Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information for:

Pd/LA-Catalyzed Decarboxylation Enabled Exclusive [5+2] Annulation toward N-Aryl Azepanes and DFT Insights

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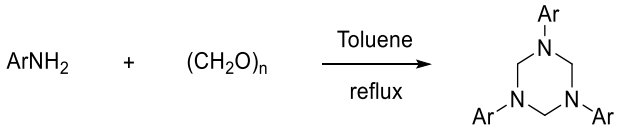
Contents:

General comments:

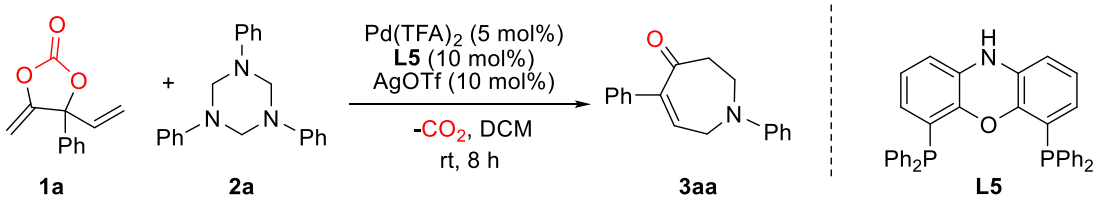
Commercially available aniline (derivatives) and solvents were purchased from Energy J&K, TCI and used without further purification. Phosphineligands **L1**, **L2**, **L4** and **L5** were purchased from Energy; **L3**[1] and **L6**[2] were prepared according to a previously reported protocol. The cyclic carbonates were synthesized according to procedures reported previously.[3] In the screening phase, the internal standard 2-methylnaphthalene was added after the reaction mixture that had been stirred at room temperature for 8 h. After that, an aliquot of the resulting mixture was taken and the yield was determined by means of ^{1}H NMR spectroscopy using $CDCl_3$ as the solvent. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded at room temperature on a Bruker AV-400 spectrometer and referenced to the residual deuterated solvent signals. All reported NMR values are given in parts per million (ppm). FT-IR measurements were carried out on a Thermo Fisher Nicolet 6700 FT-IR spectrometer or Bruker ALPHA II. High resolution mass spectra (HRMS) were obtained on a WATERS I-Class VION IMS Qtof Spectrometer. X-ray diffraction studies were performed on Bruker apex duo equipment in Frontier Institute of Science and Technology of Xi'an Jiaotong University.

General procedure for the synthesis of triazine compounds[4]



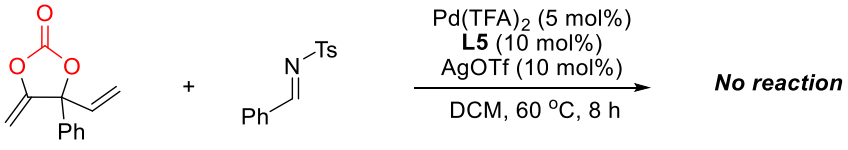
In a 100 mL round-bottomed flask equipped with a Dean-Stark apparatus, a mixture of aniline (30 mmol), paraformaldehyde (33 mmol), and toluene (50 mL) was heated with refluxing for 2 h. Then the solvent was concentrated under reduced pressure at 50 °C, a precipitate came out from the mixture. The precipitate was collected by filtration, washed with *n*-hexane several times, and dried to obtain 1,3,5-triazine.

Typical procedure for the synthesis of azepanes 3aa-3qa

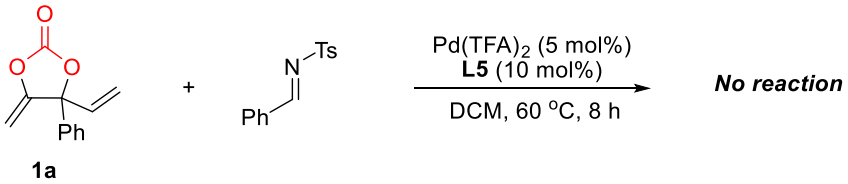


A screw-capped vial was charged with carbonate **1a** (20.2 mg, 0.1 mmol, 1.0 equiv), 1,3,5-triazine **2a** (37.8 mg, 0.12 mmol, 1.2 equiv), $Pd(TFA)_2$ (1.7 mg, 0.005 mmol, 5mol%), **L5** (5.5 mg, 0.01 mmol, 10 mol%), AgOTf (2.6 mg, 0.01 mmol, 10 mol%) and DCM (0.5 mL). The reaction mixture was stirred at room temperature for 8 h, after which the pure product was isolated (23.7 mg, 90%) by flash chromatography (PE : EA = 20 : 1) as a yellow oil.

Reaction of 1a and *N*-benzylidenetosylamide

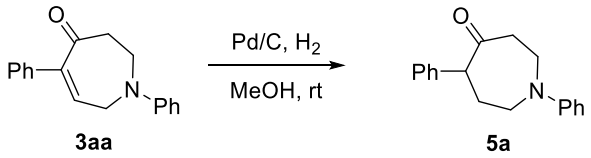


A screw-capped vial was charged with carbonate **1a** (20.2 mg, 0.1 mmol, 1.0 equiv), *N*-benzylidenetosylamide (31.1 mg, 0.12 mmol, 1.2 equiv), $Pd(TFA)_2$ (1.7 mg, 0.005 mmol, 5 mol%), **L5** (5.5 mg, 0.01 mmol, 10 mol%), AgOTf (2.6 mg, 0.01 mmol, 10 mol%) and DCM (0.5 mL). The reaction mixture was stirred at 60 °C for 8 h. After removing solvents, the residue was detected by ^{1}H NMR spectra.

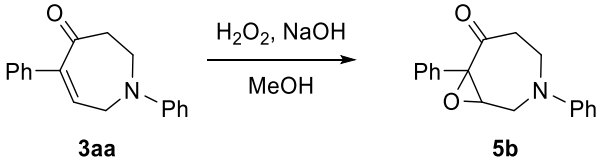


A screw-capped vial was charged with carbonate **1a** (20.2 mg, 0.1 mmol, 1.0 equiv), *N*-benzylidenetosylamide (31.1 mg, 0.12 mmol, 1.2 equiv), $Pd(TFA)_2$ (1.7 mg, 0.005 mmol, 5 mol%), **L5** (5.5 mg, 0.01 mmol, 10 mol%) and DCM (0.5 mL). The reaction mixture was stirred at 60 °C for 8 h. After removing solvents, the residue was detected by ^{1}H NMR spectra.

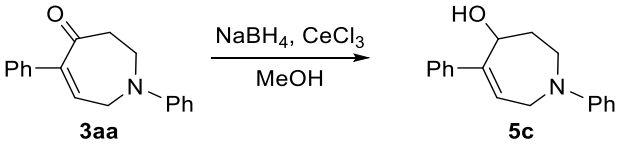
Synthetic transformations of 3aa



To a solution of **3aa** (0.1 mmol, 26.3 mg, 1.0 equiv) in MeOH (2 mL). This mixture was degassed of dissolved air and purged with an argon atmosphere. To it 10% Pd/C (10 mol%, 1.1 mg) was carefully added. The above reaction mixture was degassed and purged with hydrogen. The reaction is allowed to stir for 16 h at room temperature. After the completion of the reaction, the mixture was filtered through a celite pad and concentrated under reduced pressure and purified by flash column chromatography (PE : EA = 20 : 1) to obtain the desired product **5a** (22.8 mg, 86%) as a white solid.

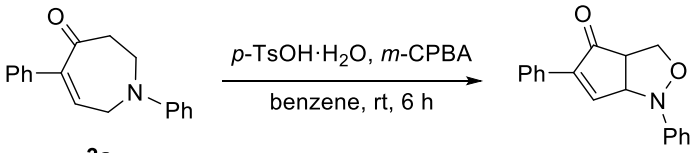


To a solution of **3aa** (0.1 mmol, 26.3 mg, 1.0 equiv) in MeOH (0.5 mL) cooled to 0 °C was added a solution of H_2O_2 (30% in water, 30 μL). To this solution was then added slowly an aqueous solution of NaOH (10%, 15 μL). The resulting solution was then stirred at 0 °C for 1 h then at room temperature for 4 h. A saturated aqueous solution of NaCl (3 mL) was then added and the product was then extracted with Et_2O (3 × 3 mL). The combined organic phases were dried over $MgSO_4$, filtered and concentrated in vacuo, to afford the crude product, which was then purified further by column chromatography (PE : EA = 20 : 1) to afford the desired product **5b** (17.0 mg, 61%) as a yellow solid.



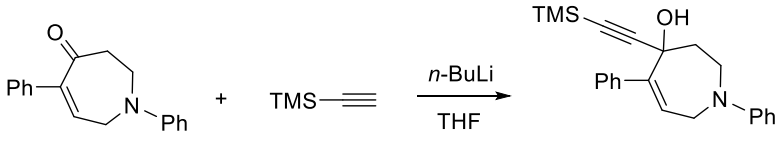
3aa **5c**

Amagnetically stirred solution of **3aa** (26.3 mg, 0.1 mmol) and $CeCl_3$ (29.5 mg, 0.12 mmol, 1.2 equiv) in methanol (1.0 mL) was cooled to 0 °C and then treated, in portions, with sodium borohydride (4.5 mg, 0.12 mmol, 1.2 equiv). The resulting mixture was stirred at 0 °C for 1 h. The reaction was quenched with water (3 mL) and the aqueous phase was extracted with ethyl acetate (3 × 3 mL). The combined organic phases were dried ($MgSO_4$), filtered, and concentrated under reduced pressure. The crude product was then purified further by column chromatography (PE : EA = 10 : 1) to afford the desired product **5c** (22.5 mg, 85%) as a yellow oil.



3a **5d**

To a solution of **3aa** (26.3 mg, 0.1 mmol) in dry benzene (1 mL) were added *m*-chloroperbenzoic acid (50.5 mg, 0.25 mmol, 85%, Energy) and a catalytic amount of *p*-toluenesulfonic acid (1.9 mg, 0.01 mmol, 10 mol%). The mixture was stirred at room temperature for 6 h. After the completion of the reaction, the mixture was quenched with H_2O and and extracted with ethyl acetate. The combined organic phases were dried ($MgSO_4$), filtered, and concentrated under reduced pressure. The crude product was then purified further by column chromatography (PE : EA = 10 : 1) to afford the desired product **5d** (16.4 mg, 59%) as a yellow solid.

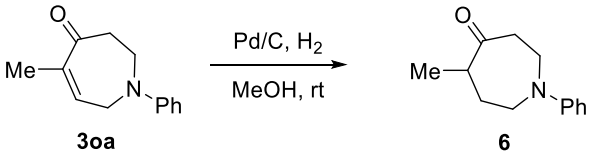


3aa **5e**

To a solution of trimethylsilylacetylene (0.31 mL, 2.2 mmol) in anhydrous THF (1 mL) was slowly added *n*-BuLi (1.25 mL, 2 mmol, 1.6 M in hexanes) at -78 °C under nitrogen atmosphere. The reaction mixture was stirred at 0 °C for 1 h. A solution of **3aa**

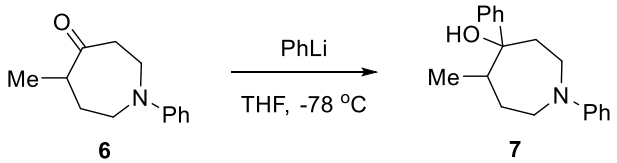
(26.3 mg, 0.1 mmol) in anhydrous THF (1 mL) was then added dropwise. The reaction mixture was stirred at rt for 8 h. After the completion of the reaction, the mixture was quenched with H_2O. The aqueous layer was extracted with ethyl acetate and the combined organic layer was washed with water and brine. The mixture was dried over $MgSO_4$ and concentrated in vacuo. Purification by column chromatography (PE : EA = 20 : 1) gave the desired product **5e** in 67% yield as a yellow oil.

Synthesis of Proheptazine derivative 8



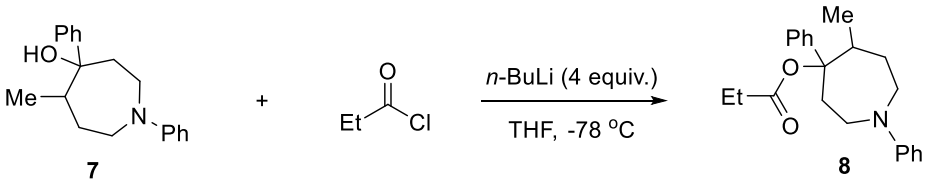
3oa **6**

To a solution of **3oa** (0.1 mmol, 20.1 mg, 1.0 equiv) in MeOH (2 mL). This mixture was degassed of dissolved air and purged with an argon atmosphere. To it 10% Pd/C (10 mol%, 1.1 mg) was carefully added. The above reaction mixture was degassed and purged with hydrogen. The reaction is allowed to stir for 16 h at room temperature. After the completion of the reaction, the mixture was filtered through a celite pad and concentrated under reduced pressure and purified by flash column chromatography (PE : EA = 10 : 1) to obtain the desired product **6** (16.8 mg, 83%) as a yellow oil.



6 **7**

To a solution of **6** (20.3 mg, 0.1 mmol) in anhydrous THF (1 mL) was slowly added PhLi (147 μL, 0.25 mmol, 1.7 M in THF) at -78 °C under nitrogen atmosphere. The reaction mixture was stirred at -78 °C for 1 h. After the completion of the reaction, the mixture was quenched with H_2O. The aqueous layer was extracted with ethyl acetate and the combined organic layer was washed with water and brine. The mixture was dried over $MgSO_4$ and concentrated in vacuo. Purification by column chromatography (PE : EA = 10 : 1) gave the desired product **7** (21.1 mg, 75%) as a yellow oil.



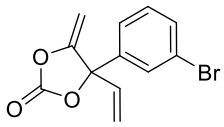
7 **8**

A solution of **7** (28.1 mg, 0.1 mmol) in anhydrous THF (1 mL) was cooled to -78 °C and treated with *n*-BuLi (250 μL, 0.4 mmol, 1.6 M in hexanes) under nitrogen atmosphere. The mixture was stirred for 1 h. A solution of propionyl chloride (35 μL, 0.4 mmol, 4.0 equiv) in anhydrous THF (1 mL) was added slowly, and the reaction was heated to 60 °C for 12 h. After the completion of the reaction, the mixture was quenched

with H_2O. The aqueous layer was extracted with ethyl acetate and the combined organic layer was washed with water and brine. The mixture was dried over $MgSO_4$ and concentrated in vacuo. Purification by column chromatography (PE : EA = 20 : 1) gave the desired product **8** (17.5 mg, 52%) as a co1orless oil.

IR, ^{1}H and ^{13}C NMR spectra, HRMS and characterization data

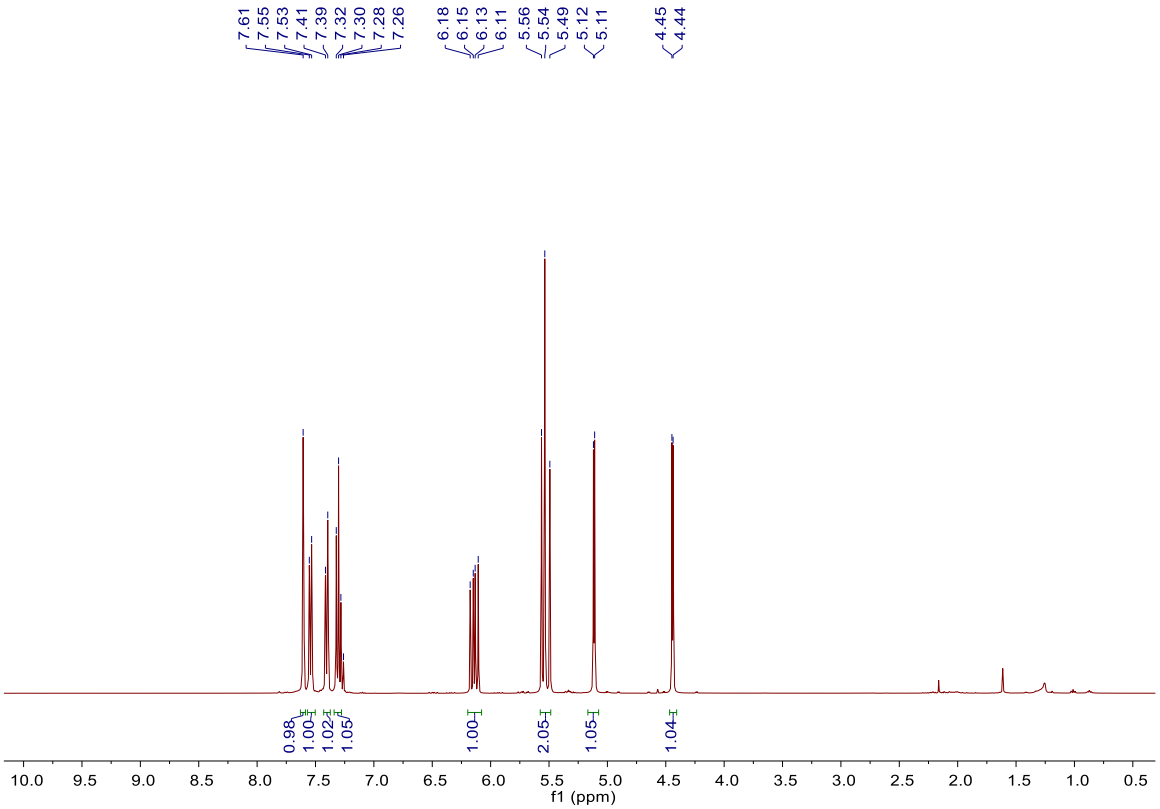
Carbonate **1l** and **1r** are new and were prepared according to a previously reported procedure.[3] All the other carbonates have been previously reported by our group.[3]



1l

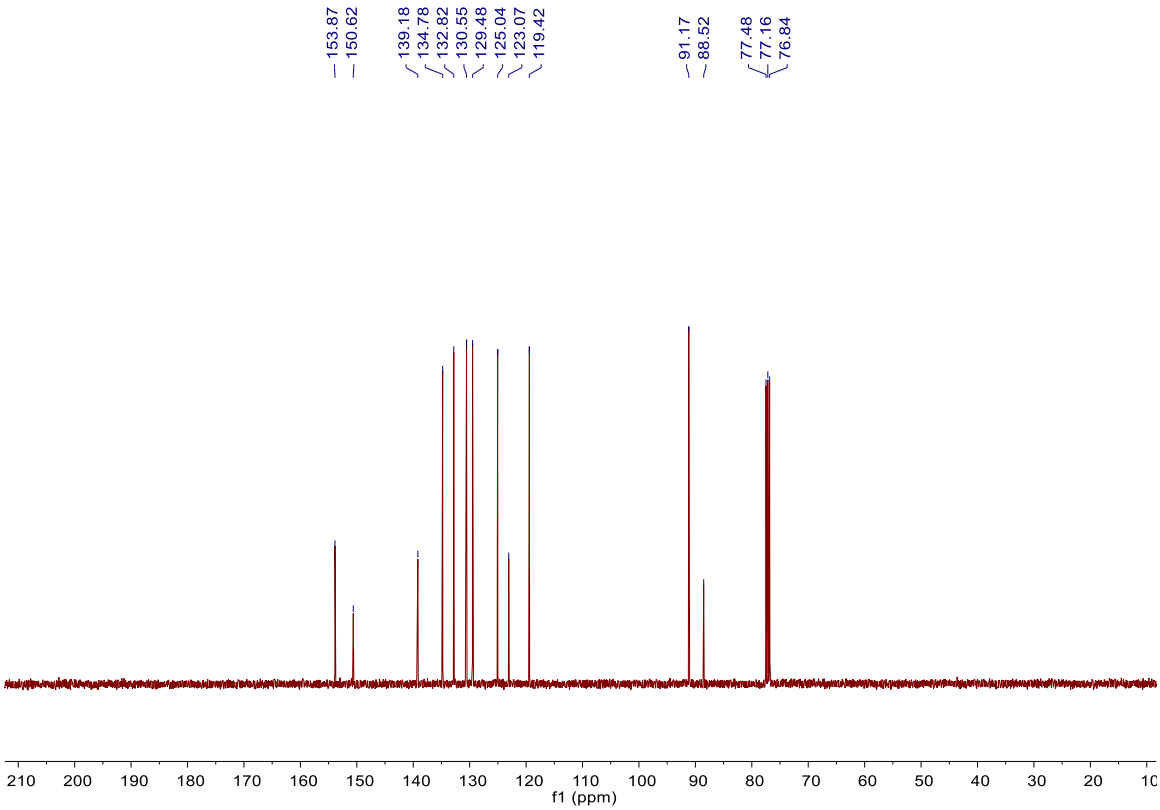
PE : EA = 19 : 1, R_f = 0.47

^{1}H NMR spectrum ($CDCl_3$)



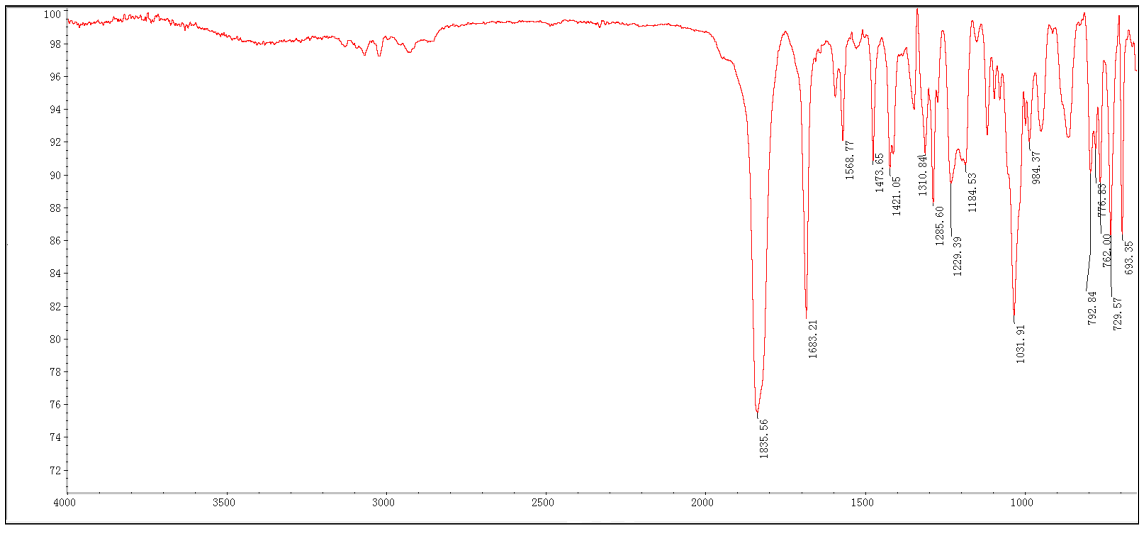
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (s, 1H), 7.54 (d, *J* = 7.9 Hz, 1H), 7.40 (d, *J* = 7.9 Hz, 1H), 7.30 (t, *J* = 7.9 Hz, 1H), 6.14 (dd, *J* = 17.1, 10.6 Hz, 1H), 5.53 (m, 2H), 5.11 (d, *J* = 4.0 Hz, 1H), 4.44 (d, *J* = 4.0 Hz, 1H).

^{13}C NMR spectrum ($CDCl_3$)

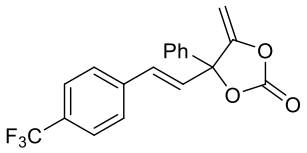


^{13}C NMR (100 MHz, $CDCl_3$) δ 153.87, 150.62, 139.18, 134.78, 132.82, 130.55, 129.48, 125.04, 123.07, 119.42, 91.17, 88.52.

IR spectrum



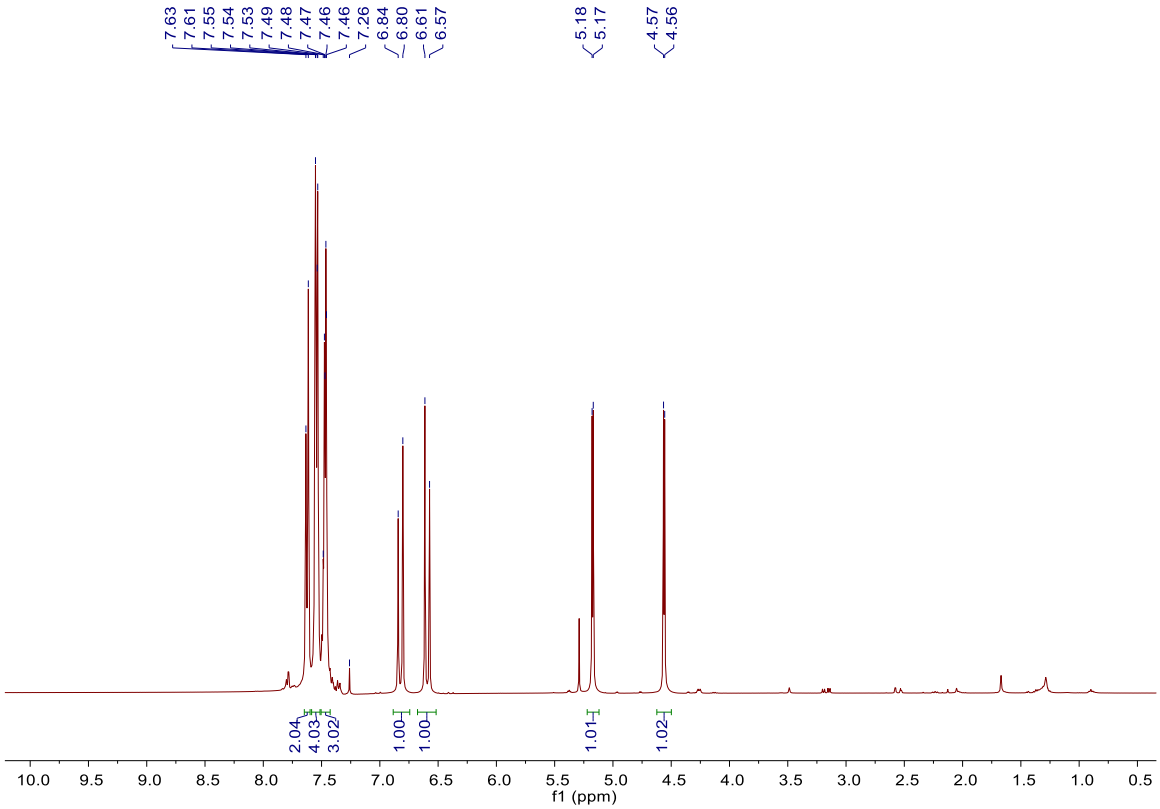
HRMS (ESI+, MeOH): *m/z* calcd. 236.9909 $(M - CO_2 + H)^+$, found: 236.9898.



1r

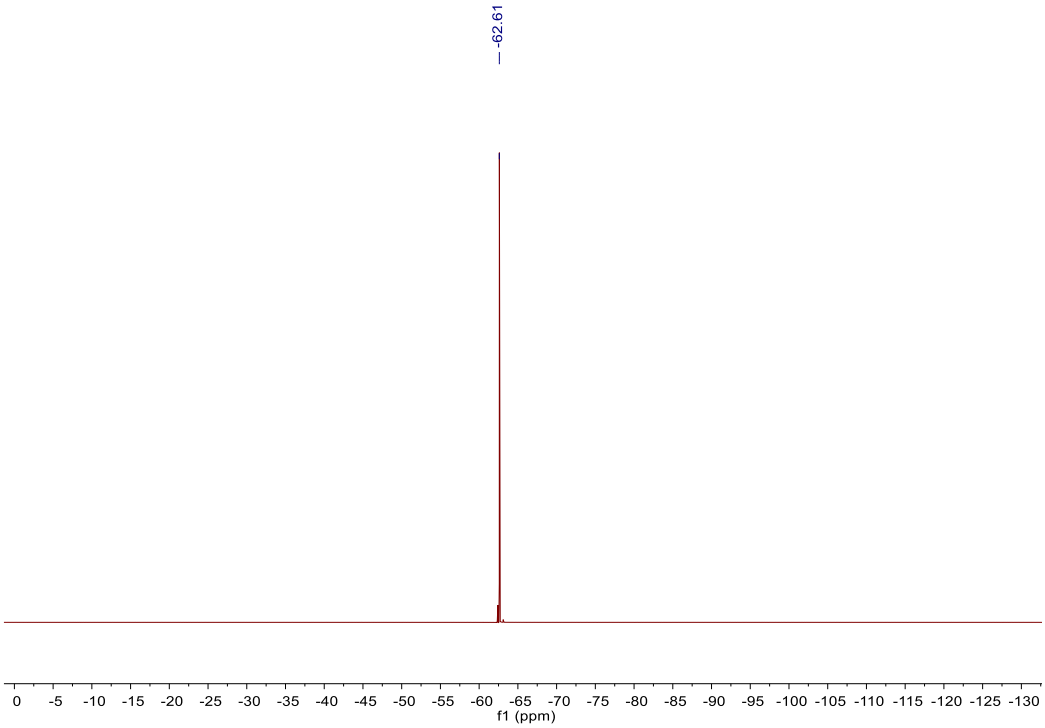
PE : EA = 4 : 1, R_f = 0.53

^{1}H NMR spectrum ($CDCl_3$)

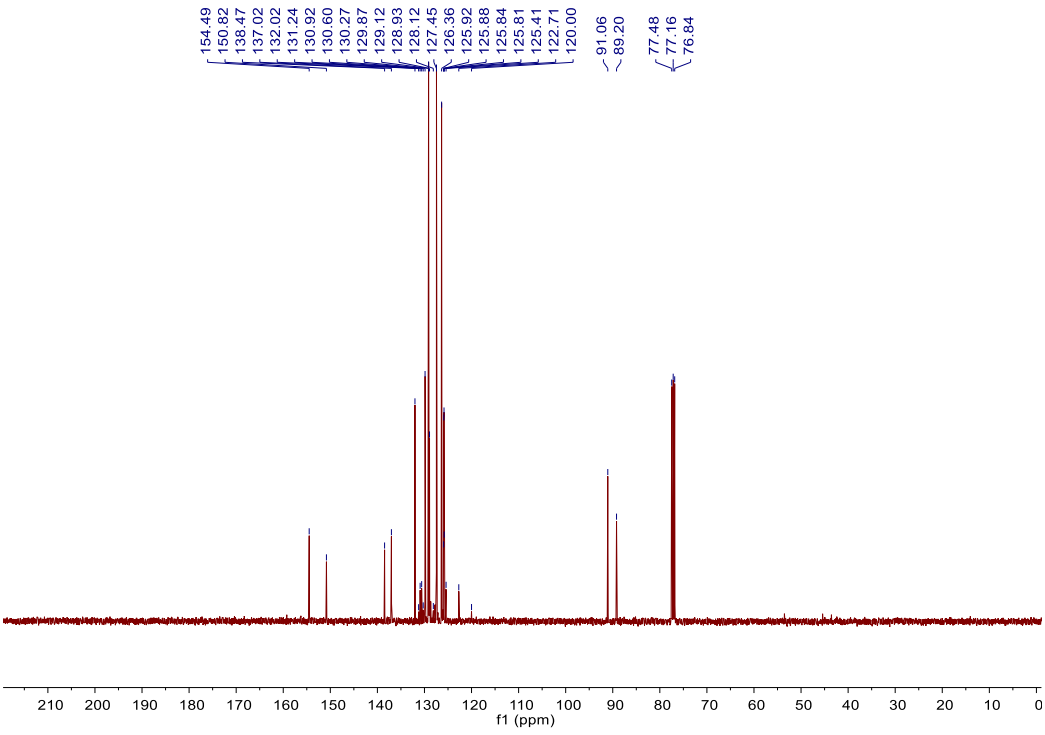


^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63-7.61 (m, 2H), 7.55-7.53 (m, 4H), 7.49-7.46 (m, 3H), 6.82 (d, *J* = 16.0 Hz, 1H), 6.59 (d, *J* = 16.0 Hz, 1H), 5.17 (d, *J* = 4.0 Hz, 1H), 4.56 (d, *J* = 4.0 Hz, 1H).

^{19}F NMR spectrum ($CDCl_3$)

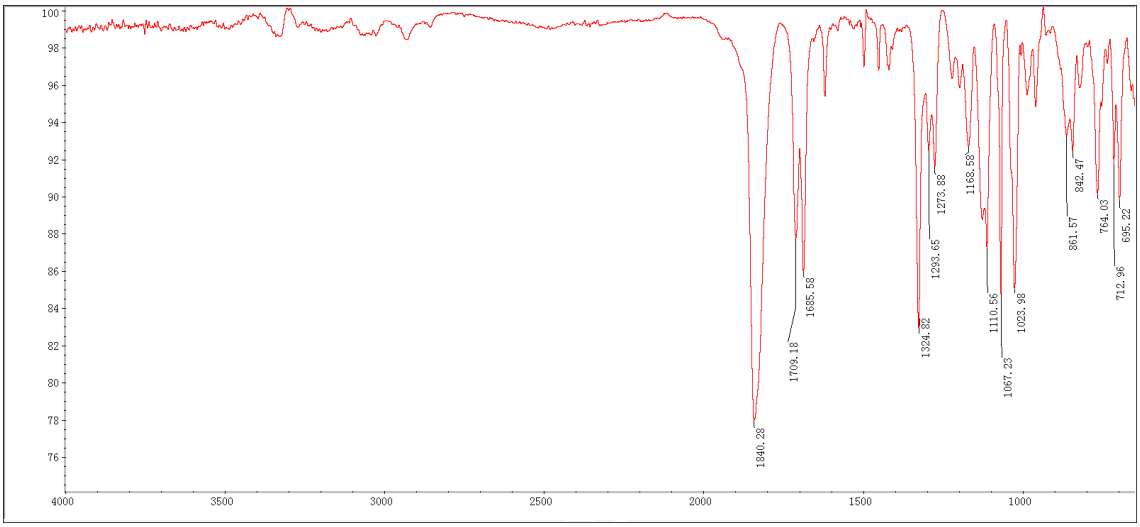


^{13}C NMR spectrum ($CDCl_3$)

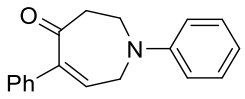


^{13}C NMR (100 MHz, $CDCl_3$) δ 154.49, 150.82, 138.47, 137.02, 132.02, 130.76 (q, J = 32.7 Hz), 129.87, 129.12, 128.93, 127.45, 126.36, 125.86 (q, J = 3.7 Hz), 124.06 (q, J = 272.1 Hz), 91.06, 89.20.

IR spectrum



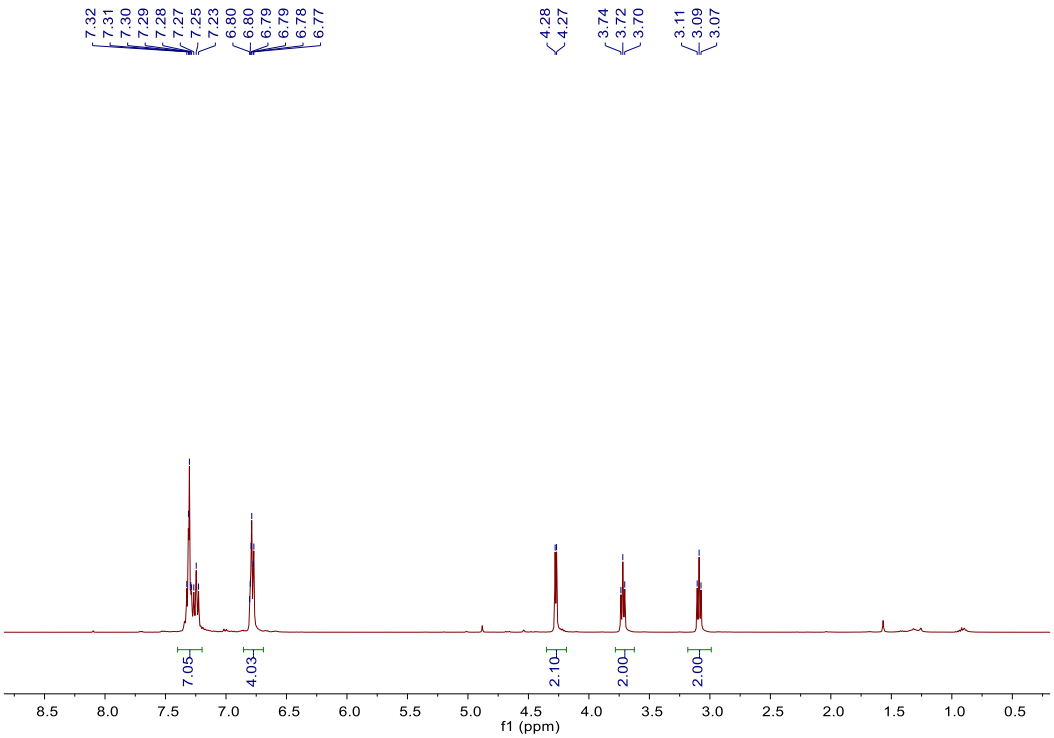
HRMS (ESI+, MeOH): *m/z* calcd. 303.0991 $(M - CO_2 + H)^+$, found: 303.0985.



3aa

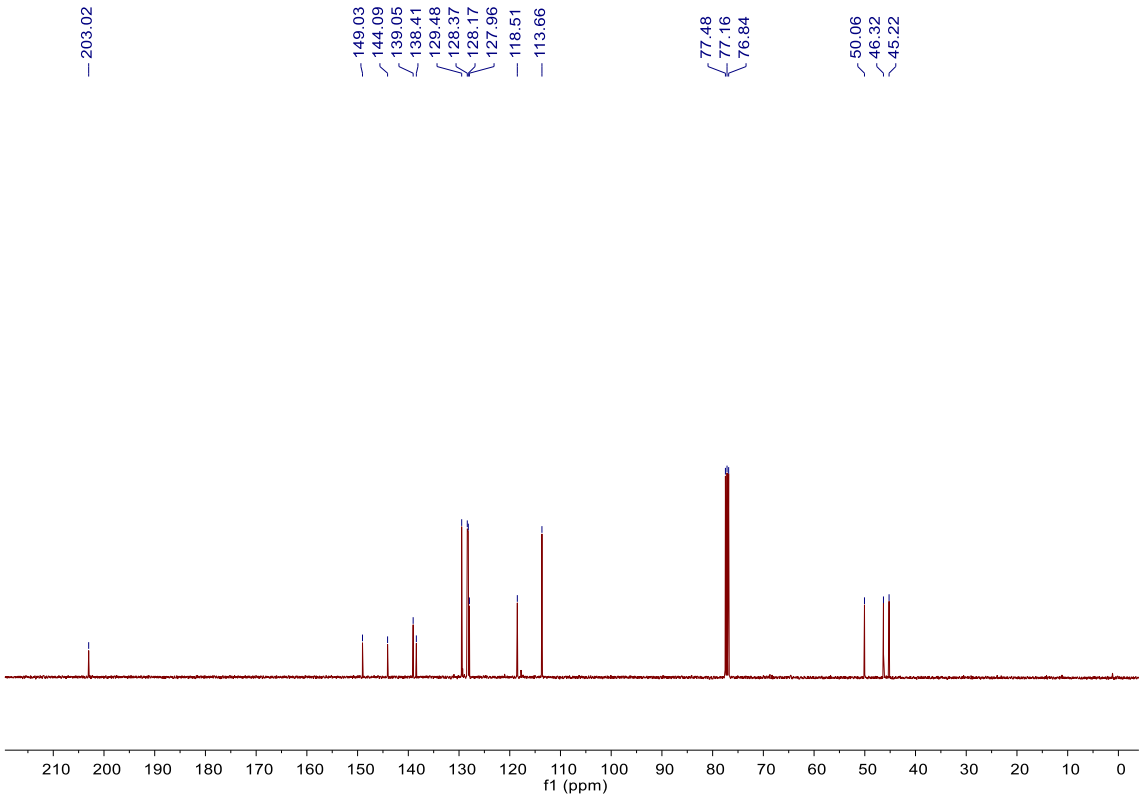
Scale: 0.1 mmol (90% yield), yellow oil, PE : EA = 5 : 1, R_f = 0.37.

^{1}H NMR spectrum ($CDCl_3$)



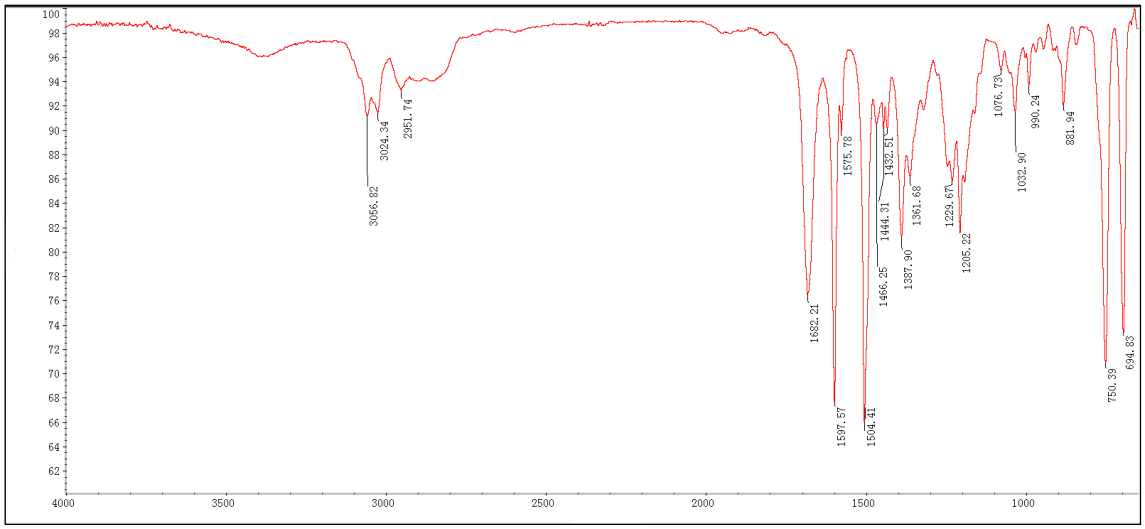
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40-7.20 (m, 7H), 6.86-6.69 (m, 4H), 4.27 (d, *J* = 4.7 Hz, 2H), 3.72 (t, *J* = 6.4 Hz, 2H), 3.09 (t, *J* = 6.4 Hz, 2H).

^{13}C NMR spectrum ($CDCl_3$)

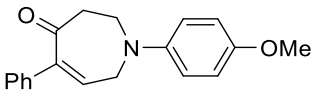


^{13}C NMR (100 MHz, $CDCl_3$) δ 203.02, 149.03, 144.09, 139.05, 138.41, 129.48, 128.37, 128.17, 127.96, 118.51, 113.66, 50.06, 46.32, 45.22.

IR spectrum



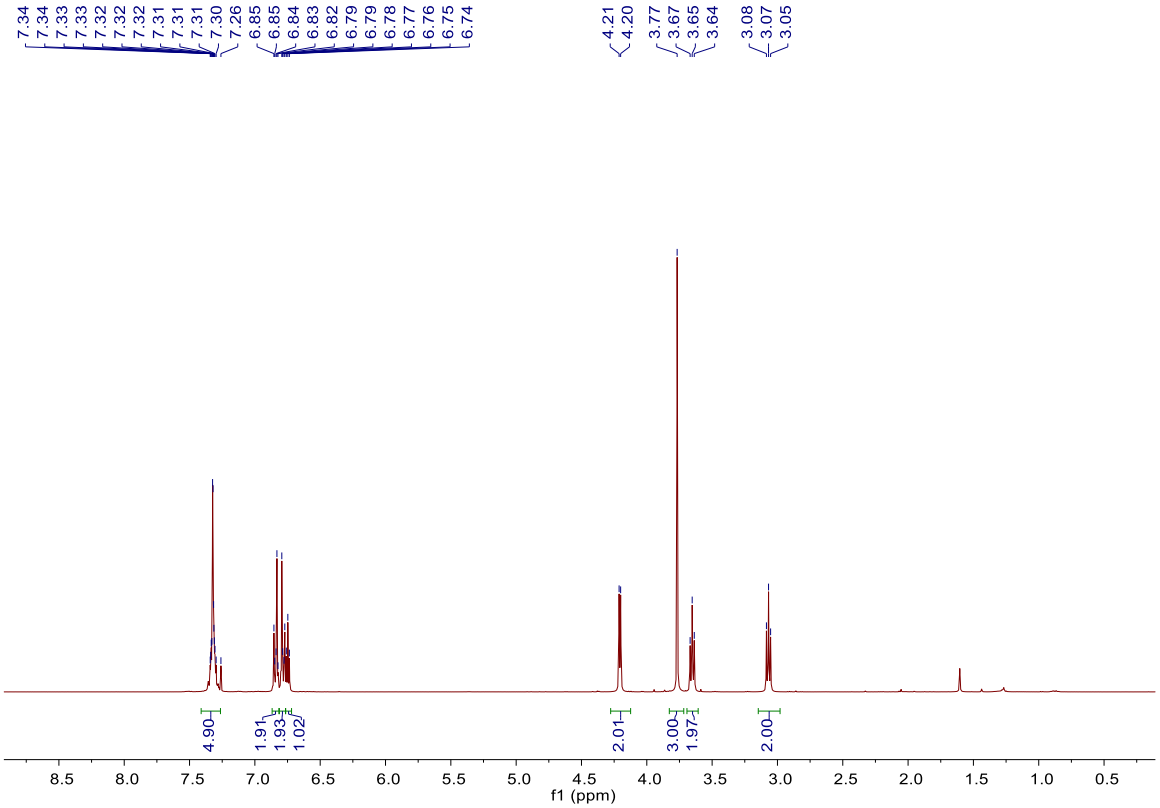
HRMS (ESI+, MeOH): *m/z* calcd. 264.1383 $(M + H)^+$, found: 264.1371.



3ab

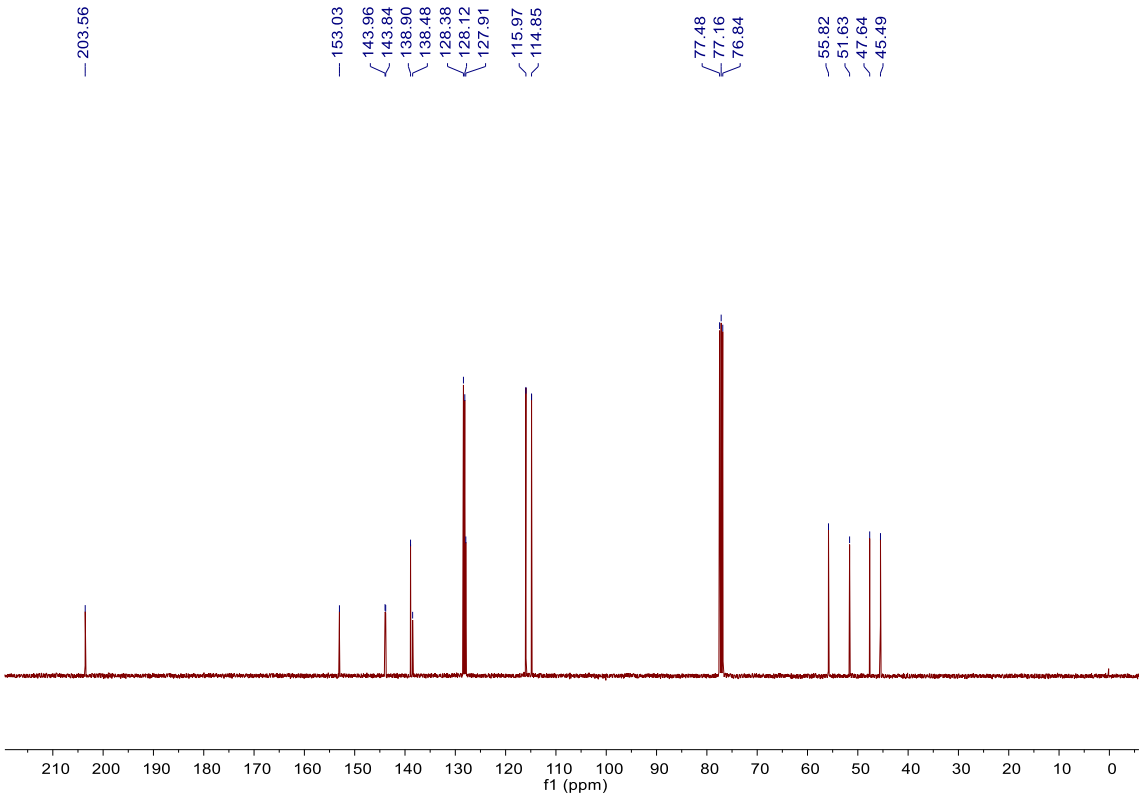
Scale: 0.1 mmol (61% yield), yellow oil, PE : EA = 5 : 1, R_f = 0.30.

^{1}H NMR spectrum ($CDCl_3$)



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41-7.26 (m, 5H), 6.87-6.82 (m, 2H), 6.81-6.77 (m, 2H), 6.75 (t, *J* = 4.7 Hz, 1H), 4.21 (d, *J* = 4.7 Hz, 2H), 3.77 (s, 3H), 3.65 (t, *J* = 6.4 Hz, 2H), 3.07 (t, *J* = 6.4 Hz, 2H).

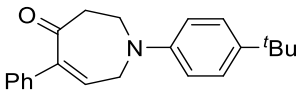
^{13}C NMR spectrum ($CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$) δ 203.56, 153.03, 143.96, 143.84, 138.90, 138.48, 128.38, 128.12, 127.91, 115.97, 114.85, 55.82, 51.63, 47.64, 45.49.

IR spectrum

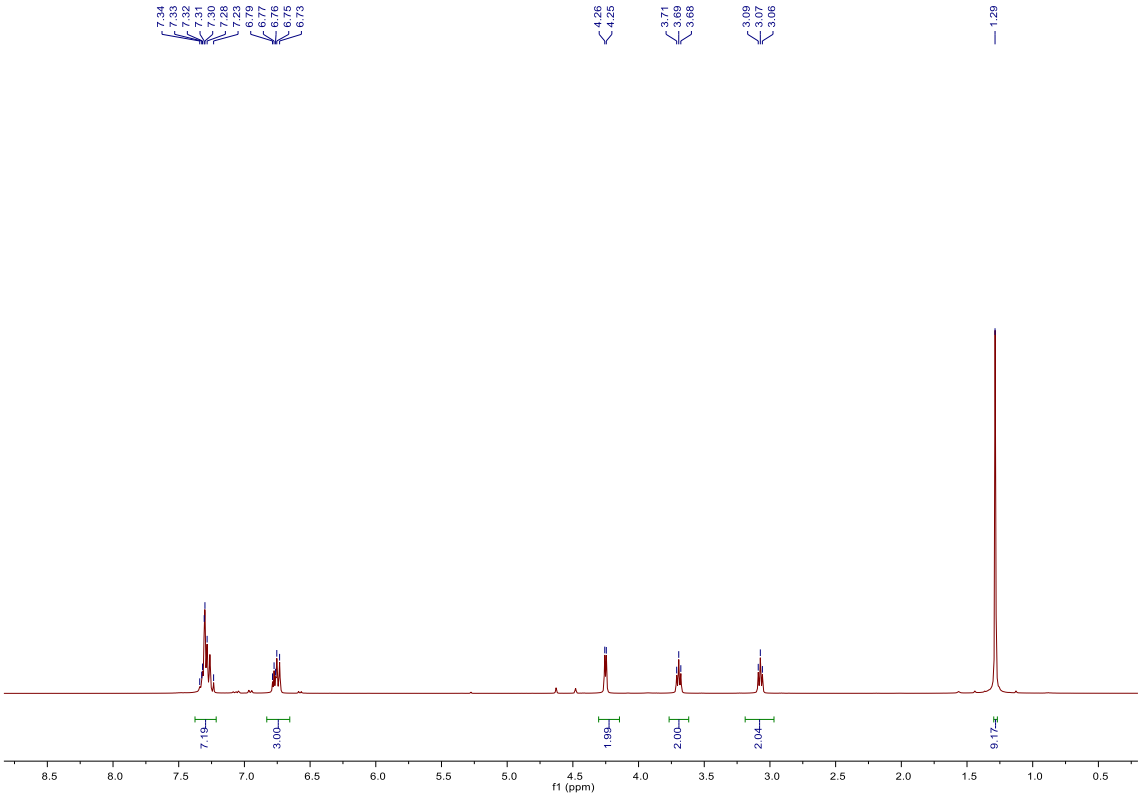
HRMS (ESI+, MeOH): *m/z* calcd. 294.1489 $(M + H)^+$, found: 294.1476.



