Water-Soluble diphosphine ligands for rhodium-catalyzed branch-selective hydroaminomethylation of vinyl arenes with anilines in water

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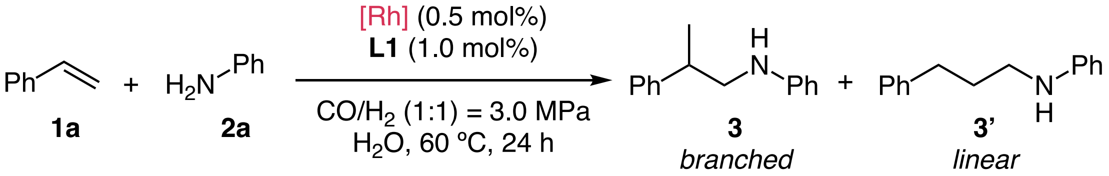
1. Supporting Tables and Schemes.

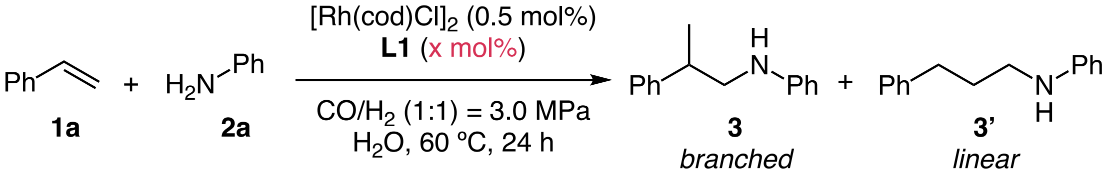
Table S1. Effect of rhodium precursor.[a]



entry	[Rh]	time	Conv. (%)	Yield of **3** (%)	*b*/*l* ratio
1	$Rh(acac)(CO)_2$	24 h	89	78	93:7
2	$[Rh(cod)Cl]_2$	24 h	>99	90	>99:1
3	$RhCl_3$	24 h	>99	80	88:12
4	$[Rh(cod)_2]BF_4$	24 h	93	79	94:6
5	-	24 h	-	-	-

[a]. Reactions were performed with **1a** (0.48 mmol) and **2a** (0.4 mmol) in H_2O (2 mL). The conversions and *b*/*l* ratios were determined with GC-MS and ^1H NMR analysis using hexadecane and CH_2Br_2 as internal standards.

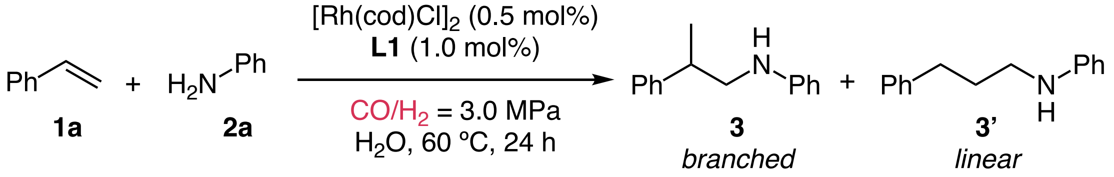
Table S2. Effect of Rh/L1 ratio. [a]



entry	x (mol%)	Conv. (%)	Yield of **3** (%)	*b*/*l* ratio
1	0.5 (Rh:**L1** = 1:1)	60	52	>99:1
2	1 (Rh:**L1** = 1:2)	>99	90	>99:1
3	2 (Rh:**L1** = 1:4)	85	64	88:12
4	4 (Rh:**L1** = 1:8)	43	23	76:24

[a]. Reactions were performed with **1a** (0.48 mmol) and **2a** (0.4 mmol) in H_2O (2 mL). The conversions and *b*/*l* ratios were determined with GC-MS and ^1H NMR analysis using hexadecane and CH_2Br_2 as internal standards.

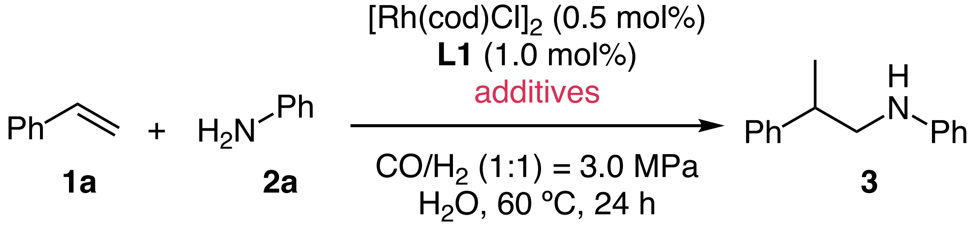
Table S3. Effect of CO/H_2 ratio. [a]

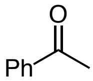
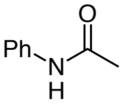
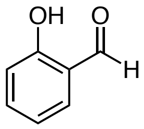


entry	CO/H_2	Conv. (%)	Yield of **3** (%)	*b*/*l* ratio
1	2:1	92	77	97:3
2	1:1	>99	90	>99:1
3	1:2	>99	86	94:6

[a]. Reactions were performed with **1a** (0.48 mmol) and **2a** (0.4 mmol) in H_2O (2 mL). The conversions and *b*/*l* ratios were determined with GC-MS and ^{1}H NMR analysis using hexadecane and CH_2Br_2 as internal standards.

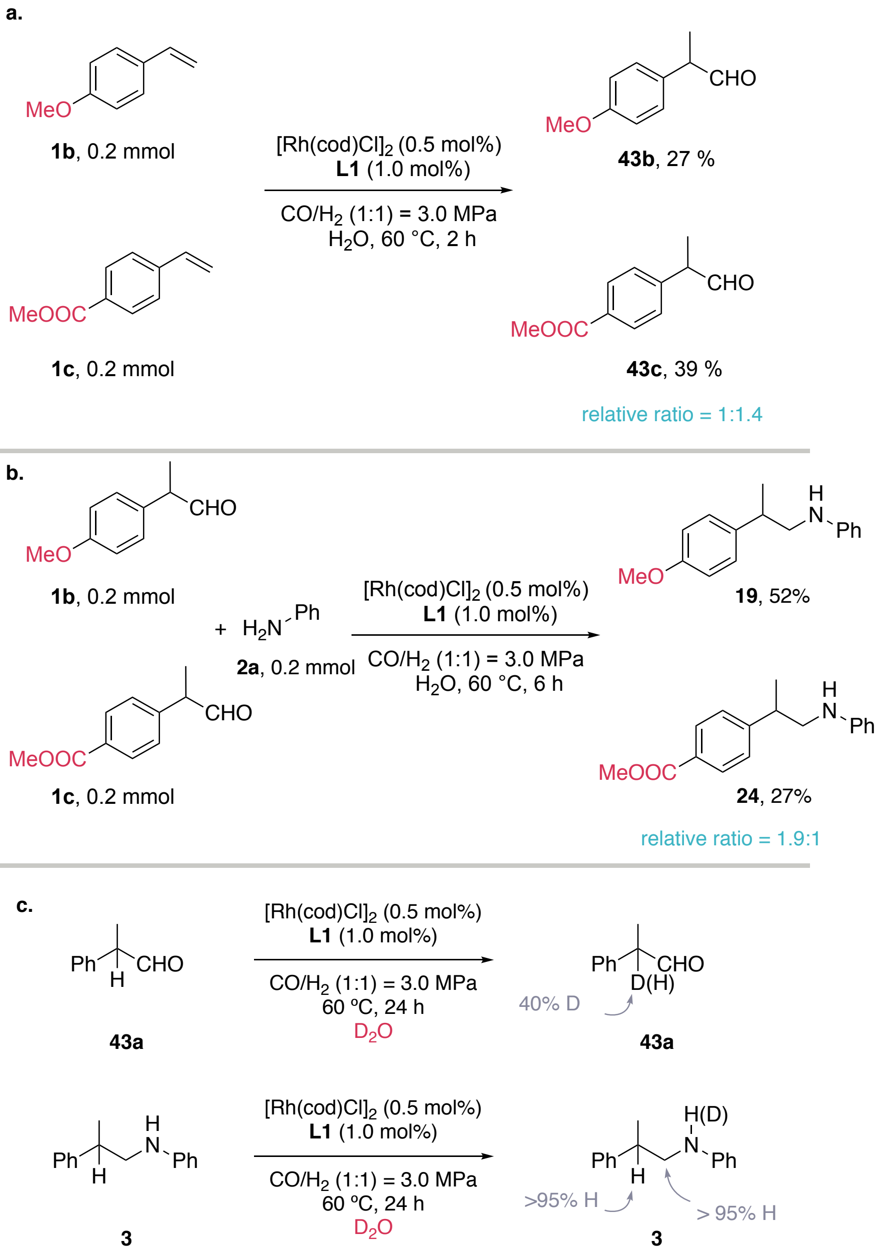
Table S4. Examination of Functional group tolerance. [a]



entry	additives	recovery of addtives	yield of **3**
1	Ph—≡	7.6%	trace
2	Ph—≡N	86%	88%
3		>99%	86%
4		>99%	90%
5[b]		5.6%	n.d.

[a]. Reactions were performed with **1a** (0.48 mmol) and **2a** (0.4 mmol) in H_2O (2 mL). The conversions and yields were determined with GC-MS using hexadecane as an internal standard. [b]. The conversions and yields were determined with ^{1}H NMR using CH_2Br_2 as an internal standard. see Scheme S2 for details.

Scheme S1. Experiments for mechanistic studies.



Scheme S2. Reductive amination of salicylic aldehyde with aniline using hydrogen.

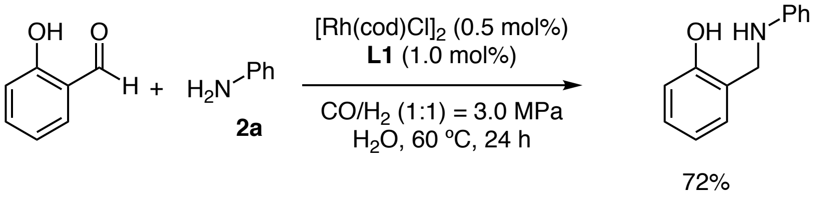
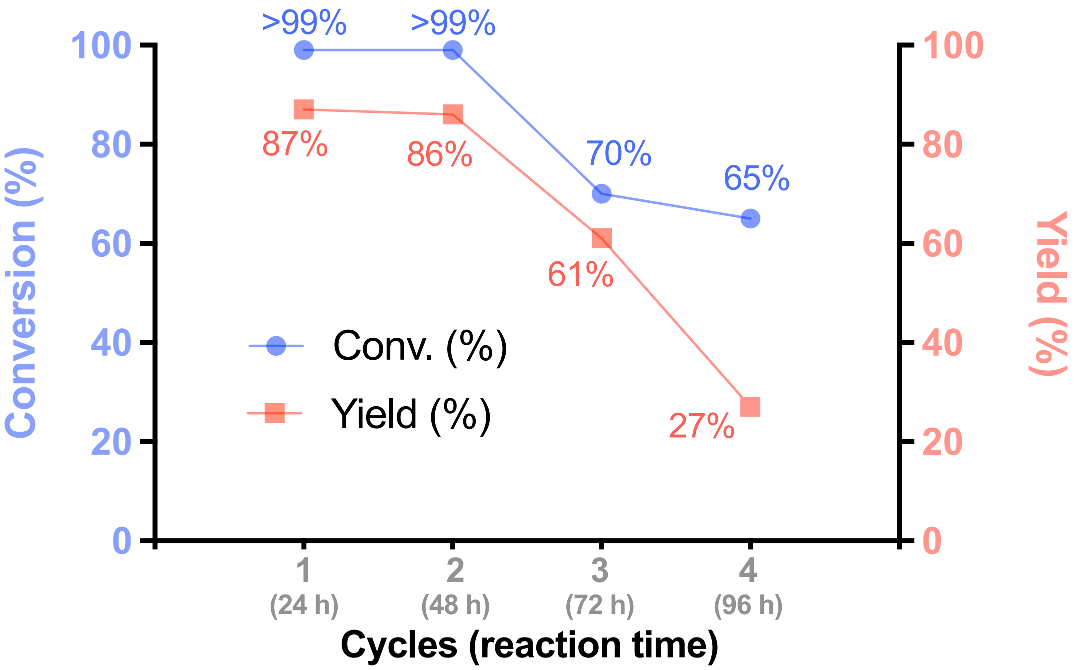


Figure S1. Catalyst Recycling Experiment.



The catalyst recycling experiments were conducted at 0.6 mmol scale in 3 mL of water. After each cycle, the crude mixture was extracted with toluene, and the organic phase was washed with brine and dried over anhydrous sodium sulfate. To the organic phase was added hexadecane, and an aliquot was analyzed by GC-MS.

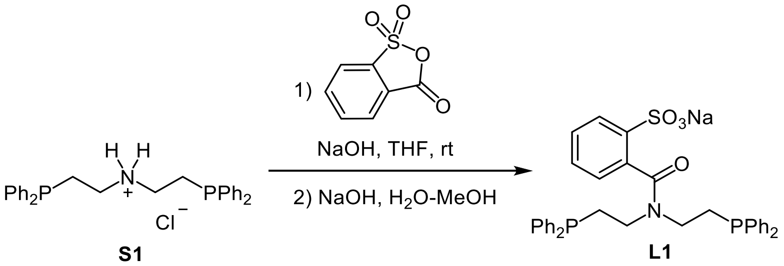
2. General information

All commercial reagents and solvents were ordered from Bidepharm, TCI and Macklin. Reagents and solvents were used as received unless otherwise noted. Where necessary, solvents were purified by passing through columns of alumina using a solvent purification system.[1] Air- and moisture sensitive synthesis were performed under nitrogen atmosphere with oven-dried glassware. Column chromatography was performed on silica gel (200-300 mesh). Thin-layer chromatography (TLC) was performed on EM reagents 0.25 mm silica 60-F plates. NMR spectra were recorded with a Bruker Avance III (400 MHz) spectrometer. ^{1}H NMR spectra were recorded at 400 MHz and ^{13}C NMR spectra were recorded at 100 MHz. Chemical shifts are reported in ppm downfield from $CDCl_3$ (δ = 7.26 ppm) for ^{1}H NMR and relative to the central $CDCl_3$ resonance (δ = 77.16 ppm) for ^{13}C NMR spectroscopy. Data are reported as follows: chemical shift [integration, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, m = multiplet), coupling constant(s) in Hertz]. GC-MS analysis was carried out on Agilent 7820A GC system and Angilent 5977B MSD. LC-MS analysis was carried out on Agilent 1260 Infinity II and Agilent 6545 LC/Q-TOF. High-resolution mass spectra (HRMS) were recorded on a Bruker microTOF Q III spectrometer with electronspray ionization (ESI). Melting points (m.p.) were recorded on an SRS–optic melting point apparatus.

3. General procedure for the preparation of the ligands L1-L6

Ligands **L1-L3** were prepared following the reported procedure.

Synthesis of L1[2]



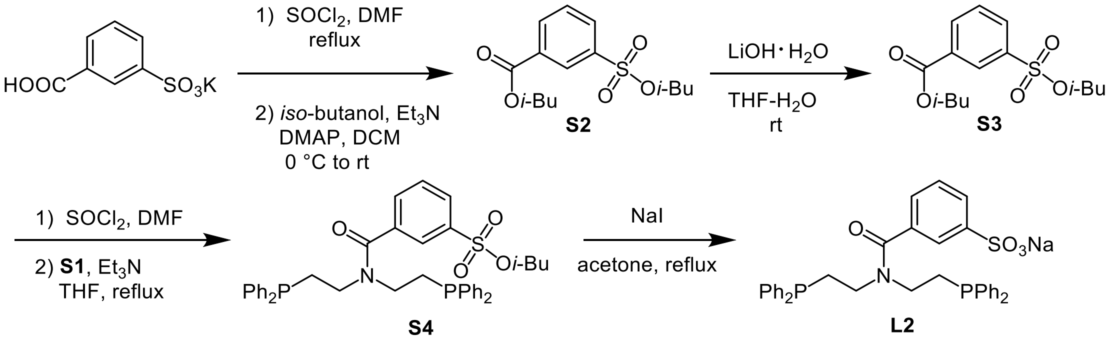
To a solution of **S1** (2.0 g, 4.18 mmol) and 2-sulfobenzoic anhydride (0.85 g, 4.60 mmol) in THF (25 mL) was added aqueous sodium hydroxide solution (25%, 2 mL) at 0 °C. The reaction mixture was stirred for 12 h at room temperature. The mixture was filtered, and the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (eluent: 5% methanol in dichloromethane with 1% acetic acid) to afford **L1-H** (2.32 g, 85%) as a white solid. This material was dissolved in 15 mL of MeOH, and 2.2 mL of 2.0 M NaOH was added dropwise with vigorous stirring. The solvent was removed under reduced pressure to give a white solid. Drying for 24 h at 0.05 torr at ambient temperature gave **L1** (2.31g, 98%) as a white hygroscopic powder.

L1. ^{1}H NMR (400 MHz, CD_3OD) δ 7.90-7.88 (1H, m), 7.46-7.39 (5H, m), 7.34-7.09 (17H, m), 7.07-7.04 (1H, m), 3.57-3.54 (2H, m),3.20-3.11 (2H, m), 2.63-2.55 (1H, m), 2.44-2.37 (1H, m), 2.26-2.18 (1H, m), 2.02-1.94 (1H, m)

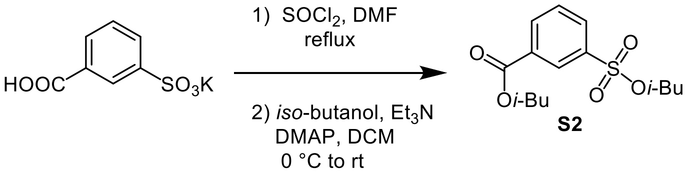
^{31}P NMR (161 MHz, CD_3OD) δ -21.14, -21.40.

HRMS (ESI): calcd for $C_{35}H_{32}NO_4P_2S$ [M-Na]$^-$: 624.1533, found: 624.1537.

Synthetic route of L2[3]

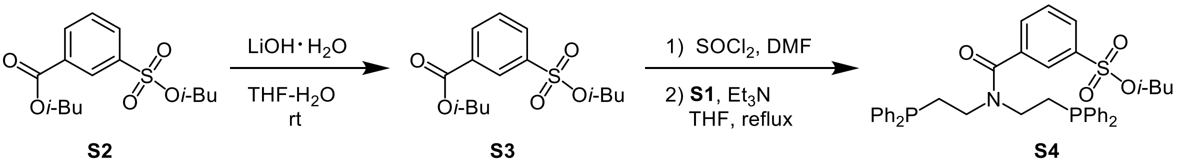


Synthesis of L2



Under a nitrogen atmosphere, the mixture of potassium 3-carboxybenzenesulfonate (4.00 g, 16.6 mmol), thionyl chloride (20 mL) and DMF (0.6 mL) was refluxed for 4 h. The mixture was cooled and evaporated to dryness. The residue was dissolved in CH_2Cl_2 and was added DMAP (0.89 mmol, 108.8 mg) and *iso*-butanol (3.28 mL, 33.2 mmol) at 0 °C. The mixture was added TEA (11.2 mL, 107.9 mmol) dropwise, and the reaction was allowed to warm to room temperature overnight. The mixture was concentrated and the residue was purified by column chromatography on silica gel (eluent: 10% ethyl acetate in petroleum ether) to afford **S2** (3.38 g, 65%) as a yellow oil.

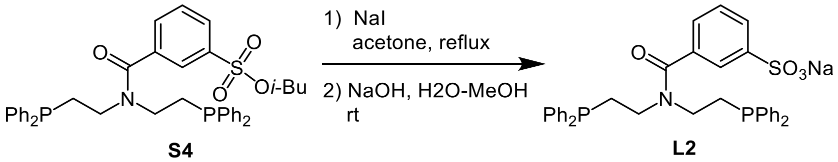
S2 ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (1H, s), 8.31 (1H, d, J = 7.8 Hz), 8.10 (1H, d, J = 7.9 Hz), 7.65 (1H, m), 4.13 (2H, d, J = 6.7 Hz), 3.80 (2H, d, J = 6.6 Hz), 2.14-2.06 (1H, m), 2.14-2.06 (1H, m), 2.00-1.91 (1H, m), 1.01 (6H, d, J = 6.8 Hz), 0.88(6H, d, J = 6.9 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.9, 137.0, 134. 6, 132.0, 131. 8, 129.6, 128.9, 71.9, 71.9, 28.2, 27.9, 19.3, 18.7.



A solution of LiOH·H_2O (0.528 g, 12.6 mmol) in water (15 mL) was added to a stirred solution of **S2** (3.3 g, 10.5 mmol) in THF (15 mL). The reaction was stirred for 5 h and was adjusted to pH = 2 by the dropwise addition of 5% hydrochloric acid. The THF was evaporated and the suspension was extracted with CH_2Cl_2. The organic phase was dried with anhydrate Na_2SO_4 and concentrated in *vacuo* to afford 3-(isobutoxysulfonyl)benzoic acid.**S3** (3.38 g, 90%) as a white solid.

A solution of the above solid (**S3**) (0.387 g, 1.5 mmol) in thionyl chloride (5 mL) was added three drops of DMF. The mixture was refluxed for 12 h. The mixture was concentrated azeotropically with THF to give a yellow-green solid. Under nitrogen atmosphere, the above solid was added to a stirred solution of triethylamine (13.7 ml, 95.0 mmol) and **S1** (0.572 g, 1.2 mmol) in dry CH_2Cl_2 at 0 °C. The reaction was allowed to warm to room temperature overnight. The solution was concentrated and the residue was purified by column chromatography on silica gel (eluent: 25% dichloromethane in petroleum ether) to afford **S4** (0.54 g, 53%) as a yellow oil.

S4 ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89-7.86 (1H, m), 7.81 (1H, s), 7.49-7.46 (4H, m), 7.43-7.41 (2H, m), 7.36-7.34 (6H, m), 7.29-7.23 (6H, m), 7.19-7.15 (4H, m), 3.78 (2H, d, J = 6.5 Hz), 3.64-3.58 (2H, m), 3.24-3.22 (2H, m), 2.45 (2H, t, J = 8.0 Hz), 2.11 (2H, t, J = 8.0 Hz), 1.98-1.87 (1H, m), 0.88 (6H, d, J = 6.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 137.8, 137.7 (d, J = 10.3 Hz), 136.8, 136.6 (d, J = 12.3 Hz), 132.8 (d, J = 19.0 Hz), 132.5 (d, J = 19.0 Hz), 131.5, 129.6, 129.2, 129.1, 128.8 (d, J = 6.8 Hz), 128.6, 126.1, 77.0, 47.1 (d, J = 26.8 Hz), 43.3 (d, J = 24.2 Hz), 29.8, 28.2, 27.9 (d, J = 15.9 Hz), 26.6 (d, J = 14.1 Hz), 18.7; ^{31}P NMR (161 MHz, $CDCl_3$) δ -21.05, -21.04.



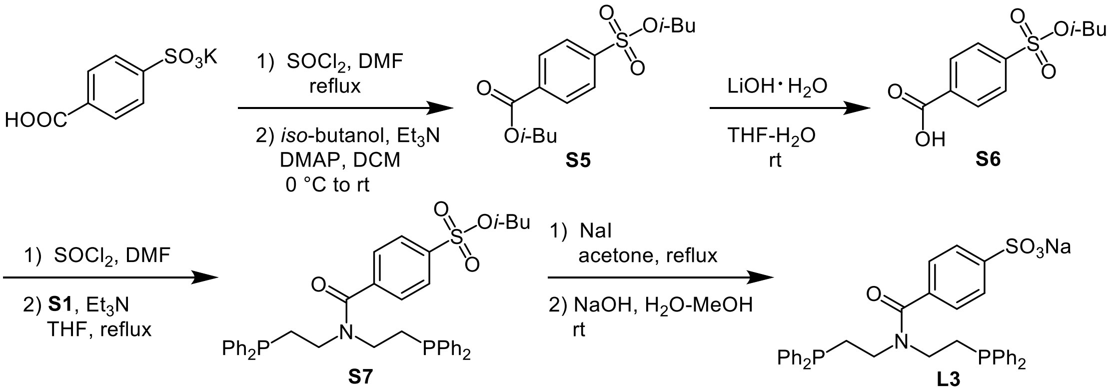
NaI (171.6 mg, 1.15 mmol) was added to a solution of **S4** (520 mg, 0.76 mmol) in dry actone. The reaction was refluxed for 24 h. The resulting precipitate was collected and purified by column chromatography on silica gel (eluent: 10% methanol in dichloromethane with 1% acetic acid) to afford **L2-H** (0.403 g, 82%) as a white solid. This material was dissolved in 3 mL of MeOH, and 0.325 mL of 2.0 M NaOH was added dropwise with vigorous stirring. The solvent was removed under reduced pressure to give a white solid. Drying for 24 h at 0.05 torr at ambient temperature gave **L2** (0.405 g, 97%) as a white hygroscopic powder.

L2 ^{1}H NMR (400 MHz, CD_3OD) δ 7.85-7.80 (2H, m), 7.42-7.38 (4H, m), 7.31-7.27 (7H, m), 7.22-7.21 (6H, m), 7.17-7.12 (5H, m), 3.58-3.52 (2H, m), 3.25-3.20 (2H, m), 2.42-2.38 (2H, m), 2.14-2.10 (2H, m).

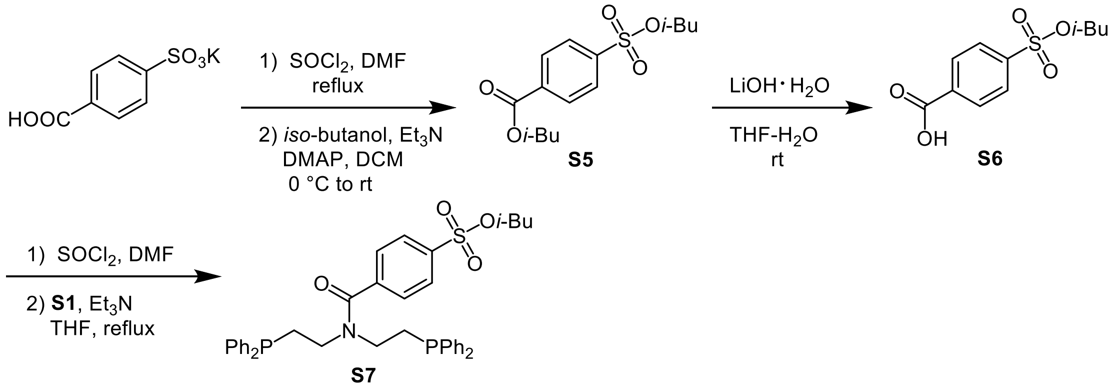
^{31}P NMR (161 MHz, CD_3OD) δ -21.28, -21.87.

HRMS (ESI): calcd for $C_{35}H_{32}NO_4P_2S$ $[M-Na]^+$: 624.1533, found: 624.1522.

Synthetic route of L3[3]



Synthesis of L3



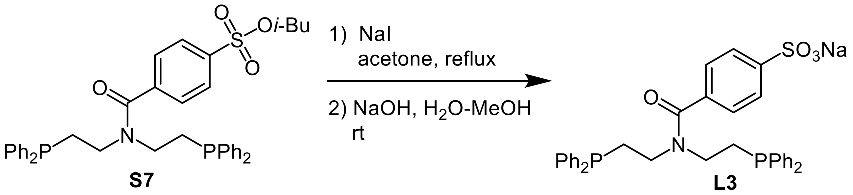
Under nitrogen atmosphere, the mixture of potassium 4-carboxybenzenesulfonate (4.00 g, 16.6 mmol), thionyl chloride (20 mL) and DMF (0.6 mL) was refluxed for 4 h. The mixture was cooled to room temperature and evaporated to dryness. The residue was dissolved in CH_2Cl_2 and was added DMAP (0.89 mmol, 108.8 mg) and *iso*-butanol (3.28 mL, 33.2 mmol) at 0 °C. The mixture was added TEA (11.2 mL, 107.9 mmol) dropwise, and the reaction was allowed to warm to room temperature overnight. The mixture was concentrated and the residue was purified by column chromatography on silica gel (eluent: 10% ethyl acetate in petroleum ether) to afford **S5** (3.27 g, 63%) as a yellow oil.

A solution of $LiOH\cdot H_2O$ (0.53 g, 12.6 mmol) in water (15 mL) was added to a stirred solution of **S5** (3.27 g, 10.4 mmol) in THF (15 mL) at room temperature. The reaction was stirred for 5 h and was adjusted to pH = 2 by the dropwise addition of 5% hydrochloric acid. The THF was evaporated and the suspension was extracted with CH_2Cl_2. The organic phase was dried with anhydrate Na_2SO_4 and concentrated in *vacuo* to afford 3-(isobutoxysulfonyl)benzoic acid. **S6** (3.58 g, 95%) as a white solid.

A solution of the above solid (**S6**) (0.258 g, 1.0 mmol) in thionyl chloride (5 mL) was added three drops of DMF. The mixture was refluxed for 12 h. The solution was evaporated azeotropically with dry THF to afford yellow-green solid. Under nitrogen atmosphere, the above solid was added to a stirred solution of triethylamine (13.7 ml, 95 mmol) and **S1** (0.382 g, 0.8 mmol) in dry CH_2Cl_2 at 0 °C. The reaction was allowed to warm to room temperature overnight. The solution was concentrated and the residue was purified by column chromatography on silica gel (eluent: 25%

dichloromethane in petroleum ether) to afford **S7** (0.347 g, 64%) as a yellow oil.

S7 ^{1}H NMR (400 MHz, CDCl$_3$) *δ* 7.76-7.74 (2H, m), 77.50-7.46 (4H, m), 7.37-7.32 (6H, m), 7.30-7.24 (8H, m), 7.18-7.14 (4H, m), 3.78 (2H, d, *J* = 6.6 Hz), 3.67-3.61 (2H, m), 3.26-3.20 (2H, m), 2.47 (2H, t, *J* = 8.0 Hz), 2.10 (2H, t, *J* = 8.0 Hz), 1.99-1.89(1H, m), 0.90 (6H, d, *J* = 6.8 Hz). ^{13}C NMR (100 MHz, CDCl$_3$) *δ* 169.7, 141.6, 137.8 (d, *J* = 11.9 Hz), 136.8, 136.6 (d, *J* = 12.0 Hz), 132.8 (d, *J* = 18.9 Hz), 132.5 (d, *J* = 18.9 Hz), 129.4, 129.1, 128.84 (d, *J* = 3.4 Hz), 128.78 (d, *J* = 3.3 Hz), 128.3, 127.2, 77.0, 46.9 (d, *J* = 27.3 Hz), 43.1 (d, *J* = 23.5 Hz), 28.2, 28.0 (d, *J* = 15.3 Hz), 26.5 (d, *J* = 14.5 Hz), 18.6; ^{31}P NMR (161 MHz, CDCl$_3$) *δ* -21.09, -22.05.



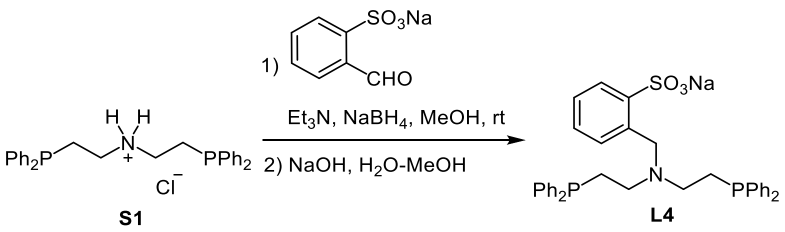
NaI (105.7 mg, 0.71 mmol) was added to a solution of the compound **S7** (0.320 g, 0.47 mmol) in dry acetone. The reaction was refluxed for 24 h. The resulting precipitate was collected and purified by column chromatography on silica gel (eluent: 10% methanol in dichloromethane with 1% acetic acid) to afford **L3-H** (0.254 g, 82%) as a white solid. This material was dissolved in 2 mL of MeOH, and 0.205 mL of 2.0 M NaOH was added dropwise with vigorous stirring. The solvent was removed under reduced pressure to give a white solid. Drying for 24 h at 0.05 torr at ambient temperature gave **L3** (0.271 g, 98%) of a white hygroscopic powder.

L3 ^{1}H NMR (400 MHz, CD$_3$OD) *δ* 7.77-7.75 (2H, m), 7.44-7.40 (4H, m), 7.32-7.21 (12H, m), 7.20-7.18 (2H, m), 7.14-7.09 (4H, m),3.62-3.56 (2H, m), 3.25-3.20 (2H, m), 2.45-2.41 (2H, m), 2.14-2.10 (2H, m).

^{31}P NMR (161 MHz, CD$_3$OD) *δ* -21.04, -21.89.

HRMS (ESI): calcd for $C_{35}H_{32}NO_4P_2S$ [M-Na]$^-$: 624.1533, found: 624.1537.

Synthesis of L4[4]



To a solution of bis(2-(diphenylphosphanyl)ethyl)ammonium chloride (2.0 g, 4.18 mmol) in MeOH (25 mL) was added Et_3N (1.45 mL, 10.45 mmol) and 2-sulfobenzaldehyde sodium salt (958 mg, 4.6 mmol) at room temperature. The reaction mixture was stirred for 16 h. $NaBH_4$ (0.158 g, 4.18 mmol) was added and the mixture was stirred at room temperature for 1 h. The reaction was quenched with water. The solution was concentrated and purified by column chromatography on silica gel (eluent: 2% methanol in dichloromethane with 1% acetic acid) to afford **L4-H** (1.38 g, 54%) as a white solid. This material was dissolved in 2 mL of MeOH, and 1.13 mL of 2.0 M NaOH was added dropwise with vigorous stirring. The solvent was removed under reduced pressure to give a white solid. Drying for 24 h at 0.05 torr at ambient temperature gave **L4** (1.37 g, 96%) of a white hygroscopic powder.

L4 ^{1}H NMR (400 MHz, CD_3OD) δ 7.98 (1H, dd, J = 7.8, 1.3 Hz), 7.49-7.45 (1H, m), 7.37-7.27 (21H, m), 7.24 (1H, dd, J = 7.5, 1.3 Hz), 4.67 (2H, s), 3.21-3.14 (4H, m), 2.42-2.36 (2H, m), 2.33-2.26 (2H, m). ^{13}C NMR (100 MHz, CD_3OD) δ146.2, 137.7 (dd, J = 12.6 Hz, 137.4 (d, J = 12.3 Hz), 134.8, 133.8 (d, J = 19.5 Hz),133.7 (d, J = 19.3 Hz), 132.3, 132.4, 131.6, 130.5(d, J = 3.3 Hz), 129.9 (d, J = 5.1 Hz), 129.1, 127.7, 57.5,51.2 (d, J = 29.0 Hz), 23.7 (d, J = 16.3 Hz). ^{31}P NMR (161 MHz, CD_3OD) δ -21.79, -21.80.

HRMS (ESI): calcd for $C_{35}H_{34}NO_3P_2S$ $[M\text{-}Na]^-$: 610.1740, found: 610.1742.

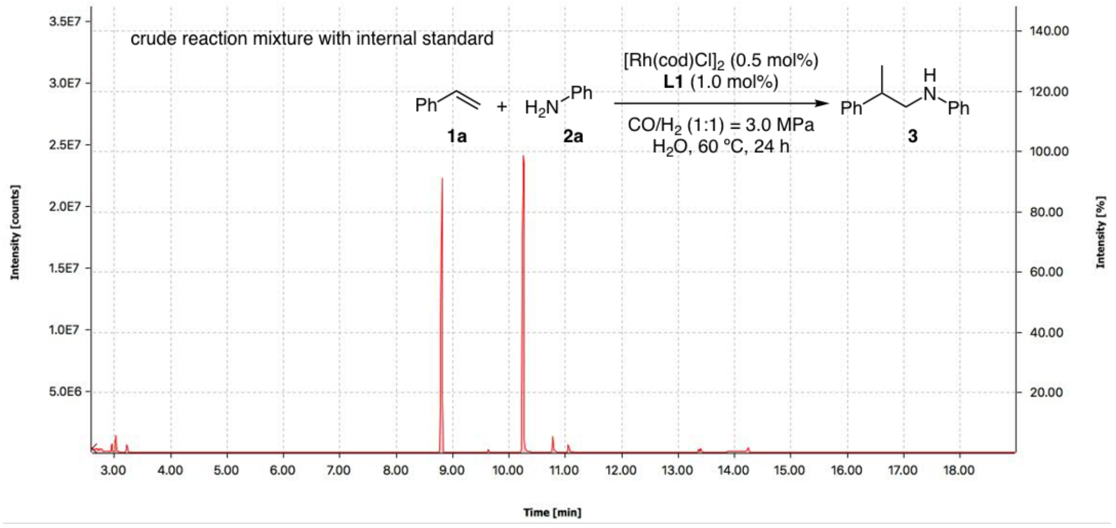
L5-L7 were prepared according to the literature methods. [5]

4. General procedure for reaction optimization

The hydroaminomethylation reactions were conducted in a batch autoclave reactor (Shaanxi Wattcas). In a typical run, chloro(1,5-cyclooctadiene)rhodium(I) dimer ([Rh(COD)Cl]$_2$, 0.99 mg, 2×10^{-3} mmol, 0.50 mol%), ligands (**L1-L8**) was dissolved in 2 mL of water and stirred for 1 hour. Substituted styrene (0.48 mmol) and aniline (0.4 mmol) were added, and the reactor was purged with nitrogen three times and then charged with 3.0 MPa syngas (CO/H_2=1:1). The mixture was stirred for 24 h at 60 °C, and the combined organic layers were dried over anhydrous sodium sulfate. An aliquot was analyzed with GC-MS using hexadecane as an internal standard. The organic layers were filtered and concentrated under reduced pressure. The residue was added CH_2Br_2 as an internal standard and further analyzed with ^{1}H NMR. The reported values are primarily based on GC-MS measurement, and ^{1}H NMR analysis showed an error within 5%.

5. Calibration curve and spectra of crude mixture of HAM reaction.

Figure S2. GC spectra of crude reaction mixtures.



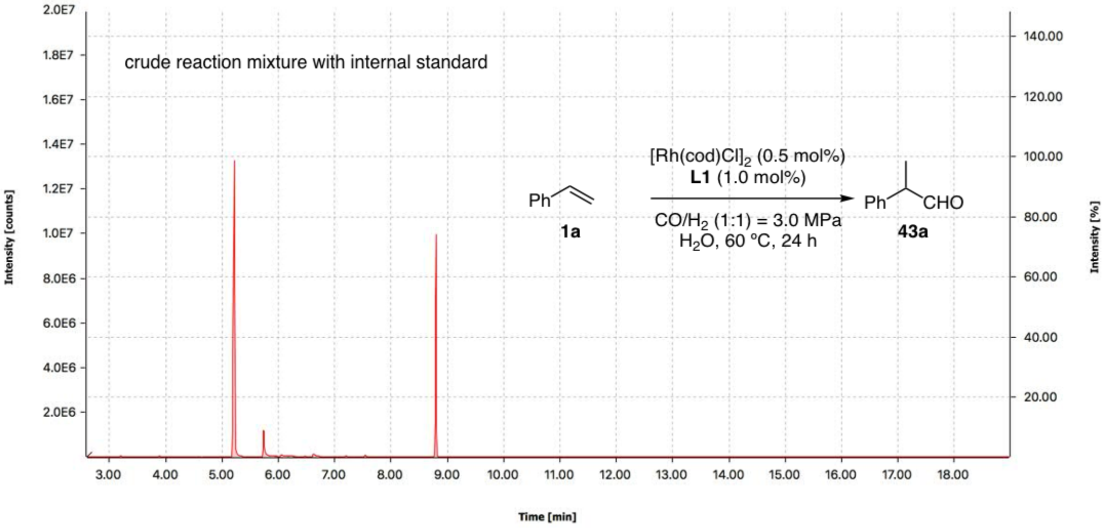
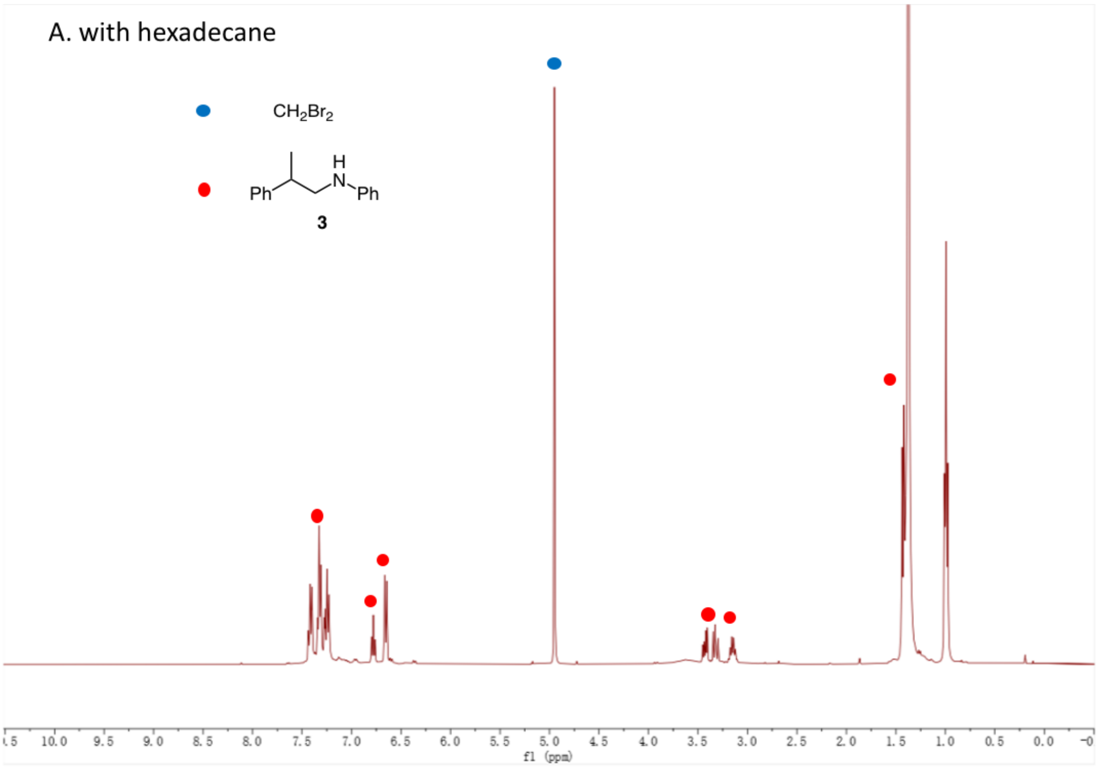


Figure S3. ^{1}H NMR spectra of crude reaction mixture.



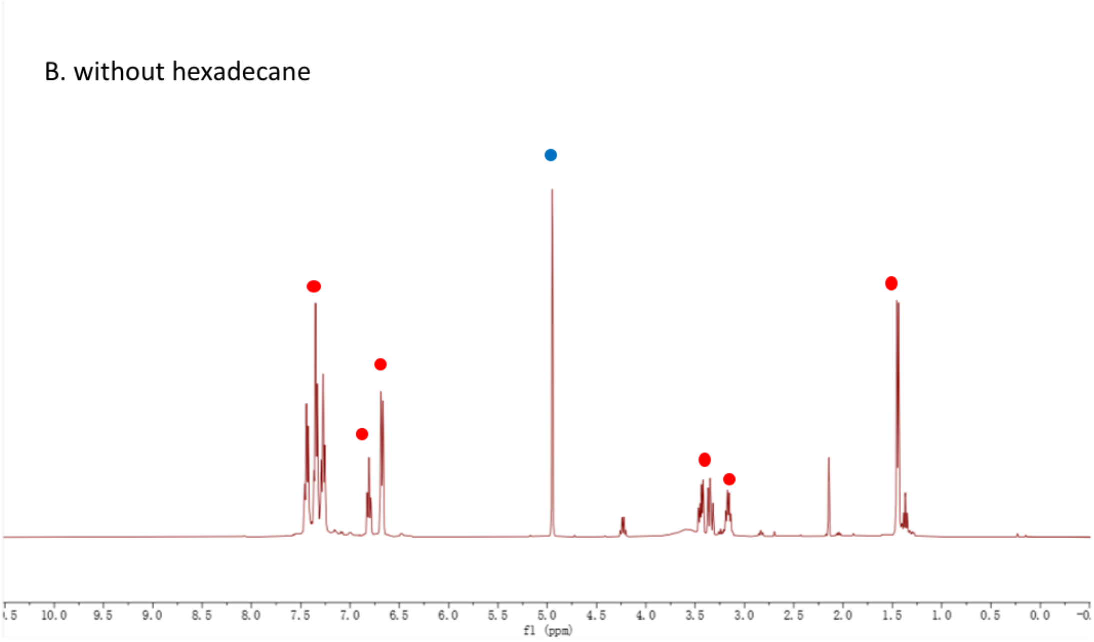


Figure S4. Calibration curve of aniline.

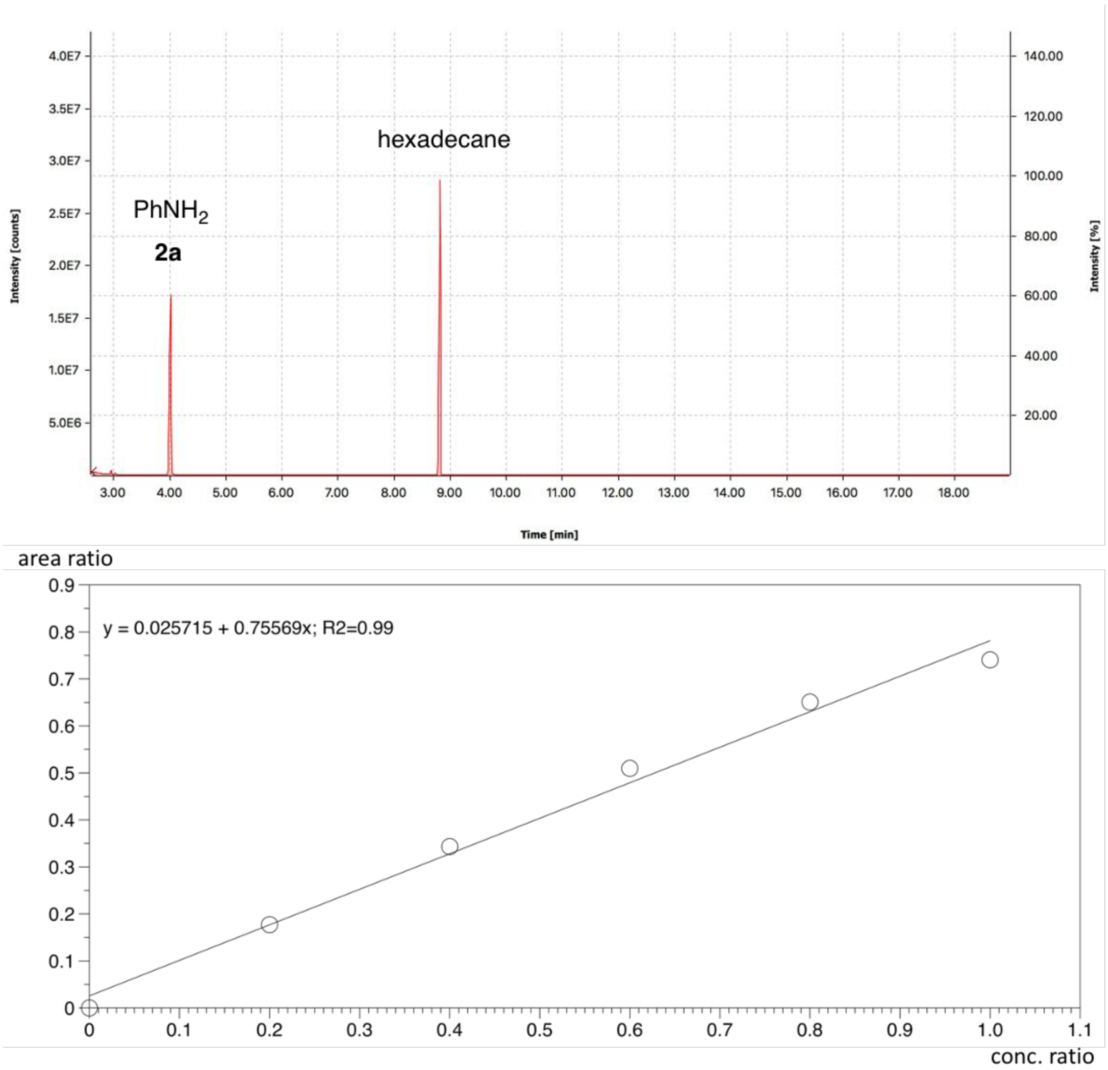


Figure S5. Calibration curve of styrene.

