Supporting Information

Visible-Light-Mediated Deaminative Three-Component Dicarbofunctionalization of Styrenes with Benzylic Radicals

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Contents

1. General information

All reactions were carried out in oven-dried glassware under an atmosphere of argon, unless otherwise stated. The solvents used were purified by distillation over standard drying agents and were stored over molecular sieves and transferred under argon. Blue LEDs (5W, λ_{max} = 455 nm; 3W, λ_{max} = 420 nm or 3W, λ_{max} = 400 nm) or UV LEDs (3W, λ_{max} = 365 nm) were used as light sources (for emission spectra of the LEDs, see figure S1).

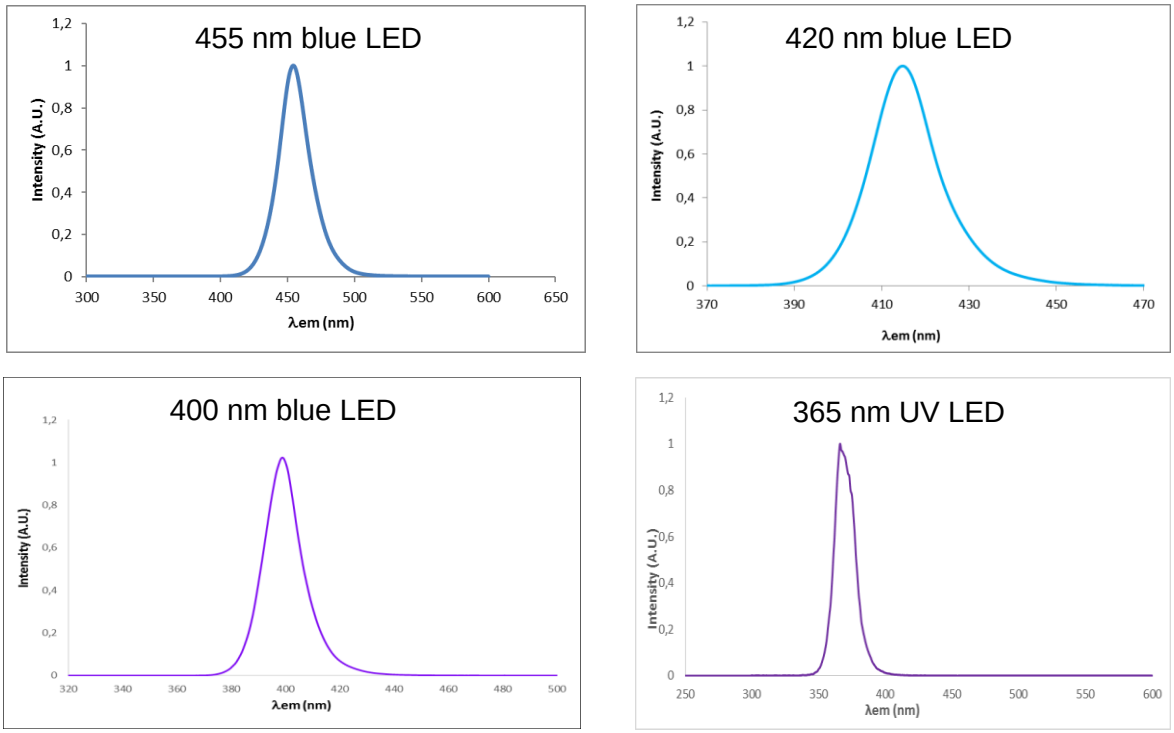


Figure S1. Emission spectra of the used LEDs.

In each case, the light source was placed ~ 5 cm from the reaction vessel. A custom made "light box" was used with 6 LEDs arranged around the reaction vessels (see figure S2). A fan attached to the apparatus was used to maintain the temperature inside the "box" at no more than 9 °C above room temperature.

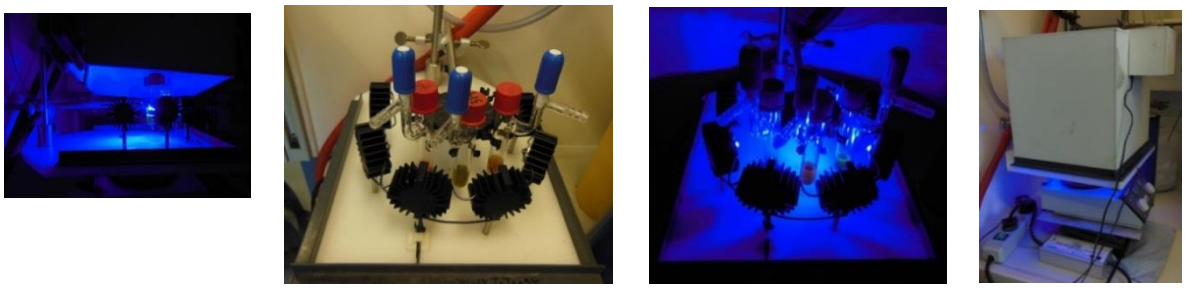


Figure S2. Photographs of the custom-made light box used for irradiation of the reaction mixtures.

2,4,6-Triphenylpyrylium tetrafluoroborate, primary amines, indoles and *α*-methylstyrene were commercially available and used as received. 4-Methoxystyrene and benzyl bromide were commercially available and filtered through a plug of basic alumina before use.

Trimethylpyrylium tetrafluoroborate was synthesized according to a literature procedure.[1] Photocatalysts [Ir(dtbbpy)(ppy)$_2$](PF$_6$) (ppy = 2-phenylpyridinato-C^2,*N*; dtbbpy = 4,4'-di-*tert*-butyl-2,2'-bipyridine),[2] *fac*-[Ir(ppy)$_3$],[3] [Ir(dtbbpy)(dF(CF$_3$)ppy)$_2$](PF$_6$) (dF(CF$_3$)ppy = 2-(2,4-difluorophenyl)-3-trifluoromethylpyridinato-C^6,*N*)[4] and [Ru(bpy)$_3$](PF$_6$)$_2$ (bpy = 2,2′-bipyridine)[5] were prepared according to literature procedures.

Flash chromatography was performed on Merck silica gel (40-63 mesh) using standard techniques. NMR-spectra were recorded on a Bruker ARX-300, AV-300, AV-400 MHz or on an Agilent DD2-500 MHz, DD2-600 MHz spectrometer. Chemicals shifts (δ) are quoted in ppm downfield of tetramethylsilane. The residual solvent signals were used as references for ^{1}H and ^{13}C NMR spectra ($CDCl_3$: δ_H = 7.26 ppm, δ_C = 77.16 ppm, CD_2Cl_2: δ_H = 5.32 ppm, δ_C = 54.00 ppm). ^{19}F NMR spectra are not calibrated by an internal reference. Coupling constants (*J*) are quoted in Hz.

GC-MS spectra were recorded on an Agilent Technologies 7890A GC-system with an Agilent 5975C VL MSD or an Agilent 5975 inert mass selective detector (EI) and a HP-5MS column (0.25 mm x 30 m, film: 0.25 µm). The major signals are quoted in *m*/*z* with the relative intensity in parentheses. The method indicated as '50_40_long' starts with the injection temperature T0 (50 °C); after holding this temperature for 3 min, the column is heated by 40 °C/min to temperature T1 (290 °C or 320 °C) and this temperature is held for an additional time t.

GC-FID analysis was undertaken on an Agilent Technologies 6890A equipped with an HP-5 quartz column (0.32 mm x 30 m, film: 0.25 µm) using flame ionization detection. Method: Initial temperature 50 °C, hold 3 min, increment 20 °C/min, final temperature 280 °C, hold 9 min. ESI mass spectra were recorded on a Bruker Daltonics MicroTof spectrometer.

Infrared spectra were recorded on a Shimadzu FTIR 8400S spectrometer. The wave numbers (ν) of recorded IR-signals are quoted in cm^{-1}.

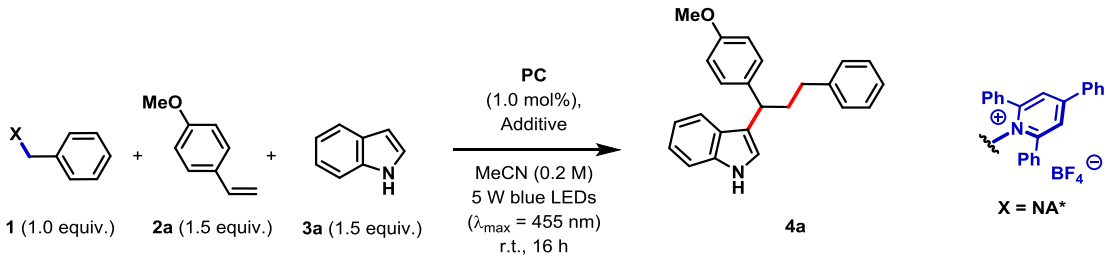
Stern-Volmer luminescence quenching studies were conducted using a Jasco FP-8300 spectrofluorometer. The following parameters were employed: Excitation bandwidth = 5 nm, data interval = 0.2 nm, scan speed = 500 nm/min, response time = 0.2 sec.

UV/Vis Absorption spectra were recorded on a Jasco V-750 UV-Visible/NIR-spectrophotometer. The samples were measured in Hellma fluorescence QS quartz cuvettes (chamber volume = 3.5 mL, H × W × D = 46 mm × 12.5 mm x 12.5 mm) fitted with a PTFE stopper.

2. Optimization studies

An oven-dried screw cap Schlenk reaction tube was charged with the benzyl radical precursor (**1**), if solid. 1*H*-Indole (**3a**) and the respective photocatalyst were added. The tube was evacuated and backfilled with argon. The respective solvent was added in a stream of argon. If liquid, the benzyl radical precursor (**1**) was added in a stream of argon, followed by 4-methoxystyrene (**2a**). The reaction mixture was degassed by three consecutive freeze-pump-thaw cycles. The solution was stirred under irradiation for the specified time in an atmosphere of argon. After the indicated reaction time triethylamine (0.1 mL per 0.1 mmol of the limiting starting material) and mesitylene (1.0 equiv.) were added to the reaction mixture. The yield was determined by calibrated GC-FID analysis.

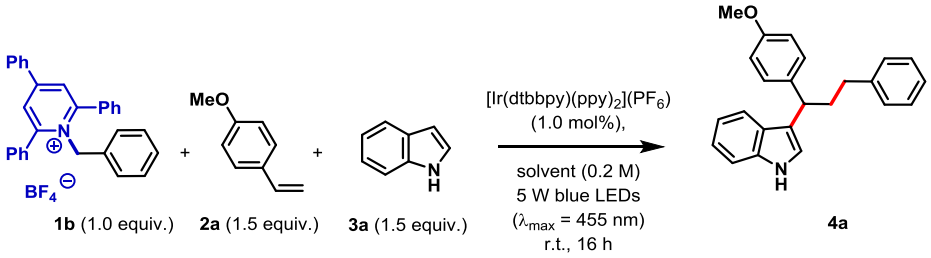
Radical precursors (0.10 mmol scale)



1 (1.0 equiv.) **2a** (1.5 equiv.) **3a** (1.5 equiv.) **4a**

X =	Additive (equiv.)	**PC**	Yield **4a** [%]
Br	-	*Ir(ppy)$_3$*	*0*
Br	-	*[Ir(dtbbpy)(ppy)$_2$](PF$_6$)*	*2*
Br	*K$_2$CO$_3$ (2.0)*	*Ir(ppy)$_3$*	*18*
Br	*K$_2$CO$_3$ (2.0)*	*[Ir(dtbbpy)(ppy)$_2$](PF$_6$)*	*15*
NA*	-	*[Ir(dtbbpy)(ppy)$_2$](PF$_6$)*	***48***

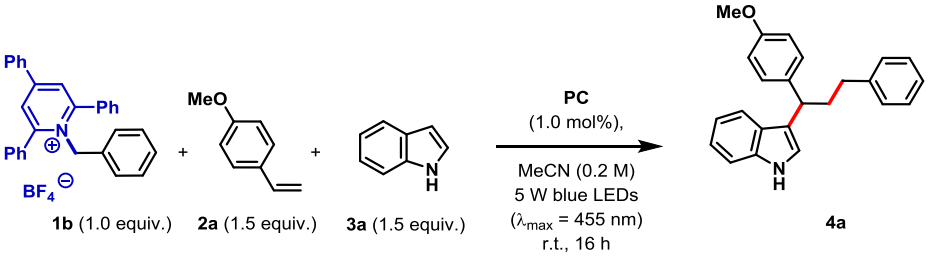
Solvent screen (0.10 mmol scale)



1b (1.0 equiv.) **2a** (1.5 equiv.) **3a** (1.5 equiv.) **4a**

Solvent	Yield **4a** [%]
MeCN	***48***
DMF	*28*
DCE	*40*
DMA	*23*
DMSO	*24*
DCM	*38*
PhCl	*41*
DME	*34*

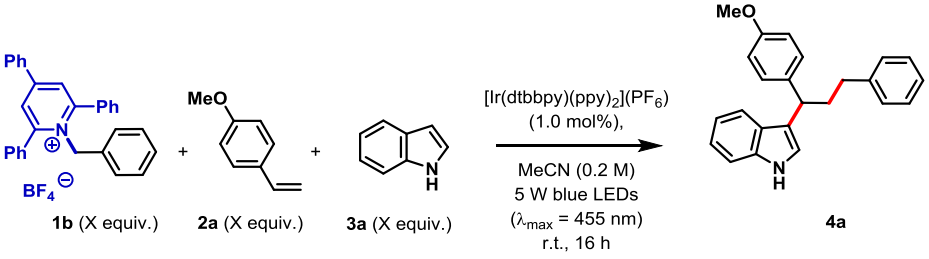
Photocatalyst screen (0.10 mmol scale)



1b (1.0 equiv.) **2a** (1.5 equiv.) **3a** (1.5 equiv.) **4a**

PC	Yield **4a** [%]
fac-Ir(ppy)$_3$	*31*
[Ir(dtbbpy)(dF(CF$_3$)ppy)$_2$](PF$_6$)	*36*
[Ru(bpy)$_3$](PF$_6$)$_2$	*12*
[Ir(dtbbpy)(ppy)$_2$](PF$_6$)	***48***

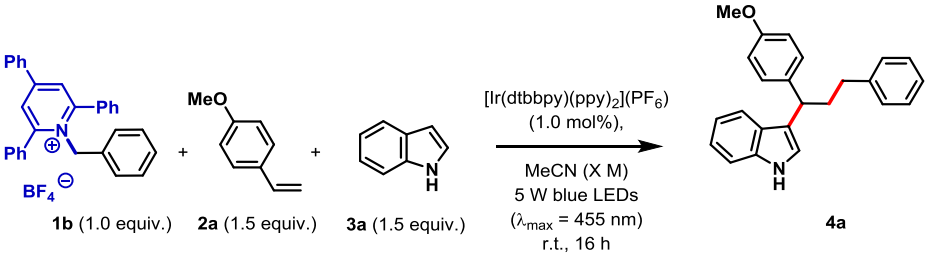
Stoichiometry (0.10 mmol scale)



1b (X equiv.) **2a** (X equiv.) **3a** (X equiv.) **4a**

Equiv. (**1b**)	Equiv. (**2a**)	Equiv. (**3a**)	Yield **4a** [%]
1.5	*1.0*	*3.0*	*24*
1.5	*1.5*	*1.0*	*39*
2.5	*1.0*	*3.0*	*21*
1.5	*1.0*	*1.5*	*33*
2.5	*1.0*	*1.5*	*19*
1.0	*1.5*	*3.0*	*40*
1.0	*2.0*	*1.5*	*54*
1.0	*2.5*	*1.5*	*58*
1.0	*3.0*	*1.5*	***60***

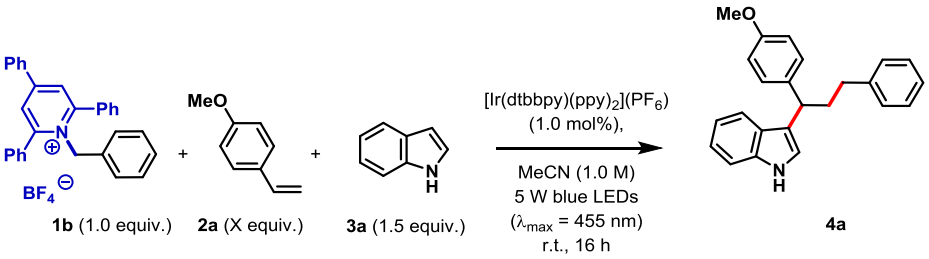
Concentration (0.10 or 0.20 mmol scale)



1b (1.0 equiv.) **2a** (1.5 equiv.) **3a** (1.5 equiv.) **4a**

Concentration [M]	Scale [mmol]	Yield **4a** [%]
0.05	*0.10*	*32*
0.1	*0.10*	*45*
0.2	*0.10*	*49*
0.4	*0.10*	*60*
0.8	*0.20*	*60*
1.0	*0.20*	***63***
2.0	*0.20*	*56*

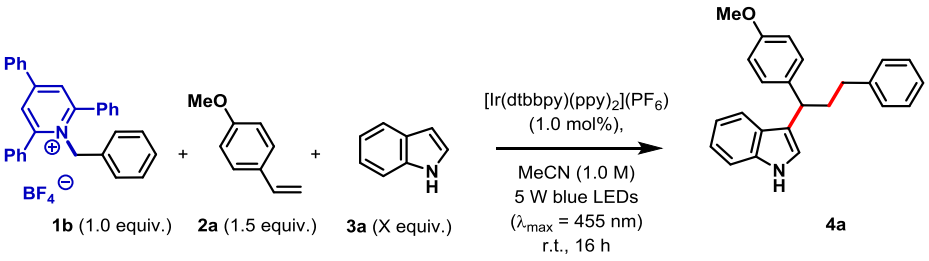
Equivalents styrene (0.20 mmol scale)



1b (1.0 equiv.) **2a** (X equiv.) **3a** (1.5 equiv.) **4a**

*Equiv. (**2a**)*	Yield **4a** [%]
1.1	*52*
1.3	*57*
1.5	***63***
1.7	*60*
2.0	*60*
2.5	*57*

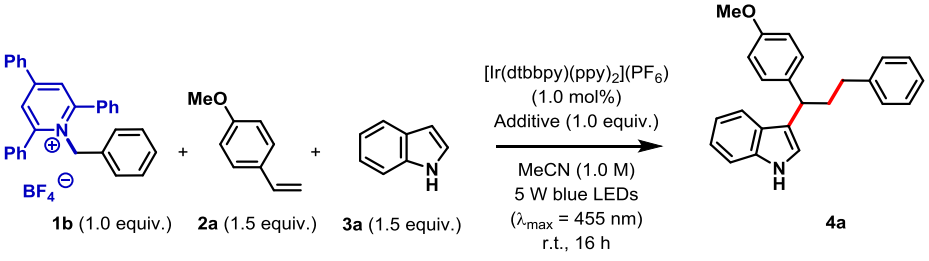
Equivalents indole (0.20 mmol scale)



1b (1.0 equiv.) **2a** (1.5 equiv.) **3a** (X equiv.) **4a**

*Equiv. (**3a**)*	Yield **4a** [%]
1.1	*59*
1.3	***63***
1.5	***63***
1.7	*59*
2.0	*61*
2.5	*61*

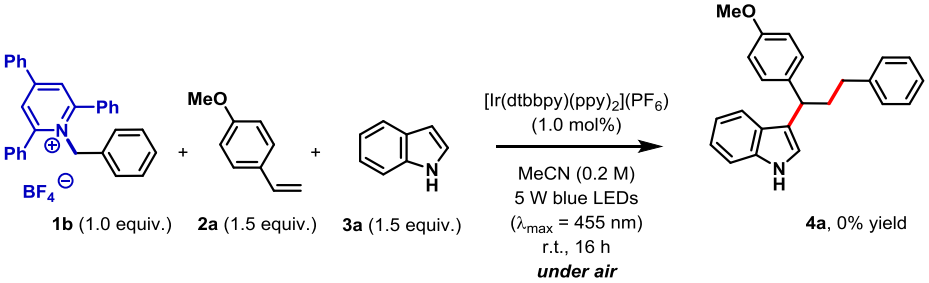
Additive screen (0.20 mmol scale)



1b (1.0 equiv.) **2a** (1.5 equiv.) **3a** (1.5 equiv.) **4a**

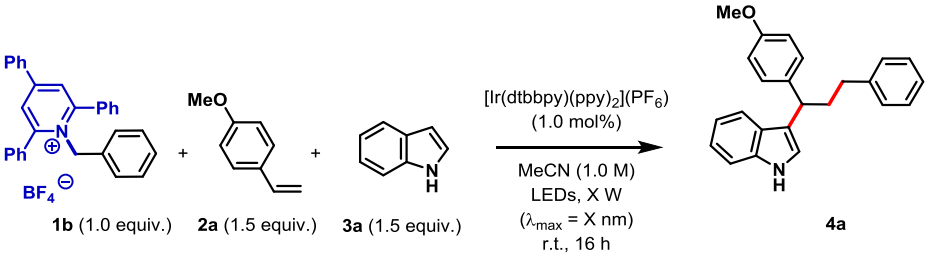
Additive	Yield **4a** [%]
NaCl	*29*
NaI	*3*
$NaPF_6$	*57*
$NaBF_4$	*64*
Pyridine	*35*
NEt_3	*12*

Reaction without exclusion of air (0.10 mmol scale)



1b (1.0 equiv.) **2a** (1.5 equiv.) **3a** (1.5 equiv.) **4a**, 0% yield

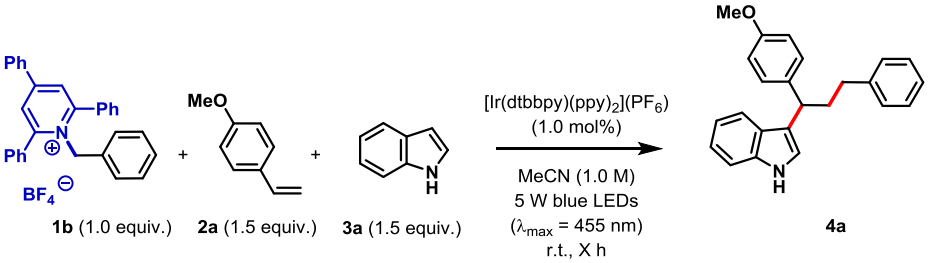
Light Sources (0.20 mmol scale)



1b (1.0 equiv.) **2a** (1.5 equiv.) **3a** (1.5 equiv.) **4a**

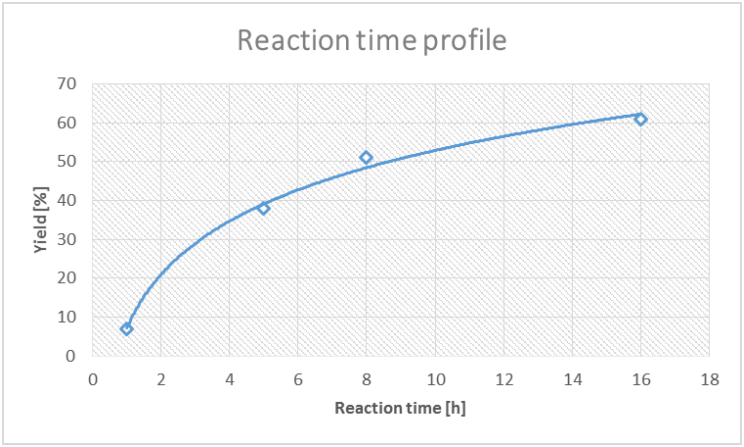
Light Source	Yield **4a** [%]
455 nm, 5 W	***63***
420 nm, 3 W	*48*
400 nm, 3 W	*31*
365 nm, 3 W	*9*

Reaction time (0.20 mmol scale)

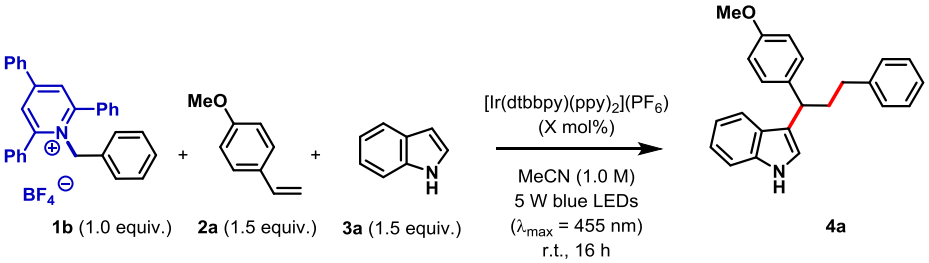


1b (1.0 equiv.) **2a** (1.5 equiv.) **3a** (1.5 equiv.) **4a**

Reaction time [h]	Yield **4a** [%]
1	*7*
5	*38*
8	*51*
16	*63*



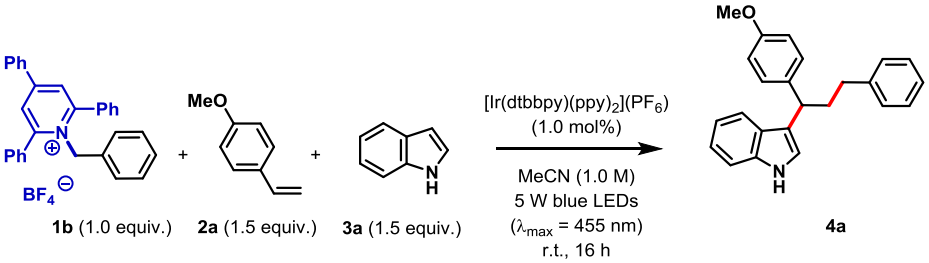
Catalyst loading (0.20 mmol scale)



1b (1.0 equiv.) **2a** (1.5 equiv.) **3a** (1.5 equiv.) **4a**

Catalyst loading [mol%]	Yield **4a** [%]
1	***63***
0.5	*50*
0.1	*30*

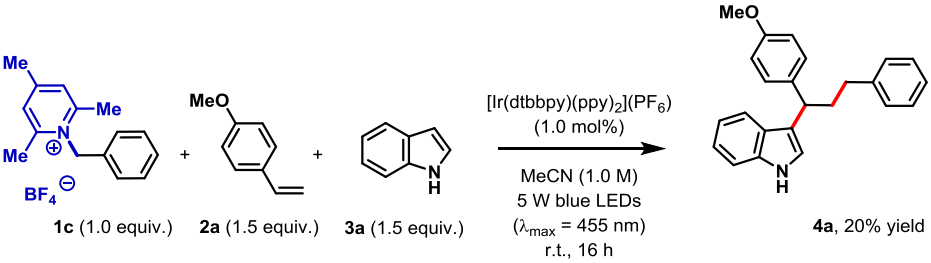
Control reactions (0.20 mmol scale)



1b (1.0 equiv.) **2a** (1.5 equiv.) **3a** (1.5 equiv.) **4a**

Deviation	Yield **4a** [%]
No Photocatalyst	*0*
No Light, 40 °C	*0*
+ TEMPO (2.0 equiv.)	*0*

Using Trimethylpyridinium salt 1c (0.30 mmol scale)



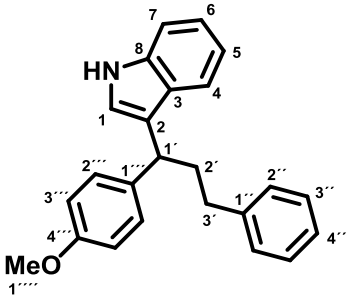
1c (1.0 equiv.) **2a** (1.5 equiv.) **3a** (1.5 equiv.) **4a**, 20% yield

3. Substrate scope

General procedure

An oven-dried screw cap Schlenk reaction tube was charged with the Katritzky salt (**1**, 0.30 mmol, 1.0 equiv.), the arene (**3**, 0.45 mmol, 1.5 equiv.), if solid, and [Ir(dtbbpy)(ppy)$_2$](PF$_6$) (2.7 mg, 0.003 mmol, 1 mol%). The tube was evacuated and backfilled with argon. Acetonitrile (0.3 mL, 1.0 M) was added in a stream of argon. The liquid arene (**3**, 0.45 mmol, 1.5 equiv.) and the styrene (**2**, 0.45 mmol, 1.5 equiv.) were added in a stream of argon. The reaction mixture was degassed by three consecutive freeze-pump-thaw cycles. The solution was stirred under irradiation (λ_{max} = 455 nm, 5 W) for 16 h in an atmosphere of argon. Triethylamine (0.3 mL) was added to the reaction mixture. The crude product was absorbed to silica and purified by column chromatography (SiO$_2$, mixtures of *n*-pentane/ethyl acetate, *n*-pentane/dichloromethane or dichloromethane/methanol).

3-(1-(4-Methoxyphenyl)-3-phenylpropyl)-1*H*-indole (4a)

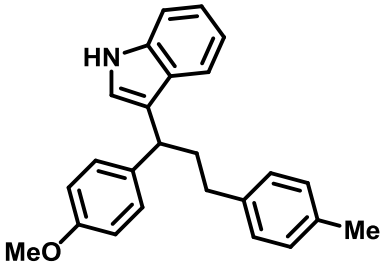


Following the general procedure the reaction was carried out with 1-benzyl-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (0.30 mmol, 145.6 mg), 4-methoxystyrene (0.45 mmol, 61 µL), 1*H*-indole (0.45 mmol, 52.7 mg), [Ir(dtbbpy)(ppy)$_2$](PF$_6$) (1.0 mol%, 2.7 mg) and acetonitrile (0.3 mL, 1.0 M). Isolation by column chromatography (SiO$_2$, *n*-pentane/dichloromethane 3:1 to 1:1). 3-(1-(4-Methoxyphenyl)-3-phenylpropyl)-1*H*-indole (**4a**) was formed in 56% yield (57.7 mg, 0.17 mmol) as a colourless oil.

***R*$_f$ (*n*-pentane/dichloromethane 1:1):** 0.4; **^{1}H NMR (600 MHz, CD$_2$Cl$_2$)** δ = 8.11 (s, 1H, N-*H*), 7.39 (dd, *J* = 7.9, 1.0 Hz, 1H, C4-*H*), 7.34 (dt, *J* = 8.1, 0.9 Hz, 1H, C7-*H*), 7.27 (dd, *J* = 8.2, 7.0 Hz, 2H, C3´´-*H*), 7.26 – 7.22 (m, 2H, C2´´´-*H*), 7.20 – 7.15 (m, 3H, C2´´-*H*, C4´´-*H*), 7.15 – 7.09 (m, 2H, C1-*H*, C6-*H*), 6.98 (ddd, *J* = 8.0, 7.0, 1.0 Hz, 1H, C5-*H*), 6.86 – 6.81 (m, 2H, C15-*H*), 4.16 – 4.12 (m, 1H, C1´-*H*), 3.76 (s, 3H, C-1´´´´-*H*), 2.70 – 2.58 (m, 2H, C-3´-*H*$_a$, C-3´-*H*$_b$), 2.50 (ddt, *J* = 13.2, 9.4, 6.7 Hz, 1H, C2´-*H*$_a$), 2.30 (dtd, *J* = 13.3, 9.0, 6.1 Hz, 1H, C2´-*H*$_b$); **^{13}C NMR (151 MHz, CD$_2$Cl$_2$)** δ = 158.5 (C$_q$, C4´´´), 143.2 (C$_q$, C1´´), 137.9 (C$_q$, C1´´´), 137.2 (C$_q$, C8), 129.4 (CH, C2´´´), 129.0 (CH, C2´´), 128.8 (CH, C3´´), 127.5 (C$_q$, C3), 126.2 (CH, C4´´), 122.4 (CH, C6), 121.5 (CH, C1), 120.9 (C$_q$, C2), 119.8 (CH, C4), 119.6 (CH, C5), 114.2 (CH, C3´´´), 111.6 (CH, C7), 55.7 (CH$_3$, C1´´´´), 42.1 (CH, C1´), 38.4 (CH$_2$, C3´), 34.8 (CH$_2$, C2´); **HRMS** *m/z* (ESI): calcd. for [C$_{24}$H$_{22}$NOClNa]$^+$ 398.1282; found 398.1271; **ATR-IR *v* (cm^{-1})** 3418, 1055, 3024, 2932, 2832, 1605, 1582, 1505, 1458, 1420, 1335, 1296, 1242, 1173, 1096, 1034, 1011, 910, 810, 741, 702.

The assignment was done by 2D-NMR experiments.

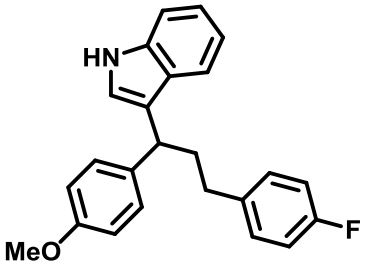
3-(1-(4-Methoxyphenyl)-3-(*p*-tolyl)propyl)-1*H*-indole (4b)



Following the general procedure the reaction was carried out with 1-(4-methylbenzyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (0.30 mmol, 149.8 mg), 4-methoxystyrene (0.45 mmol, 61 µL), 1*H*-indole (0.45 mmol, 52.7 mg), $[Ir(dtbbpy)(ppy)_2](PF_6)$ (1.0 mol%, 2.7 mg) and acetonitrile (0.3 mL, 1.0 M). Isolation by column chromatography (SiO_2, *n*-pentane/dichloromethane 3:1 to 1:1). 3-(1-(4-Methoxyphenyl)-3-(*p*-tolyl)propyl)-1*H*-indole (**4b**) was formed in 41% yield (43.6 mg, 0.12 mmol) as a colourless oil.

***R*$_f$ (*n*-pentane/dichloromethane 1:1):** 0.4; **^{1}H NMR (400 MHz, CD_2Cl_2)** δ = 8.11 (br, 1H), 7.38 (d, *J* = 8.0 Hz, 1H), 7.34 (d, *J* = 8.2 Hz, 1H), 7.28 – 7.20 (m, 2H), 7.16 – 7.02 (m, 6H), 7.02 – 6.93 (m, 1H), 6.86 – 6.78 (m, 2H), 4.13 (t, J = 7.6 Hz, 1H), 3.76 (s, 3H), 2.67 – 2.52 (m, 2H), 2.53 – 2.40 (m, 1H), 2.31 (s, 3H), 2.28 – 2.22 (m, 1H); **^{13}C NMR (101 MHz, CD_2Cl_2)** δ = 158.5, 140.0, 138.0, 137.2, 135.7, 129.5, 129.4, 128.9, 127.5, 122.4, 121.5, 121.0, 119.8, 119.6, 114.2, 111.6, 55.7, 42.1, 38.5, 34.3, 21.3; **HRMS** *m/z* (ESI): calcd. for $[C_{25}H_{25}NONa]^+$, 378.1828; found 378.1828; **ATR-IR *v* (cm^{-1})** 3418, 3048, 3024, 2924, 2854, 1512, 1458, 1242, 1180, 1034, 810, 741.

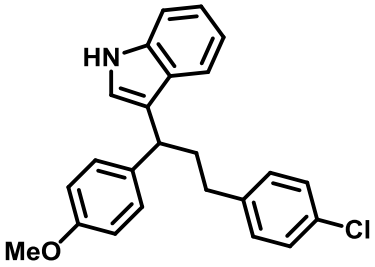
3-(3-(4-Fluorophenyl)-1-(4-methoxyphenyl)propyl)-1*H*-indole (4c)



Following the general procedure the reaction was carried out with 1-(4-Fluorobenzyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (0.30 mmol, 151.0 mg), 4-methoxystyrene (0.45 mmol, 61 µL), 1*H*-indole (0.45 mmol, 52.7 mg), $[Ir(dtbbpy)(ppy)_2](PF_6)$ (1.0 mol%, 2.7 mg) and acetonitrile (0.3 mL, 1.0 M). Isolation by column chromatography (SiO_2, *n*-pentane/ethyl acetate 10:1). 3-(3-(4-Fluorophenyl)-1-(4-methoxyphenyl)propyl)-1*H*-indole (**4c**) was formed in 53% yield (57.5 mg, 0.16 mmol) as a yellow oil.

***R*$_f$ (*n*-pentane/ethyl acetate 10:1):** 0.4; **^{1}H NMR (300 MHz, $CDCl_3$)** *δ* = 7.89 (s, 1H), 7.43 – 7.34 (m, 1H), 7.32 – 7.23 (m, 1H), 7.23 – 7.16 (m, 2H), 7.15 – 6.87 (m, 7H), 6.85 – 6.76 (m, 2H), 4.19 – 3.98 (m, 1H), 3.74 (s, 3H), 2.63 – 2.52 (m, 2H), 2.53 – 2.35 (m, 1H), 2.31 – 2.17 (m, 1H); **^{13}C NMR (75 MHz, $CDCl_3$)** *δ* = 161.3 (d, *J* = 243.1 Hz), 158.0, 138.1 (d, *J* = 3.2 Hz), 137.1, 136.6, 129.9 (d, *J* = 7.7 Hz), 129.0, 127.0, 122.1, 121.0, 120.5, 119.6, 119.4, 115.1 (d, *J* = 20.9 Hz), 113.9, 111.2, 55.3, 41.5, 38.1, 33.5; **^{19}F NMR (282 MHz, $CDCl_3$)** *δ* = -117.83; **HRMS** *m/z* (ESI): calcd. for $[C_{24}H_{22}NOFNa]^+$ 382.1578; found 382.1581; **ATR-IR *v* (cm^{-1})** 3418, 3055, 3001, 2932, 2839, 1605, 1582, 1505, 1458, 1420, 1335, 1296, 1242, 1219, 1173, 1157, 1096, 1034, 1011, 826, 764, 741, 702.

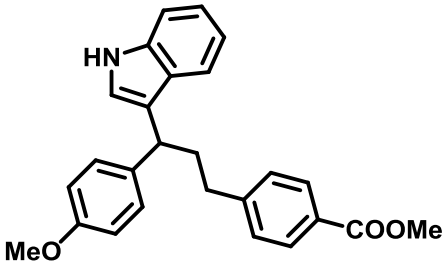
3-(3-(4-Chlorophenyl)-1-(4-methoxyphenyl)propyl)-1*H*-indole (4d)



Following the general procedure the reaction was carried out with 1-(4-chlorobenzyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (0.30 mmol, 155.9 mg), 4-methoxystyrene (0.45 mmol, 61 µL), 1*H*-indole (0.45 mmol, 52.7 mg), [Ir(dtbbpy)(ppy)$_2$](PF$_6$) (1.0 mol%, 2.7 mg) and acetonitrile (0.3 mL, 1.0 M). Isolation by column chromatography (SiO_2, *n*-pentane/dichloromethane 2:1 to 1:2). 3-(3-(4-Chlorophenyl)-1-(4-methoxyphenyl)propyl)-1*H*-indole (**4d**) was formed in 39% yield (43.7 mg, 0.12 mmol) as a white solid.

***R*$_f$ (*n*-pentane/dichloromethane 1:1):** 0.2; **^{1}H NMR (400 MHz, CD_2Cl_2)** δ = 8.12 (s, 1H), 7.42 – 7.35 (m, 1H), 7.35 (dt, *J* = 8.3, 1.0 Hz, 1H), 7.29 – 7.18 (m, 4H), 7.17 – 7.07 (m, 4H), 6.98 (ddd, *J* = 8.1, 7.0, 1.0 Hz, 1H), 6.87 – 6.79 (m, 2H), 4.18 – 4.07 (m, 1H), 3.76 (s, 3H), 2.71 – 2.54 (m, 2H), 2.48 (ddt, *J* = 13.7, 8.6, 6.8 Hz, 1H), 2.28 (dtd, *J* = 13.2, 8.7, 6.5 Hz, 1H); **^{13}C NMR (101 MHz, CD_2Cl_2)** δ = 158.6, 141.7, 137.7, 137.1, 131.8, 130.5, 129.3, 128.8, 127.4, 122.5, 121.4, 120.7, 119.8, 119.7, 114.2, 111.6, 55.7, 41.9, 38.2, 34.0; **HRMS** *m/z* (ESI): calcd. for $[C_{24}H_{22}NOClNa]^+$ 398.1282; found 398.1271; **ATR-IR *v* (cm^{-1})** 3418, 3055, 3001, 2932, 2832, 1613, 1582, 1512, 1489, 1458, 1420, 1335, 1304, 1242, 1173, 1096, 1034, 1011, 949, 810, 741, 710.

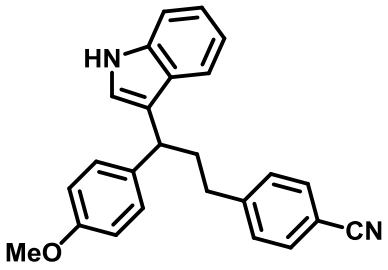
Methyl 4-(3-(1*H*-indol-3-yl)-3-(4-methoxyphenyl)propyl)benzoate (4e)



Following the general procedure the reaction was carried out with 1-(4-(methoxycarbonyl)benzyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (0.30 mmol, 163.0 mg), 4-methoxystyrene (0.45 mmol, 61 µL), 1*H*-indole (0.45 mmol, 52.7 mg), [Ir(dtbbpy)(ppy)$_2$](PF$_6$) (1.0 mol%, 2.7 mg) and acetonitrile (0.3 mL, 1.0 M). Isolation by column chromatography (SiO_2, *n*-pentane/dichloromethane 1:1 to 1:3). Methyl 4-(3-(1*H*-indol-3-yl)-3-(4-methoxyphenyl)propyl)benzoate (**4e**) was formed in 61% yield (73.5 mg, 0.18 mmol) as a yellowish solid.

***R*$_f$ (*n*-pentane/dichloromethane 1:4):** 0.2; **^{1}H NMR (400 MHz, CD_2Cl_2)** δ = 8.17 (br, 1H), 7.98 – 7.90 (m, 2H), 7.39 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.35 (dt, *J* = 8.1, 0.9 Hz, 1H), 7.29 – 7.19 (m, 4H), 7.17 – 7.06 (m, 2H), 6.99 (ddd, *J* = 8.0, 7.0, 1.0 Hz, 1H), 6.88 – 6.80 (m, 2H), 4.18 – 4.10 (m, 1H), 3.88 (s, 3H), 3.76 (s, 3H), 2.79 – 2.63 (m, 2H), 2.52 (ddt, *J* = 13.6, 8.9, 6.8 Hz, 1H), 2.38 – 2.27 (m, 1H); **^{13}C NMR (101 MHz, CD_2Cl_2)** δ = 167.5, 158.6, 148.7, 137.7, 137.2, 130.1, 129.3, 129.1, 128.4, 127.4, 122.5, 121.5, 120.7, 119.8, 119.7, 114.2, 111.6, 55.7, 52.4, 42.0, 37.9, 34.8; **HRMS** *m/z* (ESI): calcd. for $[C_{26}H_{25}NO_3Na]^+$, 422.1727; found 422.1728; **ATR-IR *v* (cm^{-1})** 3410, 3032, 2978, 2886, 2839, 1713, 1613, 1574, 1512, 1458, 1435, 1281, 1242, 1180, 1103, 1034, 1018, 964, 833, 810, 741.

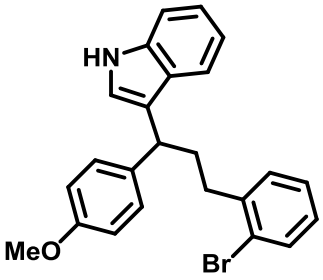
4-(3-(1*H*-Indol-3-yl)-3-(4-methoxyphenyl)propyl)benzonitrile (4f)



Following the general procedure the reaction was carried out with 1-(4-cyanobenzyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (0.30 mmol, 153.1 mg), 4-methoxystyrene (0.45 mmol, 61 µL), 1*H*-indole (0.45 mmol, 52.7 mg), [Ir(dtbbpy)(ppy)$_2$](PF$_6$) (1.0 mol%, 2.7 mg) and acetonitrile (0.3 mL, 1.0 M). Isolation by column chromatography (SiO$_2$, *n*-pentane/dichloromethane 1:1 to 1:3). 4-(3-(1*H*-Indol-3-yl)-3-(4-methoxyphenyl)-propyl)benzonitrile (**4f**) was formed in 46% yield (51.0 mg, 0.14 mmol) as a white solid.

***R*$_f$ (*n*-pentane/dichloromethane 1:4):** 0.3; **^{1}H NMR (400 MHz, CD$_2$Cl$_2$)** δ = 8.15 (br, 1H), 7.62 – 7.50 (m, 2H), 7.42 – 7.32 (m, 2H), 7.30 – 7.21 (m, 2H), 7.26 – 7.19 (m, 2H), 7.17 – 7.09 (m, 1H), 7.09 (d, *J* = 2.5 Hz, 1H), 7.03 – 6.95 (m, 1H), 6.89 – 6.78 (m, 2H), 4.18 – 4.08 (m, 1H), 3.76 (s, 3H), 2.80 – 2.63 (m, 2H), 2.51 (ddt, *J* = 13.6, 8.8, 6.9 Hz, 1H), 2.31 (dtd, *J* = 13.3, 8.8, 6.4 Hz, 1H); **^{13}C NMR (101 MHz, CD$_2$Cl$_2$)** δ = 158.6, 148.9, 137.4, 137.2, 132.7, 129.8, 129.3, 127.3, 122.5, 121.5, 120.5, 119.7, 119.7, 114.3, 111.7, 110.1, 55.7, 42.0, 37.7, 34.9 (*one carbon signal was not detected*); **HRMS** *m/z* (ESI): calcd. for [C$_{25}$H$_{22}$N$_2$ONa]$^+$, 389.1624; found 389.1628; **ATR-IR *v* (cm^{-1})** 3410, 3055, 3032, 2978, 2932, 2862, 2839, 2230, 1605, 1574, 1505, 1458, 1420, 1335, 1304, 1242, 1173, 1096, 1034, 949, 826, 741, 710, 679.

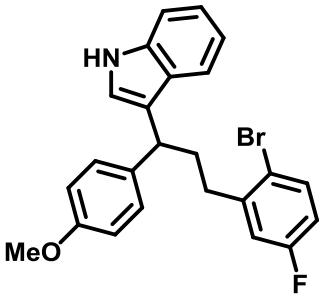
3-(3-(2-Bromophenyl)-1-(4-methoxyphenyl)propyl)-1*H*-indole (4g)



Following the general procedure the reaction was carried out with 1-(2-bromobenzyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (0.30 mmol, 169.3 mg), 4-methoxystyrene (0.45 mmol, 61 µL), 1*H*-indole (0.45 mmol, 52.7 mg), [Ir(dtbbpy)(ppy)$_2$](PF$_6$) (1.0 mol%, 2.7 mg) and acetonitrile (0.3 mL, 1.0 M). Isolation by column chromatography (SiO$_2$, *n*-pentane/dichloromethane 2:1 to 1:1). 3-(3-(2-Bromophenyl)-1-(4-methoxyphenyl)propyl)-1*H*-indole (**4g**) was formed in 61% yield (76.3 mg, 0.18 mmol) as a colourless oil.

***R*$_f$ (*n*-pentane/dichloromethane 1:1):** 0.3; **^{1}H NMR (400 MHz, CD$_2$Cl$_2$)** δ = 8.10 (br, 1H), 7.54 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.45 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.35 (dd, *J* = 8.2, 1.0 Hz, 1H), 7.32 – 7.25 (m, 2H), 7.27 – 7.17 (m, 2H), 7.18 – 7.10 (m, 2H), 7.07 (ddd, *J* = 7.9, 7.0, 2.1 Hz, 1H), 7.01 (ddd, *J* = 8.0, 7.0, 1.1 Hz, 1H), 6.89 – 6.82 (m, 2H), 4.25 – 4.20 (m, 1H), 3.77 (s, 3H), 2.83 (ddd, *J* = 13.5, 10.8, 5.5 Hz, 1H), 2.73 (ddd, *J* = 13.5, 10.7, 5.3 Hz, 1H), 2.49 (dddd, *J* = 13.2, 10.7, 6.7, 5.5 Hz, 1H), 2.29 (dddd, *J* = 13.6, 10.8, 8.5, 5.3 Hz, 1H); **^{13}C NMR (101 MHz, CD$_2$Cl$_2$)** δ = 158.6, 142.5, 137.7, 137.2, 133.3, 131.1, 129.4, 128.1, 128.0, 127.5, 124.9, 122.5, 121.5, 120.7, 119.8, 119.7, 114.2, 111.6, 55.7, 42.5, 36.9, 35.5; **HRMS** *m/z* (ESI): calcd. for [C$_{24}$H$_{22}$NOBrNa]$^+$, 442.0777; found 442.0784; **ATR-IR *v* (cm^{-1})** 3418, 3055, 3001, 2955, 2932, 2862, 2832, 1613, 1582, 1505, 1458, 1435, 1420, 1335, 1304, 1242, 1173, 1096, 1026, 949, 826, 741, 710, 656.

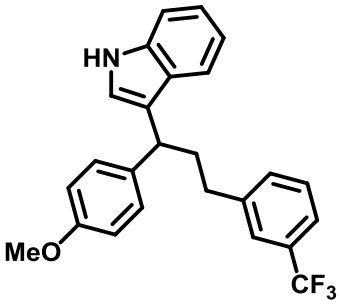
3-(3-(2-Bromo-5-fluorophenyl)-1-(4-methoxyphenyl)propyl)-1*H*-indole (4h)



Following the general procedure the reaction was carried out with 1-(2-bromo-5-fluorobenzyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (0.30 mmol, 174.7 mg), 4-methoxystyrene (0.45 mmol, 61 µL), 1*H*-indole (0.45 mmol, 52.7 mg), [Ir(dtbbpy)(ppy)$_2$](PF$_6$) (1.0 mol%, 2.7 mg) and acetonitrile (0.3 mL, 1.0 M). Isolation by column chromatography (SiO$_2$, *n*-pentane/ethyl acetate 10:1). 3-(3-(2-Bromo-5-fluorophenyl)-1-(4-methoxyphenyl)propyl)-1*H*-indole (**4h**) was formed in 63% yield (82.3 mg, 0.19 mmol) as a colourless oil.

***R*$_f$ (*n*-pentane/ethyl acetate 10:1):** 0.3; **^{1}H NMR (400 MHz, CD$_2$Cl$_2$)** δ = 8.12 (s, 1H), 7.49 (dd, *J* = 8.8, 5.5 Hz, 1H), 7.48 – 7.42 (m, 1H), 7.35 (dt, *J* = 8.1, 0.9 Hz, 1H), 7.32 – 7.24 (m, 2H), 7.18 – 7.09 (m, 2H), 7.01 (ddd, *J* = 8.0, 7.0, 1.0 Hz, 1H), 6.94 (dd, *J* = 9.6, 3.1 Hz, 1H), 6.89 – 6.81 (m, 2H), 6.84 – 6.77 (m, 1H), 4.22 (dd, *J* = 8.3, 7.0 Hz, 1H), 3.77 (s, 3H), 2.80 (ddd, *J* = 13.6, 10.8, 5.5 Hz, 1H), 2.70 (ddd, *J* = 13.6, 10.7, 5.3 Hz, 1H), 2.49 (dddd, *J* = 13.3, 10.7, 6.8, 5.6 Hz, 1H), 2.28 (dddd, *J* = 10.8, 8.2, 7.0, 4.2 Hz, 1H); **^{13}C NMR (101 MHz, CD$_2$Cl$_2$)** δ = 162.5 (d, *J* = 245.6 Hz), 158.6, 144.7 (d, *J* = 7.4 Hz), 137.5, 137.2, 134.4 (d, *J* = 8.2 Hz), 129.3, 127.4, 122.5, 121.5, 120.5, 119.8, 119.7, 119.0 (d, *J* = 3.0 Hz), 117.7 (d, *J* = 22.5 Hz), 115.1 (d, *J* = 22.5 Hz), 114.3, 111.6, 55.7, 42.5, 36.5, 35.6 (d, *J* = 1.4 Hz); **^{19}F NMR (376 MHz, CD$_2$Cl$_2$)** δ = -116.06; **HRMS** *m/z* (ESI): calcd. for [C$_{24}$H$_{21}$NOBrFNa]$^+$ 460.0683; found 460.0688; **ATR-IR *v* (cm^{-1})** 3418, 3055, 2932, 2832, 1605, 1582, 1512, 1466, 1412, 1335, 1304, 1242, 1173, 1157, 1103, 1026, 949, 872, 833, 810, 741, 710.

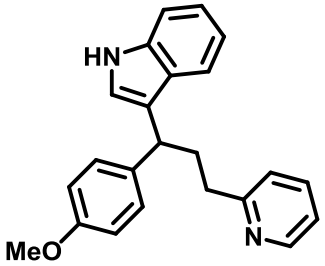
3-(1-(4-Methoxyphenyl)-3-(3-(trifluoromethyl)phenyl)propyl)-1*H*-indole (4i)



Following the general procedure the reaction was carried out with 2,4,6-triphenyl-1-(3-(trifluoromethyl)benzyl)pyridin-1-ium tetrafluoroborate (0.30 mmol, 166.0 mg), 4-methoxystyrene (0.45 mmol, 61 µL), 1*H*-indole (0.45 mmol, 52.7 mg), [Ir(dtbbpy)(ppy)$_2$](PF$_6$) (1.0 mol%, 2.7 mg) and acetonitrile (0.3 mL, 1.0 M). Isolation by column chromatography (SiO$_2$, *n*-pentane/ethyl acetate 5:1). 3-(1-(4-Methoxyphenyl)-3-(3-(trifluoromethyl)phenyl)propyl)-1*H*-indole (**4i**) was formed in 59% yield (72.3 mg, 0.18 mmol) as a white solid.

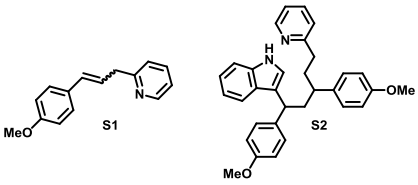
***R*$_f$ (*n*-pentane/ethyl acetate 3:1):** 0.6; **^{1}H NMR (400 MHz, CD$_2$Cl$_2$)** δ = 8.13 (s, 1H), 7.50 – 7.42 (m, 2H), 7.44 – 7.37 (m, 3H), 7.39 – 7.32 (m, 1H), 7.29 – 7.21 (m, 2H), 7.14 (ddd, *J* = 8.2, 7.0, 1.2 Hz, 1H), 7.13 – 7.08 (m, 1H), 7.04 – 6.97 (m, 1H), 6.89 – 6.81 (m, 2H), 4.19 – 4.11 (m, 1H), 3.77 (s, 3H), 2.81 – 2.64 (m, 2H), 2.61 – 2.47 (m, 1H), 2.41 – 2.27 (m, 1H); **^{13}C NMR (101 MHz, CD$_2$Cl$_2$)** δ = 158.6, 144.1, 137.6, 137.2, 132.7, 132.6, 130.8 (q, *J* = 31.7 Hz), 129.3, 127.4, 125.7 (q, *J* = 3.8 Hz), 125.0 (q, *J* = 272.2), 123.1 (q, *J* = 3.9 Hz), 122.5, 121.5, 120.6, 119.8, 119.7, 114.3, 111.7, 55.7, 42.1, 38.1, 34.6; **^{19}F NMR (376 MHz, CD$_2$Cl$_2$)** δ = -62.75; **HRMS** *m/z* (ESI): calcd. for [C$_{25}$H$_{22}$NOF$_3$Na]$^+$ 432.1546; found 432.1551; **ATR-IR *v* (cm^{-1})** 3418, 3055, 3001, 2931, 2862, 2839, 1613, 1512, 1451, 1420, 1327, 1242, 1196, 1157, 1119, 1096, 1072, 1034, 903, 833, 802, 741, 702.

3-(1-(4-Methoxyphenyl)-3-(pyridin-2-yl)propyl)-1*H*-indole (4j)



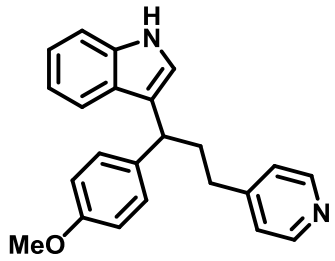
Following the general procedure the reaction was carried out with 2,4,6-triphenyl-1-(pyridin-2-ylmethyl)pyridin-1-ium tetrafluoroborate (0.30 mmol, 145.9 mg), 4-methoxystyrene (0.45 mmol, 61 µL), 1*H*-indole (0.45 mmol, 52.7 mg), [Ir(dtbbpy)(ppy)$_2$](PF$_6$) (1.0 mol%, 2.7 mg) and acetonitrile (0.3 mL, 1.0 M). Isolation by column chromatography (SiO$_2$, *n*-pentane/ethyl acetate 2:1 to 1:1).

A white solid (73.2 mg) was isolated, which was determined to contain an inseparable mixture of **4j** (84%), the Heck products **S1** (9%) and radical dimer **S2** (7%) by ^{1}H NMR spectroscopic analysis. 3-(1-(4-Methoxyphenyl)-3-(pyridin-2-yl)propyl)-1*H*-indole (**4j**) was formed in 60% yield (61.5 mg, 0.18 mmol).



***R*$_f$ (*n*-pentane/ethyl acetate 1:2):** 0.5; **^{1}H NMR (300 MHz, CD$_2$Cl$_2$)** δ = 8.61 (br, 1H), 8.53 (dd, *J* = 5.3, 2.0 Hz, 1H), 7.59 (td, *J* = 7.6, 1.9 Hz, 1H), 7.43 – 7.34 (m, 1H), 7.32 (dt, *J* = 8.1, 0.9 Hz, 1H), 7.27 – 7.18 (m, 2H), 7.16 – 7.07 (m, 4H), 6.97 (ddd, *J* = 8.0, 7.0, 1.1 Hz, 1H), 6.86 – 6.77 (m, 2H), 4.22 – 4.11 (m, 1H), 3.75 (s, 3H), 2.92 – 2.70 (m, 2H), 2.72 – 2.54 (m, 1H), 2.49 – 2.33 (m, 1H); **^{13}C NMR (75 MHz, CD$_2$Cl$_2$)** δ = 162.7, 158.5, 149.7, 137.9, 137.2, 136.8, 129.3, 127.5, 123.4, 122.3, 121.6, 121.5, 120.6, 119.8, 119.5, 114.1, 111.6, 55.7, 42.1, 37.1, 36.5; **HRMS** *m/z* (ESI): calcd. for [C$_{23}$H$_{22}$N$_2$OH]$^+$, 343.1805; found 343.1814; **ATR-IR *v* (cm^{-1})** 3418, 3163, 3055, 2947, 2924, 1589, 1512, 1458, 1435, 1242, 1180, 1034, 833, 741.

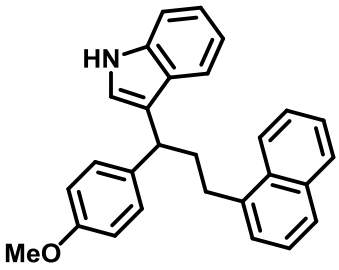
3-(1-(4-Methoxyphenyl)-3-(pyridin-4-yl)propyl)-1*H*-indole (4k)



Following the general procedure the reaction was carried out with 2,4,6-triphenyl-1-(pyridin-4-ylmethyl)pyridin-1-ium tetrafluoroborate (0.30 mmol, 145.9 mg), 4-methoxystyrene (0.45 mmol, 61 µL), 1*H*-indole (0.45 mmol, 52.7 mg), [Ir(dtbbpy)(ppy)$_2$](PF$_6$) (1.0 mol%, 2.7 mg) and acetonitrile (0.3 mL, 1.0 M). Isolation by column chromatography (SiO$_2$, dichloromethane/methanol 100:1 to 50:1). 3-(1-(4-Methoxyphenyl)-3-(pyridin-4-yl)propyl)-1*H*-indole (**4k**) was formed in 54% yield (55.6 mg, 0.16 mmol) as a white solid.

***R*$_f$ (dichloromethane/methanol 10:1):** 0.4; **^{1}H NMR (400 MHz, CDCl$_3$)** *δ* = 8.52 – 8.45 (m, 2H), 8.29 (br, 1H), 7.45 – 7.37 (m, 1H), 7.33 (dt, *J* = 8.2, 0.9 Hz, 1H), 7.27 – 7.19 (m, 2H), 7.15 (ddd, *J* = 8.2, 7.0, 1.2 Hz, 1H), 7.12 – 7.06 (m, 2H), 7.05 – 7.01 (m, 2H), 6.88 – 6.80 (m, 2H), 4.17 – 4.09 (m, 1H), 3.78 (s, 3H), 2.70 – 2.58 (m, 2H), 2.59 – 2.46 (m, 1H), 2.38 – 2.25 (m, 1H); **^{13}C NMR (101 MHz, CDCl$_3$)** *δ* = 158.1, 151.7, 149.7, 136.7, 136.7, 128.9, 126.9, 124.2, 122.2, 121.1, 120.1, 119.5, 119.4, 114.0, 111.3, 55.4, 41.6, 36.8, 33.7; **HRMS** *m/z* (ESI): calcd. for [C$_{23}$H$_{22}$N$_2$OH]$^+$ 343.1805; found 343.1804; **ATR-IR *v* (cm^{-1})** 3410, 3164, 3055, 2924, 2862, 2831, 1605, 1582, 1505, 1458, 1420, 1335, 1304, 1242, 1180, 1126, 1111, 1034, 1003, 826, 810, 741.