3ac

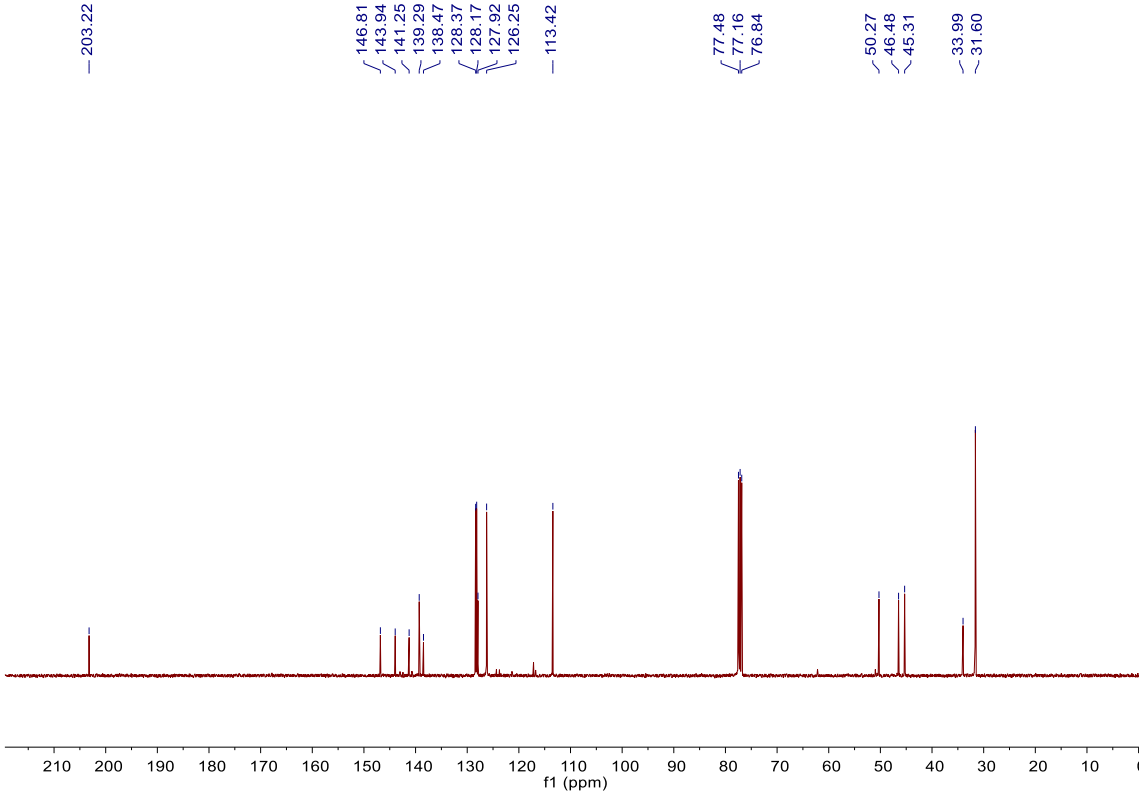
Scale: 0.1 mmol (64% yield), yellow oil, PE : EA = 5 : 1, R_f = 0.42.

^{1}H NMR spectrum ($CDCl_3$)



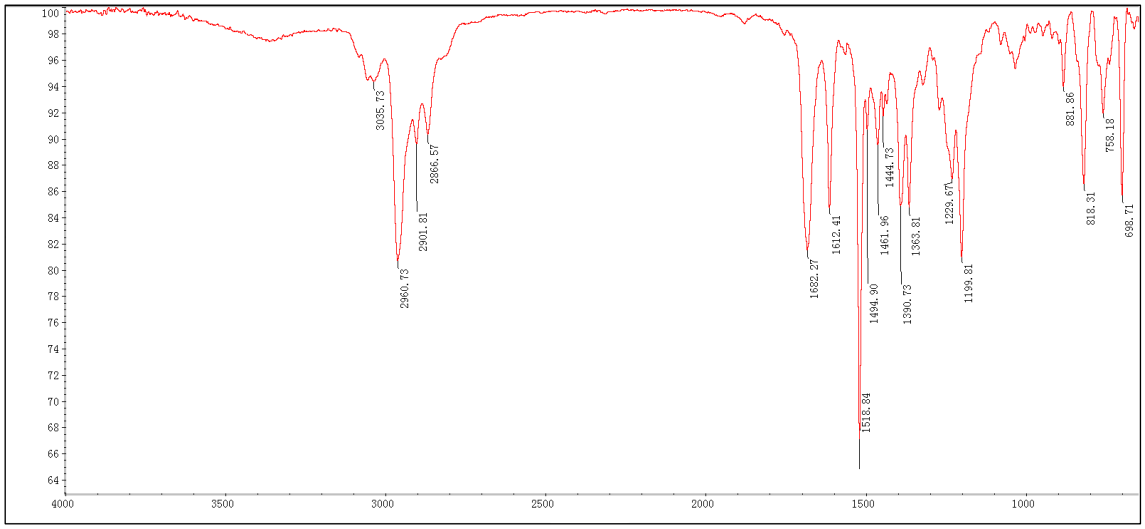
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.21 (m, 7H), 6.83-6.65 (m, 3H), 4.25 (d, *J* = 4.7 Hz, 2H), 3.69 (t, *J* = 6.4 Hz, 2H), 3.07 (t, *J* = 6.4 Hz, 2H), 1.29 (s, 9H).

^{13}C NMR spectrum ($CDCl_3$)

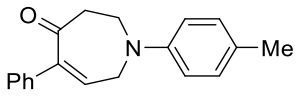


^{13}C NMR (100 MHz, $CDCl_3$) δ 203.22, 146.81, 143.94, 141.25, 139.29, 138.47, 128.37, 128.17, 127.92, 126.25, 113.42, 50.27, 46.48, 45.31, 33.99, 31.60.

IR spectrum



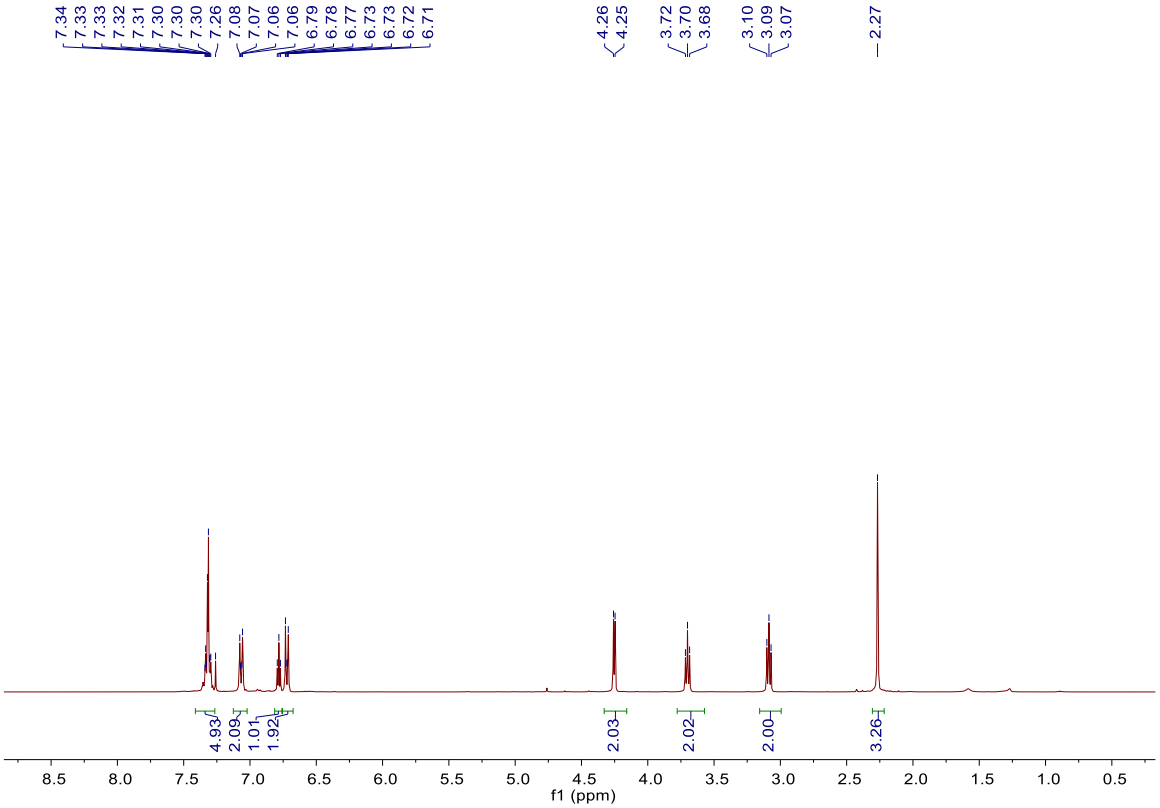
HRMS (ESI+, MeOH): *m/z* calcd. 320.2009 $(M + H)^+$, found: 320.2007.



3ad

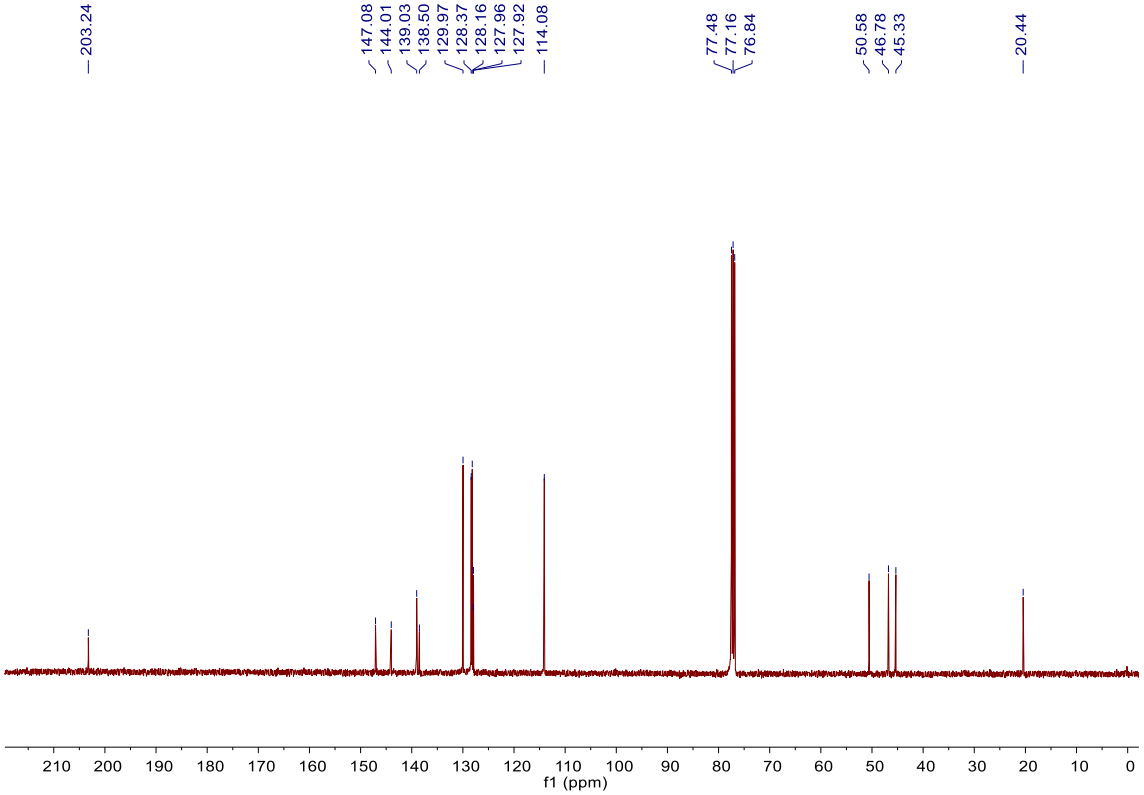
Scale: 0.1 mmol (62% yield), yellow oil, PE : EA = 5 : 1, R_f = 0.42.

^{1}H NMR spectrum ($CDCl_3$)



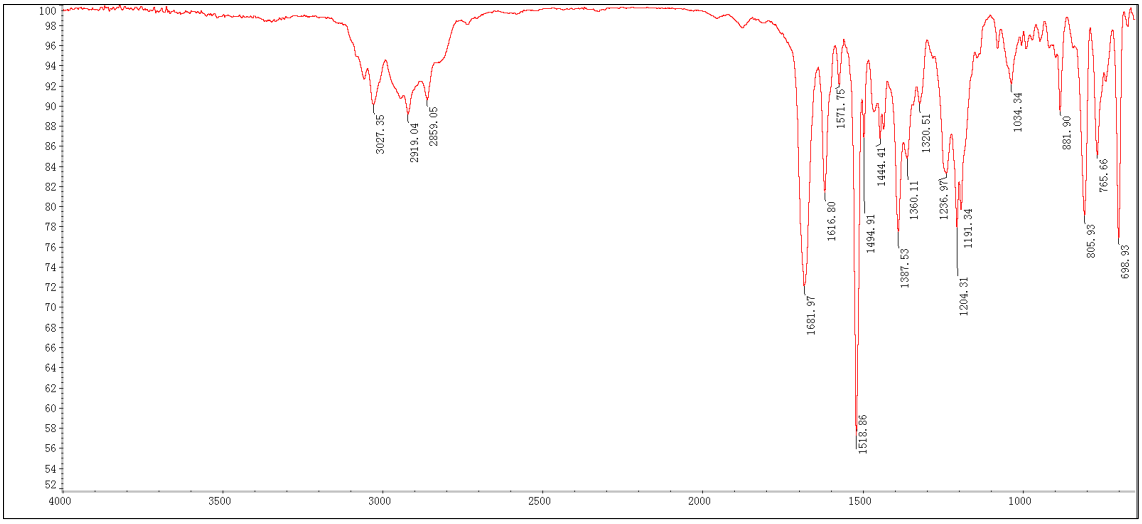
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.27 (m, 5H), 7.13-7.02 (m, 2H), 6.78 (t, *J* = 4.7 Hz, 1H), 6.75-6.67 (m, 2H), 4.25 (d, *J* = 4.7 Hz, 2H), 3.70 (t, *J* = 6.3 Hz, 2H), 3.09 (t, *J* = 6.3 Hz, 2H), 2.27 (s, 3H).

^{13}C NMR spectrum ($CDCl_3$)

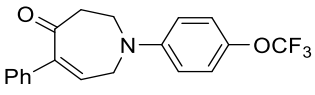


^{13}C NMR (100 MHz, $CDCl_3$) δ 203.24, 147.08, 144.01, 139.03, 138.50, 129.97, 128.37, 128.16, 127.96, 127.92, 114.08, 50.58, 46.78, 45.33, 20.44.

IR spectrum



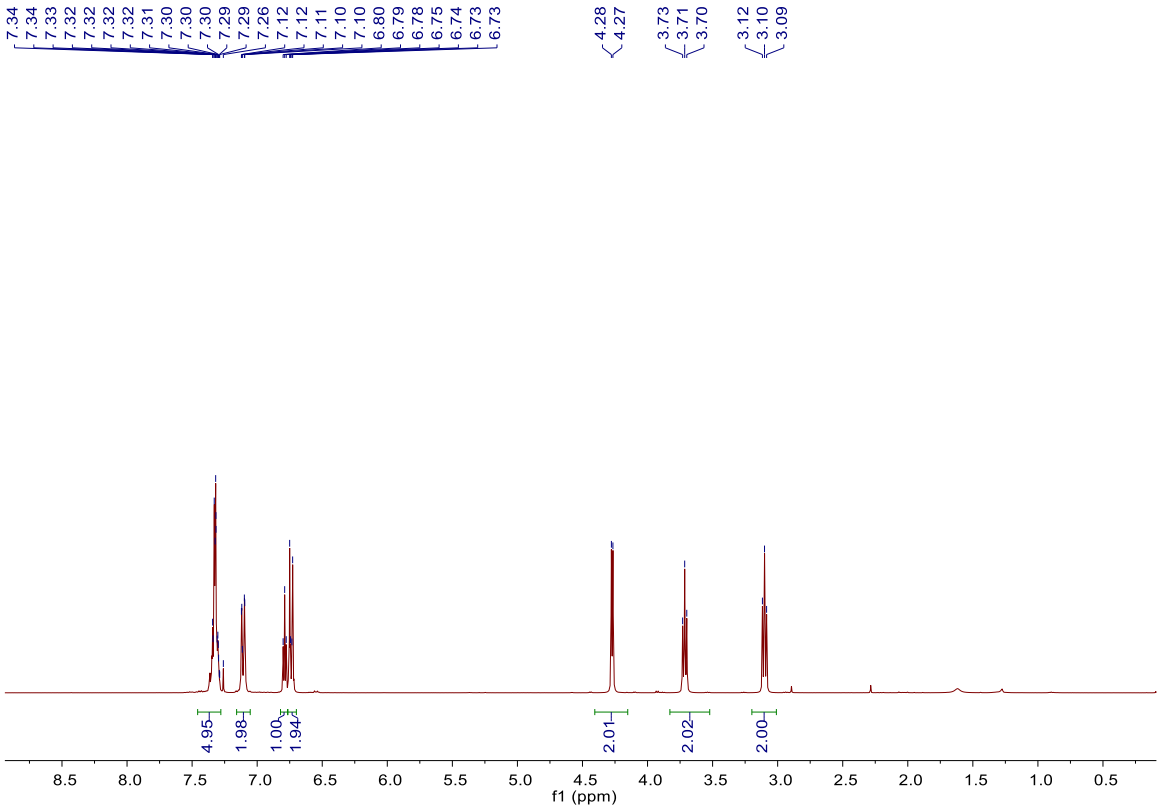
HRMS (ESI+, MeOH): *m/z* calcd. 278.1539 $(M + H)^+$, found: 278.1526.



3ae

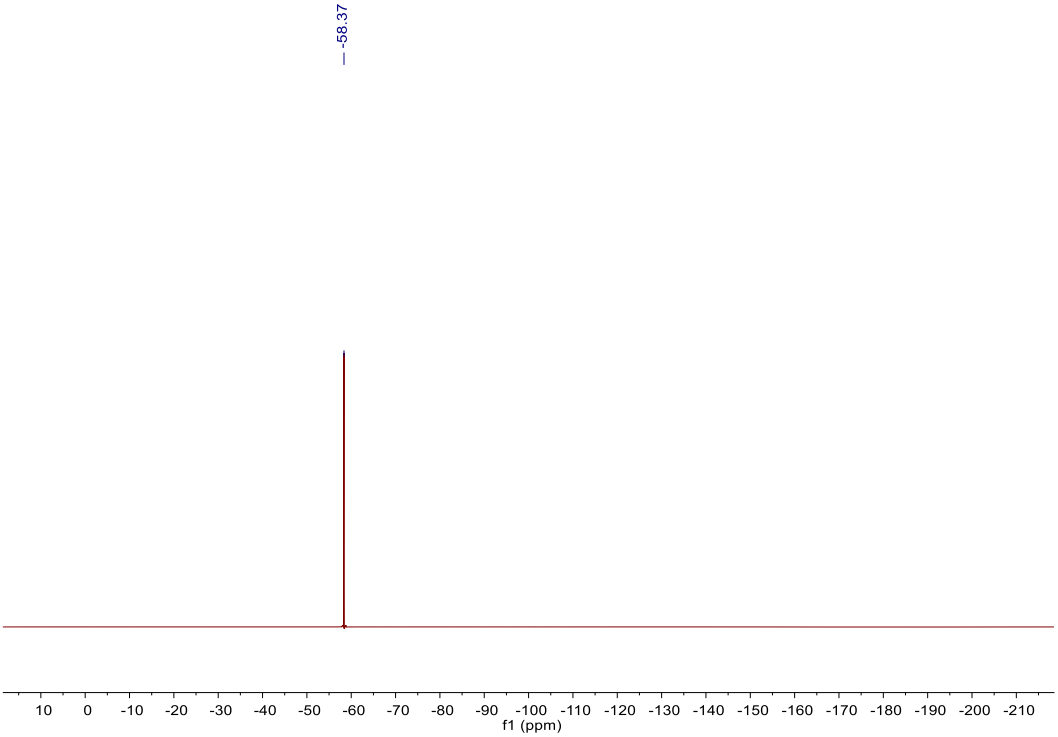
Scale: 0.1 mmol (76% yield), yellow oil, PE : EA = 5 : 1, R_f = 0.33.

^{1}H NMR spectrum ($CDCl_3$)

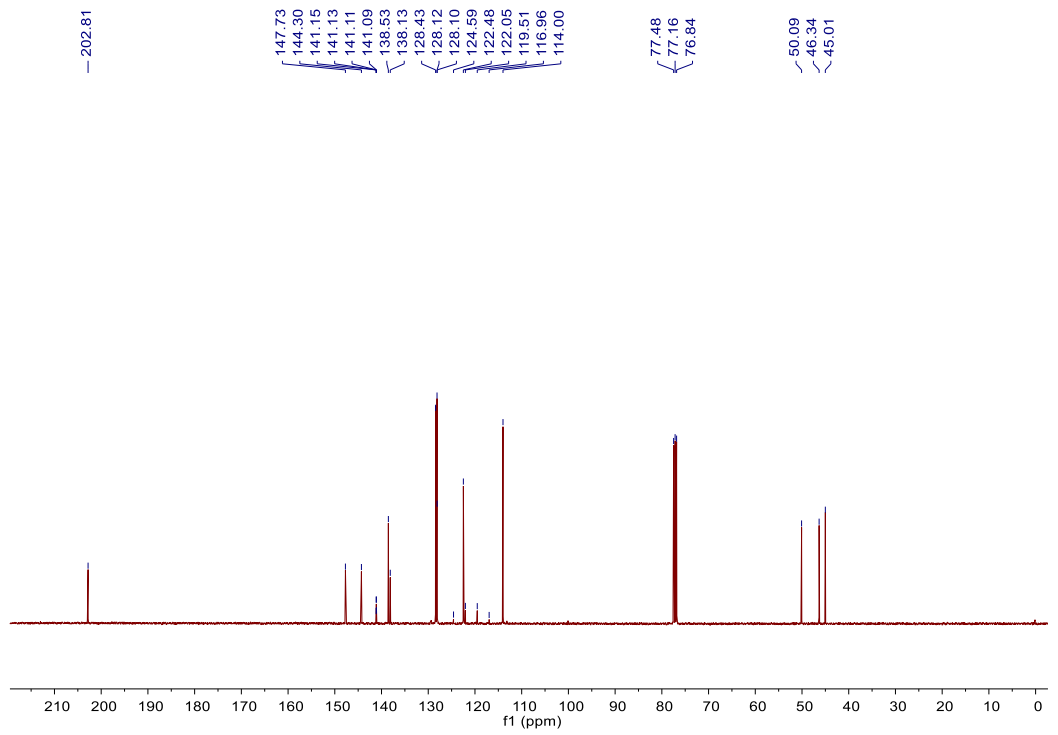


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46-7.28 (m, 5H), 7.16-7.05 (m, 2H), 6.79 (t, *J* = 4.7 Hz, 1H), 6.76-6.70 (m, 2H), 4.27 (d, *J* = 4.7 Hz, 2H), 3.71 (t, *J* = 6.4 Hz, 2H), 3.10 (t, *J* = 6.4 Hz, 2H).

^{19}F NMR spectrum ($CDCl_3$)

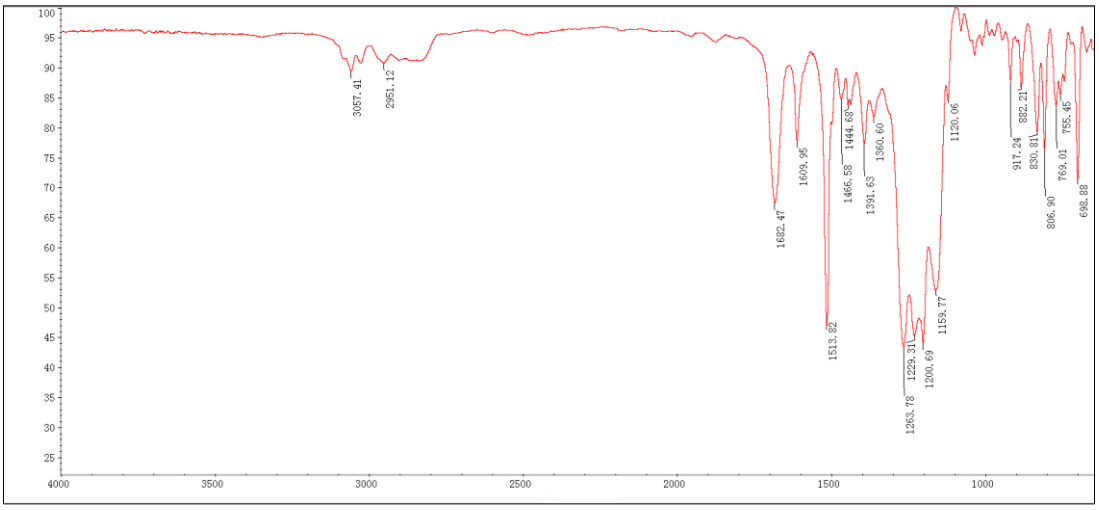


^{13}C NMR spectrum ($CDCl_3$)

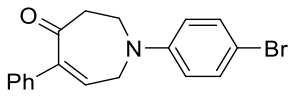


^{13}C NMR (100 MHz, $CDCl_3$) δ 202.81, 147.73, 144.30, 141.12 (q, J = 1.8 Hz), 138.53, 138.13, 128.43, 128.12, 128.10, 122.48, 120.78 (q, J = 255.6 Hz), 114.00, 50.09, 46.34, 45.01.

IR spectrum



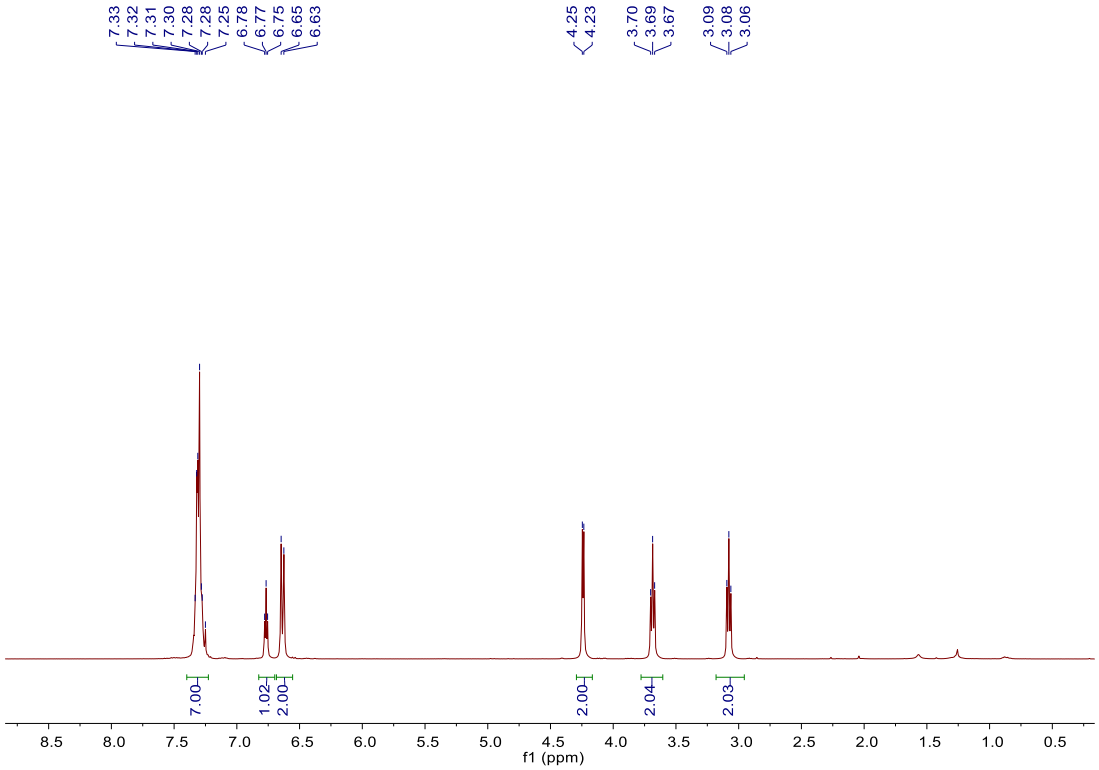
HRMS (ESI+, MeOH): *m/z* calcd. 348.1206 $(M + H)^+$, found: 348.1213.



3af

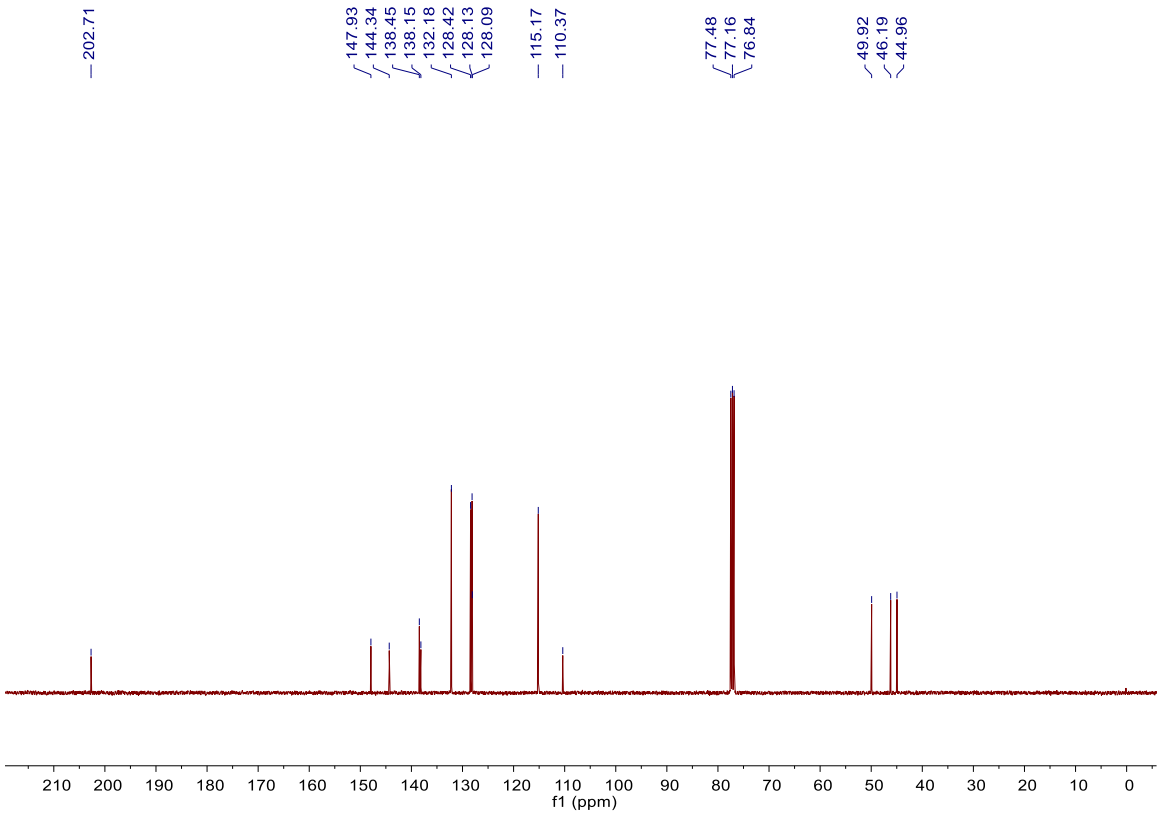
Scale: 0.1 mmol (87% yield), yellow oil, PE : EA = 5 : 1, R_f = 0.35.

^{1}H NMR spectrum ($CDCl_3$)



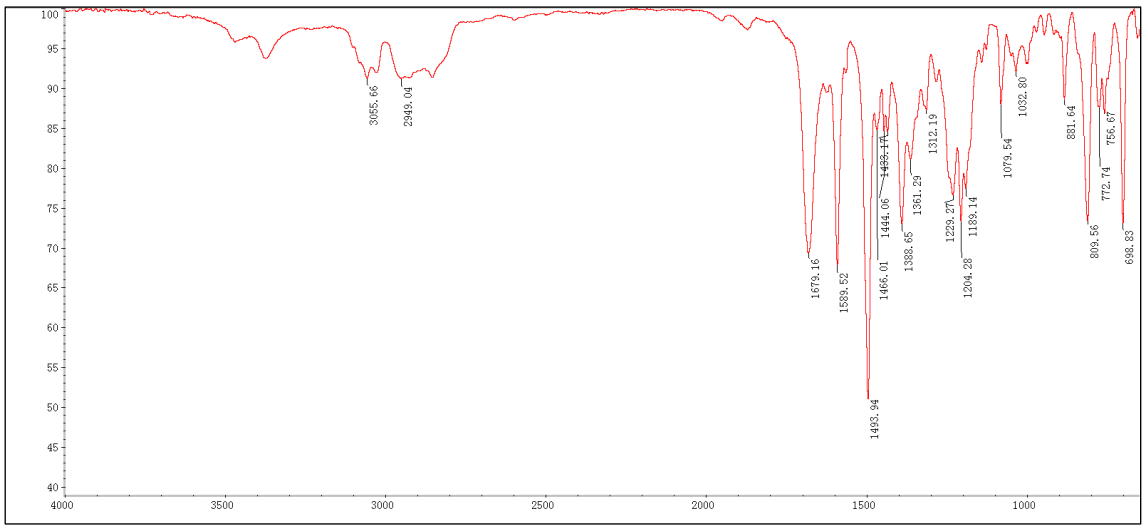
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.23 (m, 7H), 6.77 (t, *J* = 4.7 Hz, 1H), 6.64 (d, *J* = 8.6 Hz, 2H), 4.24 (d, *J* = 4.7 Hz, 2H), 3.69 (t, *J* = 6.4 Hz, 2H), 3.08 (t, *J* = 6.4 Hz, 2H).

^{13}C NMR spectrum ($CDCl_3$)

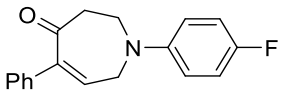


^{13}C NMR (100 MHz, $CDCl_3$) δ 202.71, 147.93, 144.34, 138.45, 138.15, 132.18, 128.42, 128.13, 128.09, 115.17, 110.37, 49.92, 46.19, 44.96.

IR spectrum



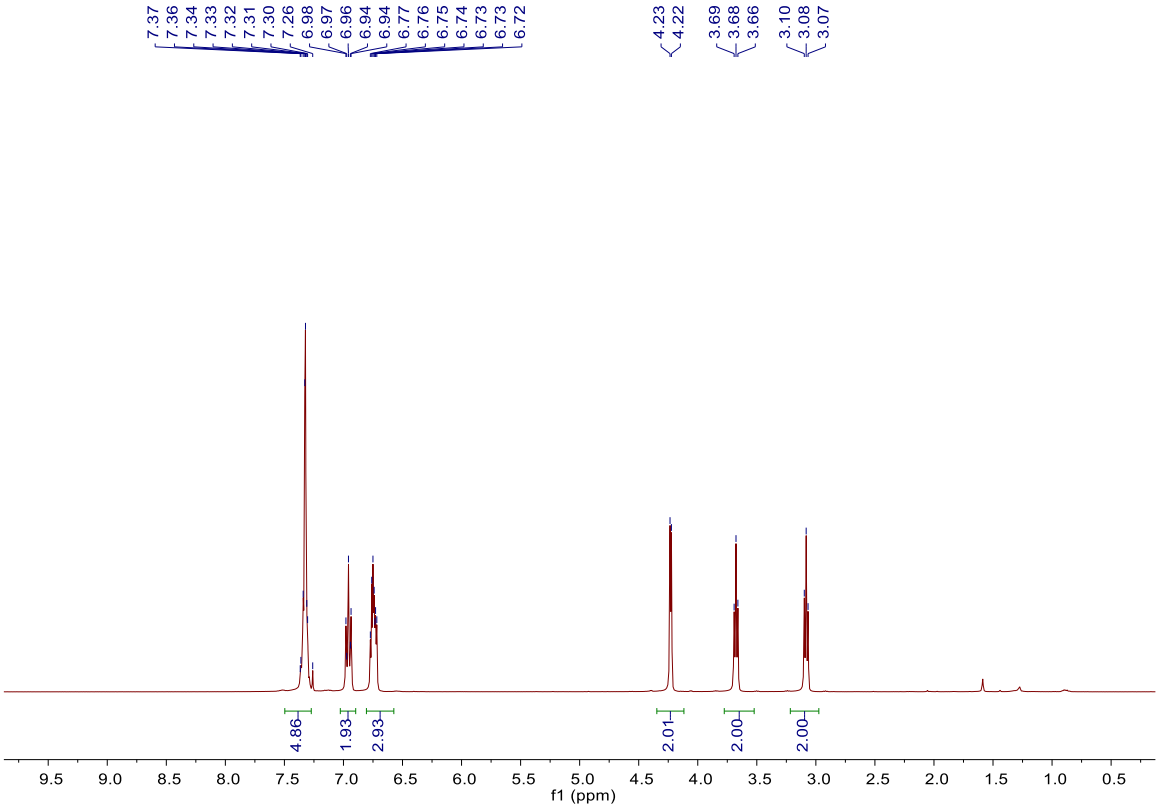
HRMS (ESI+, MeOH): *m/z* calcd. 342.0488 $(M + H)^+$, found: 342.0473.



3ag

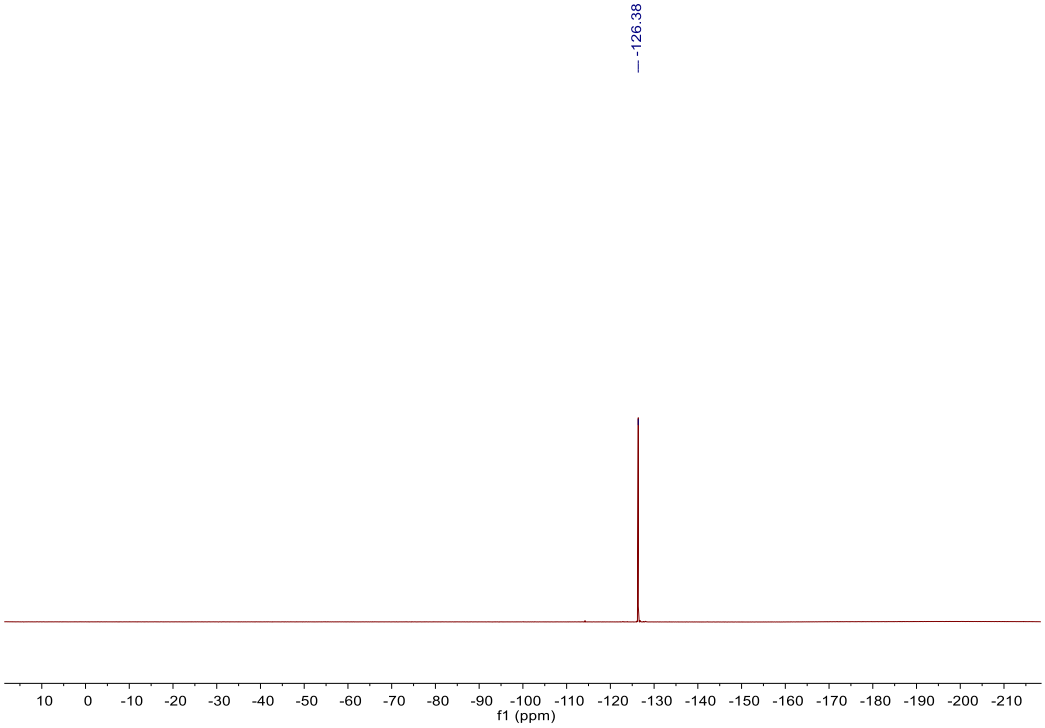
Scale: 0.1 mmol (84% yield), yellow solid, PE : EA = 5 : 1, R_f = 0.33.

^{1}H NMR spectrum ($CDCl_3$)

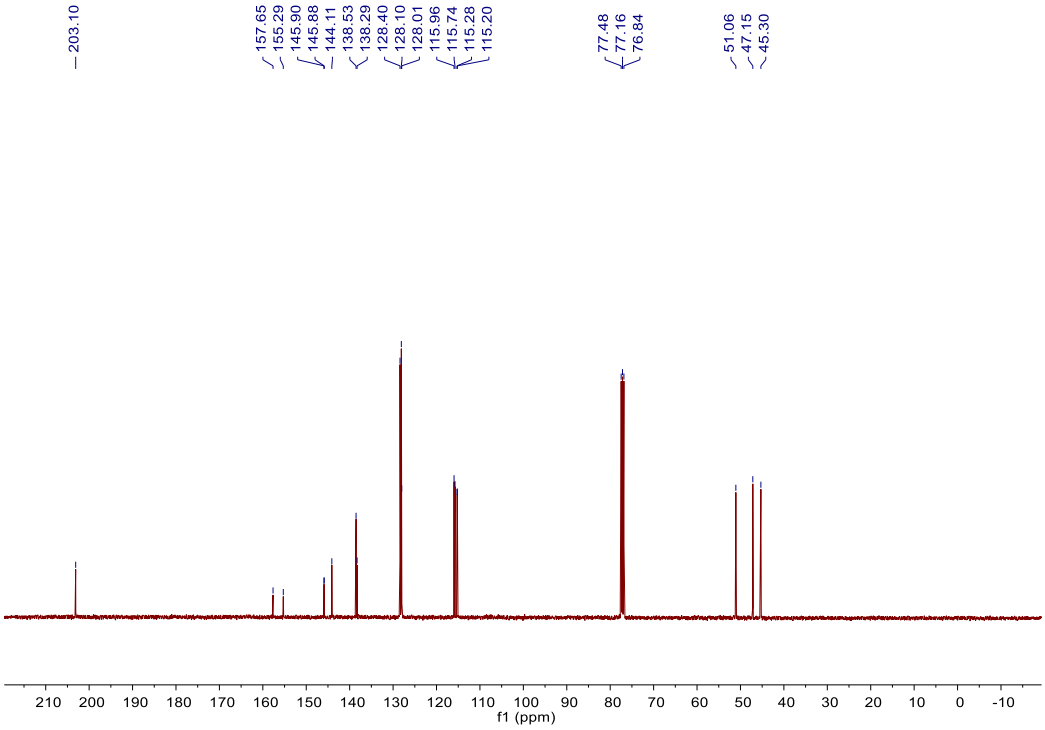


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50-7.27 (m, 5H), 7.03-6.90 (m, 2H), 6.81-6.57 (m, 3H), 4.23 (d, *J* = 4.7 Hz, 2H), 3.68 (t, *J* = 6.4 Hz, 2H), 3.08 (t, *J* = 6.4 Hz, 2H).

^{19}F NMR spectrum ($CDCl_3$)

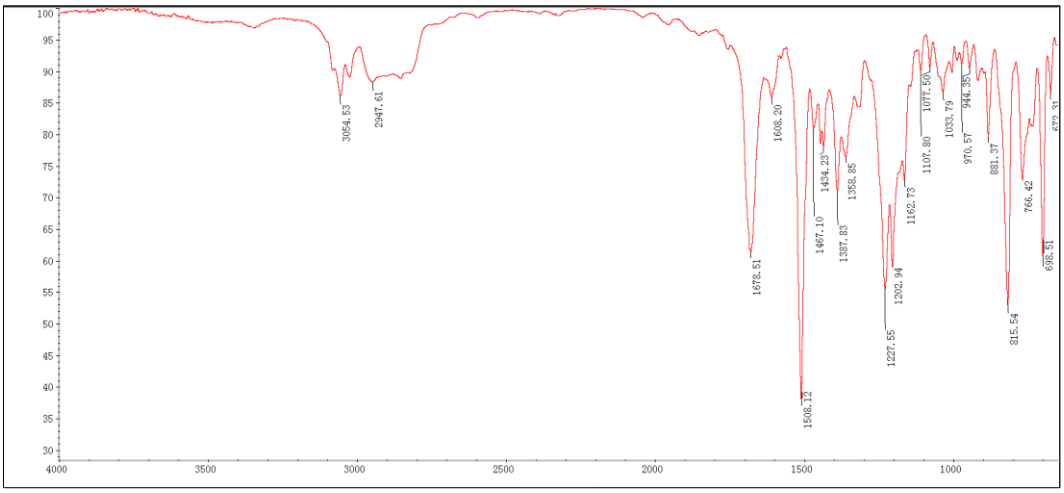


^{13}C NMR spectrum ($CDCl_3$)

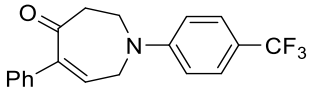


^{13}C NMR (100 MHz, $CDCl_3$) δ 203.10, 156.47 (d, *J* = 236.1 Hz), 145.89 (d, *J* = 2.1 Hz), 144.11, 138.53, 138.29, 128.40, 128.10, 128.01, 115.85 (d, *J* = 22.3 Hz), 115.24 (d, *J* = 7.5 Hz), 51.06, 47.15, 45.30.

IR spectrum



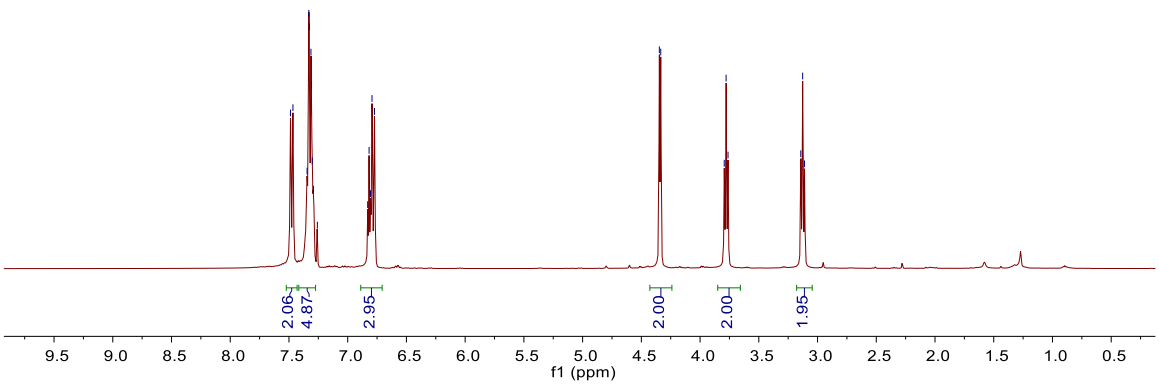
HRMS (ESI+, MeOH): *m/z* calcd. 282.1289 $(M + H)^+$, found: 282.1283.



3ah

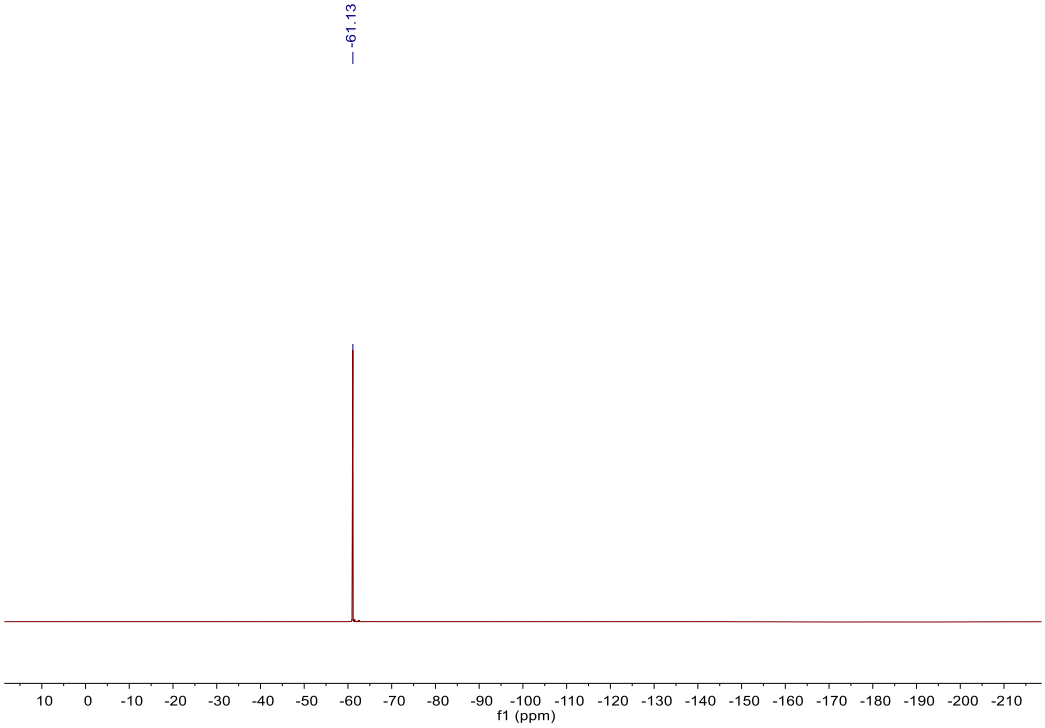
Scale: 0.1 mmol (77% yield), yellow oil, PE : EA = 5 : 1, R_f = 0.30.

