Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

A simple and convenient strategy for the oxidation of C(sp^3)–H bonds based on γ-valerolactone

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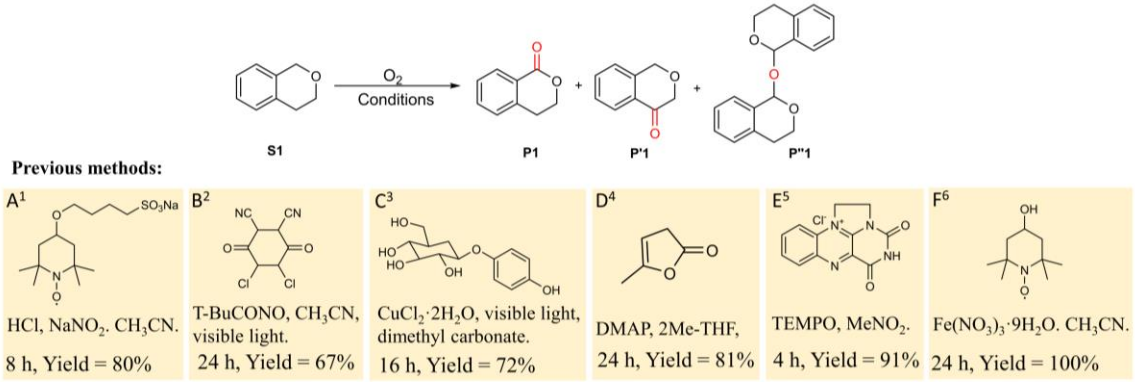
Previous work for the oxidation of isochroman



Scheme S1 C–H oxidation of isochroman over organocatalysts.[1-6]

Experimental

General Information

All the reagents and solvents in the study were analytically pure and were all purchased from Energy or Aladdin and used as received. Column chromatography was performed using 300-400 Mesh silica gel. Visualization of spots on TLC plate was accomplished with UV light (254 nm). Isochroman derivatives were prepared from corresponding phenyl ethanol derivative and 2-methoxyethoxymethyl chloride according to the reported method.[7] Benzyl ether derivatives were prepared from corresponding benzyl alcohols and haloalkanes according to the reported method.[8] Isopropylbenzene derivatives were synthesized according to reported method.[9] Isochromane-1,1-*d₂* (**S1-*d₂***) was synthesized according to reported method,[10] and the purity of **S1-*d₂*** was 98% according to ^{1}H NMR analysis. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker AV 400 or Bruker AV 500. The peaks were internally referenced to TMS (0.00 ppm). The following abbreviations were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, and br = broad. All products were identified by ^{1}H and ^{13}C NMR, HRMS.

Catalytic aerobic oxidation of isochromans

Typically, a mixture of isochroman (134 mg, 1 mmol), Ni_2Al-LDH (100 mg) and *γ*-valerolactone (2.0 g, 20 mmol) in a carousel reaction tube (Fig. S1) were magnetically stirred at 110 ℃ under 1 atm of oxygen atmosphere. The reaction was monitored by GC (Gas chromatography, the internal standard is biphenyl). The conversion of the substrate and the selectivity of 1-isochromanone were obtained on the basis of the GC analysis. The other reactions were monitored by TLC (thin-layer chromatography, petroleum ether/ethyl acetate (5:1, v/v) and analyzed through a GC-MS (SHIMADZU, GCMS-QP2010 SE). After completion of the reaction, the reaction mixture was concentrated on a rotary evaporator under vacuum, then the residue was purified by flash column chromatography on silica gel to yield isochromanones.

Fig. S1 The photographs of the reactor and the reaction.

Catalytic aerobic oxidation of isochromans without Ni_2Al-LDH

Typically, a mixture of isochroman (1.34 g, 10 mmol) and γ-valerolactone (20 g, 200 mmol) in reactor were magnetically stirred at 90 °C under 1 atm of oxygen atmosphere. The reaction was monitored by TLC (petroleum ether/ethyl acetate (5:1, v/v) and analyzed through a GC-MS (SHIMADZU, GCMS-QP2010 SE). After completion of the reaction, the reaction mixture was concentrated on a rotary evaporator under vacuum, then the residue was purified by flash column chromatography on silica gel to yield 4-isochromanone.

Catalytic aerobic oxidation of ethers

Typically, a mixture of benzyl methyl ether (122 mg, 1 mmol) and *γ*-valerolactone (2.0 g, 20 mmol) in a carousel reaction tube (Fig. S1) were magnetically stirred at 110 °C under 1 atm of oxygen atmosphere. The reaction was monitored by TLC (petroleum ether/ethyl acetate (20:1, v/v) and analyzed through a GC-MS (SHIMADZU, GCMS-QP2010 SE). After completion of the reaction, the reaction mixture was concentrated on a rotary evaporator under vacuum, then the residue was purified by flash column chromatography on silica gel to yield esters.

Catalytic aerobic oxidation of benzyl or allylic C–Hs

Typically, a mixture of benzyl or allylic C–Hs (1 mmol) and *γ*-valerolactone (2.0 g, 20 mmol) in a carousel reaction tube (Fig. S1) were magnetically stirred at 140 °C under 1 atm of oxygen atmosphere. The reaction was monitored by TLC (petroleum ether/ethyl acetate (20:1, v/v) and analyzed through a GC-MS (SHIMADZU, GCMS-QP2010 SE). After completion of the reaction, the reaction mixture was concentrated on a rotary evaporator under vacuum, then the residue was purified by flash column chromatography on silica gel to yield corresponding ketones.

Catalytic aerobic oxidation of isopropylbenzene

Typically, a mixture of cumene (120 mg, 1 mmol) and *γ*-valerolactone (2.0 g, 20 mmol) in a carousel reaction tube (Fig. S1) were magnetically stirred at 140 °C under 1 atm of oxygen atmosphere. The reaction was monitored by TLC (petroleum ether/ethyl acetate (10:1, v/v) and analyzed through a GC-MS (SHIMADZU, GCMS-QP2010 SE). After completion of the reaction, the reaction mixture was concentrated on a rotary evaporator under vacuum, then the residue was purified by flash column chromatography on silica gel to yield ketones.

Catalytic aerobic oxidation of 1-phenylethanol

Typically, a mixture of 1-phenylethanol (122 mg, 1 mmol) and *γ*-valerolactone (2.0 g, 20 mmol) in a carousel reaction tube (Fig. S1) were magnetically stirred at 110 °C under 1 atm of oxygen atmosphere. The reaction was monitored by TLC (petroleum ether/ethyl acetate (20:1, v/v) and analyzed through a GC-MS (SHIMADZU, GCMS-QP2010 SE). After completion of the reaction, the reaction mixture was concentrated on a rotary evaporator under vacuum, then the residue was purified by flash column chromatography on silica gel to yield ketones.

Catalytic aerobic oxidation of 1-benzylpiperidine

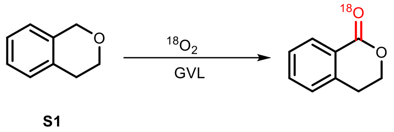
Typically, a mixture of 1-benzylpiperidine (175 mg, 1 mmol) and *γ*-valerolactone (2.0 g, 20 mmol) in a carousel reaction tube (Fig. S1) were magnetically stirred at 140 °C under 1 atm of oxygen atmosphere. The reaction was monitored by TLC (petroleum ether/ethyl acetate (20:1, v/v) and analyzed through a GC-MS (SHIMADZU, GCMS-QP2010 SE). The reaction detected no target product amide.

Electron paramagnetic resonance (EPR) experiments

X-band continuous-wave EPR spectra were obtained using a Bruker spectrometer equipped (EPR A300-10/12). The solution of isochroman (1.0 mmol), Ni_2Al-LDH (100 mg) in *γ*-valerolactone (2 mL) was stirred for 1 h at 110 °C and 100 μL of the solution was sampled in EPR tube, which were cooled 5 K prior to measurements; and other contrast reactions were tested under the same conditions. EPR analysis was carried out at low temperature on EPR spectrometer operated at 9.802 GHz.

$^{18}O_2$ isotope experiments

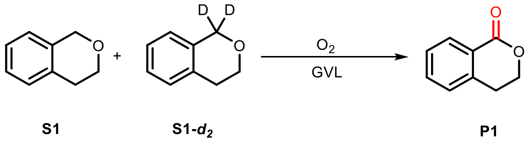
Typically, a mixture of isochroman (134 mg, 1 mmol) and *γ*-valerolactone (2 g, 20 mmol) in reactor were magnetically stirred at 110 °C under 1 atm of $^{18}O_2$ (97%) atmosphere. The reaction was analyzed through a GC-MS (SHIMADZU, GCMS-QP2010 SE).



Scheme S2 $^{18}O_2$ isotope experiments

Kinetic isotope effect studies

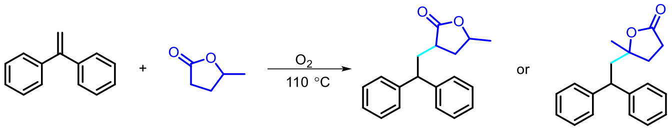
For the calculation of intramolecular isotopic value, the reaction was performed as described above except for the use of **S1-*d*$_2$** instead of **S1**. When **S1-*d*$_2$** was completely converted, Kinetic isotopic effects (KIE) values k_H/k_D were calculated based on the GC-MS analysis. On the other hand, for the calculation of intermolecular isotopic value, the reactions were performed as described above except for the use of the mixture of **S1-*d*$_2$** and **S1** as the substrates. When the substrates were completely converted, KIE values k_H/k_D were calculated based on the GC-MS analysis. For the calculation of KIE values, it was taken into account that substrates **S1-*d*$_2$** and **S1** were 99% and 99% pure, respectively.



Scheme S3 Comparison of reaction rates of isochromane and S1-*d*$_2$ for isolated kinetic isotope experiments over GVL reaction system.

Experiment for capturing the GVL radical

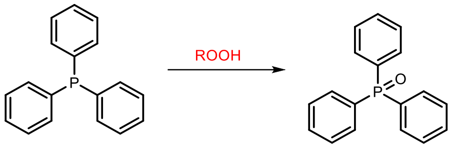
Typically, a mixture of 1,1-diphenylethylene (180 mg, 1 mmol) and *γ*-valerolactone (2.0 g, 20 mmol) in a carousel reaction tube (Fig. S1) were magnetically stirred at 110 °C reaction 6 h under 1 atm of oxygen atmosphere. The reaction system was analyzed through a GC-MS (SHIMADZU, GCMS-QP2010 SE) (Scheme S4).



Scheme S4 Capturing the GVL radical.

Experiment for capturing the peroxide intermediates

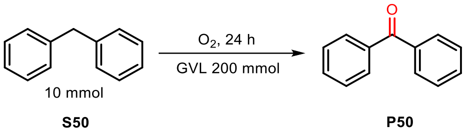
At the end of the reaction, 100 mg of Ph_3P was added into the reaction solution, the white solid was completely dissolved and the reaction solution was reduced to room temperature, and then the content of $Ph_3P=O$ was analyzed by GC-MS.



Scheme S5 Capturing the peroxide intermediates.

Scale-up experiment for the aerobic oxidation of diphenylmethane

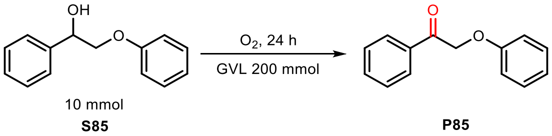
A mixture of diphenylmethane (1.68 g, 10 mmol), *γ*-valerolactone (20 g, 200 mmol) in a 50 mL round-bottom flask was magnetically stirred at 140 °C under 1 atm of oxygen atmosphere. The reaction was monitored by GC-MS (Scheme S6).



Scheme S6 Scale-up experiment.

Scale-up experiment for the aerobic oxidation of benzenemethanol

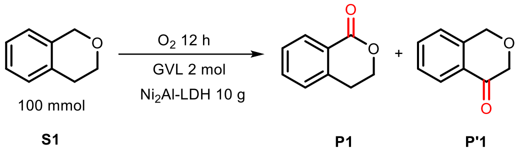
A mixture of benzenemethanol (2.14 g, 10 mmol), *γ*-valerolactone (20 g, 200 mmol) in a 50 mL round-bottom flask was magnetically stirred at 140 °C under 1 atm of oxygen atmosphere. The reaction was monitored by GC-MS (Scheme S7).



Scheme S7 Scale-up experiment.

Scale-up experiment for the aerobic oxidation of isochroman

A mixture of isochroman (13.42 g, 100 mmol), Ni_2Al-LDH (10 g), γ-valerolactone (200 g, 2 mol) in a 500 mL round-bottom flask was magnetically stirred at 110 ℃ under 1 atm of oxygen atmosphere. The reaction was monitored by GC (Scheme S8).



Scheme S8 Scale-up experiment.

Characterization of Ni_2Al-LDH

The identification of the crystallization of the prepared samples were confirmed through Powder X-ray diffraction (XRD) using a Rigaku D/max 2500 PC X-ray diffractometers with Cu-Kα (1.5402 Å) radiation. Temperature-programmed desorption of ammonia (NH_3-TPD) using a Micromeritics Autochem model 2920 instrument was carried out to evaluate the total acidity of the catalysts. The samples (~100 mg) were pretreated in vacuum at 100 °C before the samples were degassed under helium (White Martins, 99.9) flow (30 mL min^{-1}) for 1 h. Next, the materials were saturated with NH_3 (30 mL min^{-1}) by 30 min. Once saturated, the samples were purged again with helium gas (30 mL min^{-1}) to remove physiorbed/weakly adsorbed ammonia species. the NH_3-TPD was performed between 50 and 800 °C with a heating rate of 10 K min^{-1} by using a helium flow. The evolved ammonia was analyzed by on-line GC-MS provided with a TCD detector. Fourier-transformed infrared absorption of pyridine spectra (Py-FTIR) were collected on a Tensor 27 spectrophotometer. The samples were pretreated in vacuum at 80 °C for 2 h and then cooling the sample at 30 °C. Pyridine steam was subsequently introduced into the situ-cell for 30 min. Finally, the spectra were recorded at 50 °C.

Production and application of GVL

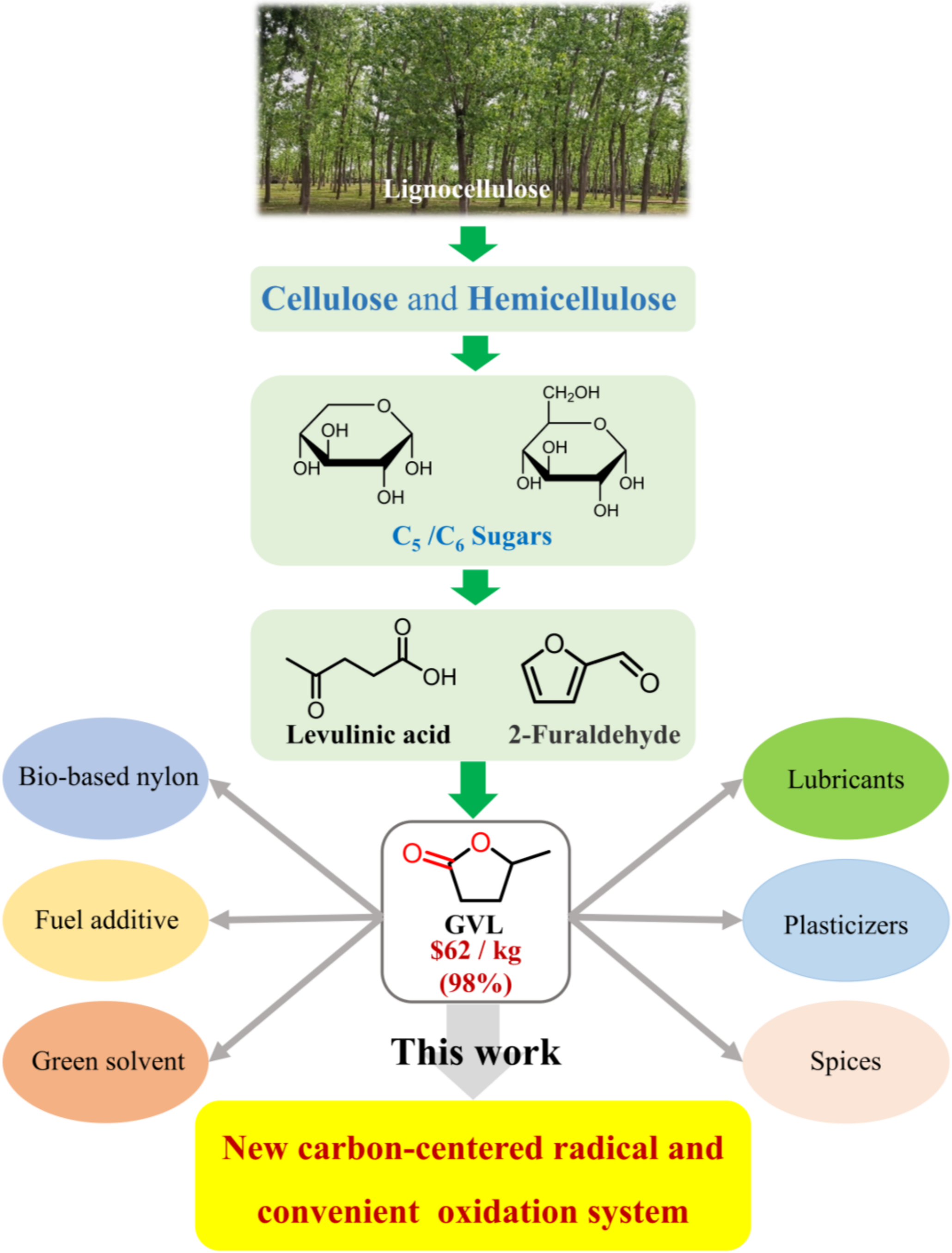
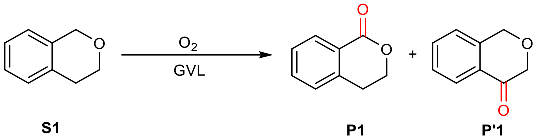


Fig. S2 Production and application of GVL.

Comparative experiments of various additives

Table S1 Effect of additives on the catalytic oxidation of isochroman[a].



Entry	Additive	Conv. /%[b]	Sel. /%[b]
1	Ni_2Mg_2Mn-LDH	>99	86
2	Ni_2Mn-LDH	>99	70
3	Mg_2Al-LDH	>99	81
4	Mg_2Fe-LDH	>99	70
5	USY/11	40	24
6	ZSM-5	56	73
7	HY/9-12	43	37
8	NaY	>99	74
9	13X	99	67
10	3Å	>99	74
11	Strongly basic anion exchange resin	93	64
12	Macroporous weakly acidic ion-exchange resin	98	76
13	*p*-toluenesulfonic acid	4	>99
14	H_3PO_4	29	27
15	Na_2CO_3	76	59
16	DMAP	9	76
17	$NiCl_2$	64	43
18	$AlCl_3$	trace	-

[a] Reaction conditions: **S1** 1 mmol, additive 100 mg, GVL 20 mmol, O_2 1 atm, 5 h; [b] Based on GC analysis using biphenyl as the internal standard substance.

Optimization of reaction conditions

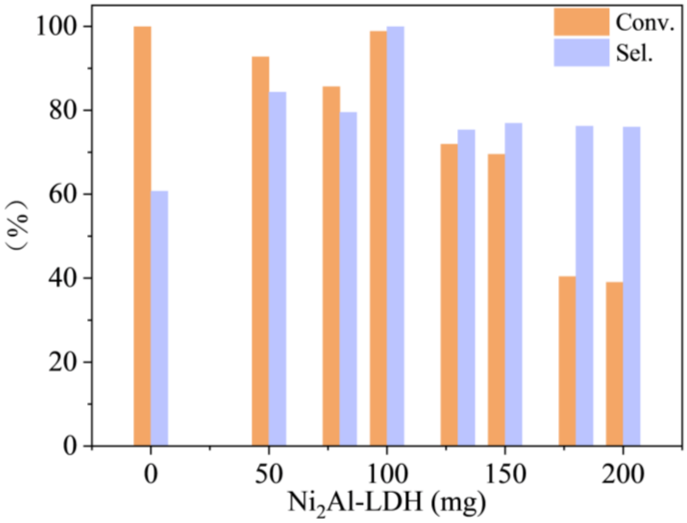


Fig. S3 Effect of the amount of Ni_2Al-LDH.

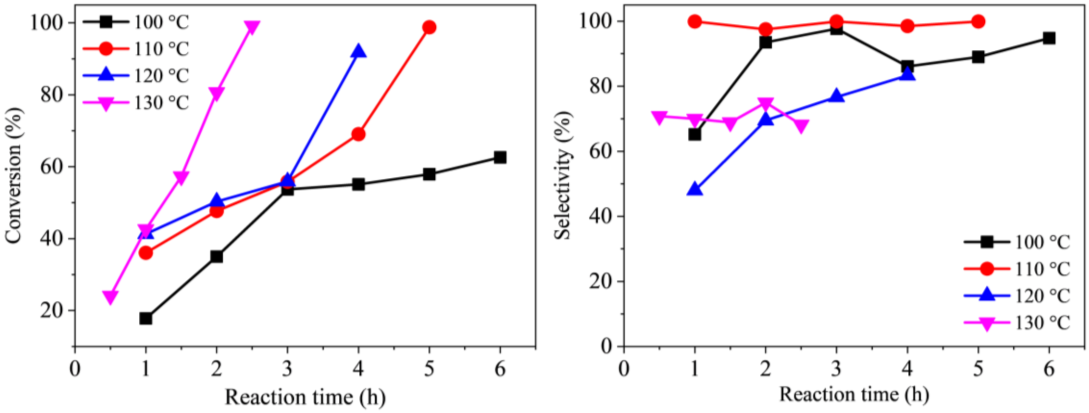


Fig. S4 Effect of the reaction temperature and reaction time.

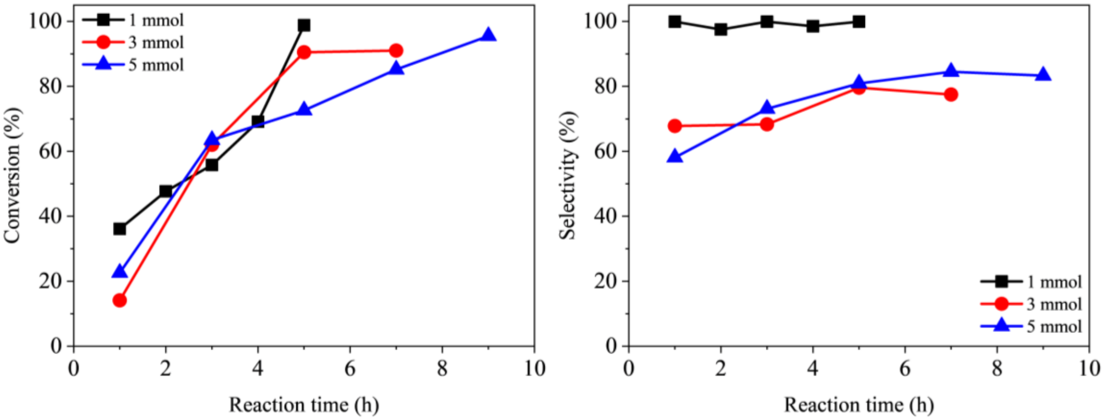


Fig. S5 Effect of the isochroman concentration.

DFT calculation method

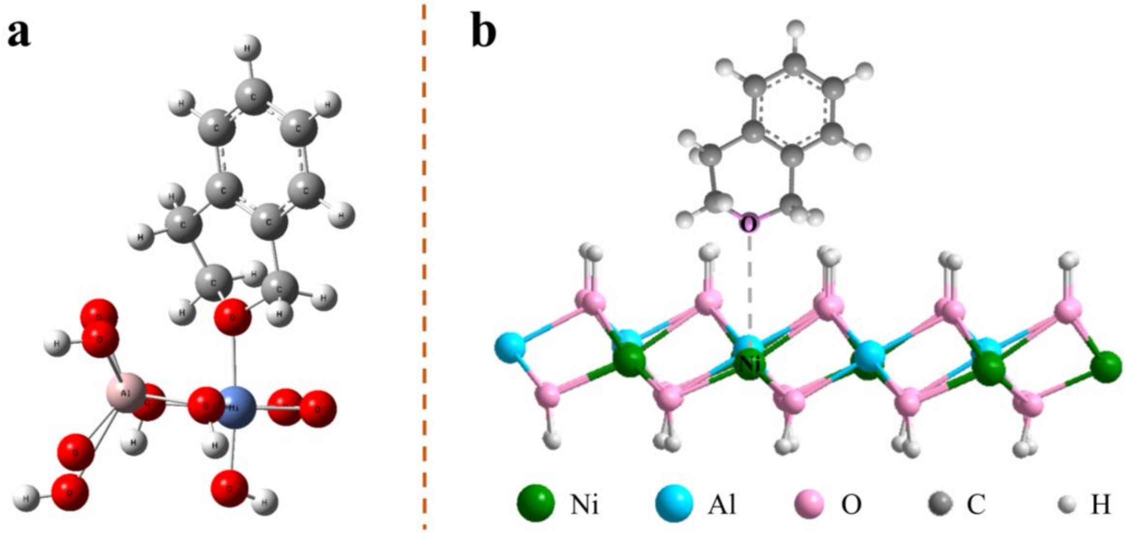


Fig. S6 Calculation of the optimized adsorption mode (a) and schematic diagram (b) of **S1** on Ni_2Al-LDH.

Determination of the HAT or SET process

The difference in reactivity between the above two substrates can reflect the reaction pathways. For the SET (Single Electron Transfer) reactions, the relative rate of C–H oxidation is 2º>3º, whereas it is 3º>2º for HAT (Hydrogen Atom Transfer) reactions.[11-13]

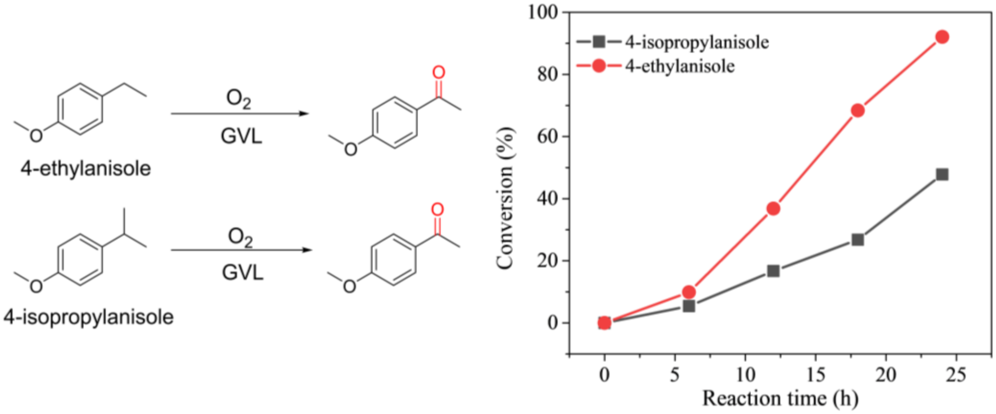


Fig. S7 Catalytic oxidation of 4-ethylanisole and 4-isopropylanisole over GVL reaction system. Reaction conditions: substrate 1 mmol, GVL 2 mL, 140 °C, O_2 (1 atm).

Electron spin density

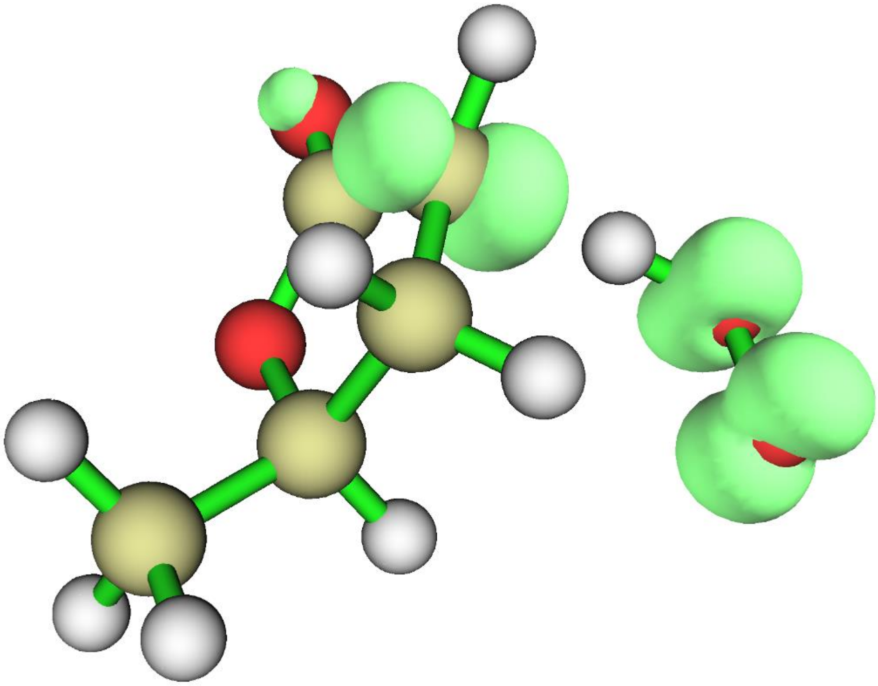


Fig. S8 The electron spin density of **TS1-β**

Experiment for capturing the GVL radical

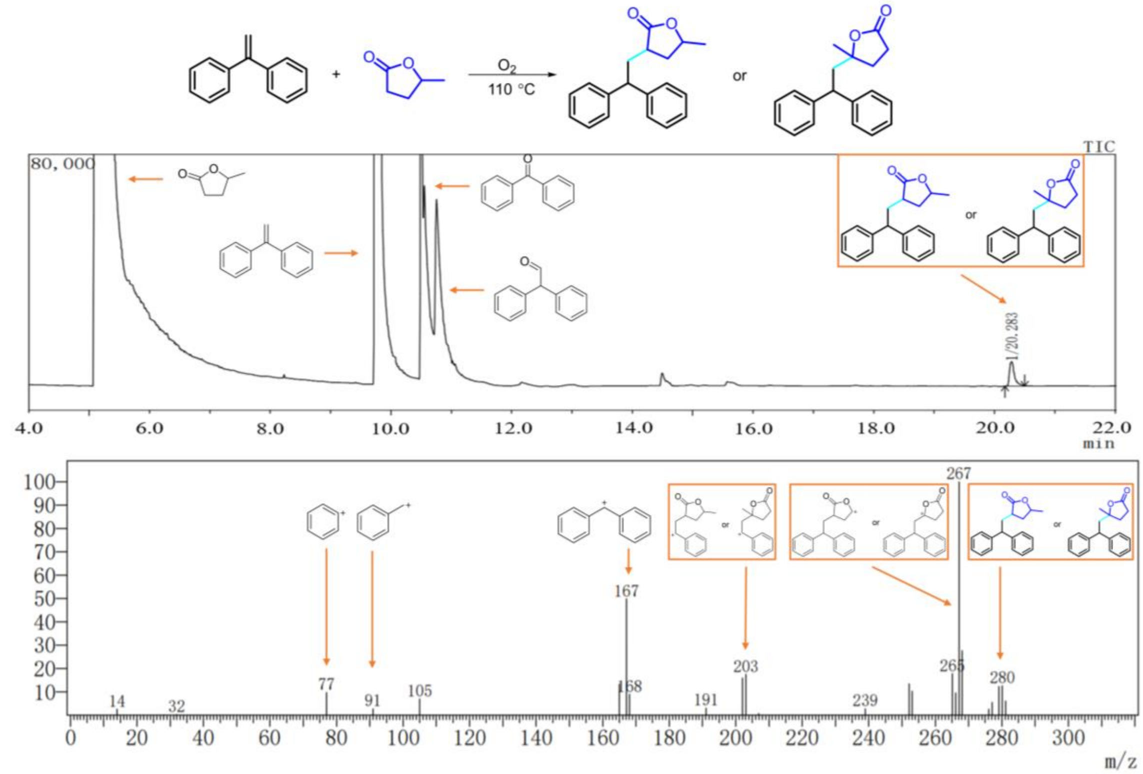


Fig. S9 GC-MS analysis the GVL reaction system in the presence of 1,1-diphenylethylene. Reaction conditions: 1,1-diphenylethylene 1 mmol, GVL 2 mmol, 110 ℃, 6 h, O_2 (1 atm).

Free energy profiles

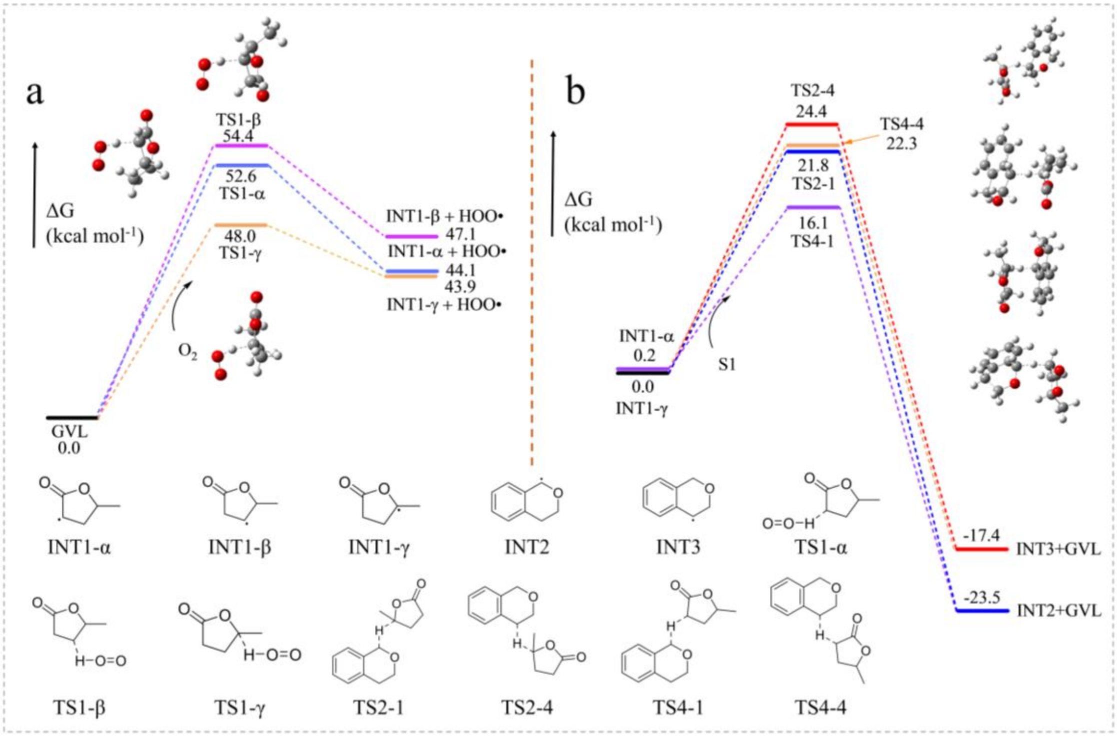


Fig. S10 Free energy profiles (kcal/mol) calculated at the M06-2x/6-31G(2df,2p) level of theory for the GVL-catalyzed oxidation of **S1**: (a) generation of active intermediates and (b) activation of **S1** through two possible intermedia.

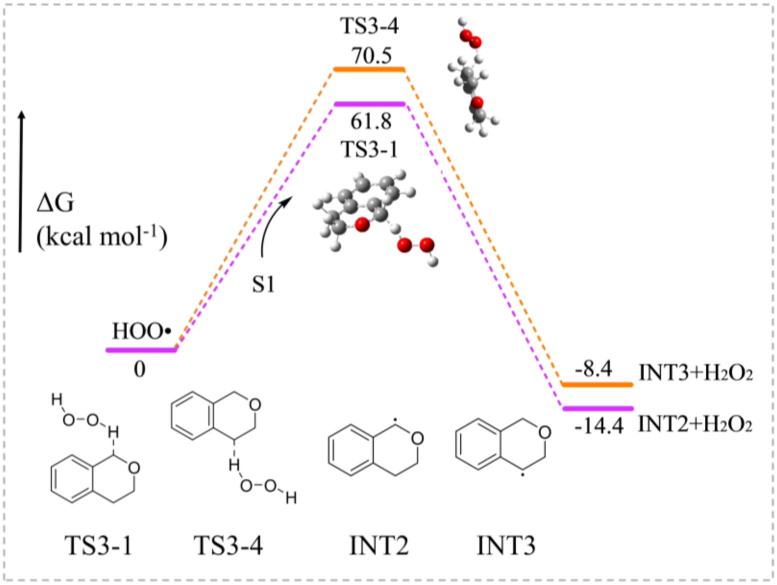


Fig. S11 Free energy profiles (kcal/mol) calculated at the M06-2x/6-31G(2df,2p) level of theory for the •OOH-catalyzed oxidation of **S1**.

Table S2 The ICP-MS results of GVL and the mixture reaction liquid.

Sample	Ni (ppm)	Al (ppm)	Ca (ppm)	Fe (ppm)	Na (ppm)	Si (ppm)	Other metals (ppm)
GVL	0.003	0.240	0.267	0.839	0.442	0.253	<0.001
Reaction mixture	0.003	0.247	-	-	-	-	-

ICP-MS total element analysis of GVL and ICP-MS analysis the reaction mixture.

Characterization of Ni_2Al-LDH

The XRD pattern of the Ni_2Al-LDH (Fig. S11a) exhibits intense typical reflections located at the angles of a hydrotalcite-like phase. The amount of acidic sites was quantified by NH_3-TPD. The result shown in Fig. S11b indicates that two peaks at 50−200°C and 250−350°C can be observed for Ni_2Al-LDH, which are related to the weak and medium acidic sites,[14] respectively. The type of acidic site of the catalyst was further identified by Py-FTIR analysis, as shown in Fig. S11c. The Py-FTIR spectra shows four main bands observed at 1607, 1574, 1490, and 1445 cm^{-1}. Among them, the band at 1445, 1574, and 1606 cm^{-1} are due to the pyridine adsorbed on Lewis acidic sites, originating from coordinatively unsaturated metal cationic sites. The band at 1490 cm^{-1} is attributed to a mixture of Lewis and Brønsted acidic site of pyridine adsorption.[15]

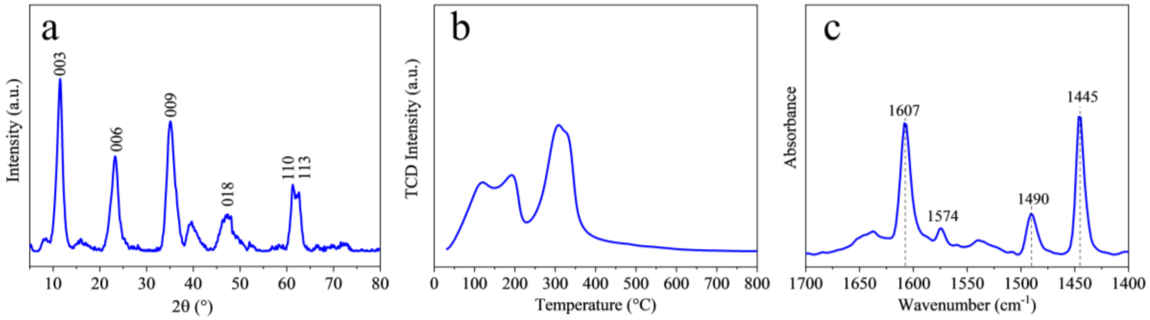


Fig. S12 XRD pattern of Ni_2Al-LDH (a), NH_3-TPD (b) and Py-FTIR (c) analysis of Ni_2Al-LDH.

Computational details

All reported structures were optimized and characterized to be minima or transition states at M06-2x[16-18]/6-31G(2df,2p) level in the gas phase.

The free energies at 298.15 K and 1 atm were obtained through frequency calculations.

All standard DFT calculations were performed with Gaussian 09 program.[19]

Table S3 Calculated energies and energy corrections.

Stationary point	Zero-point correction	Thermal correction to Energy	Thermal correction to Enthalpy	Thermal correction to Gibbs Free Energy	Sum of electronic and zero-point Energies	Sum of electronic and thermal Energies	Sum of electronic and thermal Enthalpies	Sum of electronic and thermal Free Energies
GVL	0.127135	0.133644	0.134588	0.096679	-345.557384	-345.550875	-345.549931	-345.587840
O_2	0.004048	0.006410	0.007354	-0.015905	-150.259906	-150.257544	-150.256599	-150.279858
TS1-γ	0.125815	0.135311	0.136255	0.089483	-495.754901	-495.745405	-495.744461	-495.791234
INT1-γ	0.113010	0.119821	0.120765	0.081426	-344.910940	-344.904129	-344.903184	-344.942524
•OOH	0.014602	0.017454	0.018398	-0.007549	-150.833095	-150.830243	-150.829299	-150.855246
S1	0.170365	0.176933	0.177877	0.138993	-423.850704	-423.844136	-423.843192	-423.882076
TS2-1	0.279613	0.294100	0.295044	0.235060	-768.745293	-768.730806	-768.729862	-768.789846
TS2-4	0.281416	0.294814	0.295758	0.239266	-768.743514	-768.730116	-768.729172	-768.785664
TS3-1	0.185179	0.192654	0.193598	0.151186	-574.604851	-574.597377	-574.596432	-574.638845
TS3-4	0.185588	0.192815	0.193759	0.151884	-574.591272	-574.584046	-574.583101	-574.624976
INT2	0.157317	0.164882	0.165826	0.124645	-423.241521	-423.233956	-423.233012	-423.274193
INT3	0.156769	0.164394	0.165338	0.123911	-423.231711	-423.224086	-423.223142	-423.264569
H_2O_2	0.026335	0.029217	0.030161	0.004885	-151.464650	-151.461768	-151.460824	-151.486100
TS1-α	0.125726	0.135115	0.136060	0.089225	-495.747405	-495.738017	-495.737072	-495.783907
TS1-β	0.125587	0.135170	0.136114	0.088216	-495.743683	-495.734100	-495.733156	-495.781054
INT1-α	0.113373	0.119867	0.120812	0.082238	-344.911066	-344.904571	-344.903627	-344.942201
INT1-β	0.112037	0.118982	0.119926	0.080177	-344.905460	-344.898515	-344.897571	-344.937320
TS4-1	0.280717	0.295320	0.296264	0.236729	-768.754667	-768.740065	-768.739121	-768.798656
TS4-4	0.281305	0.295785	0.296729	0.237595	-768.745108	-768.730628	-768.729684	-768.788818

Energies and cartesian coordinates for all structures

All energies are given in Hartree

TS1-α

C	0.230383	0.831223	0.888623
C	-0.077654	-0.5552	1.329688
C	0.636176	-1.414422	0.261031
H	-1.001034	1.131333	-0.041265
H	0.114529	1.714346	1.5055
H	-1.151415	-0.768549	1.372465
H	0.327265	-0.733606	2.332555
H	1.230106	-2.205254	0.718997
O	1.575334	-0.532497	-0.388415
C	-0.301398	-1.987808	-0.784719
H	0.266712	-2.505145	-1.557129
H	-0.995486	-2.691592	-0.322153
H	-0.88245	-1.192306	-1.256151
C	1.346284	0.76873	-0.082044
O	1.97843	1.678658	-0.551891
O	-2.72264	0.313491	-0.069368
O	-1.944997	1.214802	-0.543864

TS1-β

C	-0.151414	-0.649197	1.05432
C	-0.101483	0.801559	0.709889
C	0.935126	0.983034	-0.374205
H	0.27604	-0.882936	2.034786
H	-1.158372	-1.08188	1.035333
H	-0.234671	1.57776	1.456362
H	-1.50481	0.952306	-0.030341
H	0.547674	1.532911	-1.237386
O	1.229576	-0.343807	-0.832129
C	2.213554	1.645166	0.127294
H	2.963331	1.644749	-0.663626
H	2.0102	2.675443	0.423483
H	2.610425	1.101793	0.987179
C	0.692784	-1.301513	-0.032984
O	0.889669	-2.468646	-0.204813
O	-3.041826	-0.15507	-0.08224
O	-2.457571	0.918218	-0.494778

TS1-γ

C	1.209723	-1.040011	0.850258
C	0.022571	-0.204021	1.325087
C	-0.248331	0.668542	0.11733
H	1.952855	-1.270126	1.609619
H	0.889854	-1.978214	0.389982
H	0.299242	0.432291	2.174406
H	-0.853635	-0.78479	1.611867
H	-1.164273	-0.207551	-0.659804
O	0.932024	0.791973	-0.603271
C	-1.038529	1.933064	0.208717
H	-1.174699	2.378453	-0.776506

H	-2.014775	1.723959	0.647587
H	-0.514743	2.655677	0.845558
C	1.83276	-0.188446	-0.24066
O	2.901285	-0.280401	-0.762489
O	-2.852842	-0.889884	-0.053759
O	-1.991591	-0.867247	-1.006368

TS2-1

C	3.884921	-1.61492	-0.101932
C	3.854352	-0.22018	-0.038267
C	2.6526	0.474918	-0.093888
C	1.440602	-0.229516	-0.210751
C	1.47832	-1.638338	-0.303951
C	2.687366	-2.317456	-0.246582
H	4.82879	-2.142922	-0.052609
H	4.783008	0.335942	0.045034
H	0.553292	-2.187929	-0.436351
H	2.698299	-3.398275	-0.319004
O	1.458314	2.602544	0.281751
C	0.182707	0.515201	-0.302357
H	-0.385482	0.292967	-1.21787
H	-0.573289	-0.023501	0.534348
C	0.196231	2.004084	0.023765
H	-0.354706	2.17838	0.951725
H	-0.308868	2.570268	-0.771461
C	2.647628	1.979323	-0.160273
H	2.874237	2.300625	-1.187334
H	3.431549	2.381841	0.486421
C	-3.253515	1.023685	-0.368715
C	-2.748507	0.827639	1.05975
C	-1.918098	-0.442921	0.960833
H	-4.276704	1.383029	-0.454465
H	-2.613888	1.695906	-0.944529
H	-3.572448	0.636329	1.753379
H	-2.186358	1.678049	1.435818
O	-2.358388	-1.141952	-0.165642
C	-1.87644	-1.393385	2.125741
H	-0.909099	-1.895702	2.208592
H	-2.073511	-0.858628	3.053001
H	-2.645537	-2.157441	1.978238
C	-3.125872	-0.357236	-0.988523
O	-3.585307	-0.767382	-2.015115

TS2-4

C	-1.264381	2.62822	-0.243876
C	-0.546531	1.548727	-0.728105
C	-1.026807	0.236127	-0.561118
C	-2.240343	0.014448	0.090086
C	-2.960851	1.113856	0.569571
C	-2.483401	2.409866	0.409541
H	-0.881961	3.631058	-0.369239
H	0.396238	1.707116	-1.241586
H	-3.904481	0.947903	1.075469
H	-3.051715	3.246637	0.790589
O	-0.761225	-2.117731	-0.982494
C	-2.77029	-1.355688	0.28297
H	-2.924438	-1.505006	1.35071
H	-3.74295	-1.42231	-0.202923

C	-1.887272	-2.474272	-0.225579
H	-2.467397	-3.122522	-0.876495
H	-1.540158	-3.063816	0.624238
C	-0.240428	-0.856199	-1.074997
H	0.822903	-0.92031	-0.265628
H	0.114279	-0.719769	-2.092374
C	2.913667	0.387842	-0.949311
C	2.839224	-1.054457	-0.449285
C	1.70131	-0.97747	0.551513
H	3.91561	0.758886	-1.154976
H	2.312441	0.544858	-1.848888
H	3.790254	-1.349497	0.012541
H	2.614703	-1.784248	-1.229641
O	1.677204	0.359158	1.045253
C	1.423495	-2.01147	1.586494
H	0.497149	-1.777494	2.115971
H	1.318603	-2.985959	1.105618
H	2.231241	-2.075139	2.323922
C	2.301339	1.199509	0.184801
O	2.327433	2.387996	0.340549

TS3-1

C	-2.836737	-1.211494	0.08714
C	-2.580763	0.157393	0.135926
C	-1.271183	0.642846	0.026387
C	-0.215267	-0.24763	-0.136584
C	-0.476572	-1.630006	-0.183274
C	-1.777896	-2.11033	-0.07218
H	-3.845582	-1.575125	0.172905

H	-3.395796	0.850111	0.260695
H	0.343028	-2.316751	-0.30658
H	-1.96813	-3.168392	-0.109117
O	0.239429	2.418579	-0.018018
C	1.134895	0.192749	-0.254293
H	1.74974	-0.236818	0.66937
H	1.554996	-0.184888	-1.171249
C	1.338966	1.640754	-0.215175
H	1.784375	1.933153	-1.155495
H	2.025972	1.86148	0.591388
C	-1.053449	2.053124	0.092206
H	-1.421036	2.410683	1.044603
H	-1.611156	2.526159	-0.705327
O	3.003901	-1.263526	-0.35666
O	2.702289	-0.786934	0.876233
H	3.64668	-1.968998	-0.184557

TS3-4

C	2.926765	-1.100907	-0.08137
C	2.606019	0.255792	-0.156464
C	1.275152	0.678975	-0.039007
C	0.266136	-0.254553	0.154552
C	0.589897	-1.621451	0.231002
C	1.914031	-2.043688	0.113315
H	3.947777	-1.418703	-0.17258
H	3.383882	0.981132	-0.304374
H	-0.192553	-2.342449	0.378433
H	2.15404	-3.088077	0.170997
O	-0.305234	2.336665	-0.001777

C	-1.086732	0.11502	0.274913
H	-1.664781	-0.437005	-0.60438
H	-1.479402	-0.248299	1.206113
C	-1.36526	1.522706	0.150012
H	-1.883303	1.830924	1.040577
H	-2.002922	1.660543	-0.708024
C	0.990612	2.05534	-0.110862
H	1.340316	2.428204	-1.058587
H	1.513353	2.554994	0.686604
O	-3.495737	-0.790106	0.051174
O	-2.412592	-1.299616	-0.546632
H	-4.10762	-1.540214	0.126558

TS4-1

C	-2.795076	-2.156501	-0.416562
C	-1.664071	-1.452818	-0.826899
C	-1.572345	-0.085306	-0.577826
C	-2.600363	0.585041	0.103938
C	-3.720787	-0.128507	0.523613
C	-3.819434	-1.493813	0.257306
H	-2.871765	-3.219212	-0.609004
H	-0.841435	-1.96537	-1.318297
H	-4.518562	0.381977	1.052162
H	-4.694619	-2.04296	0.582079
O	0.024023	1.564809	0.114452
C	-2.403877	2.065584	0.297444
H	-2.582759	2.566254	-0.65989
H	-3.113799	2.479295	1.015415
C	-0.973467	2.373989	0.758757
H	-0.880946	2.189961	1.831393
H	-0.727299	3.420372	0.564689
C	-0.400508	0.762103	-0.939776
H	-0.491642	1.310386	-1.88406
H	0.671953	-0.02091	-1.162577
C	1.71624	-0.802501	-1.08378
C	1.629835	-1.422342	0.289075
C	2.344635	-0.372691	1.1574
H	1.641628	-1.39267	-1.990966
H	2.168376	-2.374897	0.328631
H	0.604652	-1.594797	0.626619
H	1.617147	0.359283	1.514929
O	3.231937	0.324376	0.261823
C	3.150048	-0.937334	2.305233
H	3.672998	-0.142783	2.837565
H	2.485798	-1.44874	3.005109
H	3.886264	-1.653036	1.934814
C	2.867141	0.142751	-1.032685
O	3.422312	0.696055	-1.946281

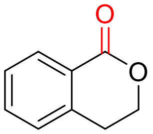
TS4-4

C	-3.32696	1.732697	-0.229908
C	-3.27093	0.420727	-0.683136
C	-2.227034	-0.42395	-0.301772
C	-1.226859	0.046157	0.562878
C	-1.287765	1.388761	1.01118
C	-2.321759	2.219379	0.615006
H	-4.141743	2.377756	-0.533715
H	-4.042964	0.041913	-1.345228

H	-0.496843	1.784184	1.647956
H	-2.352759	3.244696	0.961546
O	-0.998048	-2.550263	-0.56139
C	-0.262033	-0.906282	1.094821
H	1.15597	-0.533627	1.15698
H	-0.236296	-0.82619	2.197756
C	-0.385963	-2.351968	0.696311
H	-0.912971	-2.912897	1.483997
H	0.608123	-2.796708	0.590306
C	-2.186739	-1.840177	-0.82237
H	-2.262881	-1.807761	-1.911813
H	-3.058088	-2.398095	-0.448121
C	2.312695	-0.229637	1.207686
C	2.246509	1.265867	0.983207
C	1.72799	1.34325	-0.470162
H	2.891669	-0.730966	1.973662
H	3.203122	1.784782	1.09028
H	1.547192	1.726018	1.675461
H	0.630944	1.381604	-0.469475
O	2.131354	0.105606	-1.089881
C	2.298711	2.486673	-1.279302
H	1.938269	2.446867	-2.306951
H	1.996752	3.441669	-0.842097
H	3.388717	2.435447	-1.287446
C	2.530641	-0.801281	-0.166635
O	2.919288	-1.900342	-0.46622

Spectrometric data for the products

1-Isochromanone (**P1**)



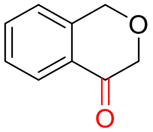
The general procedure as described above in 98% yield as colorless oil, 5 h, 145 mg.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.8 Hz, 1H), 7.53 (t, *J* = 7.3 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 1H), 7.26 (d, *J* = 7.6 Hz, 1H), 4.52 (t, *J* = 6.0 Hz, 2H), 3.05 (t, *J* = 6.0 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 165.2, 139.6, 133.7, 130.3, 127.7, 127.3, 125.3, 67.4, 27.8.

HRMS (ESI, *m/z*): calcd for $C_9H_9O_2$ $[M+H]^+$ 149.0601, found 149.0597.

4-Isochromanone (**P'1**)



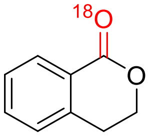
The general procedure as described above in 30% yield as colorless oil, 12 h, 80 ºC, 450 mg.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.7 Hz, 1H), 7.60 (td, *J* = 7.6, 1.2 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 1H), 7.25 (d, *J* = 7.7 Hz, 1H), 4.93 (s, 2H), 4.40 (s, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 194.1, 134.2, 127.9, 126.4, 124.5, 73.6, 67.9.

HRMS (ESI, *m/z*): calcd for $C_9H_9O_2$ $[M+H]^+$ 149.0601, found 149.0597.

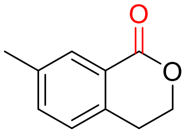
1-Isochromanone-^{18}O



The yield was 48% by GC-MS analysis after 2 h.

GC-MS: m/z (rel int.) 150 $[M^+]$ (44%), 120 (100%), 90 (89%), 63 (15%), 51 (12%).

7-Methylisochroman-1-one (**P2**)



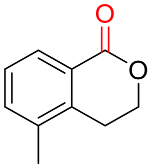
The general procedure as described above in 81% yield as colorless oil, 24 h, 131 mg.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (d, *J* = 2.7 Hz, 1H), 7.16 (d, *J* = 8.4 Hz, 1H), 7.08 (dd, *J* = 8.4, 2.7 Hz, 1H), 4.49 (t, *J* = 6.0 Hz, 2H), 3.82 (s, 3H), 2.97 (t, *J* = 6.0 Hz, 2H).

^{13}**C NMR** (126 MHz, $CDCl_3$) δ 165.2, 158.9, 131.9, 128.5, 126.0, 121.5, 113.0, 67.7, 55.6, 27.0.

HRMS (ESI, *m/z*): calcd for $C_{10}H_{11}O_2$ $[M+H]^+$ 163.0759, found 163.0754.

5-Methylisochroman-1-one (**P3**)



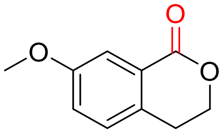
The general procedure as described above in 91% yield as colorless oil, 16 h, 147 mg.

^{1}**H NMR** (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.8 Hz, 1H), 7.40 (d, *J* = 7.5 Hz, 1H), 7.28 (t, *J* = 7.7 Hz, 1H), 4.52 (t, *J* = 6.1 Hz, 2H), 2.97 (t, *J* = 6.0 Hz, 2H), 2.33 (s, 3H).

^{13}**C NMR** (126 MHz, $CDCl_3$) δ 165.6, 138.3, 135.1, 128.2, 127.1, 125.3, 66.7, 24.9, 18.9.

HRMS (ESI, *m/z*): calcd for $C_{10}H_{11}O_2$ $[M+H]^+$ 163.0759, found 163.0754.

7-Methoxyisochroman-1-one (**P4**)



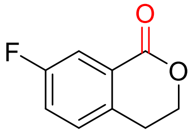
The general procedure as described above in 75% yield as colorless oil, 24 h, 147 mg.

^{1}**H NMR** (500 MHz, $CDCl_3$) δ 7.55 (d, *J* = 2.7 Hz, 1H), 7.16 (d, *J* = 8.4 Hz, 1H), 7.08 (dd, *J* = 8.4, 2.7 Hz, 1H), 4.49 (t, *J* = 6.0 Hz, 2H), 3.82 (s, 3H), 2.97 (t, *J* = 6.0 Hz, 2H).

^{13}**C NMR** (126 MHz, $CDCl_3$) δ 165.2, 158.9, 131.9, 128.5, 126.0, 121.5, 113.0, 67.67, 55.6, 27.0.

HRMS (ESI, *m/z*): calcd for $C_{10}H_{11}O_3$ $[M+H]^+$ 179.0708, found 179.0703.

7-Fluoroisochroman-1-one (**P5**)



The general procedure as described above in 90% yield as white solid, 5 h, 150 mg.

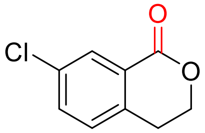
m.p. 76.0–77.1 ºC.

^{1}**H NMR** (500 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.6 Hz, 1H), 7.26 (dt, *J* = 8.0, 4.8 Hz, 2H), 4.54 (t, *J* = 6.0 Hz, 2H), 3.04 (t, *J* = 6.0 Hz, 2H).

^{13}**C NMR** (126 MHz, $CDCl_3$) δ 177.3, 160.8, 135.4, 129.2, 126.9, 121.0, 116.6, 67.5, 27.1.

HRMS (ESI, *m/z*): calcd for $C_{10}H_{11}O_2F$ $[M+H]^+$ 167.0508, found 167.0503.

7-Chloroisochroman-1-one (**P6**)



The general procedure as described above in 93% yield as yellow solid, 16 h, 170 mg.

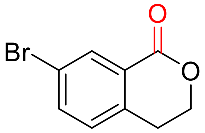
m.p. 69.3–70.3 ºC.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.45 (d, *J* = 8.1 Hz, 1H), 7.22 (d, *J* = 8.1 Hz, 1H), 4.50 (t, *J* = 6.0 Hz, 2H), 3.02 (t, *J* = 6.0 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 163.9, 137.9, 133.7, 133.5, 129.9, 128.9, 126.7, 67.3, 27.2.

HRMS (ESI, *m/z*): calcd for $C_{10}H_{11}O_2Cl$ $[M+H]^+$ 183.0209, found 183.0207.

7-Bromoisochroman-1-one (**P7**)



The general procedure as described above in 91% yield as yellow solid, 16 h, 207 mg.

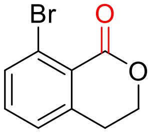
m.p. 87.7–89.9 ºC.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21 (d, *J* = 2.1 Hz, 1H), 7.66 (dd, *J* = 8.1, 2.1 Hz, 1H), 7.18 (d, *J* = 8.1 Hz, 1H), 4.54 (t, *J* = 6.0 Hz, 2H), 3.03 (t, *J* = 6.0 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 163.8, 138.3, 136.6, 133.1, 129.1, 127.0, 121.3, 67.3, 27.3.

HRMS (ESI, *m/z*): calcd for $C_{10}H_{11}O_2Br$ $[M+H]^+$ 248.9527, found 248.9522.

8-Bromoisochroman-1-one (**P8**)



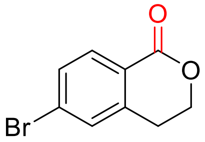
The general procedure as described above in 81% yield as colorless oil, 16 h, 184 mg.

^{1}H NMR (400 MHz,) δ 7.66 (d, *J* = 8.0 Hz, 1H), 7.32 (dd, *J* = 14.8, 7.0 Hz, 1H), 7.24 (d, *J* = 7.5 Hz, 1H), 4.47 (t, *J* = 5.8 Hz, 2H), 3.08 (t, *J* = 5.8 Hz, 2H).

^{13}C NMR (101 MHz,) δ 162.0, 142.7, 134.6, 133.5, 126.7, 124.7, 66.6, 29.3.

HRMS (ESI, *m/z*): calcd for $C_{10}H_{11}O_2Br$ $[M+H]^+$ 248.9527, found 248.9522.

6-Bromoisochroman-1-one (**P9**)



The general procedure as described above in 95% yield as white solid, 16 h, 216 mg.

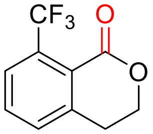
m.p. 120.9–122.1 ºC.