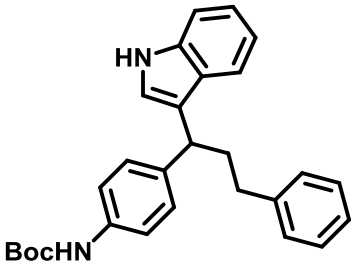
3-(1-(4-Methoxyphenyl)-3-(naphthalen-1-yl)propyl)-1*H*-indole (4l)



Following the general procedure the reaction was carried out with 1-(naphthalen-1-ylmethyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (0.30 mmol, 160.6 mg), 4-methoxystyrene (0.45 mmol, 61 µL), 1*H*-indole (0.45 mmol, 52.7 mg), $[Ir(dtbbpy)(ppy)_2](PF_6)$ (1.0 mol%, 2.7 mg) and acetonitrile (0.3 mL, 1.0 M). Isolation by column chromatography (SiO_2, *n*-pentane/dichloromethane 2:1 to 1:1). 3-(1-(4-Methoxyphenyl)-3-(naphthalen-1-yl)propyl)-1*H*-indole (**4l**) was formed in 38% yield (44.3 mg, 0.11 mmol) as a white solid.

***R*$_f$ (*n*-pentane/dichloromethane 1:1):** 0.3; **^{1}H NMR (400 MHz, CD_2Cl_2)** δ = 8.10 (br, 1H), 7.92 – 7.80 (m, 2H), 7.77 – 7.67 (m, 1H), 7.51 – 7.36 (m, 4H), 7.38 – 7.25 (m, 4H), 7.20 – 7.07 (m, 2H), 7.00 (t, *J* = 7.5 Hz, 1H), 6.91 – 6.84 (m, 2H), 4.28 (dd, *J* = 8.7, 6.5 Hz, 1H), 3.78 (s, 3H), 3.20 – 3.02 (m, 2H), 2.63 (ddt, *J* = 13.0, 10.3, 6.4 Hz, 1H), 2.51 – 2.35 (m, 1H); **^{13}C NMR (101 MHz, CD_2Cl_2)** δ = 158.6, 139.4, 137.9, 137.2, 134.5, 132.4, 129.4, 129.2, 127.4, 127.0, 126.5, 126.2, 126.1, 126.0, 124.4, 122.5, 121.4, 120.9, 119.9, 119.6, 114.2, 111.6, 55.7, 42.7, 37.8, 32.0; **HRMS** *m/z* (ESI): calcd. for $[C_{28}H_{25}NONa]^+$, 414.1828; found 414.1821; **ATR-IR *v* (cm^{-1})** 3426, 3055, 2932, 2855, 1613, 1512, 1458, 1242, 1180, 1034, 795, 779, 741.

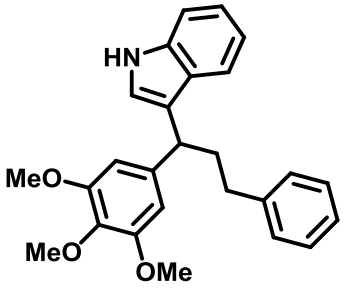
***tert*-Butyl (4-(1-(1*H*-indol-3-yl)-3-phenylpropyl)phenyl)carbamate (4m)**



Following the general procedure the reaction was carried out with 1-benzyl-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (0.30 mmol, 145.6 mg), *tert*-butyl (4-vinylphenyl)carbamate (0.45 mmol, 98.7 mg), 1*H*-indole (0.45 mmol, 52.7 mg), $[Ir(dtbbpy)(ppy)_2](PF_6)$ (1.0 mol%, 2.7 mg) and acetonitrile (0.3 mL, 1.0 M). Isolation by column chromatography (SiO_2, *n*-pentane/dichloromethane 1:1 to pure dichloromethane). *tert*-Butyl (4-(1-(1*H*-indol-3-yl)-3-phenylpropyl)-phenyl)carbamate (**4m**) was formed in 41% yield (51.9 mg, 0.12 mmol) as a white solid.

***R*$_f$ (dichloromethane):** 0.5; **^{1}H NMR (400 MHz, CD_2Cl_2)** *δ* = 8.15 (br, 1H), 7.38 (dd, *J* = 7.9, 1.0 Hz, 1H), 7.34 (dt, *J* = 8.1, 0.9 Hz, 1H), 7.32 – 7.21 (m, 6H), 7.22 – 7.14 (m, 3H), 7.16 – 7.07 (m, 2H), 6.98 (ddd, *J* = 8.0, 7.0, 1.0 Hz, 1H), 6.53 (br, 1H), 4.21 – 4.11 (m, 1H), 2.64 (ddd, *J* = 8.9, 6.6, 2.5 Hz, 2H), 2.50 (ddt, *J* = 13.6, 8.8, 6.7 Hz, 1H), 2.38 – 2.24 (m, 1H), 1.50 (s, 9H); **^{13}C NMR (101 MHz, CD_2Cl_2)** *δ* = 153.3, 143.1, 140.5, 137.2, 137.1, 129.0, 128.9, 128.8, 127.5, 126.2, 122.4, 121.6, 120.6, 119.8, 119.6, 119.1, 111.6, 80.7, 42.3, 38.3, 34.7, 28.6; **HRMS** *m/z* (ESI): calcd. for $[C_{28}H_{30}N_2O_2Na]^+$, 449.2199; found 449.2198; **ATR-IR *v* (cm^{-1})** 3418, 3055, 3024, 2978, 2932, 1862, 1705, 1613, 1597, 1520, 1458, 1412, 1389, 1366, 1312, 1227, 1157, 1096, 1057, 1018, 949, 903, 826, 741, 702.

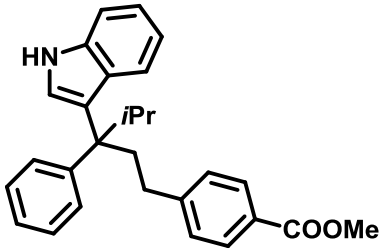
3-(3-Phenyl-1-(3,4,5-trimethoxyphenyl)propyl)-1*H*-indole (4n)



Following the general procedure the reaction was carried out with 1-benzyl-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (0.30 mmol, 145.6 mg), 1,2,3-trimethoxy-5-vinylbenzene (0.60 mmol, 116.5 mg), 1*H*-indole (0.60 mmol, 70.3 mg), [Ir(dtbbpy)(ppy)$_2$](PF$_6$) (1.0 mol%, 2.7 mg) and acetonitrile (0.3 mL, 1.0 M). Isolation by column chromatography (SiO$_2$, *n*-pentane/ethyl acetate 3:1). 3-(3-Phenyl-1-(3,4,5-trimethoxyphenyl)propyl)-1*H*-indole (**4n**) was formed in 35% yield (42.6 mg, 0.11 mmol) as a white solid.

***R*$_f$ (*n*-pentane/ethyl acetate 3:1):** 0.2; **^{1}H NMR (400 MHz, CD$_2$Cl$_2$)** δ = 8.19 (br, 1H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.36 (d, *J* = 8.2 Hz, 1H), 7.28 (t, *J* = 7.6 Hz, 2H), 7.22 – 7.09 (m, 5H), 7.01 (t, *J* = 7.5 Hz, 1H), 6.57 (s, 2H), 4.12 (t, *J* = 7.5 Hz, 1H), 3.79 (s, 6H), 3.73 (s, 3H), 2.65 (t, *J* = 7.7 Hz, 2H), 2.51 (dq, *J* = 14.8, 7.4 Hz, 1H), 2.33 (ddd, *J* = 14.0, 10.4, 7.1 Hz, 1H); **^{13}C NMR (101 MHz, CD$_2$Cl$_2$)** δ = 153.8, 143.1, 141.6, 137.1, 136.8, 129.0, 128.8, 127.5, 126.3, 122.5, 121.5, 120.5, 119.8, 119.7, 111.6, 105.5, 60.9, 56.5, 43.4, 38.3, 34.7; **HRMS** *m/z* (ESI): calcd. for [C$_{26}$H$_{27}$NO$_3$Na]$^+$, 424.1883; found 424.1883; **ATR-IR *v* (cm^{-1})** 3410, 3364, 3055, 3024, 2932, 2839, 1589, 1505, 1458, 1429, 1327, 1234, 1119, 1003, 764, 741, 702.

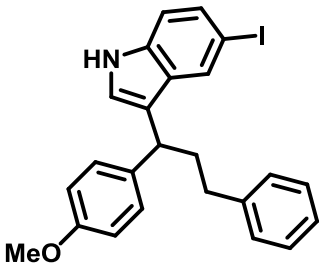
Methyl 4-(3-(1*H*-indol-3-yl)-4-methyl-3-phenylpentyl)benzoate (4o)



Following the general procedure the reaction was carried out with 1-(4-(methoxycarbonyl)benzyl-2,4,6-triphenylpyridin-1-ium (0.30 mmol, 163.0 mg), (3-methylbut-1-en-2-yl)benzene (0.45 mmol, 66 mg), 1*H*-indole (0.45 mmol, 52.7 mg), [Ir(dtbbpy)(ppy)$_2$](PF$_6$) (1.0 mol%, 2.7 mg) and acetonitrile (0.3 mL, 1.0 M) for 24 h. Isolation by column chromatography (SiO$_2$, *n*-pentane/dichloromethane 2:1 to 1:3). Methyl 4-(3-(1*H*-indol-3-yl)-4-methyl-3-phenylpentyl)benzoate (**4o**) was formed in 34% yield (42.5 mg, 0.10 mmol) as a colourless oil.

***R*$_f$ (*n*-pentane/dichloromethane 1:3):** 0.4; **^{1}H NMR (400 MHz, CD$_2$Cl$_2$)** δ = 8.28 (br, 1H), 7.92 – 7.80 (m, 2H), 7.38 (dt, *J* = 8.2, 0.9 Hz, 1H), 7.35 – 7.21 (m, 6H), 7.07 (ddd, *J* = 8.2, 7.0, 1.2 Hz, 1H), 7.06 – 6.99 (m, 2H), 6.78 (ddd, *J* = 8.0, 7.0, 1.1 Hz, 1H), 6.69 – 6.62 (m, 1H), 3.85 (s, 3H), 2.78 (hept, *J* = 6.7 Hz, 1H), 2.59 – 2.36 (m, 3H), 2.27 – 2.16 (m, 1H), 0.95 (d, *J* = 6.7 Hz, 3H), 0.92 (d, *J* = 6.7 Hz, 3H); **^{13}C NMR (101 MHz, CD$_2$Cl$_2$)** δ = 167.5, 149.6, 144.3, 137.5, 130.0, 128.9, 128.2, 127.7, 127.5, 126.4, 124.7, 123.0, 121.9, 120.6, 119.0, 111.6, 52.3, 50.9, 41.0, 31.7, 31.6, 19.1, 18.8 (*one carbon signal was not detected*); **HRMS** *m/z* (ESI): calcd. for [C$_{28}$H$_{29}$NO$_2$Na]$^+$, 434.2091; found 434.2102; **ATR-IR *v* (cm^{-1})** 3418, 3055, 3032, 2947, 1705, 1613, 1458, 1435, 1412, 1281, 1180, 1111, 1018, 856, 764, 741, 702.

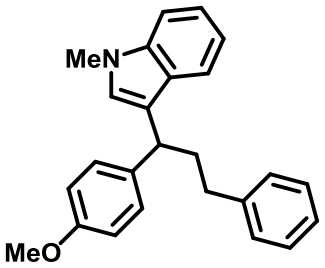
5-Iodo-3-(1-(4-methoxyphenyl)-3-phenylpropyl)-1*H*-indole (4p)



Following the general procedure the reaction was carried out with 1-benzyl-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (0.30 mmol, 145.6 mg), 4-methoxystyrene (0.45 mmol, 61 µL), 5-iodo-1*H*-indole (0.45 mmol, 109.4 mg), [Ir(dtbbpy)(ppy)$_2$](PF$_6$) (1.0 mol%, 2.7 mg) and acetonitrile (0.3 mL, 1.0 M). Isolation by column chromatography (SiO$_2$, *n*-pentane/dichloromethane 2:1 to 1:1). 5-Iodo-3-(1-(4-methoxyphenyl)-3-phenylpropyl)-1*H*-indole (**4p**) was formed in 32% yield (45.1 mg, 0.10 mmol) as a white solid.

***R*$_f$ (*n*-pentane/dichloromethane 1:1):** 0.3; **^{1}H NMR (400 MHz, CD$_2$Cl$_2$)** δ = 8.17 (br, 1H), 7.77 – 7.66 (m, 1H), 7.39 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.34 – 7.25 (m, 2H), 7.24 – 7.12 (m, 6H), 7.07 (dd, *J* = 2.5, 0.9 Hz, 1H), 6.89 – 6.82 (m, 2H), 4.10 – 4.05 (m, 1H), 3.78 (s, 3H), 2.69 – 2.57 (m, 2H), 2.51 – 2.38 (m, 1H), 2.29 (dtd, *J* = 13.2, 8.7, 6.7 Hz, 1H); **^{13}C NMR (101 MHz, CD$_2$Cl$_2$)** δ = 158.6, 143.0, 137.4, 136.1, 130.7, 130.1, 129.3, 129.0, 128.9, 128.6, 126.3, 122.4, 120.4, 114.3, 113.7, 83.0, 55.7, 41.8, 38.5, 34.6; **HRMS** *m/z* (ESI): calcd. for [C$_{24}$H$_{22}$NOINa]$^+$, 490.0638; found 490.0634; **ATR-IR *v* (cm^{-1})** 3418, 3055, 3024, 2932, 2855, 2832, 1605, 1512, 1451, 1242, 1180, 1096, 1034, 872, 826, 795, 733, 702.

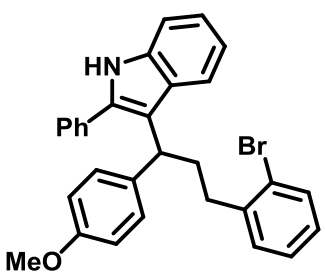
3-(1-(4-Methoxyphenyl)-3-phenylpropyl)-1-methyl-1*H*-indole (4q)



Following the general procedure the reaction was carried out with 1-benzyl-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (0.30 mmol, 145.6 mg), 4-methoxystyrene (0.45 mmol, 61 µL), 1-methyl-1*H*-indole (0.45 mmol, 56 µL), [Ir(dtbbpy)(ppy)$_2$](PF$_6$) (1.0 mol%, 2.7 mg) and acetonitrile (0.3 mL, 1.0 M). Isolation by column chromatography (SiO$_2$, *n*-pentane/ethyl acetate 20:1). 3-(1-(4-Methoxyphenyl)-3-phenylpropyl)-1-methyl-1*H*-indole (**4p**) was formed in 43% yield (45.9 mg, 0.13 mmol) as a white solid.

***R*$_f$ (*n*-pentane/ethyl acetate 10:1):** 0.3; **^{1}H NMR (400 MHz, CD$_2$Cl$_2$)** δ = 7.39 (dt, *J* = 7.9, 1.0 Hz, 1H), 7.33 – 7.22 (m, 5H), 7.23 – 7.11 (m, 4H), 7.02 – 6.93 (m, 2H), 6.88 – 6.81 (m, 2H), 4.14 (dd, *J* = 8.3, 6.8 Hz, 1H), 3.77 (s, 3H), 3.75 (s, 3H), 2.71 – 2.58 (m, 2H), 2.55 – 2.43 (m, 1H), 2.40 – 2.23 (m, 1H); **^{13}C NMR (101 MHz, CD$_2$Cl$_2$)** δ = 158.5, 143.2, 138.1, 137.9, 129.3, 129.0, 128.8, 127.9, 126.3, 126.2, 122.0, 119.9, 119.4, 119.0, 114.2, 109.7, 55.7, 42.1, 38.5, 34.8, 33.1; **HRMS** *m/z* (ESI): calcd. for [C$_{25}$H$_{25}$NONa]$^+$, 378.1828; found 378.1832; **ATR-IR *v* (cm^{-1})** 3055, 3024, 2932, 2855, 2832, 1613, 1512, 1458, 1327, 1242, 1180, 1034, 826, 741, 702.

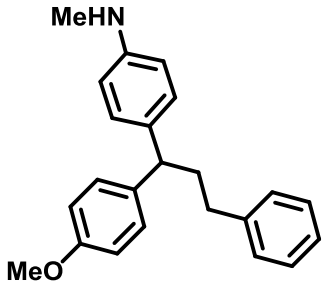
3-(3-(2-Bromophenyl)-1-(4-methoxyphenyl)propyl)-2-phenyl-1*H*-indole (4r)



Following the general procedure the reaction was carried out with 1-(2-bromobenzyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (0.30 mmol, 169.3 mg), 4-methoxystyrene (0.45 mmol, 61 µL), 2-phenyl-1*H*-indole (0.45 mmol, 87.0 mg), [Ir(dtbbpy)(ppy)$_2$](PF$_6$) (1.0 mol%, 2.7 mg) and acetonitrile (0.3 mL, 1.0 M). Isolation by column chromatography (SiO$_2$, *n*-pentane/dichloromethane 3:1 to 1:1). 3-(3-(2-Bromophenyl)-1-(4-methoxyphenyl)propyl)-2-phenyl-1*H*-indole (**4r**) was formed in 65% yield (96.9 mg, 0.20 mmol) as a white solid.

***R*f (*n*-pentane/dichloromethane 1:1):** 0.4; **^{1}H NMR (400 MHz, CD_2Cl_2)** δ = 8.23 (br, 1H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.57 – 7.36 (m, 7H), 7.33 – 7.26 (m, 2H), 7.22 – 7.13 (m, 1H), 7.10 – 6.92 (m, 4H), 6.85 – 6.74 (m, 2H), 4.41 – 4.29 (m, 1H), 3.75 (s, 3H), 2.69 – 2.44 (m, 4H); **^{13}C NMR (101 MHz, CD_2Cl_2)** δ = 158.3, 142.2, 137.9, 137.0, 136.4, 133.8, 133.1, 131.0, 129.3, 129.2, 128.5, 128.2, 128.0, 127.8, 124.8, 122.5, 121.5, 120.0, 115.4, 114.1, 111.6, 55.7, 41.3, 35.5, 35.5 (*one carbon signal was not detected*); **HRMS** *m/z* (ESI): calcd. for $[C_{30}H_{26}NOBrNa]^+$, 518.1090; found 518.1092; **ATR-IR *v* (cm^{-1})** 3403, 3055, 2987, 2831, 1605, 1512, 1489, 1451, 1304, 1242, 1180, 1157, 1026, 826, 741, 702.

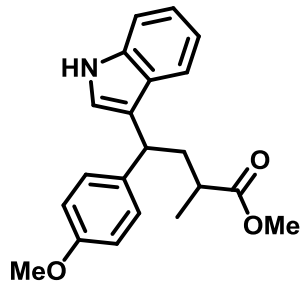
4-(1-(4-Methoxyphenyl)-3-phenylpropyl)-*N*-methylaniline (4s)



Following the general procedure the reaction was carried out with 1-benzyl-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (0.30 mmol, 145.6 mg), 4-methoxystyrene (0.45 mmol, 61 µL), *N*-methylaniline (0.45 mmol, 49 µL), $[Ir(dtbbpy)(ppy)_2](PF_6)$ (1.0 mol%, 2.7 mg) and acetonitrile (0.3 mL, 1.0 M). Isolation by column chromatography (SiO_2, *n*-pentane/ethyl acetate 20:1 to 10:1). 4-(1-(4-Methoxyphenyl)-3-phenylpropyl)-*N*-methylaniline (**4s**) was formed in 25% yield (24.8 mg, 0.08 mmol) as a colourless oil.

***R*f (*n*-pentane/ethyl acetate 4:1):** 0.4; **^{1}H NMR (300 MHz, CD_2Cl_2)** *δ* = 7.32 – 7.20 (m, 2H), 7.22 – 7.10 (m, 5H), 7.09 – 6.98 (m, 2H), 6.86 – 6.77 (m, 2H), 6.59 – 6.49 (m, 2H), 3.83 – 3.70 (m, 4H), 2.78 (s, 3H), 2.60 – 2.48 (m, 2H), 2.34 – 2.20 (m, 2H); **^{13}C NMR (101 MHz, $CDCl_3$)** *δ* = 158.4, 148.4, 143.1, 138.7, 134.5, 129.0, 129.0, 128.8, 128.8, 126.2, 114.2, 112.9, 55.7, 49.6, 38.2, 34.7, 31.2; **HRMS** *m/z* (ESI): calcd. for $[C_{23}H_{25}NOH]^+$ 332.2009; found 332.2015; **ATR-IR *v* (cm^{-1})** 3418, 3024, 2932, 2862, 2832, 1613, 1512, 1458, 1319, 1304, 1250, 1180, 1157, 1111, 1034, 826, 702.

Methyl 4-(1*H*-indol-3-yl)-4-(4-methoxyphenyl)-2-methylbutanoate (4t)

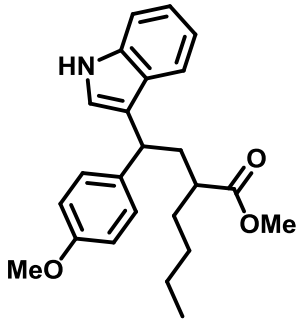


Following the general procedure the reaction was carried out with 1-(1-methoxy-1-oxopropan-2-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (0.30 mmol, 144.4 mg), 4-methoxystyrene (0.45 mmol, 61 µL), 1*H*-indole (0.45 mmol, 52.7 mg), $[Ir(dtbbpy)(ppy)_2](PF_6)$ (1.0 mol%, 2.7 mg) and acetonitrile (0.3 mL, 1.0 M). The diastereomeric ratio was determined by ^{1}H NMR spectroscopy of the crude reaction mixture. Isolation by column chromatography (SiO_2, dichloromethane). Methyl 4-(1*H*-indol-3-yl)-4-(4-methoxyphenyl)-2-methylbutanoate (**4t**) was formed in 95% yield (95.7 mg, 0.28 mmol, 1.2:1 dr). The diastereomers were separated for analytical purposes.

Major diastereomer: Colourless oil, ***R*f (dichloromethane):** 0.34; **^{1}H NMR (400 MHz, CD_2Cl_2)** δ = 8.17 (s, 1H), 7.40 (dd, J = 8.0, 1.0 Hz, 1H), 7.34 (dt, J = 8.2, 0.9 Hz, 1H), 7.26 – 7.19 (m, 2H), 7.12 (ddd, J = 8.2, 7.0, 1.2 Hz, 1H), 7.08 (d, J = 2.1 Hz, 1H), 6.99 (ddd, J = 8.0, 7.0, 1.0 Hz, 1H), 6.86 – 6.77 (m, 2H), 4.20 (t, J = 7.6 Hz, 1H), 3.75 (s, 3H), 3.58 (s, 3H), 2.49 – 2.35 (m, 2H), 2.28 – 2.14 (m, 1H), 1.23 (d, J = 6.8 Hz, 3H); **^{13}C NMR (101 MHz, CD_2Cl_2)** δ = 177.5, 158.6, 137.2, 137.1, 129.3, 127.3, 122.5, 121.5, 120.4, 119.8, 119.7, 114.2, 111.7, 55.7, 51.9, 40.2, 40.2, 38.1, 17.5; **HRMS** *m/z* (ESI): calcd. for $[C_{21}H_{23}NO_3Na]^+$ 360.1570; found 360.1575; **ATR-IR *v* (cm^{-1})** 3410, 3055, 2970, 2947, 2839, 1721, 1613, 1582, 1512, 1458, 1435, 1358, 1335, 1304, 1242, 1211, 1173, 1126, 1096, 1034, 1011, 833, 795, 741.

Minor diastereomer: Colourless oil, R_f **(dichloromethane):** 0.36; **^{1}H NMR (400 MHz, CD_2Cl_2)** δ = 8.14 (br, 1H), 7.43 (dd, *J* = 8.1, 1.0 Hz, 1H), 7.34 (dd, *J* = 8.1, 1.0 Hz, 1H), 7.24 – 7.17 (m, 2H), 7.12 (ddd, *J* = 8.2, 7.0, 1.2 Hz, 1H), 7.06 (d, *J* = 2.1 Hz, 1H), 6.99 (ddd, *J* = 8.0, 7.0, 1.1 Hz, 1H), 6.85 – 6.79 (m, 2H), 4.16 (dd, *J* = 9.1, 6.5 Hz, 1H), 3.76 (s, 3H), 3.65 (s, 3H), 2.59 (ddd, *J* = 13.4, 8.6, 6.5 Hz, 1H), 2.42 (dqd, *J* = 8.6, 7.0, 5.4 Hz, 1H), 1.98 (ddd, *J* = 13.4, 9.1, 5.5 Hz, 1H), 1.16 (d, *J* = 7.0 Hz, 3H); **^{13}C NMR (101 MHz, CD_2Cl_2)** δ = 177.5, 158.7, 137.3, 137.2, 129.4, 127.4, 122.5, 121.6, 120.4, 119.8, 119.7, 114.2, 111.6, 55.7, 52.0, 40.7, 40.5, 38.2, 18.1; **HRMS** *m/z* (ESI): calcd. for $[C_{21}H_{23}NO_3Na]^+$ 360.1570; found 360.1569; **ATR-IR *v* (cm^{-1})** 3410, 3055, 2970, 2932, 2839, 1721, 1613, 1512, 1458, 1435, 1335, 1304, 1242, 1219, 1173, 1126, 1096, 1034, 1011, 833, 810, 741.

Methyl 2-(2-(1*H*-indol-3-yl)-2-(4-methoxyphenyl)ethyl)hexanoate (4u)

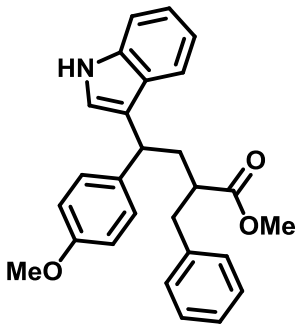


Following the general procedure the reaction was carried out with 1-(1-methoxy-1-oxohexan-2-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (0.30 mmol, 157.0 mg), 4-methoxystyrene (0.45 mmol, 61 µL), 1*H*-indole (0.45 mmol, 52.7 mg), $[Ir(dtbbpy)(ppy)_2](PF_6)$ (1.0 mol%, 2.7 mg) and acetonitrile (0.3 mL, 1.0 M). The diastereomeric ratio was determined by ^{1}H NMR spectroscopy of the crude reaction mixture. Isolation by column chromatography (SiO_2, dichloromethane). Methyl 2-(2-(1*H*-indol-3-yl)-2-(4-methoxyphenyl)-ethyl)hexanoate (**4u**) was formed in 74% yield (84.0 mg, 0.22 mmol, 1.3:1 dr). The diastereomers were separated for analytical purposes.

Major diastereomer: Colourless oil, R_f **(dichloromethane):** 0.34; **^{1}H NMR (500 MHz, CD_2Cl_2)** δ = 8.18 (br, 1H), 7.42 – 7.36 (m, 1H), 7.35 (dt, *J* = 8.2, 0.9 Hz, 1H), 7.23 – 7.18 (m, 2H), 7.12 (ddd, *J* = 8.2, 7.0, 1.2 Hz, 1H), 7.09 (dd, *J* = 2.4, 0.8 Hz, 1H), 6.98 (ddd, *J* = 8.0, 7.0, 1.0 Hz, 1H), 6.83 – 6.78 (m, 2H), 4.15 (t, *J* = 7.6 Hz, 1H), 3.75 (s, 3H), 3.56 (s, 3H), 2.46 – 2.23 (m, 3H), 1.71 – 1.54 (m, 2H), 1.35 – 1.17 (m, 4H), 0.87 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR (126 MHz, CD_2Cl_2)** δ = 177.1, 158.6, 137.6, 137.2, 129.3, 127.4, 122.5, 121.6, 120.0, 119.8, 119.7, 114.1, 111.7, 55.7, 51.7, 44.4, 40.6, 39.0, 32.9, 29.9, 23.2, 14.3; **HRMS** *m/z* (ESI): calcd. for $[C_{24}H_{29}NO_3Na]^+$ 402.2040; found 402.2040; **ATR-IR *v* (cm^{-1})** 3418, 3055, 2978, 2955, 2932, 2870, 1721, 1613, 1512, 1458, 1435, 1381, 1335, 1242, 1165, 1096, 1034, 1011, 833, 810, 741.

Minor diastereomer: White solid, R_f **(dichloromethane):** 0.40; **^{1}H NMR (500 MHz, CD_2Cl_2)** δ = 8.12 (br, 1H), 7.45 – 7.40 (m, 1H), 7.33 (dt, *J* = 8.2, 0.9 Hz, 1H), 7.23 – 7.18 (m, 2H), 7.12 (dddd, *J* = 8.2, 7.1, 1.2, 0.4 Hz, 1H), 7.03 – 6.95 (m, 2H), 6.86 – 6.80 (m, 2H), 4.08 (dd, *J* = 10.0, 5.3 Hz, 1H), 3.77 (s, 3H), 3.65 (s, 3H), 2.53 (ddd, *J* = 13.5, 9.9, 5.4 Hz, 1H), 2.31 (dddd, *J* = 9.9, 8.4, 5.7, 4.4 Hz, 1H), 2.06 (ddd, *J* = 13.5, 10.1, 4.3 Hz, 1H), 1.68 – 1.57 (m, 1H), 1.53 – 1.42 (m, 1H), 1.28 – 1.15 (m, 4H), 0.84 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR (126 MHz, CD_2Cl_2)** δ = 177.2, 158.7, 137.1, 137.0, 129.5, 127.3, 122.5, 121.5, 120.9, 119.8, 119.7, 114.2, 111.6, 55.7, 51.8, 44.2, 40.7, 39.2, 33.3, 30.0, 23.2, 14.2; **HRMS** *m/z* (ESI): calcd. for $[C_{24}H_{29}NO_3Na]^+$ 402.2040; found 402.2046; **ATR-IR *v* (cm^{-1})** 3410, 3055, 2978, 2955, 2932, 2870, 1728, 1613, 1512, 1458, 1435, 1381, 1335, 1242, 1219, 1165, 1096, 1034, 833, 810, 741.

Methyl 2-benzyl-4-(1*H*-indol-3-yl)-4-(4-methoxyphenyl)butanoate (4v)

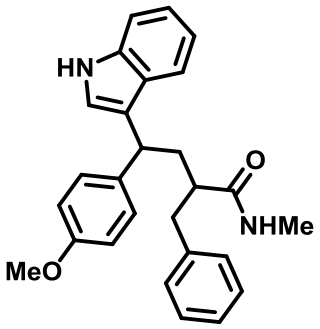


Following the general procedure the reaction was carried out with 1-(1-methoxy-1-oxo-3-phenylpropan-2-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (0.30 mmol, 167.2 mg), 4-methoxystyrene (0.45 mmol, 61 µL), 1*H*-indole (0.45 mmol, 52.7 mg), $[Ir(dtbbpy)(ppy)_2](PF_6)$ (1.0 mol%, 2.7 mg) and acetonitrile (0.3 mL, 1.0 M). The diastereomeric ratio was determined by ^{1}H NMR spectroscopy of the crude reaction mixture. Isolation by column chromatography (SiO_2, dichloromethane). Methyl 2-benzyl-4-(1*H*-indol-3-yl)-4-(4-methoxyphenyl)butanoate (**4v**) was formed in 76% yield (93.8 mg, 0.23 mmol, 1.4:1 dr). The diastereomers were separated for analytical purposes.

Major diastereomer: White solid, ***R*$_f$ (dichloromethane):** 0.41; **^{1}H NMR (400 MHz, CD_2Cl_2)** δ = 8.11 (br, 1H), 7.35 – 7.20 (m, 5H), 7.19 – 7.15 (m, 2H), 7.14 – 7.09 (m, 3H), 6.95 (ddd, *J* = 8.0, 7.0, 1.1 Hz, 1H), 6.85 (dd, *J* = 2.5, 0.9 Hz, 1H), 6.82 – 6.76 (m, 2H), 4.18 (t, *J* = 7.8 Hz, 1H), 3.74 (s, 3H), 3.50 (s, 3H), 2.97 (dd, *J* = 13.5, 8.0 Hz, 1H), 2.85 (dd, *J* = 13.5, 6.9 Hz, 1H), 2.70 (tdd, *J* = 8.1, 6.9, 5.5 Hz, 1H), 2.42 – 2.25 (m, 2H); **^{13}C NMR (101 MHz, CD_2Cl_2)** δ = 176.2, 158.6, 139.9, 137.5, 137.1, 129.6, 129.2, 128.9, 127.4, 126.9, 122.5, 121.6, 119.7, 119.7, 119.6, 114.2, 111.6, 55.7, 51.8, 46.5, 40.5, 39.1, 38.4; **HRMS** *m/z* (ESI): calcd. for $[C_{27}H_{27}NO_3Na]^+$ 436.1883; found 436.1894; **ATR-IR *v* (cm^{-1})** 3418, 3055, 3024, 2978, 2955, 2839, 1728, 1613, 1512, 1458, 1250, 1219, 1173, 1034, 841, 741, 702.

Minor diastereomer: White solid, ***R*$_f$ (dichloromethane):** 0.43; **^{1}H NMR (400 MHz, CD_2Cl_2)** δ = 8.09 (br, 1H), 7.42 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.33 (dt, *J* = 8.2, 0.9 Hz, 1H), 7.26 – 7.18 (m, 3H), 7.15 – 7.07 (m, 3H), 7.08 – 7.01 (m, 2H), 6.99 (ddd, *J* = 8.0, 7.0, 1.0 Hz, 1H), 6.94 (dd, *J* = 2.5, 1.0 Hz, 1H), 6.83 – 6.77 (m, 2H), 4.11 (dd, *J* = 10.2, 5.0 Hz, 1H), 3.77 (s, 3H), 3.58 (s, 3H), 2.96 (dd, *J* = 13.5, 7.8 Hz, 1H), 2.76 (dd, *J* = 13.5, 6.5 Hz, 1H), 2.68 – 2.50 (m, 2H), 2.17 – 2.04 (m, 1H); **^{13}C NMR (101 MHz, CD_2Cl_2)** δ = 176.3, 158.7, 139.8, 137.1, 136.6, 129.4, 129.4, 128.8, 127.3, 126.8, 122.5, 121.5, 120.8, 119.8, 119.7, 114.2, 111.6, 55.7, 51.9, 46.1, 40.6, 39.5, 38.5; **HRMS** *m/z* (ESI): calcd. for $[C_{27}H_{27}NO_3Na]^+$ 436.1883; found 436.1883; **ATR-IR *v* (cm^{-1})** 3418, 3055, 3032, 3001, 2947, 2932, 2839, 1728, 1613, 1512, 1458, 1335, 1304, 1250, 1219, 1173, 1034, 841, 810, 741, 702.

2-Benzyl-4-(1*H*-indol-3-yl)-4-(4-methoxyphenyl)-N-methylbutanamide (4w)



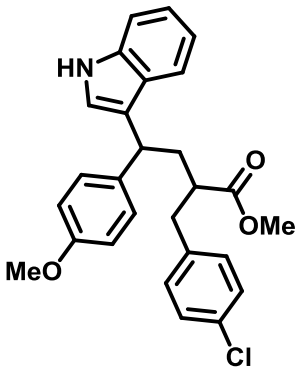
Following the general procedure the reaction was carried out with 1-(1-(methylamino)-1-oxo-3-phenylpropan-2-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (0.30 mmol, 166.9 mg), 4-methoxystyrene (0.45 mmol, 61 µL), 1*H*-indole (0.45 mmol, 52.7 mg), $[Ir(dtbbpy)(ppy)_2](PF_6)$ (1.0 mol%, 2.7 mg) and acetonitrile (0.3 mL, 1.0 M). The diastereomeric ratio was determined by ^{1}H NMR spectroscopy of the crude reaction mixture. Isolation by column chromatography (SiO_2, *n*-pentane/ethyl acetate 1:1). 2-Benzyl-4-(1*H*-indol-3-yl)-4-(4-methoxyphenyl)-N-methylbutanamide (**4w**) was formed in 82% yield (101.3 mg, 0.25 mmol, 1.6:1 dr). The diastereomers were separated for analytical purposes.

Major diastereomer: White solid, ***R*$_f$ (*n*-pentane/ethyl acetate 1:1):** 0.24; **^{1}H NMR (400 MHz, CD_2Cl_2)** δ = 8.38 (br, 1H), 7.38 – 7.31 (m, 2H), 7.28 – 7.20 (m, 2H), 7.21 – 7.07 (m, 6H), 7.01 – 6.92 (m, 2H), 6.81 – 6.74 (m, 2H), 4.97 – 4.91 (m, 1H), 4.19 – 4.11 (m, 1H), 3.73 (s, 3H),

2.94 (dd, J = 13.5, 7.2 Hz, 1H), 2.80 (dd, J = 13.4, 4.5 Hz, 1H), 2.55 (dd, J = 4.9, 1.4 Hz, 3H), 2.42 – 2.21 (m, 3H); **^{13}C NMR (101 MHz, CD_2Cl_2)** δ = 175.7, 158.5, 140.6, 138.0, 137.2, 129.5, 129.1, 128.8, 127.5, 126.7, 122.5, 121.6, 119.7, 119.6, 119.3, 114.2, 111.7, 55.7, 48.7, 40.3, 39.7, 39.4, 26.3; **HRMS** *m/z* (ESI): calcd. for $[C_{27}H_{28}N_2O_2Na]^+$ 435.2043; found 435.2052; **ATR-IR *v* (cm^{-1})** 3410, 3279, 3055, 3024, 2931, 1651, 1613, 1543, 1512, 1458, 1242, 1180, 1034, 741, 702.

Minor diastereomer: White solid, ***R*$_f$ (*n*-pentane/ethyl acetate 1:1):** 0.30; **^{1}H NMR (400 MHz, CD_2Cl_2)** δ = 8.32 (br, 1H), 7.49 (d, *J* = 8.0 Hz, 1H), 7.33 (d, *J* = 8.1 Hz, 1H), 7.27 – 7.18 (m, 2H), 7.21 – 7.07 (m, 4H), 7.08 – 7.01 (m, 2H), 7.00 (ddd, J = 8.0, 7.0, 1.1 Hz, 1H), 6.89 (d, J = 2.4 Hz, 1H), 6.85 – 6.80 (m, 2H), 5.06 (d, *J* = 5.2 Hz, 1H), 4.12 – 4.03 (m, 1H), 3.77 (s, 3H), 2.92 (dd, *J* = 13.3, 8.9 Hz, 1H), 2.70 (dd, *J* = 13.3, 5.9 Hz, 1H), 2.65 (d, *J* = 4.8 Hz, 3H), 2.62 – 2.55 (m, 1H), 2.21 – 2.12 (m, 1H), 2.10 – 2.05 (m, 1H); **^{13}C NMR (101 MHz, CD_2Cl_2)** δ = 175.6, 158.7, 140.5, 137.2, 136.7, 129.4, 129.4, 128.8, 127.2, 126.7, 122.4, 121.5, 121.1, 119.9, 119.6, 114.3, 111.6, 55.7, 48.5, 40.6, 40.3, 38.9, 26.3; **HRMS** *m/z* (ESI): calcd. for $[C_{27}H_{28}N_2O_2Na]^+$ 435.2043; found 435.2036; **ATR-IR *v* (cm^{-1})** 3418, 3279, 3055, 3024, 2931, 1651, 1613, 1543, 1512, 1458, 1242, 1180, 1034, 741.

Methyl 2-(4-chlorobenzyl)-4-(1*H*-indol-3-yl)-4-(4-methoxyphenyl)butanoate (4x)



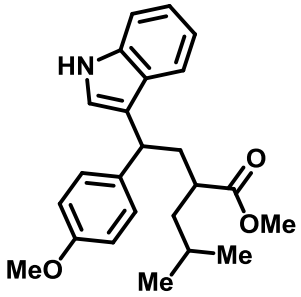
Following the general procedure the reaction was carried out with 1-(3-(4-chlorophenyl)-1-(methylamino)-1-oxopropan-2-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (0.30 mmol, 177.6 mg), 4-methoxystyrene (0.45 mmol, 61 µL), 1*H*-indole (0.45 mmol, 52.7 mg), $[Ir(dtbbpy)(ppy)_2](PF_6)$ (1.0 mol%, 2.7 mg) and acetonitrile (0.3 mL, 1.0 M). The diastereomeric ratio was determined by ^{1}H NMR spectroscopy of the crude reaction mixture. Isolation by column chromatography (SiO_2, dichloromethane). Methyl 2-(4-chlorobenzyl)-4-(1*H*-indol-3-yl)-4-(4-methoxyphenyl)butanoate (**4x**) was formed in 76% yield (102.1 mg, 0.23 mmol, 1.4:1 dr). The diastereomers were separated for analytical purposes.

Major diastereomer: White solid, ***R*$_f$ (dichloromethane):** 0.41; **^{1}H NMR (400 MHz, CD_2Cl_2)** δ = 8.14 (br, 1H), 7.34 (dt, *J* = 8.2, 0.9 Hz, 1H), 7.31 (dt, *J* = 8.0, 1.0 Hz, 1H), 7.26 – 7.20 (m, 2H), 7.22 – 7.15 (m, 2H), 7.12 (ddd, *J* = 8.2, 7.0, 1.2 Hz, 1H), 7.08 – 7.01 (m, 2H), 6.97 (ddd, *J* = 8.0, 7.0, 1.0 Hz, 1H), 6.94 – 6.88 (m, 1H), 6.84 – 6.77 (m, 2H), 4.19 (t, *J* = 7.8 Hz, 1H), 3.75 (s, 3H), 3.50 (s, 3H), 2.94 (dd, *J* = 13.6, 8.2 Hz, 1H), 2.84 (dd, *J* = 13.6, 6.7 Hz, 1H), 2.67 (tdd, *J* = 8.3, 6.7, 5.5 Hz, 1H), 2.37 (ddd, *J* = 13.7, 8.3, 7.2 Hz, 1H), 2.29 (ddd, *J* = 13.8, 8.4, 5.5 Hz, 1H); **^{13}C NMR (101 MHz, CD_2Cl_2)** δ = 176.0, 158.7, 138.5, 137.3, 137.2, 132.6, 131.0, 129.2, 128.9, 127.3, 122.5, 121.6, 119.7, 119.5, 114.2, 111.7, 55.7, 51.9, 46.4, 40.5, 38.4, 38.3 (*one carbon signal was not detected*); **HRMS** *m/z* (ESI): calcd. for $[C_{27}H_{26}NO_3ClNa]^+$ 470.1493; found 470.1497; **ATR-IR *v* (cm^{-1})** 3410, 3055, 2978, 2947, 2839, 1728, 1613, 1512, 1489, 1458, 1435, 1381, 1343, 1296, 1250, 1211, 1165, 1096, 1034, 1011, 826, 748.

Minor diastereomer: Colourless oil, ***R*$_f$ (dichloromethane):** 0.43; **^{1}H NMR (400 MHz, CD_2Cl_2)** δ = 8.10 (br, 1H), 7.42 (dd, *J* = 7.9, 1.0 Hz, 1H), 7.33 (dt, *J* = 8.2, 0.9 Hz, 1H), 7.24 – 7.17 (m, 2H), 7.17 – 7.08 (m, 3H), 7.04 – 6.95 (m, 3H), 6.94 (dd, *J* = 2.5, 1.0 Hz, 1H), 6.84 – 6.76 (m, 2H), 4.11 (dd, *J* = 10.2, 4.7 Hz, 1H), 3.77 (s, 3H), 3.59 (s, 3H), 2.93 (dd, *J* = 13.6, 7.7 Hz, 1H), 2.74 (dd, *J* = 13.6, 6.4 Hz, 1H), 2.65 – 2.51 (m, 2H), 2.13 – 2.02 (m, 1H); **^{13}C NMR (101 MHz, CD_2Cl_2)** δ = 176.1, 158.7, 138.4, 137.1, 136.5, 132.5, 130.9, 129.4, 128.9, 127.2, 122.5, 121.5, 120.7, 119.8, 119.7, 114.3, 111.6, 55.7, 52.0, 45.9, 40.6, 38.7, 38.5; **HRMS** *m/z* (ESI): calcd. for $[C_{27}H_{26}NO_3ClNa]^+$ 470.1493; found 470.1496; **ATR-IR *v* (cm^{-1})** 3410, 3055, 2978, 2955,

2839, 1721, 1512, 1489, 1458, 1335, 1304, 1242, 1219, 1173, 1096, 1034, 1011, 810, 741.

Methyl 2-(2-(1*H*-indol-3-yl)-2-(4-methoxyphenyl)ethyl)-4-methylpentanoate (4y)

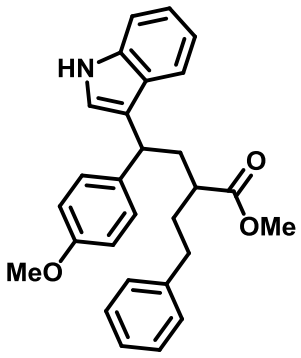


Following the general procedure the reaction was carried out with 1-(1-methoxy-4-methyl-1-oxopentan-2-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (0.30 mmol, 157.0 mg), 4-methoxystyrene (0.45 mmol, 61 µL), 1*H*-indole (0.45 mmol, 52.7 mg), $[Ir(dtbbpy)(ppy)_2](PF_6)$ (1.0 mol%, 2.7 mg) and acetonitrile (0.3 mL, 1.0 M). The diastereomeric ratio was determined by ^{1}H NMR spectroscopy of the crude reaction mixture. Isolation by column chromatography (SiO_2, dichloromethane). Methyl 2-(2-(1*H*-indol-3-yl)-2-(4-methoxyphenyl)ethyl)-4-methylpentanoate (**4y**) was formed in 79% yield (89.7 mg, 0.24 mmol, 1.4:1 dr). The diastereomers were separated for analytical purposes.

Major diastereomer: Colourless oil, R_f **(dichloromethane):** 0.34; **^{1}H NMR (400 MHz, CD_2Cl_2)** δ = 8.18 (br, 1H), 7.39 (d, *J* = 8.0 Hz, 1H), 7.35 (d, *J* = 8.1 Hz, 1H), 7.24 – 7.17 (m, 2H), 7.12 (ddd, *J* = 8.2, 7.0, 1.2 Hz, 1H), 7.08 (dd, *J* = 2.5, 0.9 Hz, 1H), 6.98 (ddd, *J* = 8.0, 7.0, 1.1 Hz, 1H), 6.85 – 6.74 (m, 2H), 4.15 (t, *J* = 7.7 Hz, 1H), 3.75 (s, 3H), 3.54 (s, 3H), 2.47 (ddt, *J* = 9.4, 8.0, 5.6 Hz, 1H), 2.38 – 2.20 (m, 2H), 1.68 – 1.44 (m, 2H), 1.40 (ddd, *J* = 13.1, 8.1, 5.2 Hz, 1H), 0.84 (d, *J* = 6.4 Hz, 3H), 0.82 (d, *J* = 6.4 Hz, 3H); **^{13}C NMR (101 MHz, CD_2Cl_2)** δ = 177.3, 158.6, 137.5, 137.2, 129.3, 127.4, 122.5, 121.5, 120.1, 119.8, 119.7, 114.1, 111.7, 55.7, 51.7, 42.6, 42.4, 40.6, 39.6, 26.7, 23.4, 22.4; **HRMS** *m/z* (ESI): calcd. for $[C_{24}H_{29}NO_3Na]^+$ 402.2040; found 402.2042; **ATR-IR *v* (cm^{-1})** 3410, 3055, 2955, 2931, 2870, 2839, 1721, 1613, 1512, 1458, 1435, 1335, 1242, 1196, 1173, 1103, 1034, 826, 741.

Minor diastereomer: Colourless oil, R_f **(dichloromethane):** 0.43; **^{1}H NMR (400 MHz, CD_2Cl_2)** δ = 8.13 (br, 1H), 7.43 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.33 (dt, *J* = 8.2, 0.9 Hz, 1H), 7.25 – 7.18 (m, 2H), 7.12 (ddd, *J* = 8.2, 7.0, 1.2 Hz, 1H), 7.03 – 6.95 (m, 2H), 6.87 – 6.80 (m, 2H), 4.08 (dd, *J* = 10.2, 5.2 Hz, 1H), 3.77 (s, 3H), 3.65 (s, 3H), 2.50 (ddd, *J* = 13.2, 10.0, 5.2 Hz, 1H), 2.40 (dddd, *J* = 10.0, 8.5, 6.0, 3.9 Hz, 1H), 2.05 (ddd, *J* = 13.2, 10.2, 3.9 Hz, 1H), 1.66 – 1.42 (m, 2H), 1.31 (ddd, *J* = 12.8, 7.2, 5.8 Hz, 1H), 0.79 (d, *J* = 6.4 Hz, 3H), 0.76 (d, *J* = 6.4 Hz, 3H); **^{13}C NMR (101 MHz, CD_2Cl_2)** δ = 177.4, 158.7, 137.2, 137.0, 129.5, 127.3, 122.5, 121.5, 120.9, 119.9, 119.6, 114.2, 111.6, 55.7, 51.8, 42.8, 42.3, 40.8, 39.5, 26.6, 23.0, 22.6; **HRMS** *m/z* (ESI): calcd. for $[C_{24}H_{29}NO_3Na]^+$ 402.2040; found 402.2045; **ATR-IR *v* (cm^{-1})** 3410, 3032, 2955, 2932, 2870, 2839, 1728, 1613, 1512, 1458, 1335, 1242, 1227, 1173, 1034, 833, 810, 741.

Methyl 4-(1*H*-indol-3-yl)-4-(4-methoxyphenyl)-2-phenethylbutanoate (4z)



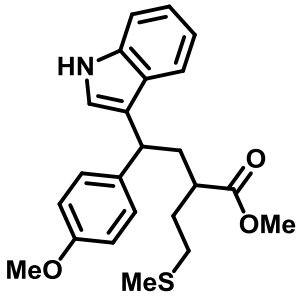
Following the general procedure the reaction was carried out with 1-(1-methoxy-1-oxo-4-phenylbutan-2-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (0.30 mmol, 171.4 mg), 4-methoxystyrene (0.45 mmol, 61 µL), 1*H*-indole (0.45 mmol, 52.7 mg), $[Ir(dtbbpy)(ppy)_2](PF_6)$ (1.0 mol%, 2.7 mg) and acetonitrile (0.3 mL, 1.0 M). The diastereomeric ratio was determined by ^{1}H NMR spectroscopy of the crude reaction mixture. Isolation by column chromatography (SiO_2, dichloromethane). Methyl 4-(1*H*-indol-3-yl)-4-(4-methoxyphenyl)-2-phenethylbutanoate (**4z**) was formed in 74%

yield (95.0 mg, 0.22 mmol, 1.3:1 dr). The diastereomers were separated for analytical purposes.

Major diastereomer: Colourless oil, R_f **(dichloromethane):** 0.32; **^{1}H NMR (500 MHz, CD_2Cl_2)** δ = 8.15 (br, 1H), 7.40 – 7.35 (m, 1H), 7.35 (dt, *J* = 8.2, 0.9 Hz, 1H), 7.28 – 7.24 (m, 2H), 7.21 – 7.10 (m, 6H), 7.05 (dd, *J* = 2.5, 0.8 Hz, 1H), 6.98 (ddd, *J* = 8.0, 7.0, 1.0 Hz, 1H), 6.81 – 6.76 (m, 2H), 4.15 (t, *J* = 7.6 Hz, 1H), 3.75 (s, 3H), 3.58 (s, 3H), 2.65 – 2.49 (m, 2H), 2.48 – 2.27 (m, 3H), 1.99 (dddd, *J* = 13.5, 9.5, 8.4, 5.9 Hz, 1H), 1.90 (dddd, *J* = 13.5, 9.7, 6.6, 4.9 Hz, 1H); **^{13}C NMR (126 MHz, CD_2Cl_2)** δ = 176.8, 158.6, 142.4, 137.3, 137.2, 129.2, 129.0, 128.9, 127.3, 126.4, 122.5, 121.7, 119.9, 119.8, 119.7, 114.2, 111.7, 55.7, 51.9, 43.8, 40.5, 38.9, 34.7, 33.9; **HRMS** *m/z* (ESI): calcd. for $[C_{28}H_{29}NO_3Na]^+$ 450.2040; found 450.2046; **ATR-IR *v* (cm^{-1})** 3418, 3055, 3024, 2978, 2947, 2862, 1728, 1613, 1512, 1458, 1335, 1242, 1173, 1096, 1034, 826, 741, 702.

Minor diastereomer: Colourless oil, R_f **(dichloromethane):** 0.36; **^{1}H NMR (500 MHz, CD_2Cl_2)** δ = 8.12 (br, 1H), 7.45 – 7.39 (m, 1H), 7.34 (dt, *J* = 8.1, 0.9 Hz, 1H), 7.26 – 7.17 (m, 4H), 7.19 – 7.09 (m, 2H), 7.11 – 7.05 (m, 2H), 7.03 – 6.96 (m, 2H), 6.86 – 6.81 (m, 2H), 4.11 (dd, *J* = 10.0, 5.5 Hz, 1H), 3.77 (s, 3H), 3.66 (s, 3H), 2.58 (ddd, *J* = 13.6, 9.7, 5.5 Hz, 1H), 2.53 (t, *J* = 8.0 Hz, 2H), 2.39 (dddd, *J* = 9.8, 8.3, 5.6, 4.4 Hz, 1H), 2.15 – 2.09 (m, 1H), 2.00 – 1.90 (m, 1H), 1.84 – 1.75 (m, 1H); **^{13}C NMR (126 MHz, CD_2Cl_2)** δ = 176.8, 158.7, 142.3, 137.1, 136.9, 129.5, 128.9, 128.8, 127.3, 126.4, 122.5, 121.5, 120.7, 119.8, 119.7, 114.3, 111.6, 55.7, 51.9, 43.8, 40.7, 39.1, 35.2, 34.0; **HRMS** *m/z* (ESI): $[C_{28}H_{29}NO_3Na]^+$ 450.2040; found 450.2036; **ATR-IR *v* (cm^{-1})** 3418, 3055, 3024, 2978, 2947, 2839, 1728, 1613, 1512, 1458, 1435, 1335, 1242, 1211, 1165, 1096, 1034, 826, 741, 702.

Methyl 4-(1*H*-indol-3-yl)-4-(4-methoxyphenyl)-2-(2-(methylthio)ethyl)butanoate (4aa)



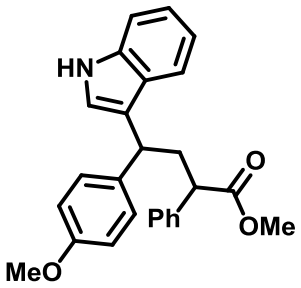
Following the general procedure the reaction was carried out with 1-(1-methoxy-4-(methylthio)-1-oxobutan-2-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (0.30 mmol, 162.4 mg), 4-methoxystyrene (0.45 mmol, 61 µL), 1*H*-indole (0.45 mmol, 52.7 mg), $[Ir(dtbbpy)(ppy)_2](PF_6)$ (1.0 mol%, 2.7 mg) and acetonitrile (0.3 mL, 1.0 M). The diastereomeric ratio was determined by ^{1}H NMR spectroscopy of the crude reaction mixture. Isolation by column chromatography (SiO_2, *n*-pentane/ethyl acetate 4:1). Methyl 4-(1*H*-indol-3-yl)-4-(4-methoxyphenyl)-2-(2-(methylthio)ethyl)butanoate (**4aa**) was formed in 56% yield (66.9 mg, 0.17 mmol, 1.4:1 dr). The diastereomers were separated for analytical purposes.

Major diastereomer: Colourless oil, R_f **(*n*-pentane/ethyl acetate 1:1):** 0.57; **^{1}H NMR (300 MHz, CD_2Cl_2)** δ = 8.18 (br, 1H), 7.43 – 7.30 (m, 2H), 7.23 – 7.19 (m, 2H), 7.15 – 7.08 (m, 2H), 6.98 (ddd, *J* = 8.1, 7.0, 1.1 Hz, 1H), 6.83 – 6.78 (m, 2H), 4.17 (t, *J* = 7.8 Hz, 1H), 3.74 (s, 3H), 3.56 (s, 3H), 2.59 – 2.22 (m, 5H), 2.04 (s, 3H), 2.00 – 1.78 (m, 2H); **^{13}C NMR (75 MHz, CD_2Cl_2)** δ = 176.4, 158.6, 137.2, 137.1, 129.4, 129.2, 127.3, 122.5, 121.6, 119.7, 119.7, 114.2, 111.7, 55.7, 51.9, 43.5, 40.4, 38.7, 32.3, 32.2, 15.6; **HRMS** *m/z* (ESI): calcd. for $[C_{23}H_{27}NO_3SNa]^+$ 420.1604; found 420.1608; **ATR-IR *v* (cm^{-1})** 3410, 3032, 2947, 2916, 2832, 1721, 1613, 1512, 1458, 1435,1265, 1242, 1173, 1034, 833, 733, 702.

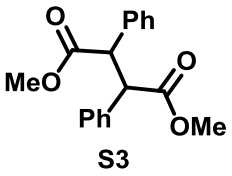
Minor diastereomer: Colourless oil, R_f **(*n*-pentane/ethyl acetate 1:1):** 0.61; **^{1}H NMR (300 MHz, CD_2Cl_2)** δ = 8.15 (s, 1H), 7.48 – 7.38 (m, 1H), 7.38 – 7.29 (m, 1H), 7.26 – 7.17 (m, 2H), 7.18 – 7.06 (m, 1H), 7.06 – 6.94 (m, 2H), 6.88 – 6.76 (m, 2H), 4.18 – 4.05 (m, 1H), 3.76 (s, 3H), 3.66 (s, 3H), 2.63 – 2.32 (m, 4H), 2.15 – 2.03 (m, 1H), 2.01 (s, 3H), 2.01 – 1.87 (m, 1H),

1.82 – 1.69 (m, 1H); **^{13}C NMR (75 MHz, CD_2Cl_2)** δ = 176.4, 158.7, 137.1, 136.8, 129.4, 127.3, 122.5, 121.5, 120.6, 119.8, 119.7, 114.2, 111.6, 55.7, 52.0, 43.4, 40.6, 39.0, 32.9, 32.2, 15.6; **HRMS** *m/z* (ESI): calcd. for $[C_{23}H_{27}NO_3SNa]^+$ 420.1604; found 420.1601; **ATR-IR *v* (cm^{-1})** 3418, 3055, 2947, 2916, 2847, 1721, 1613, 1512, 1458, 1435,1265, 1242, 1173, 1034, 833, 733, 702.

Methyl 4-(1*H*-indol-3-yl)-4-(4-methoxyphenyl)-2-phenylbutanoate (4ab)



Following the general procedure the reaction was carried out with 1-(2-methoxy-2-oxo-1-phenylethyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (0.30 mmol, 166.9 mg), 4-methoxystyrene (0.45 mmol, 61 µL), 1*H*-indole (0.45 mmol, 52.7 mg), [Ir(dtbbpy)(ppy)$_2$](PF$_6$) (1.0 mol%, 2.7 mg) and acetonitrile (0.3 mL, 1.0 M). The diastereomeric ratio was determined by ^{1}H NMR spectroscopy of the crude reaction mixture. Isolation by column chromatography (SiO_2, dichloromethane). A white solid (72.7 mg) was isolated, which was determined to contain an inseparable mixture of **4ab** (86%) and radical dimer **S3** (14%).



S3

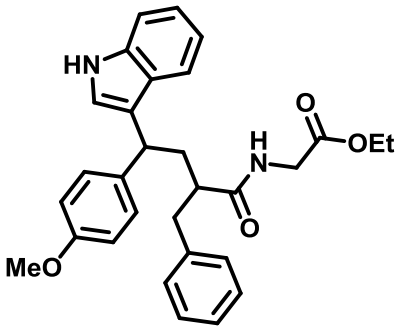
mixture of diastereomers

Methyl 4-(1*H*-indol-3-yl)-4-(4-methoxyphenyl)-2-phenylbutanoate (**4ab**) was formed in 52% yield (62.5 mg, 0.16 mmol, 1.3:1 dr). The diastereomers were separated for analytical purposes.