^{1}H NMR spectrum ($CDCl_3$)

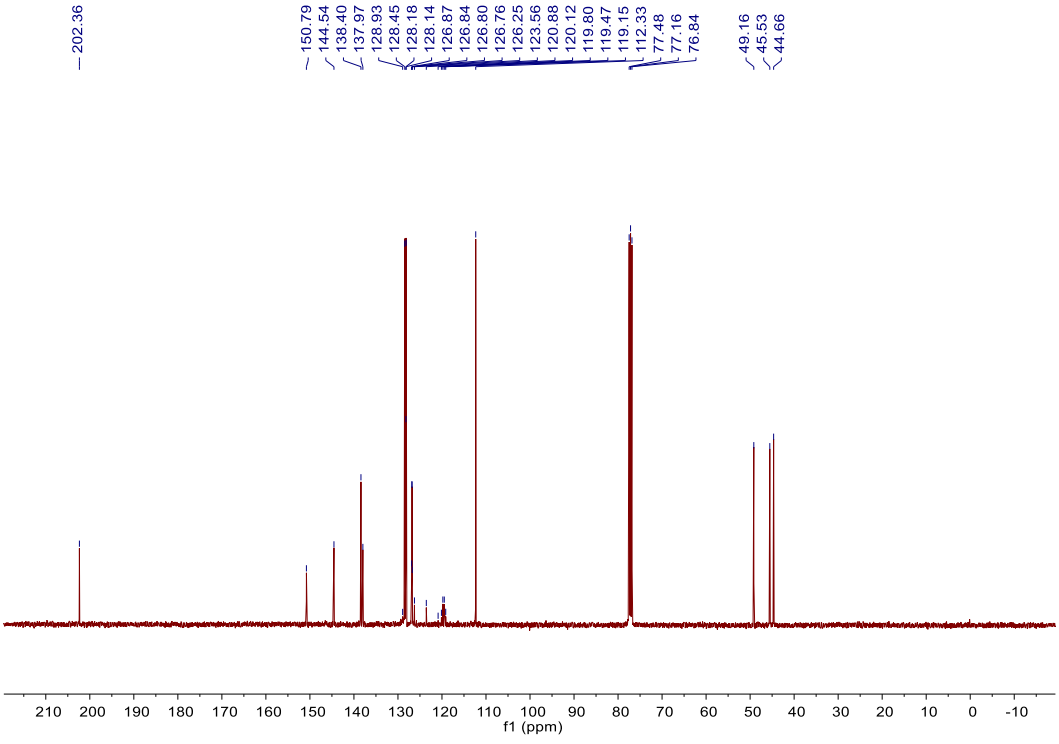


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.4 Hz, 2H), 7.42-7.27 (m, 5H), 6.89-6.71 (m, 3H), 4.34 (d, *J* = 4.7 Hz, 2H), 3.78 (t, *J* = 6.4 Hz, 2H), 3.13 (t, *J* = 6.4 Hz, 2H).

^{19}F NMR spectrum ($CDCl_3$)

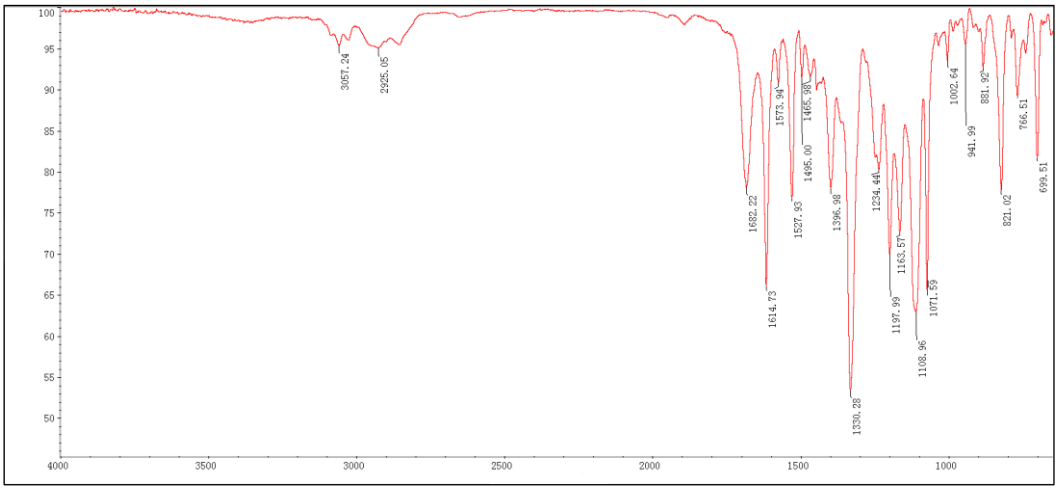


^{13}C NMR spectrum ($CDCl_3$)

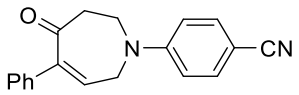


^{13}C NMR (100 MHz, $CDCl_3$) δ 202.36, 150.79, 144.54, 138.40, 137.97, 128.45, 128.18, 128.14, 126.82 (q, J = 3.7 Hz), 124.90 (q, J = 268.7 Hz), 119.64 (q, J = 32.7 Hz), 112.33, 49.16, 45.53, 44.66.

IR spectrum



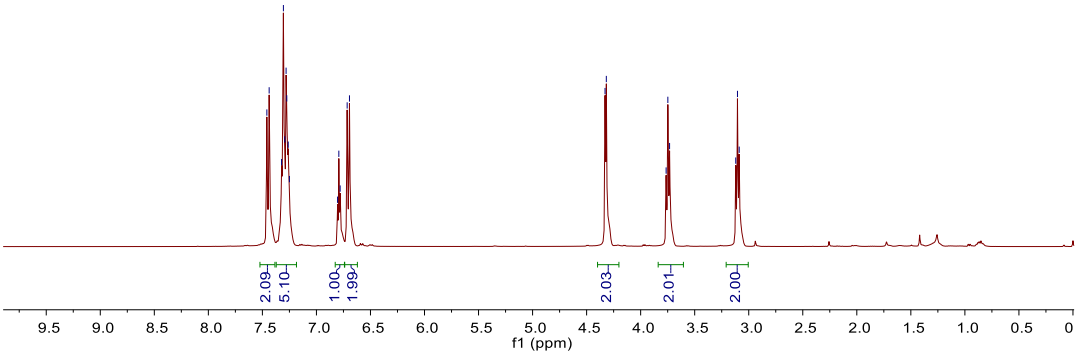
HRMS (ESI+, MeOH): *m/z* calcd. 332.1257 $(M + H)^+$, found: 332.1248.



3ai

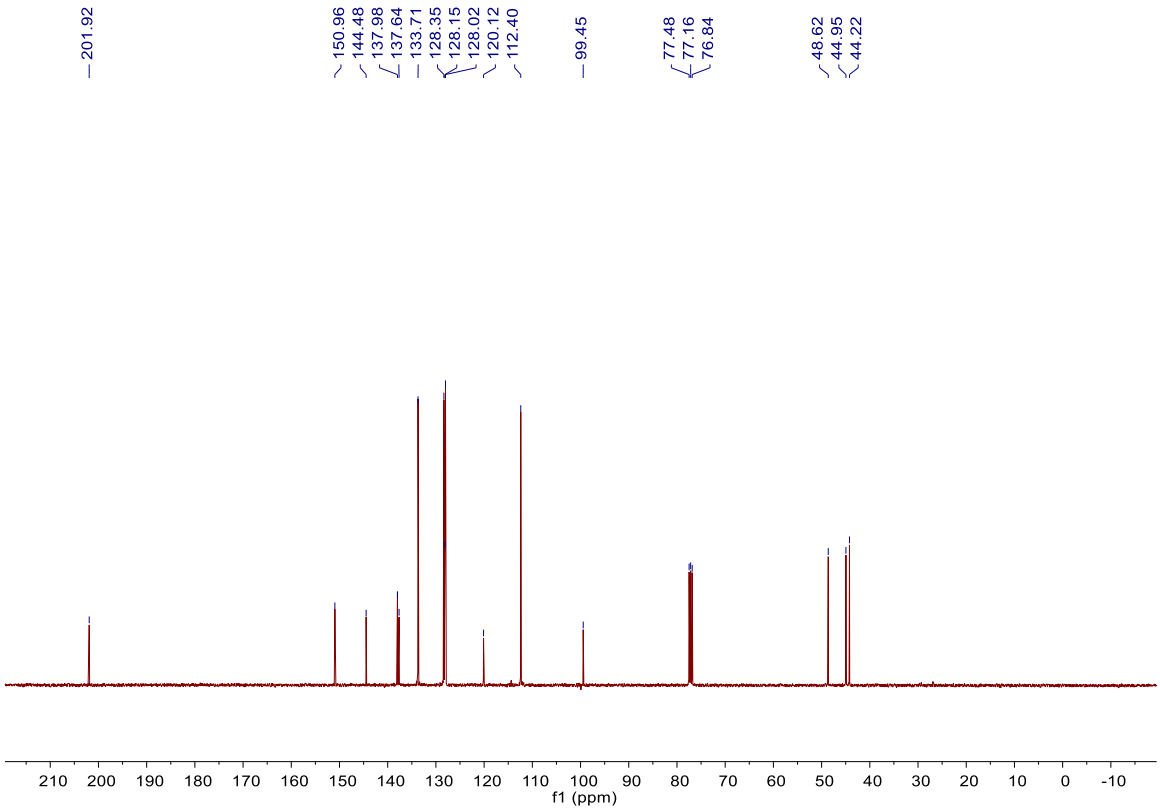
Scale: 0.1 mmol (43% yield), yellow oil, PE : EA = 3 : 1, R_f = 0.27.

^{1}H NMR spectrum ($CDCl_3$)



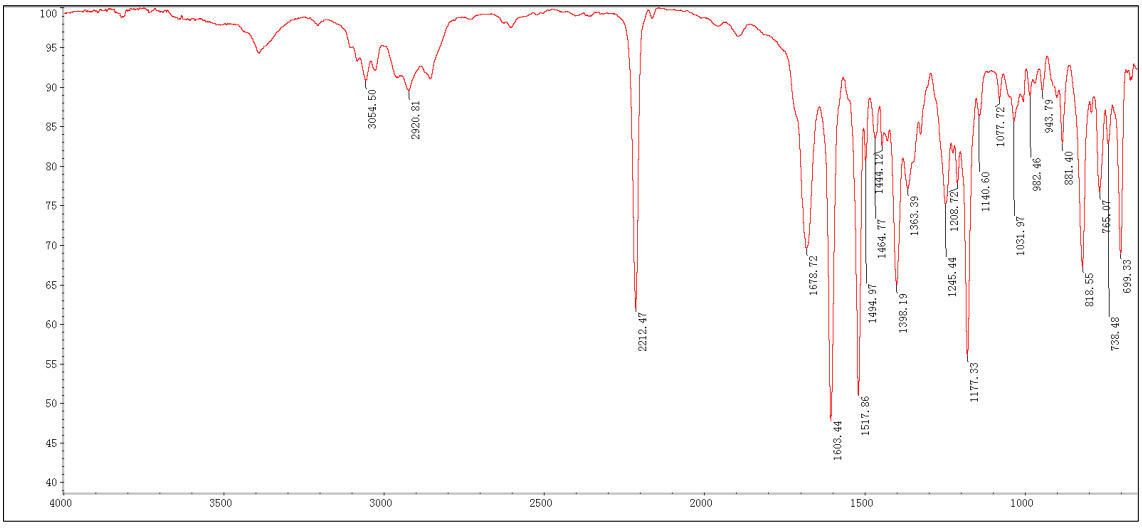
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.5 Hz, 2H), 7.37-7.18 (m, 5H), 6.79 (t, *J* = 4.8 Hz, 1H), 6.70 (d, *J* = 8.6 Hz, 2H), 4.32 (d, *J* = 4.8 Hz, 2H), 3.75 (t, *J* = 6.4 Hz, 2H), 3.10 (t, J = 6.4 Hz, 2H).

^{13}C NMR spectrum ($CDCl_3$)

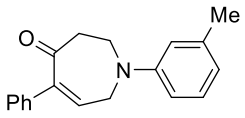


^{13}C NMR (100 MHz, $CDCl_3$) δ 201.92, 150.96, 144.48, 137.98, 137.64, 133.71, 128.35 , 128.15, 128.02, 120,12, 112.40, 99.45, 48.62, 44.95, 44.22.

IR spectrum



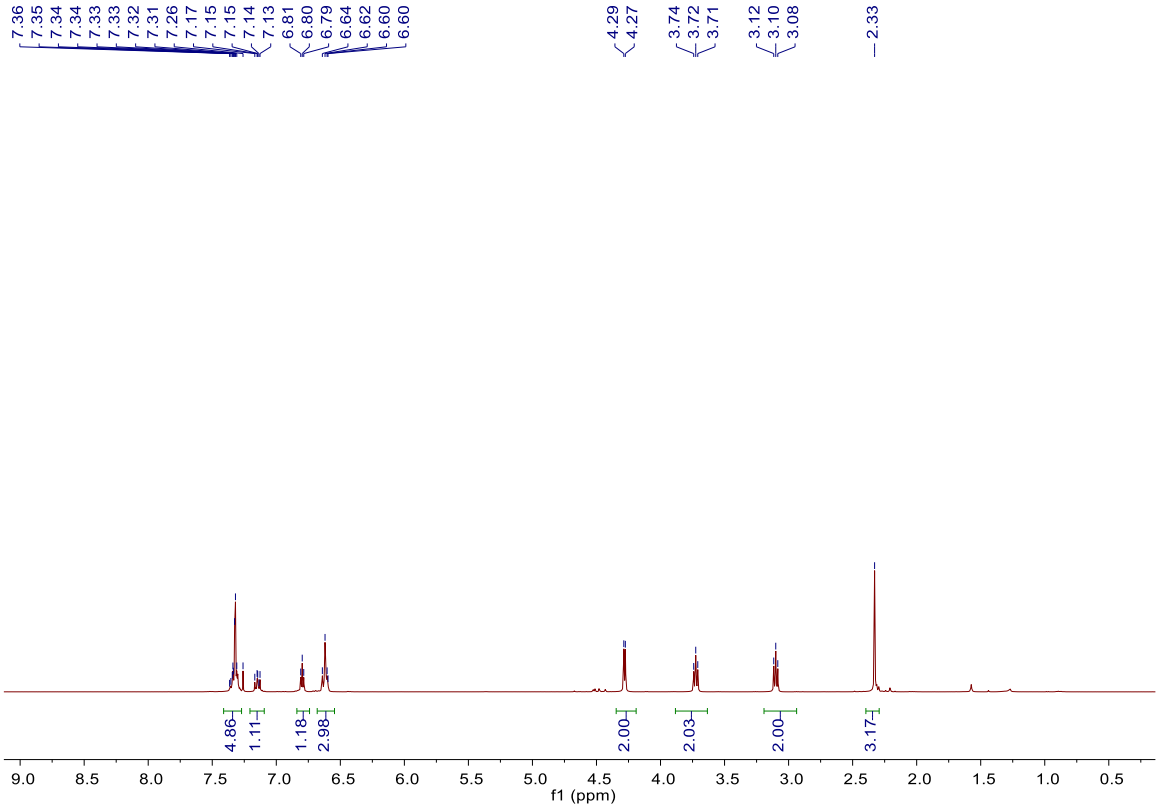
HRMS (ESI+, MeOH): *m/z* calcd. 289.1335 $(M + H)^+$, found: 289.1326.



3aj

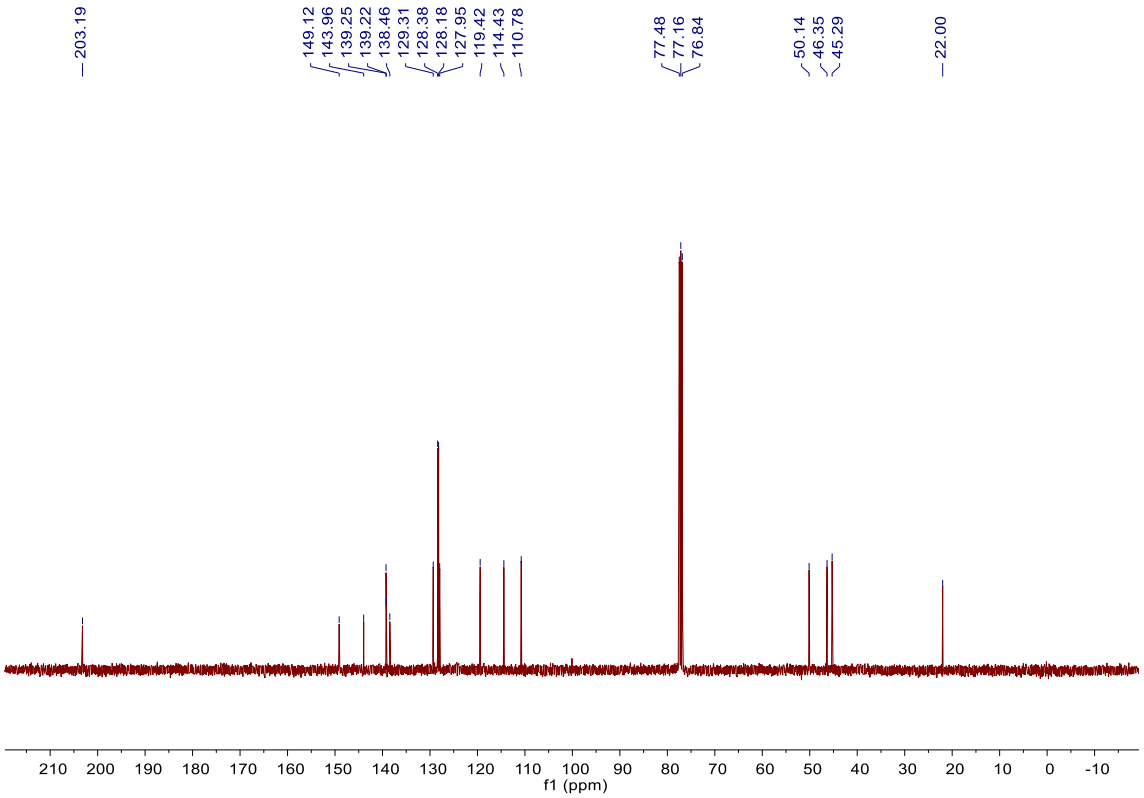
Scale: 0.1 mmol (42% yield), yellow oil, PE : EA = 5 : 1, R_f = 0.37.

^{1}H NMR spectrum ($CDCl_3$)



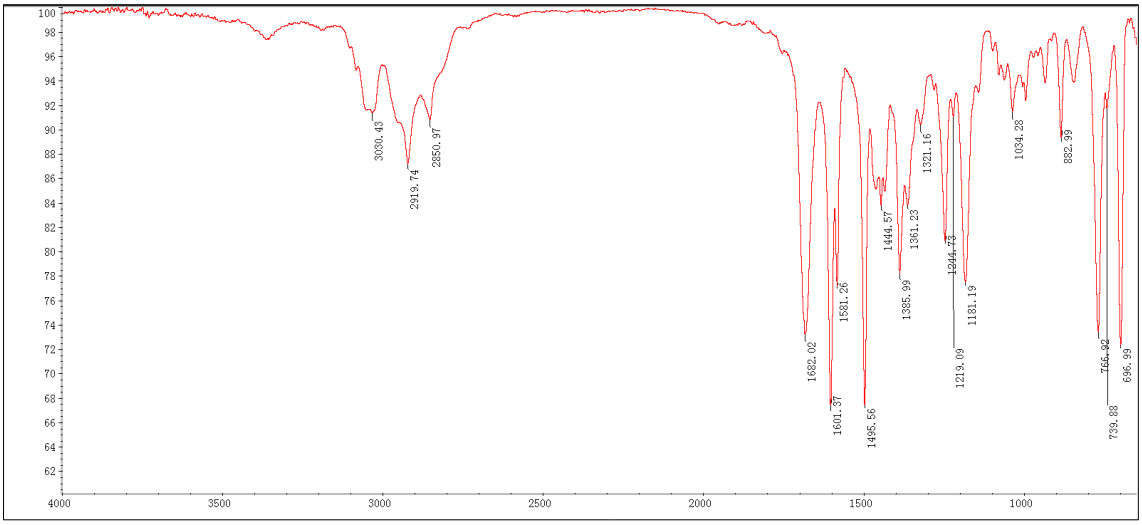
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.27 (m, 5H), 7.21-7.09 (m, 1H), 6.80 (t, *J* = 4.7 Hz, 1H), 6.68-6.55 (m, 3H), 4.28 (d, *J* = 4.7 Hz, 2H), 3.72 (t, *J* = 6.3 Hz, 2H), 3.10 (t, *J* = 6.3 Hz, 2H), 2.33 (s, 3H).

^{13}C NMR spectrum ($CDCl_3$)

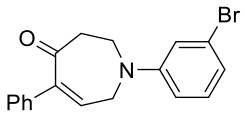


^{13}C NMR (100 MHz, $CDCl_3$) δ 203.19, 149.12, 143.96, 139.25, 139.22, 138.46, 129.31, 128.38, 128.18, 127.95, 119.42, 114.43, 110.78, 50.14, 46.35, 45.29, 22.00.

IR spectrum



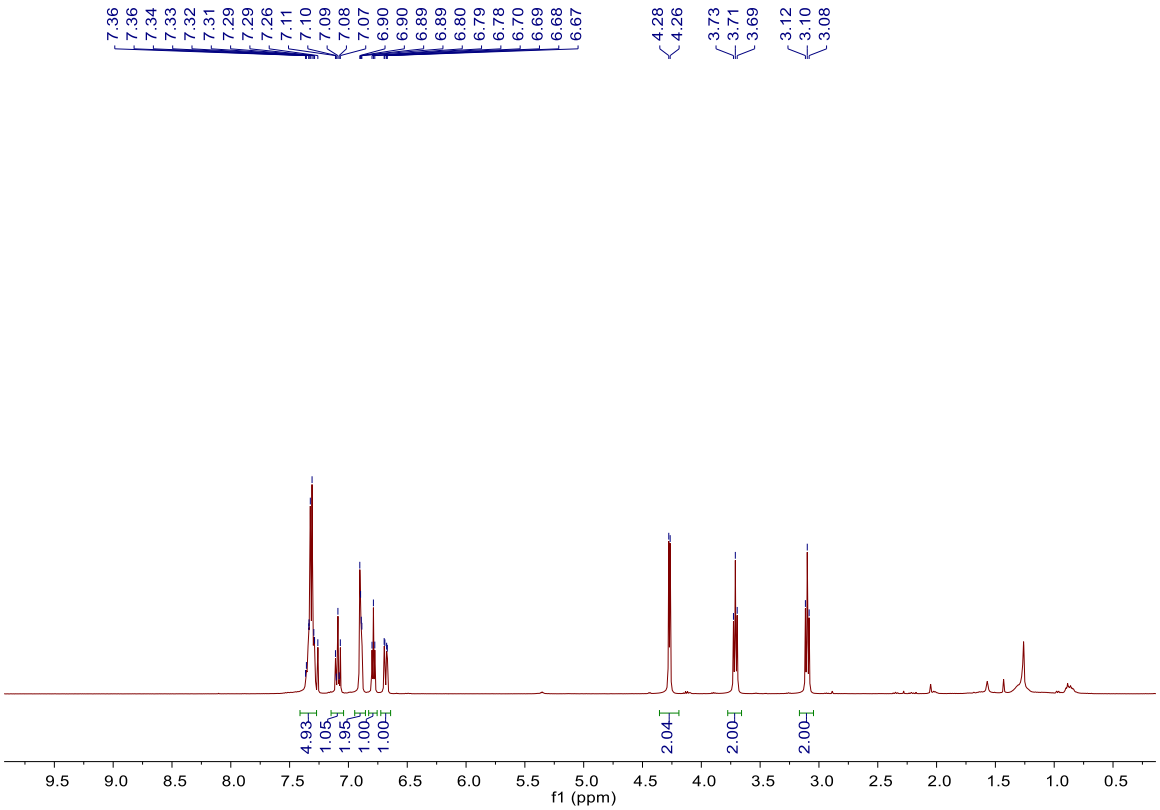
HRMS (ESI+, MeOH): *m/z* calcd. 278.1539 $(M + H)^+$, found: 278.1526.



3ak

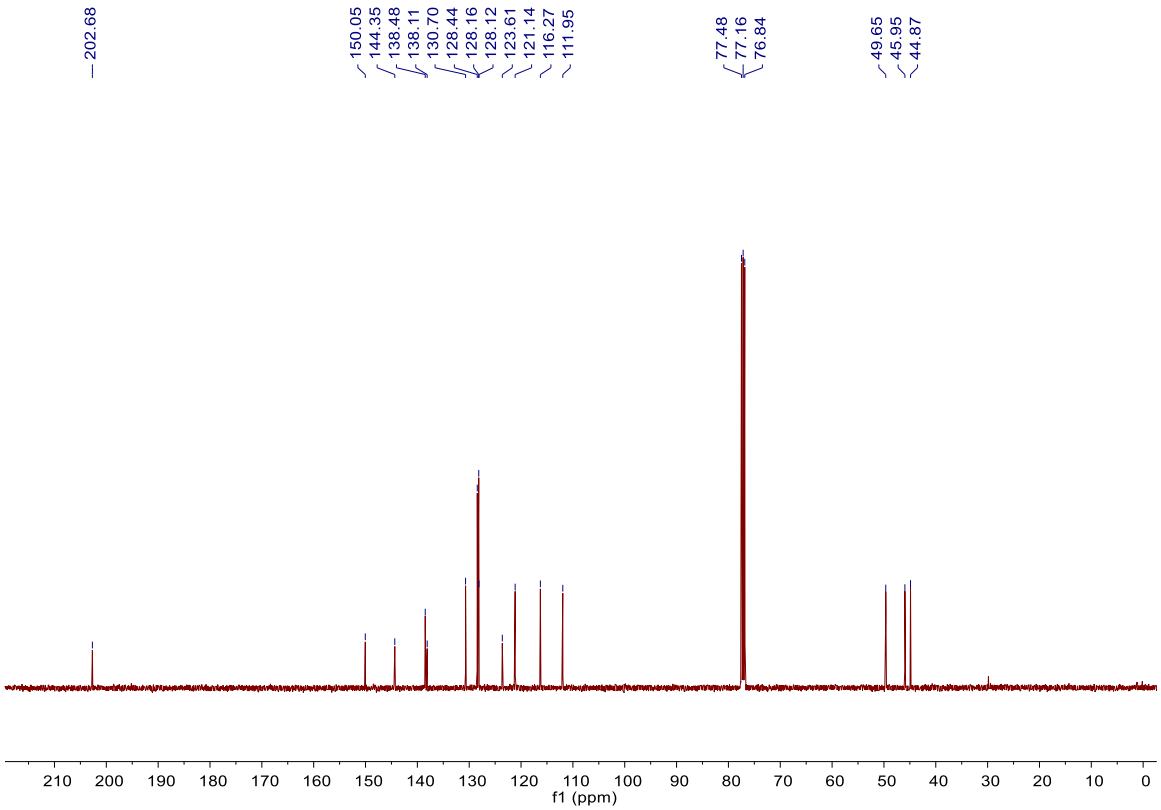
Scale: 0.1 mmol (83% yield), yellow oil, PE : EA = 5 : 1, R_f = 0.33.

^{1}H NMR spectrum ($CDCl_3$)



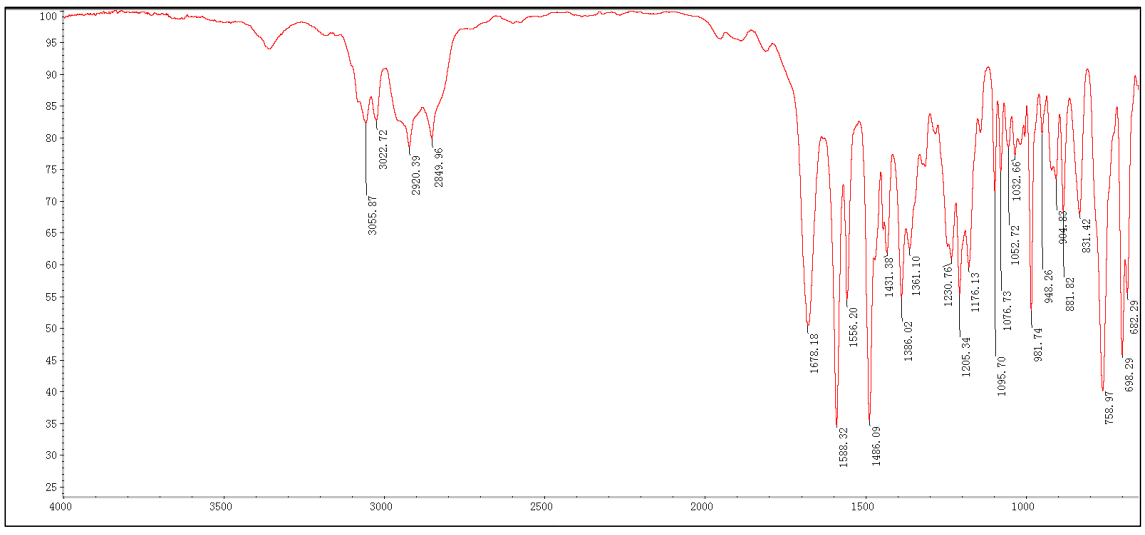
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.27 (m, 5H), 7.15-7.04 (m, 1H), 6.95-6.86 (m, 2H), 6.79 (t, *J* = 4.7 Hz, 1H), 6.68 (dd, *J* = 8.4, 2.3 Hz, 1H), 4.27 (d, *J* = 4.7 Hz, 2H), 3.71 (t, *J* = 6.3 Hz, 2H), 3.10 (t, *J* = 6.3 Hz, 2H).

^{13}C NMR spectrum ($CDCl_3$)

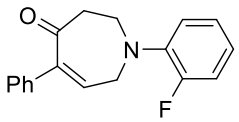


^{13}C NMR (100 MHz, $CDCl_3$) δ 202.68, 150.05, 144.35, 138.48, 138.11, 130.70, 128.44, 128.16, 128.12, 123.61, 121.14, 116.27, 111.95, 49.65, 45.95, 44.87.

IR spectrum



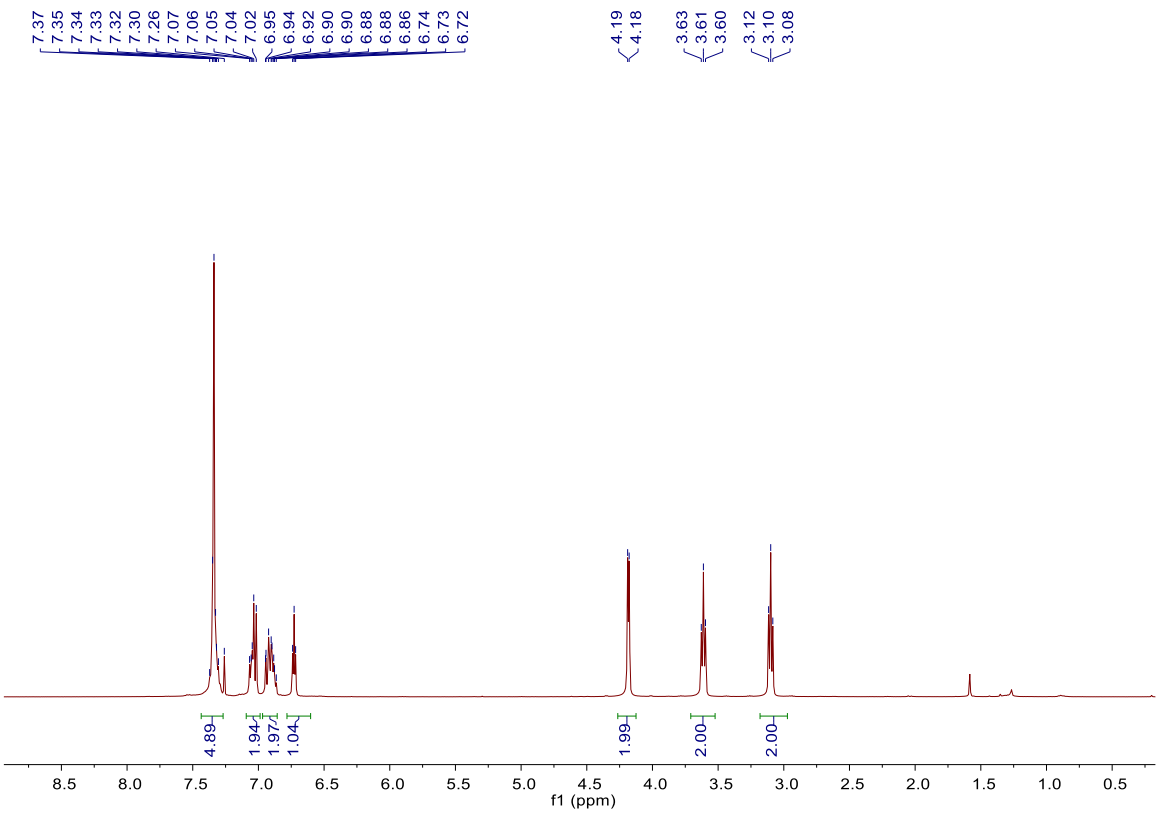
HRMS (ESI+, MeOH): *m/z* calcd. 342.0488 $(M + H)^+$, found: 342.0481.



3al

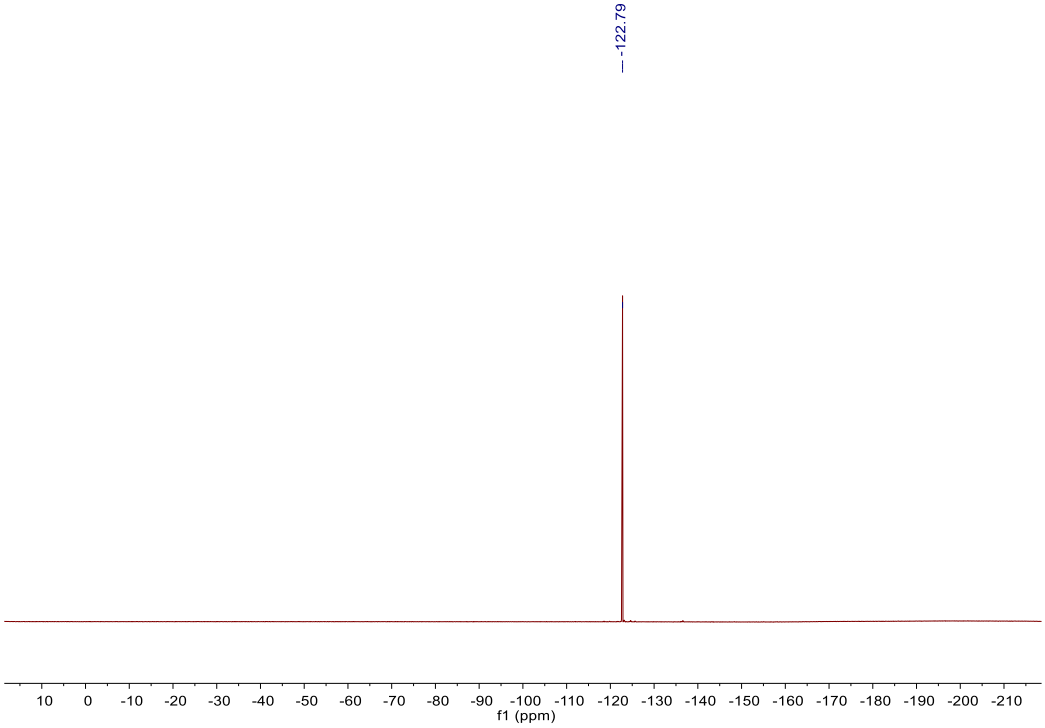
Scale: 0.1 mmol (69% yield), yellow oil, PE : EA = 5 : 1, R_f = 0.37.

^{1}H NMR spectrum ($CDCl_3$)

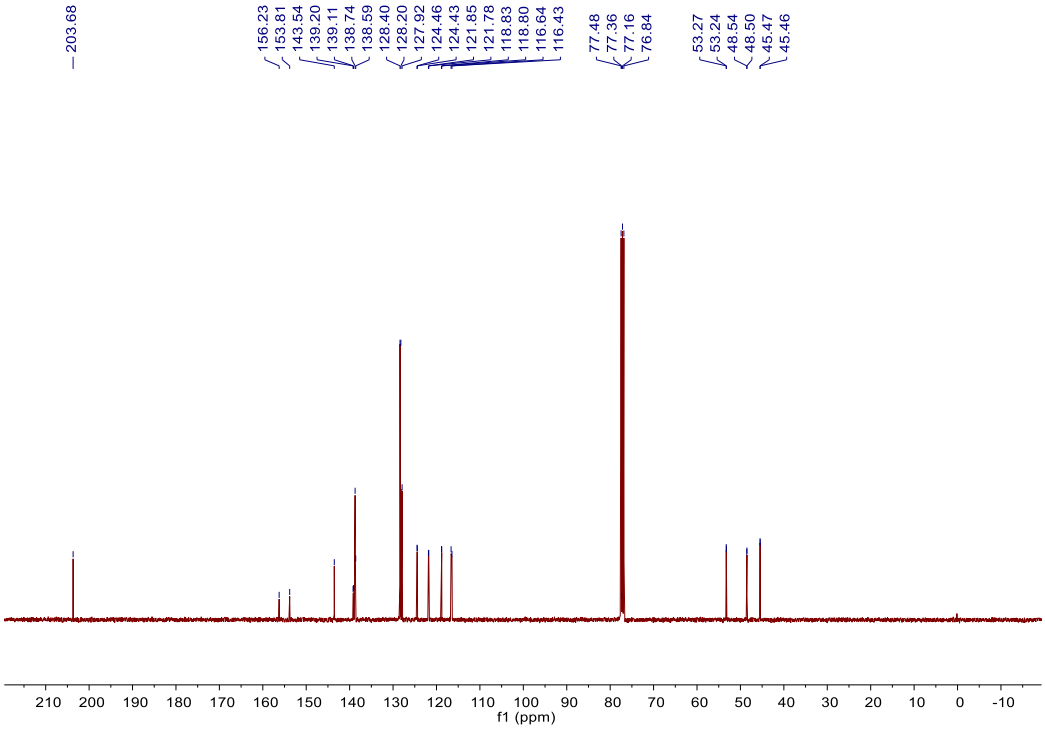


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44-7.27 (m, 5H), 7.09-6.99 (m, 2H), 6.97-6.86 (m, 2H), 6.73 (t, *J* = 4.6 Hz, 1H), 4.18 (d, *J* = 4.6 Hz, 2H), 3.61 (t, *J* = 6.4 Hz, 2H), 3.10 (t, *J* = 6.4 Hz, 2H).

^{19}F NMR spectrum ($CDCl_3$)

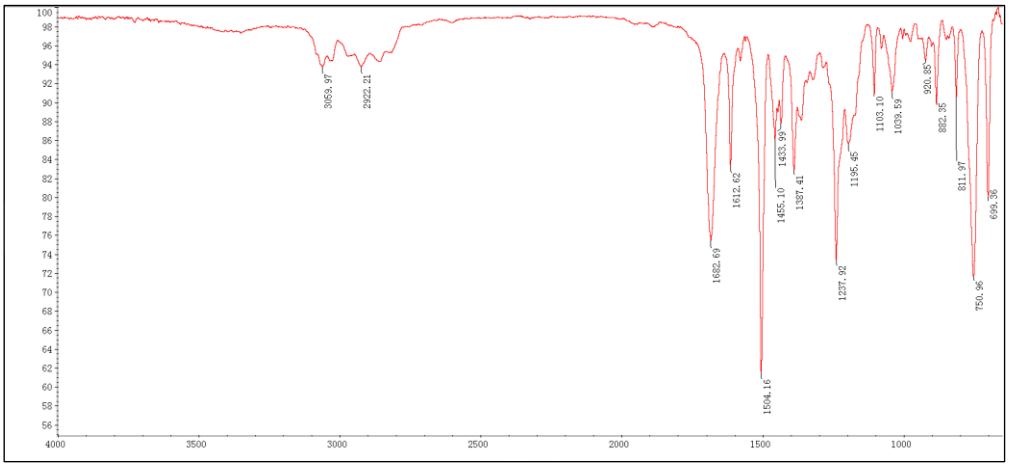


^{13}C NMR spectrum ($CDCl_3$)

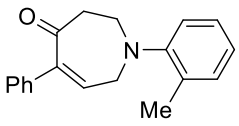


^{13}C NMR (100 MHz, $CDCl_3$) δ 203.68, 155.02 (d, J = 242.8 Hz), 143.54, 139.16 (d, J = 8.9 Hz), 138.74, 138.59, 128.40, 128.20, 127.92, 124.45 (d, J = 3.5 Hz), 121.81 (d, J = 7.7 Hz), 118.81 (d, J = 3.1 Hz), 116.54 (d, J = 20.6 Hz), 53.25 (d, J = 2.7 Hz), 48.52 (d, J = 3.5 Hz), 45.47 (d, J = 1.8 Hz).

IR spectrum



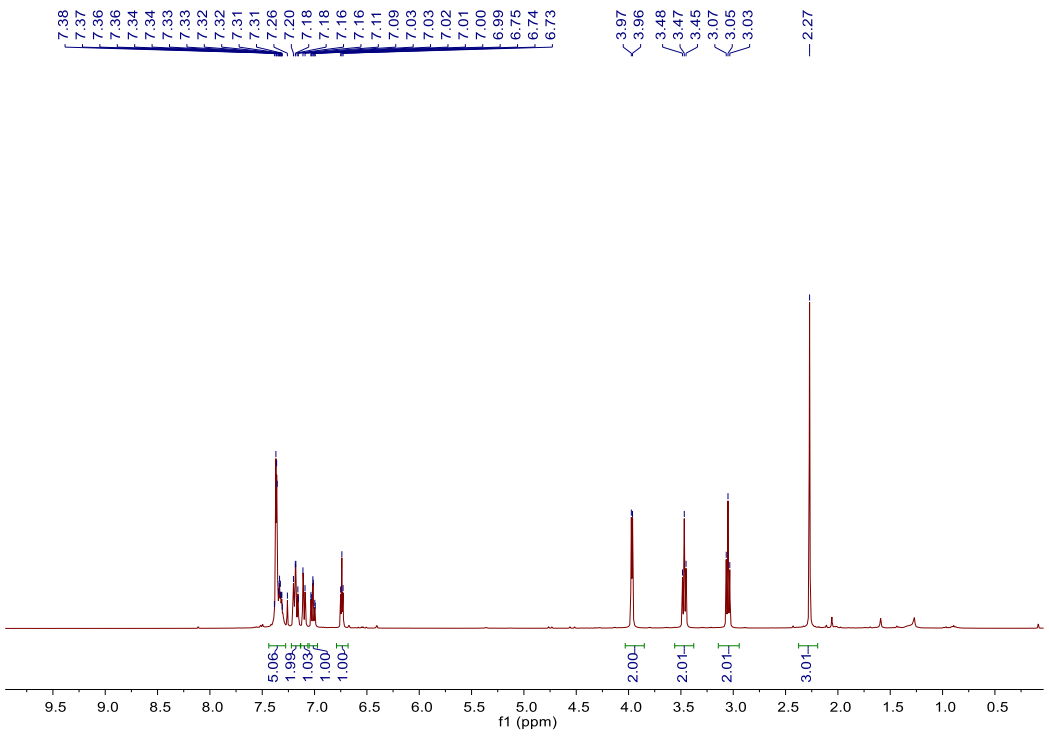
HRMS (ESI+, MeOH): *m/z* calcd. 282.1289 $(M + H)^+$, found: 282.1283.



3am

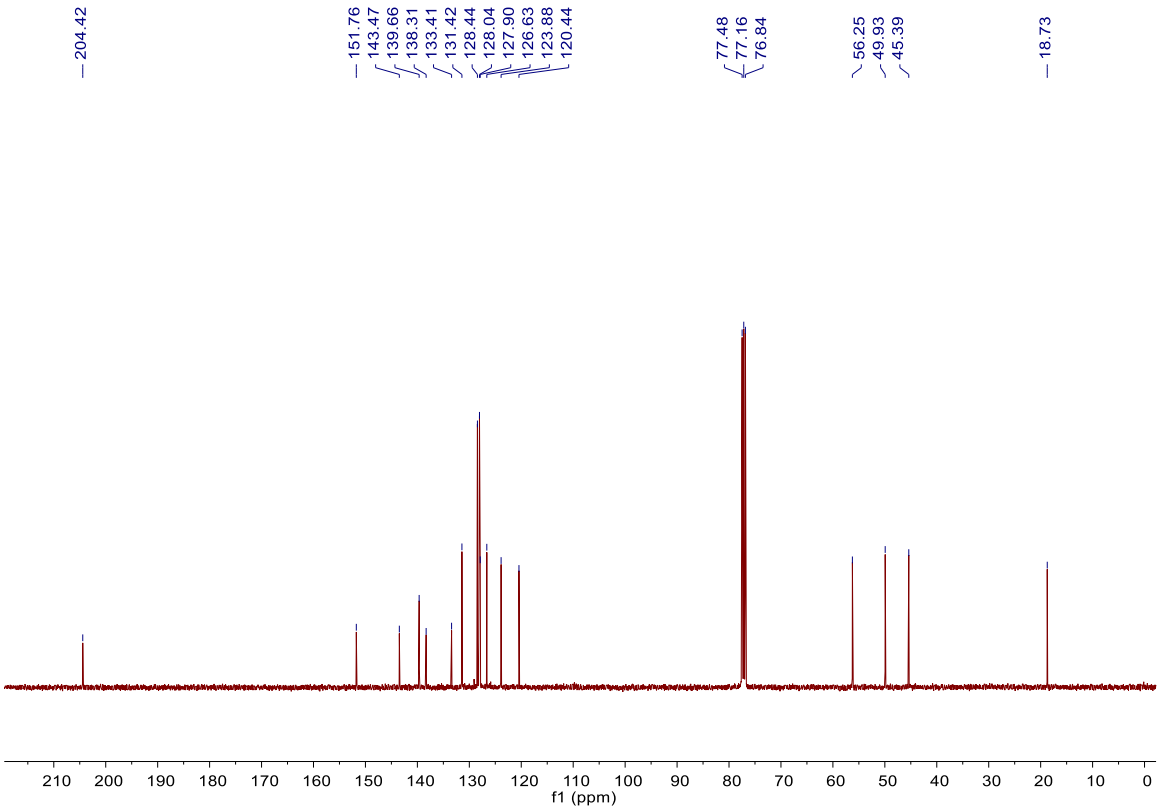
Scale: 0.1 mmol (39% yield), yellow oil, PE : EA = 10 : 1, R_f = 0.25.

^{1}H NMR spectrum ($CDCl_3$)



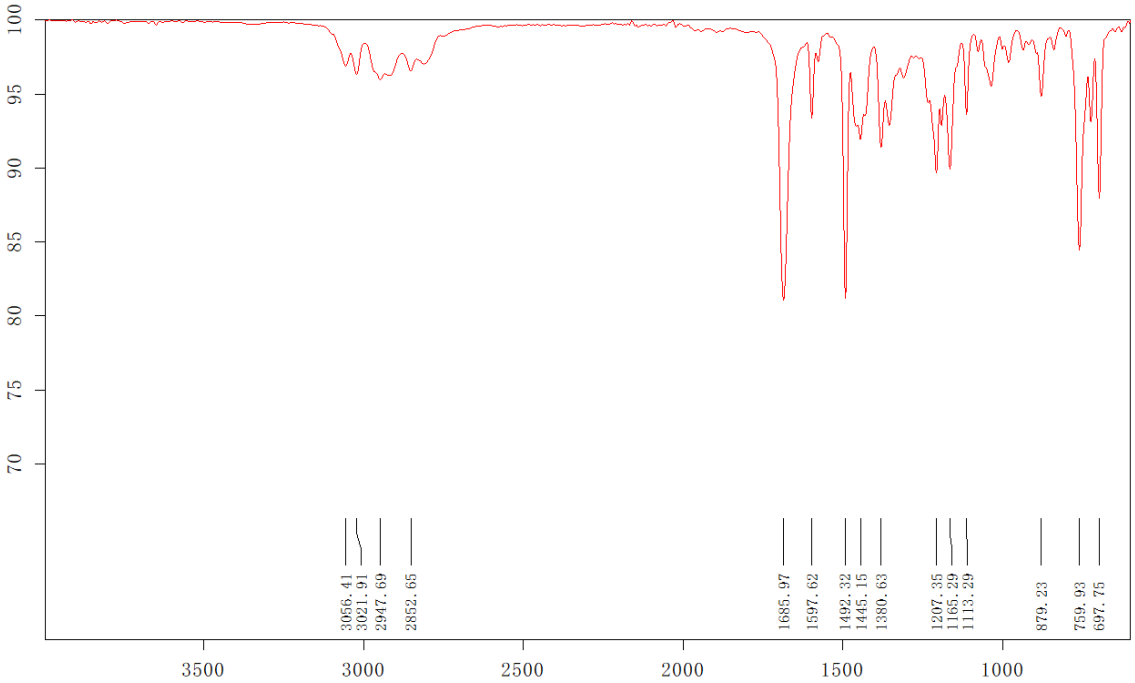
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44-7.28 (m, 5H), 7.22-7.14 (m, 2H), 7.10 (d, *J* = 8.0 Hz, 1H), 7.05-6.97 (m, 1H), 6.74 (t, *J* = 4.6 Hz, 1H), 3.97 (d, *J* = 4.4 Hz, 2H), 3.47 (t, *J* = 6.8 Hz, 2H), 3.05 (t, *J* = 6.8 Hz, 2H), 2.27 (s, 3H).

^{13}C NMR spectrum ($CDCl_3$)

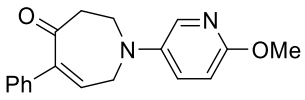


^{13}C NMR (100 MHz, $CDCl_3$) δ 204.42, 151.76, 143.47, 139.66, 138.31, 133.41, 131.42, 128.44, 128.04, 127.90, 126.63, 123.88, 120.44, 56.25, 49.93, 45.39, 18.73.

IR spectrum



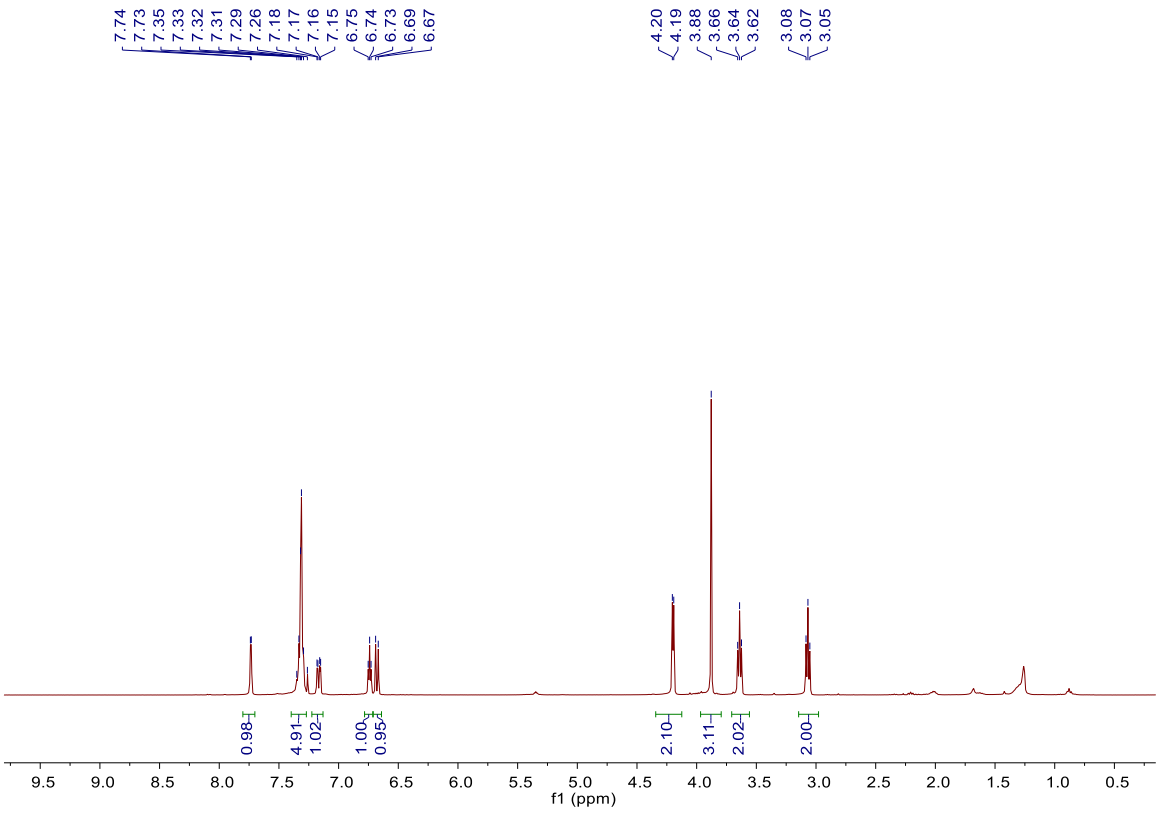
HRMS (ESI+, MeOH): *m/z* calcd. 278.1545 $(M + H)^+$, found: 278.1546.



