Supplementary Information for

Brønsted acid-catalysed conjugate addition of photochemically generated α-amino radicals to alkenylpyridines

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A. General Information

The NMR spectra were recorded at 400 MHz and 500 MHz for ^{1}H or at 100 MHz and 125 MHz for ^{13}C, respectively. The chemical shifts (δ) for ^{1}H and ^{13}C are given in ppm relative to residual signals of the solvents ($CHCl_3$ @ 7.27 ppm ^{1}H NMR, 77.00 ppm ^{13}C NMR). Coupling constants are given in Hz. The following abbreviations are used to indicate the multiplicity: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br s, broad signal.
High-resolution mass spectra (HRMS) were obtained from the ICIQ High Resolution Mass Spectrometry Unit on Waters GCT gas chromatograph coupled time-of-flight mass spectrometer (GC/MS-TOF) with electron ionization (EI) or MicroTOF II (Bruker Daltonics): HPLC-MS-TOF (ESI). X-ray data were obtained from the ICIQ X-Ray Unit using a Bruker-Nonius diffractometer equipped with an APPEX 2 4K CCD area detector. Optical rotations were measured on a Polarimeter Jasco P-1030 and are reported as follows: $[\alpha]_D$ rt (c in g per 100 mL, solvent).

The authors are indebted to the team of the Research Support Area at ICIQ.

Chromatographic purification of products was accomplished using force-flow chromatography (FC) on silica gel (35-70 mesh). For thin layer chromatography (TLC) analysis throughout this work, Merck precoated TLC plates (silica gel 60 GF_{254}, 0.25 mm) were used, using UV light as the visualising agent and an acidic mixture of ceric ammonium molybdate or basic aqueous potassium permangante ($KMnO_4$), and heat as developing agents. Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator.

Cyclic Voltammetry: Cyclic voltammetry studies was carried out on a Princeton Applied Research PARSTAT 2273 potentiostat offering compliance voltage up to ± 100 V (available at the counter electrode), ± 10 V scan range and ± 2 A current range.

Determination of Diastereomeric Ratio. The diastereomeric ratio was determined by ^{1}H NMR analysis of the crude reaction mixture through integration of diagnostic signals.

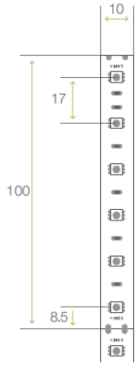
Emission Spectra. The emission spectra of the compounds were recorded in a Fluorolog Horiba Jobin Yvon spectrofluorimeter equipped with photomultiplier detector, double monochromator and 350 W xenon light source

Determination of Enantiomeric Purity: UPC^2 analysis on chiral stationary phase was performed on an Waters Acquity instrument. Waters Amy1 columns with CO_2/EtOH as the eluents were used. HPLC traces were compared to racemic samples prepared by running the reaction in the presence of an achiral catalyst.

Materials: Commercial grade reagents and solvents were purchased at the highest commercial quality from Sigma Aldrich, Fluka, Acros Organics, and Alfa Aesar and used as received, unless otherwise stated.

Light Source: Ledxon Modular 9009083 LED, Single 5050, 14.4 W, Blue purchased from the **Farnell Company :** http://pl.farnell.com/ledxon/9009083/led-single-5050-14-4w-blue/dp/2214013
Technical Data:

Operating voltage	24 VDC (± 5%)
Wattage / m	14.4 W
Wattage / Segment	1.44 W
LED type	SMD 5050 3-Chip
LED pitch	17 mm
Number of LED / m	60 pc.
Step length	100 mm / 6 LED
Dimensions in mm	1000 x 10 x 2.2
Ingress protection	IP20
PCB technology	Isolated double layer FPC
Lifetime	>36.000h LF70 @ Tc 70°C
Operating temperature	Tc min. -25°C / Tc max. +70°C

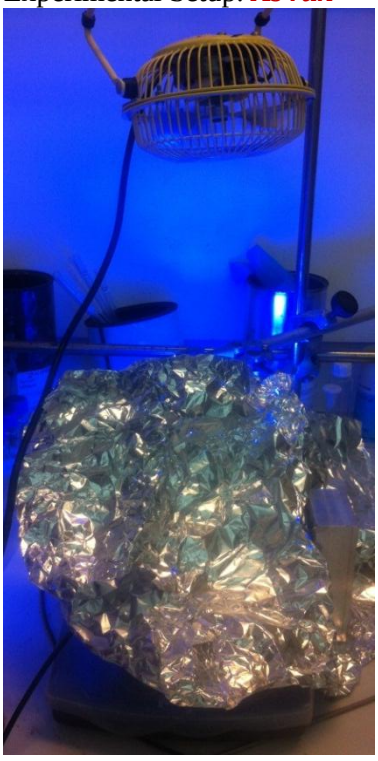


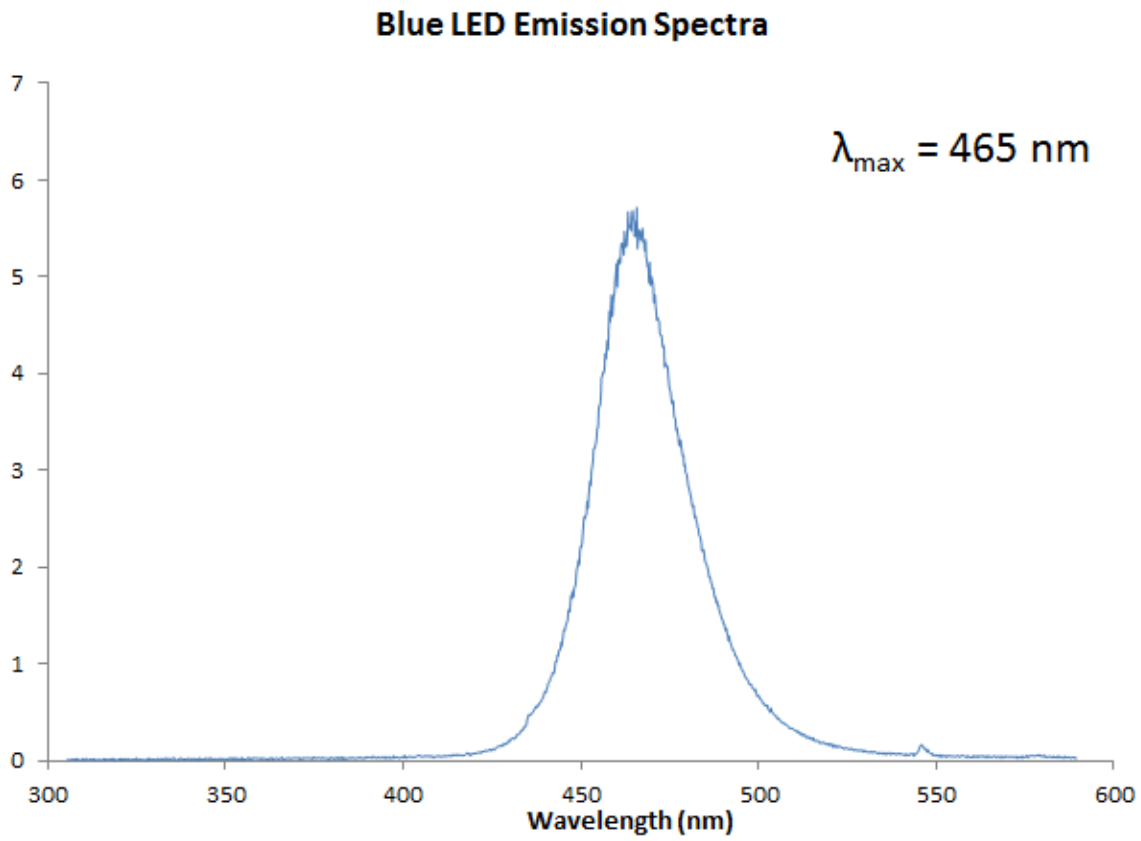
Experimnetal Setup:

Experimental Setup: light off

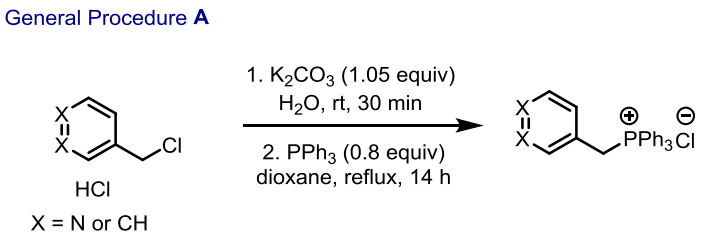
Experimental Setup: ***light on***

Experimental Setup: ***As run***

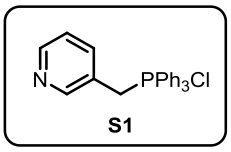



Blue LED Emission Spectra
λmax = 465 nm
7
6
5
4
3
2
1
0
300
350
400
450
500
550
600
Wavelength (nm)

B. Substrate Synthesis



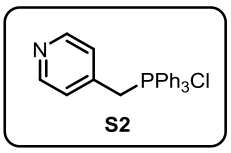
General Procedure A: The commercially available (chloromethyl)pyrdine hydrochloride (1.0 equiv) was dissolved in water (0.2 M). Potassium carbonate (1.05 equiv) was added portionwise and the solution was stirred for 30 minutes. The solution was diluted by the addition of Et_2O and the biphasic system was extracted with Et_2O (x 3). The organic layers were combined, dried, and concentrated *in vacuo*. The resulting crude product was dissolved in dioxane (0.2 M) and triphenylphosphine (0.8 equiv) was added. The solution was heated at reflux for 14 hours then cooled to room temperature. The solution was filtered and the solid was then dried under high vacuum for 1 hour to afford the corresponding *ylide*.



(Pyridin-3-ylmethyl)triphenylphosphonium chloride (S1)

The title compound was prepared according to General Procedure A using 3-(chloromethyl)pyridine hydrochloride (2.00 g, 12.2 mmol). The filtered solid was >95% pure to afford ylide **S1** (873 mg, 18%) as a peach solid. HRMS (ESI) Exact mass calculated for $C_{24}H_{21}NP$ $[M+H]^+$: 354.1406, found: 354.1410;

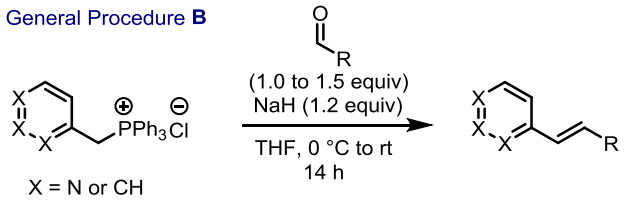
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.43 (1H, ddd, *J* = 4.9, 2.4, 1.7 Hz, Ar**H**), 8.09 (1H, q, *J* = 1.0 Hz, Ar**H**), 7.94 (1H, dq, *J* = 7.9, 2.2 Hz, Ar**H**), 7.88-7-72 (9H, m, Ar**H**), 7.70-7.57 (6H, m, Ar**H**), 7.09 (1H, ddt, *J* = 7.9, 4.8, 0.9 Hz, Ar**H**), 5.81 (2H, d, *J* = 14.9 Hz, C**H**$_2$P); **^{13}C NMR (125.6 MHz, $CDCl_3$)** δ 135.1 (CH, d, *J* = 2.9 Hz,), 134.4 (CH, d, *J* = 10.0 Hz,), 130.25 (CH, d, *J* = 12.7 Hz; **^{31}P NMR (202 MHz, $CDCl_3$)** δ 27.3.



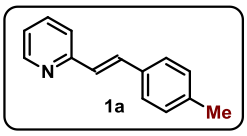
(Pyridin-4-ylmethyl)triphenylphosphonium chloride (S2)

The title compound was prepared according to General Procedure A using 3-(Chloromethyl)pyridine hydrochloride (5.00 g, 30.5 mmol). The filtered solid was >95% pure to afford ylide **S2** (1.64 mg, 14%) as a brown solid. HRMS (ESI) Exact mass calculated for $C_{24}H_{21}NP$ $[M+H]^+$: 354.1406, found: 354.1407;

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.35 (2H, dt, *J* = 5.2, 0.8 Hz, Ar**H**), 7.89-7.80 (6H, m, Ar**H**), 7.79-7.71 (3H, m, Ar**H**), 7.67-7-55 (6H, m, Ar**H**), 7.24-7.18 (2H, m, Ar**H**), 5.92 (2H, d, *J* = 15.9 Hz, C**H**$_2$P; **^{13}C NMR (125.6 MHz, $CDCl_3$)** δ 134.4 (2 x CH, d, *J* = 10.0 Hz,), 130.18 (2 x CH, d, *J* = 12.8 Hz,); **^{31}P NMR (202 MHz, $CDCl_3$)** δ 27.2.

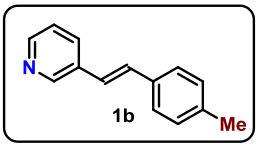


General Procedure B: Pyridyl ylide (1.0 equiv) was dissolved in THF (0.05 M) under argon and cooled to 0 °C. Sodium Hydride (1.2 equiv, 60% dispersion in mineral oil) was added portionwise and the solution was stirred for 1 hour. Aldehyde (1.0 to 1.5 equiv) was then added and the reaction was warmed to room temperature and stirred for 13 hours. The solution was diluted by the addition of EtOAc and the biphasic system was extracted with EtOAc (x 3). The organic layers were combined, dried, and concentrated *in vacuo*. The crude product was purified by FC to afford the corresponding *alkenylpyridine*.



(*E*)-2-(*p*-Tolylstyryl)pyridine (1a)

The title compound **1a** was prepared according to General Procedure B using (pyridin-2-ylmethyl)triphenylphosphonium chloride[1] (1.00 g, 2.57 mmol) and *p*-tolualdehyde (0.36 mL, 3.08 mmol). The crude product was purified by FC (95:5 hexanes:EtOAc) to afford *alkenylpyridine* **1a** (371 mg, 74%) as a white solid that displayed spectroscopic data consistent with those reported previously.[2]

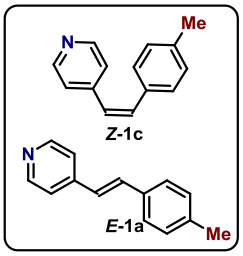


(*E*)-3-(*p*-tolylstyryl)pyridine (1b)

The title compound **1b** was prepared according to General Procedure B using (pyridin-3-ylmethyl)triphenylphosphonium chloride (500 mg, 1.28 mmol) and *o*-tolualdehyde (0.18 mL, 1.56 mmol). The crude product was purified by FC (90:10 hexanes:EtOAc) to afford *E-alkenylpyridine* **1b** (71 mg, 28%) as a white solid.

HRMS (ESI) Exact mass calculated for $C_{14}H_{14}N$ $[M+H]^+$: 196.1121, found: 196.1116;

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.72 (1H, d, *J* = 2.2 Hz, Ar**H**), 8.48 (1H, dd, *J* = 4.8, 1.6 Hz, Ar**H**), 7.82 (1H, dt, *J* = 8.0, 2.0 Hz, Ar**H**), 7.44 (2H, d, *J* = 8.1 Hz, Ar**H**), 7.28 (1H, ddd, *J* = 7.9, 4.8, 0.8 Hz, Ar**H**), 7.20 (2H, d, *J* = 7.9 Hz, Ar**H**), 7.15 (1H, d, *J* = 16.4 Hz, C**H**=CH), 7.03 (1H, d, *J* = 16.4 Hz, CH=C**H**), 2.38 (3H, s, C**H**$_3$); **^{13}C NMR (125.6 MHz, $CDCl_3$)** δ 148.5 (CH), 148.3 (CH), 138.2 (C), 133.9 (C), 133.2 (C), 132.5 (CH), 130.8 (CH), 129.5 (2 x CH), 126.6 (2 x CH), 123.9 (CH), 123.5 (CH), 21.3 (CH_3).



(*Z*)-4-(*p*-Tolylstyryl)pyridine (*Z*-1c) and (*E*)-4-(*p*-tolylstyryl)pyridine (*E*-1c)

The title compounds were prepared according to General Procedure B using (pyridin-4-ylmethyl)triphenylphosphonium chloride (1.00 g, 2.57 mmol) and *o*-tolualdehyde (0.36 mL, 3.08 mmol). The crude product was purified by FC (90:10 hexanes:EtOAc) to afford *Z-alkenylpyridine* **1c** (73 mg, 15%) as a colourless oil followed by *E-alkenylpyridine* **1c** (260 mg, 52%) as a white solid.

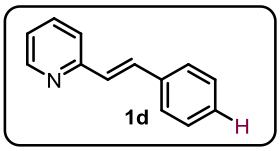
Data for (*Z*)-3-(*p*-tolylstyryl)pyridine (1c): HRMS (ESI) Exact mass calculated for $C_{14}H_{14}N$ $[M+H]^+$: 196.1121, found: 196.1118;

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.43 (2H, m, Ar**H**), 7.12-7.08 (4H, m, Ar**H**), 7.04 (2H, d, *J* = 8.0 Hz, Ar**H**), 6.73 (1H, d, *J* = 12.2 Hz, C**H**=CH), 6.42 (1H, d, *J* = 12.2 Hz, CH=C**H**), 2.31 (3H, s,

C**H**$_3$); **^{13}C NMR (125.6 MHz, CDCl$_3$)** δ 149.5 (2 x CH), 145.1 (C), 137.6 (C), 133.9 (CH), 133.0 (C), 128.9 (2 x CH), 128.5 (2 x CH), 126.6 (CH), 123.3 (2 x CH), 21.1 (CH$_3$).

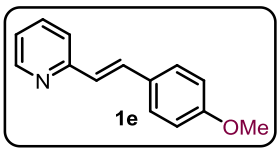
Data for (*E*)-3-(*p*-tolylstyryl)pyridine (1c): HRMS (ESI) Exact mass calculated for $C_{14}H_{14}N$ $[M+H]^+$: 196.1121, found: 196.1121;

^{1}H NMR (500 MHz, CDCl$_3$) δ 8.58-8.56 (2H, m, Ar**H**), 7.45 (2H, d, *J* = 8.1 Hz, Ar**H**), 7.38-7.34 (2H, m, Ar**H**), 7.29 (1H, d, *J* = 16.0 Hz, C**H**=CH), 7.23-7.19 (2H, m, Ar**H**), 6.98 (1H, d, *J* = 16.3 Hz, CH=C**H**), 2.39 (3H, s, C**H**$_3$); **^{13}C NMR (125.6 MHz, CDCl$_3$)** δ 150.1 (2 x CH), 144.8 (C), 138.9 (C), 133.4 (C), 133.1 (CH), 129.6 (2 x CH), 126.9 (2 x CH), 125.0 (CH), 120.7 (2 x CH), 21.3 (CH$_3$).



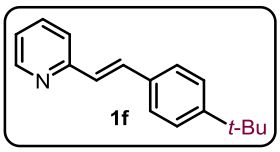
(*E*)-2-(Styryl)pyridine (1d)

The title compound **1d** was prepared according to General Procedure B using (pyridin-2-ylmethyl)triphenylphosphonium chloride (1.00 g, 2.57 mmol) and benzaldehyde (0.39 mL, 3.85 mmol). The crude product was purified by FC (95:5 hexanes:EtOAc) to afford *alkenylpyridine* **1d** (208 mg, 45%) as a white solid that displayed spectroscopic data consistent with those reported previously.[3]



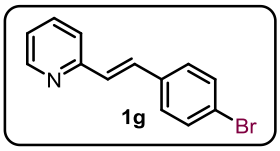
(*E*)-2-(*p*-Methoxystyryl)pyridine (1e)

The title compound **1e** was prepared according to General Procedure B using (pyridin-2-ylmethyl)triphenylphosphonium chloride (1.00 g, 2.57 mmol) and *p*-tolualdehyde (0.47 mL, 3.85 mmol). The crude product was purified by FC (95:5 hexanes:EtOAc) to afford *alkenylpyridine* **1e** (375 mg, 69%) as a white solid that displayed spectroscopic data consistent with those reported previously.[2]



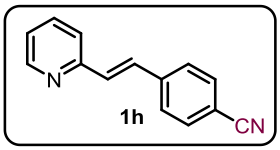
(*E*)-2-(*p*-*tert*-Butylstyryl)pyridine (1f)

The title compound **1f** was prepared according to General Procedure B using (pyridin-2-ylmethyl)triphenylphosphonium chloride (1.00 g, 2.57 mmol) and *p*-*tert*-butylbenzaldehyde (0.64 mL, 3.85 mmol). The crude product was purified by FC (95:5 hexanes:EtOAc) to afford *alkenylpyridine* **1f** (323 mg, 53%) as a white solid that displayed spectroscopic data consistent with those reported previously.[3]



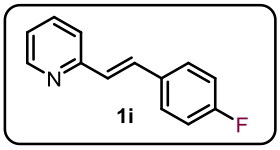
(*E*)-2-(*p*-Bromostyryl)pyridine (1g)

The title compound **1g** was prepared according to General Procedure B using (pyridin-2-ylmethyl)triphenylphosphonium chloride (1.00 g, 2.57 mmol) and *p*-bromobenzaldehyde (0.48 g, 2.57 mmol). The crude product was purified by FC (95:5 hexanes:EtOAc) to afford *alkenylpyridine* **1g** (85 mg, 13%) as a white solid that displayed spectroscopic data consistent with those reported previously.[4]



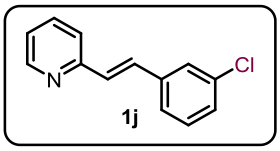
(*E*)-2-(*p*-Cyanostyryl)pyridine (1h)

The title compound **1h** was prepared according to General Procedure B using (pyridin-2-ylmethyl)triphenylphosphonium chloride (1.00 g, 2.57 mmol) and *p*-cyanobenzaldehyde (0.34 g, 2.57 mmol). The crude product was purified by FC (95:5 hexanes:EtOAc) to afford *alkenylpyridine* **1h** (387 mg, 73%) as a white solid that displayed spectroscopic data consistent with those reported previously.[2]



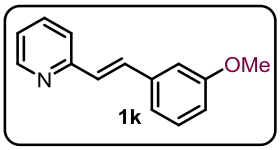
(*E*)-2-(*p*-Fluorostyryl)pyridine (1i)

The title compound **1i** was prepared according to General Procedure B using (pyridin-2-ylmethyl)triphenylphosphonium chloride (1.00 g, 2.57 mmol) and *p*-fluorobenzaldehyde (0.28 mL, 2.57 mmol). The crude product was purified by FC (95:5 hexanes:EtOAc) to afford *alkenylpyridine* **1i** (377 mg, 74%) as a cream solid that displayed spectroscopic data consistent with those reported previously.[3]



(*E*)-2-(*m*-Chlorostyryl)pyridine (1j)

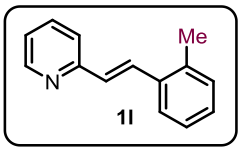
The title compound **1j** was prepared according to General Procedure B using (pyridin-2-ylmethyl)triphenylphosphonium chloride (1.00 g, 2.57 mmol) and *m*-chlorobenzaldehyde (436 mL, 2.57 mmol). The crude product was purified by FC (95:5 hexanes:EtOAc) to afford *alkenylpyridine* **1j** (275 mg, 50%) as a yellow solid that displayed spectroscopic data consistent with those reported previously.[4]



(*E*)-2-(*m*-Methoxystyryl)pyridine (1k)

The title compound **1k** was prepared according to General Procedure B using (pyridin-2-ylmethyl)triphenylphosphonium chloride (1.00 g, 2.57 mmol) and *m*-methoxybenzaldehyde (0.31 mL, 2.57 mmol). The crude product was purified by FC (95:5 hexanes:EtOAc) to afford *alkenylpyridine* **1k** (349 mg, 64%) as a colourless oil. HRMS (ESI) Exact mass calculated for $C_{14}H_{14}NO$ $[M+H]^+$: 212.1070, found: 212.1068;

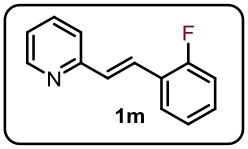
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.60 (1H, ddd, *J* = 4.8, 1.9, 0.9 Hz, Ar**H**), 7.65-7.58 (2H, m, Ar**H** + C**H**=CH), 7.37 (1H, dt, *J* = 7.9, 1.1 Hz, Ar**H**), 7.29 (1H, t, *J* = 7.9 Hz, Ar**H**), 7.20-7.10 (4H, m, Ar**H** + CH=C**H**), 6.86 (1H, ddd, *J* = 8.2, 2.6, 1.0 Hz, Ar**H**), 3.83 (3H, s, OC**H**$_3$); **^{13}C NMR (125.6 MHz, $CDCl_3$)** δ 159.8 (C), 155.4 (C), 149.5 (CH), 138.0 (C), 136.4 (CH), 132.5 (CH), 129.6 (CH), 128.2 (CH), 121.98 (CH), 121.96 (CH), 119.7 (CH), 114.1 (CH), 112.0 (CH), 55.1 (CH_3).



(*E*)-2-(*o*-Tolylstyryl)pyridine (1l)

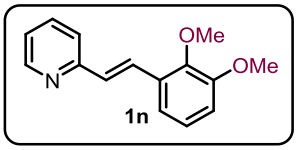
The title compound **1l** was prepared according to General Procedure B using (pyridin-2-ylmethyl)triphenylphosphonium chloride (1.00 g, 2.57 mmol) and *o*-tolualdehyde (0.36 mL, 3.08 mmol). The crude product was purified by FC (90:10 hexanes:EtOAc) to afford *alkenylpyridine* **1l** (297 mg, 59%) as a colourless oil. HRMS (ESI) Exact mass calculated for $C_{14}H_{14}N$ $[M+H]^+$: 196.1121, found: 196.1121;

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.63 (1H, ddd, *J* = 4.9, 1.9, 0.9 Hz, Ar**H**), 7.90 (1H, d, *J* = 15.9 Hz, C**H**=CH), 7.71-7.63 (2H, m, Ar**H**), 7.40 (1H, dd, *J* = 7.9, 1.1 Hz, Ar**H**), 7.28-7.17 (3H, m, Ar**H**), 7.16 (1H, ddd, *J* = 7.5, 4.9, 1.1 Hz, Ar**H**), 7.08 (1H, d, *J* = 15.9 Hz, CH=C**H**), 2.50 (3H, s, C**H**$_3$); **^{13}C NMR (125.6 MHz, $CDCl_3$)** δ 155.8 (C), 149.7 (CH), 136.54 (C), 136.49 (CH), 135.7 (C), 130.5 (2 x CH), 129.3 (CH), 128.2 (CH), 126.2 (CH), 125.7 (CH), 122.1 (CH), 120.0 (CH), 20.0 (CH_3).



(*E*)-2-(*o*-Fluorostyryl)pyridine (1m)

The title compound **1m** was prepared according to General Procedure B using (pyridin-2-ylmethyl)triphenylphosphonium chloride (1.00 g, 2.57 mmol) and *o*-fluoroobenzaldehyde (0.27 mL, 2.57 mmol). The crude product was purified by FC (90:10 cyclohexanes:EtOAc) to afford *alkenylpyridine* **1m** (298 mg, 58%) as a white solid that displayed spectroscopic data consistent with those reported previously.[5]

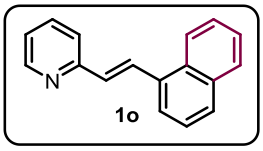


(*E*)-2-(*o*,*m*-Dimethoxystyryl)pyridine (1n)

The title compound **1n** was prepared according to General Procedure B using (pyridin-2-ylmethyl)triphenylphosphonium chloride (1.00 g, 2.57 mmol) and 2,3-dimethoxybenzaldehyde (0.43 g, 3.08 mmol). The crude product was purified by FC (95:5 cyclohexanes:EtOAc) to afford *alkenylpyridine* **1n** (154 mg, 25%) as a colourless oil.

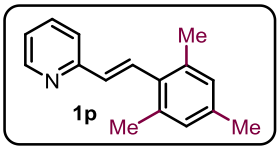
HRMS (ESI) Exact mass calculated for $C_{15}H_{16}NO_2$ $[M+H]^+$: 242.1176 , found: 242.1174.

^{1}H NMR (500 MHz, $CDCl_3$) 8.61 (1H, d, *J* = 4.6 Hz, Ar**H**), 7.89 (1H, d, *J* = 16.4 Hz, C**H**=CH), 7.65 (1H, td, *J* = 7.7, 1.9 Hz, Ar**H**), 7.47 (1H, d, *J* = 7.8 Hz, Ar**H**), 7.28 (1H, dd, *J* = 8.0, 1.5 Hz, Ar**H**), 7.24 (1H, d, *J* = 16.4 Hz, C**H**=CH), 7.13 (1H, ddd, *J* = 7.4, 4.8, 1.2 Hz, Ar**H**), 7.07 (1H, t, *J* = 8.0 Hz, Ar**H**), 3.89 (3H, s, OC**H**$_3$), 3.88 (3H, s, OC**H**$_3$); **^{13}C NMR (125.6 MHz, $CDCl_3$)** δ 156.0 (C), 153.0 (C), 149.5 (CH), 147.5 (C), 136.4 (CH), 130.8 (C), 129.6 (CH), 127.2 (CH), 124.0 (CH), 121.9 (CH), 121.6 (CH), 118.5 (CH), 112.0 (CH), 61.1 (CH_3), 55.8 (CH_3).



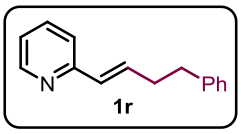
(*E*)-2-(2-Naphthalen-1-yl)pyridine (1o)

The title compound **1o** was prepared according to General Procedure B using (pyridin-2-ylmethyl)triphenylphosphonium chloride (1.00 g, 2.57 mmol) and 1-naphthaldehyde (0.35 mL, 2.57 mmol). The crude product was purified by FC (95:5 hexanes:EtOAc) to afford *alkenylpyridine* **1o** (464 mg, 78%) as a yellow oil that displayed spectroscopic data consistent with those reported previously.[6]



(*E*)-2-(2,4,6-Trimethylstyryl)pyridine (1p)

The title compound **1p** was prepared according to General Procedure B using (pyridin-2-ylmethyl)triphenylphosphonium chloride (1.00 g, 2.57 mmol) and 2,4,6-trimethylbenzaldehyde (0.45 mL, 2.57 mmol). The crude product was purified by FC (95:5 hexanes:EtOAc) to afford *alkenylpyridine* **1p** (395 mg, 69%) as a colourless oil that displayed spectroscopic data consistent with those reported previously.[3]

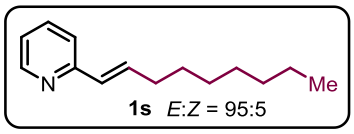


(*E*)-2-(4-Phenyl-but-1-enyl)pyridine (1r)

The title compound **1r** was prepared according to General Procedure B using (pyridin-2-ylmethyl)triphenylphosphonium chloride (1.00 g, 2.57 mmol) and hydrocinnamaldehyde (90% technical grade, 0.38 mL, 2.57 mmol). The crude product was purified by FC (90:10 hexanes:EtOAc) to afford *alkenylpyridine* **1r** (335 mg, 62%) as a colourless oil.

HRMS (ESI) Exact mass calculated for $C_{15}H_{16}N$ $[M+H]^+$: 210.1277, found: 210.1276.

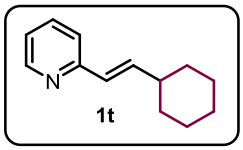
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.54 (1H, ddd, *J* = 4.8, 1.9. 0.9 Hz, Ar**H**) 7.60 (1H, td, *J* = 7.7, 1.8 Hz, Ar**H**), 7.34-7.28 (2H, m, Ar**H**), 7.26-7.19 (4H, m, Ar**H**), 7.10 (1H, ddd, *J* = 7.5, 4.8, 1.2 Hz, Ar**H**), 6.80 (1H, dt, *J* = 15.7, 6.9 Hz, CH=C**H**CH_2), 6.54 (1H, dt, *J* = 15.7, 1.6 Hz, C**H**=$CHCH_2$) 2.85 (2H, dd, *J* = 9.1 6.7 Hz, CH_2C**H**$_2$Ph), 2.67-2.56 (2H, m, C**H**$_2CH_2$Ph); **^{13}C NMR (125.6 MHz, $CDCl_3$)** δ 155.9 (C), 149.4 (CH), 141.6 (C), 136.4 (CH), 134.7 (CH), 130.4 (CH), 128.40 (2 x CH), 128.36 (2 x CH), 125.9 (CH), 121.6 (CH), 121.0 (CH), 35.4 (CH_2), 34.6 (CH_2).



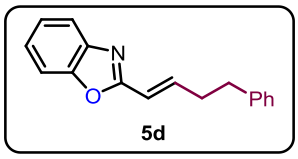
(*E*)-2-(Non-1-enyl)pyridine (1s)

The title compound **1s** was prepared according to General Procedure B using (pyridin-2-ylmethyl)triphenylphosphonium chloride (1.00 g, 2.57 mmol) and octanal (0.60 mL, 3.85 mmol). The crude product was purified by FC (95:5 cyclohexane:EtOAc) to afford *alkenylpyridine* **1s** (411 mg, 79% *E*:*Z* = 95:5) as a yellow oil.

HRMS (ESI) Exact mass calculated for $C_{14}H_{22}N$ $[M+H]^+$: 204.1747 , found: 204.1746.
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.53 (1H, dd, *J* = 4.8, 1.9 Hz, Ar**H**), 7.59 (1H, dt, *J* = 7.6, 1.9 Hz, Ar**H**), 7.24 (1H, dd, *J* = 7.9, 1.2 Hz, Ar**H**), 7.11-7.05 (1H, m, Ar**H**), 6.74 (1H, dt, *J* = 15.6, 7.0 Hz, ArCH=C**H**), 6.48 (1H, dd, *J* = 15.7, 1.7 Hz, ArC**H**=CH), 2.26 (2H, qd, *J* = 7.2, 1.6 Hz, CH=CHC**H**$_2$), 1.54-1.47 (2H, m, CH=CHCH$_2$C**H**$_2$), 1.39-1.24 (8H, m, 4 x C**H**$_2$), 0.89 (3H, t, *J* = 6.7 Hz, C**H**$_3$); **^{13}C NMR (125.6 MHz, $CDCl_3$)** δ 156.2 (C), 149.3 (CH), 136.3 (CH), 136.1 (CH), 129.8 (CH), 121.4 (CH), 120.9 (CH), 32.8 (CH_2), 31.8 (CH_2), 29.22 (CH_2), 29.16 (CH_2), 29.0 (CH_2), 22.6 (CH_2), 14.1 (CH_3).

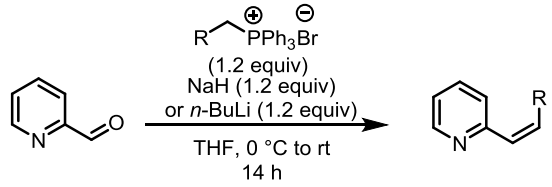


(*E*)-2-(2-Cyclohexylstyryl)pyridine (1t)
The title compound **1t** was prepared according to General Procedure B using (pyridin-2-ylmethyl)triphenylphosphonium chloride (1.00 g, 2.57 mmol) and cyclohexylcarboxaldehyde (0.47 mL, 3.85 mmol). The crude product was purified by FC (95:5 cyclohexane:EtOAc) to afford *alkenylpyridine* **1t** (370 mg, 77%) as a colourless oil that displayed spectroscopic data consistent with those reported previously.[2]

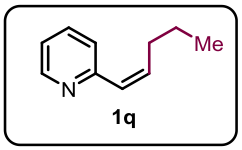


(*E*)-2-(4-Phenylbut-1-en-1-yl)benzo[d]oxazole (5d)
The title compound **5d** was prepared according to a modified variant of General Procedure B using (Benzo[d]oxazol-2-ylmethyl)triphenylphosphonium bromide (500 mg, 1.05 mmol) and hydrocinnamaldehyde (0.278 mL, 2.11 mmol, 2.0 equiv). The crude product was purified by FC (95:5 cyclohexane:EtOAc) to afford *alkenylbenzoxazole* **5d** (91 mg, 35%) as a yellow oil.
HRMS (ESI) Exact mass calculated for $C_{17}H_{16}NO$ $[M+H]^+$: 250.1226 , found: 250.1217;
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73-7.69 (1H, m, Ar**H**), 7.53-7.48 (1H, m, Ar**H**), 7.38-7.29 (5H, m, Ar**H**), 7.27-7.23 (3H, m, Ar**H**), 7.08 (1H, dt, *J* = 16.0, 6.9 Hz, CH=C**H**CH$_2$), 6.48 (1H, dt, *J* = 16.0, 1.6 Hz, C**H**=CHCH$_2$), 2.88 (2H, t, *J* = 7.7 Hz, C**H**$_2$Ph), 2.73-2.63 (2H, m, CH=CHC**H**$_2$); **^{13}C NMR (125.6 MHz, $CDCl_3$)** δ 162.3 (C), 150.2 (C), 142.8 (CH), 141.9 (C), 140.7 (CH), 128.5 (2 x CH), 128.3 (2 x CH), 126.1 (CH), 124.9 (CH), 124.3 (CH), 119.7 (CH), 117.4 (CH), 110.2 (CH), 34.7 (CH_2), 34.6 (CH_2).

General Procedure **C**



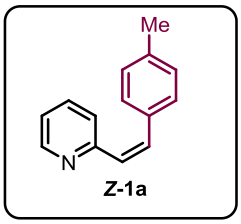
General Procedure C: Ylide (1.2 equiv) was dissolved in THF (0.05 M) under argon and cooled to 0 °C. Sodium Hydride (1.2 equiv, 60% dispersion in mineral oil) or *n*-BuLi (1.2 equiv, 2.5 M in hexanes) was added portionwise and the solution was stirred for 1 hour. Aldehyde (1.0 equiv) was then added and the reaction was warmed to room temperature and stirred for 13 hours. The solution was diluted by the addition of EtOAc and the biphasic system was extracted with EtOAc (x 3). The organic layers were combined, dried, and concentrated *in vacuo*. The crude product was purified by FC to afford the corresponding *alkenylpyridine*.



(*Z*)-2-(Prop-1-enyl)pyridine (1q)

The title compound **1q** was prepared according to General Procedure C using butyltriphenylphosphonium chloride (4.79 g, 12.0 mmol) and picolinaldehyde (0.95 mL, 10.0mmol). The crude product was purified by FC (98:02 hexanes:EtOAc) to afford *alkenylpyridine* **1q** (409 mg, 28%) as a colourless oil. HRMS (ESI) Exact mass calculated for $C_{14}H_{14}N$ $[M+H]^+$: 196.1121, found: 196.1121;

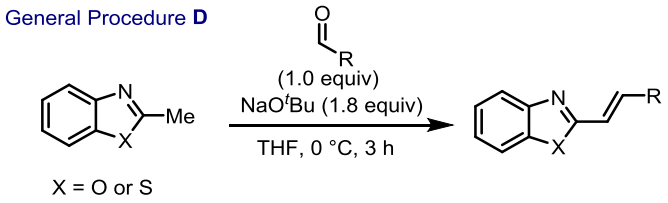
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.60 (1H, ddd, *J* = 4.9, 1.9, 1.0 Hz, Ar**H**), 7.62 (1H, td, *J* = 7.7, 1.9 Hz, Ar**H**), 7.24 (1H, dt, *J* = 7.9, 1.1 Hz, Ar**H**), 7.09 (1H, ddd, *J* = 7.6, 4.8, 1.2 Hz, Ar**H**), 6.47 (1H, dt, *J* = 11.9 Hz, 1.9 Hz, ArC**H**=CH), 5.89 (1H, dt, *J* = 11.9, 7.3 Hz, ArCH=C**H**), 2.55 (2H, qd, *J* = 7.3, 1.9 Hz, CH=CHC**H**$_2$), 1.50 (2H, app hept, *J* = 7.4 Hz, $CH_2C\mathbf{H}_2CH_3$), 0.95 (3H, t, *J* = 7.4 Hz, C**H**$_3$); **^{13}C NMR (125.6 MHz, $CDCl_3$)** δ 156.8 (C), 149.2 (CH), 137.1 (CH), 135.8 (CH), 128.6 (CH), 123.7 (CH), 121.0 (CH), 30.8 (CH_2), 22.9 (CH_2), 13.8 (CH_3).



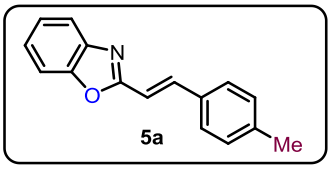
(*Z*)-2-(*p*-Tolylstyryl)pyridine (*Z*-1a)

The title compound ***Z*-1a** was prepared according to General Procedure C using (4-methylbenzyl)ltriphenylphosphonium bromide (5.51 g, 12.3 mmol) and picolinaldehyde (1.07 mL, 11.2 mmol). The crude product was purified by FC (90:10 hexanes:EtOAc) to afford *alkenylpyridine* ***Z*-1a** (450 mg, 21%) as a colourless oil.

HRMS (ESI) Exact mass calculated for $C_{14}H_{14}N$ $[M+H]^+$: 196.1121, found: 196.1129; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.59 (1H, ddd, *J* = 4.9, 1.9, 0.9 Hz, Ar**H**), 7.44 (1H, td, *J* = 7.7, 1.9 Hz, Ar**H**), 7.23-7.14 (3H, m, Ar**H**), 7.11-7.04 (3H, m, Ar**H**), 6.80 (1H, d, *J* = 12.4 Hz, C**H**=CH), 6.65 (1H, d, *J* = 12.4 Hz, CH=C**H**); **^{13}C NMR (125.6 MHz, $CDCl_3$)** δ 156.5 (C), 149.4 (CH), 137.4 (C), 135.5 (CH), 133.6 (C), 133.2 (CH), 129.7 (CH), 128.9 (2 x CH), 128.8 (2 x CH), 123.7 (CH), 121.6 (CH), 21.2 (CH_3).

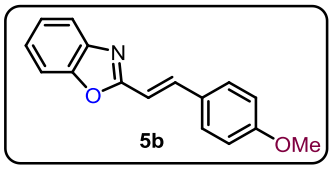


General Procedure D: Sodium *tert*-butoxide (1.8 equiv) was suspended in THF (0.5 M) under argon and cooled to 0 °C. Methylbenzoxazole or Methylbenzothiazole (1.0 equiv) was added dropwise and the solution was stirred for 30 minutes. Aldehyde (1.0 equiv) was then added and the reaction was warmed to room temperature and stirred for 2 hours. The solution was poured into water and filtered to afford the corresponding *alkenylheterocycle*.



