# Electronic Supplementary Information

## Aerobic Oxyfunctionalization of Alkynes by A Bioinspired Flavin-Metal Ion Photocatalytic System

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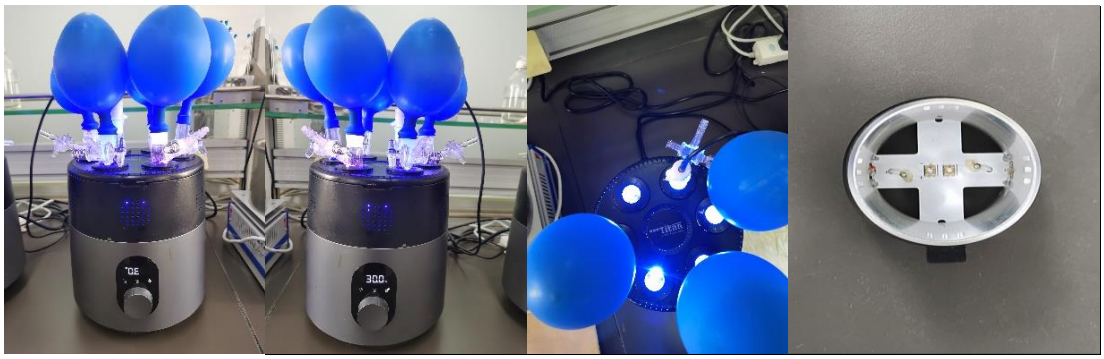
## 1. General Remarks

Nuclear magnetic resonance (NMR) spectroscopy was performed at 500 MHz ($^{1}$H-NMR), 126 MHz ($^{13}$C-NMR) and 470 MHz ($^{19}$F-NMR) on Bruker Avance III HD 500 instruments. Chemical shifts (δ) were provided in ppm and were referenced to the TMS and the residual solvent signal ($^{1}$H NMR: TMS at 0.00 ppm, $CDCl_3$ at 7.26 ppm and DMSO-$d_6$ at 2.50 ppm; $^{13}$C NMR: $CDCl_3$ at 77 ppm and DMSO-$d_6$ at 40 ppm). Gas Chromatography (GC) and mass spectra (MS) were obtained from Agilent 8890/7000D GC-MS (EI-MS, 70 eV) equipped with HP-5 MS 30 m × 0.5 mm × 0.25 μm column. HR-MS were measured by an Agilent 1290 Infinity II/6564 LC-MS system. UV-Vis spectroscope was recorded on an Agilent Cary 8454 diode array spectrophotometer. Fluorescence quenching was analyzed with a Hitachi F-7000 FL fluorescence spectrometer. cyclic voltammetry was measured by a CHI660E electrochemical workstation (Chenhua, Shanghai). The data of single crystals were collected on a SMART APEX CCD X-Ray diffractometer. The catalytic reactions were performed with a multi-station reactor perchased from Shanghai Taitan Science Co. Ltd. (P. R. China). And the temperature and irradiation power could be set and controlled by the reactor. The single crystals of **g7** and **g15** for X-ray diffraction were obtained by a slow evaporation of the corresponding hexene/DCM solutions. Unless otherwise stated, analytical pure reagents and solvents (including anhydrous solvents) were purchased from Adamas-beta® and Energy Chemical Co. Ltd. while used without further purification. Riboflavin tetraacetate (RFT) were prepared by the acetylation of RF according to literature procedure.[1] Alkynes (**a1**-**a12**, **d1**-**d20**, **d22**, **d24**-**d33**, **f1**, **f8** and **f9**) were known compounds that were prepared by the well-known Sonogashira coupling methods with the commercially available ArI and terminal alkynes.[2] The synthesis of new compounds (substrates) was performed according to previously described methods and the characterization data were presented *vide infra* (*Section 8 in SI*). All catalytic reactions were carried out in Schlenk tubes with a Teflon-coated magnetic stir bar and an air, $N_2$, or $^{18}O_2$ balloon. Synthesis and catalytic reactions were monitored by thin layer chromatography (TLC) and the products were purified by column chromatography on silica gel (200-300 mesh).

## 2. Experimental Section

**Typical procedure of photocatalytic reactions.** In a 10 mL of Schlenk tube equipped with a magnetic stirring bar, the substrates (**a1**, 0.2 mmol), RFT (3 mol%), $Sc(OTf)_3$ (6 mol%) and the anhydrous MeOH or other alcohols (2 mL) were added. Having charged with an air balloon (atmospheric pressure), then the tube was irradiated under a 3 W blue LED (450 nm) with continuous stirring at defined reaction temperature and time (see pictures below). The reaction course was monitored by TLC. After completion of the reaction, solvents were evaporated under reduced pressure. Then the residue was purified by chromatography column on silica gel by EtOAc/petroleum ether to obtain the desired products.



**Typical procedure of gram-scale reaction.** In a 100 mL of Schlenk flask equipped with a magnetic stirring bar, diphenyl acetylene (**a1**, 6 mmol), RFT (3.0 mol%), $Sc(OTf)_3$ (6.0 mol%) and MeOH (50 mL) were added. Then the mixture was stirred and irradiated under a 3 W blue LED (450 nm) at 30 $^oC$ with air bubbling (ca. 2 bubbles/sec) every 10 min by a syringe and a small pump. The reaction course was monitored by TLC. After completion of the reaction, the same work-up of typical reaction procedure was conducted to get the product.

**Typical procedure of blank experiments.** Following the typical procedure of photocatalytic reaction, the blank experiments were carried out in the absence of RFT, $Sc(OTf)_3$, light or dioxygen, respectively. After the defined time, the same work-up of typical reaction was conducted to detect the products.

**Procedure of control experiments.**

(a) With radical inhibitors: Following the typical procedure of photocatalytic reaction, 2 equivalents of TEMPO or 1,3-diphenylisobenzofuran were added to the reaction mixture under the

standard condition, respectively. After the defined time, the same work-up of typical reaction was conducted to detect the products.

(b) $^{18}$O-isotopical labelling experiment: Following the typical procedure of photocatalytic reaction, the Schlenk tube was charged with $^{18}$O-dioxygen rather than air under the standard condition. After the defined time, the same work-up of typical reaction was conducted to get the product which was further analyzed by GC-MS.

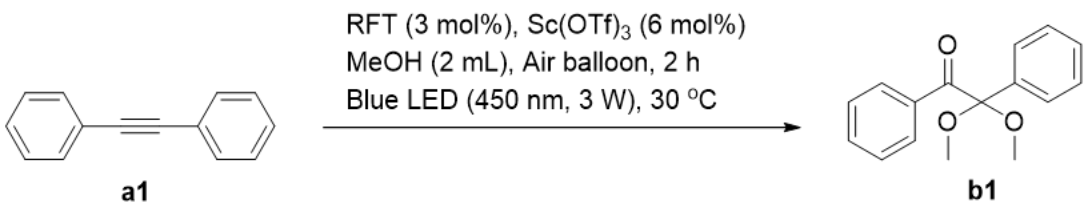
(c) Verify benzil and 1,2-diphenylethan-1-one as the possible intermediates: Following the typical procedure of photocatalytic reaction, the diketone benzil or 1,2-diphenylethan-1-one was used as the starting material instead of alkyne under the standard condition, respectively. After the defined time, the same work-up of typical reaction was conducted to detect the targeted products.

**Procedure of competitive reaction.** Following the typical procedure of photocatalytic reaction, equimolar of diphenyl acetylene (**a1**, 0.1 mmol) and its derivatives with di-*para*-substituted rings (**a2**, **a3**, **a4**, **a5**, and **a7**, each 0.1 mmol) were added under the standard condition, respectively. After 15 min, follow the same work-up with typical catalytic reaction to isolate the desired products. The relative ratio of product mixture was analyzed by $^1$H NMR. Then the relative reactivities $\log(k_X/k_H)$ (X = *t*-Bu, Me, H, F, Cl, $OCF_3$), expressed as the mole ratio of products, were plotted against the *para*-substitution constant σ to provide a Hammett relationship.

**Typical procedure of alkynediol substrates toward oxo-spiroketal products.** In a 10 mL of Schlenk tube equipped with a magnetic stirring bar, the substrate (**f1**-**f18**, 0.2 mmol), RFT (3 mol%), $Sc(OTf)_3$ (6 mol%) and 2 mL anhydrous MeCN (or mixed solvents of MeCN-DMF (v/v = 9/1) for substrates having poor solubility) were added in a batch. Having charged with an air balloon (atmospheric pressure), then the tube was irradiated under a 3 W blue LED (450 nm) with continuous stirring at defined reaction temperature and time. The reaction course was monitored by TLC. After completion of the reaction, solvents were evaporated under reduced pressure. Then the residue was purified by chromatography column on silica gel by EtOAc/petroleum ether to obtain the desired products.

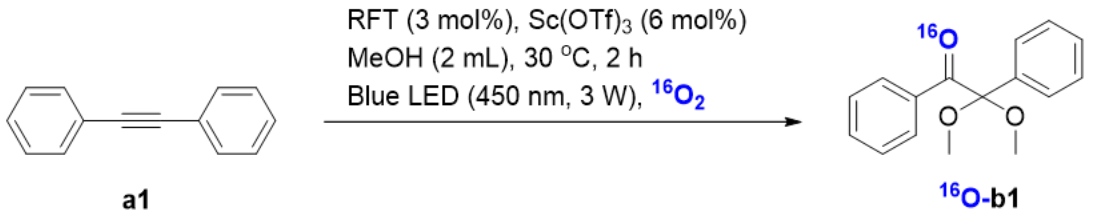
## 3. Table S1. Blank Experiments

**Table S1.** Results of blank experiments.

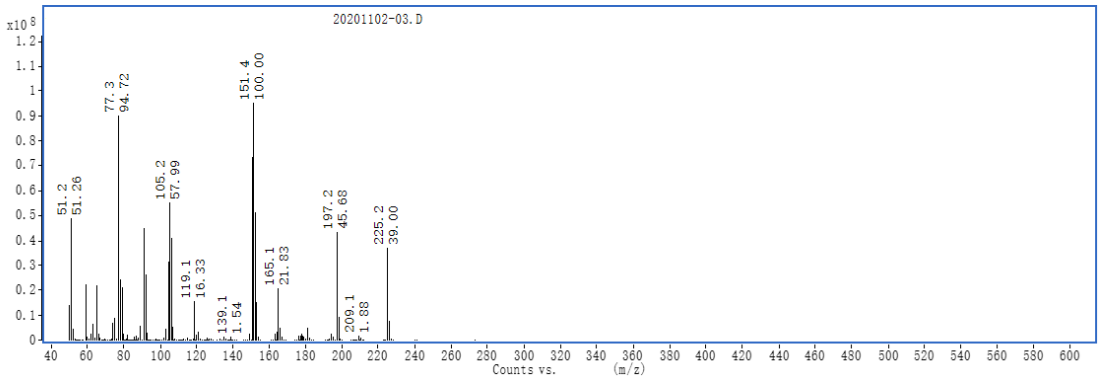


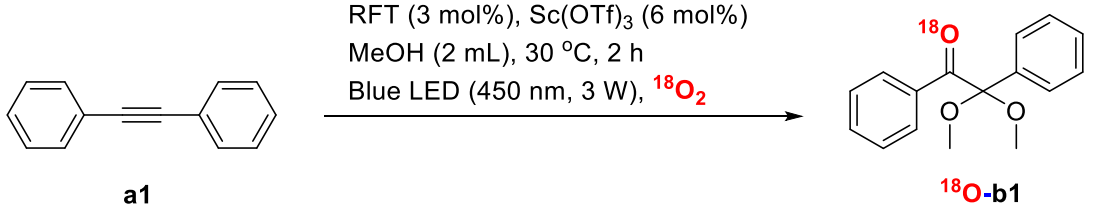

| Entry | RFT | $Sc(OTf)_3$ | *hv* | air | yield of **b1** |
|---|---|---|---|---|---|
| 1 | √ | √ | √ | √ | 90% |
| 2 | × | √ | √ | √ | trace |
| 3 | √ | × | √ | √ | trace |
| 4 | √ | √ | × | √ | trace |
| 5 | √ | √ | √ | × | trace |

## 4. GC-MS Spectra of $^{18}$O-Labelling Experiment

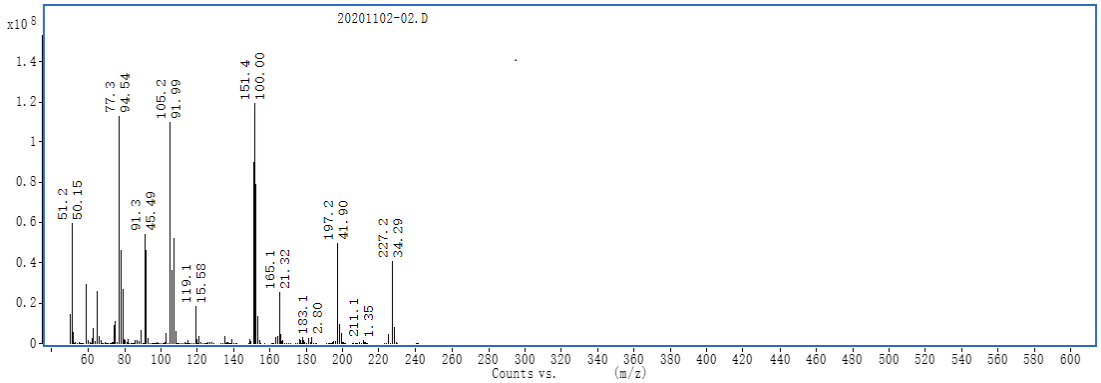



a1 $^{16}$O-b1




a1 $^{18}$O-b1



## 5. Fluorescence Quenching Experiments

All RFT solutions were excited at 440 nm and the emission intensity was collected at 510 nm.[3] In a typical experiment, to a 0.1 mM solution of RFT (or [RFT-2Sc$^{3+}$]) in MeCN was added the appropriate amount of quencher in a screw-top quartz cuvette. After degassing the sample with a stream of nitrogen for 5 minutes, the emission of the sample was collected at room temperature.

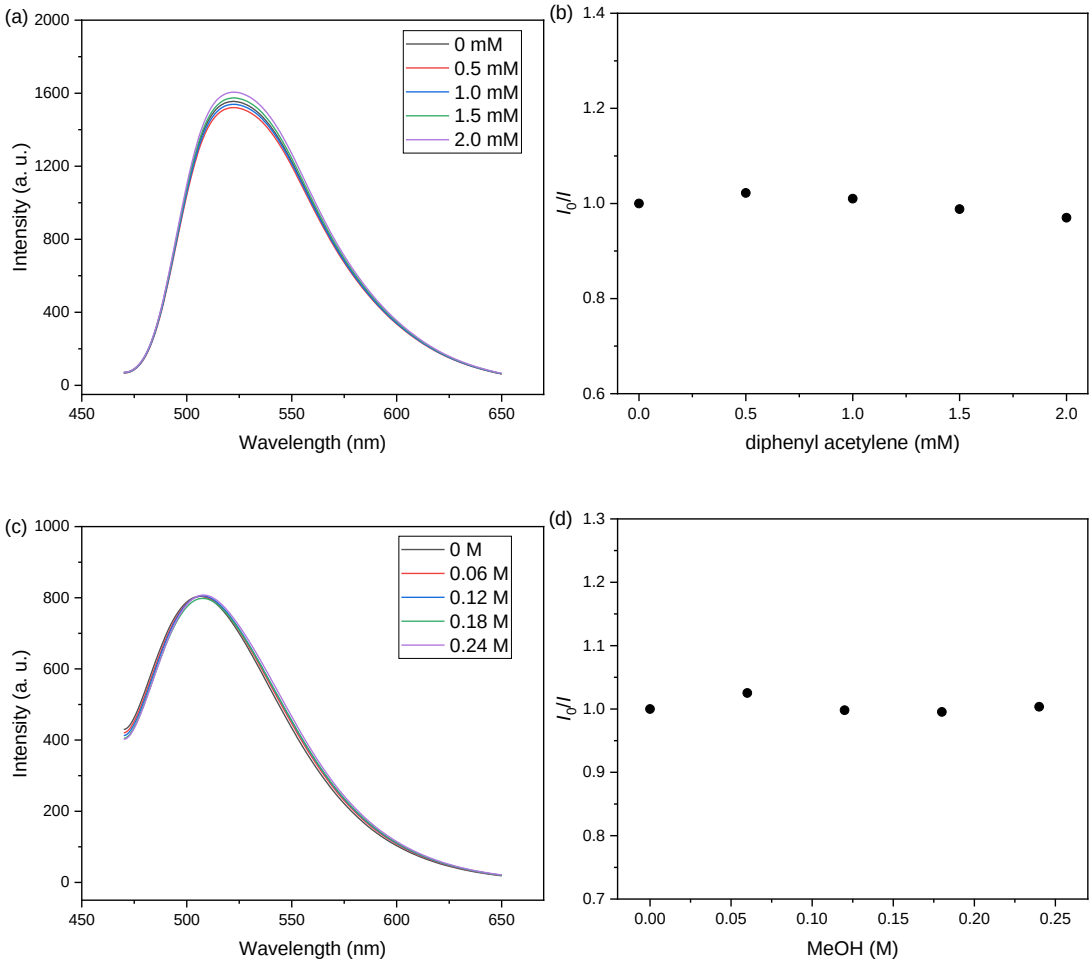



**Figure S1.** (a) Fluorescence quenching of RFT (0.1 mM) with diphenyl acetylene (**a1**) in deaerated MeCN. (b) Stern-Volmer plot of fluorescence quenching of RFT with **a1** in deaerated MeCN. (c) Fluorescence quenching of RFT (0.1 mM) with MeOH in deaerated MeCN. (d) Stern-Volmer plot of fluorescence quenching of RFT with MeOH in deaerated MeCN.

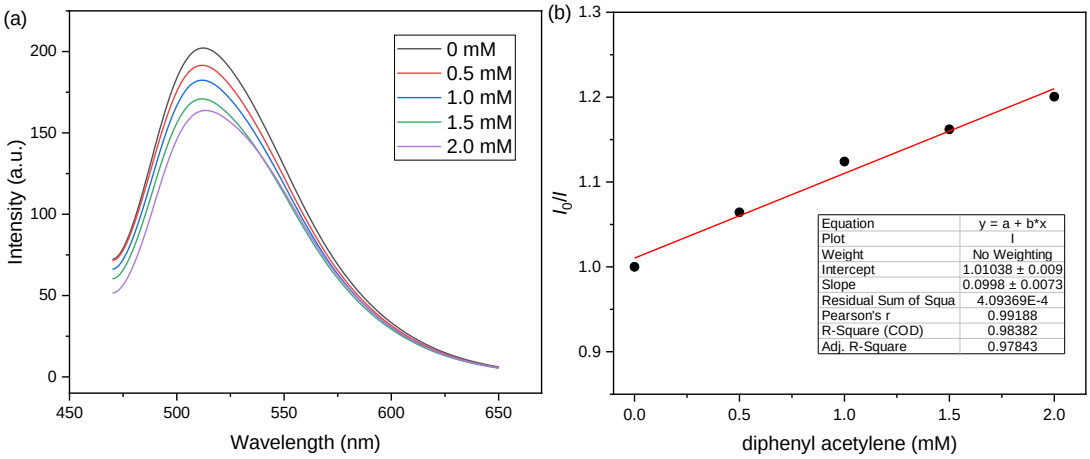



**Figure S2.** (a) Fluorescence quenching of [RFT-2Sc$^{3+}$] (0.1 mM) with diphenyl acetylene (**a1**) in deaerated MeCN. (b) Stern-Volmer plot of fluorescence quenching of RFT with **a1** in deaerated MeCN; $K_S$ = 10 $M^{-1}$.

## 6. UV-Vis Spectra

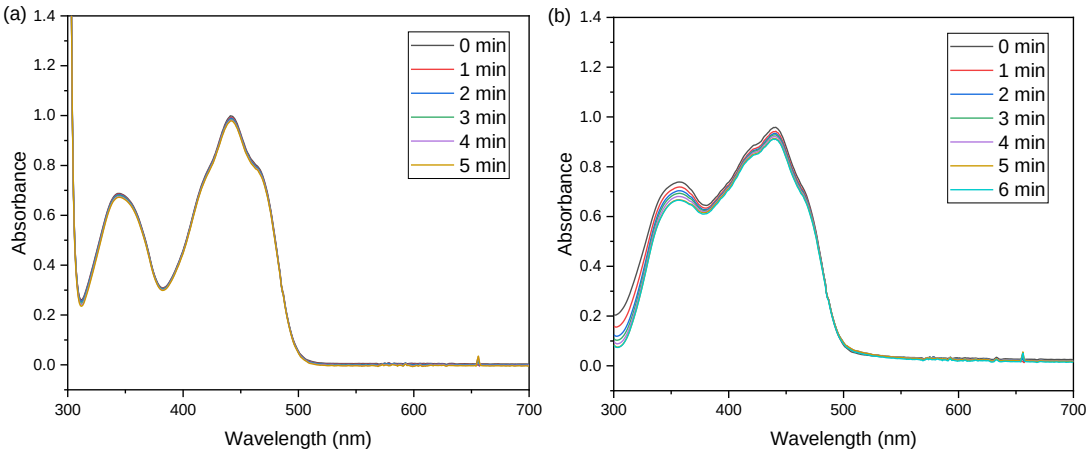



**Figure S3.** (a) UV-Vis absorption spectra of diphenyl acetylene (4 mM) and RFT (0.1 mM) in deaerated MeCN during irradiation with blue light at 298 K under nitrogen atmosphere. (b) UV-Vis absorption spectra of RFT (0.1 mM) and $Sc^{3+}$ (0.2 mM) in deaerated MeCN during irradiation with blue light at 298 K under nitrogen atmosphere.

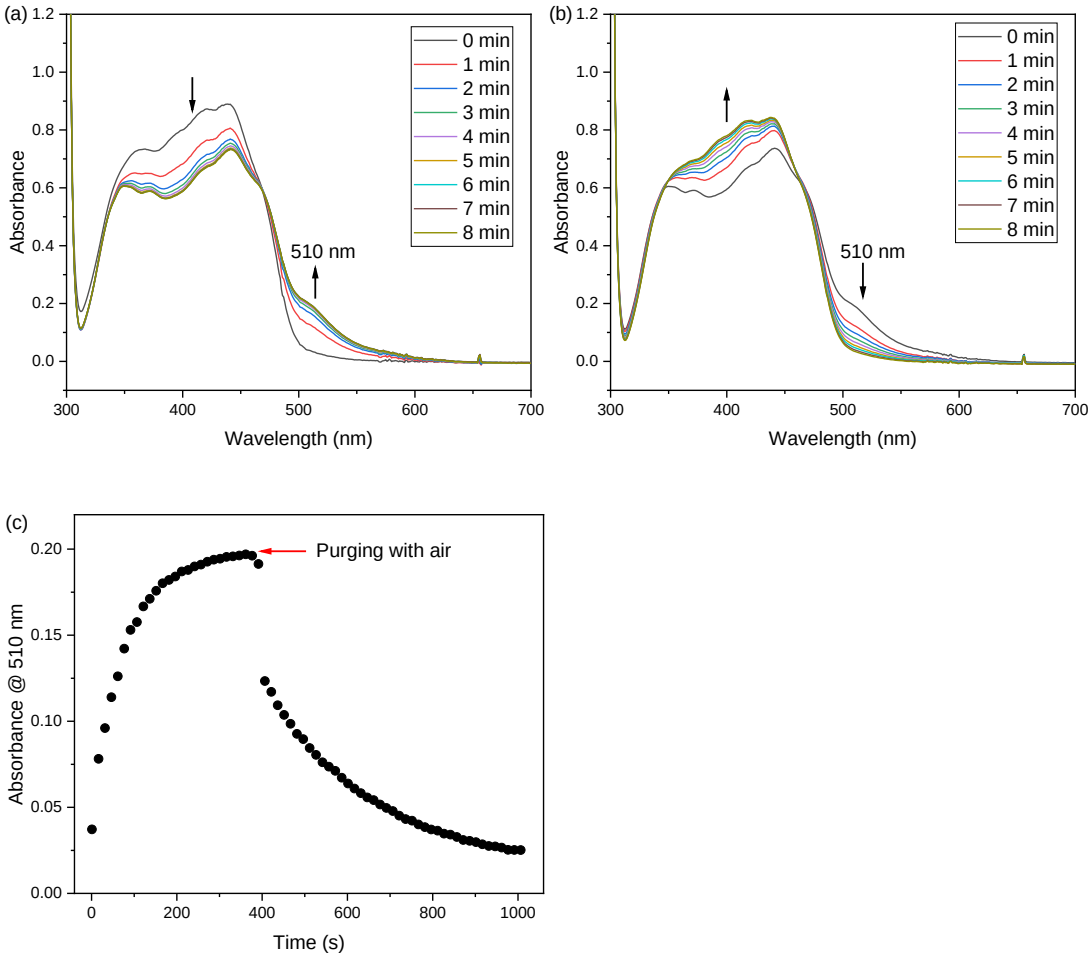



**Figure S4.** (a) UV-vis absorption spectra of diphenyl acetylene (4 mM) and RFT (0.1 mM) in the presence of $Sc(OTf)_3$ (0.2 mM) during irradiation with blue light in deaerated MeCN at 298 K under nitrogen. (b) Electronic absorption spectra of acetylene (4 mM) and RFT (0.1 mM) in the presence of $Sc(OTf)_3$ (0.2 mM) after 8 min of irradiation with blue light in deaerated MeCN and purging the solution with dioxygen. (c) Time trace of absorbance at $\lambda$ = 510 nm..

## 7. CV of Selected Alkynes

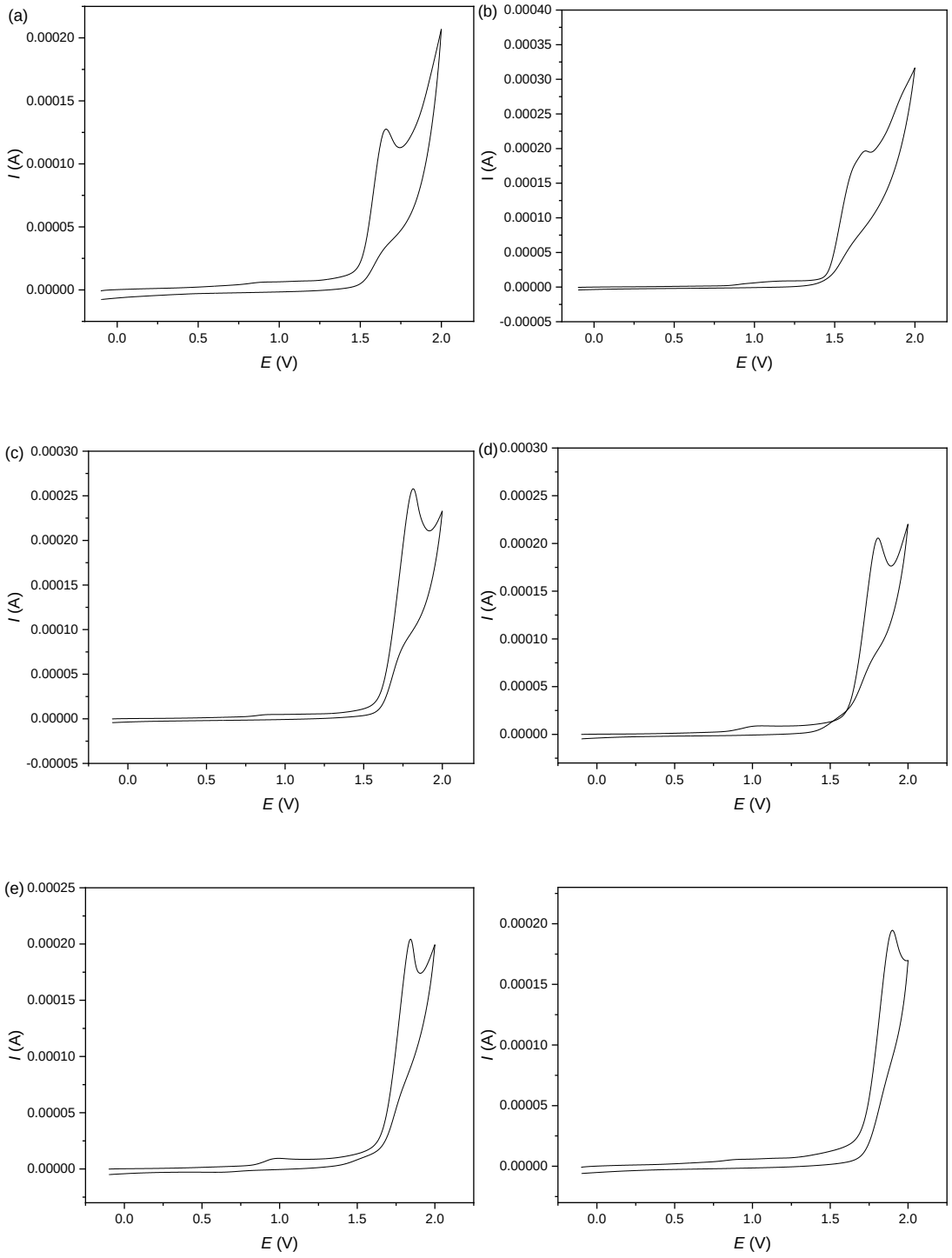
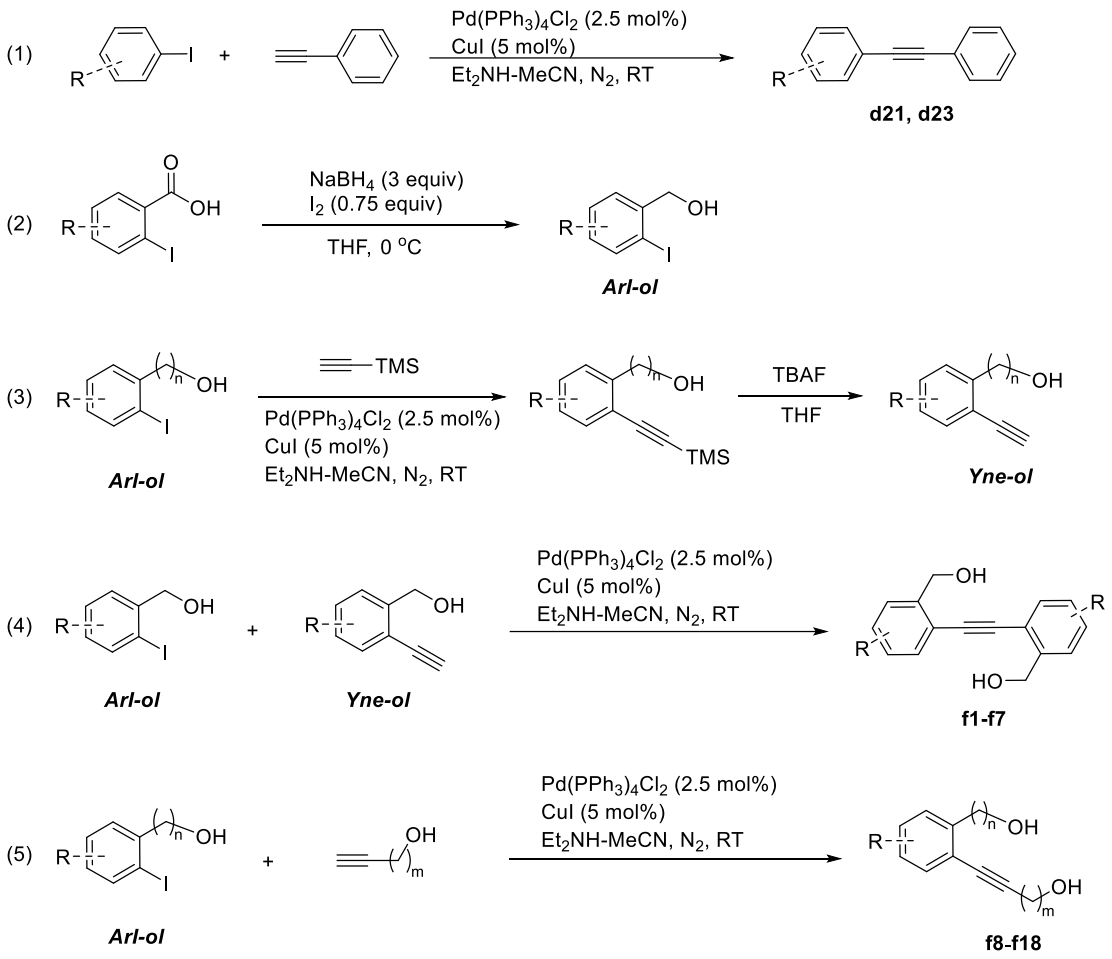



**Figure S5.** CV of (a) 1,2-bis(4-(tert-butyl)phenyl)ethyne (**a2**); (b) 1,2-di-p-tolylethyne (**a3**); (c) 1,2-diphenylethyne (**a1**); (d) 1,2-bis(4-fluorophenyl)ethyne (**a4**); (e) 1,2-bis(4-chlorophenyl)ethyne (**a5**); (f) 1,2-bis(4-(trifluoromethoxy)phenyl)ethyne (**a7**). Cyclic voltammetry (CV) conditions: alkyne (2 mM), $nBu_4NPF_6$ (0.1 M, electrolyte), deaerated and anhydrous MeCN (20 mL, solvent),

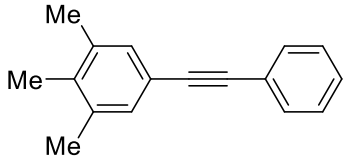
scan rate 100 mV/s, glass carbon (working electrode), Pt wire (counter electrode), Ag/AgCl (reference electrode).

## 8. Synthesis and Characterization Data of New Substrates




**Scheme S1.** Representative synthetic route of synthons and new substrates.

New diaryl acetylenes (**d21** and **d23**) were synthesized by the well-known Sonogashira coupling with commercially available aryl iodide and phenyl acetylene as the substrates. The synthons *ArI-ol*[4] and *Yne-ol*[5] were synthesized according to literature methods. The compounds **f1-f18** were also prepared by Sonogashira coupling using the corresponding *ArI-ol* and *Yne-ol* (or commercially available alkynols) as the starting materials.

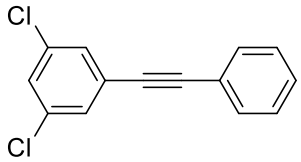



1,2,3-trimethyl-5-(phenylethynyl)benzene (**d21**)

$^{1}$H NMR (500 MHz, Chloroform-*d*) δ 7.53 – 7.48 (m, 2H), 7.34 – 7.27 (m, 3H), 7.19 (s, 2H), 2.27 (s, 6H), 2.17 (s, 3H).

$^{13}$C NMR (126 MHz, Chloroform-*d*) δ 136.56, 135.91, 131.56, 130.64, 128.31, 127.95, 123.71, 119.80, 89.90, 88.28, 20.43, 15.46.

HRMS (ESI): Cacld. for $[M+Na]^+$ 243.1150, found 243.1151.

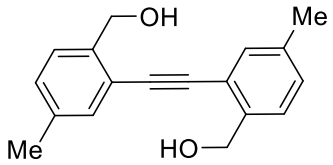



1,3-dichloro-5-(phenylethynyl)benzene (**d23**)

$^{1}$H NMR (500 MHz, Chloroform-*d*) δ 7.54 – 7.49 (m, 2H), 7.40 (d, *J* = 1.9 Hz, 2H), 7.38 – 7.34 (m, 3H), 7.32 (t, *J* = 1.9 Hz, 1H).

$^{13}$C NMR (126 MHz, Chloroform-*d*) δ 134.90, 131.75, 129.74, 128.96, 128.52, 128.47, 126.14, 122.28, 91.75, 86.67.

HRMS (ESI): Cacld. for $[M+Na]^+$ 268.9901, found 268.9898.

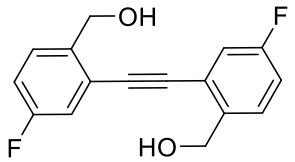



(ethyne-1,2-diylbis(4-methyl-2,1-phenylene))dimethanol (**f2**)

$^{1}$H NMR (500 MHz, DMSO-$d_6$) δ 7.43 (d, *J* = 7.8 Hz, 2H), 7.33 (d, *J* = 1.7 Hz, 2H), 7.23 (dd, *J* = 7.9, 1.8 Hz, 2H), 5.27 (t, *J* = 5.7 Hz, 2H), 4.69 (d, *J* = 5.7 Hz, 4H), 2.31 (s, 6H).

$^{13}$C NMR (126 MHz, DMSO-*d6*) δ 141.43, 136.36, 132.26, 129.89, 126.93, 120.17, 61.60, 20.83.

HRMS (ESI): Cacld. for $[M+Na]^+$ 289.1204, found 289.1206.



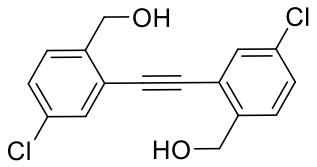

(ethyne-1,2-diylbis(4-fluoro-2,1-phenylene))dimethanol (**f3**)

$^{1}$H NMR (500 MHz, DMSO-$d_6$) δ 7.57 (dd, $J$ = 8.6, 5.9 Hz, 2H), 7.40 (dd, $J$ = 9.3, 2.7 Hz, 2H), 7.30 (td, $J$ = 8.6, 2.8 Hz, 2H), 5.41 (t, $J$ = 5.7 Hz, 2H), 4.70 (d, $J$ = 5.7 Hz, 4H).

$^{13}$C NMR (126 MHz, DMSO-$d_6$) δ 161.95, 160.01, 140.93, 140.91, 129.14, 129.07, 121.51, 121.43, 118.50, 118.32, 116.75, 116.58, 91.46, 91.43, 61.23.

$^{19}$F NMR (471 MHz, DMSO-$d_6$) δ -116.20.

HRMS (ESI): Cacld. for $[M+H]^+$ 275.0884, found 275.0885.

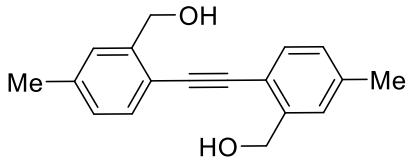



(ethyne-1,2-diylbis(4-chloro-2,1-phenylene))dimethanol (**f4**)

$^{1}$H NMR (500 MHz, DMSO-$d_6$) δ 7.63 (d, $J$ = 2.1 Hz, 2H), 7.57 (d, $J$ = 8.4 Hz, 2H), 7.51 (dd, $J$ = 8.4, 2.2 Hz, 2H), 5.46 (s, 2H), 4.71 (s, 4H).

$^{13}$C NMR (126 MHz, DMSO-$d_6$) δ 143.6, 131.6, 131.3, 129.6, 128.7, 121.6, 91.5, 61.2.

HRMS (ESI): Cacld. for $[M+Na]^+$ 329.0112, found 319.0117.

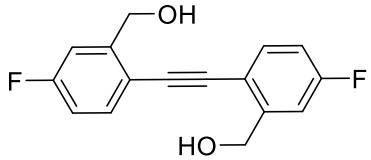



(ethyne-1,2-diylbis(5-methyl-2,1-phenylene))dimethanol (**f5**)

$^{1}$H NMR (500 MHz, Chloroform-$d$) δ 7.45 (d, $J$ = 7.7 Hz, 2H), 7.25 – 7.22 (m, 2H), 7.12 (dd, $J$ = 7.8, 1.7 Hz, 2H), 4.83 (s, 4H), 2.38 (s, 6H), 2.15 (s, 2H).

$^{13}$C NMR (126 MHz, Chloroform-$d$) δ 138.93, 132.25, 129.03, 128.54, 64.56, 21.49.

HRMS (ESI): Cacld. for $[M+Na]^+$ 289.1204, found 289.1199.



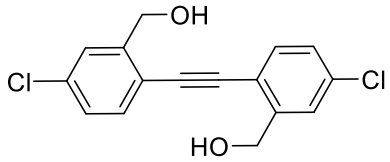

(ethyne-1,2-diylbis(5-fluoro-2,1-phenylene))dimethanol (**f6**)

$^{1}$H NMR (500 MHz, DMSO-$d_6$) δ 7.58 (dd, *J* = 8.5, 5.7 Hz, 2H), 7.33 (dd, *J* = 10.1, 2.8 Hz, 2H), 7.15 (td, *J* = 8.5, 2.8 Hz, 2H), 5.52 (t, *J* = 5.7 Hz, 2H), 4.72 (d, *J* = 5.7 Hz, 4H).

$^{13}$C NMR (126 MHz, DMSO-$d_6$) δ 163.82, 161.85, 148.00, 147.94, 134.29, 134.22, 116.08, 116.05, 114.39, 114.21, 113.63, 113.44, 90.60, 61.37.

$^{19}$F NMR (471 MHz, DMSO-$d_6$) δ -110.15.

HRMS (ESI): Cacld. for $[M+H]^+$ 275.0884, found 275.0888.

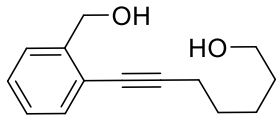



(ethyne-1,2-diylbis(5-chloro-2,1-phenylene))dimethanol (**f7**)

$^{1}$H NMR (500 MHz, DMSO-$d_6$) δ 7.60 – 7.53 (m, 4H), 7.38 (dd, *J* = 8.2, 2.3 Hz, 2H), 5.60 (t, *J* = 5.8 Hz, 2H), 4.73 (d, *J* = 5.8 Hz, 4H).

$^{13}$C NMR (126 MHz, DMSO-$d_6$) δ 147.0, 134.3, 133.8, 127.2, 126.6, 118.5, 91.8, 61.3.

HRMS (ESI): Cacld. for $[M+Na]^+$ 329.0112, found 319.0107.

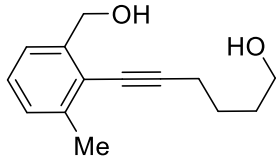



7-(2-(hydroxymethyl)phenyl)hept-6-yn-1-ol (**f10**)

$^{1}$H NMR (500 MHz, Chloroform-*d*) δ 7.42 – 7.36 (m, 2H), 7.27 (td, *J* = 7.5, 1.5 Hz, 1H), 7.21 (td, *J* = 7.5, 1.4 Hz, 1H), 4.78 (s, 2H), 3.64 (t, *J* = 6.0 Hz, 2H), 2.47 (t, *J* = 6.7 Hz, 2H), 2.37 (s, 3H), 1.60 (dddd, *J* = 26.1, 15.3, 11.9, 6.1 Hz, 6H).

$^{13}$C NMR (126 MHz, Chloroform-*d*) δ 142.3, 132.1, 128.0, 127.4, 127.4, 122.2, 95.05, 95.0, 78.5, 64.0, 62.6, 32.1, 28.4, 25.0, 19.5.

HRMS (ESI): Cacld. for $[M+H]^+$ 219.1385, found 219.1390.

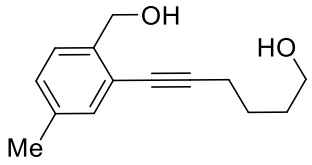



6-(2-(hydroxymethyl)-6-methylphenyl)hex-5-yn-1-ol (**f11**)

$^{1}$H NMR (500 MHz, Chloroform-*d*) δ 7.23 – 7.11 (m, 3H), 4.78 (s, 2H), 3.71 (t, *J* = 5.9 Hz, 2H), 2.56 (t, *J* = 6.4 Hz, 2H), 2.42 (s, 3H), 1.98 (s, 2H), 1.76 (dtdd, *J* = 12.3, 7.2, 5.5, 2.5 Hz, 4H).

$^{13}$C NMR (126 MHz, Chloroform-*d*) δ 142.5, 140.5, 128.6, 127.5, 124.8, 122.0, 99.3, 64.6, 62.3, 31.9, 25.2, 20.8, 19.5.

HRMS (ESI): Cacld. for $[M+Na]^+$ 241.1204, found 241.1200.

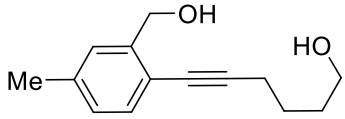



6-(2-(hydroxymethyl)-5-methylphenyl)hex-5-yn-1-ol (**f12**)

$^{1}$H NMR (500 MHz, Chloroform-*d*) δ 7.24 (d, *J* = 7.8 Hz, 1H), 7.21 (d, *J* = 1.8 Hz, 1H), 7.06 (dd, *J* = 7.8, 1.8 Hz, 1H), 4.71 (s, 2H), 3.64 (t, *J* = 6.2 Hz, 2H), 2.79 (s, 2H), 2.46 (t, *J* = 6.6 Hz, 2H), 2.29 (s, 3H), 1.78 – 1.62 (m, 4H).

$^{13}$C NMR (126 MHz, Chloroform-*d*) δ 139.3, 137.0, 132.6, 128.7, 127.4, 121.9, 94.3, 78.7, 63.6, 62.0, 31.7, 24.9, 20.8, 19.2.

HRMS (ESI): Cacld. for $[M+Na]^+$ 241.1204, found 241.1200.

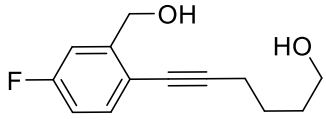



6-(2-(hydroxymethyl)-4-methylphenyl)hex-5-yn-1-ol (**f13**)

$^{1}$H NMR (500 MHz, Chloroform-*d*) δ 7.29 (d, *J* = 7.8 Hz, 1H), 7.21 – 7.17 (m, 1H), 7.02 (dd, *J* = 7.8, 1.7 Hz, 1H), 5.29 (s, 1H), 4.74 (s, 2H), 3.69 (t, *J* = 6.1 Hz, 2H), 2.48 (t, *J* = 6.6 Hz, 2H), 2.33 (s, 3H), 2.28 (s, 2H), 1.79 – 1.65 (m, 4H).

$^{13}$C NMR (126 MHz, Chloroform-*d*) δ 142.1, 138.1, 132.1, 128.3, 128.2, 119.1, 94.1, 78.6, 64.1, 62.3, 53.4, 31.8, 25.0, 21.4, 19.4.

HRMS (ESI): Cacld. for $[M+Na]^+$ 241.1204, found 241.1199.



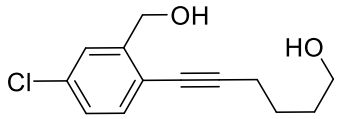

6-(4-fluoro-2-(hydroxymethyl)phenyl)hex-5-yn-1-ol (**f14**)

$^{1}$H NMR (500 MHz, Chloroform-*d*) δ 7.35 (dd, *J* = 8.5, 5.6 Hz, 1H), 7.14 (dd, *J* = 9.4, 2.7 Hz, 1H), 6.90 (td, *J* = 8.4, 2.7 Hz, 1H), 4.77 (s, 2H), 3.70 (t, *J* = 6.1 Hz, 2H), 2.48 (t, *J* = 6.6 Hz, 2H), 2.25 (s, 3H), 1.78 – 1.65 (m, 4H).

$^{13}$C NMR (126 MHz, Chloroform-*d*) δ 163.27, 161.29, 145.15, 145.09, 133.78, 133.71, 117.66, 117.64, 114.32, 114.21, 114.15, 114.03, 94.56, 94.55, 77.54, 63.39, 63.38, 62.31, 31.78, 24.98, 19.28.

$^{19}$F NMR (471 MHz, Chloroform-*d*) δ -111.40.

HRMS (ESI): Cacld. for $[M+Na]^+$ 245.0954, found 245.0950.

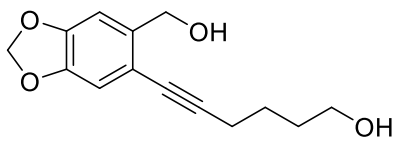



6-(4-chloro-2-(hydroxymethyl)phenyl)hex-5-yn-1-ol (**f15**)

$^{1}$H NMR (500 MHz, Chloroform-*d*) δ 7.41 (d, *J* = 2.2 Hz, 1H), 7.30 (d, *J* = 8.2 Hz, 1H), 7.18 (dd, *J* = 8.2, 2.2 Hz, 1H), 4.75 (s, 2H), 3.69 (t, *J* = 6.1 Hz, 2H), 2.48 (t, *J* = 6.6 Hz, 2H), 2.29 (s, 2H), 1.79 – 1.66 (m, 4H).

$^{13}$C NMR (126 MHz, Chloroform-*d*) δ 144.2, 133.9, 133.2, 127.4, 127.2, 120.3, 95.9, 77.6, 63.4, 62.3, 31.8, 24.9, 19.4.

HRMS (ESI): Cacld. for $[M+Na]^+$ 261.0658, found 261.0648.

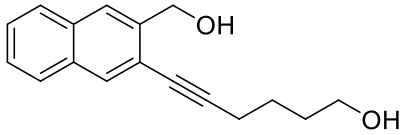



6-(6-(hydroxymethyl)benzo[d][1,3]dioxol-5-yl)hex-5-yn-1-ol (**f16**)

$^{1}$H NMR (500 MHz, Chloroform-*d*) δ 6.87 (s, 1H), 6.84 (s, 1H), 5.95 (s, 2H), 4.69 (s, 2H), 3.70 (t, *J* = 6.1 Hz, 2H), 2.47 (t, *J* = 6.6 Hz, 2H), 1.97 (s, 2H), 1.77 – 1.66 (m, 4H).

$^{13}$C NMR (126 MHz, Chloroform-*d*) δ 147.58, 146.67, 137.44, 115.36, 111.77, 108.31, 101.33, 93.24, 78.46, 63.90, 62.33, 31.84, 25.04, 19.31.

HRMS (ESI): Cacld. for $[M+Na]^+$ 271.0946, found 271.0947.

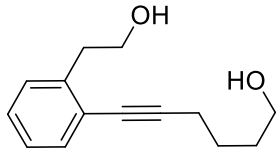



6-(3-(hydroxymethyl)naphthalen-2-yl)hex-5-yn-1-ol (**f17**)

$^1$H NMR (500 MHz, Chloroform-*d*) δ 7.91 (s, 1H), 7.80 (s, 1H), 7.79 – 7.71 (m, 2H), 7.44 (tt, *J* = 7.2, 3.5 Hz, 2H), 4.91 (s, 2H), 3.70 (t, *J* = 6.1 Hz, 2H), 2.52 (t, *J* = 6.6 Hz, 2H), 2.33 – 2.22 (m, 2H), 1.75 (dddd, *J* = 21.1, 8.7, 5.0, 2.2 Hz, 4H).

$^{13}$C NMR (126 MHz, DMSO-$d_6$) δ 140.87, 132.66, 131.97, 131.39, 127.96, 127.64, 127.08, 126.40, 124.43, 119.51, 95.74, 78.59, 61.84, 60.68, 32.20, 25.46, 19.20.

HRMS (ESI): Cacld. for $[M+H]^+$ 255.1385, found 255.1373.



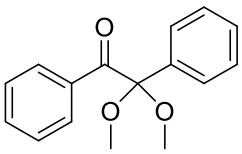

6-(2-(2-hydroxyethyl)phenyl)hex-5-yn-1-ol (**f18**)

$^1$H NMR (500 MHz, Chloroform-*d*) δ 7.38 (d, *J* = 7.6 Hz, 1H), 7.20 (d, *J* = 6.0 Hz, 2H), 7.14 (td, *J* = 6.9, 6.4, 2.6 Hz, 1H), 3.83 (t, *J* = 7.4 Hz, 2H), 3.68 (t, *J* = 6.4 Hz, 2H), 3.05 (t, *J* = 7.4 Hz, 2H), 2.86 (s, 2H), 2.49 (t, *J* = 6.6 Hz, 2H), 1.84 – 1.64 (m, 4H).

$^{13}$C NMR (126 MHz, Chloroform-*d*) δ 139.9, 132.1, 129.4, 127.7, 126.3, 123.7, 93.6, 79.5, 62.8, 62.1, 38.3, 31.7, 24.9, 19.3.

HRMS (ESI): Cacld. for $[M+H]^+$ 219.1385, found 219.1372.

## 9. Characterization Data of Isolated Compounds

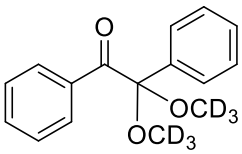


2,2-dimethoxy-1,2-diphenylethan-1-one (**b1**): Following the general procedure of catalytic reactions, the title product was purified on a silicon column with EtOAc/PE (v/v = 1/25) as the eluents and isolated as a colorless oil (45.7 mg, 90% yield).

$^{1}$H NMR (500 MHz, Chloroform-d) δ 8.06 (dd, J = 8.2, 1.4 Hz, 2H), 7.62 (dt, J = 6.3, 1.3 Hz, 2H), 7.45 – 7.39 (m, 1H), 7.35 (t, J = 7.2 Hz, 2H), 7.29 (t, J = 7.7 Hz, 3H), 3.22 (s, 6H).

$^{13}$C NMR (126 MHz, Chloroform-d) δ 195.2, 136.9, 134.3, 132.8, 130.0, 128.9, 128.5, 128.1, 126.9, 103.6, 50.1.

GC-MS (EI): [M-OMe] (225.2, 39%), [M-PhCO] (151.4, 100%)

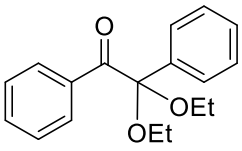


2,2-bis(methoxy-$d_3$)-1,2-diphenylethan-1-one (**b2**): Following the general procedure of catalytic reactions, the title product was purified on a silicon column with EtOAc/PE (v/v = 1/25) as the eluents and isolated as a colorless oil (47.1 mg, 90% yield).

$^{1}$H NMR (500 MHz, Chloroform-d) δ 8.06 (d, J = 7.8 Hz, 2H), 7.62 (d, J = 7.6 Hz, 2H), 7.42 (t, J = 7.4 Hz, 1H), 7.35 (t, J = 7.5 Hz, 2H), 7.29 (t, J = 7.6 Hz, 3H).

$^{13}$C NMR (126 MHz, Chloroform-d) δ 195.2, 136.9, 134.3, 132.9, 130.0, 128.9, 128.5, 128.1, 126.9, 103.5, 49.79, 49.62, 49.44, 49.27, 49.10, 48.92, 48.75.

LC-MS (ESI): found 285.1 for $[M+Na]^{+}$.

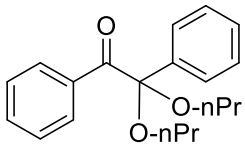


2,2-diethoxy-1,2-diphenylethan-1-one (**b3**): Following the general procedure of catalytic reactions, the title product was purified on a silicon column with EtOAc/PE (v/v = 1/25) as the eluents and isolated as a colorless solid (49.4 mg, 87% yield).

$^1$H NMR (500 MHz, Chloroform-d) δ 8.08 – 8.03 (m, 2H), 7.68 – 7.63 (m, 2H), 7.43 – 7.38 (m, 1H), 7.34 (dd, J = 8.2, 6.7 Hz, 2H), 7.28 (td, J = 10.0, 8.9, 3.0 Hz, 3H), 3.42 (dtt, J = 16.5, 9.5, 7.0 Hz, 4H), 1.20 (t, J = 7.0 Hz, 6H).

$^{13}$C NMR (126 MHz, Chloroform-d) δ 195.5, 137.8, 134.5, 132.6, 130.0, 128.7, 128.4, 128.0, 126.9, 103.1, 58.2, 15.1.

LC-MS (ESI): found 307.1 for $[M+Na]^+$.

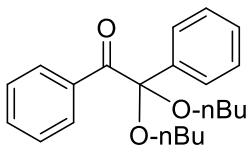



1,2-diphenyl-2,2-dipropoxyethan-1-one (**b4**): Following the general procedure of catalytic reactions, the title product was purified on a silicon column with EtOAc/PE (v/v = 1/25) as the eluents and isolated as a colorless oil (49.9 mg, 80% yield).

$^1$H NMR (500 MHz, Chloroform-d) δ 8.07 – 8.02 (m, 2H), 7.66 – 7.61 (m, 2H), 7.40 (t, J = 7.4 Hz, 1H), 7.34 (t, J = 7.5 Hz, 2H), 7.31 – 7.25 (m, 3H), 3.31 (qt, J = 9.1, 6.7 Hz, 4H), 1.61 (q, J = 7.1 Hz, 4H), 0.90 (t, J = 7.4 Hz, 6H).

$^{13}$C NMR (126 MHz, Chloroform-d) δ 195.5, 138.0, 134.6, 132.6, 130.0, 128.7, 128.4, 128.0, 126.9, 102.8, 64.0, 22.8, 10.8.

LC-MS (ESI): found 335.2 for $[M+Na]^+$.

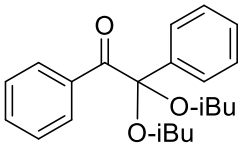



2,2-dibutoxy-1,2-diphenylethan-1-one (**b5**): Following the general procedure of catalytic reactions, the title product was purified on a silicon column with EtOAc/PE (v/v = 1/25) as the eluents and isolated as a colorless oil (51.0 mg, 75% yield).

$^1$H NMR (500 MHz, Chloroform-d) δ 8.06 – 8.01 (m, 2H), 7.63 (dt, J = 6.1, 1.4 Hz, 2H), 7.40 (td, J = 7.2, 1.4 Hz, 1H), 7.34 (t, J = 7.2 Hz, 2H), 7.30 – 7.25 (m, 3H), 3.34 (qt, J = 9.1, 6.6 Hz, 4H), 1.60 – 1.53 (m, 4H), 1.37 (dt, J = 14.9, 7.5 Hz, 4H), 0.86 (t, J = 7.4 Hz, 6H).

$^{13}$C NMR (126 MHz, Chloroform-d) δ 195.5, 138.0, 134.6, 132.6, 130.0, 128.7, 128.4, 128.0, 126.9, 102.8, 62.1, 31.7, 19.4, 13.9.

LC-MS (ESI): found 363.2 for $[M+Na]^+$.

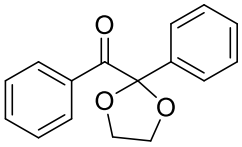



2,2-bis(isopentyloxy)-1,2-diphenylethan-1-one (**b6**): Following the general procedure of catalytic reactions, the title product was purified on a silicon column with EtOAc/PE (v/v = 1/25) as the eluents and isolated as a colorless oil (47.6 mg, 70% yield).

$^1$H NMR (500 MHz, Chloroform-d) δ 8.05 – 8.01 (m, 2H), 7.64 – 7.60 (m, 2H), 7.42 – 7.38 (m, 1H), 7.34 (dd, J = 8.2, 6.5 Hz, 2H), 7.31 – 7.25 (m, 3H), 3.16 – 3.07 (m, 4H), 1.89 (dp, J = 13.4, 6.7 Hz, 2H), 0.91 (dd, J = 6.7, 3.1 Hz, 12H).

$^{13}$C NMR (126 MHz, Chloroform-d) δ 195.5, 138.1, 134.7, 132.6, 130.0, 128.6, 128.4, 127.9, 126.9, 102.5, 68.6, 28.5, 19.6, 19.6.

HRMS (ESI): Cacld. for $[M+Na]^+$ 363.1936, found 363.1931.

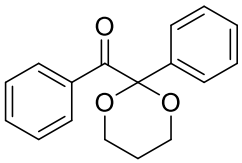



phenyl(2-phenyl-1,3-dioxolan-2-yl)methanone (**b7**): Following the general procedure of catalytic reactions, the title product was purified on a silicon column with EtOAc/PE (v/v = 1/25) as the eluents and isolated as a colorless oil (18.3 mg, 36% yield).

$^1$H NMR (500 MHz, Chloroform-*d*) δ 8.06 – 8.01 (m, 2H), 7.62 – 7.57 (m, 2H), 7.48 – 7.42 (m, 1H), 7.40 – 7.30 (m, 5H), 4.22 – 4.09 (m, 4H).

$^{13}$C NMR (126 MHz, Chloroform-*d*) δ 194.8, 137.5, 133.7, 133.0, 130.5, 129.2, 128.7, 128.1, 125.6, 109.3, 65.8.

HRMS (ESI): Cacld. for $[M+Na]^+$ 277.0841, found 277.0840.

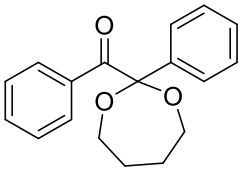


phenyl(2-phenyl-1,3-dioxan-2-yl)methanone (**b8**): Following the general procedure of catalytic reactions, the title product was purified on a silicon column with EtOAc/PE (v/v = 1/25) as the eluents and isolated as a colorless oil (24.1 mg, 45% yield).

$^1$H NMR (500 MHz, Chloroform-*d*) δ 8.14 – 8.07 (m, 2H), 7.64 (d, *J* = 7.5 Hz, 2H), 7.46 (t, *J* = 7.4 Hz, 1H), 7.39 – 7.27 (m, 5H), 4.14 – 4.00 (m, 4H), 2.08 (ddt, *J* = 18.8, 10.2, 5.1 Hz, 1H), 1.60 (dp, *J* = 13.7, 3.5 Hz, 1H).

$^{13}$C NMR (126 MHz, Chloroform-*d*) δ 196.7, 138.1, 134.5, 132.9, 130.1, 128.9, 128.5, 128.1, 126.2, 102.2, 62.9, 25.0.

HRMS (ESI): Cacld. for $[M+Na]^+$ 291.0997, found 291.0992.

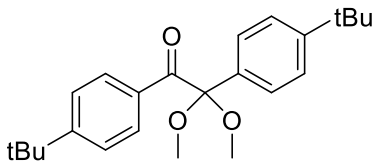


phenyl(2-phenyl-1,3-dioxepan-2-yl)methanone (**b9**): Following the general procedure of catalytic reactions, the title product was purified on a silicon column with EtOAc/PE (v/v = 1/25) as the eluents and isolated as a colorless oil (22.6 mg, 40% yield).

$^1$H NMR (500 MHz, Chloroform-*d*) δ 8.11 – 8.04 (m, 2H), 7.71 – 7.63 (m, 2H), 7.45 – 7.39 (m, 1H), 7.37 – 7.25 (m, 5H), 3.82 (tdd, *J* = 12.1, 9.2, 5.1 Hz, 4H), 1.73 (ttt, *J* = 14.9, 7.8, 3.3 Hz, 4H).

$^{13}$C NMR (126 MHz, Chloroform-*d*) δ 195.9, 138.5, 134.5, 132.5, 130.4, 128.7, 128.4, 127.9, 126.9, 104.8, 64.8, 29.1.

HRMS (ESI): Cacld. for $[M+Na]^+$ 305.1154, found 305.1163.

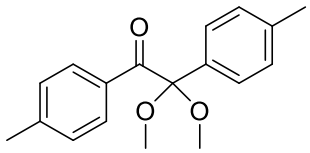



1,2-bis(4-(tert-butyl)phenyl)-2,2-dimethoxyethan-1-one (**c2**): Following the general procedure of catalytic reactions, the title product was purified on a silicon column with EtOAc/PE (v/v = 1/25) as the eluents and isolated as a colorless oil (51.1 mg, 69% yield).

$^{1}$H NMR (500 MHz, Chloroform-d) δ 8.06 – 8.01 (m, 2H), 7.57 – 7.51 (m, 2H), 7.38 – 7.30 (m, 4H), 3.19 (s, 6H), 1.28 (d, J = 3.5 Hz, 18H).

$^{13}$C NMR (126 MHz, Chloroform-d) δ 194.9, 156.409, 151.759, 133.859, 131.7, 130.1, 126.6, 125.4, 125.1, 103.8, 50.0, 35.0, 34.6, 31.3, 31.0.

LC-MS (ESI): found 391. for $[M+Na]^+$.

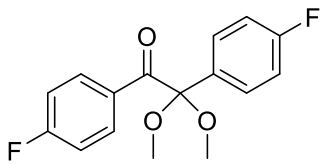



2,2-dimethoxy-1,2-di-p-tolylethan-1-one (**c3**): Following the general procedure of catalytic reactions, the title product was purified on a silicon column with EtOAc/PE (v/v = 1/25) as the eluents and isolated as a colorless oil (43.7 mg, 77% yield).

$^{1}$H NMR (500 MHz, Chloroform-d) δ 8.01 – 7.95 (m, 2H), 7.48 (d, J = 8.2 Hz, 2H), 7.14 (d, J = 8.0 Hz, 2H), 7.09 (d, J = 8.1 Hz, 2H), 3.20 (s, 6H), 2.31 (d, J = 3.4 Hz, 6H).

$^{13}$C NMR (126 MHz, Chloroform-d) δ 194.7, 143.6, 138.7, 134.1, 131.6, 130.2, 129.2, 128.8, 126.8, 103.6, 50.0, 21.6, 21.2.

LC-MS (ESI): found 307.1 for $[M+Na]^+$, 253.1 for $[M-OMe]^+$.



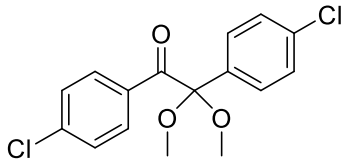
1,2-bis(4-fluorophenyl)-2,2-dimethoxyethan-1-one (**c4**): Following the general procedure of catalytic reactions, the title product was purified on a silicon column with EtOAc/PE (v/v = 1/25) as the eluents and isolated as a colorless oil (46.7 mg, 80% yield).

$^{1}$H NMR (500 MHz, Chloroform-d) δ 8.14 – 8.08 (m, 2H), 7.62 – 7.54 (m, 2H), 7.05 (t, J = 8.7 Hz, 2H), 7.02 – 6.95 (m, 2H), 3.21 (s, 6H).

$^{13}$C NMR (126 MHz, Chloroform-d) δ 193.4, 166.5, 164.5, 164.0, 162.0, 132.85, 132.77, 132.65, 132.62, 130.34, 130.31, 128.85, 128.78, 115.75, 115.58, 115.46, 115.29, 103.2, 50.1.

$^{19}$F NMR (471 MHz, Chloroform-d) δ -104.59, -112.26.

HRMS (ESI): Cacld. for $[M+Na]^+$ 315.0809, found 315.0809.

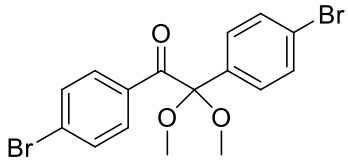



1,2-bis(4-chlorophenyl)-2,2-dimethoxyethan-1-one (**c5**): Following the general procedure of catalytic reactions, the title product was purified on a silicon column with EtOAc/PE (v/v = 1/25) as the eluents and isolated as a white solid (55.1 mg, 85% yield).

$^{1}$H NMR (500 MHz, Chloroform-d) δ 8.03 – 7.98 (m, 2H), 7.56 – 7.51 (m, 2H), 7.36 – 7.32 (m, 2H), 7.31 – 7.27 (m, 2H), 3.22 (s, 6H).

$^{13}$C NMR (126 MHz, Chloroform-d) δ 193.6, 139.6, 135.2, 132.2, 131.4, 128.9, 128.6, 128.3, 103.2, 50.2.

LC-MS (ESI): found 293.0 for $[M-OMe]^+$293.0.

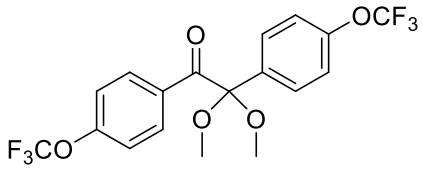



1,2-bis(4-bromophenyl)-2,2-dimethoxyethan-1-one (**c6**): Following the general procedure of catalytic reactions, the title product was purified on a silicon column with EtOAc/PE (v/v = 1/25) as the eluents and isolated as a white solid (72.7 mg, 88% yield).

$^{1}$H NMR (500 MHz, Chloroform-d) δ 7.92 (d, J = 8.7 Hz, 2H), 7.51 – 7.42 (m, 6H), 3.21 (s, 6H).

$^{13}$C NMR (126 MHz, Chloroform-d) δ 193.8, 135.7, 132.6, 131.9, 131.6, 131.5, 128.6, 128.5, 123.6, 103.2, 50.2.

HRMS (ESI): Cacld. for $[M\text{-}OMe]^+$ 380.9126 and 382.9106, found 380.9130 and 382.9112.



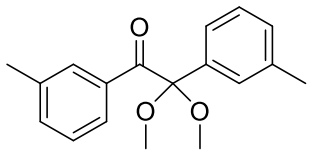

2,2-dimethoxy-1,2-bis(4-(trifluoromethoxy)phenyl)ethan-1-one (**c7**): Following the general procedure of catalytic reactions, the title product was purified on a silicon column with EtOAc/PE (v/v = 1/25) as the eluents and isolated as a colorless oil ( 62.7 mg, 74% yield).

$^1$H NMR (500 MHz, Chloroform-*d*) δ 8.16 – 8.11 (m, 2H), 7.68 – 7.63 (m, 2H), 7.24 – 7.19 (m, 2H), 7.15 (dq, *J* = 9.1, 1.1 Hz, 2H), 3.24 (s, 6H).

$^{13}$C NMR (126 MHz, Chloroform-*d*) δ 193.31, 152.52, 152.51, 149.74, 149.72, 135.15, 132.13, 132.08, 128.58, 121.35, 121.23, 120.83, 119.83, 119.30, 119.17, 103.24, 50.19.

$^{19}$F NMR (471 MHz, Chloroform-*d*) δ -57.65, -57.85.

HRMS (ESI): Cacld. for $[M+Na]^+$ 447.0643, found 447.0648.

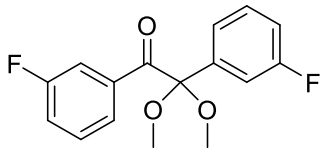



2,2-dimethoxy-1,2-di-m-tolylethan-1-one (**c8**): Following the general procedure of catalytic reactions, the title product was purified on a silicon column with EtOAc/PE (v/v = 1/25) as the eluents and isolated as a colorless oil (47.1 mg, 83% yield).

$^1$H NMR (500 MHz, Chloroform-d) δ 7.90 – 7.84 (m, 2H), 7.44 (d, J = 7.8 Hz, 1H), 7.39 (s, 1H), 7.24 (td, J = 8.0, 4.1 Hz, 2H), 7.17 (t, J = 7.9 Hz, 1H), 7.10 (d, J = 7.6 Hz, 1H), 3.20 (s, 6H), 2.31 (d, J = 6.3 Hz, 6H).

$^{13}$C NMR (126 MHz, Chloroform-d) δ 195.4, 138.1, 137.8, 136.8, 134.3, 133.7, 130.4, 129.6, 128.3, 127.9, 127.5, 127.3, 124.0, 103.6, 50.0, 21.5, 21.3.

LC-MS (ESI): found 253.1 for [M-OMe], and found 307.1 for $[M+Na]^+$.



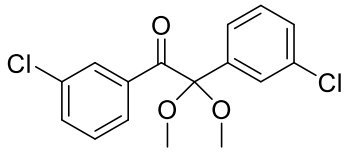
1,2-bis(3-fluorophenyl)-2,2-dimethoxyethan-1-one (**c9**): Following the general procedure of catalytic reactions, the title product was purified on a silicon column with EtOAc/PE (v/v = 1/25) as the eluents and isolated as a white solid (49.1 mg, 84% yield).

$^{1}$H NMR (500 MHz, Chloroform-*d*) δ 7.85 (dt, *J* = 7.9, 1.2 Hz, 1H), 7.76 (dt, *J* = 10.1, 2.1 Hz, 1H), 7.40 – 7.35 (m, 1H), 7.35 – 7.28 (m, 3H), 7.16 (td, *J* = 8.3, 2.6 Hz, 1H), 7.02 (ddt, *J* = 9.1, 6.0, 2.8 Hz, 1H), 3.24 (s, 6H).

$^{13}$C NMR (126 MHz, Chloroform-*d*) δ 193.53, 193.51, 163.93, 163.31, 161.96, 161.34, 139.22, 139.17, 135.90, 135.85, 130.37, 130.31, 129.94, 129.88, 125.72, 125.70, 122.61, 122.59, 120.28, 120.11, 116.81, 116.62, 116.29, 116.12, 114.24, 114.05, 103.06, 50.25.

$^{19}$F NMR (471 MHz, Chloroform-*d*) δ -111.66, -111.92.

HRMS (ESI): Cacld. for $[M+Na]^+$ 315.0809, found 315.0807.

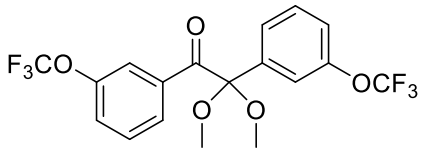


1,2-bis(3-chlorophenyl)-2,2-dimethoxyethan-1-one (**c10**): Following the general procedure of catalytic reactions, the title product was purified on a silicon column with EtOAc/PE (v/v = 1/25) as the eluents and isolated as a white solid (49.9 mg, 77% yield).

$^{1}$H NMR (500 MHz, Chloroform-d) δ 8.04 (t, J = 1.8 Hz, 1H), 7.93 (dt, J = 8.0, 1.3 Hz, 1H), 7.65 (d, J = 2.2 Hz, 1H), 7.46 – 7.41 (m, 2H), 7.32 – 7.26 (m, 3H), 3.23 (s, 6H).

$^{13}$C NMR (126 MHz, Chloroform-d) δ 193.5, 138.6, 135.4, 134.9, 134.5, 133.1, 130.0, 129.9, 129.6, 129.4, 128.1, 127.1, 125.1, 103.1, 50.3.

HRMS (ESI): Cacld. for $[M-OMe]^+$ 293.0136, found 293.0143.



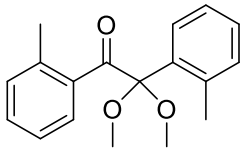
2,2-dimethoxy-1,2-bis(3-(trifluoromethoxy)phenyl)ethan-1-one (**c11**): Following the general procedure of catalytic reactions, the title product was purified on a silicon column with EtOAc/PE (v/v = 1/25) as the eluents and isolated as a colorless oil (43.2 mg, 51% yield).

$^{1}$H NMR (500 MHz, Chloroform-*d*) δ 7.98 (dt, *J* = 7.9, 1.4 Hz, 1H), 7.94 (dt, *J* = 2.4, 1.3 Hz, 1H), 7.56 (dt, *J* = 2.6, 1.2 Hz, 1H), 7.46 (dt, *J* = 7.8, 1.3 Hz, 1H), 7.38 (td, *J* = 7.9, 4.0 Hz, 2H), 7.31 (ddt, *J* = 8.2, 2.3, 1.1 Hz, 1H), 7.18 (ddt, *J* = 8.1, 2.4, 1.1 Hz, 1H), 3.26 (s, 6H).

$^{13}$C NMR (126 MHz, Chloroform-*d*) δ 193.15, 149.59, 149.57, 149.02, 149.01, 148.99, 138.94, 135.56, 130.22, 129.82, 128.13, 125.50, 125.31, 123.45, 123.40, 122.27, 121.63, 121.40, 121.35, 119.74, 119.35, 119.30, 103.05, 50.28.

$^{19}$F NMR (471 MHz, Chloroform-*d*) δ -58.06, -58.14.

HRMS (ESI): Cacld. for $[M+Na]^+$ 447.0643, found 447.0629.

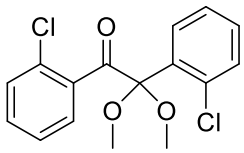



2,2-dimethoxy-1,2-di-o-tolylethan-1-one (**c12**): Following the general procedure of catalytic reactions, the title product was purified on a silicon column with EtOAc/PE (v/v = 1/25) as the eluents and isolated as a colorless oil (43.2 mg, 76% yield).

$^{1}$H NMR (500 MHz, Chloroform-d) δ 7.82 (dd, J = 7.8, 1.7 Hz, 1H), 7.67 (dd, J = 8.0, 1.4 Hz, 1H), 7.14 – 7.03 (m, 4H), 6.95 (dd, J = 7.4, 1.5 Hz, 1H), 6.92 – 6.87 (m, 1H), 3.18 (s, 6H), 2.33 (s, 3H), 2.16 (s, 3H).

$^{13}$C NMR (126 MHz, Chloroform-d) δ 197.0, 139.3, 136.7, 135.1, 134.9, 131.7, 131.6, 131.0, 129.5, 128.7, 128.4, 125.7, 124.8, 102.6, 49.7, 21.1, 19.9.

LC-MS (ESI): found 307.1 for $[M+Na]^+$, 253.1 for $[M-OMe]^+$.



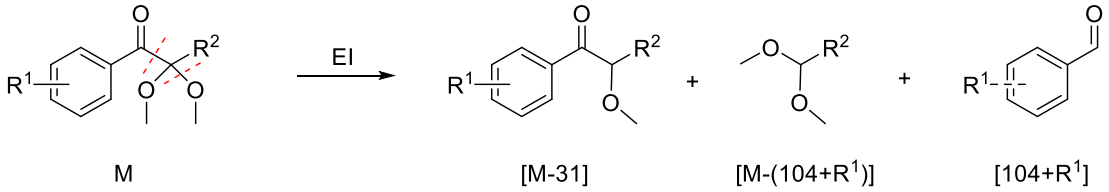
1,2-bis(2-chlorophenyl)-2,2-dimethoxyethan-1-one (**c13**): Following the general procedure of catalytic reactions, the title product was purified on a silicon column with EtOAc/PE (v/v = 1/25) as the eluents and isolated as a white solid (51.2 mg, 79% yield).

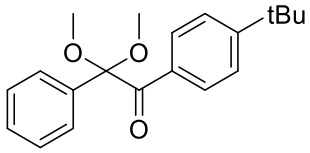
$^1$H NMR (500 MHz, Chloroform-d) δ 8.01 (d, J = 8.4 Hz, 1H), 7.69 (dd, J = 7.9, 1.6 Hz, 1H), 7.36 (dd, J = 8.1, 1.2 Hz, 1H), 7.29 (ddd, J = 7.9, 6.0, 2.5 Hz, 1H), 7.25 – 7.18 (m, 3H), 7.01 (td, J = 7.7, 1.2 Hz, 1H), 3.28 (s, 6H).

$^{13}$C NMR (126 MHz, Chloroform-d) δ 192.0, 134.7, 134.5, 133.6, 132.8, 131.7, 131.4, 130.5, 130.2, 130.1, 130.1, 126.5, 125.5, 100.7, 50.1.

LC-MS (ESI): found 293.0 for $[M\text{-}OMe]^+$.

In the case of unsymmetrical acetylenes, the assignment of products isomers was based on NMR and EI-MS. By fragments analysis in GC-MS spectra, in most cases the base peak (100% abundance) of fragments corresponded to the loss of the acyl radical with the formation of the corresponding benzylic ketal cation. Please see the scheme below.



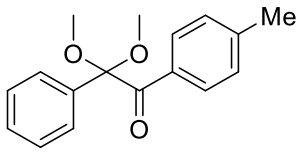

1-(4-(tert-butyl)phenyl)-2,2-dimethoxy-2-phenylethan-1-one (**e1'**, **major isomer**): Following the general procedure of catalytic reactions, the title product was purified on a silicon column with EtOAc/PE (v/v = 1/25) as the eluents and isolated as a colorless oil (40.9 mg, 65.6 % yield).

$^1$H NMR (500 MHz, Chloroform-*d*) δ 8.01 (d, *J* = 8.3 Hz, 2H), 7.66 – 7.61 (m, 2H), 7.36 (t, *J* = 7.3 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 3H), 3.21 (s, 6H), 1.27 (s, 9H).

$^{13}$C NMR (126 MHz, Chloroform-*d*) δ 194.65, 156.53, 137.08, 131.46, 130.03, 128.82, 128.49, 126.95, 125.12, 103.57, 50.05, 35.02, 30.98.

HRMS (ESI): Cacld. for $[M+Na]^+$ 335.1623, found 335.1628.

GC-MS (EI): $[M\text{-}OMe]^+$ (281.2, 39.0%), $[M\text{-}(4\text{-}tBuPh)CO]^+$ (151.4, 100%)

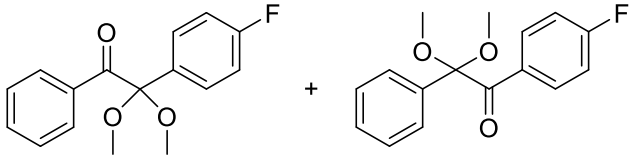



2,2-dimethoxy-2-phenyl-1-(p-tolyl)ethan-1-one (**e2'**, **major isomer**): Following the general procedure of catalytic reactions, the title product was purified on a silicon column with EtOAc/PE (v/v = 1/25) as the eluents and isolated as a colorless oil (33.3mg, 61.6 % yield).

$^{1}$H NMR (500 MHz, Chloroform-*d*) δ 7.98 (d, *J* = 8.0 Hz, 2H), 7.61 (d, *J* = 7.5 Hz, 2H), 7.34 (t, *J* = 7.5 Hz, 2H), 7.32 – 7.27 (m, 1H), 7.10 (d, *J* = 7.9 Hz, 2H), 3.21 (s, 6H).

$^{13}$C NMR (126 MHz, Chloroform-*d*) δ 194.6, 143.7, 137.1, 131.6, 130.2, 128.9, 128.8, 128.5, 126.9, 103.5, 50.0, 21.6.

GC-MS (EI): $[M\text{-}OMe]^+$ (239.2, 28.7%), $[M\text{-}(4\text{-}MePh)CO]^+$ (151.3, 100%)




**e3, major** **e3', minor**

2-(4-fluorophenyl)-2,2-dimethoxy-1-phenylethan-1-one (**e3**, **major isomer**) and 1-(4-fluorophenyl)-2,2-dimethoxy-2-phenylethan-1-one (**e3'**, minor isomer): Following the general procedure of catalytic reactions, the title products were purified on a silicon column with EtOAc/PE (v/v = 1/25) as the eluents and isolated as a colorless oil (inseparable mixture, 43.8 mg, 80% yield in total).

$^{1}$H NMR (500 MHz, Chloroform-*d*) δ 8.15 – 8.10 (m, 1H), 8.04 (dd, *J* = 8.3, 1.4 Hz, 1H), 7.63 – 7.57 (m, 2H), 7.47 – 7.41 (m, 1H), 7.39 – 7.28 (m, 3H), 7.04 (t, *J* = 8.7 Hz, 1H), 6.96 (t, *J* = 8.7 Hz, 1H), 3.22 (s, 7H).

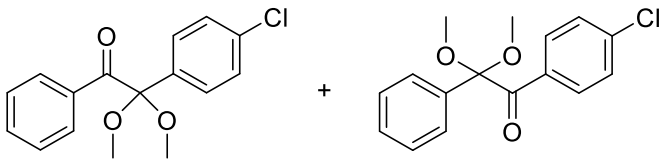
$^{13}$C NMR (126 MHz, Chloroform-*d*) δ 194.96, 193.54, 166.44, 164.41, 163.95, 161.98, 136.74, 134.13, 132.99, 132.88, 132.80, 132.78, 130.49, 130.46, 129.93, 129.02, 128.94, 128.88, 128.60, 128.20, 126.83, 115.65, 115.48, 115.35, 115.18, 103.51, 103.27, 50.07.

$^{19}$F NMR (471 MHz, Chloroform-*d*) δ -104.93, -112.53.

HRMS (ESI): Cacld. for $[M+Na]^+$ 297.0903, found 297.0911.

GC-MS (EI): **e3**: $[M\text{-}OMe]^+$ (243.2, 16.9%), $[M\text{-}PhCO]^+$ (169.3, 100%);

GC-MS (EI): **e3'**: $[M\text{-}OMe]^+$ (243.2, 12.1%), $[M\text{-}(4\text{-}FPh)CO]^+$ (151.2, 100%)




**e4, major** **e4', minor**

2-(4-chlorophenyl)-2,2-dimethoxy-1-phenylethan-1-one (**e4**, **major isomer**) and 1-(4-chlorophenyl)-2,2-dimethoxy-2-phenylethan-1-one (**e4'**, minor isomer): Following the general procedure of catalytic reactions, the title product was purified on a silicon column with EtOAc/PE (v/v = 1/25) as the eluents and isolated as a colorless oil (inseparable mixture, 43.0 mg, 74% yield in total).

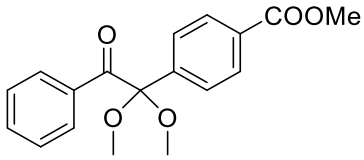
$^1$H NMR (400 MHz, Chloroform-*d*) δ 8.02 (dd, *J* = 8.2, 6.2 Hz, 6H), 7.61 – 7.52 (m, 6H), 7.48 – 7.42 (m, 1H), 7.39 – 7.23 (m, 15H), 3.22 (d, *J* = 1.3 Hz, 18H).

$^{13}$C NMR (101 MHz, Chloroform-*d*) δ 194.8, 194.0, 139.4, 136.6, 135.6, 135.0, 134.1, 133.0, 132.5, 131.5, 129.9, 129.1, 128.8, 128.6, 128.5, 128.4, 128.2, 126.9, 103.6, 103.3, 50.1, 50.1.

HRMS (ESI): Cacld. for $[M+Na]^+$ 313.0607, found 313.0614.

GC-MS (EI): **e4**: $[M\text{-}OMe]^+$ (259.1, 17.7%), $[M\text{-}PhCO]^+$ (185.2, 100%);

GC-MS (EI): **e4'**: $[M\text{-}OMe]^+$ (259.1, 16.1%), $[M\text{-}(4\text{-}FPh)CO]^+$ (151.1, 100%)



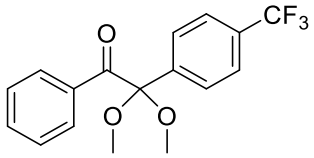

methyl 4-(1,1-dimethoxy-2-oxo-2-phenylethyl)benzoate (**e5**, **major isomer**): Following the general procedure of catalytic reactions, the title product was purified on a silicon column with EtOAc/PE (v/v = 1/25) as the eluents and isolated as a white solid (42.1 mg, 67.1 % yield).

$^1$H NMR (500 MHz, Chloroform-*d*) δ 8.03 (dd, *J* = 8.0, 5.4 Hz, 4H), 7.71 (d, *J* = 8.1 Hz, 2H), 7.44 (t, *J* = 7.4 Hz, 1H), 7.30 (t, *J* = 7.7 Hz, 2H), 3.89 (s, 3H), 3.23 (s, 6H).

$^{13}$C NMR (126 MHz, Chloroform-*d*) δ 194.6, 166.6, 141.8, 134.0, 133.1, 130.7, 129.9, 129.8, 128.3, 127.0, 103.3, 52.2, 50.2.

HRMS (ESI): Cacld. for $[M+Na]^+$ 337.1052, found 337.1053.

GC-MS (EI): $[M\text{-}OMe]^+$ (283.1, 17.6%), $[M\text{-}PhCO]^+$ (209.4, 100%).



2,2-dimethoxy-1-phenyl-2-(4-(trifluoromethyl)phenyl)ethan-1-one (**e6**): Following the general procedure of catalytic reactions, the title product was purified on a silicon column with EtOAc/PE (v/v = 1/25) as the eluents and isolated as a colorless oil (48.6 mg, 75 % yield).

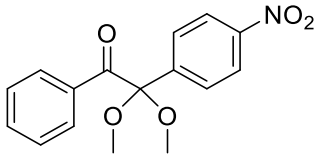
$^1$H NMR (500 MHz, Chloroform-d) δ 8.05 (d, J = 7.8 Hz, 2H), 7.76 (d, J = 8.1 Hz, 2H), 7.62 (d, J = 8.1 Hz, 2H), 7.46 (t, J = 7.4 Hz, 1H), 7.33 (t, J = 7.6 Hz, 2H), 3.24 (s, 6H).

$^{13}$C NMR (126 MHz, Chloroform-d) δ 194.5, 140.97, 133.90, 133.25, 131.18, 130.93, 129.93, 128.33, 127.42, 125.60, 125.57, 125.54, 125.51, 124.92, 122.76, 103.22, 50.24, 50.17.

$^{19}$F NMR (471 MHz, Chloroform-d) δ -62.74.

HRMS (ESI): Cacld. for $[M+Na]^+$ 347.0871, found 347.0876.

GC-MS (EI): $[M\text{-}OMe]^+$ (293.1, 11.3%), $[M\text{-}PhCO]^+$ (219.3, 100%).



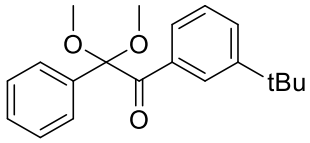
2,2-dimethoxy-2-(4-nitrophenyl)-1-phenylethan-1-one (**e7**): Following the general procedure of catalytic reactions, the title product was purified on a silicon column with EtOAc/PE (v/v = 1/25) as the eluents and isolated as a pale yellow solid (32.5 mg, 54 % yield).

$^1$H NMR (500 MHz, Chloroform-*d*) δ 8.14 (d, *J* = 8.6 Hz, 2H), 7.96 (dt, *J* = 8.4, 1.3 Hz, 2H), 7.75 (d, *J* = 8.6 Hz, 2H), 7.42 – 7.37 (m, 1H), 7.26 (t, *J* = 7.7 Hz, 2H), 3.19 (s, 6H).

$^{13}$C NMR (126 MHz, Chloroform-*d*) δ 194.0, 148.2, 144.1, 133.8, 133.5, 129.9, 128.4, 128.1, 123.8, 103.1, 50.4.

HRMS (ESI): Cacld. for $[M\text{-}OMe]^+$ 270.0767, found 270.0770.

GC-MS (EI): $[M\text{-}OMe]^+$ (270.1, 16.9%), $[M\text{-}PhCO]^+$ (196.3, 100%).



