Supplemental Information

Ruthenium(II)-Catalyzed Deoxygenation of Ketones

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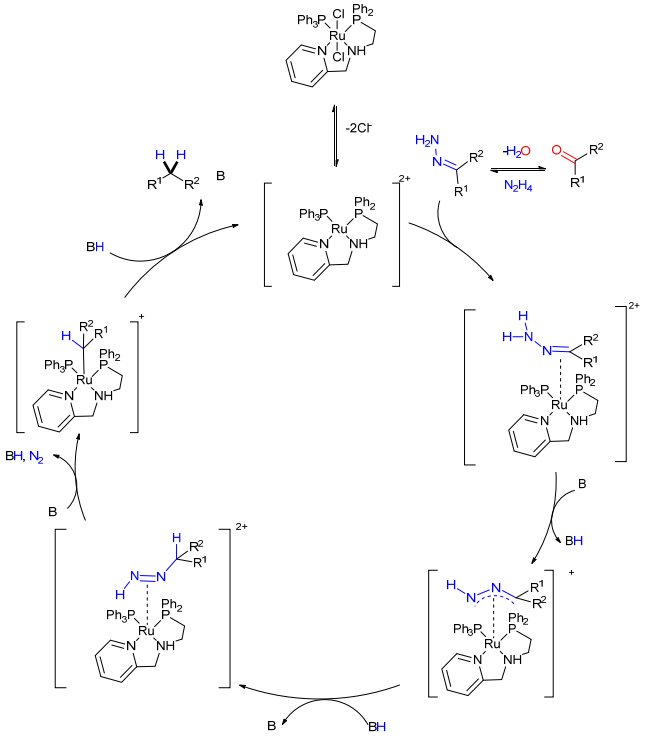
I. General Methods

All reagents and solvents were purchased from commercial sources (Sigma-Aldrich) and used without further purification unless otherwise stated. Catalysts Ru-2, Ru-3, and Ru-5 were synthesized by mixing $[(Ph_3P)_3RuCl_2]$ with one equiv of ligand. The procedure was referred to that of Ru-PNX synthesis[1] but optimized to 75°C temperature and overnight reaction time. All reactions were monitored by thin-layer chromatography (TLC). All reactions were carried out under a nitrogen atmosphere unless otherwise stated. Column chromatography was performed on silica gel (200-300 mesh) and visualized with ultraviolet light. Ethyl acetate and hexane were used as eluents.^{1}H, and ^{13}C NMR spectra were taken on Bruker AV300, Bruker AV400, Varian Mercury 400, and Varian/Agilent QANUC 500 with TMS as an internal standard and $CDCl_3$ as solvent unless otherwise stated. GC-MS analyses were performed with a Thermo TRACE 1300 ISQ LT spectrometer.

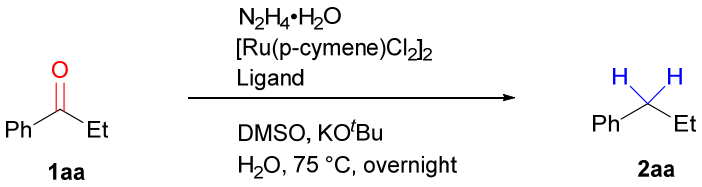
II. Mechanism

Scheme 1. Proposed mechanism for the Ru-catalyzed ketone deoxygenation



III. Optimization of Reaction Conditions

1) Table S1. Screening ligands[a]

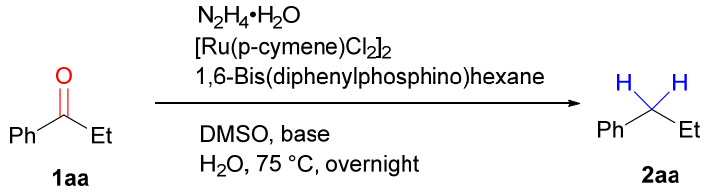


1aa **2aa**

entry	ligand	yield(%)[b]
1	PPh_3	6
2	1,2-Bis(dimethylphosphino)ethane	3
3	1,2-Bis(diphenylphosphino)ethane	10
4	1,3-Bis(diphenylphosphino)propane	12
5	1,4-Bis(diphenylphosphino)butane	10
6	1,6-Bis(diphenylphosphino)hexane	13
7	1,4-Bis(dicyclohexylphosphino)butane	14

[a] **1aa** (26.5 µL, 0.2 mmol, 1.0 equiv), $N_2H_4 \cdot H_2O$ (12 µL, 0.24 mmol, 1.2 equiv), H_2O (0.2 mL), $[Ru(p\text{-cymene})Cl_2]_2$ (1.6 mg, 0.003 mmol, 1.5 mol%), ligand (0.006 mmol, 3 mol%), KO^tBu (11.2 mg, 0.1 mmol, 0.5 equiv), additive: DMSO (2.6 µL, 0.04 mmol, 20 mol%), 75°C, overnight, under N_2. [b] Yields were determined by crude ^1H NMR using mesitylene as an internal standard.

2) Table S2. Screening bases[a]

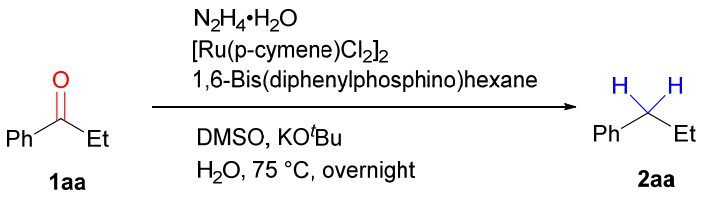


1aa **2aa**

entry	base	yield(%)[b]
1	KOH	4
2	DBU	5
3	K_3PO_4	4
4	TMP	4
5	1,8-Bis(dimethylamino)naphthalene	0
6	NaI	0
7	Cs_2CO_3	8
8	KO^tBu	19

[a] **1aa** (26.5 µL, 0.2 mmol, 1.0 equiv), $N_2H_4 \cdot H_2O$ (12 µL, 0.24 mmol, 1.2 equiv), H_2O (0.2 mL), $[Ru(p\text{-cymene})Cl_2]_2$ (1.6 mg, 0.003 mmol, 1.5 mol%), 1,6-bis(diphenylphosphino)hexane (2.7 mg, 0.006 mmol, 3 mol%), base (0.4 mmol, 2,0 equiv), additive: DMSO (2.6 µL, 0.04 mmol, 20 mol%), 75°C, overnight, under N_2. [b] Yields were determined by crude ^1H NMR using mesitylene as an internal standard.

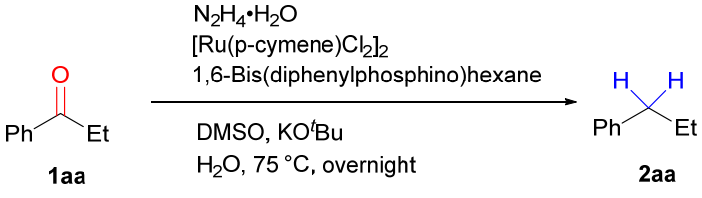
3) Table S3. Screening amount of bases[a]



entry	equivalent of KO^{t}Bu	yield(%)[b]
1	0.5	13
2	1.0	11
3	2.0	19
4	3.0	14

[a] **1aa** (26.5 μL, 0.2 mmol, 1.0 equiv), $N_2H_4 \cdot H_2O$ (12 μL, 0.24 mmol, 1.2 equiv), H_2O (0.2 mL), $[Ru(p\text{-cymene})Cl_2]_2$ (1.6 mg, 0.003 mmol, 1.5 mol%), 1,6-bis(diphenylphosphino)hexane (2.7 mg, 0.006 mmol, 3 mol%), KO^{t}Bu, additive: DMSO (2.6 μL, 0.04 mmol, 20 mol%), 75°C, overnight, under N_2. [b] Yields were determined by crude ^{1}H NMR using mesitylene as an internal standard.

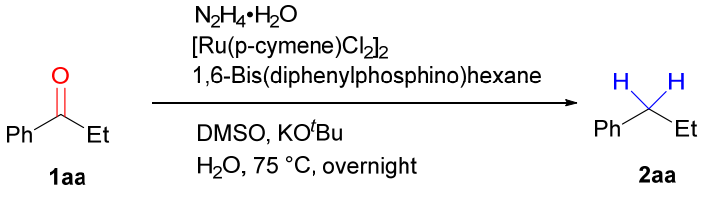
4) Table S4. Screening concentration[a]



entry	concentration (mol/L)	yield(%)[b]
1	1.0	19
2	2.0	17

[a] **1aa** (26.5 μL, 0.2 mmol, 1.0 equiv), $N_2H_4 \cdot H_2O$ (12 μL, 0.24 mmol, 1.2 equiv), H_2O, $[Ru(p\text{-cymene})Cl_2]_2$ (1.6 mg, 0.003 mmol, 1.5 mol%), 1,6-bis(diphenylphosphino)hexane (2.7 mg, 0.006 mmol, 3 mol%), KO^{t}Bu (44.8 mg, 0.4 mmol, 2.0 equiv), additive: DMSO (2.6 μL, 0.04 mmol, 20 mol%), 75°C, overnight, under N_2. [b] Yields were determined by crude ^{1}H NMR using mesitylene as an internal standard.

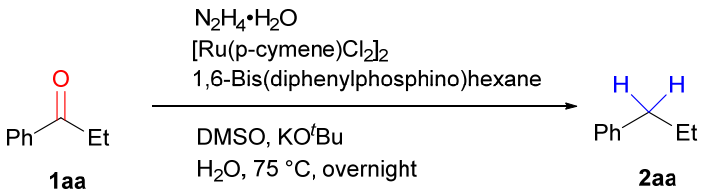
5) Table S5. Screening temperature[a]



entry	temperature (°C)	yield(%)[b]
1	75	19
2	100	7

[a] **1aa** (26.5 μL, 0.2 mmol, 1.0 equiv), $N_2H_4 \cdot H_2O$ (12 μL, 0.24 mmol, 1.2 equiv), H_2O (0.2 mL), $[Ru(p\text{-cymene})Cl_2]_2$ (1.6 mg, 0.003 mmol, 1.5 mol%), 1,6-bis(diphenylphosphino)hexane (2.7 mg, 0.006 mmol, 3 mol%), KO^{t}Bu (44.8 mg, 0.4 mmol, 2.0 equiv), additive: DMSO (2.6 μL, 0.04 mmol, 20 mol%), overnight, under N_2. [b] Yields were determined by crude ^{1}H NMR using mesitylene as an internal standard.

6) Table S6. Screening amount of additive[a]

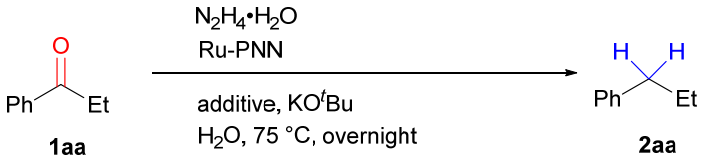


1aa **2aa**

entry	equivalent of DMSO	yield(%)[b]
1	0	3
2	0.2	19
3	0.3	17

[a] **1aa** (26.5 μL, 0.2 mmol, 1.0 equiv), $N_2H_4 \cdot H_2O$ (12 μL, 0.24 mmol, 1.2 equiv), H_2O (0.2 mL), $[Ru(p\text{-cymene})Cl_2]_2$ (1.6 mg, 0.003 mmol, 1.5 mol%), 1,6-bis(diphenylphosphino)hexane (2.7 mg, 0.006 mmol, 3 mol%), KO^tBu (44.8 mg, 0.4 mmol, 2.0 equiv), additive: DMSO, 75°C, overnight, under N_2. [b] Yields were determined by crude ^1H NMR using mesitylene as an internal standard.

7) Table S7. Screening additive[a]



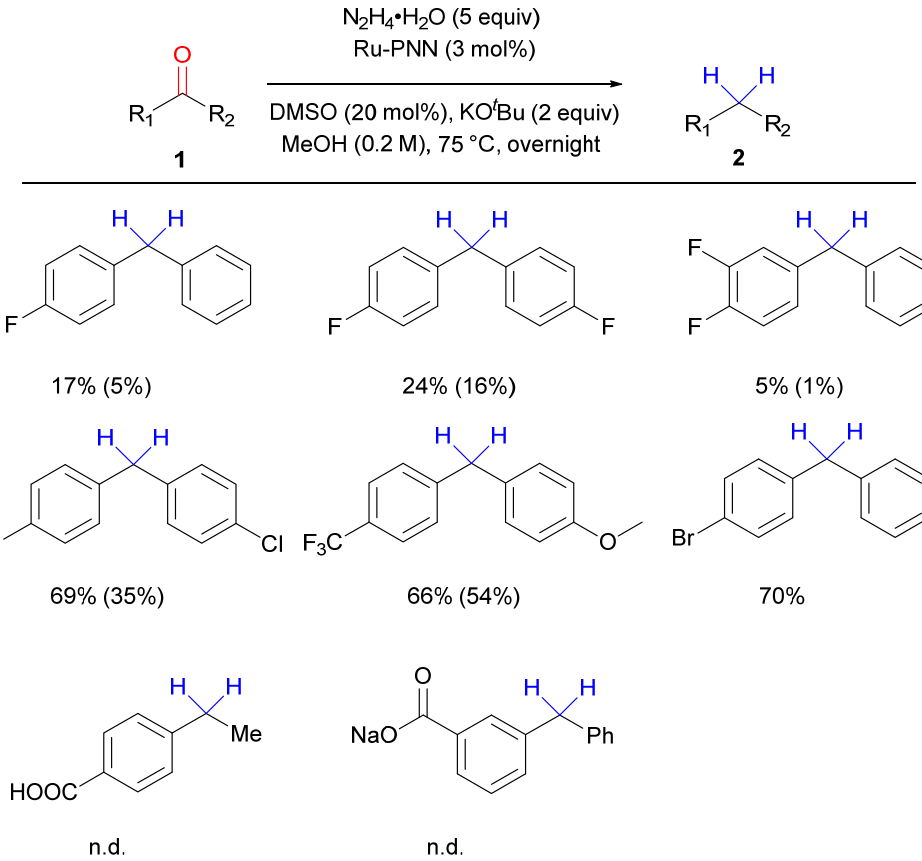
1aa **2aa**

entry	additive	yield(%)[b]
1	THF	14
2	acetone	11
3	ACN	17
4	γ–Valerolactone	14
5	HMPA	20
6	DMSO	27

[a] **1aa** (26.5 μL, 0.2 mmol, 1.0 equiv), $N_2H_4 \cdot H_2O$ (12 μL, 0.24 mmol, 1.2 equiv), H_2O (0.2 mL), Ru-PNN (4.5 mg, 0.006 mmol, 3.0 mol%), KO^tBu (44.8 mg, 0.4 mmol, 2.0 equiv), additive (0.04 mmol, 20 mol%), 75°C, overnight, under N_2. [b] Yields were determined by crude ^1H NMR using mesitylene as an internal standard.

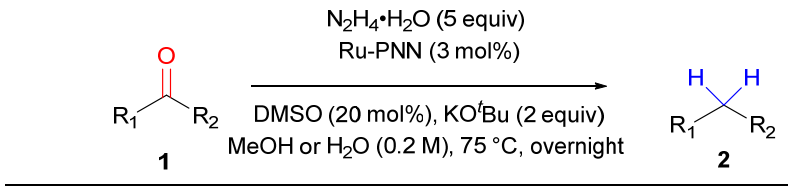
IV. Other Substrates

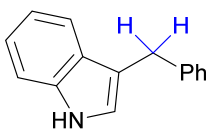
Scheme 2. Substrate scope in methanol conditions[a, b]



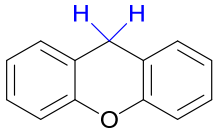
[a] **1** (0.2 mmol, 1.0 equiv), $N_2H_4 \cdot H_2O$ (50 µL, 1.0 mmol, 5.0 equiv), methanol (0.2 mL), Ru-PNN (4.5 mg, 0.006 mmol, 3 mol%), KO^tBu (44.8 mg, 0.4 mmol, 2.0 equiv), additive: DMSO (2.6 µL, 0.04 mmol, 20 mol%), 75°C, overnight, under N_2. [b] Yields were determined by crude ^1H NMR using mesitylene as an internal standard. Isolated yields were given in the parentheses.

Scheme 3. Substrates not tolerated[a]

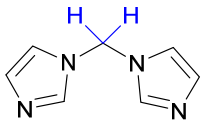




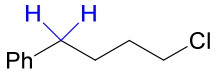
n.d.



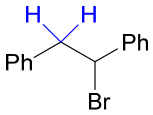
n.d.



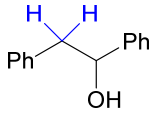
n.d.



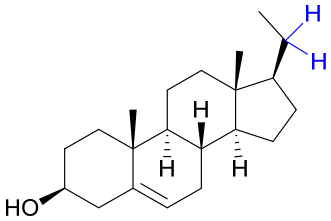
n.d.



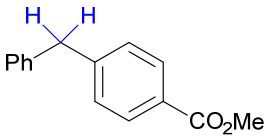
n.d.



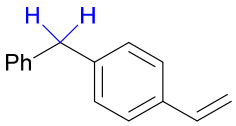
n.d.



n.d.



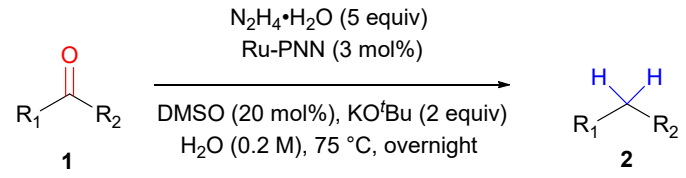
n.d.

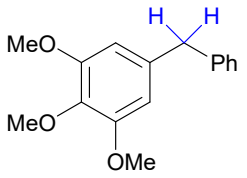


n.d.

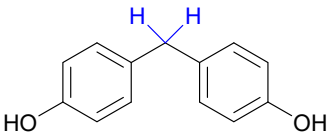
[a] **1** (0.2 mmol, 1.0 equiv), $N_2H_4 \cdot H_2O$ (50 µL, 1.0 mmol, 5.0 equiv), methanol (0.2 mL), Ru-PNN (4.5 mg, 0.006 mmol, 3 mol%), KO^tBu (44.8 mg, 0.4 mmol, 2.0 equiv), additive: DMSO (2.6 µL, 0.04 mmol, 20 mol%), 75°C, overnight, under N_2.

Scheme 4. Other substrates with poor yields[a]

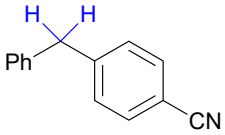




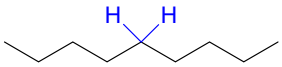
33%



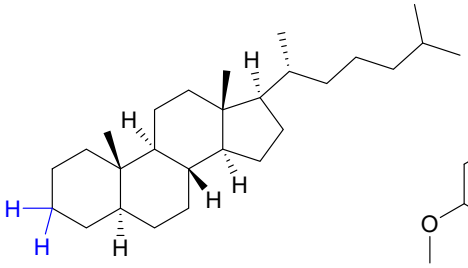
26%



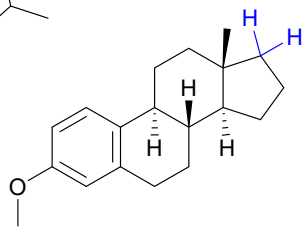
11% (in MeOH)



34% (in MeOH)



27% (in MeOH)



10% (in MeOH)

[a] **1** (0.2 mmol, 1.0 equiv), $N_2H_4 \cdot H_2O$ (50 µL, 1.0 mmol, 5.0 equiv), methanol or water (0.2 mL), Ru-PNN (4.5 mg, 0.006 mmol, 3 mol%), KO^{t}Bu (44.8 mg, 0.4 mmol, 2.0 equiv), additive: DMSO (2.6 µL, 0.04 mmol, 20 mol%), 75°C, overnight, under N_2. [b] Yields were determined by crude ^{1}H NMR using mesitylene as an internal standard. [c] Yields were determined by crude GC using mesitylene as an internal standard. Isolated yields were given in the parentheses.

V. General Procedure for the Deoxygenation of Ketones

General procedure with liquid ketones

A 10 mL V-shape microwave vial with a magnetic stir-bar was transferred to glovebox and charged with Ru-PNN (4.5 mg, 0.006 mmol, 3 mol%) and KO^{t}Bu (44.8 mg, 0.4 mmol, 2.0 equiv). The tube was capped with a rubber septum stopper and taken out from the glovebox. To the microwave vial, hydrazine monohydrate (50 µL, 1.0 mmol, 5.0 equiv), ketone (0.2 mmol, 1.0 equiv), and DMSO (2.6 µL, 0.04 mmol, 20 mol%) were charged via Hamilton microliter syringes. Solvent (0.2 mL) was added through a 1 mL plastic syringe. The tube was placed in a preheated oil bath at 75 °C and the mixture was stirred under an argon atmosphere overnight. The reaction mixture was cooled to room temperature and charged with mesitylene (9.2 µL, 0.067 mmol, 0.33 equiv). The solution was diluted with

diethyl ether filtered through anhydrous $MgSO_4$ followed by silica gel, concentrated, and then purified by column chromatography on silica gel eluting with pentane: Et_2O (100:1-10:1). The solvent was frozen in an ice-water bath and gently evacuated by vacuum to afford the products.

General procedure with solid ketones

A 10 mL V-shape microwave vial with a magnetic stir-bar was transferred to glovebox and charged with Ru-PNN (4.5 mg, 0.006 mmol, 3 mol%), KO^{t}Bu (44.8 mg, 0.4 mmol, 2.0 equiv) and ketone (0.2 mmol, 1.0 equiv). The tube was capped with a rubber septum stopper and taken out from the glovebox. To the microwave vial, hydrazine monohydrate (50 µL, 1.0 mmol, 5.0 equiv), and DMSO (2.6 µL, 0.04 mmol, 20 mol%) were charged via Hamilton microliter syringes. Solvent (0.2 mL) was added through a 1 mL plastic syringe. The tube was placed in a preheated oil bath at 75 ^oC and the mixture was stirred under an argon atmosphere overnight. The reaction mixture was cooled to room temperature and charged with mesitylene (9.2 µL, 0.067 mmol, 0.33 equiv). The solution was diluted with diethyl ether filtered through anhydrous $MgSO_4$ followed by silica gel, concentrated, and then purified by column chromatography on silica gel eluting with pentane: Et_2O (100:1-10:1). The solvent was frozen in an ice-water bath and gently evacuated by vacuum to afford the products.

General procedure with hydroxyl, amino and carboxylic acid substituted ketones

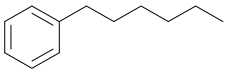
A 10 mL V-shape microwave vial with a magnetic stir-bar was transferred to glovebox and charged with Ru-PNN (4.5 mg, 0.006 mmol, 3 mol%), KO^{t}Bu (67.2 mg, 0.6 mmol, 3.0 equiv) and ketone (0.2 mmol, 1.0 equiv). The tube was capped with a rubber septum stopper and taken out from the glovebox. To the microwave vial, hydrazine monohydrate (50 µL, 1.0 mmol, 5.0 equiv), and DMSO (2.6 µL, 0.04 mmol, 20 mol%) were charged via Hamilton microliter syringes. Water (0.2 mL) was added through a 1 mL plastic syringe. The tube was placed in a preheated oil bath at 75 ^oC and the mixture was stirred under an argon atmosphere overnight. The reaction mixture was cooled to room temperature and charged with mesitylene (9.2 µL, 0.067 mmol, 0.33 equiv). The solution was diluted with diethyl ether, filtered through anhydrous $MgSO_4$ followed by silica gel, concentrated, and then purified by column chromatography on silica gel eluting with pentane: Et_2O (4:1-1:1). The solvent was frozen in an ice-water bath and gently evacuated by vacuum to afford the products.

General procedure with sodium carboxylate substituted ketones

A 10 mL V-shape microwave vial with a magnetic stir-bar was transferred to glovebox and charged with Ru-PNN (4.5 mg, 0.006 mmol, 3 mol%), KO^{t}Bu (67.2 mg, 0.6 mmol, 3.0 equiv) and ketone (0.2 mmol, 1.0 equiv). The tube was capped with a rubber septum stopper and taken out from the glovebox. To the microwave vial, hydrazine monohydrate (50 µL, 1.0 mmol, 5.0 equiv), and DMSO (2.6 µL, 0.04 mmol, 20 mol%) were charged via Hamilton microliter syringes. Water (0.2 mL) was added through a 1 mL plastic syringe. The tube was placed in a preheated oil bath at 75 ^oC and the mixture was stirred under an argon atmosphere overnight. The reaction mixture was cooled to room temperature and charged

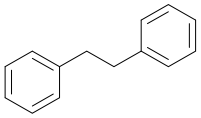
with mesitylene (9.2 µL, 0.067 mmol, 0.33 equiv). Concentrate hydrochloric acid was added dropwise until the solution became acidic. Centrifuge the slurry to isolate the products, and extract the aqueous solution with diethyl ether. Dry the organic layer, pass through a layer of silica and evacuate the solvent to afford the remaining products.

VI. Characterization of Products



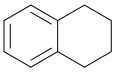
Hexylbenzene[2] (2ab)

Clear colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 – 7.24 (m, 2H), 7.18 (d, *J* = 7.5 Hz, 3H), 2.64 – 2.57 (m, 2H), 1.66 – 1.58 (m, 2H), 1.39 – 1.25 (m, 6H), 0.92 – 0.85 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.0, 128.4, 128.2, 125.5, 36.0, 31.7, 31.5, 29.0, 22.6, 14.1.



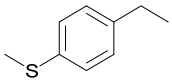
1,2-diphenylethane[3] (2b)

White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (ddd, *J* = 9.1, 6.3, 0.9 Hz, 4H), 7.25 – 7.13 (m, 6H), 2.93 (s, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.8, 128.4, 128.3, 125.9, 37.9.



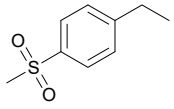
1,2,3,4-tetrahydronaphthalene[4] (2c)

Clear colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.09 (h, *J* = 4.6, 4.2 Hz, 4H), 2.80 (h, *J* = 3.1 Hz, 4H), 1.87 – 1.78 (m, *J* = 4.3 Hz, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.1, 129.1, 125.4, 29.4, 23.2.



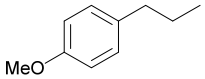
(4-ethylphenyl)(methyl)sulfane (2db)

Clear colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.18 (m, 2H), 7.16 – 7.10 (m, 2H), 2.61 (q, *J* = 7.6 Hz, 2H), 2.47 (s, 3H), 1.22 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.5, 134.9, 128.4, 127.3, 28.3, 16.5, 15.6. IR wavenumber (cm^{-1}) 2963.7, 2921.6, 2872.2, 1493.6, 1121.9, 816.8. HRMS calc. for $C_9H_{12}OSNa$ [M+Na+O]+: 191.0501; found, 191.0493.



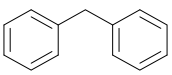
1-ethyl-4-(methylsulfonyl)benzene

Clear colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.81 (m, 2H), 7.42 – 7.35 (m, 2H), 3.04 (s, 3H), 2.75 (q, *J* = 7.6 Hz, 2H), 1.27 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.8, 137.9, 128.8, 127.5, 44.6, 28.9, 15.1. IR wavenumber (cm^{-1}) 2968.5, 2930.1, 2875.3, 1300.0, 1144.5, 547.3, 517.8. HRMS calc. for $C_9H_{12}O_2SNa$ [M+Na]+: 207.0450; found, 207.0451.



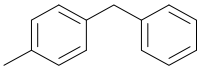
1-methoxy-4-propylbenzene[5]

Clear colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 – 7.05 (m, 2H), 6.87 – 6.78 (m, 2H), 3.79 (s, 3H), 2.53 (dd, *J* = 8.5, 6.7 Hz, 2H), 1.68 – 1.54 (m, 2H), 0.93 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.61, 134.81, 129.29, 113.61, 55.24, 37.13, 24.78, 13.77.

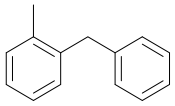


Diphenylmethane[6] (2fa)

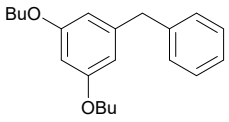
Clear colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.25 (m, 4H), 7.24 – 7.13 (m, 6H), 3.99 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.1, 128.9, 128.4, 126.1, 41.9.

1-benzyl-4-methylbenzene[7] (2fb) 

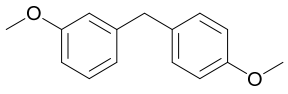
Brown liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.25 (m, 2H), 7.20 (ddt, *J* = 7.4, 3.1, 1.9 Hz, 3H), 7.15 – 7.06 (m, 4H), 3.96 (s, 2H), 2.33 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.4, 138.1, 135.5, 129.1, 128.9, 128.8, 128.4, 126.0, 41.5, 21.0.

1-benzyl-2-methylbenzene[8] (2fc) 

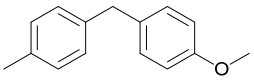
Clear colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.24 (m, 2H), 7.28 – 7.07 (m, 7H), 4.00 (s, 2H), 2.25 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.4, 138.9, 136.6, 130.3, 129.9, 128.7, 128.4, 126.4, 126.0, 125.9, 39.4, 19.7.

1-benzyl-3,5-dibutoxybenzene (2fd) 

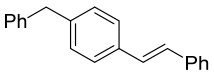
Clear colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 – 7.13 (m, 5H), 6.97 (d, *J* = 8.2 Hz, 1H), 6.45 (d, *J* = 2.4 Hz, 1H), 6.40 (dd, *J* = 8.3, 2.4 Hz, 1H), 3.97 – 3.89 (m, 6H), 1.75 (dddd, *J* = 15.3, 12.2, 7.6, 6.3 Hz, 4H), 1.55 – 1.38 (m, 4H), 0.97 (dt, *J* = 18.4, 7.4 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.9, 157.7, 141.7, 130.4, 128.8, 128.1, 125.5, 122.1, 104.4, 99.7, 67.7, 67.6, 35.5, 31.4, 31.3, 19.3, 13.9, 13.8. IR wavenumber (cm^{-1}) 3060.7, 3026.8, 2957.2, 2932.0, 2870.4, 1300.0, 1173.4. HRMS calc. for $C_{21}H_{28}O_2Na$ [M+Na]+: 335.1982; found, 335.1978.

1-methoxy-3-(4-methoxybenzyl)benzene (2ga) 

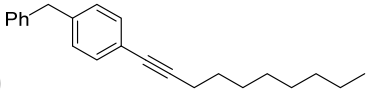
Clear yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (td, *J* = 7.7, 0.8 Hz, 1H), 7.15 – 7.07 (m, 2H), 6.87 – 6.80 (m, 2H), 6.80 – 6.74 (m, 1H), 6.77 – 6.69 (m, 2H), 3.90 (s, 2H), 3.78 (s, 3H), 3.77 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.7, 158.0, 143.2, 133.0, 129.8, 129.4, 121.2, 114.6, 113.9, 111.2, 55.3, 55.1, 41.0. IR wavenumber (cm^{-1}) 3029.4, 2998.3, 2954.8, 2933.2, 2834.1.4, 1280.3. HRMS calc. for $C_{15}H_{16}NaO_2$ [M+Na]+: 251.1043; found, 251.1034.

1-methoxy-4-(4-methylbenzyl)benzene[9] (2gb) 

Clear yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 – 7.03 (m, 6H), 6.90 – 6.79 (m, 2H), 3.89 (s, 2H), 3.78 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.9, 138.5, 135.4, 133.5, 129.8, 129.1, 128.7, 113.8, 55.2, 40.6, 21.0.

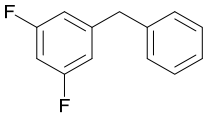
(E)-1-benzyl-4-styrylbenzene (2h) 

White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.47 (m, 2H), 7.47 – 7.41 (m, 2H), 7.35 (dd, *J* = 8.4, 6.9 Hz, 2H), 7.35 – 7.26 (m, 2H), 7.29 – 7.19 (m, 2H), 7.20 (td, *J* = 6.1, 1.8 Hz, 4H), 7.08 (d, *J* = 1.6 Hz, 2H), 4.00 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.0, 140.7, 137.4, 135.3, 129.3, 128.9, 128.6, 128.5, 128.5, 128.1, 127.5, 126.6, 126.4, 126.1, 41.7. IR wavenumber (cm^{-1}) 3079.0, 3053.5, 3022.3, 2921.0, 2852.5, 1491.5, 1448.5, 1416.8. HRMS calc. for $C_{21}H_{19}$ [M+H]+: 271.14813; found, 271.14840.

1-benzyl-4-(dec-1-yn-1-yl)benzene (2i) 

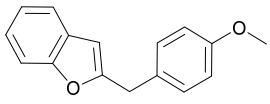
Clear yellow liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 – 7.26 (m, 4H), 7.25 – 7.13 (m, 3H), 7.13 – 7.07 (m, 2H), 3.96 (s, 2H), 2.38 (t, *J* = 7.1 Hz, 2H), 1.43 (p, *J* = 7.0 Hz, 2H), 1.37 – 1.21 (m, 10H), 0.97 – 0.77 (m, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 140.7, 140.5, 131.6, 128.9, 128.8, 128.5, 126.1, 121.8, 90.1, 80.4, 41.7, 31.8, 29.2, 29.1, 28.9, 28.8, 22.7, 19.4, 14.1. IR wavenumber (cm^{-1}) 3027.0, 2953.9, 2924.0, 2854.0, 1508.1, 1494.4, 696.6. HRMS calc. for $C_{23}H_{29}$ [M+H]+: 305.22638; found, 305.22638.



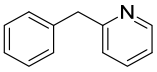
1-benzyl-3,5-difluorobenzene (2j)

Clear colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.13 (m, 5H), 6.71 (t, *J* = 1.9 Hz, 1H), 6.69 (t, *J* = 2.0 Hz, 1H), 6.64 (tt, *J* = 9.0, 2.4 Hz, 1H), 3.95 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.0 (dd, *J* = 12.8, 248.0 Hz), 145.0 (t, *J* = 9.0 Hz), 139.4, 128.9, 128.7, 126.6, 111.6 (dd, *J* = 6.3, 12.6 Hz), 101.6 (t, *J* = 25.5 Hz), 41.6 (t, *J* = 2.6 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -110.4 – -110.5 (m, *J*=1.9 Hz, 7.5 Hz). IR wavenumber (cm^{-1}) 3087.8, 3063.5, 3029.2, 2919.3, 1737.5, 1623.2, 1115.5, 971.9, 700.1. HRMS calc. for $C_{13}H_9F_2$ [M-H]+: 203.06778; found, 203.06705.



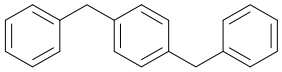
2-(4-methoxybenzyl)benzofuran (2k)

Clear colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 – 7.44 (m, 1H), 7.41 (dq, *J* = 8.1, 0.9 Hz, 1H), 7.28 – 7.14 (m, 4H), 6.91 – 6.84 (m, 2H), 6.35 (q, *J* = 1.0 Hz, 1H), 4.06 (d, *J* = 1.0 Hz, 2H), 3.81 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.5, 158.3, 154.9, 129.9, 129.2, 128.8, 123.3, 122.5, 120.4, 114.0, 110.9, 103.1, 55.3, 34.1. IR wavenumber (cm^{-1}) 3033.4, 2997.9, 2954.4, 2933.2, 2905.5, 2834.4, 1510.2, 1300.5. HRMS calc. for $C_{16}H_{14}O_2Na$ [M+Na]+: 261.08860; found, 261.08815.



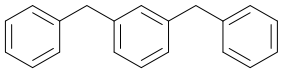
2-benzylpyridine[10] (2l)

Clear colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.55 (dt, *J* = 4.6, 1.7 Hz, 1H), 7.58 (td, *J* = 7.7, 1.9 Hz, 1H), 7.34 – 7.25 (m, 4H), 7.25 – 7.18 (m, 1H), 7.11 (dd, *J* = 7.5, 4.6 Hz, 2H), 4.17 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.0, 149.3, 139.5, 136.6, 129.1, 128.6, 126.4, 123.1, 121.2, 44.7.



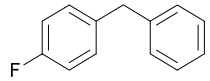
1,4-dibenzylbenzene[12]

White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.24 (m, 4H), 7.19 (tt, *J* = 6.4, 1.2 Hz, 6H), 7.10 (s, 4H), 3.95 (s, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.2, 138.8, 129.0, 128.9, 128.4, 126.0, 41.5.



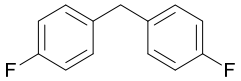
1,3-dibenzylbenzene

White cloudy oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (dd, *J* = 8.0, 6.6 Hz, 4H), 7.24 – 7.15 (m, 7H), 7.11 – 6.99 (m, 3H), 3.95 (s, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.2, 141.1, 129.6, 128.9, 128.6, 128.4, 126.7, 126.0, 41.9. IR wavenumber (cm^{-1}) 3059.4, 3023.8, 2960.7, 2912.2, 2899.5, 2833.3, 722.5, 696.0. HRMS calc. for $C_{20}H_{17}$ [M-H]+: 257.13248; found, 257.13182.



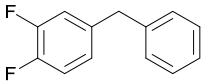
1-benzyl-4-fluorobenzene[13] (2m)

Clear colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.27 (m, 2H), 7.23 – 7.20 (m, 1H), 7.20 – 7.12 (m, 4H), 7.01 – 6.91 (m, 2H), 3.95 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.4 (d, *J* = 263.9 Hz) 140.9 (d, *J* =1.0 Hz), 136.7 (d, *J* = 3.2 Hz) 130.3 (d, *J* = 7.8 Hz) 128.8, 128.5, 126.2, 115.27 (d, *J* = 21.2 Hz), 41.1. ^{19}F NMR (471 MHz, $CDCl_3$) δ -117.4 (t, *J* = 6.8 Hz).

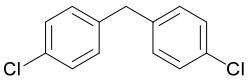


bis(4-fluorophenyl)methane[14] (2n)

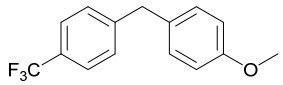
Clear colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.15 – 7.08 (m, 4H), 7.02 – 6.93 (m, 4H), 3.92 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.5 (d, *J* = 244 Hz), 136.6 (d, *J* = 3.8 Hz), 130.2 (d, *J* = 7.6 Hz), 115.3 (d, *J* = 21.4 Hz), 40.2. ^{19}F NMR (471 MHz, $CDCl_3$) δ -110.5 (d, *J* = 8.4 Hz), -117.2 (dt, *J* = 8.5, 5.1 Hz).

4-benzyl-1,2-difluorobenzene (2o) 

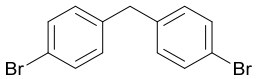
Clear colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.27 (m, 2H), 7.26 – 7.20 (m, 1H), 7.19 – 7.12 (m, 2H), 7.06 (dt, *J* = 10.3, 8.3 Hz, 1H), 6.96 (ddd, *J* = 11.3, 7.6, 2.2 Hz, 1H), 6.92 – 6.86 (m, 1H), 3.93 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.2 (dd, *J* = 75.6, 248.0 Hz), 149.5 (dd, *J* = 75.6, 248.0 Hz), 140.1, 138.1, 128.8, 128.7, 126.5, 125.1 – 124.4 (m), 117.6 (d, *J* = 16.6 Hz), 117.0 (d, *J* = 17.2 Hz), 41.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ -138.2 (dddd, *J* = 21.2, 11.4, 8.2, 1.4 Hz), -141.9 – -142.1 (m, *J* = 3.8, 11.3 Hz). IR wavenumber (cm^{-1}) 3066.3, 3029.7, 2911.0, 2837.1, 751.3, 715.9. HRMS calc. for $C_{13}H_9F_2$ [M-H]+: 203.06778; found, 203.06690.

bis(4-chlorophenyl)methane[15] (2p) 

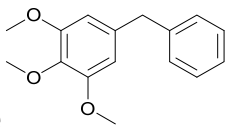
Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 – 7.23 (m, 4H), 7.15 – 7.07 (m, 4H), 3.92 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.0, 132.1, 130.2, 128.8, 40.5.

1-methoxy-4-(4-(trifluoromethyl)benzyl)benzene (2q) 

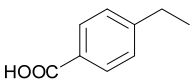
Clear colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.1 Hz, 2H), 7.36 – 7.23 (m, 2H), 7.14 – 7.04 (m, 2H), 6.92 – 6.80 (m, 2H), 3.98 (s, 2H), 3.79 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.2, 145.7, 132.1, 129.9, 129.0, 128.5, 125.4 (q, *J* = 4.2, 3.6 Hz), 114.1, 55.3, 40.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.4 (s). IR wavenumber (cm^{-1}) 3006.1, 2934.3, 2837.5, 1510.8, 1323.0, 1113.4, 1065.3. HRMS calc. for $C_{15}H_{12}OF_3$ [M-H]+: 265.08457; found, 265.08389.

bis(4-bromophenyl)methane (2r) 

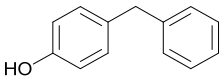
Pale yellow oil, solidify at room temperature.^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 – 7.34 (m, 4H), 7.09 – 6.94 (m, 4H), 3.88 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.4, 131.6, 130.6, 120.2, 40.6. IR wavenumber (cm^{-1}) 2937.2, 2919.1, 2851.0, 1483.6, 1066.5, 1009.3, 826.7, 805.2. HRMS calc. for $C_{13}H_9Br_2$ [M-H]+: 322.90655; found, 322.90871.

5-benzyl-1,2,3-trimethoxybenzene 

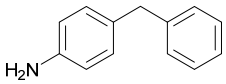
Clear colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.15 (m, 5H), 6.40 (s, 2H), 3.93 (s, 2H), 3.82 (s, 3H), 3.81 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 206.9, 153.2, 128.8, 128.5, 126.2, 105.9, 60.9, 56.0, 42.2, 30.9. IR wavenumber (cm^{-1}) 2925.4, 1127.3, 1008.4. HRMS calc. for $C_{16}H_{19}O_3$ [M+H]+: 259.13287; found, 259.13261.

4-propylbenzoic acid[16] (2s) 

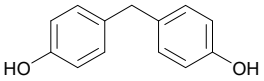
White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 – 8.00 (m, 2H), 7.33 – 7.24 (m, 2H), 2.73 (q, *J* = 7.6 Hz, 2H), 1.27 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.1, 150.8, 130.4, 128.0, 126.6, 29.0, 15.2.

4-benzylphenol[17] (2ta) 

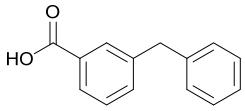
White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.24 (m, 2H), 7.26 – 7.14 (m, 3H), 7.10 – 7.02 (m, 2H), 6.80 – 6.71 (m, 2H), 4.59 (s, 1H), 3.92 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.8, 141.5, 133.4, 130.1, 128.8, 128.4, 126.0, 115.3, 41.0.

4-benzylaniline[18] (2tb) 

Clear colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.23 (m, 2H), 7.18 (td, J = 5.3, 2.8 Hz, 3H), 7.02 – 6.94 (m, 2H), 6.67 – 6.59 (m, 2H), 3.88 (s, 2H), 3.57 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.5, 141.9, 131.2, 129.8, 128.8, 128.3, 125.8, 115.3, 41.1.

4,4'-methylenediphenol[19] 

White solid. ^{1}H NMR (400 MHz, CD_3OD) δ 7.08 – 6.82 (m, 4H), 6.82 – 6.41 (m, 4H), 3.75 (s, 2H). ^{13}C NMR (126 MHz, CD_3OD) δ 156.5, 134.2, 130.7, 116.1, 41.1, 30.7.

3-benzylbenzoic acid (2u) 

White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (dt, J = 9.1, 1.7 Hz, 2H), 7.46 – 7.34 (m, 2H), 7.34 – 7.26 (m, 2H), 7.26 – 7.15 (m, 3H), 4.04 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.4, 141.6, 140.3, 134.3, 130.6, 129.6, 128.9, 128.7, 128.6, 128.1, 126.3, 41.7. IR wavenumber (cm^{-1}) 3021.6, 299.9, 2916.2, 2849.6, 2671.3, 2561.5, 1683.0. HRMS calc. for $C_{14}H_{12}NaO_2$ [M+Na]+: 235.0730; found, 235.0725.