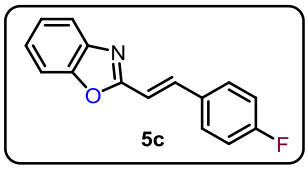
(*E*)-2-(4-Methylstyryl)benzo[d]oxazole (5a)

The title compound **5a** was prepared according to General Procedure D using 2-methylbenzoxazole (1.44 g, 10.8 mmol) and *p*-tolualdehyde (1.27 mL, 10.8 mmol) to afford *alkenylbenzoxazole* **5a** (2.25 g, 89%) as a biege solid that displayed spectroscopic data consistent with those reported previously.[7]



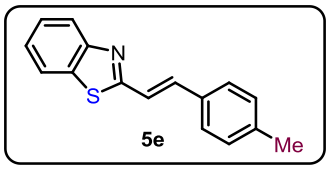
(*E*)-2-(4-Methoxystyryl)benzo[d]oxazole (5b)

The title compound **5b** was prepared according to General Procedure D using 2-methylbenzoxazole (1.44 g, 10.8 mmol) and *p*-methoxybenzaldehyde (1.31 mL, 10.8 mmol) to afford *alkenylbenzoxazole* **5b** (2.46 g, 91%) as a biege solid that displayed spectroscopic data consistent with those reported previously.[8]



(*E*)-2-(4-Fluorostyryl)benzo[d]oxazole (5c)

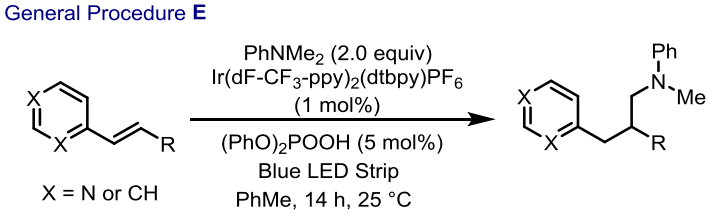
The title compound **5c** was prepared according to General Procedure D using 2-methylbenzoxazole (0.72 g, 5.4 mmol) and *p*-fluorobenzaldehyde (0.58 mL, 5.4 mmol) to afford *alkenylbenzoxazole* **5c** (1.13 g, 87%) as a yellow solid that displayed spectroscopic data consistent with those reported previously.[7]



(*E*)-2-(4-Methylstyryl)benzo[d]thiazole (5e)

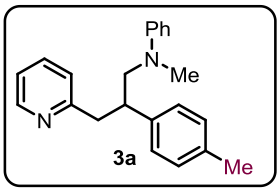
The title compound **5e** was prepared according to General Procedure D using 2-methylbenzothiazole (1.61 g, 10.8 mmol) and *p*-tolualdehyde (1.27 mL, 10.8 mmol) to afford *alkenylbenzothiazole* **5e** (264 mg, 10%) as a yellow solid that displayed spectroscopic data consistent with those reported previously.[7]

C. General Procedure for the Brønsted Acid-Catyalysed Addition of Photochemically Generatred α-Amino Radicals to Alkenylpyridines



General Procedure E: Alkenylpyridine (1.0 equiv), [Ir{dF(CF_3)ppy}$_2$(dtbbpy)]PF_6 (1 mol%) and diphenyl phosphate (5 mol%) were added to a Schlenk tube and the vessel was evacuated and backfilled with argon twice. Toluene (0.1 M) and dimethylaniline (2.0 equiv) were added and the Schlenk tube was sealed. The solution was subjected to 3 freeze-pump-thaw cycles and was then irradiated for 14 hours by blue LED´s. The solution was diluted with EtOAc and partitioned between EtOAc and 1M NaOH solution. The biphasic system was extracted with EtOAc (x 3). The organic layers were combined, dried, and concentrated *in vacuo*. The crude product was purified by FC to afford the corresponding *amine*.

D. Characterisation of Products

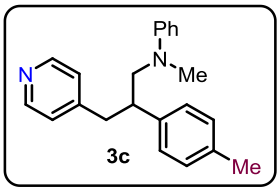


N-Methyl-N-(3-(pyridin-2-yl)-2-(p-tolyl)propyl)aniline (3a)

The title compound **3a** was prepared according to General Procedure E using (*E*)-2-(*p*-tolylstyryl)pyridine (59 mg, 0.3 mmol). The crude product was purified by FC (95:5 cyclohexane:EtOAc) to afford *amine* **3a** (83 mg, 87%) as a beige solid.

HRMS (ESI) Exact mass calculated for $C_{22}H_{25}N_2$ $[M+H]^+$: 317.2012, found: 317.2006;

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.52 (1H, ddd, *J* = 4.9, 1.9, 0.9 Hz, Ar**H**), 7.48 (1H, dt, *J* = 7.7, 1.9 Hz, Ar**H**), 7.20-7.15 (2H, m, Ar**H**), 7.09-7.04 (5H, m, Ar**H**), 6.97)1H, dt, *J* = 7.8, 1.1 Hz, Ar**H**), 6.65 (1H, tt, *J* = 7.3, 1.0 Hz, Ar**H**), 6.59-6.52 (2H, m, Ar**H**), 3.74 (1H, dd, *J* = 14.6, 6.3 Hz, NtC**H**$_2$), 3.64-3.55 (1H, m, C**H**CH_2N), 3.39 (1H, dd, *J* = 14.6, 8.3 Hz, NC**H**$_2$), 3.22 (1H, dd, *J* = 13.8, 7.0 Hz, ArC**H**$_2$), 3.11 (1H, dd, *J* = 13.8, 8.2 Hz, ArC**H**$_2$), 2.66 (3H, s, NC**H**$_3$), 2.30 (3H, s, ArC**H**$_3$); **^{13}C NMR (125.6 MHz, $CDCl_3$)** δ 160.1 (C), 149.1 (CH), 149.0 (C), 139.9 (C), 135.94 (CH), 135.86 (C), 129.02 (2 x CH), 128.98 (2 x CH), 127.8 (2 x CH), 123.4 (CH), 121.0 (CH), 115.7 (CH), 111.8 (2 x CH), 59.2 (CH_2), 44.0 (CH), 42.2 (CH), 39.3 (CH_3), 21.0 (CH_3).



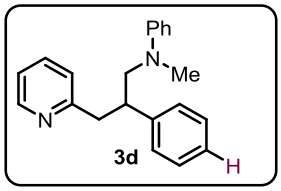
N-Methyl-N-(3-(pyridin-4-yl)-2-(p-tolyl)propyl)aniline (3c)

The title compound **3c** was prepared according to General Procedure E using (*E*)-4-(*p*-tolylstyryl)pyridine (59 mg, 0.3 mmol). The crude product was purified by FC (95:5 cyclohexane:EtOAc) to afford *amine* **3c** (81 mg, 85%) as a biege solid.

HRMS (ESI) Exact mass calculated for $C_{22}H_{25}N_2$ $[M+H]^+$: 317.2012, found: 317.2008.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.42-8.38 (2H, m, Ar**H**), 7.24 (2H, dd, *J* = 8.9, 7.2 Hz, Ar**H**), 7.11-7.07 (2H, m, Ar**H**), 7.02 (2H, d, *J* = 8.1 Hz, Ar**H**), 6.97-6.93 (2H, m, Ar**H**), 6.73 (1H, tt, *J* = 7.3, 1.0 Hz, Ar**H**), 6.63 (2H, dt, *J* = 7.8, 1.0 Hz, Ar**H**), 3.70 (1H, dd, *J* = 14.7, 7.2 Hz, NC**H**$_2$), 3.43 (1H, dd, *J* = 14.7, 7.4 Hz, NC**H**$_2$), 3.31 (1H, dtd, *J* = 9.6, 7.3, 5.5 Hz, NCH_2C**H**), 3.97 (1H, dd, *J* = 13.7, 5.6 Hz, ArC**H**$_2$), 2.91 (1H, dd, *J* = 13.7, 9.6 Hz, ArC**H**$_2$), 2.76 (3H, s, NC**H**$_3$), 2.33 (3H, s, ArC**H**$_3$); **^{13}C NMR (125.6 MHz, $CDCl_3$)** δ 149.4 (2 x CH), 149.2 (C), 148.9 (C), 138.8 (C), 136.3 (C), 129.21 (2

x CH), 129.15 (2 x CH), 127.6 (2 x CH), 124.3 (2 x CH), 116.2 (CH), 111.9 (2 x CH), 59.3 (CH_2), 45.1 (CH), 39.5 (CH_3), 39.2 (CH_2), 21.0 (CH_3).

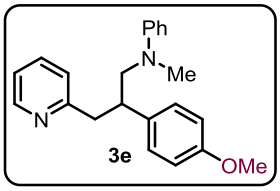


N-Methyl-N-(2-phenyl-3-(pyridin-2-yl)propyl)aniline (3d)

The title compound **3d** was prepared according to General Procedure E using (*E*)-2-(styryl)pyridine (54 mg, 0.3 mmol). The crude product was purified by FC (95:5 cyclohexane:EtOAc) to afford *amine* **3d** (57 mg, 63%) as a yellow oil.

(ESI) Exact mass calculated for $C_{21}H_{23}N_2$ $[M+H]^+$: 303.1856, found: 303.1854.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.54 (1H, ddd, *J* = 4.9, 1.8, 0.9 Hz, Ar**H**), 7.48 (1H, td, *J* = 7.6, 1.8 Hz, Ar**H**), 7.28-7.23 (2H, m, Ar**H**), 7.22-7.17 (5H, m, Ar**H**), 7.70 (1H, ddd, *J* = 7.5, 4.9, 1.1 Hz, Ar**H**), 6.97 (1H, dt, *J* = 7.8, 1.1 Hz, Ar**H**), 6.67 (1H, tt, *J* = 7.2, 1.0 Hz, Ar**H**), 6.57 (2H, dt, *J* = 7.8, 1.0 Hz, Ar**H**), 3.78 (1H, dd, *J* = 14.6, 6.1 Hz, NC$\mathbf{H}_2$), 3.65 (1H, tt, *J* = 8.2, 6.5 Hz, C**H**), 3.43 (1H, dd, *J* = 14.6, 8.4 Hz, NC$\mathbf{H}_2$), 3.26 (1H, dd, *J* = 13.8, 7.0 Hz, ArC$\mathbf{H}_2$), 3.15 (1H, dd, *J* = 13.8, 8.2 Hz, ArC$\mathbf{H}_2$), 2.65 (3H, s, NC$\mathbf{H}_3$); **^{13}C NMR (125.6 MHz, $CDCl_3$)** δ 160.0 (C), 149.1 (CH), 149.0 (C), 143.0 (C), 136.0 (CH), 129.0 (2 x CH), 128.3 (2 x CH), 128.0 (2 x CH), 126.5 (CH), 123.5 (CH), 121.1 (CH), 115.8 (CH), 111.8 (2 x CH), 59.2 (CH_2), 44.4 (CH), 42.1 (CH_2), 39.3 (CH_3).

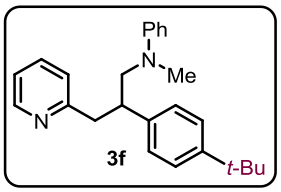


N-(2-(4-Methoxyphenyl)-3-(pyridin-2-yl)propyl)-N-methylaniline (3e)

The title compound **3e** was prepared according to General Procedure E using (*E*)-2-(*p*-methoxystyryl)pyridine (63 mg, 0.3 mmol). The crude product was purified by FC (90:10 cyclohexane:EtOAc) to afford *amine* **3e** (64 mg, 64%) as a beige solid.

HRMS (ESI) Exact mass calculated for $C_{22}H_{25}N_2O$ $[M+H]^+$: 333.1961, found: 333.1965;

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.53 (1H, ddd, *J* = 4.9, 1.9, 0.9 Hz, Ar**H**), 7.48 (1H, td, *J* = 7.7, 1.9 Hz, Ar**H**), 7.23-7.15 (2H, m, Ar**H**), 7.13-7.04 (3H, m, Ar**H**), 6.96 (1H, dt, *J* = 7.8, 1.0 Hz, Ar**H**), 6.82-6.77 (2H, m, Ar**H**), 6.67 (1H, tt, *J* = 7.2, 1.0 Hz, Ar**H**), 6.57 (2H, dd, *J* = 8.9, 1.0 Hz, Ar**H**), 3.77 (3H, s, OC$\mathbf{H}_3$), 3.75 (1H, dd, *J* = 14.6, 6.1 Hz, NC$\mathbf{H}_2$), 3.69 (1H, tt, *J* = 8.3, 6.5 Hz, C**H**), 3.37 (1H, dd, *J* = 14.6, 8.4 Hz, NC$\mathbf{H}_2$), 3.22 (1H, dd, *J* = 13.7, 6.9 Hz, ArC$\mathbf{H}_2$), 3.10 (1H, dd, *J* = 13.7, 8.4 Hz, ArC$\mathbf{H}_2$), 2.66 (3H, s, NC$\mathbf{H}_3$); **^{13}C NMR (125.6 MHz, $CDCl_3$)** δ 160.1 (C), 158.1 (C), 149.1 (CH), 149.0 (C), 136.0 (CH), 135.0 (C), 129.0 (2 x CH), 128.8 (2 x CH), 123.5 (CH), 121.0 (CH), 115.7 (CH), 113.7 (2 x CH), 111.8 (2 x CH), 59.3 (CH_2), 55.1 (CH_3), 43.6 (CH), 42.3 (CH_2), 39.3 (CH_3).



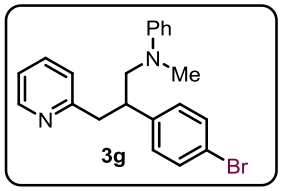
N-(2-(4-(*tert*-Butyl)phenyl)-3-(pyridin-2-yl)propyl)-N-methylaniline (3f)

The title compound **3f** was prepared according to General Procedure E using (*E*)-2-(*p-tert*-butylstyryl)pyridine (71 mg, 0.3 mmol). The crude product was purified by FC (90:10 cyclohexane:EtOAc) to afford *amine* **3f** (59 mg, 55%) as a beige solid.

HRMS (ESI) Exact mass calculated for $C_{25}H_{31}N_2$ $[M+H]^+$: 359.2482, found: 359.2479;

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.54 (1H, ddd, *J* = 4.9, 1.9, 0.9 Hz, Ar**H**), 7.49 (1H, td, *J* = 7.7, 1.9 Hz, Ar**H**), 7.30-7.24 (2H, m, Ar**H**), 7.17 (2H, dd, *J* = 8.8, 7.2 Hz, Ar**H**), 7.16-7.09 (2H, m, Ar**H**), 7.08 (1H, ddd, *J* = 7.5, 4.9, 1.1 Hz, Ar**H**), 7.00 (1H, dt, *J* = 7.8, 1.1 Hz, Ar**H**), 6.65 (1H, tt, *J* = 6.9, 1.0 Hz, Ar**H**), 6.54 (2H, dt, *J* = 7.8, 1.0 Hz, Ar**H**), 3.73 (1H, dd, *J* = 14.6, 6.3 Hz, NC$\mathbf{H}_2$), 3.65-3.56 (1H, m, C**H**), 3.40 (1H, dd, *J* = 14.6, 8.1 Hz, NC$\mathbf{H}_2$), 3.23 (1H, dd, *J* = 13.8, 7.3 Hz, ArC$\mathbf{H}_2$), 3.15 (1H, dd, *J* = 13.8, 7.8 Hz, ArC$\mathbf{H}_2$), 2.95 (3H, s, NC$\mathbf{H}_2$), 1.30 (9H, s, C(C$\mathbf{H}_3$)$_3$); **^{13}C NMR (125.6 MHz, $CDCl_3$)** δ 160.3 (C), 149.3 (C), 149.1 (CH), 139.9 (C), 136.0 (CH), 129.0 (2 x CH), 127.5 (2

x CH), 125.2 (2 x CH), 123.5 (CH), 121.1 (CH), 115.7 (CH), 111.8 (2 x CH), 59.1 (CH_2), 43.8 (CH), 42.2 (CH_2), 39.2 (CH_3), 34.3 (C), 31.4 (3 x CH_3), one quarternary aromatic peak is missing.

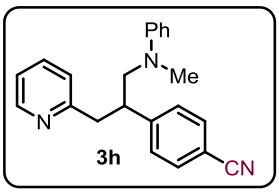


N-(2-(4-Bromophenyl)-3-(pyridin-2-yl)propyl)-N-methylaniline (3g)

The title compound **3g** was prepared according to General Procedure E using (*E*)-2-(*p*-bromostyryl)pyridine (78 mg, 0.3 mmol). The crude product was purified by FC (90:10 cyclohexane:EtOAc) to afford *amine* **3g** (96 mg, 84%) as a brown oil.

HRMS (ESI) Exact mass calculated for $C_{21}H_{22}N_2Br$ $[M+H]^+$: 381.0961, found: 381.0959;

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.53 (1H, d, *J* = 4.3 Hz, Ar**H**), 7.50 (1H, td, *J* = 7.7, 1.9 Hz, Ar**H**), 7.40-7.34 (2H, m, Ar**H**), 7.24-7.16 (2H, m, Ar**H**), 7.11-7.04 (3H, m, Ar**H**), 6.96 (1H, dt, *J* = 7.7, 1.1 Hz, Ar**H**), 6.68 (1H, tt, *J* = 6.9, 0.9 Hz, Ar**H**), 6.57 (2H, dt, *J* = 7.9, 1.1 Hz, Ar**H**), 3.77 (1H, dd, *J* = 14.5, 5.9 Hz, NC**H**$_2$), 3.65 (1H, ddd, *J* = 14.8, 8.4, 6.4 Hz, NCH_2C**H**), 3.38 (1H, dd, *J* = 14.5, 8.5 Hz, NC**H**$_2$), 3.23 (1H, dd, *J* = 13.8, 6.8 Hz, ArC**H**$_2$), 3.09 (1H, dd, *J* = 13.8, 8.4 Hz, ArC**H**$_2$), 2.66 (3H, s, NC**H**$_3$); **^{13}C NMR (125.6 MHz, $CDCl_3$)** δ 159.5 (C), 149.2 (CH), 148.9 (C), 142.0 (C), 136.1 (CH), 131.4 (2 x CH), 129.7 (2 x CH), 129.1 (2 x CH), 123.5 (CH), 121.2 (CH), 120.2 (C), 116.0 (CH), 111.9 (2 x CH), 59.1 (CH_2), 43.9 (CH), 41.9 (CH_2), 39.4 (CH_3).

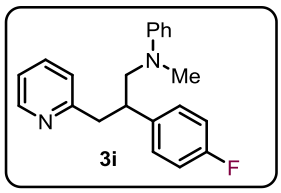


N-(2-(4-Cyanophenyl)-3-(pyridin-2-yl)propyl)-N-methylaniline (3h)

The title compound **3h** was prepared according to General Procedure E using (*E*)-2-(*p*-cyanostyryl)pyridine (62 mg, 0.3 mmol). The crude product was purified by FC (90:10 cyclohexane:EtOAc) to afford *amine* **3h** (61 mg, 62%) as a yellow oil.

HRMS (ESI) Exact mass calculated for $C_{22}H_{22}N_3$ $[M+H]^+$: 328.1808, found: 328.1805;

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.53 (1H, dd, *J* = 5.4, 1.7 Hz, Ar**H**), 7.56-7.50 (3H, m, Ar**H**), 7.33-7.28 (2H, m, Ar**H**), 7.22-7.16 (2H, m, Ar**H**), 7.11 (1H, ddd, *J* = 7.6, 4.9, 1.1 Hz, Ar**H**), 6.98 (1H, d, *J* = 7.8 Hz, Ar**H**), 6.69 (1H, t, *J* = 7.2 Hz, Ar**H**), 6.56 (2H, d, *J* = 7.7 Hz, Ar**H**), 3.84-3.74 (2H, m, NC**H**$_2$), 3.47-3.39 (1H, m, C**H**), 3.28 (1H, dd, *J* = 14.0, 6.4 Hz, ArC**H**$_2$), 3.16-3.08 (1H, m, ArC**H**$_2$), 2.65 (3H, s, C**H**$_3$); **^{13}C NMR (125.6 MHz, $CDCl_3$)** δ 158.8 (C), 149.0 (CH), 148.9 (C), 135.5 (CH), 132.1 (2 x CH), 129.1 (2 x CH), 128.8 (2 x CH), 123.5 (CH), 121.5 (CH), 118.8 (C), 116.4 (CH), 112.0 (2 x CH), 110.4 (C), 58.9 (CH_2), 44.5 (CH), 41.3 (CH_2), 39.4 (CH_3).

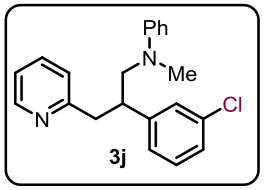


N-(2-(4-Fluorophenyl)-3-(pyridin-2-yl)propyl)-N-methylaniline (3i)

The title compound **3i** was prepared according to General Procedure E using (*E*)-2-(*p*-fluorostyryl)pyridine (60 mg, 0.3 mmol). The crude product was purified by FC (95:5 hexanes:EtOAc) to afford *amine* **3i** (74 mg, 77%) as a light brown solid.

HRMS (ESI) Exact mass calculated for $C_{21}H_{22}N_2F$ $[M+H]^+$: 321.1762, found: 321.1763;

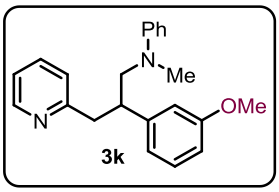
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.52 (1H, ddd, *J* = 4.9, 1.9, 0.9 Hz, Ar**H**), 7.49 (1H, dt, *J* = 7.7, 1.9 Hz, Ar**H**), 7.21-7.16 (2H, m, Ar**H**), 7.15-7.10 (2H, m, Ar**H**), 7.07 (1H, ddd, *J* = 7.5, 4.9, 1.2 Hz, Ar**H**), 6.97-6.90 (3H, m, Ar**H**), 6.67 (1H, tt, *J* = 7.3, 1.0 Hz, Ar**H**), 6.58-6.54 (2H, m, Ar**H**), 3.76 (1H, dd, *J* = 14.6, 6.0 Hz, NC**H**$_2$), 3.64 (1H, tt, *J* = 8.4, 6.4 Hz, CH_2C**H**), 3.37 (1H, dd, *J* = 14.6, 8.6 Hz, NC**H**$_2$), 3.23 (1H, dd, *J* = 13.8, 6.9 Hz, ArC**H**$_2$), 3.08 (1H, dd, *J* = 13.8, 8.4 Hz, ArC**H**$_2$), 2.65 (3H, s, NC**H**$_3$); **^{13}C NMR (125.6 MHz, $CDCl_3$)** δ 161.6 (d, *J* = 244.2 Hz, C), 159.7 (C), 149.2 (CH), 148.9 (C), 138.6 (d, *J* = 3.3 HZ, C), 136.1 (CH), 129.3 (d, *J* = 7.8 Hz, 2 x CH), 129.1 (2 x CH), 123.5 (CH), 121.2 (CH), 115.9 (CH), 115.2 (d, *J* = 21.2 Hz, 2 x CH), 111.9 (2 x CH), 59.3 (CH_2), 43.7 (CH), 42.2 (CH_2), 39.4 (CH_3); **^{19}F NMR (376 MHz, $CDCl_3$)** δ -116.7.



N-(2-(3-Chlorophenyl)-3-(pyridin-2-yl)propyl)-N-methylaniline (3j)

The title compound **3j** was prepared according to General Procedure E using (*E*)-2-(*m*-chlorostyryl)pyridine (65 mg, 0.3 mmol). The crude product was purified by FC (95:5 cyclohexane:EtOAc) to afford *amine* **3j** (41 mg, 44%) as a yellow oil.

HRMS (ESI) Exact mass calculated for $C_{21}H_{22}N_2Cl$ $[M+H]^+$: 337.1466, found: 337.1467; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.54 (1H, ddd, *J* = 4.9, 1.9, 0.9 Hz, Ar**H**), 7.51 (1H, td, *J* = 7.7, 1.8 Hz, Ar**H**), 7.23-7.14 (5H, m, Ar**H**), 7.13-7.04 (2H, m, Ar**H**), 6.98 (1H, dt, *J* = 7.9, 1.1 Hz, Ar**H**), 6.68 (1H, tt, *J* = 7.1, 0.9 Hz, Ar**H**), 6.57 (2H, dt, *J* = 7.8, 1.0 Hz, Ar**H**), 3.76 (1H, dd, *J* = 14.4, 6.1 Hz, NC**H**$_2$), 3.66 (1H, qd, *J* = 8.2, 6.4 Hz, NCH$_2$C**H**), 3.40 (1H, dd, *J* = 14.5, 8.3 Hz, NC**H**$_2$), 3.24 (1H, dd, *J* = 13.9, 7.0 Hz, ArC**H**$_2$), 3.11 (1H, dd, *J* = 13.9, 8.2 Hz, ArC**H**$_2$), 2.68 (3H, s, NC**H**$_3$); **^{13}C NMR (125.6 MHz, $CDCl_3$)** δ 159.4 (C), 149.0 (CH), 148.9 (C), 145.2 (C), 136.3 (CH), 134.2 (C), 129.6 (CH), 129.1 (2 x CH), 128.0 (CH), 126.7 (CH), 126.3 (CH), 123.6 (CH), 121.3 (CH), 116.1 (CH), 112.0 (2 x CH), 59.0 (CH$_2$), 44.2 (CH), 41.8 (CH$_2$), 39.4 (CH$_3$).

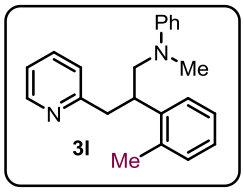


N-(2-(3-Methoxyphenyl)-3-(pyridin-2-yl)propyl)-N-methylaniline (3k)

The title compound **3k** was prepared according to General Procedure E using (*E*)-2-(*m*-methoxystyryl)pyridine (63 mg, 0.3 mmol). The crude product was purified by FC (85:15 cyclohexane:EtOAc) to afford *amine* **3k** (79 mg, 75%) as a beige solid.

HRMS (ESI) Exact mass calculated for $C_{22}H_{25}N_2O$ $[M+H]^+$: 333.1961, found: 333.1958;

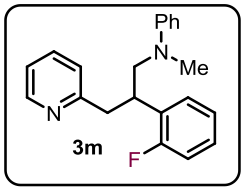
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.54 (1H, ddd, *J* = 4.9, 1.9 0.8 Hz, Ar**H**), 7.49 (1H, td, *J* = 7.6, 1.9 Hz, Ar**H**), 7.22-7.16 (3H, m, Ar**H**), 7.08 (1H, ddd, *J* = 7.5, 4.9, 1.2 Hz, Ar**H**), 6.99 (1H, dt, *J* = 7.9, 1.1 Hz, Ar**H**), 6.82 (1H, dt, *J* = 7.5, 1.3 Hz, Ar**H**), 6.76-6.72 (2H, m, Ar**H**), 6.67 (1H, tt, *J* = 7.2, 1.0 Hz, Ar**H**), 6.58 (2H, dt, *J* = 7.8, 1.0 Hz, Ar**H**), 3.78 (1H, dd, *J* = 14.6, 6.1 Hz, C**H**$_2$N) 3.74 (3H, s, OC**H**$_3$), 3.63 (1H, tt, *J* = 8.1, 6.4 Hz, C**H**CH$_2$N), 3.43 (1H, dd, *J* = 14.6, 8.3 Hz,C**H**$_2$N) 3.23 (1H, dd, *J* = 13.8, 7.1 Hz, ArC**H**$_2$), 3.13 (1H, dd, *J* = 13.8, 8.1 Hz, ArC**H**$_2$), 2.68 (3H, s, NC**H**$_3$); **^{13}C NMR (125.6 MHz, $CDCl_3$)** δ 159.9 (C), 159.5 (C), 149.1 (CH), 148.9 (C), 144.8 (C), 136.0 (CH), 129.3 (CH), 129.0 (2 x CH), 123.5 (CH), 121.1 (CH), 120.2 (CH), 115.7 (CH), 113.8 (CH), 111.8 (2 x CH), 111.7 (CH), 59.0 (CH$_2$), 55.1 (CH$_3$), 44.4 (CH), 42.1 (CH$_2$), 39.3 (CH$_3$).



N-Methyl-N-(3-(pyridin-2-yl)-2-(o-tolyl)propyl)aniline (3l)

The title compound **3l** was prepared according to General Procedure E using (*E*)-2-(*o*-tolylstyryl)pyridine (59 mg, 0.3 mmol). The crude product was purified by FC (90:10 cyclohexane:EtOAc) to afford *amine* **3l** (49 mg, 52%) as a beige solid. HRMS (ESI) Exact mass calculated for $C_{22}H_{25}N_2$ $[M+H]^+$: 317.2012, found: 317.2019;

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.52 (1H, ddd, *J* = 4.9, 1.8, 0.9 Hz, Ar**H**), 7.45 (1H, td, *J* = 7.7, 1.9 Hz, Ar**H**), 7.40 (1H, dd, *J* = 7.7, 1.4 Hz, Ar**H**), 7.25-7.16 (3H, m, Ar**H**), 7.11-7.04 (2H, m, Ar**H**), 7.03-6.99 (1H, m, Ar**H**), 6.88 (1H, d, *J* = 7.8 Hz, Ar**H**), 6.66 (1H, tt, *J* = 7.2, 1.0 Hz, Ar**H**), 6.58 (2H, dt, *J* = 7.8, 1.0 Hz, Ar**H**), 3.96 (1H, tt, *J* = 8.3, 6.3 Hz, NCH$_2$C**H**), 3.84 (1H, dd, *J* = 14.7, 6.1 Hz, NC**H**$_2$), 3.43 (1H, dd, *J* = 14.7, 8.3 Hz, NC**H**$_2$), 3.26 (1H, dd, *J* = 13.5, 6.7 Hz, ArC**H**$_2$), 3.08 (1H, dd, *J* = 13.5, 8.5 Hz, ArC**H**$_2$), 2.66 (3H, s, NC**H**$_3$), 2.00 (3H, s, ArC**H**$_3$); **^{13}C NMR (125.6 MHz, $CDCl_3$)** δ 160.1 (C), 149.10 (CH), 149.07 (C), 141.5 (C), 136.8 (C), 135.9 (CH), 130.2 (CH), 129.1 (2 x CH), 126.3 (CH), 126.04 (CH), 126.00 (CH), 123.4 (CH), 121.1 (CH), 115.8 (CH), 111.7 (2 x CH), 59.0 (CH$_2$), 42.7 (CH$_2$), 39.21 (CH$_3$), 39.17 (CH), 19.6 (CH$_3$).

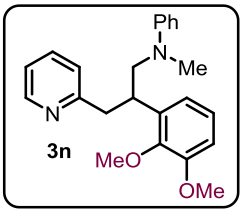


N-(2-(2-Fluorophenyl)-3-(pyridin-2-yl)propyl)-N-methylaniline (3m)

The title compound **3m** was prepared according to General Procedure E using (*E*)-2-(*o*-fluorostyryl)pyridine (60 mg, 0.3 mmol). The crude product was purified by FC (95:5 cyclohexane:EtOAc) to afford *amine* **3m** (83 mg, 86%) as a yellow oil.

HRMS (ESI) Exact mass calculated for $C_{21}H_{22}N_2F$ $[M+H]^+$: 321.1762, found: 321.1767.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.51 (1H, ddd, *J* = 4.9, 1.9, 0.9 Hz, Ar**H**), 7.47 (1H, td, *J* = 7.7, 1.9 Hz, Ar**H**), 7.22-7.11 (4H, m, Ar**H**), 7.05 (1H, ddd, *J* = 7.6, 4.9, 1.2 Hz, Ar**H**), 7.02-6.93 (3H, m, Ar**H**), 6.67 (1H, tt, *J* = 7.3, 1.0 Hz, Ar**H**), 6.64-6.60 (2H, m, Ar**H**), 3.91 (1H, tt, *J* = 8.5, 6.7 Hz, C**H**Ar), 3.75 (1H, dd, *J* = 14.7, 6.7 Hz, NC$\mathbf{H}_2$), 3.62 (1H, dd, *J* = 14.7, 8.2 Hz, NC$\mathbf{H}_2$), 3.31 (1H, dd, *J* = 13.7, 6.5 Hz, ArC$\mathbf{H}_2$), 3.21 (1H, dd, *J* = 13.8, 8.9 Hz, ArC$\mathbf{H}_2$), 2.77 (3H, s, NC$\mathbf{H}_3$); **^{13}C NMR (125.6 MHz, $CDCl_3$)** δ 161.4 (C, d, *J* = 245.0 Hz), 159.8 (C), 149.1 (CH), 149.0 (C), 136.1 (CH), 130.2 (CH, d, *J* = 5.7 Hz), 129.3 (C, d, *J* = 14.2 Hz), 129.0 (2 x CH), 128.1 (CH, d, *J* = 8.5 Hz), 124.0 (1H, d, *J* = 3.3 Hz), 123.2 (CH), 121.1 (CH), 116.0 (CH), 115.5 (CH, d, *J* = 22.7 Hz), 111.9 (2 x CH), 57.3 (CH_2, d, *J* = 1.9 Hz), 40.7 (CH_2, d, *J* = 2.3 Hz), 39.9 (CH), 39.0 (CH_3); **^{19}F NMR (376 MHz, $CDCl_3$)** δ -116.3.



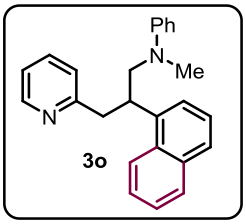
N-(2-(2,3-Dimethoxyphenyl)-3-(pyridin-2-yl)propyl)-N-methylaniline (3n)

The title compound **3n** was prepared according to General Procedure E using (*E*)-2-(*o*,*m*-dimethoxystyryl)pyridine (59 mg, 0.3 mmol). The crude product was purified by FC (90:10 cyclohexane:EtOAc) to afford *amine* **3n** (81 mg, 75%) as a yellow oil.

HRMS (ESI) Exact mass calculated for $C_{23}H_{27}N_2O_2$ $[M+H]^+$: 363.2067, found: 363.2057.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.48 (1H, ddd, *J* = 4.9,1.8 0.9 Hz, Ar**H**), 7.45 (!H, td, *J* = 7.7, 1.9 Hz, Ar**H**), 7.22-7.18 (2H, m, Ar**H**), 7.04-7.00 (2H, m, Ar**H**), 6.99 (1H, dt, *J* = 7.6, 0.9 Hz, Ar**H**), 6.94 (1H, dd, *J* = 7.9, 1.5 Hz, Ar**H**), 6.75 (1H, dd, *J* = 8.1, 1.5 Hz, Ar**H**), 6.71-6.65 (3H, m, Ar**H**), 4.12 (1H, dq, *J* = 9.5, 7.1 Hz, $NCH_2C\mathbf{H}$), 3.83 (3H, s, OC$\mathbf{H}_3$), 3.65-3.53 (5H, m, OC$\mathbf{H}_3$ + NC$\mathbf{H}_2$), 3.30 (1H, dd, *J* = 13.9, 6.1 Hz, ArC$\mathbf{H}_2$), 3.15 (1H, dd, *J* = 13.9, 9.5 Hz, ArC$\mathbf{H}_2$), 2.86 (3H, s, NC$\mathbf{H}_3$);

^{13}C NMR (125.6 MHz, $CDCl_3$) δ 160.3 (C), 152.7 (C), 149.3 (C), 148.9 (CH), 147.5 (C), 136.1 (C), 135.9 (CH), 129.0 (2 x CH), 123.8 (CH), 123.2 (CH), 120.9 (CH), 119.9 (CH), 115.8 (CH), 111.9 (2 x CH), 110.3 (CH), 60.6 (CH_3), 58.6 (CH_2), 55.5 (CH_3), 41.4 (CH_2), 39.3 (CH_3), 38.0 (CH).



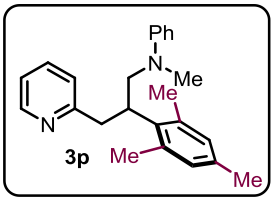
N-Methyl-N-(2-(naphthalen-1-yl)-3-(pyridin-2-yl)propyl)aniline (3o)

The title compound **3o** was prepared according to General Procedure E using (*E*)-2-(*2*-naphthalen-1-yl)pyridine (69 mg, 0.3 mmol). The crude product was purified by FC (95:5 cyclohexane:EtOAc) to afford *amine* **3o** (79 mg, 75%) as a yellow gum.

HRMS (ESI) Exact mass calculated for $C_{25}H_{25}N_2$ $[M+H]^+$: 353.2012, found: 353.2014:

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.52 (1H, ddd, *J* = 4.9, 1.8, 0.9 Hz, Ar**H**), 7.98 (1H, br s, Ar**H**), 7.81 (1H, d, *J* = 8.1 Hz, Ar**H**), 7.73 (1H, d, *J* = 8.2 Hz, Ar**H**), 7.58 (1H, br s, Ar**H**), 7.49 (1H, br s, Ar**H**), 7.46-7.33 (3H, m, Ar**H**), 7.23-7.14 (2H, m, Ar**H**), 7.02 (1H, ddd, *J* = 7.5, 4.9, 1.2 Hz, Ar**H**), 6.93 (1H, d, *J* = 7.8 Hz, Ar**H**), 6.69 (1H, tt, *J* = 7.3, 1.1 Hz, Ar**H**), 6.63-6.53 (2H, m, Ar**H**), 4.62 (1H, br s, C**H**), 4.04-3.92 (1H, m, NC$\mathbf{H}_2$), 3.57 (1H, br s, NC$\mathbf{H}_2$), 3.45 (1H, dd, *J* = 13.9, 7.0 Hz, ArC$\mathbf{H}_2$), 3.36-3.26 (1H, m, ArC$\mathbf{H}_2$), 2.60 (3H, s, NC$\mathbf{H}_3$); **^{13}C NMR (125.6 MHz, $CDCl_3$)** δ 160.0 (C), 149.1

(CH), 149.0 (C),139.9 (C),135.9 (CH), 133.8 (C),132.3 (C), 129.0 (2 x CH), 128.5 (CH), 126. (CH), 125.7 (CH), 125.35 (CH), 125.34 (CH), 123.7 (CH), 123.4 (CH), 123.3 (CH), 121.1 (CH), 115.8 (CH), 111.8 (2 x CH), 59.2 (CH_2), 42.6 (CH_2), 39.1 (CH_3), 38.7 (CH).

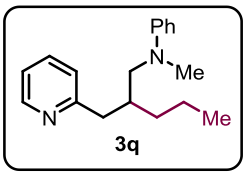


N-(2-Mesityl-3-(pyridin-2-yl)propyl)-N-methylaniline (3p)

The title compound **3p** was prepared according to General Procedure E using (*E*)-2-(2,4,6-trimethylstyryl)pyridine (67 mg, 0.3 mmol). The crude product was purified by FC (95:5 cyclohexane:EtOAc) to afford *amine* **3p** (59 mg, 57%) as a brown oil.

HRMS (ESI) Exact mass calculated for $C_{24}H_{29}N_2$ $[M+H]^+$: 345.2325, found: 345.2315;

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.55 (1H, ddd, *J* = 4.9, 1.9, 0.9 Hz, Ar**H**), 7.50 (1H, td, *J* = 7.6, 1.9 Hz, Ar**H**), 7.20-7.06 (3H, m, Ar**H**), 6.91 (1H, dd, *J* = 7.8, 1.1 Hz, Ar**H**), 6.86 (1H, s, Ar**H**), 6.71 (1H, s, Ar**H**), 6.65 (1H, tt, *J* = 7.1, 0.9 Hz, Ar**H**), 6.53-6.50 (2H, m, Ar**H**), 4.01-3.93 (2H, m, NC**H**$_2$ + C**H**Ar), 3.73-3.64 (1H, m, NC**H**$_2$), 3.35 (1H, dd, *J* = 13.3, 7.3 Hz, ArC**H**$_2$), 3.24 (1H, dd, *J* = 13.3, 7.2 Hz, ArC**H**$_2$), 2.67 (3H, s, NC**H**$_3$), 2.61 (3H, s, ArC**H**$_3$), 2.25 (3H, s, ArC**H**$_3$), 1.92 (3H, s, ArC**H**$_3$); **^{13}C NMR (125.6 MHz, $CDCl_3$)** δ 160.9 (C), 148.92 (CH), 148.85 (C), 137.6 (C), 136.2 (C), 136.1 (CH), 135.9 (C), 135.4 (C), 130.9 (CH), 129.2 (CH), 129.0 (2 x CH), 123.3 (CH), 121.1 (CH), 115. 6 (CH), 111.7 (2 x CH), 55.8 (CH_2), 41.1 (CH_2), 40.4 (CH), 40.0 (CH_3), 21.8 (CH_3), 21.3 (CH_3), 20.6 (CH_3).

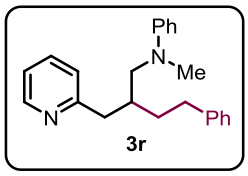


N-Methyl-N-(2-(pyridin-2-ylmethyl)pentyl)aniline (3q)

The title compound **3q** was prepared according to General Procedure E using (*Z*)-2-(propen-1-yl)pyridine (44 mg, 0.3 mmol). The crude product was purified by FC (95:5 cyclohexane:EtOAc) to afford *amine* **3q** (57 mg, 71%) as a brown oil.

HRMS (ESI) Exact mass calculated for $C_{18}H_{25}N_2$ $[M+H]^+$: 269.2012, found: 269.2010;

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.59-8.54 (1H, m, Ar**H**), 7.57 (1H, td, *J* = 7.6, 1.9 Hz, Ar**H**), 7.23-7.16 (2H, m, Ar**H**), 7.14-7.08 (2H, m, Ar**H**), 6.71-6.61 (3H, m, Ar**H**), 3.24 (2H, d, *J* = 7.3 Hz, NC**H**$_2$), 2.92 (3H, s, NC**H**$_3$), 2.85-2.75 (2H, m, ArC**H**$_2$), 2.43 (1H, qd, *J* = 7.0, 4.6 Hz, C**H**), 1.44-1.26 (4H, m, C**H**$_2$C**H**$_2$CH$_3$), 0.87 (3H, t, *J* = 7.0 Hz, CH$_2$C**H**$_3$); **^{13}C NMR (125.6 MHz, $CDCl_3$)** δ 161.1 (C), 149.8 (C), 149.0 (CH), 136.1 (CH), 129.0 (2 x CH), 123.5 (CH), 120.9 (CH), 115.7 (CH), 112.0 (2 x CH), 57.3 (CH_2), 41.1 (CH_2), 39.3 (CH_3), 37.7 (CH), 34.4 (CH_2), 19.8 (CH_2), 14.5 (CH_3).



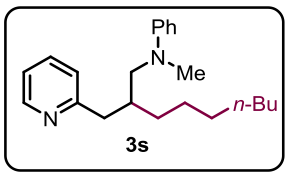
N-Methyl-N-(4-phenyl-2-(pyridin-2-ylmethyl)butyl)aniline (3r)

The title compound **3r** was prepared according to General Procedure E using (*E*)-2-(4-phenyl-but-1-enyl)pyridine (63 mg, 0.3 mmol). The crude product was purified by FC (95:5 cyclohexane:EtOAc) to afford *amine* **3r** (72 mg, 73%) as a brown oil.

HRMS (ESI) Exact mass calculated for $C_{23}H_{27}N_2$ $[M+H]^+$: 331.2169, found: 331.2168.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.60 (1H, dd, *J* = 5.0, 1.8 Hz, Ar**H**), 7.60 (1H, td, *J* = 7.7, 1.9 Hz, Ar**H**), 7.27-7.05 (9H, m, Ar**H**), 6.75-6.62 (5H, m, Ar**H**), 3.33 (2H, dd, *J* = 7.4, 1.7 Hz, NC**H**$_2$), 2.90 (3H, s, NC**H**$_3$), 2.87 (2H, d, *J* = 7.1 Hz, ArC**H**$_2$), 2.65 (2H, ddd, *J* = 9.3, 6.6, 2.2 Hz, CHCH$_2$C**H**$_2$Ph), 2.48 (1H, app hept, *J* = 7.0 HZ, CH$_2$C**H**CH$_2$), 1.74 (1H, dddd, *J* = 14.7, 9.4, 7.0, 5.5 Hz, CHC**H**$_2$CH$_2$Ph), 1.70-1.61 (1H, m, CHC**H**$_2$CH$_2$Ph); **^{13}C NMR (125.6 MHz, $CDCl_3$)** δ 160.8 (C), 149.8 (C), 149.1 (CH), 142.4 (C), 136.2 (CH), 129.0 (2 x CH), 128.3 (4 x CH), 125.7 (CH),

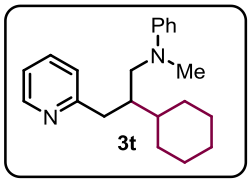
123.5 (CH), 121.1 (CH), 115.9 (CH), 112.2 (2 x CH), 57.3 (CH), 41.2 (CH), 39.3 (CH_2), 37.5 (CH_2), 33.9 (CH), 33.0 (CH_3).



N-Methyl-N-(2-(pyridin-2-ylmethyl)nonyl)aniline (3s)

The title compound **3s** was prepared according to General Procedure E using (*E*)-2-(non-1-enyl)pyridine (61 mg, 0.3 mmol). The crude product was purified by FC (95:5 cyclohexane:EtOAc) to afford *amine* **3s** (83 mg, 85%) as a colourless oil.

