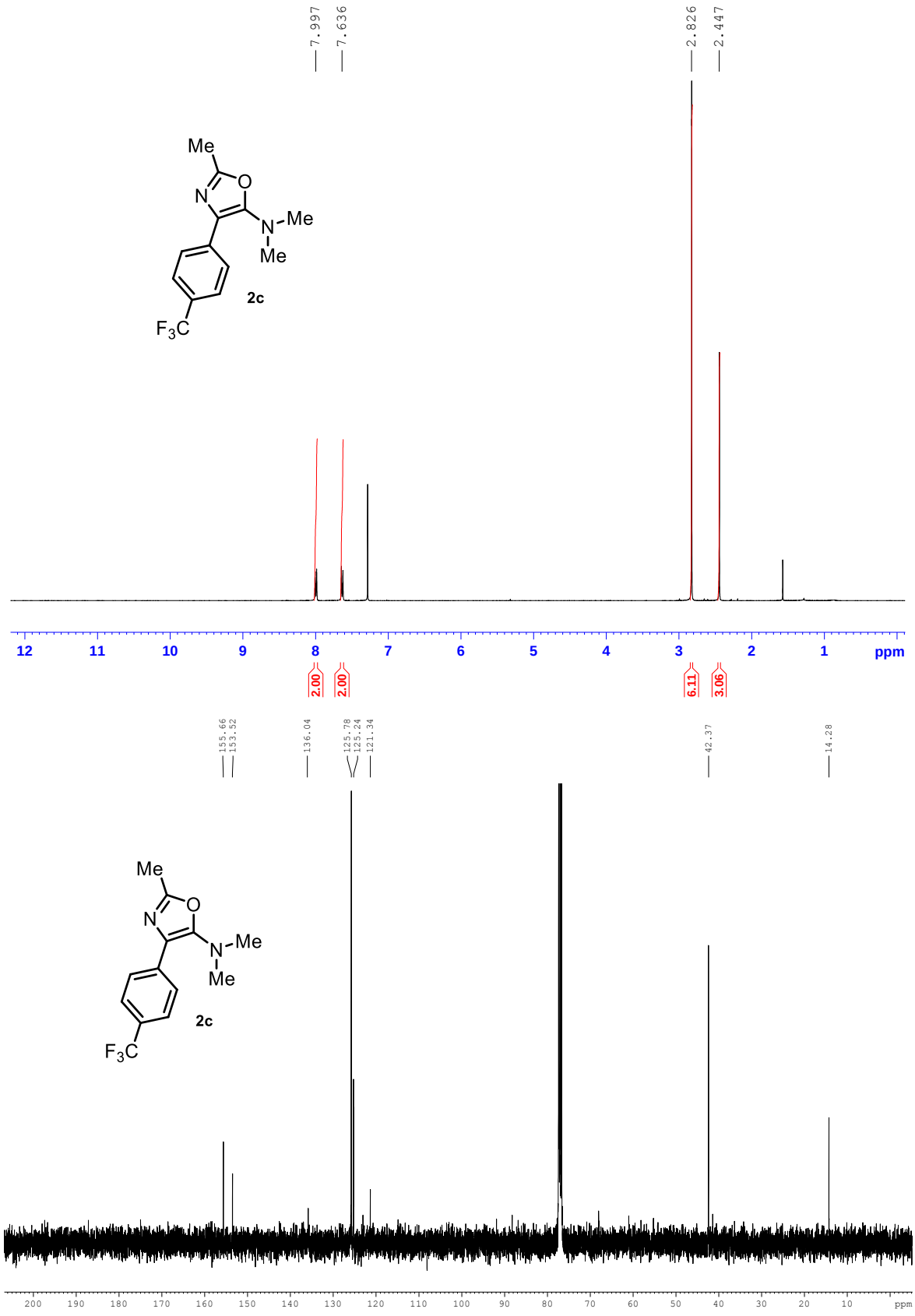

168.540
143.266
137.498
136.589
134.216
133.591
132.497
131.913
130.048
129.527
129.247
128.822
128.503
127.285
124.936
52.385
50.221
49.762
37.107
O
O
S
O
N
N
O
NO2
1m
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