Major diastereomer: White solid, ***R*$_f$ (dichloromethane):** 0.45; **^{1}H NMR (600 MHz, CD_2Cl_2)** δ = 8.13 (br, 1H), 7.37 – 7.26 (m, 6H), 7.25 – 7.22 (m, 1H), 7.18 – 7.15 (m, 2H), 7.11 – 7.08 (m, 2H), 6.93 (ddd, *J* = 8.0, 7.0, 1.0 Hz, 1H), 6.85 – 6.82 (m, 2H), 3.95 (dd, *J* = 9.3, 6.2 Hz, 1H), 3.77 (s, 3H), 3.56 (s, 3H), 3.51 (dd, *J* = 8.6, 6.5 Hz, 1H), 2.74 (ddd, *J* = 13.7, 9.4, 6.5 Hz, 1H), 2.66 (ddd, *J* = 13.7, 8.6, 6.2 Hz, 1H); **^{13}C NMR (151 MHz, CD_2Cl_2)** δ = 174.8, 158.8, 139.5, 137.2, 136.7, 129.5, 129.2, 128.9, 127.9, 127.3, 122.5, 121.5, 120.5, 119.7, 119.7, 114.3, 111.6, 55.7, 52.4, 49.9, 39.9, 39.8; **HRMS** *m/z* (ESI): calcd. for $[C_{26}H_{25}NO_3Na]^+$ 422.1727; found 422.1725; **ATR-IR *v* (cm^{-1})** 3418, 3063, 3032, 3001, 2932, 1736, 1512, 1458, 1250, 1180, 1157, 1034, 741.

Minor diastereomer: White solid, ***R*$_f$ (dichloromethane):** 0.50; **^{1}H NMR (300 MHz, CD_2Cl_2)** δ = 8.16 (br, 1H), 7.42 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.37 – 7.33 (m, 1H), 7.32 – 7.25 (m, 3H), 7.23 – 7.12 (m, 5H), 7.06 – 6.97 (m, 2H), 6.85 – 6.80 (m, 2H), 4.05 (t, *J* = 7.8 Hz, 1H), 3.76 (s, 3H), 3.65 (s, 3H), 3.54 (dd, *J* = 8.6, 6.5 Hz, 1H), 3.00 (ddd, *J* = 13.6, 8.6, 7.2 Hz, 1H), 2.36 (ddd, *J* = 13.6, 8.4, 6.5 Hz, 1H); **^{13}C NMR (75 MHz, CD_2Cl_2)** δ = 174.8, 158.7, 139.9, 137.2, 137.0, 129.2, 129.2, 128.5, 127.8, 127.3, 122.5, 121.8, 119.9, 119.9, 119.7, 114.3, 111.6, 55.7, 52.5, 50.0, 40.3, 40.2; **HRMS** *m/z* (ESI): calcd. for $[C_{26}H_{25}NO_3Na]^+$ 422.1727; found 422.1716; **ATR-IR *v* (cm^{-1})** 3418, 3055, 3032, 3009, 2947, 1728, 1512, 1451, 1435, 1250, 1227, 1180, 1157, 1034, 741.

Ethyl (2-benzyl-4-(1*H*-indol-3-yl)-4-(4-methoxyphenyl)butanoyl)glycinate (4ac)

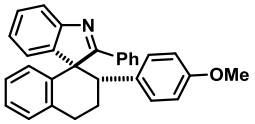


ollowing the general procedure the reaction was carried out with 1-(1-((2-ethoxy-2-oxoethyl)amino)-1-oxo-3 phenylpropan-2-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (0.30 mmol, 188.5 mg), 4-methoxystyrene (0.45 mmol, 61 µL), 1*H*-indole (0.45 mmol, 52.7 mg), $[Ir(dtbbpy)(ppy)_2](PF_6)$ (1.0 mol%, 2.7 mg) and acetonitrile (0.6 mL, 0.5 M). The diastereomeric ratio was determined by ^{1}H NMR spectroscopy of the crude reaction mixture. Isolation by column chromatography (SiO_2, *n*-pentane/ethyl acetate 4:1 to 2:1). Ethyl (2-benzyl-4-(1*H*-indol-3-yl)-4-(4-methoxyphenyl)butanoyl)glycinate (**4ac**) was formed in 79% yield (115.1 mg, 0.24 mmol, 1.3:1 dr). The diastereomers were separated for analytical purposes.

Major diastereomer: Colourless oil, **R_f (*n*-pentane/ethyl acetate 2:1):** 0.20; **^{1}H NMR (400 MHz, CD_2Cl_2)** δ = 8.24 (br, 1H), 7.40 – 7.31 (m, 2H), 7.24 (dd, *J* = 8.0, 6.3 Hz, 2H), 7.22 – 7.14 (m, 3H), 7.15 – 7.07 (m, 3H), 7.01 – 6.90 (m, 2H), 6.83 – 6.72 (m, 2H), 5.54 (t, *J* = 5.3 Hz, 1H), 4.25 (dd, *J* = 9.1, 6.8 Hz, 1H), 4.15 (q, *J* = 7.2 Hz, 2H), 3.91 (dd, *J* = 18.1, 5.5 Hz, 1H), 3.81 – 3.68 (m, 4H), 2.97 (dd, *J* = 13.5, 8.0 Hz, 1H), 2.79 (dd, *J* = 13.5, 6.5 Hz, 1H), 2.44 (p, *J* = 7.8 Hz, 1H), 2.40 – 2.24 (m, 2H), 1.24 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR (101 MHz, CD_2Cl_2)** δ = 175.4, 170.2, 158.5, 140.3, 138.0, 137.2, 129.6, 129.1, 128.8, 127.4, 126.8, 122.5, 121.9, 119.9, 119.7, 119.1, 114.2, 111.7, 61.9, 55.7, 48.1, 41.8, 40.2, 39.5, 39.1, 14.5; **HRMS** *m/z* (ESI): calcd. for $[C_{30}H_{32}N_2O_4Na]^+$ 507.2254; found 507.2267; **ATR-IR *v* (cm^{-1})** 3410, 3302, 3063, 3032, 2978, 2932, 2839, 1736, 1651, 1613, 1512, 1458, 1373, 1242, 1196, 1180, 1111, 1026, 957, 826, 741, 702.

Minor diastereomer: Colourless oil, **R_f (*n*-pentane/ethyl acetate 2:1):** 0.25; **^{1}H NMR (300 MHz, CD_2Cl_2)** δ = 8.18 (br, 1H), 7.48 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.32 (dt, *J* = 8.1, 1.0 Hz, 1H), 7.28 – 7.01 (m, 8H), 6.99 (ddd, *J* = 8.1, 7.0, 1.1 Hz, 1H), 6.89 (dd, *J* = 2.5, 1.0 Hz, 1H), 6.86 – 6.78 (m, 2H), 5.66 (t, *J* = 5.4 Hz, 1H), 4.25 – 4.11 (m, 3H), 4.07 (dd, *J* = 18.1, 5.9 Hz, 1H), 3.82 – 3.69 (m, 4H), 2.95 (dd, *J* = 13.5, 8.5 Hz, 1H), 2.71 (dd, *J* = 13.5, 6.5 Hz, 1H), 2.59 (ddd, *J* = 13.4, 10.2, 4.7 Hz, 1H), 2.28 (dddd, *J* = 10.1, 8.2, 6.4, 3.7 Hz, 1H), 2.09 (ddd, *J* = 13.4, 11.0, 3.7 Hz, 1H), 1.26 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR (75 MHz, CD_2Cl_2)** δ = 175.3, 170.3, 158.7, 140.1, 137.1, 136.7, 129.5, 129.4, 128.8, 127.2, 126.7, 122.4, 121.4, 121.2, 119.9, 119.6, 114.3, 111.6, 61.9, 55.7, 47.8, 41.7, 40.3, 40.0, 38.9, 14.5; **HRMS** *m/z* (ESI): calcd. for $[C_{30}H_{32}N_2O_4Na]^+$ 507.2254; found 507.2256; **ATR-IR *v* (cm^{-1})** 3410, 3302, 3055, 3032, 2978, 2932, 2839, 1744, 1651, 1613, 1512, 1458, 1373, 1242, 1204, 1180, 1111, 1026, 741, 702.

***rac*-(2'*S*,3*S*)-2'-(4-Methoxyphenyl)-2-phenyl-3',4'-dihydro-2'*H*-spiro[indole-3,1'-naphthalene] (5a)**

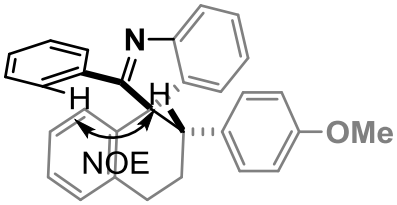


A flame dried Schlenk tube was filled with 3-(3-(2-Bromophenyl)-1-(4-methoxyphenyl)propyl)-2-phenyl-1*H*-indole (**4r**) (49.5 mg, 0.10 mmol, 1.0 equiv.). Inside a glovebox P(*t*-Bu)$_3$-Pd-G2 (2.6 mg, 0.005 mmol, 5.0 mol%) and cesium carbonate (33.6 mg, 0.17 mmol, 1.7 equiv.) were added. In a stream of argon toluene (1.0 mL, 0.1 M) was added. The reaction mixture was degassed by three consecutive freeze-pump-thaw cycles. The reaction mixture was stirred in an argon atmosphere at 100 °C for 17 h. After the reaction cooled down to room temperature the solvent was evaporated. The diastereomeric ratio was determined by ^{1}H NMR spectroscopic analysis of the crude product. Isolation by column chromatography (SiO_2,dichloromethane). *rac*-(2'*S*,3*S*)-2'-(4-Methoxyphenyl)-2-phenyl-3',4'-dihydro-2'*H*-

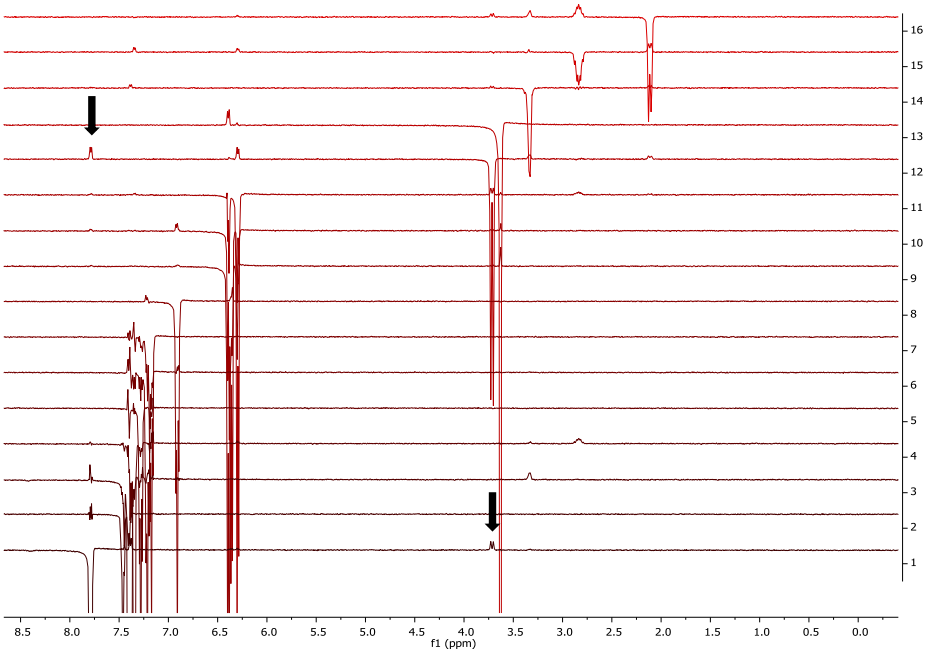
spiro[indole-3,1'-naphthalene] (**5a**) was formed in 80% yield (33.3 mg, 0.080 mmol, >20:1 dr) as a yellow solid.

***R*$_f$ (dichloromethane):** 0.3; **^{1}H NMR (500 MHz, CD_2Cl_2)** δ = 7.80 – 7.74 (m, 2H), 7.48 – 7.41 (m, 1H), 7.41 – 7.35 (m, 4H), 7.33 (ddd, *J* = 7.3, 1.2, 0.6 Hz, 1H), 7.27 (td, *J* = 7.6, 1.2 Hz, 1H), 7.20 (ddd, *J* = 7.7, 7.2, 1.3 Hz, 1H), 7.16 (td, *J* = 7.4, 1.1 Hz, 1H), 6.90 (tdt, *J* = 7.9, 1.4, 0.7 Hz, 1H), 6.41 – 6.35 (m, 2H), 6.34 (ddd, *J* = 7.8, 1.3, 0.5 Hz, 1H), 6.31 – 6.25 (m, 2H), 3.70 (dd, *J* = 13.3, 2.6 Hz, 1H), 3.61 (s, 3H), 3.37 – 3.28 (m, 2H), 2.82 (tdd, *J* = 13.4, 10.6, 7.2 Hz, 1H), 2.10 (ddt, *J* = 13.4, 5.1, 2.7 Hz, 1H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ = 182.0, 158.7, 154.9, 147.1, 136.3, 136.2, 133.7, 132.5, 131.1, 130.6, 129.4, 129.4, 129.1, 128.5, 128.0, 127.6, 127.2, 125.9, 124.8, 121.3, 112.8, 67.5, 55.4, 47.6, 30.8, 26.9; **HRMS** *m/z* (ESI): calcd. for $[C_{30}H_{25}NONa]^+$ 438.1828; found 438.1835.

The assignment of the structure was performed by 2D NMR spectroscopy. By NOE the diastereomer was assigned.



NOE spectrum:



4. Starting materials

Synthesis of pyridinium salts

All literature known pyridinium salts were synthesized according to previous reports.[6]

General procedure A[7]

Under an argon atmosphere a flame-dried Schlenk tube was charged with the respective amine (2.0 equiv.) dissolved in dichloromethane (0.25 M). Acetic acid (0.05 mL, 0.9 mmol) was added. 2,4,6-Triphenylpyrylium tetrafluoroborate (1.0 equiv.) was added and the mixture stirred for the indicated time at ambient temperature. Diethyl ether was added and the resulting suspension stirred for at least 1 h to complete the precipitation process. The solid was collected by filtration, washed with ether (5 x) and, if necessary, purified by recrystallization.

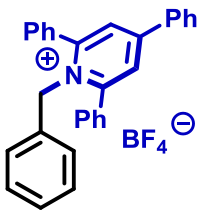
Amine hydrochlorides as starting materials: Under an argon atmosphere a flame-dried Schlenk tube was charged with the respective amine (2.0 equiv.) dissolved in dichloromethane (0.25 M). Triethylamine (2.0 equiv.) was added and the mixture stirred for 30 min at ambient temperature. Acetic acid (0.05 mL, 0.9 mmol) was added. 2,4,6-Triphenylpyrylium tetrafluoroborate (1.0 equiv.) was added and the mixture stirred for the indicated time at ambient temperature. After precipitation with diethyl ether the solid was collected by filtration, washed with water (5x) and ether (5x) and, if necessary, purified by recrystallization.

General procedure B[8]

A Schlenk tube was charged with 2,4,6-triphenylpyrylium tetrafluoroborate (1.0 equiv.) and, if solid, the corresponding primary amine (1.2 equiv.). Ethanol (1.0 M) was added to the reaction vessel and the tube sealed. No precautions to protect the reaction mixture from air and moisture were taken. The reaction mixture was heated to 85-90 °C and after the indicated time cooled to ambient temperature. If precipitation occurred during this step, the solid was collected by filtration and washed with ethanol and diethyl ether. In case no precipitation occurred, diethyl ether was added to the reaction mixture and the resulting suspension stirred at room temperature for at least 1 h to complete the precipitation process. The solid was collected by filtration, washed with diethyl ether (5x), and recrystallized, if necessary.

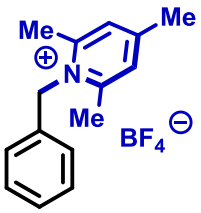
Amine hydrochlorides as starting materials: A Schlenk tube was charged with the primary amine (1.2 equiv.). Ethanol (1.0 M) and triethylamine (1.2 equiv.) were added to the reaction vessel and the tube sealed. No precautions to protect the reaction mixture from air and moisture were taken. The reaction mixture was stirred for 30 min. Then 2,4,6-triphenylpyrylium tetrafluoroborate (1.0 equiv.) was added. The reaction mixture was heated to 85-90 °C and after the indicated time cooled to ambient temperature. If precipitation occurred during this step, the solid was collected by filtration and washed with water, ethanol and diethyl ether. In case no precipitation occurred, diethyl ether was added to the reaction mixture and the resulting suspension stirred at room temperature for at least 1 h to complete the precipitation process. The solid was collected by filtration, washed with water (5x) and diethyl ether (5x), and recrystallized, if necessary.

1-Benzyl-2,4,6-triphenylpyridin-1-ium tetrafluoroborate



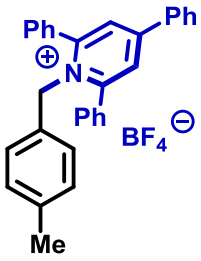
Following general procedure **A** the reaction was carried out with 2,4,6-triphenylpyrylium tetrafluoroborate (10.0 mmol, 3.96 g), phenylmethanamine (2.2 mL, 20.0 mmol), acetic acid (0.05 mL, 0.9 mmol) and dichloromethane (40 mL, 0.25 M) for 2 h. 1-Benzyl-2,4,6-triphenylpyridin-1-ium tetrafluoroborate was formed in 85% yield (4.14 g, 8.5 mmol) as a white solid. **^{1}H NMR (300 MHz, $CDCl_3$)** δ = 7.91 (s, 2H), 7.83 – 7.74 (m, 2H), 7.67 – 7.59 (m, 4H), 7.60 – 7.39 (m, 9H), 7.20 – 7.03 (m, 3H), 6.45 (d, *J* = 7.0 Hz, 2H), 5.75 (s, 2H); **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 157.7, 156.4, 134.2, 133.9, 132.9, 132.5, 131.1, 129.9, 129.3, 129.2, 128.9, 128.4, 128.3, 126.7, 126.3, 58.4; **^{19}F NMR (282 MHz, $CDCl_3$)** δ = -152.90, -152.95; **HRMS** *m/z* (ESI): calcd. for $[C_{30}H_{24}N]^+$ 398.1903; found 398.1909; **ATR-IR *v* (cm^{-1})** 3063, 1620, 1559, 1095, 1049, 1003, 772, 756, 695.

1-Benzyl-2,4,6-trimethylpyridin-1-ium tetrafluoroborate



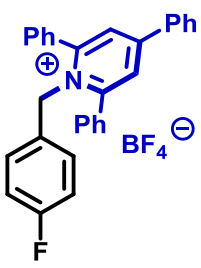
Following general procedure **A** the reaction was carried out with 2,4,6-trimethylpyrylium tetrafluoroborate (5.94 g, 15.0 mmol), phenylmethanamine (3.3 mL, 30.0 mmol), acetic acid (0.05 mL, 0.9 mmol) and dichloromethane (60 mL, 0.25 M) for 2 h. The crude product was purified by recrystallization from ethanol/dichloromethane. 1-Benzyl-2,4,6-trimethylpyridin-1-ium tetrafluoroborate was formed in 89% yield (6.47 g, 13.3 mmol) as a white solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ = 7.57 (s, 2H), 7.43 – 7.29 (m, 3H), 6.86 (dd, *J* = 8.0, 1.6 Hz, 2H), 5.77 (s, 2H), 2.71 (s, 6H), 2.58 (s, 3H); **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 158.9, 155.3, 131.7, 129.9, 128.9, 128.8, 125.1, 55.5, 21.8, 21.3; **^{19}F NMR (282 MHz, $CDCl_3$)** δ = -153.05, -153.11; **HRMS** *m/z* (ESI): calcd. for $[C_{15}H_{18}N]^+$ 212.1434; found 212.1442; **ATR-IR *v* (cm^{-1})** 3017, 1643, 1481, 1096, 1049, 1026, 856, 756.

1-(4-Methylbenzyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate



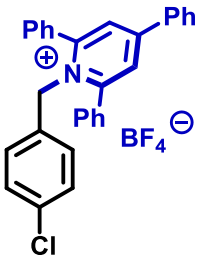
Following general procedure **A** the reaction was carried out with 2,4,6-triphenylpyrylium tetrafluoroborate (2.5 mmol, 1.00 g), *p*-tolylmethanamine (0.64 mL, 5.0 mmol), acetic acid (0.05 mL, 0.9 mmol) and dichloromethane (10 mL, 0.25 M) for 3 h. The crude product was purified by recrystallization from diethyl ether/dichloromethane. 1-(4-Methylbenzyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate was formed in 89% yield (1.11 g, 2.2 mmol) as a white solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ = 7.90 (s, 2H), 7.81 – 7.75 (m, 2H), 7.67 – 7.60 (m, 4H), 7.60 – 7.40 (m, 9H), 6.89 (d, *J* = 7.9 Hz, 2H), 6.32 (d, *J* = 8.1 Hz, 2H), 5.71 (s, 2H), 2.22 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ = 157.7, 156.3, 138.3, 133.9, 132.9, 132.5, 131.2, 131.0, 129.9, 129.6, 129.3, 129.2, 128.3, 126.7, 126.3, 58.2, 21.2; **^{19}F NMR (282 MHz, $CDCl_3$)** δ = -153.16, -153.21; **HRMS** *m/z* (ESI): calcd. for $[C_{31}H_{26}N]^+$ 412.2060; found 412.2067; **ATR-IR *v* (cm^{-1})** 3055, 1620, 1559, 1543, 1049, 1034, 787, 764, 748, 702.

1-(4-Fluorobenzyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate



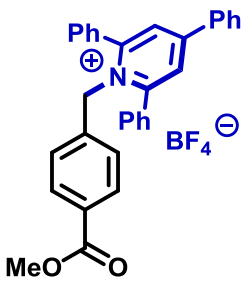
Following general procedure **B** the reaction was carried out with 2,4,6-triphenylpyrylium tetrafluoroborate (2.5 mmol, 0.990 g), (4-fluorophenyl)-methanamine (0.34 mL, 3.0 mmol) ethanol (2.5 mL, 1.0 M) for 4 h. After cooling to ambient temperature and addition of diethyl ether, no solid precipitated. The solvent was removed under reduced pressure and the residue purified by column chromatography (SiO_2, dichloromethane/acetone 8:1) and recrystallization from ethanol. 1-(4-Fluorobenzyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate was formed in 38% yield (0.475 g, 0.94 mmol) as a white solid. **^{1}H NMR (300 MHz, $CDCl_3$)** δ = 7.91 (s, 2H), 7.78 (dd, J = 8.2, 1.6 Hz, 2H), 7.69 – 7.61 (m, 4H), 7.60 – 7.41 (m, 9H), 6.85 – 6.71 (m, 2H), 6.49 – 6.35 (m, 2H), 5.75 (s, 2H); **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 162.4 (d, *J* = 248.9 Hz), 157.6, 156.6, 141.3, 133.8, 132.9, 132.6, 131.2, 129.9, 129.4, 129.2, 128.4 (d, *J* = 8.4 Hz), 128.3, 126.8, 116.0 (d, *J* = 21.9 Hz), 57.7; **^{19}F NMR (282 MHz, $CDCl_3$)** *δ* = -112.49, -152.90, -152.95; **HRMS** *m/z* (ESI): calcd. for $[C_{30}H_{23}NF]^+$ 416.1809; found 416.1812; **ATR-IR *v* (cm^{-1})** 3063, 1620, 1559, 1512, 1227, 1049, 1034, 895, 795, 748, 702.

1-(4-Chlorobenzyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate



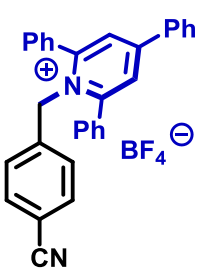
Following general procedure **B** the reaction was carried out with 2,4,6-triphenylpyrylium tetrafluoroborate (2.5 mmol, 0.990 g), (4-chlorophenyl)methanamine (0.36 mL, 3.0 mmol) ethanol (2.5 mL, 1.0 M) for 4 h. On addition of diethyl ether a solid precipitated. The solid was collected by filtration and washed with diethyl ether (5x5 mL). The crude product was recrystallized from ethanol/acetone. 1-(4-Chlorobenzyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate was formed in 80% yield (1.04 g, 2.0 mmol) as a white solid. **^{1}H NMR (300 MHz, $CDCl_3$)** δ = 7.89 (s, 2H), 7.80 – 7.71 (m, 2H), 7.68 – 7.60 (m, 4H), 7.58 – 7.39 (m, 9H), 7.06 (d, *J* = 8.0 Hz, 2H), 6.41 (d, *J* = 8.1 Hz, 2H), 5.73 (s, 2H); **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 157.5, 156.6, 134.3, 133.8, 132.7, 132.5, 132.5, 131.2, 129.9, 129.4, 129.2, 129.1, 128.3, 127.9, 126.8, 57.7; **^{19}F NMR (282 MHz, $CDCl_3$)** *δ* = -152.68, -152.73; **HRMS** *m/z* (ESI): calcd. for $[C_{30}H_{23}NCl]^+$ 432.1514; found 432.1523; **ATR-IR *v* (cm^{-1})** 3063, 1620, 1559, 1543, 1512, 1489, 1420, 1342, 1165, 1049, 1034, 895, 787, 764, 741, 702.

1-(4-(Methoxycarbonyl)benzyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate



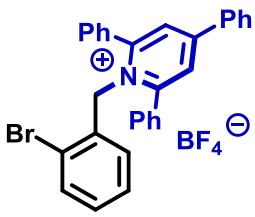
Following general procedure **A** the reaction was carried out with 2,4,6-triphenylpyrylium tetrafluoroborate (1.25 mmol, 0.495 g), methyl 4-(aminomethyl)benzoate hydrochloride (0.504 g, 2.5 mmol), triethylamine (0.35 mL, 2.5 mL), acetic acid (0.05 mL, 0.9 mmol) and dichloromethane (5 mL, 0.25 M) for 5 h. 1-(4-(Methoxycarbonyl)benzyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate was formed in 87% yield (0.592 g, 1.1 mmol) as a white solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ = 7.94 (s, 2H), 7.82 – 7.74 (m, 4H), 7.67 – 7.60 (m, 4H), 7.61 – 7.40 (m, 9H), 6.58 (d, *J* = 7.9 Hz, 2H), 5.81 (s, 2H), 3.86 (s, 3H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 166.3, 157.6, 156.8, 139.0, 133.8, 132.6, 131.3, 130.1, 130.1, 129.9, 129.4, 129.2, 128.4, 126.8, 126.3, 58.0, 52.4 (*one carbon signal was not detected*); **^{19}F NMR (376 MHz, $CDCl_3$)** *δ* = -152.78, -152.83; **HRMS** *m/z* (ESI): calcd. for $[C_{32}H_{26}NO_2]^+$ 456.1958; found 456.1960; **ATR-IR *v* (cm^{-1})** 3070, 1728, 1620, 1559, 1420, 1281, 1049, 1026, 756, 694.

1-(4-Cyanobenzyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate



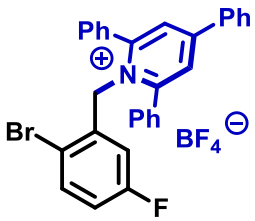
Following general procedure **B** the reaction was carried out with 2,4,6-triphenylpyrylium tetrafluoroborate (1.25 mmol, 0.495 g), 4-(aminomethyl)benzonitrile hydrochloride (0.253 g, 1.5 mmol), triethylamine (0.21 mL, 1.5 mmol) and ethanol (2.5 mL, 1.0 M) for 4 h. On addition of diethyl ether a slurry precipitate formed. The solvent was removed under reduced pressure and the residue dissolved in dichloromethane. Diethyl ether was added and the precipitated solid collected and washed with water (5x) and diethyl ether (5x). 1-(4-Cyanobenzyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate was formed in 30% yield (0.187 g, 0.4 mmol) as a white solid. **^{1}H NMR (300 MHz, $CDCl_3$)** δ = 7.94 (s, 2H), 7.79 (d, *J* = 7.4 Hz, 2H), 7.70 – 7.35 (m, 15H), 6.66 (d, *J* = 7.8 Hz, 2H), 5.84 (s, 2H); **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 157.6, 157.1, 139.2, 133.7, 132.8, 132.7, 132.5, 131.4, 123.0, 129.5, 129.2, 128.4, 127.3, 126.9, 118.0, 112.3, 57.9; **^{19}F NMR (282 MHz, $CDCl_3$)** *δ* = -152.51, -152.56; **HRMS** *m/z* (ESI): calcd. for $[C_{31}H_{23}N_2]^+$ 423.1856; found 423.1864; **ATR-IR *v* (cm^{-1})** 3063, 2230, 1620, 1559, 1057, 702.

1-(2-Bromobenzyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate



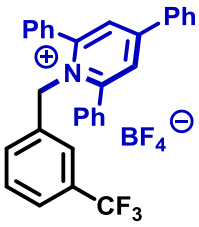
Following general procedure **A** the reaction was carried out with 2,4,6-triphenylpyrylium tetrafluoroborate (0.495 g, 1.25 mmol), (2-bromophenyl)methanamine (0.465 g, 2.5 mmol), acetic acid (0.05 mL, 0.9 mmol) and dichloromethane (5 mL, 0.25 M) for 2 h. 1-(2-Bromobenzyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate was formed in 97% yield (0.687 g, 1.2 mmol) as a white solid. **^{1}H NMR (400 MHz, $CDCl_3$)** *δ* = 7.92 (s, 2H), 7.84 – 7.76 (m, 2H), 7.66 – 7.59 (m, 4H), 7.60 – 7.39 (m, 9H), 7.26 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.15 (t, *J* = 7.3 Hz, 1H), 7.03 (td, *J* = 7.7, 1.4 Hz, 1H), 6.59 (d, *J* = 7.5 Hz, 1H), 5.75 (s, 2H); **^{13}C NMR (101 MHz, $CDCl_3$)** *δ* = 157.9, 156.8, 134.0, 133.4, 133.0, 132.7, 132.5, 131.2, 129.9, 129.4, 129.1, 129.0, 128.4, 128.1, 126.9, 121.8, 59.1 (*one carbon signal was not detected*); **^{19}F NMR (376 MHz, $CDCl_3$)** *δ* = -152.81, -152.87; **HRMS** *m/z* (ESI): calcd. for $[C_{30}H_{23}NBr]^+$ 476.1008; found 476.1004; **ATR-IR *v* (cm^{-1})** 3063, 1620, 1559, 1543, 1466, 1412, 1150, 1096, 1026, 895, 756, 741, 694.

1-(2-Bromo-5-fluorobenzyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate



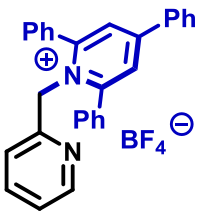
Following general procedure **A** the reaction was carried out with 2,4,6-triphenylpyrylium tetrafluoroborate (0.495 g, 1.25 mmol), (2-bromo-5-fluorophenyl)methanamine (0.510 g, 2.5 mmol), acetic acid (0.05 mL, 0.9 mmol) and dichloromethane (5 mL, 0.25 M) for 2 h. 1-(2-Bromo-5-fluorobenzyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate was formed in 97% yield (0.707 g, 1.2 mmol) as a white solid. **^{1}H NMR (400 MHz, $CDCl_3$)** *δ* = 7.98 (s, 2H), 7.92 – 7.80 (m, 2H), 7.72 – 7.62 (m, 4H), 7.63 – 7.43 (m, 9H), 7.28 – 7.22 (m, 1H), 6.78 (td, *J* = 8.2, 2.9 Hz, 1H), 6.26 (dd, *J* = 8.9, 2.9 Hz, 1H), 5.78 (s, 2H); **^{13}C NMR (151 MHz, $CDCl_3$)** *δ* = 161.9 (d, *J* = 249.4 Hz), 158.0, 157.0, 135.5 (d, *J* = 7.2 Hz), 134.6 (d, *J* = 8.0 Hz), 133.8, 132.7, 132.7, 131.4, 123.0, 129.5, 129.2, 128.4, 126.8, 117.2 (d, *J* = 22.2 Hz), 116.6 (d, *J* = 24.5 Hz), 116.2 (d, *J* = 3.4 Hz), 59.0; **^{19}F NMR (282 MHz, $CDCl_3$)** *δ* = -112.90, -152.75, -152.81; **HRMS** *m/z* (ESI): calcd. for $[C_{30}H_{22}NBrF]^+$ 494.0914; found 494.0914; **ATR-IR *v* (cm^{-1})** 3071, 1620, 1559, 1096, 1080, 1049, 1034, 772, 756, 702.

2,4,6-Triphenyl-1-(3-(trifluoromethyl)benzyl)pyridin-1-ium tetrafluoroborate



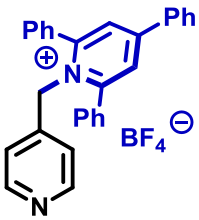
Following general procedure **B** the reaction was carried out with 2,4,6-triphenylpyrylium tetrafluoroborate (2.5 mmol, 0.990 g), (3-(trifluoromethyl)phenyl)methanamine (0.43 mL, 3.0 mmol) ethanol (2.5 mL, 1.0 M) for 4 h. On addition of diethyl ether only a slurry precipitate formed. The solvent was removed under reduced pressure and the residue purified by column chromatography (SiO_2, dichloromethane/acetone 4:1). 2,4,6-Triphenyl-1-(3-(trifluoromethyl)benzyl)pyridin-1-ium tetrafluoroborate was formed in 46% yield (0.63 g, 1.1 mmol) as a white solid. **^{1}H NMR (300 MHz, $CDCl_3$)** δ = 7.93 (s, 2H), 7.84 – 7.71 (m, 2H), 7.68 – 7.35 (m, 14H), 7.32 – 7.22 (m, 1H), 6.79 (d, *J* = 7.6 Hz, 1H), 6.57 (s, 1H), 5.83 (s, 2H); **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 157.5, 156.8, 134.9, 133.7, 132.7, 132.6, 131.3, 131.3 (q, *J* = 33.2 Hz), 130.0, 129.9, 129.9, 129.5, 129.2, 128.3, 126.8, 123.4 (q, *J* = 272.5 Hz), 125.2 (q, *J* = 3.6 Hz), 123.7 (q, *J* = 3.6 Hz), 57.7; **^{19}F NMR (282 MHz, $CDCl_3$)** *δ* = -62.90, -152.68, -152.74; **HRMS** *m/z* (ESI): calcd. for $[C_{31}H_{23}NF_3]^+$ 466.1777; found 466.1794; **ATR-IR *v* (cm^{-1})** 3063, 1620, 1559, 1327, 1119, 1049, 1034, 787, 764, 702.

2,4,6-Triphenyl-1-(pyridin-2-ylmethyl)pyridin-1-ium tetrafluoroborate



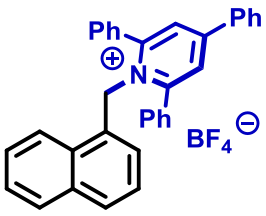
Following general procedure **A** the reaction was carried out with 2,4,6-triphenylpyrylium tetrafluoroborate (0.495 g, 1.25 mmol), pyridin-2-ylmethanamine (0.26 mL, 2.5 mmol), acetic acid (0.05 mL, 0.9 mmol) and dichloromethane (5 mL, 0.25 M) for 2 h. The crude product was purified by recrystallization from ethanol 2,4,6-Triphenyl-1-(pyridin-2-ylmethyl)pyridin-1-ium tetrafluoroborate was formed in 73% yield (0.443 g, 0.9 mmol) as a white solid. **^{1}H NMR (400 MHz, $CDCl_3$)** *δ* = 8.44 (d, *J* = 4.9 Hz, 1H), 7.95 (s, 2H), 7.87 – 7.77 (m, 2H), 7.71 – 7.35 (m, 14H), 7.15 (dd, *J* = 7.5, 5.0 Hz, 1H), 6.57 (d, *J* = 8.0 Hz, 1H), 5.81 (s, 2H); **^{13}C NMR (75 MHz, $CDCl_3$)** *δ* = 157.6, 156.1, 153.2, 149.1, 137.1, 134.1, 133.0, 132.3, 130.9, 129.9, 129.0, 129.0, 128.2, 126.2, 123.3, 122.1, 59.0; **^{19}F NMR (282 MHz, $CDCl_3$)** *δ* = -153.17, -153.22; **HRMS** *m/z* (ESI): calcd. for $[C_{29}H_{23}N_2]^+$ 399.1856; found 399.1887; **ATR-IR *v* (cm^{-1})** 3063, 1620, 1559,l 1543, 1049, 1034, 995, 764, 702.

2,4,6-Triphenyl-1-(pyridin-4-ylmethyl)pyridin-1-ium tetrafluoroborate



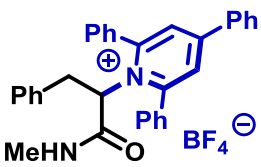
Following general procedure **A** the reaction was carried out with 2,4,6-triphenylpyrylium tetrafluoroborate (0.991 g, 2.5 mmol), pyridin-4-ylmethanamine (0.51 mL, 5.0 mmol), acetic acid (0.05 mL, 0.9 mmol) and dichloromethane (10 mL, 0.25 M) for 2 h. The crude product was purified by recrystallization from ethanol/acetone. 2,4,6-Triphenyl-1-(pyridin-4-ylmethyl)pyridin-1-ium tetrafluoroborate was formed in 78% yield (0.950 g, 0.9 mmol) as a white solid. **^{1}H NMR (300 MHz, $CDCl_3$)** *δ* = 8.37 (d, *J* = 5.9 Hz, 2H), 7.98 (s, 2H), 7.81 (dd, *J* = 8.1, 1.6 Hz, 2H), 7.71 – 7.39 (m, 13H), 6.52 (d, *J* = 6.1 Hz, 2H), 5.79 (s, 2H); **^{13}C NMR (101 MHz, $CDCl_3$)** *δ* = 157.6, 157.3, 148.9, 144.7, 133.7, 132.8, 132.3, 131.5, 130.0, 129.6, 129.2, 128.4, 126.9, 121.7, 57.2; **^{19}F NMR (282 MHz, $CDCl_3$)** *δ* = -152.51, -152.57; **HRMS** *m/z* (ESI): calcd. for $[C_{29}H_{23}N_2]^+$ 399.1856; found 399.1867; **ATR-IR *v* (cm^{-1})** 3063, 1620, 1559, 1049, 1034, 918, 772, 725, 694.

1-(Naphthalen-1-ylmethyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate



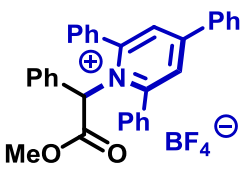
Following general procedure **A** the reaction was carried out with 2,4,6-triphenylpyrylium tetrafluoroborate (0.495 g, 1.25 mmol), naphthalen-1-ylmethanamine (0.37 mL, 2.5 mmol), acetic acid (0.05 mL, 0.9 mmol) and dichloromethane (5 mL, 0.25 M) for 2 h. The crude product was purified by recrystallization from ethanol/diethyl ether. 1-(Naphthalen-1-ylmethyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate was formed in 64% yield (0.430 g, 0.80 mmol) as a white solid. **^{1}H NMR (300 MHz, $CDCl_3$)** δ = 7.98 (s, 2H), 7.82 (d, *J* = 7.2 Hz, 2H), 7.71 (d, *J* = 8.3 Hz, 2H), 7.66 – 7.46 (m, 7H), 7.43 – 7.21 (m, 10H), 6.64 (d, *J* = 7.0 Hz, 1H), 6.18 (s, 2H); **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 157.9, 156.5, 133.9, 133.2, 132.5, 132.4, 131.0, 130.9, 129.9, 129.3, 129.1, 129.0, 128.9, 128.6, 128.3, 127.1, 126.8, 126.6, 124.8, 123.2, 122.0, 56.0; **^{19}F NMR (282 MHz, $CDCl_3$)** δ = -152.97, -153.02; **HRMS** *m/z* (ESI): calcd. for $[C_{34}H_{26}N]^+$ 448.2060; found 448.2054; **ATR-IR *v* (cm^{-1})** 3063, 2978, 1620, 1559, 1049, 1034, 795, 764, 702.

1-(1-(Methylamino)-1-oxo-3-phenylpropan-2-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate



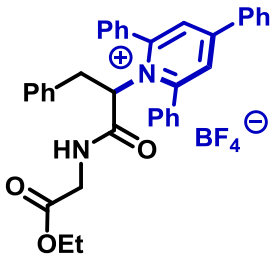
Following general procedure **B** the reaction was carried out with 2,4,6-triphenylpyrylium tetrafluoroborate (4.0 mmol, 1.59 g), 2-amino-*N*-methyl-3-phenylpropanamide (0.856 g, 4.8 mmol) ethanol (4.0 mL, 1.0 M) for 4 h. On addition of diethyl ether only a slurry precipitate formed. The solvent was removed under reduced pressure and the residue purified by column chromatography (SiO_2, dichloromethane/acetone 20:1 to 5:1). 1-(1-(Methylamino)-1-oxo-3-phenylpropan-2-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate was formed in 31% yield (0.681 g, 1.2 mmol) as a yellowish solid. **^{1}H NMR (300 MHz, $CDCl_3$)** δ = 8.03 – 7.29 (m, 16H), 7.24 – 7.07 (m, 4H), 6.90 (d, *J* = 5.0 Hz, 1H), 6.73 – 6.56 (m, 2H), 5.62 (dd, *J* = 8.2, 6.0 Hz, 1H), 3.28 (dd, *J* = 14.8, 6.0 Hz, 1H), 3.18 (dd, *J* = 14.8, 8.3 Hz, 1H), 2.73 (d, *J* = 4.5 Hz, 3H); **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 166.5, 157.9, 156.6, 135.6, 133.7, 132.7, 132.4, 131.6, 129.9, 129.7, 129.3, 129.1, 128.8, 128.5, 128.1, 127.8, 71.3, 36.9, 27.3; **^{19}F NMR (282 MHz, $CDCl_3$)** δ = -152.47, -152.52; **HRMS** *m/z* (ESI): calcd. for $[C_{33}H_{29}N_2O]^+$ 469.2274; found 469.2258; **ATR-IR *v* (cm^{-1})** 3395, 3063, 2970, 1681, 1620, 1559, 1528, 1057, 910, 764, 733, 702.

1-(2-Methoxy-2-oxo-1-phenylethyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate



Following general procedure **A** the reaction was carried out with 2,4,6-triphenylpyrylium tetrafluoroborate (1.25 mmol, 0.495 g), methyl 2-amino-2-phenylacetate hydrochloride (0.504 g, 2.5 mmol), triethylamine (0.35 mL, 2.5 mL), acetic acid (0.05 mL, 0.9 mmol) and dichloromethane (5 mL, 0.25 M) for 3 h. 1-(2-Methoxy-2-oxo-1-phenylethyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate was formed in 48% yield (0.328 g, 0.60 mmol) as a white solid. **^{1}H NMR (300 MHz, $CDCl_3$)** δ = 7.96 (s, 2H), 7.91 – 7.65 (m, 4H), 7.64 – 7.29 (m, 9H), 7.15 – 6.95 (m, 5H), 6.85 – 6.70 (m, 3H), 3.89 (s, 3H); **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 167.7, 157.5, 157.3, 133.7, 133.0, 132.5, 131.0, 130.7, 129.7, 129.1, 129.0, 128.8, 128.7, 128.6, 128.6, 128.2, 71.7, 54.1; **^{19}F NMR (282 MHz, $CDCl_3$)** δ = -152.47, -152.52; **HRMS** *m/z* (ESI): calcd. for $[C_{32}H_{26}NO_2]^+$ 456.1958; found 456.1960; **ATR-IR *v* (cm^{-1})** 3071, 1751, 1620, 1559, 1227, 1157, 1057, 1034, 995, 926, 756, 694.

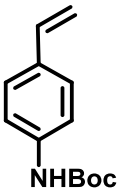
1-(1-((2-Ethoxy-2-oxoethyl)amino)-1-oxo-3-phenylpropan-2-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate



Following a modification of general procedure **B** the reaction was carried out with 2,4,6-triphenylpyrylium tetrafluoroborate (2.0 mmol, 0.792 g), 1-((2-ethoxy-2-oxoethyl)amino)-1-oxo-3-phenylpropan-2-aminium 2,2,2-trifluoroacetate (1.46 g, 4.0 mmol), triethylamine (0.56 mL, 4.0 mmol) and anhydrous ethanol (4.0 mL, 0.5 M) for 16 h. On addition of diethyl ether only a slurry precipitate formed. The solvent was removed under reduced pressure and the residue purified by column chromatography (SiO_2, dichloromethane/acetone 5:1 to 2:1). 1-(1-((2-Ethoxy-2-oxoethyl)amino)-1-oxo-3-phenylpropan-2-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate was formed in 68% yield (0.851 g, 1.4 mmol) as a yellowish solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ = 7.91 (s, 2H), 7.85 – 7.76 (m, 2H), 7.77 – 7.28 (m, 13H), 7.24 – 7.11 (m, 3H), 7.00 (br, 1H), 6.70 (d, *J* = 7.0 Hz, 2H), 5.76 (t, *J* = 7.0 Hz, 1H), 4.16 (q, *J* = 7.0 Hz, 2H), 3.97 (dd, *J* = 17.7, 5.6 Hz, 1H), 3.87 (dd, *J* = 17.7, 4.8 Hz, 1H), 3.37 (dd, *J* = 15.0, 6.8 Hz, 1H), 3.04 (dd, *J* = 15.0, 7.0 Hz, 1H), 1.25 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ = 168.7, 167.1, 157.7, 156.9, 135.7, 133.9, 132.7, 132.5, 131.6, 129.9, 129.8, 129.4, 129.2, 128.8, 128.6, 128.2, 127.9, 71.2, 61.6, 42.1, 36.9, 14.3; **^{19}F NMR (282 MHz, $CDCl_3$)** δ = -152.43, -152.48; **HRMS** *m/z* (ESI): calcd. for $[C_{36}H_{33}N_2O_3]^+$ 541,2486; found 541.2488; **ATR-IR *v* (cm^{-1})** 3379, 3063, 2986, 2940, 1736, 1682, 1620, 1559, 1543, 1497, 1204, 1157, 1057, 1026, 764, 702.

Synthesis of other starting materials

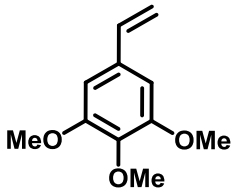
***tert*-Butyl (4-vinylphenyl)carbamate**



4-Vinylaniline (0.78 mL, 6.7 mmol, 1.0 equiv.) was added to a solution of di-*tert*-butyl dicarbonate (1.60 g, 7.3 mmol, 1.1 equiv.) in water (8 mL, 0.8 M). On addition a cloudy suspension formed. The reaction mixture was stirred for 23 h at ambient temperature. After that time ethyl acetate (10 mL) was added and the layers separated. The aqueous layer was extracted with ethyl acetate (3 x 10 mL). The combined organic layers were washed with brine and dried over $MgSO_4$. After filtration the solvent was removed under reduced pressure. The crude product was purified by column chromatography (SiO_2, *n*-pentane/ethyl acetate 10:1). *tert*-Butyl (4-vinylphenyl)carbamate was obtained in 99% yield (1.45 g, 6.6 mmol) as a white solid. **R_f (*n*-pentane/ethyl acetate 5:1):** 0.7; **^{1}H NMR (300 MHz, CD_2Cl_2)** δ = 7.39 – 7.31 (m, 4H), 6.65 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.65 (d, *J* = 17.6 Hz, 1H), 5.16 (dd, *J* = 10.9, 1.0 Hz, 1H), 1.52 (s, 9H); **^{13}C NMR (75 MHz, CD_2Cl_2)** δ = 152.8, 138.1, 136.3, 132.6, 127.0, 118.5, 112.5, 80.7, 28.5; **HRMS** *m/z* (ESI): calcd. for $[C_{13}H_{17}NO_2Na]^+$, 242.1151; found 242.1158; **ATR-IR *v* (cm^{-1})** 3379, 2986, 1697, 1520, 1505, 1319, 1234, 1150, 1057, 903, 833, 772.

^{1}H and ^{13}C spectra are in agreement with those reported in the literature.[9]

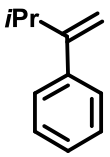
1,2,3-Trimethoxy-5-vinylbenzene



A flame dried Schlenk flask was charged with methyltriphenylphosphonium bromide (5.72 g, 16.0 mmol, 1.0 equiv.) and anhydrous diethyl ether (50 mL, 0.3 M). After cooling to 0 °C *n*-buthyllithium (1.6 M in hexane, 10 mL, 16.0 mmol, 1.0 equiv.) was dropwise added over 10 min. The resulting yellow suspension was stirred at 0 °C for 30 min. Then 3,4,5-trimethoxybenzaldehyde (3.14 g, 16.0 mmol, 1.0 equiv.) was added and the reaction mixture stirred for 16 h at ambient temperature. Water (100 mL) was added and the layers were separated. The aqueous layer was extracted with diethyl ether (3 x 100 mL) and the combined organic layers dried over $MgSO_4$. After filtration the solvent was removed under reduced pressure. The crude product was purified by column chromatography (SiO_2, *n*-pentane/ethyl acetate 20:1 to 10:1). 1,2,3-Trimethoxy-5-vinylbenzene was obtained in 44% yield (1.37 g, 7.1 mmol) as a colourless oil. ***R*$_f$ (*n*-pentane/ethyl acetate 5:1)**: 0.4; **^{1}H NMR (300 MHz, $CDCl_3$)** δ = 6.64 (dd, *J* = 17.4, 10.9 Hz, 1H), 6.64 (s, 2H), 5.66 (d, *J* = 17.5 Hz, 1H), 5.21 (d, *J* = 10.9 Hz, 1H), 3.88 (s, 6H), 3.85 (s, 3H); **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 153.4, 138.1, 136.9, 133.4, 113.4, 103.4, 61.0, 56.2; **GC-MS** t_r (min) = 7.62: *m/z* (EI): 194.1 $[M]^+$, 179.1, 151.1, 136.1, 121.1, 108.1, 91.0, 77.0, 65.0, 51.0, 39.0.

^{1}H and ^{13}C spectra are in agreement with those reported in the literature.[10]

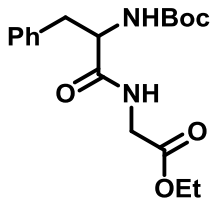
(3-Methylbut-1-en-2-yl)benzene



A flame dried Schlenk flask was charged with methyltriphenylphosphonium bromide (5.72 g, 16.0 mmol, 1.0 equiv.) and anhydrous diethyl ether (50 mL, 0.3 M). After cooling to 0 °C *n*-buthyllithium (1.6 M in hexane, 10 mL, 16.0 mmol, 1.0 equiv.) was dropwise added over 10 min. The resulting yellow suspension was stirred at 0 °C for 30 min. Then 2-methyl-1-phenylpropan-1-one (2.4 mL, 16.0 mmol, 1.0 equiv.) was added and the reaction mixture stirred for 16 h at ambient temperature. Water (100 mL) was added and the layers were separated. The aqueous layer was extracted with diethyl ether (3 x 100 mL) and the combined organic layers dried over $MgSO_4$. After filtration the solvent was removed under reduced pressure. The crude product was purified by column chromatography (SiO_2, *n*-pentane). The resulting colourless liquid was further purified by Kugelrohr distillation. (3-Methylbut-1-en-2-yl)benzene was obtained in 73% yield (1.71 g, 11.7 mmol) as a colourless liquid. ***R*$_f$ (*n*-pentane)**: 0.7; **^{1}H NMR (400 MHz, $CDCl_3$)** δ = 7.42 – 7.30 (m, 4H), 7.33 – 7.24 (m, 1H), 5.17 (d, *J* = 1.4 Hz, 1H), 5.09 – 5.04 (m, 1H), 5.20 – 5.14 (m, 1H), 2.87 (pd, *J* = 6.9, 1.4 Hz, 1H), 1.13 (d, *J* = 6.9 Hz, 6H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ = 156.0, 143.0, 128.3, 127.2, 126.8, 110.1, 32.5, 22.2; **GC-MS** t_r (min) = 6.05: *m/z* (EI): 146.1 $[M]^+$, 131.1, 115.0, 103.0, 91.0, 77.0, 63.0, 51.0, 39.0.

^{1}H and ^{13}C spectra are in agreement with those reported in the literature.[11]

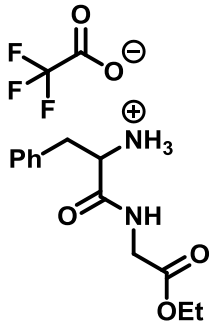
Ethyl (*tert*-butoxycarbonyl)phenylalanylglycinate



A flame dried Schlenk flask was charged with *L*-(tert-butoxycarbonyl)phenylalanine (6.37 g, 24.0 mmol, 1.2 equiv.), *N*-(3-dimethylaminopropyl)-*N′*-ethylcarbodiimide hydrochloride (8.63 g, 45.0 mmol, 2.3 equiv.) and 1-hydroxybenzotriazole hydrate (6.08 g, 45.0 mmol, 2.3 equiv.). Then anhydrous dimethylformamide (70 mL) was added and the resulting clear yellowish solution stirred for 1 h at ambient temperature under an argon atmosphere. Ethyl glycinate hydrochloride (2.79 g, 20 mmol, 1.0 equiv.) and triethylamine (8.5 mL, 61.0 mmol, 3.1 equiv.) were added and the cloudy solution stirred at ambient temperature for 70 h under an argon atmosphere. Water (30 mL) was added and the mixture extracted with ethyl acetate (4 x 60 mL). The combined organic layers were washed with hydrochloric acid (1 M, 60 mL), saturated aqueous sodium hydrogencarbonate solution (60 mL) and brine (2 x 60 mL). The organic layer was dried over sodium sulfate, filtered and the solvent removed under reduced pressure. The crude product was purified by column chromatography (SiO_2, *n*-pentane/ethyl acetate 10:1 to 3:1). Ethyl (*tert*-butoxycarbonyl)phenylalanylglycinate was obtained as a light yellow solid in 97% yield (6.79 g, 19.4 mmol). ***R*$_f$ (*n*-pentane/ethyl acetate 3:1)**: 0.1; **^{1}H NMR (300 MHz, $CDCl_3$)** δ = 7.38 – 7.18 (m, 5H), 6.48 (br, 1H), 5.05 (br, 1H), 4.52 – 4.34 (m, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 4.06 (dd, *J* = 18.3, 5.3 Hz, 1H), 3.94 (dd, *J* = 18.4, 5.0 Hz, 1H), 3.22 – 2.98 (m, 2H), 1.42 (s, 9H), 1.30 (t, *J* = 7.1 Hz, 3H); **HRMS** *m/z* (ESI): calcd. for $[C_{18}H_{26}N_2O_5Na]^+$, 373.1734; found 373.1756.

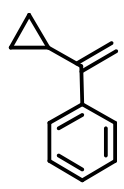
The ^{1}H spectrum is in agreement with the one reported in the literature.[12]

1-((2-Ethoxy-2-oxoethyl)amino)-1-oxo-3-phenylpropan-2-aminium 2,2,2-trifluoroacetate



A solution of ethyl (*tert*-butoxycarbonyl)phenylalanylglycinate (6.79 g, 19.4 mmol, 1.0 equiv.) in dichloromethane (60 mL) was treated with trifluoroacetic acid (10 mL, 131 mmol, 6.7 equiv.) over 2 min at ambient temperature under air. The reaction solution was stirred for 16 h at ambient temperature. The solvent was removed under reduced pressure and the residue taken up in water (60 mL). The aqueous layer was washed with dichloromethane (60 mL). The solvent of the aqueous layer was removed by lyophilization. 1-((2-Ethoxy-2-oxoethyl)amino)-1-oxo-3-phenylpropan-2-aminium 2,2,2-trifluoroacetate was obtained as a colourless oil in 99% yield (7.00 g, 19.2 mmol). **^{1}H NMR (400 MHz, CD_3OD)** δ = 7.41 – 7.21 (m, 5H), 4.22 – 4.11 (m, 3H), 3.99 – 3.90 (m, 2H), 3.31 – 3.18 (m, 2H), 3.05 (dd, *J* = 14.2, 8.1 Hz, 1H), 1.25 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR (101 MHz, CD_3OD)** δ = 169.5, 168.9, 161.3 (q, *J* = 35.0 Hz), 134.1, 129.2, 128.7, 127.5, 116.7 (q, *J* = 291.8 Hz), 61.1, 54.3, 40.6, 37.2, 13.0; **HRMS** *m/z* (ESI): calcd. for $[C_{13}H_{19}N_2O_3]^+$, 251.1390; found 251.1404.

(1-Cyclopropylvinyl)benzene



A flame dried Schlenk flask was charged with methyltriphenylphosphonium bromide (5.72 g, 16.0 mmol, 1.0 equiv.) and anhydrous diethyl ether (50 mL, 0.3 M). After cooling to 0 °C *n*-buthyllithium (1.6 M in hexane, 10 mL, 16.0 mmol, 1.0 equiv.) was dropwise added over 10 min. The resulting yellow suspension was stirred at 0 °C for 30 min. Then cyclopropyl(phenyl)methanone (2.2 mL, 16.0 mmol, 1.0 equiv.) was added and the reaction mixture stirred for 16 h at ambient temperature. Water (100 mL) was added and the layers were separated. The aqueous layer was extracted with

diethyl ether (3 x 100 mL) and the combined organic layers dried over $MgSO_4$. After filtration the solvent was removed under reduced pressure. The crude product was purified by column chromatography (SiO_2, *n*-pentane). The resulting colourless liquid was further purified by Kugelrohr distillation. (1-Cyclopropylvinyl)benzene was obtained in 73% yield (1.67 g, 11.6 mmol) as a colourless liquid. ***R*f (*n*-pentane)**: 0.7; **^{1}H NMR (300 MHz, $CDCl_3$)** δ = 7.75 – 7.57 (m, 2H), 7.44 – 7.28 (m, 3H), 5.32 (s, 1H), 4.98 (s, 1H), 1.69 (td, *J* = 8.3, 4.2 Hz, 1H), 0.94 – 0.78 (m, 2H), 0.72 – 0.57 (m, 2H); **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 149.5, 141.8, 128.3, 127.6, 126.3, 109.1, 15.8, 6.8; **GC-MS** t_r (min) = 6.52: *m/z* (EI): 144.1 $[M]^+$, 129.1, 115.1, 103.1, 91.0, 77.0, 63.0, 51.0, 39.0.

^{1}H and ^{13}C spectra are in agreement with those reported in the literature.[13]

5. Mechanistic studies

5.1 Stern-Volmer luminescence quenching studies

All samples were prepared under oxygen-free conditions. The photocatalysts and potential quenchers were weighed into vials and placed inside a glovebox under a positive pressure of argon. Acetonitrile was degassed by argon sparging for one hour. Stern-Volmer luminescence quenching studies were carried out using a 2 x 10^{-6} M solution of $[Ir(dtbbpy)(ppy)_2](PF_6)$ and variable concentrations of 1-benzyl-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (**1b**), 1-cyclohexyl-2,4,6-triphenylpyridin-1-ium tetrafluoroborate, 4-methoxystyrene, *α*-methylstyrene and indole in dry and degassed acetonitrile at room temperature under an argon atmosphere. The samples were prepared in 1.4 mL quartz cuvettes, equipped with PTFE stoppers, and sealed with parafilm inside an argon filled glove-box. The solutions were irradiated at 420 nm and the luminescence was measured at 560 nm (I_0 = emission intensity of the photocatalyst in isolation at the specified wavelength; I = observed intensity as a function of the quencher concentration).