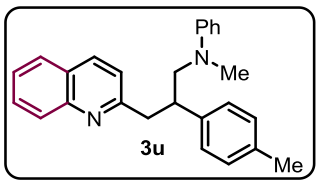
HRMS (ESI) Exact mass calculated for $C_{19}H_{33}N_2$ $[M+H]^+$: 325.2638, found: 325.3626; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.56 (1H, dd, *J* = 5.4, 2.0 Hz, Ar**H**), 7.56 (1H, td, *J* = 7.6, 1.9 Hz, Ar**H**), 7.22-7.17 (2H, m, Ar**H**), 7.11 (2H, ddt, *J* = 7.5, 2.7, 1.1 Hz, Ar**H**), 6.69-6.61 (3H, m, Ar**H**), 3.25 (2H, d, *J* = 7.3 Hz, NC$\mathbf{H}_2$), 2.92 (3H, s, NC$\mathbf{H}_3$), 2.80 (2H, dd, *J* = 7.1, 4.6 Hz, ArC$\mathbf{H}_2$), 2.48-2.37 (1H, m, C**H**), 1.47-1.19 (12H, m, CH(C$\mathbf{H}_2$)$_6$CH_3), 0.88 (3H, t, *J* = 7.0 Hz, CH_2C$\mathbf{H}_3$); **^{13}C NMR (125.6 MHz, $CDCl_3$)** δ 161.2 (C), 149.8 (C), 149.1 (CH), 136.0 (CH), 128.9 (2 x CH), 123.4 (CH), 120.9 (CH), 115.7 (CH), 112.0 (2 x CH), 57.3 (CH_2), 41.2 (CH_2), 39.2 (CH_3), 37.9 (CH), 32.1 (CH_2), 31.8 (CH_2), 29.9 (CH_2), 29.1 (CH_2), 26.6 (CH_2), 22.6 (CH_2), 14.1 (CH_3).



N-(2-Cyclohexyl-3-(pyridin-2-yl)propyl)-N-methylaniline (3t)

The title compound **3t** was prepared according to General Procedure E using (*E*)-2-(2-cyclohexylstyryl)pyridine (56 mg, 0.3 mmol). The crude product was purified by FC (95:5 cyclohexane:EtOAc) to afford *amine* **3t** (78 mg, 84%) as a yellow oil.

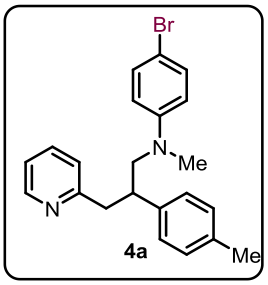
HRMS (ESI) Exact mass calculated for $C_{21}H_{29}N_2$ $[M+H]^+$: 309.2325, found: 309.2313; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.55 (1H, ddd, *J* = 4.9, 1.9, 1.0 Hz, Ar**H**), 7.56 (1H, td, *J* = 7.7, 1.9 Hz, Ar**H**), 7.20-7.13 (2H, m, Ar**H**), 7.12-7.08 (2H, m, Ar**H**), 6.64 (1H, tt, *J* = 7.2, 1.0 Hz, Ar**H**), 6.55 (2H, dt, *J* = 7.8, 1.1 Hz, Ar**H**), 3.31 (1H, dd, *J* = 14.6, 7.8 Hz, NC$\mathbf{H}_2$), 3.22 (1H, dd, *J* = 14.7, 7.0 Hz, NC$\mathbf{H}_2$), 2.89 (1H, dd, *J* = 13.8, 5.9 Hz, ArC$\mathbf{H}_2$), 2.85 (3H, s, NC$\mathbf{H}_3$), 2.66 (1H, dd, *J* = 13.8, 8.6 Hz, ArC$\mathbf{H}_2$), 2.36 (1H, ddt, *J* = 13.7, 10.7, 5.4 Hz, NCH$_2$C**H**), 1.82-1.77 (3H, m, C$\mathbf{H}_2$), 1.71-1.64 (2H, m, C$\mathbf{H}_2$), 1.53-1.42 (1H, m,C$\mathbf{H}_2$), 1.27-1.13 (5H, m, C$\mathbf{H}_2$); **^{13}C NMR (125.6 MHz, $CDCl_3$)** δ 161.7 (C), 149.8 (C), 148.9 (CH), 136.1 (CH), 128.9 (2 x CH), 123.4 (CH), 120.9 (CH), 115.7 (CH), 112.0 (2 x CH), 54.0 (CH_2), 43.0 (CH), 39.1 (CH_3), 38.8 (CH), 37.8 (CH_2), 30.3 (CH_2), 28.9 (CH_2), 27.0 (CH_2), 26.83 (CH_2), 26.76 (CH_2).



N-Methyl-N-(3-(quinolin-2-yl)-2-(p-tolyl)propyl)aniline (3u)

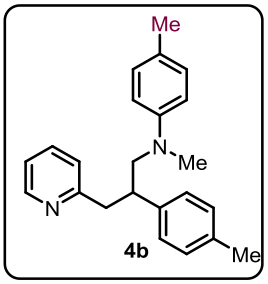
The title compound **3u** was prepared according to General Procedure E using (*E*)-2-(4-methylstyryl)quinoline (74 mg, 0.3 mmol). The crude product was purified by FC (98:2 cyclohexane:EtOAc) to afford *amine* **3u** (62 mg, 56%) as a yellow oil.

HRMS (ESI) Exact mass calculated for $C_{26}H_{27}N_2$ $[M+H]^+$: 367.2169, found: 367.2177; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.13 (1H app s, Ar**H**), 7.99 (1H, d, *J* = 8.4 Hz, Ar**H**), 7.76 (1H, dd, *J* = 8.1, 1.4 Hz, Ar**H**), 7.71 (1H, ddd, *J* = 8.5, 6.8, 1.4 Hz, Ar**H**), 7.50 (1H, ddd, *J* = 8.1, 6.8, 1.2 Hz, Ar**H**), 7.20-7.13 (5H, m, Ar**H**), 7.07 (2H, d, *J* = 7.7 Hz, Ar**H**), 6.69-6.62 (1H, m, Ar**H**), 6.61 (2H, dd, *J* = 8.9, 1.0 Hz, Ar**H**), 3.91-3.73 (2H, m, C**H** + NC$\mathbf{H}_2$), 3.49-3.32 (3H, m, NC$\mathbf{H}_2$ + ArC$\mathbf{H}_2$), 2.65 (3H, s, NC$\mathbf{H}_3$), 2.30 (3H, s, ArC$\mathbf{H}_3$); **^{13}C NMR (125.6 MHz, $CDCl_3$)** δ 160.6 (C), 160.4 (C), 148.9 (C), 147.7 (C), 140.0 (C), 136.0 (C), 129.5 (CH), 129.1 (2 x CH), 129.0 (2 x CH), 128.8 (CH), 127.9 (2 x CH), 127.5 (CH), 126.7 (CH), 125.9 (CH), 121.8 (CH), 115.7 (CH), 111.9 (2 x CH), 59.4 (CH_2), 43.4 (CH), 39.5 (CH_2), 21.0 (CH_3).



4-Bromo-N-methyl-N-(3-(pyridin-2-yl)-2-(p-tolyl)propyl)aniline (4a)

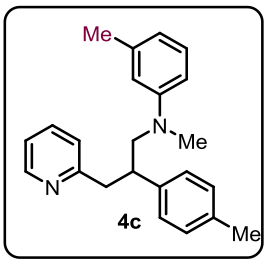
The title compound **4a** was prepared according to General Procedure E using (*E*)-2-(*p*-tolylstyryl)pyridine (59 mg, 0.3 mmol) and 4-bromo-*N*,*N*,-dimethylaniline (120 mg, 0.6 mmol). The crude product was purified by FC (95:5 cyclohexane:EtOAc) to afford *amine* **4a** (82 mg, 69%) as a orange gum. HRMS (ESI) Exact mass calculated for $C_{22}H_{24}N_2Br$ $[M+H]^+$: 395.1117, found: 395.1116; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.54 (1H, ddd, *J* = 5.0. 1.7, 0.8 Hz, Ar**H**), 7.51 (1H, td, *J* = 7.7, 1.9 Hz, Ar**H**), 7.26-7.20 (2H, m, Ar**H**), 7.12-7.04 (5H, m, Ar**H**), 6.99 (1H, dt, *J* = 7.8, 1.1 Hz, Ar**H**), 6.42-6.36 (2H, m, Ar**H**), 3.73 (1H, dd, *J* = 14.4, 5.8 Hz, NC**H**$_2$), 3.57 (1H, qd, *J* = 7.8, 5.7 Hz, NCH$_2$C**H**), 3.35 (1H, dd, *J* = 14.4, 8.6 Hz, NC**H**$_2$), 3.20 (1H, dd, *J* = 13.8, 7.3 Hz, ArC**H**$_2$), 3.11 (1H, dd, *J* = 13.8, 7.9 Hz, ArC**H**$_2$), 2.59 (3H, s, NC**H**$_3$), 2.30 (3H, s, ArC**H**$_3$); **^{13}C NMR (125.6 MHz, $CDCl_3$)** δ 159.8 (C), 148.9 (CH, 147.8 (C), 139.6 (C), 136.3 (CH),136.1 (C), 131.6 (2 x CH), 129.1 (2 x CH), 127.7 (2 x CH), 123.6 (CH), 121.2 (CH), 113.4 (2 x CH), 107.5 (C), 59.0 (CH$_2$), 43.6 (CH), 42.0 (CH$_2$), 39.5 (CH$_3$), 21.0 (CH$_3$).



N,4-Dimethyl-N-(3-(pyridin-2-yl)-2-(p-tolyl)propyl)aniline (4b)

The title compound **4b** was prepared according to General Procedure E using (*E*)-2-(*p*-tolylstyryl)pyridine (59 mg, 0.3 mmol) and *N*,*N*,4-trimethylaniline (81 mg, 0.6 mmol). The crude product was purified by FC (95:5 cyclohexane:EtOAc) to afford *amine* **4b** (75 mg, 76%) as a yellow gum.

HRMS (ESI) Exact mass calculated for $C_{23}H_{27}N_2$ $[M+H]^+$: 331.2169, found: 331.2172; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.52 (1H, ddd, *J* = 4.9,1 .9, 0.9, Hz, Ar**H**), 7.48 (1H, td, *J* = 7.7, 1.9 Hz, Ar**H**), 7.10-7.04 (5H, m, Ar**H**), 7.02-6.95 (3H, m, Ar**H**), 6.52-6.48 (2H, m, Ar**H**), 3.70 (1H, dd, *J* = 14.5, 6.3 Hz, NC**H**$_2$), 3,58 (1H, tt, *J* = 8.2, 6.6 Hz, NCH$_2$C**H**), 3.37 (1H, dd, *J* = 14.5, 8.1 Hz, NC**H**$_2$), 3.24 (1H, dd, *J* = 13.8, 6.9 Hz, ArC**H**$_2$), 3.11 (1H, dd, *J* = 13.8, 8.4 Hz, ArC**H**$_2$), 2.65 (3H, s, NC**H**$_3$), 2.31 (3H, s, ArC**H**$_3$), 2.25 (3H, s, ArC**H**$_3$); **^{13}C NMR (125.6 MHz, $CDCl_3$)** δ 160.2 (C), 149.0 (CH), 147.1 (C), 140.0 (C), 136.0 (CH), 135.8 (C), 129.5 (2 x CH), 129.0 (2 x CH), 127.8 (2 x CH), 124.9 (C), 123.5 (CH), 121.0 (CH), 112.1 (2 x CH), 59.5 (CH$_2$), 44.1 (CH), 42.2 (CH$_2$), 39.4 (CH$_3$), 21.0 (CH$_3$), 20.2 (CH$_3$).



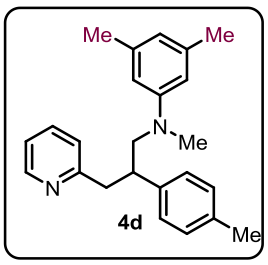
N,3-Dimethyl-N-(3-(pyridin-2-yl)-2-(p-tolyl)propyl)aniline (4c)

The title compound **4c** was prepared according to General Procedure E using (*E*)-2-(*p*-tolylstyryl)pyridine (59 mg, 0.3 mmol) and *N*,*N*,3-trimethylaniline (87 µL, 0.6 mmol). The crude product was purified by FC (95:5 cyclohexane:EtOAc) to afford *amine* **4c** (75 mg, 78%) as a yellow oil.

HRMS (ESI) Exact mass calculated for $C_{23}H_{27}N_2$ $[M+H]^+$: 331.2168, found: 331.2169;

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.56 (1H, ddd, *J* = 5.0, 1.9, 0.9 Hz, Ar**H**), 7.52 (1H, td, *J* = 7.6, 1.8 Hz, Ar**H**), 7.16-7.06 (6H, m, Ar**H**), 7.03 (1H, dt, *J* = 7.8, 1.1 Hz, Ar**H**), 6.51 (1H, d, *J* = 7.4 Hz, Ar**H**), 6.40 (1H, dd, *J* = 8.3, 2.6 Hz, Ar**H**), 6.35 (1H, t, *J* = 1.9 Hz, Ar**H**), 3.75 (1H, dd, *J* = 14.6, 6.0 Hz, NC**H**$_2$), 3.61 (1H, qd, *J* = 7.8, 6.0 Hz, C**H**Ar), 3.37 (1H, dd, *J* = 14.6, 8.3 Hz, NC**H**$_2$), 3.25 (1H, dd, *J* = 13.8, 7.4 Hz, ArC**H**$_2$), 3.14 (1H, dd, *J* = 13.8, 7.9 Hz, ArC**H**$_2$), 2.66 (3H, s, NC**H**$_3$), 2.32 (3H, s, ArC**H**$_3$), 2.28 (3H, s, ArC**H**$_3$); **^{13}C NMR (125.6 MHz, $CDCl_3$)** δ 160.2 (C), 149.1 (C), 148.9 (CH), 140.1 (C), 138.5 (C), 136.1 (CH), 135.9 (C), 129.0 (2 x CH), 128.8 (CH), 127.8 (2 x CH),

123.5 (CH), 121.1 (CH), 116.7 (CH), 112.6 (CH), 109.0 (CH), 59.1 (CH_2), 44.0 (CH), 42.1 (CH_2), 39.4 (CH_3), 21.9 (CH_3), 21.0 (CH_3).

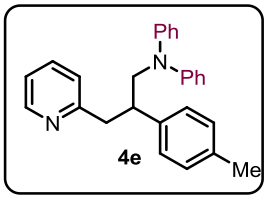


N,3,5-Trimethyl-N-(3-(pyridin-2-yl)-2-(p-tolyl)propyl)aniline (4d)

The title compound **4d** was prepared according to General Procedure E using (*E*)-2-(*p*-tolylstyryl)pyridine (59 mg, 0.3 mmol) and *N*,*N*,3,5-tetramethylaniline (90 µL, 0.6 mmol). The crude product was purified by FC (95:5 cyclohexane:EtOAc) to afford *amine* **4d** (52 mg, 50%, 95% purity) as a yellow oil.

HRMS (ESI) Exact mass calculated for $C_{24}H_{29}N_2$ $[M+H]^+$: 345.2247, found: 345.2294;

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.55 (1H, ddd, *J* = 4.9, 1.9 0.9 Hz, Ar**H**), 7.54 (1H, td, *J* = 7.7, 1.9 Hz, Ar**H**), 7.19-7.03 (7H, m, Ar**H**), 6.33 (1H, s, Ar**H**), 6.15 (2H, s, Ar**H**), 3.72 (1H, dd, *J* = 14.5, 5.9 Hz, NC$\mathbf{H}_2$), 3.57 (1H, qd, *J* = 7.8, 5.8 Hz, $NCH_2C\mathbf{H}$), 3.33 (1H, dd, *J* = 14.6, 8.3 Hz, NC$\mathbf{H}_2$), 3.24 (1H, dd, *J* = 13.8, 7.7 Hz, ArC$\mathbf{H}_2$), 3.14 (1H, dd, *J* = 13.8, 7.6 Hz, ArC$\mathbf{H}_2$), 2.62 (3H, s, NC$\mathbf{H}_3$), 2.31 (3H, s, ArC$\mathbf{H}_3$), 2.22 (6H, s, 2 x ArC$\mathbf{H}_3$); **^{13}C NMR (125.6 MHz, $CDCl_3$)** δ 160.2 (C), 149.2 (C), 148.7 (C), 140.2 (C), 138.4 (2 x C), 136.5 (CH), 135.9 (C), 120.1 (2 x CH), 127.8 (2 x CH), 123.7 (CH), 121.2 (CH), 117.9 (CH), 109.9 (2 x CH), 59.2 (CH_2), 44.1 (CH), 39.5 (CH_2), 21.8 (2 x CH_3), 21.0 (CH_3).

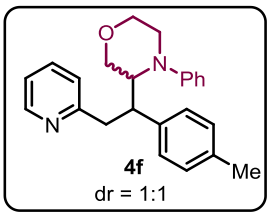


N-Phenyl-N-(3-(pyridin-2-yl)-2-(p-tolyl)propyl)aniline (4e)

The title compound **4e** was prepared according to General Procedure E using (*E*)-2-(*p*-tolylstyryl)pyridine (59 mg, 0.3 mmol) and N-methyl-N-phenylaniline (105 µL, 0.6 mmol). The crude product was purified by FC (99.5:0.5 CH_2Cl_2:MeOH to afford *amine* **4e** (74 mg, 65%) as a yellow oil.

HRMS (ESI) Exact mass calculated for $C_{27}H_{27}N_2$ $[M+H]^+$: 379.2169, found: 379.2157;

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.52 (1H, ddd, *J* = 4.9, 1.9, 0.9 Hz, Ar**H**), 7.48 (1H, td, *J* = 7.7, 1.9 Hz, Ar**H**), 7.18 (4H, dd, *J* = 8.6, 7.3 Hz, Ar**H**), 7.07 (1H, ddd, *J* = 7.5, 4.9, 1.1 Hz, Ar**H**), 7.03 (4H, s, Ar**H**), 6.95 (1H, dt, *J* = 7.9, 1.1 Hz, Ar**H**), 6.91 (2H, tt, *J* = 7.3, 1.1 Hz, Ar**H**), 6.79-6.76 (4H, m, Ar**H**), 4.09 (1H, dd, *J* = 14.7, 6.3 Hz, NC$\mathbf{H}_2$), 3.85 (1H, dd, *J* = 14.7, 8.4 Hz, NC$\mathbf{H}_2$), 3.63 (1H, tt, *J* = 8.4, 6.6. Hz, $NCH_2C\mathbf{H}$), 3.33 (1H, dd, *J* = 13.8, 6.9 Hz, ArC$\mathbf{H}_2$), 3.14 (1H, dd, *J* = 13.8, 8.4 Hz, ArC$\mathbf{H}_2$), 2.30 (3H, s, ArC$\mathbf{H}_3$); **^{13}C NMR (125.6 MHz, $CDCl_3$)** δ δ 160.1 (C), 148.9 (CH), 148.4 (2 x C), 139.5 (C), 136.1 (CH), 135.9 (C), 129.01 (4 x CH), 128.98 (2 x CH), 127.9 (2 x CH), 123.4 (CH), 121.2 (4 x CH), 121.12 (2 x CH), 121.07 (CH), 58.6 (CH_2), 43.8 (CH), 42.3 (CH_2), 21.0 (CH_3).

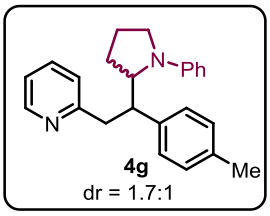


4-Phenyl-3-(2-(pyridin-2-yl)-1-(p-tolyl)ethyl)morpholine (4f)

The title compound **4f** was prepared according to General Procedure E using (*E*)-2-(*p*-tolylstyryl)pyridine (59 mg, 0.3 mmol) and *N*-phenylmorpholine (98 mg, 0.6 mmol). The crude product was purified by FC (80:20 cyclohexane:EtOAc) to give an inseparable mixture of the two diastereromers of *amine* **4f** (45 mg, 42%, dr 1.15:1).

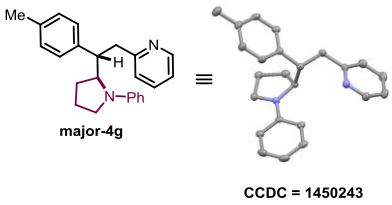
Diastereromeric Mixture: HRMS (ESI) Exact mass calculated for $C_{24}H_{27}N_2O$ $[M+H]^+$: 359.2118, found: 359.2111. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.45 (1H, ddd, *J* = 5.0, 1.8, 0.9 Hz, Ar**H**), 8.41 (1H, ddd, *J* = 5.0, 1.9, 0.9 Hz, Ar**H**), 7.34 (1H, td, *J* = 7.7, 1.9 Hz, Ar**H**), 7.32-7.26 (3H, m, Ar**H**), 7.18-7.14 (2H, m, Ar**H**), 7.04 (4H, app q, *J* = 8.1 Hz, Ar**H**), 6.98-6.91 (6H, m, Ar**H**), 6.84 (2H, d, *J* = 7.8 Hz, Ar**H**), 6.80-6.73 (4H, m, Ar**H**), 6.68 (1H, dd, *J* = 7.9, 1.1 Hz, Ar**H**), 6.62 (1H, dd, *J* = 7.8, 1.1 Hz, Ar**H**), 4.18-4.08 (2H, m, $OC\mathbf{H}_2$ + C**H**), 4.00 (1H, dd, *J* = 10.8, 3.3 Hz, C**H**), 3.98-3.95 (1H, m, $OC\mathbf{H}_2$), 3.94-3.87 (2H, m, $OC\mathbf{H}_2$ + C**H**), 3.85 (1H, ddd, *J* = 11.3, 7.5, 3.9 Hz, C**H**), 3.79 (1H, dd, *J* = 11.5, 3.0 Hz, $OC\mathbf{H}_2$), 3.76-3.63 (3H, m, 2 x $OC\mathbf{H}_2$ + C$\mathbf{H}_2$),

3.58-3.48 (2H, m, OC**H**$_2$), 3.48-3.44 (1H, m, C**H**$_2$), 3.44-3.36 (2H, m, C**H**$_2$), 2.23-3.16 (2H, m, C**H**$_2$), 3.10 (1H, dt, *J* = 12.9, 3.4 Hz, C**H**$_2$), 2.27 (3H, s, ArC**H**$_3$), 2.18 (3H, s, ArC**H**$_3$); **^{13}C NMR (125.6 MHz, CDCl$_3$)** δ 160.4 (C), 160.2 (C), 150.4 (C), 150.3 (C), 148.7 (CH), 148.6 (CH), 138.7 (C), 137.5, (C), 135.9 (CH), 135.7 (CH), 135.5 (2 x C), 129.5 (2 x CH), 129.2 (2 x CH), 128.9 (2 x CH), 128.5 (2 x CH), 128.4 (2 x CH), 128.4 (2 x CH), 123.6 (CH), 123.2 (CH), 120.8 (CH), 120.7 (CH), 119.2 (CH), 117.50 (2 x CH), 117.46 (CH), 114.2 (2 x CH), 67.2 (CH$_2$), 67.1 (CH$_2$), 66.5 (CH$_2$), 66.3 (CH$_2$), 60.6 (CH), 59.6 (CH), 46.0 (CH$_2$), 45.0 (CH), 44.2 (CH), 42.3 (CH$_2$), 41.7 (CH$_2$), 40.2 (CH$_2$), 21.0 ((CH$_3$), 20.9 (CH$_3$),



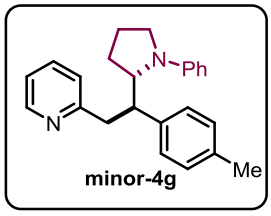
2-(2-(1-Phenylpyrrolidin-2-yl)-2-(p-tolyl)ethyl)pyridine (4g)

The title compound **4g** was prepared according to General Procedure E using (*E*)-2-(*p*-tolylstyryl)pyridine (59 mg, 0.3 mmol) and *N*-phenylpyrrolidine (88 mg, 0.6 mmol). The crude product was purified by FC (95:5 cyclohexane:EtOAc) to afford the major diastereomer of *amine* **4g** (35 mg) as a white solid followed by mixed fractions (40 mg) and finally the minor diastereomer of *amine* **4g** (20 mg, 95% pure) to give a total of *amine* **4g** (95 mg, 92%).



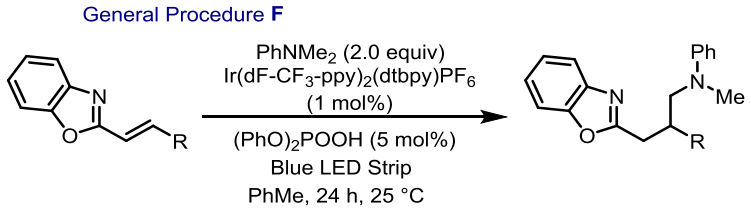
Major Diastereomer: HRMS (ESI) Exact mass calculated for $C_{24}H_{27}N_2$ $[M+H]^+$: 343.2169, found: 343.2177

^{1}H NMR (500 MHz, CDCl$_3$) δ 8.58 (1H, ddd, *J* = 4.9, 1.9, 0.9 Hz, Ar**H**), 7.54 (1H, td, *J* = 7.7, 1.9 Hz, Ar**H**), 7.26-7.17 (2H, m, Ar**H**), 7.15-7.02 (6H, m, Ar**H**), 6.72-6.63 (1H, m, Ar**H**), 6.58-6.54 (2H, m, Ar**H**), 4.00 (1H, ddd, *J* = 8.4, 4.6, 1.6 Hz, NC**H**), 3.76 (td, *J* = 7.9, 4.6 Hz, ArC**H**), 3.28 (2H, d, *J* = 7.9 Hz, ArC**H**$_2$), 3.11 (1H, td, *J* = 8.8, 2.3 Hz, NC**H**$_2$), 2.99 (1H, 9.2, 7.4 Hz, NC**H**$_2$), 2.32 (3H, s, ArC**H**$_3$), 2.01-1.91 (1H, m, NCHC**H**$_2$), 1.84 (1H, tt, *J* = 12.3, 8.0 Hz, NCH$_2$C**H**$_2$), 1.61 (1H, dddd, *J* = 15.1, 7.6, 4.9, 2.2 Hz, NCH$_2$C**H**$_2$), 1.05-0.95 (1H, m, NCHC**H**$_2$): **^{13}C NMR (125.6 MHz, CDCl$_3$)** δ 160.6 (C), 149.0 (CH), 147.5 (C), 138.2 (C), 136.2 (CH), 135.8 (C), 129.1 (2 x CH), 128.61 (2 x CH), 128.56 (2 x CH), 123.5 (CH), 121.1 (CH), 115.3 (CH), 112.1 (2 x CH), 61.5 (CH), 49.0 (CH$_2$), 45.6 (CH), 40.3 (CH$_2$), 26.8 (CH$_2$), 23.1 (CH$_2$), 21.0 (CH$_3$).

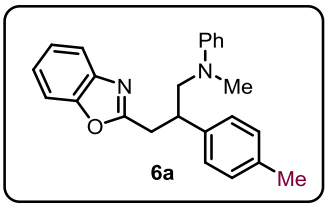


Minor Diastereomer: HRMS (ESI) Exact mass calculated for $C_{24}H_{27}N_2$ $[M+H]^+$: 343.2169, found: 343.2165. **^{1}H NMR (500 MHz, CDCl$_3$)** δ 8.37 (1H, ddd, *J* = 5.0, 1.9, 0.9 Hz, Ar**H**), 7.38 (1H, t, *J* = 7.7 Hz, Ar**H**), 7.29-7.23 (4H, m, Ar**H**), 7.10 (2H, d, *J* = 7.7 Hz, Ar**H**), 6.97 (1H, t, *J* = 6.1 Hz, Ar**H**), 6.88 (1H, d, *J* = 7.9 Hz, Ar**H**), 6.77-6.74 (2H, m, Ar**H**), 6.72 (1H, ddd, *J* = 7.3, 6.7, 1.0 Hz, Ar**H**), 4.11 (1H, dt, *J* = 8.4, 3.3 Hz, NC**H**), 3.93 (1H, ddd, *J* = 9.6, 6.3, 3.5 Hz, ArC**H**), 3.53 (1H, ddd, *J* = 9.2, 7.9, 3.7 Hz, NC**H**$_2$), 3.33-3.26 (2H, m, ArC**H**$_2$), 3.21 (1H, dt, *J* = 9.1, 7.7 Hz, NC**H**$_2$), 2.30 (3H, s, ArC**H**$_3$), 2.16 (1H, ddd, *J* = 12.6, 7.5, 3.6 Hz, NCHC**H**$_2$), 2.08-2.00 (1H, m, NCH$_2$C**H**$_2$), 1.91-1.79 (2H, m, NCHC**H**$_2$ + NCH$_2$C**H**$_2$); **^{13}C NMR (125.6 MHz, CDCl$_3$)** δ 160.3 (C), 147.7 (CH), 138.3 (C), 135.9 (C), 129.13 (2 x CH), 129.10 (2 x CH), 128.6 (C), 128.3 (2 x CH), 123.0 (CH), 120.9 (CH), 115.9 (CH), 112.8 (2 x CH), 112.1 (CH), 63.6 (CH), 50.6 (CH$_2$), 46.1 (CH), 27.0 (CH$_2$), 24.2 (CH$_2$), 21.0 (CH$_3$).

E. General Procedure for the Brønsted Acid-Catyalysed Addition of Photochemically Generatred α-Amino Radicals to Alkenylbenzoxazoles



General Procedure F: Alkenylbenzoxazole (1.0 equiv), [Ir{dF(CF_3)ppy}$_2$(dtbbpy)]PF_6 (1 mol%) and diphenyl phosphate (5 mol%) were added to a Schlenk tube and the vessel was evacuated and backfilled with argon twice. Toluene (0.1 M) and dimethylaniline (2.0 equiv) were added and the Schlenk tube was sealed. The solution was subjected to 3 freeze-pump-thaw cycles and was then irradiated for 24 hours by blue LED´s. The solution was diluted with EtOAc and partioned between EtOAc and 1M NaOH solution. The biphasic system was extracted with EtOAc (x 3). The organic layers were combined, dried, and concentrated *in vacuo*. The crude product was purified by FC to afford the corresponding *amine*.

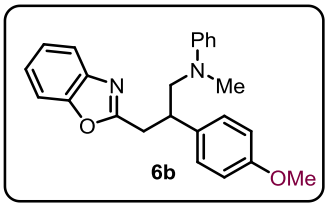


N-(3-(Benzo[d]oxazol-2-yl)-2-(p-tolyl)propyl)-N-methylaniline (6a)

The title compound **6a** was prepared according to General Procedure F using (*E*)-2-(4-methylstyryl)benzo[d]oxazole (71 mg, 0.3 mmol) The crude product was purified by FC (95:5 cyclohexane:EtOAc) to afford *amine* **6a** (68 mg, 64%) as a yellow oil.

HRMS (ESI) Exact mass calculated for $C_{24}H_{25}N_2O$ $[M+H]^+$: 357.1961, found: 357.1958;

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67-7.60 (1H, m, Ar**H**), 7.45-7.39 (1H, m, Ar**H**), 7.29-7.24 (2H, m, Ar**H**), 7.24-7.18 (2H, m, Ar**H**), 7.17-7.14 (2H, m, Ar**H**), 7.09 (2H, d, *J* = 7.9 Hz, Ar**H**), 6.73-6.64 (3H, m, Ar**H**), 3.87-3.70 (2H, m, NC**H**$_2$ + C**H**), 3.46 (1H, dd, *J* = 14.1, 7.0 Hz, NC**H**$_2$), 3.37 (1H, dd, *J* = 15.3, 6.7 Hz, ArC**H**$_2$), 3.28 (1H, dd, *J* = 15.3, 8.0 Hz, ArC**H**$_2$), 2.75 (3H, s, NC**H**$_3$), 2.30 (3H, s, ArC**H**$_3$); **^{13}C NMR (125.6 MHz, $CDCl_3$)** δ 165.4 (C), 150.7 (C), 149.0 (C), 141.2 (C), 138.5 (C), 136.5 (C), 129.3 (2 x CH), 129.1 (2 x CH), 127.4 (2 x CH), 124.4 (CH), 124.0 (CH), 119.5 (CH), 116.3 (CH), 112.1 (2 x CH), 110.2 (CH), 59.3 (CH_2), 41.8 (CH), 39.5 (CH_3), 32.7 (CH_2), 21.0 (CH_3).



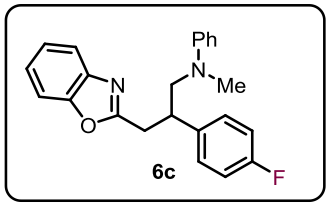
N-(3-(Benzo[d]oxazol-2-yl)-2-(4-methoxyphenyl)propyl)-N-methylaniline (6b)

The title compound **6b** was prepared according to General Procedure F using (*E*)-2-(4-methoxystyryl)benzo[d]oxazole (75 mg, 0.3 mmol) The crude product was purified by FC (98:2 cyclohexane:EtOAc) to afford *amine* **6b** (71 mg, 64%) as a yellow oil.

HRMS (ESI) Exact mass calculated for $C_{24}H_{25}N_2O_2$ $[M+H]^+$: 373.1911, found: 373.1909;

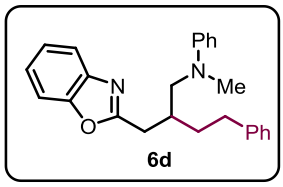
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67-7.64 (1H, m, Ar**H**), 7.46-7.42 (1H, m, Ar**H**), 7.31-7.26 (3H, m, Ar**H**), 7.25-7.21 (2H, m, Ar**H**), 7.20-7.17 (2H, m, Ar**H**), 6.86-6.82 (2H, m, Ar**H**), 6.72 (1H, tt, *J* = 7.2, 1.0 Hz, Ar**H**), 6.69 (2H, dt, *J* = 7.8, 1.0 Hz, Ar**H**), 3.85-3.77 (2H, m, NC**H**$_2$ + NCH$_2$C**H**), 3.78 (3H, s, OC**H**$_3$), 3.49-3.42 (1H, m, NC**H**$_2$), 3.38 (1H, dd, *J* = 15.3, 6.7 Hz, ArC**H**$_2$), 3.28 (1H, dd, *J* = 15.3, 8.2 Hz, ArC**H**$_2$), 2.76 (3H, s, NC**H**$_3$); **^{13}C NMR (125.6 MHz, $CDCl_3$)** δ 165.4 (C), 158.5 (C),

150.7 (C), 148.9 (C), 141.2 (C), 133.6 (C), 129.1 (2 x CH), 128.5 (2 x CH), 124.4 (CH), 124.0 (CH), 119.5 (CH), 116.2 (CH), 114.0 (2 x CH), 112.1 (2 x CH), 110.2 (CH), 59.3 (CH_2), 55.1 (CH_3), 41.4 (CH), 39.5 (CH_3), 32.8 (CH_2).



N-(3-(Benzo[d]oxazol-2-yl)-2-(4-fluorophenyl)propyl)-N-methylaniline (6c)

The title compound **6c** was prepared according to General Procedure F using (*E*)-2-(4-fluorostyryl)benzo[d]oxazole (72 mg, 0.3 mmol) The crude product was purified by FC (90:10 cyclohexane:EtOAc) to afford *amine* **6c** (76 mg, 70%) as a yellow oil. HRMS (ESI) Exact mass calculated for $C_{23}H_{22}N_2FO$ $[M+H]^+$: 361.1711, found: 361.1699; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.67-7.61 (1H, m, Ar**H**), 7.46-7.41 (1H, m, Ar**H**), 7.32-7.18 (6H, m, Ar**H**), 6.97 (2H, t, *J* = 8.7 Hz, Ar**H**), 6.72 (1H, tt, *J* = 7.3, 0.9 Hz, Ar**H**), 6.67 (2H, dt, *J* = 7.9, 1.0 Hz, Ar**H**), 3.92-3.74 (2H, m, C**H** + NC**H**$_2$), 3.51-3.22 (3H, m, NC**H**$_2$ + ArC**H**$_2$), 2.74 (3H, s, C**H**$_3$); **^{13}C NMR (125.6 MHz, $CDCl_3$)** δ 165.0 (C), 161.8 (C, d, *J* = 245 Hz), 150.7 (C), 148.8 (C), 141.2 (C), 137.2 (C, d, *J* = 3.3 Hz), 129.2 (2 x CH), 129.1 (2 x CH, d, *J* = 8.0 Hz), 124.6 (CH), 124.1 (CH), 119.6 (CH), 116.5 (CH), 115.5 (2 x CH, d, *J* = 21.2 Hz), 112.1 (2 x CH), 110.2 (CH), 59.3 (CH_2), 41.5 (CH), 39.5 (CH_3), 32.6 (CH_2); **^{19}F NMR (376 MHz, $CDCl_3$)** δ -115.7.

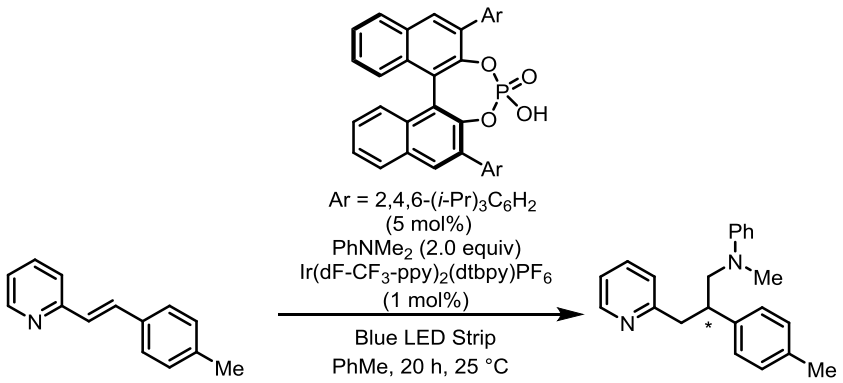


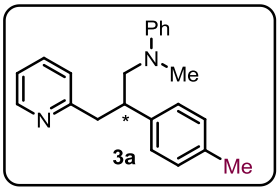
N-(2-(Benzo[d]oxazol-2-ylmethyl)-4-phenylbutyl)-N-methylaniline (6d)

The title compound **6d** was prepared according to General Procedure F using (*E*)-2-(4-phenylbut-1-en-1-yl)benzo[d]oxazole (75 mg, 0.3 mmol) The crude product was purified by FC (95:5 cyclohexane:EtOAc) to afford *amine* **6d** (78 mg, 70%) as a yellow oil.

HRMS (ESI) Exact mass calculated for $C_{25}H_{27}N_2O$ $[M+H]^+$: 371.2118, found: 371.2116. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.74-7.68 (1H, m, Ar**H**), 7.54-7.44 (1H, m, Ar**H**), 7.36-7.30 (2H, m, Ar**H**), 7.28-7.17 (5H, m, Ar**H**), 7.16-7.12 (2H, m, Ar**H**), 6.72 (3H, br s, Ar**H**), 3.47-3.3 (2H, m, NC**H**$_2$), 3.04 (2H, qd, *J* = 15.2, 6.6 Hz, ArC**H**$_2$CH), 2.97 (3H, s, NC**H**$_3$), 2.73 (2H, dddd, *J* = 16.4, 13.7, 11.8, 6.3 Hz, ArC**H**$_2$CH$_2$), 2.61 (1H, app p, *J* = 6.8 Hz, NCH$_2$C**H**), 1.87-1.72 (2H, m, ArCH$_2$C**H**$_2$); **^{13}C NMR (125.6 MHz, $CDCl_3$)** δ 165.8 (C), 150.7 (C), 149.6 (C), 141.8 (C), 141.3 (C), 129.1 (CH), 129.1 (CH), 128.4 (2 x CH), 128.3 (2 x CH), 125.9 (CH), 124.5 (CH), 124.1 (CH), 119.6 (CH), 116.4 (CH), 112.4 (2 x CH), 110.3 (2 x CH), 57.2 (CH_2), 39.5 (CH_3), 35.6 (CH), 33.7 (CH_2), 33.0 (CH_2), 31.1 (CH_2).

G. Enantioselective Procedure for the Brønsted Acid-Catalysed Addition of Photochemical Generated α-Amino Radicals to Alkenylpyridines

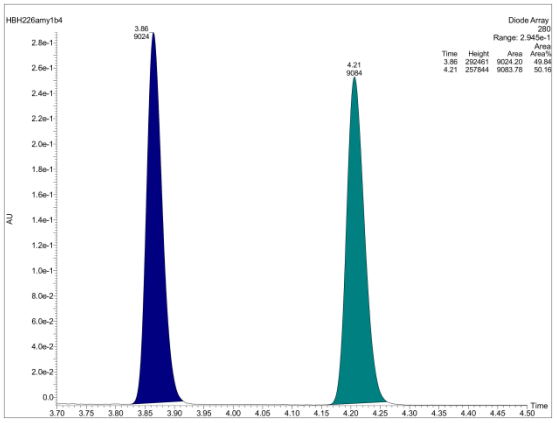


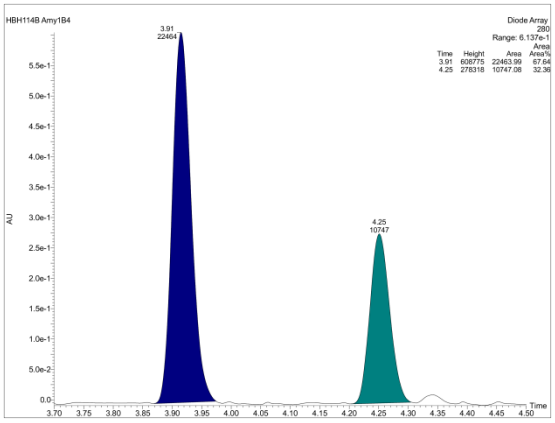


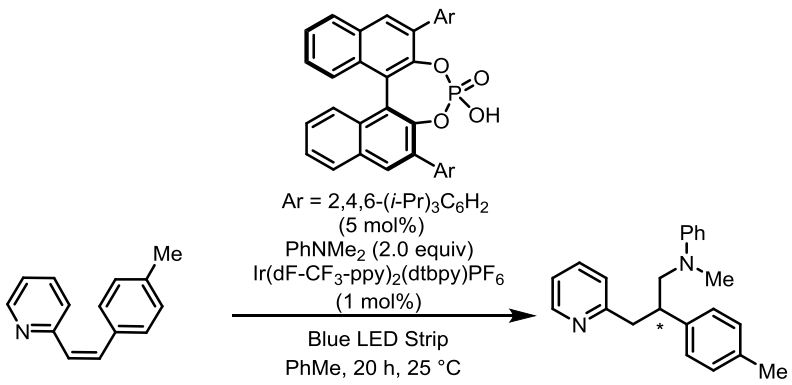
N-Methyl-N-(3-(pyridin-2-yl)-2-(p-tolyl)propyl)aniline (3a)

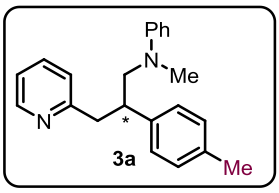
(*E*)-2-(*p*-Tolylstyryl)pyridine (59 mg, 0.3 mmol). [Ir{dF(CF_3)ppy}$_2$(dtbbpy)]PF_6 (3.4 mg, 1 mol%) and *(S)*-3,3′-bis(2,4,6-triisopropylphenyl)-1,1′-binaphthyl-2,2′-diyl hydrogenphosphate (11.3 mg, 5 mol%) were added to a Schlenk tube and the vessel was evacuated and backfilled with argon twice. Toluene (3 mL) and dimethylaniline (76 µL, 2.0 equiv) were added and the Schlenk tube was sealed. The solution was subjected to 3 freeze-pump-thaw cycles and was then irradiated for 20 hours by blue LED´s. The solution was diluted with EtOAc and partitioned between EtOAc and 1M NaOH solution. The biphasic system was extracted with EtOAc (x 3). The organic layers were combined, dried, and concentrated *in vacuo*. The crude product was purified by FC (5% EtOAc in cyclohexane) to afford the *amine* **3a** (77 mg, 81%) as a white gum.

The enantiomeric excess was determined by UPC^2 analysis on a Waters Amy1 column, 100:0 CO_2:EtOH to 60:40 CO_2:EtOH for 9 minutes with curve of "6", λ= 280 nm: τ major = 3.91 min, τ minor = 4.25 min (35% ee); $[\alpha]_D^{28}$ = 27.9 (c= 0.9, $CHCl_3$, 35% ee).