3an

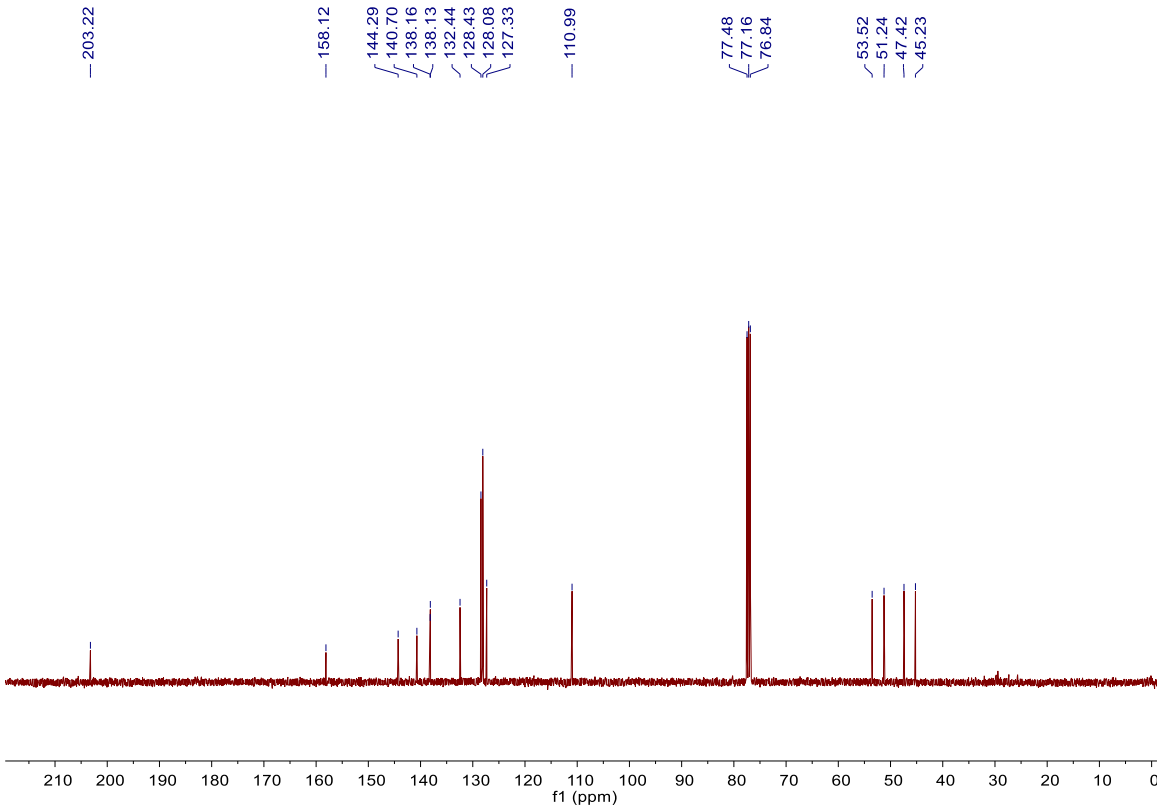
Scale: 0.1 mmol (38% yield), yellow oil, PE : EA = 3 : 1, R_f = 0.25.

^{1}H NMR spectrum ($CDCl_3$)



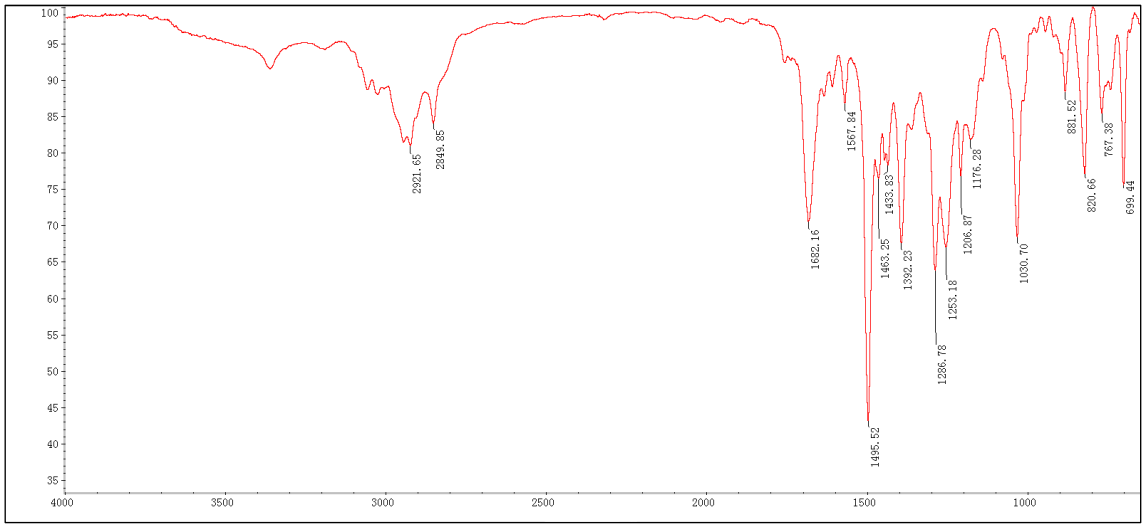
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 3.0 Hz, 1H), 7.40-7.27 (m, 5H), 7.17 (dd, *J* = 9.0, 3.1 Hz, 1H), 6.74 (t, *J* = 4.8 Hz, 1H), 6.68 (d, *J* = 8.9 Hz, 1H), 4.20 (d, *J* = 4.7 Hz, 2H), 3.88 (s, 3H), 3.64 (t, *J* = 6.4 Hz, 2H), 3.07 (t, *J* = 6.4 Hz, 2H).

^{13}C NMR spectrum ($CDCl_3$)

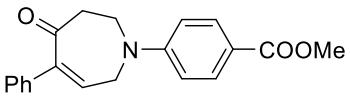


^{13}C NMR (100 MHz, $CDCl_3$) δ 203.22, 158.12, 144.29, 140.70, 138.16, 138.13, 132.44, 128.43, 128.08, 127.33, 110.99, 53.52, 51.24, 47.42, 45.23.

IR spectrum



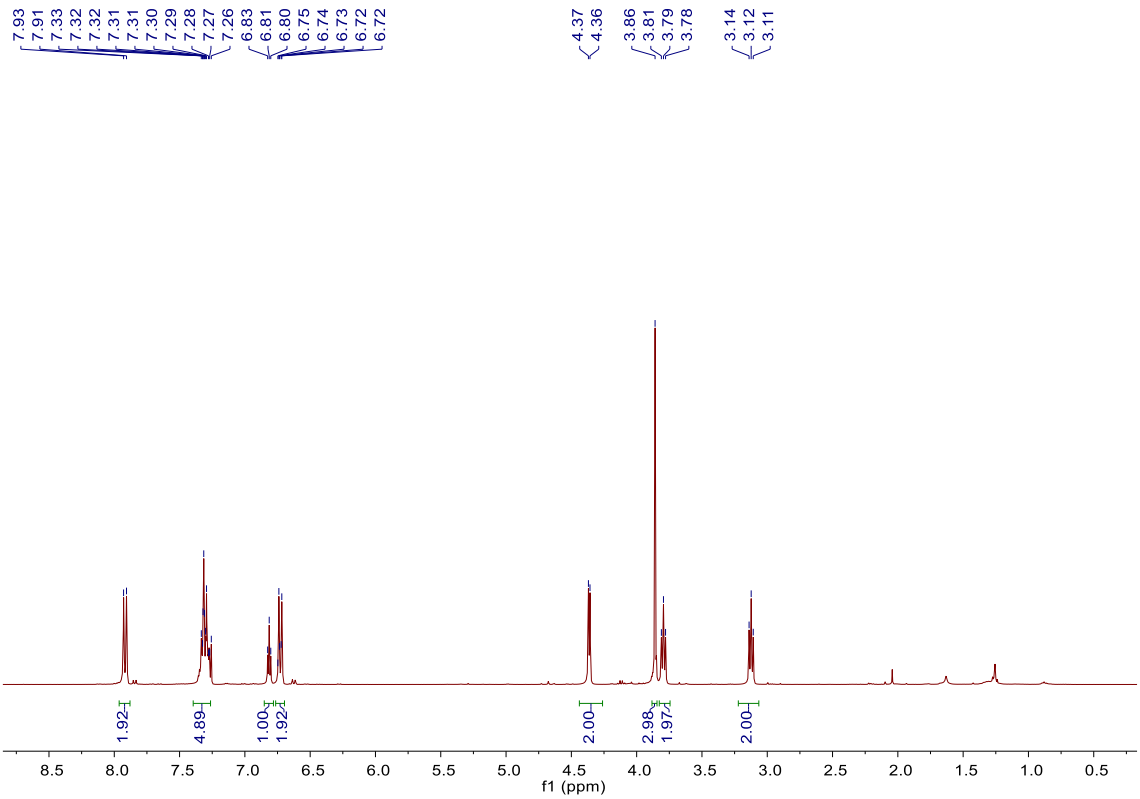
HRMS (ESI+, MeOH): *m/z* calcd. 295.1441 $(M + H)^+$, found: 295.1432.



3ao

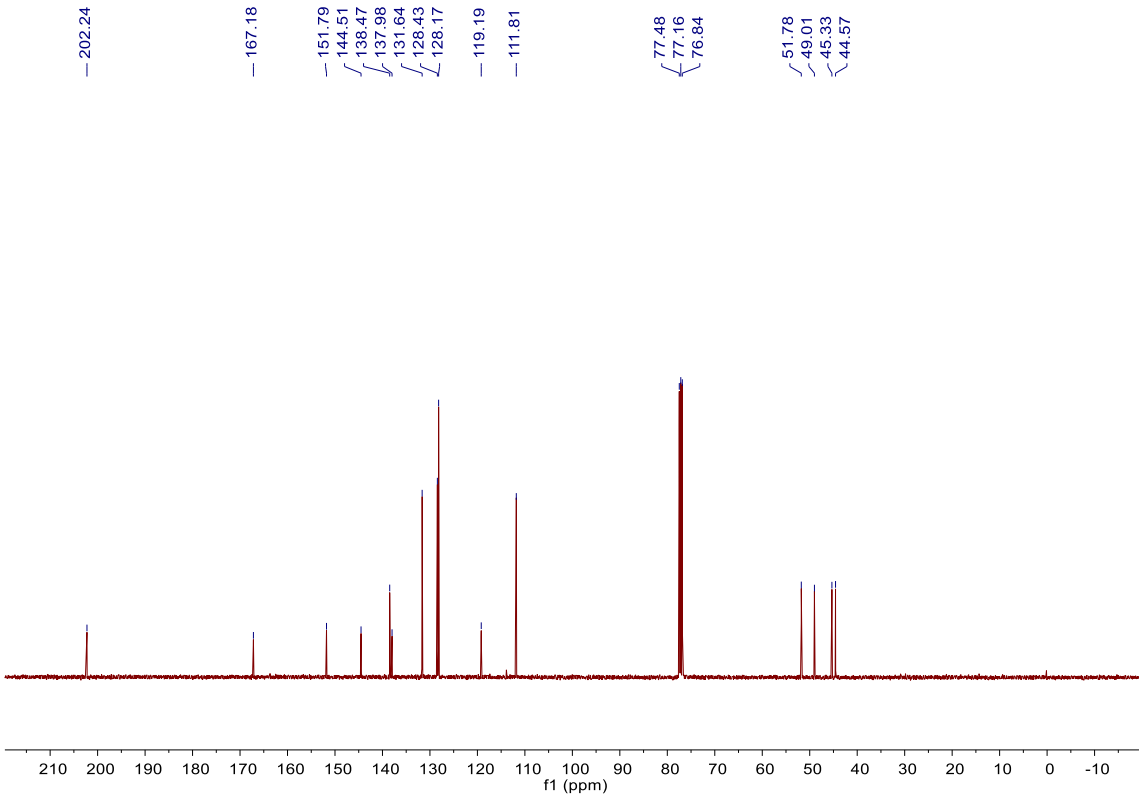
Scale: 0.1 mmol (79% yield), white solid, PE : EA = 3 : 1, R_f = 0.27.

^{1}H NMR spectrum ($CDCl_3$)



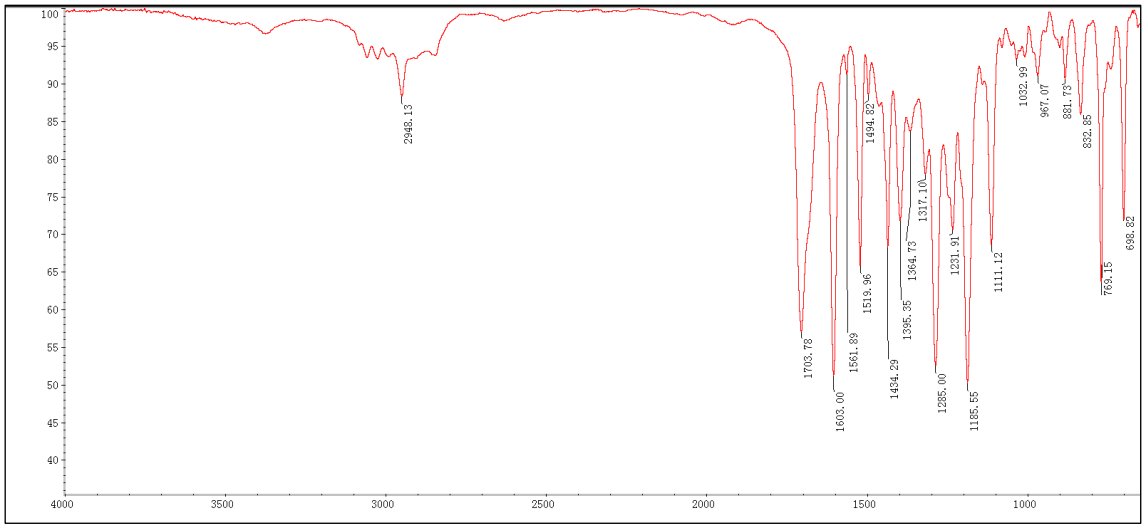
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 9.0 Hz, 2H), 7.40-7.26 (m, 5H), 6.81 (t, *J* = 4.8 Hz, 1H), 6.76-6.70 (m, 2H), 4.36 (d, *J* = 4.8 Hz, 2H), 3.86 (s, 3H), 3.79 (t, *J* = 6.4 Hz, 2H), 3.12 (t, *J* = 6.4 Hz, 2H).

^{13}C NMR spectrum ($CDCl_3$)

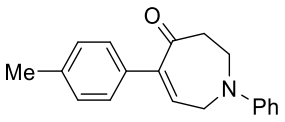


^{13}C NMR (100 MHz, $CDCl_3$) δ 202.24, 167.18, 151.79, 144.51, 138.47, 137.98, 131.64, 128.43, 128.17, 119.19, 111.81, 51.78, 49.01, 45.33, 44.57.

IR spectrum



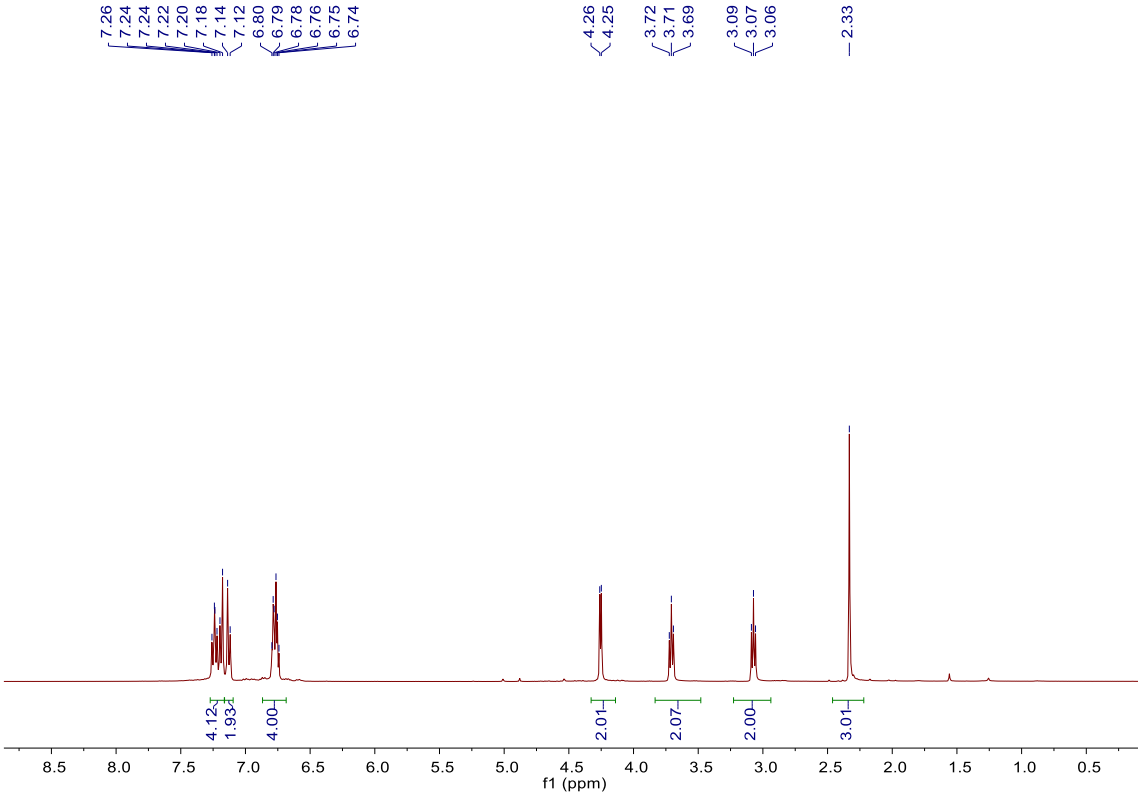
HRMS (ESI+, MeOH): *m/z* calcd. 322.1438 $(M + H)^+$, found: 322.1431.



3ba

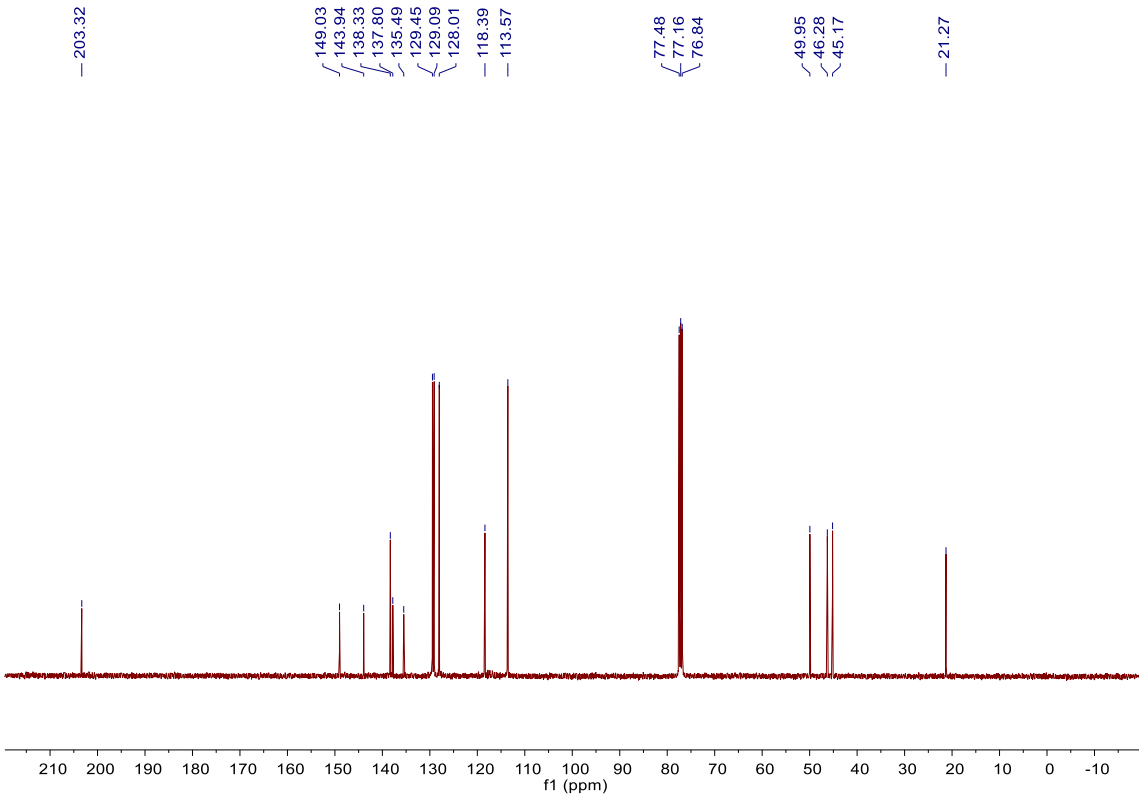
Scale: 0.1 mmol (74% yield), yellow oil, PE : EA = 5 : 1, R_f = 0.40.

^{1}H NMR spectrum ($CDCl_3$)



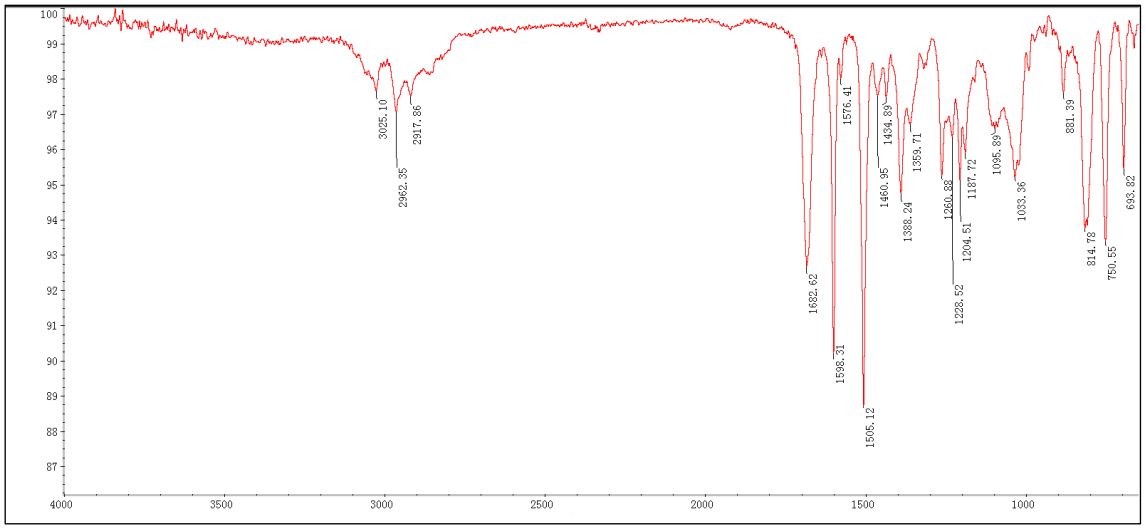
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27-7.16 (m, 4H), 7.13 (d, *J* = 7.9 Hz, 2H), 6.87-6.69 (m, 4H), 4.25 (d, *J* = 4.8 Hz, 2H), 3.71 (t, *J* = 6.4 Hz, 2H), 3.07 (t, *J* = 6.4 Hz, 2H), 2.33 (s, 3H).

^{13}C NMR spectrum ($CDCl_3$)

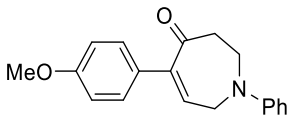


^{13}C NMR (100 MHz, $CDCl_3$) δ 203.32, 149.03, 143.94, 138.33, 137.80, 135.49, 129.45, 129.09, 128.01, 118.39, 113.57, 49.95, 46.28, 45.17, 21.27.

IR spectrum



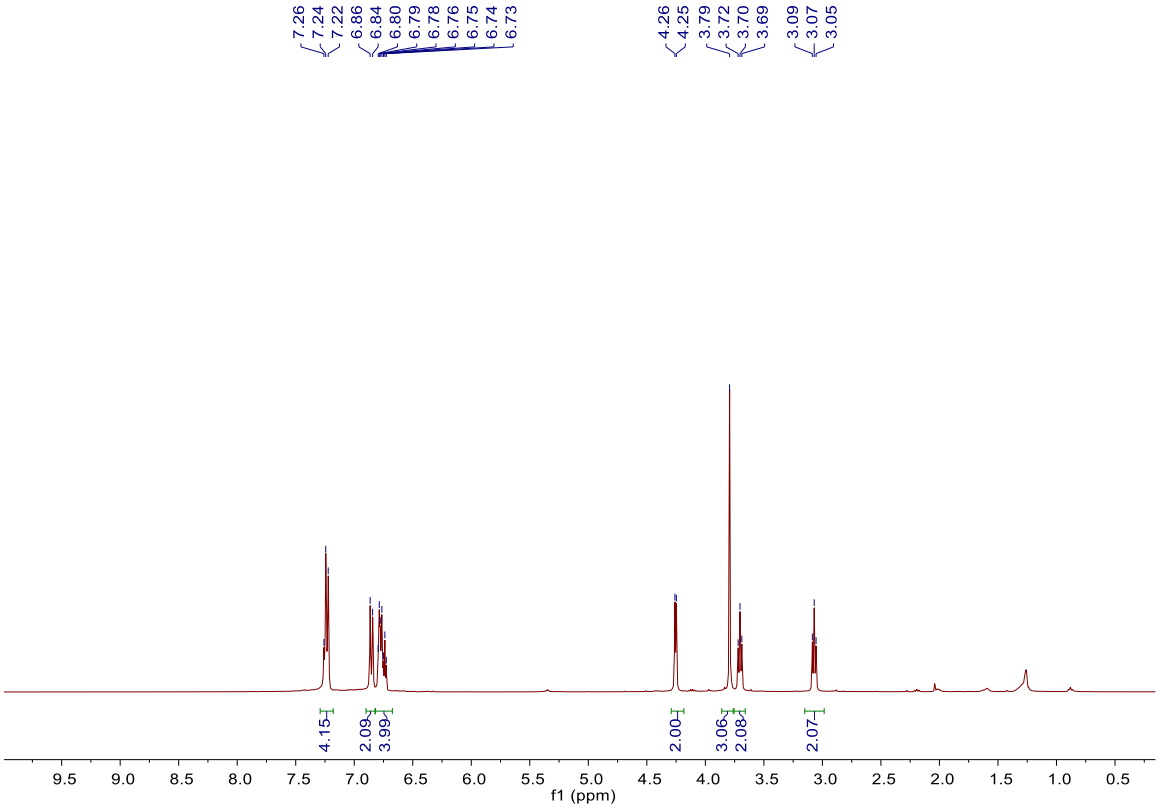
HRMS (ESI+, MeOH): *m/z* calcd. 278.1539 $(M + H)^+$, found: 278.1526.



3ca

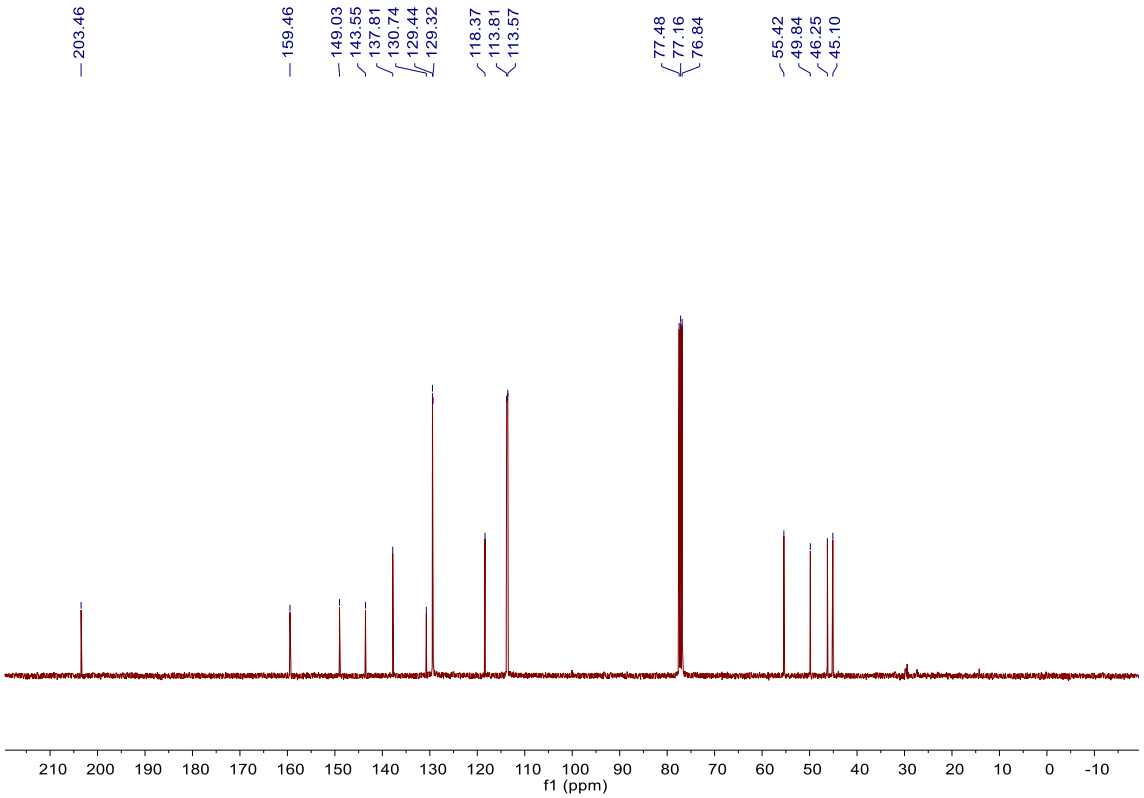
Scale: 0.1 mmol (71% yield), yellow oil, PE : EA = 5 : 1, R_f = 0.30.

^{1}H NMR spectrum ($CDCl_3$)



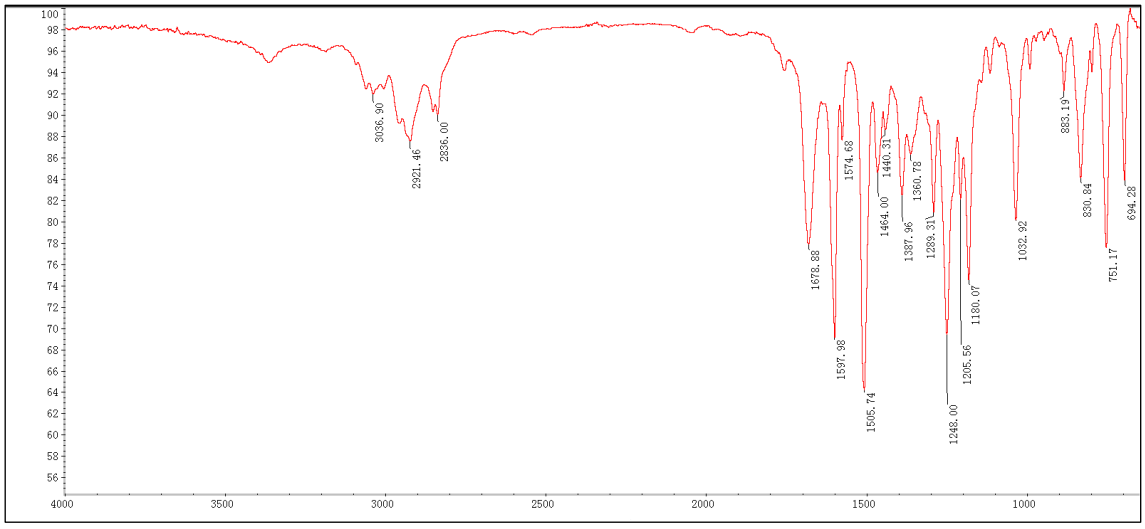
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (d, *J* = 8.5 Hz, 4H), 6.85 (d, *J* = 8.5 Hz, 2H), 6.82-6.67 (m, 4H), 4.25 (d, *J* = 4.8 Hz, 2H), 3.79 (s, 3H), 3.70 (t, *J* = 6.4 Hz, 2H), 3.07 (t, *J* = 6.4 Hz, 2H).

^{13}C NMR spectrum ($CDCl_3$)

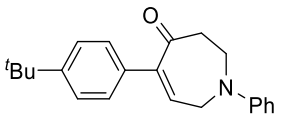


^{13}C NMR (100 MHz, $CDCl_3$) δ 203.46, 159.46, 149.03, 143.55, 137.81, 130.74, 129.44, 129.32, 118.37, 113.81, 113.57, 55.42, 49.84, 46.25, 45.10.

IR spectrum



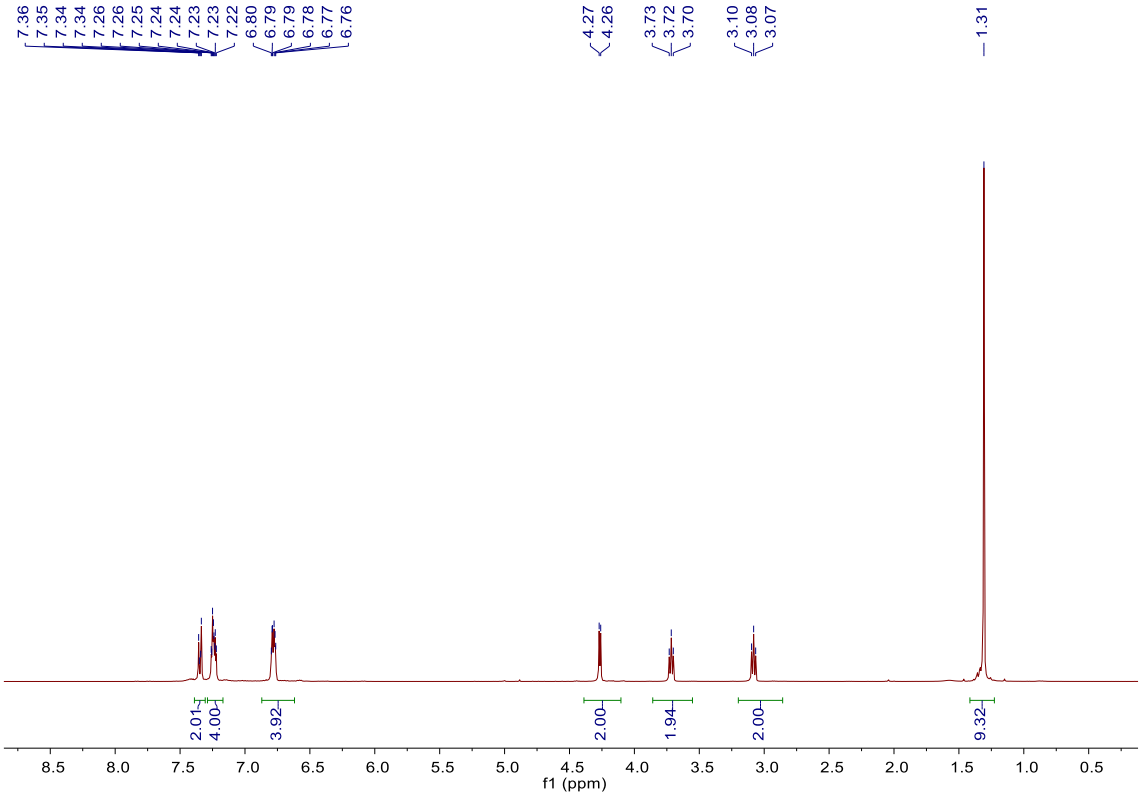
HRMS (ESI+, MeOH): *m/z* calcd. 294.1489 $(M + H)^+$, found: 294.1484.



3da

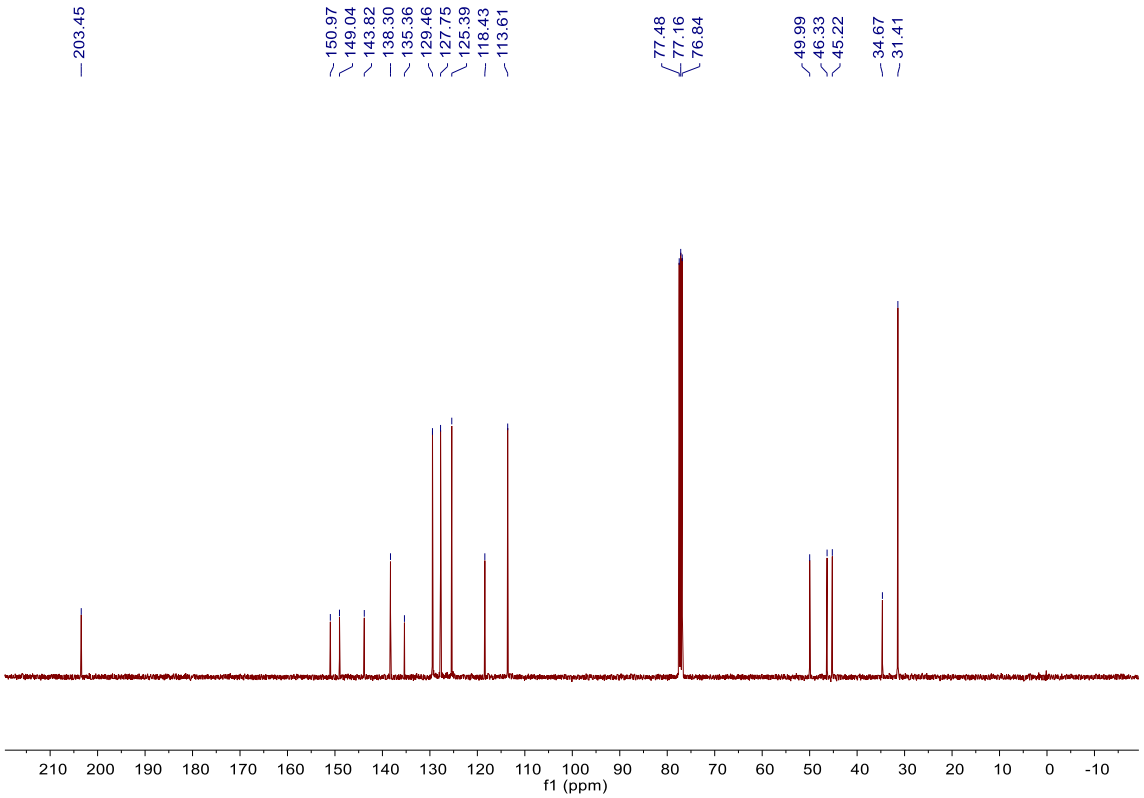
Scale: 0.1 mmol (67% yield), yellow solid, PE : EA = 5 : 1, R_f = 0.42.

^{1}H NMR spectrum ($CDCl_3$)



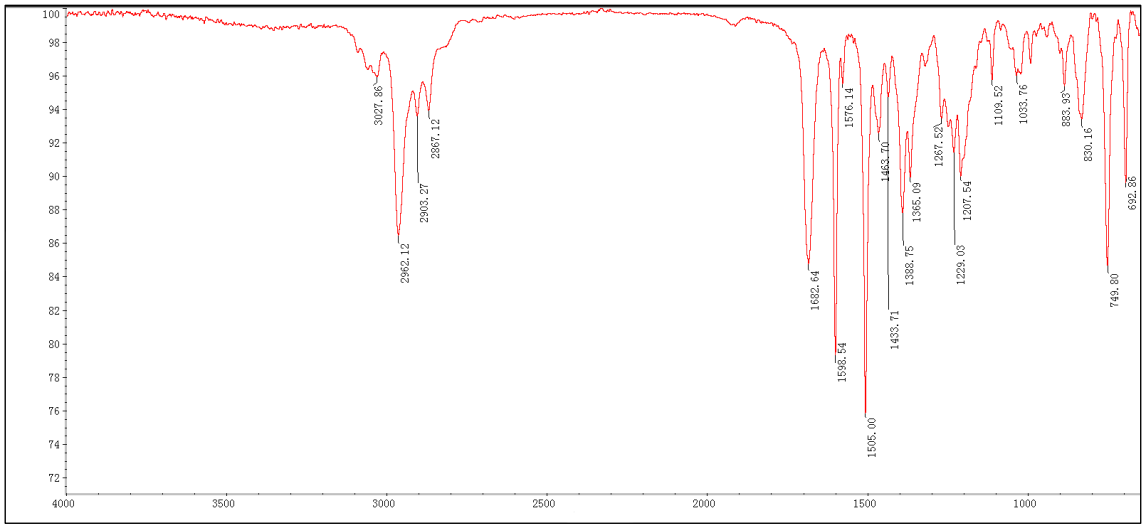
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.31 (m, 2H), 7.29-7.17 (m, 4H), 6.87-6.62 (m, 4H), 4.27 (d, *J* = 4.7 Hz, 2H), 3.72 (t, *J* = 6.3 Hz, 2H), 3.08 (t, *J* = 6.3 Hz, 2H), 1.31 (s, 9H).

^{13}C NMR spectrum ($CDCl_3$)

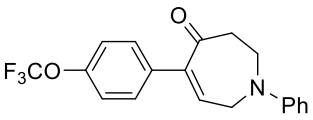


^{13}C NMR (100 MHz, $CDCl_3$) δ 203.45, 150.97, 149.04, 143.82, 138.30, 135.36, 129.46, 127.75, 125.39, 118.43, 113.61, 49.99, 46.33, 45.22, 34.67, 31.41.

IR spectrum



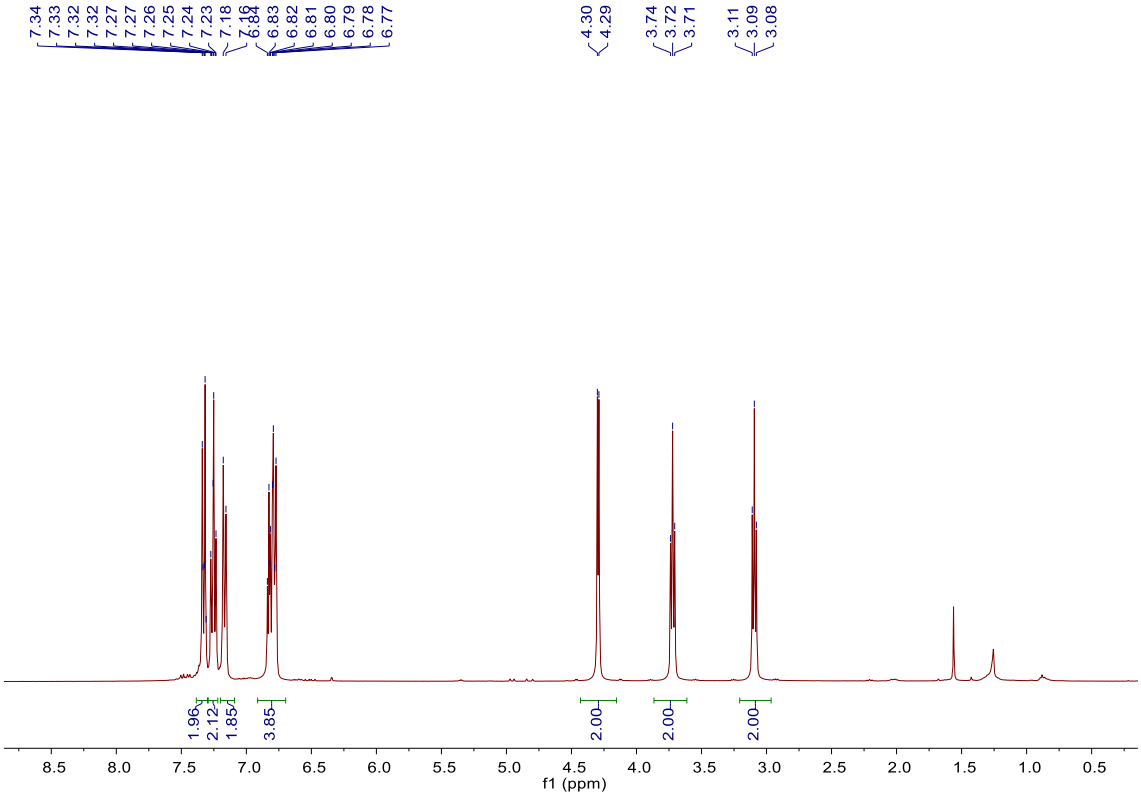
HRMS (ESI+, MeOH): *m/z* calcd. 320.2009 $(M + H)^+$, found: 320.1999.



3ea

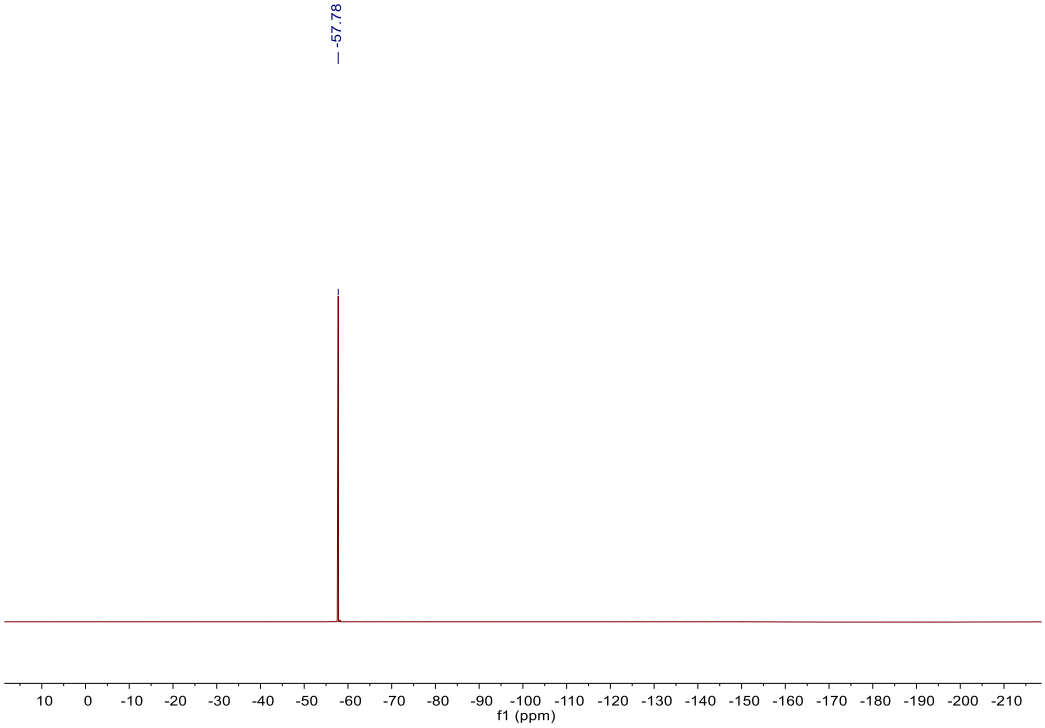
Scale: 0.1 mmol (65% yield), yellow oil, PE : EA = 5 : 1, R_f = 0.37.

^{1}H NMR spectrum ($CDCl_3$)

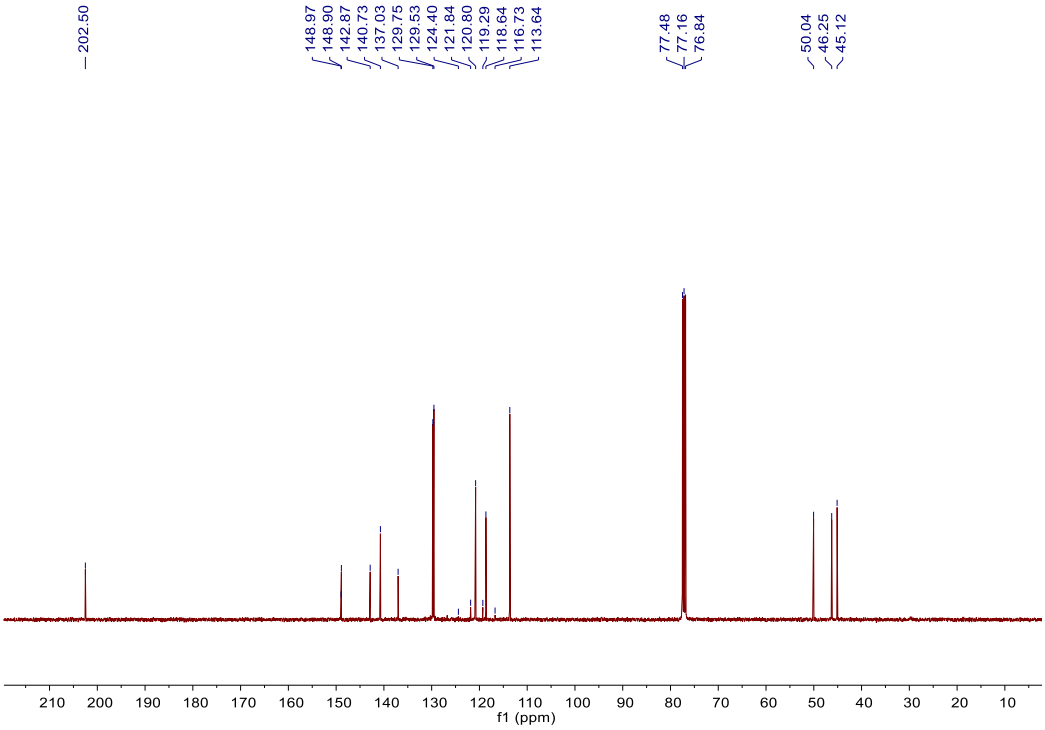


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.30 (m, 2H), 7.29-7.22 (m, 2H), 7.17 (d, *J* = 8.3 Hz, 2H), 6.91-6.70 (m, 4H), 4.29 (d, *J* = 4.7 Hz, 2H), 3.72 (t, *J* = 6.4 Hz, 2H), 3.09 (t, *J* = 6.4 Hz, 2H).