VII. References

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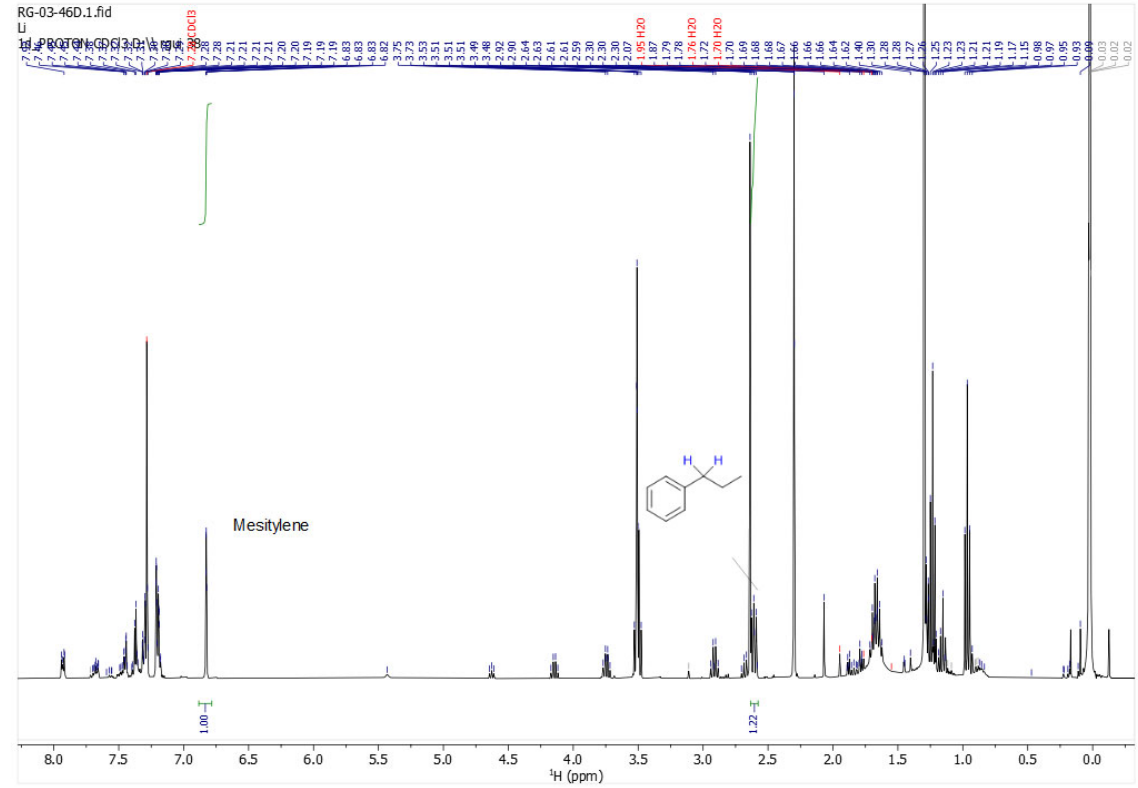
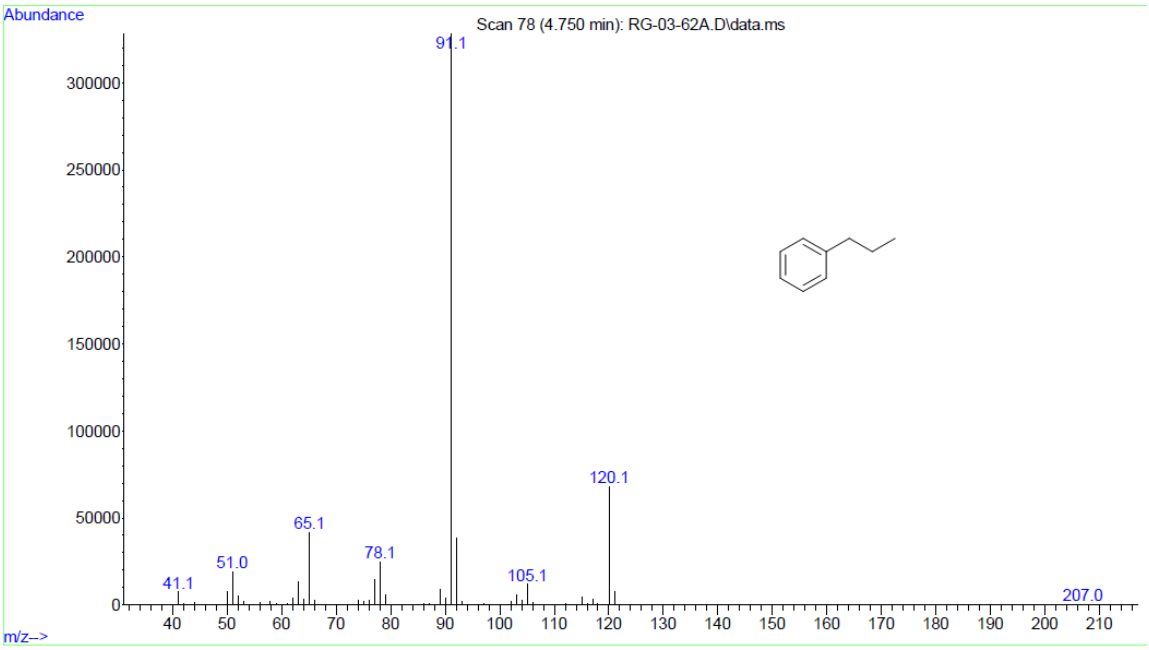
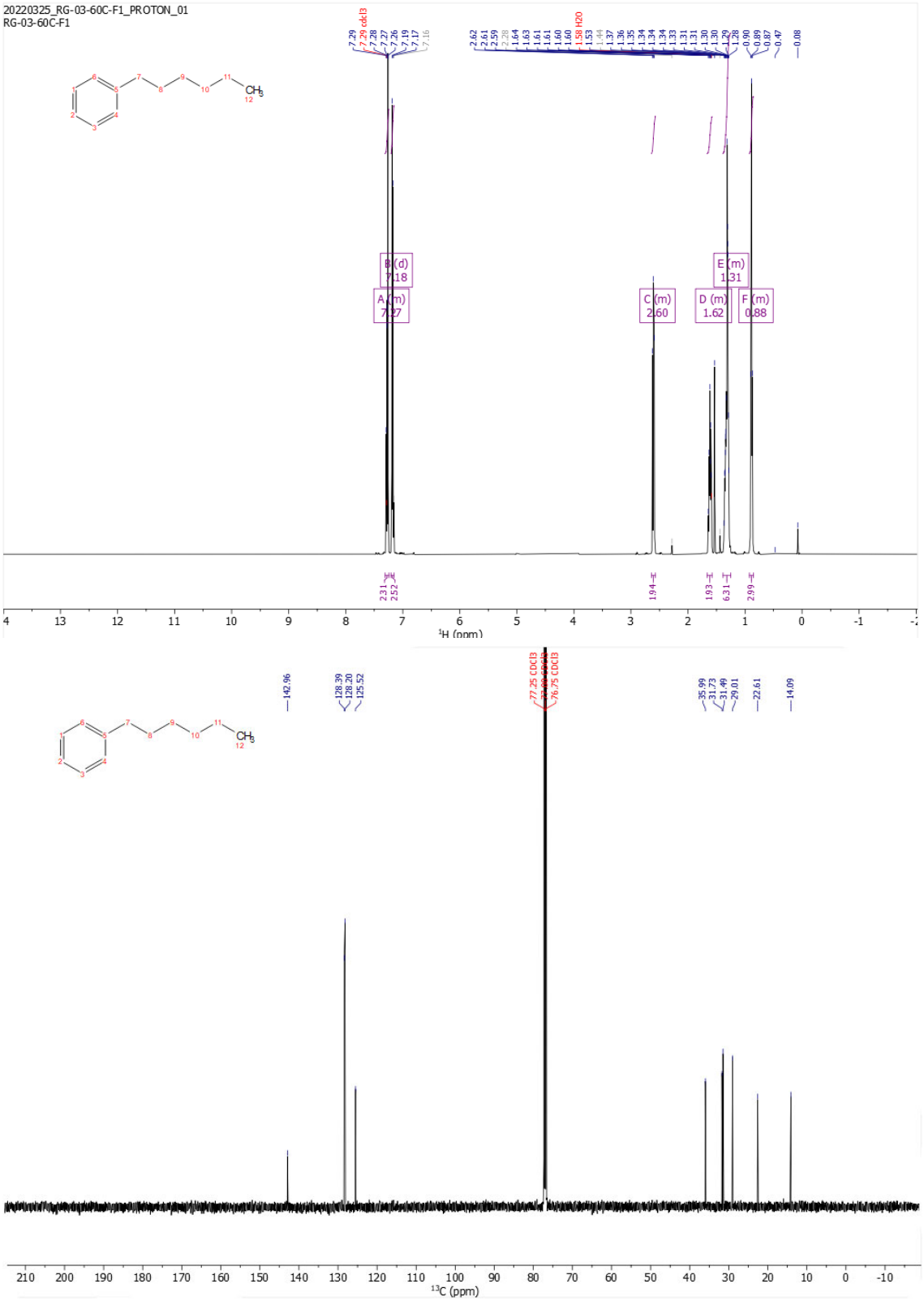
VIII. Copies of 1H NMR and 13C NMR



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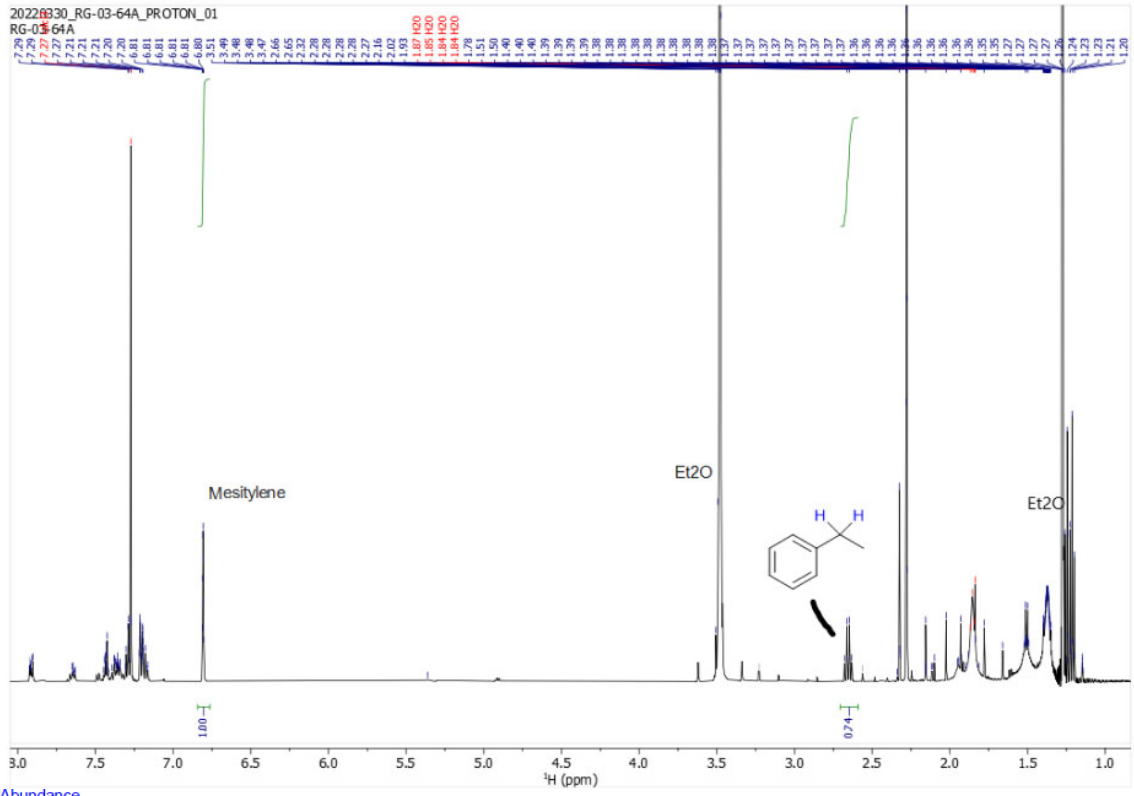
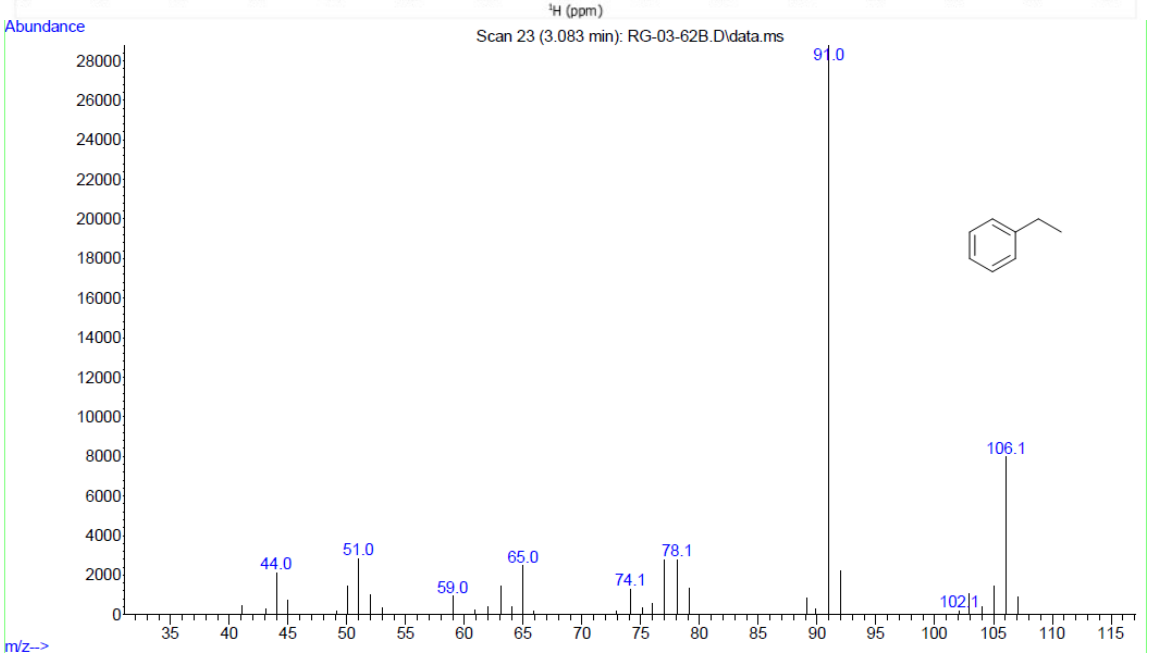
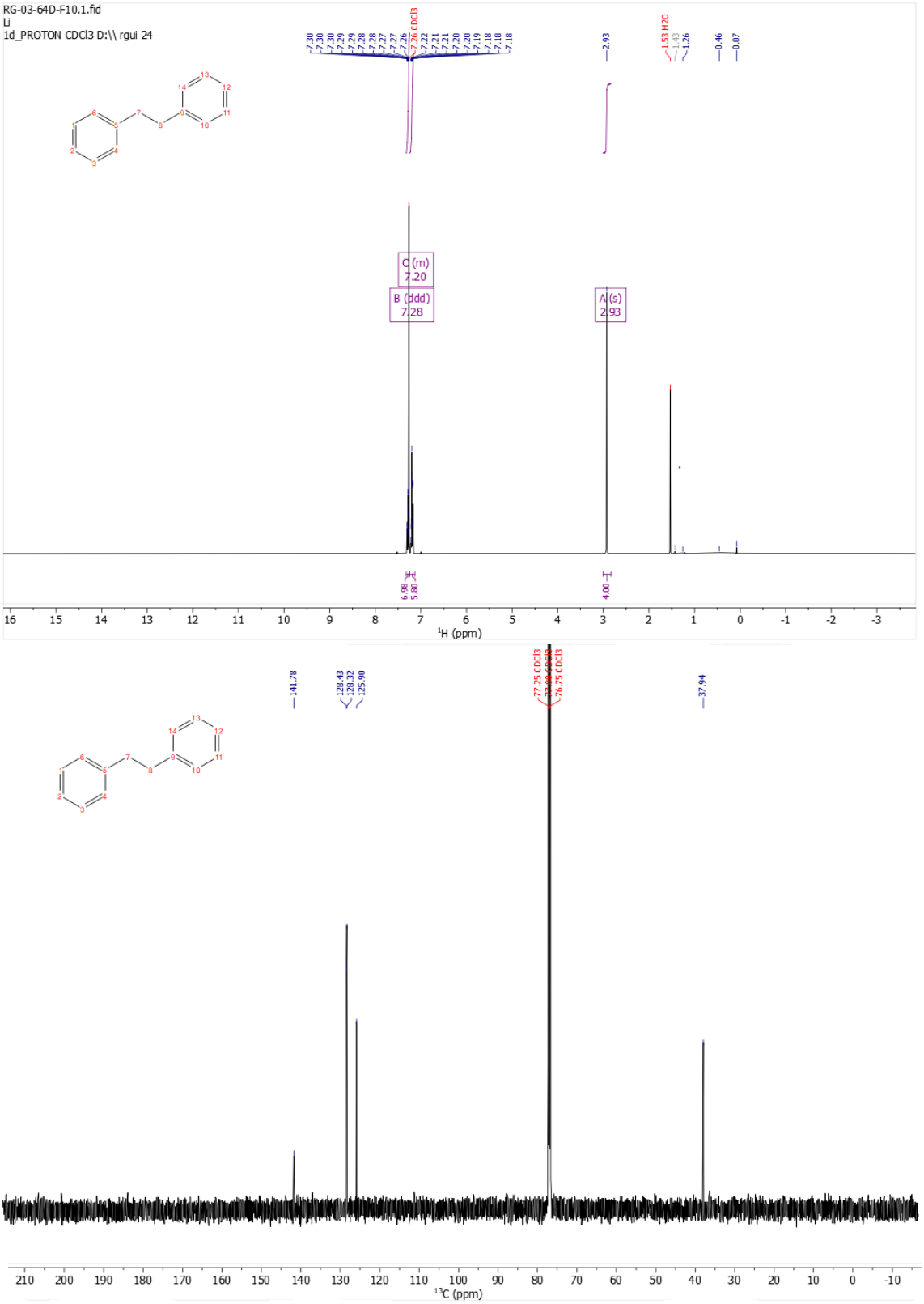
RG-03-60C-F1
B (d) 7.18
A (m) 7.27
C (m) 2.60
D (m) 1.62
E (m) 1.31
F (m) 0.88
¹H (ppm)
142.96
128.39
128.20
125.52
77.25 CDCl3
76.75 CDCl3
35.99
31.73
31.49
29.01
22.61
14.09
¹³C (ppm)


Mesitylene
Et2O
Et2O
H
H
1.00
0.74
¹H (ppm)


Abundance
Scan 23 (3.083 min): RG-03-62B.D\data.ms
91.0
106.1
44.0
51.0
59.0
65.0
74.1
78.1
102.1
m/z-->


RG-03-64D-F10.1.fid
Li
1d_PROTON CDCl3 D:\\ rgui 24
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2.93
1.53 H2O
0.46
0.07
C (m)
7.20
B (ddd)
7.28
A (s)
2.93
6.98
5.80
4.00
¹H (ppm)
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128.43
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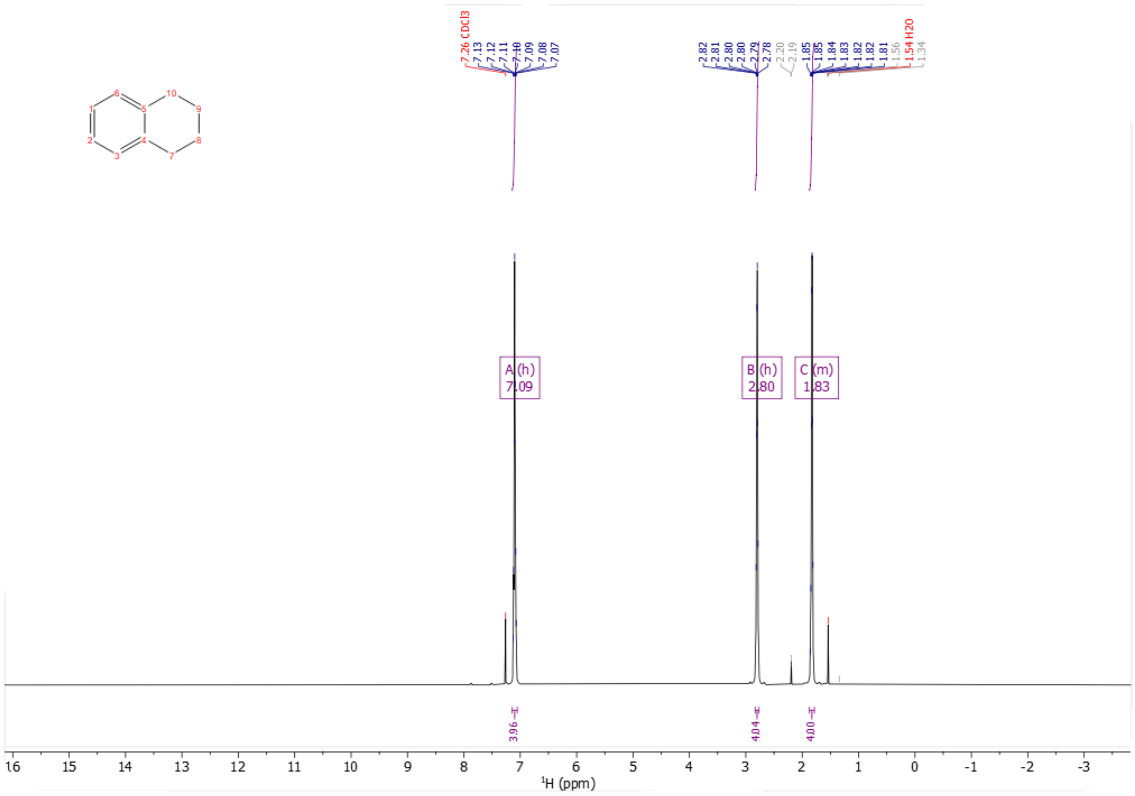
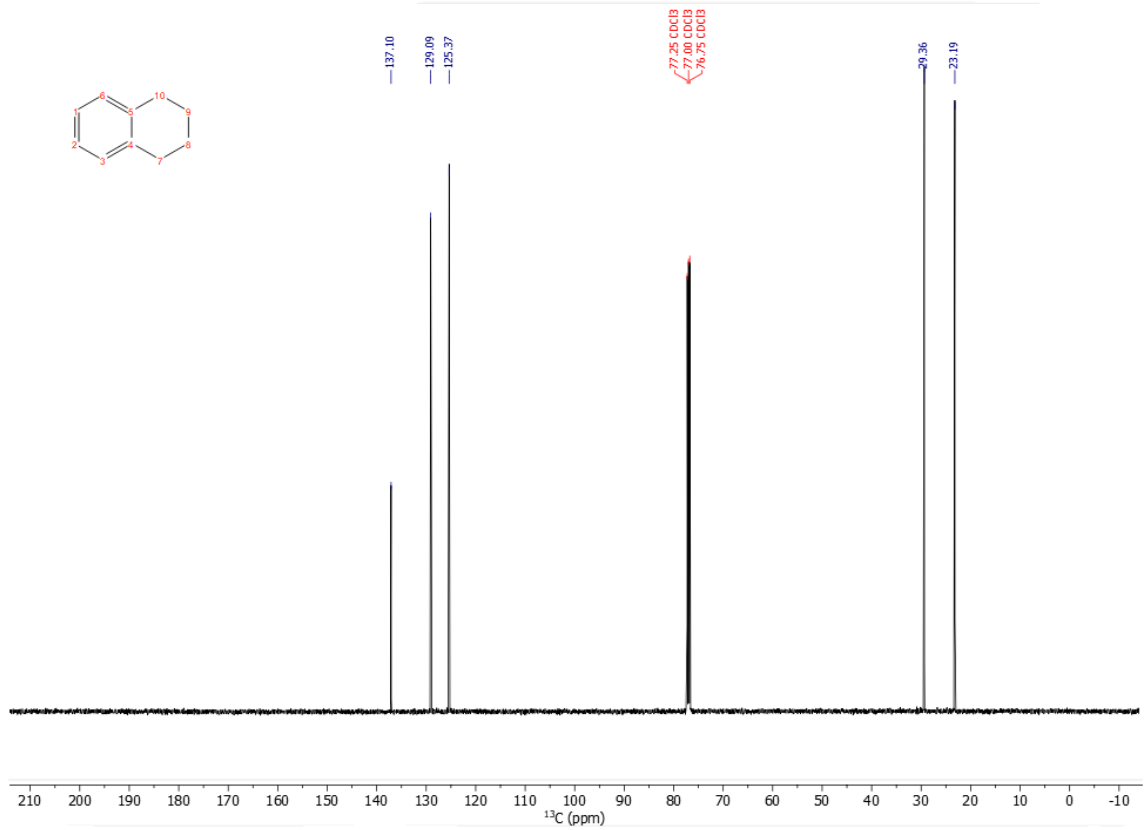
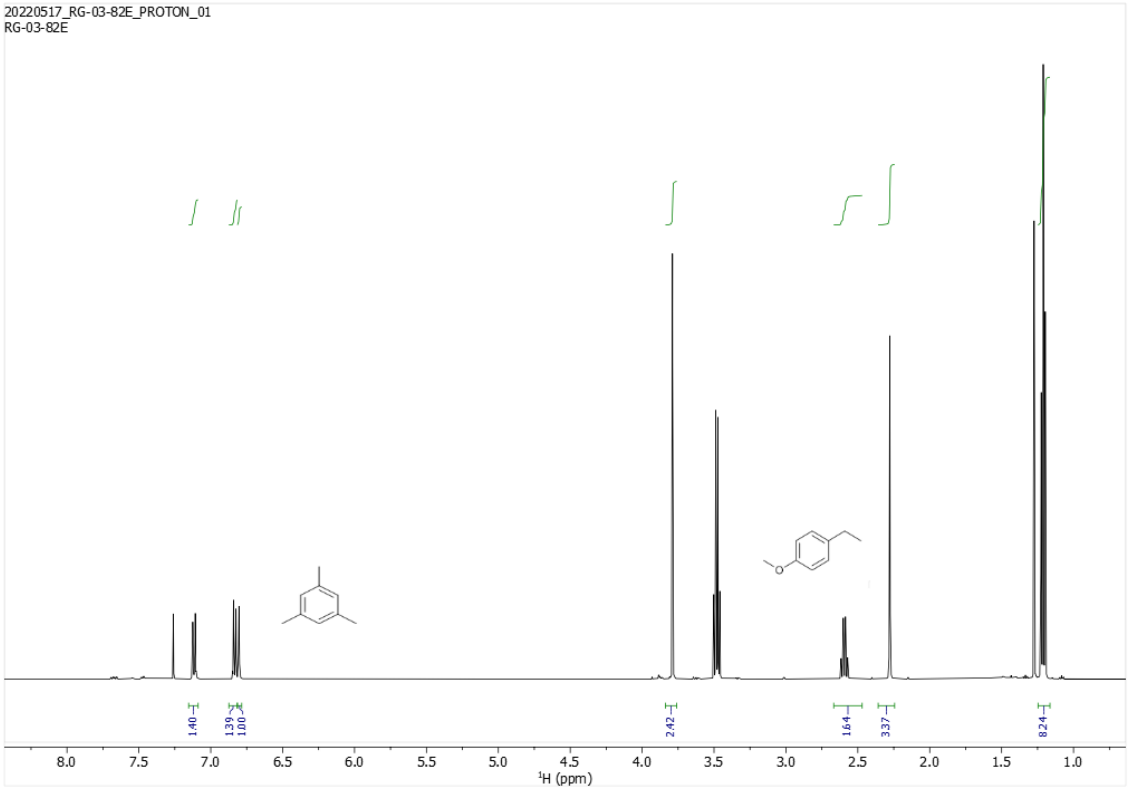
77.25 CDCl3
76.75 CDCl3
37.94
¹³C (ppm)


7.26 CDCl3
7.13
7.12
7.11
7.10
7.09
7.08
7.07
2.82
2.81
2.80
2.80
2.79
2.78
2.20
2.16
1.85
1.85
1.84
1.83
1.82
1.82
1.81
1.56
1.54 H2O
1.34
A (h)
7.09
B (h)
2.80
C (m)
1.83
3.96
4.04
4.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
¹H (ppm)


137.10
129.09
125.37
77.25 CDCl3
77.00 CDCl3
76.75 CDCl3
29.36
23.19
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
¹³C (ppm)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RG-03-82E
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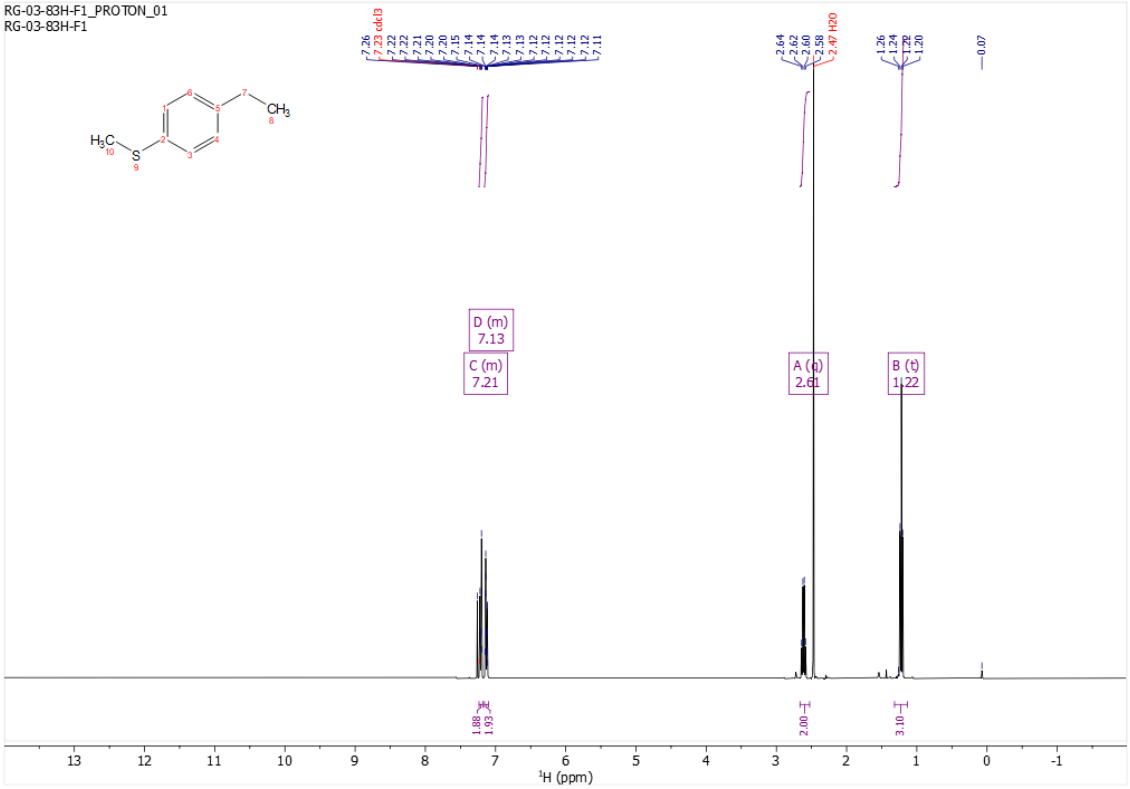
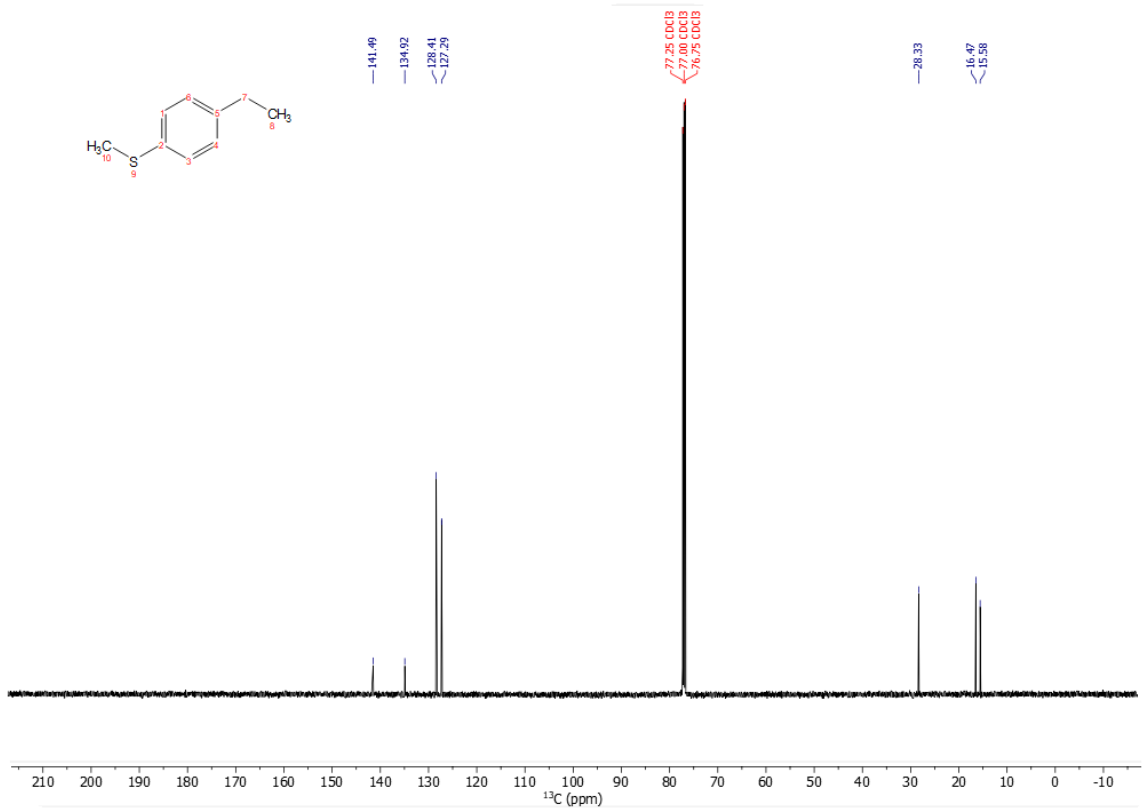
1.00
2.42
1.64
3.37
8.24
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
¹H (ppm)


RG-03-83H-F1_PROTON_01
RG-03-83H-F1
7.26
7.23 cdcl3
7.22
7.22
7.21
7.20
7.20
7.15
7.14
7.14
7.13
7.13
7.12
7.12
7.12
7.12
7.12
7.11
2.64
2.62
2.60
2.58
2.47 H2O
1.26
1.24
1.22
1.20
0.07
D (m)
7.13
C (m)
7.21
A (q)
2.61
B (t)
1.22
1.88
1.93
2.00
3.10
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
¹H (ppm)


141.49
134.92
128.41
127.29
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76.75 CDCl3
28.33
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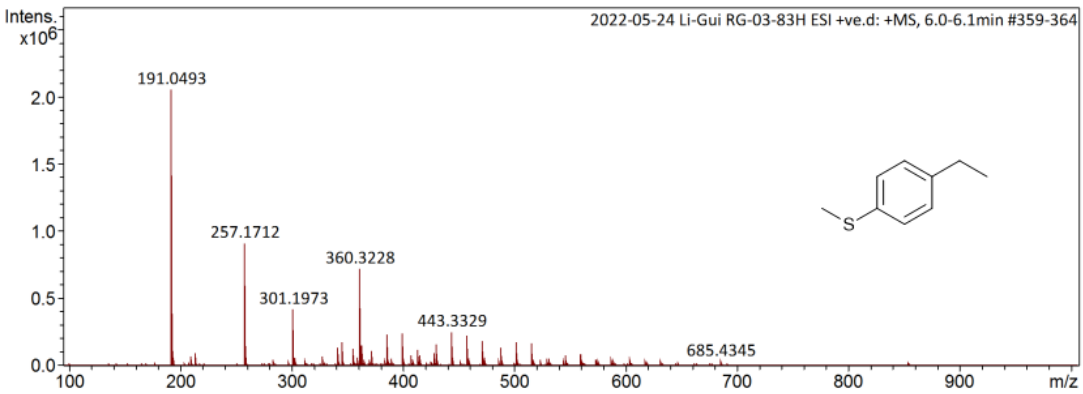
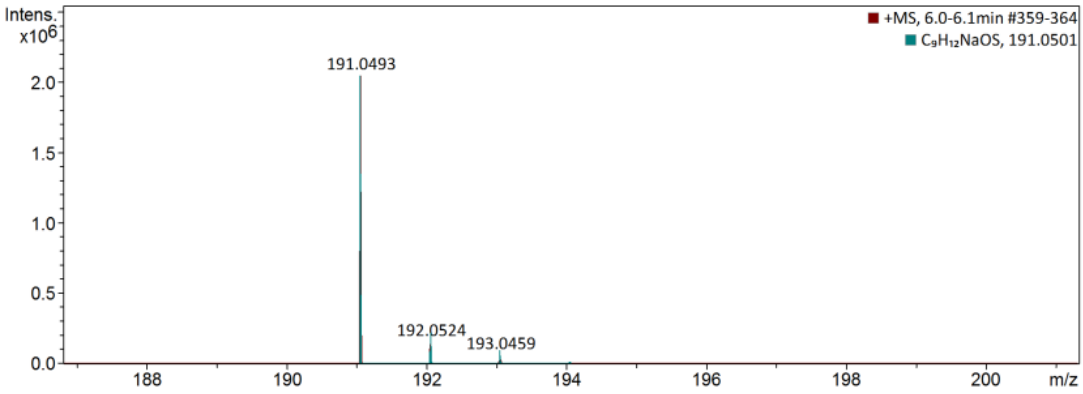
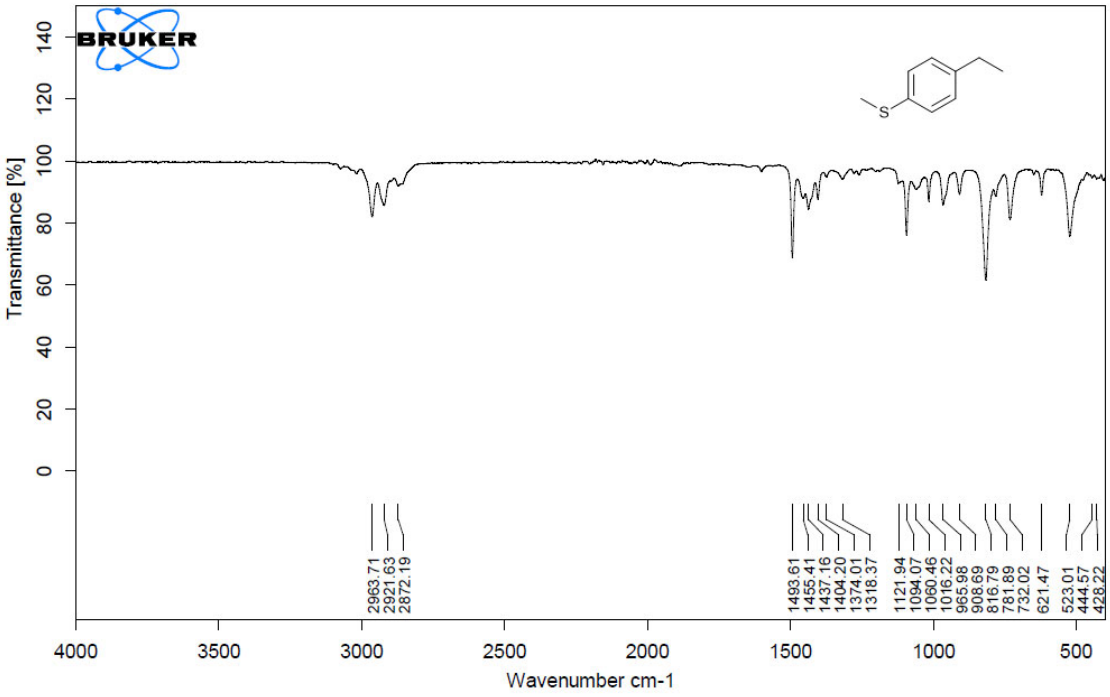
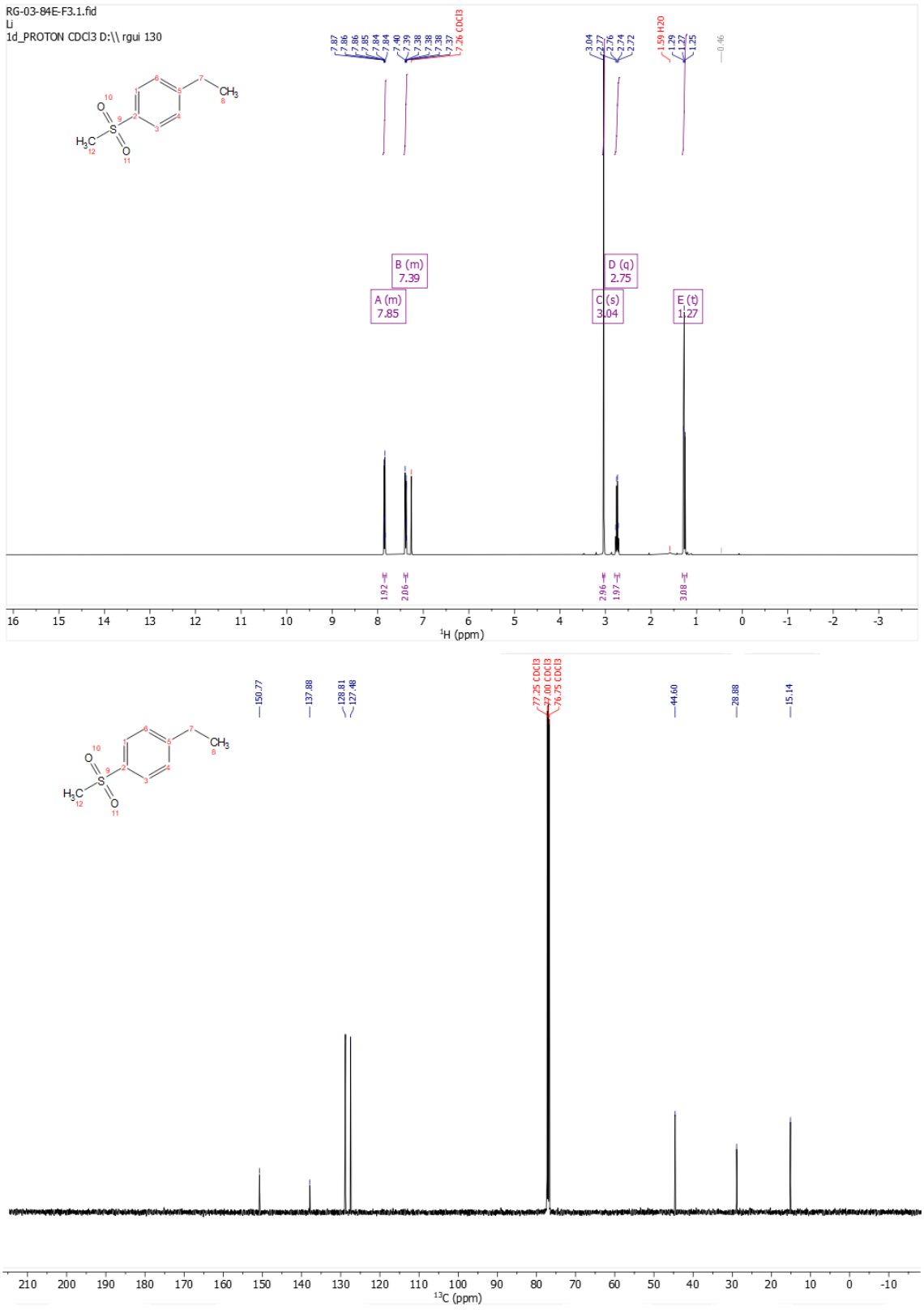
15.58
CH3
H3C
S
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
13C (ppm)





Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# mSigma	Score	rdb	e⁻ Conf	N-Rule
191.0493	1	C6H11N2O3S	191.0485	-4.2	14.0	1	100.00	2.5	even	ok
	1	C9H12NaOS	191.0501	4.2	21.7	1	100.00	3.5	even	ok

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7.86
7.86
7.85
7.84
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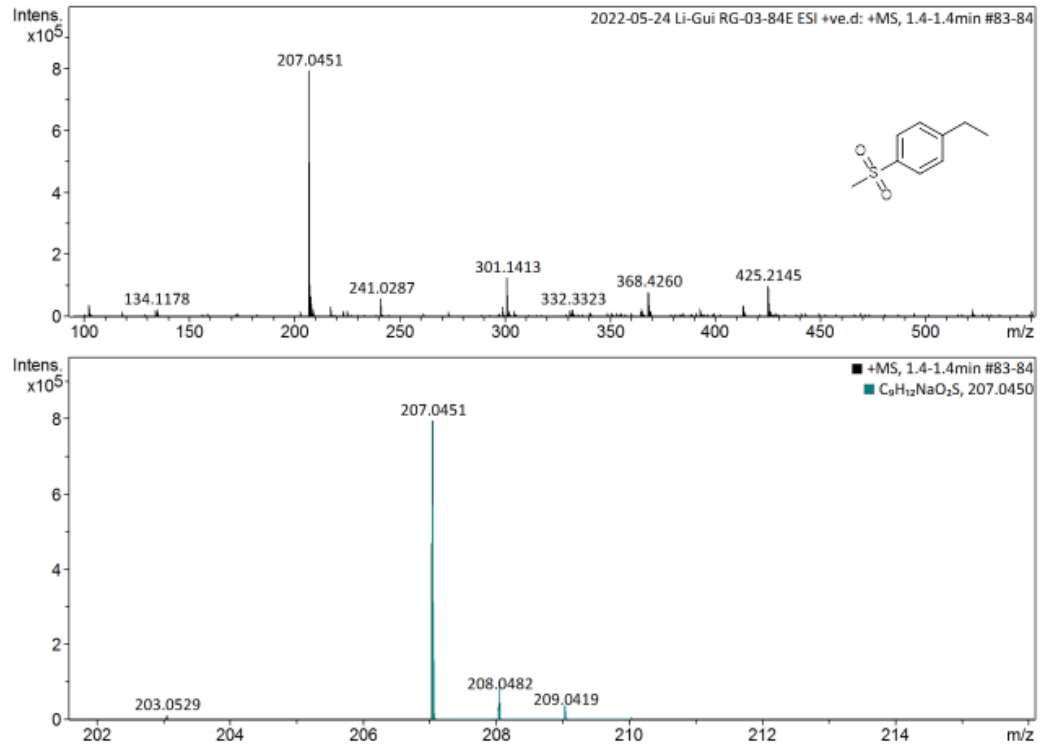
7.39
7.38
7.38
7.38
7.37
7.26 CDCl3
3.04
2.77
2.76
2.74
2.72
1.59 H2O
1.29
1.27
1.25
0.46
B (m)
7.39
A (m)
7.85
D (q)
2.75
C (s)
3.04
E (t)
1.27
1.92
2.06
2.96
1.97
3.08
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
¹H (ppm)
150.77
137.88
128.81
127.48
77.25 CDCl3
77.00 CDCl3
76.75 CDCl3
44.60
28.88
15.14
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
¹³C (ppm)



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# mSigma	Score	rdb	e¯ Conf	N-Rule
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	2	C7H7N6S	207.0447	-1.5	17.6	2	100.00	7.5	even	ok
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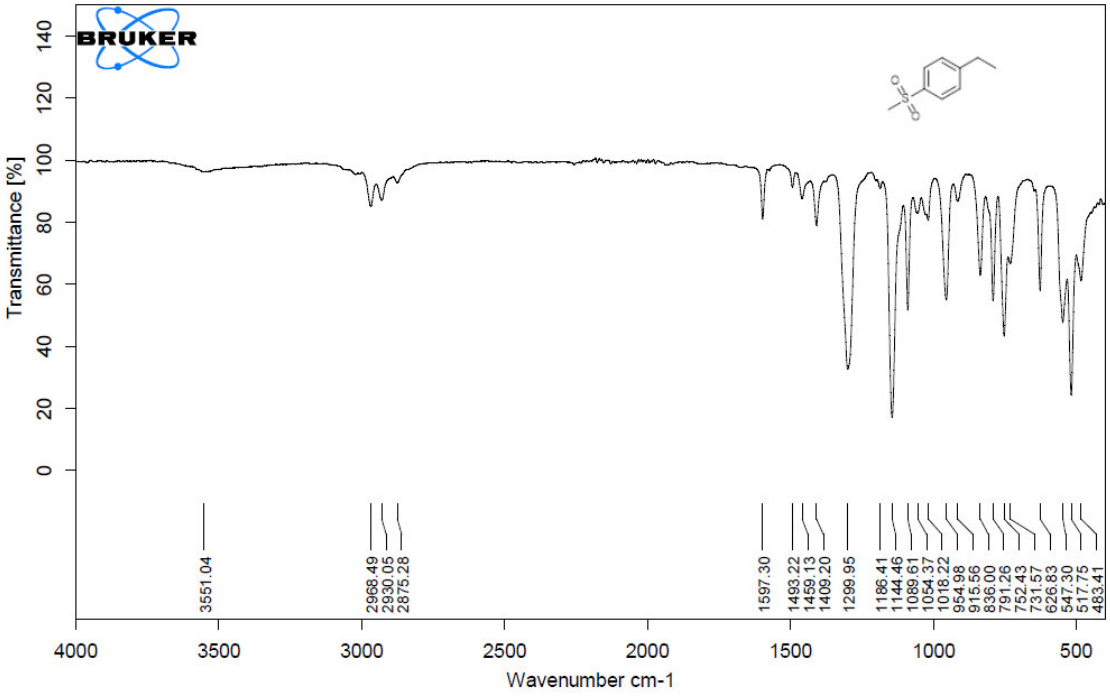

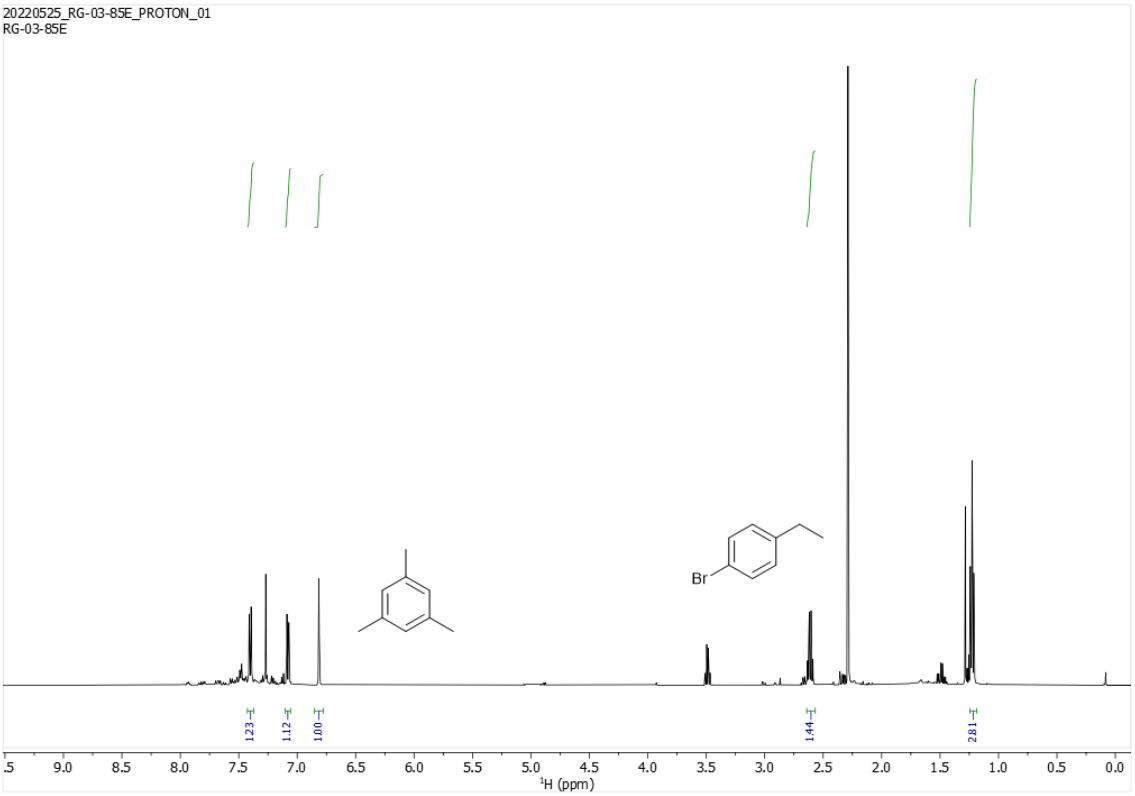
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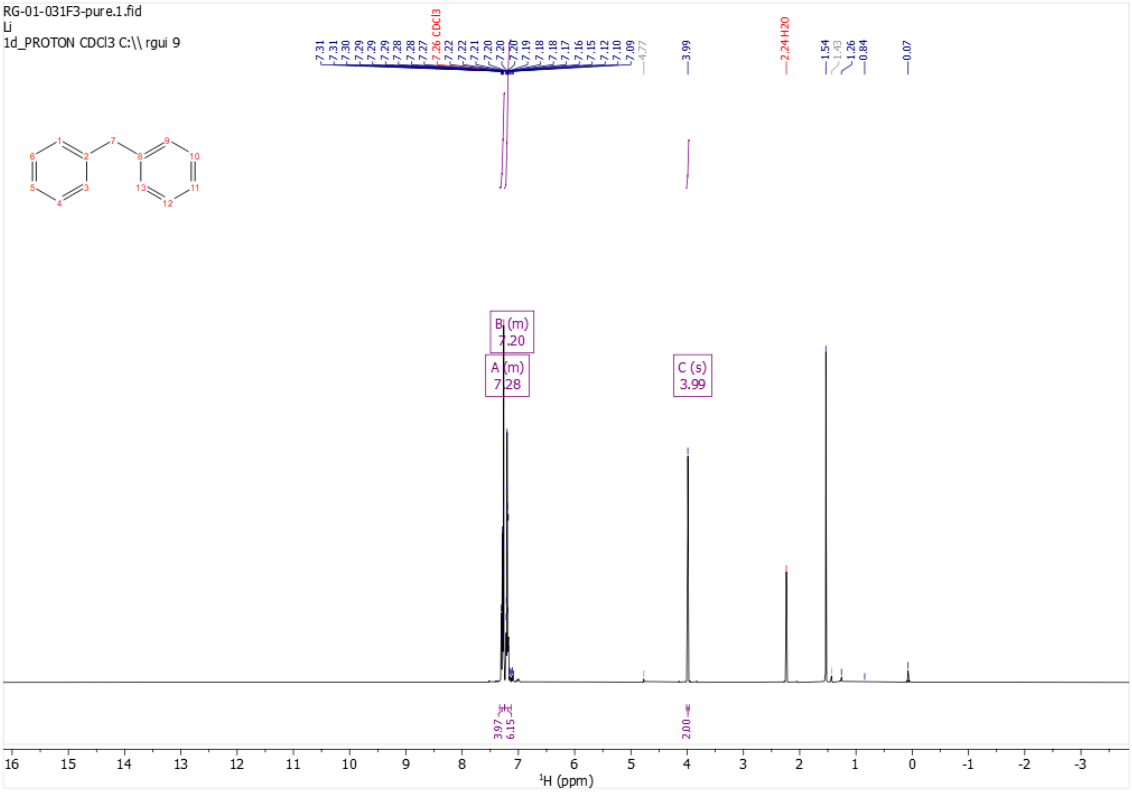
¹H (ppm)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2.24 H2O
3.99
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7.20
A (m)
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C (s)
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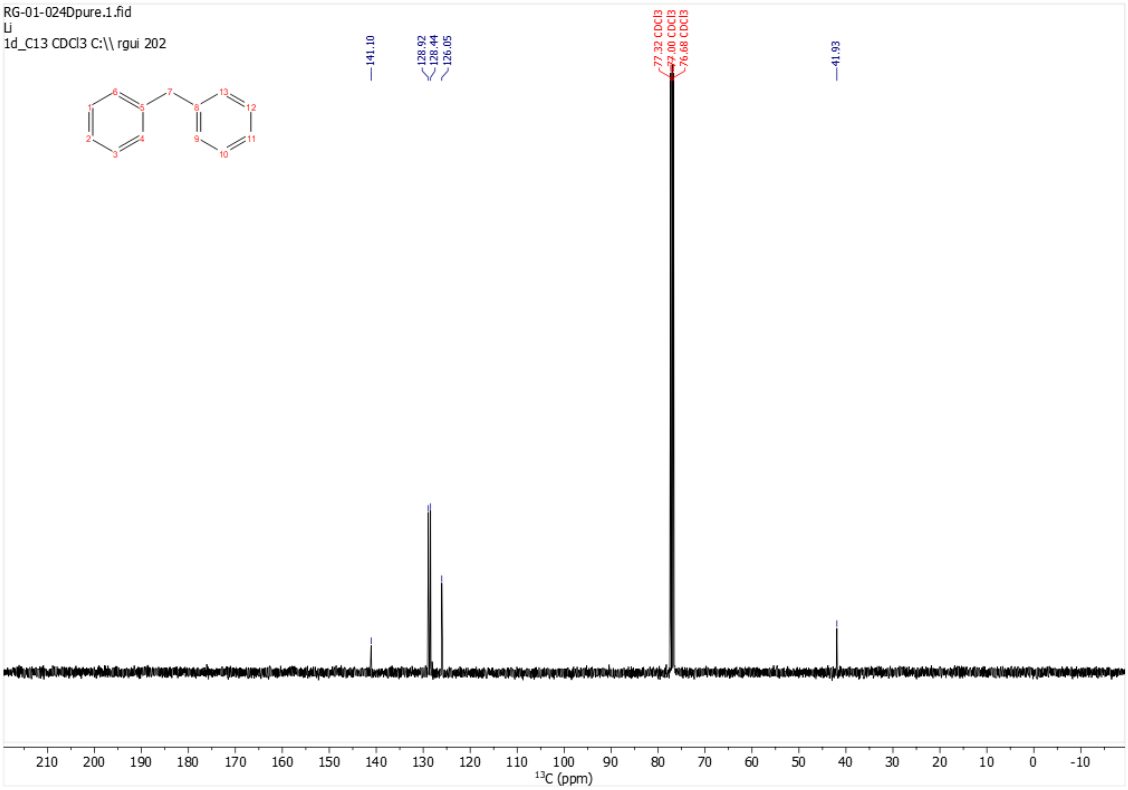
6.15
2.00
¹H (ppm)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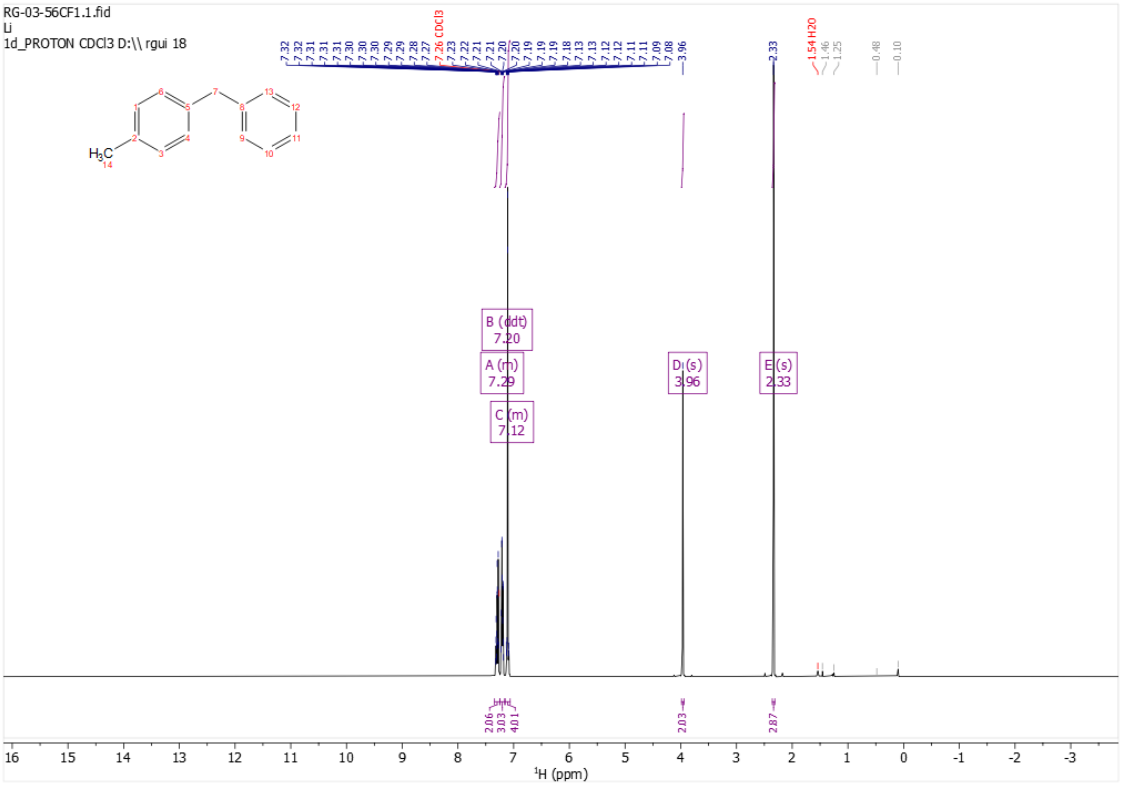
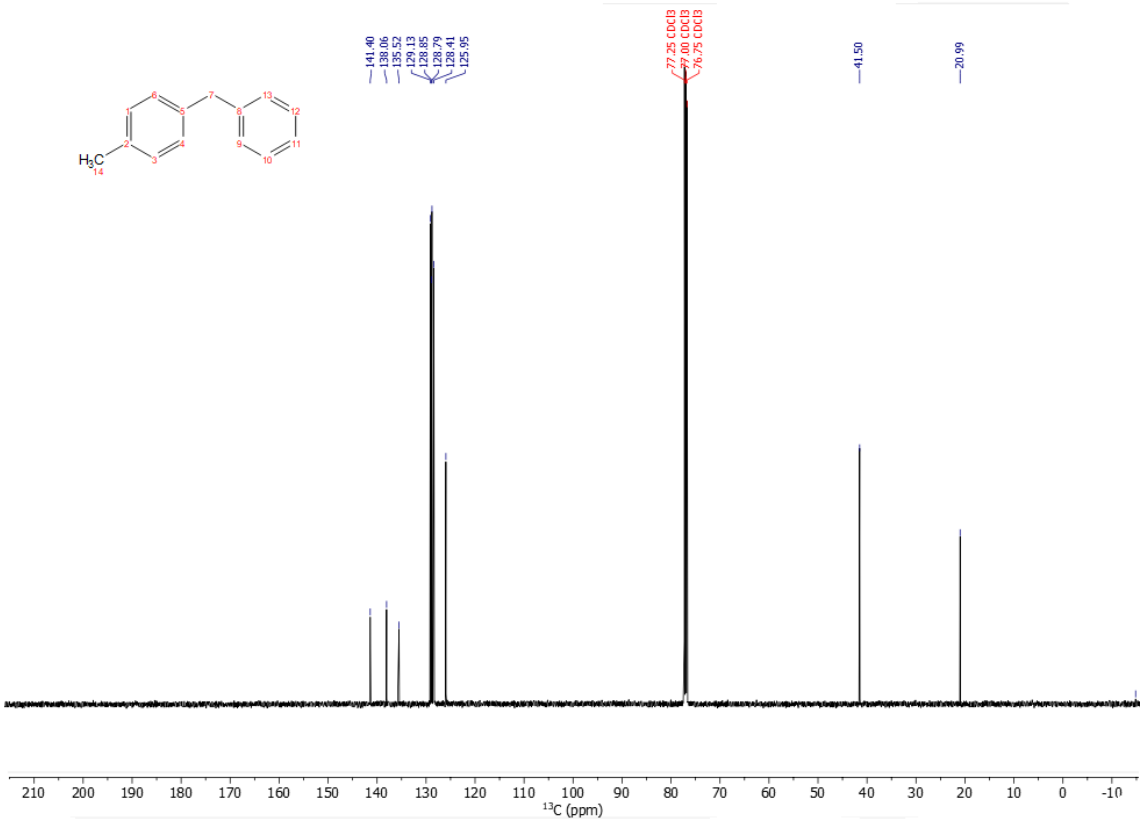
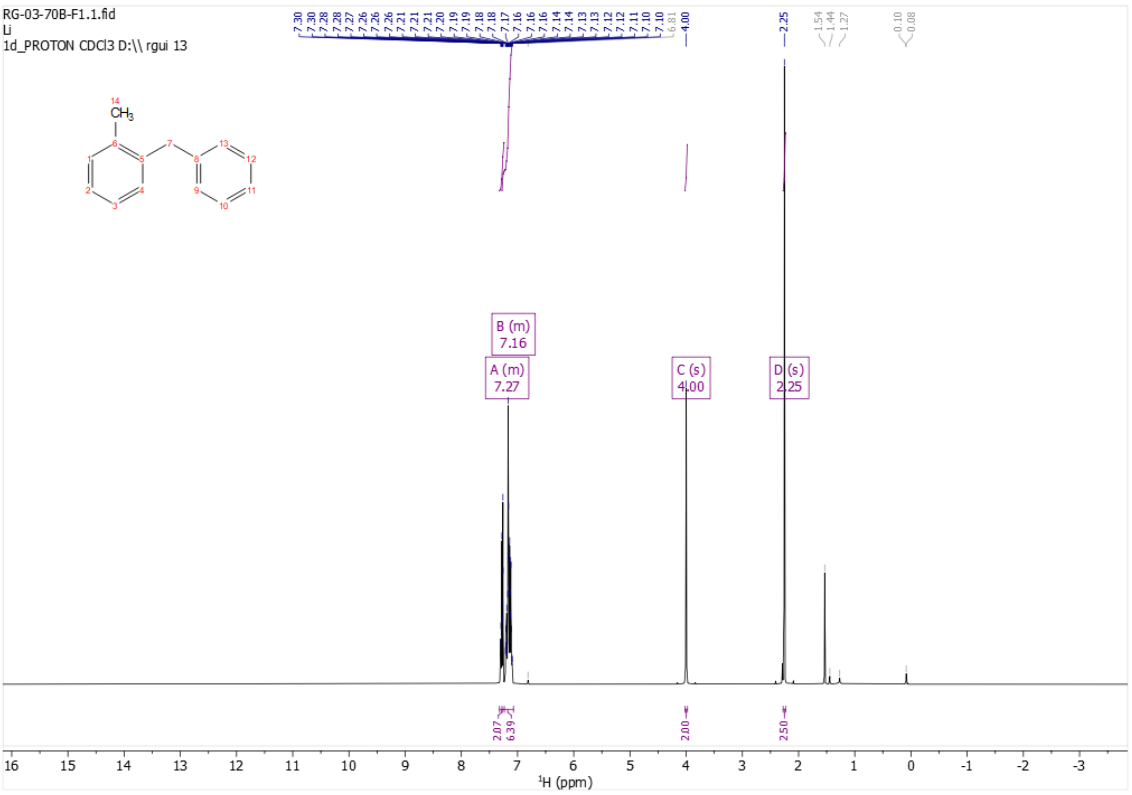
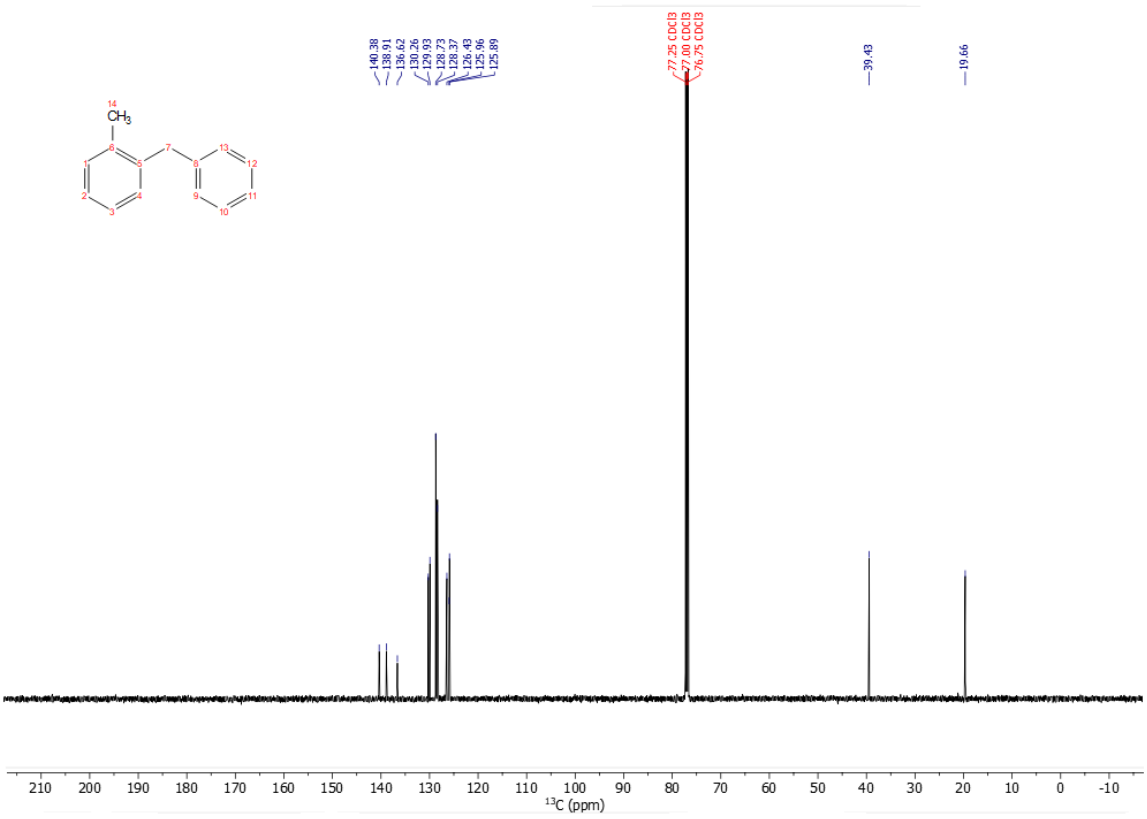
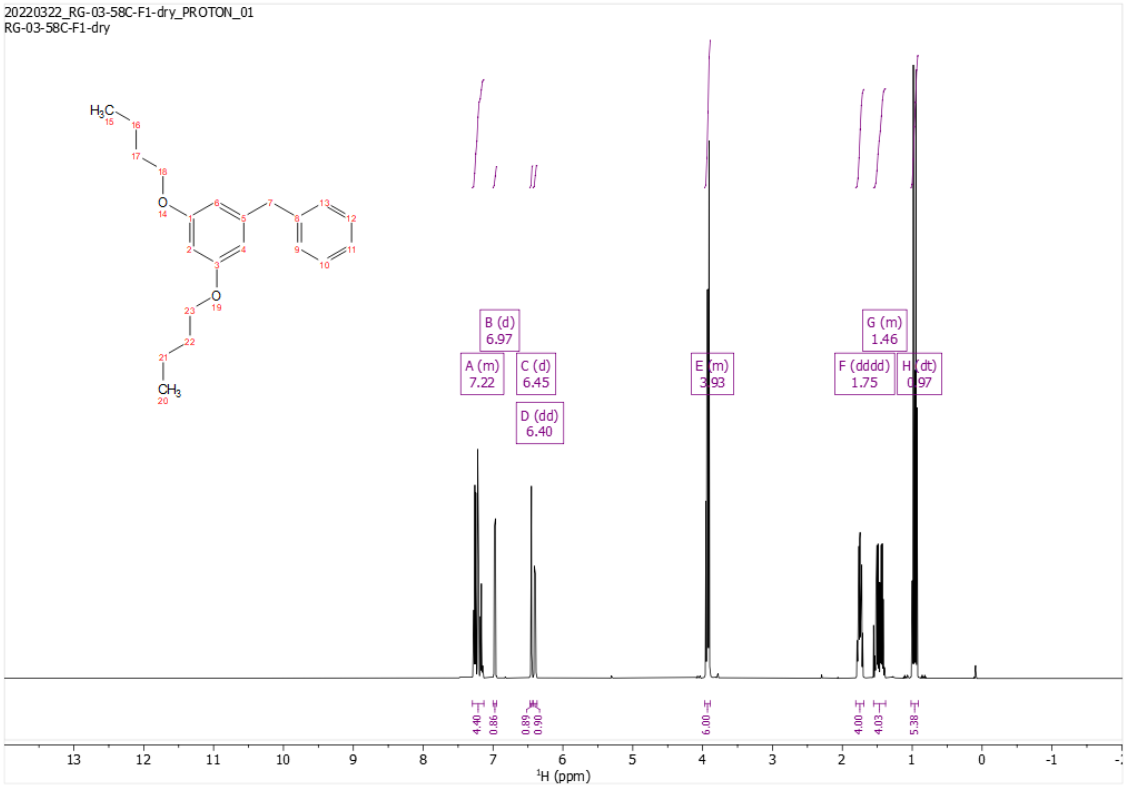
^{13}C (ppm)

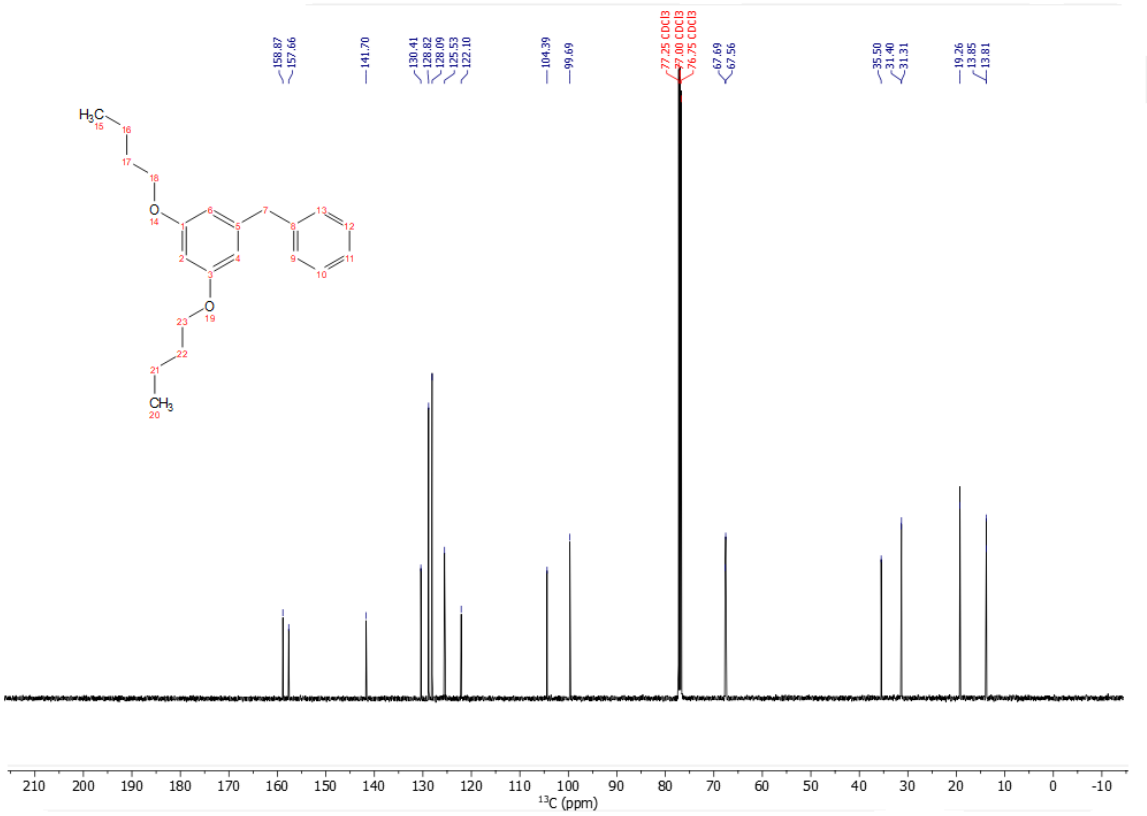

RG-03-56CF1.1.fid
Li
1d_PROTON CDCl3 D:\\ rgui 18
7.26 CDCl3
3.96
2.33
1.54 H2O
B (ddt)
7.20
A (m)
7.29
C (m)
7.12
D (s)
3.96
E (s)
2.33
2.06
2.03
4.01
2.03
2.87
^{1}H (ppm)

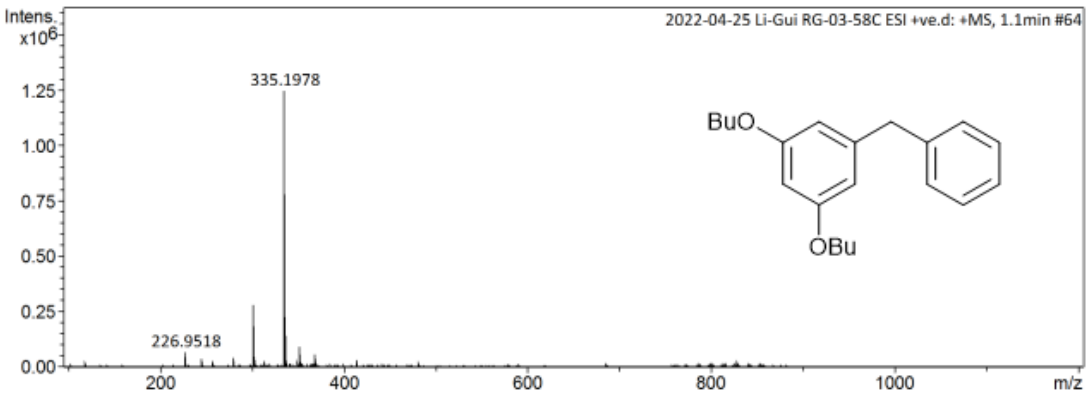

141.40
138.06
135.52
129.13
128.95
128.79
128.41
125.95
77.25 CDCl3
77.00 CDCl3
76.75 CDCl3
41.50
20.99
H3C
14
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
13C (ppm)

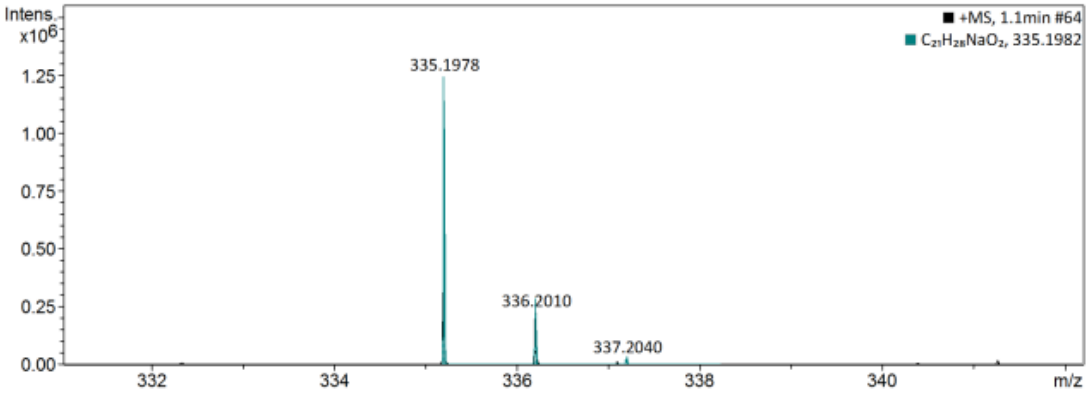

RG-03-70B-F1.1.fid
Li
1d_PROTON CDCl3 D:\\ rgui 13
7.30
7.30
7.28
7.28
7.27
7.26
7.26
7.21
7.21
7.20
7.19
7.19
7.18
7.17
7.16
7.16
7.16
7.14
7.14
7.13
7.13
7.12
7.12
7.11
7.10
6.81
4.00
2.25
1.54
1.44
1.27
0.10
0.08
CH3
14
B (m)
7.16
A (m)
7.27
C (s)
4.00
D (s)
2.25
2.07
6.39
2.00
2.50
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
1H (ppm)


140.38
138.01
136.62
130.26
129.93
128.73
128.37
126.43
125.96
125.89
77.25 CDCl3
77.00 CDCl3
76.75 CDCl3
39.43
19.66
^{13}C (ppm)

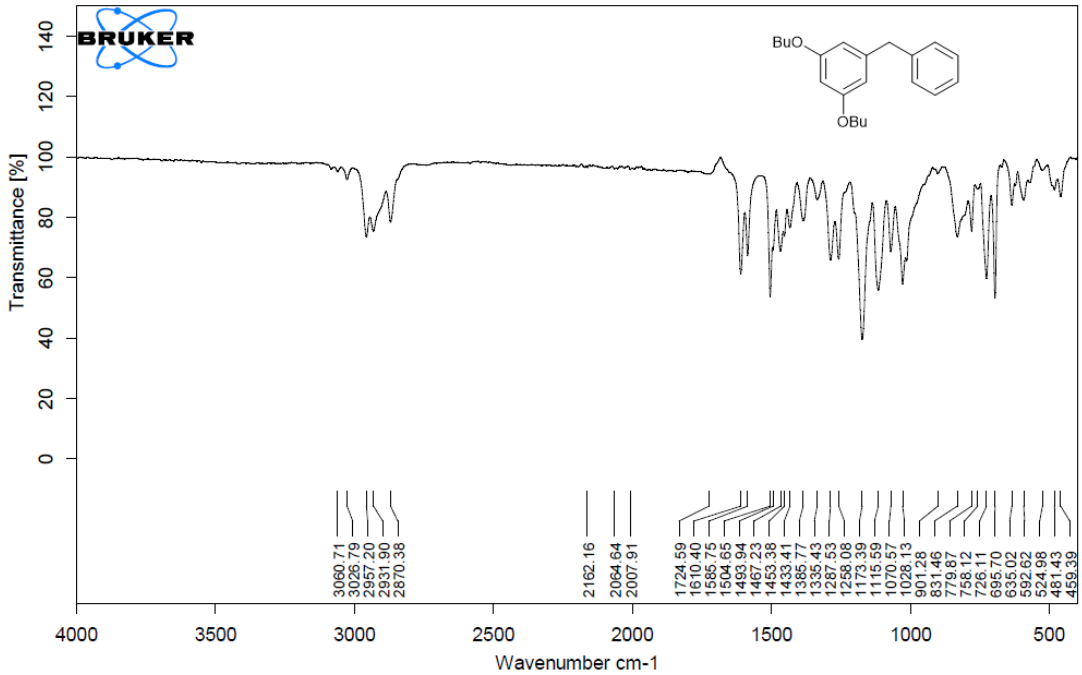

20220322_RG-03-58C-F1-dry_PROTON_01
RG-03-58C-F1-dry
B (d) 6.97
A (m) 7.22
C (d) 6.45
D (dd) 6.40
E (m) 3.93
G (m) 1.46
F (dddd) 1.75
H (dt) 0.97
^{1}H (ppm)

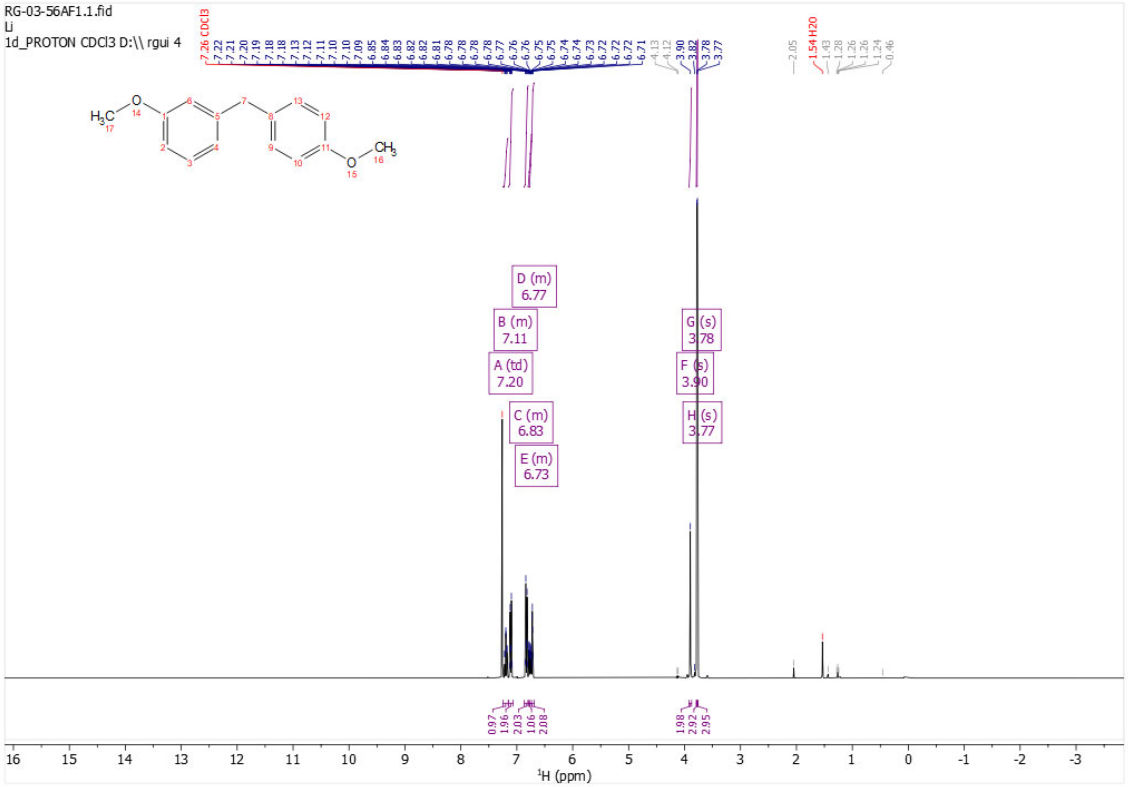

158.87
157.66
141.70
130.41
128.82
128.09
125.53
122.10
104.39
99.69
77.25 CDCl3
77.00 CDCl3
76.75 CDCl3
67.69
67.56
35.50
31.40
31.31
19.26
13.85
13.81
H3C
O
O
CH3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
13C (ppm)

