Supporting Information

Simple Amine-Directed *meta*-Selective C−H Arylation via Pd/Norbornene Catalysis

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Table of Contents

I. Materials and methods

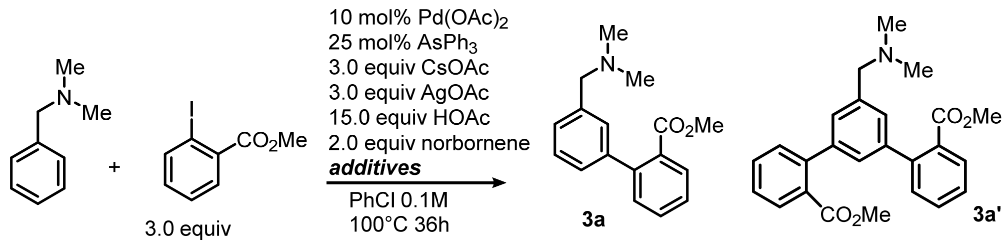
Unless stated otherwise, all reactions were run in vials sealed with PTFE lined caps, purchased from Qorpak. Chlorobenzene (99% HPLC level) was directly used as received from Arcos. Triphenylarsine ($AsPh_3$, 99%), Copper acetate monohydrate (99%) and palladium acetate (98%) were purchased from Strem and used as received. Cesium acetate (CsOAc) and lithium acetate dihydrate were purchased from Alfa and used as received. All commercially available substrates were used without further purification. Thin layer chromatography (TLC) analysis was run on silica gel plates purchased from EMD Chemical (silica gel 60, F254). Gas chromatography (GC) data was obtained from Agilent 7820A GC system, equipped with Agilent 19091J-413 column and a FID detector. GC yield of **3a** and **3a'** was determined using standard curves with dodecane as internal standard. Mass spectra were recorded on an Autospec or Agilent 6150. Accurate masses from high-resolution mass spectra were reported for the molecular ion $[M+Na]^+$, $[M]^+$ or $[M+H]^+$. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian Gemini (400 MHz for ^{1}H, 100 MHz for ^{13}C). Chemical shifts are reported as parts per million (ppm) using residual solvent signals as internal standard ($CDCl_3$, δ = 7.26 ppm for ^{1}H NMR, δ = 77.00 ppm for ^{13}C NMR; DMSO-d_6, δ = 2.50 ppm for ^{1}H NMR, δ = 39.50 ppm for ^{13}C NMR; MeCN-d_3, δ = 1.94 ppm for ^{1}H NMR, δ = 1.32, 118.26 ppm for ^{13}C NMR). Data for ^{1}H NMR were presented as following: chemical shifts (δ, ppm), multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, tt = triplet of triplets, td = triplet of doublets, m = multiplet), coupling constant (Hz), and integration. The chemical shifts of peaks found were reported for ^{13}NMR spectra. Infrared spectra were obtained from a Nicolet iS5 FTIR spectrometer.

General procedure for reaction-condition screening

The reaction was run at a 0.2 mmol scale based on the limiting reagent. A 4 mL vial was charged with palladium salt, ligand, additives, benzylamine derivative, aryl iodide, chlorobenzene (1.8 mL) and HOAc. The vial was sealed with a PTFE lined cap and heated in a pie-block at 100 °C for 36 hours under stirring. Then the mixture was allowed to cool to room temperature. The saturated potassium carbonate aqueous solution (2 mL) was carefully added to the vial to make the whole solution basic. The vial were kept stirring at room temperature for 15 min before the solid was filtered. The filter cake was further washed with ethyl acetate (containing 8% triethylamine), filtrate were collected together with the aqueous phase. The appropriate amount of dodecane (~10 mg) was added as the internal standard to the filtrate. The mixture was stirred for an additional 5 min. The filtrate was directly used for GC analysis.

GC instrument conditions: inlet temperature: 250 °C, detector temperature: 300 °C, hydrogen flow: 40 mL/min, air flow: 400 mL/min, column + makeup flow: 30 mL/min. Method: 50 °C hold for 0 min, followed by a temperature increase of 10°C/min to 320 °C, hold 0 min (total run time: 27 min). Yields of the products and byproducts are calculated using standard curves with dodecane as the internal standard. Full details of the control reactions are listed below (Tables S1-S4).

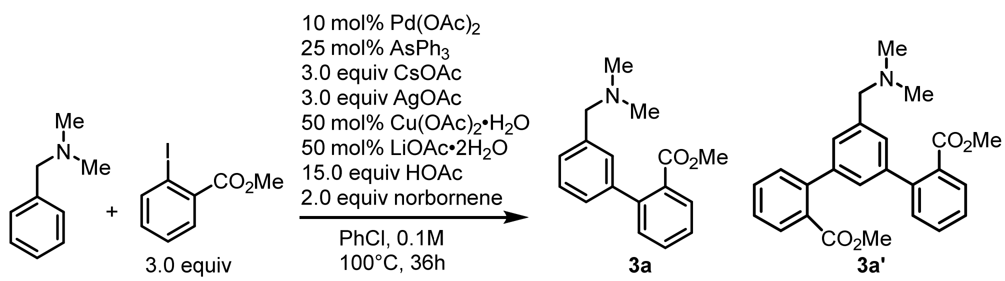
Table S1. Full details of salts effect:[a]



Additives	yield of **3a**	yield of **3a'**	Total yield
None	7%	53%	60%
50 mol% $Cu(OAc)_2 \cdot H_2O$	8%	48%	54%
50 mol% $LiOAc \cdot 2H_2O$	10%	54%	64%
50 mol% $Cu(OAc)_2 \cdot H_2O$ and 50 mol% $LiOAc \cdot 2H_2O$	9%	60%	69%
KOAc instead of CsOAc	8%	46%	54%
NaOAc instead of CsOAc	9%	42%	51%
50 mol% of $Zn(OAc)_2$	10%	47%	57%
None 130°C 18h	13%	47%	60%

[a] *All yields were determined by GC using dodecane as the internal standard.*

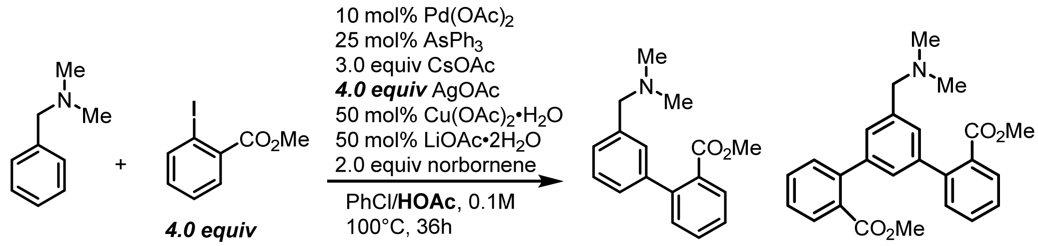
Table S2. Selected ligand and solvent effect: [a]



Change from above conditions	yield of **3a**	yield of **3a'**	Total yield
None	2%	60%	62%
tAmyOH instead of PhCl	15.5%	26.5%	42%
TFE instead of PhCl	0%	0%	0%
PPh_3 instead of $AsPh_3$	15%	12%	27%
SPhos instead of $AsPh_3$	13%	12%	25%

[a] *All yields were determined by GC using dodecane as the internal standard.*

Table S3. Acetic acid equivalent effect: [a]

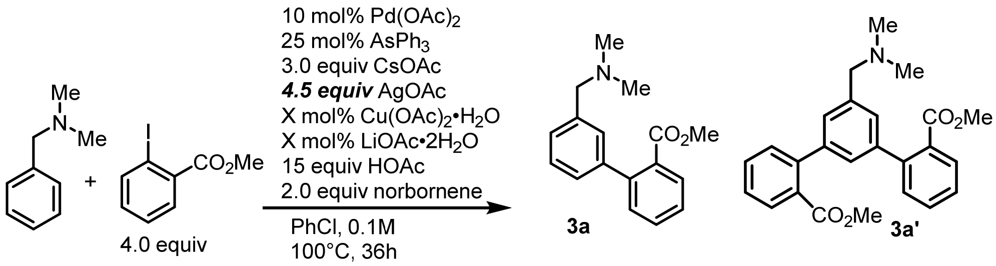


3a
3a'

	recovery yield of **1a**	yield of **3a**	yield of **3a'**	**Total yield**
PhCl/HOAc = 1 : 1	39%	4%	2.2%	6.2%
PhCl/HOAc = 3 : 1	6%	14%	19%	33%
PhCl/HOAc = 5 : 1	3%	12.3%	27.6%	40%
PhCl/HOAc = 10 : 1 (15 equiv)	1%	12.4%	43.5%	56%
HOAc 5.0 equiv	33%	20%	6%	26%
HOAc 1.0 equiv	41%	7%	4%	11%

[a]*All yields were determined by GC using dodecane as the internal standard.*

Table S4. The salts equivalent effect: [a]

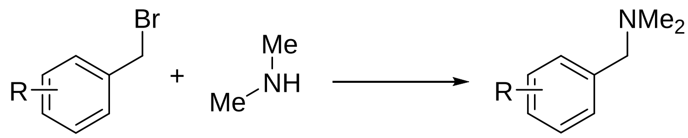


	yield of **3a**	yield of **3a'**	**Total yield**
No $Cu(OAc)_2$•H_2O and LiOAc•$2H_2O$	4%	54%	58%
No $Cu(OAc)_2$•H_2O No LiOAc•$2H_2O$ with 1.0 equiv CsOAc	4%	48%	33%
50 mol% $Cu(OAc)_2$•H_2O 50 mol% LiOAc•$2H_2O$	2%	67%	69%
50 mol% $Cu(OAc)_2$•H_2O No LiOAc•$2H_2O$	2%	63%	65%
No $Cu(OAc)_2$•H_2O 50 mol% LiOAc•$2H_2O$	6%	53%	59%
100 mol% $Cu(OAc)_2$•H_2O 50 mol% LiOAc•$2H_2O$	2%	66%	68%
50 mol% $Cu(OAc)_2$•H_2O 100 mol% LiOAc•$2H_2O$	2%	72%	74%
100 mol% $Cu(OAc)_2$•H_2O 100 mol% LiOAc•$2H_2O$	1%	70%	71%
50 mol% $Cu(OAc)_2$•H_2O 50 mol% LiOAc•$2H_2O$ Under N_2	15%	43%	58%

[a]*All yields were determined by GC using dodecane as the internal standard.*

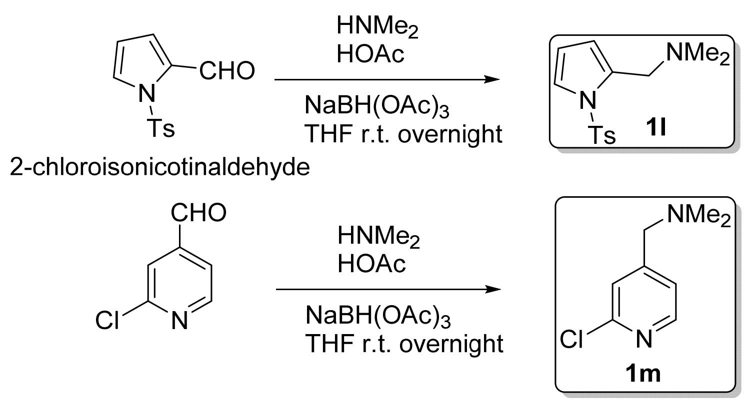
II. Synthesis of benzylamine derivatives

Most benzylamine substrates used in this work are known compounds, and substrates **1l** and **1m**. **1a, 1d** and**1j** are commercially available. The known benzylamine were all synthesized from corresponding benzyl halide and dimethyl amine. We used a slight modified protocol.[1]



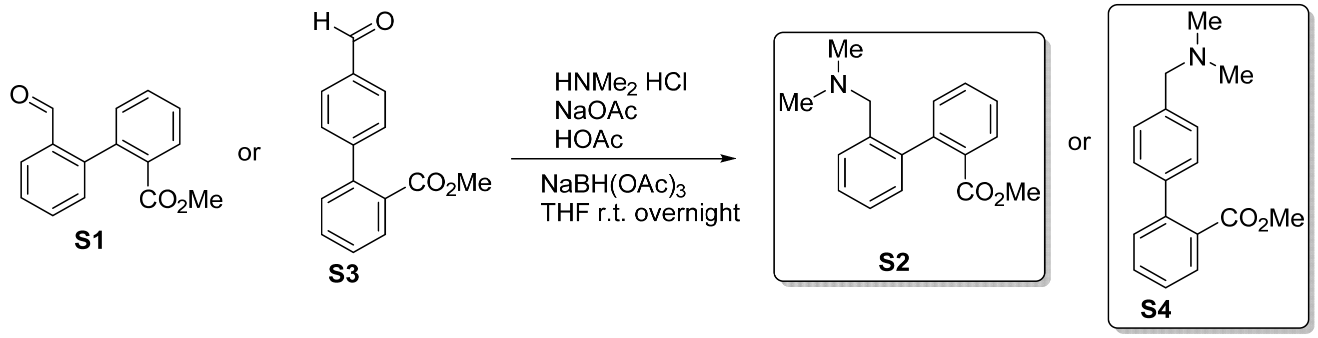
To a solution of benzylic bromide (1.0 equiv, 10 mmol) in ether (1 M) was added 50 wt.% aqueous dimethylamine solution (5 equiv) at room temperature. After stirring for 12 hours at the same temperature, the resulting mixture was transferred to a separatory funnel. The aqueous phase was removed and the organic phase was extracted with 10 wt.% aqueous citric acid solution twice. The combined aqueous extracts were treated with sodium hydroxide to keep pH slightly above 12. The mixture was extracted with ether and the combined organic extracts were washed with brine. The solution was dried over mageniusm sulfate and concentrated. The crude product were found pure based on NMR, was used without further purification. Further vacuum distillation can be adapted to remove all the colorful impurity.

1l and **1m** were synthesized from corresponding benzaldehyde through reductive amination：



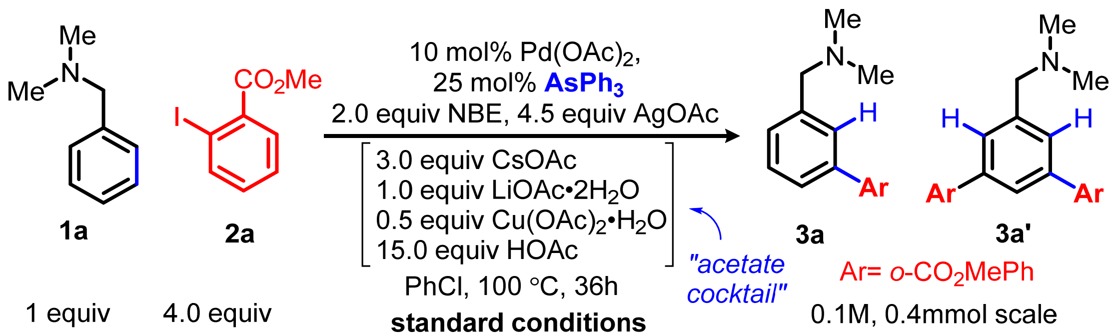
To solution of 1-tosyl-1*H*-pyrrole-2-carbaldehyde[2] or 2-chloroisonicotinaldehyde (10 mmol) in 20 mL tetrahydrofuran was added 2.0M dimethylamine solution in THF (10 ml, 20 mmol), acetic acid (1.2 g, 20 mmol). After being cooled in an ice bath for 5 min, sodium triacetoxyborohydride (4.2 g, 20 mmol) was added portion wise with stirring. The solution was further stirred at room temperature overnight. After monitored by TLC till full conversion, the solution was concentrated under vacuum. The residue was then dissolved by diethyl ether (20 mL) and extracted by 10% citric acid solution (30 mL x 3). The aqueous layer was neutralized by adding potassium hydroxide at zero degree and extracted by diethyl ether (30 mL x 3). The Combined organic layer was dried over magnesium sulfate and concertrated under vacuum to give the desired product **1l** as a pale brown solid or **1m** as an oil which were analytically pure and directly used as in the C−H activation reaction.

General Procedure for synthesis ortho and para products.



To solution of aldehyde **S1**[3] or **S3**[4] (0.55 g, 2.29 mmol) in 20 mL tetrahydrofuran was added dimethylamine hydrochloride (0.37g, 4.58 mmol), sodium acetate (0.18 g, 3.66 mmol), acetic acid (0.07 g, 1.15 mmol). After being cooled in an ice bath for 5 minutes, sodium triacetoxyborohydride (1.07 g, 5.04 mmol) was added portionwise with stirring. The solution was further stirred at room temperature overnight. After monitored by TLC till a full conversion, the solution was concentrated under vacuum. The residue was then dissolved by diethyl ether (20 mL) and extracted by 10% citric acid solution (30 mL x 3). The aqueous layer was neutralized by adding potassium hydroxide at zero degree and extracted by diethyl ether (30 mL x 3). The combined organic layer was dried over magnesium sulfate and concertrated under vacuum to give the desired product **S2** or **S4** as an oil which were analytically pure and directly used as the standard for GC-analysis.

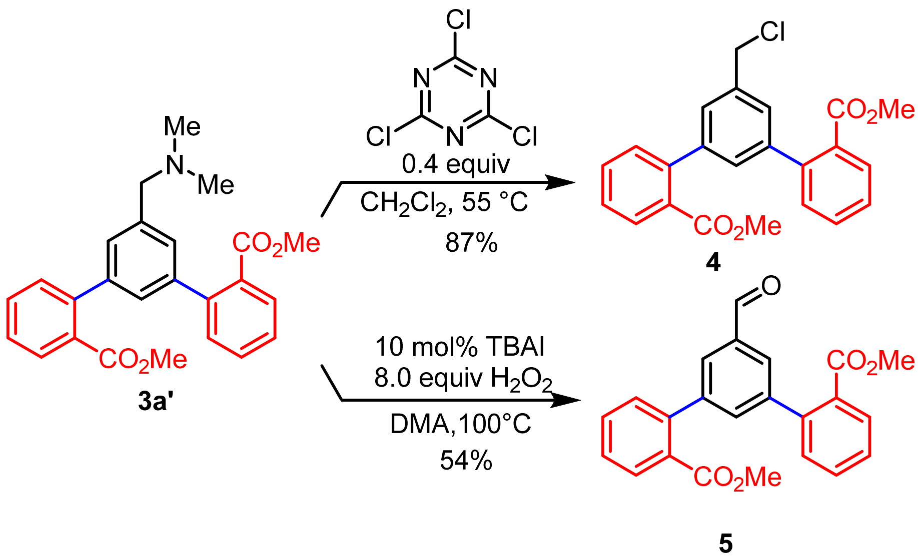
III.General Procedure for the meta-Arylation of benzylamine derivative with simple aryl iodide.



Unless stated otherwise, an 8 mL vial was charged with benzyl amine (0.4 mmol, 1.0 equiv), aryl iodide (1.6 mmol, 4.0 equiv), $Pd(OAc)_2$ (9.0 mg, 0.1 equiv), norbornene (75.7 mg, 2.0 equiv), triphenylarsine (30.6 mg, 0.25 equiv), AgOAc (300 mg, 4.5 equiv), $Cu(OAc)_2$ H_2O (40.2 mg, 0.5 equiv.), LiOAc $2H_2O$ (40.1 mg, 1.0 equiv), CsOAc (235 mg, 1.2 equiv), HOAc (360 µL, 15.0 equiv) and PhCl (3.5 mL). The vial was sealed with a PTFE lined cap and heated in a pie-block at 100 °C for 36 hours under stirring. The mixture was allowed to cool to room temperature. The saturated potassium carbonate aqueous solution (4 mL) was carefully added to the vial to make the whole solution alkaline. The vial was kept stirring at room temperature for 15 min before the solid was filtered. The filter cake was further washed with ethyl acetate (containing 8% triethylamine, roughly about 20 mL), the filtrate were collected together with aqueous phase. The aqueous phase was isolated and further extracted with dichloromethane three times (8 mL x 3). The organic phase were combined and dried with magnesium sulfate. The magnesium sulfate were removed by filtration and solution were concentrated under vacuum, the residue was purified by chromatography on silica gel.

For other substrates in the Table 2 and Table 3, the equivalent of the aryl iodide, the equivalent of AgOAc and the reaction temperature were adopted as indicated in the manuscript. The rest of procedure was exactly the same as what we described here.

Conversion of the amine DG to other FGs:



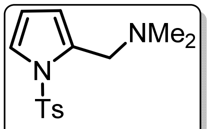
Chlorination:

In a 4 mL vial, a solution of **3a'** (72.1 mg, 0.179 mmol) and cyanuric chloride (12.9 mg, 0.07 mmol) in 1 mL dicholoromethane was sealed and heated at 55 °C for 18 hours. When the reaction showed a full conversion monitored by TLC, the solvent was removed under vacuum. The residue was directly purified by silica gel flash column chromatography (from hexane : ethyl acetate = 20:1 to hexane : ethyl acetate = 10:1) to give product **4** (61.1 mg, 87% yield) as a colorless oil.

Oxidation:

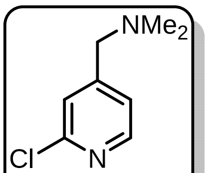
In a 4 mL vial, **3a'** (150.1 mg, 0.40 mmol) and tetrabutylammonium iodide (15.0 mg, 0.04 mmol) were dissolved in 1.5 mL dimethylacetamide. A solution of 30% hydrogen peroxide (0.33 mL, 3.2 mmol) was quickly added to the vial. The vial was then sealed and heated with stirring at 100 °C for 24 hours. (Positive pressure was generated in the vial, thus be careful when opening it.) The reaction was worked up with aqueous $NaHCO_3$, and then extracted with ethyl acetate (10 mL x 4). The combined organic layer was dried over magnesium sulfate, concentrated under vacuum, and purified by silica gel column chromatography (from hexane : ethyl acetate = 10:1 to hexane : ethyl acetate = 5:1) to give product **5** in 74.5 mg (54% yield) as a colorless oil.

IV. Characterization of new compound



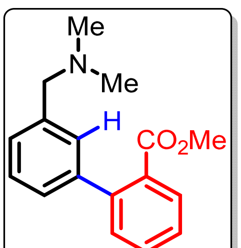
1l

(**1l**): brown solid, mp = 71.5 °C to 73.0 °C. R_f = 0.37 (Hex/EA = 3:1 with 3% v/v Et_3N). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.4 Hz, 2H), 7.30 (dd, *J* = 3.4, 1.8 Hz, 1H), 7.24 (d, *J* = 8.1 Hz, 2H), 6.19 (t, *J* = 3.3 Hz, 1H), 6.13 – 6.10 (m, 1H), 3.50 (s, 2H), 2.38 (s, 3H), 2.04 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.16, 136.89, 132.73, 129.21, 127.11, 123.16, 114.67, 110.78, 55.00, 44.53, 21.53. **IR** (KBr, cm^{-1}) 2942, 2816, 2774, 1366, 1175, 1148, 1131, 1091, 1054. **HRMS** calcd $C_{14}H_{19}N_2O_2S$ $[M+H]^+$: 279.1162. Found: 279.1164.



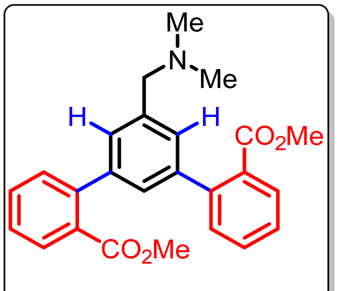
1m

(**1m**): yellow oil. R_f = 0.38 (Hex/EA = 3:1 with 3% v/v Et_3N). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 5.1Hz, 1H), 7.32–7.27 (m, 1H), 7.18–7.14 (m, 1H), 3.38 (s, 2H), 2.22 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 151.82, 151.66, 149.47, 124.00, 122.41, 62.51, 45.45.**IR** (KBr, cm^{-1}) 2970,2870, 2823, 2776, 1594, 1551, 1384, 1143, 913. **HRMS** calcd $C_8H_{12}ClN_2$ $[M+H]^+$: 171.0684. Found: 171.0681.



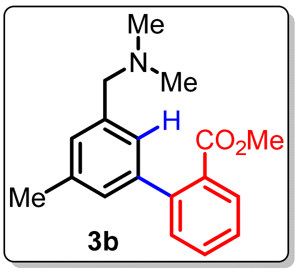
3a

(**3a**): 23% yield (reaction time: 12 hours). Colorless oil. R_f = 0.33 (Hex/EA = 5:1 with 4% v/v Et_3N). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 – 7.75 (m, 1H), 7.50 – 7.44 (m, 1H), 7.38 – 7.23 (m, 5H), 7.21 – 7.16 (m, 1H), 3.59 (s, 3H), 3.44 (s, 2H), 2.23 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.81, 142.10, 141.00, 138.20, 130.91, 130.62, 130.45, 129.45, 128.87, 127.76, 127.73, 126.84, 63.94, 51.59, 45.02. **IR** (KBr, cm^{-1}) 2947, 2815, 2769, 1724, 1288, 1253, 1125, 1090, 1050. **HRMS** calcd $C_{17}H_{20}NO_2$ $[M+H]^+$: 270.1489. Found: 270.1490.



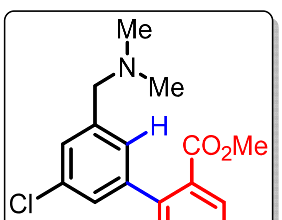
3a'

(3a'): 70% (reaction time: 36 hours). Yellow oil. R_f = 0.19 (Hex/EA = 5:1 with 4% v/v Et_3N). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 (ddd, *J* = 7.7, 1.5, 0.6 Hz, 2H), 7.56 – 7.48 (m, 2H), 7.44 – 7.36 (m, 4H), 7.25 (d, *J* = 1.8 Hz, 2H), 7.17 (t, *J* = 1.7 Hz, 1H), 3.65 (s, 6H), 3.49 (s, 2H), 2.27 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.12, 142.08, 141.12, 138.43, 131.12, 130.98, 130.73, 129.71, 128.02, 127.14, 127.04, 64.18, 51.90, 45.34.. **IR** (KBr, cm^{-1}) 2948, 2815, 2771, 1727, 1293, 1254, 1126, 1097, 1074. **HRMS** calcd $C_{25}H_{26}NO_4$ $[M+H]^+$: 404.1862. Found: 404.1859.



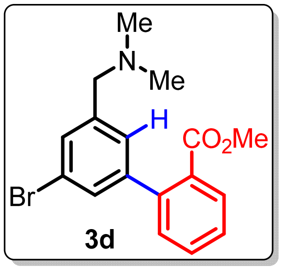
3b

(3b): 73% yield. Yellow oil. R_f = 0.29 (Hex/EA = 5:1 with 4% v/v Et_3N). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 – 7.76 (m, 1H), 7.53 – 7.46 (m, 1H), 7.41 – 7.34 (m, 2H), 7.14 (s, 1H), 7.03 (s, 2H), 3.63 (s, 3H), 3.41 (s, 2H), 2.38 (s, 3H), 2.25 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.27, 142.35, 141.03, 138.59, 137.62, 131.02, 130.93, 130.61, 129.54, 128.70, 127.69, 126.92, 126.28, 64.29, 51.84, 45.39, 21.29. **IR** (KBr, cm^{-1}) 2947, 2815, 2771, 1724, 1598, 1433, 1291, 1253, 1125, 1098, 1071, 1042. **HRMS** calcd $C_{18}H_{22}NO_2$ $[M+H]^+$: 284.1645. Found: 284.1647.



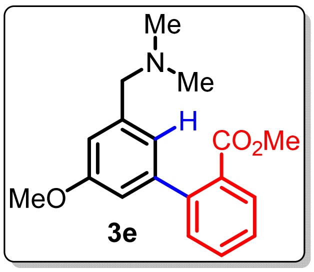
3c

(3c): 72% yield. Colorless oil. R_f = 0.36 (Hex/EA = 5:1 with 4% v/v Et_3N). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 (ddd, *J* = 7.7, 1.5, 0.5 Hz, 1H), 7.51 (td, *J* = 7.5, 1.5 Hz, 1H), 7.41 (td, *J* = 7.6, 1.4 Hz, 1H), 7.37 – 7.28 (m, 1H), 7.34 – 7.28 (m, 1H), 7.20 (t, *J* = 1.8 Hz, 1H), 7.12 (t, *J* = 1.5 Hz, 1H), 3.65 (s, 3H), 3.41 (s, 2H), 2.24 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.52, 142.85, 141.04, 140.62, 133.69, 131.30, 130.55, 130.54, 129.90, 127.66, 127.54, 127.24, 126.95, 63.65, 51.92, 45.31. **IR** (KBr, cm^{-1}) 2947, 2818, 2772, 1730, 1577, 1456, 1435, 1289, 1254, 1126, 1095, 1065. **HRMS** calcd $C_{17}H_{19}ClNO_2$ $[M+H]^+$: 304.1104. Found: 304.1101.