^{19}F NMR spectrum ($CDCl_3$)

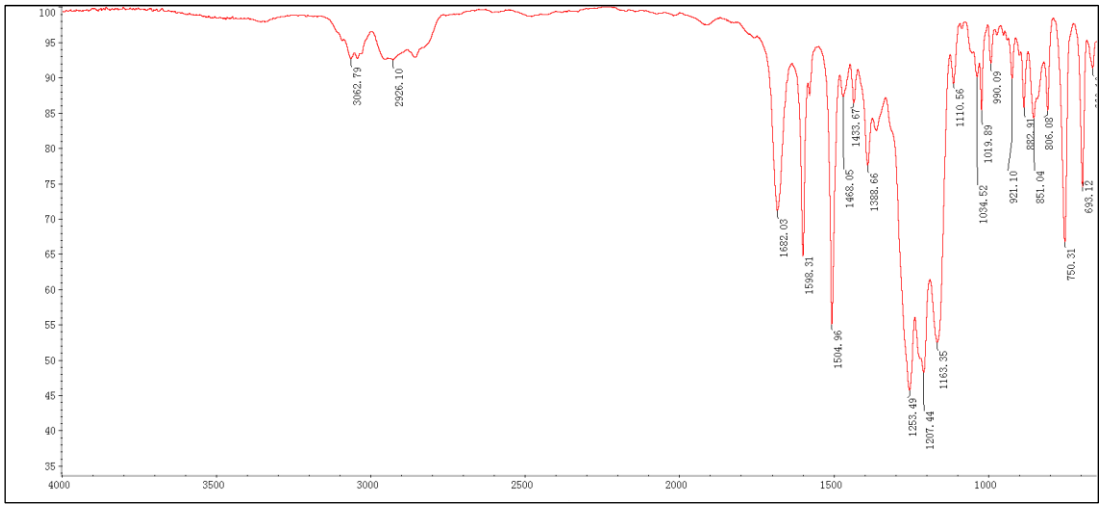


^{13}C NMR spectrum ($CDCl_3$)

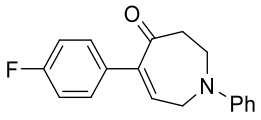


^{13}C NMR (100 MHz, $CDCl_3$) δ 202.50, 148.97, 148.90, 142.87, 140.73, 137.03, 129.75, 129.53, 120.80, 120.57 (q, J = 255.8 Hz), 118.64, 113.64, 50.04, 46.25, 45.12.

IR spectrum



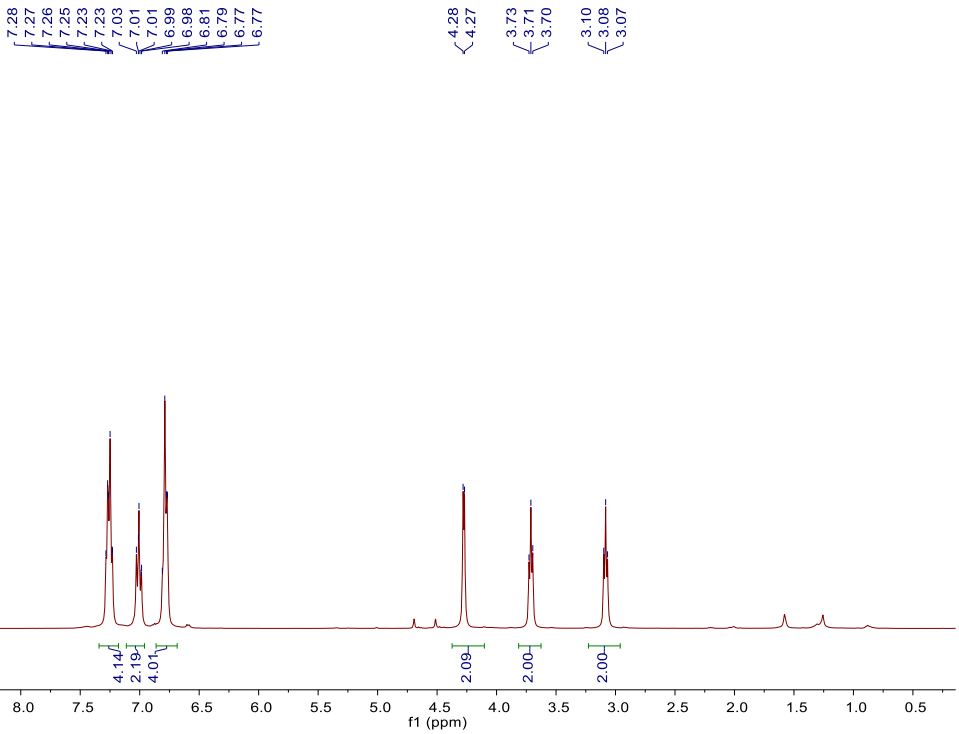
HRMS (ESI+, MeOH): *m/z* calcd. 348.1206 $(M + H)^+$, found: 348.1195.



3fa

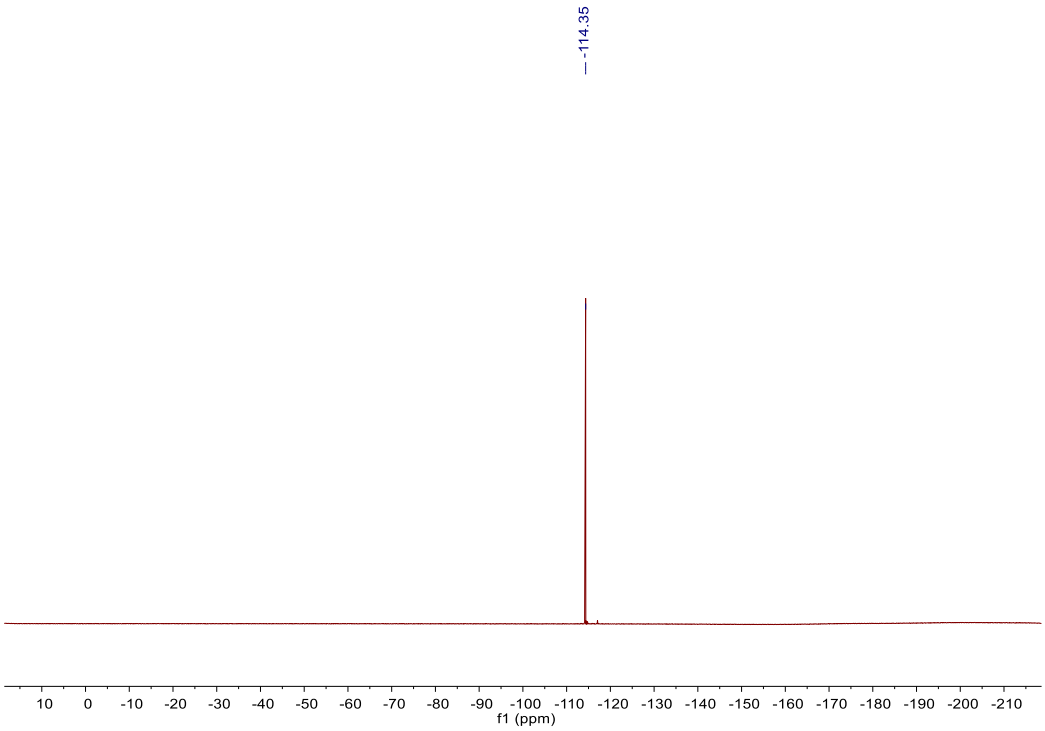
Scale: 0.1 mmol (83% yield), yellow solid, PE : EA = 5 : 1, R_f = 0.35.

^{1}H NMR spectrum ($CDCl_3$)

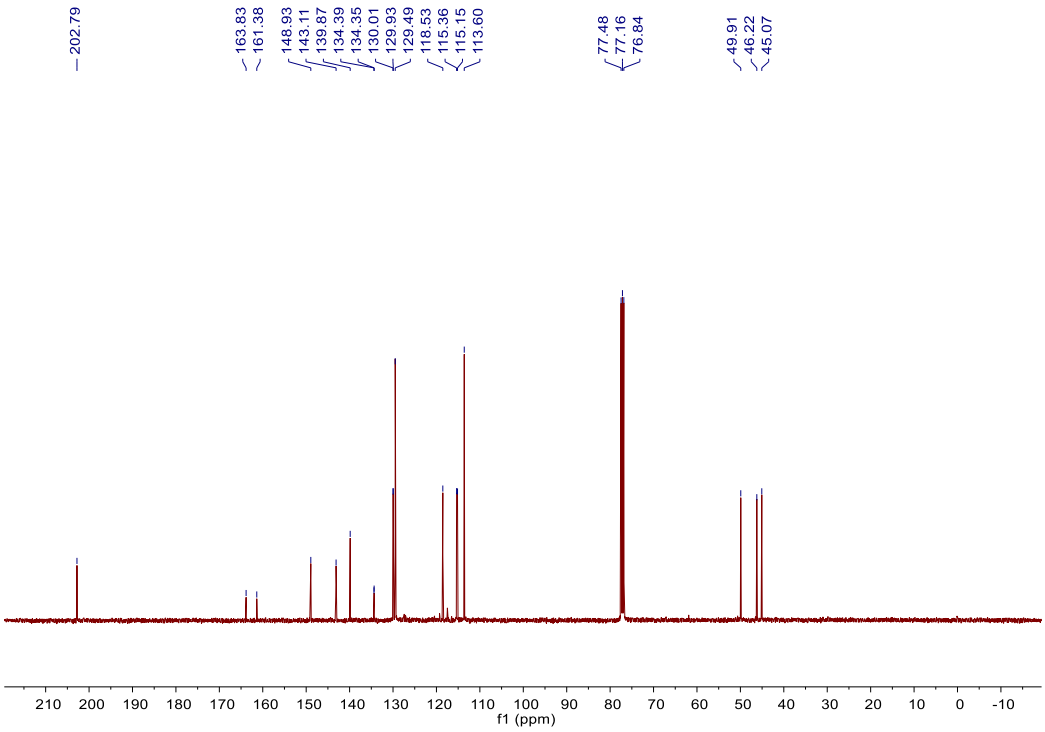


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.18 (m, 4H), 7.11-6.96 (m, 2H), 6.86-6.68 (m, 4H), 4.28 (d, *J* = 4.8 Hz, 2H), 3.71 (t, *J* = 6.4 Hz, 2H), 3.08 (t, *J* = 6.4 Hz, 2H).

^{19}F NMR spectrum ($CDCl_3$)

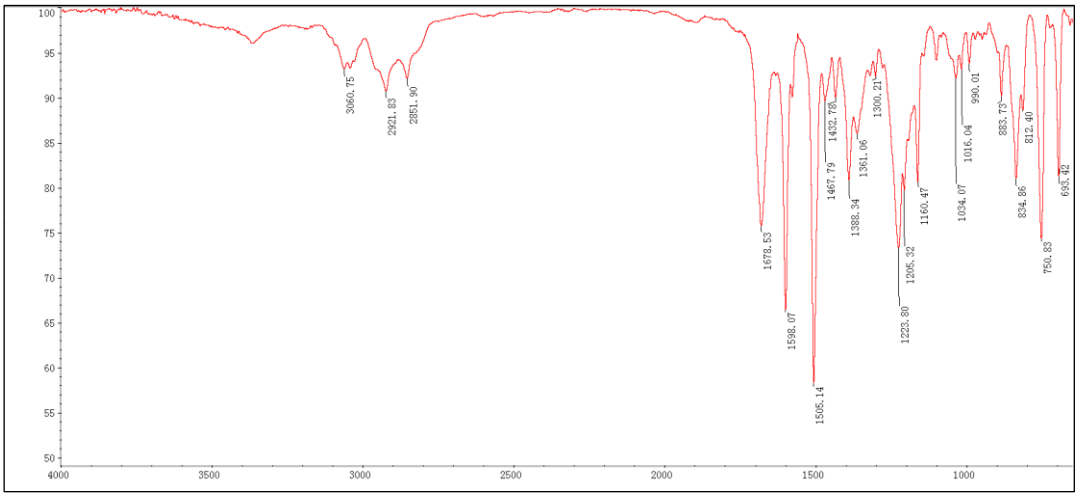


^{13}C NMR spectrum ($CDCl_3$)

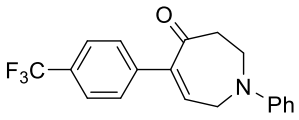


^{13}C NMR (100 MHz, $CDCl_3$) δ 202.79, 162.61 (d, *J* = 245.7 Hz), 148.93, 143.11, 139.87, 134.37 (d, *J* = 3.3 Hz), 129.97 (d, *J* = 8.1 Hz), 129.49, 118.53, 115.25 (d, *J* = 21.4 Hz), 113.60, 49.91, 46.22, 45.07.

IR spectrum



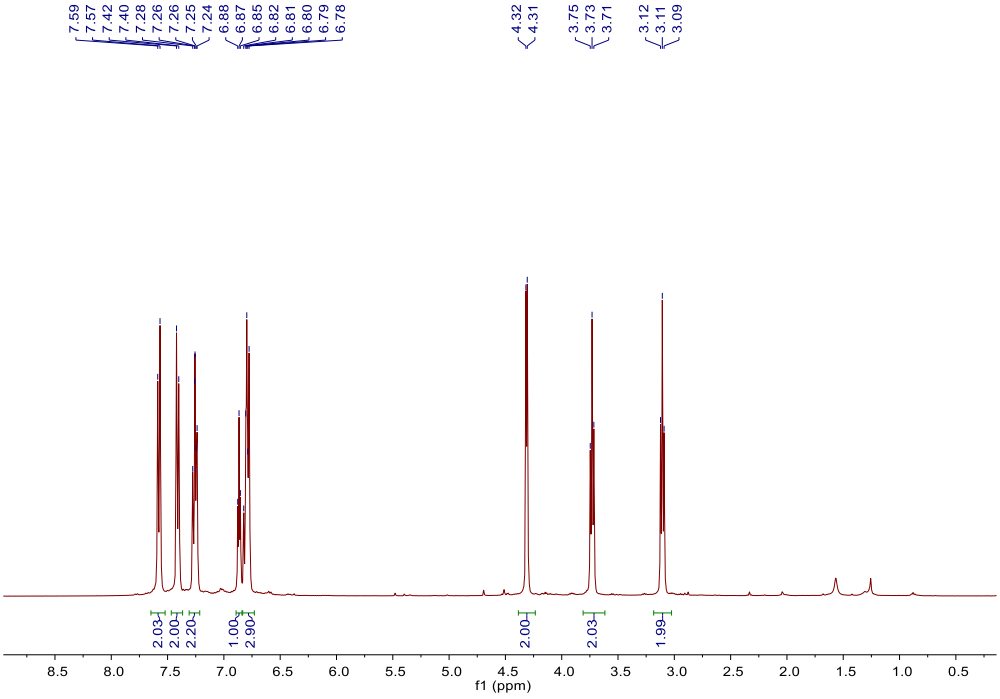
HRMS (ESI+, MeOH): *m/z* calcd. 282.1289 $(M + H)^+$, found: 282.1383.



3ga

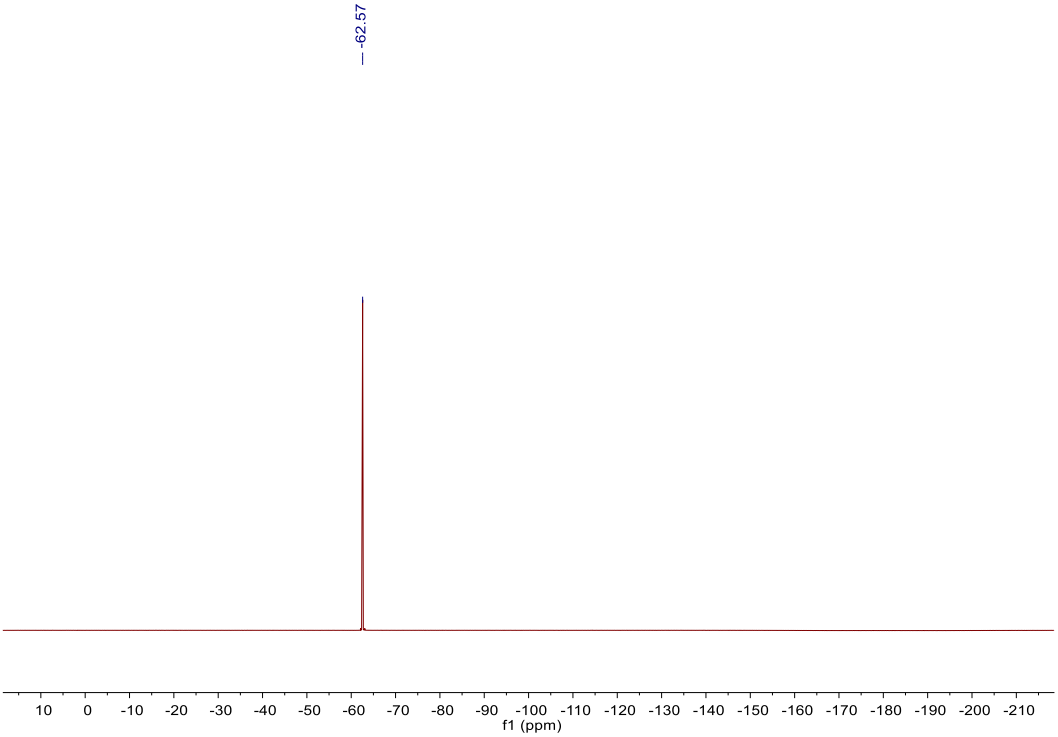
Scale: 0.1 mmol (69% yield), yellow oil, PE : EA = 5 : 1, R_f = 0.35.

^{1}H NMR spectrum ($CDCl_3$)

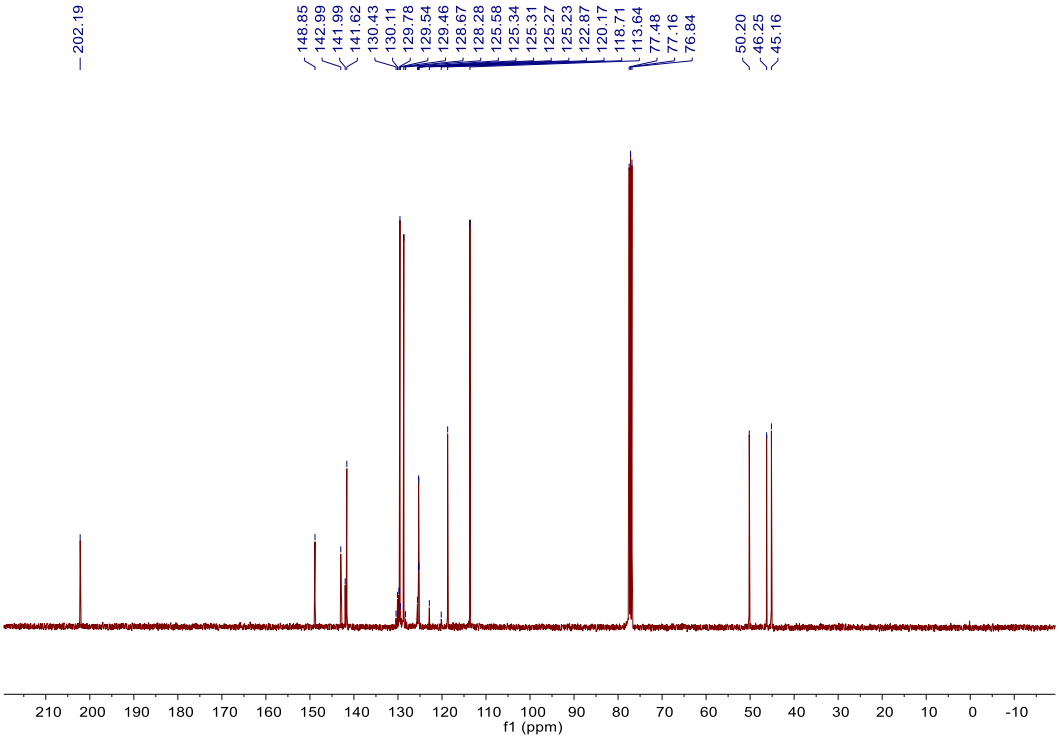


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.0 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.31-7.21 (m, 2H), 6.87 (t, *J* = 4.7 Hz, 1H), 6.83-6.73 (m, 3H), 4.31 (d, *J* = 4.7 Hz, 2H), 3.73 (t, *J* = 6.4 Hz, 2H), 3.11 (t, *J* = 6.4 Hz, 2H).

^{19}F NMR spectrum ($CDCl_3$)

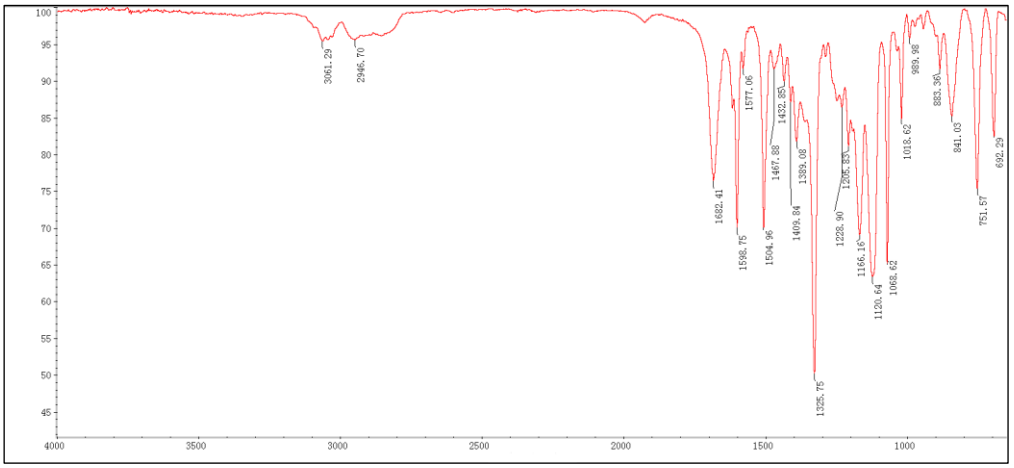


^{13}C NMR spectrum ($CDCl_3$)

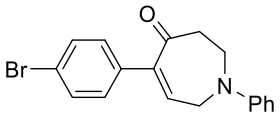


^{13}C NMR (100 MHz, $CDCl_3$) δ 202.19 , 148.85, 142.99, 141.99, 141.62, 129.95 (q, J = 32.6 Hz), 129.54, 128.67, 125.29 (q, J = 3.8 Hz), 124.22 (q, J = 270.3 Hz), 118.71, 113.64, 50.20, 46.25, 45.16.

IR spectrum



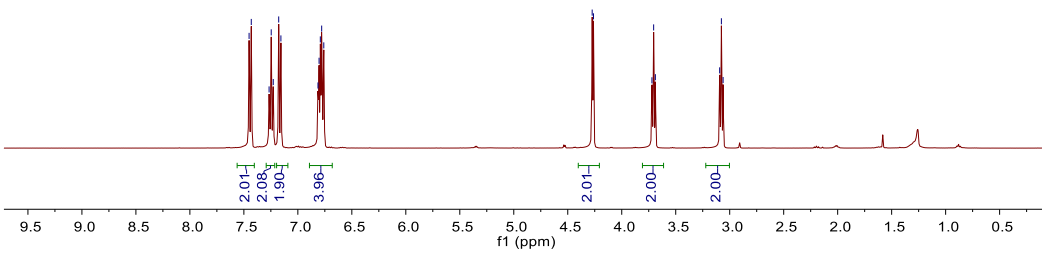
HRMS (ESI+, MeOH): *m/z* calcd. 332.1257 $(M + H)^+$, found: 332.1252.



3ha

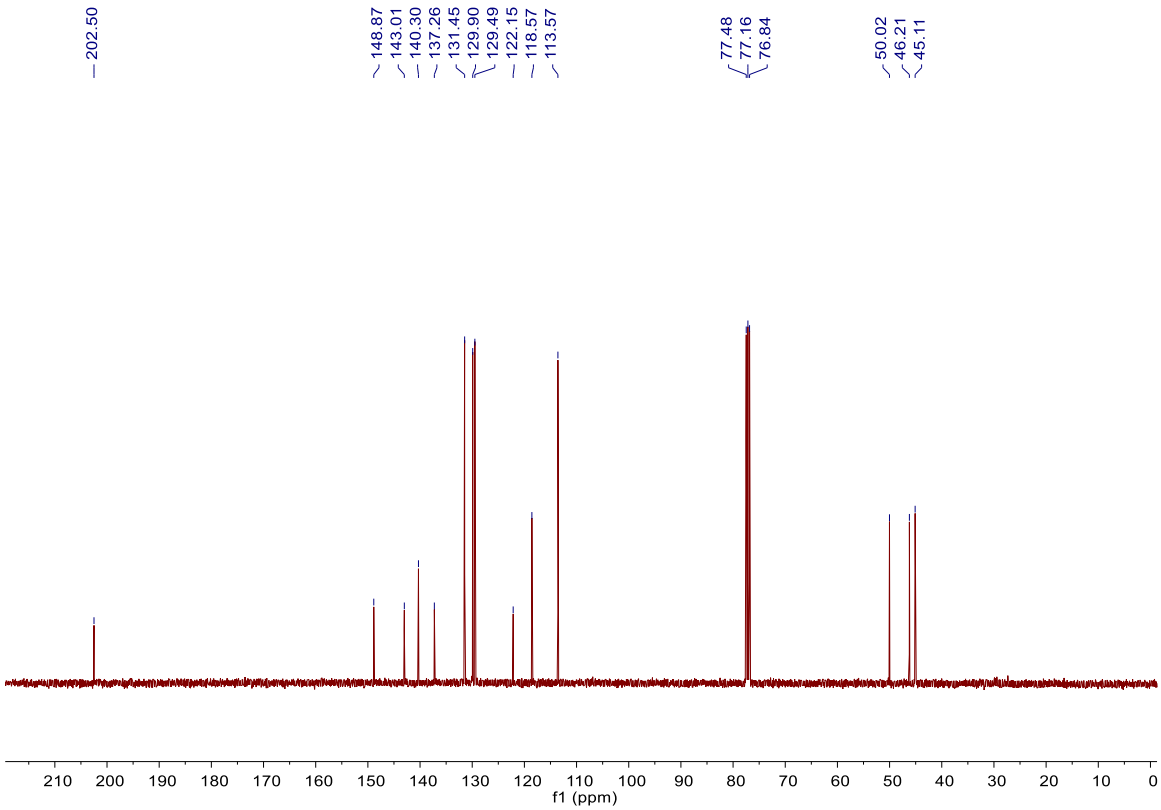
Scale: 0.1 mmol (74% yield), yellow oil, PE : EA = 5 : 1, R_f = 0.35.

^{1}H NMR spectrum ($CDCl_3$)



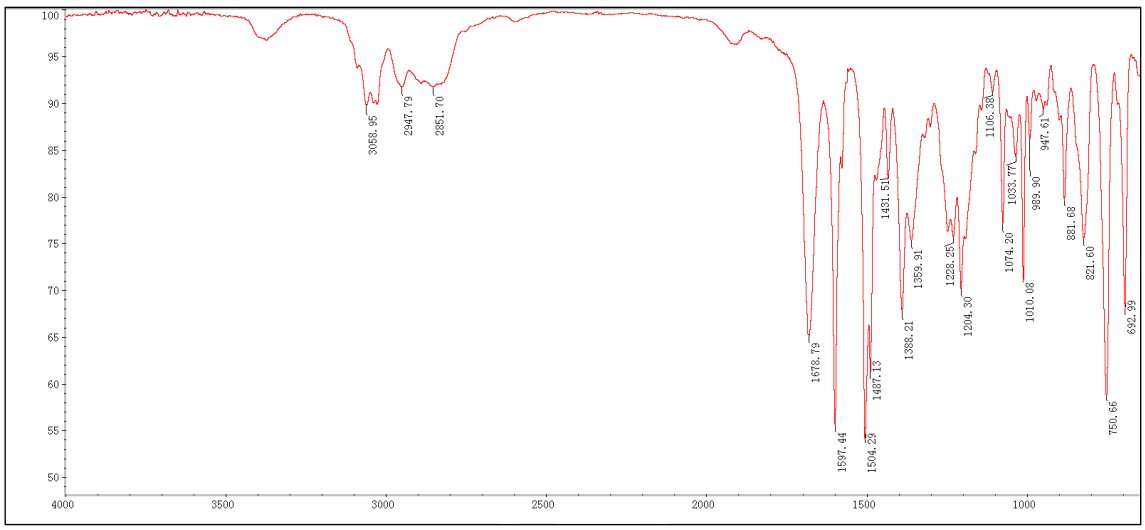
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.1 Hz, 2H), 7.25 (t, *J* = 7.7 Hz, 2H), 7.17 (d, *J* = 8.1 Hz, 2H), 6.89-6.68 (m, 4H), 4.27 (d, *J* = 4.8 Hz, 2H), 3.70 (t, *J* = 6.4 Hz, 2H), 3.08 (t, *J* = 6.3 Hz, 2H).

^{13}C NMR spectrum ($CDCl_3$)

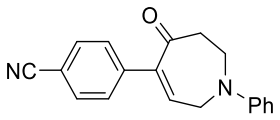


^{13}C NMR (100 MHz, $CDCl_3$) δ 202.50, 148.87, 143.01, 140.30, 137.26, 131.45, 129.90, 129.49, 122.15, 118.57, 113.57, 50.02, 46.21, 45.11.

IR spectrum



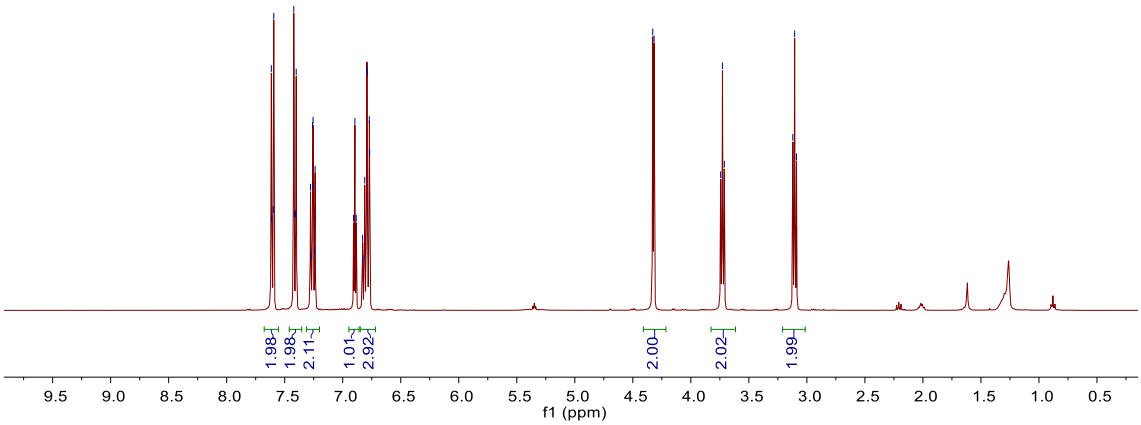
HRMS (ESI+, MeOH): *m/z* calcd. 342.0488 $(M + H)^+$, found: 342.0478.



3ia

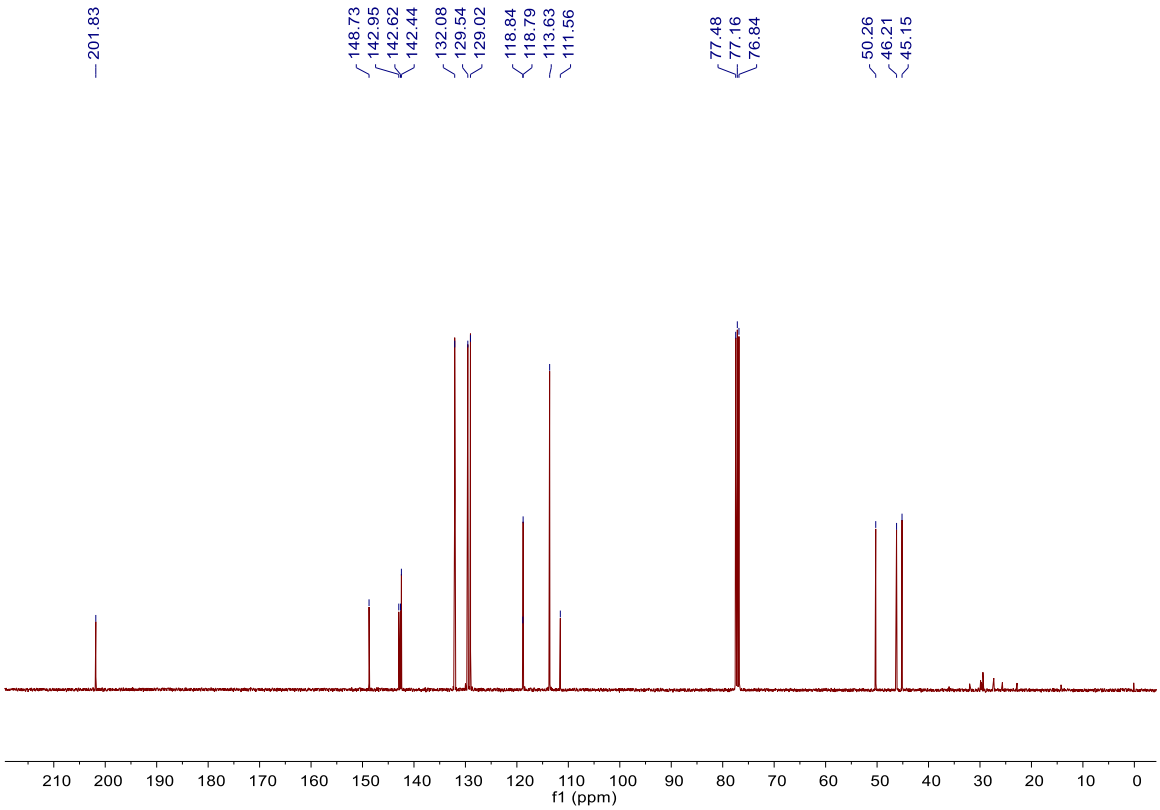
Scale: 0.1 mmol (61% yield), yellow oil, PE : EA = 3:1, R_f = 0.27.

^{1}H NMR spectrum ($CDCl_3$)



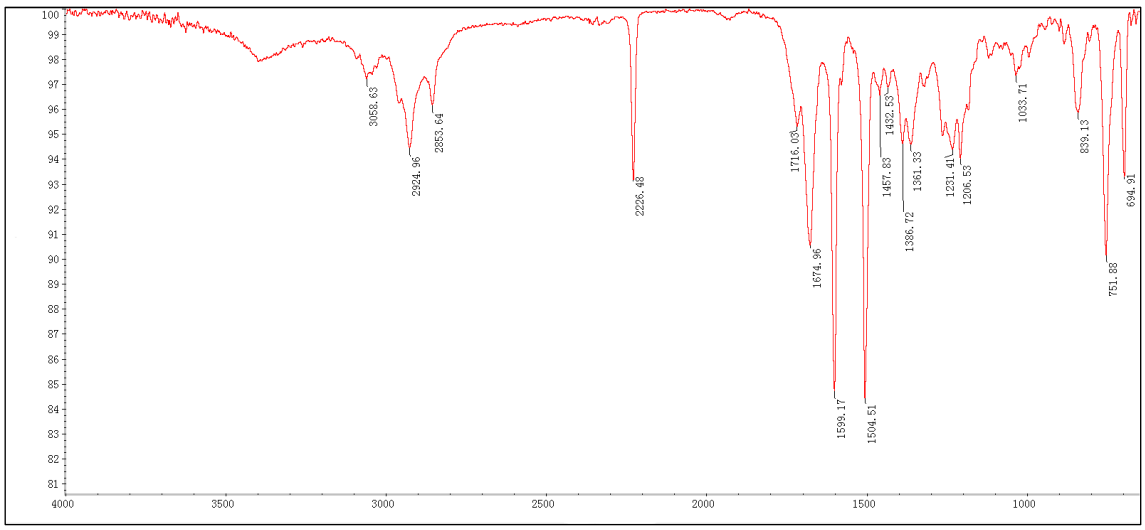
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68-7.55 (m, 2H), 7.46-7.35 (m, 2H), 7.31-7.20 (m, 2H), 6.89 (t, *J* = 4.6 Hz, 1H), 6.85-6.72 (m, 3H), 4.32 (d, *J* = 4.6 Hz, 2H), 3.73 (t, *J* = 6.4 Hz, 2H), 3.11 (t, *J* = 6.4 Hz, 2H).

^{13}C NMR spectrum ($CDCl_3$)

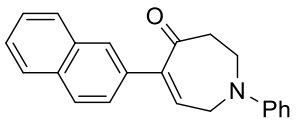


^{13}C NMR (100 MHz, $CDCl_3$) δ 201.83, 148.73, 142.95, 142.62, 142.44, 132.08, 129.54, 129.02, 118.84, 118.79, 113.63, 111.56, 50.26, 46.21, 45.15.

IR spectrum



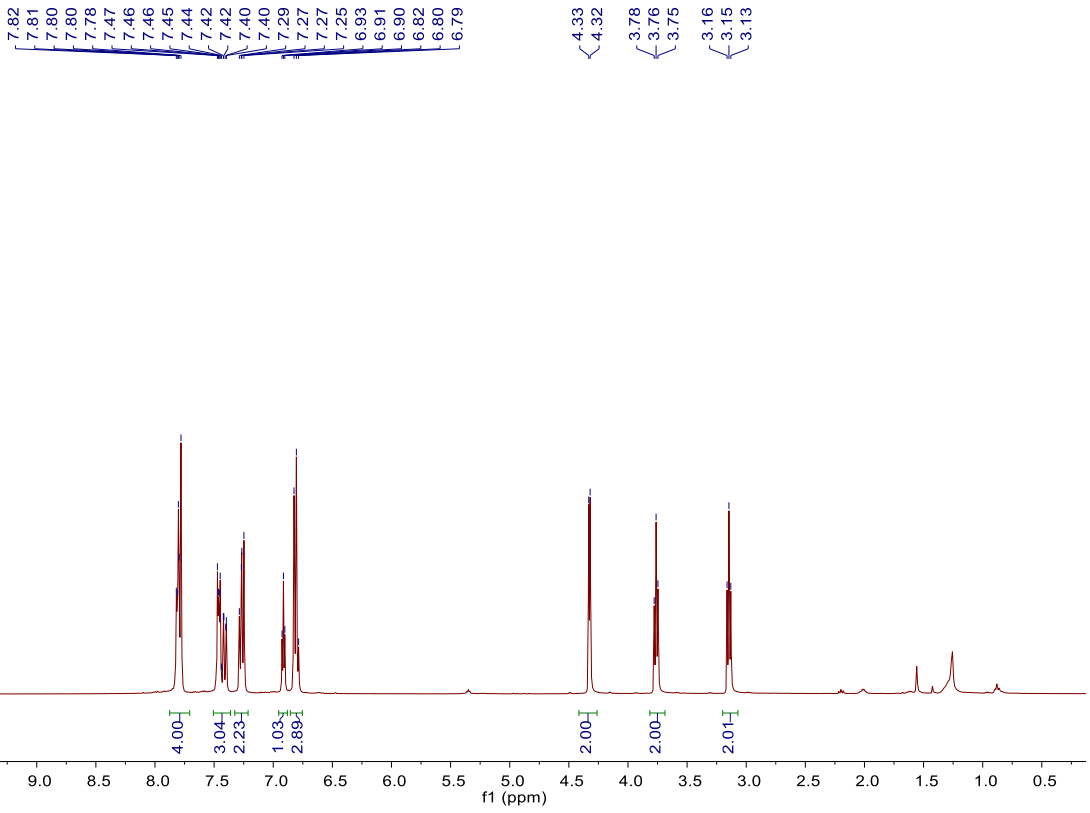
HRMS (ESI+, MeOH): *m/z* calcd. 289.1335 $(M + H)^+$, found: 289.1323.



3ja

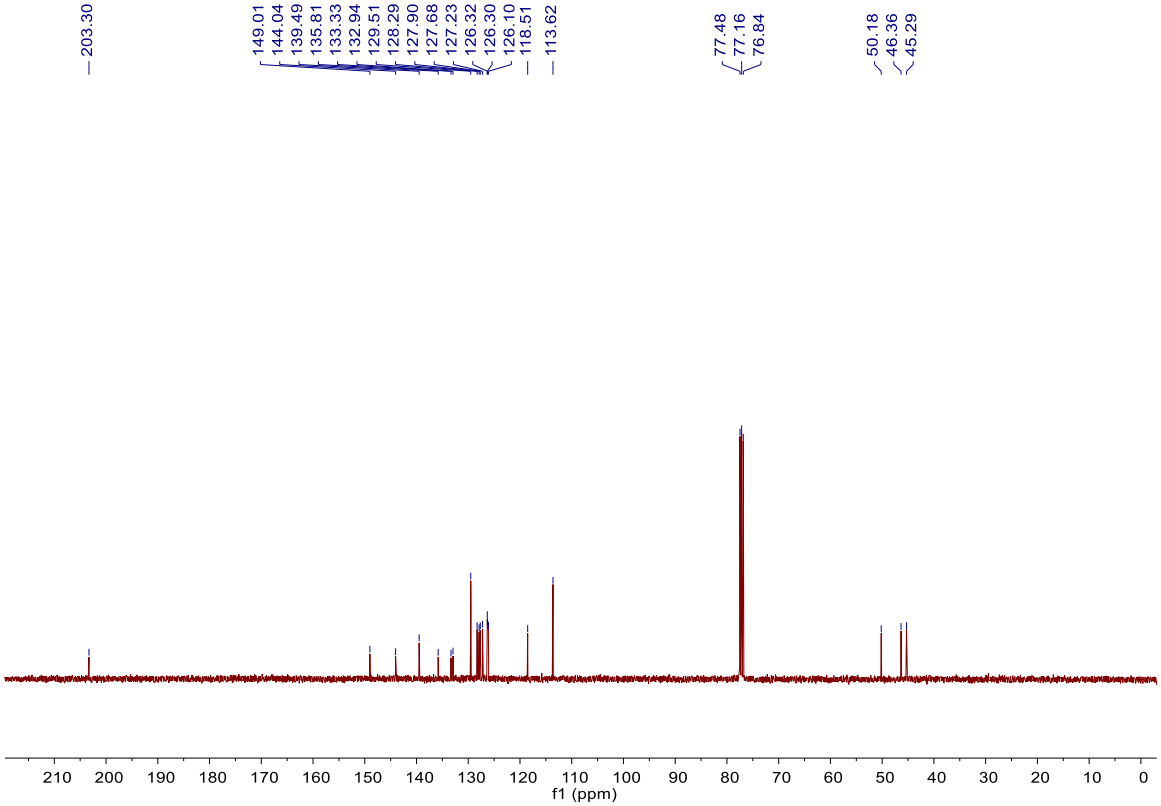
Scale: 0.1 mmol (72% yield), white solid, PE : EA = 5 : 1, R_f = 0.37.

^{1}H NMR spectrum ($CDCl_3$)



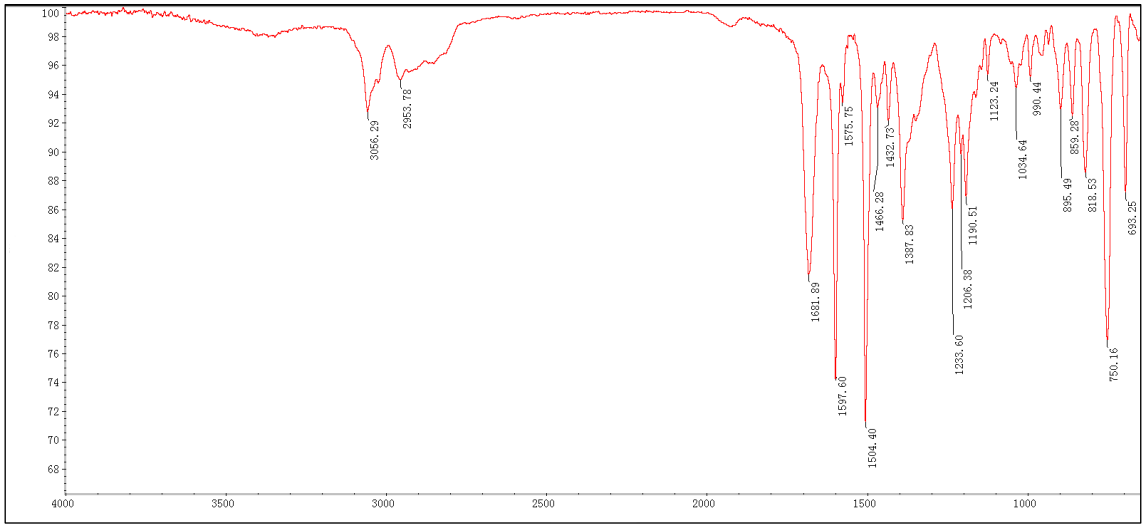
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88-7.71 (m, 4H), 7.51-7.36 (m, 3H), 7.33-7.21 (m, 2H), 6.91 (t, *J* = 4.7 Hz, 1H), 6.86-6.75 (m, 3H), 4.33 (d, *J* = 4.7 Hz, 2H), 3.76 (t, *J* = 6.3 Hz, 2H), 3.15 (t, *J* = 6.3 Hz, 2H).

^{13}C NMR spectrum ($CDCl_3$)

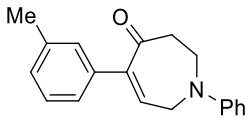


^{13}C NMR (100 MHz, $CDCl_3$) δ 203.30, 149.01, 144.04, 139.49, 135.81, 133.33, 132.94, 129.51, 128.29, 127.90, 127.68, 127.23, 126.32, 126.30, 126.10, 118.51, 113.62, 50.18, 46.36, 45.29.

IR spectrum



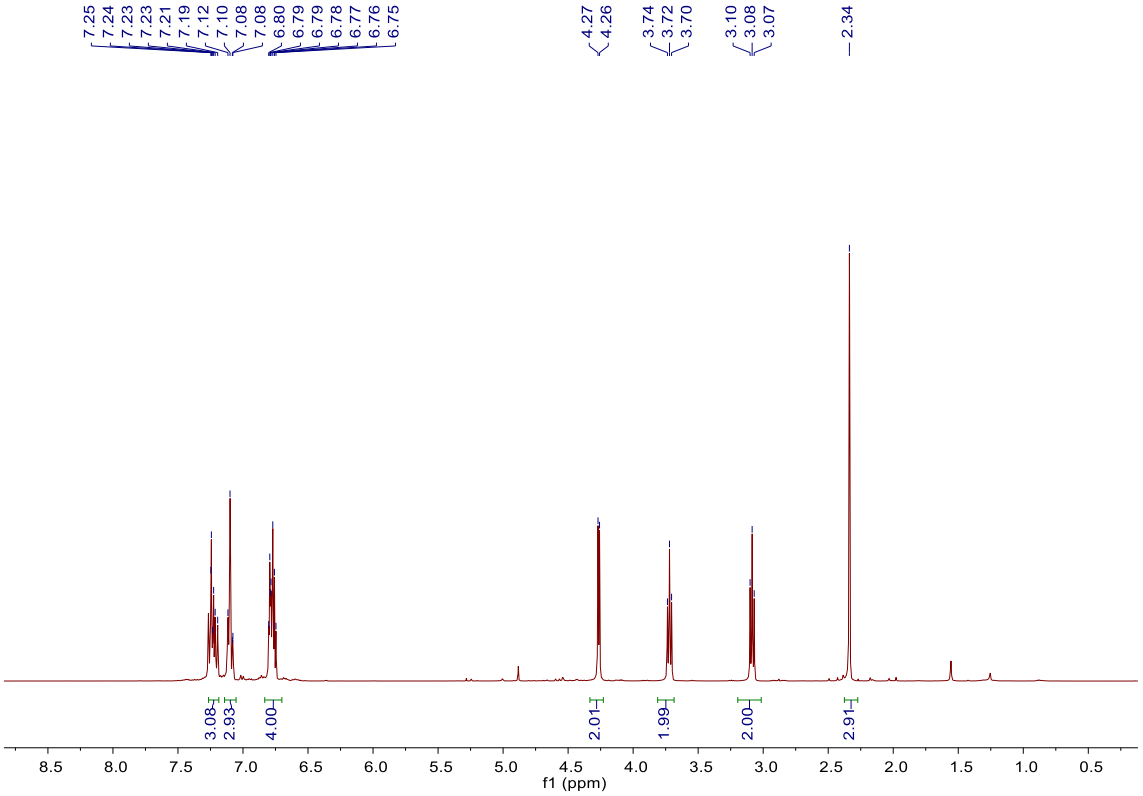
HRMS (ESI+, MeOH): *m/z* calcd. 314.1539 $(M + H)^+$, found: 314.1536.



3ka

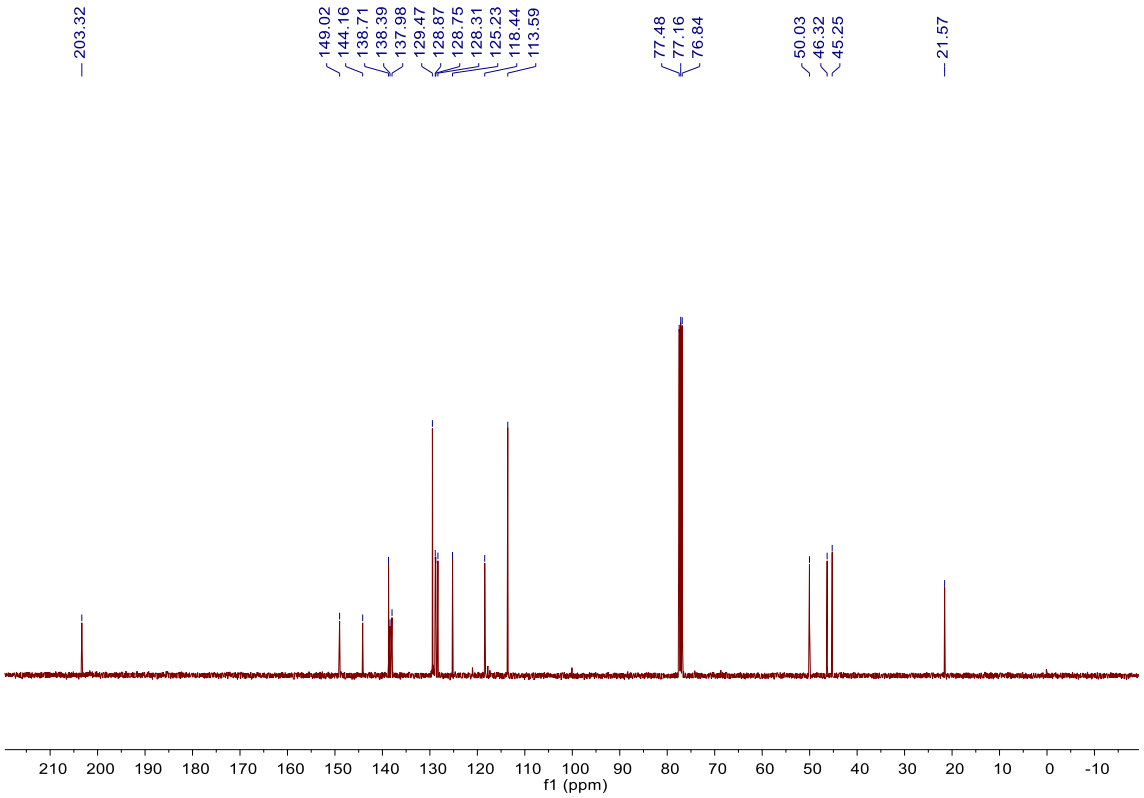
Scale: 0.1 mmol (74% yield), yellow oil, PE : EA = 5 : 1, R_f = 0.37.