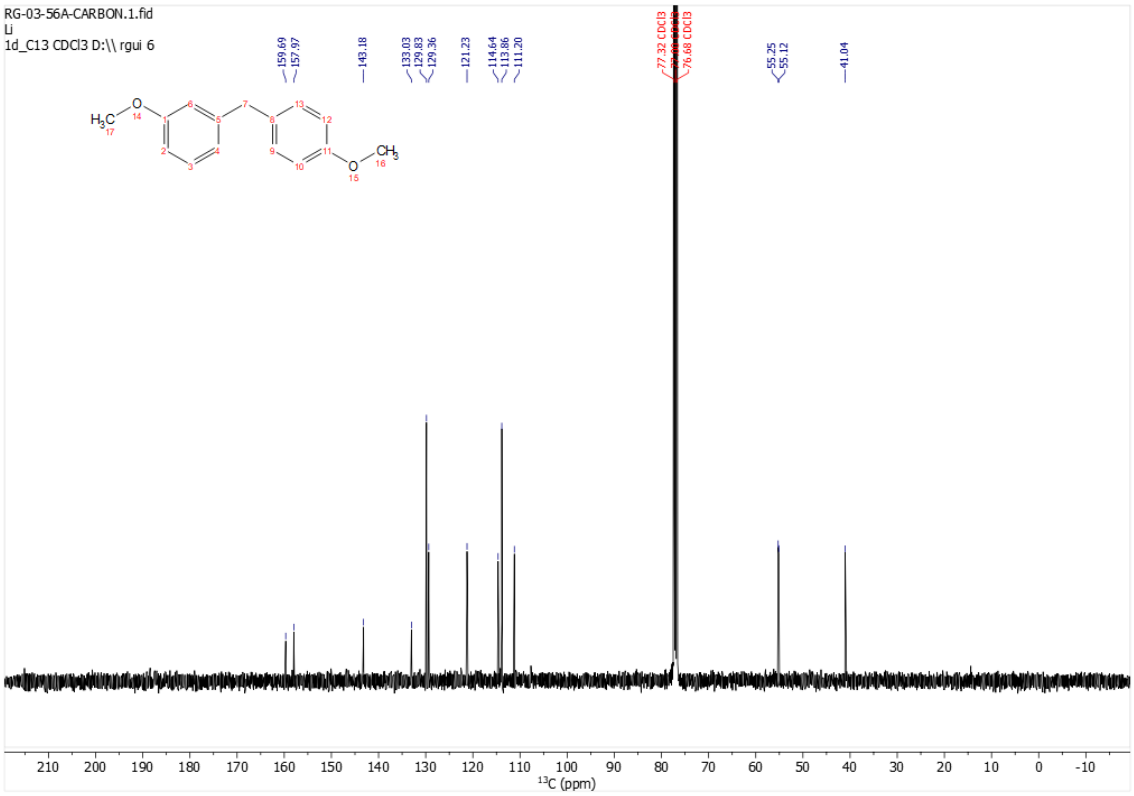


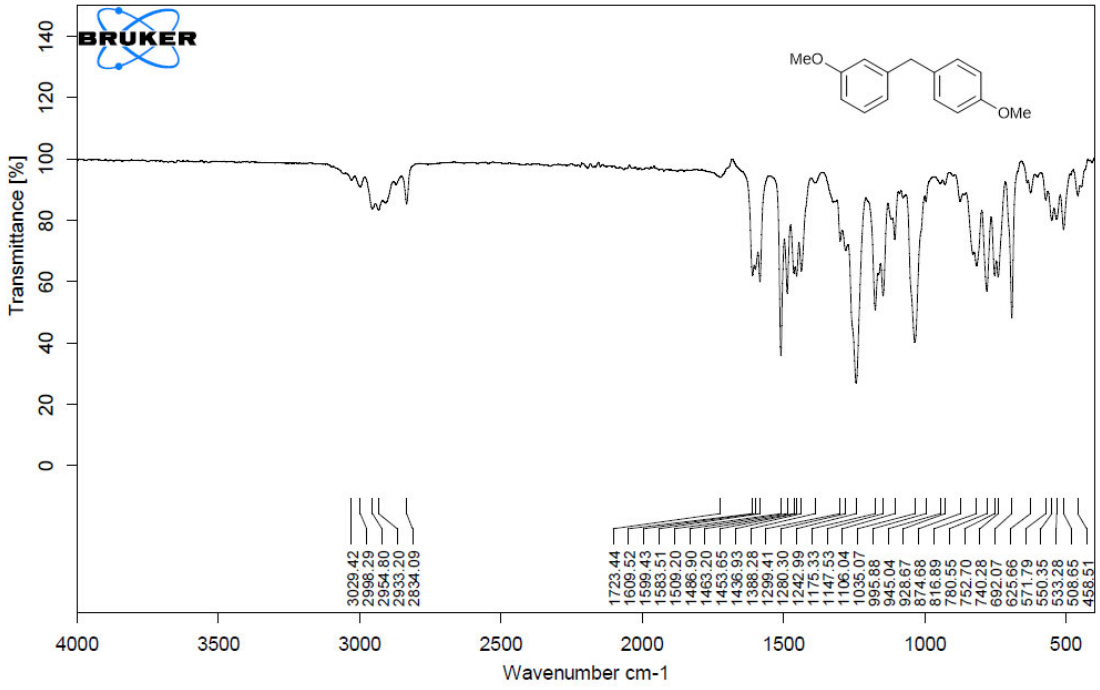


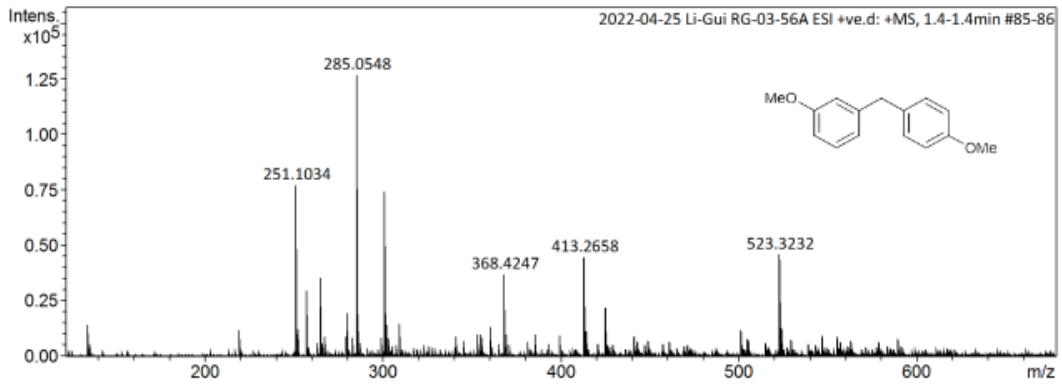
Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# mSigma	Score	rdb	e⁻ Conf	N-Rule
335.1978	1	C18H27N2O4	335.1965	-3.7	15.9	1	74.16	6.5	even	ok
	2	C19H23N6	335.1979	0.3	28.9	2	100.00	11.5	even	ok
	1	C21H28NaO2	335.1982	1.1	29.9	1	100.00	7.5	even	ok

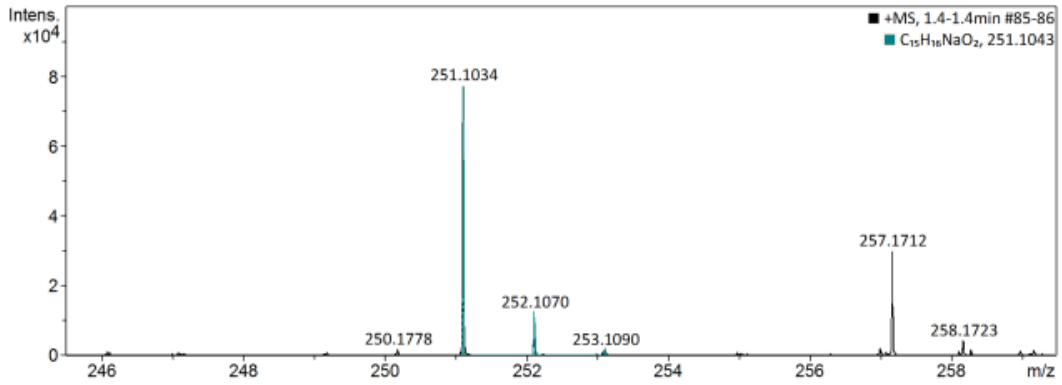



RG-03-56AF1.1.fid
Li
1d_PROTON CDCl3 D:\\ rgui 4
D (m)
6.77
B (m)
7.11
A (td)
7.20
C (m)
6.83
E (m)
6.73
G (s)
3.78
F (s)
3.90
H (s)
3.77
¹H (ppm)

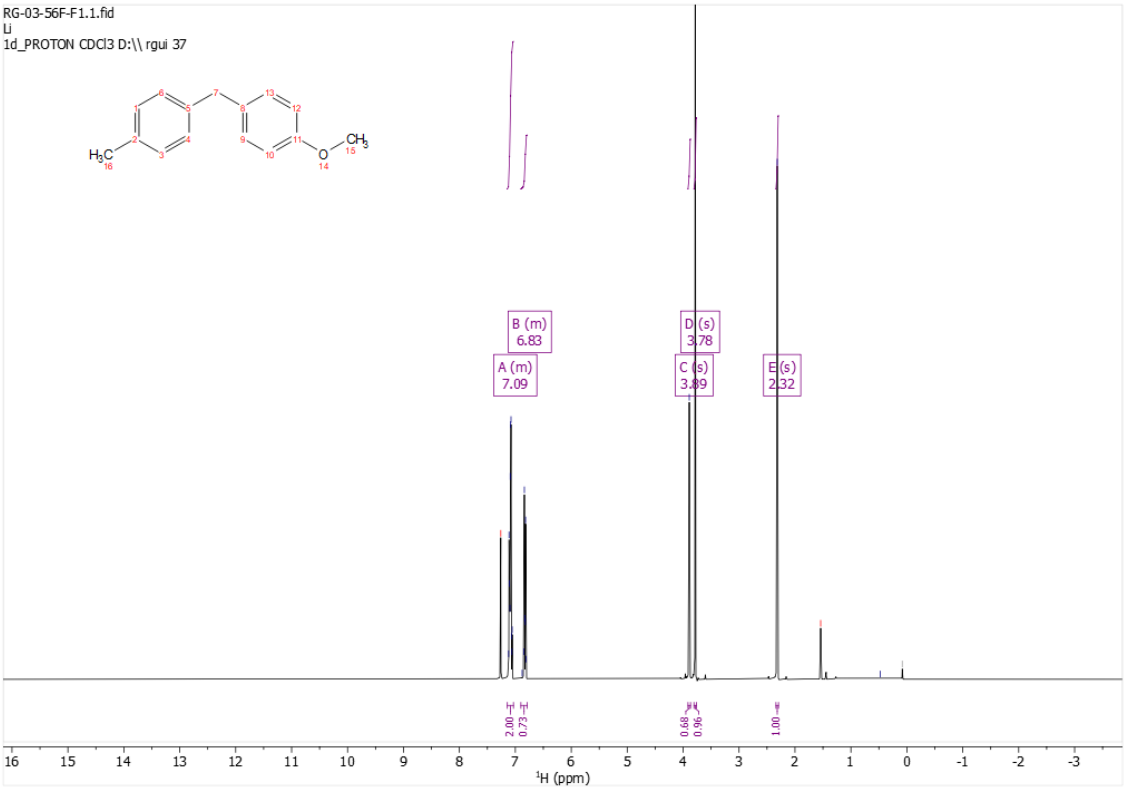

RG-03-56A-CARBON.1.fid
Li
1d_C13 CDCl3 D:\\ rgui 6
¹³C (ppm)

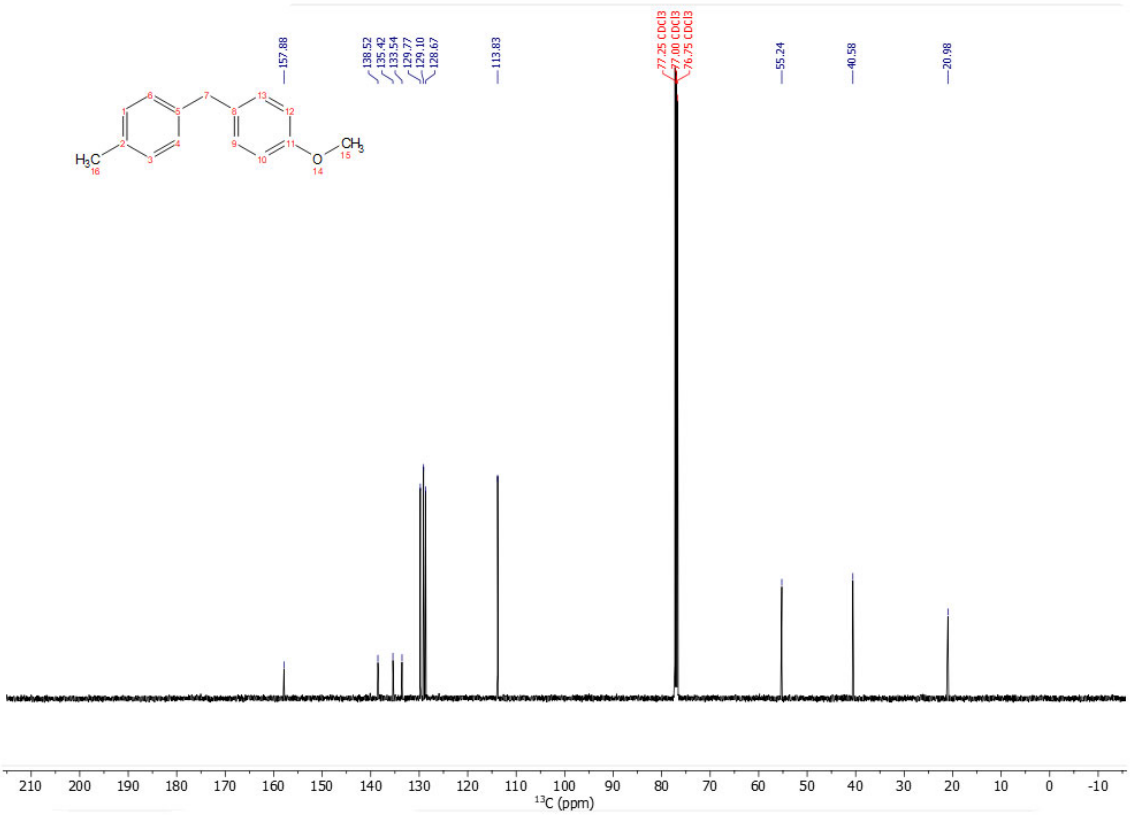


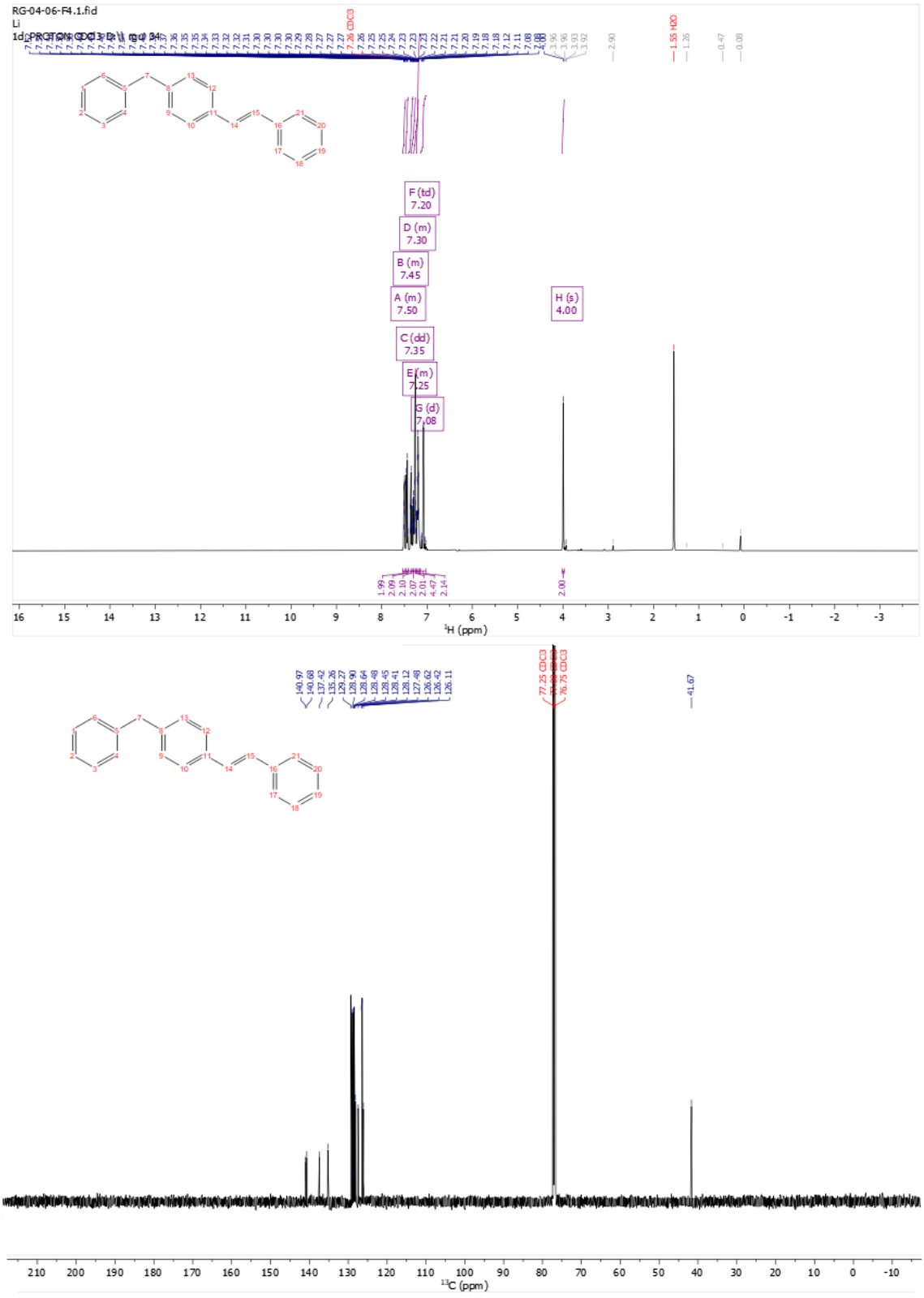


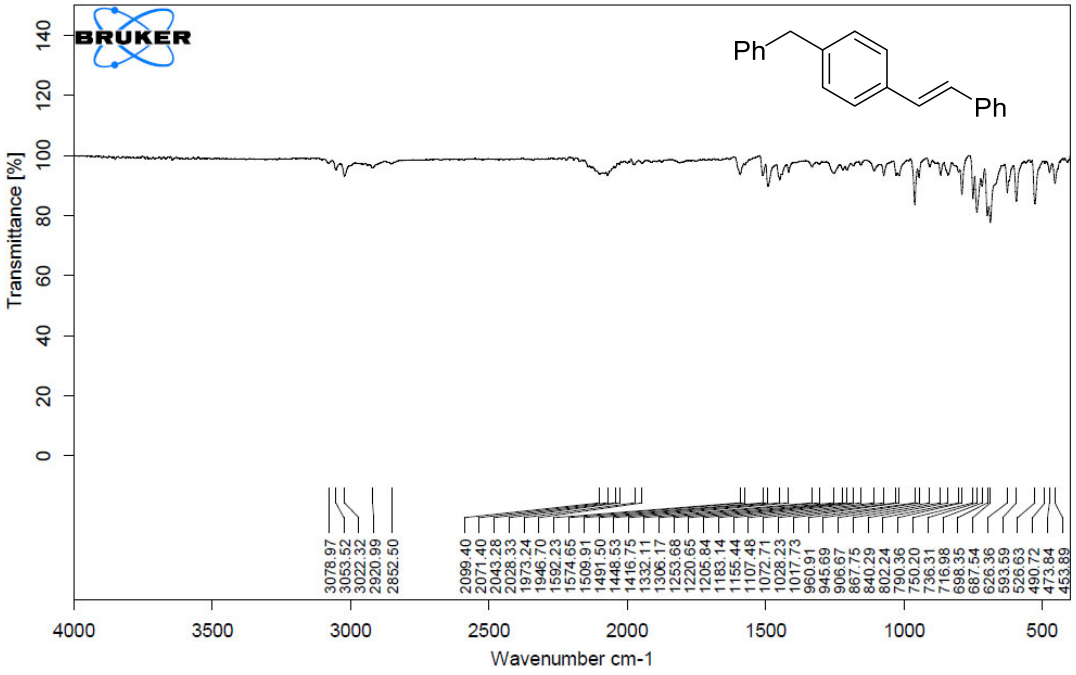


Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# mSigma	Score	rdb	e⁻ Conf	N-Rule
251.1034	1	C13H11N6	251.1040	2.1	5.4	1	100.00	11.5	even	ok
	2	C12H15N2O4	251.1026	-3.2	9.5	2	81.05	6.5	even	ok
	1	C15H16NaO2	251.1043	3.2	4.8	1	100.00	7.5	even	ok

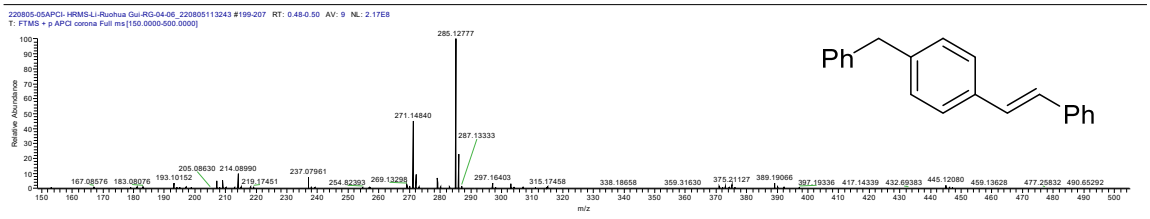

RG-03-56F-F1.1.fid
Li
1d_PROTON CDCl3 D:\\ rgui 37
B (m)
6.83
A (m)
7.09
D (s)
3.78
C (s)
3.89
E (s)
2.32
2.00
0.73
0.68
0.96
1.00
^{1}H (ppm)

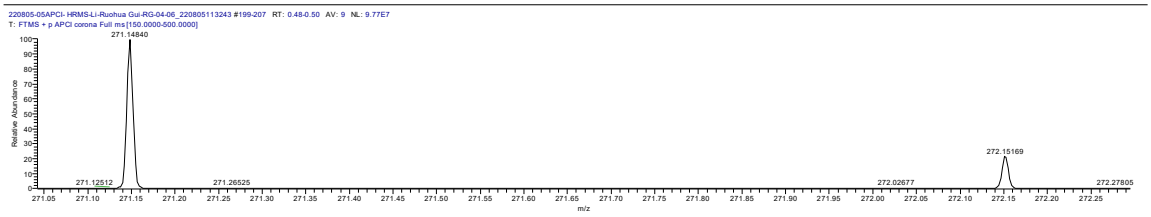

157.88
138.52
135.42
133.54
129.77
129.10
128.67
113.83
77.25 CDCl3
77.00 CDCl3
76.75 CDCl3
55.24
40.58
20.98
^{13}C (ppm)


RG-04-06-F4.1.fid
Li
F (td)
7.20
D (m)
7.30
B (m)
7.45
A (m)
7.50
C (dd)
7.35
E (m)
7.25
G (d)
7.08
H (s)
4.00
1.99
2.09
2.10
2.07
2.01
4.47
2.14
2.00
^{1}H (ppm)
140.97
140.68
137.42
135.26
129.27
128.90
128.64
128.48
128.45
128.41
127.12
126.69
126.62
126.42
126.11
77.25 CDCl3
76.75 CDCl3
41.67
^{13}C (ppm)



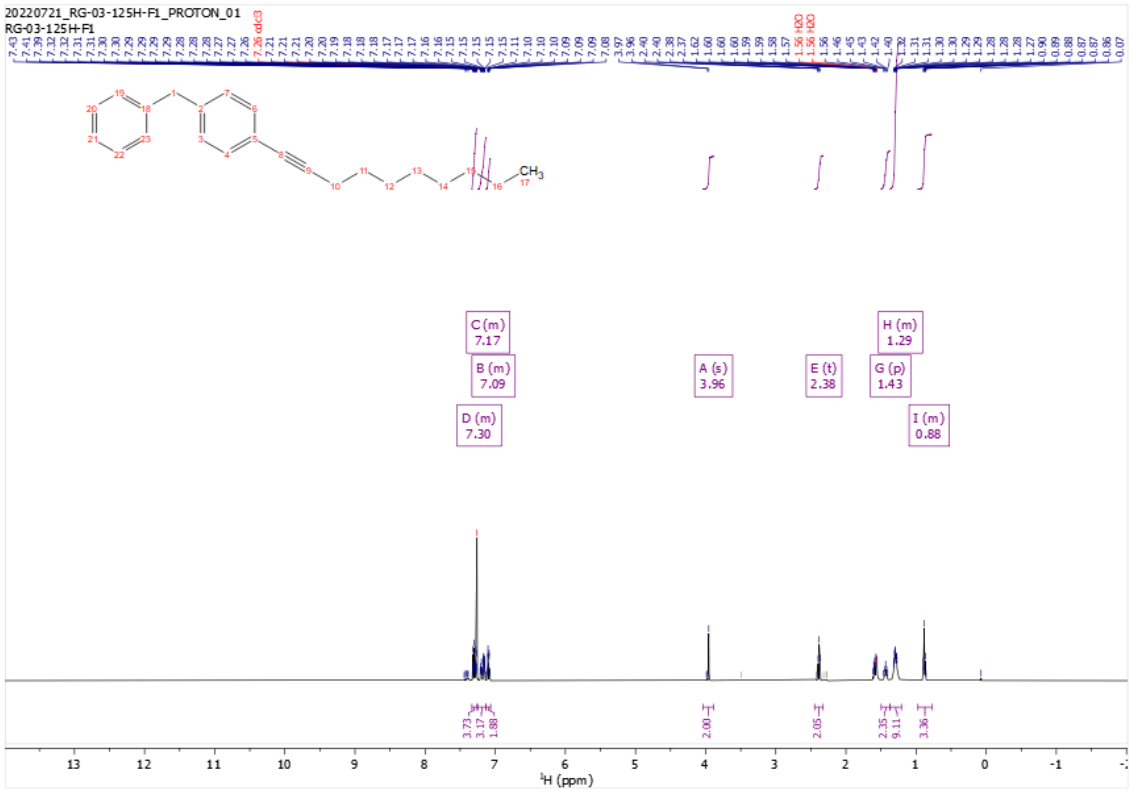
220805-05APCI- HRMS-Li-Ruohua Gui-RG-... 08/05/22 11:32:43

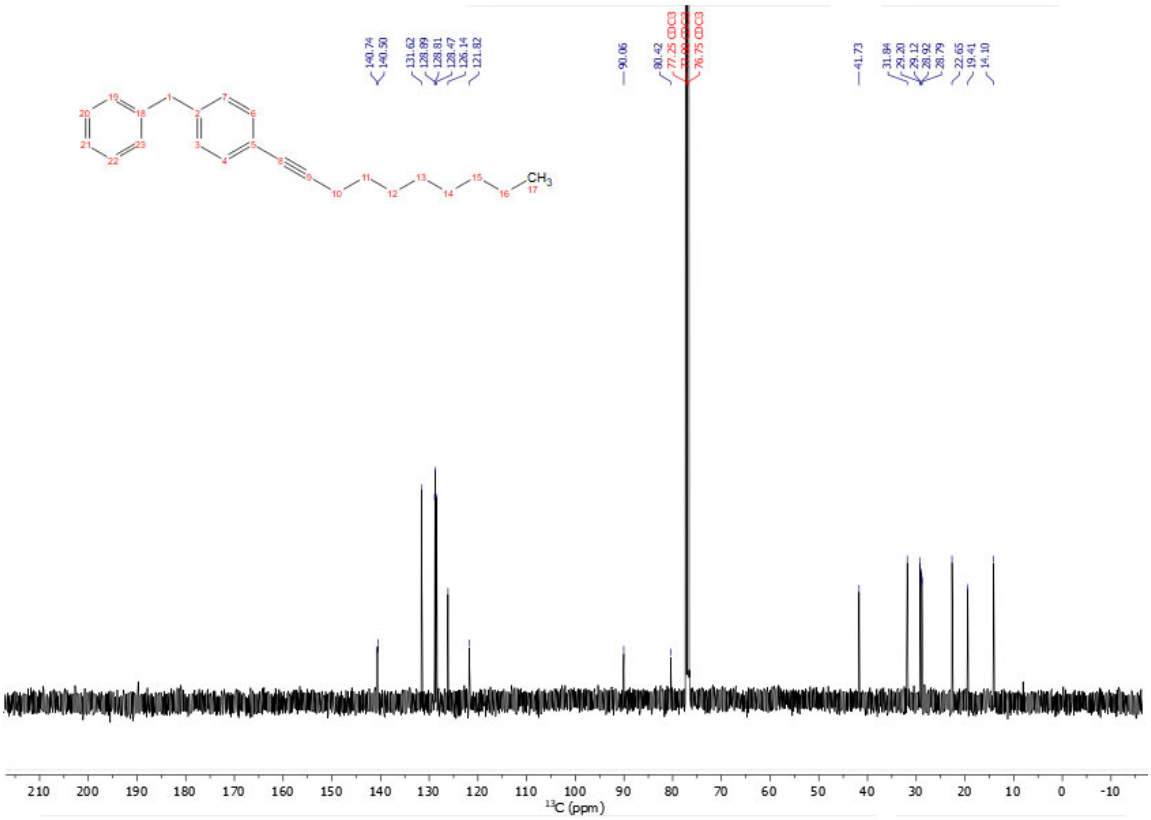


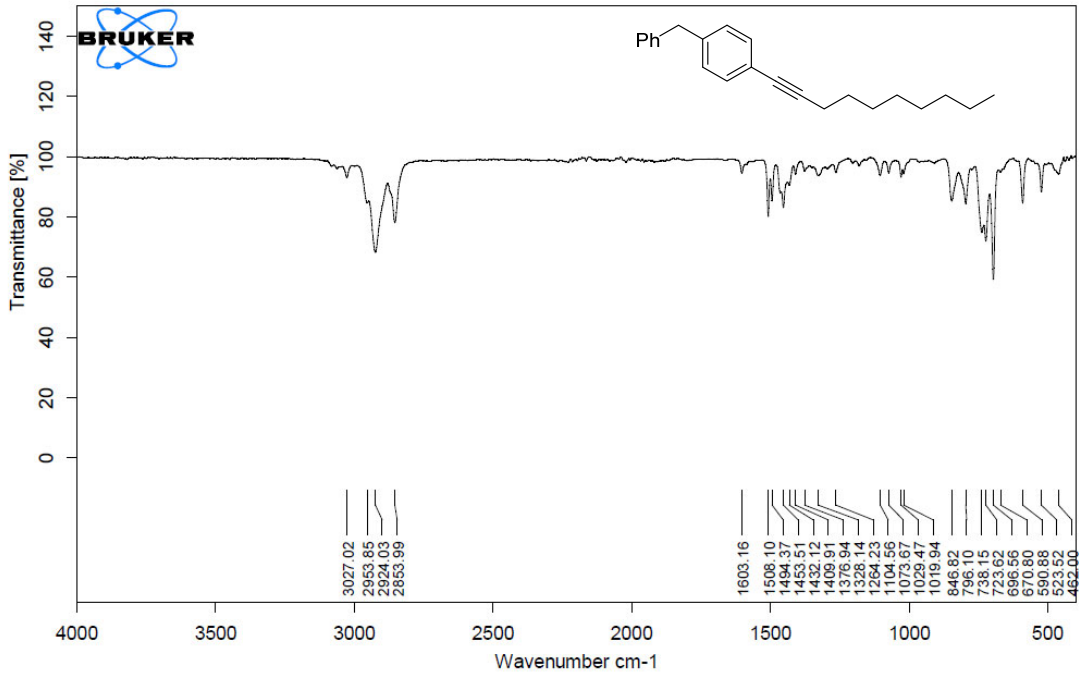


220805-05APCI- HRMS-Li-Ruohua Gui-RG-04-06_220805113243#199-207 RT: 0.48-0.50 AV: 9
T: FTMS + p APCI corona Full ms [150.0000-500.0000]
m/z= 271.13892-271.15714

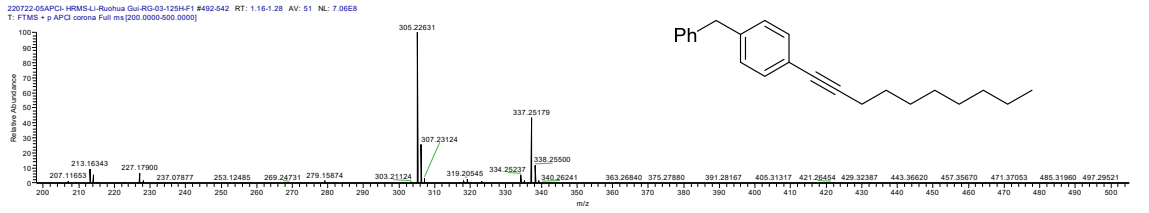
m/z	Intensity	Relative	Resolution	Charge	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
271.14840	97683528.0	100.00	34248.36	1.00	271.14813	1.01	12.5	$C_{21}H_{19}$

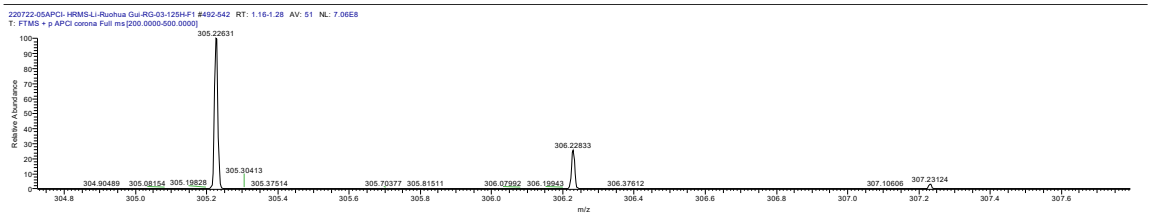

20220721_RG-03-125H-F1_PROTON_01
RG-03-125H-F1
C (m) 7.17
B (m) 7.09
D (m) 7.30
A (s) 3.96
E (t) 2.38
H (m) 1.29
G (p) 1.43
I (m) 0.88
^{1}H (ppm)


^{13}C (ppm)



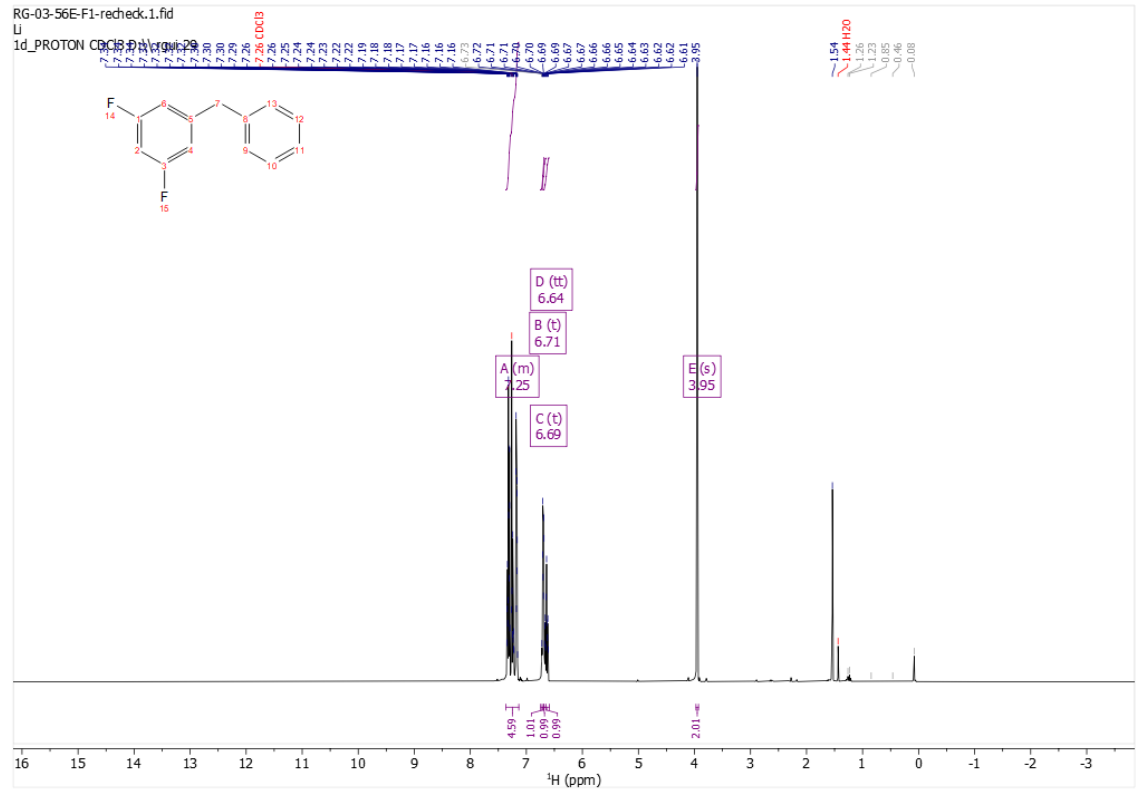
220722-05APCI- HRMS-Li-Ruohua Gui-RG-... 07/22/22 12:25:37

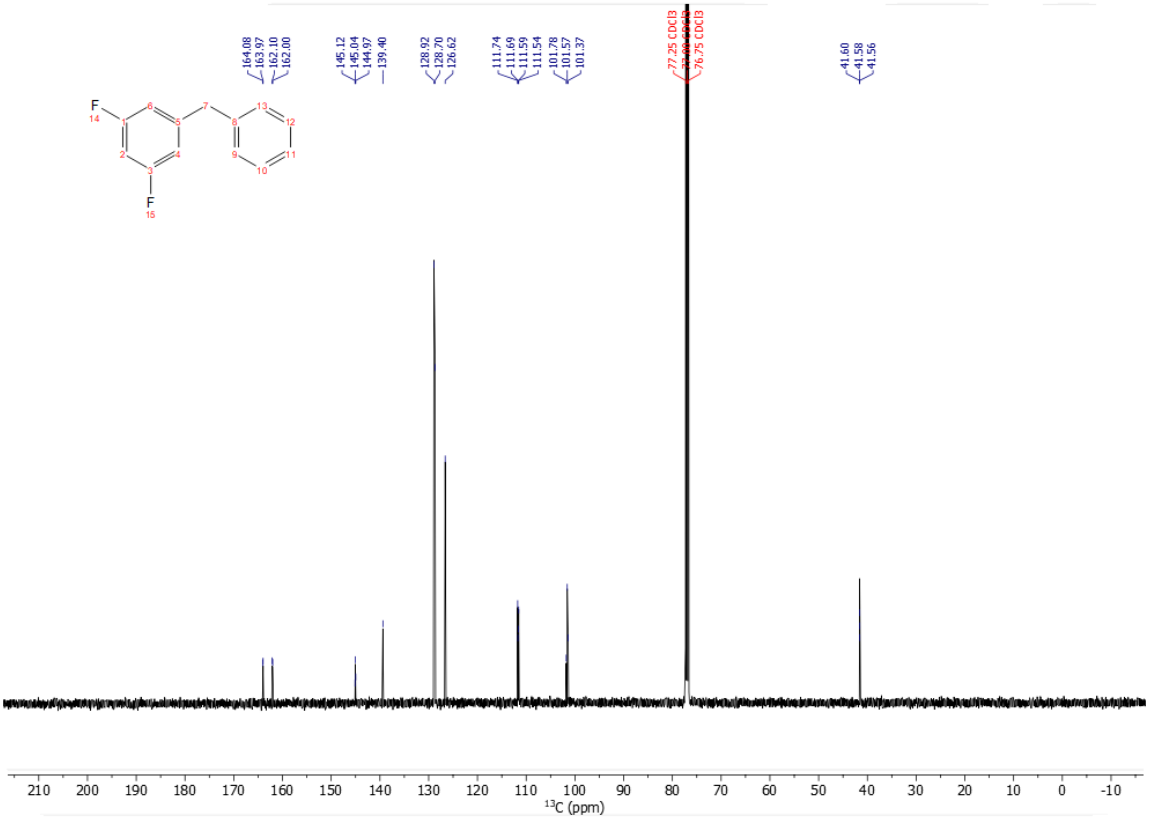


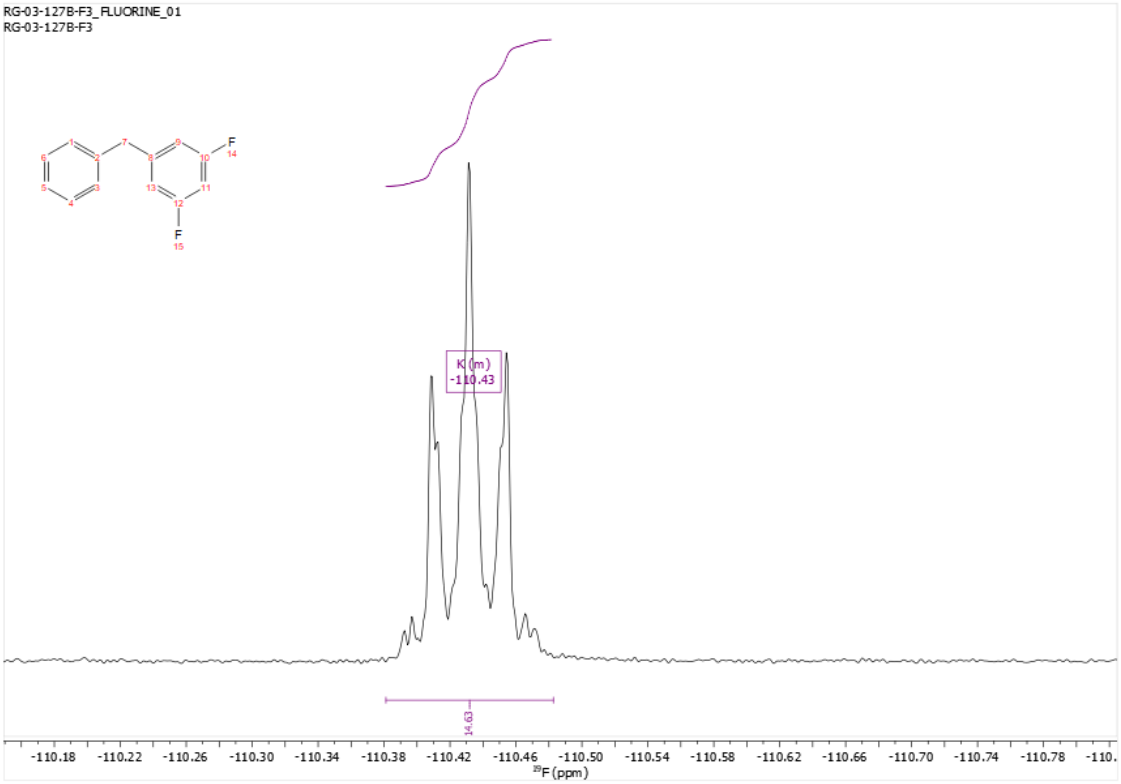


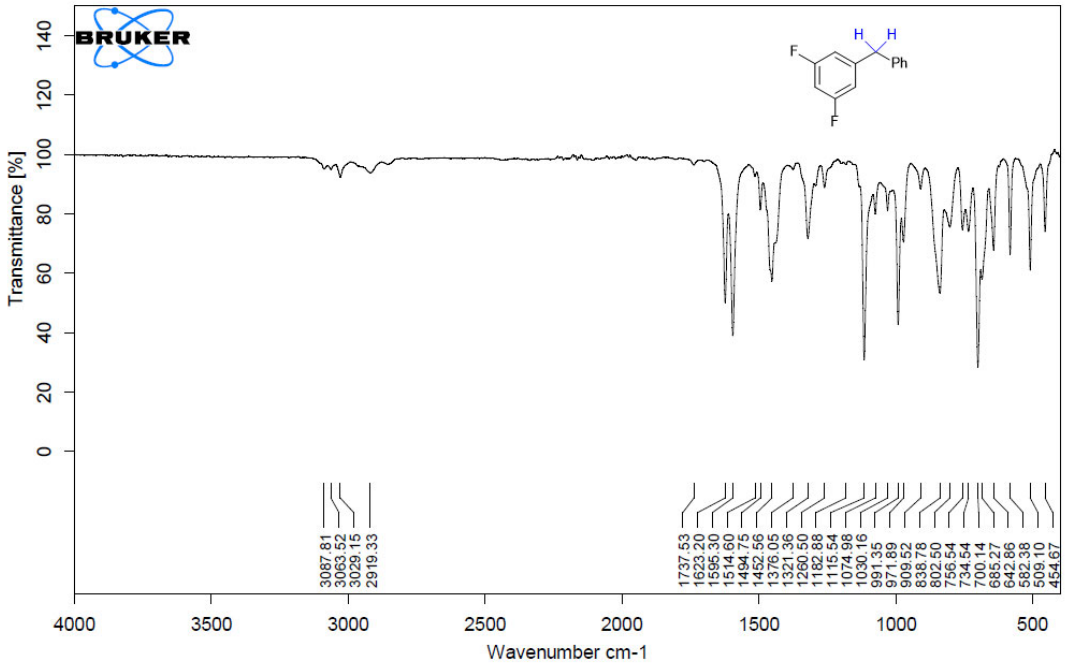
220722-05APCI- HRMS-Li-Ruohua Gui-RG-03-125H-F1#492-542 RT: 1.16-1.28 AV: 51
T: FTMS + p APCI corona Full ms [200.0000-500.0000]
m/z= 305.21277-305.25133

m/z	Intensity	Relative	Resolution	Charge	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
305.22631	733372224.0	100.00	29638.38	1.00	305.22638	-0.22	9.5	$C_{23}H_{29}$