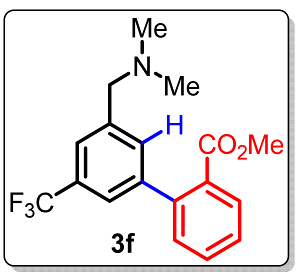
3d

(3d): 65% yield. Colorless oil. R_f = 0.39 (Hex/EA = 5:1 with 4% v/v Et_3N). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.52 (td, *J* = 7.5, 1.5 Hz, 1H), 7.48 – 7.46 (m, 1H), 7.42 (td, *J* = 7.6, 1.3 Hz, 1H), 7.36 (t, *J* = 1.8 Hz, 1H), 7.34 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.17 (t, *J* = 1.6 Hz, 1H), 3.66 (s, 3H), 3.42 (s, 2H), 2.25 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.57, 143.15, 140.96, 140.87, 131.35, 130.62, 130.60, 130.57, 129.96, 129.88, 127.77, 127.61, 121.93, 63.65, 51.99, 45.36. **IR** (KBr, cm^{-1}) 2947, 2818, 2772, 1730, 1456, 1434, 1289, 1254, 1126, 1095, 1064, 1042. **HRMS** calcd $C_{17}H_{19}BrNO_2$ $[M+H]^+$: 348.0594. Found: 348.0597



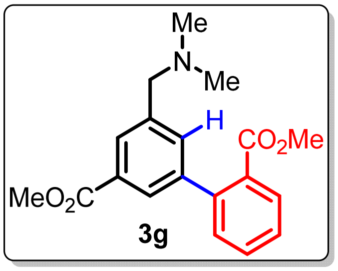
3e

(3e): 80% yield. Colorless oil. R_f = 0.21 (Hex/EA = 5:1 with 4% v/v Et_3N). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 – 7.76 (m, 1H), 7.53 – 7.47 (m, 1H), 7.42 – 7.36 (m, 2H), 6.88 (s, 1H), 6.83 (s, 1H), 6.77 (s, 1H), 3.82 (s, 3H), 3.63 (s, 3H), 3.42 (s, 2H), 2.25 (s, 6H).**^{13}C NMR** (101 MHz, $CDCl_{33}$) δ 169.16, 159.36, 142.34, 142.06, 140.15, 131.04, 130.96, 130.50, 129.51, 127.10, 121.65, 113.15, 112.75, 64.29, 55.24, 51.90, 45.36. **IR** (KBr, cm^{-1}) 2947, 2816, 2773, 1727, 1594, 1456, 1292, 1255, 1212, 913. **HRMS** calcd $C_{18}H_{21}NNaO_3$ $[M+Na]^+$: 322.1414. Found: 322.1404.

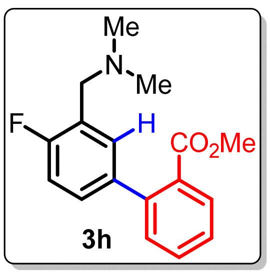


3f

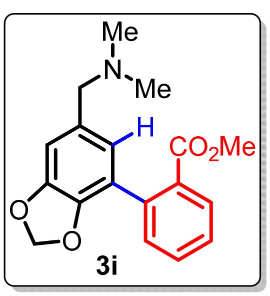
(3f): 55% yield. Colorless oil. R_f = 0.41 (Hex/EA = 5:1 with 4% v/v Et_3N). **^{1}H NMR** (400 MHz, acetonitrile-*d*$_3$) δ 7.83 (ddd, *J* = 7.7, 1.5, 0.5 Hz, 1H), 7.64 –7.58 (m, 2H), 7.53 – 7.46 (m, 3H), 7.42 (ddd, *J* = 7.6, 1.3, 0.5 Hz, 1H), 3.62 (s, 3H), 3.49 (s, 2H), 2.20 (s, 6H).**^{13}C NMR** (101 MHz, Acetonitrile-*d*$_3$) δ 169.23 , 143.05 , 141.98 , 141.52 , 133.60 (d, *J* = 1.5 Hz), 132.57 , 131.93 , 131.63 , 130.75 , 130.68 (q, *J* = 31.9 Hz), 128.98 , 125.44 (q, *J* = 271.6 Hz), 125.12 (q, *J* = 3.9 Hz), 124.51 (q, *J* = 3.8 Hz), 63.88 , 52.60 , 45.54 . **^{19}F NMR** (376 MHz, Acetonitrile-*d*$_3$) δ -62.83. **IR** (KBr, cm^{-1}) 2950, 2820, 2776, 1726, 1458, 1437, 1346, 1293, 1253, 1164, 1125. **HRMS** calcd $C_{18}H_{19}F_3NO_2$ $[M+H]^+$: 338.1362. Found: 338.1364.



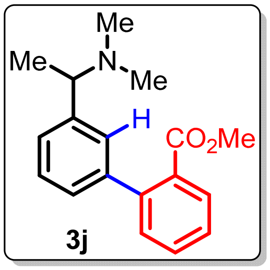
(3g): 45% yield. Colorless oil. R_f = 0.41 (Hex/EA = 5:1 with 4% v/v Et_3N). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 (t, *J* = 1.7 Hz, 1H), 7.90 (t, *J* = 1.7 Hz, 1H), 7.86 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.52 (td, *J* = 7.5, 1.4 Hz, 1H), 7.45 (t, *J* = 1.7 Hz, 1H), 7.42 (td, *J* = 7.6, 1.4 Hz, 1H), 7.36 (dd, *J* = 7.6, 1.3 Hz, 1H), 3.90 (s, 3H), 3.62 (s, 3H), 3.48 (s, 2H), 2.25 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.47, 166.94, 141.65, 141.57, 139.13, 133.54, 131.38, 130.77, 130.42, 130.01, 129.93, 128.89, 128.23, 127.49, 63.81, 52.05, 51.90, 45.32. **IR** (KBr, cm^{-1}) 2950, 2818, 2774, 1724, 1457, 1436, 1328, 1292, 1238, 1126, 1097, 913. **HRMS** calcd $C_{19}H_{22}NO_4$ $[M+H]^+$: 328.1543. Found: 328.1541.



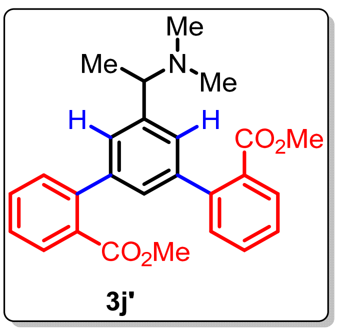
(3h): 47% yield. Colorless oil. R_f = 0.46 (Hex/EA = 5:1 with 4% v/v Et_3N). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85 – 7.80 (m, 1H), 7.54 – 7.46 (m, 1H), 7.43 – 7.37 (m, 1H), 7.34 (d, *J* = 7.6, 0.7 Hz, 1H), 7.29 (dd, *J* = 7.0, 2.4 Hz, 1H), 7.21 – 7.12 (m, 1H), 7.06 (t, *J* = 9.4, 8.4, 0.9 Hz, 1H), 3.65 (s, 3H), 3.56 – 3.42 (m, 2H), 2.28 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.68 , 160.71 (d, *J* = 246.8 Hz), 141.46 , 137.00 (d, *J* = 3.7 Hz), 131.41 (d, *J* = 4.7 Hz), 131.16 , 130.69 , 130.58 , 129.75 , 128.55 (d, *J* = 8.3 Hz), 127.12 , 124.87 (d, *J* = 15.2 Hz), 114.81 (d, *J* = 22.8 Hz), 56.53 (d, *J* = 1.6 Hz), 51.82 , 45.12. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -120.43. **IR** (KBr, cm^{-1}) 2948, 2820, 2778, 1729, 1503, 1479, 1289, 1249, 1126, 1087, 913. **HRMS** calcd $C_{17}H_{19}FNO_2$ $[M+H]^+$: 288.1394. Found: 288.1395.



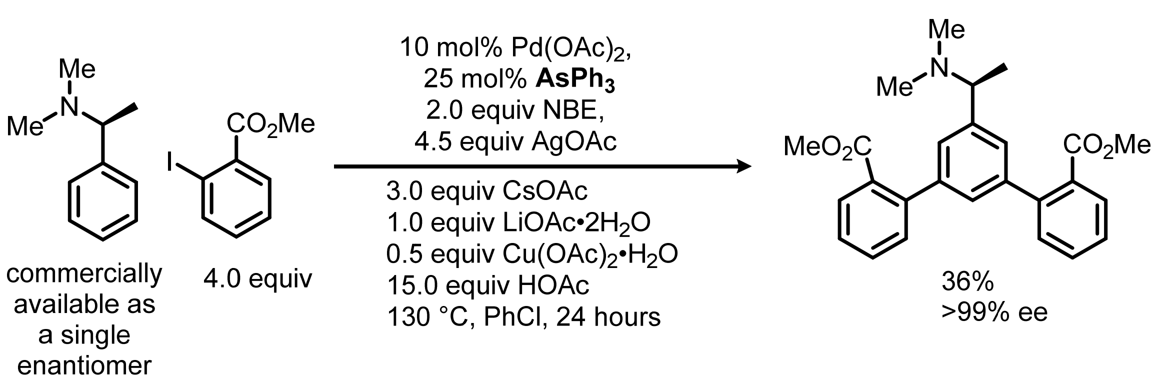
(3i): 32% yield. Colorless oil. R_f = 0.21 (Hex/EA = 5:1 with 4% v/v Et_3N). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.54 (td, *J* = 7.5, 1.4 Hz, 1H), 7.47 – 7.38 (m, 2H), 6.84 (d, *J* = 1.6 Hz, 1H), 6.75 (d, *J* = 1.5 Hz, 1H), 5.91 (s, 2H), 3.72 (s, 3H), 3.37 (s, 2H), 2.25 (s, 6H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.45, 147.13, 143.68, 136.35, 132.80, 131.58, 130.97, 130.80, 130.04, 127.62, 122.72, 122.15, 108.69, 100.94, 64.12, 52.00, 45.22. **IR** (KBr, cm^{-1}) 2948, 2617, 2772, 1726, 1420, 1291, 1256, 1192, 1126, 1096, 1046, 913. **HRMS** calcd $C_{19}H_{22}NO_4$ $[M+H]^+$: 314.1389. Found: 314.1387.



(3j): 33% yield. Colorless oil. R_f = 0.43 (Hex/EA = 5:1 with 4% v/v Et_3N). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 – 7.78 (m, 1H), 7.55 – 7.49 (m, 1H), 7.43 – 7.38 (m, 2H), 7.38 – 7.33 (m, 1H), 7.31 – 7.26 (m, 1H), 7.25 – 7.18 (m, 2H), 3.61 (s, 3H), 3.27 (q, J = 6.7 Hz, 1H), 2.21 (s, 6H), 1.39 (d, J = 6.7 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.21, 143.87, 142.42, 141.15, 131.08, 130.98, 130.65, 129.63, 127.95, 127.60, 127.02, 126.78, 126.37, 65.89, 51.86, 43.24, 20.34. **IR** (KBr, cm^{-1}) 2976, 2950, 2816, 2769, 1725, 1290, 1126, 1088, 1050, 931. **HRMS** calcd $C_{18}H_{21}NNaO_2$ $[M+Na]^+$: 306.1465. Found: 306.1467.

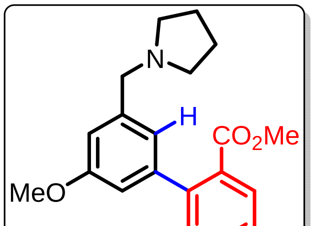


(3j'): 31% yield. Colorless oil. R_f = 0.23 (Hex/EA = 5:1 with 4% v/v Et_3N). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 (ddd, J = 7.7, 1.5, 0.6 Hz, 2H), 7.51 (ddd, J = 7.7, 7.2, 1.4 Hz, 2H), 7.44 – 7.36 (m, 4H), 7.22 (dd, J = 1.7, 0.5 Hz, 2H), 7.18 (t, J = 1.7 Hz, 1H), 3.65 (s, 6H), 3.30 (q, J = 6.7 Hz, 1H), 2.23 (s, 6H), 1.40 (d, J = 6.7 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.20, 143.70, 142.13, 141.11, 131.13, 131.07, 130.68, 129.66, 127.11, 126.76, 126.56, 65.81, 51.89, 43.26, 20.47.**IR** (KBr, cm^{-1}) 2950, 2817, 2769, 1727, 1595, 1433, 1293, 1254, 1126, 913. **HRMS** calcd $C_{26}H_{27}NNaO_4$ $[M+Na]^+$: 440.1832. Found: 440.1837.



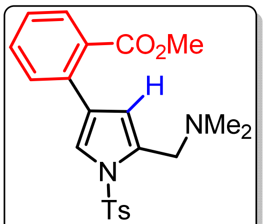
For chiral (S)-(−)-**3j',** it was directly synthesized from commercially available (*S*)-(−)-*N*,*N*-dimethyl-1-phenylethylamine by following the general procedure at 130°C.

Chiral HPLC (Chiralpak IA, hexane : isopropanol (with 0.5% V/V diethylamine) = 98.5:1.5, 1 mL/min, 254 nm): t_s = 28.65 min, t_r =31.34 min. $[\alpha]_D^{20}$ = -13° (c 1.0, $CDCl_3$) at >99 % ee.



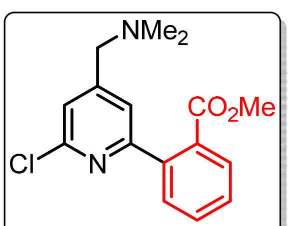
3k

(3k): 17% yield. Yellow oil. R_f = 0.54 (Hex/EA = 5:1 with 4% v/v Et_3N). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 – 7.74 (m, 1H), 7.54 – 7.46 (m, 1H), 7.44 – 7.36 (m, 2H), 6.91 (dd, *J* = 2.5, 1.4 Hz, 1H), 6.86 (t, *J* = 1.5 Hz, 1H), 6.76 (dd, *J* = 2.5, 1.6 Hz, 1H), 3.82 (s, 3H), 3.64 (s, 3H), 3.62 (s, 2H), 2.58 – 2.47 (m, 4H), 1.83 – 1.74 (m, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.25, 159.35, 142.32, 142.16, 140.62, 131.06, 131.03, 130.56, 129.53, 127.12, 121.51, 113.27, 112.48, 60.62, 55.30, 54.12, 51.95, 23.44. **IR** (KBr, cm^{-1}) 2951, 2784, 1727, 1594, 1292, 1252, 1211, 1126, 913. **HRMS** calcd $C_{20}H_{23}NNaO_3$ $[M+Na]^+$: 348.1570. Found: 348.1559.



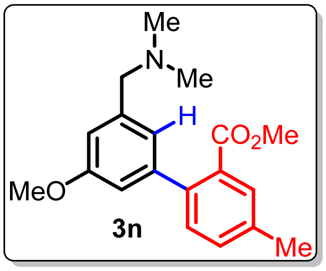
3l

(3k): 48% yield. Brown oil. R_f = 0.36 (Hex/EA = 3:1 with 4% v/v Et_3N). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84 – 7.78 (m, 2H), 7.67 (ddd, *J* = 7.7, 1.5, 0.5 Hz, 1H), 7.47 - 7.43 (m, 1H), 7.41 - 7.37 (m, 2H), 7.35 – 7.29 (m, 1H), 7.28 – 7.24 (m, 2H), 6.21 (dd, *J* = 1.9, 0.9 Hz, 1H), 3.71 (s, 3H), 3.52 (s, 2H), 2.39 (s, 3H), 2.07 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.41, 144.27, 136.80, 133.63, 132.70, 131.04, 130.79, 129.93, 129.33, 129.24, 127.16, 126.88, 125.43, 120.57, 115.68, 54.95, 51.99, 44.50, 21.52. **IR** (KBr, cm^{-1}) 2949, 2869, 2818, 1727, 1366, 1291, 1175, 1133, 1103, 913. **HRMS** calcd $C_{22}H_{25}N_2O_4S$ $[M+H]^+$: 413.1530. Found: 413.1535.



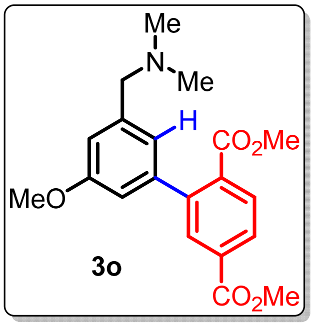
3m

(3m): 66% yield. Brown oil. R_f = 0.35 (Hex/EA = 3:1 with 4% v/v Et_3N). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.78 (ddd, *J* = 7.6, 1.4, 0.6 Hz, 1H), 7.61 – 7.51 (m, 2H), 7.49 – 7.44 (m, 1H), 7.39 (dd, *J* = 1.2, 0.6 Hz, 1H), 7.28 (dd, *J* = 1.3, 0.7 Hz, 1H), 3.75 (s, 3H), 3.46 (s, 2H), 2.28 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.05, 158.67, 152.06, 150.68, 139.04, 131.70, 131.00, 129.59, 128.72, 122.38, 121.19, 62.71, 52.14, 45.56. **IR** (KBr, cm^{-1}) 2979, 2947, 2869, 1728, 1595, 1548, 1291, 1258, 1127, 913. **HRMS** calcd $C_{16}H_{18}ClN_2O_2$ $[M+H]^+$: 305.1051. Found: 305.1056.



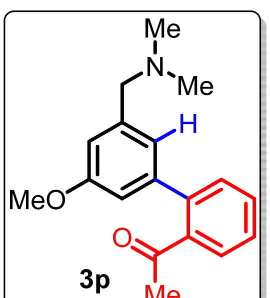
3n

(3l): 70% yield. Colorless oil. R_f = 0.21 (Hex/EA = 5:1 with 4% v/v Et_3N). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.59 (dt, *J* = 1.6, 0.7 Hz, 1H), 7.33 – 7.27 (m, 2H), 6.86 (dd, *J* = 2.5, 1.4 Hz, 1H), 6.81 (t, *J* = 1.5 Hz, 1H), 6.75 (dd, *J* = 2.5, 1.6 Hz, 1H), 3.81 (s, 3H), 3.63 (s, 3H), 3.41 (s, 2H), 2.40 (s, 3H), 2.24 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.34, 159.32, 142.27, 140.06, 139.18, 136.95, 131.75, 130.74, 130.40, 129.98, 121.67, 112.92, 112.78, 64.30, 55.19, 51.84, 45.34, 20.84.**IR** (KBr, cm^{-1}) 2946, 2816, 2772, 1732, 1594, 1456, 1434, 1296, 1253, 1204, 826. **HRMS** calcd $C_{19}H_{24}NO_3$ $[M+H]^+$: 314.1751. Found: 314.1752.



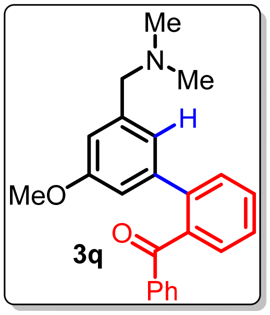
3o

(3m): 71% yield. Colorless oil. R_f = 0.19 (Hex/EA = 3:1 with 4% v/v Et_3N). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01 (d, J = 1.7 Hz, 1H), 7.97 (dd, J = 8.0, 1.7 Hz, 1H), 7.74 (dd, J = 7.9, 1.4 Hz, 1H), 6.84 (s, 1H), 6.79 (s, 1H), 6.72 (s, 1H), 3.86 (s, 3H), 3.76 (s, 3H), 3.60 (s, 3H), 3.36 (s, 2H), 2.18 (s, 6H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.38, 165.91, 159.37, 141.93, 141.10, 140.40, 134.89, 132.04, 131.33, 129.32, 127.91, 121.31, 113.44, 112.54, 64.10, 55.11, 52.20, 52.02, 45.23.**IR** (KBr, cm^{-1}) 2950, 2817, 2773, 1727, 1594, 1456, 1434, 1284, 1250, 1209, 1116, 913. **HRMS** calcd $C_{20}H_{23}NO_5$ $[M+H]^+$: 358.1649. Found: 358.1649.



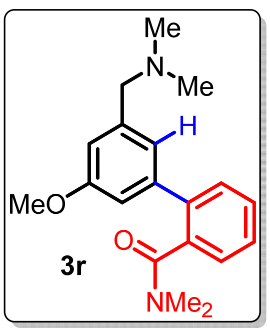
3p

(3n): 31% yield. Colorless oil. R_f = 0.24 (Hex/EA = 5:1 with 4% v/v Et_3N). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56 – 7.45 (m, 2H), 7.43 – 7.35 (m, 2H), 6.92 (s, 1H), 6.86 (s, 1H), 6.78 (s, 1H), 3.82 (s, 3H), 3.42 (s, 2H), 2.24 (s, 6H), 2.02 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 204.81, 159.80, 141.84, 141.03, 140.82, 140.32, 130.58, 130.03, 127.71, 127.44, 122.11, 113.78, 113.29, 64.14, 55.33, 45.35, 30.37. **IR** (KBr, cm^{-1}) 2941, 2816, 2772, 1688, 1592, 1456, 1361, 1332, 1276, 1238, 1211, 1146, 1030. **HRMS** calcd $C_{18}H_{21}NO_2$ $[M+H]^+$: 284.1645. Found: 284.1646.



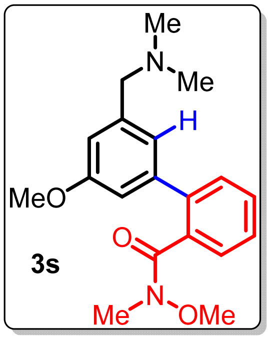
3q

(3o): 58% yield. Colorless oil. R_f = 0.22 (Hex/EA = 5:1 with 4% v/v Et_3N). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64 – 7.59 (m, 2H), 7.58 – 7.42 (m, 4H), 7.39 – 7.33 (m, 1H), 7.22 (s, 2H), 6.77 (t, *J* = 1.5 Hz, 1H), 6.71 – 6.68 (m, 1H), 6.67 – 6.61 (m, 1H), 3.67 (s, 3H), 3.25 (s, 2H), 2.09 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 198.83, 159.31, 141.18, 140.70, 140.45, 138.95, 137.21, 132.63, 130.21, 129.71, 129.63, 128.57, 127.92, 127.20, 122.25, 113.57, 113.40, 64.04, 55.16, 45.24.. **IR** (KBr, cm^{-1}) 2942, 2817, 2771, 1728, 1667, 1594, 1456, 1285, 1254, 1212, 1148, 928. **HRMS** calcd $C_{23}H_{24}NO_2$ $[M+H]^+$: 346.1802. Found: 346.1804.



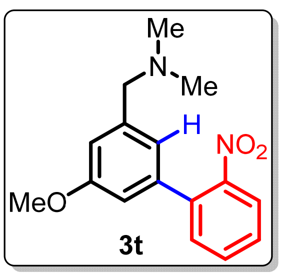
3r

(3p): 60% yield. Colorless oil. R_f = 0.29 (Hex/EA = 1:1 with 4% v/v Et_3N). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44 – 7.33 (m, 4H), 6.97 (s, 1H), 6.93 – 6.90 (m, 1H), 6.89 – 6.85 (m, 1H), 3.80 (s, 3H), 3.46 – 3.35 (m, 2H), 2.85 (s, 3H), 2.44 (s, 3H), 2.23 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.25, 159.57, 141.06, 140.56, 138.45, 135.64, 129.29, 129.15, 127.66, 127.31, 121.56, 113.99, 112.47, 64.20, 55.32, 45.35, 37.99, 34.54. **IR** (KBr, cm^{-1}) 2939, 2856, 2816, 2772, 1633, 1593, 1456, 1394, 1210, 913. **HRMS** calcd $C_{19}H_{25}N_2O_2$ $[M+H]^+$: 313.1911. Found: 313.1913.

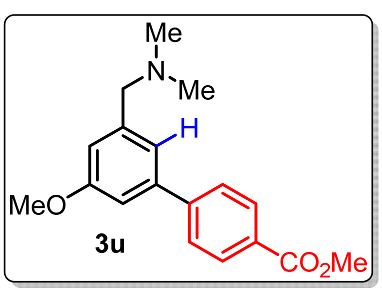


(3q): 53% yield. Colorless oil. R_f = 0.37 (Hex/EA = 1:1 with 4% v/v Et_3N). This compound has several rotamers at r.t. in $CDCl_3$. Both proton and 13 carbon were taken in DMSO-*d6* at 100°C.

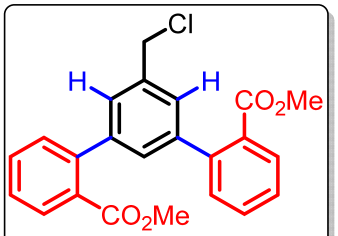
^{1}H NMR (600 MHz, DMSO-d_6) δ 7.49 (dd, *J* = 7.4, 1.6 Hz, 1H), 7.43 (ddd, *J* = 14.6, 7.4, 1.4 Hz, 2H), 7.38 (dd, *J* = 7.6, 1.6 Hz, 1H), 6.94 (d, *J* = 1.7 Hz, 1H), 6.87 (dt, *J* = 7.8, 2.1 Hz, 2H), 3.79 (s, 3H), 3.41 (s, 2H), 3.06 – 2.90 (m, 6H), 2.20 (s, 6H).**^{13}C NMR** (151 MHz, DMSO-d_6) δ 158.84, 140.44, 140.18, 138.20, 134.67, 128.63, 128.57, 126.38, 126.19, 120.72, 113.04, 112.25, 62.94, 59.73, 54.71, 54.69, 44.32.**IR** (KBr, cm^{-1}): 2938, 2816, 2773, 1652, 1593, 1457, 1364, 1332, 1214. **HRMS** calcd $C_{19}H_{25}N_2O_3$ $[M+H]^+$: 329.1860. Found: 329.1862.



(3r): 66% yield. Yellow oil. R_f = 0.43 (Hex/EA = 5:1 with 4% v/v Et_3N). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 (dd, *J* = 8.5, 1.4 Hz, 1H), 7.62 – 7.55 (m, 1H), 7.49 – 7.41 (m, 2H), 6.91 (s, 1H), 6.83 (s, 1H), 6.79 – 6.73 (m, 1H), 3.81 (s, 3H), 3.41 (s, 2H), 2.24 (s, 6H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.70, 149.23, 140.96, 138.38, 136.11, 132.08, 131.78, 128.07, 123.88, 120.86, 113.95, 112.42, 64.11, 55.27, 45.33.**IR** (KBr, cm^{-1}) 2942, 2818, 2774, 1572, 1529, 1457, 1361, 1213, 913. **HRMS** calcd $C_{16}H_{19}N_2O_3$ $[M+H]^+$: 287.1390. Found: 287.1390.

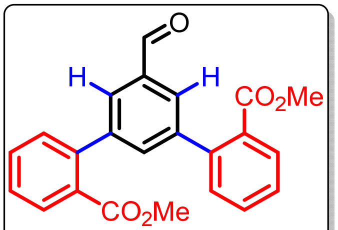


(3u): 4% yield. Pale yellow oil. R_f = 0.41 (Hex/EA = 5:1 with 4% v/v Et_3N). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.12 – 8.05 (m, 2H), 7.69 – 7.62 (m, 2H), 7.16 (t, *J* = 1.5 Hz, 1H), 7.05 (dd, *J* = 2.5, 1.6 Hz, 1H), 6.92 (dd, *J* = 2.5, 1.3 Hz, 1H), 3.94 (s, 3H), 3.87 (s, 3H), 3.46 (s, 2H), 2.28 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.99, 160.10, 145.45, 141.24, 129.98, 129.06, 128.94, 127.11, 120.40, 113.91, 111.91, 64.43, 55.43, 52.12, 45.48. **IR** (KBr, cm^{-1}) 2979, 2949, 2869, 1726, 1363, 1286, 1175, 1134, 913. **HRMS** calcd $C_{18}H_{22}NO_3$ $[M+H]^+$: 300.1594. Found: 300.1599.