^{1}H NMR (400 MHz,) δ 7.94 (d, *J* = 8.3 Hz, 1H), 7.53 (dd, *J* = 8.3, 1.9 Hz, 1H), 7.46 (s, 1H), 4.54 (t, *J* = 5.9 Hz, 2H), 3.06 (t, *J* = 6.0 Hz, 2H).

^{13}C NMR (101 MHz,) δ 164.4, 141.3, 132.0, 131.2, 130.4, 128.8, 124.2, 67.2, 27.6.

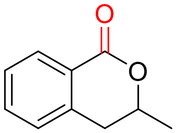
HRMS (ESI, *m/z*): calcd for $C_{10}H_{11}O_2Br$ $[M+H]^+$ 248.9527, found 248.9522.

8-(Trifluoromethyl)isochroman-1-one (P10)



The general procedure as described above in 0% yield, 40 h.

3-Methylisochroman-1-one (**P11**)



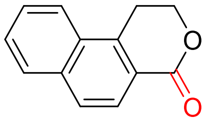
The general procedure as described above in 83% yield as colorless oil, 5 h, 134 mg.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.8 Hz, 1H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.33 (t, *J* = 7.6 Hz, 1H), 7.20 (d, *J* = 7.6 Hz, 1H), 4.65 - 4.60 (m, 1H), 2.91 - 2.88 (m, 2H), 1.47 (d, *J* = 6.3 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 165.6, 139.2, 133.7, 130.1, 127.6, 127.4, 124.9, 75.1, 34.8, 20.9.

HRMS (ESI, *m/z*): calcd for $C_{10}H_{11}O_2$ $[M+H]^+$ 163.0759, found 163.0754.

1,2-Dihydro-4*H*-benzo[f]isochromen-4-one (**P12**)



The general procedure as described above in 69% yield as orange solid, 24 h, 137 mg.

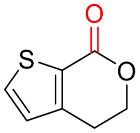
m.p. 106.7–108.4 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.6 Hz, 1H), 8.03 – 7.95 (m, 1H), 7.88 (dd, *J* = 6.6, 2.8 Hz, 1H), 7.80 (d, *J* = 8.6 Hz, 1H), 7.70 – 7.55 (m, 2H), 4.64 (t, *J* = 6.1 Hz, 2H), 3.39 (t, *J* = 6.1 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.5, 138.6, 135.6, 129.8, 128.9, 128.7, 127.7, 127.3, 125.1, 124.4, 122.4, 66.7, 24.2.

HRMS (ESI, *m/z*): calcd for $C_{13}H_{11}O_2$ $[M+H]^+$ 199.0759, found 199.0754.

4,5-Dihydro-7*H*-thieno[2,3-c]pyran-7-one (**P13**)



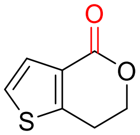
The general procedure as described above in 80% yield as colorless oil, 24 h, 123 mg.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 5.3 Hz, 1H), 7.18 (d, *J* = 5.3 Hz, 1H), 4.60 (t, *J* = 6.1 Hz, 2H), 3.17 (t, *J* = 6.1 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.3, 149.0, 128.1, 126.9, 124.0, 67.7, 24.6.

HRMS (ESI, *m/z*): calcd for $C_7H_7O_2S$ $[M+H]^+$ 155.0167, found 155.0161.

6,7-Dihydro-4*H*-thieno[3,2-c]pyran-4-one (**P14**)



The general procedure as described above in 62% yield as pale yellow solid, 24 h, 95 mg.

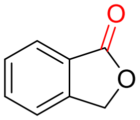
m.p. 86.2–87.4 ºC.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (d, *J* = 5.0 Hz, 1H), 7.01 (d, *J* = 4.9 Hz, 1H), 4.58 (t, *J* = 6.2 Hz, 2H), 3.02 (t, *J* = 6.2 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 161.3, 147.6, 134.5, 126.6, 122.5, 68.4, 21.1.

HRMS (ESI, *m/z*): calcd for $C_7H_7O_2S$ $[M+H]^+$ 155.0167, found 155.0161.

Isobenzofuran-1(3*H*)-one (**P15**)



The general procedure as described above in 90% yield as white solid, 16 h, 120 mg.

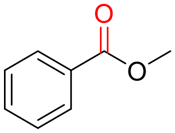
m.p. 72.9–74.1 ºC.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (s, 1H), 7.63 – 7.56 (m, 1H), 7.44 (d, *J* = 7.1 Hz, 2H), 5.23 (s, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 171.1, 146.6, 134.0, 128.9, 125.4, 122.3, 69.7.

HRMS (ESI, *m/z*): calcd for $C_8H_7O_2$ $[M+H]^+$ 135.0446, found 135.0441.

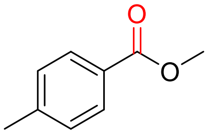
Methyl benzoate (P16) is known compound.



The yield was 75% by GC-MS analysis after 12 h.

GC-MS : *m/z* (rel int.) 136 [M$^+$] (28%), 105 (100%), 77 (52%), 51 (19%), 43 (31%).

Methyl 4-methylbenzoate (**P17**)



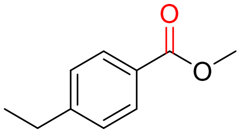
The general procedure as described above in 76% yield as colorless oil, 12 h, 114 mg.

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.93 (d, *J* = 8.1 Hz, 2H), 7.23 (d, *J* = 8.1 Hz, 2H), 3.89 (s, 3H), 2.40 (s, 3H).

^{13}C NMR (126 MHz, CDCl$_3$) δ 167.1, 143.5, 129.6, 129.0, 127.4, 51.9, 21.6.

HRMS (ESI, *m/z*): calcd for $C_9H_{11}O_2$ [M+H]$^+$ 151.0758, found 151.0754.

Methyl 4-ethylbenzoate (**P18**)



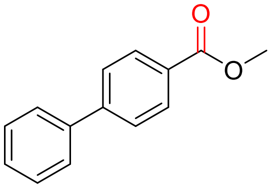
The general procedure as described above in 66% yield as colorless oil, 8 h, 108 mg.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.95 (d, *J* = 8.3 Hz, 2H), 7.26 (d, *J* = 8.4 Hz, 2H), 3.90 (s, 3H), 2.70 (q, *J* = 7.6 Hz, 2H), 1.05 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 167.1, 149.7, 129.7, 127.9, 127.6, 51.9, 28.9, 15.2.

HRMS (ESI, *m/z*): calcd for $C_{10}H_{13}O_2$ [M+H]$^+$ 165.0915, found 165.0910.

Methyl [1,1'-biphenyl]-4-carboxylate (**P19**)



The general procedure as described above in 44% yield as white solid, 5 h, 93 mg.

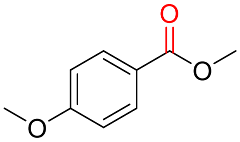
m.p. 119.1–119.8 ºC.

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.15 – 8.05 (m, 2H), 7.67 – 7.58 (m, 4H), 7.48 – 7.42 (m, 2H), 7.38 (ddd, *J* = 7.3, 3.7, 1.3 Hz, 1H), 3.92 (s, 3H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 167.0, 145.7, 140.0, 130.1, 129.0, 128.9, 128.2, 127.3, 127.1, 52.2.

HRMS (ESI, *m/z*): calcd for $C_{14}H_{13}O_2$ $[M+H]^+$ 213.0915, found 213.0910.

Methyl 4-methoxybenzoate (**P20**)



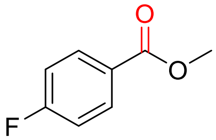
The general procedure as described above in 61% yield as colorless oil, 5 h, 101 mg.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 – 7.98 (m, 2H), 6.95 – 6.91 (m, 2H), 3.90 (s, 3H), 3.86 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 166.9, 163.3, 131.6, 122.6, 113.6, 55.4, 51.8.

HRMS (ESI, *m/z*): calcd for $C_9H_{11}O_3$ $[M+H]^+$ 167.0708, found 167.0703.

Methyl 4-fluorobenzoate (**P21**)



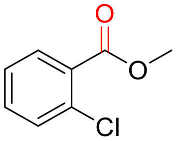
The general procedure as described above in 54% yield as colorless oil, 12 h, 83 mg.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 – 8.01 (m, 2H), 7.13 – 7.05 (m, 2H), 3.90 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 166.7, 166.1, 132.0, 126.4, 115.4, 52.1.

HRMS (ESI, *m/z*): calcd for $C_8H_8O_2F$ $[M+H]^+$ 155.0508, found 155.0503.

Methyl 2-chlorobenzoate (**P22**)



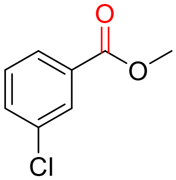
The general procedure as described above in 54% yield as colorless oil, 12 h, 51 mg.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (dd, J = 7.7, 1.5 Hz, 1H), 7.42 (dtd, J = 9.7, 8.0, 1.5 Hz, 2H), 7.30 (ddd, J = 7.6, 7.2, 1.6 Hz, 1H), 3.92 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.1, 133.7, 132.5, 131.4, 131.0, 130.0, 126.5, 52.3.

HRMS (ESI, *m/z*): calcd for $C_8H_8O_2Cl$ $[M+H]^+$ 171.0210, found 171.0207.

Methyl 3-chlorobenzoate (**P23**)



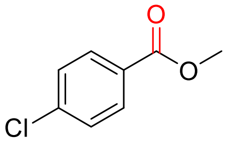
The general procedure as described above in 61% yield as colorless oil, 12 h, 104 mg.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (t, *J* = 1.8 Hz, 1H), 7.90 (d, *J* = 7.8 Hz, 1H), 7.50 (dd, *J* = 8.0, 0.9 Hz, 1H), 7.35 (t, *J* = 7.9 Hz, 1H), 3.90 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 165.8, 134.5, 132.9, 131.8, 129.7, 129.6, 127.7, 52.3.

HRMS (ESI, *m/z*): calcd for $C_8H_8O_2Cl$ $[M+H]^+$ 171.0210, found 171.0207.

Methyl 4-chlorobenzoate (**P24**)



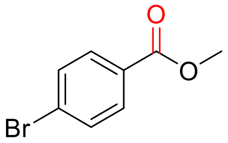
The general procedure as described above in 99% yield as colorless oil, 12 h, 168 mg.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 – 7.94 (m, 2H), 7.40 (d, *J* = 8.5 Hz, 2H), 3.91 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 166.2, 139.3, 131.0, 128.7, 128.6, 52.2.

HRMS (ESI, *m/z*): calcd for $C_8H_8O_2Cl$ $[M+H]^+$ 171.0210, found 171.0207.

Methyl 4-bromobenzoate (**P25**)



The general procedure as described above in 96% yield as white solid, 10 h, 206 mg.

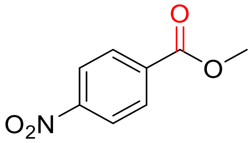
m.p. 114.6–115.0 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.4 Hz, 2H), 7.58 (d, *J* = 8.4 Hz, 2H), 3.91 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4, 131.7, 131.1, 129.0, 128.0, 52.3.

HRMS (ESI, *m/z*): calcd for $C_8H_8O_2Br$ $[M+H]^+$ 214.9707, found 214.9702.

Methyl 4-nitrobenzoate (**P26**)



The general procedure as described above in 89% yield as yellow solid, 40 h, 161 mg.

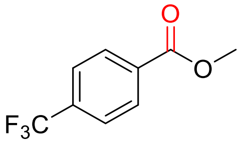
m.p. 96.7–97.9 ºC.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.25 (d, *J* = 8.8 Hz, 2H), 8.19 – 8.15 (m, 2H), 3.95 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 165.1, 150.5, 135.4, 130.7, 123.5, 52.8.

HRMS (ESI, *m/z*): calcd for $C_8H_8O_4N$ $[M+H]^+$ 182.0452, found 182.0448.

Methyl 4-(trifluoromethyl)benzoate (**P27**)



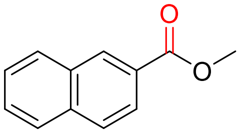
The general procedure as described above in 89% yield as colorless oil, 16 h, 181 mg.

^{1}H NMR (500 MHz, CDCl$_3$) δ 8.11 (d, *J* = 8.2 Hz, 2H), 7.66 (d, *J* = 8.2 Hz, 2H), 3.91 (s, 3H).

^{13}C NMR (126 MHz, CDCl$_3$) δ 165.7, 133.3, 129.9, 125.3, 124.7, 52.4.

HRMS (ESI, *m/z*): calcd for $C_9H_8O_2F_3$ $[M+H]^+$ 205.0476, found 205.0471.

Methyl 2-naphthoate (**P28**)



The general procedure as described above in 25% yield as white solid, 24 h, 46 mg.

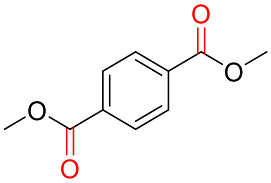
m.p. 72.5–73.3 ºC.

^{1}H NMR (500 MHz, CDCl$_3$) δ 8.65 (s, 1H), 8.10 (dd, *J* = 8.6, 1.5 Hz, 1H), 7.98 (d, *J* = 8.1 Hz, 1H), 7.94 – 7.89 (m, 2H), 7.60 (ddd, *J* = 15.0, 14.1, 7.0 Hz, 2H), 4.01 (s, 3H).

^{13}C NMR (126 MHz, CDCl$_3$) δ 167.3, 135.5, 132.5, 131.1, 129.4, 128.3, 128.2, 127.8, 127.4, 126.7, 125.3, 52.3.

HRMS (ESI, *m/z*): calcd for $C_{12}H_{11}O_2$ $[M+H]^+$ 187.0759, found 187.0754.

Dimethyl terephthalate (**P29**)



The general procedure as described above in 86% yield as white solid, 12 h, 167 mg.

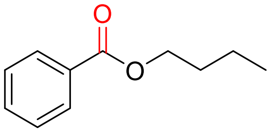
m.p. 142.2–143.1 ºC.

^{1}H NMR (500 MHz, CDCl$_3$) δ 8.09 (s, 4H), 3.94 (s, 6H).

^{13}C NMR (126 MHz, CDCl$_3$) δ 166.3, 133.9, 129.5, 52.4.

HRMS (ESI, *m/z*): calcd for $C_{10}H_{11}O_4$ $[M+H]^+$ 195.0652, found 195.0652.

Butyl benzoate (**P30**)



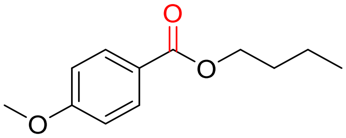
The general procedure as described above in 61% yield as colorless oil, 10 h, 108 mg.

^{1}H NMR (500 MHz, CDCl$_3$) δ 8.09 – 8.03 (m, 2H), 7.59 – 7.53 (m, 1H), 7.44 (dd, *J* = 10.7, 4.8 Hz, 2H), 4.34 (t, *J* = 6.6 Hz, 2H), 1.79 – 1.74 (m, 2H), 1.53 – 1.47 (m, 2H), 1.00 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, CDCl$_3$) δ 166.7, 132.8, 130.5, 129.53, 128.3, 64.8, 30.8, 19.3, 13.8.

HRMS (ESI, *m/z*): calcd for $C_{11}H_{15}O_2$ [M+H]$^+$ 179.1071, found 179.1067.

Butyl 4-methoxybenzoate (**P31**)



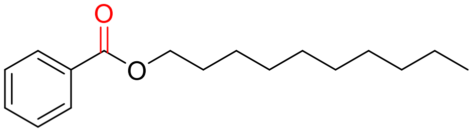
The general procedure as described above in 25% yield as colorless oil, 12 h, 52 mg.

^{1}H NMR (500 MHz, CDCl$_3$) δ 8.05 – 7.98 (m, 2H), 6.96 – 6.90 (m, 2H), 4.31 (t, *J* = 6.6 Hz, 2H), 3.87 (s, 3H), 1.76 (dt, *J* = 14.5, 6.6 Hz, 2H), 1.53 – 1.45 (m, 2H), 0.99 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, CDCl$_3$) δ 166.5, 163.2, 131.5, 123.0, 113.6, 64.5, 55.4, 30.8, 19.3, 13.8.

HRMS (ESI, *m/z*): calcd for $C_{12}H_{17}O_3$ [M+H]$^+$ 209.1177, found 209.1172.

Decyl benzoate (**P32**)



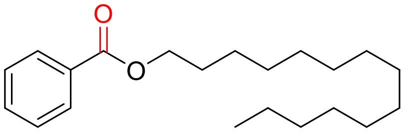
The general procedure as described above in 74% yield as colorless oil, 10 h, 194 mg.

^{1}H NMR (300 MHz, CDCl$_3$) δ 8.04 (dd, *J* = 5.2, 3.3 Hz, 2H), 7.60 – 7.50 (m, 1H), 7.43 (dd, *J* = 10.3, 4.6 Hz, 2H), 4.31 (t, *J* = 6.7 Hz, 2H), 1.81 – 1.71 (m, 2H), 1.66 – 1.51 (m, 2H), 1.27 (s, 12H), 0.88 (t, *J* = 6.7 Hz, 3H).

^{13}C NMR (75 MHz, CDCl$_3$) δ 166.7, 132.8, 130.5, 129.5, 128.3, 65.2, 31.9, 29.6, 29.3, 29.3, 28.7, 26.1, 22.7, 14.1.

HRMS (ESI, *m/z*): calcd for $C_{17}H_{27}O_2$ [M+H]$^+$ 263.2011, found 263.2006.

Tetradecyl benzoate (P33)



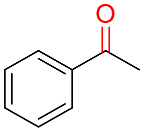
The general procedure as described above in 89% yield as colorless oil, 10 h, 283 mg.

^{1}**H NMR** (300 MHz, CDCl$_3$) δ 8.07 – 8.02 (m, 2H), 7.59 – 7.51 (m, 1H), 7.47 – 7.39 (m, 2H), 4.31 (t, *J* = 6.7 Hz, 2H), 1.82 – 1.70 (m, 2H), 1.44 (dd, *J* = 8.5, 5.0 Hz, 2H), 1.26 (s, 20H), 0.88 (t, *J* = 6.7 Hz, 3H).

^{13}**C NMR** (75 MHz, CDCl$_3$) δ 166.7, 132.8, 130.6, 129.6, 128.3, 65.2, 32.0, 29.7, 29.7, 29.6, 29.6, 29.4, 29.3, 28.7, 26.1, 22.7, 14.2.

HRMS (ESI, *m/z*): calcd for $C_{21}H_{35}O_2$ $[M+H]^+$ 319.2137, found 319.2632.

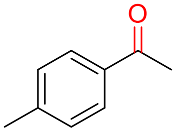
Acetophenone (P34, P62 and P82) is known compound.



The yield was 56% (and >99%) by GC-MS analysis after 24 h.

GC-MS : *m/z* (rel int.) 120 [M$^+$] (30%), 105 (88%), 77 (64%), 56 (37%), 52 (22%), 43 (100%), 27 (12%).

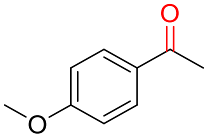
1-(*p*-Tolyl)ethan-1-one (P35) is known compound.



The yield was 76% by GC-MS analysis after 24 h.

GC-MS : *m/z* (rel int.) 134 [M$^+$] (30%), 119 (100%), 91 (72%), 65 (21%), 39 (10%).

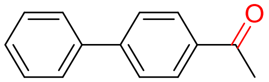
1-(4-Methoxyphenyl)ethan-1-one (P36 and P63) is known compound.



The yield was 48% and 92% by GC-MS analysis after 24 h.

GC-MS : *m/z* (rel int.) 150 [M$^+$] (35%), 135 (100%), 107 (24%), 92 (18%), 77 (32%), 64 (11%), 43 (11%).

1-([1,1'-Biphenyl]-4-yl)ethan-1-one (P37 and P66)



The general procedure as described above in 63% (and 80%) yield as white solid, 24 h, 123 mg (and 157 mg).

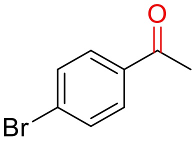
m.p. 119.1–119.8 ºC.

^{1}H NMR (500 MHz, CDCl$_3$) δ 8.06 (d, *J* = 8.3 Hz, 2H), 7.71 (d, *J* = 8.3 Hz, 2H), 7.66 (d, *J* = 7.4 Hz, 2H), 7.50 (t, *J* = 7.6 Hz, 2H), 7.43 (t, *J* = 7.3 Hz, 1H), 2.67 (s, 3H).

^{13}C NMR (126 MHz, CDCl$_3$) δ 197.8, 145.8, 139.9, 135.8, 129.9, 128.9, 128.3,127.3 127.2, 26.7.

HRMS (ESI, *m/z*): calcd for $C_{14}H_{13}O$ [M+H]$^+$ 197.0966, found 197.0961.

1-(4-Bromophenyl)ethan-1-one (**P38 and P67**)



The general procedure as described above in 76% (and 94%) yield as yellow solid, 24 h, 151 mg (and 187 mg).

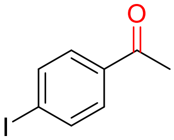
m.p. 117.3–118.5 ºC.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.84 – 7.79 (m, 2H), 7.62 – 7.58 (m, 2H), 2.58 (s, 3H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 197.1, 135.8, 131.9, 129.9, 128.3, 26.6.

HRMS (ESI, *m/z*): calcd for C_8H_8OBr [M+H]$^+$ 198.9758, found 198.9753.

1-(4-Iodophenyl)ethan-1-one (**P39 and P76**)



The general procedure as described above in 32% (and 72%) yield as yellow solid, 12 h, 79 mg (and 177 mg).

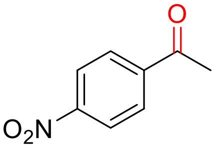
m.p. 81.5–83.4 ºC.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.85 – 7.81 (m, 2H), 7.69 – 7.64 (m, 2H), 2.58 (s, 3H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 197.4, 137.9, 136.3, 129.7, 101.1, 26.5.

HRMS (ESI, *m/z*): calcd for C_8H_8OI [M+H]$^+$ 246.9618, found 246.9614.

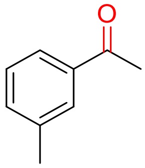
Methyl 4-nitrobenzoate (P40) is known compound.



The yield was 53% by GC-MS analysis after 24 h.

GC-MS : *m/z* (rel int.) 165 [M$^+$] (23%), 150 (100%), 120 (18%), 104 (42%), 92 (22%), 76 (22%), 50 (14%), 43 (35%).

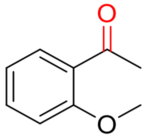
1-(*m*-tolyl)ethan-1-one (P41) is known compound.



The yield was 69% by GC-MS analysis after 24 h.

GC-MS : *m/z* (rel int.) 134 [M$^+$] (37%), 122 (34%), 119 (100%), 105 (48%), 91 (97%), 77 (31%), 65 (27%), 57 (21%), 51 (19%), 39 (19%).

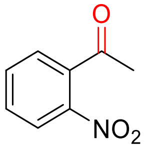
1-(2-Methoxyphenyl)ethan-1-one (P42 and P71) is known compound.



The yield was 31% (and 17%) by GC-MS analysis after 40 h (24 h).

GC-MS : *m/z* (rel int.) 150 [M$^+$] (18%), 135 (100%), 92 (16%), 77 (42%), 43 (12%).

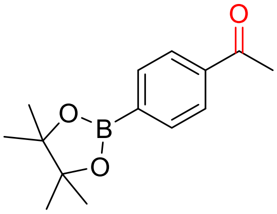
1-(2-Nitrophenyl)ethan-1-one (P43) is known compound.



The yield was 76% by GC-MS analysis after 24 h.

GC-MS : *m/z* (rel int.) 165 [M$^+$] (1.5%), 150 (100%), 123 (20%), 76 (26%), 51 (48%), 43 (58%).

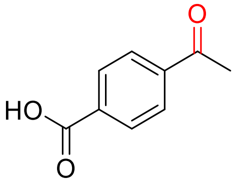
1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-one (P44)



The yield was only 6% after 48 h.

GC-MS : *m/z* (rel int.) 246 [M$^+$] (21%), 231 (100%), 160 (29%), 147 (67%), 131 (16%), 103 (15%), 85 (17%), 58 (12%), 43 (35%).

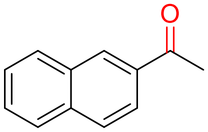
4-Acetylbenzoic acid (P45) is known compound.



The yield was 55% by GC-MS analysis after 24 h.

GC-MS : *m/z* (rel int.) 164 [M^+] (19%), 149 (100%), 121 (36%), 65 (36%), 50 (11%), 43 (16%).

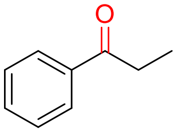
1-(Naphthalen-2-yl)ethan-1-one (P46 and P86) is known compound.



The yield was 47% (and 9%) by GC-MS analysis after 5 h (and 24 h).

GC-MS : *m/z* (rel int.) 170 [M^+] (47%), 155 (90%), 127 (100%), 101 (9%), 77 (16%), 63 (17%).

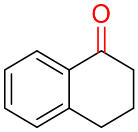
Propiophenone (P47 and P83) is known compound.



The yield was 59% (and 98%) by GC-MS analysis after 24 h (24 h).

GC-MS : *m/z* (rel int.) 134 [M^+] (17%), 105 (100%), 77 (50%), 51 (17%).

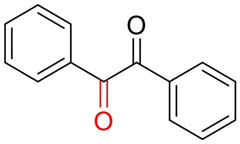
3,4-Dihydronaphthalen-1(*2H*)-one (P48) is known compound.



The yield was 44% by GC-MS analysis after 24 h.

GC-MS : *m/z* (rel int.) 146 [M^+] (68%), 131 (13%), 118 (100%), 115 (15%), 90 (71%), 63 (12%).

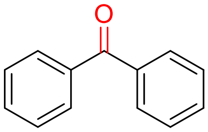
Benzil (P49) is known compound.



The yield was 44% by GC-MS analysis after 12 h.

GC-MS : *m/z* (rel int.) 210 [M^+] (3%), 105 (100%), 77 (37%), 51 (11%).

Benzophenone (P50)



The general procedure as described above in 90% yield as white solid, 24 h, 164 mg.

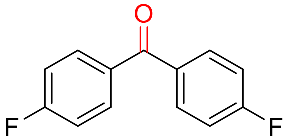
m.p. 48.3–50.4 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.74 (m, 4H), 7.57 (t, *J* = 7.4 Hz, 2H), 7.46 (t, *J* = 7.6 Hz, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 196.8, 137.6, 132.5, 130.1, 128.3.

HRMS (ESI, *m/z*): calcd for $C_{13}H_{10}O$ $[M+H]^+$ 183.0806, found 183.0804.

Bis(4-Fluorophenyl)methanone (**P51**).



The general procedure as described above in 94% yield as white solid, 24 h, 205 mg.

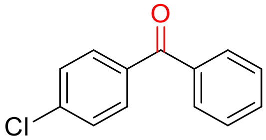
m.p. 107.8–108.8 ºC.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 – 7.78 (m, 4H), 7.20 – 7.13 (m, 4H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 193.7, 166.4, 164.4, 133.7, 132.5, 115.6, 115.5.

HRMS (ESI, *m/z*): calcd for $C_{13}H_9OF_2$ $[M+H]^+$ 219.0619, found 219.0616.

(4-Chlorophenyl)(phenyl)methanone (**P52**)



The general procedure as described above in 96% yield as white solid, 24 h, 149 mg.

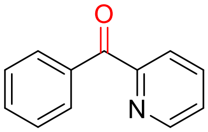
m.p. 108.1–109.4 ºC.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 – 7.73 (m, 4H), 7.63 – 7.58 (m, 1H), 7.52 – 7.45 (m, 4H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 195.4, 138.9, 137.2, 135.9, 132.7, 131.45, 129.9, 128.6, 128.4.

HRMS (ESI, *m/z*): calcd for $C_{13}H_{10}OCl$ $[M+H]^+$ 217.0418, found 217.0415.

Phenyl(pyridin-2-yl)methanone (**P53**)



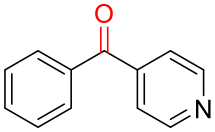
The general procedure as described above in 51% yield as colorless oil, 24 h, 93 mg.

^{1}H NMR (300 MHz, CDCl$_3$) δ 8.75 – 8.67 (m, 1H), 8.10 – 7.97 (m, 3H), 7.88 (td, *J* = 7.7, 1.7 Hz, 1H), 7.58 (ddd, *J* = 6.5, 4.5, 1.3 Hz, 1H), 7.47 (ddd, *J* = 8.4, 3.8, 0.7 Hz, 3H).

^{13}C NMR (75 MHz, CDCl$_3$) δ 193.9, 155.1, 148.6, 137.1, 136.3, 132.9, 131.0, 128.2, 126.2, 124.6.

HRMS (ESI, *m/z*): calcd for $C_{12}H_{10}ON$ [M+H]$^+$ 184.0759, found 184.0757.

Phenyl(pyridin-4-yl)methanone (**P54**)



The general procedure as described above in 96% yield as yellow solid, 24 h, 176 mg.

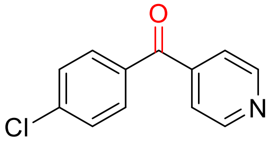
m.p. 70.4–72.4 ºC.

^{1}H NMR (500 MHz, CDCl$_3$) δ 8.83 (d, *J* = 5.8 Hz, 2H), 7.89 – 7.80 (m, 2H), 7.69 – 7.64 (m, 1H), 7.60 (dd, *J* = 4.4, 1.6 Hz, 2H), 7.53 (t, *J* = 7.8 Hz, 2H).

^{13}C NMR (126 MHz, CDCl$_3$) δ 195.2, 150.3, 144.4, 135.9, 133.6, 130.2, 128.7, 122.9.

HRMS (ESI, *m/z*): calcd for $C_{12}H_{10}ON$ [M+H]$^+$ 184.0759, found 184.0757.

(4-Chlorophenyl)(pyridin-4-yl)methanone (**P55**)



The general procedure as described above in 97% yield as white solid, 24 h, 211 mg.

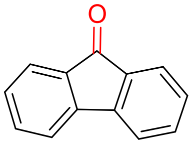
m.p. 76.0–77.1 ºC.

^{1}H NMR (500 MHz, CDCl$_3$) δ 8.77 (dd, *J* = 4.3, 1.6 Hz, 2H), 7.75 – 7.69 (m, 2H), 7.51 (dd, *J* = 4.3, 1.6 Hz, 2H), 7.46 – 7.41 (m, 2H).

^{13}C NMR (126 MHz, CDCl$_3$) δ 193.8, 150.4, 143.9, 140.1, 134.1, 131.5, 129.0, 122.7.

HRMS (ESI, *m/z*): calcd for $C_{12}H_9ONCl$ [M+H]$^+$ 218.0370, found 218.0367.

9H-fluoren-9-one (**P56**)



The general procedure as described above in 98% yield as yellow solid, 24 h, 176 mg.

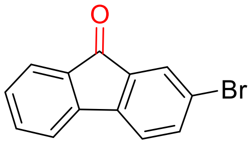
m.p. 83.9–84.4 ºC.

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.66 (d, *J* = 7.4 Hz, 2H), 7.52 – 7.46 (m, 4H), 7.32 – 7.27 (m, 2H).

^{13}C NMR (126 MHz, CDCl$_3$) δ 194.0, 144.4, 134.7, 134.1, 129.1, 124.3, 120.3.

HRMS (ESI, *m/z*): calcd for $C_{13}H_9O$ [M+H]$^+$ 181.0651, found 181.0648.

2-Bromo-9*H*-fluoren-9-one (P57)



The general procedure as described above in 91% yield as yellow solid, 24 h, 236 mg.

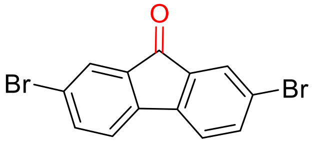
m.p. 144.7–147.0 ºC.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (d, *J* = 1.8 Hz, 1H), 7.59 (d, *J* = 7.3 Hz, 1H), 7.53 (dd, *J* = 7.9, 1.9 Hz, 1H), 7.45 (ddd, *J* = 16.6, 11.5, 4.1 Hz, 2H), 7.29 (ddd, *J* = 8.6, 5.2, 1.5 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 192.3, 143.6, 142.9, 137.0, 135.7, 135.0, 133.6, 129.4, 127.4, 124.5, 122.9, 121.7, 120.4.

HRMS (ESI, *m/z*): calcd for $C_{13}H_8OBr$ [M+H]$^+$ 258.9758, found 258.9753.

2,7-Dibromo-9*H*-fluoren-9-one (P58)



The general procedure as described above in 95% yield as yellow solid, 24 h, 321 mg.

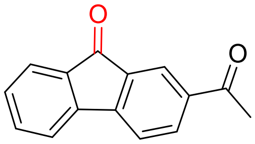
m.p. 202.2–203.2 ºC.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76 (d, *J* = 1.6 Hz, 2H), 7.64 (d, *J* = 1.9 Hz, 1H), 7.61 (d, *J* = 1.9 Hz, 1H), 7.40 – 7.36 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 191.0, 142.3, 137.5, 135.3, 127.9, 123.3, 121.9.

HRMS (ESI, *m/z*): calcd for $C_{13}H_7OBr_2$ [M+H]$^+$ 338.8839, found 338.8838.

2-Acetyl-9*H*-fluoren-9-one (P59)



The general procedure as described above in 98% yield as yellow solid, 24 h, 217 mg.

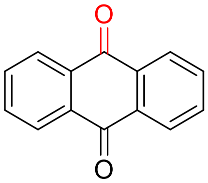
m.p. 162.3–163.0 ºC.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15 – 8.07 (m, 2H), 7.66 (d, *J* = 7.3 Hz, 1H), 7.58 – 7.49 (m, 3H), 7.35 (td, *J* = 7.3, 0.9 Hz, 1H), 2.61 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 196.5, 192.6, 148.4, 143.2, 137.7, 135.0, 134.9, 134.8, 134.2, 130.2, 124.6, 124.0, 121.3, 120.4, 26.7.

HRMS (ESI, *m/z*): calcd for $C_{15}H_{11}O_2$ [M+H]$^+$ 223.0758, found 223.0754.

Anthracene-9,10-dione (**P60**)



The general procedure as described above in 98% yield as yellow solid, 24 h, 204 mg.

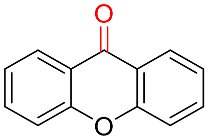
m.p. 286.0–287.8 ºC.

^{1}**H NMR** (400 MHz, $CDCl_3$) δ 8.32 (dd, *J* = 5.3, 3.3 Hz, 4H), 7.81 (dd, *J* = 5.4, 3.2 Hz, 4H).

^{13}**C NMR** (101 MHz, $CDCl_3$) δ 183.2, 134.2, 133.5, 127.3.

HRMS (ESI, *m/z*): calcd for $C_{14}H_9O_2$ $[M+H]^+$ 209.0599, found 209.0597.

9*H*-Xanthen-9-one (**P61**)



The general procedure as described above in 95% yield as white solid, 186 mg, 24 h.

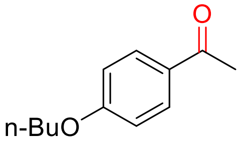
m.p. 176.8–177.5 ºC.

^{1}**H NMR** (500 MHz, $CDCl_3$) δ 8.32 (d, *J* = 7.9 Hz, 2H), 7.72 – 7.66 (m, 2H), 7.45 (d, *J* = 8.2 Hz, 2H), 7.39 – 7.32 (m, 2H).

^{13}**C NMR** (126 MHz, $CDCl_3$) δ 177.2, 156.1, 134.8, 126.7, 123.9, 121.8, 118.0.

HRMS (ESI, *m/z*): calcd for $C_{13}H_9O_2$ $[M+H]^+$ 197.0599, found 197.0597.

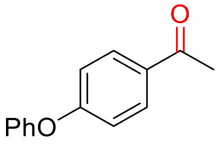
1-(4-Butoxyphenyl)ethan-1-one (**P64**) is known compound.



The yield was only 14% after 24 h.

GC-MS : *m/z* (rel int.) 192 $[M^+]$ (20%), 177 (10%), 121 (100%), 93 (9%), 43 (9%), 29 (12%).

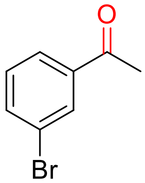
1-(4-Phenoxyphenyl)ethan-1-one (**P65**) is known compound.



The yield was only 7% after 24 h.

GC-MS : *m/z* (rel int.) 212 $[M^+]$ (47%), 197 (100%), 141 (22%), 115 (22%), 77 (15%), 51 (12%).

1-(3-Bromophenyl)ethan-1-one (**P68**)



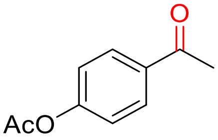
The general procedure as described above in 91% yield as colorless oil, 34 h, 181 mg.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (t, *J* = 1.8 Hz, 1H), 7.89 – 7.85 (m, 1H), 7.68 (ddd, *J* = 7.9, 2.0, 1.0 Hz, 1H), 7.34 (t, *J* = 7.9 Hz, 1H), 2.59 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 196.8, 138.7, 136.0, 131.3, 130.2, 126.9, 122.9, 26.6.

HRMS (ESI, *m/z*): calcd for C_8H_8OBr $[M+H]^+$ 198.9758, found 198.9753.

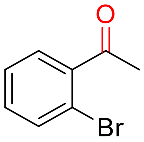
4-Acetylphenyl acetate (**P70**) is known compound.



The yield was 75% by GC-MS analysis after 24 h.

GC-MS : *m/z* (rel int.) 178 [M^+] (9%), 136 (31%), 121 (100%), 93 (16%), 65 (12%), 43 (29%).

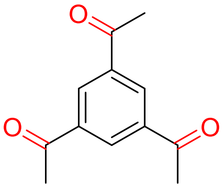
1-(2-Bromophenyl)ethan-1-one (**P72**) is known compound.



The yield was 12% by GC-MS analysis after 24 h.

GC-MS : *m/z* (rel int.) 200 [M^+] (26%), 197 (26%), 185 (98%), 183 (100%), 155 (35%), 77 (13%), 76 (30%), 75 (29%), 50 (31%), 43 (46%),

1,1',1''-(Benzene-1,3,5-triyl)tris(ethan-1-one) (**P73**)



The general procedure as described above in 81% yield as white solid, 48 h, 165 mg.

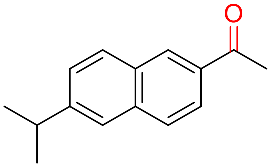
m.p. 164.1–164.7 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (s, 3H), 2.73 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 196.7, 137.9, 131.7, 26.8.

HRMS (ESI, *m/z*): calcd for $C_{12}H_{13}O_3$ $[M+H]^+$ 205.0863, found 205.0859.

1-(6-Isopropylnaphthalen-2-yl)ethan-1-one (**P74**)



The general procedure as described above in 47% yield as yellow solid, 5 h, 100 mg.

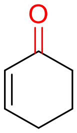
m.p. 70.5–71.7 ºC.

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.41 (s, 1H), 7.99 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.87 (d, *J* = 8.5 Hz, 1H), 7.81 (d, *J* = 8.6 Hz, 1H), 7.66 (s, 1H), 7.45 (dd, *J* = 8.5, 1.7 Hz, 1H), 3.08 (dt, *J* = 13.8, 6.9 Hz, 1H), 2.69 (s, 3H), 1.34 (d, *J* = 6.9 Hz, 6H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 198.1, 149.5, 136.0, 133.9, 131.1, 130.0, 129.6, 128.1, 126.8, 124.1, 124.0, 34.4, 26.7, 23.8.

HRMS (ESI, *m/z*): calcd for $C_{15}H_{17}O$ $[M+H]^+$ 213.1279, found 213.1274.

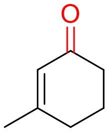
Cyclohex-2-en-1-one (**P75**) is known compound.



The yield was 64% by GC-MS analysis after 24 h.

GC-MS : *m/z* (rel int.) 96 [M$^+$] (40%), 68 (100%), 40 (19%), 39 (22%).

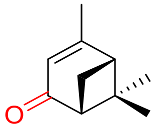
3-Methylcyclohex-2-en-1-one (**P76**) is known compound.



The yield was 46% by GC-MS analysis after 20 h.

GC-MS : *m/z* (rel int.) 110 [M$^+$] (43%), 82 (100%), 54 (34%), 39 (31%).

(1R,5R)-4,6,6-Trimethylbicyclo[3.1.1]hept-3-en-2-one (**P77**)



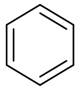
The general procedure as described above in 62% yield as colorless oil, 20 h, 93 mg.

^{1}H NMR (400 MHz, CDCl$_3$) δ 5.74 (dd, *J* = 3.0, 1.5 Hz, 1H), 2.81 (dt, *J* = 9.2, 5.5 Hz, 1H), 2.66 (td, *J* = 6.1, 1.6 Hz, 1H), 2.45 – 2.40 (m, 1H), 2.09 (d, *J* = 9.2 Hz, 1H), 2.02 (d, *J* = 1.5 Hz, 3H), 1.50 (s, 3H), 1.01 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 204.5, 170.6, 121.1, 57.5, 54.3, 49.7, 40.9, 26.6, 23.6, 22.0.

HRMS (ESI, *m/z*): calcd for $C_{10}H_{15}O$ $[M+H]^+$ 151.1119, found 151.1117.

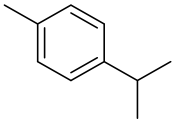
Benzene (**P78**) is known compound.



The yield was 97% by GC-MS analysis after 10 h.

GC-MS : *m/z* (rel int.) 78[M^+] (100%), 77 (24%), 52 (17%), 51 (15%), 50 (13%), 39 (11%).

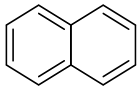
***p*-Cymene** (**P79**) is known compound.



The yield was 90% by GC-MS analysis after 3 h.

GC-MS : *m/z* (rel int.) 134[M^+] (27%), 119 (100%), 117 (14%), 91 (26%).

Naphthalene (**P80**)



The general procedure as described above in 88% yield as white solid, 24 h, 113 mg.

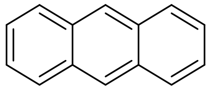
m.p. 84.1–85.2 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.77 (m, 4H), 7.49 – 7.41 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 133.6, 128.0, 125.9.

GC-MS : *m/z* (rel int.) 128[M^+] (100%), 127 (13%), 102 (10%), 64 (10%).

Anthracene (**P81**)



The general procedure as described above in 89% yield as white solid, 10 h, 158 mg.

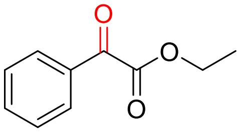
m.p. 219.5–220.4 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (s, 2H), 8.00 (dd, J = 6.4, 3.2 Hz, 4H), 7.45 (dd, J = 6.6, 3.2 Hz, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 131.7, 128.2, 126.3, 125.4.

GC-MS : *m/z* (rel int.) 178[M^+] (100%), 176 (18%), 89 (21%), 76 (16%).

Ethyl 2-oxo-2-phenylacetate (**P84**)



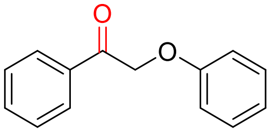
The general procedure as described above in 89% yield as colorless oil, 24 h, 158 mg.

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.07 – 7.95 (m, 2H), 7.66 (t, *J* = 7.4 Hz, 1H), 7.51 (t, *J* = 7.8 Hz, 2H), 4.45 (q, *J* = 7.1 Hz, 2H), 1.42 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 186.5, 163.9, 135.0, 130.0, 128.9, 62.4, 14.1.

HRMS (ESI, *m/z*): calcd for $C_{10}H_{11}O_3$ [M+H]$^+$ 179.0708, found 179.0703.

2-Phenoxy-1-phenylethan-1-one (**P85**)



The general procedure as described above in 60% yield as white solid, 24 h, 127 mg.

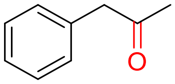
m.p. 72.5–74.4 ºC.

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.05 – 7.94 (m, 2H), 7.64 – 7.55 (m, 1H), 7.48 (dd, *J* = 10.7, 4.7 Hz, 2H), 7.33 – 7.25 (m, 2H), 7.04 – 6.87 (m, 3H), 5.26 (s, 2H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 194.6, 158.0, 134.6, 134.0, 129.6, 128.9, 128.2, 121.7, 114.8, 70.7.

HRMS (ESI, *m/z*): calcd for $C_{14}H_{12}O_2$ [M+H]$^+$ 213.0912, found 213.0910.

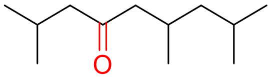
1-Phenylpropan-2-one (**P87**) is known compound.



The yield was 69% by GC-MS analysis after 34 h.

GC-MS : *m/z* (rel int.) 134 [M$^+$] (16%), 105 (100%), 77 (49%), 51 (15%).

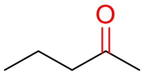
2,6,8-Trimethylnonan-4-one (**P88**) is known compound.



The yield was 86% by GC-MS analysis after 34 h.

GC-MS : *m/z* (rel int.) 184 [M$^+$] (3%) 127 (35%), 109, (41%), 101 (21%), 100 (18%), 85 (68%), 84 (21%), 83 (32%), 69 (13%), 57 (100%), 43 (38%), 41 (35%), 29 (16%).

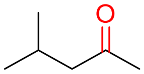
Pentan-2-one (**P89**) is known compound.



The yield was 75% by GC-MS analysis after 24 h.

GC-MS : *m/z* (rel int.) 86 [M$^+$] (21%), 58 (10%), 43 (100%), 41 (12%), 27 (15%).

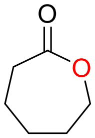
4-Methylpentan-2-one (**P90**) is known compound.



The yield was 81% by GC-MS analysis after 40 h.

GC-MS : *m/z* (rel int.) 100 [M$^+$] (18%), 85 (20%), 58 (53%), 57 (31%), 43 (100%), 41 (23%), 29 (16%).

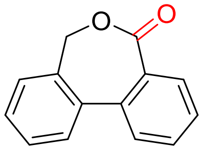
Oxepan-2-one (**P91**) is known compound.



The yield was 71% by GC-MS analysis after 24 h.

GC-MS : *m/z* (rel int.) 114 [M$^+$] (11%), 84 (25%), 70 (12%), 56 (40%), 55 (100%), 42 (67%), 41 (34%), 39 (16%), 29 (15%), 28 (23%), 27 (18%).

7*H*-Dibenzo[c,e]oxepin-5-one (**P92**)



The general procedure as described above in 80% yield as white solid, 28 h, 168 mg.

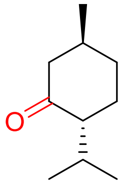
m.p. 102.6–105.0 ºC.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.63 (dtd, *J* = 16.2, 7.8, 1.2 Hz, 3H), 7.54 – 7.49 (m, 2H), 7.43 (dtd, *J* = 8.5, 7.4, 1.2 Hz, 2H), 5.01 (d, *J* = 26.9 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 170.3, 139.0, 137.3, 134.9, 132.7, 131.9, 130.7, 130.2, 128.8, 128.7, 128.6, 128.5, 69.2.

HRMS (ESI, *m/z*): calcd for $C_{14}H_{10}O_2Na$ [M+Na]$^+$ 233.0573, found 233.0570.

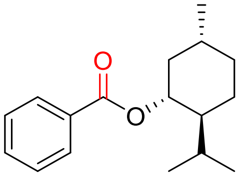
Menthone (**P93**) is known compound.



The yield was 71% by GC-MS analysis after 40 h

GC-MS : *m/z* (rel int.) 154 [M$^+$] (24%), 139 (36%), 112 (100%), 111 (28%), 98 (10%), 97 (35%), 95 (21%), 70 (32%), 69 (73%), 55 (51%), 39 (20%), 27 (15%).

(-)-Menthyl benzoate (P94)



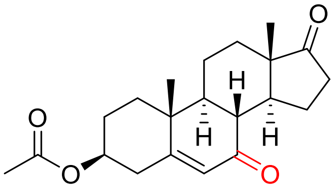
The general procedure as described above in 81% yield as colorless oil, 6 h, 211 mg.

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.05 – 7.89 (m, 2H), 7.45 (t, *J* = 7.4 Hz, 1H), 7.34 (t, *J* = 7.6 Hz, 2H), 4.85 (td, *J* = 10.9, 4.4 Hz, 1H), 2.07 – 2.01 (m, 1H), 1.93 – 1.85 (m, 1H), 1.68 – 1.58 (m, 2H), 1.52 – 1.43 (m, 2H), 1.04 (dd, *J* = 19.3, 7.2 Hz, 2H), 0.83 (dd, *J* = 6.8, 3.2 Hz, 7H), 0.71 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 165.0, 131.6, 129.8, 128.5, 127.2, 73.7, 46.2, 39.9, 33.3, 30.4, 25.4, 22.6, 21.0, 19.7, 15.5.

HRMS (ESI, *m/z*): calcd for $C_{17}H_{24}O_2Na$ [M+ Na]$^+$ 283.1669, found 283.1670.

Androst-5-en-3-ol-7,17-dione acetate (P95)



The general procedure as described above in 71% yield as white solid, 5 h, 245 mg.

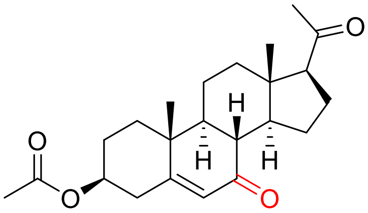
m.p. 142.2–149.7 ºC.

^{1}H NMR (400 MHz, CDCl$_3$) δ 5.74 (d, *J* = 1.4 Hz, 1H), 4.75 – 4.66 (m, 1H), 2.85 – 2.75 (m, 1H), 2.58 (dd, *J* = 5.1, 3.2 Hz, 1H), 2.52 – 2.41 (m, 3H), 2.19 – 2.08 (m, 2H), 2.06 (s, 4H), 1.84 – 1.58 (m, 8H), 1.36 – 1.29 (m, 1H), 1.26 (s, 3H), 0.90 (s, 3H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 200.5, 170.0, 164.8, 126.3, 71.8, 49.8, 47.7, 45.5, 44.2, 38.3, 37.7, 35.8, 35.4, 30.6, 27.2, 24.0, 21.1, 20.4, 17.2, 14.1, 13.6.

HRMS (ESI, *m/z*): calcd for $C_{21}H_{28}O_4Na$ [M+Na]$^+$ 367.1880, found 367.1887.

7-Keto-dehydroepiandrosterone acetate (P96)



The general procedure as described above in 79% yield as white solid, 5 h, 294 mg.

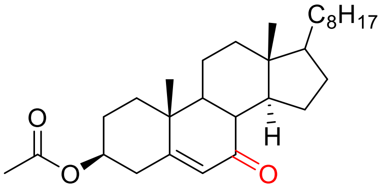
m.p. 122.2–126.7 ºC.

^{1}H NMR (400 MHz, CDCl$_3$) δ 5.71 (s, 1H), 4.76 – 4.67 (m, 1H), 2.52 (ddd, *J* = 9.1, 4.9, 2.9 Hz, 4H), 2.27 (t, *J* = 11.2 Hz, 1H), 2.14 (s, 4H), 2.07 – 1.98 (m, 6H), 1.72 (dd, *J* = 10.2, 5.6 Hz, 3H), 1.61 – 1.54 (m, 2H), 1.49 – 1.36 (m, 4H), 1.23 (s, 3H), 0.66 (s, 3H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 209.6, 201.1, 170.2, 164.3, 126.4, 72.0, 62.2, 49.9, 49.5, 45.1, 44.3, 38.3, 37.7, 37.6, 35.9, 31.6, 27.2, 26.4, 23.5, 21.2, 21.0, 17.2, 13.2.

HRMS (ESI, *m/z*): calcd for $C_{23}H_{32}O_4Na$ [M+ Na]$^+$ 395.2193, found 395.2190.

7-Ketocholesterol acetate (**P97**)



The general procedure as described above in 55% yield as yellow solid, 12 h, 243 mg.

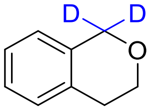
m.p. 139.9–144.1 ºC.

^{1}H NMR (400 MHz, CDCl$_3$) δ 5.70 (d, *J* = 1.5 Hz, 1H), 4.79 – 4.65 (m, 1H), 2.55 – 2.37 (m, 3H), 2.23 (t, *J* = 11.2 Hz, 1H), 2.06 – 1.96 (m, 6H), 1.92 – 1.85 (m, 1H), 1.72 – 1.66 (m, 1H), 1.57 – 1.48 (m, 4H), 1.35 (dd, *J* = 7.4, 4.2 Hz, 7H), 1.26 (d, *J* = 5.8 Hz, 3H), 1.23 – 1.07 (m, 5H), 1.01 (d, *J* = 9.9 Hz, 1H), 0.92 (d, *J* = 6.5 Hz, 3H), 0.86 (dd, *J* = 6.6, 1.8 Hz, 6H), 0.68 (s, 3H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 201.9, 170.3, 163.8, 126.7, 72.2, 54.8, 49.9, 49.8, 45.4, 43.1, 39.5, 38.7, 38.3, 37.7, 36.2, 36.0, 35.7, 28.5, 28.0, 27.4, 26.3, 23.8, 22.8, 22.6, 21.3, 21.2, 18.9, 17.3, 12.0.

HRMS (ESI, *m/z*): calcd for $C_{29}H_{47}O_3$ [M+ H]$^+$ 443.3520, found 443.3519.

Isochromane-1,1-*d*$_2$ (**S1-*d*$_2$**)



The general procedure as described above in 60% yield colorless oil.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.20 – 7.09 (m, 3H), 7.01 – 6.91 (m, 1H), 3.97 (t, *J* = 5.7 Hz, 2H), 2.85 (t, *J* = 5.7 Hz, 2H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 134.8, 133.3, 129.0, 126.4, 126.0, 124.5, 65.4, 28.4.

HRMS (ESI, *m/z*): calcd for $C_9H_9OD_2$ [M+H]$^+$ 137.0934, found 137.0930.