^{1}H NMR spectrum ($CDCl_3$)



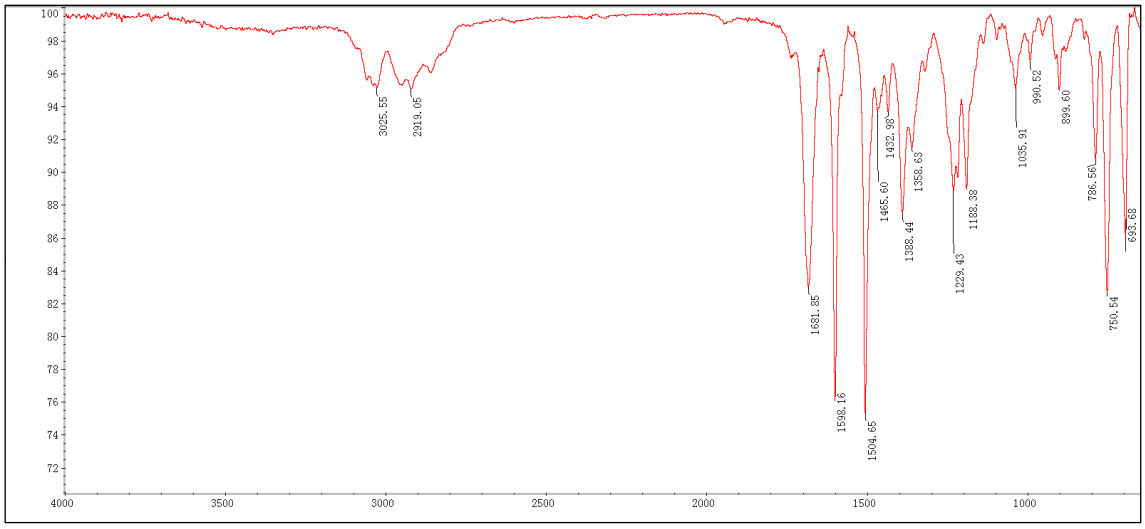
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26-7.19 (m, 3H), 7.14-7.05 (m, 3H), 6.83-6.70 (m, 4H), 4.26 (d, *J* = 4.7 Hz, 2H), 3.72 (t, *J* = 6.4 Hz, 2H), 3.08 (t, *J* = 6.4 Hz, 2H), 2.34 (s, 3H).

^{13}C NMR spectrum ($CDCl_3$)

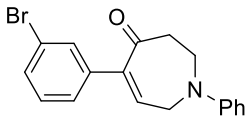


^{13}C NMR (100 MHz, $CDCl_3$) δ 203.32, 149.02, 144.16, 138.71, 138.39, 137.98, 129.47, 128.87, 128.75, 128.31, 125.23, 118.44, 113.59, 50.03, 46.32, 45.25, 21.57.

IR spectrum



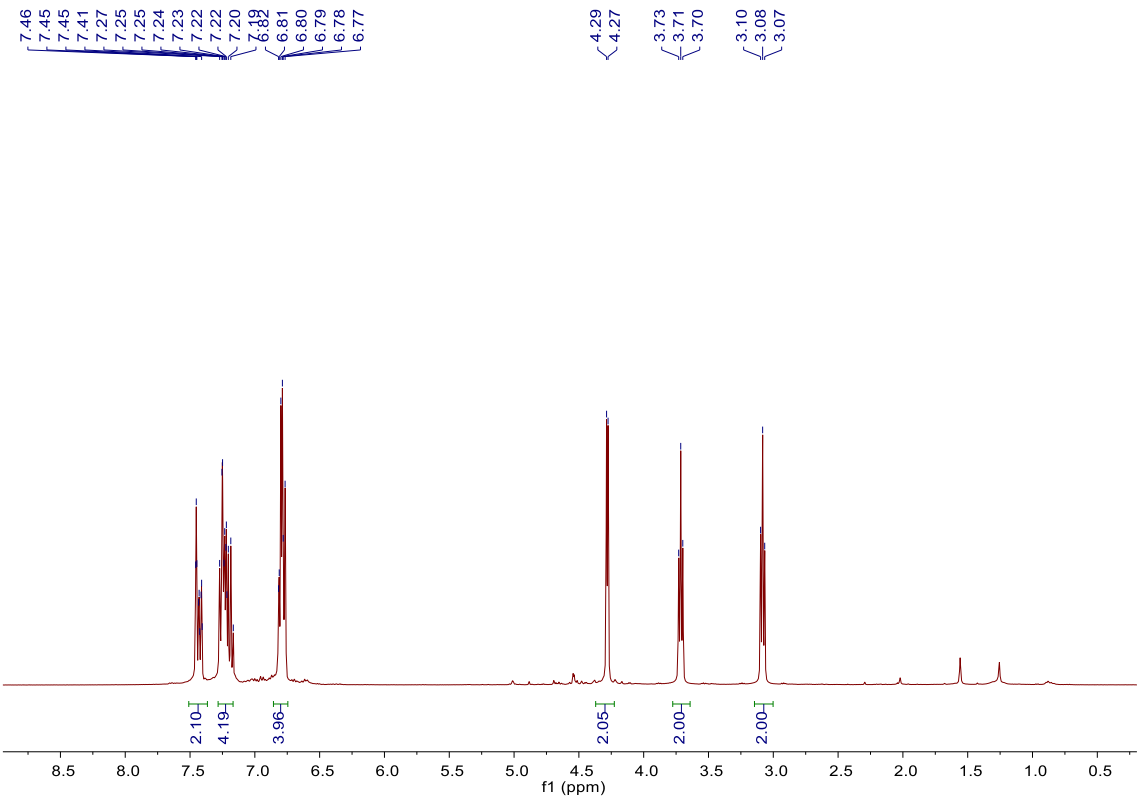
HRMS (ESI+, MeOH): *m/z* calcd. 278.1539 $(M + H)^+$, found: 278.1530.



3la

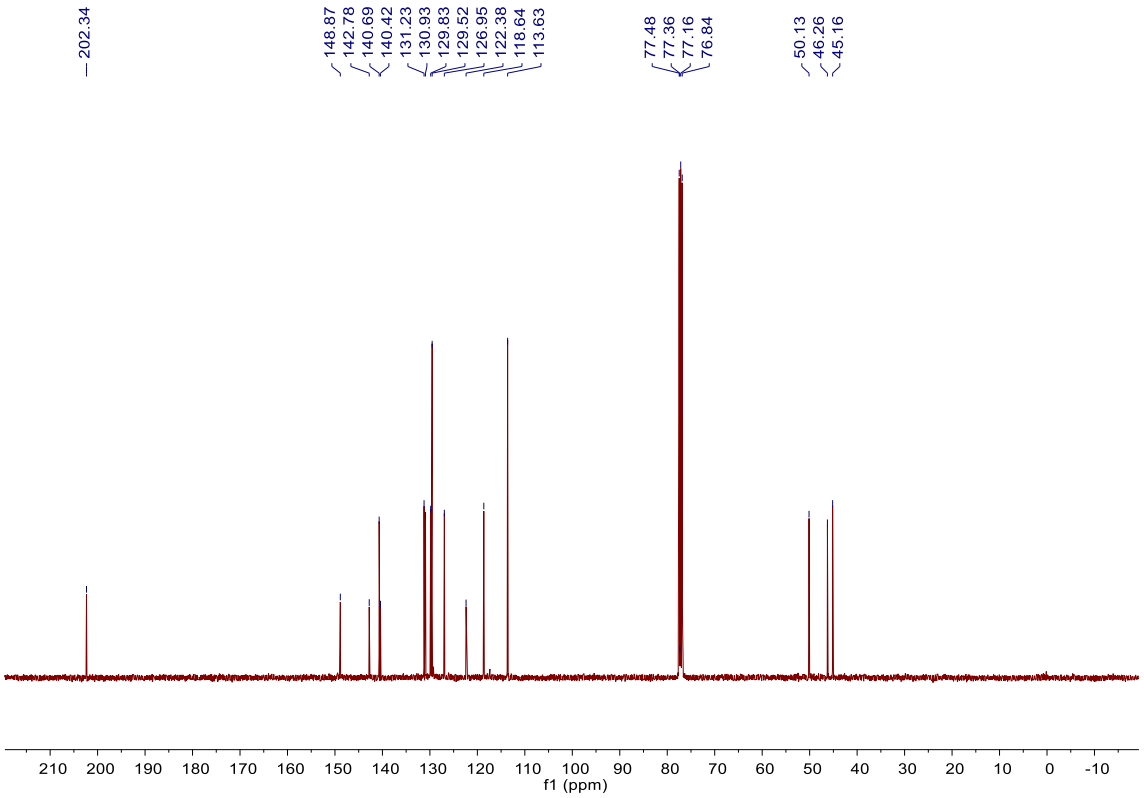
Scale: 0.1 mmol (64% yield), yellow oil, PE : EA = 5 : 1, R_f = 0.37.

^{1}H NMR spectrum ($CDCl_3$)



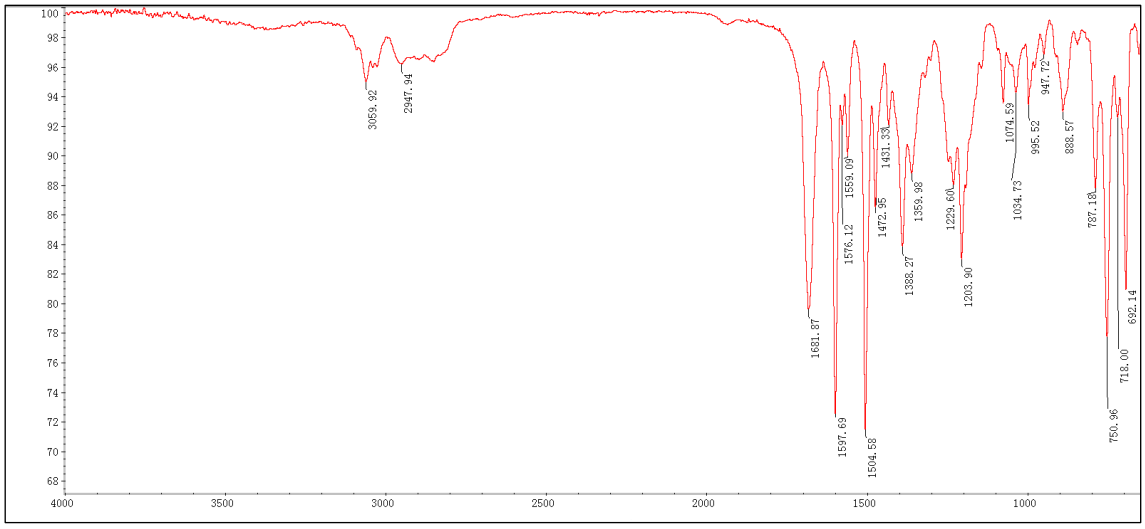
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51-7.37 (m, 2H), 7.28-7.17 (m, 4H), 6.86-6.75 (m, 4H), 4.28 (d, *J* = 4.6 Hz, 2H), 3.71 (t, *J* = 6.4 Hz, 2H), 3.08 (t, *J* = 6.4 Hz, 2H).

^{13}C NMR spectrum ($CDCl_3$)

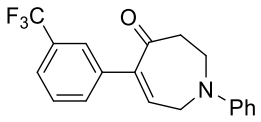


^{13}C NMR (100 MHz, $CDCl_3$) δ 202.34, 148.87, 142.78, 140.69, 140.42, 131.23, 130.93, 129.83, 129.52, 126.95, 122.38, 118.64, 113.63, 50.13, 46.26, 45.16.

IR spectrum



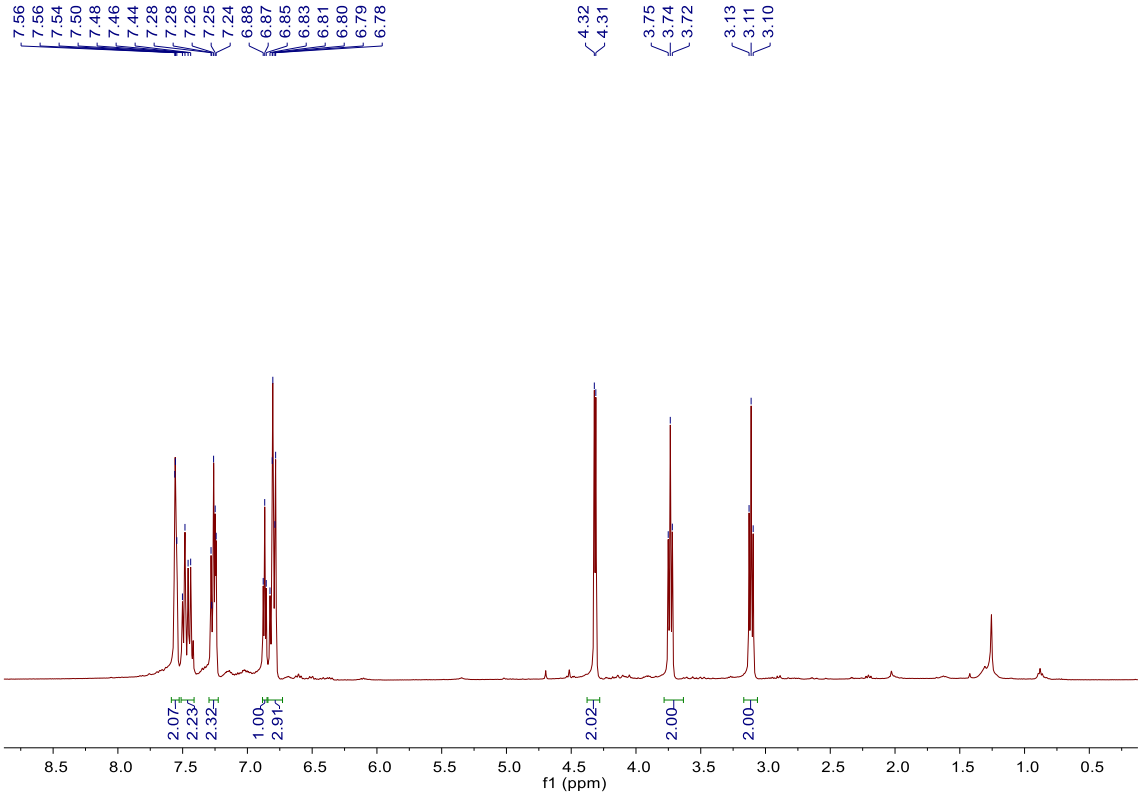
HRMS (ESI+, MeOH): *m/z* calcd. 342.0488 $(M + H)^+$, found: 342.0474.



3ma

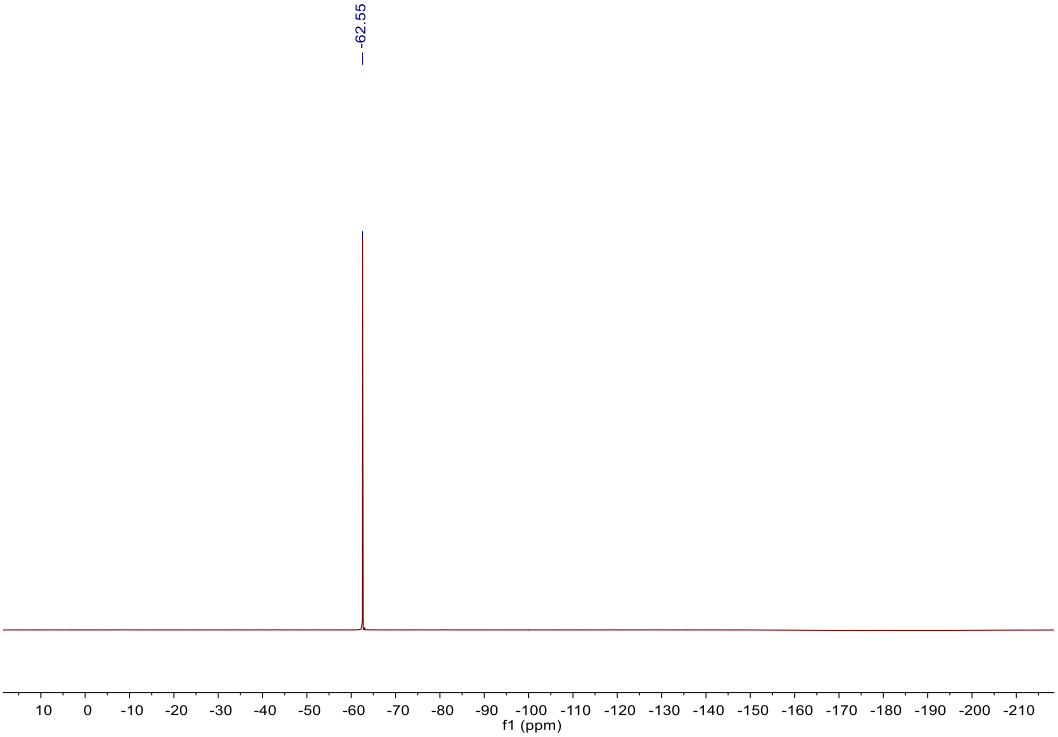
Scale: 0.1 mmol (61% yield), yellow oil, PE : EA = 5 : 1, R_f = 0.37.

^{1}H NMR spectrum ($CDCl_3$)

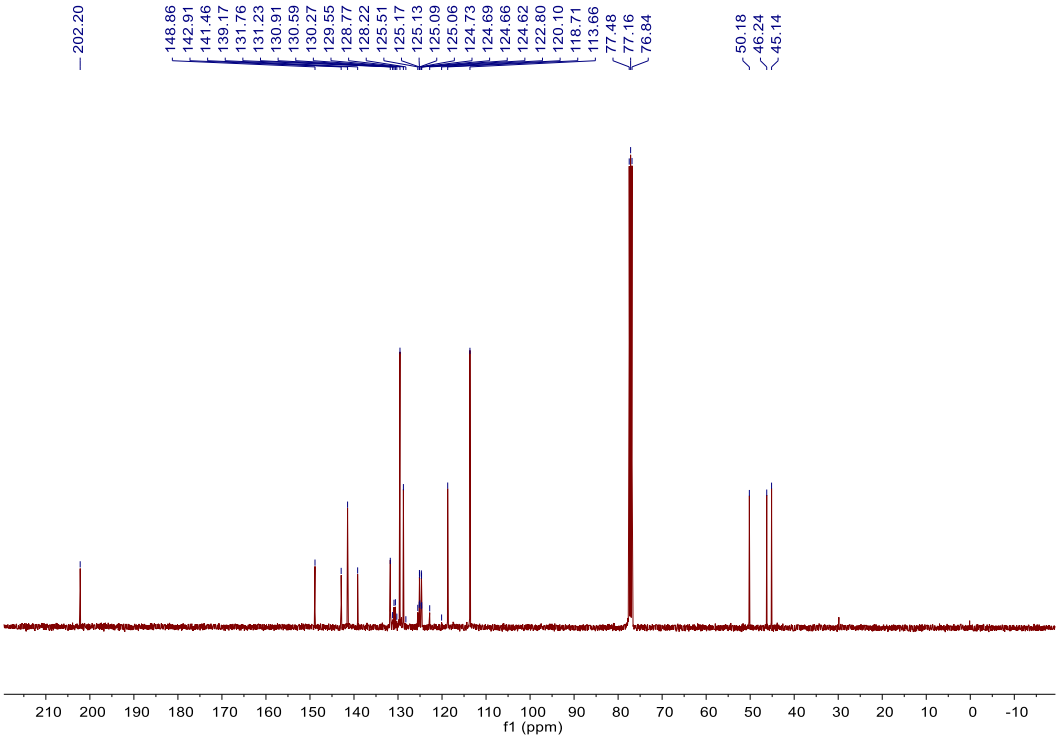


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59-7.53 (m, 2H), 7.51-7.41 (m, 2H), 7.30-7.23 (m, 2H), 6.87 (t, *J* = 4.7 Hz, 1H), 6.84-6.73 (m, 3H), 4.32 (d, *J* = 4.7 Hz, 2H), 3.74 (t, *J* = 6.4 Hz, 2H), 3.11 (t, *J* = 6.4 Hz, 2H).

^{19}F NMR spectrum ($CDCl_3$)

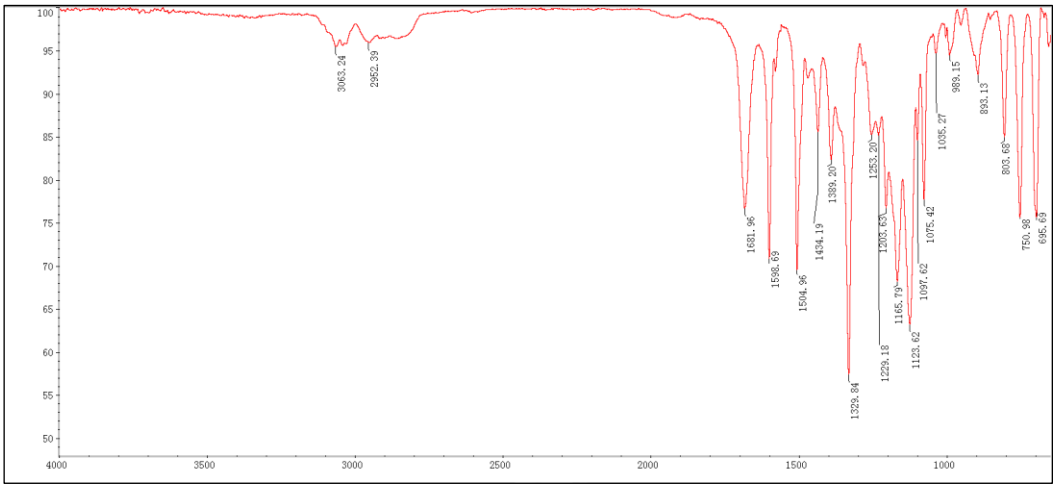


^{13}C NMR spectrum ($CDCl_3$)

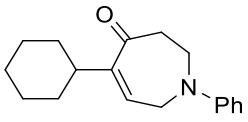


^{13}C NMR (100 MHz, $CDCl_3$) δ 202.20, 148.86, 142.91, 141.46, 139.17, 131.76, 130.75 (q, *J* = 32.1 Hz), 129.55, 128.77, 125.11 (q, *J* = 3.8 Hz), 124.68 (q, *J* = 3.8 Hz), 124.16 (q, J = 270.6 Hz), 118.71, 113.66, 50.18, 46.24, 45.14.

IR spectrum



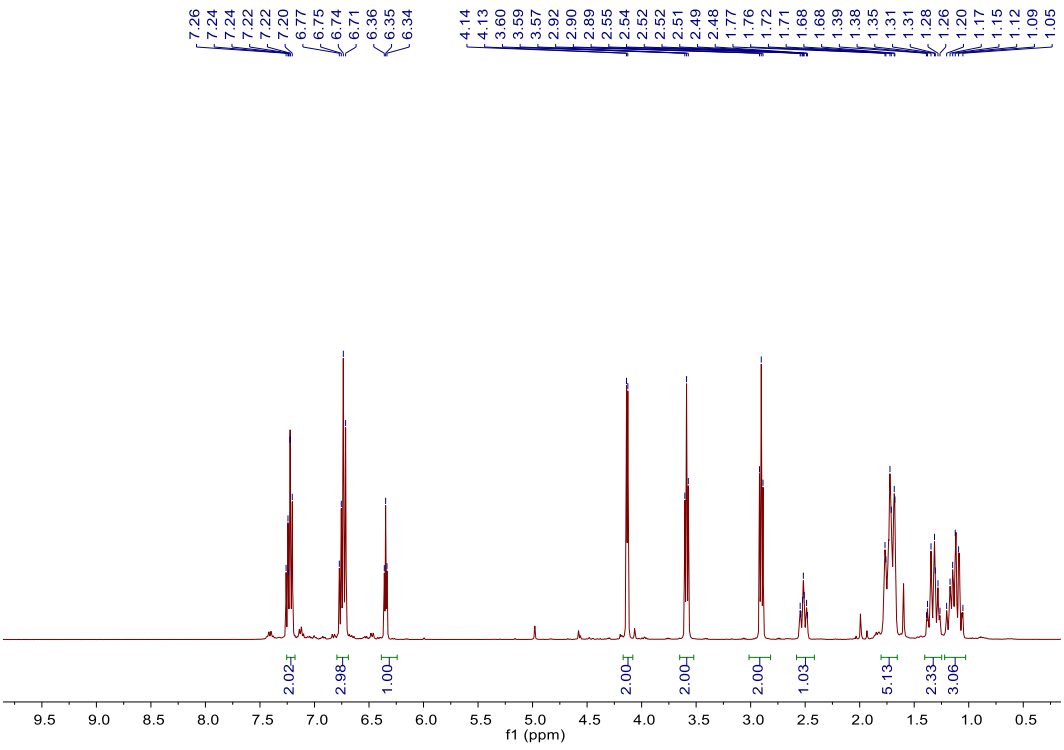
HRMS (ESI+, MeOH): *m/z* calcd. 332.1257 $(M + H)^+$, found: 332.1255.



3na

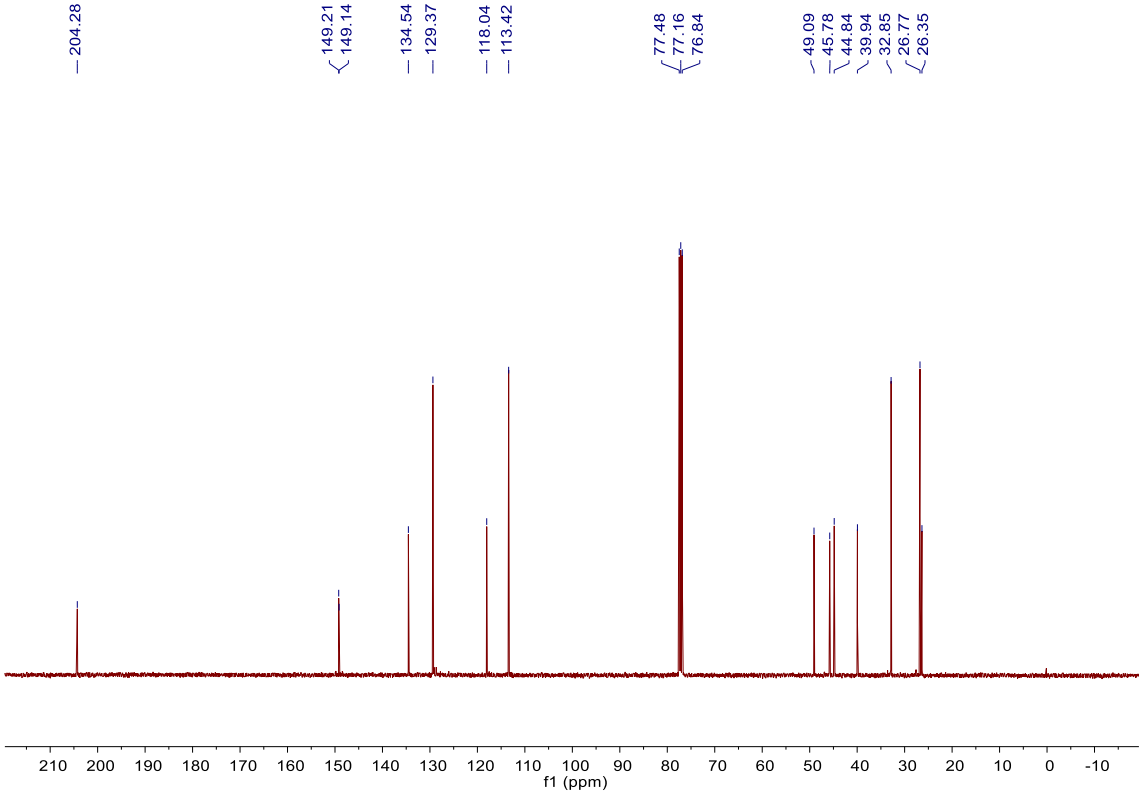
Scale: 0.1 mmol (73% yield), yellow oil, PE : EA = 10 : 1, R_f = 0.33.

^{1}H NMR spectrum ($CDCl_3$)



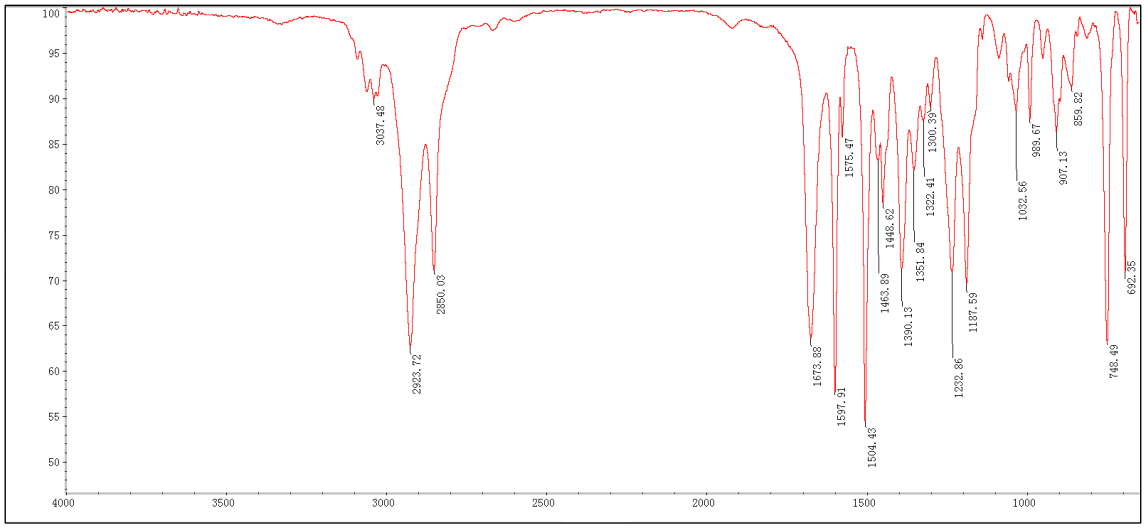
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25-7.18 (m, 2H), 6.79-6.69 (m, 3H), 6.35 (t, *J* = 4.9 Hz, 1H), 4.13 (d, *J* = 4.8 Hz, 2H), 3.59 (t, *J* = 6.4 Hz, 2H), 2.90 (t, *J* = 6.4 Hz, 2H), 2.58-2.42 (m, 1H), 1.80-1.66 (m, 5H), 1.40-1.25 (m, 2H), 1.22-1.03 (m, 3H).

^{13}C NMR spectrum ($CDCl_3$)

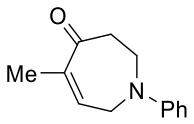


^{13}C NMR (100 MHz, $CDCl_3$) δ 204.28, 149.21, 149.14, 134.54, 129.37, 118.04, 113.42, 49.09, 45.78, 44.84, 39.94, 32.85, 26.77, 26.35.

IR spectrum



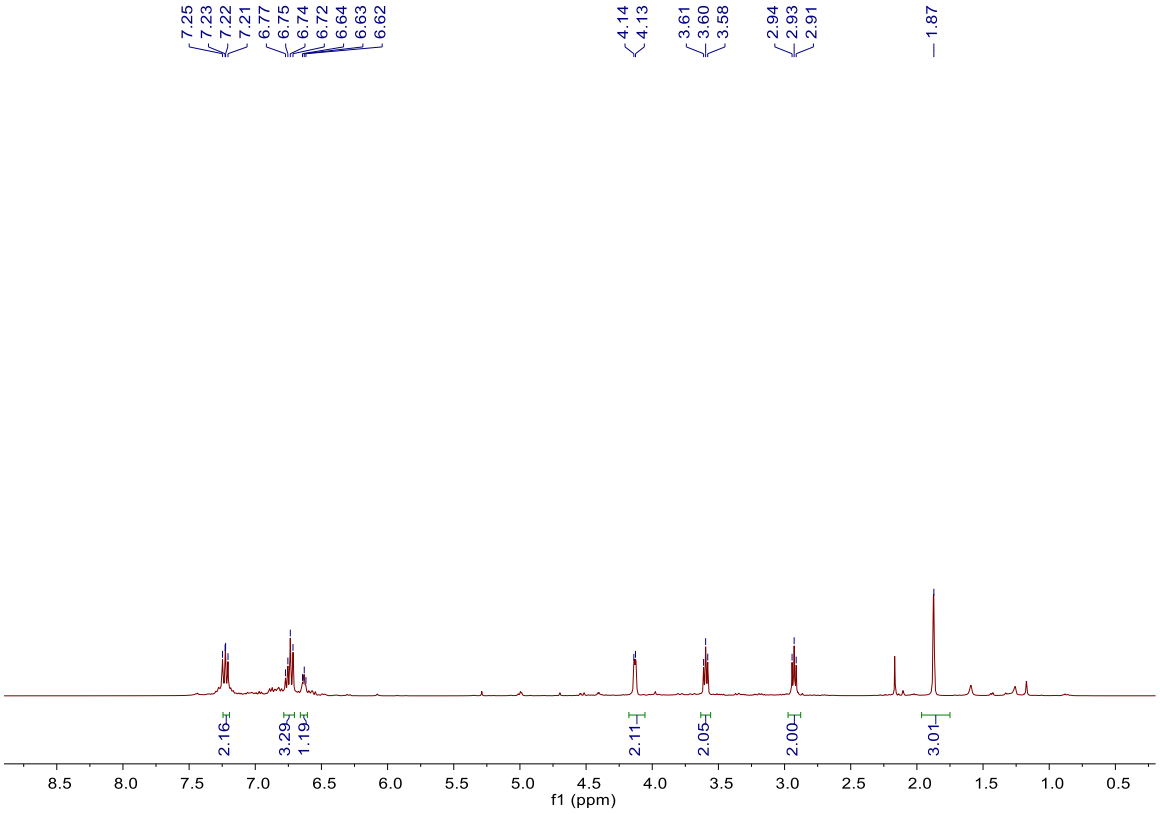
HRMS (ESI+, MeOH): *m/z* calcd. 270.1852 $(M + H)^+$, found: 270.1841.



3oa

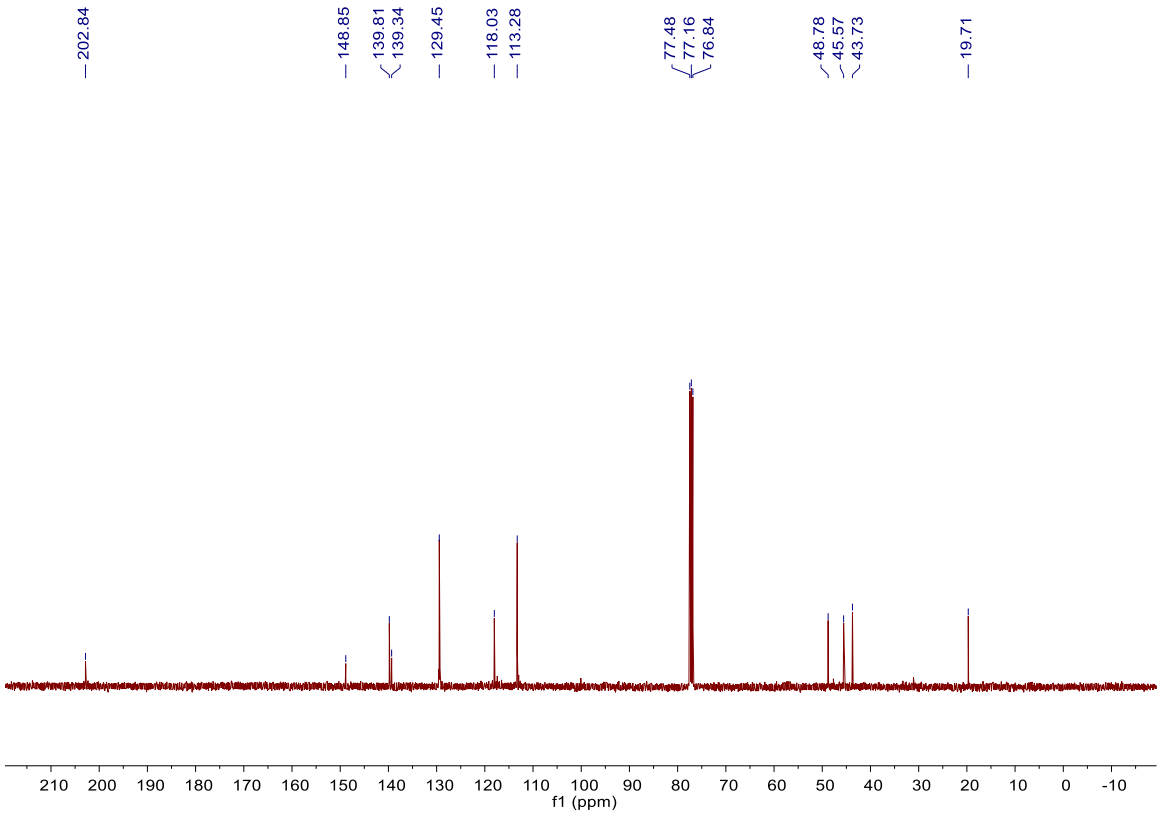
Scale: 0.1 mmol (52% yield), yellow oil, PE : EA = 10 : 1, R_f = 0.40.

^{1}H NMR spectrum ($CDCl_3$)



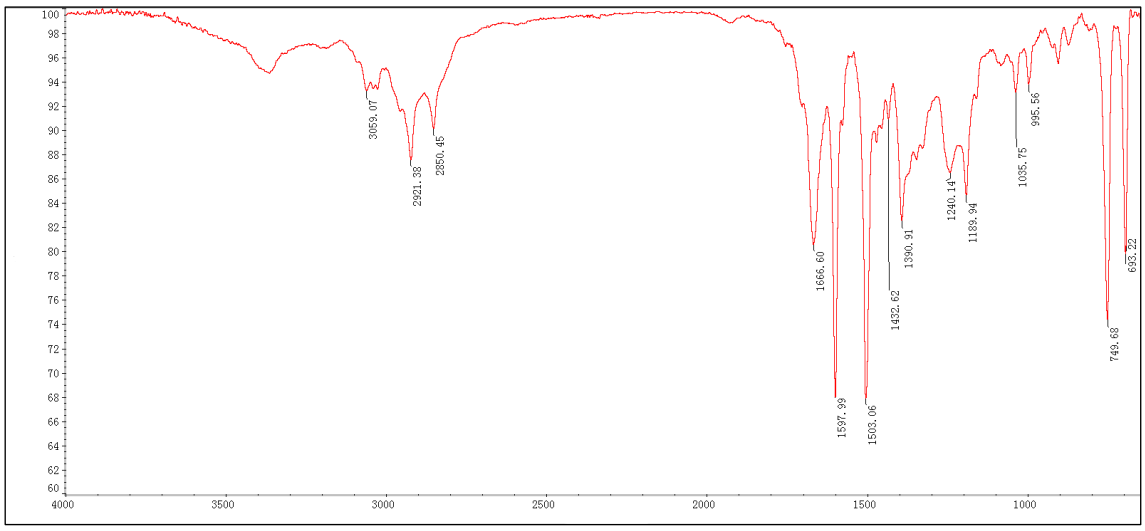
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24-7.19 (m, 2H), 6.78-6.70 (m, 3H), 6.63 (t, *J* = 4.8 Hz, 1H), 4.13 (d, *J* = 4.8 Hz, 2H), 3.60 (t, *J* = 6.2 Hz, 2H), 2.93 (t, *J* = 6.2 Hz, 2H), 1.87 (s, 3H).

^{13}C NMR spectrum ($CDCl_3$)

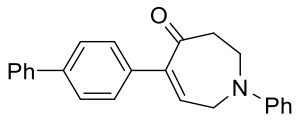


^{13}C NMR (100 MHz, $CDCl_3$) δ 202.84, 148.85, 139.81, 139.34, 129.45, 118.03, 113.28, 48.78, 45.57, 43.73, 19.71.

IR spectrum



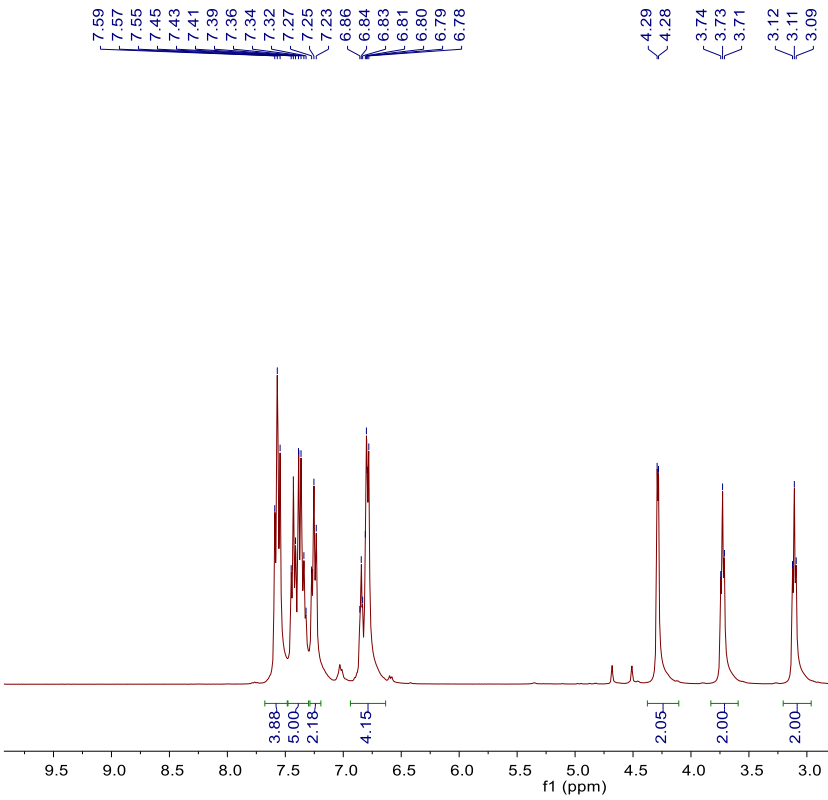
HRMS (ESI+, MeOH): *m/z* calcd. 202.1226 $(M + H)^+$, found: 202.1226.



3pa

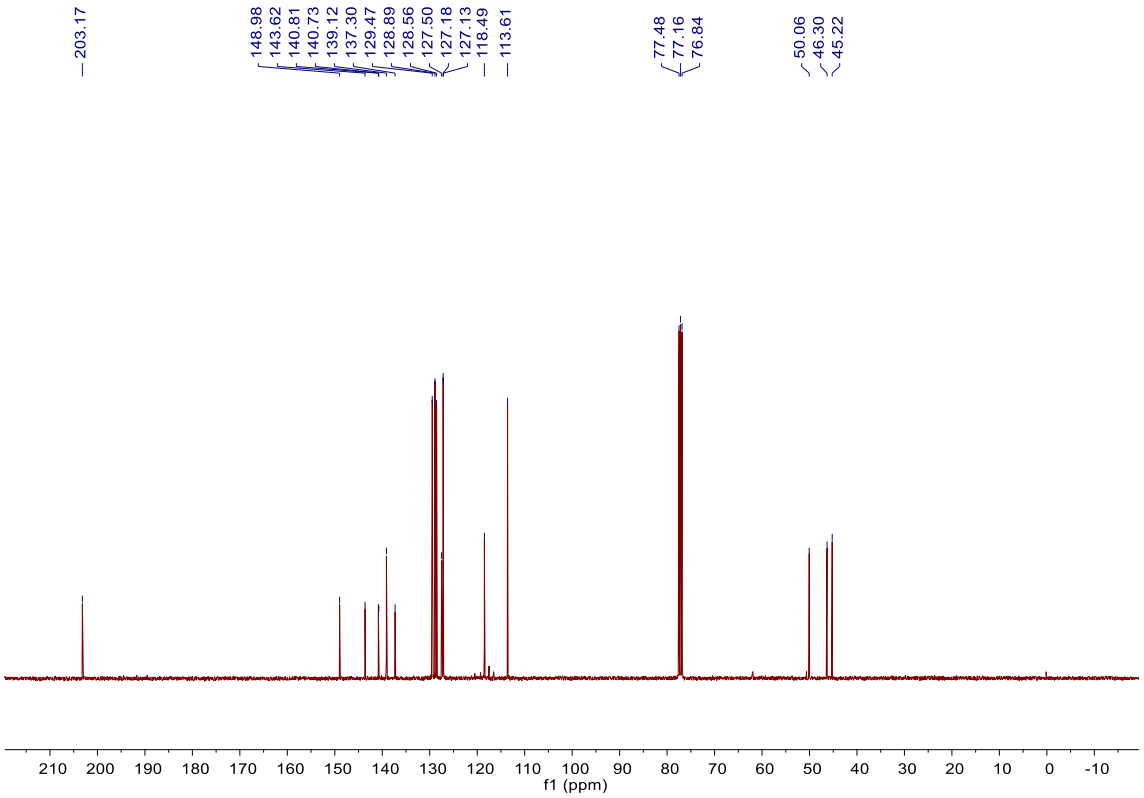
Scale: 0.1 mmol (72% yield), white solid, PE : EA = 5 : 1, R_f = 0.35.

^{1}H NMR spectrum ($CDCl_3$)



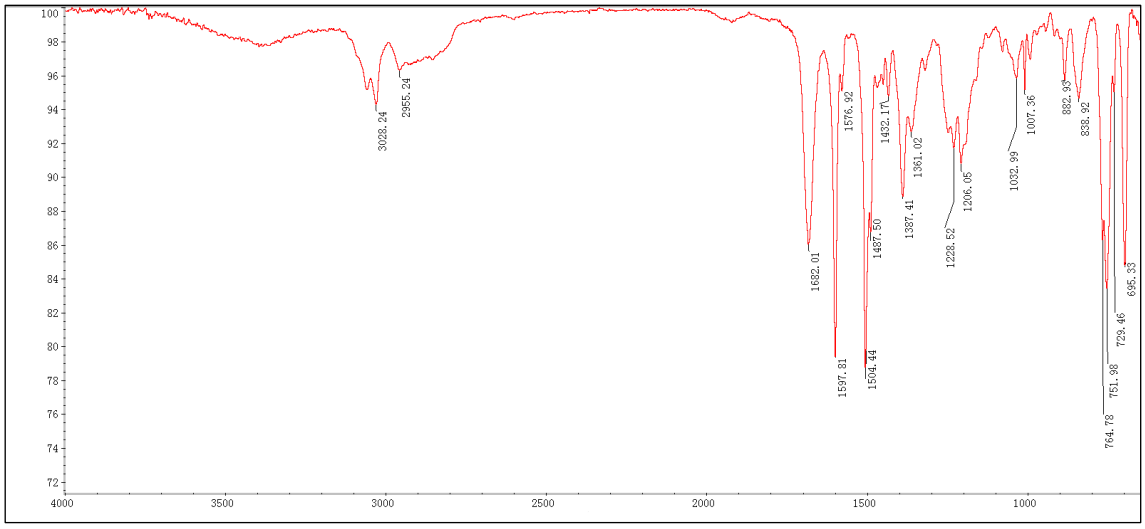
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (t, *J* = 9.2 Hz, 4H), 7.48-7.30 (m, 5H), 7.25 (t, *J* = 8.0 Hz, 2H), 6.94-6.63 (m, 4H), 4.29 (d, *J* = 4.8 Hz, 2H), 3.73 (t, *J* = 6.4 Hz, 2H), 3.11 (t, *J* = 6.4 Hz, 2H).

^{13}C NMR spectrum ($CDCl_3$)

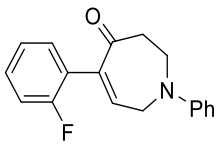


^{13}C NMR (100 MHz, $CDCl_3$) δ 203.17, 148.98, 143.62, 140.81, 140.73, 139.12, 137.30, 129.47, 128.89, 128.56, 127.50, 127.18, 127.13, 118.49, 113.61, 50.06, 46.30, 45.22.

IR spectrum



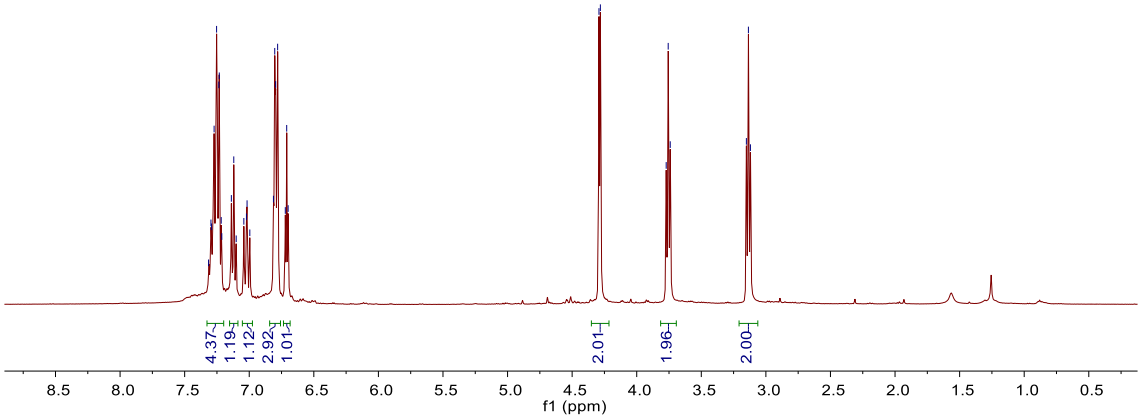
HRMS (ESI+, MeOH): *m/z* calcd. 340.1696 $(M + H)^+$, found: 340.1690.



3qa

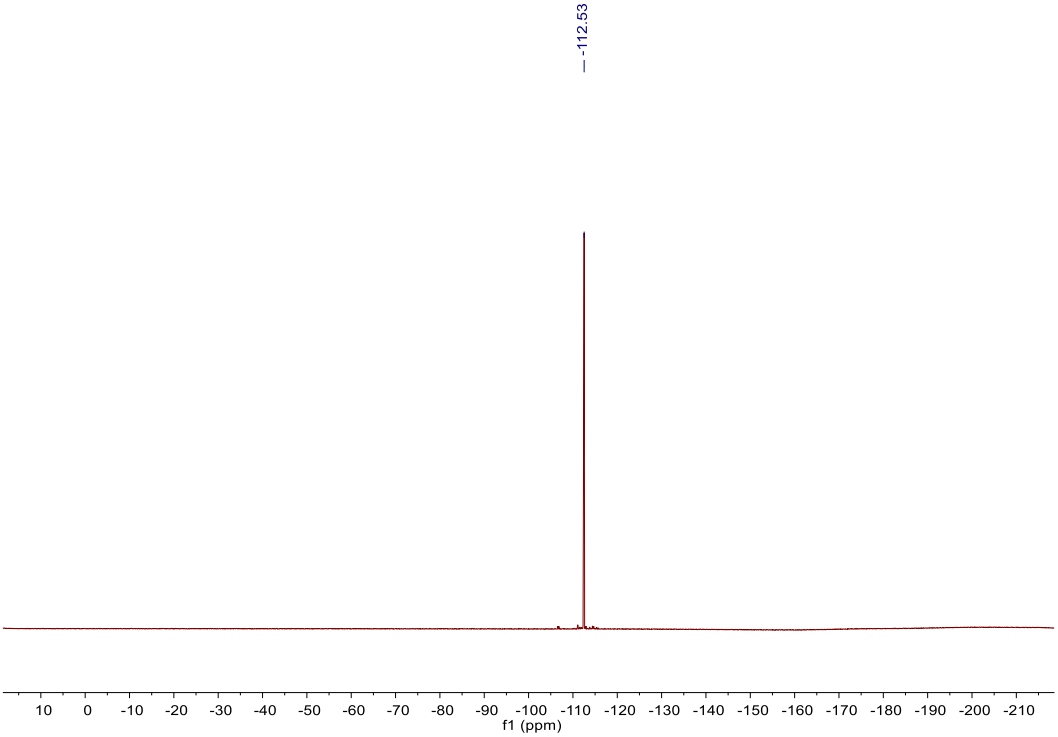
Scale: 0.1 mmol (64% yield), yellow oil, PE : EA = 5 : 1, R_f = 0.38.