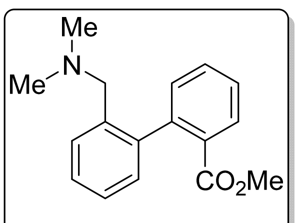
4

(4): 87% yield. Colorless oil. R_f = 0.34 (Hex/EA = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85 (ddd, *J* = 7.7, 1.4, 0.6 Hz, 2H), 7.54 (td, *J* = 7.5, 1.5 Hz, 2H), 7.46 – 7.39 (m, 4H), 7.33 (d, *J* = 1.7 Hz, 2H), 7.25 (t, *J* = 1.7 Hz, 1H), 4.65 (s, 2H), 3.68 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.90, 141.68, 141.46, 136.99, 131.30, 130.87, 130.64, 129.90, 128.37, 127.48, 52.04, 46.04. **IR** (KBr, cm^{-1}) 2950, 1725, 1596, 1434, 1294, 1255, 1127, 1098, 1074, 913. **HRMS** calcd $C_{23}H_{19}ClNaO_4$ $[M+Na]^+$: 417.0864. Found: 417.0859.



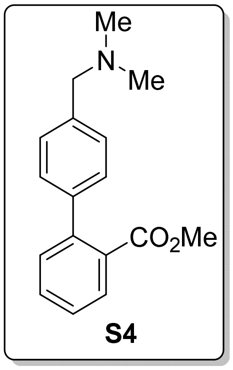
5

(5): 55% yield. Colorless oil. R_f = 0.23 (Hex/EA = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.08 (s, 1H), 7.92 (ddd, *J* = 7.8, 1.5, 0.5 Hz, 2H), 7.82 (d, *J* = 1.8 Hz, 2H), 7.56 (td, *J* = 7.5, 1.4 Hz, 2H), 7.50 (t, *J* = 1.7 Hz, 1H), 7.49 – 7.44 (m, 2H), 7.40 (ddd, *J* = 7.6, 1.4, 0.5 Hz, 2H), 3.68 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 191.95, 168.18, 142.14, 141.10, 135.98, 134.40, 131.59, 130.80, 130.34, 130.24, 128.35, 127.85, 52.03. **IR** (KBr, cm^{-1}) 2951, 1726, 1699, 1597, 1434, 1294, 1258, 1166, 1127, 913. **HRMS** calcd $C_{23}H_{18}NaO_5$ $[M+Na]^+$: 397.1046. Found: 397.1047.



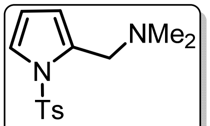
S2

(S2): 43% yield. Colorless oil. R_f = 0.44 (Hex/EA = 5:1 with 4% v/v Et_3N). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 (ddd, *J* = 7.8, 1.5, 0.5 Hz, 1H), 7.55 – 7.46 (m, 2H), 7.42 (td, *J* = 7.6, 1.4 Hz, 1H), 7.33 (td, *J* = 7.5, 1.5 Hz, 1H), 7.29 – 7.20 (m, 2H), 7.12 – 7.06 (m, 1H), 3.57 (s, 3H), 3.21 – 2.95 (m, 2H), 2.06 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.67, 142.15, 141.70, 136.36, 131.08, 131.04, 130.79, 129.70, 128.76, 128.71, 127.15, 127.07, 126.11, 61.21, 51.70, 45.26.**IR** (KBr, cm^{-1}) 2947, 2815, 2769, 1732, 1456, 1289, 1253, 1127, 1085, 913. **HRMS** calcd $C_{17}H_{20}NO_2$ $[M+H]^+$: 270.1489. Found: 270.1488.

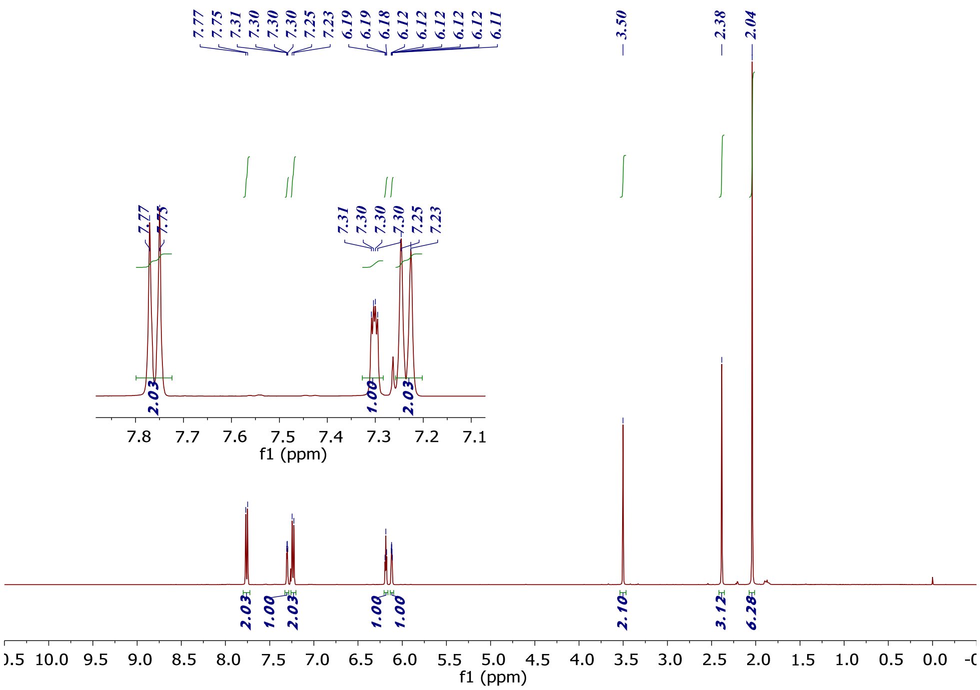


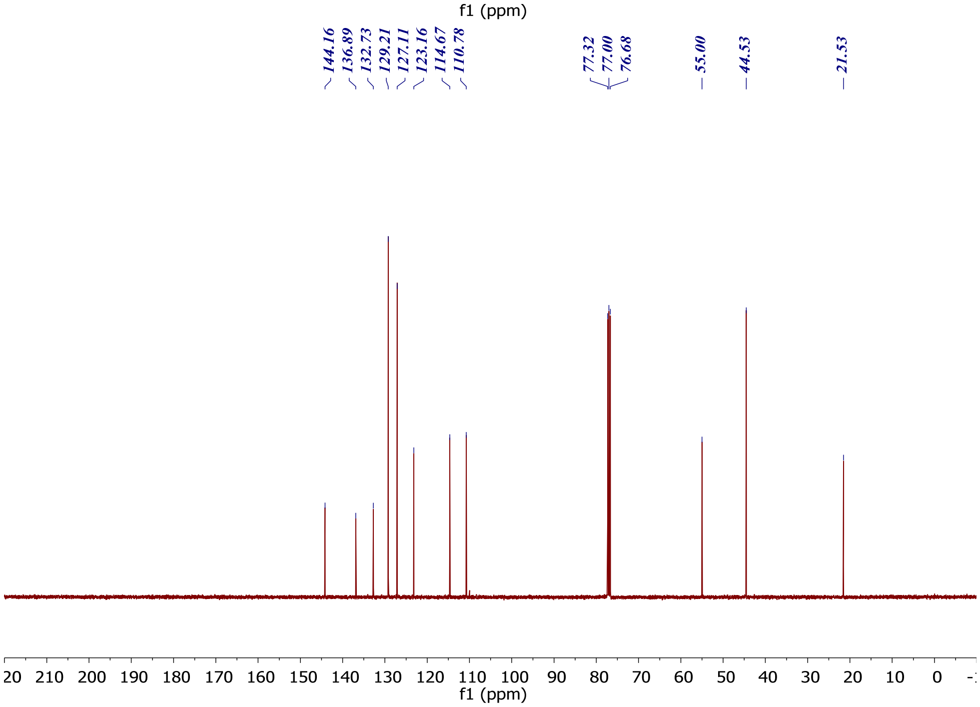
(S2): 45% yield. Colorless oil. R_f = 0.35 (Hex/EA = 5:1 with 4% v/v Et_3N). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 (ddd, *J* = 7.6, 1.4, 0.7 Hz, 1H), 7.52 (td, *J* = 7.5, 1.4 Hz, 1H), 7.44 – 7.37 (m, 2H), 7.36 – 7.31 (m, 2H), 7.27 (d, *J* = 7.0 Hz, 2H), 3.62 (s, 3H), 3.47 (s, 2H), 2.27 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.27 , 142.20 , 140.03 , 137.83 , 131.19 , 130.89 , 130.65 , 129.72 , 128.81 , 128.18 , 127.05 , 64.12 , 51.88 , 45.41 .**IR** (KBr, cm^{-1}) 2947, 2816, 2769, 1727, 1447, 1433, 1287, 1253, 1126, 1089. **HRMS** calcd $C_{17}H_{20}NO_2$ $[M+H]^+$: 270.1489. Found: 270.1481.

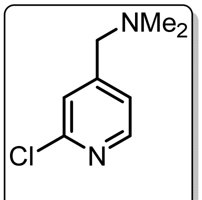
V. ^{1}H- and ^{13}C-NMR spectra



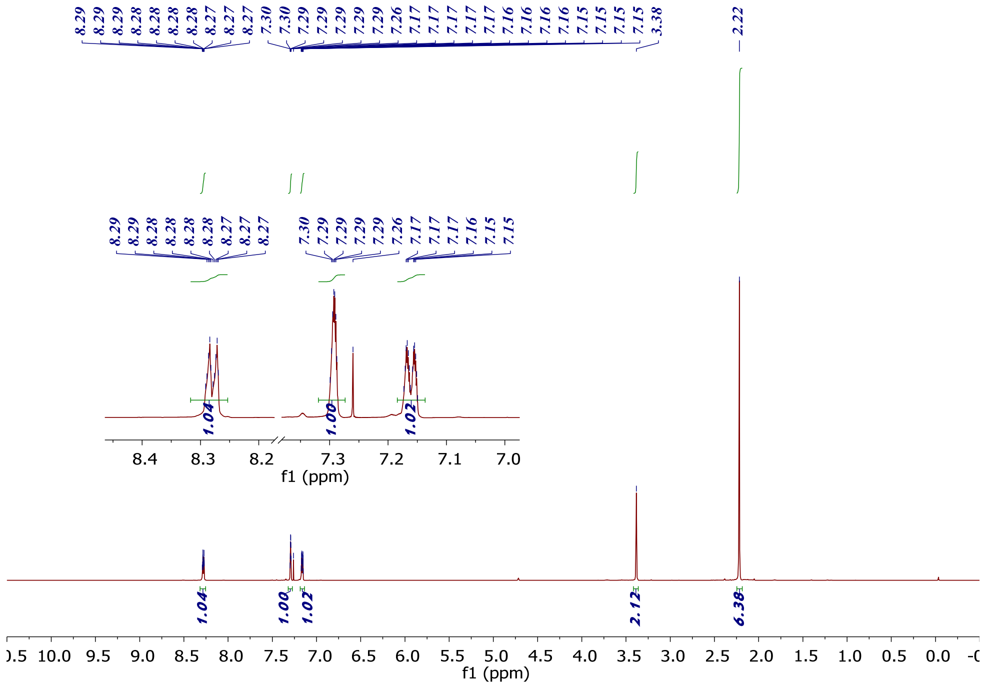
1m

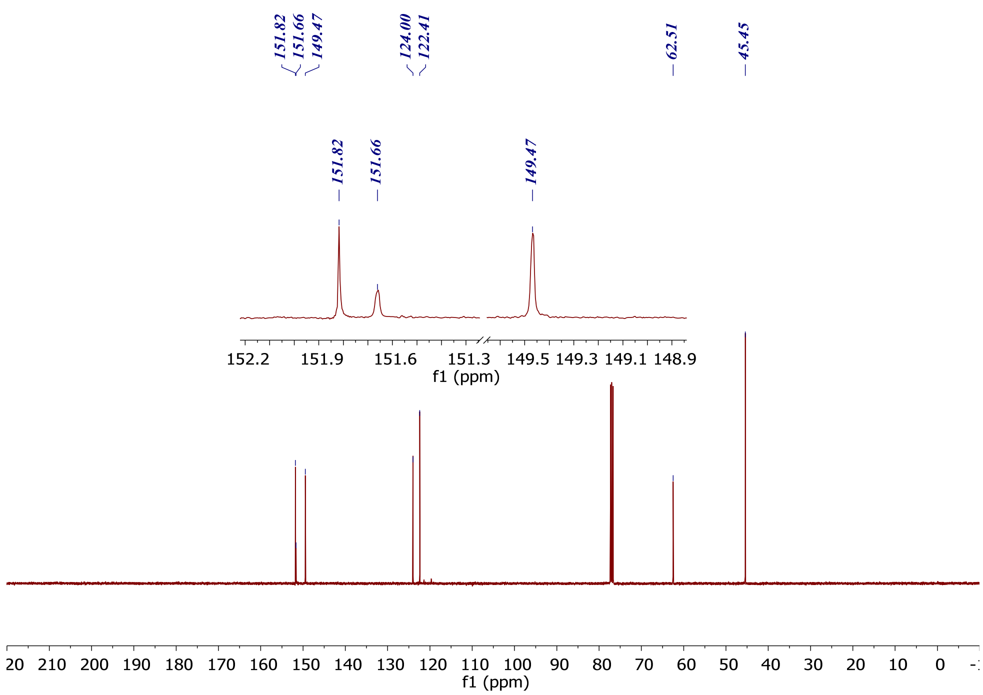


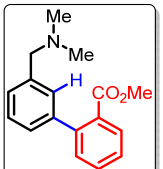




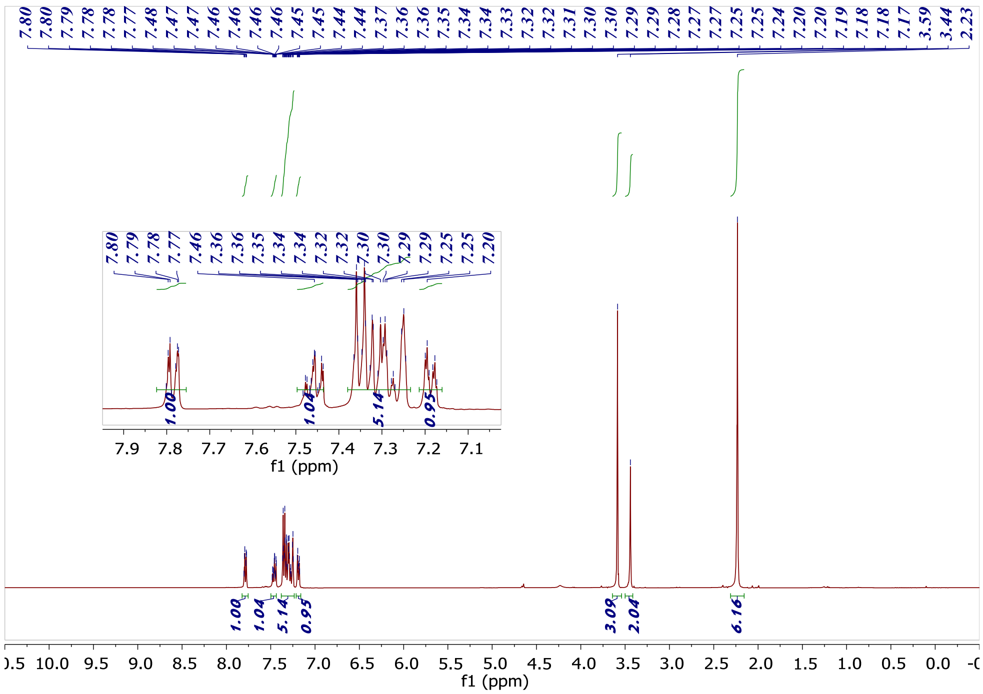
1l






Me
N
Me
H
CO2Me

3a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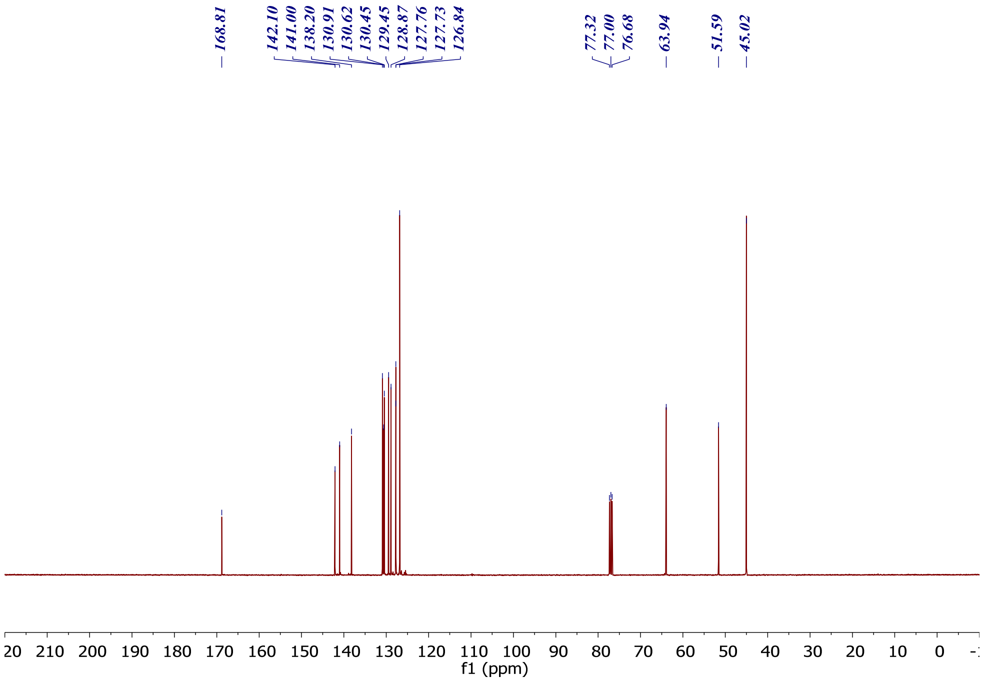
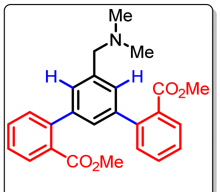
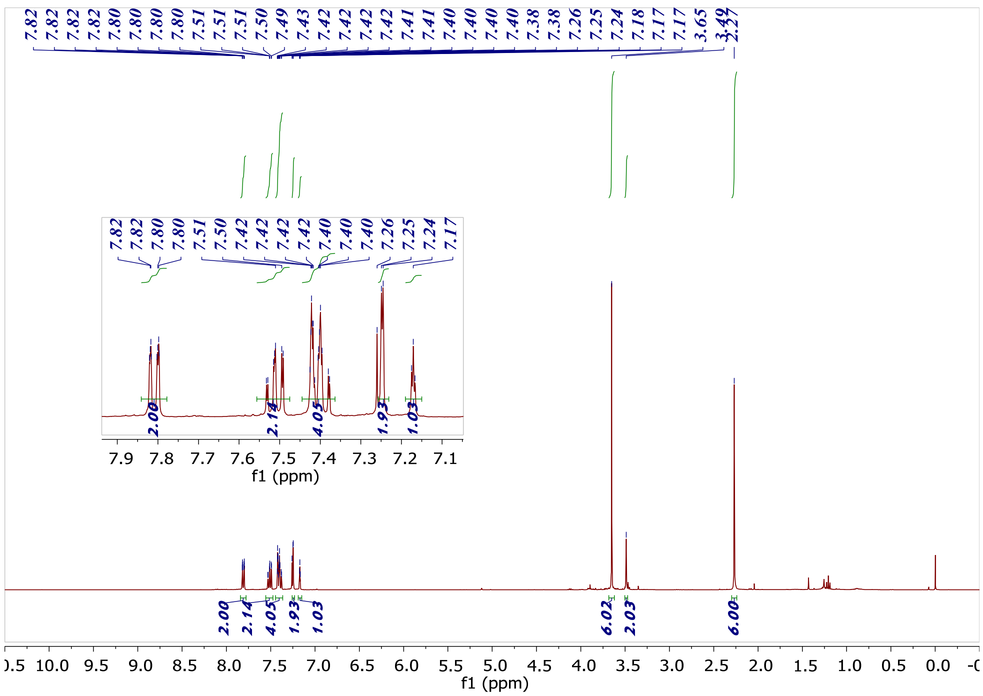
7.80 7.79 7.78 7.77 7.46 7.36 7.36 7.35 7.34 7.34 7.32 7.30 7.30 7.29 7.29 7.25 7.25 7.20
1.00
1.04
5.14
0.95
7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1
f1 (ppm)
1.00
1.04
5.14
0.95
3.09
2.04
6.16
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


168.81
142.10 141.00 138.20 130.91 130.62 130.45 129.45 128.87 127.76 127.73 126.84
77.32 77.00 76.68
63.94
51.59
45.02
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Me
N
Me
H
H
CO2Me
CO2Me

3a'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7.82
7.82
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7.80
7.80
7.80
7.51
7.51
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7.50
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7.42
7.42
7.42
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7.41
7.41
7.40
7.40
7.40
7.40
7.38
7.38
7.26
7.25
7.24
7.18
7.17
7.17
3.65
3.49
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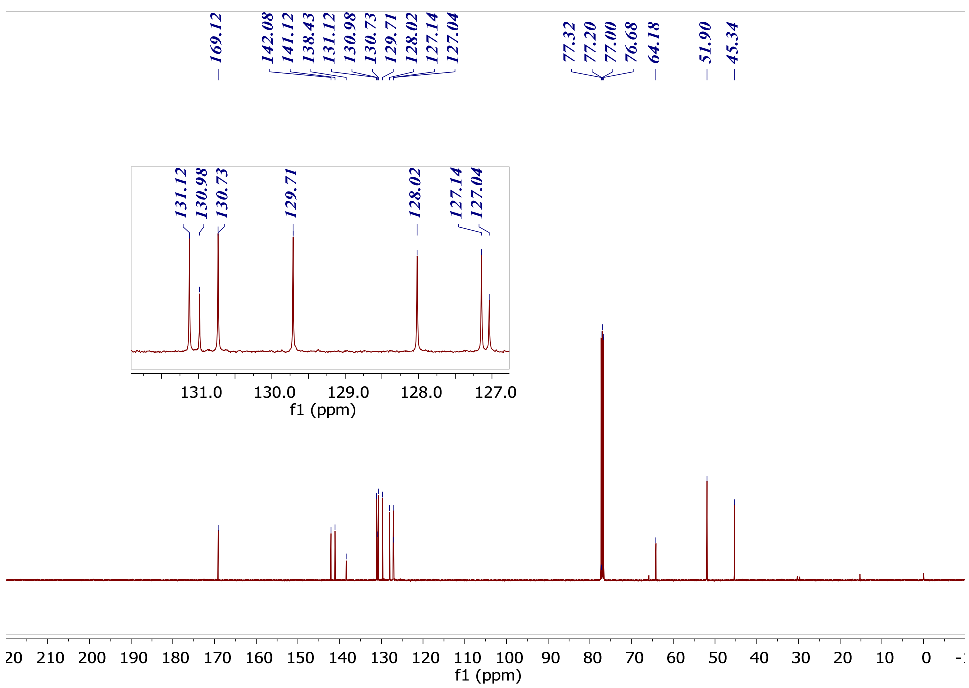
2.00
2.14
4.05
1.93
1.03
6.02
2.03
6.00
f1 (ppm)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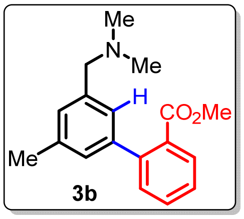
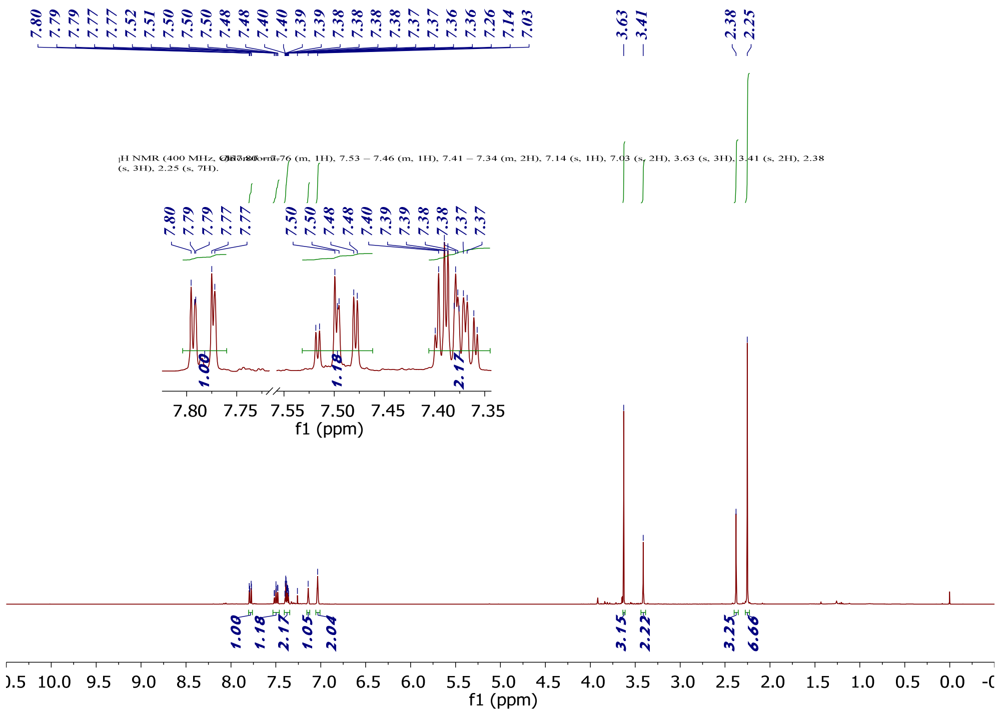
142.08
141.12
138.43
131.12
130.98
130.73
129.71
128.02
127.14
127.04
77.32
77.20
77.00
76.68
64.18
51.90
45.34
f1 (ppm)


Me
N
Me
H
CO2Me
Me
3b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3.63
3.41
2.38
2.25
1H NMR (400 MHz, Chloroform) δ 7.80 – 7.76 (m, 1H), 7.53 – 7.46 (m, 1H), 7.41 – 7.34 (m, 2H), 7.14 (s, 1H), 7.03 (s, 2H), 3.63 (s, 3H), 3.41 (s, 2H), 2.38 (s, 3H), 2.25 (s, 7H).
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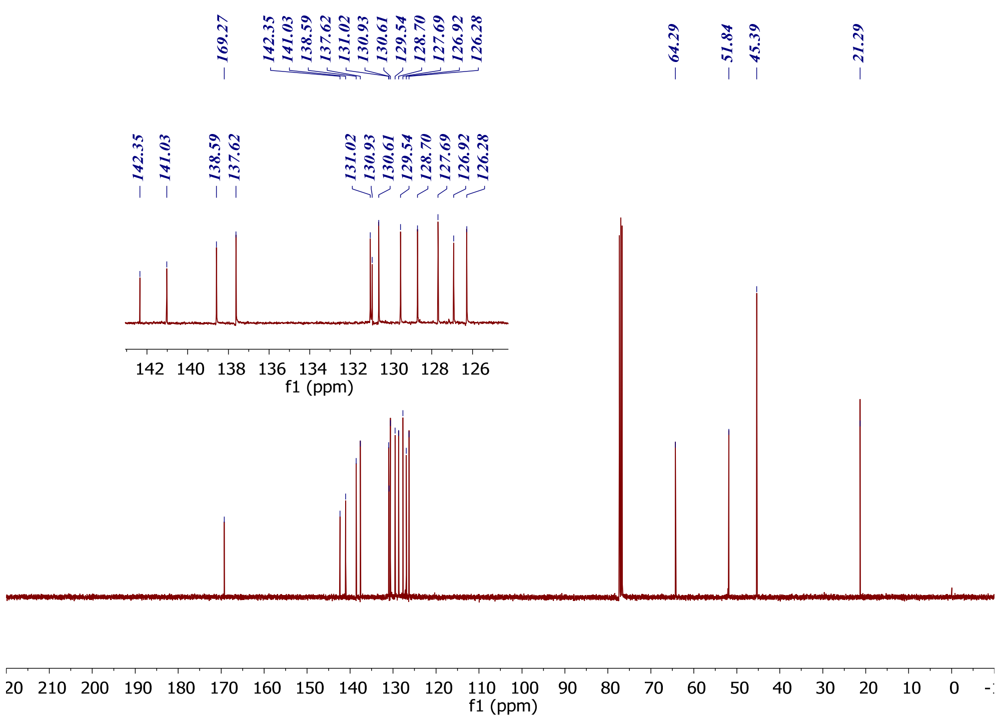
1.18
2.17
1.05
2.04
3.15
2.22
3.25
6.66
f1 (ppm)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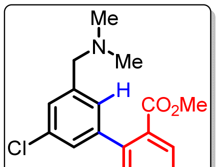
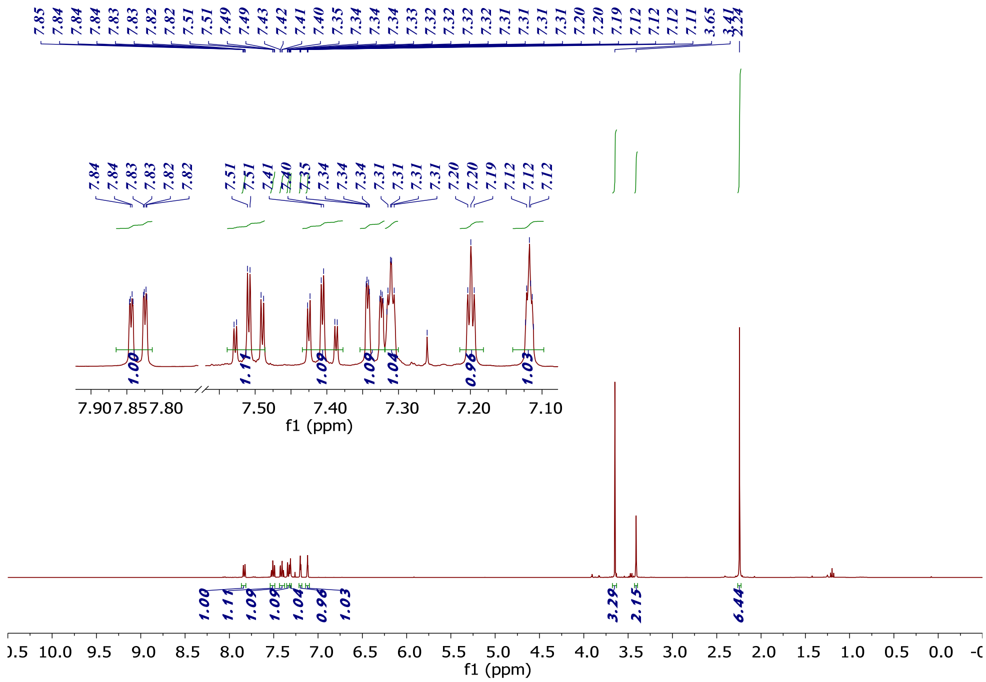
142.35 141.03 138.59 137.62 131.02 130.93 130.61 129.54 128.70 127.69 126.92 126.28
64.29
51.84
45.39
21.29
f1 (ppm)