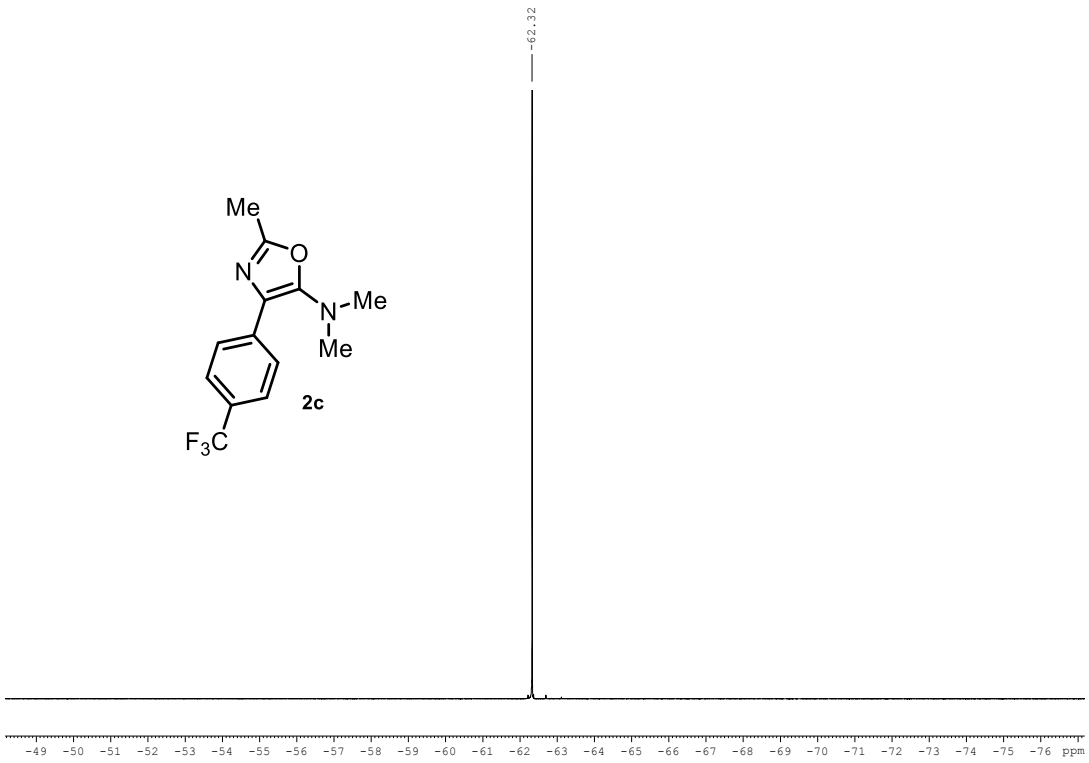
5.2. Products – Oxazoles

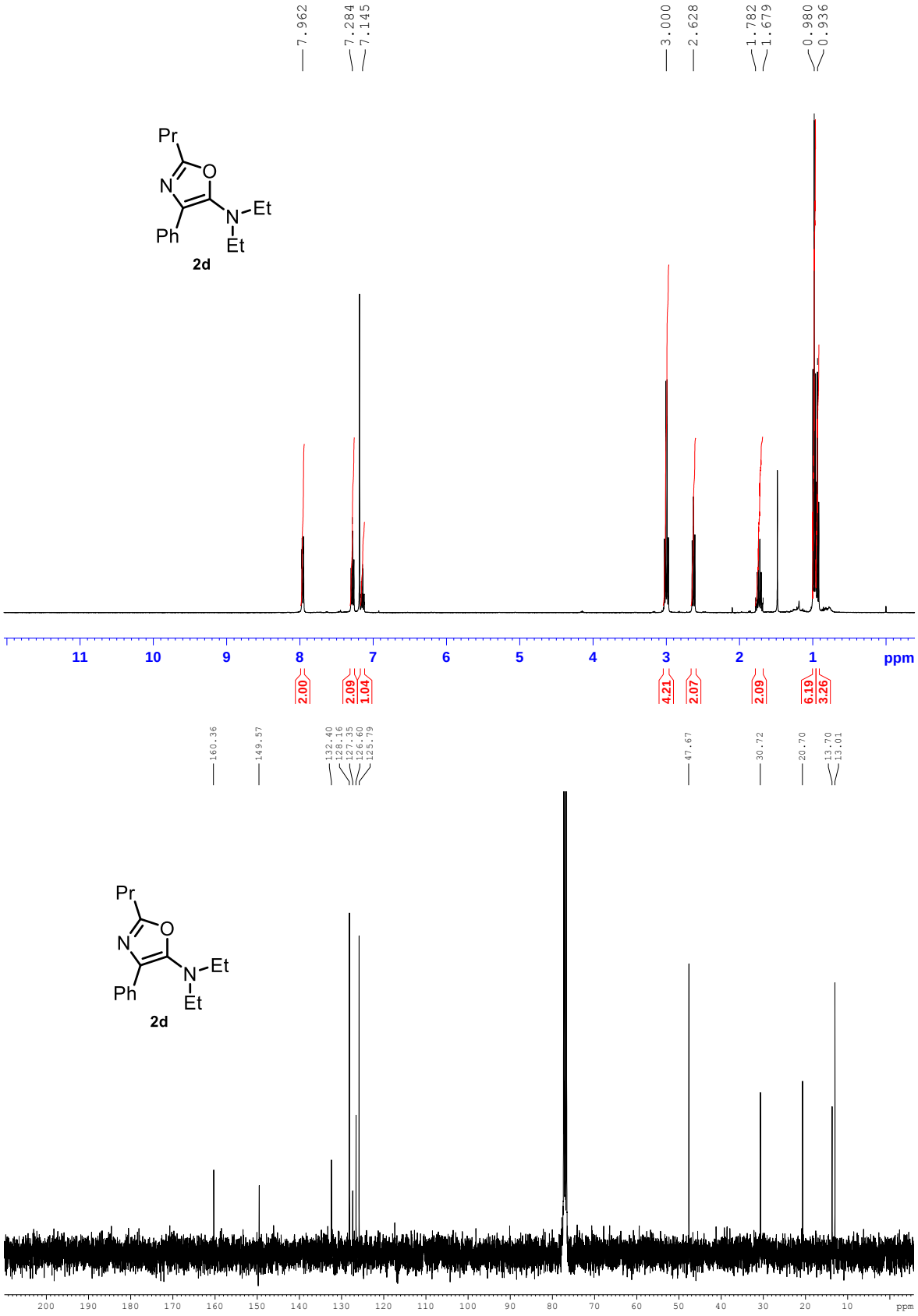


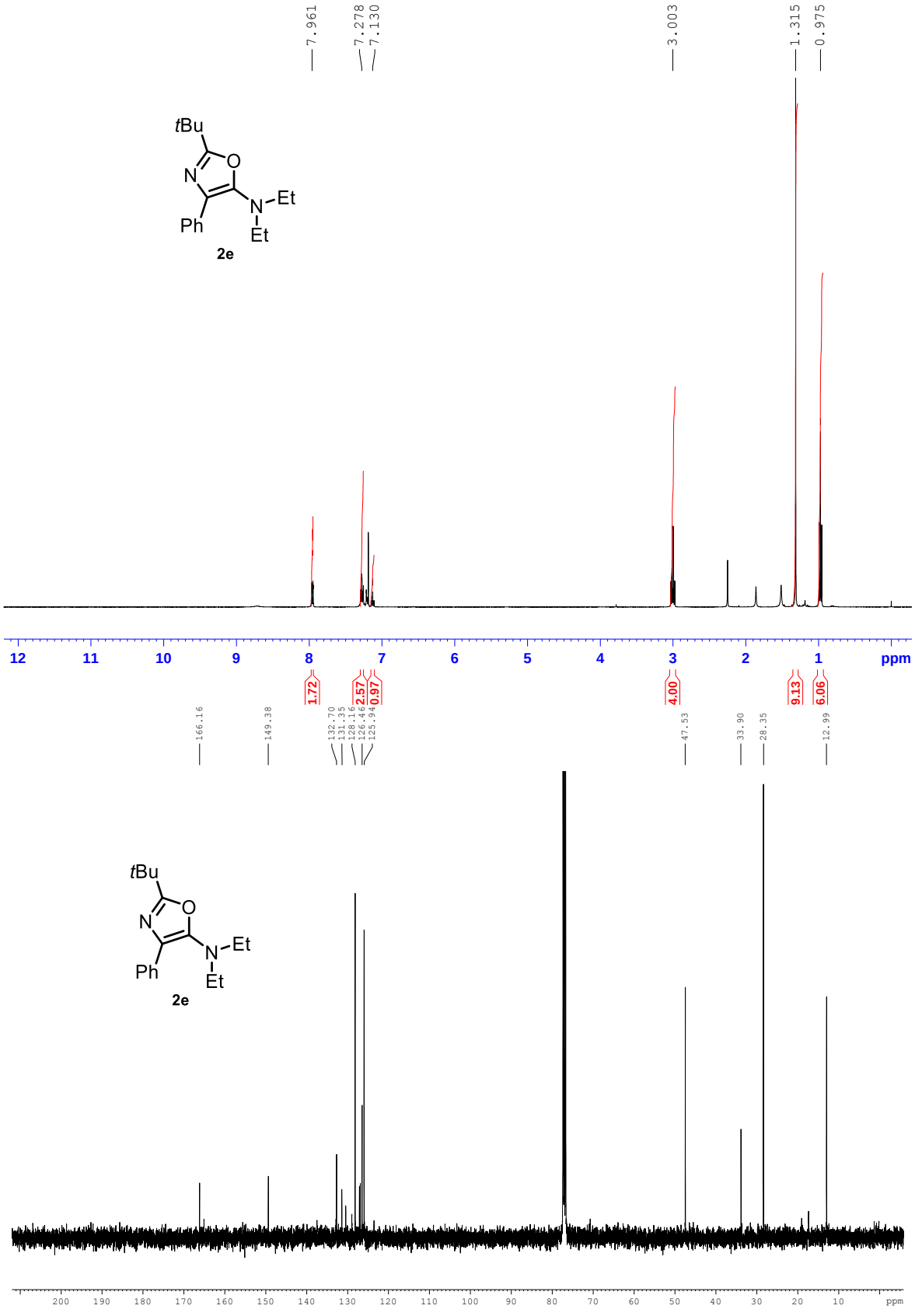


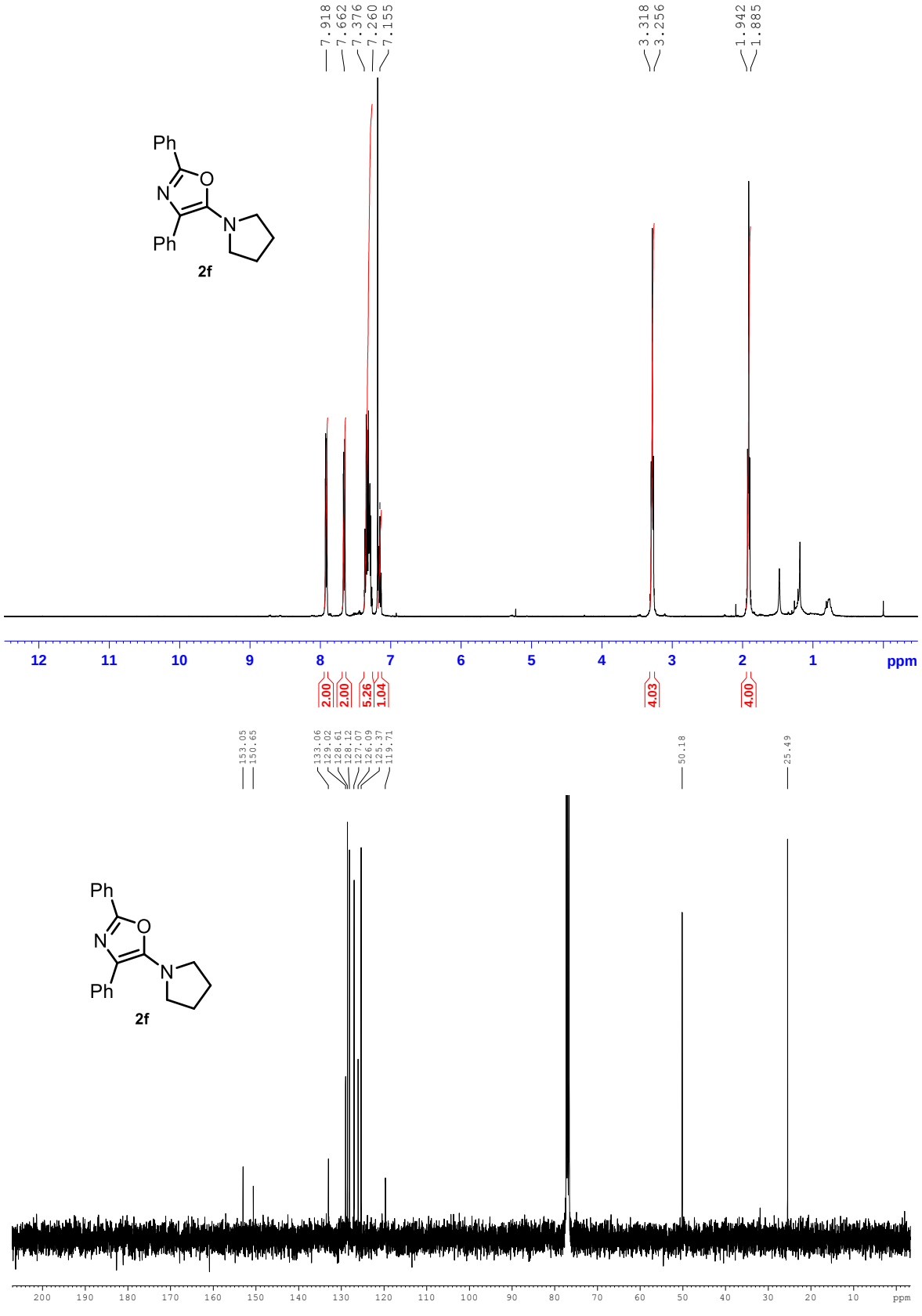

7.952
7.287
7.149
2.995
2.350
0.985
Me
O
N
Ph
N
Et
Et
2b
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.92
2.04
1.00
4.23
3.12
6.05
156.89
149.76
132.25
128.22
127.63
126.65
125.82
47.66
14.54
13.02
Me
O
N
Ph
N
Et
Et
2b
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

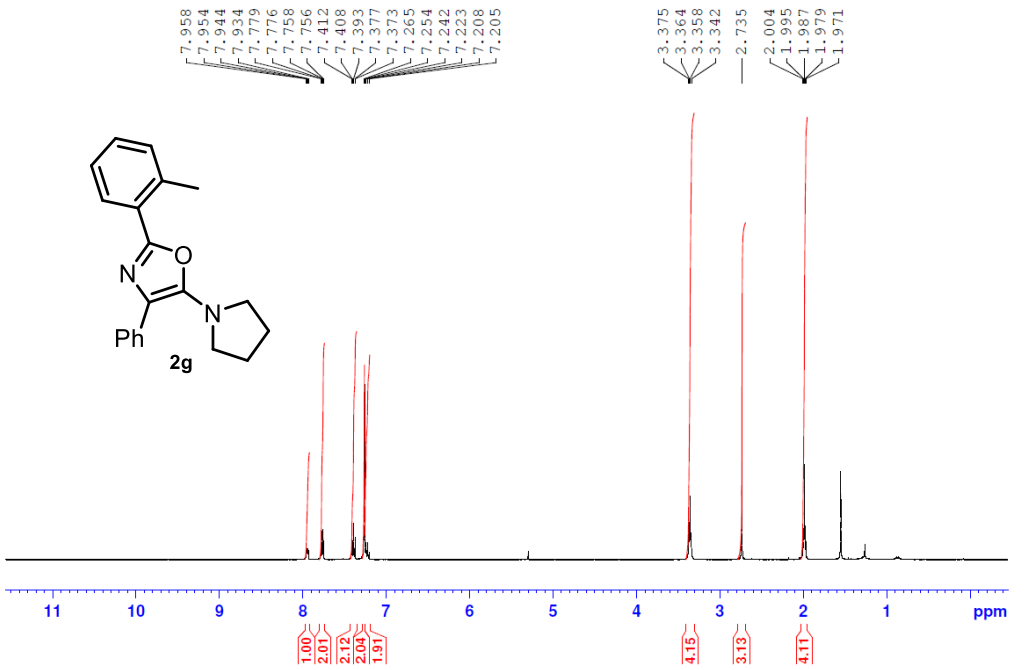

7.997
7.636
2.826
2.447
Me
O
N
N-Me
Me
2c
F3C
12
11
10
9
8
7
6
5
4
3
2
1
ppm
2.00
2.00
6.11
3.06
155.66
153.52
136.04
125.78
125.24
121.34
42.37
14.28
Me
O
N
N-Me
Me
2c
F3C
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

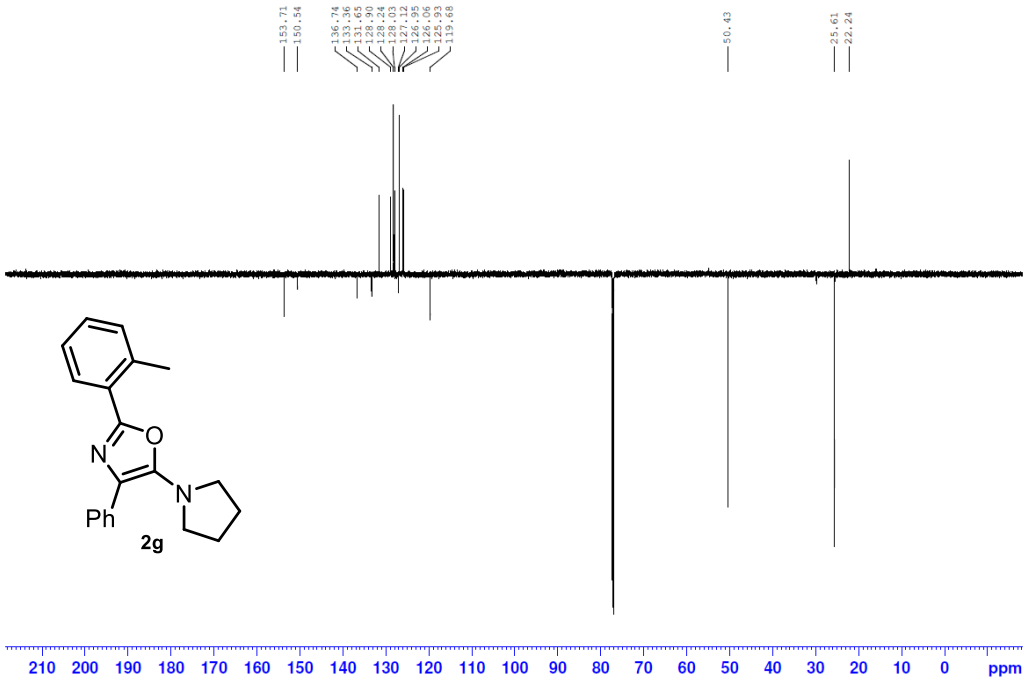

-62.32
Me
O
N
N
Me
Me
2c
F3C
-49 -50 -51 -52 -53 -54 -55 -56 -57 -58 -59 -60 -61 -62 -63 -64 -65 -66 -67 -68 -69 -70 -71 -72 -73 -74 -75 -76 ppm

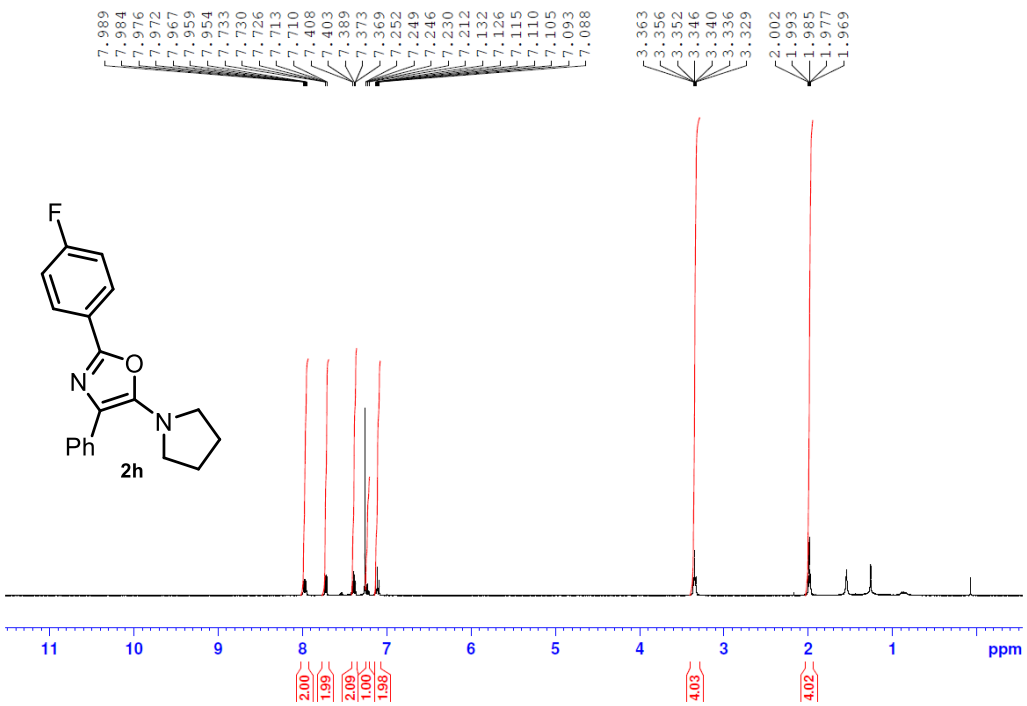

7.962
7.284
7.145
3.000
2.628
1.782
1.679
0.980
0.936
Pr
O
N
Et
N
Et
Ph
2d
11
10
9
8
7
6
5
4
3
2
1
ppm
2.00
2.09
1.04
4.21
2.07
2.09
6.19
3.26
160.36
149.57
132.40
128.16
127.35
126.60
125.79
47.67
30.72
20.70
13.70
13.01
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


7.961
7.278
7.130
3.003
1.315
0.975
tBu
N
O
N
Et
Et
Ph
2e
12
11
10
9
8
7
6
5
4
3
2
1
ppm
1.72
2.57
0.97
4.00
9.13
6.06
166.16
149.38
132.70
131.35
128.16
126.46
125.94
47.53
33.90
28.35
12.99
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


7.918
7.662
7.376
7.260
7.155
3.318
3.256
1.942
1.885
Ph
O
N
N
Ph
2f
12
11
10
9
8
7
6
5
4
3
2
1
ppm
2.00
2.00
5.26
1.04
4.03
4.00
153.05
150.65
133.06
129.02
128.61
128.12
127.07
126.09
125.37
119.71
50.18
25.49
Ph
O
N
N
Ph
2f
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


7.958
7.954
7.944
7.934
7.779
7.776
7.758
7.756
7.412
7.408
7.393
7.377
7.373
7.265
7.254
7.242
7.223
7.208
7.205
3.375
3.364
3.358
3.342
2.735
2.004
1.995
1.987
1.979
1.971
Ph
2g
11
10
9
8
7
6
5
4
3
2
1
ppm
1.00
2.01
2.12
2.04
1.91
4.15
3.13
4.11


153.71
150.54
136.74
133.36
131.65
128.90
128.24
128.03
127.12
126.95
126.06
125.93
119.68
50.43
25.61
22.24
Ph
2g
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