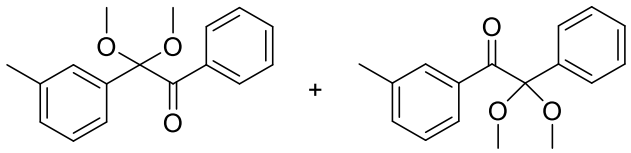

1-(3-(tert-butyl)phenyl)-2,2-dimethoxy-2-phenylethan-1-one (**e8'**, **major isomer**): Following the general procedure of catalytic reactions, the title product was purified on a silicon column with EtOAc/PE (v/v = 1/25) as the eluents and isolated as a colorless oil (28.8 mg, 46.1 % yield).

$^1$H NMR (500 MHz, Chloroform-*d*) δ 8.07 – 8.02 (m, 2H), 7.64 (t, *J* = 1.8 Hz, 1H), 7.44 – 7.39 (m, 2H), 7.33 – 7.26 (m, 4H), 3.22 (d, *J* = 1.1 Hz, 6H), 1.28 (s, 9H).

$^{13}$C NMR (126 MHz, Chloroform-*d*) δ 195.4, 151.5, 136.4, 134.5, 132.7, 129.9, 128.1, 128.0, 125.6, 124.2, 124.1, 103.9, 50.1, 34.8, 31.3.

HRMS (ESI): Cacld. for $[M+Na]^+$ 335.1623, found 335.1630.

GC-MS (EI): $[M-OMe]^+$ (281.2, 3.2%), $[M-(4\text{-tBuPh})CO]^+$ (151.4, 100%).




**e9**, minor **e9', major**

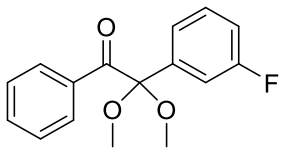
2,2-dimethoxy-1-phenyl-2-(m-tolyl)ethan-1-one (**e9**, minor isomer) and 2,2-dimethoxy-2-phenyl-1-(m-tolyl)ethan-1-one (**e9'**, **major isomer**): Following the general procedure of catalytic reactions, the title product was purified on a silicon column with EtOAc/PE (v/v = 1/25) as the eluents and isolated as a colorless oil (inseparable mixtures, 40.0 mg, 74% yield in total).

$^1$H NMR (500 MHz, Chloroform-*d*) δ 7.98 (dd, *J* = 8.3, 1.5 Hz, 2H), 7.79 (d, *J* = 7.6 Hz, 3H), 7.60 (dt, *J* = 6.2, 1.4 Hz, 1H), 7.56 – 7.51 (m, 3H), 7.44 – 7.41 (m, 1H), 7.39 – 7.13 (m, 16H), 7.09 (td, *J* = 7.6, 1.4 Hz, 2H), 7.03 (d, *J* = 7.5 Hz, 1H), 3.15 – 3.12 (m, 16H), 2.25 (s, 3H), 2.23 (s, 5H).

$^{13}$C NMR (126 MHz, Chloroform-*d*) δ 195.3, 195.3, 138.3, 137.9, 137.0, 136.7, 134.3, 134.23, 133.7, 133.2, 132.8, 131.0, 130.4, 130.0, 129.7, 129.3, 128.9, 128.6, 128.5, 128.5, 128.4, 128.1, 128.0, 127.6, 127.4, 127.3, 126.9, 124.0, 103.6, 103.6, 50.0, 21.5, 21.3.

GC-MS (EI): **e9**: $[M-OMe]^+$ (239.2, 9.4%), $[M-PhCO]^+$ (165.2, 100%);

GC-MS (EI): **e9'**: $[M-OMe]^+$ (239.1, 17.9%), $[M-(3\text{-MePh})CO]^+$ (151.1, 100%)



2-(3-fluorophenyl)-2,2-dimethoxy-1-phenylethan-1-one (**e10**, **major isomer**): Following the general procedure of catalytic reactions, the title product was purified on a silicon column with EtOAc/PE (v/v = 1/25) as the eluents and isolated as a colorless oil (32.8 mg, 59.9% yield).

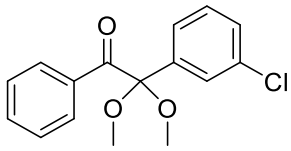
$^{1}$H NMR (500 MHz, Chloroform-*d*) δ 8.05 (dd, *J* = 8.2, 1.5 Hz, 2H), 7.48 – 7.43 (m, 1H), 7.41 (dt, *J* = 9.9, 2.0 Hz, 1H), 7.37 – 7.28 (m, 4H), 7.03 – 6.97 (m, 1H), 3.23 (s, 6H).

$^{13}$C NMR (126 MHz, Chloroform-*d*) δ 194.63, 163.88, 161.92, 139.66, 139.61, 134.04, 133.09, 130.22, 130.16, 129.93, 128.24, 122.67, 122.64, 116.06, 115.89, 114.27, 114.08, 103.02, 103.00, 50.16.

$^{19}$F NMR (471 MHz, Chloroform-*d*) δ -111.97.

HRMS (ESI): Cacld. for $[M+Na]^+$ 297.0903, found 297.0910.

GC-MS (EI): $[M-OMe]^+$ (243.1, 7.1%), $[M-PhCO]^+$ (169.3, 100%);



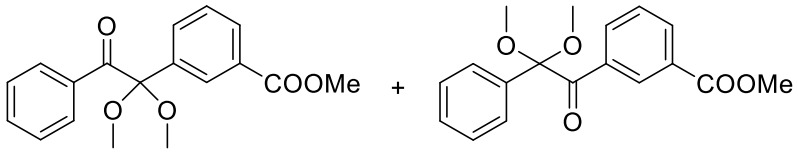
2-(3-chlorophenyl)-2,2-dimethoxy-1-phenylethan-1-one (**e11**, **major isomer**): Following the general procedure of catalytic reactions, the title product was purified on a silicon column with EtOAc/PE (v/v = 1/25) as the eluents and isolated as a colorless oil (32.7 mg, 56.3% yield).

$^{1}$H NMR (500 MHz, Chloroform-*d*) δ 8.08 – 8.02 (m, 2H), 7.69 (dd, *J* = 2.1, 1.1 Hz, 1H), 7.49 – 7.42 (m, 2H), 7.33 (t, *J* = 7.7 Hz, 2H), 7.29 – 7.25 (m, 2H), 3.22 (d, *J* = 0.8 Hz, 6H).

$^{13}$C NMR (126 MHz, Chloroform-*d*) δ 194.6, 139.1, 134.7, 134.0, 133.1, 129.9, 129.9, 129.2, 128.3, 127.1, 125.2, 103.0, 50.2.

HRMS (ESI): Cacld. for $[M+Na]^+$ 313.0607, found 313.0612.

GC-MS (EI): $[M-OMe]^+$ (259.1, 19.4%), $[M-PhCO]^+$ (185.2, 100%);




**e12, major** **e12'**, minor

methyl 3-(1,1-dimethoxy-2-oxo-2-phenylethyl)benzoate (**e12**, **major isomer**) and methyl 3-(2,2-dimethoxy-2-phenylacetyl)benzoate (**e12'**, minor isomer): Following the general procedure of catalytic reactions, the title product was purified on a silicon column with EtOAc/PE (v/v = 1/25) as the eluents and isolated as a colorless oil (inseparable mixtures, 52.8 mg, 84% yield in total).

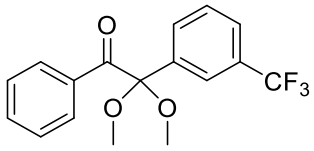
$^1$H NMR (500 MHz, Chloroform-*d*) δ 8.75 (t, *J* = 1.8 Hz, 1H), 8.37 (t, *J* = 1.8 Hz, 3H), 8.24 (dt, *J* = 7.9, 1.5 Hz, 1H), 8.10 (dt, *J* = 7.8, 1.5 Hz, 1H), 8.07 – 8.03 (m, 7H), 8.00 (dt, *J* = 7.7, 1.5 Hz, 4H), 7.77 (dt, *J* = 8.0, 1.5 Hz, 4H), 7.66 – 7.60 (m, 2H), 7.46 – 7.41 (m, 7H), 7.38 (ddd, *J* = 11.0, 9.2, 6.9 Hz, 4H), 7.31 (t, *J* = 7.8 Hz, 10H), 3.92 (s, 10H), 3.91 (s, 4H), 3.24 (d, *J* = 1.7 Hz, 29H).

$^{13}$C NMR (126 MHz, Chloroform-*d*) δ 194.7, 194.4, 166.6, 166.2, 137.6, 136.5, 134.4, 134.1, 134.0, 133.6, 133.1, 131.4, 131.2, 130.6, 130.3, 130.2, 130.0, 129.1, 128.8, 128.6, 128.4, 128.3, 128.0, 126.9, 103.6, 103.2, 52.3, 52.2, 50.2, 50.1.

HRMS (ESI): Cacld. for $[M+Na]^+$ 337.1052, found 337.1057.

GC-MS (EI): **e12**: $[M\text{-}OMe]^+$ (283.1, 7.4%), $[M\text{-}PhCO]^+$ (209.2, 100%);

GC-MS (EI): **e12'**: $[M\text{-}OMe]^+$ (283.1, 8.1%), $[M\text{-}(3\text{-}COOMePh)CO]^+$ (151.2, 100%)




2,2-dimethoxy-1-phenyl-2-(3-(trifluoromethyl)phenyl)ethan-1-one (**e13**): Following the general procedure of catalytic reactions, the title product was purified on a silicon column with EtOAc/PE (v/v = 1/25) as the eluents and isolated as a colorless oil (53.8 mg, 83 % yield).

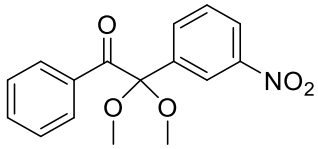
$^1$H NMR (500 MHz, Chloroform-*d*) δ 7.97 (d, *J* = 7.9 Hz, 2H), 7.91 (s, 1H), 7.67 (d, *J* = 7.8 Hz, 1H), 7.49 (d, *J* = 7.8 Hz, 1H), 7.38 (q, *J* = 7.3 Hz, 2H), 7.25 (t, *J* = 7.7 Hz, 2H), 3.16 (s, 6H).

$^{13}$C NMR (126 MHz, Chloroform-*d*) δ 194.55, 138.19, 133.89, 133.17, 131.14, 130.88, 130.35, 129.85, 129.10, 128.28, 125.85, 125.82, 125.79, 125.77, 124.94, 123.86, 123.83, 123.80, 123.77, 122.77, 103.11, 50.19.

$^{19}$F NMR (471 MHz, Chloroform-*d*) δ -62.59.

HRMS (ESI): Cacld. for $[M+Na]^+$ 347.0871, found 347.0875.

GC-MS (EI): $[M-F]^+$ (305.1, 2.0%), $[M-OMe]^+$ (293.1, 12.8%), $[M-PhCO]^+$ (219.0, 100%).



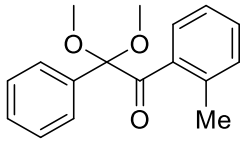

2,2-dimethoxy-2-(3-nitrophenyl)-1-phenylethan-1-one (**e14**): Following the general procedure of catalytic reactions, the title product was purified on a silicon column with EtOAc/PE (v/v = 1/25) as the eluents and isolated as a pale yellow solid (26.5 mg, 44 % yield).

$^1$H NMR (500 MHz, Chloroform-*d*) δ 8.62 (t, *J* = 2.0 Hz, 1H), 8.18 (ddd, *J* = 8.2, 2.3, 1.1 Hz, 1H), 8.09 – 8.03 (m, 2H), 7.86 (dt, *J* = 7.7, 1.3 Hz, 1H), 7.54 (t, *J* = 8.0 Hz, 1H), 7.50 – 7.45 (m, 1H), 7.34 (t, *J* = 7.9 Hz, 2H), 3.27 (s, 6H).

$^{13}$C NMR (126 MHz, Chloroform-*d*) δ 194.1, 148.5, 139.5, 133.7, 133.4, 133.0, 129.9, 129.8, 128.5, 124.0, 122.1, 102.9, 50.4.

HRMS (ESI): Cacld. for $[M-OMe]^+$ 270.0767, found 270.0770.

GC-MS (EI): $[M-OMe]^+$ (270.1, 7.3%), $[M-PhCO]^+$ (196.0, 100%).

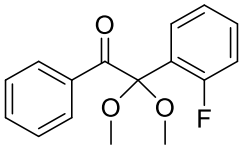



2,2-dimethoxy-2-phenyl-1-(o-tolyl)ethan-1-one (**e15'**, **major isomer**): Following the general procedure of catalytic reactions, the title product was purified on a silicon column with EtOAc/PE (v/v = 1/25) as the eluents and isolated as a colorless oil (23.3 mg, 43.2 % yield).

$^1$H NMR (500 MHz, Chloroform-*d*) δ 7.61 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.53 (dt, *J* = 6.2, 1.7 Hz, 2H), 7.36 – 7.28 (m, 3H), 7.27 – 7.22 (m, 1H), 7.12 (d, *J* = 7.6 Hz, 1H), 7.07 (t, *J* = 7.6 Hz, 1H), 3.28 (s, 6H), 2.17 (s, 3H).

$^{13}$C NMR (126 MHz, Chloroform-*d*) δ 199.4, 138.2, 136.5, 136.2, 131.1, 130.5, 128.8, 128.5, 128.4, 127.2, 124.6, 104.5, 50.2, 20.4.

GC-MS (EI): $[M-OMe]^+$ (239.1, 16.9%), $[M-(2MePh)CO]^+$ (151.0, 100%).



2-(2-fluorophenyl)-2,2-dimethoxy-1-phenylethan-1-one (**e16**, **major isomer**): Following the general procedure of catalytic reactions, the title product was purified on a silicon column with EtOAc/PE (v/v = 1/25) as the eluents and isolated as a colorless oil (26.7 mg, 48.8% yield).

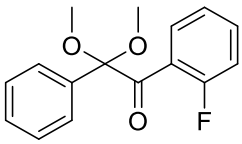
$^{1}$H NMR (500 MHz, Chloroform-*d*) δ 7.99 (ddd, *J* = 9.9, 5.4, 3.6 Hz, 3H), 7.44 – 7.39 (m, 1H), 7.33 – 7.25 (m, 3H), 7.22 (td, *J* = 7.6, 1.2 Hz, 1H), 6.90 (ddd, *J* = 10.8, 8.1, 1.2 Hz, 1H), 3.25 (s, 6H).

$^{13}$C NMR (126 MHz, Chloroform-*d*) δ 193.18, 160.64, 158.65, 134.30, 132.78, 131.01, 130.94, 129.72, 128.89, 128.87, 128.05, 125.38, 125.29, 123.94, 123.91, 116.20, 116.03, 99.84, 99.82, 49.98.

$^{19}$F NMR (471 MHz, Chloroform-*d*) δ -112.67.

HRMS (ESI): Cacld. for $[M+Na]^+$ 297.0903, found 297.0910.

GC-MS (EI): $[M-OMe]^+$ (243.1, 25.0%), $[M-PhCO]^+$ (169.1, 100%).



1-(2-fluorophenyl)-2,2-dimethoxy-2-phenylethan-1-one (**e16'**, minor isomer): Following the general procedure of catalytic reactions, the title product was purified on a silicon column with EtOAc/PE (v/v = 1/25) as the eluents and isolated as a colorless oil (17.1 mg, 31.2% yield).

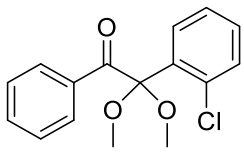
$^{1}$H NMR (500 MHz, Chloroform-*d*) δ 7.59 – 7.55 (m, 2H), 7.41 – 7.33 (m, 5H), 7.05 – 6.98 (m, 2H), 3.28 (s, 6H).

$^{13}$C NMR (126 MHz, Chloroform-*d*) δ 196.08, 161.25, 159.21, 136.04, 132.78, 132.71, 129.81, 129.80, 129.10, 128.48, 127.30, 125.89, 125.79, 123.26, 123.23, 116.44, 116.27, 103.97, 50.30.

$^{19}$F NMR (471 MHz, Chloroform-*d*) δ -112.17.

HRMS (ESI): Cacld. for $[M+Na]^+$ 297.0903, found 297.0910.

GC-MS (EI): $[M-OMe]^+$ (243.1, 6.7%), $[M-(2\text{-F-Ph})CO]^+$ (151.2, 100%).



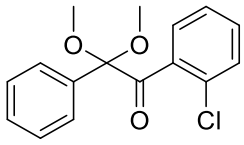
1-(2-chlorophenyl)-2,2-dimethoxy-2-phenylethan-1-one (**e17**, **major isomer**): Following the general procedure of catalytic reactions, the title product was purified on a silicon column with EtOAc/PE (v/v = 1/25) as the eluents and isolated as a colorless oil (29.5 mg, 50.8% yield).

$^{1}$H NMR (500 MHz, Chloroform-d) δ 8.15 (dd, J = 7.9, 1.7 Hz, 1H), 7.93 – 7.87 (m, 2H), 7.41 – 7.33 (m, 2H), 7.26 – 7.18 (m, 4H), 3.24 (s, 6H).

$^{13}$C NMR (126 MHz, Chloroform-*d*) δ 193.1, 135.5, 135.0, 132.4, 132.4, 130.7, 130.2, 129.6, 129.5, 127.9, 126.5, 100.3, 49.9.

HRMS (ESI): Cacld. for $[M+Na]^+$ 313.0607, found 313.0611.

GC-MS (EI): $[M-OMe]^+$ (259.1, 18.5%), $[M-PhCO]^+$ (185.3, 100%).



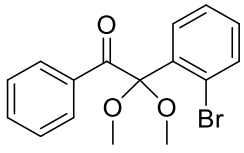
1-(2-chlorophenyl)-2,2-dimethoxy-2-phenylethan-1-one (**e17'**, minor isomer): Following the general procedure of catalytic reactions, the title product was purified on a silicon column with EtOAc/PE (v/v = 1/25) as the eluents and isolated as a colorless oil (18.1 mg, 31.2% yield).

$^{1}$H NMR (500 MHz, Chloroform-*d*) δ 7.57 – 7.49 (m, 2H), 7.34 (td, *J* = 12.8, 11.6, 6.4 Hz, 4H), 7.27 (ddd, *J* = 15.1, 10.2, 4.8 Hz, 2H), 7.13 (t, *J* = 7.6 Hz, 1H), 3.34 (s, 6H).

$^{13}$C NMR (126 MHz, Chloroform-*d*) δ 197.6, 137.0, 135.7, 131.9, 131.0, 130.3, 129.2, 128.8, 128.5, 127.6, 125.6, 104.5, 50.5.

HRMS (ESI): Cacld. for $[M+Na]^+$ 313.0607, found 313.0611.

GC-MS (EI): $[M-OMe]^+$ (259.0, 12.5%), $[M-(2\text{-Cl-Ph})CO]^+$ (151.0, 95.6%).

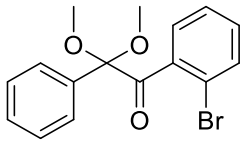


1-(2-bromophenyl)-2,2-dimethoxy-2-phenylethan-1-one (**e18**, **major isomer**): Following the general procedure of catalytic reactions, the title product was purified on a silicon column with EtOAc/PE (v/v = 1/25) as the eluents and isolated as a aple yellow solid (31.9 mg, 47.8% yield).

$^1$H NMR (500 MHz, Chloroform-d) δ 8.17 (dd, J = 7.9, 1.7 Hz, 1H), 7.89 (dd, J = 8.1, 1.5 Hz, 2H), 7.44 – 7.35 (m, 3H), 7.24 (t, J = 7.8 Hz, 2H), 7.15 (td, J = 7.6, 1.8 Hz, 1H), 3.24 (s, 6H).

$^{13}$C NMR (126 MHz, Chloroform-d) δ 193.1, 137.0, 135.4, 134.3, 132.4, 130.3, 130.1, 129.6, 127.0, 121.5, 100.9, 50.0.

GC-MS (EI): $[M\text{-}OMe]^+$ (303.1, 1.7%), $[M\text{-}PhCO]^+$ (229.2, 100%).

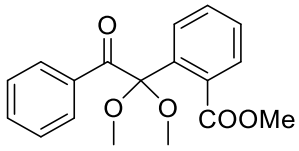



1-(2-bromophenyl)-2,2-dimethoxy-2-phenylethan-1-one (**e18'**, minor isomer): Following the general procedure of catalytic reactions, the title product was purified on a silicon column with EtOAc/PE (v/v = 1/25) as the eluents and isolated as a pale yellow solid (22.2 mg, 33.2% yield).

$^1$H NMR (500 MHz, Chloroform-*d*) δ 7.56 – 7.50 (m, 3H), 7.37 – 7.32 (m, 3H), 7.28 (dt, *J* = 7.5, 3.7 Hz, 1H), 7.19 (dd, *J* = 5.9, 3.4 Hz, 2H), 3.34 (s, 6H).

$^{13}$C NMR (126 MHz, Chloroform-*d*) δ 197.9, 138.7, 135.7, 133.7, 131.1, 129.2, 129.0, 128.5, 127.7, 126.1, 120.5, 104.5, 50.5.

GC-MS (EI): $[M\text{-}OMe]^+$ (303.0, 4.3%), $[M\text{-}(2\text{-}Br\text{-}Ph)CO]^+$ (151.0, 100%).



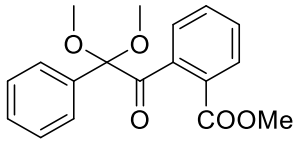

methyl 2-(1,1-dimethoxy-2-oxo-2-phenylethyl)benzoate (**e19**, **major isomer**): Following the general procedure of catalytic reactions, the title product was purified on a silicon column with EtOAc/PE (v/v = 1/25) as the eluents and isolated as a white solid (31.3 mg, 49.9% yield).

$^1$H NMR (500 MHz, Chloroform-*d*) δ 7.95 (dd, *J* = 8.0, 1.4 Hz, 2H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.48 – 7.33 (m, 4H), 7.31 – 7.26 (m, 2H), 3.76 (s, 3H), 3.22 (s, 6H).

$^{13}$C NMR (126 MHz, Chloroform-*d*) δ 193.3, 169.7, 135.5, 135.5, 132.3, 132.3, 130.2, 129.4, 128.8, 128.7, 128.5, 128.0, 102.0, 51.7, 50.2.

HRMS (ESI): Cacld. for $[M+Na]^+$ 337.1052, found 337.1058.

GC-MS (EI): $[M-OMe]^+$ (283.1, 2.5%), $[M-PhCO]^+$ (209.2, 100%).



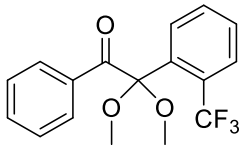

methyl 2-(2,2-dimethoxy-2-phenylacetyl)benzoate (**e19'**, minor isomer): Following the general procedure of catalytic reactions, the title product was purified on a silicon column with EtOAc/PE (v/v = 1/25) as the eluents and isolated as a white solid (17.6 mg, 28.1% yield).

$^{1}$H NMR (500 MHz, Chloroform-*d*) δ 7.71 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.43 (ddd, *J* = 7.8, 6.1, 2.4 Hz, 3H), 7.31 (qd, *J* = 7.2, 6.7, 2.2 Hz, 4H), 7.15 (dd, *J* = 7.8, 1.3 Hz, 1H), 3.81 (s, 3H), 3.34 (s, 6H).

$^{13}$C NMR (126 MHz, Chloroform-*d*) δ 198.7, 168.2, 137.5, 136.2, 132.0, 130.3, 130.2, 129.2, 129.0, 128.9, 128.2, 127.7, 104.8, 52.5, 50.5.

HRMS (ESI): Cacld. for $[M+Na]^+$ 337.1052, found 337.1058.

GC-MS (EI): $[M-OMe]^+$ (283.1, 3.2%), $[M-(2\text{-}COOMe\text{-}Ph)CO]^+$ (151.2, 100%).




2,2-dimethoxy-2-phenyl-1-(2-(trifluoromethyl)phenyl)ethan-1-one (**e20**, **major isomer**): Following the general procedure of catalytic reactions, the title product was purified on a silicon column with EtOAc/PE (v/v = 1/25) as the eluents and isolated as a colorless oil (42.1 mg, 65 % yield).

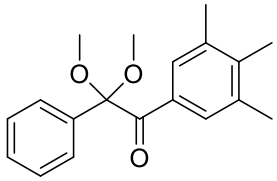
$^{1}$H NMR (500 MHz, DMSO-d6) δ 8.23 (d, J = 8.0 Hz, 1H), 7.85 – 7.81 (m, 2H), 7.80 – 7.73 (m, 2H), 7.60 (t, J = 7.6 Hz, 1H), 7.52 – 7.47 (m, 1H), 7.38 (t, J = 7.8 Hz, 2H), 3.15 (s, 6H).

$^{13}$C NMR (126 MHz, Chloroform-d) δ 193.3, 136.5, 135.6, 132.3, 131.6, 130.4, 129.5, 129.2, 128.0, 127.76, 127.74, 127.71, 127.66, 127.60, 126.97, 124.80, 122.62, 120.44, 101.5, 50.1.

$^{19}$F NMR (471 MHz, Chloroform-d) δ -57.44.

HRMS (ESI): Cacld. for $[M+Na]^+$ 347.0871, found 347.0867.

GC-MS (EI): $[M-OMe]^+$ (293.1, 13.0%), $[M-PhCO]^+$ (219.2, 100%).



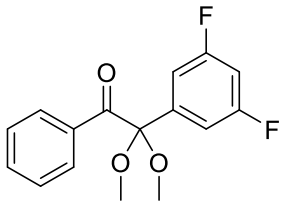
2,2-dimethoxy-2-phenyl-1-(3,4,5-trimethylphenyl)ethan-1-one (**e21'**, **major isomer**): Following the general procedure of catalytic reactions, the title product was purified on a silicon column with EtOAc/PE (v/v = 1/25) as the eluents and isolated as a white solid (29.8 mg, 50% yield).

$^1$H NMR (500 MHz, Chloroform-*d*) δ 7.72 (s, 2H), 7.63 – 7.59 (m, 2H), 7.37 – 7.32 (m, 2H), 7.31 – 7.26 (m, 1H), 3.21 (s, 6H), 2.22 (s, 6H), 2.12 (s, 3H).

$^{13}$C NMR (126 MHz, Chloroform-*d*) δ 194.91, 141.20, 137.35, 136.20, 131.26, 129.20, 128.72, 128.41, 126.87, 103.56, 50.00, 20.62, 15.80.

HRMS (ESI): Cacld. for $[M+Na]^+$ 321.1467, found 321.1463.

GC-MS (EI): $[M-OMe]^+$ (267.1, 20.4%), [M-(3,4,5-triMePh) CO]$^+$ (151.4, 100%)



2-(3,5-difluorophenyl)-2,2-dimethoxy-1-phenylethan-1-one (**e22**, **major isomer**): Following the general procedure of catalytic reactions, the title product was purified on a silicon column with EtOAc/PE (v/v = 1/25) as the eluents and isolated as a colorless oil (31.5 mg, 54% yield).

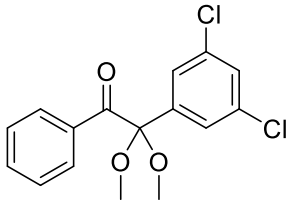
$^1$H NMR (500 MHz, Chloroform-*d*) δ 8.08 – 8.03 (m, 2H), 7.51 – 7.46 (m, 1H), 7.38 – 7.32 (m, 2H), 7.20 – 7.14 (m, 2H), 6.75 (tt, *J* = 8.7, 2.4 Hz, 1H), 3.24 (s, 6H).

$^{13}$C NMR (126 MHz, Chloroform-*d*) δ 194.09, 164.14, 164.04, 162.16, 162.06, 141.30, 141.23, 141.16, 133.85, 133.31, 129.88, 128.37, 110.30, 110.25, 110.14, 110.09, 104.76, 104.55, 104.35, 102.67, 102.65, 50.27.

$^{19}$F NMR (471 MHz, Chloroform-*d*) δ -108.33.

HRMS (ESI): Cacld. for $[M+Na]^+$ 315.0809, found 315.0807;

GC-MS (EI): $[M-OMe]^+$ (261.1, 25.1%), $[M-PhCO]^+$ (186.8, 100%).



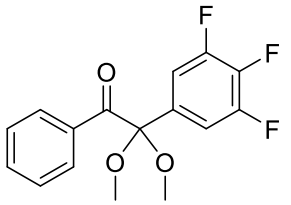

2-(3,5-dichlorophenyl)-2,2-dimethoxy-1-phenylethan-1-one (**e23**, **major isomer**): Following the general procedure of catalytic reactions, the title product was purified on a silicon column with EtOAc/PE (v/v = 1/25) as the eluents and isolated as a white solid (45.5 mg, 70% yield).

$^1$H NMR (500 MHz, Chloroform-*d*) δ 8.07 – 8.03 (m, 2H), 7.53 (d, *J* = 2.0 Hz, 2H), 7.51 – 7.47 (m, 1H), 7.39 – 7.34 (m, 2H), 7.30 (t, *J* = 1.9 Hz, 1H), 3.23 (s, 6H).

$^{13}$C NMR (126 MHz, Chloroform-*d*) δ 194.04, 140.62, 135.44, 133.77, 133.39, 129.92, 129.27, 128.43, 125.52, 102.64, 50.32.

HRMS (ESI): Cacld. for $[M+Na]^+$ 347.0218, found 347.0209;

GC-MS (EI): $[M-OMe]^+$ (293.0, 11.4%), $[M-PhCO]^+$ (219.3, 100%).




2,2-dimethoxy-1-phenyl-2-(3,4,5-trifluorophenyl)ethan-1-one (**e24**, **major isomer**): Following the general procedure of catalytic reactions, the title product was purified on a silicon column with EtOAc/PE (v/v = 1/25) as the eluents and isolated as a colorless oil (42.8 mg, 70% yield).

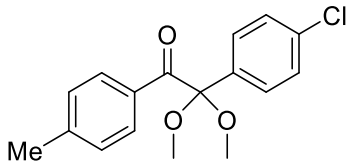
$^1$H NMR (500 MHz, Chloroform-*d*) δ 8.06 – 8.02 (m, 2H), 7.52 – 7.47 (m, 1H), 7.39 – 7.34 (m, 2H), 7.31 – 7.24 (m, 2H), 3.24 (s, 6H).

$^{13}$C NMR (126 MHz, Chloroform-*d*) δ 193.95, 152.34, 152.31, 152.26, 152.23, 150.34, 150.31, 150.26, 150.23, 140.97, 138.95, 133.75, 133.63, 133.62, 133.58, 133.53, 133.43, 129.84, 128.45, 111.59, 111.54, 111.45, 111.41, 102.39, 50.30.

$^{19}$F NMR (471 MHz, Chloroform-*d*) δ -132.62, -132.67, -158.76, -158.80, -158.84.

HRMS (ESI): Cacld. for $[M+Na]^+$ 333.0714, found 333.0704;

GC-MS (EI): $[M-OMe]^+$ (279.1, 25.0%), $[M-PhCO]^+$ (205.4, 100%)



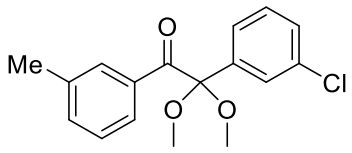

2-(4-chlorophenyl)-2,2-dimethoxy-1-(p-tolyl)ethan-1-one (**e25**, **major isomer**): Following the general procedure of catalytic reactions, the title product was purified on a silicon column with EtOAc/PE (v/v = 1/25) as the eluents and isolated as a white solid (40.6 mg, 67 % yield).

$^1$H NMR (500 MHz, Chloroform-*d*) δ 7.96 (d, *J* = 8.0 Hz, 2H), 7.58 – 7.52 (m, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 3.21 (s, 6H), 2.33 (s, 3H).

$^{13}$C NMR (126 MHz, Chloroform-*d*) δ 194.2, 144.0, 135.7, 134.9, 131.4, 130.1, 129.0, 128.8, 128.4, 103.2, 50.1, 21.6.

HRMS (ESI): Cacld. for $[M+Na]^+$ 327.0764, found 327.0770.

GC-MS (EI): $[M-OMe]^+$ (273.1, 5.8%), $[M-(4\text{-}MePh)CO]^+$ (185.2, 100%);



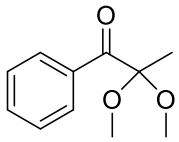

2-(3-chlorophenyl)-2,2-dimethoxy-1-(m-tolyl)ethan-1-one (**e26**, **major isomer**): Following the general procedure of catalytic reactions, the title product was purified on a silicon column with EtOAc/PE (v/v = 1/25) as the eluents and isolated as a white solid (40.1 mg, 66 % yield).

$^1$H NMR (500 MHz, Chloroform-*d*) δ 7.85 (d, *J* = 5.5 Hz, 2H), 7.68 (s, 1H), 7.45 (t, *J* = 4.2 Hz, 1H), 7.30 – 7.24 (m, 3H), 7.20 (t, *J* = 7.9 Hz, 1H), 3.22 (s, 6H), 2.33 (s, 3H).

$^{13}$C NMR (126 MHz, Chloroform-*d*) δ 194.72, 139.22, 138.06, 134.67, 133.95, 130.38, 129.85, 129.14, 128.11, 127.20, 127.11, 125.15, 103.04, 50.18, 21.36.

HRMS (ESI): Cacld. for $[M+Na]^+$ 327.0764, found 327.0771.

GC-MS (EI): $[M-OMe]^+$ (273.1, 4.0%), $[M-(3\text{-}MePh)CO]^+$ (185.2, 100%).

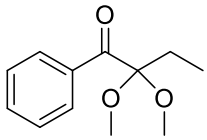


2,2-dimethoxy-1-phenylpropan-1-one (**e27'**): Following the general procedure of catalytic reactions, the title product was purified on a silicon column with EtOAc/PE (v/v = 1/25) as the eluents and isolated as a colorless oil (18.2 mg, 47% yield).

$^{1}$H NMR (500 MHz, Chloroform-d) δ 8.22 – 8.16 (m, 2H), 7.58 – 7.52 (m, 1H), 7.44 (t, J = 7.8 Hz, 2H), 3.34 (s, 6H), 1.61 (s, 3H).

$^{13}$C NMR (126 MHz, Chloroform-d) δ 197.11, 134.43, 133.08, 130.09, 128.33, 103.07, 49.85, 21.42.

GC-MS (EI): $[M-Me]^+$ (179.1, 3.4%), $[M-OMe]^+$ (163.2, 34%), $[M-PhCO]^+$ (89.3, 100%).

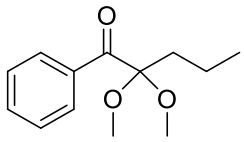


2,2-dimethoxy-1-phenylbutan-1-one (**e28'**): Following the general procedure of catalytic reactions, the title product was purified on a silicon column with EtOAc/PE (v/v = 1/25) as the eluents and isolated as a colorless oil (31.6 mg, 76% yield).

$^{1}$H NMR (500 MHz, Chloroform-d) δ 8.24 – 8.19 (m, 2H), 7.58 – 7.53 (m, 1H), 7.44 (t, J = 7.8 Hz, 2H), 3.32 (s, 6H), 2.05 (q, J = 7.6 Hz, 2H), 0.74 (t, J = 7.6 Hz, 3H).

$^{13}$C NMR (126 MHz, Chloroform-d) δ 197.0, 135.1, 133.0, 129.8, 128.3, 105.41, 49.6, 27.0, 7.3.

GC-MS (EI): $[M-OMe]^+$ (177.2, 31.9%), $[M-PhCO]^+$ (103.3, 100%).

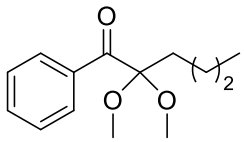


2,2-dimethoxy-1-phenylpentan-1-one (**e29'**): Following the general procedure of catalytic reactions, the title product was purified on a silicon column with EtOAc/PE (v/v = 1/25) as the eluents and isolated as a colorless oil (32.0 mg, 72% yield).

$^{1}$H NMR (500 MHz, Chloroform-d) δ 8.24 – 8.17 (m, 2H), 7.58 – 7.53 (m, 1H), 7.44 (t, J = 7.8 Hz, 2H), 3.31 (s, 6H), 2.02 – 1.95 (m, 2H), 1.21 – 1.11 (m, 2H), 0.81 (t, J = 7.4 Hz, 3H).

$^{13}$C NMR (126 MHz, Chloroform-d) δ 197.12, 135.11, 133.01, 129.87, 128.36, 104.94, 49.56, 36.35, 16.42, 14.09.

GC-MS (EI): $[M\text{-}OMe]^+$ (191.3, 53.6%), $[M\text{-}PhCO]^+$ (117.4, 100%).



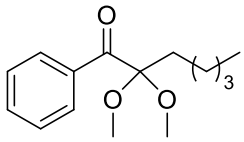
2,2-dimethoxy-1-phenylhexan-1-one (**e30'**): Following the general procedure of catalytic reactions, the title product was purified on a silicon column with EtOAc/PE (v/v = 1/25) as the eluents and isolated as a colorless oil (35.4 mg, 75% yield).

$^1$H NMR (500 MHz, Chloroform-d) δ 8.24 – 8.17 (m, 2H), 7.58 – 7.53 (m, 1H), 7.44 (t, J = 7.8 Hz, 2H), 3.31 (s, 6H), 2.04 – 1.97 (m, 2H), 1.24 – 1.15 (m, 2H), 1.15 – 1.07 (m, 2H), 0.78 (t, J = 7.2 Hz, 3H).

$^{13}$C NMR (126 MHz, Chloroform-d) δ 197.1, 135.1, 133.0, 129.8, 128.3, 105.0, 49.5, 33.9, 25.0, 22.6, 13.7.

HRMS (ESI): Cacld. for $[M+Na]^+$ 259.1310, found 259.1315.

GC-MS (EI): $[M\text{-}OMe]^+$ (205.3, 29.6%), $[M\text{-}PhCO]^+$ (131.4, 100%).



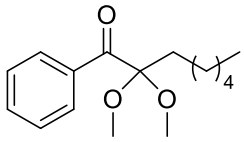
2,2-dimethoxy-1-phenylheptan-1-one (**e31'**): Following the general procedure of catalytic reactions, the title product was purified on a silicon column with EtOAc/PE (v/v = 1/25) as the eluents and isolated as a colorless oil (18.0 mg, 36% yield).

$^1$H NMR (500 MHz, Chloroform-d) δ 8.20 (d, J = 7.6 Hz, 2H), 7.58 – 7.53 (m, 1H), 7.44 (t, J = 7.6 Hz, 2H), 3.31 (s, 6H), 1.99 (dd, J = 9.7, 5.8 Hz, 2H), 1.21 – 1.10 (m, 6H), 0.78 (t, J = 6.8 Hz, 3H).

$^{13}$C NMR (126 MHz, Chloroform-d) δ 197.1, 135.2, 133.0, 129.8, 128.3, 105.0, 49.6, 34.1, 31.7, 22.6, 22.2, 13.8.

HRMS (ESI): Cacld. for $[M+Na]^+$ 273.1467, found 273.1475.

GC-MS (EI): $[M\text{-}OMe]^+$ (219.2, 23.7%), $[M\text{-}PhCO]^+$ (145.3, 100%).

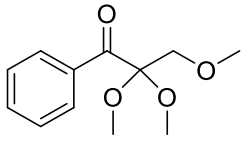


2,2-dimethoxy-1-phenyloctan-1-one (**e32'**): Following the general procedure of catalytic reactions, the title product was purified on a silicon column with EtOAc/PE (v/v = 1/25) as the eluents and isolated as a colorless oil (33.8 mg, 46% yield).

$^{1}$H NMR (500 MHz, Chloroform-d) δ 8.20 (dt, J = 8.3, 1.2 Hz, 2H), 7.59 – 7.52 (m, 1H), 7.44 (t, J = 7.7 Hz, 2H), 3.31 (s, 6H), 2.03 – 1.96 (m, 2H), 1.15 (q, J = 16.3, 11.1 Hz, 8H), 0.79 (t, J = 6.7 Hz, 3H).

$^{13}$C NMR (126 MHz, Chloroform-d) δ 197.1, 135.2, 133.0, 129.8, 128.3, 105.0, 49.6, 34.2, 31.4, 29.2, 22.8, 22.4, 13.9.

GC-MS (EI): $[M\text{-}OMe]^+$ (233.2, 17.5%), $[M\text{-}PhCO]^+$ (159.3, 100%).

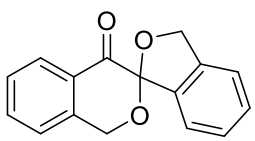


2,2,3-trimethoxy-1-phenylpropan-1-one (**e33'**): Following the general procedure of catalytic reactions, the title product was purified on a silicon column with EtOAc/PE (v/v = 1/25) as the eluents and isolated as a colorless oil (19.7 mg, 44% yield).

$^{1}$H NMR (500 MHz, Chloroform-d) δ 8.14 – 8.11 (m, 2H), 7.56 – 7.51 (m, 1H), 7.43 (dd, J = 8.4, 7.2 Hz, 2H), 3.77 (s, 2H), 3.36 (s, 6H), 3.26 (s, 3H).

$^{13}$C NMR (126 MHz, Chloroform-d) δ 197.7, 136.2, 132.7, 129.9, 128.0, 103.3, 72.1, 59.5, 49.9.

GC-MS (EI): $[M\text{-}OMe]^+$ (193.1, 1.5%), $[M\text{-}PhCO]^+$ (119.3, 94.8%).

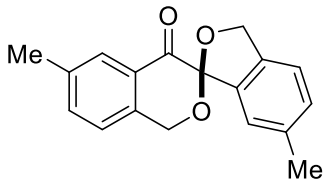


3*H*-spiro[isobenzofuran-1,3'-isochroman]-4'-one (**g1**): Following the general procedure of catalytic reactions, the title product was purified on a silicon column with EtOAc/PE (v/v = 1/25) as the eluents and isolated as a white solid (25.1 mg, 50% yield).

$^1$H NMR (500 MHz, Chloroform-*d*) δ 8.11 (d, *J* = 7.8 Hz, 1H), 7.60 (t, *J* = 7.5 Hz, 1H), 7.45 (t, *J* = 7.4 Hz, 2H), 7.36 (ddd, *J* = 22.9, 15.0, 7.5 Hz, 3H), 7.25 (d, *J* = 7.3 Hz, 1H), 5.52 (d, *J* = 15.7 Hz, 1H), 5.36 (d, *J* = 12.5 Hz, 1H), 5.21 (d, *J* = 12.5 Hz, 1H), 4.90 (d, *J* = 15.7 Hz, 1H).

$^{13}$C NMR (126 MHz, Chloroform-*d*) δ 188.3, 141.7, 140.3, 136.7, 134.1, 129.9, 128.9, 128.0, 127.7, 127.7, 124.1, 123.5, 120.9, 108.3, 73.6, 63.1.

HRMS (ESI): Cacld. for $[M+H]^+$ 253.0865, found 253.0869.

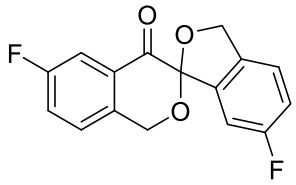



6,6'-dimethyl-3H-spiro[isobenzofuran-1,3'-isochroman]-4'-one (**g2**): Following the general procedure of catalytic reactions, the title product was purified on a silicon column with EtOAc/PE (v/v = 1/25) as the eluents and isolated as a white solid (27.4 mg, 49% yield).

$^1$H NMR (500 MHz, Chloroform-*d*) δ 7.93 – 7.89 (m, 1H), 7.41 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.25 – 7.22 (m, 1H), 7.19 (d, *J* = 7.9 Hz, 1H), 7.16 – 7.12 (m, 2H), 5.47 (d, *J* = 15.5 Hz, 1H), 5.30 (d, *J* = 12.2 Hz, 1H), 5.16 (d, *J* = 12.2 Hz, 1H), 4.86 (d, *J* = 15.5 Hz, 1H), 2.42 (s, 3H), 2.39 (s, 3H).

$^{13}$C NMR (126 MHz, Chloroform-*d*) δ 188.65, 138.86, 137.95, 137.52, 137.41, 137.04, 135.05, 130.84, 128.69, 127.65, 124.04, 123.73, 120.62, 108.21, 73.49, 62.98, 21.32, 21.09.

HRMS (ESI): Cacld. for $[M+Na]^+$ 303.0997, found 303.0986.



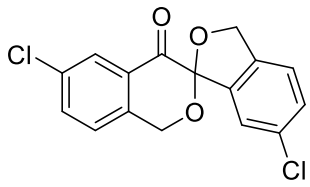

6,6'-difluoro-3*H*-spiro[isobenzofuran-1,3'-isochroman]-4'-one (**g3**): Following the general procedure of catalytic reactions, the title product was purified on a silicon column with EtOAc/PE (v/v = 1/25) as the eluents and isolated as a white solid (31.7 mg, 55% yield).

$^1$H NMR (500 MHz, Chloroform-*d*) δ 7.76 (dd, *J* = 8.6, 2.7 Hz, 1H), 7.32 (td, *J* = 8.4, 2.7 Hz, 1H), 7.29 – 7.22 (m, 2H), 7.16 (td, *J* = 8.6, 2.4 Hz, 1H), 7.03 (dd, *J* = 8.0, 2.3 Hz, 1H), 5.49 – 5.43 (m, 1H), 5.33 – 5.27 (m, 1H), 5.16 (d, *J* = 12.2 Hz, 1H), 4.88 (d, *J* = 15.5 Hz, 1H).

$^{13}$C NMR (126 MHz, Chloroform-*d*) δ 186.80, 163.74, 163.11, 161.78, 161.14, 138.46, 138.39, 137.43, 137.40, 135.69, 135.67, 130.39, 130.34, 126.32, 126.26, 122.27, 122.20, 121.87, 121.69, 117.61, 117.42, 113.74, 113.57, 110.86, 110.67, 107.51, 73.26, 62.65.

$^{19}$F NMR (471 MHz, Chloroform-*d*) δ -112.90, -114.35.

HRMS (ESI): Cacld. for $[M+H]^+$ 289.0676, found 289.0672.

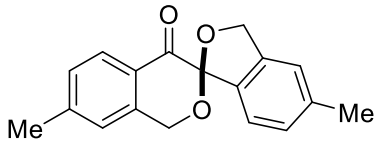



6,6'-dichloro-3*H*-spiro[isobenzofuran-1,3'-isochroman]-4'-one (**g4**): Following the general procedure of catalytic reactions, the title product was purified on a silicon column with EtOAc/PE (v/v = 1/25) as the eluents and isolated as a white solid (39.0 mg, 61% yield).

$^{1}$H NMR (500 MHz, Chloroform-*d*) δ 8.06 (d, *J* = 2.2 Hz, 1H), 7.57 (dd, *J* = 8.2, 2.3 Hz, 1H), 7.42 (dd, *J* = 8.1, 1.9 Hz, 1H), 7.32 (d, *J* = 1.8 Hz, 1H), 7.26 – 7.19 (m, 2H), 5.44 (dd, *J* = 15.8, 1.0 Hz, 1H), 5.30 (dd, *J* = 12.6, 1.0 Hz, 1H), 5.18 – 5.12 (m, 1H), 4.87 (d, *J* = 15.8 Hz, 1H).

$^{13}$C NMR (126 MHz, Chloroform-*d*) δ 186.6, 139.7, 138.7, 138.2, 134.2, 134.2, 134.0, 130.3, 129.9, 127.4, 125.8, 124.0, 122.1, 107.6, 73.3, 62.7

HRMS (ESI): Cacld. for $[M+H]^+$ 321.0085, found 321.0080.

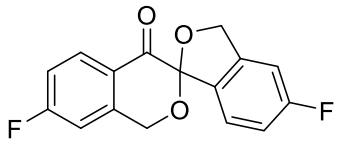



5,7'-dimethyl-3H-spiro[isobenzofuran-1,3'-isochroman]-4'-one (**g5**): Following the general procedure of catalytic reactions, the title product was purified on a silicon column with EtOAc/PE (v/v = 1/25) as the eluents and isolated as a white solid (26.9 mg, 48% yield).

$^{1}$H NMR (500 MHz, Chloroform-*d*) δ 8.00 (d, *J* = 8.0 Hz, 1H), 7.25 – 7.20 (m, 2H), 7.20 – 7.17 (m, 1H), 7.11 (d, *J* = 1.4 Hz, 1H), 7.03 (s, 1H), 5.46 (d, *J* = 15.6 Hz, 1H), 5.29 (d, *J* = 12.4 Hz, 1H), 5.15 (d, *J* = 12.5 Hz, 1H), 4.83 (d, *J* = 15.6 Hz, 1H), 2.43 (s, 3H), 2.41 (s, 3H).

$^{13}$C NMR (126 MHz, Chloroform-*d*) δ 188.24, 145.12, 141.78, 140.60, 139.90, 134.18, 128.97, 128.69, 127.77, 126.56, 124.39, 123.08, 121.31, 108.30, 73.37, 63.04, 22.01, 21.55.

HRMS (ESI): Cacld. for $[M+Na]^+$ 303.0997, found 303.0992.



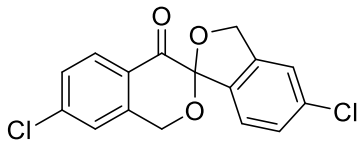
5,7'-difluoro-3H-spiro[isobenzofuran-1,3'-isochroman]-4'-one (**g6**): Following the general procedure of catalytic reactions, the title product was purified on a silicon column with EtOAc/PE (v/v = 1/25) as the eluents and isolated as a white solid (29.9 mg, 52% yield).

$^1$H NMR (500 MHz, Chloroform-*d*) δ 8.13 (dd, *J* = 8.7, 5.6 Hz, 1H), 7.30 (dd, *J* = 8.4, 4.8 Hz, 1H), 7.11 (dtd, *J* = 20.0, 8.7, 2.4 Hz, 2H), 7.00 (dd, *J* = 8.3, 2.2 Hz, 1H), 6.93 (dd, *J* = 8.7, 2.4 Hz, 1H), 5.47 (d, *J* = 15.9 Hz, 1H), 5.30 (d, *J* = 12.9 Hz, 1H), 5.16 (d, *J* = 12.9 Hz, 1H), 4.86 (d, *J* = 15.9 Hz, 1H).

$^{13}$C NMR (126 MHz, Chloroform-*d*) δ 186.62, 167.13, 165.08, 163.10, 144.69, 144.62, 142.75, 142.68, 132.30, 132.28, 131.10, 131.02, 125.40, 125.38, 125.19, 125.12, 115.76, 115.74, 115.58, 115.55, 110.98, 110.80, 108.29, 108.10, 107.76, 73.11, 73.08, 62.84, 62.82.

$^{19}$F NMR (471 MHz, Chloroform-*d*) δ -101.87, -111.65.

HRMS (ESI): Cacld. for $[M+H]^+$ 289.0676, found 289.0671.

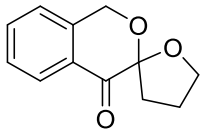


5,7'-dichloro-3H-spiro[isobenzofuran-1,3'-isochroman]-4'-one (**g7**): Following the general procedure of catalytic reactions, the title product was purified on a silicon column with EtOAc/PE (v/v = 1/25) as the eluents and isolated as a white solid (34 mg, 53% yield).

$^1$H NMR (500 MHz, Chloroform-*d*) δ 8.02 (d, *J* = 8.3 Hz, 1H), 7.40 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.36 (dd, *J* = 8.2, 1.8 Hz, 1H), 7.30 (s, 1H), 7.27 – 7.22 (m, 2H), 5.44 (d, *J* = 15.8 Hz, 1H), 5.28 (d, *J* = 12.8 Hz, 1H), 5.14 (d, *J* = 12.8 Hz, 1H), 4.83 (d, *J* = 15.9 Hz, 1H).

$^{13}$C NMR (126 MHz, Chloroform-*d*) δ 186.9, 143.1, 142.2, 140.8, 136.1, 135.0, 129.4, 128.5, 128.4, 127.1, 124.7, 124.3, 121.3, 107.8, 73.1, 62.6.

HRMS (ESI): Cacld. for $[M+H]^+$ 321.0085, found 321.0090.

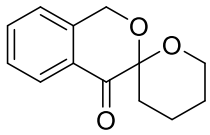


4,5-dihydro-3H-spiro[furan-2,3'-isochroman]-4'-one (**g8**): Following the general procedure of catalytic reactions, the title product was purified on a silicon column with EtOAc/PE (v/v = 1/25) as the eluents and isolated as a colorless oil (16.7 mg, 41% yield).

$^1$H NMR (500 MHz, Chloroform-*d*) δ 8.05 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.53 (td, *J* = 7.6, 1.3 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 1H), 7.17 (d, *J* = 7.7 Hz, 1H), 5.28 (d, *J* = 15.5 Hz, 1H), 4.70 (d, *J* = 15.5 Hz, 1H), 4.12 (td, *J* = 8.0, 5.7 Hz, 1H), 4.05 (q, *J* = 7.4 Hz, 1H), 2.78 (dt, *J* = 13.0, 8.8 Hz, 1H), 2.23 – 2.05 (m, 2H), 1.99 (ddd, *J* = 12.8, 8.2, 4.4 Hz, 1H).

$^{13}$C NMR (126 MHz, Chloroform-*d*) δ 188.9, 141.9, 133.8, 128.6, 127.5, 127.4, 124.0, 105.7, 70.3, 61.8, 32.8, 24.9.

HRMS (ESI): Cacld. for $[M+H]^+$ 205.0865, found 205.0862.

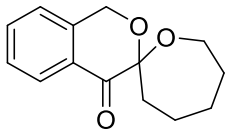


3',4',5',6'-tetrahydrospiro[isochromane-3,2'-pyran]-4-one (**g9**): Following the general procedure of catalytic reactions, the title product was purified on a silicon column with EtOAc/PE (v/v = 1/25) as the eluents and isolated as a colorless oil (27.9 mg, 64% yield).

$^1$H NMR (500 MHz, Chloroform-*d*) δ 8.04 (d, *J* = 7.8 Hz, 1H), 7.52 (t, *J* = 7.5 Hz, 1H), 7.36 (t, *J* = 7.6 Hz, 1H), 7.16 (d, *J* = 7.8 Hz, 1H), 5.10 (d, *J* = 15.4 Hz, 1H), 4.71 (d, *J* = 15.5 Hz, 1H), 3.85 (dd, *J* = 12.1, 3.1 Hz, 2H), 2.35 (td, *J* = 13.5, 4.8 Hz, 1H), 1.89 (qt, *J* = 13.2, 4.1 Hz, 1H), 1.75 (tdd, *J* = 23.0, 10.4, 4.2 Hz, 2H), 1.68 – 1.56 (m, 2H).

$^{13}$C NMR (126 MHz, Chloroform-*d*) δ 189.2, 141.5, 133.6, 127.9, 127.6, 127.4, 123.9, 96.2, 63.2, 60.5, 27.8, 24.7, 17.9.

HRMS (ESI): Cacld. for $[M+H]^+$ 219.1021, found 219.1025.

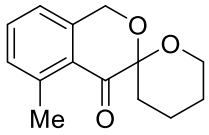


spiro[isochromane-3,2'-oxepan]-4-one (**g10**): Following the general procedure of catalytic reactions, the title product was purified on a silicon column with EtOAc/PE (v/v = 1/25) as the eluents and isolated as a colorless oil (13.4 mg, 29% yield).

$^1$H NMR (500 MHz, Chloroform-*d*) δ 8.03 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.52 (td, *J* = 7.5, 1.4 Hz, 1H), 7.37 (t, *J* = 7.6 Hz, 1H), 7.15 (d, *J* = 7.7 Hz, 1H), 5.14 (d, *J* = 15.5 Hz, 1H), 4.69 (d, *J* = 15.5 Hz, 1H), 3.99 – 3.92 (m, 1H), 3.80 – 3.74 (m, 1H), 2.55 – 2.48 (m, 1H), 1.90 – 1.83 (m, 3H), 1.76 – 1.67 (m, 3H), 1.49 – 1.38 (m, 1H).

$^{13}$C NMR (126 MHz, Chloroform-*d*) δ 190.3, 141.7, 133.4, 128.4, 127.5, 127.4, 123.7, 100.0, 64.7, 61.3, 35.5, 30.7, 30.2, 23.6.

HRMS (ESI): Cacld. for $[M+Na]^+$ 255.0997, found 255.1002.

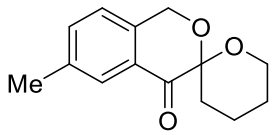


5-methyl-3',4',5',6'-tetrahydrospiro[isochromane-3,2'-pyran]-4-one (**g11**): Following the general procedure of catalytic reactions, the title product was purified on a silicon column with EtOAc/PE (v/v = 1/25) as the eluents and isolated as a colorless oil (19.4 mg, 42% yield).

$^1$H NMR (500 MHz, Chloroform-*d*) δ 7.37 (t, *J* = 7.6 Hz, 1H), 7.14 (d, *J* = 7.6 Hz, 1H), 7.00 (d, *J* = 7.7 Hz, 1H), 5.10 (d, *J* = 15.4 Hz, 1H), 4.72 (d, *J* = 15.4 Hz, 1H), 3.89 – 3.80 (m, 2H), 2.66 (s, 3H), 2.32 (td, *J* = 13.5, 4.8 Hz, 1H), 1.89 (qt, *J* = 13.3, 4.0 Hz, 1H), 1.82 – 1.68 (m, 2H), 1.62 (dddd, *J* = 20.2, 13.3, 3.8, 1.7 Hz, 2H).

$^{13}$C NMR (126 MHz, Chloroform-*d*) δ 191., 142.6, 142.3, 132.8, 130.9, 126.1, 121.8, 96.5, 63.2, 61.2, 28.2, 24.9, 22.6, 18.1.

HRMS (ESI): Cacld. for $[M+H]^+$ 233.1178, found 219.1170.

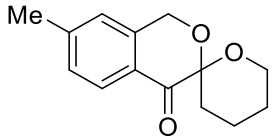


6-methyl-3',4',5',6'-tetrahydrospiro[isochromane-3,2'-pyran]-4-one (**g12**): Following the general procedure of catalytic reactions, the title product was purified on a silicon column with EtOAc/PE (v/v = 1/25) as the eluents and isolated as a colorless oil (20.4 mg, 44% yield).

$^1$H NMR (500 MHz, Chloroform-*d*) δ 7.84 (d, *J* = 1.7 Hz, 1H), 7.34 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.06 (d, *J* = 7.8 Hz, 1H), 5.07 (d, *J* = 15.2 Hz, 1H), 4.69 (d, *J* = 15.3 Hz, 1H), 3.89 – 3.80 (m, 2H), 2.40 – 2.30 (m, 4H), 1.89 (qt, *J* = 13.3, 4.1 Hz, 1H), 1.82 – 1.69 (m, 2H), 1.62 (ddddd, *J* = 15.5, 13.5, 5.9, 3.4, 1.8 Hz, 2H).

$^{13}$C NMR (126 MHz, Chloroform-*d*) δ 189.6, 138.8, 137.3, 134.7, 127.8, 127.7, 123.9, 96.2, 63.2, 60.5, 27.9, 24.8, 21.1, 18.0.

HRMS (ESI): Cacld. for $[M+H]^+$ 233.1178, found 219.1172.

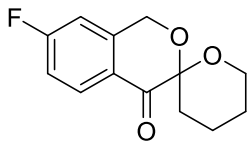



7-methyl-3',4',5',6'-tetrahydrospiro[isochromane-3,2'-pyran]-4-one (**g13**): Following the general procedure of catalytic reactions, the title product was purified on a silicon column with EtOAc/PE (v/v = 1/25) as the eluents and isolated as a colorless oil (20.9 mg, 45% yield).

$^1$H NMR (500 MHz, Chloroform-*d*) δ 7.94 (d, *J* = 7.9 Hz, 1H), 7.17 (dd, *J* = 8.0, 1.5 Hz, 1H), 6.96 (s, 1H), 5.07 (d, *J* = 15.4 Hz, 1H), 4.67 (d, *J* = 15.4 Hz, 1H), 3.89 – 3.79 (m, 2H), 2.42 – 2.31 (m, 4H), 1.89 (qt, *J* = 13.3, 4.1 Hz, 1H), 1.82 – 1.69 (m, 2H), 1.67 – 1.56 (m, 2H).

$^{13}$C NMR (126 MHz, DMSO-$d_6$) δ 189.1, 144.7, 141.6, 128.5, 127.8, 125.6, 124.2, 96.3, 63.1, 60.5, 27.8, 24.8, 21.9, 17.9.

HRMS (ESI): Cacld. for $[M+H]^+$ 233.1178, found 219.1171.



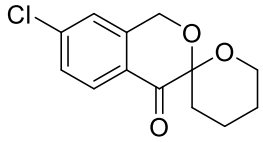

7-fluoro-3',4',5',6'-tetrahydrospiro[isochromane-3,2'-pyran]-4-one (**g14**): Following the general procedure of catalytic reactions, the title product was purified on a silicon column with EtOAc/PE (v/v = 1/25) as the eluents and isolated as a colorless oil (24.1 mg, 51% yield).

$^{1}$H NMR (500 MHz, Chloroform-*d*) δ 8.07 (dd, *J* = 8.7, 5.7 Hz, 1H), 7.05 (td, *J* = 8.6, 2.5 Hz, 1H), 6.85 (dd, *J* = 8.7, 2.5 Hz, 1H), 5.08 (d, *J* = 15.6 Hz, 1H), 4.70 (d, *J* = 15.6 Hz, 1H), 3.84 (dd, *J* = 9.4, 2.3 Hz, 2H), 2.35 (td, *J* = 13.6, 5.0 Hz, 1H), 1.88 (qt, *J* = 13.3, 4.1 Hz, 1H), 1.83 – 1.69 (m, 2H), 1.67 – 1.57 (m, 2H).

$^{13}$C NMR (126 MHz, Chloroform-*d*) δ 187.88, 166.79, 164.75, 144.65, 144.58, 131.03, 130.95, 124.61, 124.59, 115.37, 115.20, 110.73, 110.55, 96.22, 63.25, 60.32, 60.30, 27.66, 24.69, 17.86.

$^{19}$F NMR (471 MHz, Chloroform-*d*) δ -103.01.

HRMS (ESI): Cacld. for $[M+Na]^+$ 259.0746, found 259.0750.

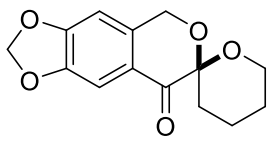



7-chloro-3',4',5',6'-tetrahydrospiro[isochromane-3,2'-pyran]-4-one (**g15**): Following the general procedure of catalytic reactions, the title product was purified on a silicon column with EtOAc/PE (v/v = 1/25) as the eluents and isolated as a white solid (26.2 mg, 52% yield).

$^{1}$H NMR (500 MHz, Chloroform-*d*) δ 7.98 (d, *J* = 8.4 Hz, 1H), 7.34 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.18 (d, *J* = 2.2 Hz, 1H), 5.07 (dt, *J* = 15.7, 1.0 Hz, 1H), 4.68 (d, *J* = 15.7 Hz, 1H), 3.84 (dd, *J* = 9.1, 2.3 Hz, 2H), 2.33 (td, *J* = 13.5, 4.9 Hz, 1H), 1.88 (qt, *J* = 13.1, 4.0 Hz, 1H), 1.83 – 1.69 (m, 2H), 1.66 – 1.58 (m, 2H).

$^{13}$C NMR (126 MHz, Chloroform-*d*) δ 188.3, 143.2, 140.1, 129.4, 128.1, 126.4, 124.0, 96.2, 63.3, 60.1, 27.6, 24.7, 17.9.

HRMS (ESI): Cacld. for $[M+H]^+$ 253.0631, found 253.0625..

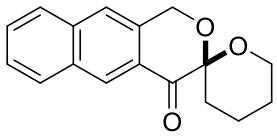



3,4,5,6-tetrahydrospiro[pyran-2,7'-[1,3]dioxolo[4,5-g]isochromen]-8'(5'H)-one (**g16**): Following the general procedure of catalytic reactions, the title product was purified on a silicon column with EtOAc/PE (v/v = 1/25) as the eluents and isolated as a white solid (12.0 mg, 23% yield).

$^1$H NMR (500 MHz, Chloroform-*d*) δ 6.84 (d, *J* = 8.7 Hz, 2H), 5.94 (s, 2H), 4.53 (s, 2H), 3.56 (t, *J* = 6.5 Hz, 2H), 2.45 (t, *J* = 6.8 Hz, 2H), 1.80 (dq, *J* = 8.7, 6.6 Hz, 2H), 1.73 – 1.65 (m, 2H).

$^{13}$C NMR (126 MHz, Chloroform-*d*) δ 147.37, 146.85, 134.55, 117.18, 111.58, 109.56, 101.26, 92.43, 78.94, 71.15, 69.88, 28.71, 25.44, 19.22.

HRMS (ESI): Cacld. for $[M+Na]^+$ 285.0739, found 285.0743.

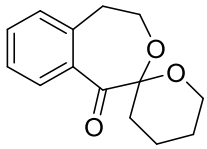


3',4',5',6'-tetrahydrospiro[benzo[g]isochromene-3,2'-pyran]-4(1H)-one (**g17**): Following the general procedure of catalytic reactions, the title product was purified on a silicon column with EtOAc/PE (v/v = 1/25) as the eluents and isolated as a white solid (17.6 mg, 33% yield).

$^1$H NMR (500 MHz, Chloroform-*d*) δ 8.67 (d, *J* = 2.2 Hz, 1H), 7.99 (d, *J* = 8.3 Hz, 1H), 7.83 (d, *J* = 8.3 Hz, 1H), 7.66 – 7.57 (m, 2H), 7.52 (tt, *J* = 6.8, 1.6 Hz, 1H), 5.30 (dt, *J* = 14.9, 1.9 Hz, 1H), 4.91 (dd, *J* = 15.1, 2.2 Hz, 1H), 3.91 (ddddd, *J* = 15.7, 9.1, 6.6, 4.8, 2.2 Hz, 2H), 2.43 (tdd, *J* = 13.6, 4.8, 2.2 Hz, 1H), 2.02 – 1.88 (m, 1H), 1.88 – 1.75 (m, 2H), 1.75 – 1.63 (m, 2H).

$^{13}$C NMR (126 MHz, Chloroform-*d*) δ 189.94, 136.39, 135.69, 132.09, 129.97, 129.76, 128.98, 127.40, 126.37, 122.41, 96.80, 63.04, 60.57, 31.45, 30.21, 28.08, 24.80, 18.01.

HRMS (ESI): Cacld. for $[M+Na]^+$ 291.0997, found 291.0999.



3',4,4',5,5',6'-hexahydro-1H-spiro[benzo[d]oxepine-2,2'-pyran]-1-one (**g18**): Following the general procedure of catalytic reactions, the title product was purified on a silicon column with EtOAc/PE (v/v = 1/25) as the eluents and isolated as a colorless oil (14.4 mg, 31% yield).

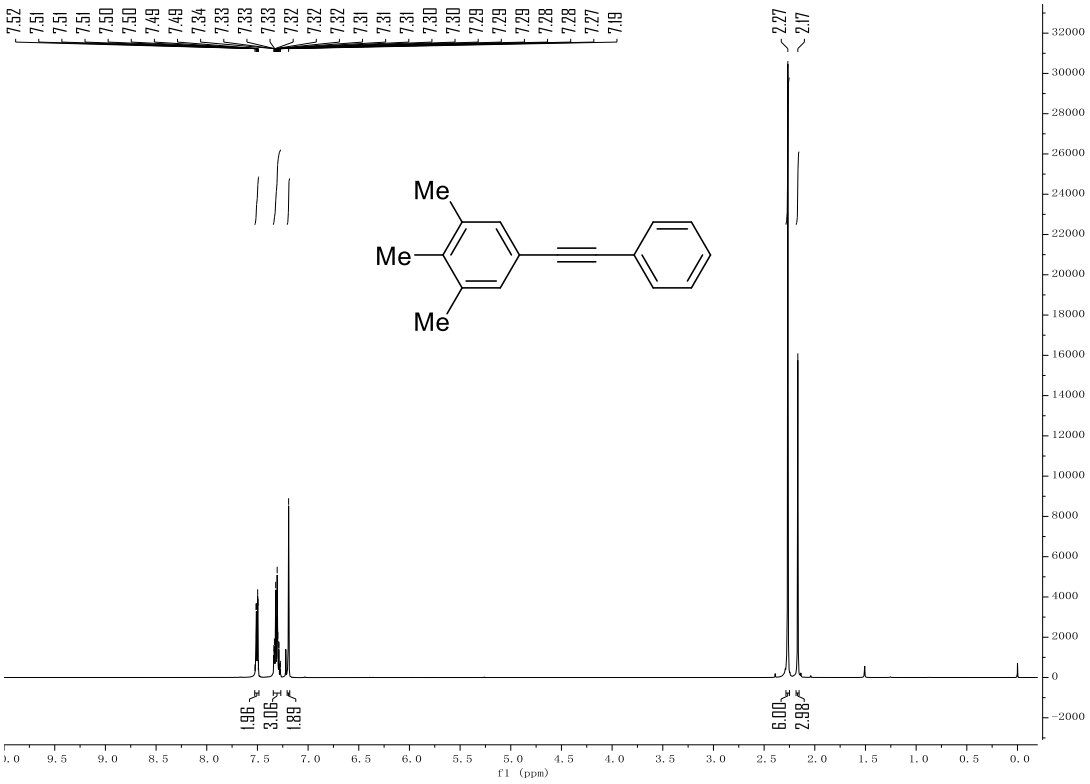
$^1$H NMR (500 MHz, Chloroform-*d*) δ 7.52 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.43 (td, *J* = 7.6, 1.5 Hz, 1H), 7.32 – 7.27 (m, 1H), 7.20 (d, *J* = 7.6 Hz, 1H), 4.18 (ddd, *J* = 11.9, 7.4, 4.1 Hz, 1H), 3.98 (ddd, *J* = 12.1, 7.0, 4.6 Hz, 1H), 3.90 – 3.83 (m, 2H), 3.27 (ddd, *J* = 16.5, 7.0, 4.1 Hz, 1H), 3.15 (ddd, *J* = 16.5, 7.5, 4.7 Hz, 1H), 1.89 – 1.54 (m, 6H).

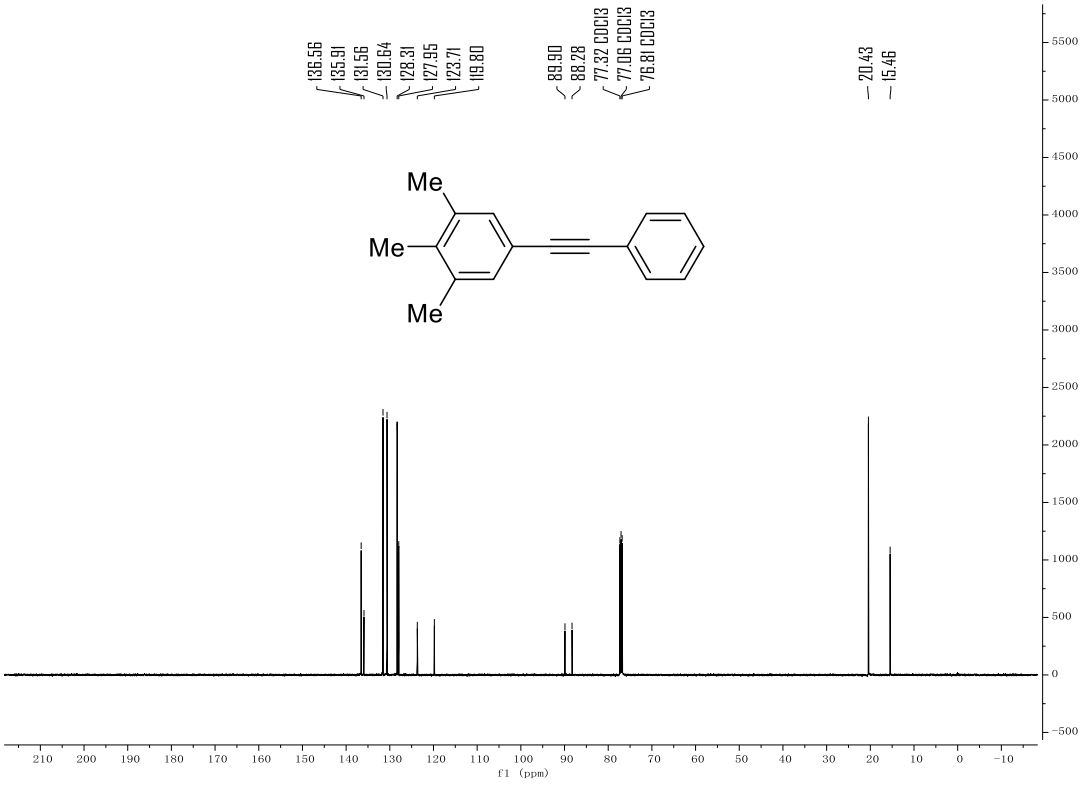
$^{13}$C NMR (126 MHz, Chloroform-*d*) δ 204.6, 138.0, 137.8, 131.8, 129.4, 128.9, 126.6, 101.8, 62.6, 35.8, 31.9, 24.6, 18.4.

HRMS (ESI): Cacld. for $[M+Na]^+$ 255.0997, found 255.0988.

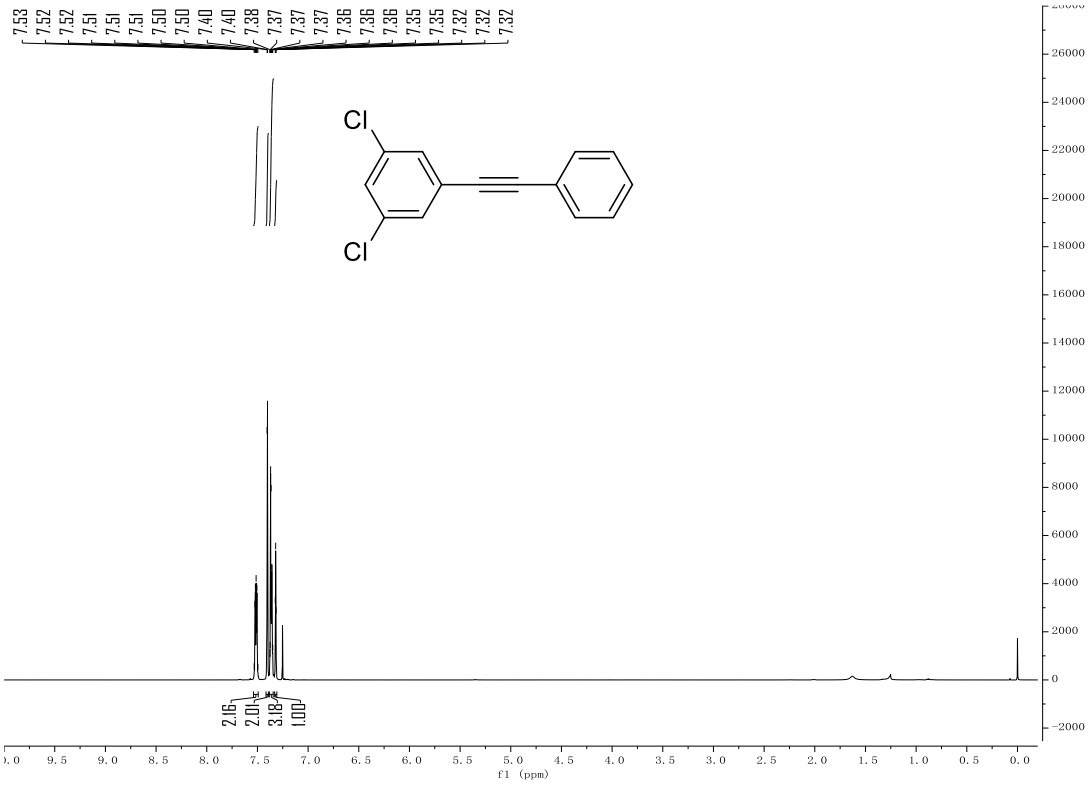
## 10. NMR Spectra of Isolated Compounds

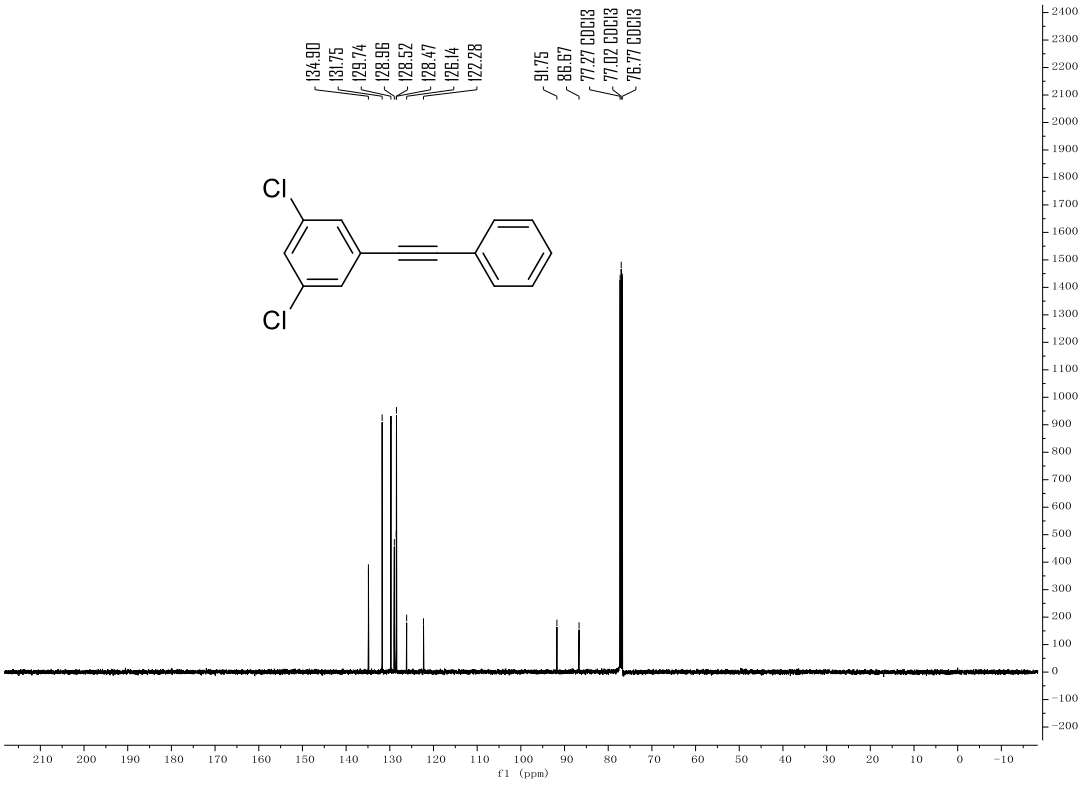
1,2,3-trimethyl-5-(phenylethynyl)benzene (**d21**)



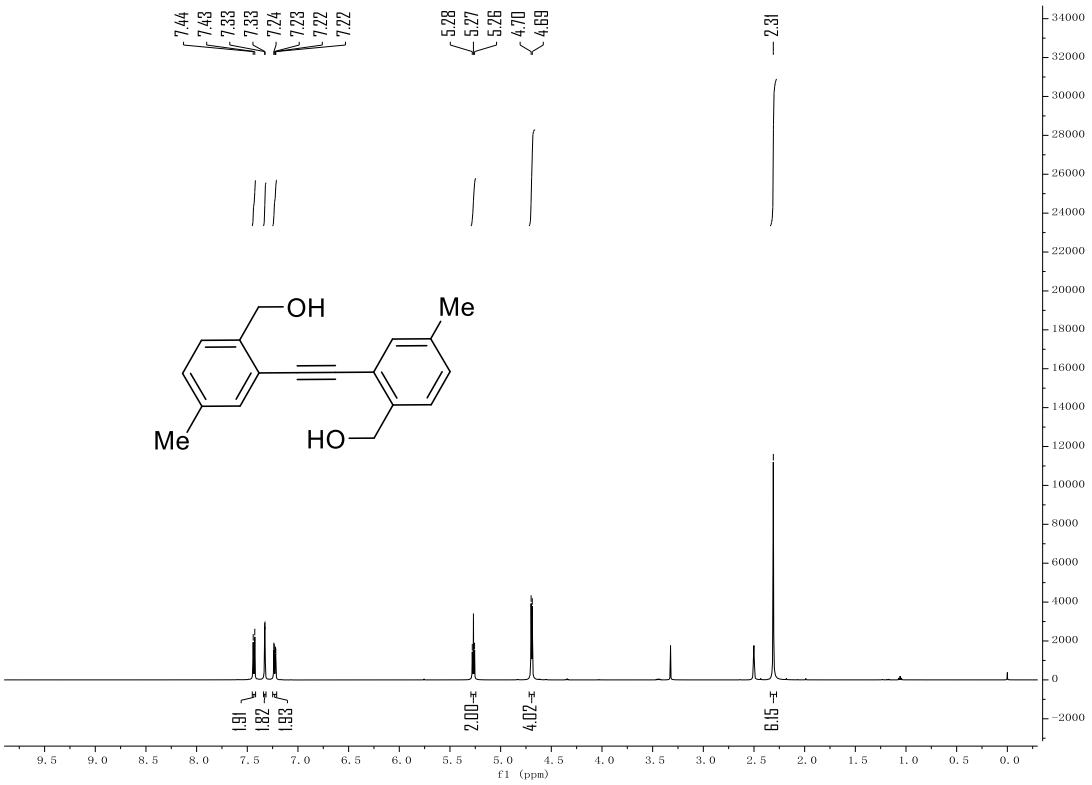



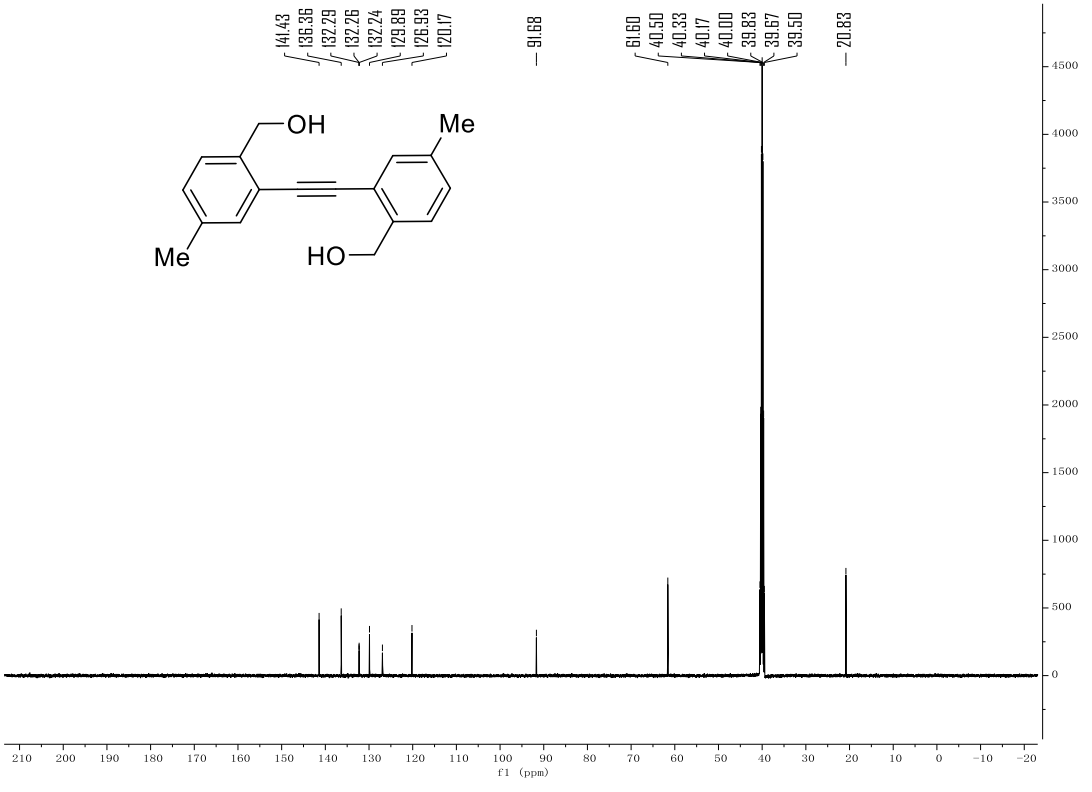
1,3-dichloro-5-(phenylethynyl)benzene (**d23**)



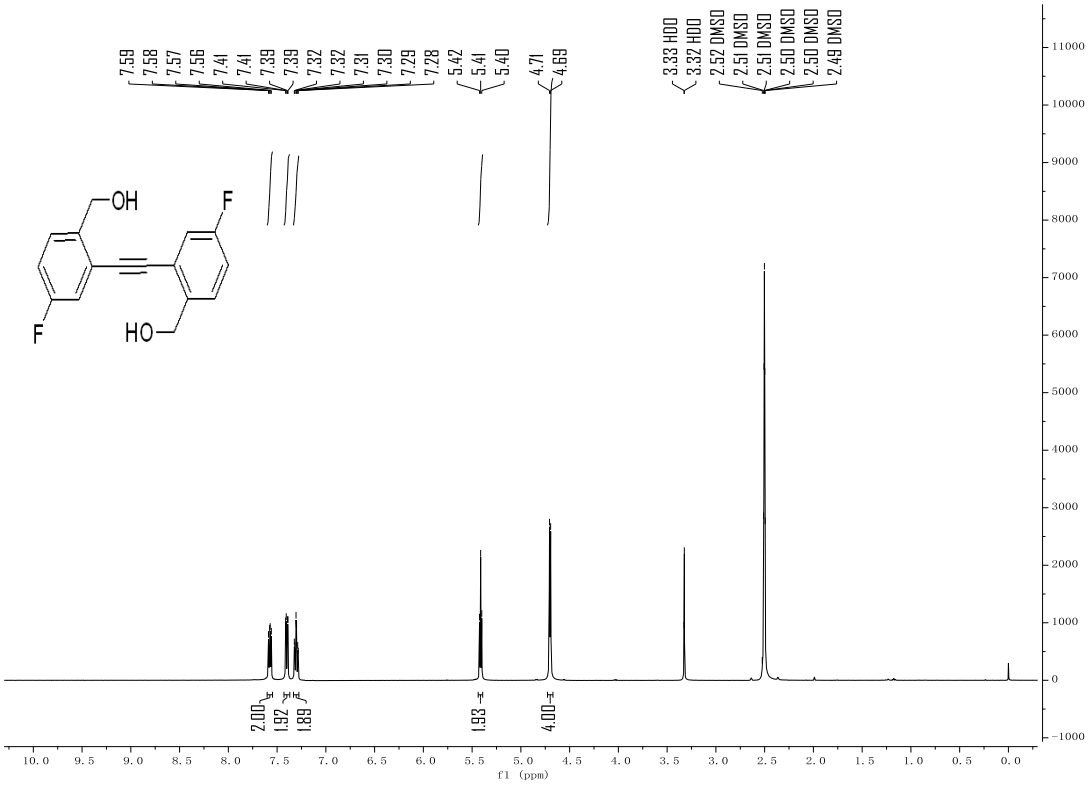



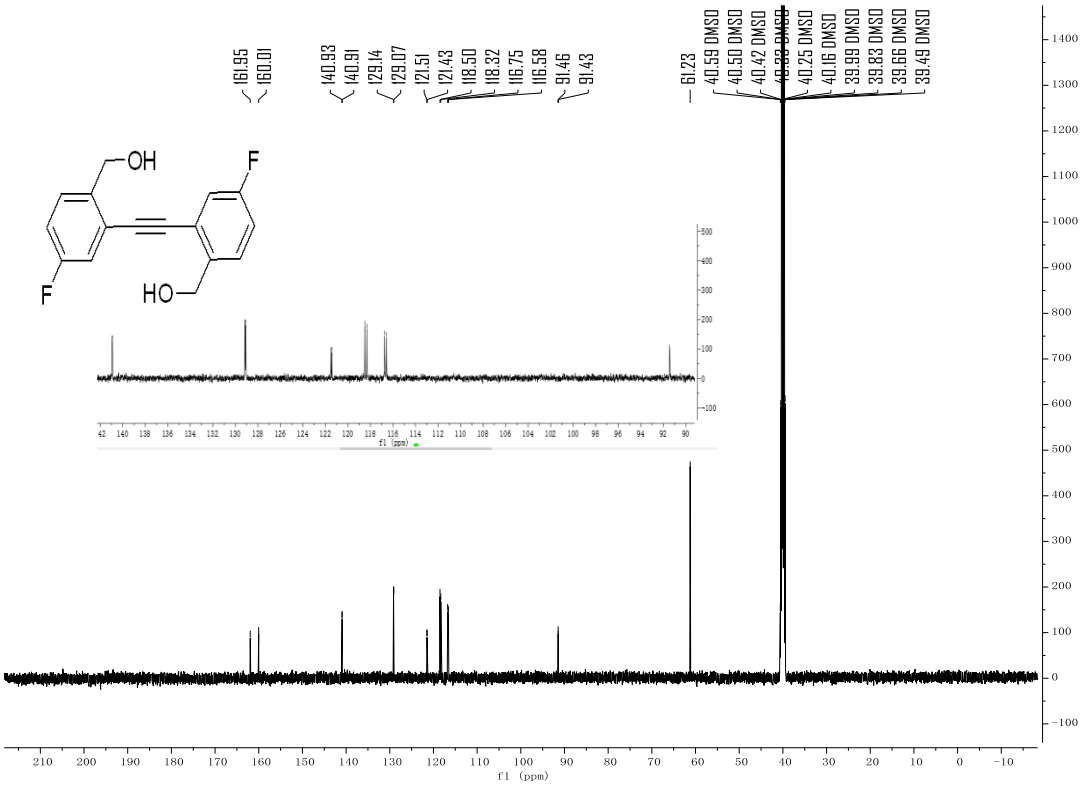
(ethyne-1,2-diylbis(4-methyl-2,1-phenylene))dimethanol (**f2**)