Me
N
Me
H
CO2Me
Cl

3c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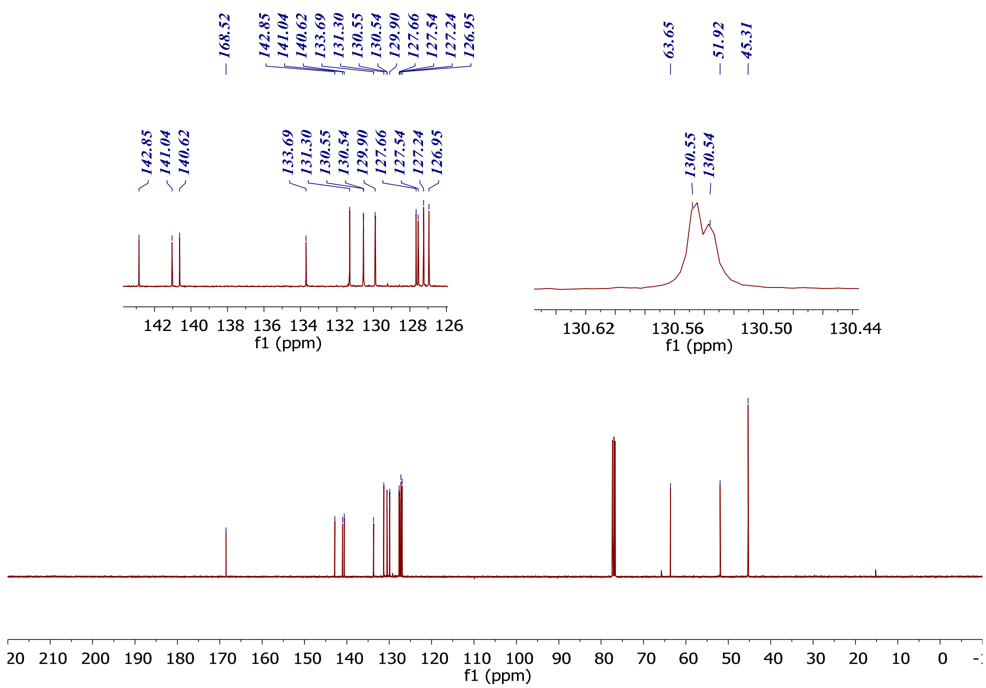
1.09
1.09
1.04
0.96
1.03
3.29
2.15
6.44
f1 (ppm)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141.04
140.62
133.69
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130.55
130.54
129.90
127.66
127.54
127.24
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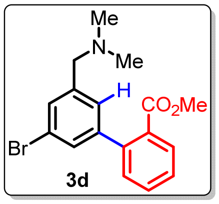
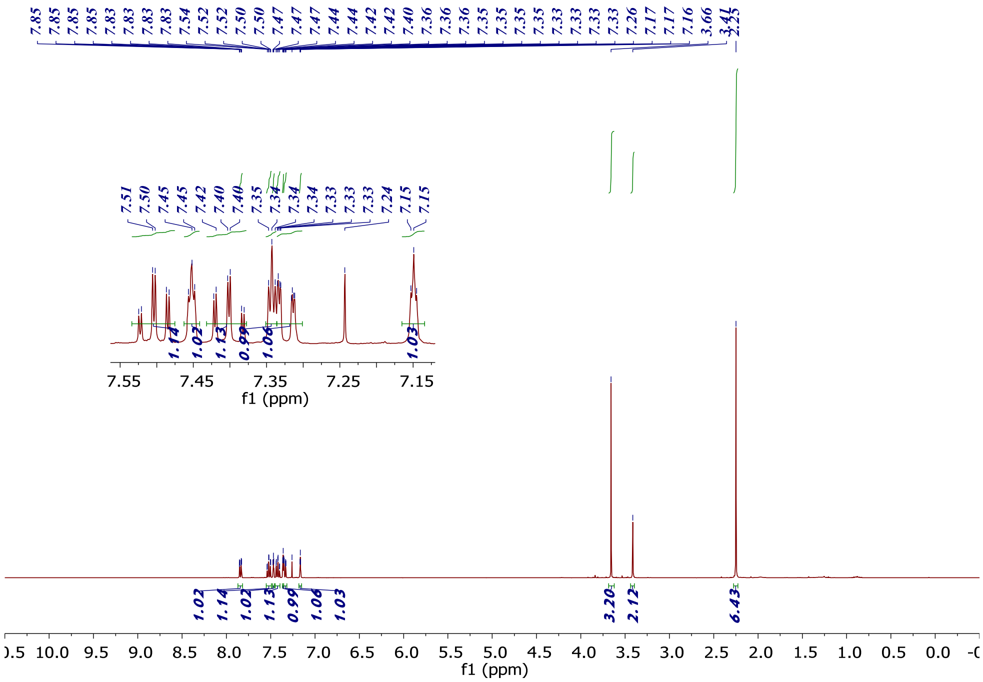
51.92
45.31
f1 (ppm)


Me
N
Me
H
CO2Me
Br

3d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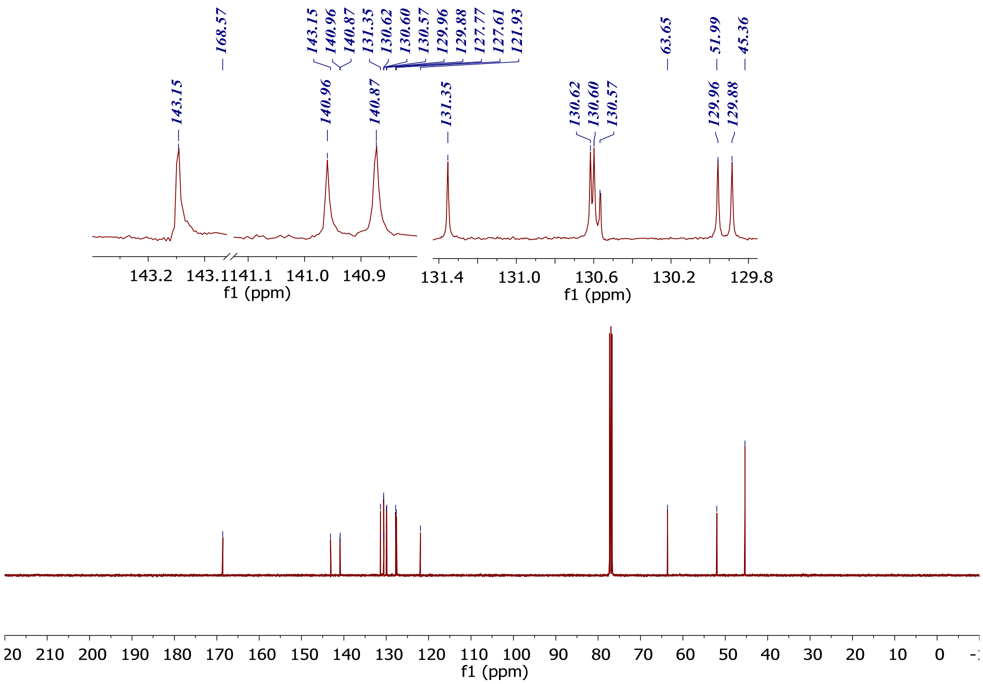
7.51 7.50 7.45 7.45 7.42 7.40 7.40 7.35 7.34 7.34 7.33 7.33 7.33 7.24 7.15 7.15
1.14 1.02 1.13 0.99 1.06 1.03
7.55 7.45 7.35 7.25 7.15
f1 (ppm)
1.02 1.14 1.02 1.13 0.99 1.06 1.03 3.20 2.12 6.43
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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63.65
51.99
45.36
143.15 140.96 140.87
143.2 143.1 141.1 141.0 140.9
f1 (ppm)
131.35 130.62 130.60 130.57 129.96 129.88
131.4 131.0 130.6 130.2 129.8
f1 (ppm)
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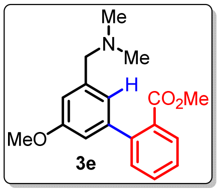
f1 (ppm)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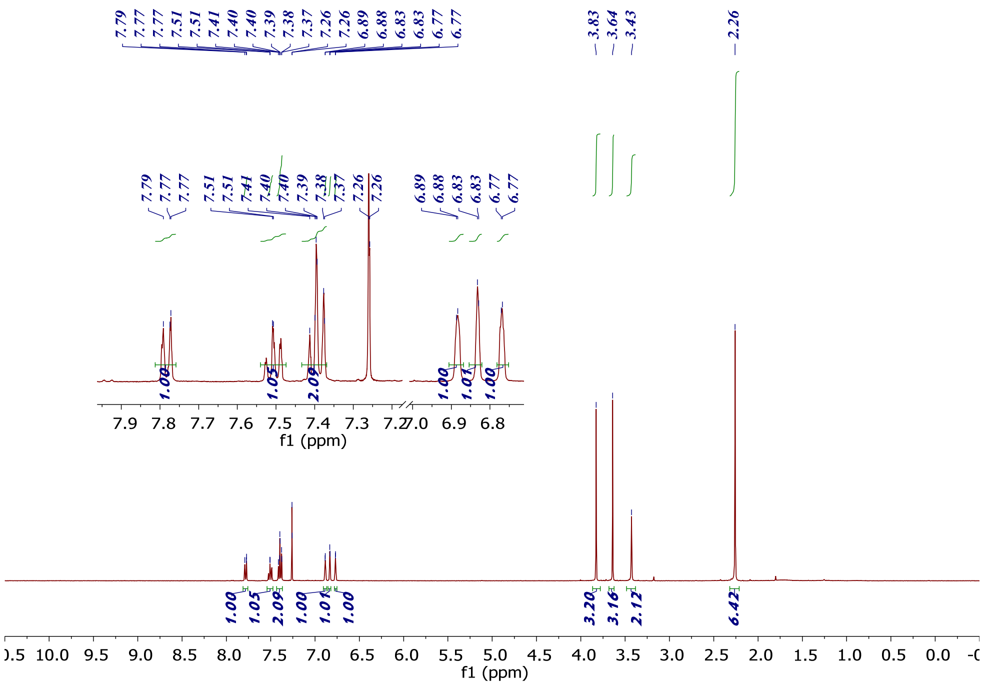
N
Me
H
CO2Me
MeO
3e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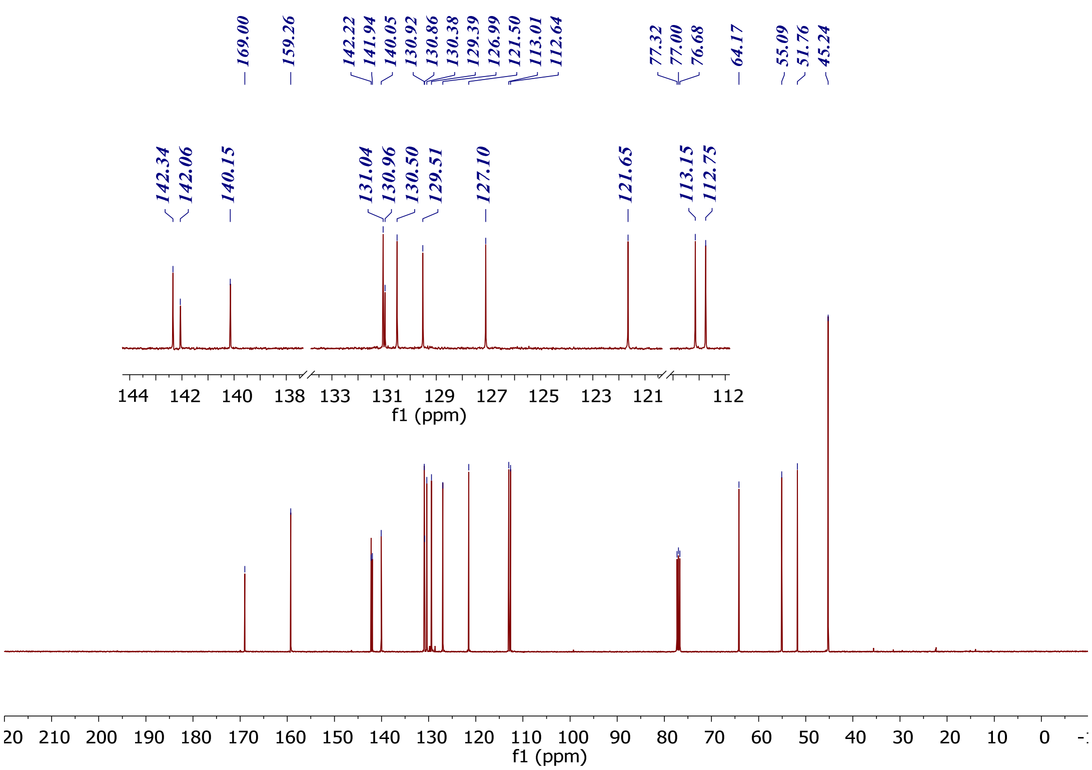
3.83 3.64 3.43
2.26
1.00 1.05 2.09 1.00 1.01 1.00
3.20 3.16 2.12
6.42
f1 (ppm)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159.26
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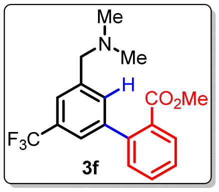
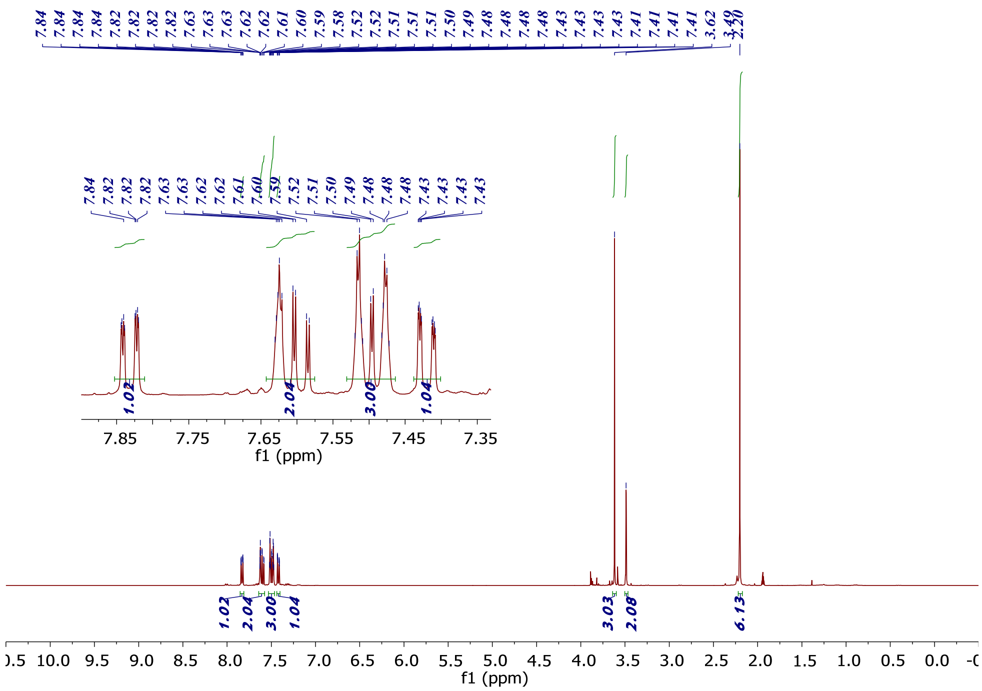
77.32 77.00 76.68
64.17
55.09 51.76 45.24
142.34 142.06 140.15 131.04 130.96 130.50 129.51 127.10 121.65 113.15 112.75
f1 (ppm)


Me
N
Me
H
CO2Me
F3C
3f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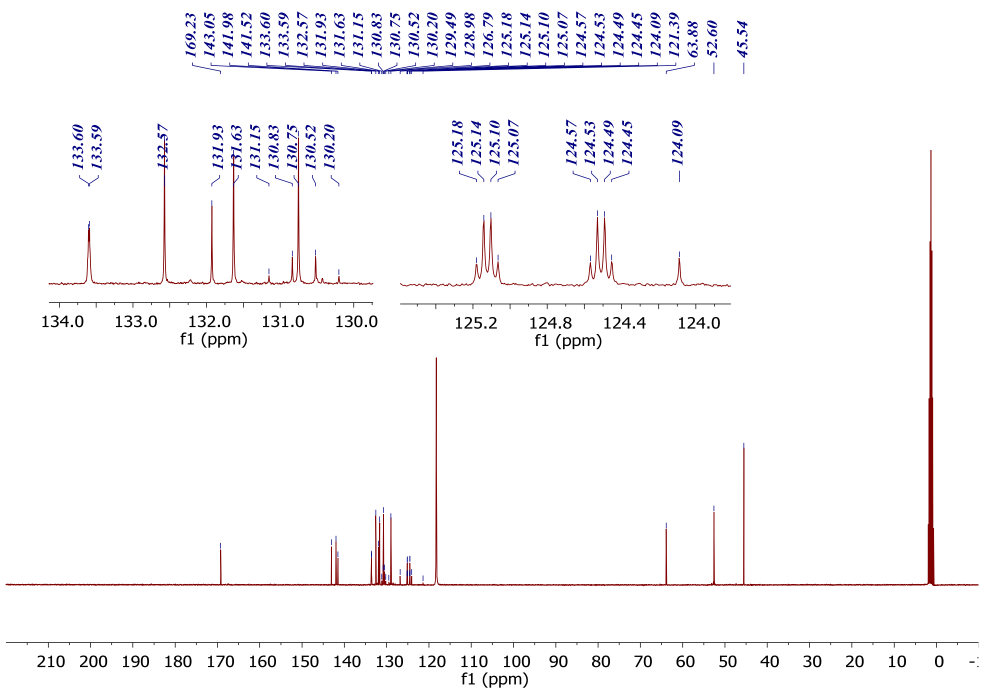
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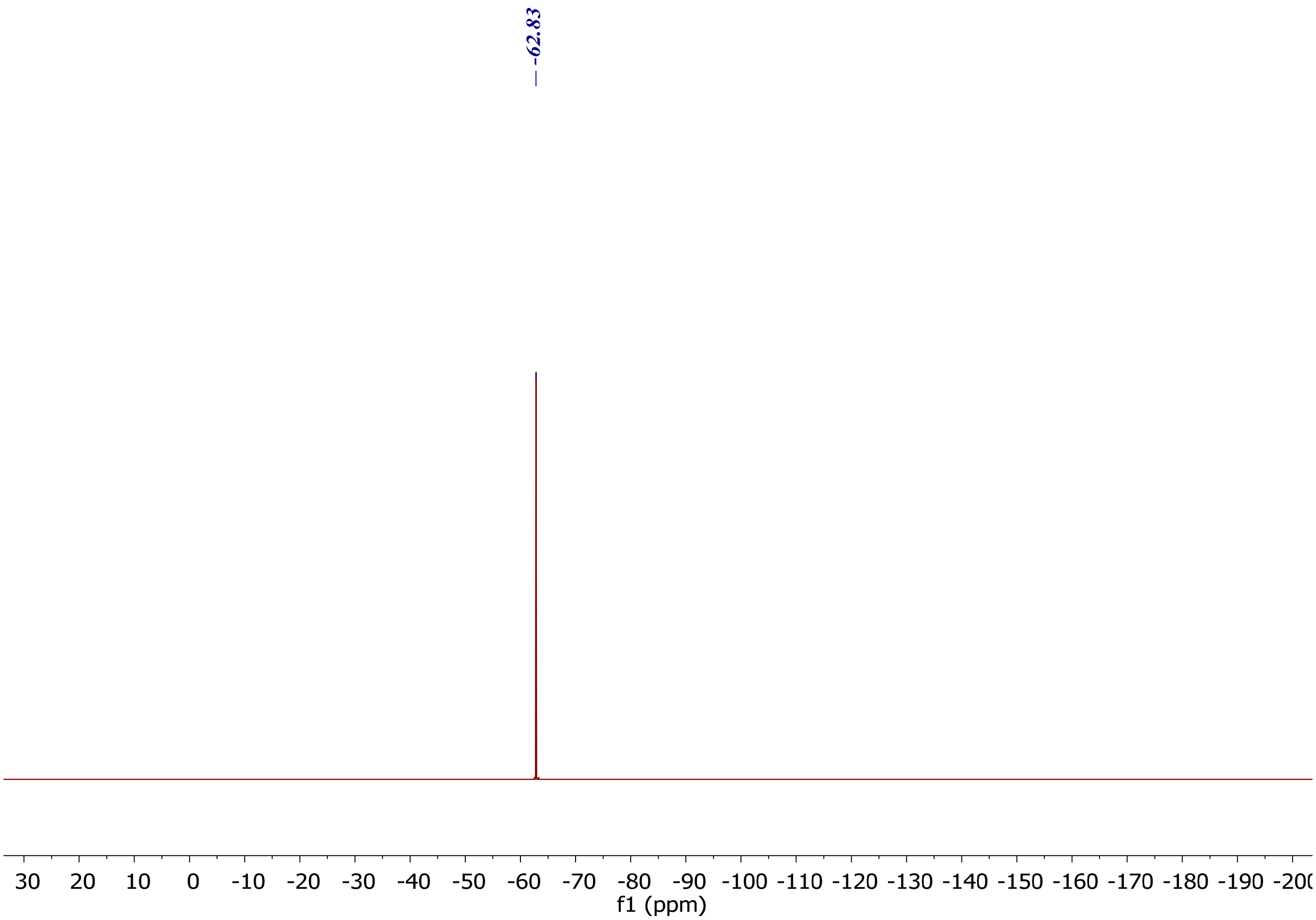

-62.83
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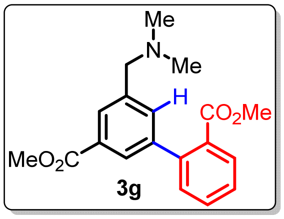
f1 (ppm)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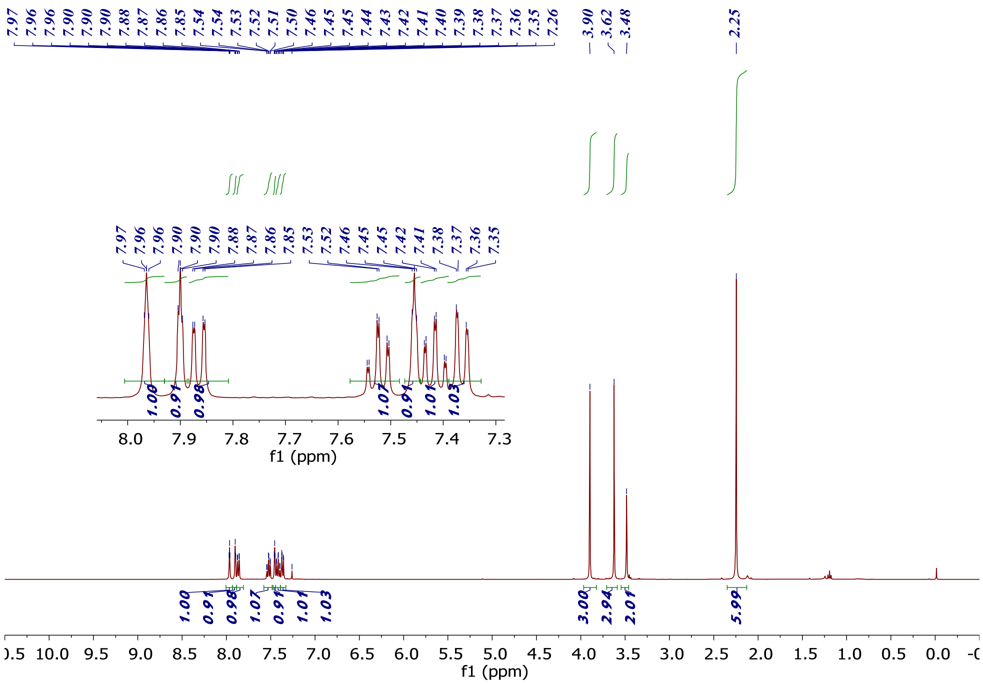
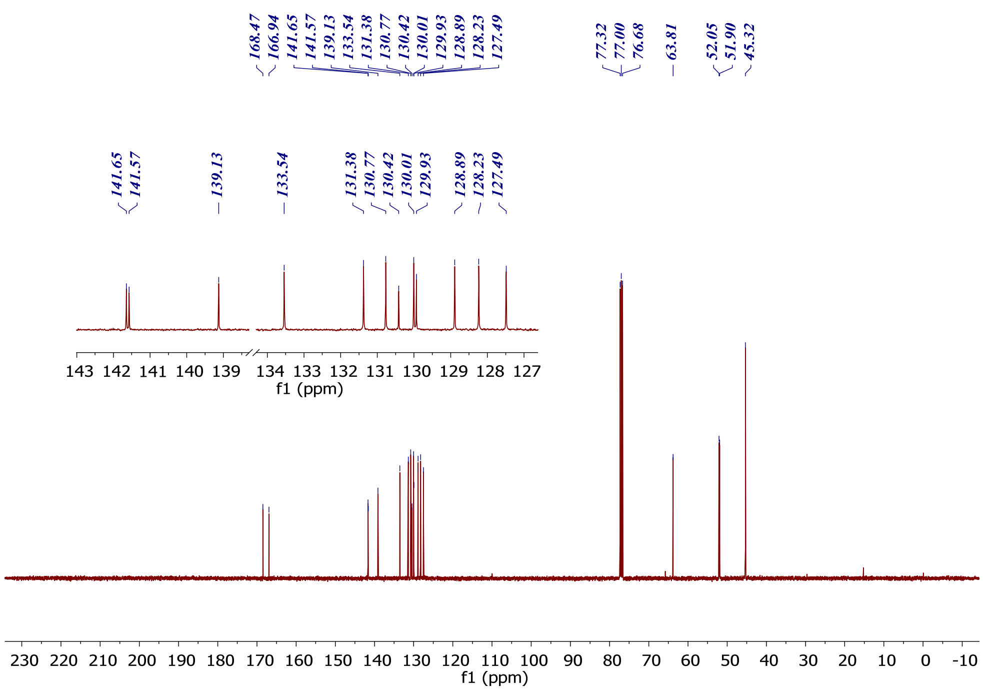
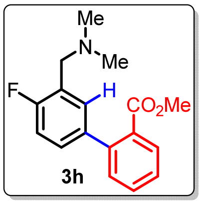
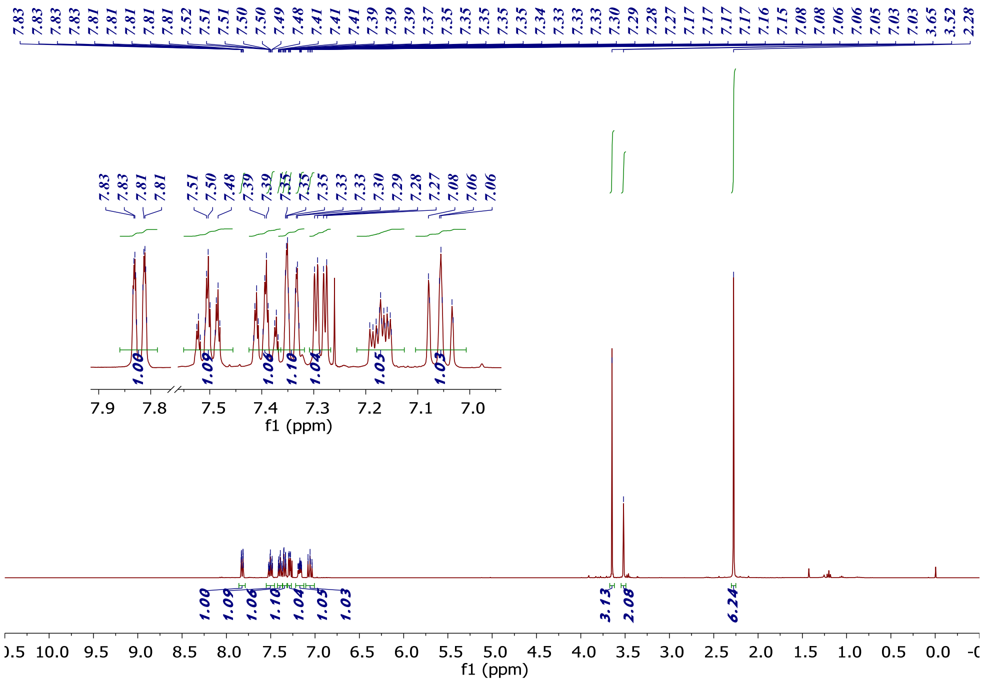
Me
H
CO2Me
MeO2C
3g