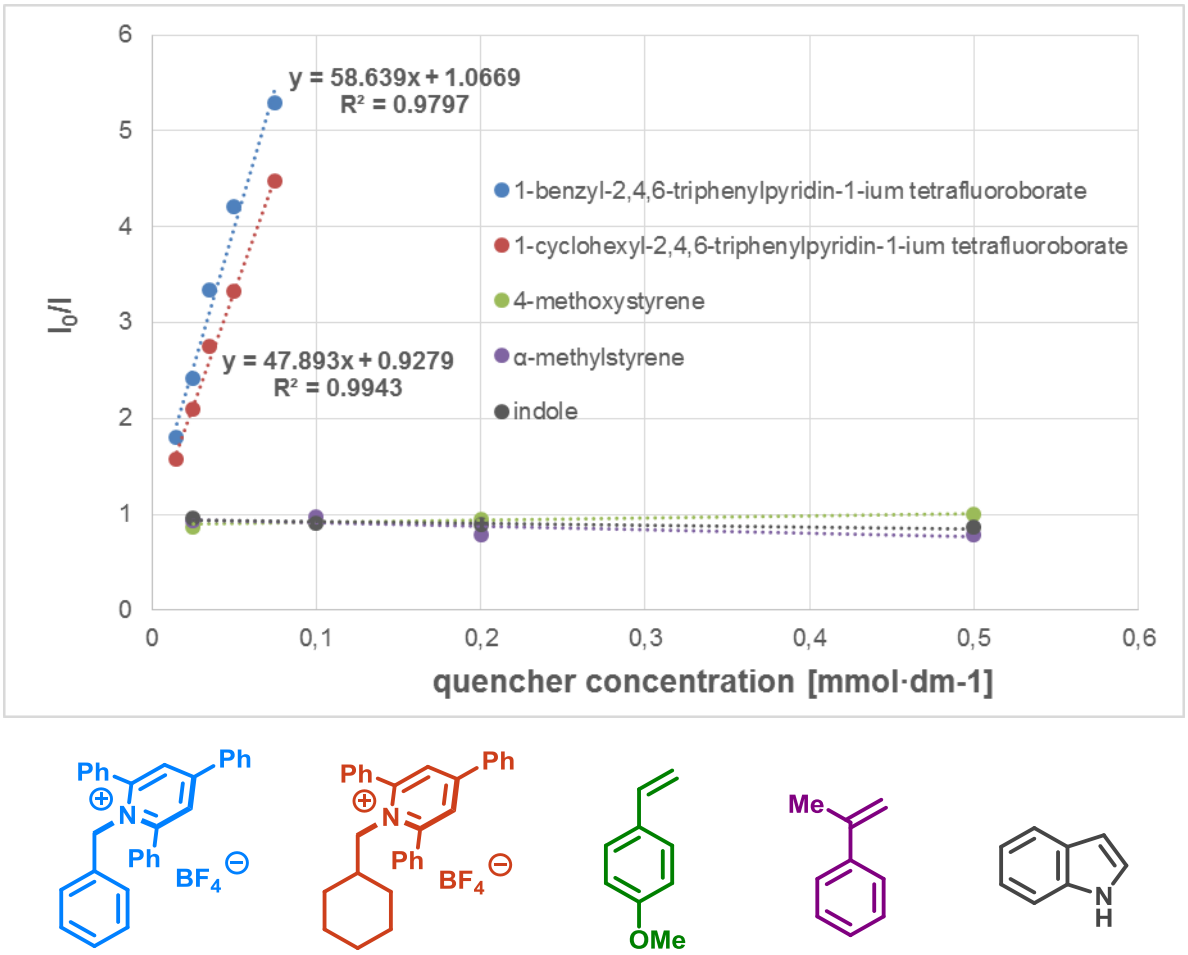
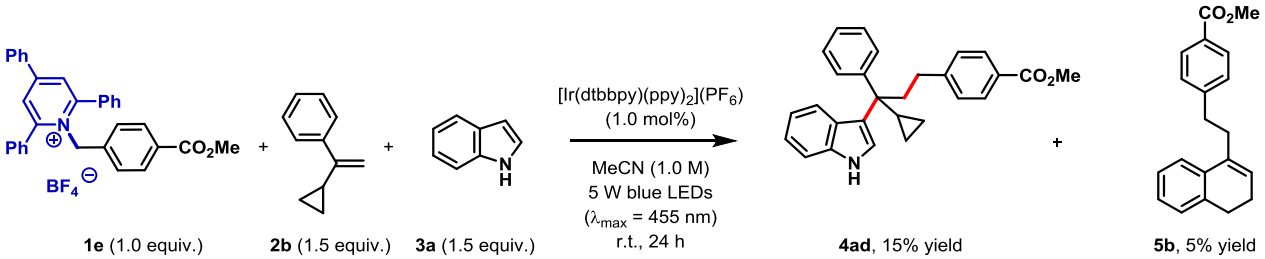


Figure S3. Stern-Volmer plot of components of the reaction mixture.

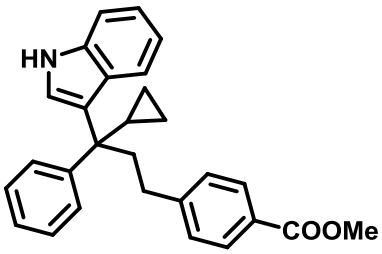
5.2 Radical clock study



An oven-dried screw cap Schlenk reaction tube was charged with 1-(4-(methoxycarbonyl)benzyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (0.30 mmol, 163.0 mg), 1*H*-indole (0.45 mmol, 52.7 mg) and [Ir(dtbbpy)(ppy)$_2$](PF$_6$) (1.0 mol%, 2.7 mg). The tube was evacuated and backfilled with argon. Acetonitrile (0.3 mL, 1.0 M) was added in a stream of argon. (1-Cyclopropylvinyl)benzene (**2b**, 0.45 mmol, 65 mg) was added in a stream of argon. The reaction mixture was degassed by three consecutive freeze-pump-thaw cycles. The solution was stirred under irradiation (λ_{max} = 455 nm, 5 W) for 24 h in an atmosphere of argon. Triethylamine (0.3 mL) was added to the reaction mixture. The crude product was absorbed to silica and purified by column chromatography (SiO$_2$, mixtures of *n*-pentane/ethyl acetate).

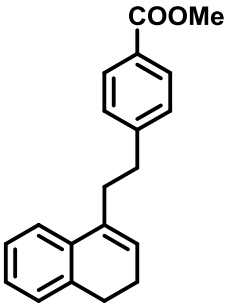
Two fractions of the crude reaction mixture were isolated.

Methyl 4-(3-cyclopropyl-3-(1*H*-indol-3-yl)-3-phenylpropyl)benzoate (4ad)



Fraction 1 (**4ad**): White solid, 18.0 mg (0.04 mmol, 15% yield), ***R*$_f$ (*n*-pentane/ethyl acetate 3:1):** 0.4; **^{1}H NMR (300 MHz, CD$_2$Cl$_2$)** δ = 8.23 (br, 1H), 7.87 (d, *J* = 8.3 Hz, 2H), 7.40 – 7.27 (m, 4H), 7.31 – 7.16 (m, 3H), 7.19 – 7.10 (m, 2H), 7.05 (ddd, *J* = 8.2, 6.2, 2.0 Hz, 1H), 6.83 – 6.70 (m, 2H), 3.86 (s, 3H), 2.74 – 2.37 (m, 4H), 1.77 (tt, *J* = 8.4, 5.6 Hz, 1H), 0.58 – 0.39 (m, 2H), 0.08 – -0.09 (m, 2H); **^{13}C NMR (75 MHz, CD$_2$Cl$_2$)** δ = 167.5, 149.7, 145.6, 137.4, 130.0, 129.3, 129.0, 128.2, 128.0, 127.2, 126.5, 124.2, 122.0, 121.8, 121.7, 119.4, 111.6, 52.3, 46.9, 43.4, 32.0, 18.8, 2.0, 1.8; **HRMS** *m/z* (ESI): calcd. for [C$_{28}$H$_{27}$NO$_2$Na]$^+$ 432.1934; found 432.1936; **ATR-IR *v* (cm^{-1})** 3410, 3055, 3001, 2924, 2855, 1721, 1705, 1613, 1458, 1435, 1281, 1180, 1111, 1018, 764, 741, 702.

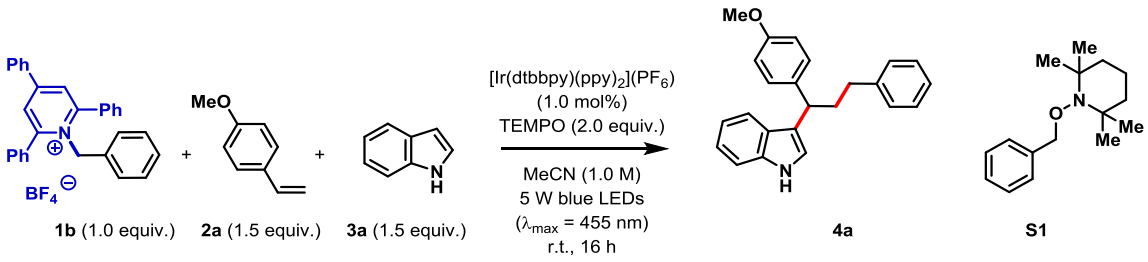
Methyl 4-(2-(3,4-dihydronaphthalen-1-yl)ethyl)benzoate (5b)



Fraction 2 (**5b**): Colourless oil, 4.6 mg (0.02 mmol, 5% yield), containing trace amounts of an unknown impurity ***R*$_f$ (*n*-pentane/ethyl acetate 10:1):** 0.4; **^{1}H NMR (500 MHz, CD$_2$Cl$_2$)** δ = 7.96 – 7.90 (m, 2H), 7.30 (d, *J* = 7.9 Hz, 1H), 7.29 – 7.24 (m, 2H), 7.24 – 7.19 (m, 1H), 7.18 – 7.13 (m, 1H), 7.17 – 7.12 (m, 1H), 5.81 (tt, *J* = 4.5, 1.1 Hz, 1H), 3.88 (s, 3H), 2.90 (dd, *J* = 9.3, 6.4 Hz, 2H), 2.79 – 2.72 (m, 2H), 2.74 – 2.67 (m, 2H), 2.24 – 2.16 (m, 2H); **^{13}C NMR (126 MHz, CD$_2$Cl$_2$)** δ = 167.5, 148.4, 137.6, 136.0, 135.1, 130.0, 129.2, 128.5, 128.2, 127.2, 126.9, 126.3, 123.0, 52.4, 35.4, 34.9, 28.9, 23.7; **HRMS** *m/z* (ESI): calcd. for [C$_{20}$H$_{20}$O$_2$Na]$^+$ 315.1356;

found 315.1375; **ATR-IR *v* (cm^{-1})** 3055, 3024, 2932, 2832, 1721, 1613, 1435, 1281, 1180, 1103, 1018, 764, 702.

5.3 TEMPO trapping experiment



An oven-dried screw cap Schlenk reaction tube was charged with 1-benzyl-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (0.30 mmol, 145.6 mg), 1*H*-indole (0.45 mmol, 52.7 mg), [Ir(dtbbpy)(ppy)$_2$](PF$_6$) (1.0 mol%, 2.7 mg) and (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO, 0.60 mmol, 93.8 mg). The tube was evacuated and backfilled with argon. Acetonitrile (0.3 mL, 1.0 M) was added in a stream of argon. 4-Methoxystyrene (0.45 mmol, 61 µL) was added in a stream of argon. The reaction mixture was degassed by three consecutive freeze-pump-thaw cycles. The solution was stirred under irradiation (λ_{max} = 455 nm, 5 W) for 16 h in an atmosphere of argon. An aliquot of the solution was submitted to ESI-HR mass spectrometry. The solvent was removed under reduced pressure and the crude reaction mixture investigated by ^{1}H NMR spectroscopy using dibromomethane (0.30 mmol, 21.0 µL) as an internal standard.

The crude NMR spectrum showed the presence of all starting materials:

Compound	Amount [mmol]
1b	0.095-0.100
2a	0.065-0.070
3a	0.140-0.150

A part of compound **2a** was presumably lost during the removal of the solvent under reduced pressure due to its volatility.

The formation of the desired product **4a** was not observed, presumably the desired reaction did not take place. The formation of radical adduct **S4** was not observed in the HR-MS trace of the crude reaction mixture.

5.4 Side-product analysis

The reaction to form product **4j** under the standard reaction conditions led to the isolation of a mixture of products. From HR-ESI MS it was observed that the ternary mixture contained masses putatively corresponding to isomeric Heck products and a product with two equivalents of styrene incorporated (Figure S4). The amount of the compounds was then determined from the ^{1}H NMR spectrum of the isolated mixture (Figure S5). Heck product presumably stems from elimination of a proton after radical-polar crossover. The presence of the dimeric product

hints towards occurrence of radical polymerization as side reaction. It is probable, that also higher oligomers and polymers are present in the reaction mixture.

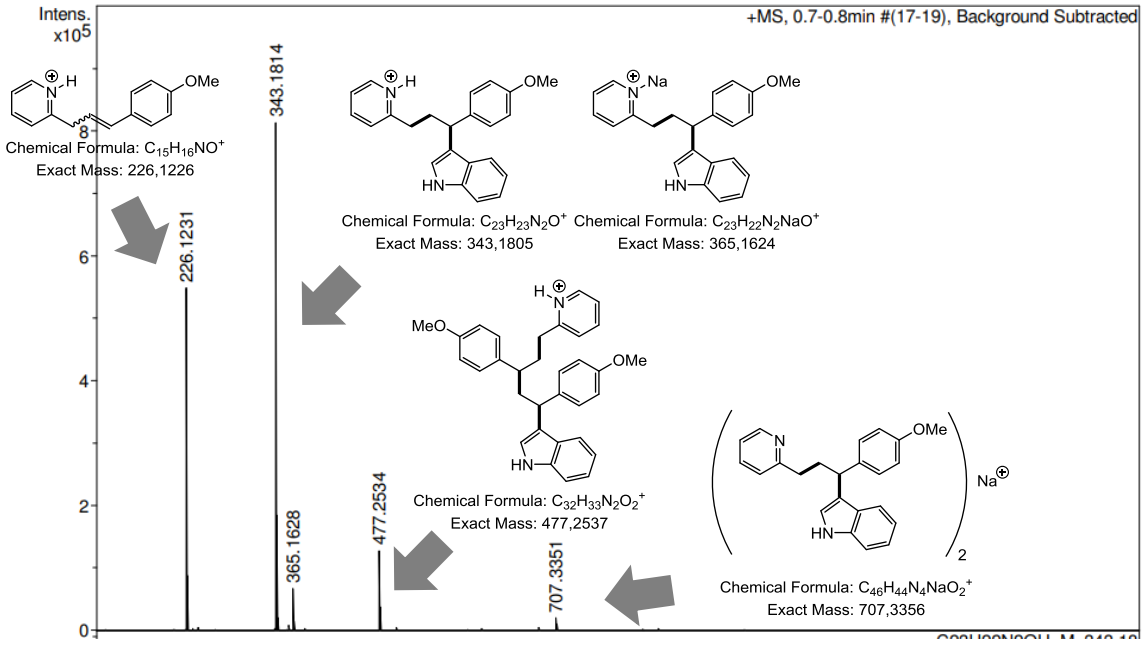


Figure S4. HR-ESI MS spectrum of the isolated ternary mixture of the reaction to form **4j**.

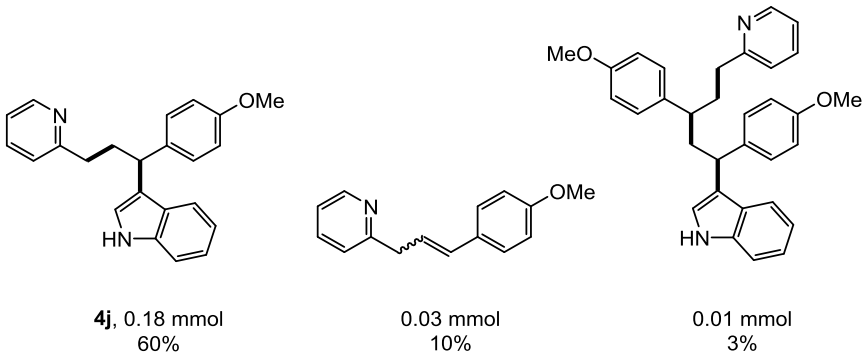


Figure S5. Components of the isolated mixture under standard scope conditions.

In the reaction towards formation of dicarbofunctionalization product **4p** a GC-MS analysis of the crude reaction mixture provided evidence for the presence of further side-products (Figure S6). Besides starting materials and fragmentation product 2,4,6-triphenylpyridine, the presence of side-products has been observed as suggested by the mass spectra corresponding to the chromatographic peaks. Benzyl dimer, presumably arising from radical recombination of two benzyl radicals, was observed. A peak tentatively suggesting the presence of isomeric Heck-type products was observed, supporting their presence in the reaction mixture. Also hints for direct benzylation of indole were found. Hydroarylation side-product arising presumably from an ionic reaction between styrene and indole was seen additionally. Even though the formation of this product does not involve consumption of the limiting reagent, a decrease in styrene and indole concentration can be inferred to lower the selectivity for radical addition of benzylic radicals involved.

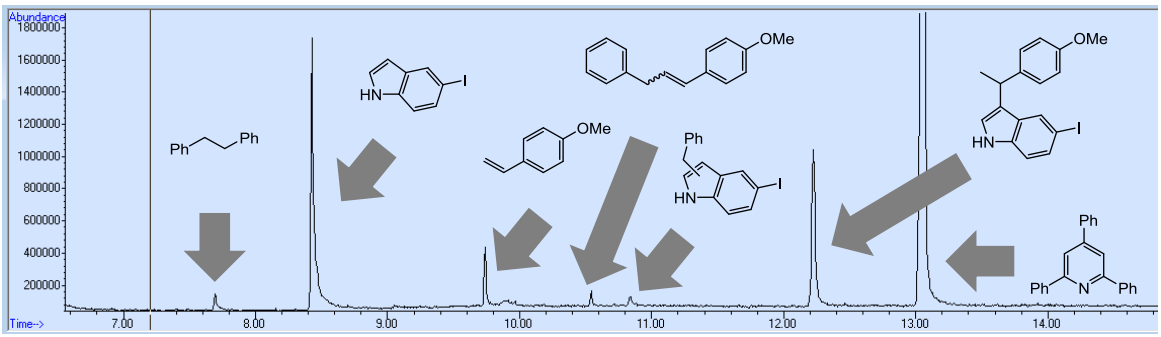


Figure S6. Analysis of side products in the formation of **4p** by GC-MS.

6. Literature

(1) Greulich, T. W.; Daniliuc, C. G.; Studer, A. *N*-Aminopyridinium Salts as Precursors for N-Centered Radicals – Direct Amidation of Arenes and Heteroarenes. *Org. Lett.* **2015**, *17*, 254–257.

(2) a) Sprouse, S.; King, K. A.; Spellane, P. J.; Watts, R. J. Photophysical effects of metal-carbon .sigma. bonds in ortho-metalated complexes of iridium(III) and rhodium(III). *J. Am. Chem. Soc.* **1984**, *106*, 6647–6653; b) Slinker, J. D.; Gorodetsky, A. A.; Lowry, M. S.; Wang, J.; Parker, S.; Rohl, R.; Bernhard, S.; Malliaras, G. G. Efficient Yellow Electroluminescence from a Single Layer of a Cyclometalated Iridium Complex. *J. Am. Chem. Soc.* **2004**, *126*, 2763–2767.

(3) Tamayo, A. B.; Alleyne, B. D.; Djurovich, P. I.; Lamansky, S.; Tsyba, I.; Ho, N. N.; Bau, R.; Thompson, M. E. Synthesis and Characterization of Facial and Meridional Tris-cyclometalated Iridium(III) Complexes. *J. Am. Chem. Soc.* **2003**, *125*, 7377–7387.

(4) Hanss, D.; Freys, J. C.; Bernardinelli, G.; Wenger, O. S. Cyclometalated Iridium(III) Complexes as Photosensitizers for Long-Range Electron Transfer: Occurrence of a Coulomb Barrier. *Eur. J. Inorg. Chem.* **2009**, *32*, 4850–4859.

(5) Ischay, M. A.; Lu, Z.; Yoon, T. P. [2+2] Cycloadditions by Oxidative Visible Light Photocatalysis. *J. Am. Chem. Soc.* **2010**, *132*, 8572–8574.

(6) Klauck, F. J. R.; James, M. J.; Glorius, F. Deaminative Strategy for the Visible-Light-Mediated Generation of Alkyl Radicals. *Angew. Chem. Int. Ed.* **2017**, *56*, 12336–12339.

(7) Awartani, R.; Sakizadeh, K.; Gabrielsen, B. The preparation and reactions of phenyl-substituted pyrylium and pyridinium salts: Nucleophilic substitution of an amino group by pyridine. *J. Chem. Educ.* **1986**, *63*, 172–176.

(8) Basch, C. H.; Liao, J.; Xu, J.; Piane, J. J.; Watson, M. P. Harnessing Alkyl Amines as Electrophiles for Nickel-Catalyzed Cross Couplings via C–N Bond Activation. *J. Am. Chem. Soc.* **2017**, *139*, 5313–5316.

(9) Seo, H.; Liu, A.; Jamison, T. F. Direct β-Selective Hydrocarboxylation of Styrenes with CO_2 Enabled by Continuous Flow Photoredox Catalysis. *J. Am. Chem. Soc.* **2017**, *139*, 13969–13972.

(10) Faler, C. A.; Joullié, M. M. The Kulinkovich Reaction in the Synthesis of Constrained *N,N*-Dialkyl Neurotransmitter Analogues. *Org. Lett.* **2007**, *9*, 1987–1990.

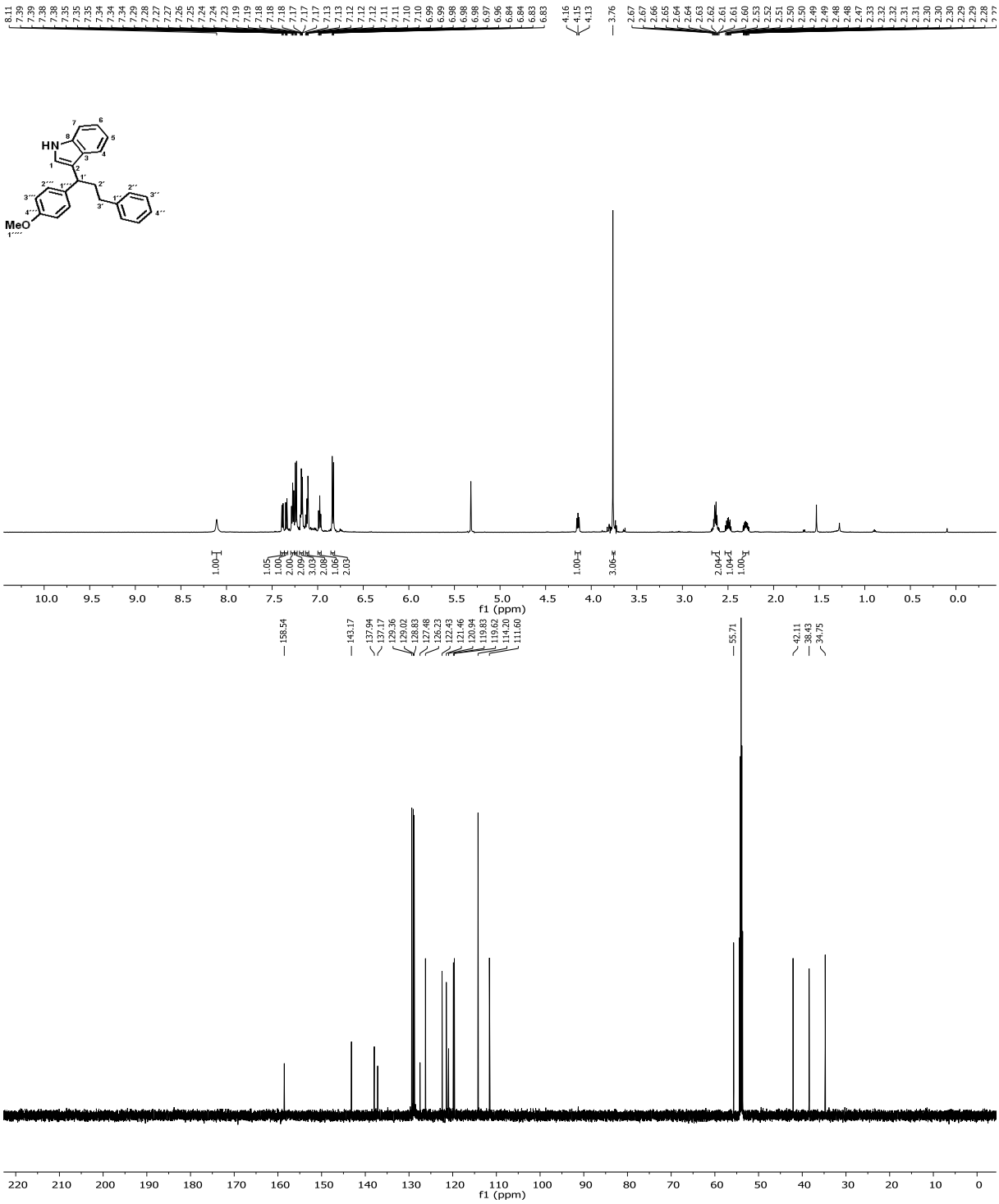
(11) Adam, W.; Bosio, S. G.; Turro, N. J.; Wolff, B. T. Enecarbamates as Selective Substrates in Oxidations: Chiral-Auxiliary-Controlled Mode Selectivity and Diastereoselectivity in the [2+2] Cycloaddition and Ene Reaction of Singlet Oxygen and in the Epoxidation by DMD and *m*CPBA. *J. Org. Chem.* **2004**, *69*, 1704–1715.

(12) López-Cobeñas, A.; Cledera, P.; Sánchez, J. D.; López-Alvarado, P.; Ramos, M. T.; Avendaño, C.; Menéndez, J. C. Microwave-Assisted Synthesis of 2,5-Piperazinediones under Solvent-Free Conditions. *Synthesis* **2005**, *19*, 3412–3422.

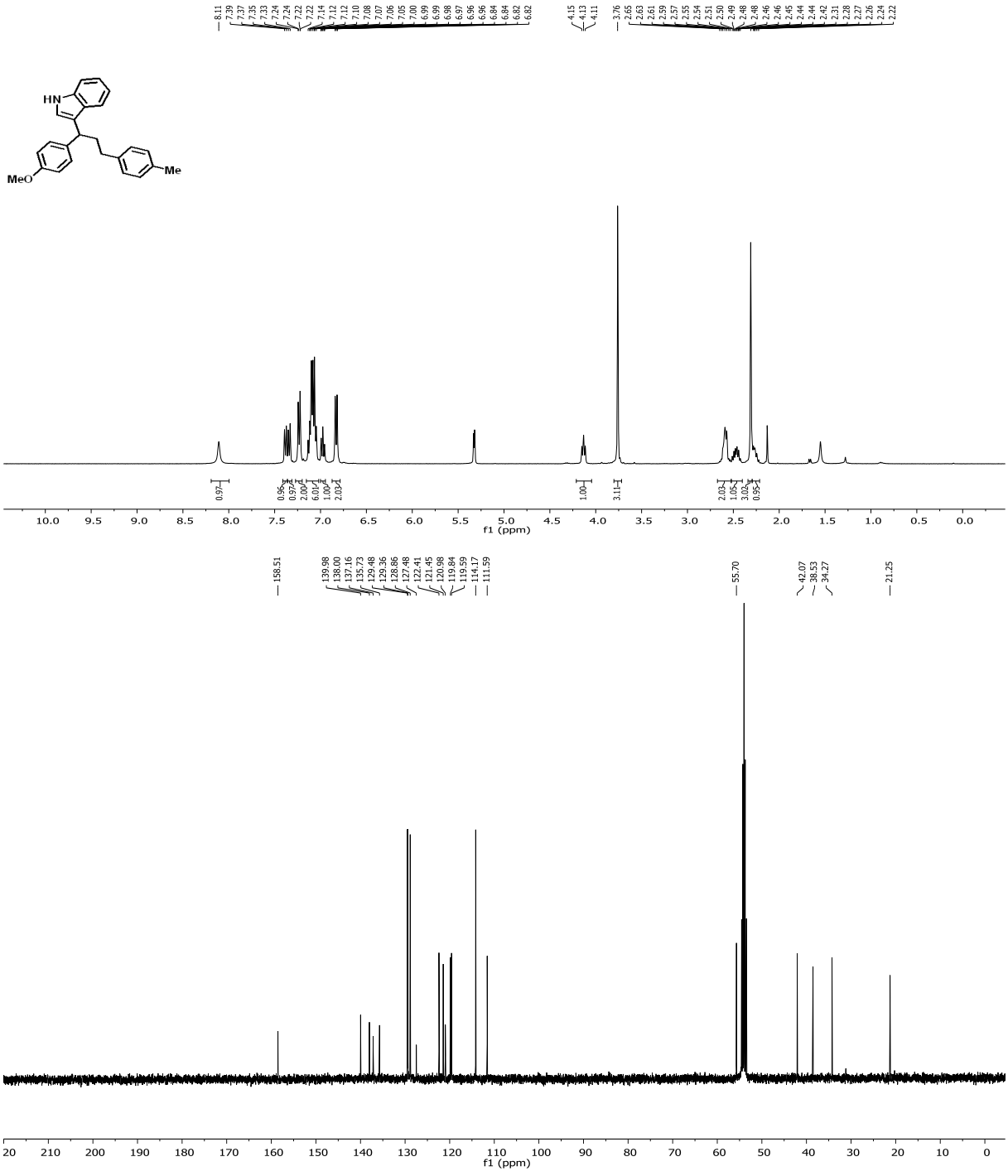
(13) Han, P.; Wang, R.; Wang, D. Z. Electronic polarizability-based stereochemical model for Sharpless AD reactions. *Tetrahedron* **2011**, *67*, 8873–8878.

7. NMR spectra

3-(1-(4-Methoxyphenyl)-3-phenylpropyl)-1*H*-indole (4a)



3-(1-(4-Methoxyphenyl)-3-(p-tolyl)propyl)-1*H*-indole (4b)



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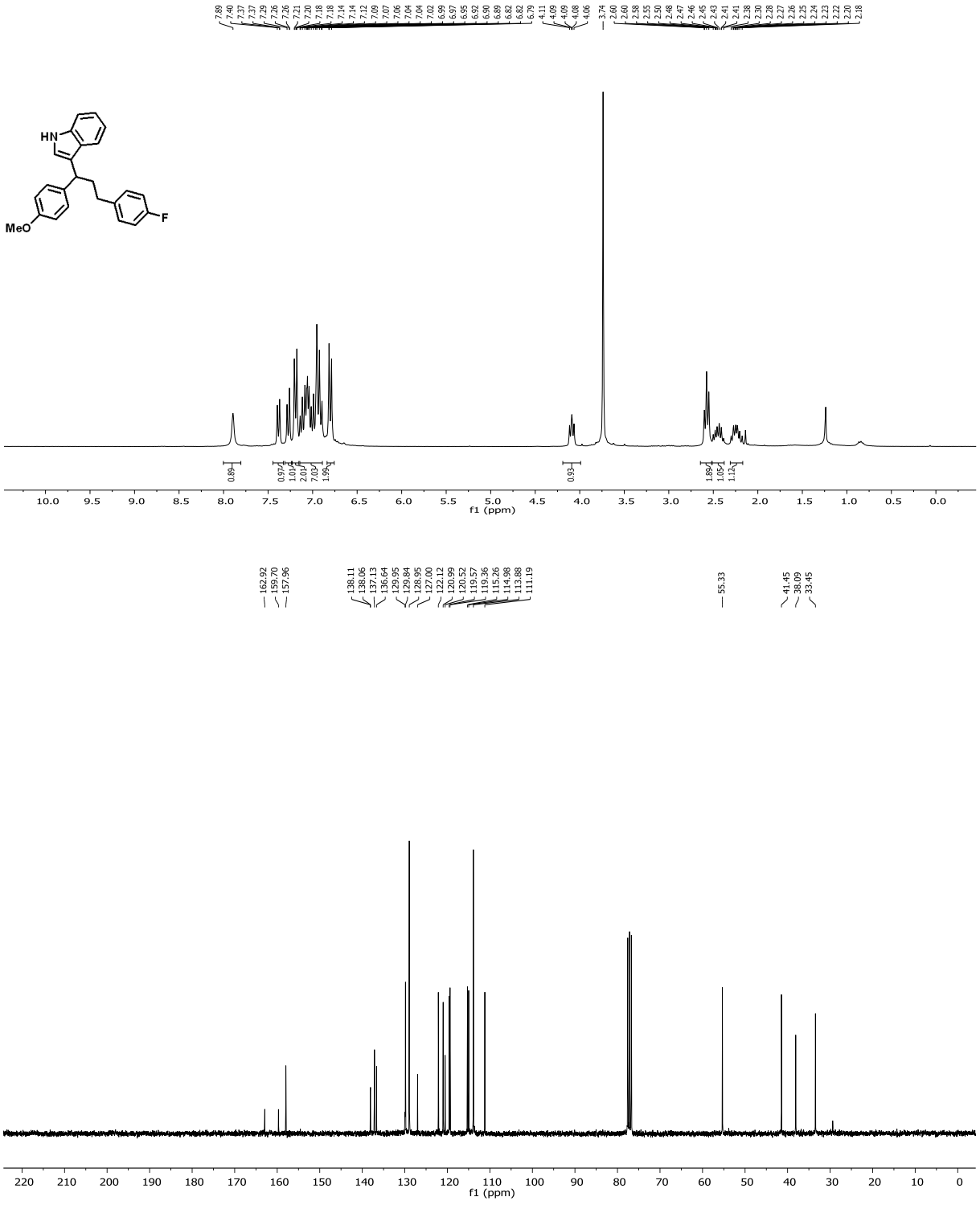
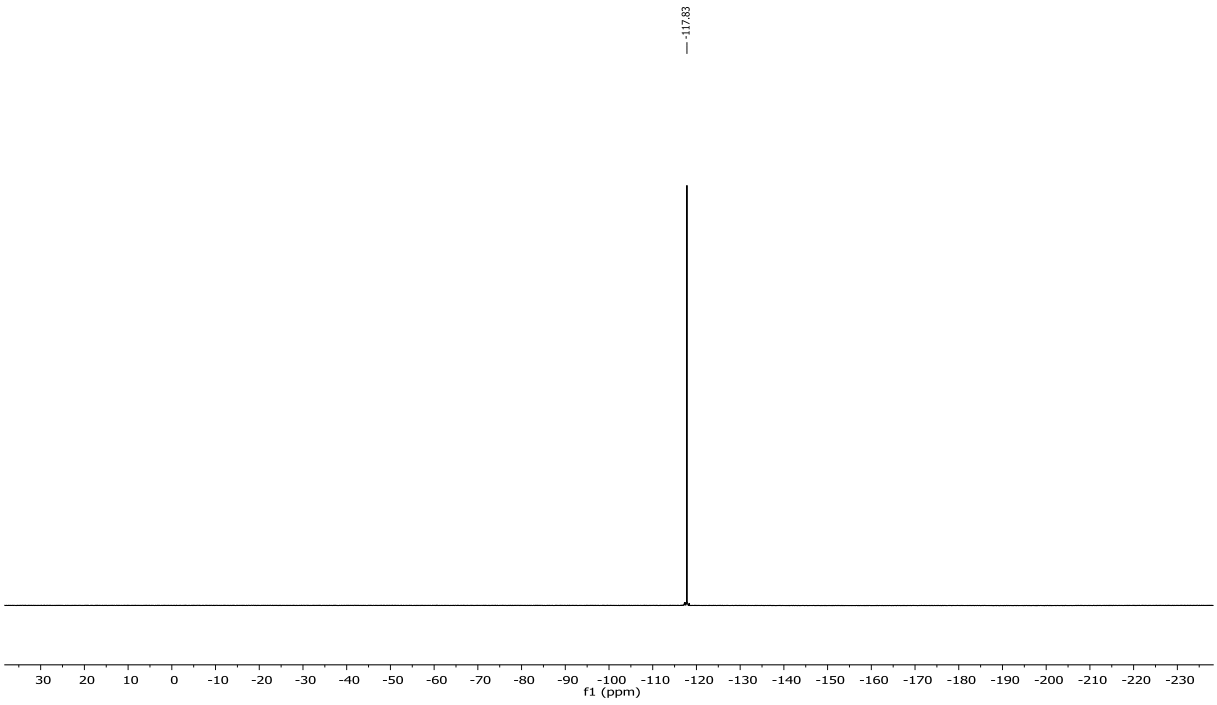
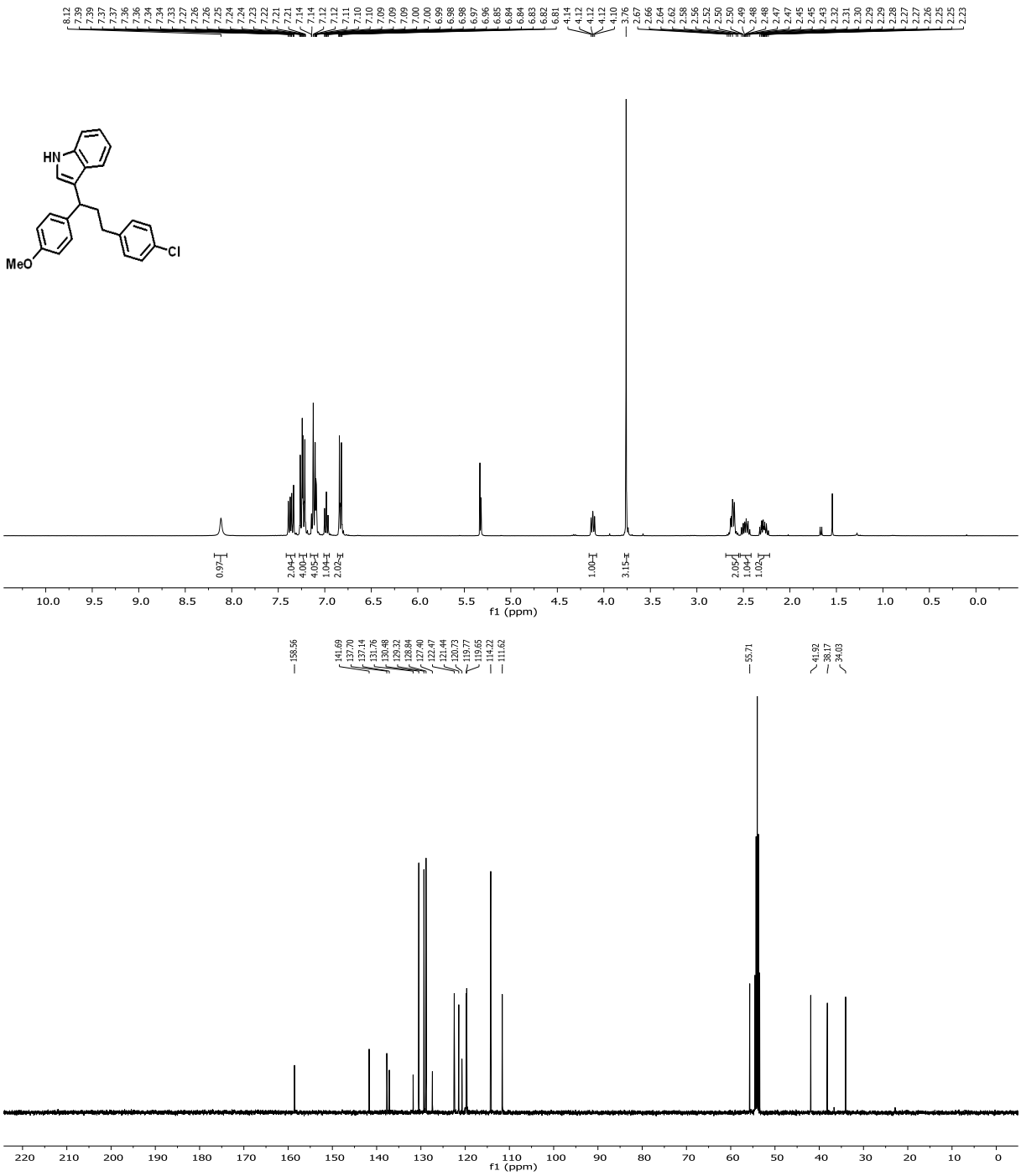
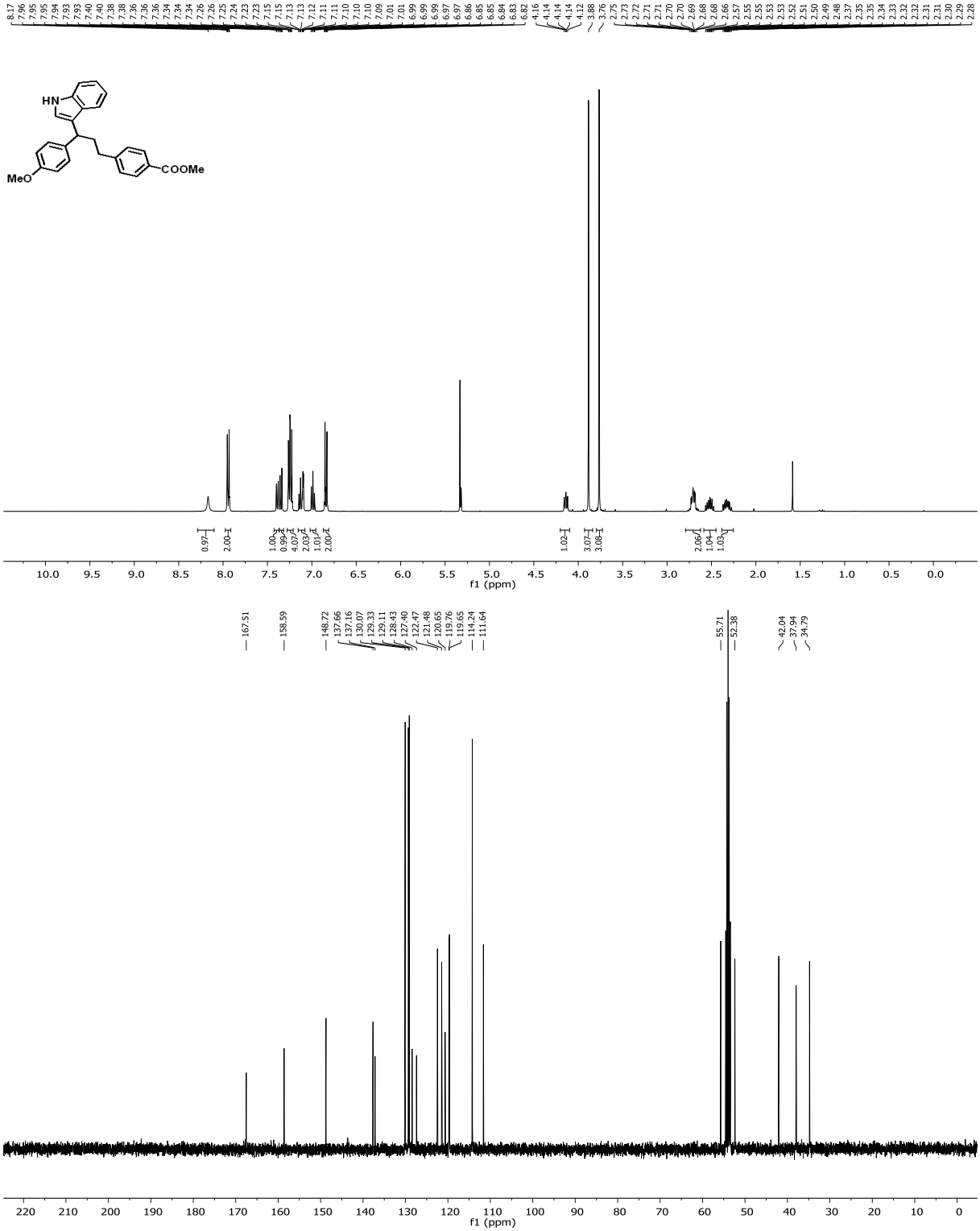



-117.83
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230
f1 (ppm)

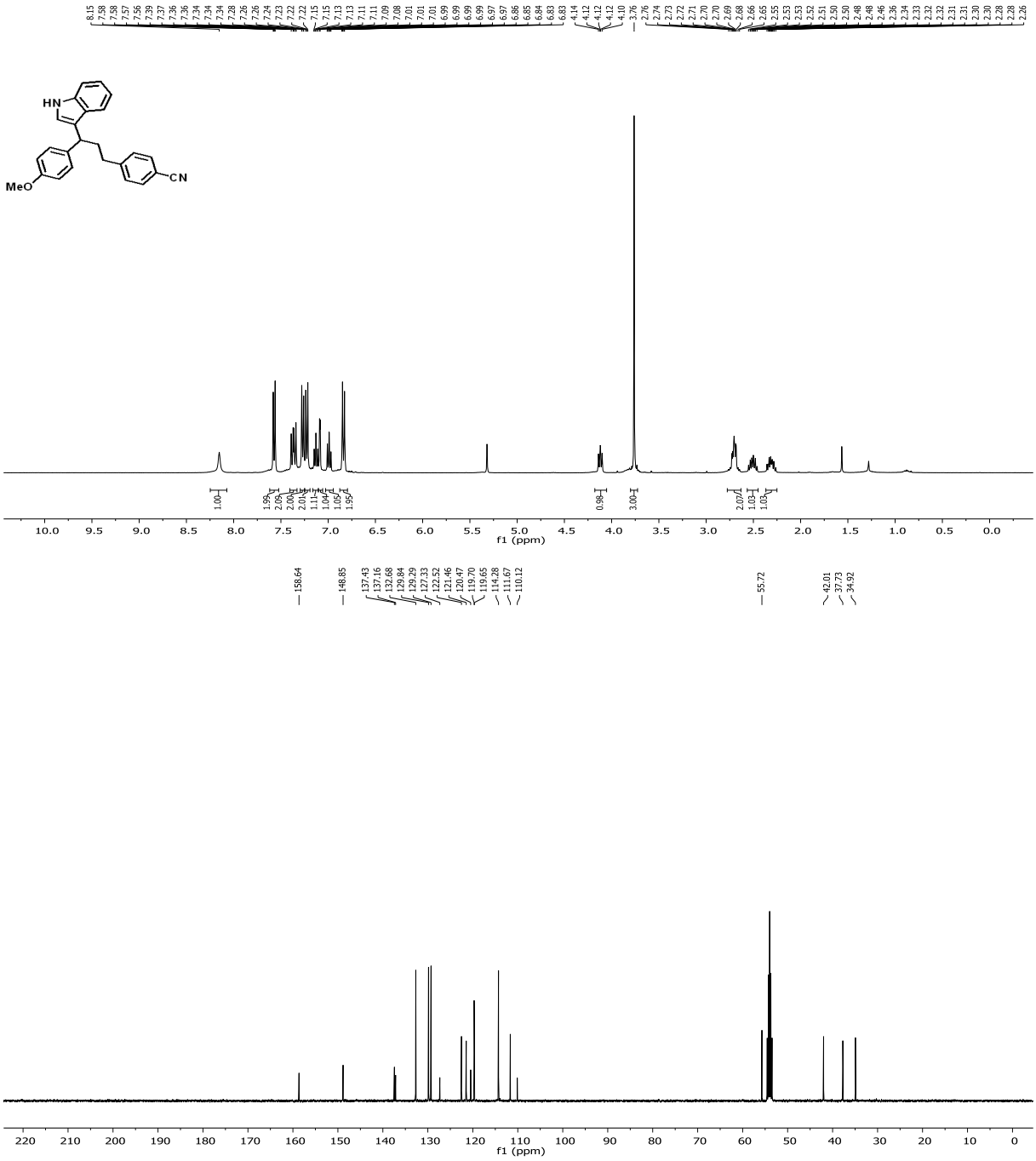
3-(3-(4-Chlorophenyl)-1-(4-methoxyphenyl)propyl)-1*H*-indole (4d)



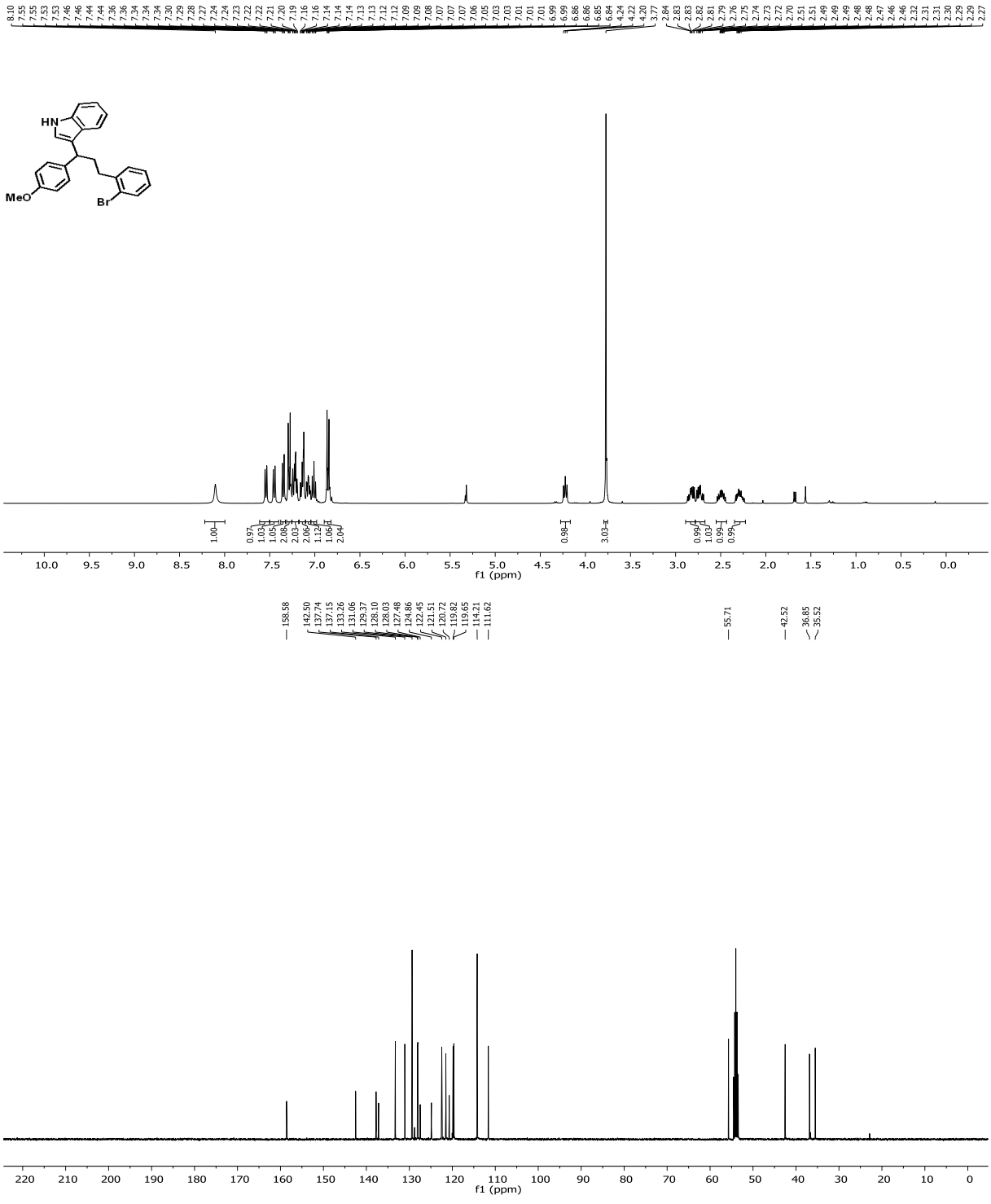
Methyl 4-(3-(1*H*-indol-3-yl)-3-(4-methoxyphenyl)propyl)benzoate (4e)



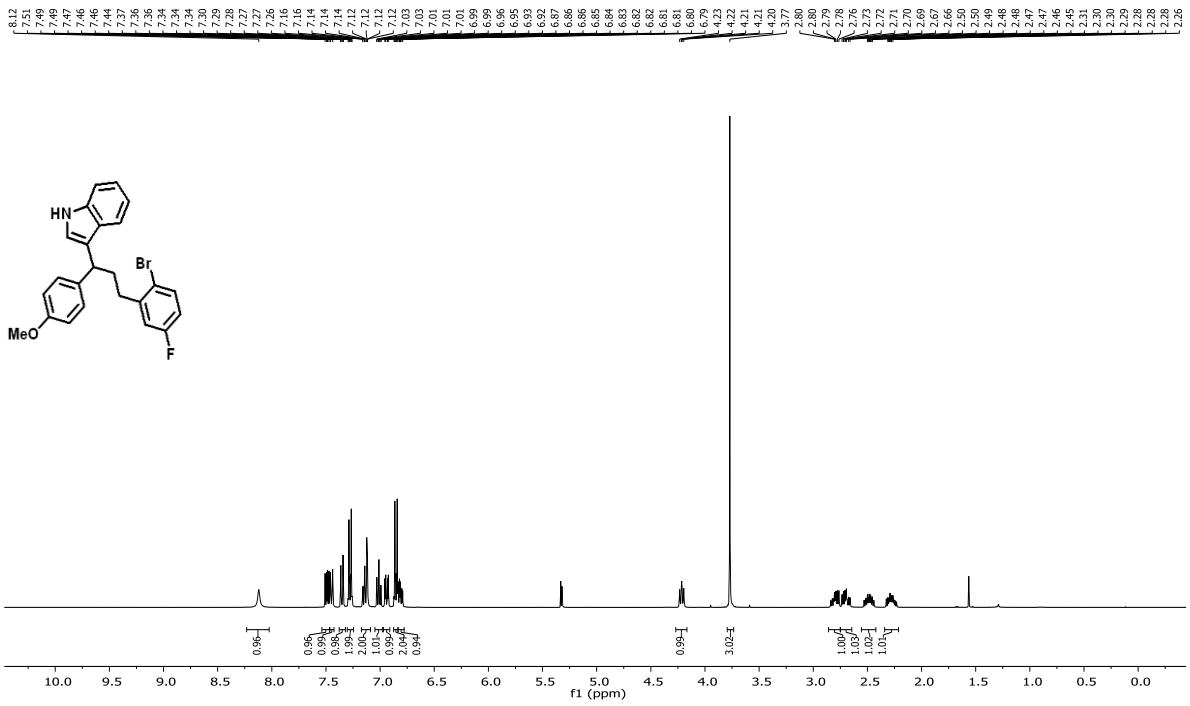
4-(3-(1*H*-indol-3-yl)-3-(4-methoxyphenyl)propyl)benzonitrile (4f)

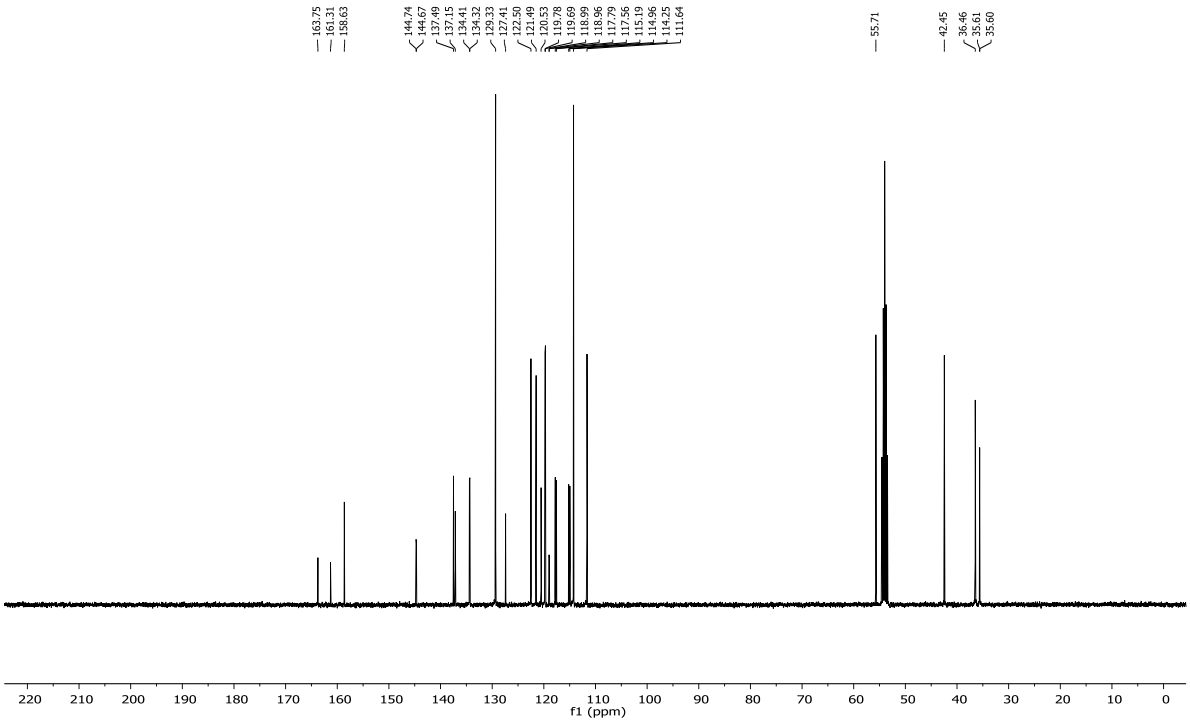


3-(3-(2-Bromophenyl)-1-(4-methoxyphenyl)propyl)-1*H*-indole (4g)



3-(3-(2-Bromo-5-fluorophenyl)-1-(4-methoxyphenyl)propyl)-1*H*-indole (4h)