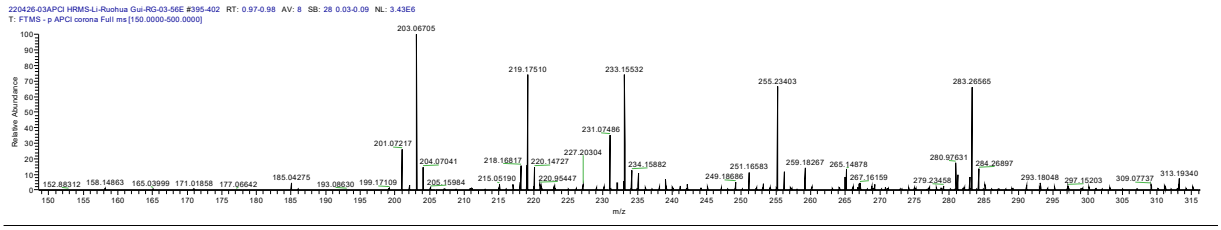

RG-03-56E-F1-recheck.1.fid
Li
1d_PROTON CDCl3 D1 1 1 qqui 29
D (tt)
6.64
B (t)
6.71
A (m)
7.25
C (t)
6.69
E (s)
3.95
4.59
1.01
0.99
0.99
2.01
1H (ppm)

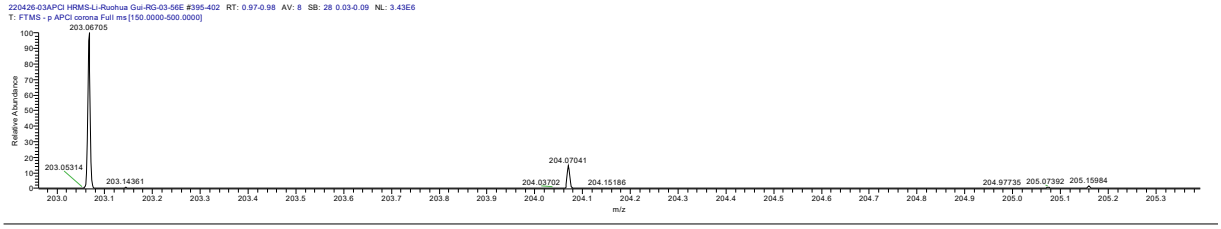

164.08
163.97
162.10
162.00
145.12
145.04
144.97
139.40
128.92
128.70
126.62
111.74
111.69
111.59
111.54
101.78
101.57
101.37
77.25 CDCl3
76.75 CDCl3
41.60
41.58
41.56
13C (ppm)


RG-03-127B-F3_FLUORINE_01
RG-03-127B-F3
K (m)
-110.43
14.63
-110.18
-110.22
-110.26
-110.30
-110.34
-110.38
-110.42
-110.46
-110.50
-110.54
-110.58
-110.62
-110.66
-110.70
-110.74
-110.78
^{19}F (ppm)



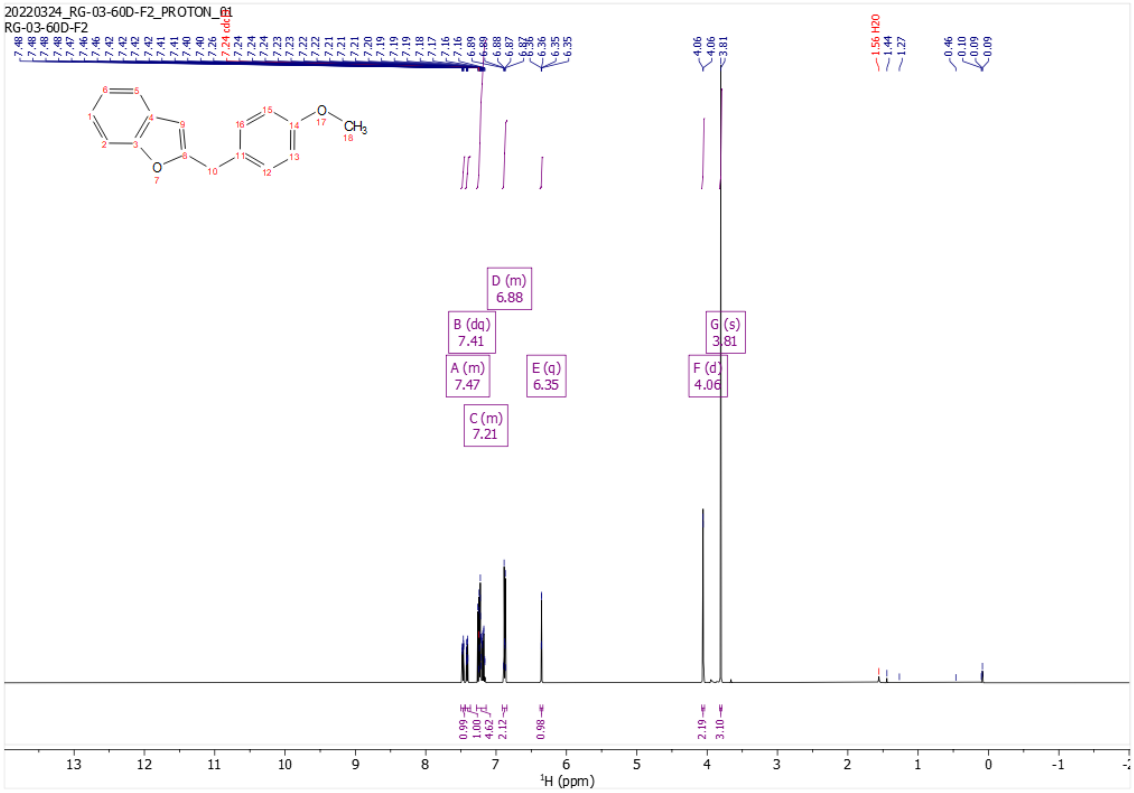
220426-03APCI HRMS-Li-Ruohua Gui-RG-0... 04/26/22 10:01:21

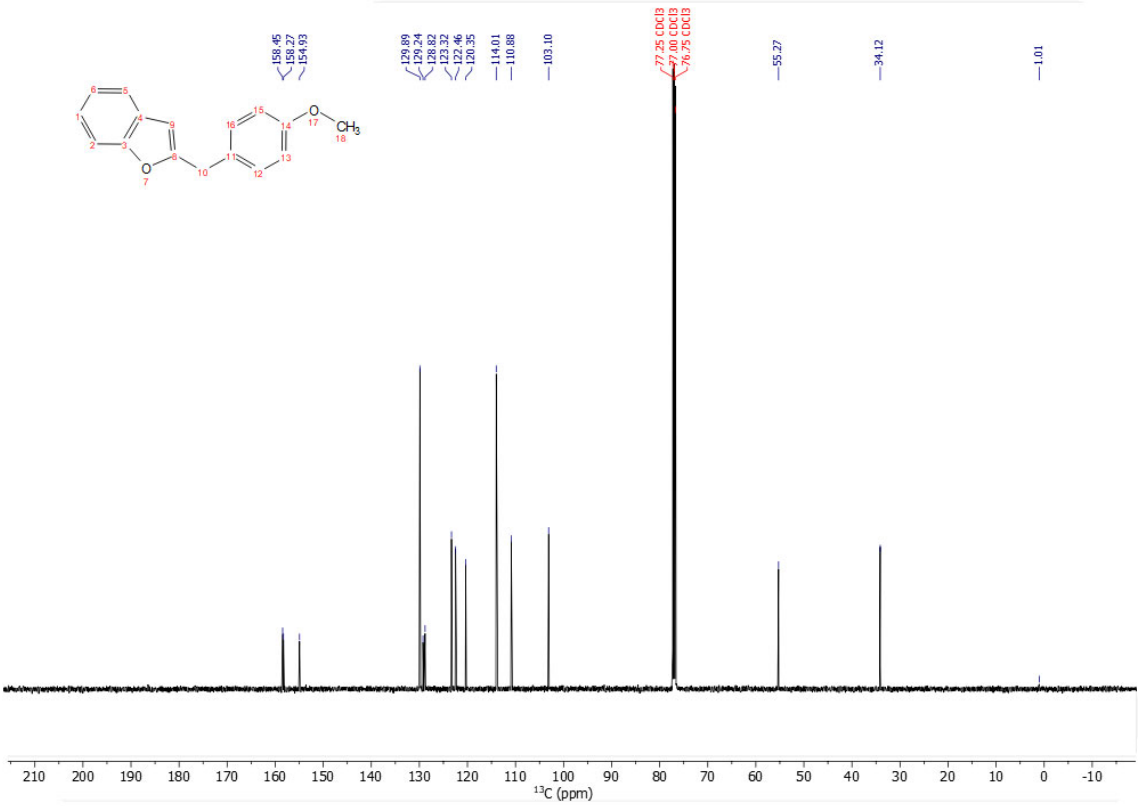




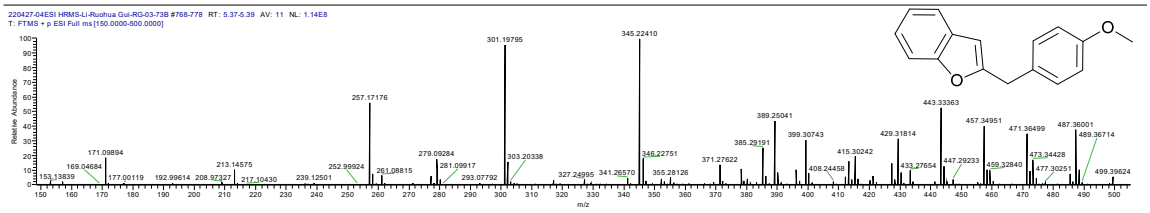
220426-03APCI HRMS-Li-Ruohua Gui-RG-03-56E#395-402 RT: 0.97-0.98 AV: 8
SB: 28 0.03-0.09
T: FTMS - p APCI corona Full ms [150.0000-500.0000]
m/z= 203.05635-203.07357

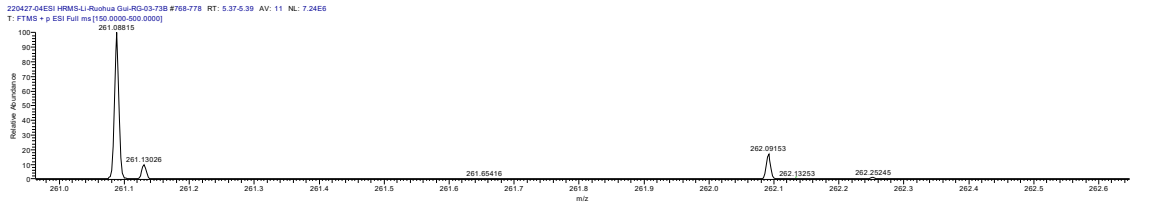
m/z	Intensity	Relative	Resolution	Charge	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
203.06705	3481768.8	100.00	35440.10	1.00	203.06778	-3.60	8.5	$C_{13}H_9F_2$


20220324_RG-03-60D-F2_PROTON_01
RG-03-60D-F2
D (m)
6.88
B (dq)
7.41
G (s)
3.81
A (m)
7.47
E (q)
6.35
F (d)
4.06
C (m)
7.21
1.56 H2O
¹H (ppm)


158.45
158.27
154.93
129.89
129.24
128.82
123.32
122.46
120.35
114.01
110.88
103.10
77.25 CDCl3
77.00 CDCl3
76.75 CDCl3
55.27
34.12
1.01
¹³C (ppm)

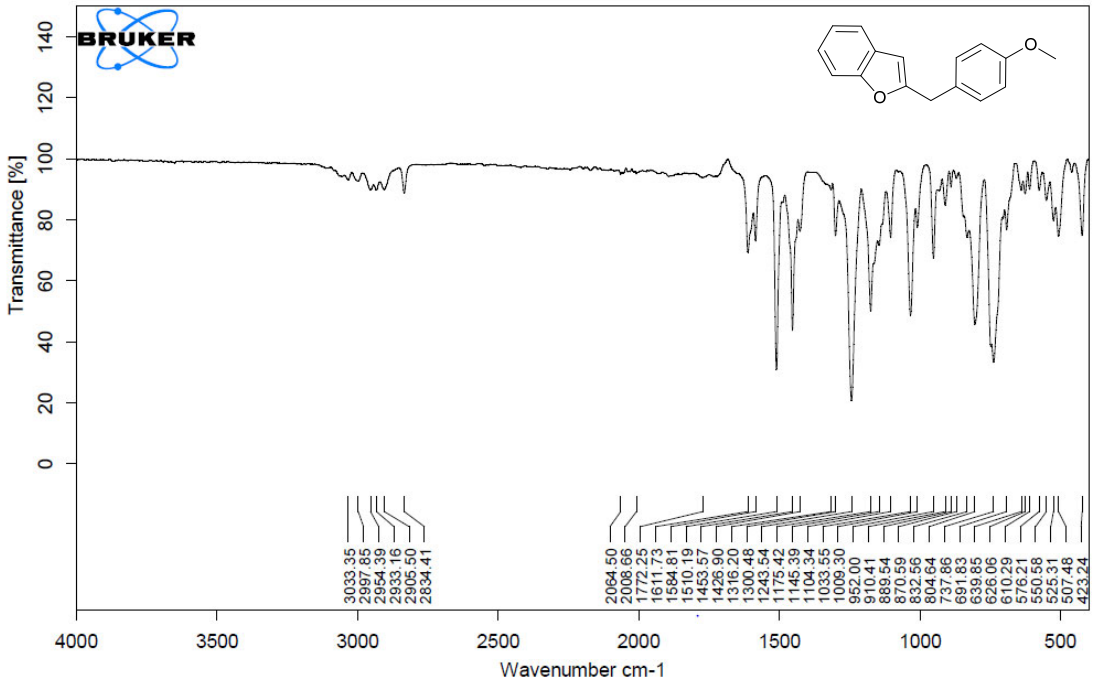
220427-04ESI HRMS-Li-Ruohua Gui-RG-03... 04/27/22 10:57:33

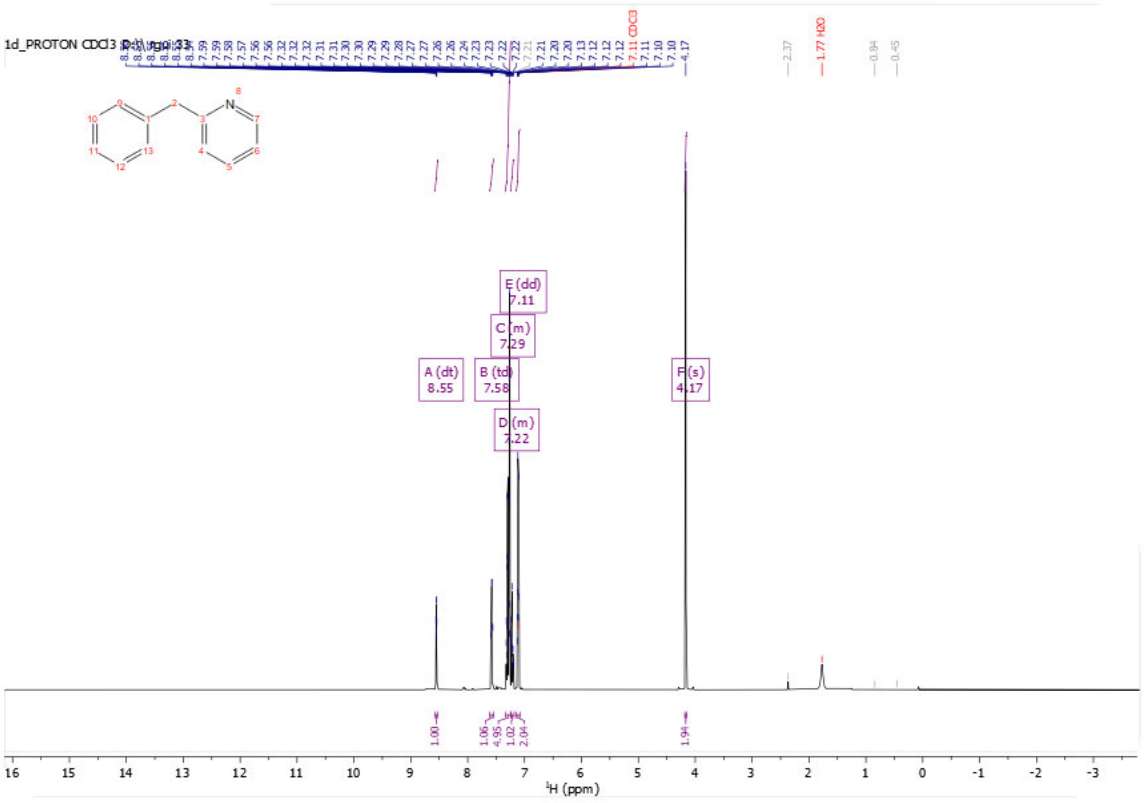


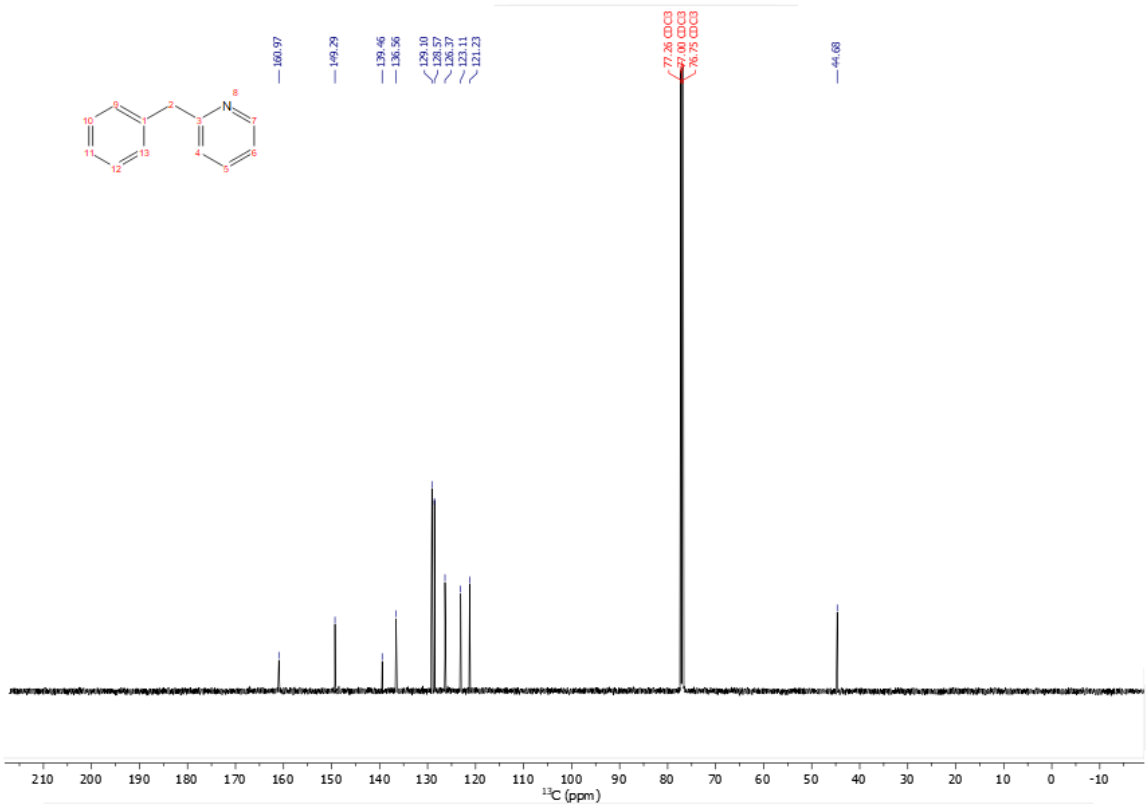


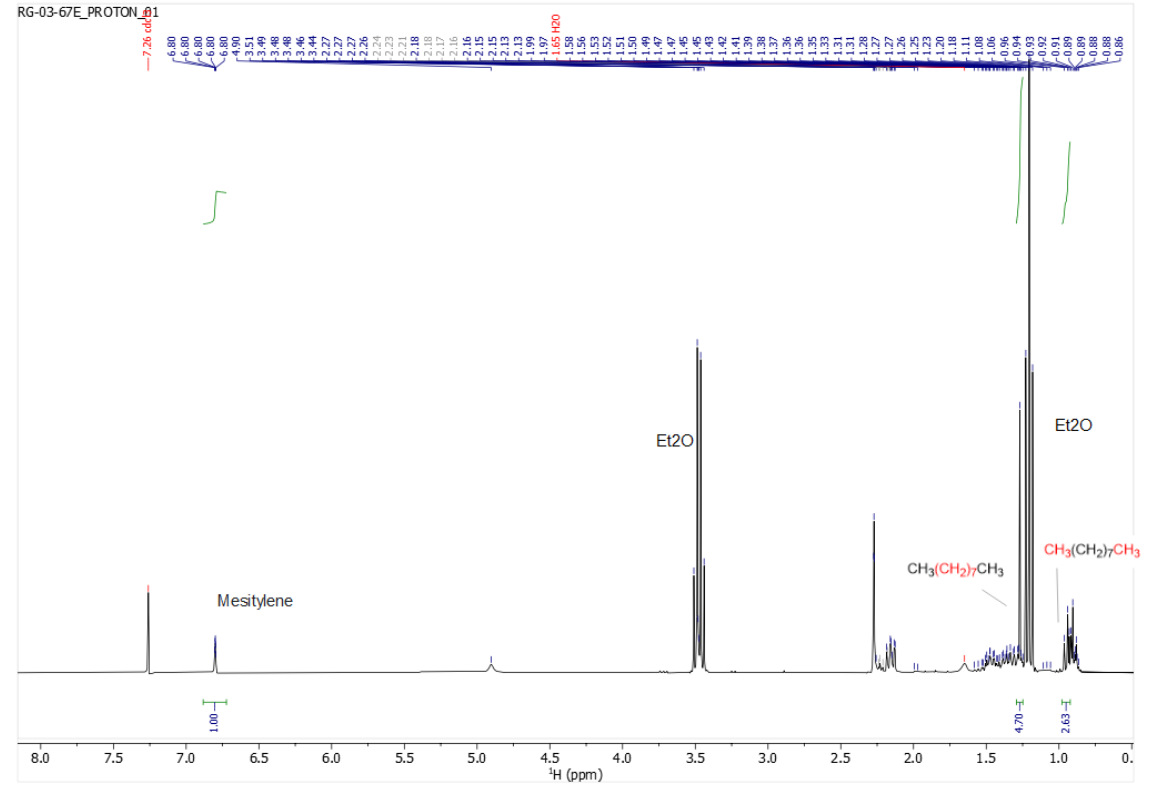
220427-04ESI HRMS-Li-Ruohua Gui-RG-03-73B#768-778 RT: 5.37-5.39 AV: 11
T: FTMS + p ESI Full ms [150.0000-500.0000]
m/z= 261.08186-261.09564

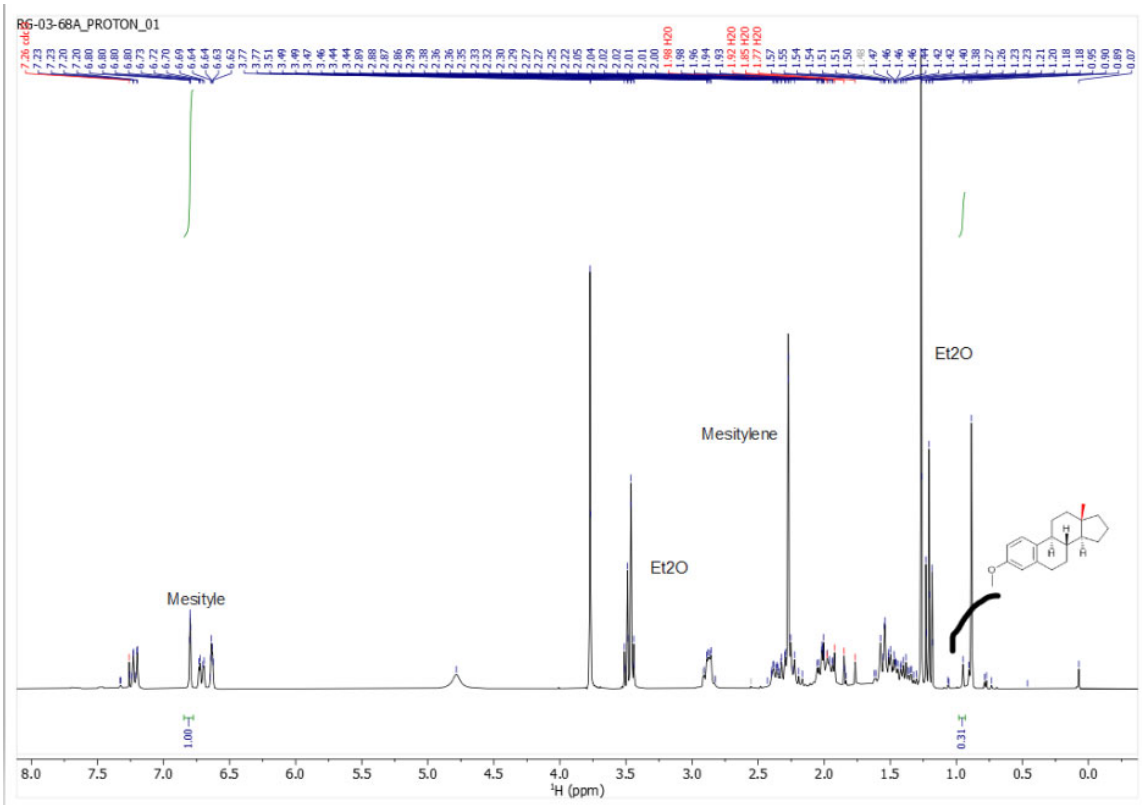
m/z	Intensity	Relative	Resolution	Charge	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
261.08815	7278741.5	100.00	34251.95	1.00	261.08860	-1.72	9.5	$C_{16}H_{14}O_2Na$

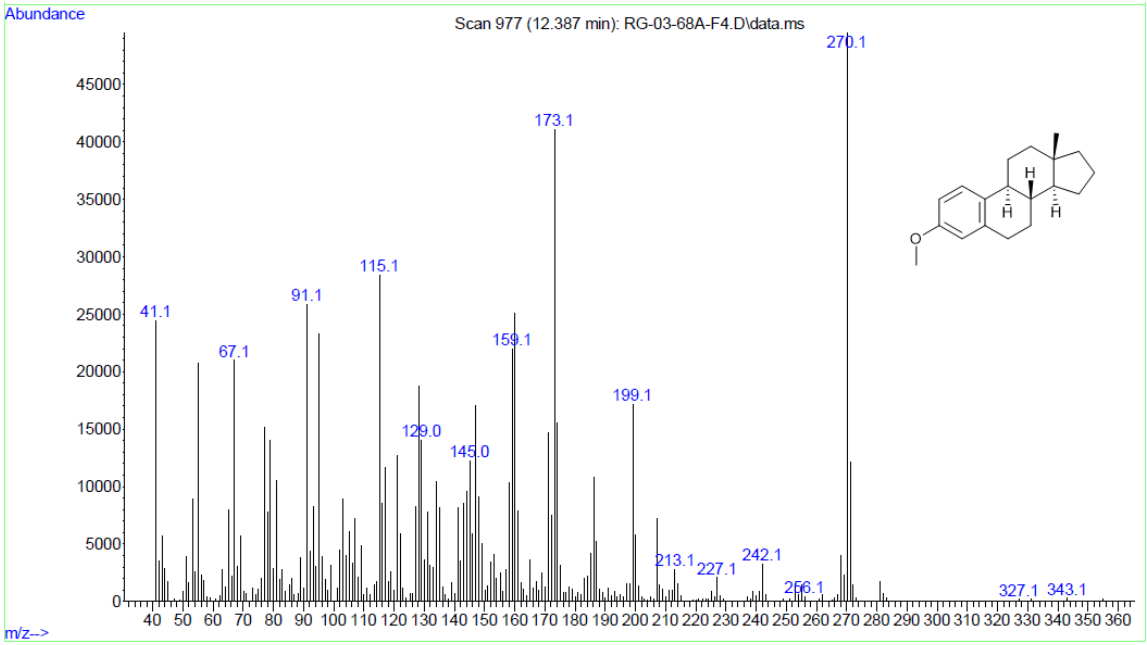


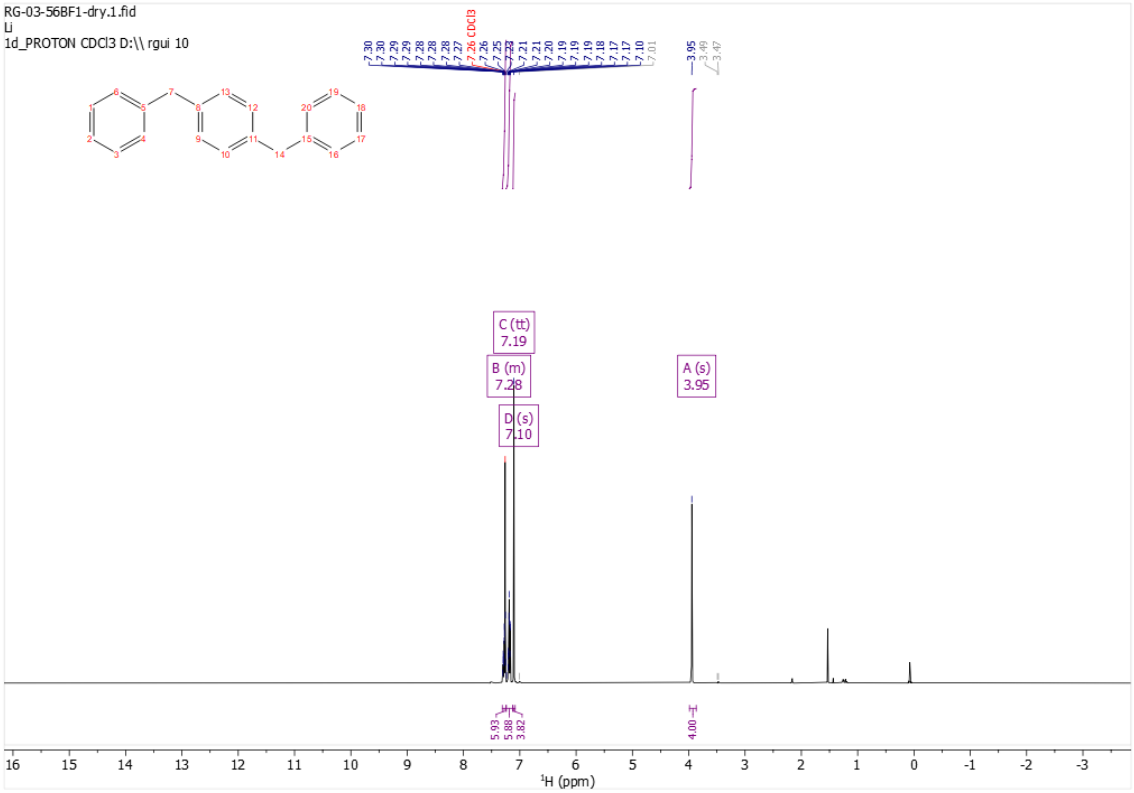

E (dd)
7.11
C (m)
7.29
A (dt)
8.55
B (tdd)
7.58
F (s)
4.17
D (m)
7.22
1.00
1.06
4.95
1.02
2.04
1.94
¹H (ppm)

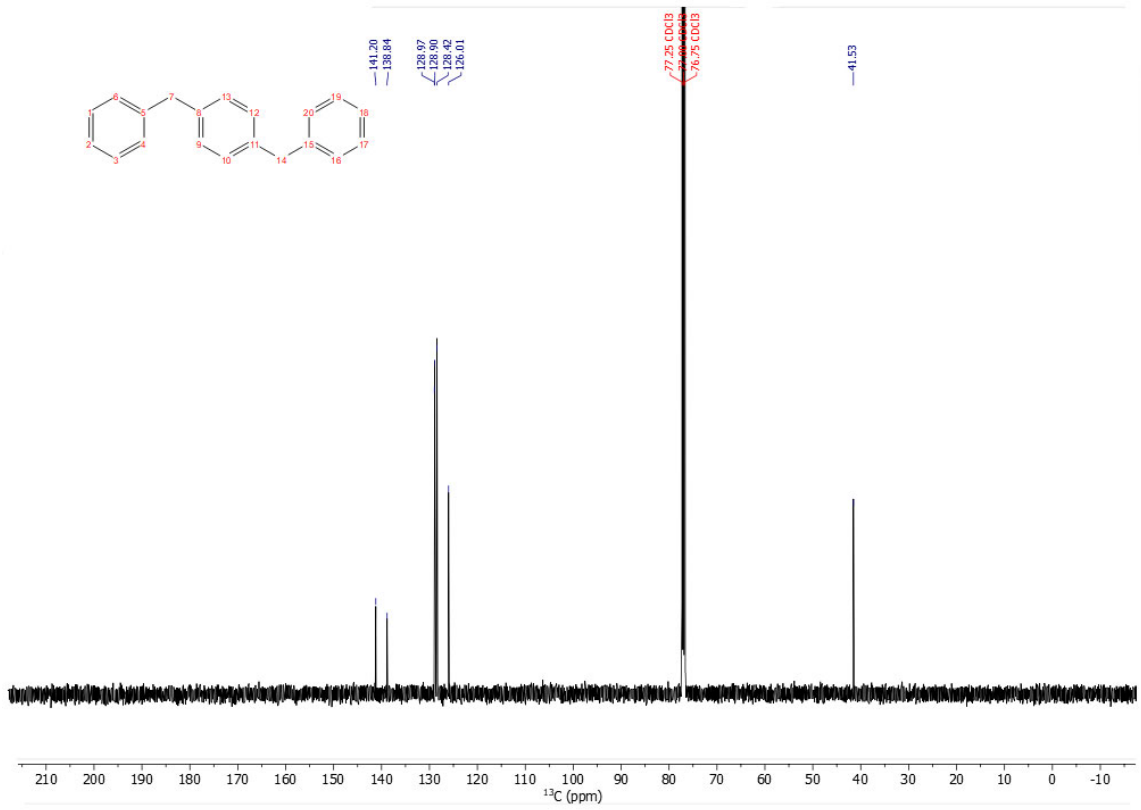

160.97
149.29
139.46
136.56
129.10
128.57
126.37
123.11
121.23
77.26 CDCl3
77.00 CDCl3
76.75 CDCl3
44.68
¹³C (ppm)

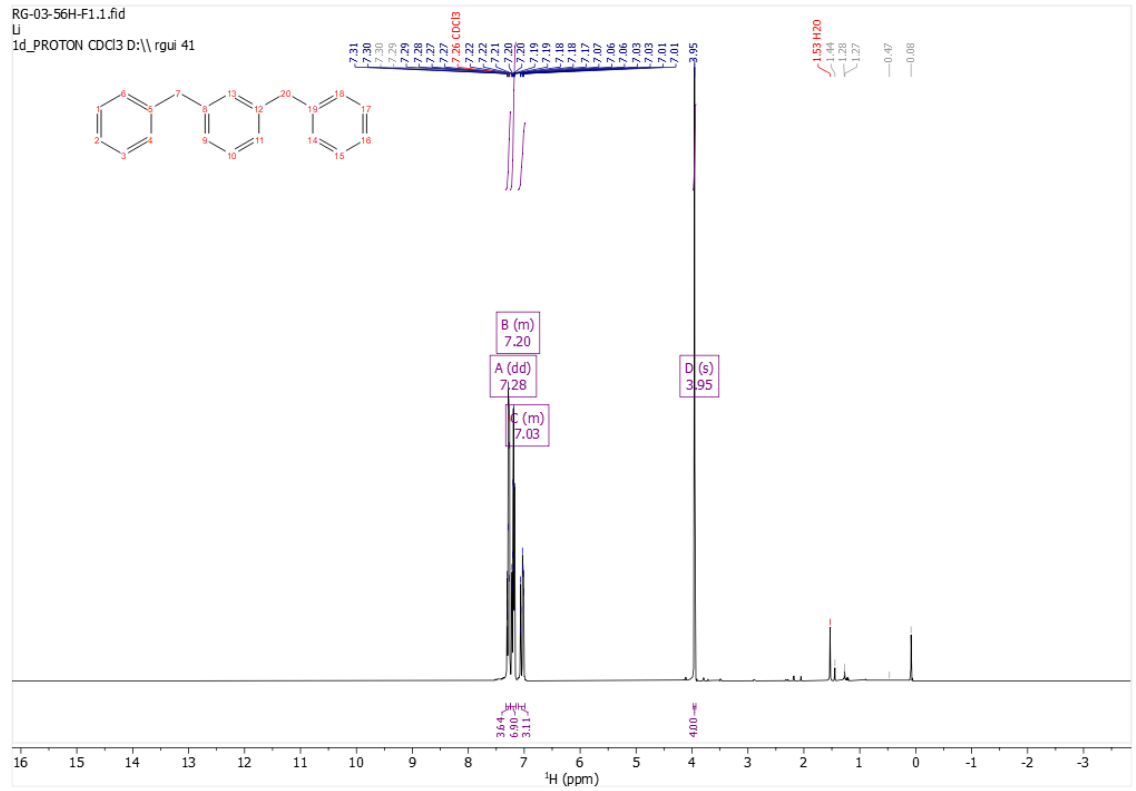

RG-03-67E_PROTON_01
Et2O
Et2O
Mesitylene
CH3(CH2)7CH3
CH3(CH2)7CH3
1.00
4.70
2.63
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.
1H (ppm)

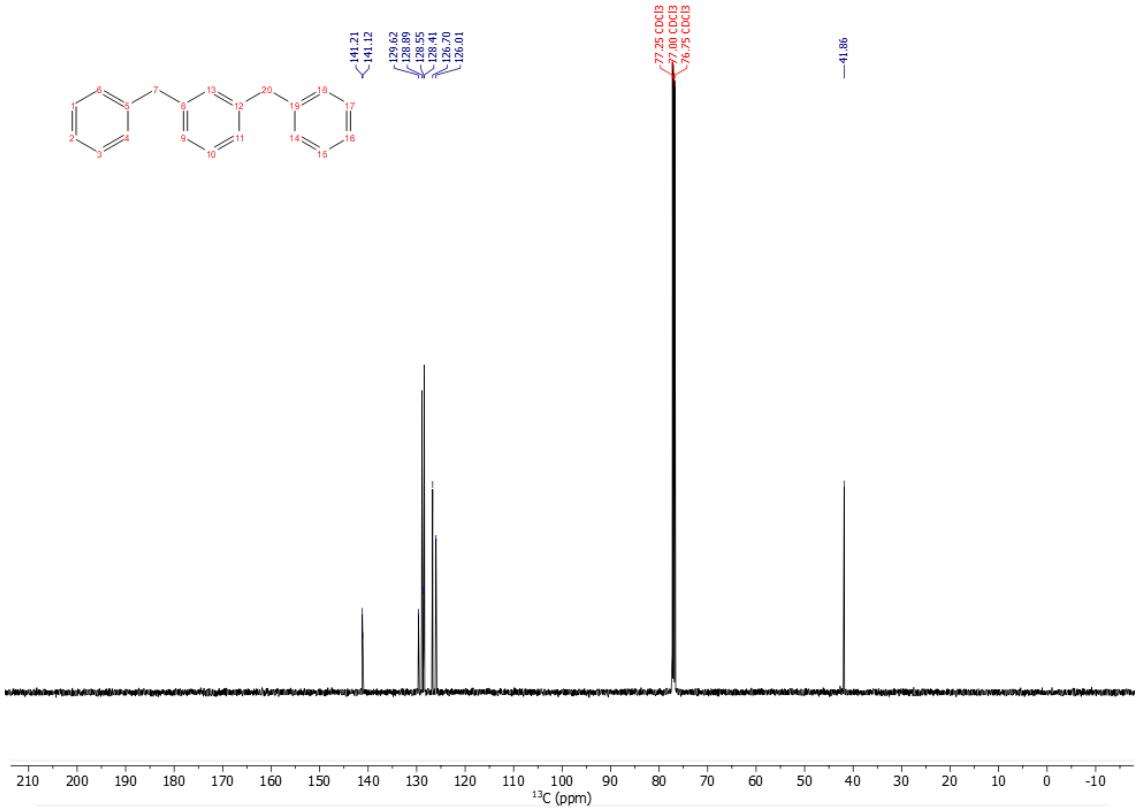

RG-03-68A_PROTON_01
Et2O
Mesitylene
Et2O
Mesityle
1.00
0.31
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
1H (ppm)

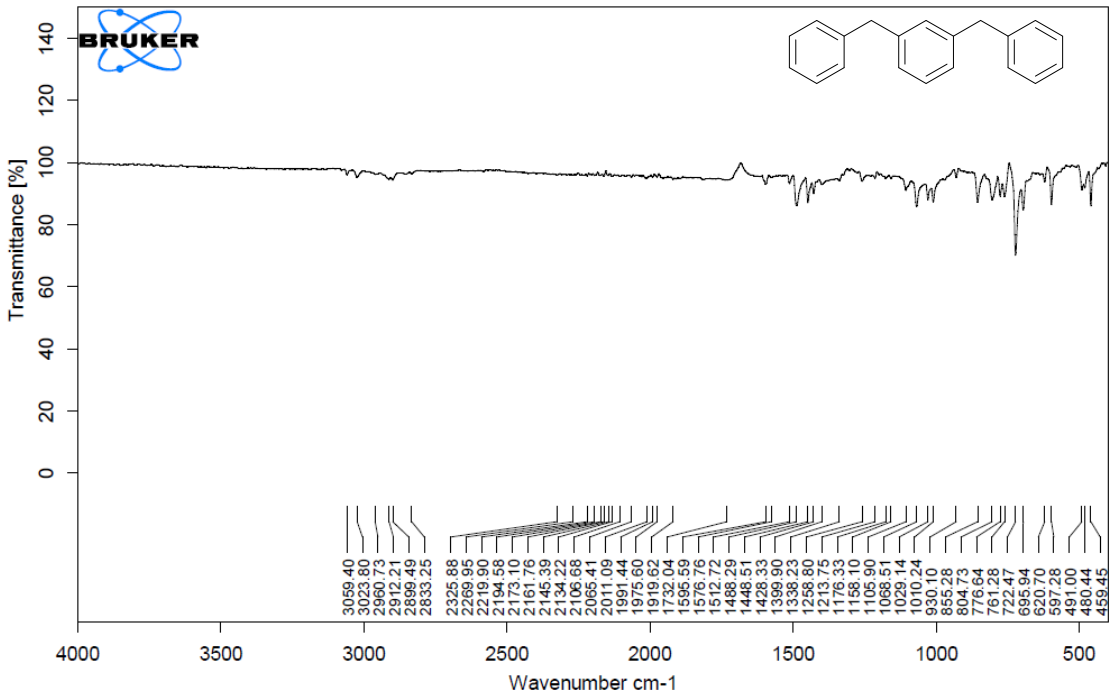

Abundance
Scan 977 (12.387 min): RG-03-68A-F4.D\data.ms
270.1
173.1
115.1
91.1
41.1
67.1
159.1
199.1
129.0
145.0
213.1
227.1
242.1
256.1
327.1
343.1
m/z-->