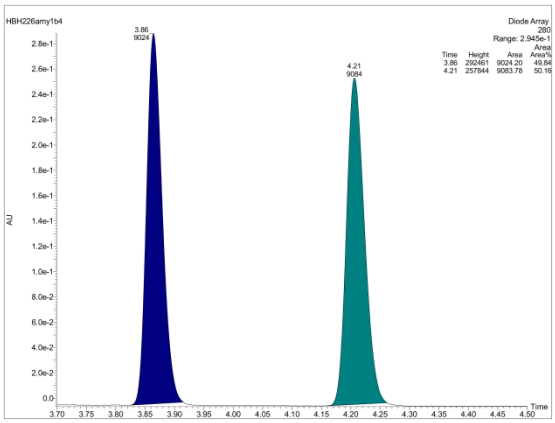


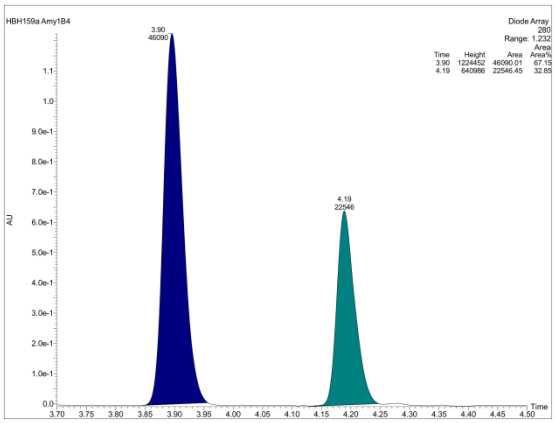


N-Methyl-N-(3-(pyridin-2-yl)-2-(p-tolyl)propyl)aniline (3a)

(*Z*)-2-(*p*-Tolylstyryl)pyridine (59 mg, 0.3 mmol). [Ir{dF(CF_3)ppy}$_2$(dtbbpy)]PF_6 (3.4 mg, 1 mol%) and *(S)*-3,3′-bis(2,4,6-triisopropylphenyl)-1,1′-binaphthyl-2,2′-diyl hydrogenphosphate (11.3 mg, 5 mol%) were added to a Schlenk tube and the vessel was evacuated and backfilled with argon twice. Toluene (3 mL) and dimethylaniline (76 µL, 2.0 equiv) were added and the Schlenk tube was sealed. The solution was subjected to 3 freeze-pump-thaw cycles and was then irradiated for 20 hours by blue LED´s. The solution was diluted with EtOAc and partitioned between EtOAc and 1M NaOH solution. The biphasic system was extracted with EtOAc (x 3). The organic layers were combined, dried, and concentrated *in vacuo*. The crude product was purified by FC (5% EtOAc in cyclohexane) to afford the *amine* **3a** (69 mg, 73%) as a white gum.

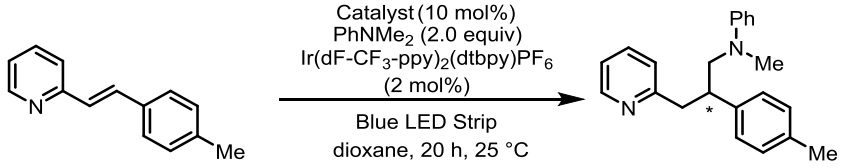
The enantiomeric excess was determined by UPC^2 analysis on a Waters Amy1 column, 100:0 CO_2:EtOH to 60:40 CO_2:EtOH for 9 minutes with curve of "6", λ= 280 nm: τ major = 3.91 min, τ minor = 4.25 min (34% ee); $[\alpha]_D^{28}$ = +27.5 (c= 1.0, $CHCl_3$, 34% ee).

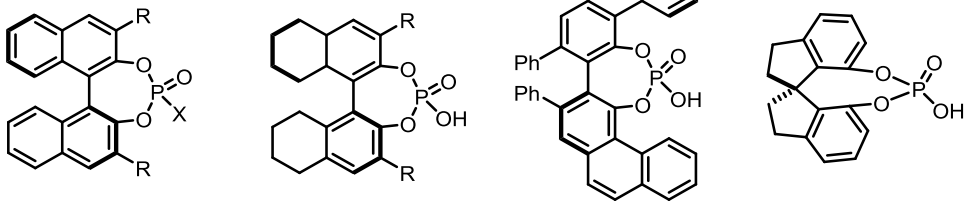




Screening Data:

Catalyst Screening:





1 R = H, X =OH
2 R = 9-Anthrancenyl, X = OH
3 R = 3,5-CF_3-C_6H_3, X = OH
4 R = 2,4,6-(*i*-Pr)$_3$-C_6H_2, X = OH
5 R = 2,4,6-(*i*-Pr)$_3$-C_6H_2 X NHTf

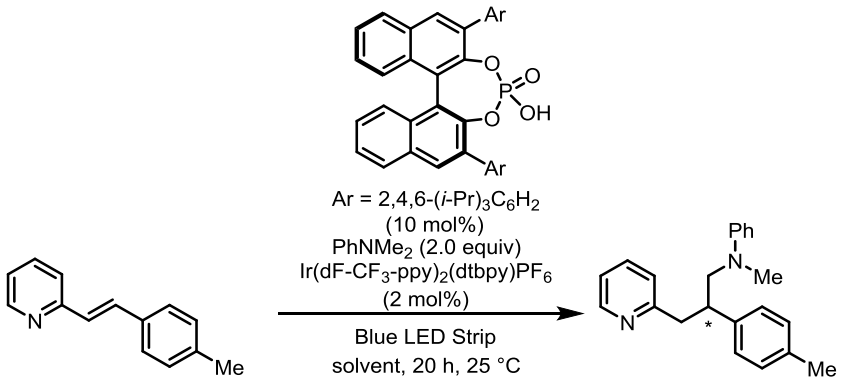
6 R = 4-Ph-C_6H_4
7 R = Phenyl
8 R = *t*-Bu

9

10

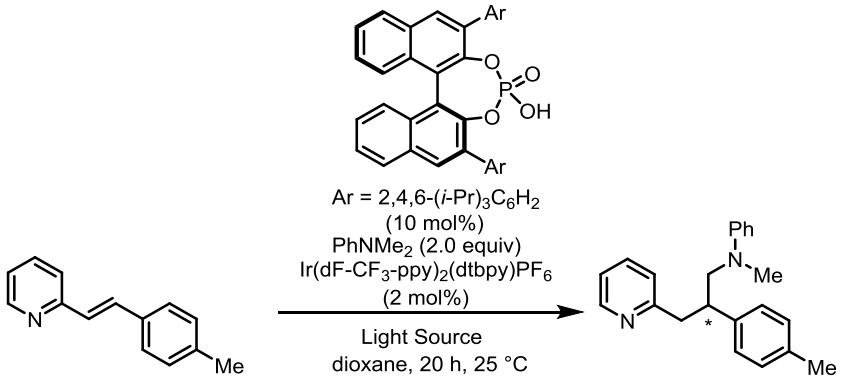
Catalyst	Conversion (by UPC^2 or NMR)	%ee
1	**95%**	**0%**
2	**90%**	**19%**
3	**48%**	**19%**
4	**95%**	**26%**
5	**93%**	**18%**
6	**95%**	**10%**
7	**95%**	**10%**
8	**95%**	**10%**
9	**34%**	**1%**
10	**74%**	**4%**

Solvent Screening:



Solvent	Conversion (by UPC^2 or NMR)	%ee
dioxane	95%	26%
CH_2Cl_2	66%	15%
MeCN	14%	6%
PhMe	95%	35%
benzene	95%	34%
cyclohexane	95%	26%
THF	95%	23%

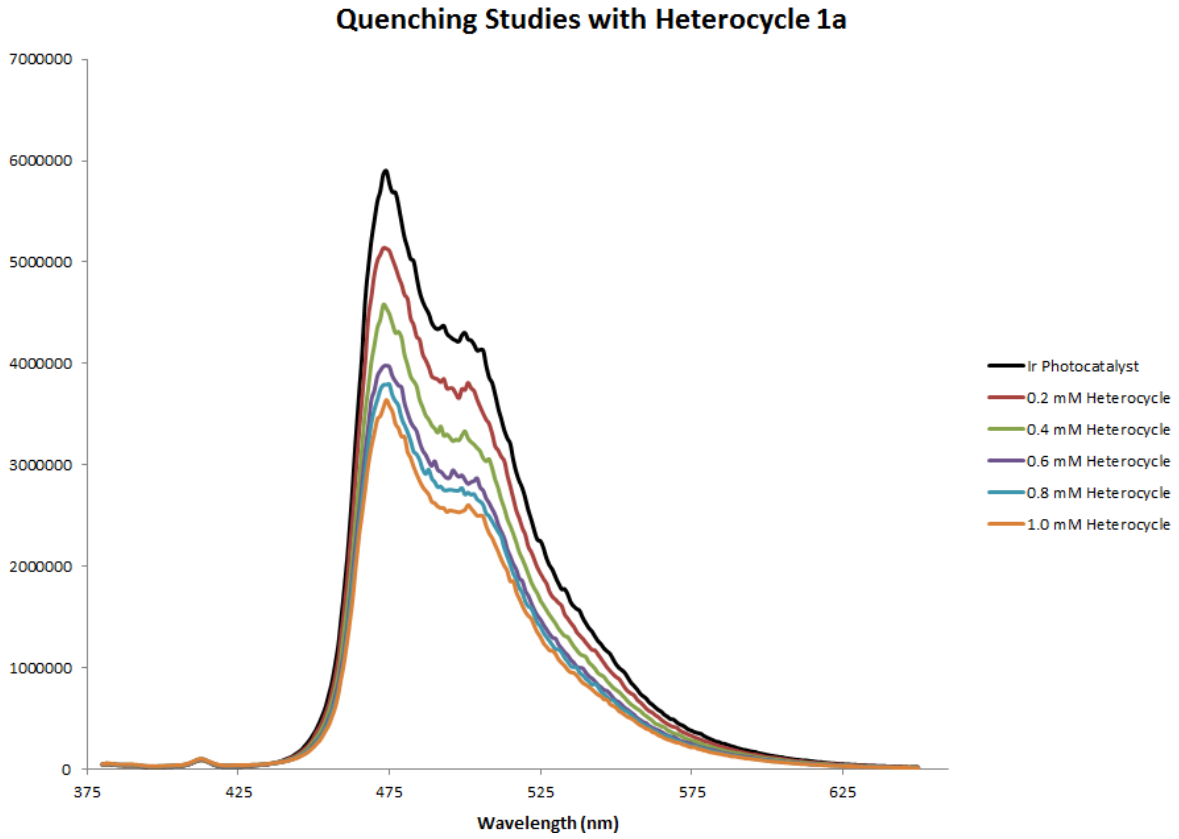
Light Source Screening:

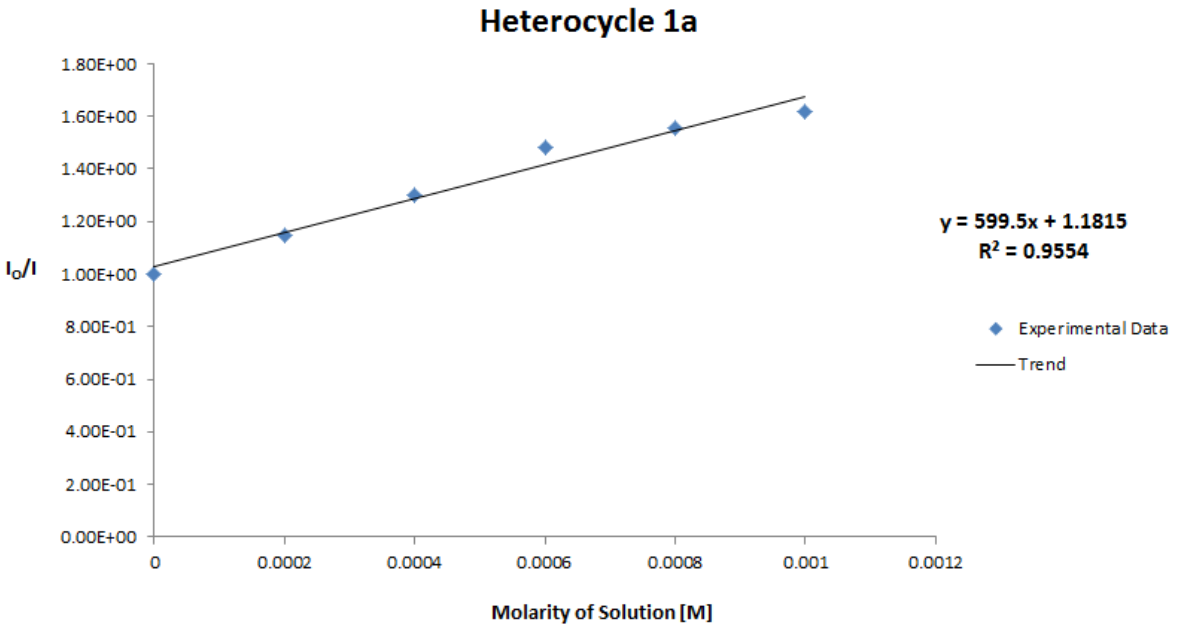


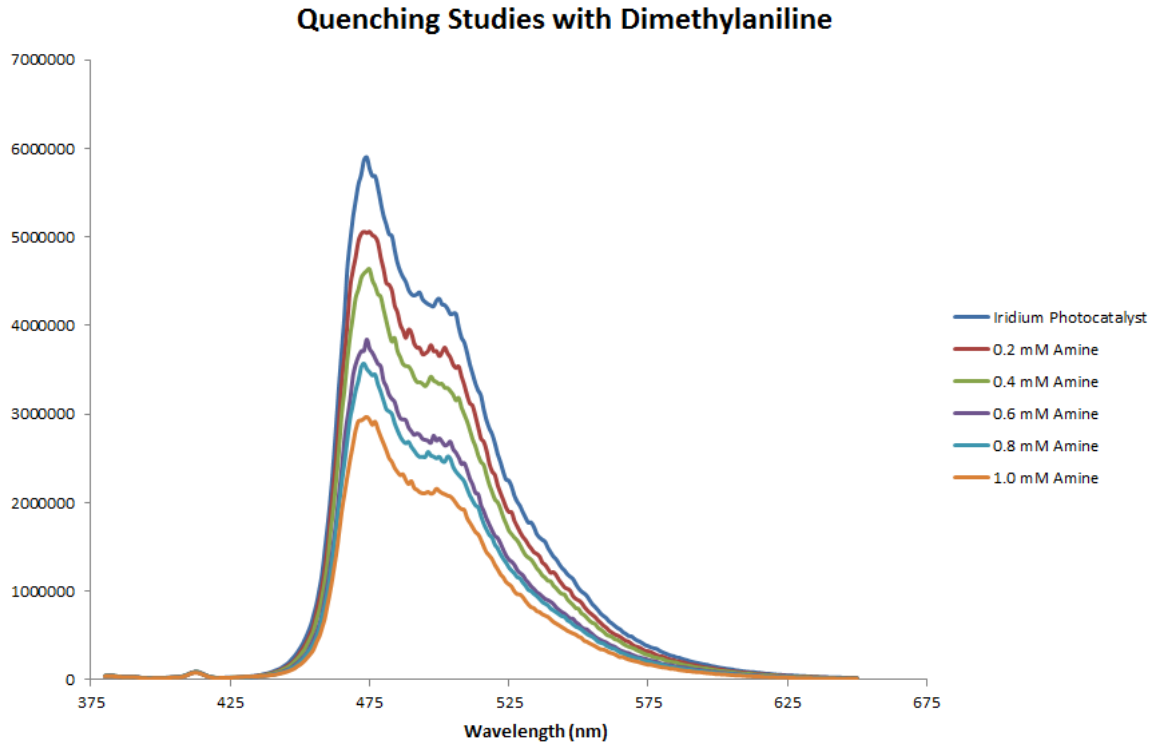
Light Source	Temperature (°C)	Conversion (by UPC^2 or NMR)	%ee
Blue LED Strip	20 °C	95%	26%
Blue LED Strip	40 °C	95%	26%
Single Blue LED	rt	0%	N/A
Single White LED	rt	0%	N/A
CFL	rt	95%	26%

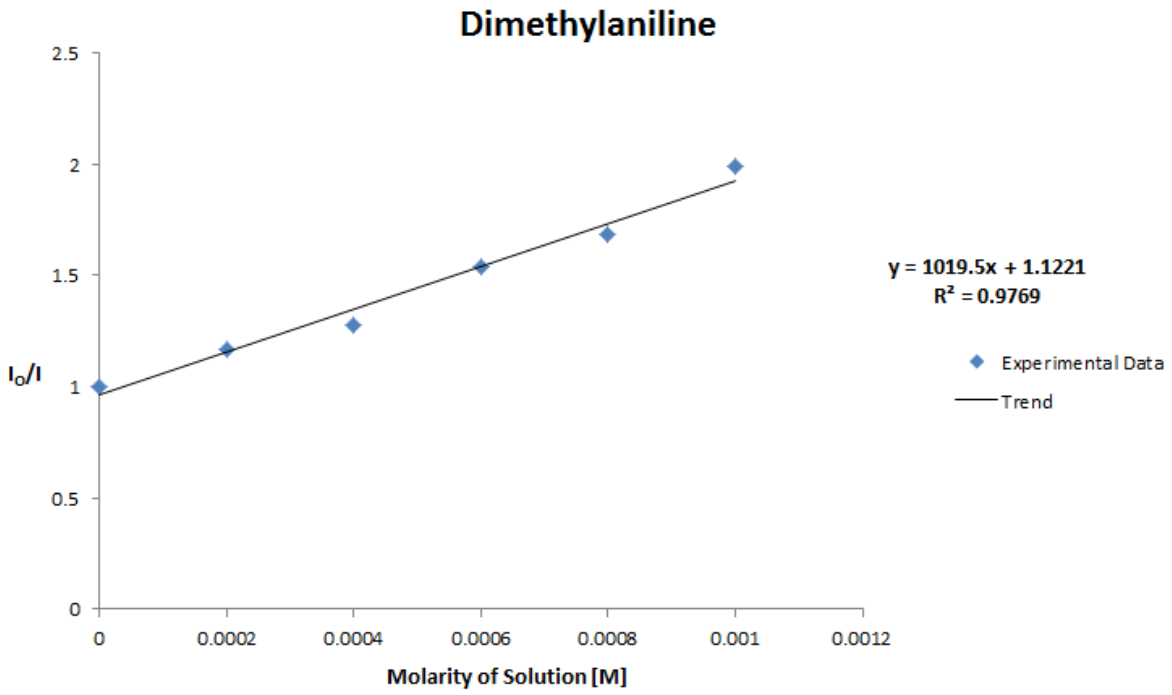
H. Stern-Volmer Quenching Studies

75 mL of PhMe was degassed through 3 freeze-pump-thaw repetitions and was used to prepare a 10^{-4} M solution of $(Ir(dF(CF_3)ppy)_2(dtbbpy)PF_6$ (25 mL), a 2 M solution of heterocycle **1a** (10 mL), and a 2 M solution of dimethylaniline **2** (10 mL). To prepare each solution for study, 0.6 mL of the Ir standard solution was added to the appropriate volume of quencher solution and the total volume was increased to 2 mL using degassed toluene. The iridium was excited at 380 nm.

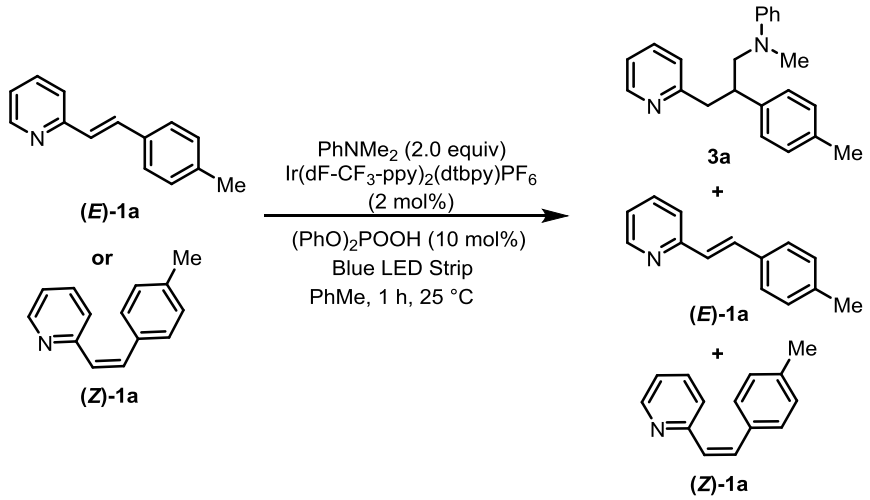



Heterocycle 1a
1.80E+00
1.60E+00
1.40E+00
1.20E+00
1.00E+00
8.00E-01
6.00E-01
4.00E-01
2.00E-01
0.00E+00
I0/I
0
0.0002
0.0004
0.0006
0.0008
0.001
0.0012
Molarity of Solution [M]
y = 599.5x + 1.1815
R2 = 0.9554
Experimental Data
Trend


Quenching Studies with Dimethylaniline
7000000
6000000
5000000
4000000
3000000
2000000
1000000
0
375
425
475
525
575
625
675
Wavelength (nm)
Iridium Photocatalyst
0.2 mM Amine
0.4 mM Amine
0.6 mM Amine
0.8 mM Amine
1.0 mM Amine


Dimethylaniline
2.5
2
1.5
1
0.5
0
I_o/I
0
0.0002
0.0004
0.0006
0.0008
0.001
0.0012
Molarity of Solution [M]
y = 1019.5x + 1.1221
R^2 = 0.9769
Experimental Data
Trend

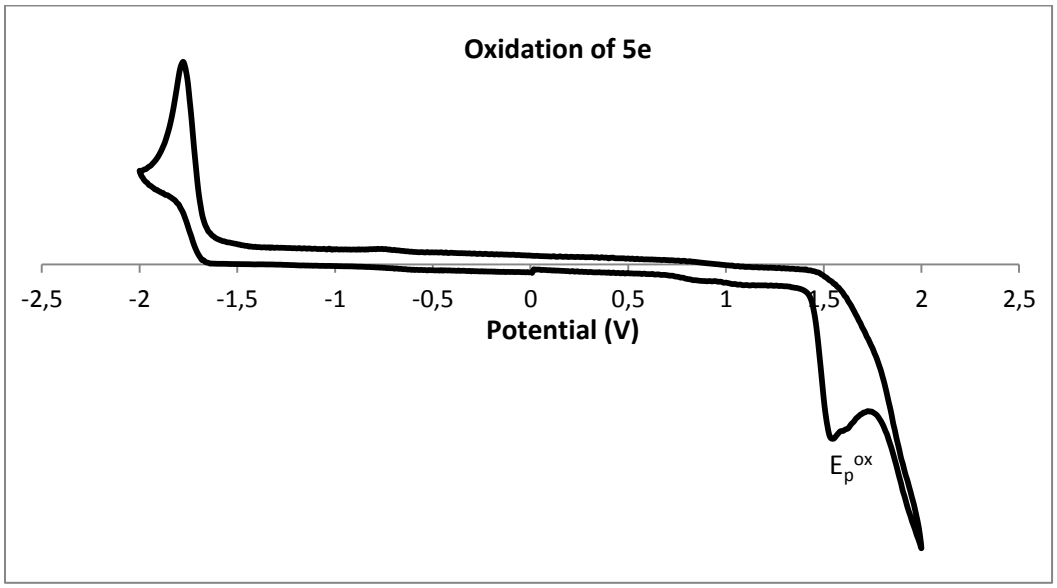
I. Study of the Reaction



Reaction with (*E*)-1a: Reaction composition after 1 hour (yields determined by ^{1}H NMR using trimethoxybenzene as internal standard) = **(*E*)-1a** = 45%, **(*Z*)-1a** = 20%, **3a** = 18%. ***E*:*Z*** = 2.25.

Reaction with (*Z*)-1a: Reaction composition after 1 hour (yields determined by ^{1}H NMR using trimethoxybenzene as internal standard) = **(*E*)-1a** = 51%, **(*Z*)-1a** = 27%, **3a** = 7%. ***E*:*Z*** = 1.89.

K. Cyclic Voltammetry



Cyclic voltammogram of **5e** [0.002 M] in [0.1 M] $TBAPF_6$ in CH_3CN. Sweep rate: 100 mV/s. Graphite electrode working electrode, Ag/AgCl (KCl saturated) reference electrode, Pt wire auxiliary electrode. E_p^{ox} = +1.45 V; This indicates that the oxidation of the dimethylaniline (E_p^{ox} = + 0.81V) occurs more readily that the oxidation of **5e**.

K. References

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2. D. Mao, G. Hon, S. Wu, X. Liu, J. Yu, and L. Wang, *Eur. J. Org. Chem.* 2014, **14**, 3009-3019

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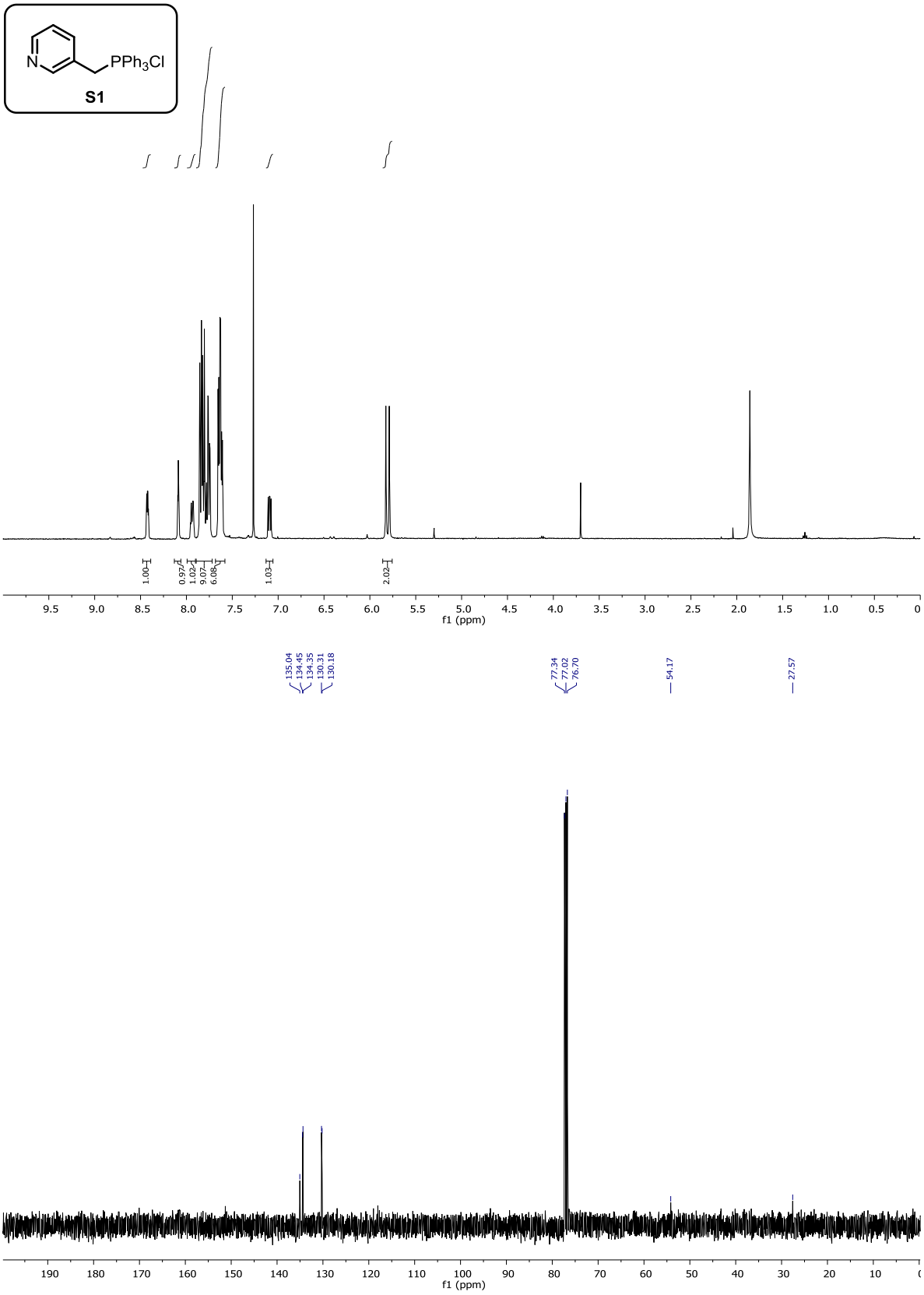
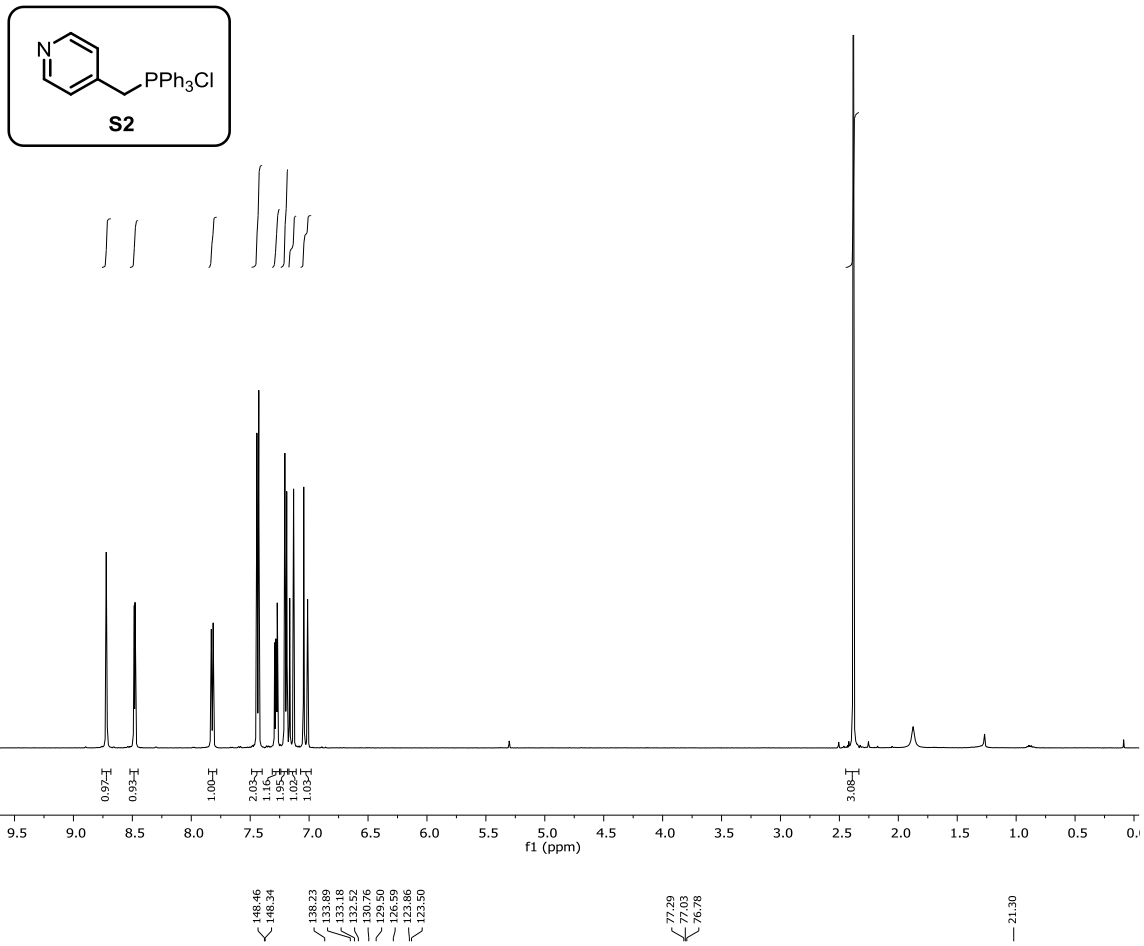
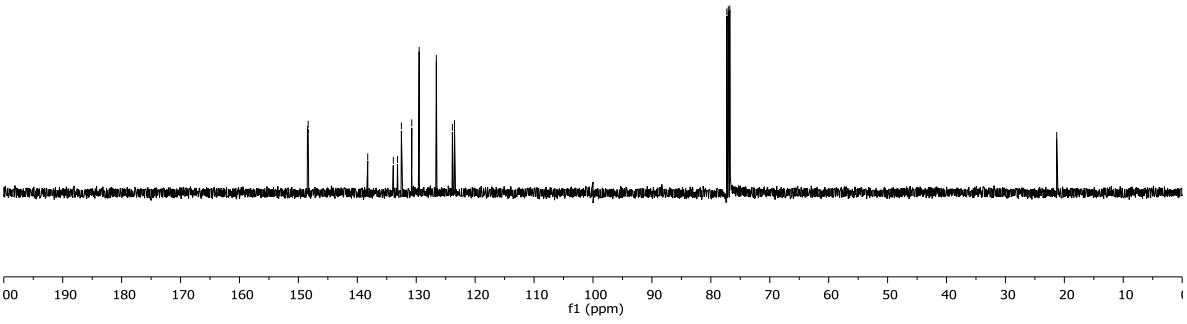
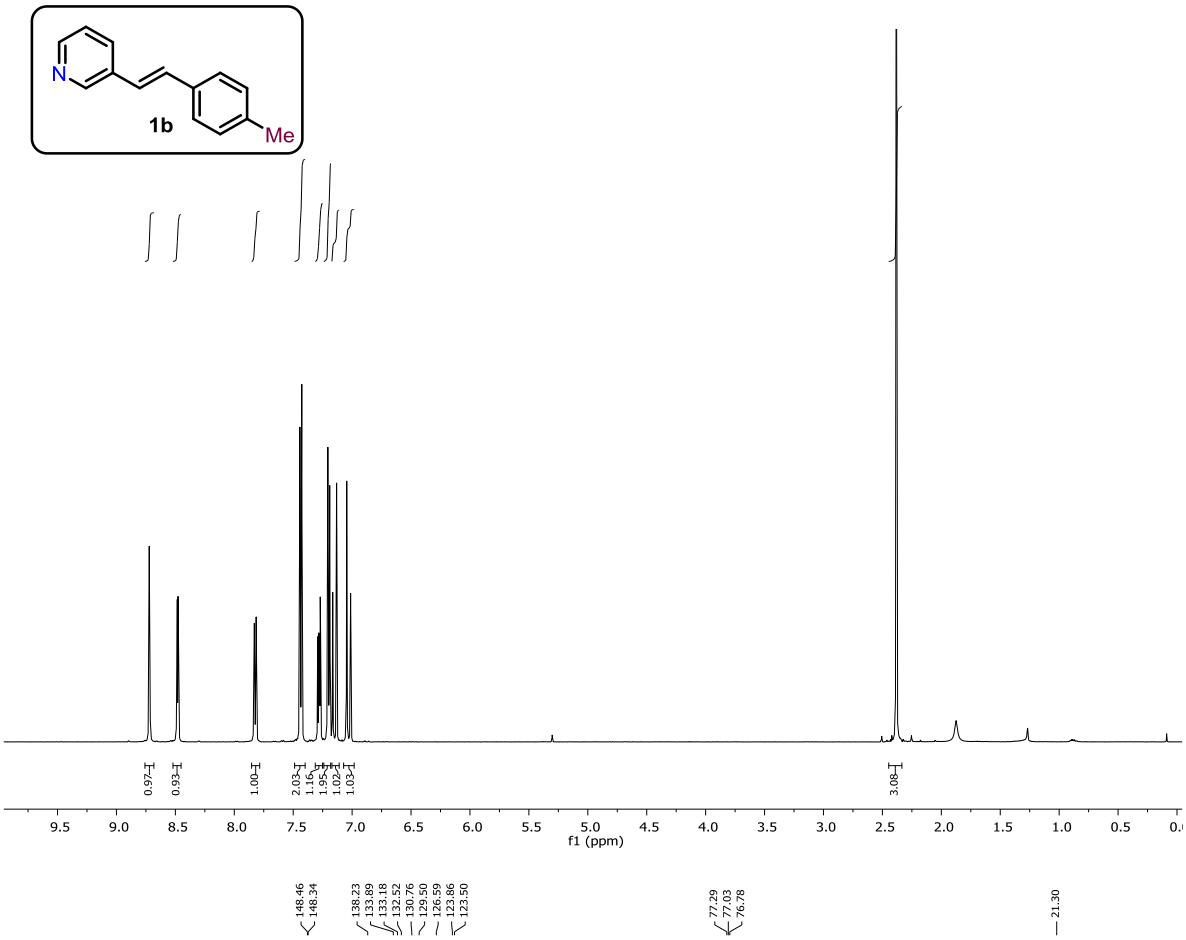

PPh3Cl
S1
1.00
0.97
1.02
9.07
6.08
1.03
2.02
f1 (ppm)
135.04
134.45
134.35
130.31
130.18
77.34
77.02
76.70
54.17
27.57
f1 (ppm)

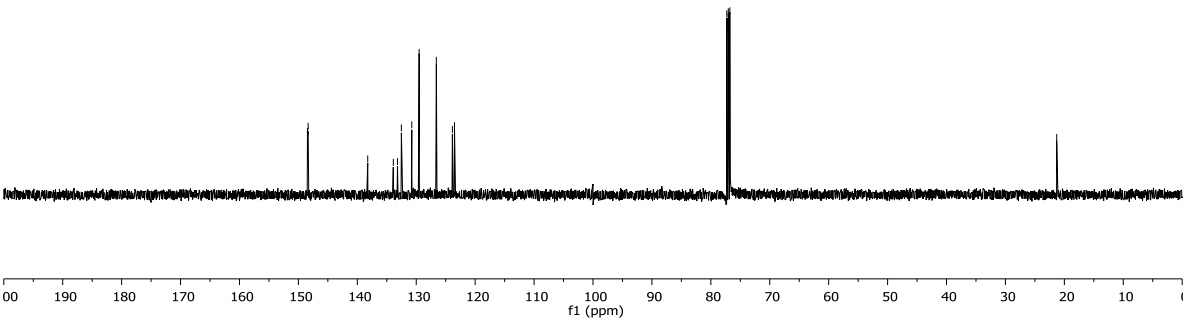

N
PPh3Cl
S2
0.97
0.93
1.00
2.03
1.16
1.95
1.02
1.03
3.08
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

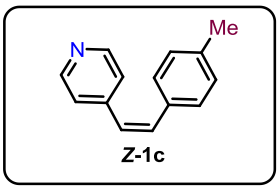
148.46
148.34
138.23
133.89
133.18
132.52
130.76
129.50
126.59
123.86
123.50
77.29
77.03
76.78
21.30


190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


N
1b
Me
0.97
0.93
1.00
2.03
1.16
1.95
1.02
1.03
3.08
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 0.5
f1 (ppm)

148.46
148.34
138.23
133.89
133.18
132.52
130.76
129.50
126.59
123.86
123.50
77.29
77.03
76.78
21.30

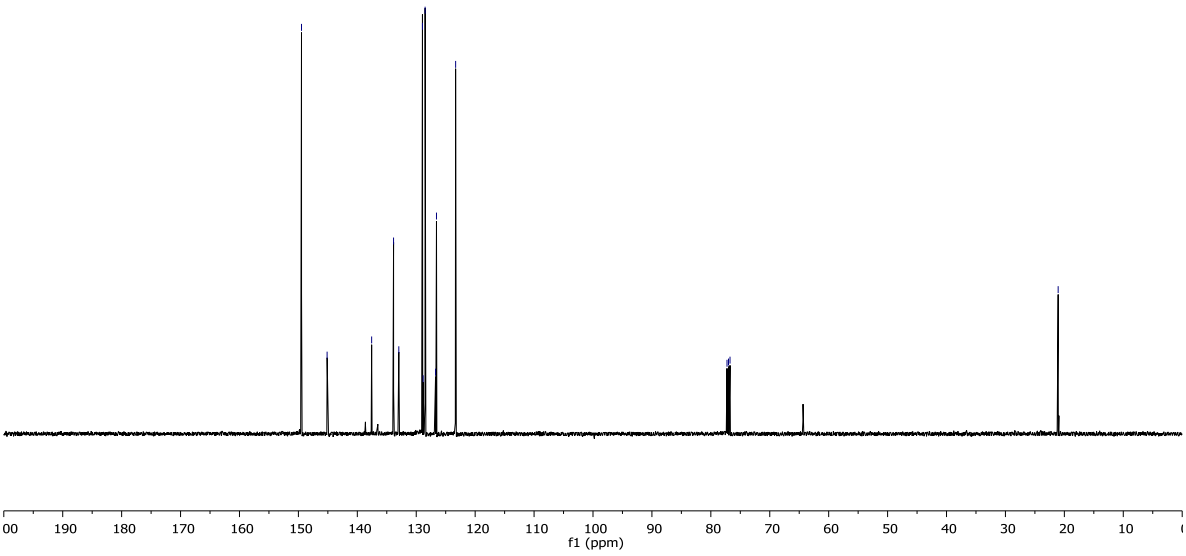

00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

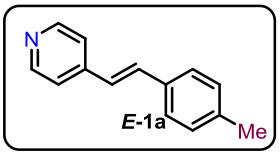

Me
N

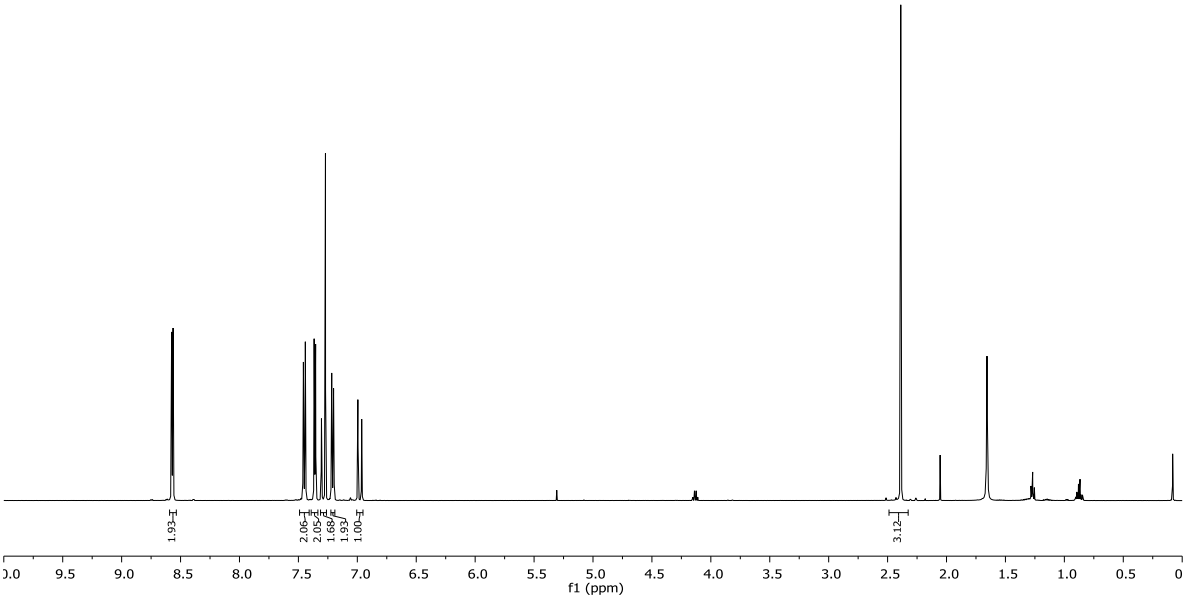
***Z*-1c**

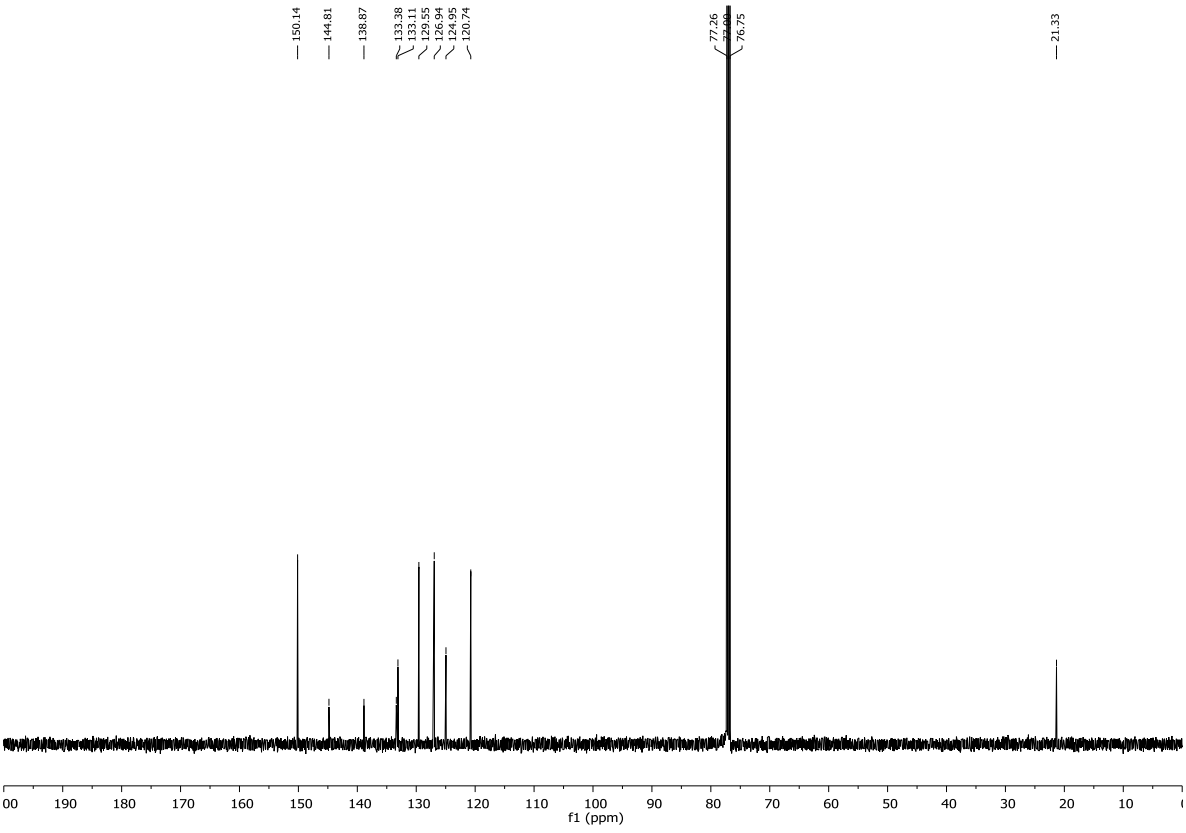
1.93
3.85
1.95
1.00
1.00
3.02
f1 (ppm)