(ethyne-1,2-diylbis(4-fluoro-2,1-phenylene))dimethanol (**f3**)

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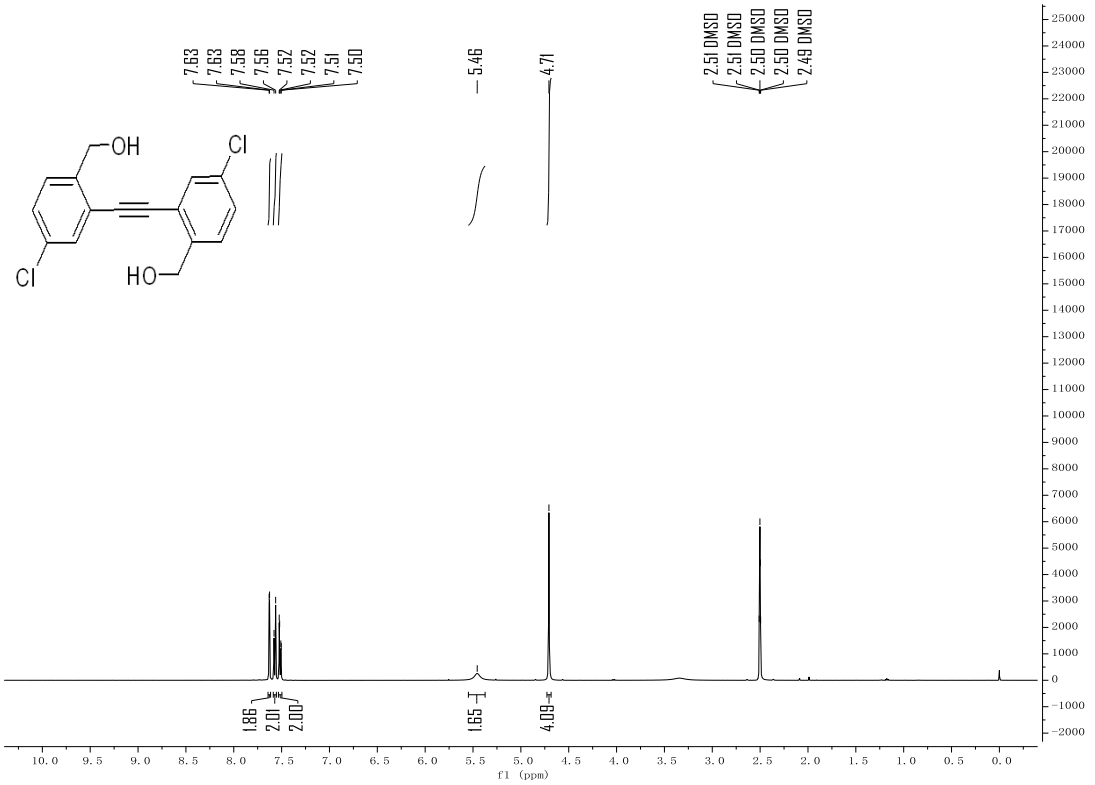
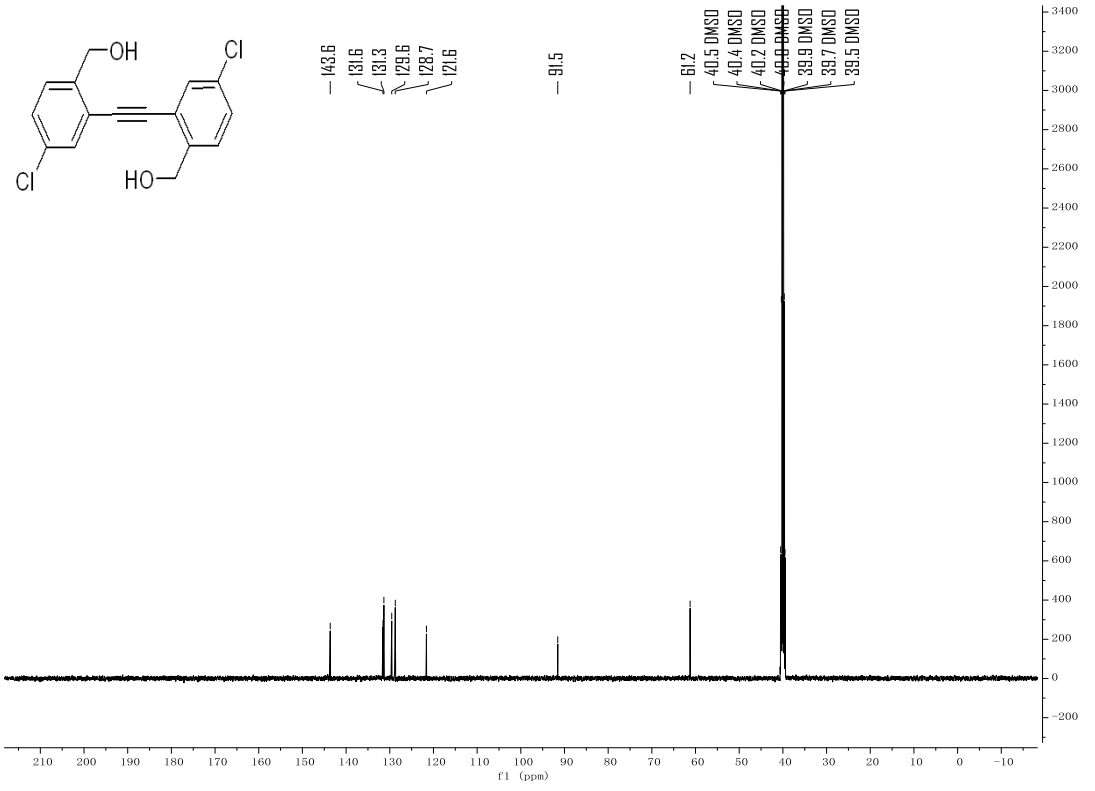
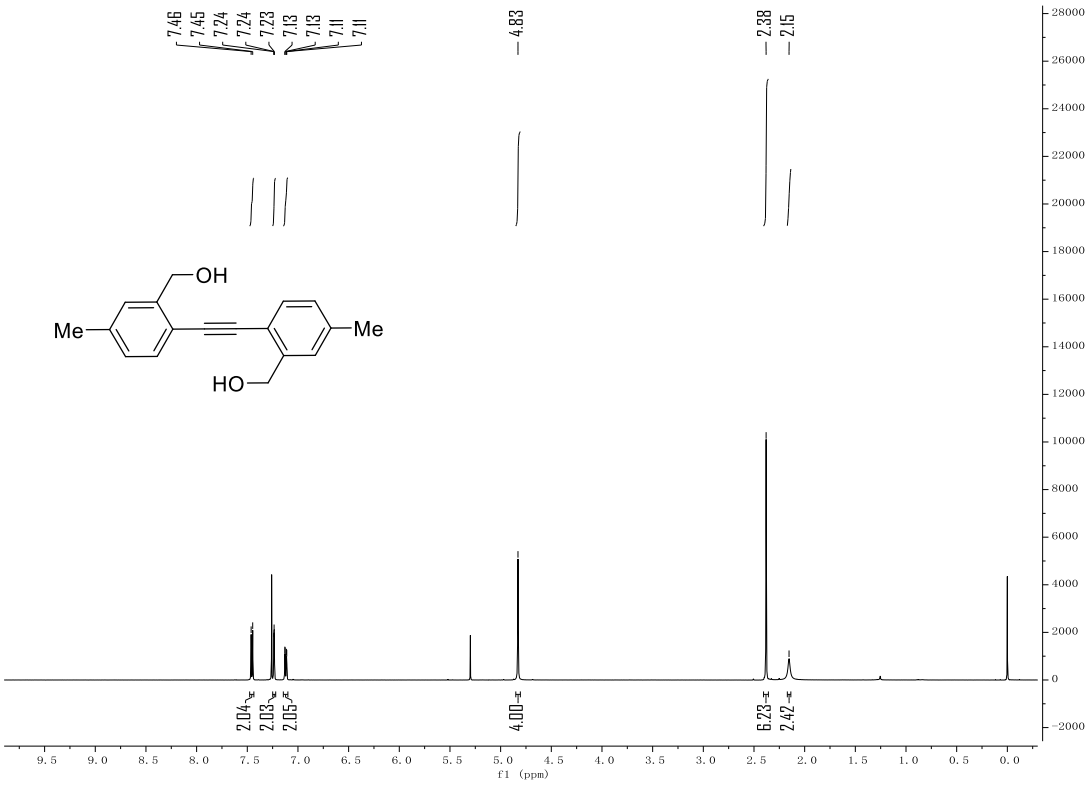
f1 (ppm)

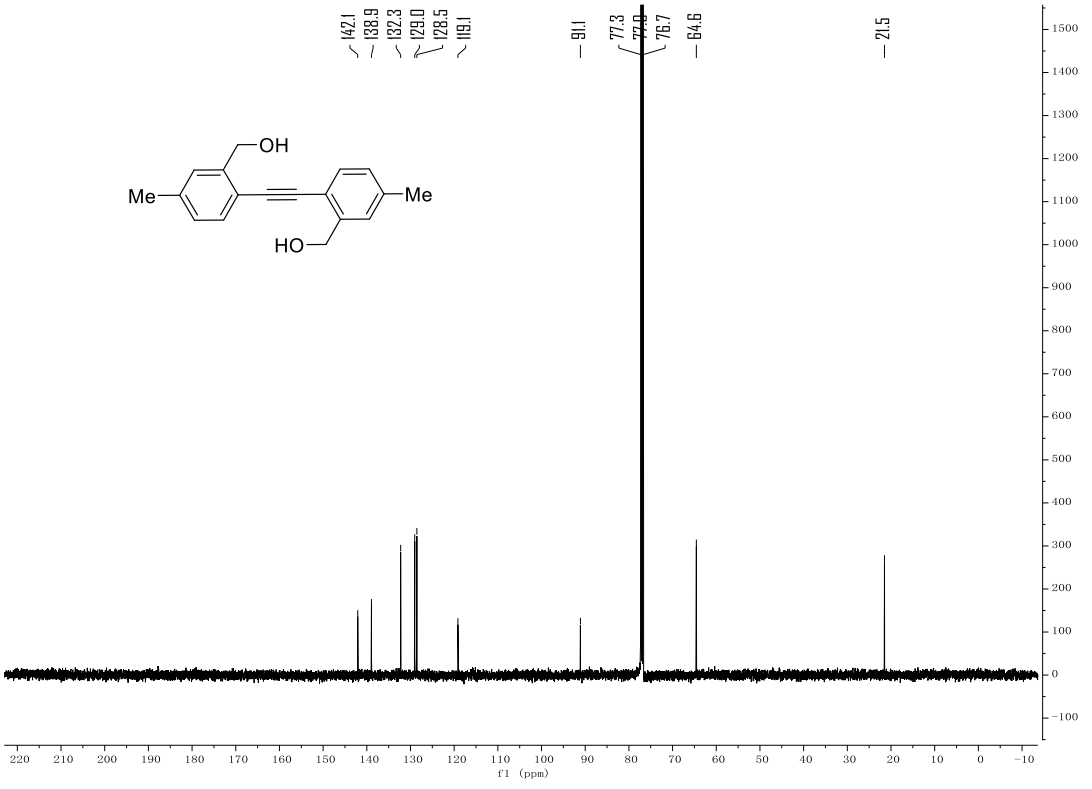
(ethyne-1,2-diylbis(4-chloro-2,1-phenylene))dimethanol (**f4**)



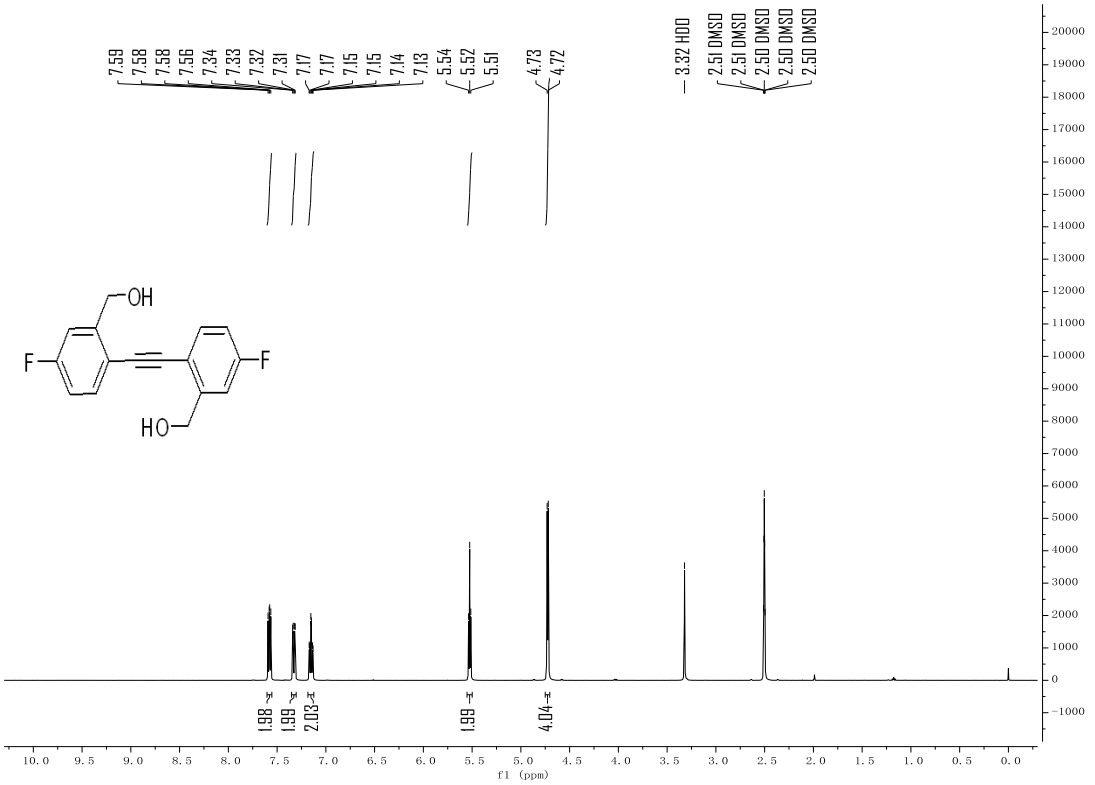



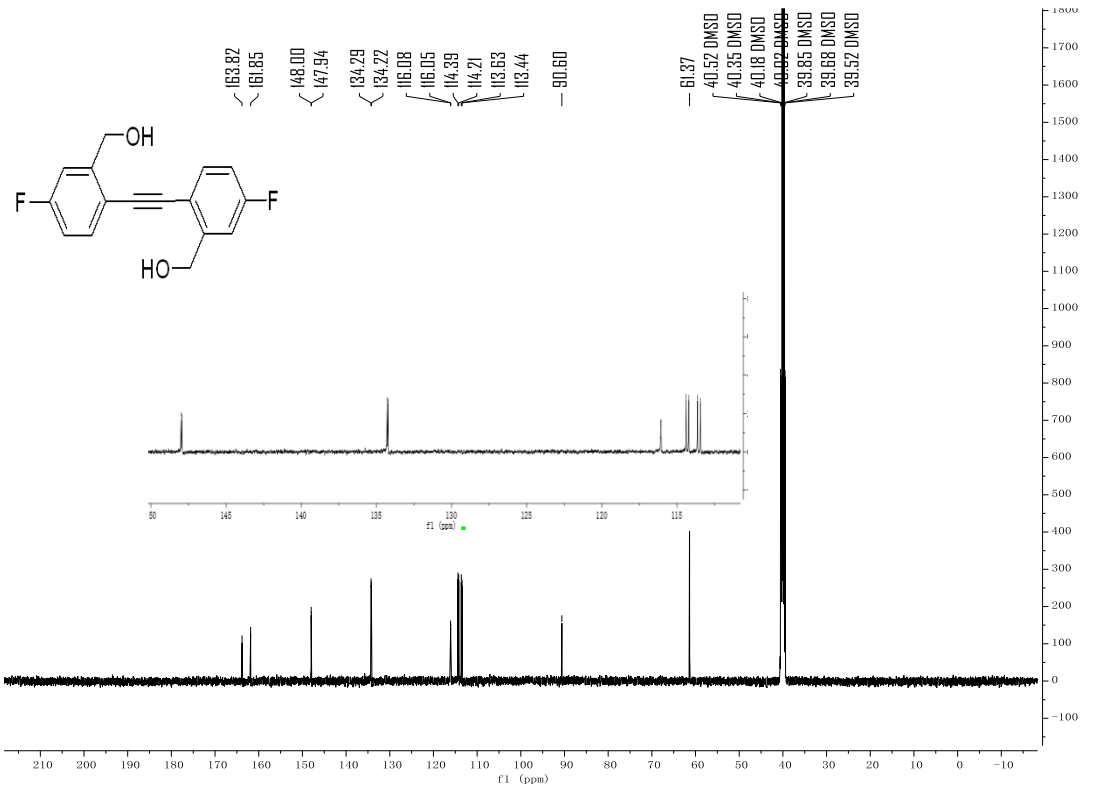
(ethyne-1,2-diylbis(5-methyl-2,1-phenylene))dimethanol (**f5**)

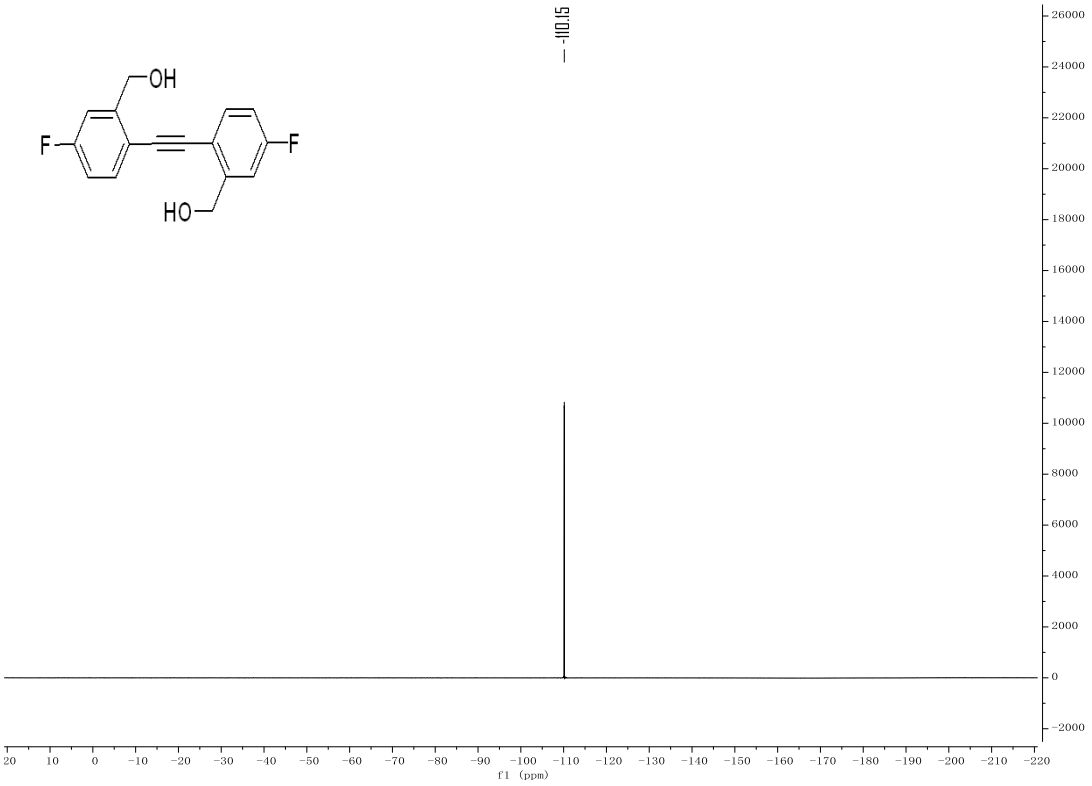


(ethyne-1,2-diylbis(5-fluoro-2,1-phenylene))dimethanol (**f6**)

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-2000
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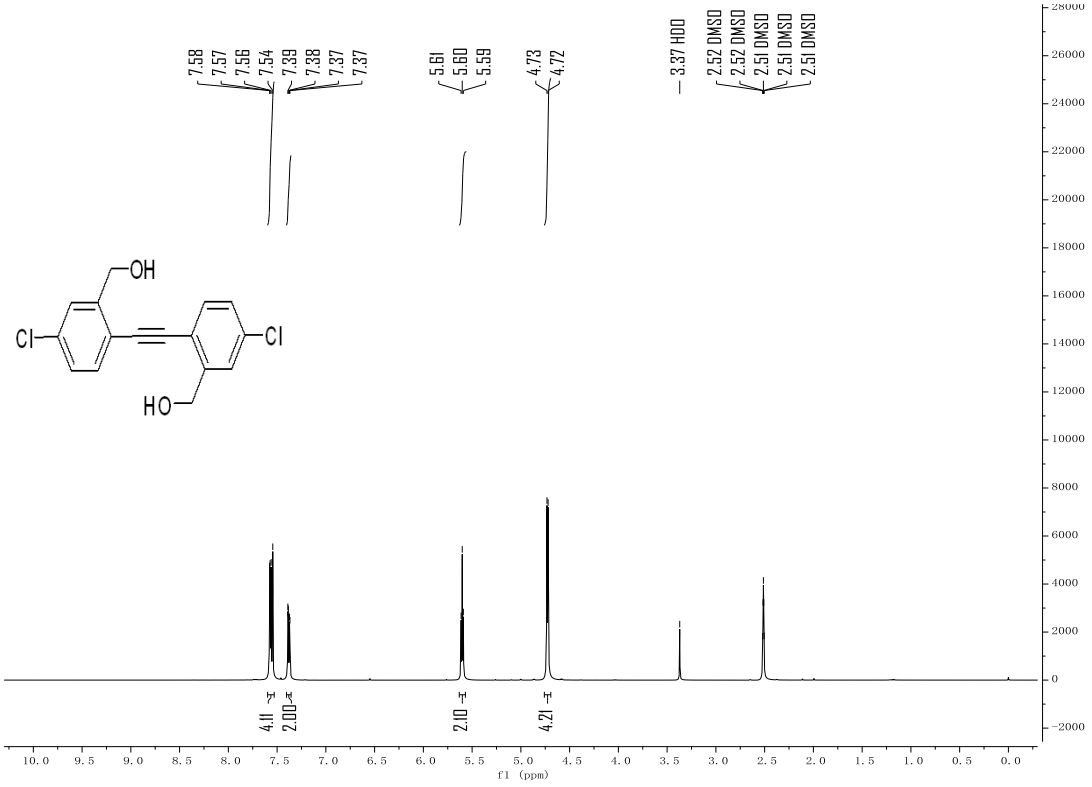
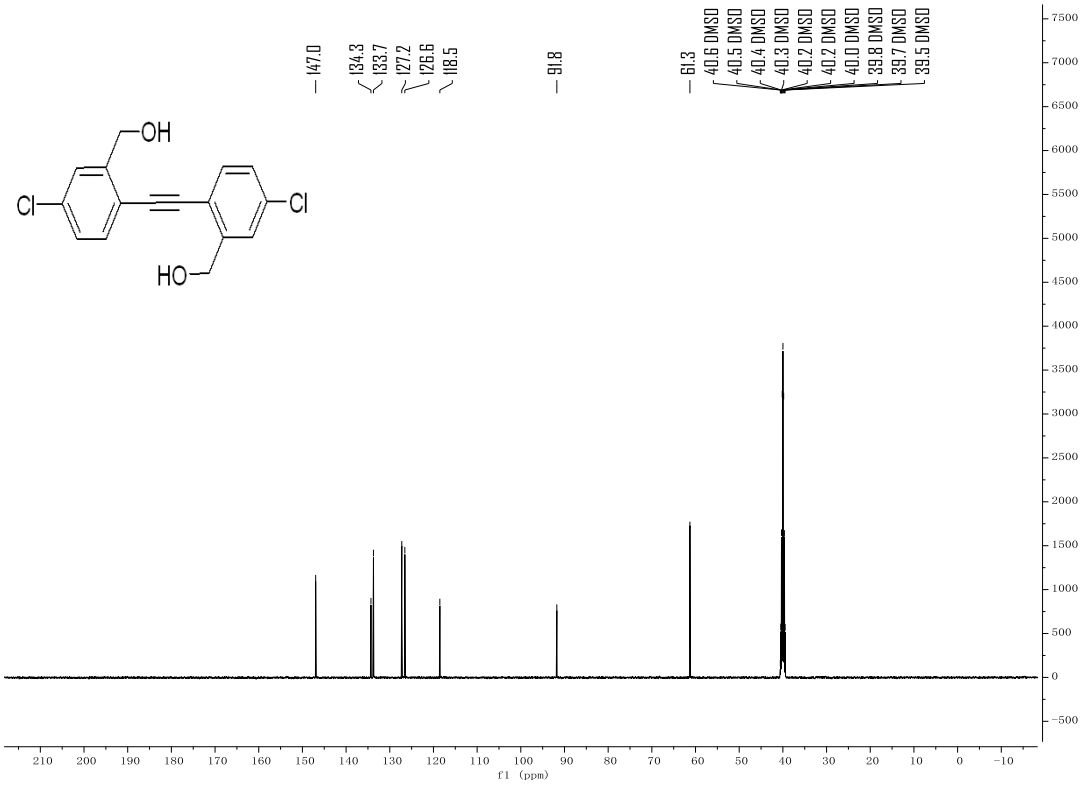
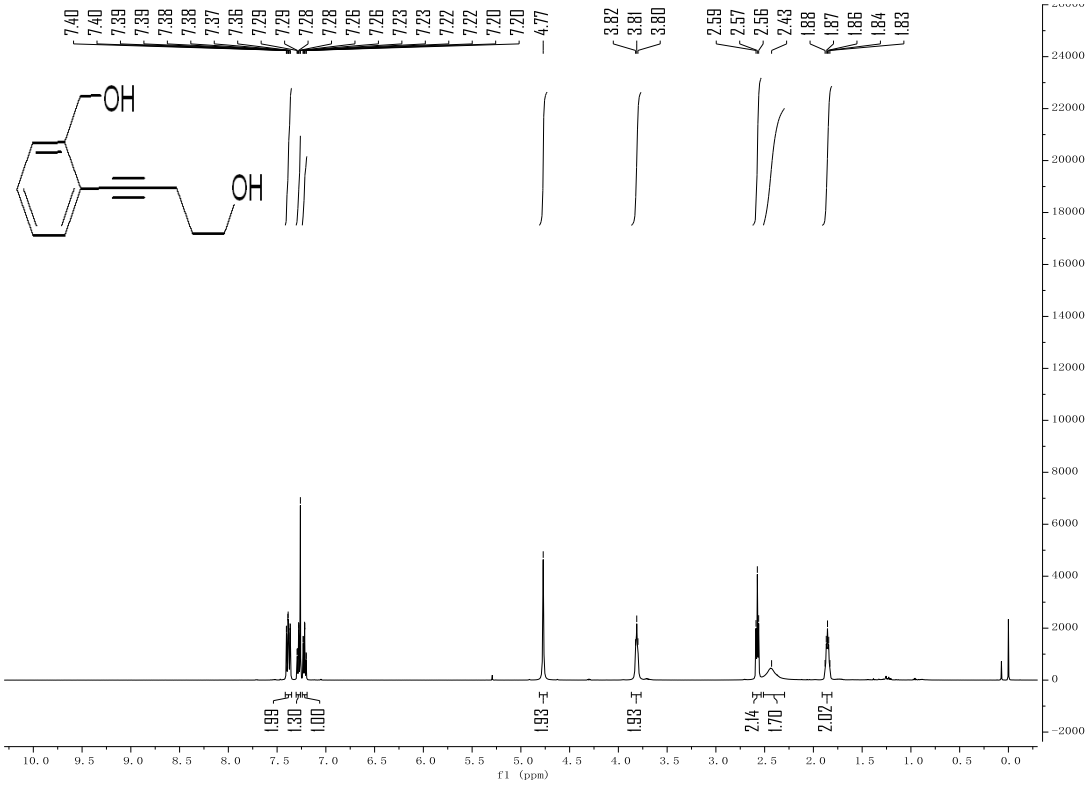
f1 (ppm)

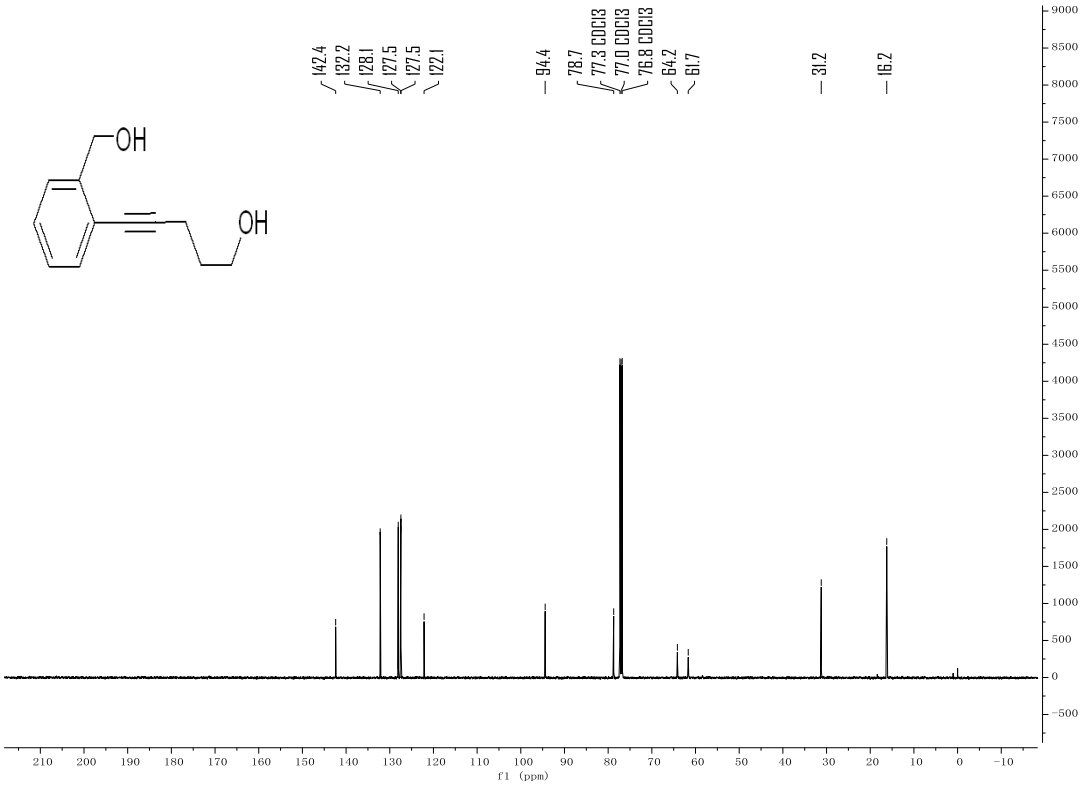
(ethyne-1,2-diylbis(5-chloro-2,1-phenylene))dimethanol (**f7**)



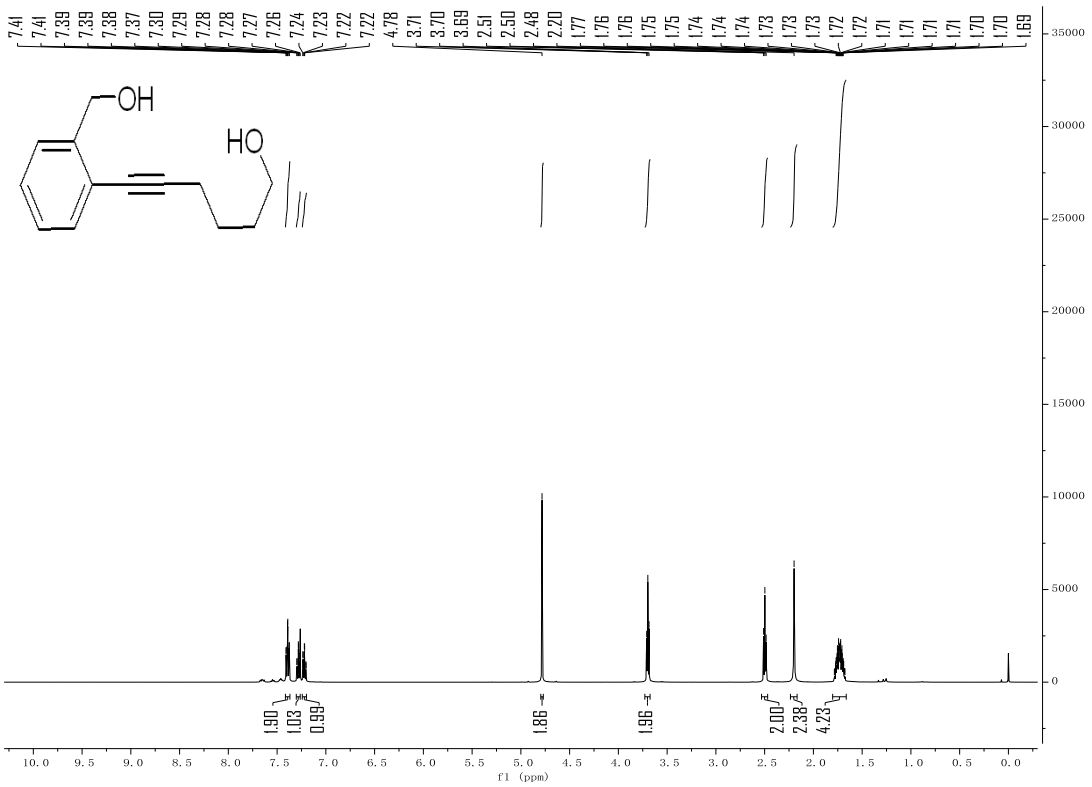



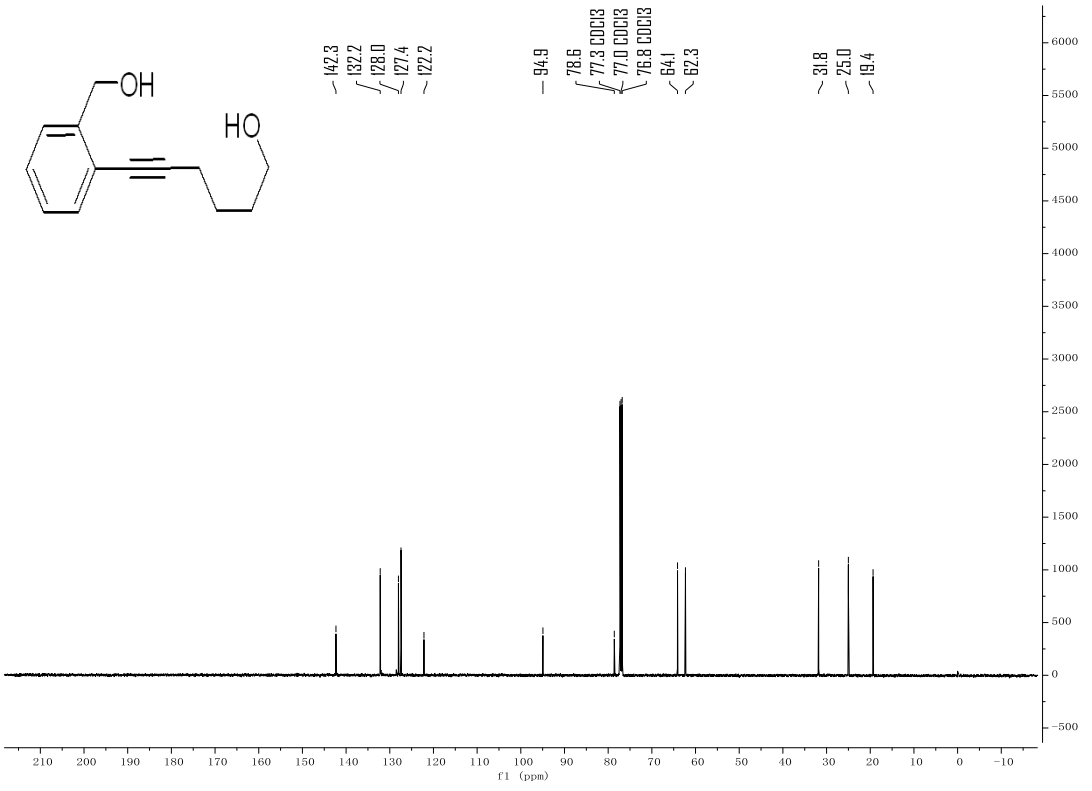
5-(2-(hydroxymethyl)phenyl)pent-4-yn-1-ol (**f8**)



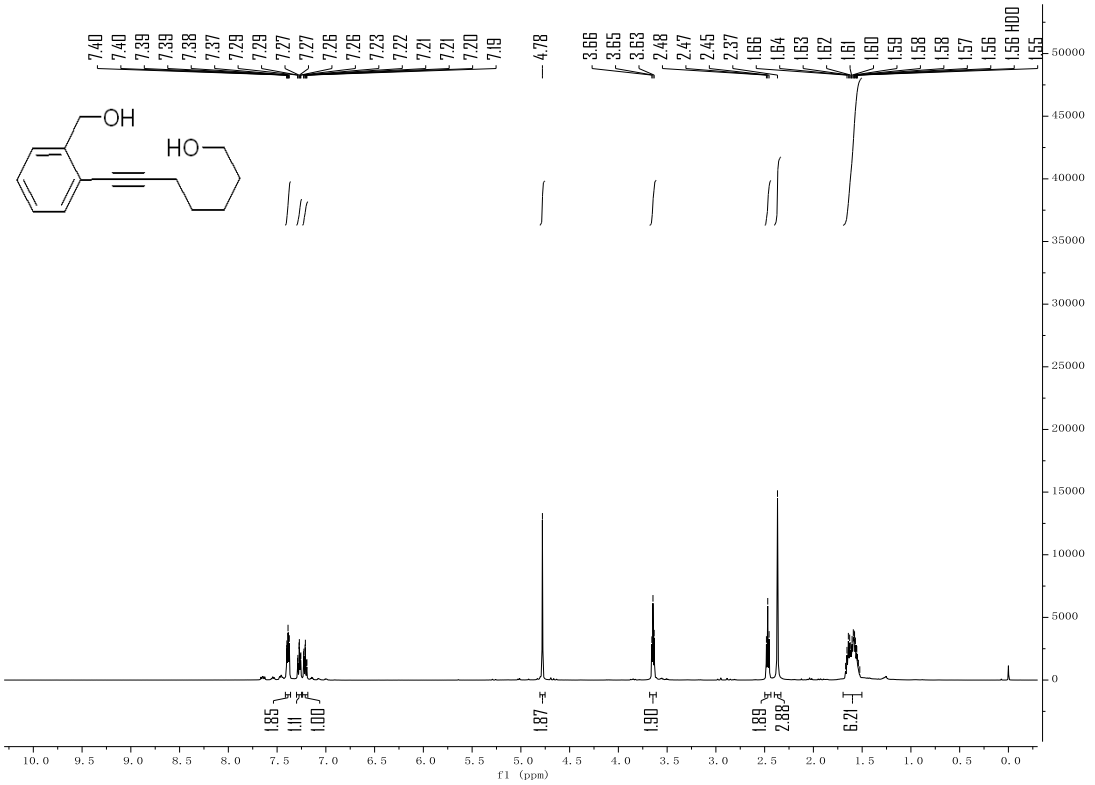



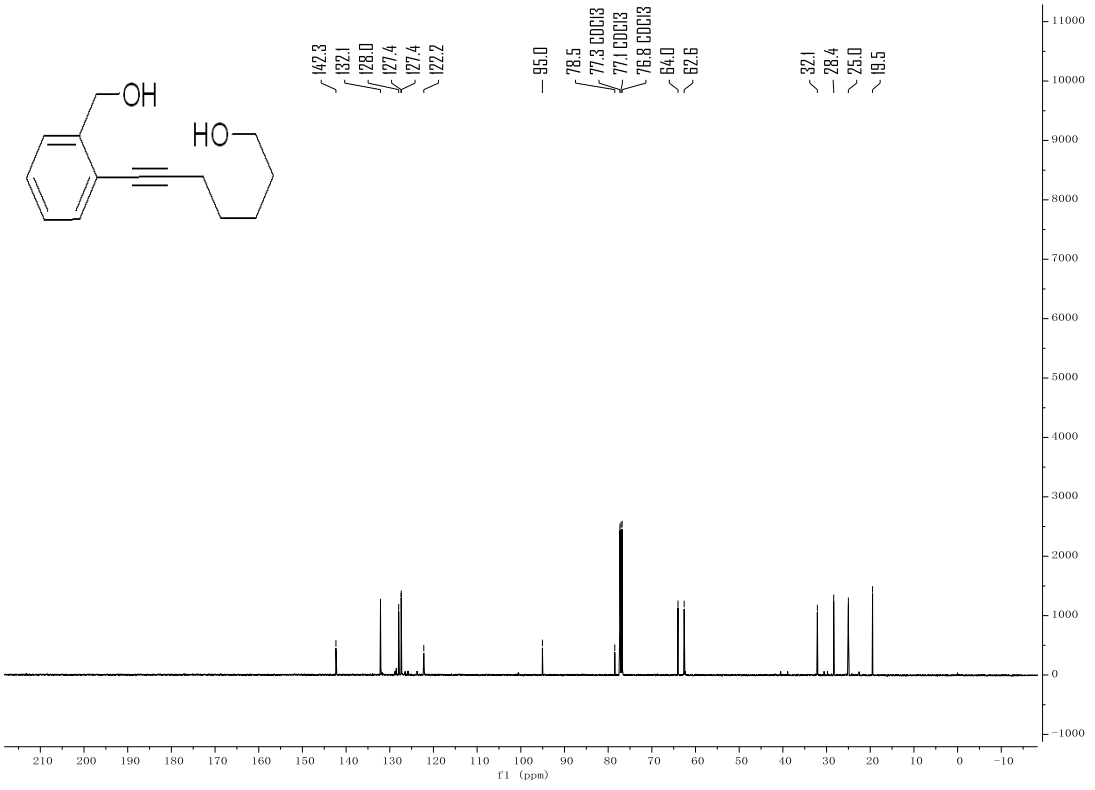
6-(2-(hydroxymethyl)phenyl)hex-5-yn-1-ol (**f9**)



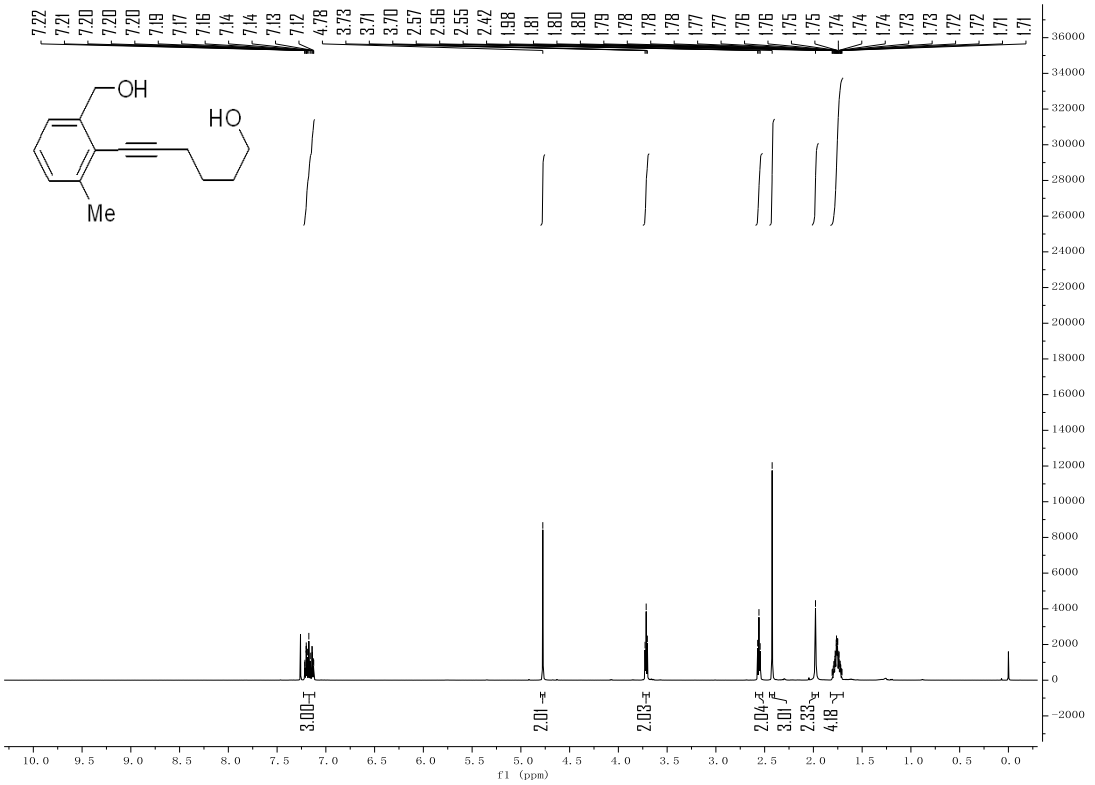



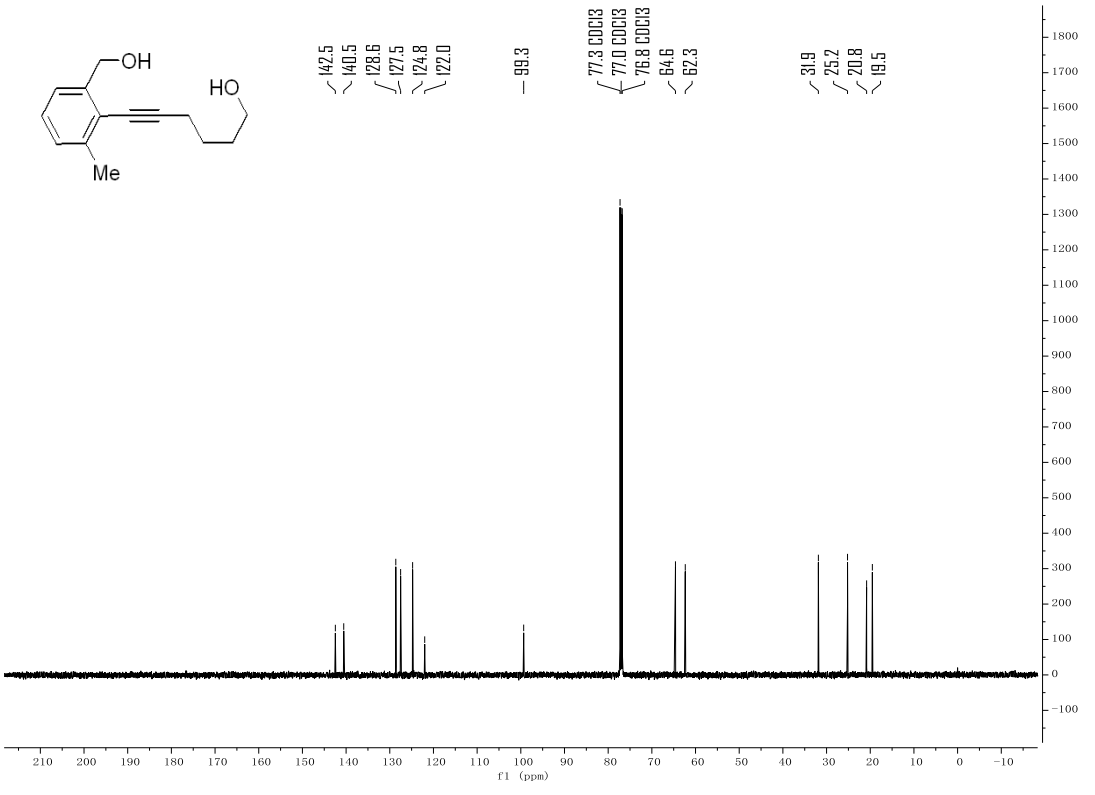
7-(2-(hydroxymethyl)phenyl)hept-6-yn-1-ol (**f10**)



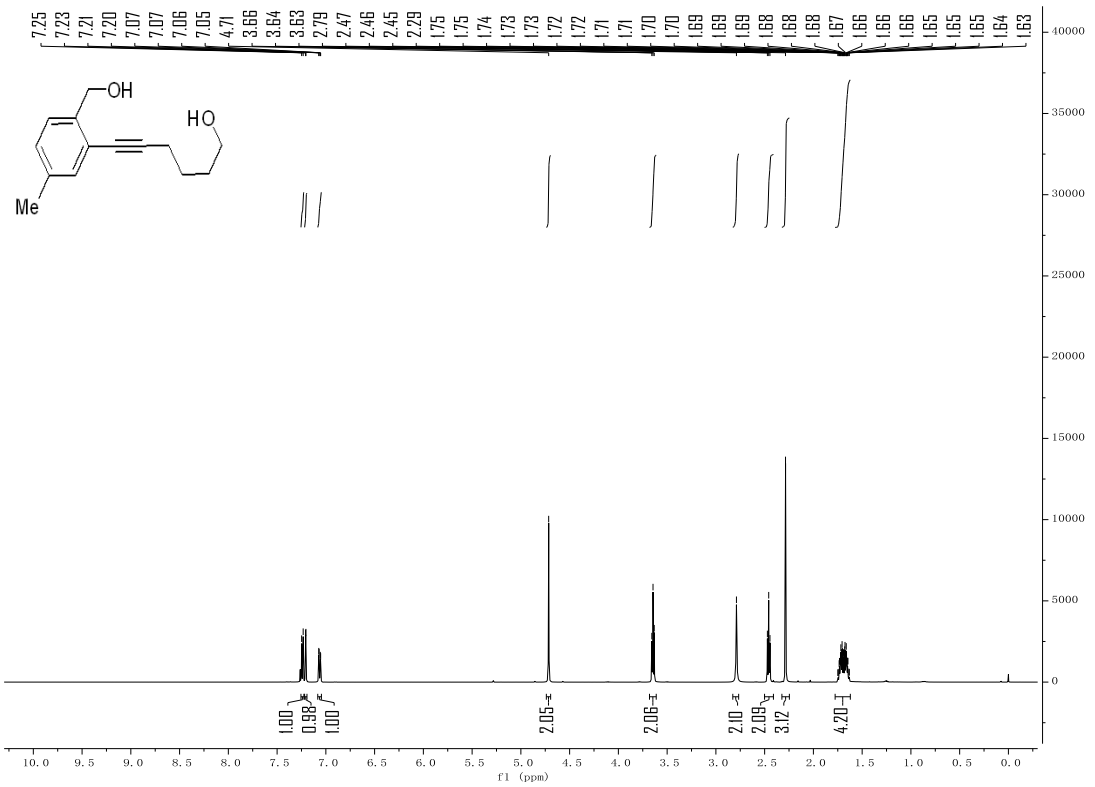



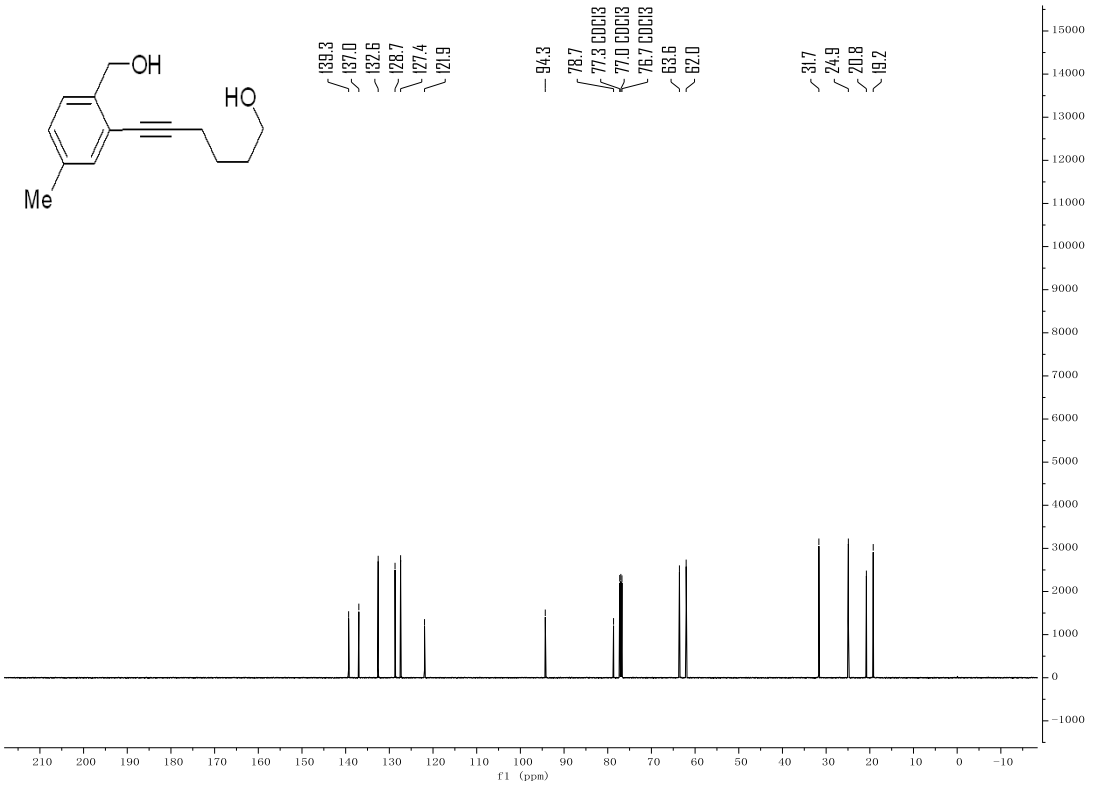
6-(2-(hydroxymethyl)-6-methylphenyl)hex-5-yn-1-ol (**f11**)



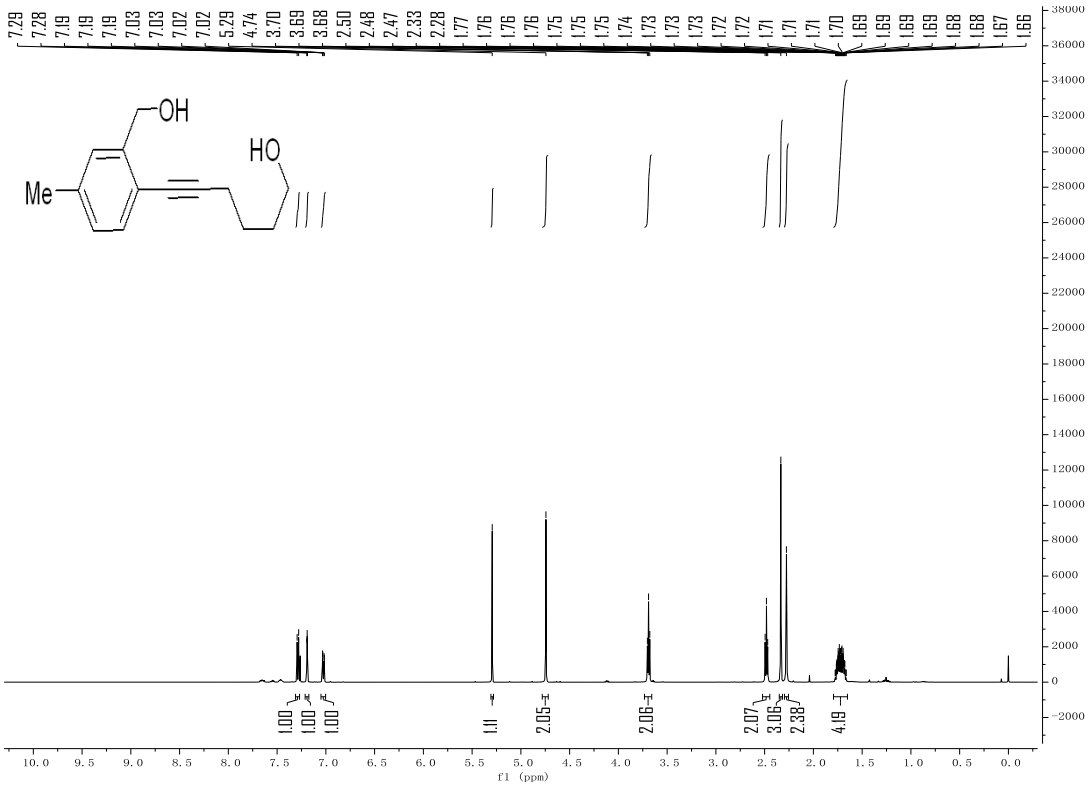



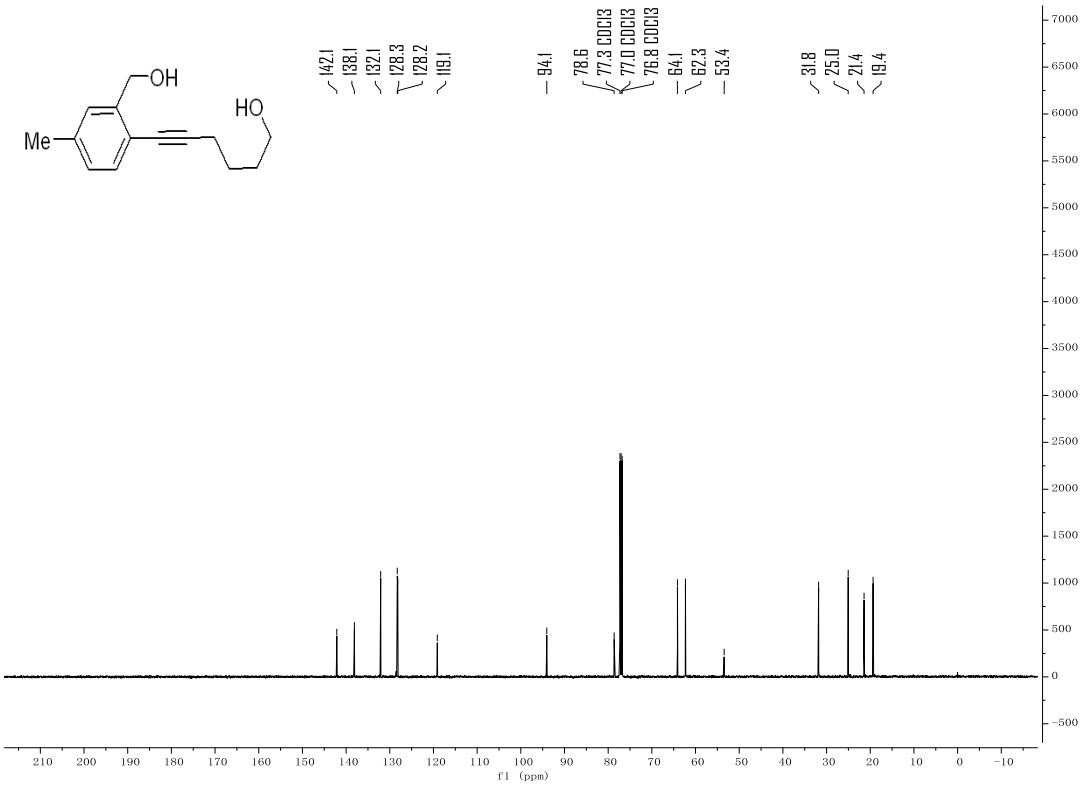
6-(2-(hydroxymethyl)-5-methylphenyl)hex-5-yn-1-ol (**f12**)



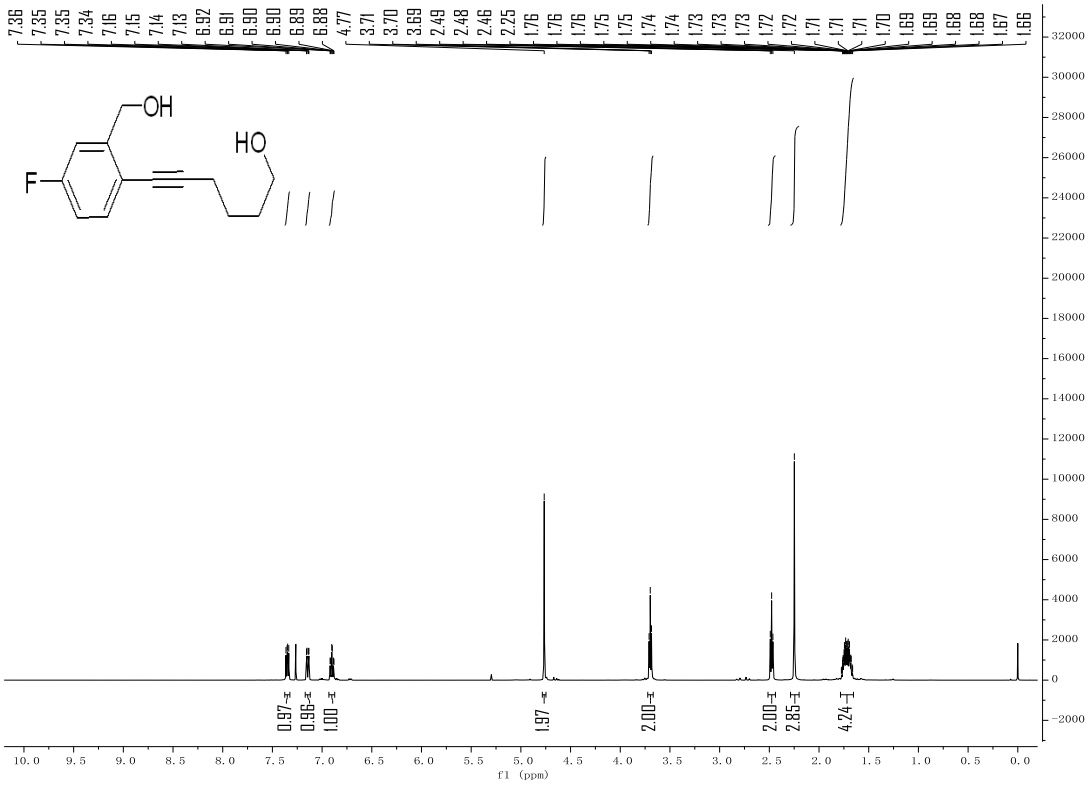



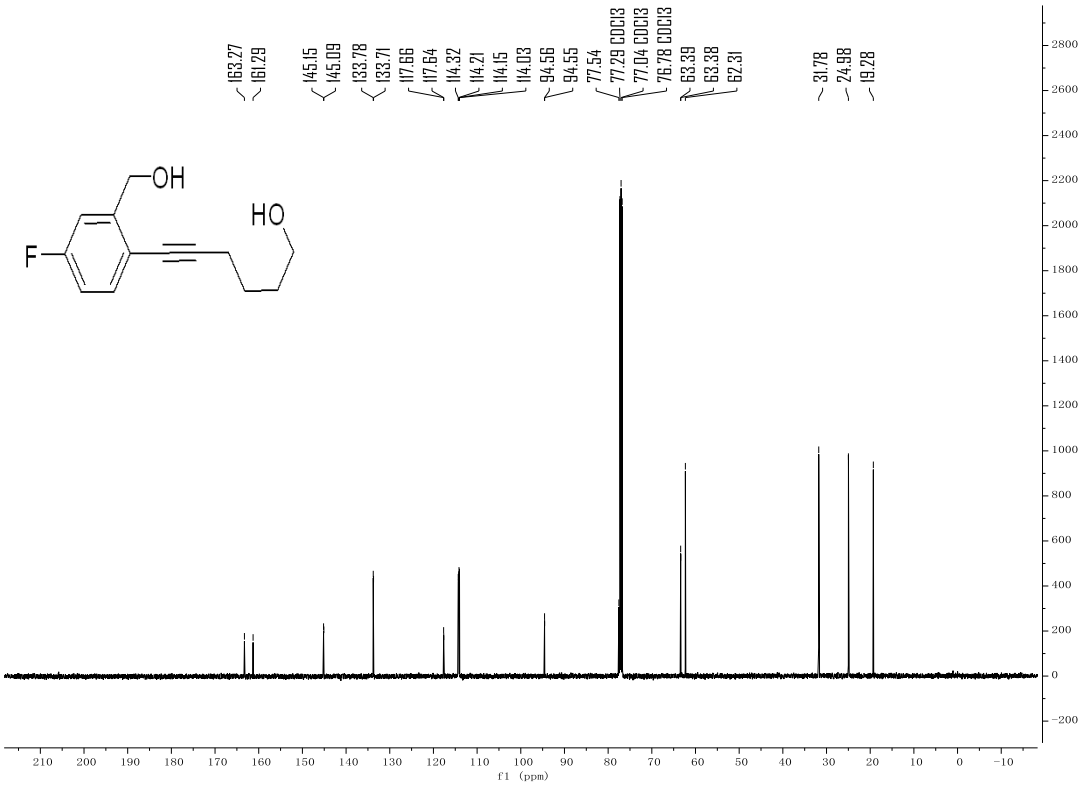
6-(2-(hydroxymethyl)-4-methylphenyl)hex-5-yn-1-ol (**f13**)

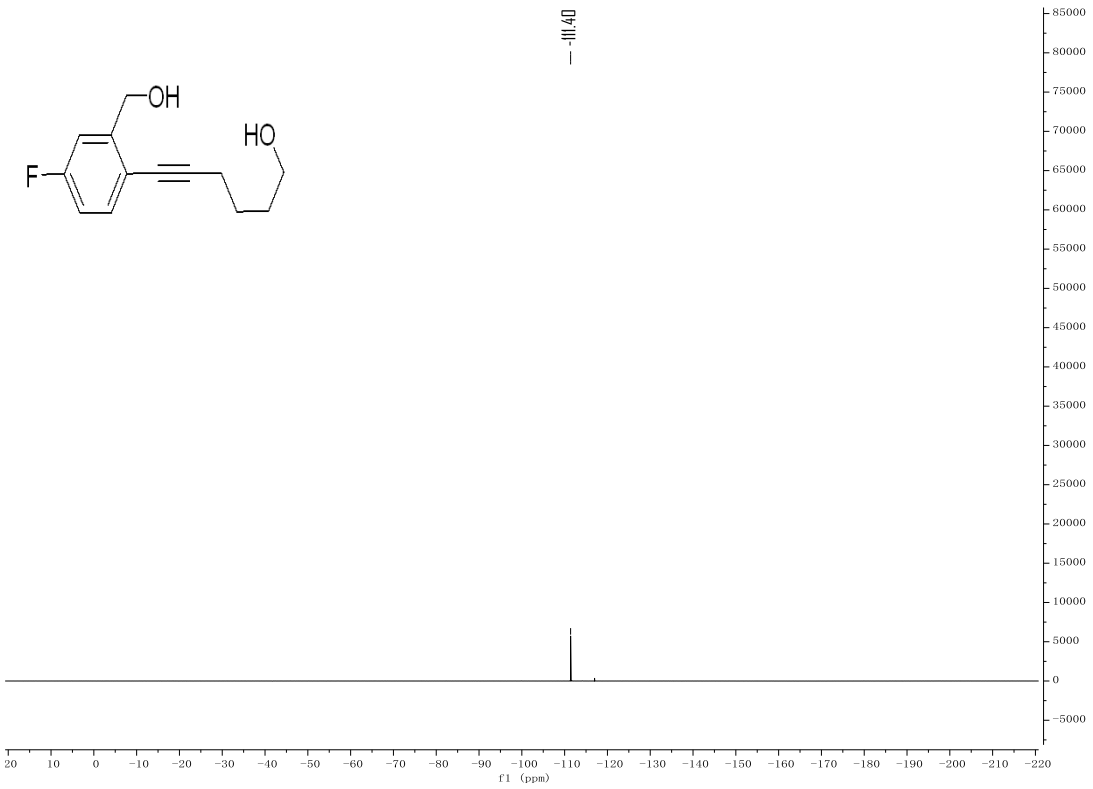


6-(4-fluoro-2-(hydroxymethyl)phenyl)hex-5-yn-1-ol (**f14**)

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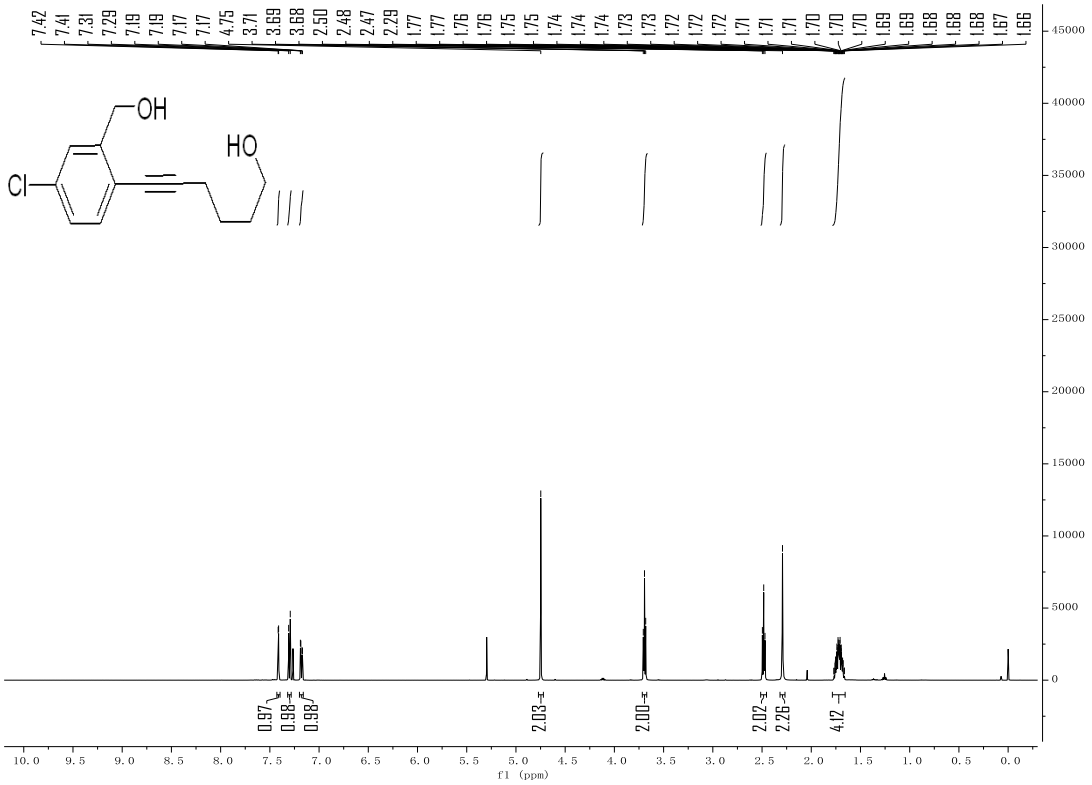
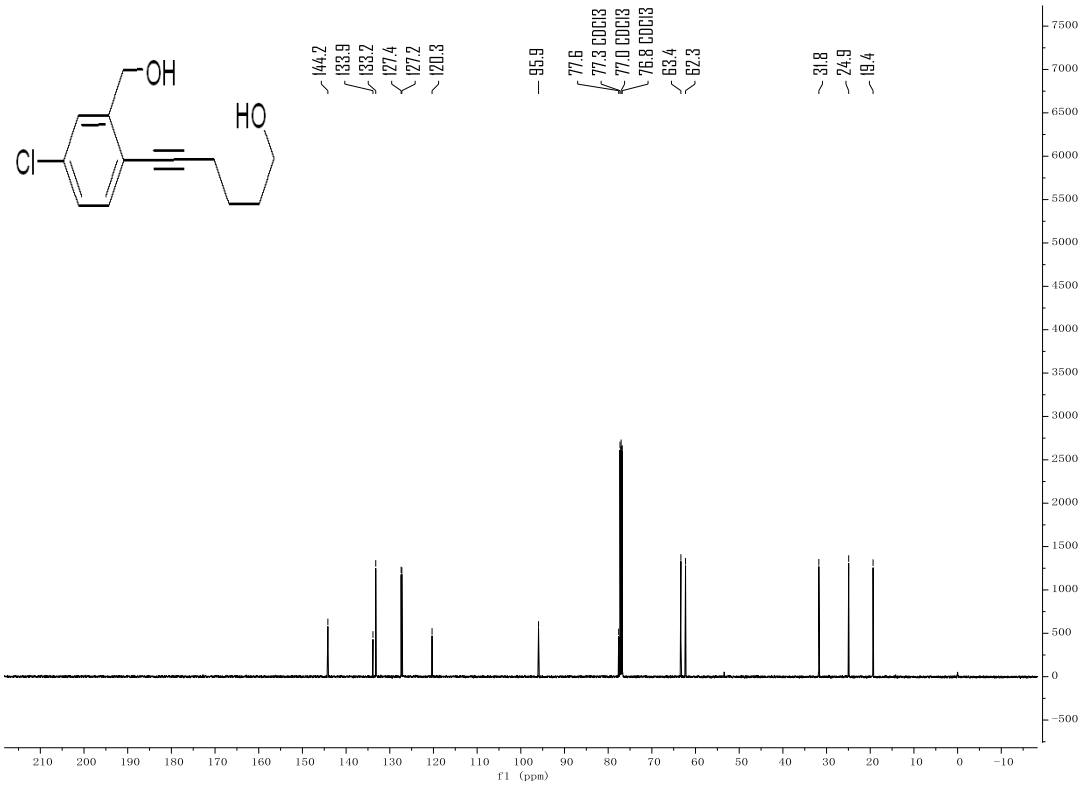
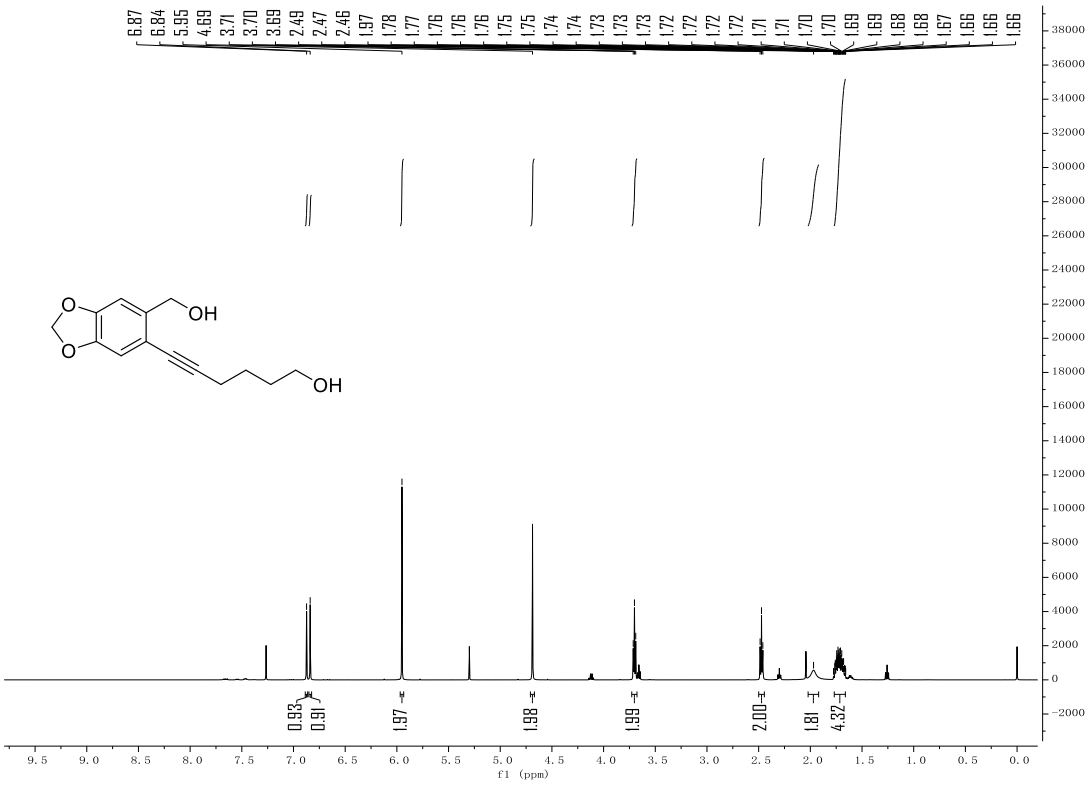
f1 (ppm)

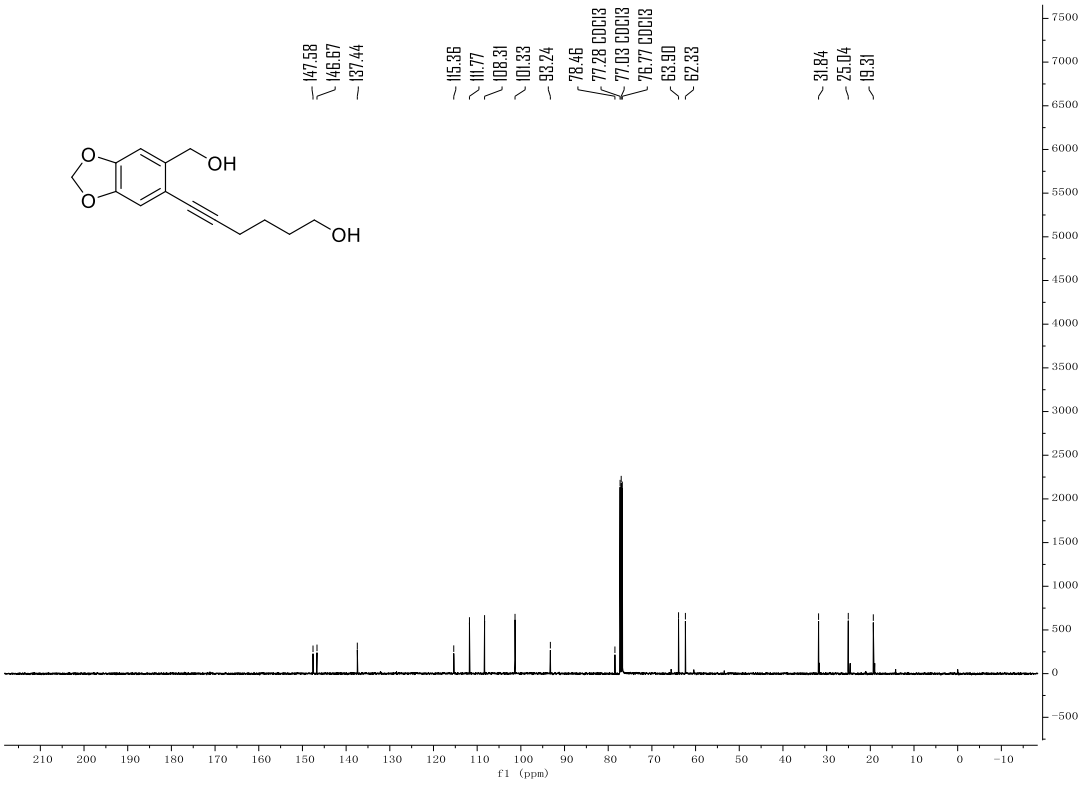
6-(4-chloro-2-(hydroxymethyl)phenyl)hex-5-yn-1-ol (**f15**)



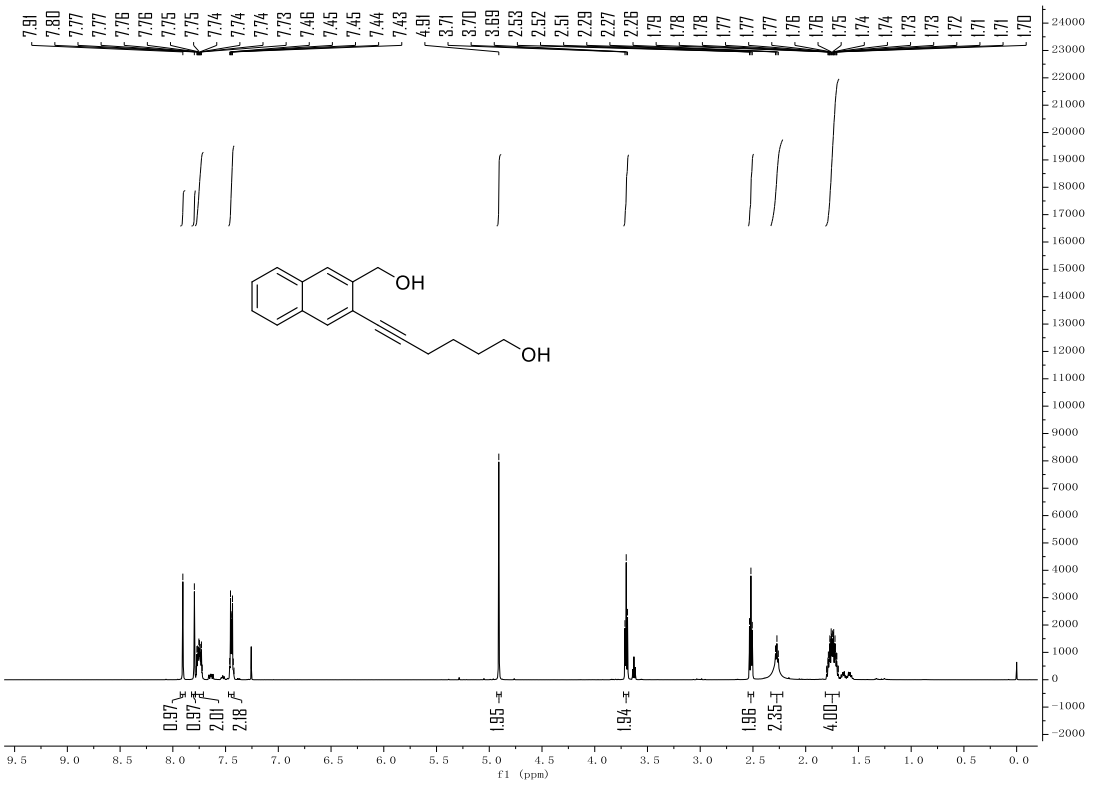



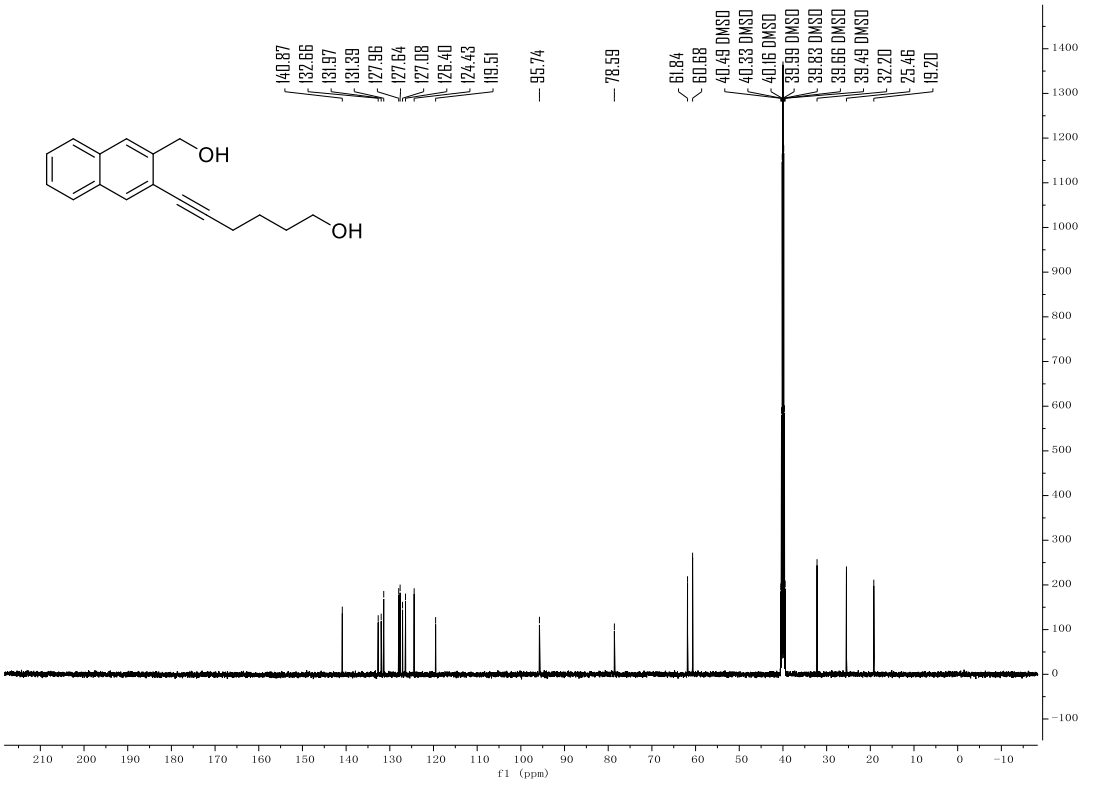
6-(6-(hydroxymethyl)benzo[d][1,3]dioxol-5-yl)hex-5-yn-1-ol (**f16**)



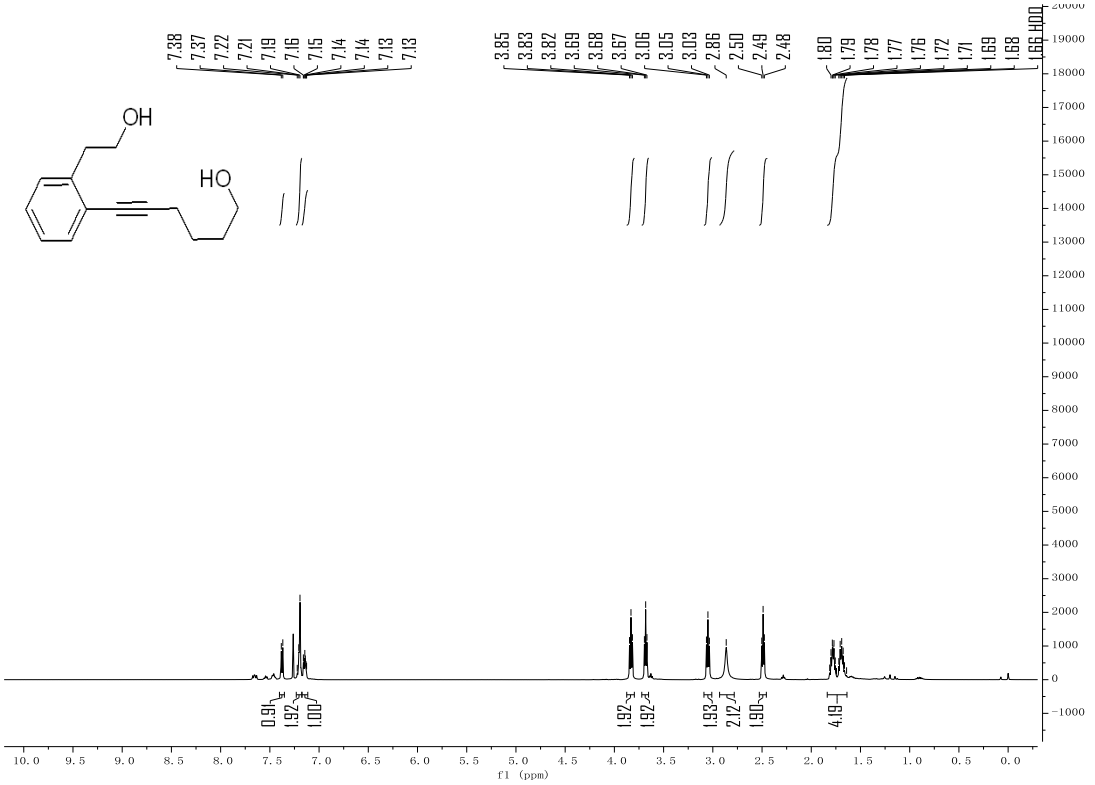



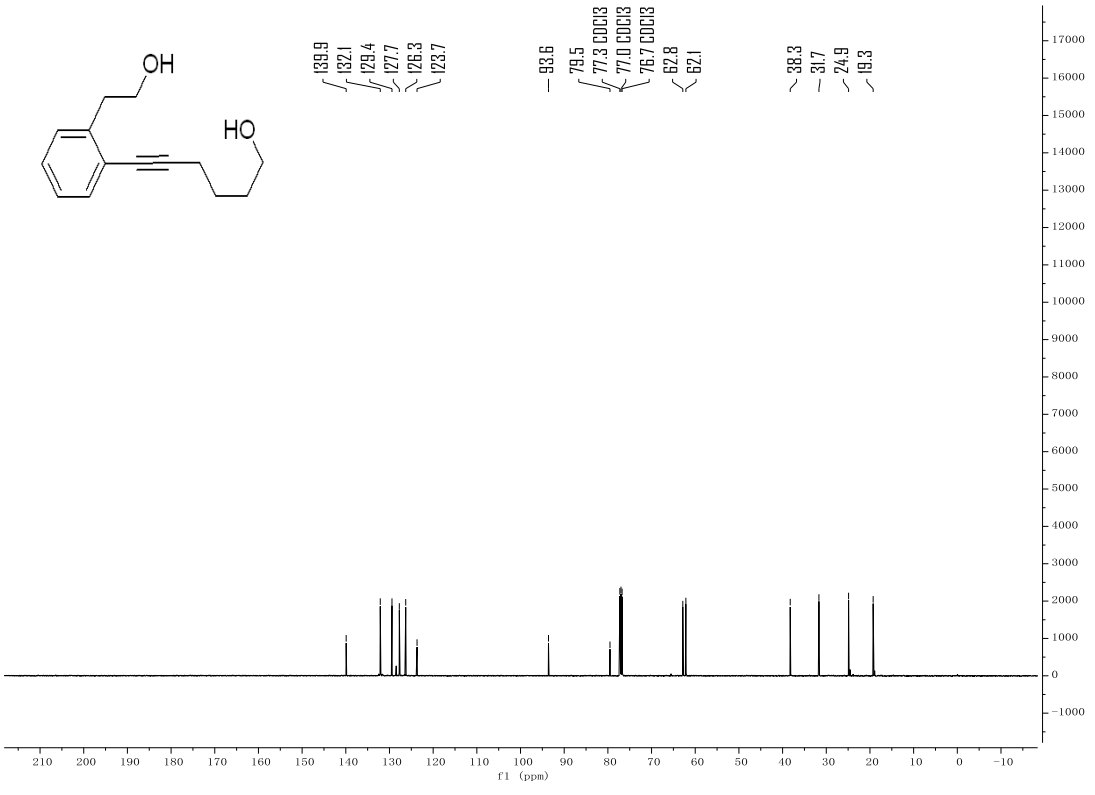
6-(3-(hydroxymethyl)naphthalen-2-yl)hex-5-yn-1-ol (**f17**)