7.989
7.984
7.976
7.972
7.967
7.959
7.954
7.733
7.730
7.726
7.713
7.710
7.408
7.403
7.389
7.373
7.369
7.252
7.249
7.246
7.230
7.212
7.132
7.126
7.115
7.110
7.105
7.093
7.088
3.363
3.356
3.352
3.346
3.340
3.336
3.329
2.002
1.993
1.985
1.977
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O
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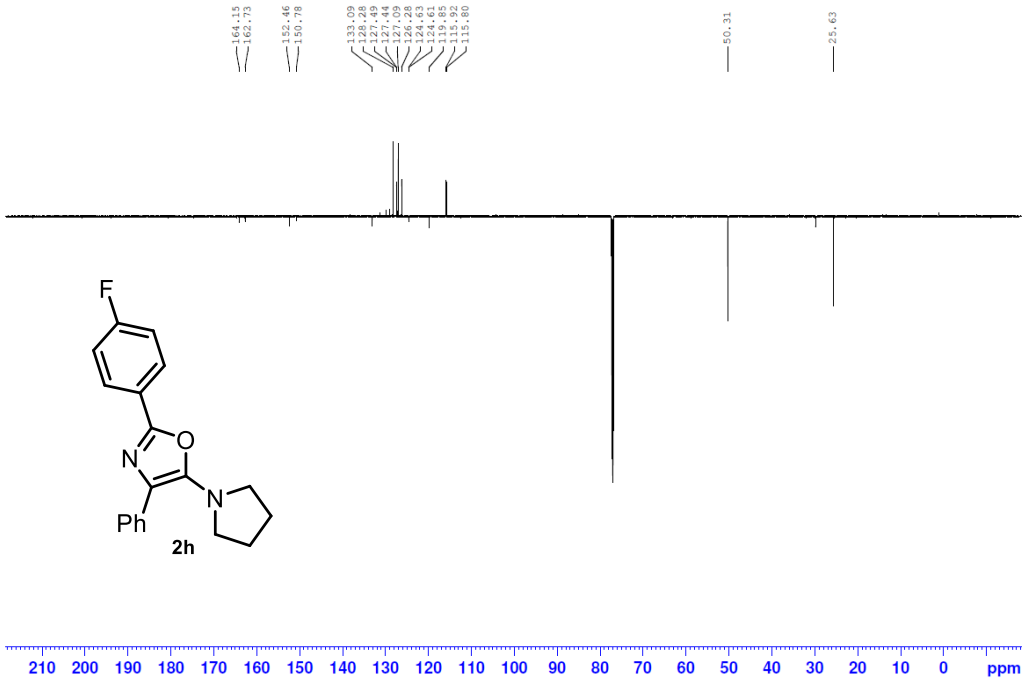
N
Ph
2h
11
10
9
8
7
6
5
4
3
2
1
ppm
2.00
1.99
2.09
1.00
1.98
4.03
4.02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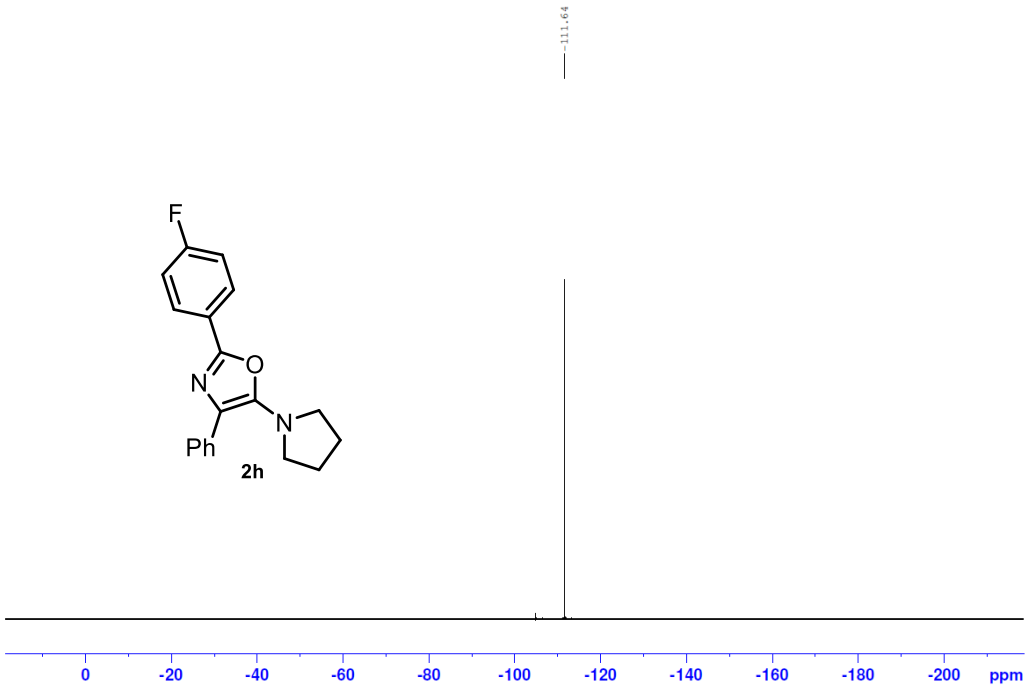
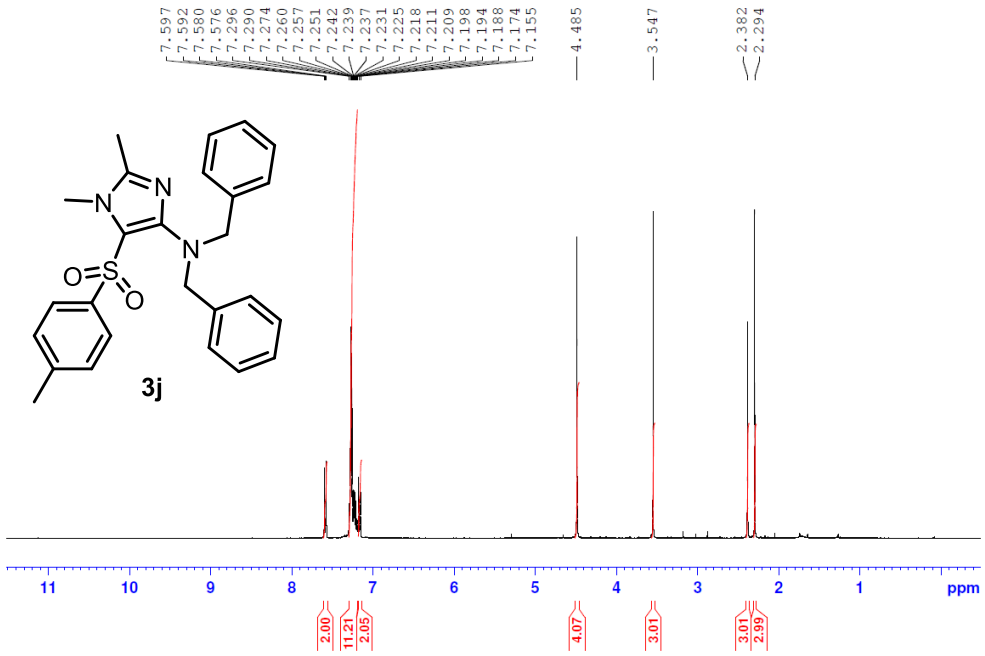
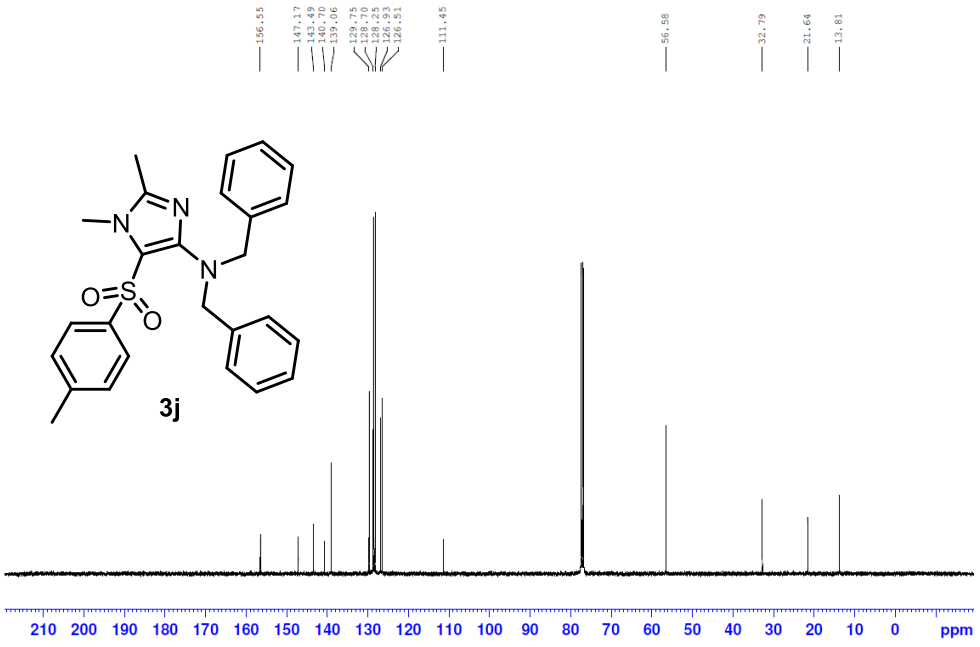
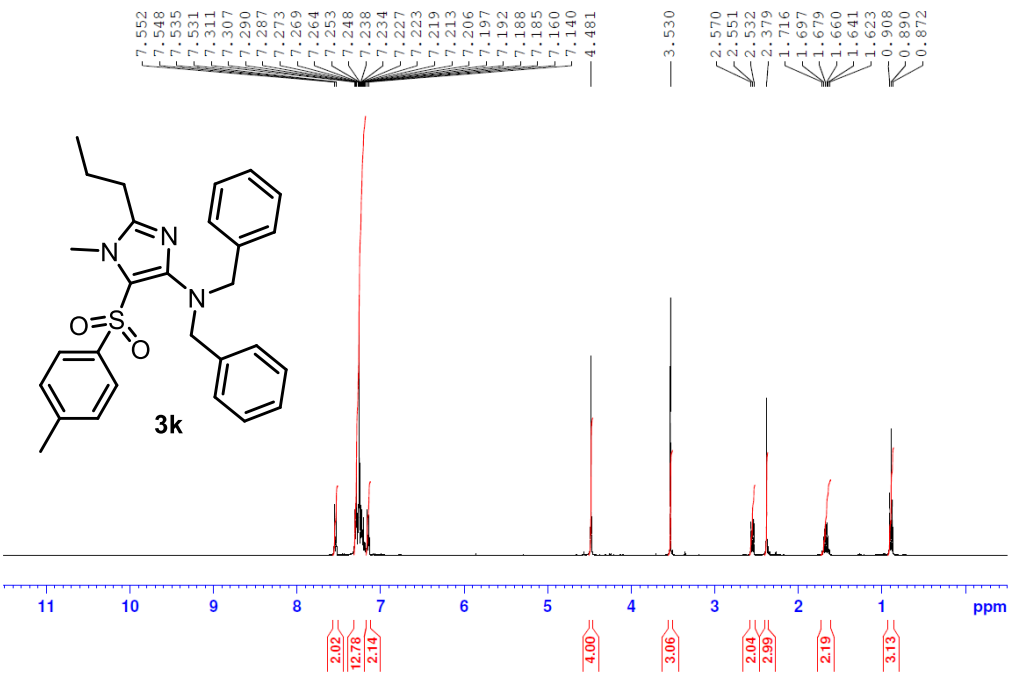
162.73
152.46
150.78
133.09
128.28
127.49
127.44
127.09
126.28
124.63
124.61
119.85
115.92
115.80
50.31
25.63
F
O
N
N
Ph
2h
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