RG-03-56BF1-dry.1.fid
1d_PROTON CDCl3 D:\\ rgui 10
C (tt)
7.19
B (m)
7.28
D (s)
7.10
A (s)
3.95
5.93
5.88
3.82
4.00
¹H (ppm)

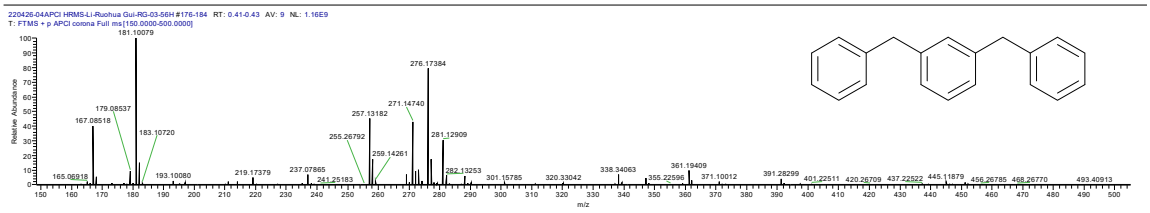

141.20
138.84
128.97
128.90
128.42
126.01
77.25 CDCl3
77.00 CDCl3
76.75 CDCl3
41.53
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
13C (ppm)


RG-03-56H-F1.1.fid
Li
1d_PROTON CDCl3 D:\\ rgui 41
7.31
7.30
7.30
7.29
7.29
7.28
7.28
7.27
7.27
7.26 CDCl3
7.22
7.22
7.21
7.20
7.20
7.19
7.19
7.18
7.18
7.17
7.17
7.07
7.06
7.06
7.03
7.03
7.01
7.01
3.95
1.53 H2O
1.44
1.28
1.27
0.47
0.08
B (m)
7.20
A (dd)
7.28
C (m)
7.03
D (s)
3.95
3.64
6.90
3.11
4.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
1H (ppm)


141.21
141.12
129.62
128.89
128.55
128.44
126.70
126.01
77.25 CDCl3
77.00 CDCl3
76.75 CDCl3
41.86
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
13C (ppm)


BRUKER
Transmittance [%]
0 20 40 60 80 100 120 140
3059.40
3023.80
2960.73
2912.21
2899.49
2833.25
2325.88
2269.95
2219.90
2194.58
2173.10
2161.76
2145.39
2134.22
2106.68
2065.41
2011.09
1991.44
1975.60
1919.62
1732.04
1595.59
1576.76
1512.72
1488.29
1448.51
1428.33
1399.90
1338.23
1258.80
1213.75
1176.33
1158.10
1105.90
1068.51
1029.14
1010.24
930.10
855.28
804.73
776.64
761.28
722.47
695.94
620.70
587.28
491.00
480.44
459.45
4000 3500 3000 2500 2000 1500 1000 500
Wavenumber cm-1

220426-04APCI HRMS-Li-Ruohua Gui-RG-0... 04/26/22 10:14:59

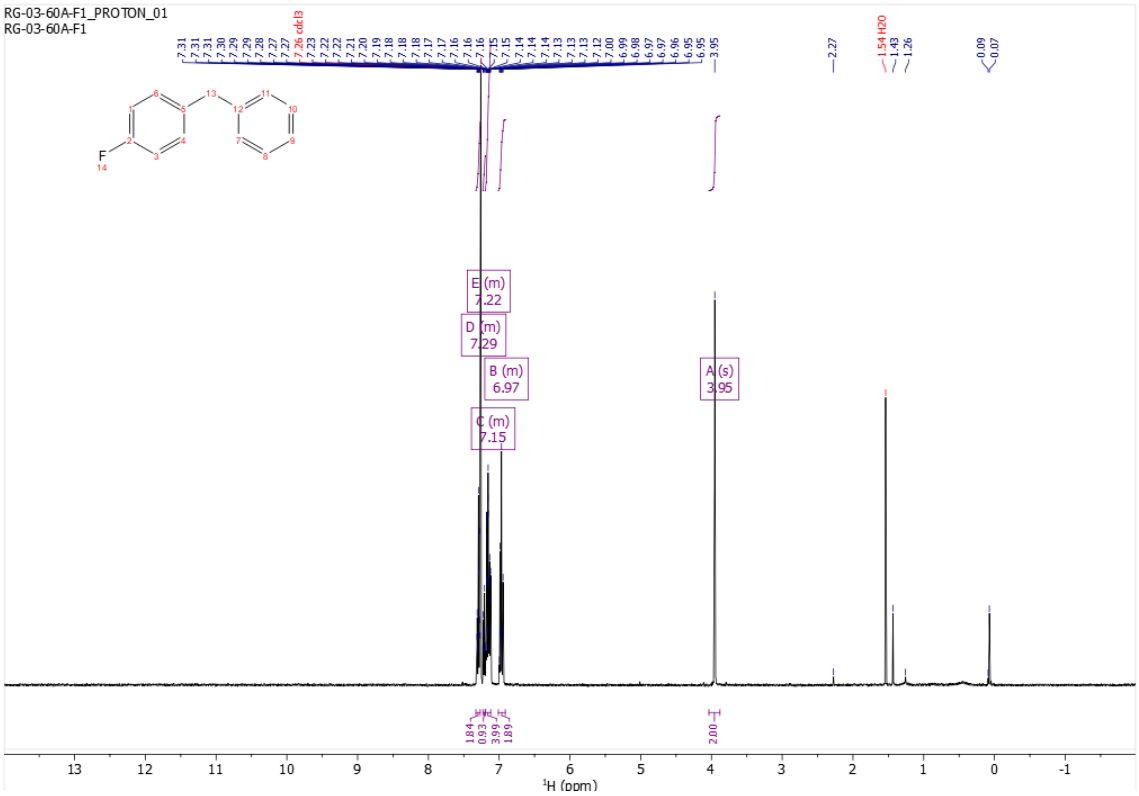


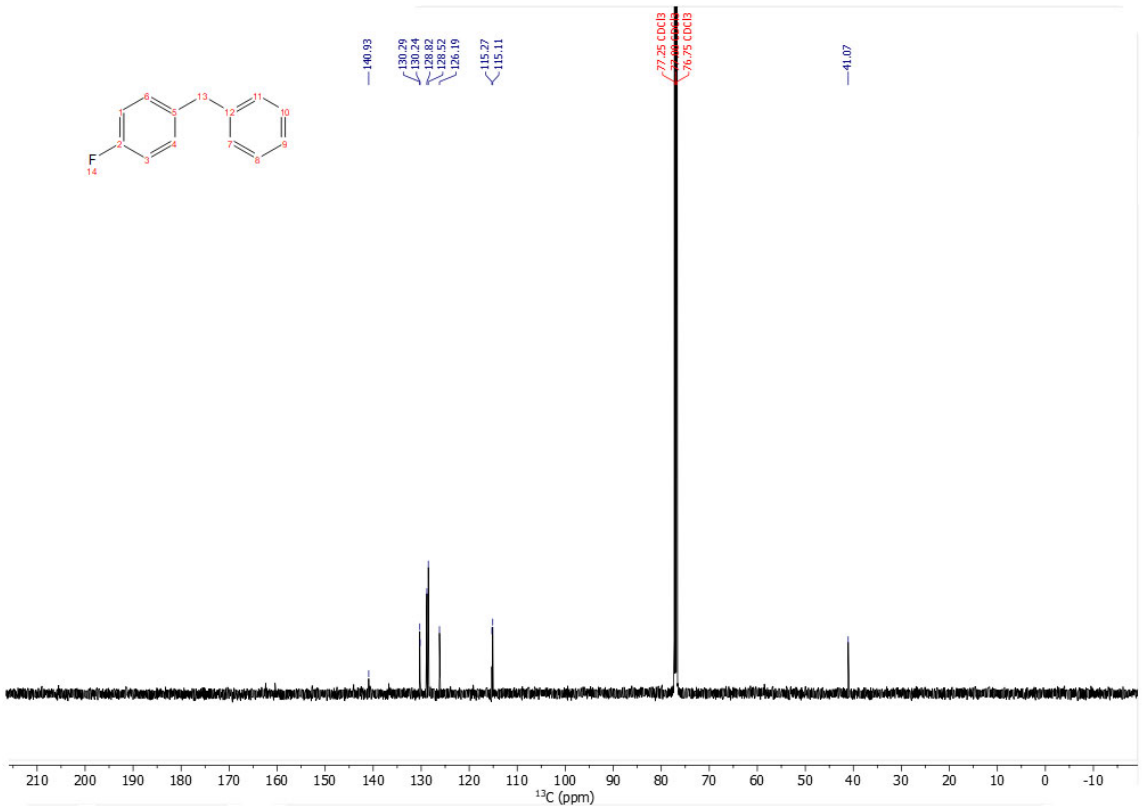
220426-04APCI HRMS-Li-Ruohua Gui-RG-03-56H#176-184 RT: 0.41-0.43 AV: 9
T: FTMS + p APCI corona Full ms [150.0000-500.0000]
m/z= 281.11514-281.13894

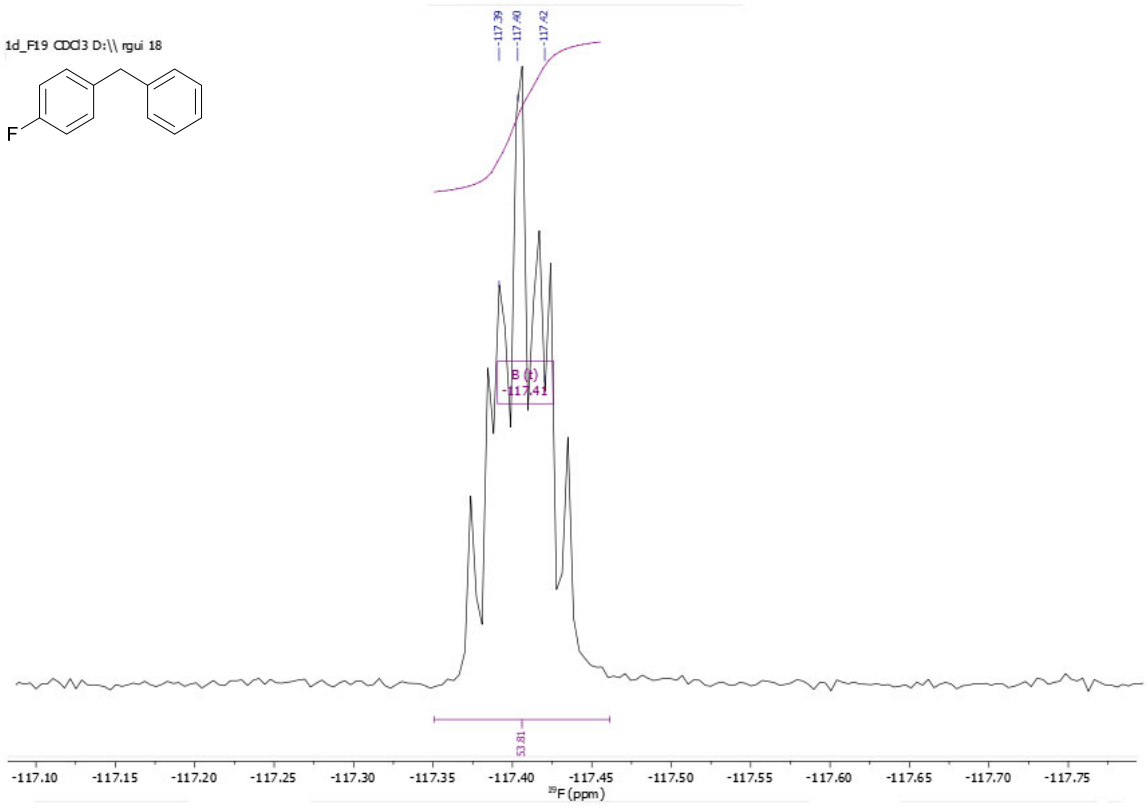
m/z	Intensity	Relative	Resolution	Charge	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
281.12909	359434112.0	100.00	31789.59	1.00	281.12845	2.27	10.5	$C_{17}H_{17}O_2N_2$
					281.13007	-3.49	11.5	$C_{20}H_{18}Na$

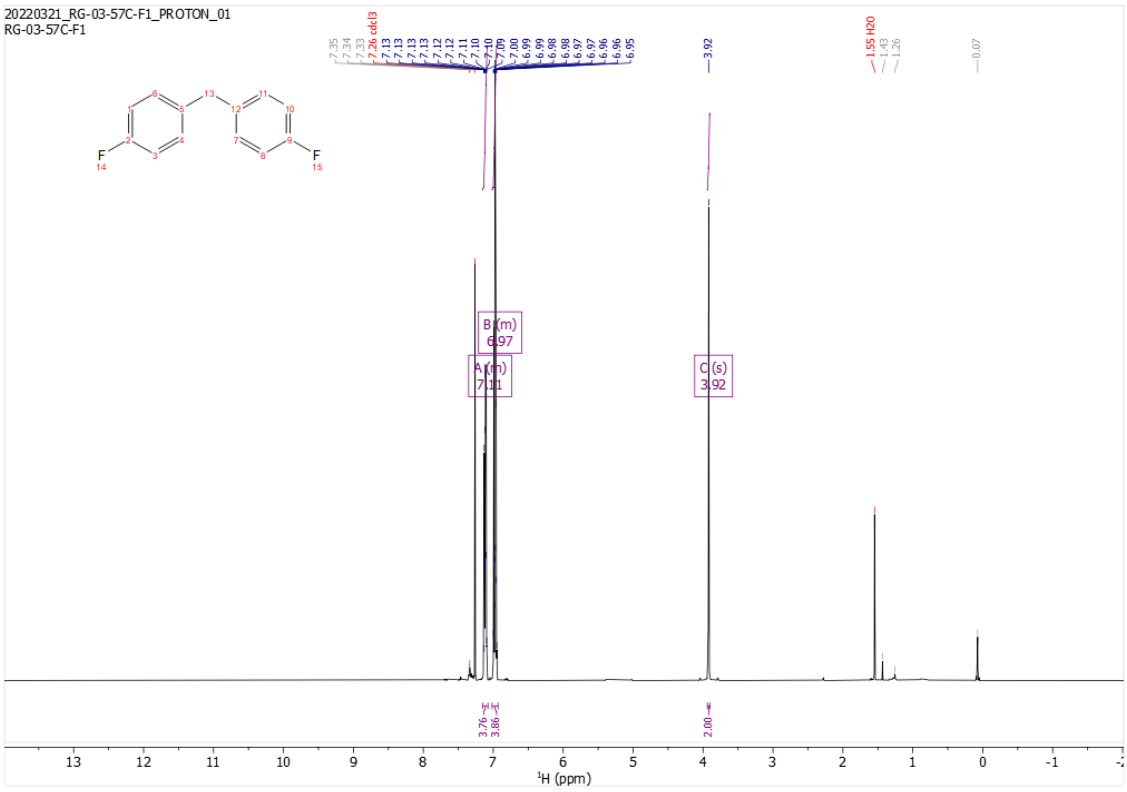
220426-04APCI HRMS-Li-Ruohua Gui-RG-03-56H#176-184 RT: 0.41-0.43 AV: 9
T: FTMS + p APCI corona Full ms [150.0000-500.0000]
m/z= 257.12449-257.13669

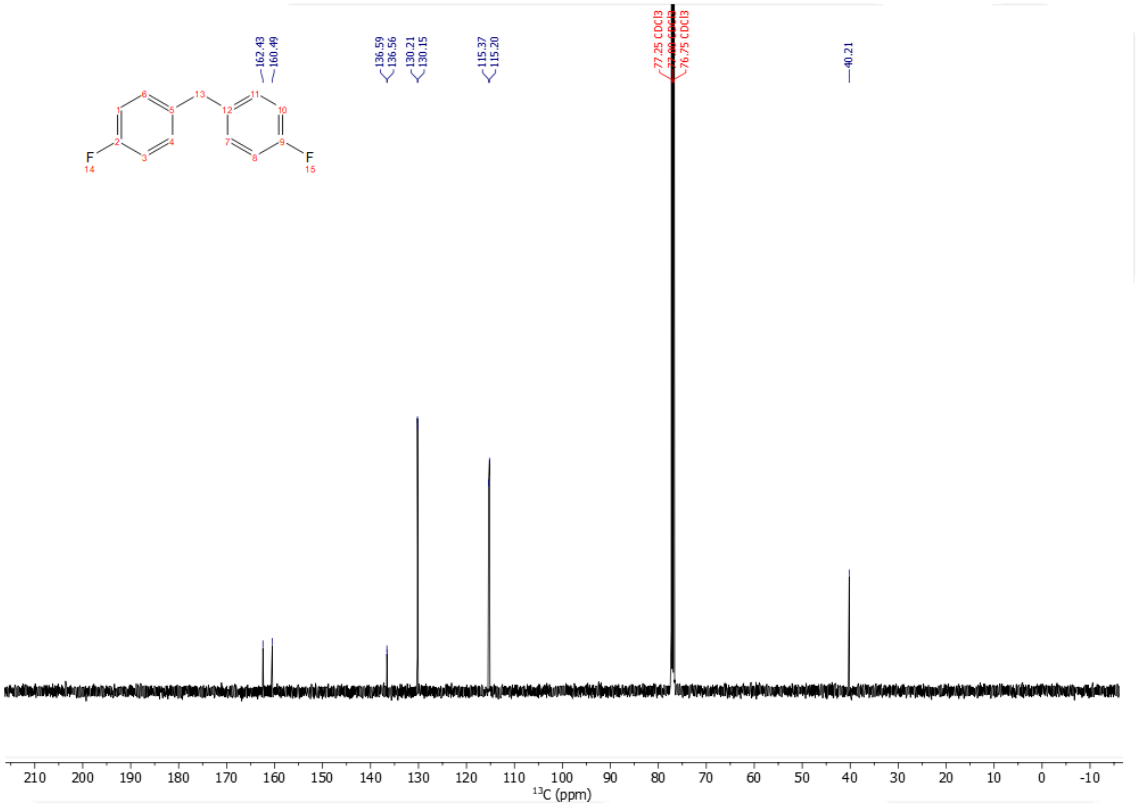
m/z	Intensity	Relative	Resolution	Charge	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
257.13182	540994112.0	100.00	32786.08	1.00	257.13248	-2.57	12.5	$C_{20}H_{17}$

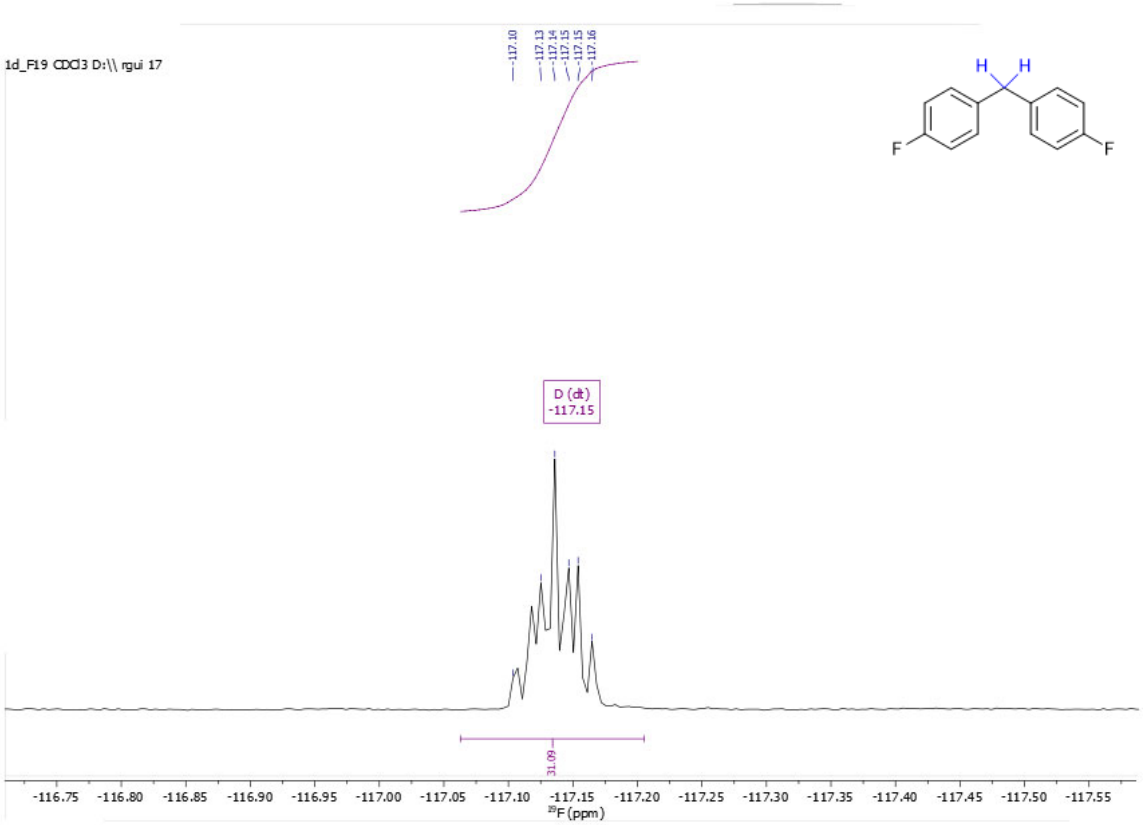


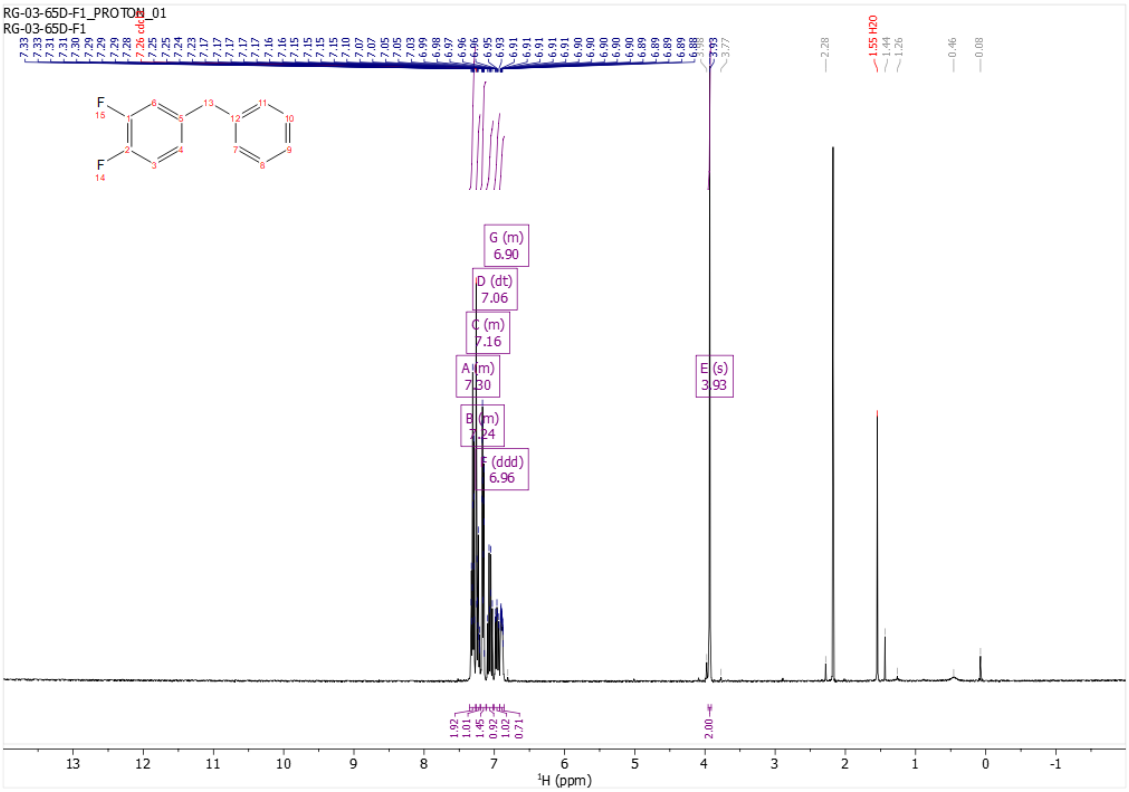

140.93
130.39
130.24
128.82
128.52
126.19
115.27
115.11
77.25 CDCl3
76.75 CDCl3
41.07
F
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
13C (ppm)

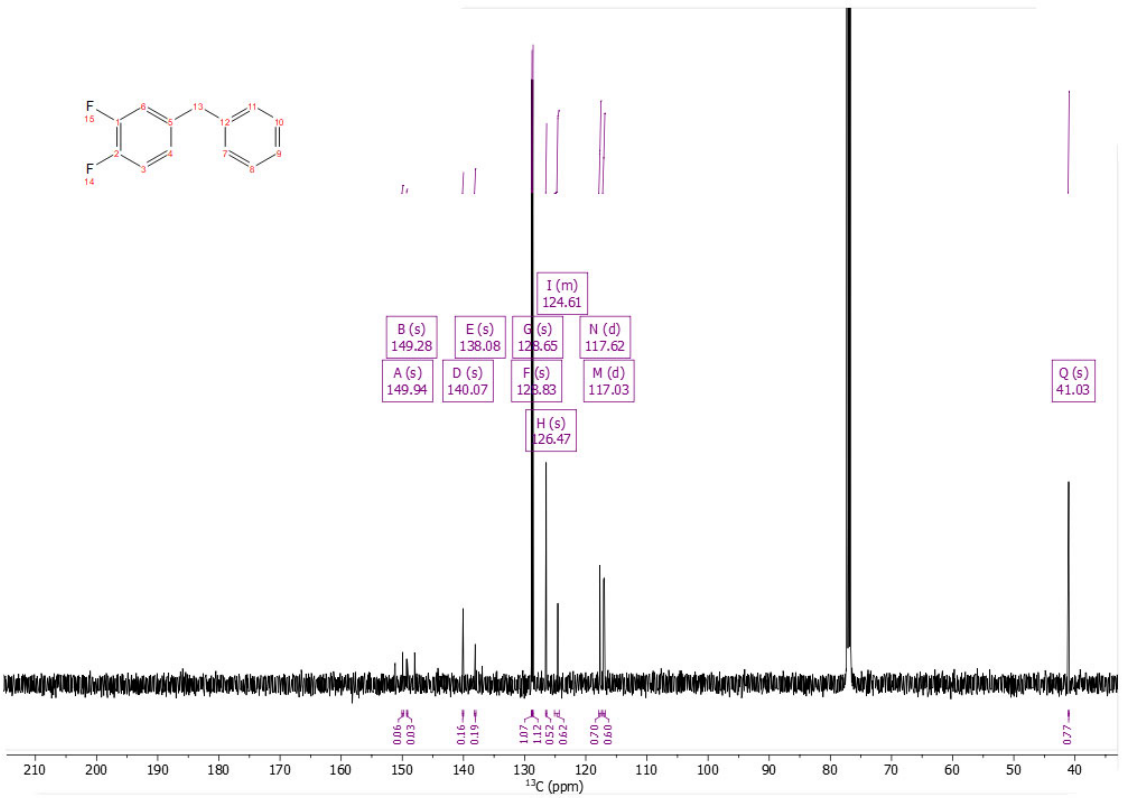

1d_F19 CDCl3 D:\\ rgui 18
F
-117.39
-117.40
-117.42
B (a)
-117.41
53.81
-117.10 -117.15 -117.20 -117.25 -117.30 -117.35 -117.40 -117.45 -117.50 -117.55 -117.60 -117.65 -117.70 -117.75
19F (ppm)

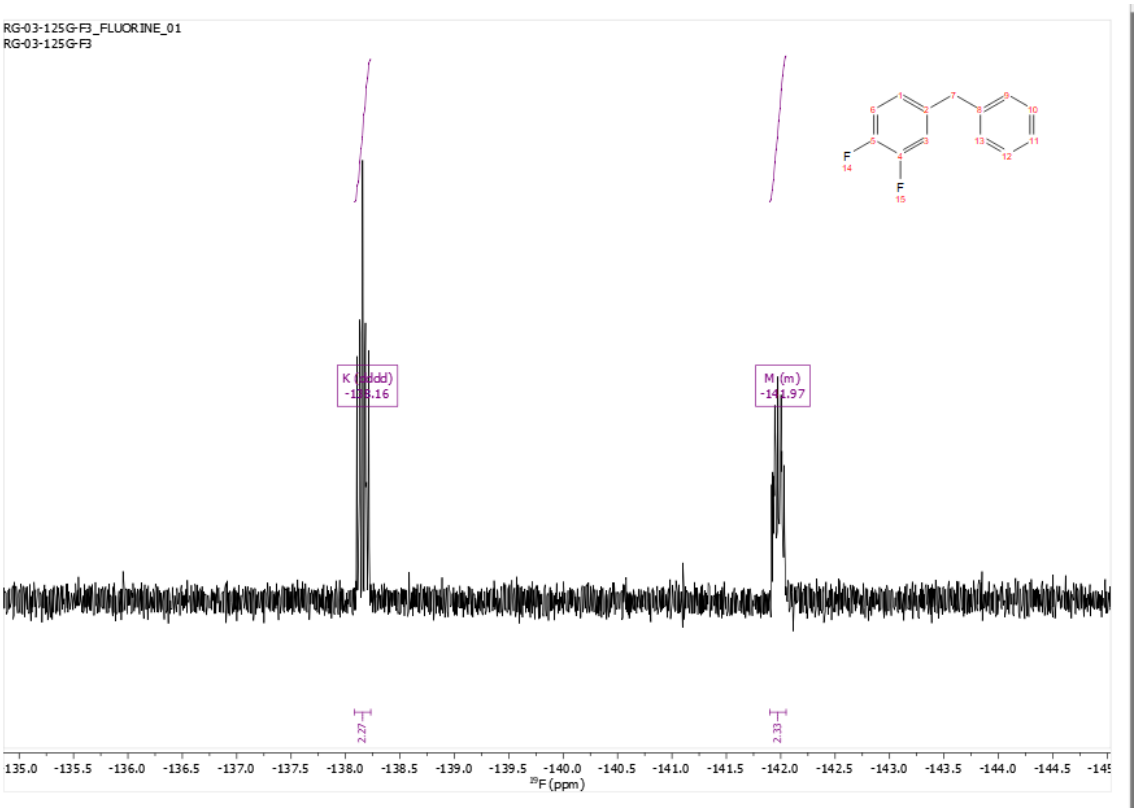

20220321_RG-03-57C-F1_PROTON_01
RG-03-57C-F1
B (m)
6.97
A (m)
7.11
C (s)
3.92
3.76
3.86
2.00
1H (ppm)

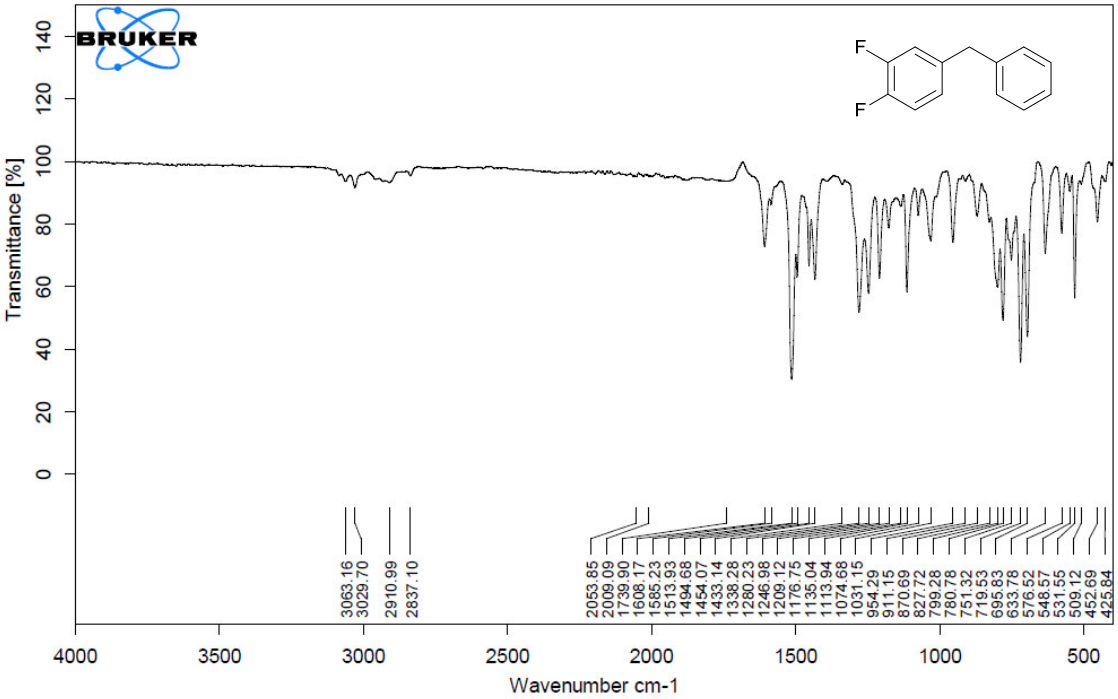

162.43
160.49
136.59
136.56
130.21
130.15
115.37
115.20
77.25 CDCl3
76.75 CDCl3
40.21
13C (ppm)


1d_F19 CDCl3 D:\\ rgui 17
-117.10
-117.13
-117.14
-117.15
-117.15
-117.16
H
H
F
F
D (dt)
-117.15
31.09
-116.75
-116.80
-116.85
-116.90
-116.95
-117.00
-117.05
-117.10
-117.15
-117.20
-117.25
-117.30
-117.35
-117.40
-117.45
-117.50
-117.55
^{19}F (ppm)

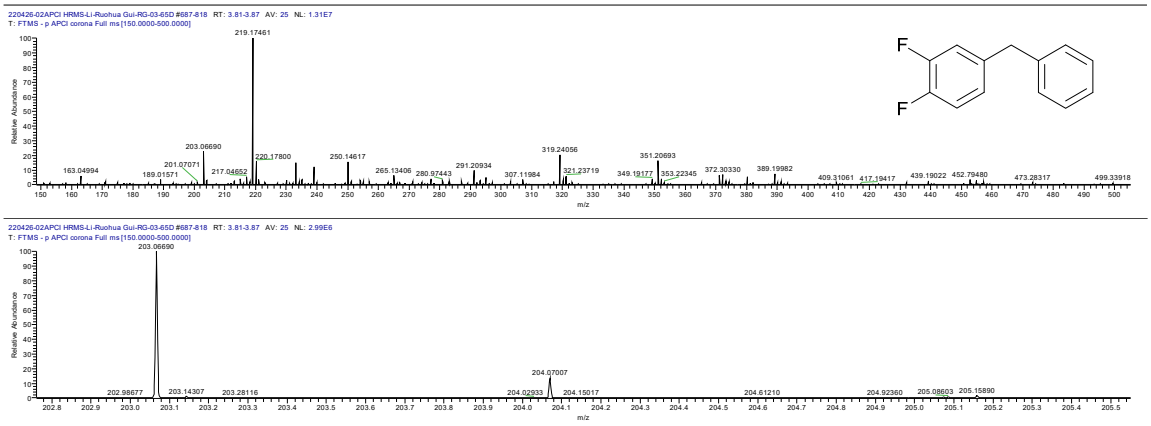

RG-03-65D-F1_PROTON_01
RG-03-65D-F1
G (m)
6.90
D (dt)
7.06
C (m)
7.16
A (m)
7.30
B (m)
7.24
F (ddd)
6.96
E (s)
3.93
1.55 H2O
2.28
0.46
0.08
1.92
1.01
1.45
0.92
1.02
0.71
2.00
¹H (ppm)


I (m)
124.61
B (s)
149.28
E (s)
138.08
G (s)
128.65
N (d)
117.62
A (s)
149.94
D (s)
140.07
F (s)
128.83
M (d)
117.03
H (s)
126.47
Q (s)
41.03
0.06
0.03
0.16
0.19
1.07
1.12
0.52
0.62
0.70
0.60
0.77
¹³C (ppm)


RG-03-125G-F3_FLUORINE_01
RG-03-125G-F3
K (dddd)
-138.16
M (m)
-141.97
2.27
2.33
135.0 -135.5 -136.0 -136.5 -137.0 -137.5 -138.0 -138.5 -139.0 -139.5 -140.0 -140.5 -141.0 -141.5 -142.0 -142.5 -143.0 -143.5 -144.0 -144.5
19F (ppm)

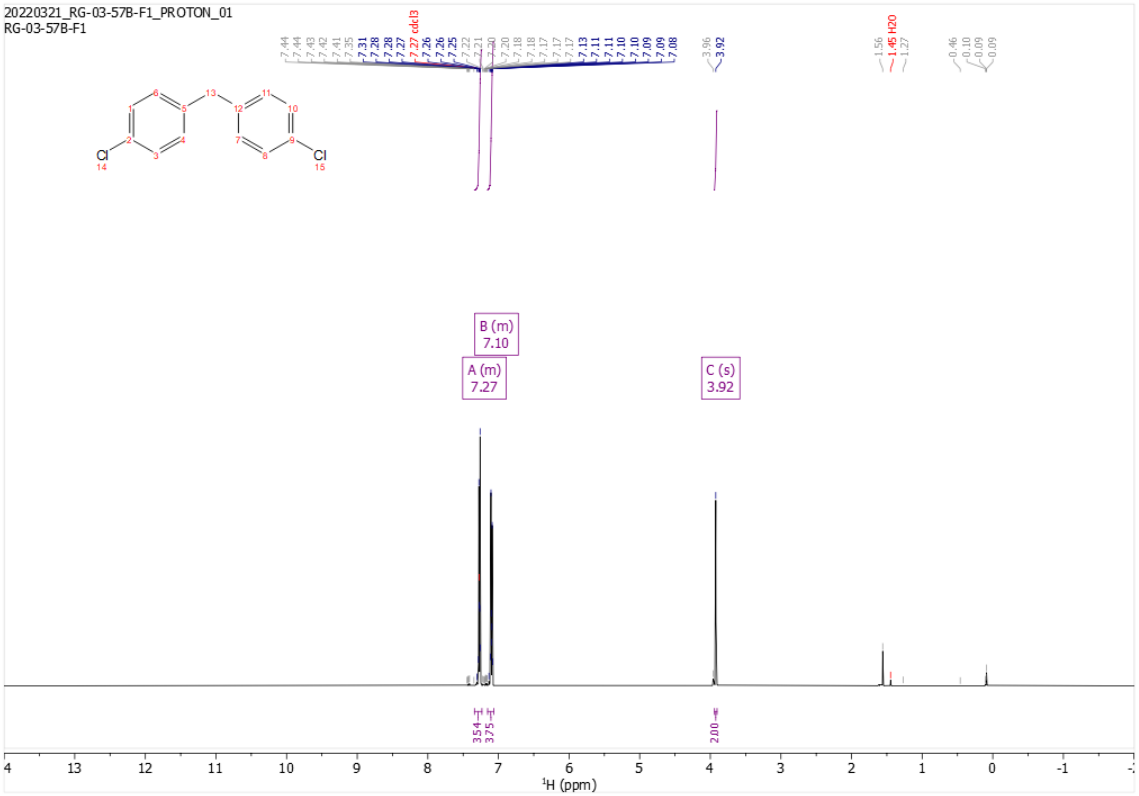

BRUKER
Transmittance [%]
0 20 40 60 80 100 120 140
3063.16
3029.70
2910.99
2837.10
2053.85
2009.09
1739.90
1608.17
1585.23
1513.93
1494.68
1454.07
1433.14
1338.28
1280.23
1246.98
1209.12
1176.75
1135.04
1113.94
1074.68
1031.15
954.29
911.15
870.69
827.72
799.28
780.78
751.32
719.53
695.83
633.78
576.52
548.57
531.55
509.12
452.69
425.84
4000 3500 3000 2500 2000 1500 1000 500
Wavenumber cm-1

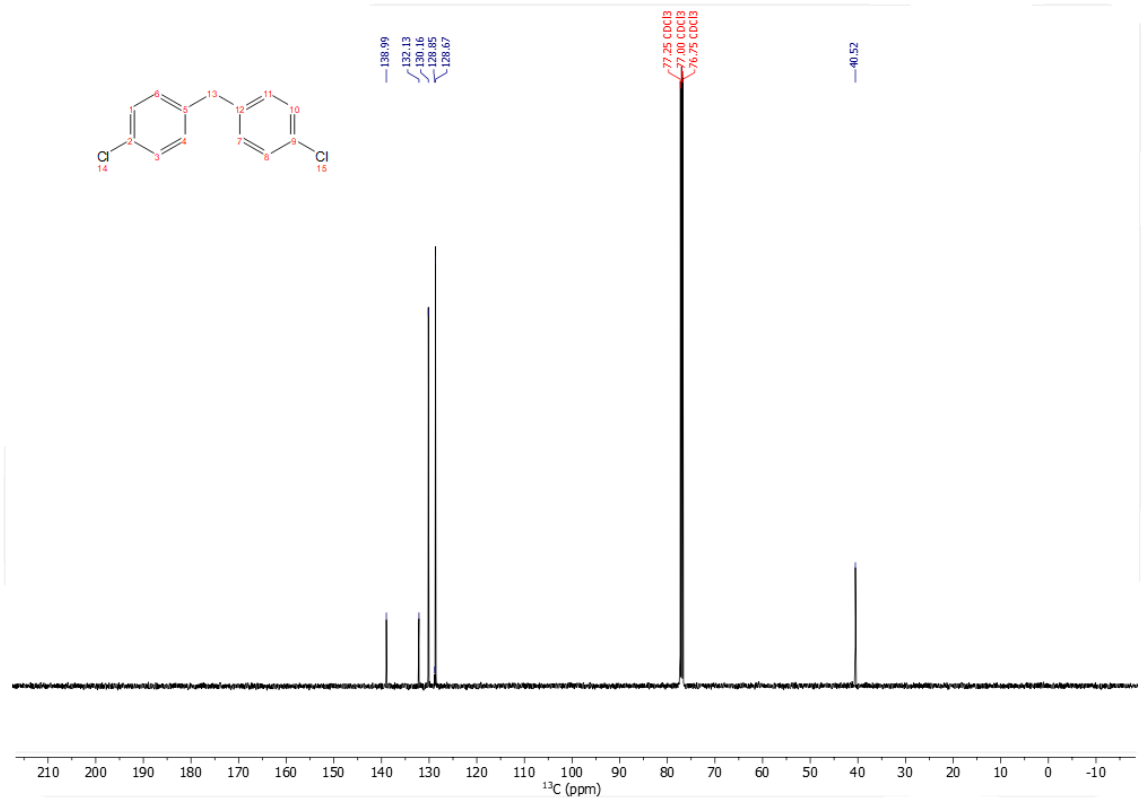
220426-02APCI HRMS-Li-Ruohua Gui-RG-0... 04/26/22 09:29:33