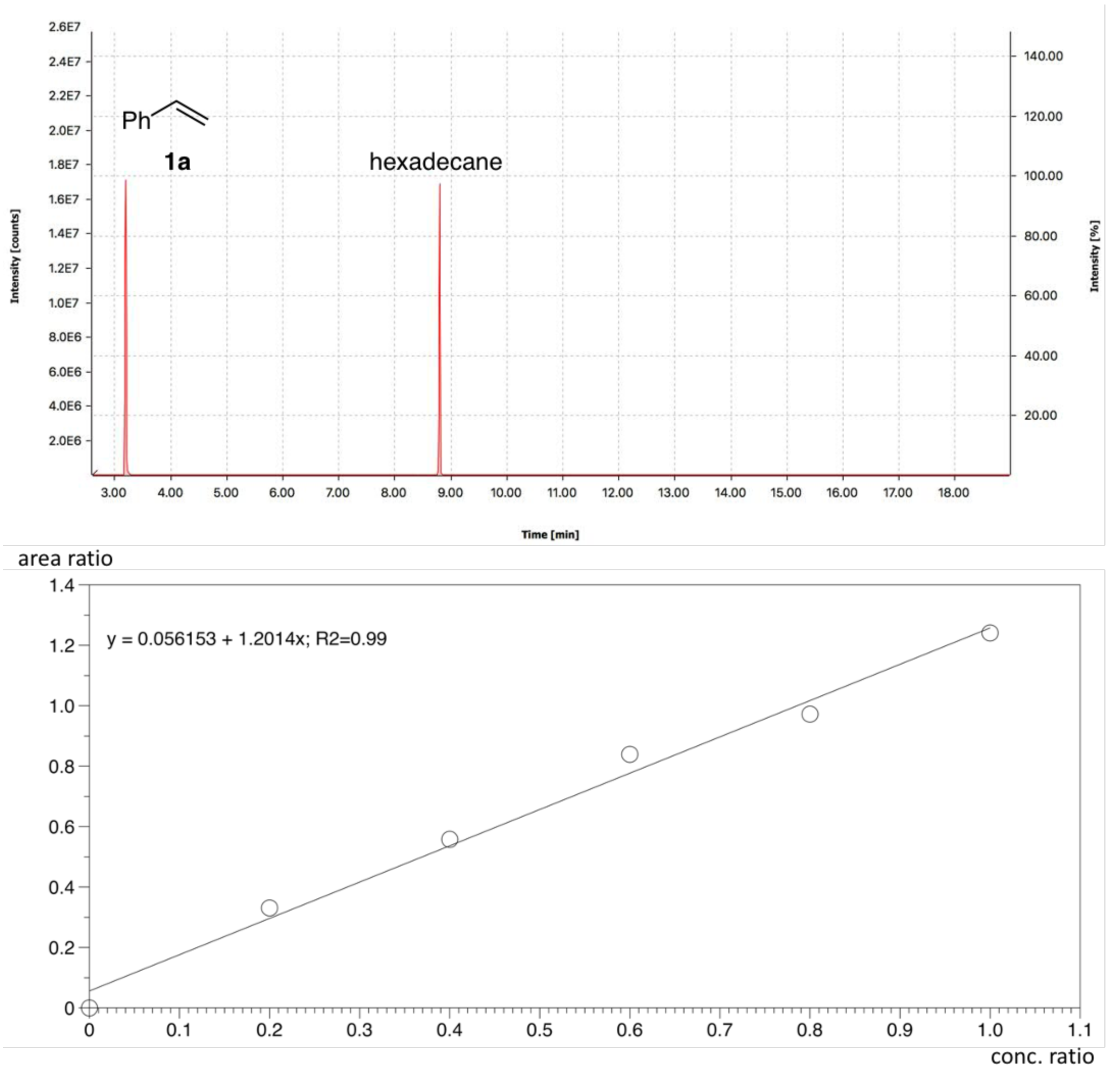


Figure S6. Calibration curve of HAM product 3.

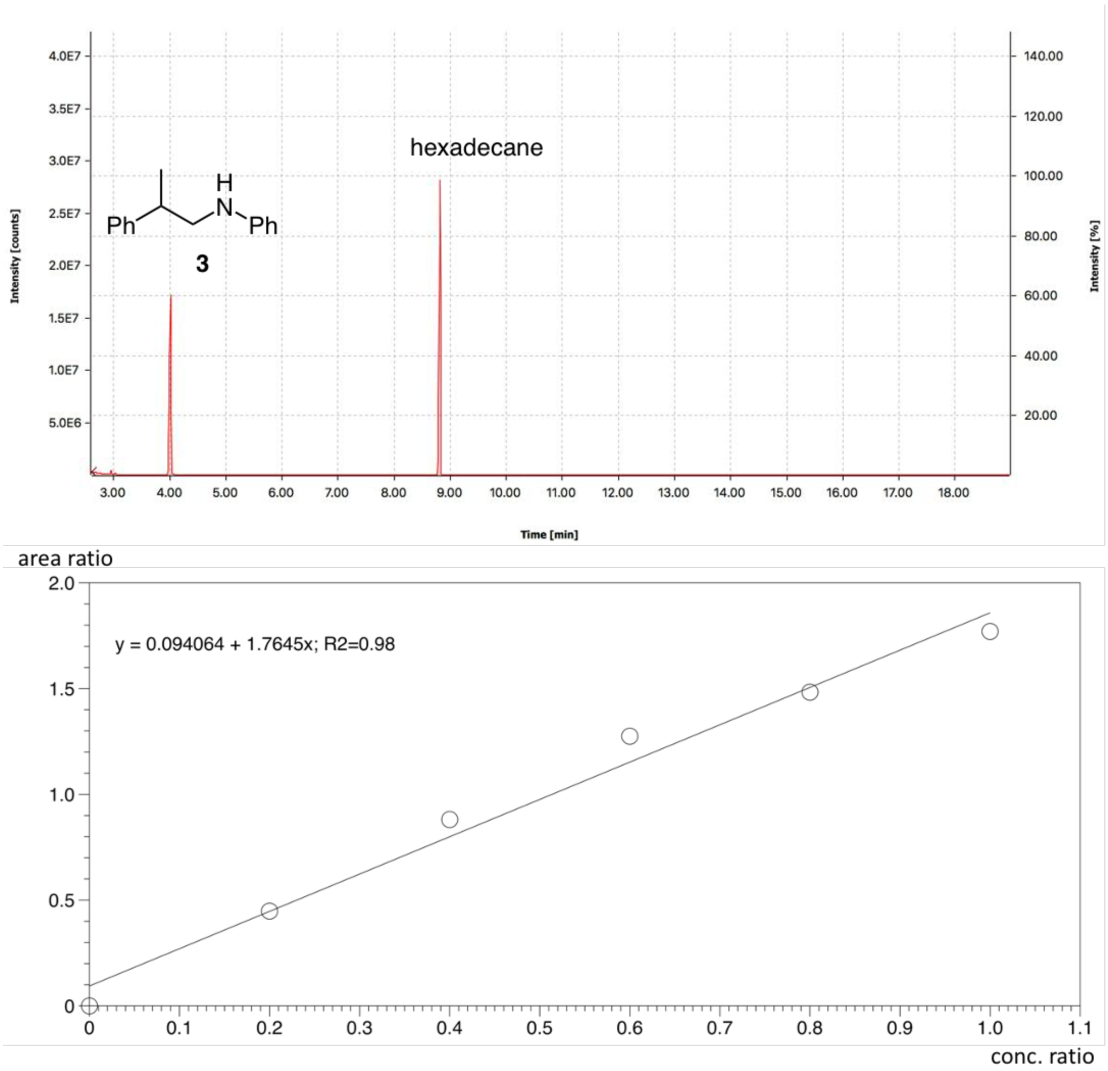
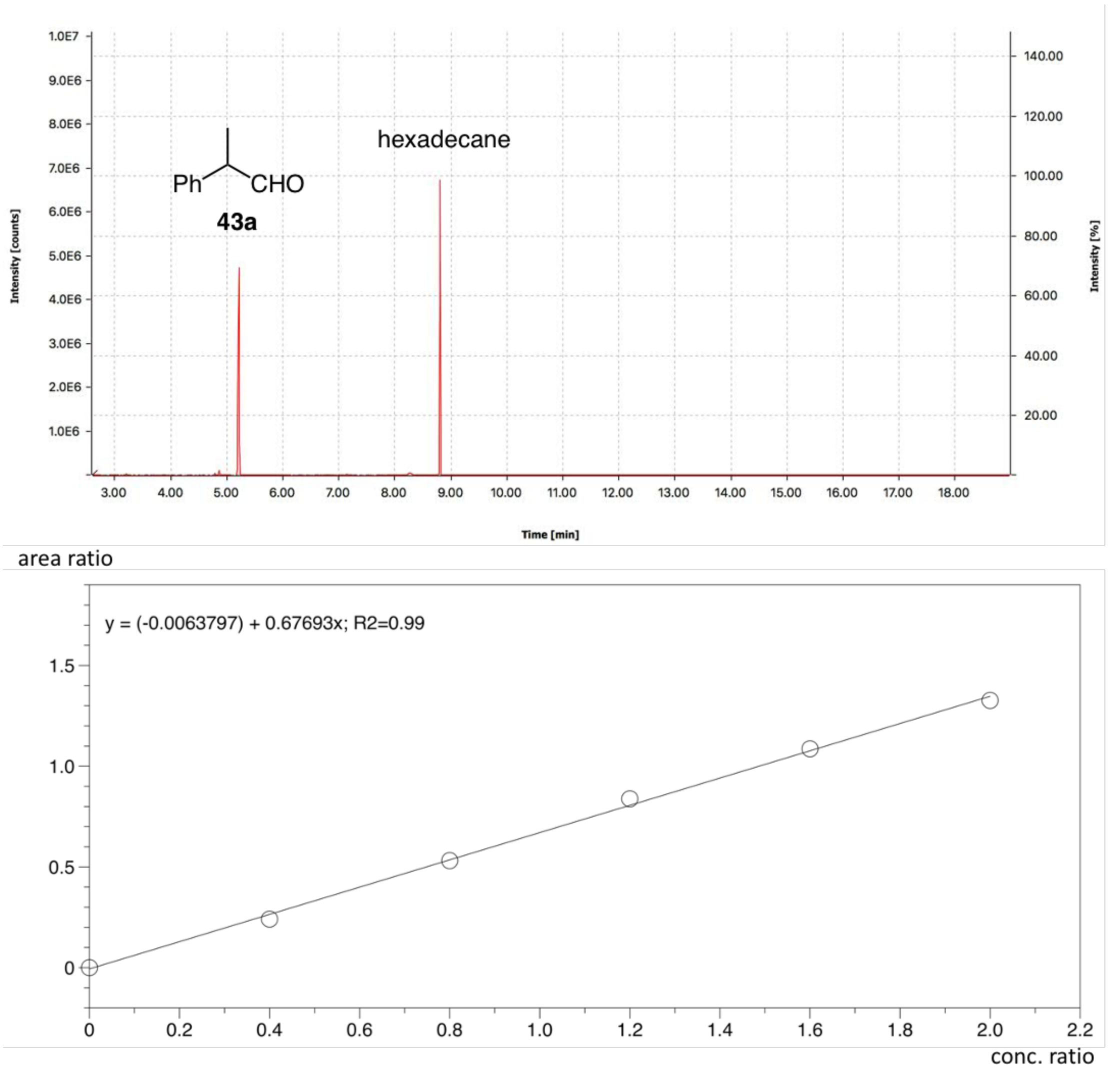


Figure S7. Calibration curve of aldehyde 43a.



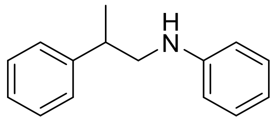
6. General procedure for hydroaminomethylation

The hydroaminomethylation reactions were conducted in a batch autoclave reactor (Shaanxi Wattcas). In a typical run, chloro(1,5-cyclooctadiene)rhodium(I) dimer ([Rh(COD)Cl]$_2$, 0.99 mg, 2×10^{-3} mmol, 0.50 mol%), ligand (0.004 mmol,1.0 mmol %, Rh/L = 1:2) was dissolved in 2 mL of water and stirred for 1 hour. Substituted styrene (0.48 mmol) and aniline (0.4 mmol) were added, and the reactor was purged with nitrogen three times and then charged with 3.0 MPa syngas (CO/H_2=1:1). The mixture was stirred for 24 h at 60 °C. The reaction mixture was extracted with ethyl acetate, and the combined organic layers were analyzed with GC-MS. The organic layers were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure. The residue was purified by column chromatography (eluent: 2-5% ethyl acetate in petroleum ether).

5. Gram-scale hydroaminomethylation

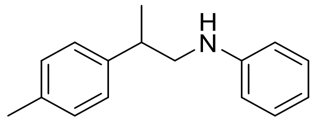
The Gram-scale hydroaminomethylation reaction was conducted in a batch autoclave reactor (Shaanxi Wattcas). Chloro(1,5-cyclooctadiene) rhodium(I) dimer ([Rh(COD)Cl]$_2$, 49.3 mg, 0.1 mmol, 0.5 mmol%), **L1** (129.5 mg, 0.2mmol, Rh/L = 1:2) was dissolved in 100 mL of water and stirred for 1 hour. Styrene (2.50 g, 24 mmol) and aniline (1.86 g, 20 mmol) were added, and the reactor was purged with nitrogen three times and then charged with 3.0 MPa syngas (CO/H_2=1:1). The mixture was stirred for 24 h at 60°C. The reaction mixture was extracted with ethyl acetate, and the combined organic layers were analyzed with GC-MS. The organic layers were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (eluent: 2% ethyl acetate in pertroleum ether) to provide **3** (3.59 g, 85%) as a light-yellow oil.

7. Characterization data of aromatic amines



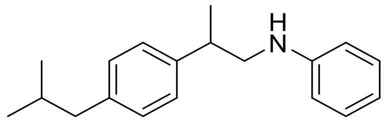
***N*-(2-phenylpropyl)aniline** (**3**)[6] light yellow oil, 82% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.29 (2H, m), 7.23-7.19 (3H, m), 7.16-7.12 (2H, m), 6.69-6.65 (1H, tt, J = 7.3, 1.1 Hz), 6.55-6.53 (2H, m), 3.54 (1H, s), 3.31 (1H, dd, J = 12.4, 6.2 Hz), 3.21 (1H, dd, J = 12.4, 8.2 Hz), 3.07-2.98 (1H, m), 1.31 (3H, d, J = 7.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.2, 144.6, 129.3, 128.8, 127.3, 126.7, 117.4, 113.0, 51.0, 39.3, 19.8.



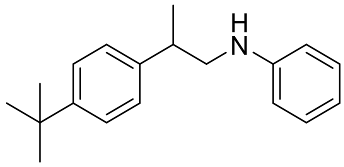
***N*-(2-(*p*-tolyl)propyl)aniline** (**4**) [7] light yellow oil, 87% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17-7.09 (6H, m), 6.67 (1H, tt, J = 7.3, 1.1 Hz), 6.55 (2H, dd, J = 8.7, 1.2 Hz), 3.55 (1H, brs), 3.30 (1H, dd, J = 12.3, 6.2 Hz), 3.19 (1H, dd, J = 12.3, 8.3 Hz), 3.05-2.96 (1H, m), 2.32 (3H, s), 1.30 (3H, d, J = 7.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.3, 141.6, 136.2, 129.5, 129.3, 127.2, 117.4, 113.1, 51.0, 38.9, 21.1, 20.0.



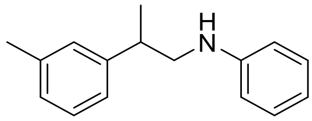
***N*-(2-(4-isobutylphenyl) propyl)aniline** (**5**) [8] light yellow oil, 45% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21-7.12 (6H, m), 6.71 (1H, tt, J = 7.2, 1.1 Hz), 6.60 (2H, dd, J = 8.6, 1.2 Hz), 3.62 (1H, brs), 3.35 (1H, dd, J = 12.2, 6.2 Hz), 3.24 (1H, dd, J = 12.2, 8.2 Hz), 3.06 (1H, m), 2.49 (2H, d, J = 7.2 Hz), 1.94-1.84 (1H, m), 1.35 (3H, d, J = 6.7 Hz), 0.94 (6H, d, J = 6.6 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.3, 141.8, 140.1, 129.5, 129.3, 127.1, 117.4, 113.1, 51.1, 45.2, 38.9, 30.4, 22.6, 19.9.



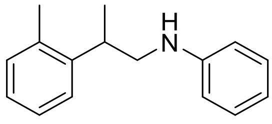
***N*-(2-(4-(tert-butyl)phenyl)propyl)aniline** (**6**) [7] light yellow oil, 56% yield.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.38-7.36 (2H, m), 7.20-7.16 (4H, m), 6.71 (1H, tt, J = 7.3, 1.1 Hz), 6.60 (2H, dd, J = 8.6, 1.1 Hz), 3.64 (1H, brs), 3.34 (1H, dd, J = 12.3, 6.3 Hz), 3.25 (1H, dd, J = 12.3, 8.0 Hz), 3.05 (1H, m), 1.36-1.34 (12H, m). ^{13}C NMR (100 MHz, CDCl$_3$) δ 149.5, 148.3, 141.5, 129.3, 127.0, 125.7, 117.4, 113.1, 51.1, 38.8, 34.6, 31.5, 19.9.



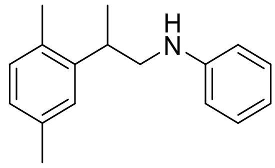
***N*-(2-(*m*-tolyl)propyl)aniline** (**7**) [6] light yellow oil, 75% yield.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.22-7.13 (3H, m), 7.05-7.00 (3H, m), 6.67 (1H, tt, J = 7.2, 1.0 Hz), 6.7-6.54 (2H, dd, J = 8.6, 1.0 Hz), 3.56 (1H, brs), 3.31 (1H, dd, J = 12.3, 6.3 Hz), 3.21 (1H, dd, J = 12.3, 8.2 Hz), 3.04-2.95 (1H, m), 2.34 (3H, s), 1.31 (3H, d, J = 7.0 Hz). ^{13}C NMR (100 MHz, CDCl$_3$) δ 148.3, 144.6, 138.3, 129.3, 128.7, 128.1, 127.5, 124.4, 117.4, 113.1, 51.0, 39.3, 21.6, 19.9.



***N*-(2-(*o*-tolyl)propyl)aniline** (**8**) [6] light yellow oil, 63% yield.

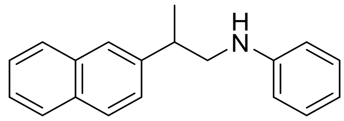
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.23-7.20 (2H, m), 7.17-7.12 (4H, m), 6.68 (1H, tt, J = 7.2, 1.1 Hz), 6.57 (2H, dd, J = 8.7, 1.1 Hz), 3.37-3.28 (3H, m), 2.29 (3H, s), 1.28 (3H, d, J = 6.3 Hz). ^{13}C NMR (100 MHz, CDCl$_3$) δ 148.3, 142.8, 136.3, 130.7, 129.4, 126.6, 126.3, 125.4, 117.4, 113.02, 50.3, 34.2, 19.73, 19.68.



N-(2-(2,5-dimethylphenyl)propyl)aniline (**9**) light yellow oil, 73% yield.

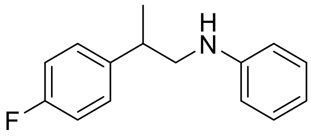
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.24-7.20 (2H, m), 7.13-7.09 (2H, m), 7.01 (1H, dd, J = 7.7, 1.9 Hz), 6.75 (1H, tt, J = 7.2, 1.1 Hz), 6.65-6.63 (2H, m), 3.41-3.33 (3H, m), 2.38 (3H, s), 2.32 (3H, s), 1.34 (3H, d, J = 6.5 Hz). ^{13}C NMR (100 MHz, CDCl$_3$) δ 148.4, 142.5, 135.9, 133.1, 130.5, 129.3, 127.1, 126.1, 117.4, 113.0, 50.3, 34.2, 21.3, 19.8, 19.2.

HRMS (ESI): calcd for $C_{17}H_{22}N$ $[M+H]^+$: 240.1747, found: 240.1749.



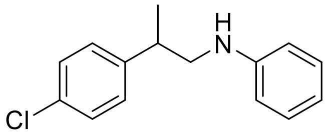
N-(2-(naphthalen-2-yl)propyl)aniline (**10**)[7] light yellow oil, 53% yield.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.89-7.85 (3H, m), 7.72 (1H, s), 7.56-7.48 (2H, m), 7.43 (1H, dd, J = 8.5, 1.7 Hz), 7.24-7.20 (2H, m), 6.76 (1H, tt, J = 7.5, 1.1 Hz), 6.63 (2H, dd, J = 8.6, 1.0 Hz), 3.49 (1H, dd, J = 12.3, 6.0 Hz), 3.39 (1H, dd, J = 12.3, 8.3 Hz), 3.33-3.24 (1H, m), 1.48 (3H, d, J = 6.9 Hz). ^{13}C NMR (100 MHz, CDCl$_3$) δ 148.2, 142.0, 133.7, 132.6, 129.4, 128.5, 127.8, 127.7, 126.2, 126.0, 125.64, 125.62, 117.5, 113.1, 50.8, 39.5, 20.0.



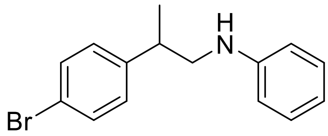
N-(2-(4-fluorophenyl)propyl)aniline (**11**)[9] light yellow oil, 71% yield.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.21-7.15 (4H, m), 7.04-7.00 (2H, m), 6.70 (1H, tt, J = 7.3, 1.1 Hz), 6.58 (2H, dd, J= 8.7, 1.1 Hz), 3.34 (1H, dd, J = 6.1, 12.5 Hz), 3.20 (1H, dd, J= 12.4, 8.3 Hz), 3.10-3.02 (1H, m), 1.32 (3H, d, J = 6.9 Hz). ^{13}C NMR (100 MHz, CDCl$_3$) δ 161.7 (d, J = 244.0 Hz), 148.1, 140.3 (d, J = 3.2 Hz), 129.4, 128.8 (d, J = 7.8 Hz), 117.6, 115.6 (d, J = 21.1 Hz), 113.1, 61.1, 38.6, 20.0.



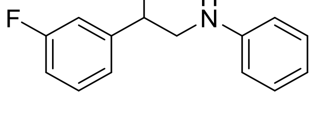
N-(2-(4-chlorophenyl)propyl)aniline (**12**) [7] light yellow oil, 80% yield.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.35-7.32 (2H, m), 7.23-7.18 (4H, m), 6.75 (1H, tt, J = 7.3, 1.1 Hz), 6.61 (2H, dd, J = 7.6, 1.0 Hz), 3.37 (1H, dd, J = 12.5, 6.1 Hz), 3.24(1H, dd, J = 12.5, 8.3 Hz), 3.13-3.04 (1H, m), 1.35 (3H, d, J = 6.9 Hz). ^{13}C NMR (100 MHz, CDCl$_3$) δ 148.0, 143.1, 132.3, 129.4, 128.9, 128.7, 117.6, 113.0, 50.9, 38.7, 19.7.



N-(2-(4-bromophenyl)propyl)aniline (**13**) [10] light yellow oil, 84% yield.

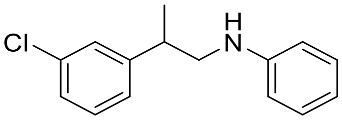
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.48-7.46 (2H, m), 7.22-7.17 (2H, m), 7.14-7.11 (2H, m), 6.73 (1H, dd, J= 7.4, 1.1 Hz), 6.59 (2H, dd, J= 8.7, 1.1 Hz), 3.57 (1H, brs), 3.34 (1H, dd, J = 12.5, 6.1 Hz), 3.20 (1H, dd, J = 12.5, 8.4 Hz), 3.08-3.00 (1H, m), 1.31 (3H, d, J = 7.0 Hz). ^{13}C NMR (100 MHz, CDCl$_3$) δ 148.0, 143.7, 131.9, 129.4, 129.2, 120.5, 117.6, 113.1, 50.9, 38.8, 19.7.



N-(2-(3-fluorophenyl)propyl)aniline (14) light yellow oil, 87% yield.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.31-7.25 (1H, m), 7.19-7.14 (2H, m), 7.00 (1H, dt, J = 7.7, 1.3 Hz), 6.95-6.90 (2H, m), 6.70 (1H, tt, J= 7.2, 1.1 Hz), 6.57 (2H, dd, J = 8.7, 1.1 Hz), 3.58 (1H, brs), 3.33 (1H, dd, J = 12.6, 6.2 Hz), 3.22 (1H, dd, J = 12.5, 8.1 Hz), 3.11-3.02 (1H, m), 1.32 (3H, d, J = 7.0 Hz). ^{13}C NMR (100 MHz, CDCl$_3$) δ 163.2 (d, J = 245.8 Hz), 148.0, 147.4 (d, J = 6.9 Hz), 130.2 (d, J = 8.4 Hz), 129.4, 123.1 (d, J = 2.9 Hz), 117.6, 114.2 (d, J = 21.0 Hz), 113.6 (d, J = 21.0 Hz), 113.1, 50.9, 39.2 (d, J = 1.7 Hz), 19.7.

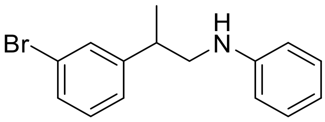
HRMS (ESI): calcd for $C_{15}H_{17}FN$ $[M+H]^+$: 230.1340, found:230.1337.



N-(2-(3-chlorophenyl)propyl)aniline (**15**) light yellow oil, 76% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27-7.20 (3H, m), 7.19-7.14 (2H, m), 7.10 (1H, dt, J = 7.2, 1.5 Hz), 6.70 (1H, tt, J = 7.3, 1.1 Hz), 6.57 (2H, dd, J = 8.6, 1.1 Hz), 3.56 (1H, brs), 3.32 (1H, dd, J = 12.6, 6.3 Hz), 3.22 (1H, dd, J = 12.6, 8.1 Hz), 3.08-2.99 (1H, m), 1.32 (3H, d, J = 7.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.0, 146.9, 134.6, 130.0, 129.4, 127.5, 127.0, 125.7, 117.6, 113.1, 50.9, 39.2, 19.7.

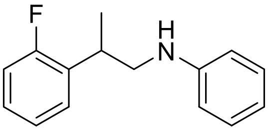
HRMS (ESI): calcd for $C_{15}H_{17}ClN$ $[M+H]^+$: 246.1044, found: 246.1042.



N-(2-(3-bromophenyl)propyl)aniline (**16**) light yellow oil, 80% yield.

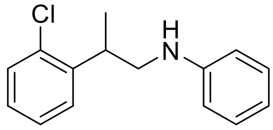
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.37 (2H, m), 7.22-7.14 (4H, m), 6.71 (1H, tt, J = 7.2, 1.1 Hz), 6.59 (2H, dd, J = 8.6, 1.1 Hz), 3.58 (1H, brs), 3.34 (1H, dd, J = 12.6, 6.3 Hz), 3.23 (1H, dd, J = 12.6, 8.1 Hz), 3.09-3.00 (1H, m), 1.33 (3H, d, J = 7.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.0, 147.2, 130.4, 130.4, 129.9, 129.4, 126.2, 122.9, 117.6, 113.1, 50.9, 39.2, 19.7.

HRMS (ESI): calcd for $C_{15}H_{17}BrN$ $[M+H]^+$: 290.0539, found: 290.0539.



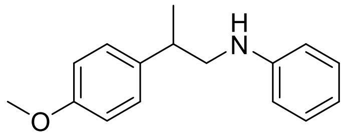
N-(2-(2-fluorophenyl)propyl)aniline (**17**) light yellow oil, 86% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26-7.01 (6H, m), 6.68 (1H, tt, J = 7.3, 1.1 Hz), 6.60-6.58 (2H, m), 3.65 (1H, brs), 3.43-3.26 (3H, m), 1.34 (3H, d, J = 6.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.2 (d, J = 245.0 Hz), 148.2, 131.3 (d, J = 14.6 Hz), 129.4, 128.3 (d, J = 5.1 Hz), 128.1 (d, J = 8.4 Hz), 124.5 (d, J = 3.4 Hz), 117.4, 115.7 (d, J = 22.7 Hz), 112.9, 49.8 (d, J = 1.5 Hz), 32.9 (d, J = 1.3 Hz), 18.5 (d, J = 1.3 Hz). HRMS (ESI): calcd for $C_{15}H_{17}FN$ $[M+H]^+$: 230.1340, found: 230.1336.



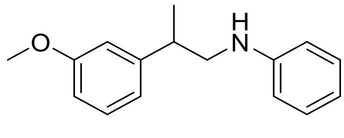
***N*-(2-(2-chlorophenyl)propyl)aniline** (**18**) [9] light yellow oil, 74% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (1H, dd, J = 7.9, 1.2 Hz), 7.30-7.22 (2H, m), 7.18-7.14 (3H, m), 6.68 (1H, tt, J = 7.3, 1.1 Hz), 6.60 (2H, dd, J = 8.6, 1.1 Hz), 3.69-3.60 (2H, m), 3.37 (1H, dd, J = 12.3, 7.3 Hz), 3.25 (1H, dd, J = 12.3, 7.0 Hz), 1.32 (3H, d, J = 6.9 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.2, 141.9, 134.3, 129.9, 129.3, 127.8, 127.5, 127.3, 117.4, 112.9, 49.9, 35.4, 18.9.



***N*-(2-(4-methoxyphenyl)propyl)aniline** (**19**) [7] light yellow oil, 90% yield.

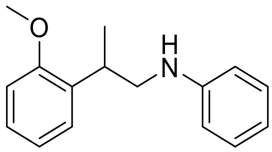
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16-7.10 (4H, m), 6.86-6.83 (2H, m), 6.68 (1H, tt, J = 7.3, 1.1 Hz), 6.57 (2H, dd, J = 8.7, 1.1 Hz), 3.76 (3H, s), 3.29 (1H, dd, J = 12.3, 6.2 Hz), 3.16 (1H, dd, J = 12.3, 8.3 Hz), 3.03-2.94 (1H, m), 1.28 (3H, d, J = 7.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.3, 147.9, 136.5, 129.3, 128.2, 117.6, 114.1, 113.3, 55.3, 51.3, 38.3, 20.0.



***N*-(2-(3-methoxyphenyl)propyl)aniline** (**20**) light yellow oil, 86% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25-7.21 (1H, m), 7.18-7.12 (2H, m), 6.81 (1H, dt, J = 7.7, 1.3 Hz), 6.78-6.75 (2H, m), 6.67 (1H, tt, J = 7.2, 1.1 Hz), 6.55 (2H, dd, J = 8.6, 1.1 Hz), 3.77 (3H, s), 3.31 (1H, dd, J = 12.4, 6.1 Hz), 3.20 (1H, dd, J = 12.3, 8.3 Hz), 3.06-2.97 (1H, m), 1.31 (3H, d, *J* = 7.0 Hz). ^{13}C NMR (100 MHz, CDCl$_3$) *δ* 157.4, 148.6, 132.8, 129.3, 127.5, 127.1, 120.9, 117.0, 112.8, 110.7, 55.5, 50.2, 32.1, 18.4.

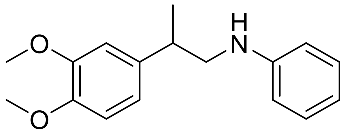
HRMS (ESI): calcd for $C_{16}H_{20}NO$ [M+H]$^+$: 242.1539, found: 242.1541.



***N*-(2-(2-methoxyphenyl)propyl)aniline** (**21**) light yellow oil, 71% yield.

^{1}H NMR (400 MHz, CDCl$_3$) *δ* 7.25-7.20 (2H, m), 7.19-7.14 (2H, m), 6.98-6.94 (1H, m), 6.90 (1H, dd, *J* = 8.6, 1.3 Hz), 6.67 (1H, tt, *J* = 7.3, 1.1 Hz), 6.61 (2H, dd, *J* = 8.7, 1.1 Hz), 3.85 (3H, s), 3.60-3.51 (1H, m), 3.34 (1H, dd, *J* = 12.0, 7.4 Hz), 3.21 (1H, dd, *J* = 12.0, 6.8 Hz), 1.32 (3H, dd, *J* = 7.0 Hz). ^{13}C NMR (100 MHz, CDCl$_3$) *δ* 159.9, 148.2, 146.3, 129.7, 129.3, 119.7, 117.4, 113.3, 113.0, 111.7, 55.2, 50.9, 39.3, 19.8.

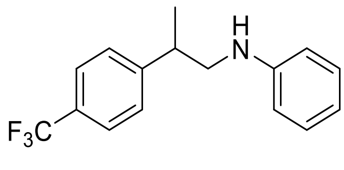
HRMS (ESI): calcd for $C_{16}H_{20}NO$ [M+H]$^+$: 242.1539, found: 242.1537.



***N*-(2-(3,4-dimethoxyphenyl)propyl)aniline** (**22**) light yellow oil, 71% yield.

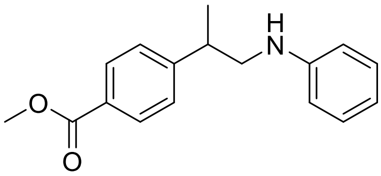
^{1}H NMR (400 MHz, CDCl$_3$) *δ* 7.19-7.14 (2H, m), 6.84 (1H, d, *J* = 8.2 Hz), 6.78 (1H, dd, *J* = 8.2, 2.0 Hz), 6.73-6.67 (2H, m), 6.58 (2H, dd, *J* = 8.7, 1.1 Hz), 3.88 (3H, s), 3.87 (3H, s), 3.35 (1H, dd, *J* = 12.3, 5.9 Hz), 3.17 (1H, dd, *J* = 12.3, 8.6 Hz), 3.06-2.97 (1H, m), 1.33 (3H, d, *J* = 6.9 Hz). ^{13}C NMR (100 MHz, CDCl$_3$) *δ* 149.1, 148.2, 147.8, 137.1, 129.4, 119.1, 117.5 113.2, 111.4, 110.6, 56.03, 55.96, 51.1, 38.9, 20.0.

HRMS (ESI): calcd for $C_{17}H_{22}NO_2$ [M+H]$^+$: 272.1645, found: 272.1648.



***N*-(2-(4-(trifluoromethyl)phenyl)propyl)aniline** (**23**)[7] light yellow oil, 85% yield.

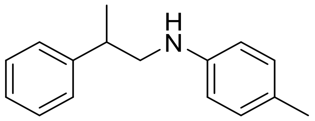
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.59 (2H, d, J = 8.0 Hz), 7.34 (2H, d, J = 8.1 Hz), 7.20-7.15 (2H, m), 6.72 (1H, tt, J = 7.3, 1.1 Hz), 6.58 (2H, dd, J = 8.7, 1.1 Hz), 3.57 (1H, brs), 3.38 (1H, dd, J = 12.6, 6.2 Hz), 3.27 (1H, dd, J = 12.7, 8.2 Hz), 3.19-3.10 (1H, m), 1.36 (3H, d, J = 6.9 Hz). ^{13}C NMR (100 MHz, CDCl$_3$) δ 148.9, 147.9, 129.6, 129.1 (q, J = 32.4 Hz), 127.8, 125.7 (q, J = 3.8 Hz), 124.3 (q, J = 272.0 Hz), 117.7, 113.1, 50.8, 39.3, 19.6.



methyl 4-(1-(phenylamino)propan-2-yl)benzoate (**24**) light yellow oil, 79% yield.

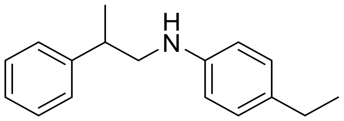
^{1}H NMR (400 MHz, CDCl$_3$) δ 8.04 (2H, d, J = 8.0 Hz), 7.32 (2H, d, J = 8.1 Hz), 7.20 (2H, t, J = 7.7 Hz), 6.76-6.72 (1H, m), 6.59-6.61 (2H, m), 3.94 (3H, s), 3.39 (1H, dd, J = 12.6, 6.2 Hz), 3.29 (1H, dd, J = 12.6, 8.1 Hz), 3.20-3.12 (1H, m), 1.37 (3H, d, J = 6.4 Hz). ^{13}C NMR (100 MHz, CDCl$_3$) δ 167.0, 150.1, 147.9, 130.0, 129.3, 128.6, 127.4, 117.5, 113.0, 52.1, 50.7, 39.3, 19.5.

HRMS (ESI): calcd for $C_{17}H_{20}NO_2$ [M+H]$^+$: 270.1489, found: 270.1492.



4-methyl-*N*-(2-phenylpropyl)aniline (**25**) [7] light yellow oil, 74% yield.

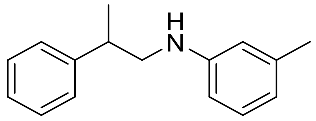
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.34-7.31 (2H, m), 7.25-7.21 (3H, m), 6.97 (2H, d, J = 8.1 Hz), 6.51 (2H, d, J = 8.4 Hz), 3.32 (1H, dd, J = 12.3, 6.2 Hz), 3.21 (1H, dd, J = 12.3, 8.2 Hz), 3.09-3.02 (1H, m), 2.23 (3H, s), 1.32 (3H, d, J = 7.0 Hz).^{13}C NMR (100 MHz, CDCl$_3$) δ 146.0, 144.8, 129.9, 128.8, 127.4, 126.7, 113.3, 51.5, 39.3, 20.5, 19. 9.



4-ethyl-*N*-(2-phenylpropyl)aniline (**26**) light yellow oil, 90% yield.

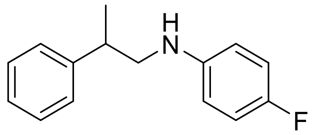
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46-7.42 (2H, m), 7.37-7.32 (3H, m), 7.12 (2H, d, J = 8.4 Hz), 6.64 (2H, d, J = 8.5 Hz), 3.43 (1H, dd, J = 12.3, 6.2 Hz), 3.33 (1H, dd, J = 12.3, 8.2 Hz), 3.19-3.14 (1H, m), 2.66 (2H, q, J = 7.6 Hz), 1.44 (3H, d, J = 7.0 Hz), 1.31 (3H, t, J = 7.6 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.1, 144.7, 133.2, 128.7, 128.6, 127.3, 126.7, 113.2, 51.3, 39.3, 28.0, 19.9, 16.1.

HRMS (ESI): calcd for $C_{17}H_{22}N$ $[M+H]^+$: 240.1747, found: 240.1746.



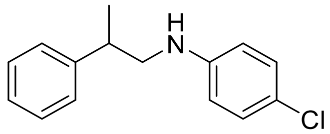
3-methyl-*N*-(2-phenylpropyl)aniline (**27**) [7] light yellow oil, 68% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.39 (2H, m), 7.34-7.30 (3H, m), 7.15-7.11 (1H, m), 6.60 (1H, d, J = 7.5 Hz), 6.48-6.45 (2H, m), 3.41 (1H, dd, J = 12.3, 6.2 Hz), 3.30 (1H, dd, J = 12.3, 8.2 Hz), 3.17-3.08 (1H, m), 2.35 (3H, s), 1.41 (3H, d, J = 7.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.2, 144.7, 139.1, 129.2, 128.8, 127.4, 126.7, 118.4, 113.8, 110.2, 51.0, 39.3, 21.7, 19.9.



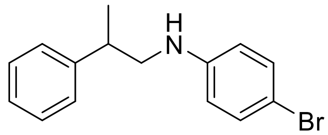
4-fluoro-*N*-(2-phenylpropyl)aniline (**28**) [7] light yellow oil, 80% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (2H, t, J = 7.4 Hz), 7.24-7.17 (3H, m), 6.87-6.82 (2H, m), 6.48-6.44 (2H, m), 3.27 (1H, dd, J = 12.2, 6.1 Hz), 3.16 (1H, dd, J = 12.2, 8.4 Hz), 3.05-2.96 (1H, m), 1.30 (3H, d, J = 6.9 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.8 (d, J = 235.0 Hz), 144.5 (d, J = 1.9 Hz), 144.5, 128.8, 127.3, 126.8, 115.7 (d, J =22.3 Hz), 113.8 (d, J = 7.3 Hz), 51.6, 39.2, 19.8.



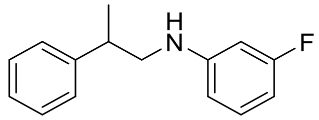
4-chloro-*N*-(2-phenylpropyl)aniline (**29**) [7] light yellow oil, 82% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.29 (2H, m), 7.25-7.18 (3H, m), 7.10-7.06 (2H, m), 6.47-6.43 (2H, m), 3.55 (1H, brs), 3.28 (1H, dd, *J* = 12.4, 6.1 Hz), 3.17 (1H, dd, *J* = 12.4, 8.4 Hz), 3.06-2.97 (1H, m), 1.31(3H, d, *J* = 6.9 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 146.7, 144.4, 129.1, 128.0, 127.3, 126.8, 121.9, 114.1, 51.0, 39.2, 19.8.



4-bromo-*N*-(2-phenylpropyl)aniline (**30**) [7] light yellow oil, 78% yield.

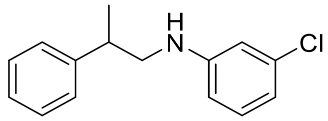
^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.32-7.28 (2H, m), 7.24-7.16 (5H, m), 6.40-6.36 (2H, m), 3.56 (1H, brs), 3.25 (1H, dd, *J* = 12.4, 6.1 Hz), 3.15 (1H, dd, *J* = 12.4, 8.4 Hz), 3.04-2.95 (1H, m), 1.29 (3H, d, *J* = 7.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 147.1, 144.3, 131.9, 128.8, 127.3, 126.8, 114.5, 108.8, 50.8, 39.1, 19. 8.



3-fluoro-*N*-(2-phenylpropyl)aniline (**31**) light yellow oil, 71% yield.

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.32 (2H, t, *J* = 7.4 Hz), 7.25-7.19 (3H, m), 7.04 (1H, dd, *J* = 8.0, 15.1 Hz), 6.35 (1H, m), 6.29-6.22 (2H, m), 3.68 (1H, brs), 3.29 (1H, dd, *J* = 12.4, 6.1 Hz), 3.19 (1H, dd, *J* = 12.4, 8.4 Hz), 3.07-2.98 (1H, m), 1.32 (3H, d, *J* = 7.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 164.2 (d, *J* = 243.0 Hz), 150.0 (d, *J* = 10.7 Hz), 144.3, 130.3 (d, *J* = 10.3 Hz), 128.8, 127.3, 126.9, 108.9 (d, *J* = 2.3 Hz), 103.7 (d, *J* = 21.6 Hz), 99.5 (d, *J* = 25.3 Hz), 50.8, 39.2, 19.8.

HRMS (ESI): calcd for $C_{15}H_{17}FN$ [M+H]$^+$: 230.1340, found: 230.1337.

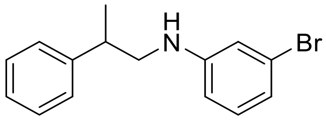


3-chloro-*N*-(2-phenylpropyl)aniline (**32)** light yellow oil, 73% yield.

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.41-7.37 (2H, m), 7.32-7.26 (3H, m), 7.09 (1H, t, *J* = 7.3 Hz), 6.70 (1H, ddd, *J* = 7.9, 2.0, 0.9 Hz), 6.59 (1H, t, *J* = 2.2 Hz), 6.46 (1H, ddd, *J* = 0.6, 2.2, 8.2 Hz), 3.70 (1H, brs), 3.36 (1H, dd, *J* = 12.4, 6.1 Hz), 3.25 (1H, dd, *J* =

12.4, 8.4 Hz), 3.13-3.05 (1H, m), 1.39 (3H, d, *J* = 7.0 Hz). ^{13}C NMR (100 MHz, CDCl$_3$) *δ* 149.3, 144.3, 135.1, 130.3, 128.9, 127.3, 126.9, 117.2, 112.5, 111.3, 50.7, 39.2, 19.8.

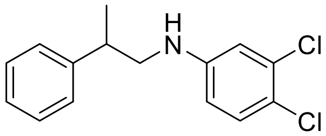
HRMS (ESI): calcd for $C_{15}H_{17}ClN$ [M+H]$^+$: 246.1044, found: 246.1043.



3-bromo-*N*-(2-phenylpropyl) aniline (**33**) light yellow oil, 87% yield.

^{1}H NMR (400 MHz, CDCl$_3$) *δ* 7.32-7.28 (2H, m), 7.23-7.15 (3H, m), 6.94 (1H, m), 6.76 (1H, d, *J* = 7.8 Hz), 6.65 (1H, s), 6.40 (1H, dd, *J* = 8.2, 2.3 Hz), 3.59 (1H, brs), 3.25 (1H, dd, *J* = 12.4, 6.1 Hz), 3.15 (1H, dd, *J* = 12.3, 8.4 Hz), 3.03-2.94 (1H, m), 1.29 (3H, d, *J* = 7.0 Hz). ^{13}C NMR (100 MHz, CDCl$_3$) *δ* 149.4, 144.2, 130.5, 128.8, 127.3, 126.8, 123.3, 120.0, 115.3, 111.7, 50.6, 39.2, 19.8.

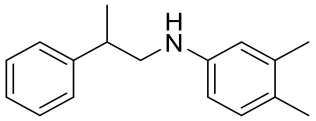
HRMS (ESI): calcd for $C_{15}H_{17}BrN$ [M+H]$^+$: 290.0539, found: 290.0540.



3,4-dichloro-*N*-(2-phenylpropyl)aniline (**34**) light yellow oil, 94% yield.

^{1}H NMR (400 MHz, CDCl$_3$) *δ* 7.35-7.30 (2H, m), 7.26-7.18 (3H, m), 7.13 (1H, d, *J* = 8.8 Hz), 6.59 (1H, d, *J* =2.7 Hz), 6.34 (1H, dd, *J* = 8.8, 2.8 Hz), 3.63 (1H, brs), 3.27 (1H, dd, *J* = 12.4, 6.0 Hz), 3.16 (1H, dd, *J* = 12.4, 8.6 Hz), 3.05-2.96 (1H, m), 1.32 (3H, d, *J* = 7.0 Hz). ^{13}C NMR (100 MHz, CDCl$_3$) *δ* 147.7, 144.0, 132.8, 130.6, 128.9, 127.3, 127.0, 119.6, 113.9, 112.7, 50.8, 39.2, 19.8.

HRMS (ESI): calcd for $C_{15}H_{16}Cl_2N$ [M+H]$^+$: 280.0654, found: 280.0654.

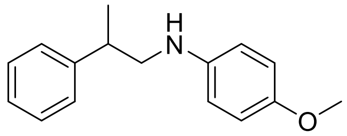


3,4-dimethyl-*N*-(2-phenylpropyl)aniline (**35**) light yellow oil, 83% yield.

^{1}H NMR (400 MHz, CDCl$_3$) *δ* 7.43-7.39 (2H, m), 7.34-7.29 (3H, m), 7.01 (1H, d, *J* =

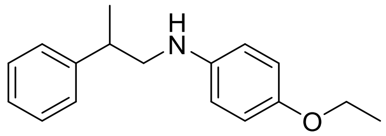
8.0 Hz), 6.49 (1H, d, J = 2.6 Hz), 6.44 (1H, dd, J = 8.1, 2.6 Hz), 3.39 (1H, dd, J = 12.3, 6.3 Hz), 3.29 (1H, dd, J = 12.3, 8.1 Hz), 3.17-3.09 (1H, m), 2.27 (3H, s), 2.23 (3H, s), 1.41 (3H, d, J = 7.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.4, 144.8, 137.4, 130.4, 128.8, 127.4, 126. 7, 125.4, 115.0, 110.5, 51.4, 39.3, 20.2, 19.9, 18.8.

HRMS (ESI): calcd for C17H21N $[M+H]^+$: 240.1747, found: 240.1746.



4-methoxy-*N*-(2-phenylpropyl)aniline (**36**) [7] light yellow oil, 71% yield.

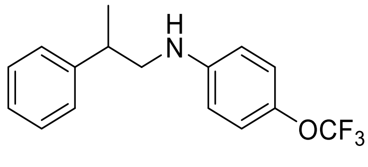
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.29 (2H, m), 7.24-7.19 (3H, m), 6.76-6.73 (2H, m), 6.54-6.51 (2H, m), 3.72 (3H, s), 3.28 (1H, dd, J = 12.2, 6.1 Hz), 3.17 (1H, dd, J = 12.2, 8.3 Hz), 3.07-2.98 (1H, m), 1.31 (3H, d, J = 7.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.1, 144.7, 142.4, 128.7, 127.3, 126. 7, 114.9, 114.4, 55.8, 52.0, 39.3, 19.9.



4-ethoxy-*N*-(2-phenylpropyl)aniline (**37**) light yellow oil, 93% yield,

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.30 (2H, m), 7.25-7.20 (3H, m), 6.78-6.74 (2H, m), 6.54-6.50 (2H, m), 3.95 (2H, q, J = 7.0 Hz), 3.29 (1H, dd, J = 12.2, 6.1 Hz), 3.18 (1H, dd, J = 12.2, 8.3 Hz), 3.08-2.99 (1H, m), 1.36 (3H, t, J = 7.0 Hz), 1.32 (3H, d, J = 7.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.4, 144.7, 142.4, 128.7, 127.3, 126.7, 115.8, 114.4, 64.1, 52.0, 39.3, 19.9, 15.1.

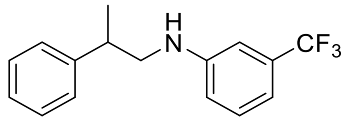
HRMS (ESI): calcd for $C_{17}H_{22}NO$ $[M+H]^+$: 256.1696, found: 256.1698.