^{1}H NMR spectrum ($CDCl_3$)

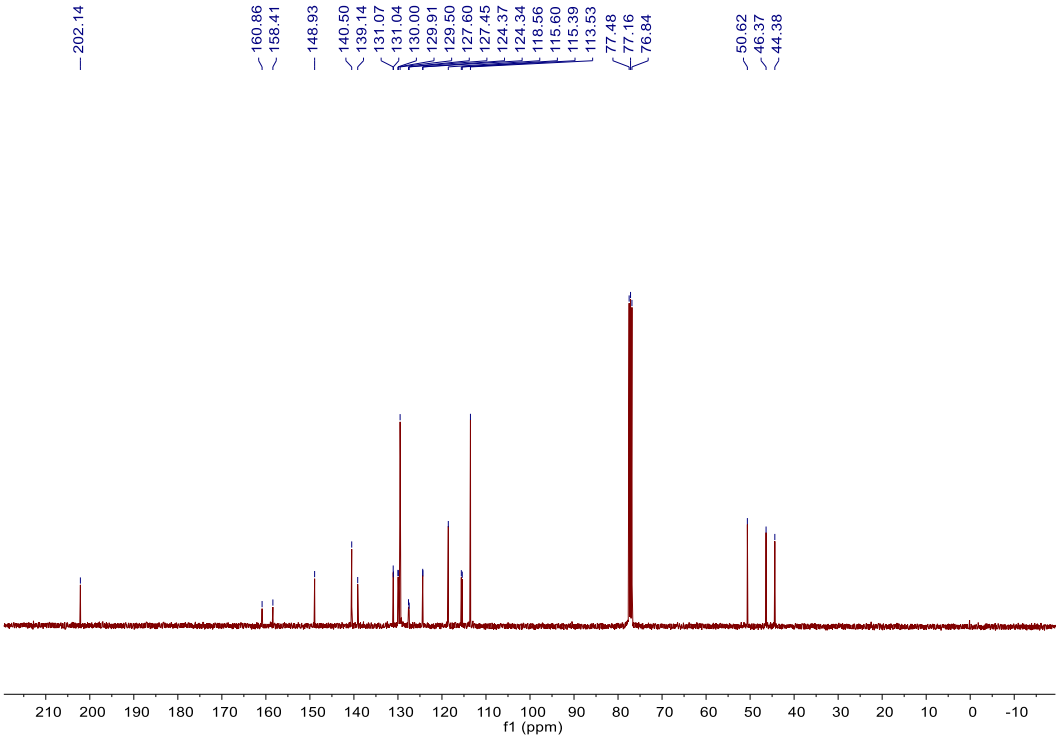


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.20 (m, 4H), 7.12 (t, *J* = 7.5 Hz, 1H), 7.05-6.98 (m, 1H), 6.84-6.76 (m, 3H), 6.71 (t, *J* = 4.4 Hz, 1H), 4.29 (d, *J* = 4.4 Hz, 2H), 3.76 (t, *J* = 6.3 Hz, 2H), 3.14 (t, *J* = 6.3 Hz, 2H).

^{19}F NMR spectrum ($CDCl_3$)

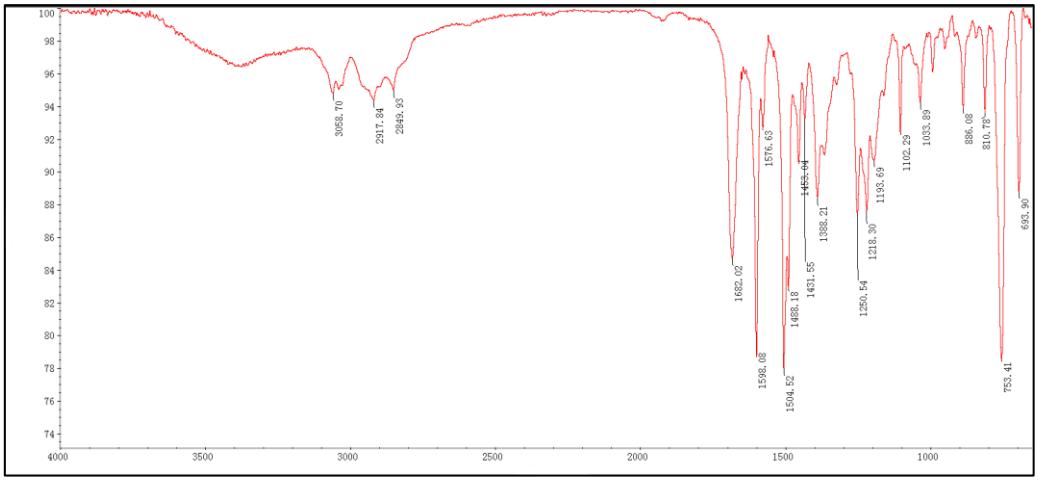


^{13}C NMR spectrum ($CDCl_3$)

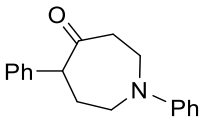


^{13}C NMR (100 MHz, $CDCl_3$) δ 202.14, 159.63 (d, J = 245.3 Hz), 148.93, 140.50, 139.14, 131.05 (d, J = 3.7 Hz), 129.95 (d, J = 8.3 Hz), 129.50, 127.52 (d, J = 15.1 Hz), 124.36 (d, J = 3.4 Hz), 118.56 , 115.49 (d, J = 21.8 Hz), 113.53, 50.62, 46.37, 44.38.

IR spectrum



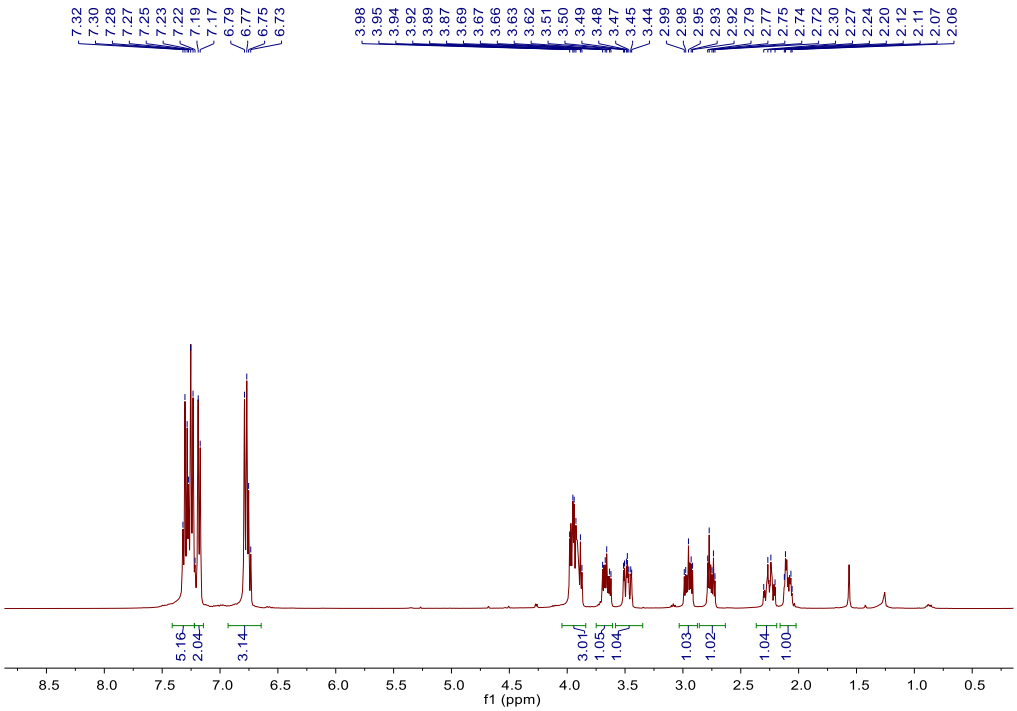
HRMS (ESI+, MeOH): *m/z* calcd. 282.1289 $(M + H)^+$, found: 282.1283.



4a

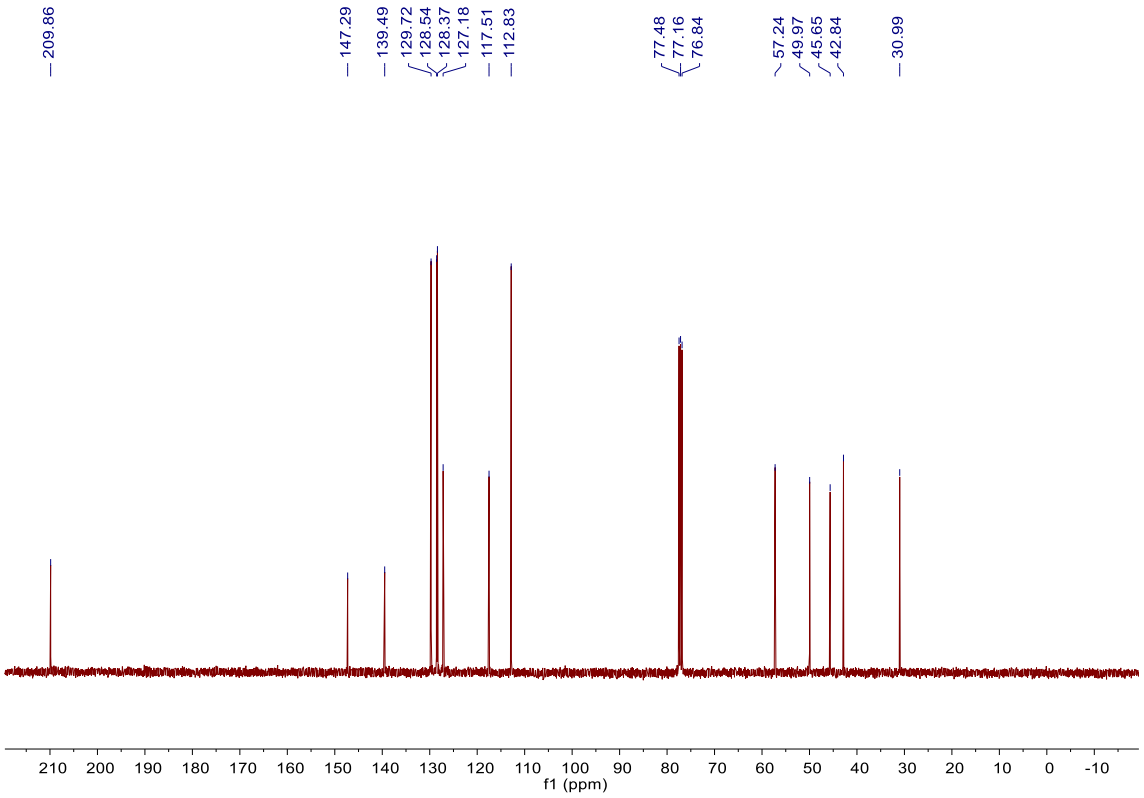
Scale: 0.1 mmol (86% yield), white solid, PE : EA = 5 : 1, R_f = 0.38.

^{1}H NMR spectrum ($CDCl_3$)



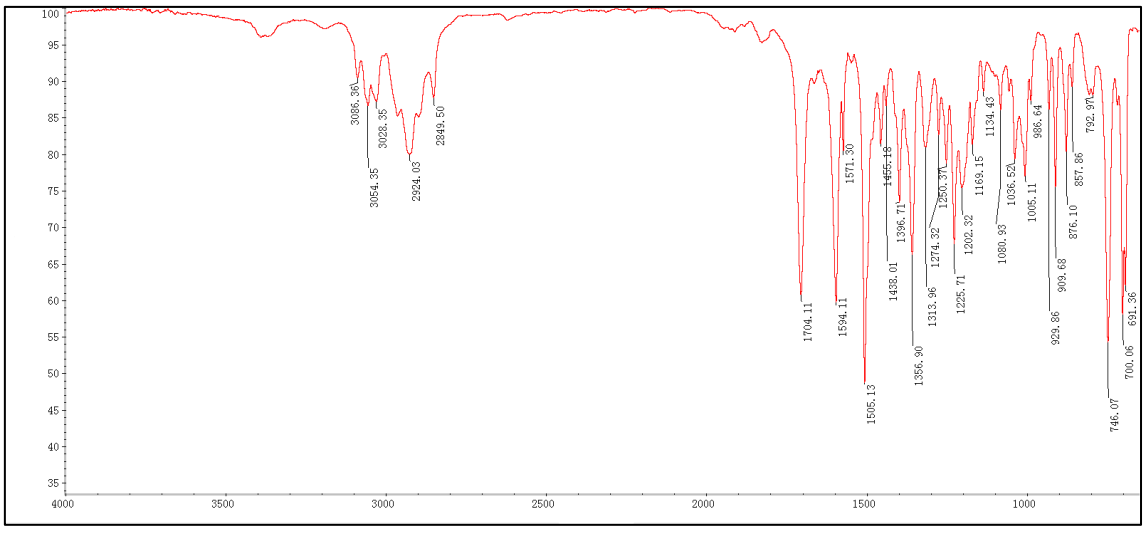
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.22 (m, 5H), 7.18 (d, *J* = 6.8 Hz, 2H), 6.76 (dd, *J* = 14.0, 7.6 Hz, 3H), 4.05-3.84 (m, 3H), 3.75-3.61 (m, 1H), 3.58-3.35 (m, 1H), 3.03-2.87 (m, 1H), 2.86-2.63 (m, 1H), 2.37-2.19 (m, 1H), 2.16-2.02 (m, 1H).

^{13}C NMR spectrum ($CDCl_3$)

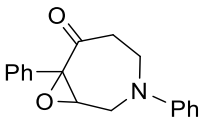


^{13}C NMR (100 MHz, $CDCl_3$) δ 209.86, 147.29, 139.49, 129.72, 128.54, 128.37, 127.18, 117.51, 112.83, 57.24, 49.97, 45.65, 42.84, 30.99.

IR spectrum



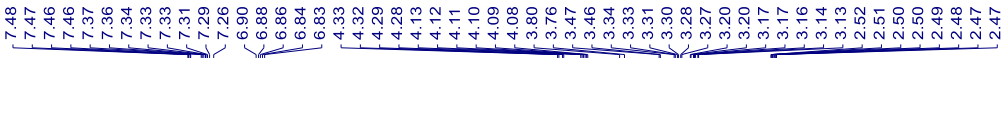
HRMS (ESI+, MeOH): *m/z* calcd. 266.1539 $(M + H)^+$, found: 266.1526.

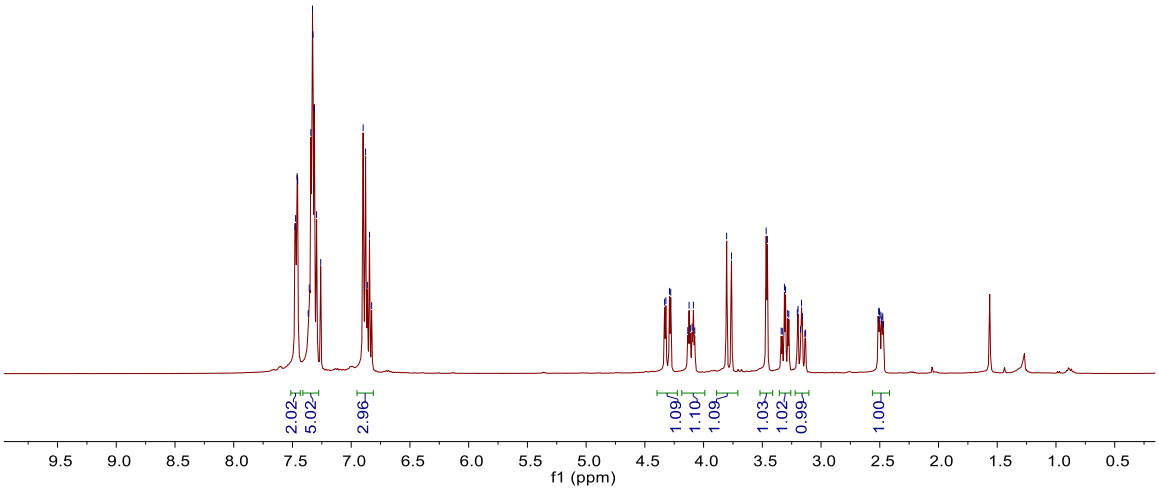


4b

Scale: 0.1 mmol (61% yield), yellow solid, PE : EA = 5 : 1, R_f = 0.45.

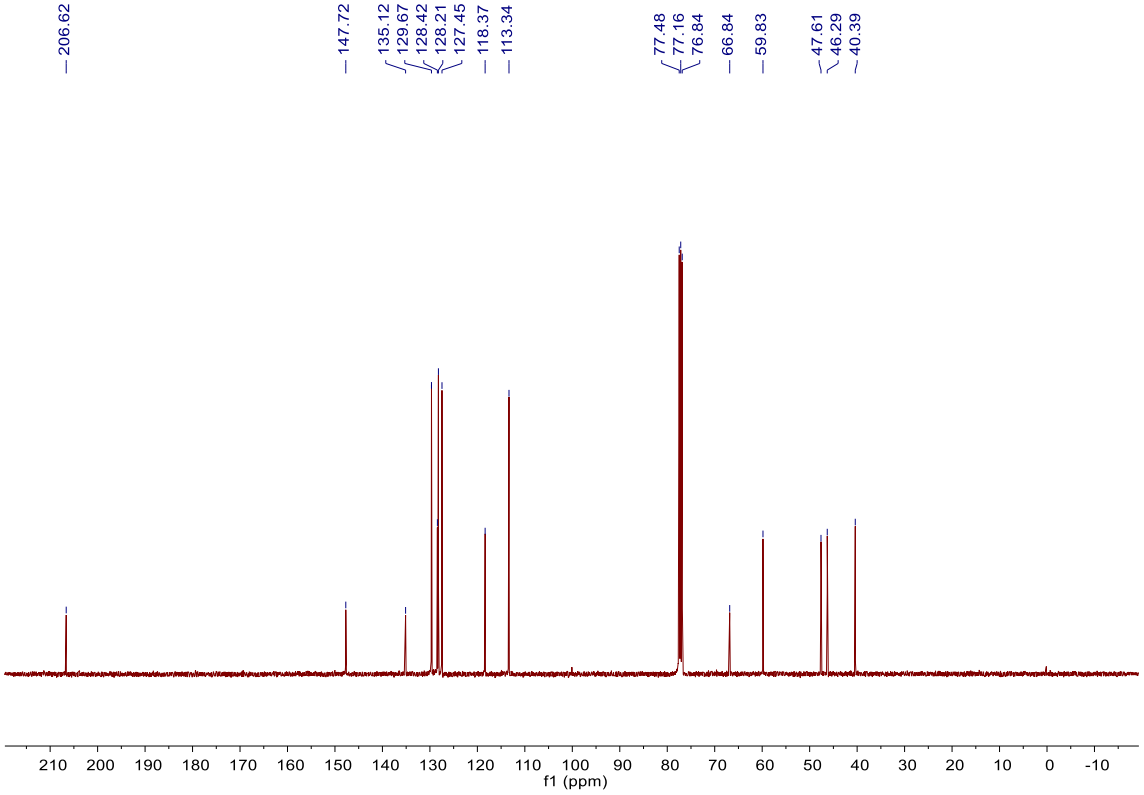
^{1}H NMR spectrum ($CDCl_3$)





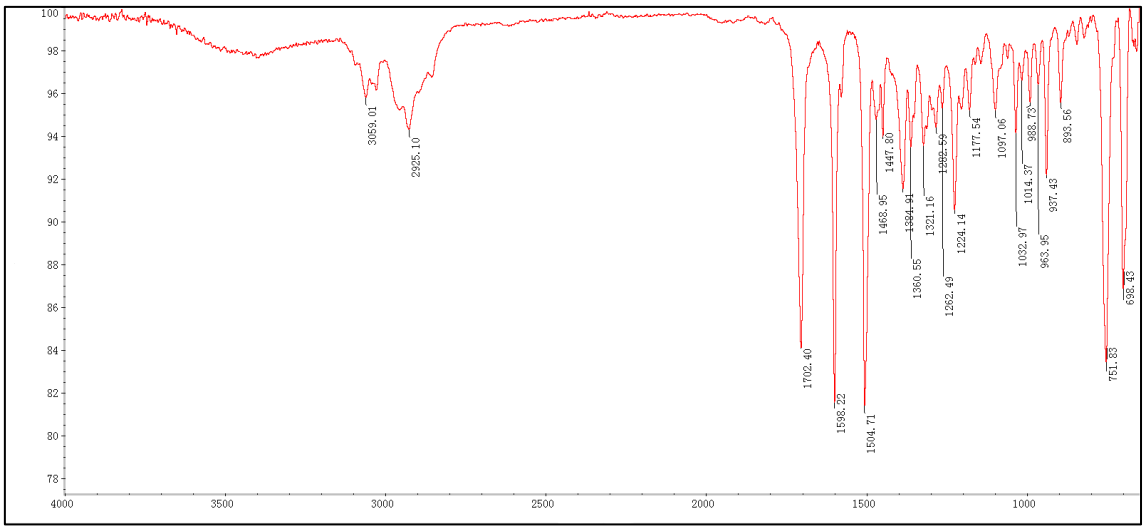
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (dd, *J* = 7.4, 2.2 Hz, 2H), 7.41-7.28 (m, 5H), 6.95-6.81 (m, 3H), 4.31 (dd, *J* = 16.6, 4.3 Hz, 1H), 4.10 (dt, *J* = 14.8, 4.6 Hz, 1H), 3.78 (d, *J* = 16.5 Hz, 1H), 3.46 (d, *J* = 4.2 Hz, 1H), 3.31 (td, *J* = 11.1, 3.8 Hz, 1H), 3.22-3.10 (m, 1H), 2.56-2.42 (m, 1H).

^{13}C NMR spectrum ($CDCl_3$)

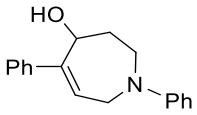


^{13}C NMR (100 MHz, $CDCl_3$) δ 206.62, 147.72, 135.12, 129.67, 128.42, 128.21, 127.45, 118.37, 113.34, 66.84, 59.83, 47.61, 46.29, 40.39.

IR spectrum



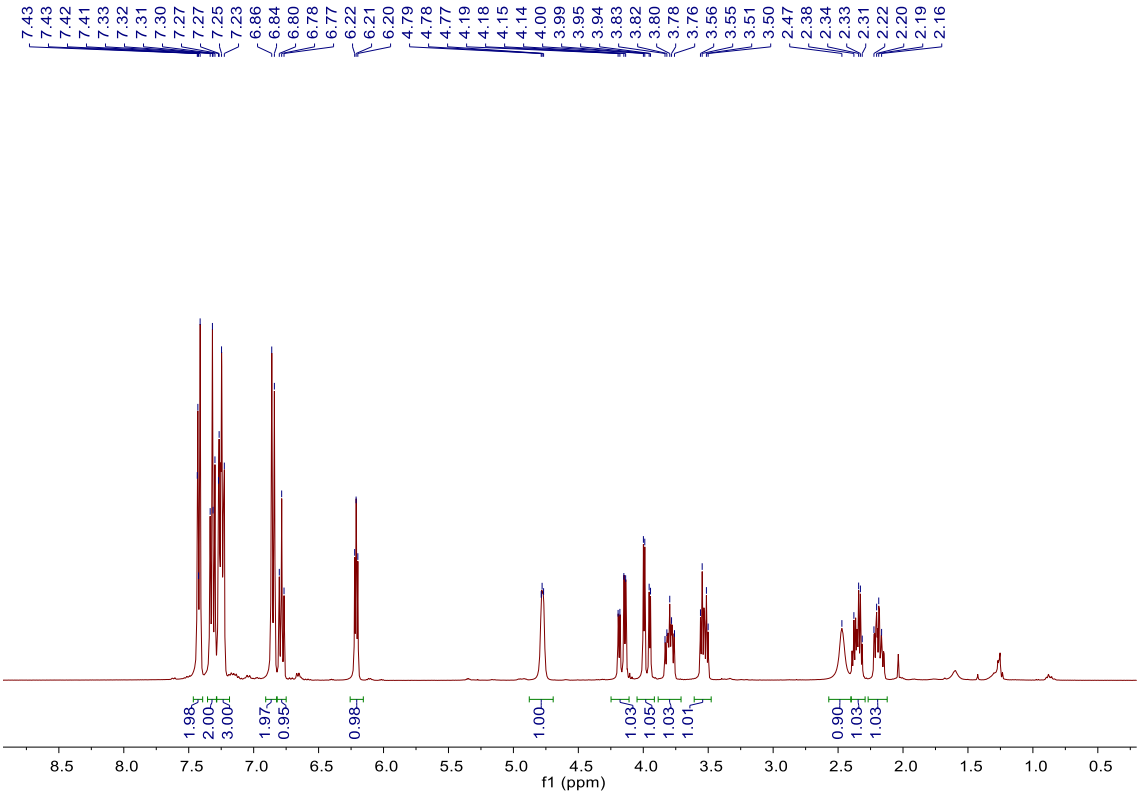
HRMS (ESI+, MeOH): *m/z* calcd. 280.1332 $(M + H)^+$, found: 280.1322.



4c

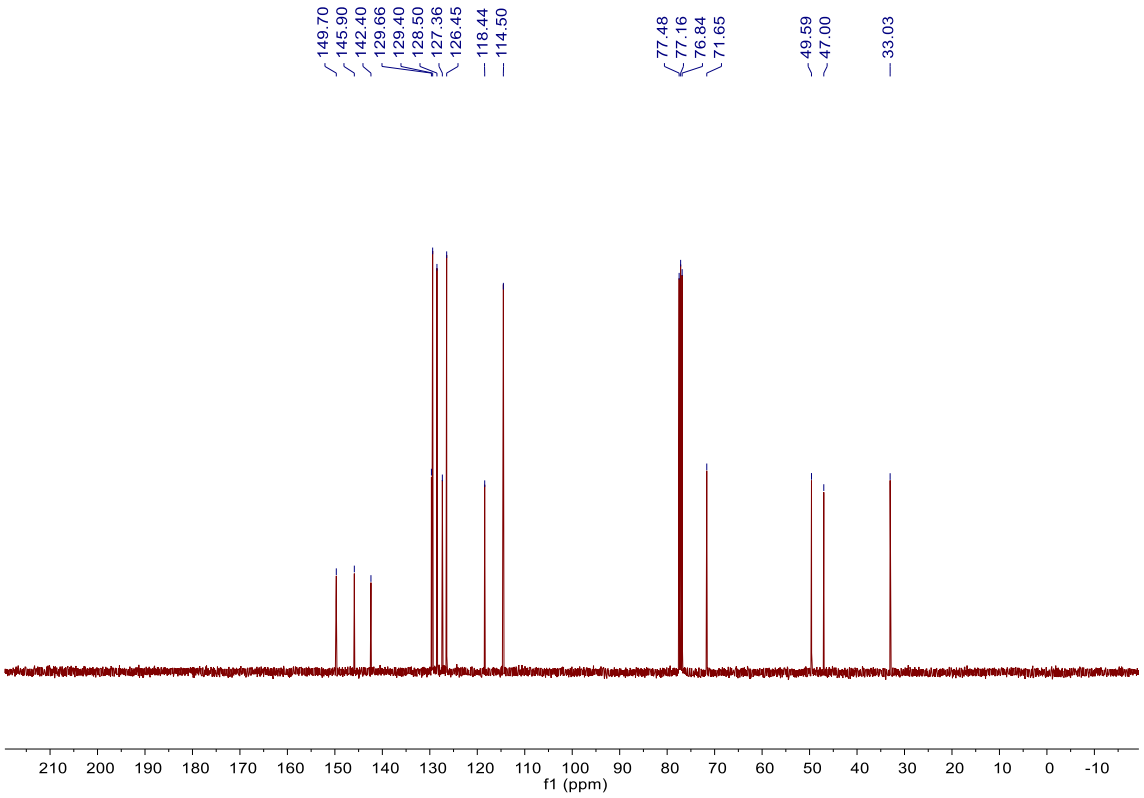
Scale: 0.1 mmol (85% yield), yellow oil, PE : EA = 5 : 1, R_f = 0.25.

^{1}H NMR spectrum ($CDCl_3$)



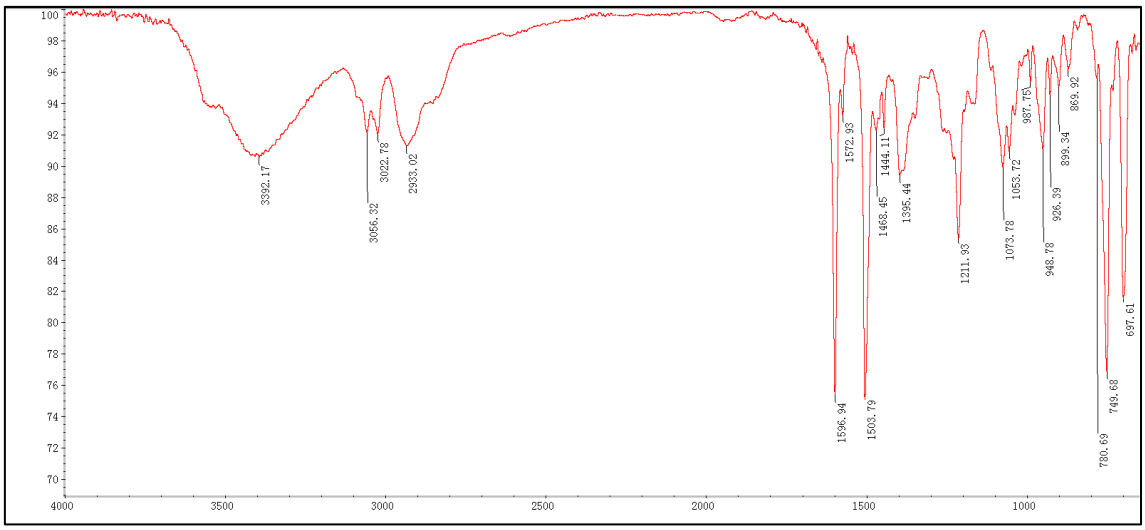
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46-7.39 (m, 2H), 7.36-7.29 (m, 2H), 7.28-7.19 (m, 3H), 6.85 (d, *J* = 8.2 Hz, 2H), 6.78 (t, *J* = 7.3 Hz, 1H), 6.26-6.16 (m, 1H), 4.88-4.69 (m, 1H), 4.16 (dd, *J* = 17.7, 5.5 Hz, 1H), 3.97 (dd, *J* = 17.7, 4.2 Hz, 1H), 3.89-3.71 (m, 1H), 3.61-3.48 (m, 1H), 2.47 (s, 1H), 2.40-2.29 (m, 1H), 2.27-2.12 (m, 1H).

^{13}C NMR spectrum ($CDCl_3$)

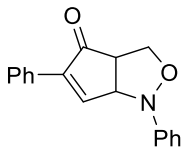


^{13}C NMR (100 MHz, $CDCl_3$) δ 149.70, 145.90, 142.40, 129.66, 129.40, 128.50, 127.36, 126.45, 118.44, 114.50, 71.65, 49.59, 47.00, 33.03.

IR spectrum



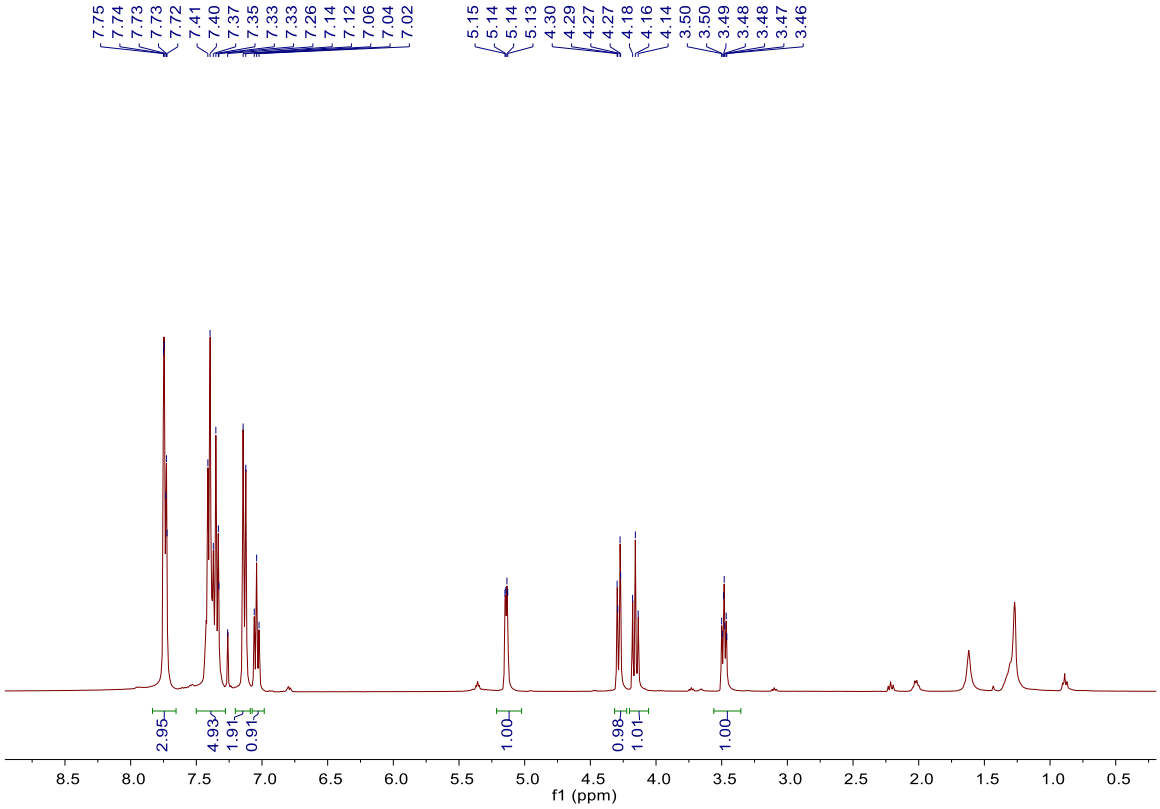
HRMS (ESI+, MeOH): *m/z* calcd. 248.1434 $[M - OH]^+$, found: 248.1428.



4d

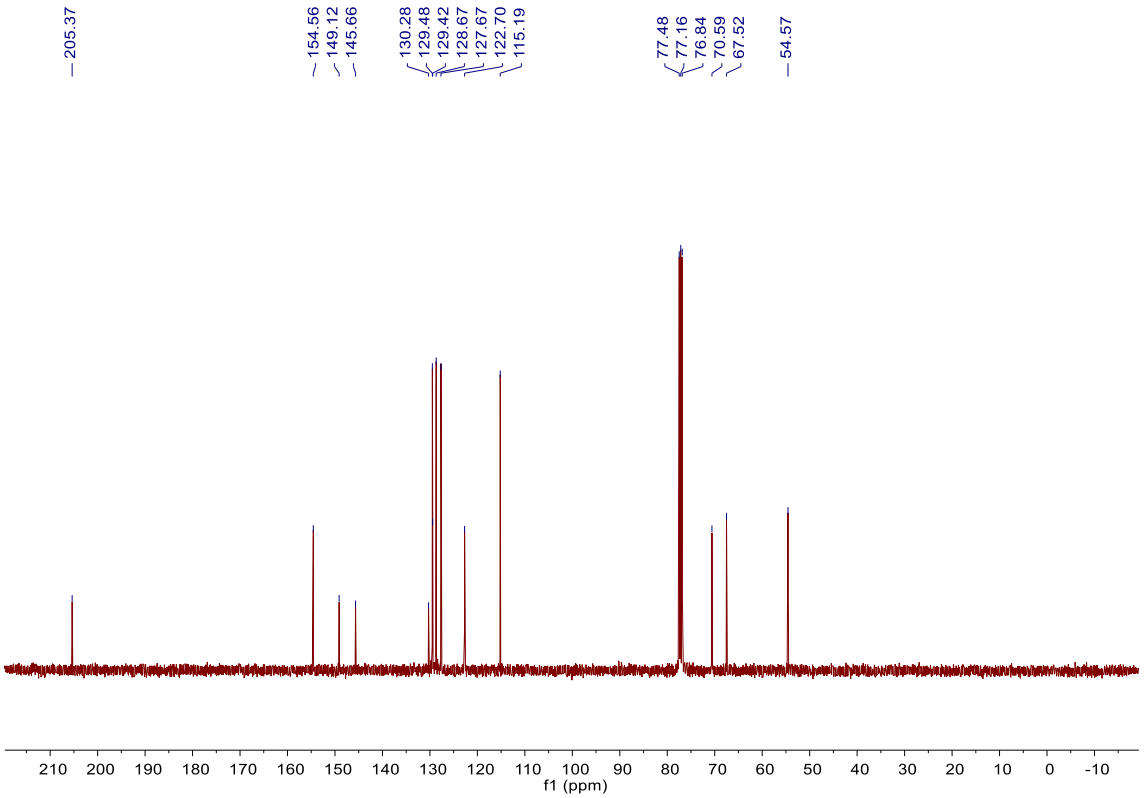
Scale: 0.1 mmol (59% yield), yellow solid, PE : EA = 5 : 1, R_f = 0.37.

^{1}H NMR spectrum ($CDCl_3$)



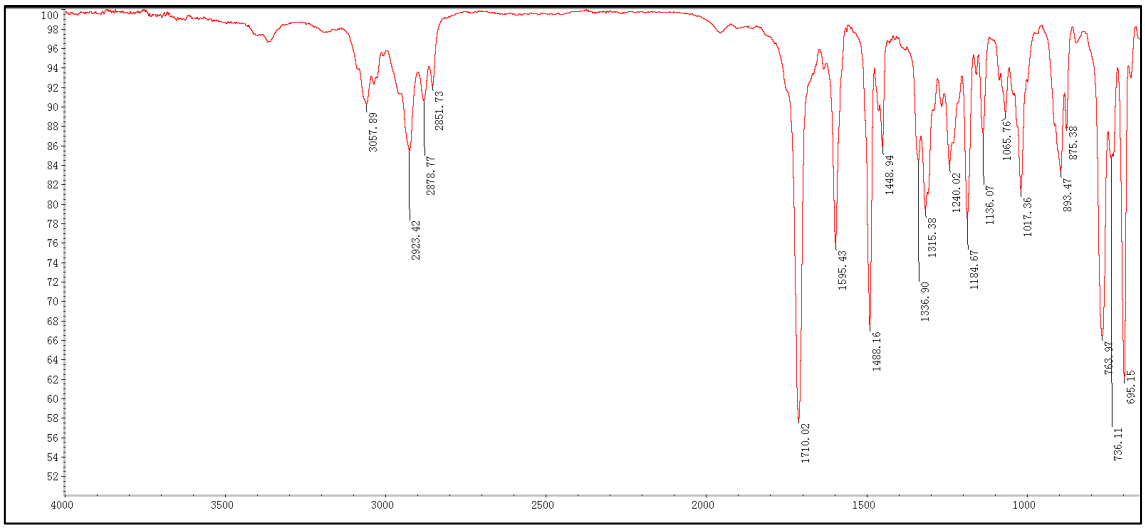
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83-7.65 (m, 3H), 7.50-7.28 (m, 5H), 7.13 (d, *J* = 8.0 Hz, 2H), 7.04 (t, *J* = 7.3 Hz, 1H), 5.14 (dd, *J* = 6.0, 2.5 Hz, 1H), 4.32-4.22 (m, 1H), 4.16 (t, *J* = 8.5 Hz, 1H), 3.56-3.35 (m, 1H).

^{13}C NMR spectrum ($CDCl_3$)

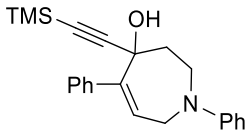


^{13}C NMR (100 MHz, $CDCl_3$) δ 205.37, 154.56, 149.12, 145.66, 130.28, 129.48, 129.42, 128.67, 127.67, 122.70, 115.19, 70.59, 67.52, 54.57.

IR spectrum



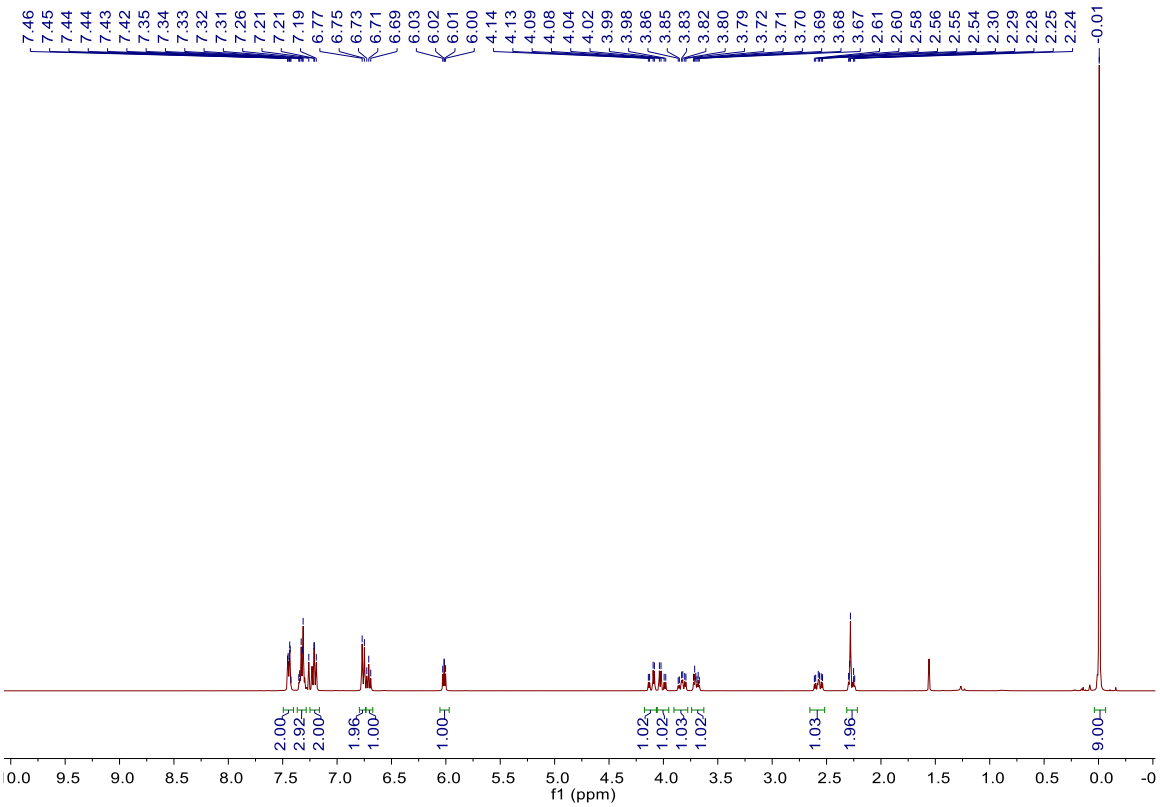
HRMS (ESI+, MeOH): *m/z* calcd. 278.1176 $(M + H)^+$, found: 278.1166.



4e

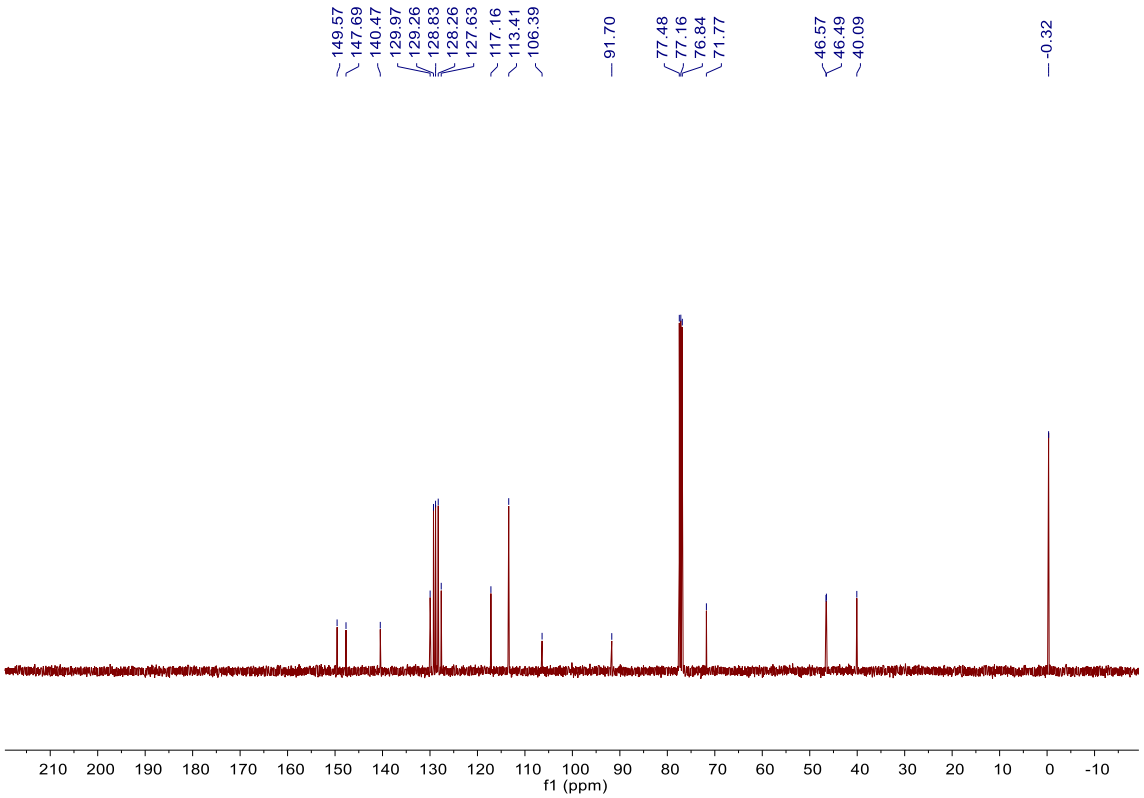
Scale: 0.1 mmol (67% yield), yellow oil, PE : EA = 5 : 1, R_f = 0.37.

^{1}H NMR spectrum ($CDCl_3$)



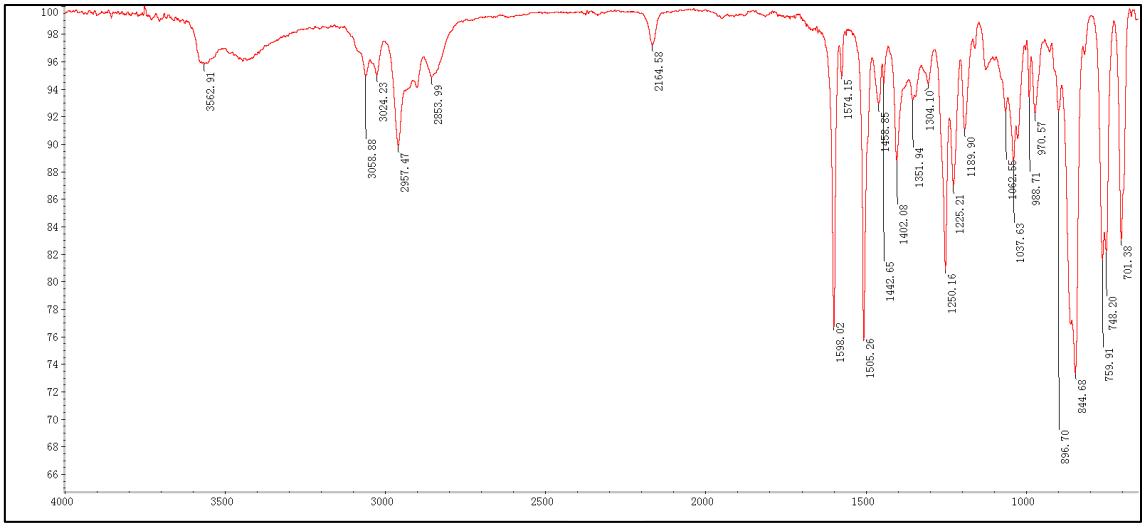
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49-7.40 (m, 2H), 7.37-7.28 (m, 3H), 7.25-7.16 (m, 2H), 6.76 (d, *J* = 8.2 Hz, 2H), 6.71 (t, *J* = 7.2 Hz, 1H), 6.05-5.97 (m, 1H), 4.11 (dd, *J* = 17.5, 4.6 Hz, 1H), 4.01 (dd, *J* = 17.5, 6.0 Hz, 1H), 3.83 (td, *J* = 12.0, 11.5, 4.3 Hz, 1H), 3.70 (dt, *J* = 12.8, 4.3 Hz, 1H), 2.65-2.52 (m, 1H), 2.31-2.22 (m, 2H), -0.01 (s, 9H).

^{13}C NMR spectrum ($CDCl_3$)

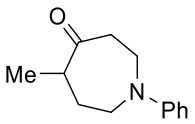


^{13}C NMR (100 MHz, $CDCl_3$) δ 149.57, 147.69, 140.47, 129.97, 129.26, 128.83, 128.26, 127.63, 117.16, 113.41, 106.39, 91.70, 71.77, 46.57, 46.49, 40.09, -0.32.