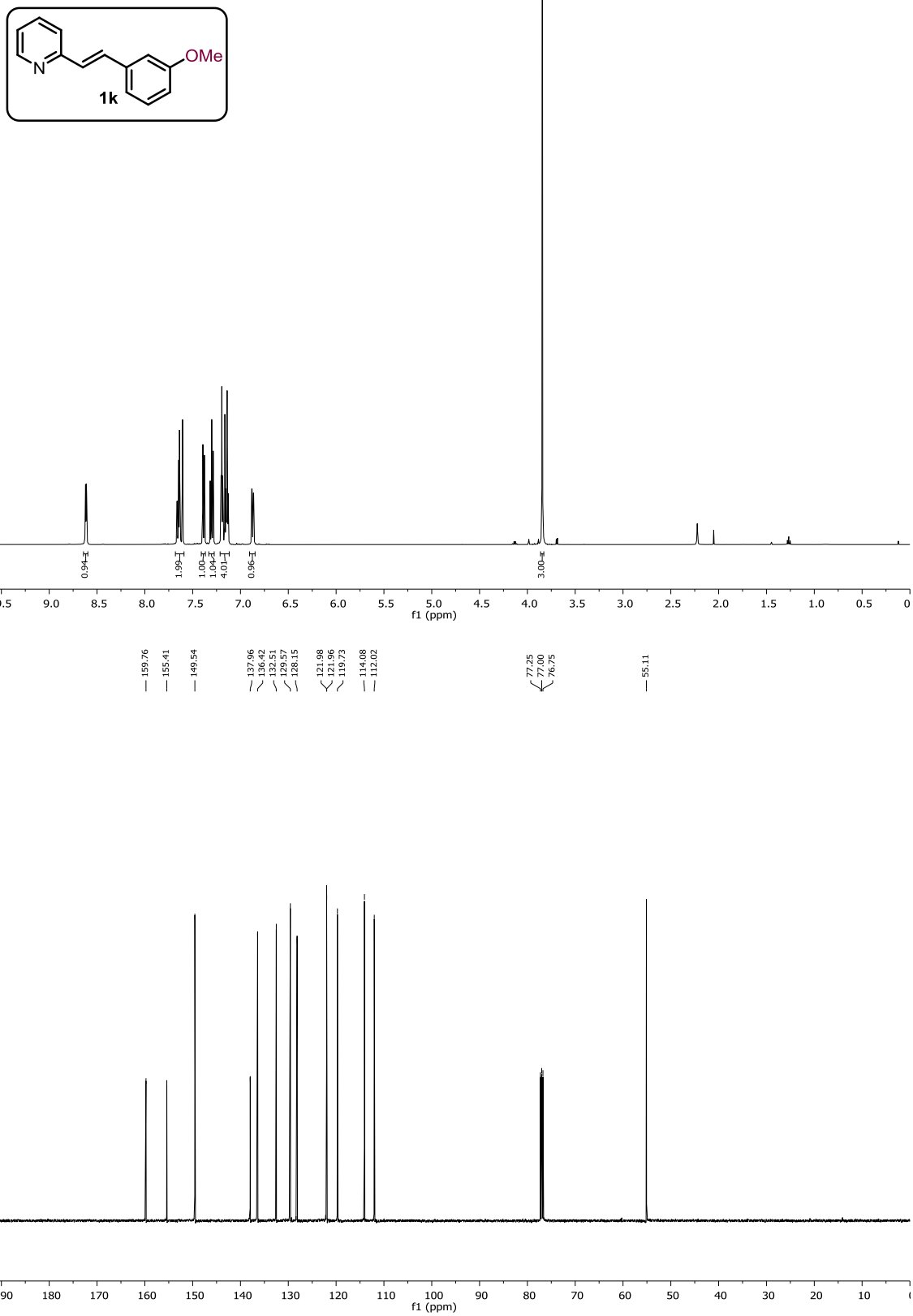

149.47
145.13
137.57
133.85
132.96
128.94
128.83
128.49
126.72
126.56
123.31
77.26
77.00
76.75
21.05

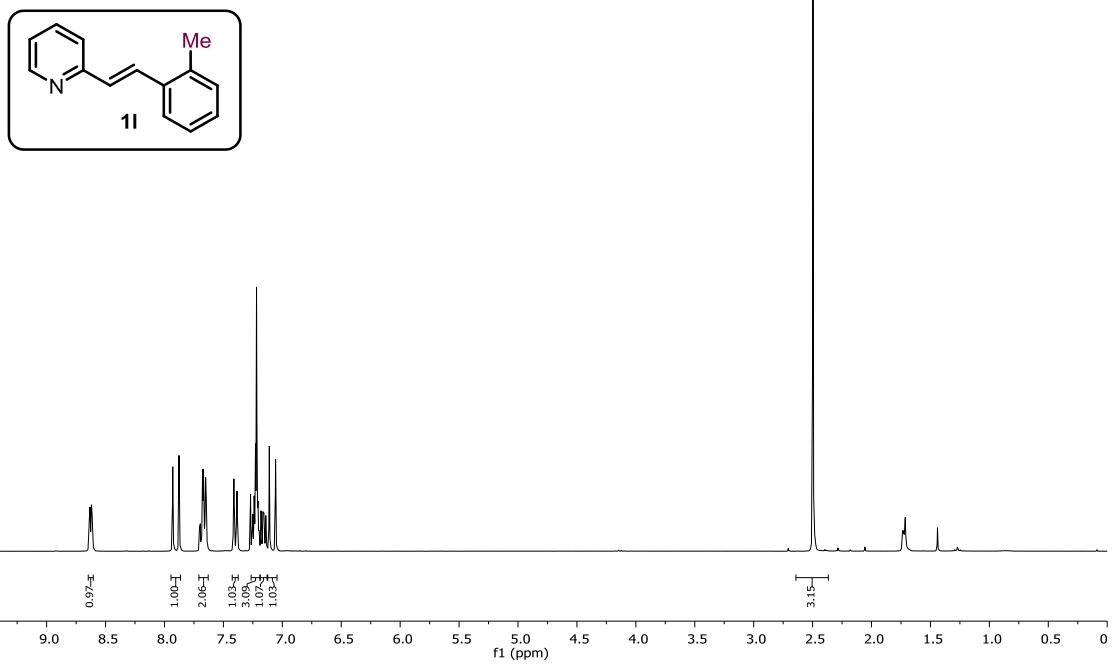

f1 (ppm)

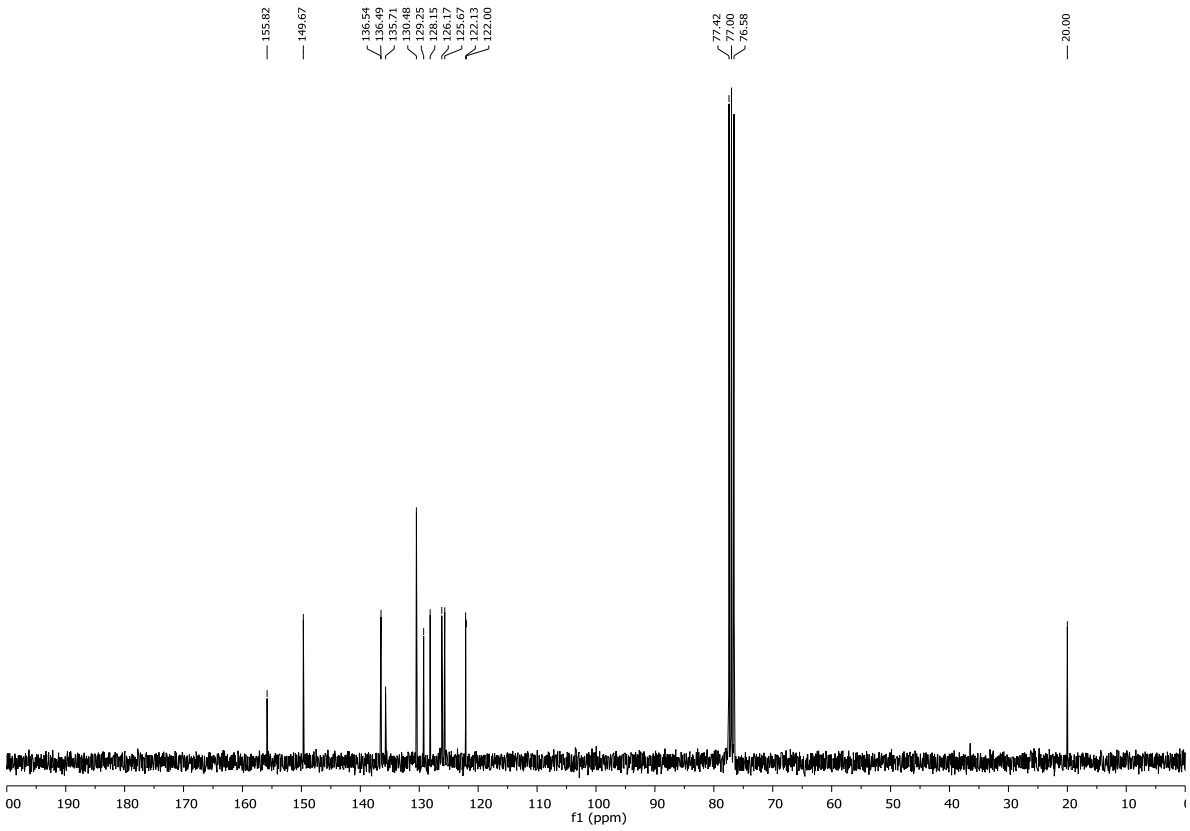

N
E-1a
Me

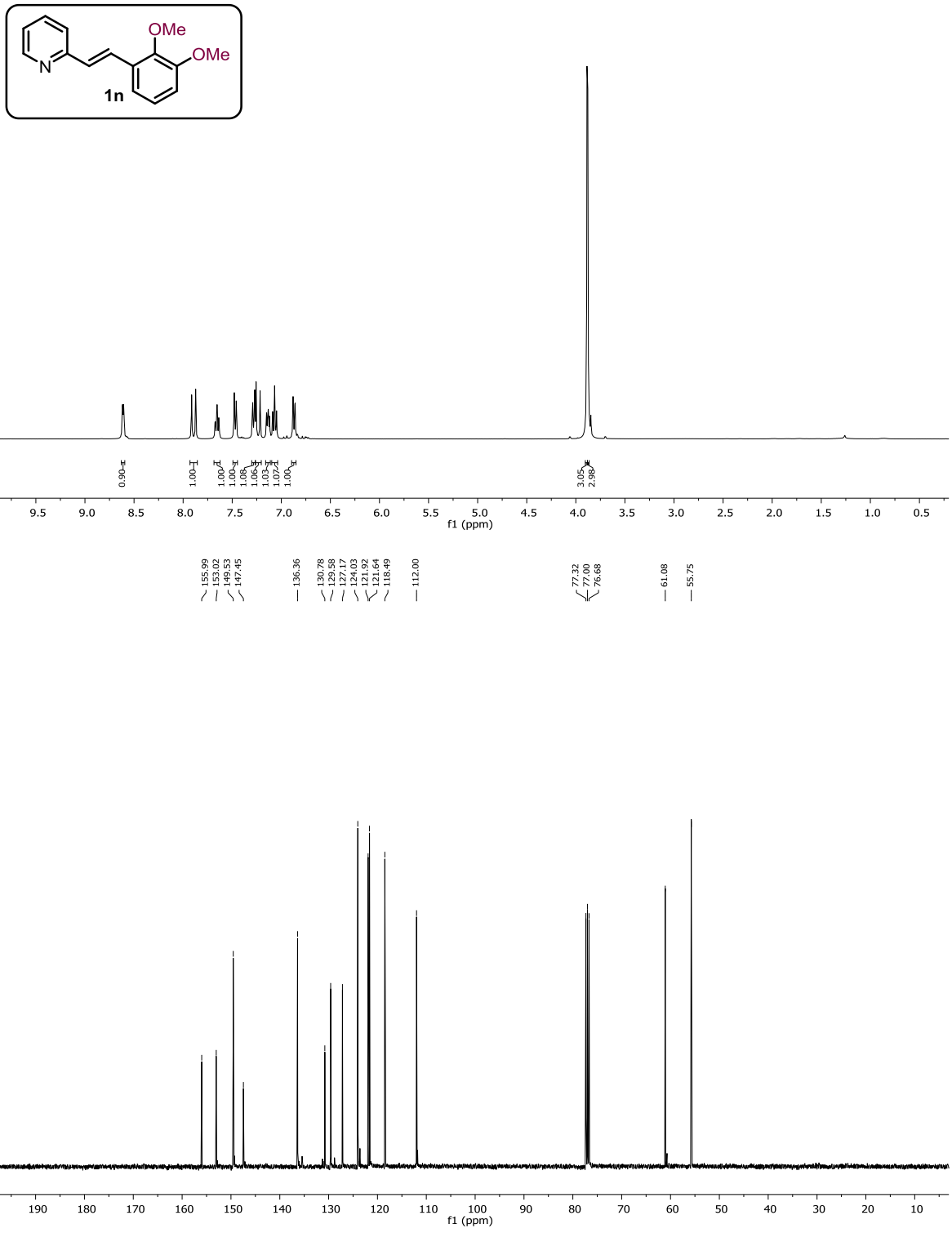

1.93
2.06
2.05
1.68
1.93
1.00
3.12
f1 (ppm)

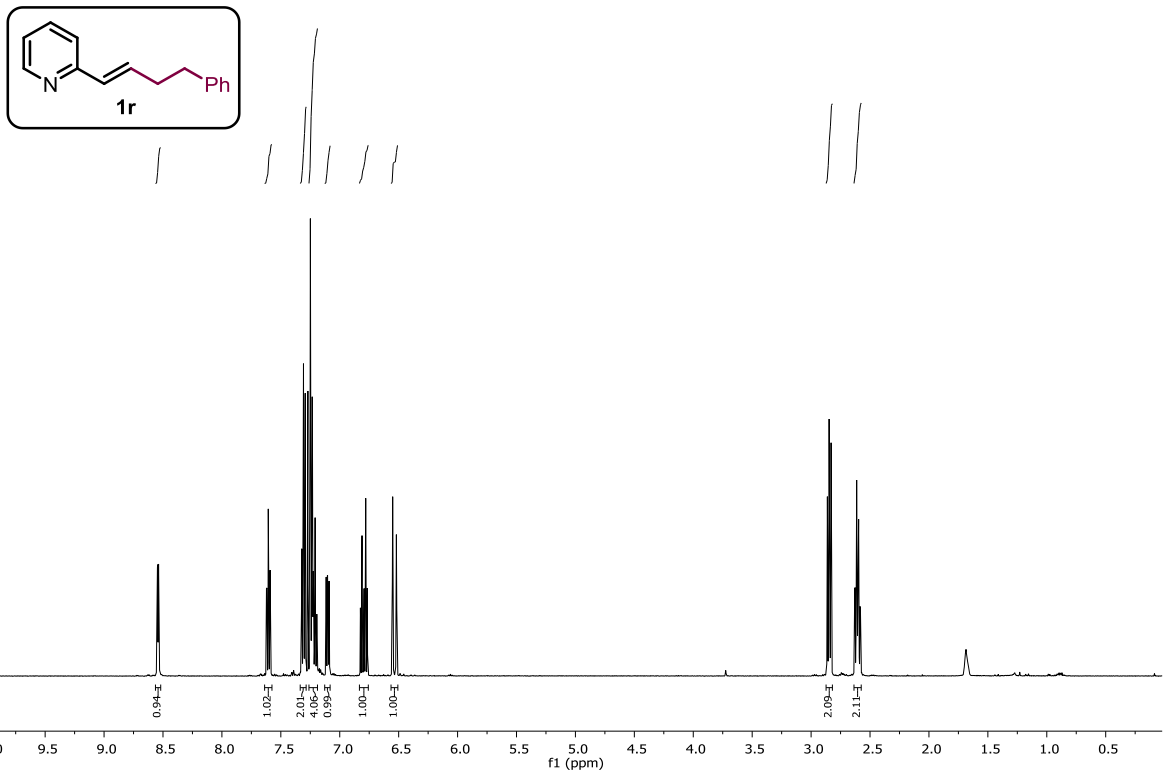

150.14
144.81
138.87
133.38
133.11
129.55
126.94
124.95
120.74
77.26
77.00
76.75
21.33
f1 (ppm)

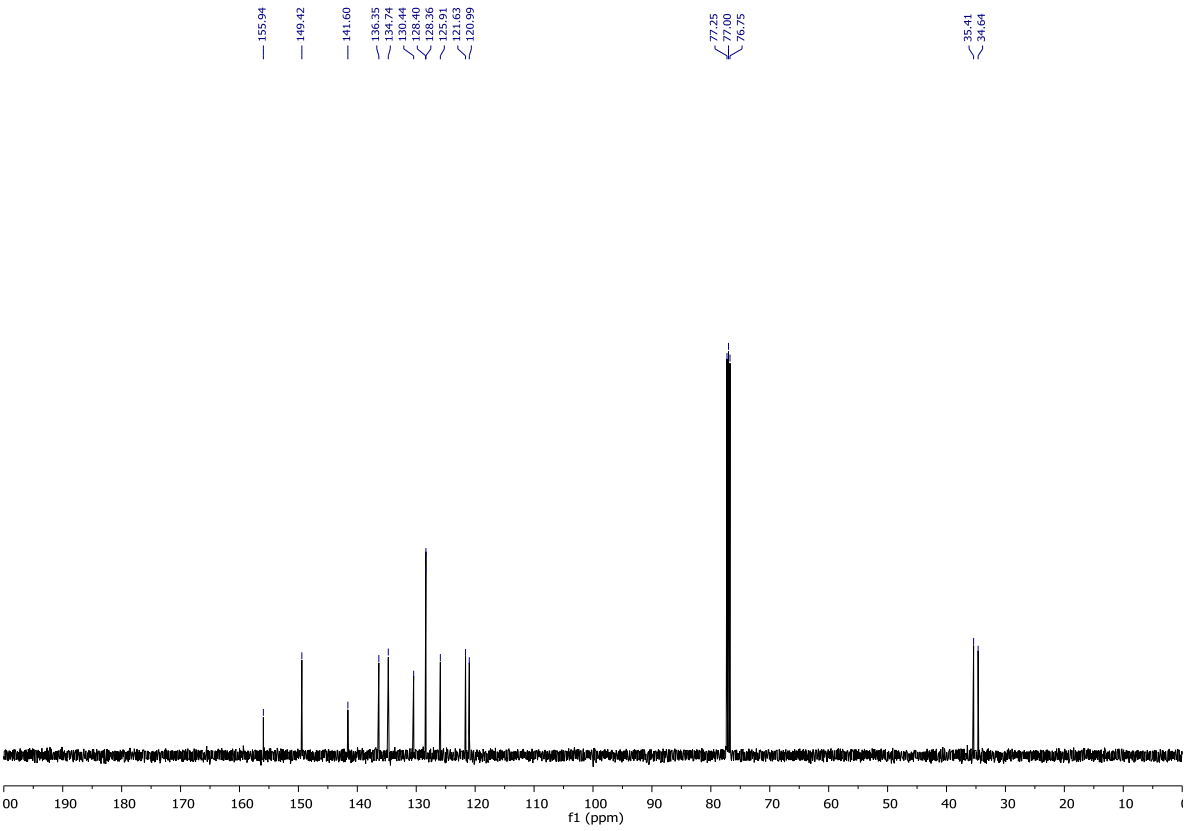

OMe
1k
0.94
1.99
1.00
1.04
4.01
0.96
3.00
f1 (ppm)
159.76
155.41
149.54
137.96
136.42
132.51
129.57
128.15
121.98
121.96
119.73
114.08
112.02
77.25
77.00
76.75
55.11
f1 (ppm)

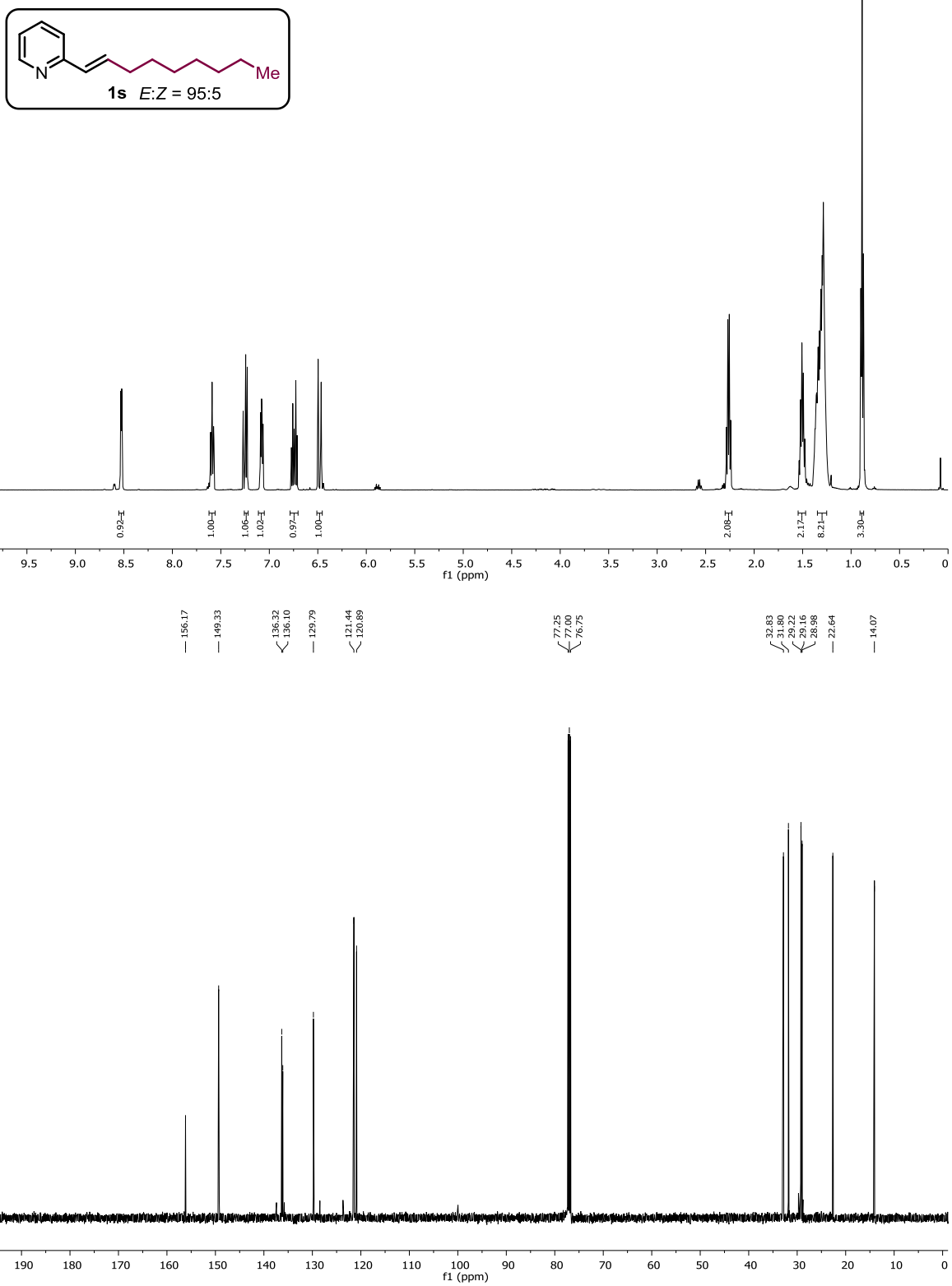

Me
N
1l
0.97
1.00
2.06
1.03
3.09
1.07
1.03
3.15
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
f1 (ppm)


155.82
149.67
136.54
136.49
135.71
130.48
129.25
128.15
126.17
125.67
122.13
122.00
77.42
77.00
76.58
20.00
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


OMe
OMe
N
1n
0.90
1.00
1.00
1.00
1.08
1.06
1.03
1.07
1.00
3.05
2.98
f1 (ppm)
155.99
153.02
149.53
147.45
136.36
130.78
129.58
127.17
124.03
121.92
121.64
118.49
112.00
77.32
77.00
76.68
61.08
55.75
f1 (ppm)


N
Ph
1r
0.94
1.02
2.01
4.06
0.99
1.00
1.00
2.09
2.11
f1 (ppm)


155.94
149.42
141.60
136.35
134.74
130.44
128.40
128.36
125.91
121.63
120.99
77.25
77.00
76.75
35.41
34.64
f1 (ppm)


Me
1s E:Z = 95:5
0.92
1.00
1.06
1.02
0.97
1.00
2.08
2.17
8.21
3.30
f1 (ppm)
156.17
149.33
136.32
136.10
129.79
121.44
120.89
77.25
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76.75
32.83
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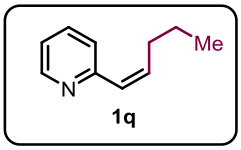
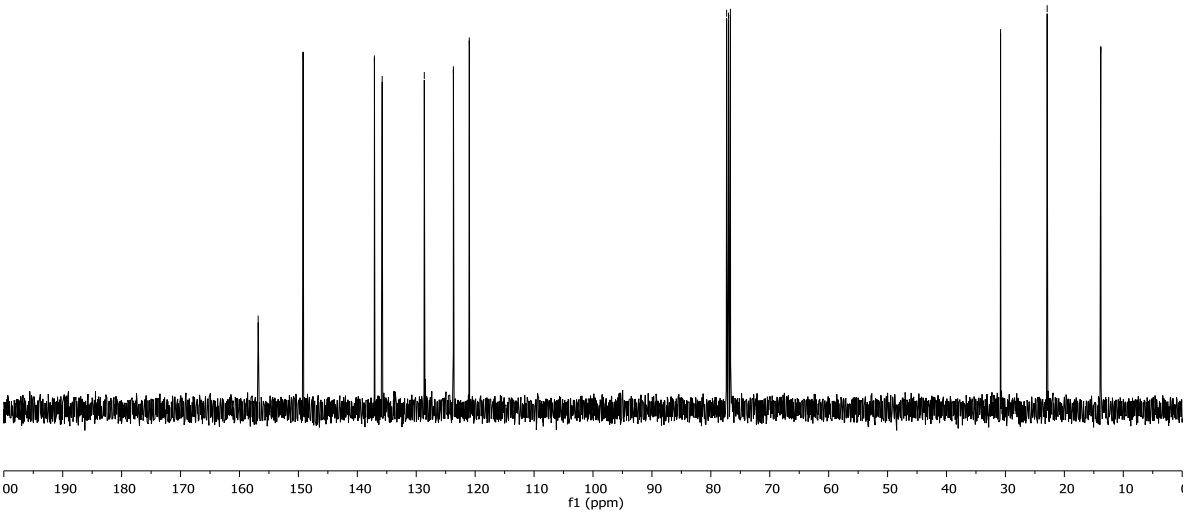
29.22
29.16
28.98
22.64
14.07
f1 (ppm)

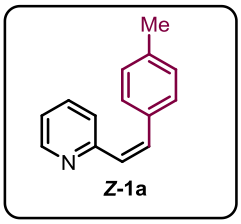

Me
N

1q

1.00
1.07
1.04
1.06
1.06
1.09
2.23
2.29
3.37
f1 (ppm)

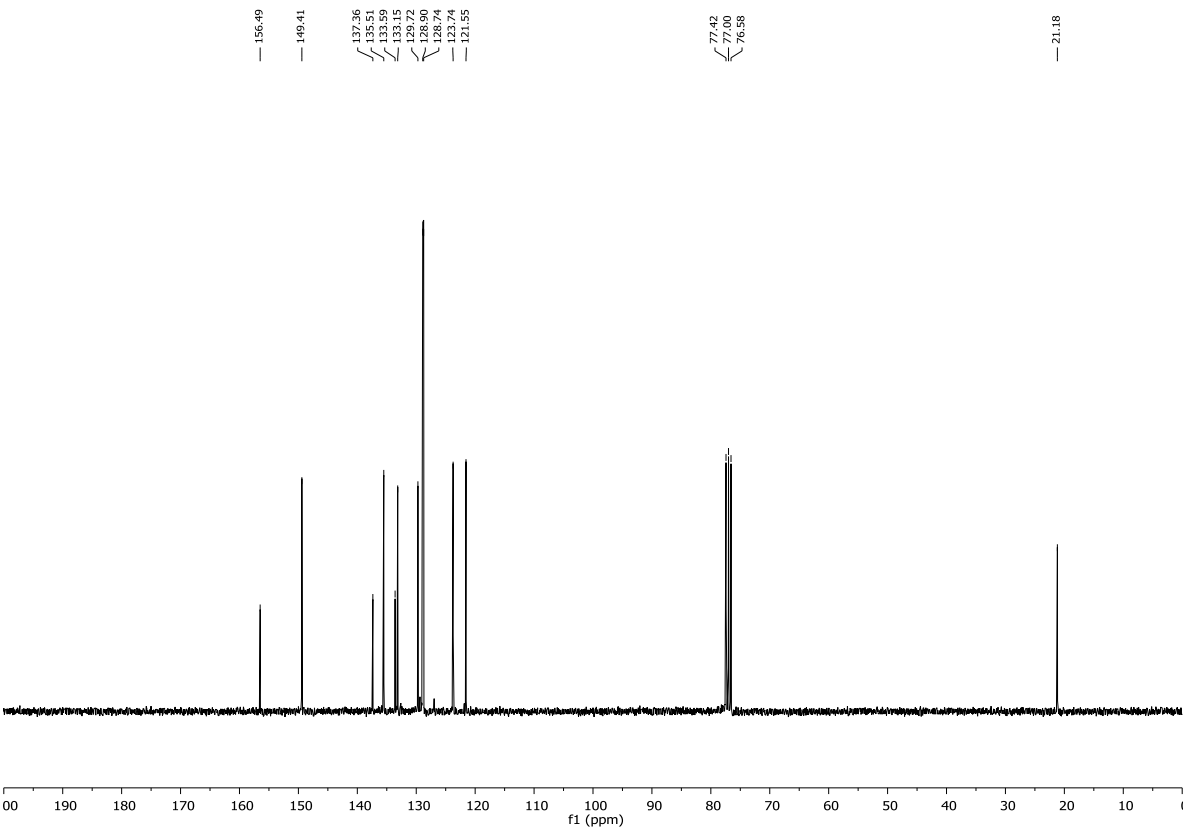

156.82
149.20
137.10
135.78
128.63
123.69
120.99
77.32
77.00
76.68
30.83
22.92
13.82

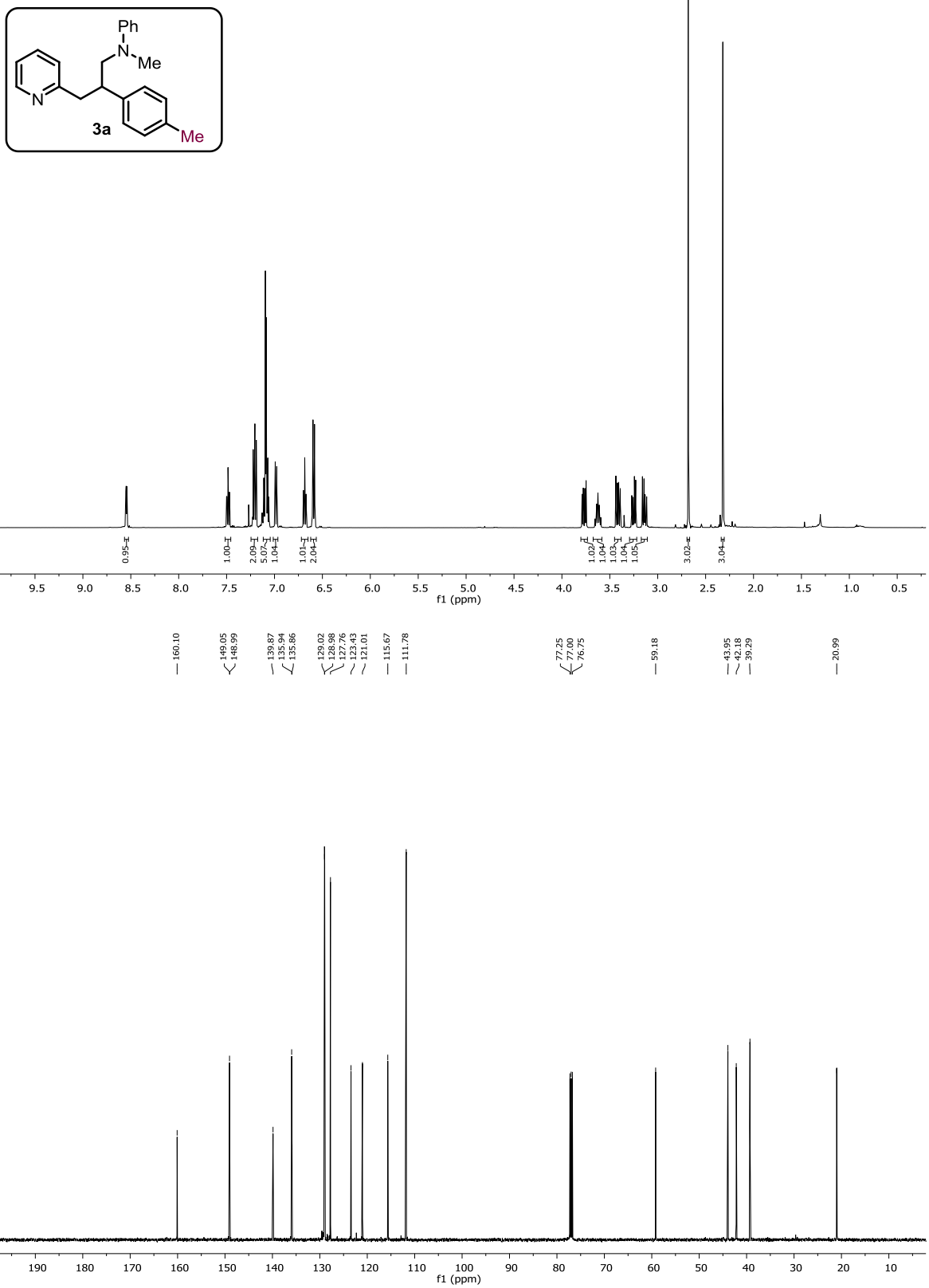

f1 (ppm)

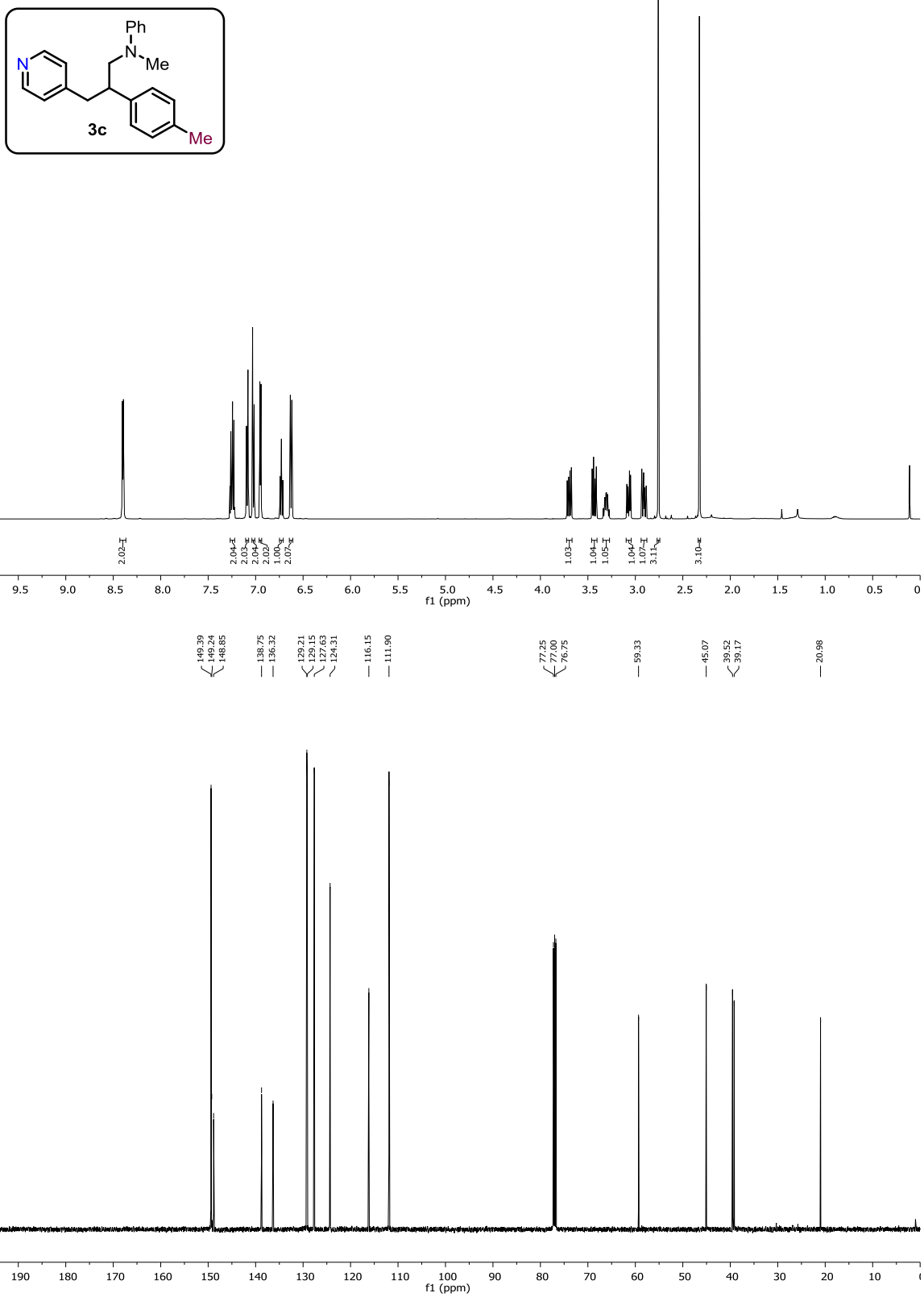

Me
N

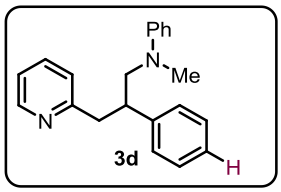
***Z*-1a**

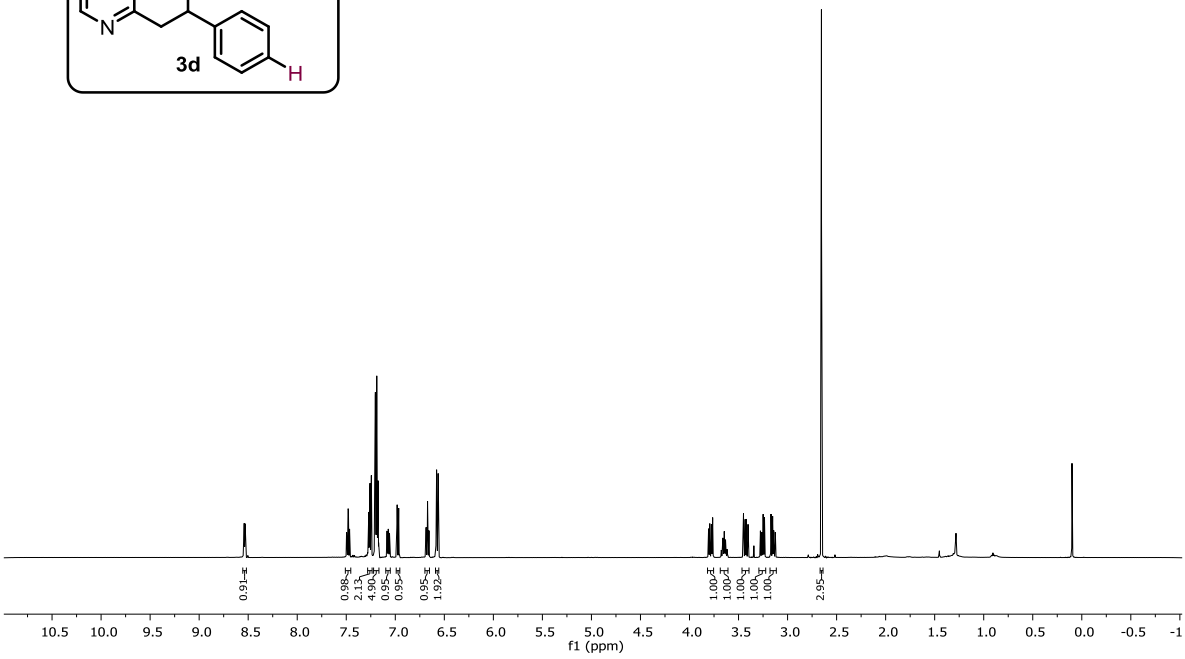
1.00
1.03
3.11
3.09
1.03
1.03
3.03
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
f1 (ppm)