***N*-(2-phenylpropyl)-4-(trifluoromethoxy)aniline** (**38**) light yellow oil, 85% yield.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.34-7.30 (2H, m), 7.25-7.19 (3H, m), 6.99 (2H, d, *J* = 8.0 Hz), 6.49-6.45 (2H, m), 3.60 (1H, brs), 3.29 (1H, dd, *J* = 12.3, 6.1 Hz), 3.19 (1H, dd, *J* = 8.4, 12.3 Hz), 3.06-2.98 (1H, m), 1.32 (3H, d, *J* = 7.0 Hz). ^{13}C NMR (100 MHz, CDCl$_3$) δ 147.0, 144.4, 140.4 (q, *J* = 1.9 Hz), 128.9, 127.3, 126.9, 124.7, 120.9 (q, *J* = 255.0 Hz), 113.2, 51.1, 39.3, 19.8.

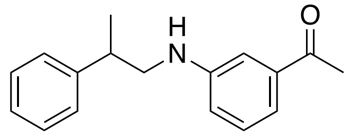
HRMS (ESI): calcd for $C_{16}H_{17}F_3NO$ [M+H]$^+$: 296.1257, found: 296.1257.



***N*-(2-phenylpropyl)-3-(trifluoromethyl)aniline (39)** light yellow oil, 86% yield.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.36-7.32 (2H, m), 7.27-7.19 (4H, m), 6.90 (1H, d, *J* = 7.6 Hz), 6.74 (1H, s), 6.67 (1H, d, *J* = 8.2 Hz), 3.75 (1H, brs), 3.35 (1H, dd, *J* = 12.1, 5.9 Hz), 3.27-3.22 (1H, m), 3.09-3.00 (1H, m), 1.35 (3H, d, *J* = 7.0 Hz). ^{13}C NMR (100 MHz, CDCl$_3$) δ 148.4, 144.2, 131.6 (q, *J* = 31.6 Hz), 129.7, 128.9, 127.3, 127.0, 124.5 (q, *J* = 272.3 Hz), 116.0, 113.8 (q, *J* =3.9 Hz), 109.0 (q, *J* = 3.9 Hz), 50.7, 39.4, 19.9.

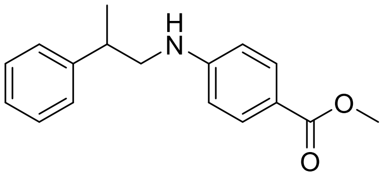
HRMS (ESI): calcd for $C_{16}H_{17}F_3N$ [M+H]$^+$: 280.1308, found: 280.1305.



1-(3-((2-phenylpropyl)amino)phenyl)ethan-1-one (**40**) colorless oil, 77% yield.

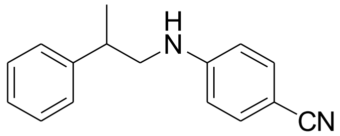
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.42-7.33 (m, 2H), 7.32-7.21 (m, 4H), 7.18 (t, *J* = 2.0 Hz, 1H), 6.79-6.76 (m, 1H), 3.78 (brs, 1H), 3.43 (dd, *J* = 12.3, 6.0 Hz, 1H), 3.30 (dd, *J* = 12.3, 8.4 Hz, 1H), 3.12-3.06 (m, 1H), 2.59 (s, 3H), 1.38 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 198.8, 148.3, 144.2, 138.1, 129.3, 128.8, 127.3, 126.8, 117.8, 117.7, 111.5, 50.7, 39.3, 26.8, 19.8.

HRMS (ESI): calcd for $C_{17}H_{19}NO_2$ [M+H]$^+$: 254.1539, found: 254.1537.



methyl 4-((2-phenylpropyl)amino)benzoate (**41**)[11] light yellow oil, 86% yield.

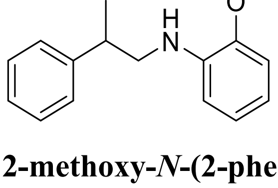
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.85-7.82 (2H, m), 7.34-7.30 (2H, m), 7.25-7.19 (3H, m), 6.50-6.48 (2H, m), 4.08 (1H, brs), 3.82 (3H, s), 3.40-3.33 (1H, m), 3.29-3.23 (1H, m), 3.08-2.99 (1H, m), 1.33 (3H, d, J = 7.0 Hz). ^{13}C NMR (100 MHz, CDCl$_3$) δ 167.4, 151.9, 144.1, 131.6, 128.8, 127.3, 126.9, 118.3, 111.6, 51.6, 50.2, 39.3, 19.7.



4-((2-phenylpropyl)amino)benzonitrile (**42**) light yellow oil, 43% yield.

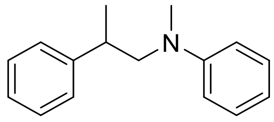
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.40-7.32 (4H, m), 7.28-7.25 (1H, m), 7.22-7.19 (2H, m), 6.52-6.48 (2H, m), 4.13 (1H, brs), 3.37 (1H, dd, J = 12.8, 6.5 Hz), 3.30-3.23 (1H, m), 3.07-3.01 (1H, m), 1.35 (3H, d, J = 7.0 Hz). ^{13}C NMR (100 MHz, CDCl$_3$) δ 151.2, 143.8, 133.8, 129.0, 127.3, 127.1, 120.6, 112.4, 98.7, 50.1, 39.3, 19.8.

HRMS (ESI): calcd for $C_{17}H_{22}N$ [M+H]$^+$: 237.1386, found: 237.1384.



2-methoxy-*N*-(2-phenylpropyl)aniline (**43**)[12] light yellow oil, 30% yield.

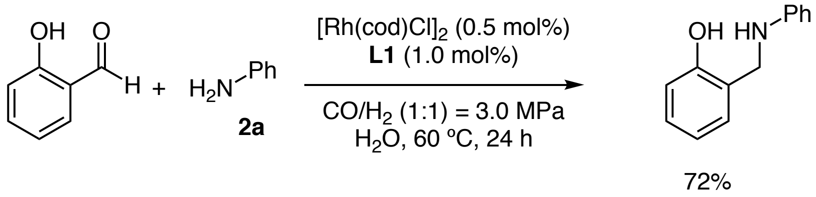
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.33-7.29 (2H, m), 7.24-7.19 (3H, m), 6.86 (1H, td, J = 7.6, 1.5 Hz), 6.74-6.71 (1H, m), 6.66-6.62 (2H, m), 4.24 (1H, brs), 3.73 (3H, s), 3.33-3.23 (2H, m), 3.11-3.03 (1H, m), 1.34 (3H, d, J = 6.9 Hz). ^{13}C NMR (100 MHz, CDCl$_3$) δ 146.9, 144.9, 138.2, 128.6, 127.3, 126.6, 121.4, 116.4, 110.0, 109.6, 55.5, 51.0, 39.2, 19.7.



***N*-methyl-*N*-(2-phenylpropyl)aniline** (**44**) [13] light yellow oil, 40% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.28 (2H, m), 7.26-7.19 (5H, m), 6.70-6.65 (3H, m), 3.49 (1H, dd, J = 14.6, 7.6 Hz), 3.38 (1H, dd, J = 14.7, 7.1 Hz), 3.24-3.15 (1H, m), 2.74 (3H, s), 1.29 (3H, d, J = 7.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.1, 145.3, 129.3, 128.6, 127.4, 126.5, 115.8, 111.8, 61.1, 39.7, 38.34, 18.9.

8. Reductive amination of Salicylic aldehyde with aniline.



The reductive amination was conducted in a batch autoclave reactor (Shaanxi Wattcas). Chloro(1,5-cyclooctadiene)rhodium(I) dimer ($[Rh(COD)Cl]_2$, 0.99 mg, 2×10^{-3} mmol, 0.50 mol%), ligand (0.004 mmol,1.0 mmol %, Rh/L = 1:2) was dissolved in 2 mL of water and stirred for 1 hour. Salicyclic aldehyde (58.4 mg, 0.48 mmol) and aniline (37.3 mg, 0.4 mmol) were added, and the reactor was purged with nitrogen three times and then charged with 3.0 MPa syngas (CO/H_2=1:1). The mixture was stirred for 24 h at 60 °C. The reaction mixture was extracted with ethyl acetate. The organic layers were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure. The residue was purified by column chromatography (eluent: 25% ethyl acetate in petroleum ether) to afford 2-((phenylamino)methyl)phenol as a white solid (60.4 mg, 76%).

2-((phenylamino)methyl)phenol. mp. 117.0-118.5 ºC. ^{1}H NMR (400 MHz, MeOD) δ 7.23 (dd, J = 7.5, 1.7 Hz, 1H), 77.12-7.05 (m, 3H), 6.82-6.73 (m, 2H), 6.73-6.60 (m, 3H), 4.30 (s, 2H).

9. References

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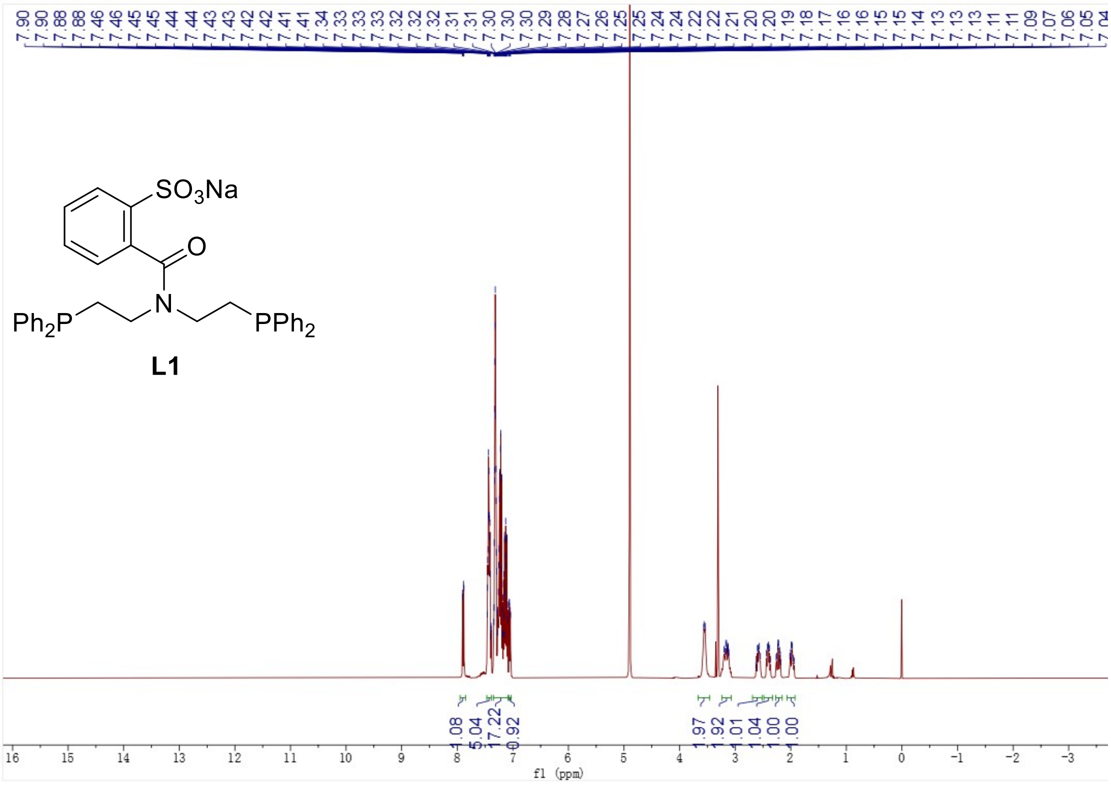
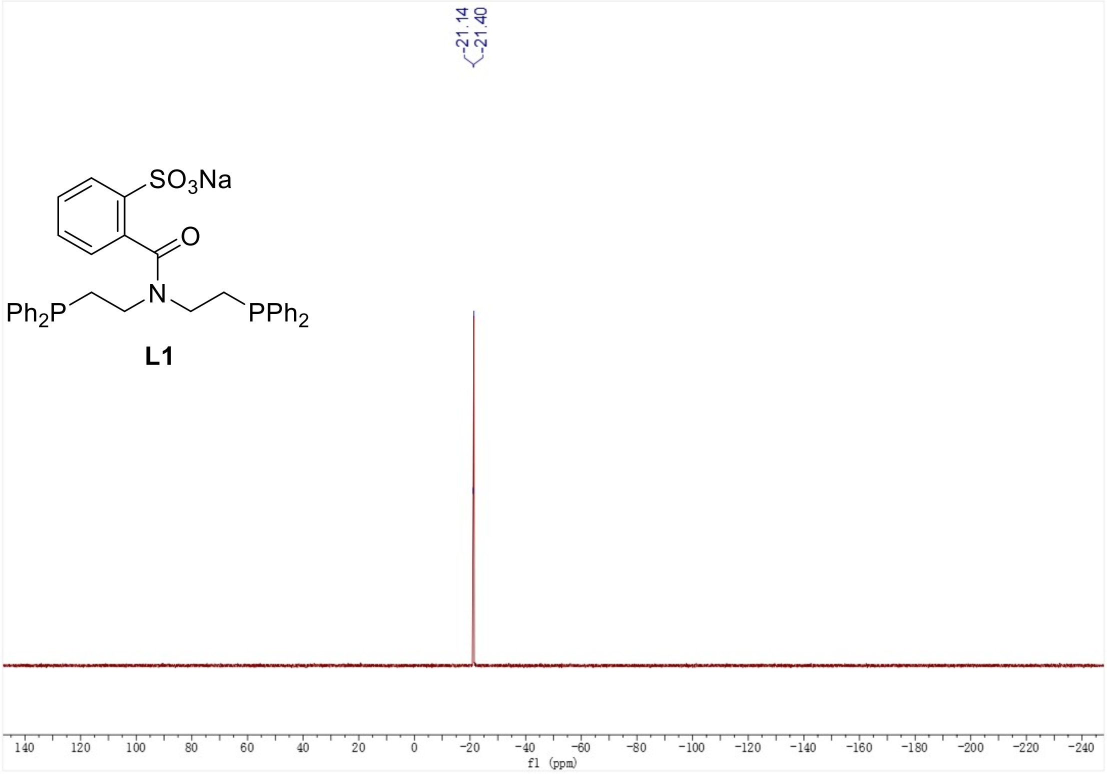
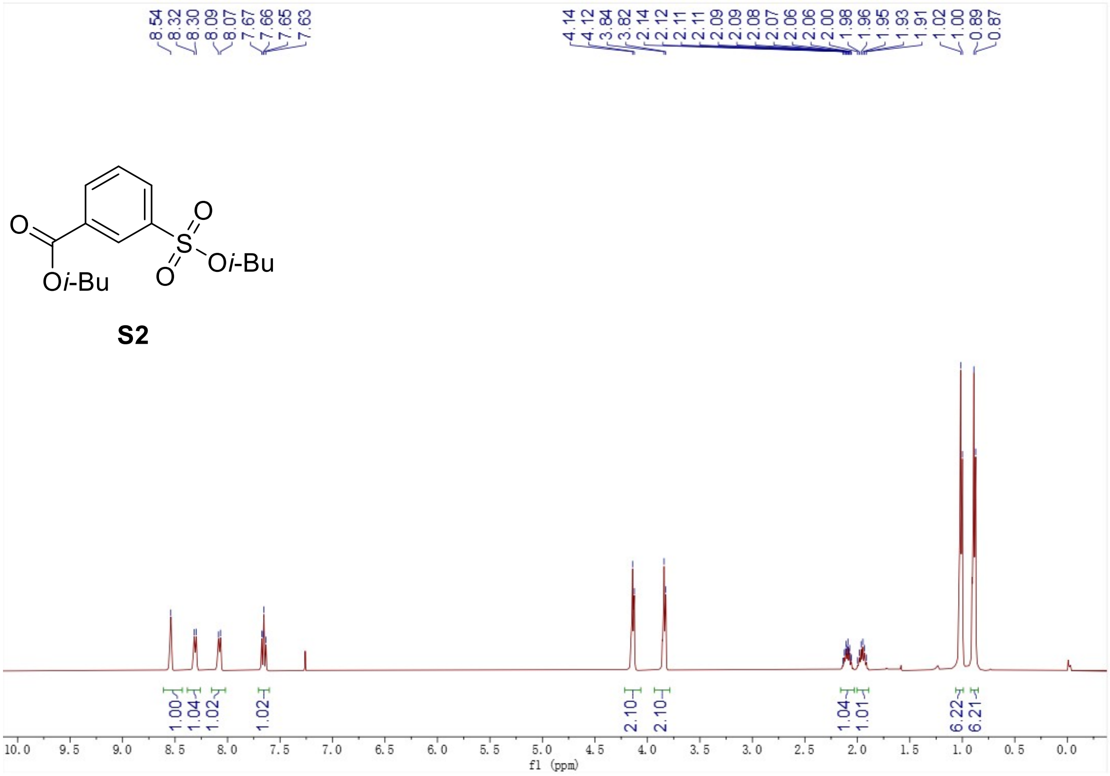
10. NMR spectra.



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2.09
2.08
2.07
2.06
2.00
1.98
1.96
1.95
1.93
1.91
1.02
1.00
0.89
0.87
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O
S
O
O*i*-Bu
O*i*-Bu
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1.04
1.02
1.02
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1.04
1.01
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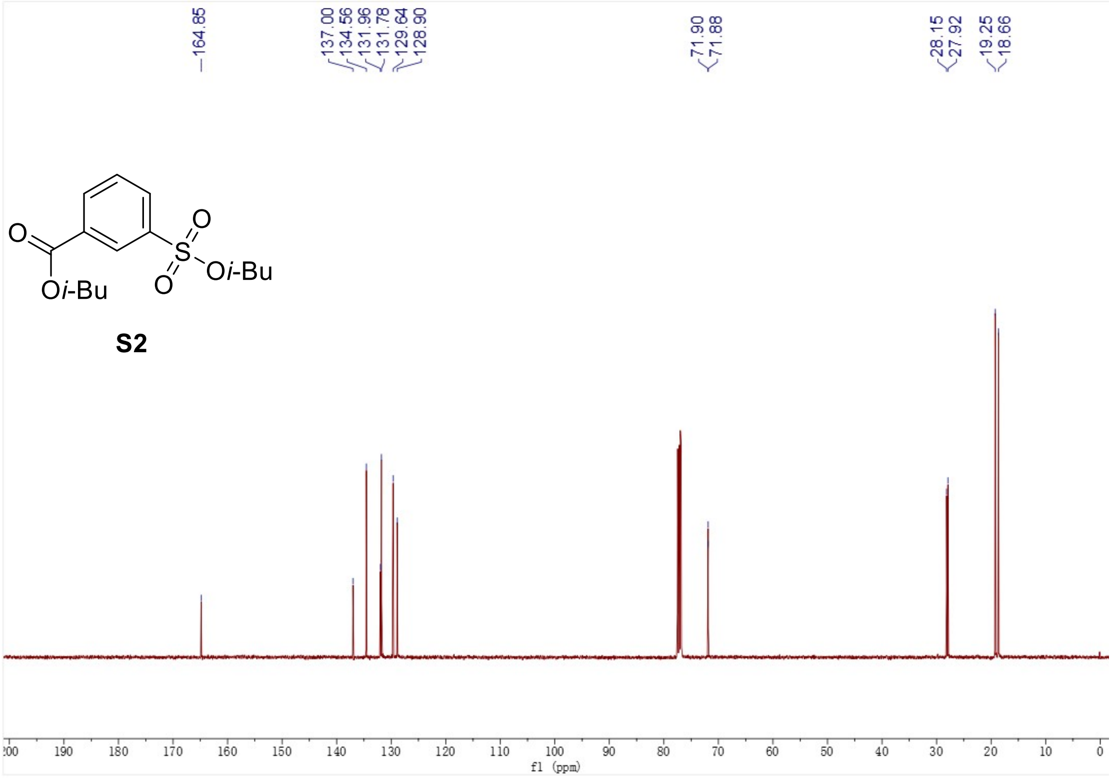
S2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18.66
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O
S
O
O*i*-Bu
O*i*-Bu
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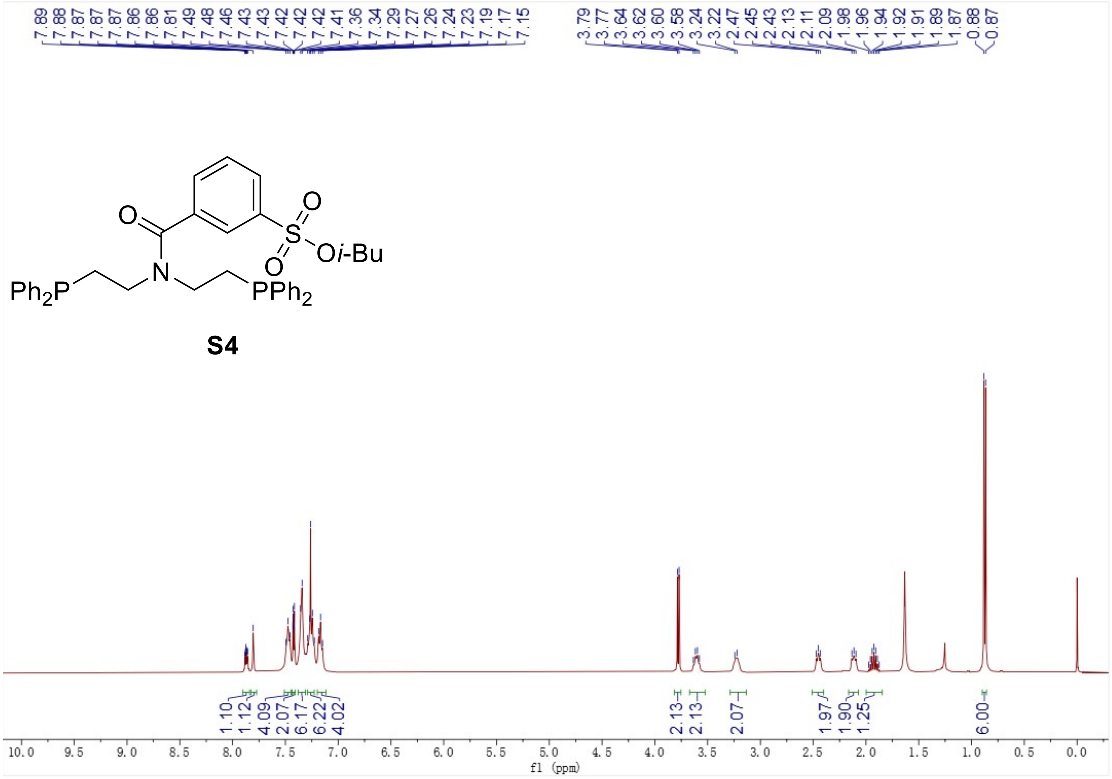
f1 (ppm)

S2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3.79 3.77 3.64 3.62 3.60 3.58 3.24 3.22 2.47 2.45 2.43 2.13 2.11 2.09 1.98 1.96 1.94 1.92 1.91 1.89 1.87 0.88 0.87
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N
Ph2P
PPh2
S
O
O
Oi-Bu
S4
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6.00
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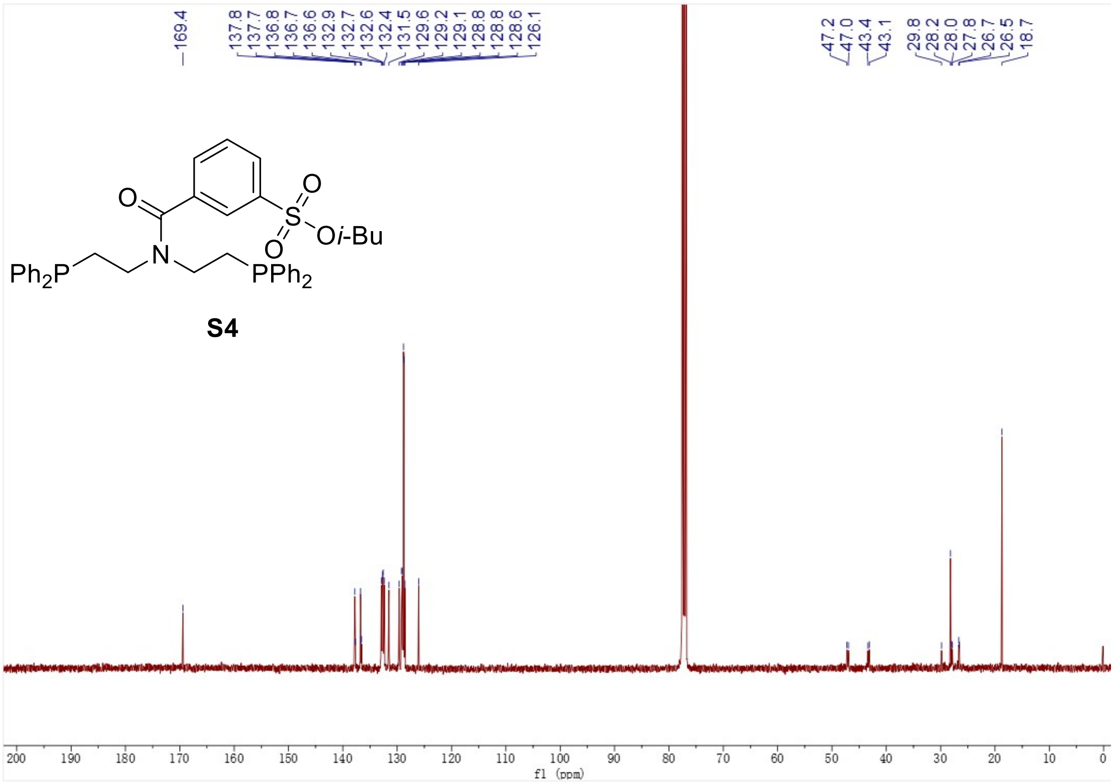
f1 (ppm)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47.2 47.0 43.4 43.1
29.8 28.2 28.0 27.8 26.7 26.5 18.7
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S
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O
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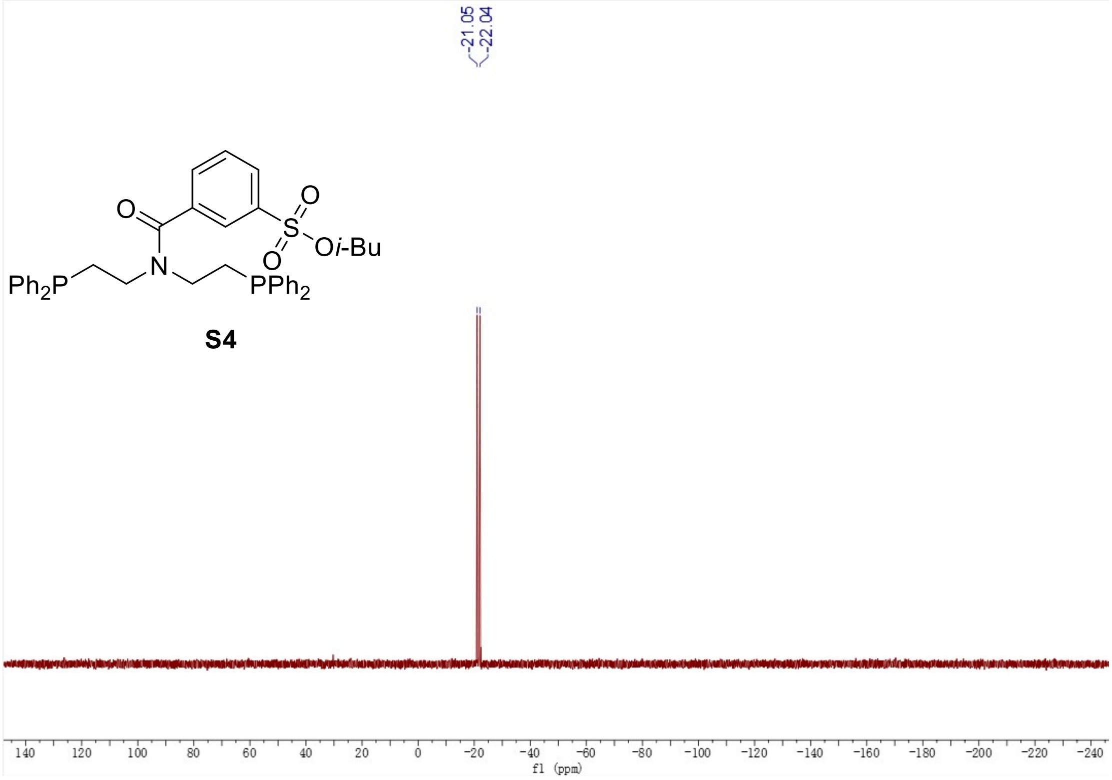
f1 (ppm)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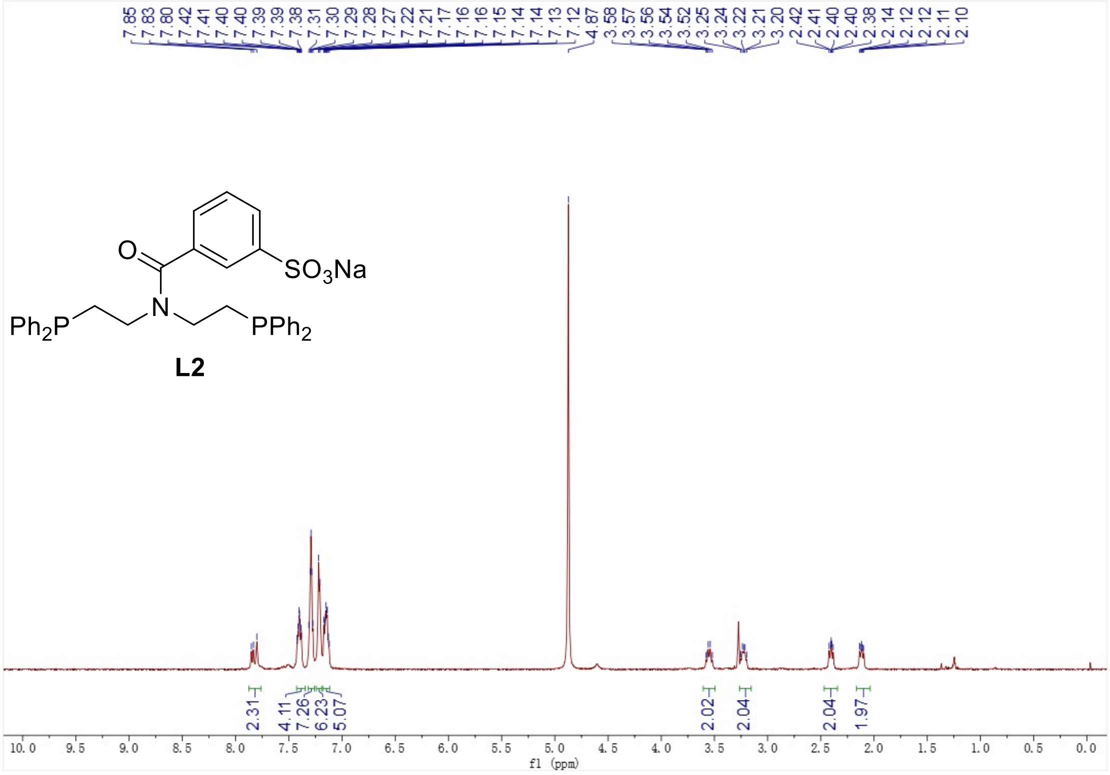
S4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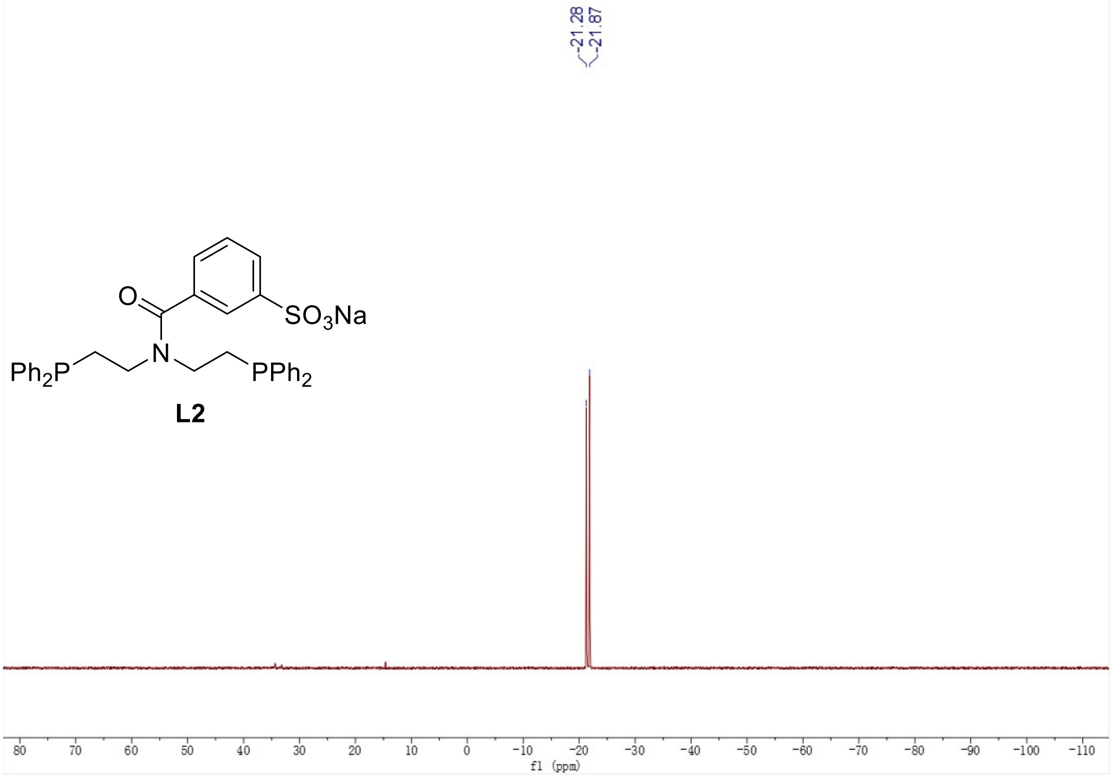
L2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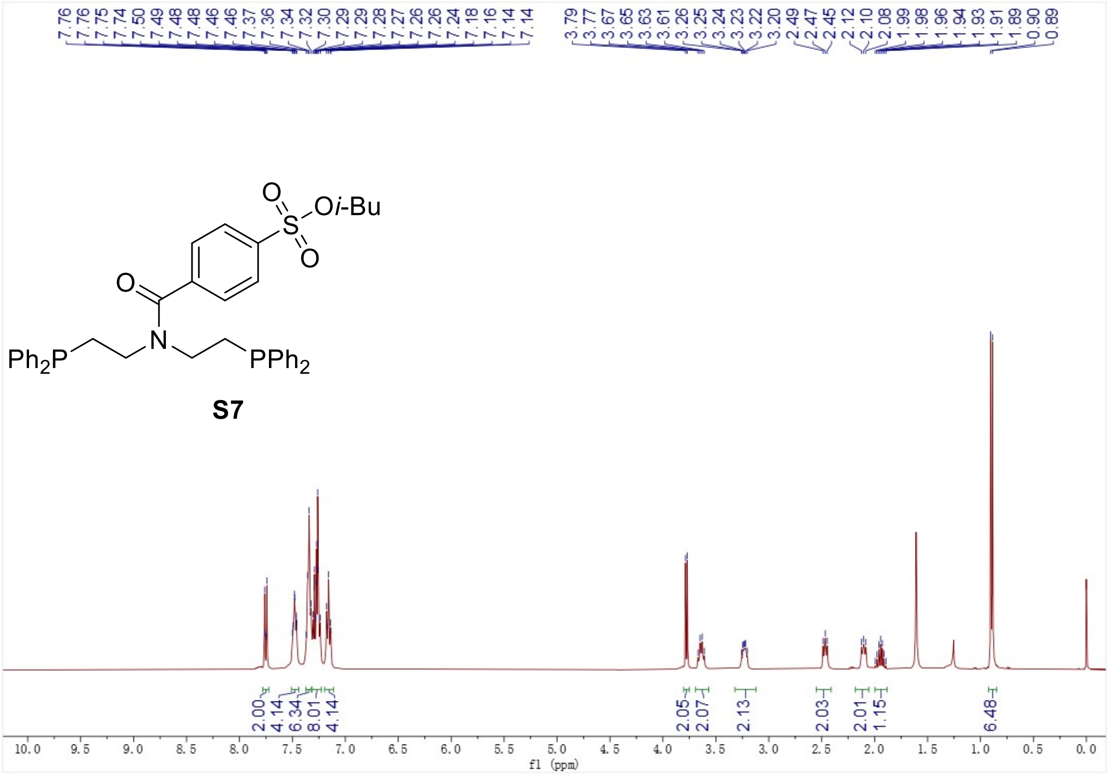
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3.79 3.77 3.67 3.65 3.63 3.61 3.26 3.25 3.24 3.23 3.22 3.20 2.49 2.47 2.45 2.12 2.10 2.08 1.99 1.98 1.96 1.94 1.93 1.91 1.89 0.90 0.89
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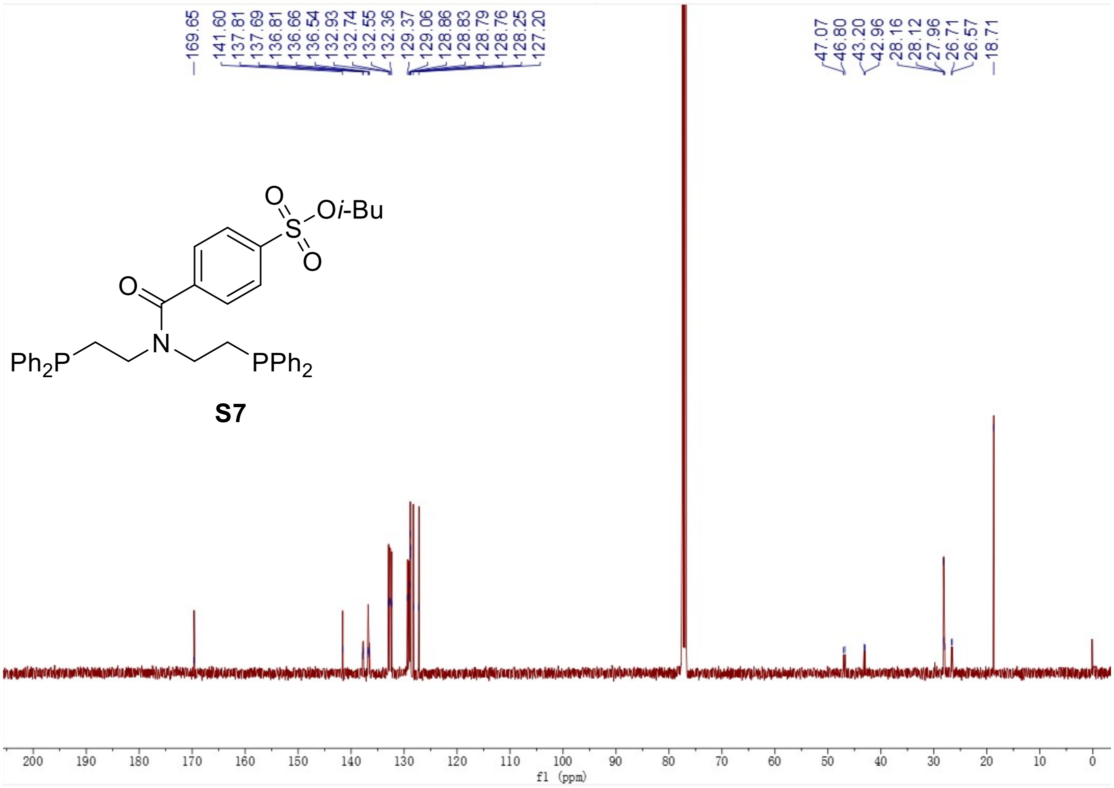
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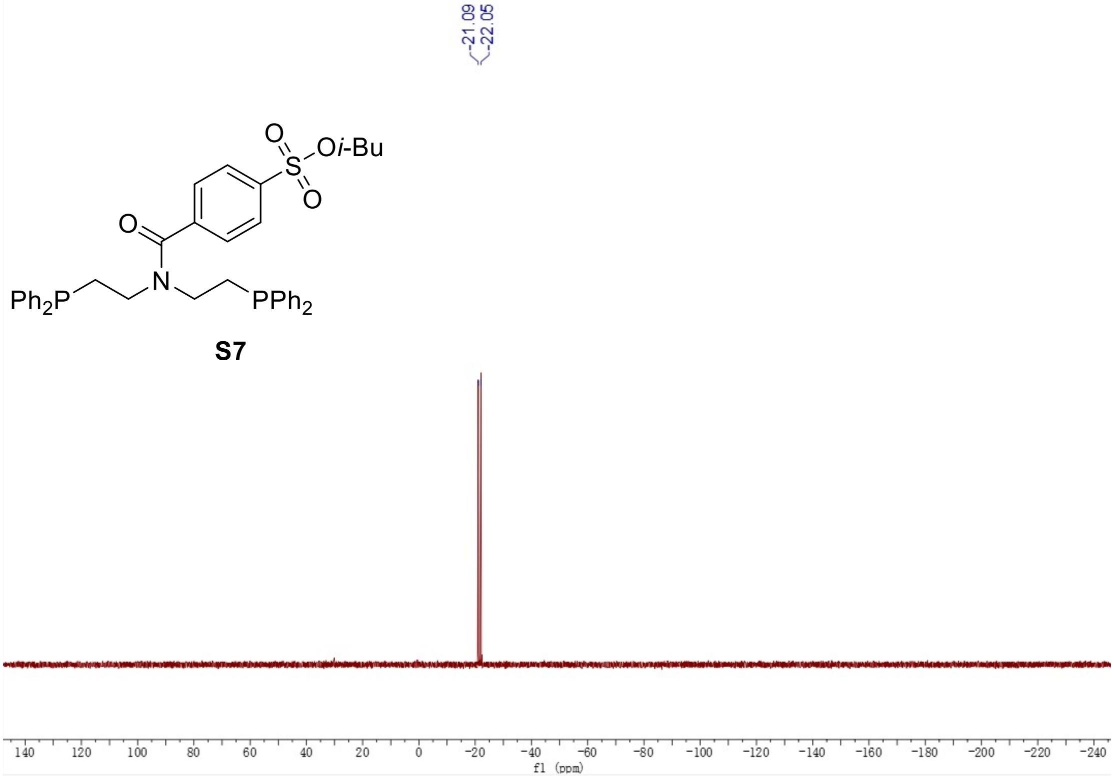
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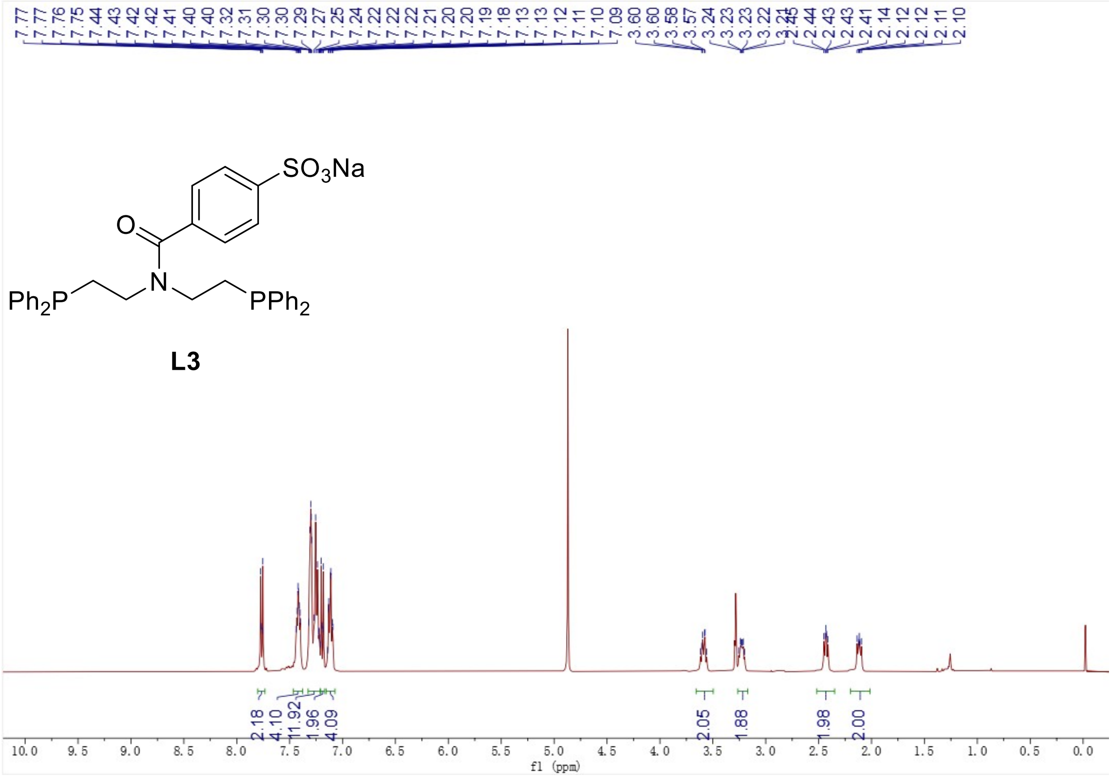
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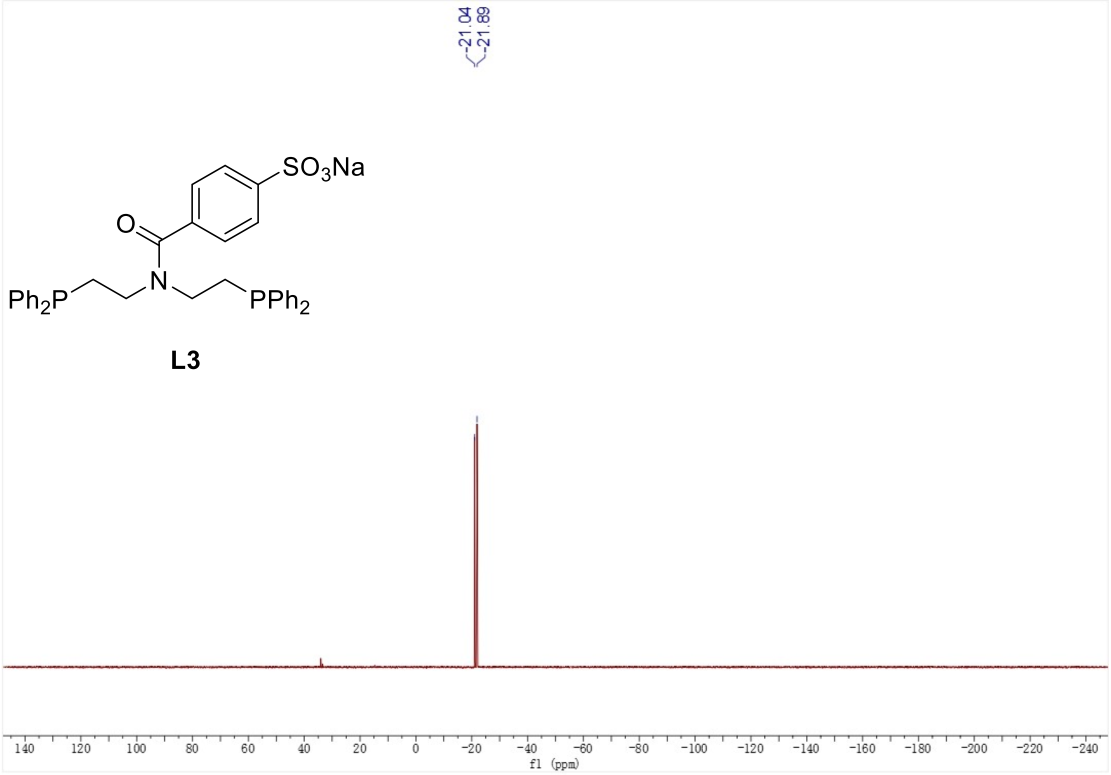
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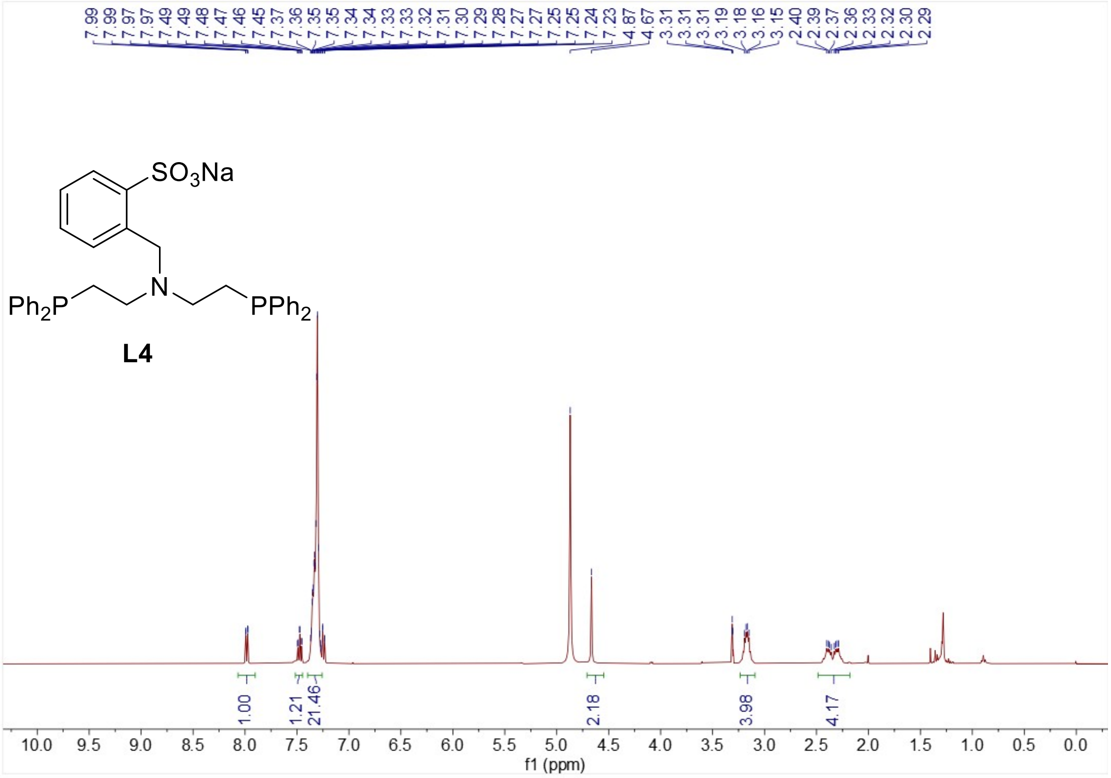
f1 (ppm)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7.34
7.33
7.33
7.32
7.31
7.30
7.29
7.28
7.27
7.27
7.25
7.25
7.24
7.23
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3.31
3.31
3.31
3.19
3.18
3.16
3.15
2.40
2.39
2.37
2.36
2.33
2.32
2.30
2.29
SO3Na
Ph2P
N
PPh2
L4
1.00
1.21
21.46
2.18
3.98
4.17
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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2.5
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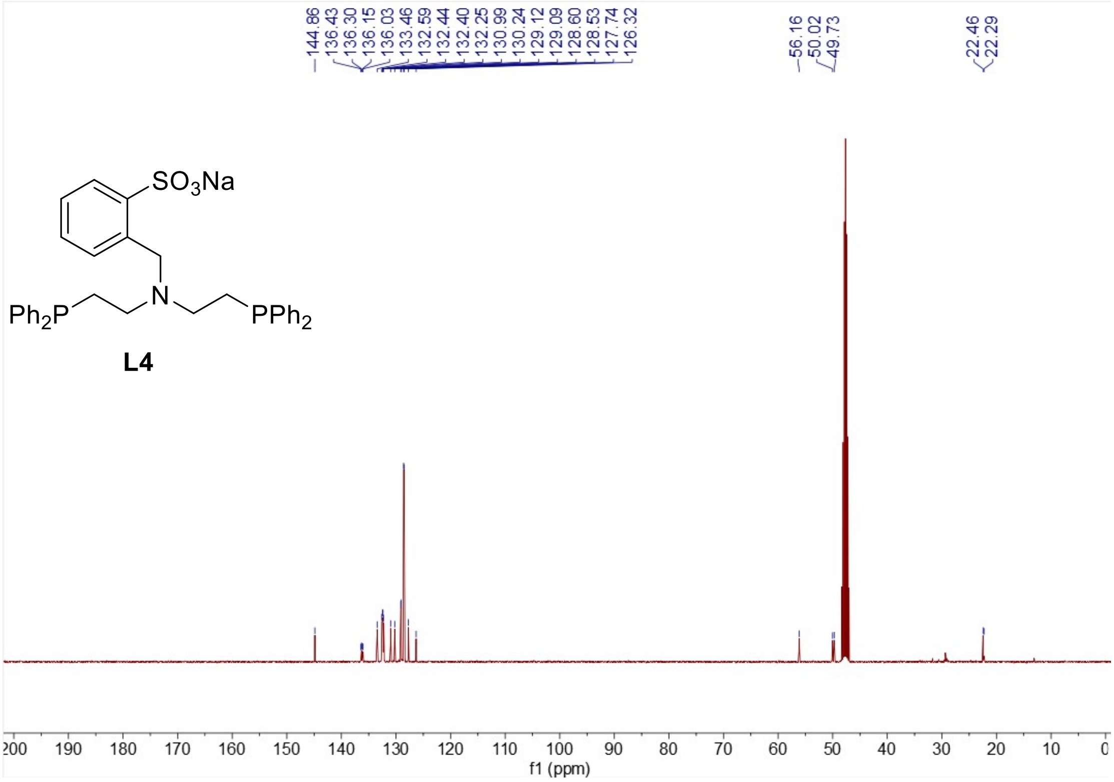
f1 (ppm)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132.25
130.99
130.24
129.12
129.09
128.60
128.53
127.74
126.32
56.16
50.02
49.73
22.46
22.29
SO3Na
Ph2P
N
PPh2
L4
200
190
180
170
160
150
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130
120
110
100
90
80
70
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50
40
30
20
10
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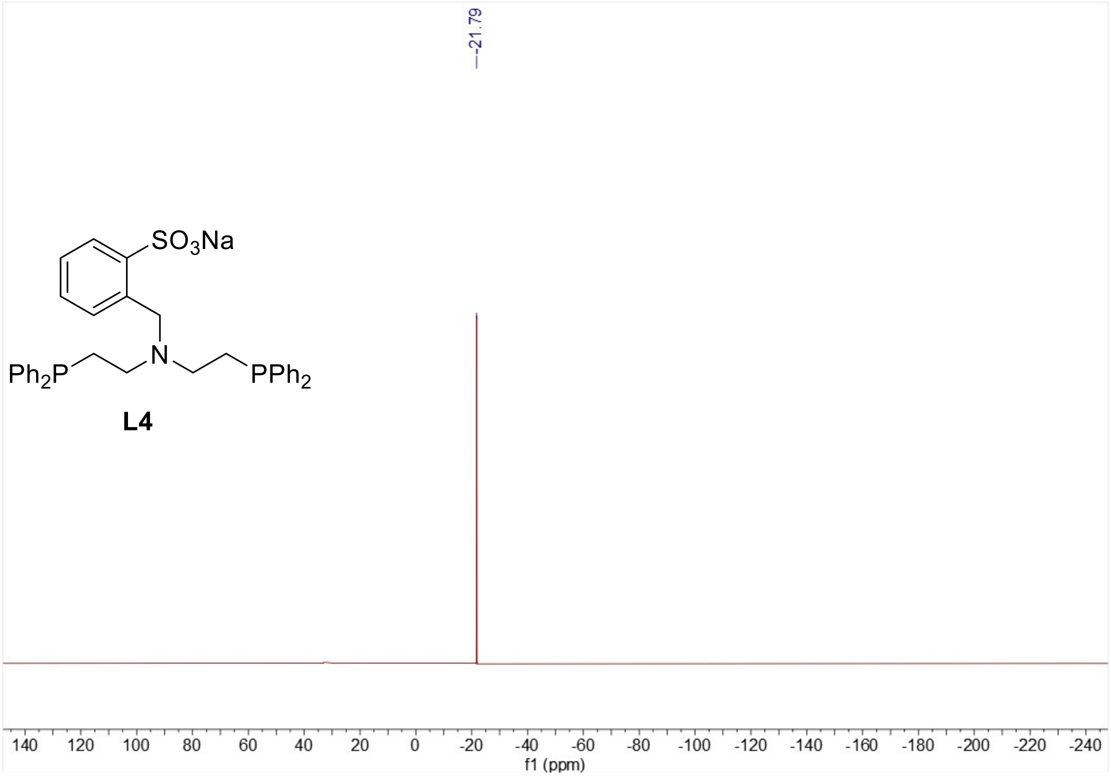
f1 (ppm)