163.75
161.31
158.63
144.74
144.67
137.49
137.15
134.41
134.32
129.33
127.41
122.50
121.49
120.53
119.78
119.69
119.09
118.96
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111.64
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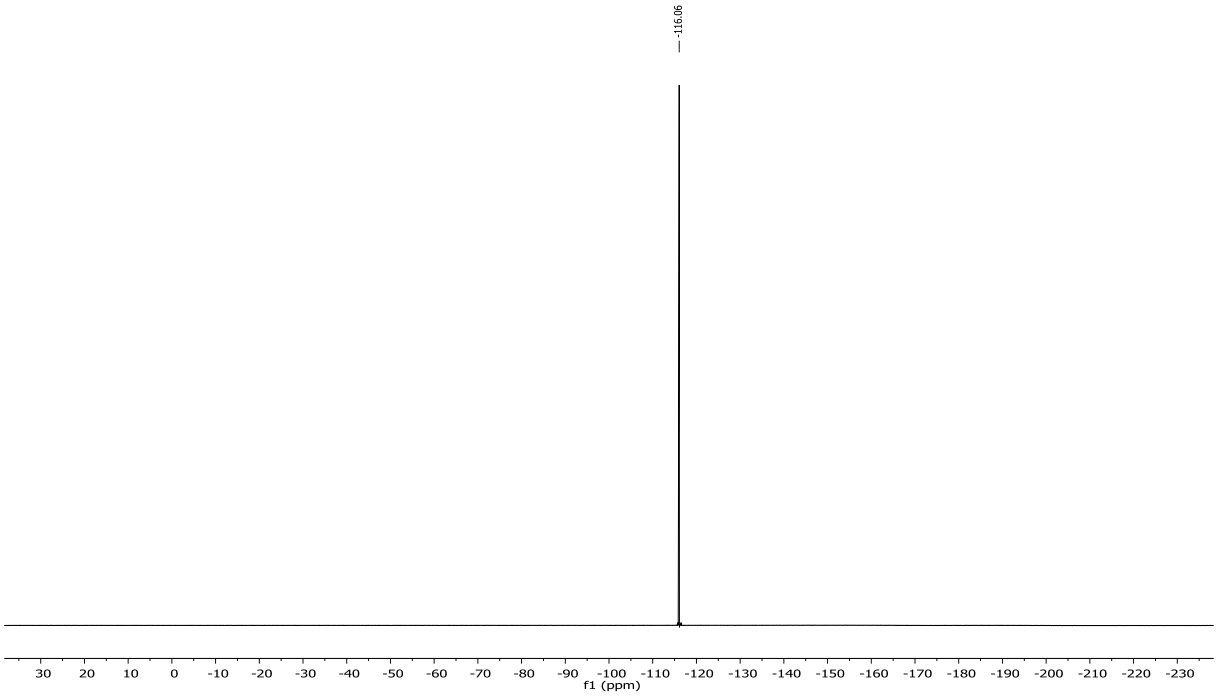
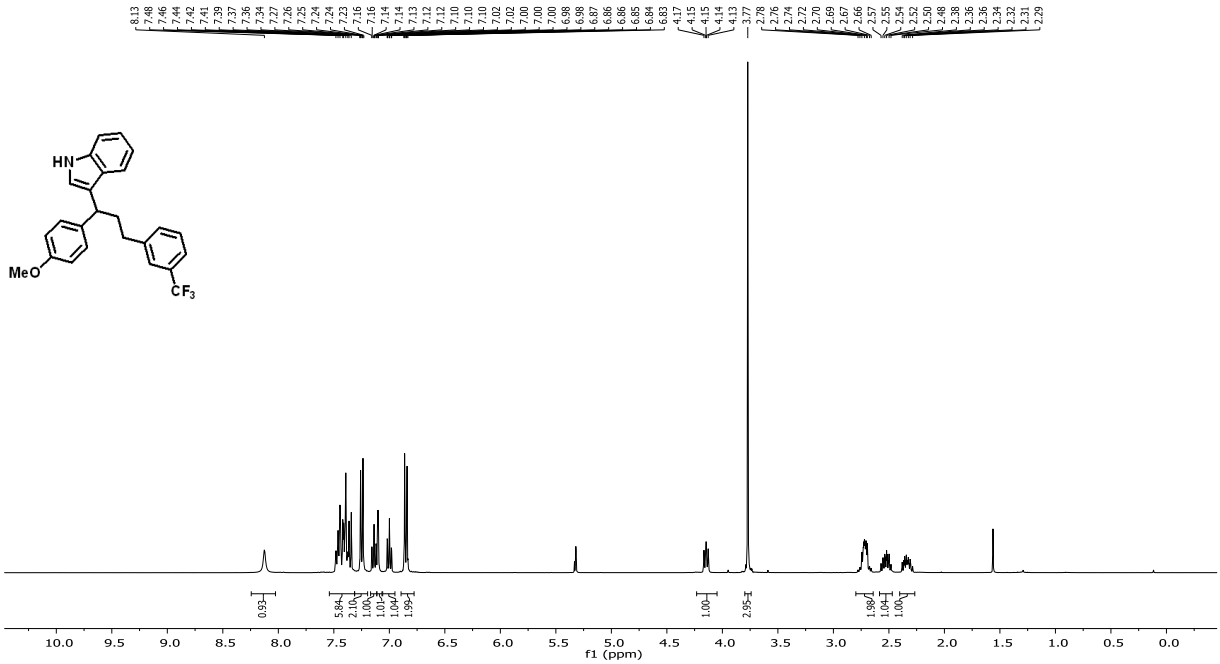
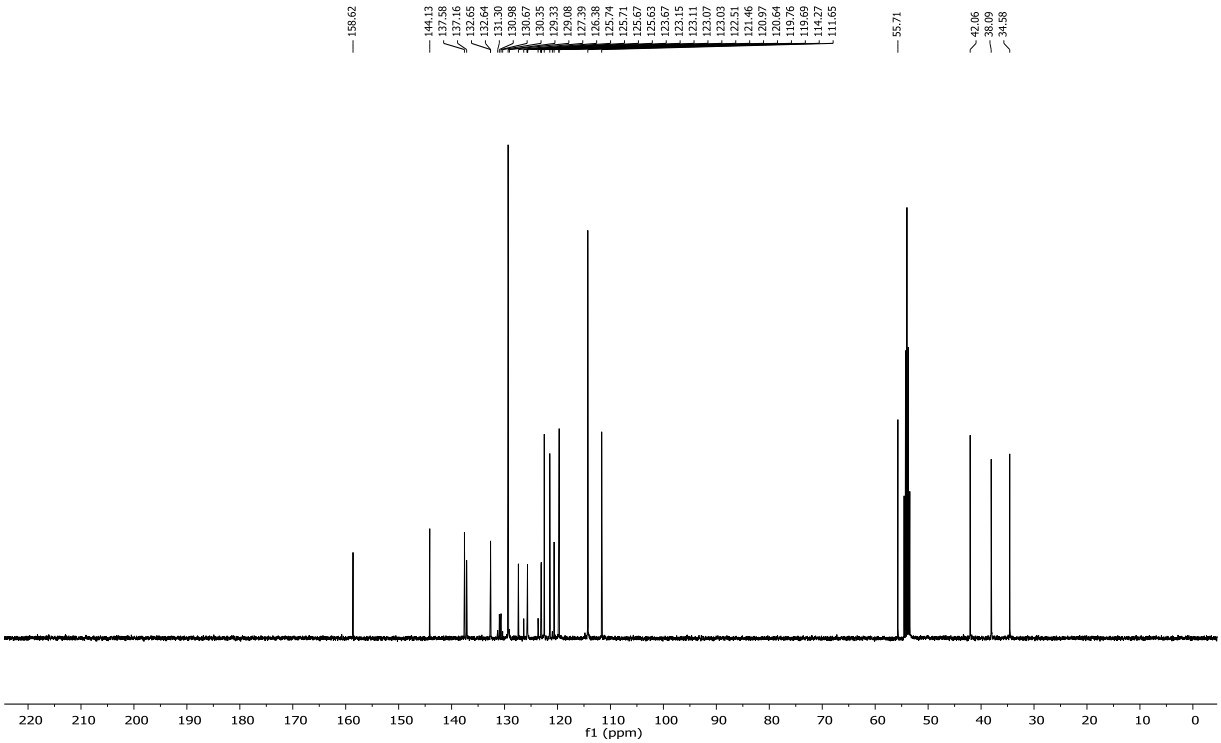
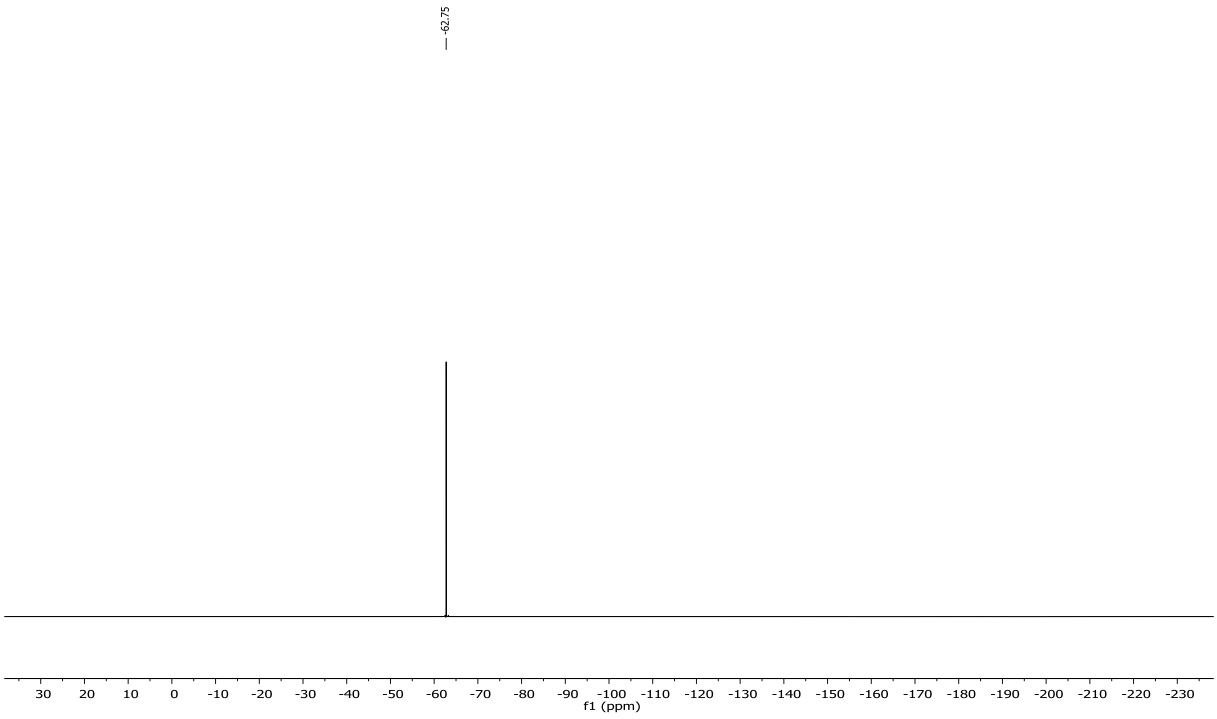
42.45
36.46
35.61
35.60
f1 (ppm)


-116.06
f1 (ppm)

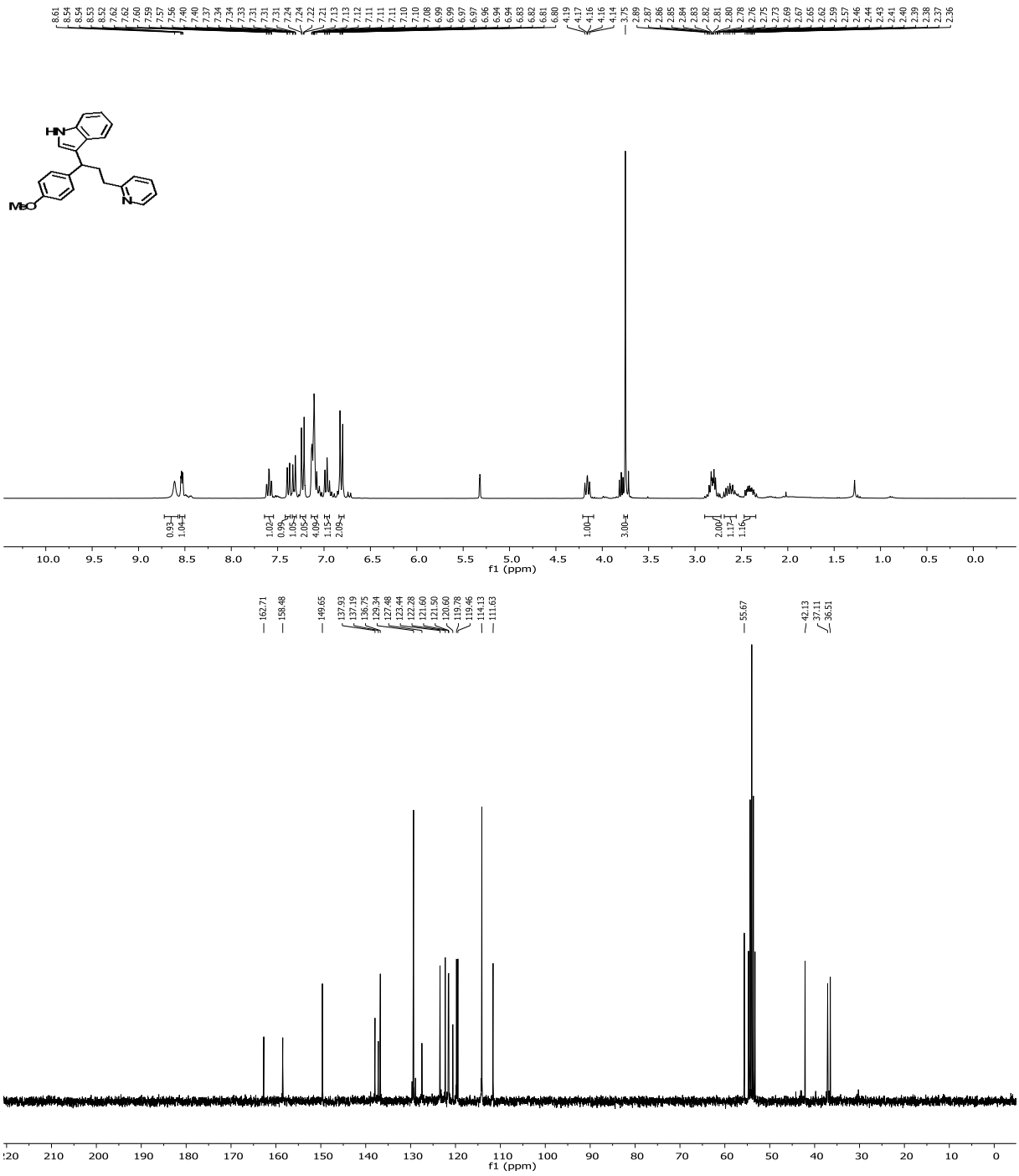
3-(1-(4-Methoxyphenyl)-3-(3-(trifluoromethyl)phenyl)propyl)-1*H*-indole (4i)



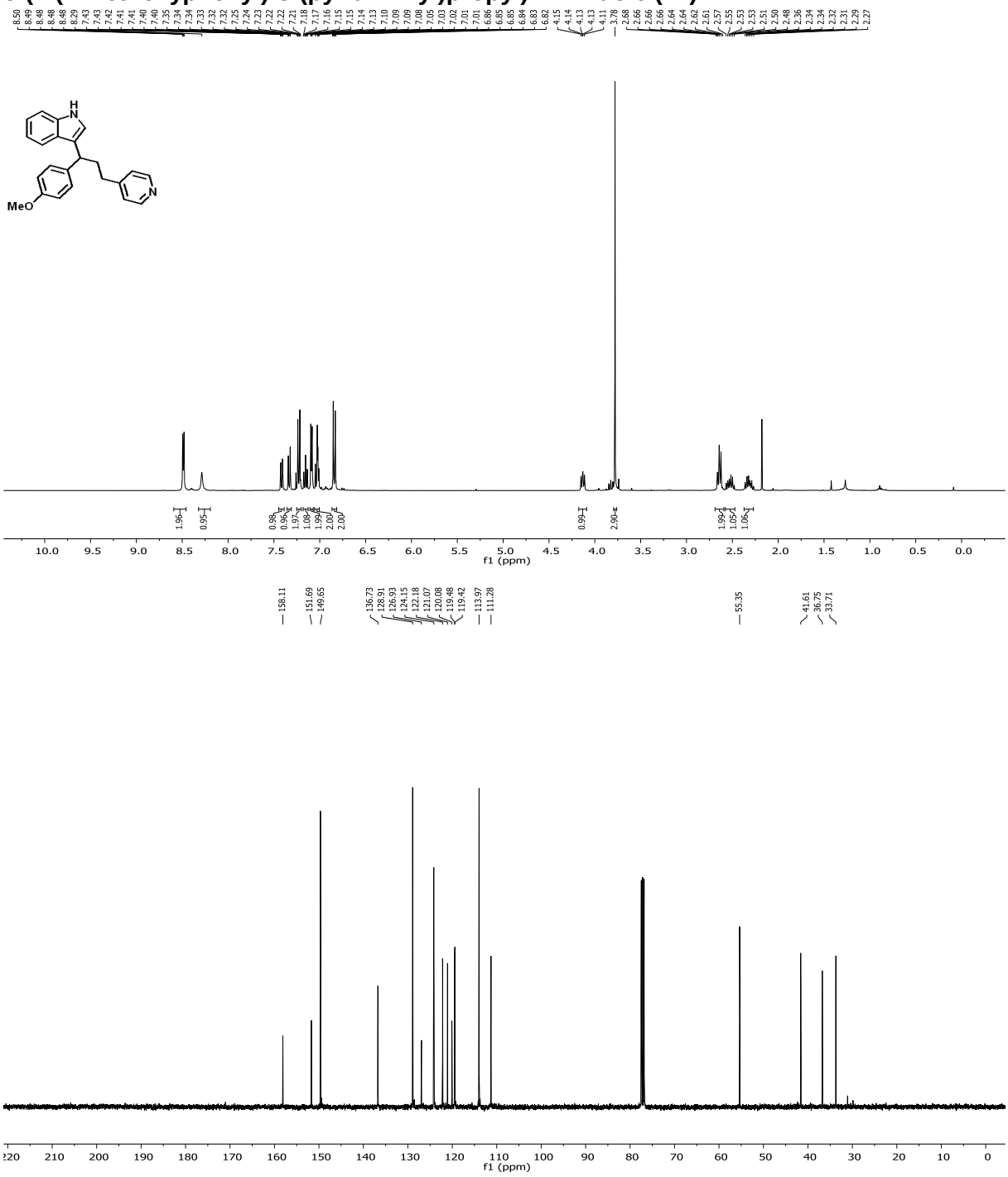



-62.75
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230
f1 (ppm)

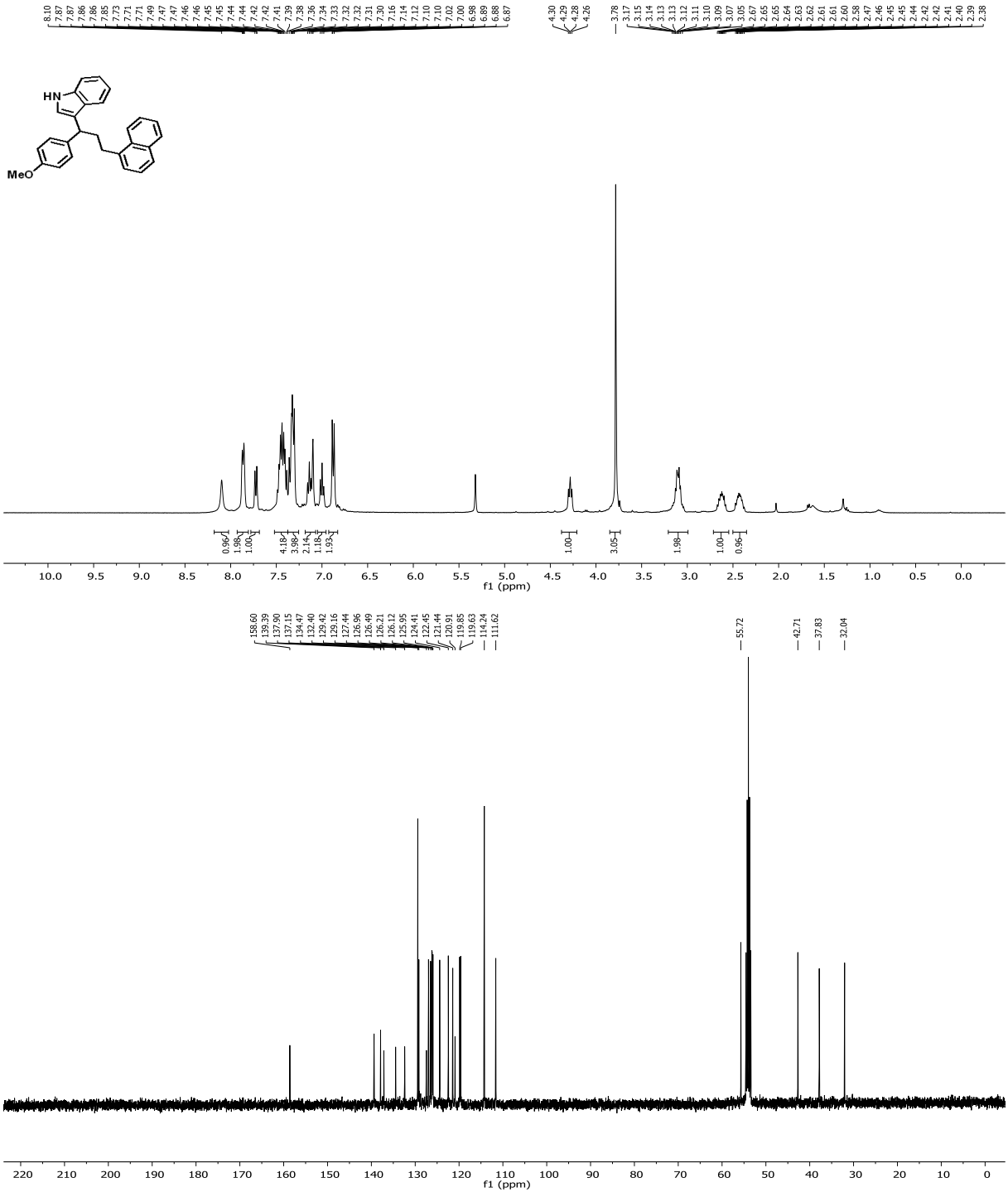
3-(1-(4-Methoxyphenyl)-3-(pyridin-2-yl)propyl)-1*H*-indole (4j)



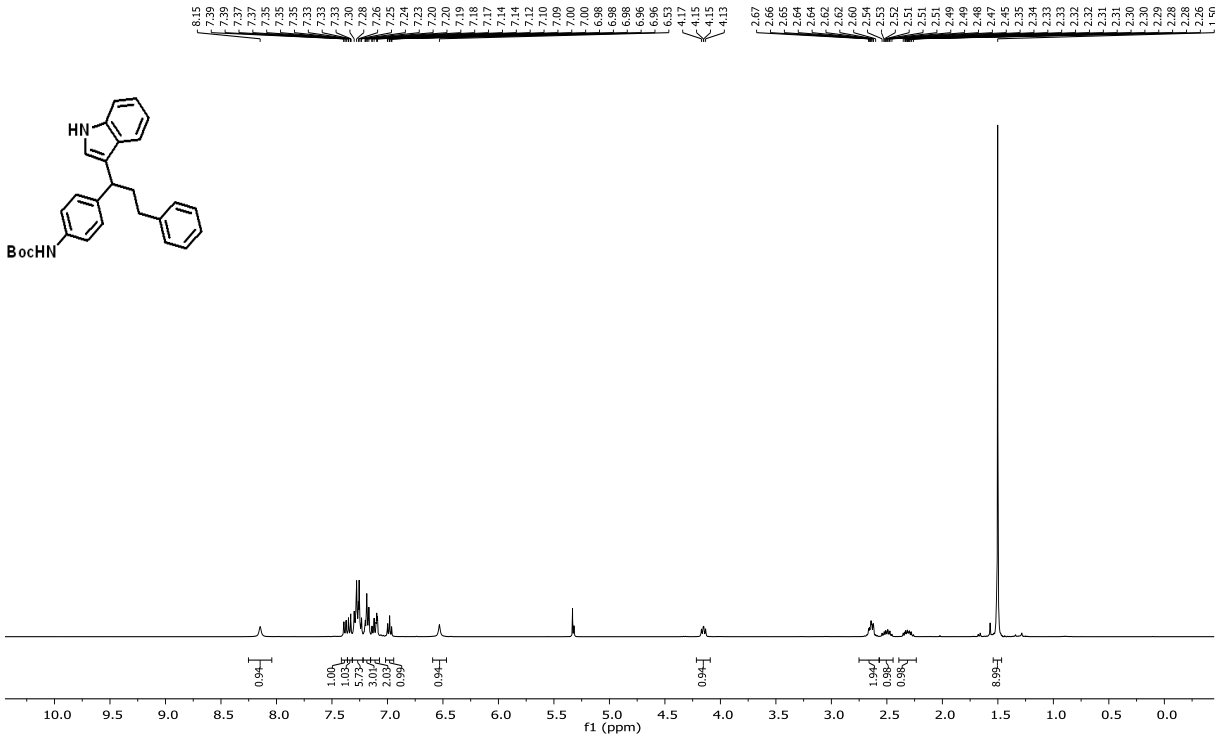
3-(1-(4-Methoxyphenyl)-3-(pyridin-4-yl)propyl)-1*H*-indole (4k)

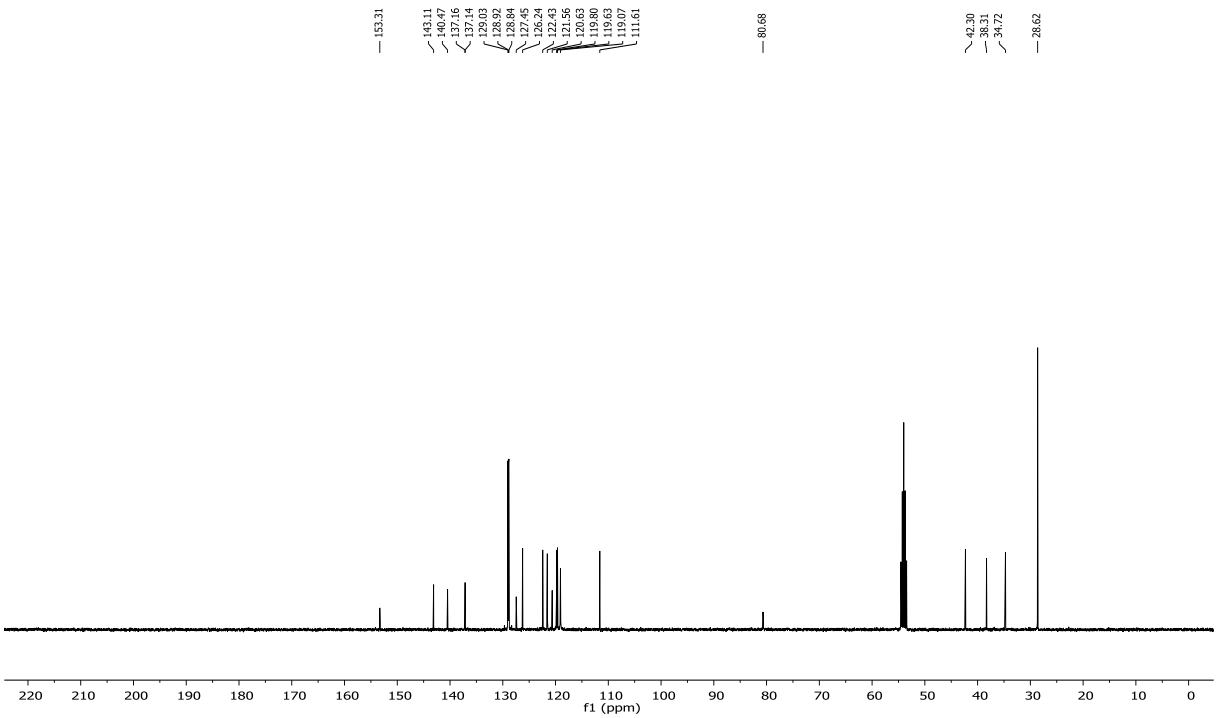


3-(1-(4-Methoxyphenyl)-3-(naphthalen-1-yl)propyl)-1*H*-indole (4l)

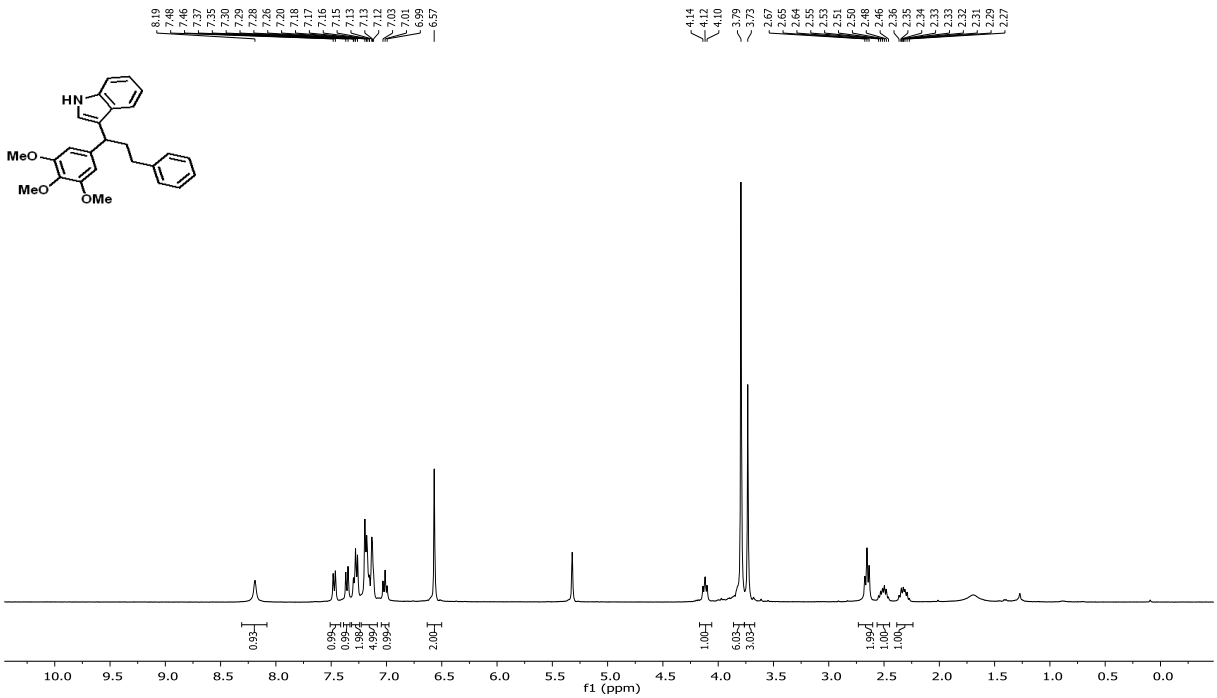


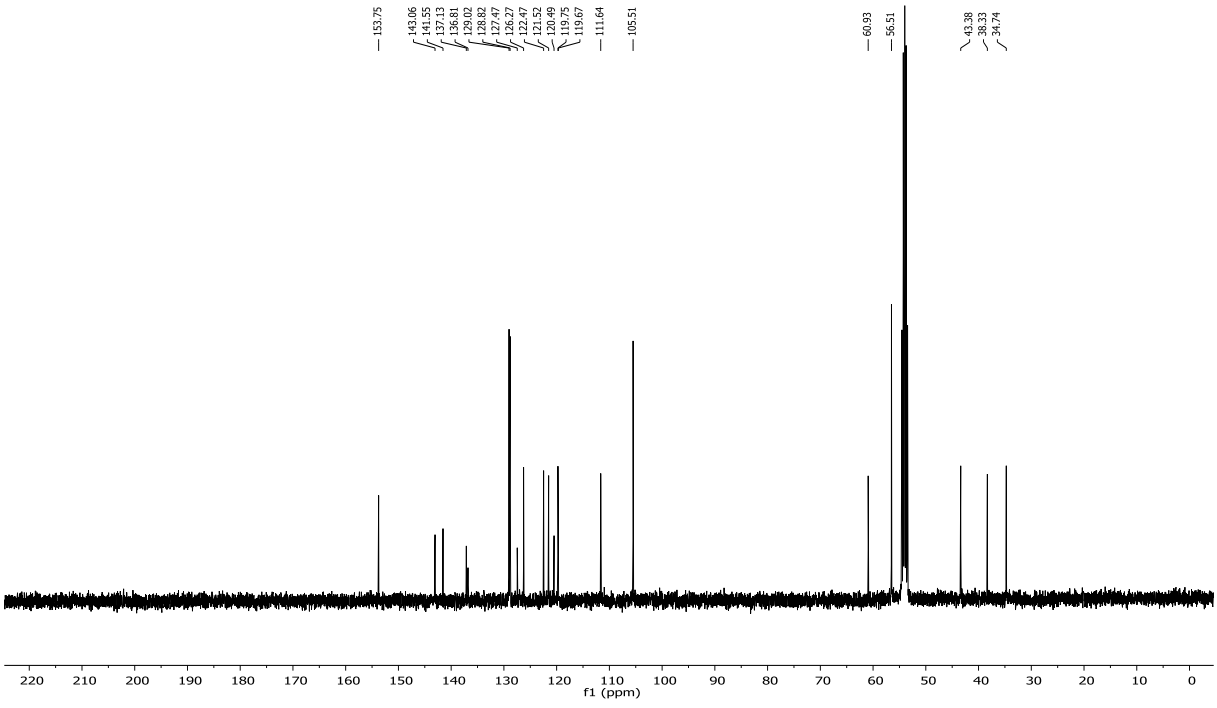
tert-Butyl (4-(1-(1*H*-indol-3-yl)-3-phenylpropyl)phenyl)carbamate (4m)



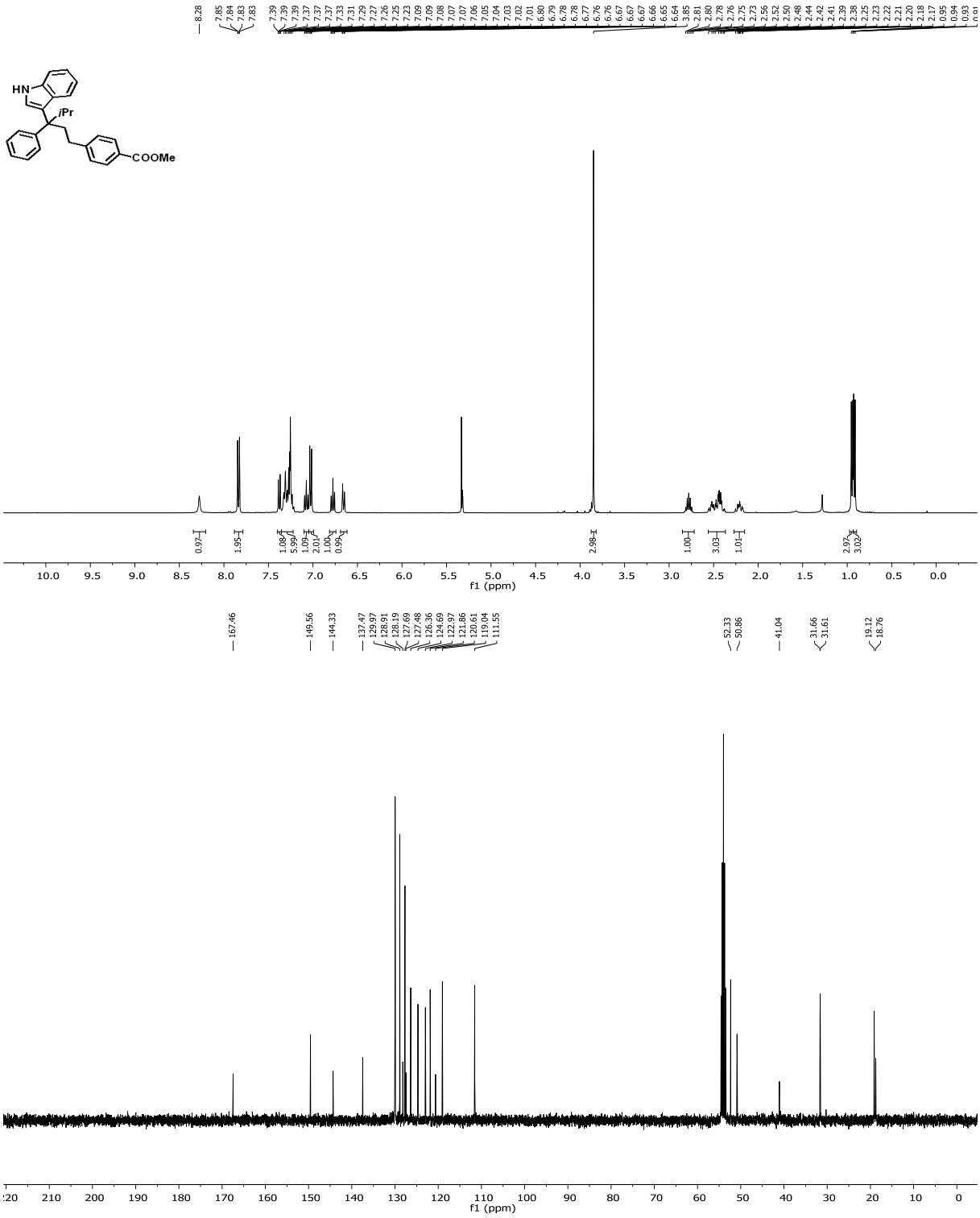


3-(3-Phenyl-1-(3,4,5-trimethoxyphenyl)propyl)-1*H*-indole (4n)

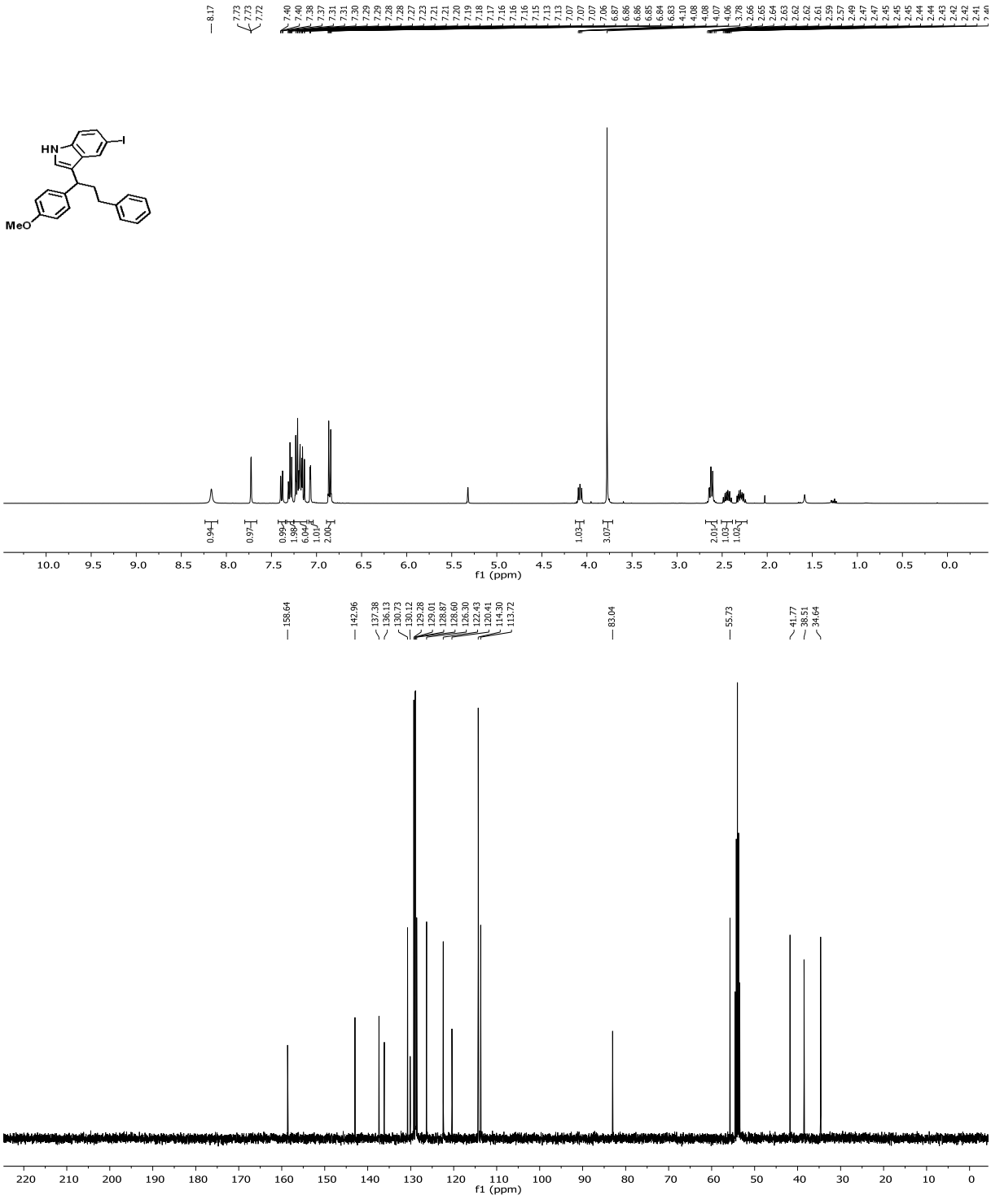




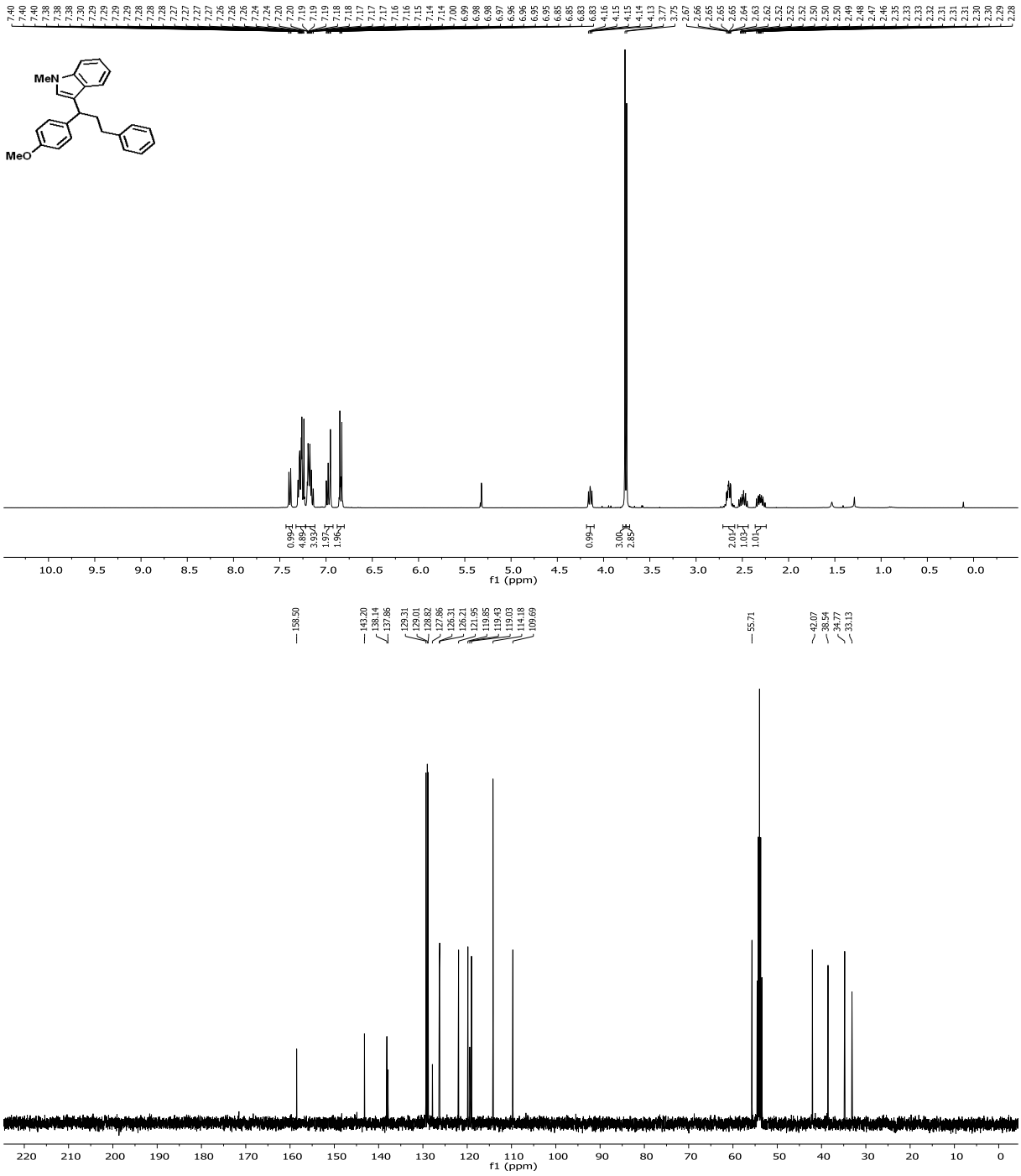
Methyl 4-(3-(1*H*-indol-3-yl)-4-methyl-3-phenylpentyl)benzoate (4o)



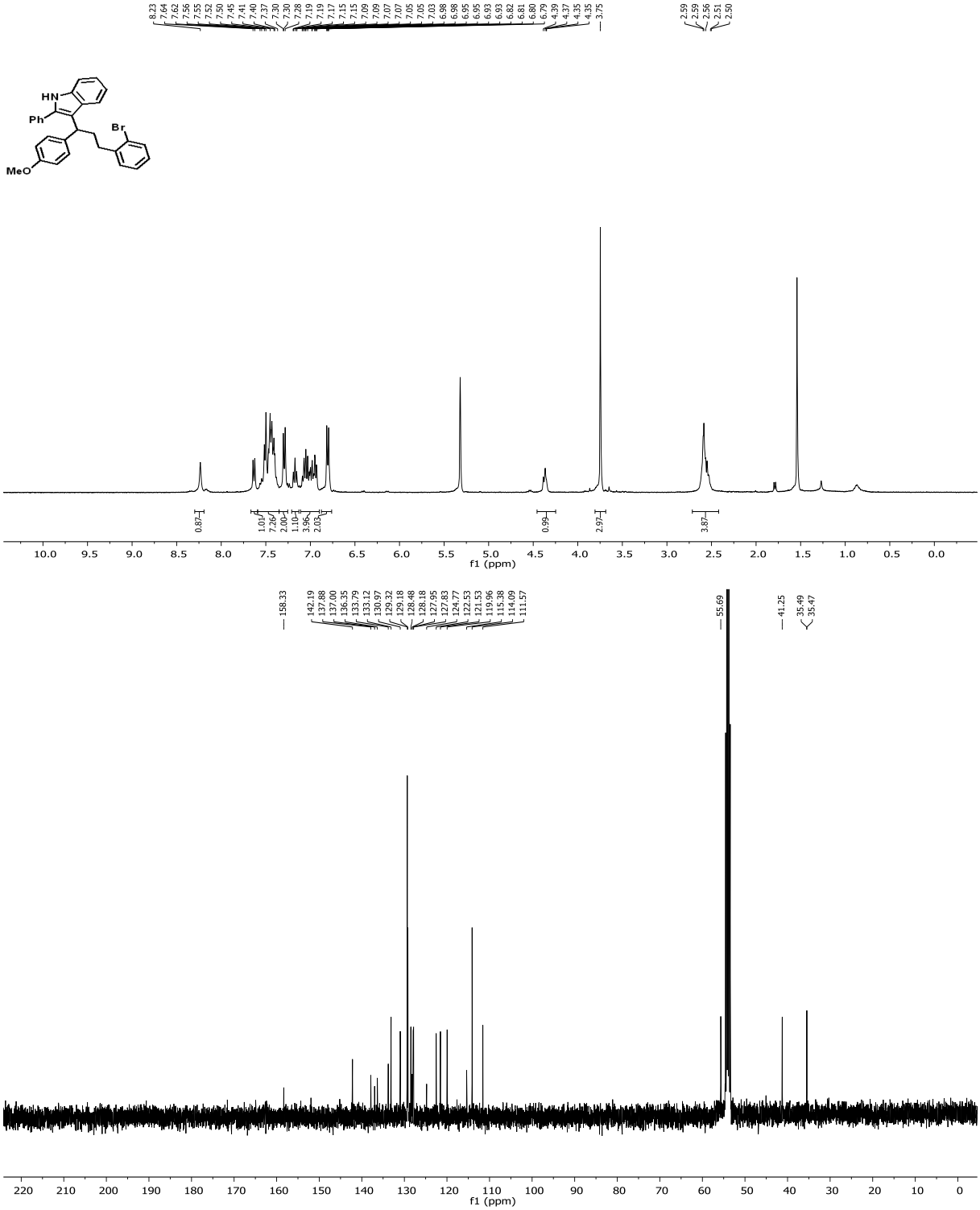
5-Iodo-3-(1-(4-methoxyphenyl)-3-phenylpropyl)-1*H*-indole (4p)



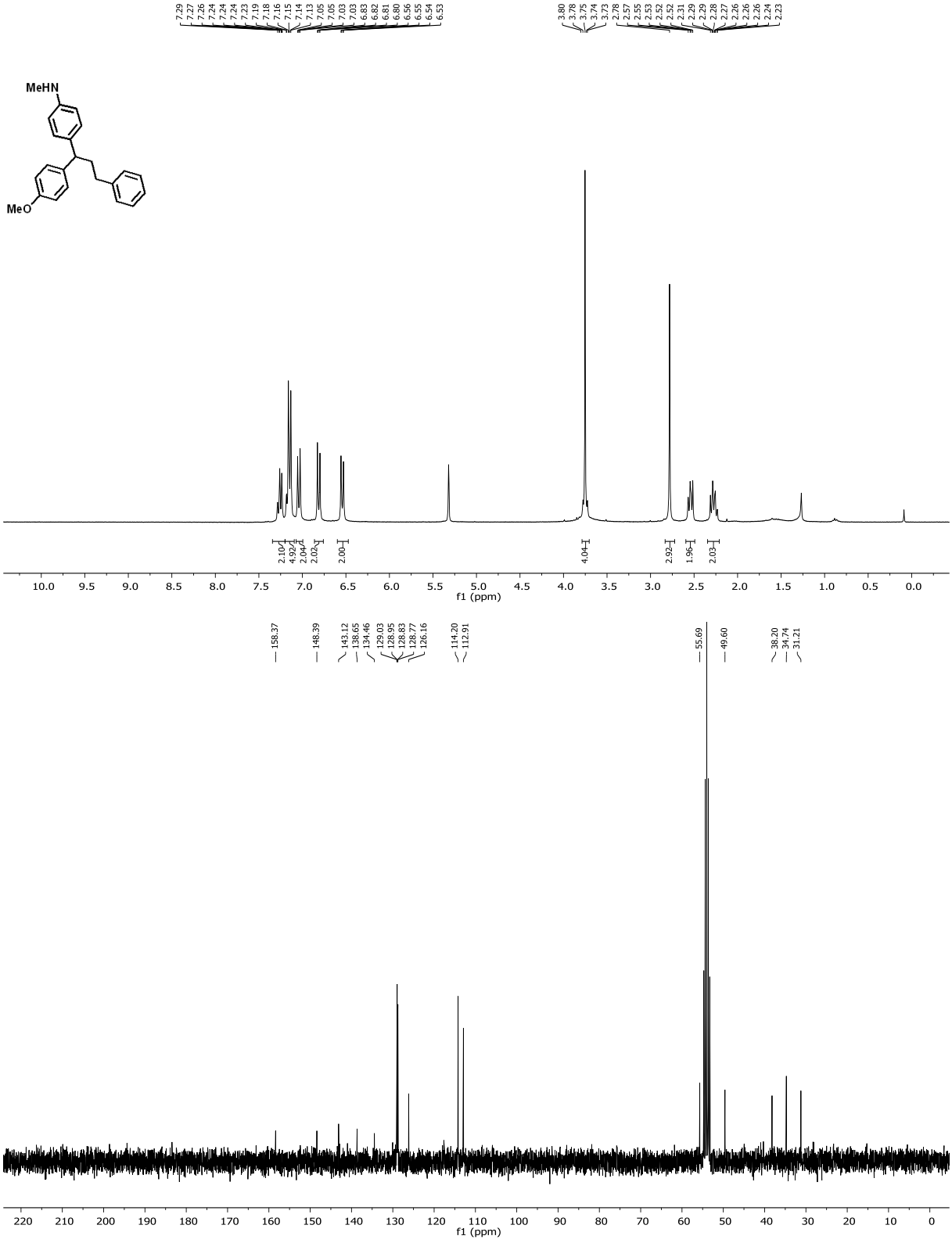
3-(1-(4-Methoxyphenyl)-3-phenylpropyl)-1-methyl-1*H*-indole (4q)



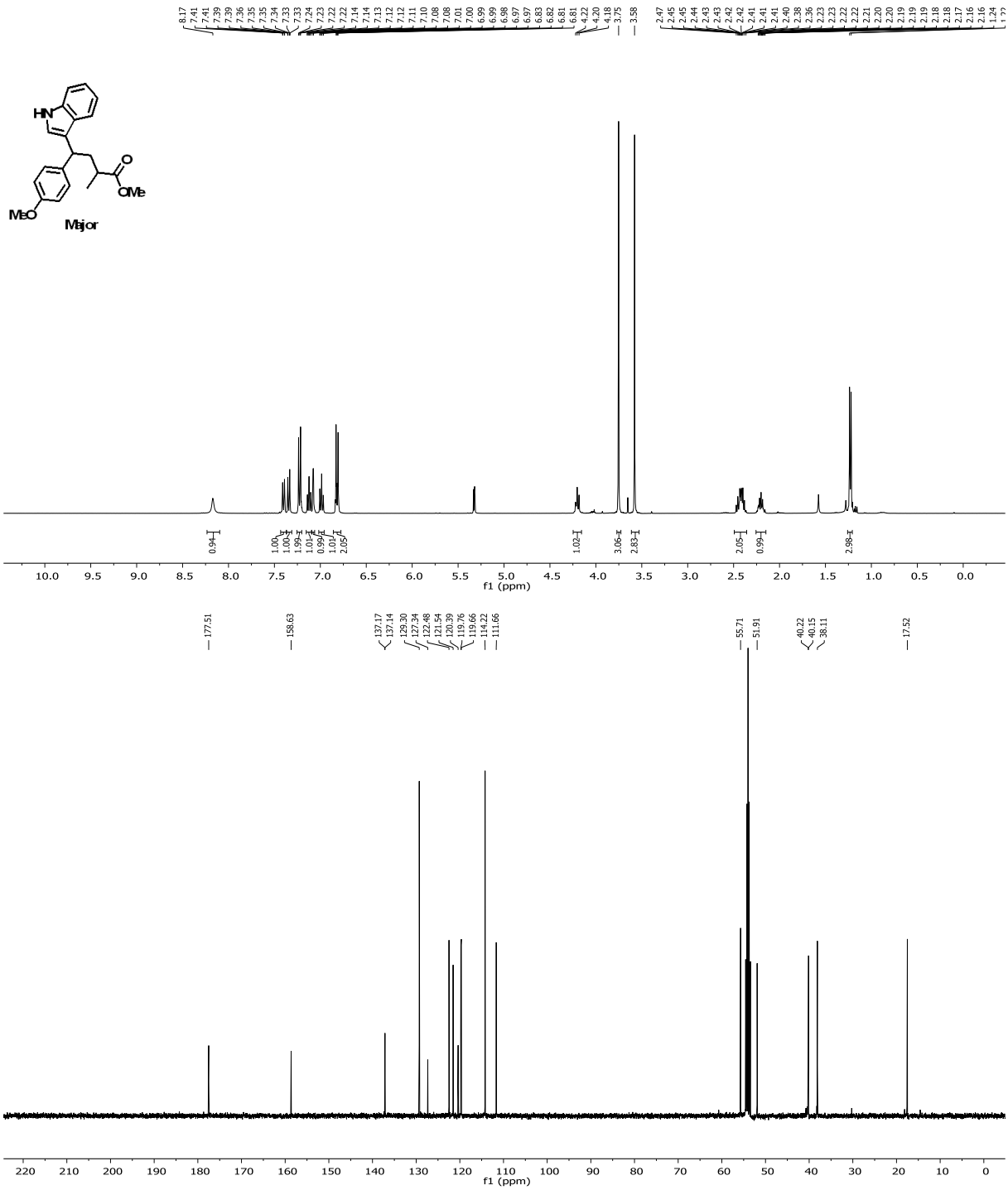
3-(3-(2-Bromophenyl)-1-(4-methoxyphenyl)propyl)-2-phenyl-1*H*-indole (4r)

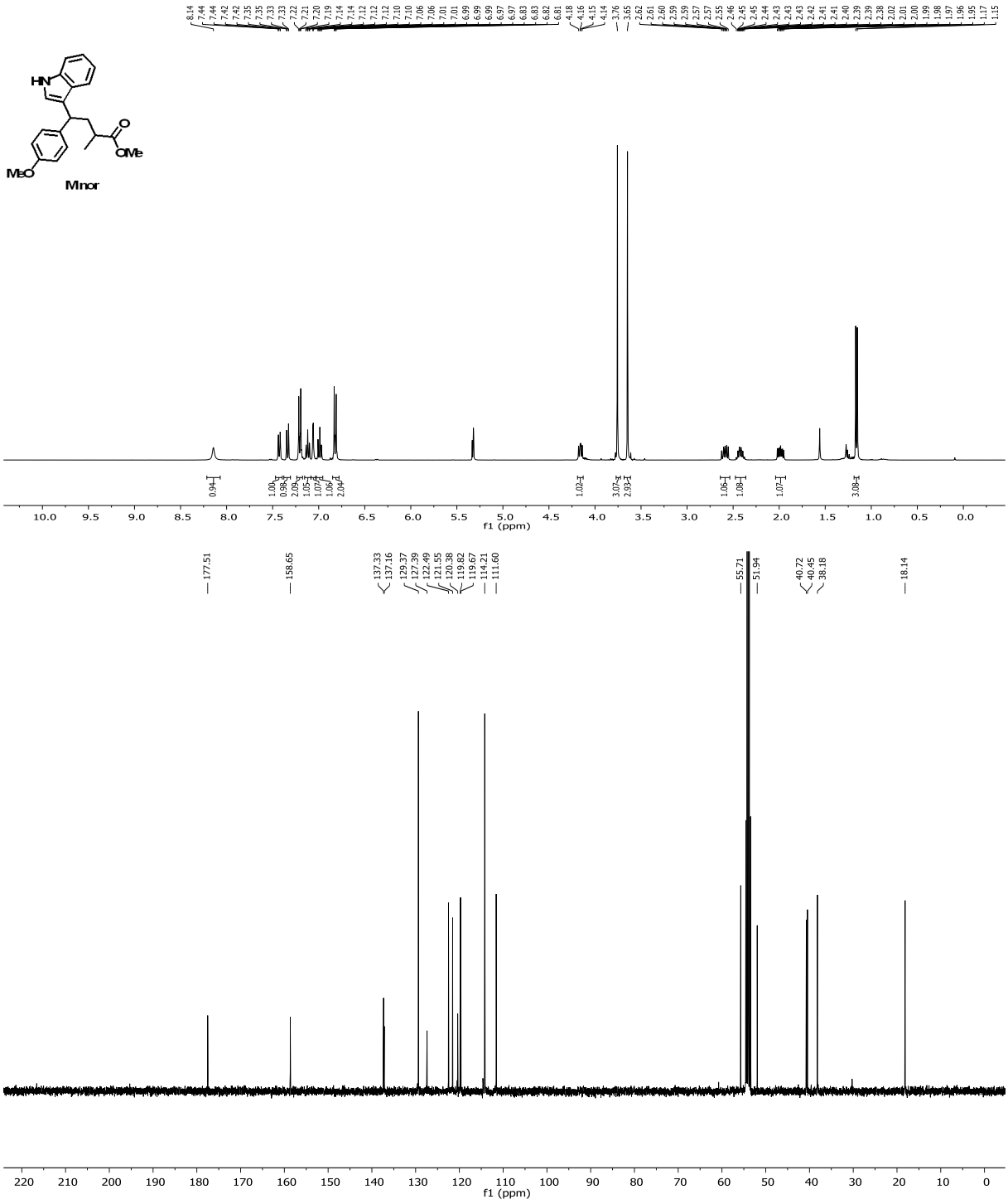


4-(1-(4-Methoxyphenyl)-3-phenylpropyl)-*N*-methylaniline (4s)

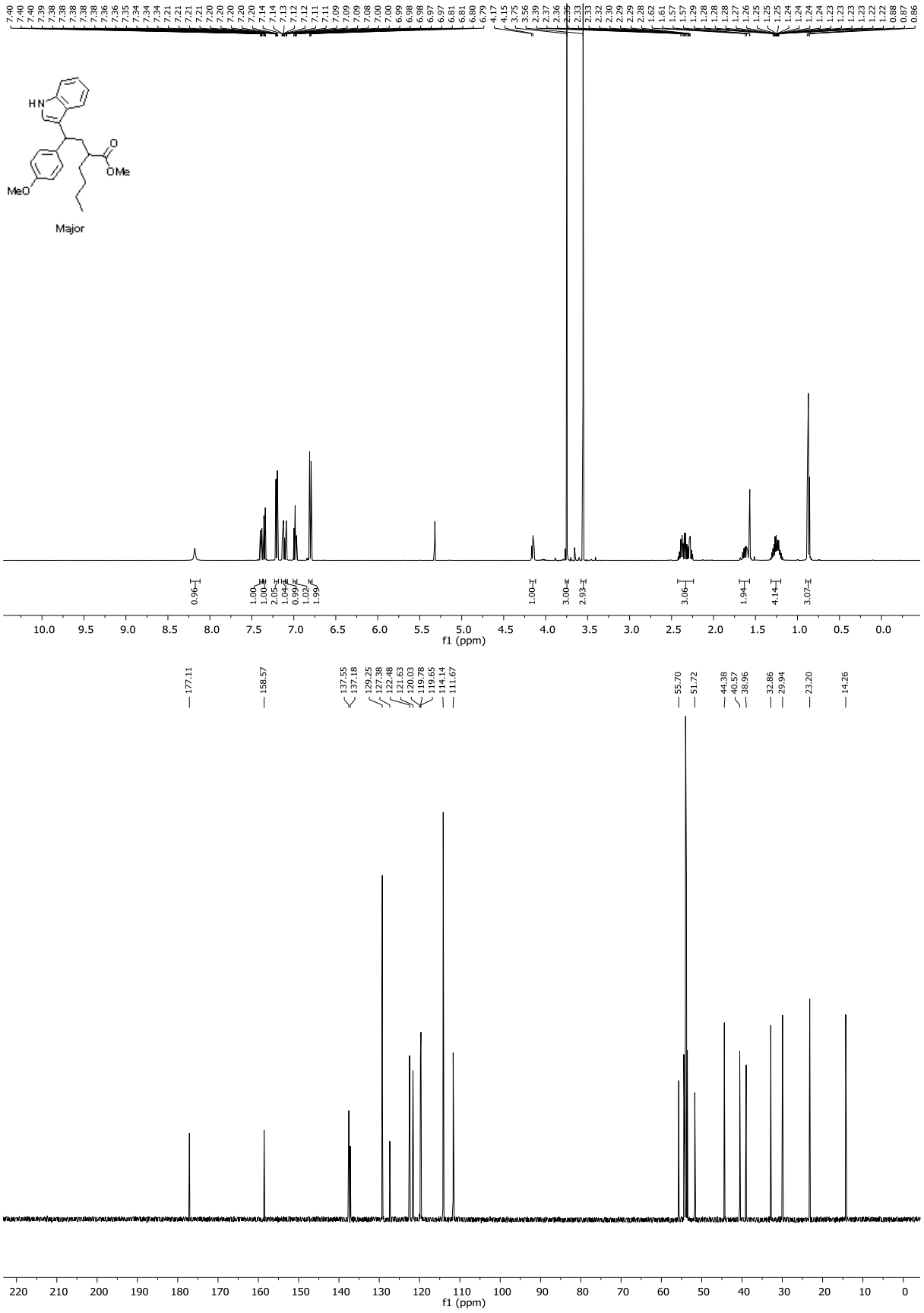


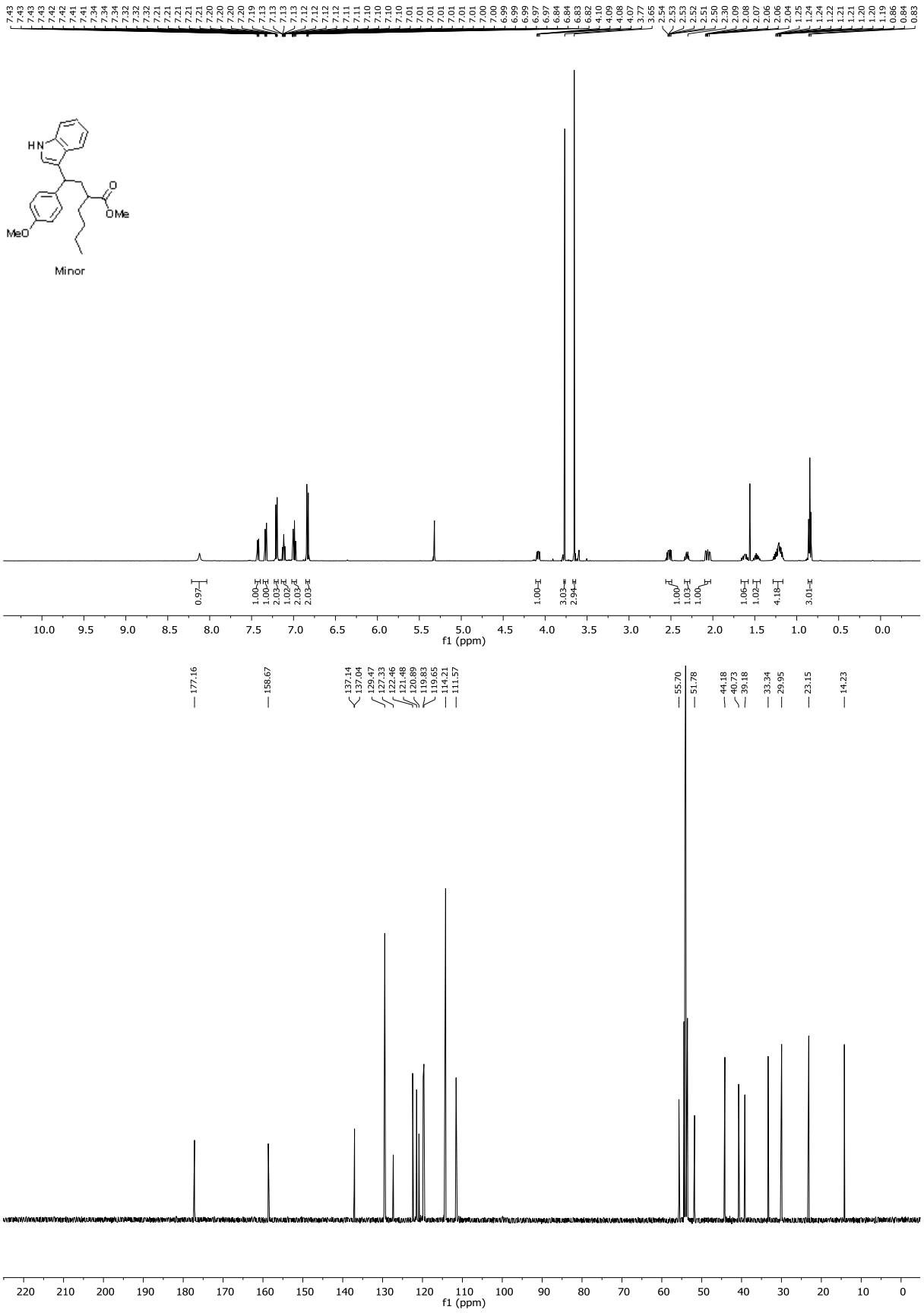
Methyl 4-(1*H*-indol-3-yl)-4-(4-methoxyphenyl)-2-methylbutanoate (4t)