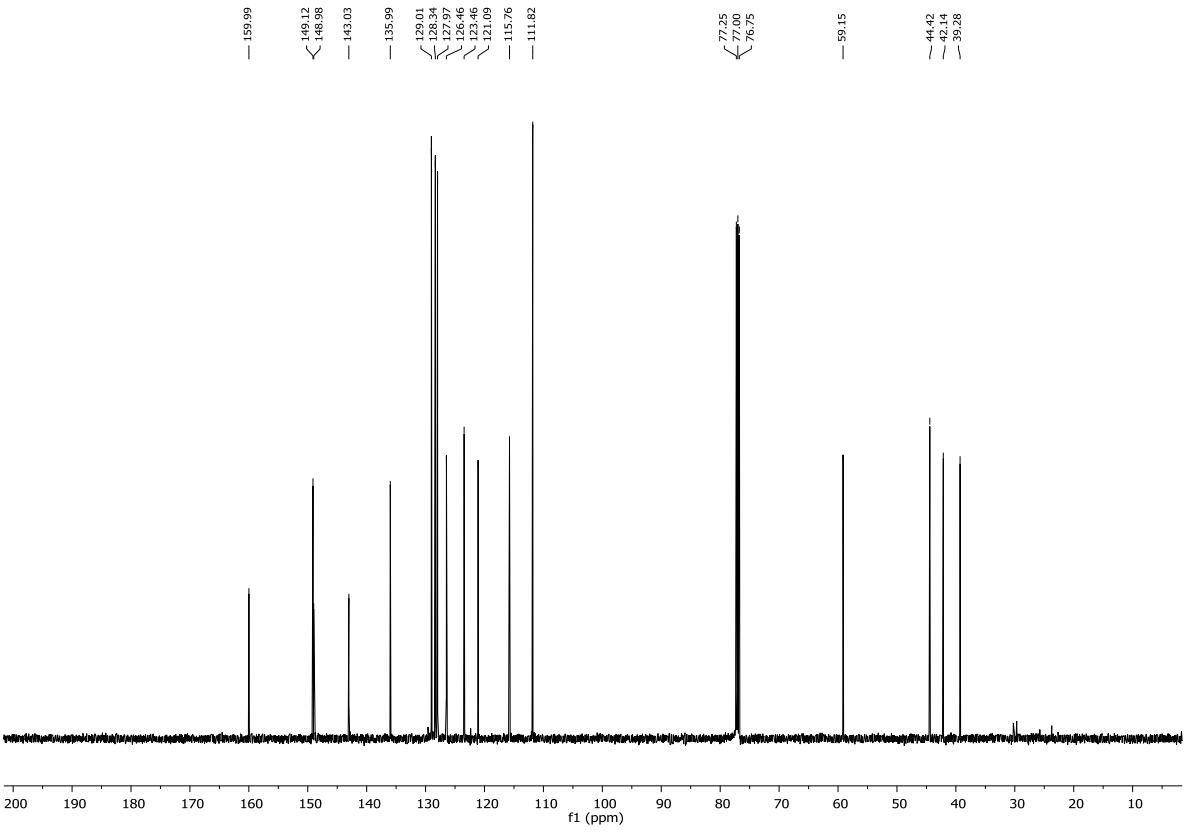

156.49
149.41
137.36
135.51
133.59
133.15
129.72
128.90
128.74
123.74
121.55
77.42
77.00
76.58
21.18
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

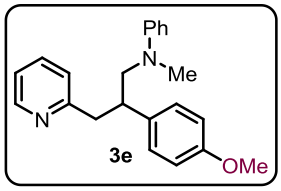

Ph
N
Me
N
3a
Me
0.95
1.00
2.09
5.07
1.04
1.01
2.04
1.02
1.04
1.03
1.04
1.05
3.02
3.04
f1 (ppm)
160.10
149.05
148.99
139.87
135.94
135.86
129.02
128.98
127.76
123.43
121.01
115.67
111.78
77.25
77.00
76.75
59.18
43.95
42.18
39.29
20.99
f1 (ppm)


Ph
N
Me
N
3c
Me
2.02
2.04
2.03
2.04
2.02
1.00
2.07
1.03
1.04
1.05
1.04
1.07
3.11
3.10
f1 (ppm)
149.39
149.24
148.85
138.75
136.32
129.21
129.15
127.63
124.31
116.15
111.90
77.25
77.00
76.75
59.33
45.07
39.52
39.17
20.98
f1 (ppm)


Ph
N
Me
N
3d
H


0.91
0.98
2.13
4.90
0.95
0.95
1.92
1.00
1.00
1.00
1.00
1.00
2.95
10.5 10.0 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 0.5 0.0 -0.5 -1
f1 (ppm)


159.99
149.12
148.98
143.03
135.99
129.01
128.34
127.97
126.46
123.46
121.09
115.76
111.82
77.25
77.00
76.75
59.15
44.42
42.14
39.28
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)



160.09
158.13
149.08
148.99
135.97
134.96
129.01
128.83
123.47
121.04
115.69
113.73
111.79
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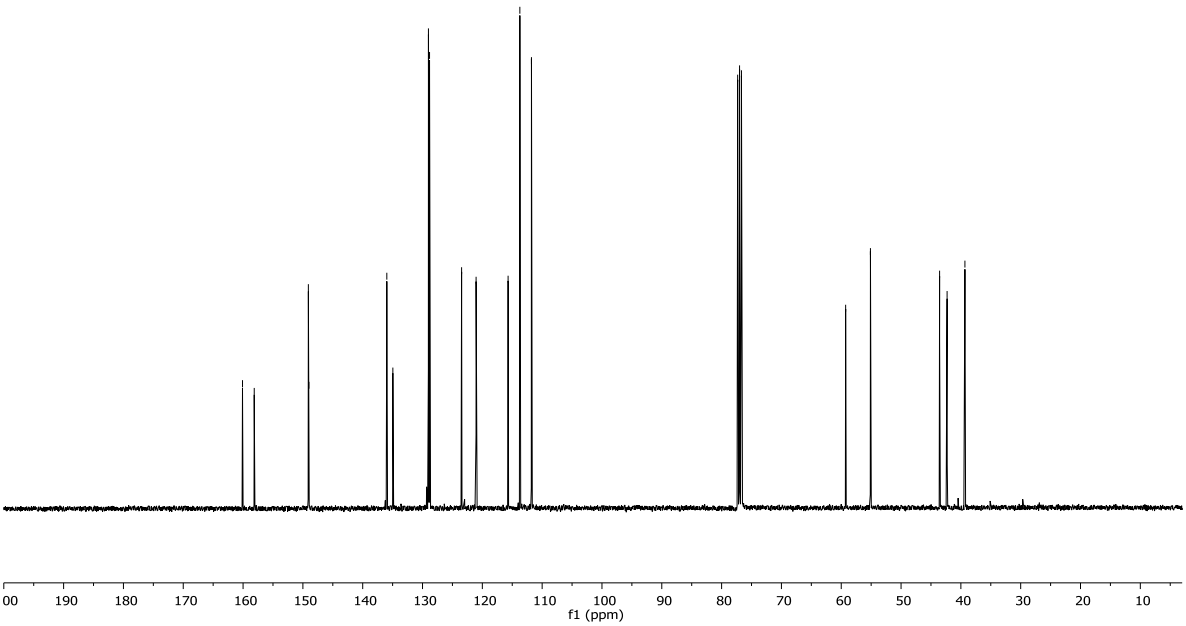
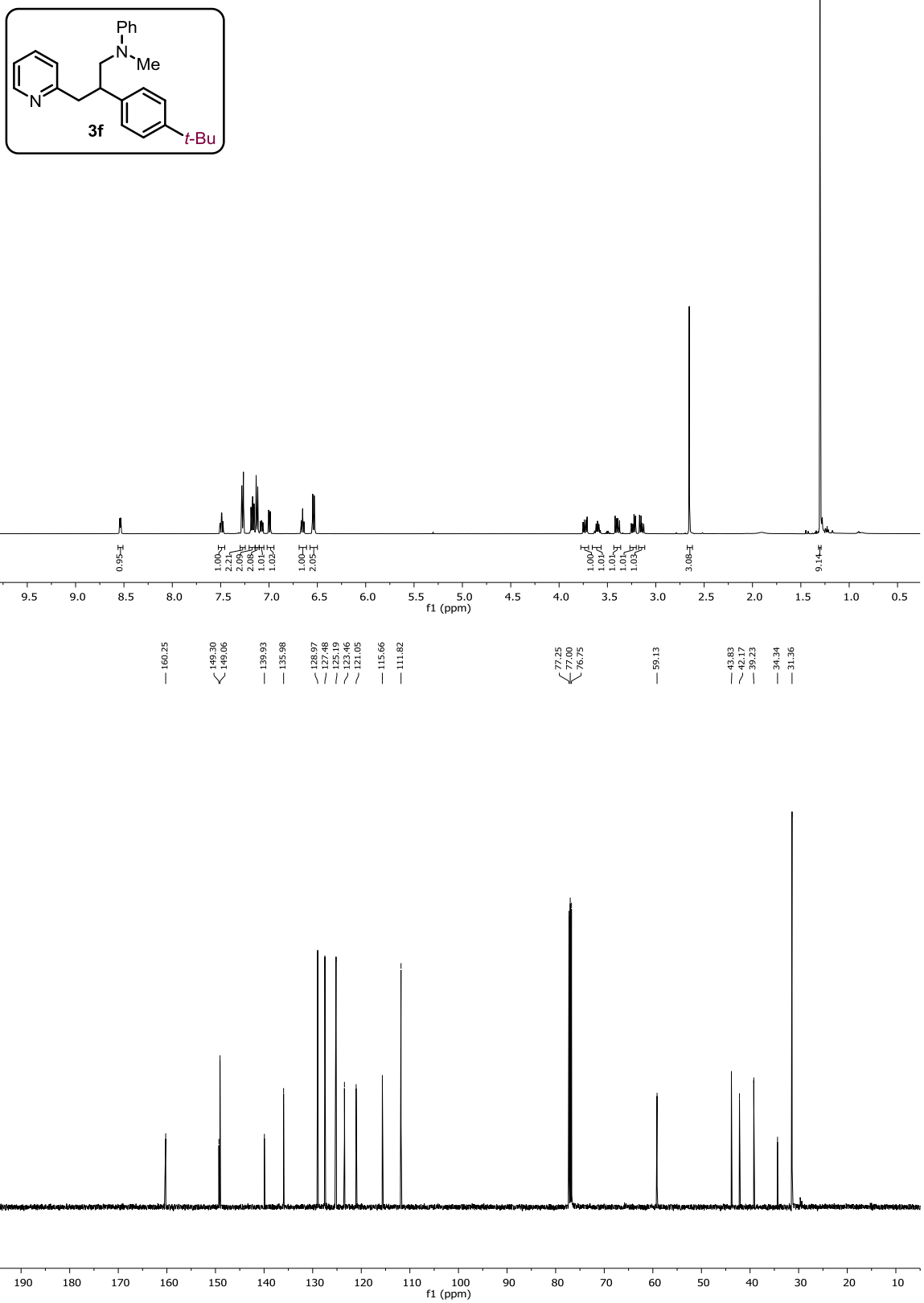
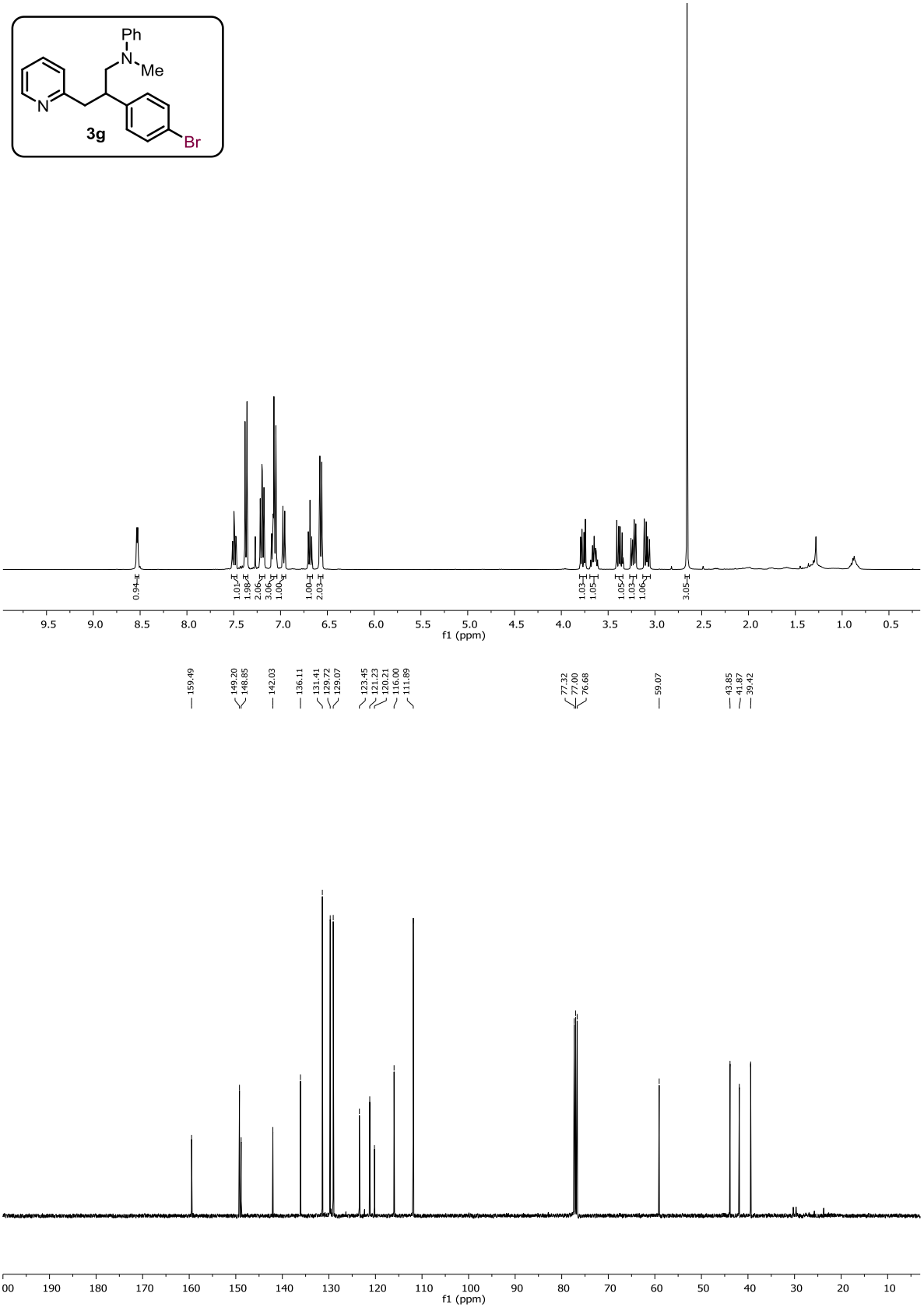
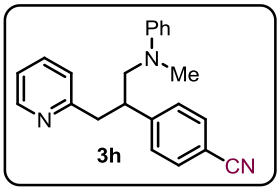
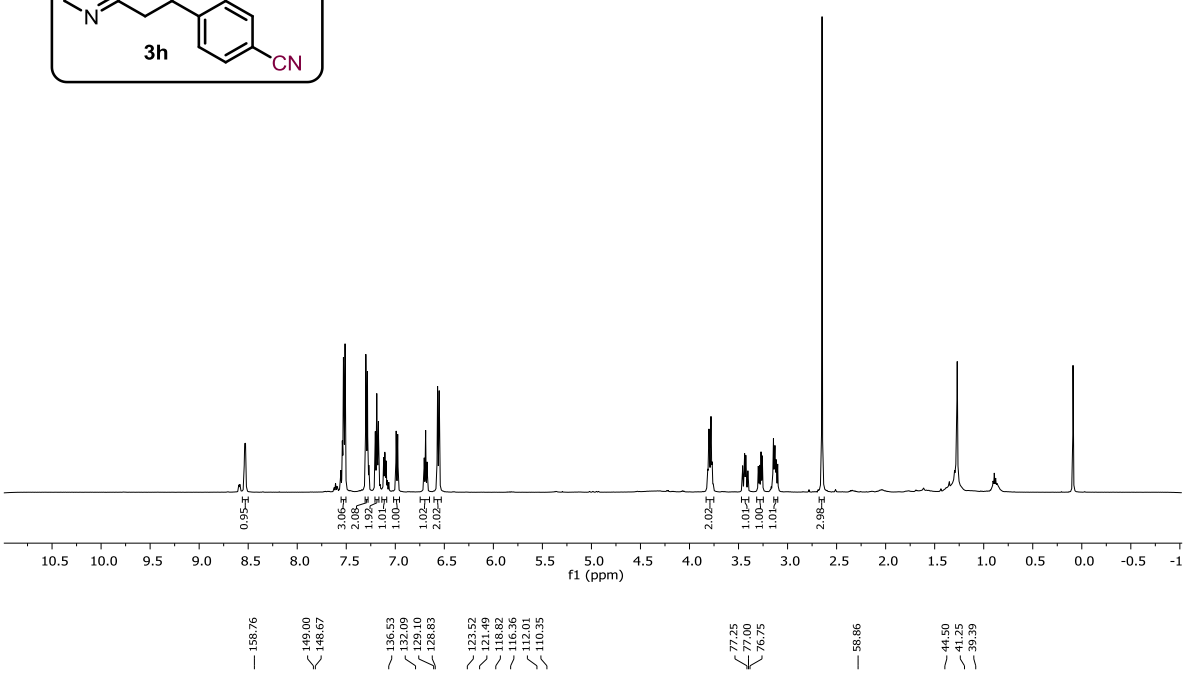
76.68
59.26
55.12
43.56
42.30
39.33



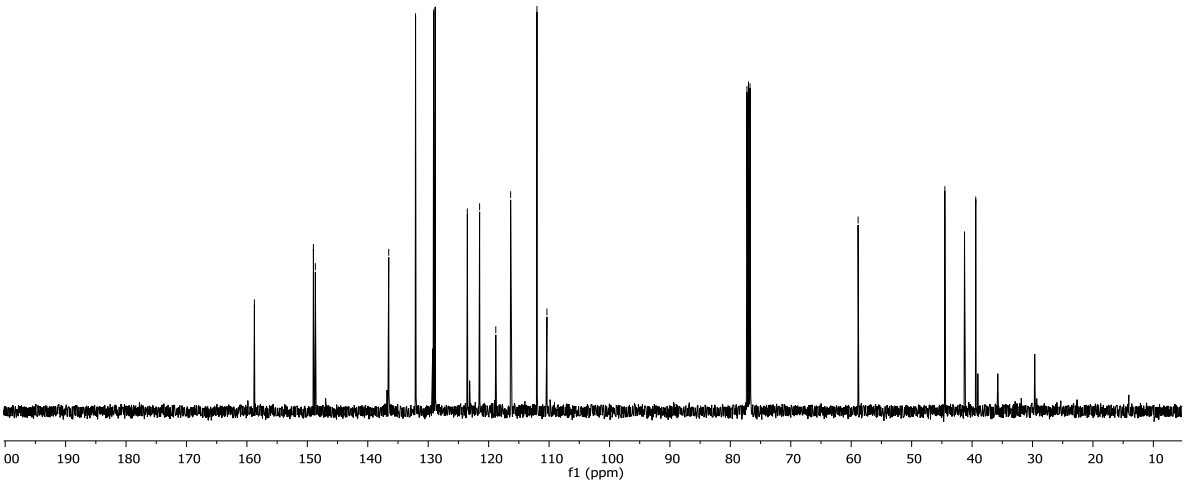

Ph
N
Me
N
3f
t-Bu
0.95
1.00
2.21
2.09
2.08
1.01
1.02
1.00
2.05
1.00
1.01
1.01
1.01
1.03
3.08
9.14
f1 (ppm)
160.25
149.30
149.06
139.93
135.98
128.97
127.48
125.19
123.46
121.05
115.66
111.82
77.25
77.00
76.75
59.13
43.83
42.17
39.23
34.34
31.36
f1 (ppm)

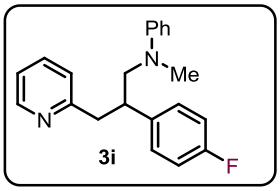

Ph
N
Me
N
3g
Br
0.94
1.01
1.98
2.06
3.06
1.00
1.00
2.03
1.03
1.05
1.05
1.03
1.06
3.05
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)
159.49
149.20
148.85
142.03
136.11
131.41
129.72
129.07
123.45
121.23
120.21
116.00
111.89
77.32
77.00
76.68
59.07
43.85
41.87
39.42
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


Ph
N
Me
N
3h
CN


0.95
3.06
2.08
1.92
1.01
1.00
1.02
2.02
2.02
1.01
1.00
1.01
2.98
10.5 10.0 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 0.5 0.0 -0.5 -1
f1 (ppm)

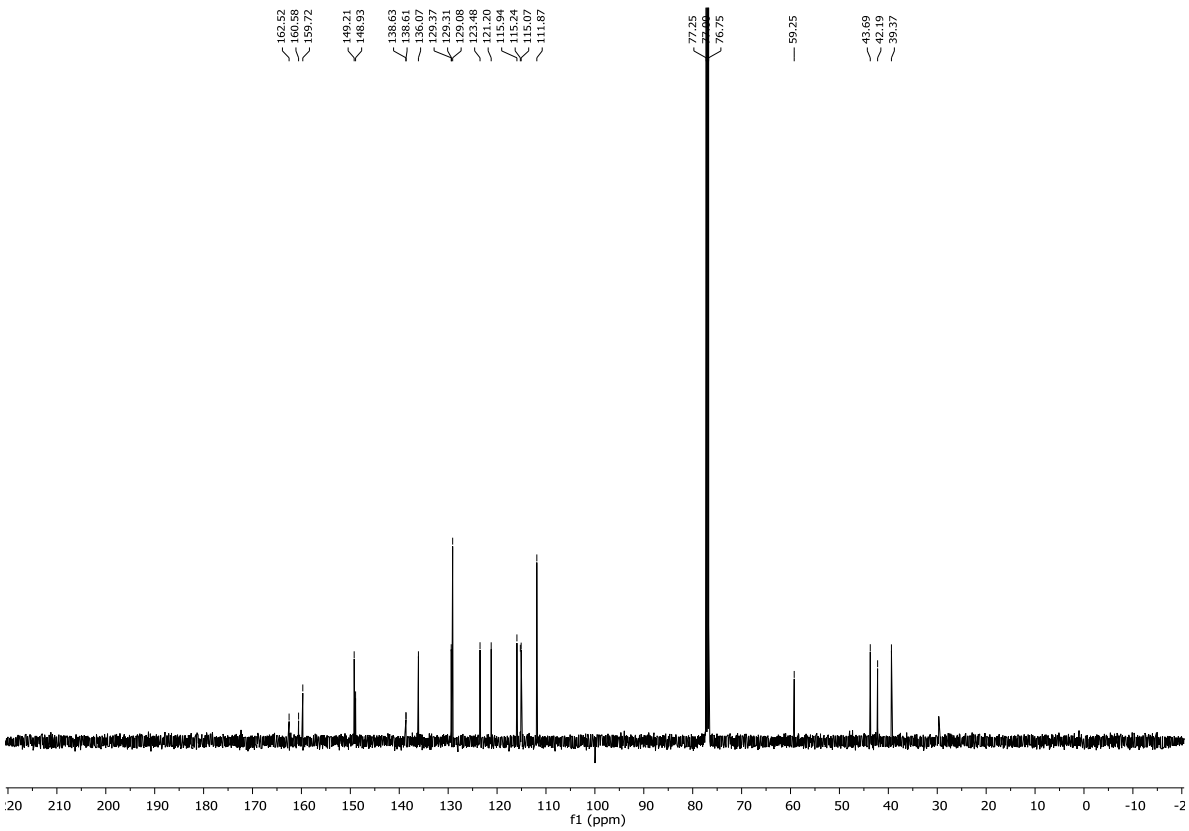
158.76
149.00
148.67
136.53
132.09
129.10
128.83
123.52
121.49
118.82
116.36
112.01
110.35
77.25
77.00
76.75
58.86
44.50
41.25
39.39

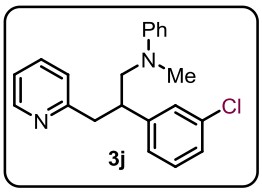

00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


Ph
N
Me
N
F

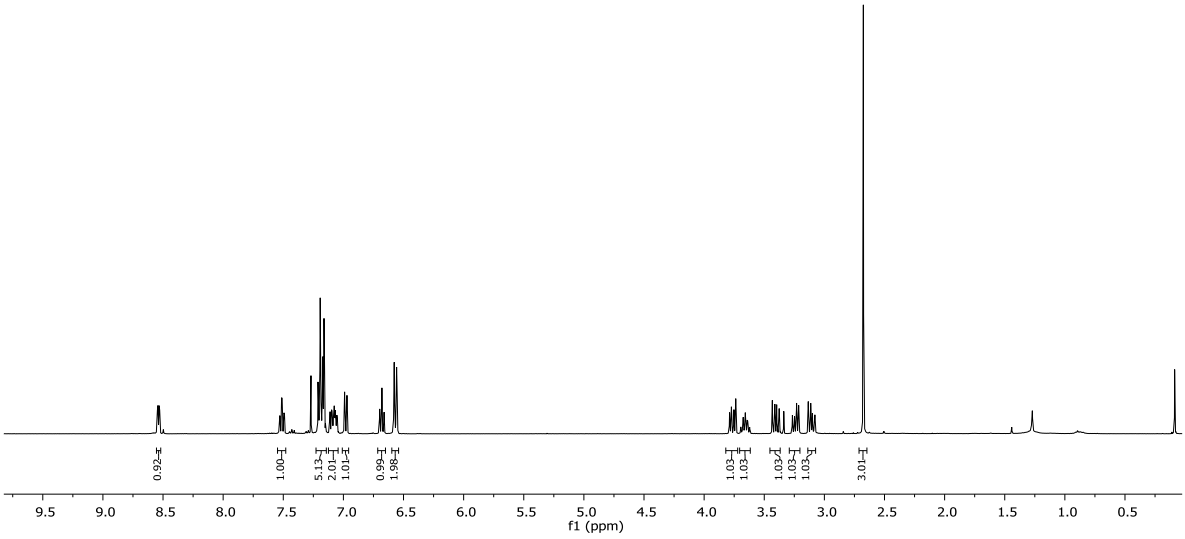
3i

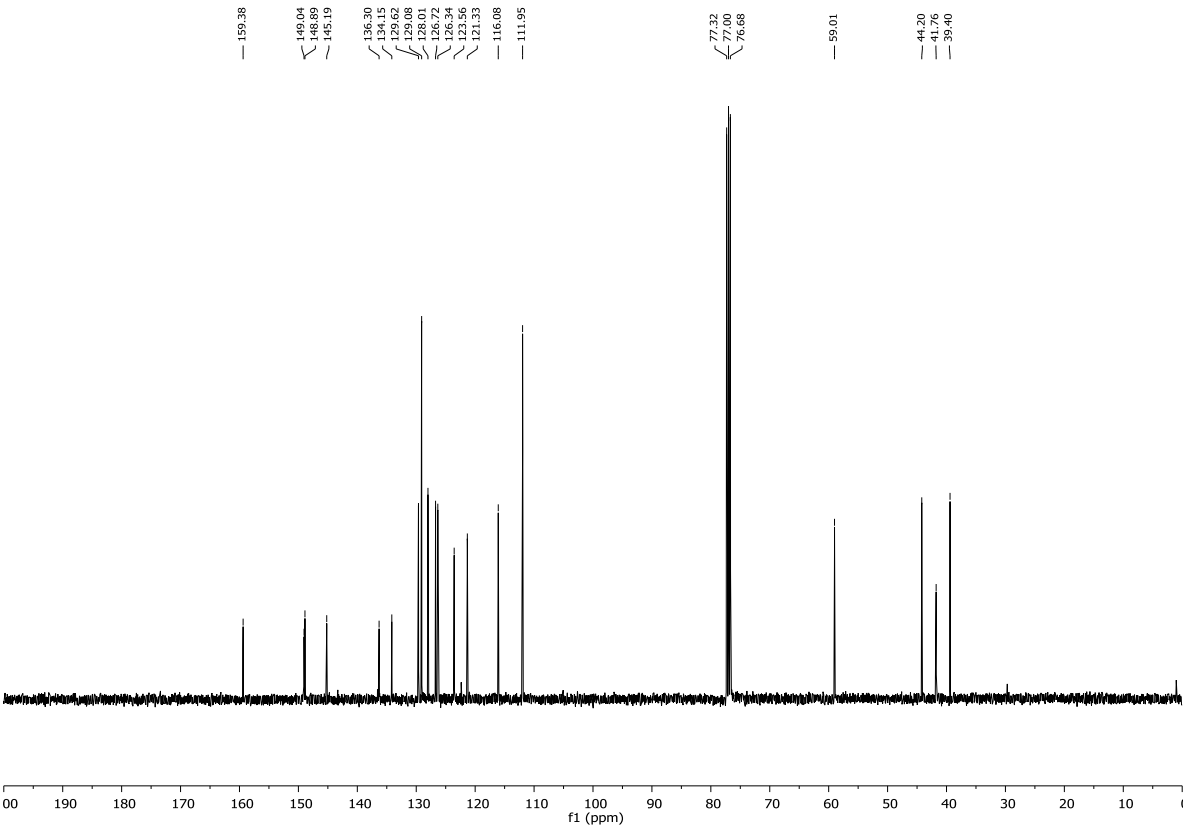
0.96
1.00
2.02
2.06
1.00
3.01
1.00
2.04
1.07
1.05
1.05
1.06
1.05
3.10
f1 (ppm)

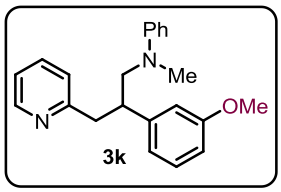

162.52
160.58
159.72
149.21
148.93
138.63
138.61
136.07
129.37
129.31
129.08
123.48
121.20
115.94
115.24
115.07
111.87
77.25
77.00
76.75
59.25
43.69
42.19
39.37
f1 (ppm)


Ph
N
Me
N
Cl

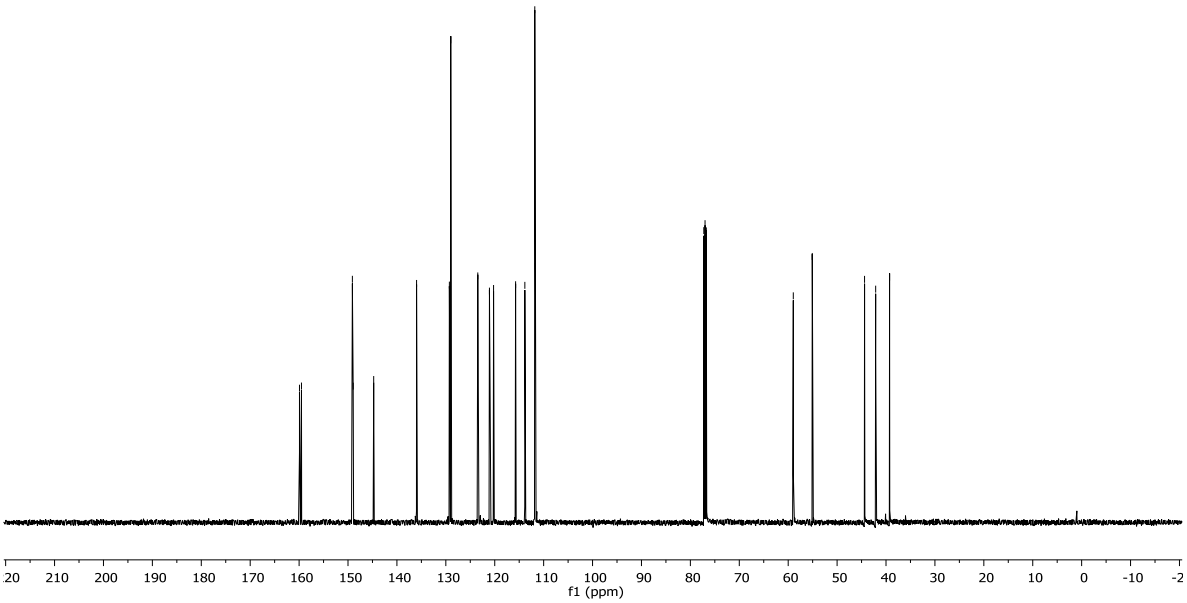
3j

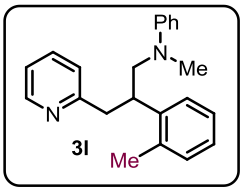

0.92
1.00
5.13
2.01
1.01
0.99
1.98
1.03
1.03
1.03
1.03
3.01
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

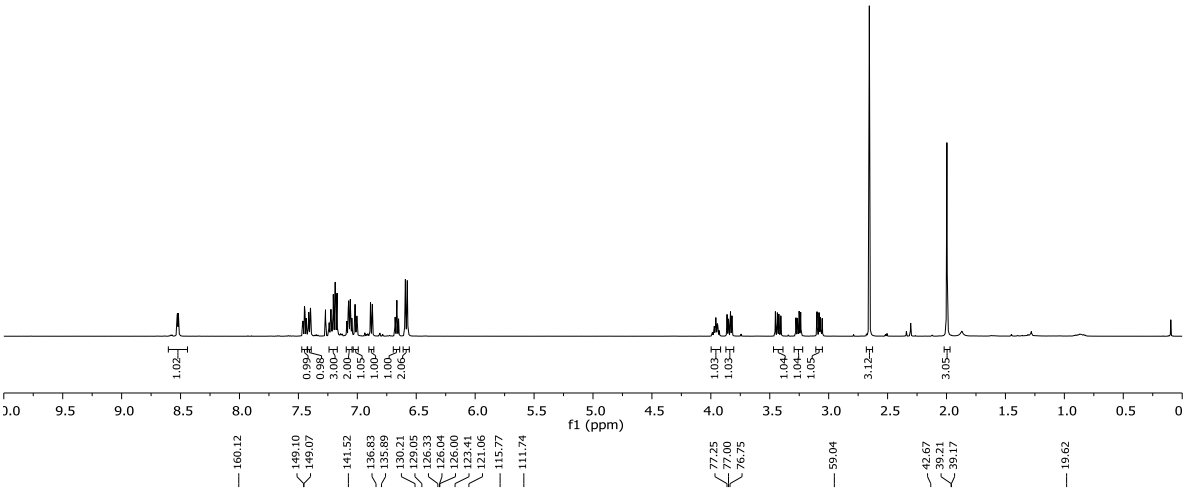

159.38
149.04
148.89
145.19
136.30
134.15
129.62
129.08
128.01
126.72
125.54
123.56
121.33
116.08
111.95
77.32
77.00
76.68
59.01
44.20
41.76
39.40
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)



159.92
159.51
149.11
148.94
144.75
135.98
129.27
128.99
123.47
121.08
120.24
115.23
113.84
111.81
111.74
77.25
77.00
76.74
58.96
55.08
44.39
42.11
39.27




Ph
N
Me
N
3l
Me


1.02
0.99
0.98
3.00
2.00
1.05
1.00
1.00
2.06
1.03
1.03
1.04
1.04
1.05
3.12
3.05
f1 (ppm)
160.12
149.10
149.07
141.52
136.83
135.89
130.21
129.05
126.33
126.04
126.00
123.41
121.06
115.77
111.74
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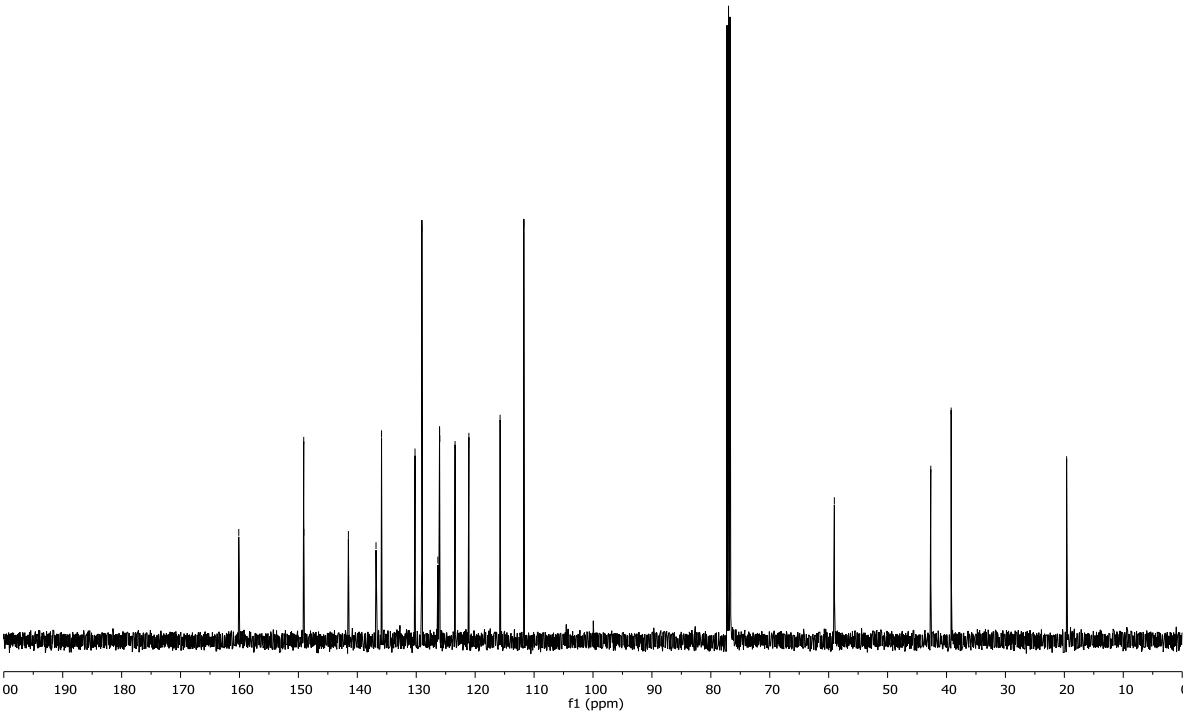
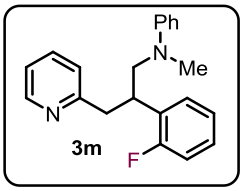
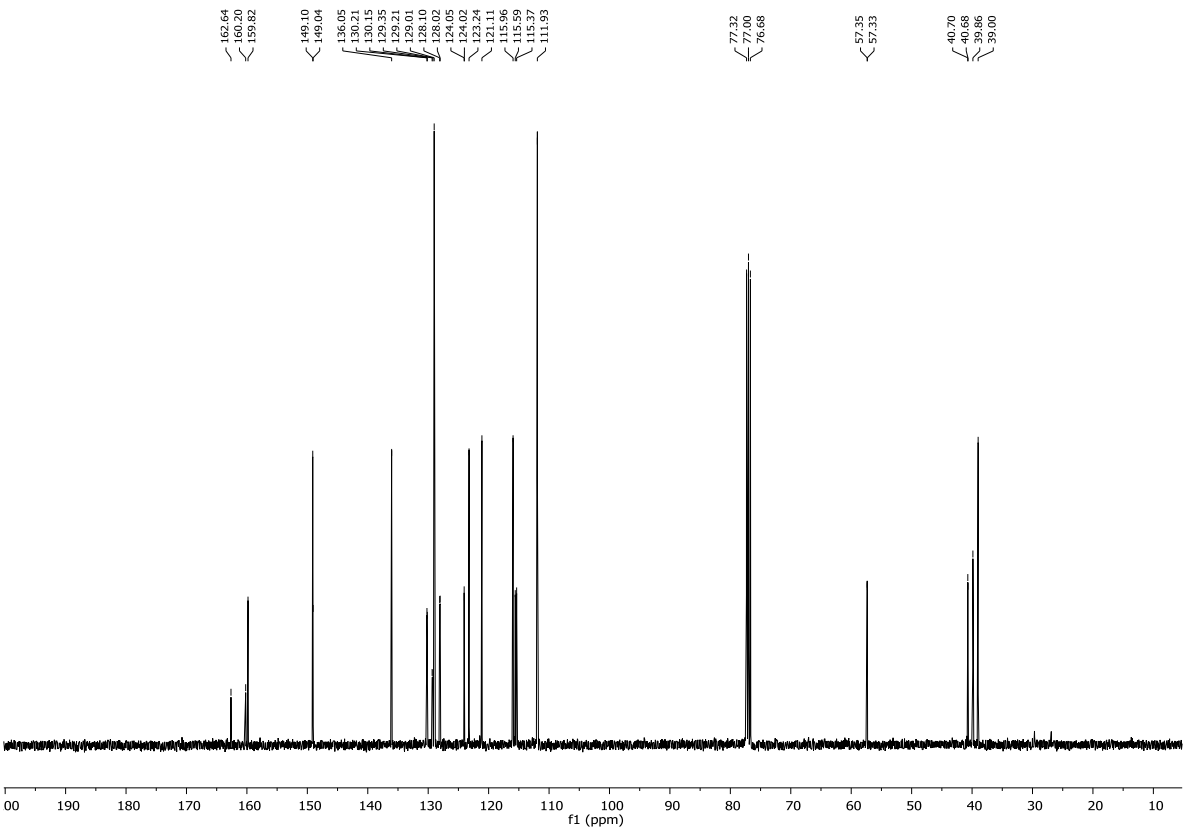
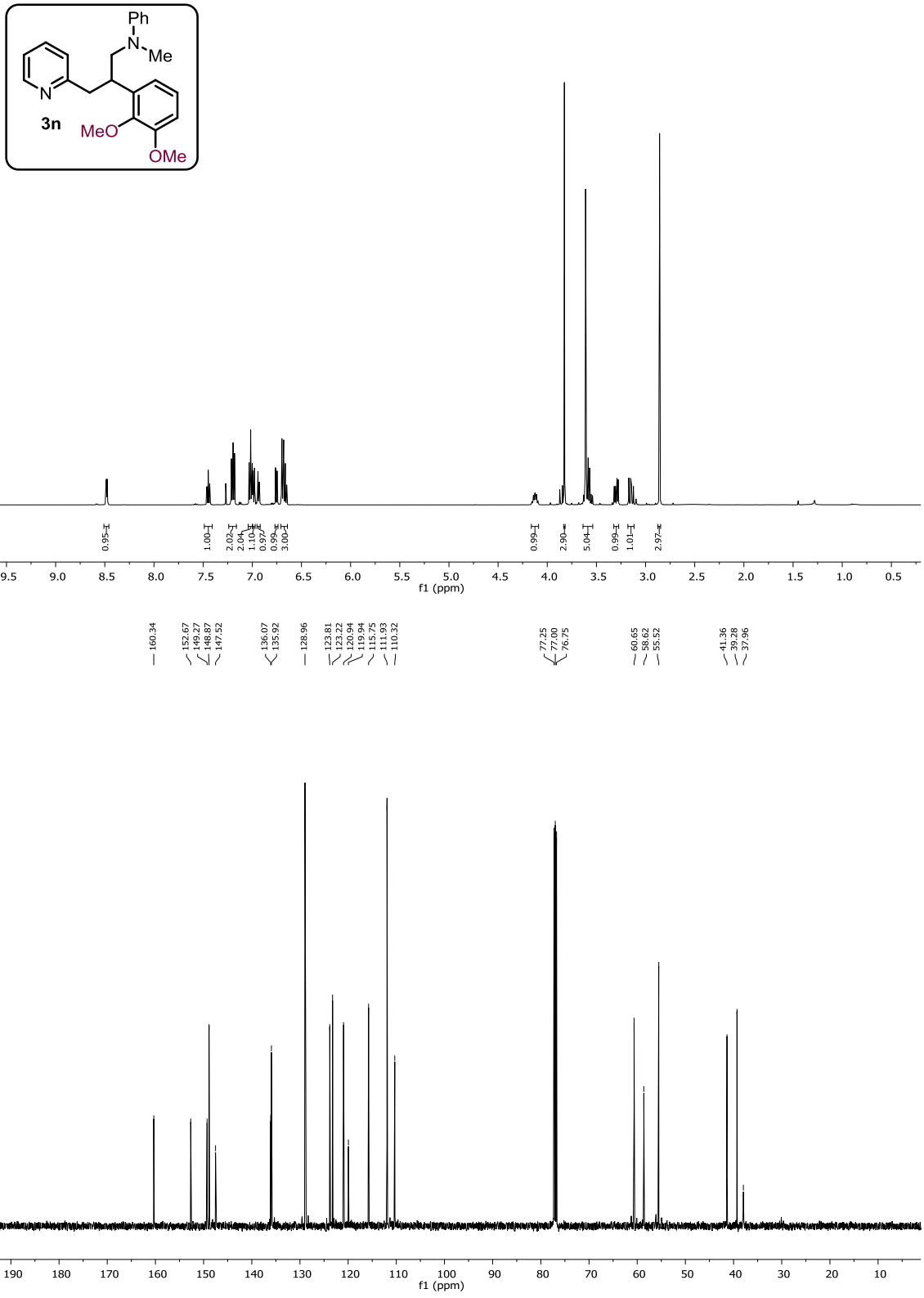
77.00
76.75
59.04
42.67
39.21
39.17
19.62