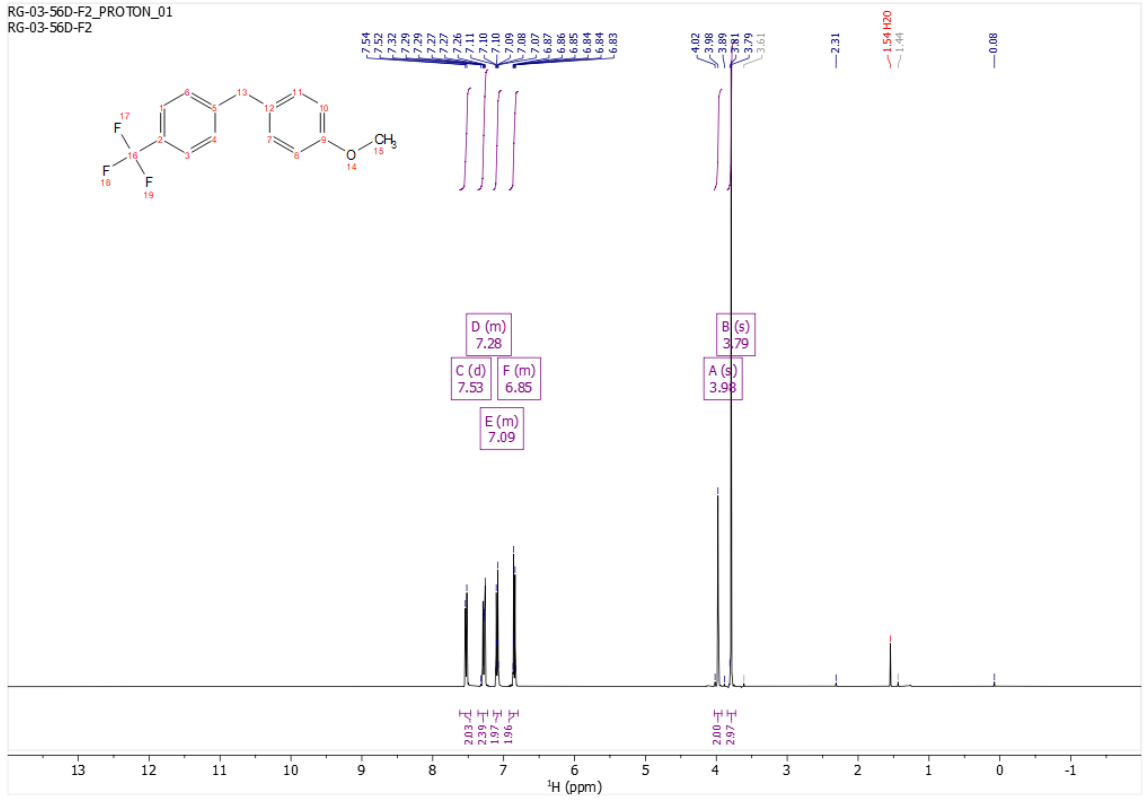


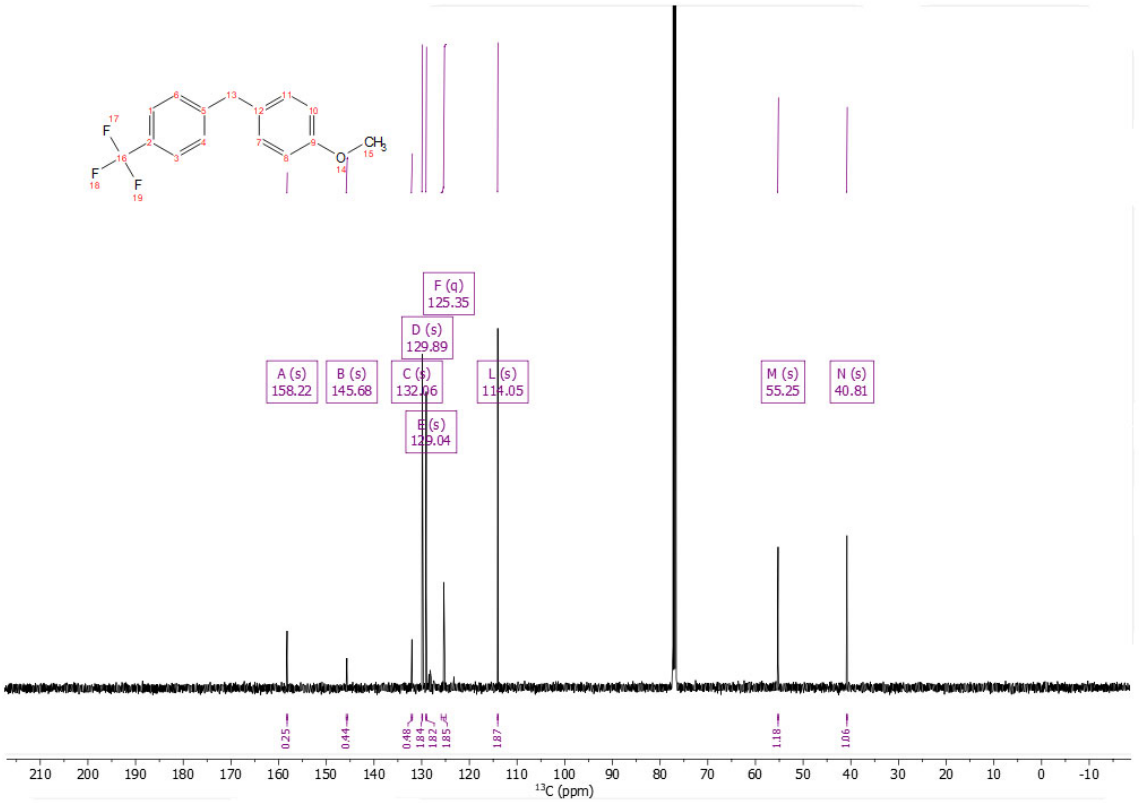
220426-02APCI HRMS-Li-Ruohua Gui-RG-03-65D#794-818 RT: 3.81-3.87 AV: 25
T: FTMS - p APCI corona Full ms [150.0000-500.0000]
m/z= 203.05677-203.07653

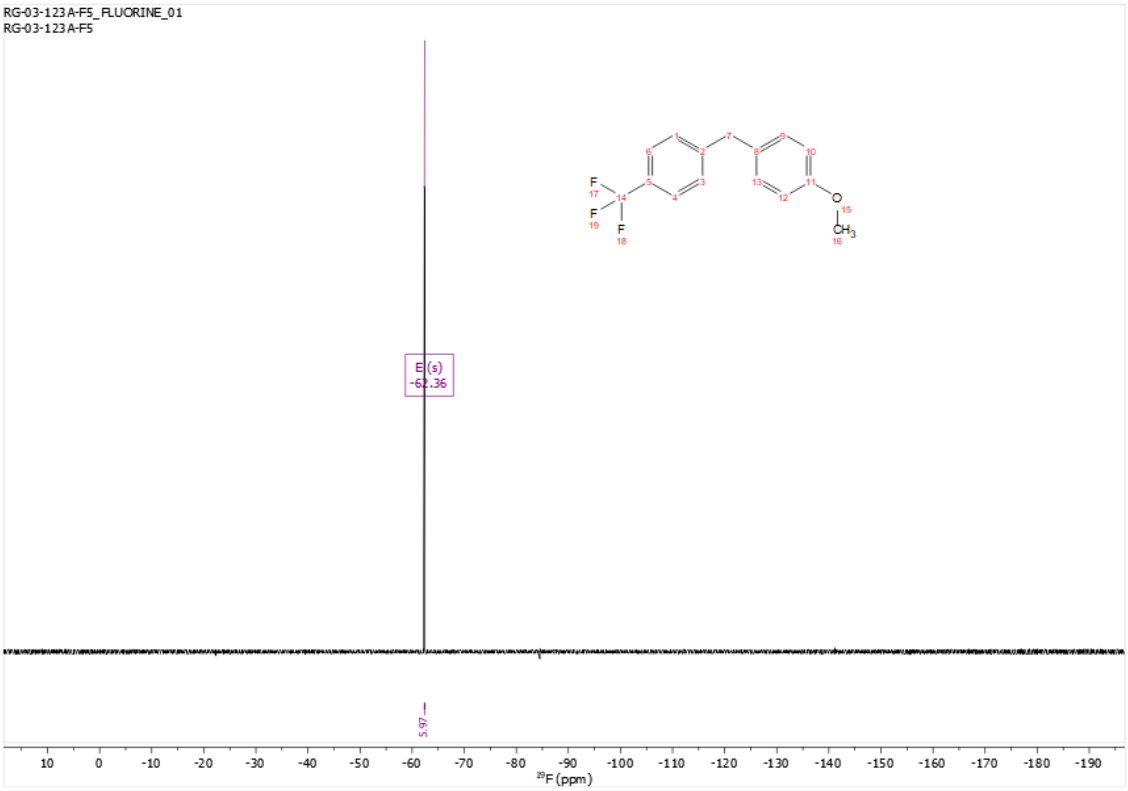
m/z	Intensity	Relative	Resolution	Charge	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
203.06690	3029890.3	100.00	37057.96	1.00	203.06778	-4.36	8.5	$C_{13}H_9F_2$

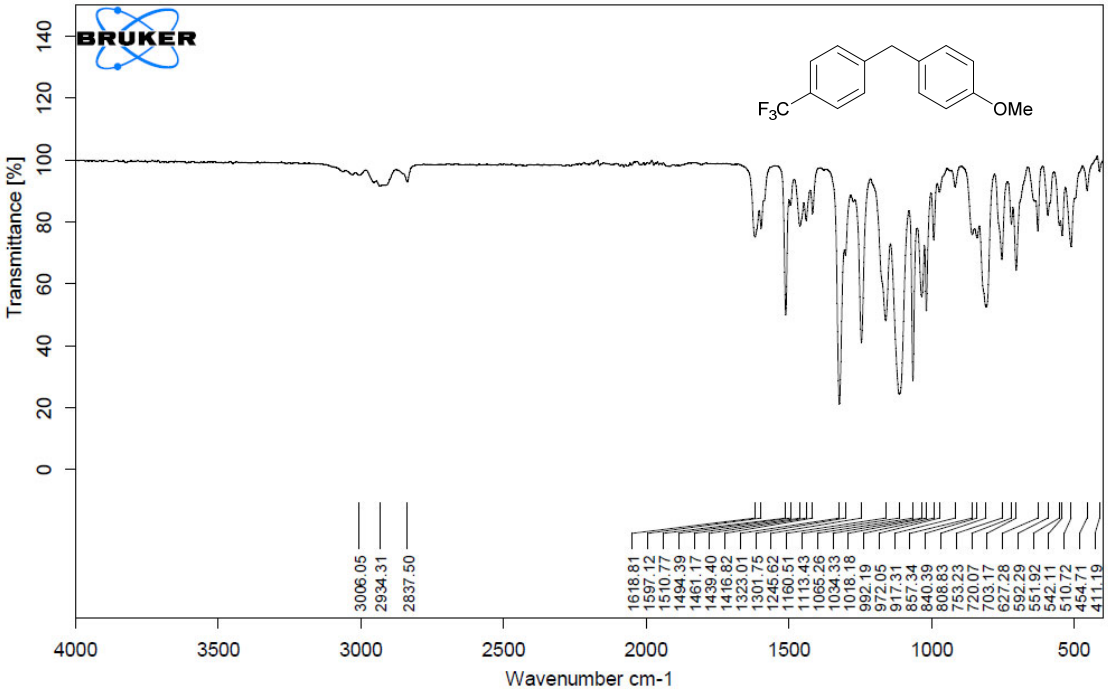



138.99
132.13
130.16
128.85
128.67
77.25 CDCl3
77.00 CDCl3
76.75 CDCl3
40.52
Cl
Cl
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
13C (ppm)

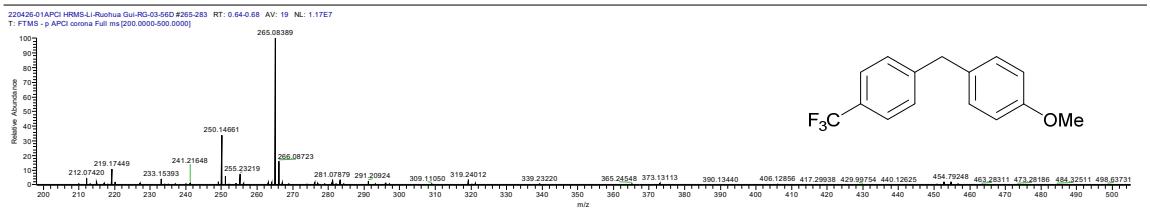

RG-03-56D-F2_PROTON_01
RG-03-56D-F2
7.54
7.52
7.32
7.29
7.29
7.27
7.27
7.26
7.11
7.10
7.09
7.08
7.07
6.87
6.86
6.85
6.84
6.84
6.83
4.02
3.98
3.89
3.81
3.79
3.61
2.31
1.54 H2O
1.44
0.08
F
F
F
O
CH3
D (m)
7.28
C (d)
7.53
F (m)
6.85
E (m)
7.09
B (s)
3.79
A (s)
3.98
2.03
2.39
1.97
1.96
2.00
2.97
13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
1H (ppm)

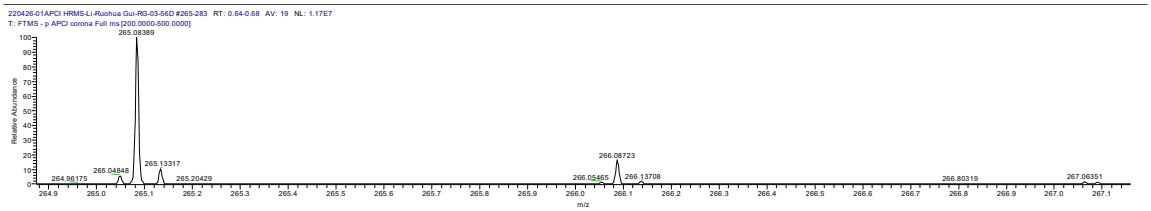

F (q)
125.35
D (s)
129.89
A (s)
158.22
B (s)
145.68
C (s)
132.06
L (s)
114.05
M (s)
55.25
N (s)
40.81
E (s)
129.04
0.25
0.44
0.48
1.84
1.82
1.85
1.87
1.18
1.06
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
13C (ppm)


RG-03-123A-F5_FLUORINE_01
RG-03-123A-F5
E (s)
-62.36
5.97
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
19F (ppm)



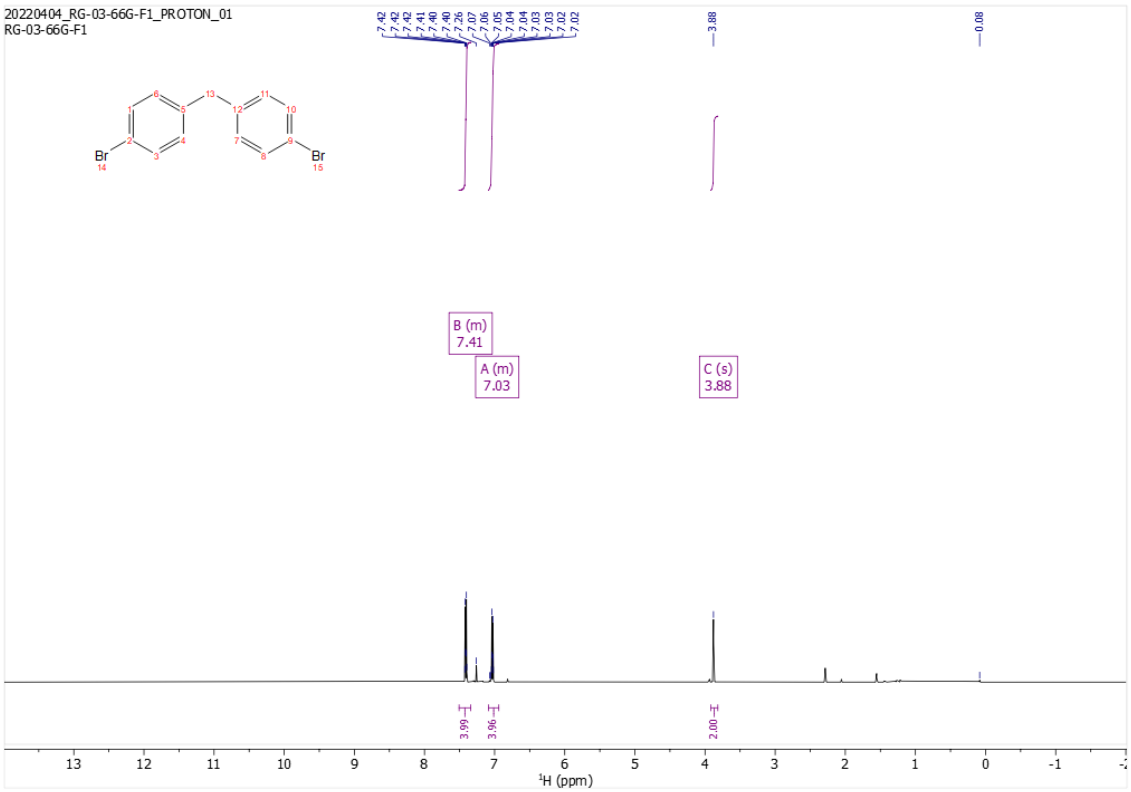
220426-01APCI HRMS-Li-Ruohua Gui-RG-0... 04/26/22 09:16:23

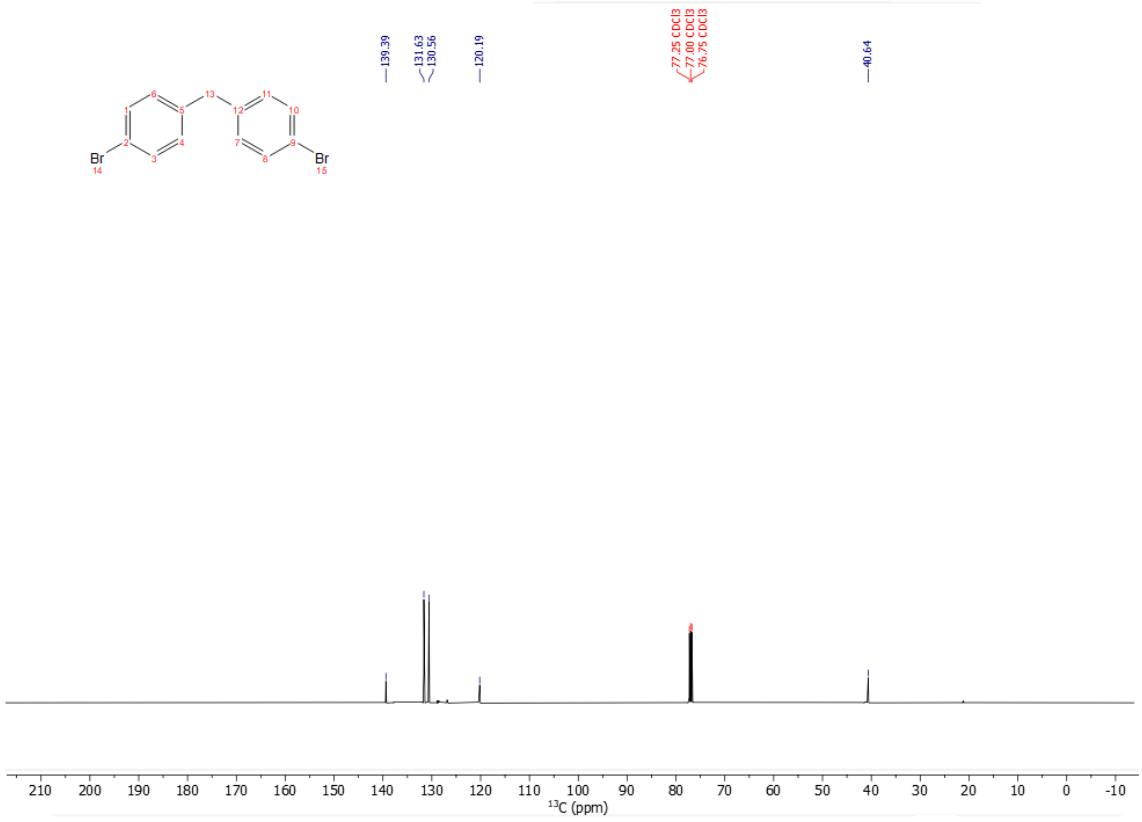


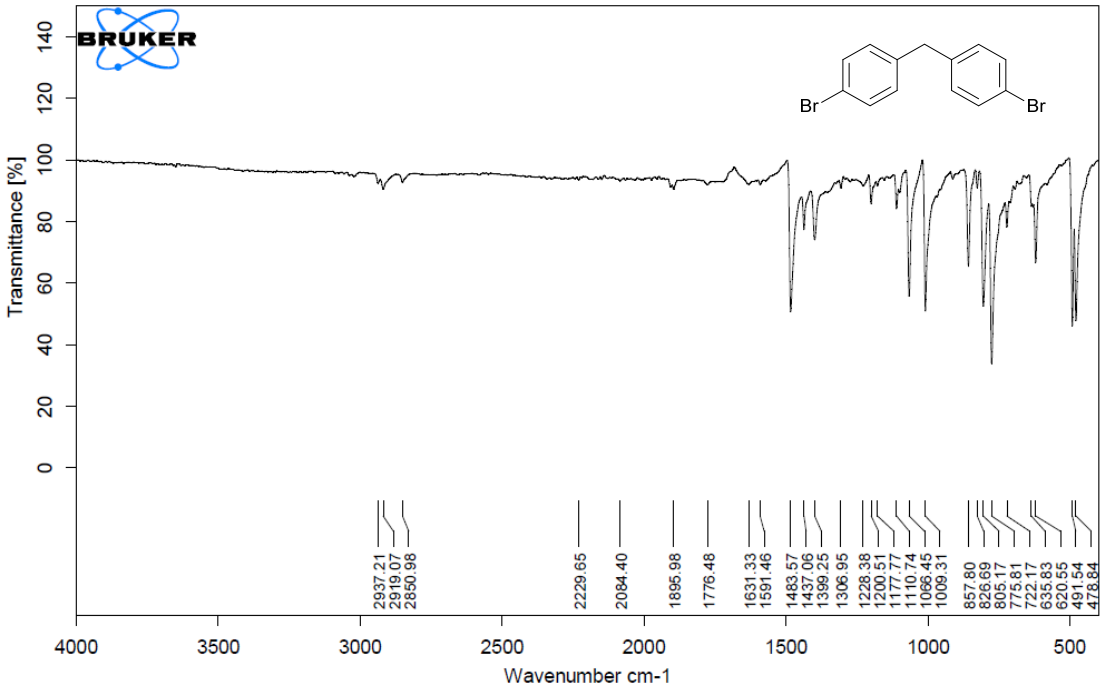


220426-01APCI HRMS-Li-Ruohua Gui-RG-03-56D#265-283 RT: 0.64-0.68 AV: 19
T: FTMS - p APCI corona Full ms [200.0000-500.0000]
m/z= 265.07368-265.09134

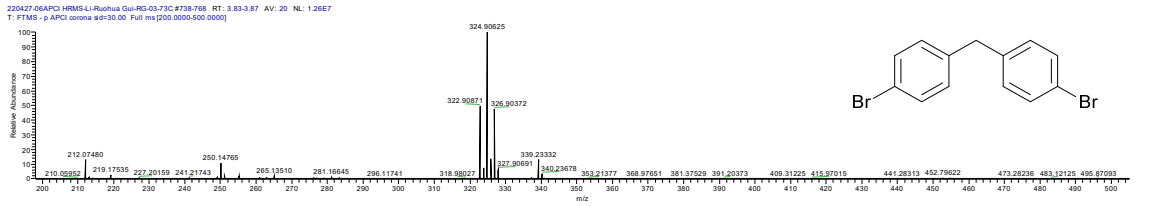
m/z	Intensity	Relative	Resolution	Charge	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
265.08389	11671075.0	100.00	33269.82	1.00	265.08457	-2.56	8.5	$C_{15}H_{12}OF_3$

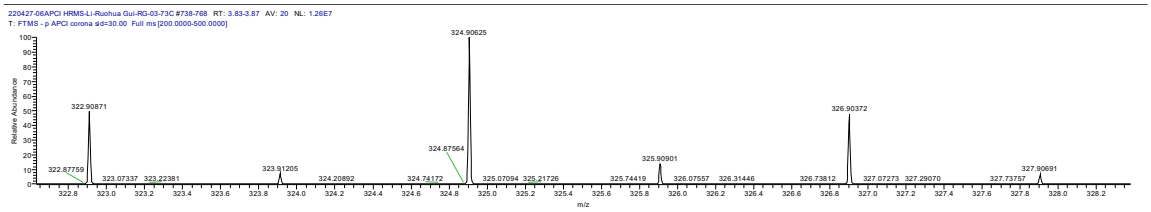

20220404_RG-03-66G-F1_PROTON_01
RG-03-66G-F1
7.42
7.42
7.42
7.41
7.40
7.40
7.26
7.07
7.06
7.05
7.04
7.04
7.03
7.03
7.02
7.02
3.88
0.08
Br
14
Br
15
B (m)
7.41
A (m)
7.03
C (s)
3.88
3.99
3.96
2.00
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
¹H (ppm)


139.39
131.63
130.56
120.19
77.25 CDCl3
77.00 CDCl3
76.75 CDCl3
40.64
Br
14
Br
15
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
¹³C (ppm)



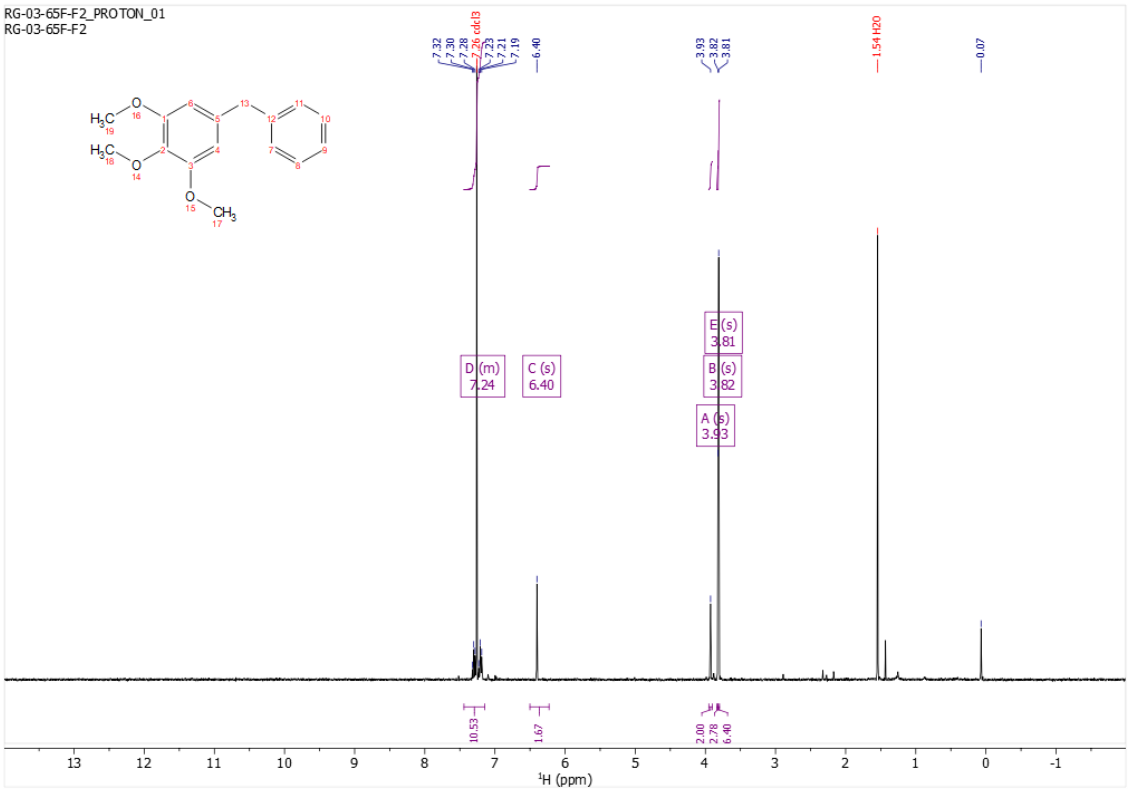
220427-06APCI HRMS-Li-Ruohua Gui-RG-0... 04/27/22 13:33:03

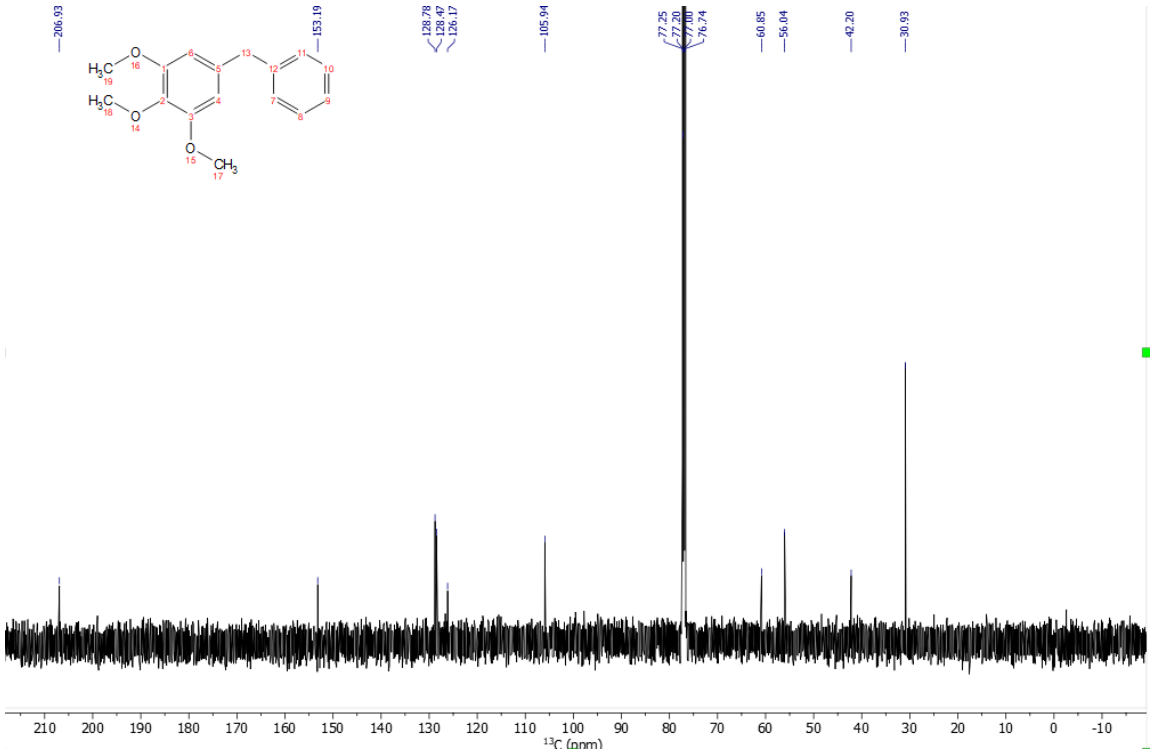


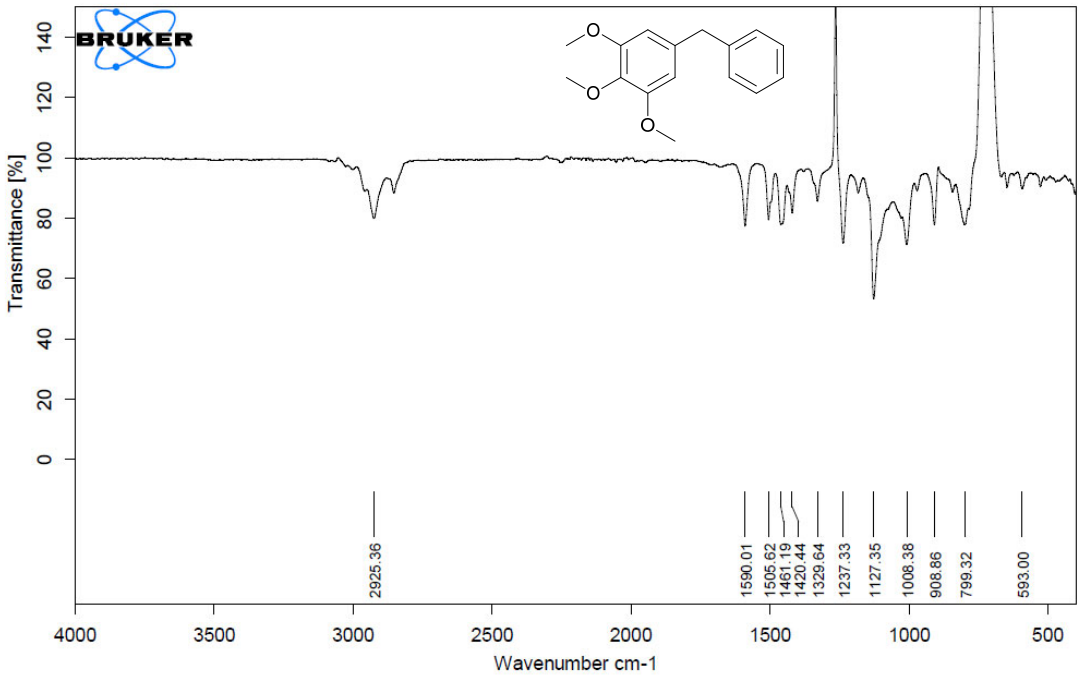


220427-06APCI HRMS-Li-Ruohua Gui-RG-03-73C#738-757 RT: 3.83-3.87 AV: 20
T: FTMS - p APCI corona sid=30.00 Full ms [200.0000-500.0000]
m/z= 322.88909-322.92982

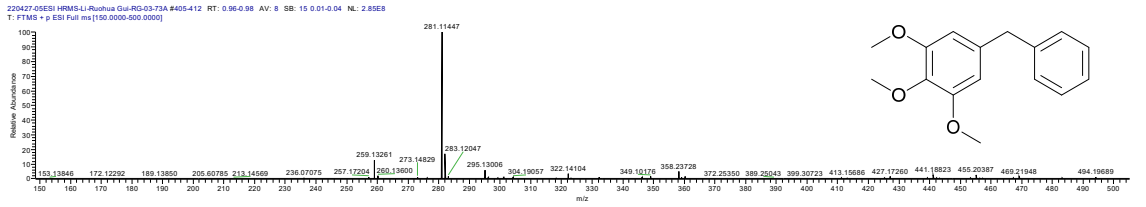
m/z	Intensity	Relative	Resolution	Charge	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
322.90871	6347600.0	100.00	29559.04	1.00	322.90655	2.16	8.5	$C_{13}H_9Br_2$


RG-03-65F-F2_PROTON_01
RG-03-65F-F2
7.32
7.30
7.28
CDCl3
7.26
7.23
7.21
7.19
6.40
3.93
3.82
3.81
1.54 H2O
0.07
D (m)
7.24
C (s)
6.40
E (s)
3.81
B (s)
3.82
A (s)
3.93
10.53
1.67
2.00
2.78
6.40
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
¹H (ppm)


206.93
153.19
128.78
128.47
126.17
105.94
77.25
77.00
76.74
60.85
56.04
42.20
30.93
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
¹³C (ppm)



220427-05ESI HRMS-Li-Ruohua Gui-RG-03... 04/27/22 11:12:41

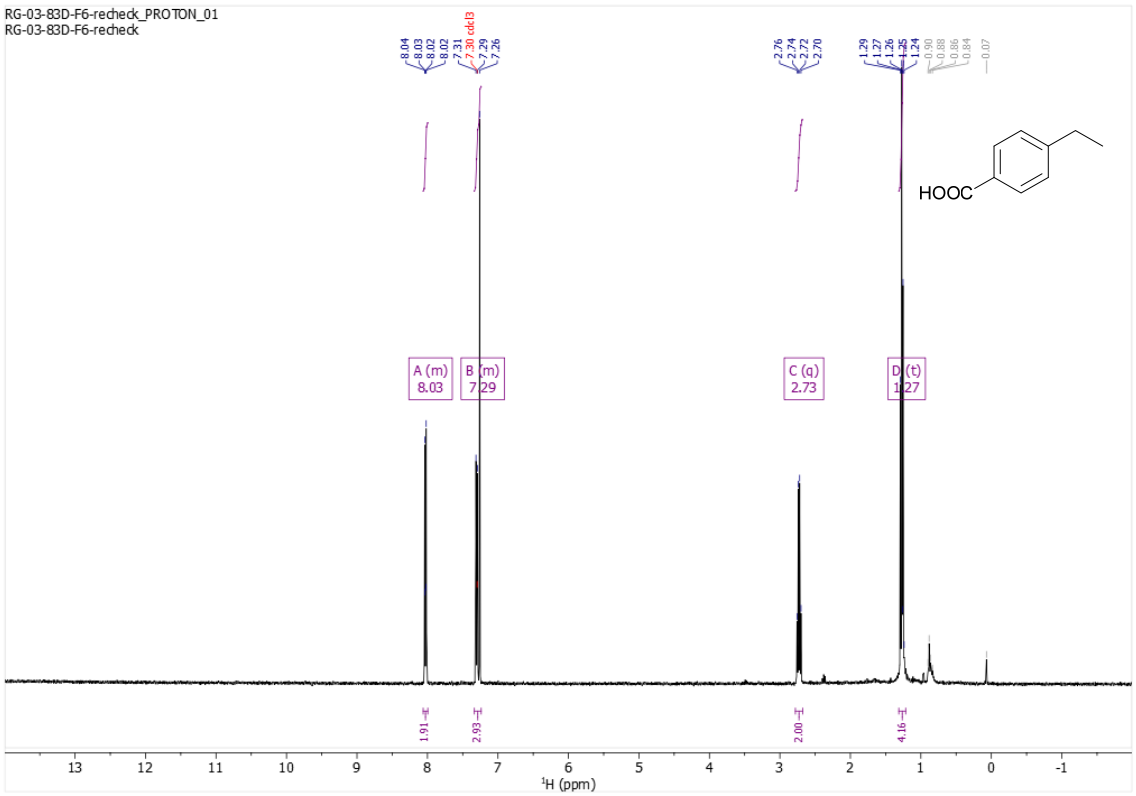


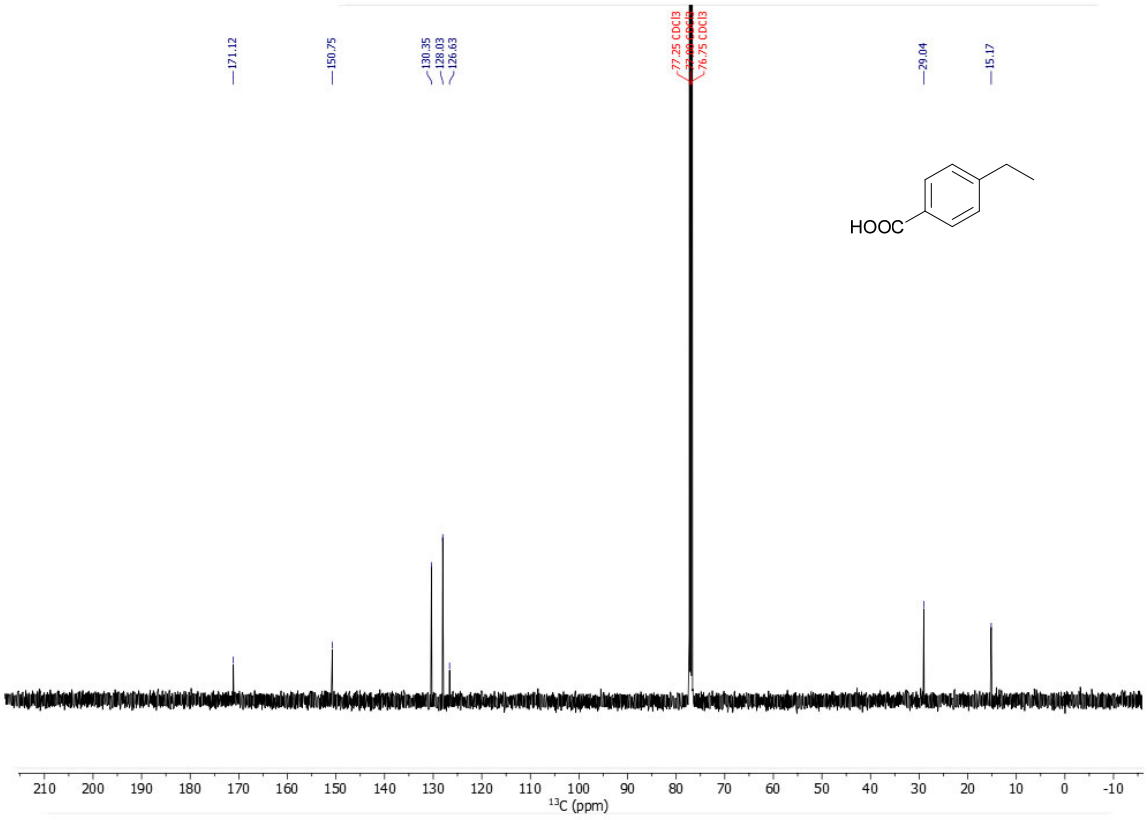
220427-05ESI HRMS-Li-Ruohua Gui-RG-03-73A#405-412 RT: 0.96-0.98 AV: 8
SB: 15 0.01-0.04
T: FTMS + p ESI Full ms [150.0000-500.0000]
m/z= 259.12429-259.13792

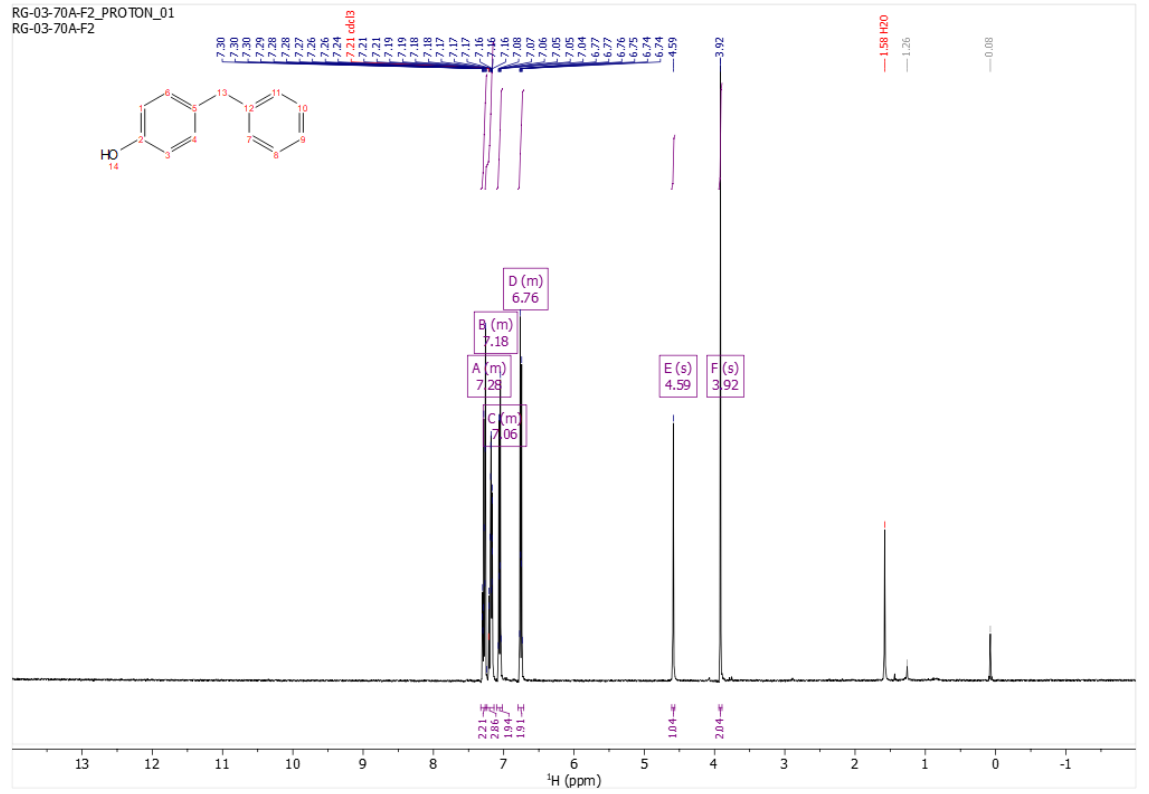
m/z	Intensity	Relative	Resolution	Charge	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
259.13261	37041412.0	100.00	34239.50	1.00	259.13287	-1.00	7.5	$C_{16}H_{19}O_3$