-111.64
F
N
O
N
Ph
2h
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm

5.3. Products – Imidazoles



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7.287
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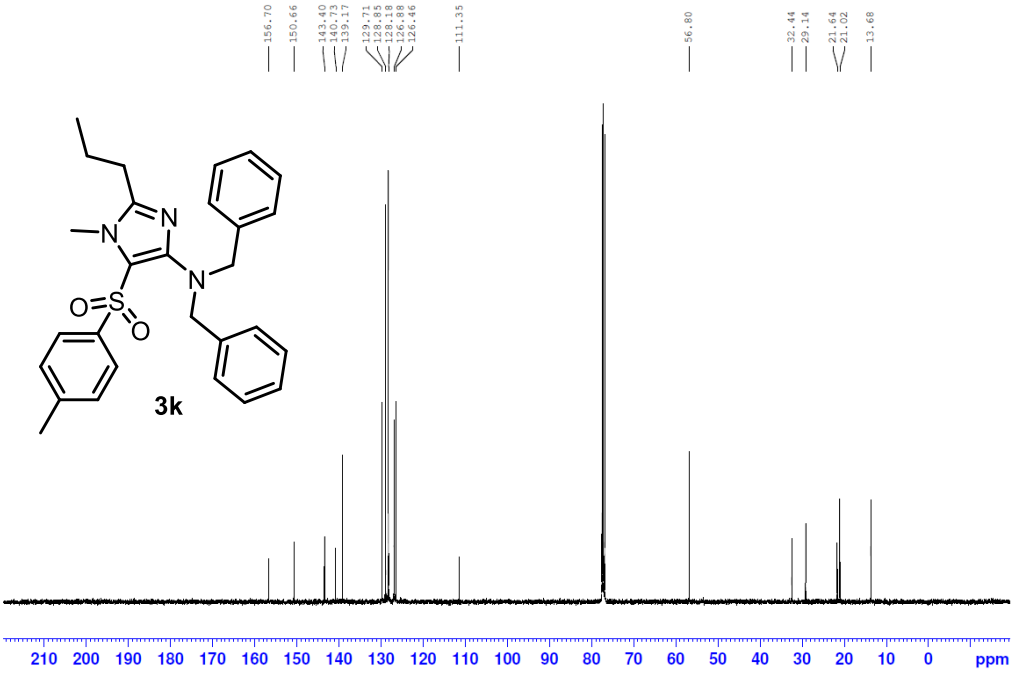
7.269
7.264
7.253
7.248
7.238
7.234
7.227
7.223
7.219
7.213
7.206
7.197
7.192
7.188
7.185
7.160
7.140
4.481
3.530
2.570
2.551
2.532
2.379
1.716
1.697
1.679
1.660
1.641
1.623
0.908
0.890
0.872
3k
11
10
9
8
7
6
5
4
3
2
1
ppm
2.02
12.78
2.14
4.00
3.06
2.04
2.99
2.19
3.13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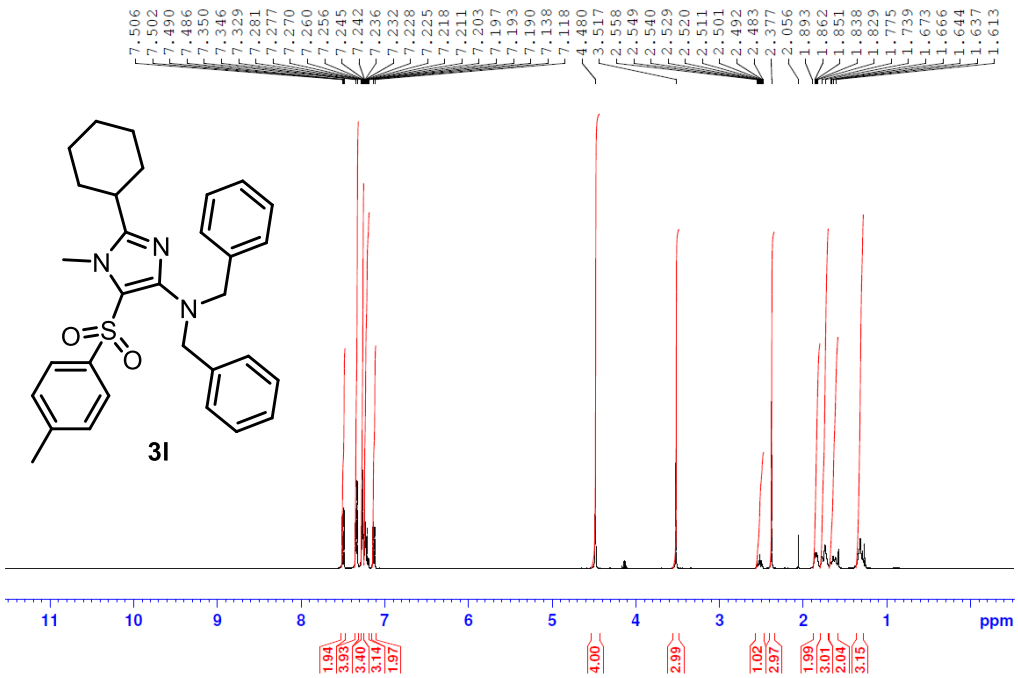
140.73
139.17
129.71
128.85
128.18
126.88
126.46
111.35
56.80
32.44
29.14
21.64
21.02
13.68
3k
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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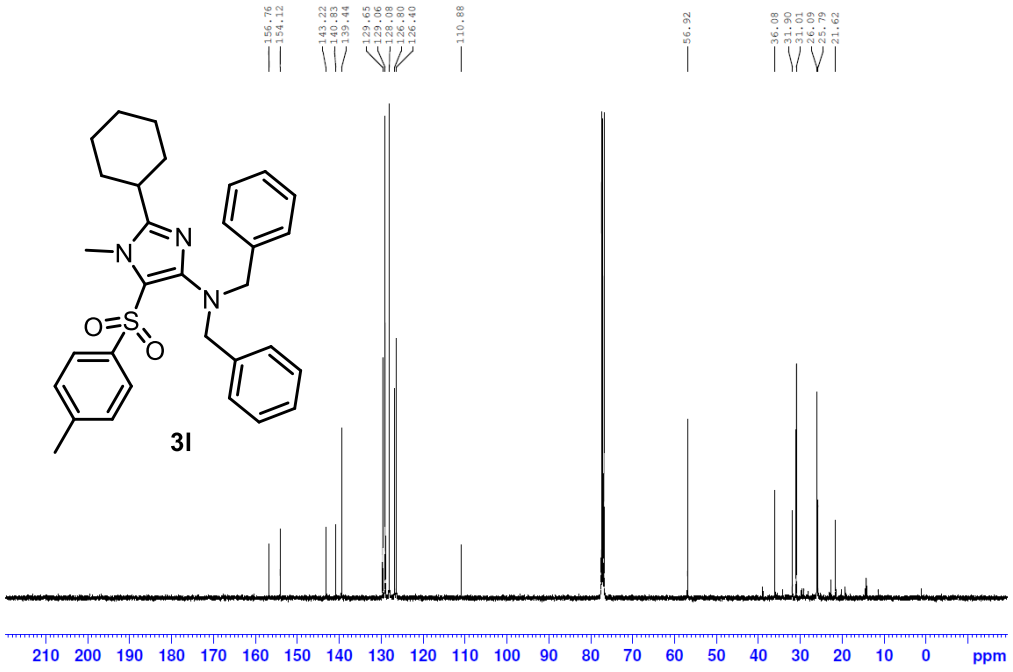
7.277
7.270
7.260
7.256
7.245
7.242
7.236
7.232
7.228
7.225
7.218
7.211
7.203
7.197
7.193
7.190
7.138
7.118
4.480
3.517
2.558
2.549
2.540
2.529
2.520
2.511
2.501
2.492
2.483
2.377
2.056
1.893
1.862
1.851
1.838
1.829
1.775
1.739
1.673
1.666
1.644
1.637
1.613
3I
11 10 9 8 7 6 5 4 3 2 1 ppm
1.94 3.93 3.40 3.14 1.97 4.00 2.99 1.02 2.97 1.99 3.01 2.04 3.15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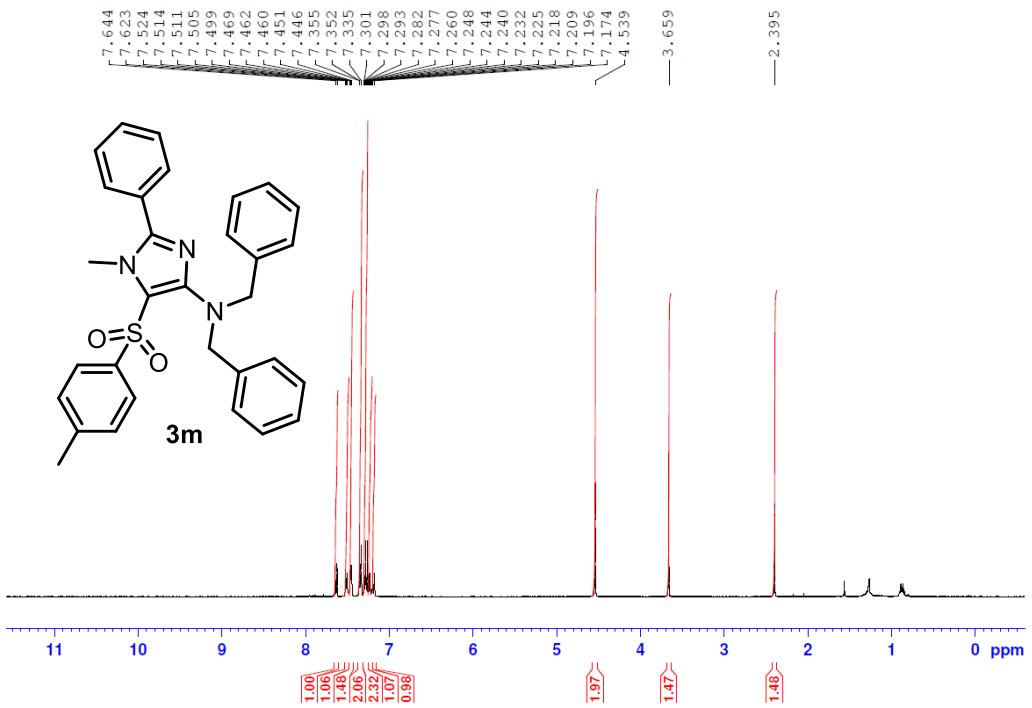
143.22
140.83
139.44
129.65
129.06
128.08
126.80
126.40
110.88
56.92
36.08
31.90
31.01
26.09
25.79
21.62
3I
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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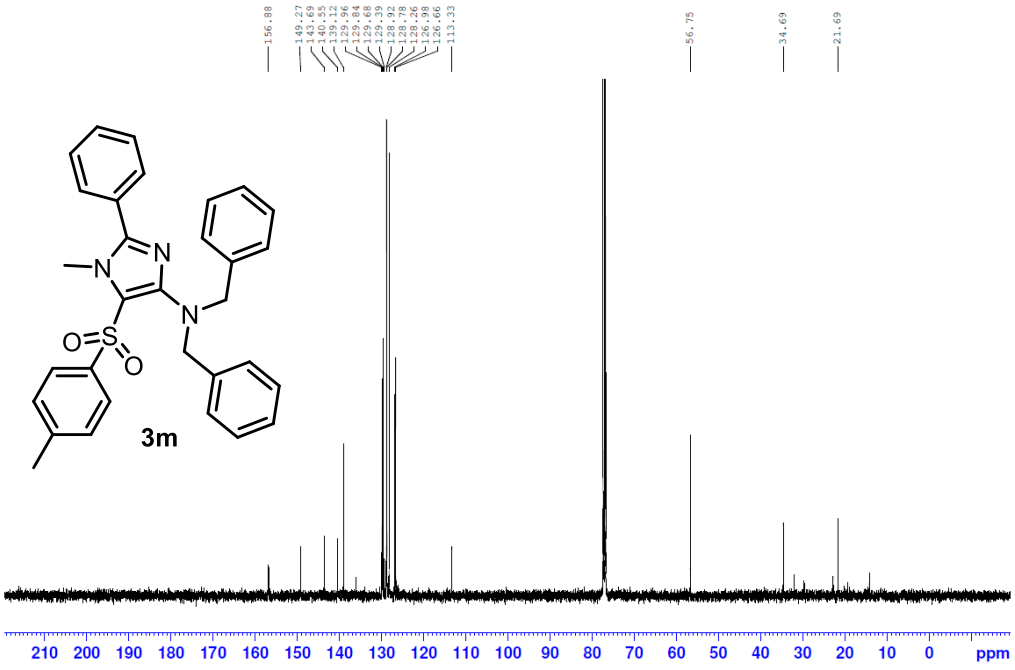
7.524
7.514
7.511
7.505
7.499
7.469
7.462
7.460
7.451
7.446
7.355
7.352
7.335
7.301
7.298
7.293
7.282
7.277
7.260
7.248
7.244
7.240
7.232
7.225
7.218
7.209
7.196
7.174
4.539
3.659
2.395
3m
11 10 9 8 7 6 5 4 3 2 1 0 ppm