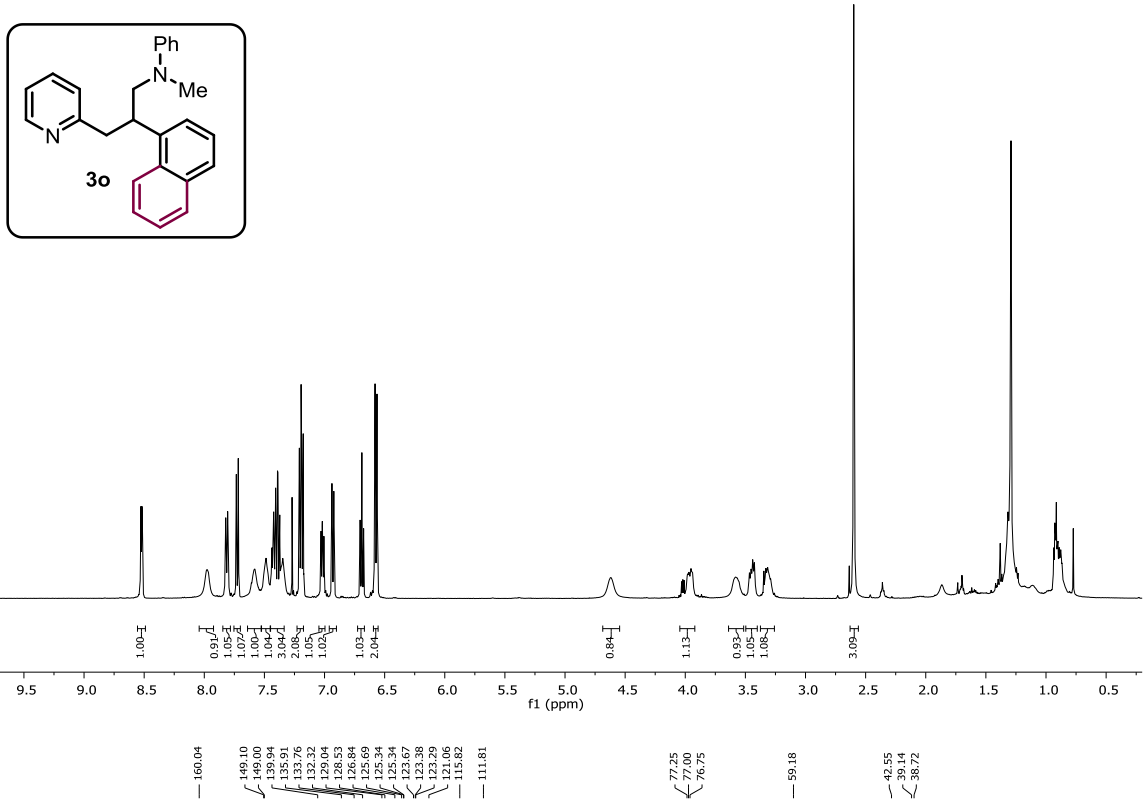

f1 (ppm)


Ph
N
Me
N
3m
F

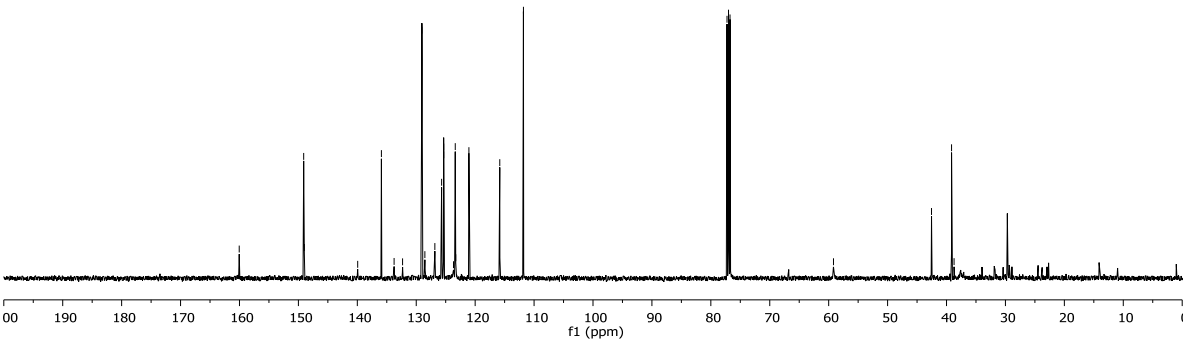
0.96
1.00
4.12
1.03
3.01
1.04
2.02
1.05
1.06
1.05
1.08
1.04
3.08
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

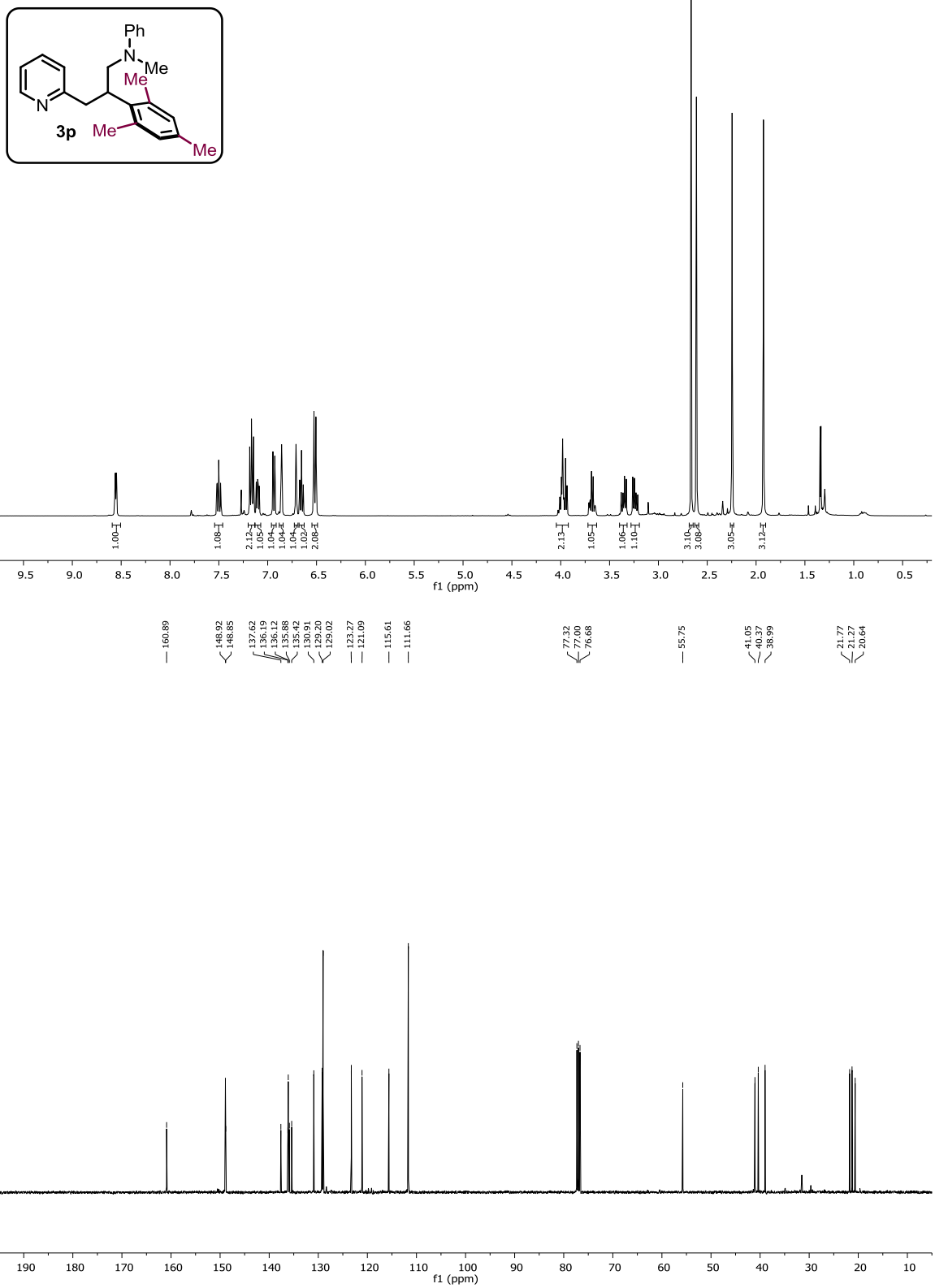

162.64
160.20
159.82
149.10
149.04
136.05
130.21
130.15
129.35
129.21
129.01
128.10
128.02
124.05
124.02
123.24
121.11
115.96
115.59
115.37
111.93
77.32
77.00
76.68
57.35
57.33
40.70
40.68
39.86
39.00
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

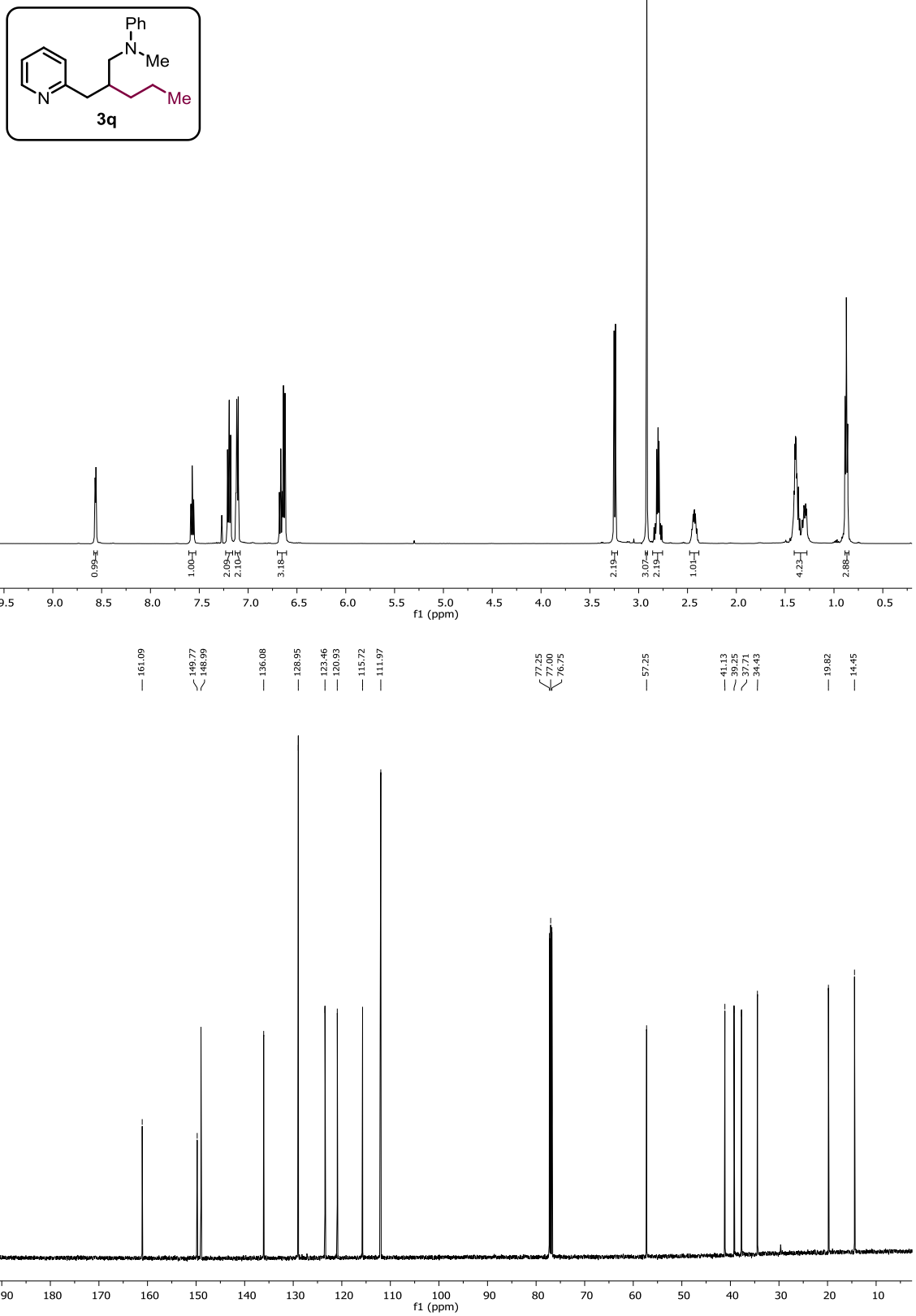

Ph
N
Me
N
3n
MeO
OMe
0.95
1.00
2.03
2.04
1.10
0.97
0.99
3.00
0.99
2.90
5.04
0.99
1.01
2.97
f1 (ppm)
160.34
152.67
149.27
148.87
147.52
136.07
135.92
128.96
123.81
123.22
120.94
119.94
115.75
111.93
110.32
77.25
77.00
76.75
60.65
58.62
55.52
41.36
39.28
37.96
f1 (ppm)

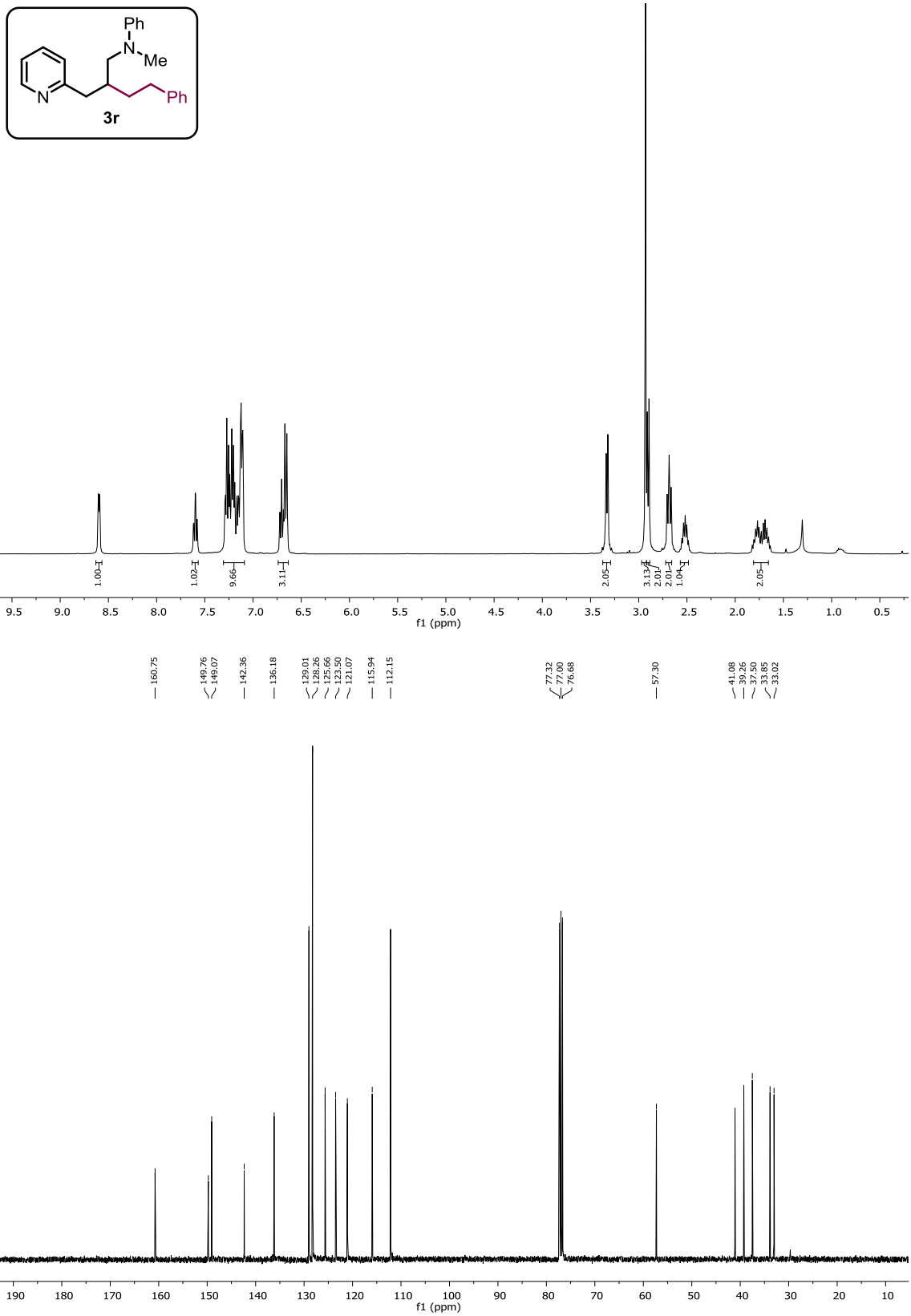

Ph
N
Me
N
3o
1.00
0.91
1.05
1.02
1.00
1.04
3.04
2.08
1.05
1.02
1.03
2.04
0.84
1.13
0.93
1.05
1.08
3.09
f1 (ppm)

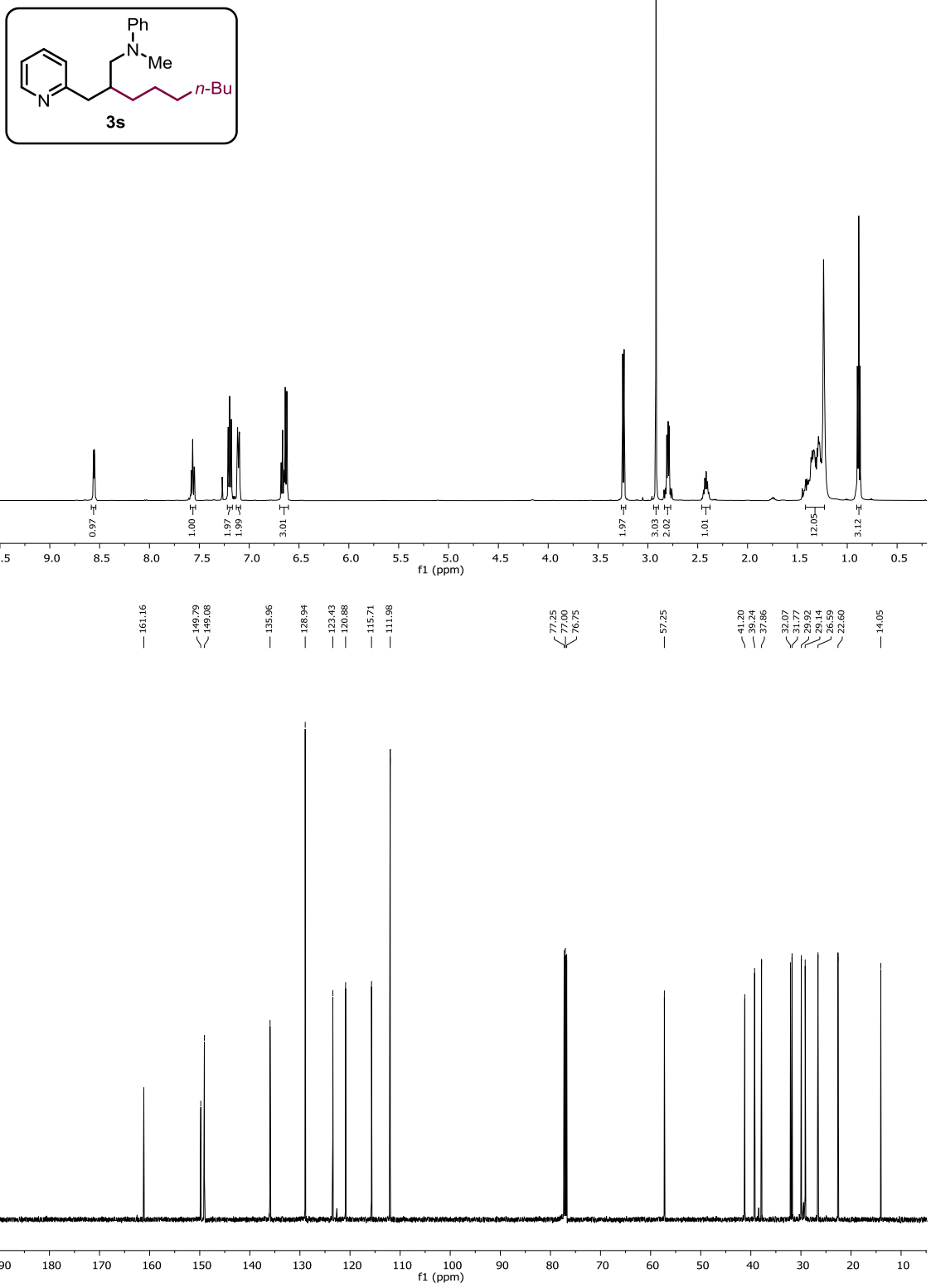
160.04
149.10
149.00
139.94
135.91
133.76
132.32
129.04
128.53
126.84
125.69
125.34
125.34
123.67
123.38
123.29
121.06
115.82
111.81
77.25
77.00
76.75
59.18
42.55
39.14
38.72

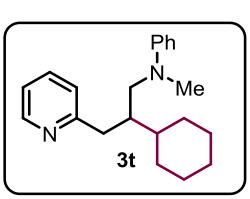

f1 (ppm)


Ph
N
Me
Me
N
3p
Me
Me
1.00
1.08
2.12
1.05
1.04
1.04
1.04
1.02
2.08
2.13
1.05
1.06
1.10
3.10
3.08
3.05
3.12
f1 (ppm)
160.89
148.92
148.85
137.62
136.19
136.12
135.88
135.42
130.91
129.20
129.02
123.27
121.09
115.61
111.66
77.32
77.00
76.68
55.75
41.05
40.37
38.99
21.77
21.27
20.64
f1 (ppm)


Ph
N
Me
N
Me
3q
0.99
1.00
2.09
2.10
3.18
2.19
3.07
2.19
1.01
4.23
2.88
f1 (ppm)
161.09
149.77
148.99
136.08
128.95
123.46
120.93
115.72
111.97
77.25
77.00
76.75
57.25
41.13
39.25
37.71
34.43
19.82
14.45
f1 (ppm)

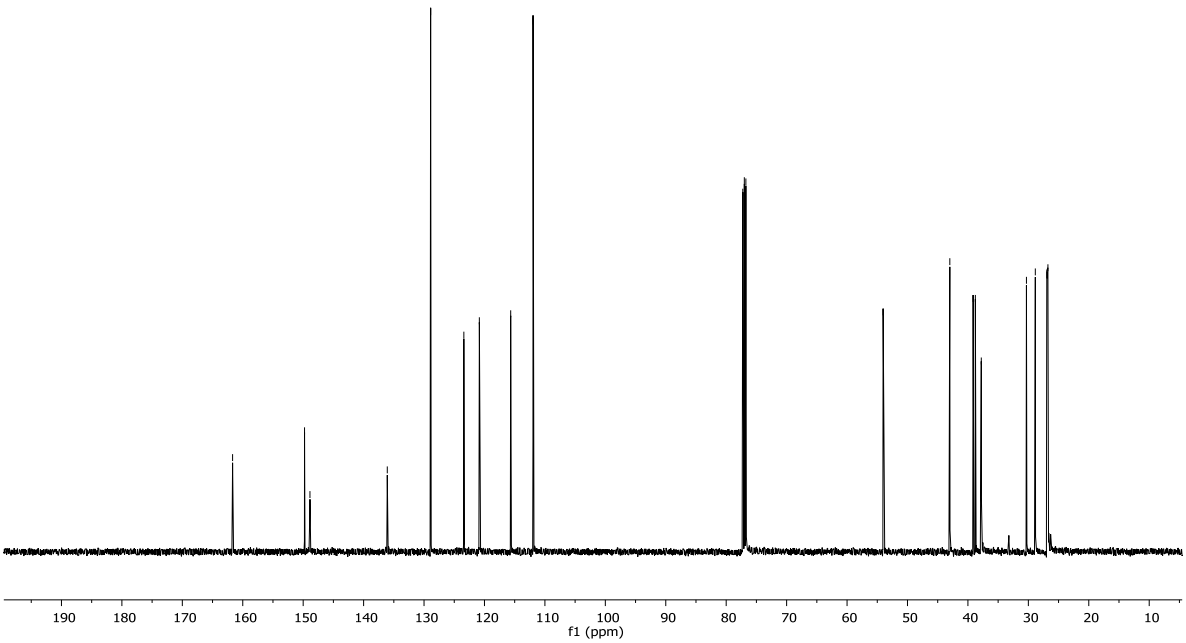

Ph
N
Me
N
Ph
3r
1.00
1.02
9.66
3.11
2.05
3.13
2.01
2.01
1.04
2.05
f1 (ppm)
160.75
149.76
149.07
142.36
136.18
129.01
128.26
125.66
123.50
121.07
115.94
112.15
77.32
77.00
76.68
57.30
41.08
39.26
37.50
33.85
33.02
f1 (ppm)

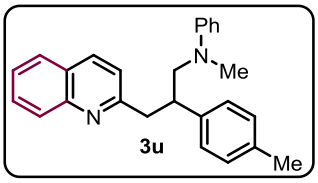

Ph
N
Me
n-Bu
N
3s
0.97
1.00
1.97
1.99
3.01
1.97
3.03
2.02
1.01
12.05
3.12
f1 (ppm)
161.16
149.79
149.08
135.96
128.94
123.43
120.88
115.71
111.98
77.25
77.00
76.75
57.25
41.20
39.24
37.86
32.07
31.77
29.92
29.14
26.59
22.60
14.05
f1 (ppm)


Ph
N
Me
N
3t

0.97
0.97
2.02
2.03
0.98
2.02
1.03
1.02
1.12
3.03
1.00
1.01
3.02
2.06
1.04
5.19
f1 (ppm)

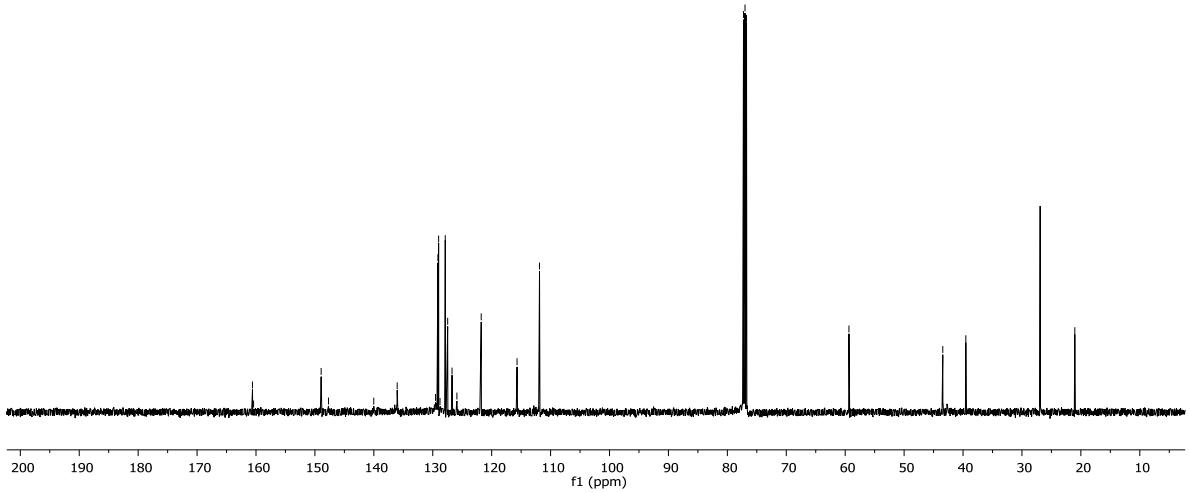

161.68
149.78
148.88
136.08
128.91
123.41
120.85
115.66
111.96
77.25
77.00
76.74
54.03
42.99
39.14
38.77
37.79
30.32
28.85
26.95
26.83
26.76

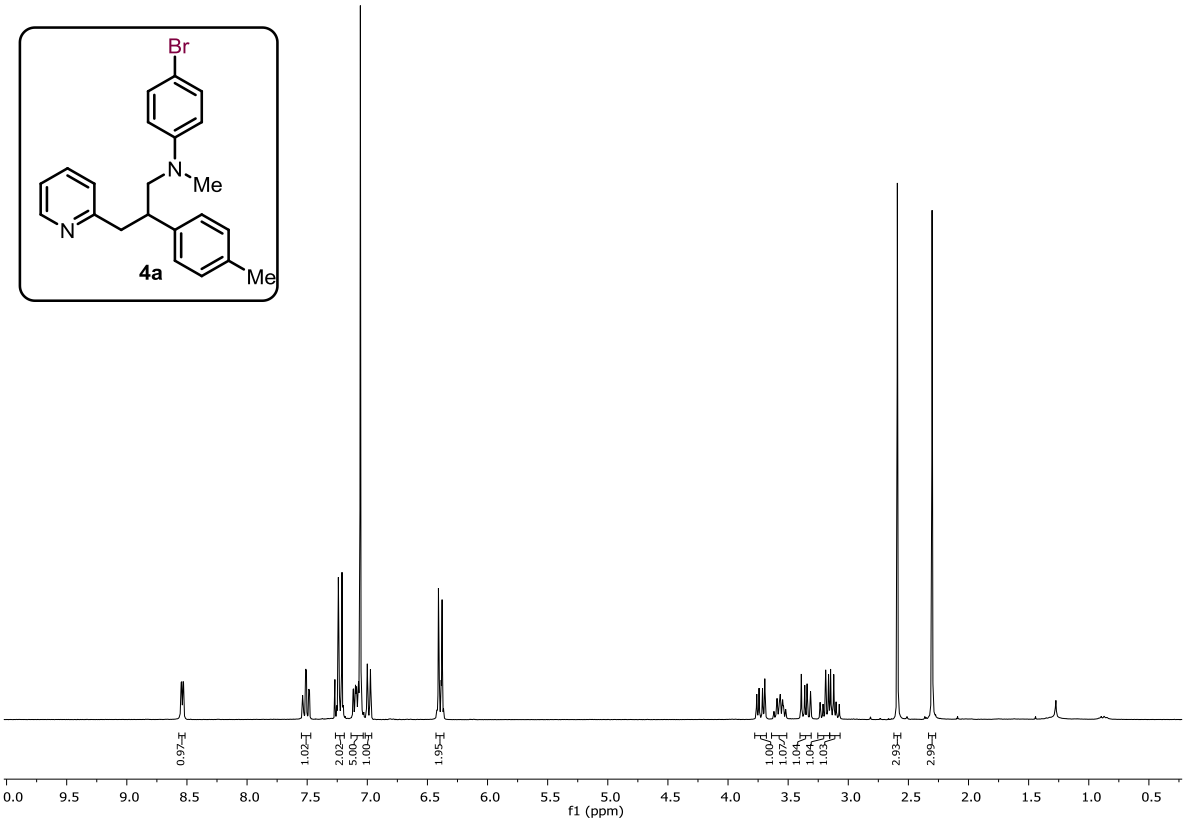

f1 (ppm)

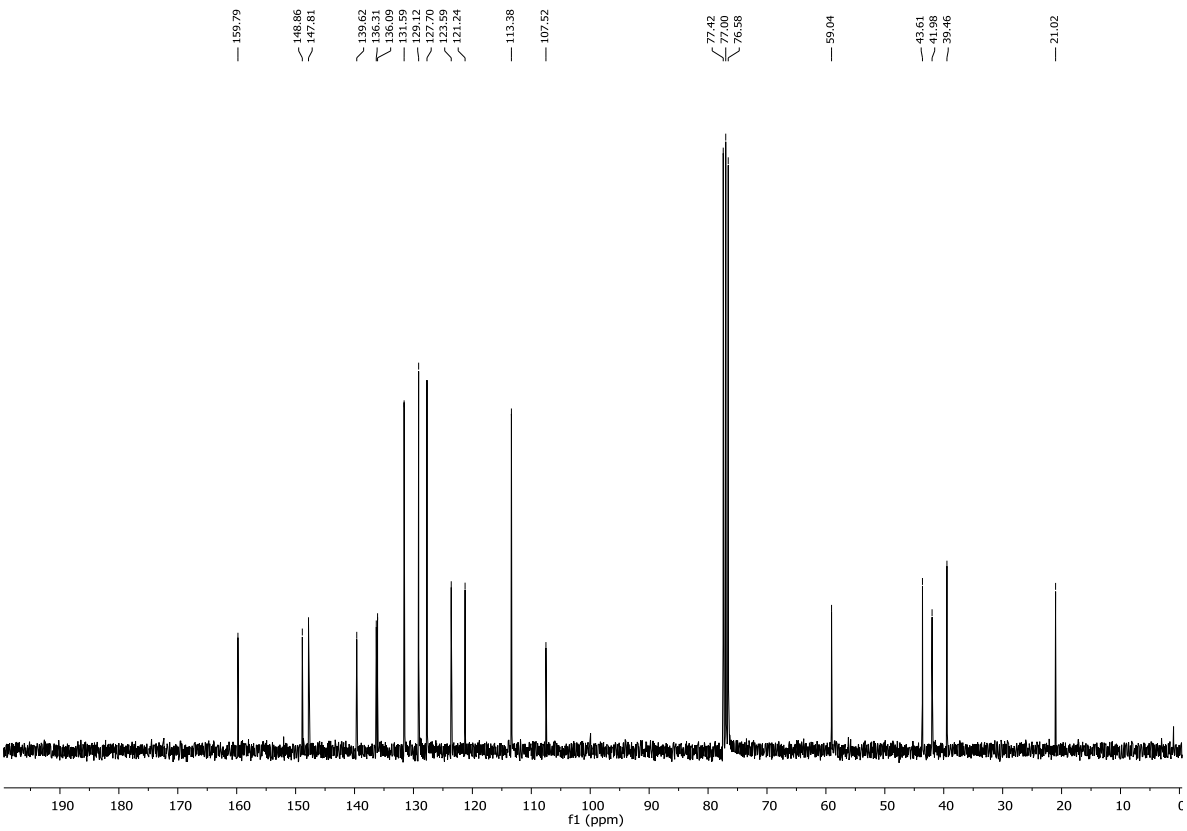

Ph
N
Me
N
3u
Me

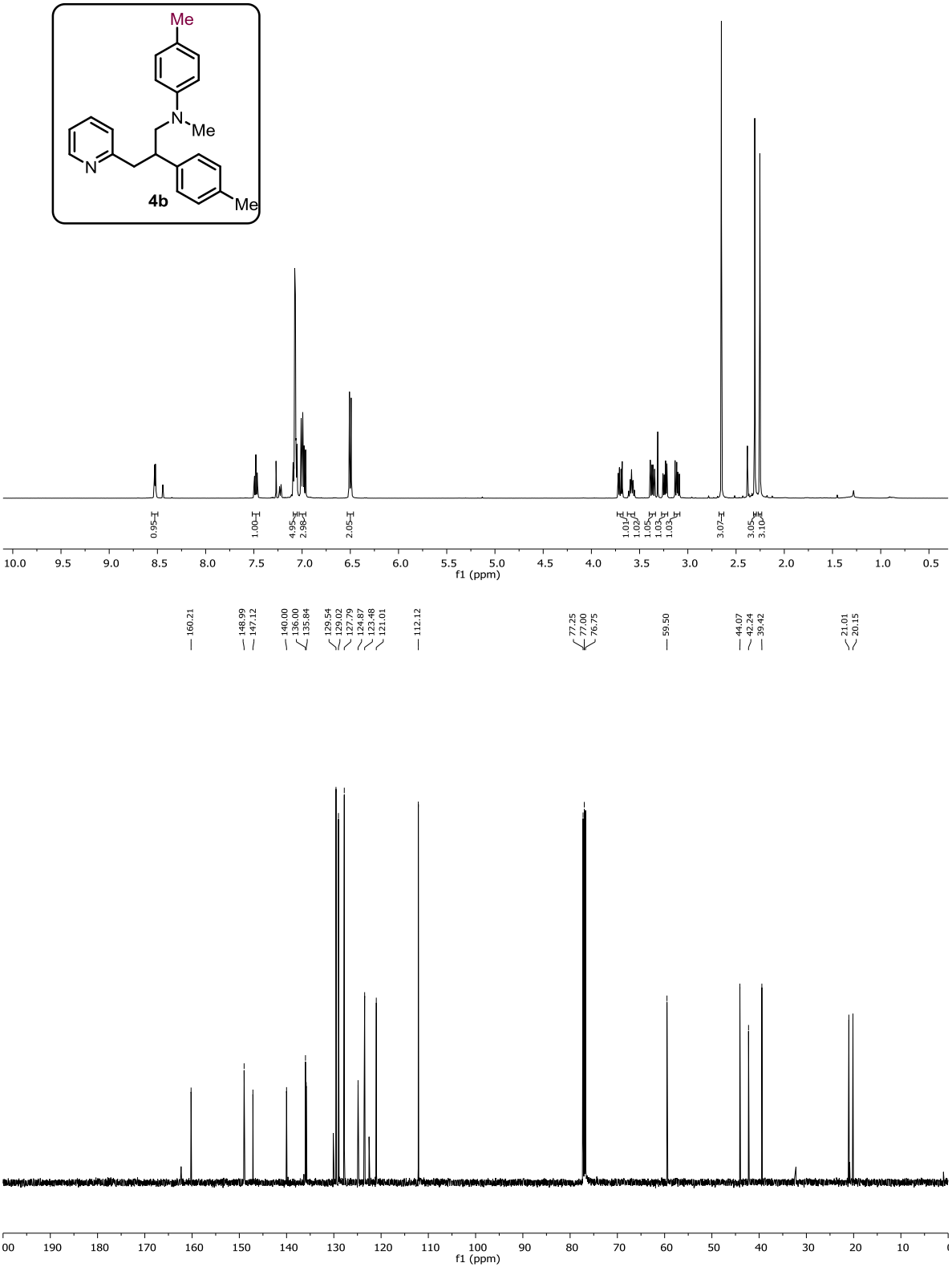
0.78
0.94
1.02
0.99
1.00
5.11
2.06
1.05
2.02
2.04
3.00
3.03
3.11
f1 (ppm)

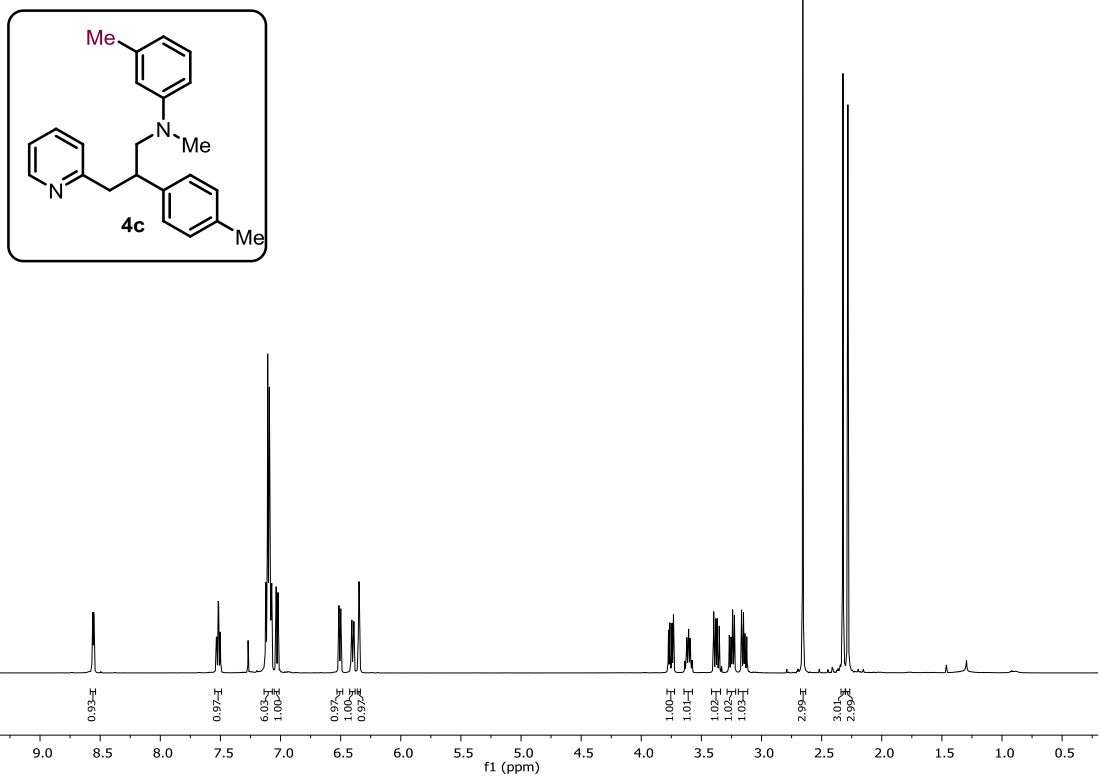

160.60
160.41
148.94
147.69
140.01
136.04
129.53
129.13
129.00
128.77
127.88
127.47
126.73
125.90
121.77
115.69
111.88
77.25
77.00
76.75
59.36
43.44
39.52
21.03

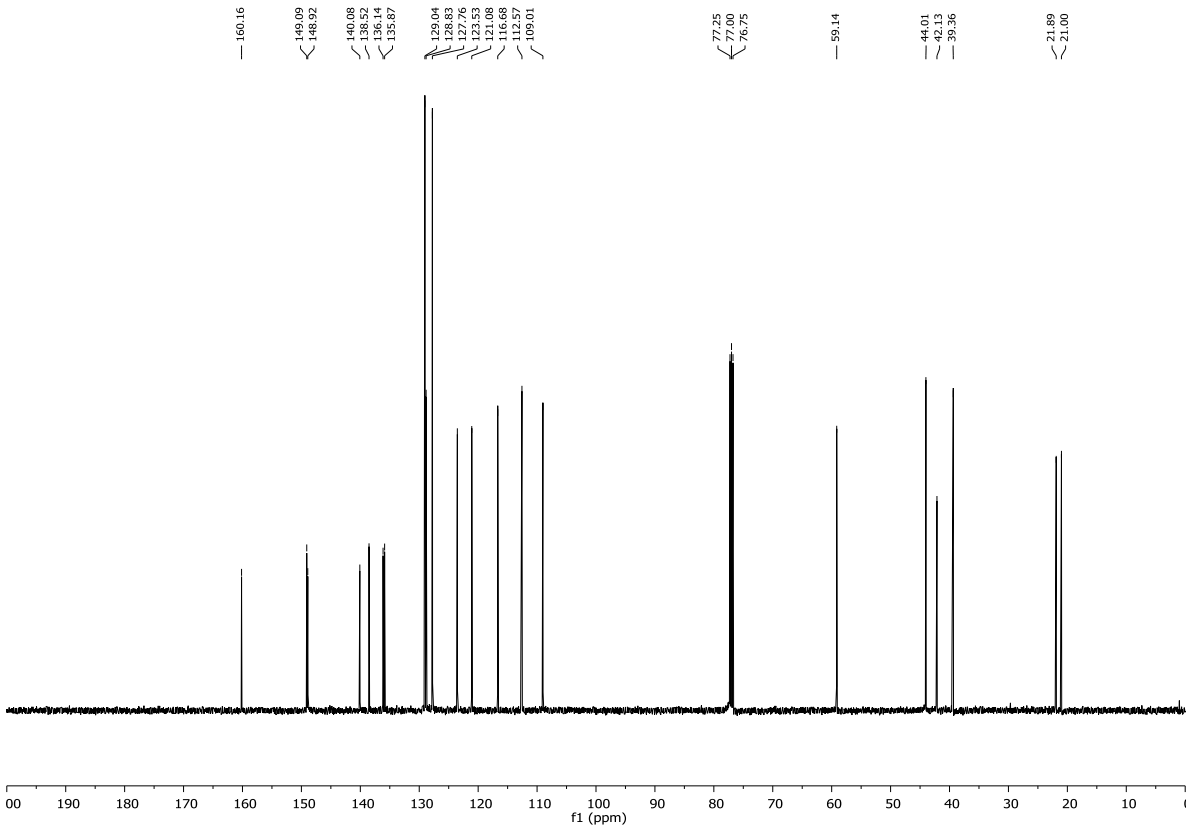

f1 (ppm)


Br
N
Me
N
Me
4a
0.97
1.02
2.02
5.00
1.00
1.95
1.00
1.07
1.04
1.04
1.03
2.93
2.99
f1 (ppm)