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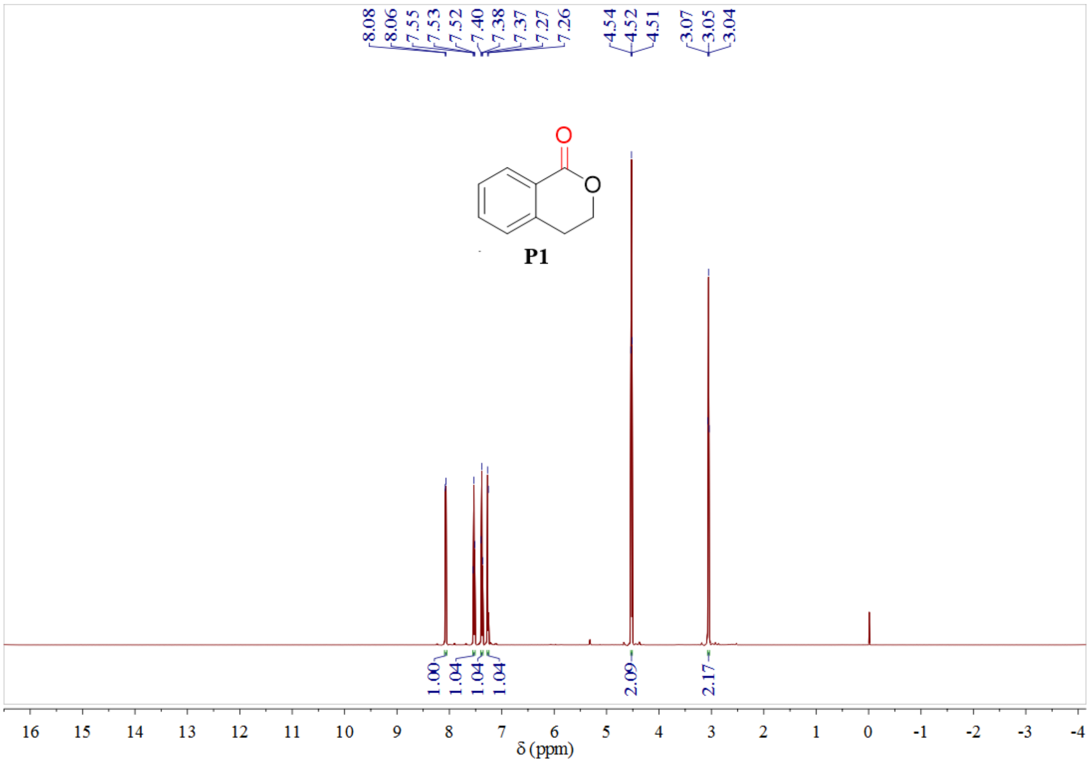
NMR Spectra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P1
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1.04
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2.09
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13
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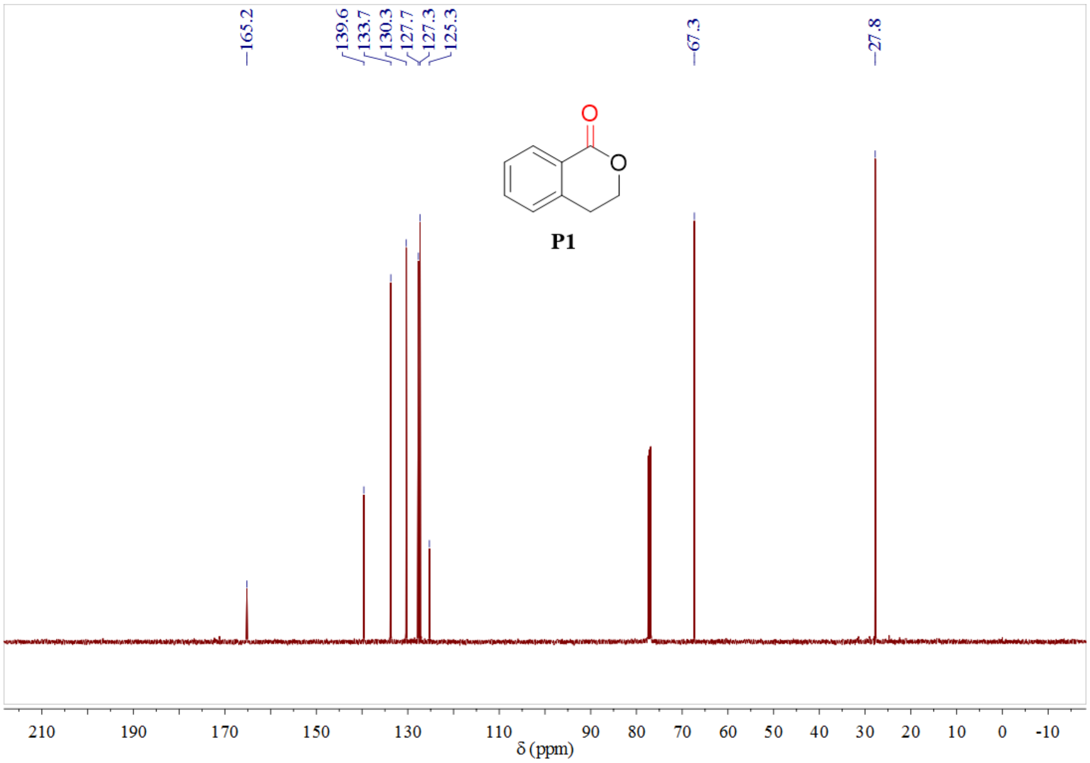
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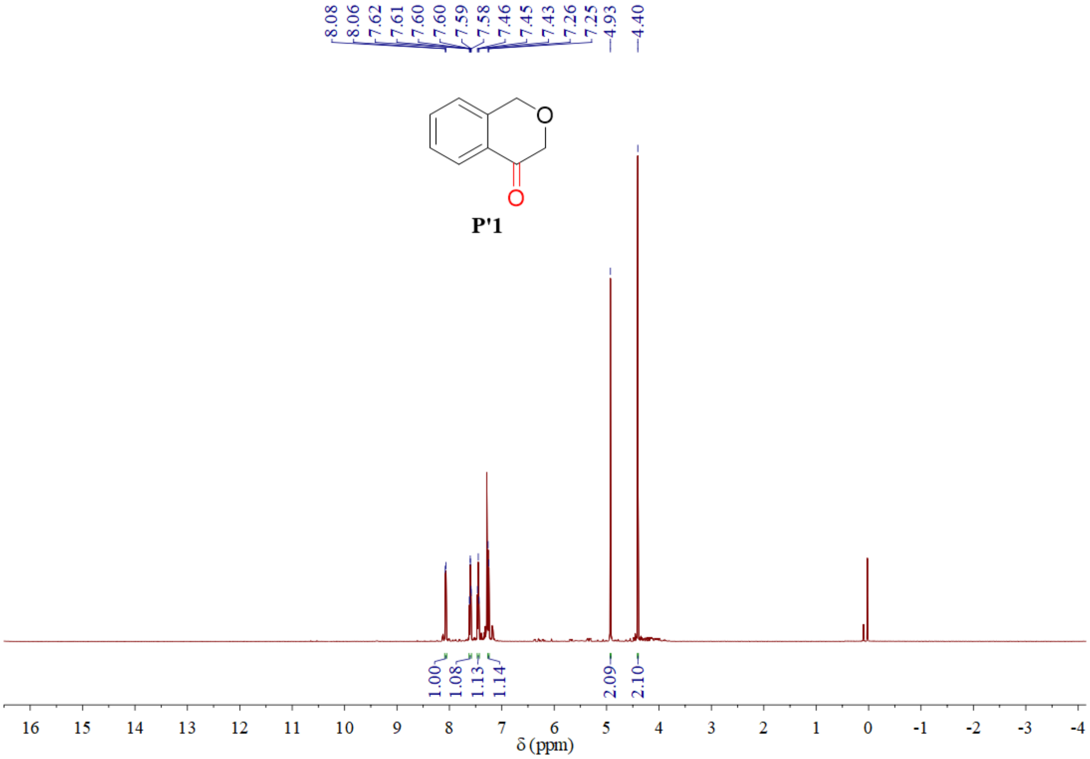
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O
P'1
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2.09
2.10
16
15
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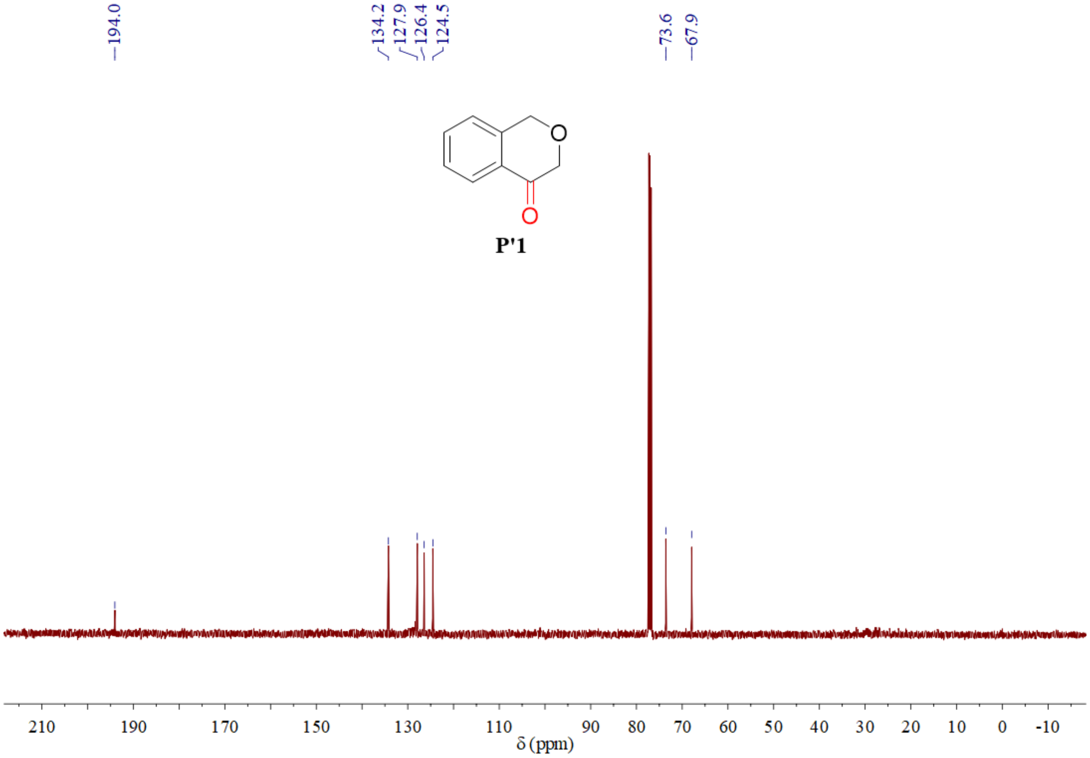
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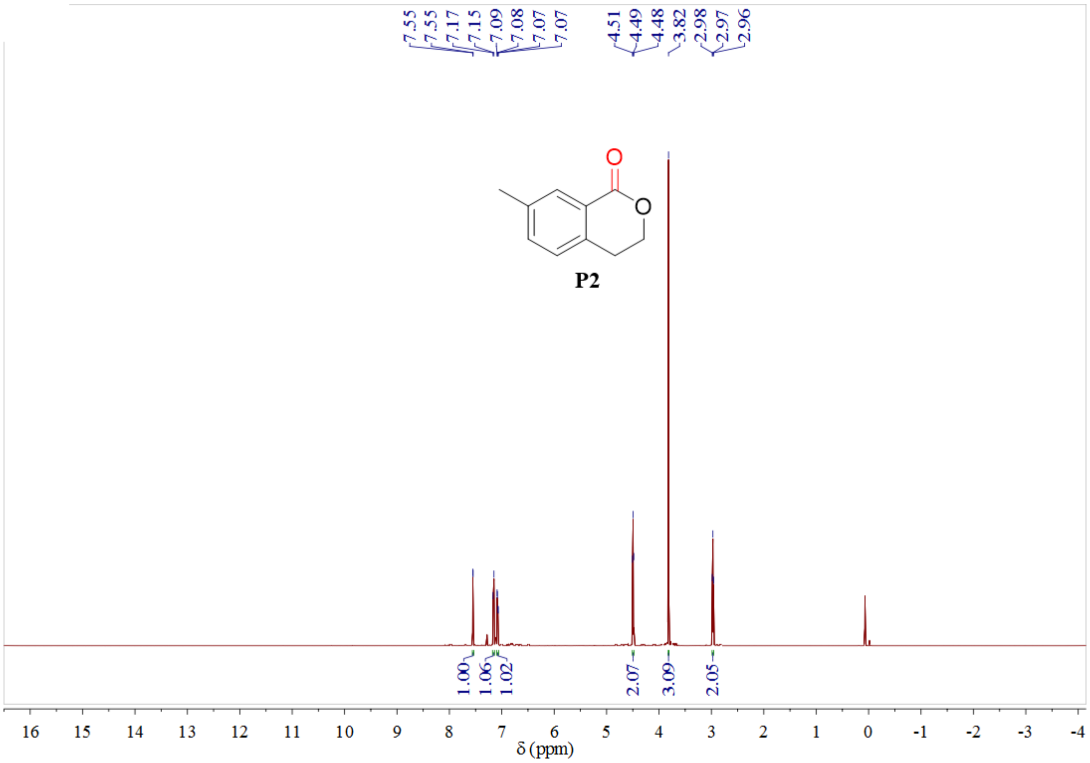
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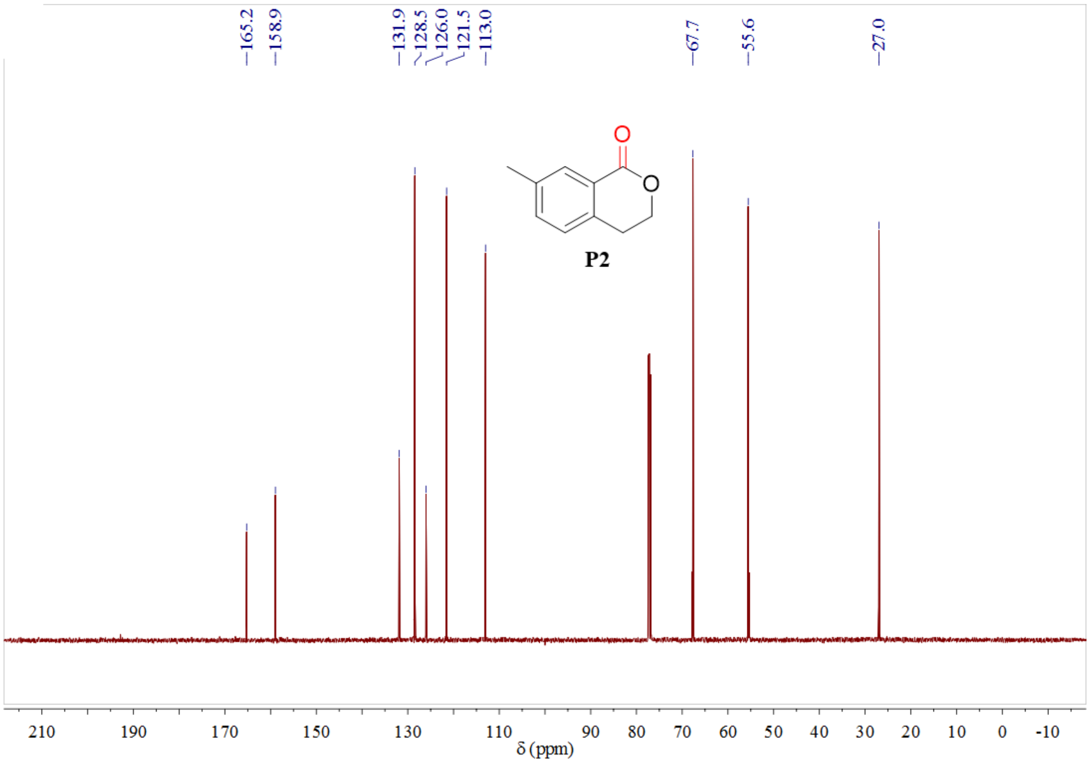
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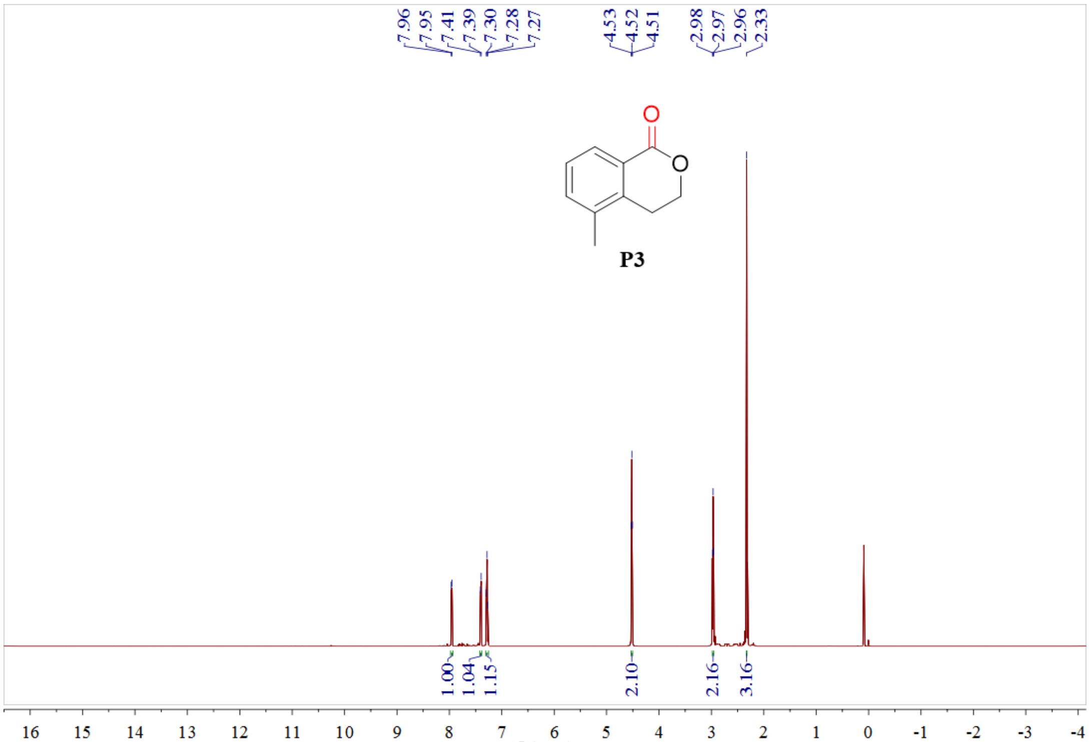
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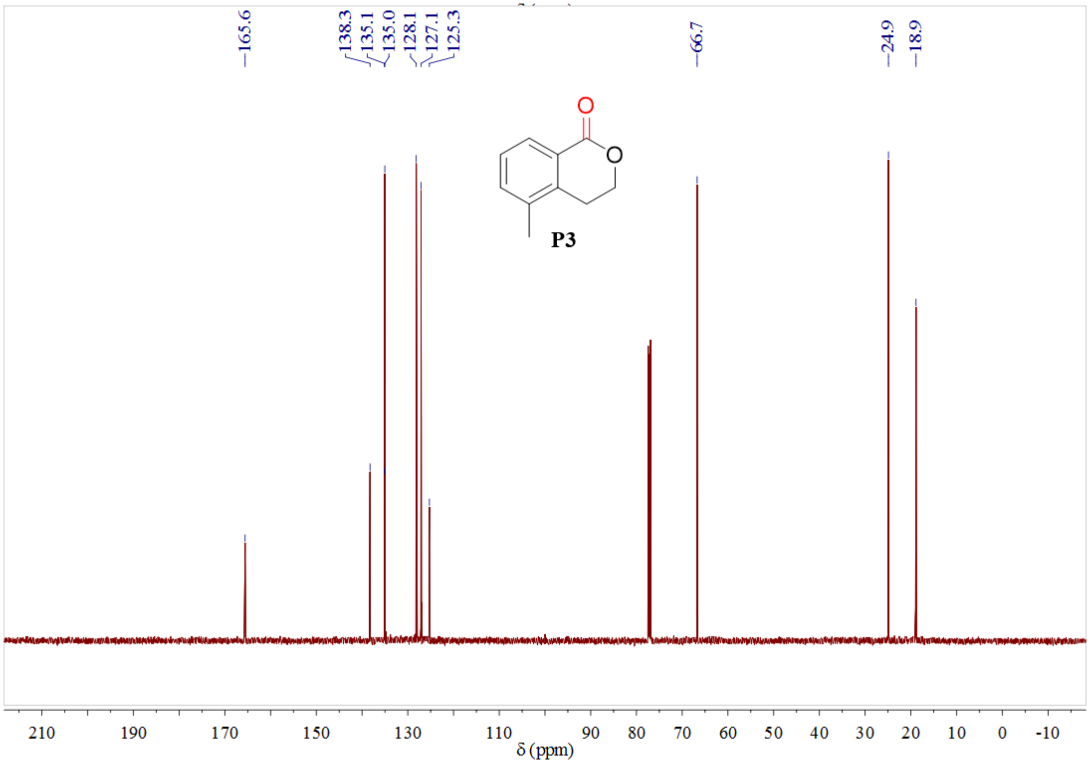
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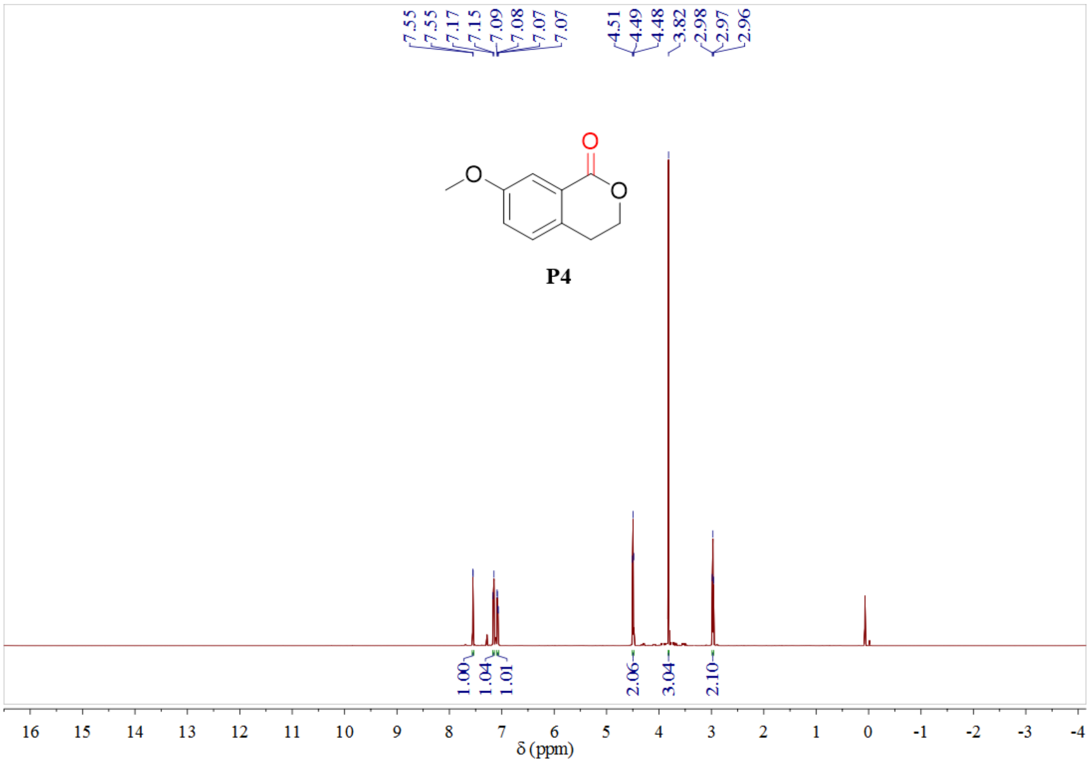
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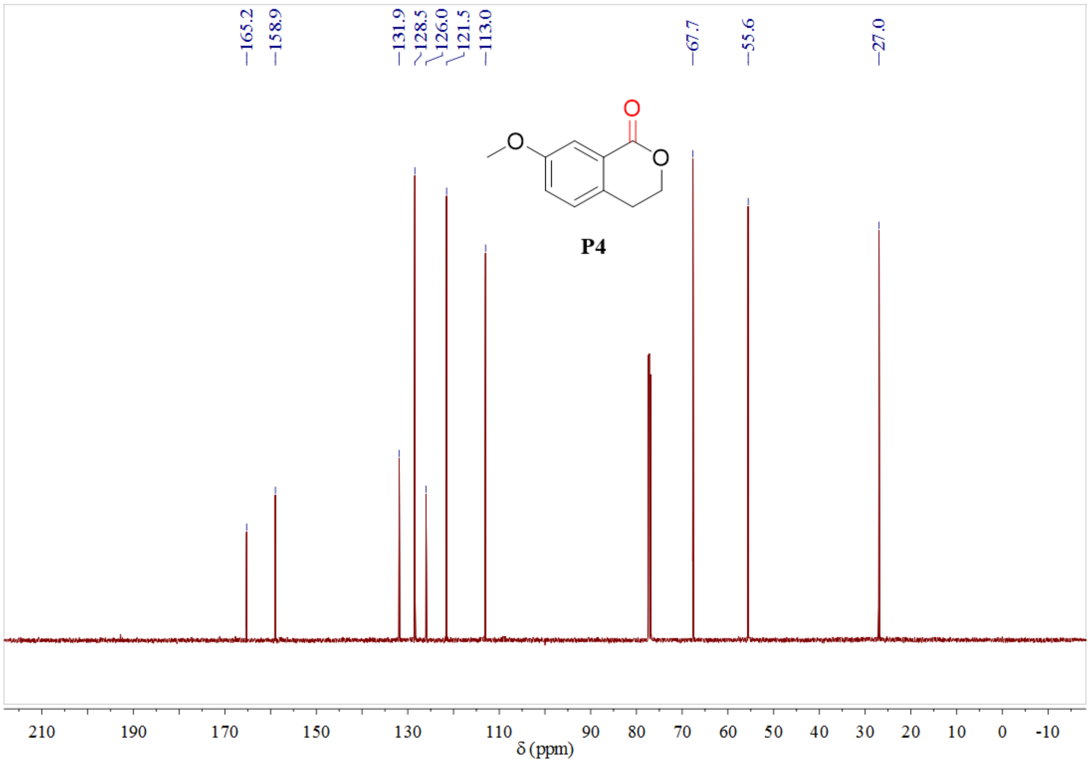
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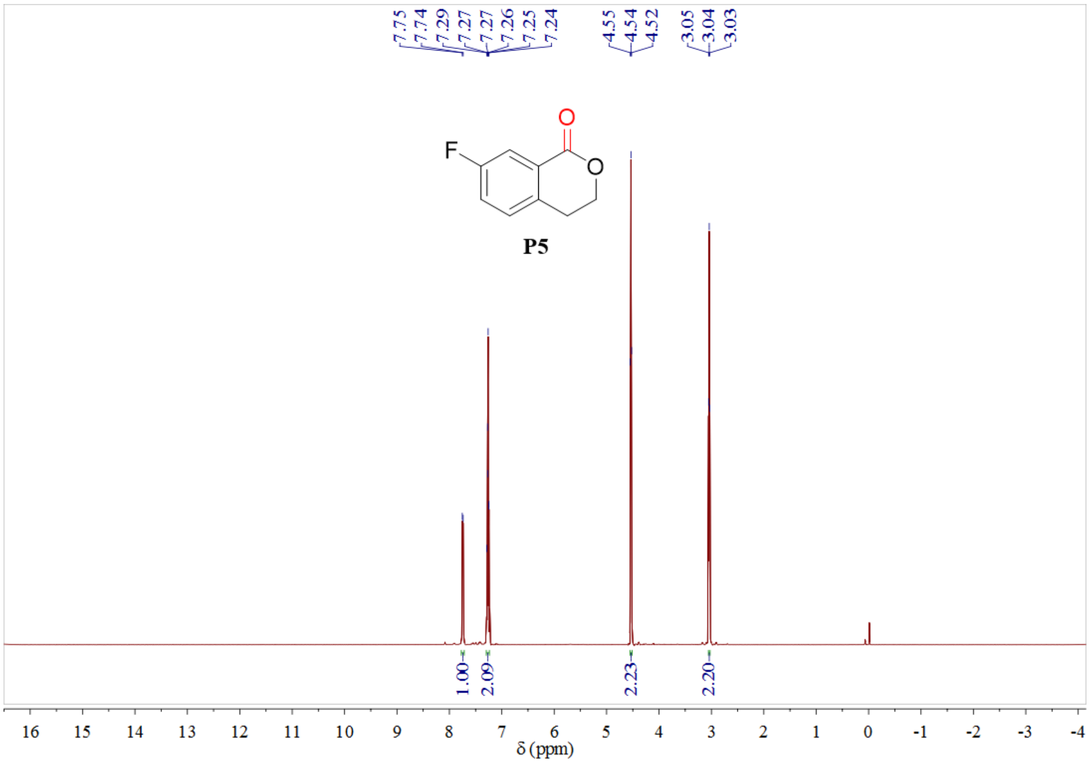
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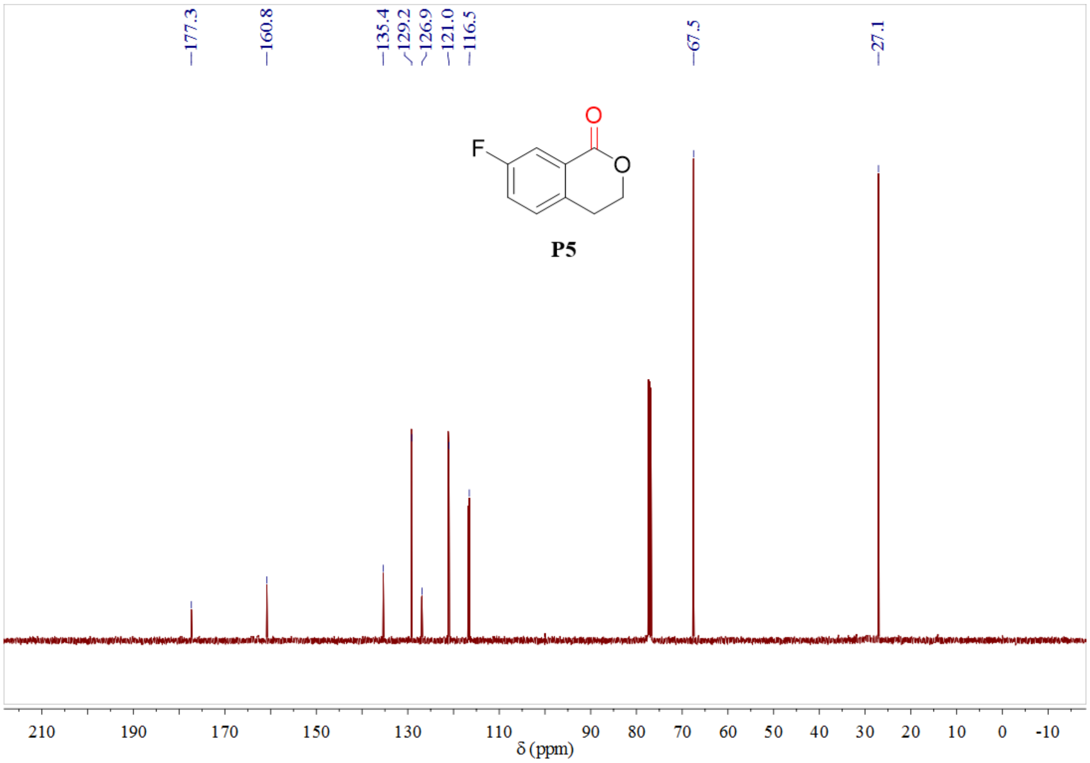
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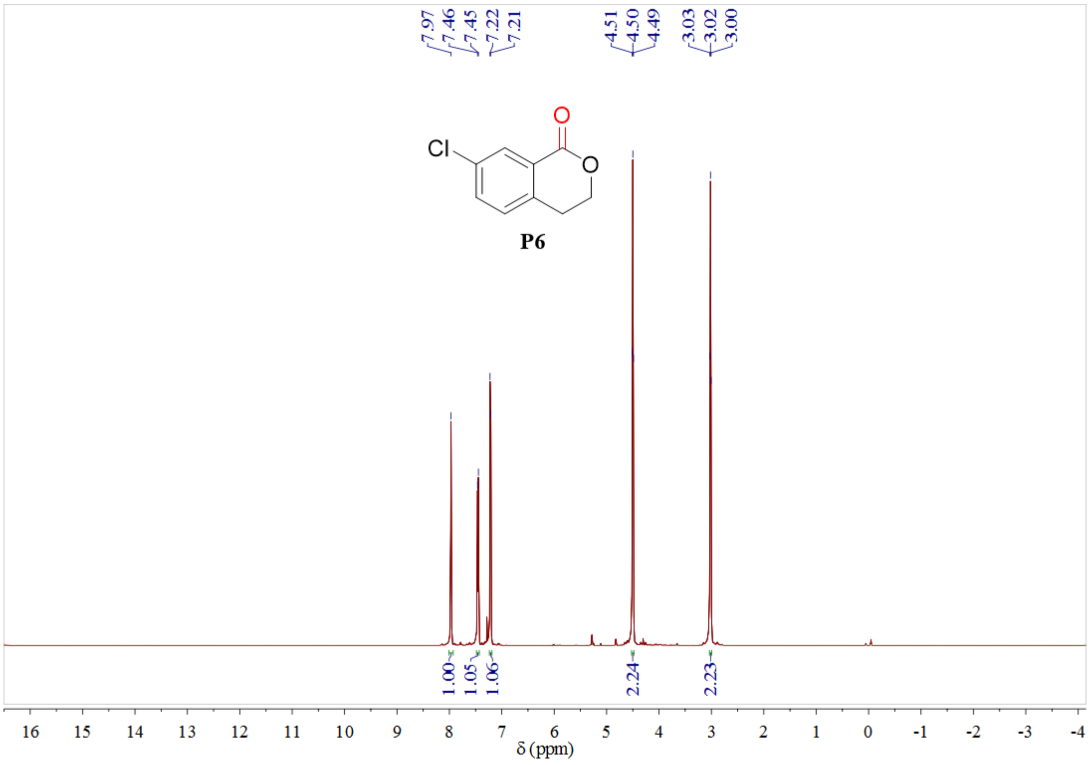
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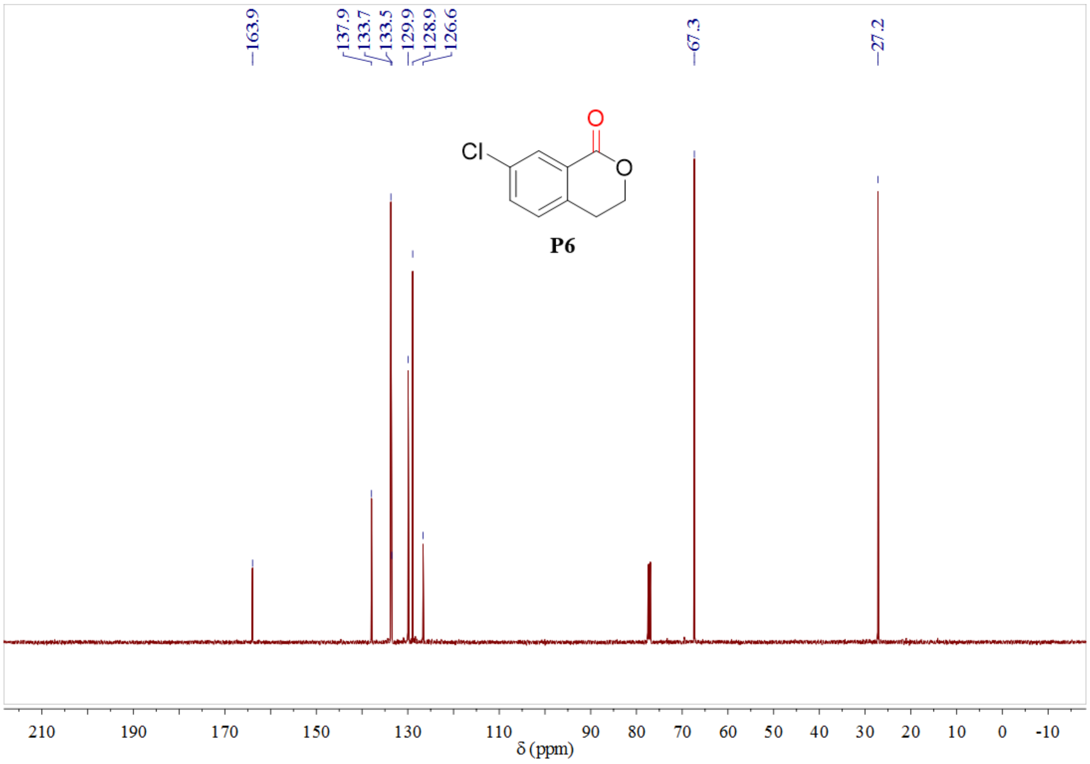
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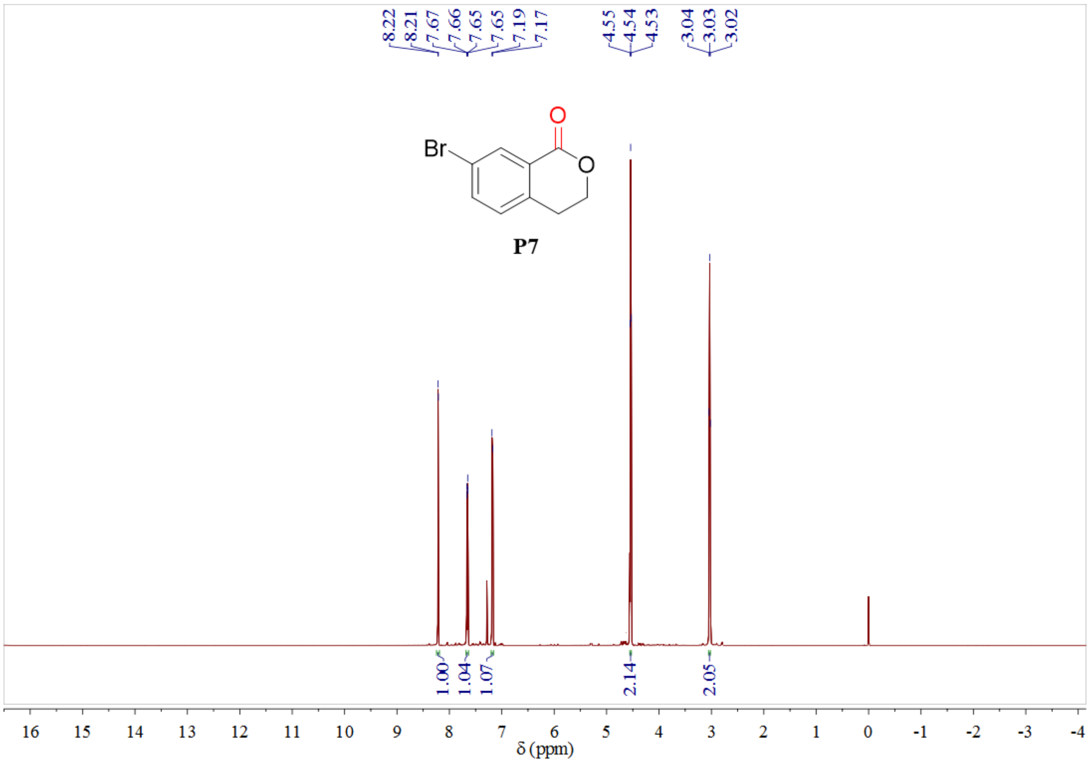
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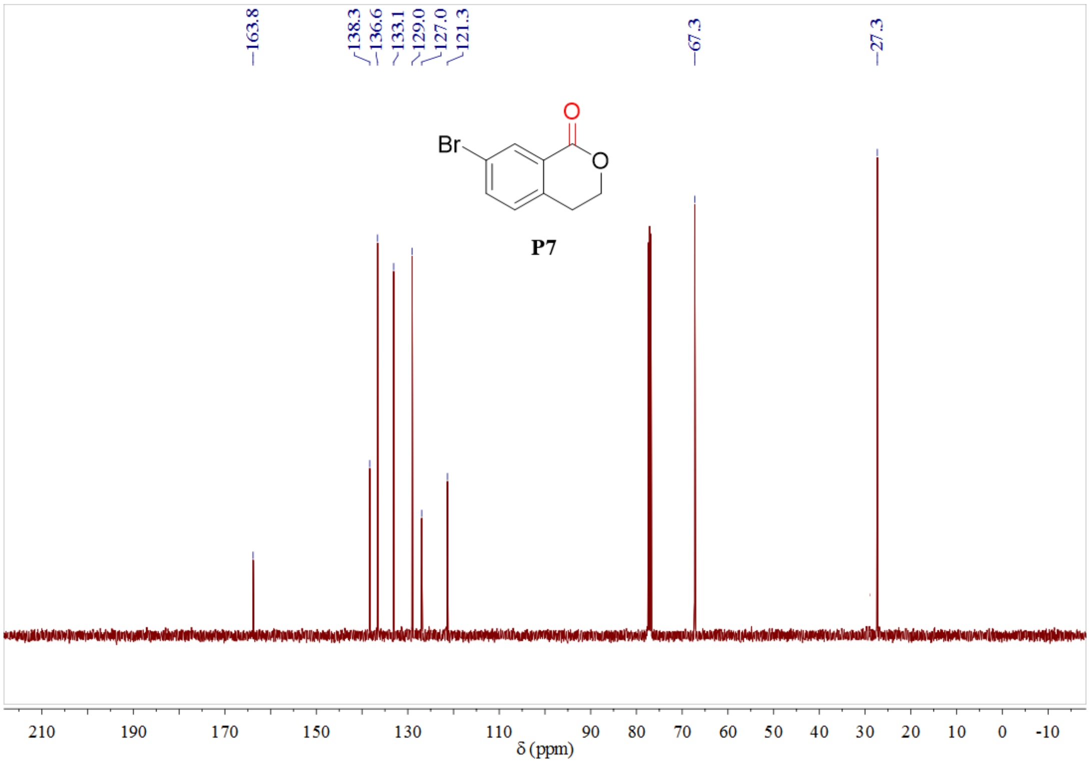
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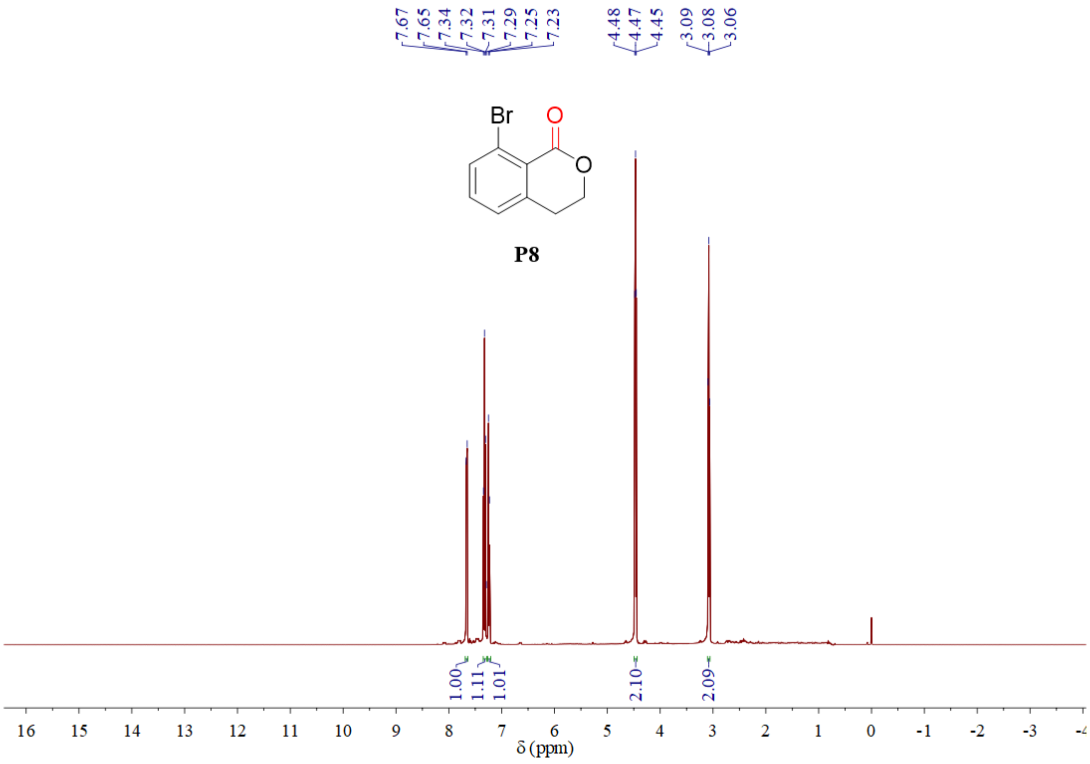
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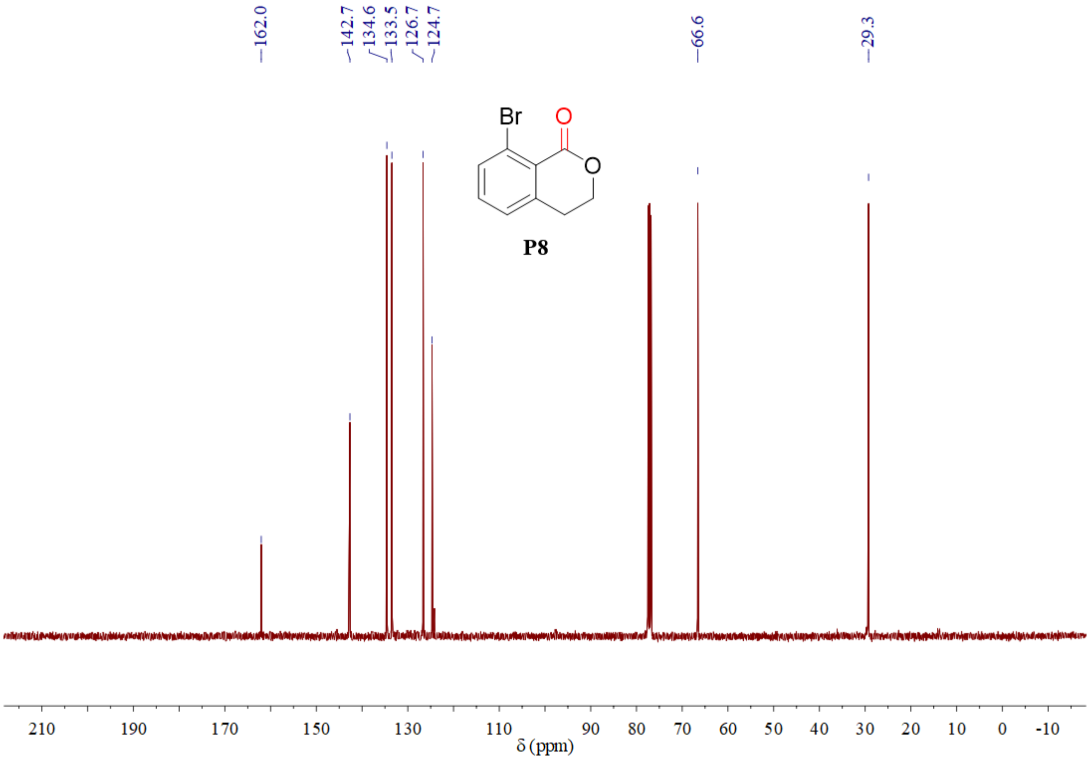
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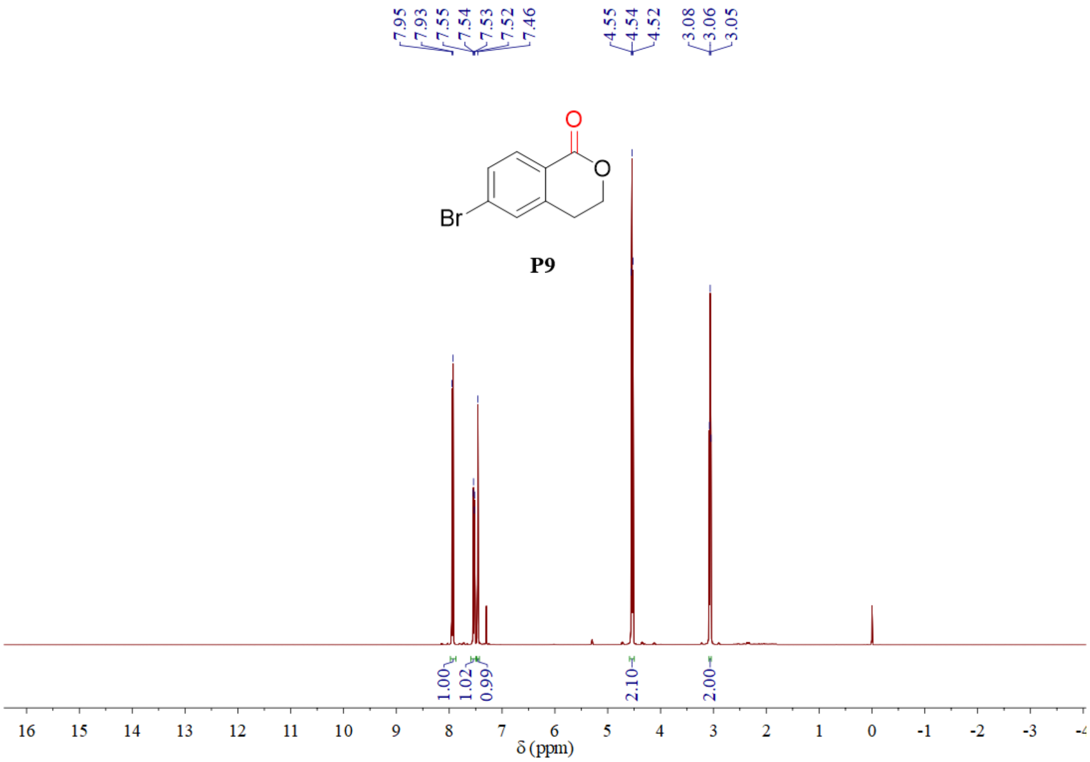
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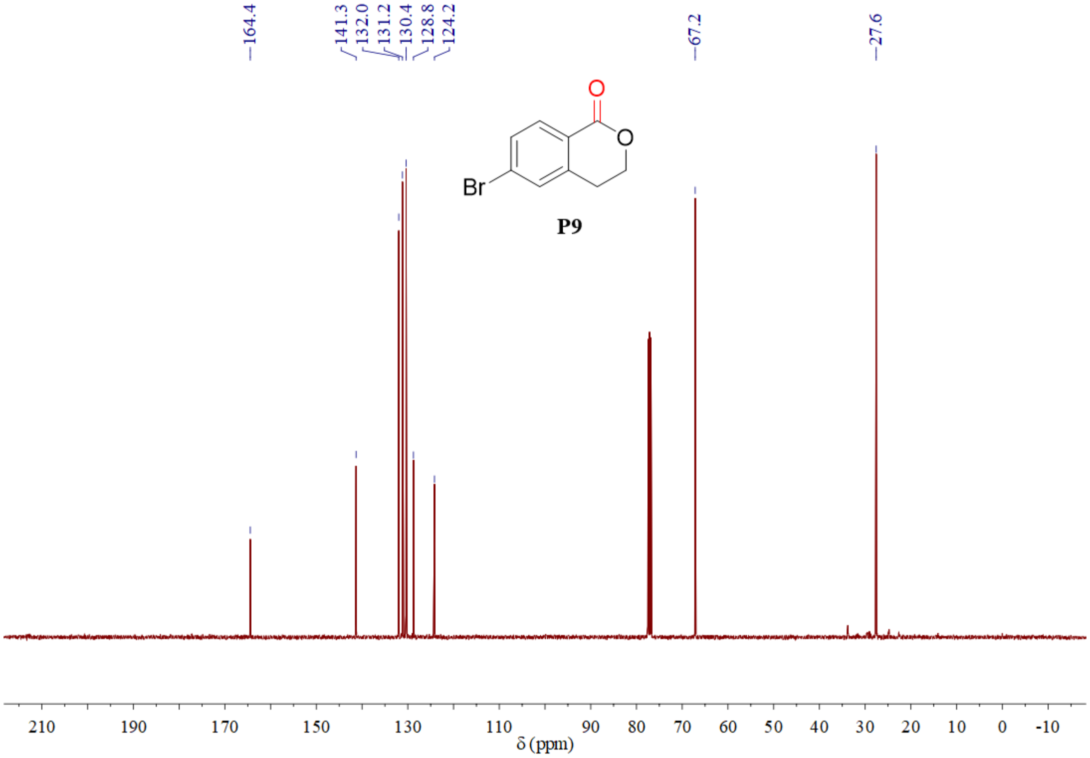
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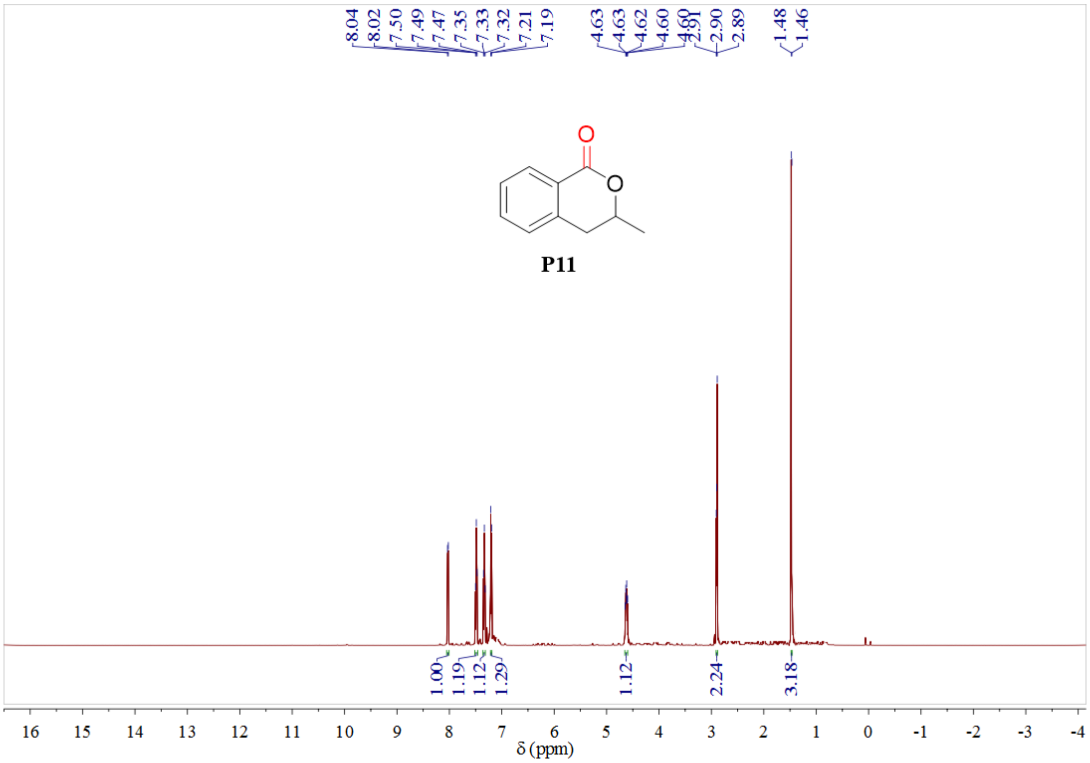
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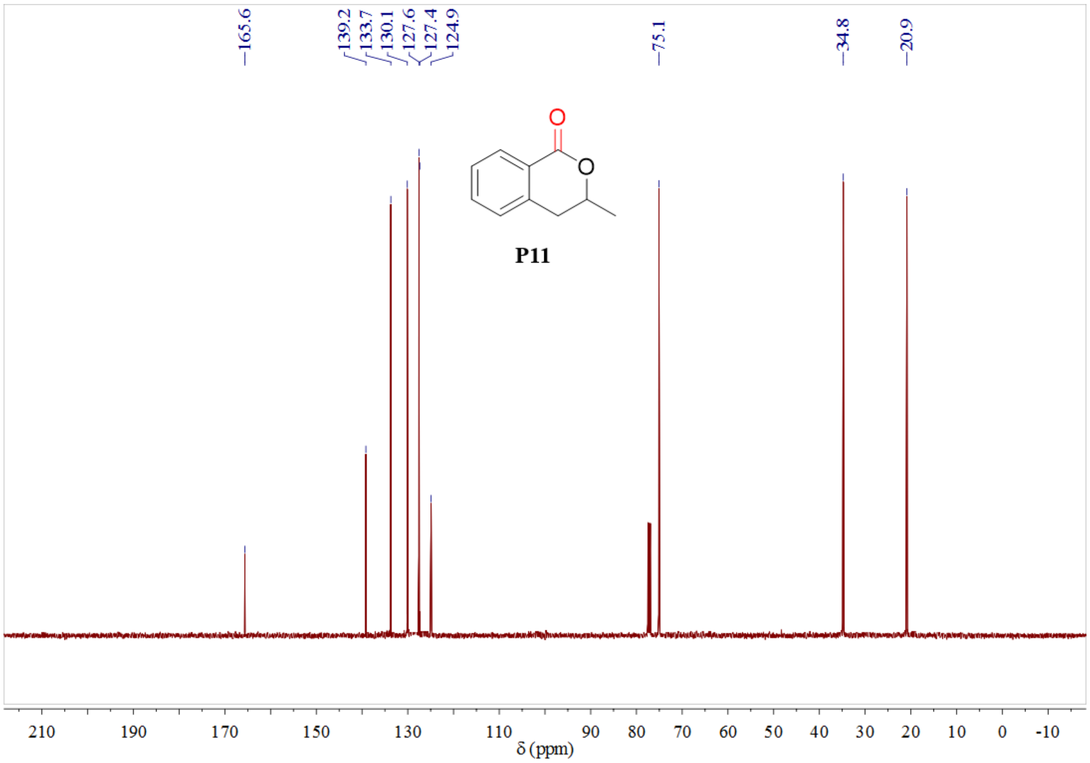
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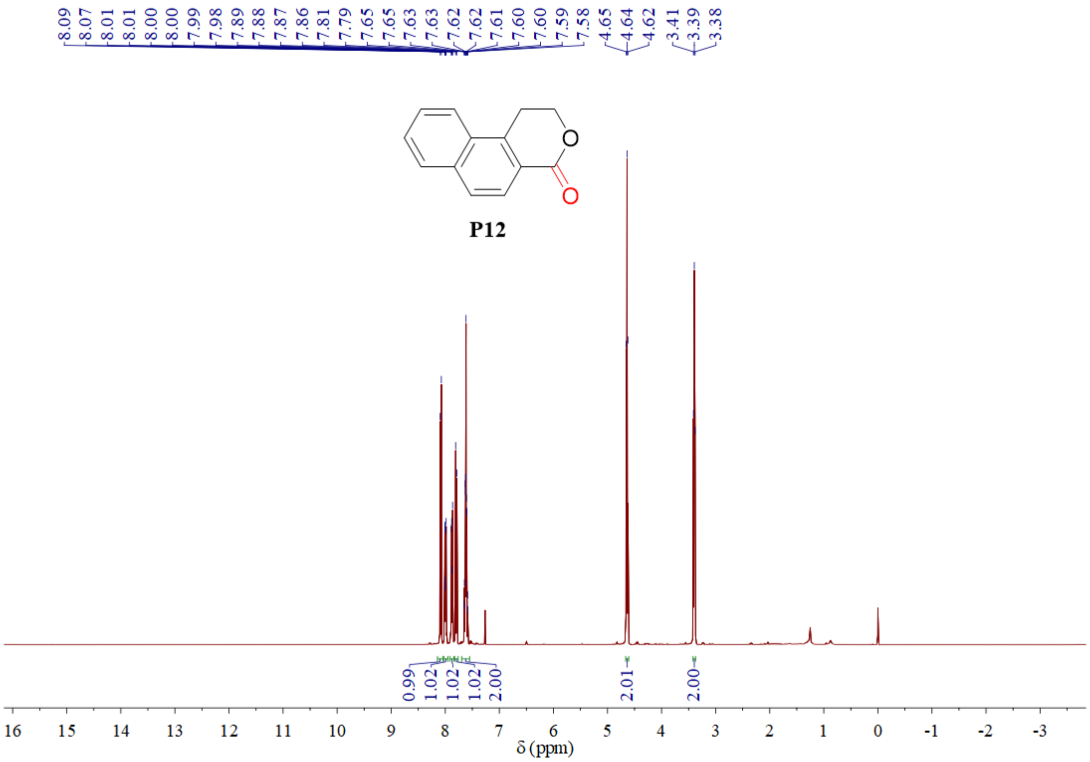
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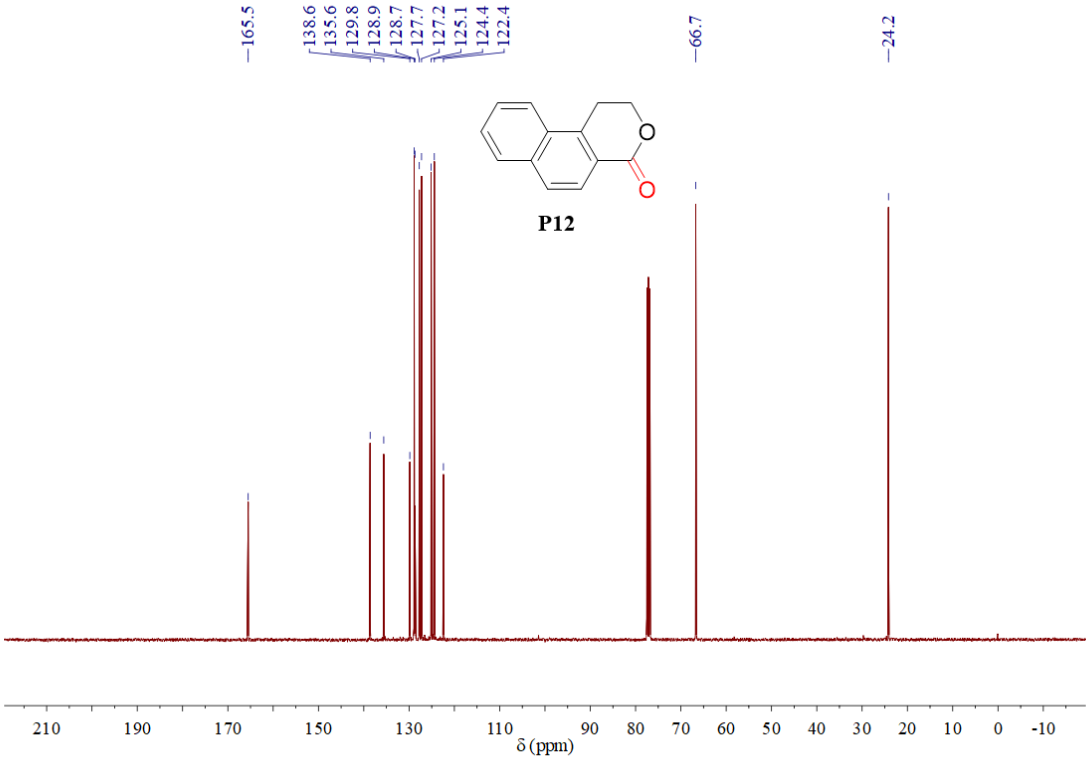
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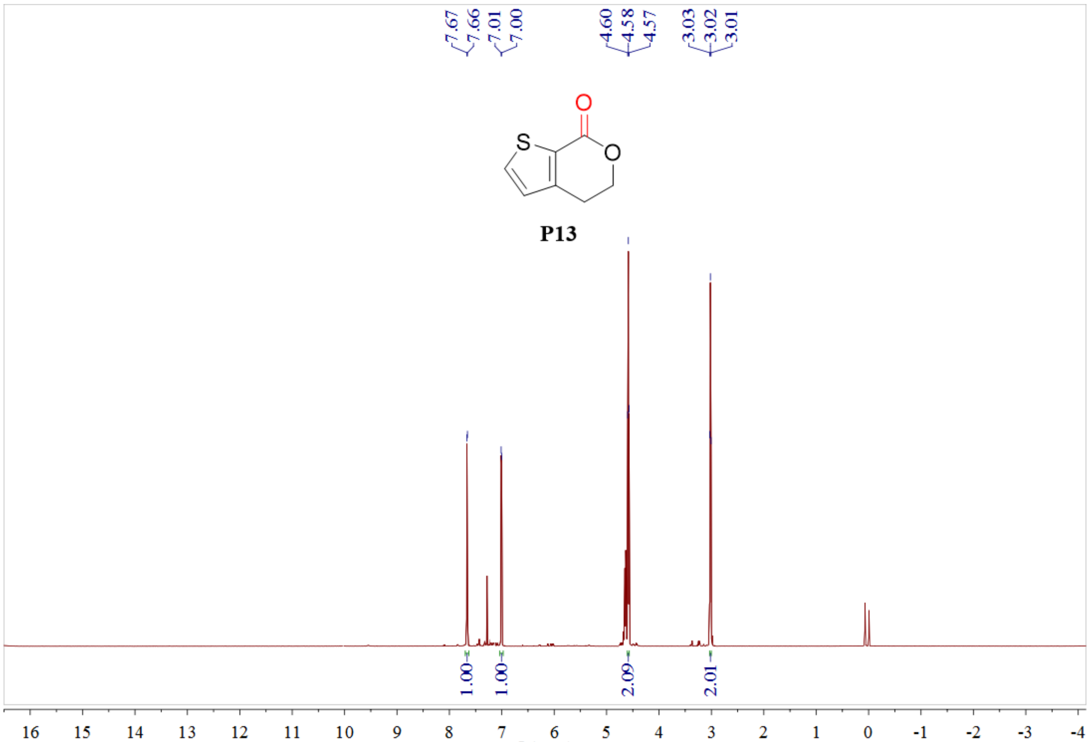
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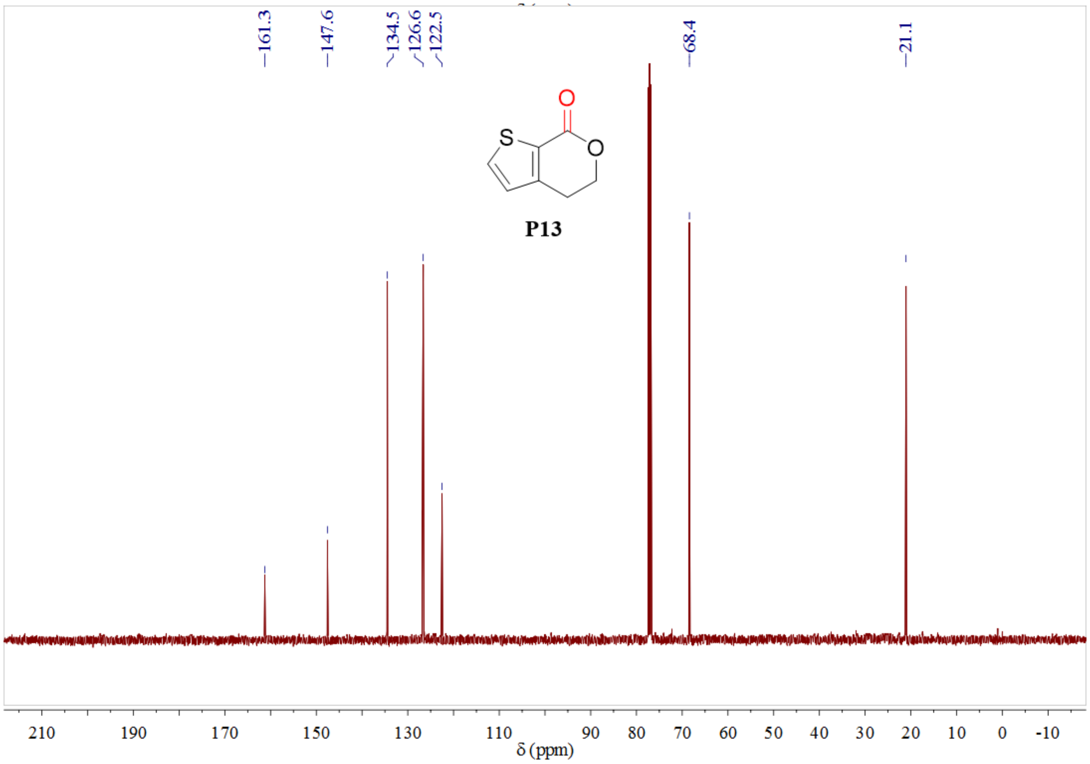
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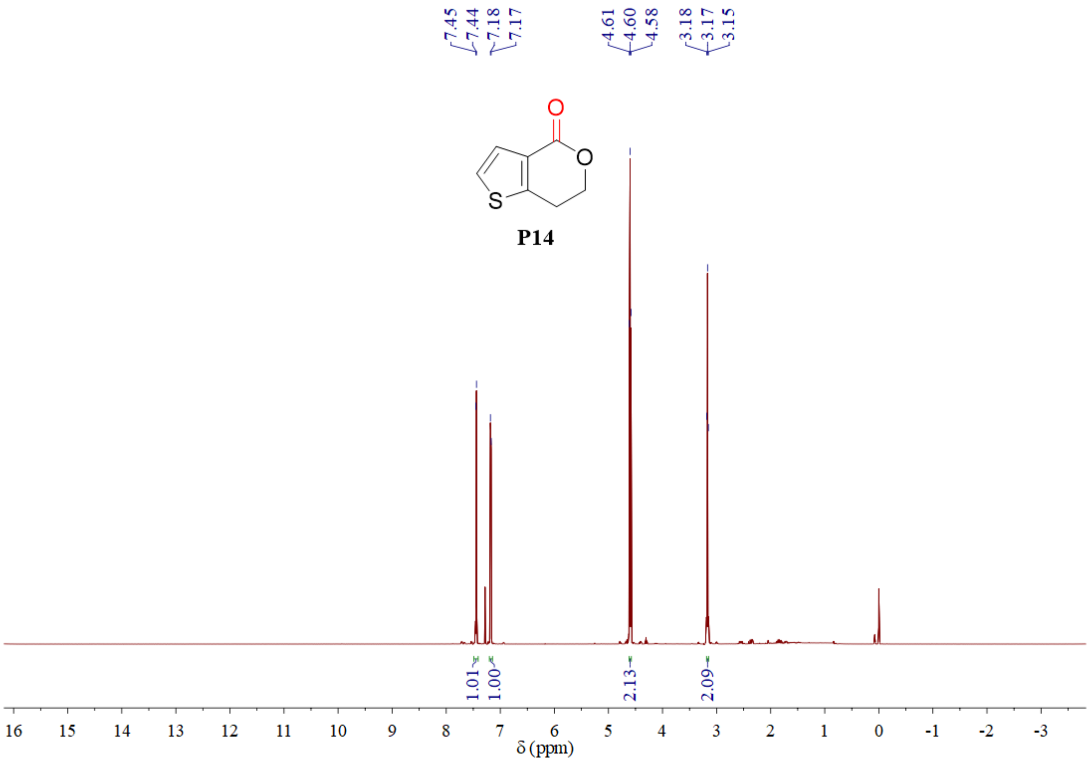
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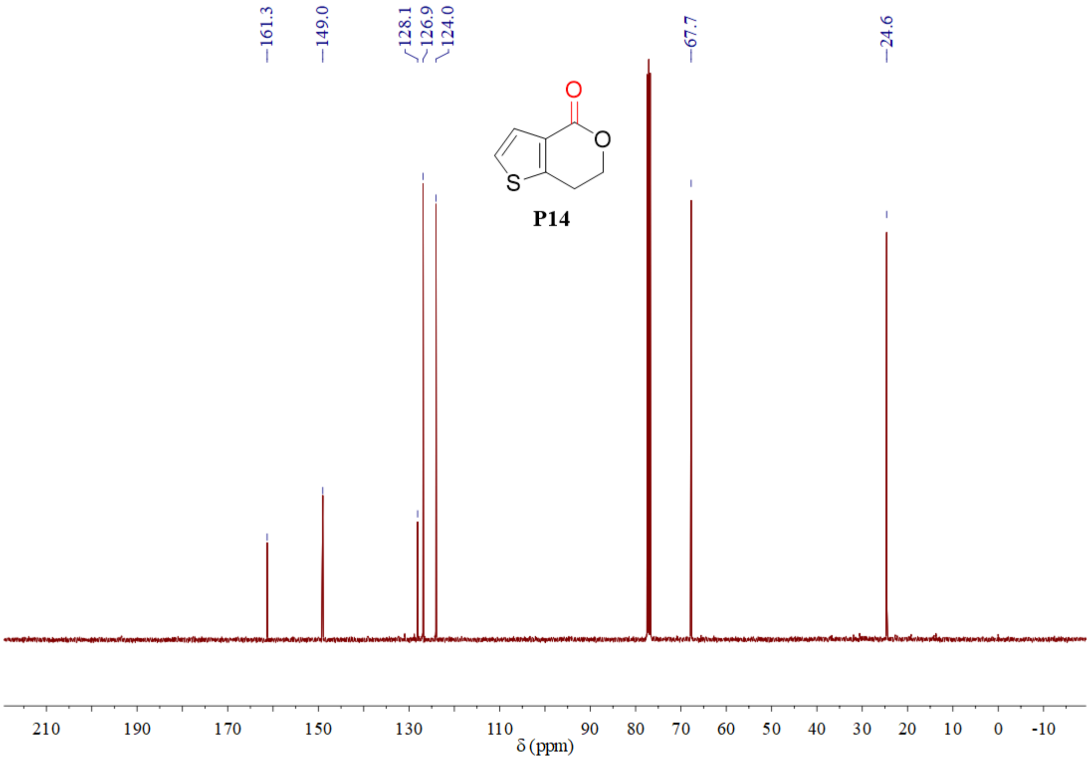
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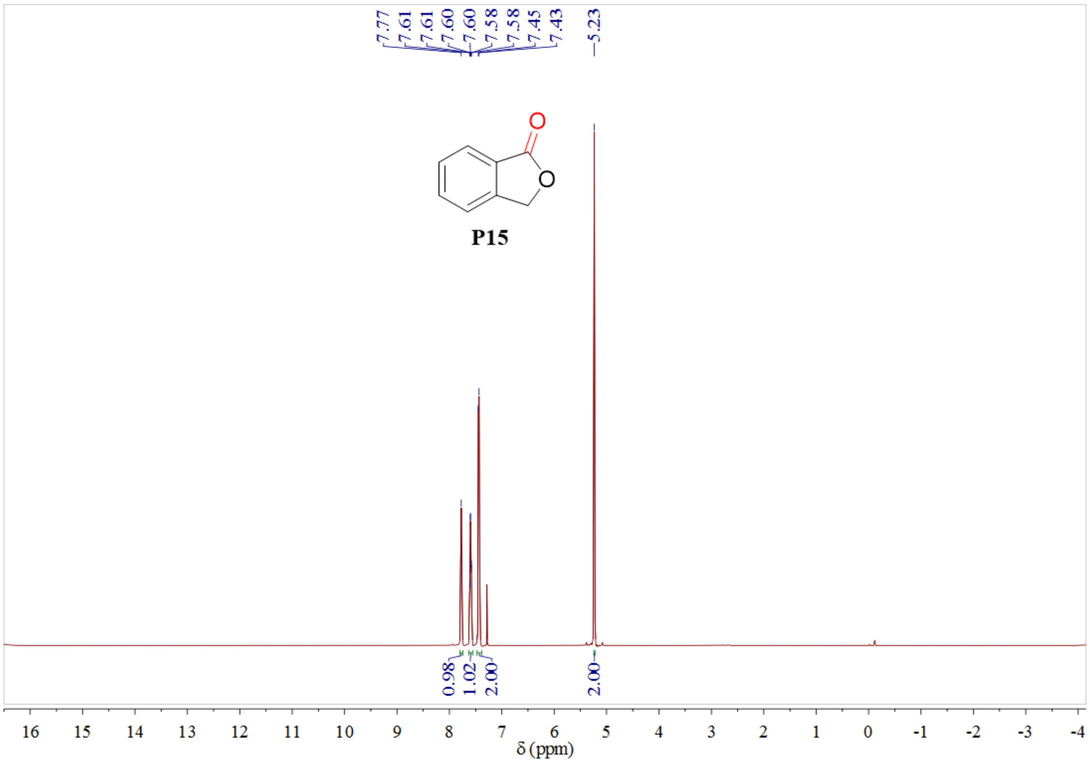
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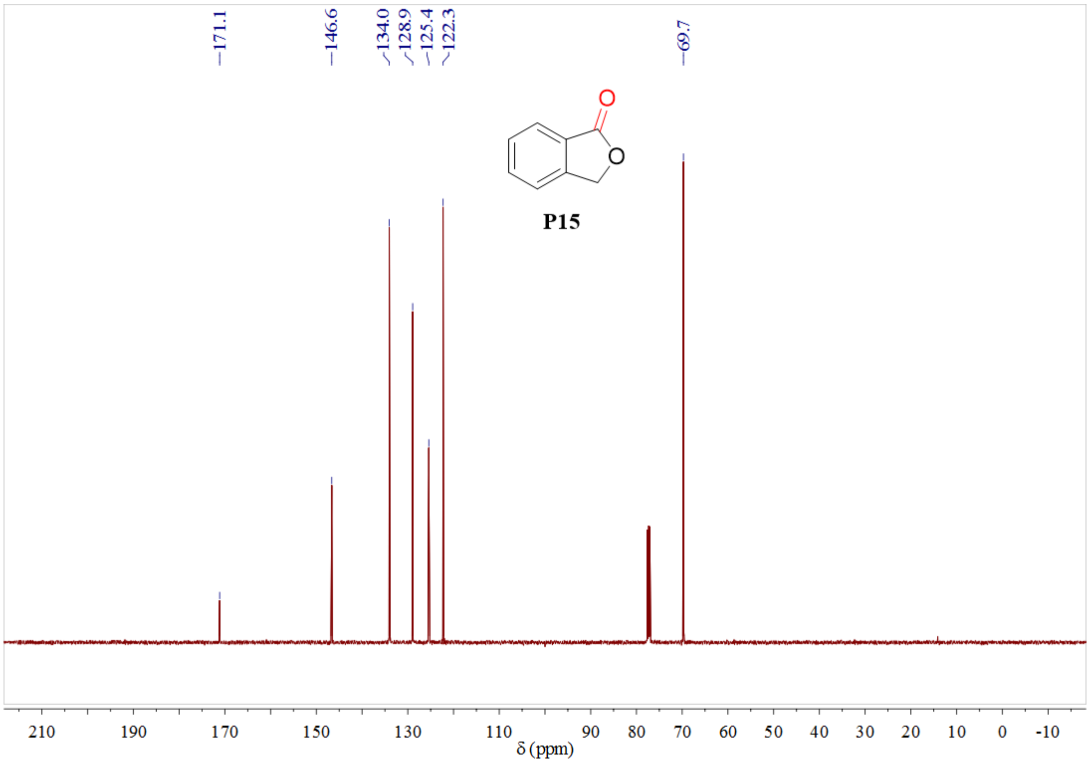
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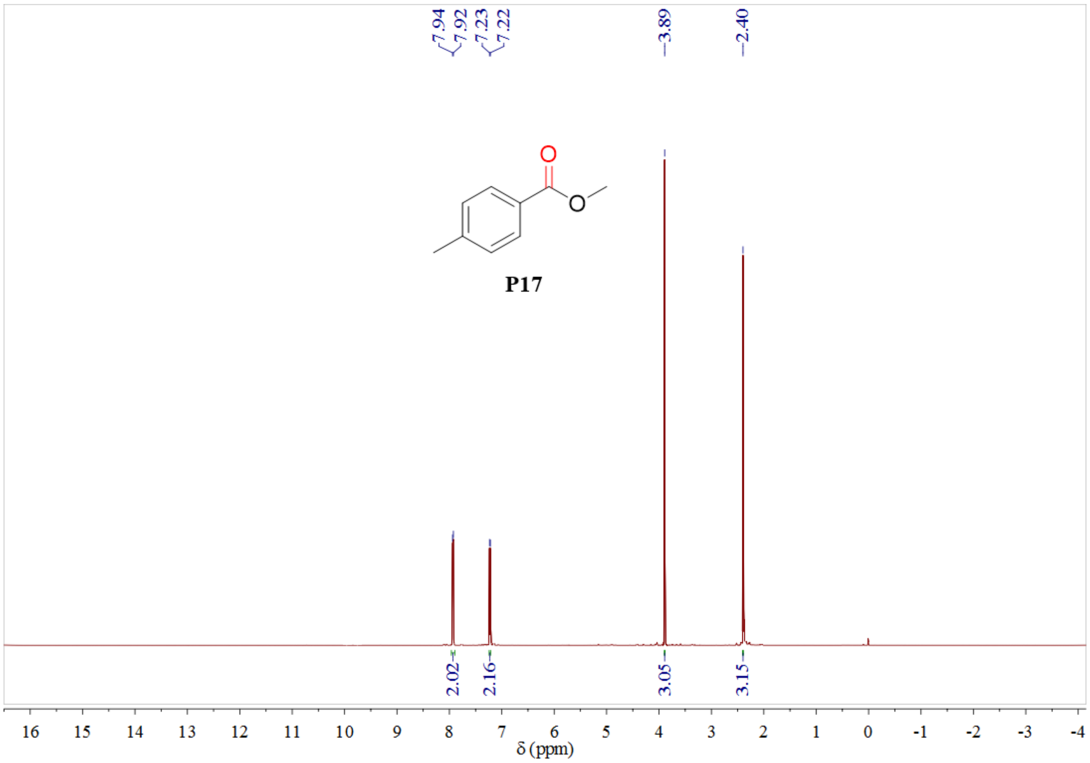
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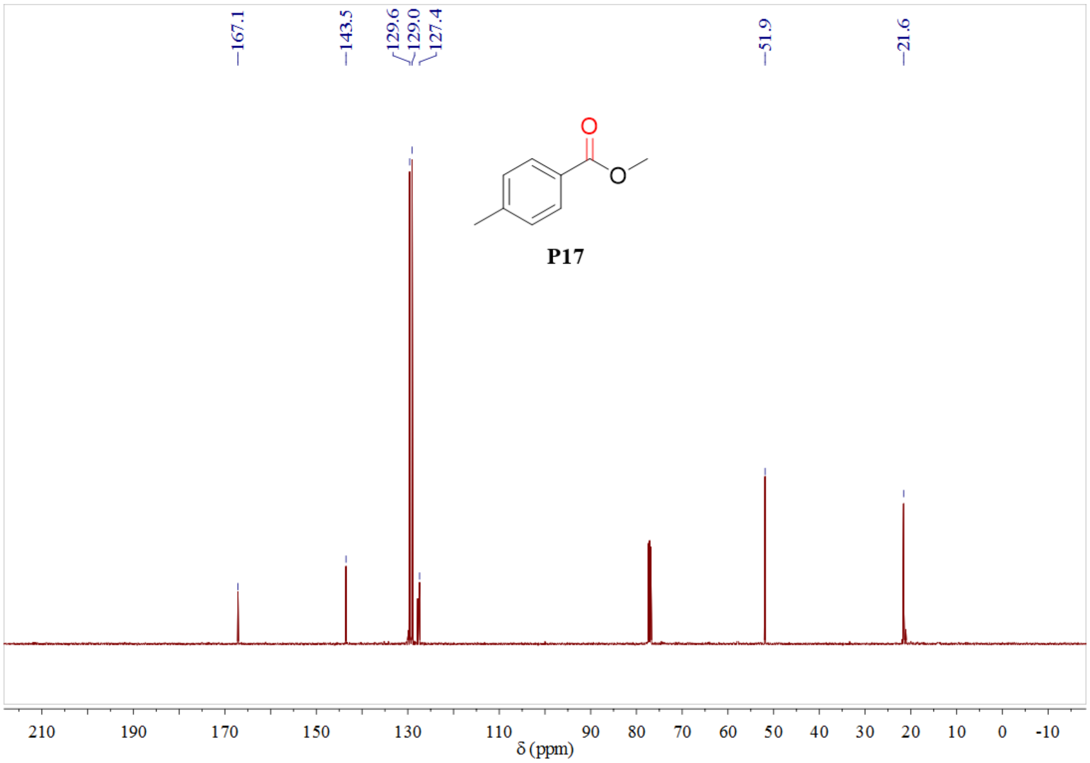
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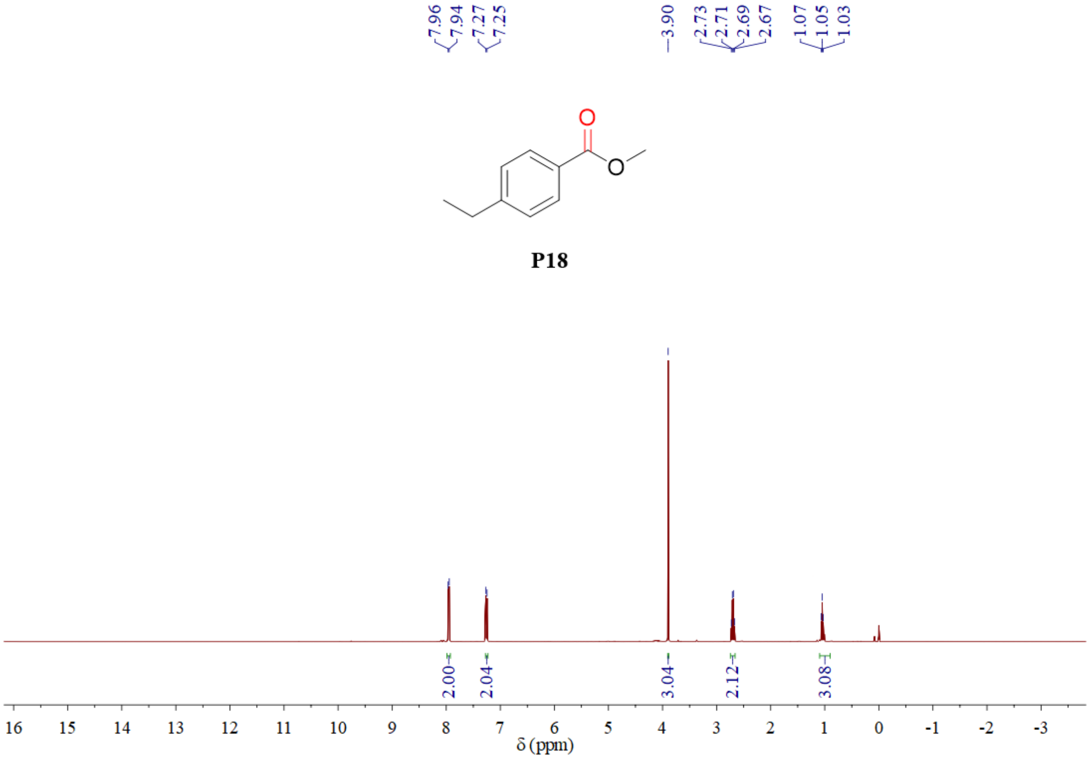
δ (ppm)