1.00 1.06 1.48 2.06 2.32 1.07 0.98 1.97 1.47 1.48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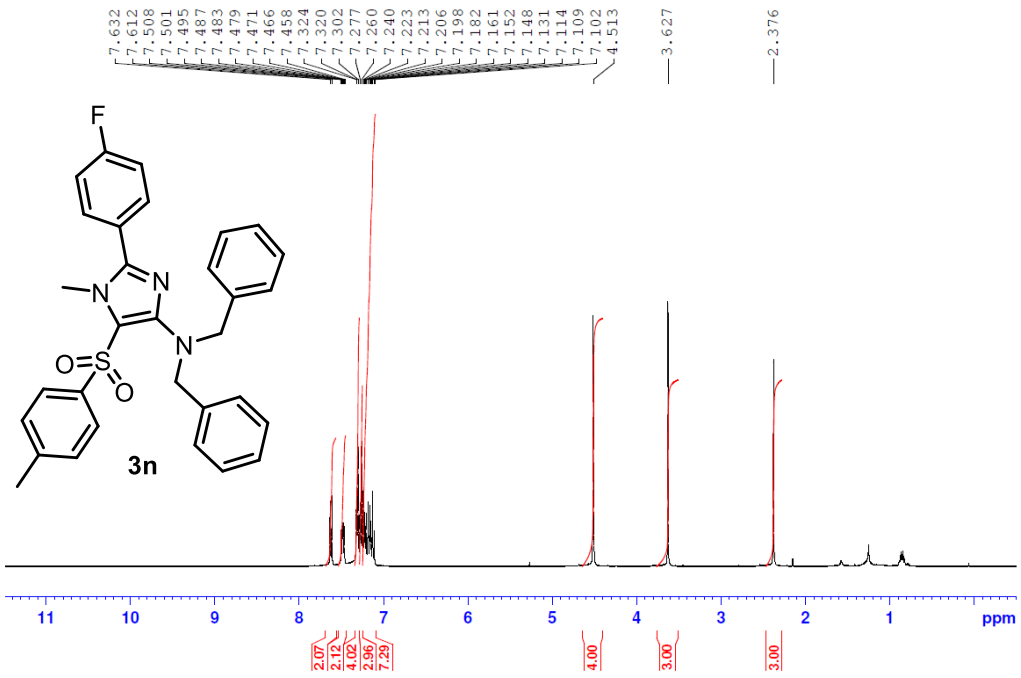
140.55
139.12
139.06
129.84
129.68
129.39
128.92
128.78
128.26
126.98
126.66
113.33
56.75
34.69
21.69
3m
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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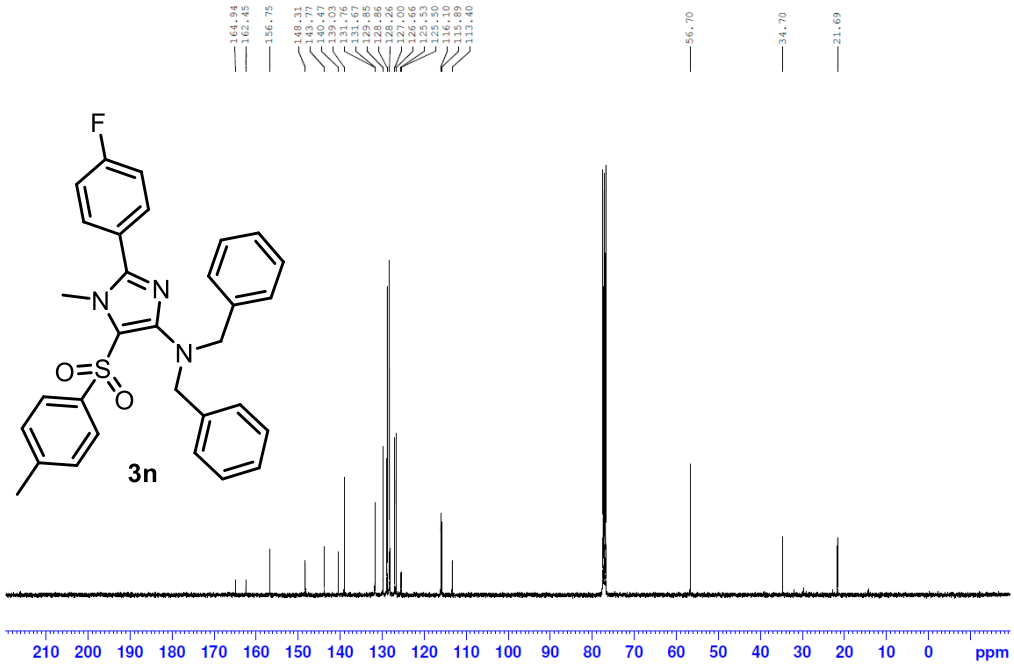
7.487
7.483
7.479
7.471
7.466
7.458
7.324
7.320
7.302
7.277
7.260
7.240
7.223
7.213
7.206
7.198
7.182
7.161
7.152
7.148
7.131
7.114
7.109
7.102
4.513
3.627
2.376
F
N
N
N
O=S=O
3n
11
10
9
8
7
6
5
4
3
2
1
ppm
2.07
2.12
4.02
2.96
7.29
4.00
3.00
3.00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148.31
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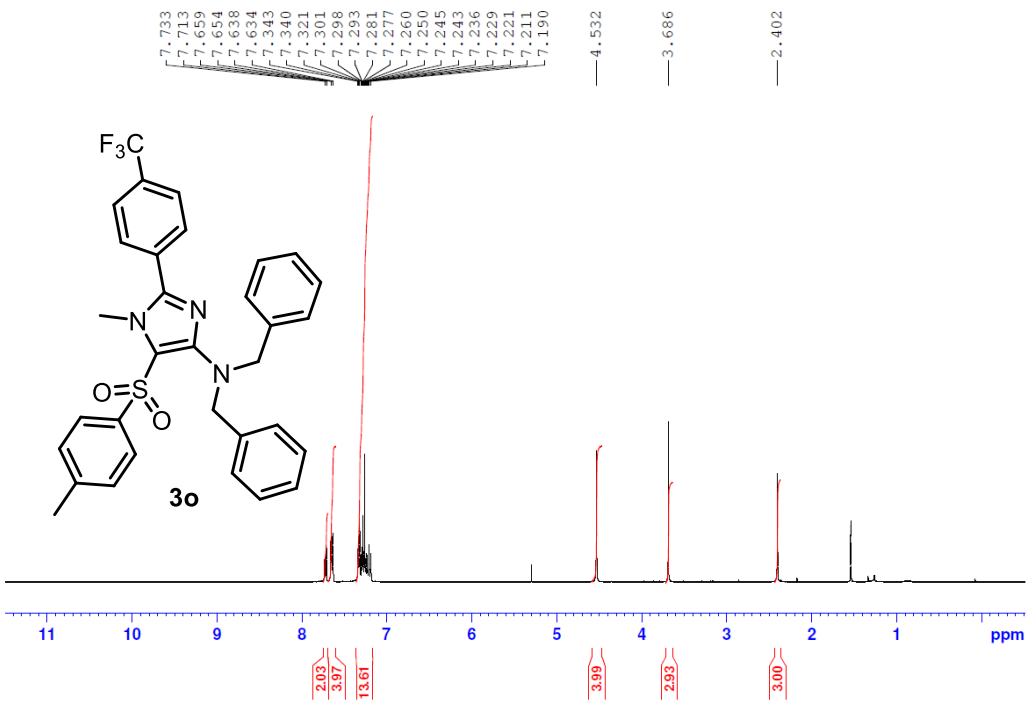
140.47
139.03
131.76
131.67
129.85
128.86
128.26
127.00
126.66
125.53
125.50
116.10
115.89
113.40
56.70
34.70
21.69
F
N
N
N
O=S=O
3n
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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7.659
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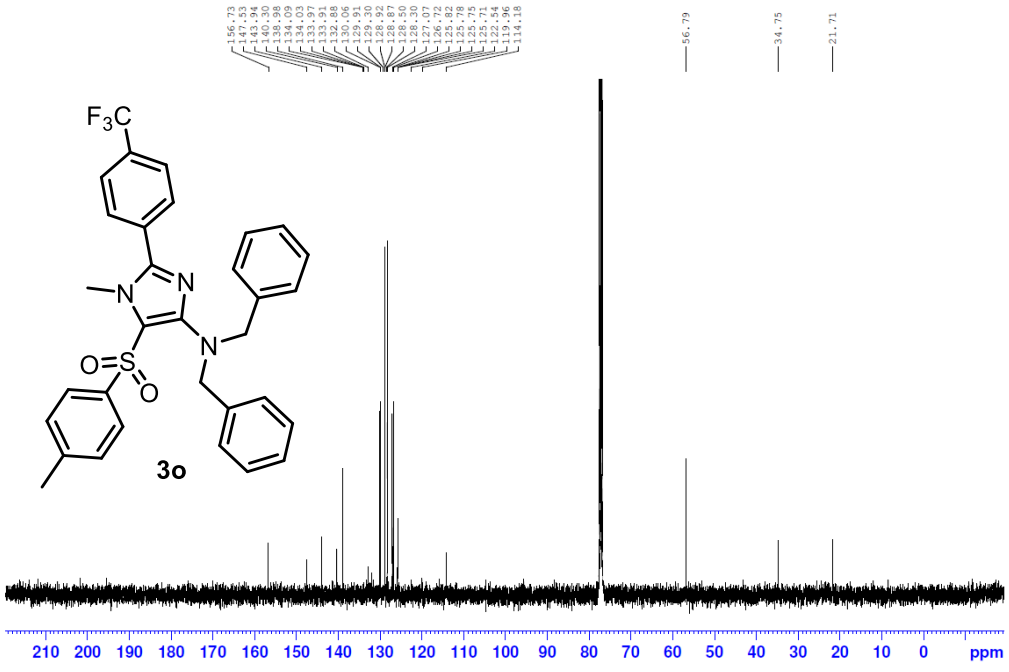
7.634
7.343
7.340
7.321
7.301
7.298
7.293
7.281
7.277
7.260
7.250
7.245
7.243
7.236
7.229
7.221
7.211
7.190
4.532
3.686
2.402
F3C
N
N
O=S=O
3o
11 10 9 8 7 6 5 4 3 2 1 ppm
2.03
3.97
13.61
3.99
2.93
3.00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143.94
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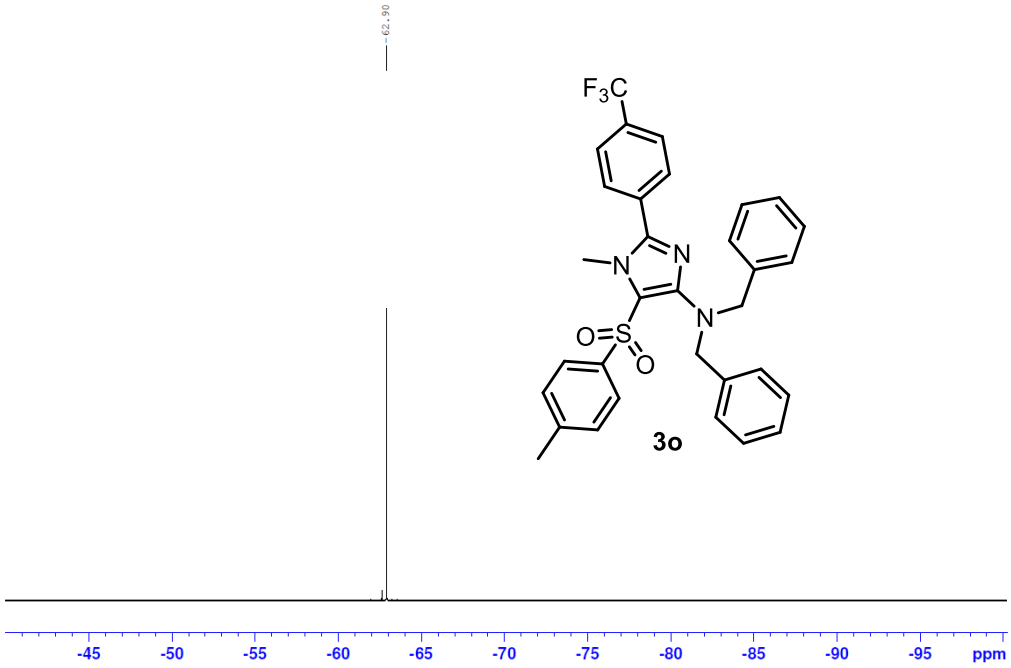
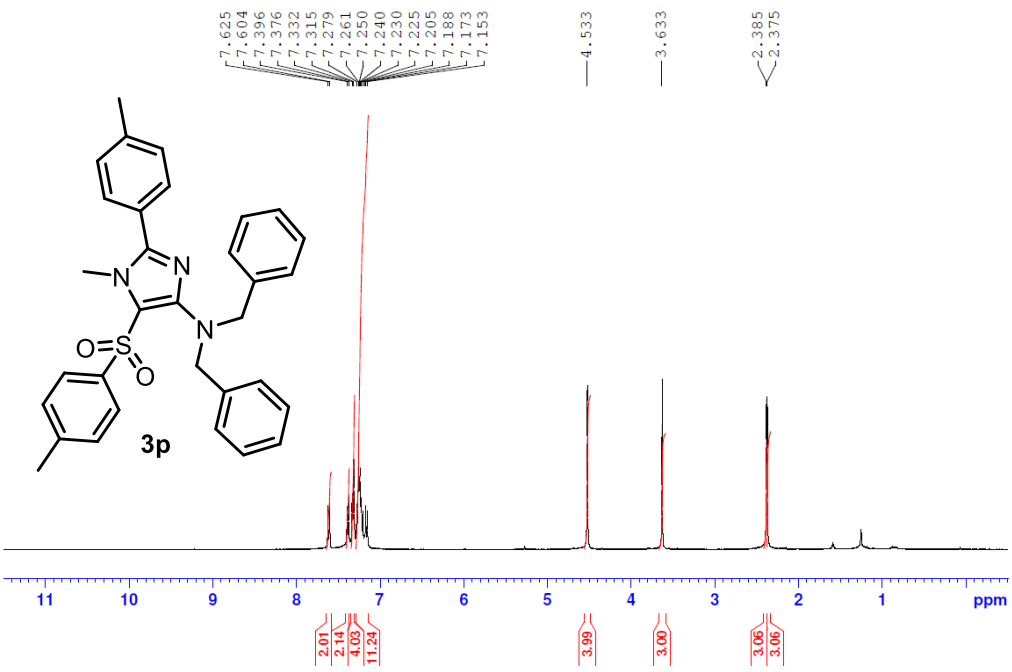
136.98
134.09
134.03
133.97
133.91
132.88
130.06
129.91
129.30
128.92
128.87
128.50
128.30
127.07
126.72
125.82
125.78
125.75
125.71
122.54
119.96
114.18
56.79
34.75
21.71
F3C
N
N
O=S=O
3o
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