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SO3Na
Ph2P
N
PPh2
L4
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120
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80
60
40
20
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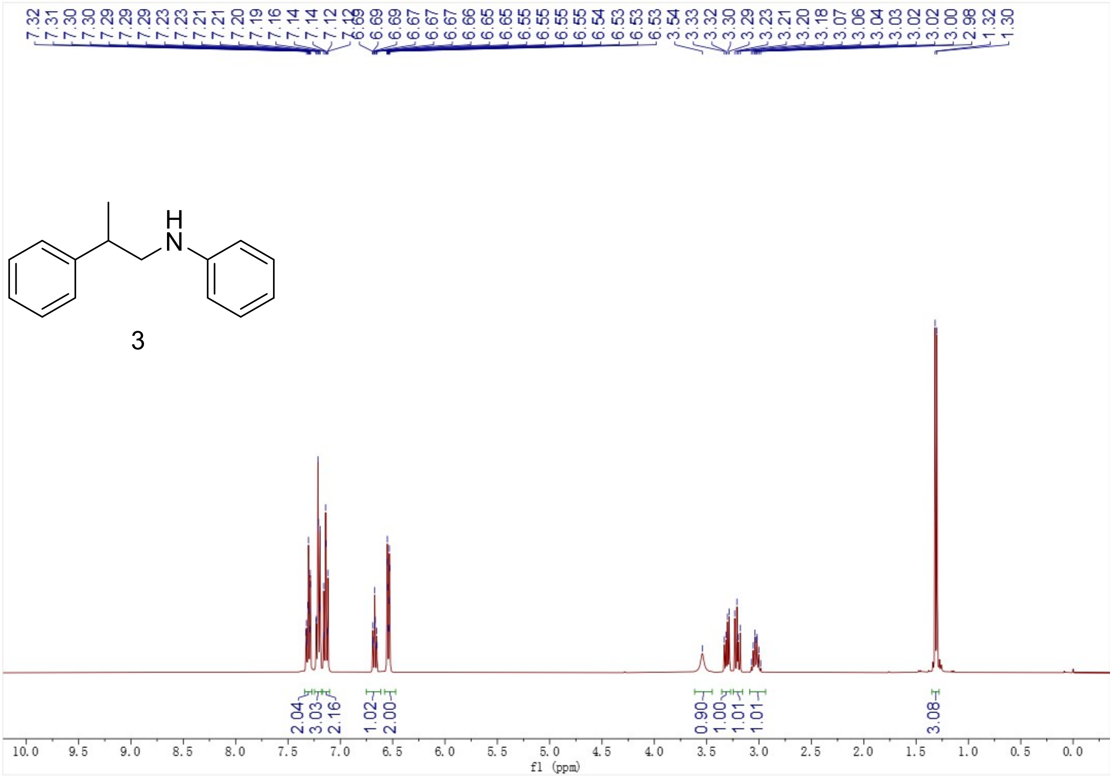
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
f1 (ppm)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7.14
7.14
7.12
7.12
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6.69
6.67
6.67
6.66
6.65
6.65
6.55
6.55
6.55
6.54
6.53
6.53
6.53
3.54
3.33
3.32
3.30
3.29
3.23
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3.20
3.18
3.07
3.06
3.04
3.03
3.02
3.02
3.00
2.98
1.32
1.30
H
N
3
2.04
3.03
2.16
1.02
2.00
0.90
1.00
1.01
1.01
3.08
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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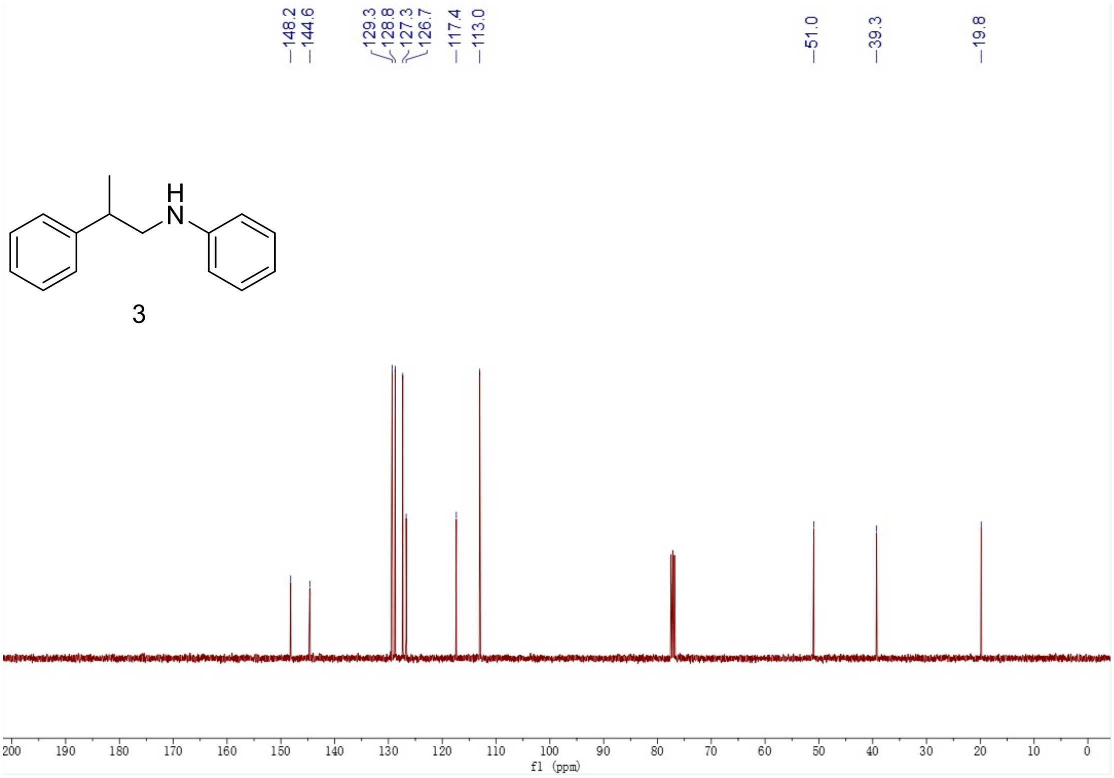
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19.8
H
N
3
200
190
180
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150
140
130
120
110
100
90
80
70
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50
40
30
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10
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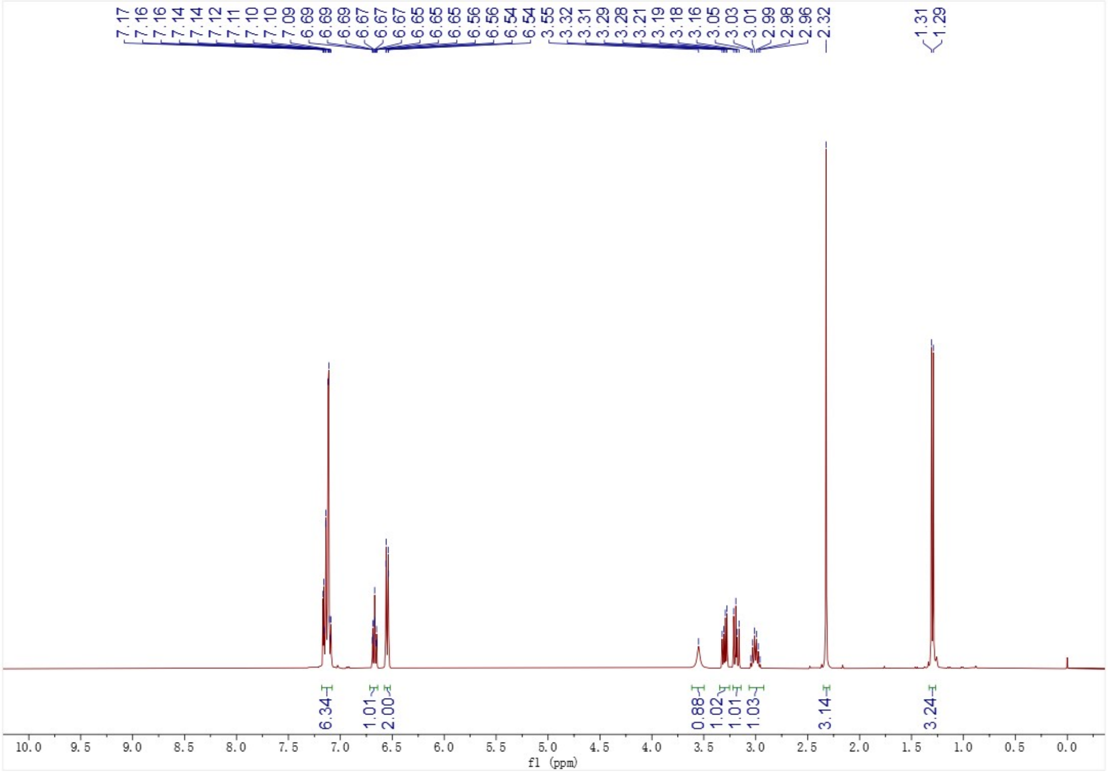
f1 (ppm)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7.09
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6.67
6.65
6.65
6.56
6.56
6.54
3.55
3.32
3.31
3.29
3.28
3.21
3.19
3.18
3.16
3.05
3.03
3.01
2.99
2.98
2.96
2.32
1.31
1.29
6.34
1.01
2.00
0.88
1.02
1.01
1.03
3.14
3.24
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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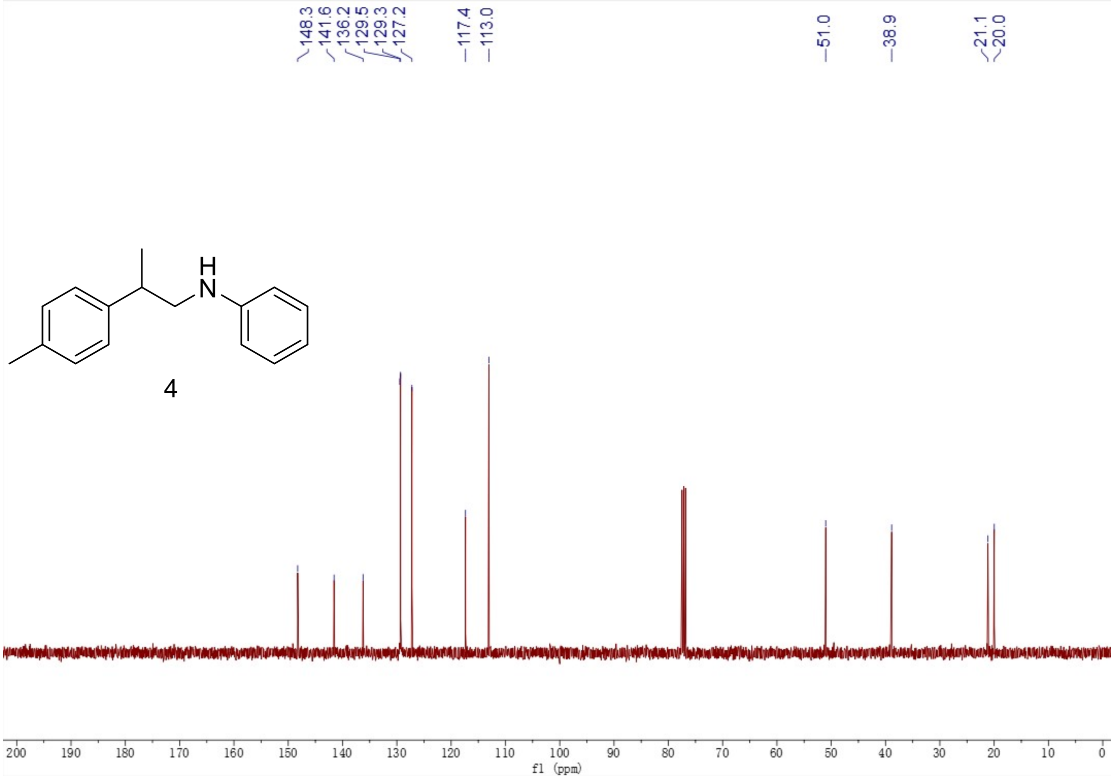
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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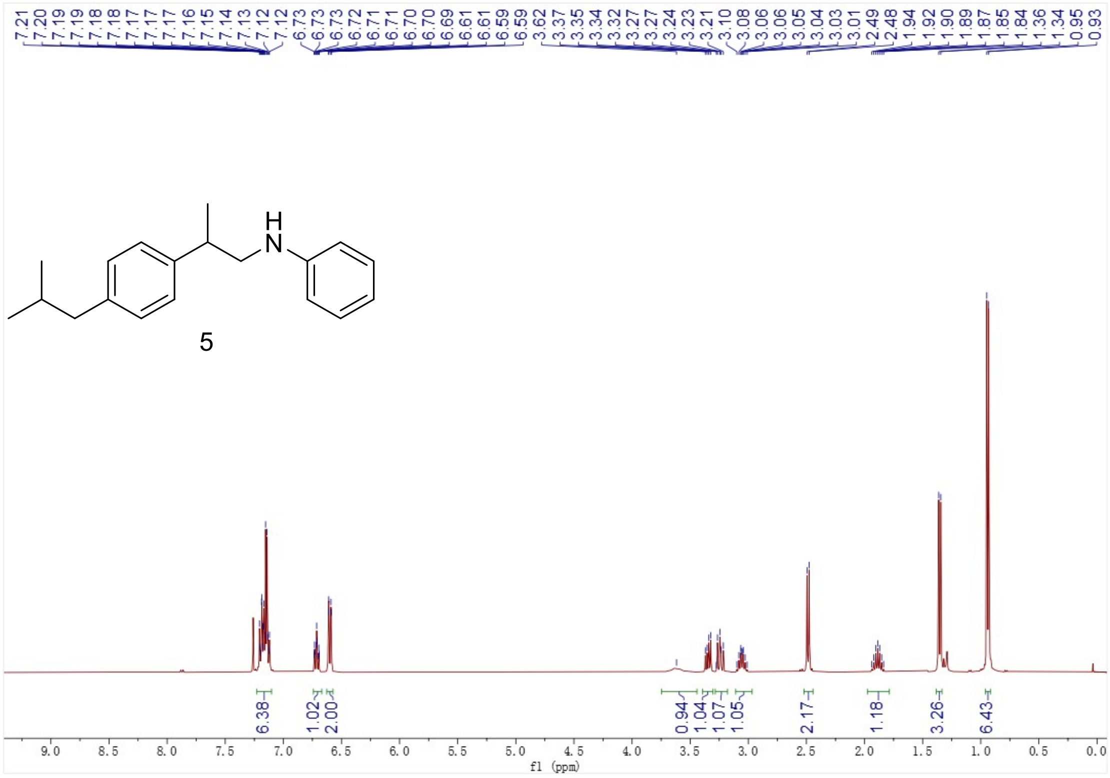
141.6
136.2
129.5
129.3
127.2
117.4
113.0
51.0
38.9
21.1
20.0
H
N
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

4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7.20
7.19
7.19
7.18
7.17
7.17
7.17
7.16
7.15
7.14
7.13
7.12
7.12
6.73
6.73
6.72
6.71
6.71
6.70
6.69
6.61
6.61
6.59
6.59
3.62
3.37
3.35
3.34
3.32
3.27
3.24
3.23
3.21
3.10
3.08
3.06
3.05
3.04
3.03
3.01
2.49
2.48
1.94
1.92
1.90
1.89
1.87
1.85
1.84
1.36
1.34
0.95
0.93
H
N
6.38
1.02
2.00
0.94
1.04
1.07
1.05
2.17
1.18
3.26
6.43
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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3.5
3.0
2.5
2.0
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1.0
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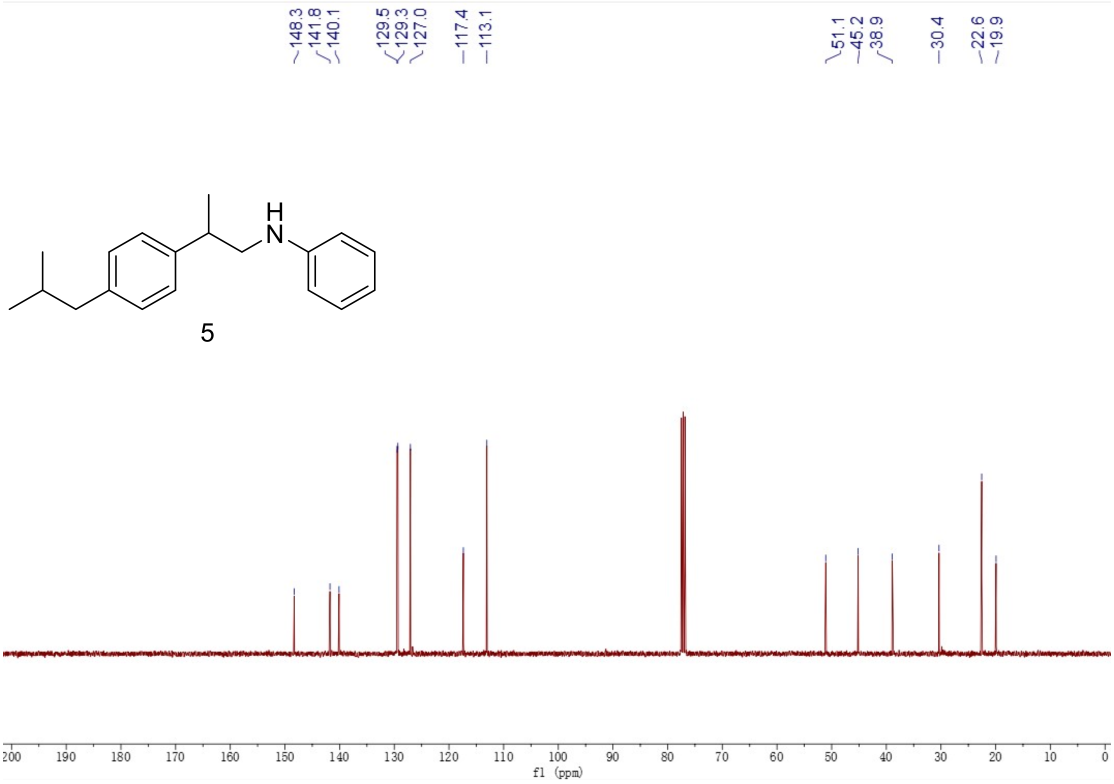
0.0
f1 (ppm)


5
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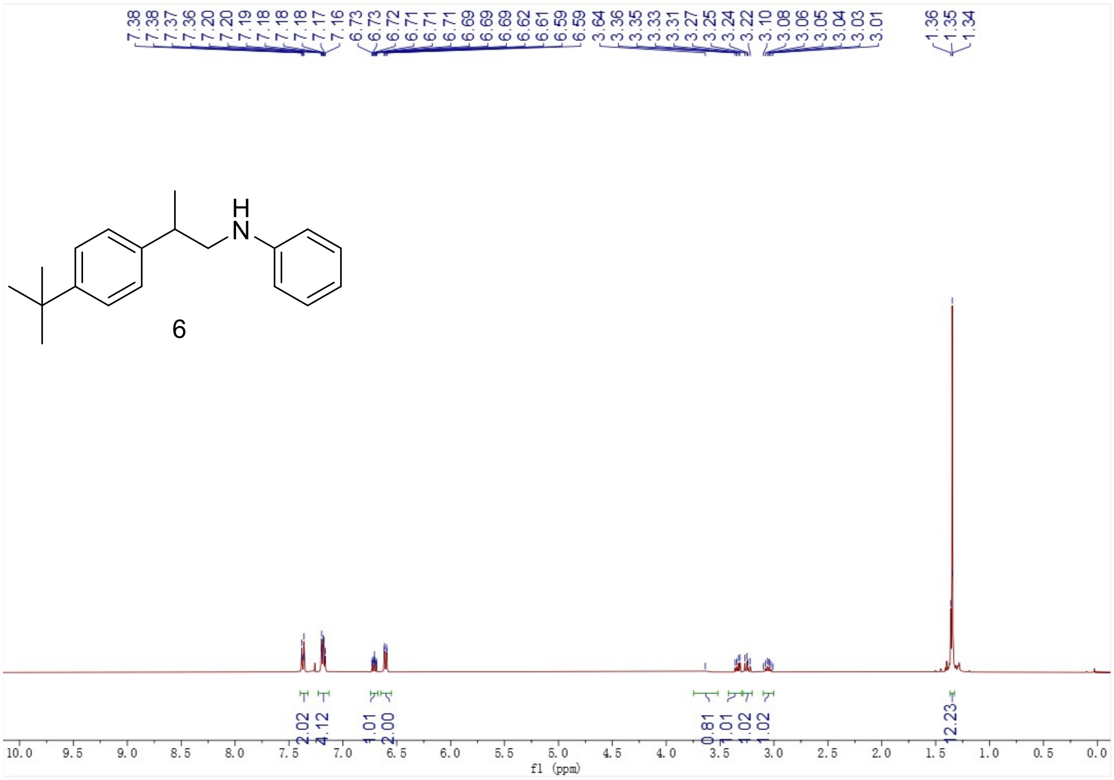
140.1
129.5
129.3
127.0
117.4
113.1
51.1
45.2
38.9
30.4
22.6
19.9
H
N
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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6.71
6.71
6.69
6.69
6.62
6.61
6.59
6.59
3.64
3.36
3.35
3.33
3.31
3.27
3.25
3.24
3.22
3.10
3.08
3.06
3.05
3.04
3.03
3.01
1.36
1.35
1.34
H
N
6
2.02
4.12
1.01
2.00
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1.01
1.02
1.02
12.23
10.0
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9.0
8.5
8.0
7.5
7.0
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6.0
5.5
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2.5
2.0
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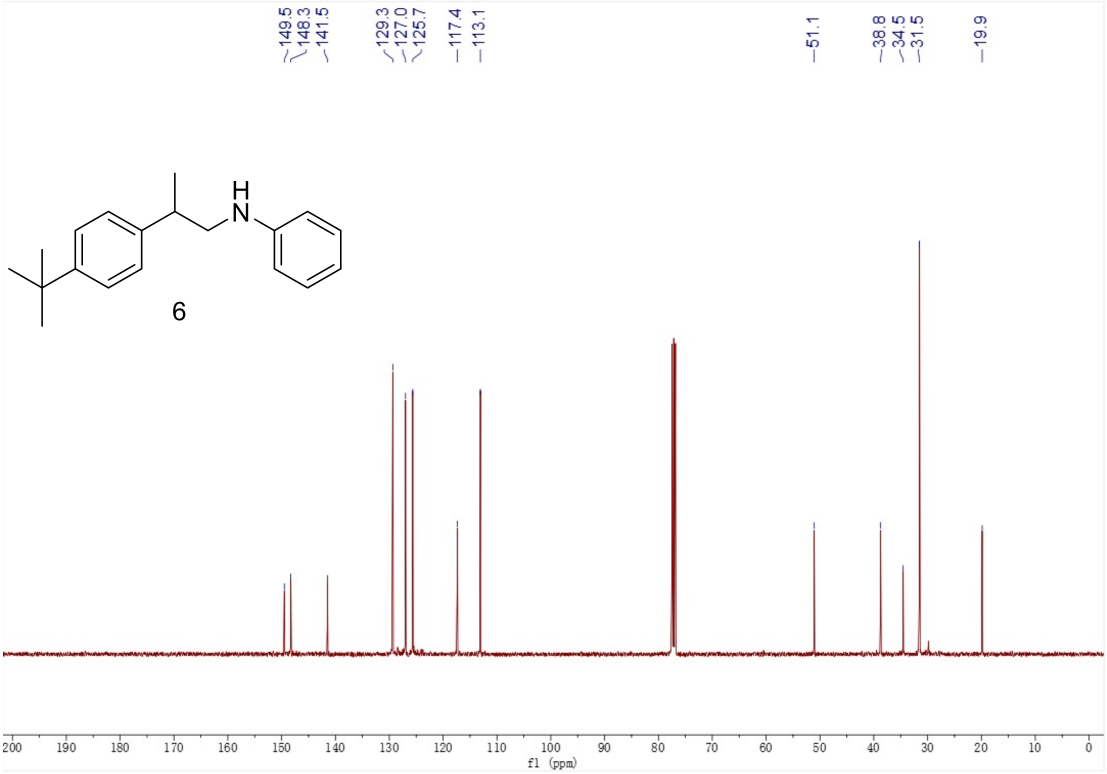
1.0
0.5
0.0
f1 (ppm)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113.1
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38.8
34.5
31.5
19.9
H
N
6
200
190
180
170
160
150
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130
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110
100
90
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70
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50
40
30
20
10
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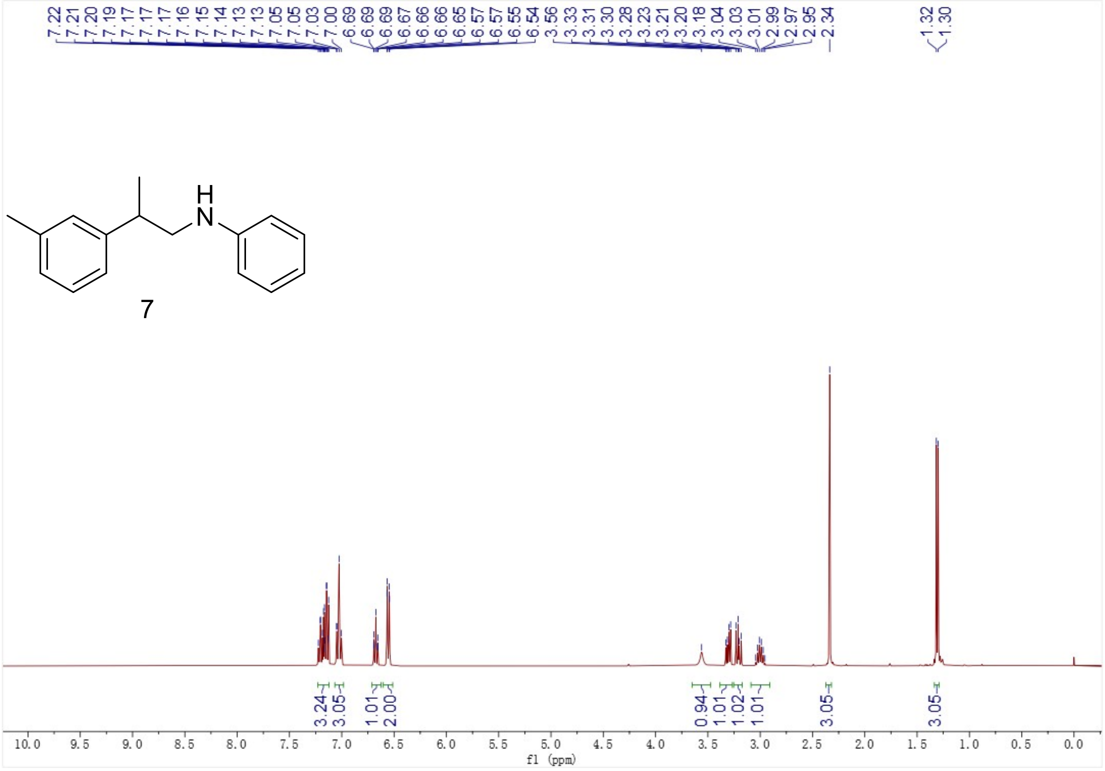
f1 (ppm)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7.13
7.13
7.05
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6.65
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6.57
6.55
6.54
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3.33
3.31
3.30
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3.20
3.18
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3.03
3.01
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1.30
H
N
7
3.24
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1.01
2.00
0.94
1.01
1.02
1.01
3.05
3.05
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9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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2.0
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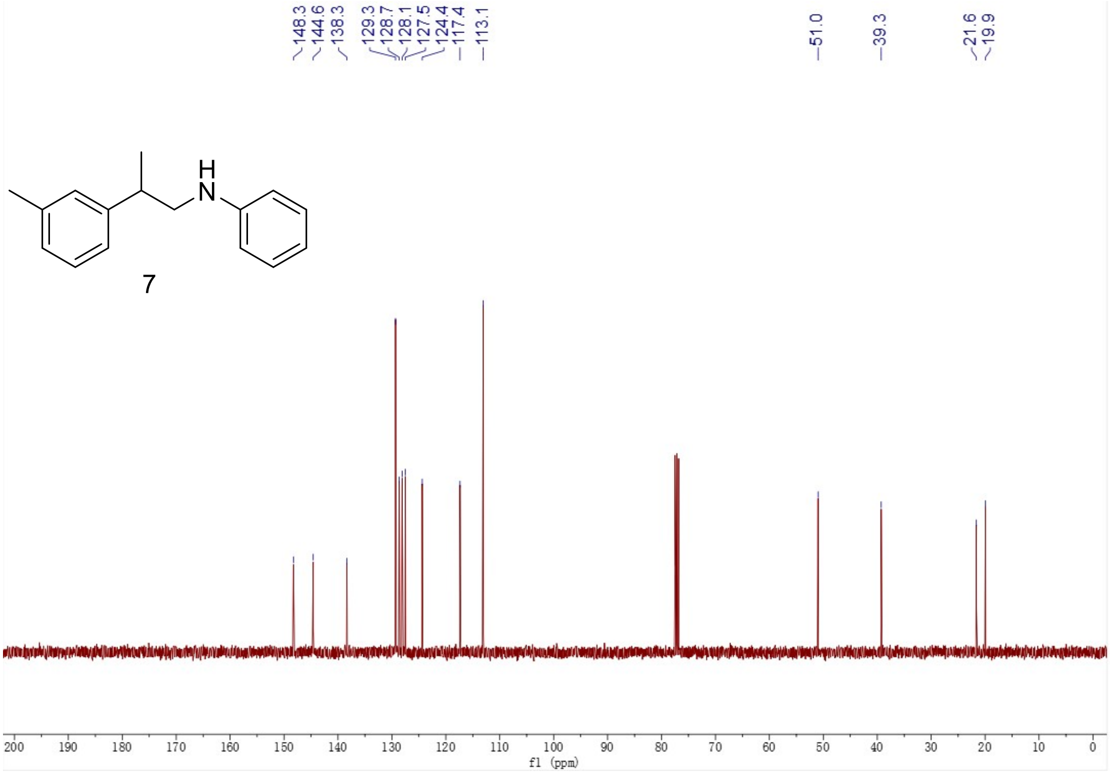
0.0
f1 (ppm)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127.5
124.4
117.4
113.1
51.0
39.3
21.6
19.9
H
N
7
200
190
180
170
160
150
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130
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110
100
90
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70
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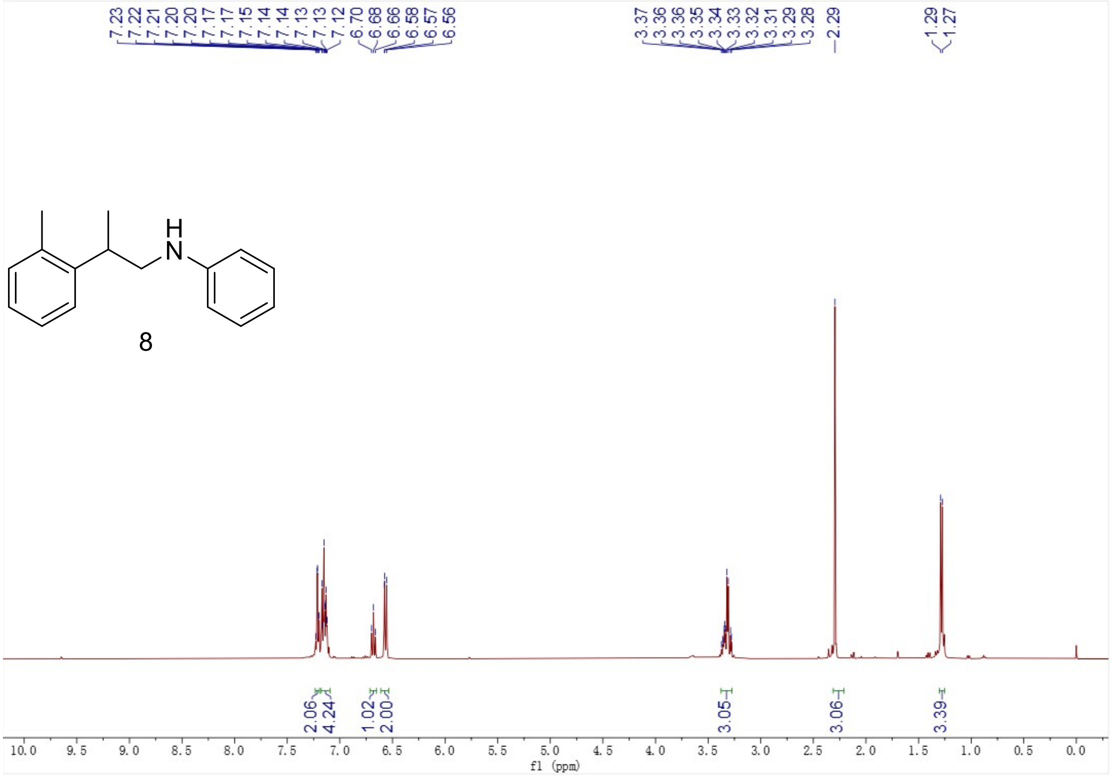
0
f1 (ppm)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6.57
6.56
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3.36
3.36
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3.34
3.33
3.32
3.31
3.29
3.28
2.29
1.29
1.27
H
N
8
2.06
4.24
1.02
2.00
3.05
3.06
3.39
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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4.5
4.0
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3.0
2.5
2.0
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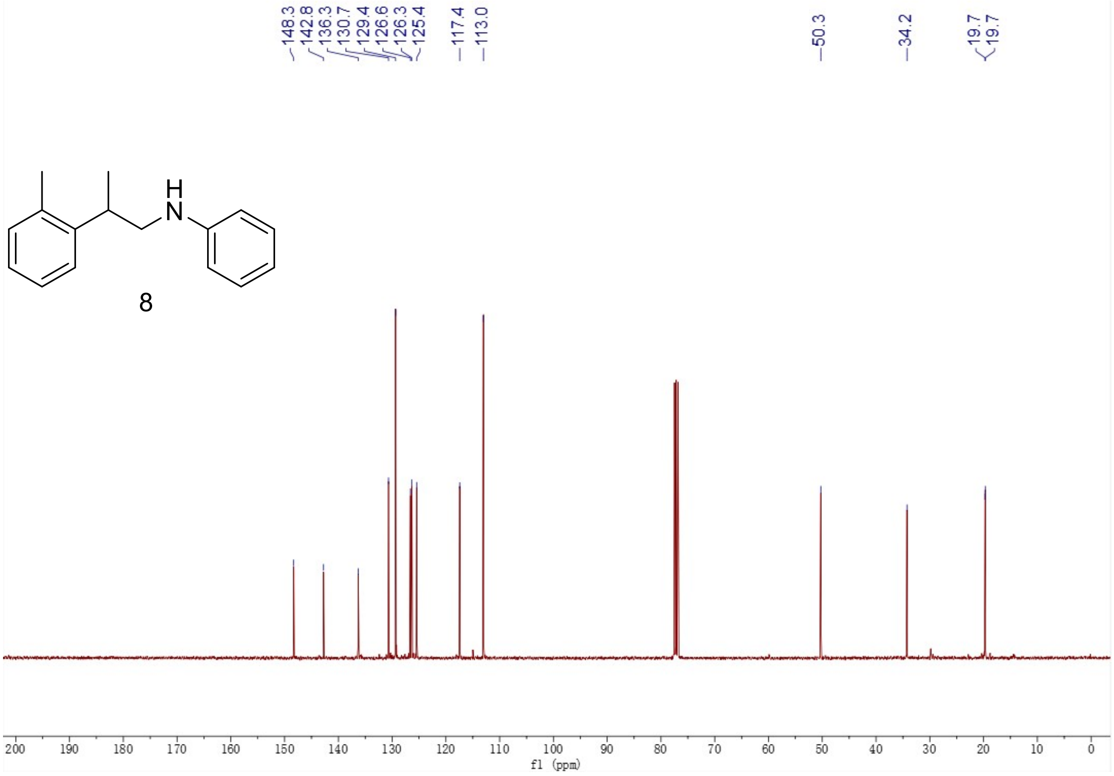
0.5
0.0
f1 (ppm)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126.3
125.4
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113.0
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19.7
19.7
H
N
8
200
190
180
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150
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130
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110
100
90
80
70
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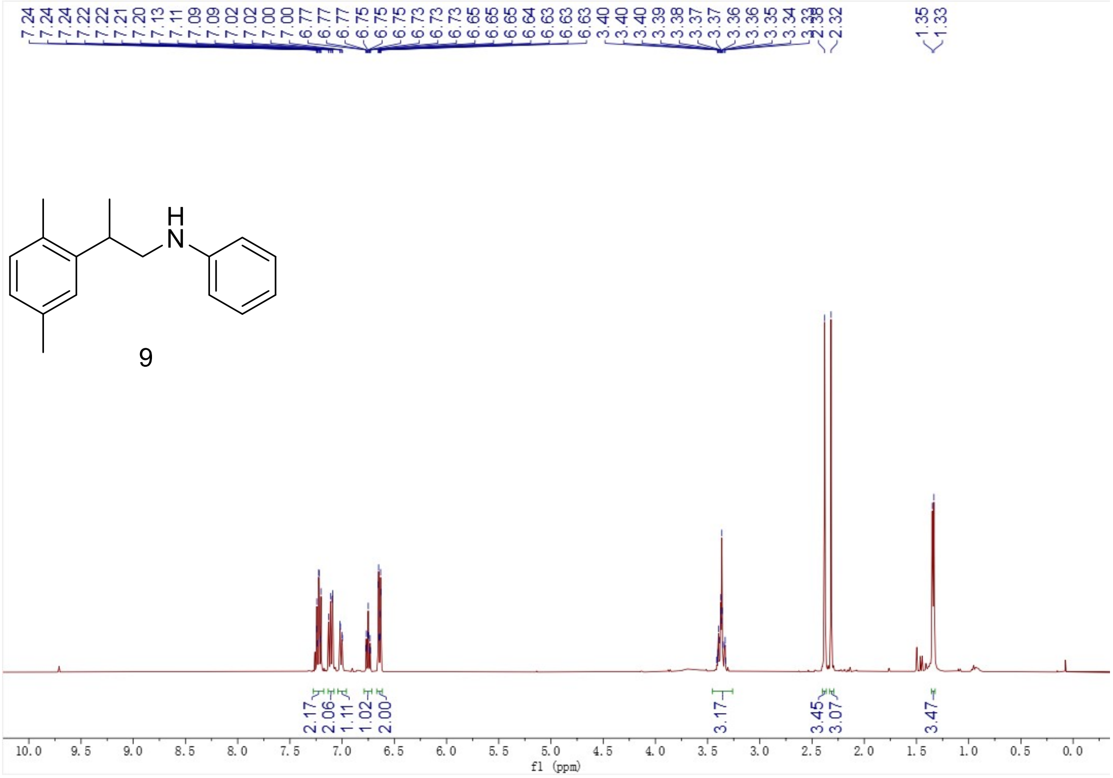
50
40
30
20
10
0
f1 (ppm)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7.02
7.02
7.00
7.00
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6.77
6.77
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6.75
6.75
6.73
6.73
6.73
6.65
6.65
6.65
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6.63
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3.33
2.38
2.32
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1.33
H
N
9
2.17
2.06
1.11
1.02
2.00
3.17
3.45
3.07
3.47
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9.0
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6.5
6.0
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3.0
2.5
2.0
1.5
1.0
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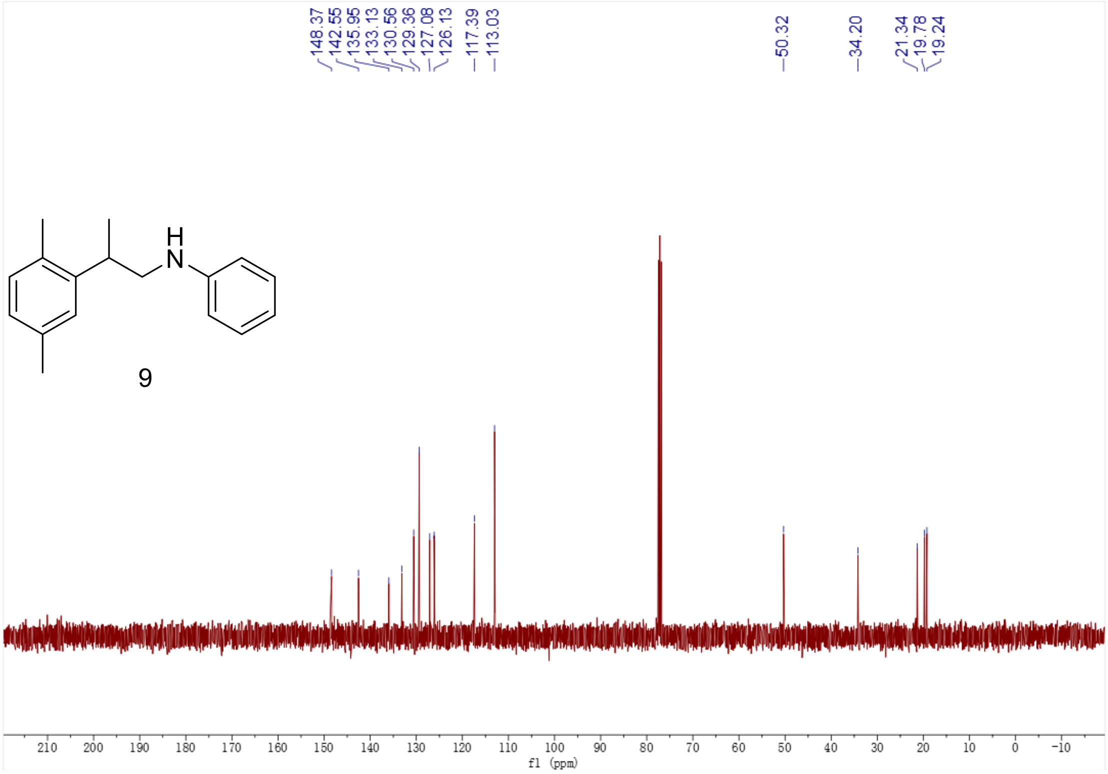
f1 (ppm)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126.13
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113.03
50.32
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21.34
19.78
19.24
H
N
9
210
200
190
180
170
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140
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120
110
100
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80
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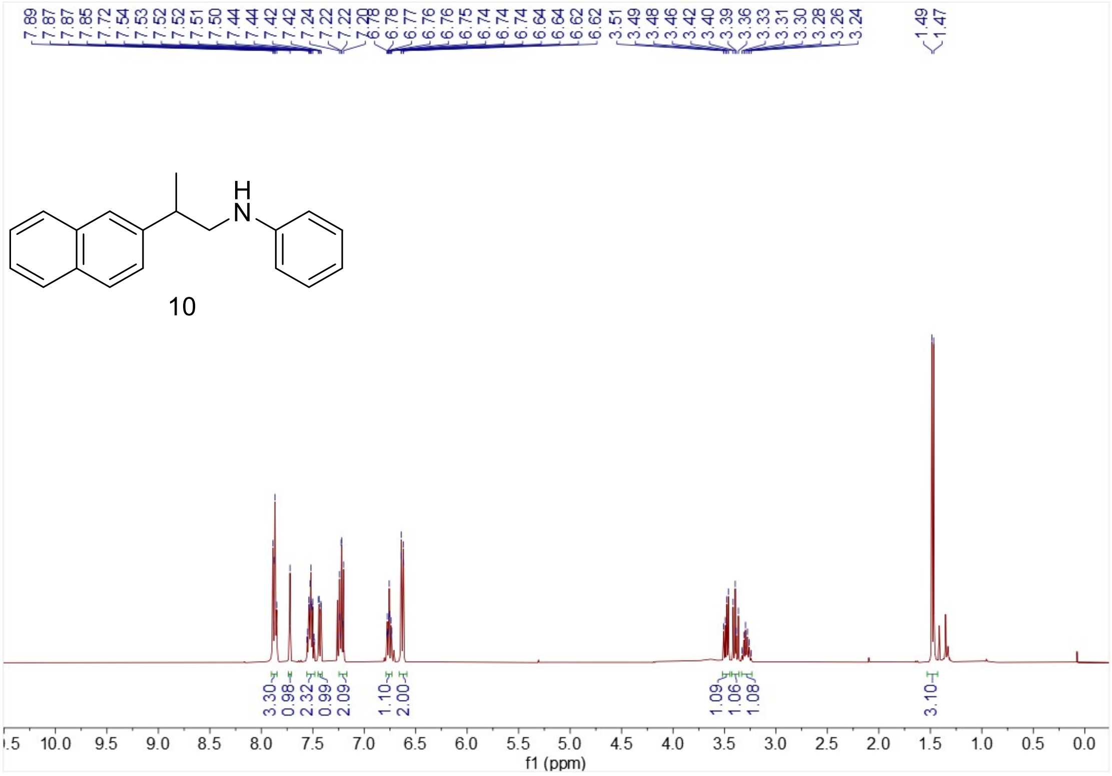
60
50
40
30
20
10
0
-10
f1 (ppm)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6.74
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6.62
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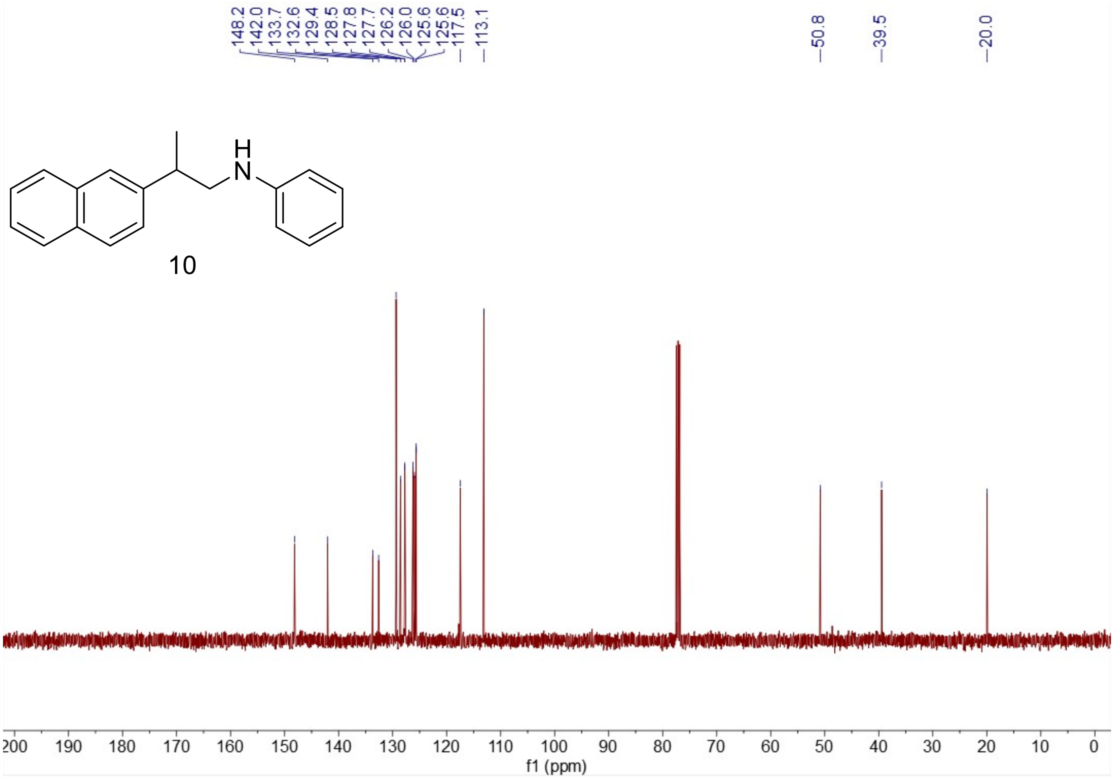
3.39
3.36
3.33
3.31
3.30
3.28
3.26
3.24
1.49
1.47
H
N
10
3.30
0.98
2.32
0.99
2.09
1.10
2.00
1.09
1.06
1.08
3.10
.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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127.8
127.7
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126.0
125.6
125.6
117.5
113.1
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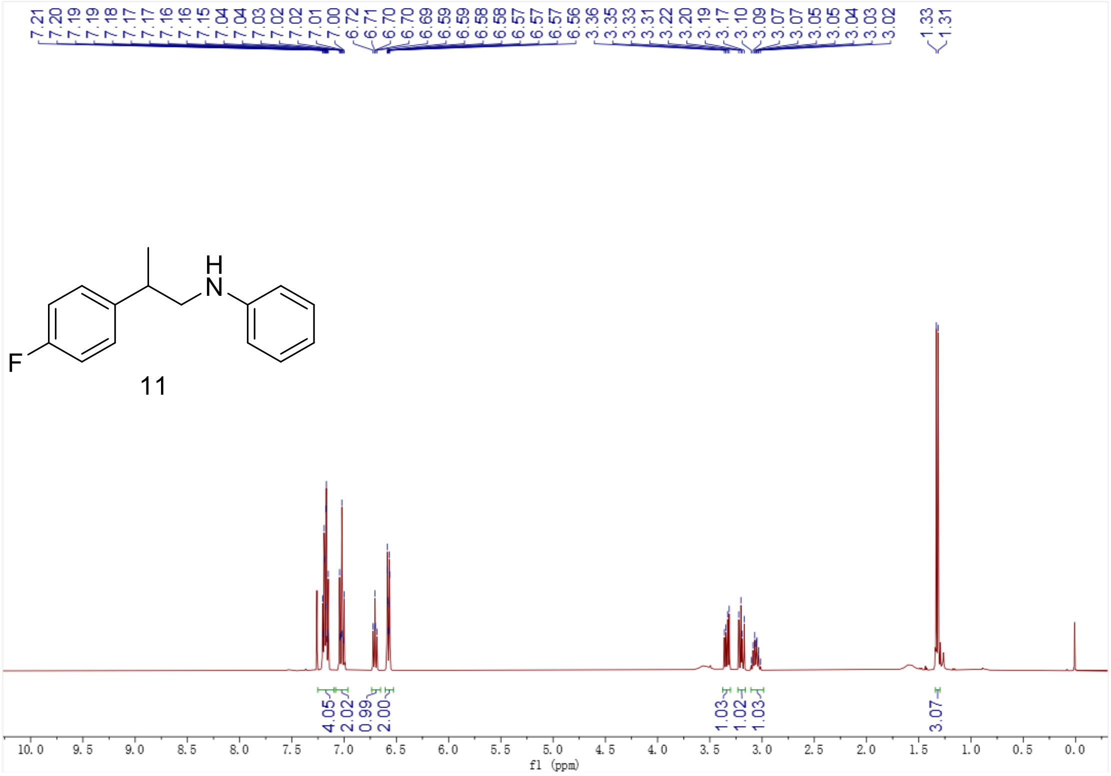
39.5
20.0
H
N
10
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.03
7.02
7.02
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6.58
6.58
6.57
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6.56
3.36
3.35
3.33
3.31
3.22
3.20
3.19
3.17
3.10
3.09
3.07
3.07
3.05
3.05
3.04
3.03
3.02
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1.31
H
N
F
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2.00
1.03
1.02
1.03
3.07
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9.0
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6.0
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1.5
1.0
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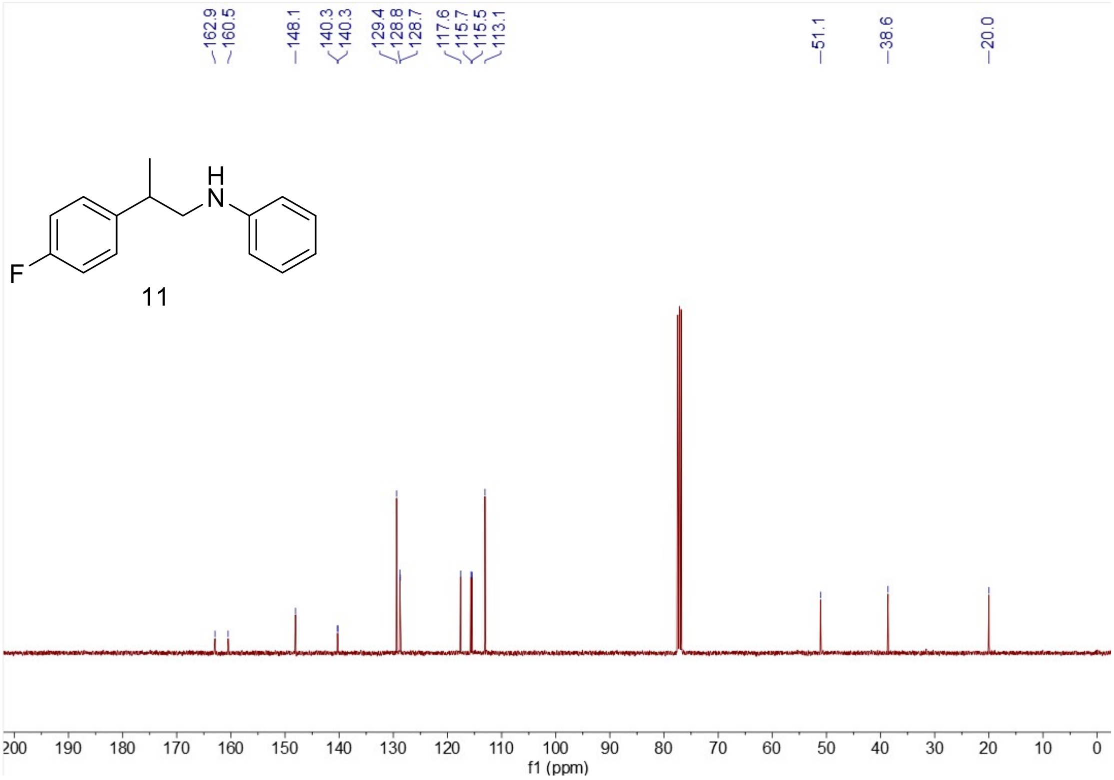
0.0
f1 (ppm)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115.7
115.5
113.1
51.1
38.6
20.0
H
N
F
11
200
190
180
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130
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110
100
90
80
70
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50
40
30
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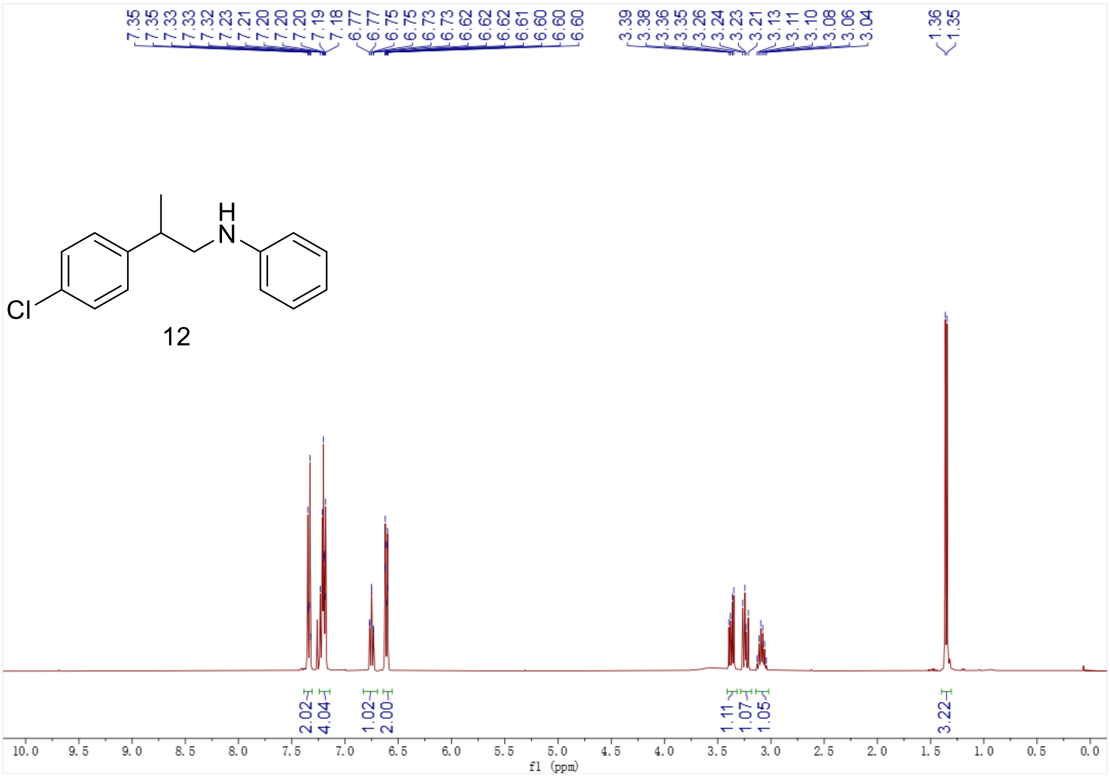
10
0
f1 (ppm)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6.60
3.39
3.38
3.36
3.35
3.26
3.24
3.23
3.21
3.13
3.11
3.10
3.08
3.06
3.04
1.36
1.35
H
N
Cl
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4.04
1.02
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1.05
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7.0
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6.0
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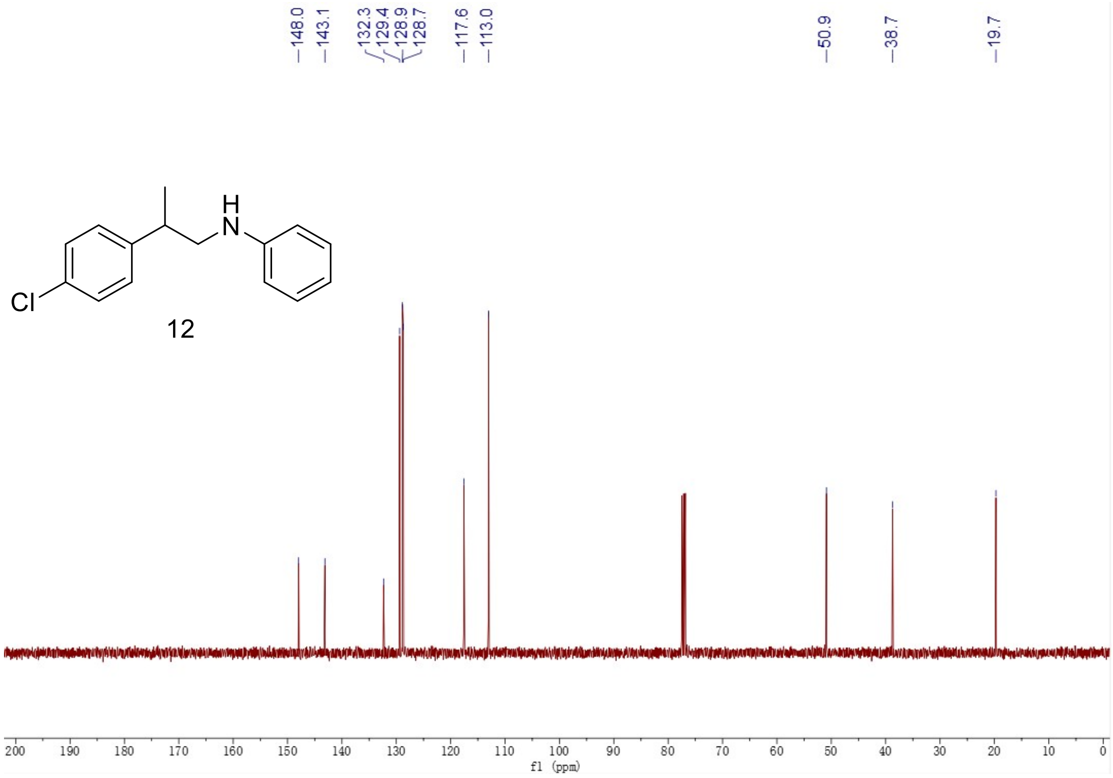
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