159.79
148.86
147.81
139.62
136.31
136.09
131.59
129.12
127.70
123.59
121.24
113.38
107.52
77.42
77.00
76.58
59.04
43.61
41.98
39.46
21.02
f1 (ppm)


Me
N
Me
N
4b
Me
0.95
1.00
4.95
2.98
2.05
1.01
1.02
1.05
1.03
1.03
3.07
3.05
3.10
10.0 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 0.5
f1 (ppm)
160.21
148.99
147.12
140.00
136.00
135.84
129.54
129.02
127.79
124.87
123.48
121.01
112.12
77.25
77.00
76.75
59.50
44.07
42.24
39.42
21.01
20.15
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


Me
N
Me
N
4c
Me
0.93
0.97
6.03
1.00
0.97
1.00
0.97
1.00
1.01
1.02
1.02
1.03
2.99
3.01
2.99
f1 (ppm)


160.16
149.09
148.92
140.08
138.52
136.14
135.87
129.04
128.83
127.76
123.53
121.08
116.68
112.57
109.01
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77.00
76.75
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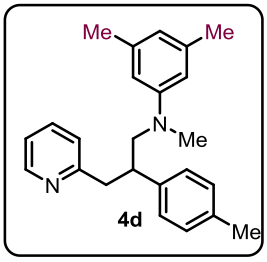
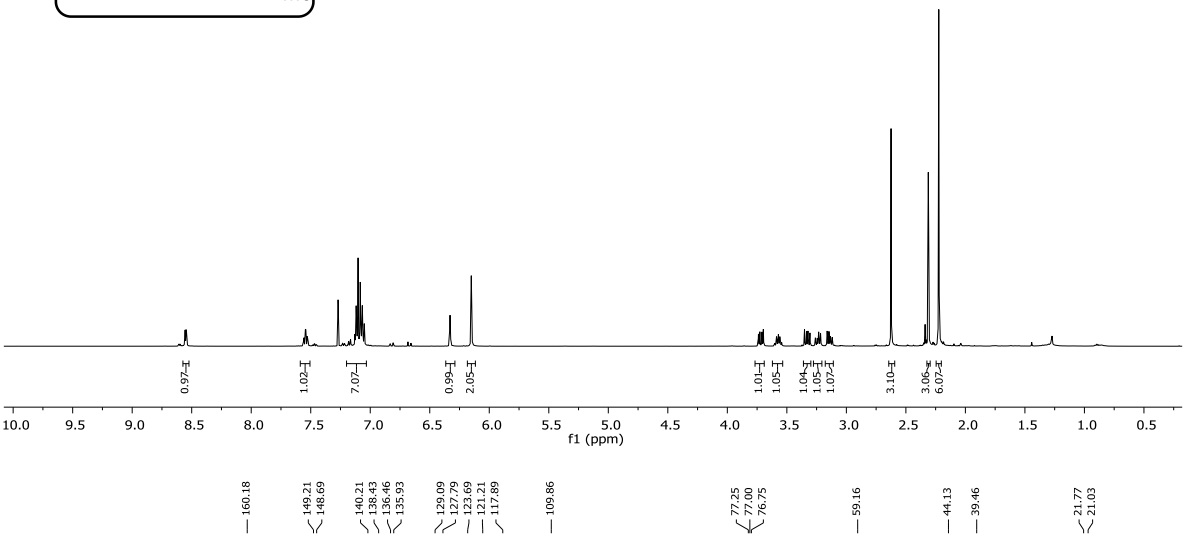
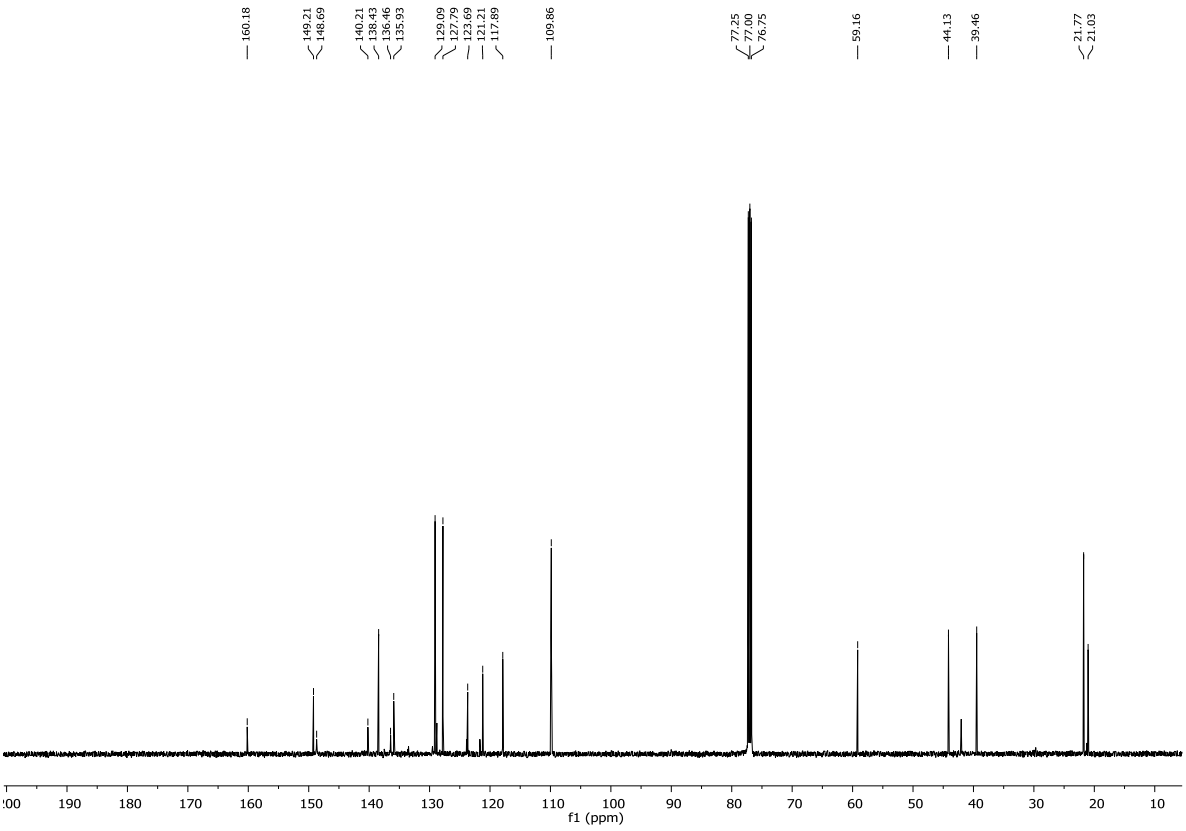
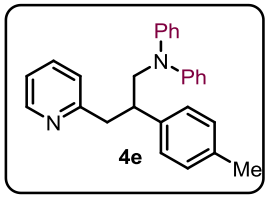
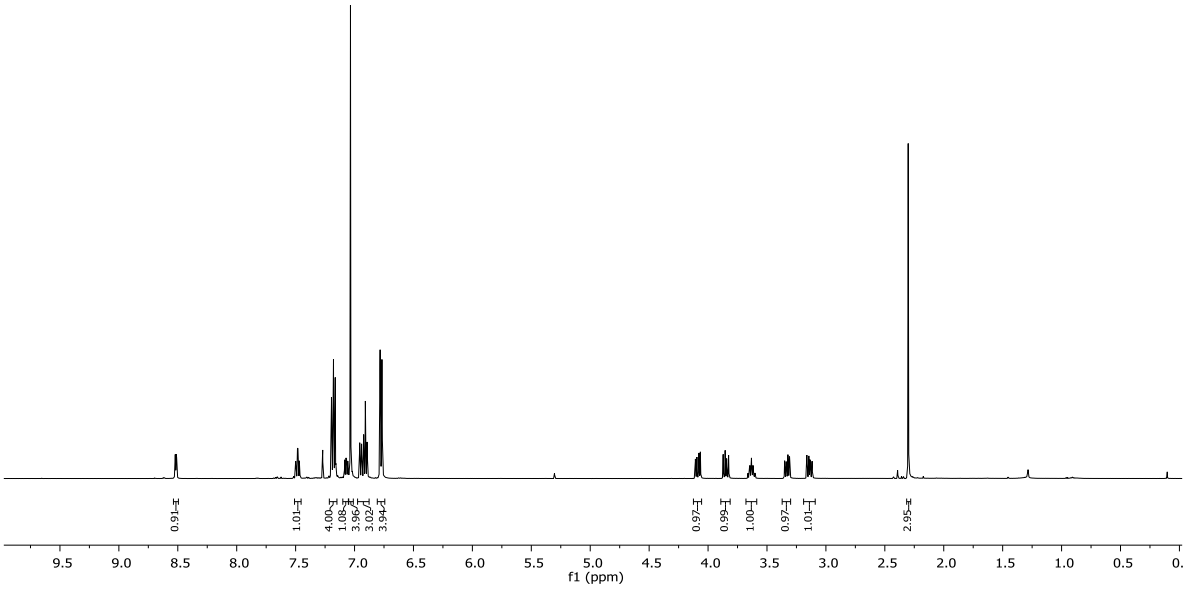
44.01
42.13
39.36
21.89
21.00
f1 (ppm)

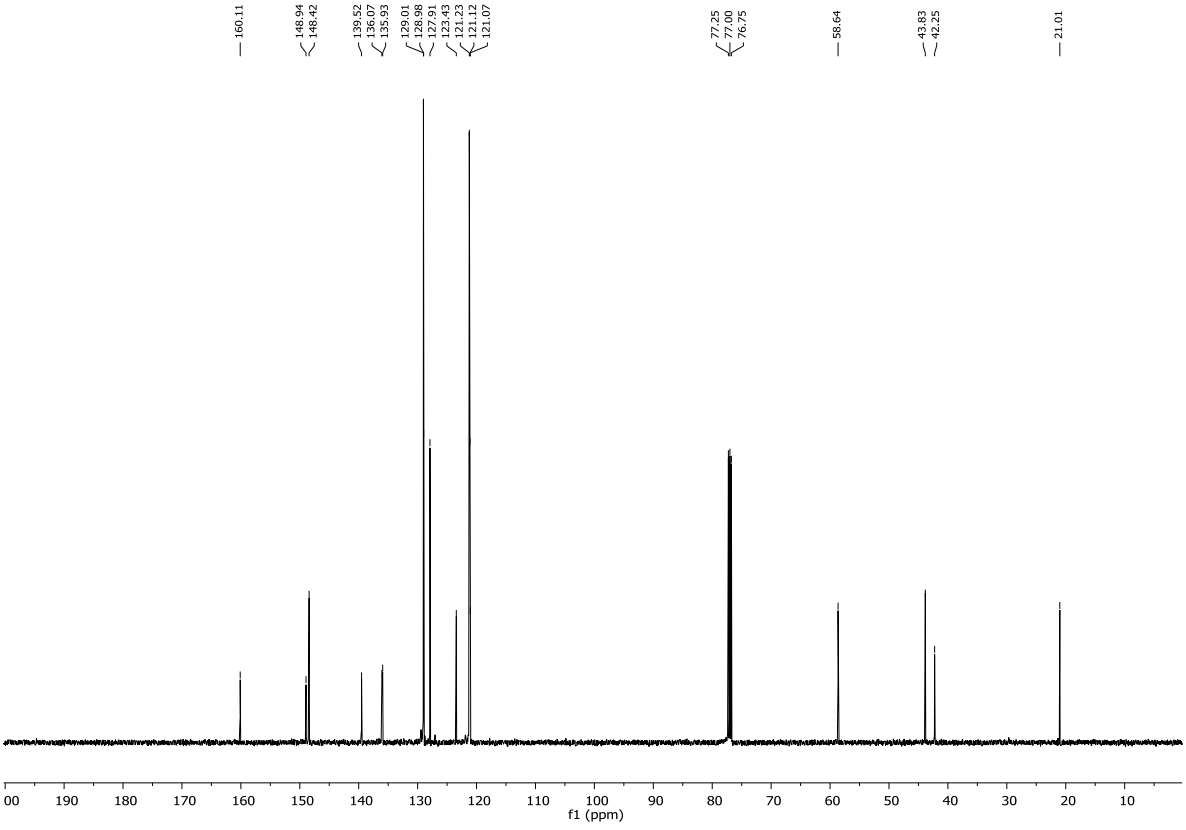

Me
Me
N
Me
N
4d
Me

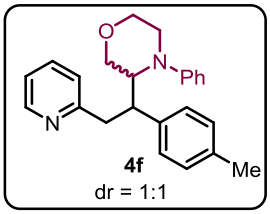

0.97
1.02
7.07
0.99
2.05
1.01
1.05
1.04
1.05
1.07
3.10
3.06
6.07
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


160.18
149.21
148.69
140.21
138.43
136.46
135.93
129.09
127.79
123.69
121.21
117.89
109.86
77.25
77.00
76.75
59.16
44.13
39.46
21.77
21.03
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


Ph
N
Ph
N
4e
Me

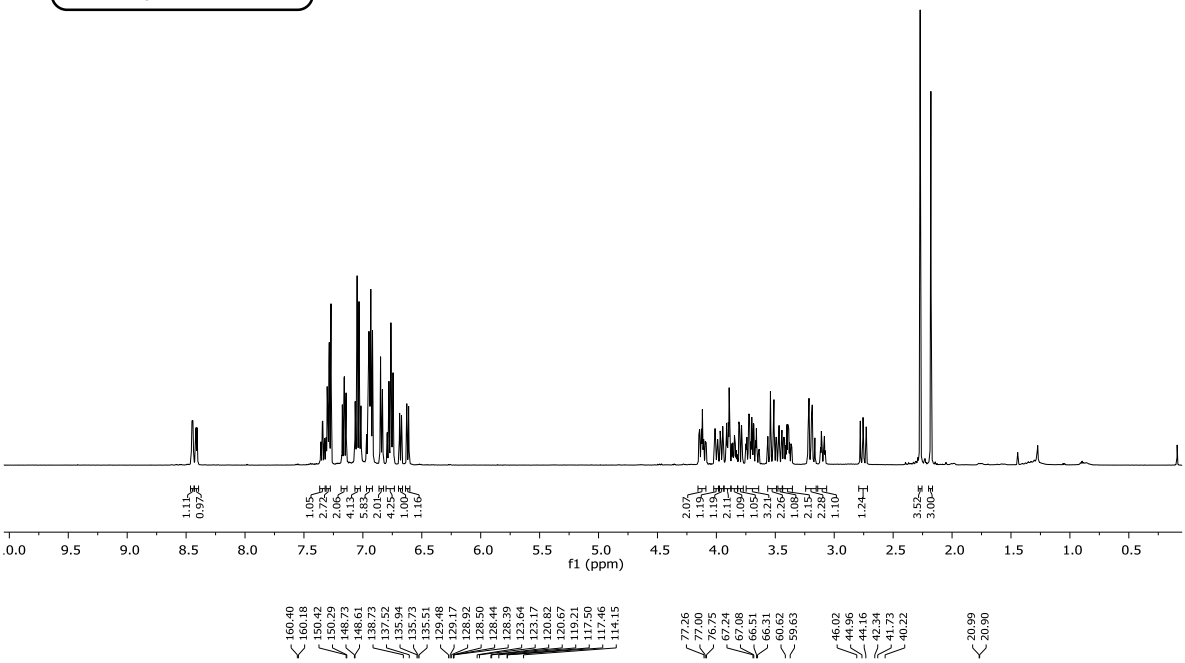

0.91
1.01
4.00
1.08
3.96
3.02
3.94
0.97
0.99
1.00
0.97
1.01
2.95
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.
f1 (ppm)


160.11
148.94
148.42
139.52
136.07
135.93
129.01
128.98
127.91
123.43
121.23
121.12
121.07
77.25
77.00
76.75
58.64
43.83
42.25
21.01
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

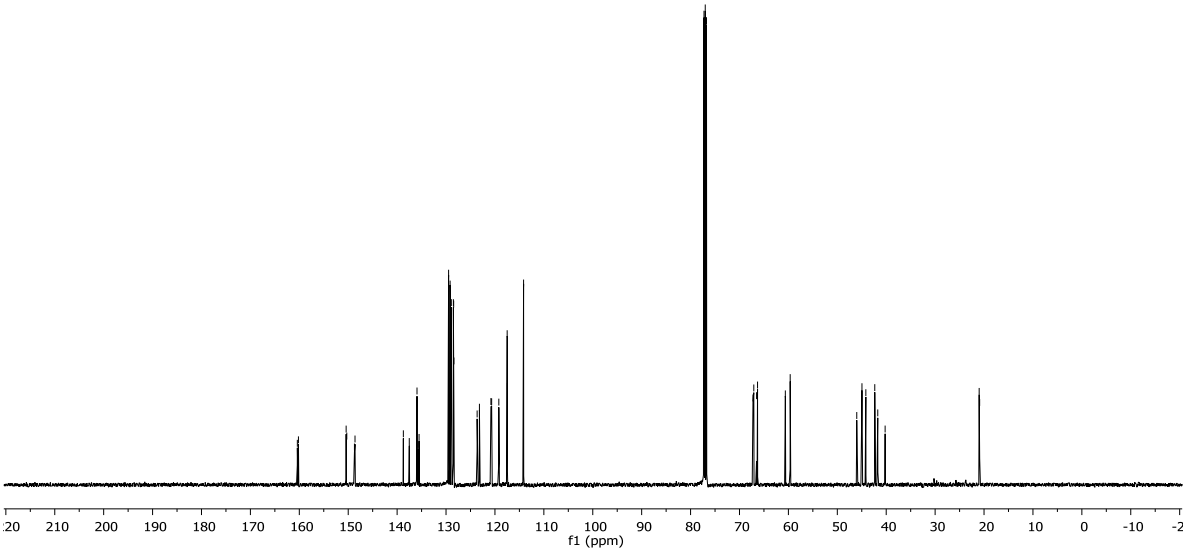

O
N
Ph
N
Me

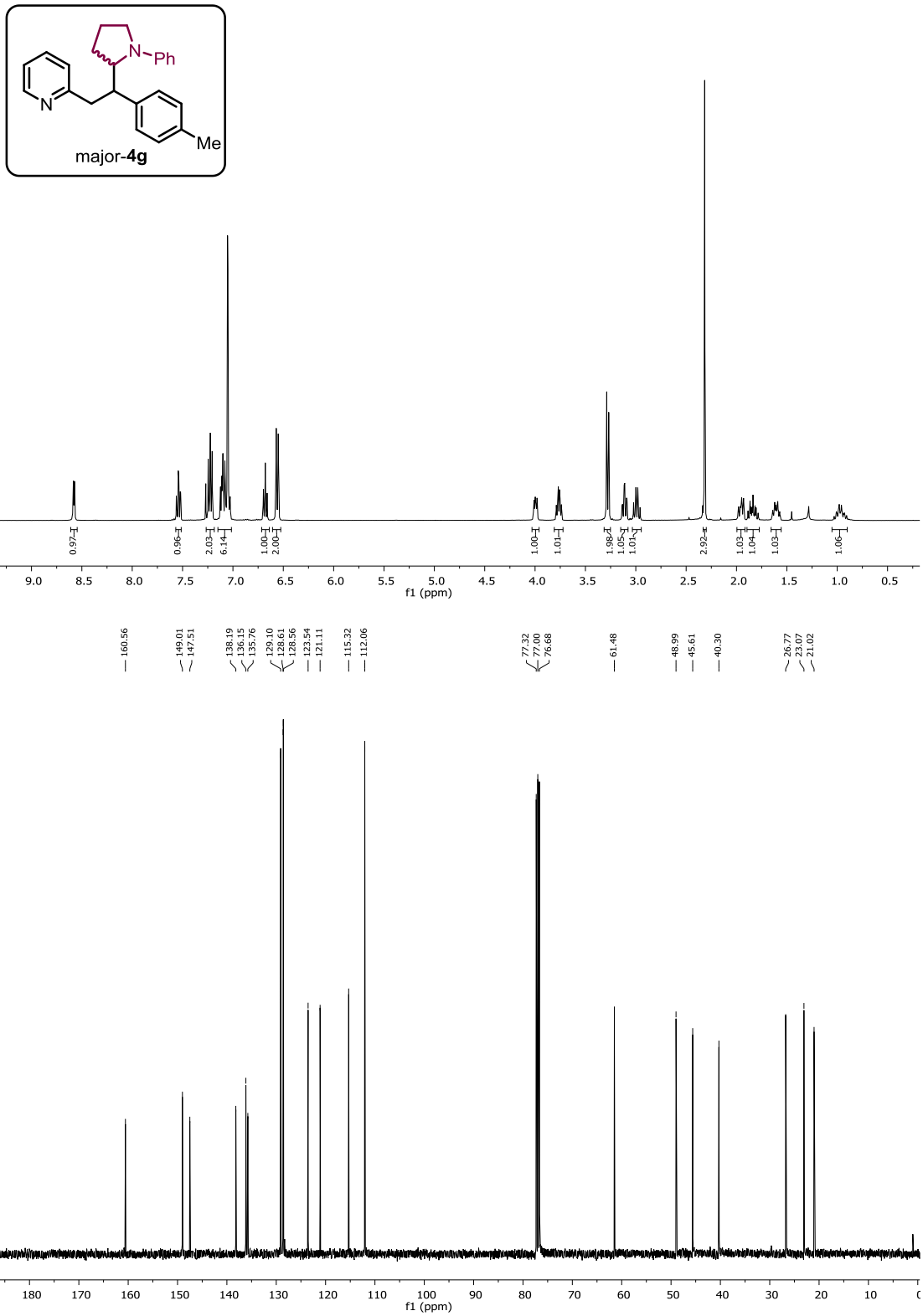
4f

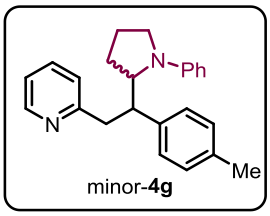
dr = 1:1


1.11
0.97
1.05
2.72
2.66
4.13
5.83
2.01
4.25
1.00
1.16
2.07
1.19
1.19
2.11
1.09
1.05
3.21
2.26
1.08
2.15
2.28
1.10
1.24
3.52
3.00
f1 (ppm)

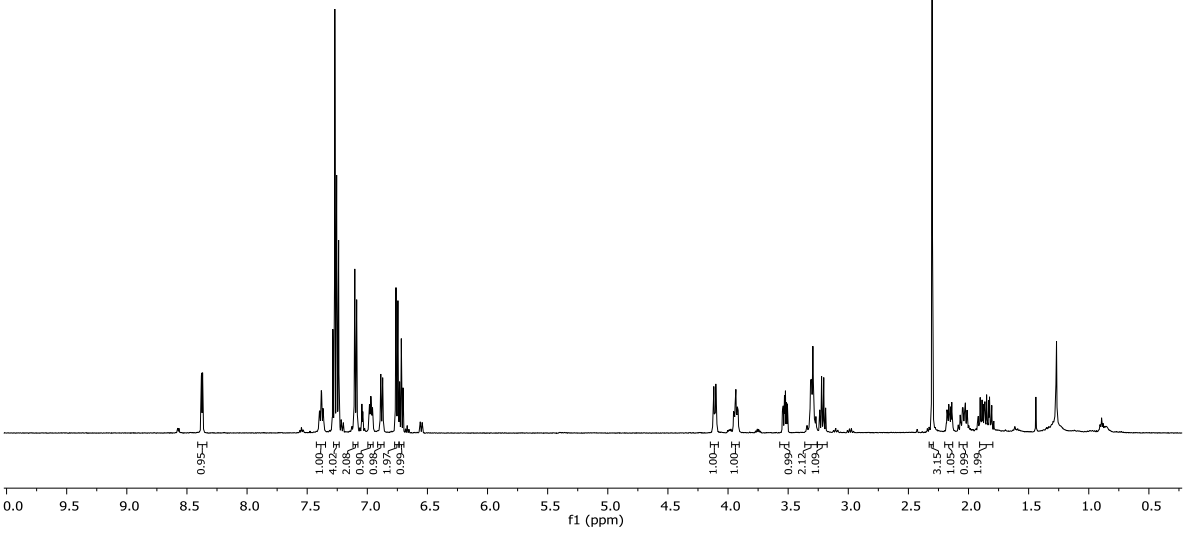
160.40
160.18
150.42
150.29
148.73
148.61
138.73
137.52
135.94
135.73
135.51
129.48
129.17
128.92
128.50
128.44
128.39
123.64
123.17
120.82
120.67
119.21
117.50
117.46
114.15
77.26
77.00
76.75
67.24
67.08
66.51
66.31
60.62
59.63
46.02
44.96
44.16
42.34
41.73
40.22
20.99
20.90

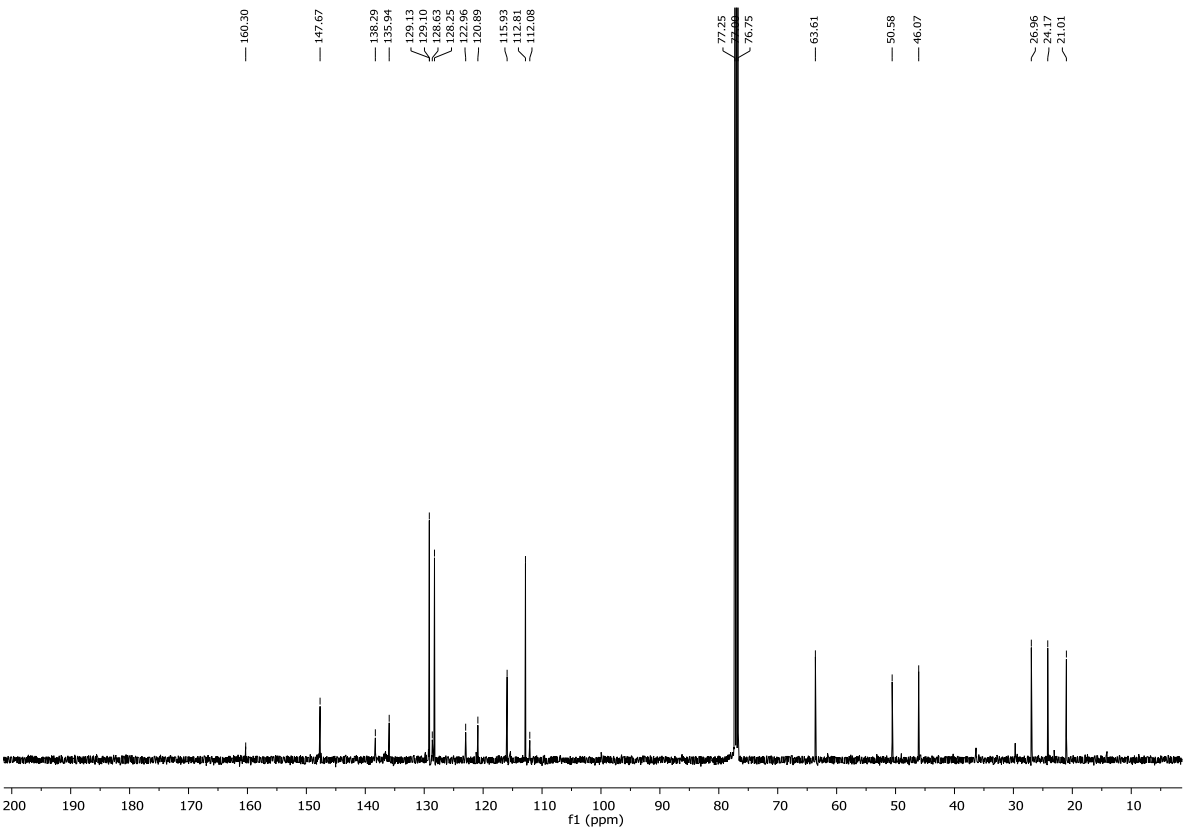

f1 (ppm)

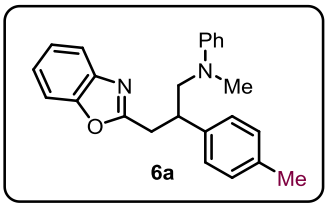

N
Ph
N
Me
major-4g
0.97
0.96
2.03
6.14
1.00
2.00
1.00
1.01
1.98
1.05
1.01
2.92
1.03
1.04
1.03
1.06
f1 (ppm)
160.56
149.01
147.51
138.19
136.15
135.76
129.10
128.61
128.56
123.54
121.11
115.32
112.06
77.32
77.00
76.68
61.48
48.99
45.61
40.30
26.77
23.07
21.02
f1 (ppm)


N
Ph
N
Me

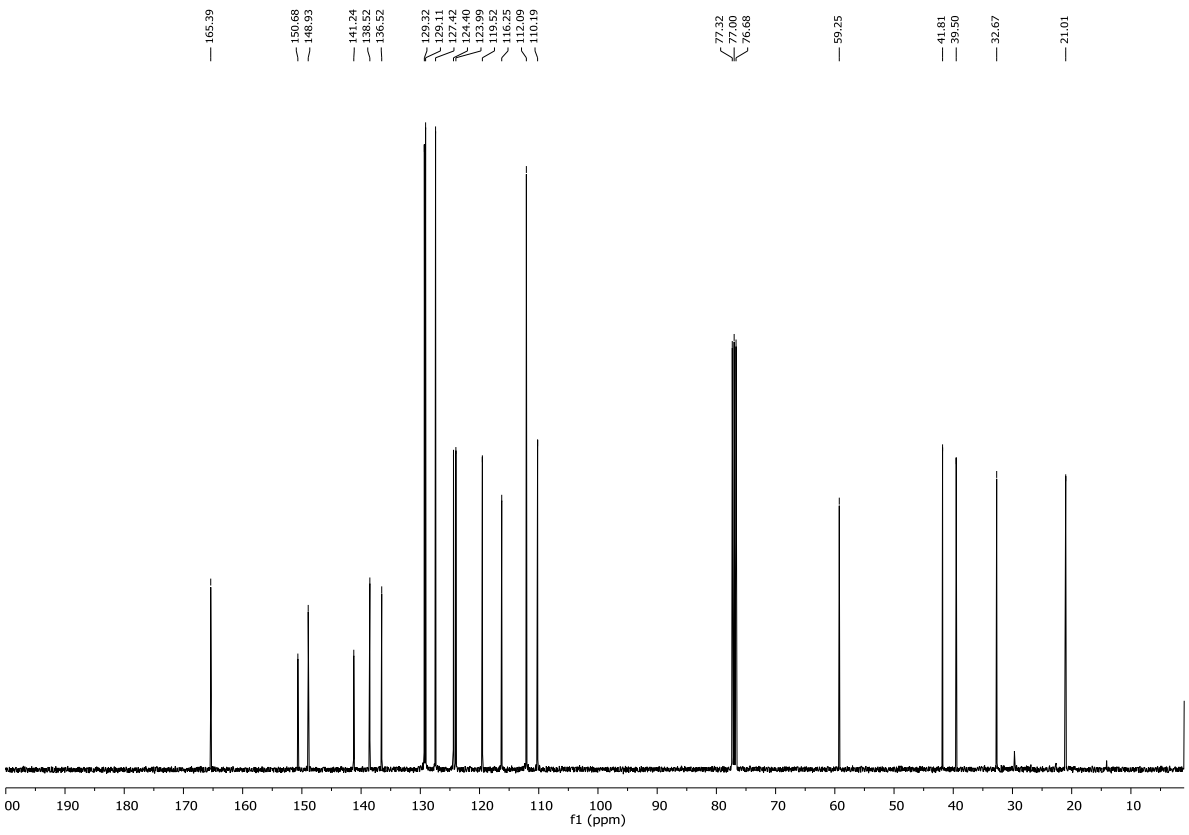
minor-**4g**

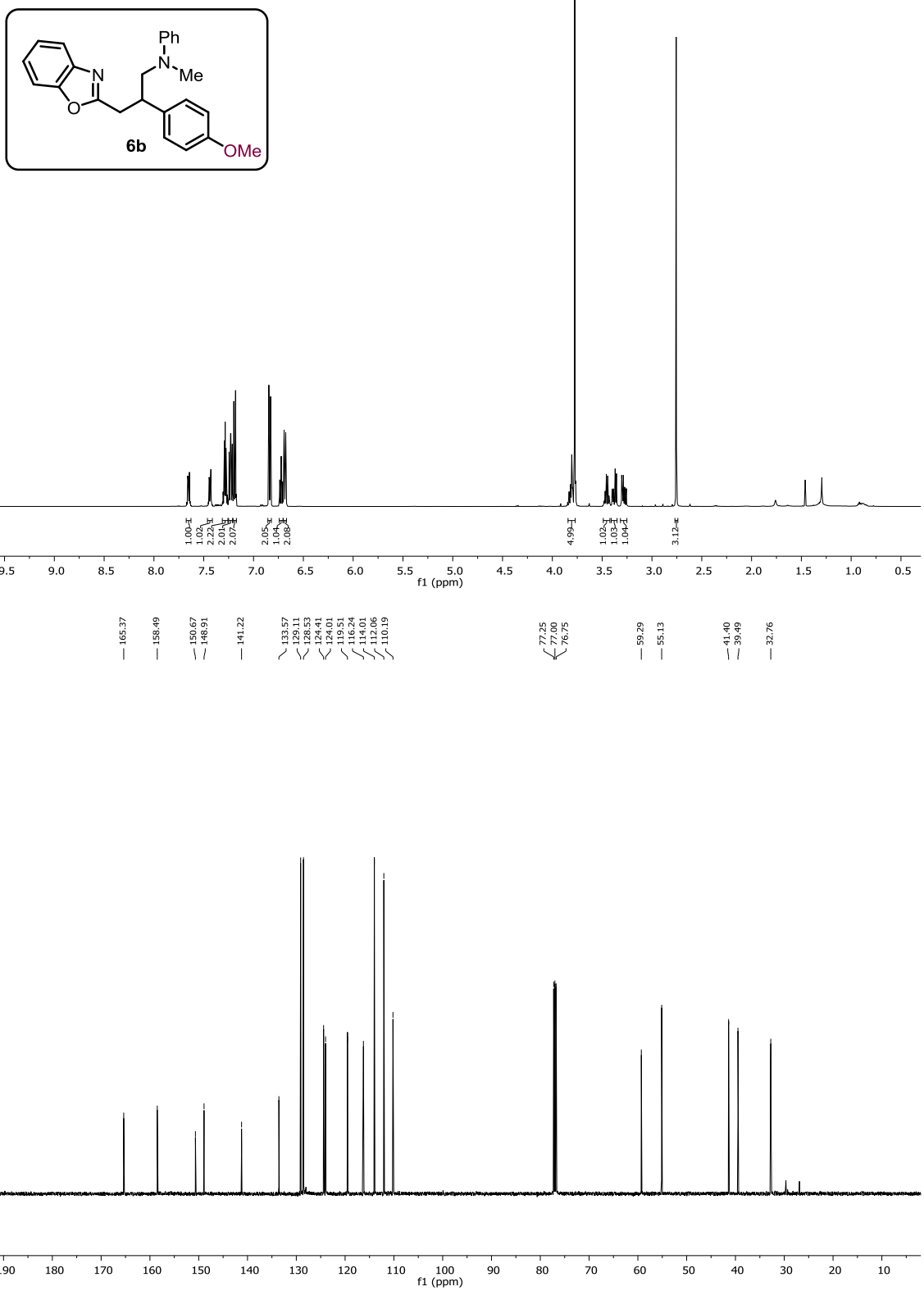

0.95
1.00
4.02
2.08
0.90
0.98
1.97
0.99
1.00
1.00
0.99
2.12
1.05
3.15
1.05
0.99
1.99
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

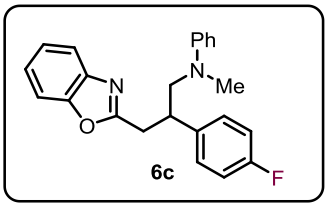

160.30
147.67
138.29
135.94
129.13
129.10
128.63
128.25
122.96
120.89
115.93
112.81
112.08
77.25
77.00
76.75
63.61
50.58
46.07
26.96
24.17
21.01
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


Ph
N
Me
N
O
6a
Me

1.00
1.02
2.09
2.03
2.03
2.05
3.08
2.11
1.04
1.06
1.03
3.12
3.06
f1 (ppm)

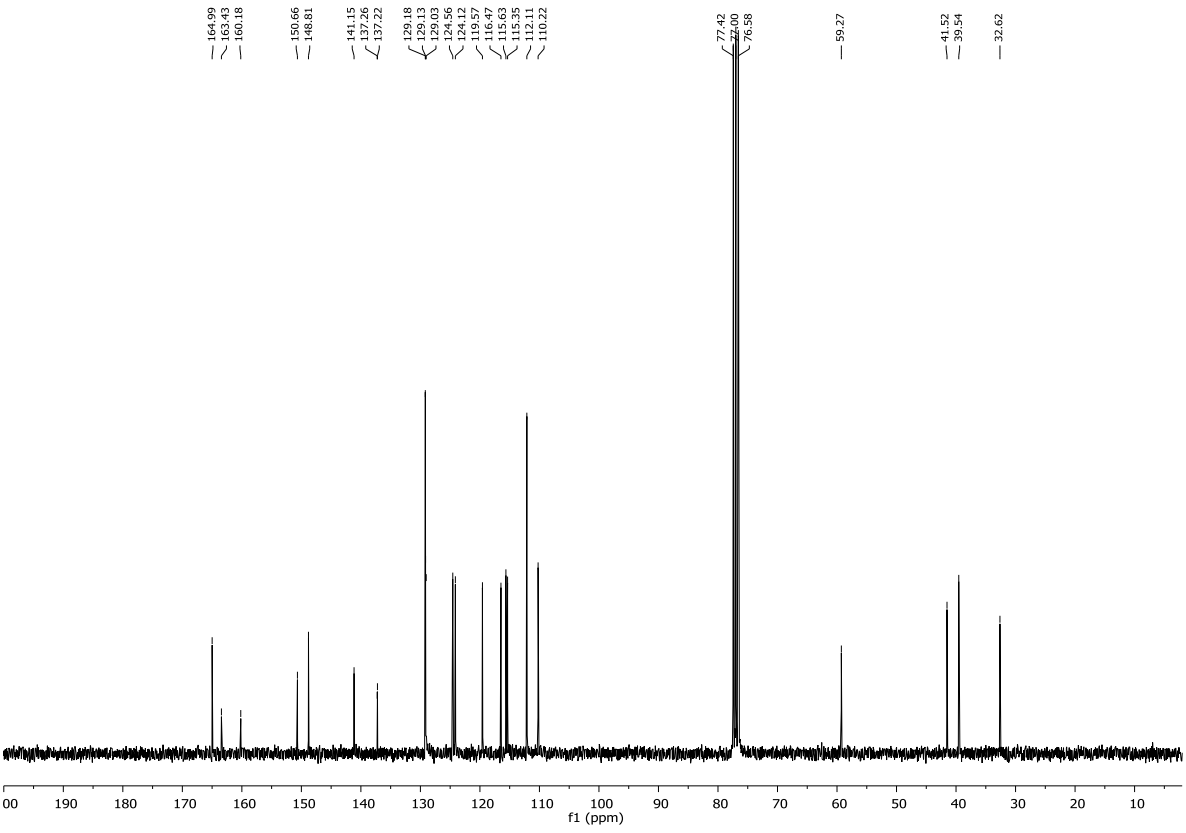

165.39
150.68
148.93
141.24
138.52
136.52
129.32
129.11
127.42
124.40
123.99
115.52
115.25
112.09
110.19
77.32
77.00
76.68
59.25
41.81
39.50
32.67
21.01
f1 (ppm)

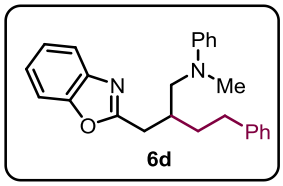

Ph
N
Me
N
O
6b
OMe
1.00
1.02
2.22
2.01
2.07
2.05
1.04
2.08
4.99
1.02
1.03
1.04
3.12
f1 (ppm)
165.37
158.49
150.67
148.91
141.22
133.57
129.11
128.53
124.41
124.01
119.51
116.24
114.01
112.06
110.19
77.25
77.00
76.75
59.29
55.13
41.40
39.49
32.76
f1 (ppm)


Ph
N
Me
N
O
F

6c

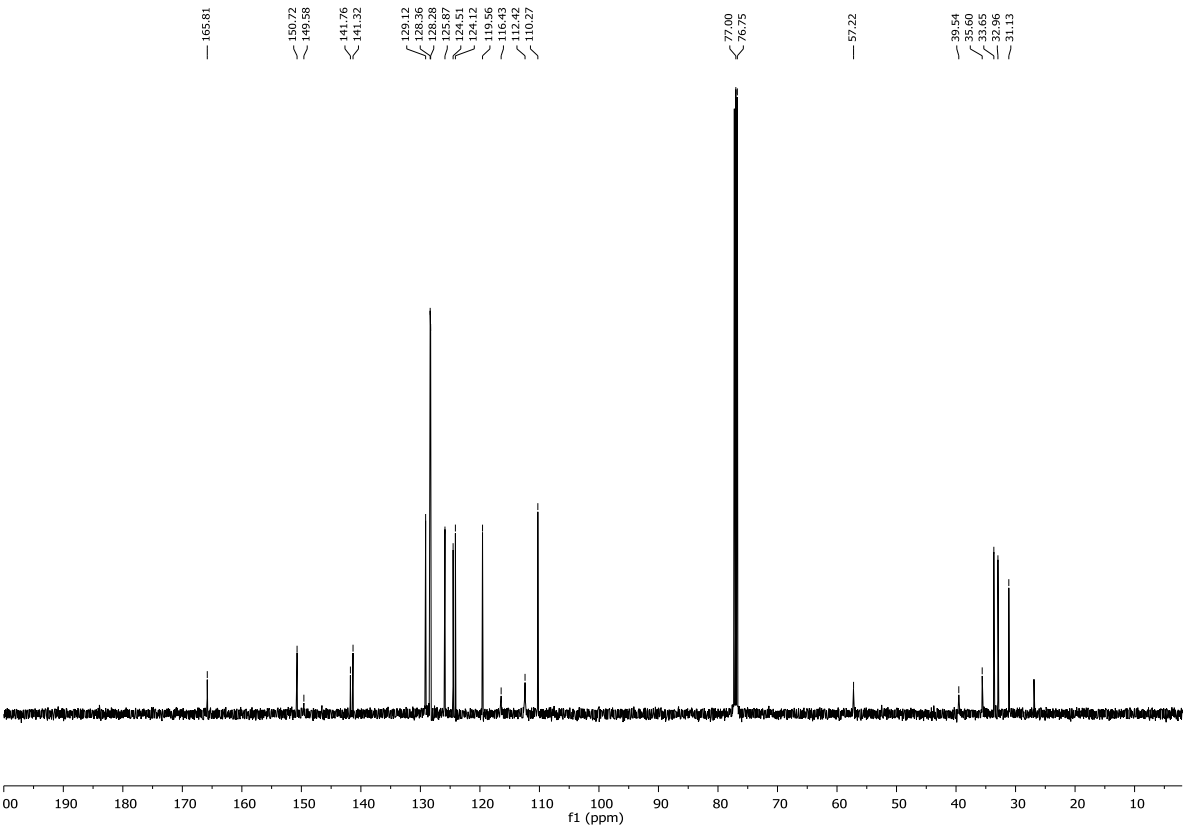
1.00
1.03
6.11
1.94
2.84
1.91
2.93
2.85
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


164.99
163.43
160.18
150.66
148.81
141.15
137.26
137.22
129.18
129.13
129.03
124.56
124.12
119.57
116.47
115.63
115.35
112.11
110.22
77.42
77.00
76.58
59.27
41.52
39.54
32.62
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


Ph
N
Me
N
O
Ph

6d

0.94
0.98
2.14
4.96
1.98
2.82
2.01
2.10
3.02
2.05
0.98
2.05
f1 (ppm)


165.81
150.72
149.58
141.76
141.32
129.12
128.36
128.28
125.87
124.51
124.12
119.56
116.43
112.42
110.27
77.00
76.75
57.22
39.54
35.60
33.65
32.96
31.13
f1 (ppm)