P18

7.96
7.94
7.27
7.25
3.90
2.73
2.71
2.69
2.67
1.07
1.05
1.03
O
O
2.00
2.04
3.04
2.12
3.08
16
15
14
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9
8
7
6
5
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3
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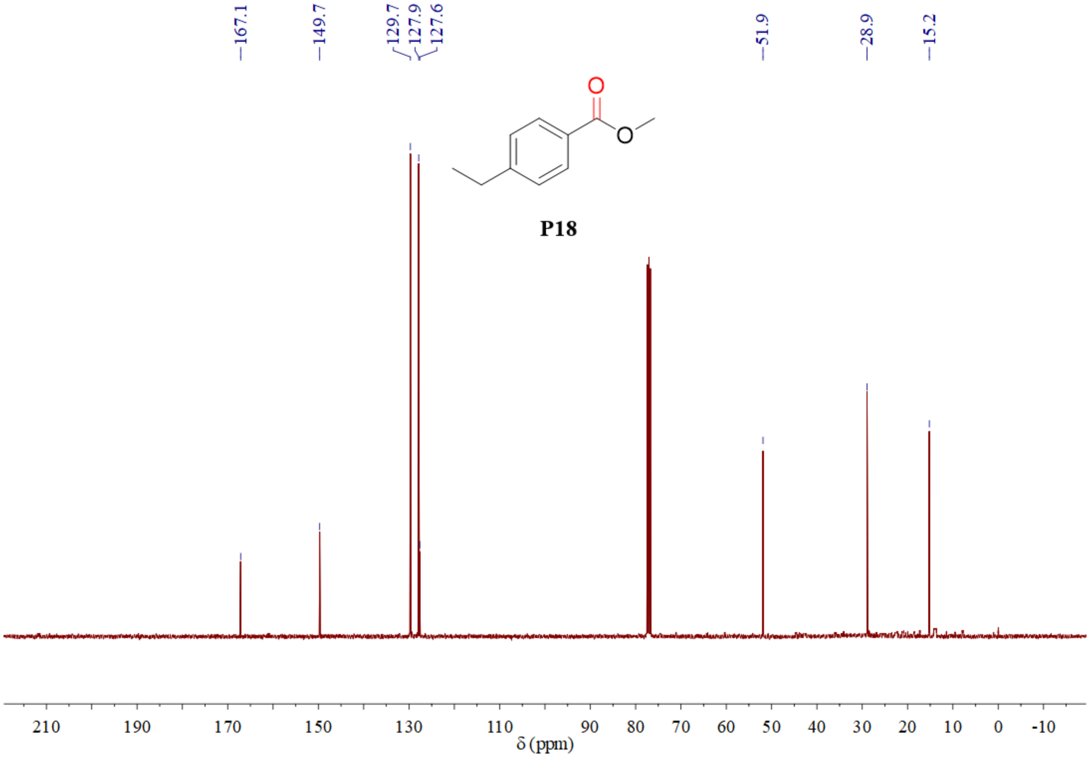
-2
-3
δ (ppm)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127.6
51.9
28.9
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O
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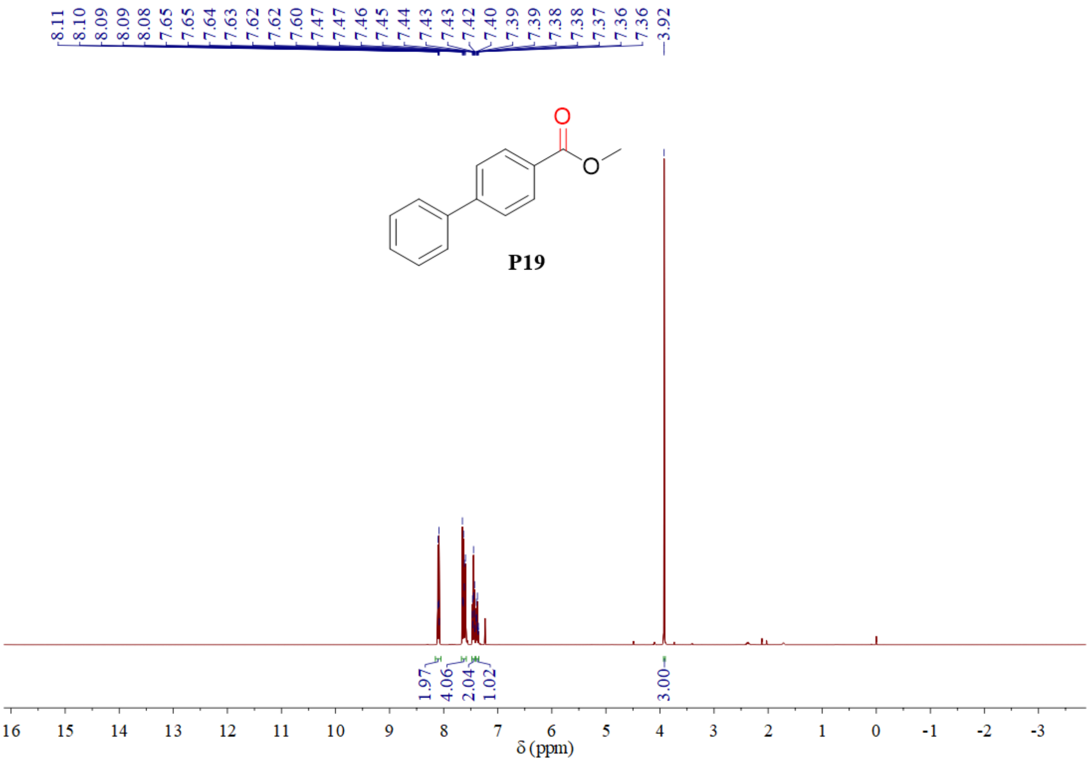
δ (ppm)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7.43
7.42
7.40
7.39
7.39
7.38
7.38
7.37
7.36
7.36
3.92
O
O
P19
1.97
4.06
2.04
1.02
3.00
16
15
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12
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9
8
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5
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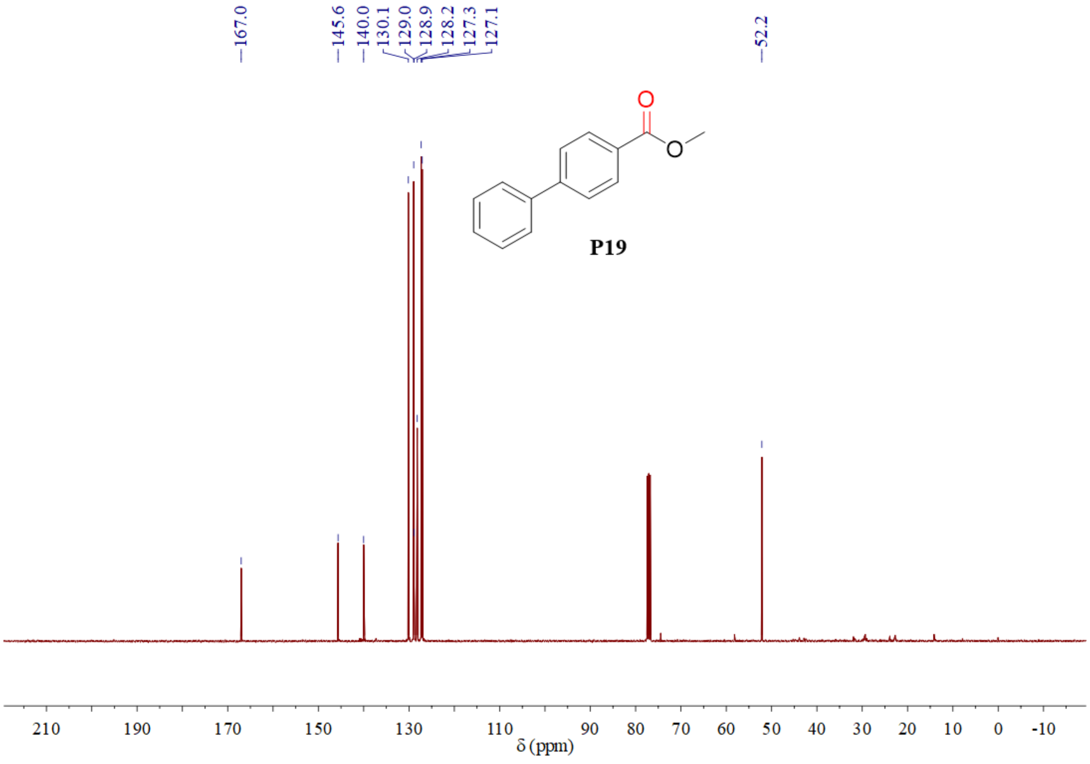
-2
-3
δ (ppm)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128.9
128.2
127.3
127.1
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O
O
P19
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150
130
110
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80
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50
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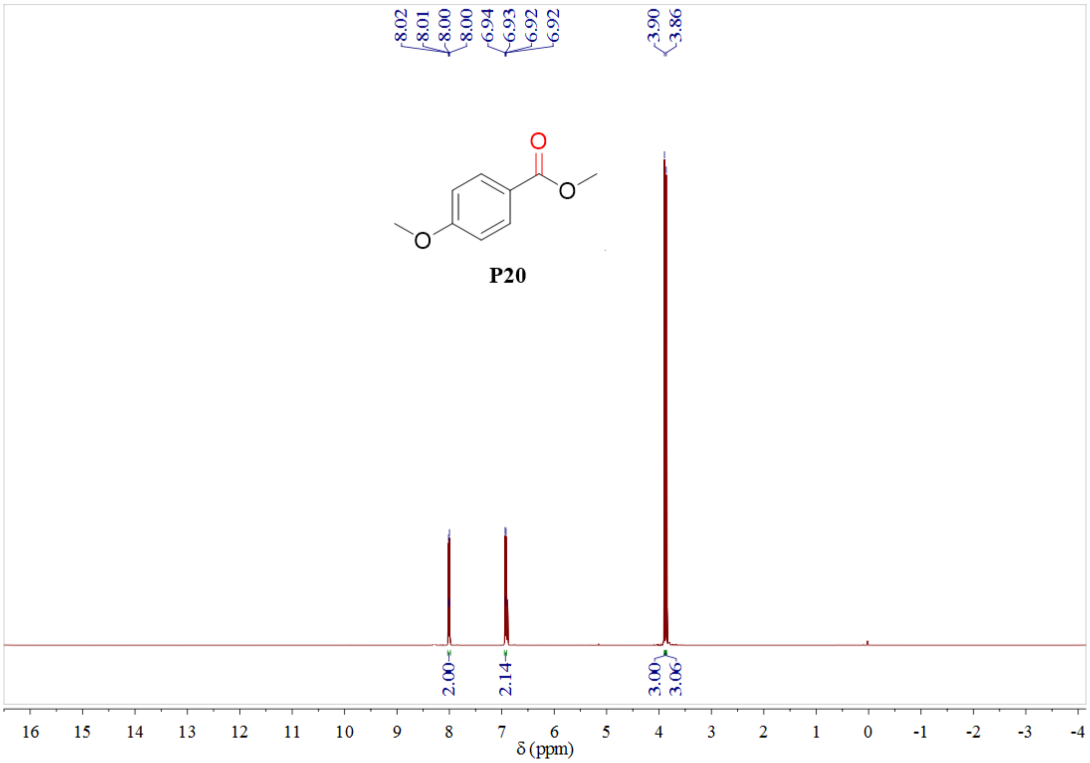
0
-10
δ (ppm)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6.92
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P20
2.00
2.14
3.00
3.06
16
15
14
13
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0
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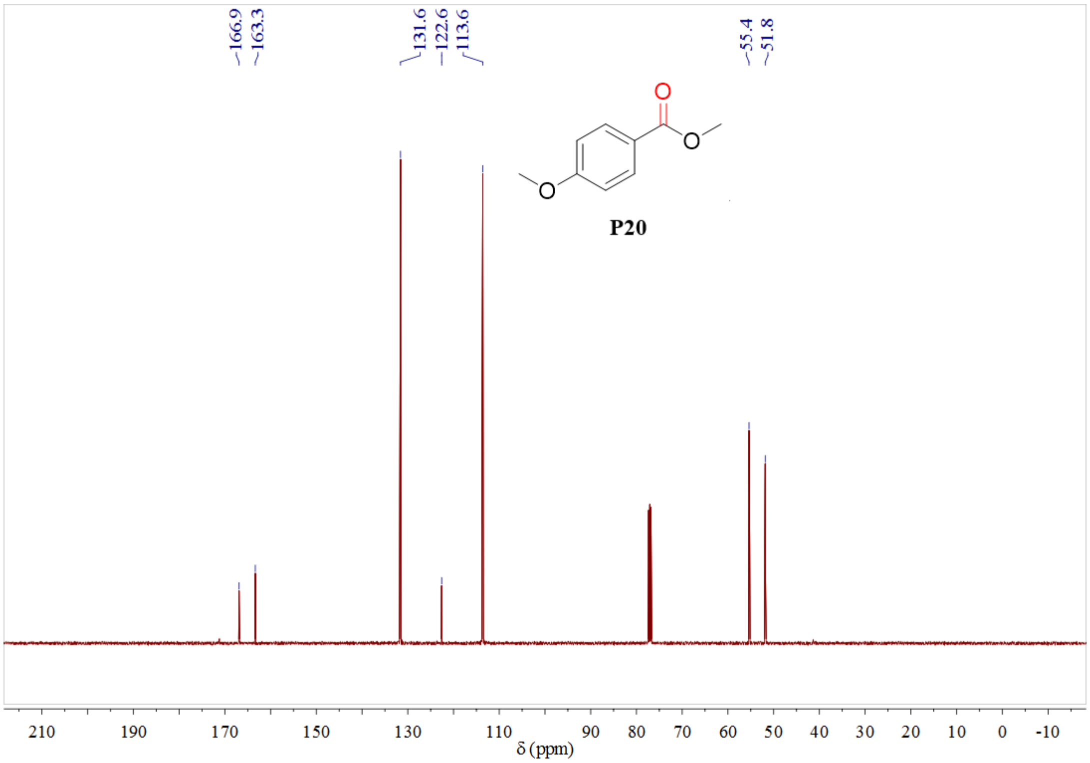
-2
-3
-4
δ (ppm)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122.6
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P20
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30
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0
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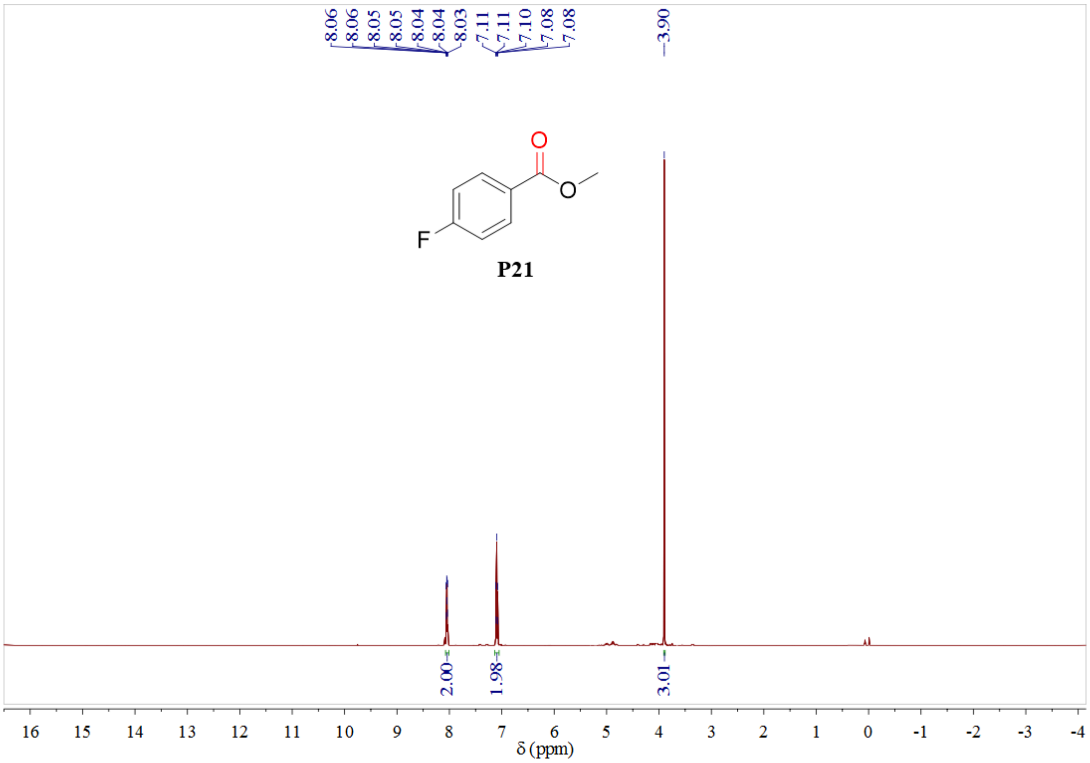
δ (ppm)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8.05
8.05
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8.03
7.11
7.11
7.10
7.08
7.08
3.90
O
O
F
P21
2.00
1.98
3.01
16
15
14
13
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8
7
6
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4
3
2
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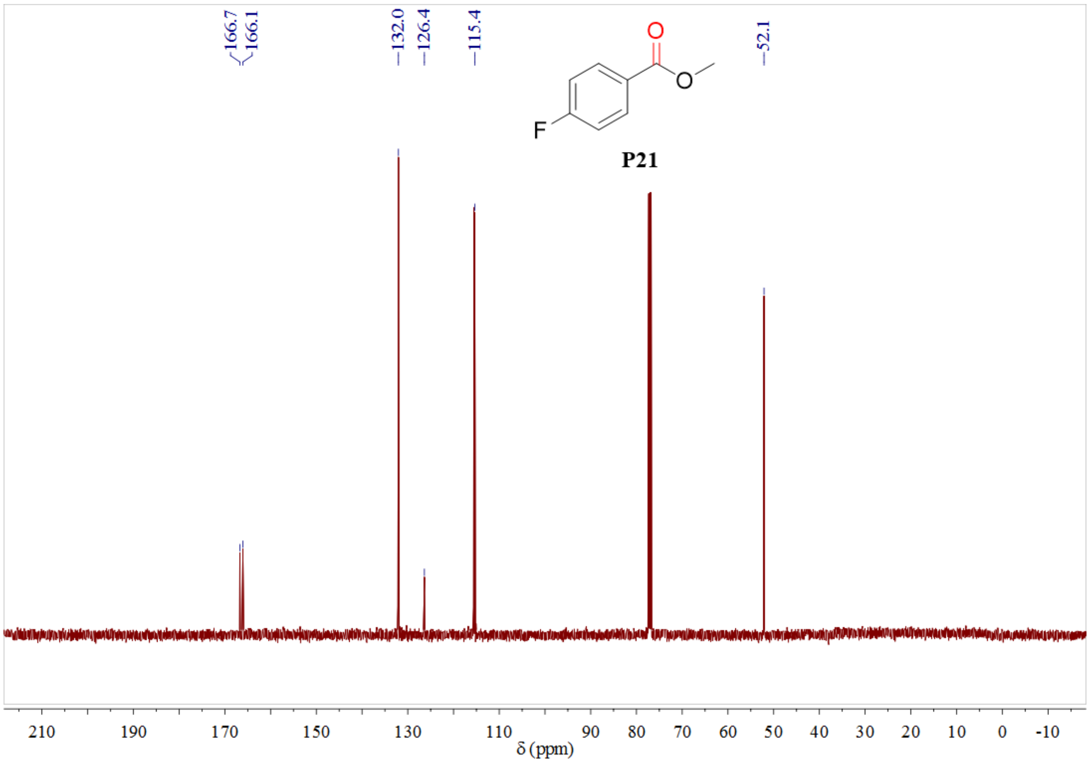
0
-1
-2
-3
-4
δ (ppm)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115.4
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O
F
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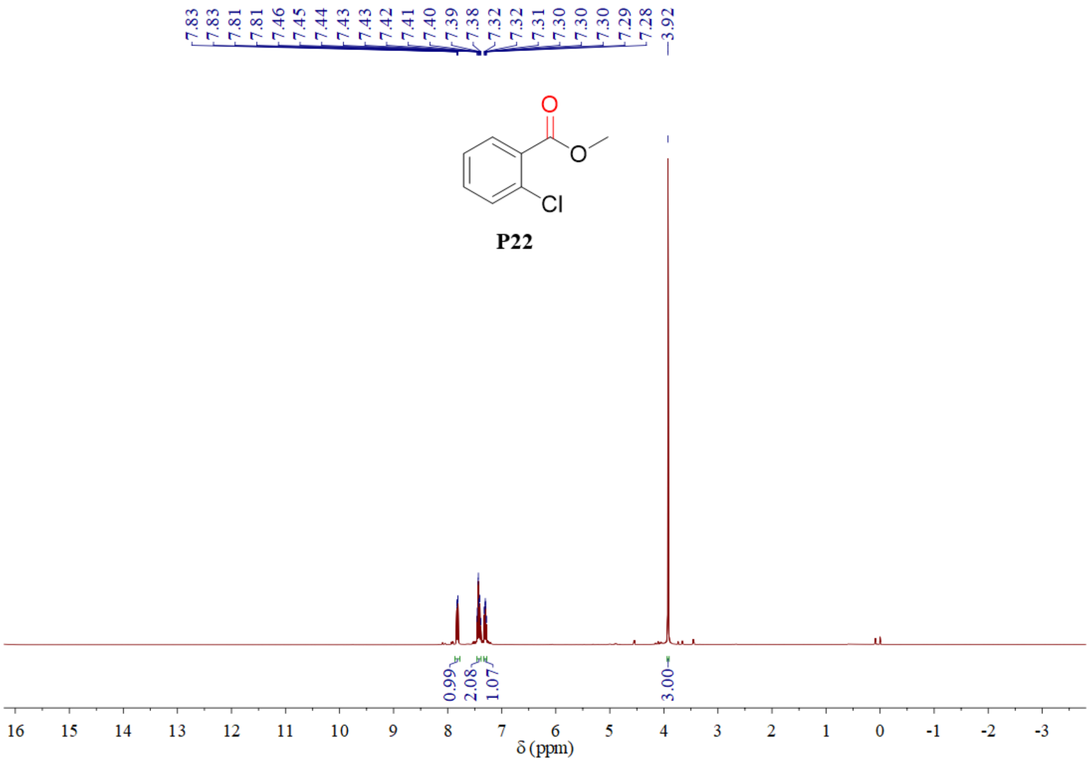
δ (ppm)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7.39
7.38
7.32
7.32
7.31
7.30
7.30
7.30
7.29
7.28
3.92
O
O
Cl
P22
0.99
2.08
1.07
3.00
16
15
14
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12
11
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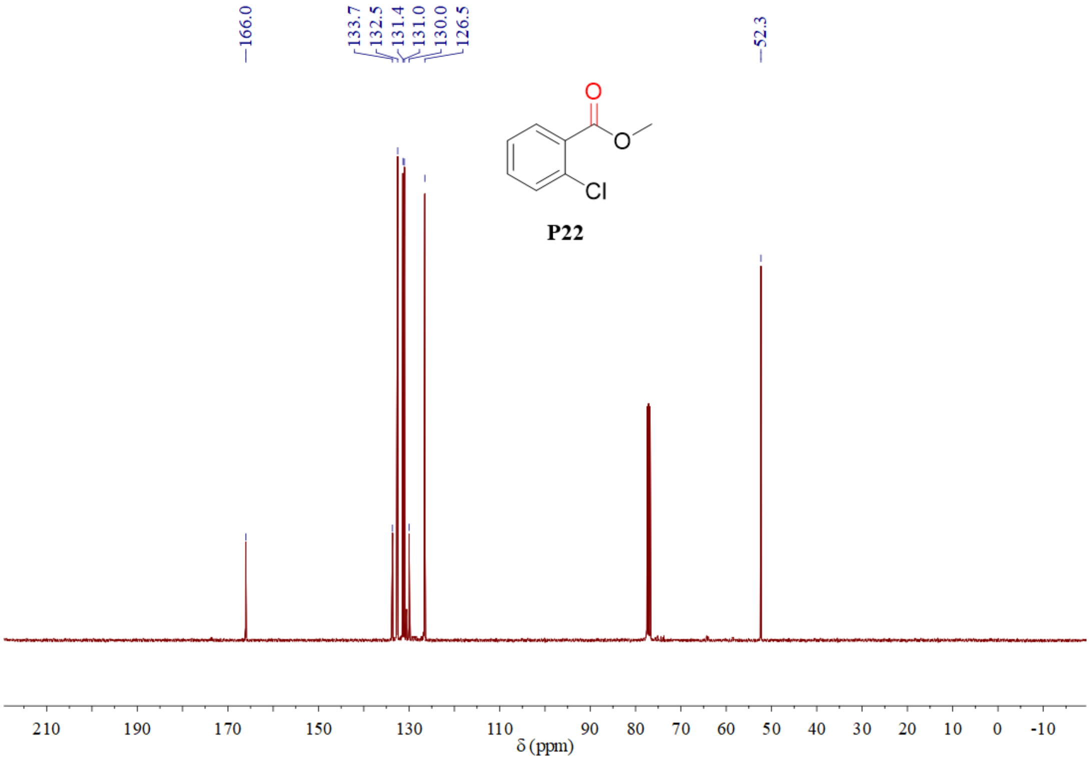
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
δ (ppm)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130.0
126.5
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O
Cl
P22
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150
130
110
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80
70
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50
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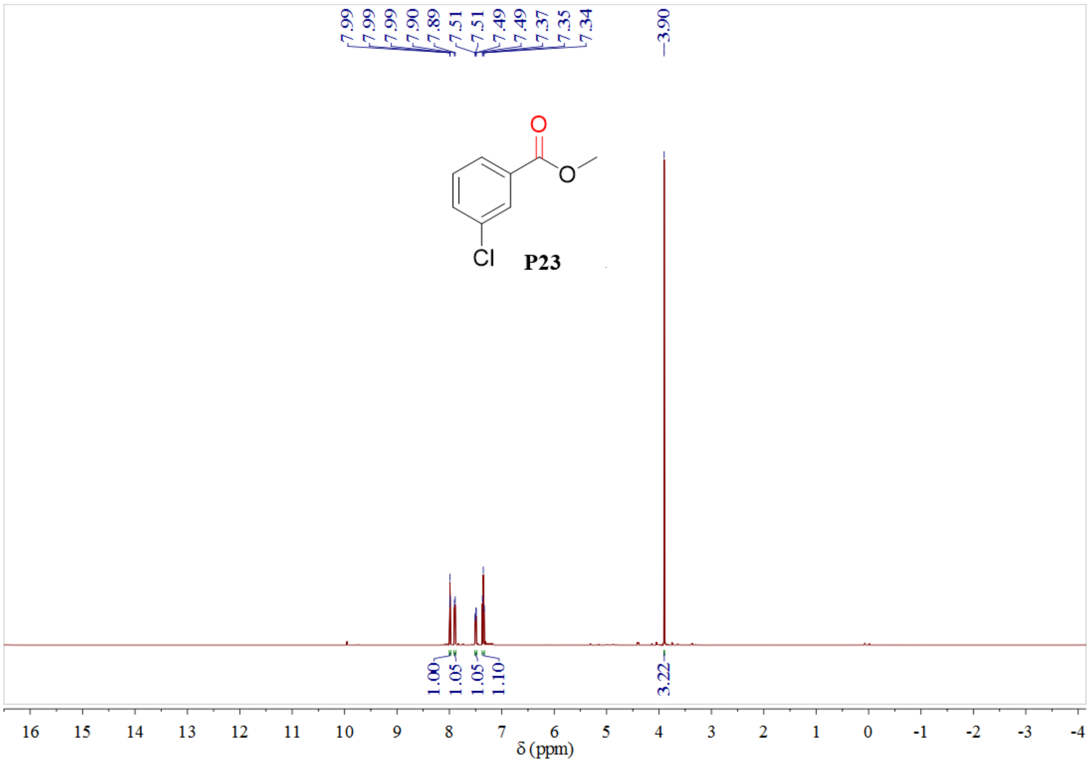
30
20
10
0
-10
δ (ppm)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7.49
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7.37
7.35
7.34
3.90
O
O
Cl
P23
1.00
1.05
1.05
1.10
3.22
16
15
14
13
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6
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4
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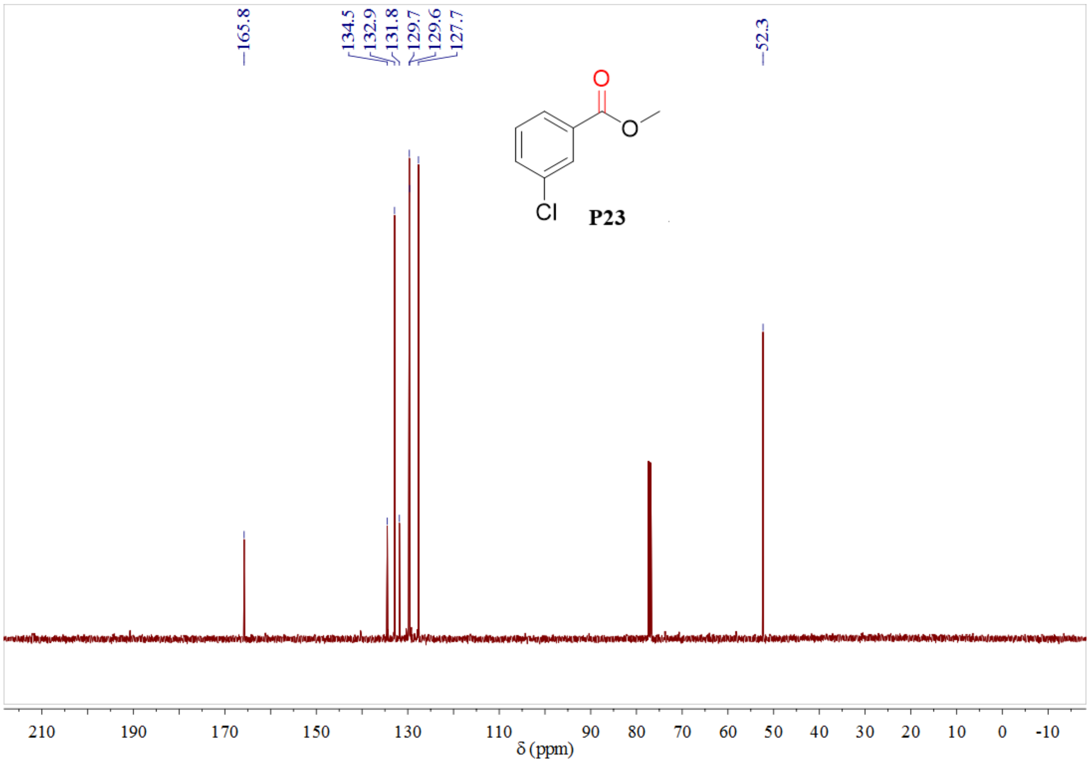
0
-1
-2
-3
-4
δ (ppm)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134.5
132.9
131.8
129.7
129.6
127.7
52.3
O
O
Cl
P23
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150
130
110
90
80
70
60
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30
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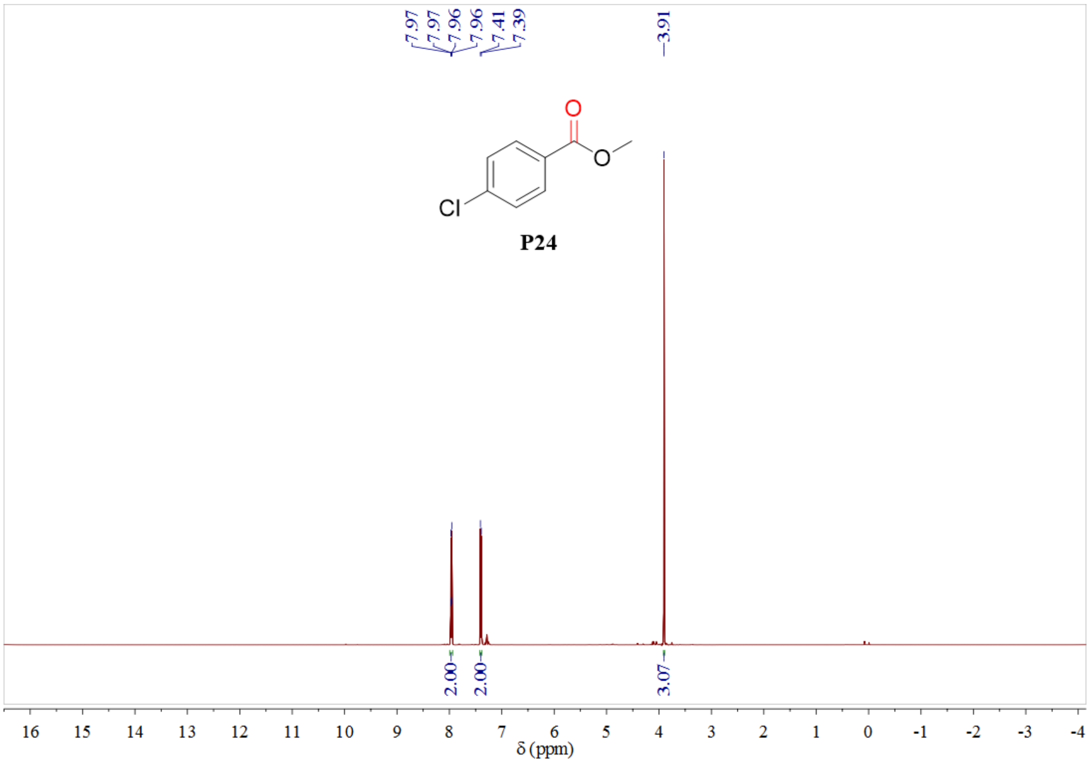
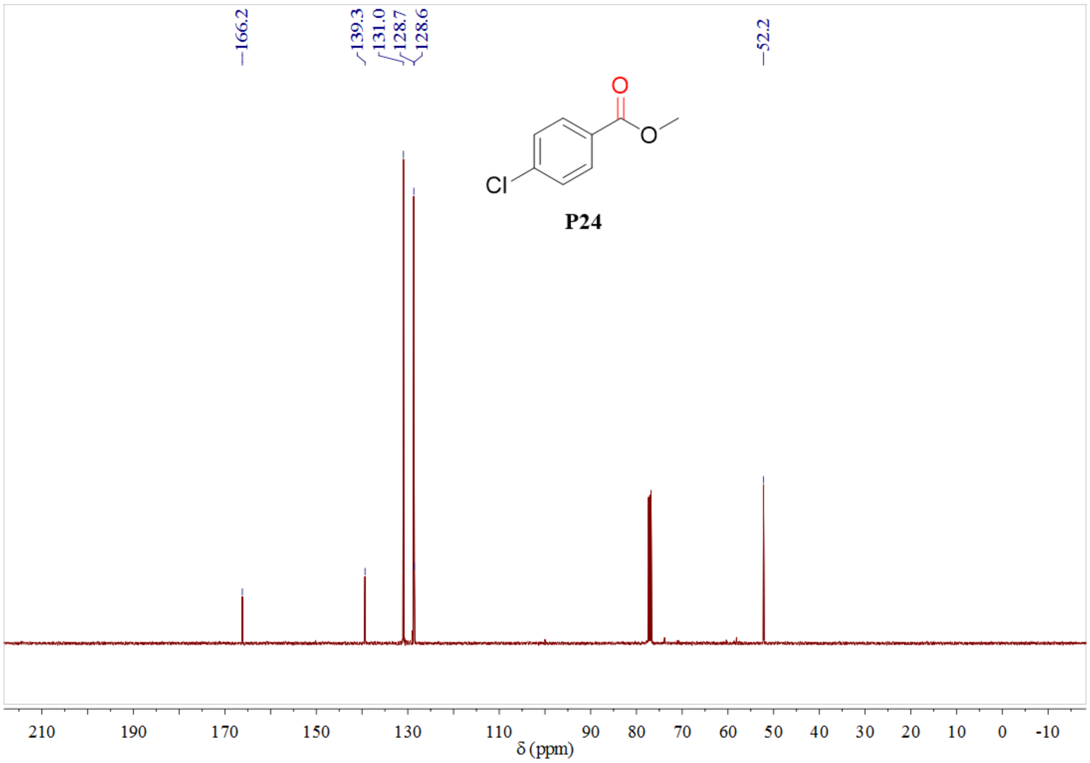
0
-10
δ (ppm)