12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Cl
200
190
180
170
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120
110
100
90
80
70
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30
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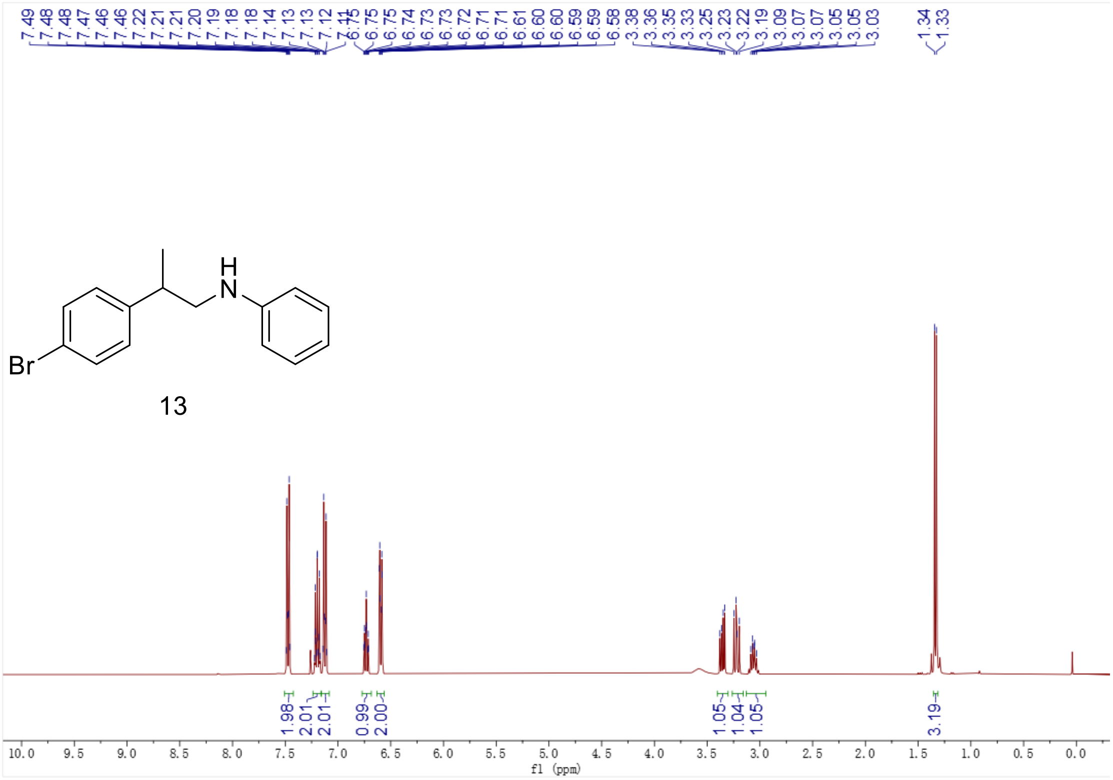
0
f1 (ppm)

12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7.13
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6.75
6.75
6.74
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6.73
6.72
6.71
6.71
6.61
6.60
6.60
6.59
6.59
6.58
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3.36
3.35
3.33
3.25
3.23
3.22
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3.09
3.07
3.05
3.05
3.03
1.34
1.33
H
N
Br
1.98
2.01
2.01
0.99
2.00
1.05
1.04
1.05
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9.5
9.0
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7.0
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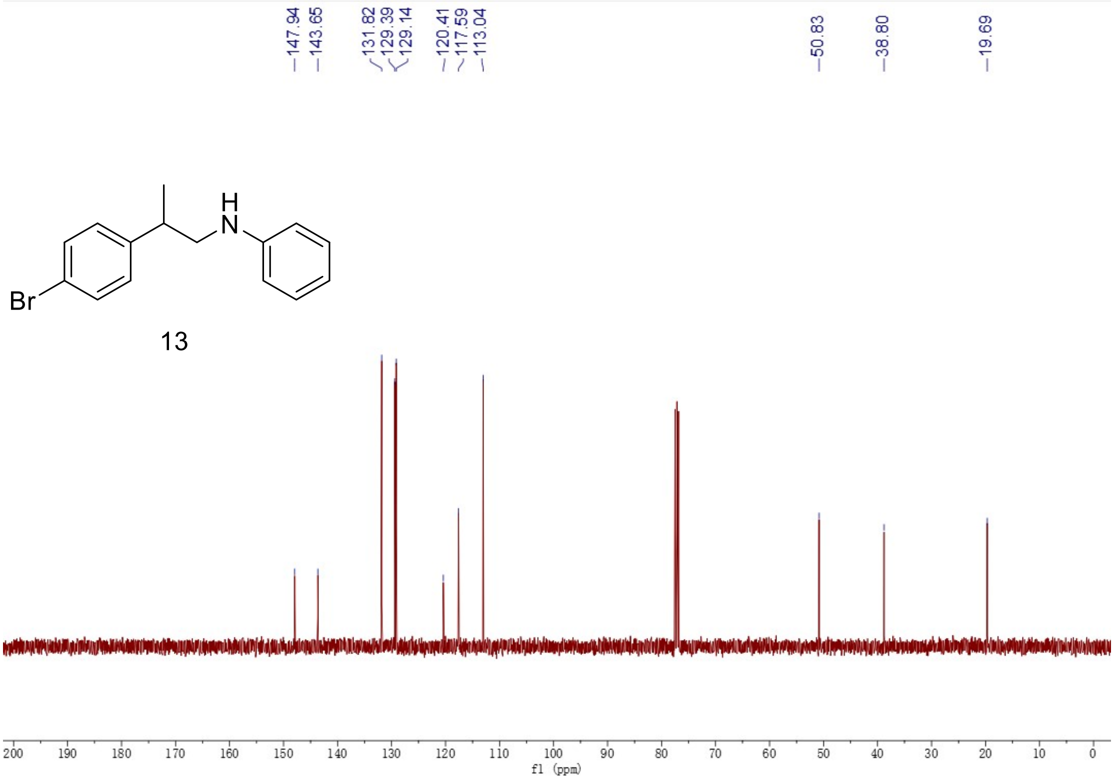
f1 (ppm)

13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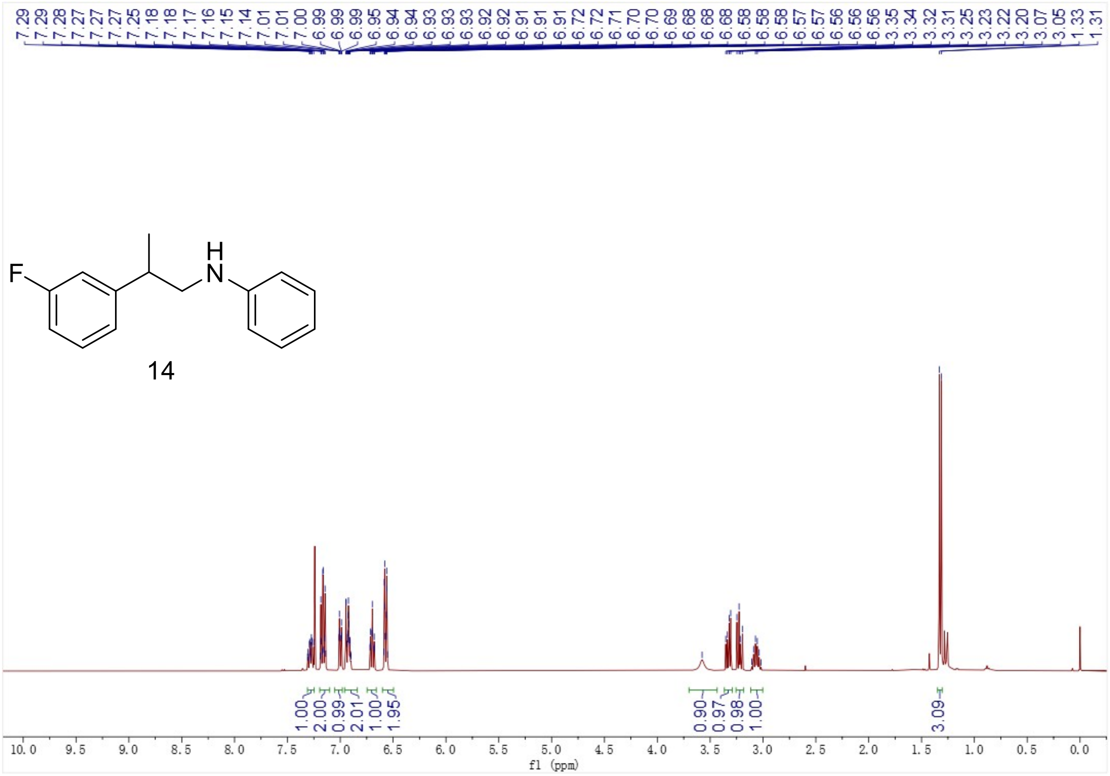
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3.23
3.22
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3.05
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1.31
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2.00
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0.97
0.98
1.00
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10.0
9.5
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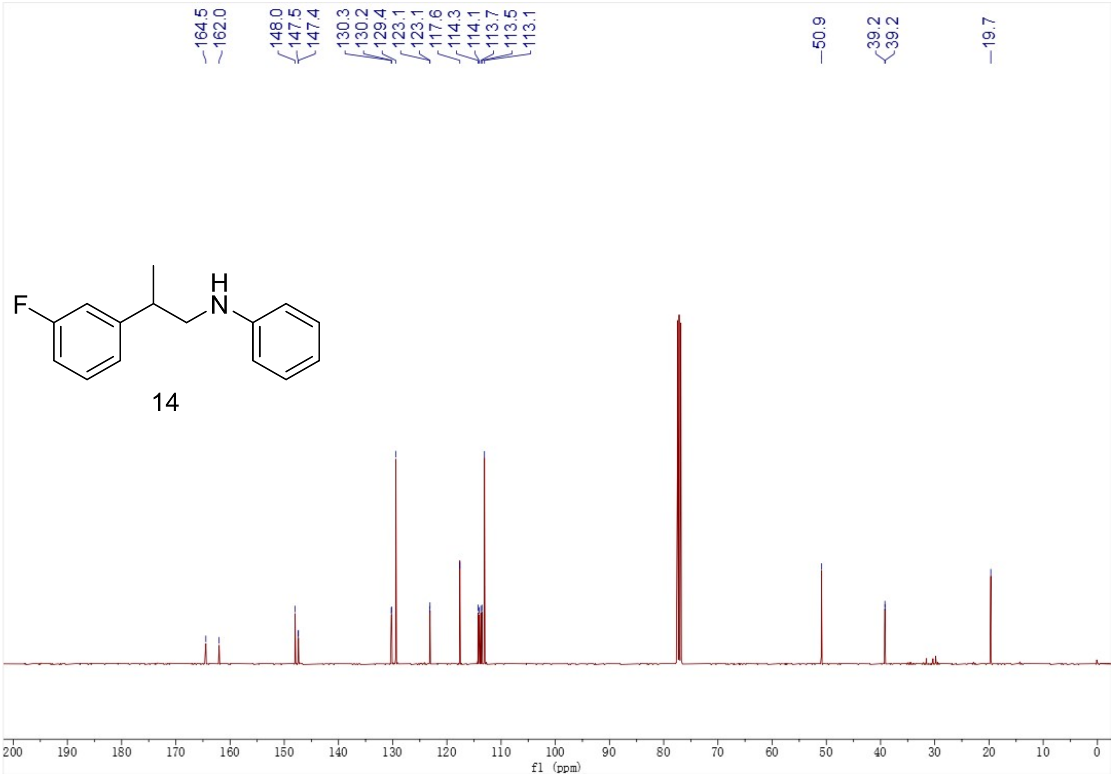
14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114.3
114.1
113.7
113.5
113.1
50.9
39.2
39.2
19.7
F
H
N
200
190
180
170
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80
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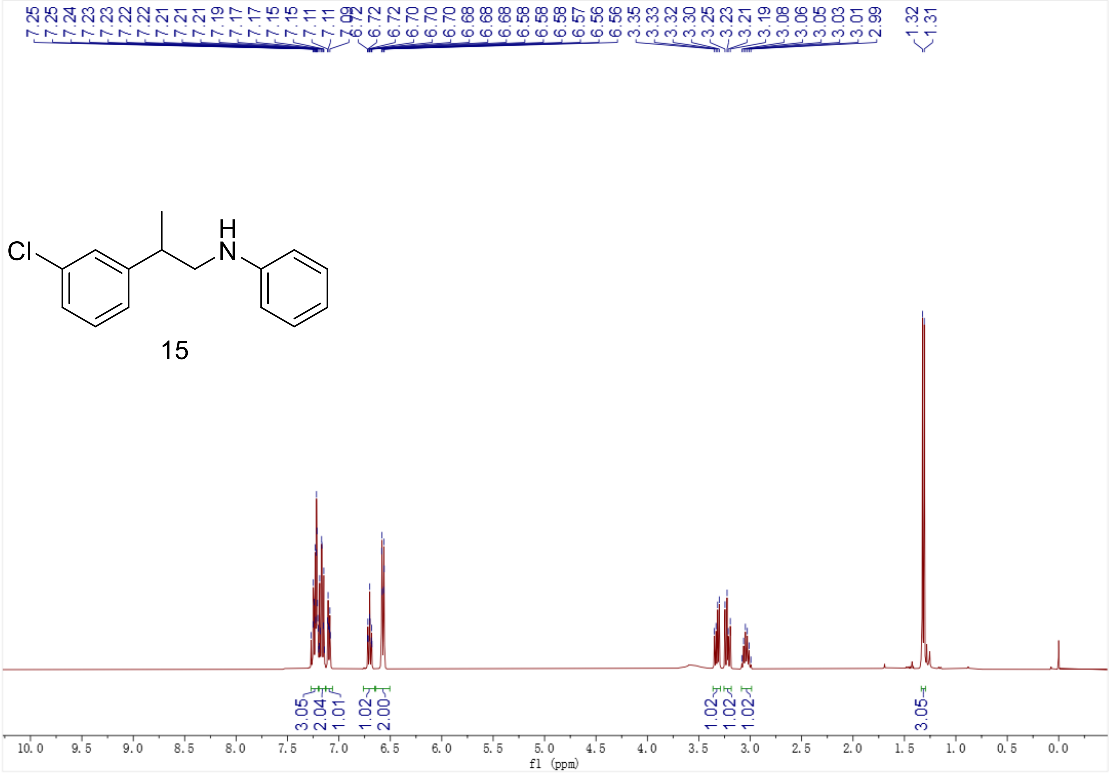
0
f1 (ppm)