62.90
F3C
N
N
N
O=S=O
3o
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
ppm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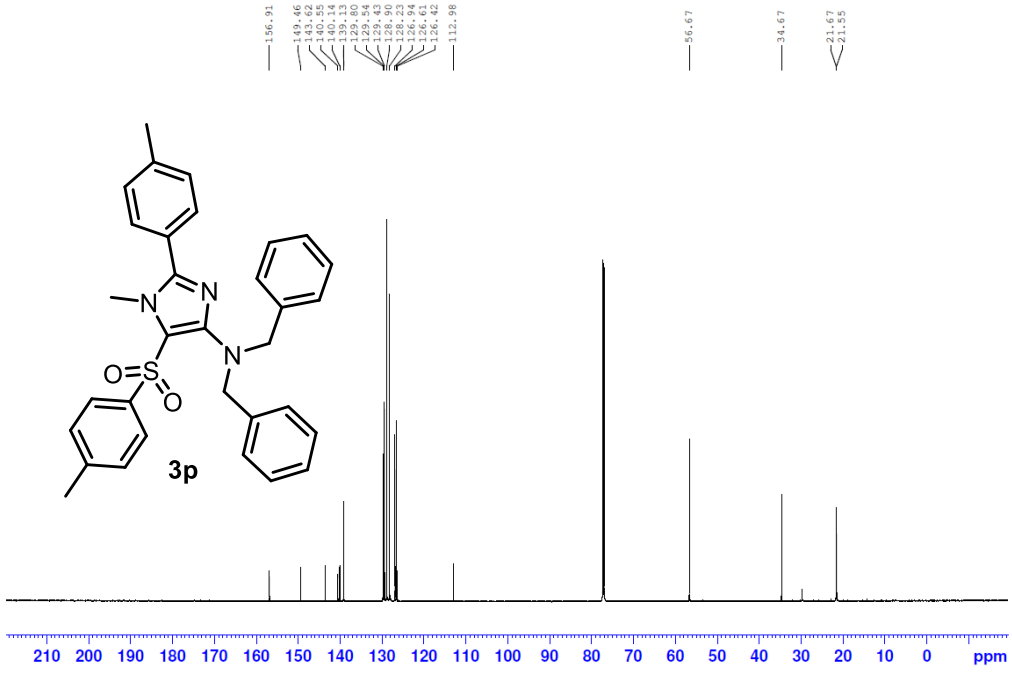
7.396
7.376
7.332
7.315
7.279
7.261
7.250
7.240
7.230
7.225
7.205
7.188
7.173
7.153
4.533
3.633
2.385
2.375
3p
11
10
9
8
7
6
5
4
3
2
1
ppm
2.01
2.14
4.03
11.24
3.99
3.00
3.06
3.06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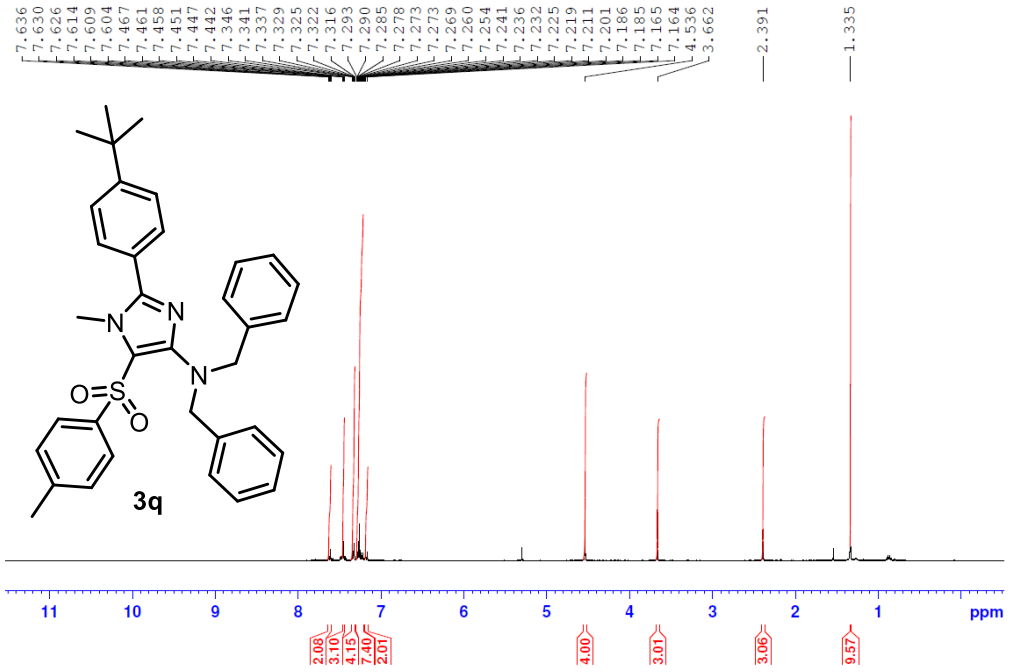
129.54
129.43
128.90
128.23
126.94
126.61
126.42
112.98
56.67
34.67
21.67
21.55
3p
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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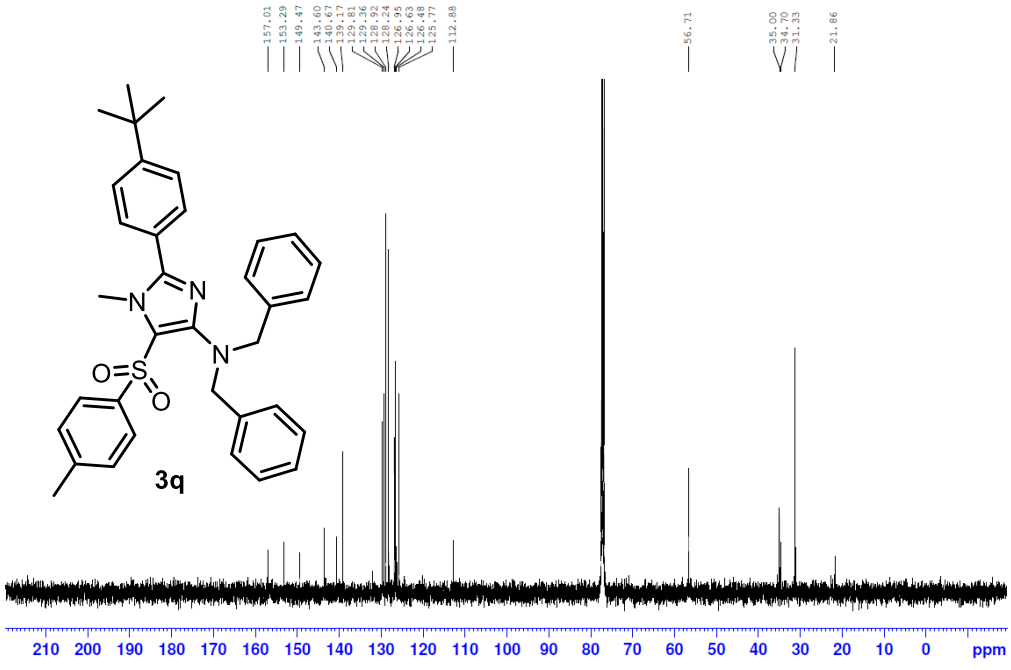
7.442
7.346
7.341
7.337
7.329
7.325
7.322
7.316
7.293
7.290
7.285
7.278
7.273
7.273
7.269
7.260
7.254
7.241
7.236
7.232
7.225
7.219
7.211
7.201
7.186
7.185
7.165
7.164
4.536
3.662
2.391
1.335
3q
11
10
9
8
7
6
5
4
3
2
1
ppm
2.08
3.10
4.15
7.40
2.01
4.00
3.01
3.06
9.57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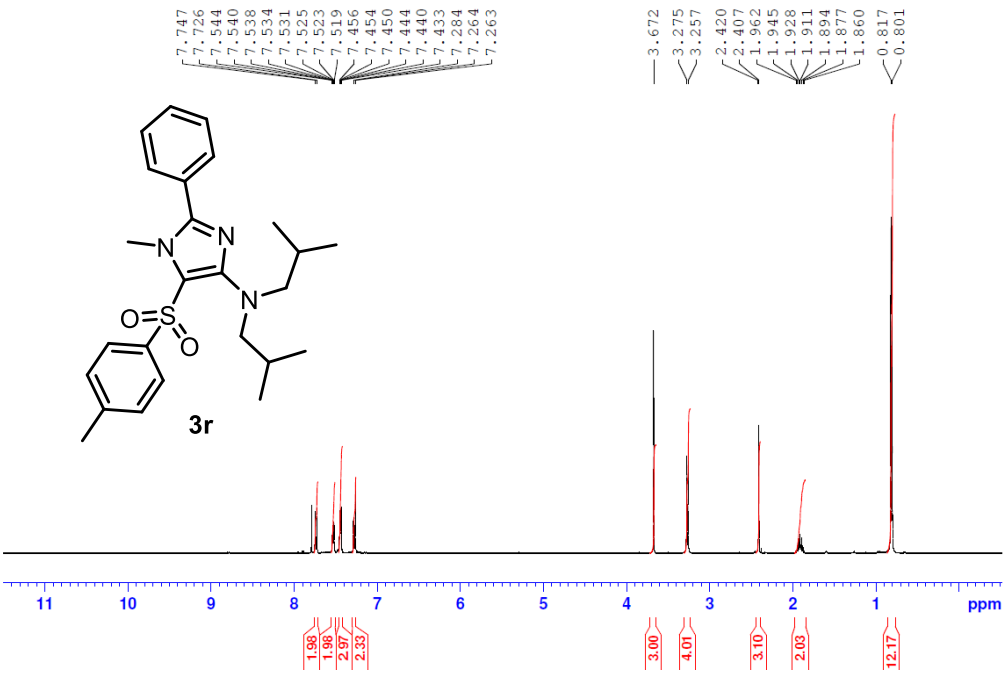
129.36
128.92
128.24
126.95
126.63
126.48
125.77
112.88
56.71
35.00
34.70
31.33
21.86
3q
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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7.525
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7.454
7.450
7.444
7.440
7.433
7.284
7.264
7.263
3.672
3.275
3.257
2.420
2.407
1.962
1.945
1.928
1.911
1.894
1.877
1.860
0.817
0.801
3r
11
10
9
8
7
6
5
4
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ppm
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1.98
2.97
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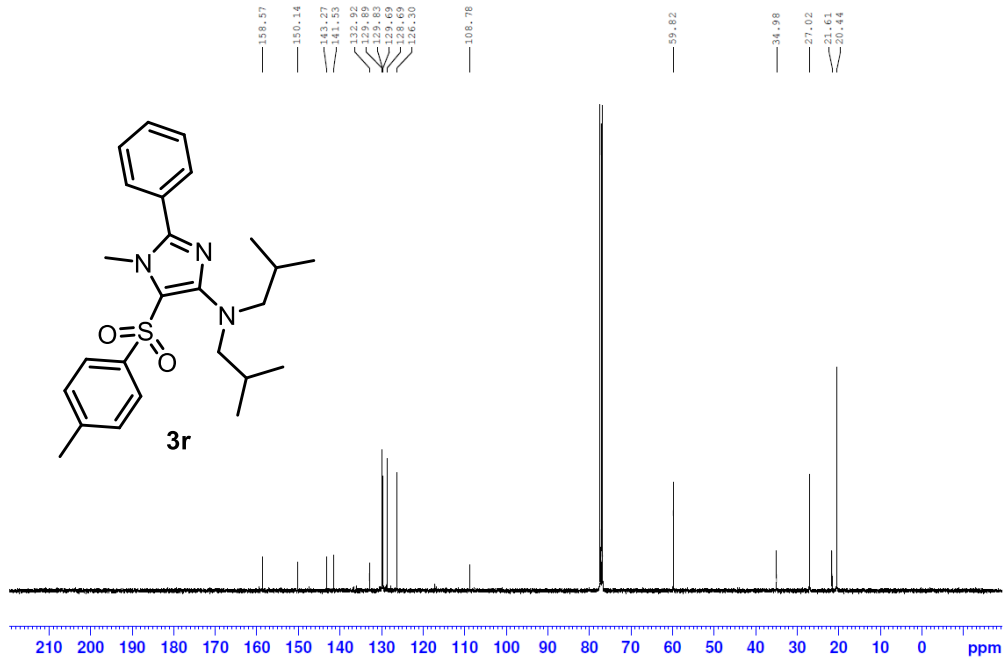
3.00
4.01
3.10
2.03
12.17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129.69
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108.78
59.82
34.98
27.02
21.61
20.44
3r
210
200
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180
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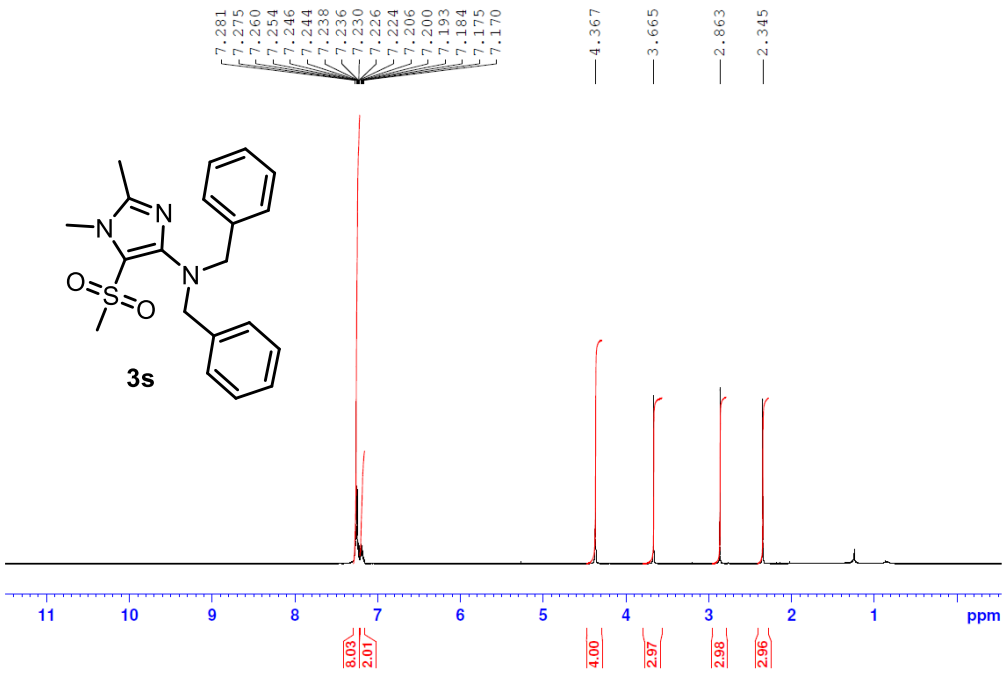
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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7.226
7.224
7.206
7.200
7.193
7.184
7.175
7.170
4.367
3.665
2.863
2.345
3s
11
10
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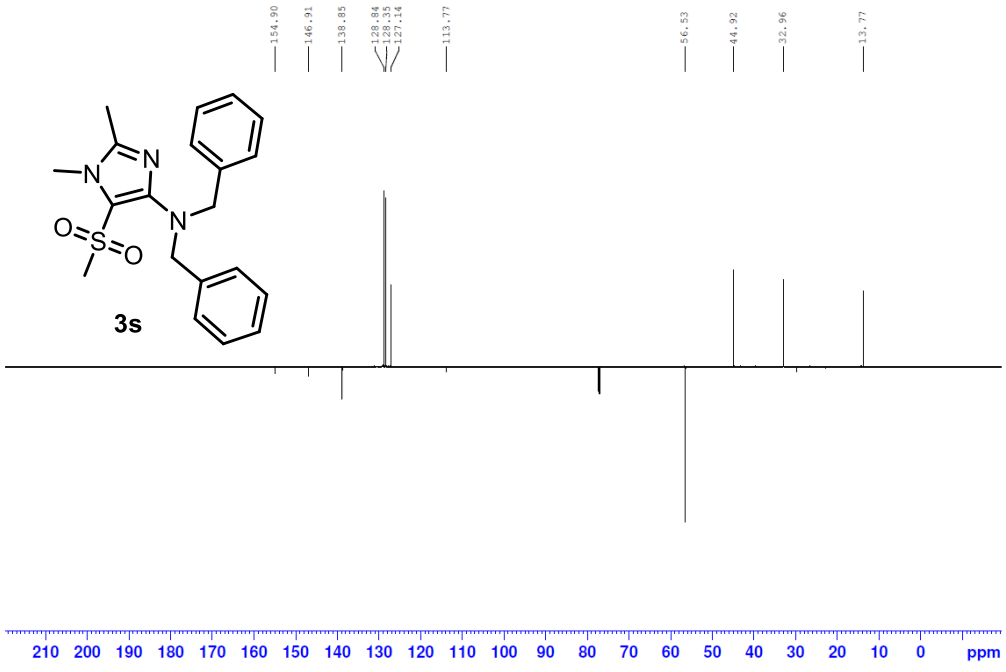
6
5
4
3
2
1
ppm
8.03
2.01
4.00
2.97
2.98
2.96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128.35
127.14
113.77
56.53
44.92
32.96
13.77
3s
210
200
190
180
170
160
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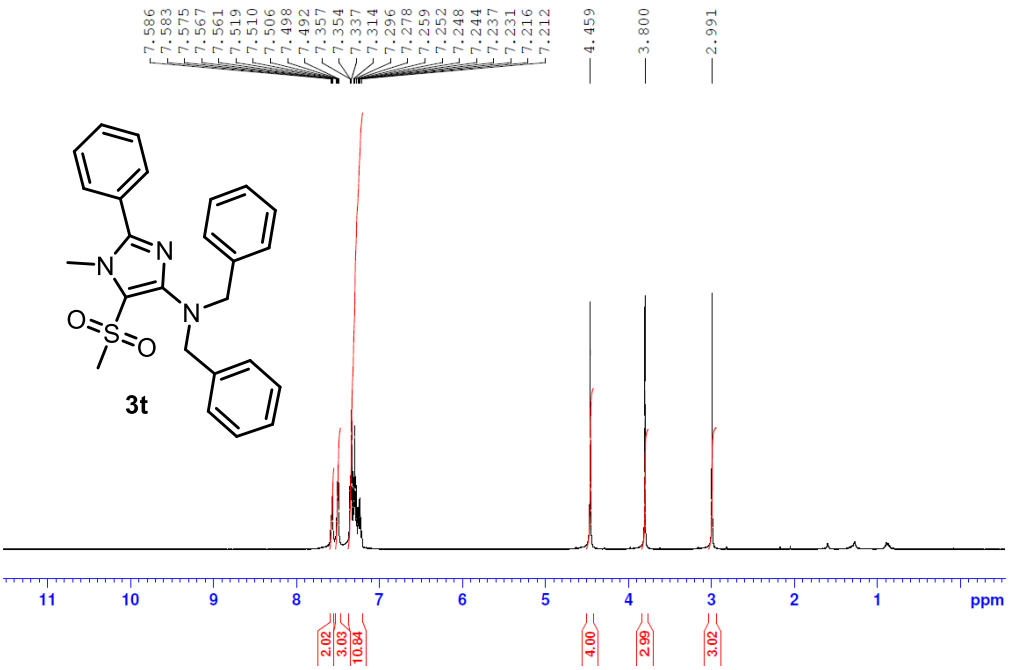
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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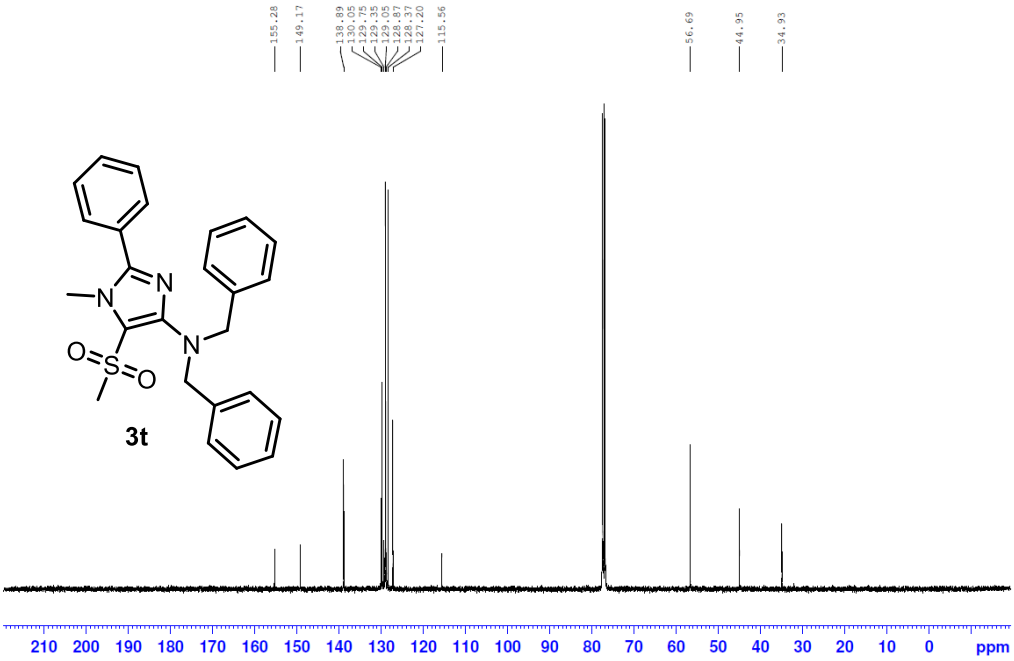
7.337
7.314
7.296
7.278
7.259
7.252
7.248
7.244
7.237
7.231
7.216
7.212
4.459
3.800
2.991
3t
11
10
9
8
7
6
5
4
3
2
1
ppm
2.02
3.03
10.84
4.00
2.99
3.02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129.75
129.35
129.05
128.87
128.37
127.20
115.56
56.69
44.95
34.93
3t
210
200
190
180
170
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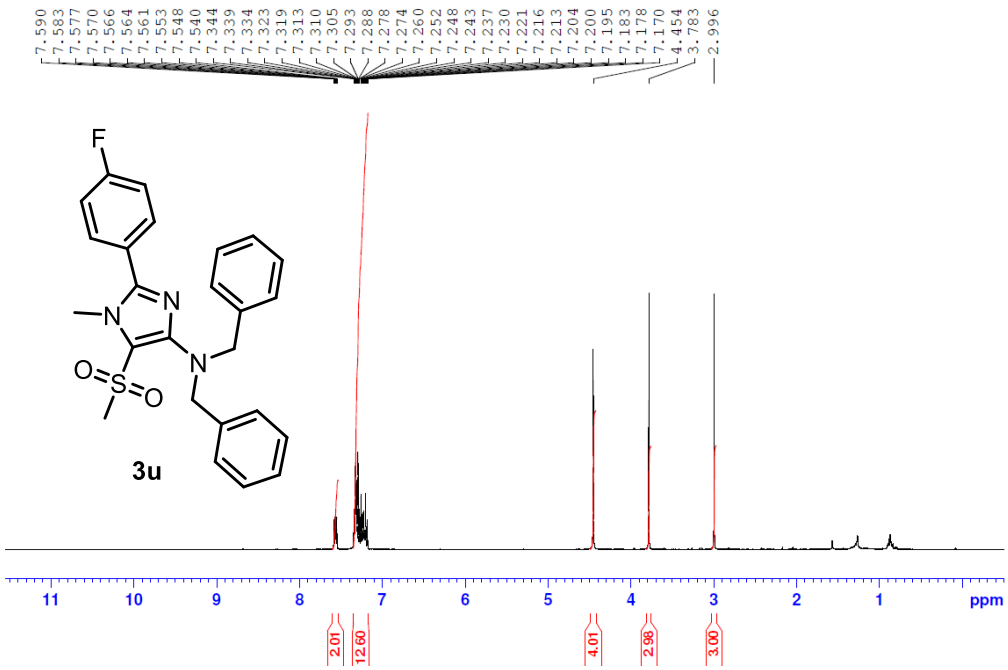
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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7.334
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7.319
7.313
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7.293
7.288
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7.274
7.260
7.252
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7.243
7.237
7.230
7.221
7.216
7.213
7.204
7.200
7.195
7.183
7.178
7.170
4.454
3.783
2.996
F
N
N
N
O
S
O
3u
11
10
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8
7
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2
1
ppm
2.01
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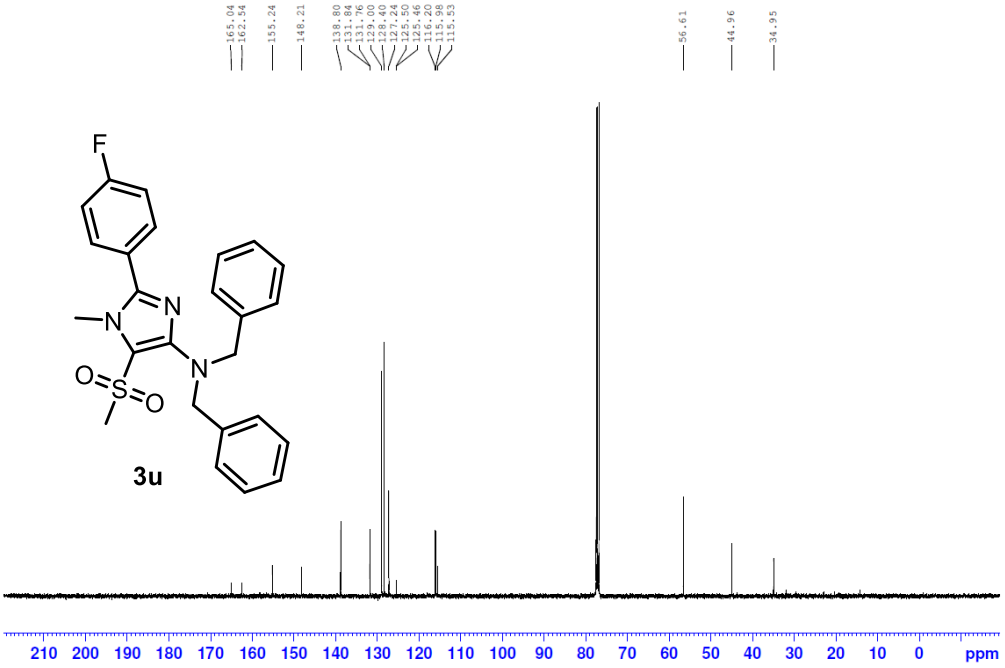
4.01
2.98
3.00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131.84
131.76
131.00
128.40
127.24
125.50
125.46
116.20
115.98
115.53
56.61
44.96
34.95
F
N
N
N
O
S
O
3u
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