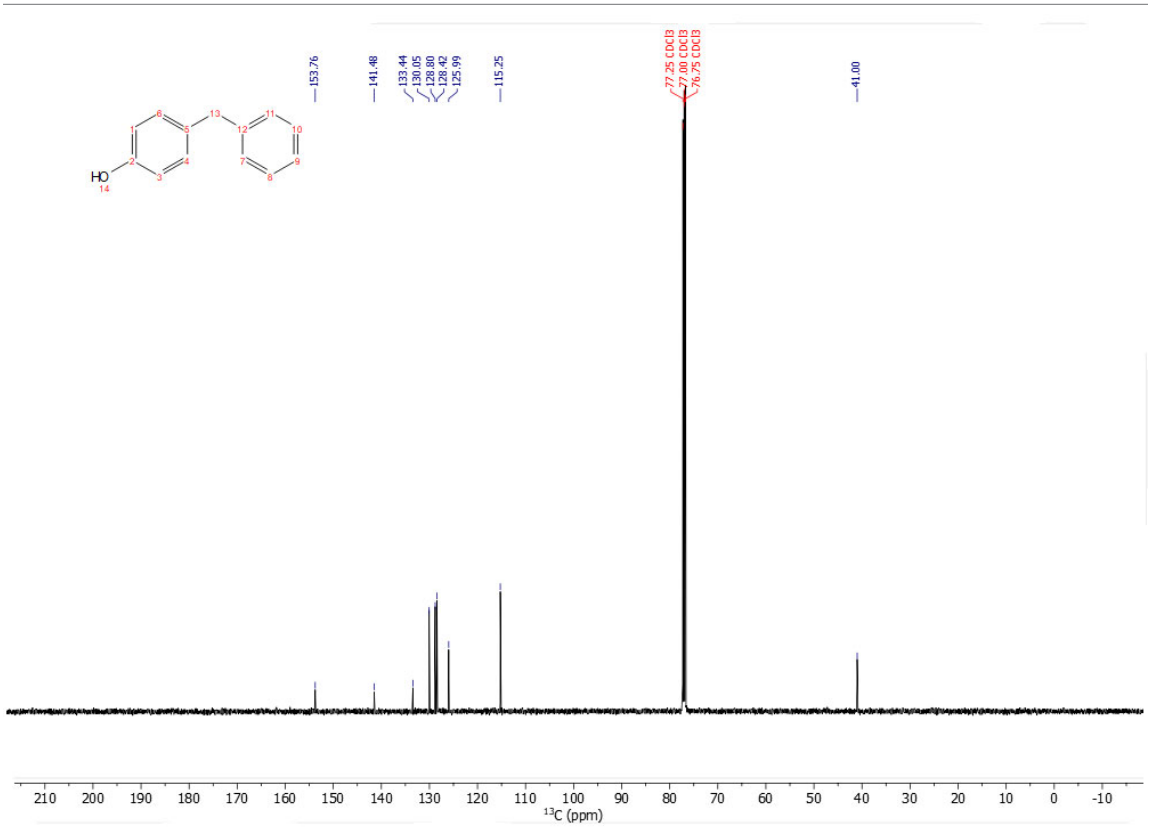
220427-05ESI HRMS-Li-Ruohua Gui-RG-03-73A#405-412 RT: 0.96-0.98 AV: 8
SB: 15 0.01-0.04
T: FTMS + p ESI Full ms [150.0000-500.0000]
m/z= 281.10455-281.12109

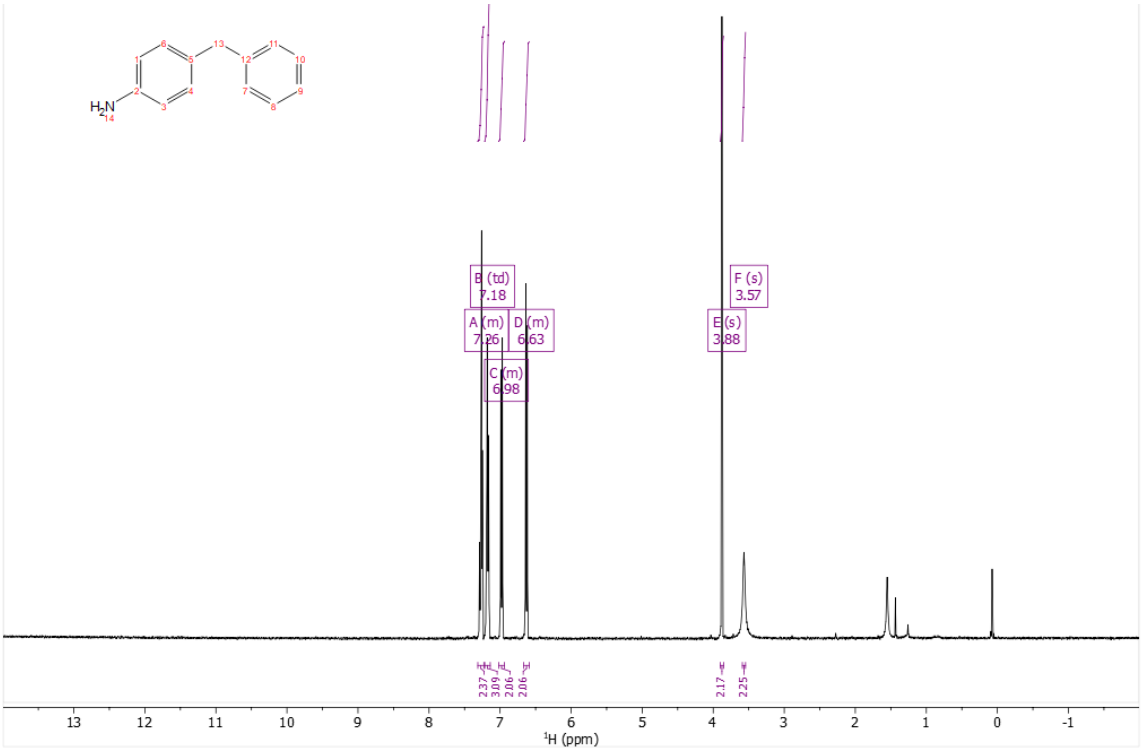
m/z	Intensity	Relative	Resolution	Charge	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
281.11447	285351200.0	100.00	32858.57	1.00	281.11482	-1.22	7.5	$C_{16}H_{18}O_3Na$

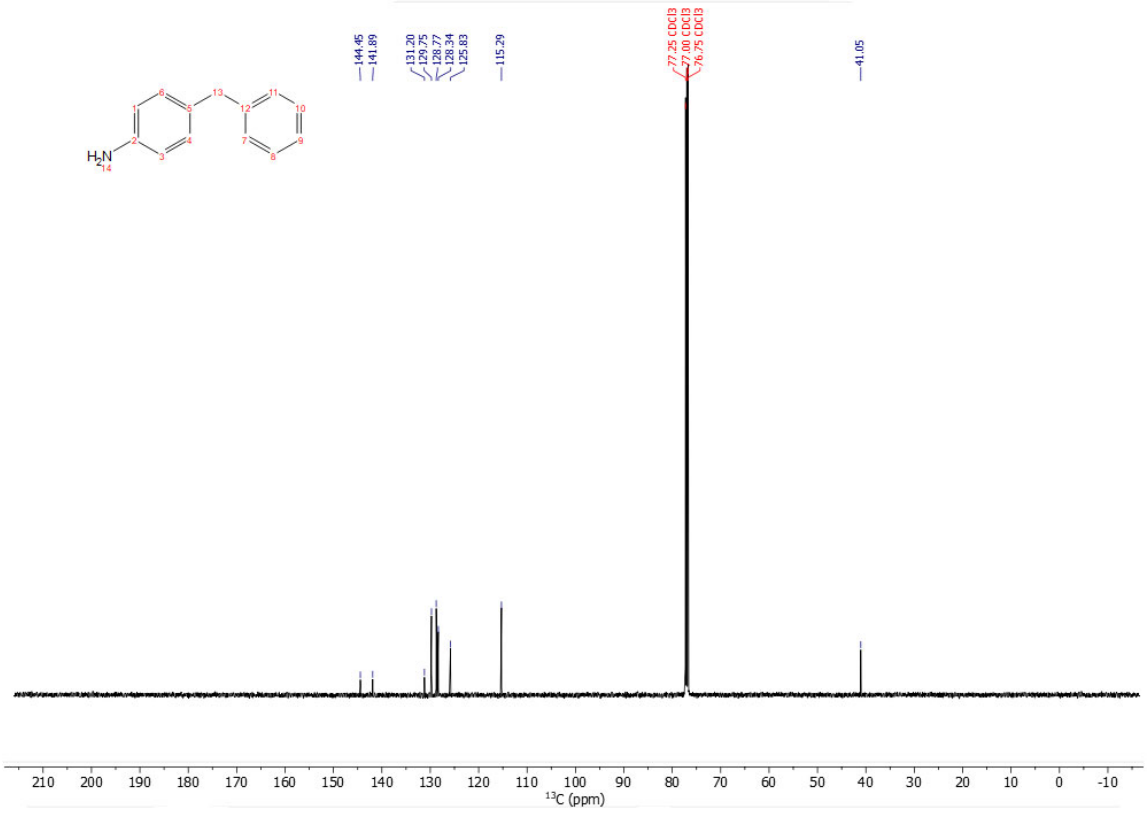

RG-03-83D-F6-recheck_PROTON_01
RG-03-83D-F6-recheck
8.04
8.03
8.02
8.02
7.31
7.30 cdcl3
7.29
7.26
2.76
2.74
2.72
2.70
1.29
1.27
1.26
1.25
1.24
1.90
0.88
0.86
0.84
0.07
HOOC
A (m)
8.03
B (m)
7.29
C (q)
2.73
D (t)
1.27
1.91
2.93
2.00
4.16
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
¹H (ppm)

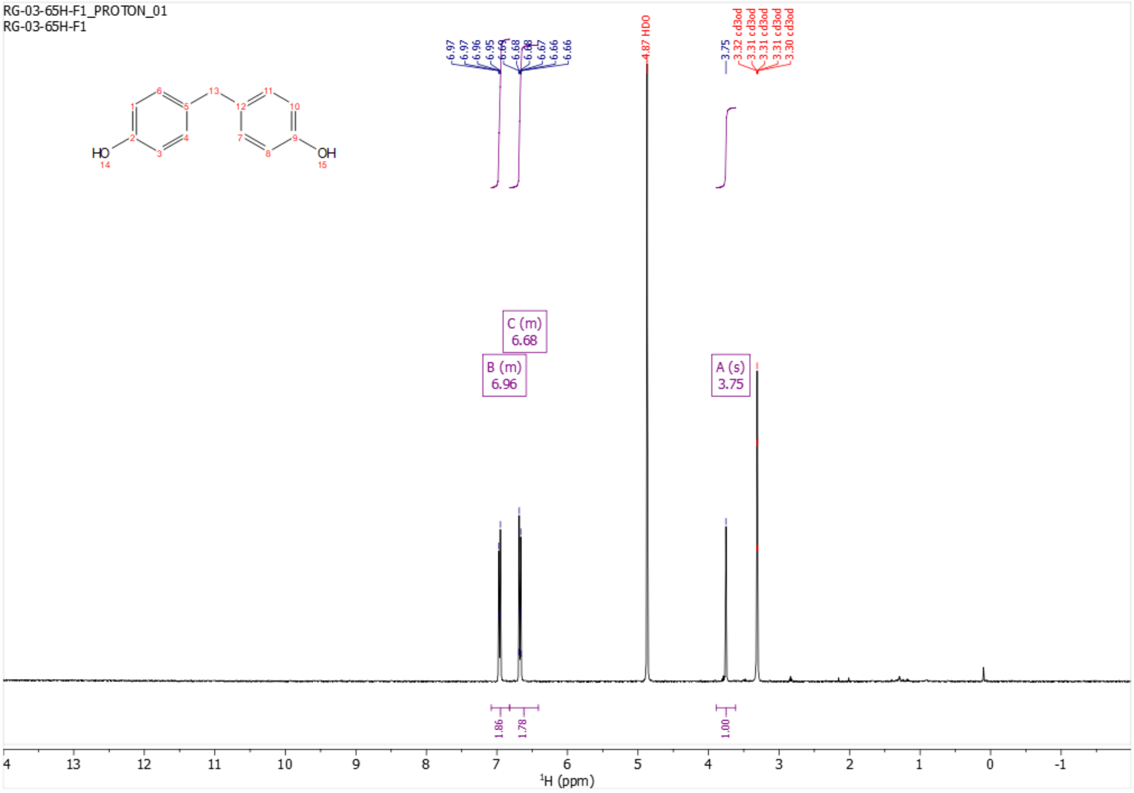

171.12
150.75
130.35
128.03
126.63
77.25 CDCl3
76.75 CDCl3
29.04
15.17
HOOC
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
¹³C (ppm)

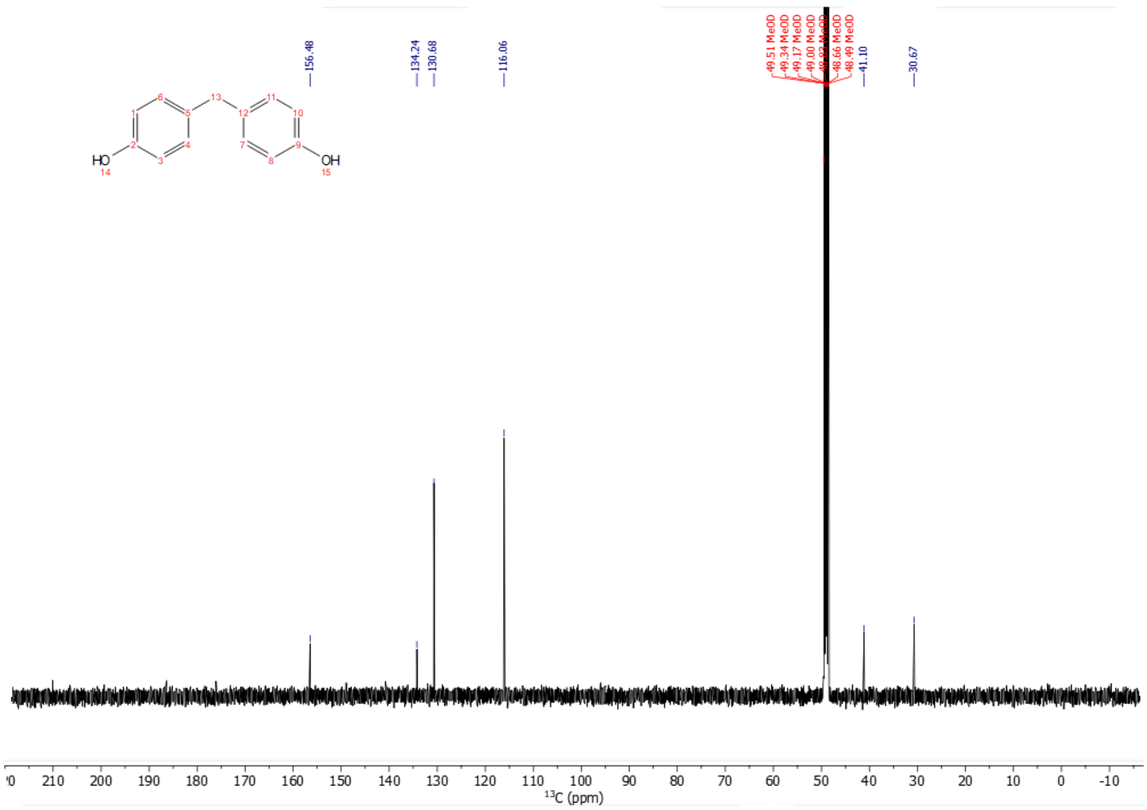

RG-03-70A-F2_PROTON_01
RG-03-70A-F2
D (m) 6.76
B (m) 7.18
A (m) 7.28
C (m) 7.06
E (s) 4.59
F (s) 3.92
1.58 H2O
1H (ppm)

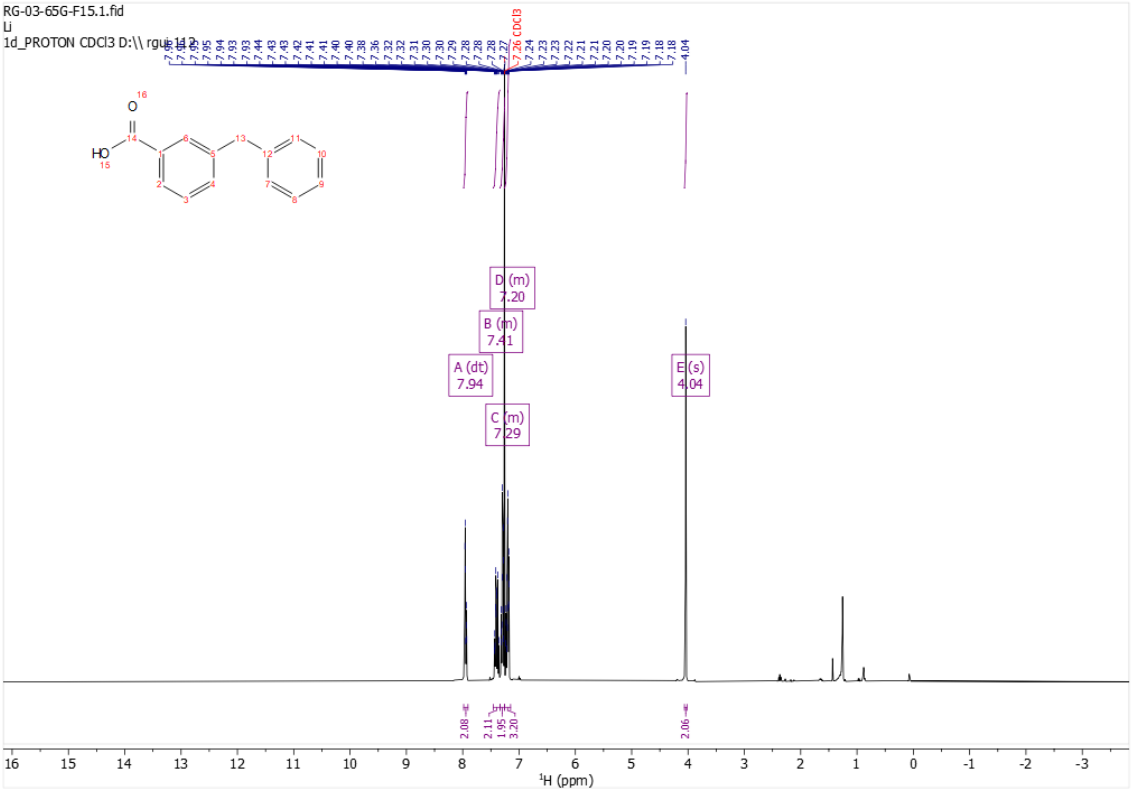

153.76
141.48
133.44
130.05
128.80
128.42
125.99
115.25
77.25 CDCl3
77.00 CDCl3
76.75 CDCl3
41.00
13C (ppm)

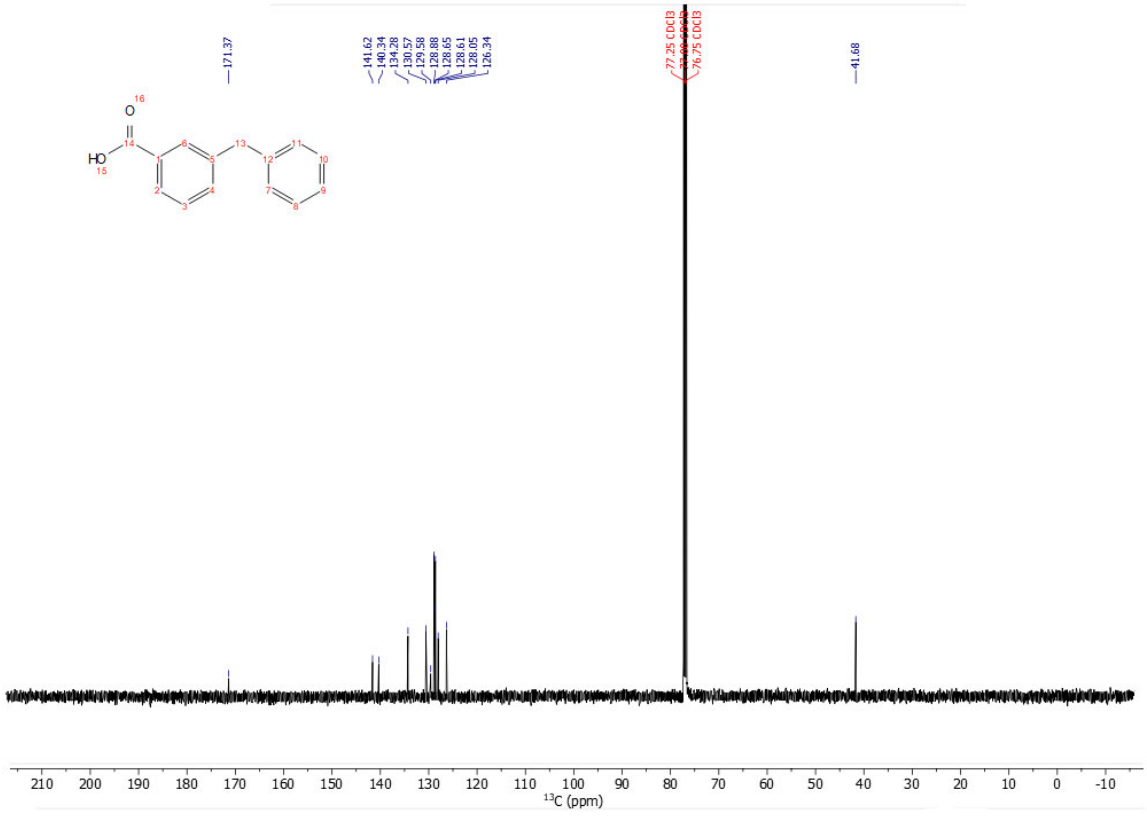

B (td)
7.18
A (m)
7.26
D (m)
6.63
C (m)
6.98
F (s)
3.57
E (s)
3.88
2.37
3.09
2.06
2.06
2.17
2.25
^{1}H (ppm)

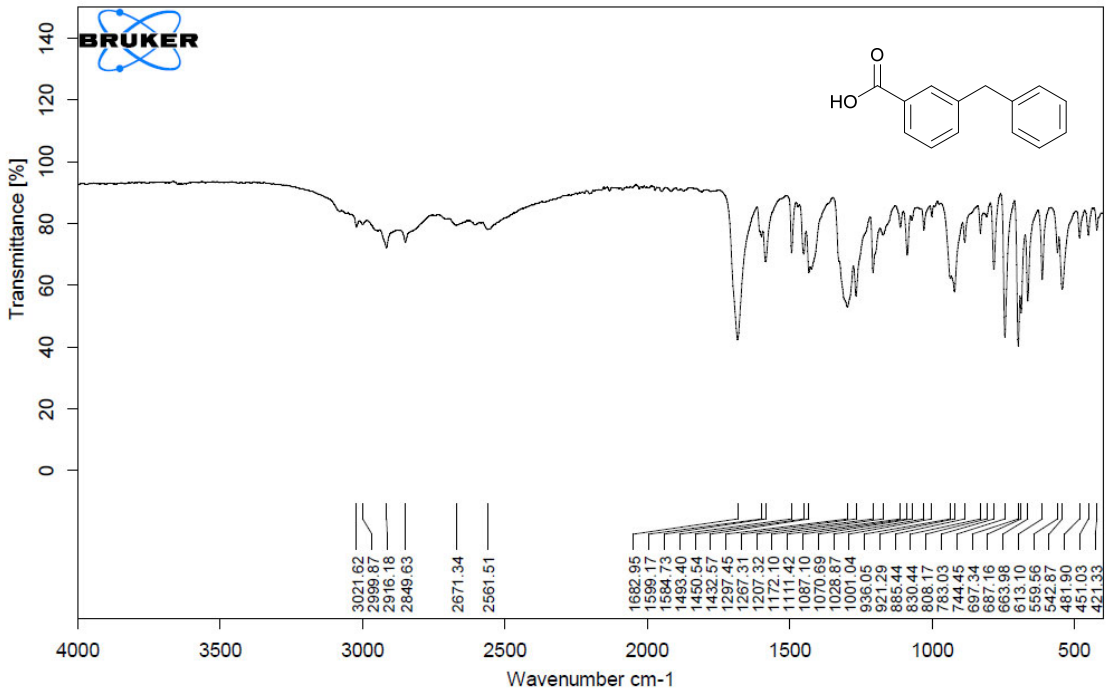

144.45
141.89
131.20
129.75
128.77
128.34
125.83
115.29
77.25 CDCl3
77.00 CDCl3
76.75 CDCl3
41.05
^{13}C (ppm)

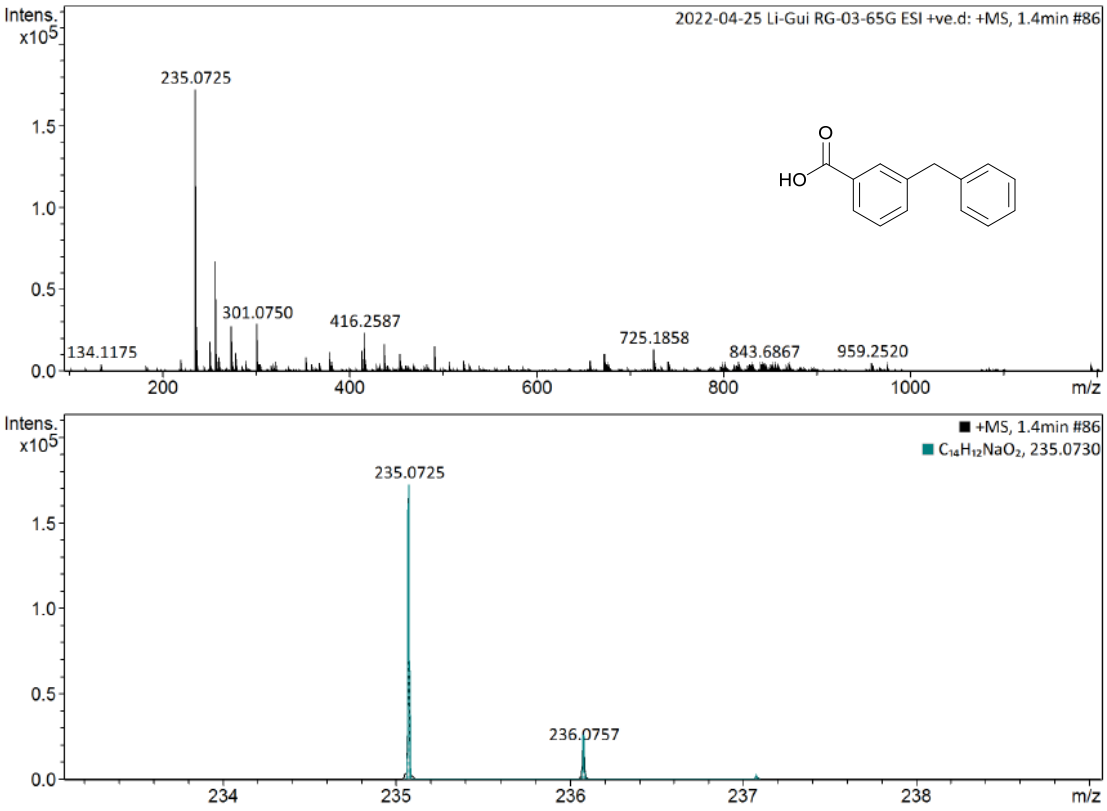

RG-03-65H-F1_PROTON_01
RG-03-65H-F1
6.97
6.97
6.96
6.95
6.69
6.68
6.68
6.67
6.66
6.66
4.87 HDO
3.75
3.32 cd3od
3.31 cd3od
3.31 cd3od
3.31 cd3od
3.30 cd3od
C (m)
6.68
B (m)
6.96
A (s)
3.75
1.86
1.78
1.00
HO
OH
14
15
^{1}H (ppm)


156.48
134.24
130.68
116.06
49.51 MeOD
49.34 MeOD
49.17 MeOD
49.00 MeOD
48.83 MeOD
48.66 MeOD
48.49 MeOD
41.10
30.67
HO
OH
14
15
^{13}C (ppm)


RG-03-65G-F15.1.fid
1d_PROTON CDCl3 D:\\ rgu 1d 2
D (m)
7.20
B (m)
7.41
A (dt)
7.94
E (s)
4.04
C (m)
7.29
2.08
2.11
1.95
3.20
2.06
¹H (ppm)


171.37
141.62
140.34
134.28
130.57
129.58
128.88
128.65
128.61
128.05
126.34
77.25 CDCl3
76.75 CDCl3
41.68
¹³C (ppm)

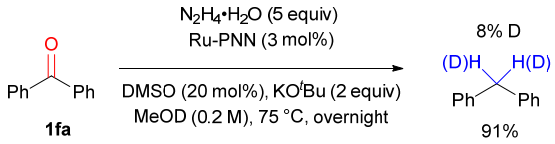

BRUKER
HO
O
Transmittance [%]
0
20
40
60
80
100
120
140
3021.62
2999.87
2916.18
2849.63
2671.34
2561.51
1682.95
1599.17
1584.73
1493.40
1450.54
1432.57
1297.45
1267.31
1207.32
1172.10
1111.42
1087.10
1070.69
1028.87
1001.04
936.05
921.29
885.44
830.44
808.17
783.03
744.45
697.34
687.16
663.98
613.10
559.96
542.87
481.90
451.03
421.33
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1



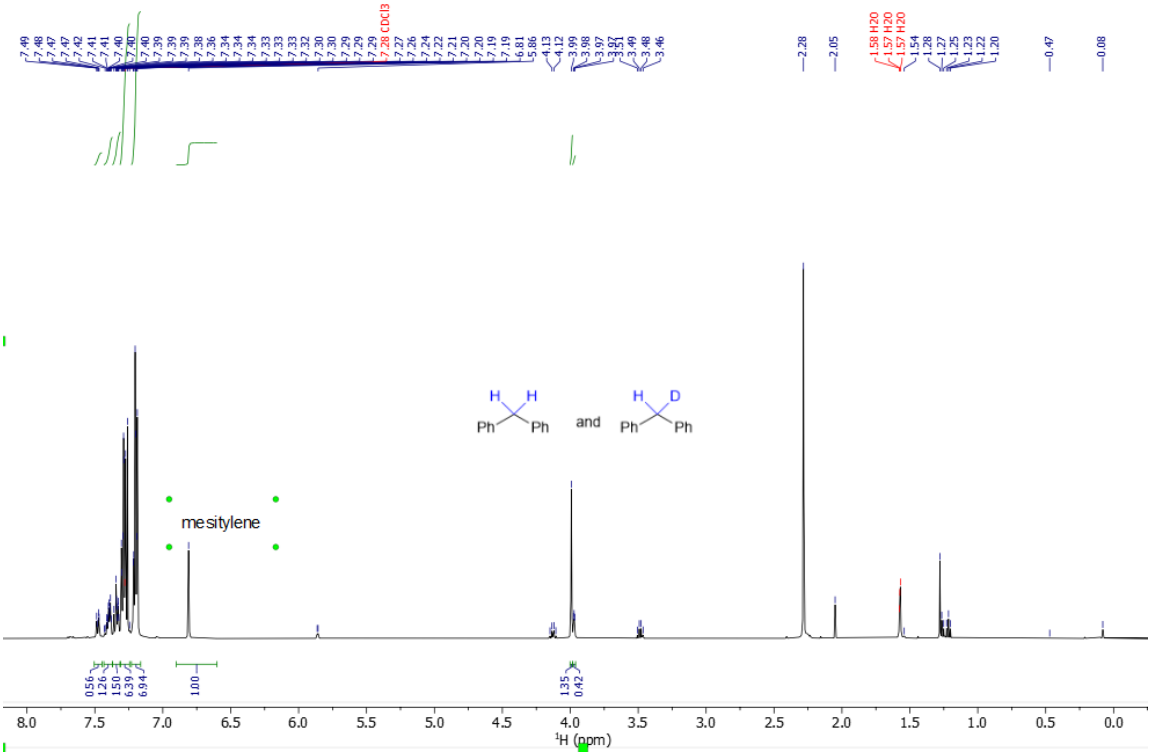
Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# mSigma	Score	rdb	e¯ Conf	N-Rule
235.0725	1	C12H7N6	235.0727	0.6	22.4	1	100.00	12.5	even	ok
	1	C14H12NaO2	235.0730	1.8	23.1	1	100.00	8.5	even	ok
257.0545	1	C12H6N6Na	257.0546	0.4	14.6	1	100.00	12.5	even	ok
	1	C12H6N6Na	257.0546	0.4	14.6	1	100.00	12.5	even	ok
	2	C14H11Na2O2	257.0549	1.5	15.1	2	87.61	8.5	even	ok

IX. Mechanism study

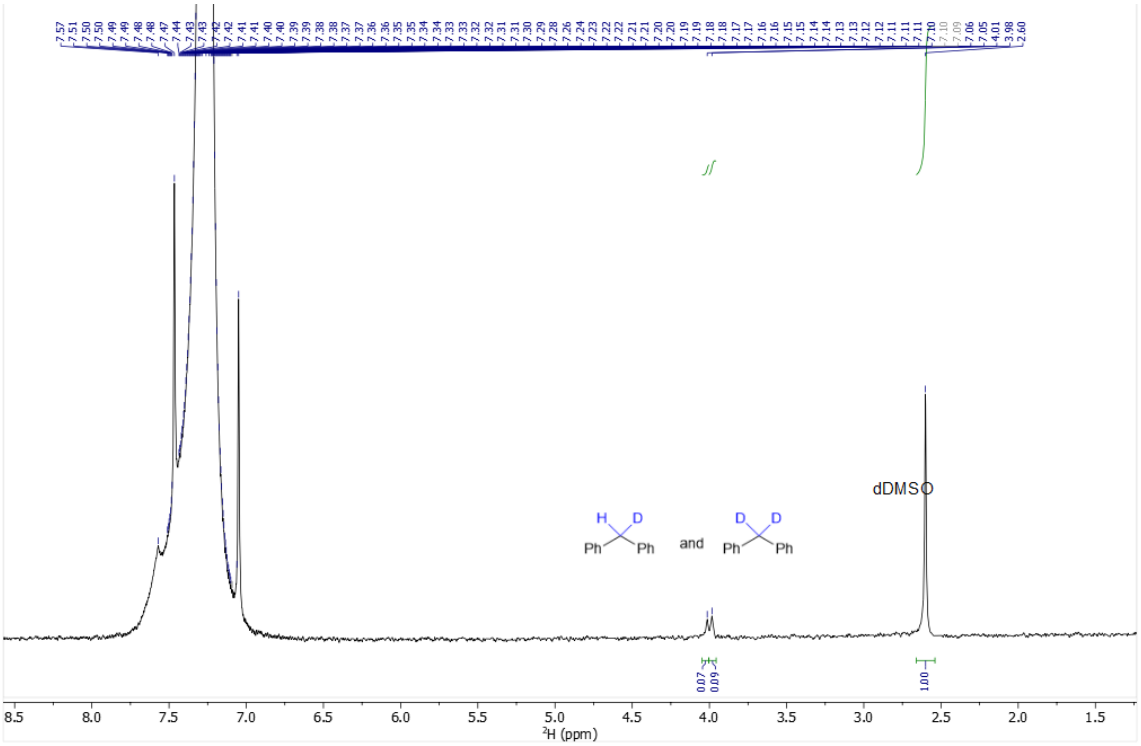
Scheme 5. Reaction in d-methanol



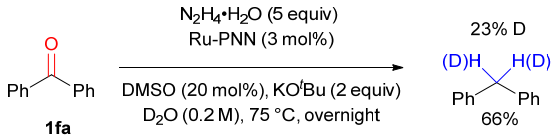
^{1}H NMR data



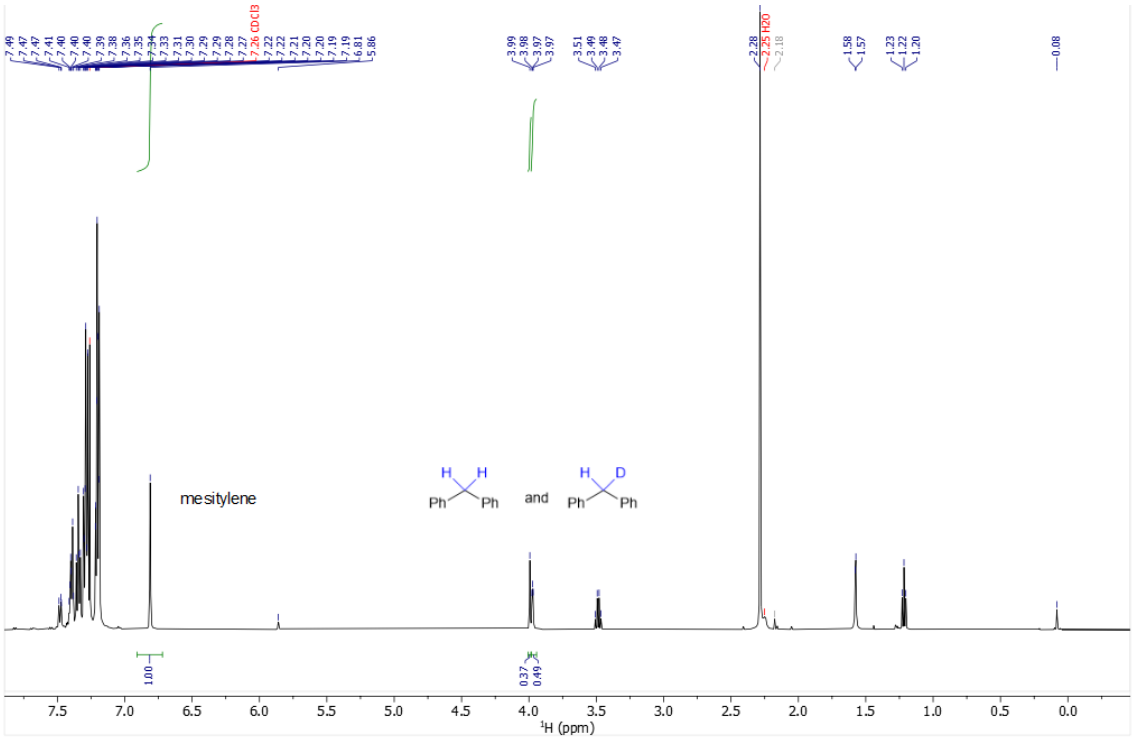
^{2}D NMR data


dDMSO
H D
Ph Ph
and
D D
Ph Ph
0.07
0.09
1.00
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
^{2}H (ppm)

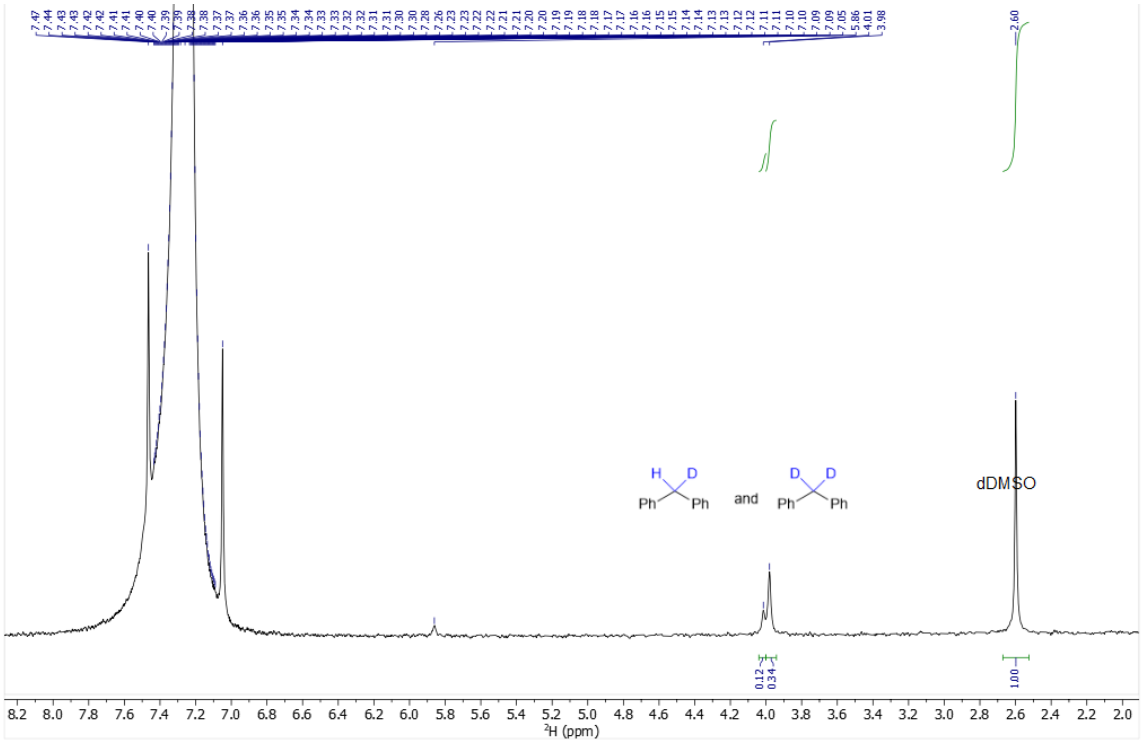
Scheme 6. Reaction in d-methanol



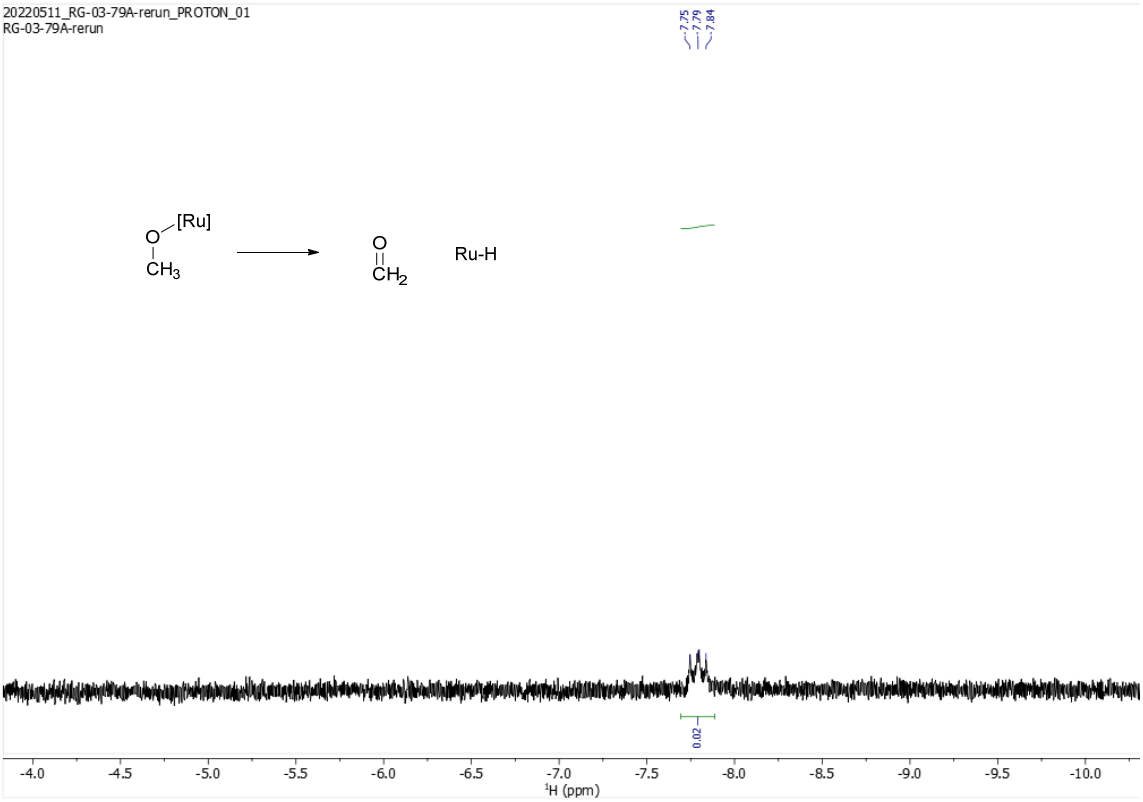
^{1}H NMR data



^{2}D NMR data



Scheme 7. In situ ^{1}H NMR of Ru-H species



Scheme 8. Control Experiments