7.97
7.97
7.96
7.96
7.41
7.39
3.91
O
O
Cl
P24
2.00
2.00
3.07
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
-4
δ (ppm)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139.3
131.0
128.7
128.6
52.2
O
O
Cl
P24
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190
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150
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110
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80
70
60
50
40
30
20
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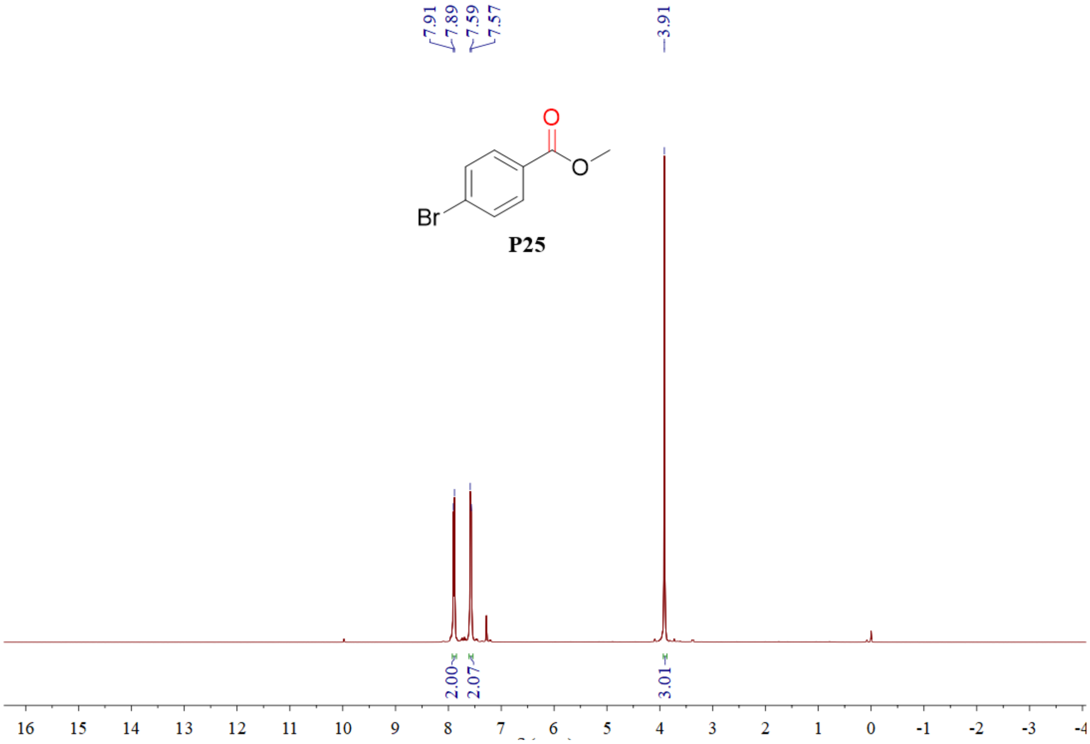
0
-10
δ (ppm)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Br
O
O
P25
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2.07
3.01
16
15
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12
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10
9
8
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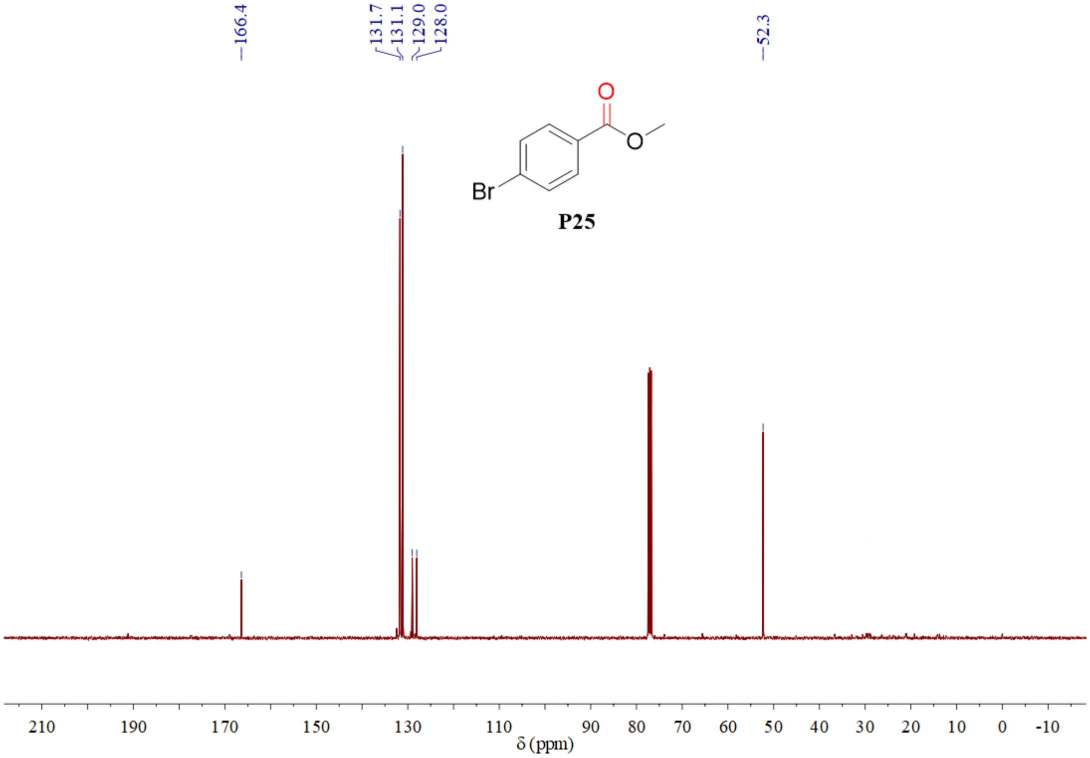
6
5
4
3
2
1
0
-1
-2
-3
-4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128.0
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Br
O
O
P25
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150
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110
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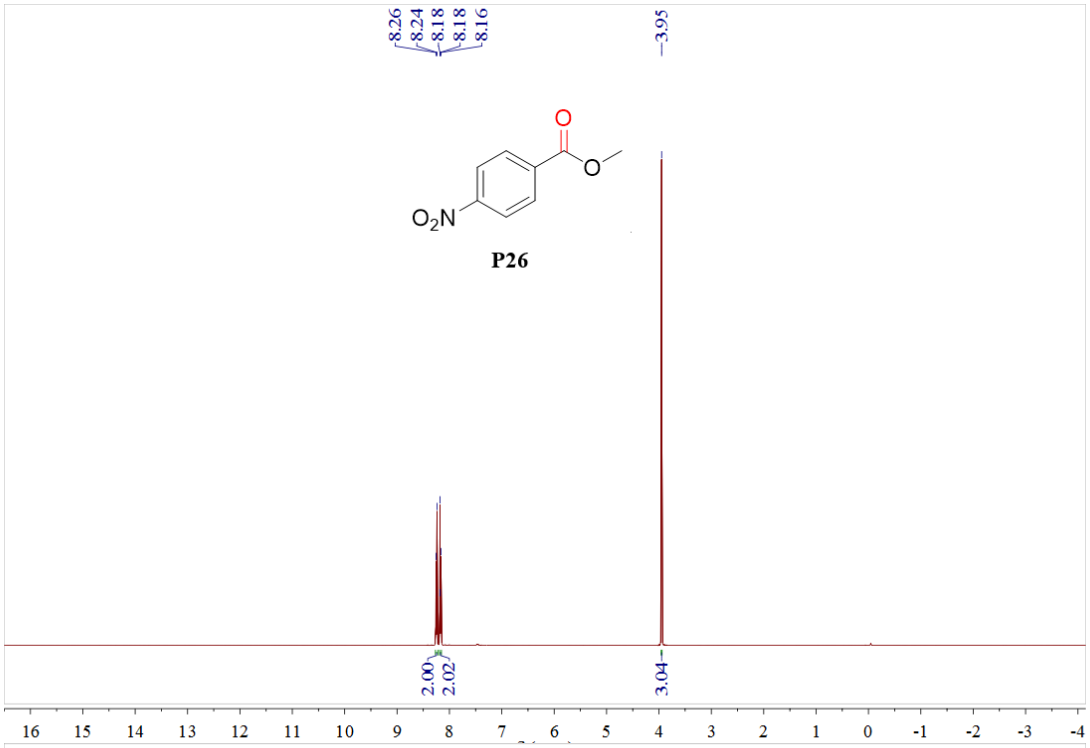
80
70
60
50
40
30
20
10
0
-10
δ (ppm)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8.18
8.16
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O
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P26
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3.04
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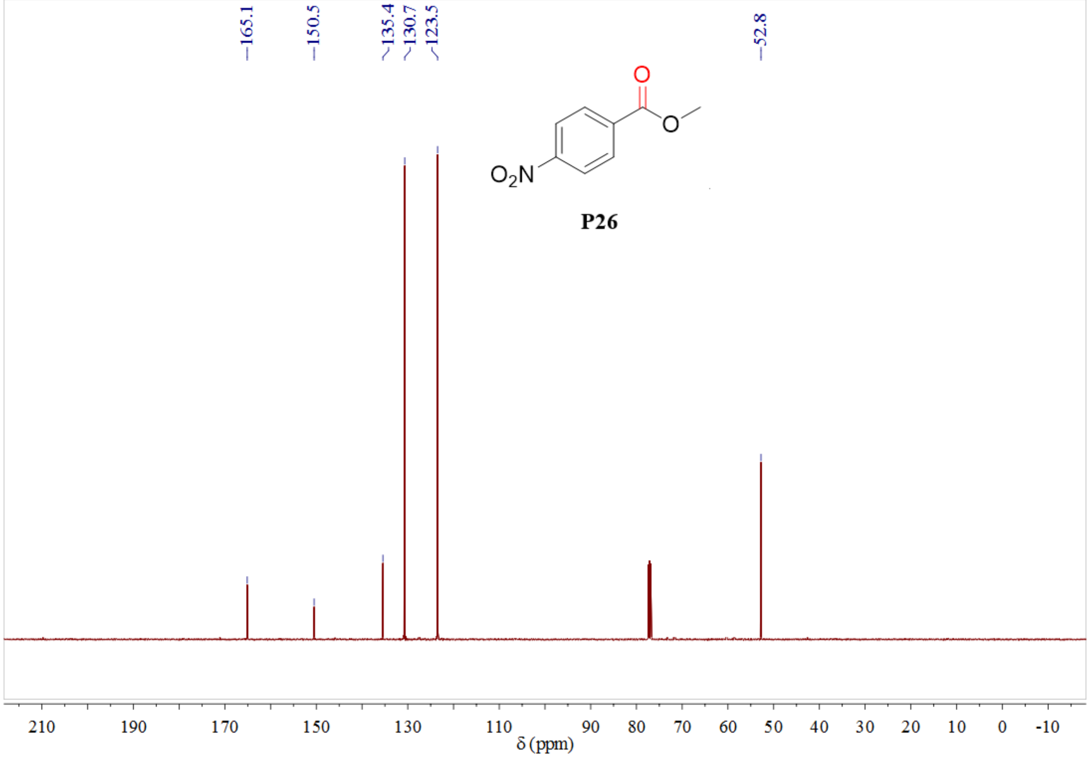
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150.5
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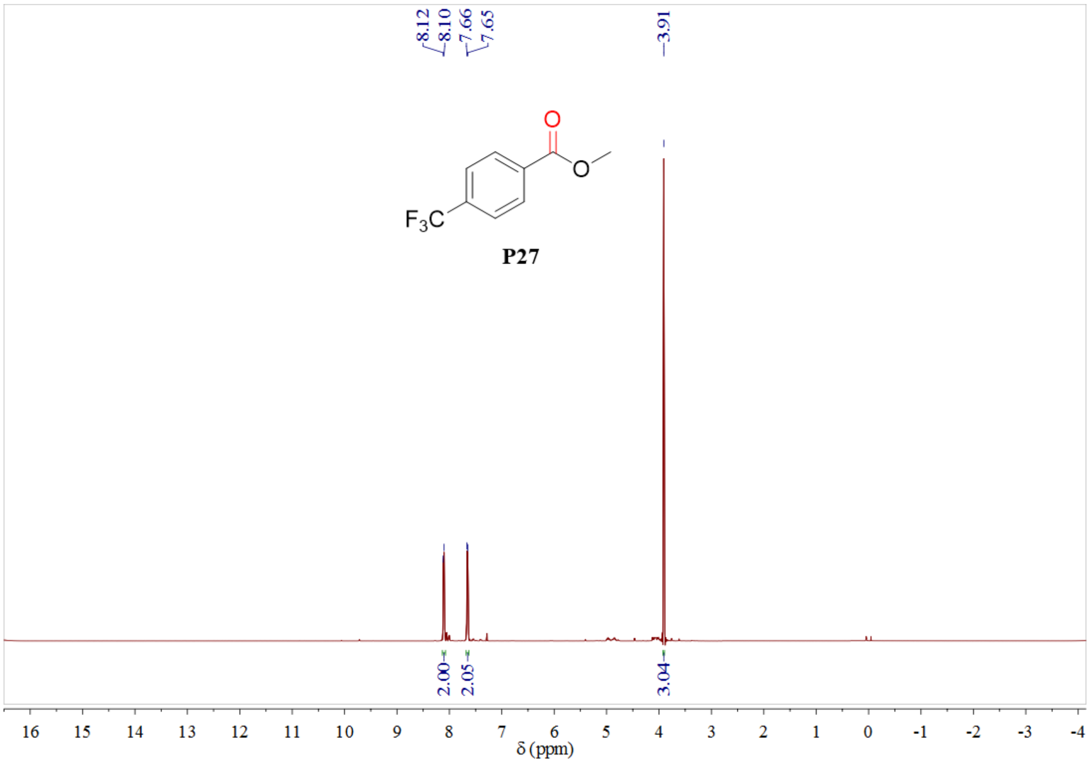
52.8
O
O
O_2N
P26
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
δ (ppm)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7.65
3.91
F3C
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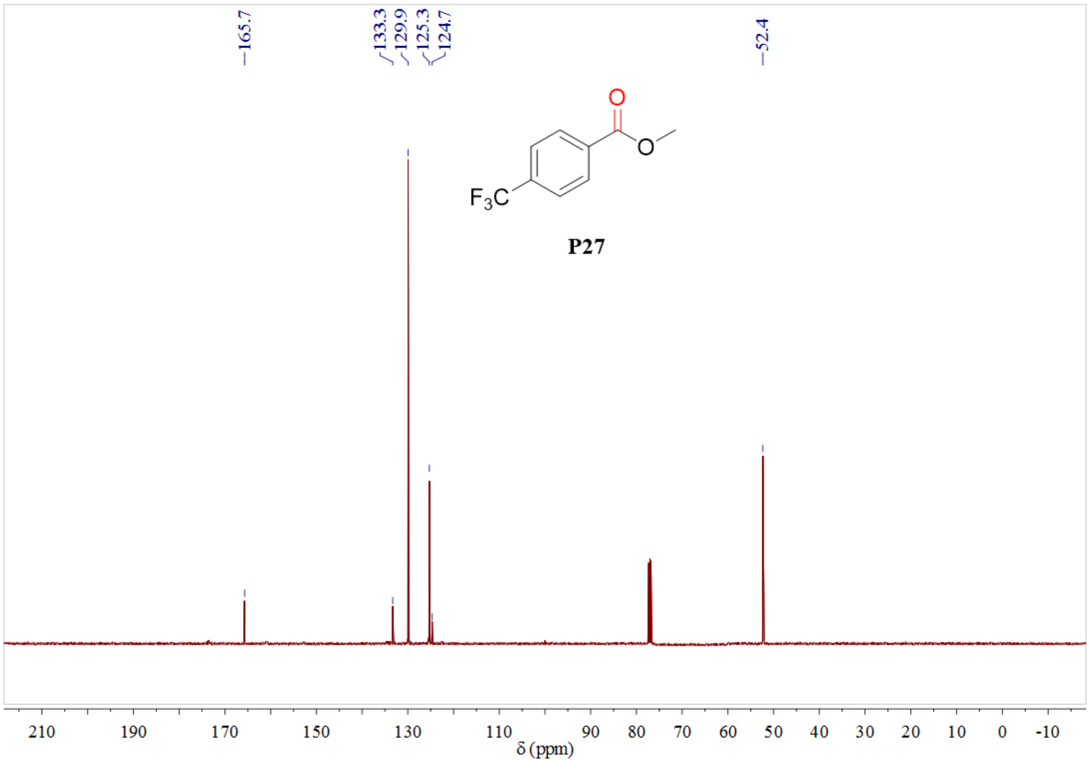
O
P27
2.00
2.05
3.04
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
δ (ppm)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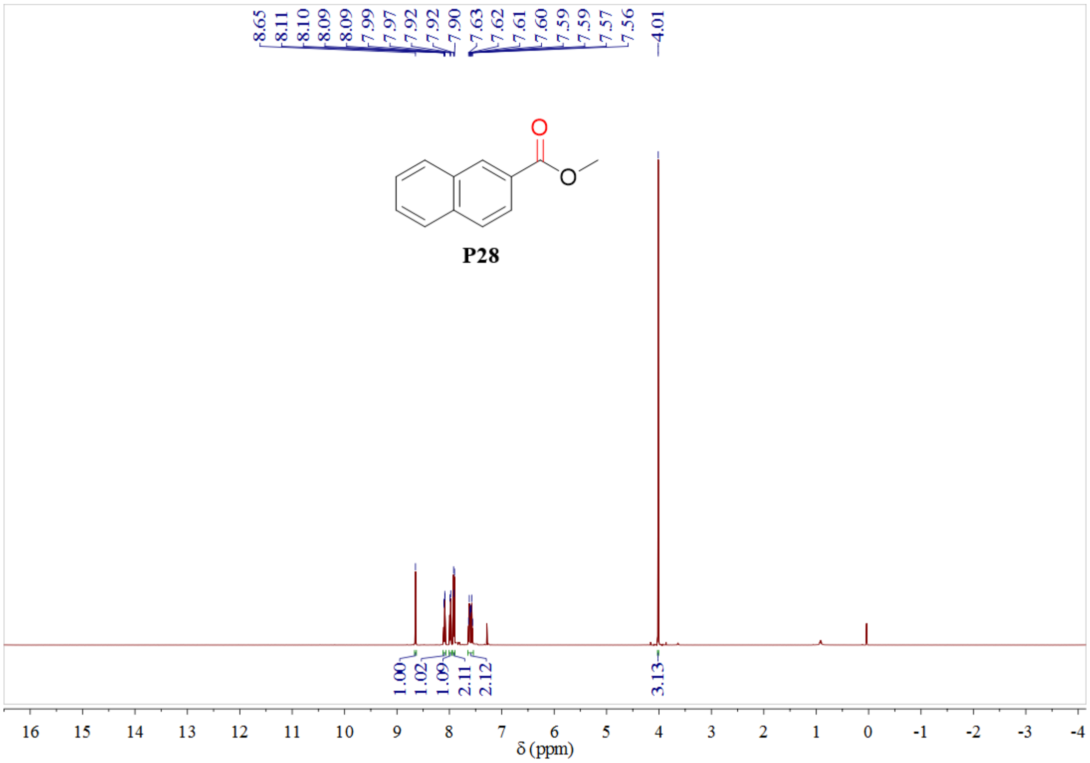
52.4
F3C
O
O
P27
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
δ (ppm)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7.62
7.61
7.60
7.59
7.59
7.57
7.56
4.01
P28
1.00
1.02
1.09
2.11
2.12
3.13
16
15
14
13
12
11
10
9
8
7
6
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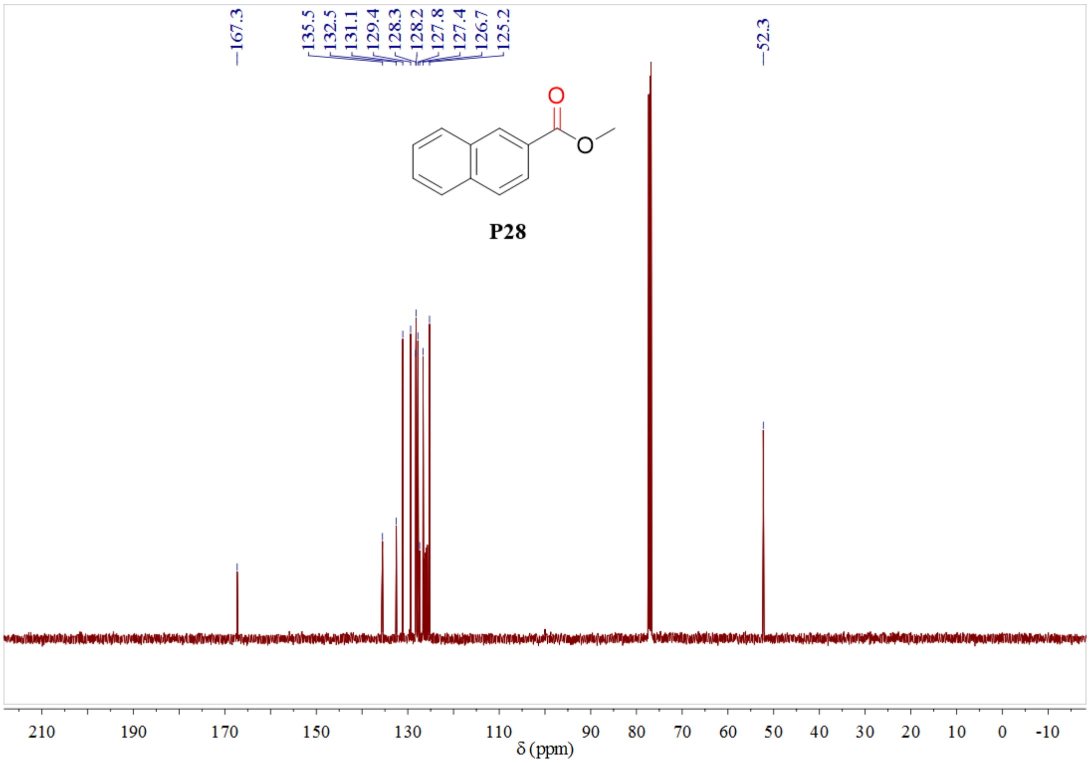
4
3
2
1
0
-1
-2
-3
-4
δ (ppm)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129.4
128.3
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127.8
127.4
126.7
125.2
52.3
P28
210
190
170
150
130
110
90
80
70
60
50
40
30
20
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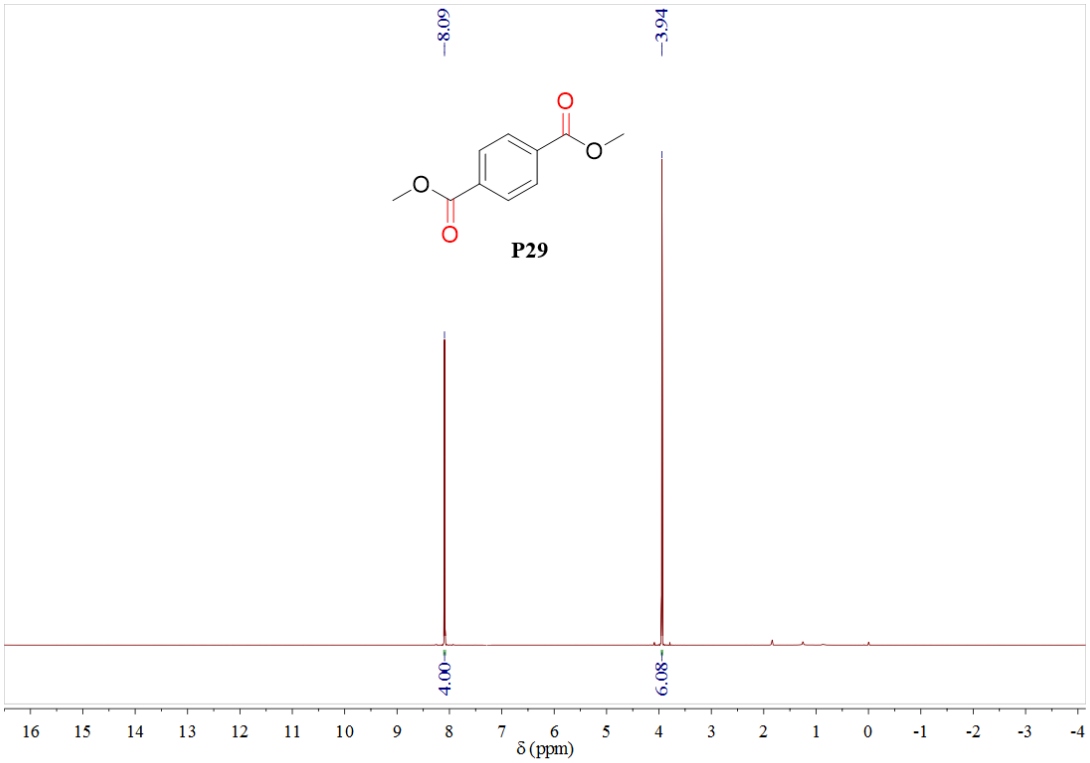
0
-10
δ (ppm)



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O
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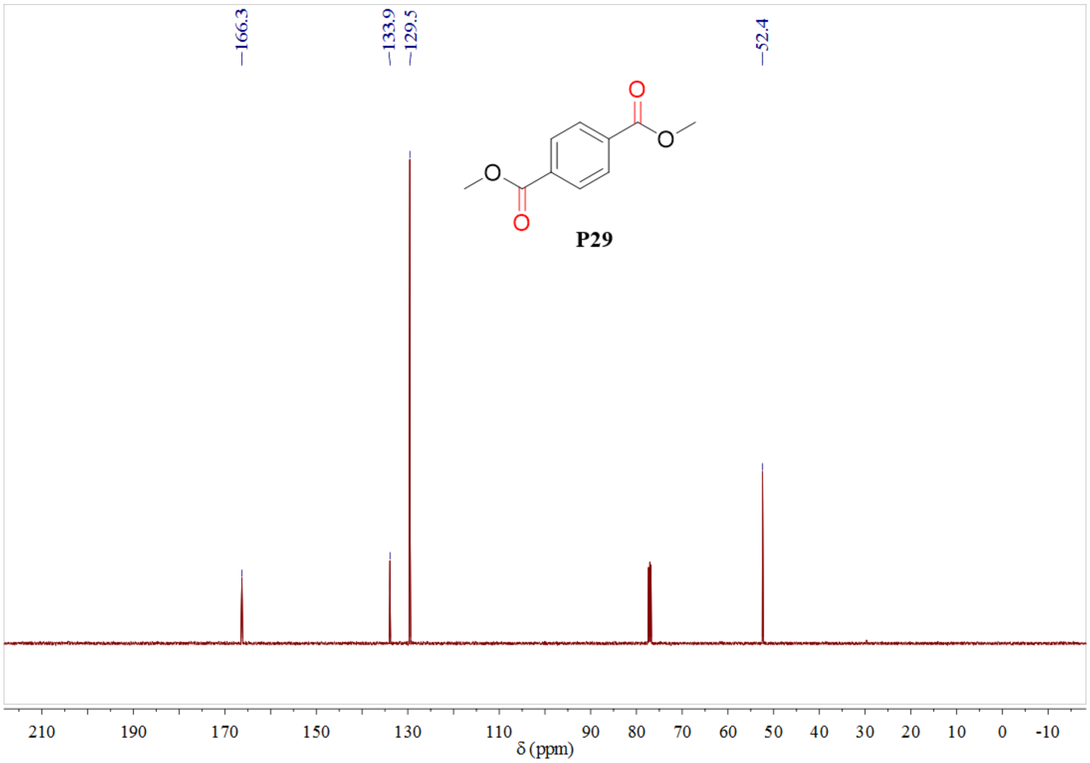
O
P29
4.00
6.08
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
δ (ppm)



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52.4
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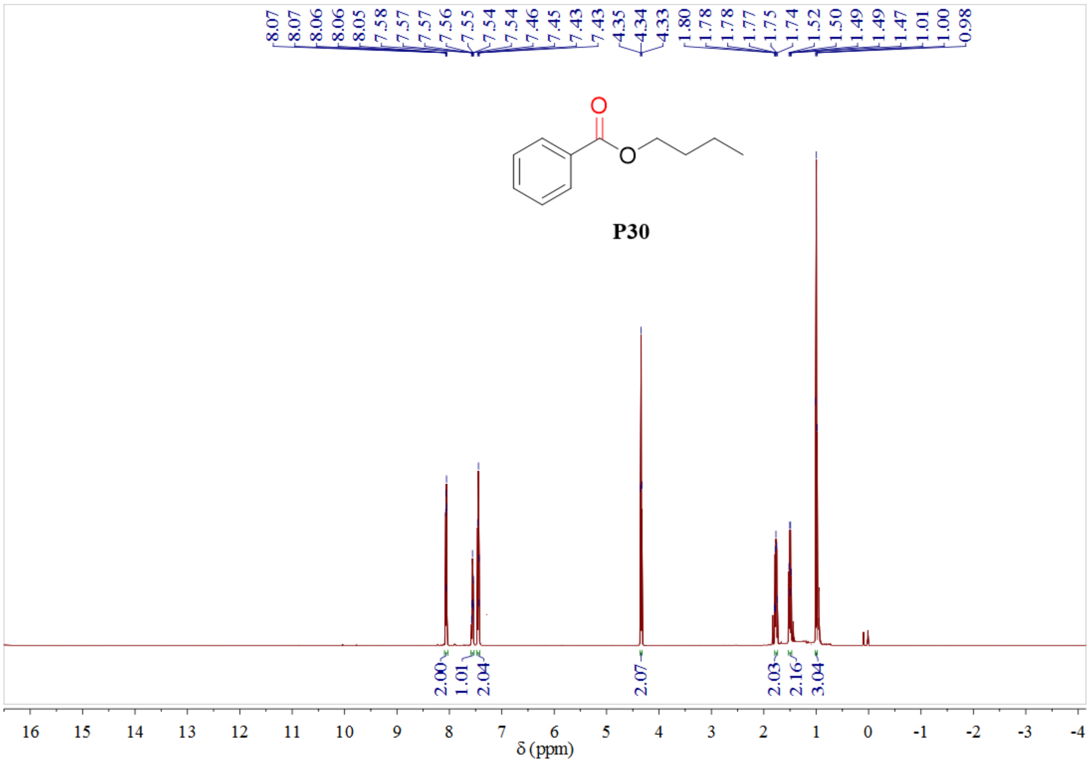
O
O
O
P29
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
δ (ppm)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7.45
7.43
7.43
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4.34
4.33
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1.78
1.78
1.77
1.75
1.74
1.52
1.50
1.49
1.49
1.47
1.01
1.00
0.98
O
O
P30
2.00
1.01
2.04
2.07
2.03
2.16
3.04
16
15
14
13
12
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6
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4
3
2
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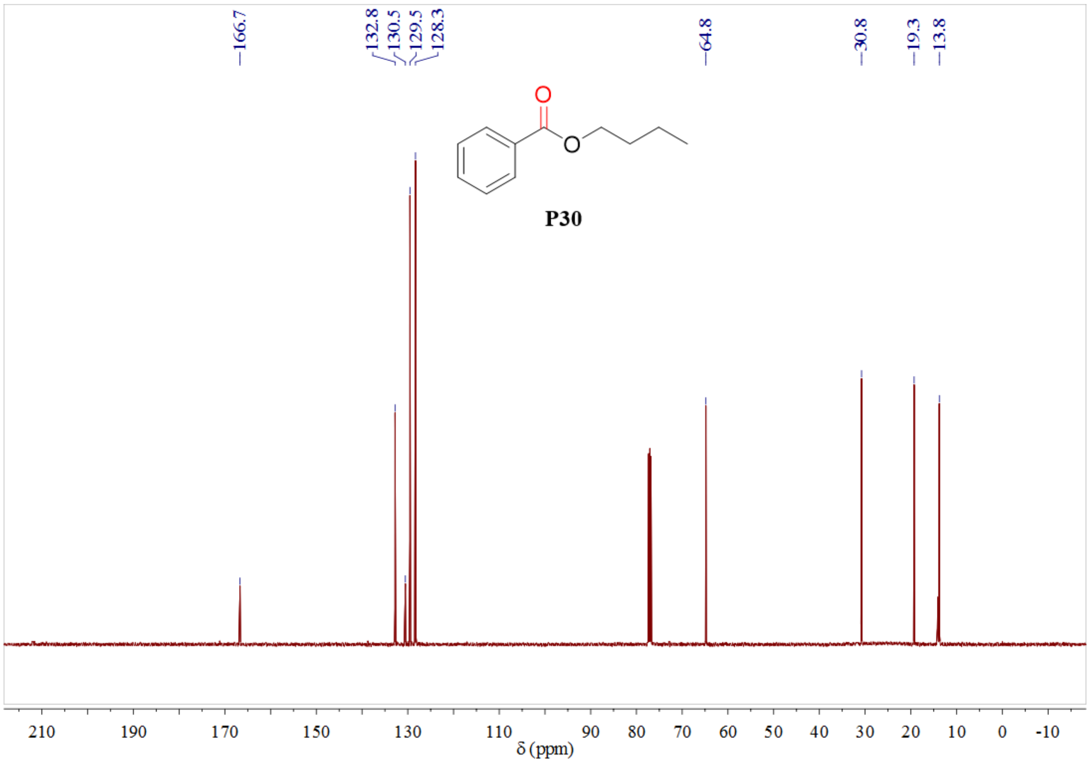
0
-1
-2
-3
-4
δ (ppm)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19.3
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O
O
P30
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150
130
110
90
80
70
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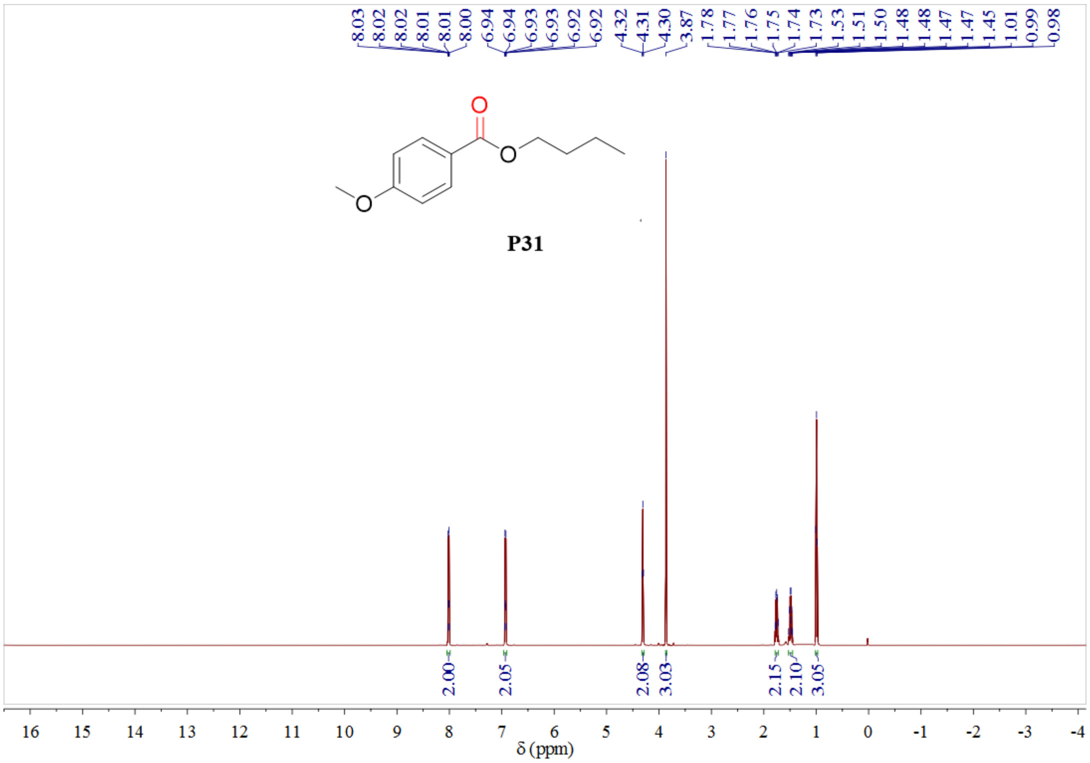
50
40
30
20
10
0
-10
δ (ppm)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6.93
6.93
6.92
6.92
4.32
4.31
4.30
3.87
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1.77
1.76
1.75
1.74
1.73
1.53
1.51
1.50
1.48
1.48
1.47
1.47
1.45
1.01
0.99
0.98
O
O
O
P31
2.00
2.05
2.08
3.03
2.15
2.10
3.05
16
15
14
13
12
11
10
9
8
7
6
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4
3
2
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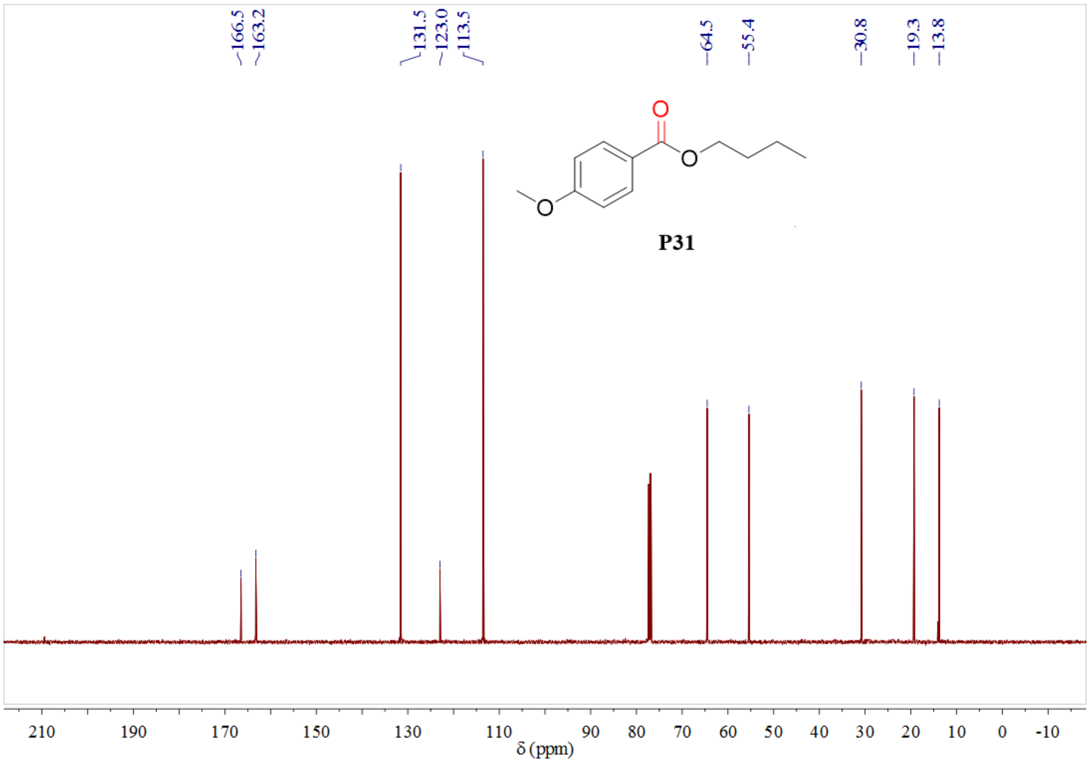
0
-1
-2
-3
-4
δ (ppm)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30.8
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13.8
O
O
O
P31
210
190
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150
130
110
90
80
70
60
50
40
30
20
10
0
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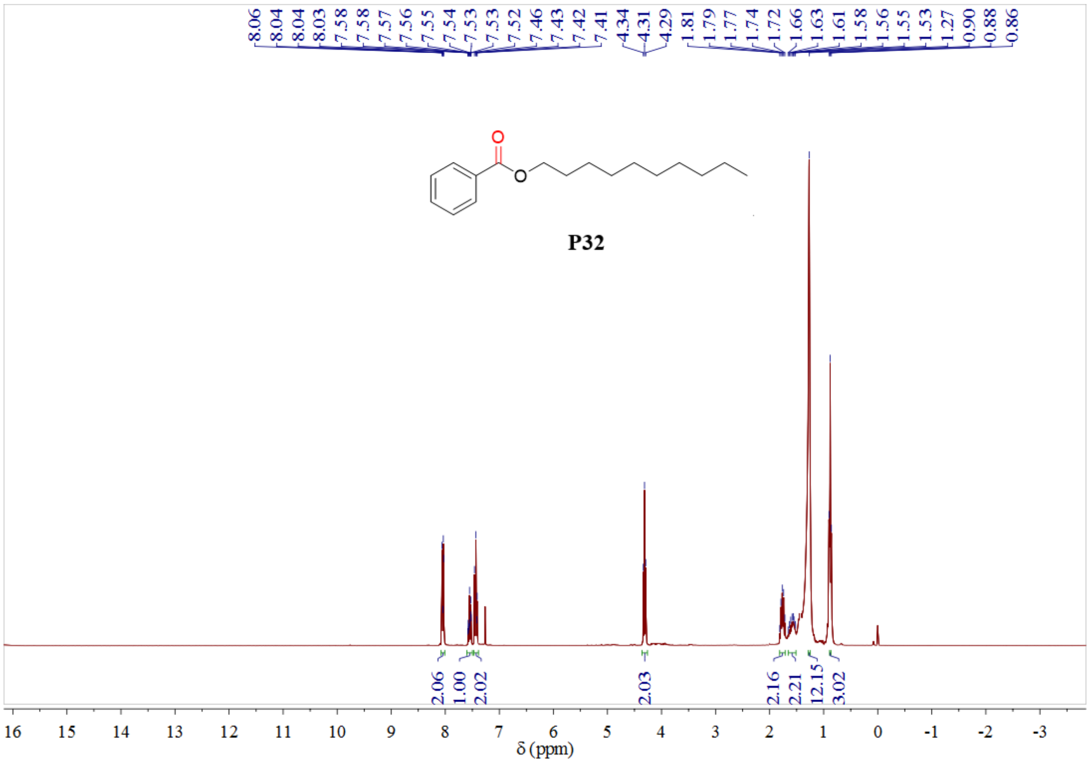
δ (ppm)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8.03
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7.52
7.46
7.43
7.42
7.41
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4.31
4.29
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1.79
1.77
1.74
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1.63
1.61
1.58
1.56
1.55
1.53
1.27
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0.88
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O
O
P32
2.06
1.00
2.02
2.03
2.16
2.21
12.15
3.02
16
15
14
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12
11
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9
8
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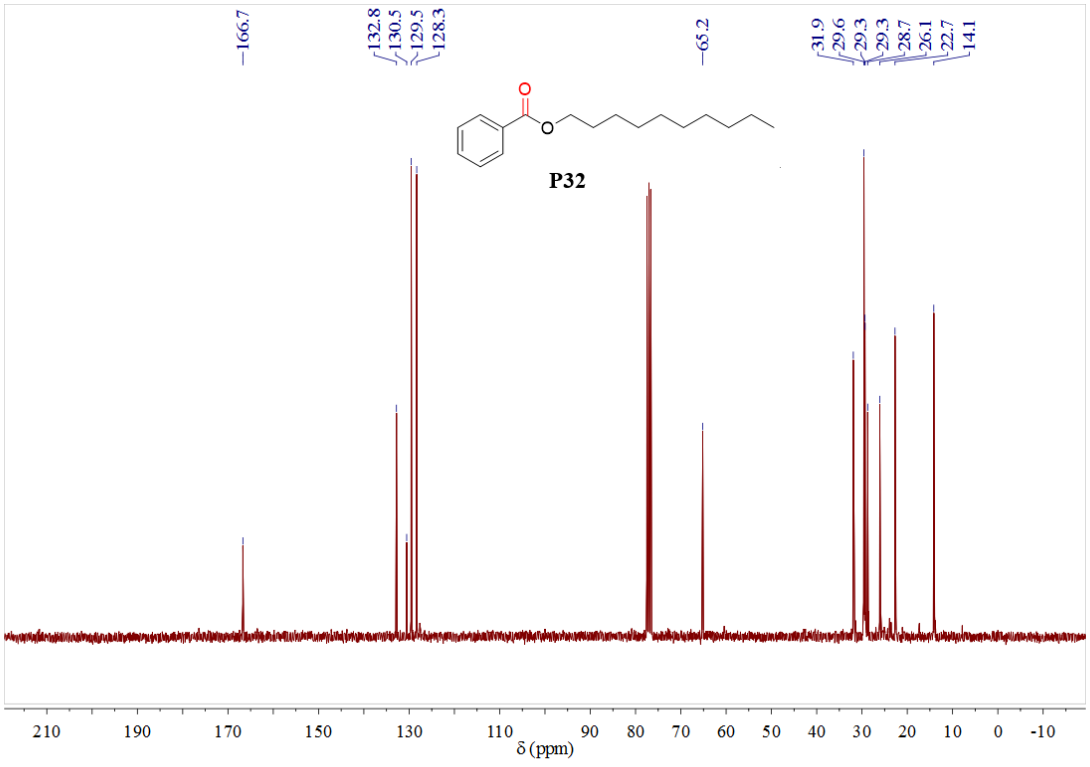
6
5
4
3
2
1
0
-1
-2
-3
δ (ppm)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129.5
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65.2
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29.6
29.3
29.3
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22.7
14.1
O
O
P32
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150
130
110
90
80
70
60
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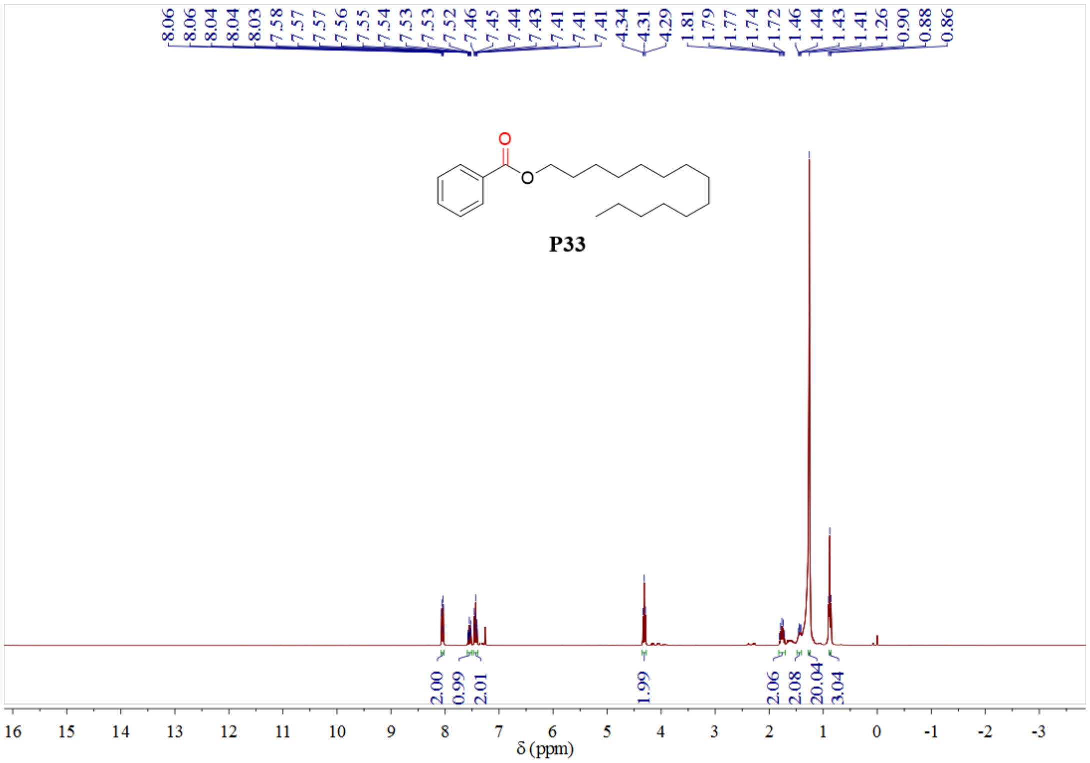
40
30
20
10
0
-10
δ (ppm)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8.06
8.04
8.04
8.03
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7.57
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7.52
7.46
7.45
7.44
7.43
7.41
7.41
7.41
4.34
4.31
4.29
1.81
1.79
1.77
1.74
1.72
1.46
1.44
1.43
1.41
1.26
0.90
0.88
0.86
O
O
P33
2.00
0.99
2.01
1.99
2.06
2.08
20.04
3.04
16
15
14
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12
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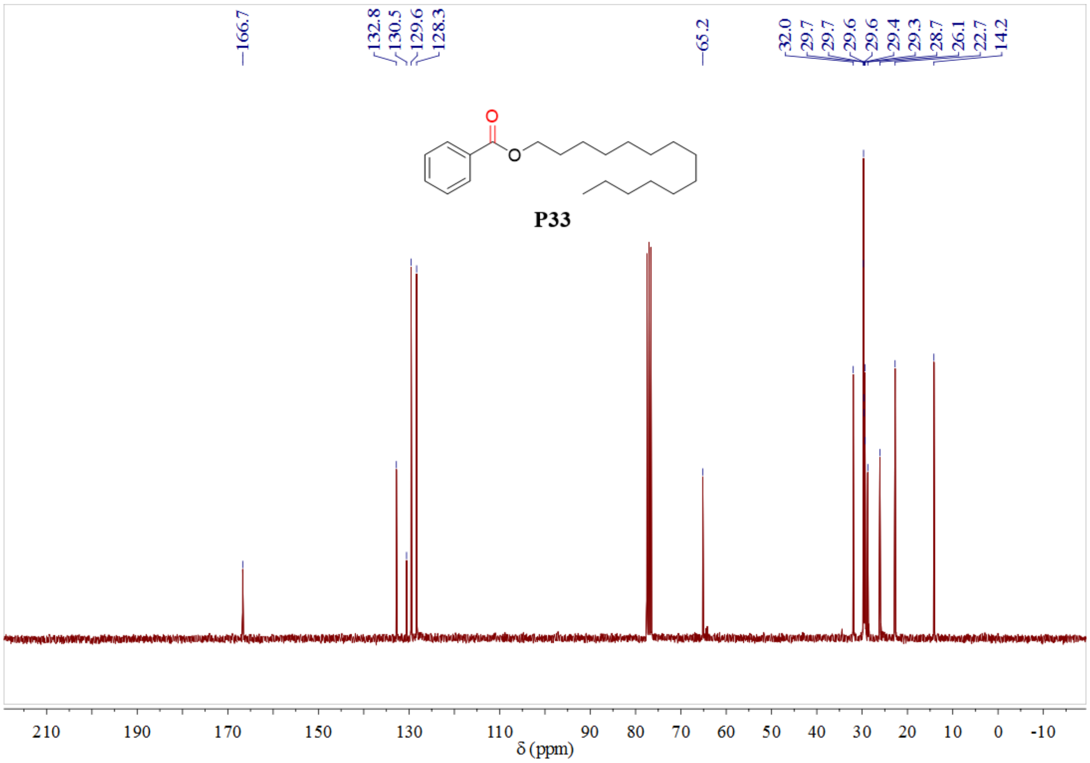
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
δ (ppm)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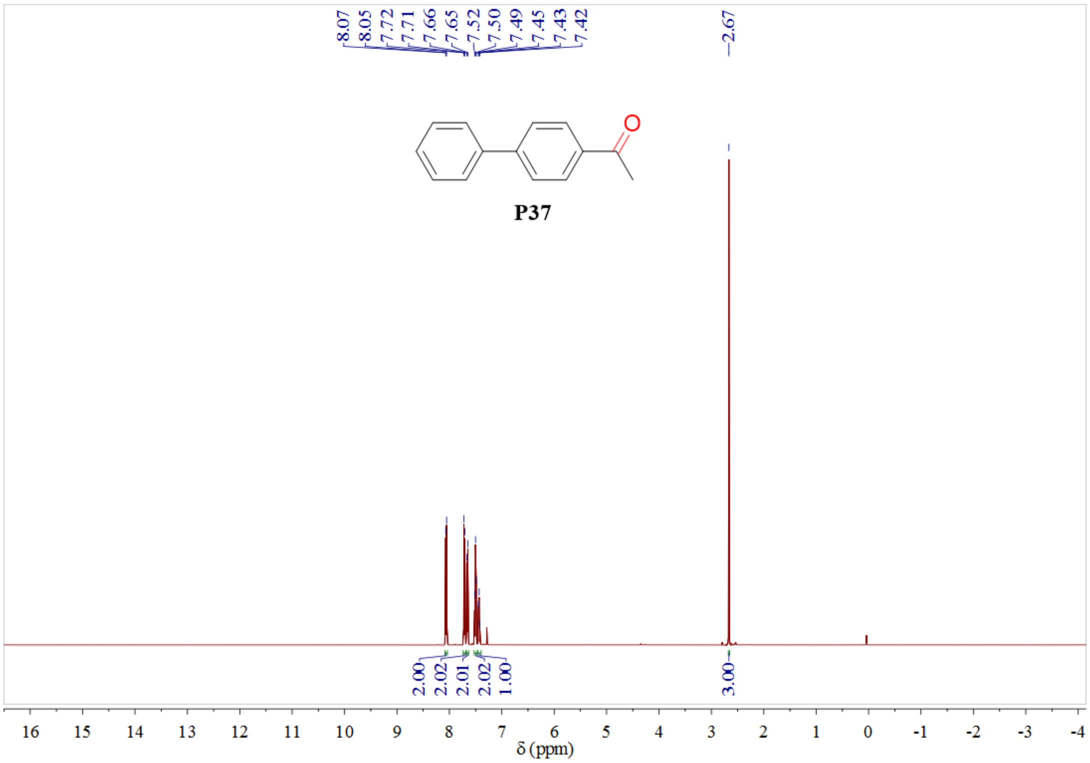
29.3
28.7
26.1
22.7
14.2
O
O
P33
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
δ (ppm)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8.05
7.72
7.71
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7.65
7.52
7.50
7.49
7.45
7.43
7.42
2.67
P37
2.00
2.02
2.01
2.02
1.00
3.00
16
15
14
13
12
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10
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8
7
6
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4
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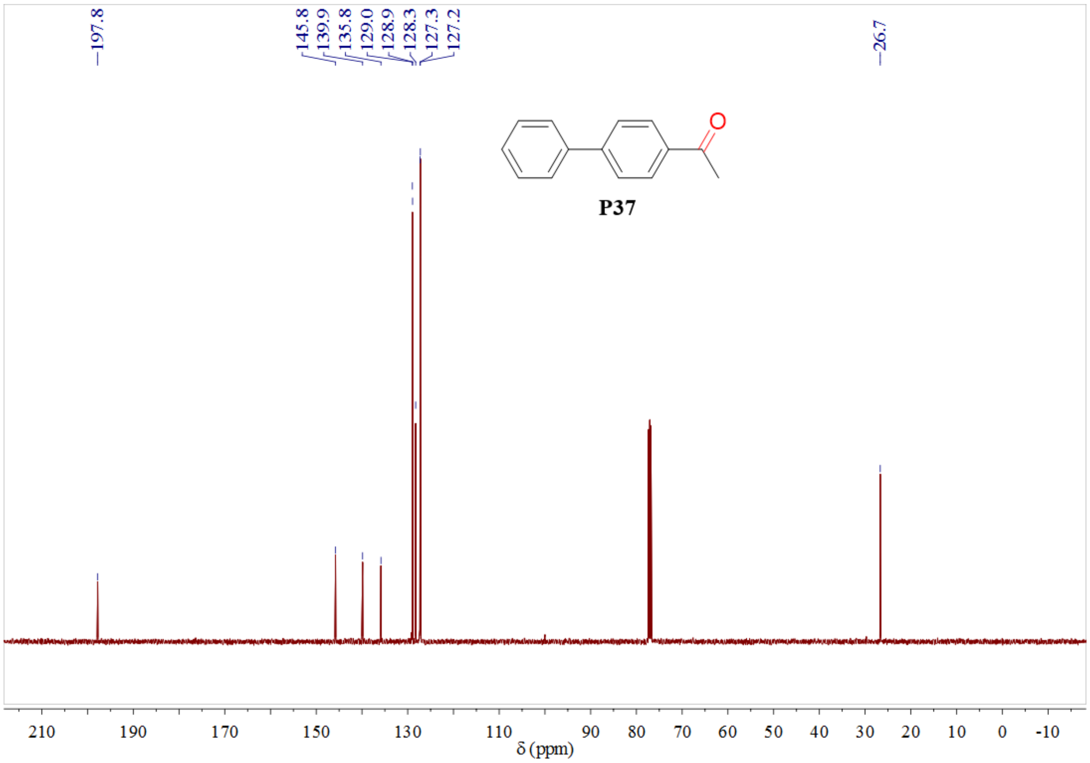
2
1
0
-1
-2
-3
-4
δ (ppm)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139.9
135.8
129.0
128.9
128.3
127.3
127.2
26.7
P37
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190
170
150
130
110
90
80
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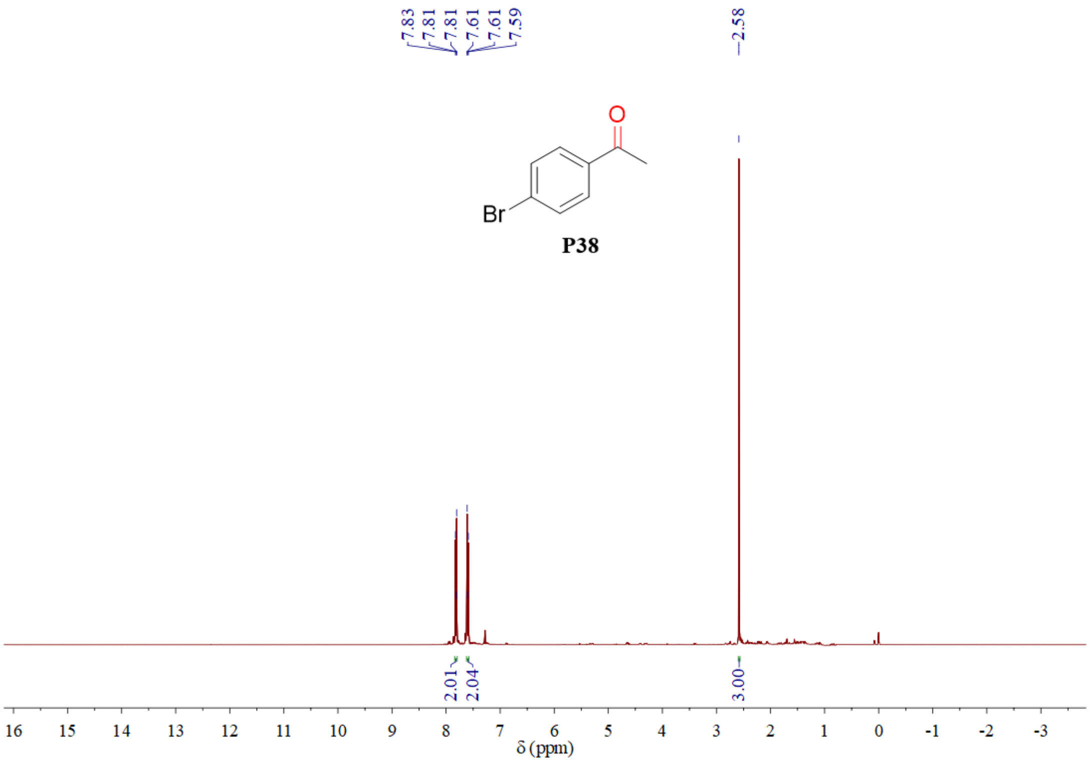
60
50
40
30
20
10
0
-10
δ (ppm)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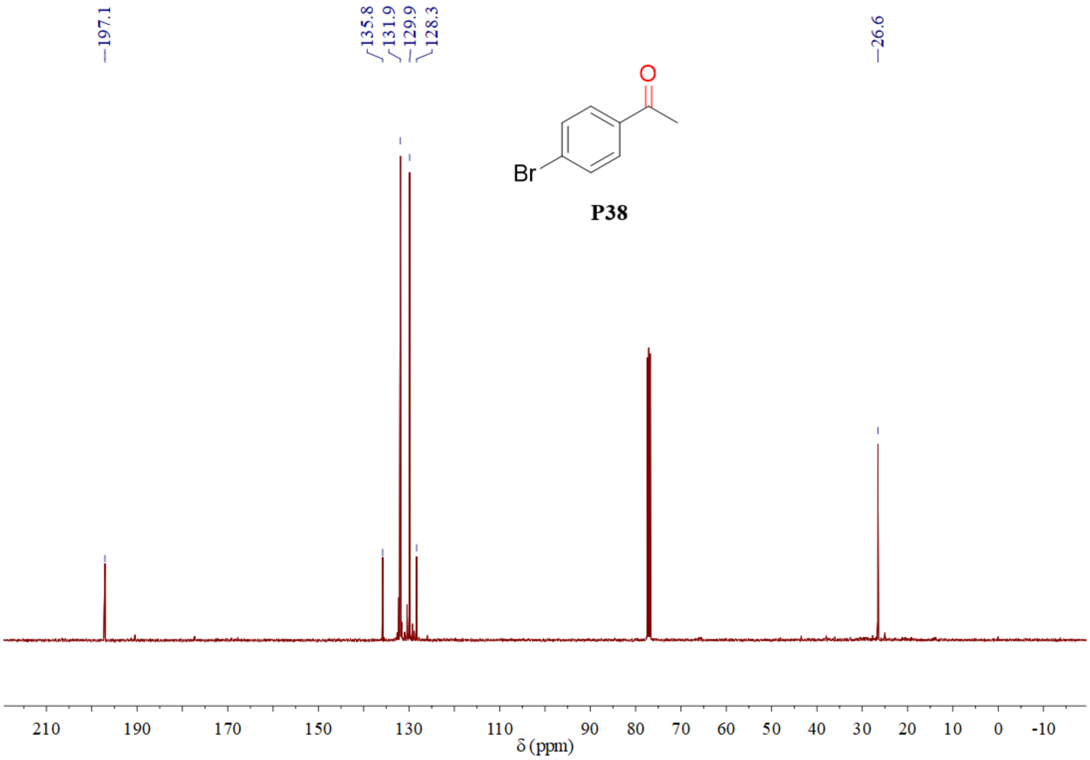
7.81
7.81
7.61
7.61
7.59
2.58
O
Br
P38
2.01
2.04
3.00
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
δ (ppm)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129.9
128.3
26.6
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Br
P38
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150
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110
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80
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60
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30
20
10
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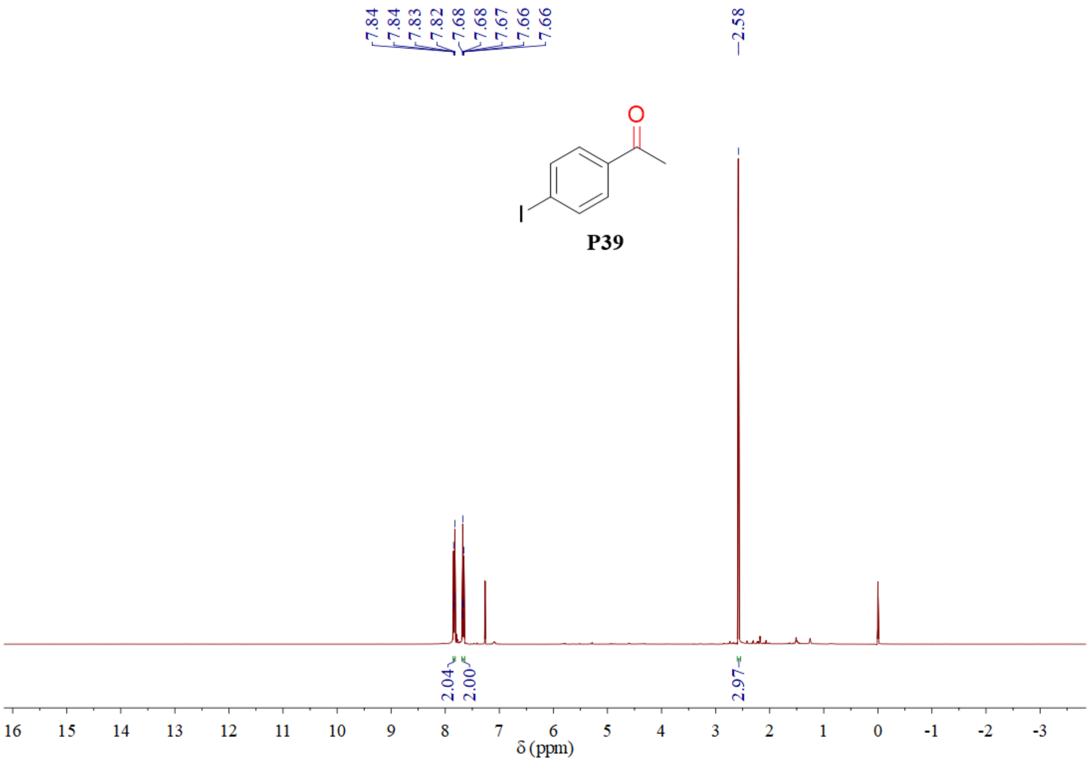
-10
δ (ppm)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7.84
7.83
7.82
7.68
7.68
7.67
7.66
7.66
2.58
O
I
P39
2.04
2.00
2.97
16
15
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12
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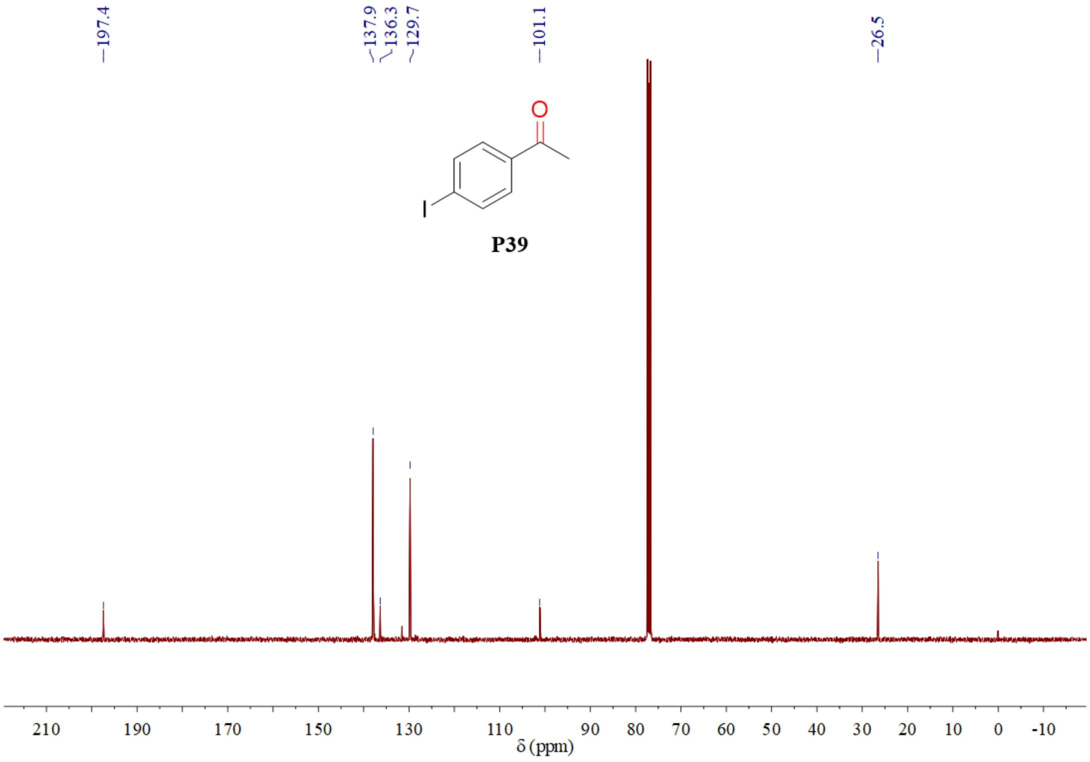
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
δ (ppm)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136.3
129.7
101.1
26.5
O
I
P39
210
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150
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50
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30
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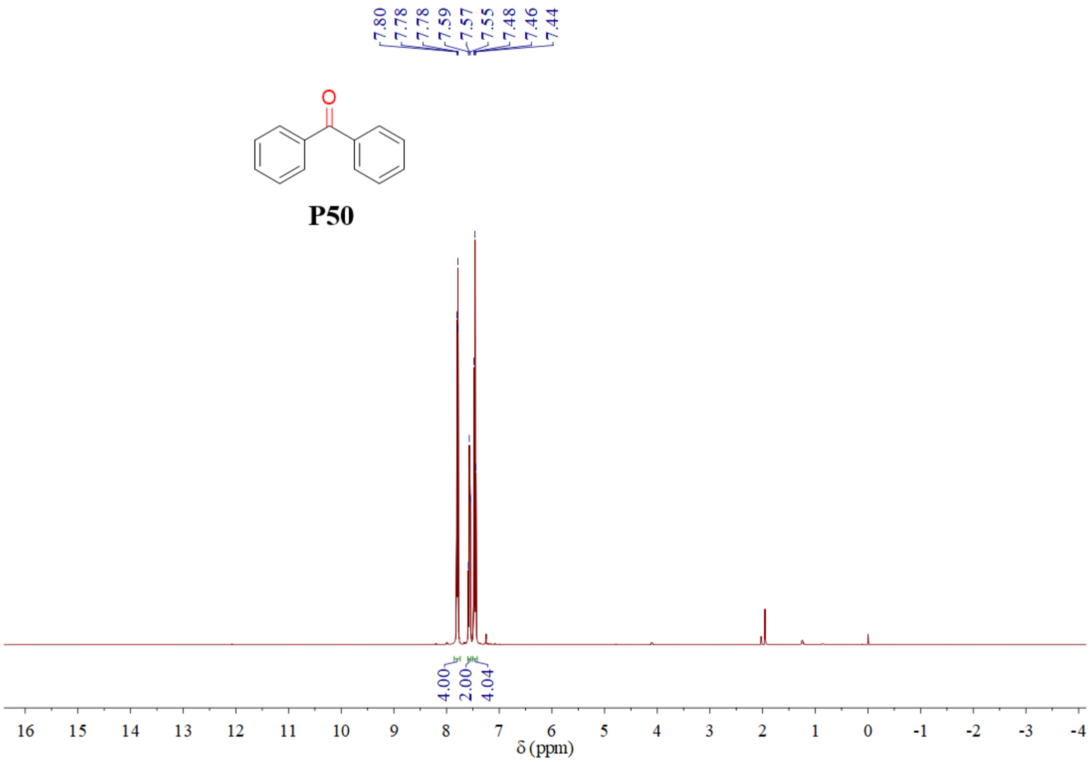
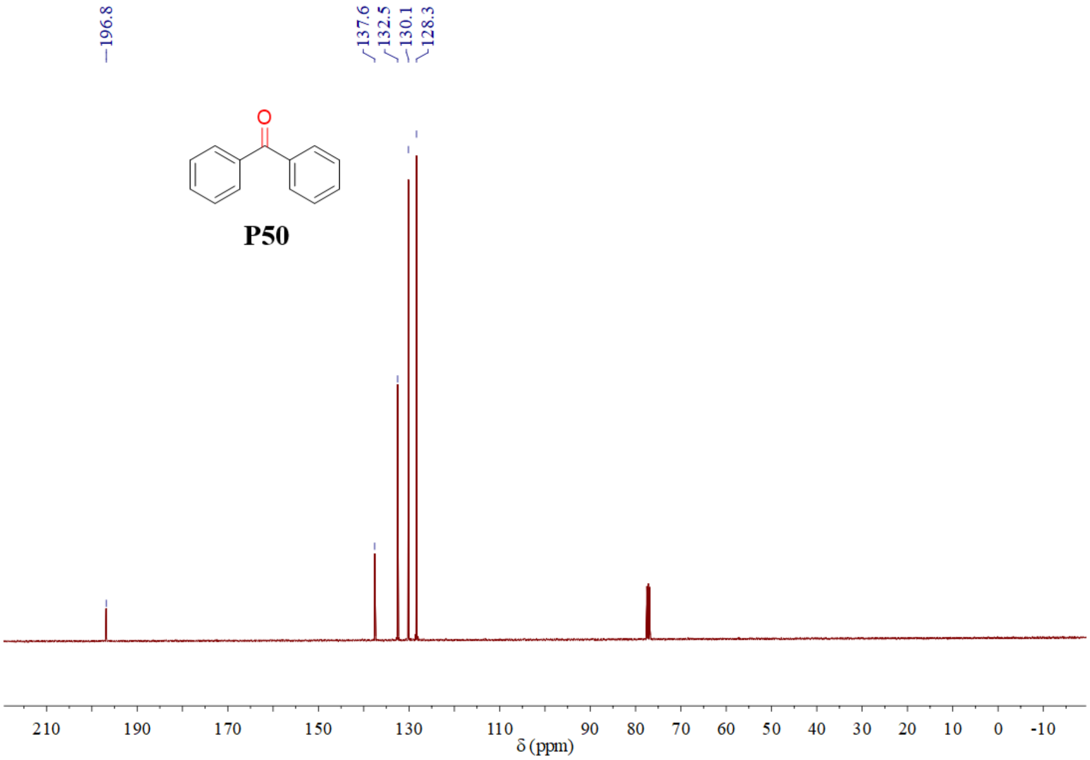
δ (ppm)