6. Computational Details

All structures were optimized at the B3LYP-D3/6-31+G(d,p) level of theory.[5–7] The nature of all stationary points (minima and transition states) was verified through computation of the vibrational frequencies. The thermal corrections to the Gibbs free energy were combined with single point energies calculated at the RI-MP2/def2-TZVP//B3LYP-D3/6-31+G(d,p) level[8] to yield Gibbs free energies (G_{298}) at 298.15 K (all energies are reported in kcal mol^{-1}). The density-based solvation model SMD[9] (for geometry optimization) and Conductor-like screening model COSMO[10] (for RI-MP2 single-point calculations) were applied to consider solvent effects. The DFT calculations have been performed with the Gaussian09 program package,[11] whereas for the RI-MP2 single point calculations the Turbomole V7.0 program package[12] was used. Computed structures were visualized using the Chemcraft software.[13]

Cartesian coordinates (the most stable ($\Delta G_{298,MeCN}$) conformations as computed at the RI-MP2-COSMO/def2-TZVP//B3LYP-D3-SMD/6-31+G(d,p) level of theory

A

S	-1.968644	-1.135411	-0.990484
O	-1.910880	-2.599398	-1.130261
O	-1.697321	-0.271881	-2.150752
N	-0.761738	-0.726827	0.184677
C	1.548718	0.256933	-2.129401
C	-0.617514	0.662157	0.430442
C	0.146490	1.449383	-0.371007
H	-1.158826	1.093721	1.266404
N	0.907537	0.808489	-1.349576
N	0.201349	2.825481	-0.412198
C	-0.713754	3.535589	0.480558
C	1.511252	3.471630	-0.579213
H	2.086429	2.986162	-1.369642
H	1.345404	4.511173	-0.868278
H	2.091302	3.446183	0.354103
H	-1.729805	3.152089	0.354772
H	-0.422536	3.439529	1.536896
H	-0.699689	4.592770	0.208890
C	2.327948	-0.442520	-3.112215
H	3.291010	-0.729477	-2.677552
H	1.773263	-1.335473	-3.422096
H	2.483180	0.216661	-3.973038
C	-3.542289	-0.673953	-0.285578
C	-3.990610	0.642928	-0.429776
C	-4.263882	-1.613251	0.459116
C	-5.190456	1.014427	0.177742
H	-3.424150	1.358224	-1.015734
C	-5.462276	-1.221243	1.053099
H	-3.902702	-2.630879	0.559977
C	-5.942975	0.093707	0.925179
H	-5.550960	2.032570	0.060615
H	-6.035687	-1.948894	1.621027
C	-7.229166	0.504768	1.595273
H	-7.618047	1.437569	1.177209
H	-7.994697	-0.271092	1.490637
H	-7.068992	0.659633	2.669848
C	-0.824706	-1.538318	1.418995
H	-0.906112	-2.592853	1.156087
H	0.110240	-1.381527	1.960702
H	-1.667633	-1.246830	2.059234

TS_{A-B}

S	1.695629	1.070049	-0.984006
O	3.028534	0.472099	-0.894179
O	1.553973	2.535687	-0.564446
N	0.660710	0.287797	0.115535
C	1.040233	2.934531	1.157375
C	-0.692101	0.738293	0.093219
C	-1.070598	1.915174	0.677274
H	-1.412023	0.084004	-0.381681
N	-0.112820	2.664770	1.383272
N	-2.314359	2.478993	0.616708
C	-3.358384	1.735838	-0.081243
C	-2.768792	3.389703	1.671717
H	-3.151152	2.837504	2.541555
H	-1.952991	4.037454	1.995077
H	-3.568483	4.013503	1.267082
H	-4.240237	2.372357	-0.164826
H	-3.022721	1.471275	-1.088525
H	-3.634816	0.815714	0.454344
C	2.236608	3.563026	1.705129
H	3.039489	2.823117	1.777955
H	2.562214	4.377644	1.052653
H	1.987174	3.946033	2.698782
C	1.067390	0.991214	-2.640472
C	1.498458	-0.069823	-3.445388
C	0.087930	1.896559	-3.067485
C	0.938350	-0.210134	-4.713308
H	2.253782	-0.764540	-3.094079
C	-0.455560	1.731253	-4.338935
H	-0.230267	2.713340	-2.430968
C	-0.043118	0.681489	-5.178731
H	1.268783	-1.025725	-5.349886
H	-1.211787	2.429770	-4.685540
C	-0.622327	0.536403	-6.561184
H	-0.521602	-0.487777	-6.931463
H	-1.680260	0.816127	-6.580099
H	-0.097485	1.196728	-7.263542
C	0.819184	-1.183265	0.168492
H	0.353364	-1.671992	-0.695418
H	1.877295	-1.438645	0.220727
H	0.327983	-1.516347	1.084407

B

S	-0.165469	-1.494634	0.051325
O	-0.465744	-2.918620	0.125849
O	0.753327	-1.052691	-1.188881
N	0.841001	-1.010298	1.320181
C	2.214779	-1.045667	-1.111777
C	1.221642	0.359459	1.258399
C	2.218667	0.753859	0.398281
H	0.722751	1.030201	1.944787
N	2.836900	-0.169296	-0.458647
N	2.743517	2.016049	0.358462
C	2.170279	3.024351	1.243253
C	3.331674	2.526154	-0.884097
H	3.857257	1.729075	-1.409886
H	2.559192	2.941992	-1.546882
H	4.046687	3.313957	-0.636423
H	1.126817	3.254375	0.980302
H	2.206188	2.684382	2.282151
H	2.760125	3.938091	1.159492
C	2.783416	-2.096334	-1.987133
H	3.870959	-2.018471	-1.998020
H	2.481560	-3.083330	-1.618807
H	2.389129	-1.987653	-3.003288
C	-1.605556	-0.512915	-0.224259
C	-1.509826	0.769207	-0.784961
C	-2.812984	-1.025512	0.272662
C	-2.667787	1.537424	-0.861775
H	-0.569688	1.148870	-1.163561
C	-3.951185	-0.231350	0.180227
H	-2.865063	-2.015642	0.712702
C	-3.899650	1.055497	-0.384946
H	-2.613242	2.528871	-1.301319
H	-4.895230	-0.617379	0.552907
C	-5.147463	1.887759	-0.503219
H	-5.664454	1.658222	-1.443999
H	-5.844260	1.676560	0.313291
H	-4.915935	2.956772	-0.506019
C	0.425937	-1.520260	2.649088
H	0.155359	-2.573981	2.576297
H	1.298818	-1.422151	3.296102
H	-0.406020	-0.937694	3.058789

TS_{B-C}

S	1.825036	0.010196	0.467950
O	3.272193	-0.013350	0.709631
O	1.205546	1.519121	0.338065
N	0.829319	-0.432340	1.966885
C	0.811322	2.285850	1.482422
C	-0.530190	-0.294351	1.780665
C	-1.097464	0.984813	1.775612
H	-1.124165	-1.185962	1.618349
N	-0.305249	2.102477	2.048908

N	-2.410167	1.207371	1.590613
C	-3.323353	0.081382	1.399061
C	-3.001595	2.546222	1.575493
H	-2.229382	3.306096	1.676624
H	-3.531386	2.696683	0.629159
H	-3.715343	2.645942	2.400315
H	-3.040213	-0.503495	0.516538
H	-3.324956	-0.574490	2.276620
H	-4.329206	0.473234	1.251450
C	1.783171	3.362964	1.789939
H	1.413367	3.979008	2.610081
H	2.746219	2.916763	2.063234
H	1.948412	3.980801	0.900805
C	1.387192	-0.601993	-1.136088
C	0.142975	-0.287581	-1.705241
C	2.242900	-1.562661	-1.697828
C	-0.220873	-0.932721	-2.884855
H	-0.508146	0.453946	-1.259247
C	1.852672	-2.182612	-2.879219
H	3.191265	-1.807364	-1.231094
C	0.620311	-1.882516	-3.489318
H	-1.174060	-0.690152	-3.345272
H	2.513062	-2.913859	-3.336214
C	0.229182	-2.552098	-4.778785
H	0.724618	-2.059661	-5.625552
H	0.539723	-3.601629	-4.787849
H	-0.850041	-2.500073	-4.947099
C	1.277712	-1.755664	2.449244
H	2.367176	-1.814171	2.417559
H	0.955887	-1.825030	3.490950
H	0.836373	-2.579224	1.876888

C

S	2.541951	-1.561668	-0.052237
O	2.204849	-2.029880	1.669661
O	1.574111	-2.227458	-0.972954
N	-0.055904	0.857345	3.057084
C	1.031797	-1.808856	2.282224
C	-1.169673	0.355246	2.706916
C	-1.170214	-0.978454	2.033763
H	-2.128377	0.853322	2.863984
N	-0.006378	-1.490796	1.602768
N	-2.307712	-1.575555	1.740199
C	-2.330200	-2.868448	1.043077
C	-3.628312	-1.012274	2.087964
H	-3.846415	-0.143080	1.462454
H	-4.374734	-1.782399	1.901066
H	-3.668208	-0.740084	3.143254
H	-3.068725	-2.812892	0.240225
H	-1.347206	-3.091975	0.633241
H	-2.622579	-3.650276	1.750681
C	1.118306	-2.076683	3.754195
H	0.170613	-1.869921	4.250919
H	1.387235	-3.127826	3.903827
H	1.909742	-1.460472	4.189389
C	2.071354	0.169323	0.070825
C	2.894232	1.016222	0.819089
C	0.943617	0.649041	-0.600356
C	2.556731	2.366282	0.917239
H	3.771960	0.634317	1.333899
C	0.626639	2.000165	-0.493912
H	0.323041	-0.029445	-1.175963
C	1.420141	2.876248	0.269937
H	3.179982	3.029203	1.510454
H	-0.255360	2.383553	-1.000166
C	1.043835	4.330287	0.385802
H	1.162210	4.839878	-0.578277
H	-0.006429	4.438372	0.679136
H	1.664253	4.849142	1.121570
C	-0.052762	2.152933	3.706351
H	-1.051569	2.590321	3.838558
H	0.436385	2.047604	4.681715
H	0.572171	2.828537	3.111598

$TS_{C\text{-}D}$

S	5.246464	5.614071	-3.648532
O	6.215379	6.543697	-2.413440
O	3.986627	6.386167	-3.862885
N	7.355237	4.325876	-1.046927
C	6.137983	6.087881	-1.164925
C	6.548731	3.580568	-0.418470
C	5.189843	4.199149	-0.245836
H	6.806003	2.599261	-0.025929
N	5.052945	5.389743	-0.790036
N	4.186028	3.589702	0.379234
C	2.906854	4.297212	0.499427
C	4.173098	2.175314	0.763853
H	5.160913	1.727008	0.697047
H	3.819677	2.094958	1.794597
H	3.489275	1.627083	0.106999
H	3.074118	5.323676	0.831168
H	2.392332	4.315564	-0.468322
H	2.287979	3.773663	1.228057
C	6.937822	6.918871	-0.201635

H	7.927546	7.131387	-0.609572
H	6.400902	7.864457	-0.061257
H	7.020195	6.411143	0.760255
C	6.384931	6.068463	-4.955321
C	6.072595	7.103384	-5.839013
C	7.560816	5.319997	-5.086175
C	6.968941	7.401067	-6.864888
H	5.145557	7.656820	-5.727641
C	8.444787	5.635835	-6.115982
H	7.788432	4.509582	-4.398059
C	8.165420	6.679265	-7.016882
H	6.736109	8.202871	-7.560209
H	9.361353	5.063209	-6.227840
C	9.143503	7.028315	-8.108476
H	8.650850	7.545823	-8.936758
H	9.925250	7.693419	-7.719401
H	9.640900	6.134460	-8.497871
C	8.747380	4.018652	-1.284705
H	9.035666	3.038307	-0.889469
H	8.933146	4.062150	-2.362251
H	9.353410	4.800930	-0.814732

D

S	-2.179778	0.064232	-1.551757
O	-2.003617	0.767709	-0.236059
O	-1.071932	-1.294526	-1.561316
N	0.704234	-0.612376	-0.120229
C	0.301385	-0.968048	-1.567294
C	1.242762	0.547416	-0.115057
C	1.219397	1.064627	-1.511715
H	1.617622	1.012453	0.788640
N	0.627330	0.207654	-2.310764
N	1.749497	2.232506	-1.890480
C	1.621919	2.619547	-3.296456
C	2.195965	3.273848	-0.962907
H	2.349156	2.879806	0.039990
H	3.144027	3.681856	-1.322096
H	1.454020	4.079307	-0.920347
H	0.603576	2.967181	-3.509982
H	2.327830	3.425324	-3.501313
H	1.844796	1.766262	-3.940366
C	1.063228	-2.209875	-2.010145
H	2.137168	-2.044255	-1.892478
H	0.755011	-3.078708	-1.424171
H	0.835072	-2.383733	-3.063572
C	-3.598690	-1.029666	-1.383838
C	-4.181065	-1.547367	-2.544914
C	-4.113894	-1.315958	-0.118215
C	-5.292119	-2.382394	-2.425062
H	-3.776358	-1.311763	-3.525934
C	-5.225364	-2.152235	-0.018556
H	-3.652836	-0.890132	0.767625
C	-5.830524	-2.696123	-1.165070
H	-5.749621	-2.793948	-3.320669
H	-5.630850	-2.386177	0.962180
C	-7.054059	-3.569260	-1.051061
H	-7.048707	-4.362126	-1.805723
H	-7.126246	-4.028221	-0.060573
H	-7.963620	-2.975275	-1.207999
C	0.476064	-1.500800	1.011475
H	1.120885	-2.376741	0.905389
H	0.702128	-0.970279	1.935725
H	-0.568794	-1.815142	0.990692