14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6.57
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3.33
3.32
3.30
3.25
3.23
3.21
3.19
3.08
3.06
3.05
3.03
3.01
2.99
1.32
1.31
Cl
H
N
15
3.05
2.04
1.01
1.02
2.00
1.02
1.02
1.02
3.05
10.0
9.5
9.0
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8.0
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5.5
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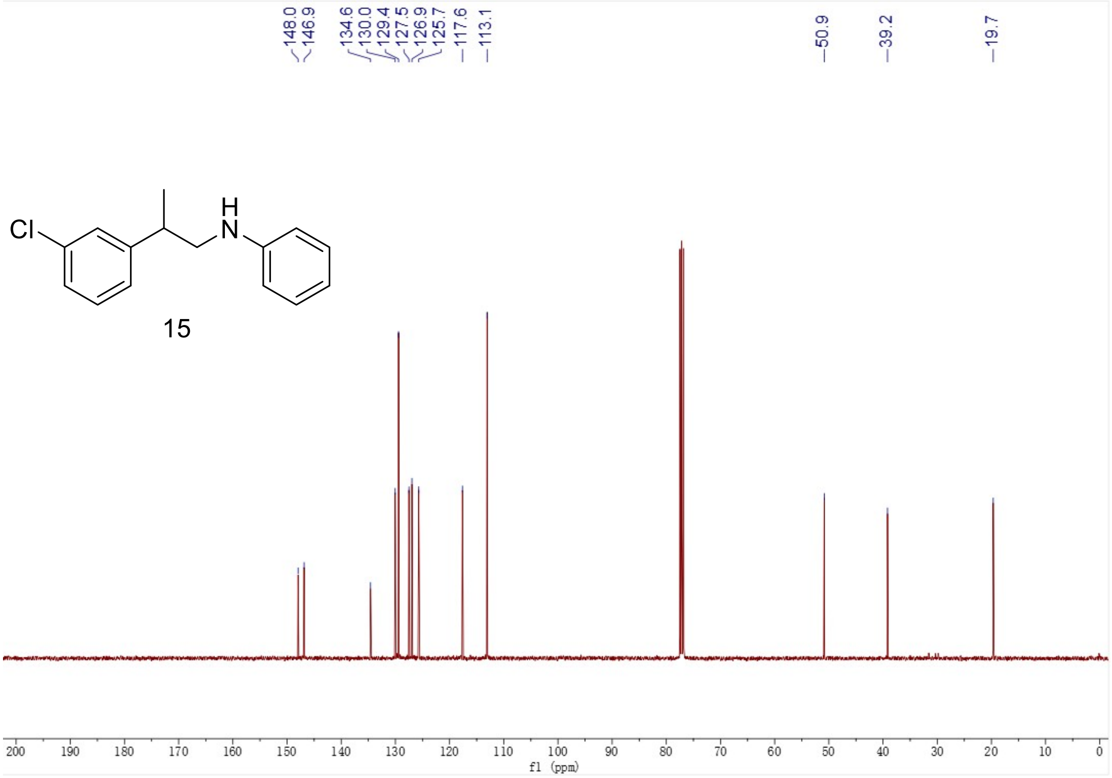
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39.2
19.7
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H
N
15
200
190
180
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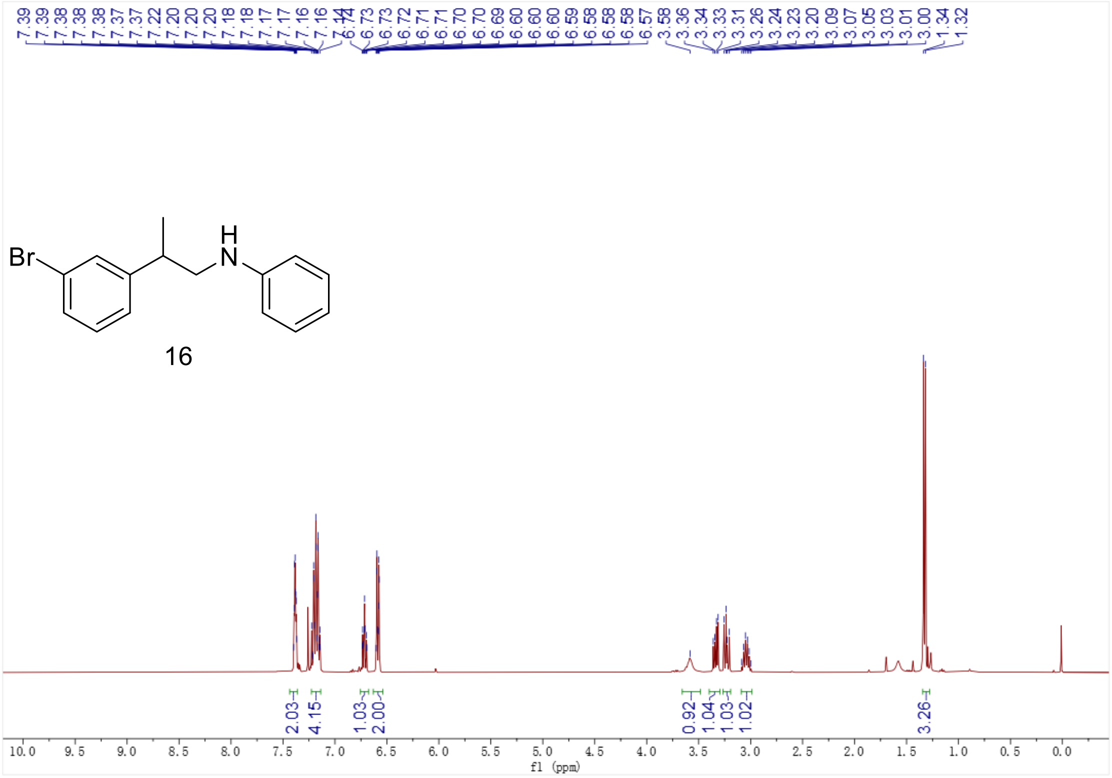
f1 (ppm)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6.72
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6.71
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6.58
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6.58
6.57
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3.34
3.33
3.31
3.26
3.24
3.23
3.20
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3.03
3.01
3.00
1.34
1.32
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N
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1.04
1.03
1.02
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7.0
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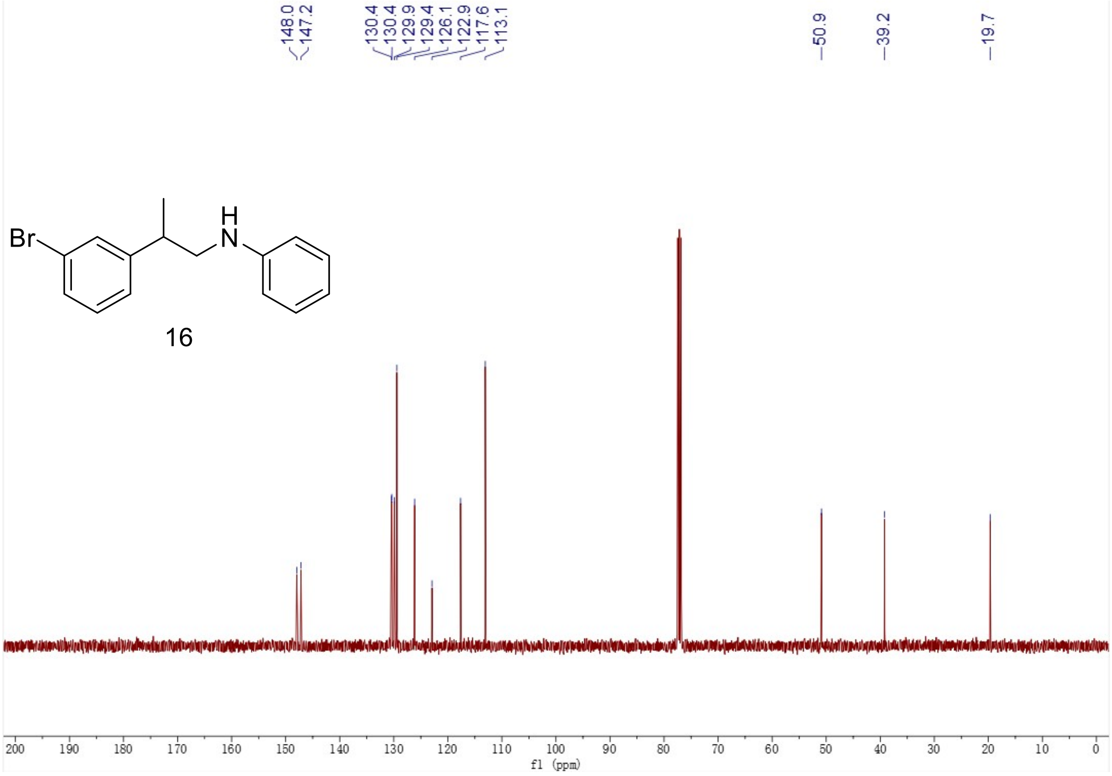
0.0
f1 (ppm)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N
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200
190
180
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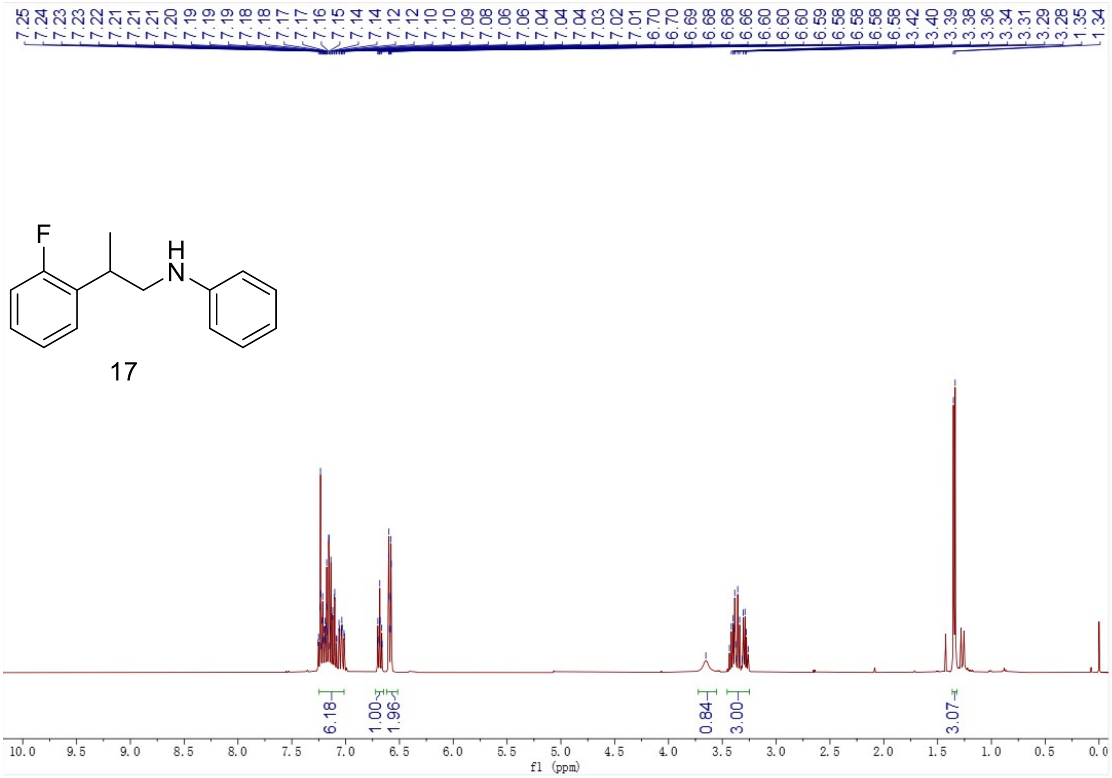
f1 (ppm)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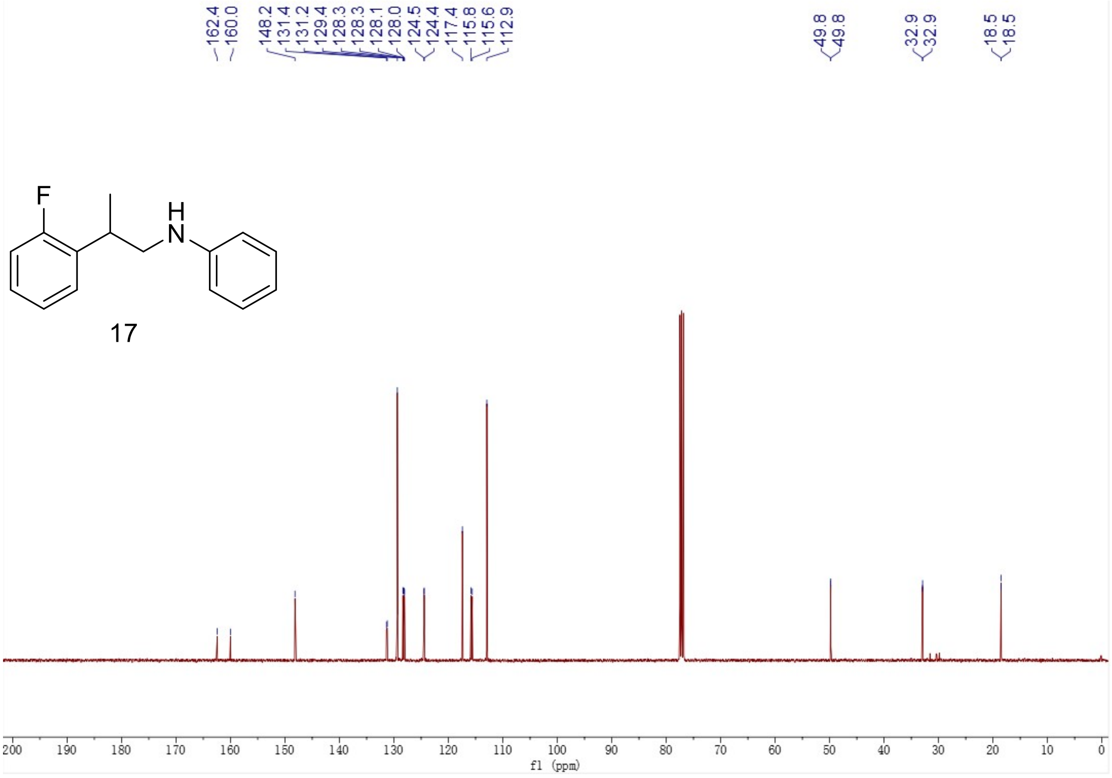
f1 (ppm)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32.9
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18.5
F
H
N
17
200
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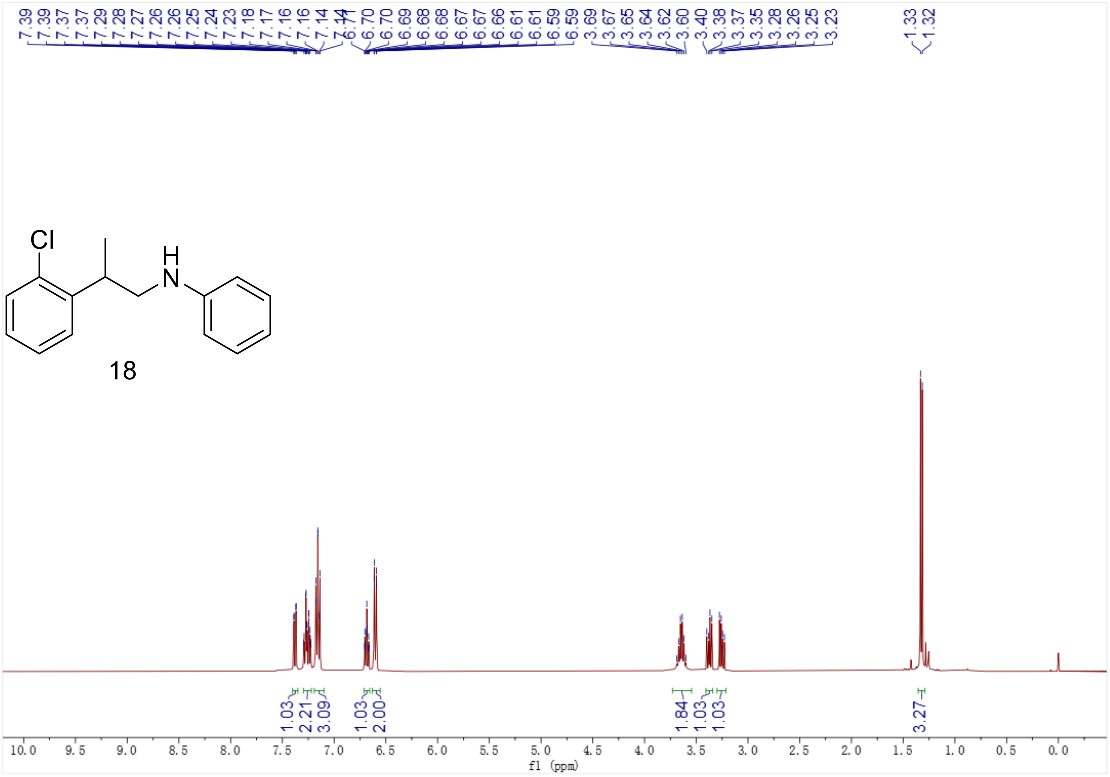
f1 (ppm)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3.26
3.25
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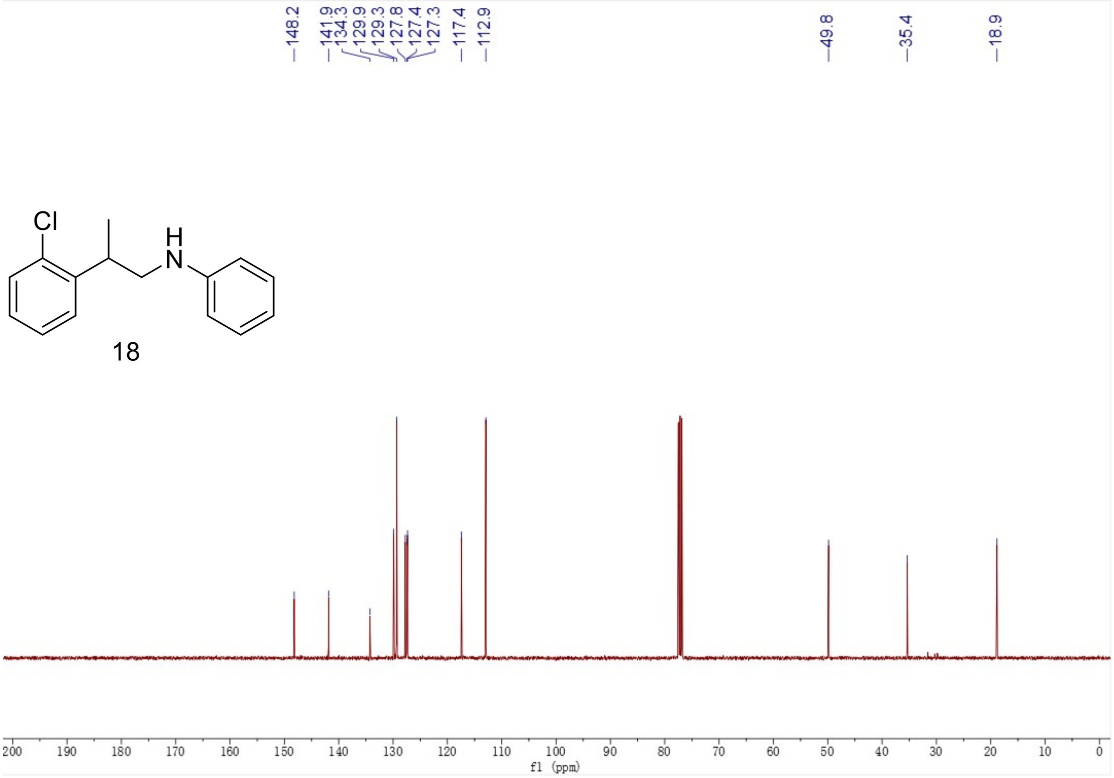
0.0
f1 (ppm)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Cl
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N
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200
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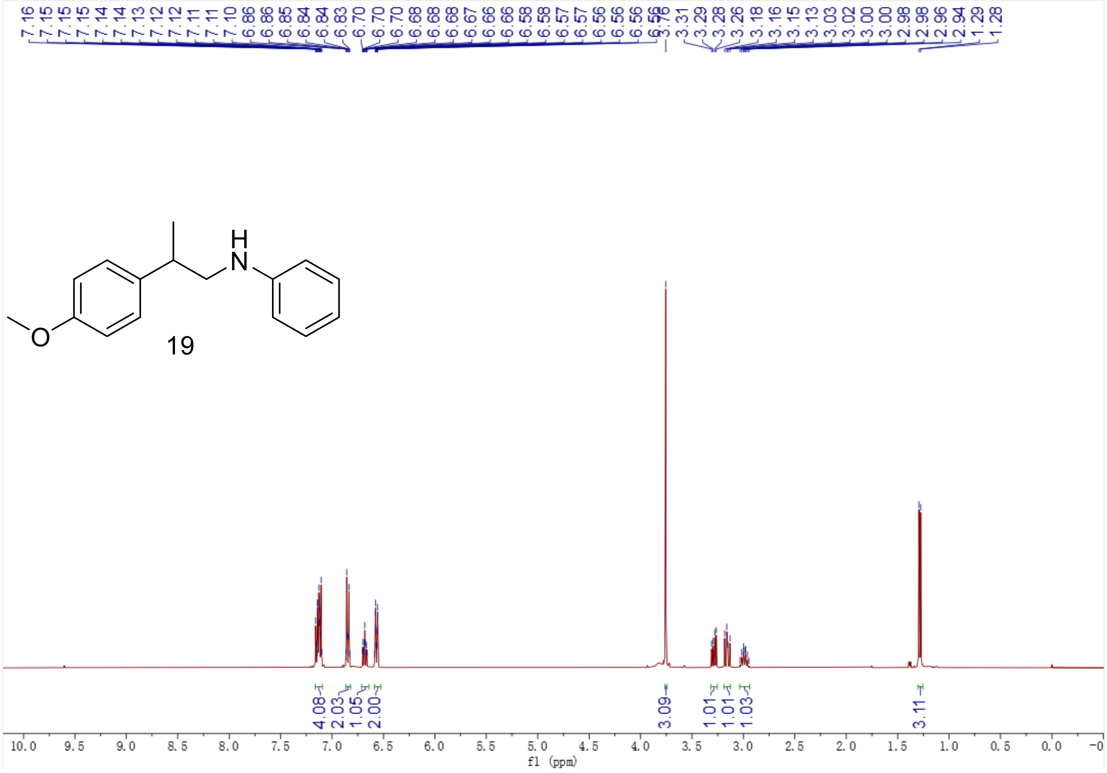
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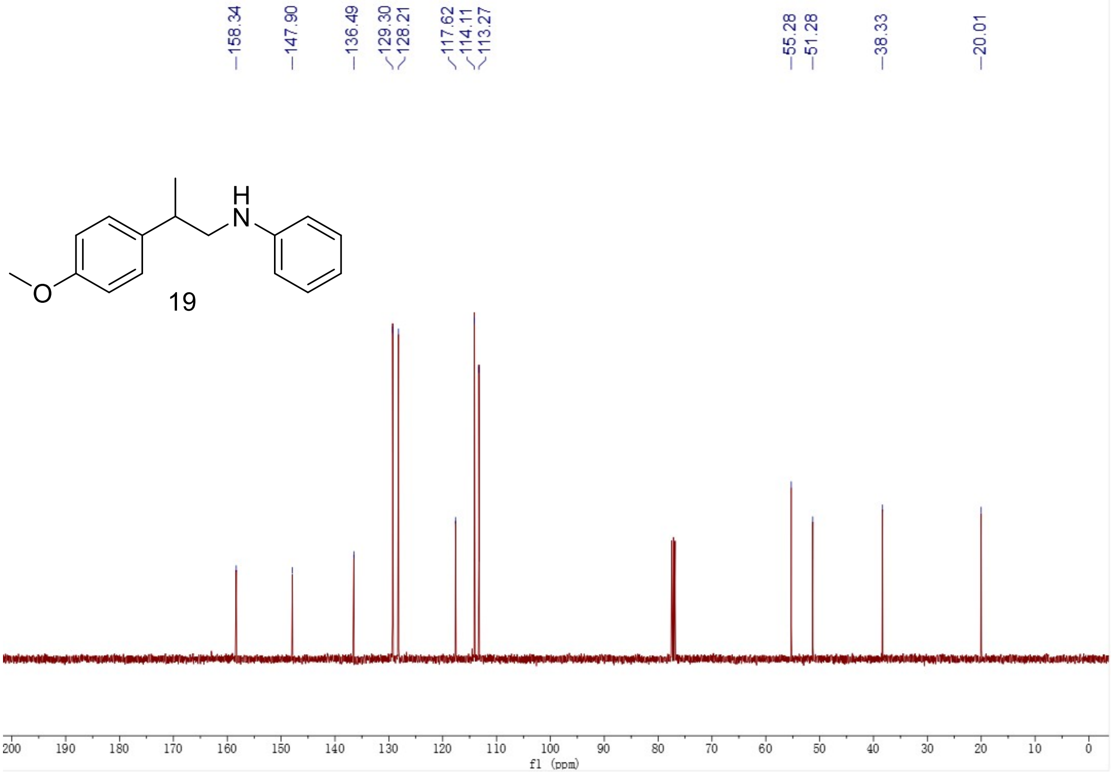
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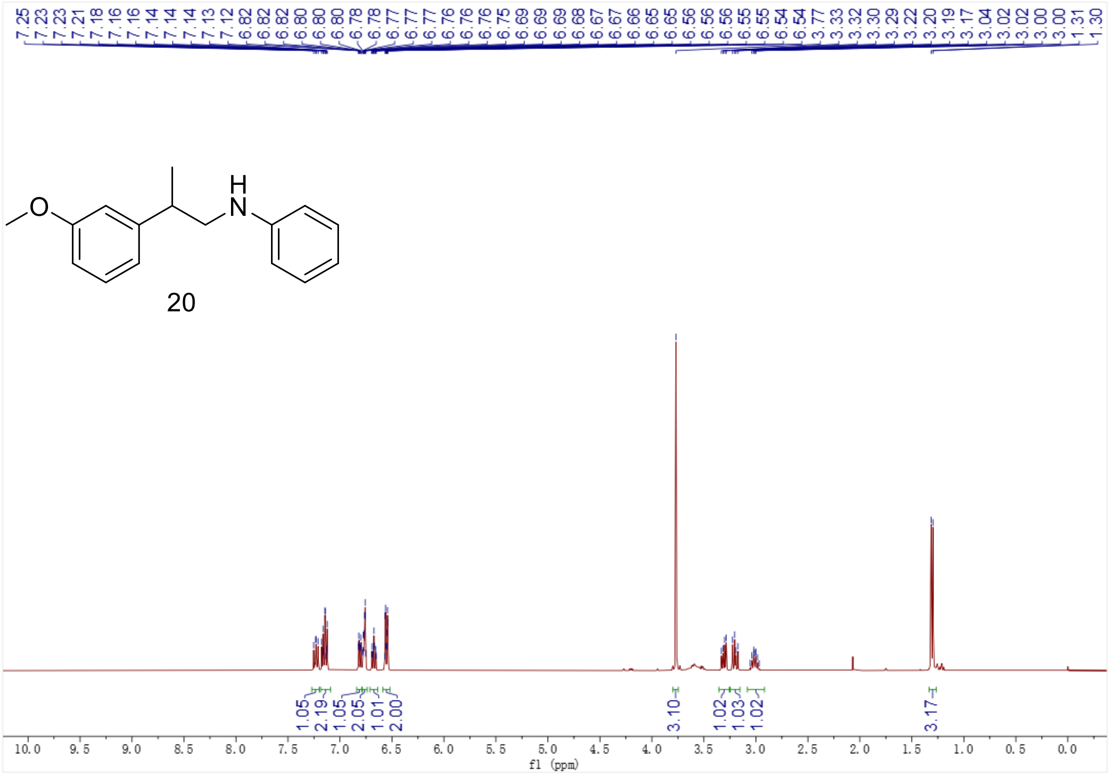
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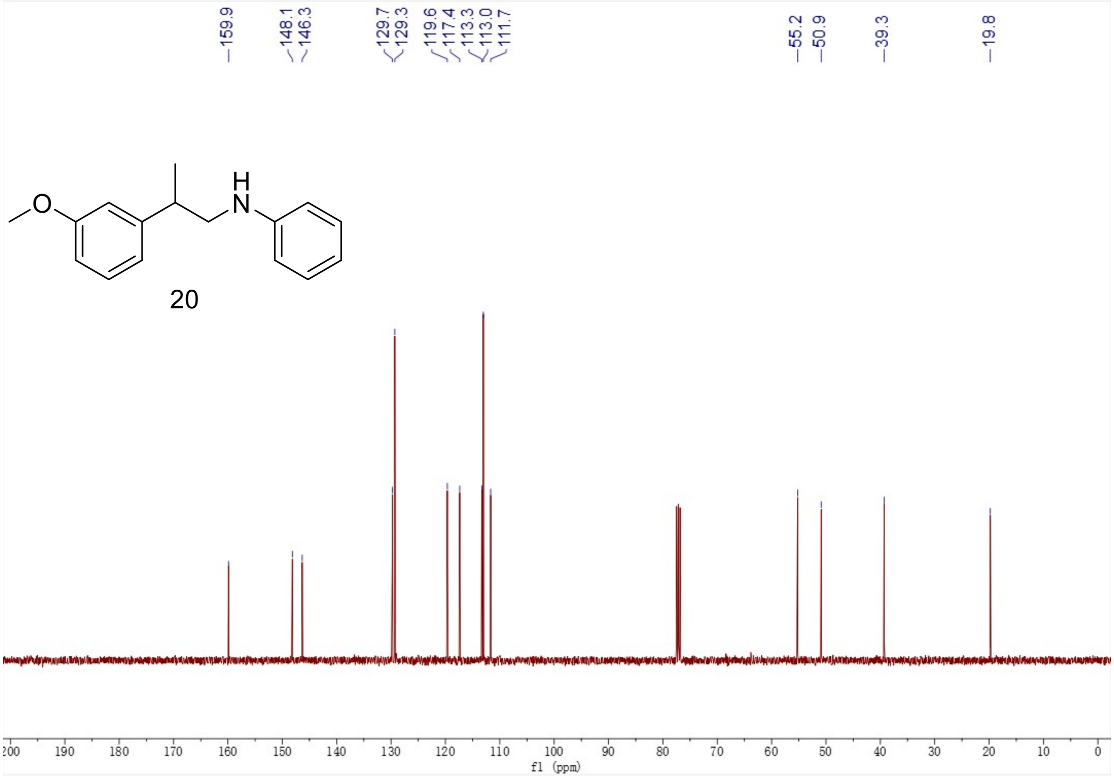
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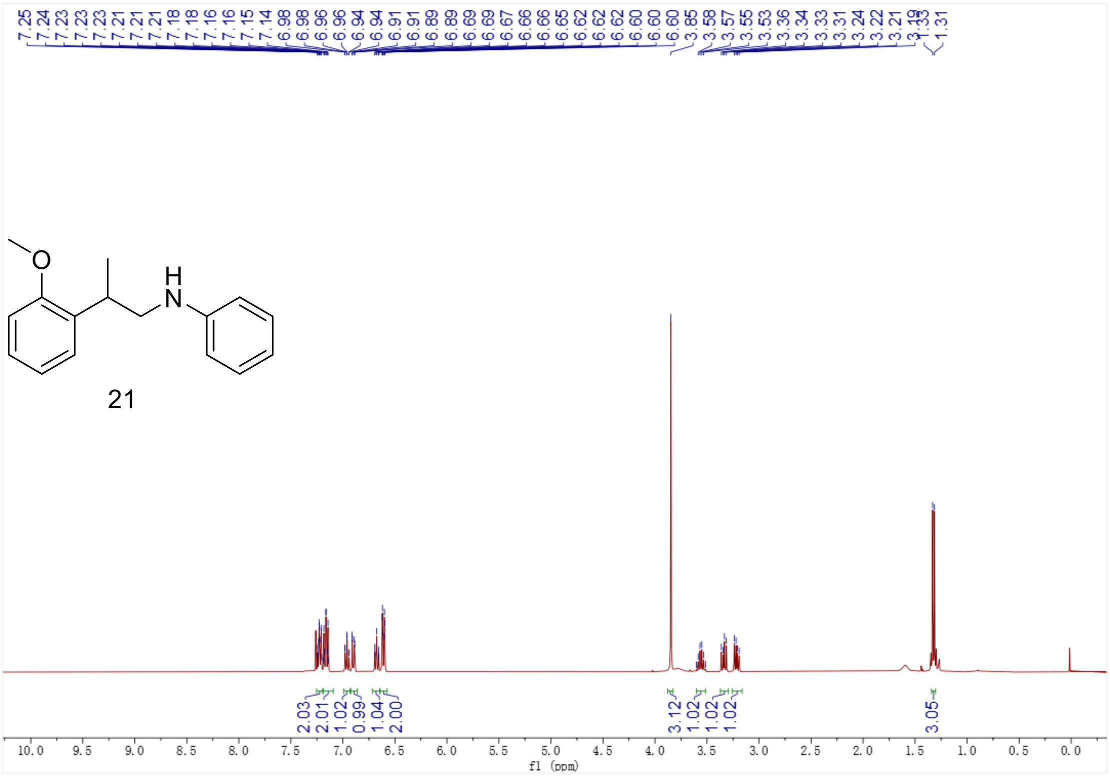
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1.31
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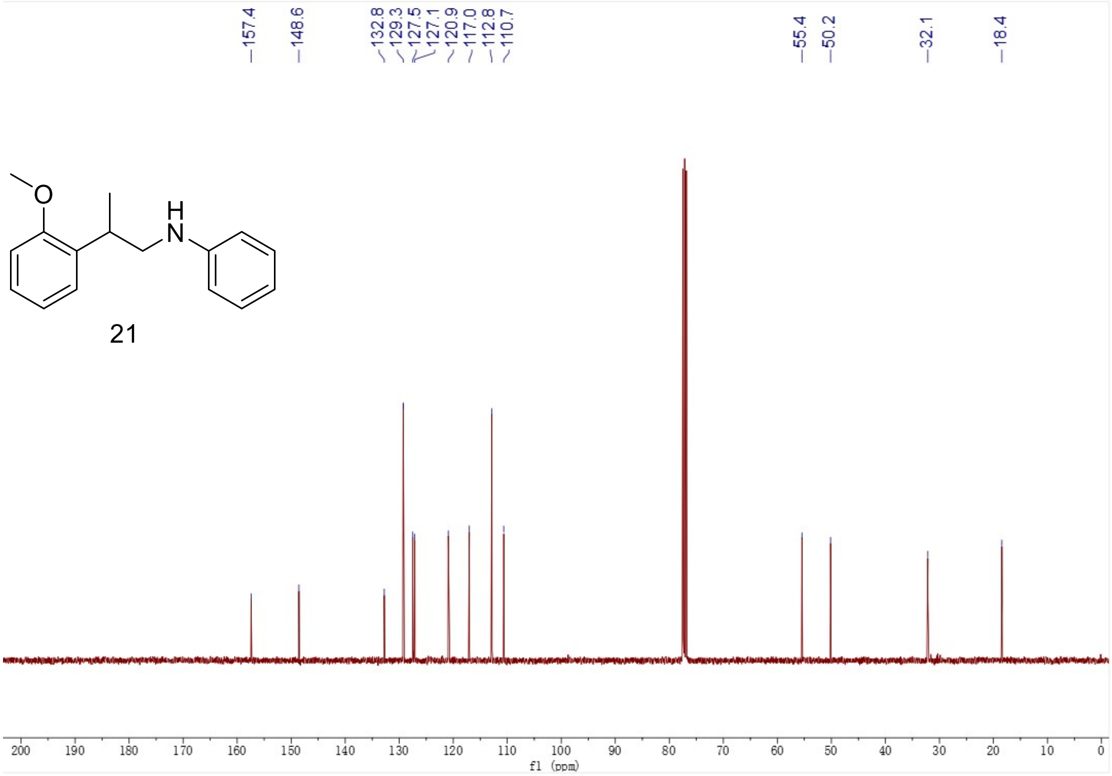
f1 (ppm)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110.7
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O
H
N
21
200
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180
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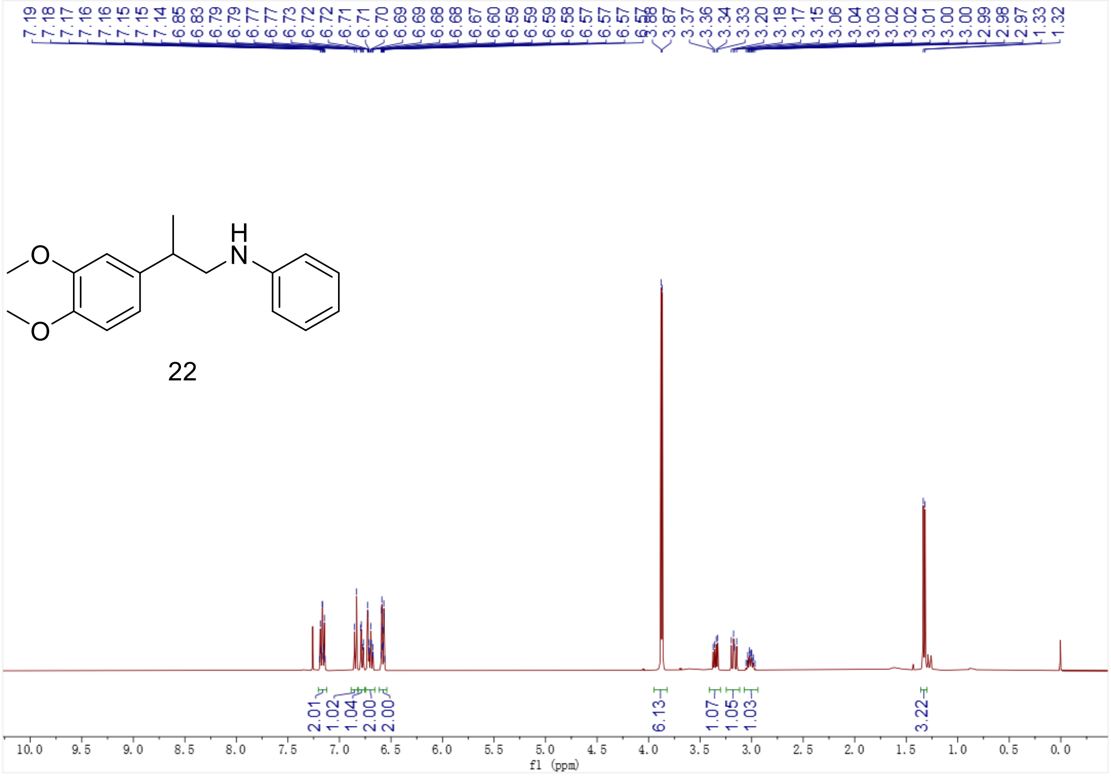
f1 (ppm)


22

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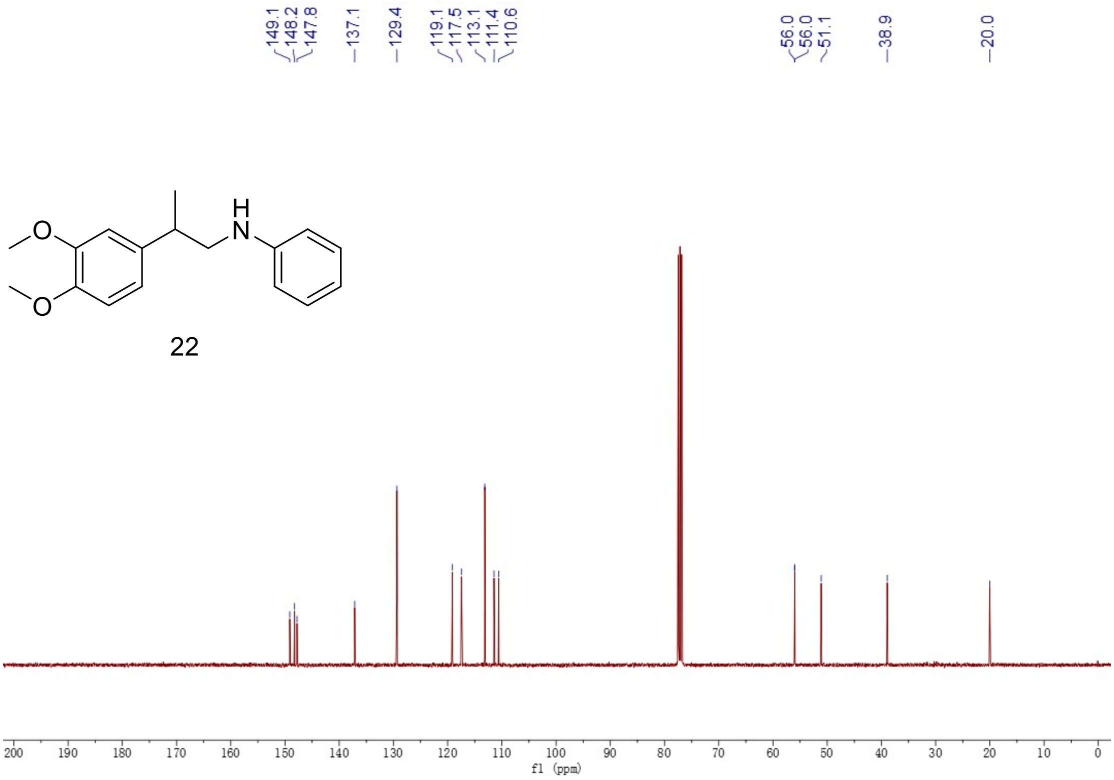
22

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N
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190
180
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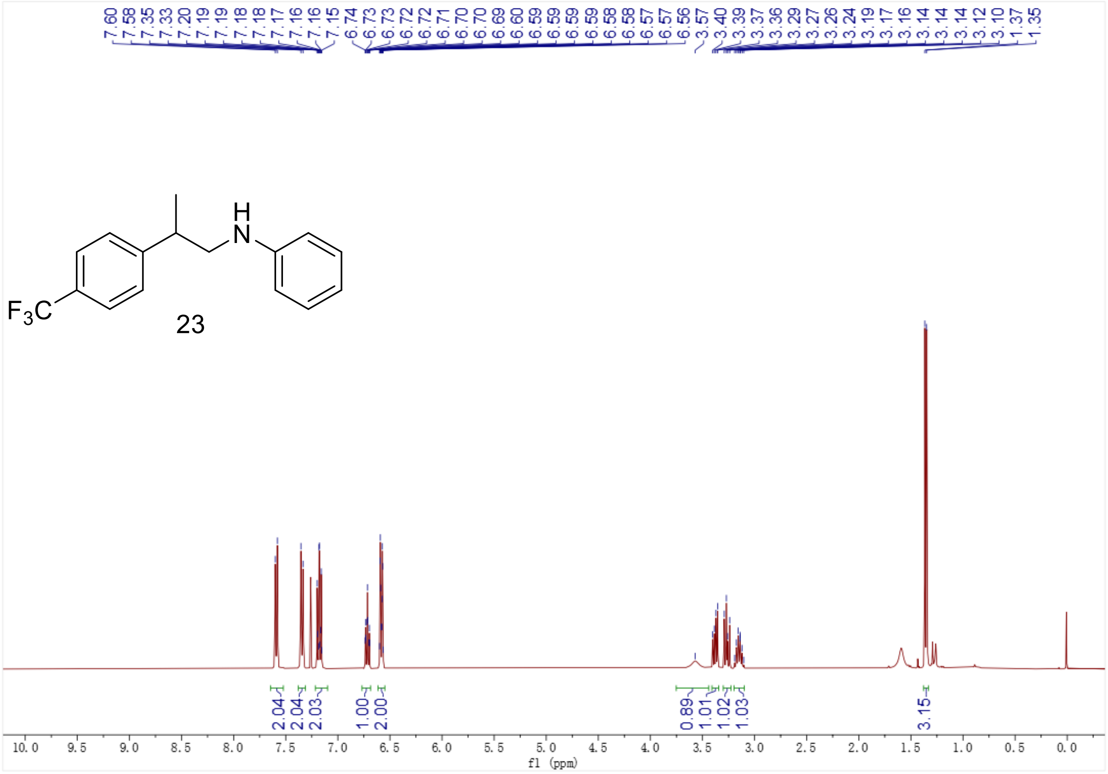
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6.73
6.73
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6.71
6.70
6.70
6.69
6.60
6.59
6.59
6.59
6.59
6.58
6.57
6.57
6.56
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3.29
3.27
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3.24
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1.35
H
N
F_3C
23
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2.04
2.03
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2.00
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1.02
1.03
3.15
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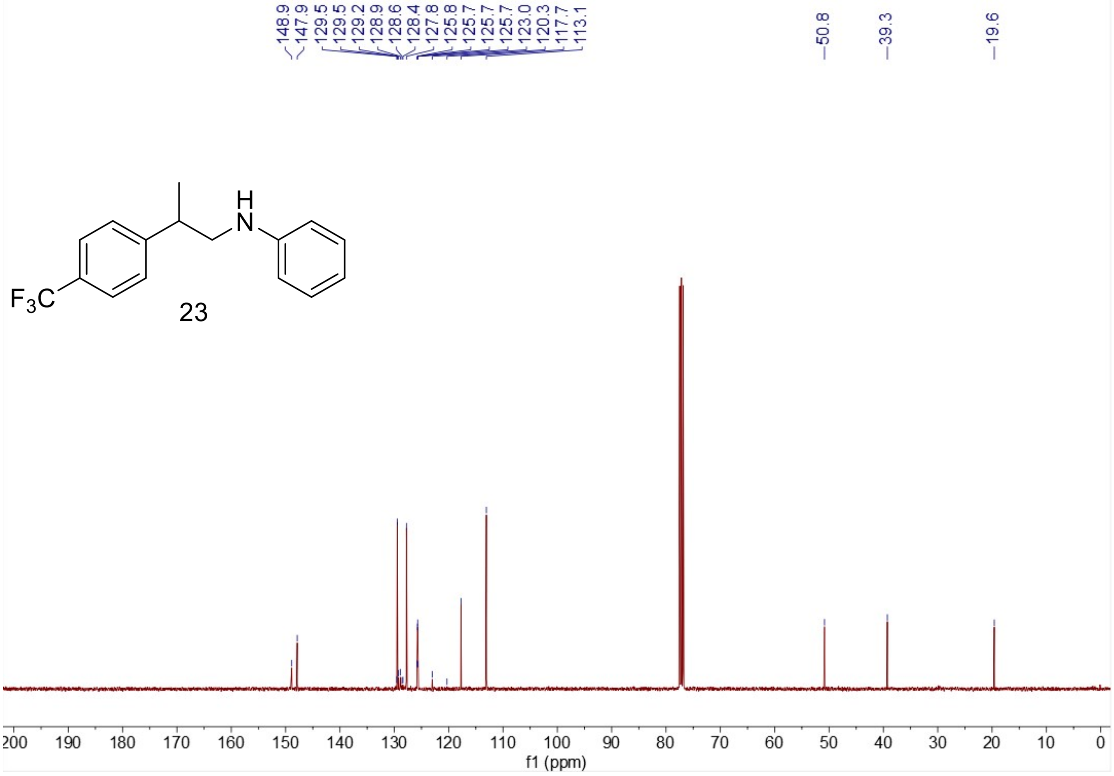
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117.7
113.1
50.8
39.3
19.6
H
N
F_3C
23
200
190
180
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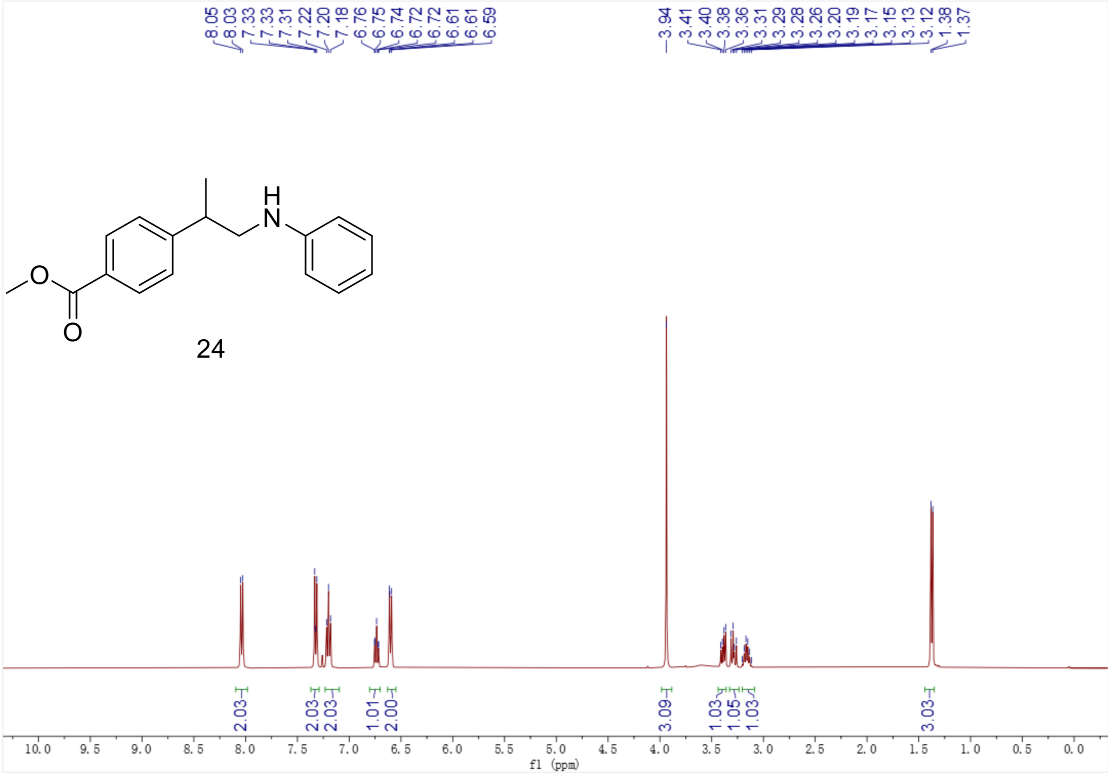
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3.41
3.40
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3.31
3.29
3.28
3.26
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3.19
3.17
3.15
3.13
3.12
1.38
1.37
O
O
H
N
2.03
2.03
2.03
1.01
2.00
3.09
1.03
1.05
1.03
3.03
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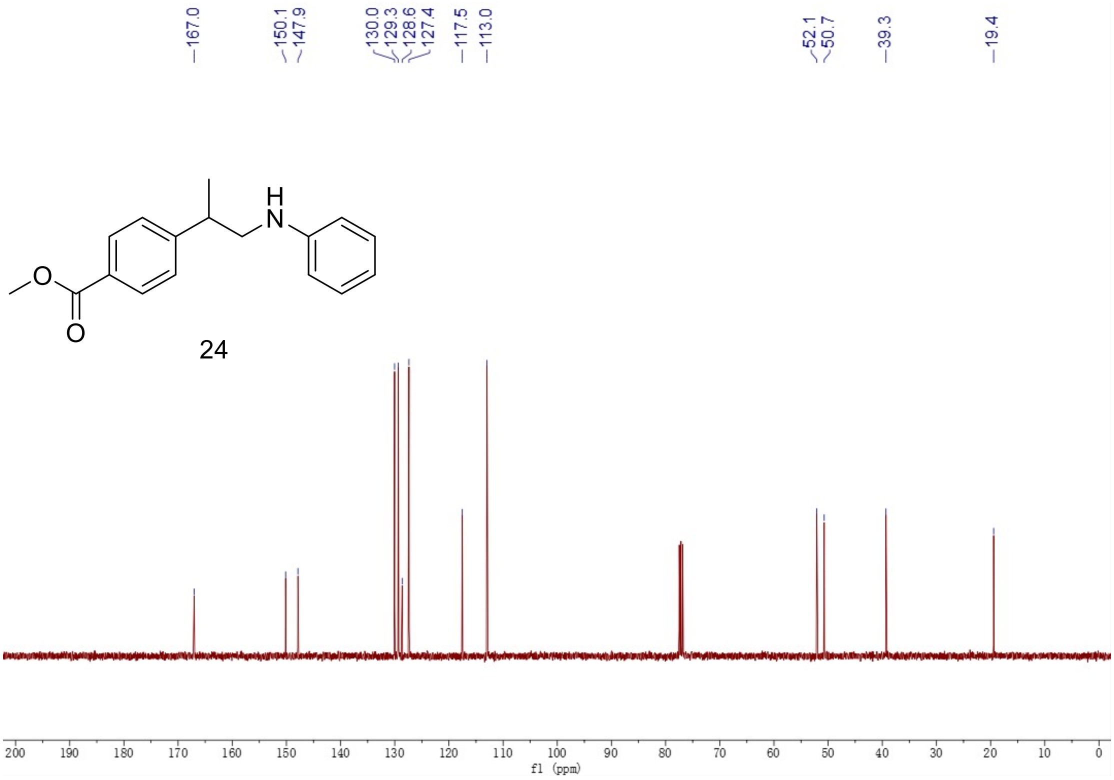
24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O
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N
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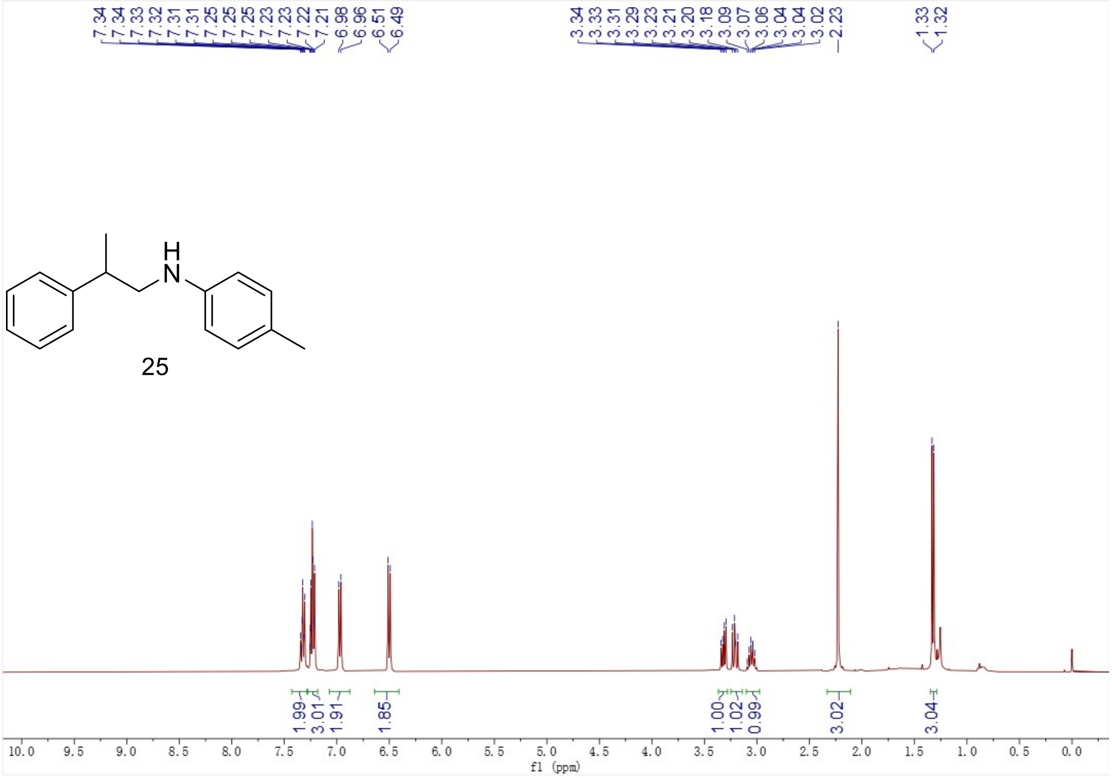
f1 (ppm)

24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6.51
6.49
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3.31
3.29
3.23
3.21
3.20
3.18
3.09
3.07
3.06
3.04
3.04
3.02
2.23
1.33
1.32
H
N
1.99
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1.91
1.85
1.00
1.02
0.99
3.02
3.04
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8.0
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7.0
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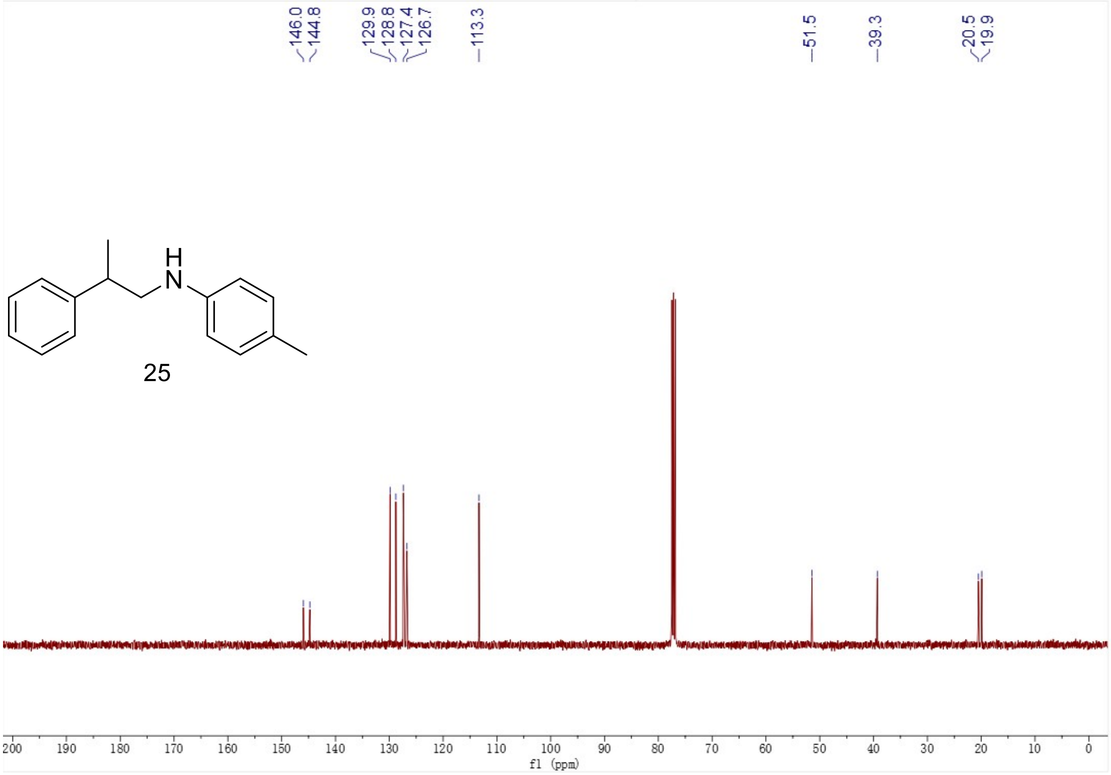
25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200
190
180
170
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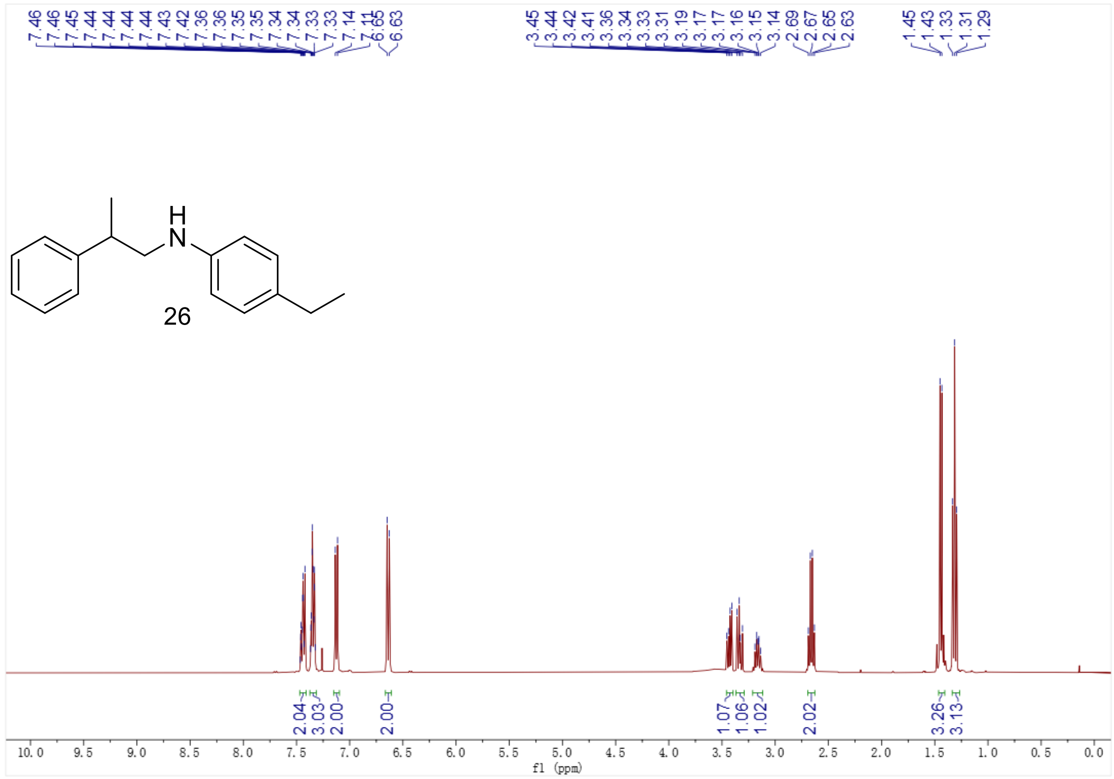
10
0
f1 (ppm)

25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6.65
6.63
3.45
3.44
3.42
3.41
3.36
3.34
3.33
3.31
3.19
3.17
3.17
3.16
3.15
3.14
2.69
2.67
2.65
2.63
1.45
1.43
1.33
1.31
1.29
H
N
26
2.04
3.03
2.00
2.00
1.07
1.06
1.02
2.02
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3.13
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9.0
8.5
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7.0
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6.0
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5.0
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4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