7.80
7.78
7.78
7.59
7.57
7.55
7.48
7.46
7.44
O
P50
4.00
2.00
4.04
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
-4
δ (ppm)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137.6
132.5
130.1
128.3
O
P50
210
190
170
150
130
110
90
80
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60
50
40
30
20
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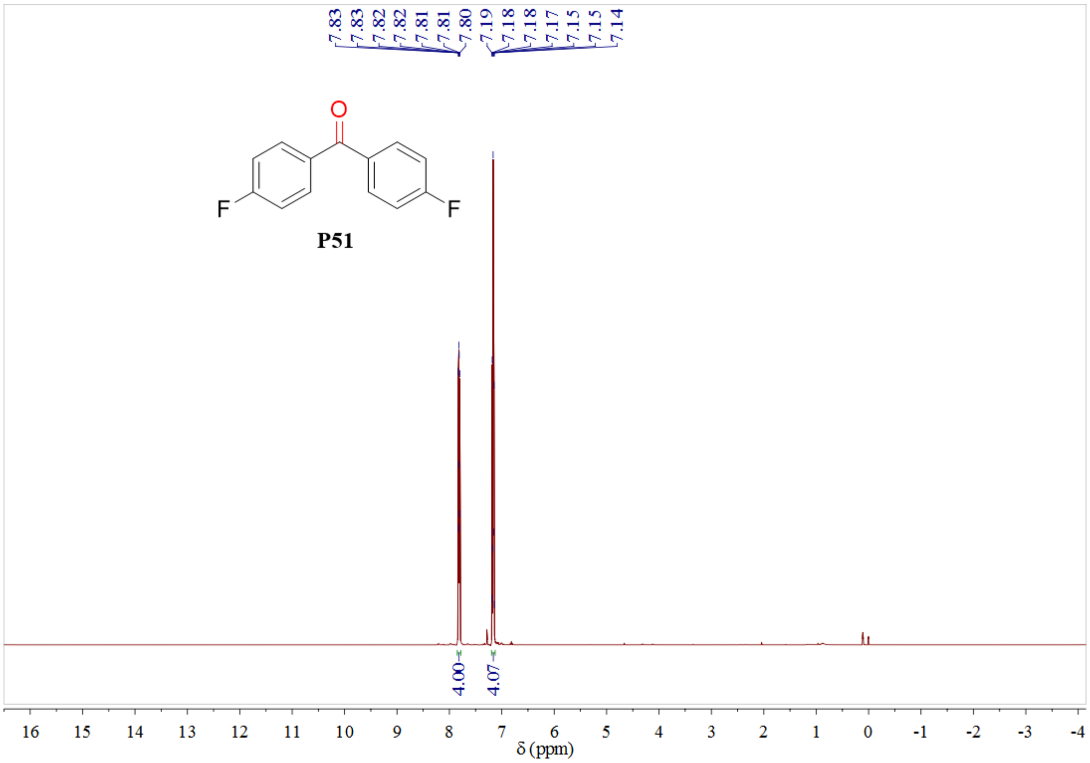
0
-10
δ (ppm)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7.82
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7.81
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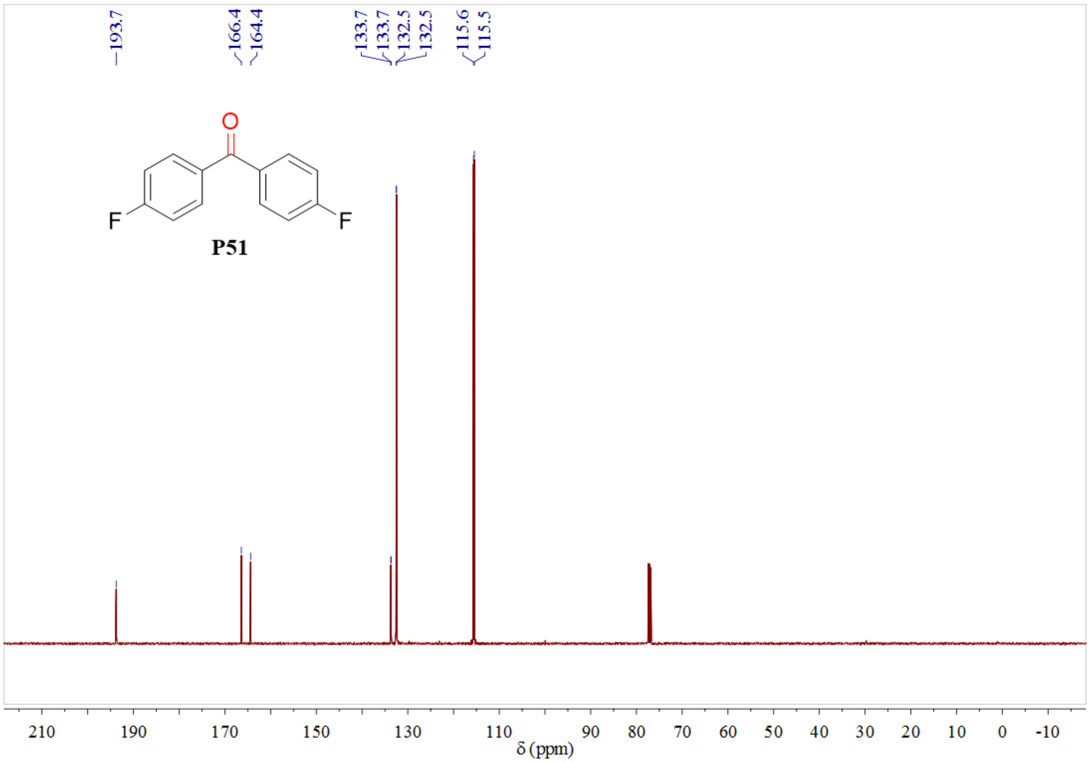
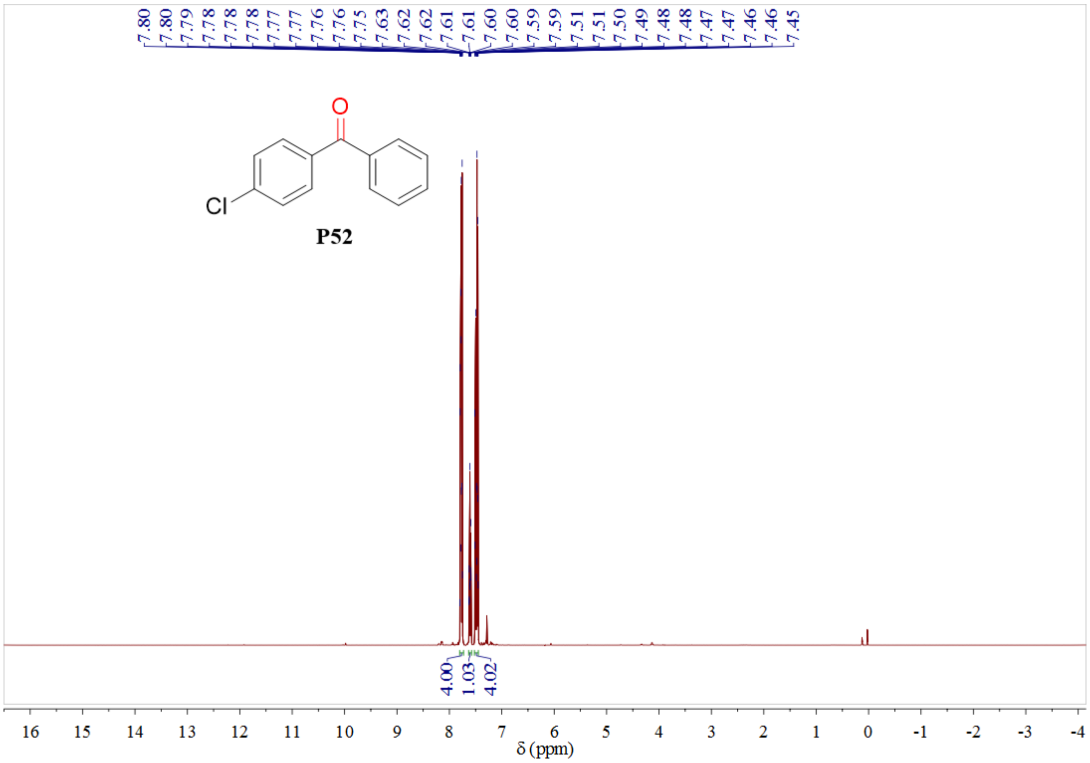
7.18
7.17
7.15
7.15
7.14
O
F
F
P51
4.00
4.07
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
-4
δ (ppm)


193.7
166.4
164.4
133.7
133.7
132.5
132.5
115.6
115.5
O
F
F
P51
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
δ (ppm)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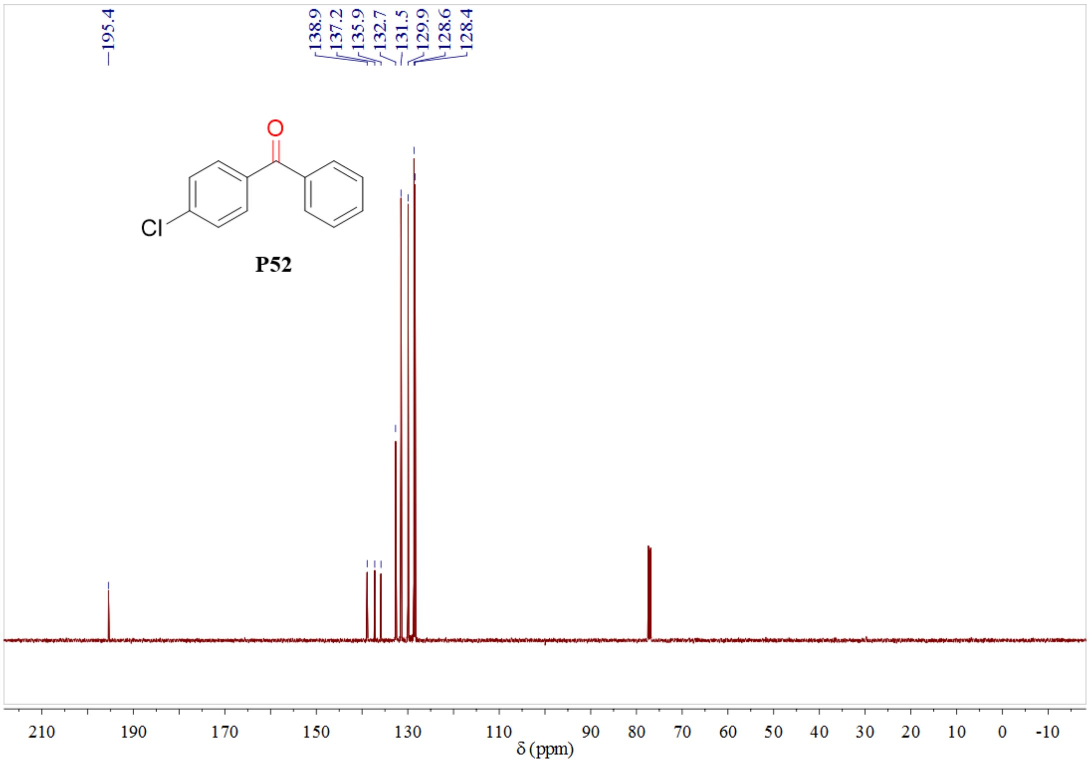
7.75
7.63
7.62
7.62
7.61
7.61
7.60
7.60
7.59
7.59
7.51
7.51
7.50
7.49
7.48
7.48
7.47
7.47
7.46
7.46
7.45
O
Cl
P52
4.00
1.03
4.02
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
-4
δ (ppm)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138.9
137.2
135.9
132.7
131.5
129.9
128.6
128.4
O
Cl
P52
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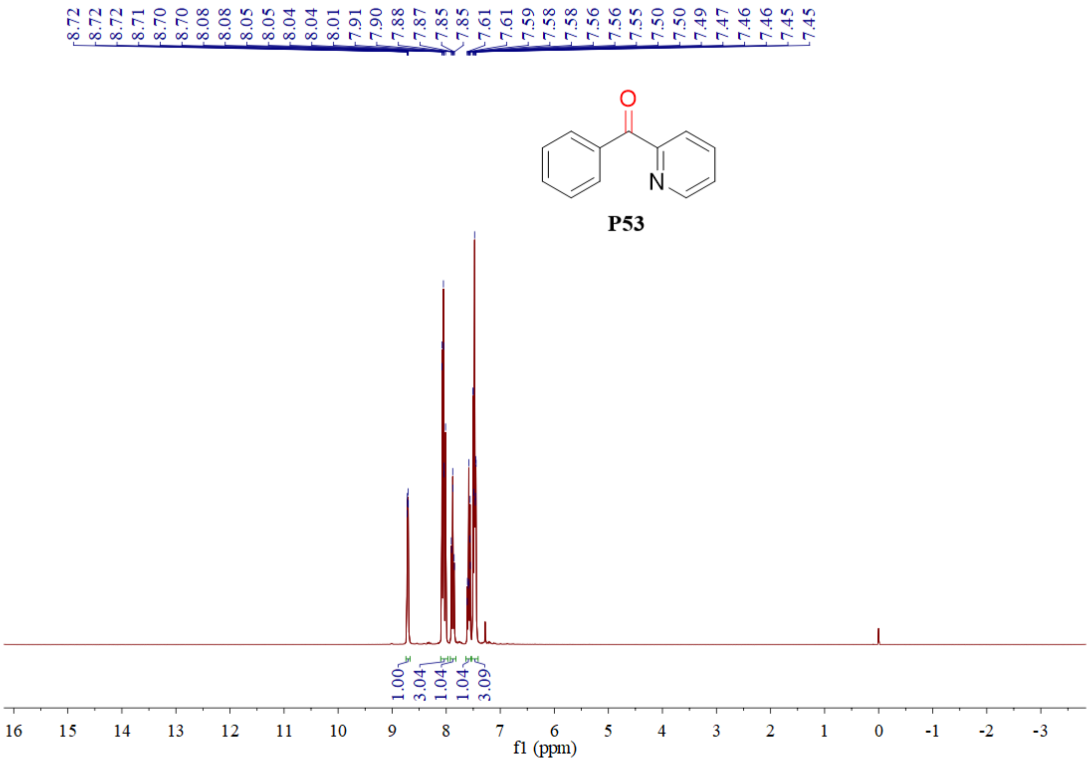
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
δ (ppm)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8.70
8.08
8.08
8.05
8.05
8.04
8.04
8.01
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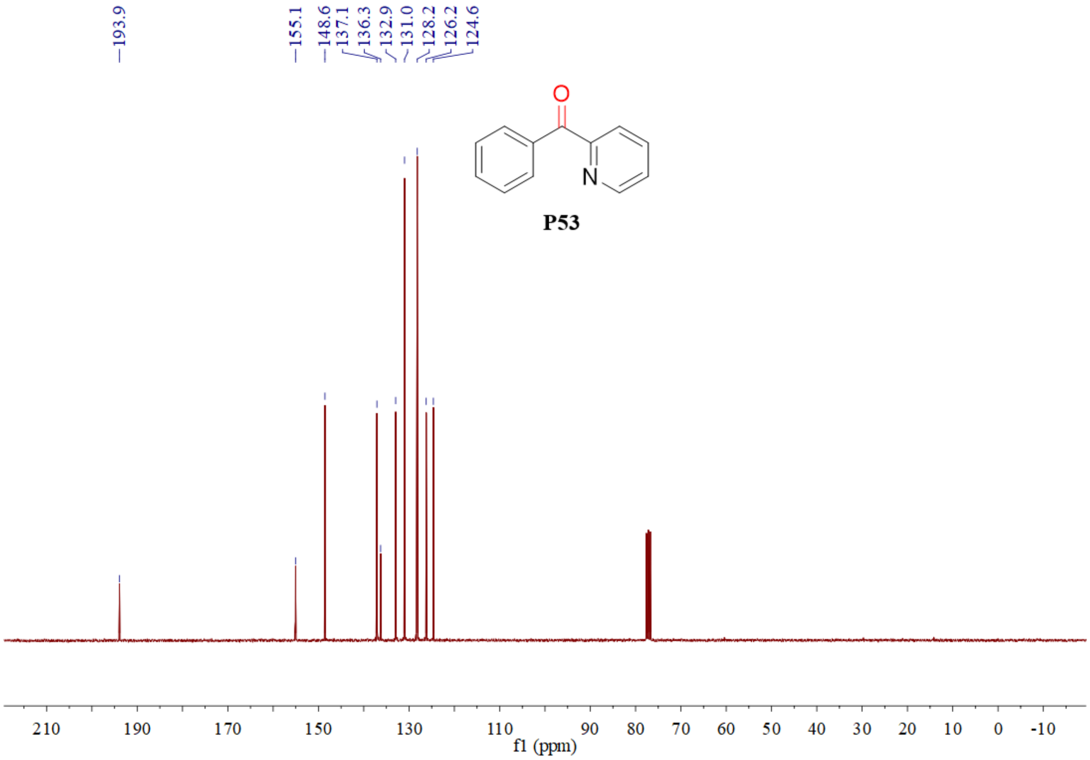
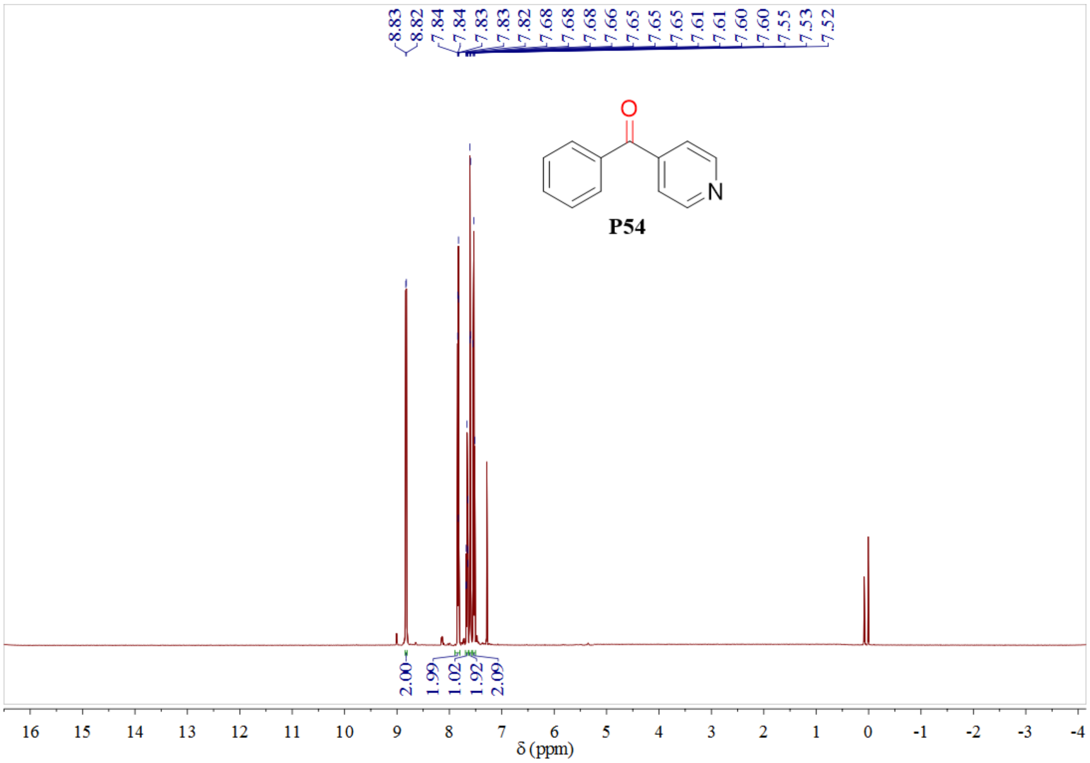
7.90
7.88
7.87
7.85
7.85
7.61
7.61
7.59
7.58
7.58
7.56
7.56
7.55
7.50
7.50
7.49
7.47
7.46
7.46
7.45
7.45
O
N
P53
1.00
3.04
1.04
1.04
3.09
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)


193.9
155.1
148.6
137.1
136.3
132.9
131.0
128.2
126.2
124.6
O
N
P53
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.84
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7.82
7.68
7.68
7.68
7.66
7.65
7.65
7.65
7.61
7.61
7.60
7.60
7.55
7.53
7.52
O
N
P54
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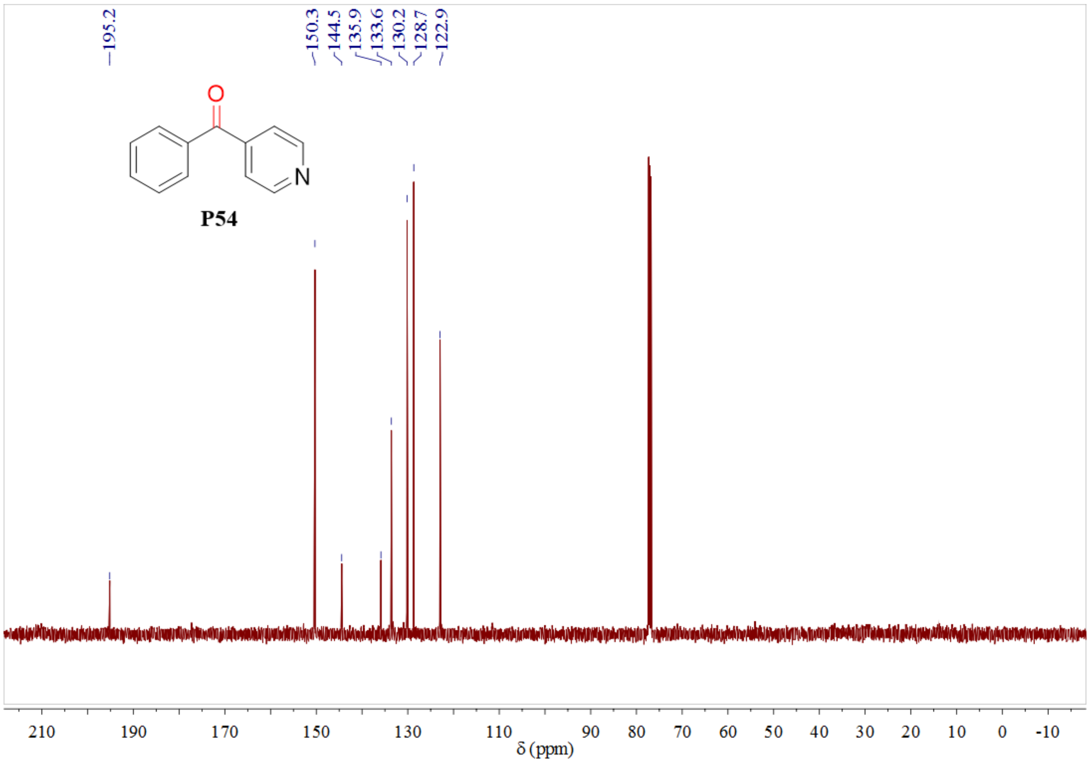
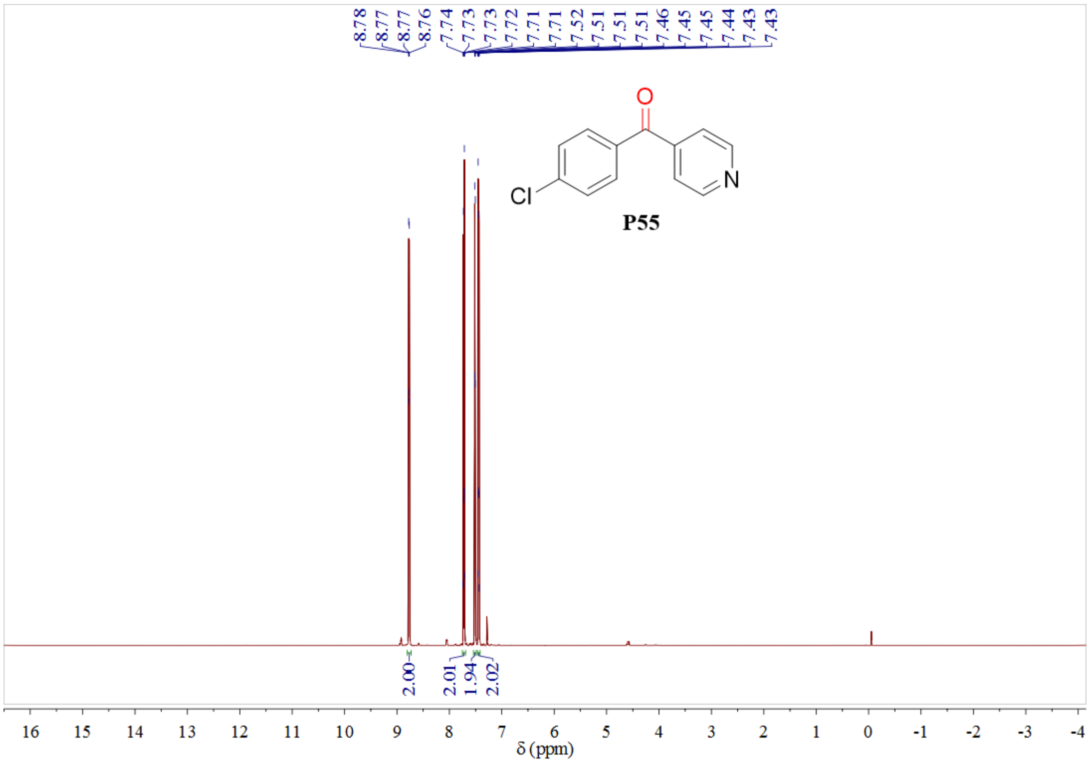
1.99
1.02
1.92
2.09
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
δ (ppm)


195.2
150.3
144.5
135.9
133.6
130.2
128.7
122.9
O
N
P54
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
δ (ppm)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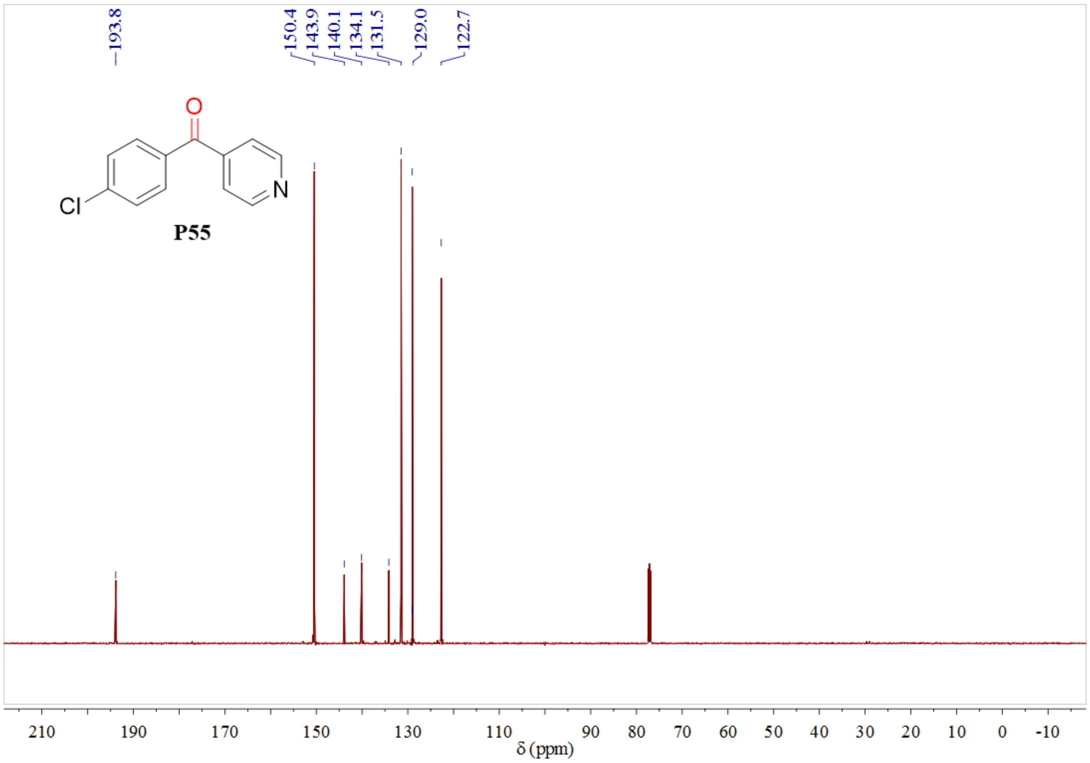
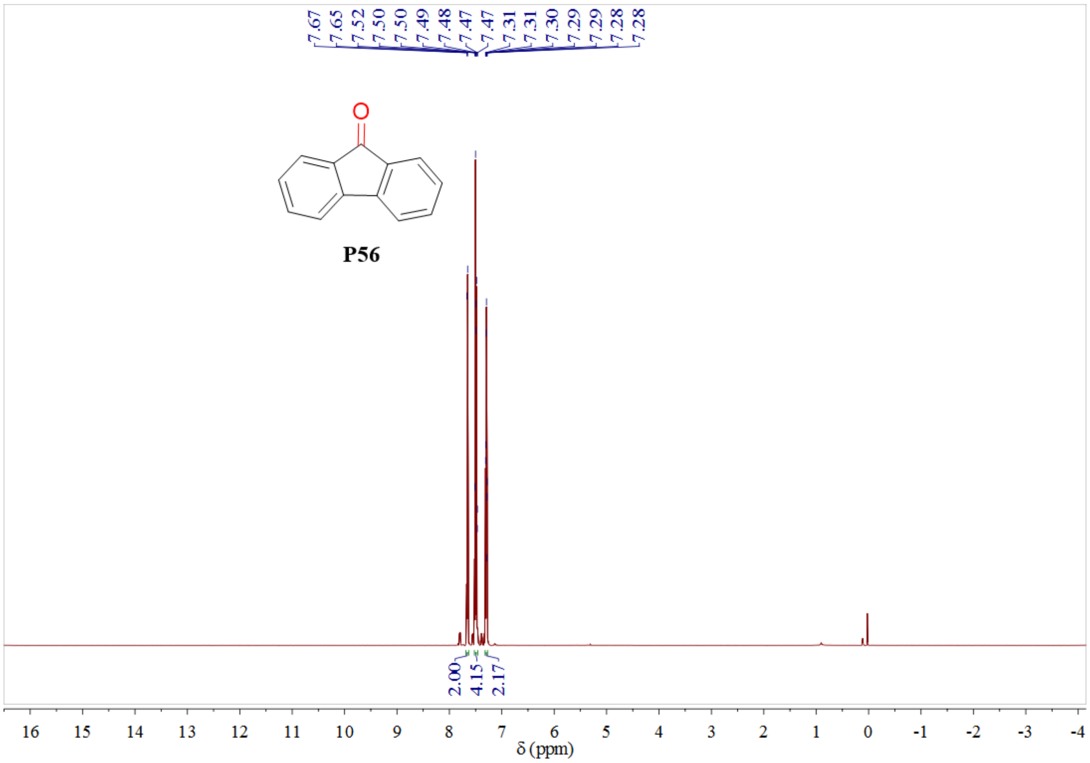
7.73
7.73
7.72
7.71
7.71
7.52
7.51
7.51
7.51
7.46
7.45
7.45
7.44
7.43
7.43
O
Cl
N
P55
2.00
2.01
1.94
2.02
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
-4
δ (ppm)


193.8
150.4
143.9
140.1
134.1
131.5
129.0
122.7
O
Cl
N
P55
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
δ (ppm)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7.52
7.50
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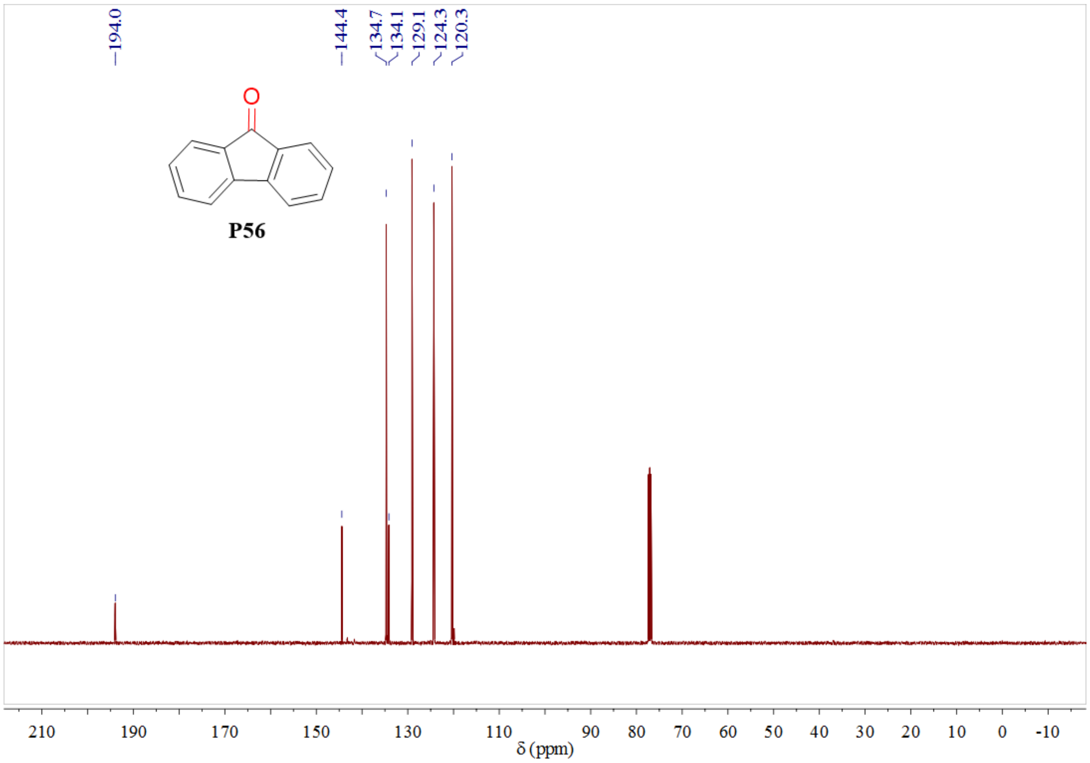
7.49
7.48
7.47
7.47
7.31
7.31
7.30
7.29
7.29
7.28
7.28
P56
2.00
4.15
2.17
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
δ (ppm)


194.0
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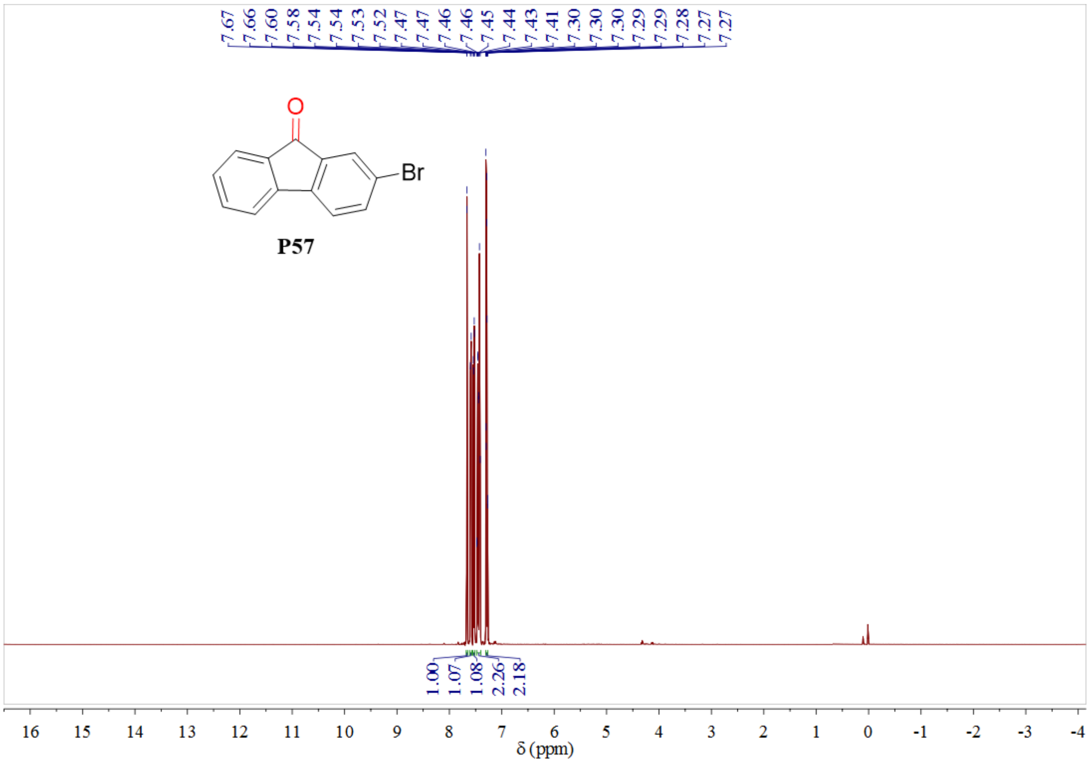
134.7
134.1
129.1
124.3
120.3
P56
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
δ (ppm)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7.52
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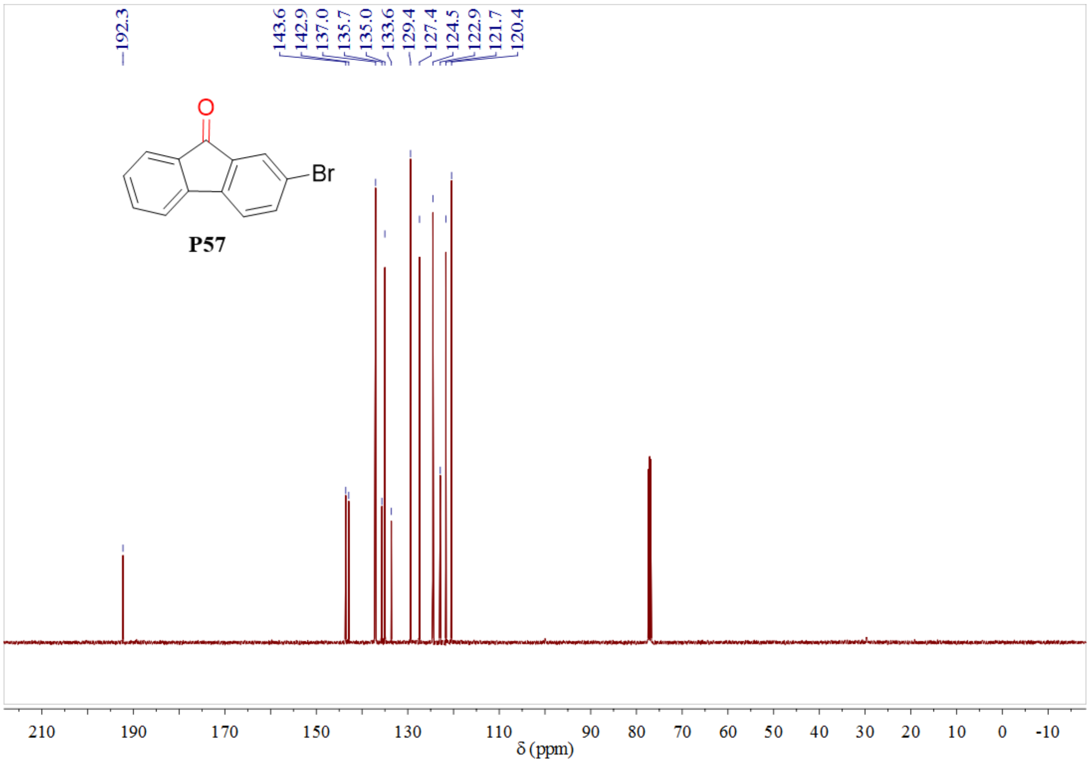
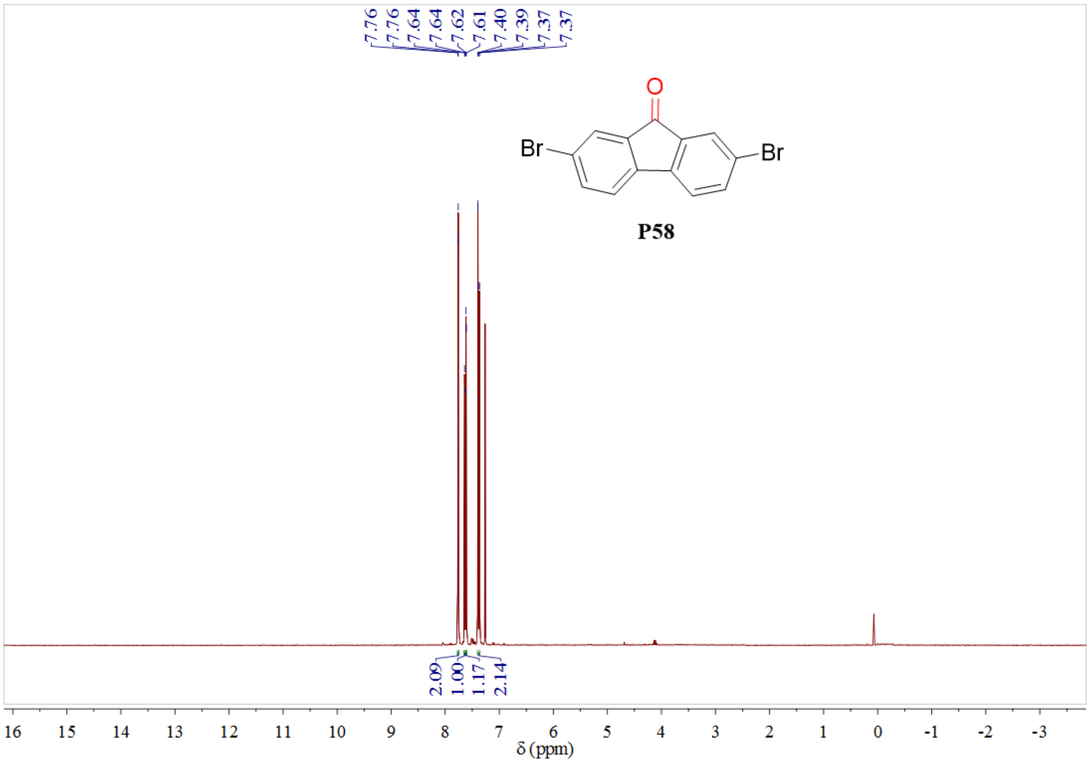
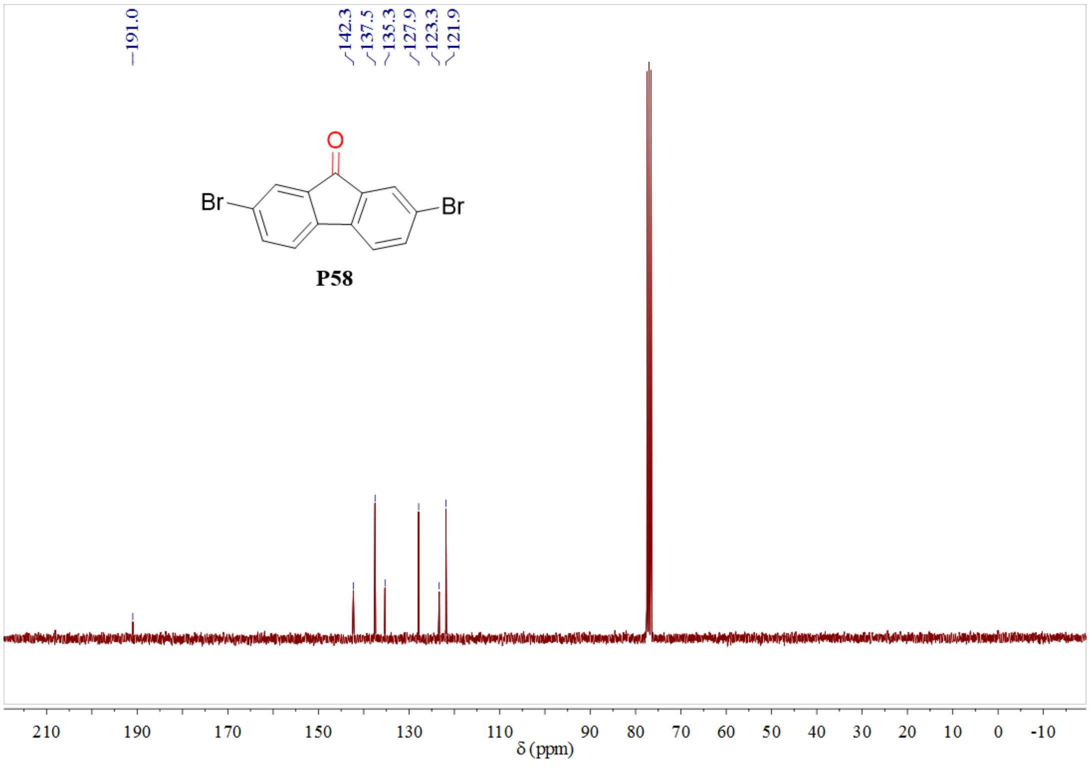
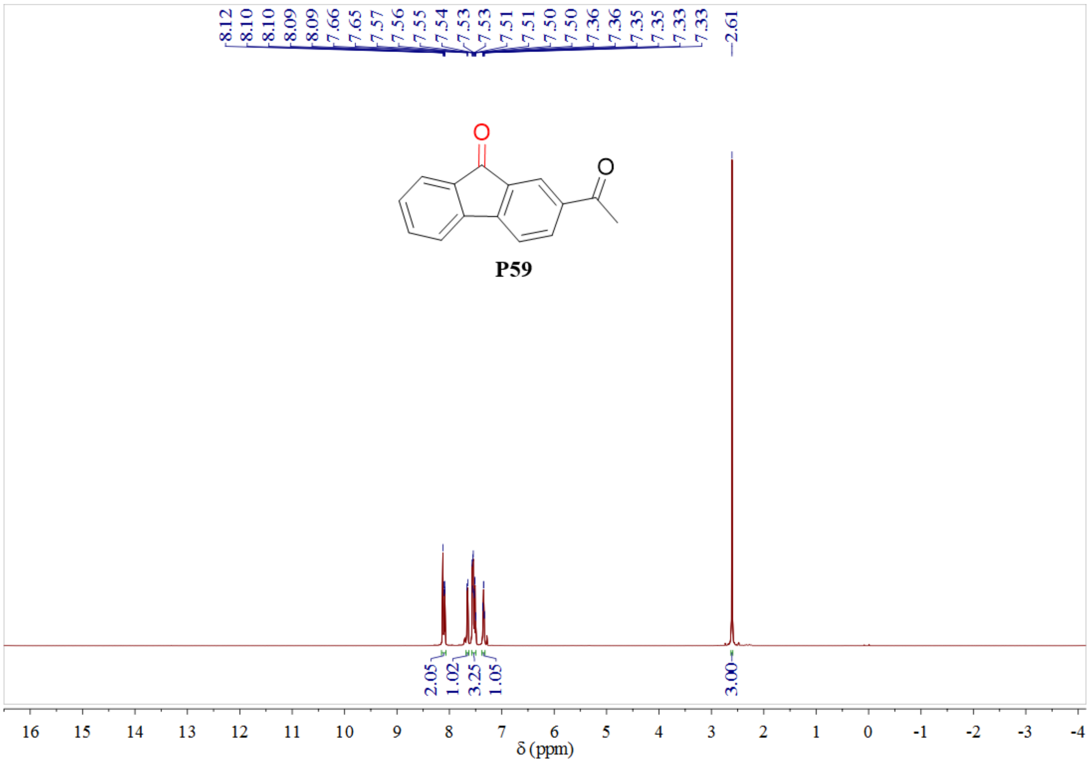
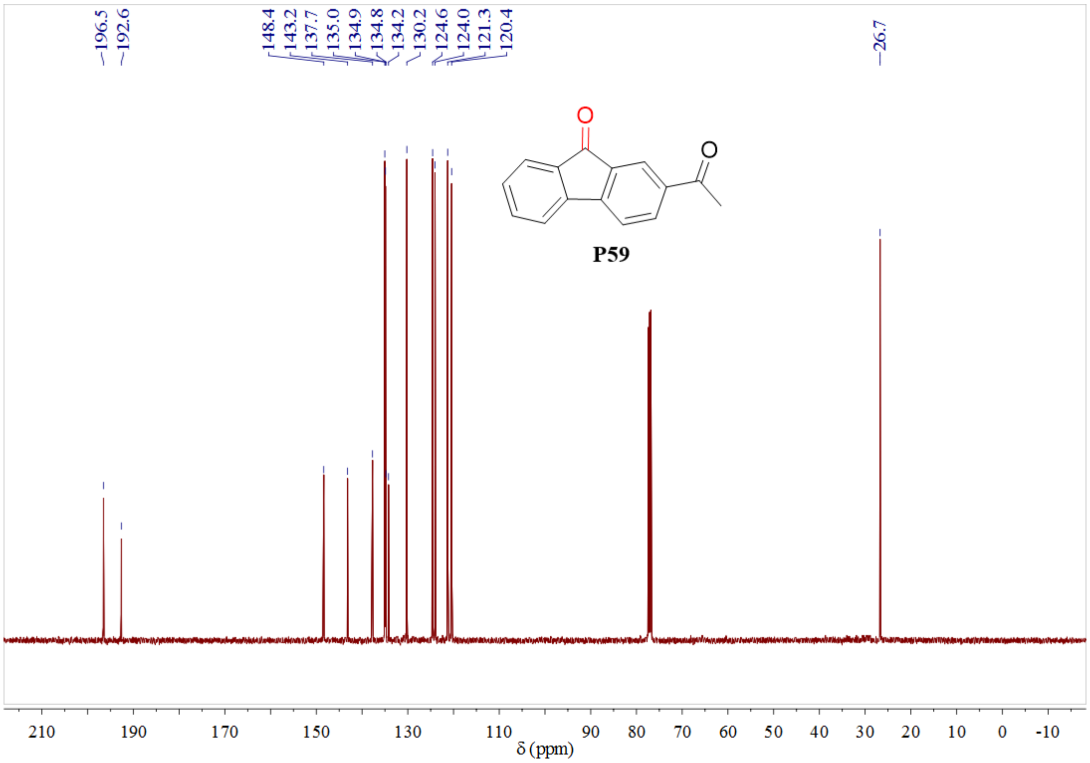
7.47
7.46
7.46
7.45
7.44
7.43
7.41
7.30
7.30
7.29
7.29
7.28
7.27
7.27
O
Br
P57
1.00
1.07
1.08
2.26
2.18
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
-4
δ (ppm)

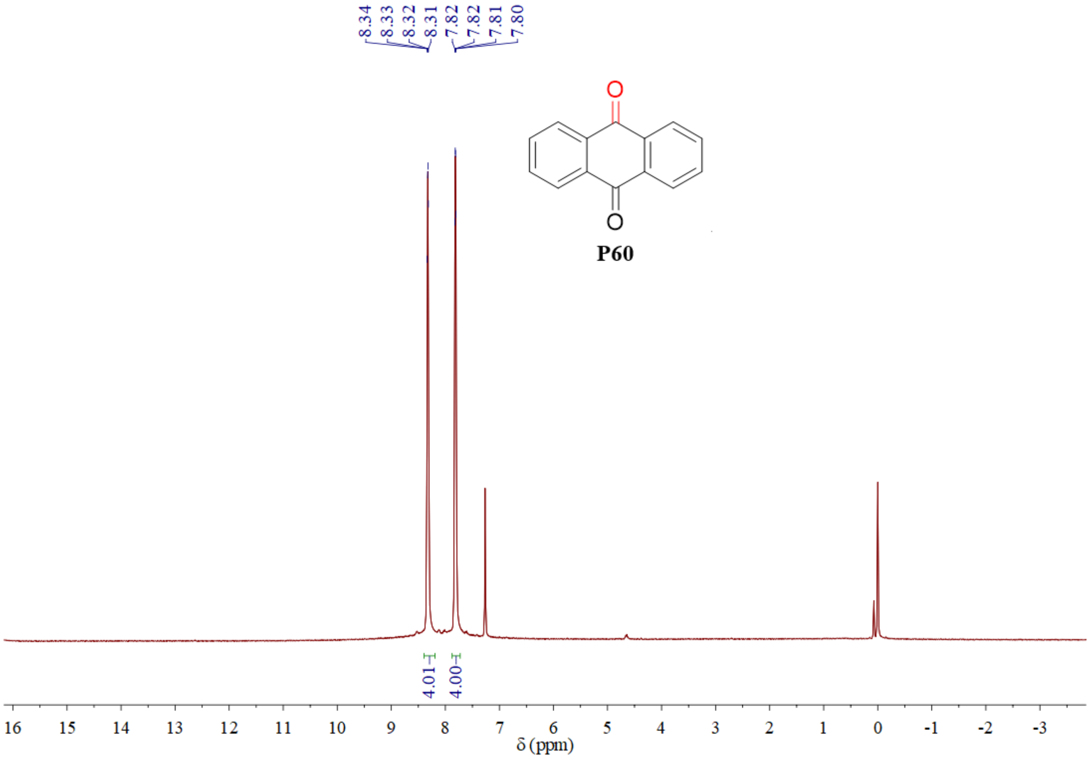

192.3
143.6
142.9
137.0
135.7
135.0
133.6
129.4
127.4
124.5
122.9
121.7
120.4
O
Br
P57
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
δ (ppm)


7.76
7.76
7.64
7.64
7.62
7.61
7.40
7.39
7.37
7.37
O
Br
Br
P58
2.09
1.00
1.17
2.14
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
δ (ppm)


191.0
142.3
137.5
135.3
127.9
123.3
121.9
O
Br
Br
P58
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
δ (ppm)


8.12
8.10
8.10
8.09
8.09
7.66
7.65
7.57
7.56
7.55
7.54
7.53
7.53
7.51
7.51
7.50
7.50
7.36
7.36
7.35
7.35
7.33
7.33
2.61
O
O
P59
2.05
1.02
3.25
1.05
3.00
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
-4
δ (ppm)


196.5
192.6
148.4
143.2
137.7
135.0
134.9
134.8
134.2
130.2
124.6
124.0
121.3
120.4
26.7
O
O
P59
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
δ (ppm)