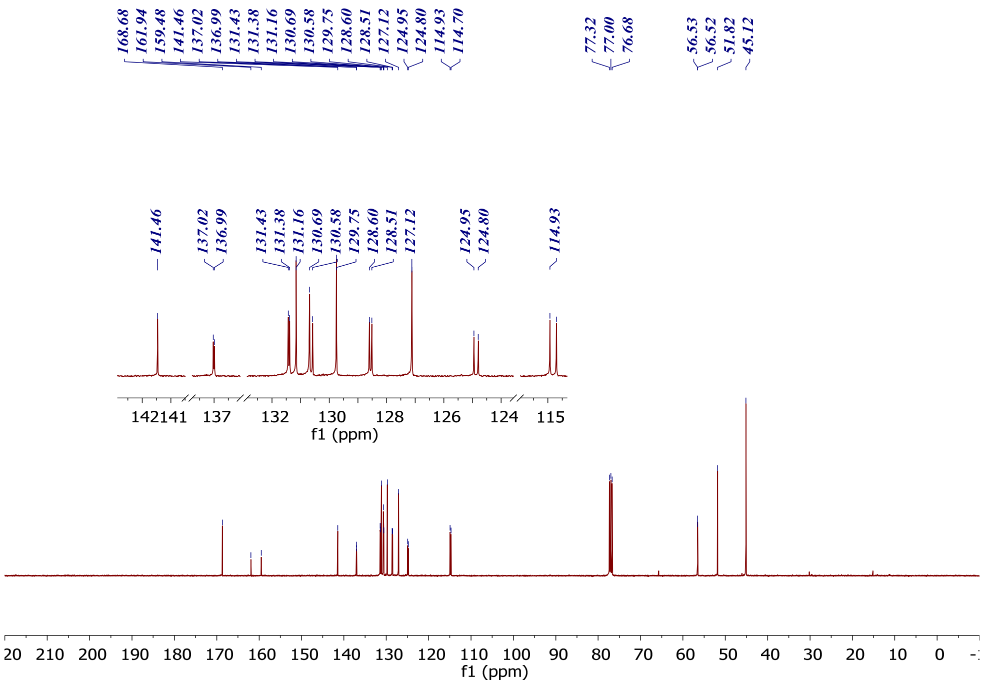

7.97 7.96 7.96 7.90 7.90 7.90 7.88 7.87 7.86 7.85 7.54 7.54 7.53 7.52 7.51 7.50 7.46 7.45 7.45 7.44 7.43 7.42 7.41 7.40 7.39 7.38 7.37 7.36 7.35 7.26
3.90 3.62 3.48
2.25
1.00 0.91 0.98 1.07 0.91 1.01 1.03
3.00 2.94 2.01
5.99
f1 (ppm)

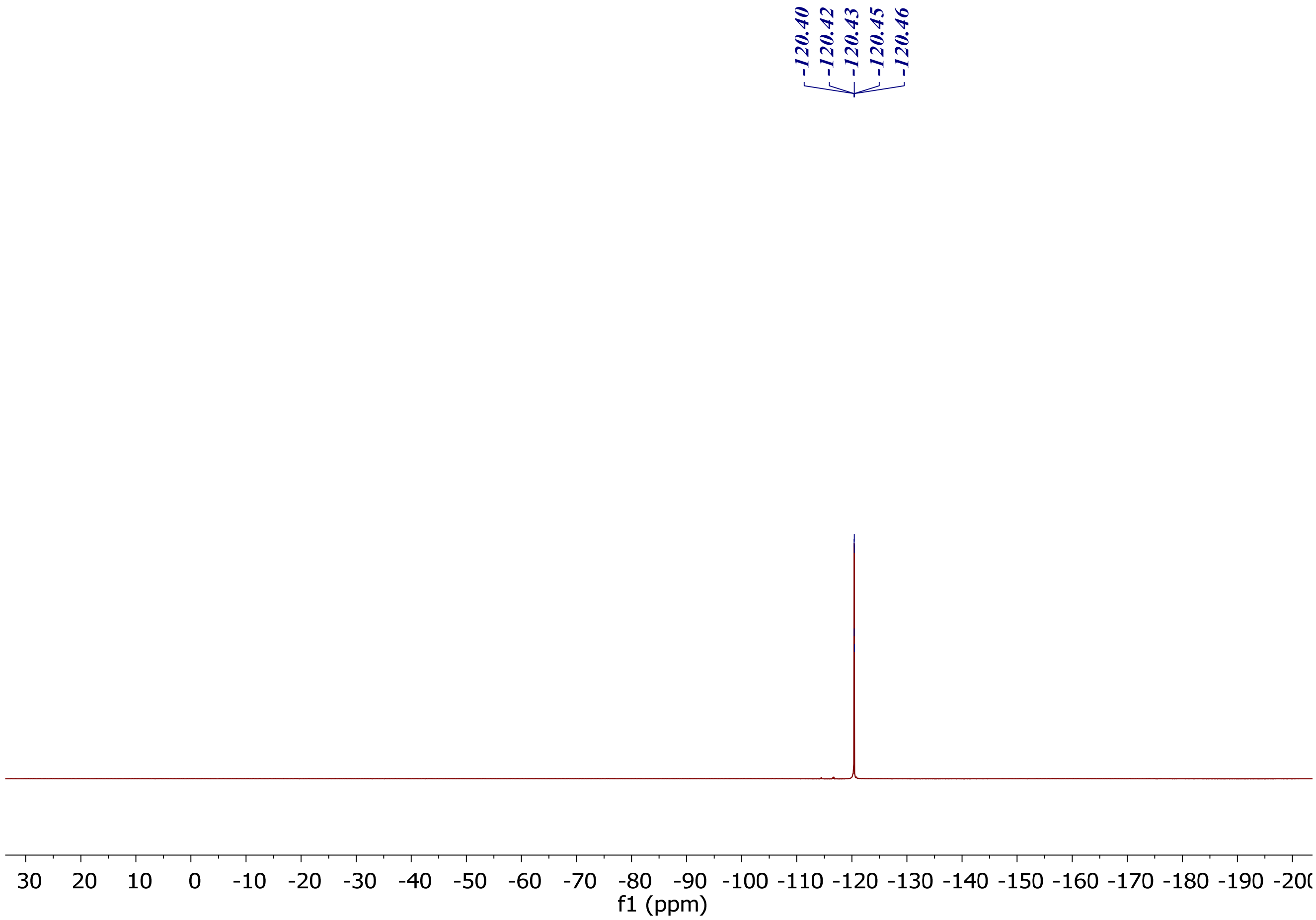

168.47 166.94 141.65 141.57 139.13 133.54 131.38 130.77 130.42 130.01 129.93 128.89 128.23 127.49
77.32 77.00 76.68
63.81
52.05 51.90 45.32
f1 (ppm)

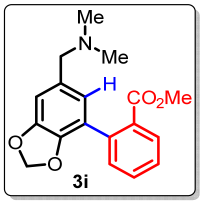


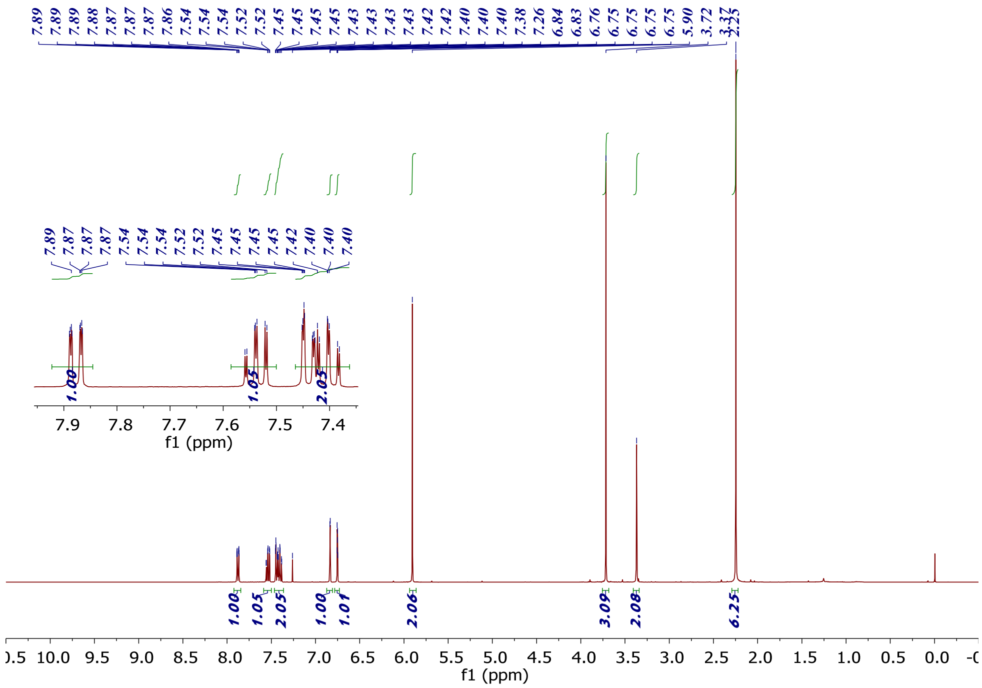
3h

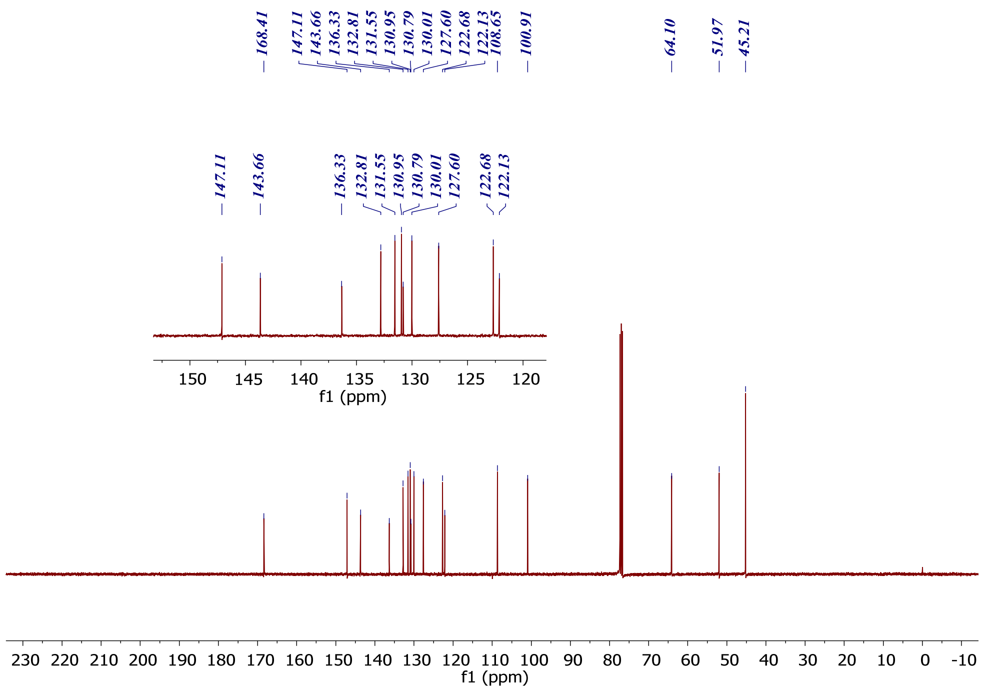


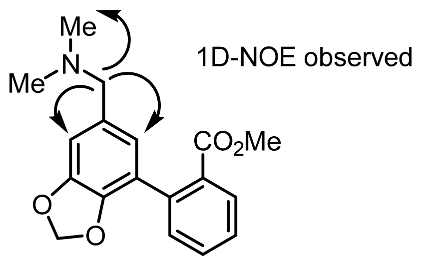



-120.40
-120.42
-120.43
-120.45
-120.46
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

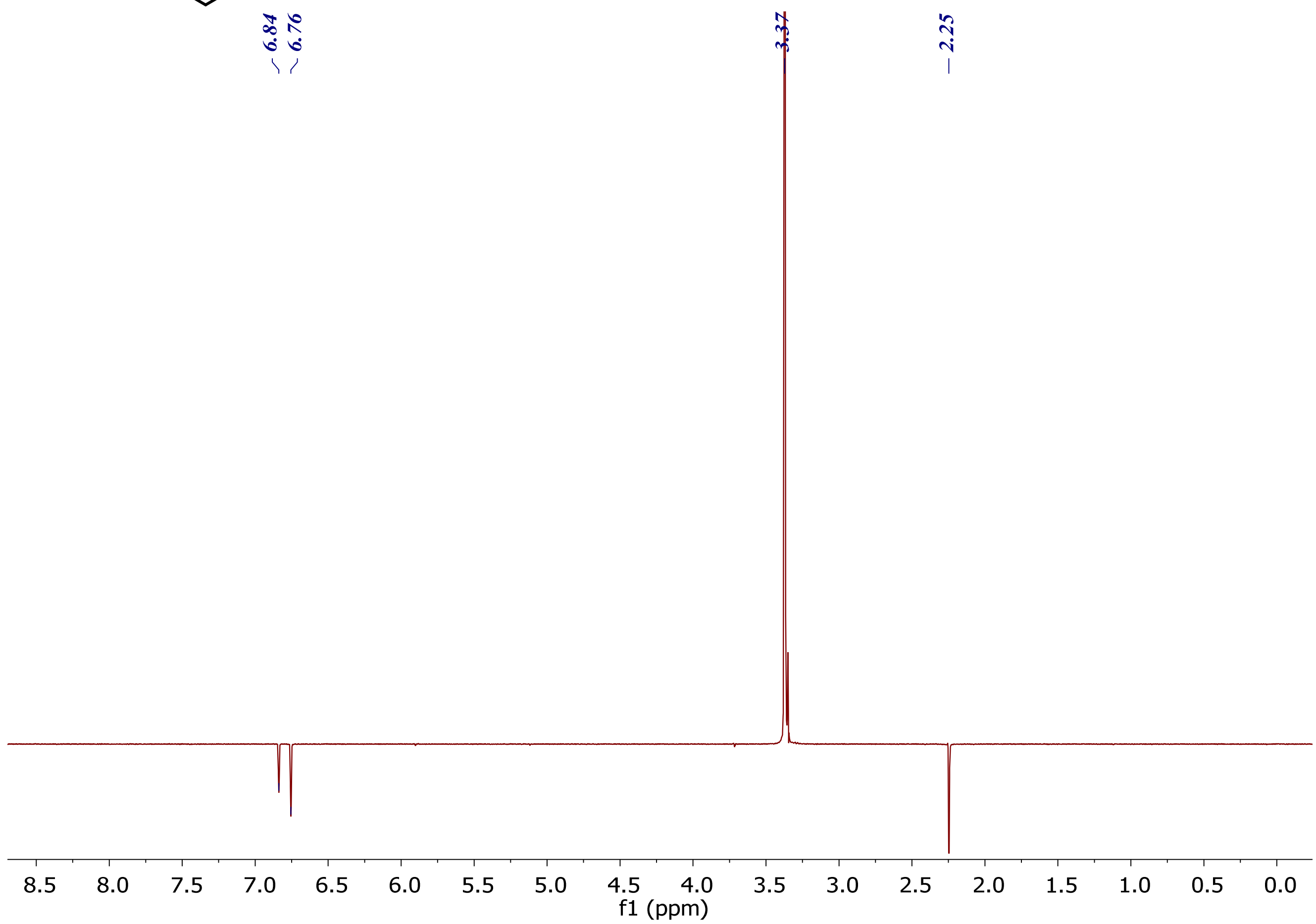

Me
N
Me
H
CO2Me
O
O
3i


7.89 7.89 7.89 7.88 7.87 7.87 7.87 7.86 7.54 7.54 7.54 7.52 7.52 7.45 7.45 7.45 7.45 7.43 7.43 7.43 7.43 7.42 7.42 7.40 7.40 7.40 7.38 7.26 6.84 6.83 6.76 6.75 6.75 6.75 6.75 5.90 3.72 3.37 2.25
7.89 7.87 7.87 7.87 7.54 7.54 7.54 7.52 7.52 7.45 7.45 7.45 7.45 7.42 7.40 7.40 7.40 7.40
1.00 1.05 2.03
7.9 7.8 7.7 7.6 7.5 7.4
f1 (ppm)
1.00 1.05 2.05 1.00 1.01 2.06 3.09 2.08 6.25
0.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

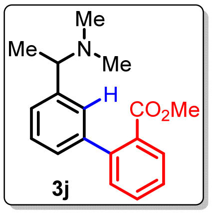

168.41 147.11 143.66 136.33 132.81 131.55 130.95 130.79 130.01 127.60 122.68 122.13 108.65 100.91 64.10 51.97 45.21
147.11 143.66 136.33 132.81 131.55 130.95 130.79 130.01 127.60 122.68 122.13
150 145 140 135 130 125 120
f1 (ppm)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

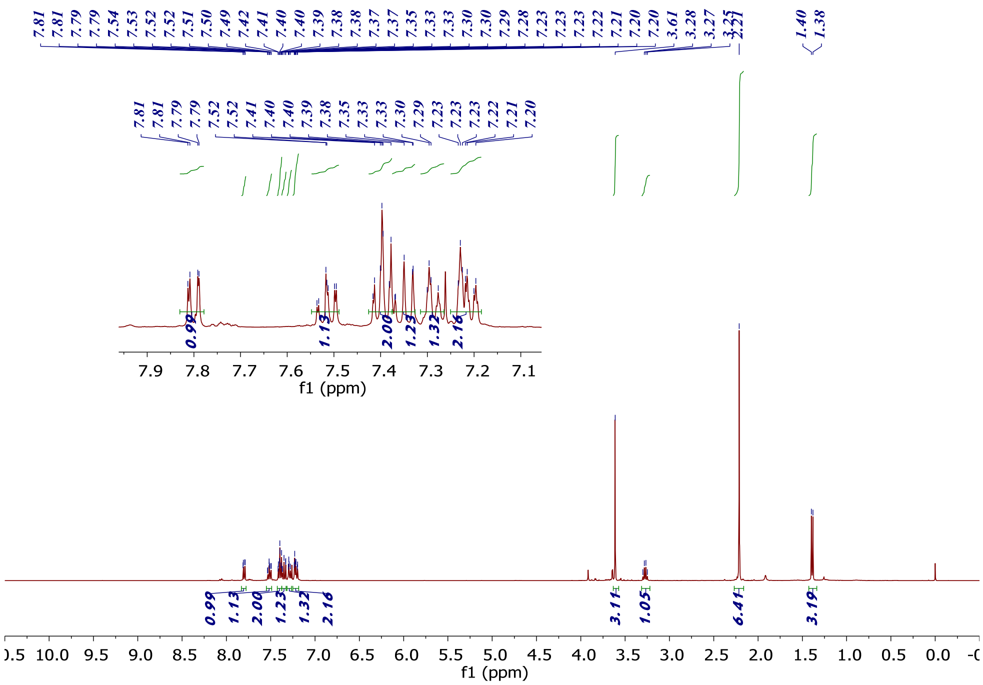


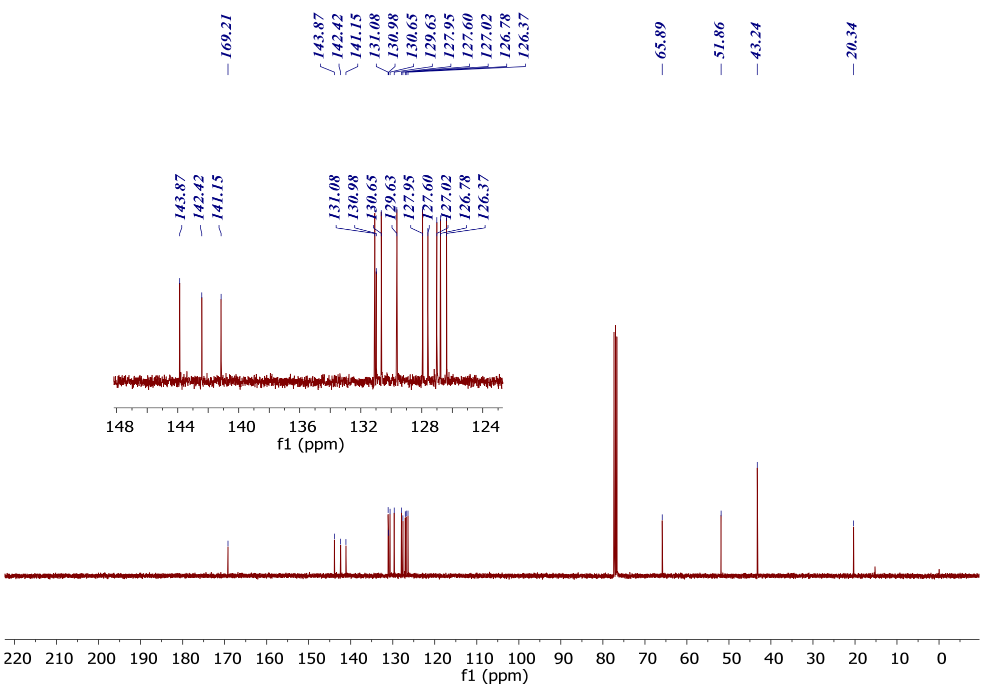
Me
N
Me
CO2Me
O
O
1D-NOE observed

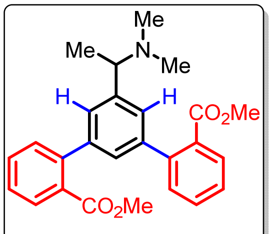


6.84
6.76
3.37
2.25
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

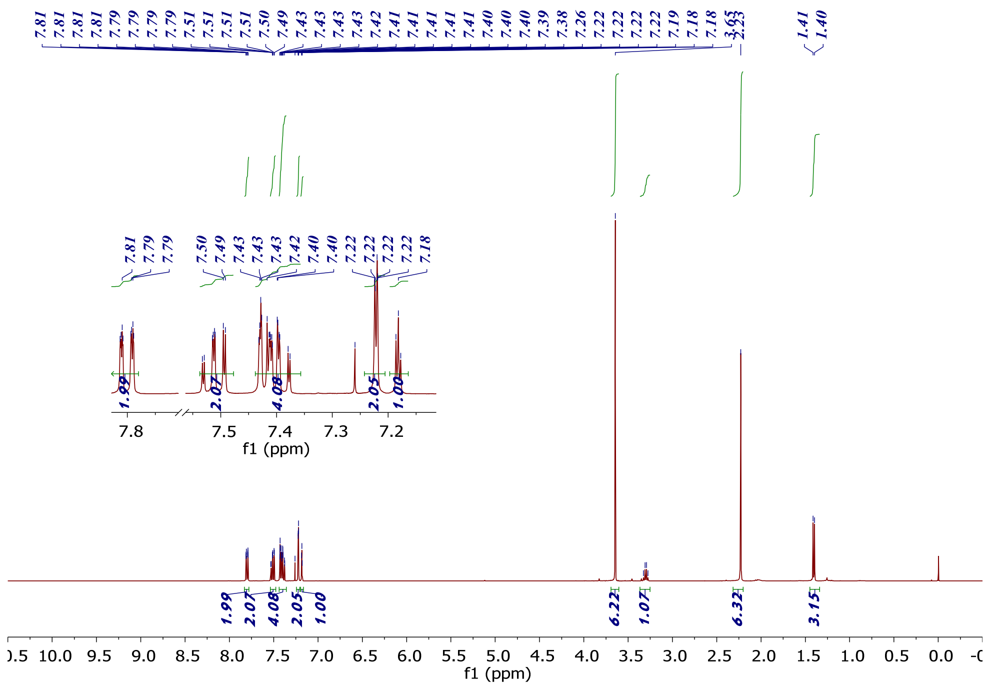

Me
Me
N
Me
H
CO2Me
3j

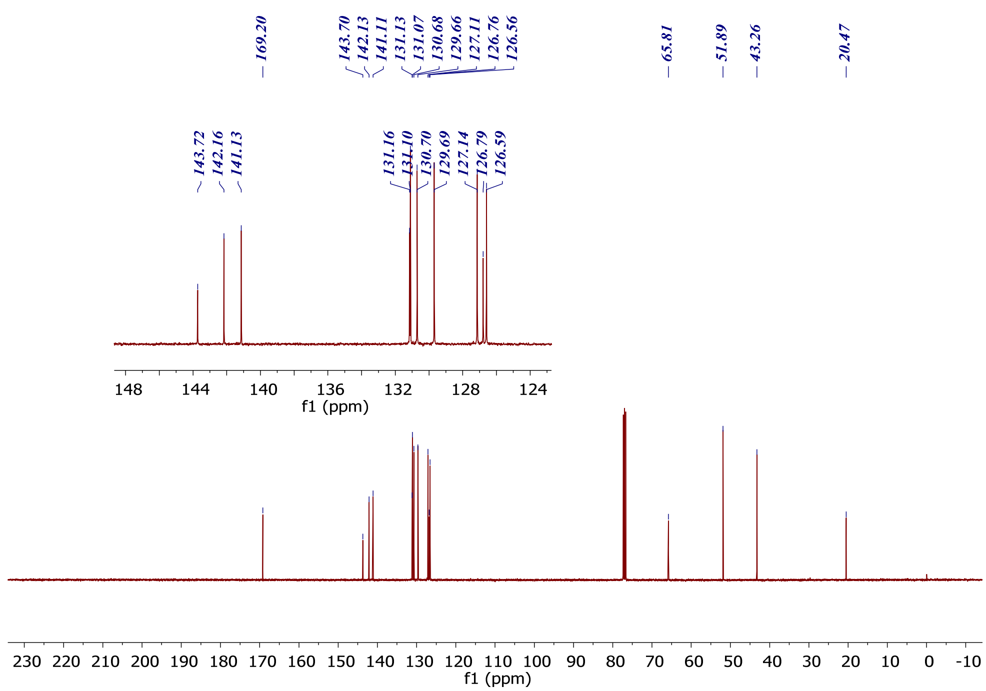

7.81
7.81
7.79
7.79
7.54
7.53
7.52
7.52
7.51
7.50
7.49
7.42
7.41
7.40
7.40
7.39
7.38
7.38
7.37
7.37
7.35
7.33
7.33
7.30
7.30
7.29
7.28
7.23
7.23
7.23
7.22
7.21
7.20
7.20
3.61
3.28
3.27
3.25
2.21
1.40
1.38
0.99
1.13
2.00
1.23
1.32
2.16
7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1
f1 (ppm)
3.11
1.05
6.41
3.19
10.0 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)