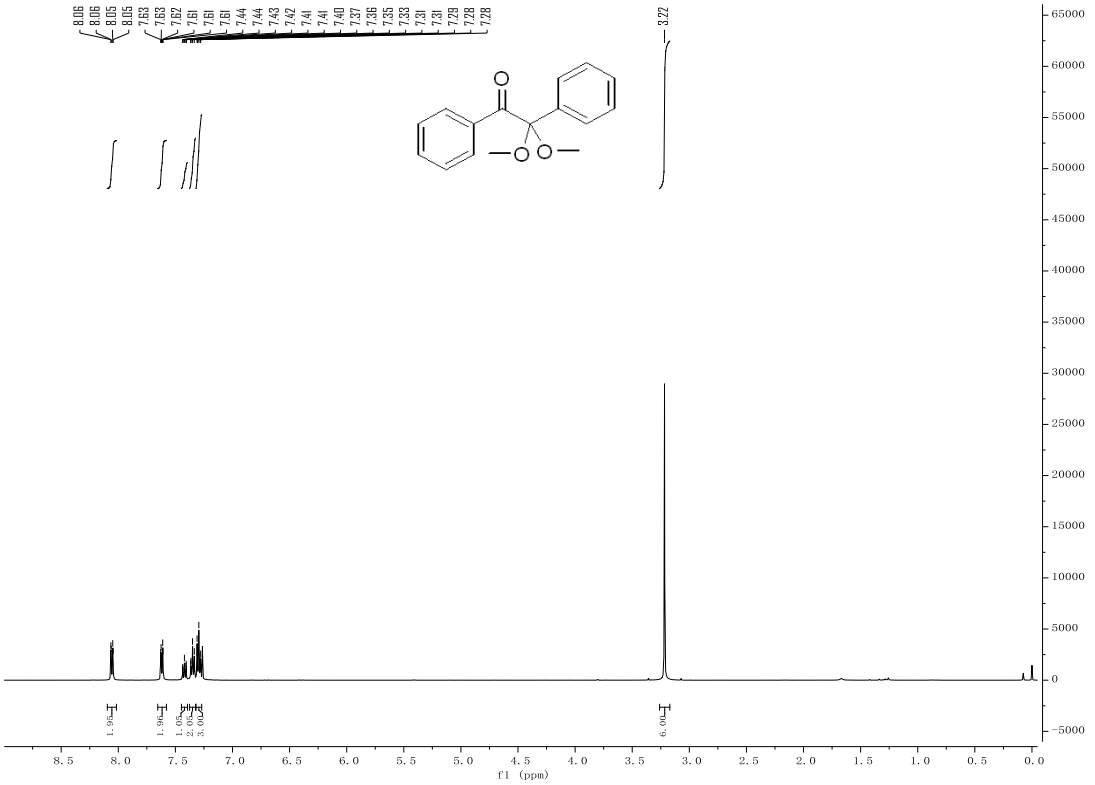



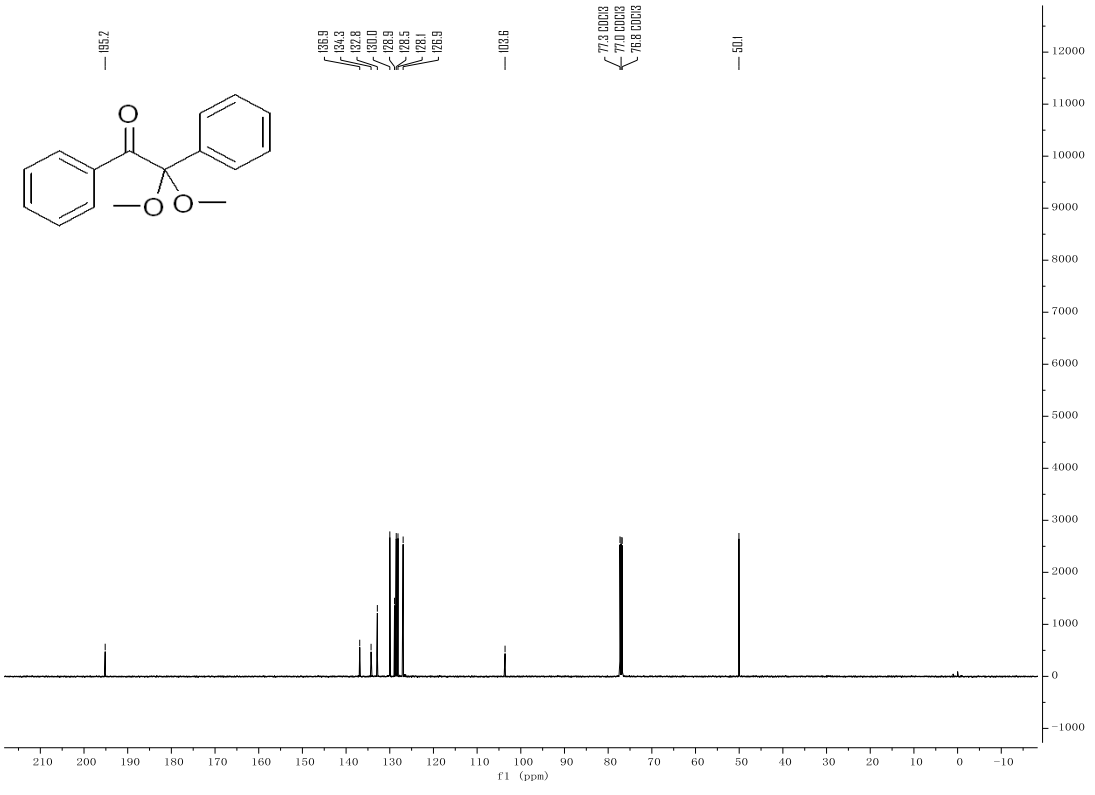
6-(2-(2-hydroxyethyl)phenyl)hex-5-yn-1-ol (**f18**)



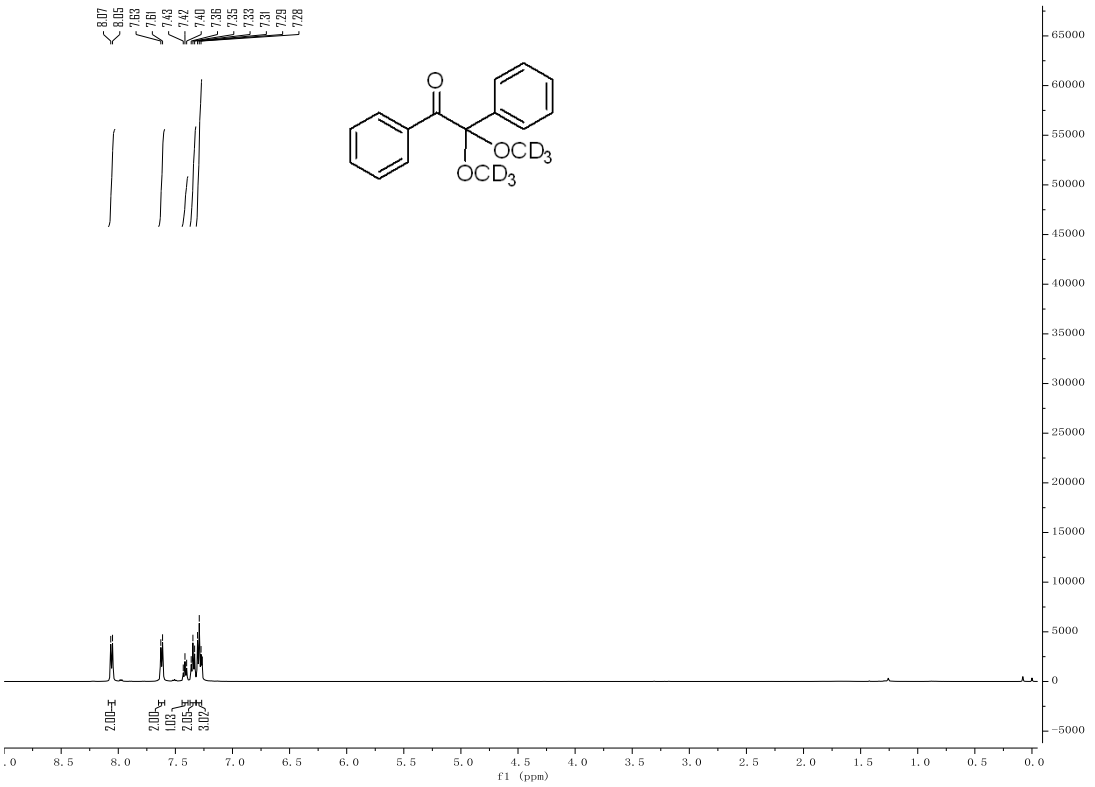



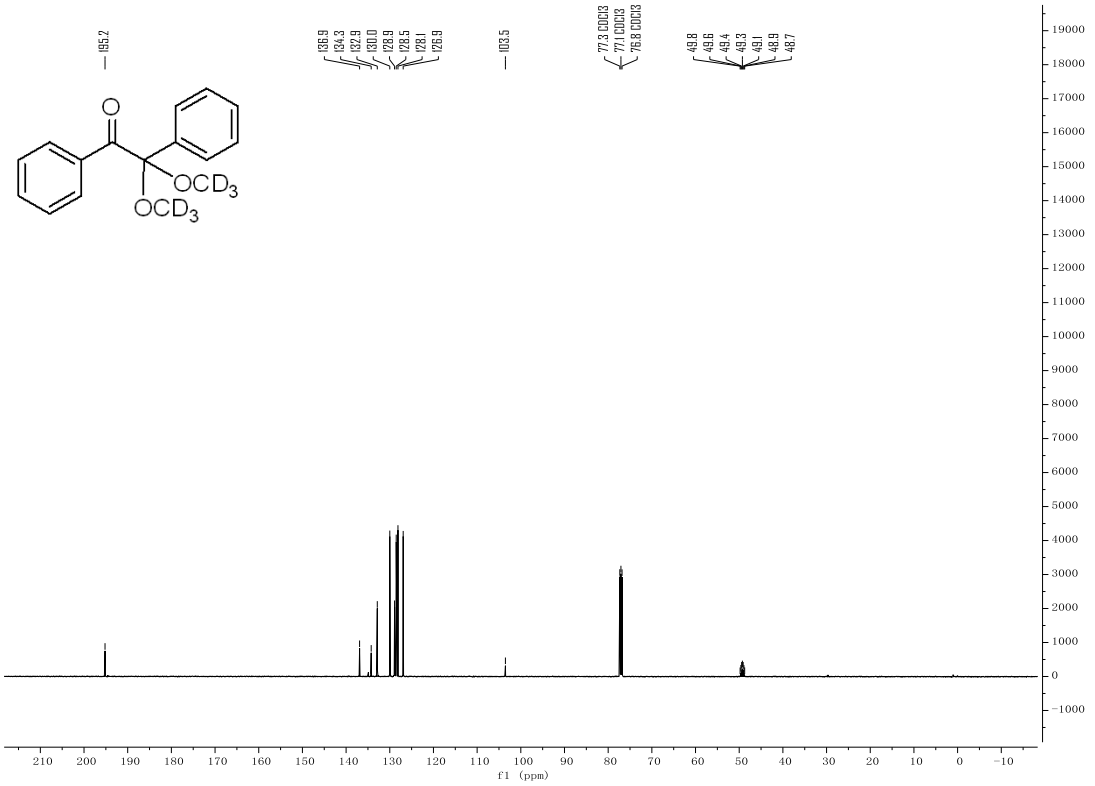
2,2-dimethoxy-1,2-diphenylethan-1-one (**b1**)



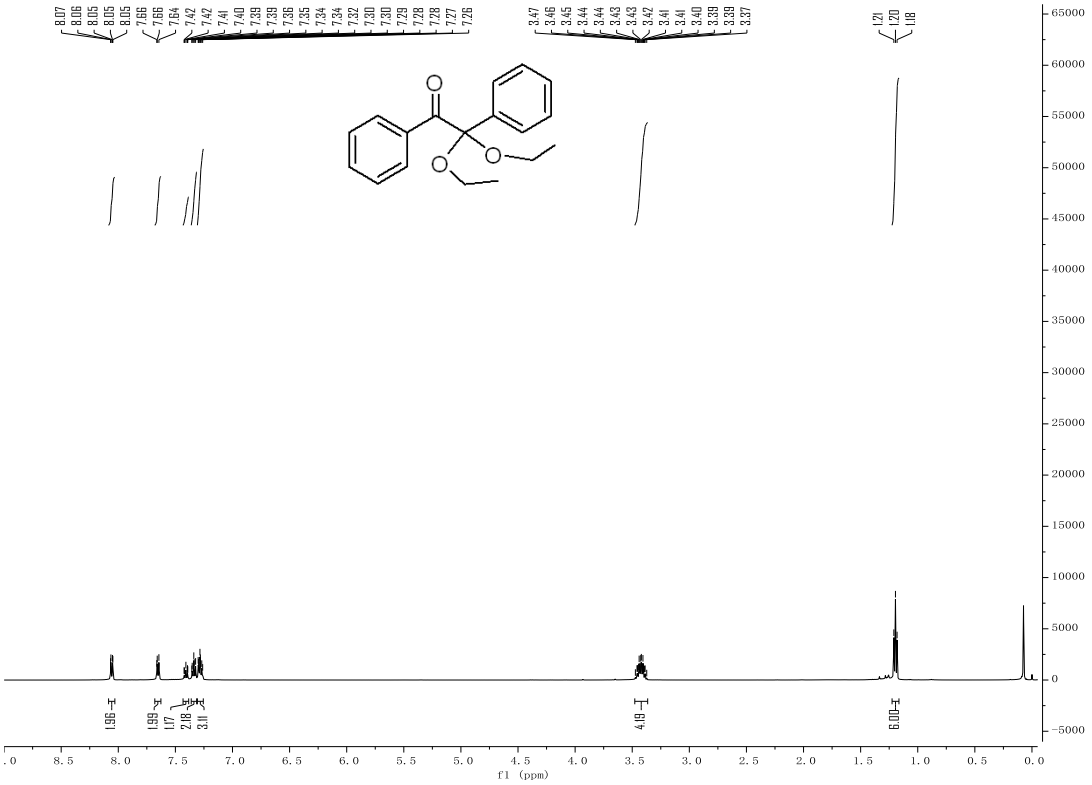



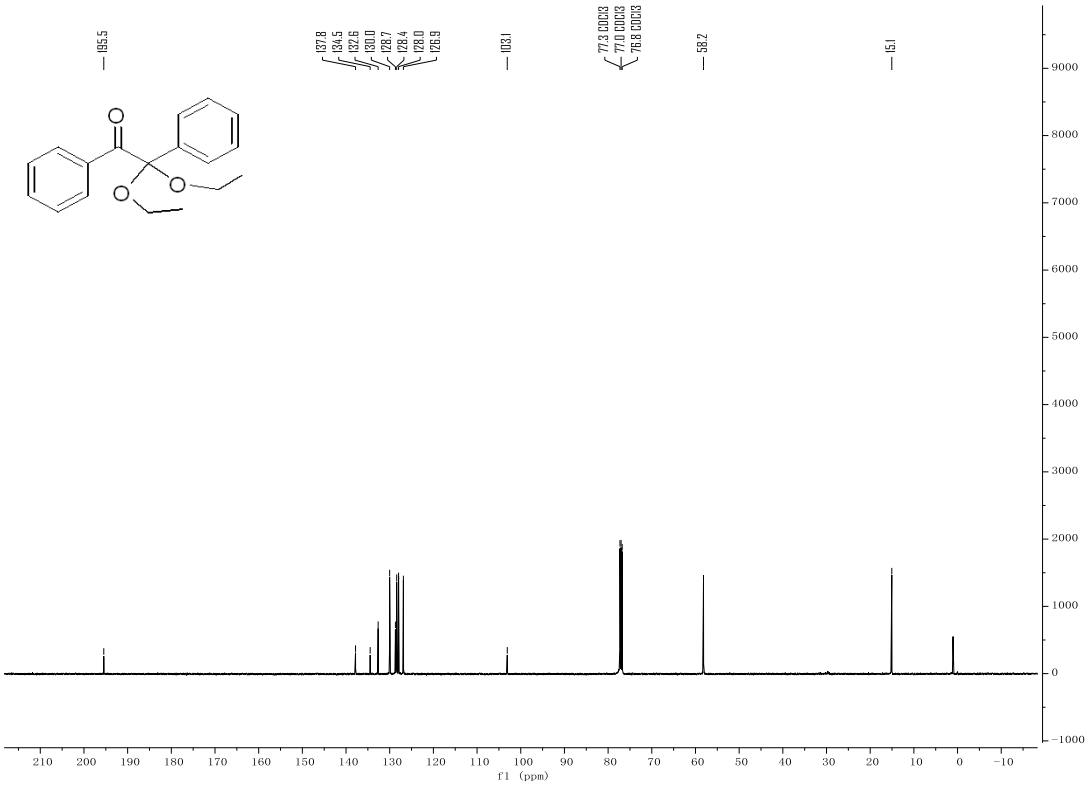
2,2-bis(methoxy-d3)-1,2-diphenylethan-1-one (**b2**)



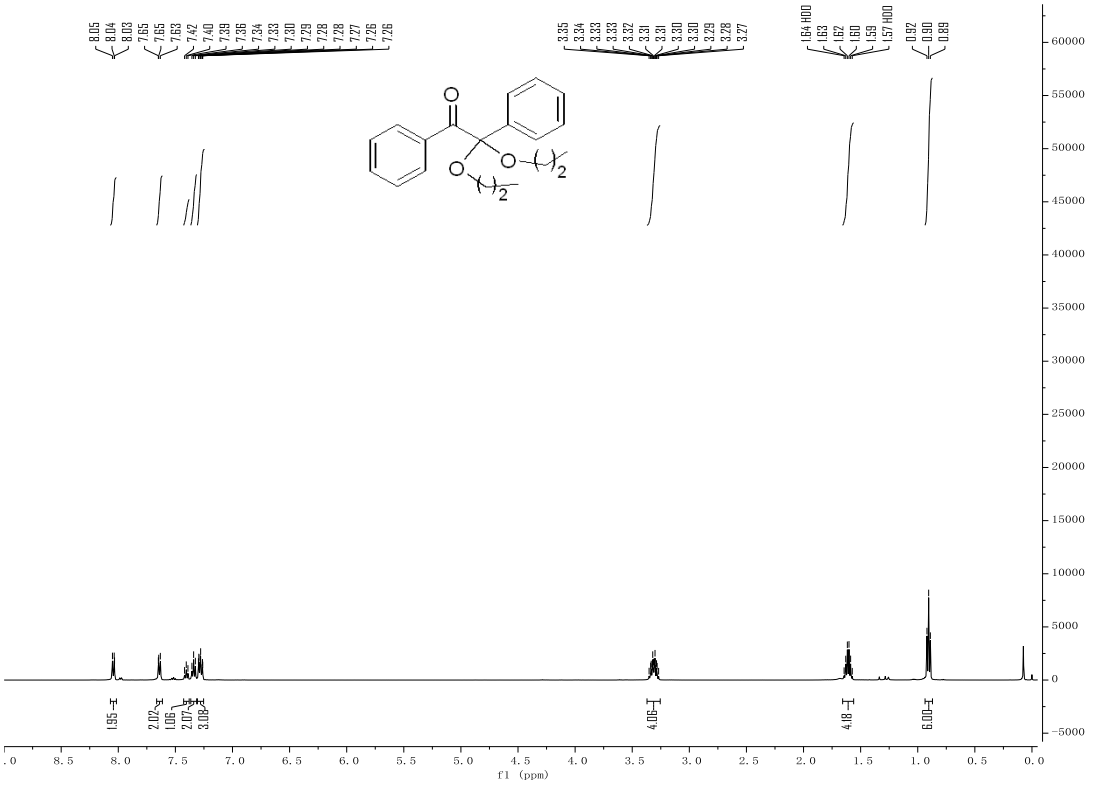



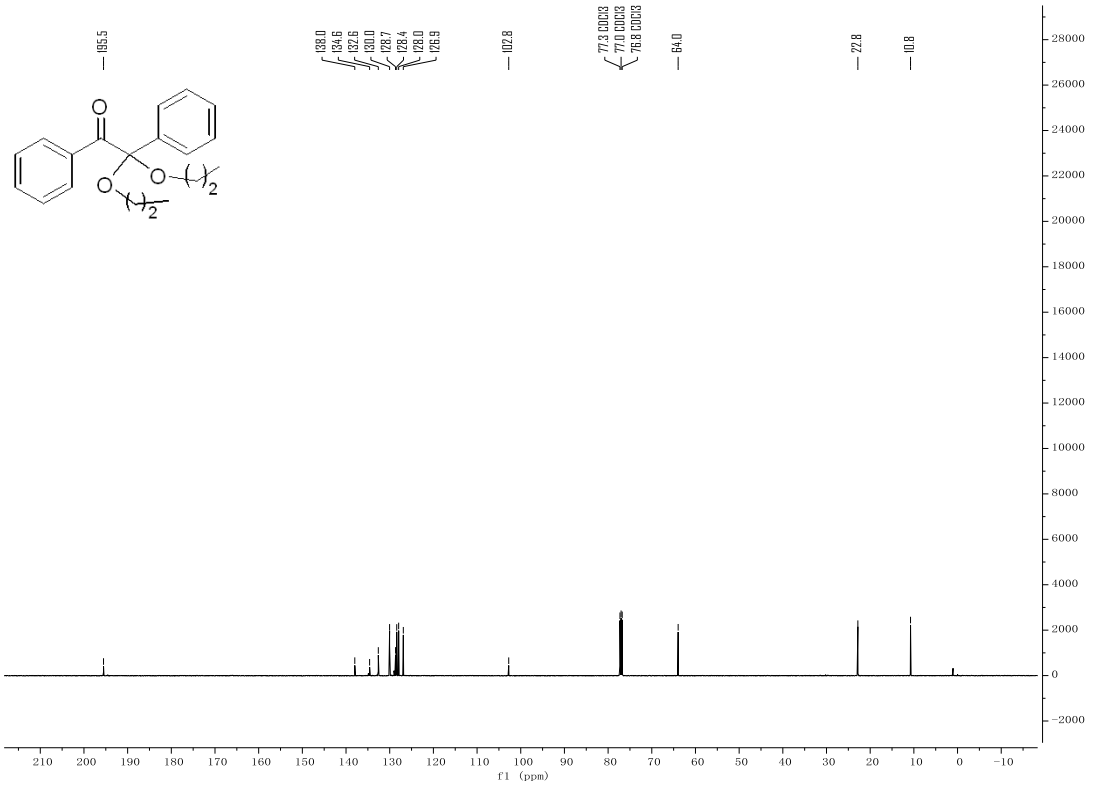
2,2-diethoxy-1,2-diphenylethan-1-one (**b3**)



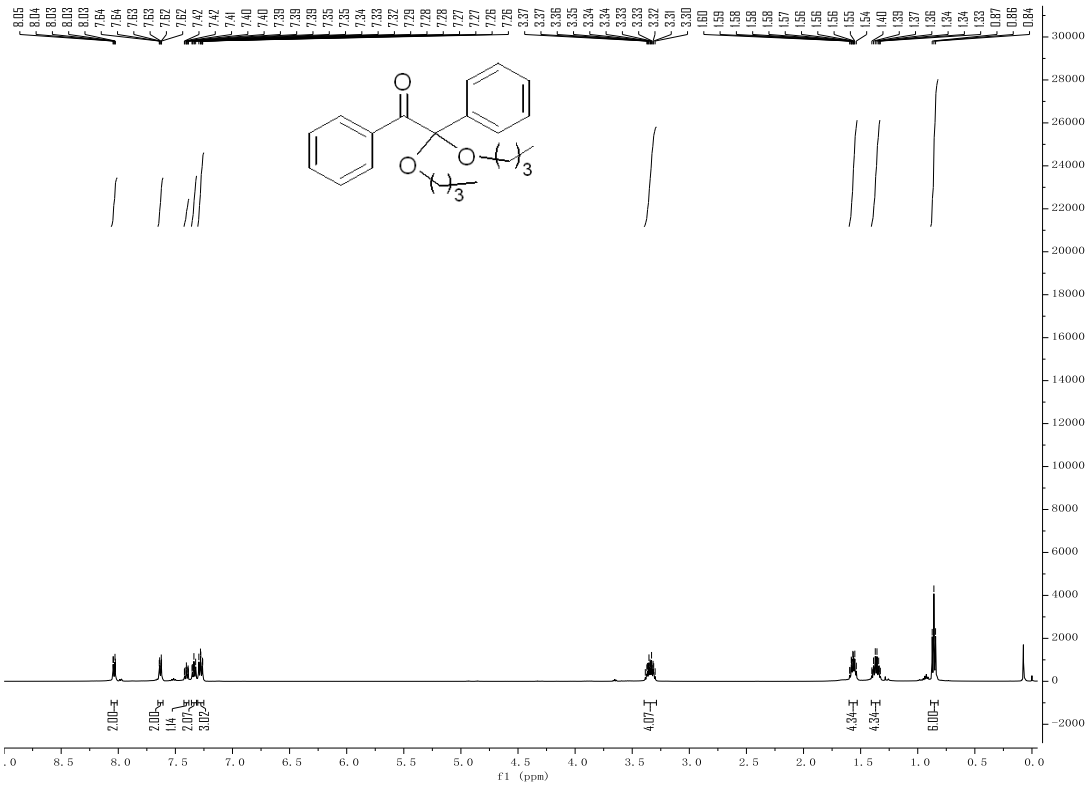



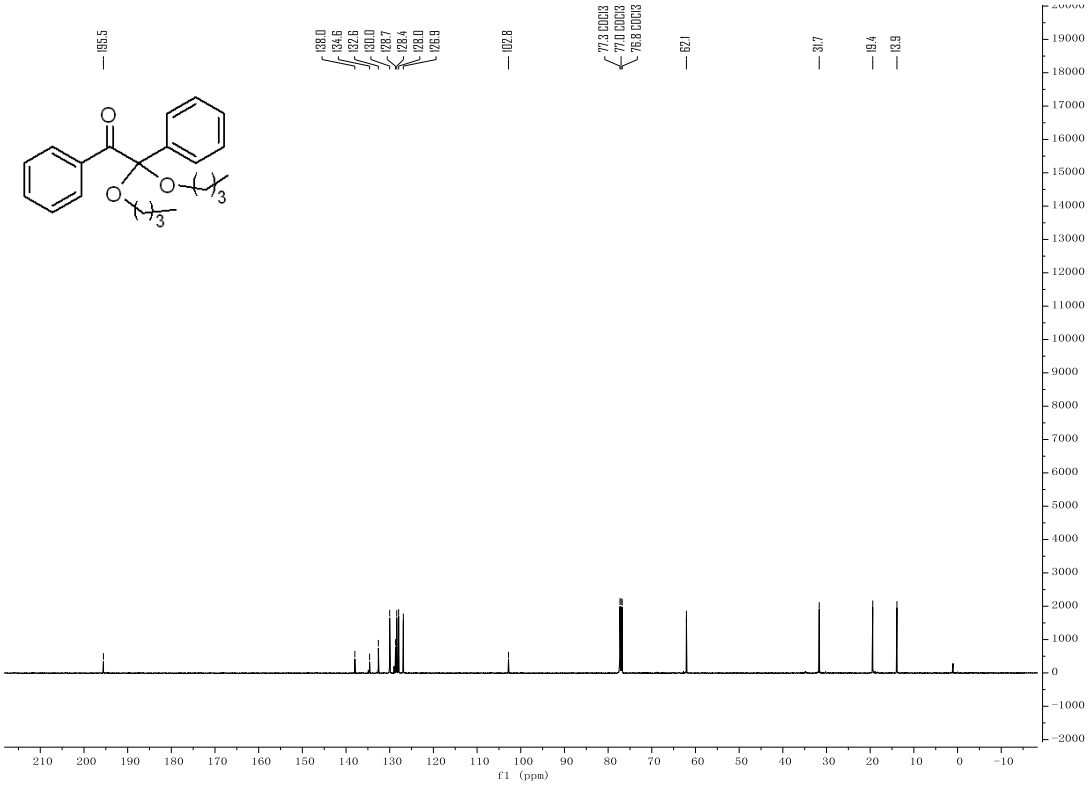
1,2-diphenyl-2,2-dipropoxyethan-1-one (**b4**)



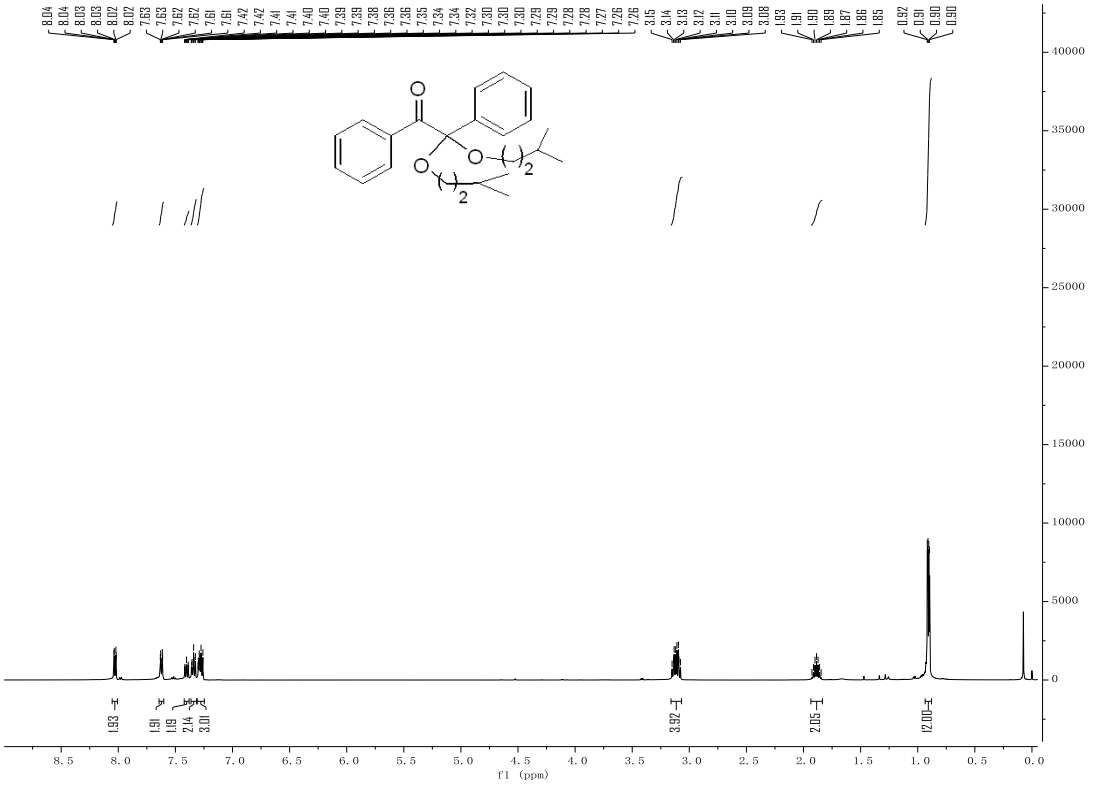



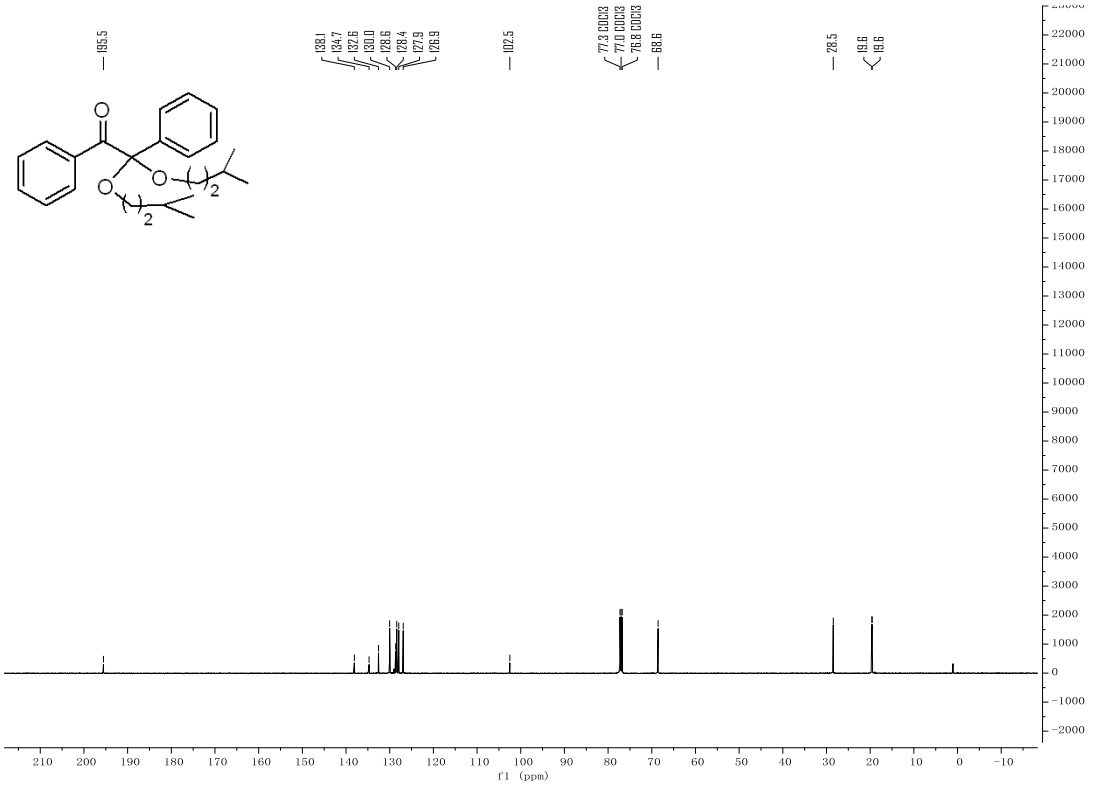
2,2-dibutoxy-1,2-diphenylethan-1-one (**b5**)



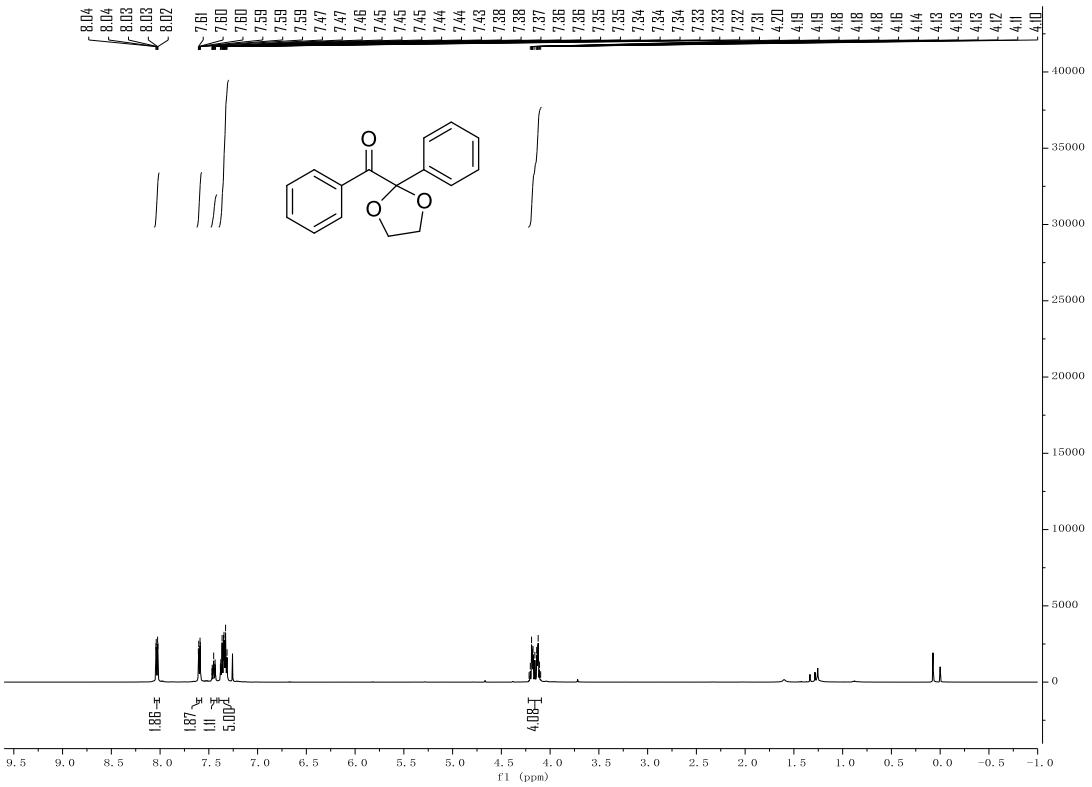


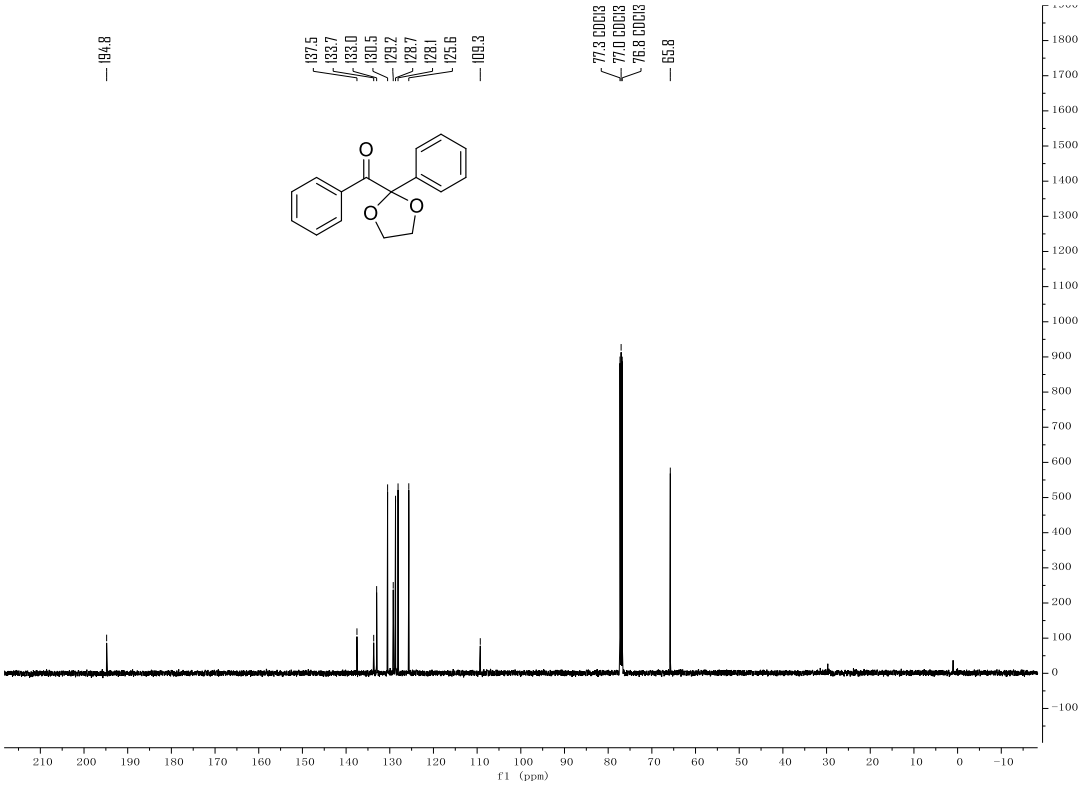
2,2-bis(isopentyloxy)-1,2-diphenylethan-1-one (**b6**)



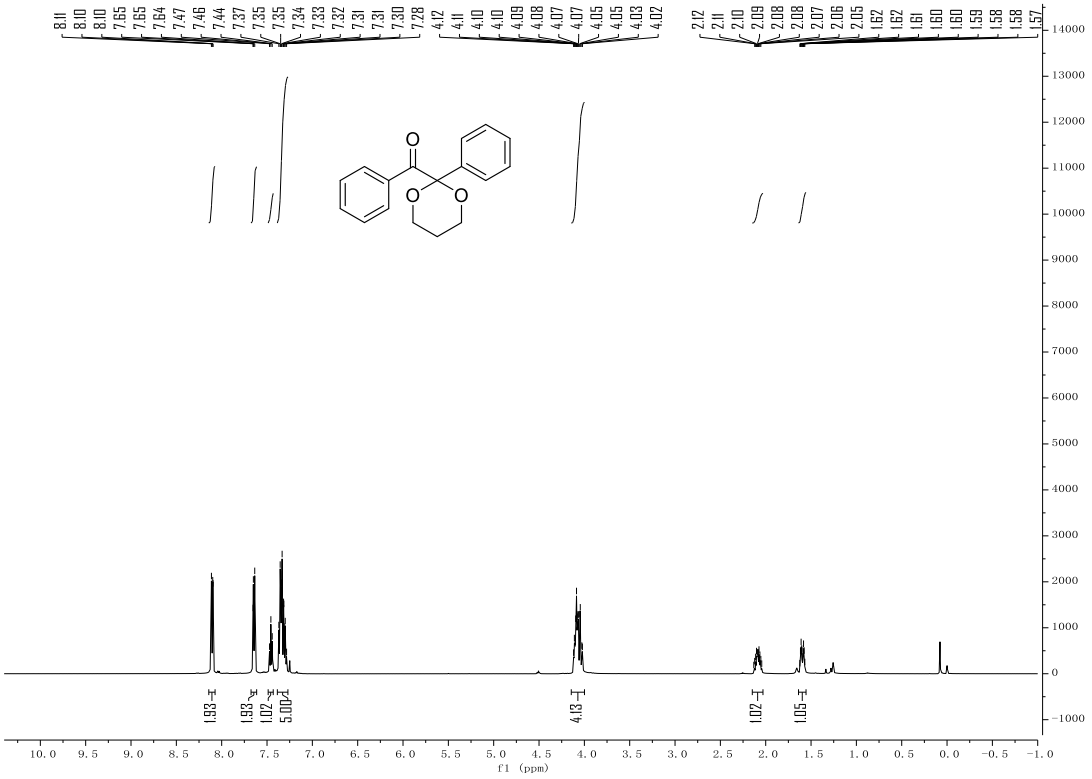


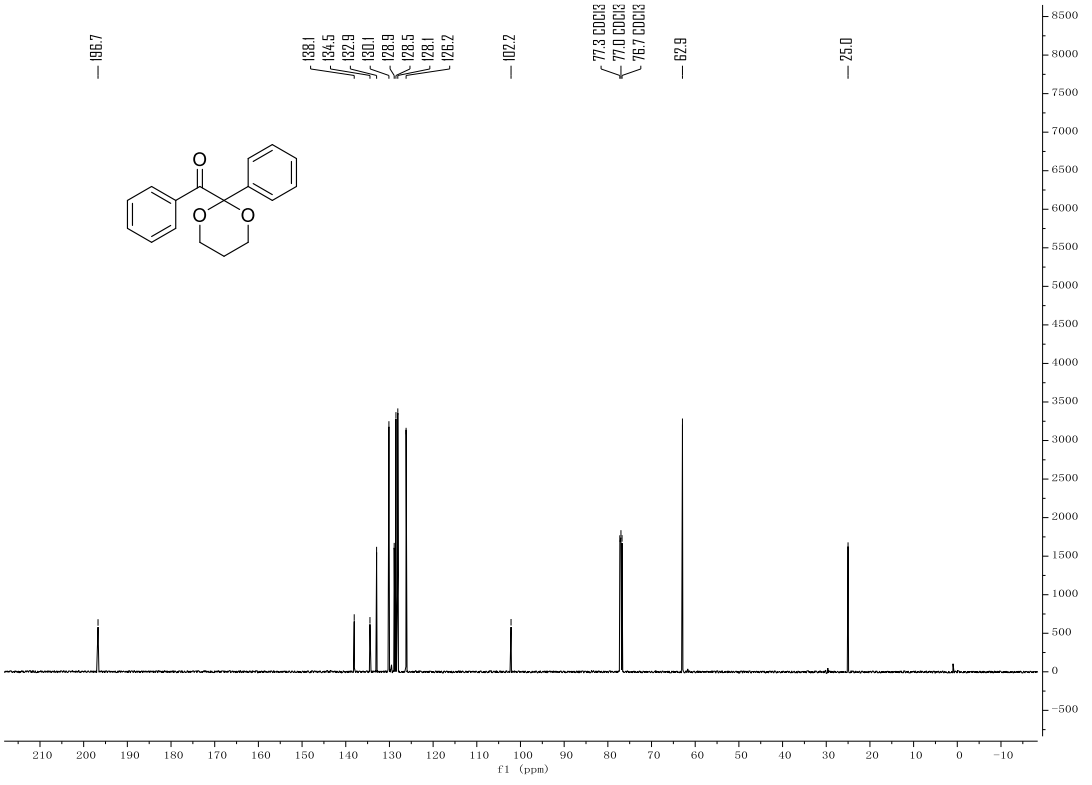
phenyl(2-phenyl-1,3-dioxolan-2-yl)methanone (**b7**)



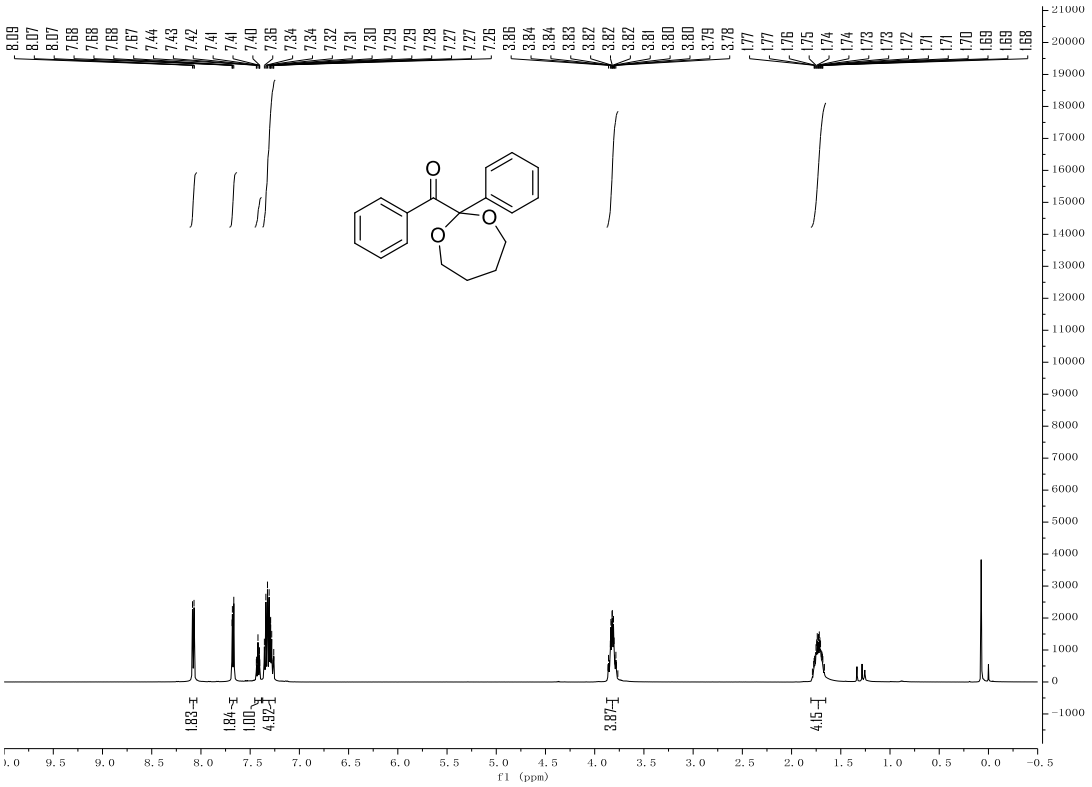



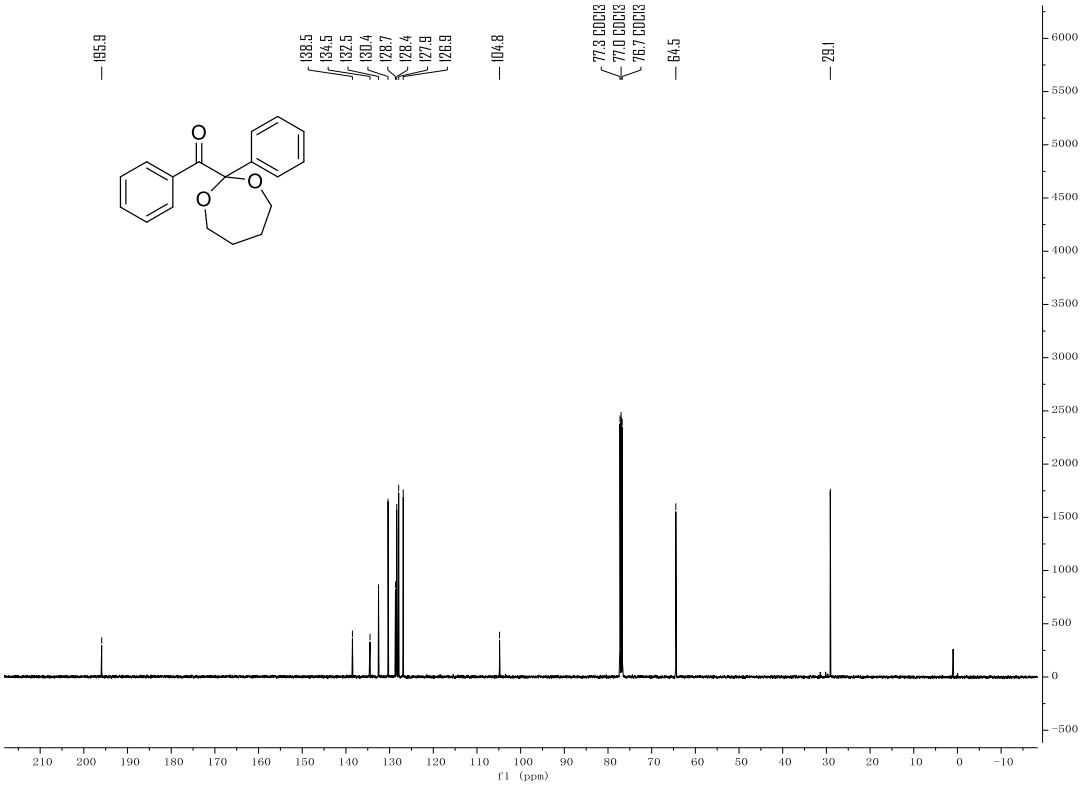
phenyl(2-phenyl-1,3-dioxan-2-yl)methanone (**b8**)



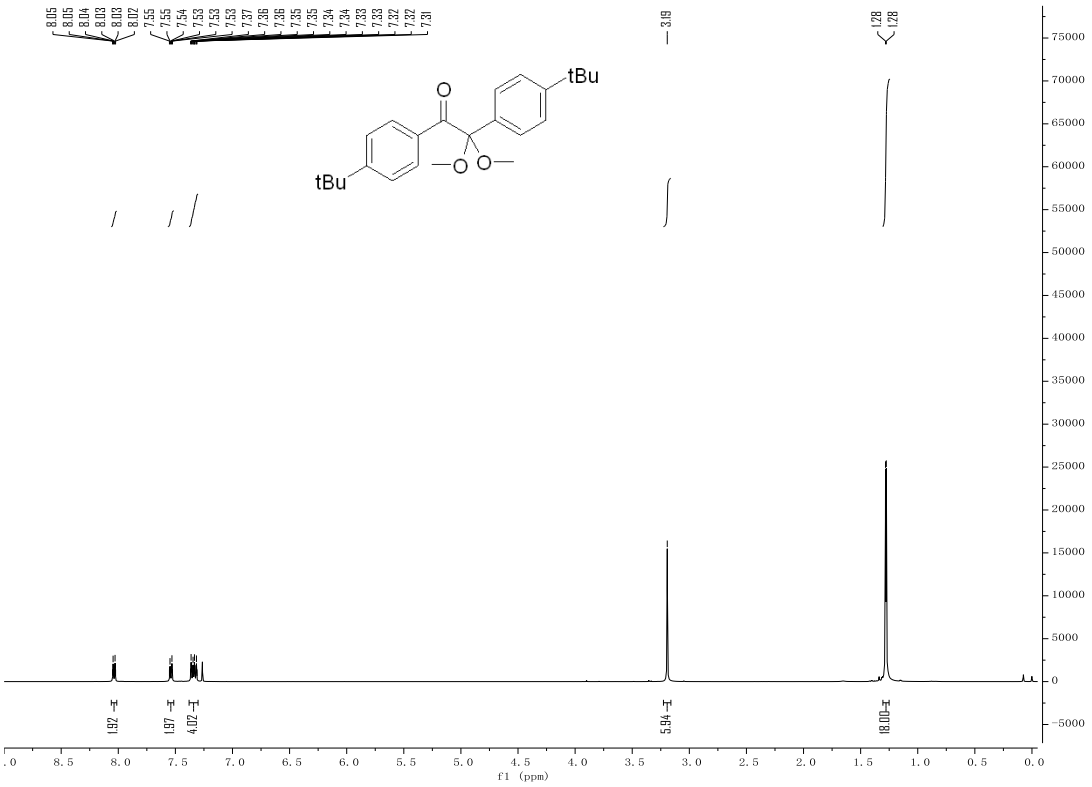



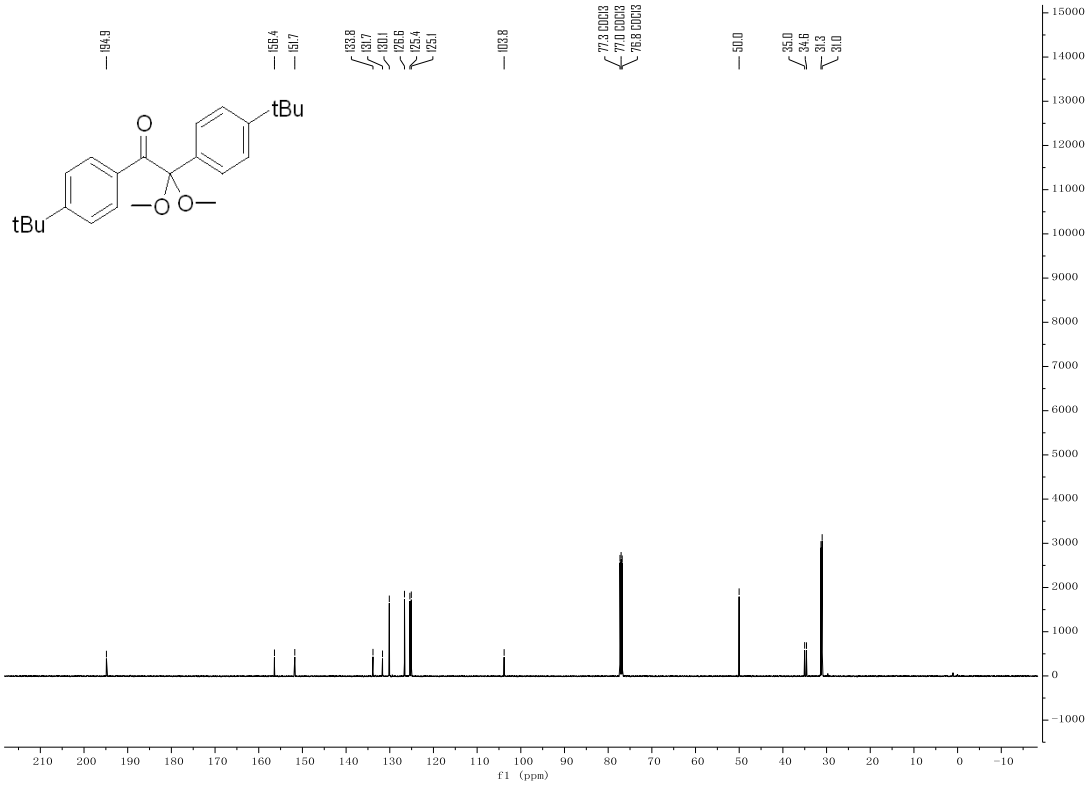
phenyl(2-phenyl-1,3-dioxepan-2-yl)methanone (**b9**)



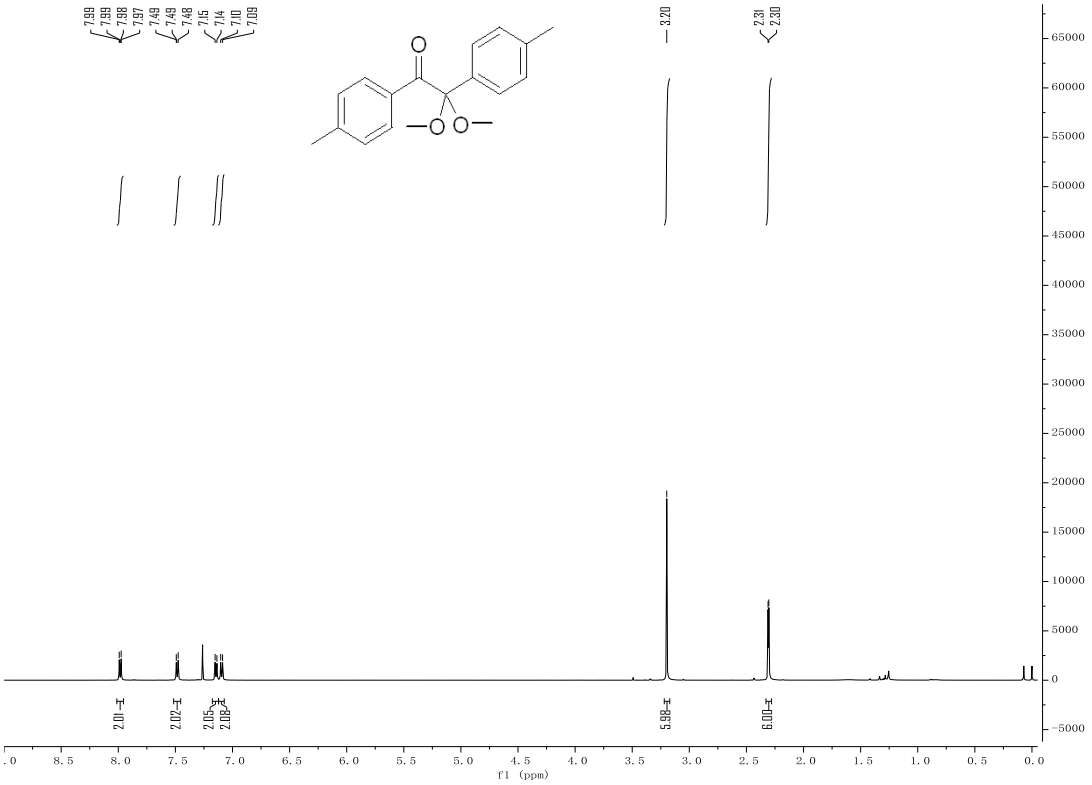



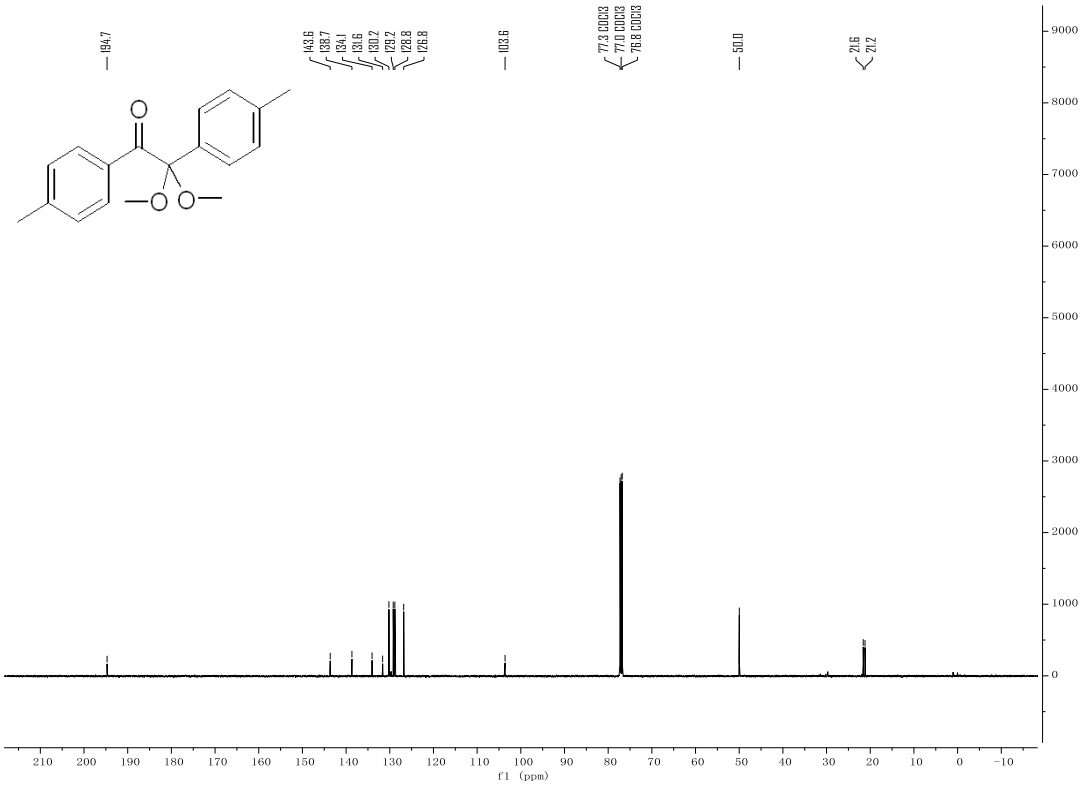
1,2-bis(4-(tert-butyl)phenyl)-2,2-dimethoxyethan-1-one (**c2**)



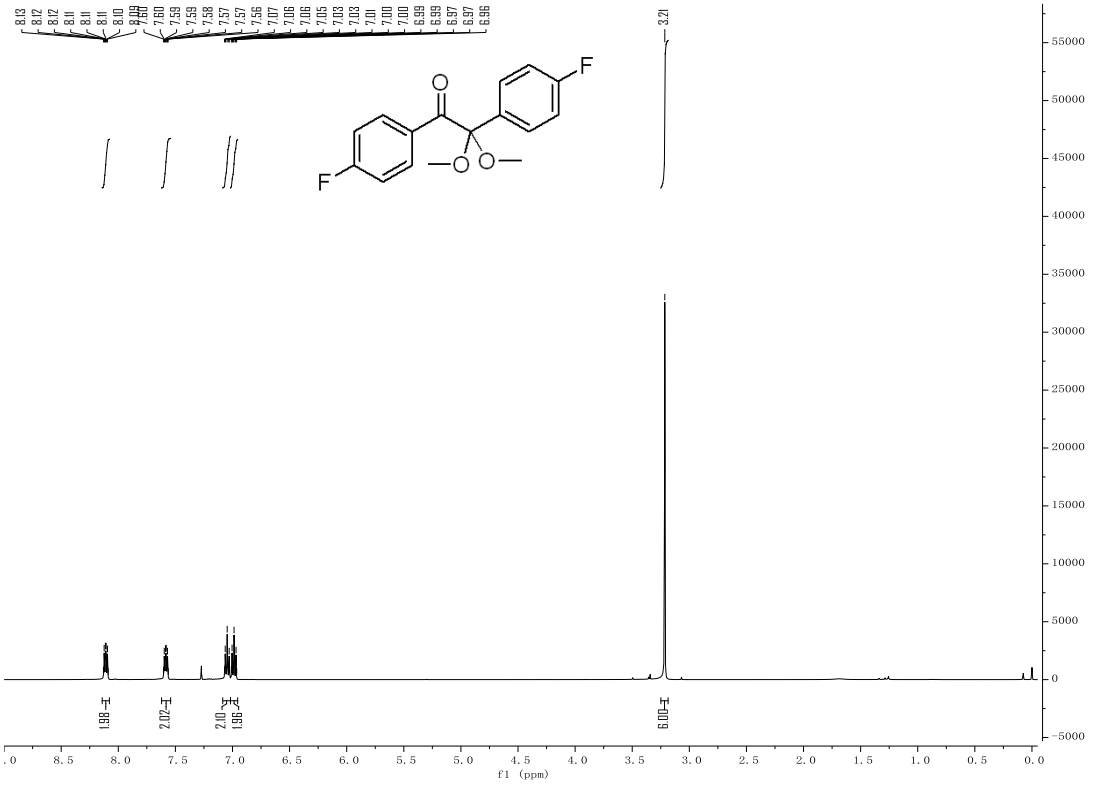



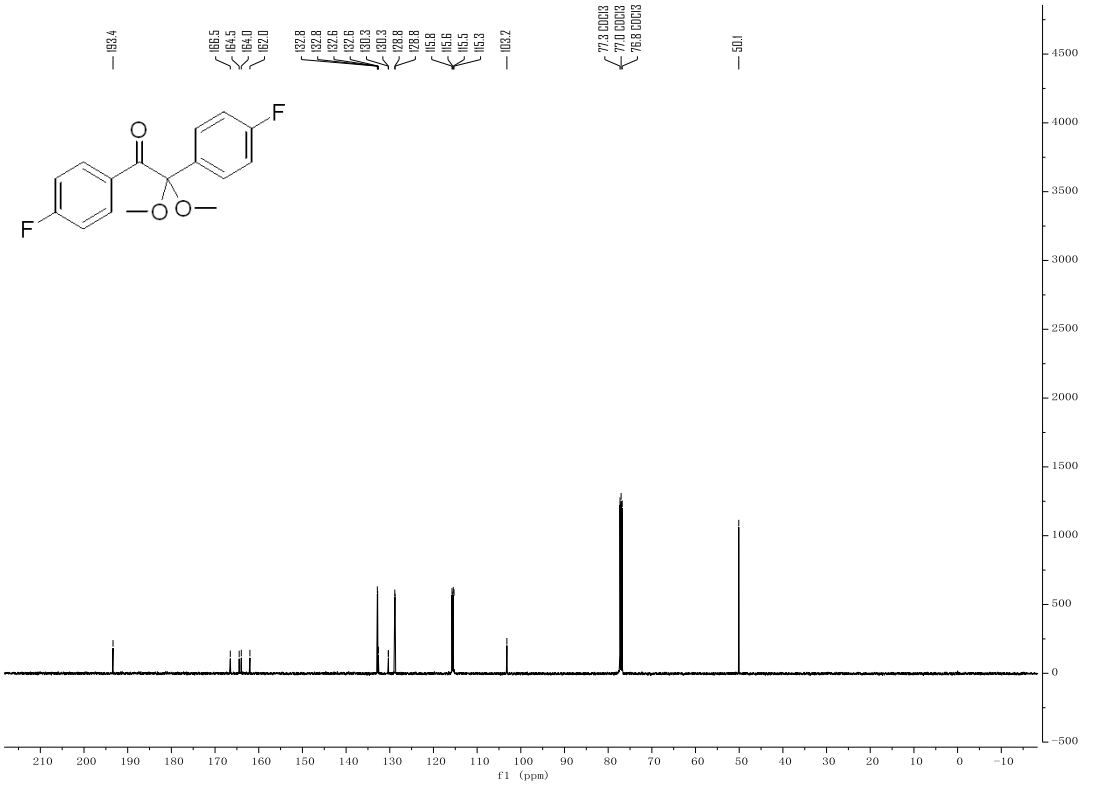
2,2-dimethoxy-1,2-di-*p*-tolylethan-1-one (**c3**)

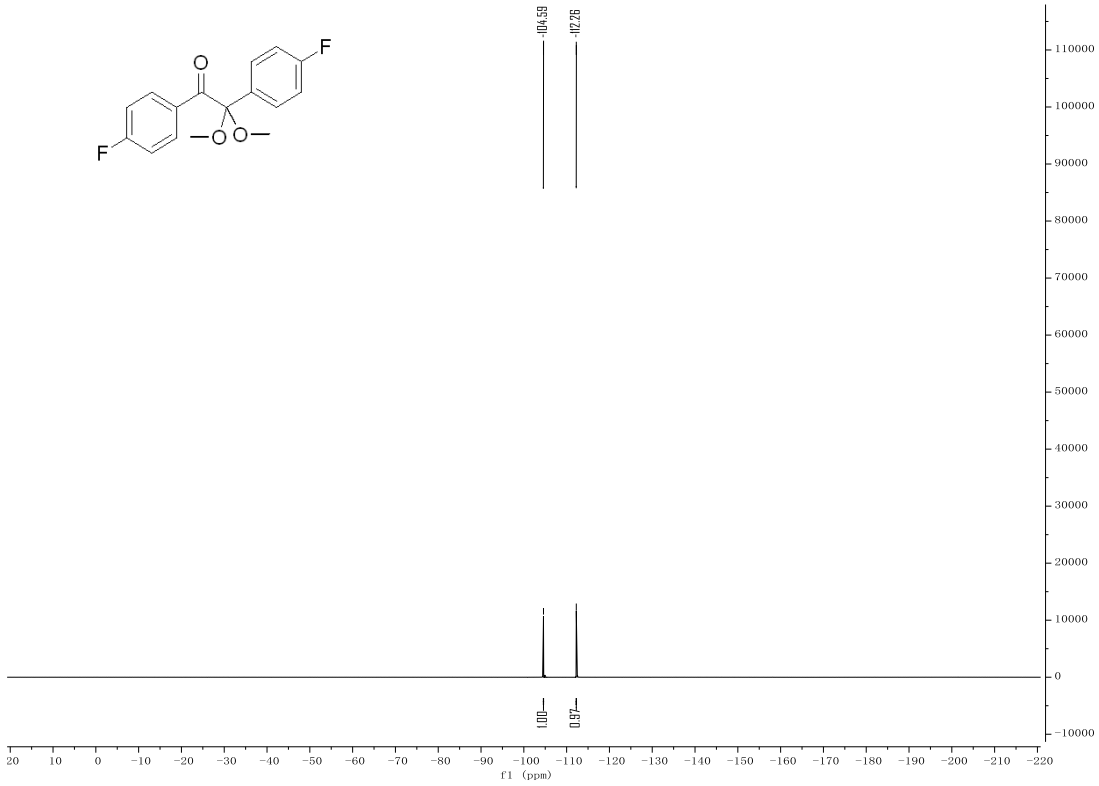


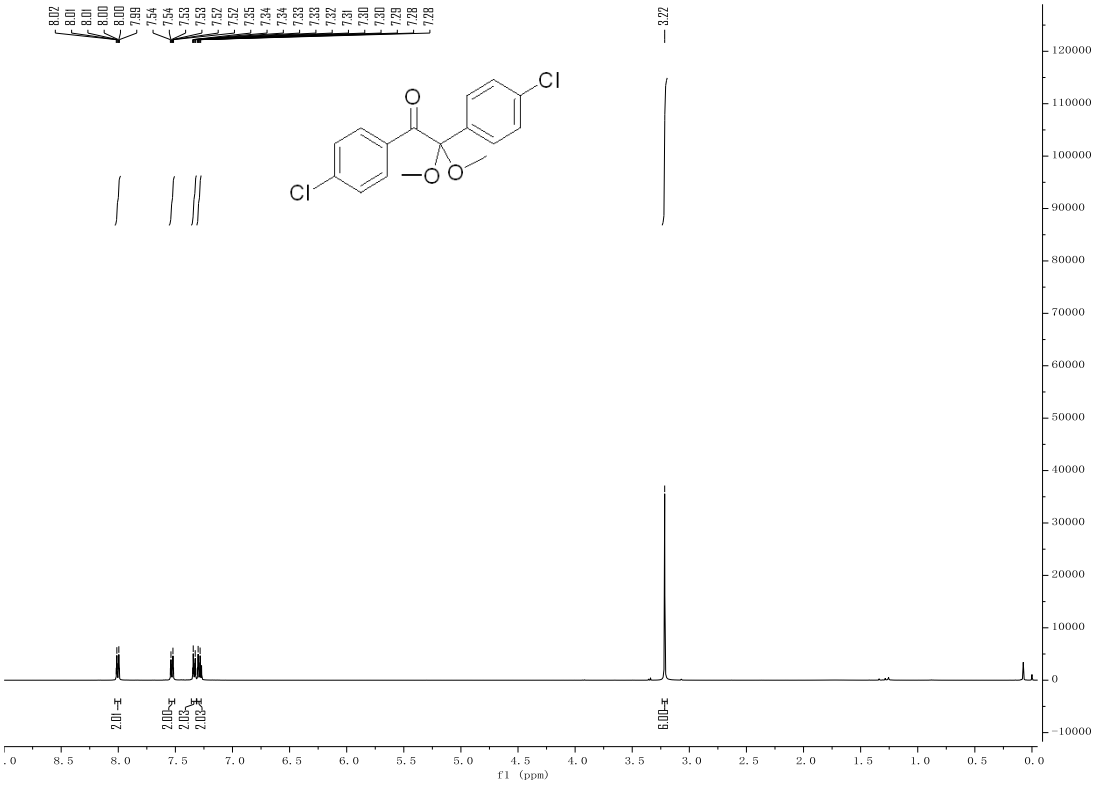
1,2-bis(4-fluorophenyl)-2,2-dimethoxyethan-1-one (**c4**)

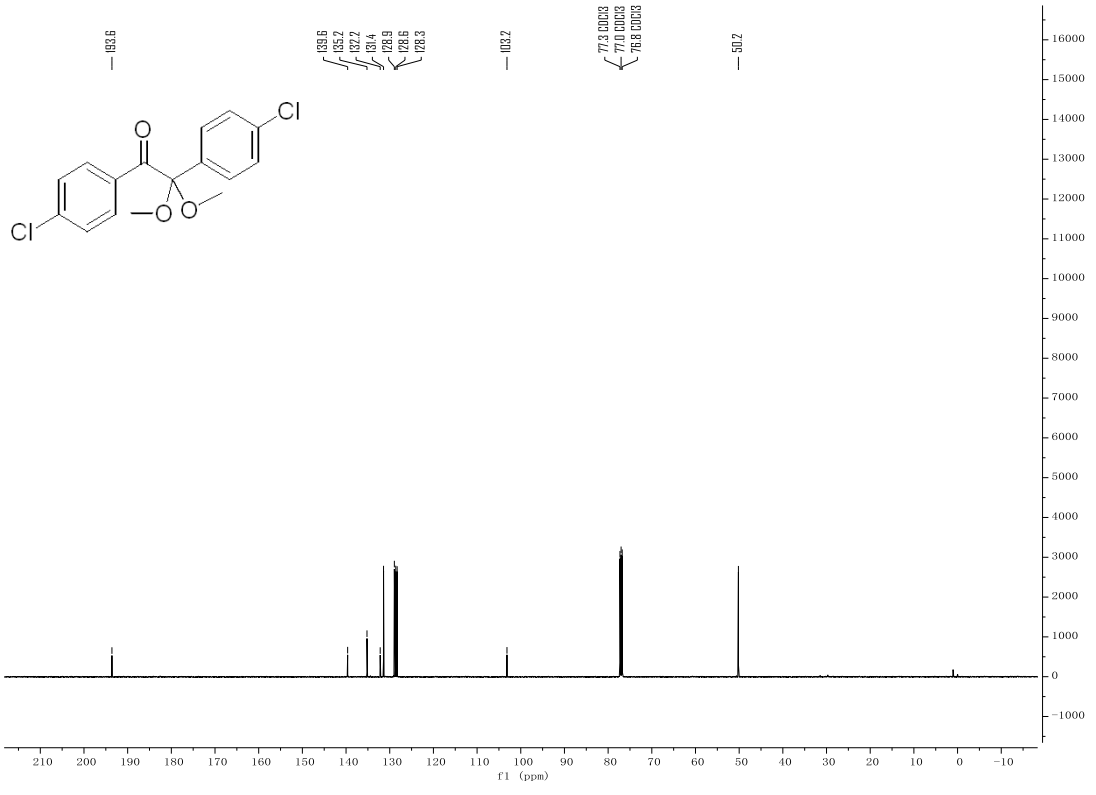


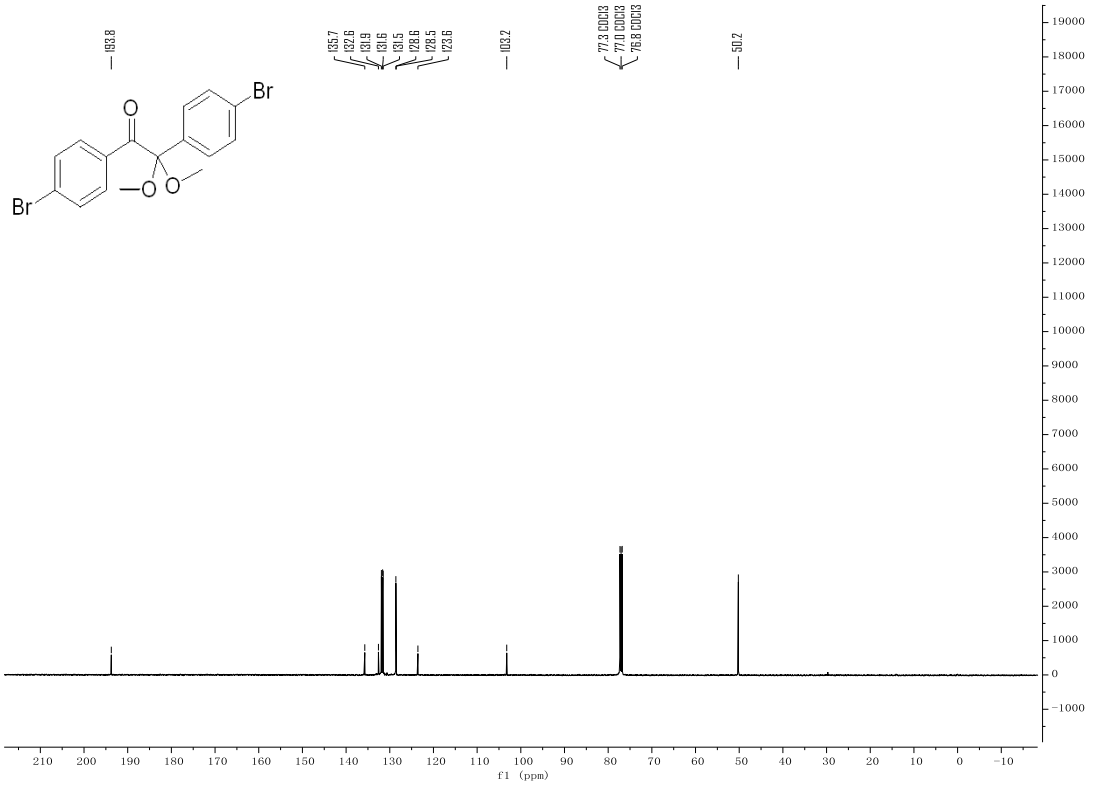

F
O
O
O
F
-104.593
-107.276
1.00
0.97
f1 (ppm)

1,2-bis(4-chlorophenyl)-2,2-dimethoxyethan-1-one (**c5**)

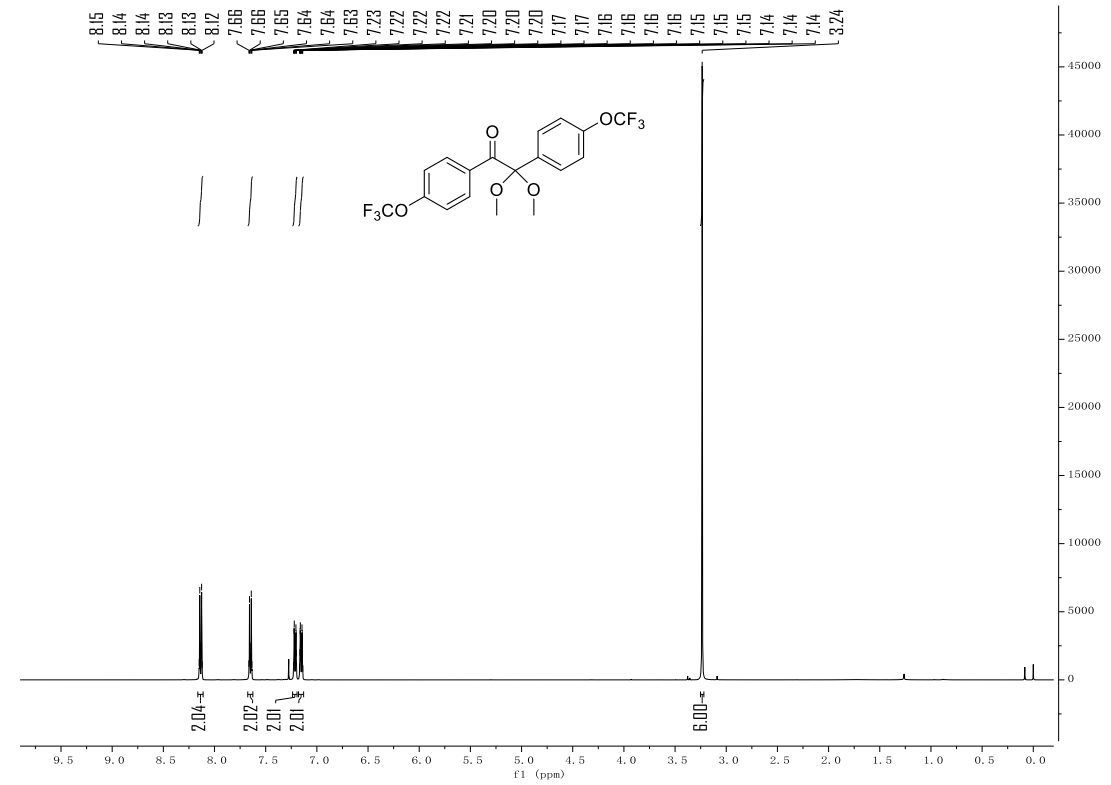


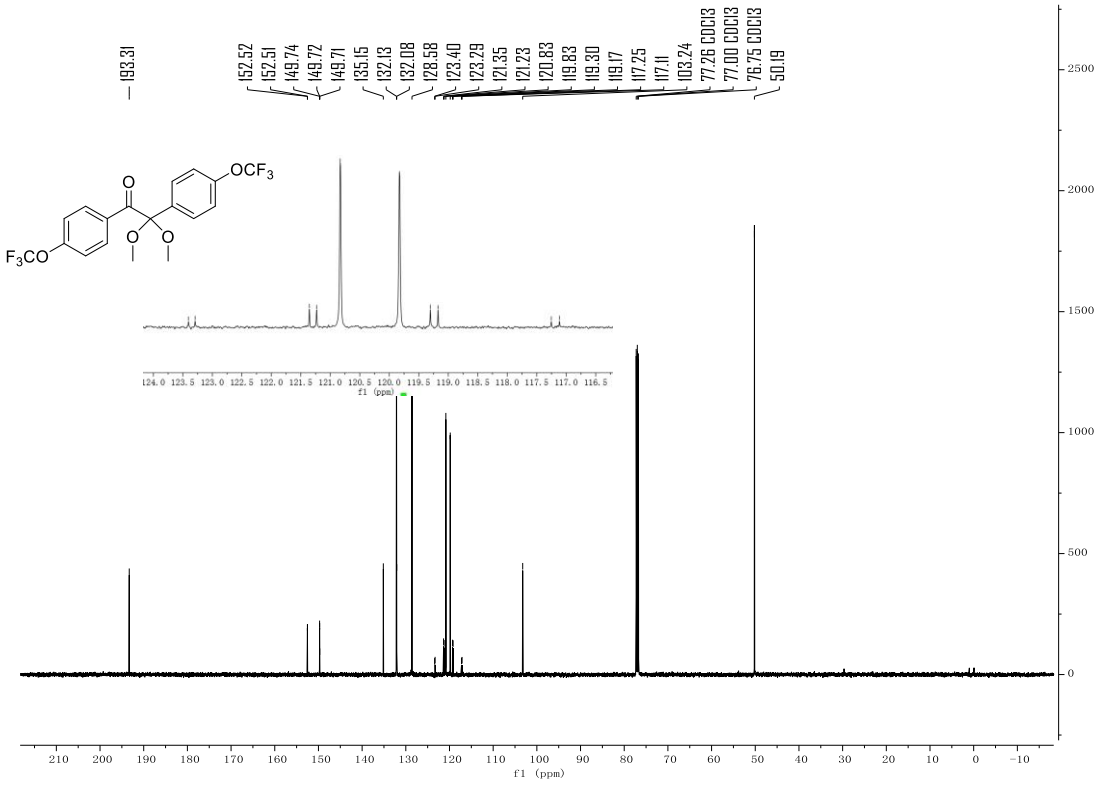



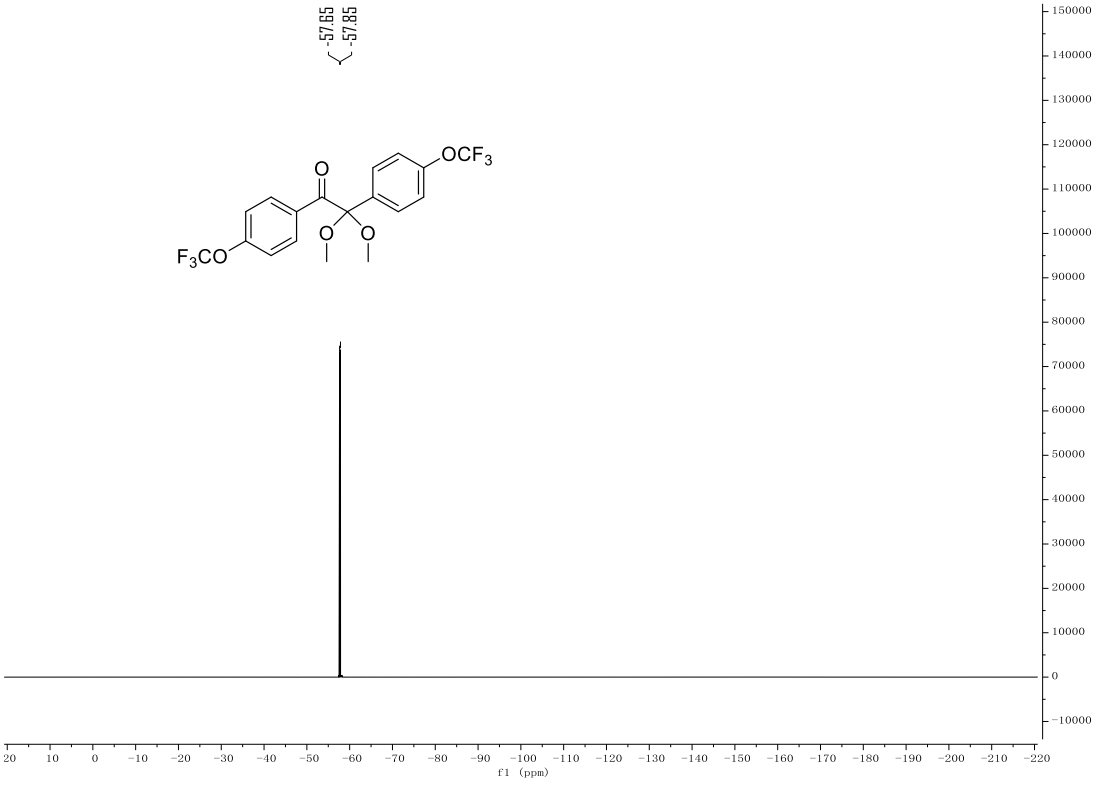
1,2-bis(4-bromophenyl)-2,2-dimethoxyethan-1-one (**c6**)