P60
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8.33
8.32
8.31
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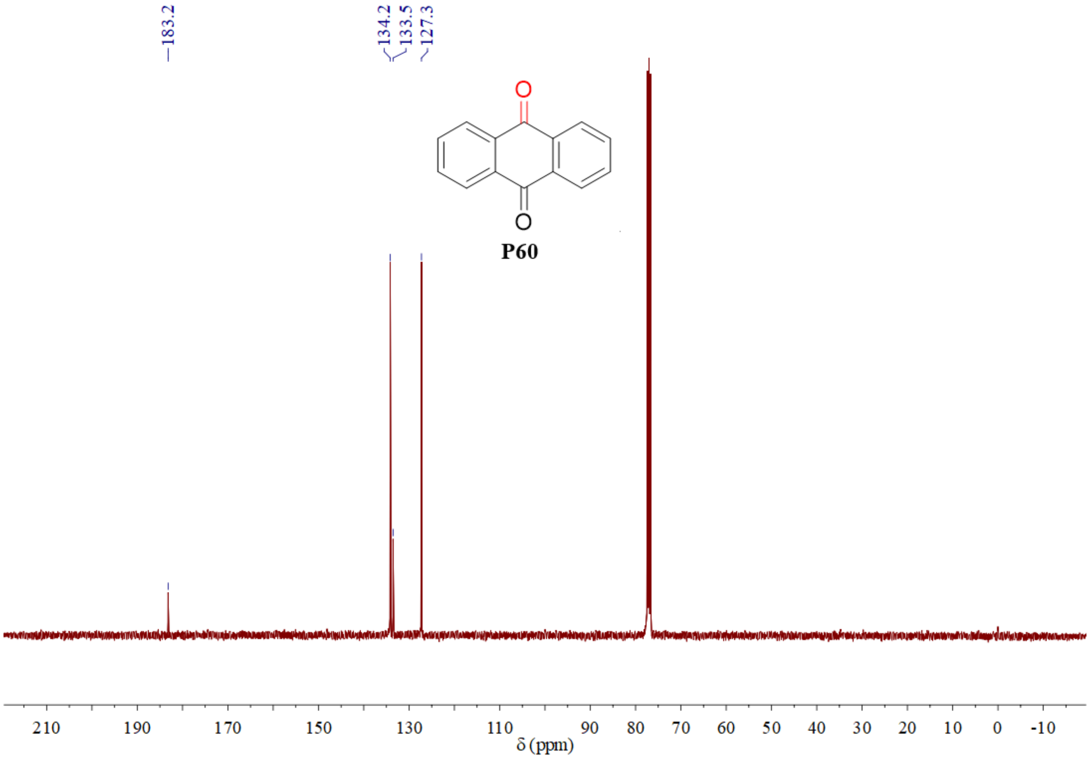
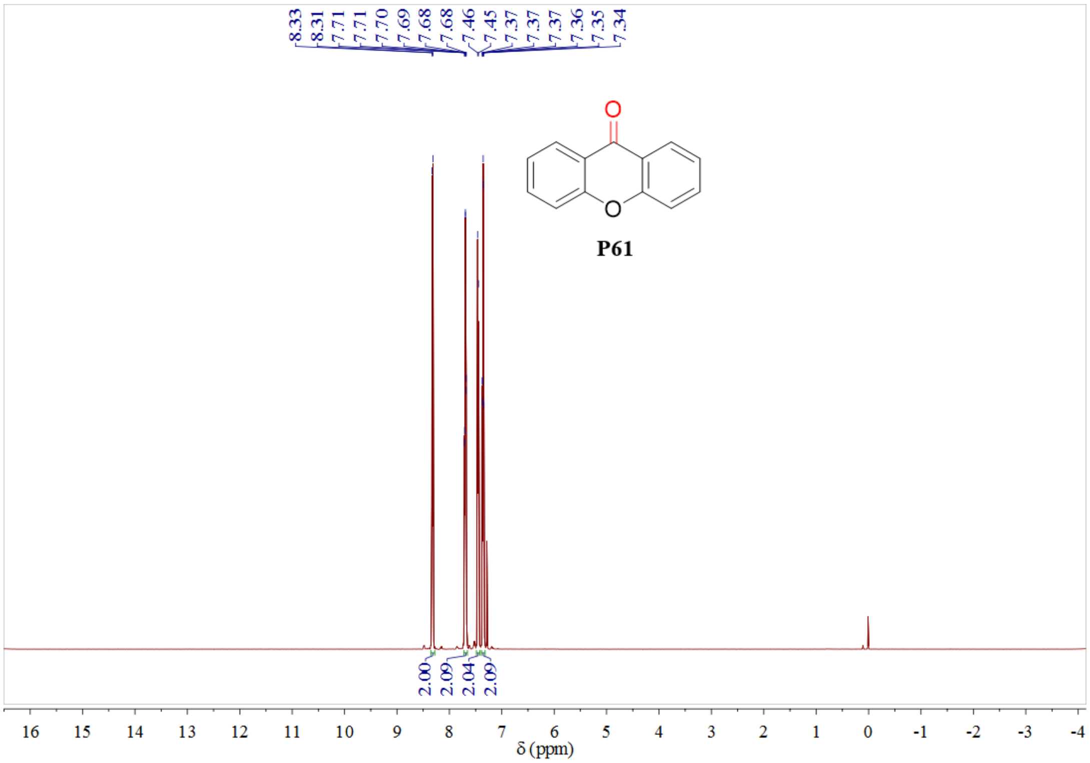
7.82
7.81
7.80
4.01
4.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
δ (ppm)


P60
183.2
134.2
133.5
127.3
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
δ (ppm)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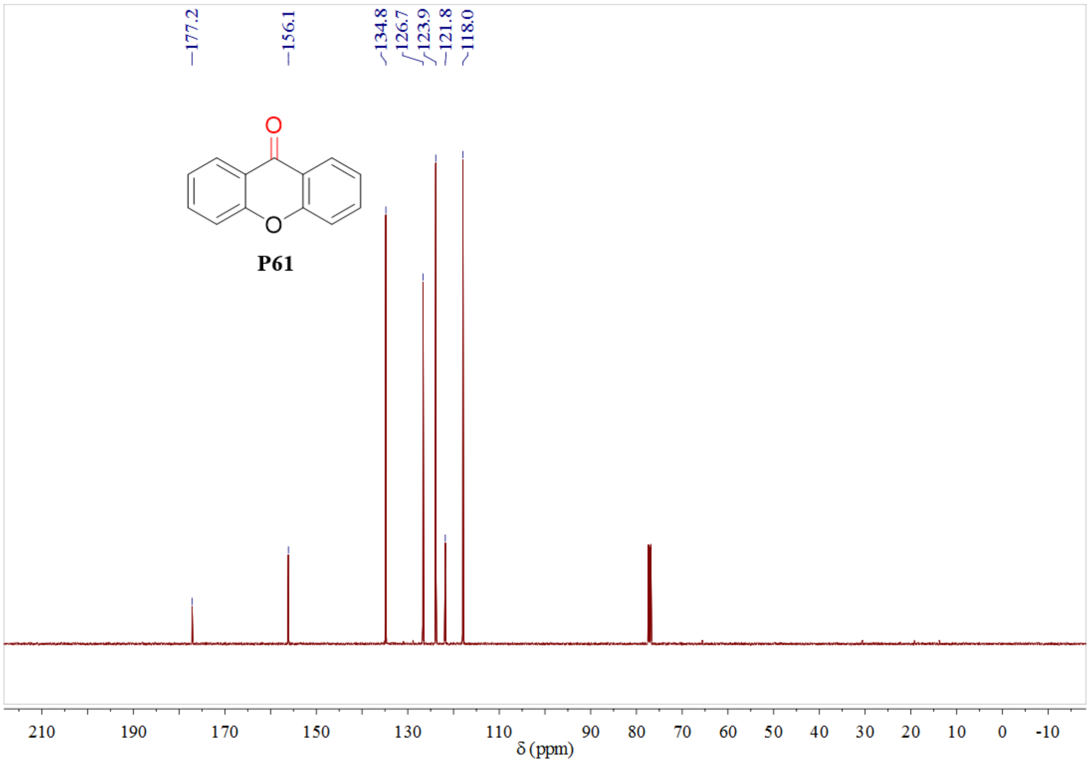
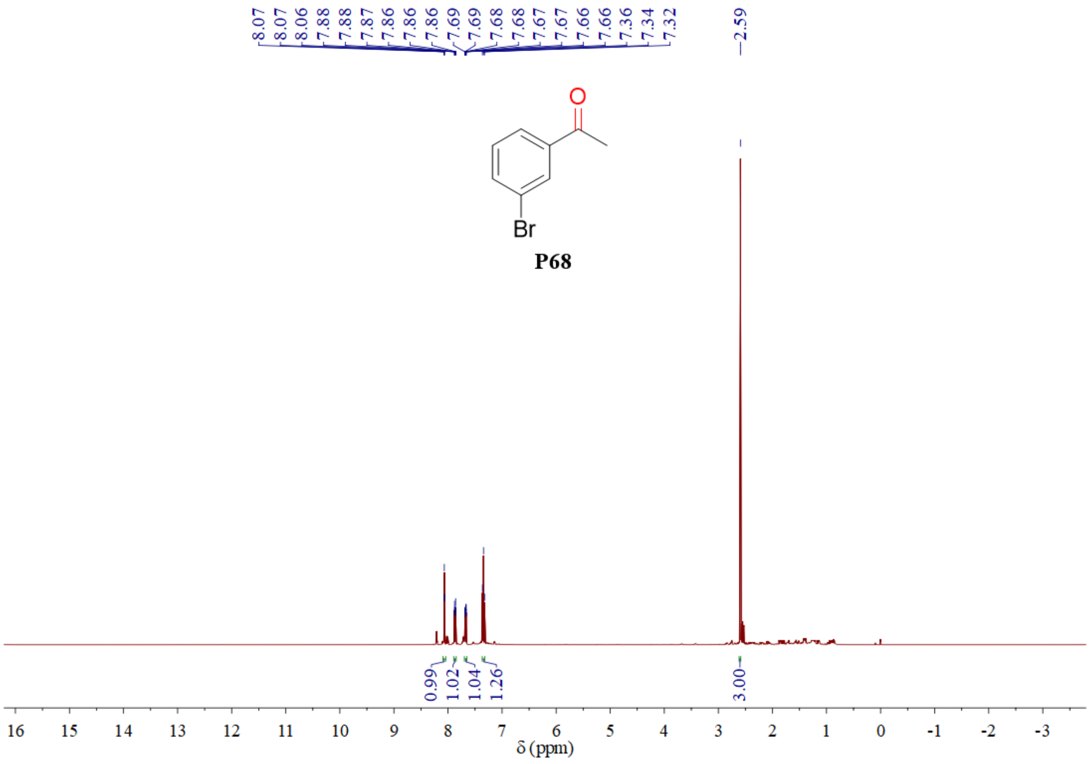
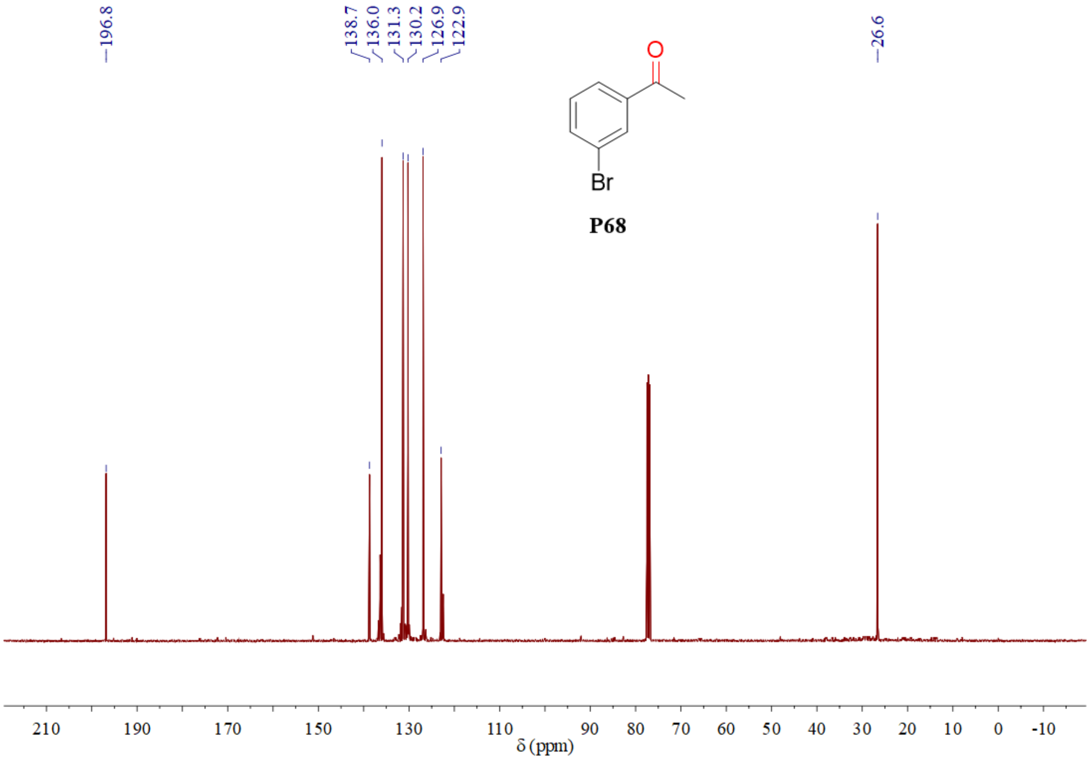
7.69
7.68
7.68
7.46
7.45
7.37
7.37
7.37
7.36
7.35
7.34
O
O
P61
2.00
2.09
2.04
2.09
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
δ (ppm)


177.2
156.1
134.8
126.7
123.9
121.8
118.0
O
O
P61
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
δ (ppm)



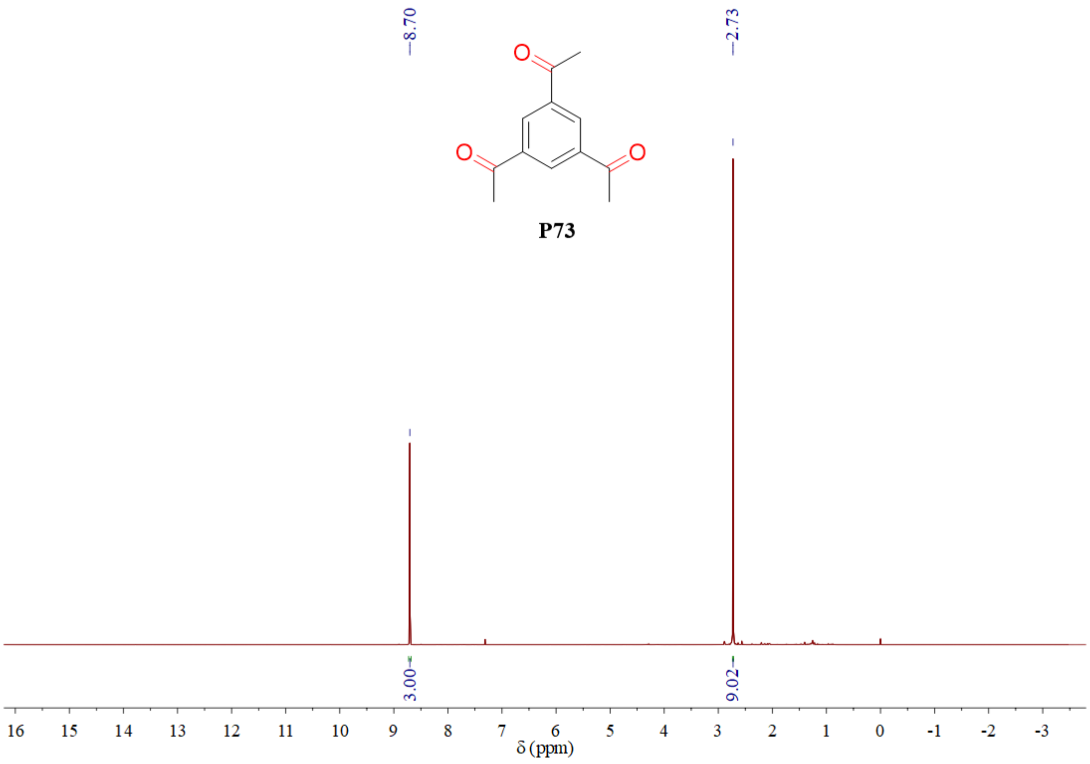
P68

8.07
8.07
8.06
7.88
7.88
7.87
7.86
7.86
7.86
7.69
7.69
7.68
7.68
7.67
7.67
7.66
7.66
7.36
7.34
7.32
2.59
O
Br
0.99
1.02
1.04
1.26
3.00
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
δ (ppm)



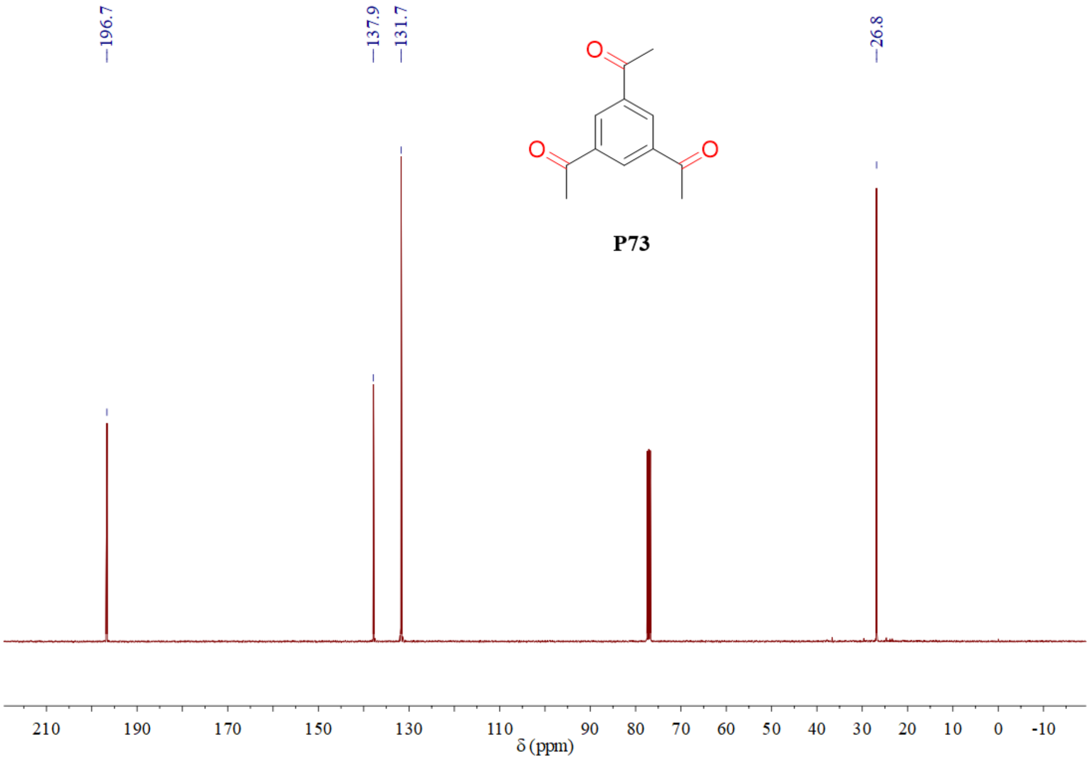
P68

196.8
138.7
136.0
131.3
130.2
126.9
122.9
26.6
O
Br
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
δ (ppm)



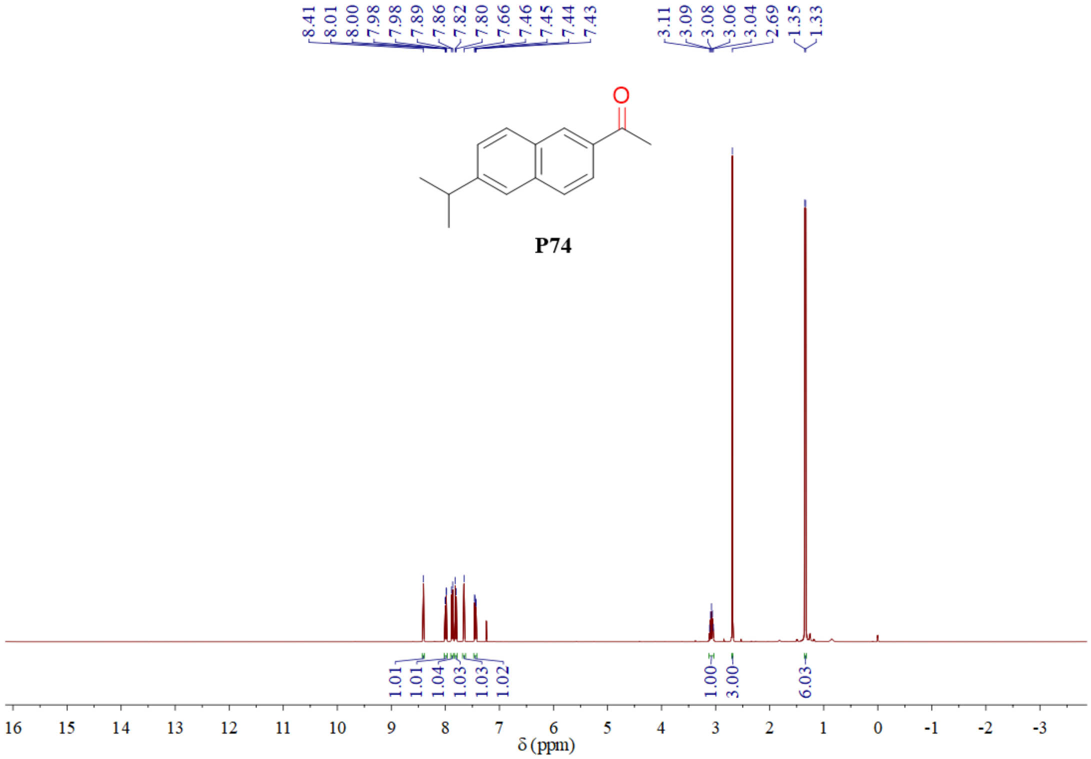
8.70
2.73
3.00
9.02
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
δ (ppm)

P73

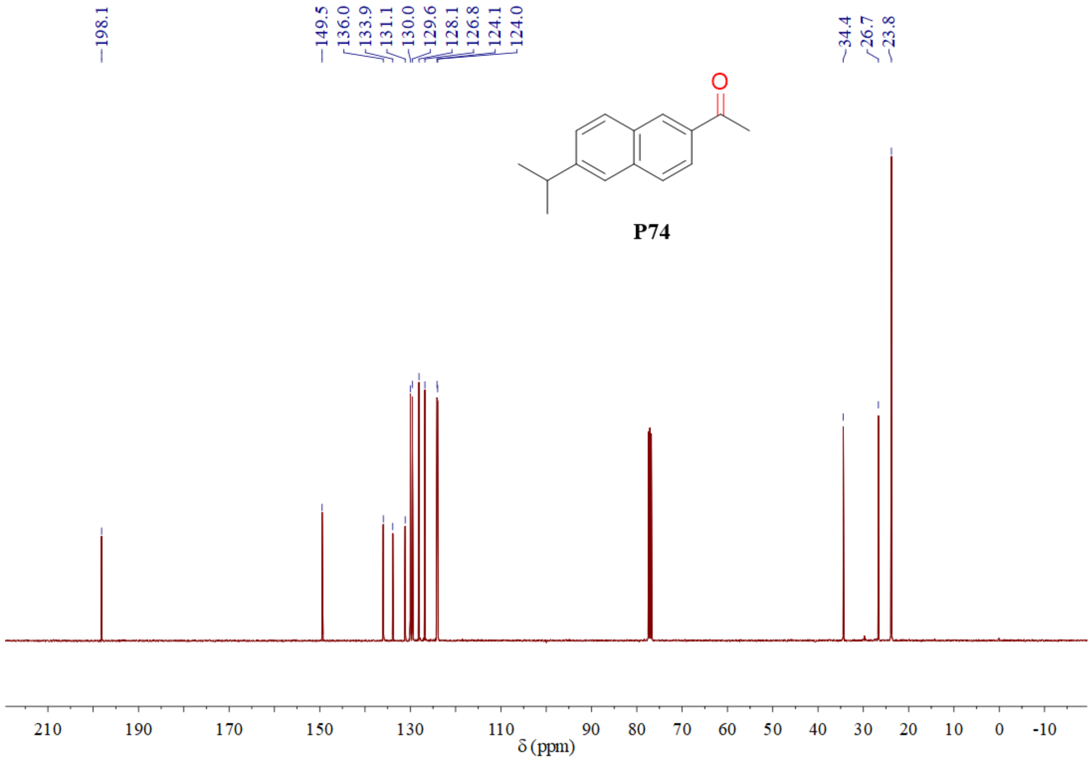


196.7
137.9
131.7
26.8
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
δ (ppm)

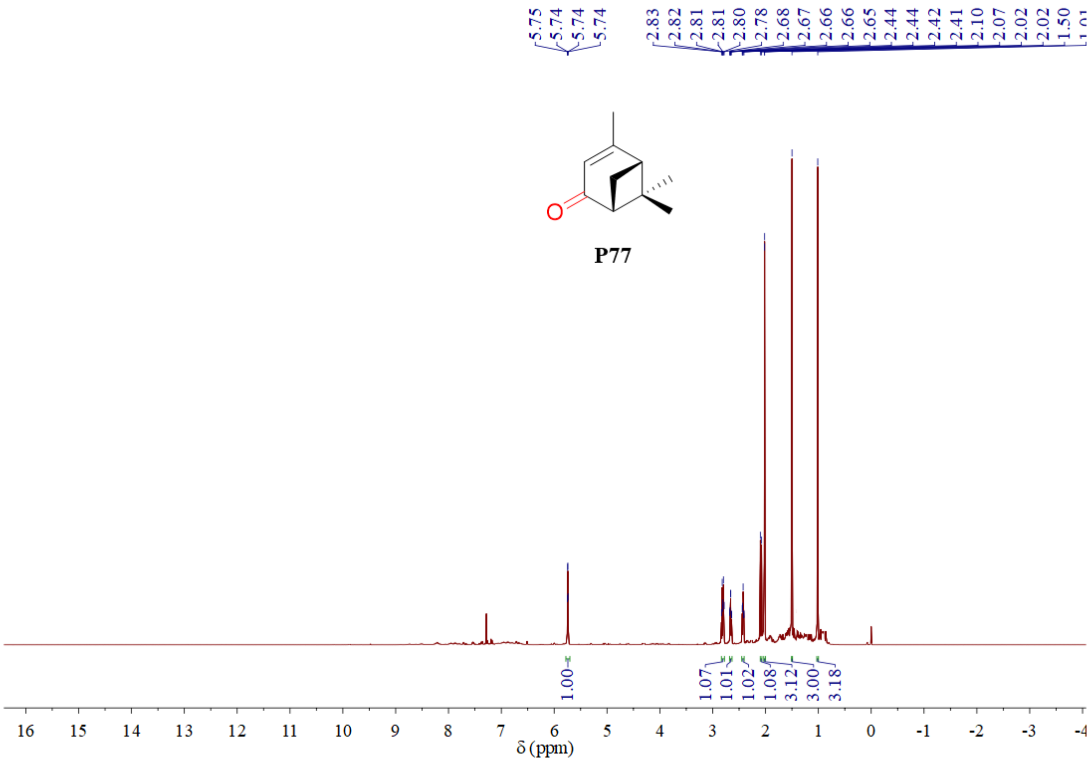
P73

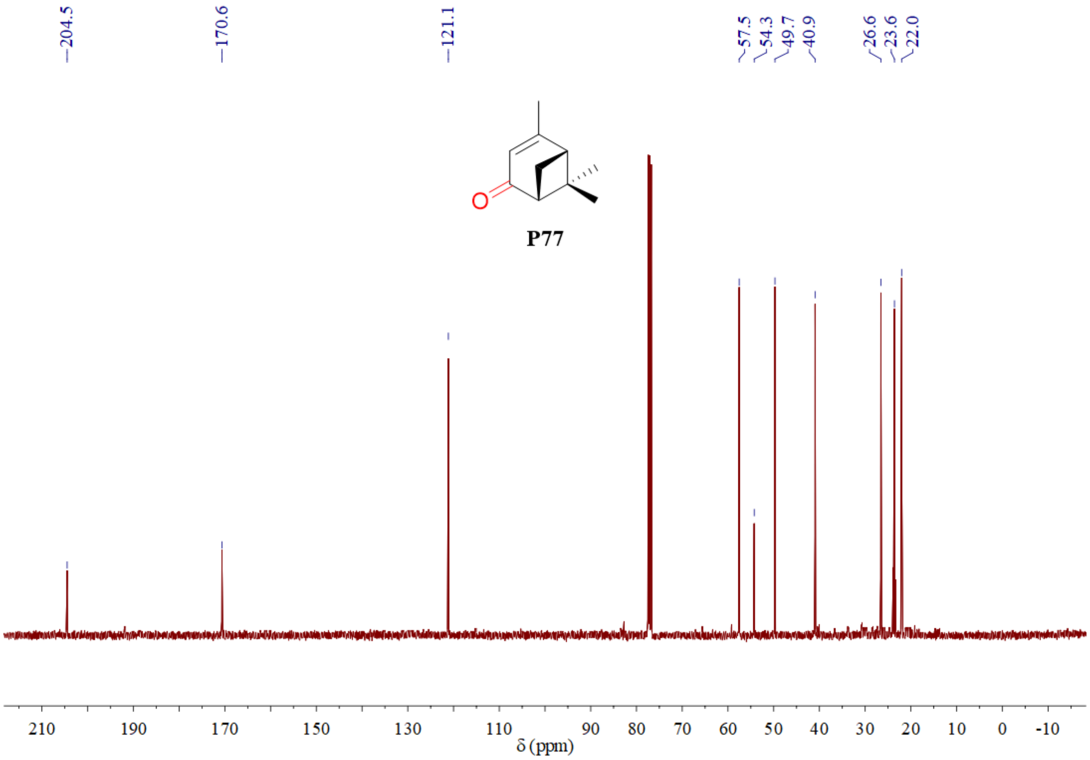

8.41
8.01
8.00
7.98
7.98
7.89
7.86
7.82
7.80
7.66
7.46
7.45
7.44
7.43
3.11
3.09
3.08
3.06
3.04
2.69
1.35
1.33
O
1.01
1.01
1.04
1.03
1.03
1.02
1.00
3.00
6.03
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
δ (ppm)

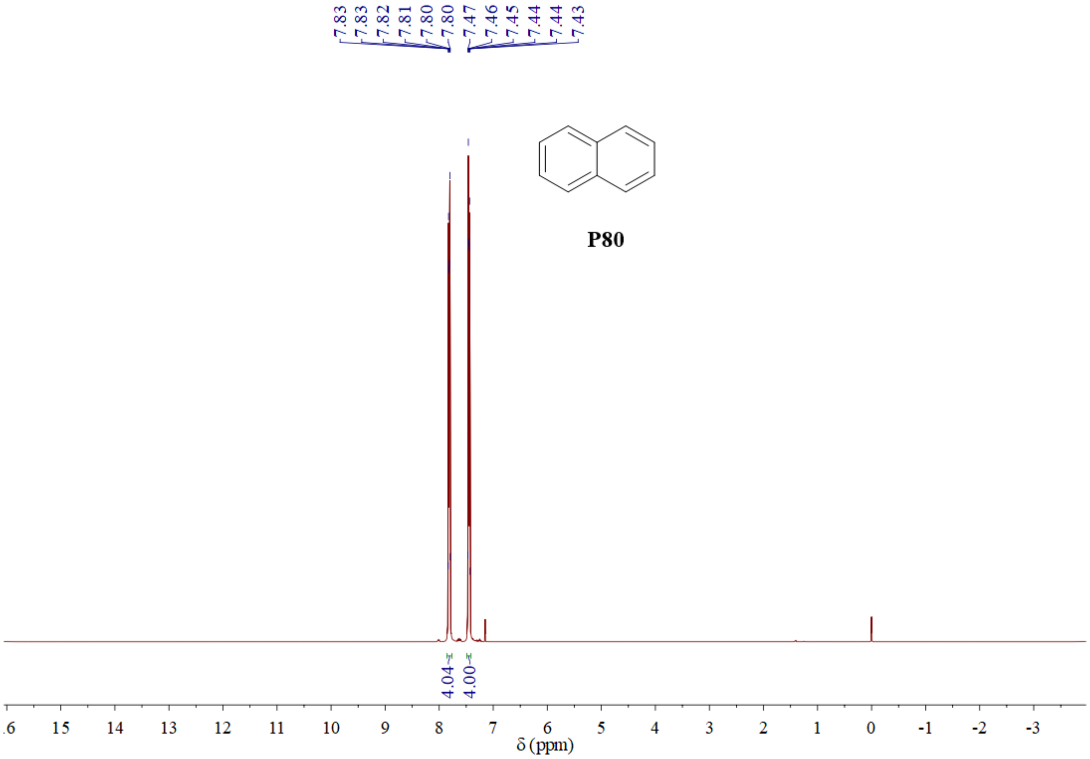
P74


198.1
149.5
136.0
133.9
131.1
130.0
129.6
128.1
126.8
124.1
124.0
34.4
26.7
23.8
O
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
δ (ppm)

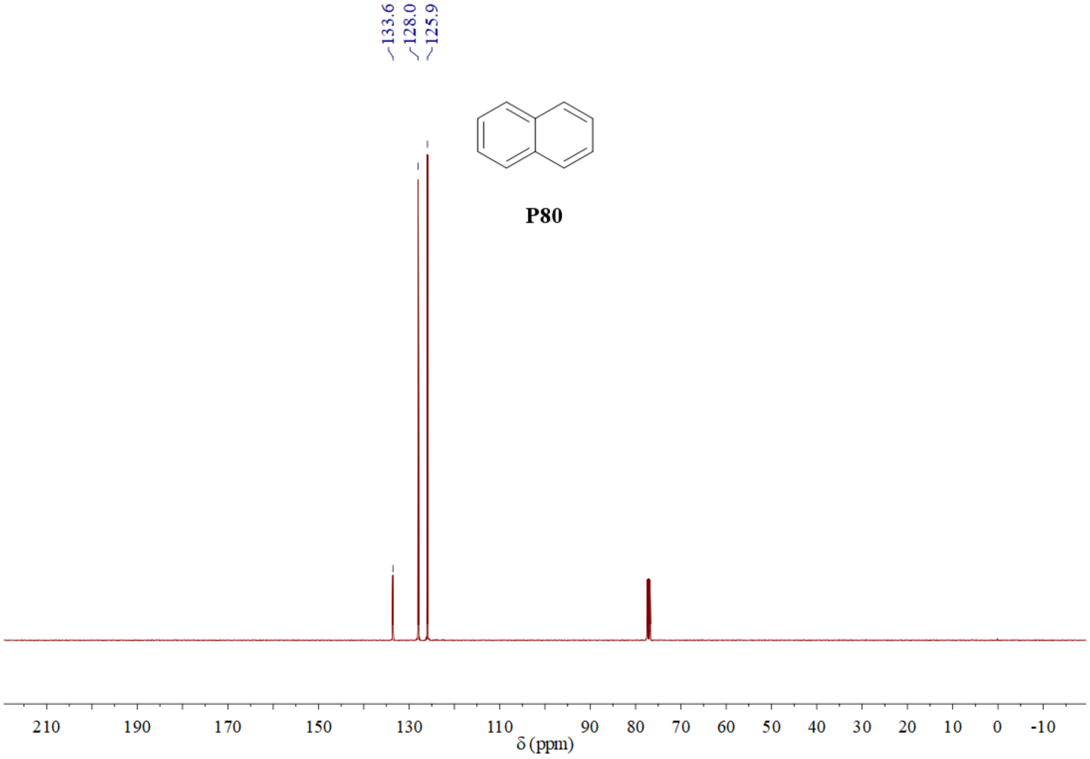
P74


5.75
5.74
5.74
5.74
2.83
2.82
2.81
2.81
2.80
2.78
2.68
2.67
2.66
2.66
2.65
2.44
2.44
2.42
2.41
2.10
2.07
2.02
2.02
1.50
O
P77
1.00
1.07
1.01
1.02
1.08
3.12
3.00
3.18
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
δ (ppm)

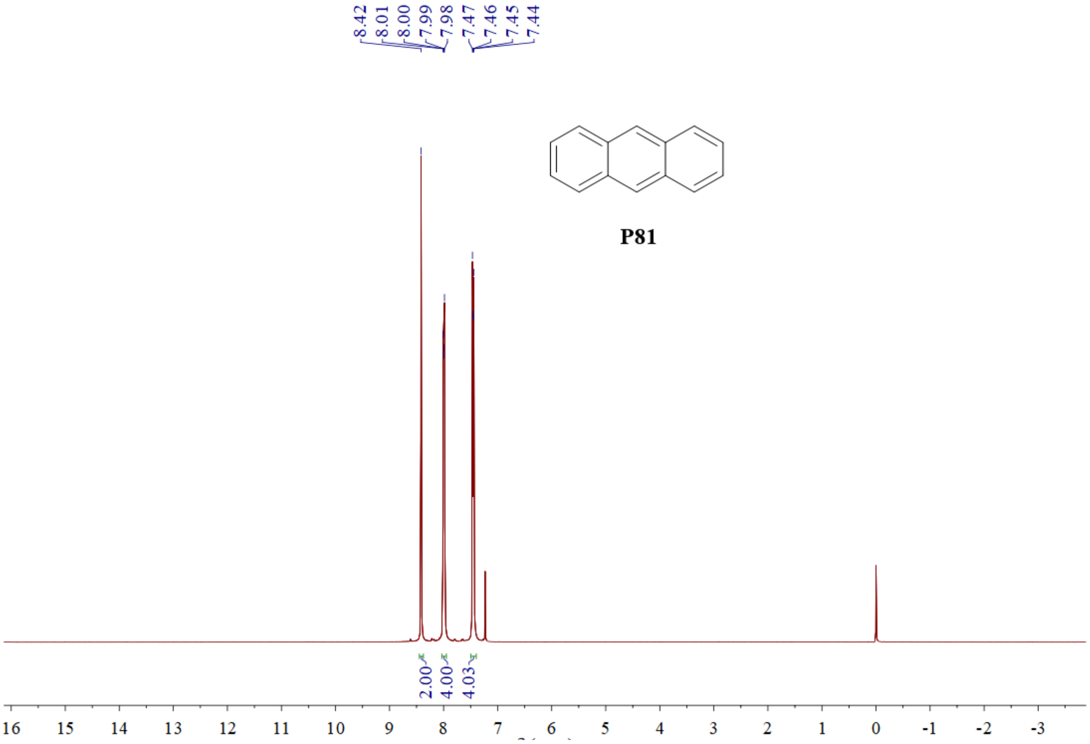

204.5
170.6
121.1
57.5
54.3
49.7
40.9
26.6
23.6
22.0
O
P77
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
δ (ppm)


7.83
7.83
7.82
7.81
7.80
7.80
7.47
7.46
7.45
7.44
7.44
7.43
4.04
4.00
.6
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
δ (ppm)

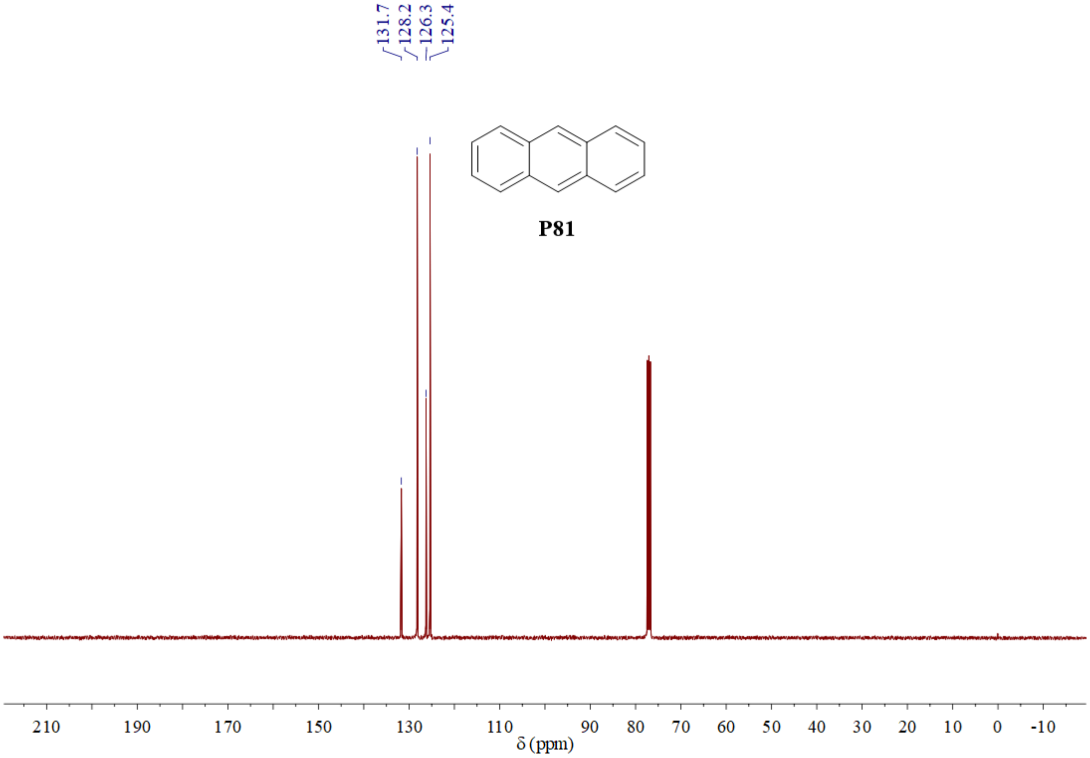
P80


133.6
128.0
125.9
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
δ (ppm)

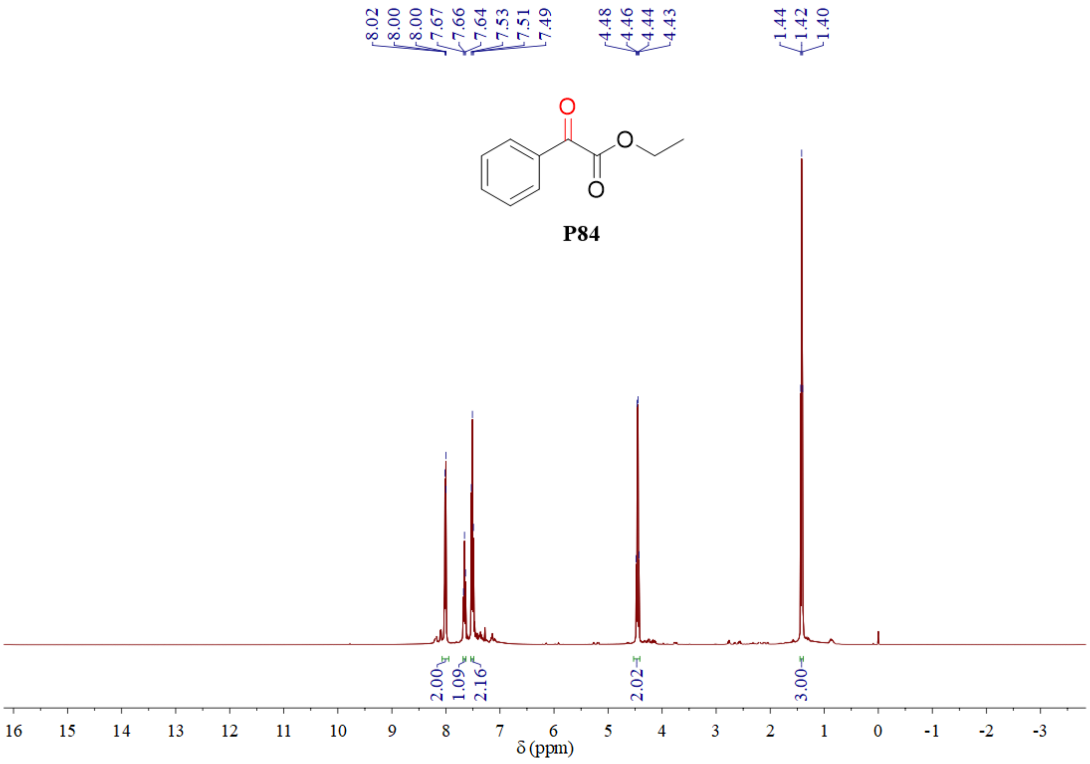
P80

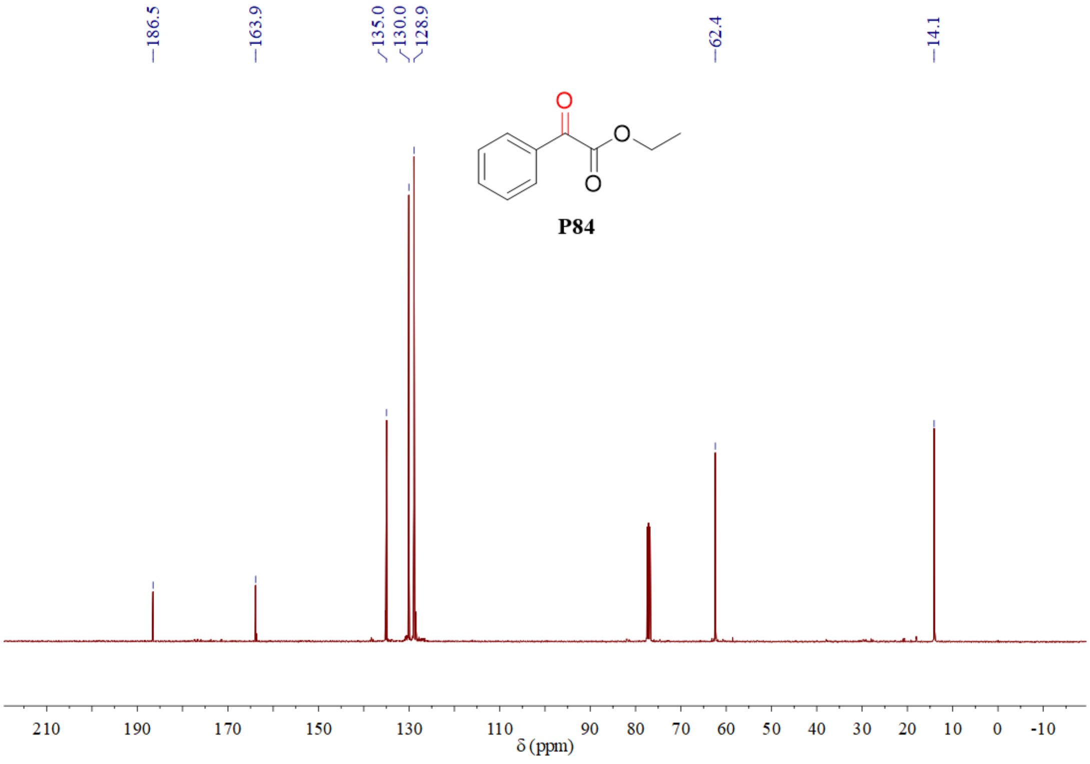

8.42
8.01
8.00
7.99
7.98
7.47
7.46
7.45
7.44
2.00
4.00
4.03
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3

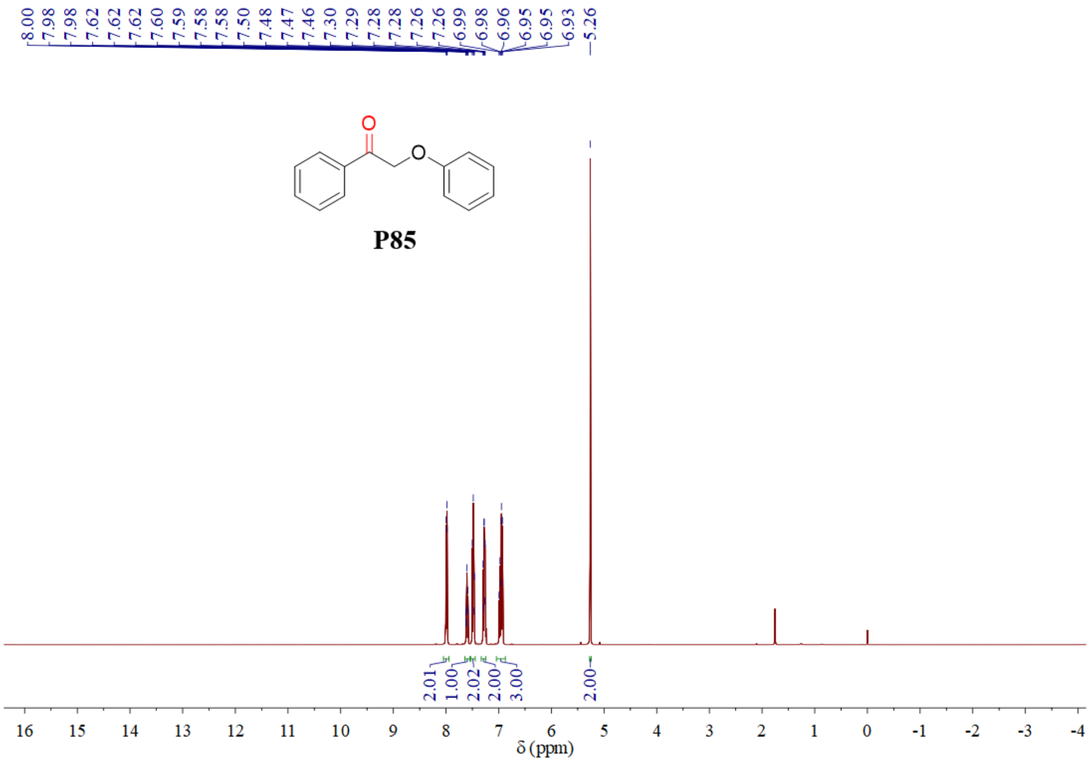
P81

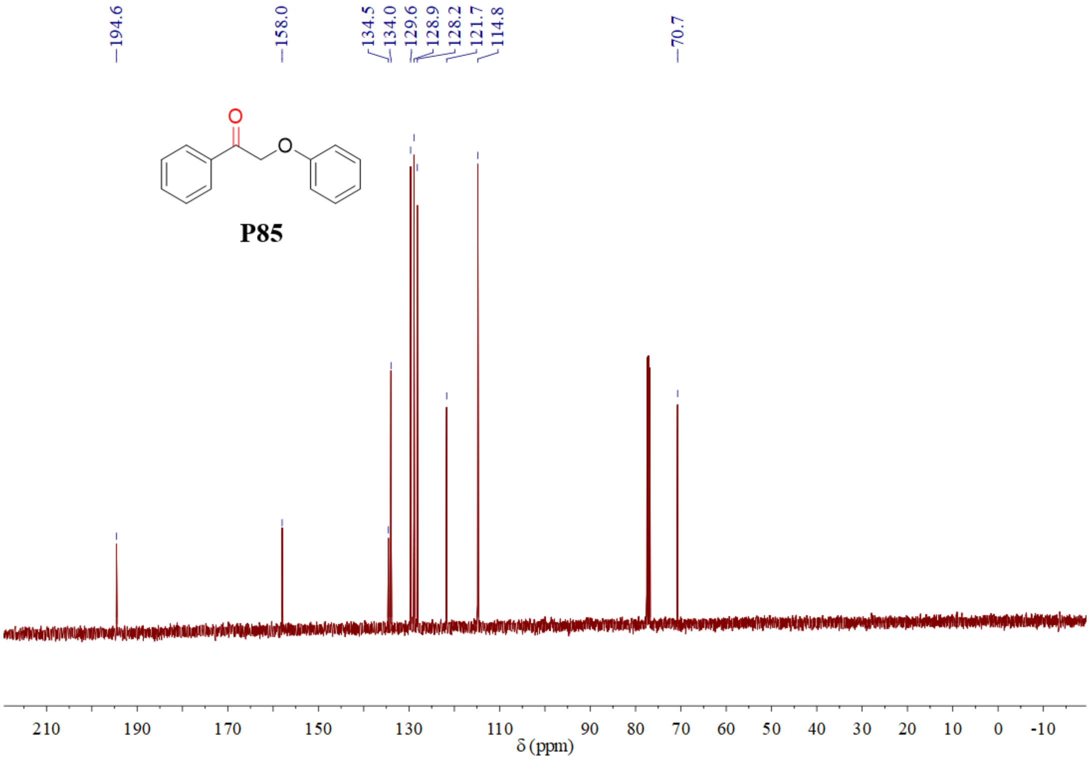

131.7
128.2
126.3
125.4
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
δ (ppm)

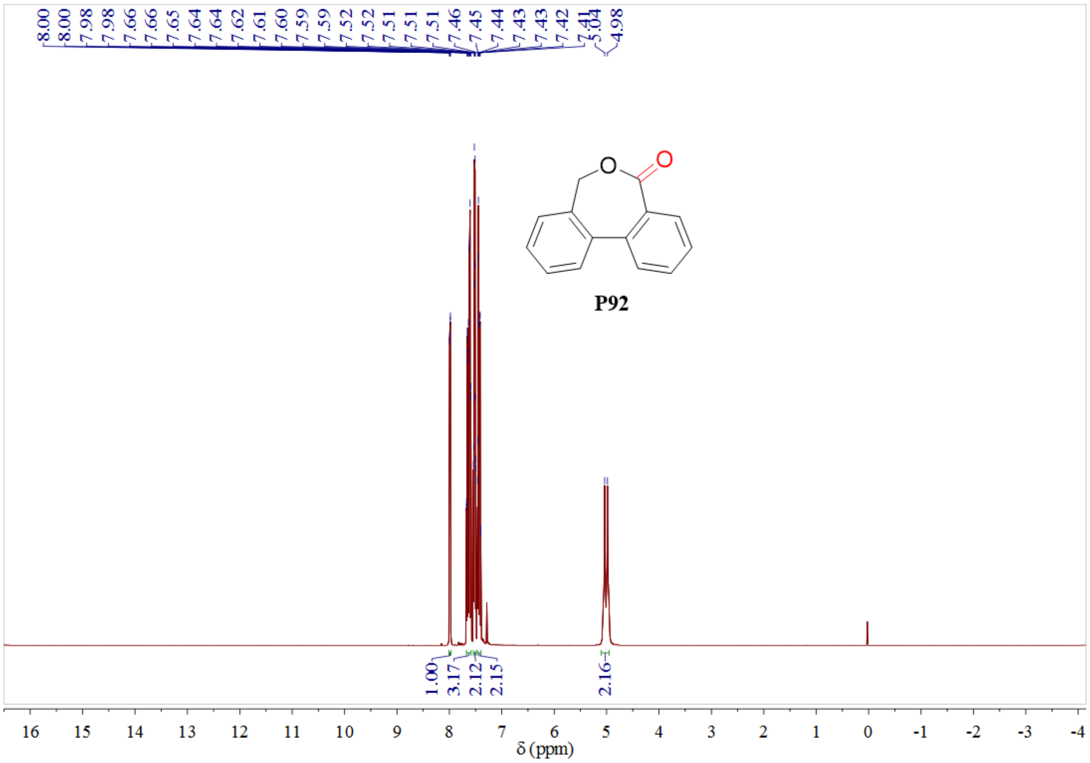
P81

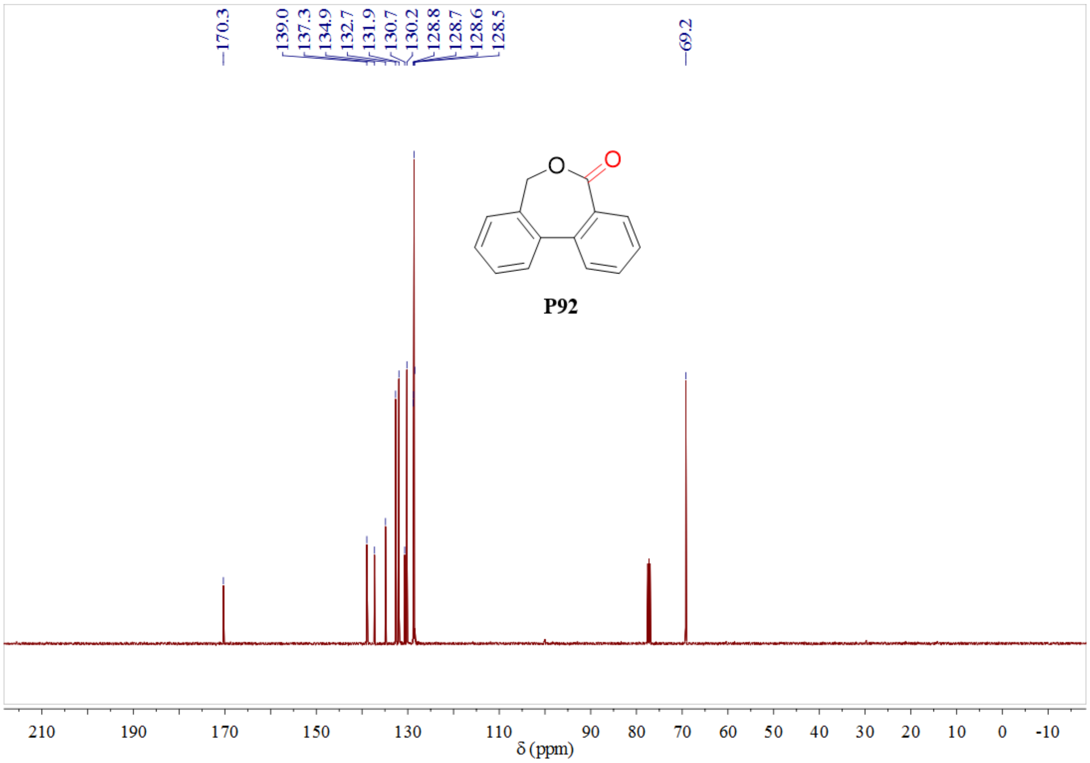

P84
8.02
8.00
8.00
7.67
7.66
7.64
7.53
7.51
7.49
4.48
4.46
4.44
4.43
1.44
1.42
1.40
O
O
O
2.00
1.09
2.16
2.02
3.00
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
δ (ppm)

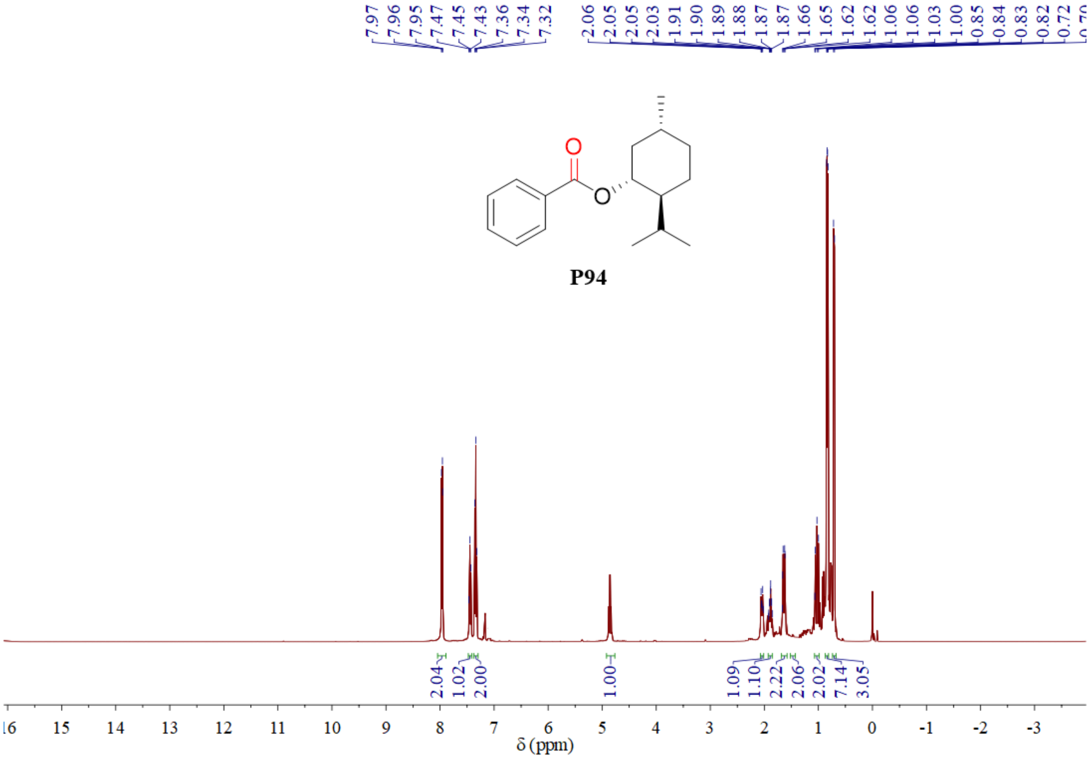

P84
186.5
163.9
135.0
130.0
128.9
62.4
14.1
O
O
O
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
δ (ppm)

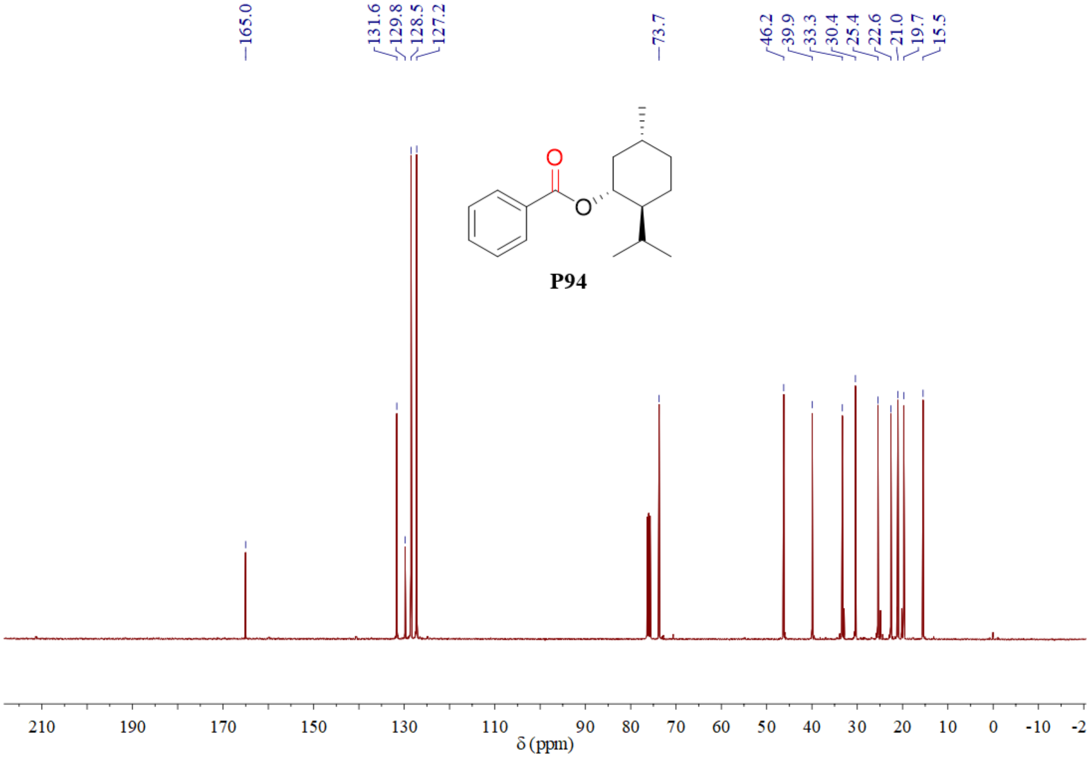

8.00
7.98
7.98
7.62
7.62
7.62
7.60
7.59
7.58
7.58
7.50
7.48
7.47
7.46
7.30
7.29
7.28
7.28
7.26
7.26
6.99
6.98
6.96
6.95
6.95
6.93
5.26
P85
2.01
1.00
2.02
2.00
3.00
2.00
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
-4
δ (ppm)