IR spectrum

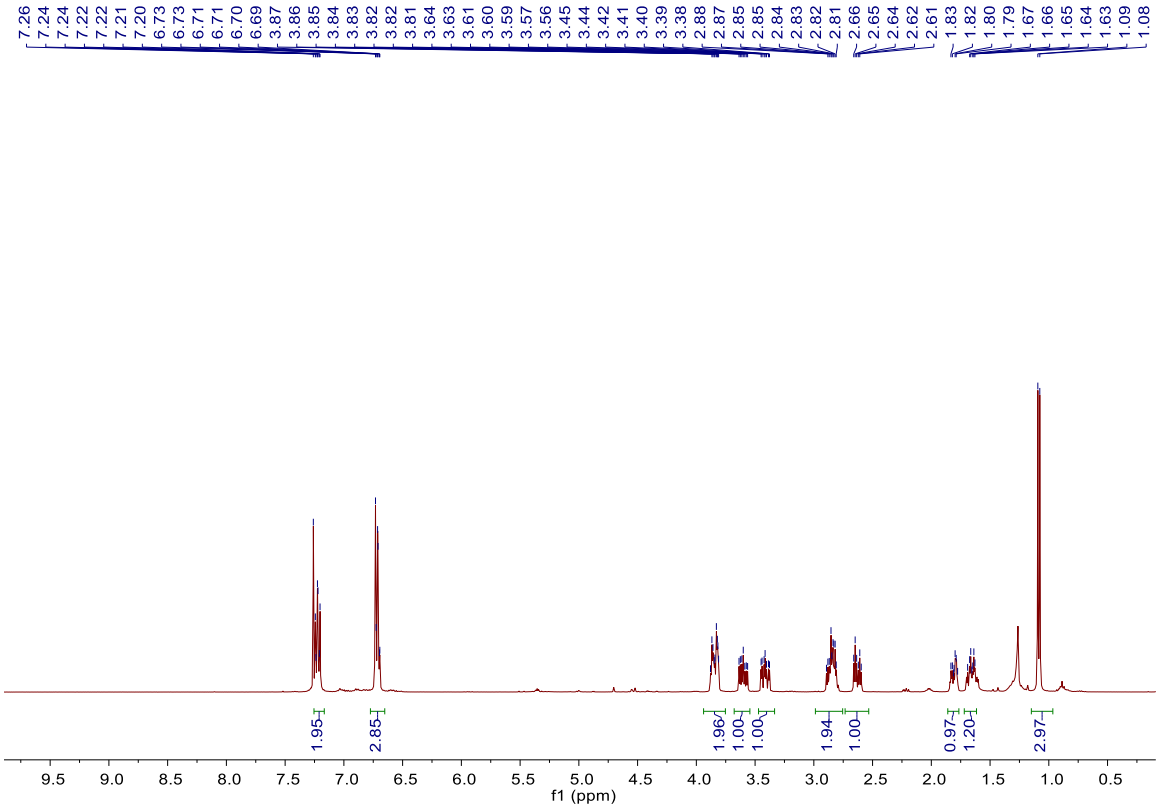


HRMS (ESI+, MeOH): *m/z* calcd. 360.1778 $(M + H)^+$, found: 360.1793.



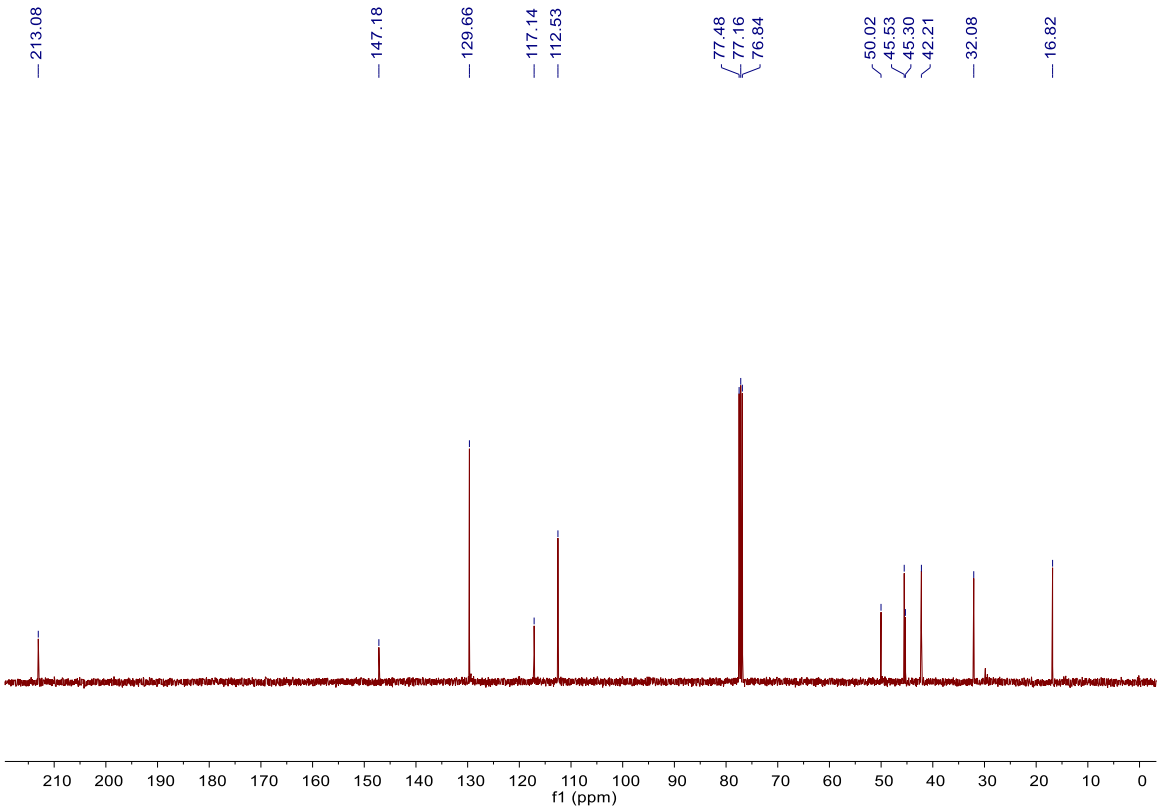
Scale: 0.1 mmol (83% yield), yellow oil, PE : EA = 10 : 1, R_f = 0.20.

^{1}H NMR spectrum ($CDCl_3$)



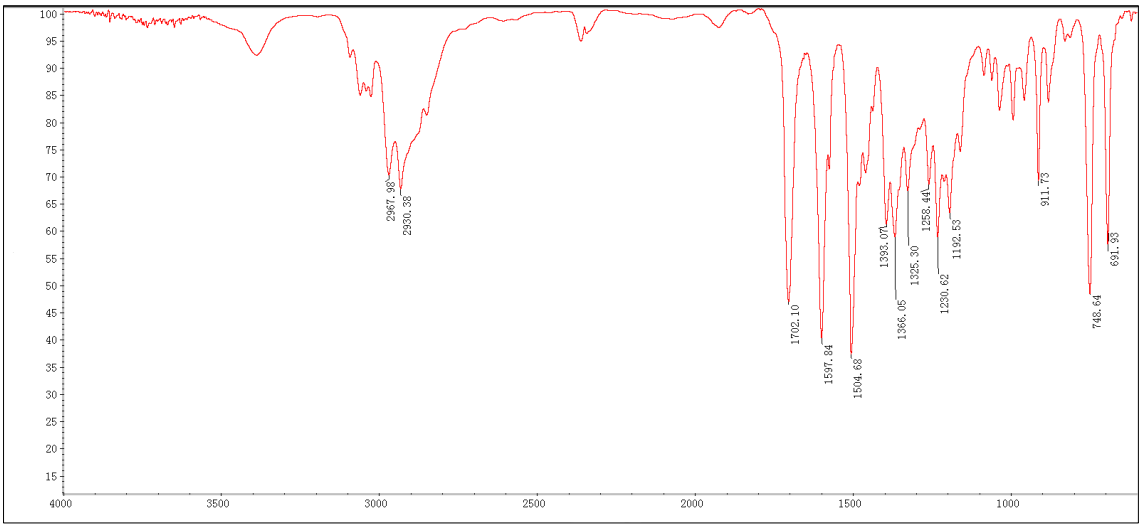
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25-7.17 (m, 2H), 6.77-6.65 (m, 3H), 3.94-3.75 (m, 2H), 3.68-3.54 (m, 1H), 3.47-3.33 (m, 1H), 2.99-2.75 (m, 2H), 2.63 (dt, *J* = 15.6, 4.9 Hz, 1H), 1.86-1.77 (m, 1H), 1.72-1.62 (m, 1H), 1.09 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR spectrum ($CDCl_3$)

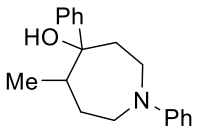


^{13}C NMR (100 MHz, $CDCl_3$) δ 213.08, 147.18, 129.66, 117.14, 112.53, 50.02, 45.53, 45.30, 42.21, 32.08, 16.82.

IR spectrum

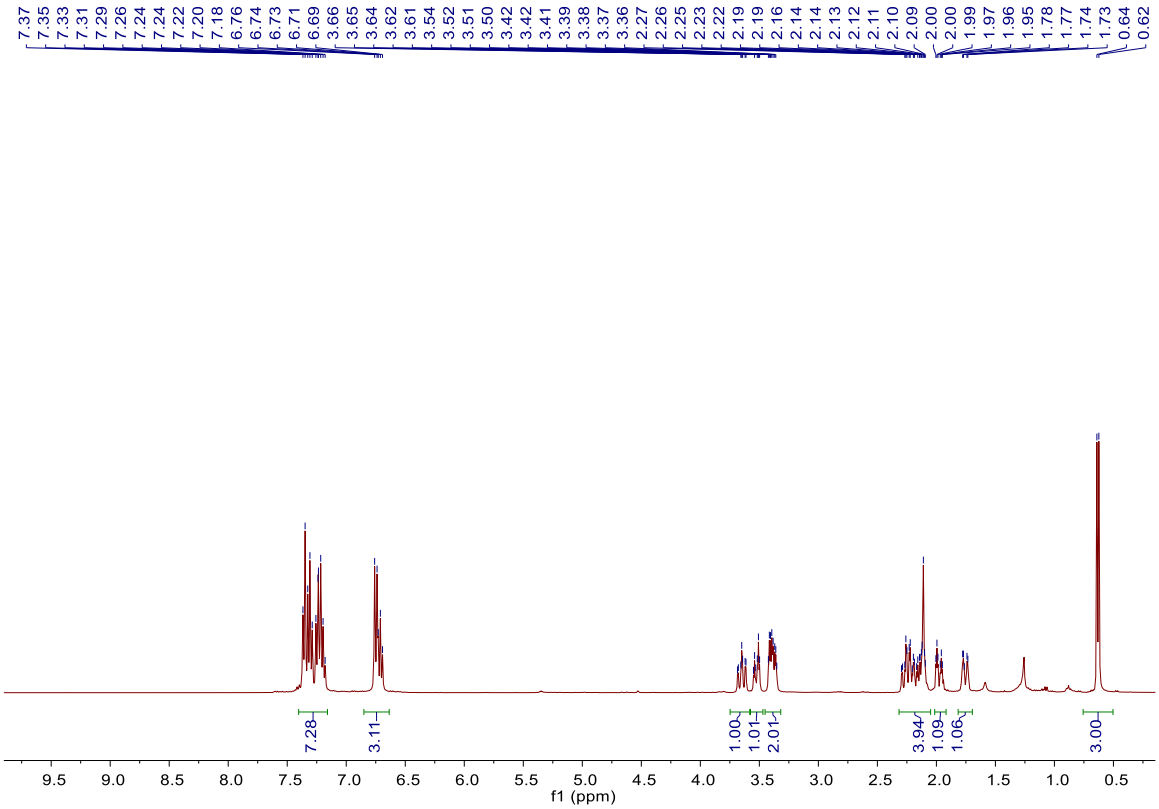


HRMS (ESI+, MeOH): *m/z* calcd. 204.1388 $(M + H)^+$, found: 204.1393.



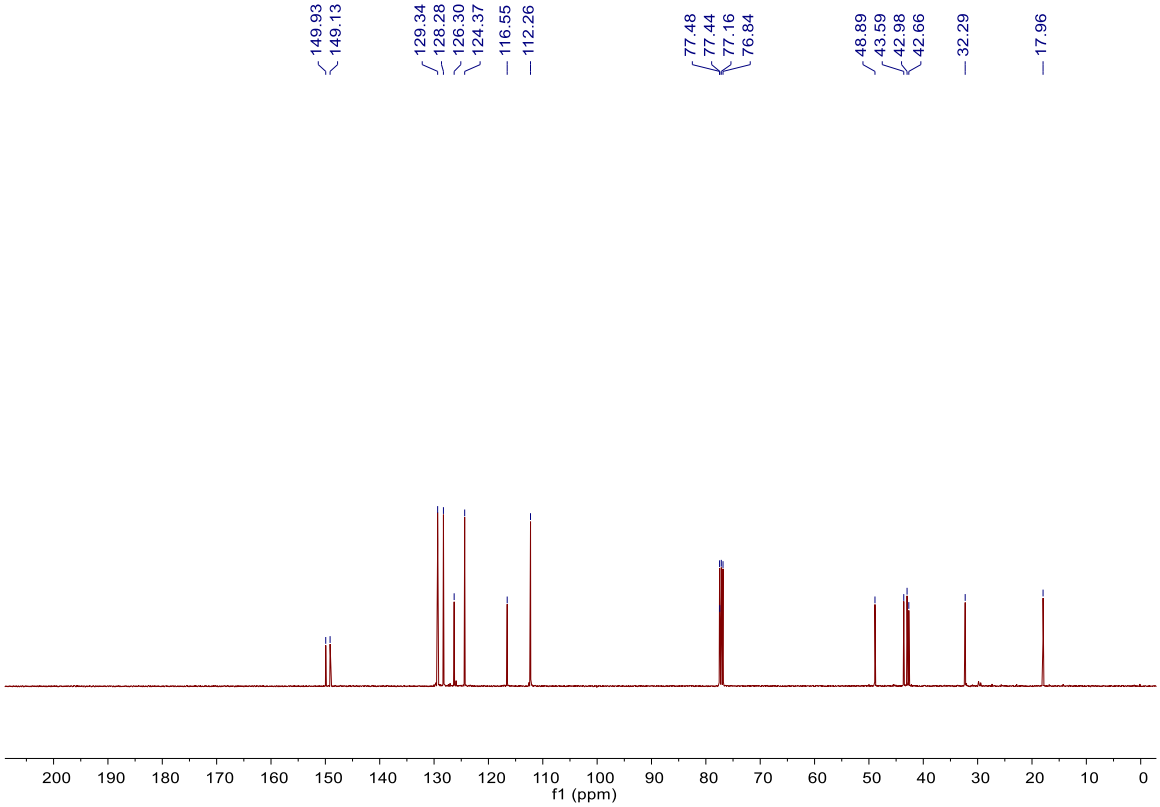
Scale: 0.1 mmol (75% yield), yellow oil, PE : EA = 10 : 1, R_f = 0.30.

^{1}H NMR spectrum ($CDCl_3$)



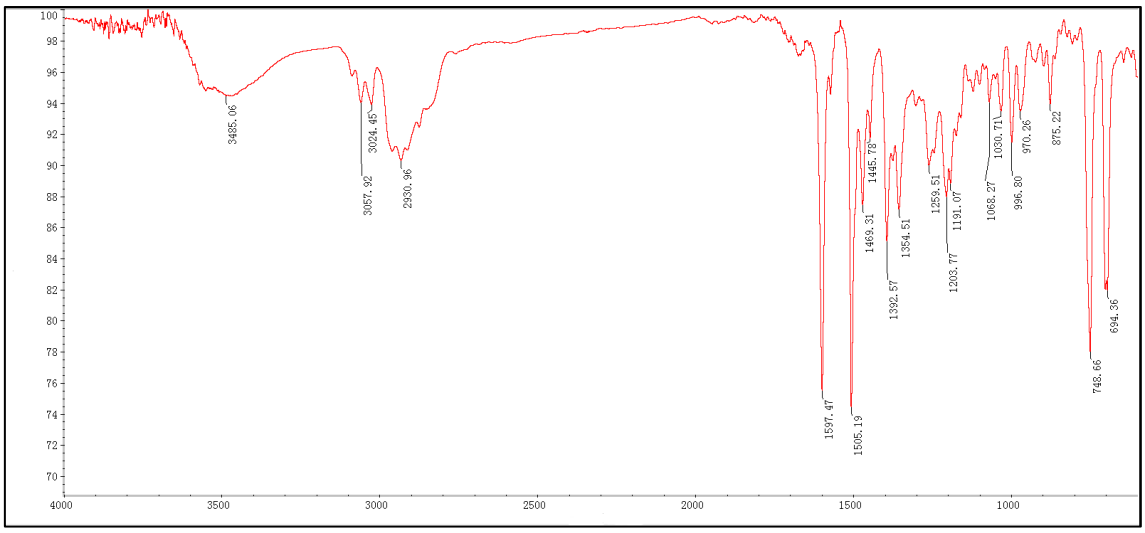
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.16 (m, 7H), 6.85-6.64 (m, 3H), 3.75-3.58 (m, 1H), 3.52 (dt, *J* = 13.1, 3.8 Hz, 1H), 3.45-3.32 (m, 2H), 2.32-2.05 (m, 4H), 2.01-1.92 (m, 1H), 1.82-1.70 (m, 1H), 0.63 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR spectrum ($CDCl_3$)

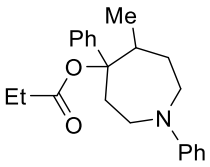


^{13}C NMR (100 MHz, $CDCl_3$) δ 149.93, 149.13, 129.34, 128.28, 126.30, 124.37, 116.55, 112.26, 77.44, 48.89, 43.59, 42.98, 42.66, 32.29, 17.96.

IR spectrum

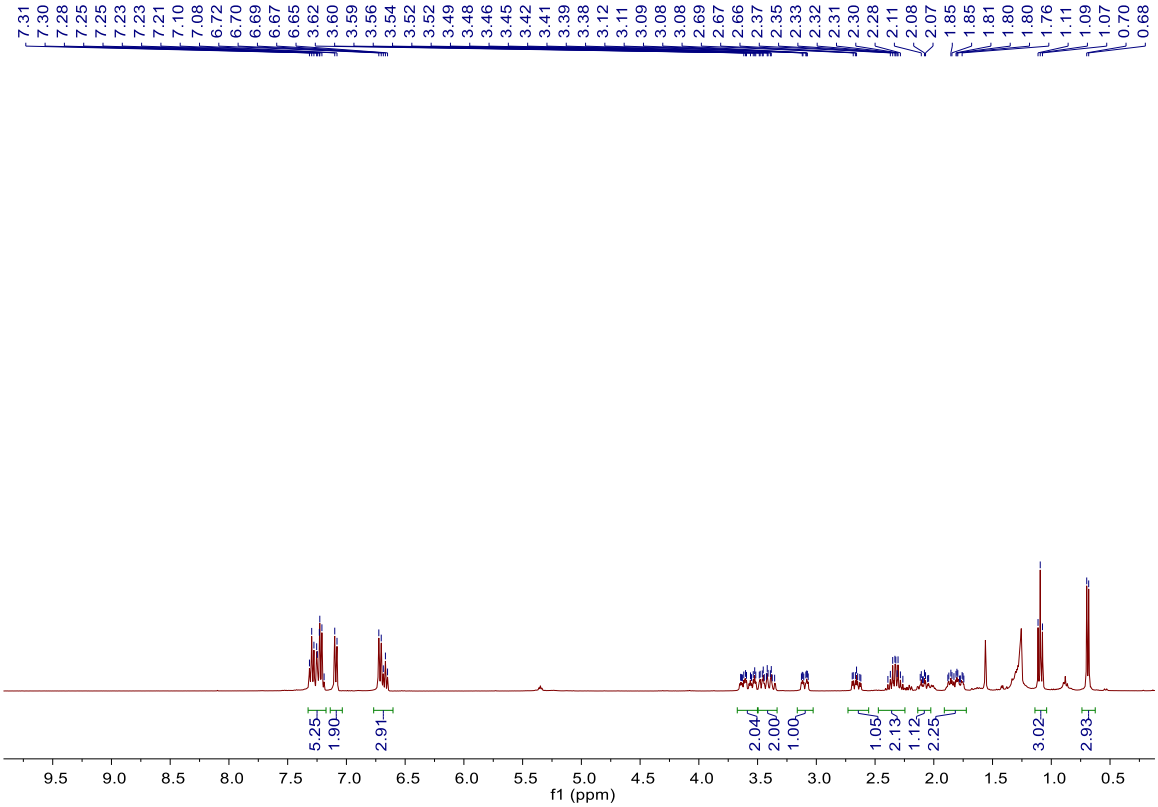


HRMS (ESI+, MeOH): *m/z* calcd. 282.1858 $(M + H)^+$, found: 282.1862.



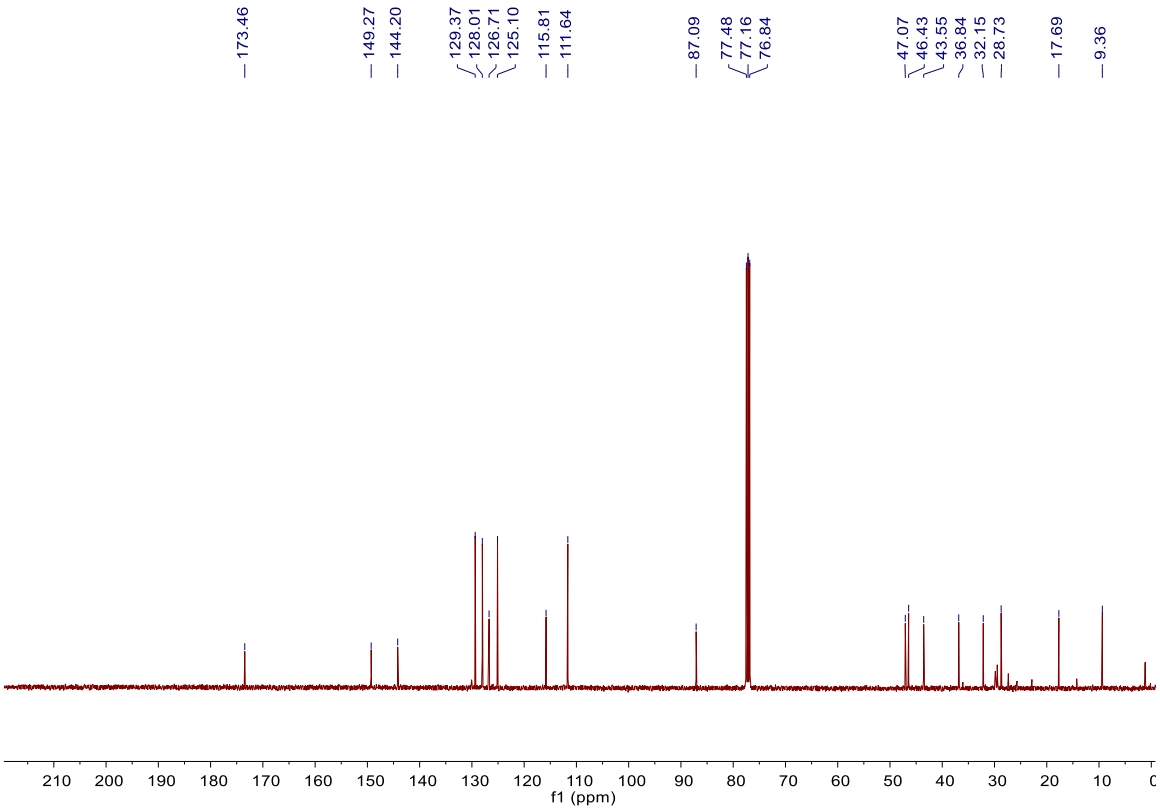
Scale: 0.1 mmol (52% yield), colorless oil, PE : EA = 10 : 1, R_f = 0.50.

^{1}H NMR spectrum ($CDCl_3$)



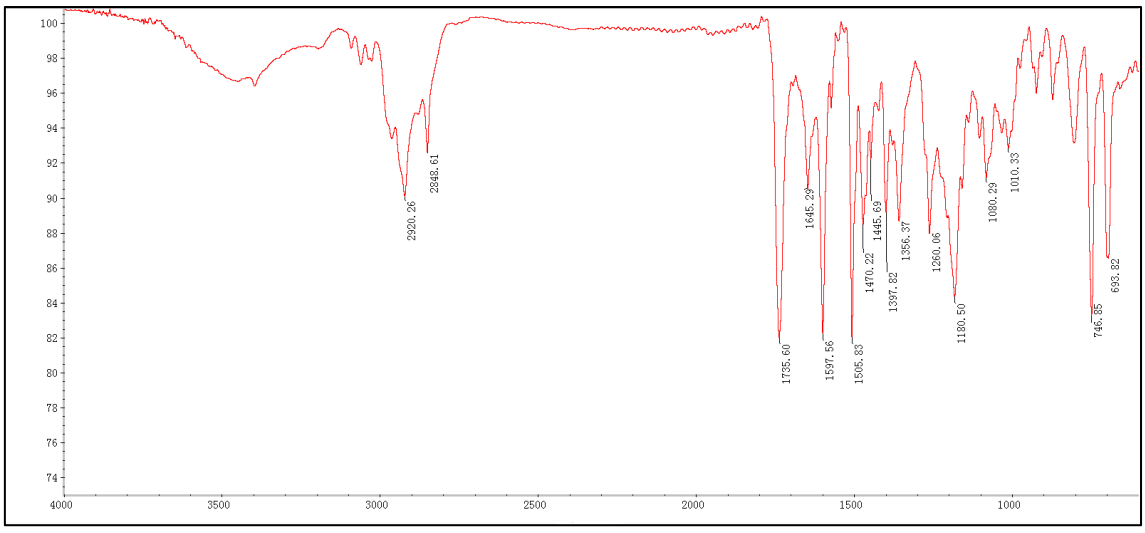
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.17 (m, 5H), 7.09 (d, *J* = 7.7 Hz, 2H), 6.77-6.60 (m, 3H), 3.67-3.50 (m, 2H), 3.50-3.33 (m, 2H), 3.16-3.03 (m, 1H), 2.73-2.55 (m, 1H), 2.47-2.25 (m, 2H), 2.14-2.03 (m, 1H), 1.91-1.72 (m, 2H), 1.09 (t, *J* = 7.6 Hz, 3H), 0.69 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR spectrum ($CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$) δ 173.46, 149.27, 144.20, 129.37, 128.01, 126.71, 125.10, 115.81, 111.64, 87.09, 47.07, 46.43, 43.55, 36.84, 32.15, 28.73, 17.69, 9.36.

IR spectrum

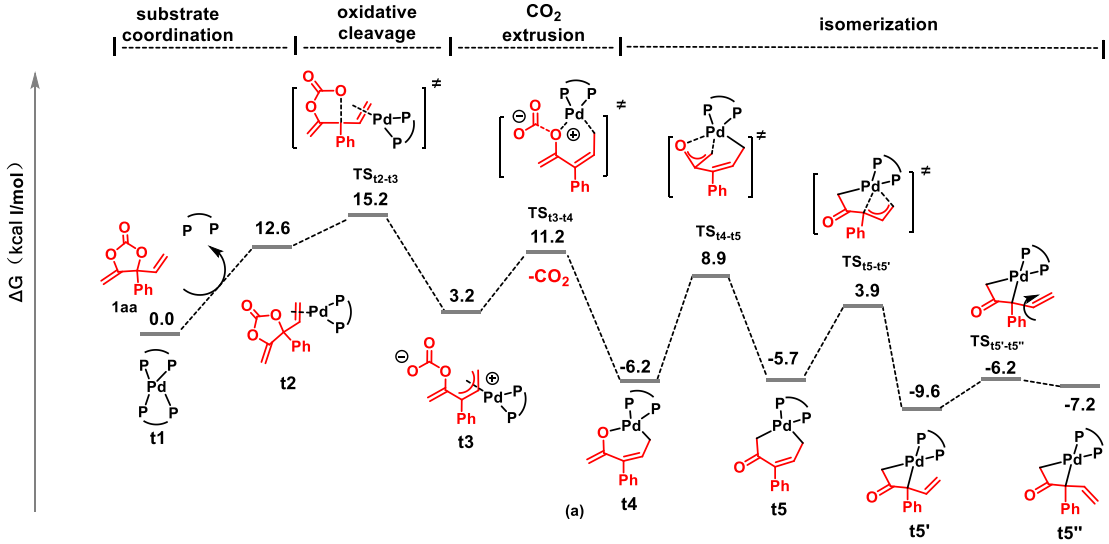


HRMS (ESI+, MeOH): *m/z* calcd. 338.2115 $(M + H)^+$, found: 338.2121.

Computational Methods

All the calculations were carried out via Density functional theory (DFT) calculation using Gaussian 09[5] with the B97D[6] functional. Geometric structures of all species in this work were optimized in gas phase at T=298.15K and 1 atm pressure. Frequency calculation were performed to determine all the stationary points (no imaginary frequency) and transition state structures (only one imaginary frequency). The 6-31+G*[7] basis set was used for the atoms (C、H、O、N、P、S、F). And the LANL2DZ basis set was used for Pd and Ag atoms[8] with the polarization functions added for Pd (f = 1.72) and Ag (f = 1.611).[9] In addition, the intrinsic reaction coordinate (IRC) calculation[10] were applied to conform the connection of each transition state to its corresponding appropriate intermediates, reactants, or products. Solvent effects were computed by using the SMD[11] model at the same level of theory while LANL2DZ basis set for Pd and Ag atoms and 6-311++G**[12] basis set for all other atoms. Dichloromethane (ε=8.93) was used as the solvent, corresponding to the experimental conditions, and Bondi atomic radii[13] used for the SMD calculation. All 3D molecular structures were generated by using the CYLview (Version) program.[14]

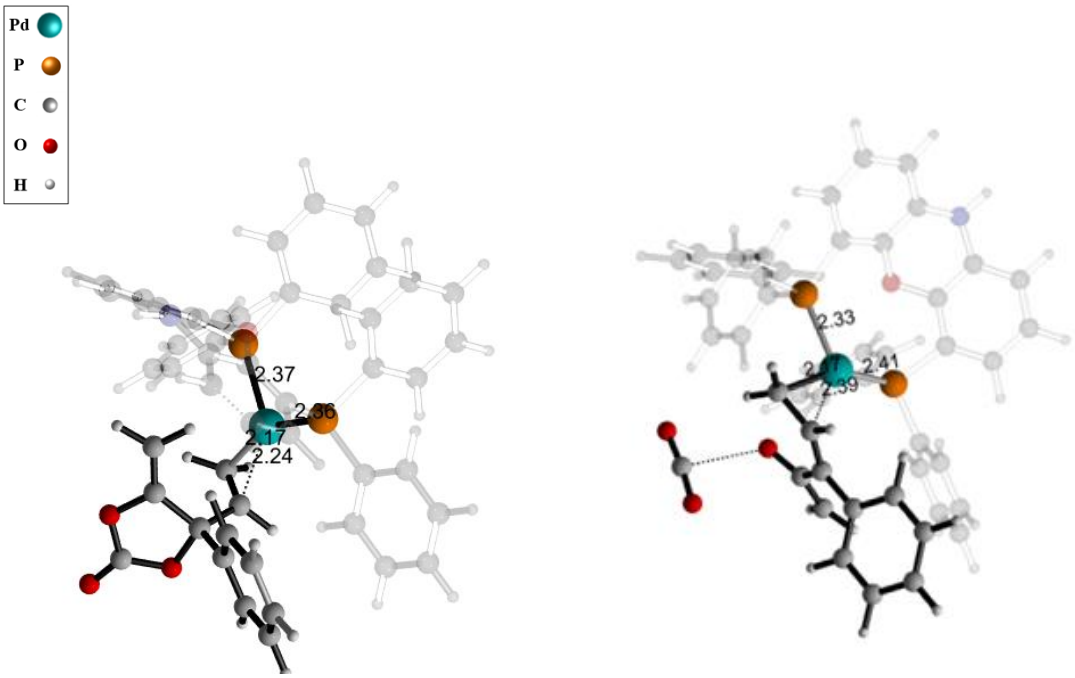
Scheme S1. The free energy profiles for the formation of t5, t5' and t5"



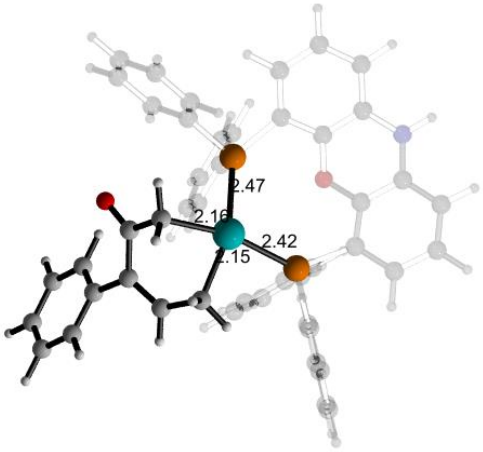
Scheme S1. The free energy profiles (in kcal/mol) for the formation of intermediates **t5**, **t5'** and **t5"**.

Table S1. The gas phase relative electronic energies (ΔEgas), gas phase relative free energies (ΔGgas) and solvation corrected relative electronic energies (ΔEsol) calculated for species involved in the process of ligand exchange, oxidative cleavage, CO_2 extrusion and isomerization.

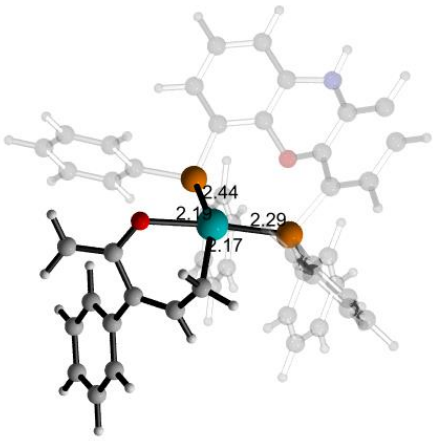
Species	ΔGgas	ΔEgas	ΔEsol
t1	0.0	0.0	0.0
t2	19.7	25.7	18.6
t3	14.3	26.4	15.3
t4	5.4	25.1	13.5
t5	6.4	26.7	14.6
t5'	3.3	22.9	10.0
t5''	7.1	27.2	12.9
TS_{t2-3}	29.1	37.0	23.1
TS_{t3-4}	22.4	35.2	23.9
TS_{t4-5}	24.0	46.7	31.5
$TS_{t5-5'}$	18.8	37.2	22.3
$TS_{t5'-5''}$	6.5	26.4	13.7



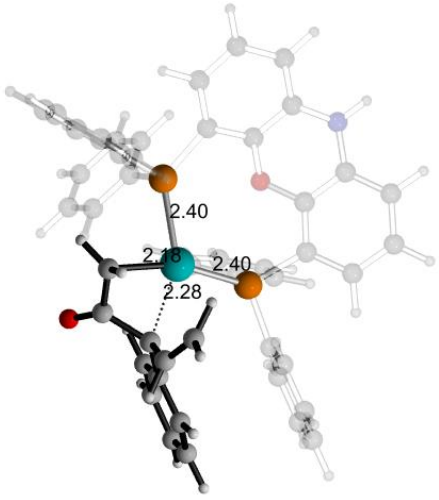
t2 **t3**



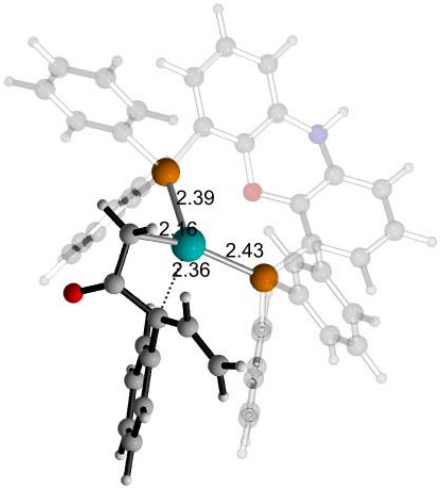
t4



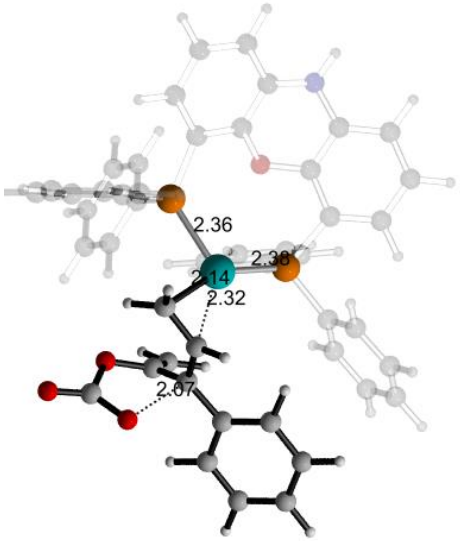
t5



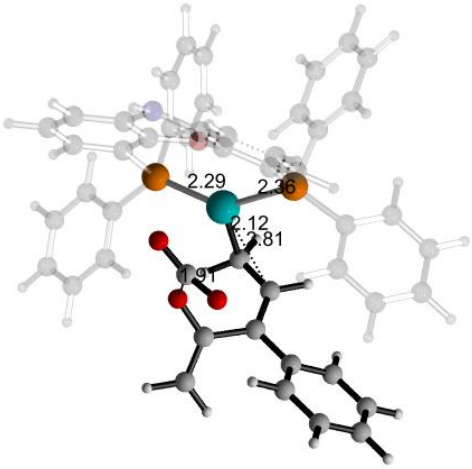
t5'



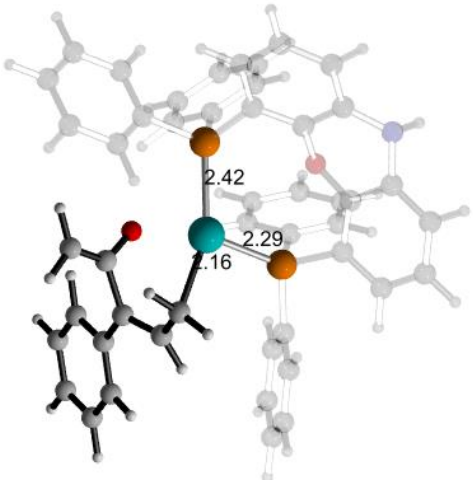
t5''



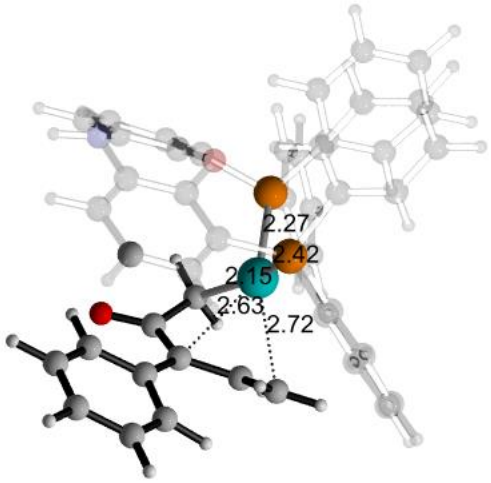
$TS_{t2\text{-}t3}$



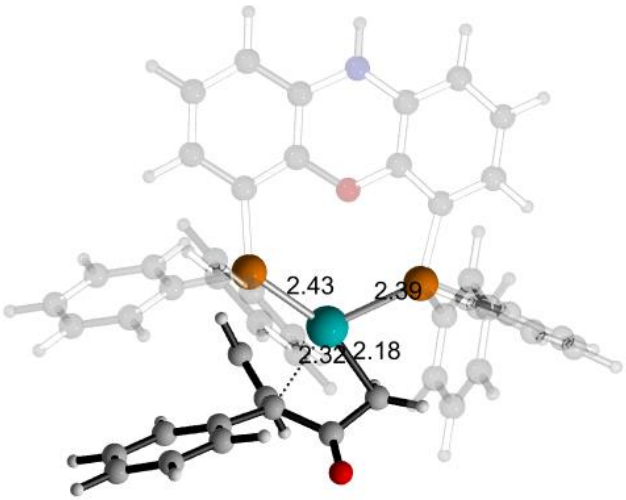
$TS_{t3\text{-}t4}$



$TS_{t4\text{-}t5}$



$TS_{t5\text{-}t5'}$

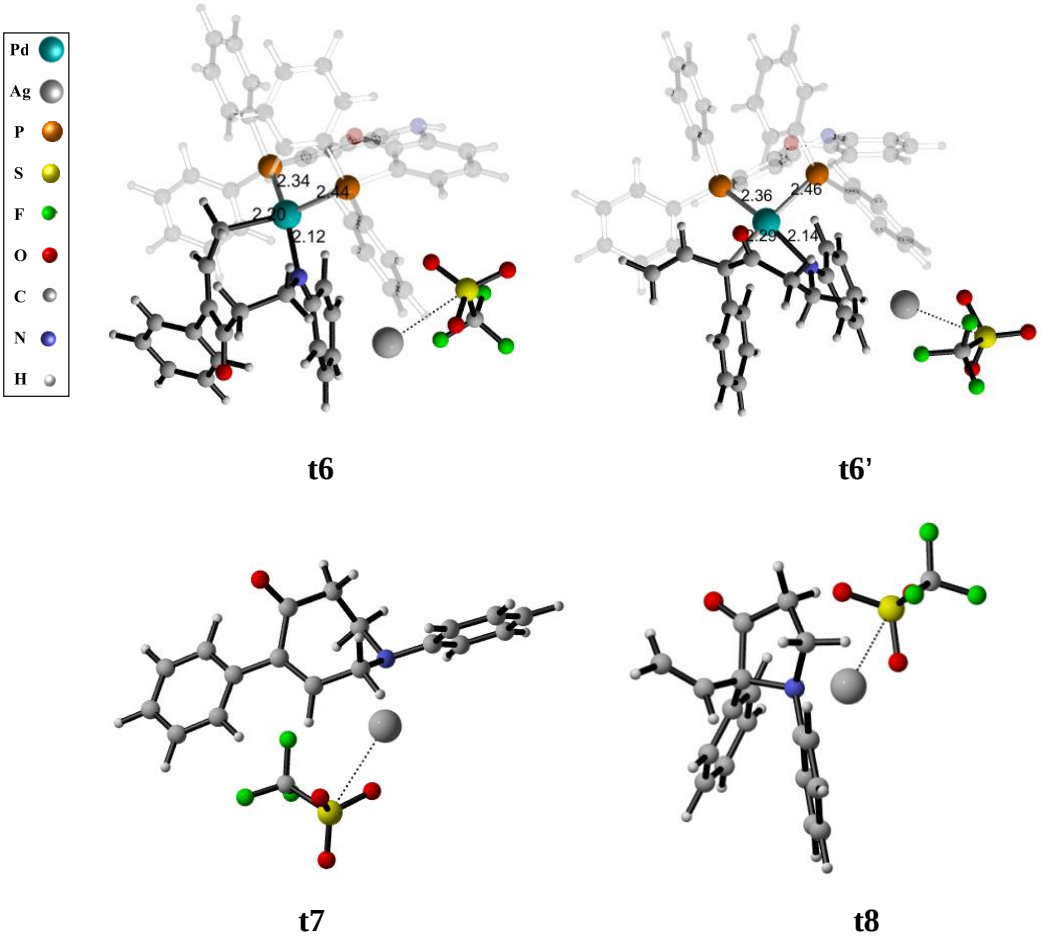


$TS_{t5'\text{-}5''}$

Figure S1. Optimized geometries with partial structural parameters (distances in Å) for the species involved in the process of ligand exchange, oxidative cleavage, CO_2 extrusion and isomerization. Unimportant hydrogen and carbon atoms are transparent for clarity.

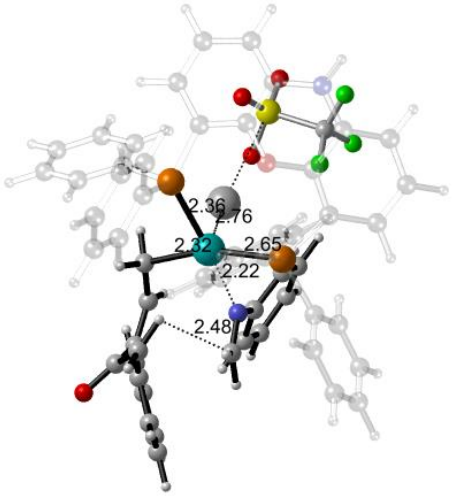
Table S2. The gas phase relative electronic energies (ΔEgas), gas phase relative free energies (ΔGgas) and solvation corrected relative electronic energies (ΔEsol) calculated for species involved in the process of amine insertion and reductive elimination.

Species	ΔGgas	ΔEgas	ΔEsol
t6	-12.6	-13.8	-15.9
t6'	-12.2	-12.0	-15.4
t7	-38.7	-47.4	-48.1
t8	-39.3	-46.6	-43.9
TS_{t5-t6}	15.9	18.1	7.5
$TS_{t5''-t6'}$	16.9	18.8	18.9
TS_{t6-t7}	1.2	3.2	1.5
$TS_{t6'-t8}$	6.9	8.9	7.6
TS_{t7-t8}	2.9	-2.2	1.7

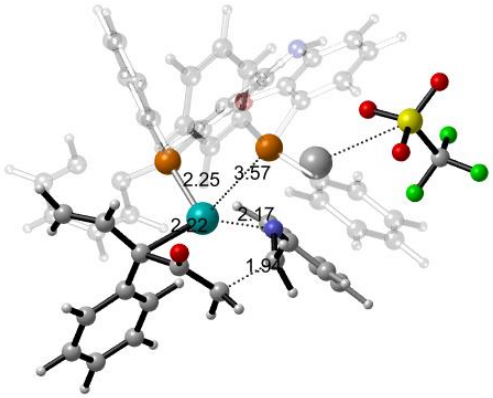


t6 **t6'**

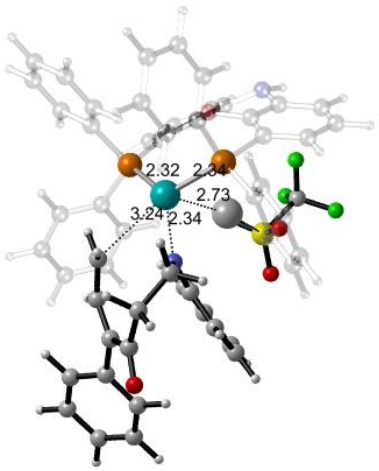
t7 **t8**



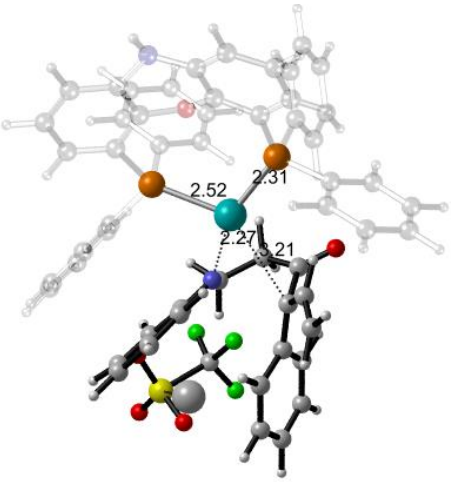
$TS_{t5\text{-}t6}$



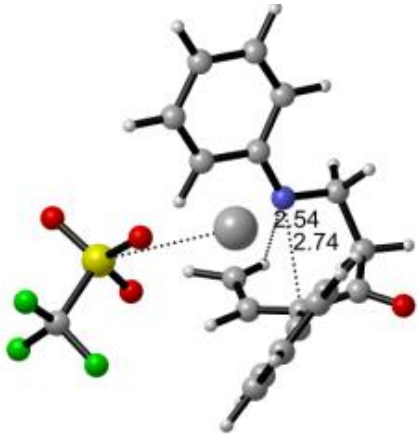
$TS_{t5''\text{-}t6'}$



$TS_{t6\text{-}t7}$



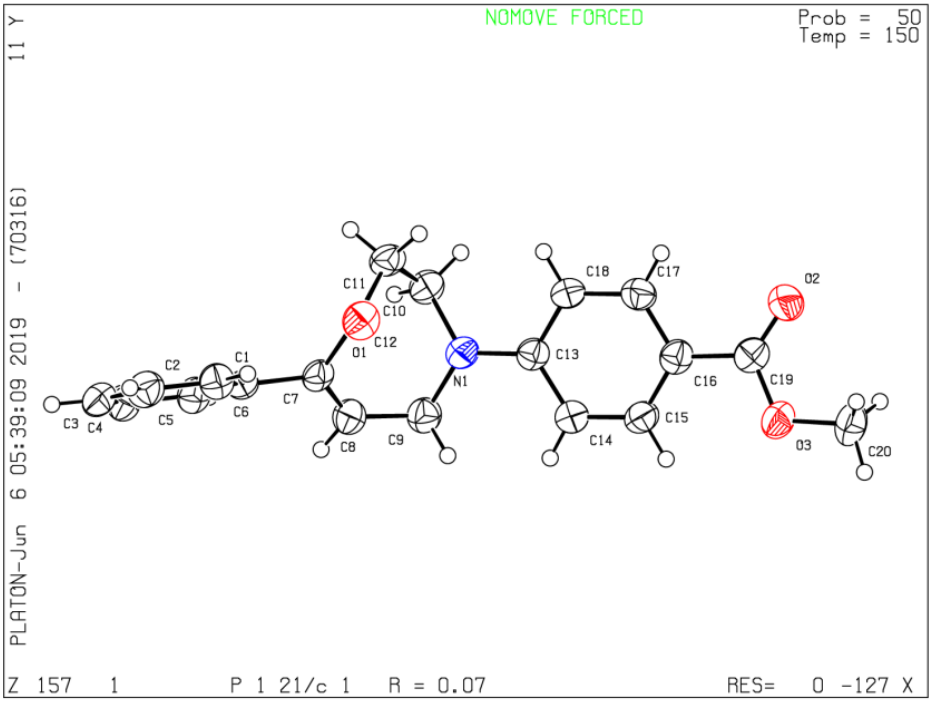
$TS_{t6'\text{-}t8}$



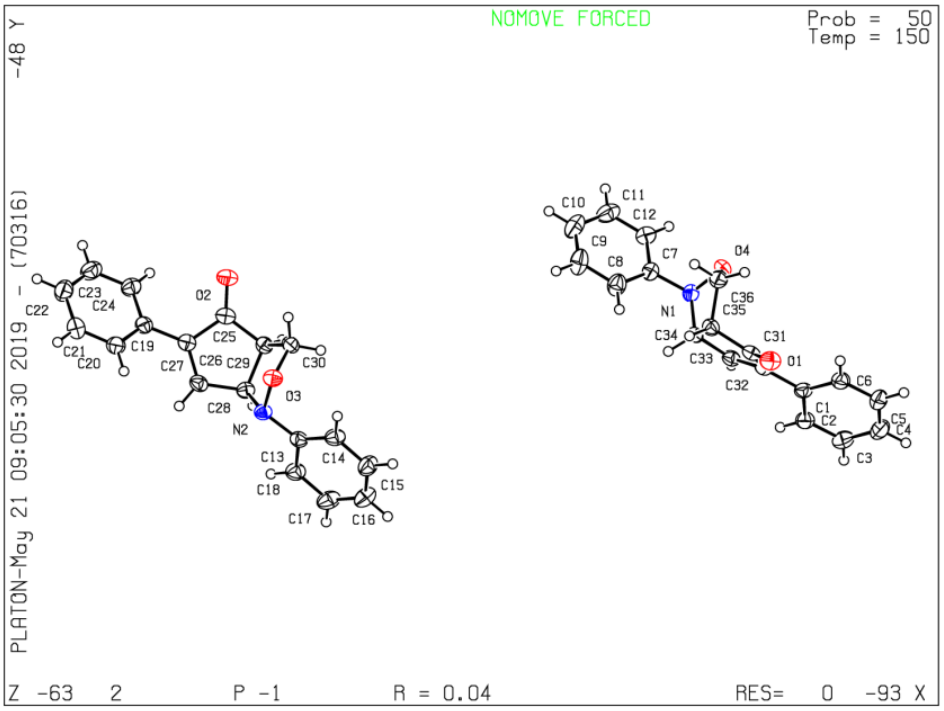
$TS_{t7\text{-}t8}$

Figure S2. Optimized geometries with partial structural parameters (distances in Å) for the species involved in the process of amine insertion and reductive elimination. Unimportant hydrogen and carbon atoms are transparent for clarity.

X-ray molecular structures of 3ao and 5d



X-ray molecular structure of **3ao**



X-ray molecular structure of **5d**

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