169.21
143.87
142.42
141.15
131.08
130.98
130.65
129.63
127.95
127.60
127.02
126.78
126.37
65.89
51.86
43.24
20.34
148 144 140 136 132 128 124
f1 (ppm)
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)


Me
Me
N
Me
H
H
CO2Me
CO2Me

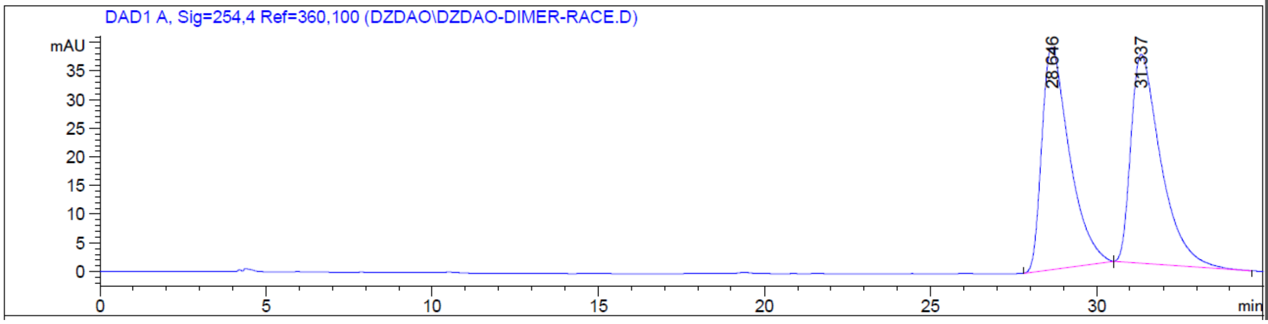
3j'


7.81 7.81 7.81 7.81 7.79 7.79 7.79 7.79 7.51 7.51 7.51 7.51 7.50 7.49 7.43 7.43 7.43 7.42 7.41 7.41 7.41 7.41 7.40 7.40 7.40 7.39 7.38 7.26 7.22 7.22 7.22 7.22 7.22 7.19 7.18 7.18 3.65 2.23
1.41 1.40
7.81 7.79 7.79 7.50 7.49 7.43 7.43 7.43 7.42 7.40 7.40 7.22 7.22 7.22 7.22 7.18
1.99 2.07 4.08 2.05 1.00
7.8 7.5 7.4 7.3 7.2
f1 (ppm)
1.99 2.07 4.08 2.05 1.00 6.22 1.07 6.32 3.15
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


169.20
143.70 142.13 141.11 131.13 131.07 130.68 129.66 127.11 126.76 126.56
65.81
51.89
43.26
20.47
143.72 142.16 141.13
131.16 131.10 130.70 129.69 127.14 126.79 126.59
148 144 140 136 132 128 124
f1 (ppm)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

Chiral HPLC conditions for racemic sample **3j'**

```
Data File C:\CHEM32\2\DATA\DZDAO\DZDAO-DIMER-RACE.D
Sample Name: dzdao-dimer-race

    =====================================================================
    Acq. Operator   : SYSTEM
    Acq. Instrument : 1260                          Location : Vial 1
    Injection Date  : 4/17/2015 9:57:54 PM
                                                  Inj Volume : 1.000 µl
    Acq. Method     : C:\CHEM32\2\METHODS\LIN.M
    Last changed    : 4/17/2015 9:27:49 PM by SYSTEM
                      (modified after loading)
    Analysis Method : C:\CHEM32\2\METHODS\DEF_LC.M
    Last changed    : 4/9/2015 11:01:36 PM by SYSTEM
    Sample Info     : IF 1.0 mL/min Hex:IPA:Et2NH=98.5:1.5:0.01
```



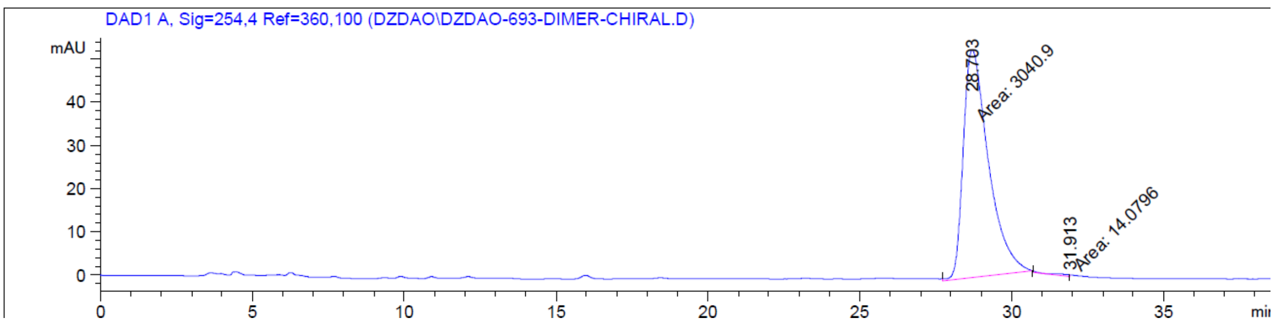
Data File C:\CHEM32\2\DATA\DZDAO\DZDAO-DIMER-RACE.D
Sample Name: dzdao-dimer-race

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.646	BB	0.8614	2246.63452	38.80727	49.5323
2	31.337	BBA	0.9459	2289.05762	36.49050	50.4677
Totals :				4535.69214	75.29777	

Chiral HPLC conditions for enantiopure sample **3j’**

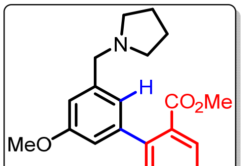
```
Data File C:\CHEM32\2\DATA\DZDAO\DZDAO-693-DIMER-CHIRAL.D
Sample Name: dzdao-693-dimer-chiral

    =====================================================================
    Acq. Operator   : SYSTEM
    Acq. Instrument : 1260                            Location : Vial 1
    Injection Date  : 4/17/2015 10:35:56 PM
                                                    Inj Volume : 1.000 µl
    Acq. Method     : C:\CHEM32\2\METHODS\LIN.M
    Last changed    : 4/17/2015 9:27:49 PM by SYSTEM
                      (modified after loading)
    Analysis Method : C:\CHEM32\2\METHODS\DEF_LC.M
    Last changed    : 4/9/2015 11:01:36 PM by SYSTEM
    Sample Info     : IF 1.0 mL/min Hex:IPA:Et2NH=98.5:1.5:0.01


    Additional Info : Peak(s) manually integrated
```



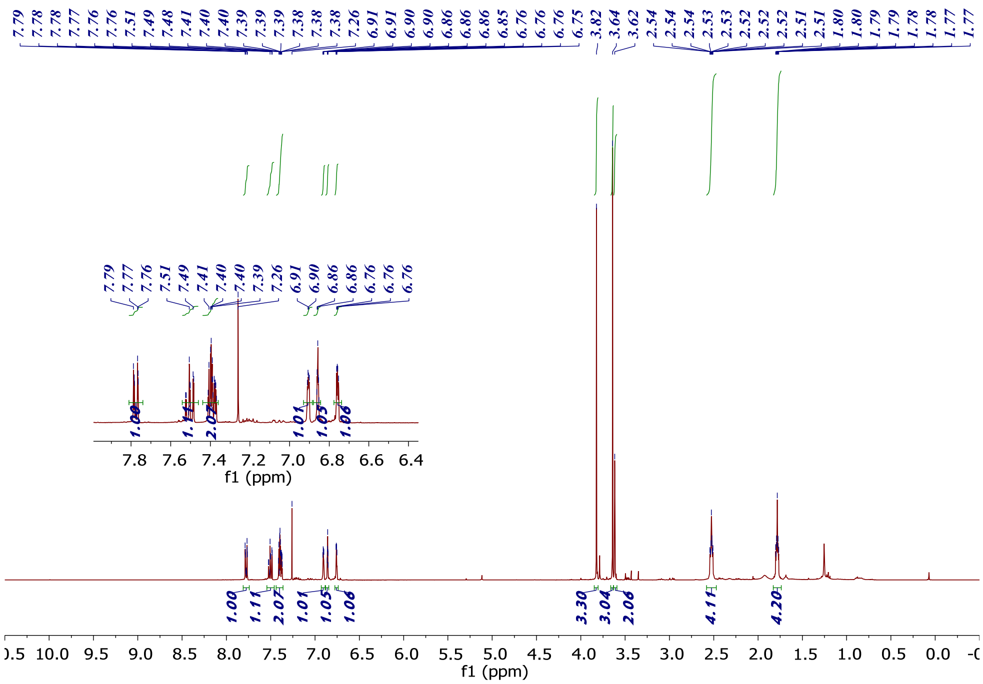
Data File C:\CHEM32\2\DATA\DZDAO\DZDAO-693-DIMER-CHIRAL.D
Sample Name: dzdao-693-dimer-chiral

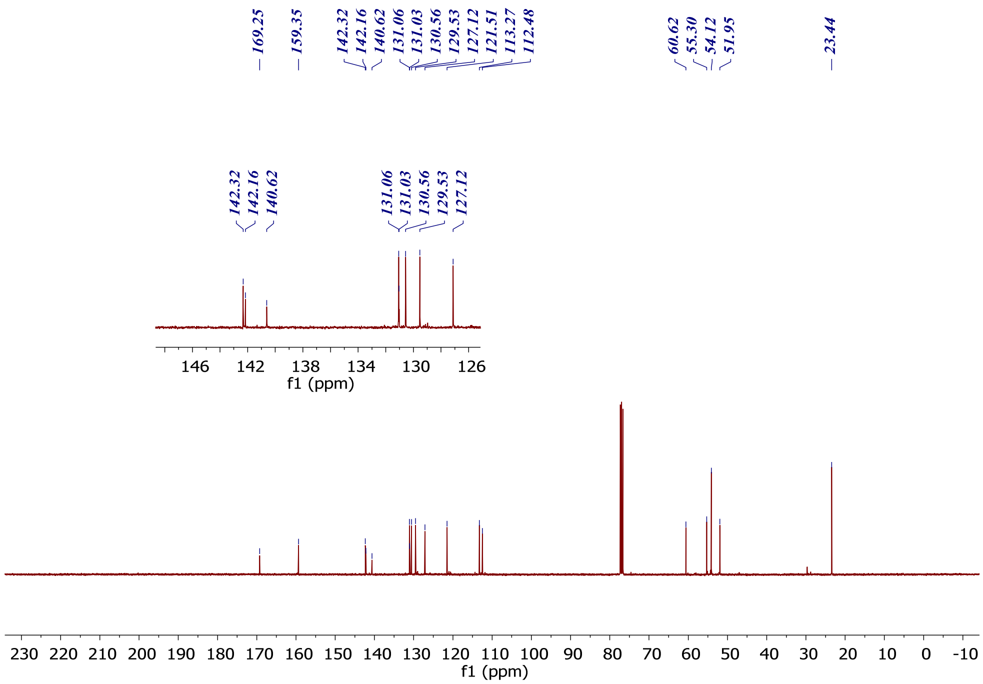
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

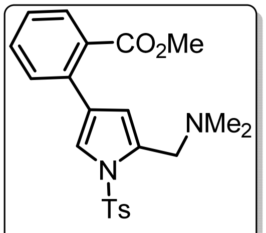
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.703	MM	0.9604	3040.89551	52.76996	99.5391
2	31.913	MM	0.6126	14.07957	3.83043e-1	0.4609
Totals :				3054.97507	53.15300	



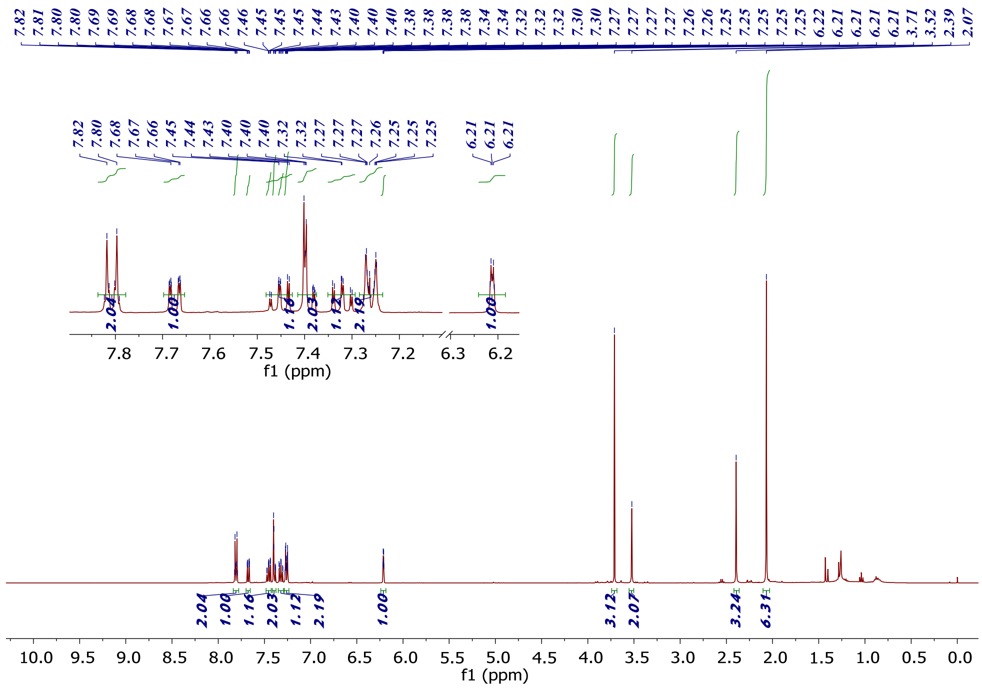
3k

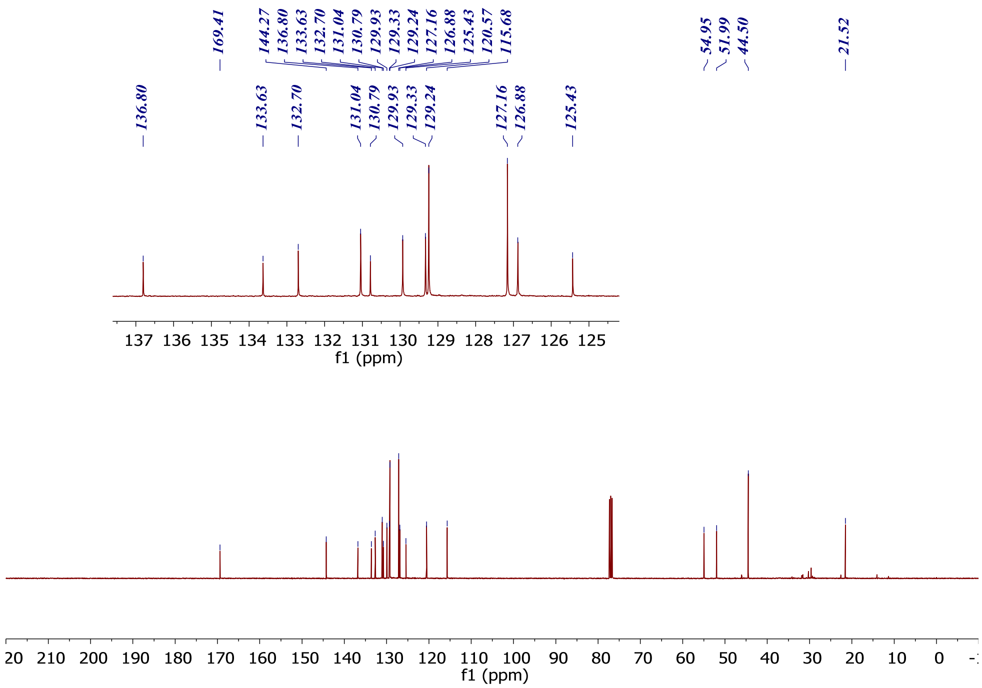

7.79 7.78 7.78 7.77 7.76 7.76 7.51 7.49 7.48 7.41 7.40 7.40 7.39 7.39 7.39 7.38 7.38 7.38 7.26 6.91 6.91 6.90 6.90 6.86 6.86 6.86 6.85 6.76 6.76 6.76 6.75 3.82 3.64 3.62 2.54 2.54 2.54 2.53 2.53 2.52 2.52 2.52 2.51 2.51 1.80 1.80 1.79 1.79 1.78 1.78 1.77 1.77
1.00 1.11 2.07 1.01 1.05 1.06 3.30 3.04 2.06 4.11 4.20
f1 (ppm)

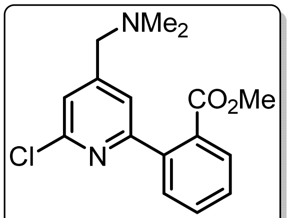

169.25 159.35 142.32 142.16 140.62 131.06 131.03 130.56 129.53 127.12 121.51 113.27 112.48 60.62 55.30 54.12 51.95 23.44
f1 (ppm)



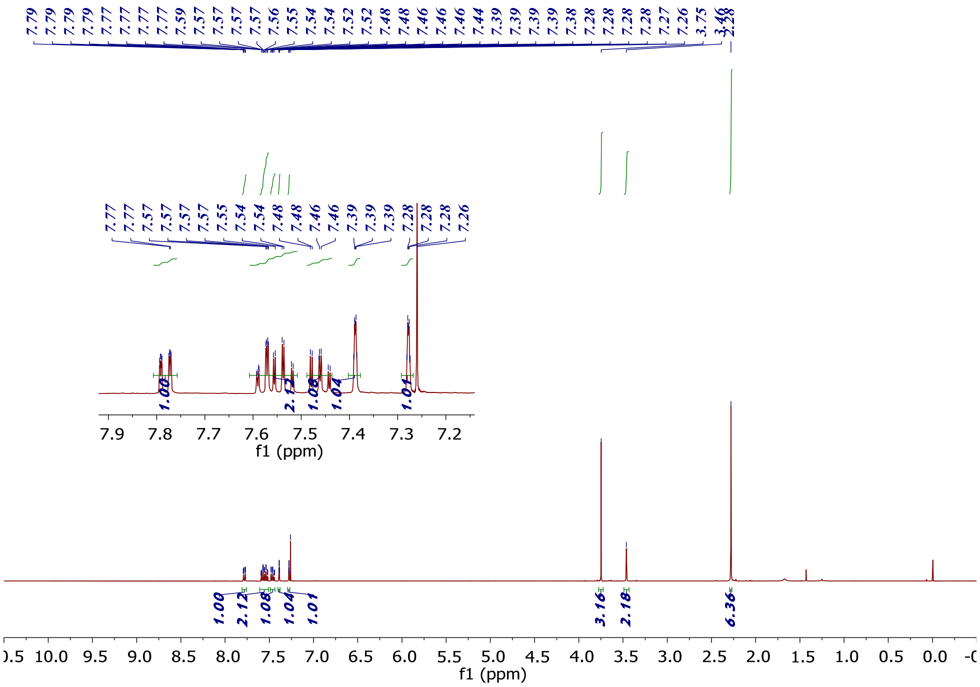
3l

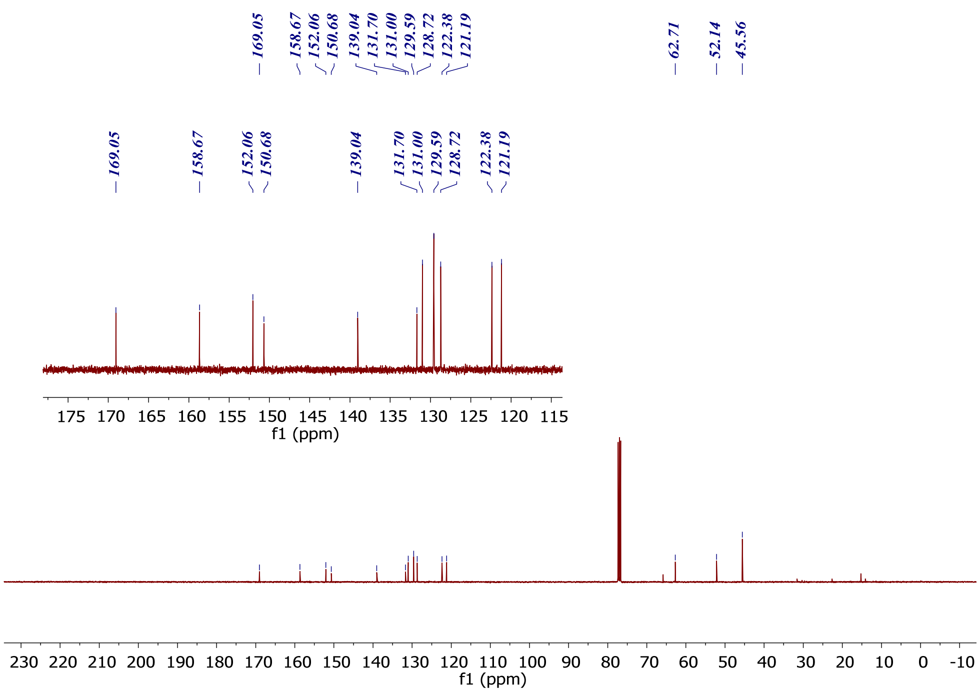


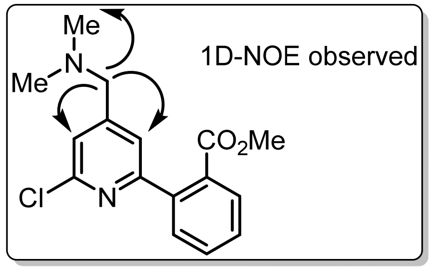


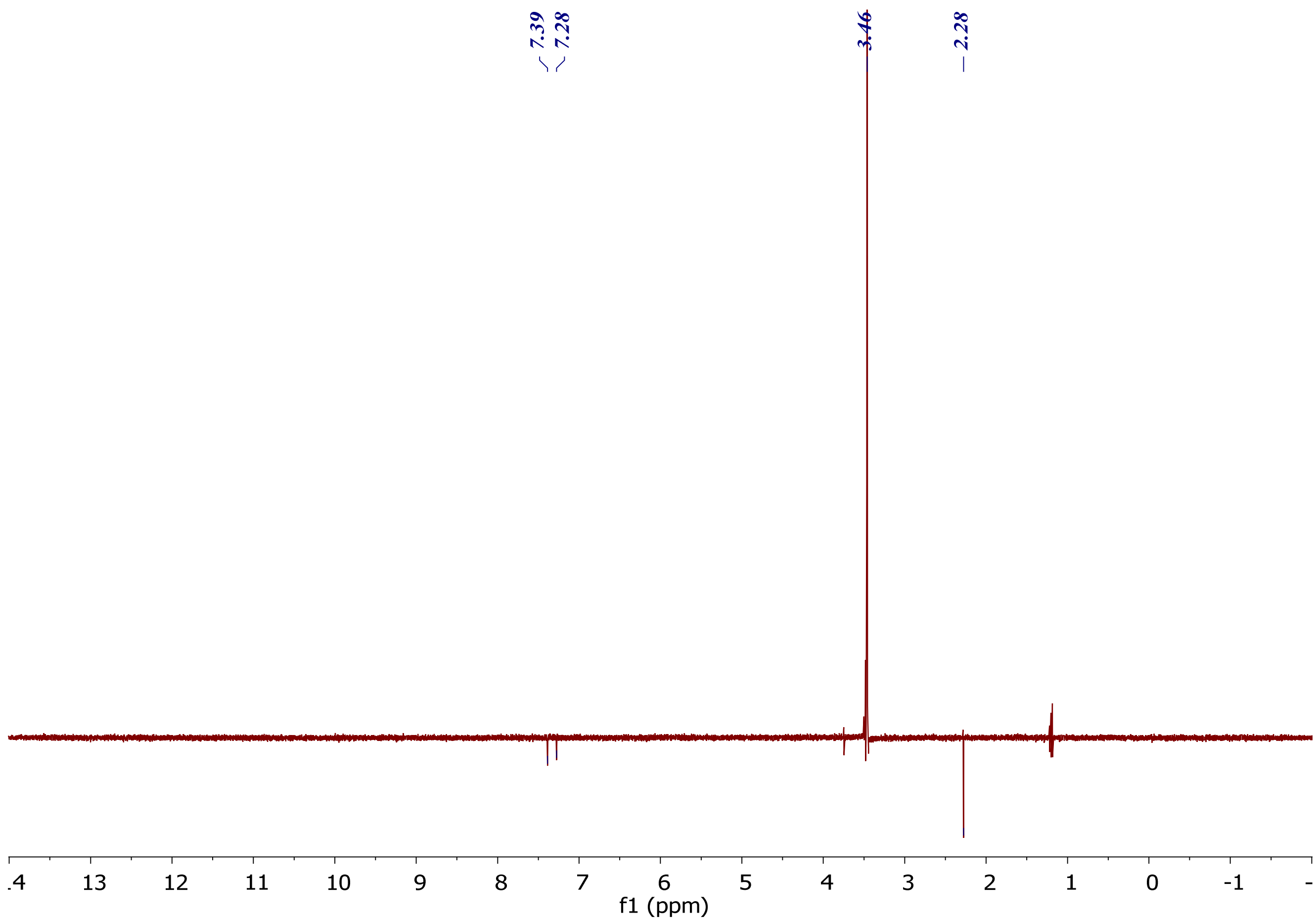


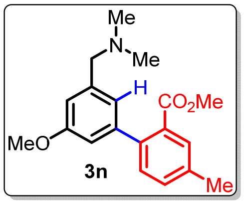
3m

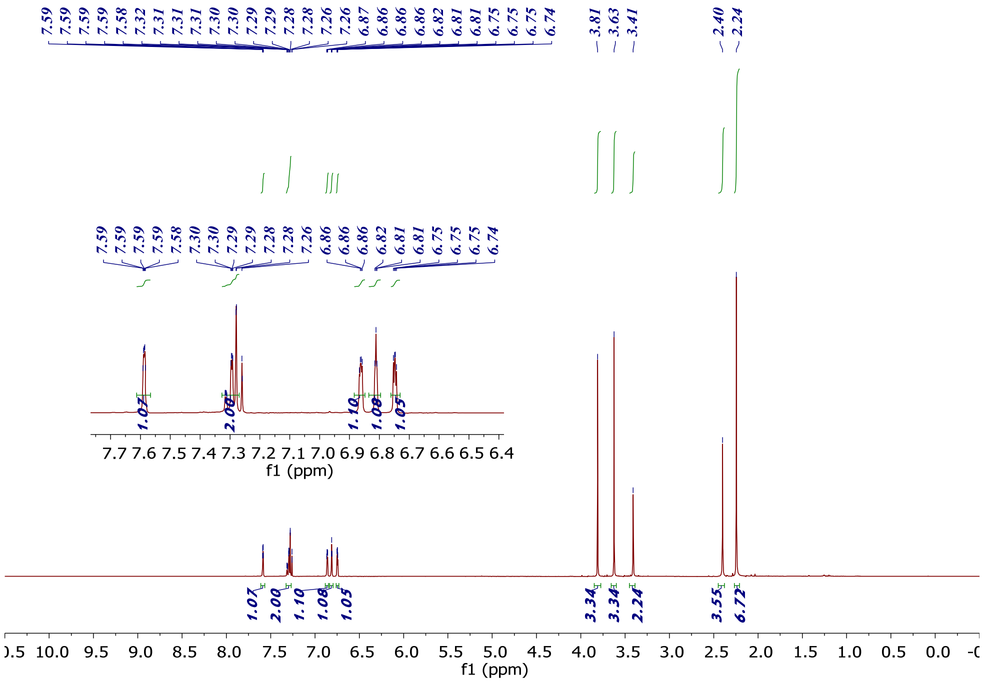


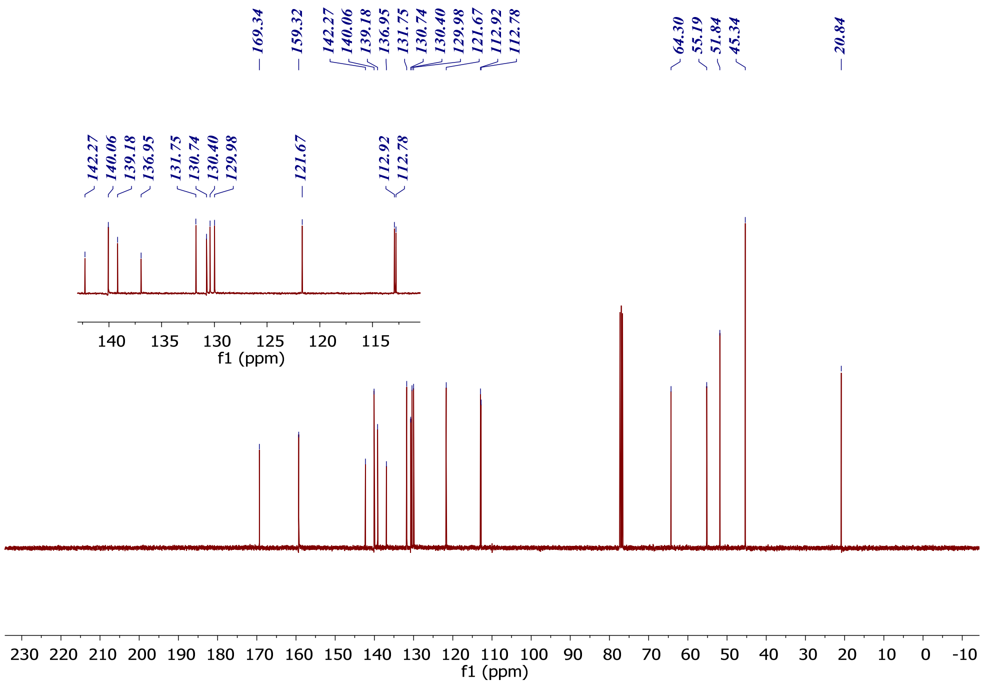


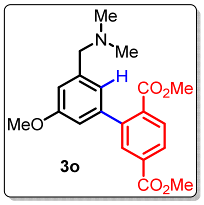

Me
N
Me
1D-NOE observed
CO2Me
Cl
N


7.39
7.28
3.46
2.28
.4
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-
f1 (ppm)