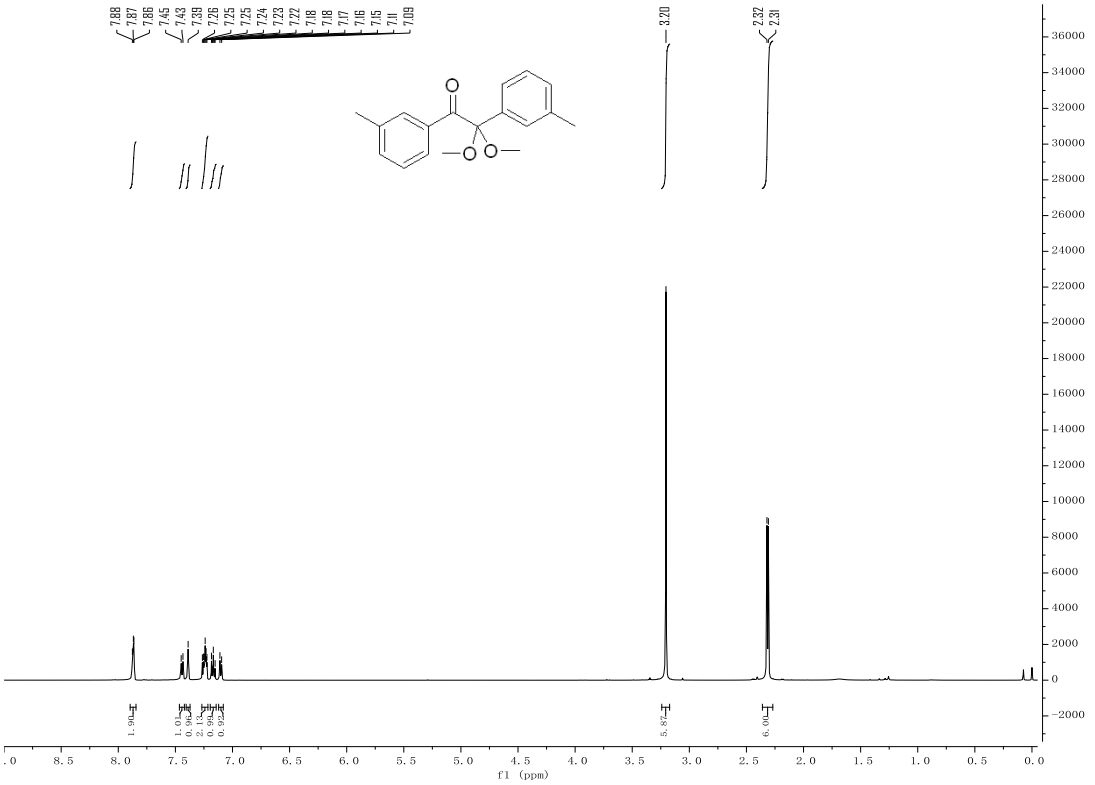
2,2-dimethoxy-1,2-bis(4-(trifluoromethoxy)phenyl)ethan-1-one (**c7**)

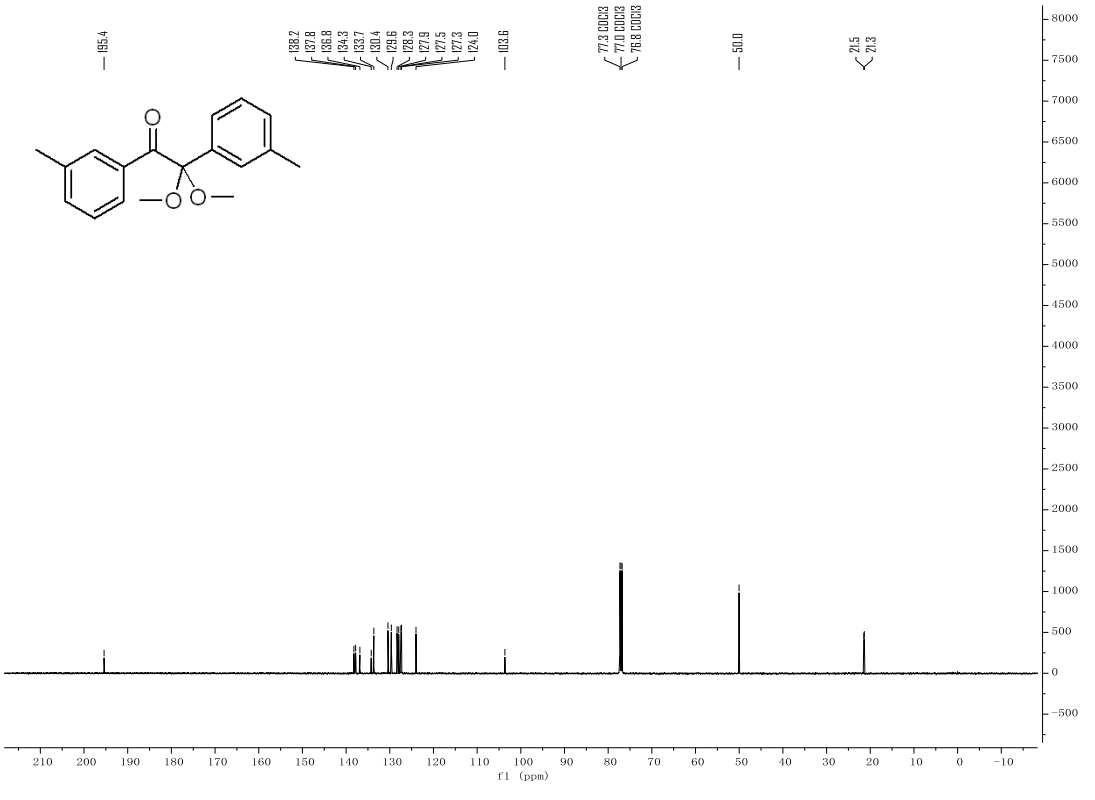


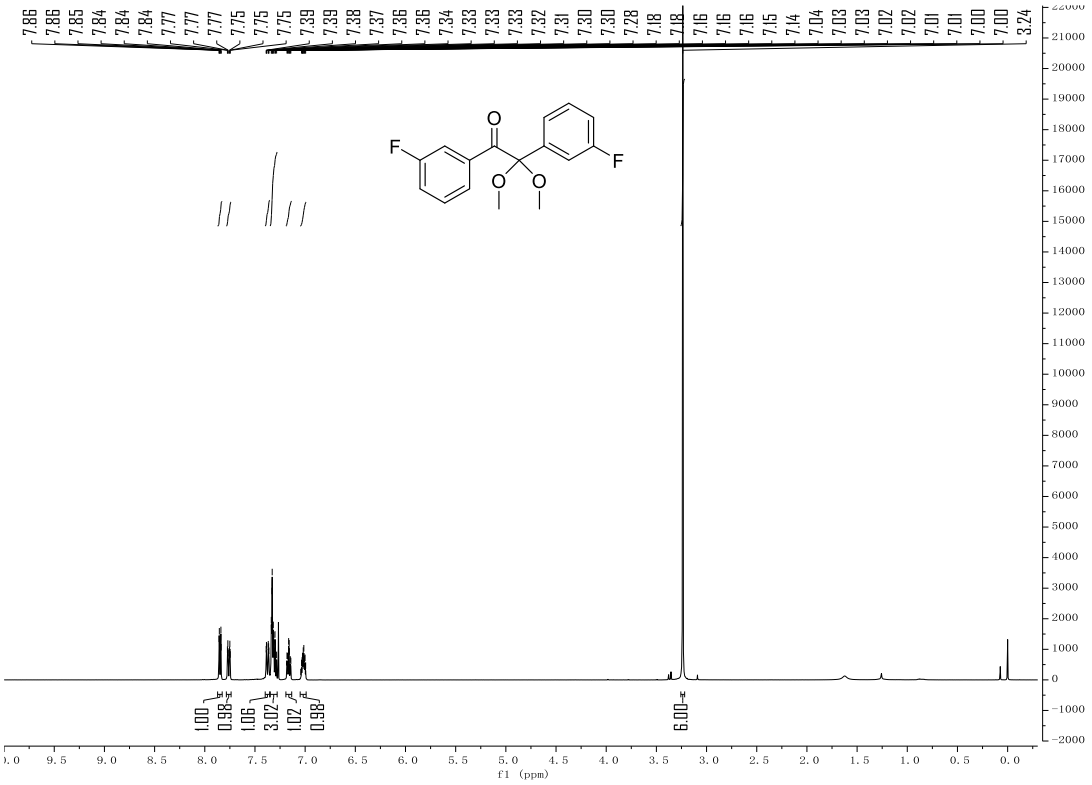

-57.65
-57.85
O
OCF3
O
O
F3CO
150000
140000
130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)

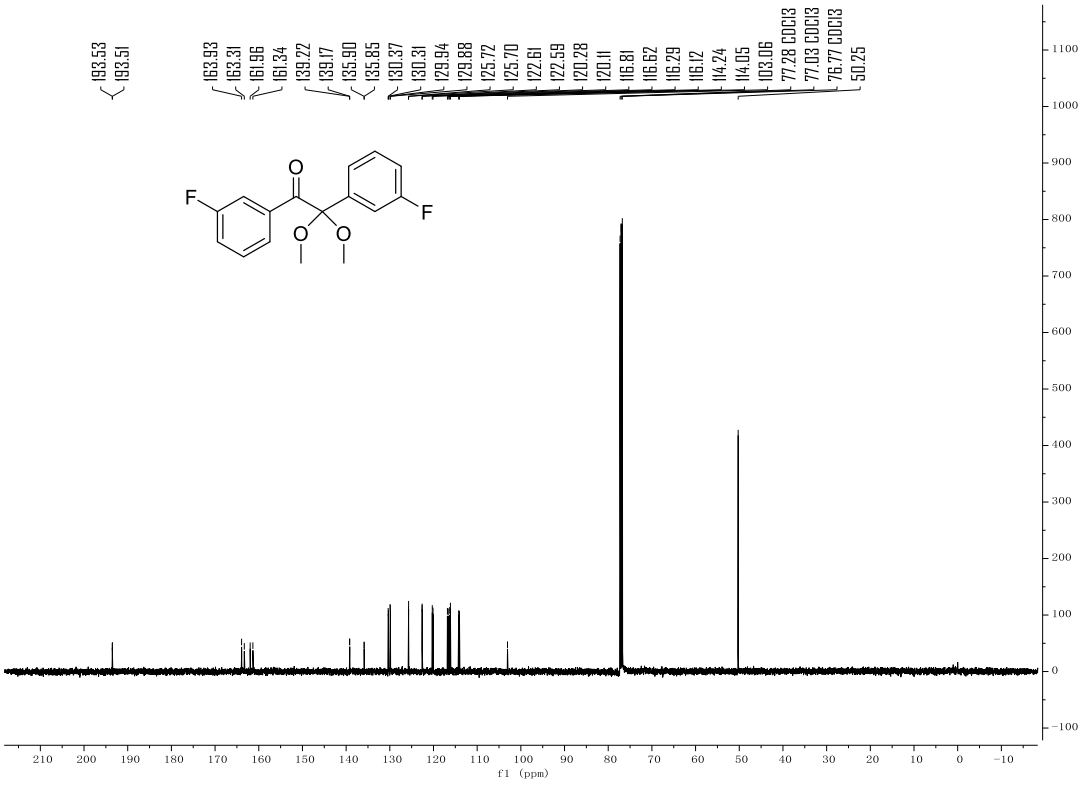
2,2-dimethoxy-1,2-di-*m*-tolylethan-1-one (**c8**)

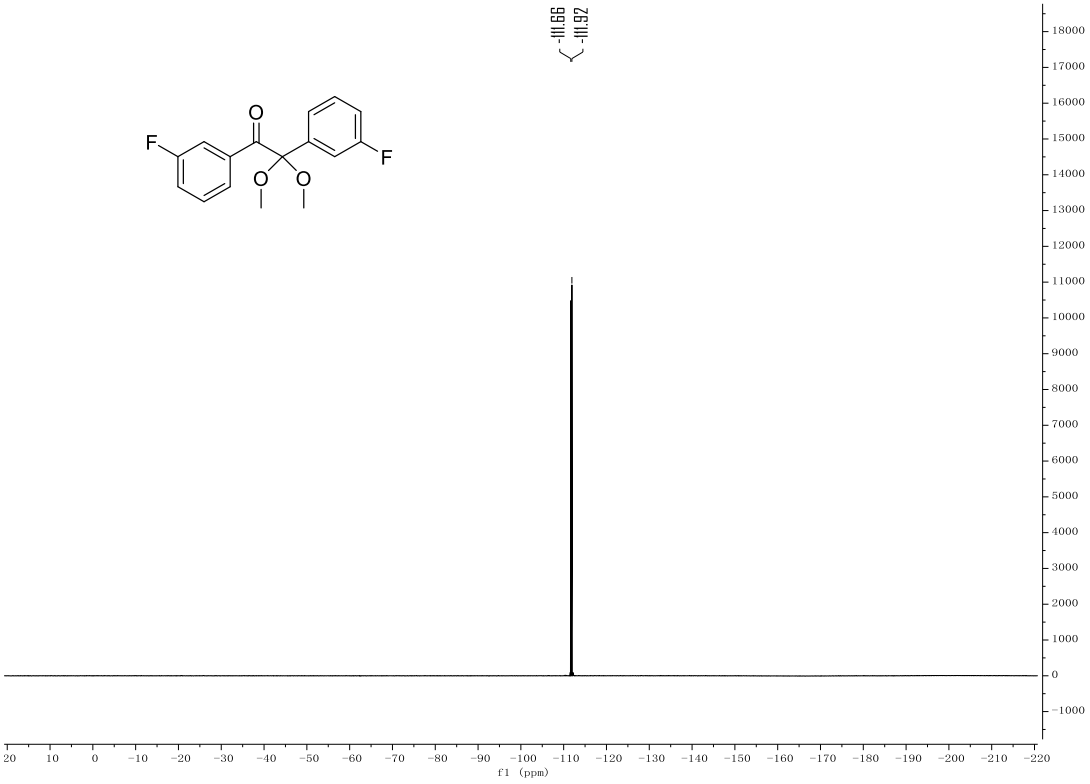


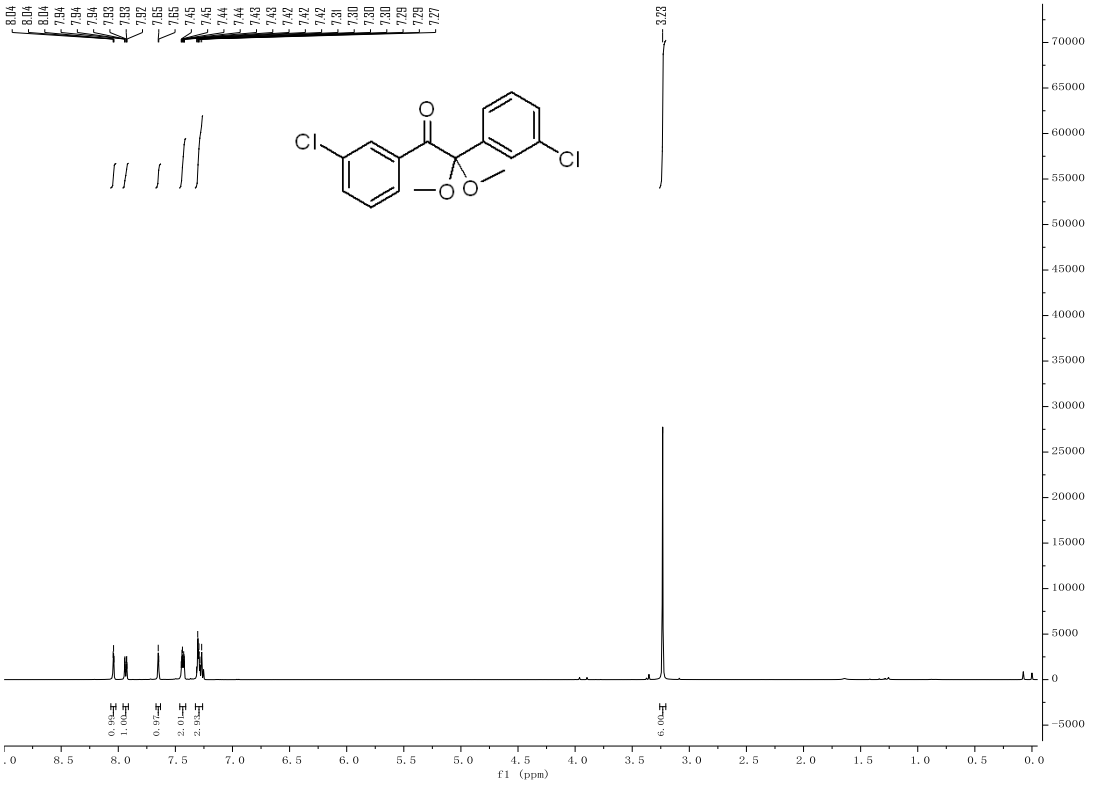
1,2-bis(3-fluorophenyl)-2,2-dimethoxyethan-1-one (**c9**)

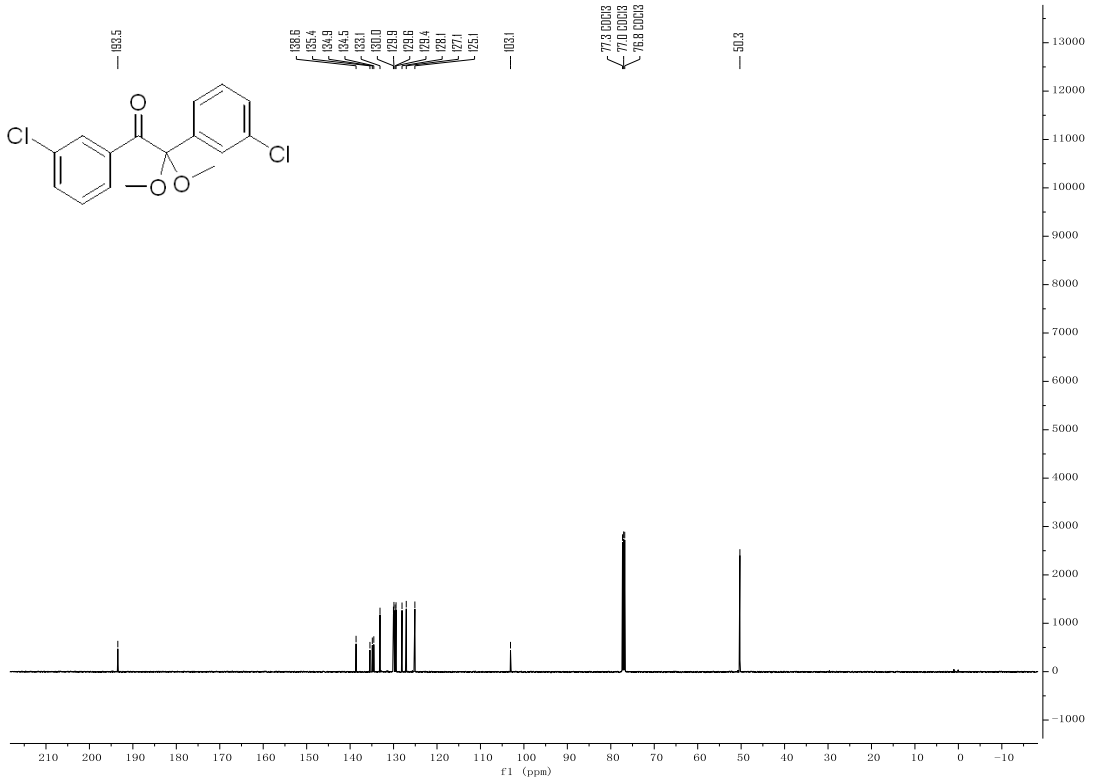


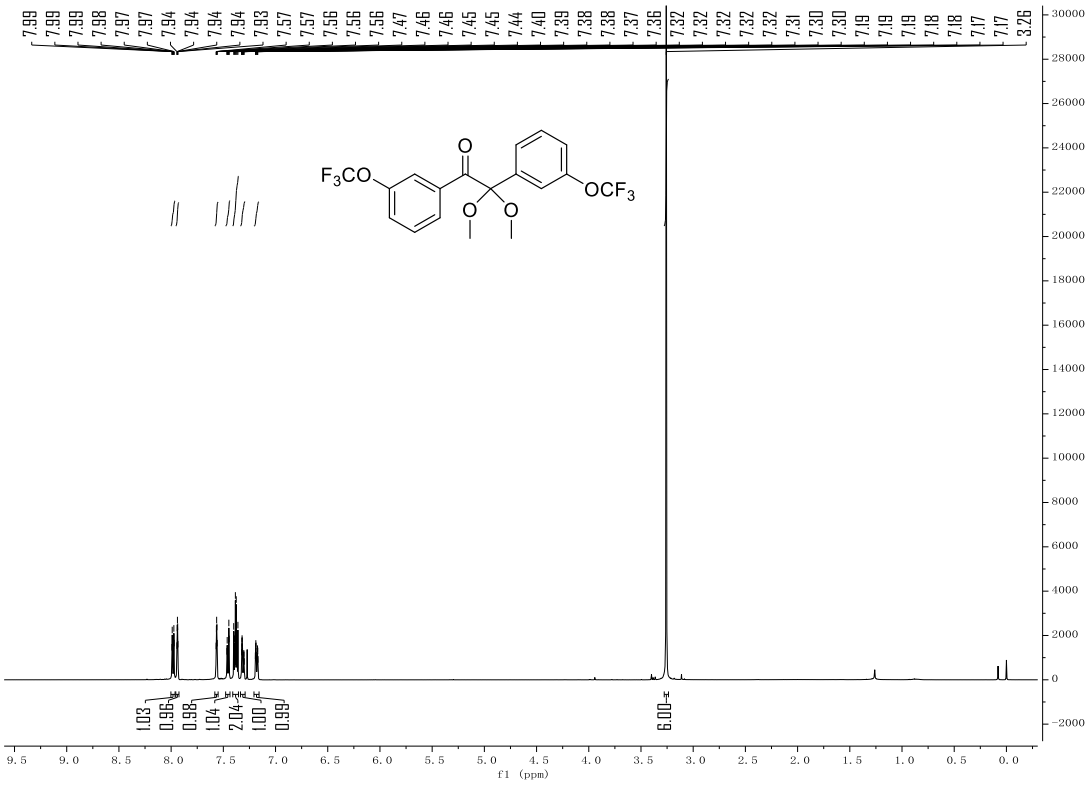

-111.66
-111.92
F
O
O
O
F
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)

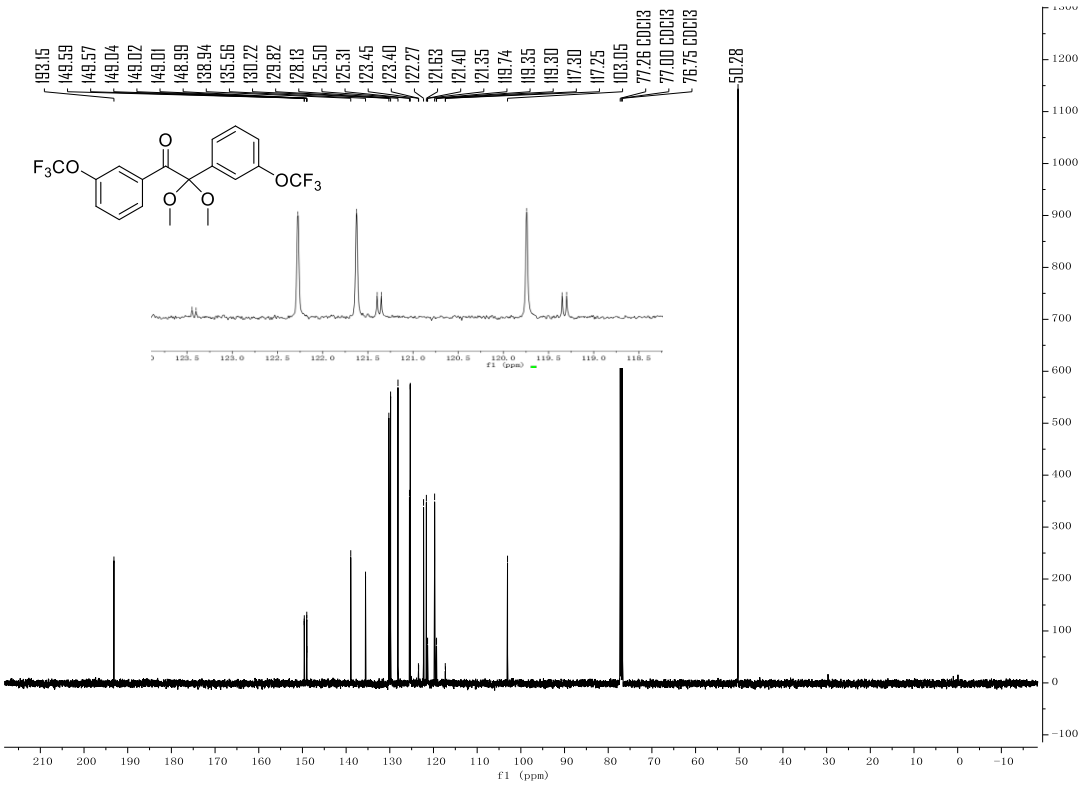
1,2-bis(3-chlorophenyl)-2,2-dimethoxyethan-1-one (**c10**)

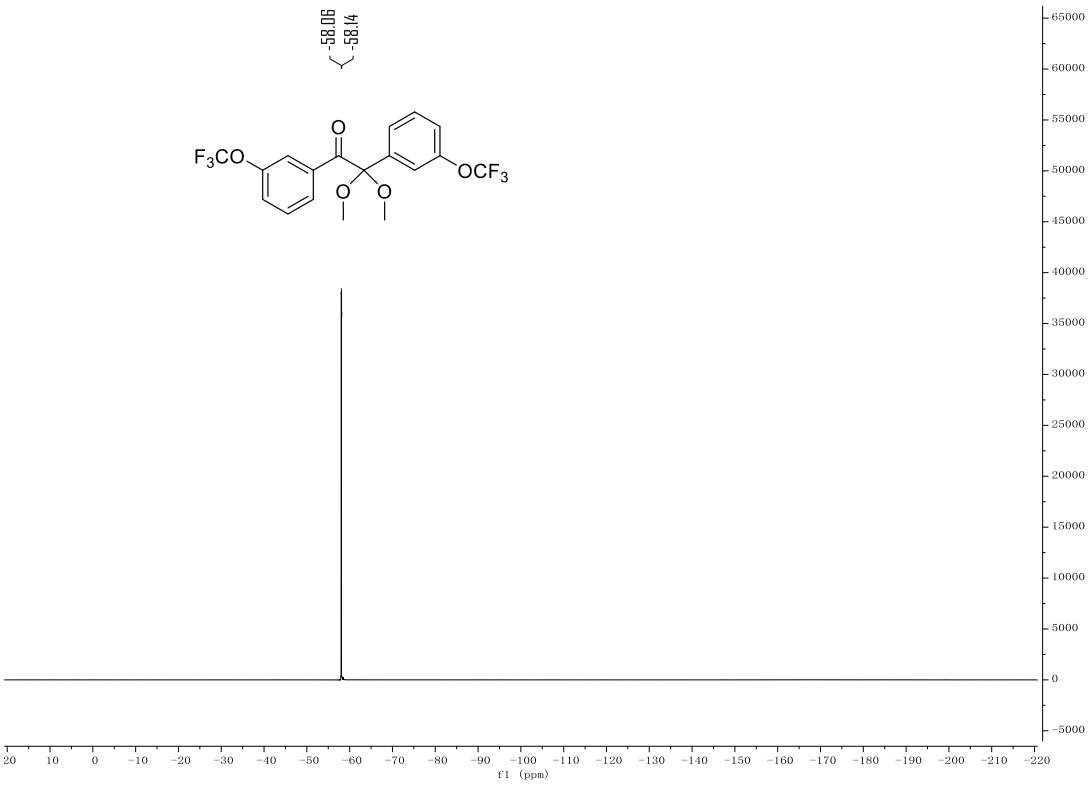


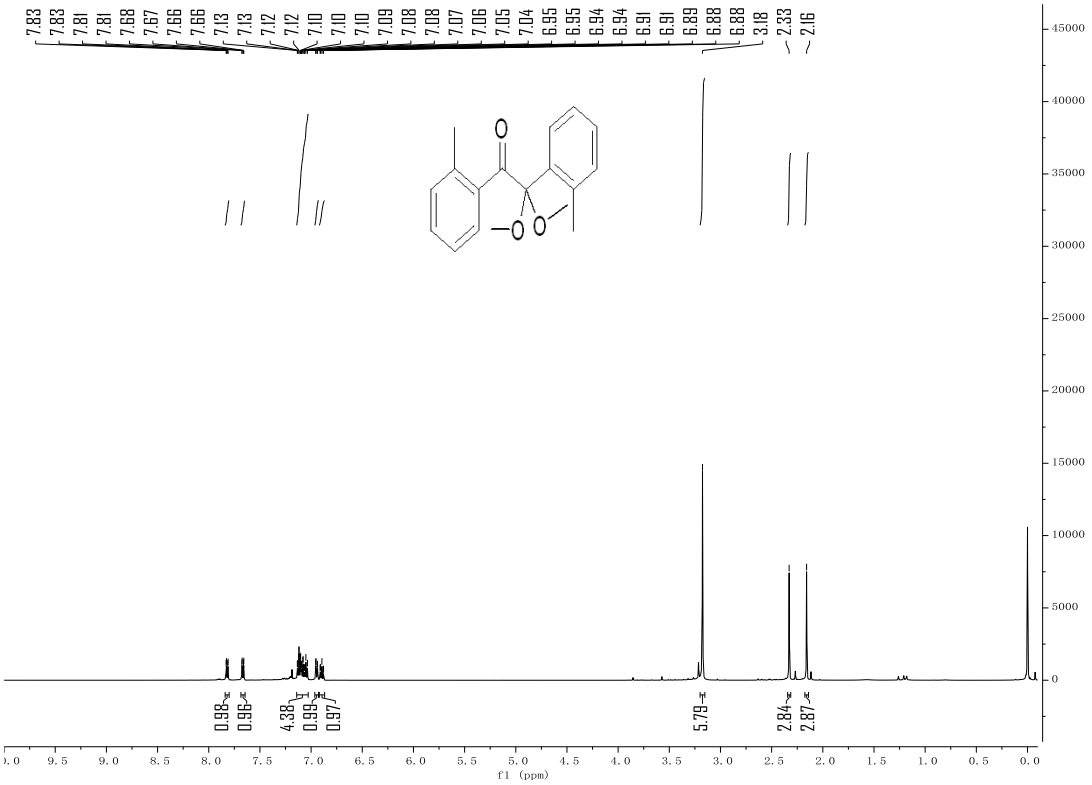
2,2-dimethoxy-1,2-bis(3-(trifluoromethoxy)phenyl)ethan-1-one (**c11**)

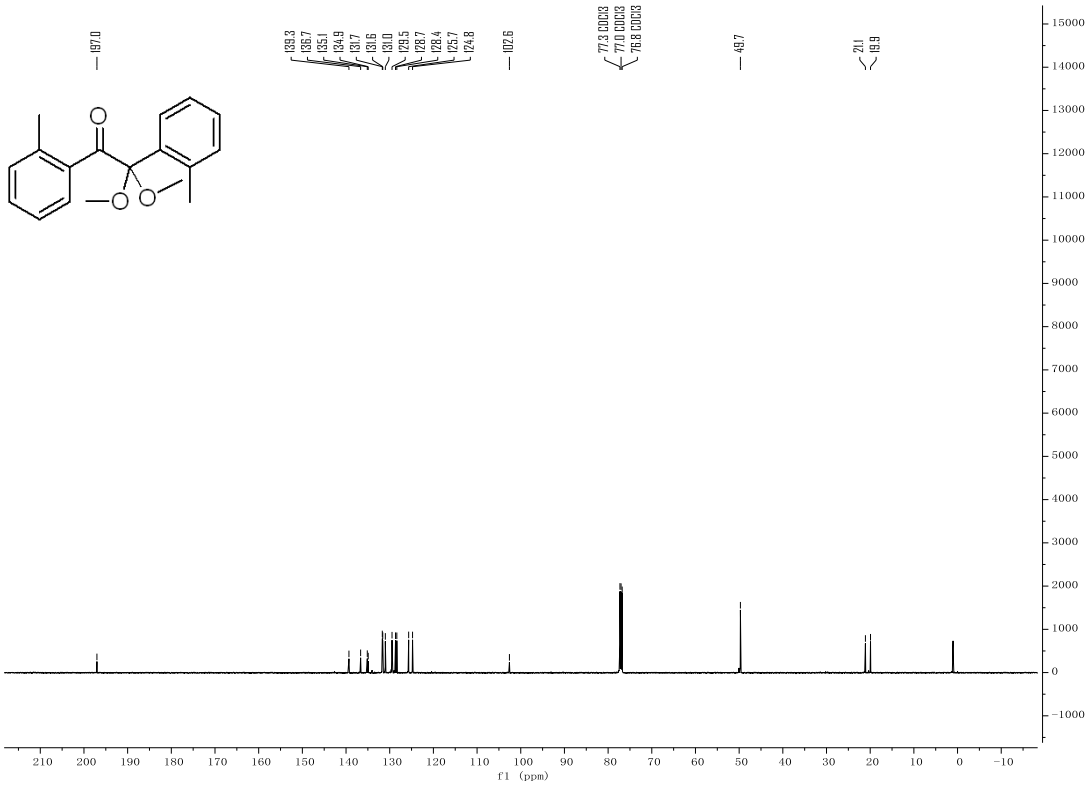


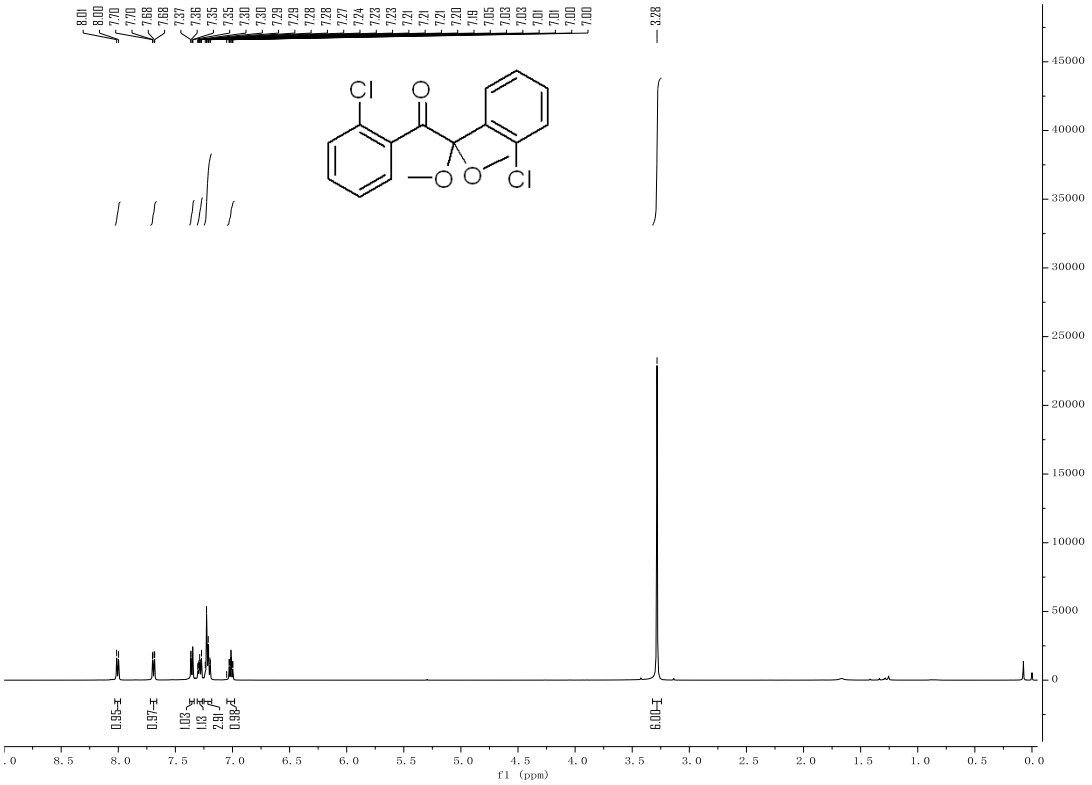

-58.06
-58.14
F3CO
OCF3
O
O
O
65000
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)

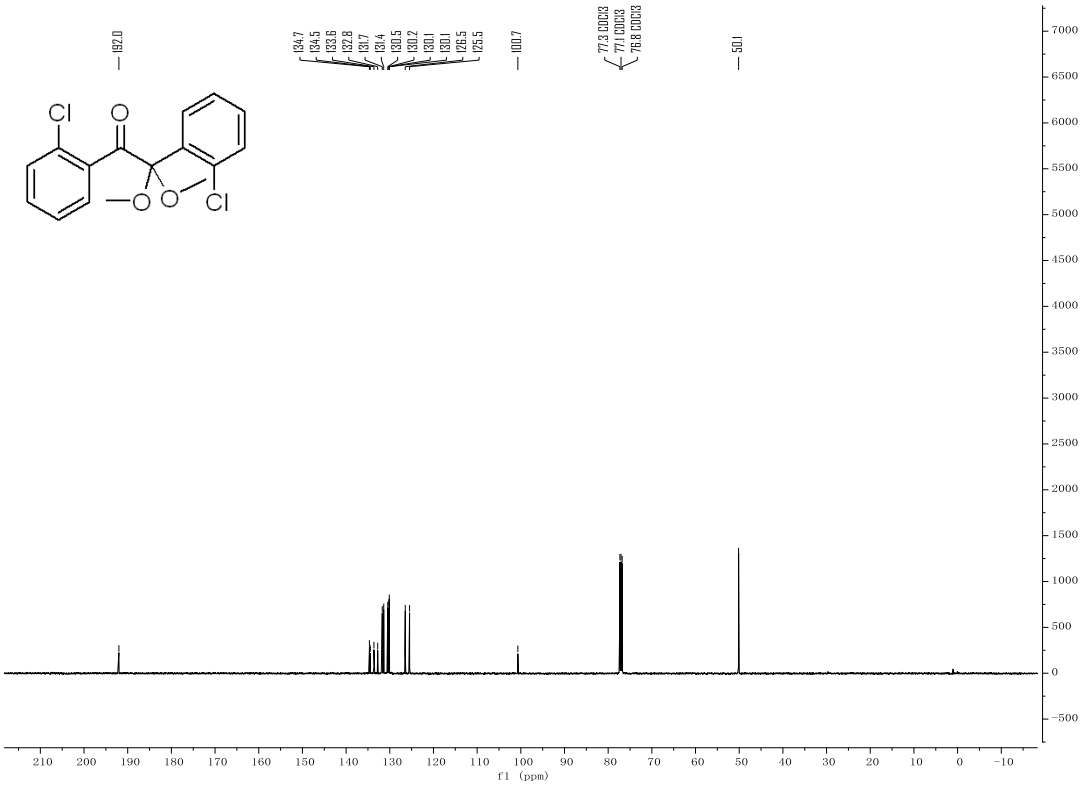
2,2-dimethoxy-1,2-di-*o*-tolylethan-1-one (**c12**)



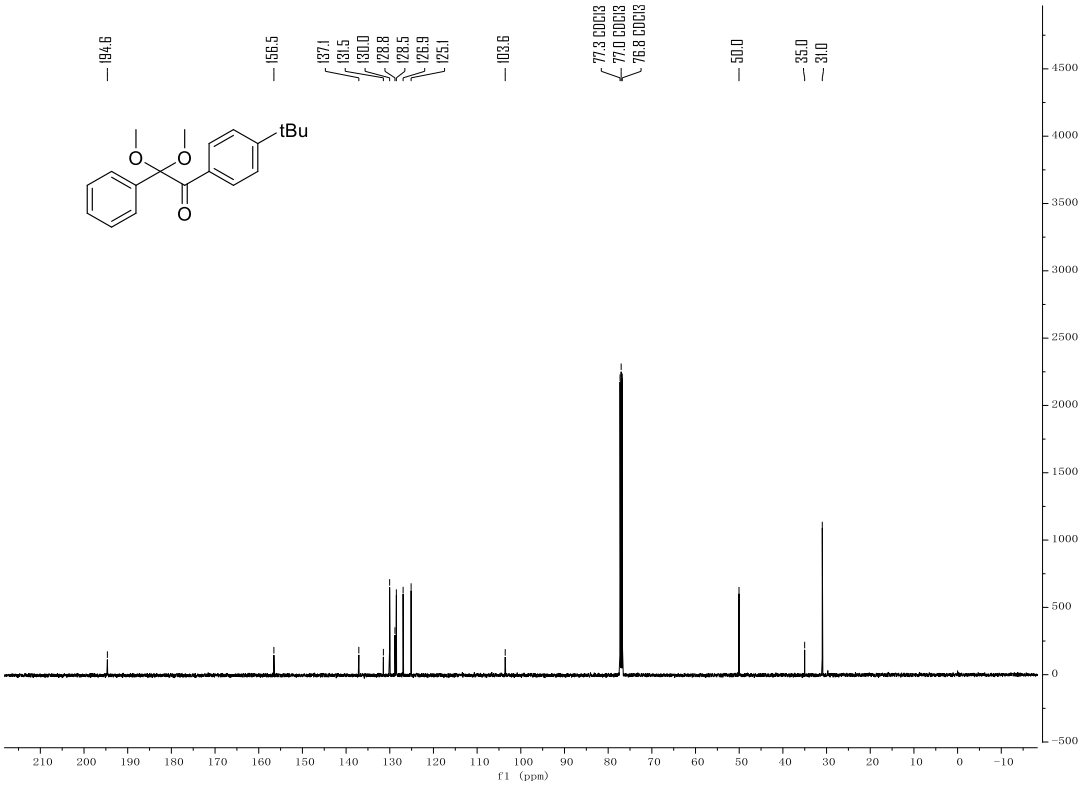



1,2-bis(2-chlorophenyl)-2,2-dimethoxyethan-1-one (**c13**)

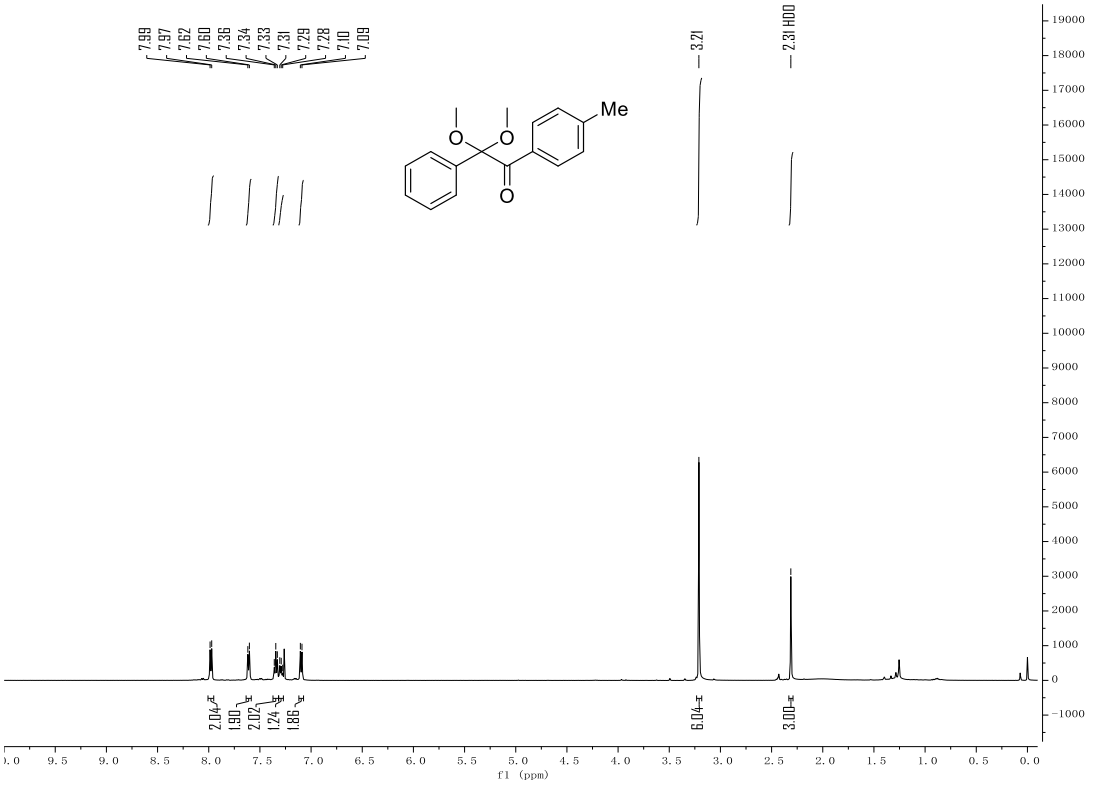


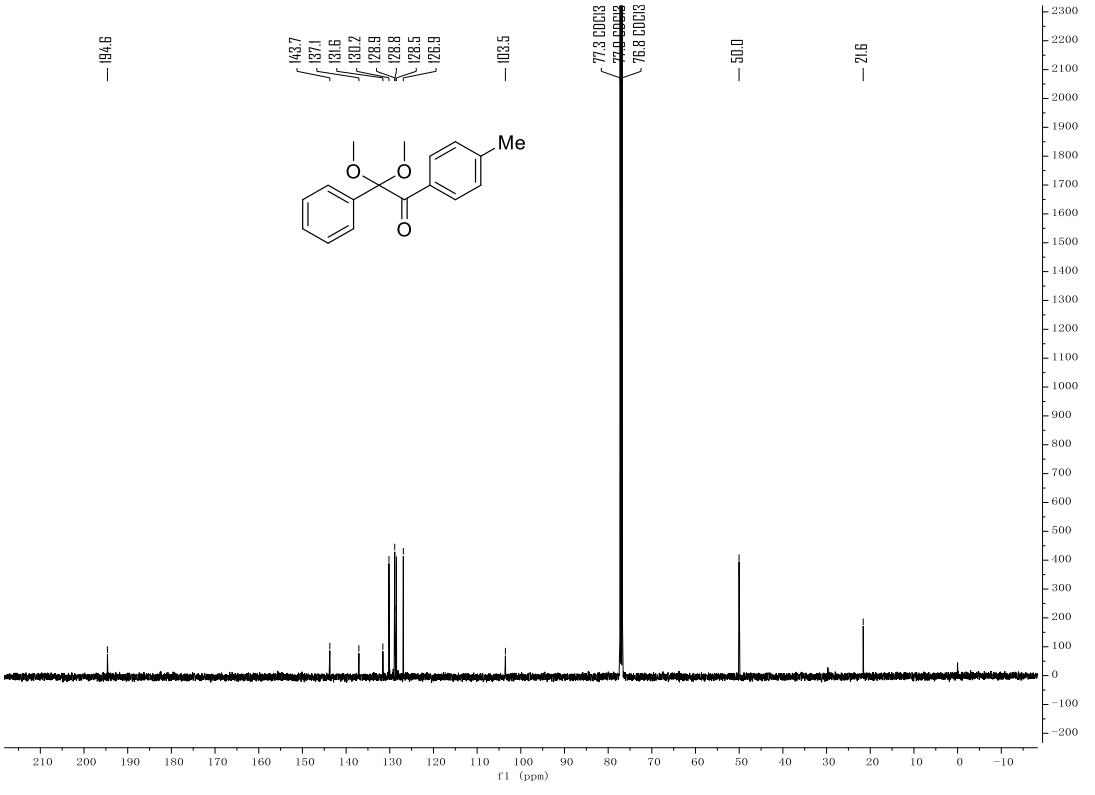



1-(4-(tert-butyl)phenyl)-2,2-dimethoxy-2-phenylethan-1-one (**e1', major isomer**)

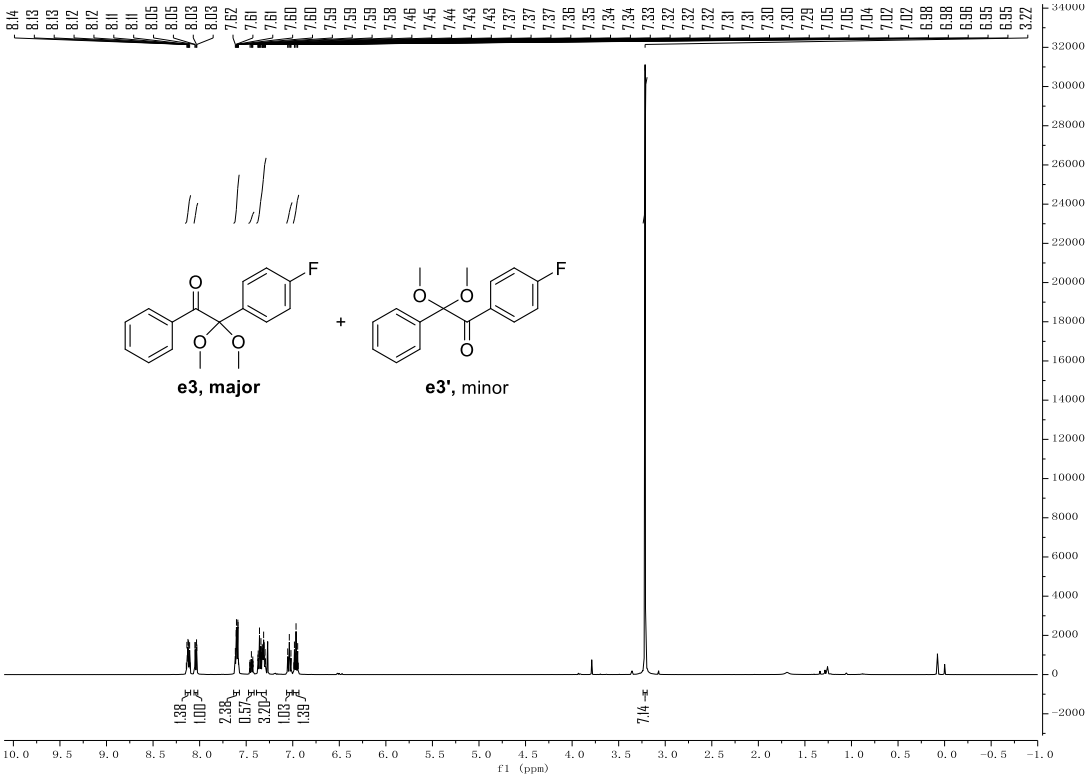



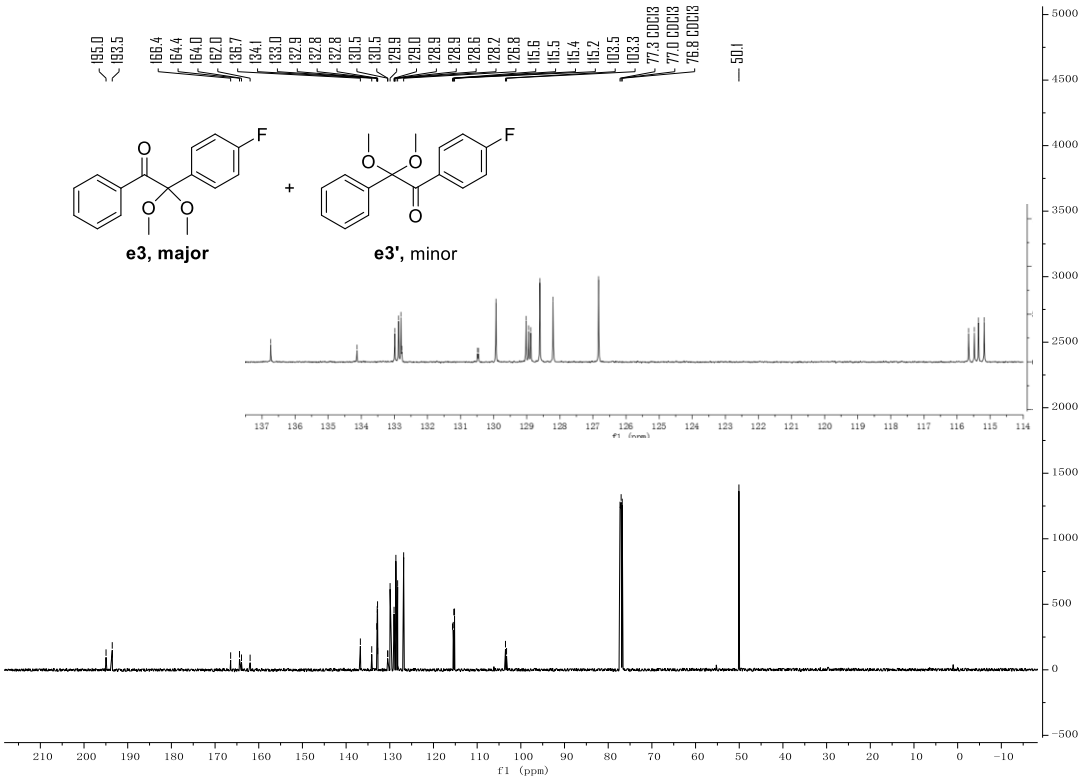
2,2-dimethoxy-2-phenyl-1-(p-tolyl)ethan-1-one (**e2', major isomer**)

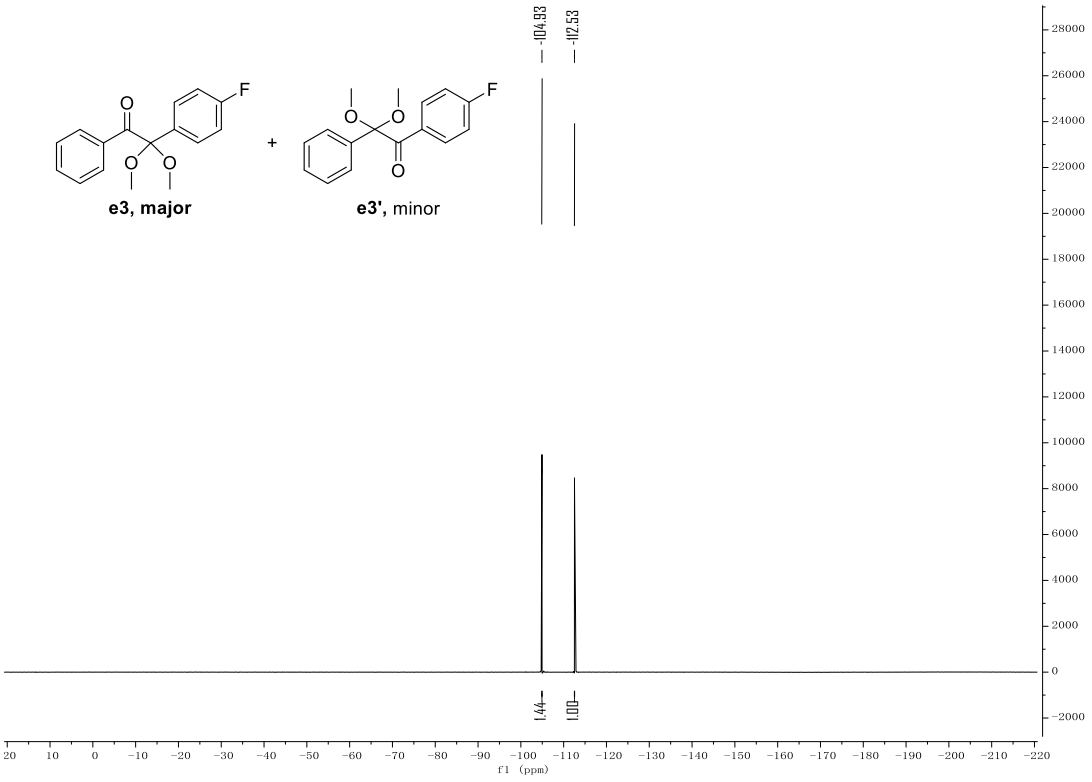


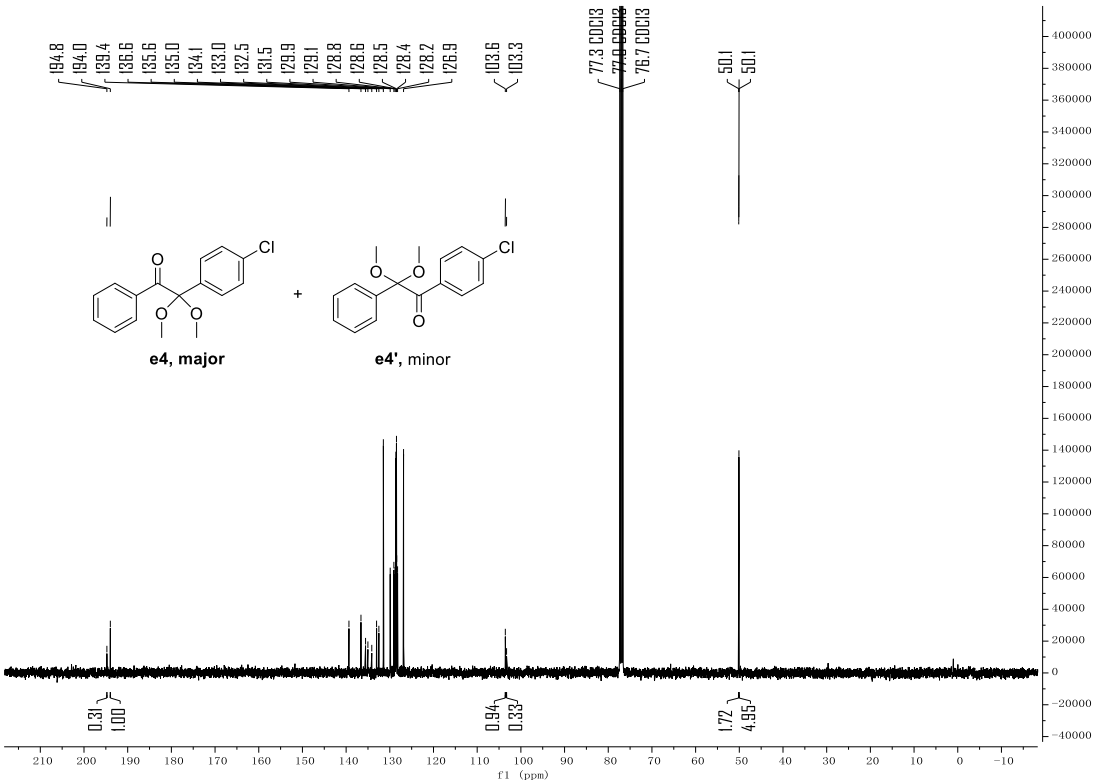
2-(4-fluorophenyl)-2,2-dimethoxy-1-phenylethan-1-one (**e3**, **major isomer**) and 1-(4-fluorophenyl)-2,2-dimethoxy-2-phenylethan-1-one (**e3'**, minor isomer) (Inseparable)



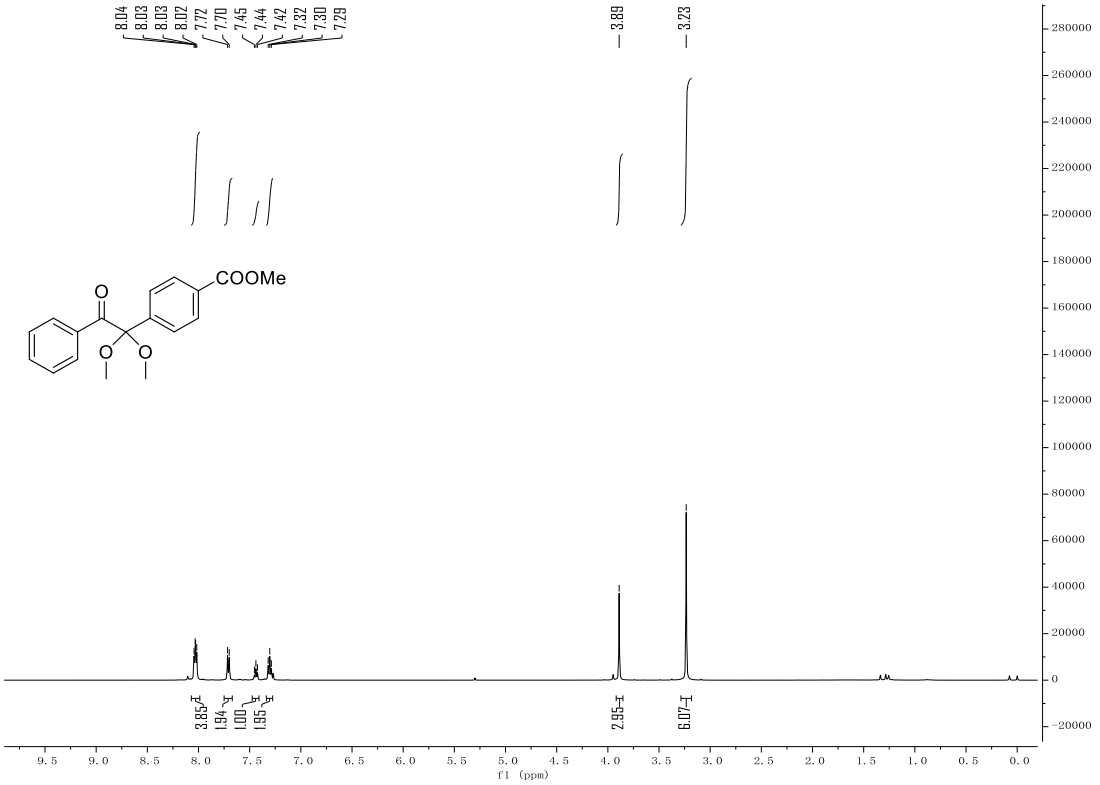



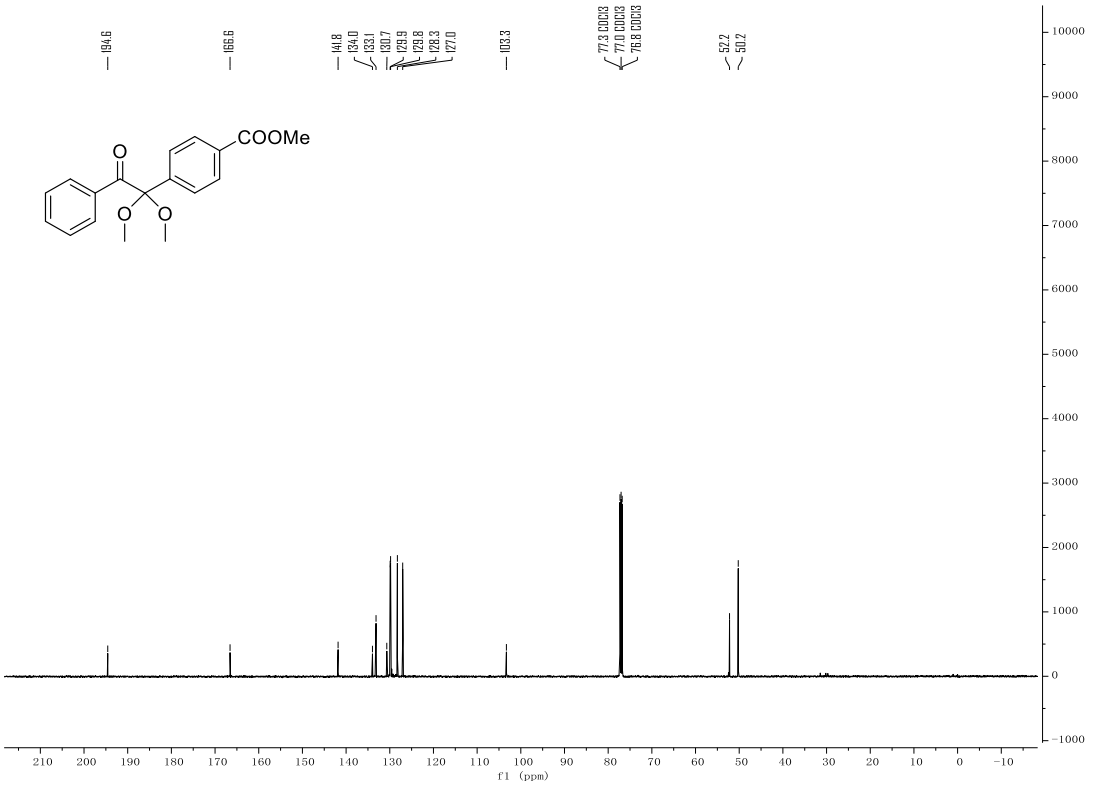

F
O
O
O
e3, major
+
O
O
O
F
e3', minor
-104.93
-112.53
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
1.44
1.00
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
f1 (ppm)

2-(4-chlorophenyl)-2,2-dimethoxy-1-phenylethan-1-one (**e4**, **major isomer**) and 1-(4-chlorophenyl)-2,2-dimethoxy-2-phenylethan-1-one (**e4'**, minor isomer) (Inseparable)

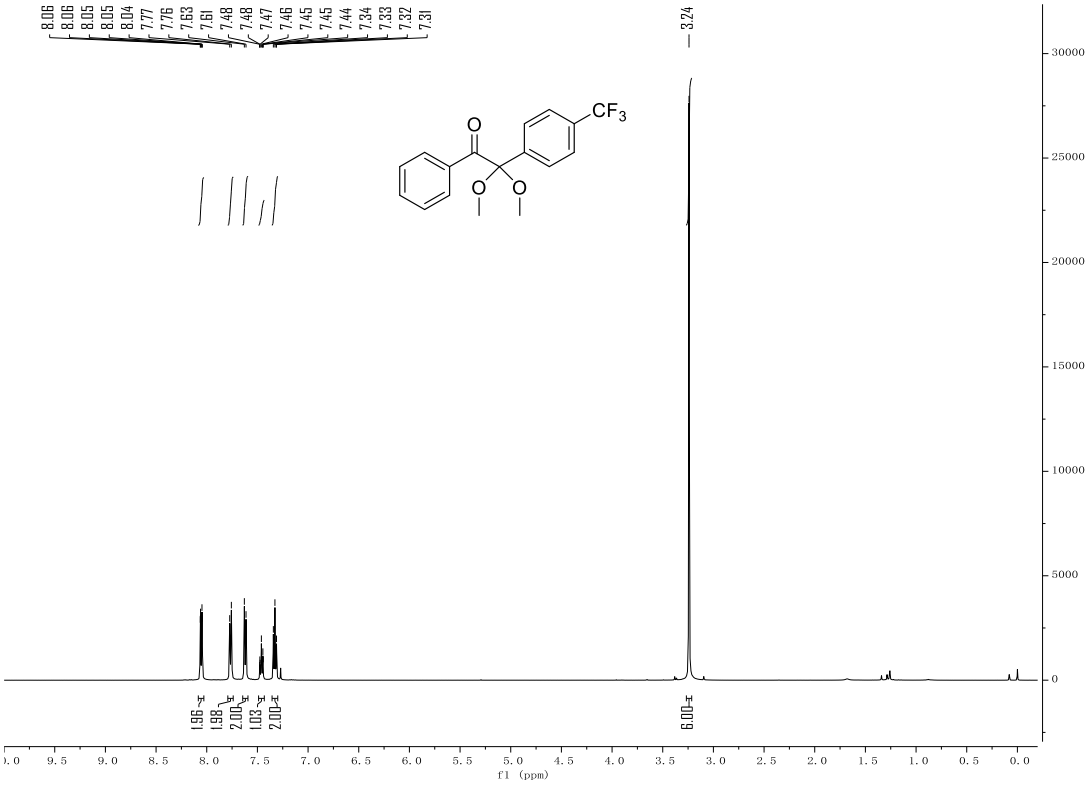



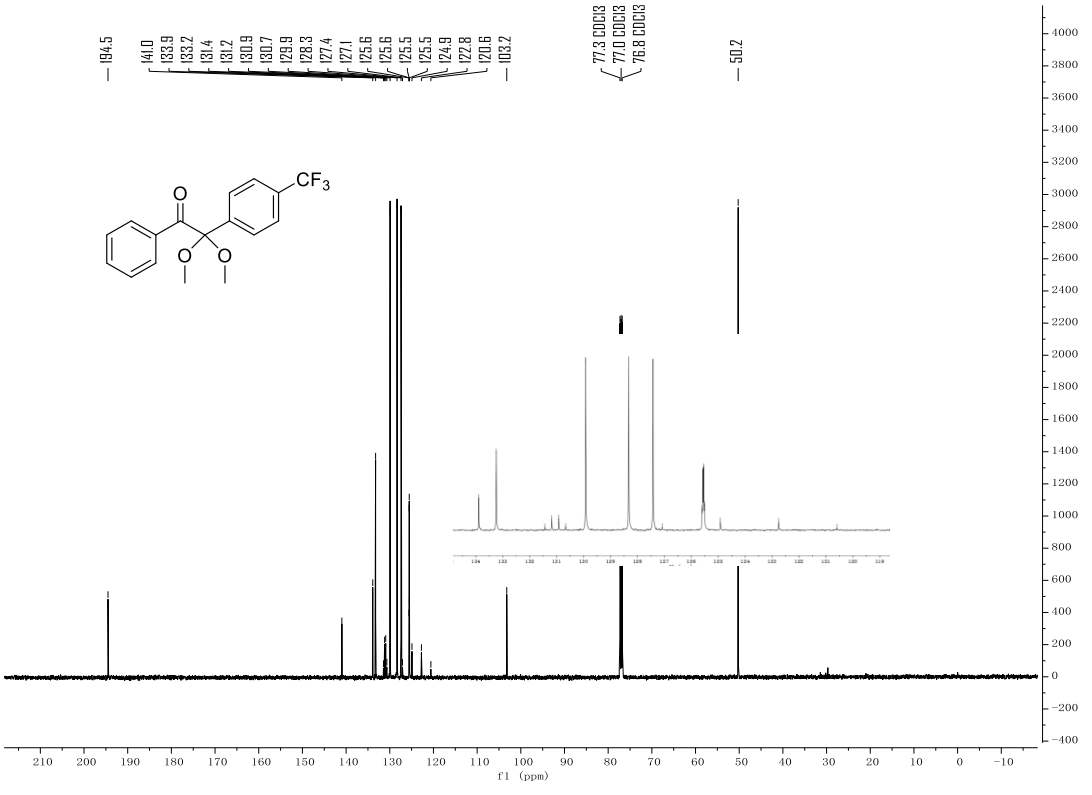
methyl 4-(1,1-dimethoxy-2-oxo-2-phenylethyl)benzoate (**e5**, **major isomer**)

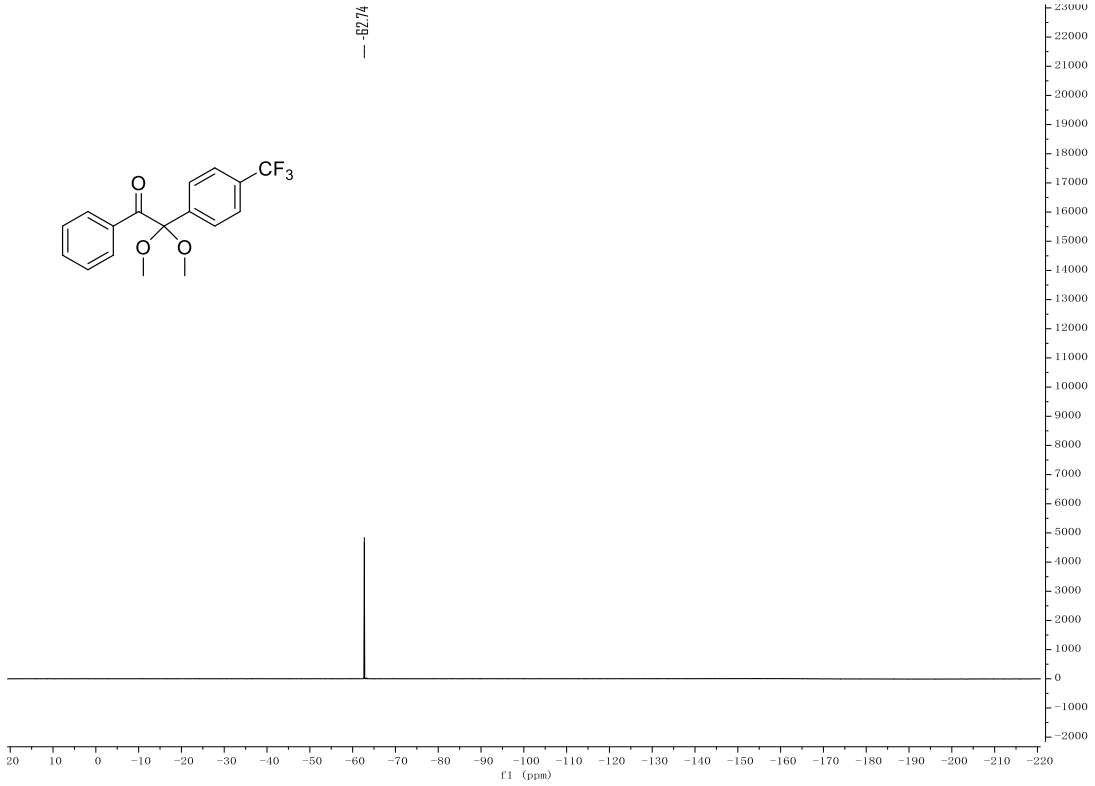


2,2-dimethoxy-1-phenyl-2-(4-(trifluoromethyl)phenyl)ethan-1-one (**e6**)

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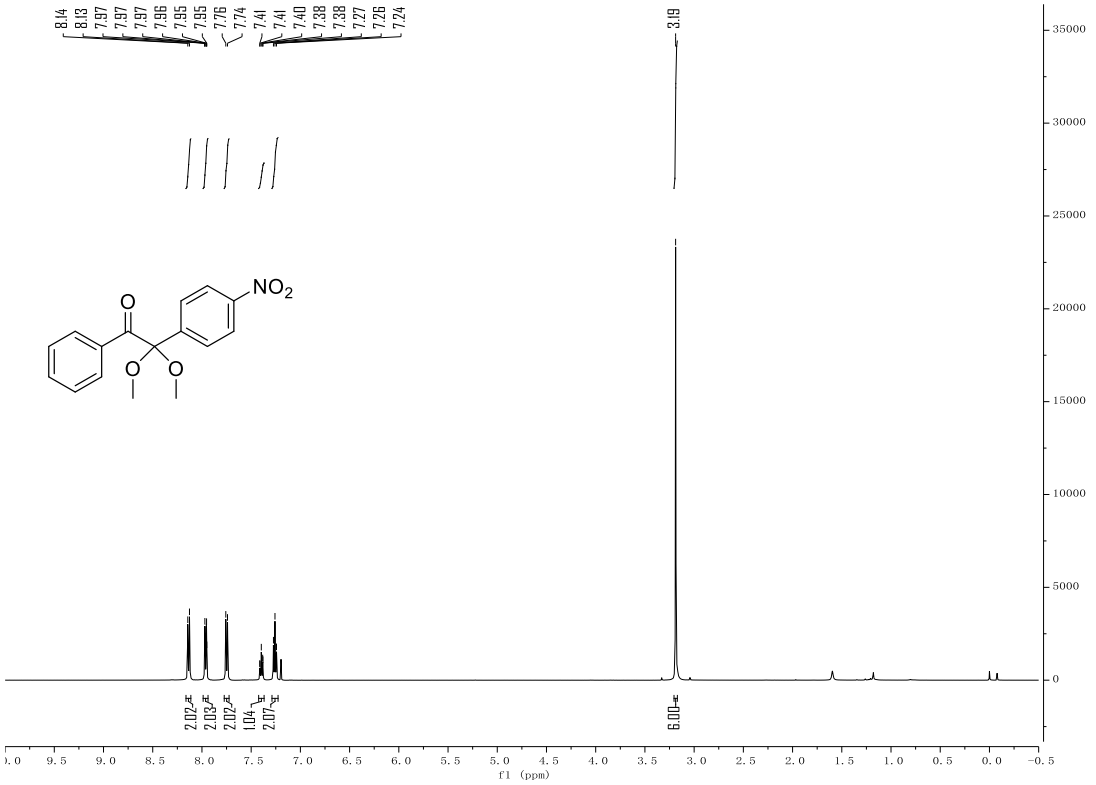
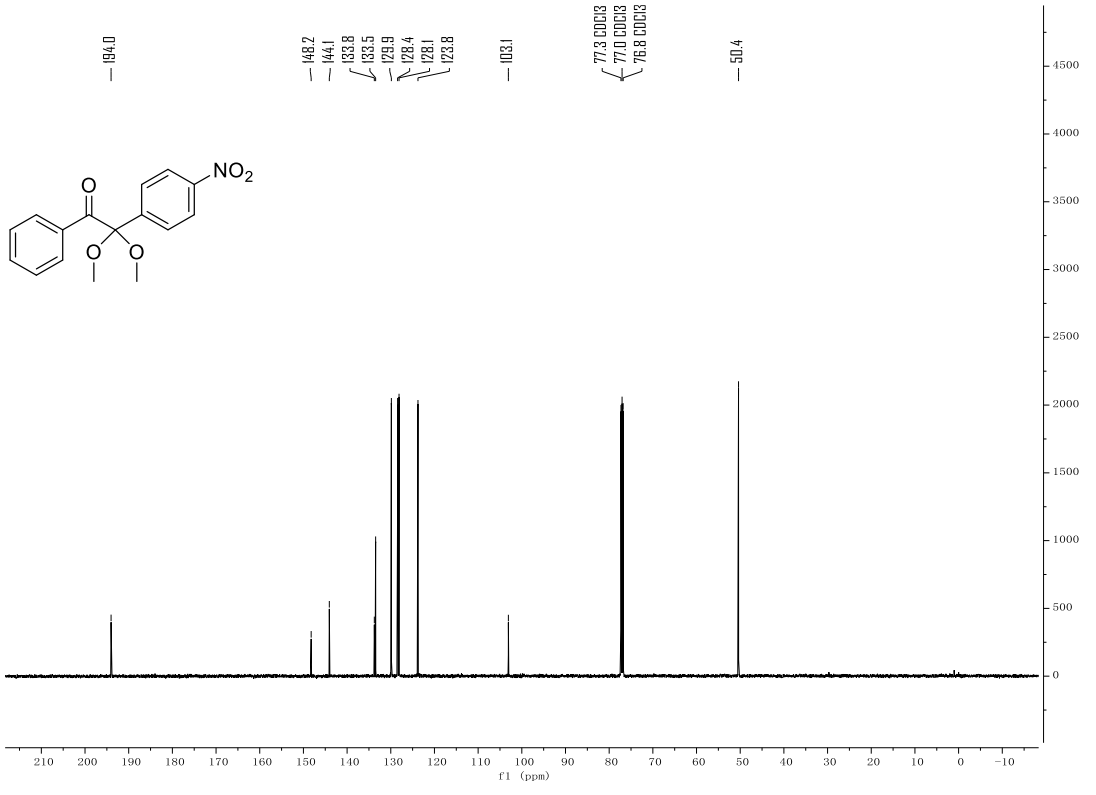
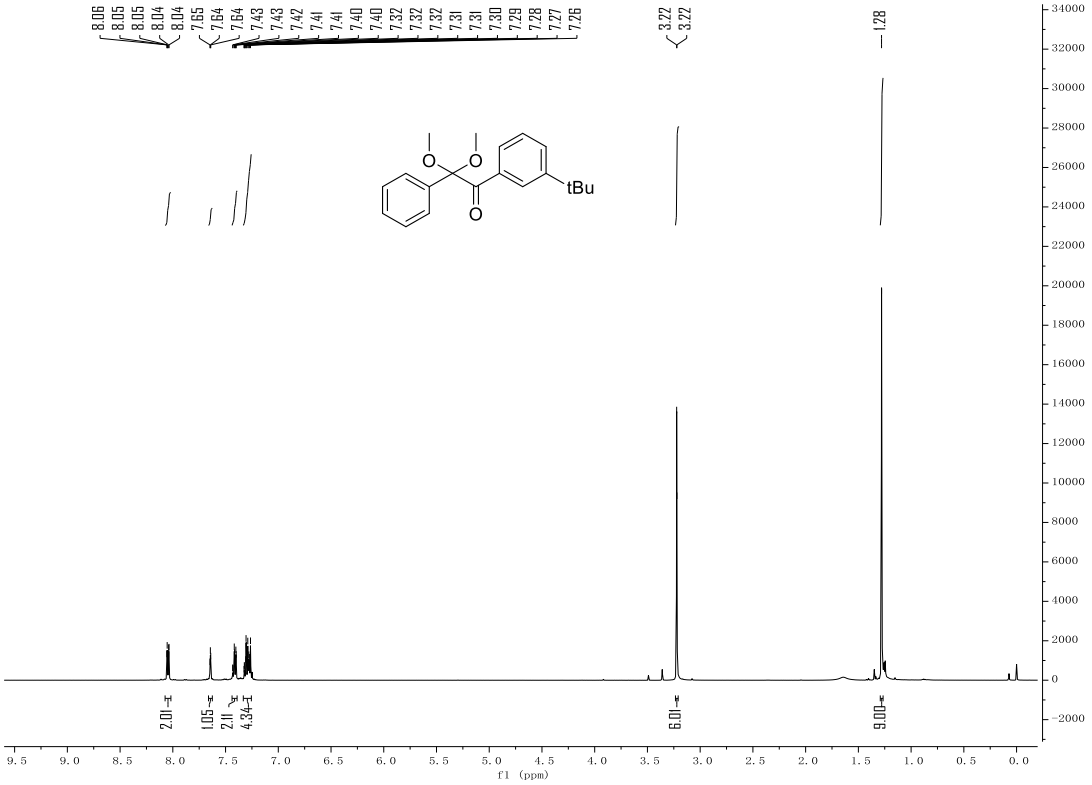
f1 (ppm)

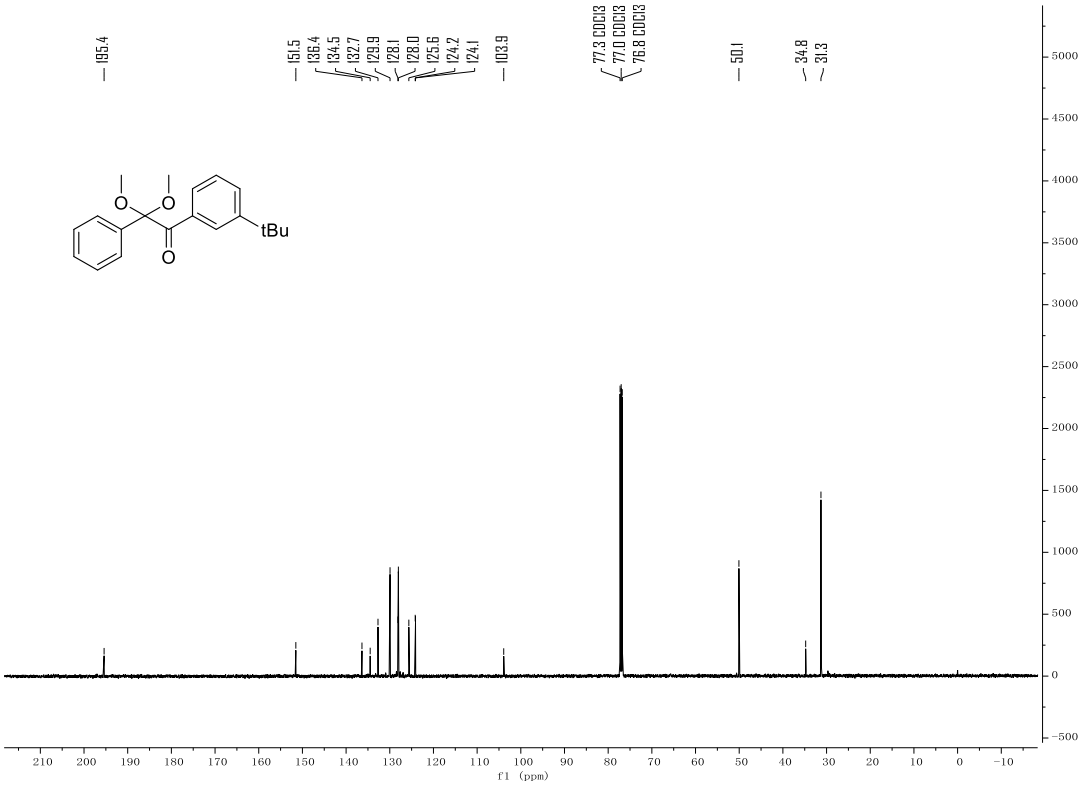
2,2-dimethoxy-2-(4-nitrophenyl)-1-phenylethan-1-one (**e7**)



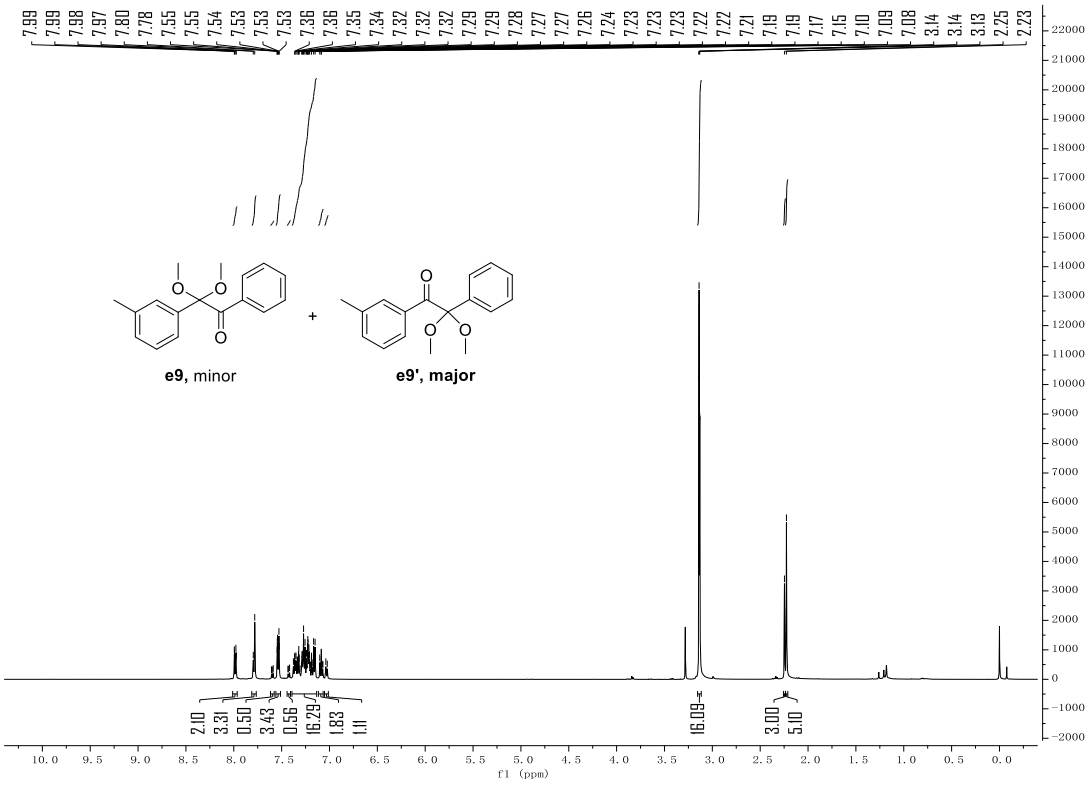



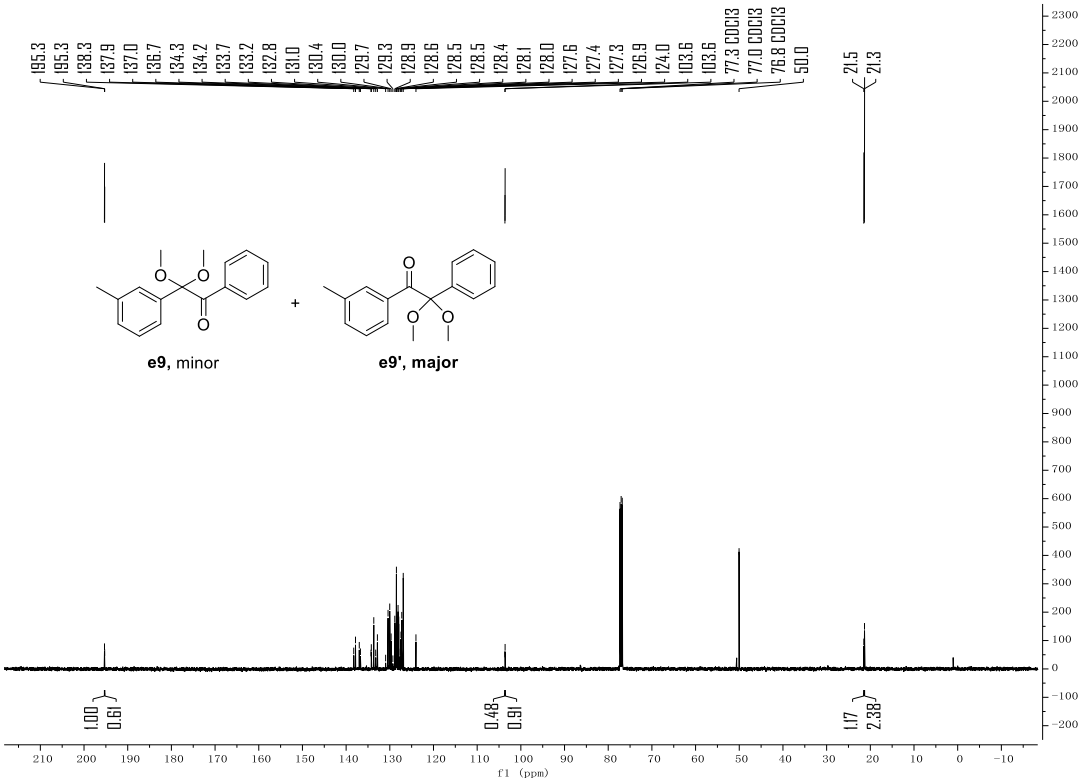
1-(3-(tert-butyl)phenyl)-2,2-dimethoxy-2-phenylethan-1-one (**e8'**, **major isomer**)



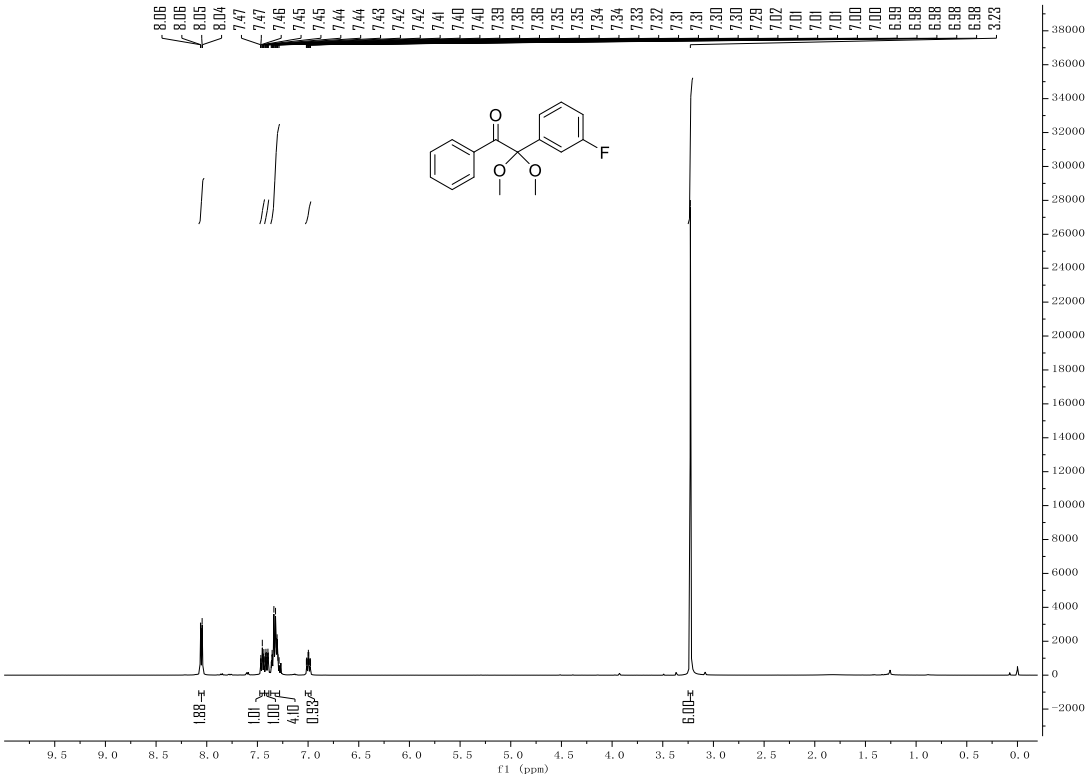



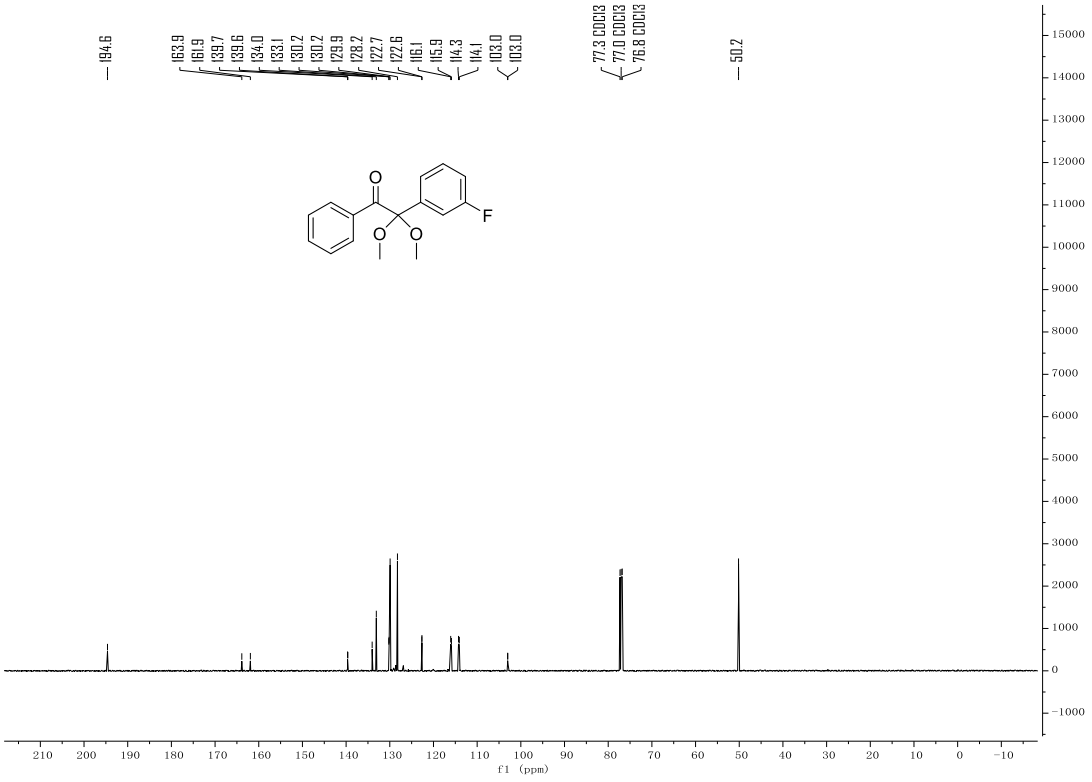
2,2-dimethoxy-1-phenyl-2-(m-tolyl)ethan-1-one (**e9**, minor isomer) and 2,2-dimethoxy-2-phenyl-1-(m-tolyl)ethan-1-one (**e9'**, **major isomer**): Inseparable.