146.1
144.7
133.2
128.7
128.6
127.3
126.7
113.2
77.5
77.2
76.8
51.3
39.3
28.0
19.9
16.1
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N
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200
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180
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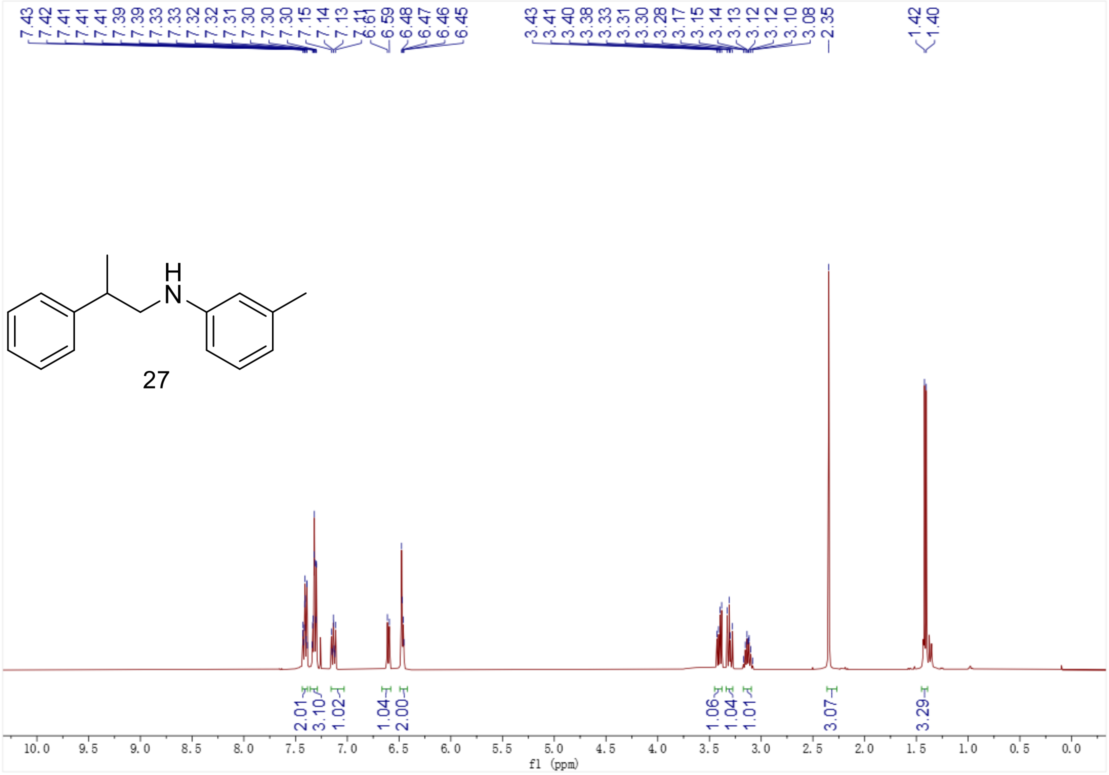
f1 (ppm)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3.14
3.13
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N
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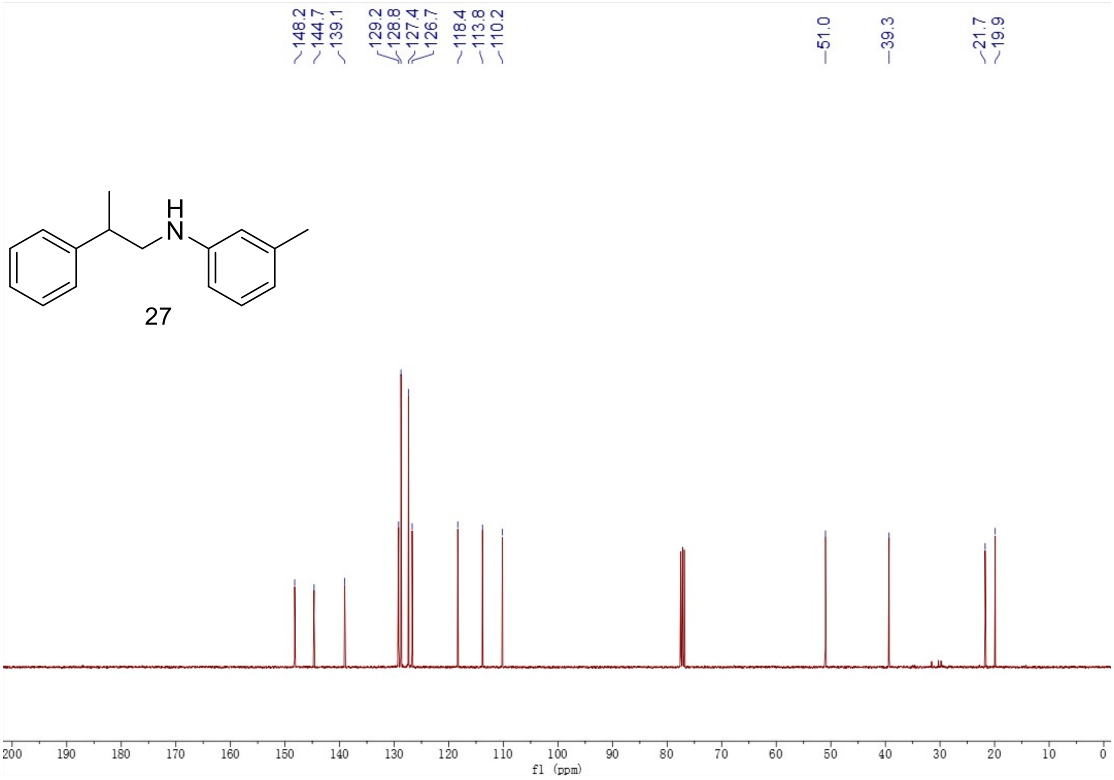
f1 (ppm)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N
27
200
190
180
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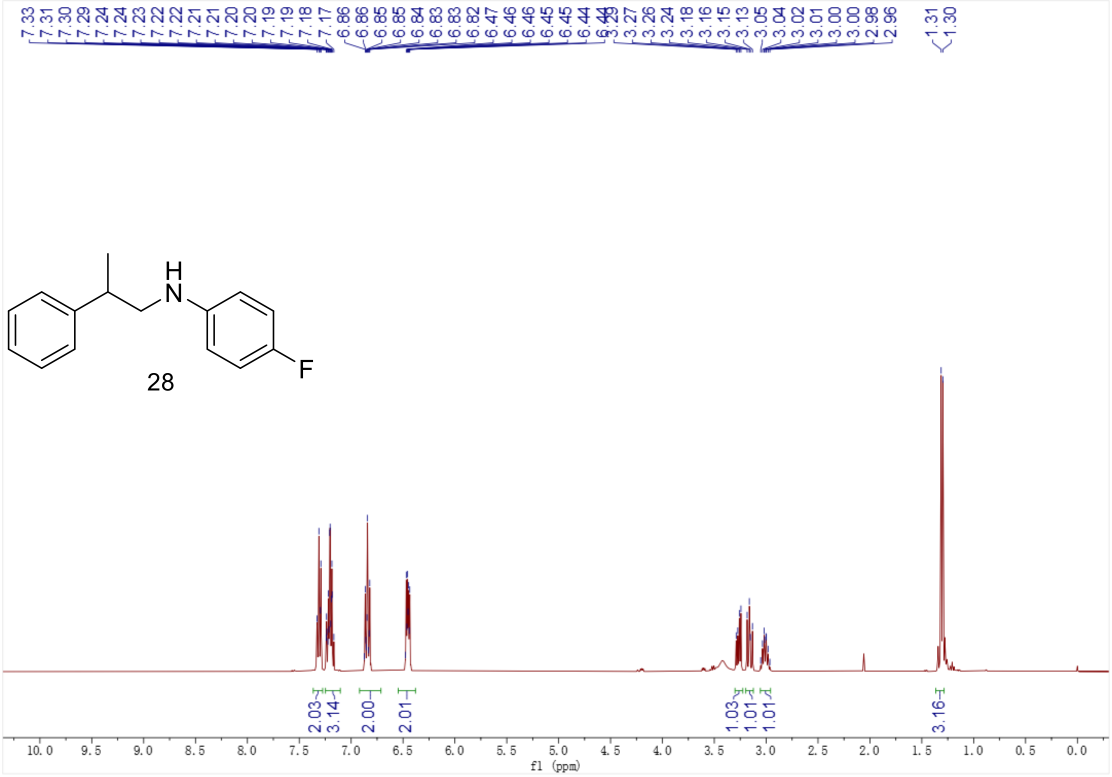
f1 (ppm)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7.19
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7.17
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6.82
6.47
6.46
6.45
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6.44
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3.27
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3.00
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N
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1.01
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7.5
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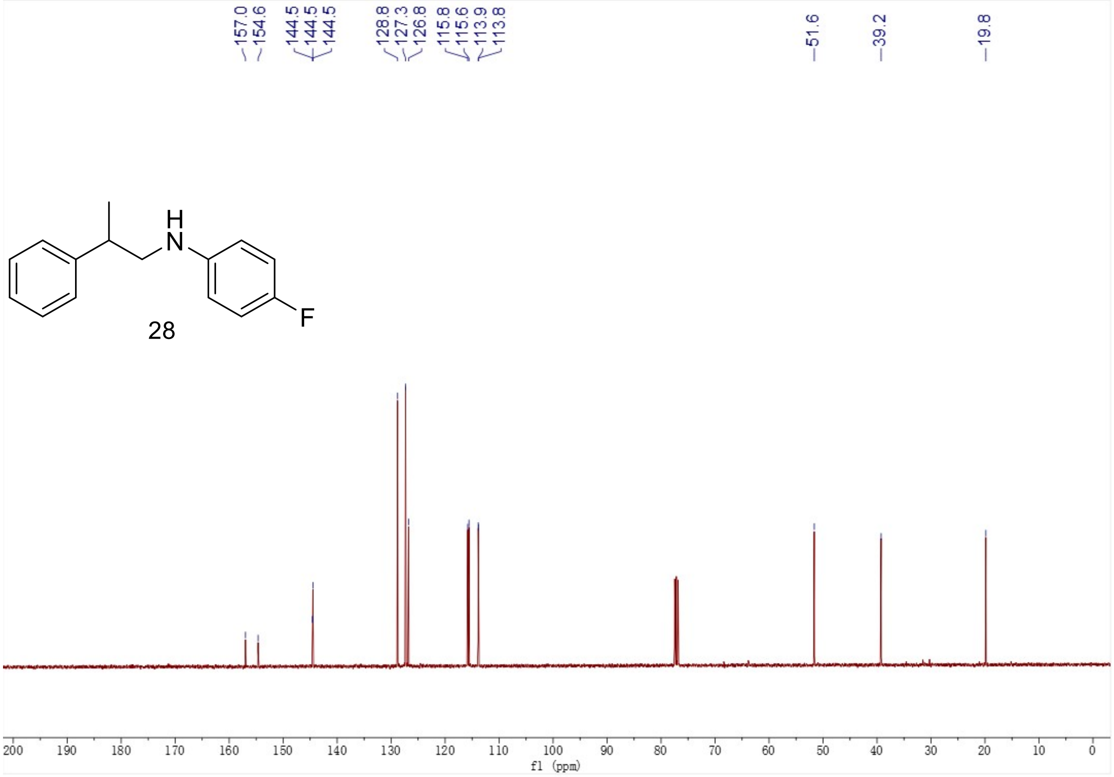
f1 (ppm)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39.2
19.8
H
N
F
28
200
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180
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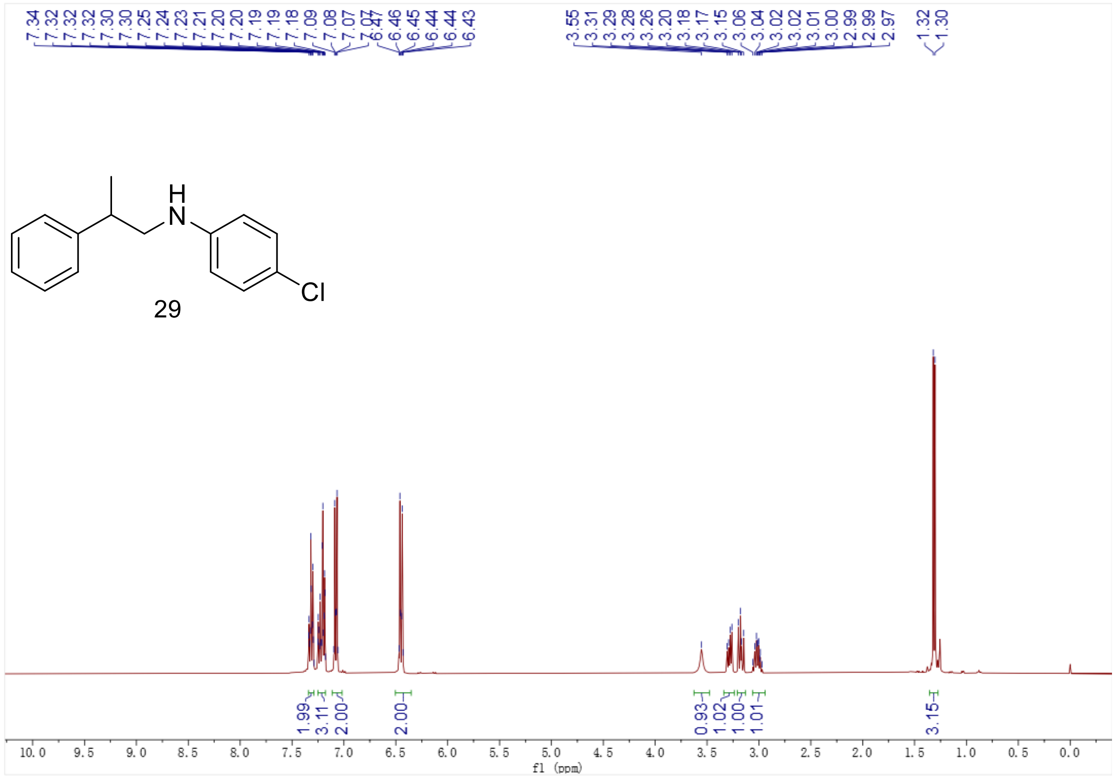
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7.07
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6.43
3.55
3.31
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3.06
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3.02
3.01
3.00
2.99
2.97
1.32
1.30
H
N
Cl
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2.00
0.93
1.02
1.00
1.01
3.15
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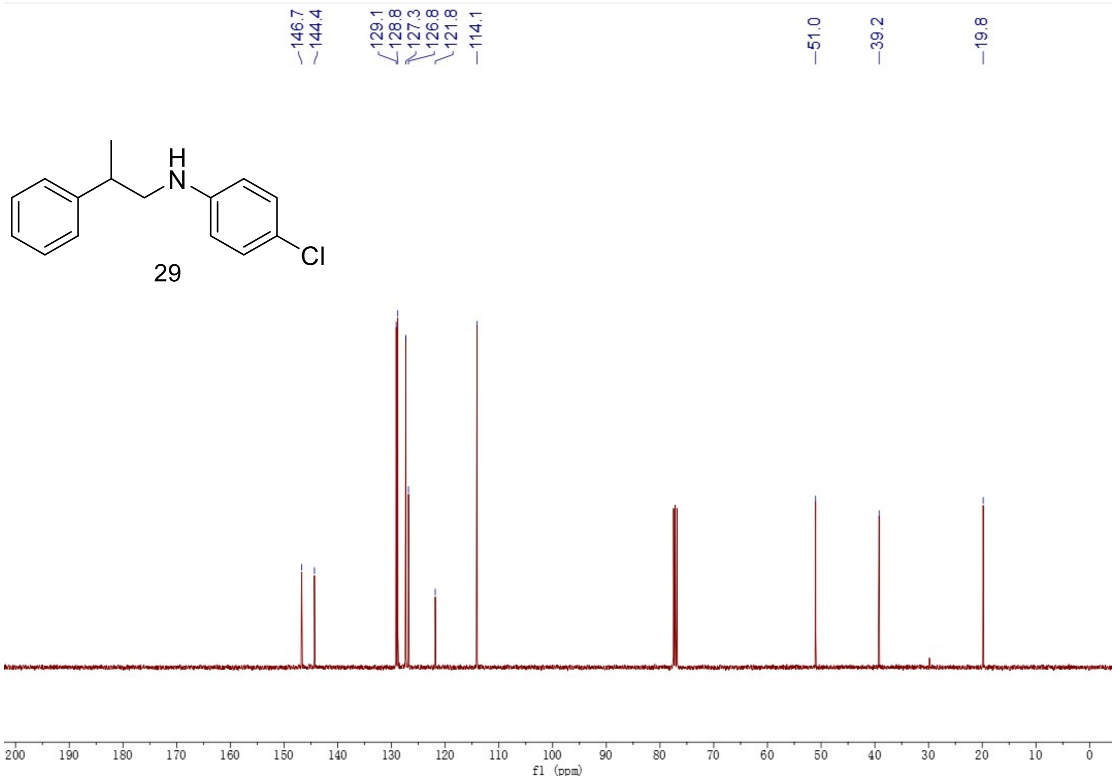
f1 (ppm)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N
Cl
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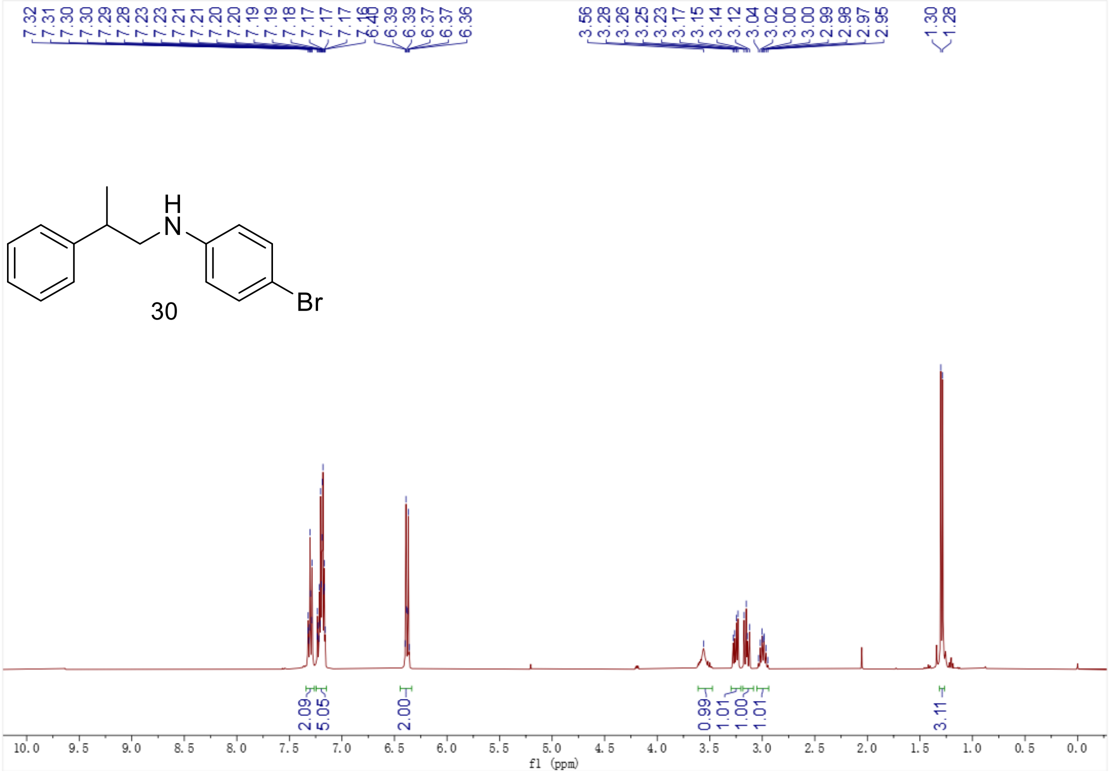
f1 (ppm)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H
N
Br
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5.05
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1.01
1.00
1.01
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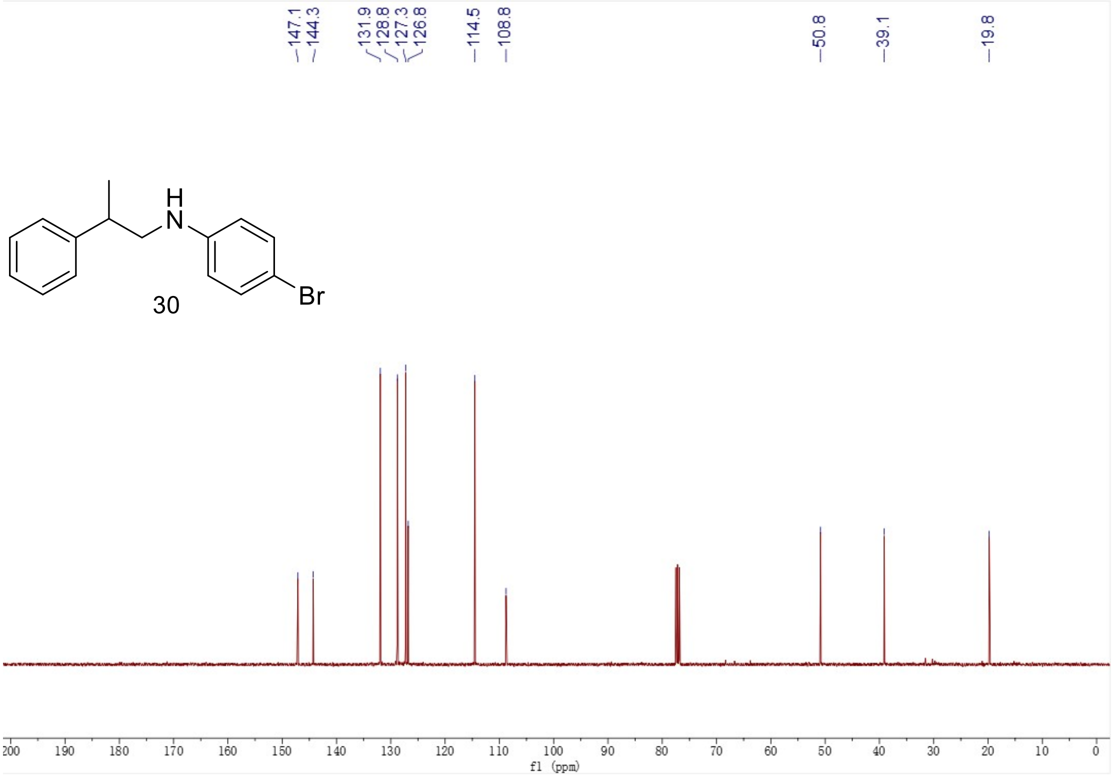
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19.8
H
N
Br
30
200
190
180
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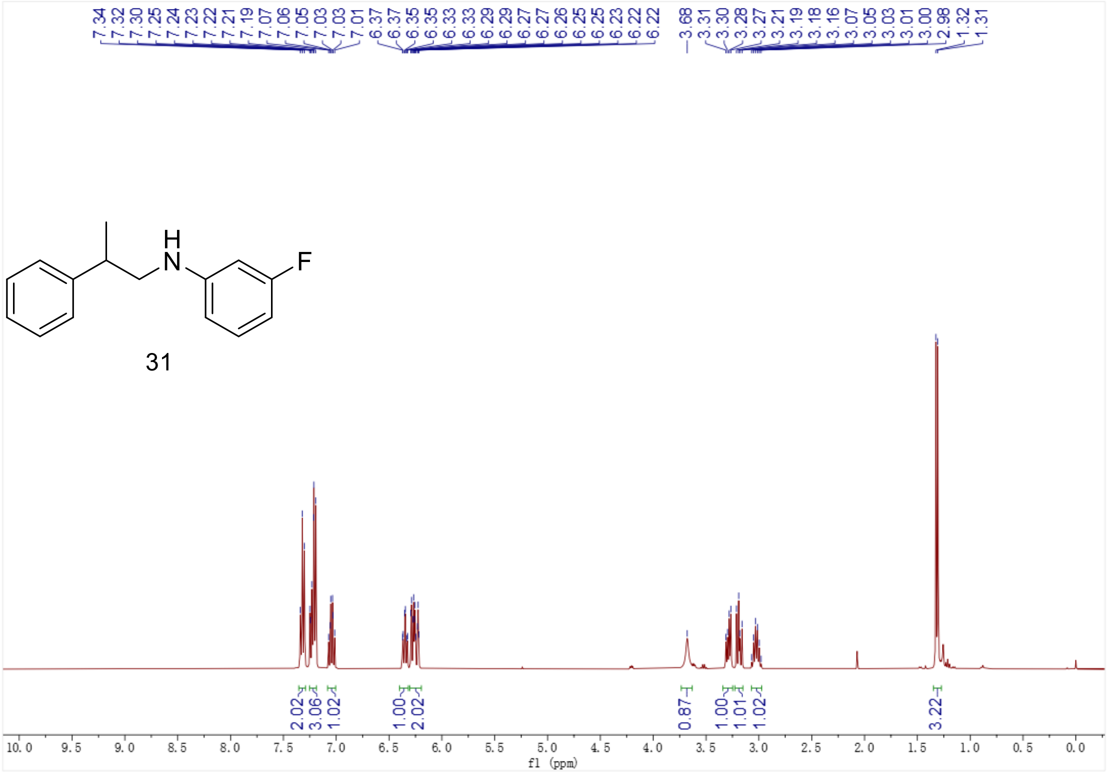
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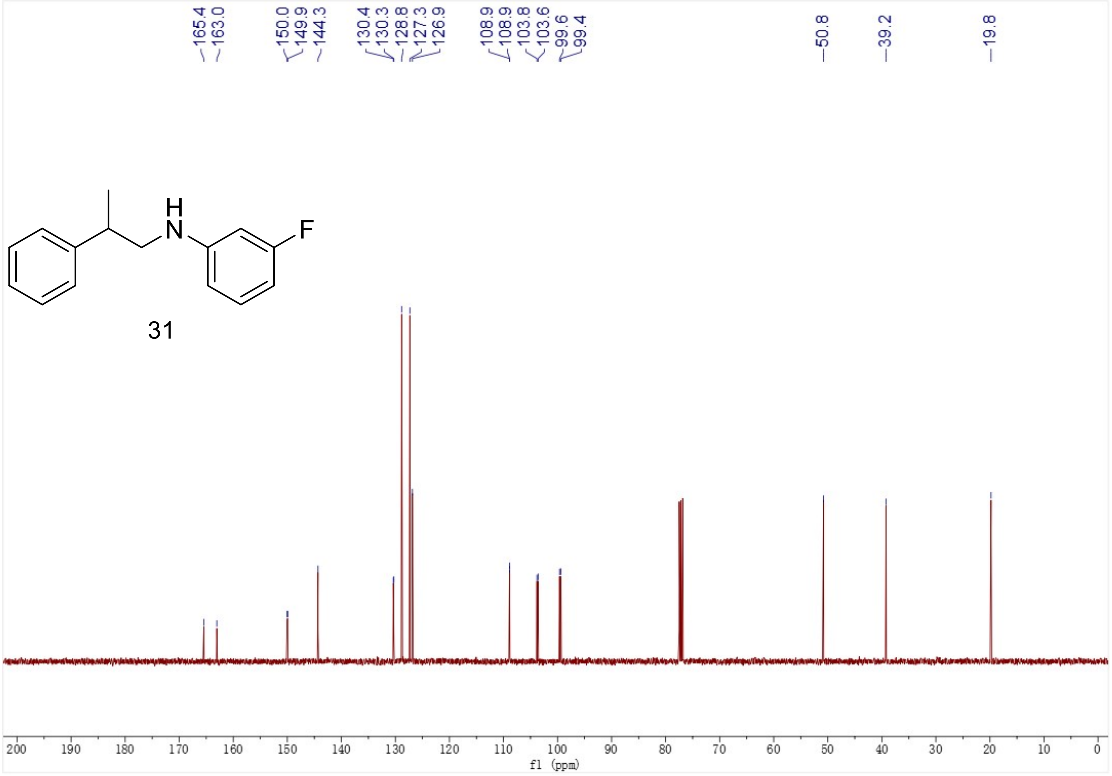
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99.4
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F
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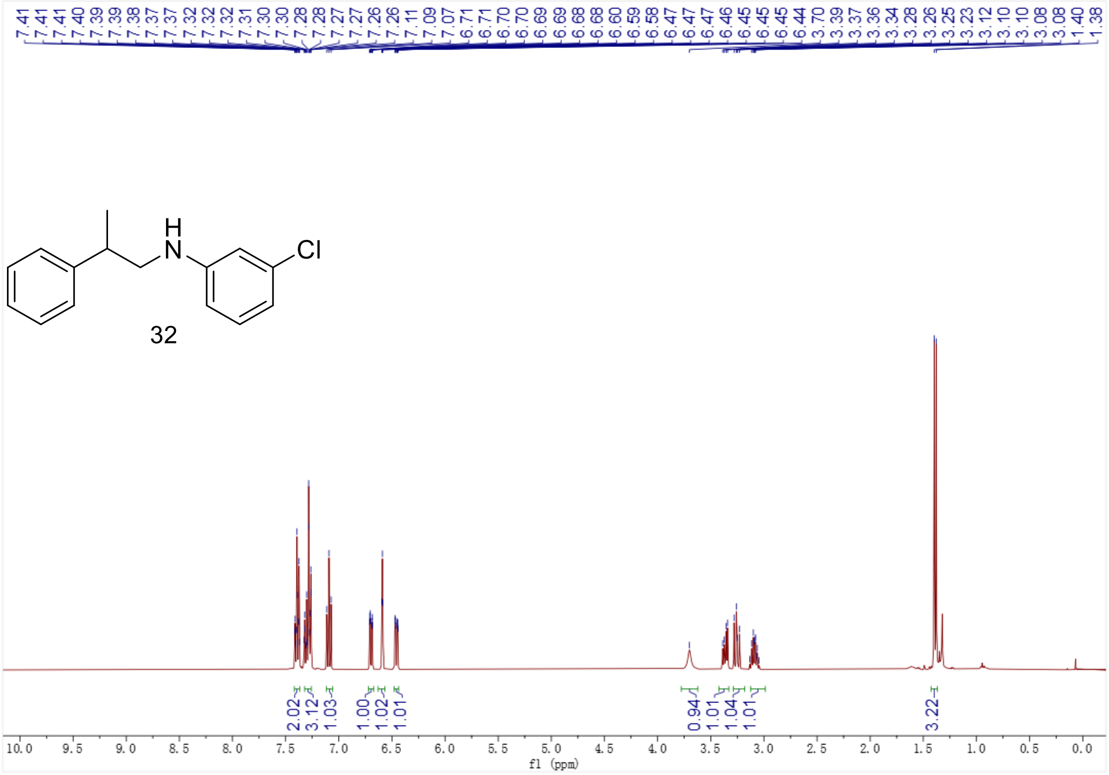
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3.08
3.08
1.40
1.38
H
N
Cl
32
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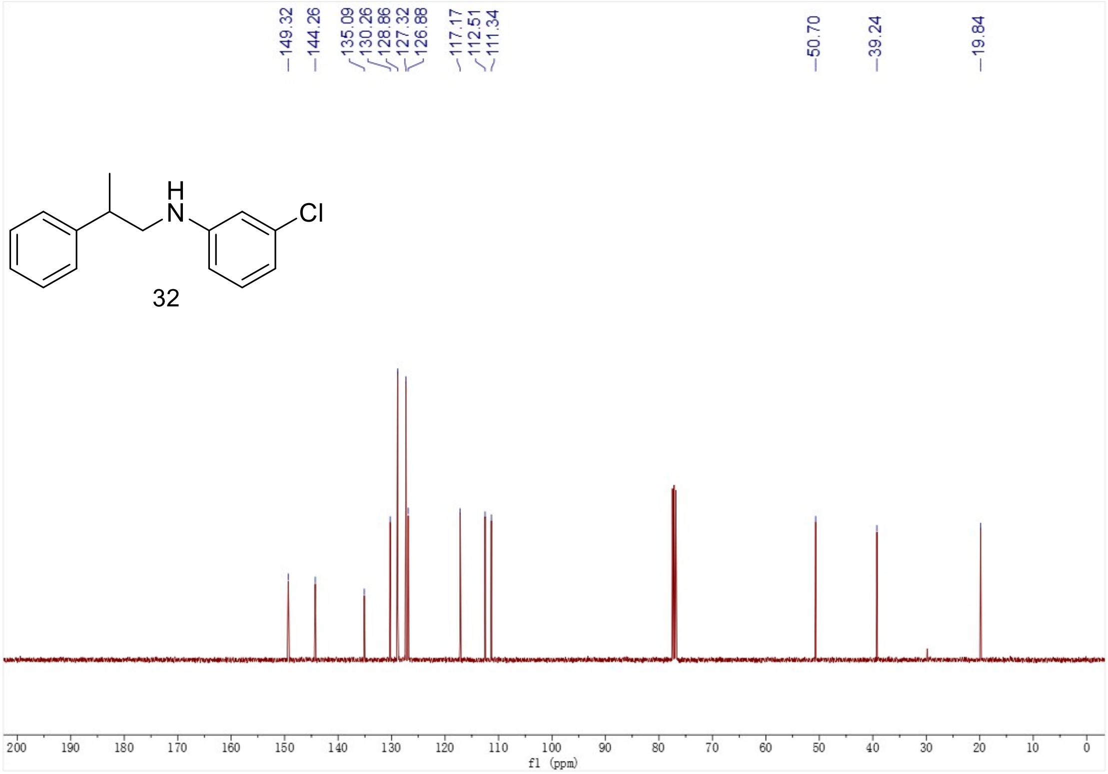
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H
N
Cl
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200
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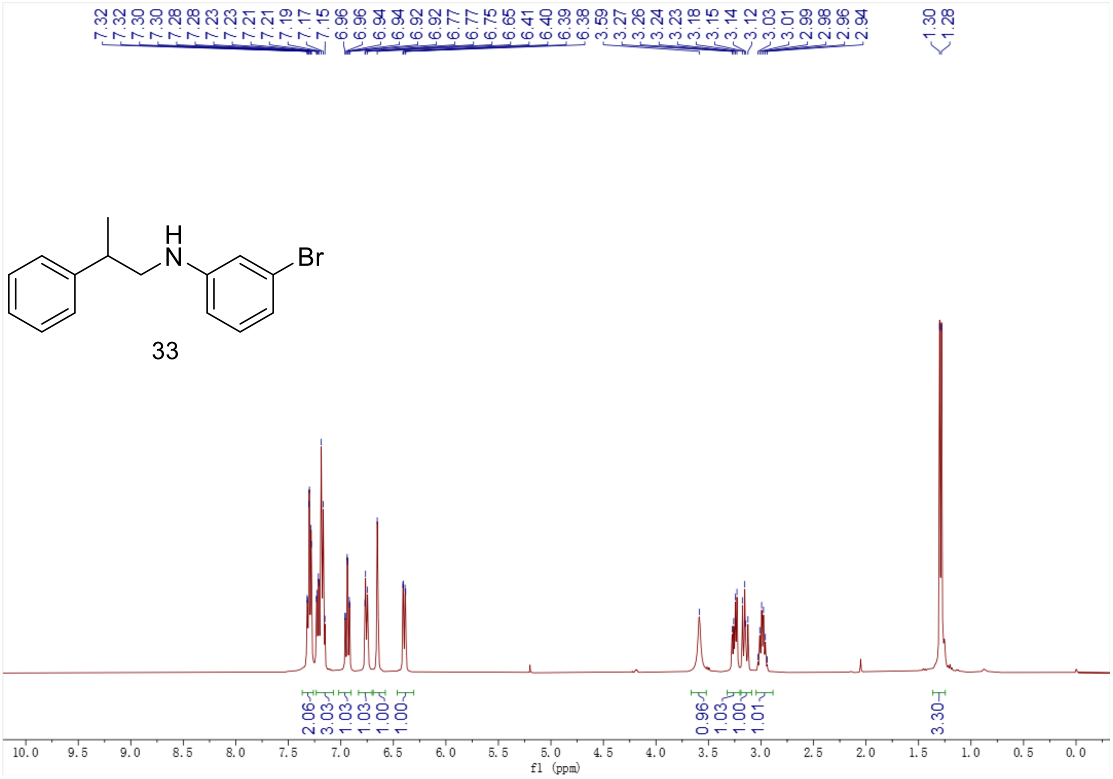
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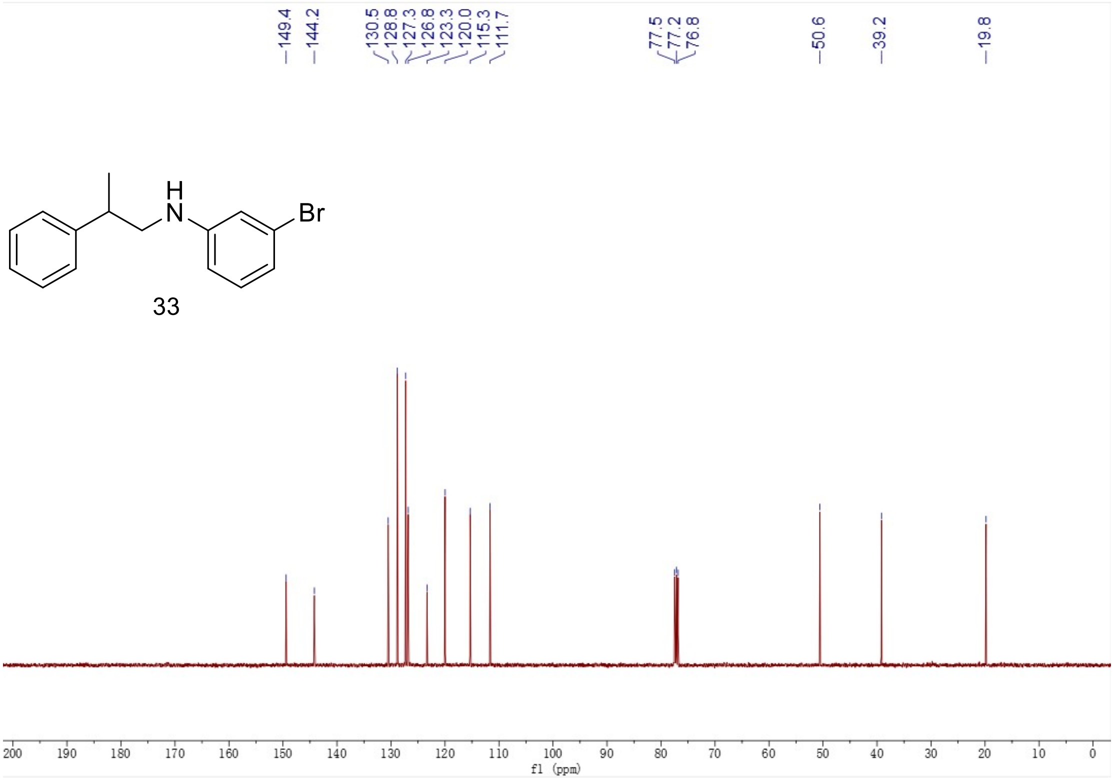
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H
N
Br
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20
10
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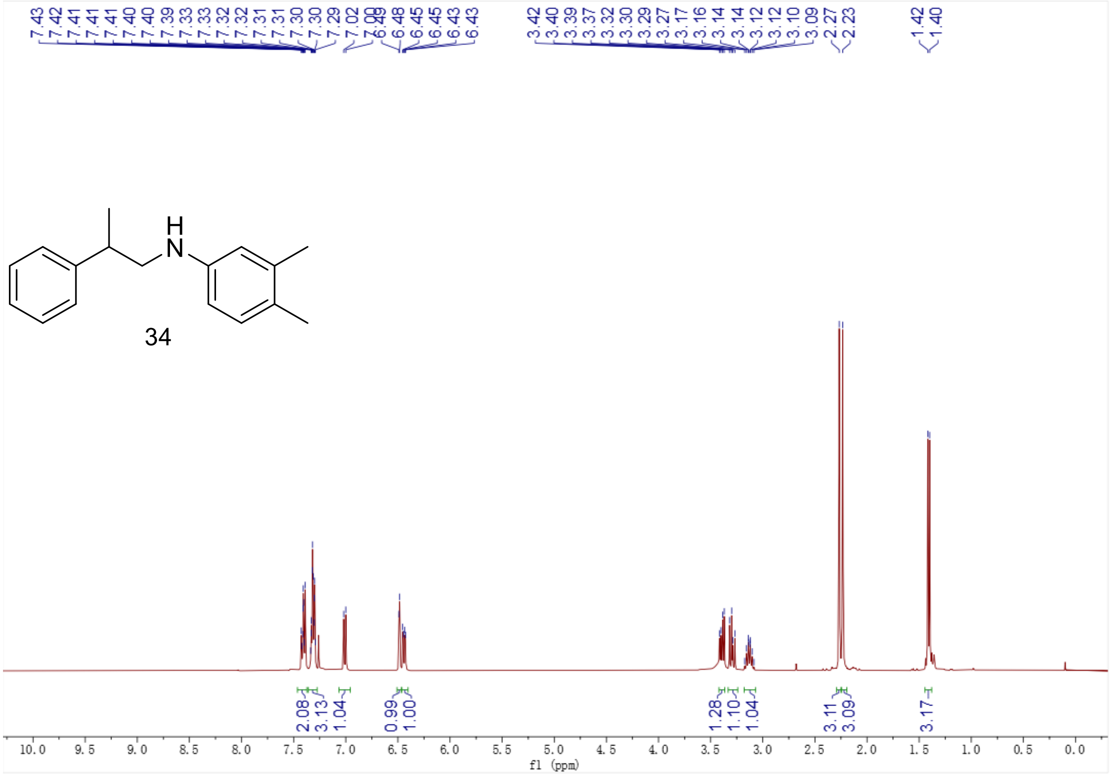
f1 (ppm)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1.10
1.04
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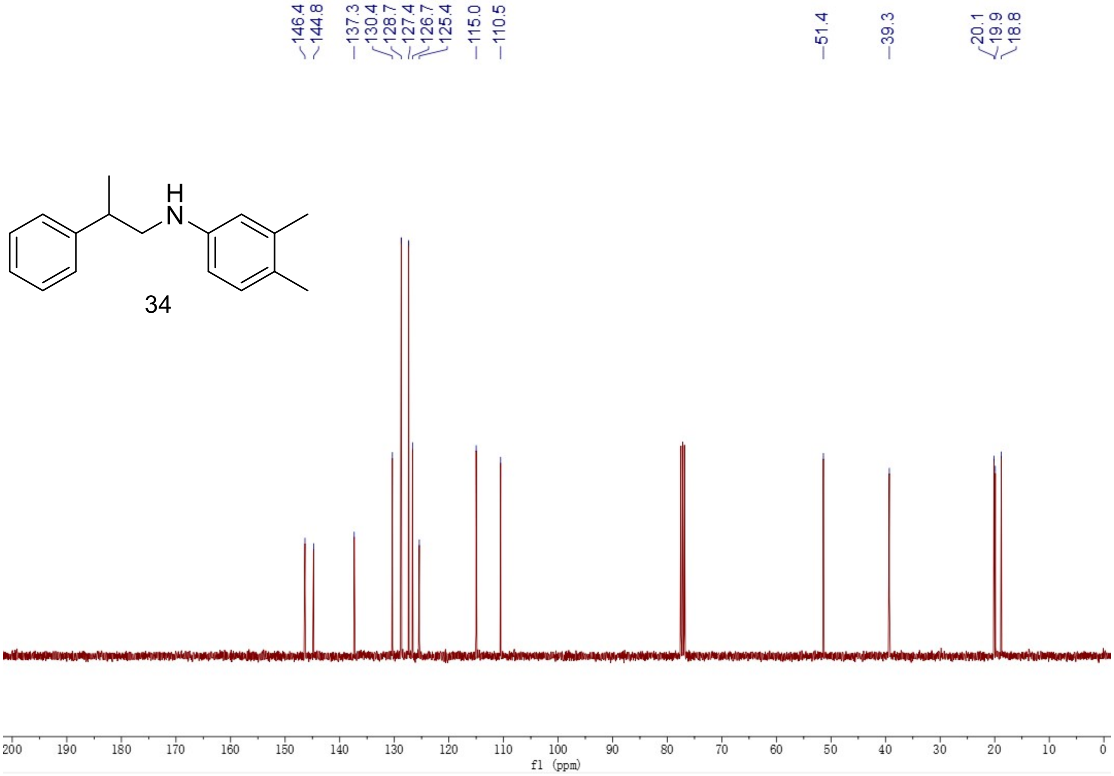
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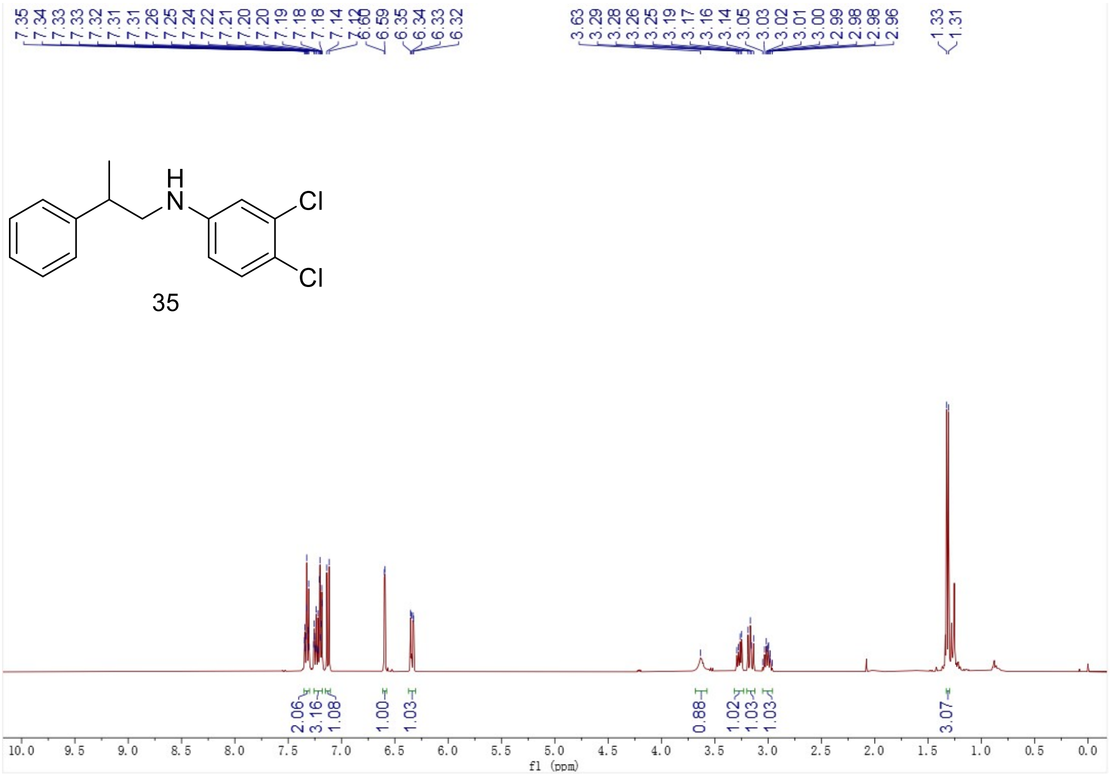