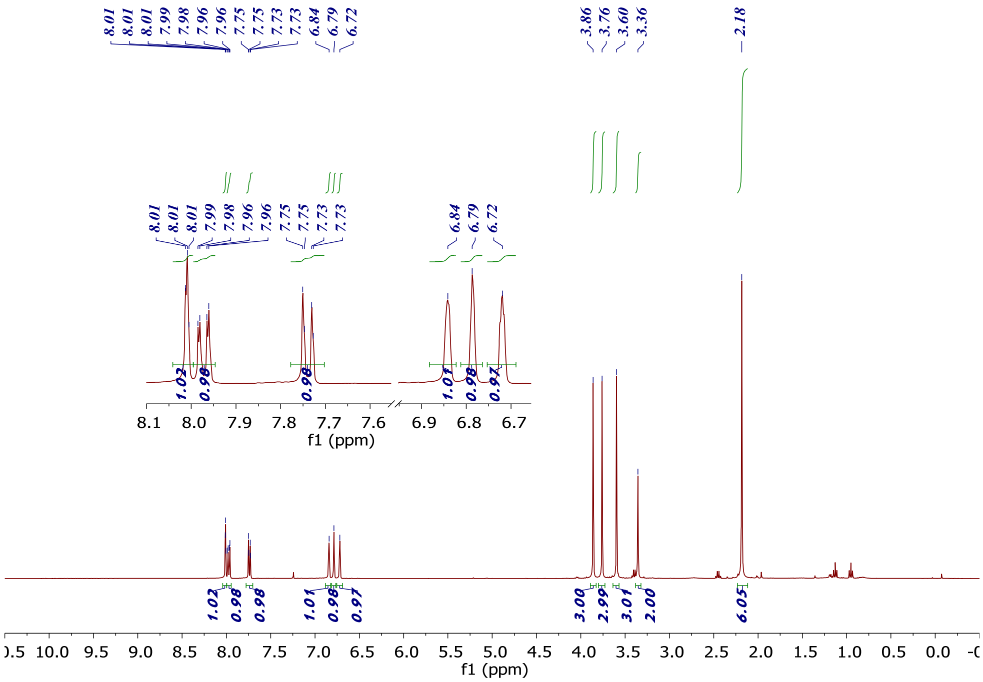

Me
N
Me
H
CO2Me
MeO
3n
Me

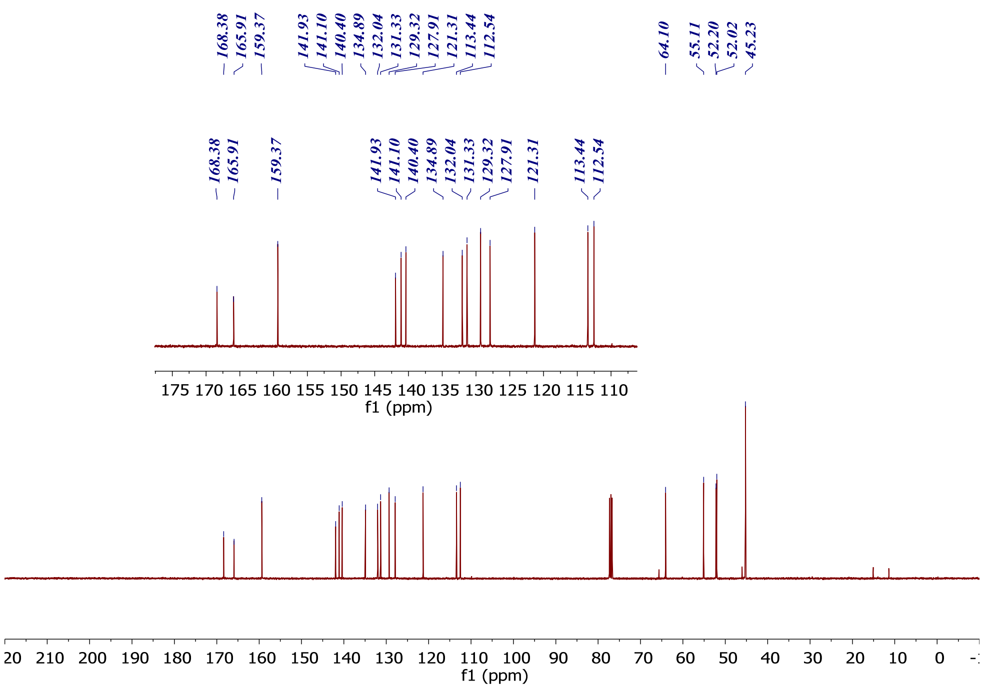

7.59 7.59 7.59 7.59 7.58 7.32 7.31 7.31 7.31 7.30 7.30 7.29 7.29 7.28 7.28 7.26 7.26 6.87 6.86 6.86 6.86 6.82 6.81 6.81 6.75 6.75 6.75 6.74
3.81 3.63 3.41
2.40 2.24
1.07 2.00 1.10 1.08 1.05 3.34 3.34 2.24 3.55 6.72
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 6.5 6.4
f1 (ppm)

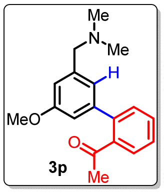

169.34 159.32 142.27 140.06 139.18 136.95 131.75 130.74 130.40 129.98 121.67 112.92 112.78
64.30 55.19 51.84 45.34 20.84
140 135 130 125 120 115
f1 (ppm)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

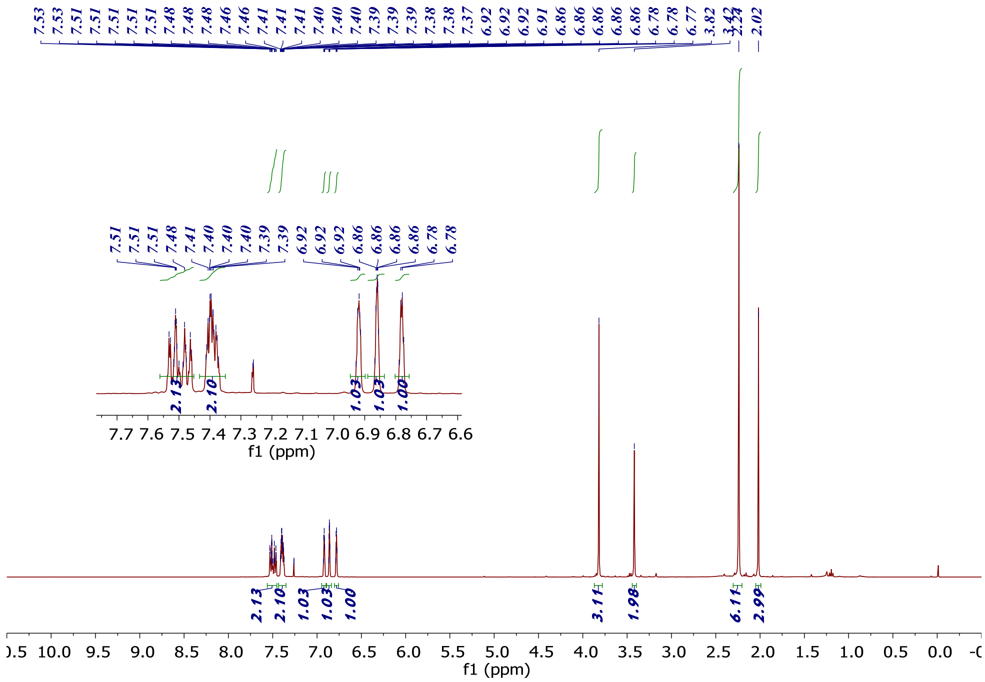


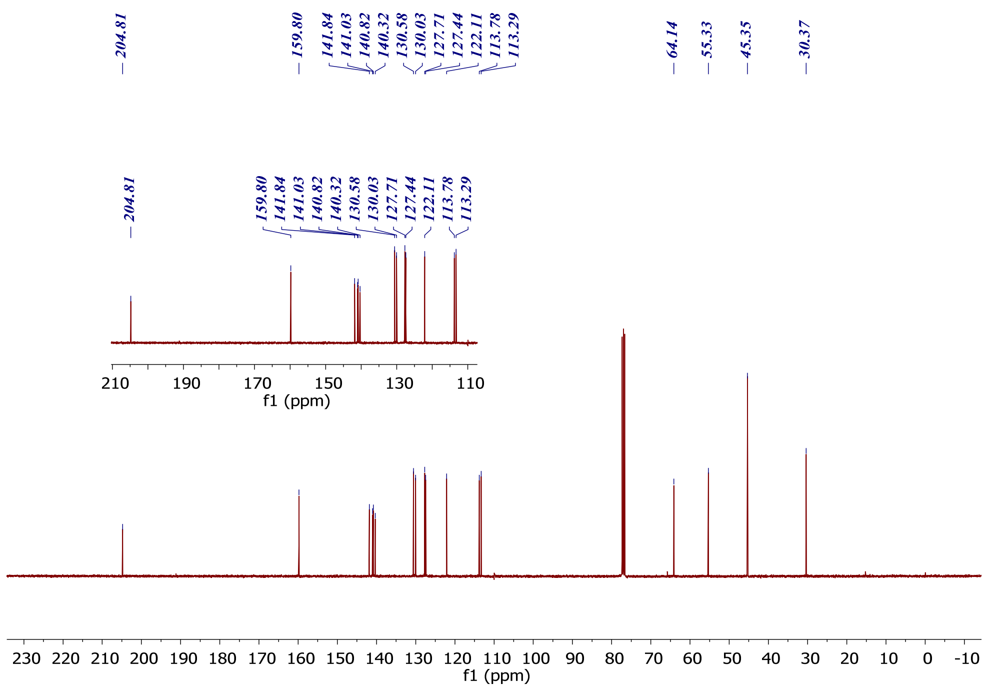
3o

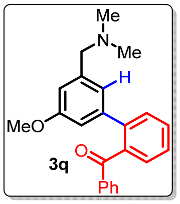


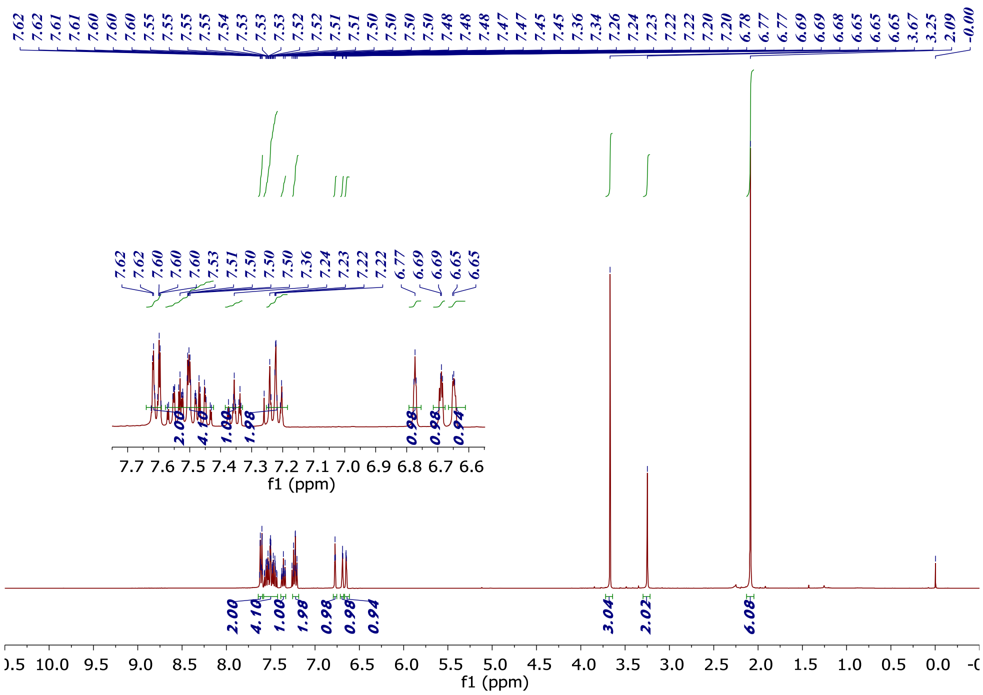


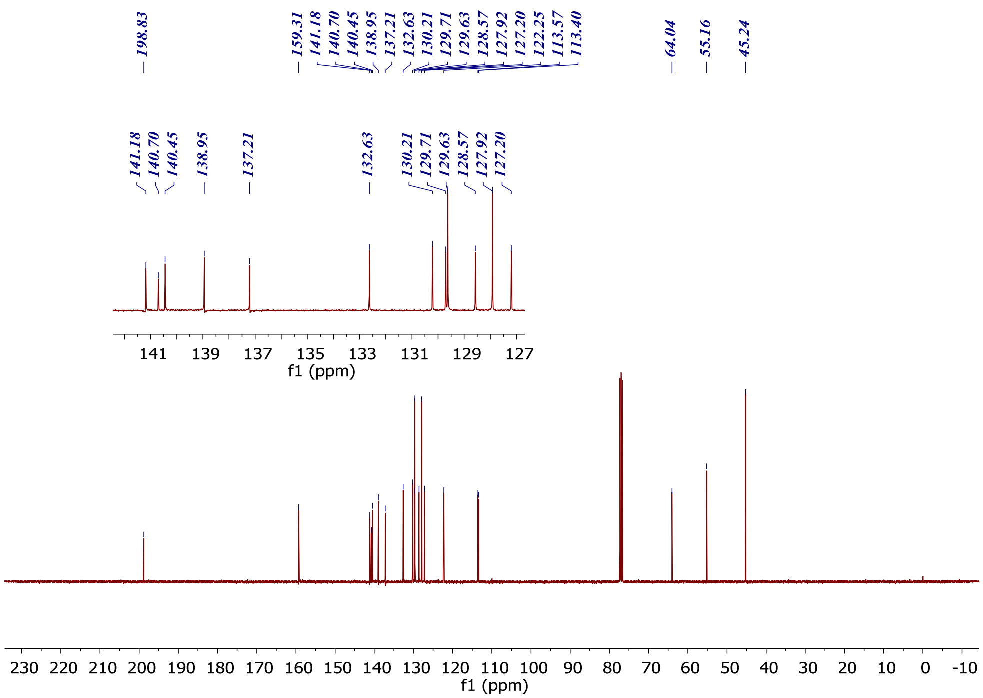

Me
N
Me
H
MeO
O
Me
3p

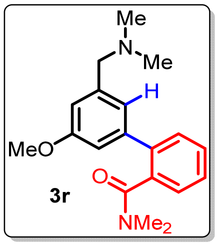

7.53 7.53 7.51 7.51 7.51 7.51 7.51 7.48 7.48 7.48 7.46 7.46 7.41 7.41 7.41 7.40 7.40 7.40 7.39 7.39 7.39 7.38 7.38 7.37 6.92 6.92 6.92 6.91 6.86 6.86 6.86 6.86 6.86 6.78 6.78 6.77 3.82 3.42 2.24 2.02
7.51 7.51 7.51 7.48 7.41 7.40 7.40 7.40 7.39 7.39 6.92 6.92 6.92 6.86 6.86 6.86 6.86 6.86 6.78 6.78
2.13 2.10 1.03 1.03 1.00
7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6
f1 (ppm)
2.13 2.10 1.03 1.03 1.00 3.11 1.98 6.11 2.99
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


204.81
159.80 141.84 141.03 140.82 140.32 130.58 130.03 127.71 127.44 122.11 113.78 113.29
64.14
55.33
45.35
30.37
210 190 170 150 130 110
f1 (ppm)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

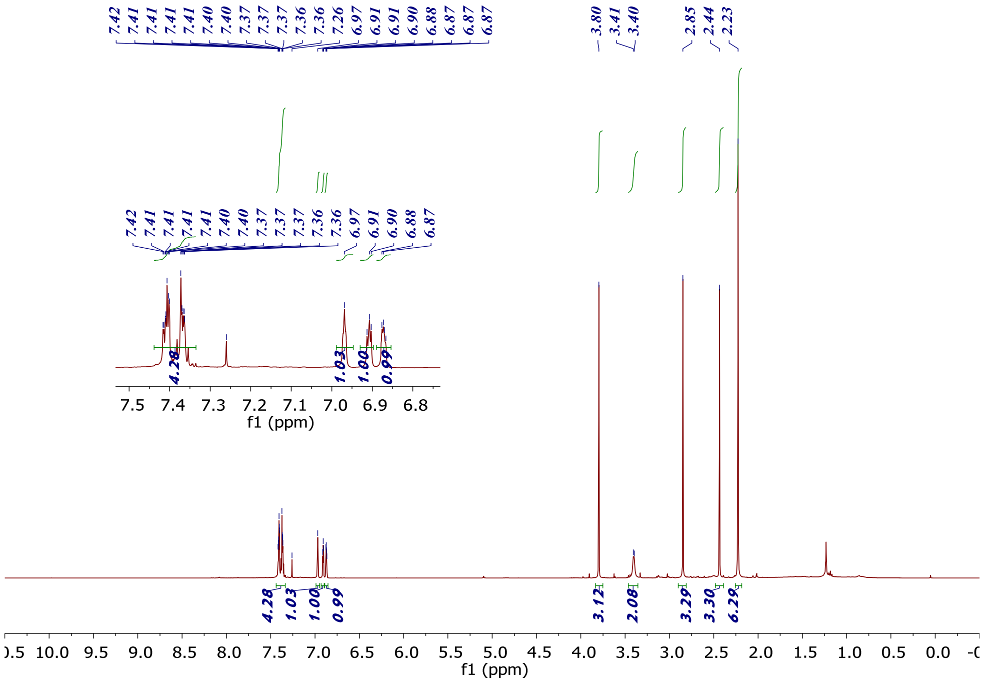

Me
N
Me
H
MeO
O
3q
Ph

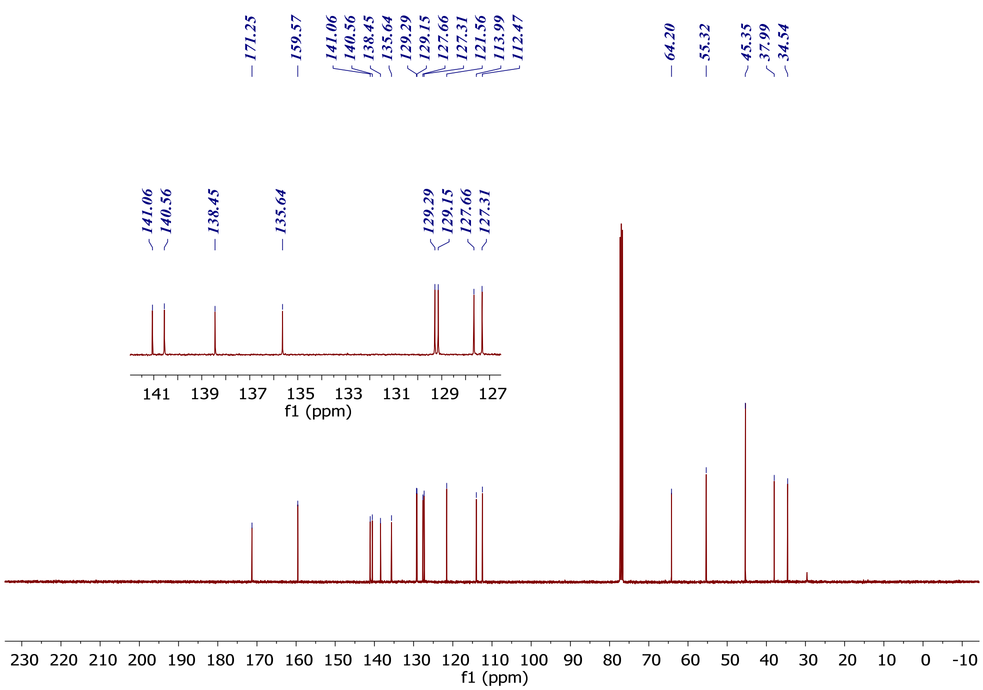

7.62 7.62 7.61 7.61 7.60 7.60 7.60 7.55 7.55 7.55 7.55 7.55 7.54 7.53 7.53 7.53 7.52 7.52 7.51 7.51 7.50 7.50 7.50 7.50 7.48 7.48 7.47 7.47 7.45 7.45 7.36 7.34 7.26 7.24 7.23 7.22 7.22 7.22 7.20 7.20 6.78 6.77 6.77 6.69 6.69 6.68 6.65 6.65 6.65 6.65 3.67 3.25 2.09 -0.00
2.00 4.10 1.00 1.98 0.98 0.98 0.94 3.04 2.02 6.08
f1 (ppm)

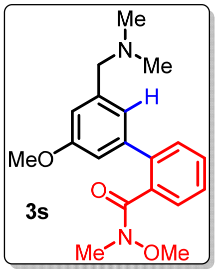

198.83 159.31 141.18 140.70 140.45 138.95 137.21 132.63 130.21 129.71 129.63 128.57 127.92 127.20 122.25 113.57 113.40 64.04 55.16 45.24
f1 (ppm)



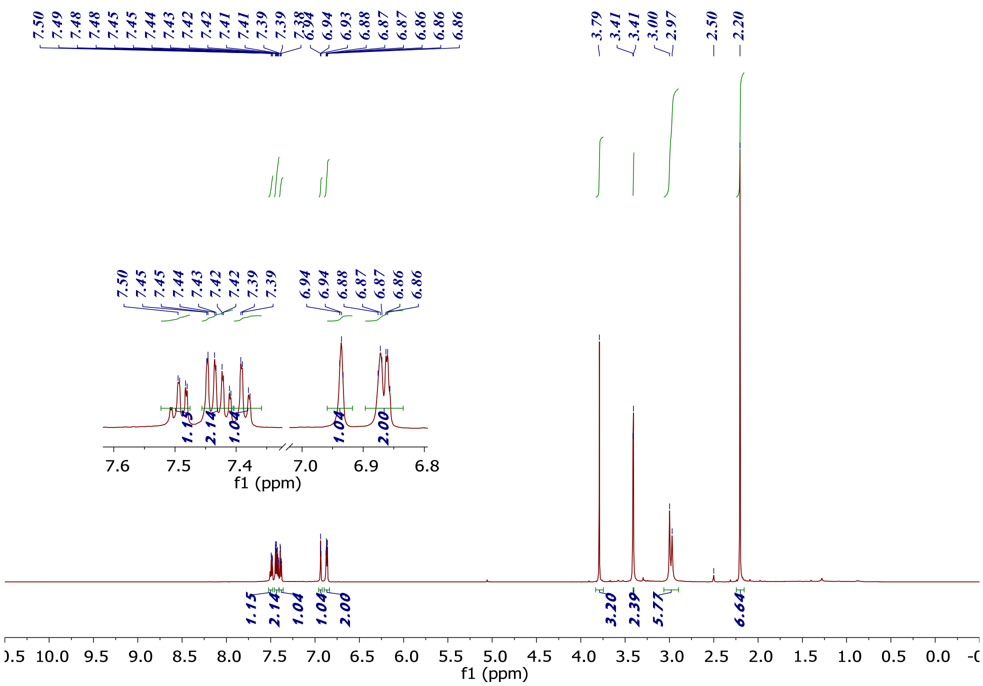
3r

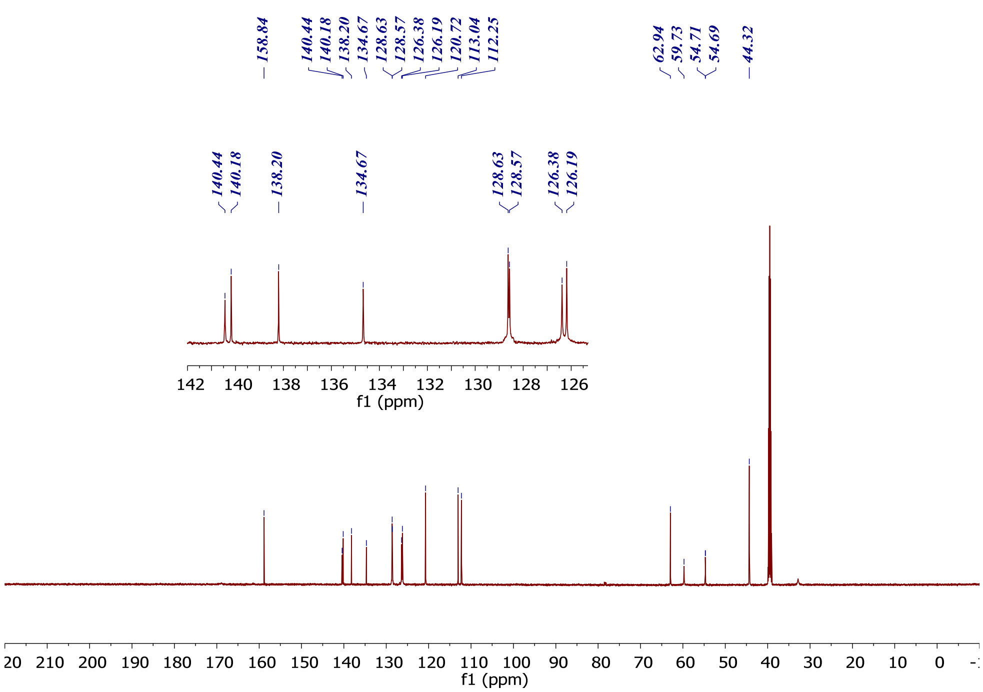


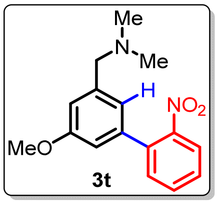




taken in DMSO-*d6* at 100°C.