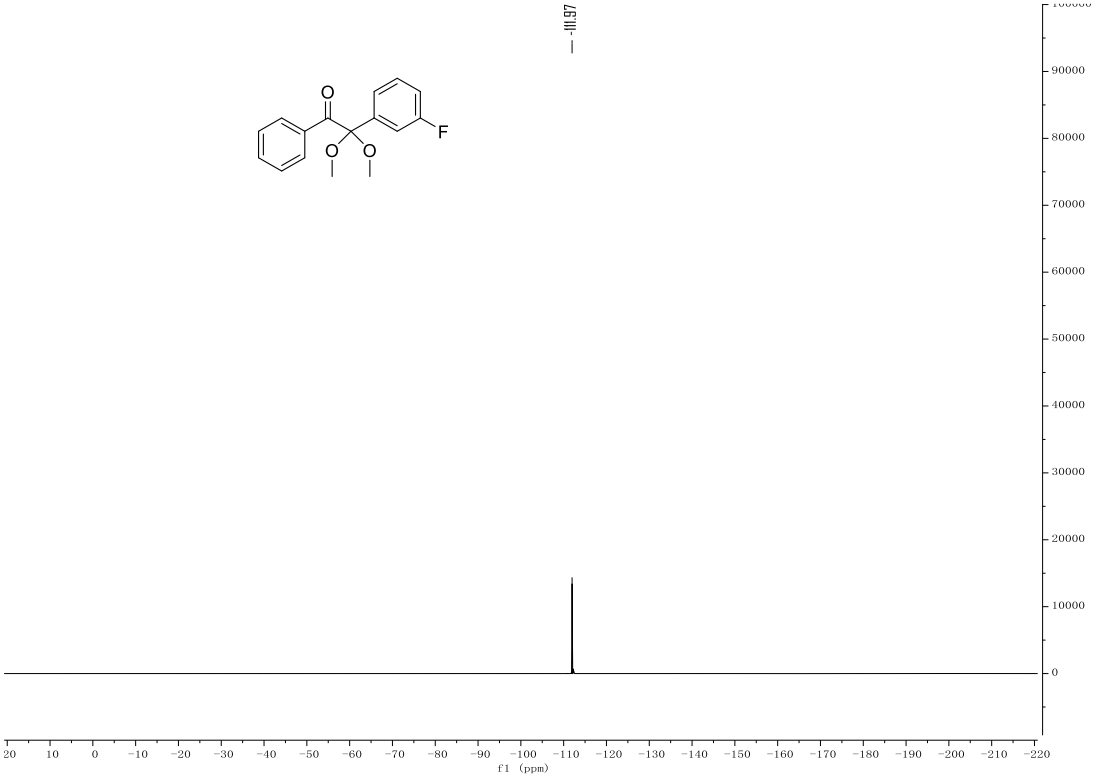


2-(3-fluorophenyl)-2,2-dimethoxy-1-phenylethan-1-one (**e10**, **major isomer**)

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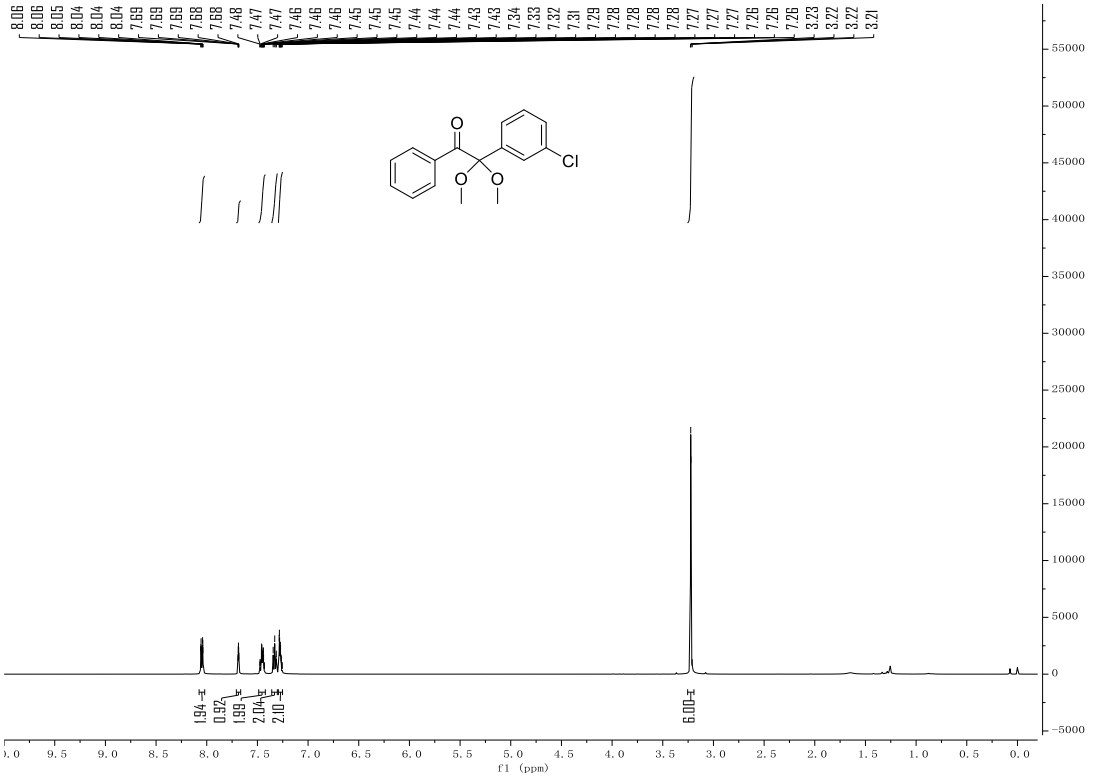
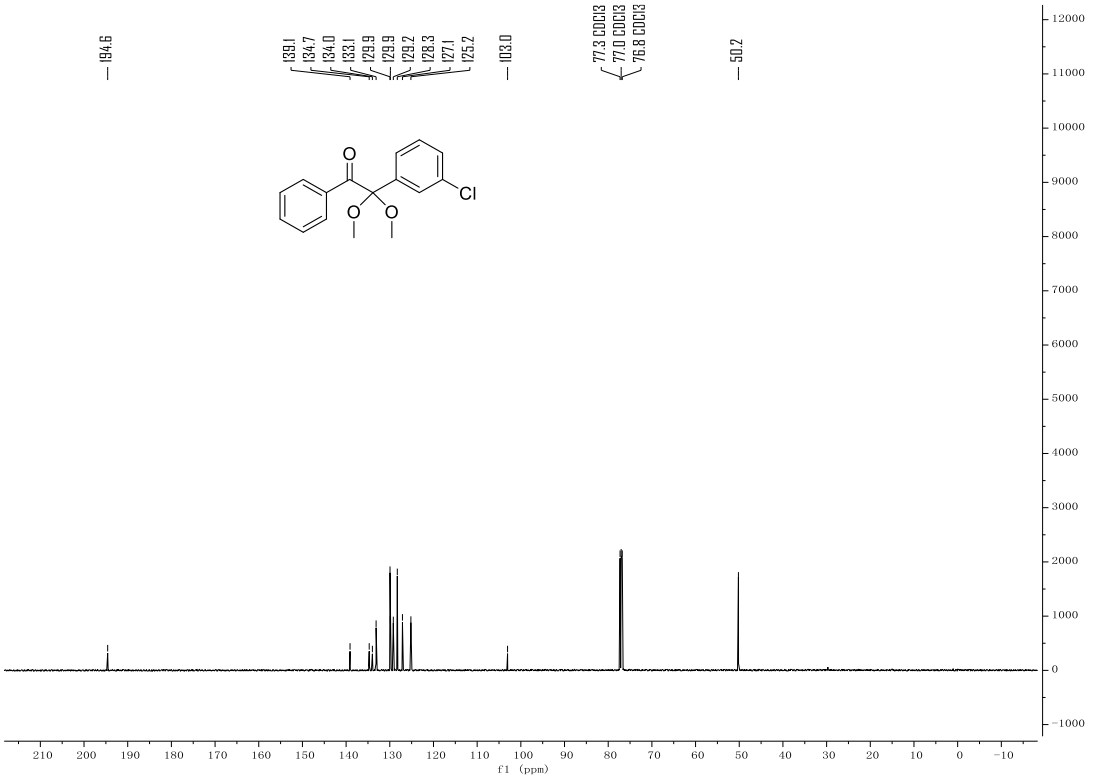
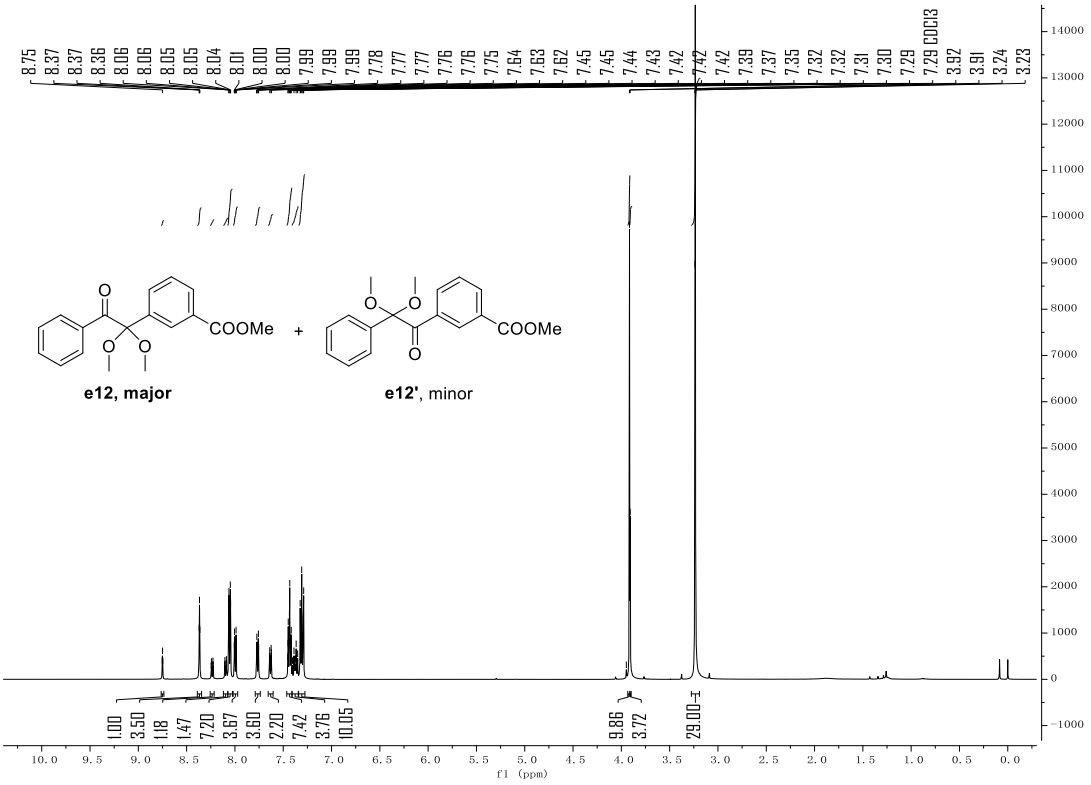
f1 (ppm)

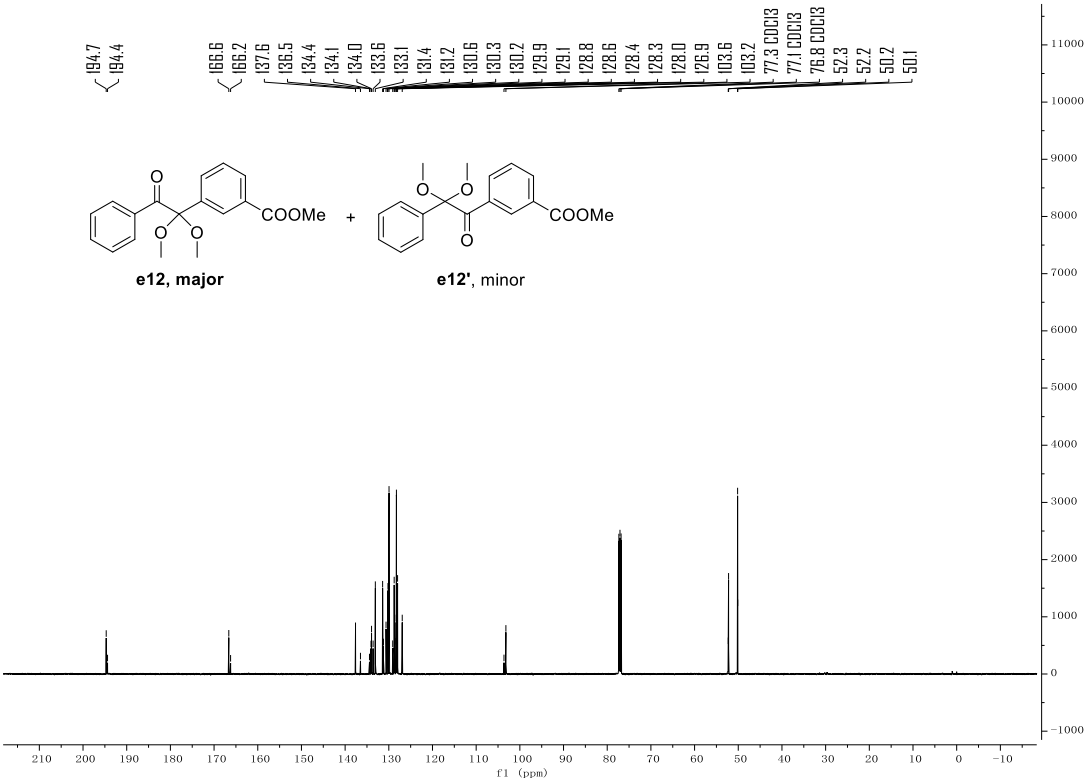
2-(3-chlorophenyl)-2,2-dimethoxy-1-phenylethan-1-one (**e11**, **major isomer**)



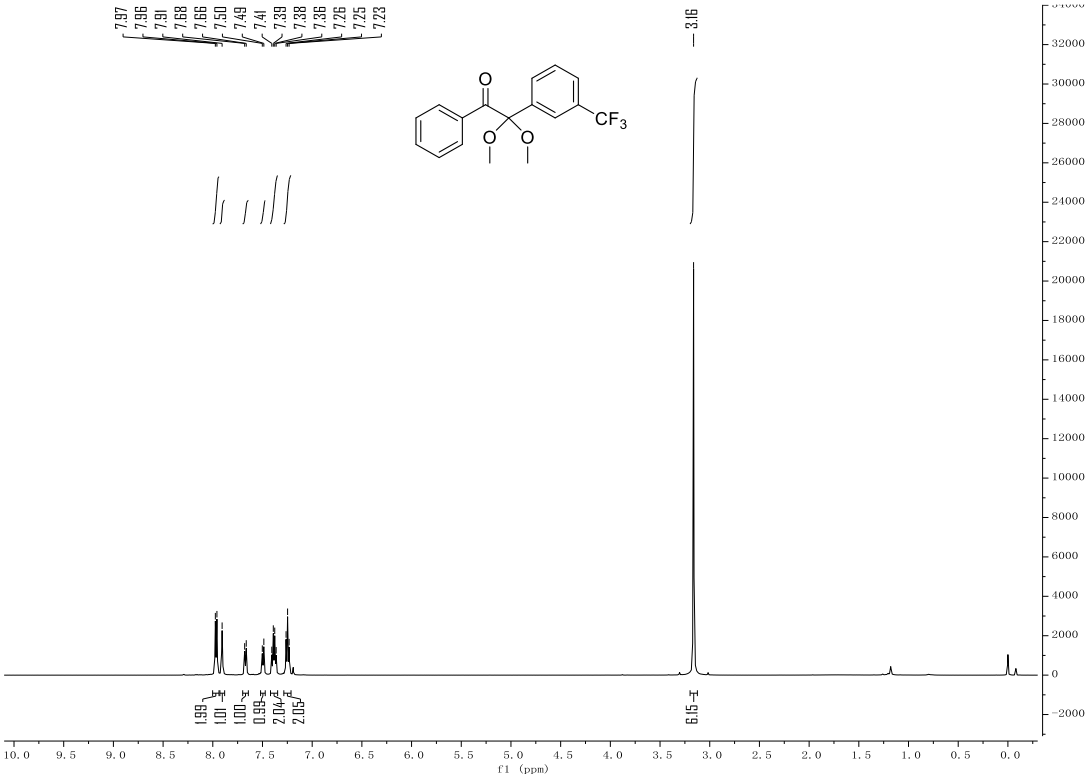



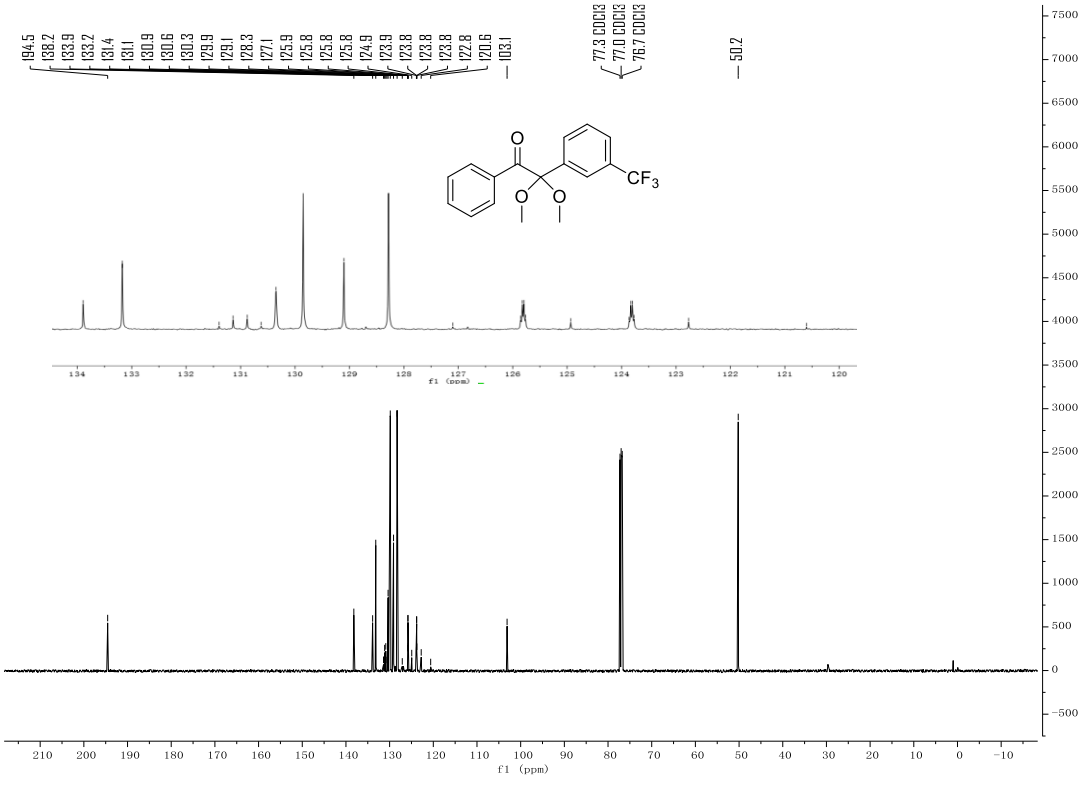
methyl 3-(1,1-dimethoxy-2-oxo-2-phenylethyl)benzoate (**e12**, **major isomer**) and methyl 3-(2,2-dimethoxy-2-phenylacetyl)benzoate (**e12'**, minor isomer): Inseparable.



2,2-dimethoxy-1-phenyl-2-(3-(trifluoromethyl)phenyl)ethan-1-one (**e13**)

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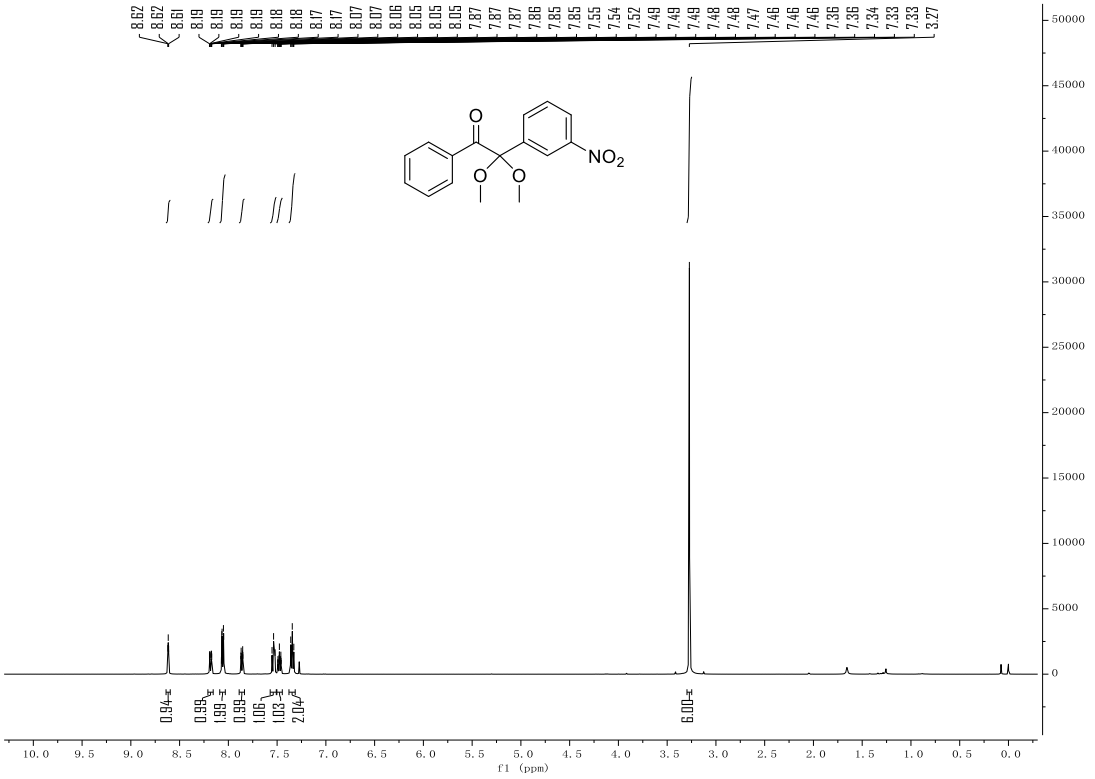
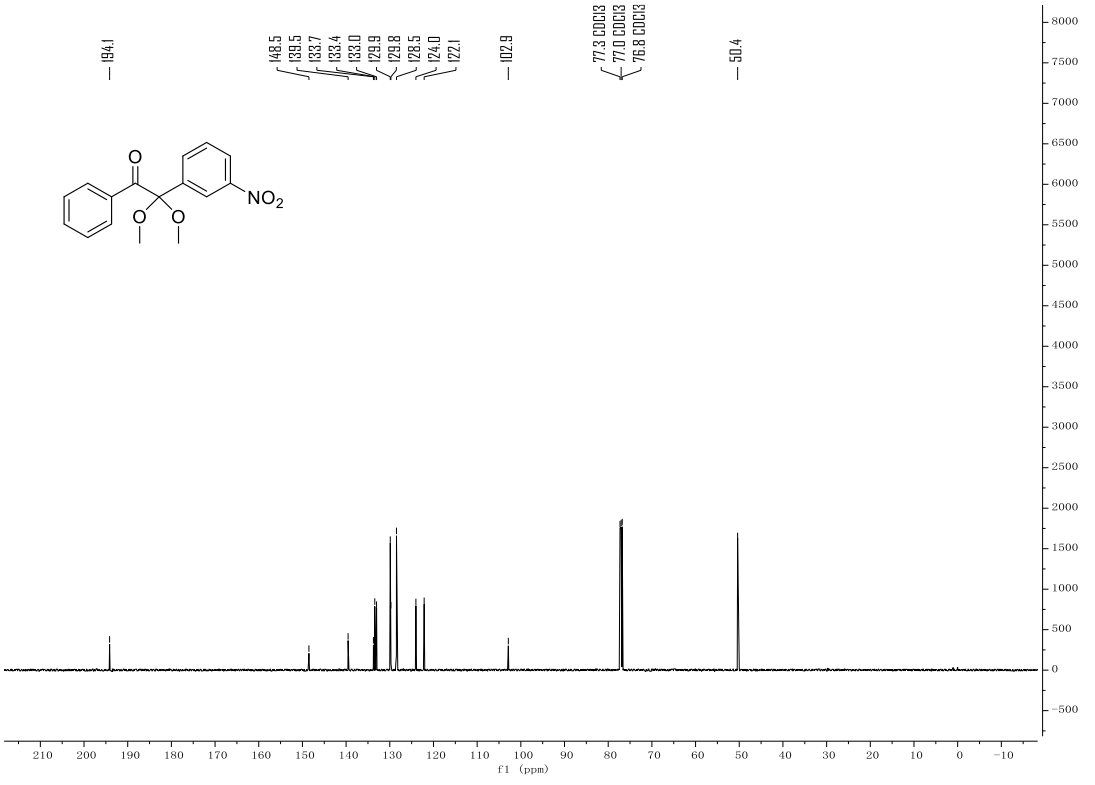
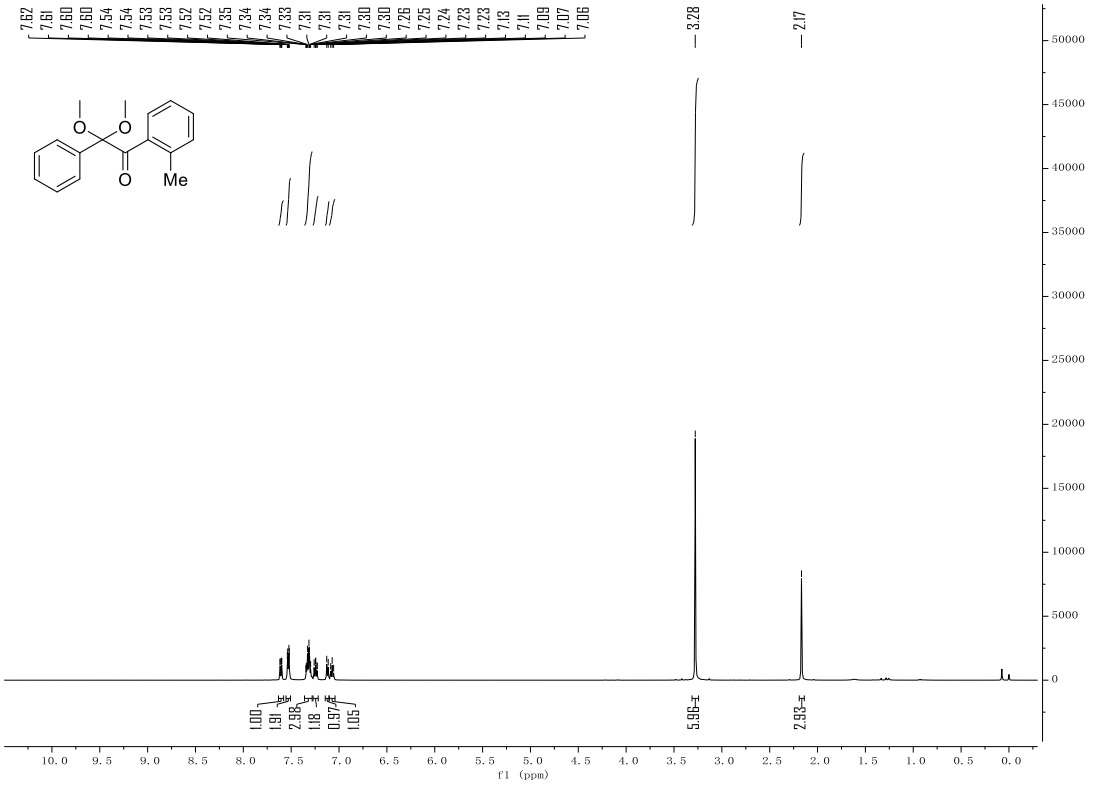
f1 (ppm)

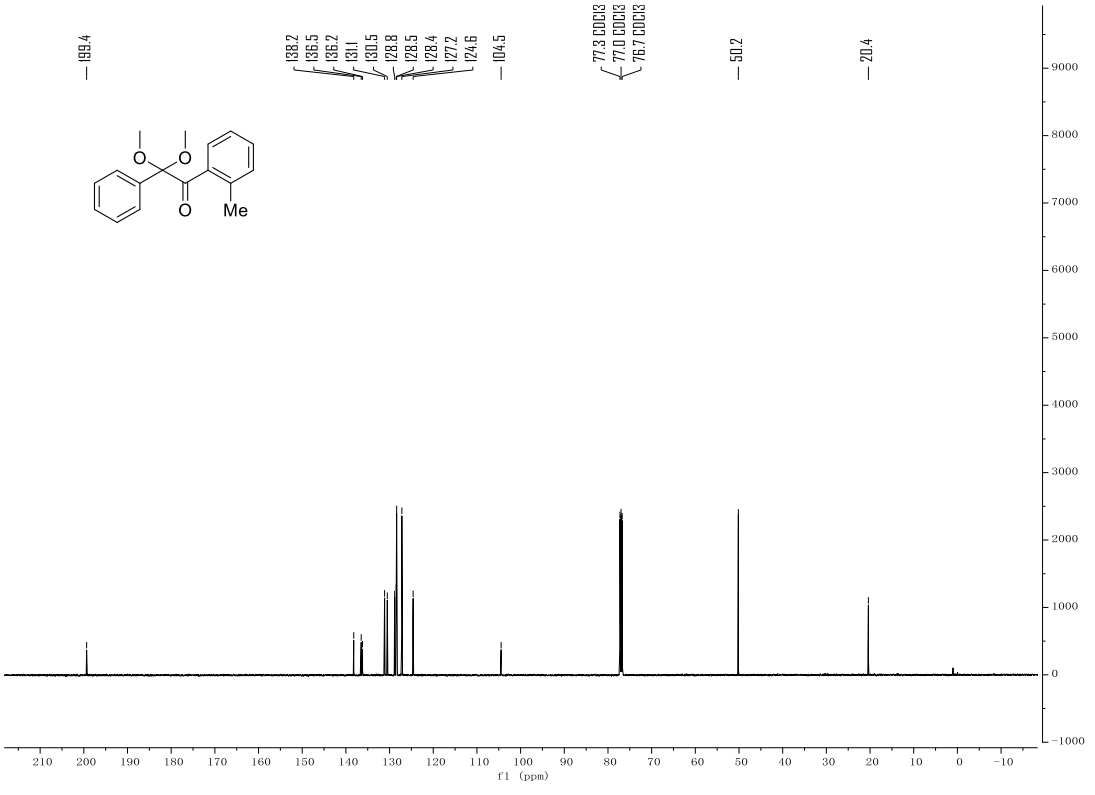
2,2-dimethoxy-2-(3-nitrophenyl)-1-phenylethan-1-one (**e14**)



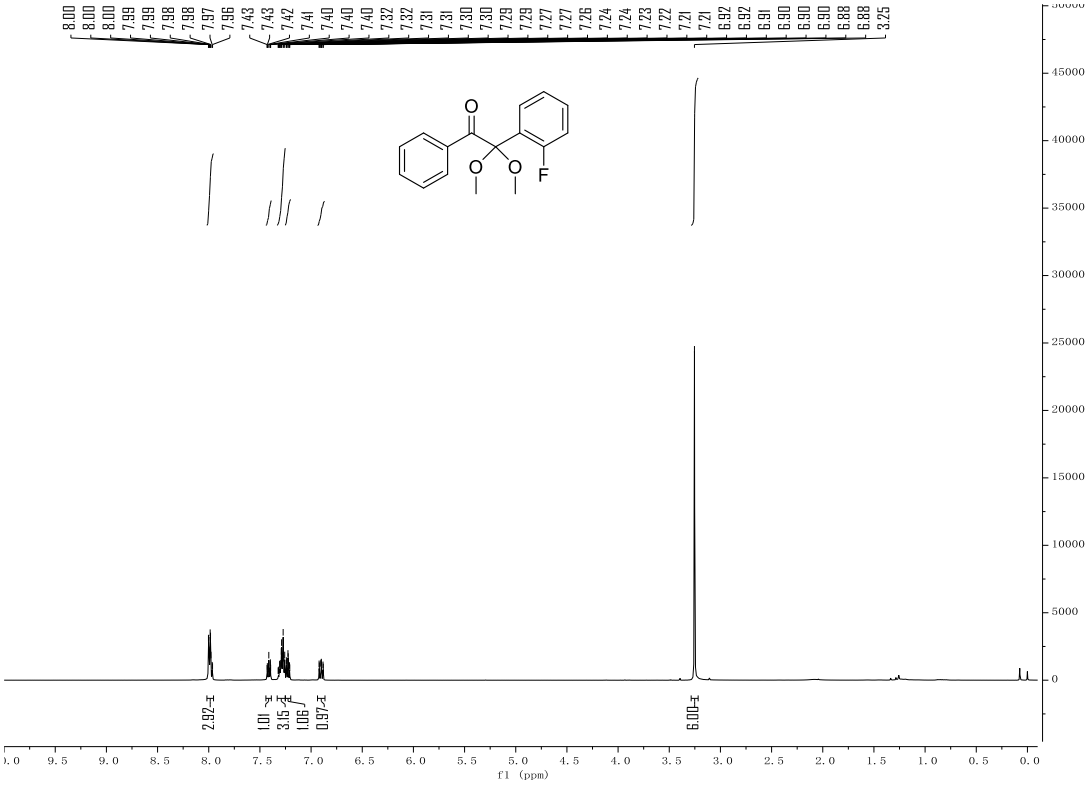



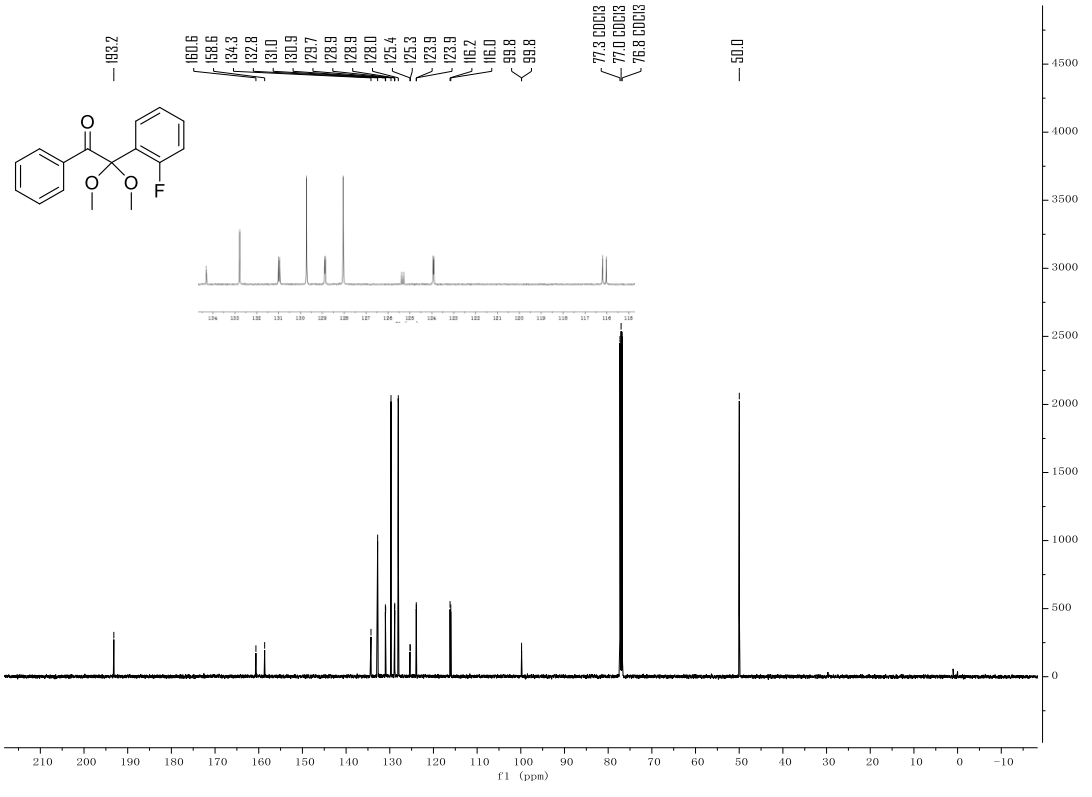
2,2-dimethoxy-2-phenyl-1-(o-tolyl)ethan-1-one (**e15'**, **major isomer**)

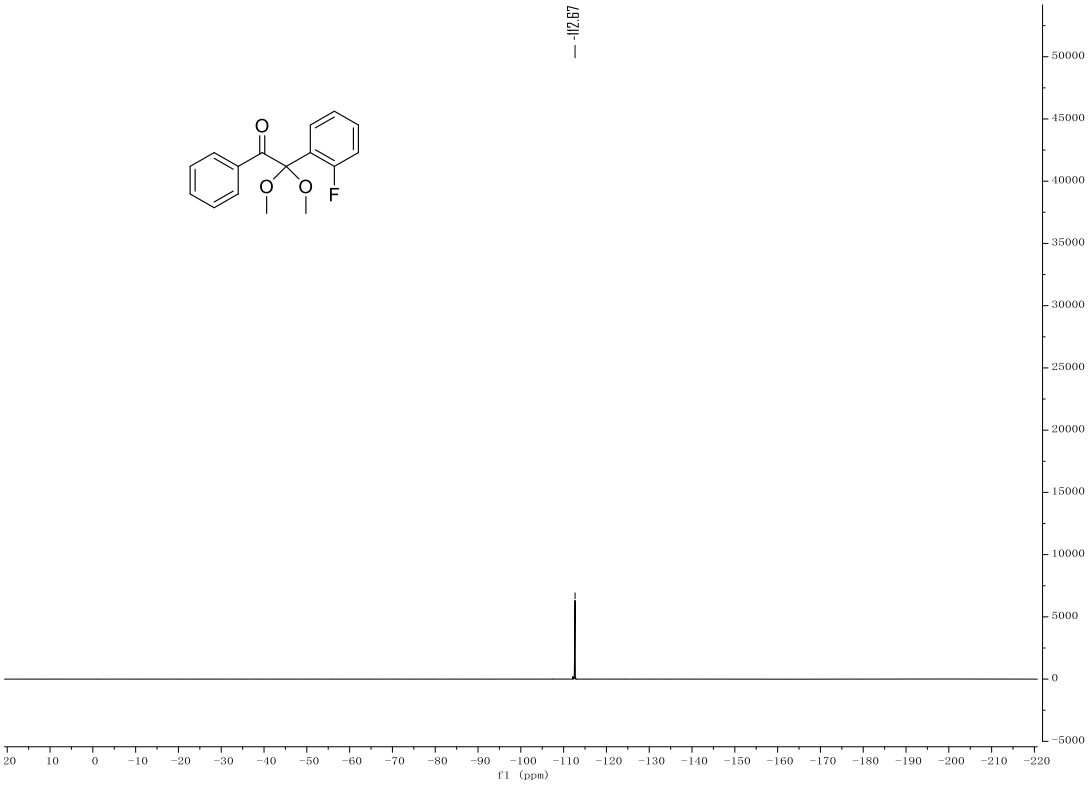


2-(2-fluorophenyl)-2,2-dimethoxy-1-phenylethan-1-one (**e16**, **major isomer**)

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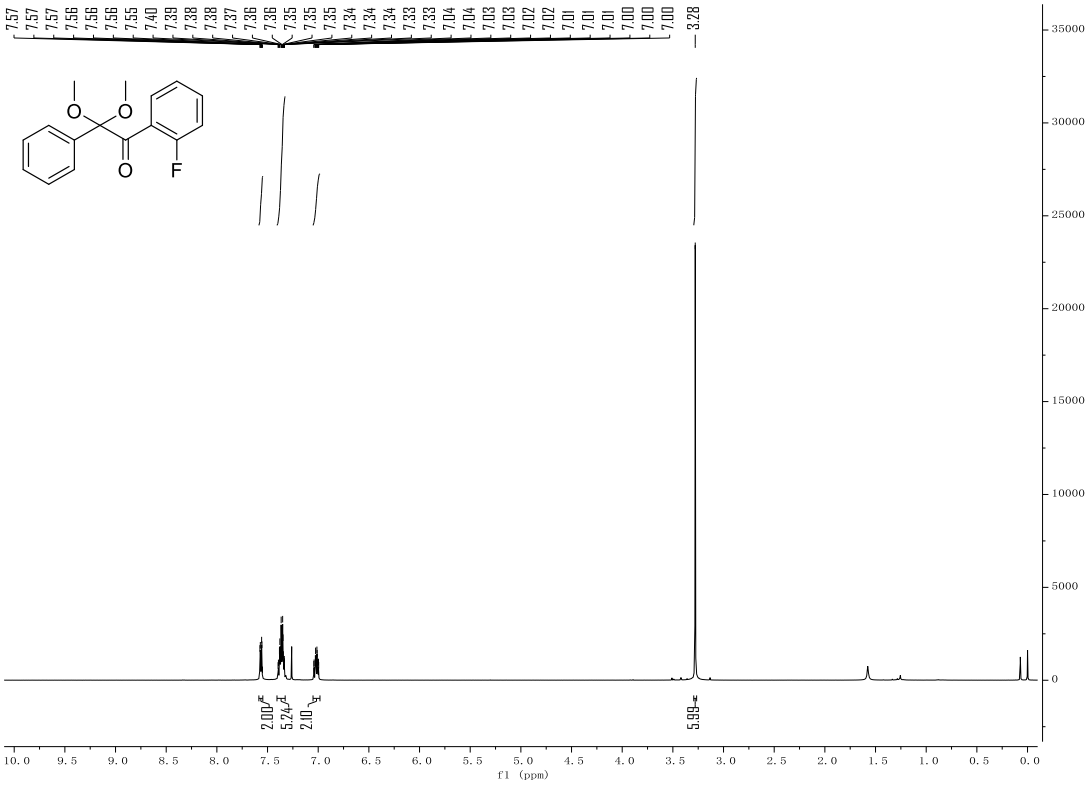
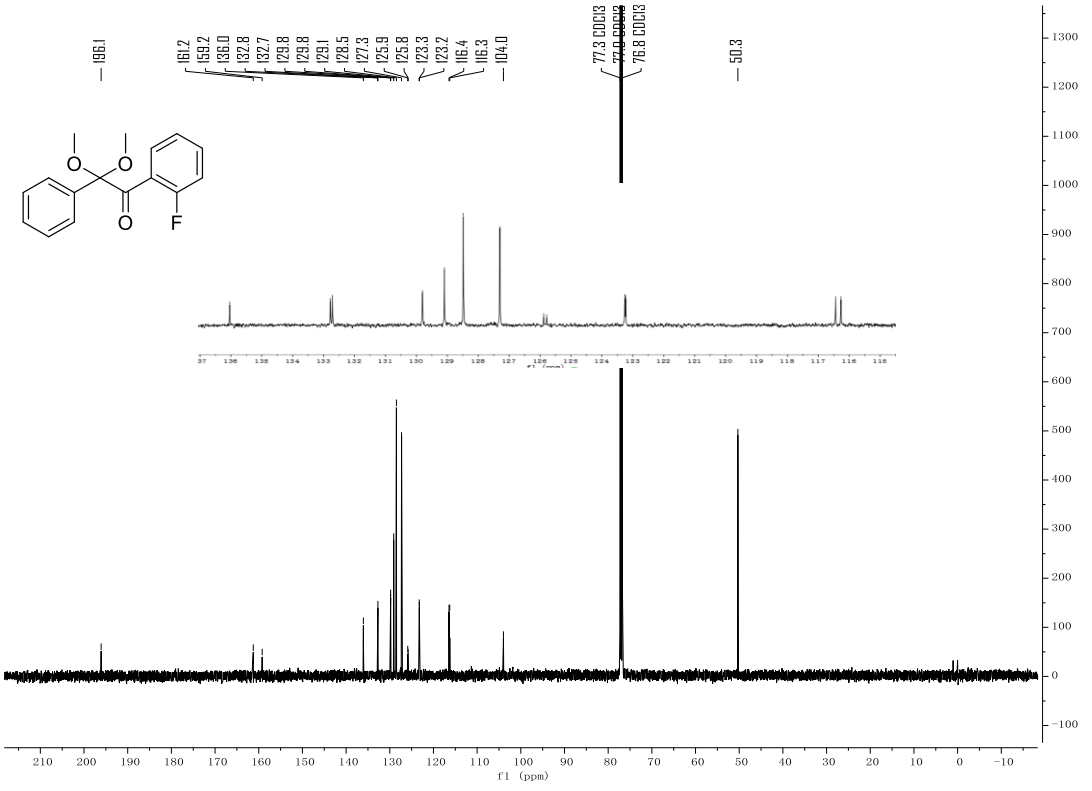
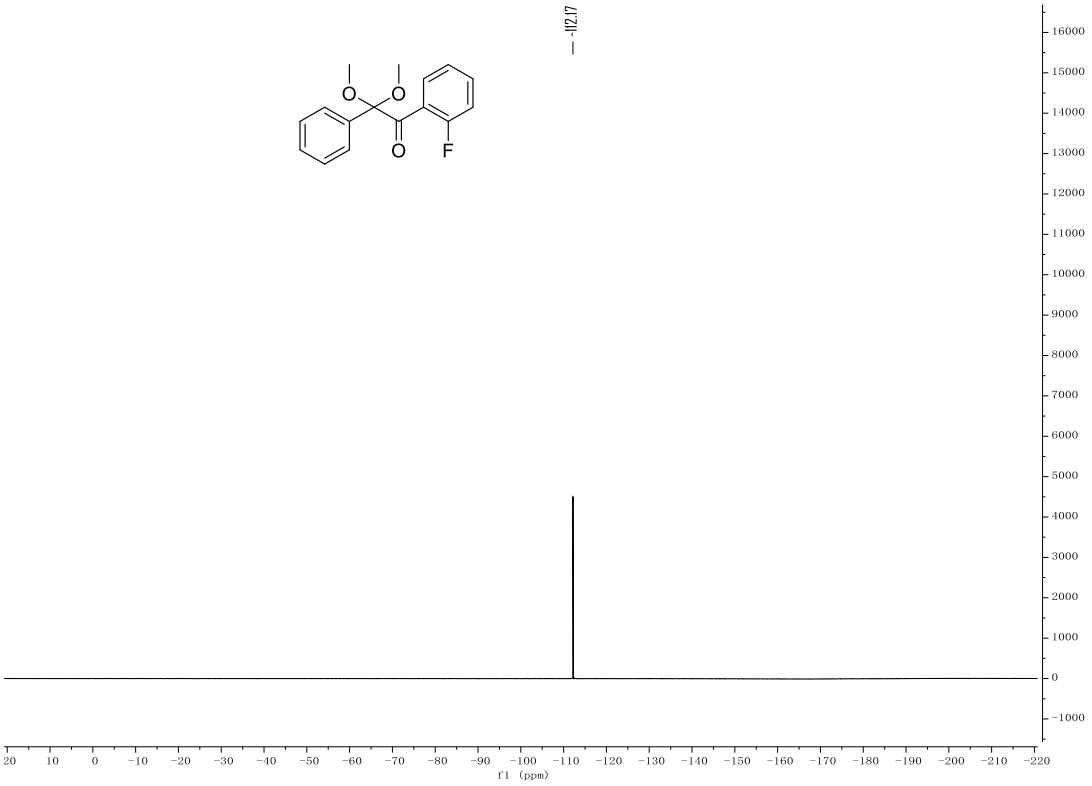
f1 (ppm)

1-(2-fluorophenyl)-2,2-dimethoxy-2-phenylethan-1-one (**e16'**, minor isomer)

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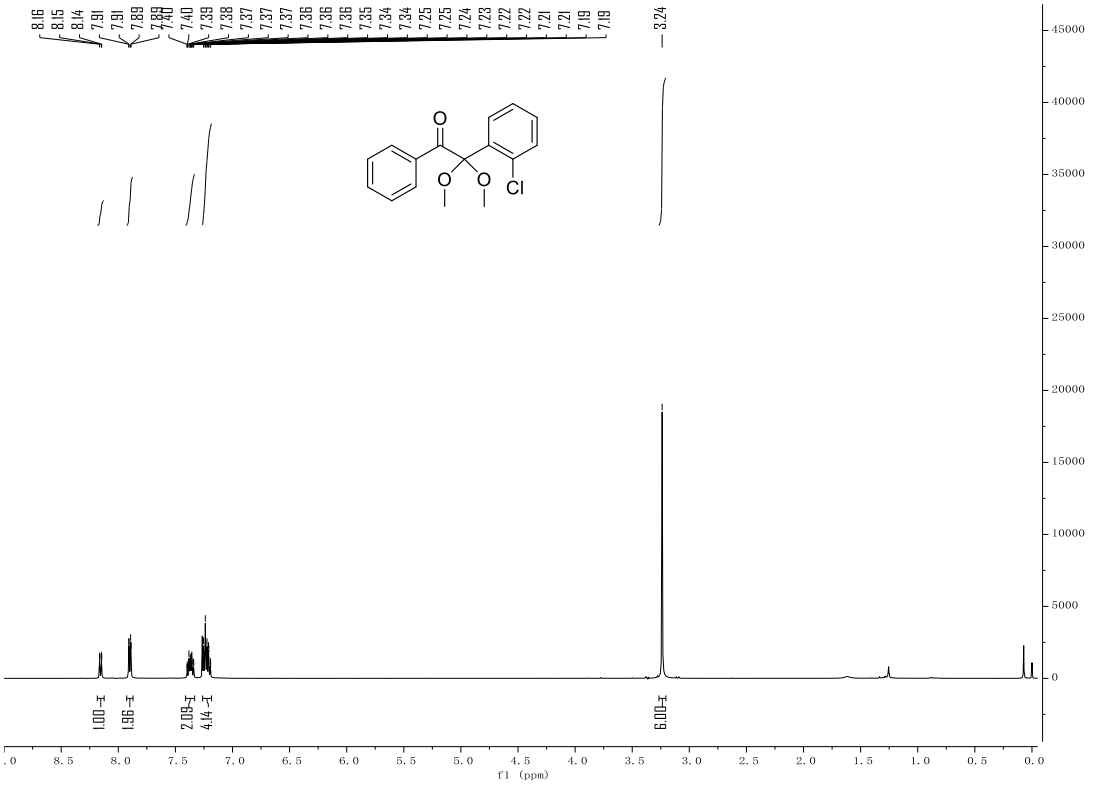
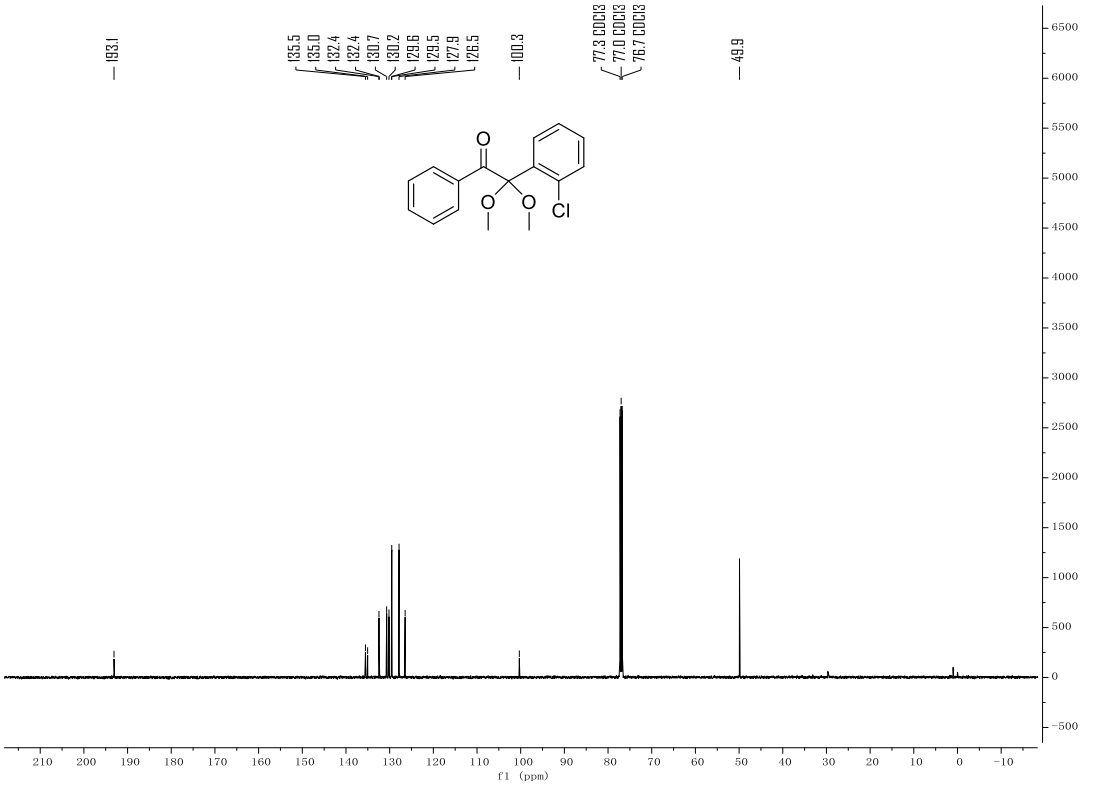
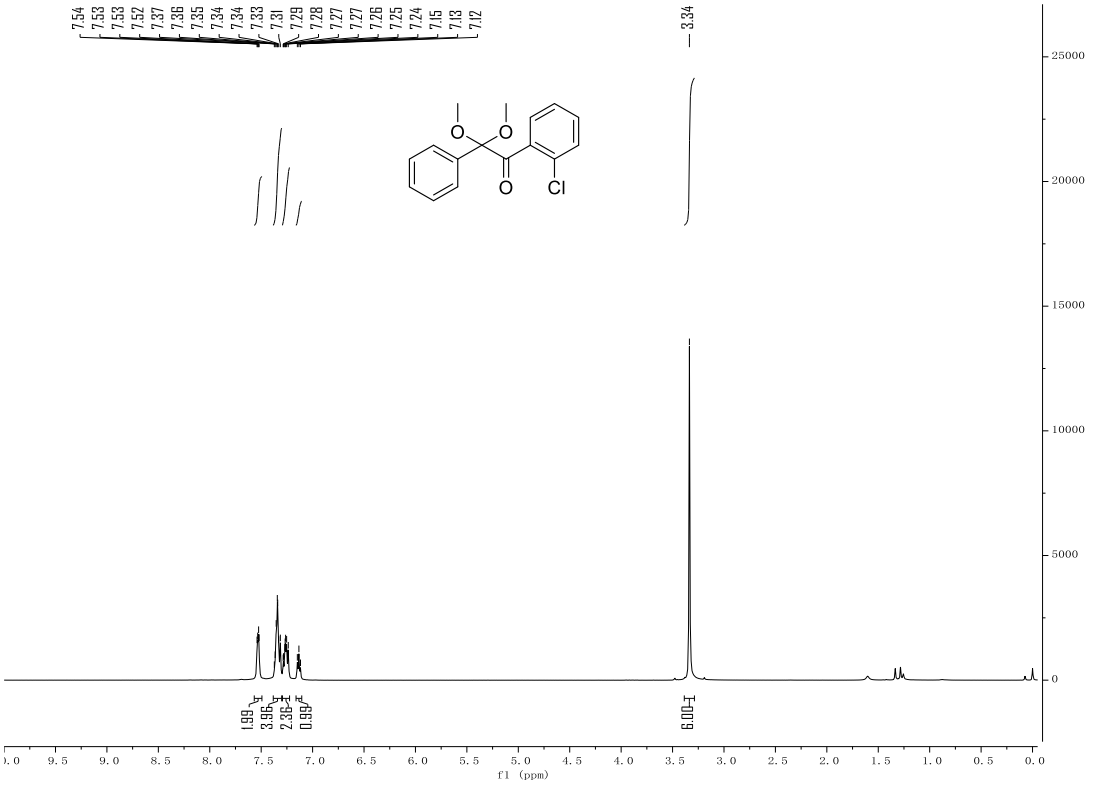
f1 (ppm)

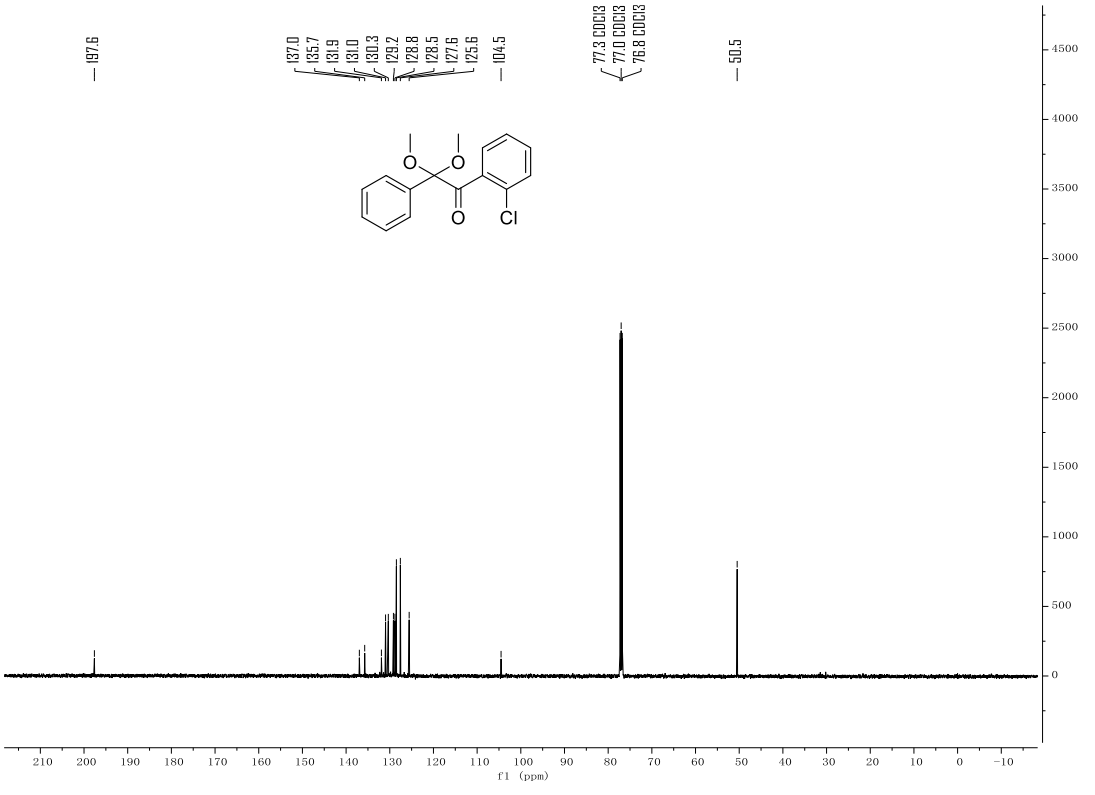
1-(2-chlorophenyl)-2,2-dimethoxy-2-phenylethan-1-one (**e17**, **major isomer**)



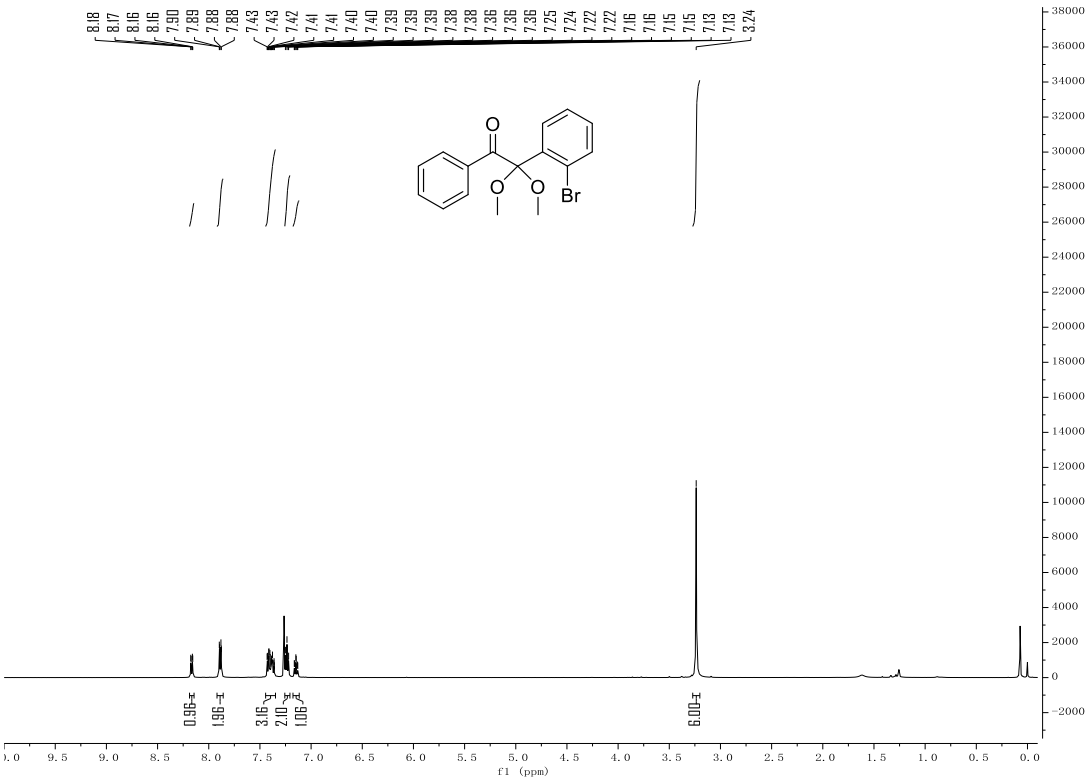



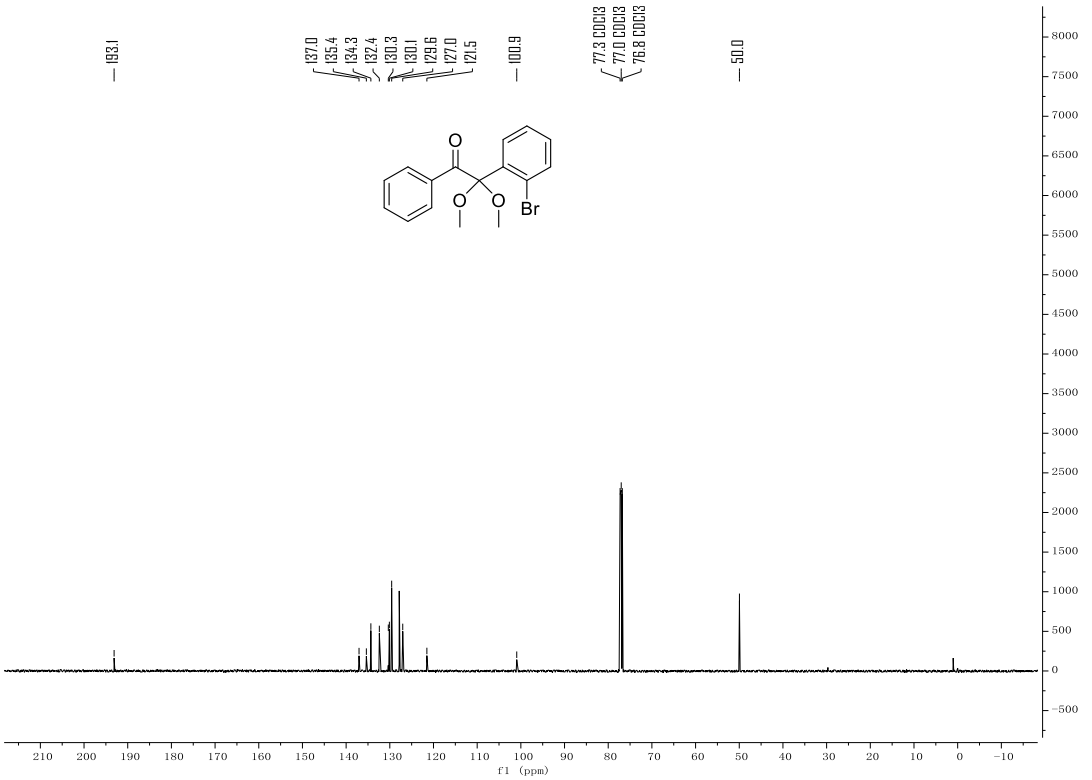
1-(2-chlorophenyl)-2,2-dimethoxy-2-phenylethan-1-one (**e17'**, minor isomer)



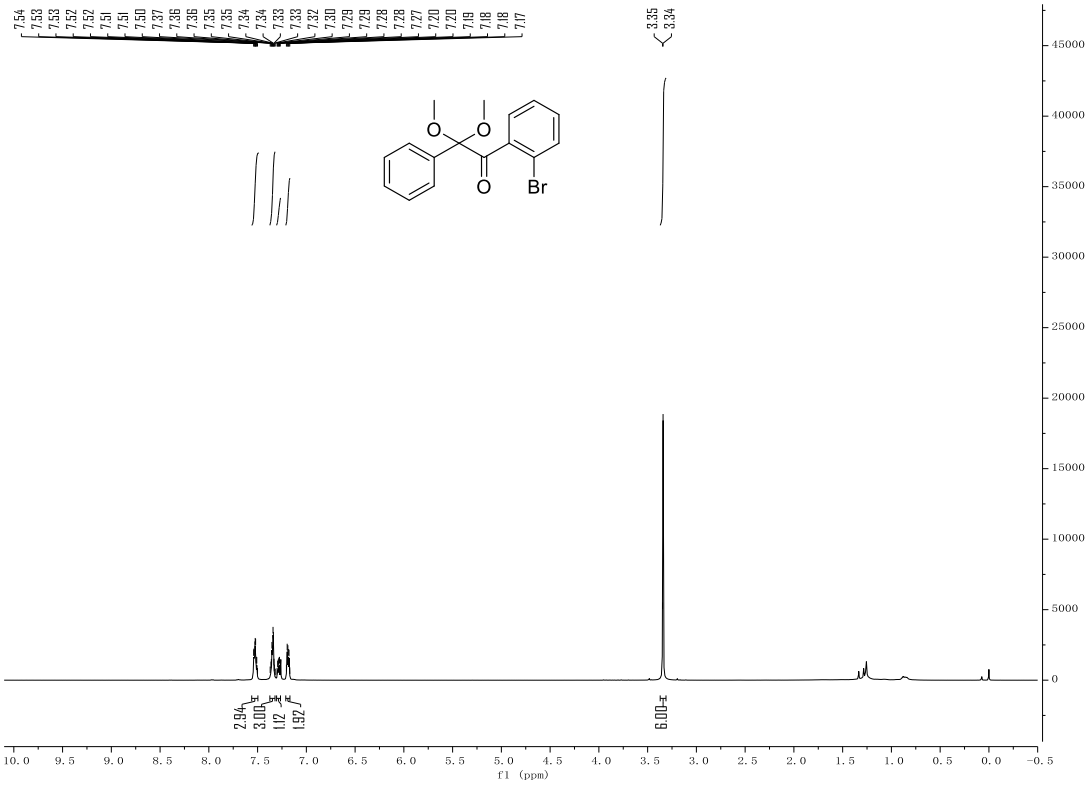



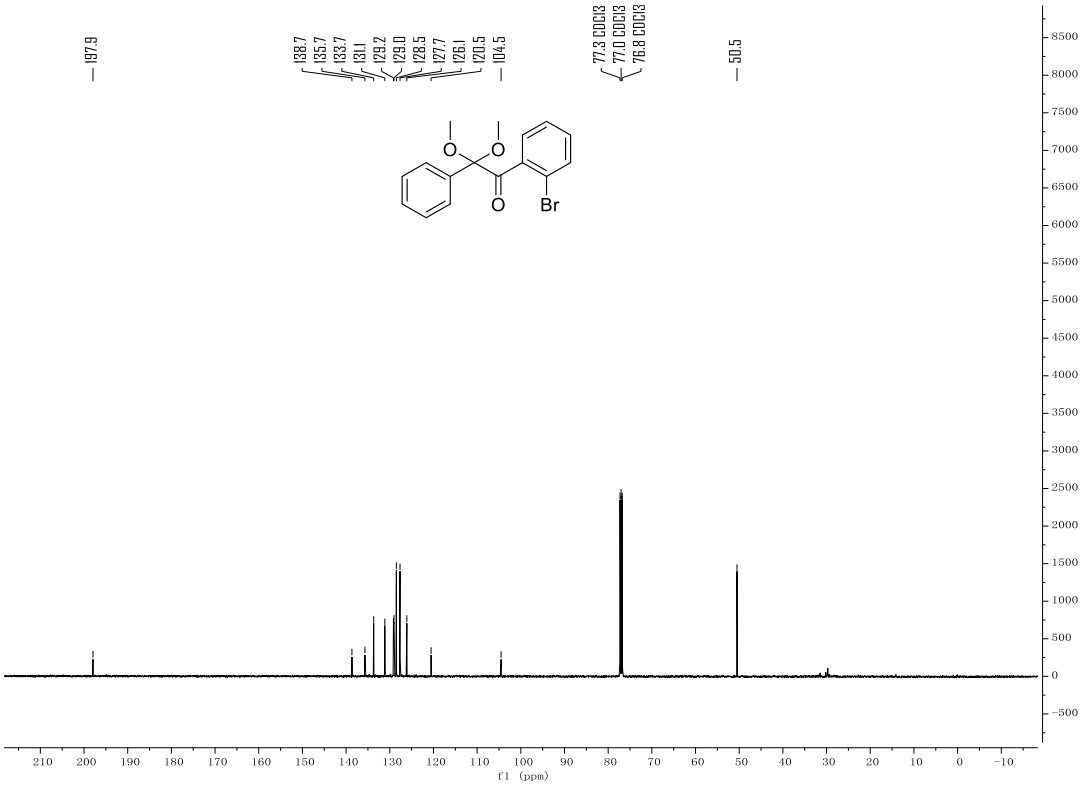
1-(2-bromophenyl)-2,2-dimethoxy-2-phenylethan-1-one (**e18**, **major isomer**)



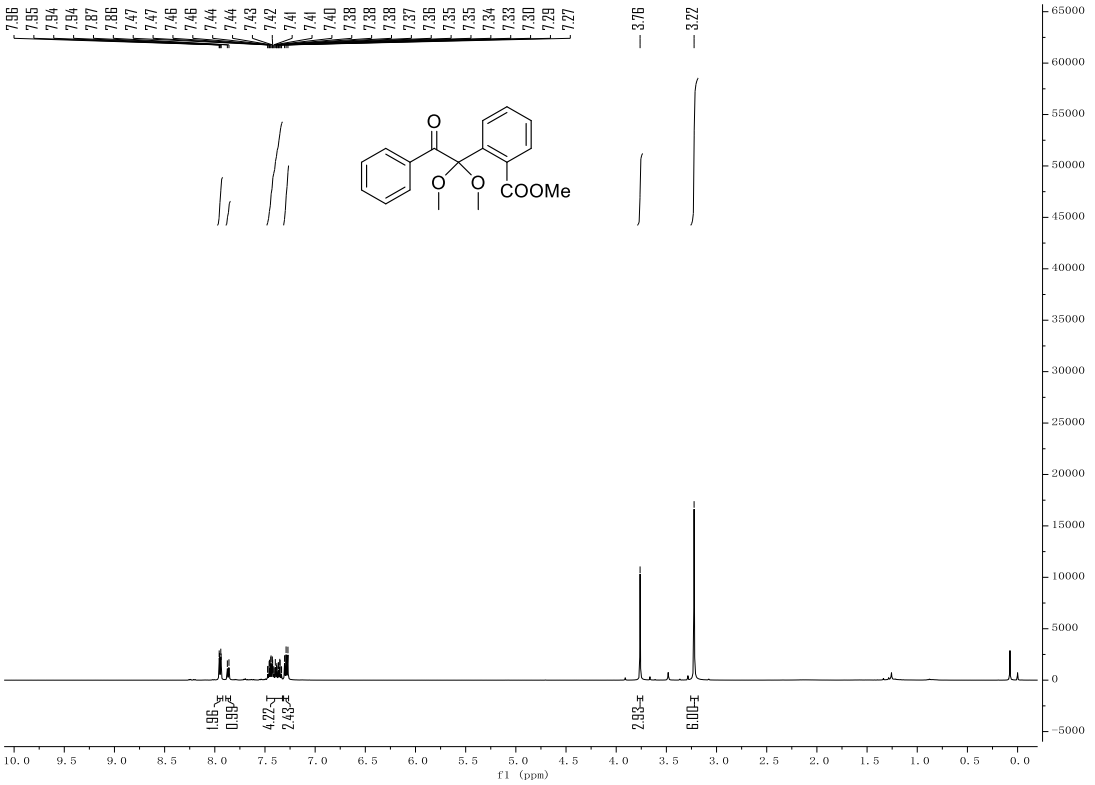



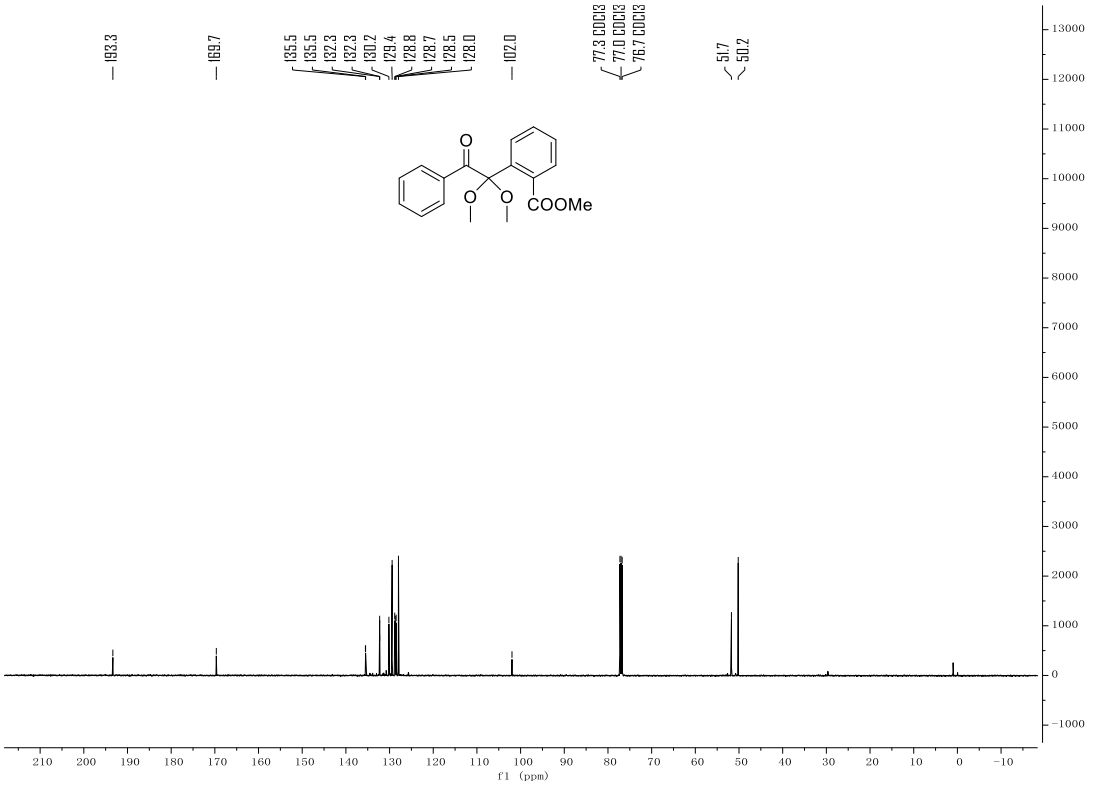
1-(2-bromophenyl)-2,2-dimethoxy-2-phenylethan-1-one (**e18'**, minor isomer)



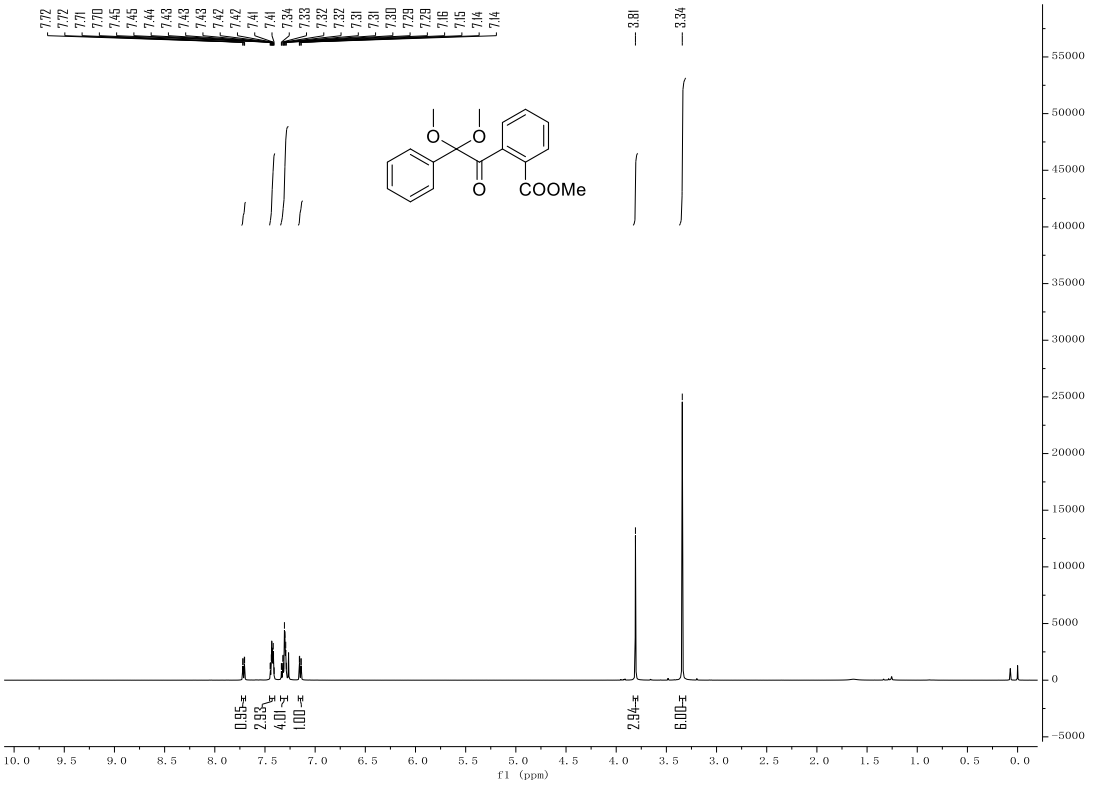



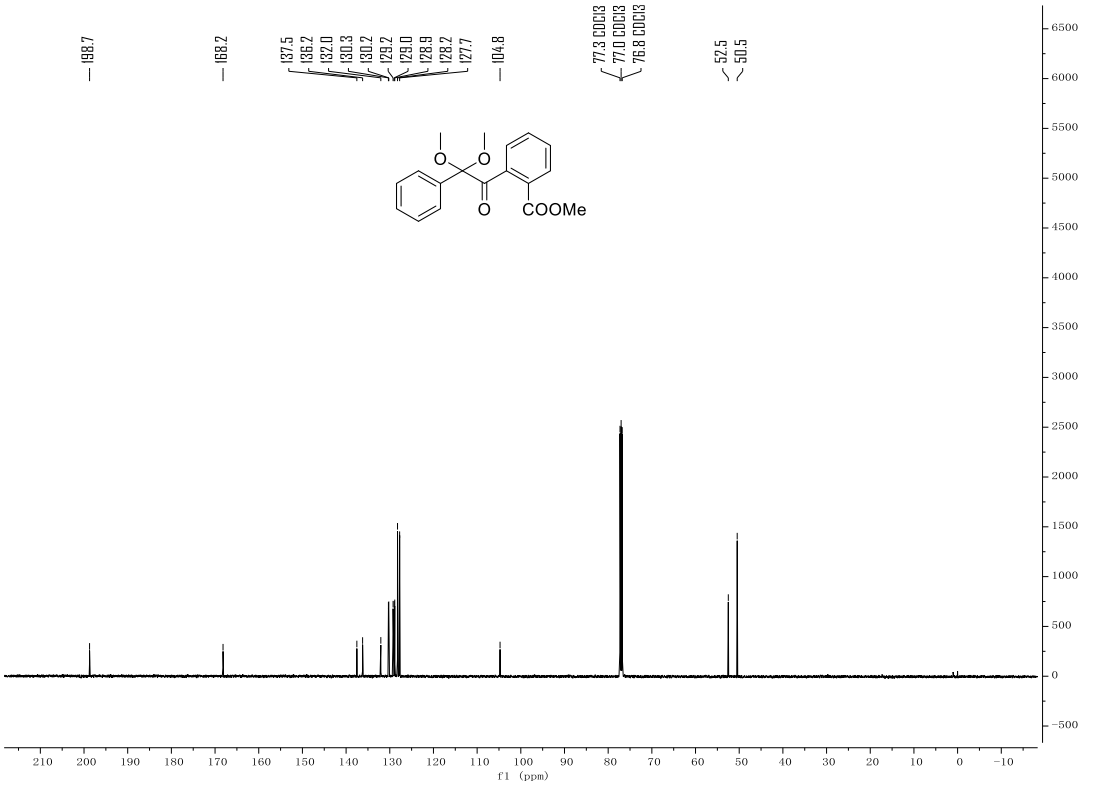
methyl 2-(1,1-dimethoxy-2-oxo-2-phenylethyl)benzoate (**e19**, **major isomer**)



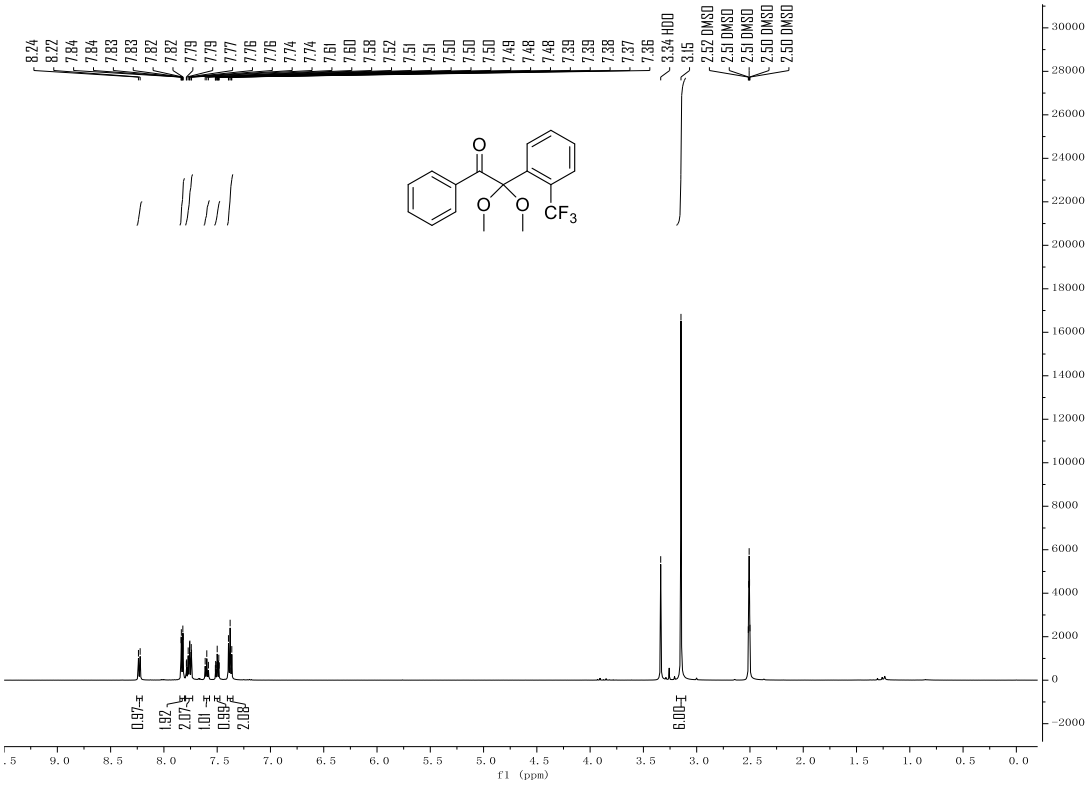



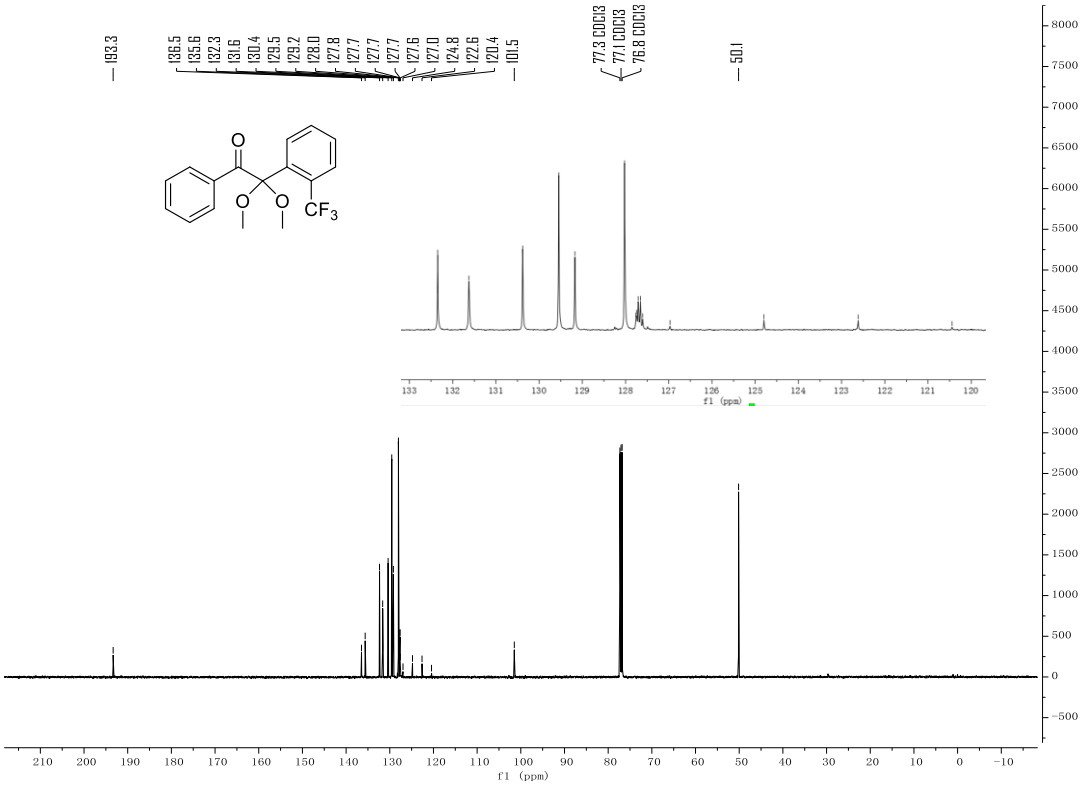
methyl 2-(2,2-dimethoxy-2-phenylacetyl)benzoate (**e19'**, minor isomer)