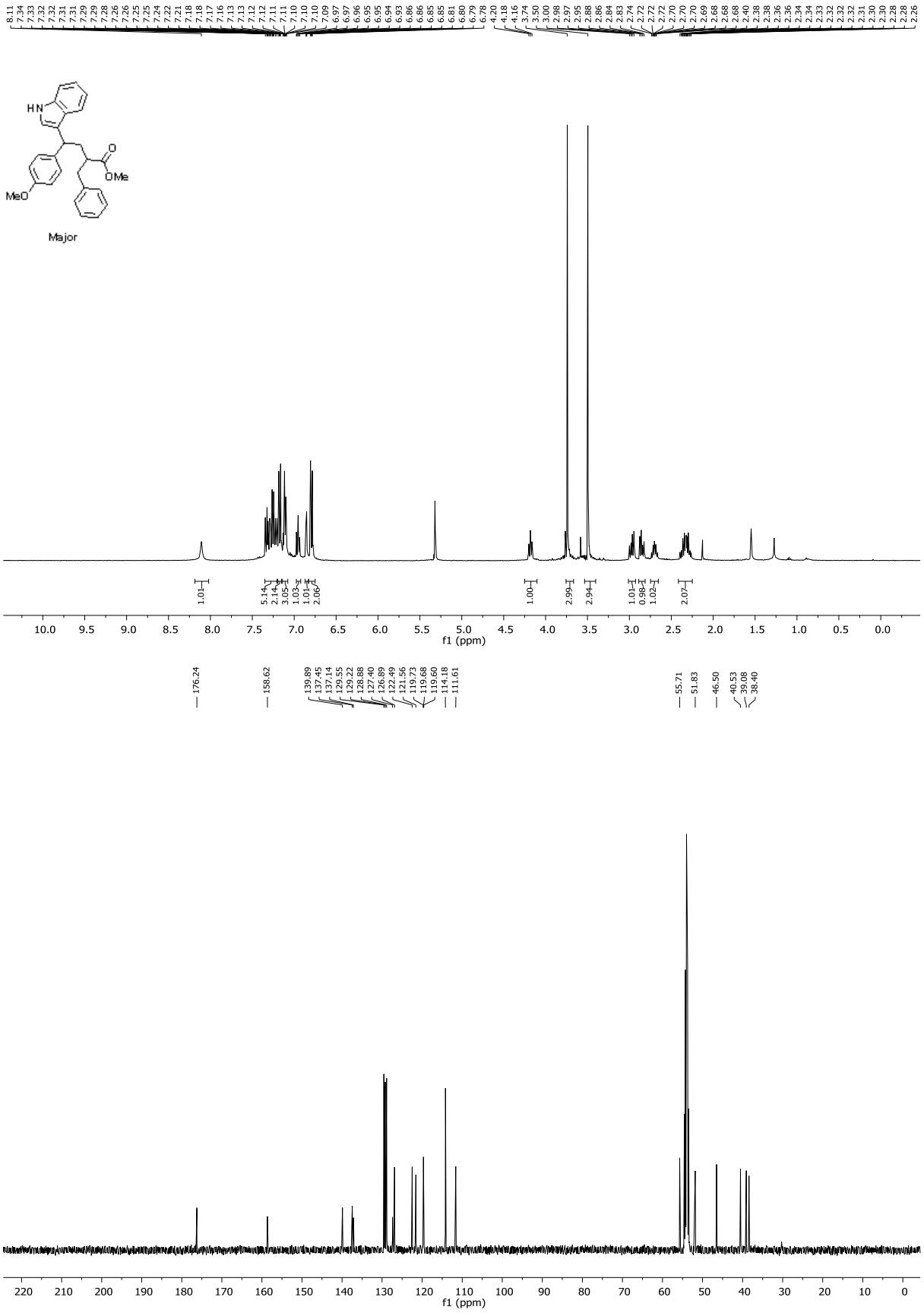

HN
O
OMe
MeO
Minor
f1 (ppm)
f1 (ppm)

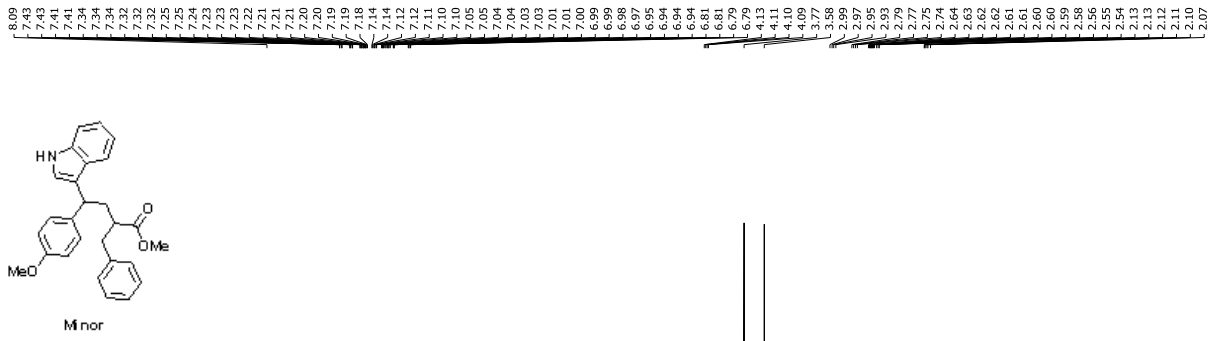
Methyl 2-(2-(1*H*-indol-3-yl)-2-(4-methoxyphenyl)ethyl)hexanoate (4u)




HN
O
OMe
MeO
Minor
f1 (ppm)
f1 (ppm)

Methyl 2-benzyl-4-(1*H*-indol-3-yl)-4-(4-methoxyphenyl)butanoate (4v)

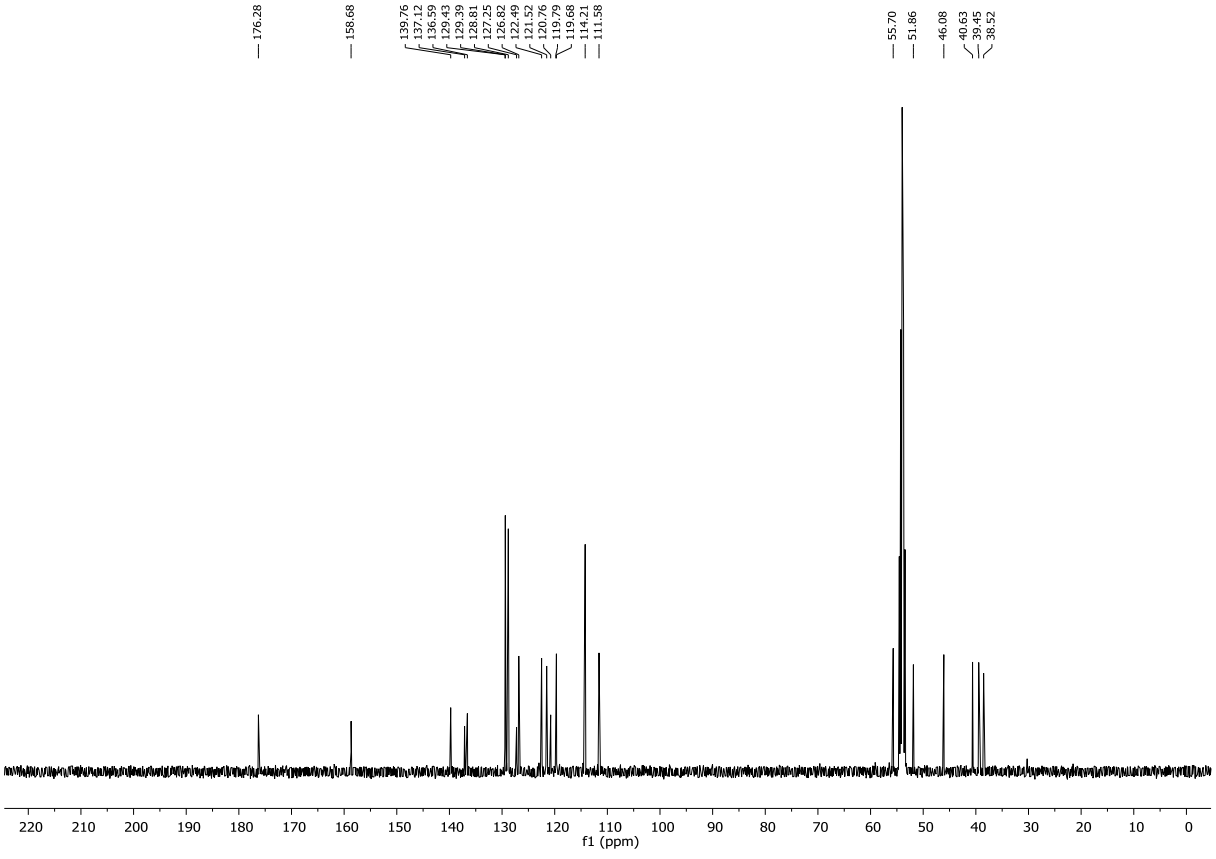




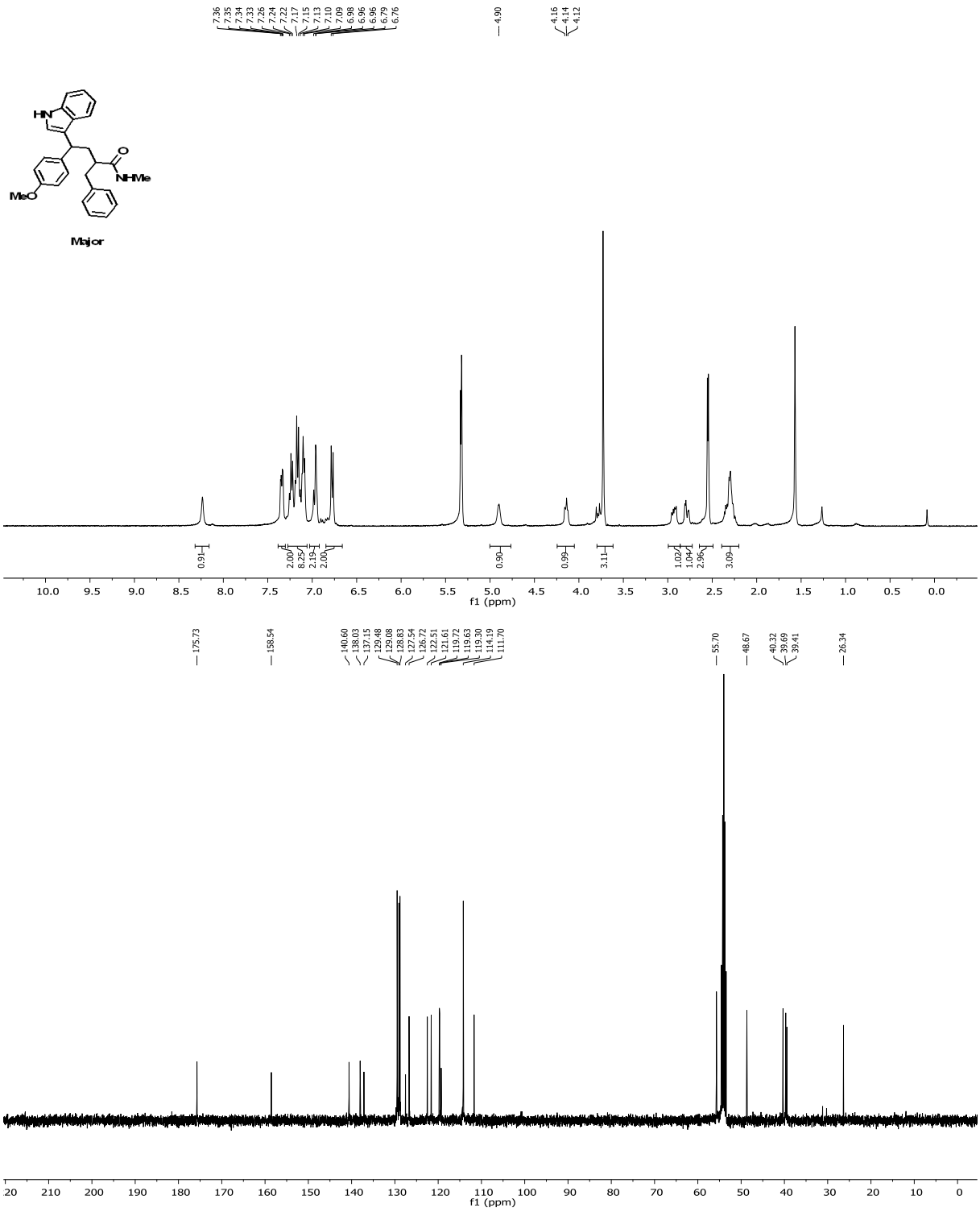
HN
O
OMe
MeO

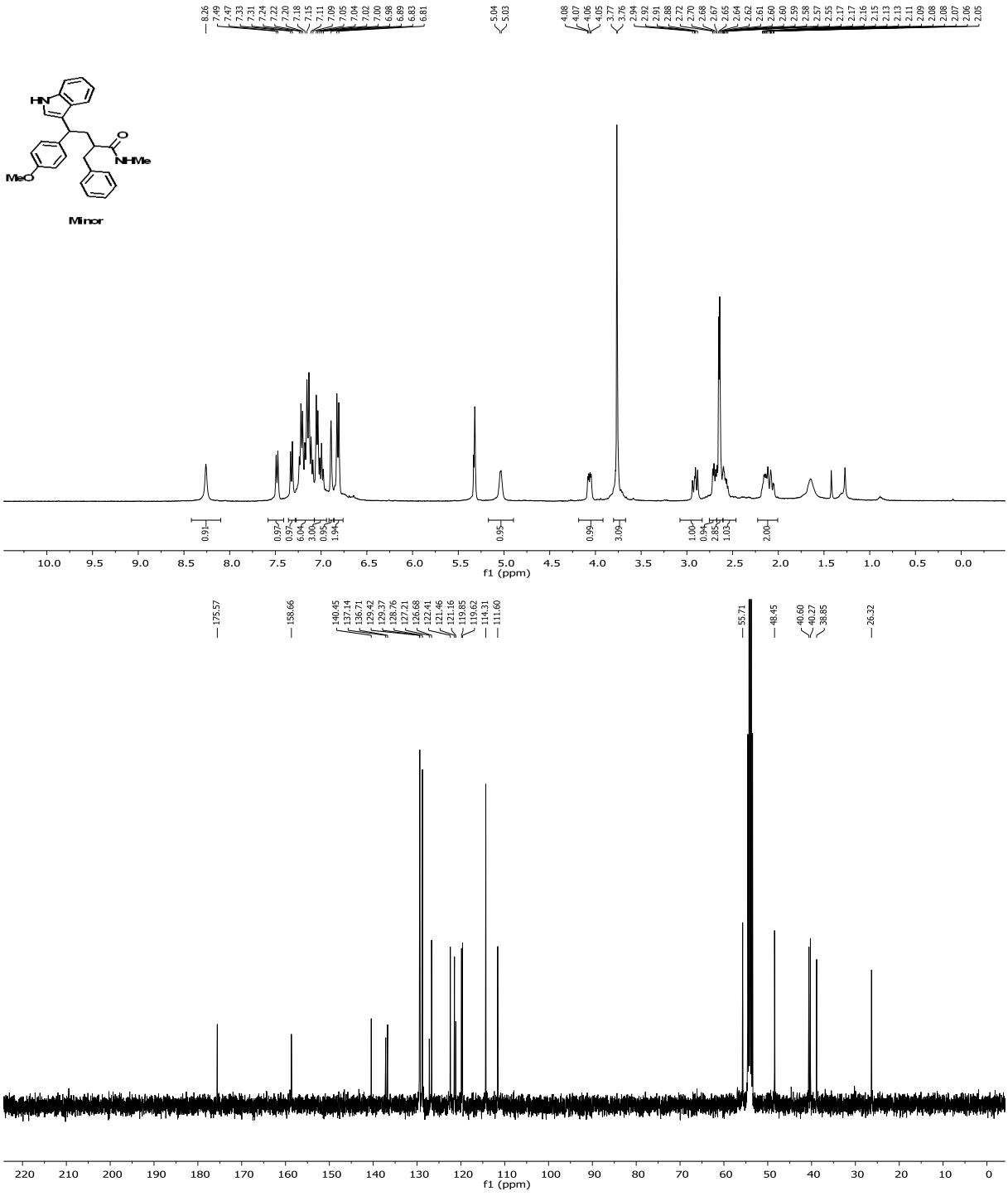
Minor

1.00
0.99
1.06
3.95
2.96
2.10
1.09
1.03
2.04
1.02
3.02
3.02
1.00
1.04
2.03
1.03
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
f1 (ppm)

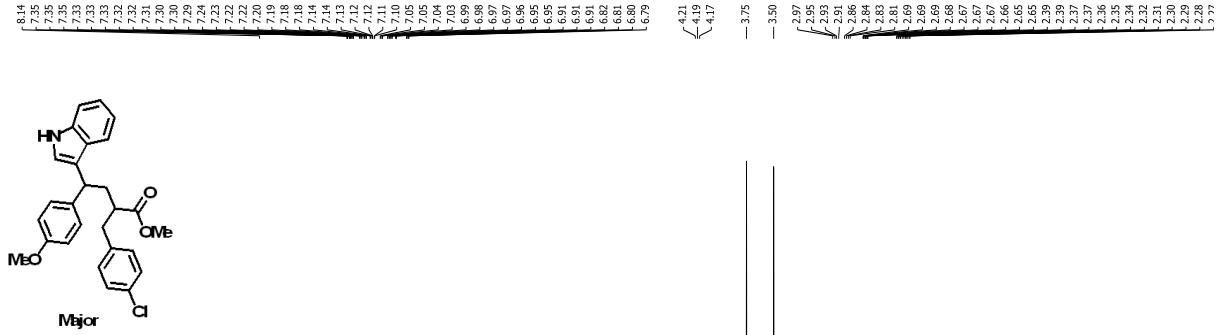

176.28
158.68
139.76
137.12
136.59
129.43
129.39
128.81
127.25
126.82
122.49
121.52
120.76
119.79
119.68
114.21
111.58
55.70
51.86
46.08
40.63
39.45
38.52
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

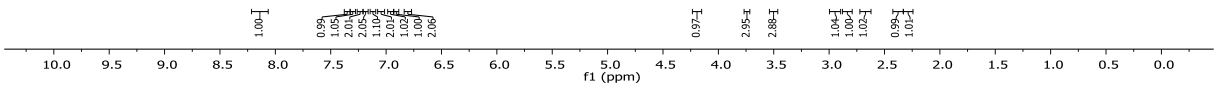
2-Benzyl-4-(1*H*-indol-3-yl)-4-(4-methoxyphenyl)-N-methylbutanamide (4w)

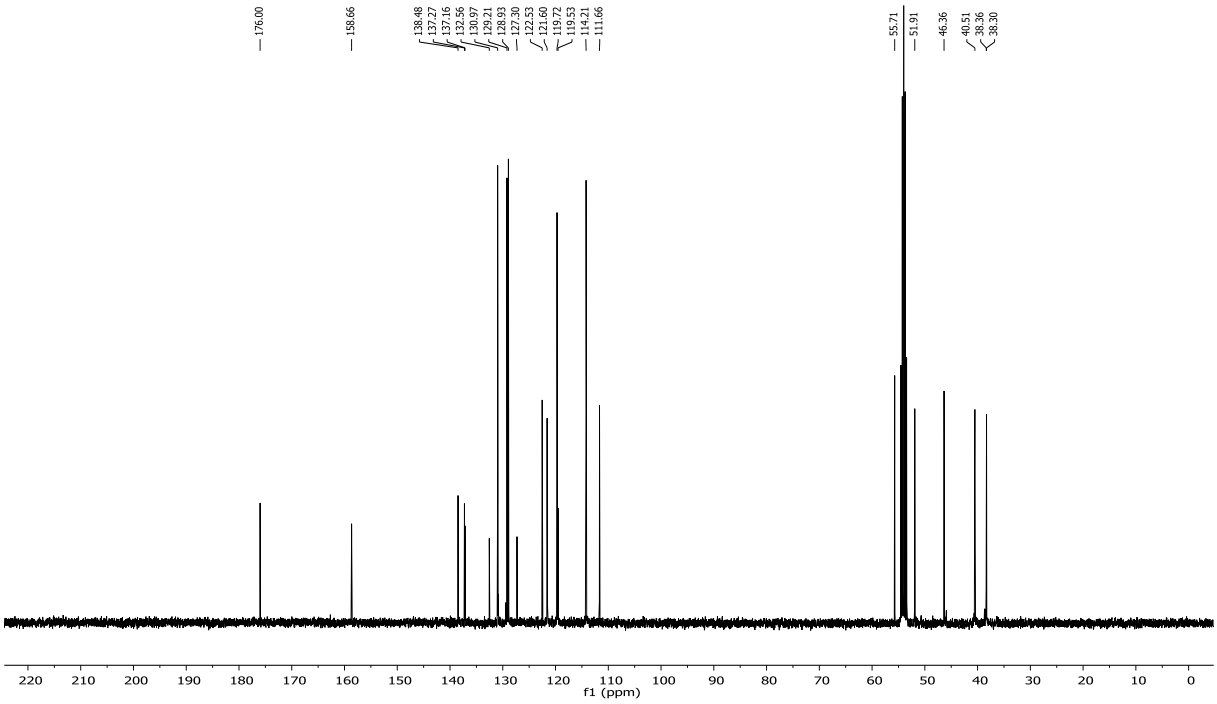


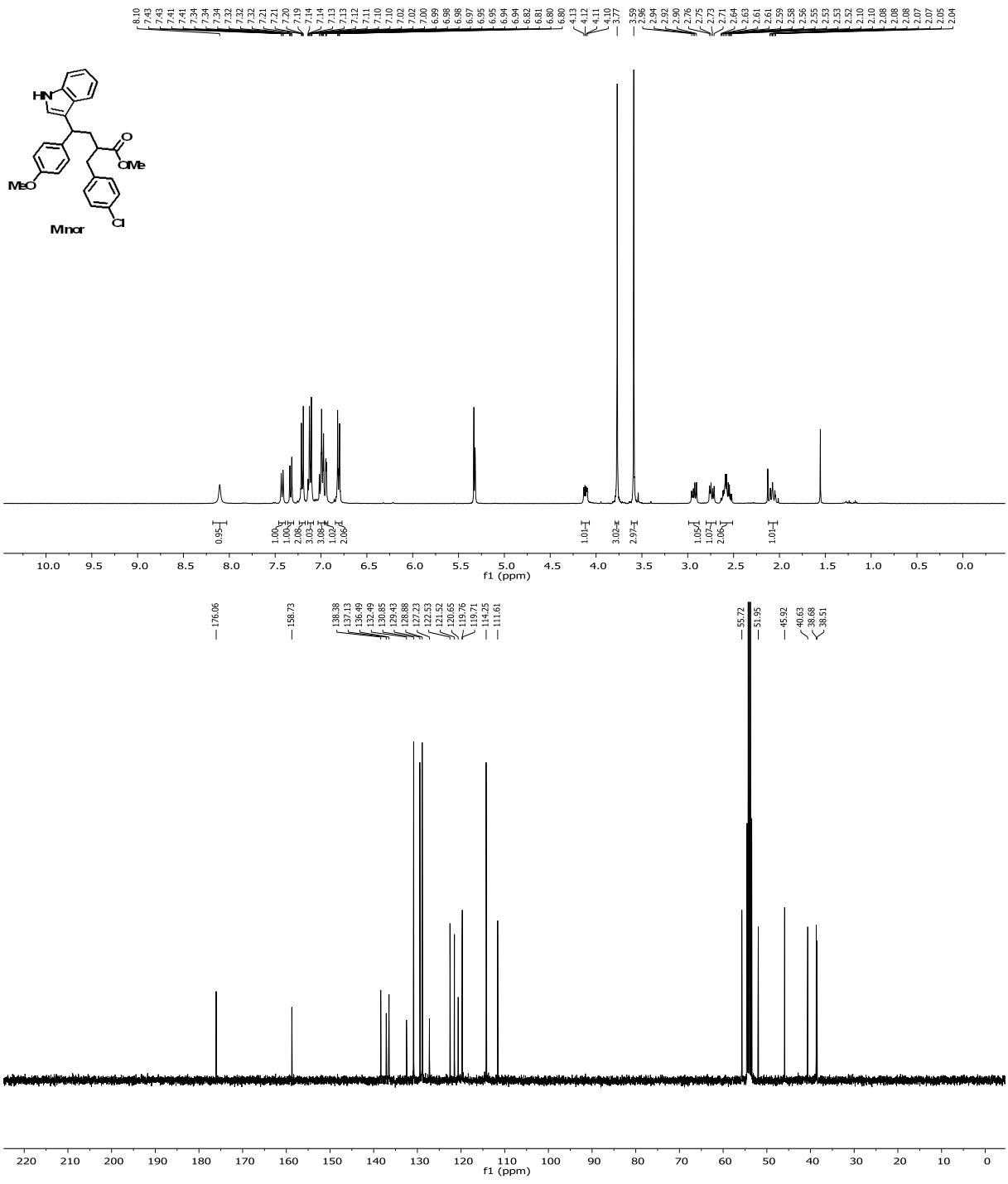

HN
O
NHMe
MeO
Minor
f1 (ppm)
f1 (ppm)

Methyl 2-(4-chlorobenzyl)-4-(1*H*-indol-3-yl)-4-(4-methoxyphenyl)butanoate (4x)

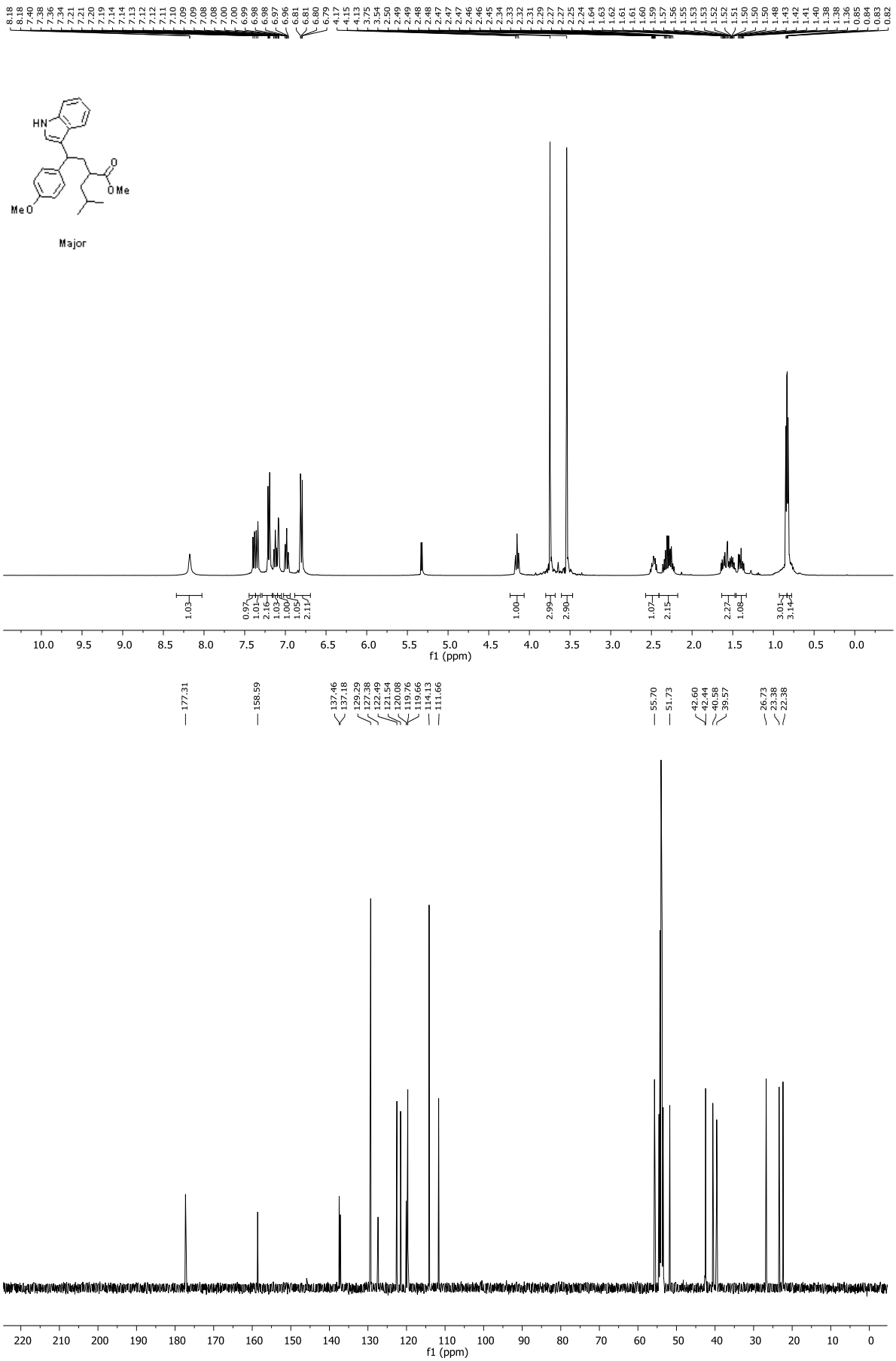


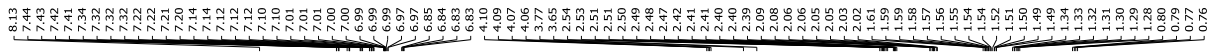


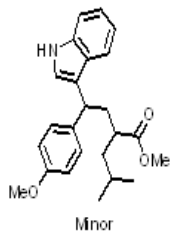



HN
O
OMe
MeO
Cl
Minor
f1 (ppm)
f1 (ppm)

Methyl 2-(2-(1*H*-indol-3-yl)-2-(4-methoxyphenyl)ethyl)-4-methylpentanoate (4y)

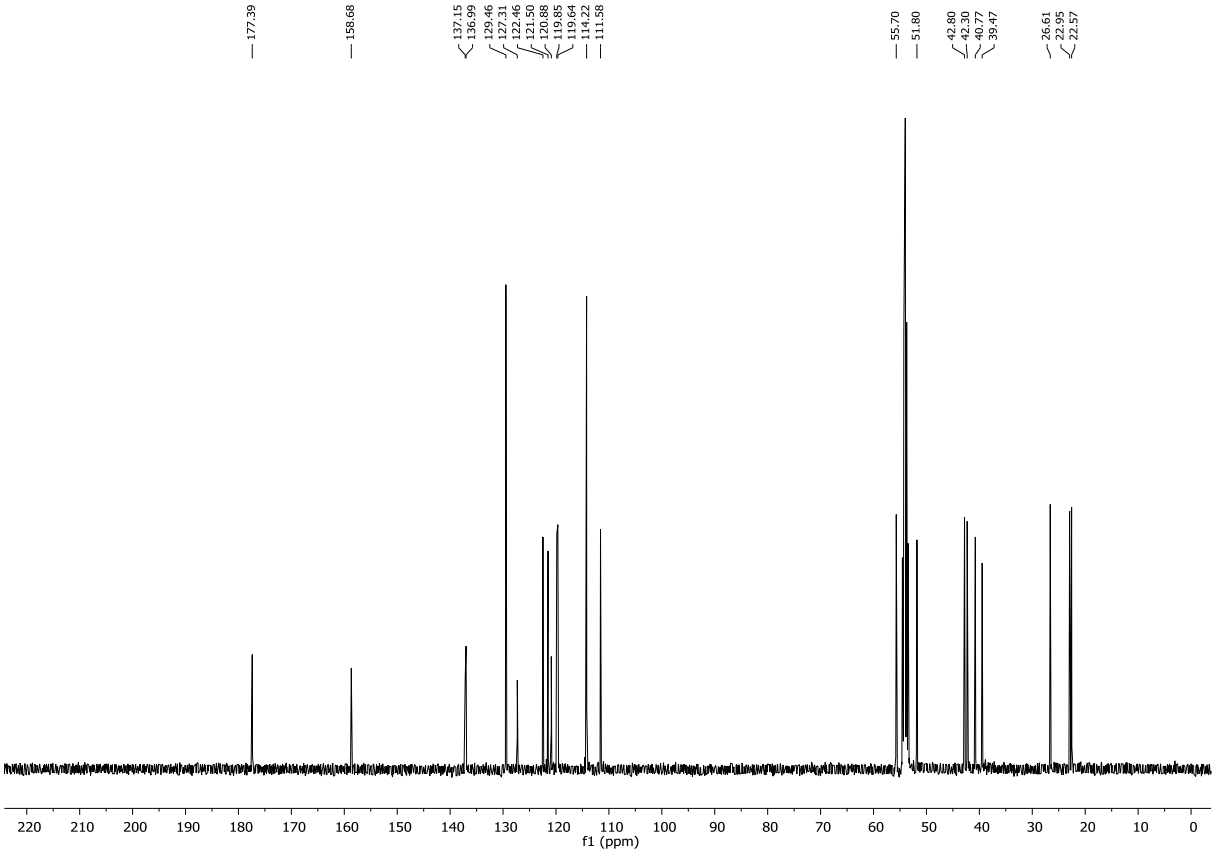




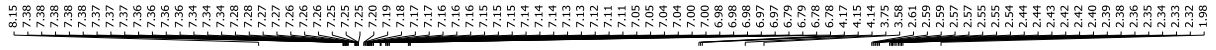

HN
O
OMe
MeO

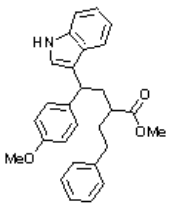
Minor

0.98
0.99
0.99
1.97
1.04
1.97
1.96
0.99
3.03
3.00
1.03
1.04
0.99
2.15
1.12
3.03
2.97
f1 (ppm)

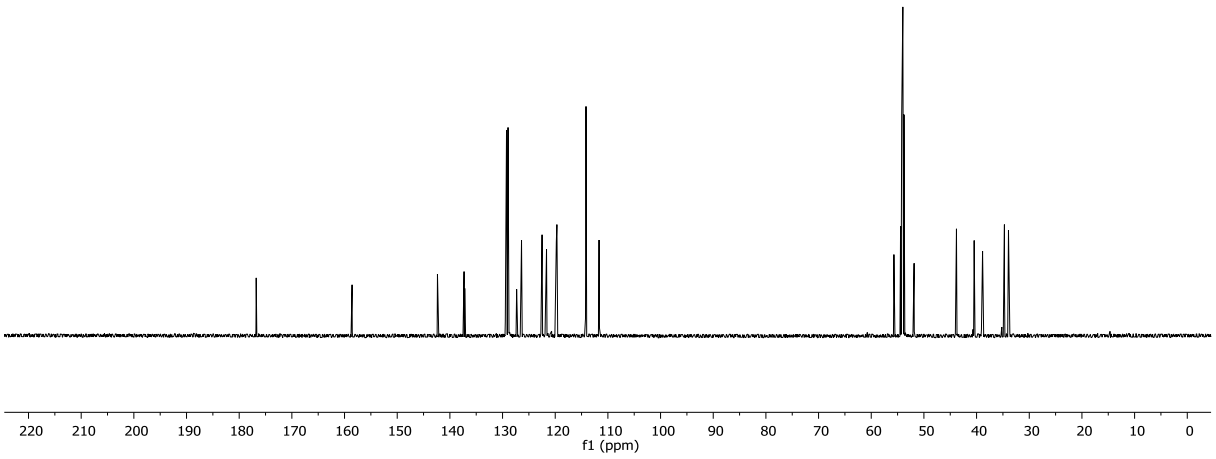

177.39
158.68
137.15
136.99
129.46
127.31
122.46
121.50
120.88
119.85
119.64
114.22
111.58
55.70
51.80
42.80
42.30
40.77
39.47
26.61
22.95
22.57
f1 (ppm)

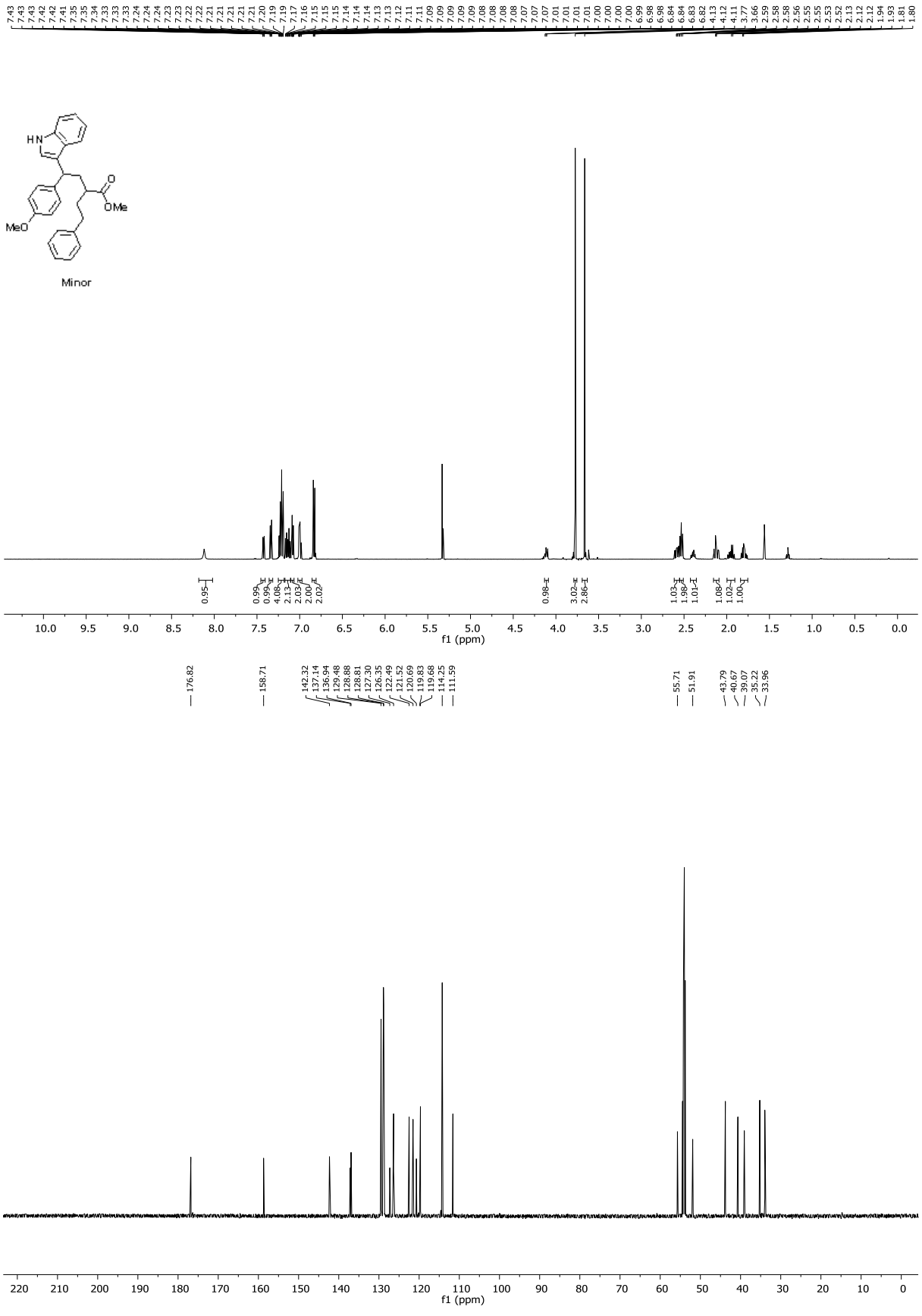
Methyl 4-(1*H*-indol-3-yl)-4-(4-methoxyphenyl)-2-phenethylbutanoate (4z)



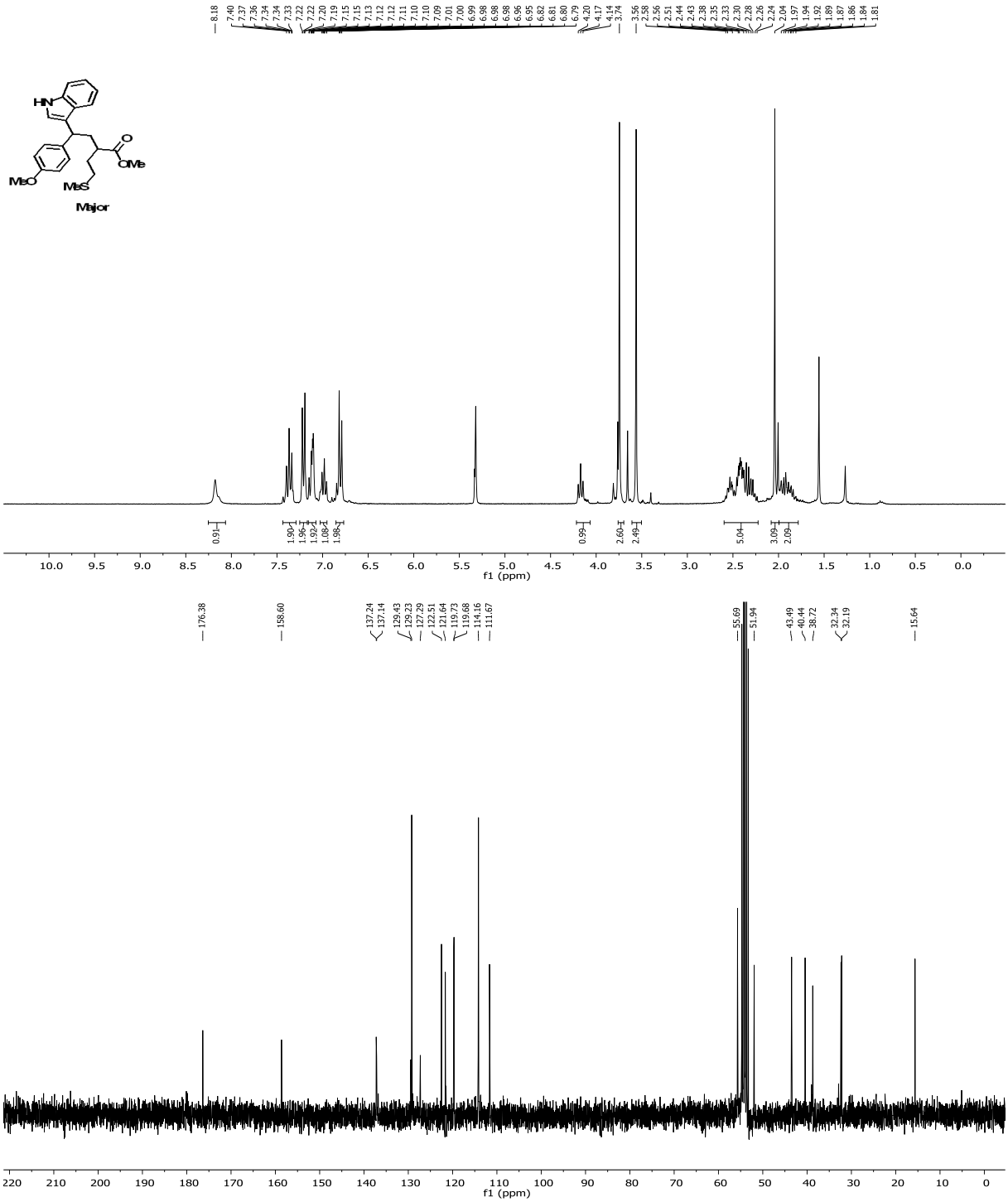


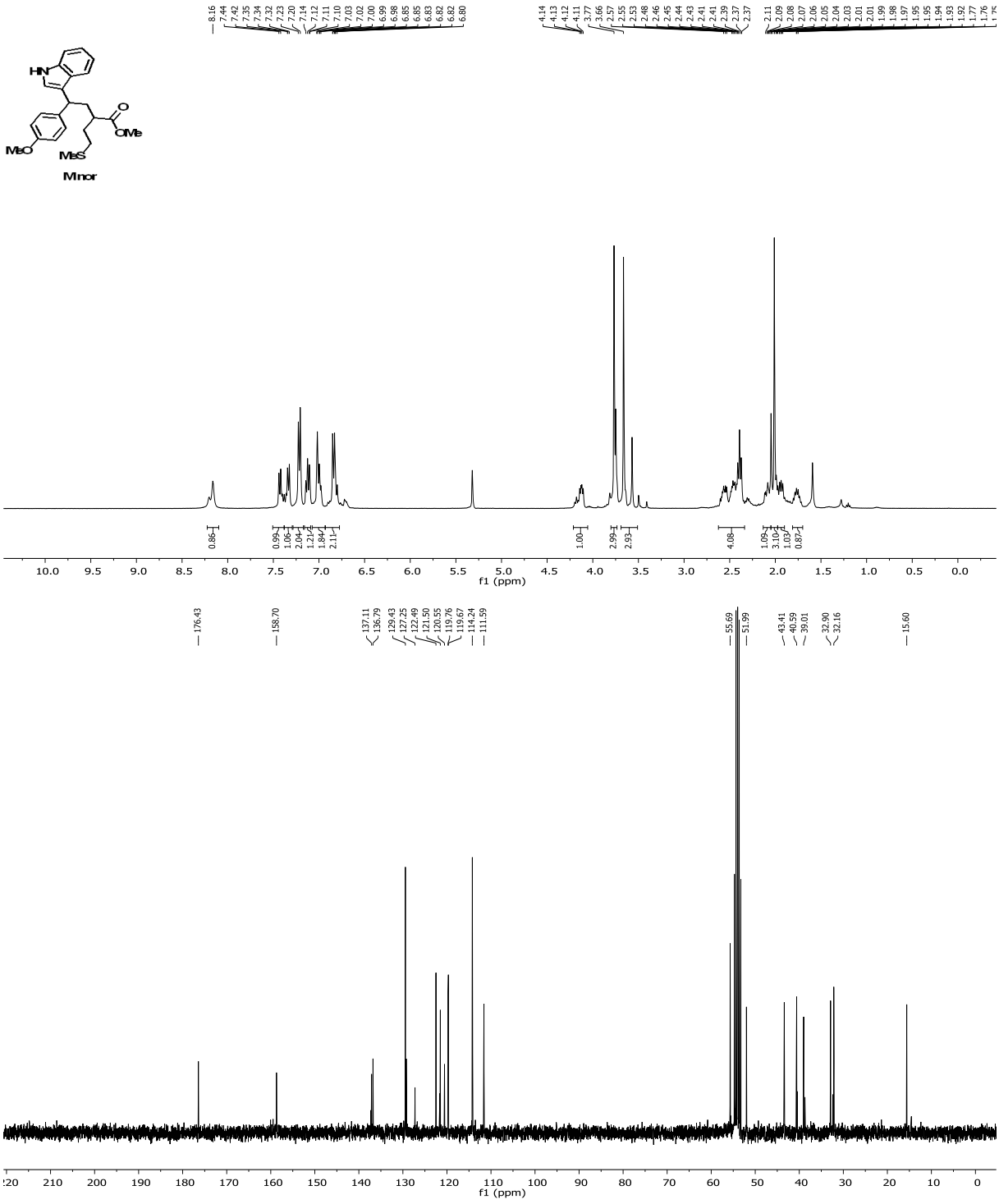
Major



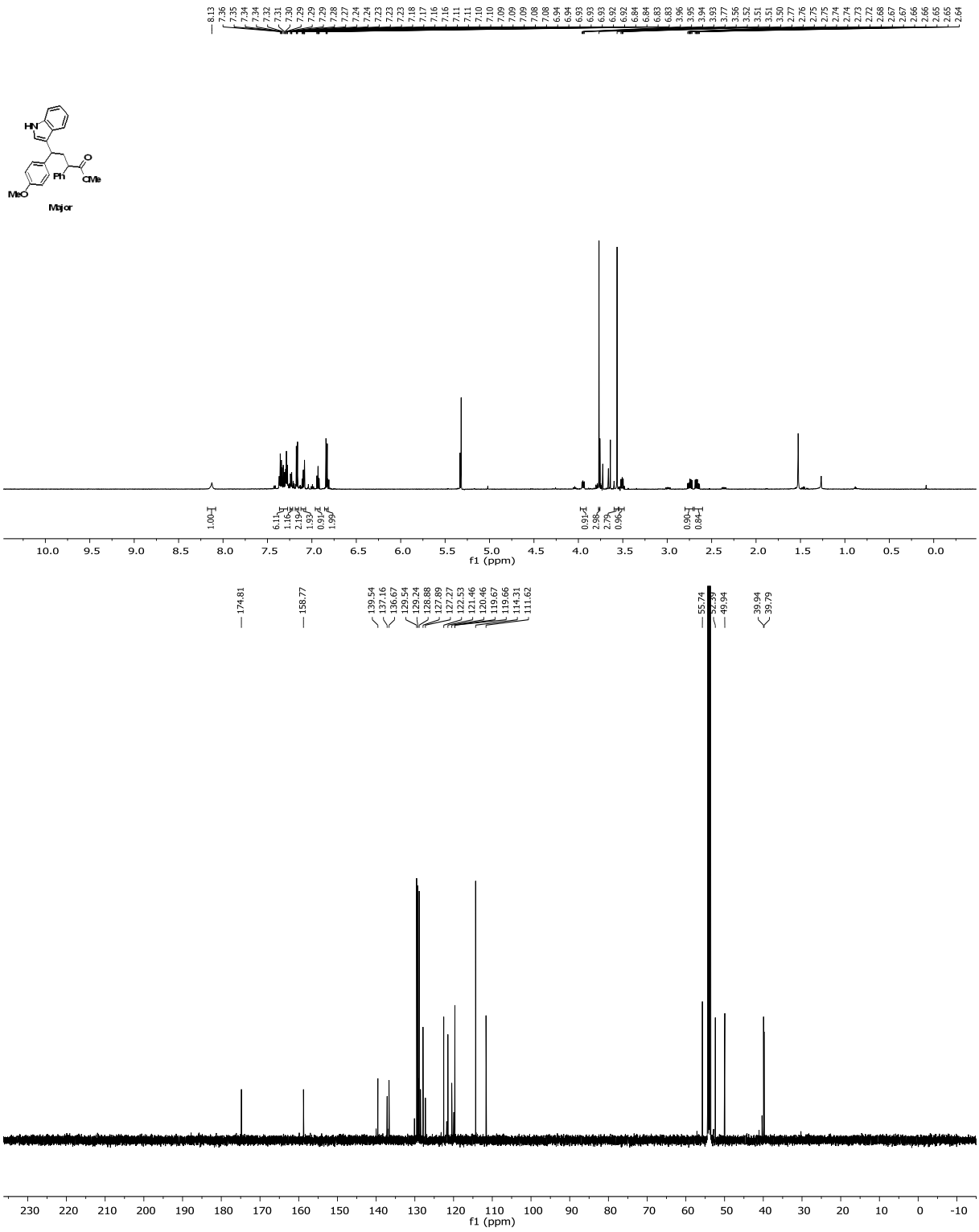

HN
O
OMe
MeO
Minor
f1 (ppm)
f1 (ppm)

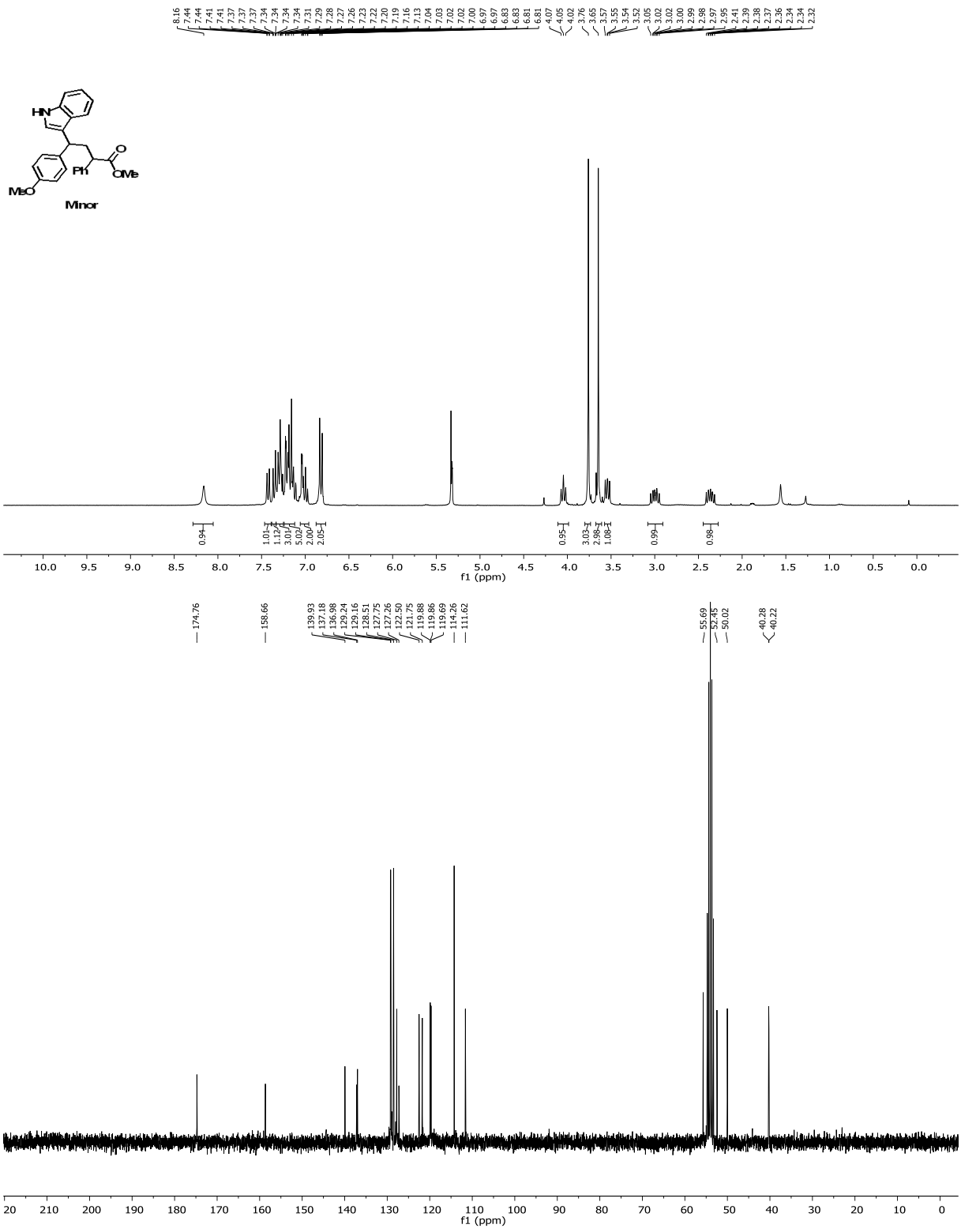
Methyl 4-(1*H*-indol-3-yl)-4-(4-methoxyphenyl)-2-(2-(methylthio)ethyl)butanoate (4aa)



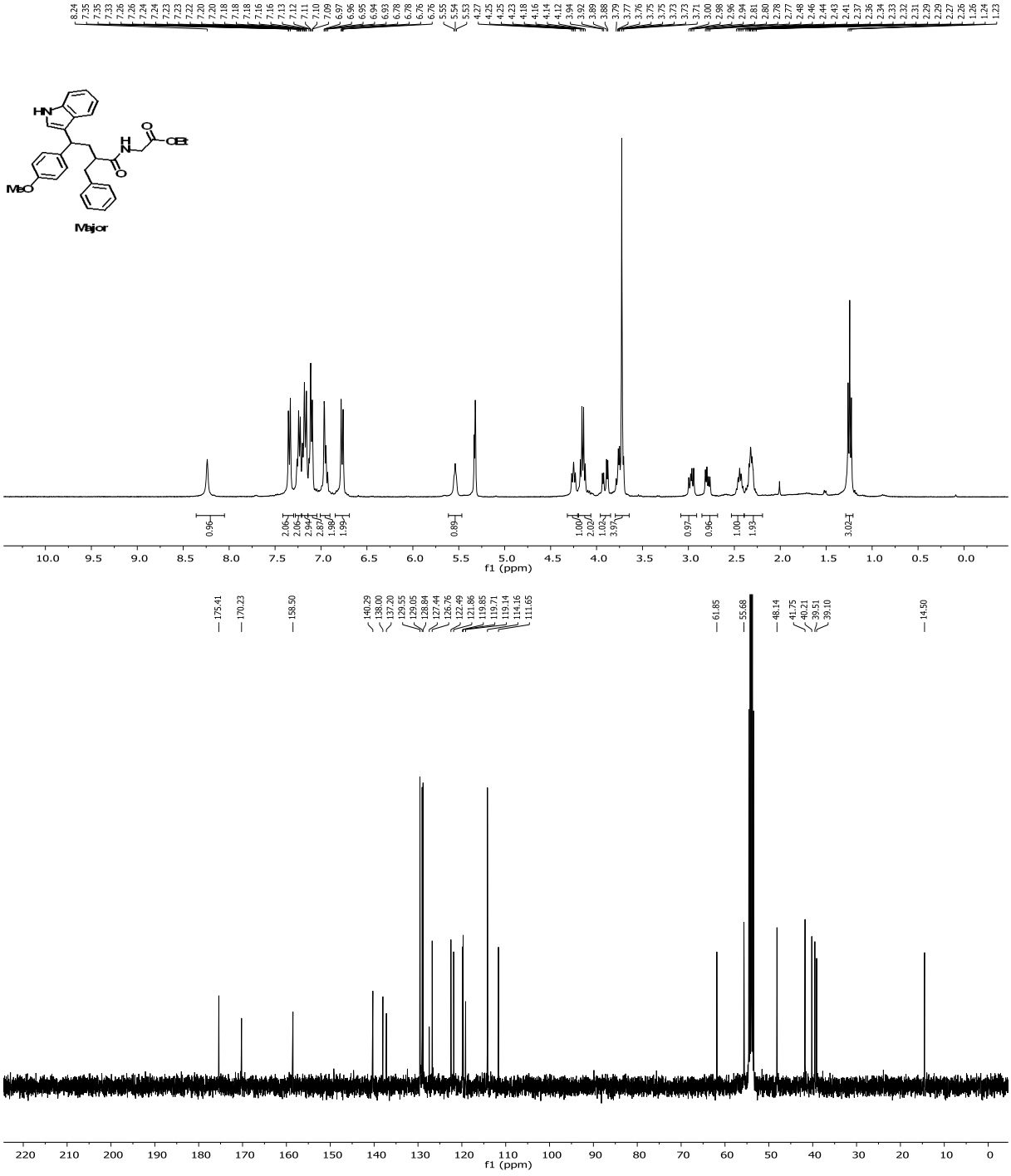

HN
O
OMe
MeO
MeS
Minor
f1 (ppm)
f1 (ppm)