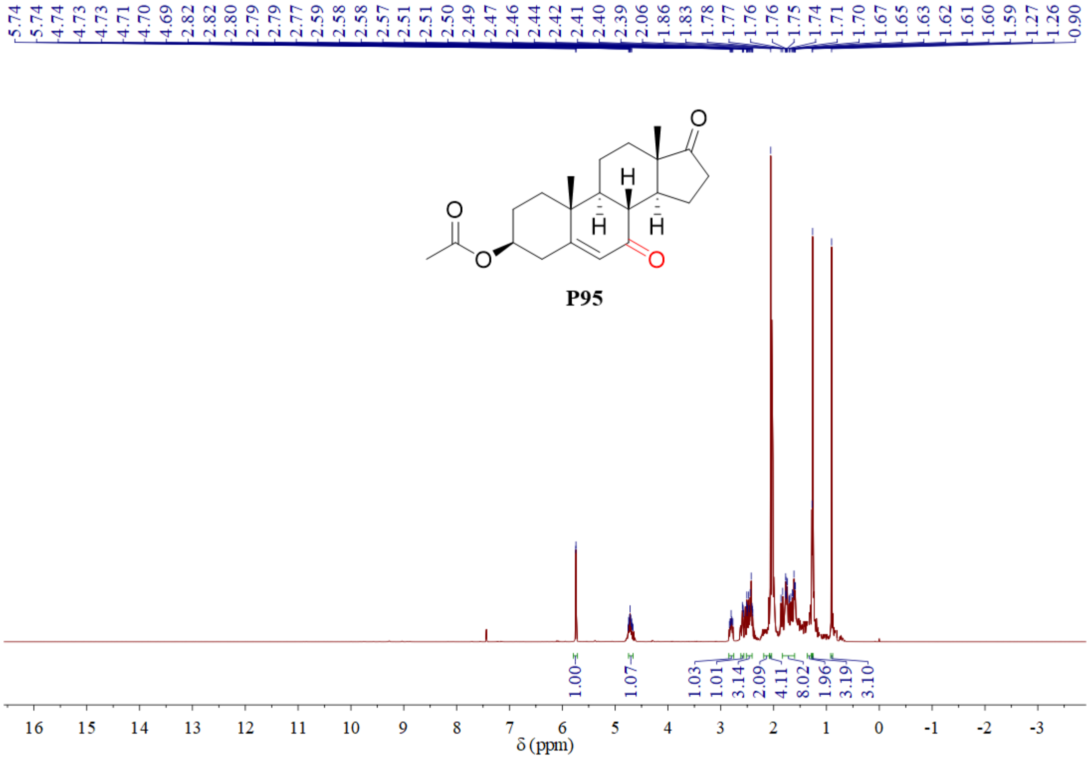

194.6
158.0
134.5
134.0
129.6
128.9
128.2
121.7
114.8
70.7
P85
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
δ (ppm)

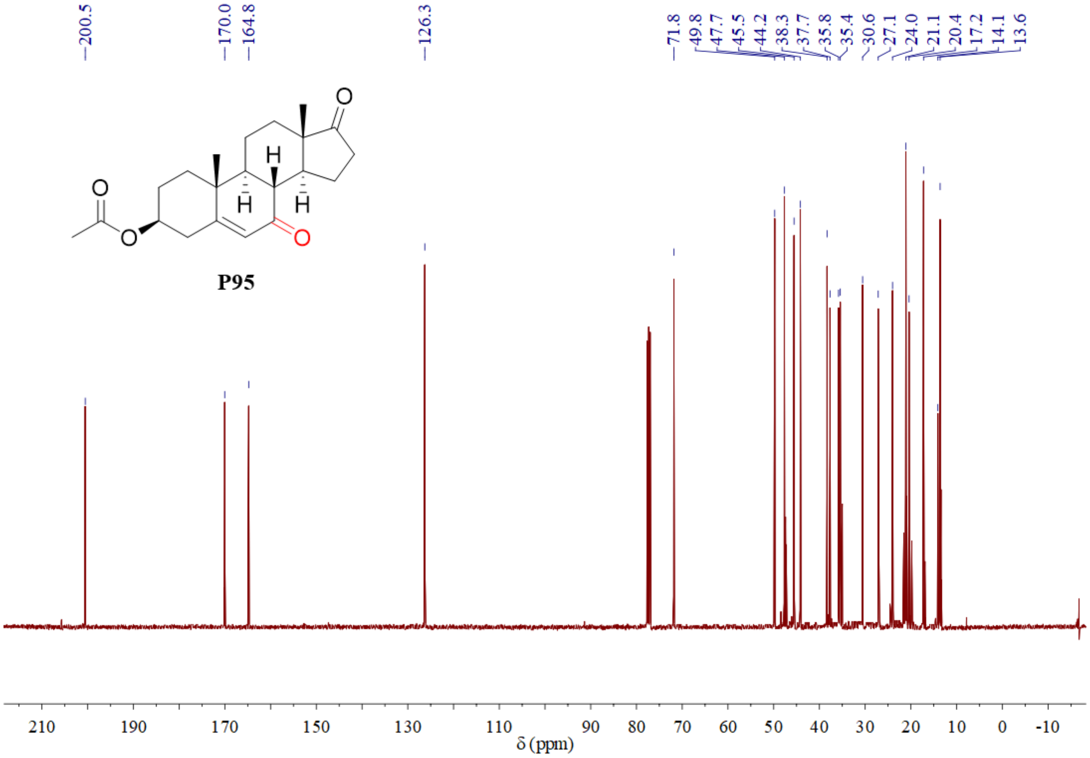

8.00
8.00
7.98
7.98
7.66
7.66
7.65
7.64
7.64
7.62
7.61
7.60
7.59
7.59
7.52
7.52
7.51
7.51
7.51
7.46
7.45
7.44
7.43
7.43
7.42
7.41
5.04
4.98
O
O
P92
1.00
3.17
2.12
2.15
2.16
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
-4
δ (ppm)

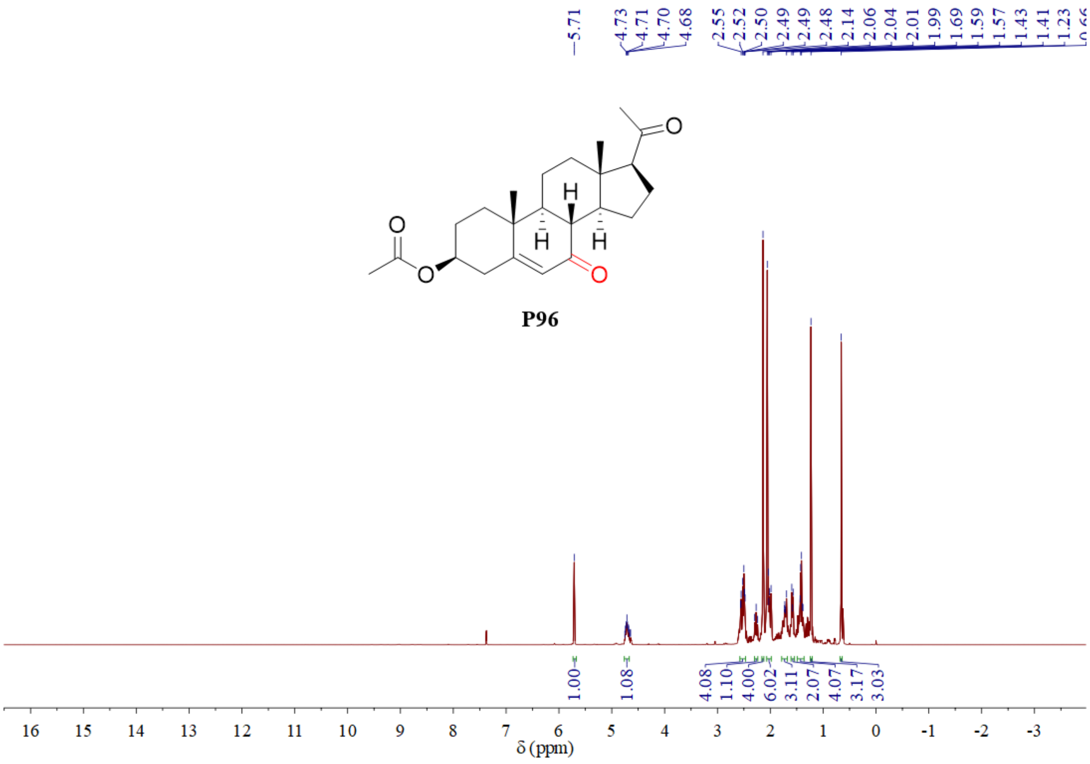

170.3
139.0
137.3
134.9
132.7
131.9
130.7
130.2
128.8
128.7
128.6
128.5
69.2
O
O
P92
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
δ (ppm)

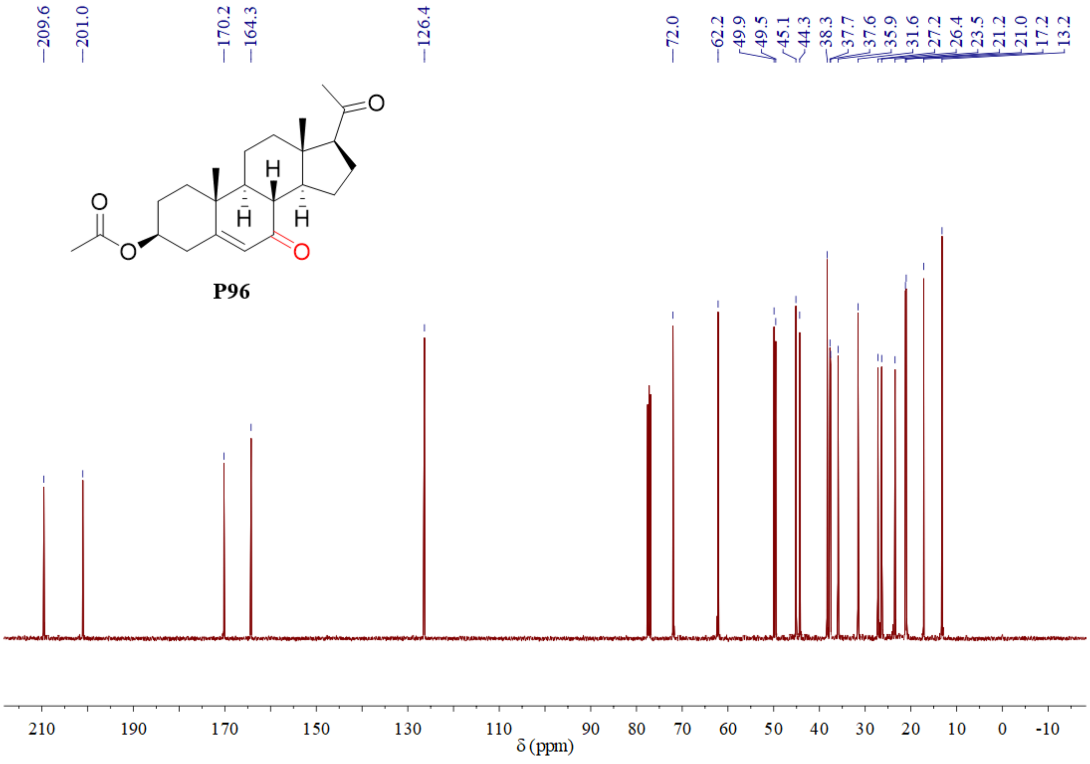

7.97
7.96
7.95
7.47
7.45
7.43
7.36
7.34
7.32
2.06
2.05
2.05
2.03
1.91
1.90
1.89
1.88
1.87
1.87
1.66
1.65
1.62
1.62
1.06
1.06
1.03
1.00
0.85
0.84
0.83
0.82
0.72
O
O
P94
2.04
1.02
2.00
1.00
1.09
1.10
2.22
2.06
2.02
7.14
3.05
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
δ (ppm)

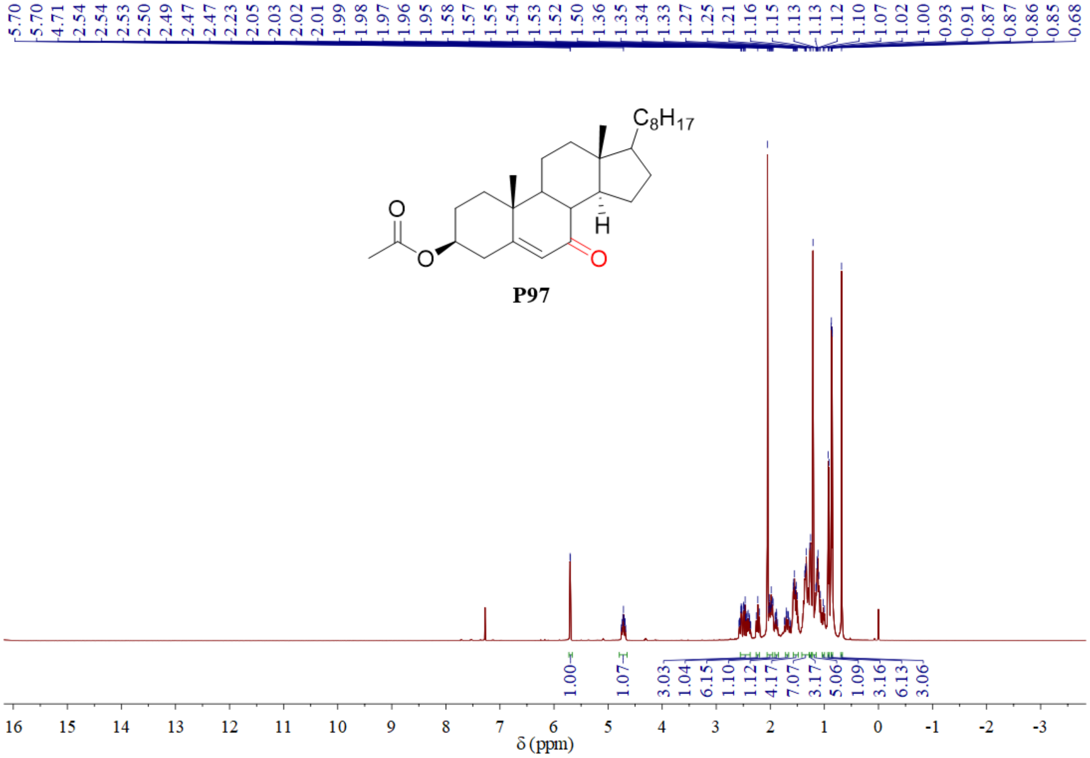

165.0
131.6
129.8
128.5
127.2
73.7
46.2
39.9
33.3
30.4
25.4
22.6
21.0
19.7
15.5
O
O
P94
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
δ (ppm)

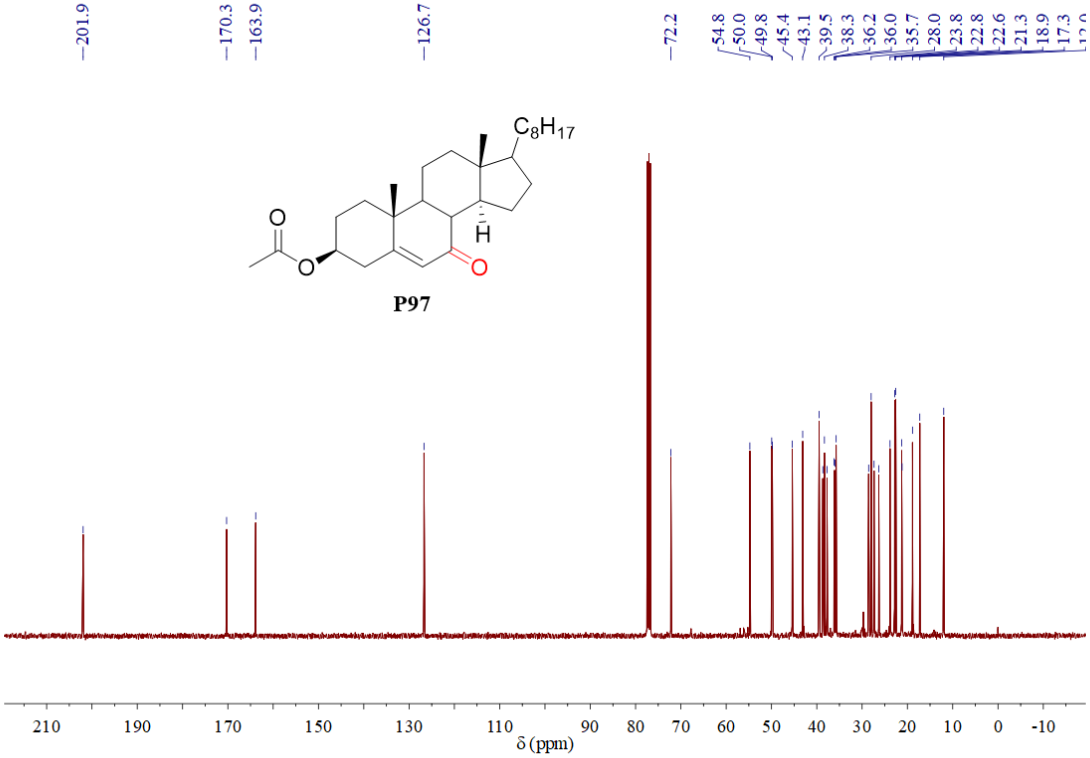

5.74
5.74
4.74
4.74
4.73
4.73
4.71
4.70
4.69
2.82
2.82
2.80
2.79
2.79
2.77
2.59
2.58
2.58
2.57
2.51
2.51
2.50
2.49
2.47
2.46
2.44
2.42
2.41
2.40
2.39
2.06
1.86
1.83
1.78
1.77
1.76
1.76
1.75
1.74
1.71
1.70
1.67
1.65
1.63
1.62
1.61
1.60
1.59
1.27
1.26
0.90
O
H
O
O
H
H
O
P95
1.00
1.07
1.03
1.01
3.14
2.09
4.11
8.02
1.96
3.19
3.10
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
δ (ppm)

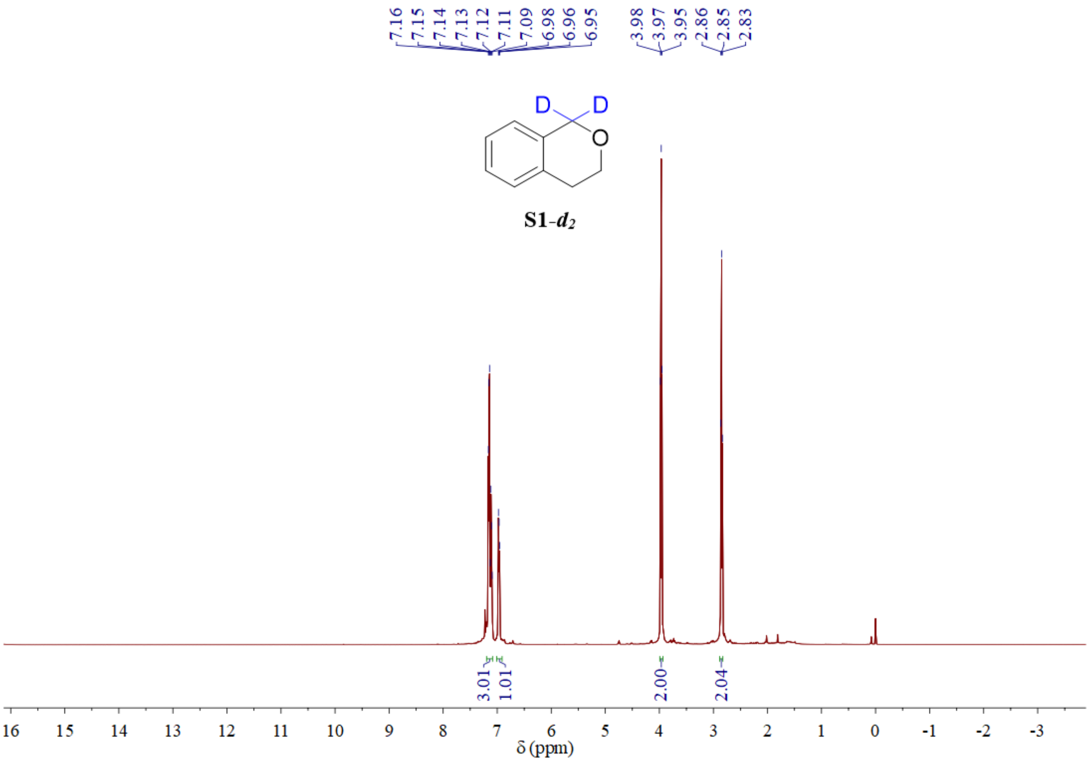

200.5
170.0
164.8
126.3
71.8
49.8
47.7
45.5
44.2
38.3
37.7
35.8
35.4
30.6
27.1
24.0
21.1
20.4
17.2
14.1
13.6
O
H
O
O
H
H
O
P95
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
δ (ppm)

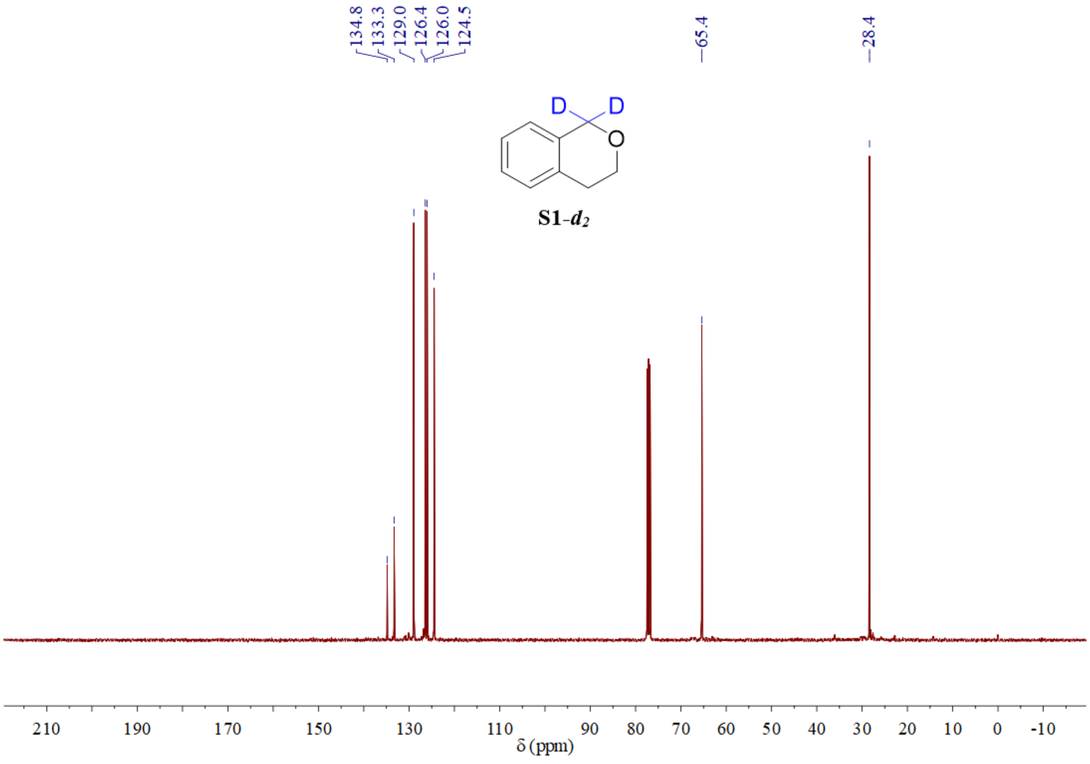

5.71
4.73
4.71
4.70
4.68
2.55
2.52
2.50
2.49
2.49
2.48
2.14
2.06
2.04
2.01
1.99
1.69
1.59
1.57
1.43
1.41
1.23
P96
1.00
1.08
4.08
1.10
4.00
6.02
3.11
2.07
4.07
3.17
3.03
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
δ (ppm)


209.6
201.0
170.2
164.3
126.4
72.0
62.2
49.9
49.5
45.1
44.3
38.3
37.7
37.6
35.9
31.6
27.2
26.4
23.5
21.2
21.0
17.2
13.2
P96
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
δ (ppm)

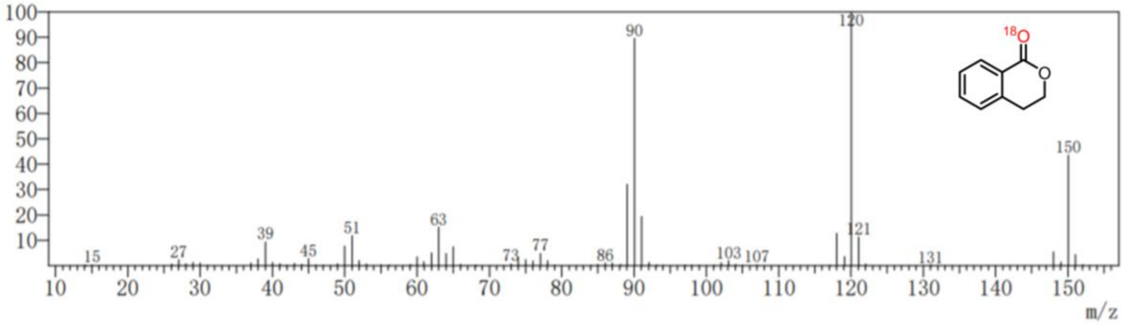

5.70
5.70
4.71
2.54
2.54
2.53
2.50
2.49
2.47
2.47
2.23
2.05
2.03
2.02
2.01
1.99
1.98
1.97
1.96
1.95
1.58
1.57
1.55
1.54
1.53
1.52
1.50
1.36
1.35
1.34
1.33
1.27
1.25
1.21
1.16
1.15
1.13
1.13
1.12
1.10
1.07
1.02
1.00
0.93
0.91
0.87
0.87
0.86
0.85
0.68
C8H17
O
O
H
O
P97
1.00
1.07
3.03
1.04
6.15
1.10
1.12
4.17
7.07
3.17
5.06
1.09
3.16
6.13
3.06
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
δ (ppm)

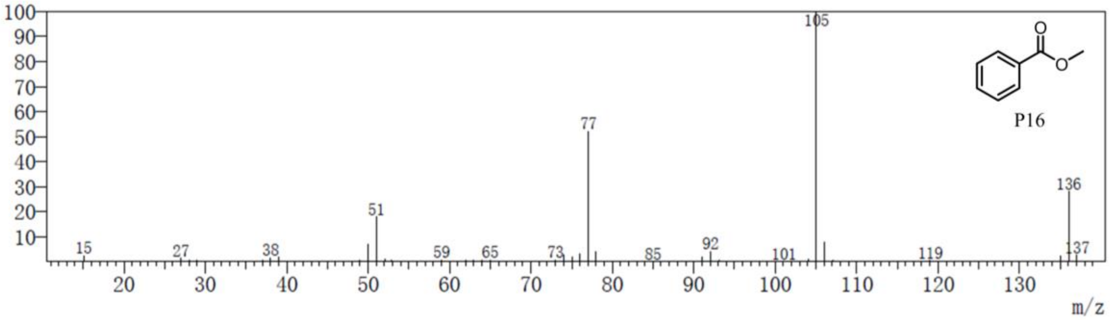

201.9
170.3
163.9
126.7
72.2
54.8
50.0
49.8
45.4
43.1
39.5
38.3
36.2
36.0
35.7
28.0
23.8
22.8
22.6
21.3
18.9
17.3
C8H17
O
O
H
O
P97
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
δ (ppm)


7.16
7.15
7.14
7.13
7.12
7.11
7.09
6.98
6.96
6.95
3.98
3.97
3.95
2.86
2.85
2.83
D
D
O
S1-d_2
3.01
1.01
2.00
2.04
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
δ (ppm)

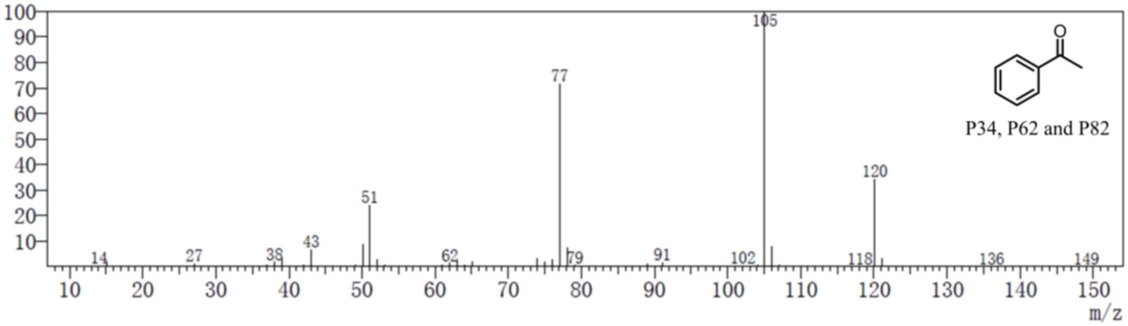

134.8
133.3
129.0
126.4
126.0
124.5
65.4
28.4
D
D
O
S1-d_2
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
δ (ppm)

MS Spectra

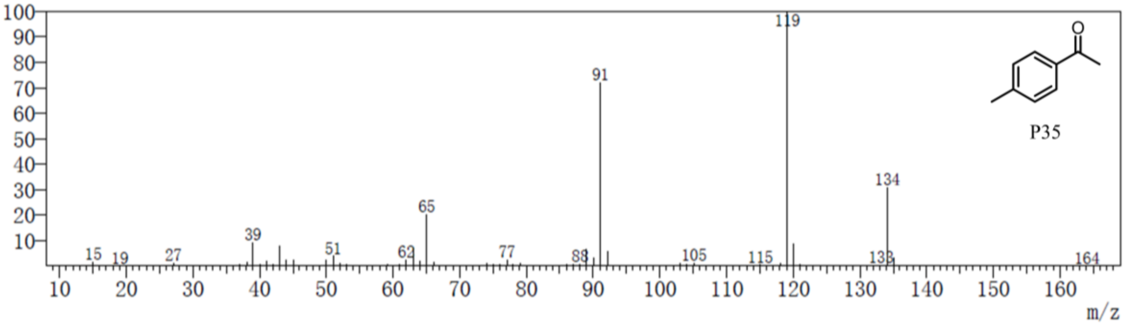




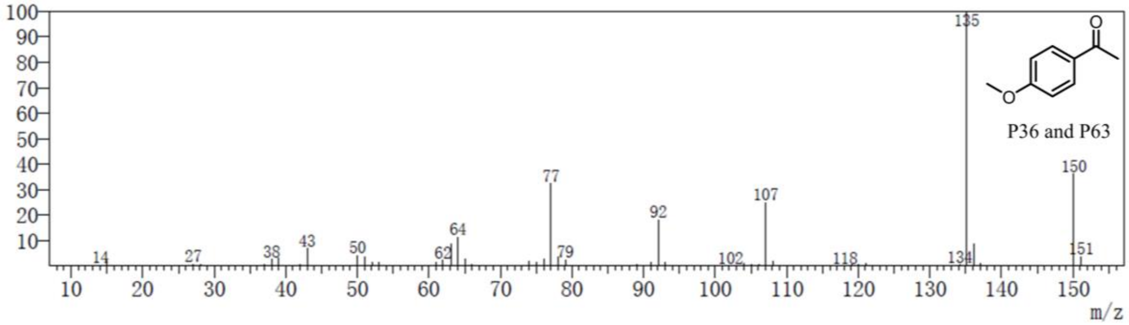
P16

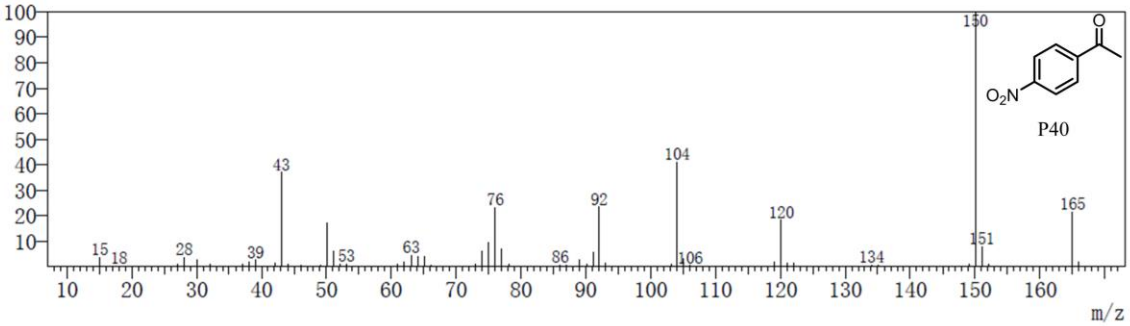


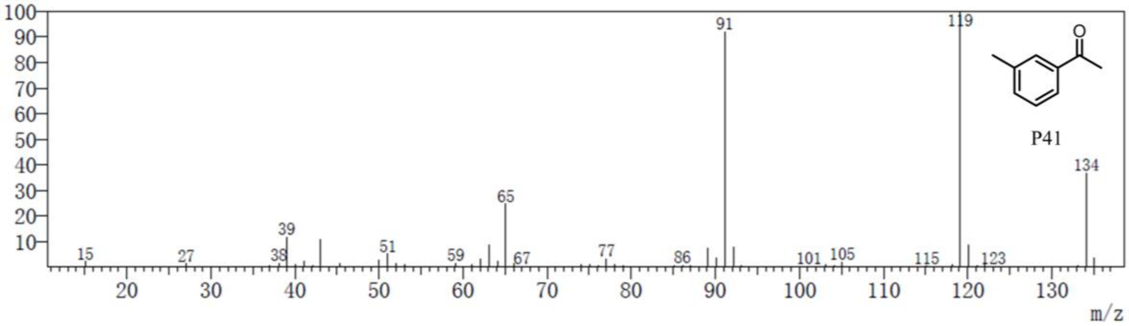
P34, P62 and P82

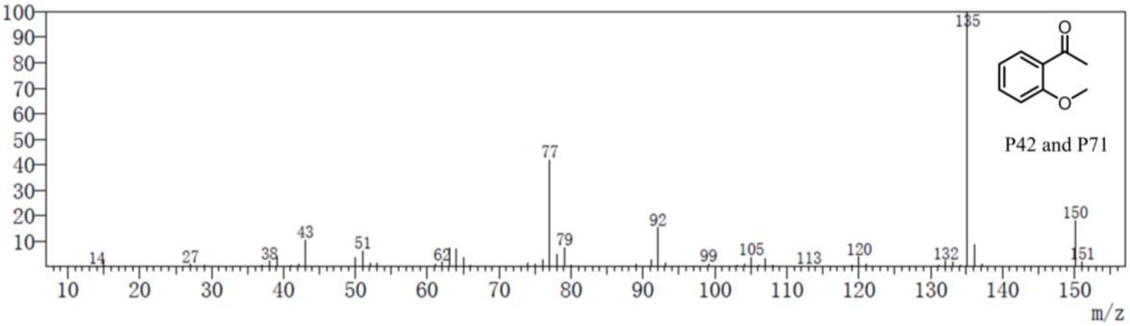


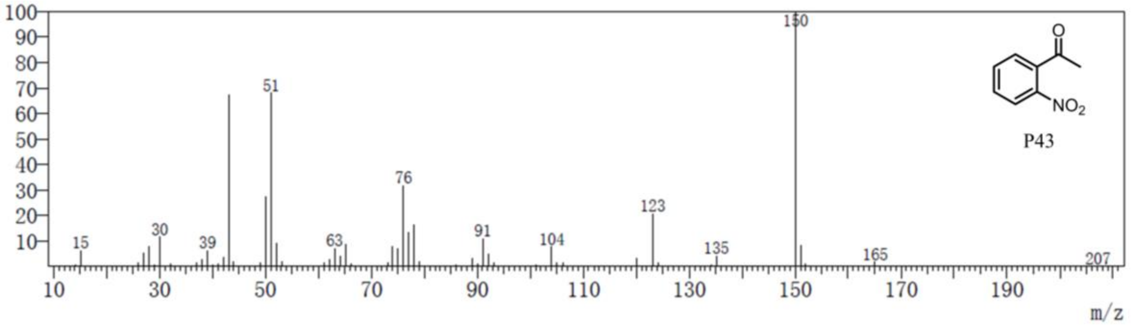
P35

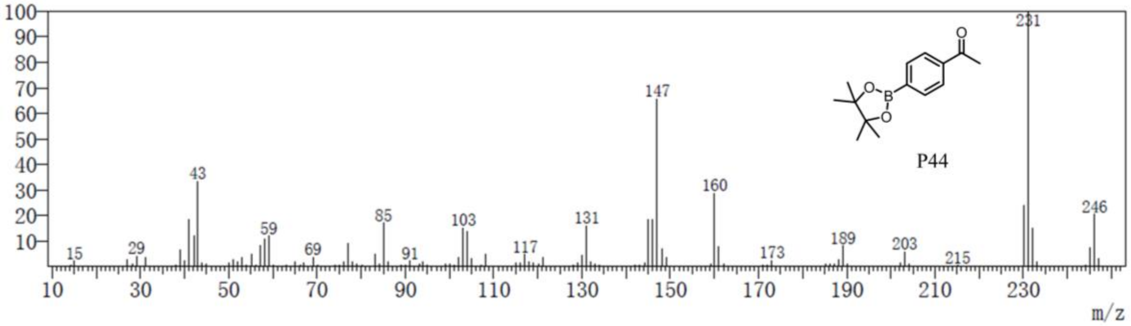

P36 and P63


P40


P41


P42 and P71


P43
NO2
O
100
90
80
70
60
50
40
30
20
10
15
30
39
51
63
76
91
104
123
135
150
165
207
10 30 50 70 90 110 130 150 170 190
m/z


P44
O
B
O
O
100
90
80
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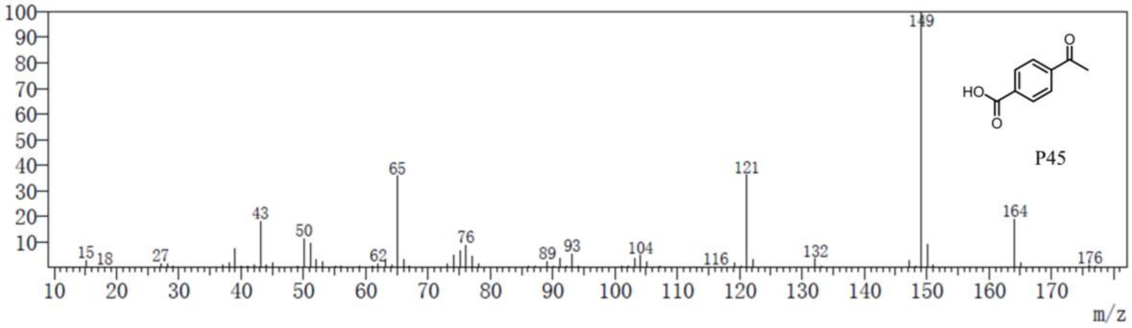
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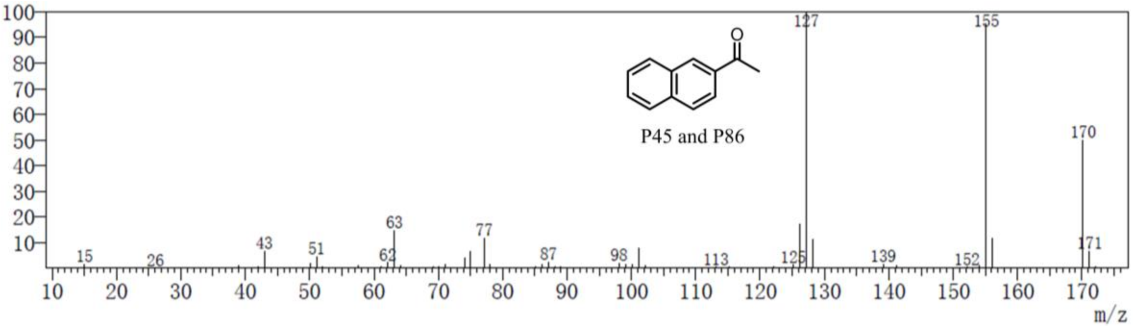
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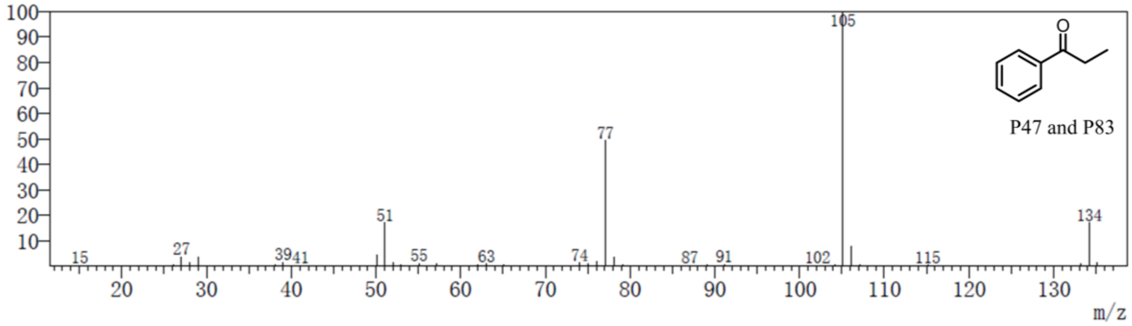

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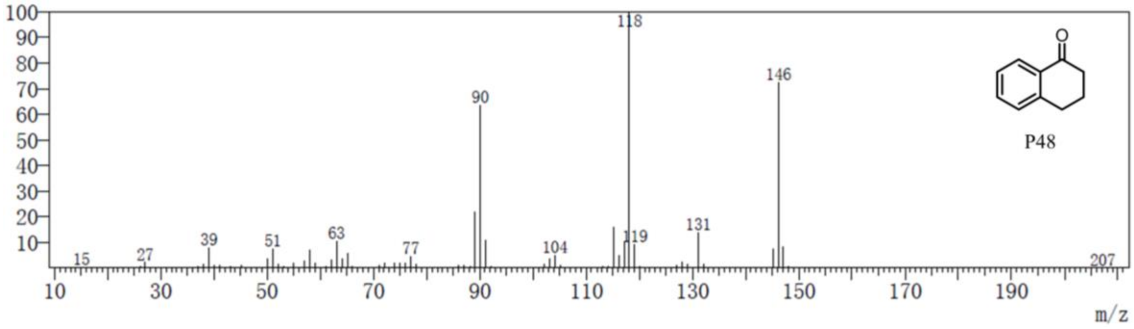

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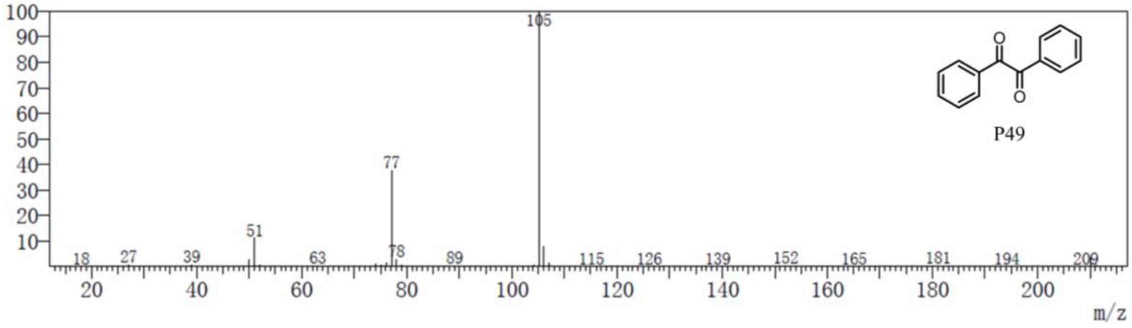

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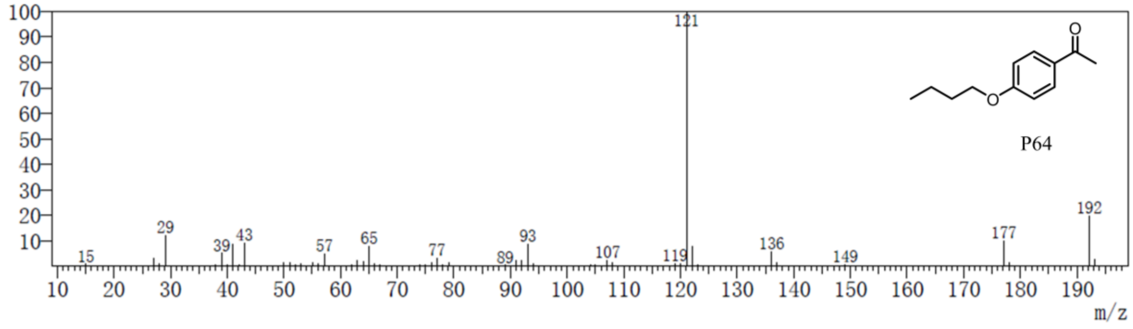

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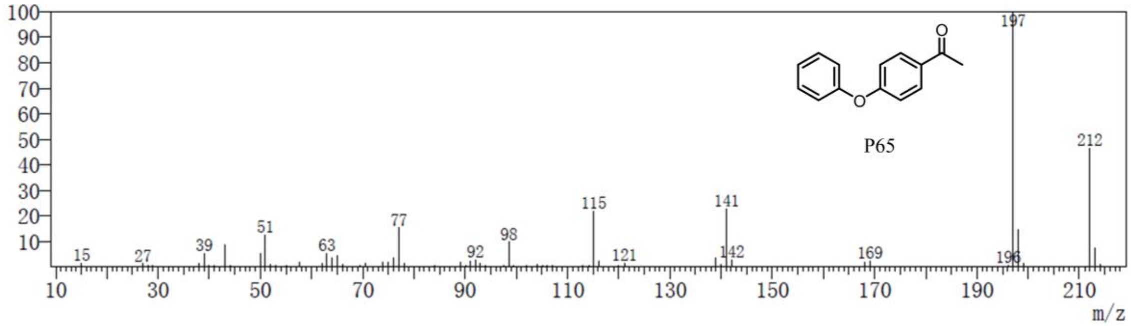

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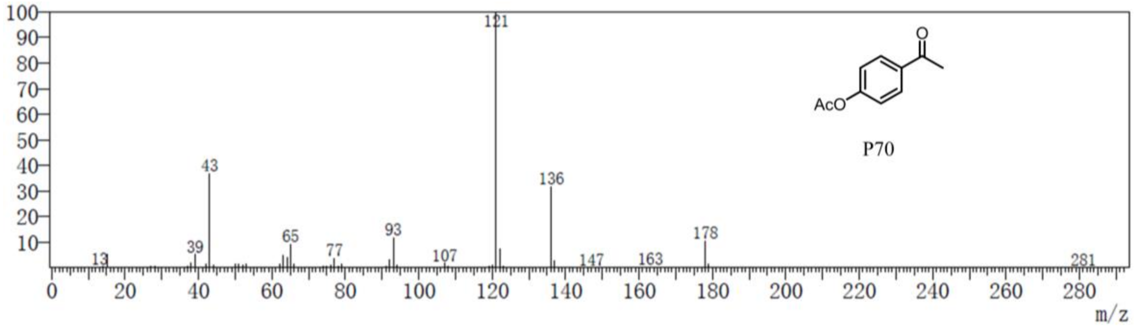

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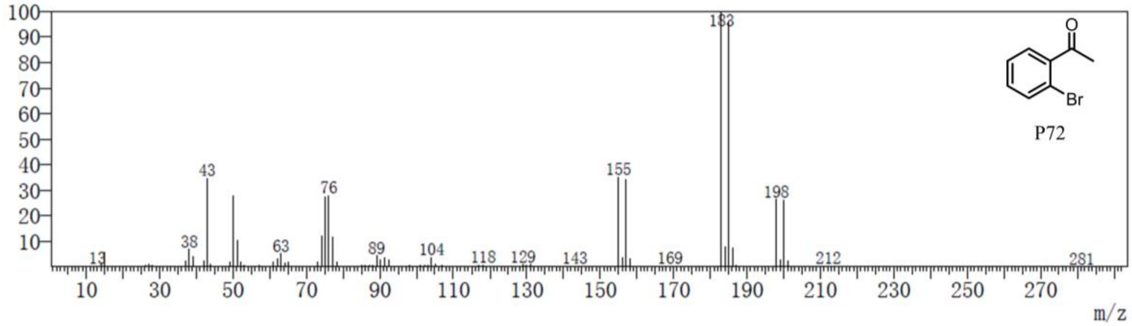

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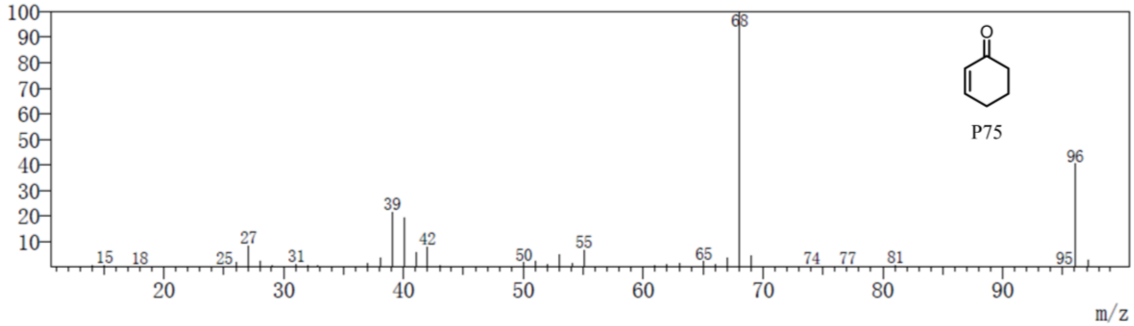

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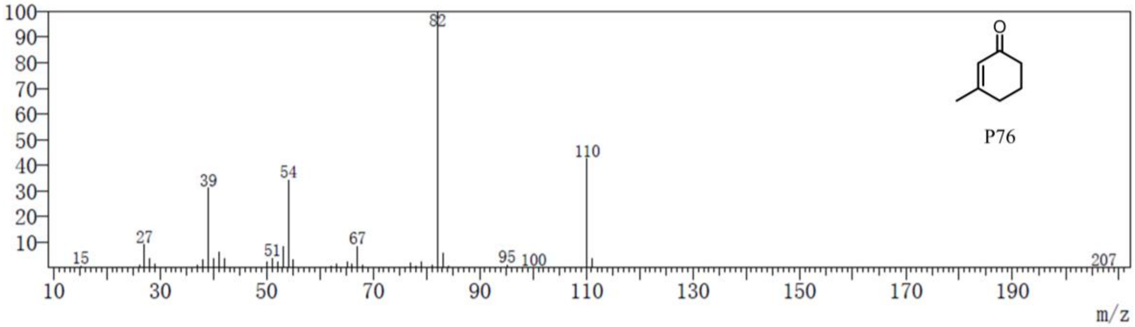

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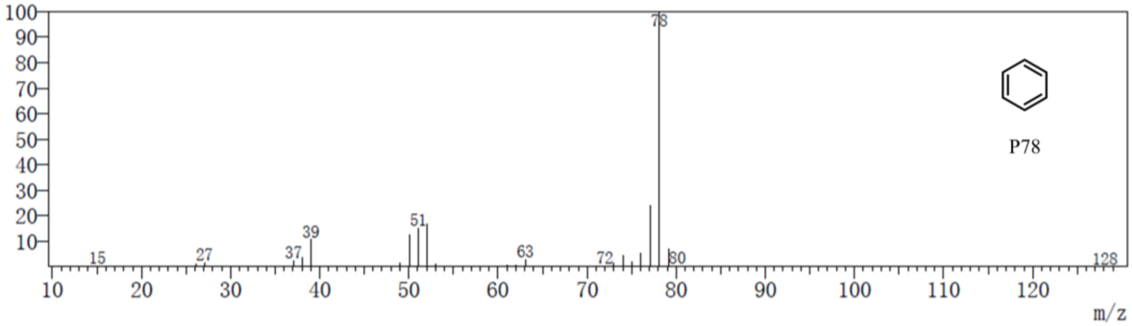

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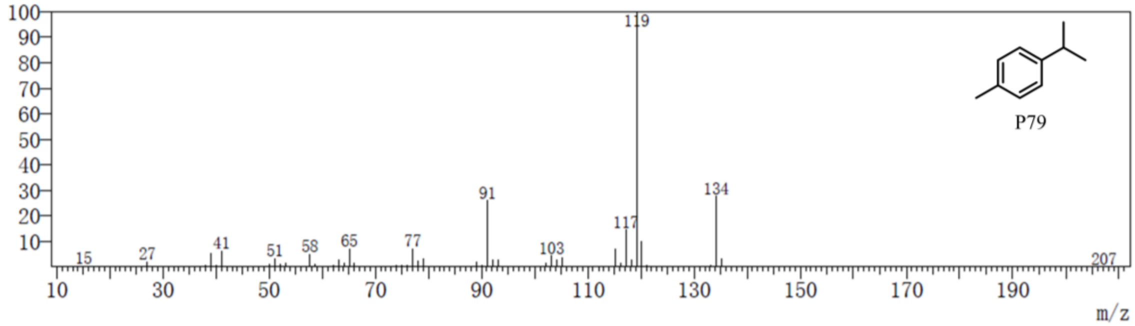

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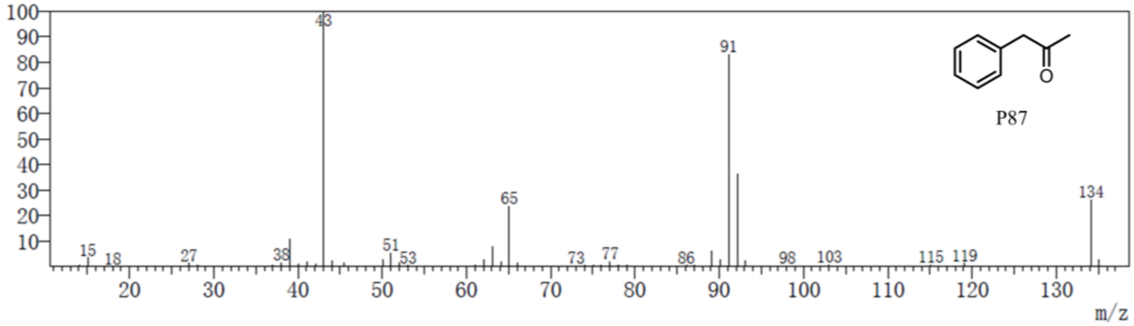

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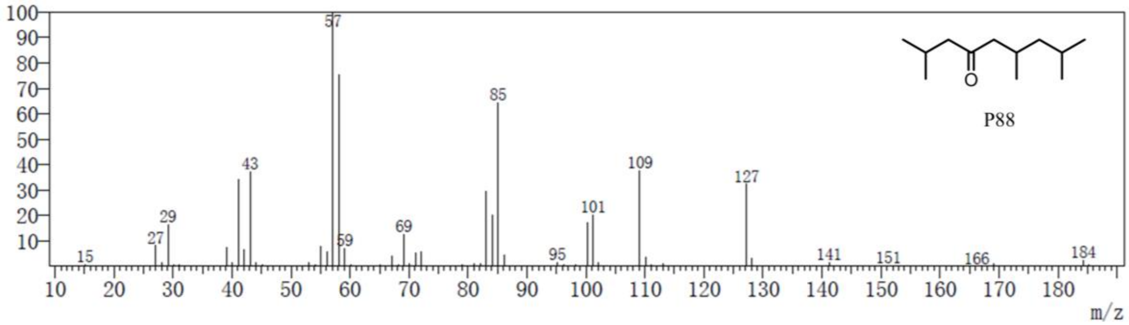

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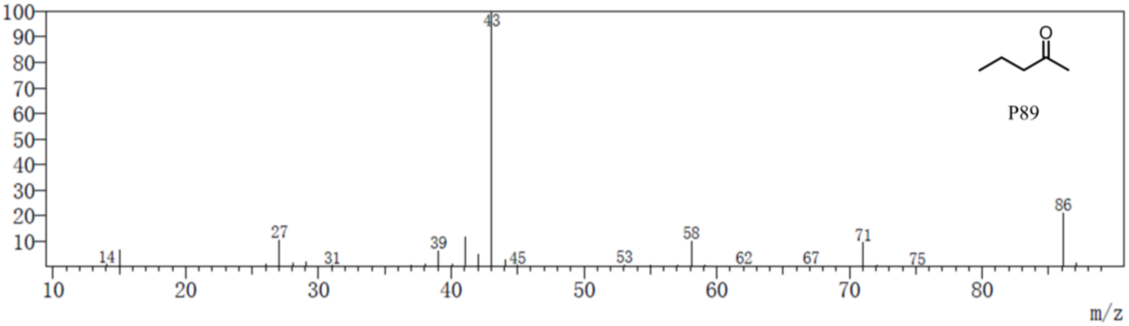

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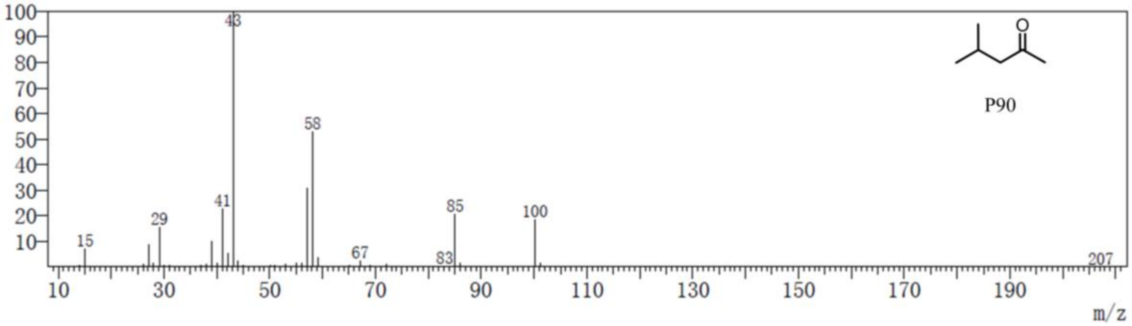

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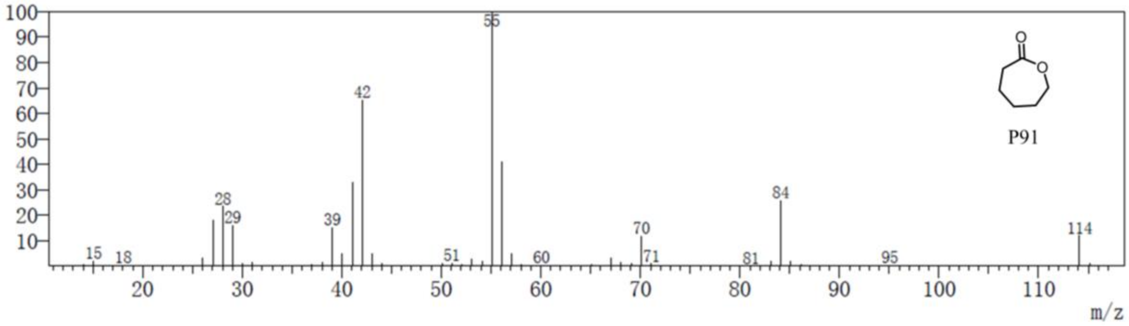

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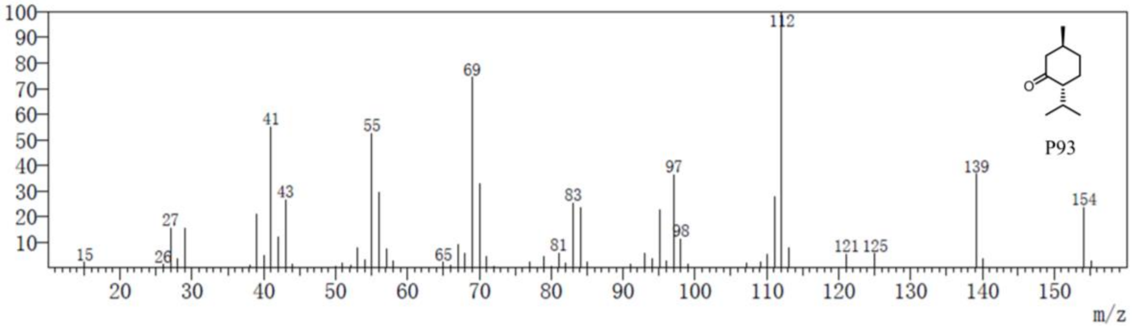
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