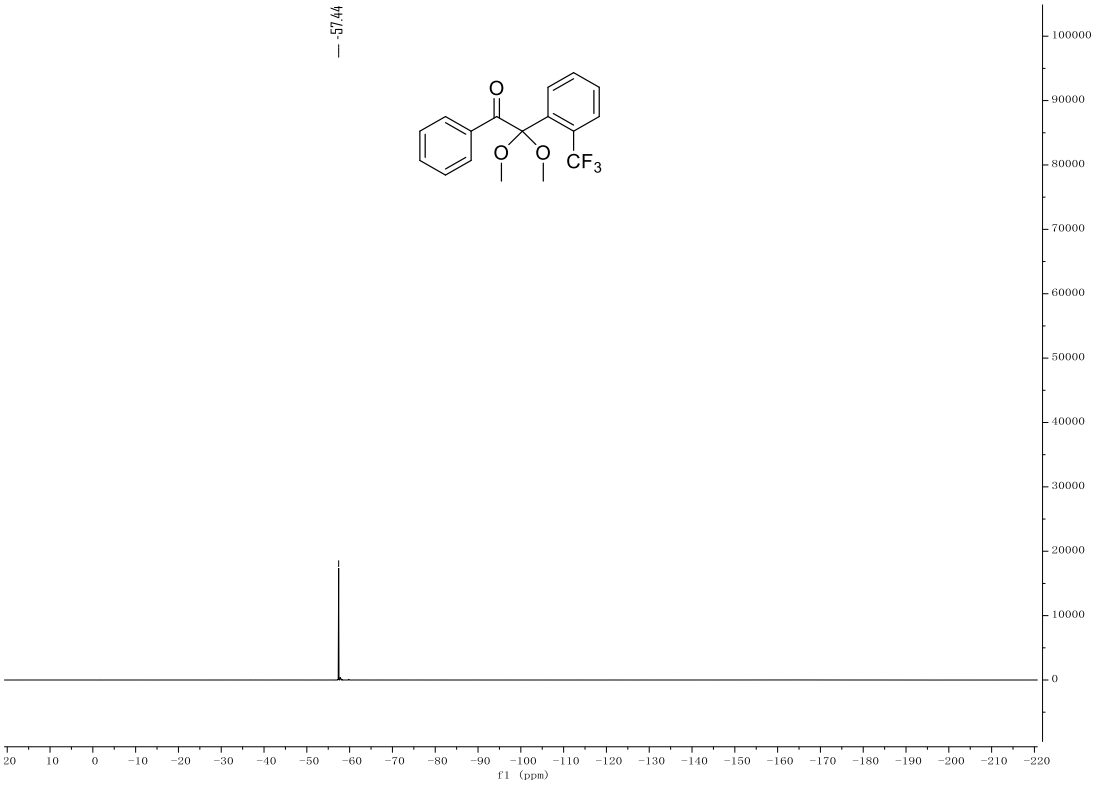


2,2-dimethoxy-2-phenyl-1-(2-(trifluoromethyl)phenyl)ethan-1-one (**e20**, **major isomer**)

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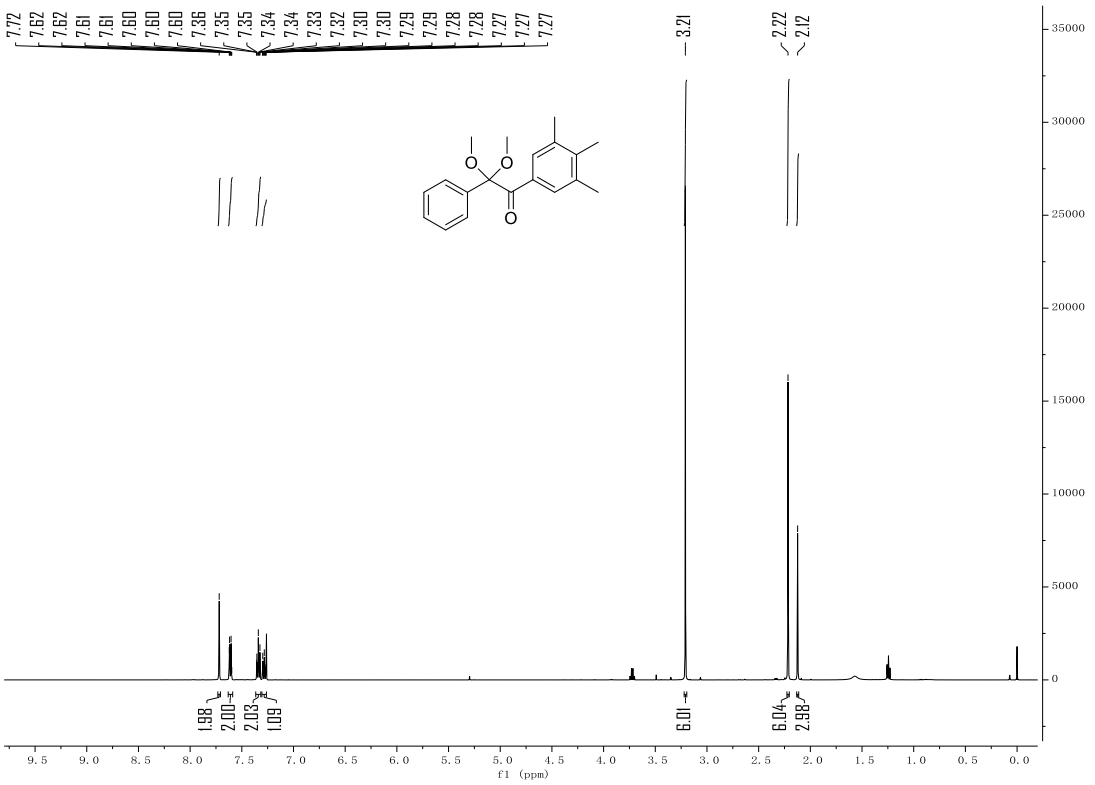
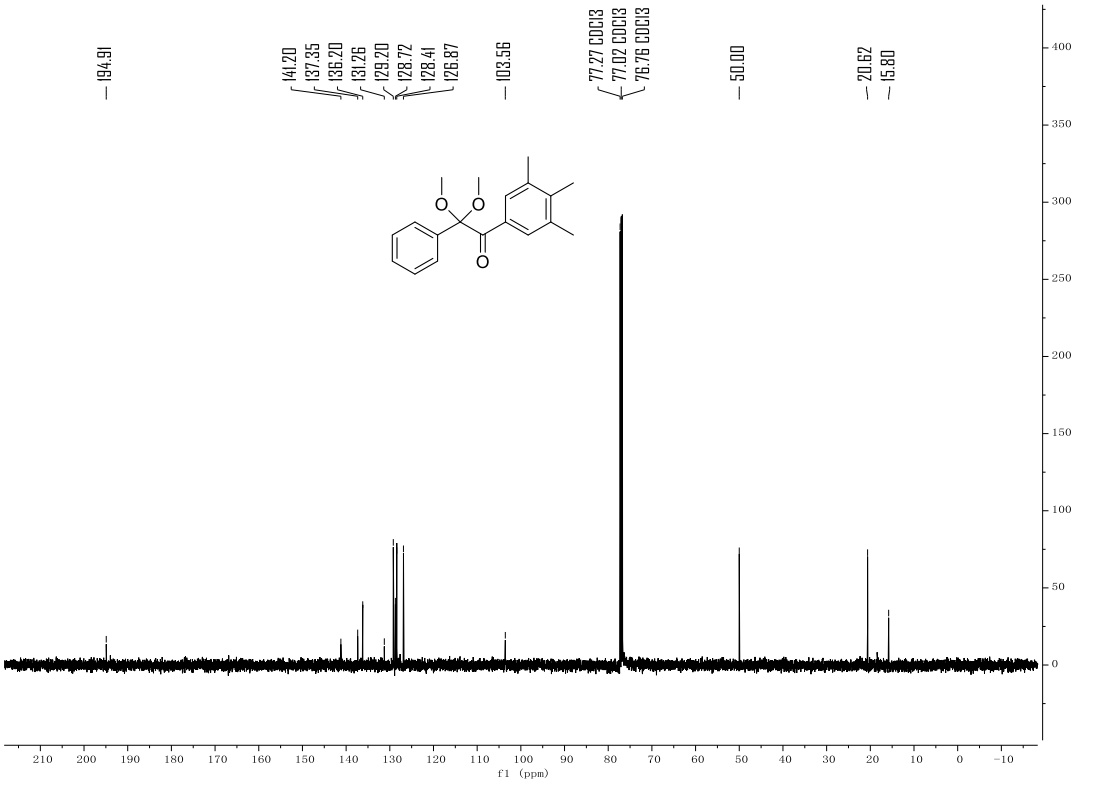
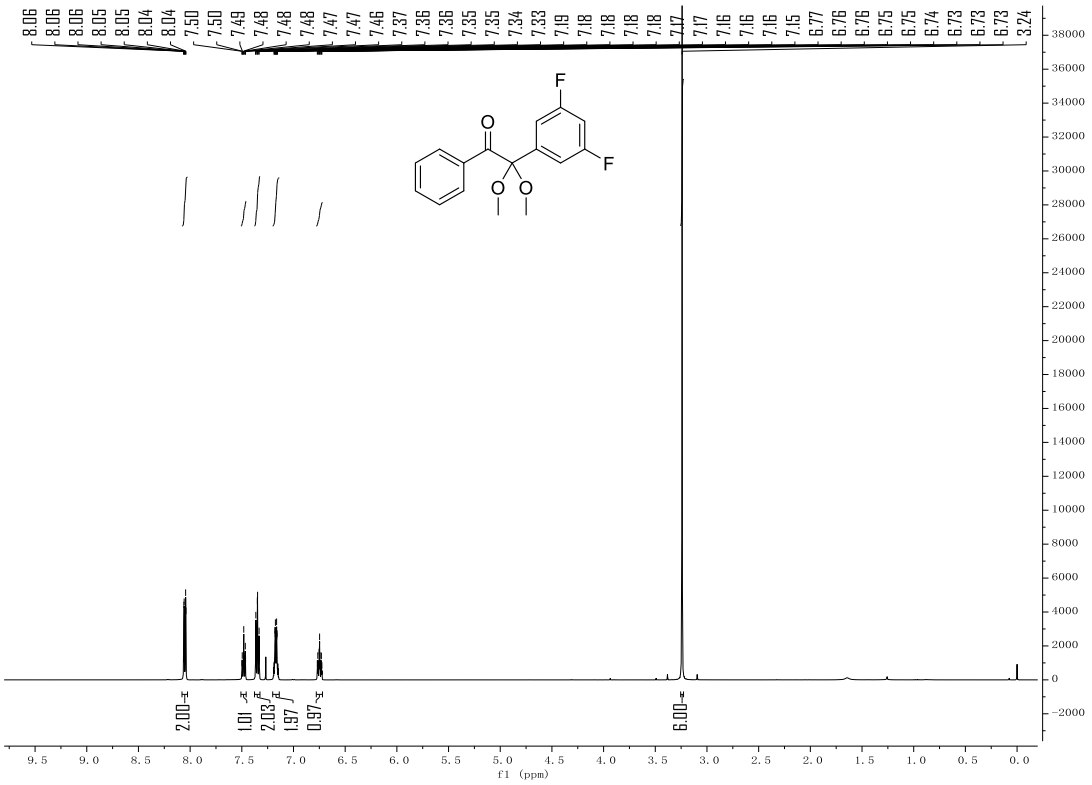
f1 (ppm)

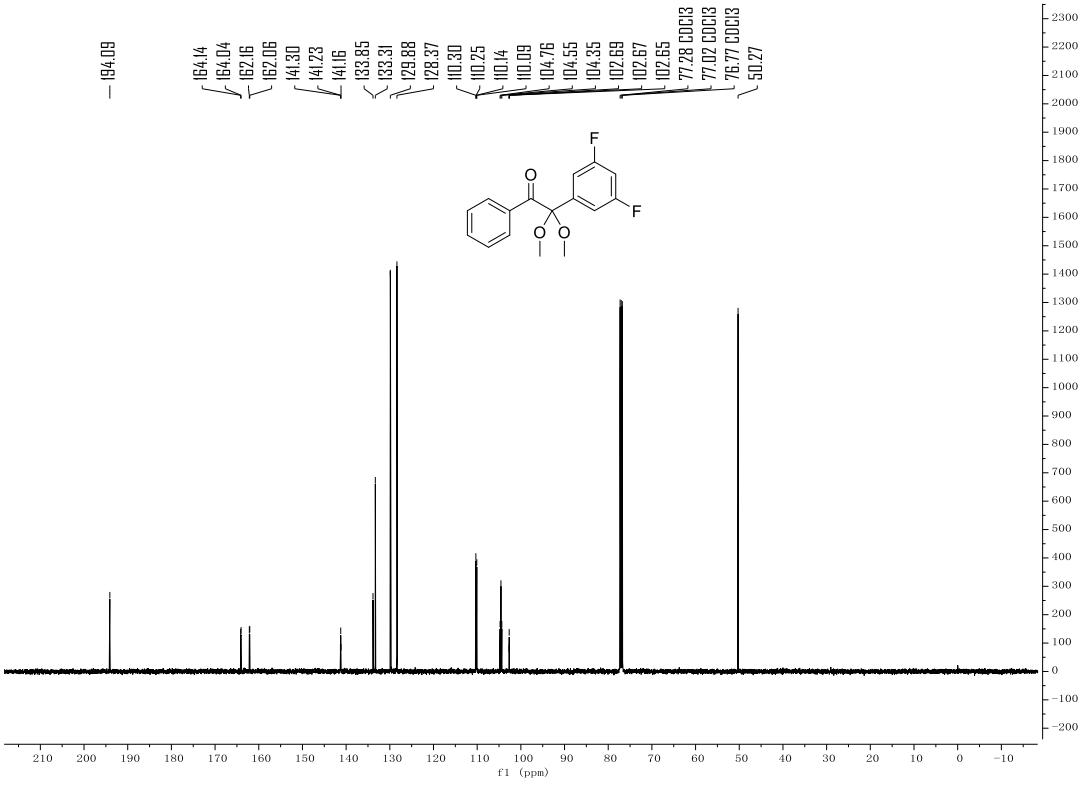
2,2-dimethoxy-2-phenyl-1-(3,4,5-trimethylphenyl)ethan-1-one (**e21', major isomer**)

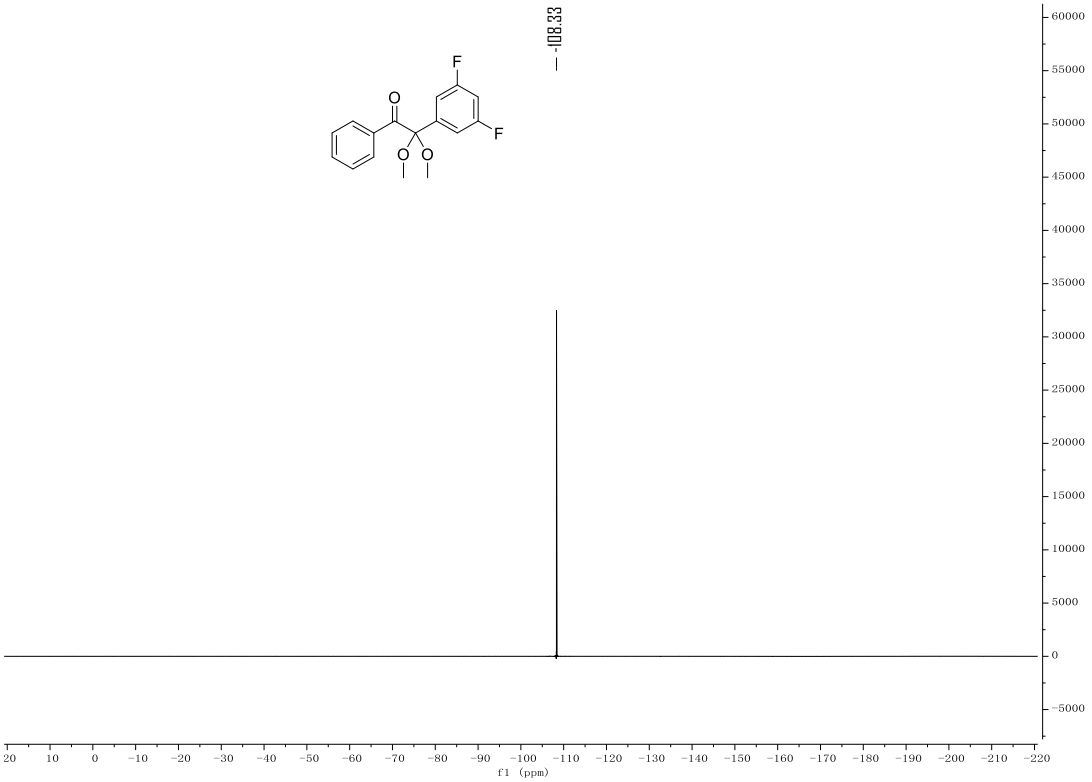


2-(3,5-difluorophenyl)-2,2-dimethoxy-1-phenylethan-1-one (**e22, major isomer**)

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F
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F
O
O
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45000
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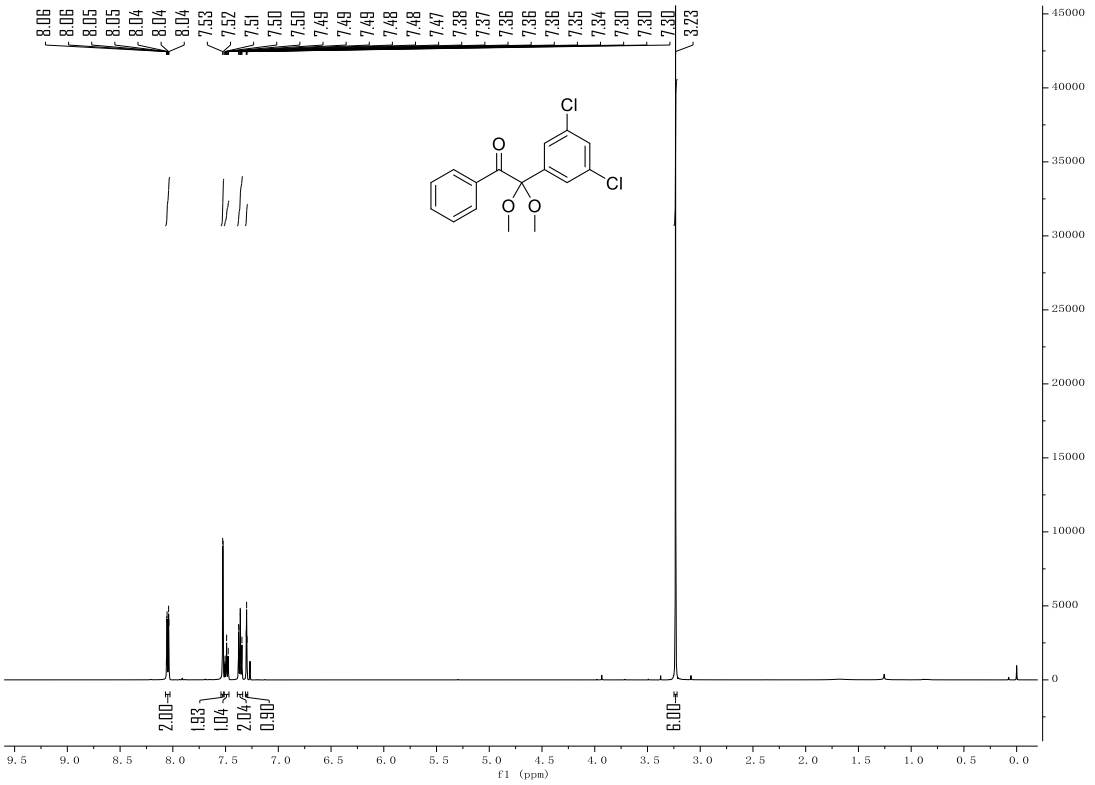
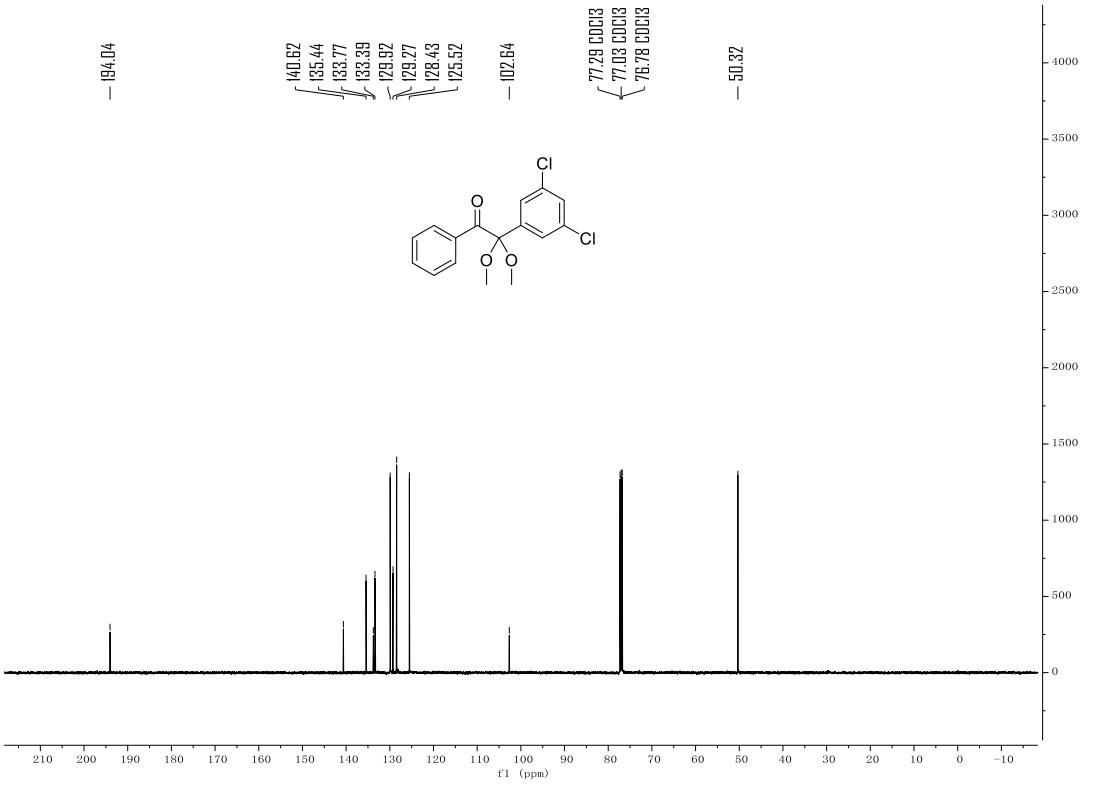
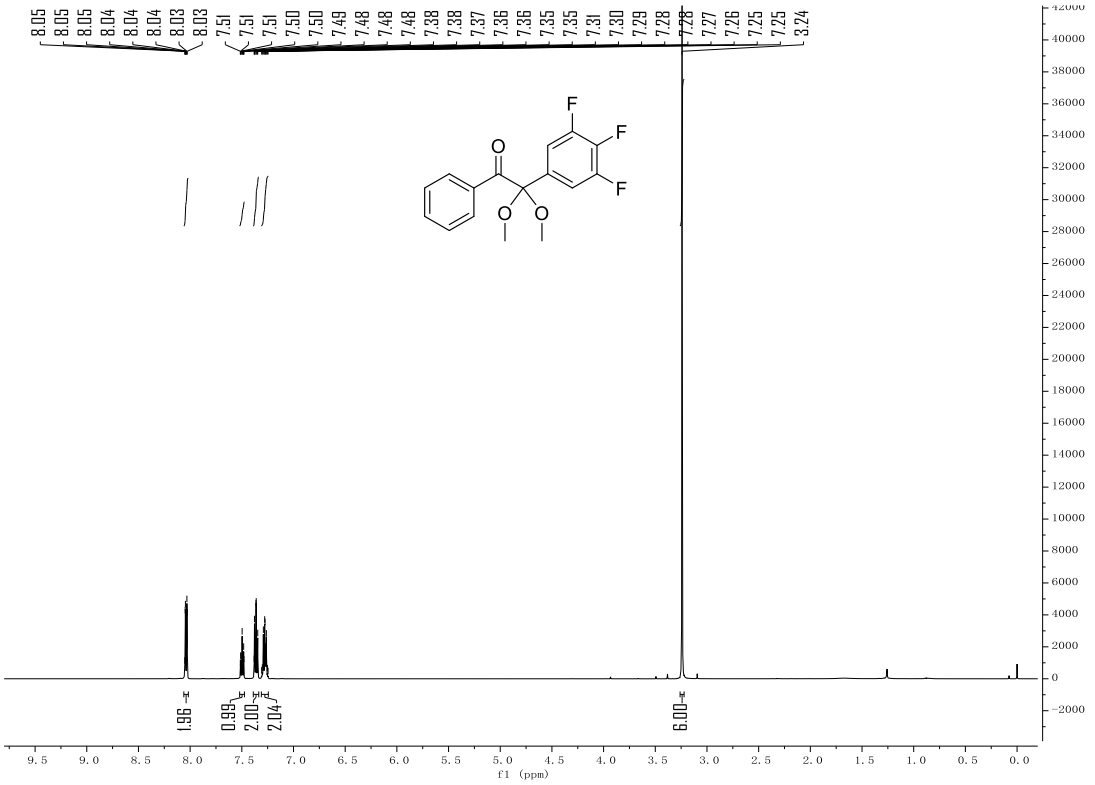
30000
25000
20000
15000
10000
5000
0
-5000
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)

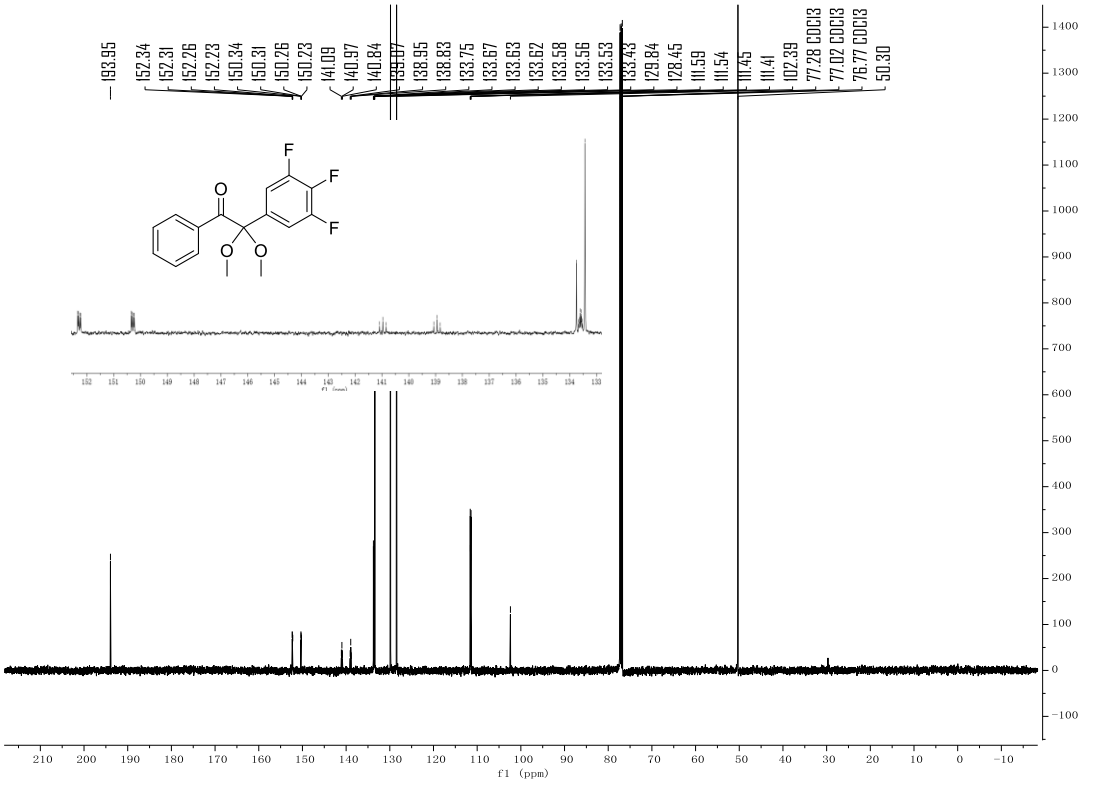
2-(3,5-dichlorophenyl)-2,2-dimethoxy-1-phenylethan-1-one (**e23, major isomer**)

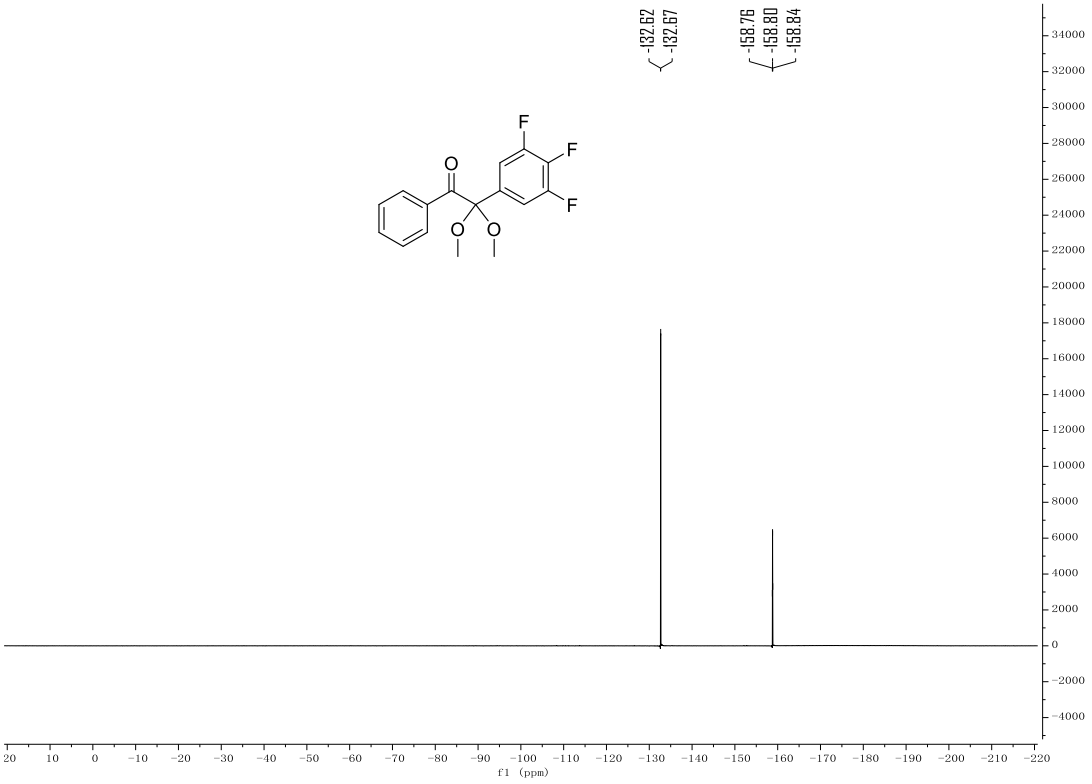


2,2-dimethoxy-1-phenyl-2-(3,4,5-trifluorophenyl)ethan-1-one (**e24, major isomer**)

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F
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F
O
O
O
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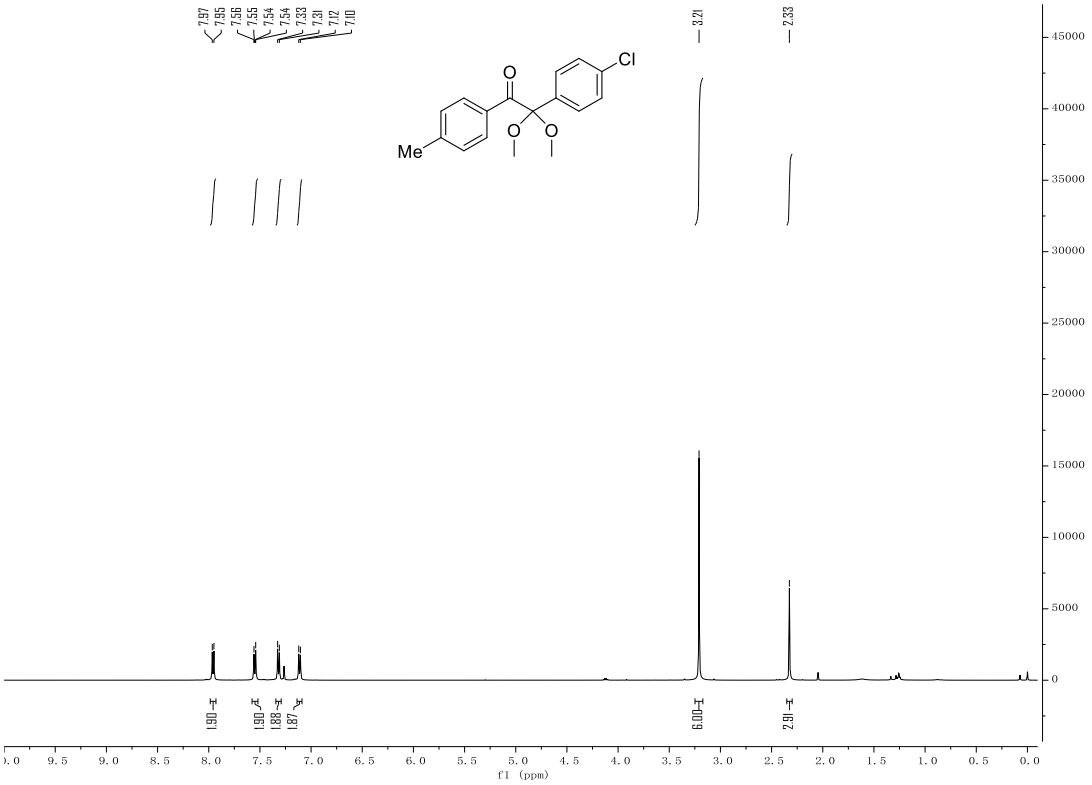
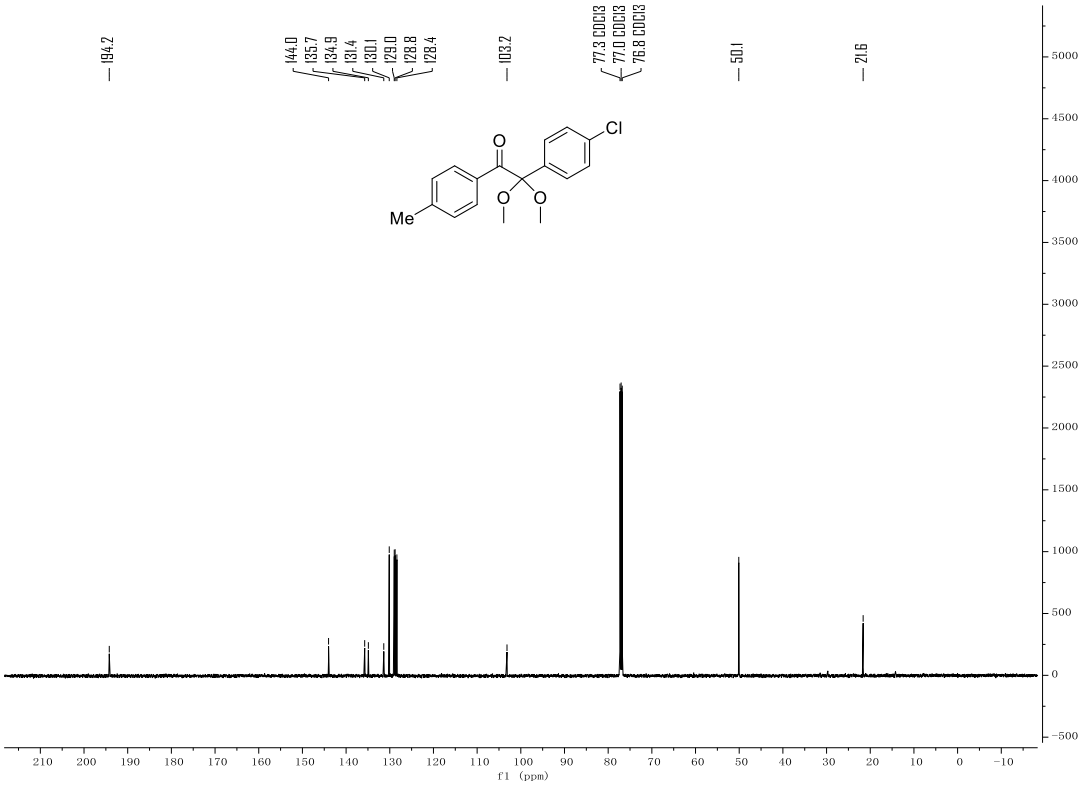
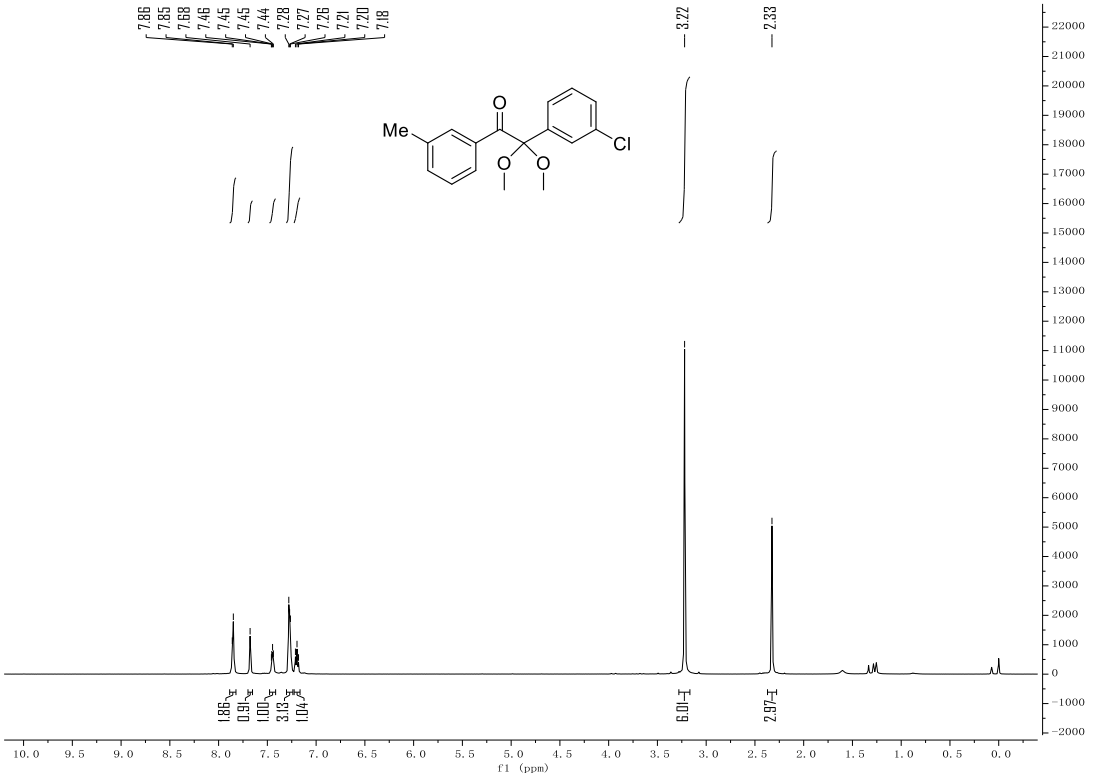
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
-4000
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)

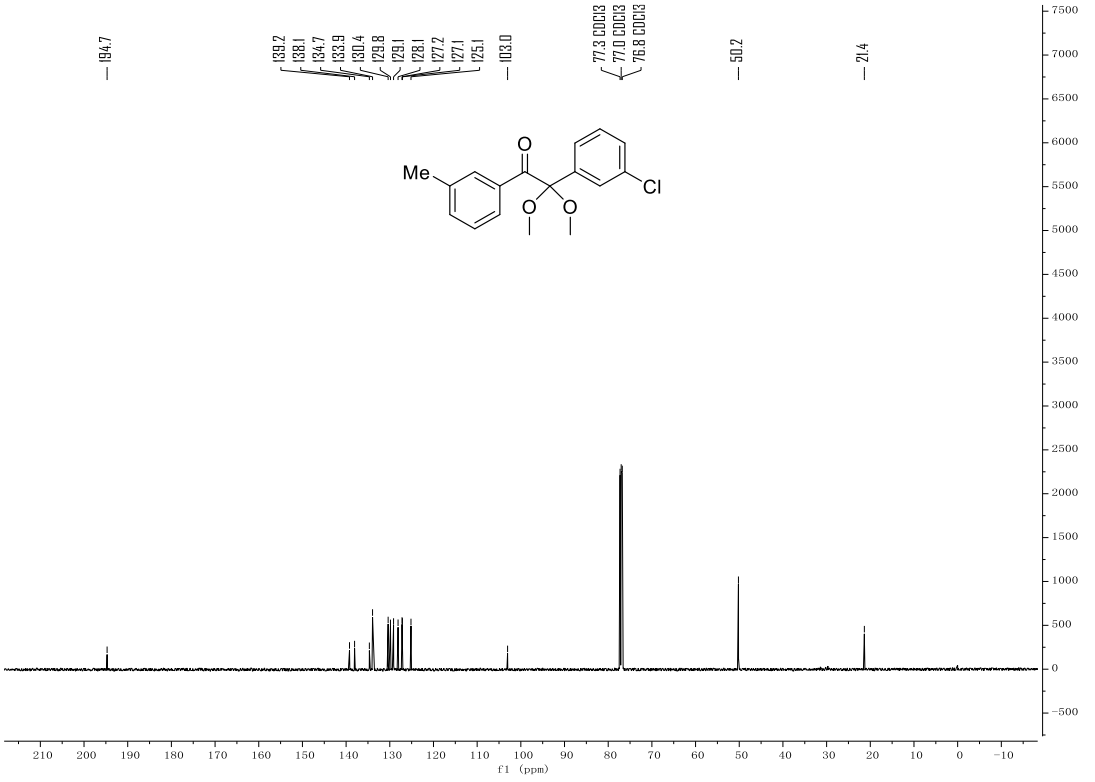
2-(4-chlorophenyl)-2,2-dimethoxy-1-(p-tolyl)ethan-1-one (**e25**, **major isomer**)



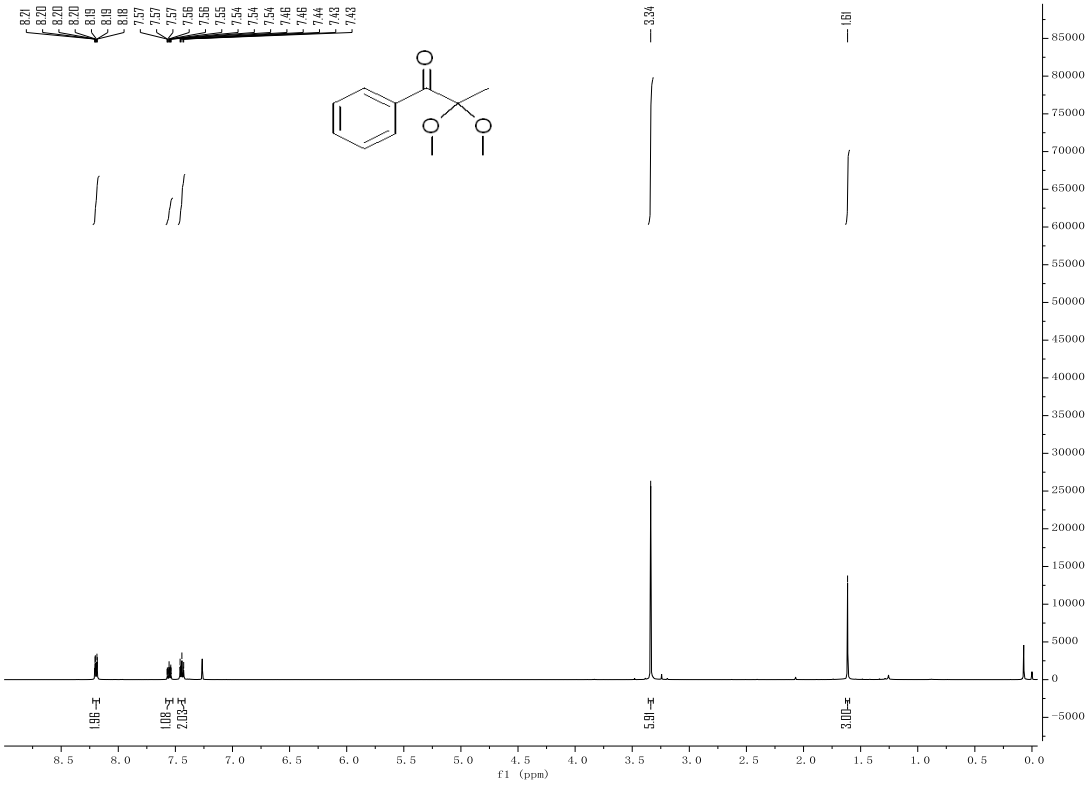



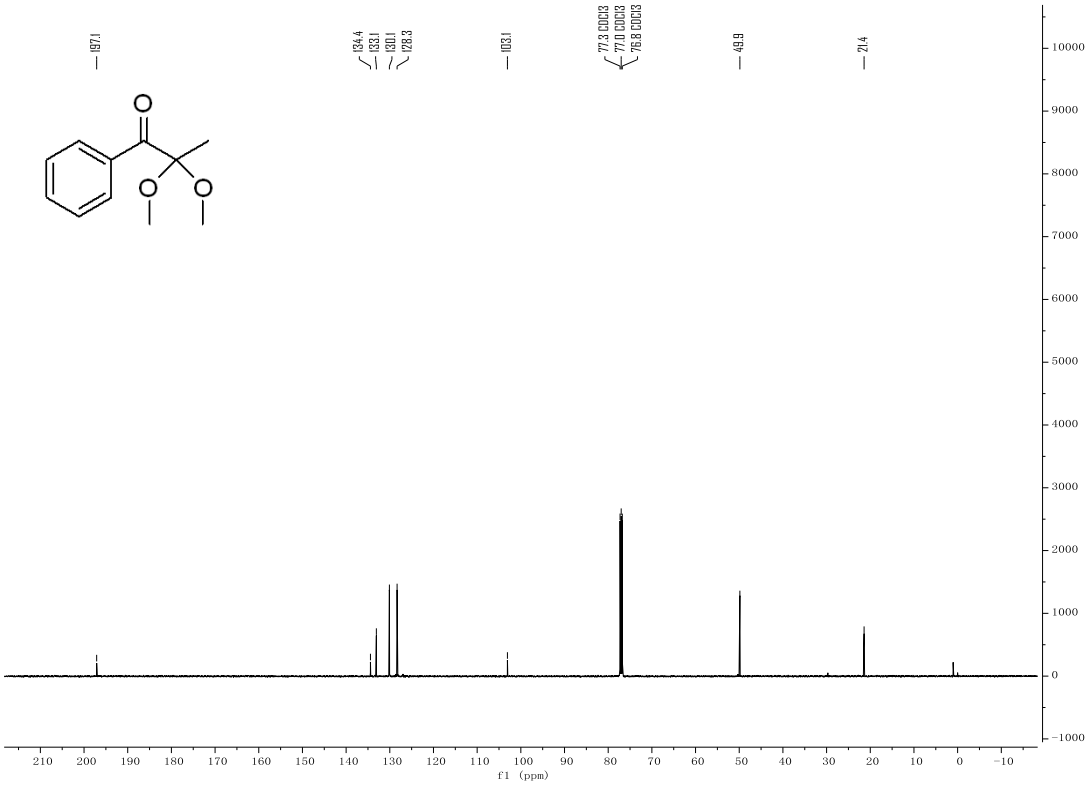
2-(3-chlorophenyl)-2,2-dimethoxy-1-(m-tolyl)ethan-1-one (**e26**, **major isomer**)



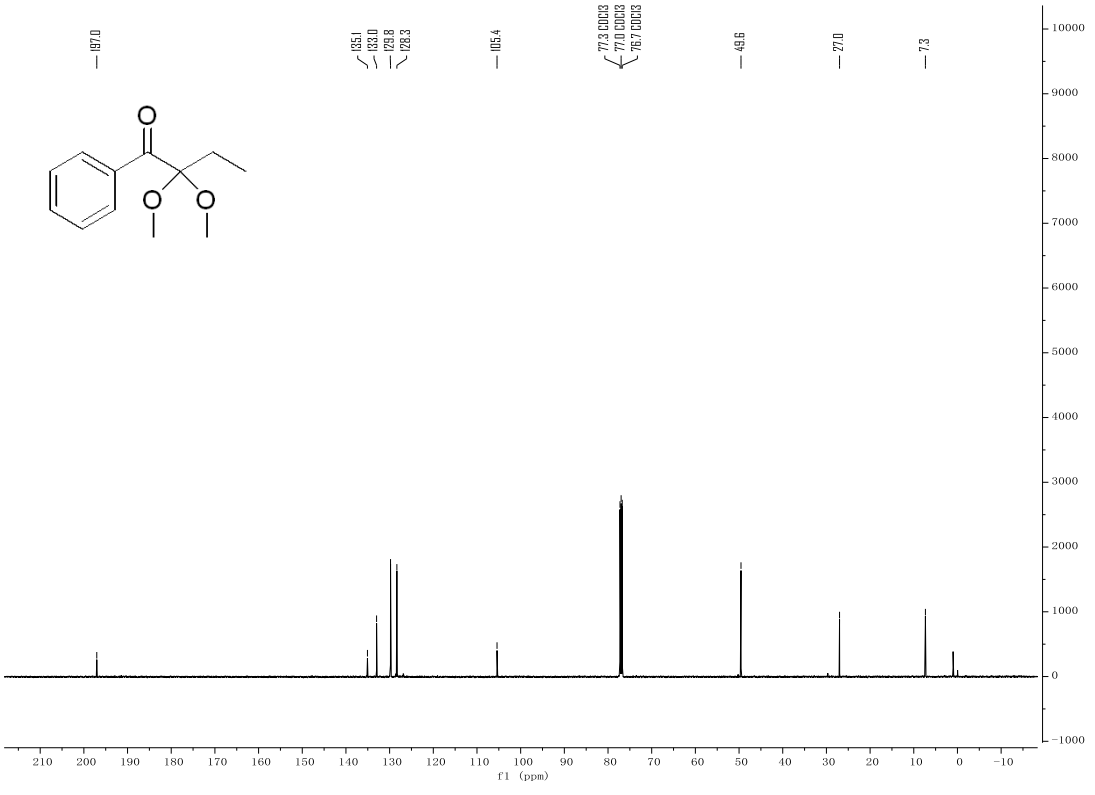



2,2-dimethoxy-1-phenylpropan-1-one (**e27', major isomer**)

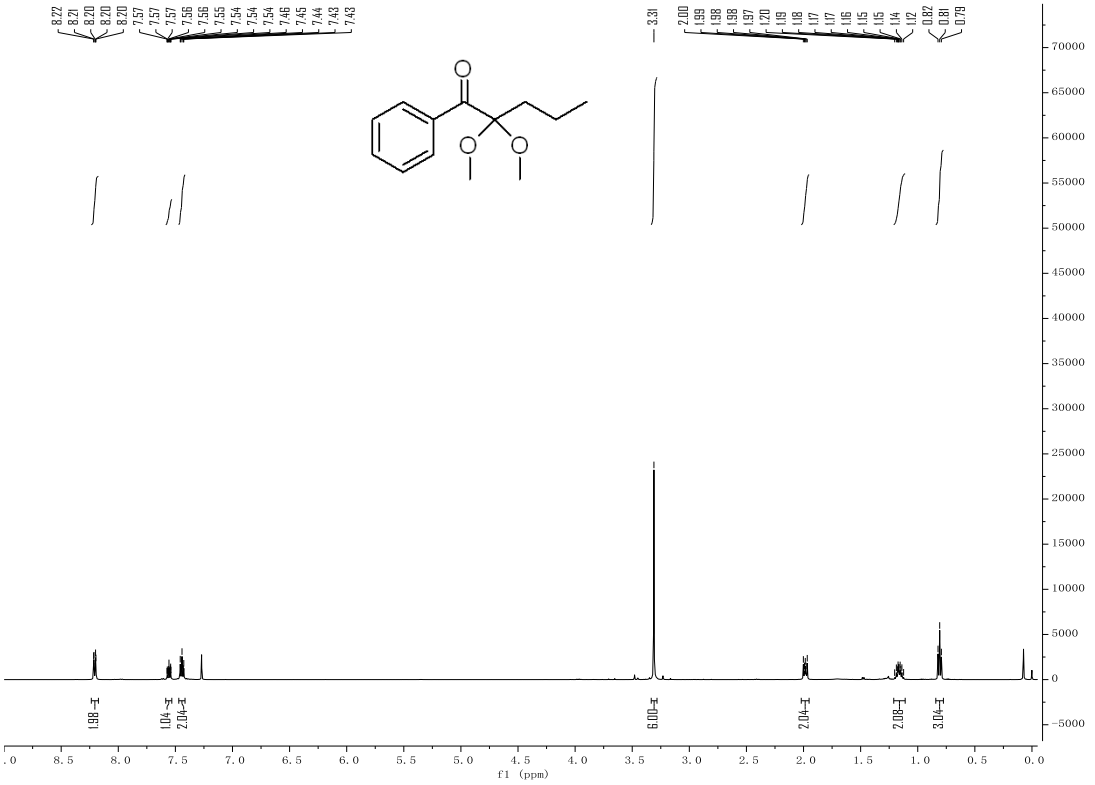


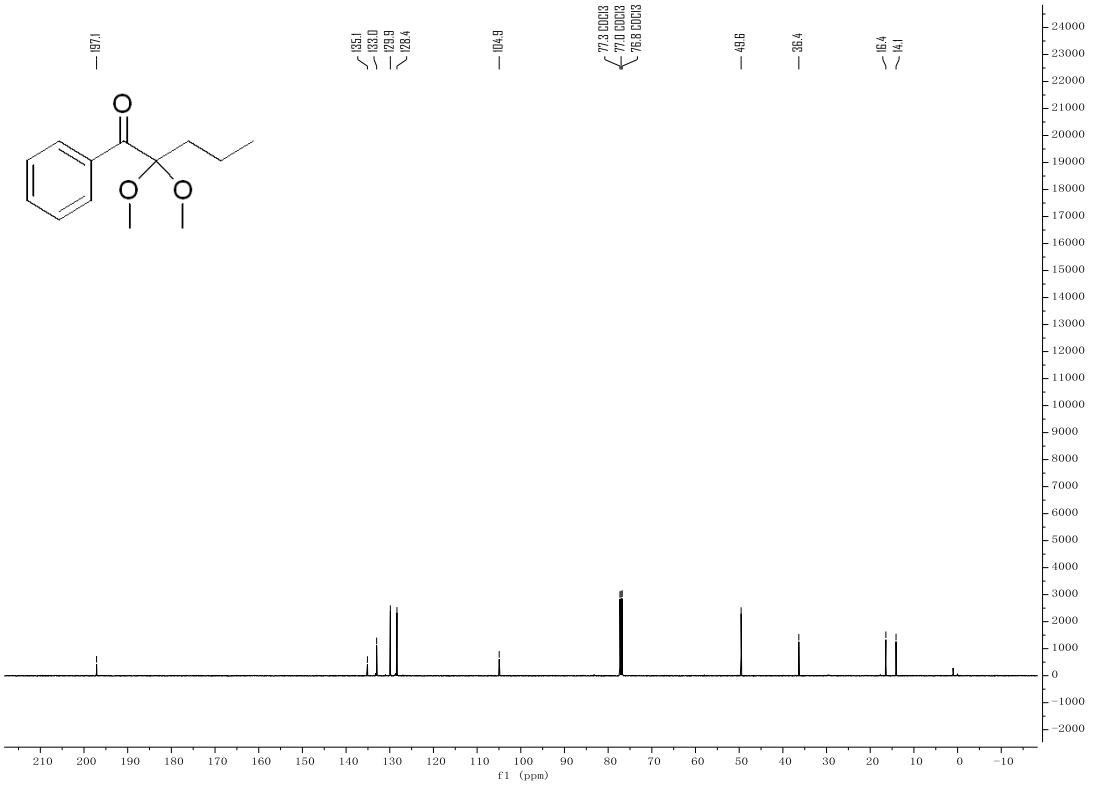



2,2-dimethoxy-1-phenylbutan-1-one (**e28', major isomer**)

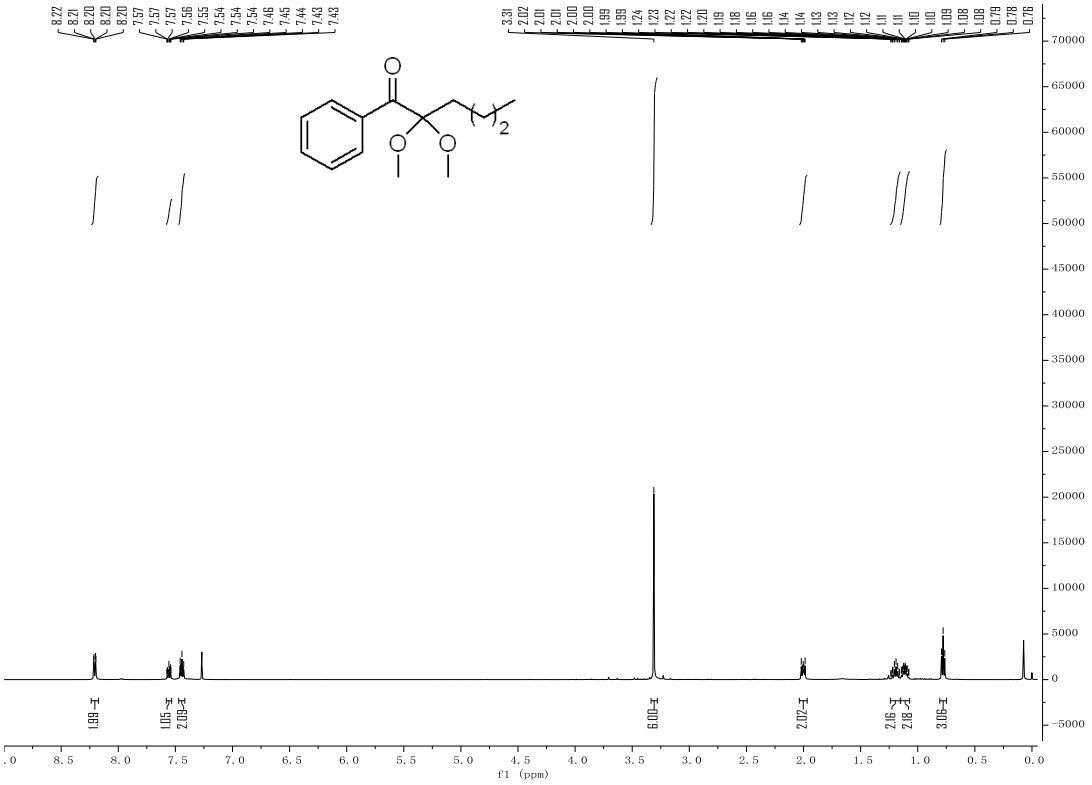



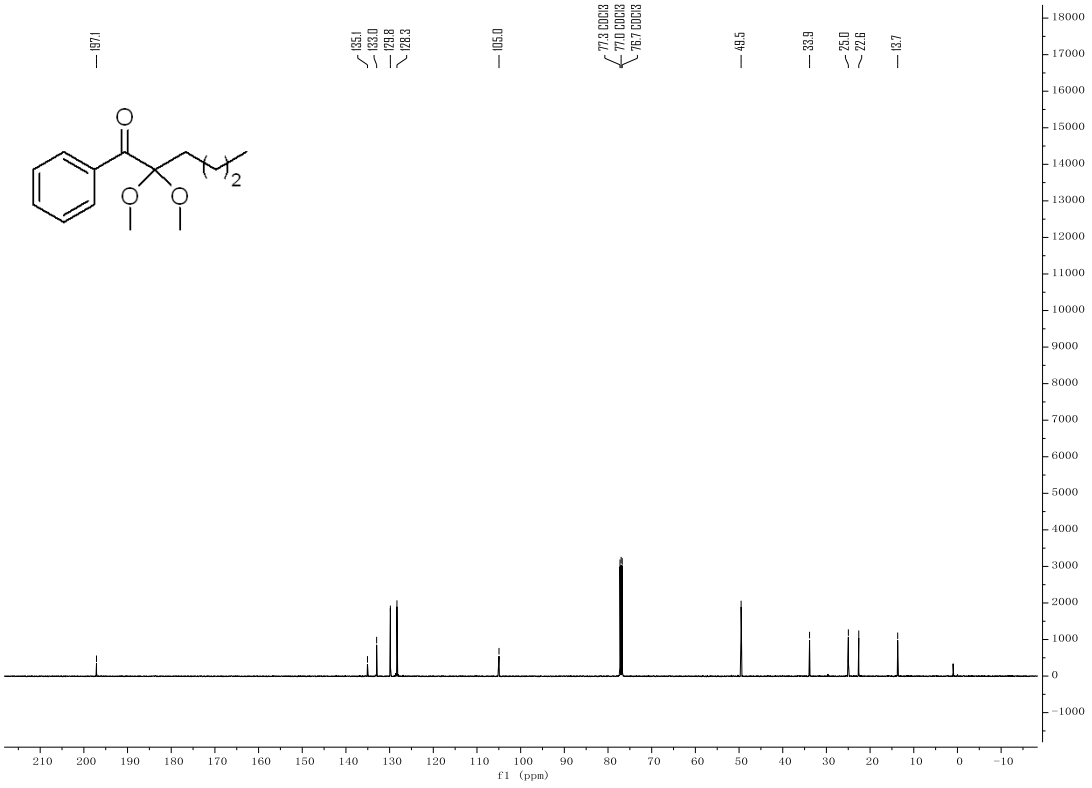
2,2-dimethoxy-1-phenylpentan-1-one (**e29', major isomer**)



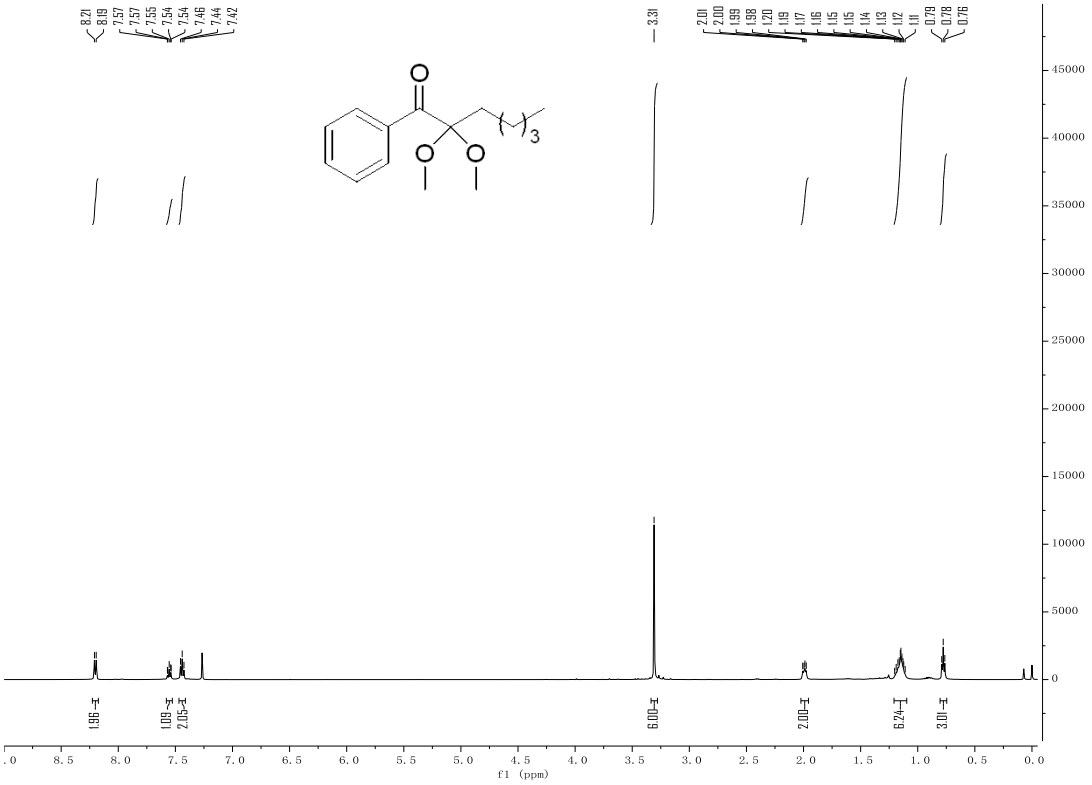



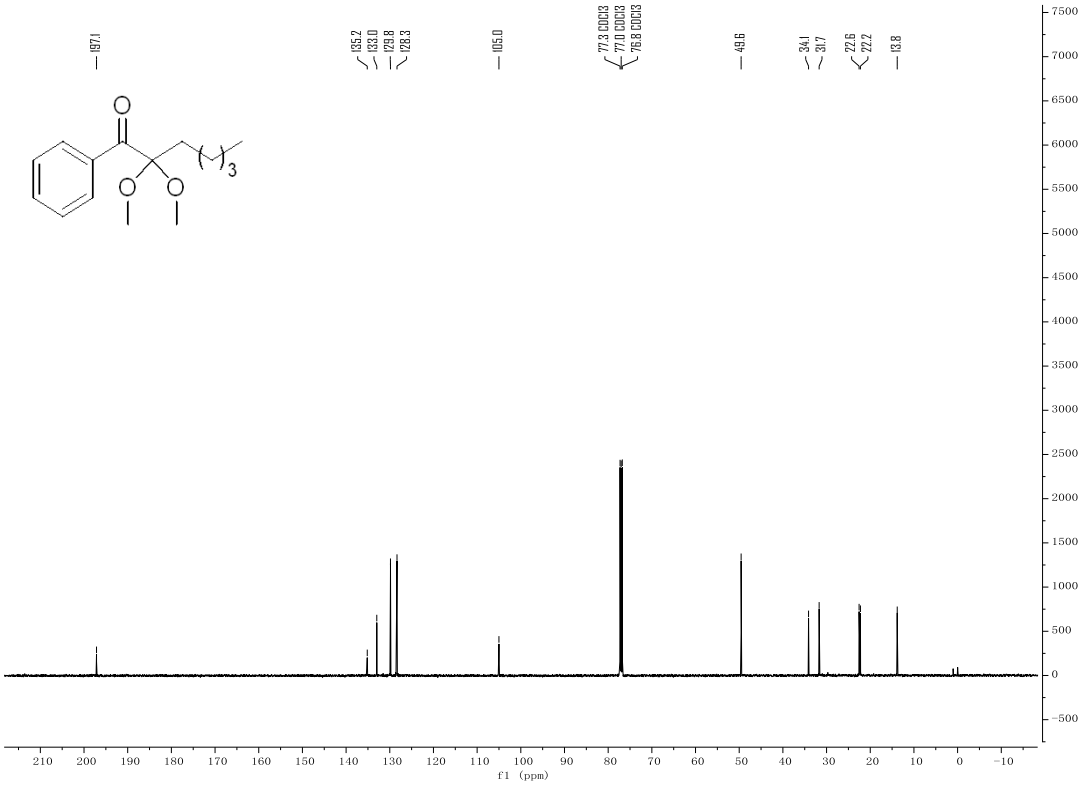
2,2-dimethoxy-1-phenylhexan-1-one (**e30', major isomer**)



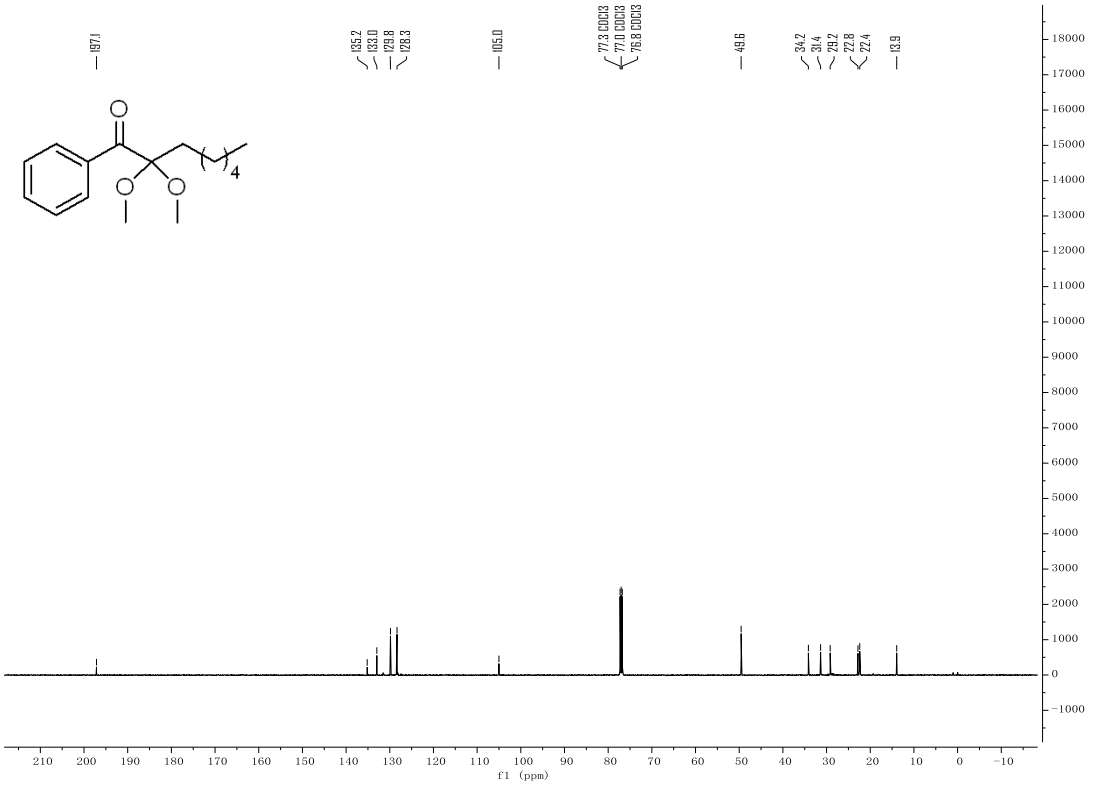


2,2-dimethoxy-1-phenylheptan-1-one (**e31', major isomer**)

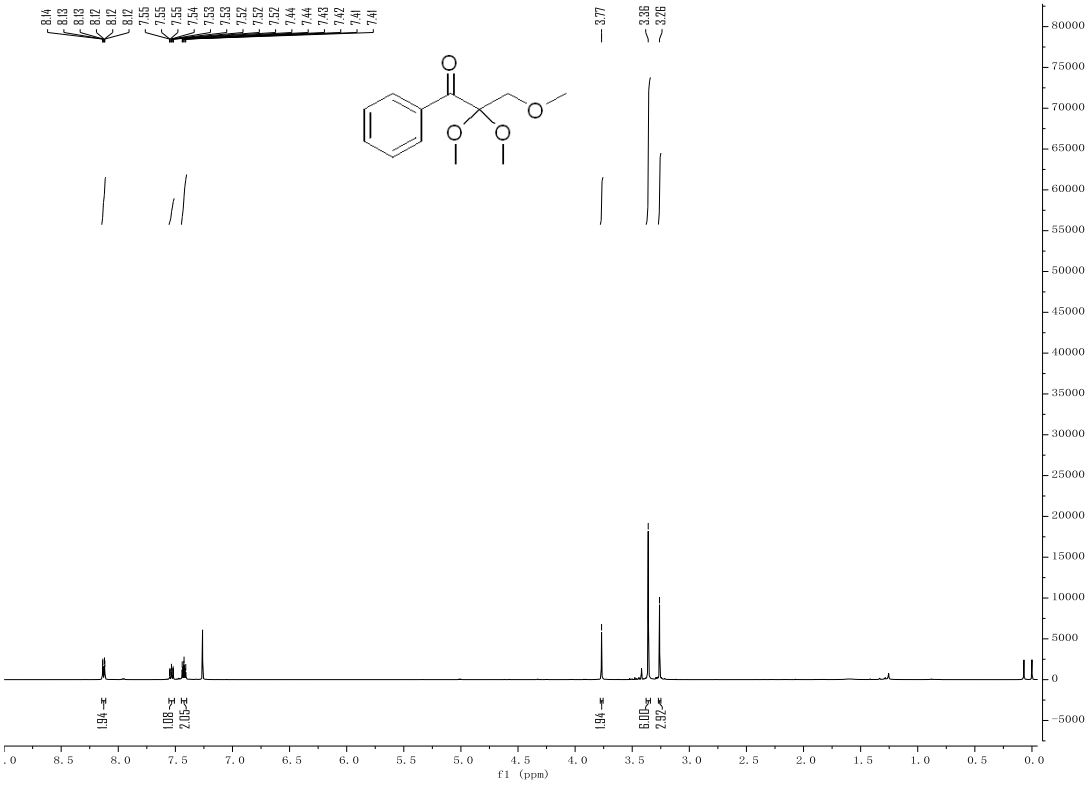


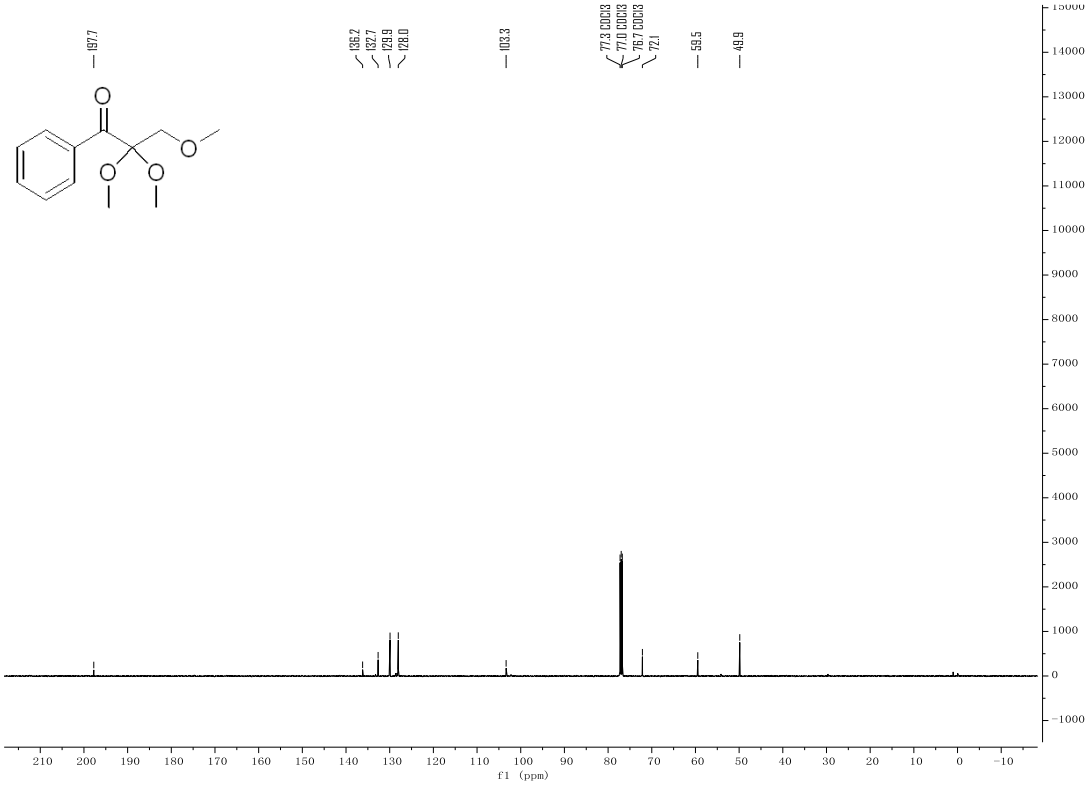



2,2-dimethoxy-1-phenyloctan-1-one (**e32', major isomer**)

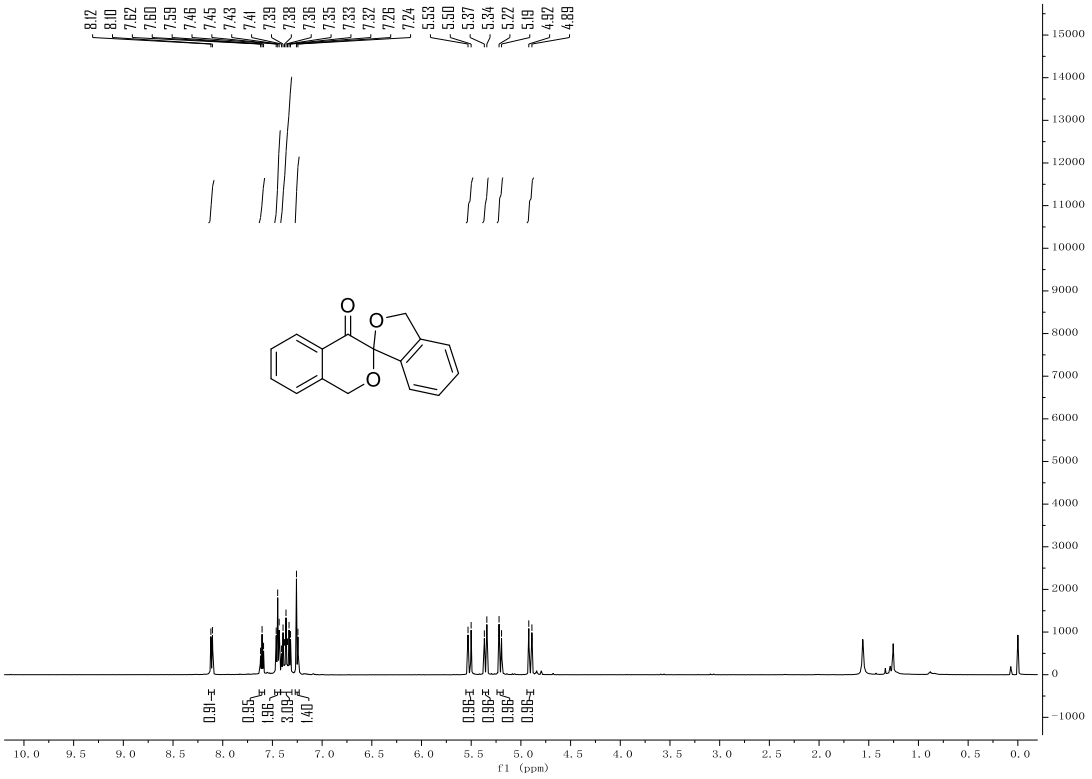



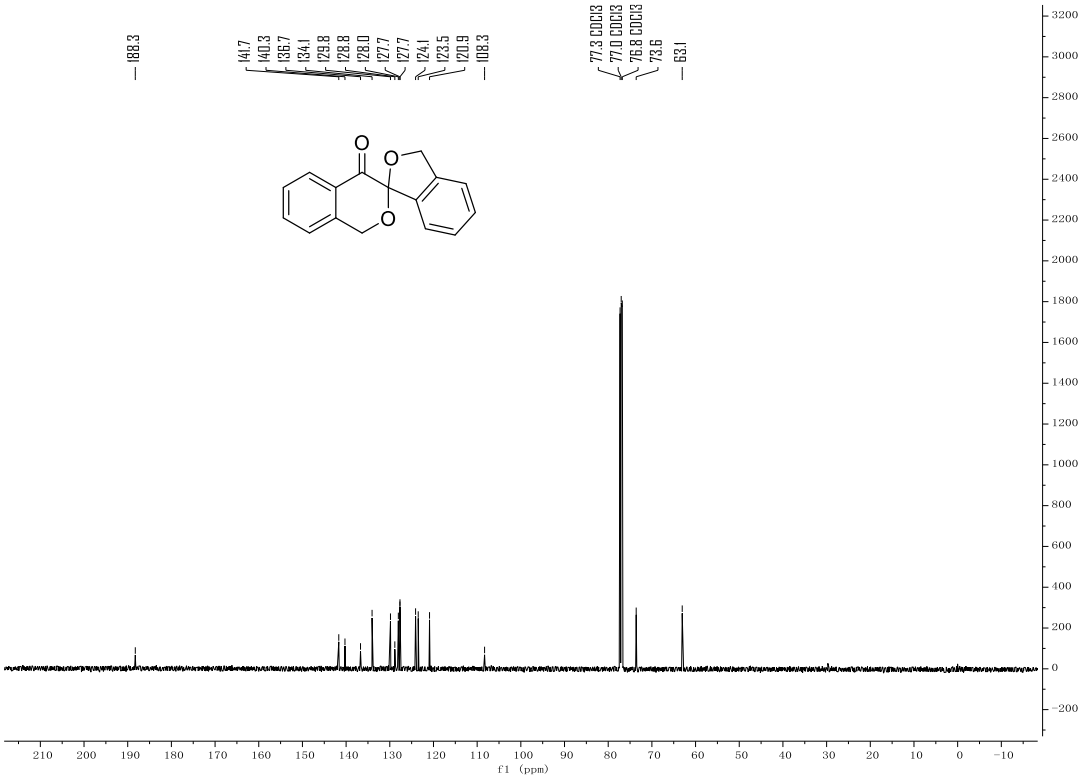
2,2,3-trimethoxy-1-phenylpropan-1-one (**e33', major isomer**)



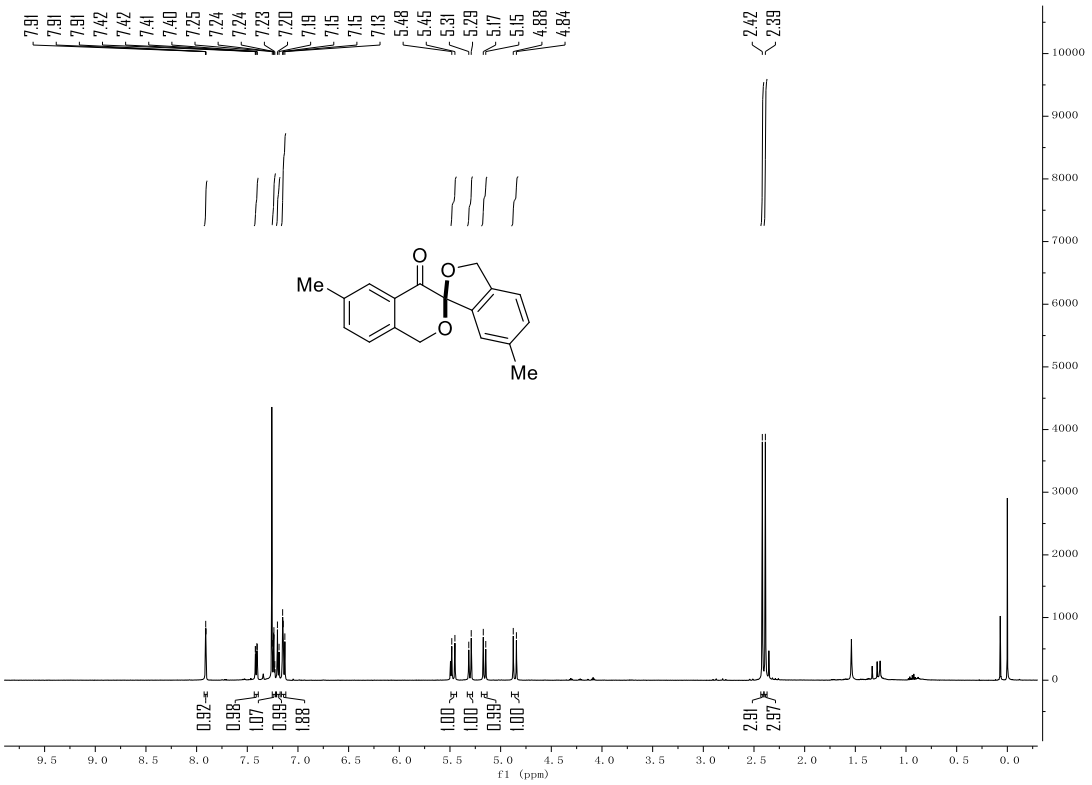



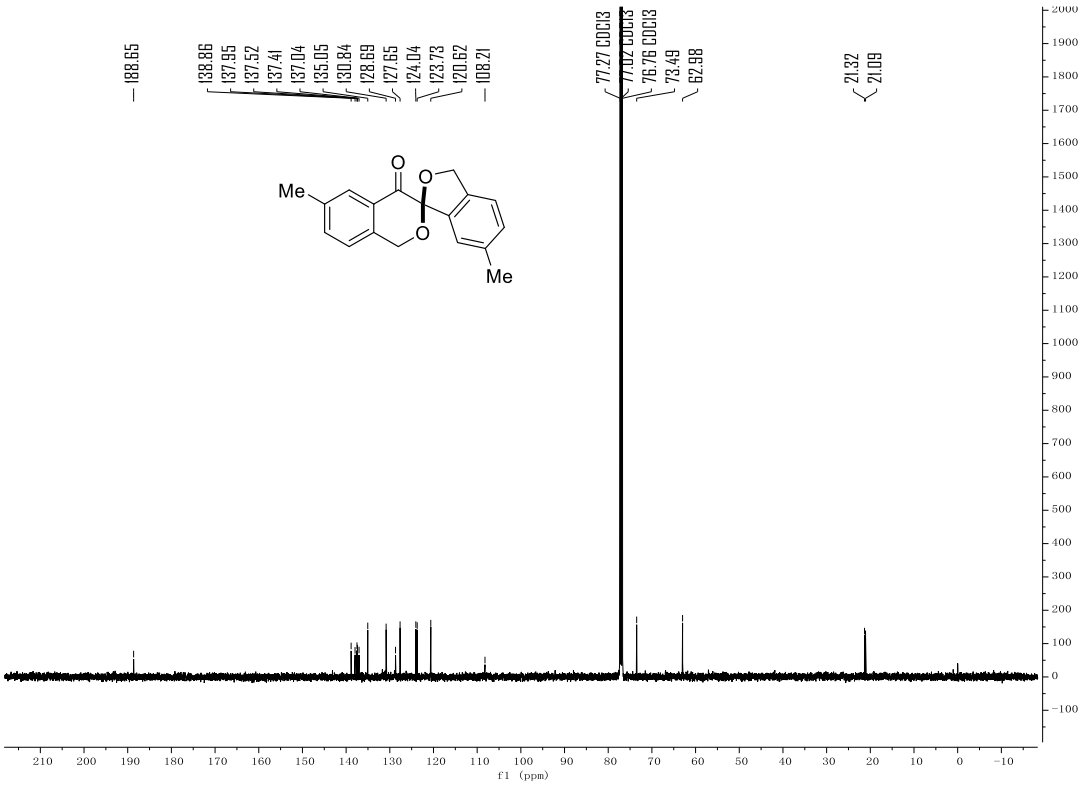
3H-spiro[isobenzofuran-1,3'-isochroman]-4'-one (**g1**)