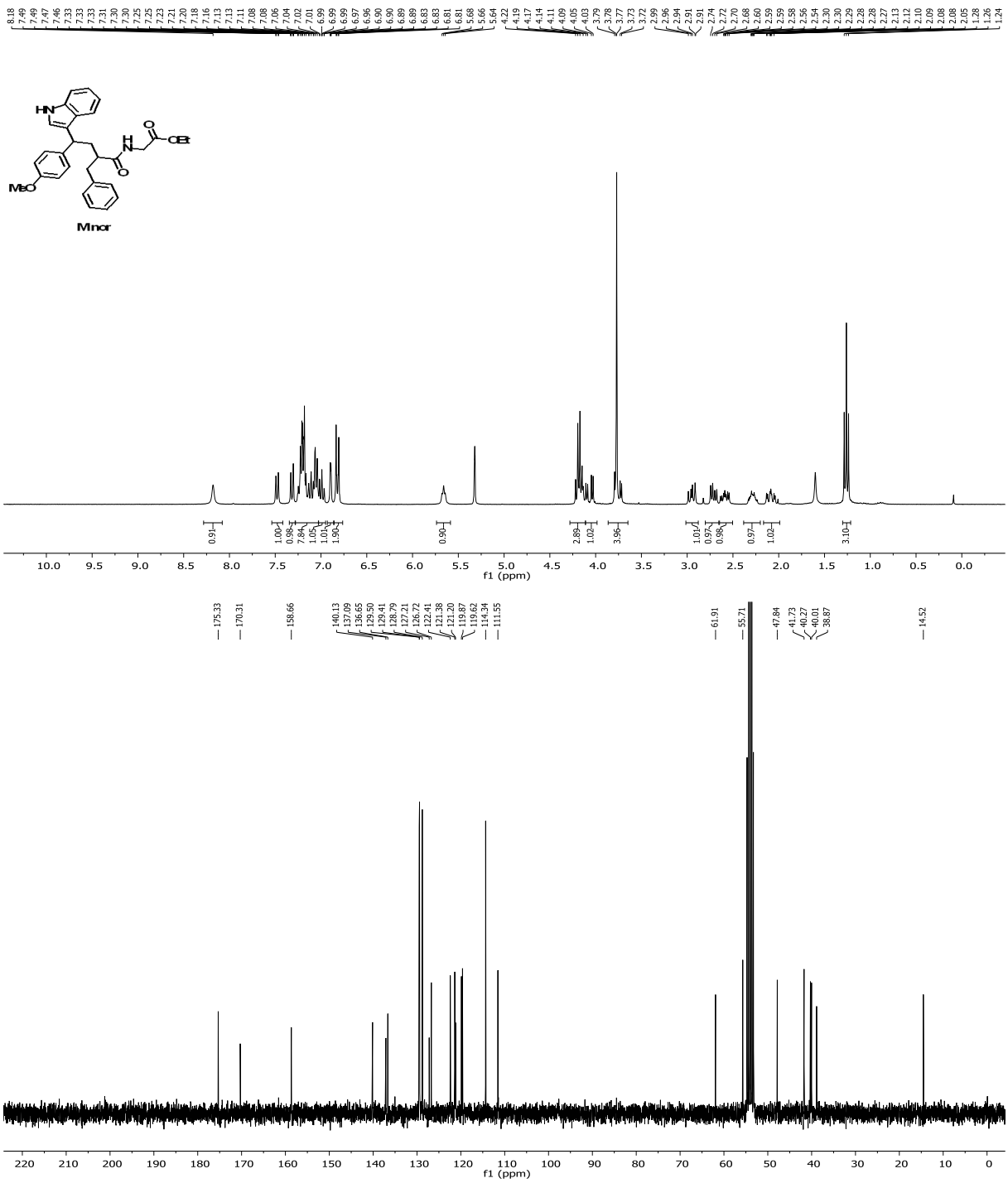
Methyl 4-(1*H*-indol-3-yl)-4-(4-methoxyphenyl)-2-phenylbutanoate (4ab)



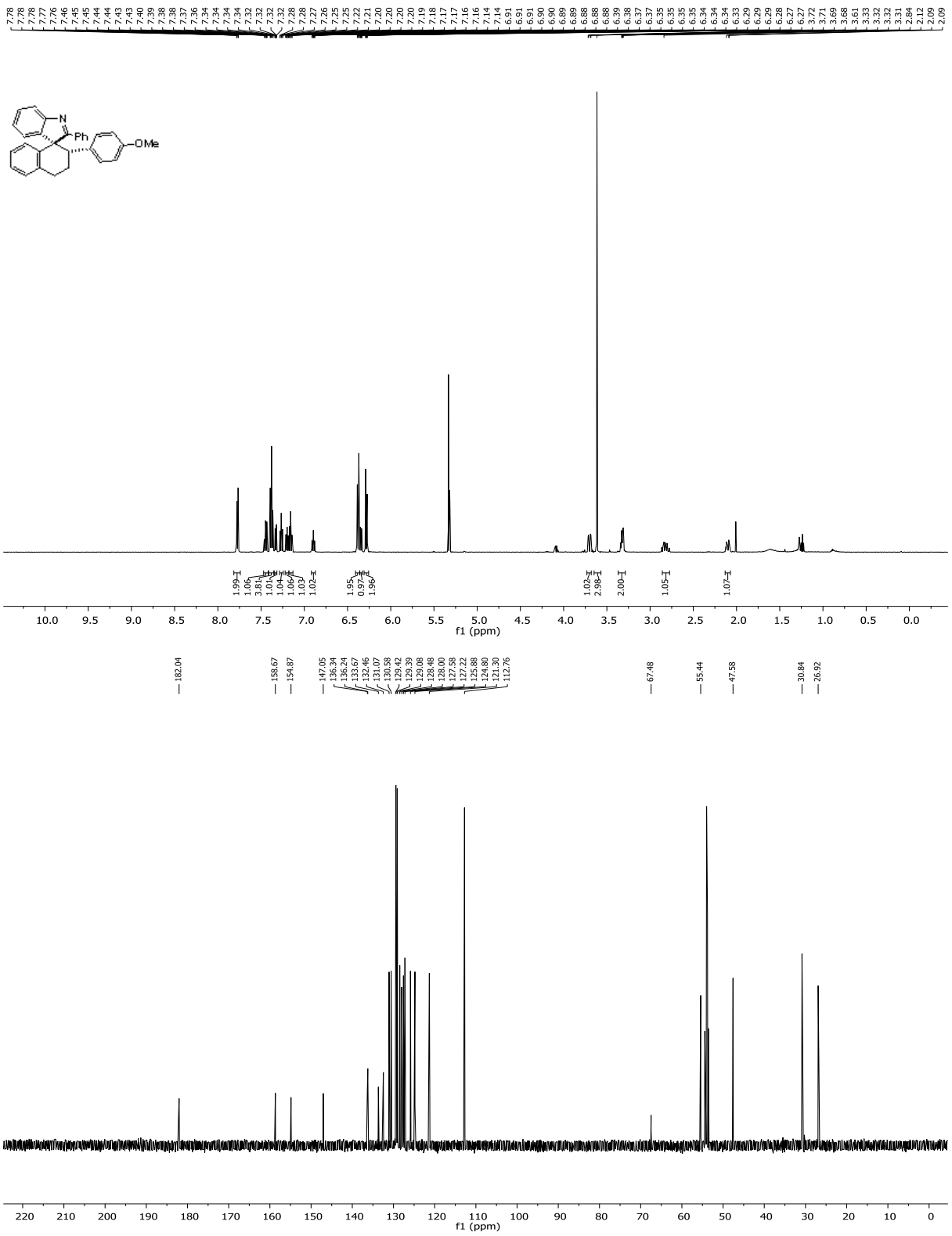

Minor
f1 (ppm)
f1 (ppm)

Ethyl (2-benzyl-4-(1*H*-indol-3-yl)-4-(4-methoxyphenyl)butanoyl)glycinate (4ac)



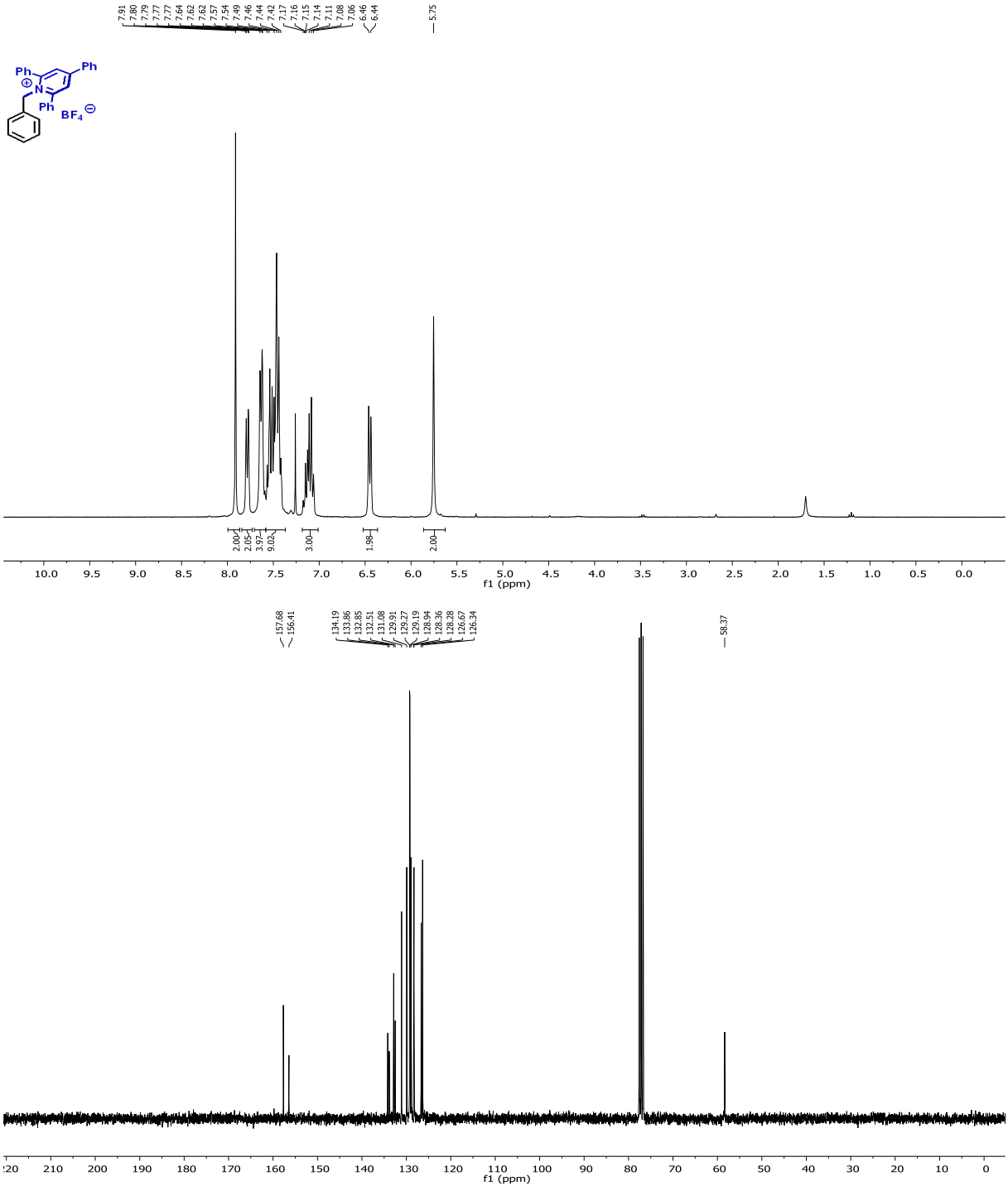

Minor
f1 (ppm)
f1 (ppm)

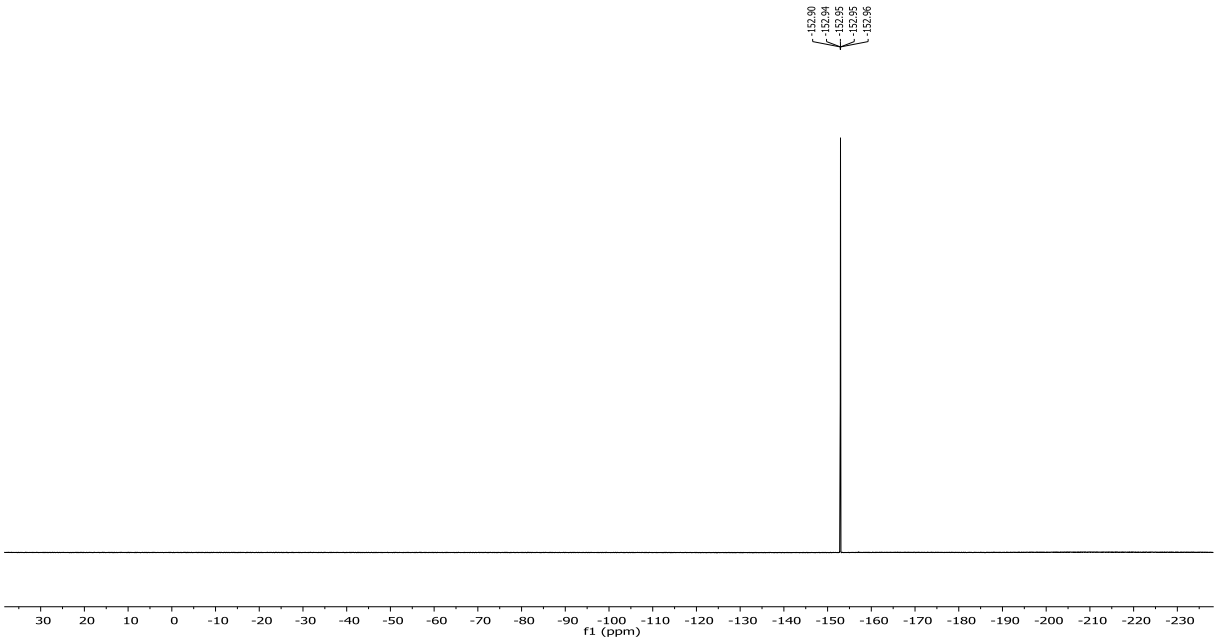
rac-(2'_S_,3_S_)-2'-(4-Methoxyphenyl)-2-phenyl-3',4'-dihydro-2'_H_-spiro[indole-3,1'-naphthalene] (5a)



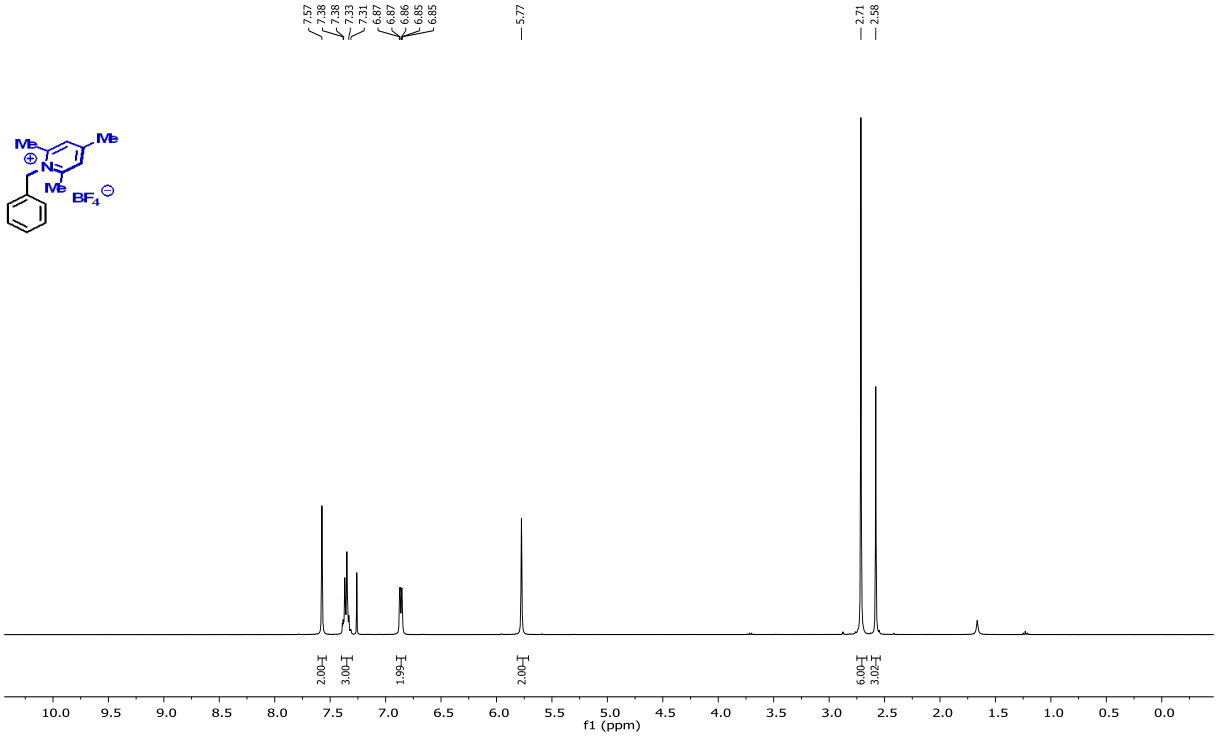
Starting materials

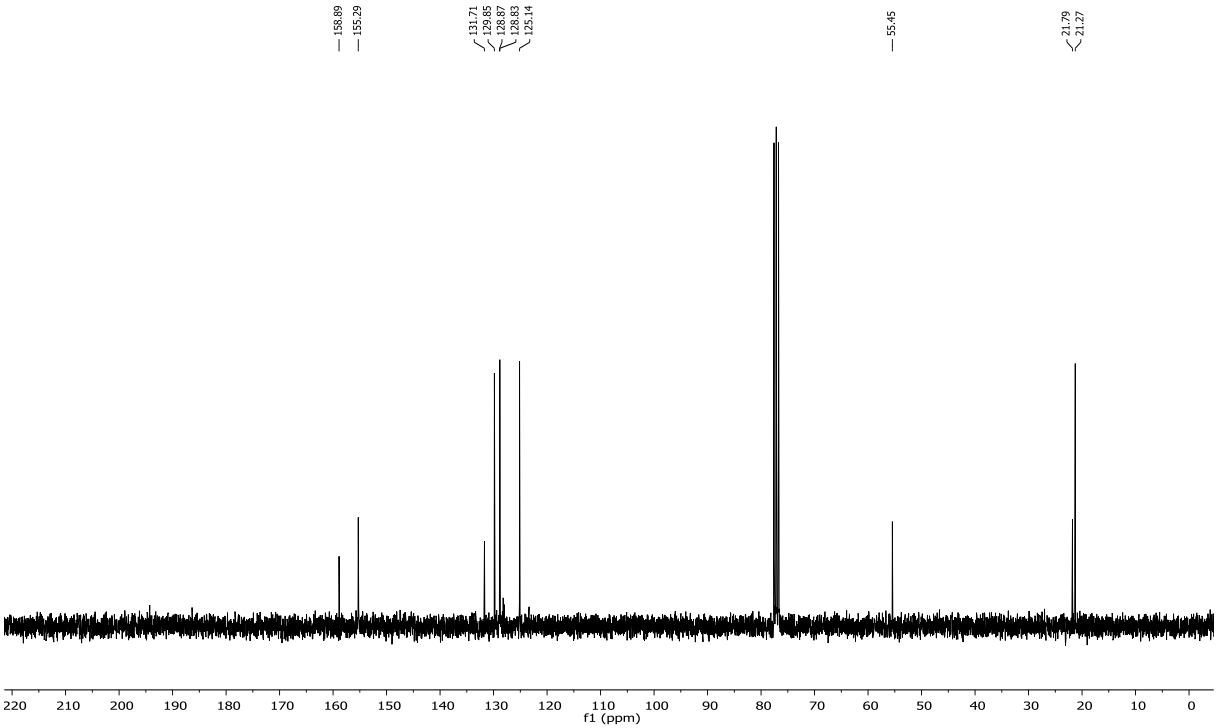
1-Benzyl-2,4,6-triphenylpyridin-1-ium tetrafluoroborate

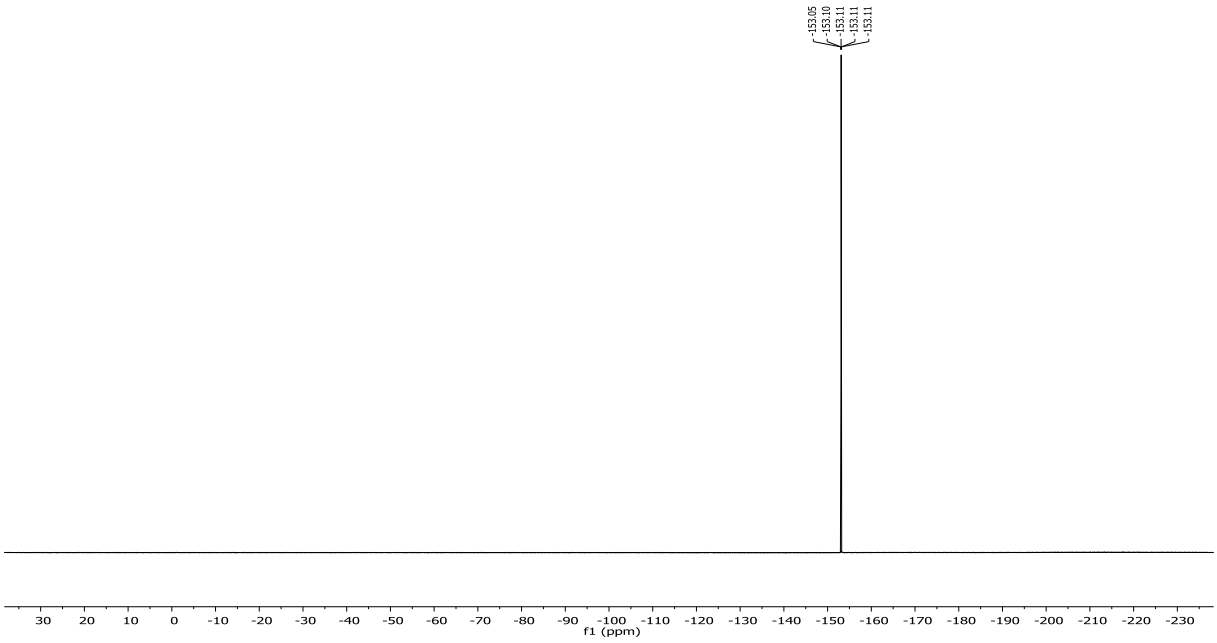



-152.90
-152.94
-152.95
-152.95
-152.96
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230
f1 (ppm)

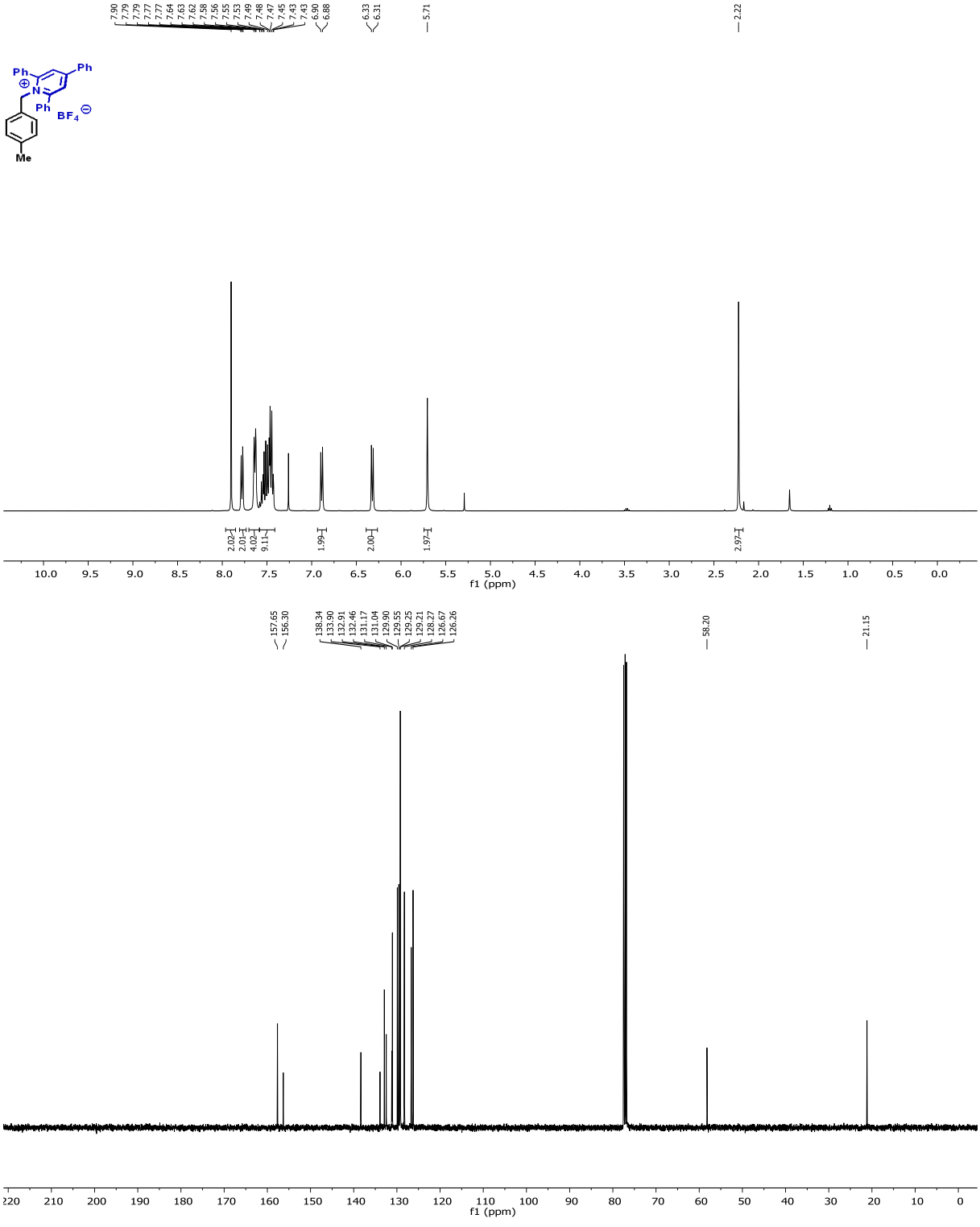
1-Benzyl-2,4,6-trimethylpyridin-1-ium tetrafluoroborate

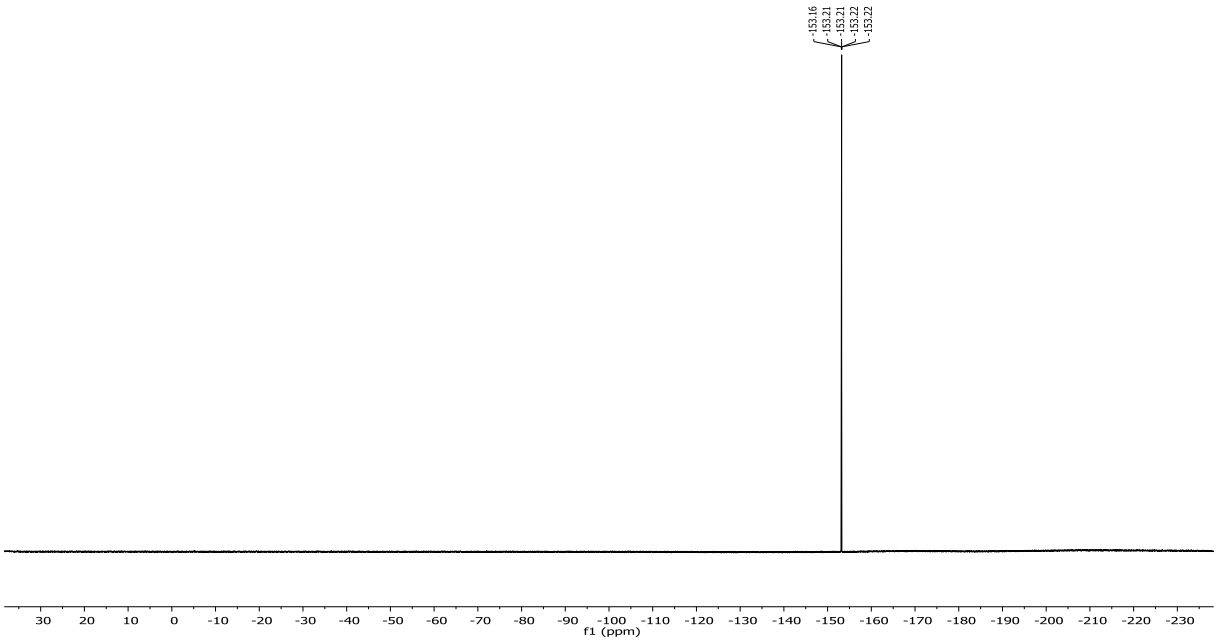




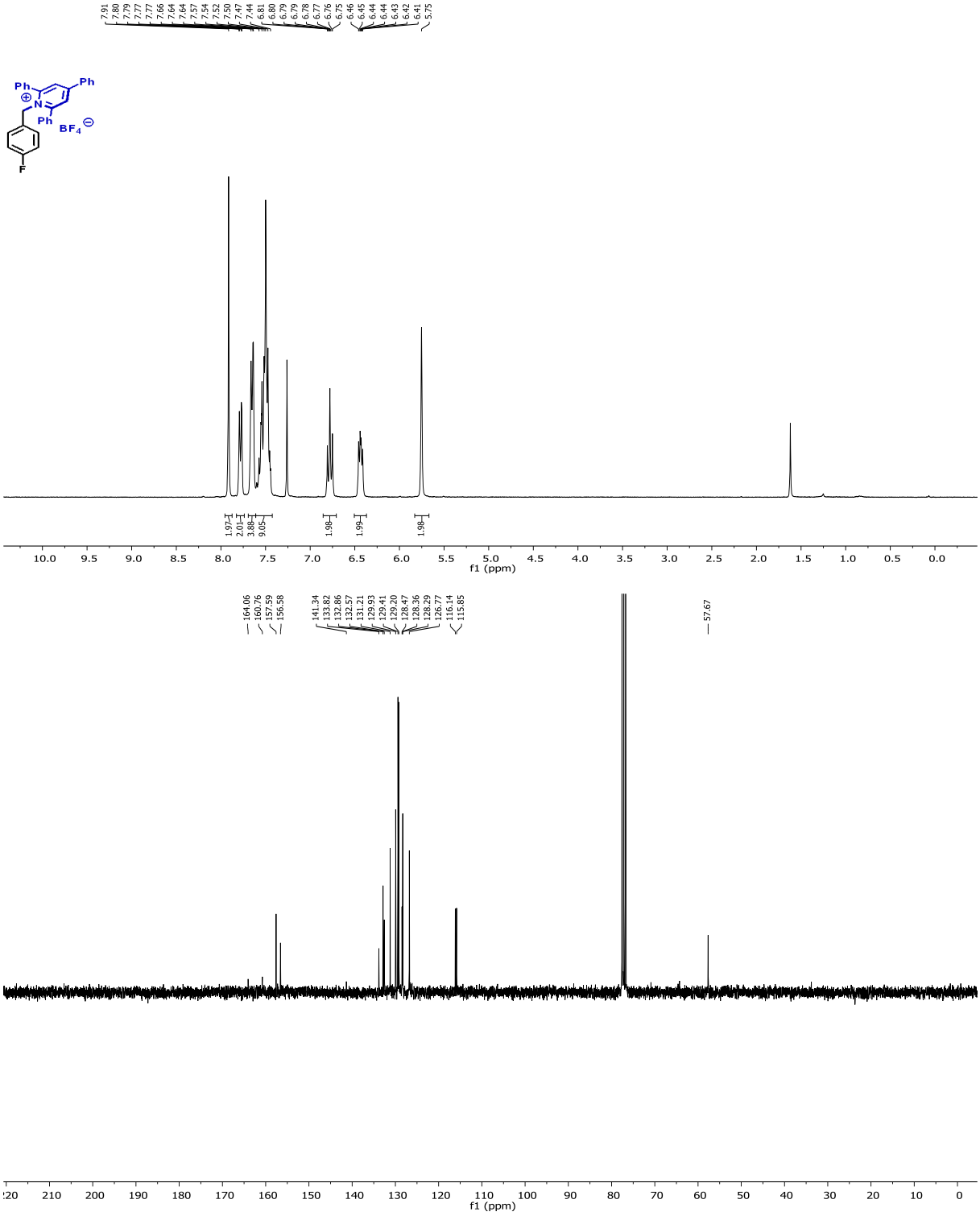

-153.05
-153.10
-153.11
-153.11
-153.11
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230
f1 (ppm)

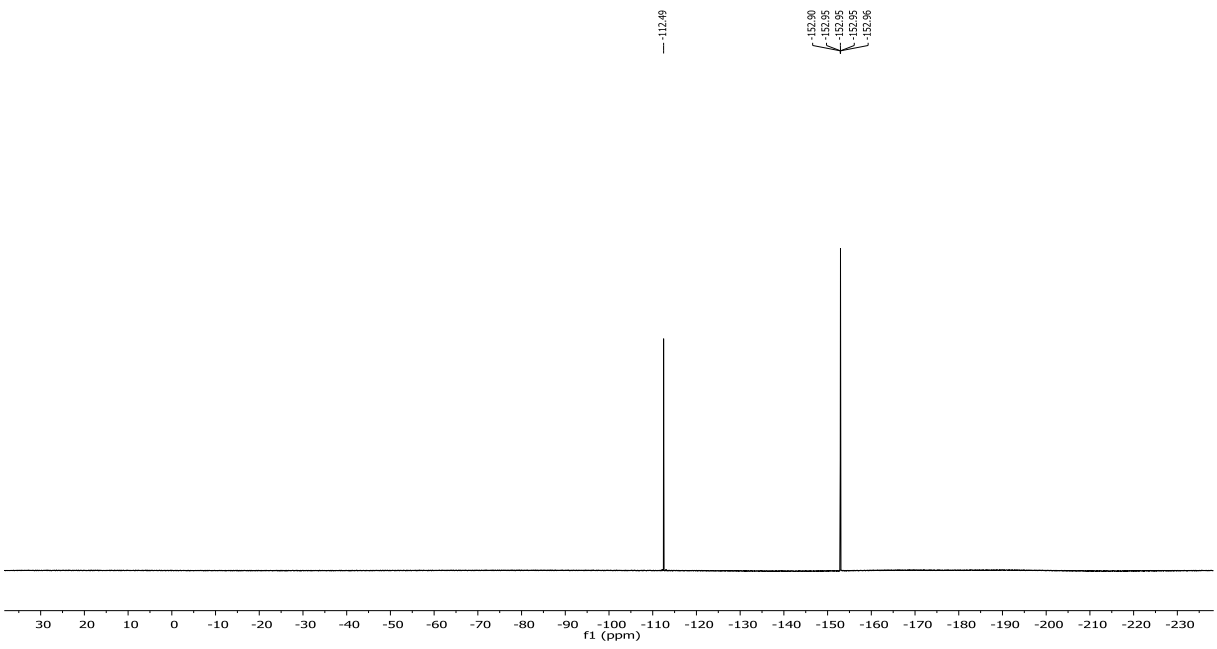
1-(4-Methylbenzyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate



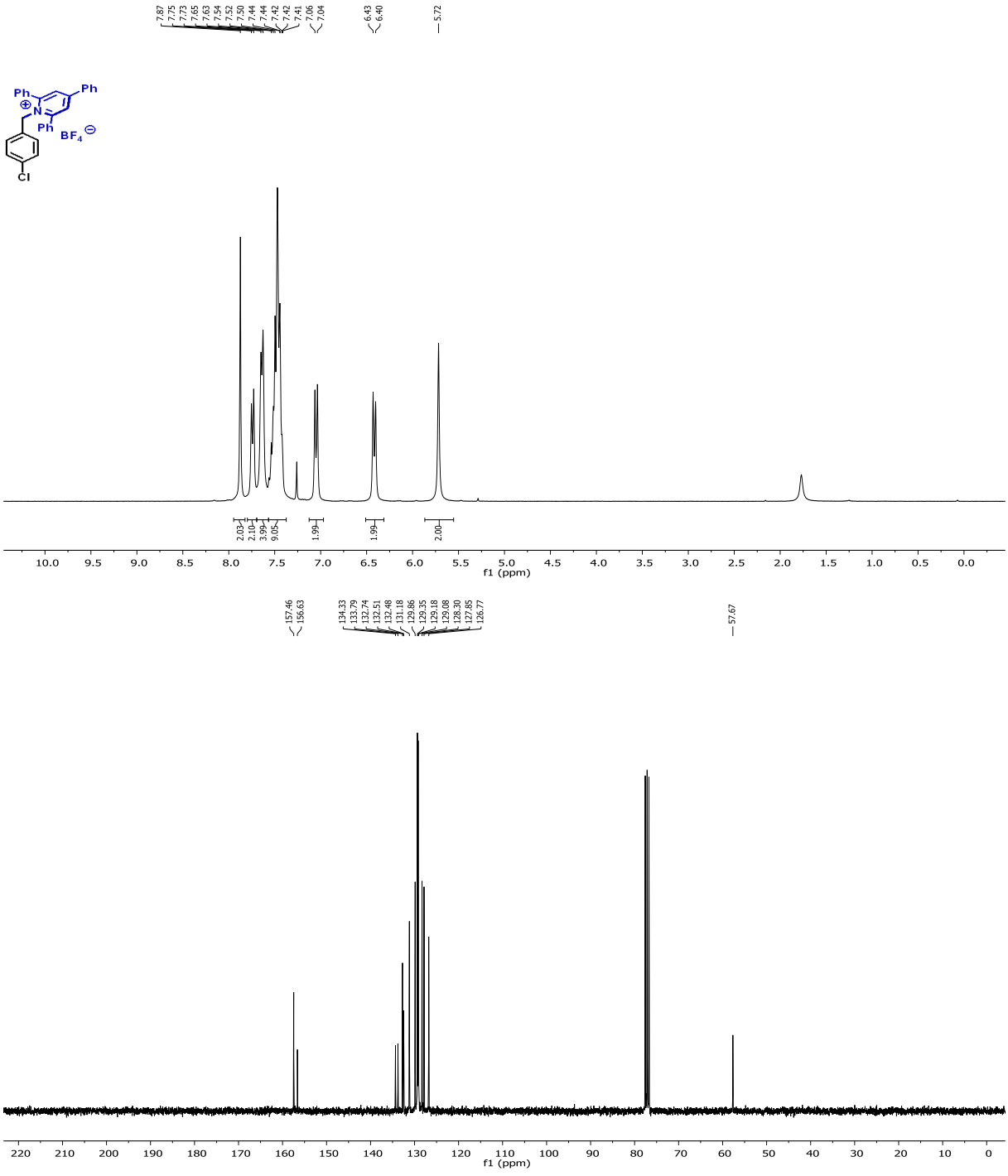

-153.16
-153.21
-153.21
-153.22
-153.22
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230
f1 (ppm)

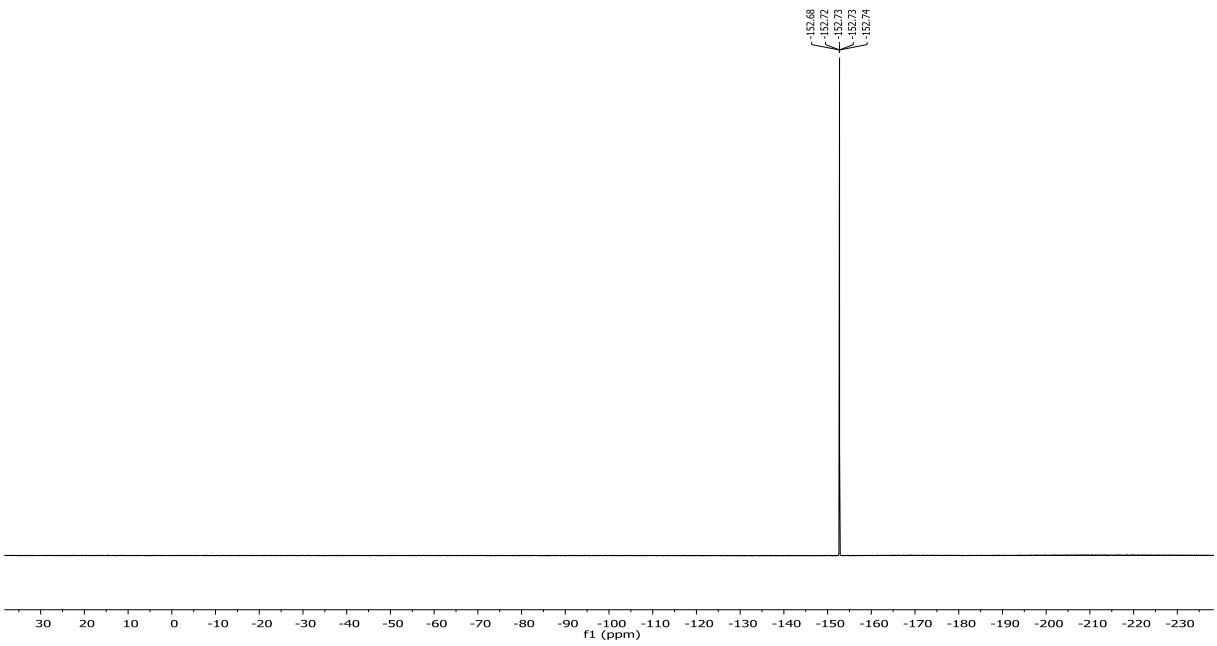
1-(4-Fluorobenzyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate



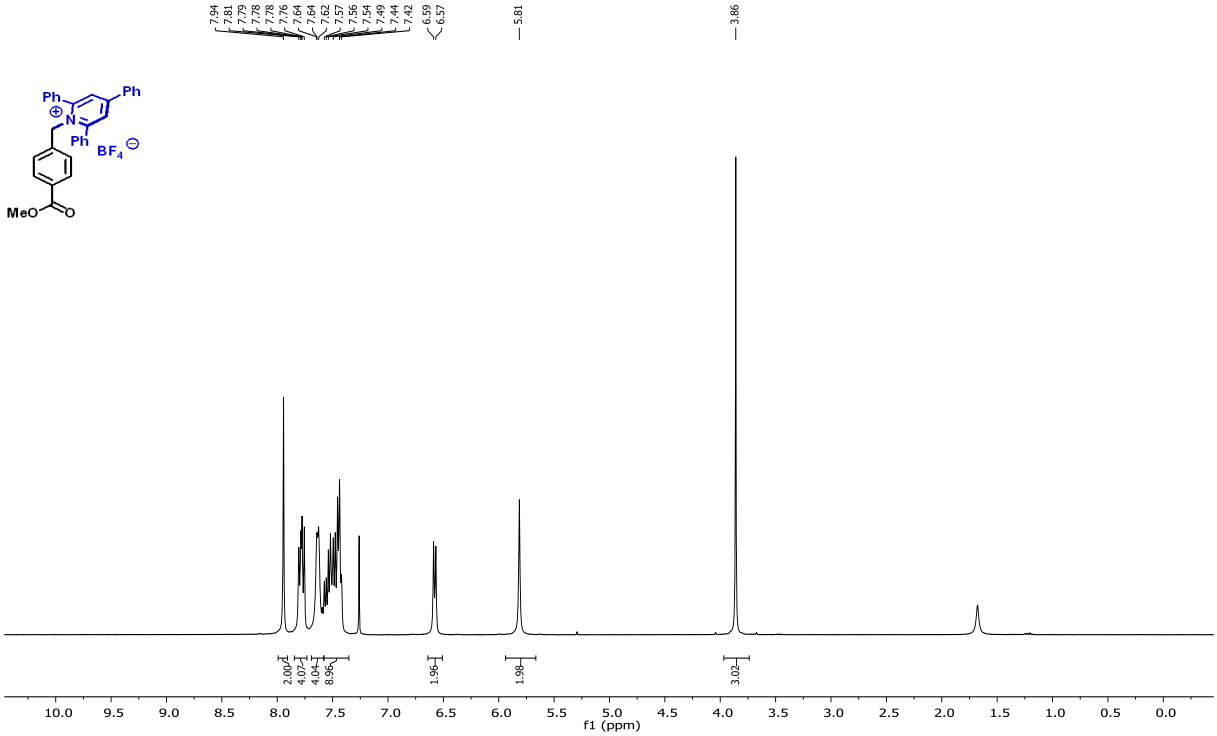

-112.49
-152.90
-152.95
-152.95
-152.95
-152.96
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230
f1 (ppm)

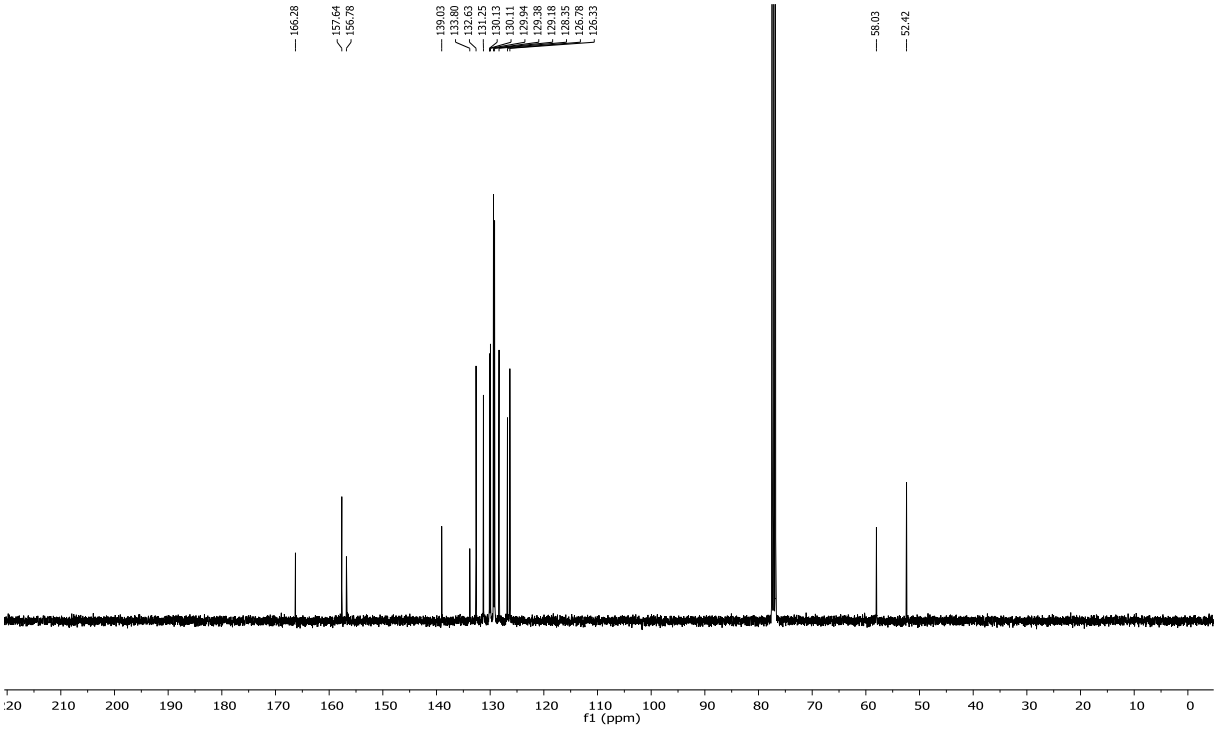
1-(4-Chlorobenzyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate

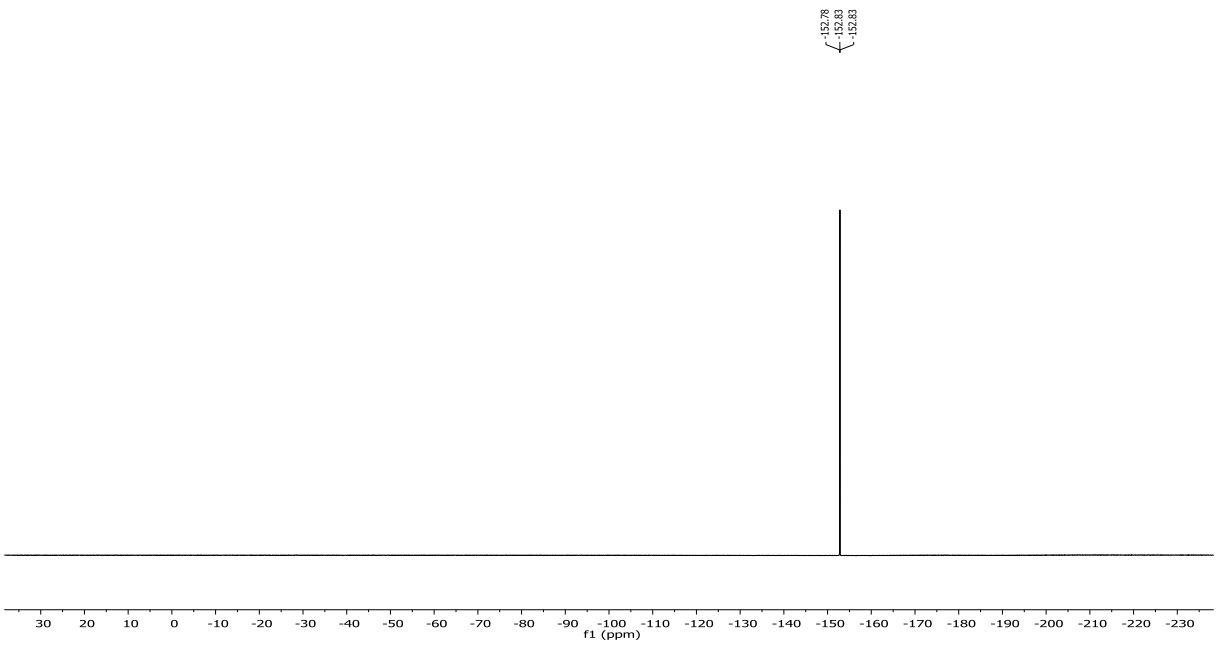



-152.68
-152.72
-152.73
-152.73
-152.74
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230
f1 (ppm)

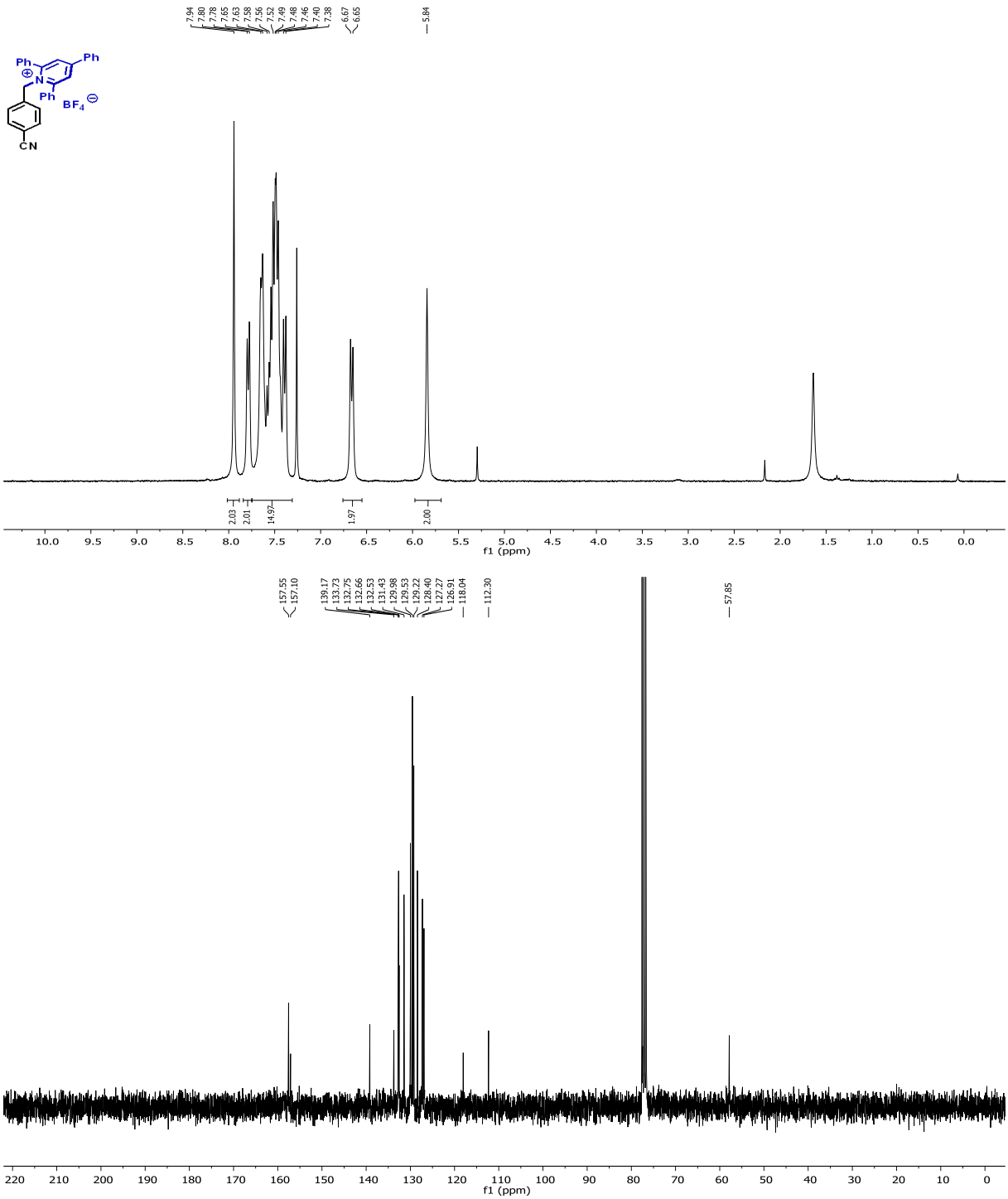
1-(4-(Methoxycarbonyl)benzyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate

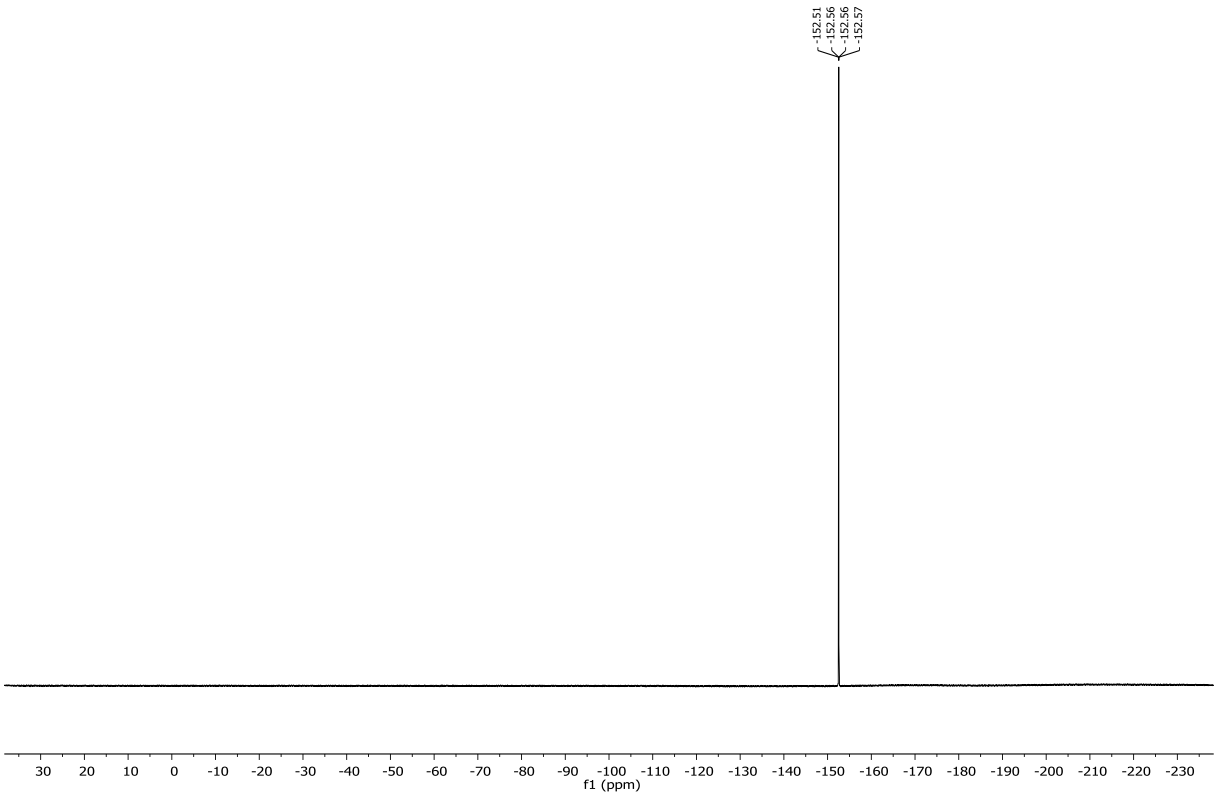




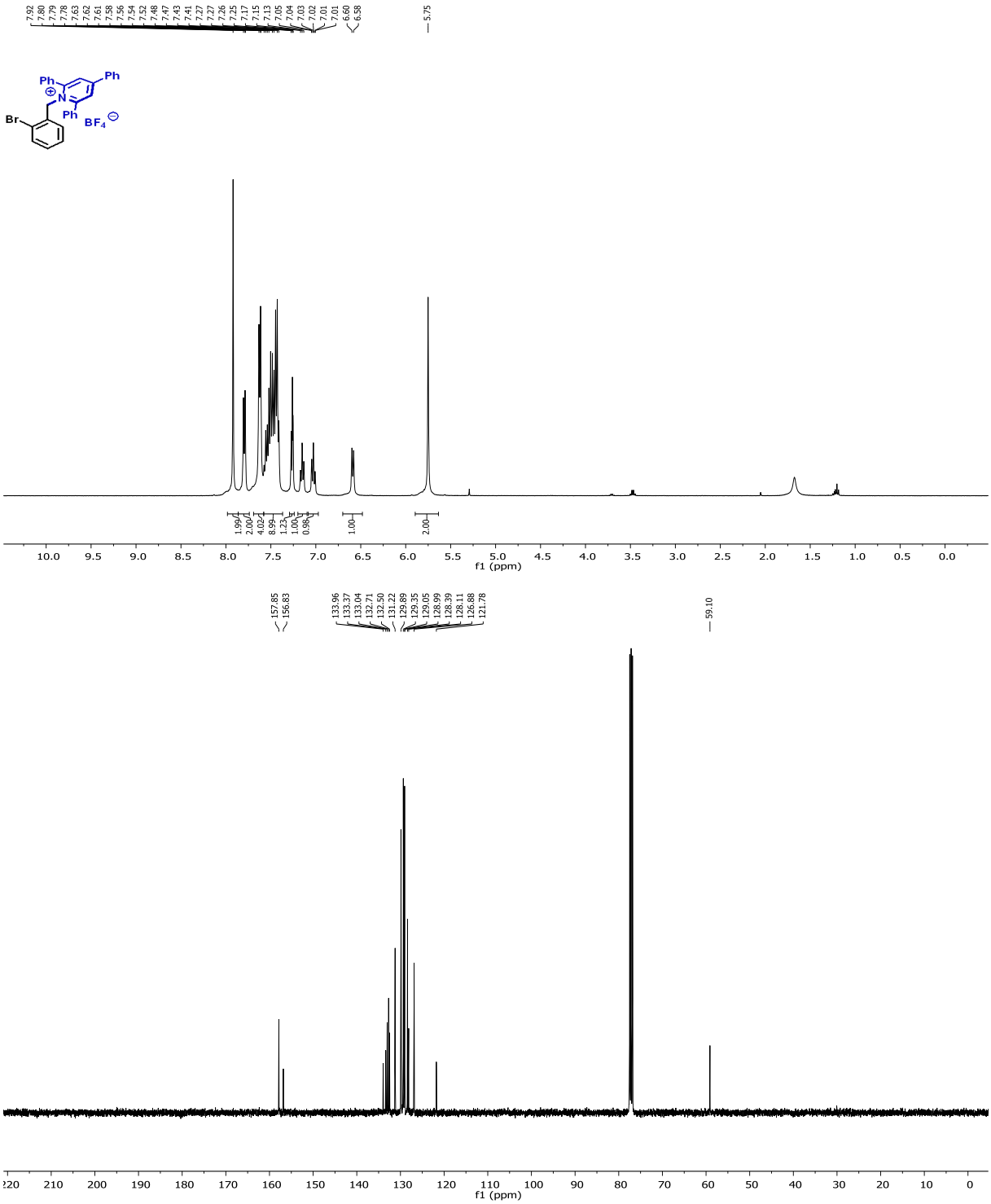

-152.78
-152.83
-152.83
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230
f1 (ppm)