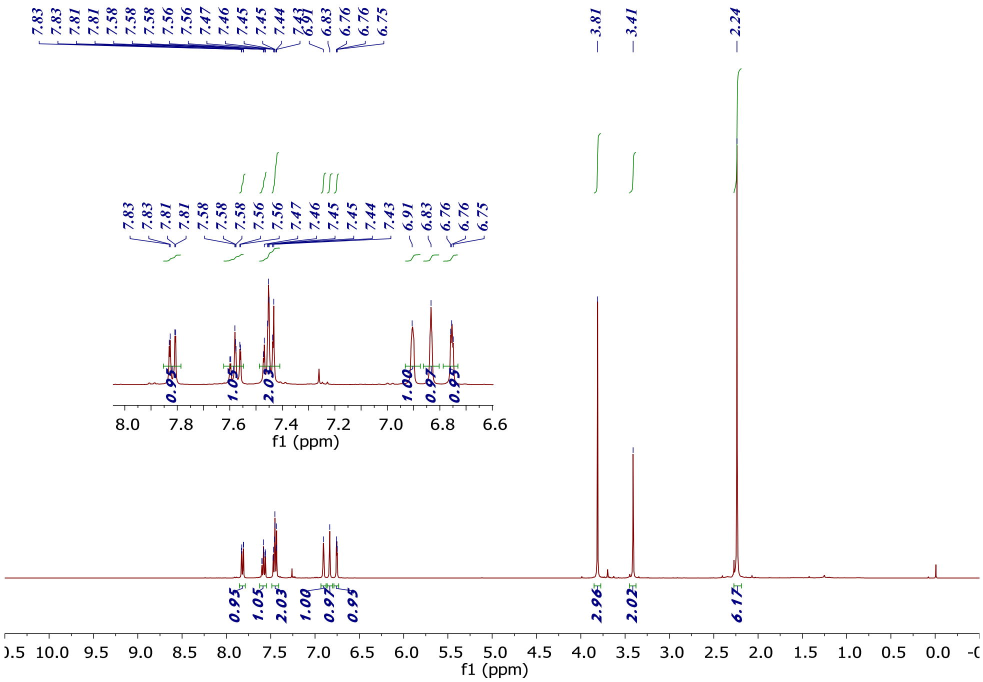




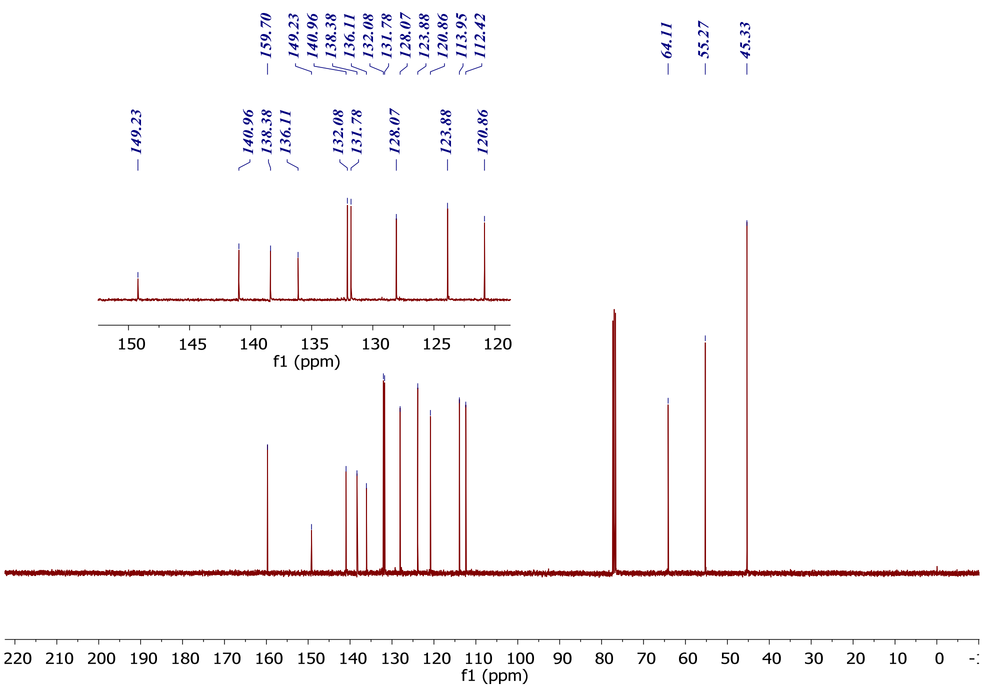


Me
N
Me
H
NO2
MeO

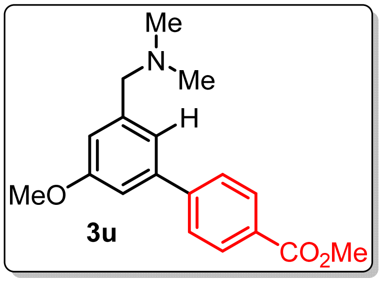
3t

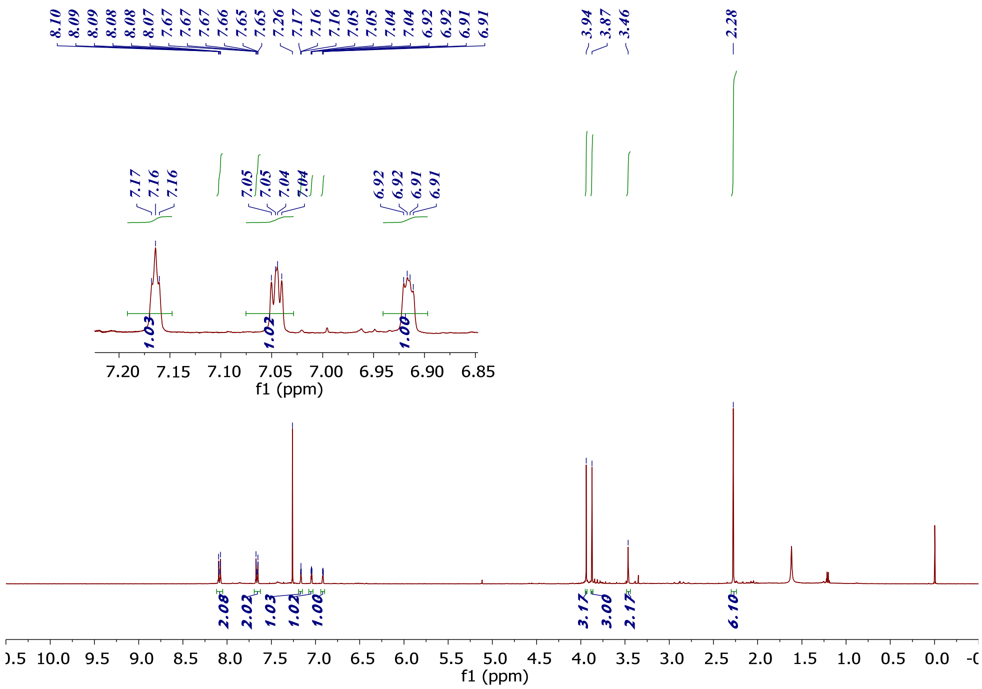


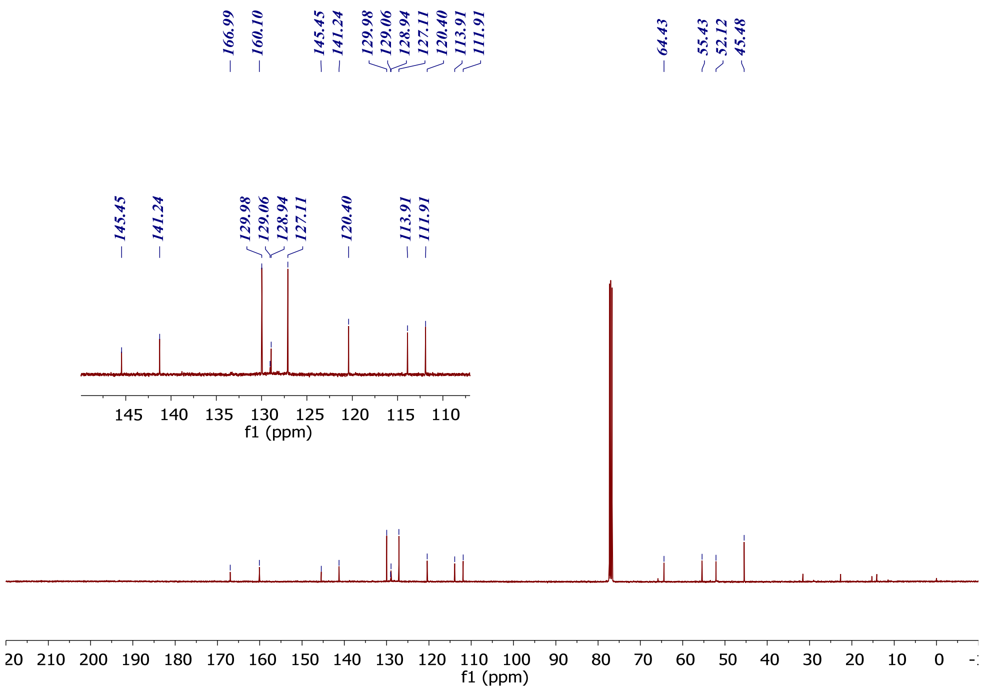
7.83
7.83
7.81
7.81
7.58
7.58
7.58
7.56
7.56
7.47
7.46
7.45
7.45
7.44
7.43
6.91
6.83
6.76
6.76
6.75
3.81
3.41
2.24
0.95
1.05
2.03
1.00
0.97
0.95
2.96
2.02
6.17
8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6
f1 (ppm)
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

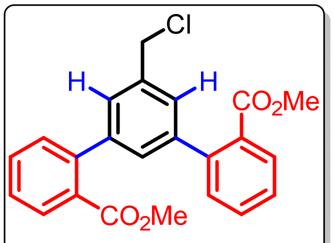


159.70
149.23
140.96
138.38
136.11
132.08
131.78
128.07
123.88
120.86
113.95
112.42
64.11
55.27
45.33
150 145 140 135 130 125 120
f1 (ppm)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

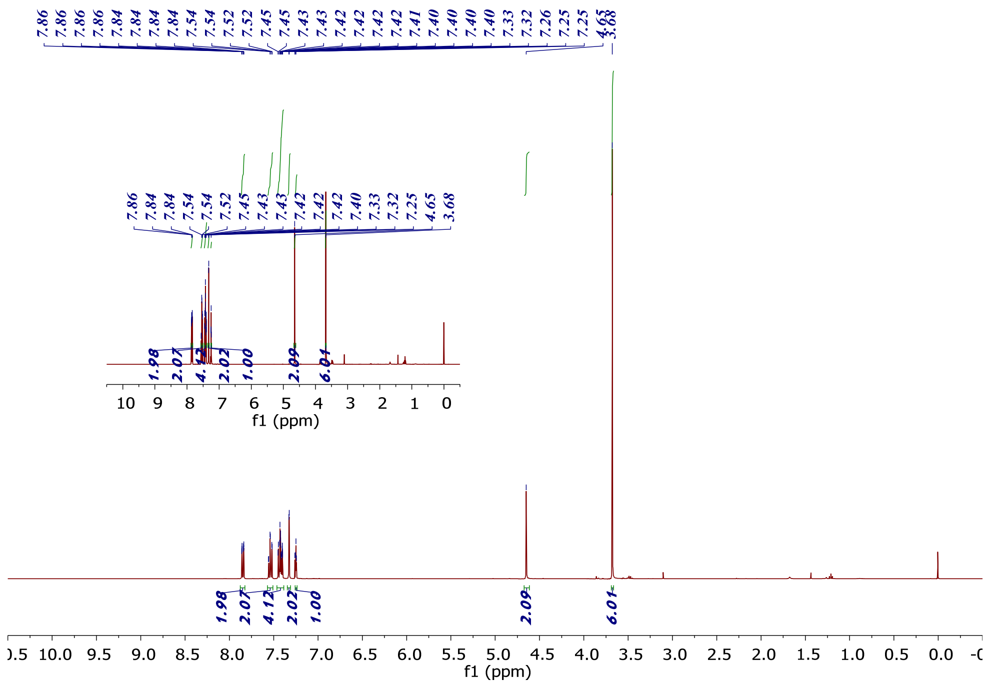

Me
N
Me
H
MeO
3u
CO2Me

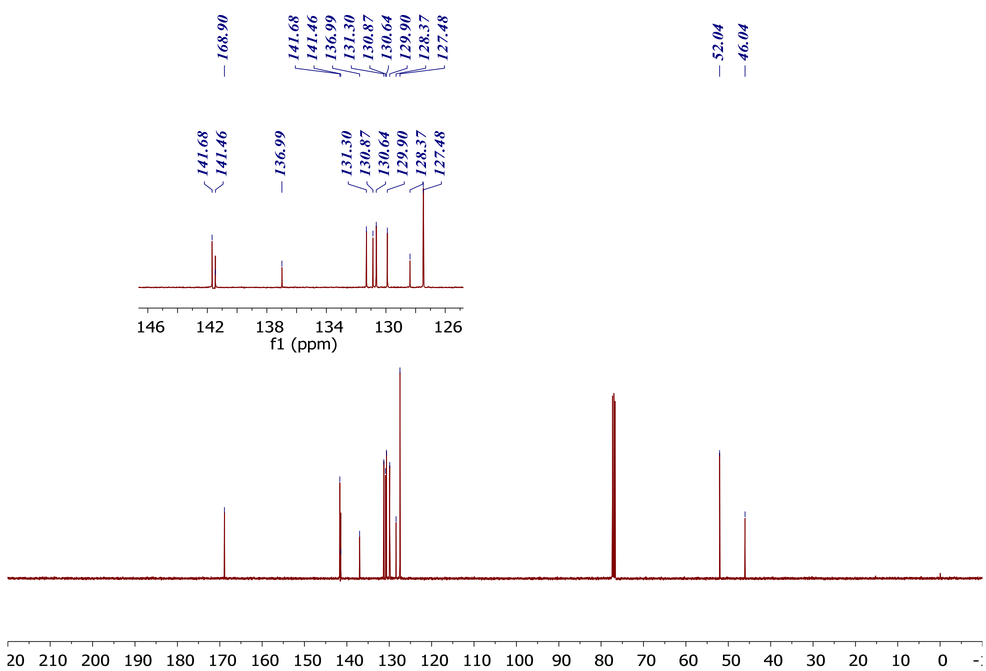

8.10 8.09 8.09 8.08 8.08 8.07 7.67 7.67 7.67 7.66 7.65 7.65 7.26 7.17 7.16 7.16 7.05 7.05 7.04 7.04 6.92 6.92 6.91 6.91
3.94 3.87 3.46
2.28
7.17 7.16 7.16
7.05 7.05 7.04 7.04
6.92 6.92 6.91 6.91
1.03 1.03 1.00
7.20 7.15 7.10 7.05 7.00 6.95 6.90 6.85
f1 (ppm)
2.08 2.02 1.03 1.02 1.00
3.17 3.00 2.17
6.10
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

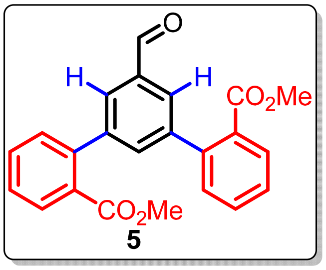

166.99 160.10 145.45 141.24 129.98 129.06 128.94 127.11 120.40 113.91 111.91
64.43 55.43 52.12 45.48
145.45 141.24 129.98 129.06 128.94 127.11 120.40 113.91 111.91
145 140 135 130 125 120 115 110
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

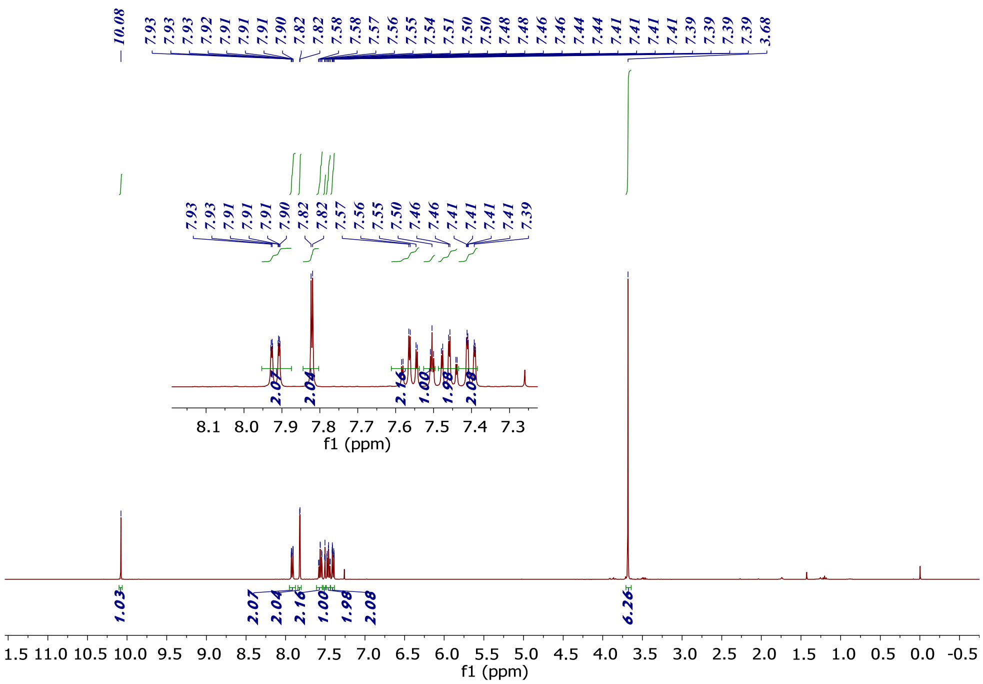


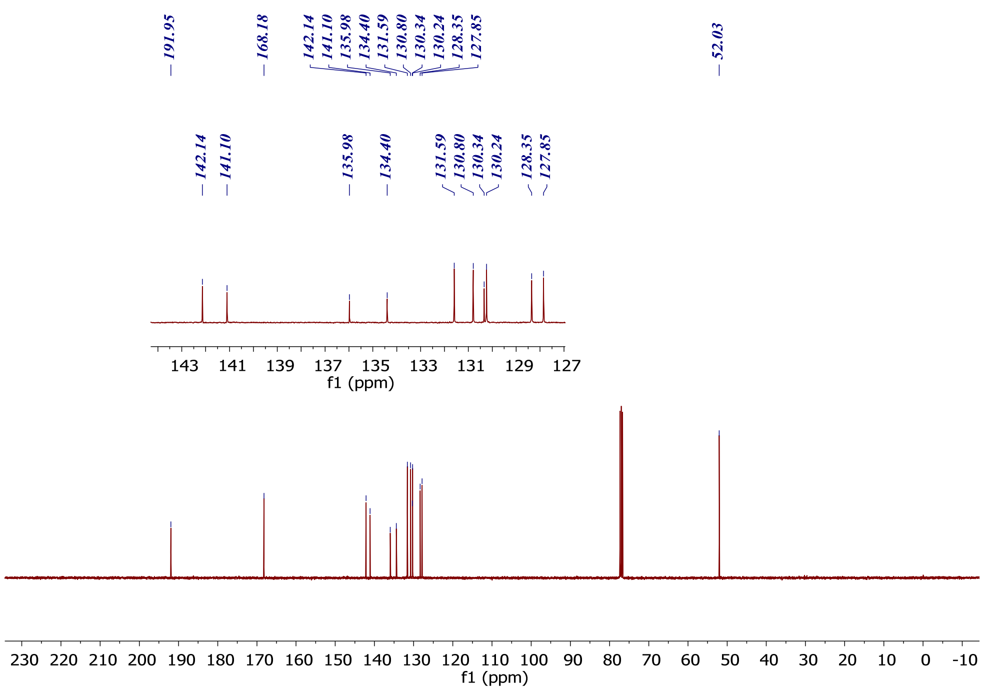
4

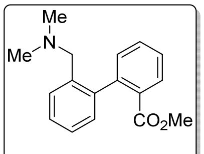




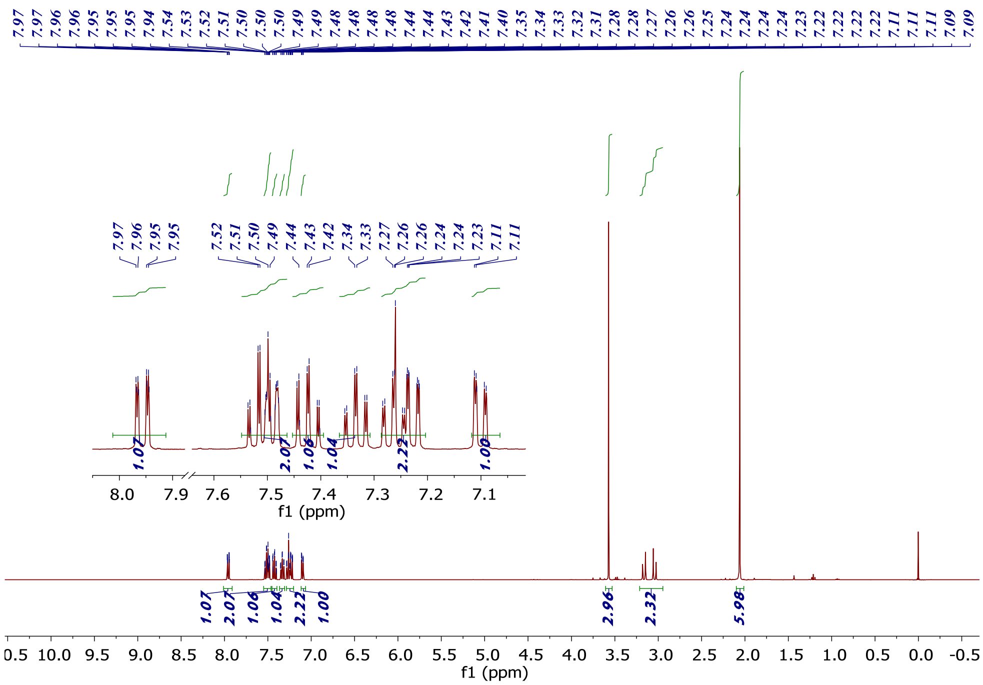

H
H
CO2Me
CO2Me
5

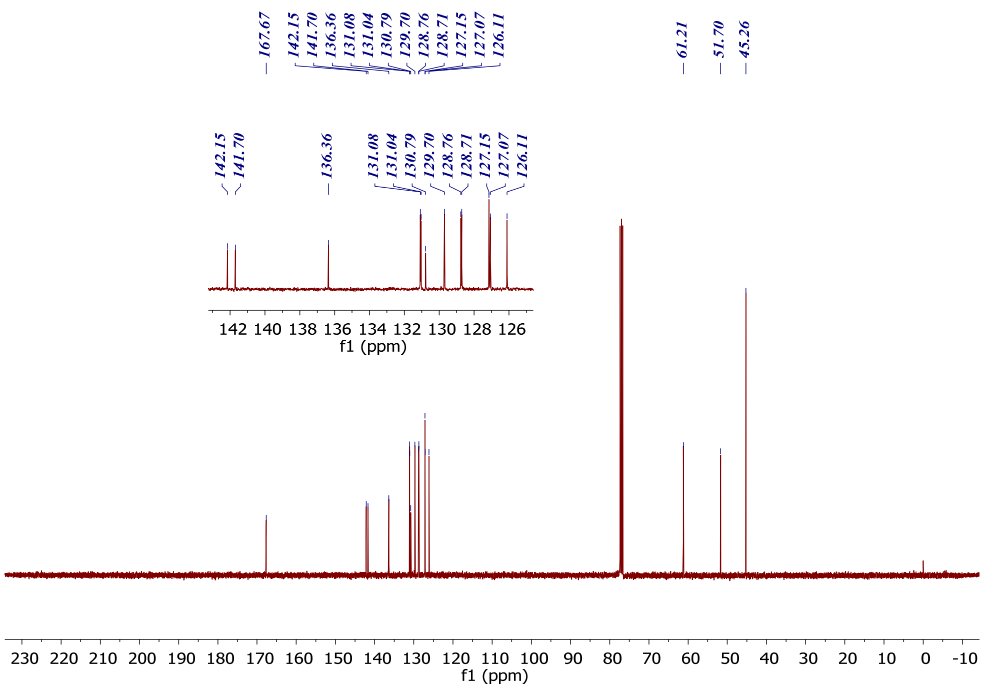

10.08
7.93 7.93 7.93 7.92 7.91 7.91 7.91 7.90 7.82 7.82 7.58 7.58 7.57 7.56 7.55 7.54 7.51 7.50 7.50 7.48 7.48 7.46 7.46 7.44 7.44 7.41 7.41 7.41 7.41 7.39 7.39 7.39 7.39 3.68
7.93 7.93 7.91 7.91 7.91 7.90 7.82 7.82 7.57 7.56 7.55 7.50 7.46 7.46 7.41 7.41 7.41 7.41 7.39
2.07 2.04 2.16 1.00 1.98 2.08
8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3
f1 (ppm)
1.03 2.07 2.04 2.16 1.00 1.98 2.08 6.26
1.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

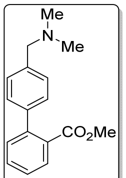

191.95
168.18
142.14 141.10 135.98 134.40 131.59 130.80 130.34 130.24 128.35 127.85
52.03
143 141 139 137 135 133 131 129 127
f1 (ppm)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



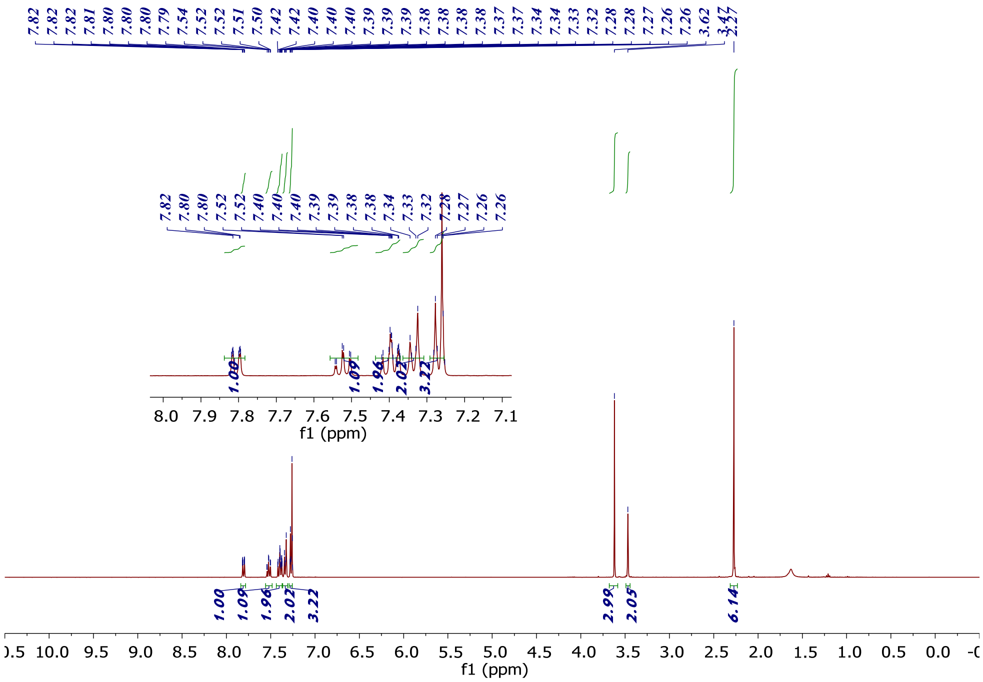
S2

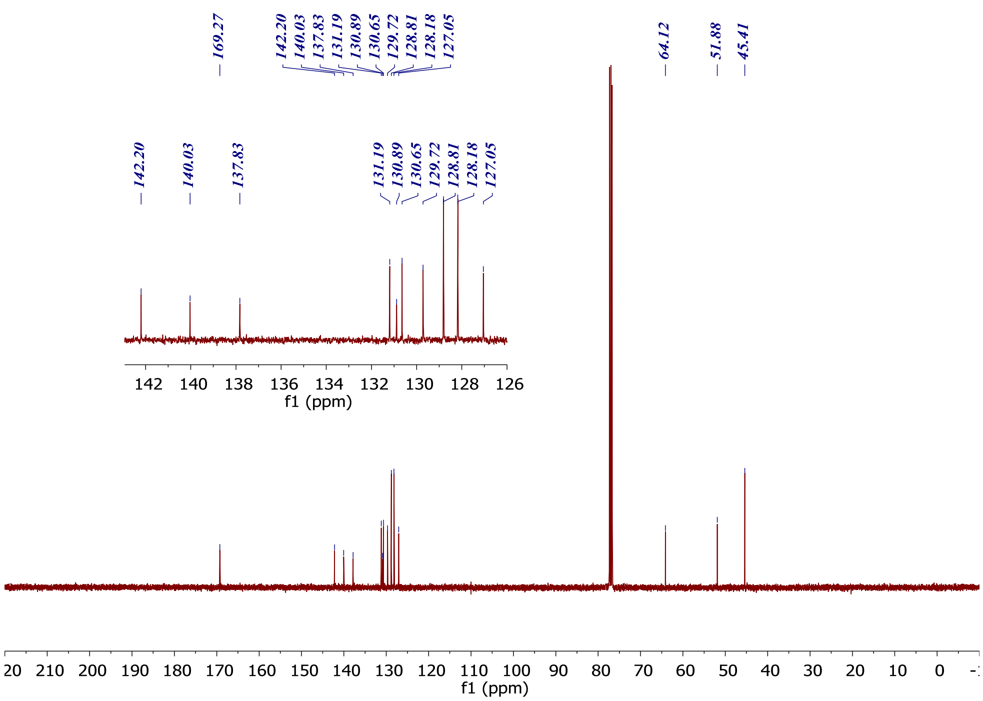






S4





VI. References

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(2) Waser, J.; Gaspar, B.; Nambu, H.; Carreira, E. M. *J. Am. Chem. Soc.* **2006**, *128*, 11693.
(3) Knowles, J. P.; Oconnor, V. E.; Whiting, A. *Org. Biomol. Chem.* **2011**, *9*, 1876.
(4) Wang, Y.; Gulevich, A. V.; Gevorgyan, V. *Chem. Eur. J.* **2013**, *19*, 15836.