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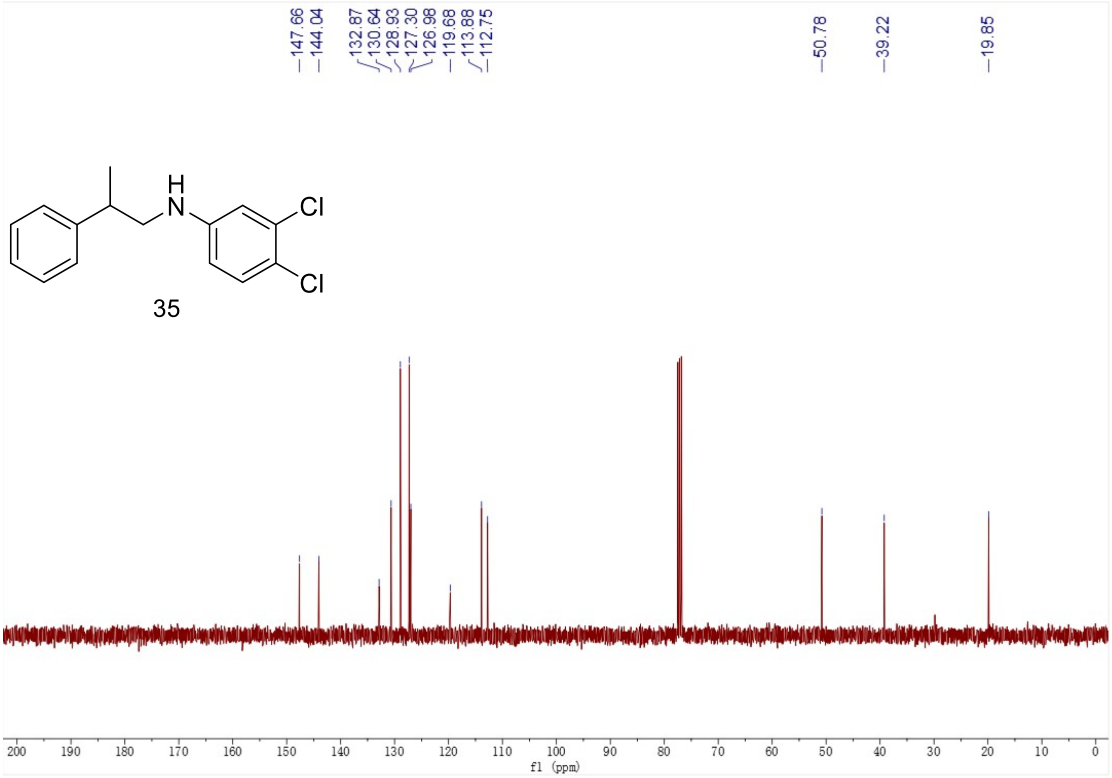
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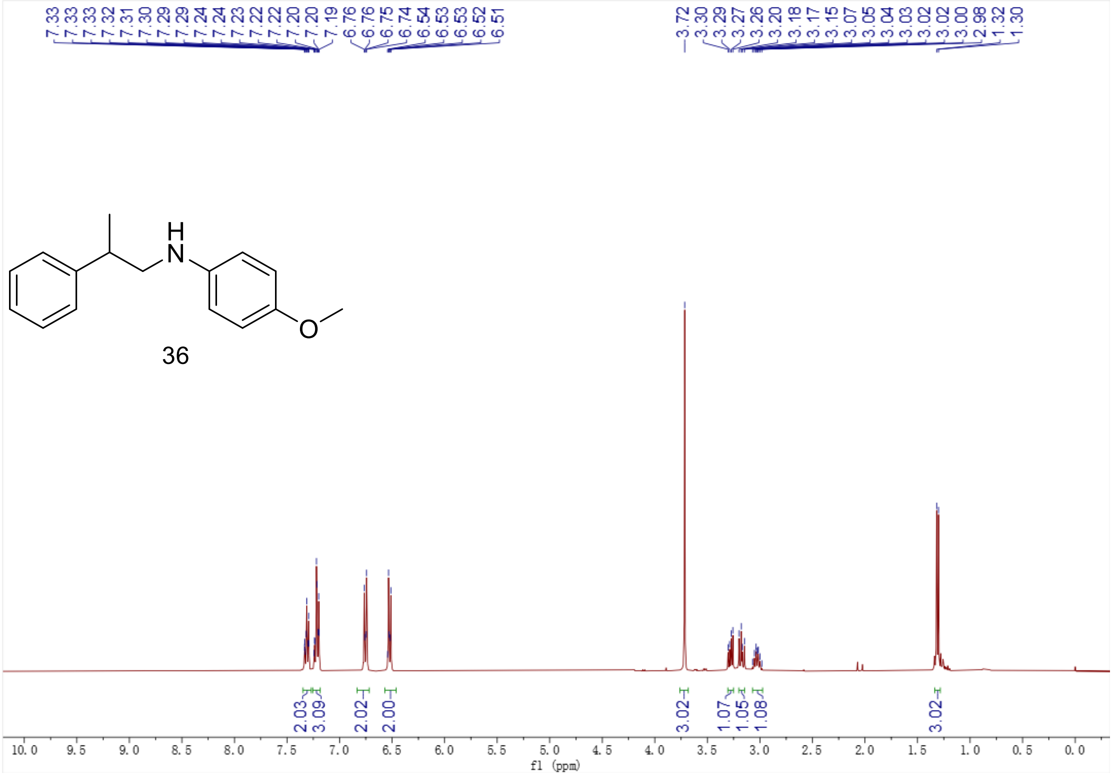
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1.05
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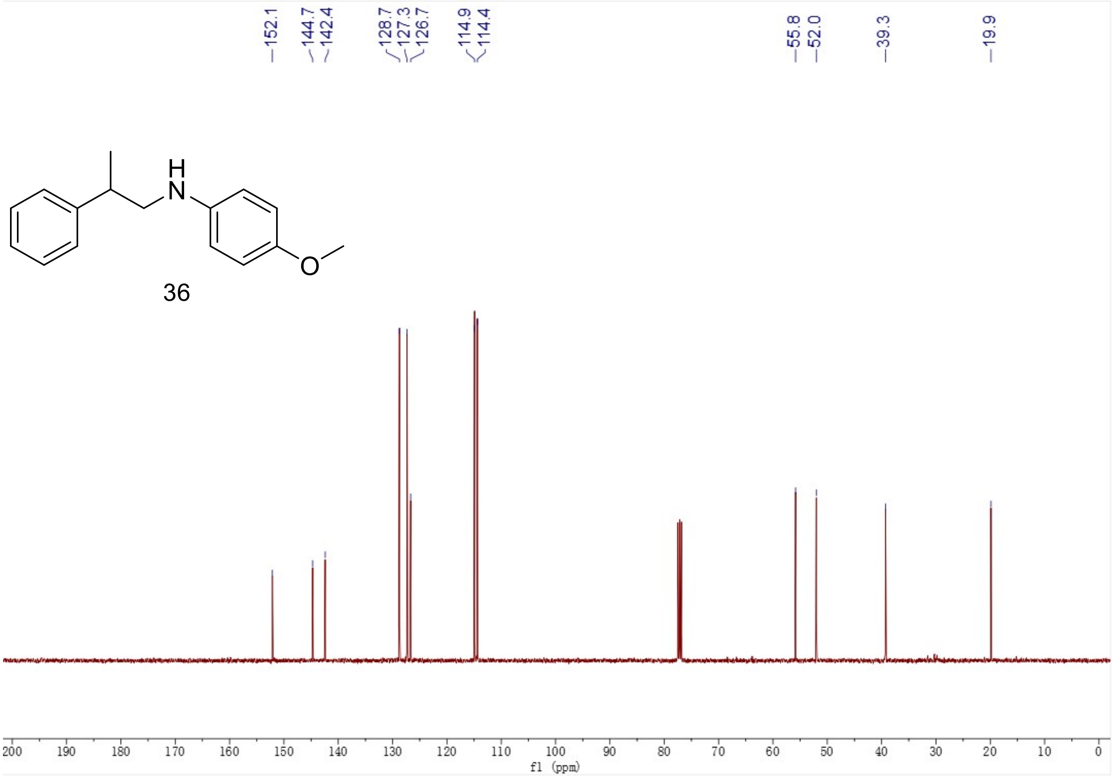
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N
O
36
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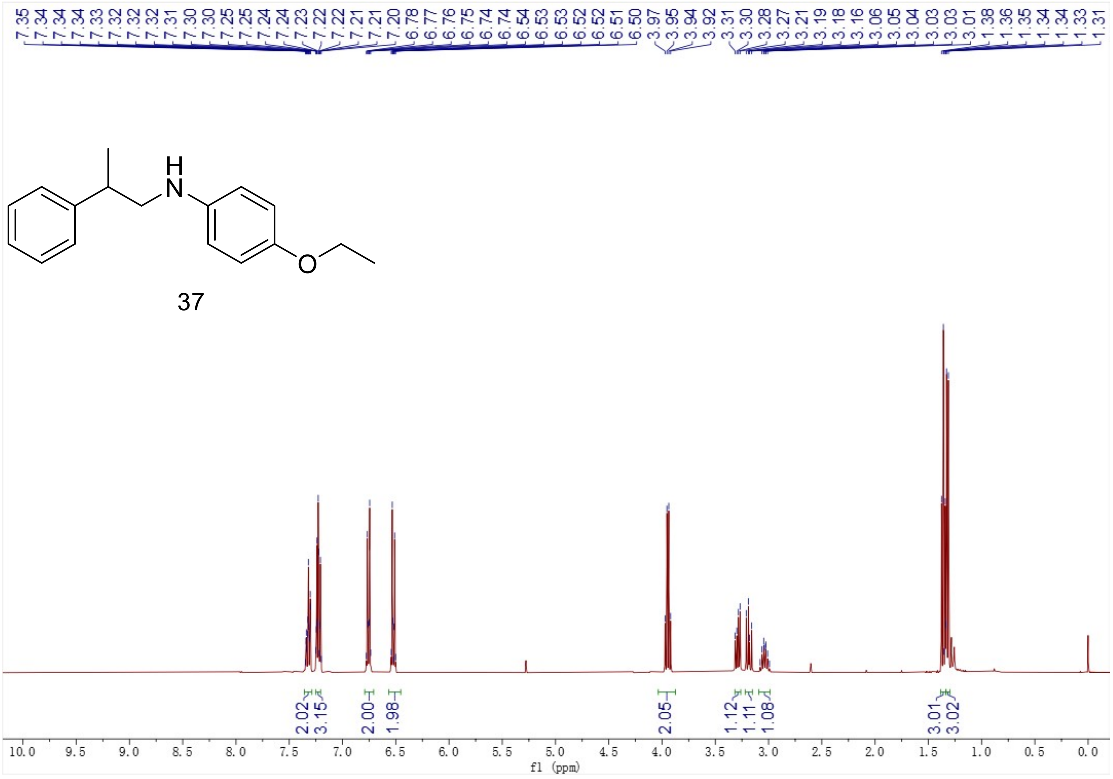
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1.11
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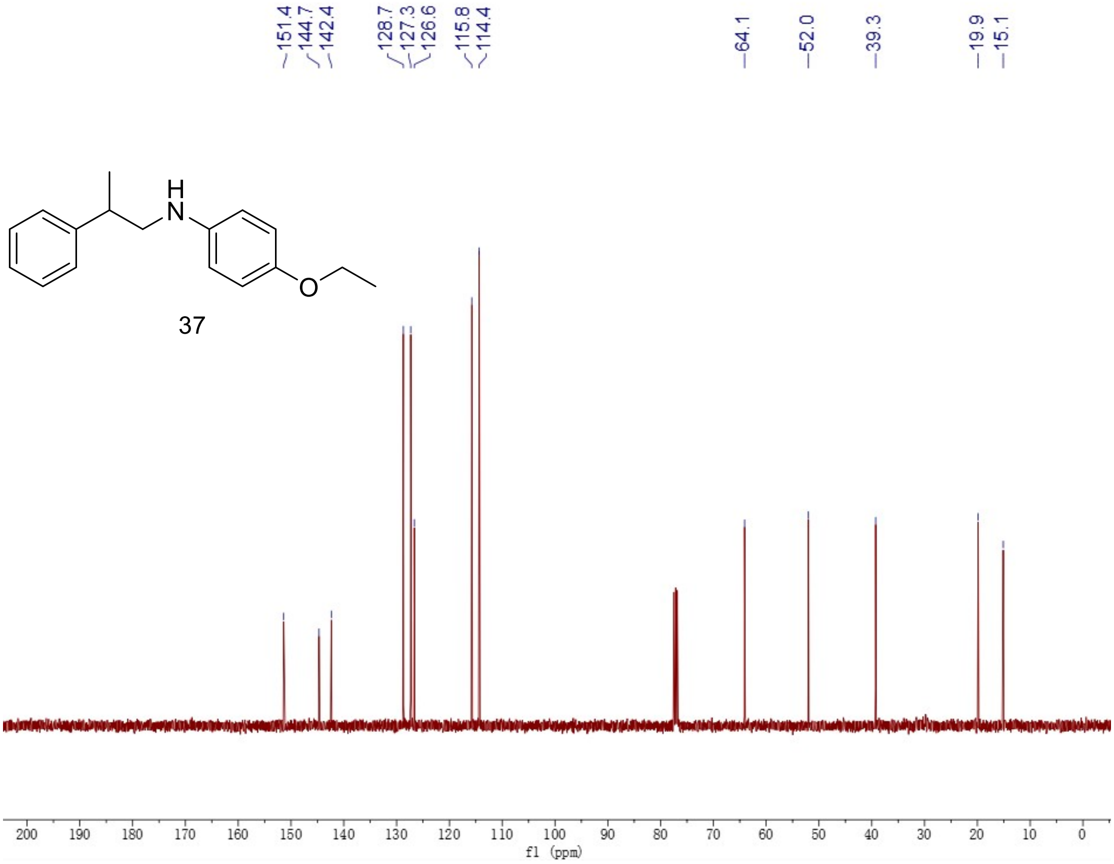
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H
N
O
37
200
190
180
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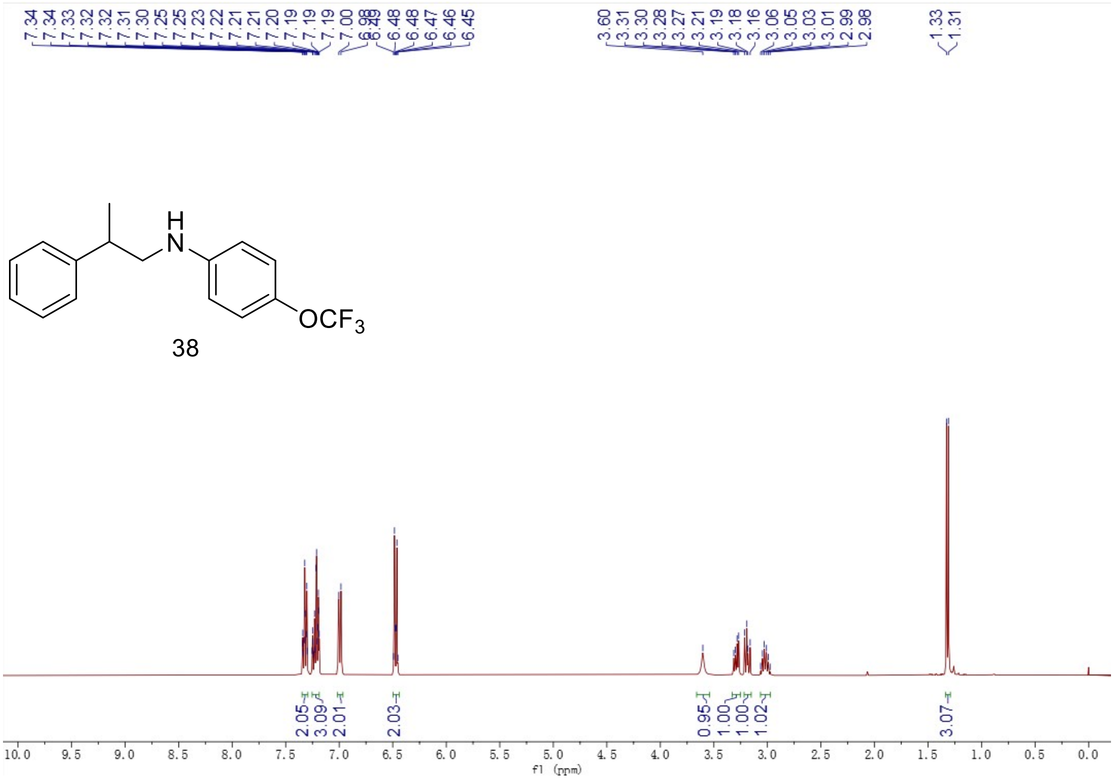
f1 (ppm)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3.01
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1.31
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OCF3
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2.03
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1.00
1.00
1.02
3.07
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6.0
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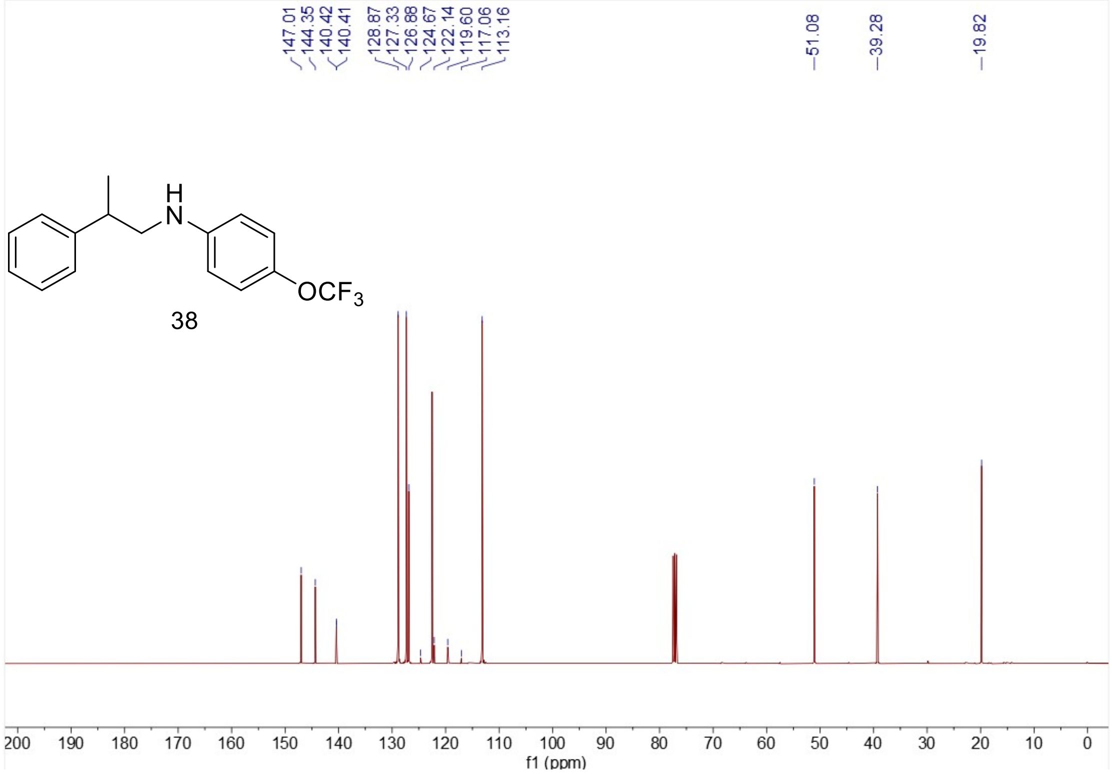
0.0
f1 (ppm)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H
N
OCF3
38
200
190
180
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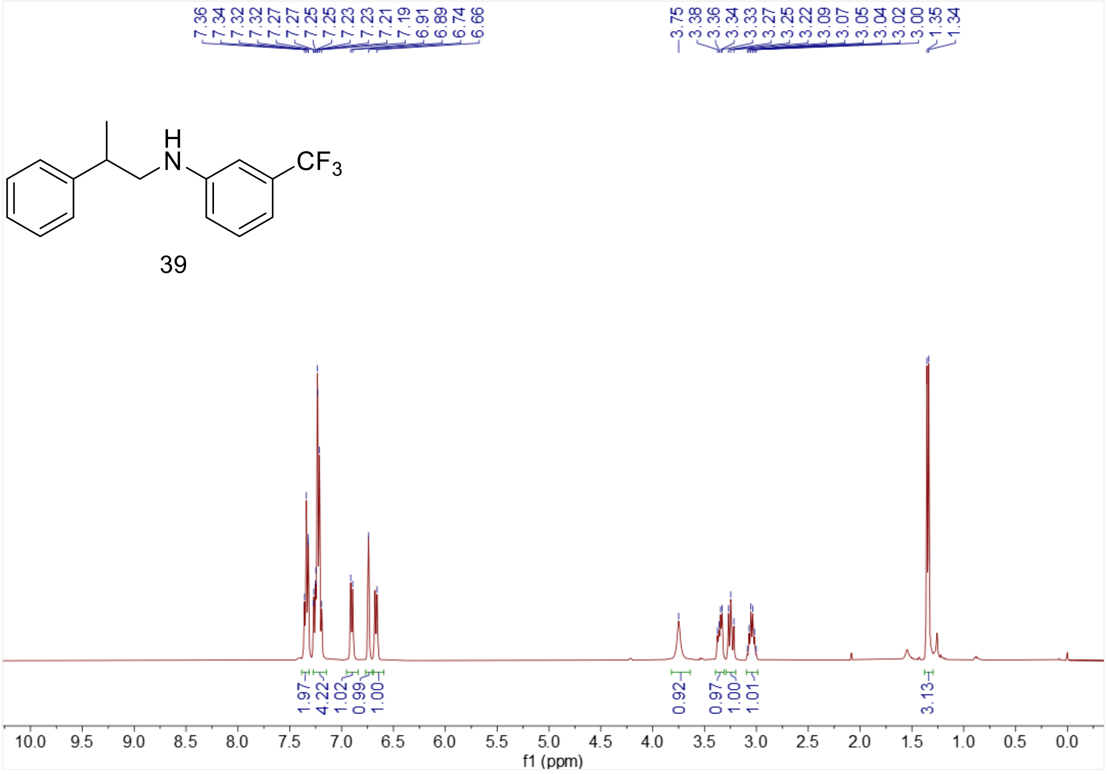
f1 (ppm)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H
N
CF3
39
1.97 4.22 1.02 0.99 1.00
0.92 0.97 1.00 1.01
3.13
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
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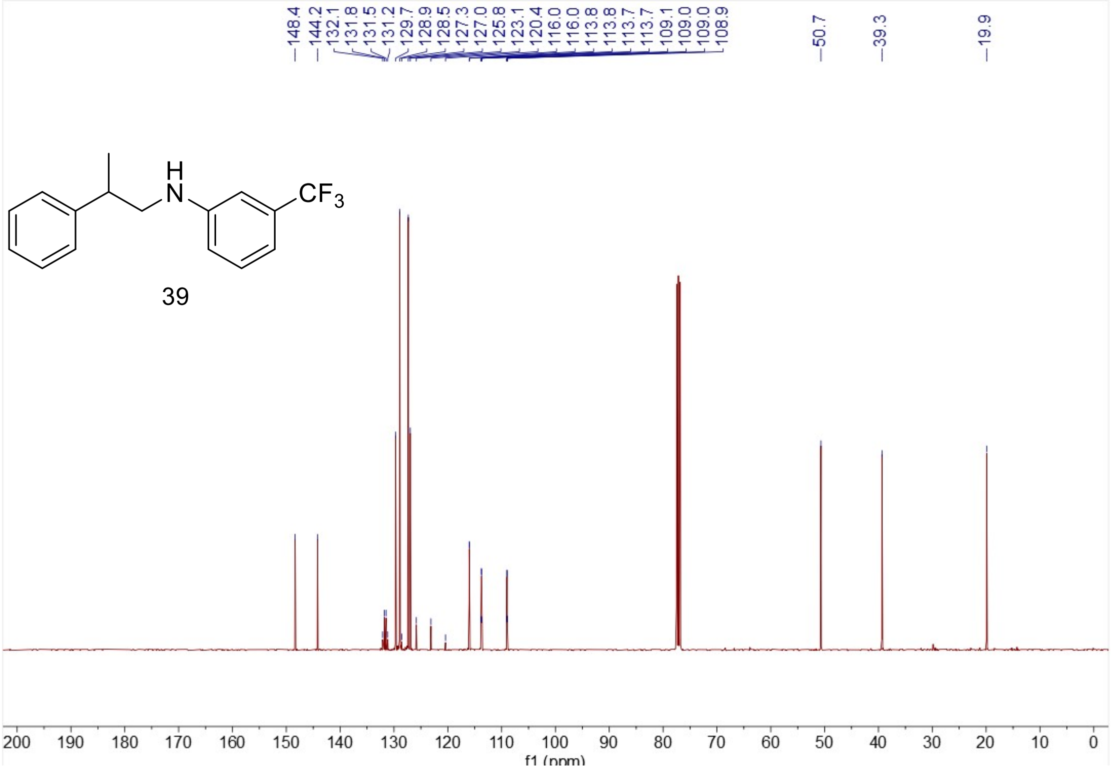
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CF3
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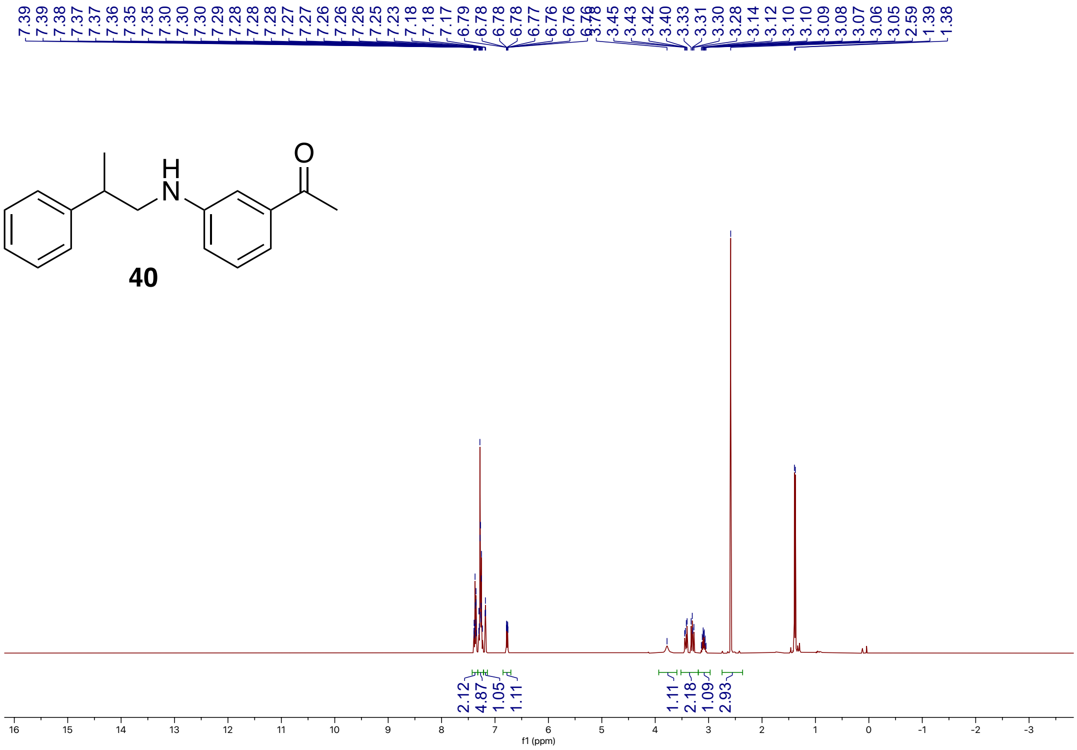
f1 (ppm)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-2
-3
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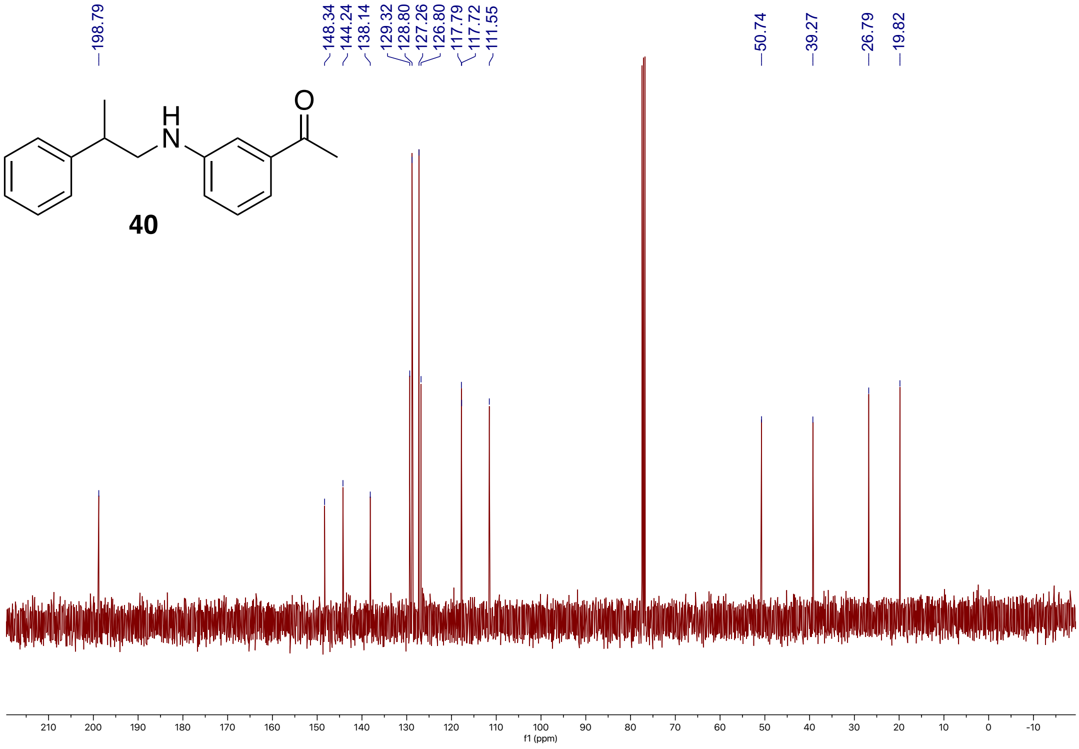
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19.82
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O
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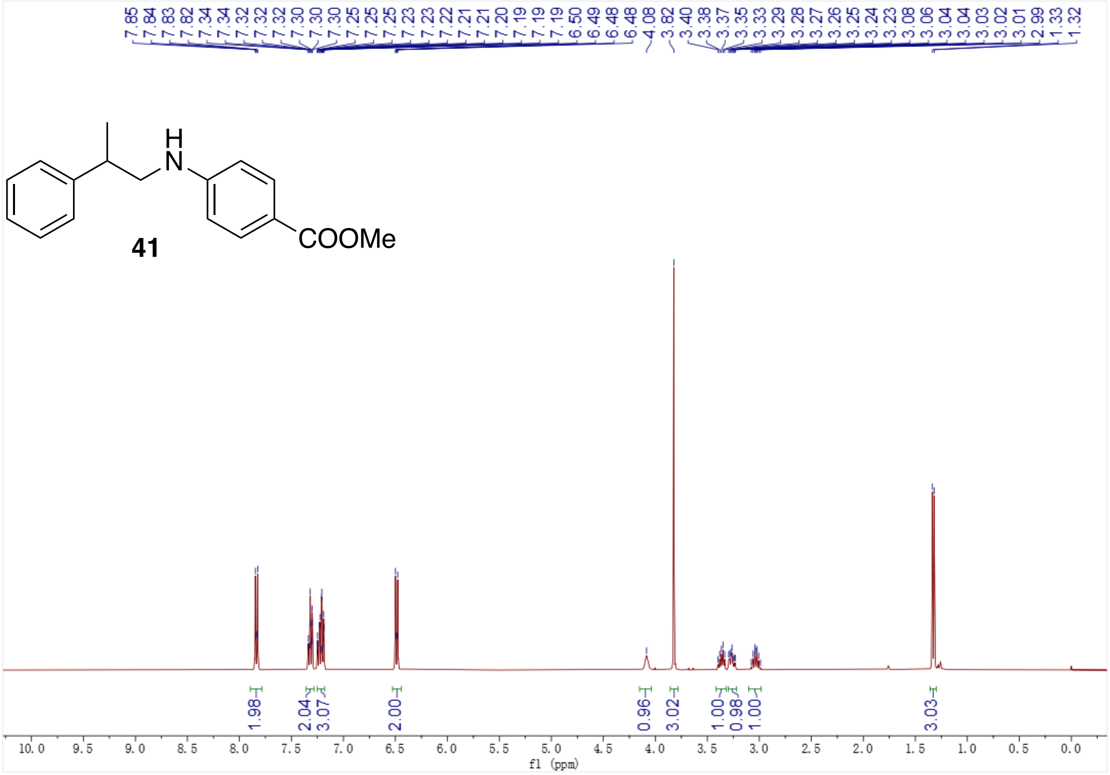
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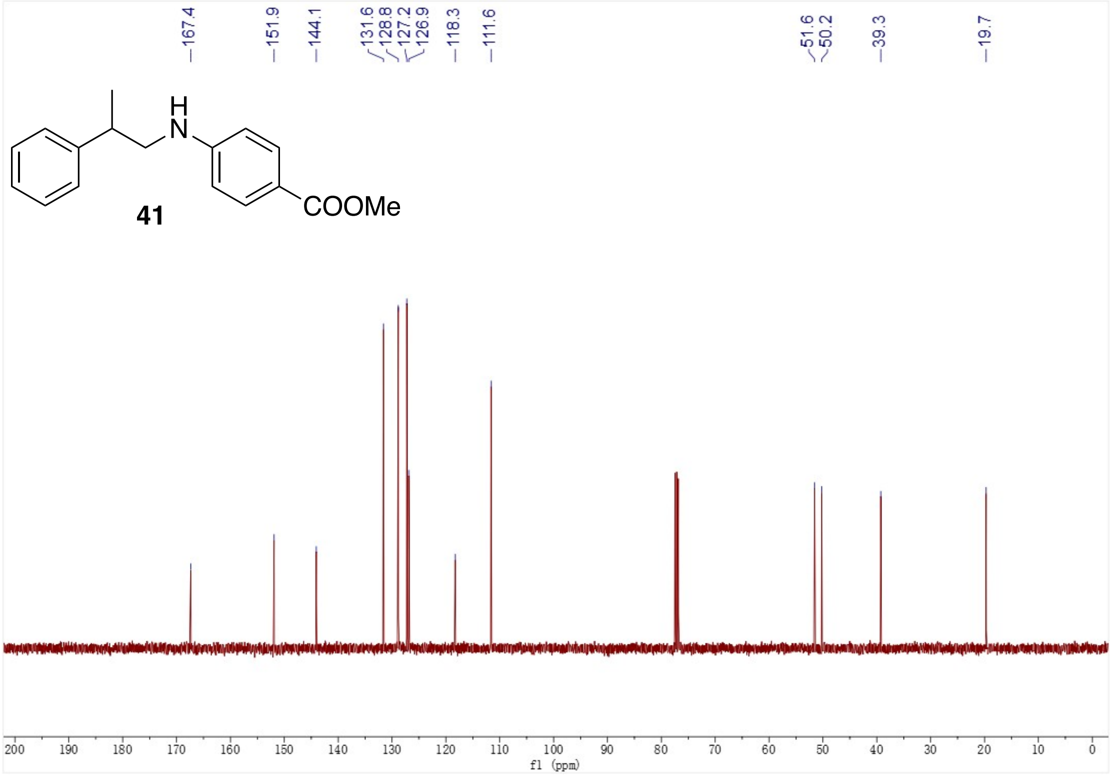
41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COOMe
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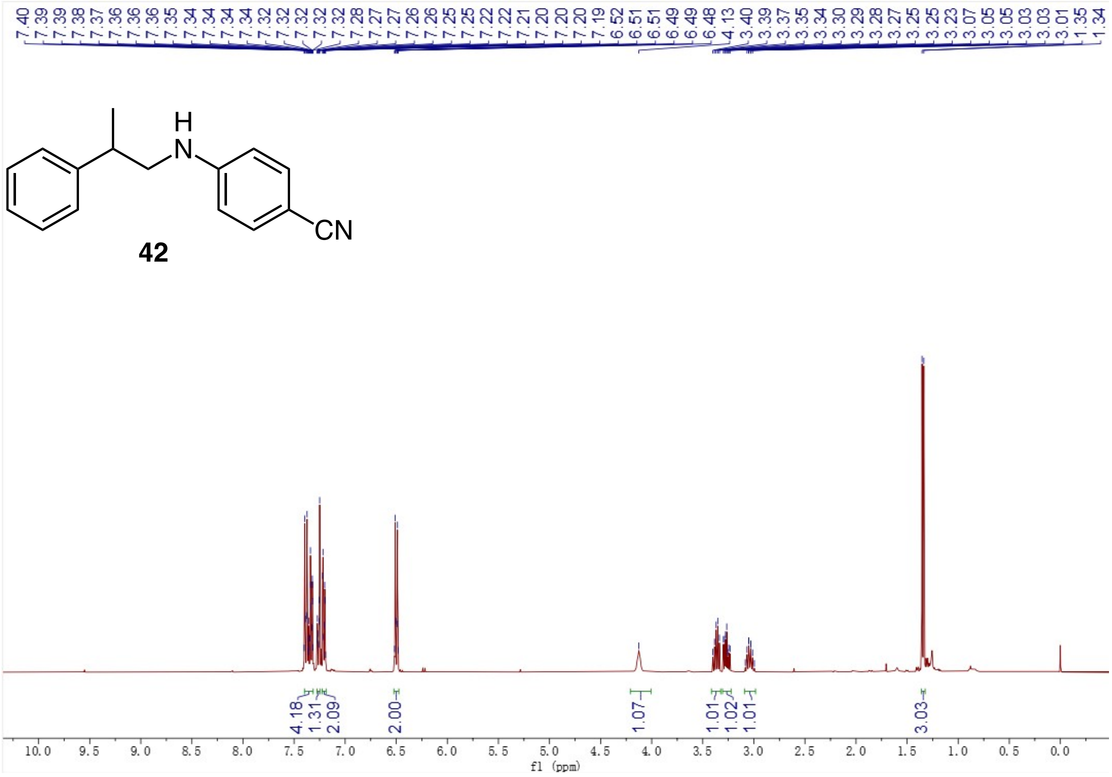
41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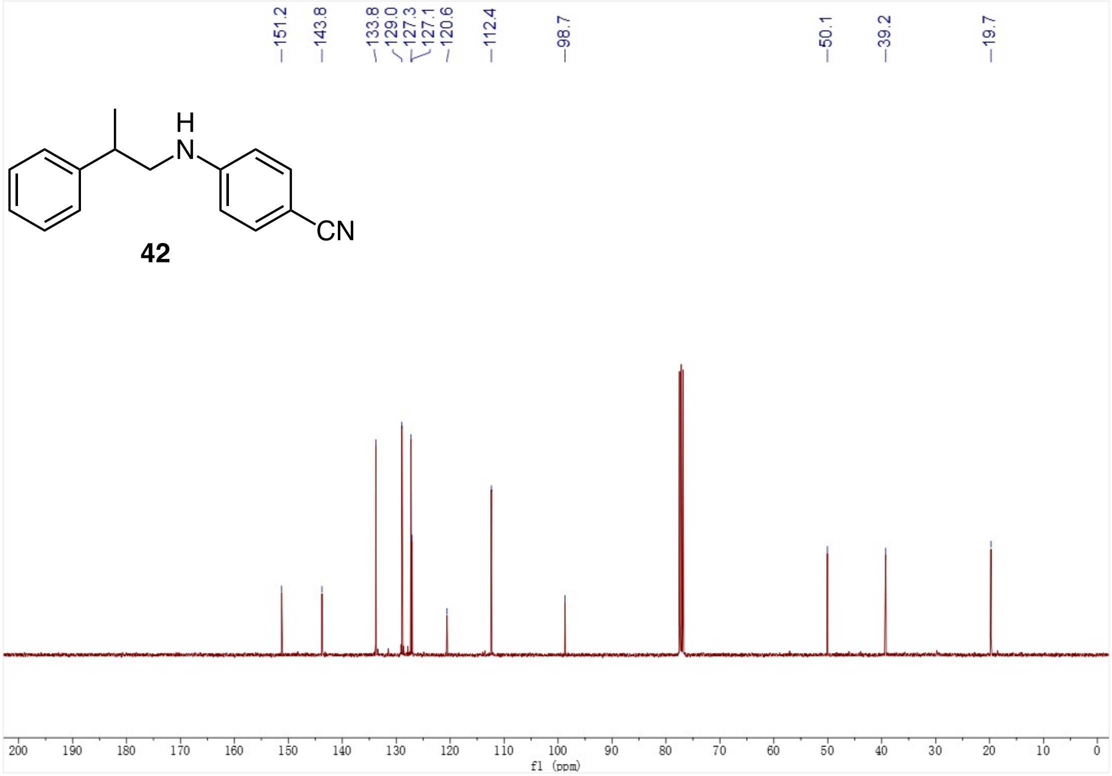
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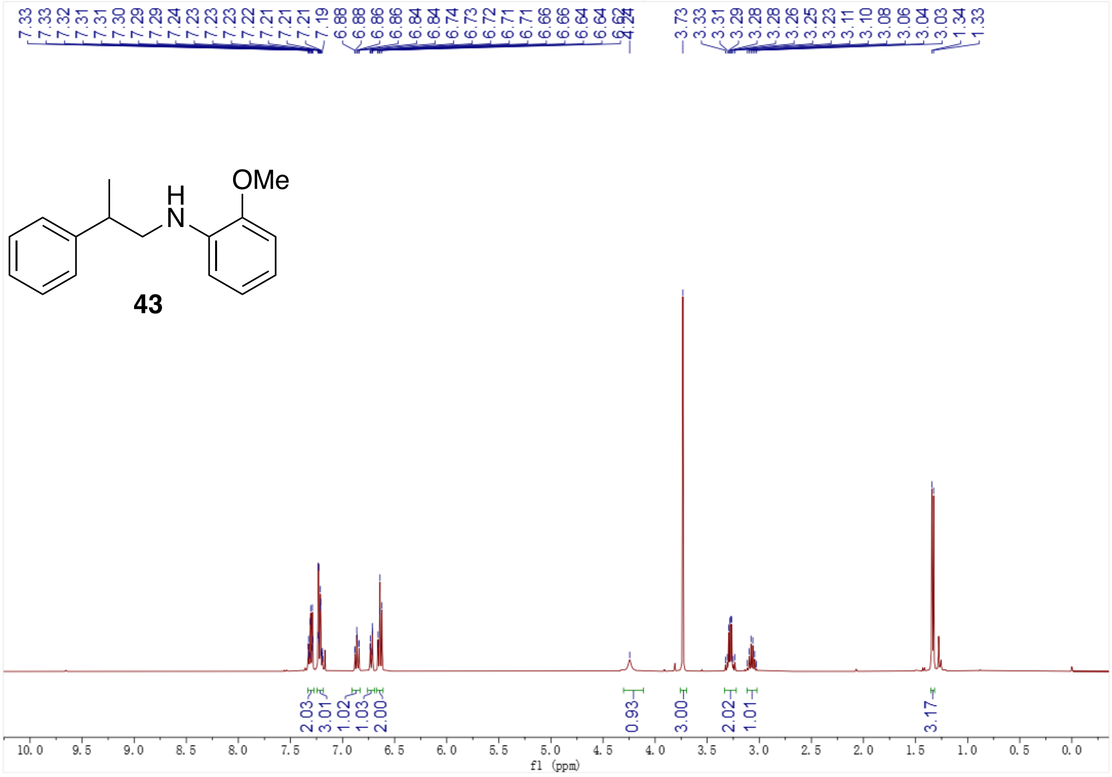
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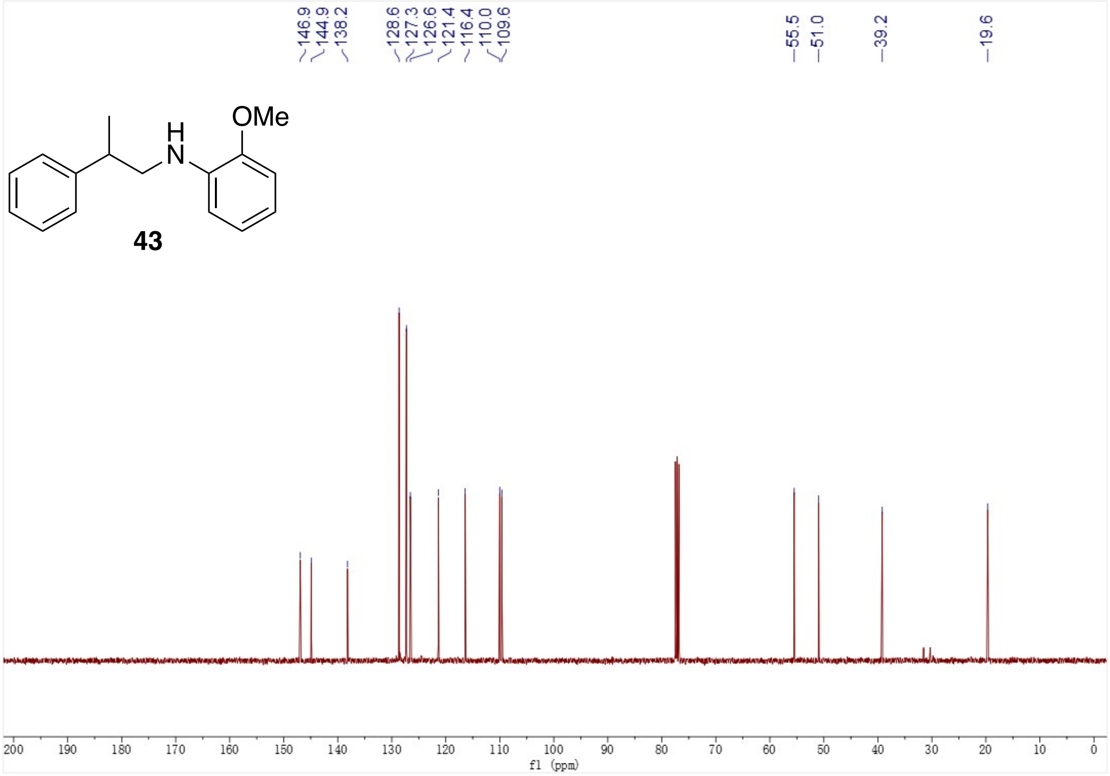
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OMe
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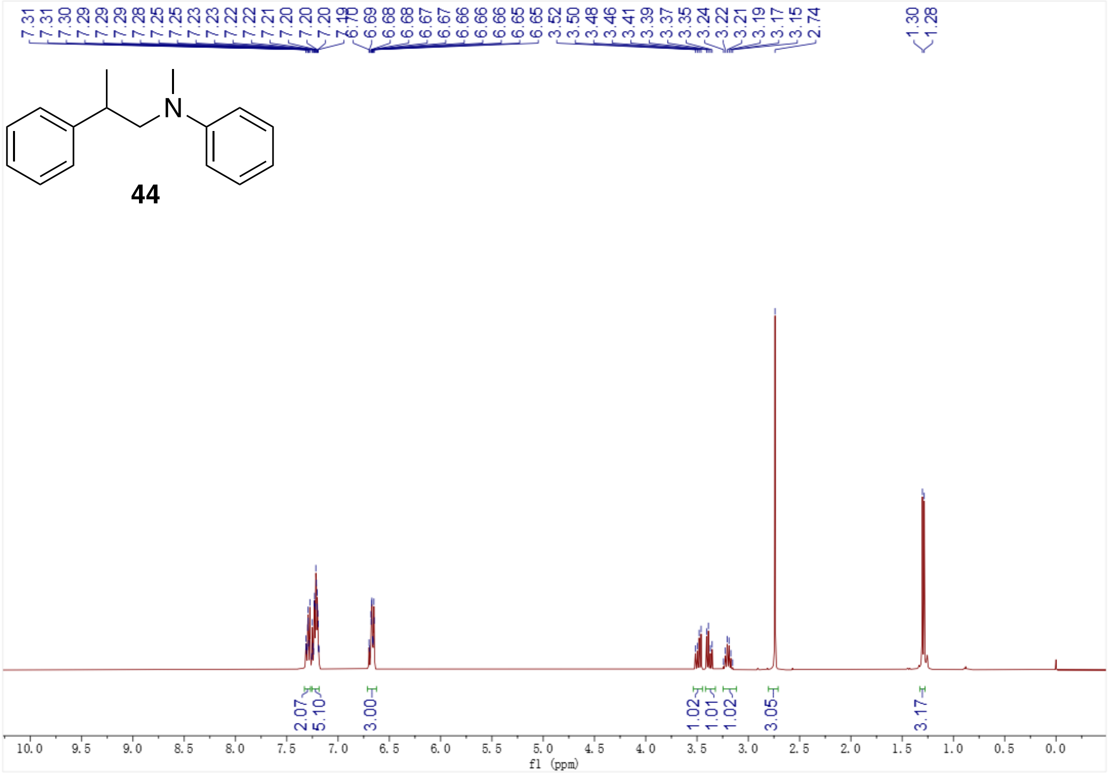
f1 (ppm)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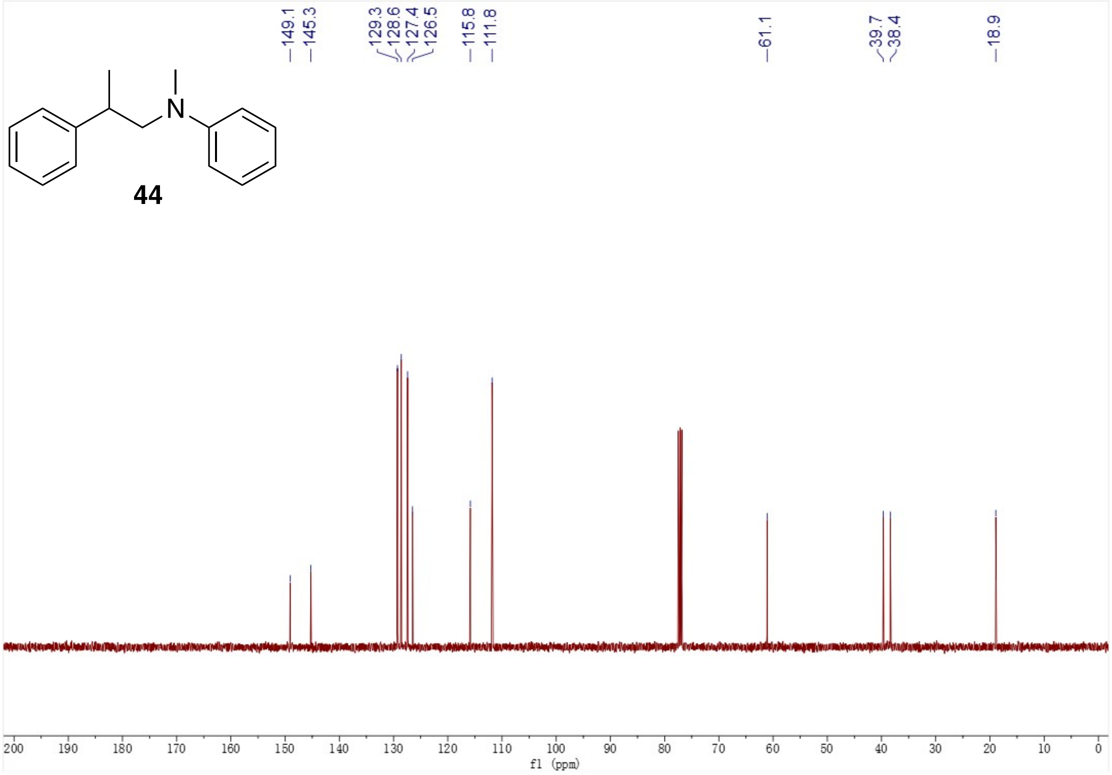
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39.7
38.4
18.9
N
44
200
190
180
170
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140
130
120
110
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90
80
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50
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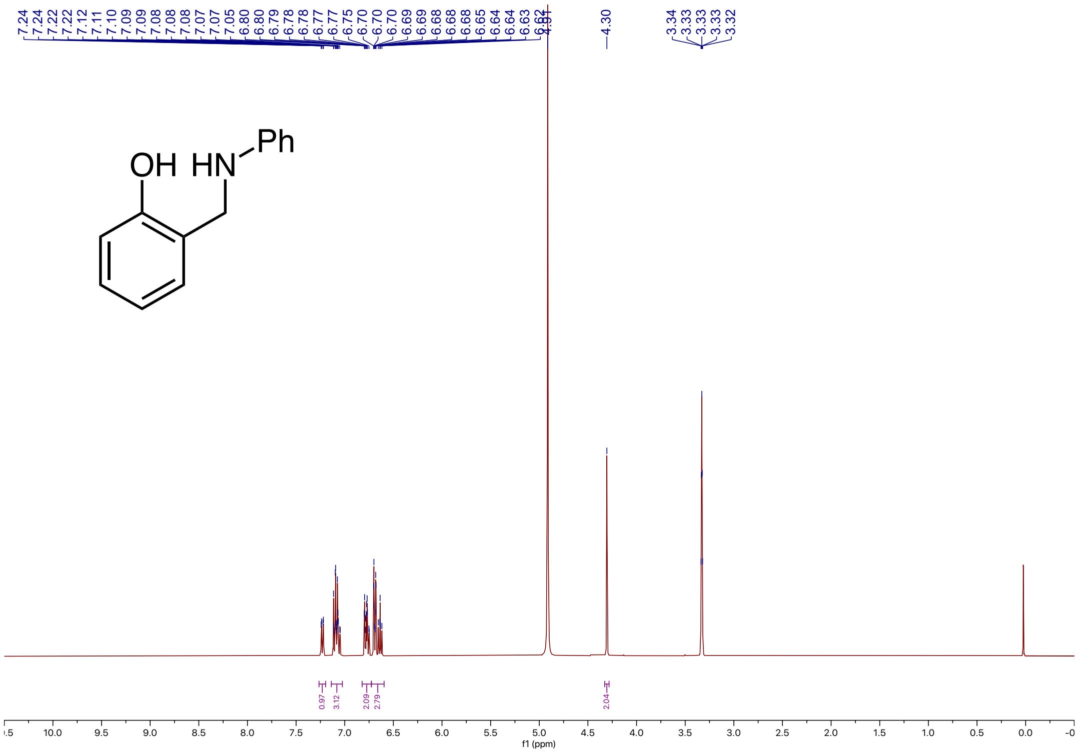
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7.24
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7.10
7.09
7.09
7.08
7.08
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6.80
6.80
6.79
6.78
6.78
6.77
6.77
6.75
6.70
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6.70
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6.69
6.68
6.68
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6.65
6.64
6.64
6.63
6.62
4.91
4.30
3.34
3.33
3.33
3.33
3.32
OH
HN
Ph
0.97
3.12
2.09
2.79
2.04
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
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f1 (ppm)