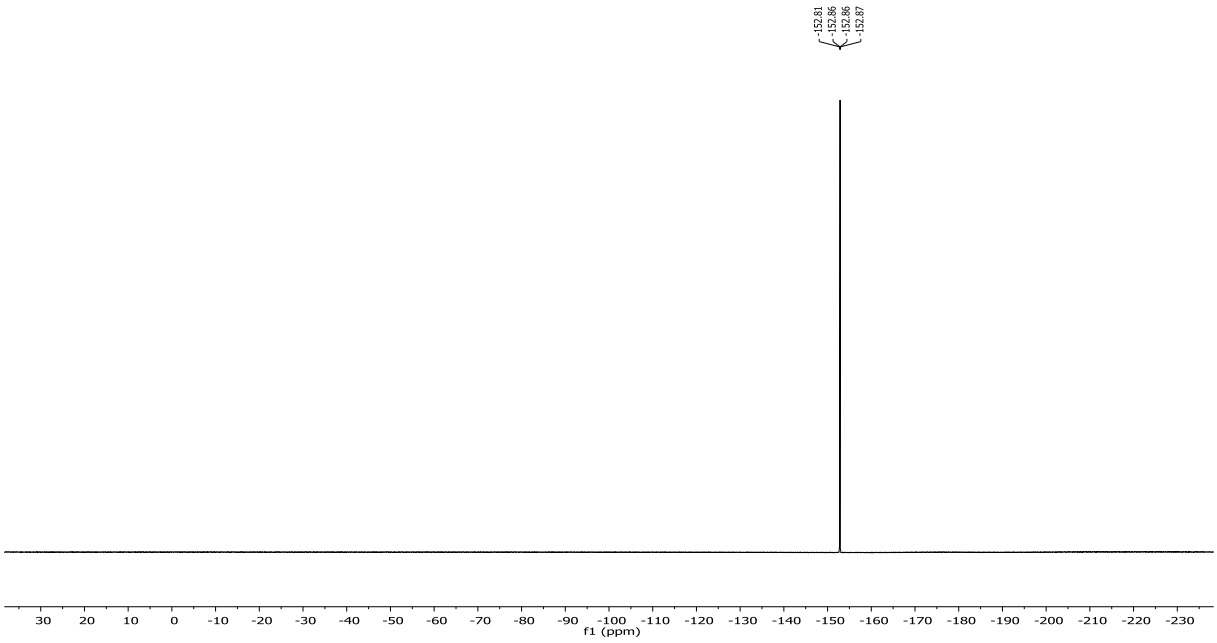
1-(4-Cyanobenzyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate



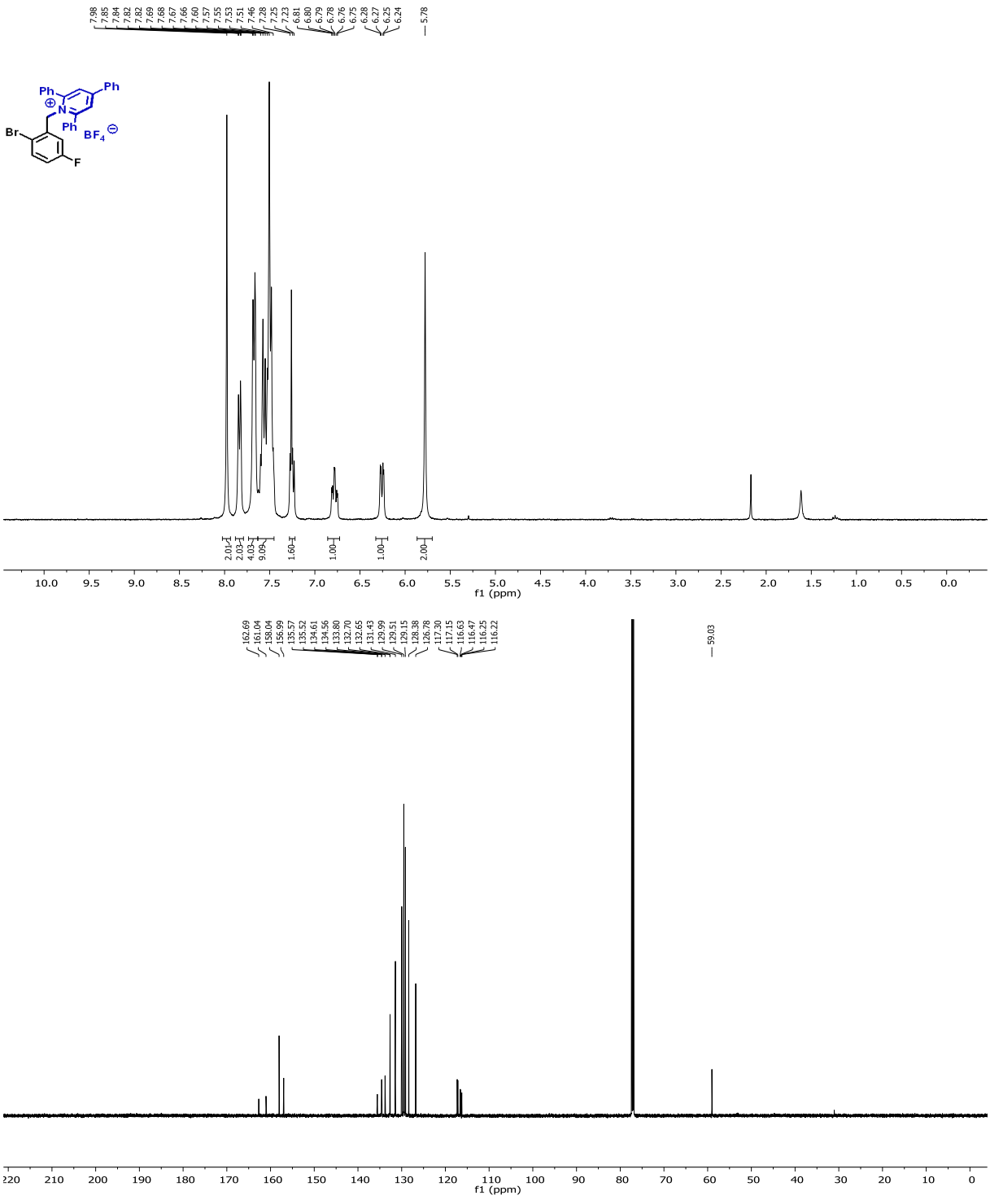

-152.51
-152.56
-152.56
-152.57
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230
f1 (ppm)

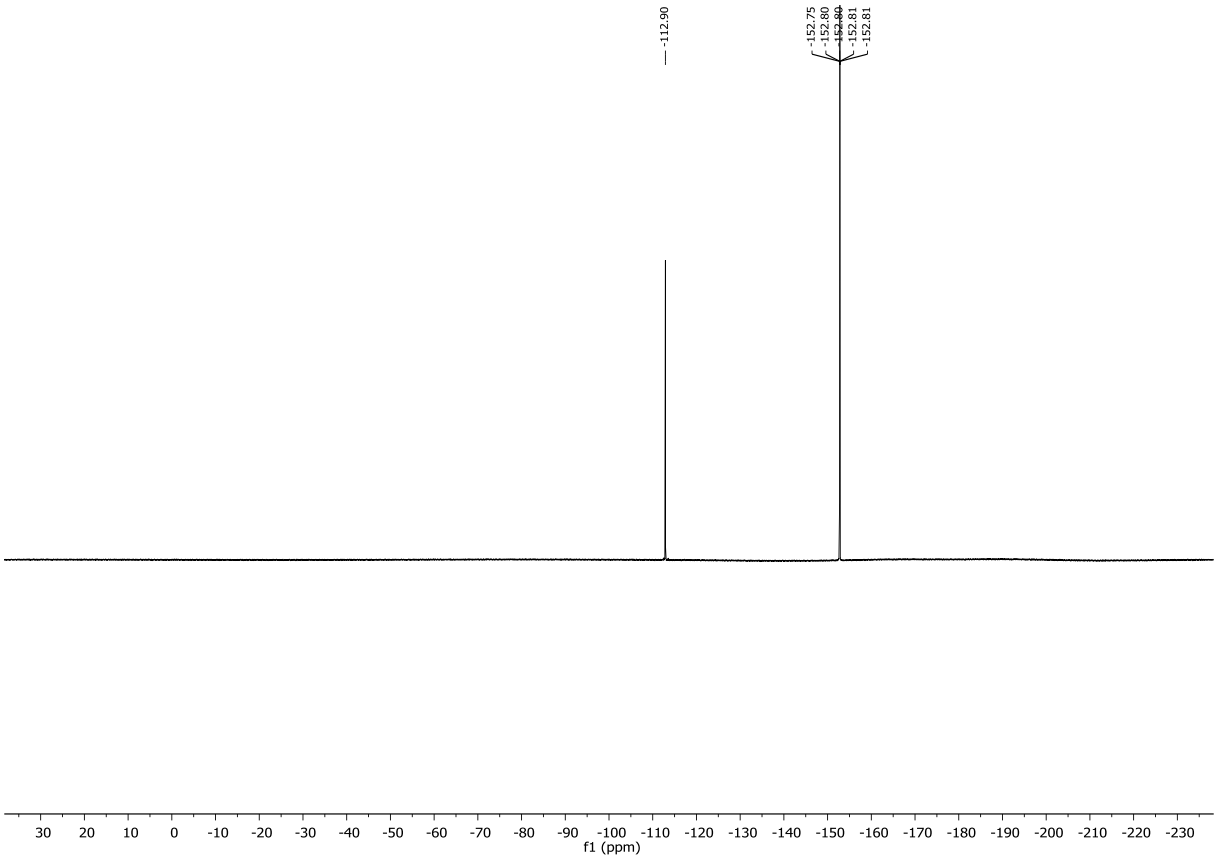
1-(2-Bromobenzyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate



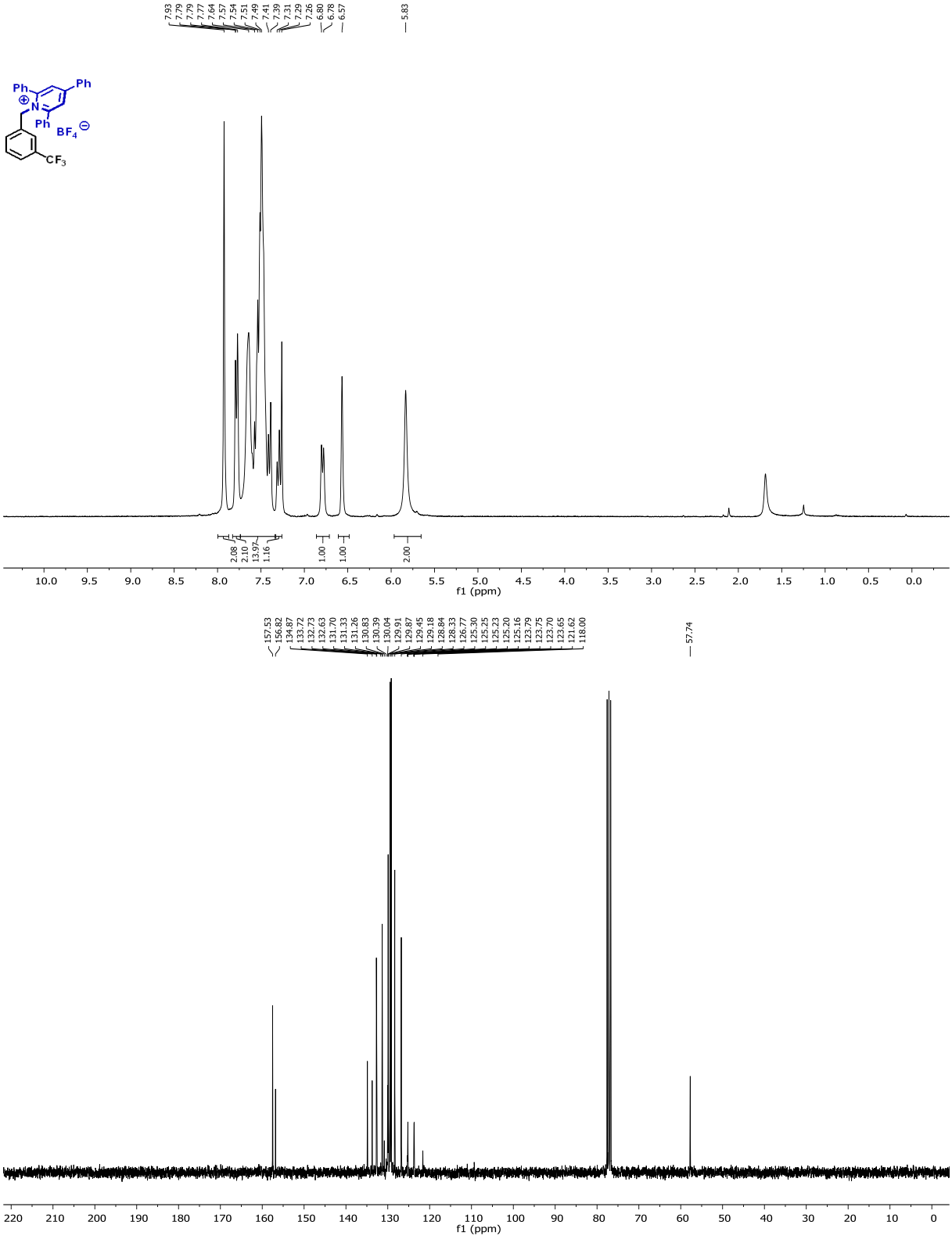

-152.81
-152.86
-152.86
-152.87
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230
f1 (ppm)

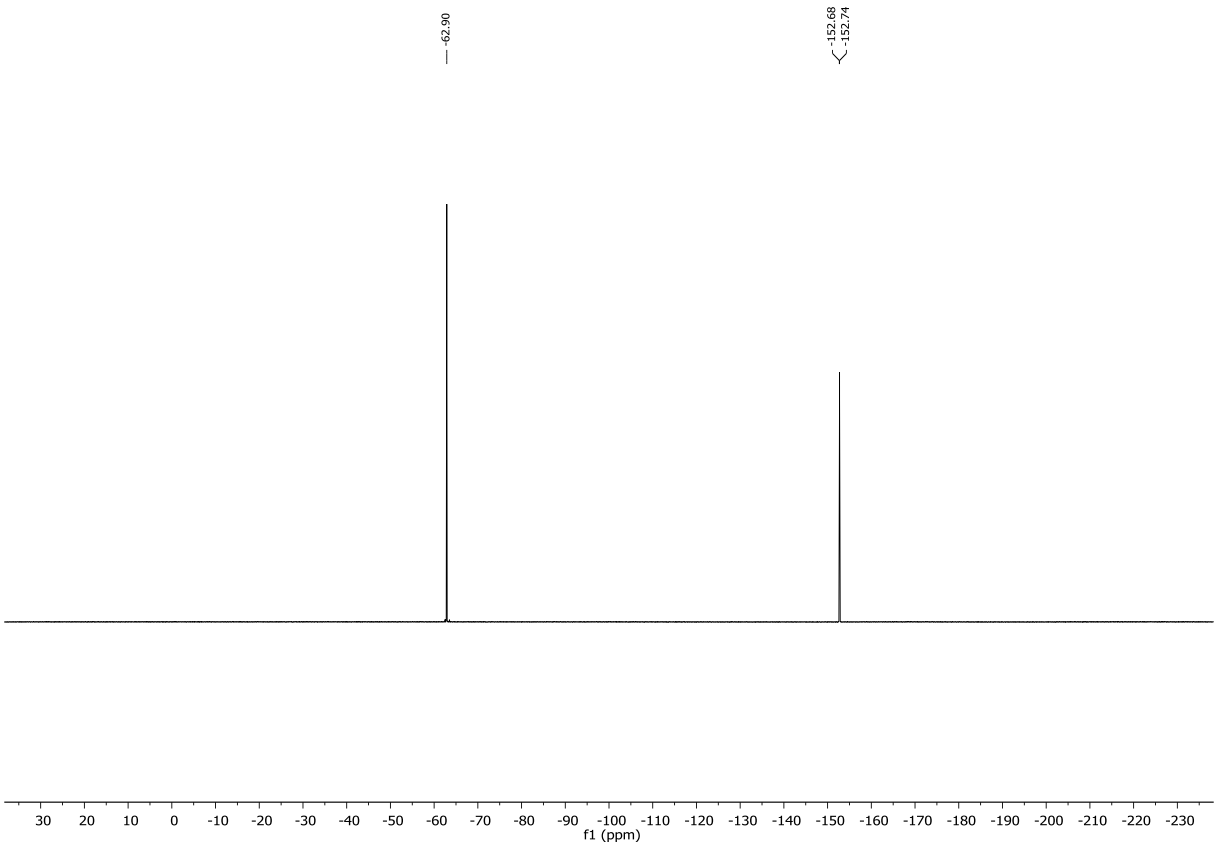
1-(2-Bromo-5-fluorobenzyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate



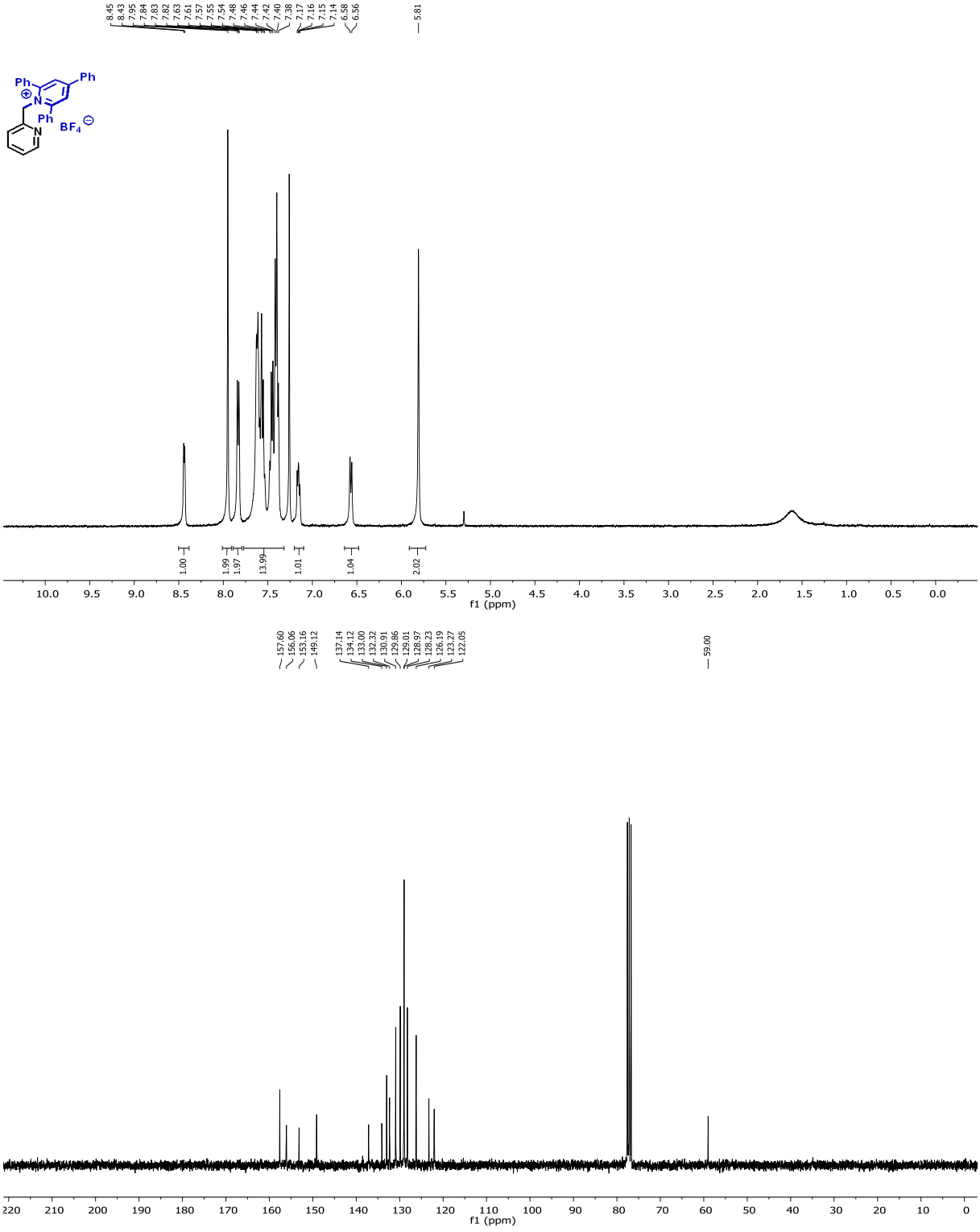

-112.90
-152.75
-152.80
-152.81
-152.81
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230
f1 (ppm)

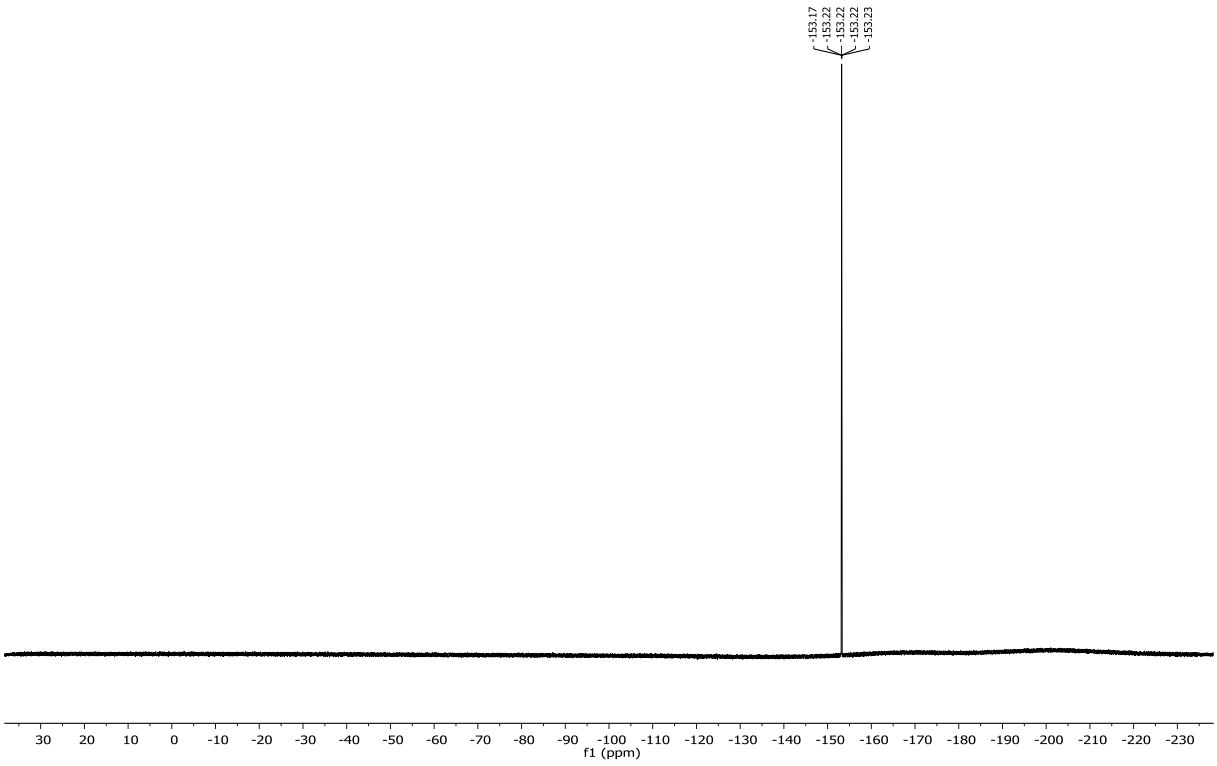
2,4,6-Triphenyl-1-(3-(trifluoromethyl)benzyl)pyridin-1-ium tetrafluoroborate



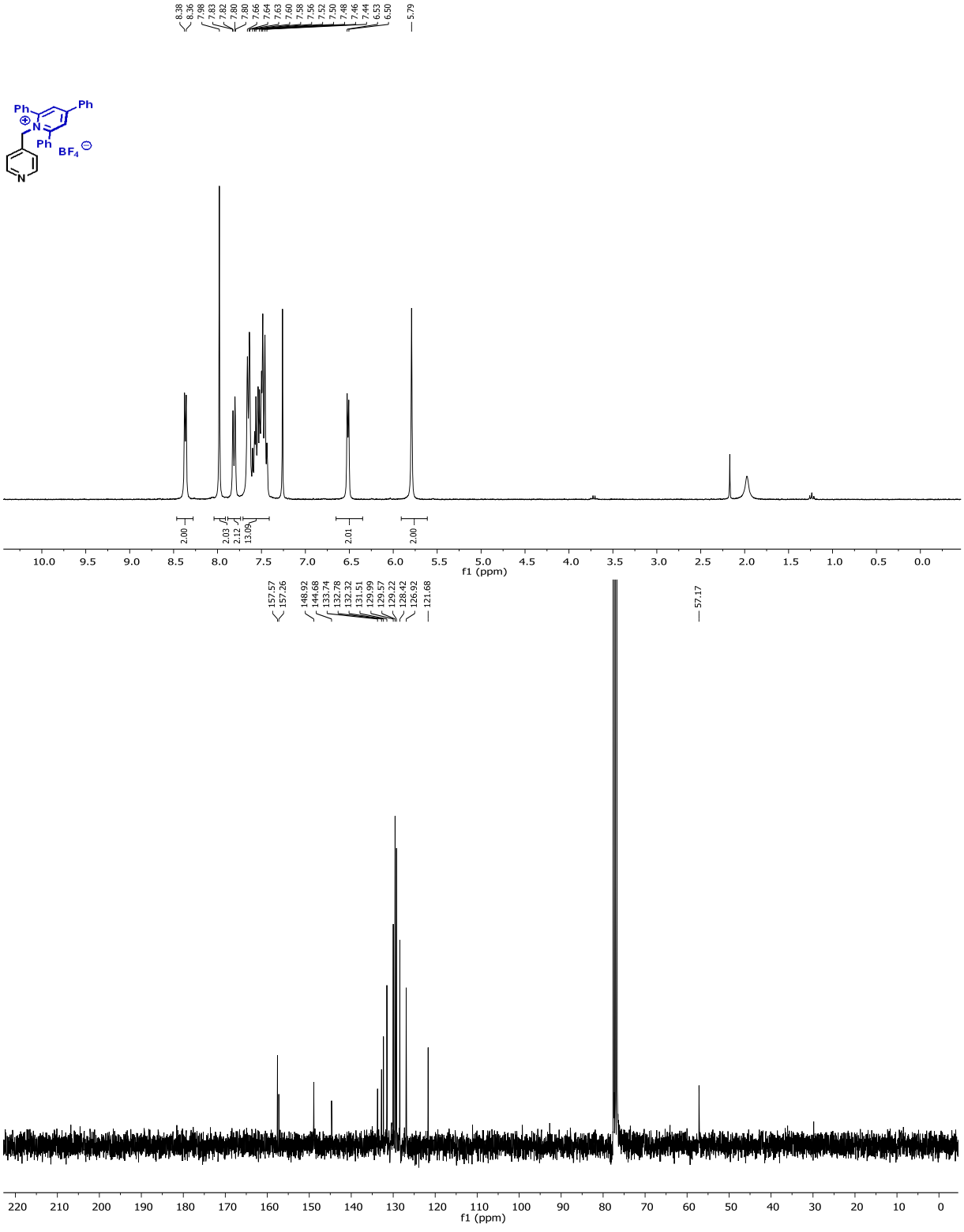

-62.90
-152.68
-152.74
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230
f1 (ppm)

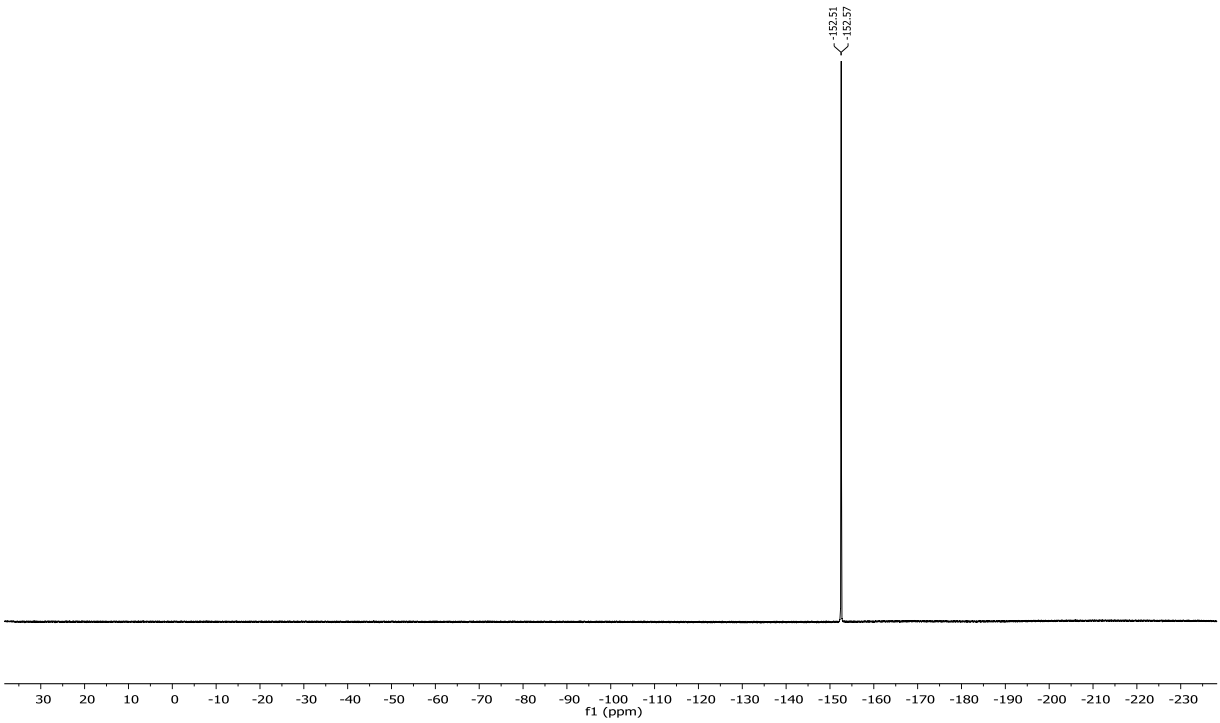
2,4,6-Triphenyl-1-(pyridin-2-ylmethyl)pyridin-1-ium tetrafluoroborate



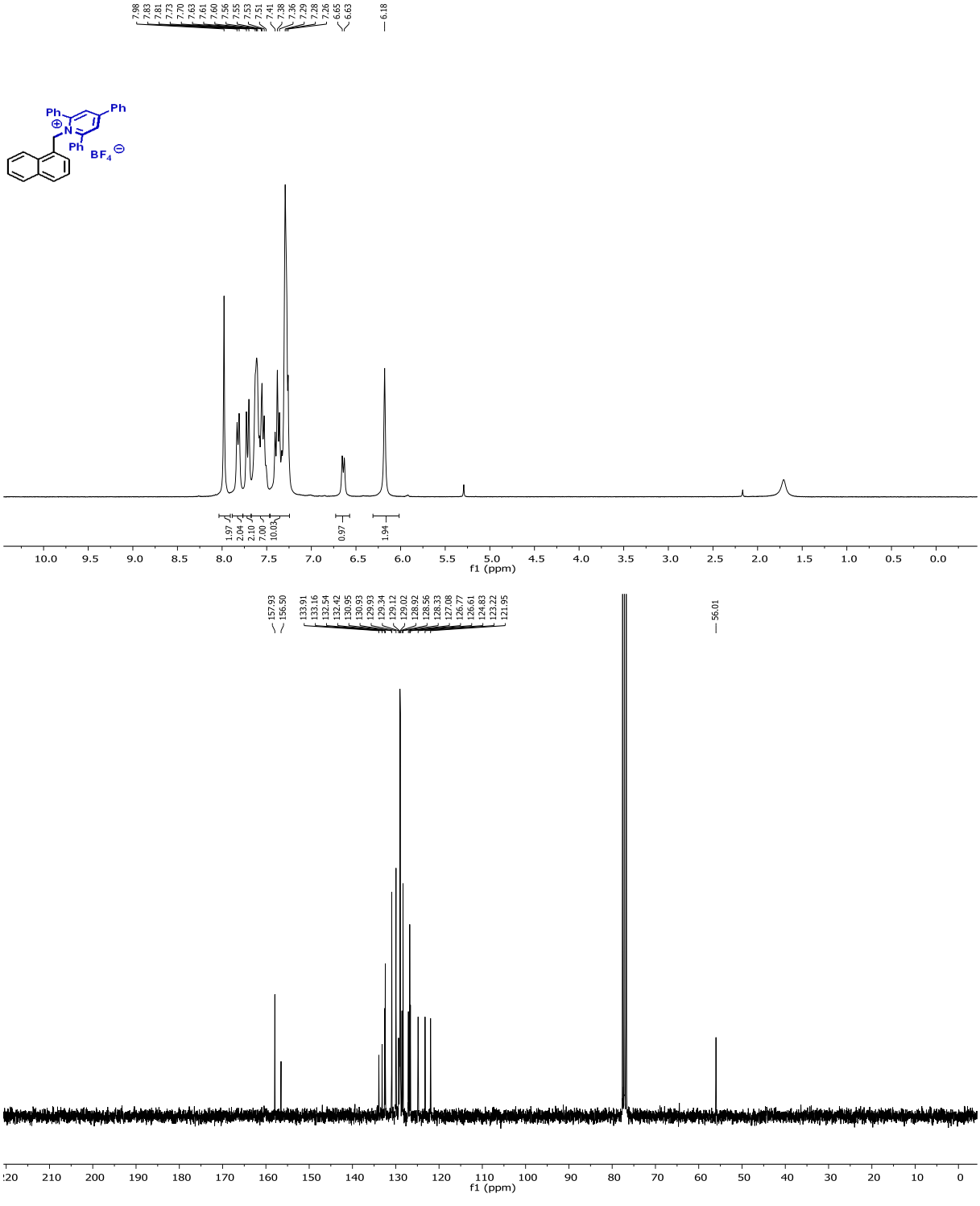

-153.17
-153.22
-153.22
-153.22
-153.23
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230
f1 (ppm)

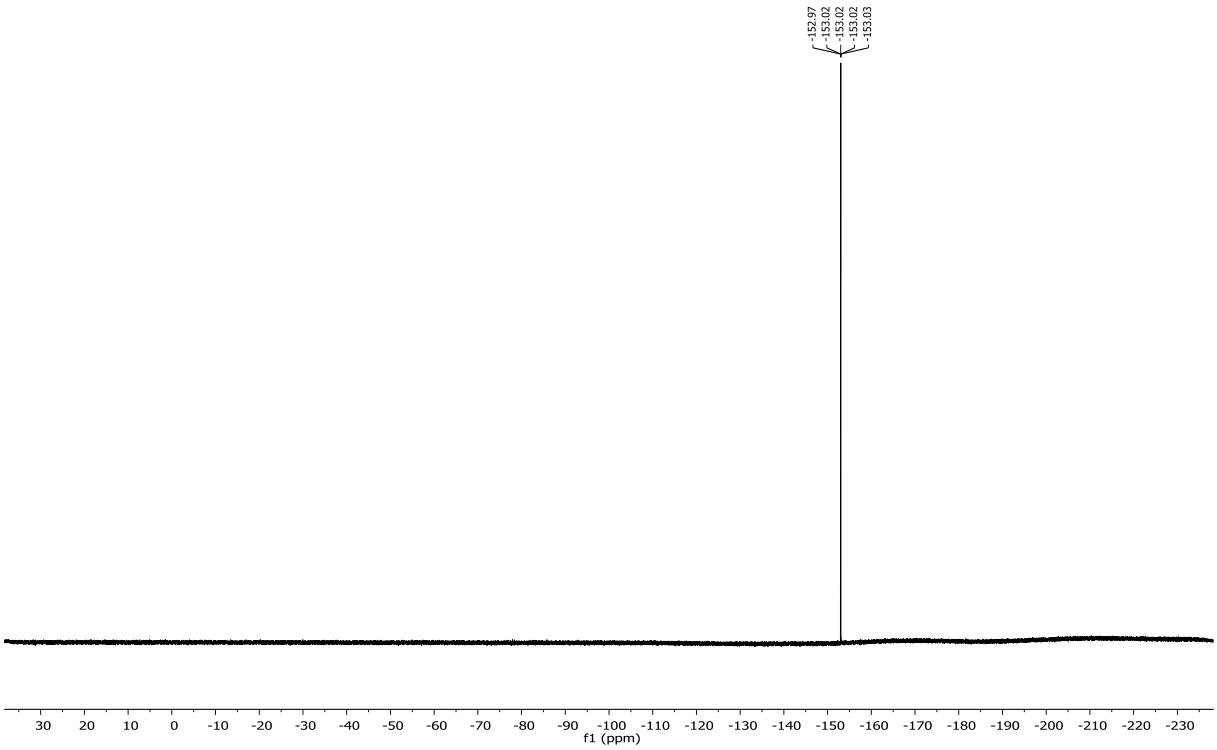
2,4,6-Triphenyl-1-(pyridin-4-ylmethyl)pyridin-1-ium tetrafluoroborate



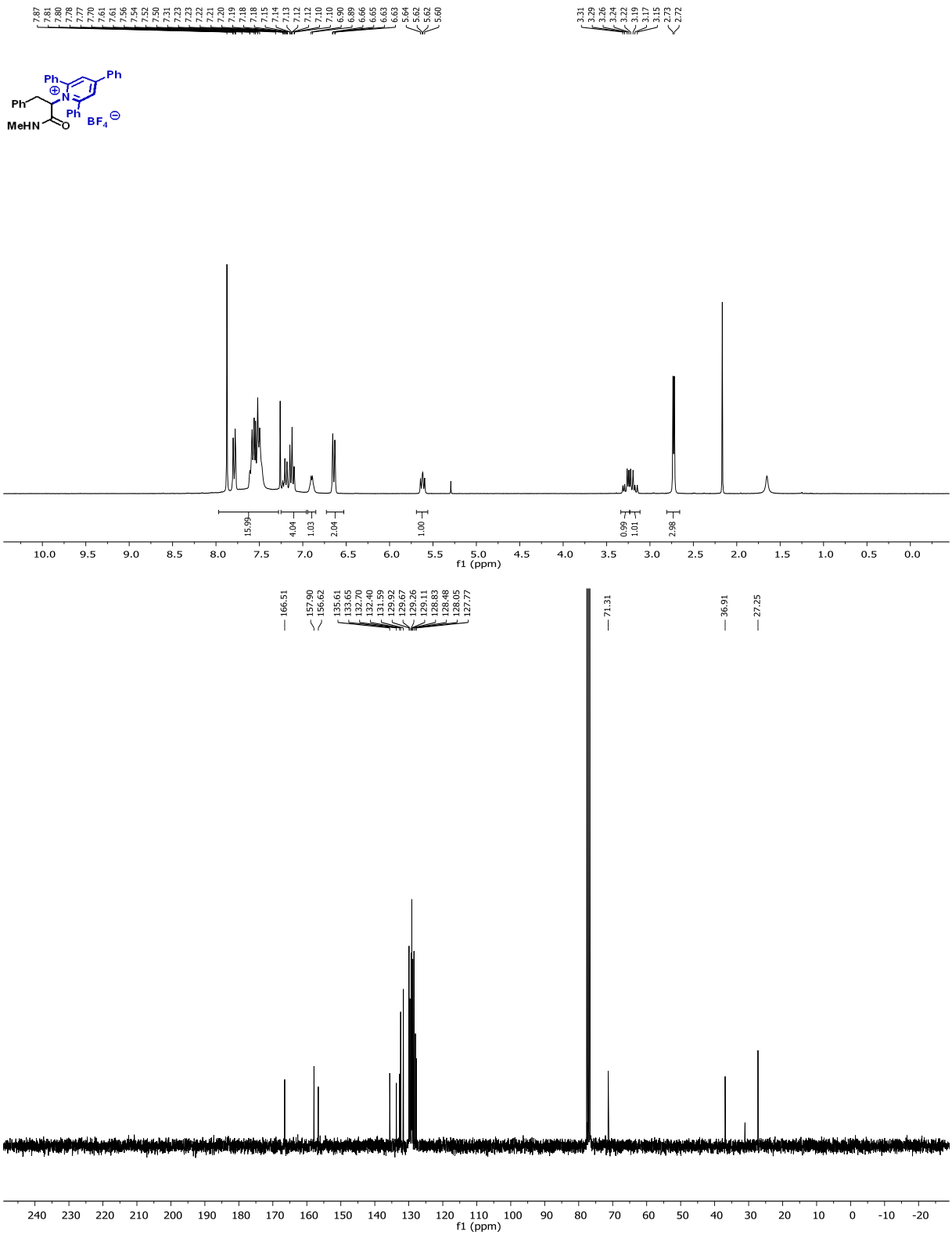

-152.51
-152.57
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230
f1 (ppm)

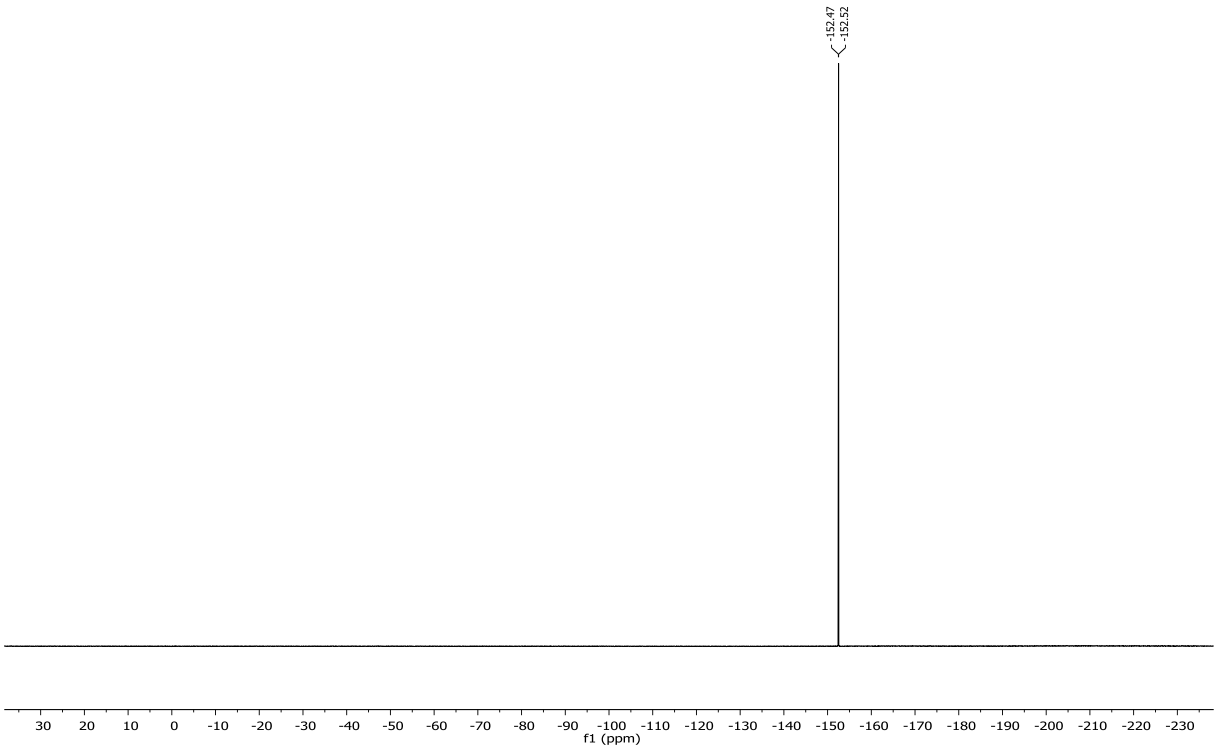
1-(Naphthalen-1-ylmethyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate



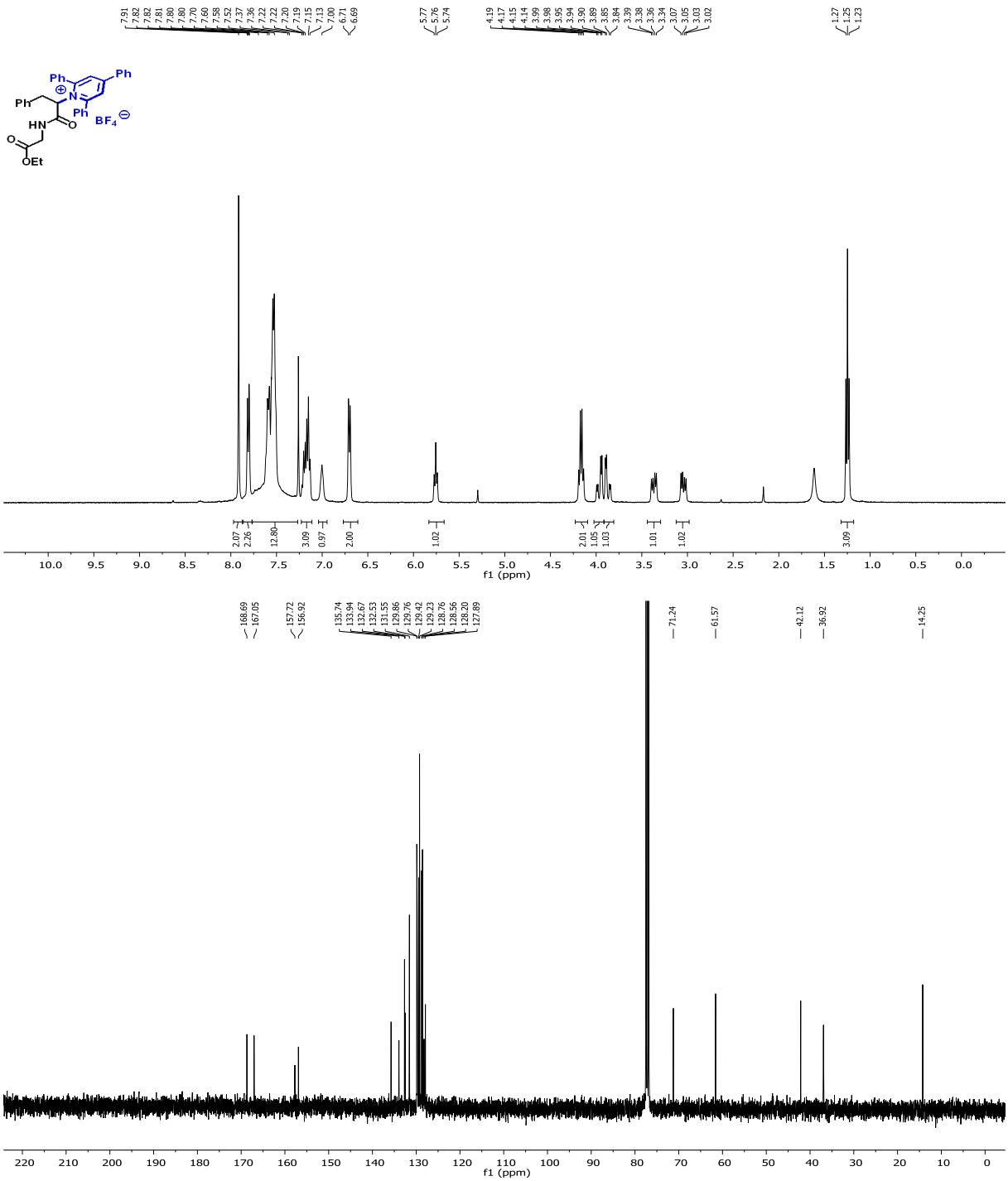

-152.97
-153.02
-153.02
-153.02
-153.03
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230
f1 (ppm)

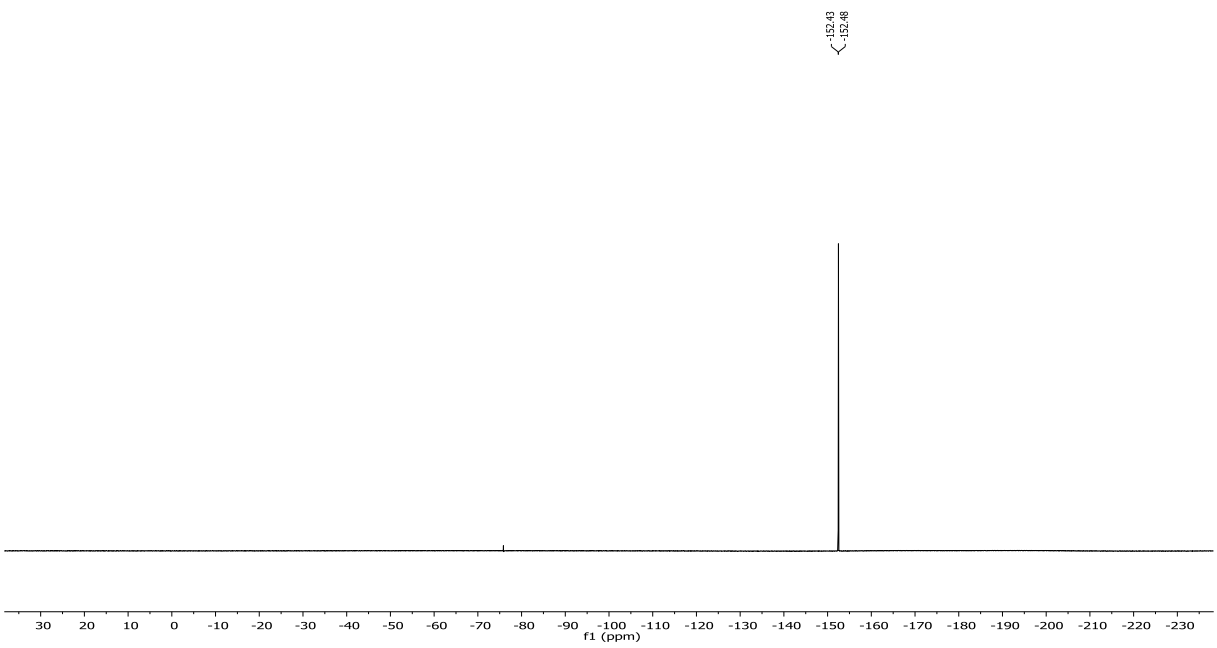
1-(1-(Methylamino)-1-oxo-3-phenylpropan-2-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate



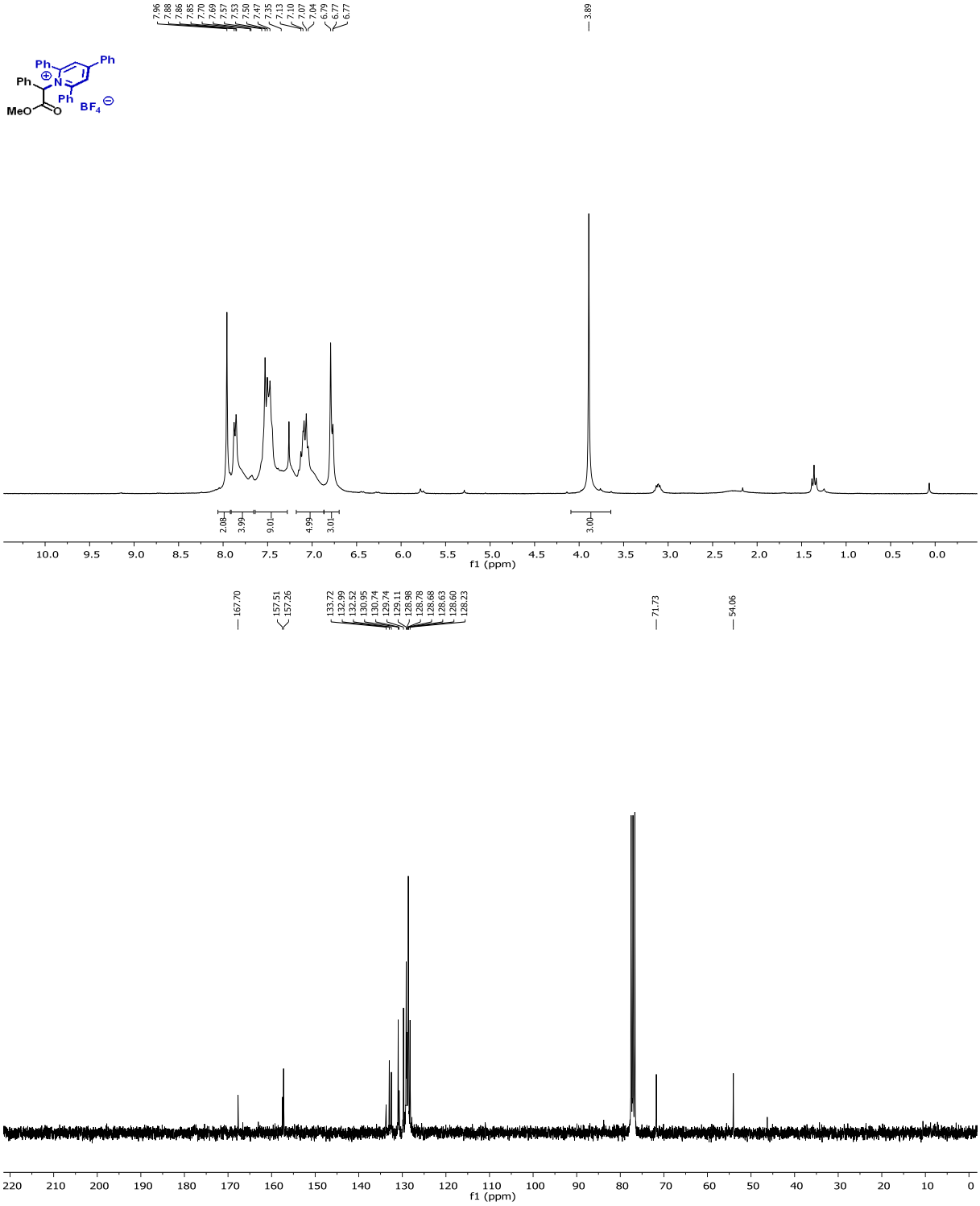

-152.47
-152.52
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230
f1 (ppm)

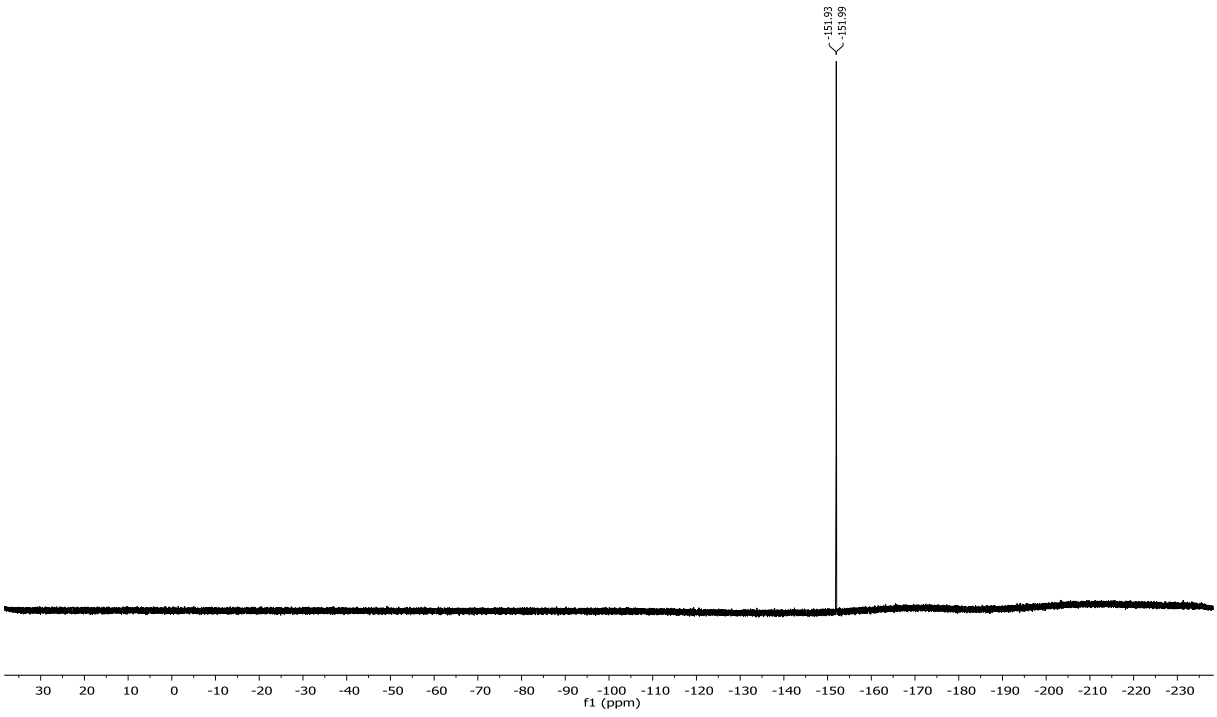
1-(1-((2-Ethoxy-2-oxoethyl)amino)-1-oxo-3-phenylpropan-2-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate



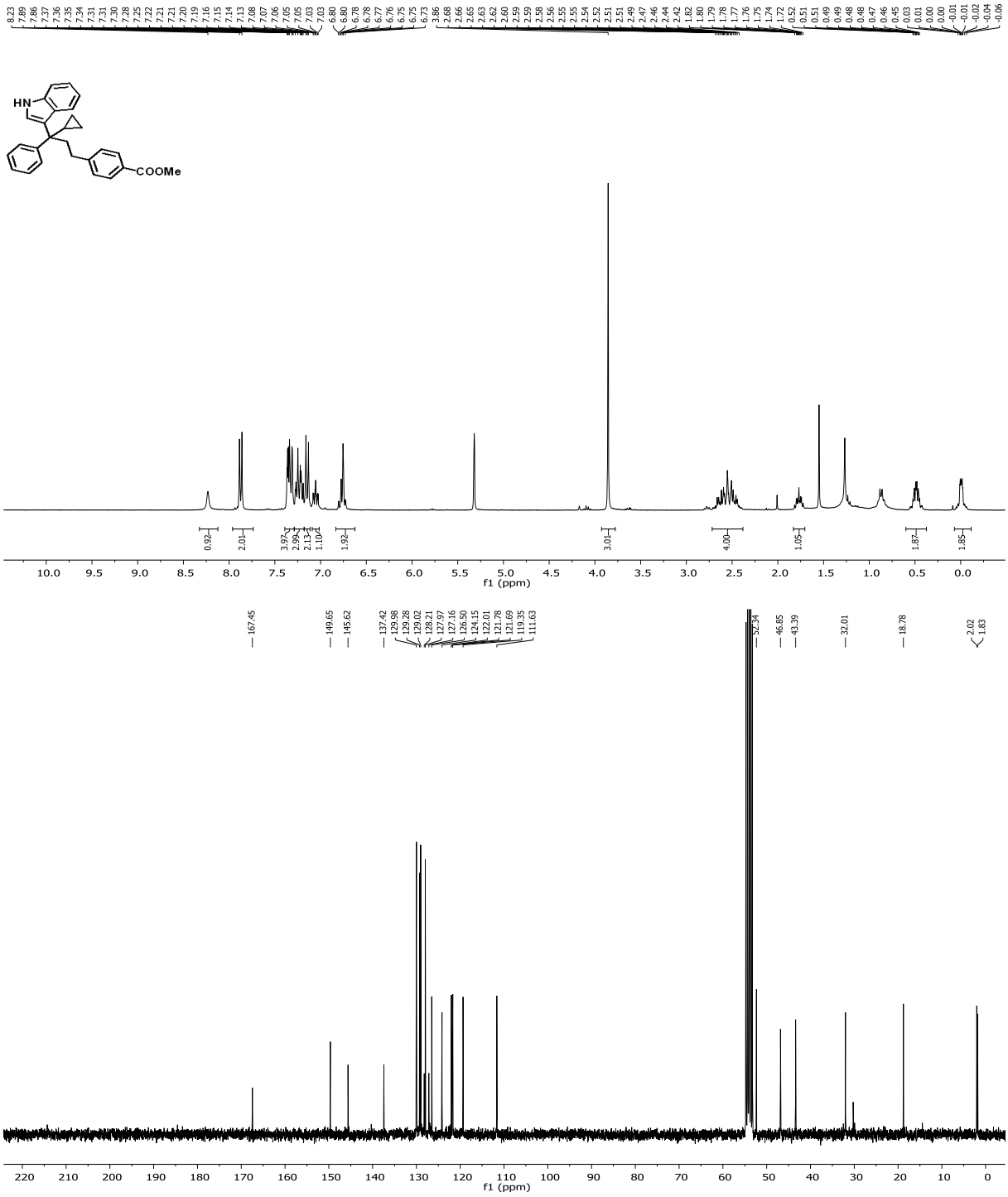

-152.43
-152.48
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230
f1 (ppm)

1-(2-Methoxy-2-oxo-1-phenylethyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate




-151.93
-151.99
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230
f1 (ppm)

Methyl 4-(3-cyclopropyl-3-(1*H*-indol-3-yl)-3-phenylpropyl)benzoate (4ad)



Methyl 4-(2-(3,4-dihydronaphthalen-1-yl)ethyl)benzoate (5b)