TS_{D-E}

S	-0.105626	-0.999393	-0.774017
O	-0.144570	-2.142844	-1.761464
O	-0.781596	-1.381162	0.614003
N	-2.927449	-0.269818	-0.021893
C	-2.104847	-0.068049	1.176211
C	-2.658563	0.690643	-0.849701
C	-1.765720	1.627022	-0.118037
H	-3.068077	0.738544	-1.849717
N	-1.518670	1.133804	1.110910
N	-1.304673	2.770552	-0.579836
C	-0.371079	3.564181	0.227901
C	-1.546592	3.266457	-1.937384
H	-1.925505	4.289201	-1.870569
H	-0.596139	3.270270	-2.480453
H	-2.267268	2.650294	-2.469278
H	0.653020	3.338776	-0.090000
H	-0.579136	4.621290	0.054579
H	-0.488918	3.324396	1.282689
C	-2.466227	-0.731204	2.450705
H	-1.638790	-0.608595	3.151474
H	-3.352961	-0.233829	2.861304
H	-2.679151	-1.791000	2.311176
C	1.622226	-0.828805	-0.231506
C	2.637298	-1.467616	-0.944603
C	1.906967	0.006669	0.850028
C	3.961818	-1.281757	-0.542597
H	2.394347	-2.105632	-1.788254
C	3.237782	0.182093	1.235075
H	1.106783	0.503658	1.390482

C	4.283448	-0.456497	0.548108
H	4.757944	-1.785077	-1.085719
H	3.465277	0.822149	2.083471
C	5.722536	-0.257694	0.955399
H	5.801998	0.330278	1.874225
H	6.221772	-1.219697	1.117820
H	6.280519	0.265133	0.169080
C	-3.775675	-1.436568	-0.253541
H	-3.164222	-2.333911	-0.141774
H	-4.573156	-1.435832	0.492441
H	-4.189936	-1.374205	-1.258316

E

S	0.144882	1.778243	-0.026540
O	0.403638	2.845999	0.959640
O	-0.280271	2.121560	-1.397635
N	-2.504362	1.549519	0.429411
C	-3.171872	0.935878	-0.563235
C	-1.328625	0.778379	0.722634
C	-1.603662	-0.467295	-0.092516
H	-1.113834	0.670937	1.785674
N	-2.663580	-0.261211	-0.902749
N	-0.907148	-1.581510	-0.070490
C	0.035424	-1.945961	0.994316
C	-1.193901	-2.648181	-1.040996
H	-0.264906	-3.189900	-1.226617
H	-1.939747	-3.333509	-0.625616
H	-1.565238	-2.217794	-1.969382
H	0.078272	-1.183280	1.767844
H	-0.313397	-2.883195	1.438204
H	1.028933	-2.098622	0.569003
C	-4.385815	1.515734	-1.183314
H	-5.178615	1.610893	-0.431847
H	-4.171673	2.520763	-1.562022
H	-4.730520	0.875867	-1.995226
C	1.543450	0.685249	-0.103980
C	2.380082	0.576136	1.011221
C	1.765091	-0.054474	-1.270875
C	3.462911	-0.297505	0.947245
H	2.192447	1.163571	1.903700
C	2.853740	-0.922069	-1.310089
H	1.107989	0.051129	-2.127078
C	3.713925	-1.060939	-0.206273
H	4.126063	-0.384583	1.803090
H	3.041345	-1.497398	-2.212144
C	4.866388	-2.029039	-0.252511
H	4.527594	-3.033889	0.030963
H	5.287453	-2.097576	-1.260158
H	5.659315	-1.739166	0.442874
C	-2.819781	2.840890	1.040236
H	-2.420272	3.662928	0.440186
H	-3.902511	2.940051	1.124580
H	-2.379283	2.868618	2.036739

7. X-Ray Analysis

The X-ray intensity data were measured on Bruker D8 Venture diffractometer equipped with multilayer monochromators, Cu K/a INCOATEC micro focus sealed tube and Kryoflex II cooling device. The structures were solved by *direct methods* and refined by *full-matrix least-squares techniques*. Non-hydrogen atoms were refined with *anisotropic displacement parameters*. Hydrogen atoms were inserted at calculated positions and refined with a riding model respectively as rotating groups. The following software was used: *Bruker SAINT software package*[14] using a narrow-frame algorithm for frame integration, *SADABS*[15] for absorption correction, *OLEX2*[16] for structure solution, refinement, molecular diagrams and graphical user-interface, *Shelxle*[17] for refinement and graphical user-interface *SHELXS-2013*[18] for structure solution, *SHELXL-2013*[19] for refinement, *Platon*[20] for symmetry check. Experimental data and CCDC-Codes can be found in Table 1. Crystal data, data collection parameters, and structure refinement details are given in Tables 2, 3, 4 and 5. Molecular structures in "Ortep View" are displayed in Figure 1 and 2.

Table 1 Experimental parameter and CCDC-Code.

Sample	Machine	Source	Temp.	Detector Distance	Time/ Frame	#Frames	Frame width	CCDC
	Bruker		[K]	[mm]	[s]		[°]	
2a	D8	Cu	100	40	50	1672	0.7	1537944
3j	D8	Cu	100	40	2	2910	0.8	1553624

5-(Indolin-1-yl)-2-methyl-4-phenyloxazole [2a] for "Organic letters".

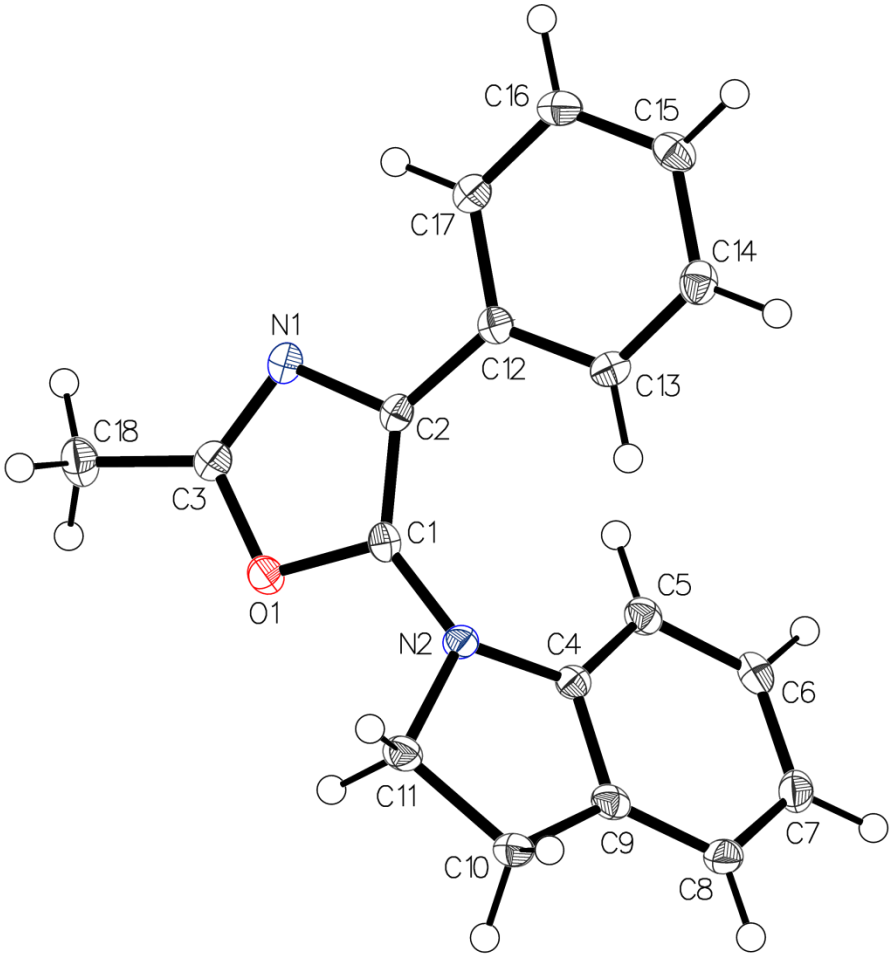

Figure 1 Crystal structure of [**2a**], drawn with 50% displacement ellipsoids. Bond precision: C-C=0.0020Å.

Table 2 Data collection and structure refinement of [**2a**].

Index ranges	$-14 \le h \le 14$, $-8 \le k \le 8$, $-19 \le l \le 19$	**Theta range for data collection [°]**	11.164 to 144.136	
Reflections number	10676	**Data / restraints / parameters**	2670/0/191	
Refinement method	Least squares	**Final R indices**	all data	R1 = 0.0515, wR2 = 0.0923
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$		$I>2\sigma(I)$	R1 = 0.0385, wR2 = 0.0870
Goodness-of-fit on F^2	1.024	**Weighting scheme**	$w=1/[\sigma^2(F_o^2)+(0.0413P)^2+0.4157P]$	
Largest diff. peak and hole [e $Å^{-3}$]	0.19/-0.20		where $P=(F_o^2+2F_c^2)/3$	

Table 3 Sample and crystal data of [**2a**].

Chemical formula	C18H16N2O	**Crystal system**	monoclinic	
Formula weight [g/mol]	276.33	**Space group**	*P21/c*	
Temperature [K]	100	**Z**	4	
Measurement method	\f and \w scans	**Volume [Å^3]**	1371.97(9)	
Radiation (Wavelength [Å])	CuKα (λ = 1.54178)	**Unit cell dimensions [Å] and [°]**	12.1454(5)	90
Crystal size / [mm^3]	0.332 × 0.042 × 0.019		7.1266(2)	97.206(3)
Crystal habit	clear colourless needle		15.9769(6)	90
Density (calculated) / [g/cm^3]	1.338	**Absorption coefficient / [mm^{-1}]**	0.664	
Abs. correction Tmin	0.6614	**Abs. correction Tmax**	0.7536	
Abs. correction type	multi-scan	**F(000) [e$^-$]**	584	

***N,N*-Dibenzyl-1,2-dimethyl-5-tosyl-*1H*-imidazol-4-amine [3j] for "Organic letters".**

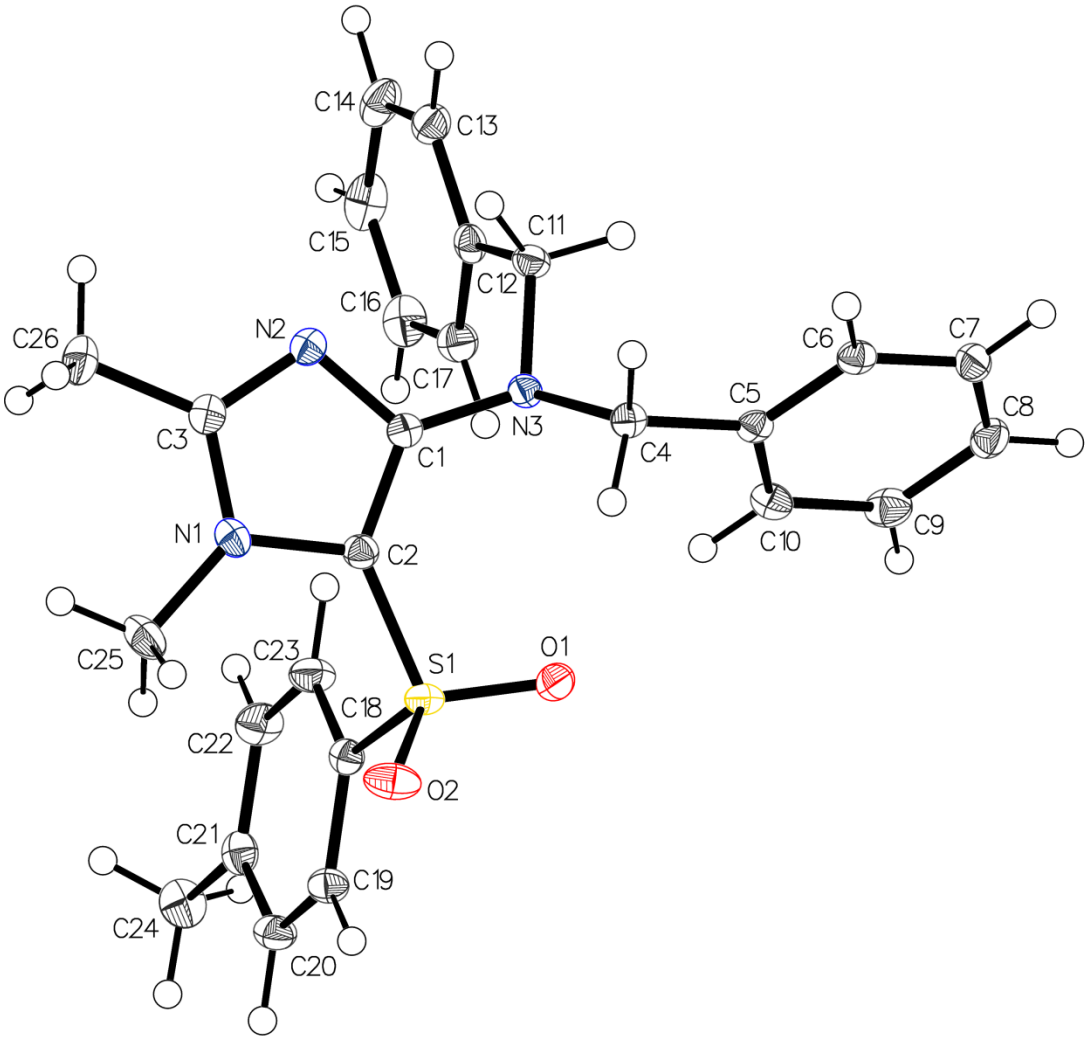

Figure 2 Crystal structure of [**3j**], drawn with 50% displacement ellipsoids. Bond precision: C-C=0.0020Å.

Table 4 Sample and crystal data of [**3j**].

Chemical formula	C26H27N3O2S	**Crystal system**	triclinic	
Formula weight [g/mol]	445.56	**Space group**	*P-1*	
Temperature [K]	100	**Z**	2	
Measurement method	\f and \w scans	**Volume [Å^3]**	1117.35(19)	
Radiation (Wavelength [Å])	CuKα (λ = 1.54178)	**Unit cell dimensions [Å] and [°]**	9.3234(9)	78.305(3)
Crystal size / [mm^3]	0.816 × 0.561 × 0.404		9.9427(10)	78.596(3)
Crystal habit	clear brown block		13.0102(13)	73.067(3)
Density (calculated) / [g/cm^3]	1.324	**Absorption coefficient / [mm^{-1}]**	1.513	
Abs. correction Tmin	0.5616	**Abs. correction Tmax**	0.7536	
Abs. correction type	multi-scan	**F(000) [e$^-$]**	472	

Table 5 Data collection and structure refinement of [**3g**].

Index ranges	$-11 \le h \le 11$, $-12 \le k \le 12$, $-16 \le l \le 16$	**Theta range for data collection [°]**	10.028 to 145.794	
Reflections number	17436	**Data / restraints / parameters**	4389/0/292	
Refinement method	Least squares	**Final R indices**	all data	R1 = 0.0375, wR2 = 0.0947
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$		I>2σ(I)	R1 = 0.0365, wR2 = 0.0939
Goodness-of-fit on F^2	1.069	**Weighting scheme**	$w=1/[\sigma^2(F_o^2)+(0.0466P)^2+0.5788P]$	
Largest diff. peak and hole [e Å^{-3}]	0.45/-0.47		where $P=(F_o^2+2F_c^2)/3$	

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