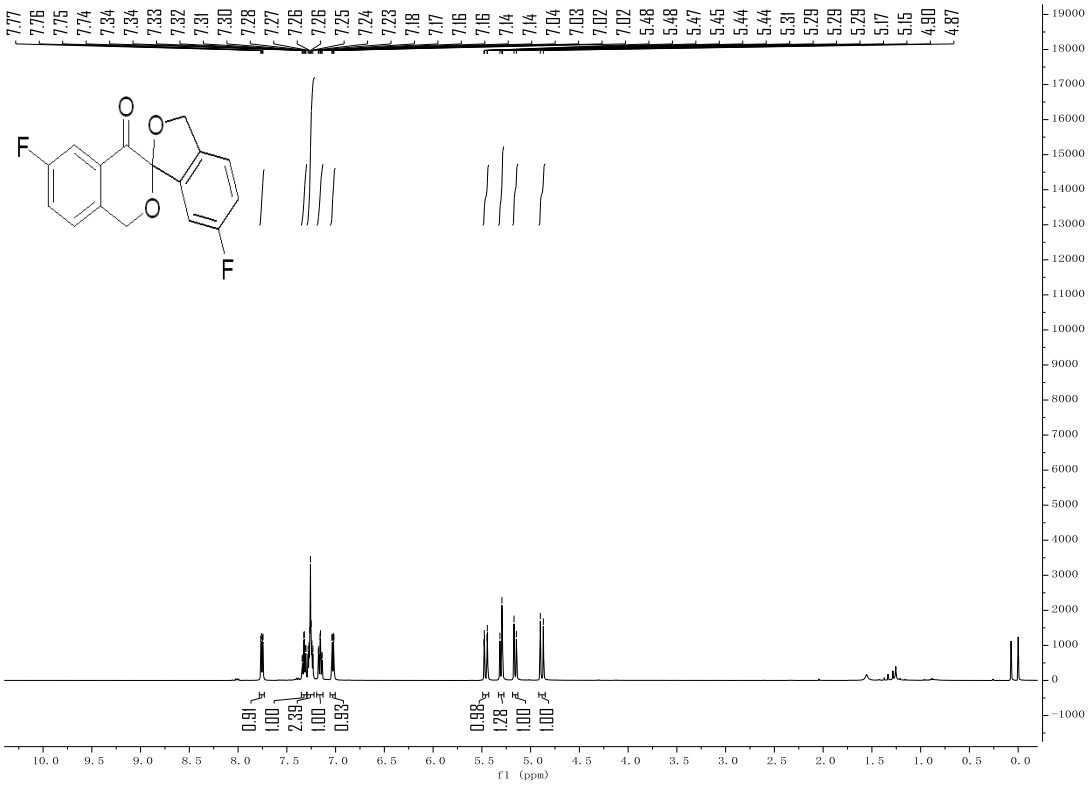



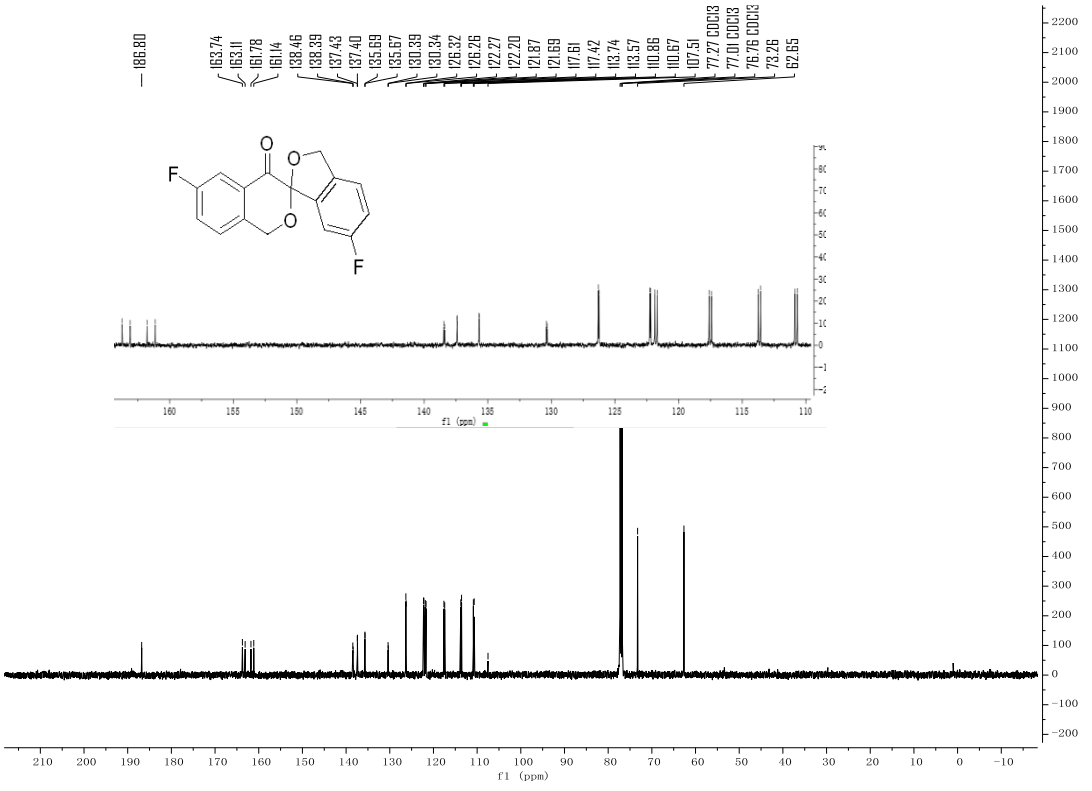
6,6'-dimethyl-3H-spiro[isobenzofuran-1,3'-isochroman]-4'-one (**g2**)

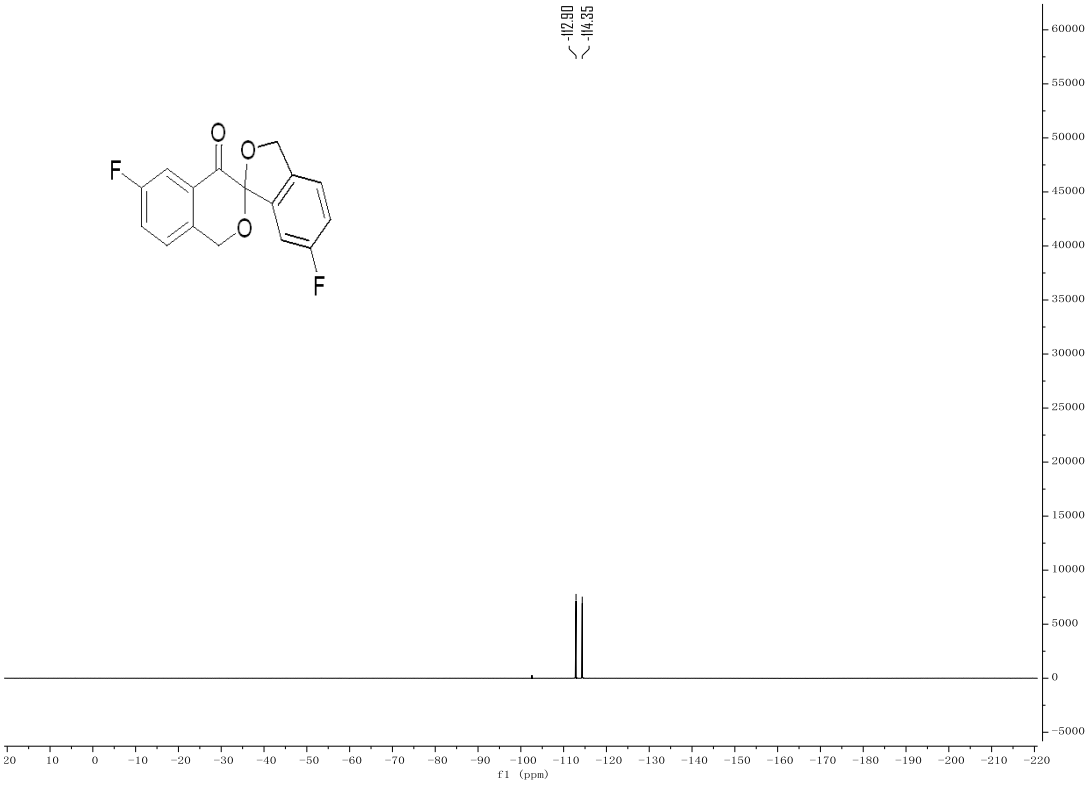


6,6'-difluoro-3H-spiro[isobenzofuran-1,3'-isochroman]-4'-one (**g3**)

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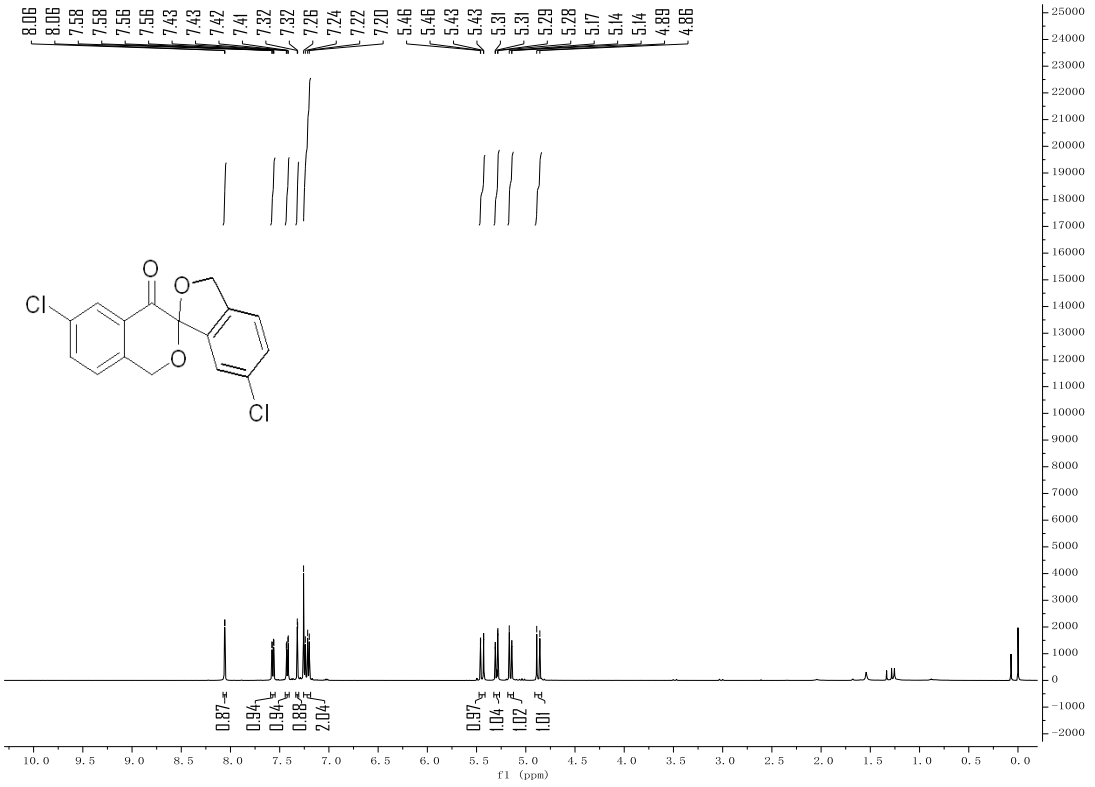
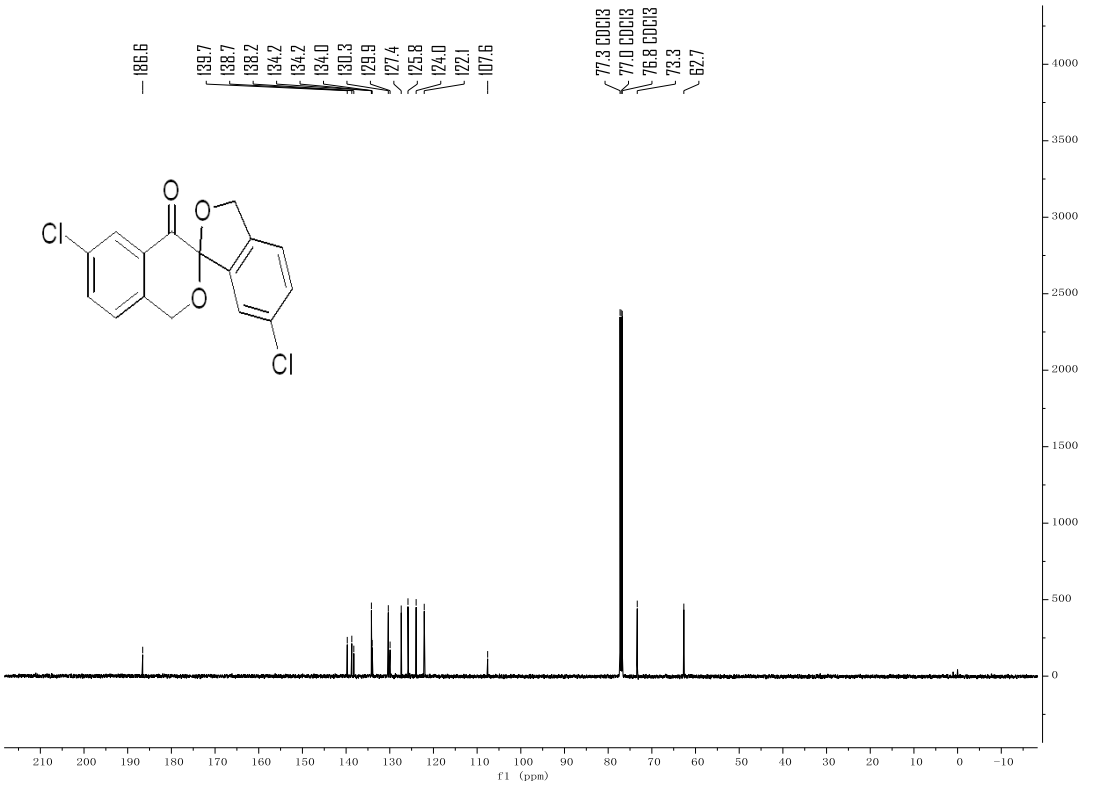
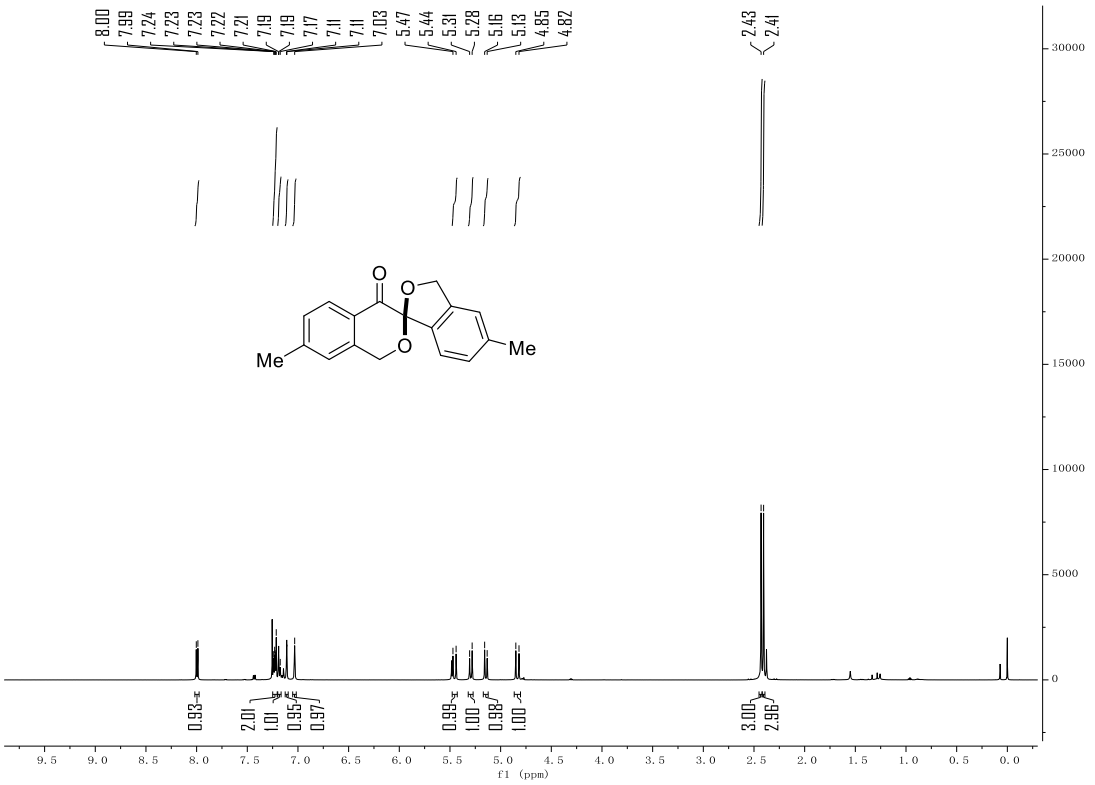
-114.35
F
O
O
O
F
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)

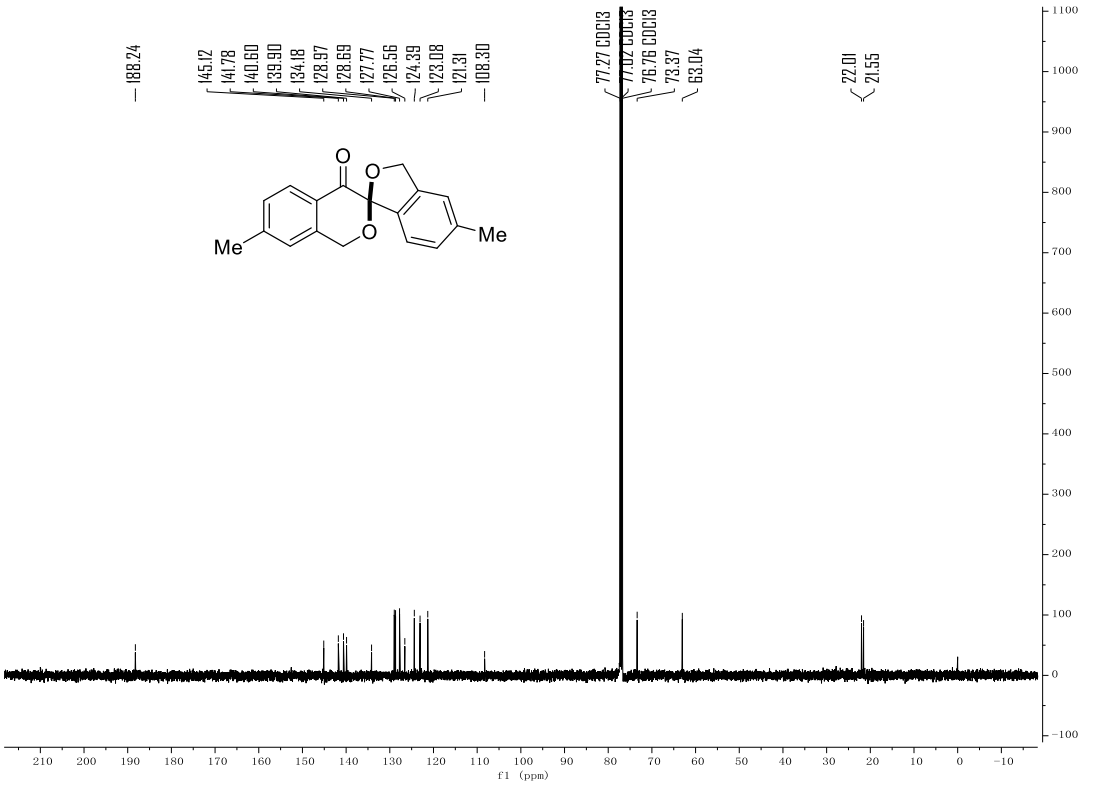
6,6'-dichloro-3H-spiro[isobenzofuran-1,3'-isochroman]-4'-one (**g4**)



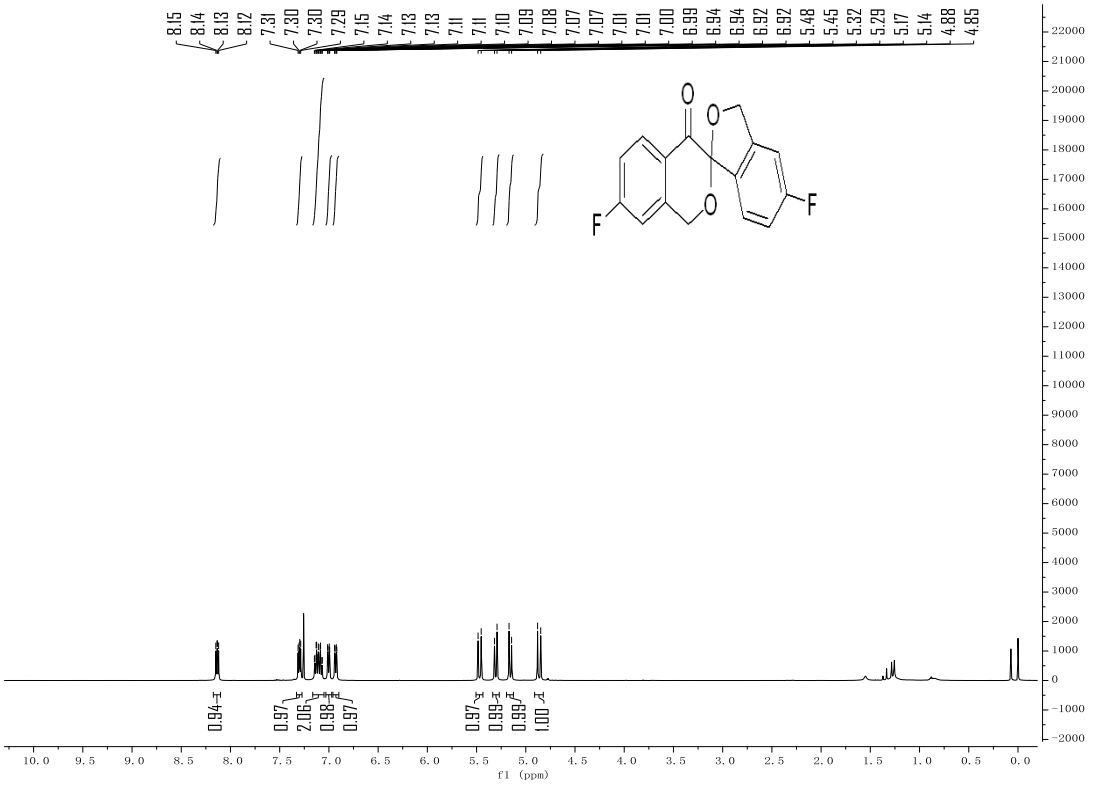



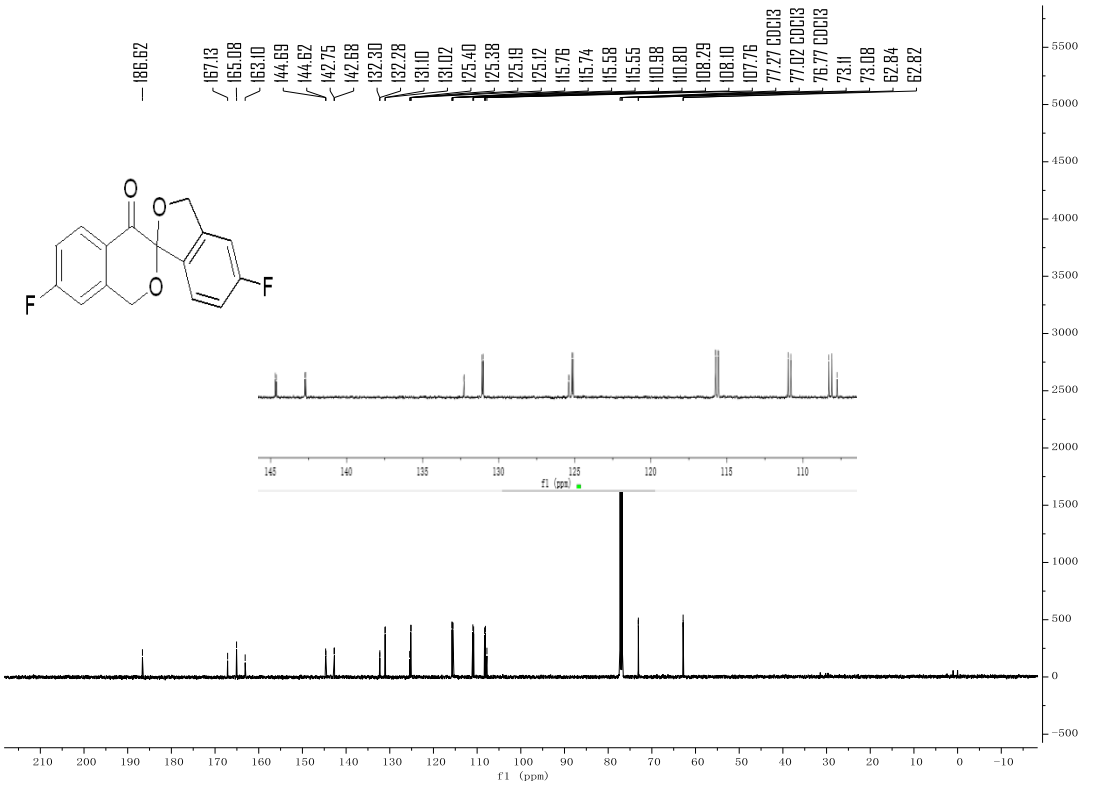
5,7'-dimethyl-3H-spiro[isobenzofuran-1,3'-isochroman]-4'-one (**g5**)

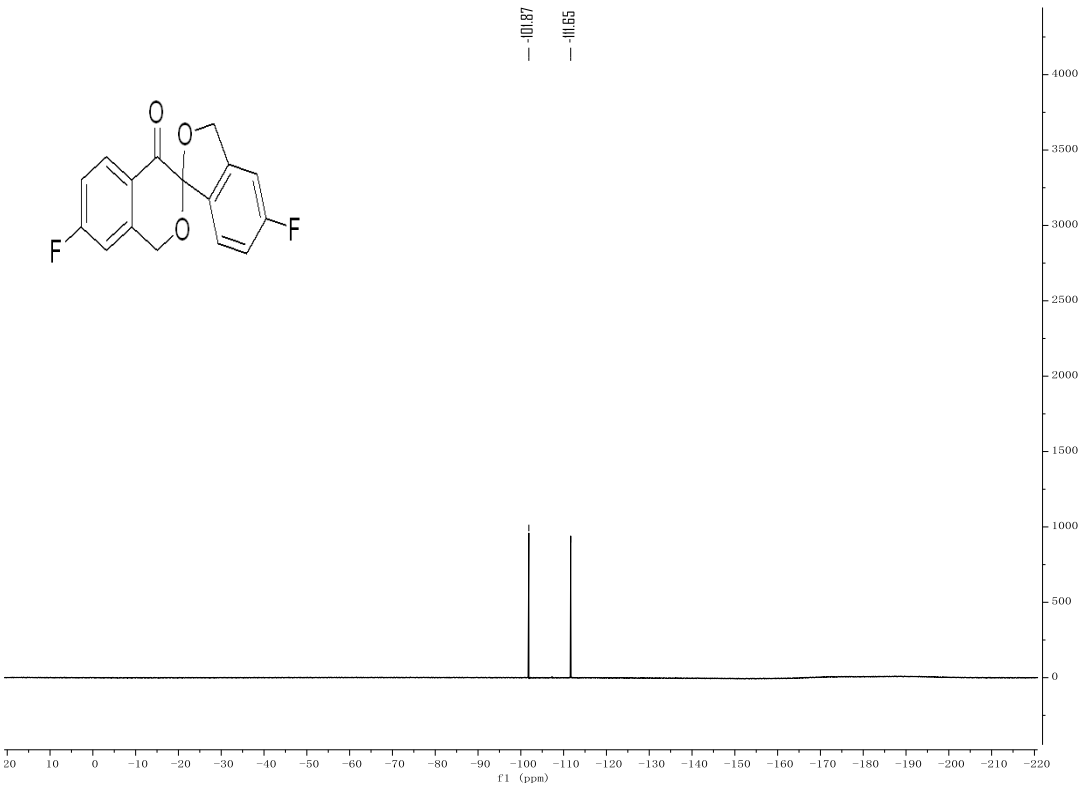


5,7'-difluoro-3H-spiro[isobenzofuran-1,3'-isochroman]-4'-one (**g6**)

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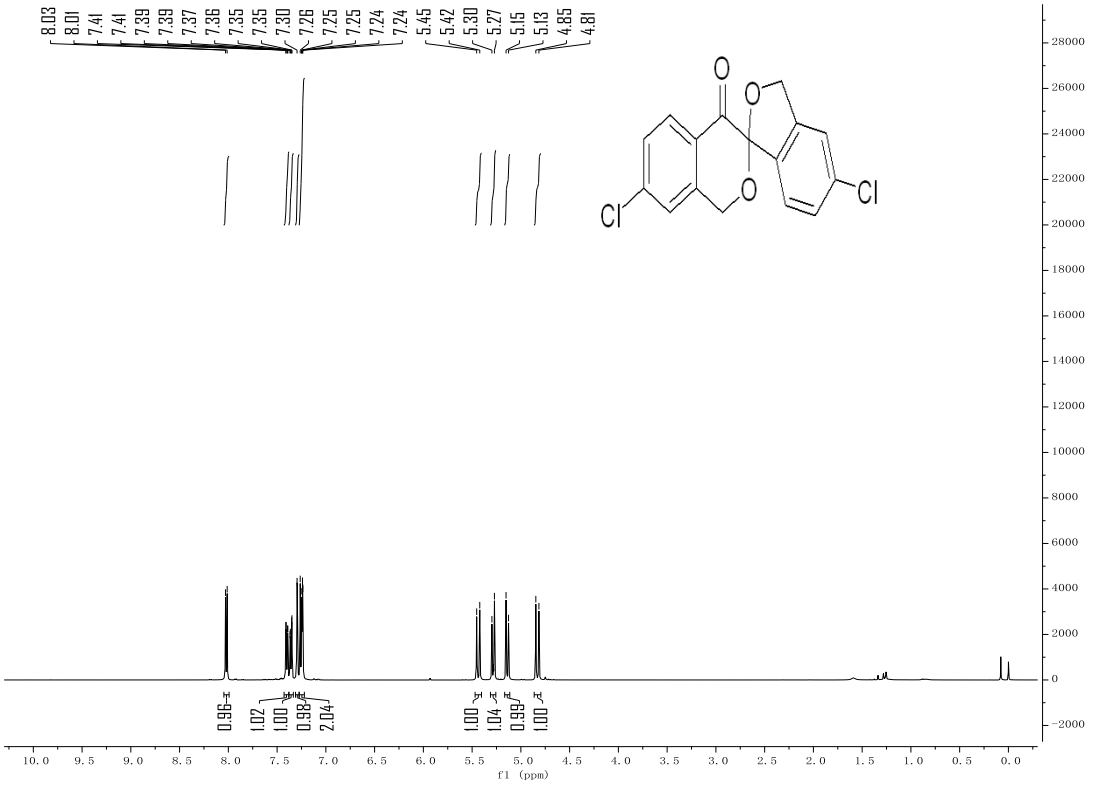
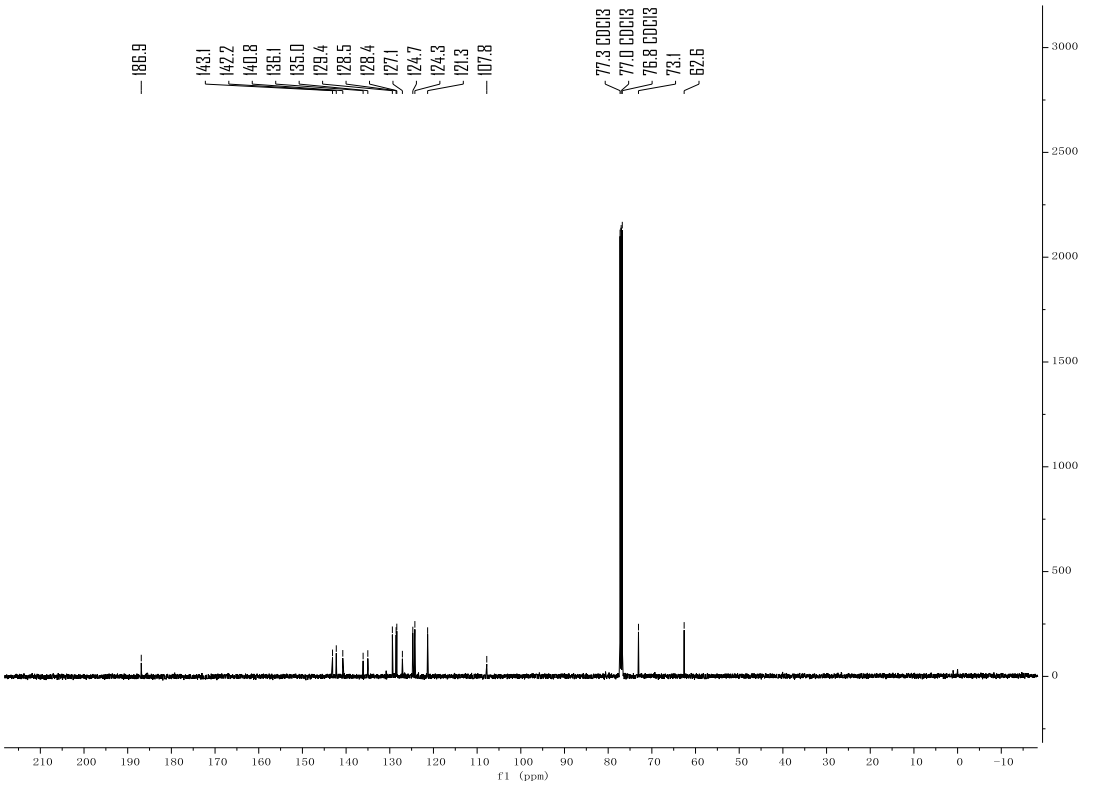
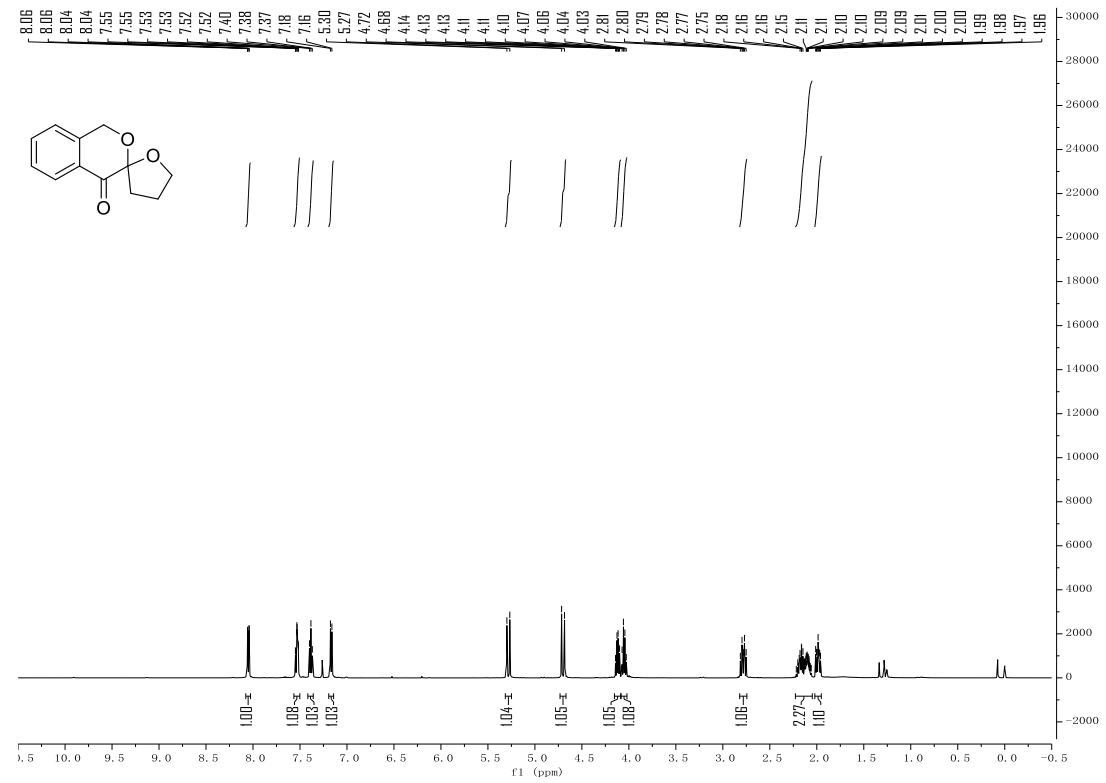
3000
2500
2000
1500
1000
500
0
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)
O
O
O
F
F

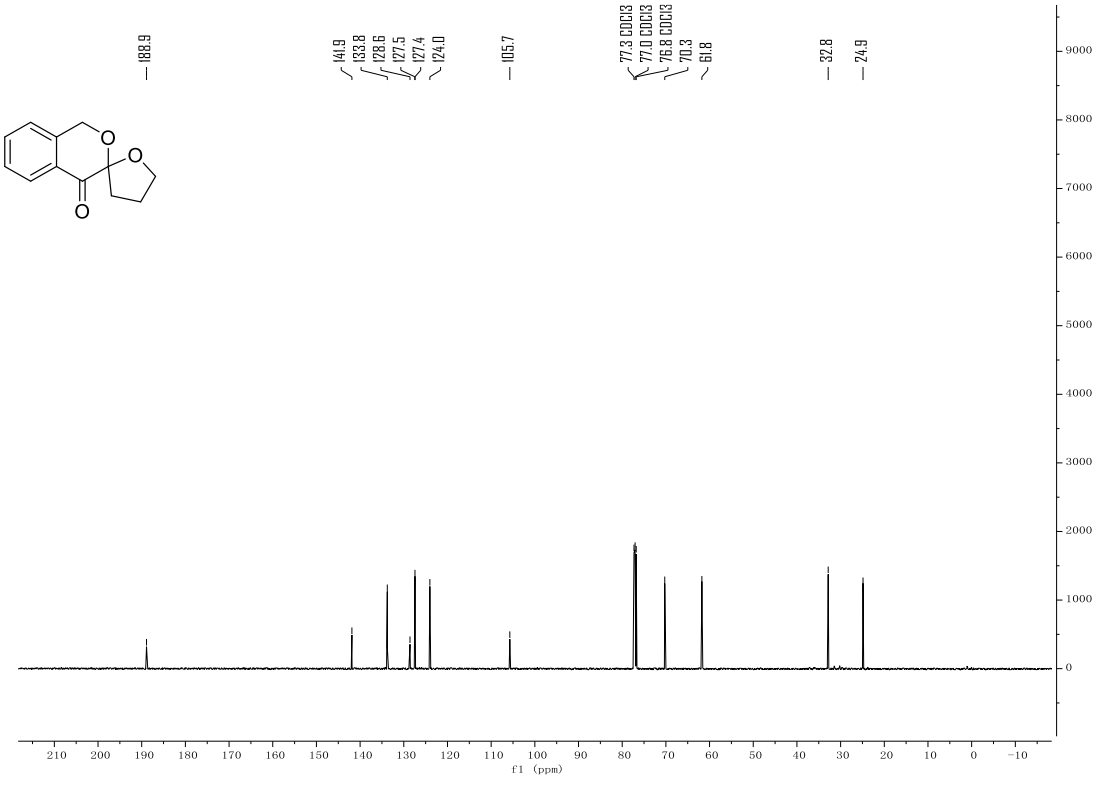
5,7'-dichloro-3H-spiro[isobenzofuran-1,3'-isochroman]-4'-one (**g7**)



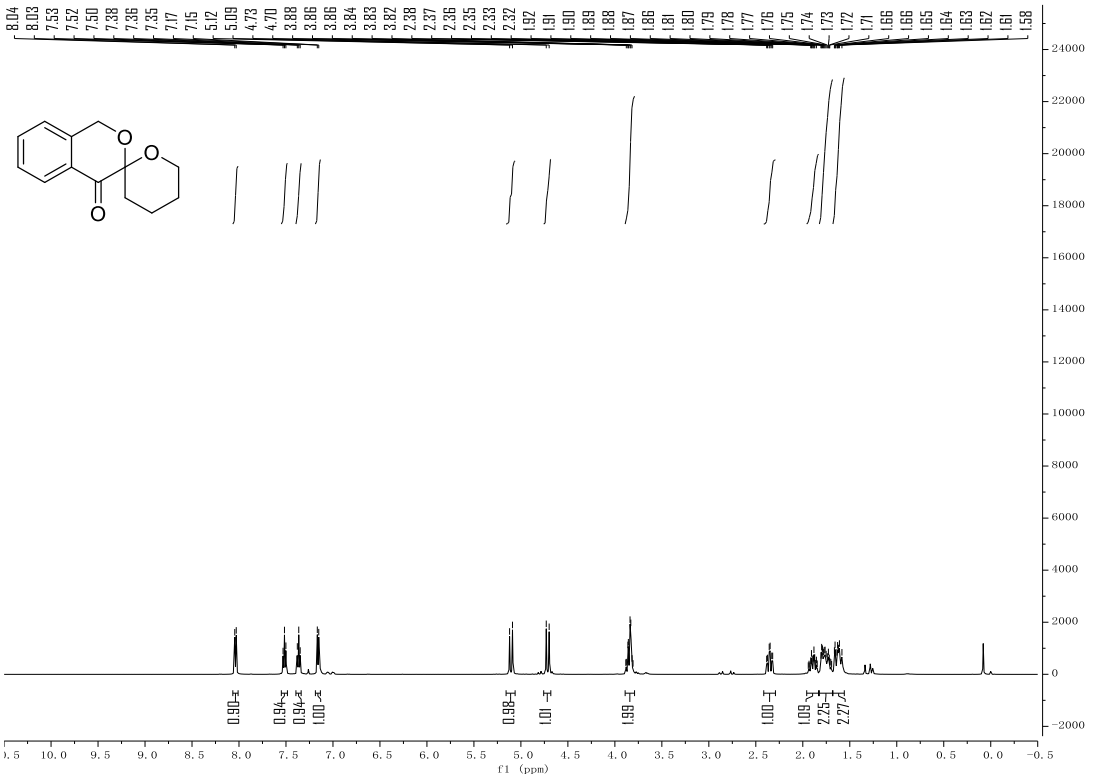



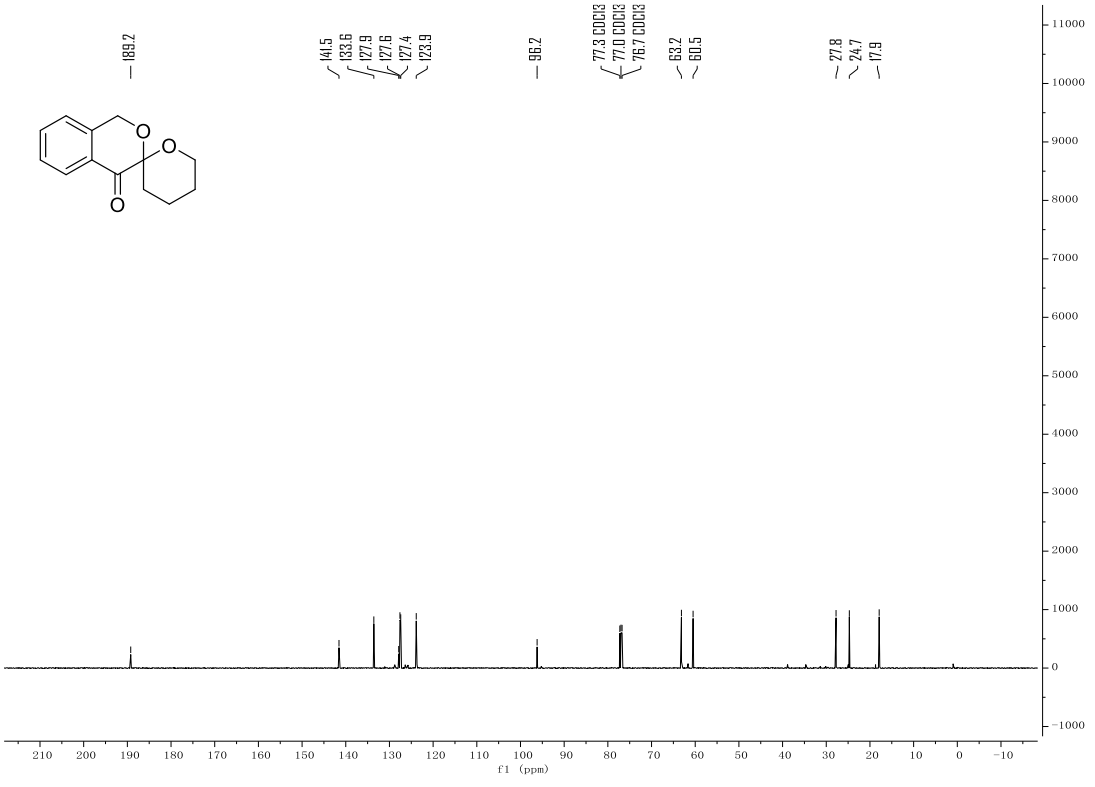
4,5-dihydro-3H-spiro[furan-2,3'-isochroman]-4'-one (**g8**)



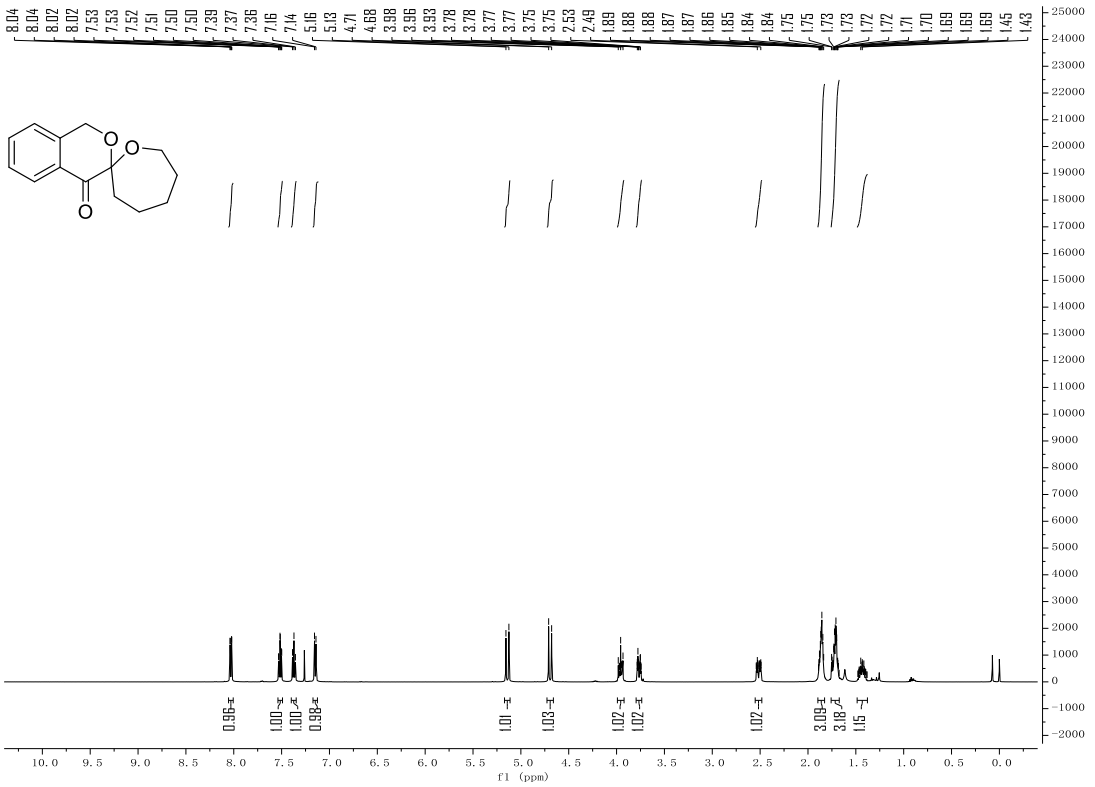



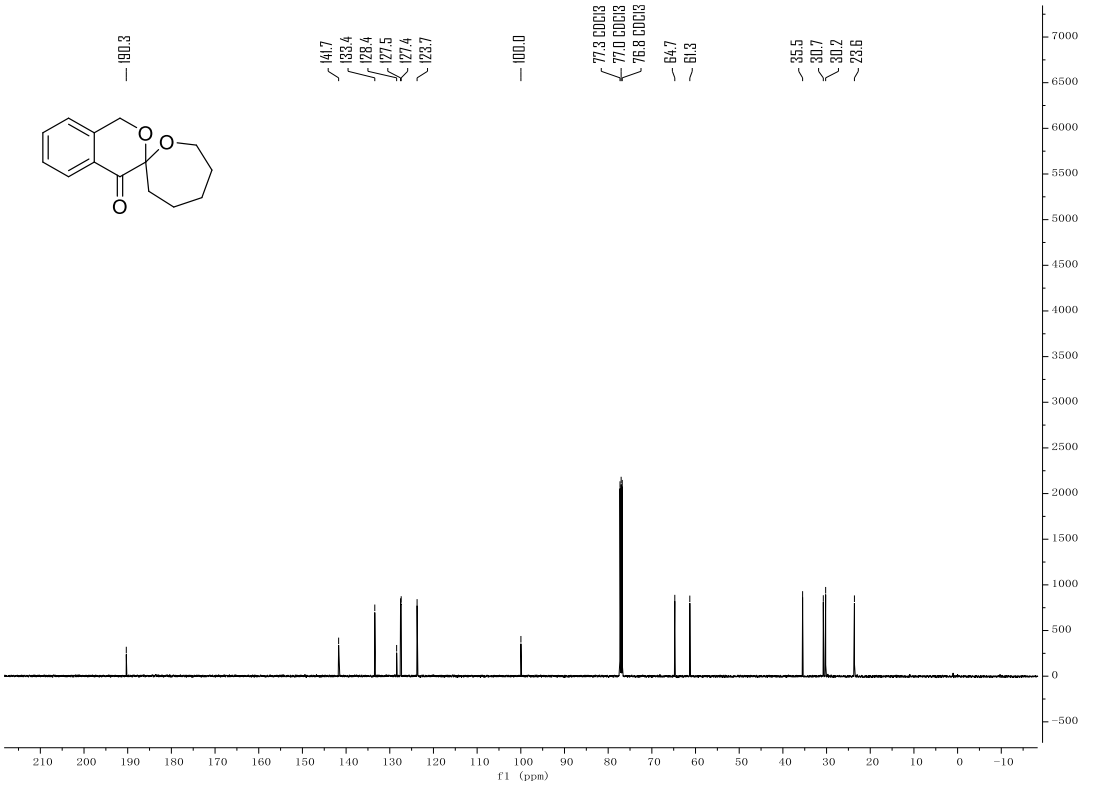
3',4',5',6'-tetrahydrospiro[isochromane-3,2'-pyran]-4-one (**g9**)



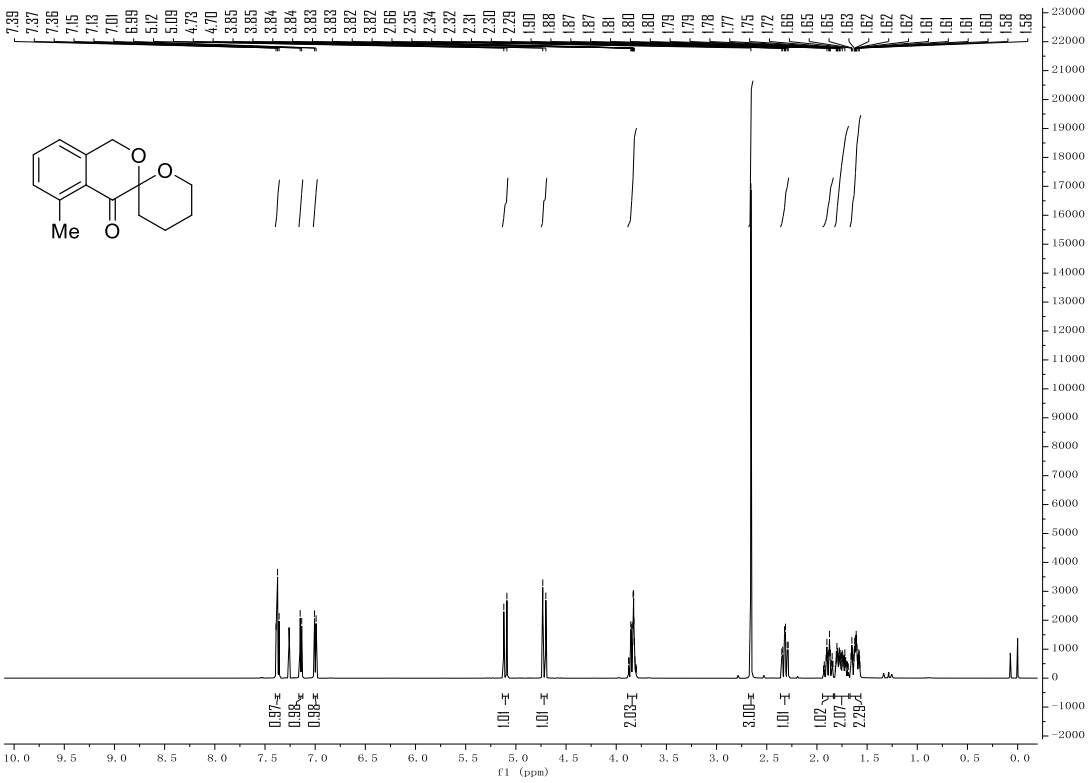



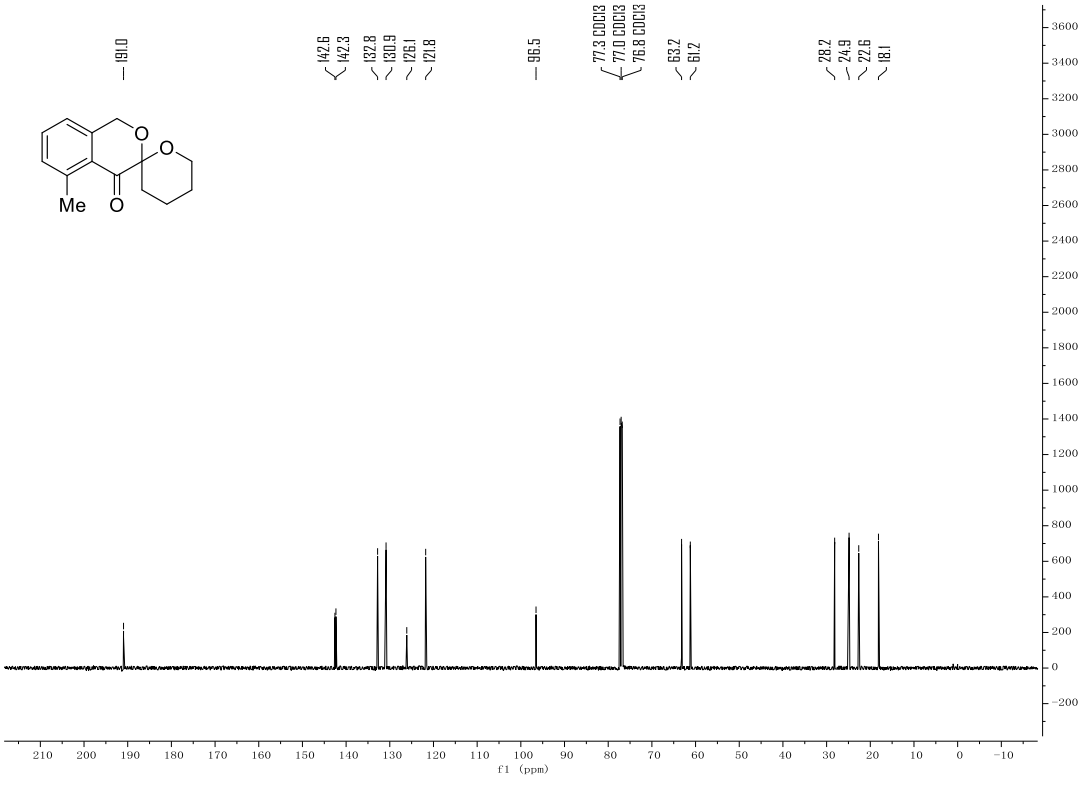
spiro[isochromane-3,2'-oxepan]-4-one (**g10**)



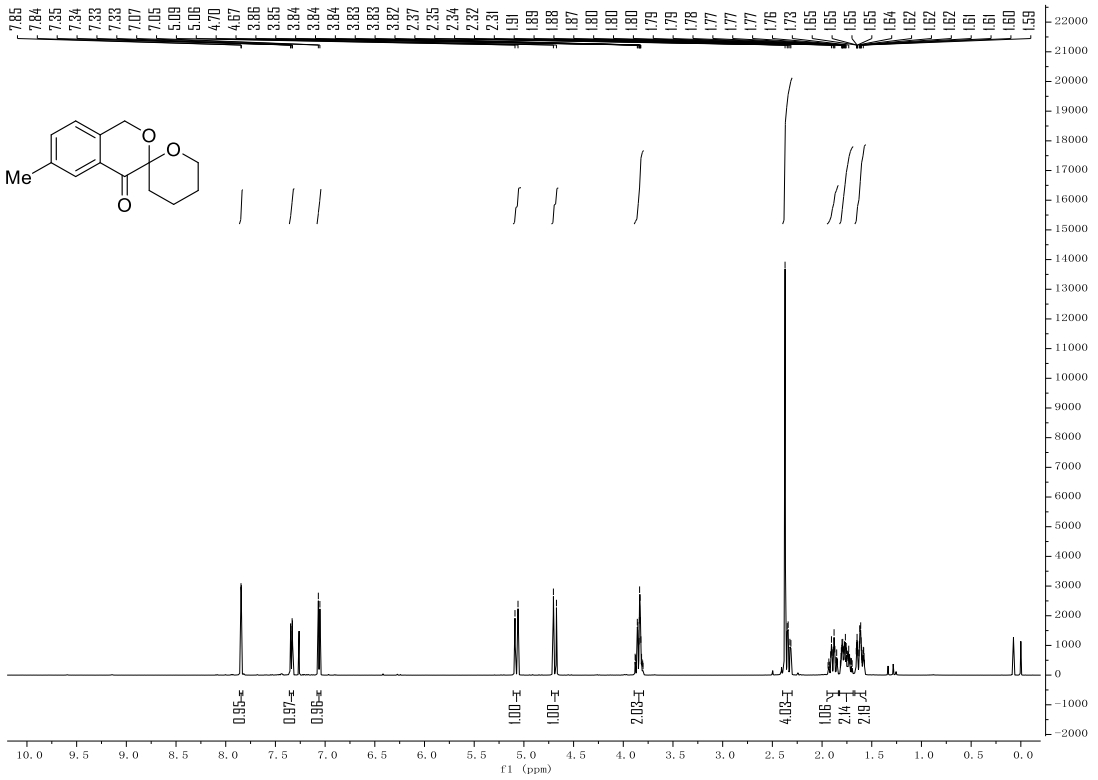



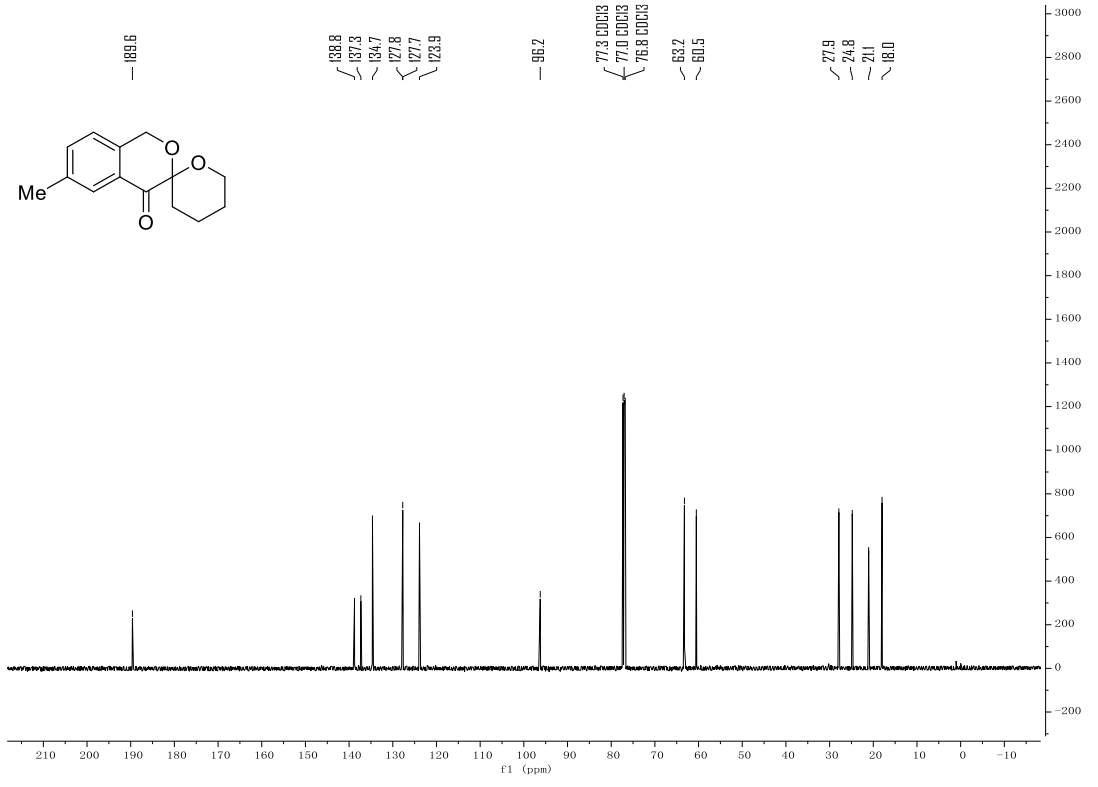
5-methyl-3',4',5',6'-tetrahydrospiro[isochromane-3,2'-pyran]-4-one (**g11**)



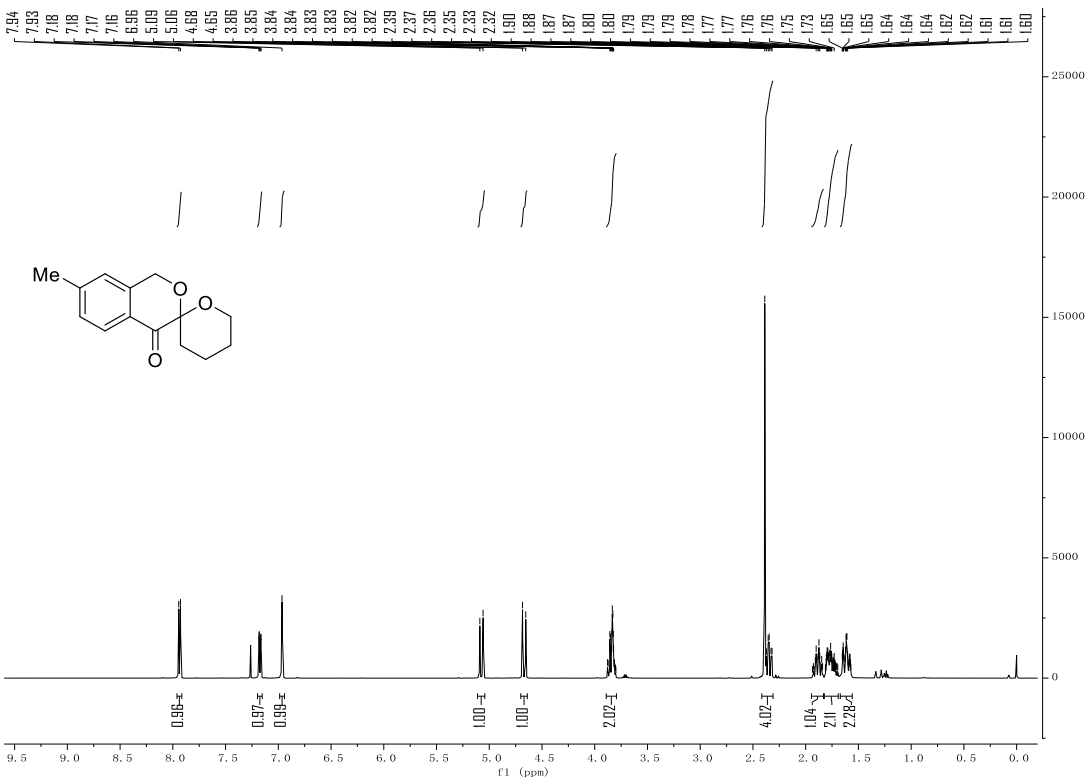



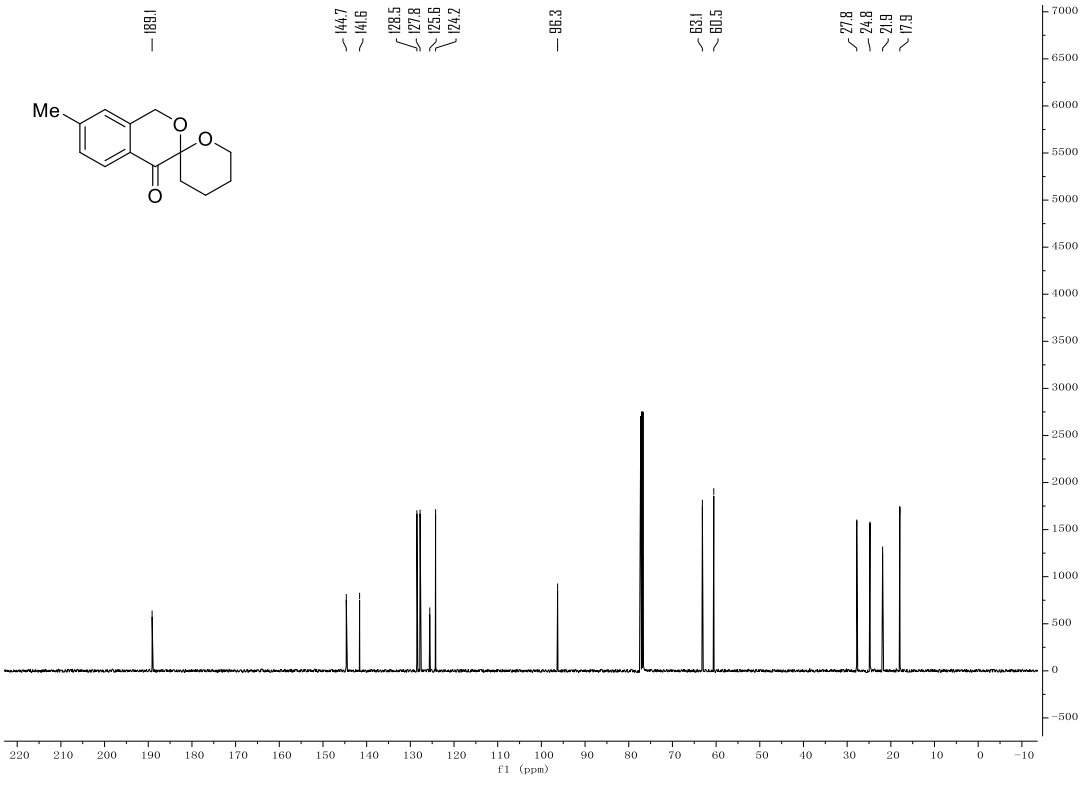
6-methyl-3',4',5',6'-tetrahydrospiro[isochromane-3,2'-pyran]-4-one (**g12**)



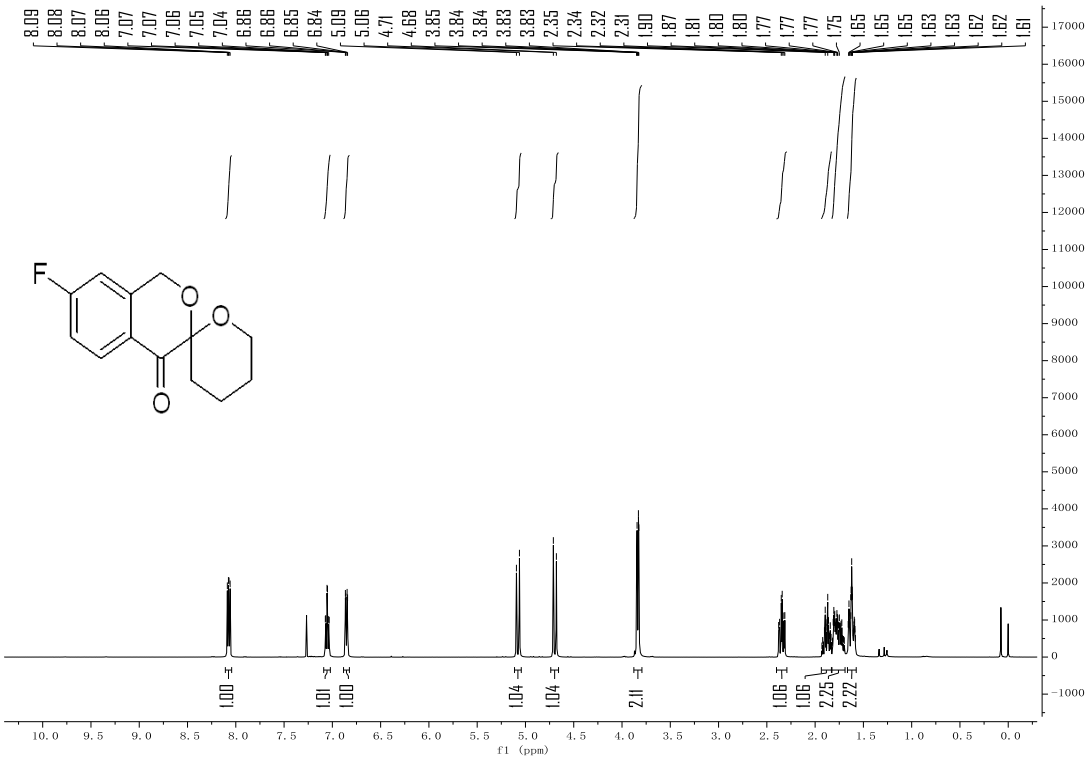



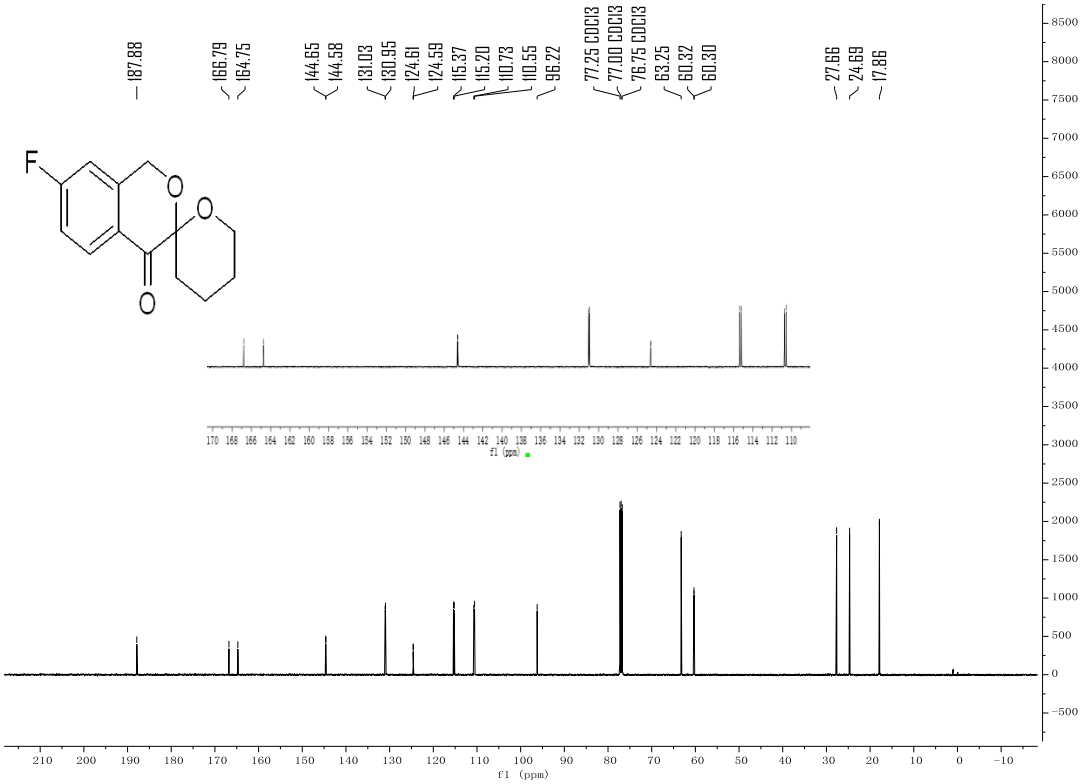
7-methyl-3',4',5',6'-tetrahydrospiro[isochromane-3,2'-pyran]-4-one (**g13**)

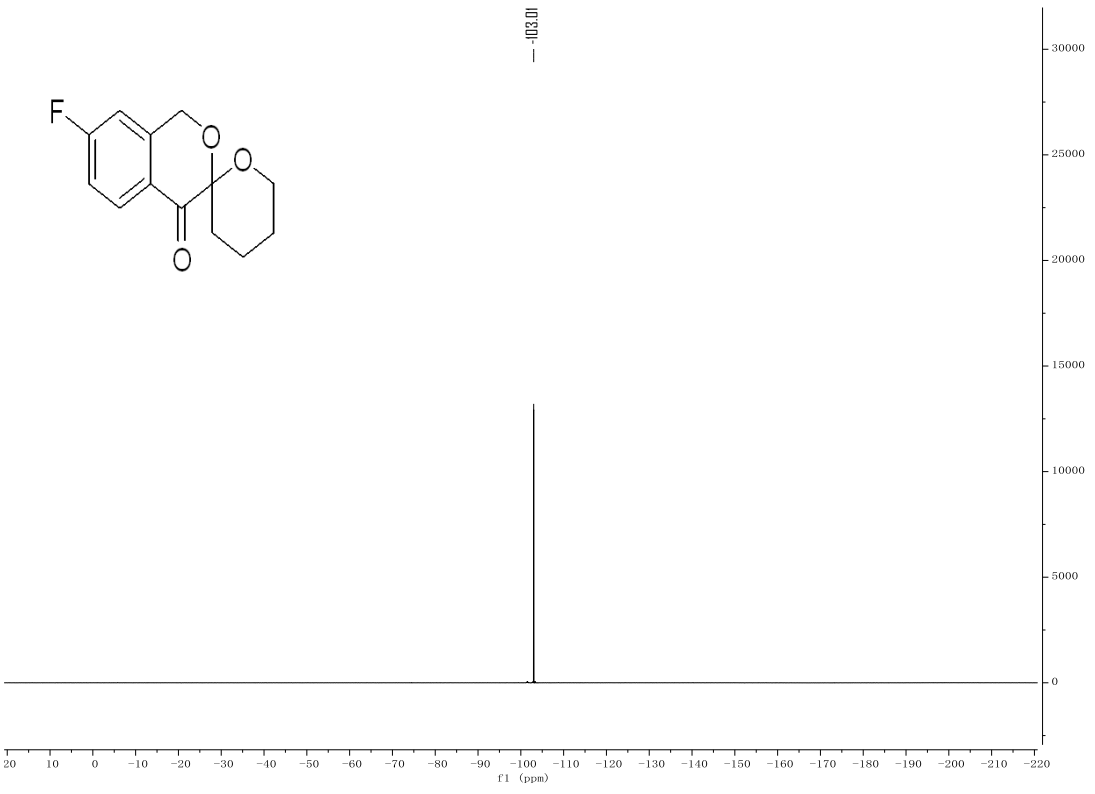


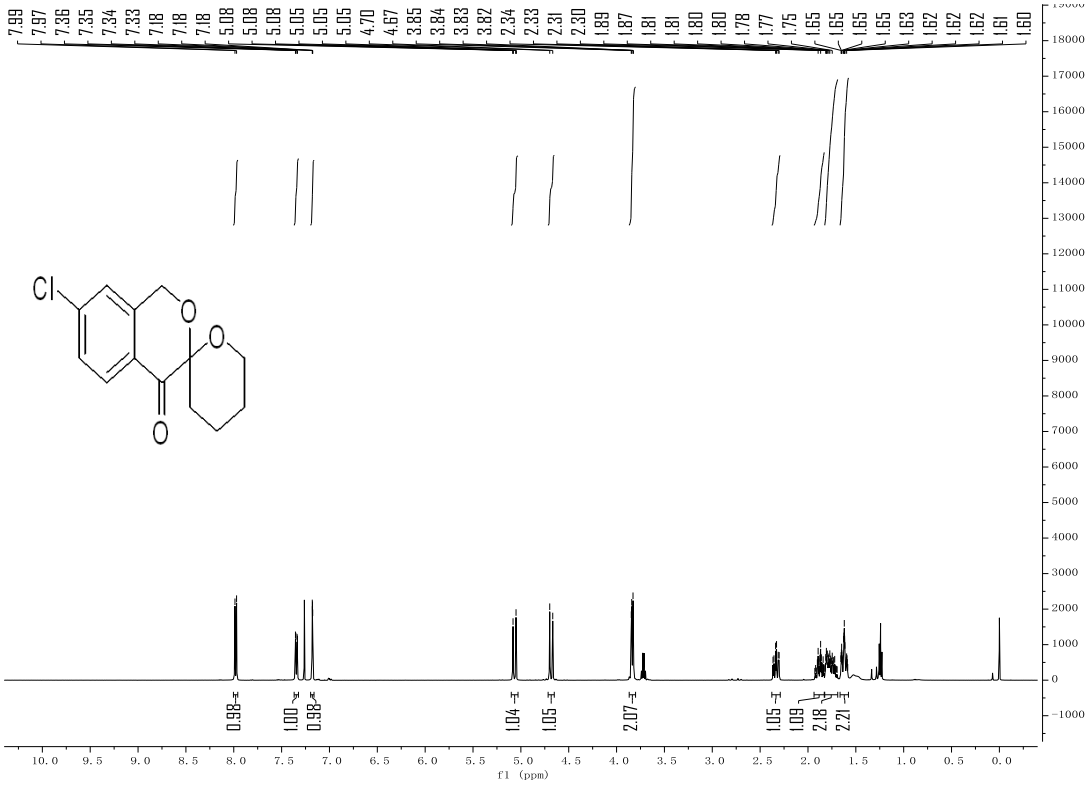
7-fluoro-3',4',5',6'-tetrahydrospiro[isochromane-3,2'-pyran]-4-one (**g14**)

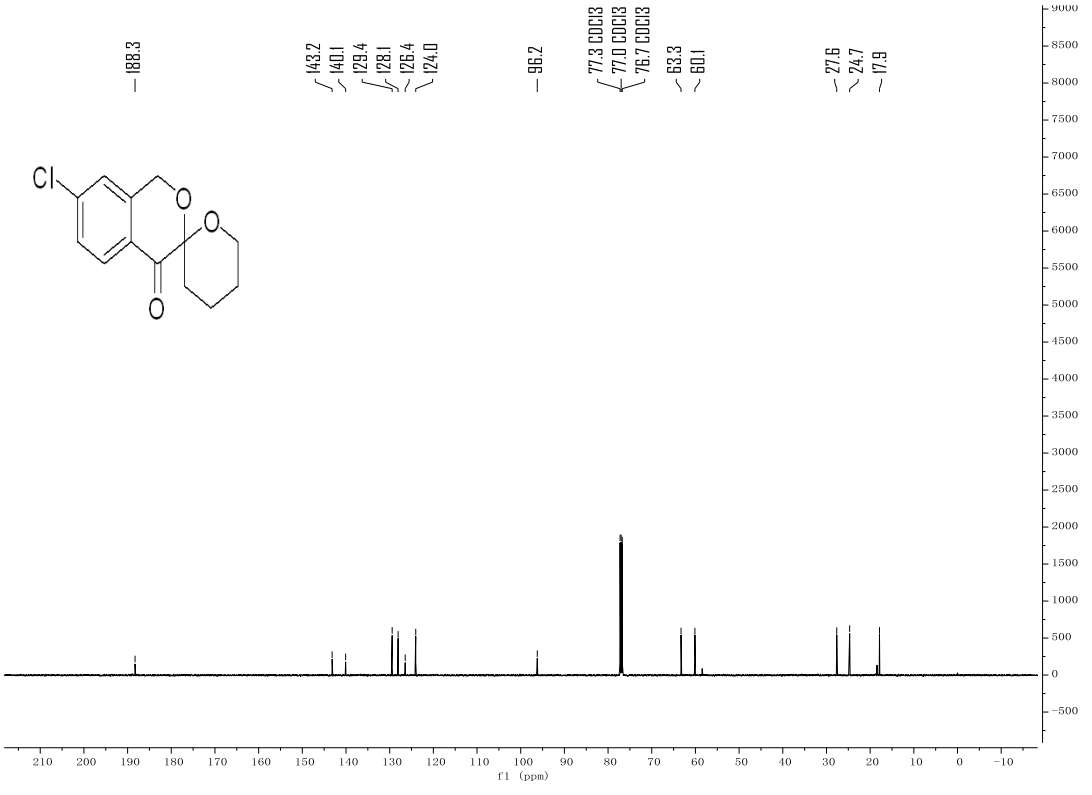


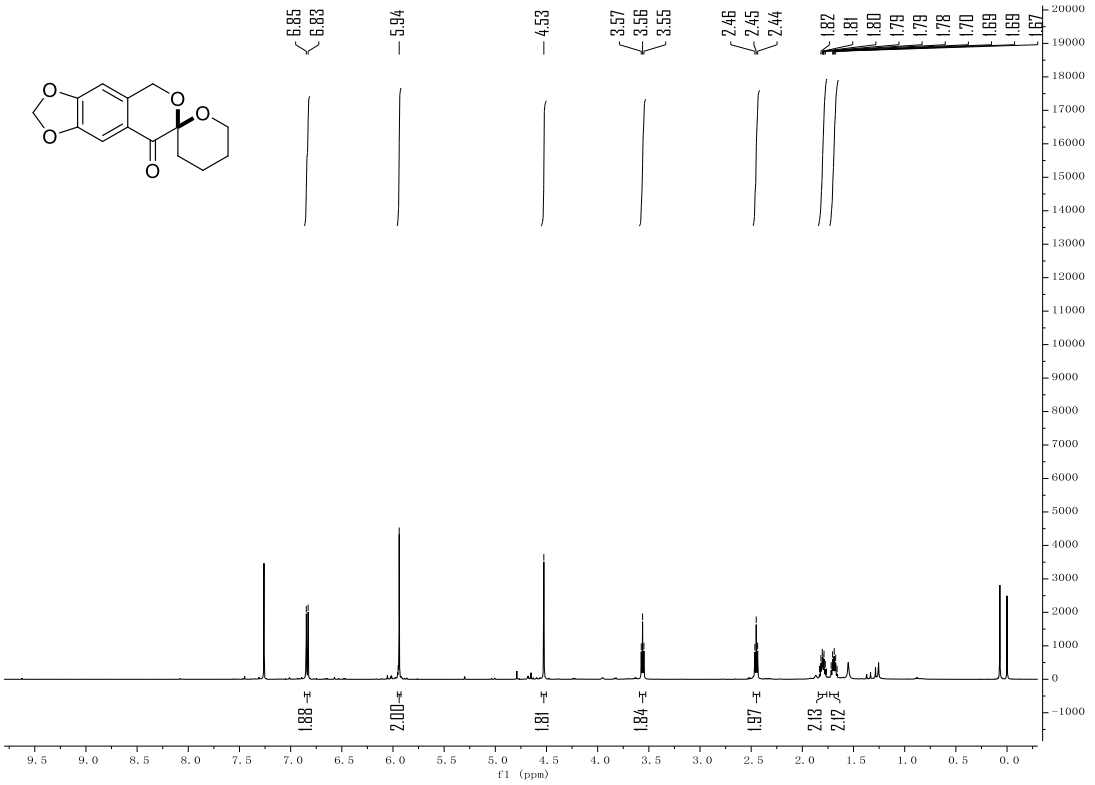

-103.01
F
O
O
O
30000
25000
20000
15000
10000
5000
0
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)

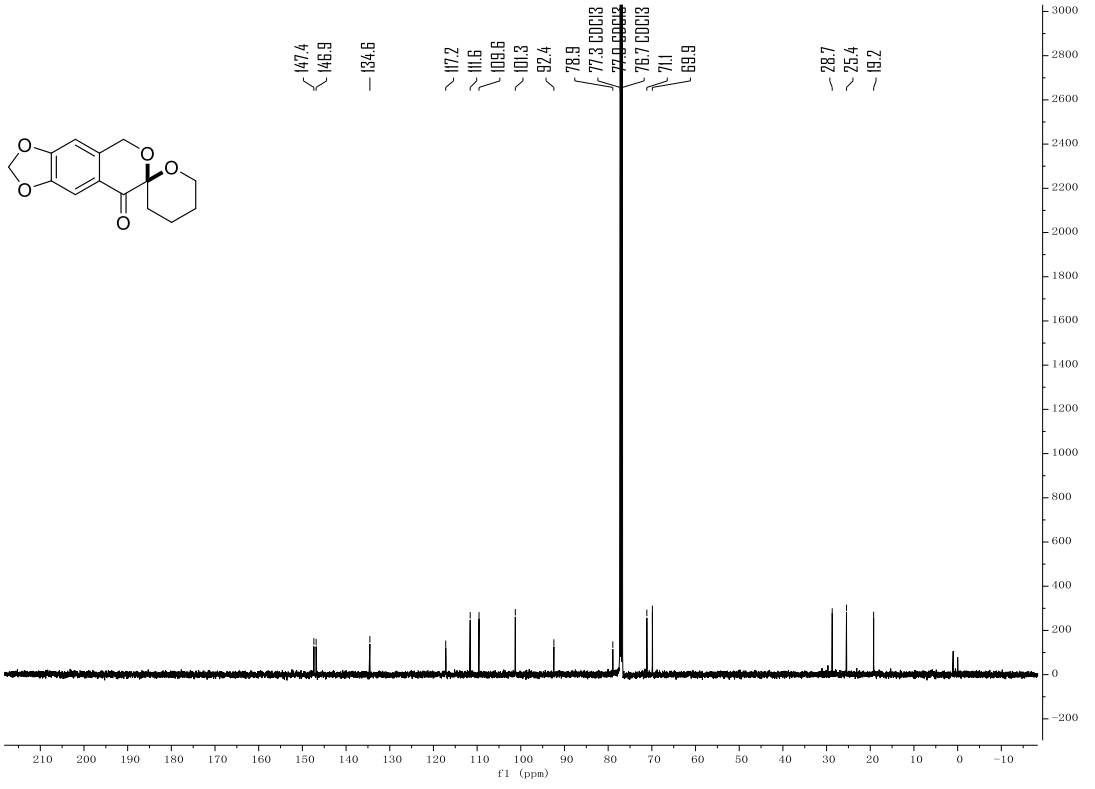
7-chloro-3',4',5',6'-tetrahydrospiro[isochromane-3,2'-pyran]-4-one (**g15**)



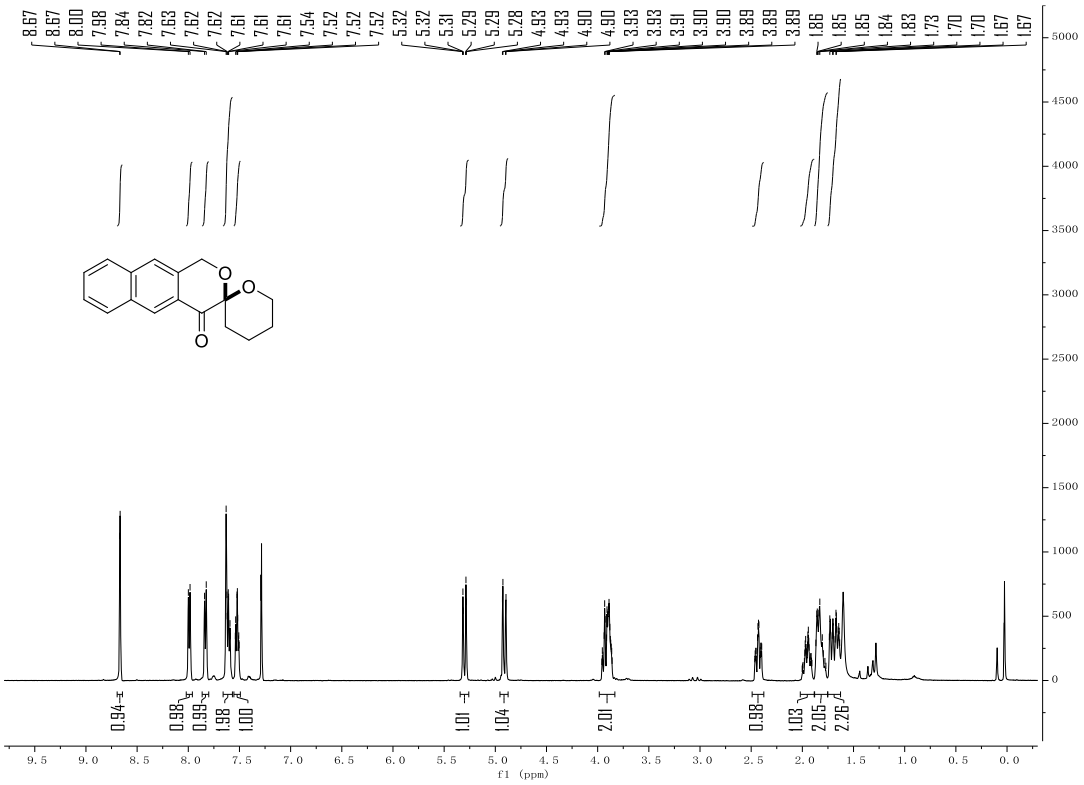



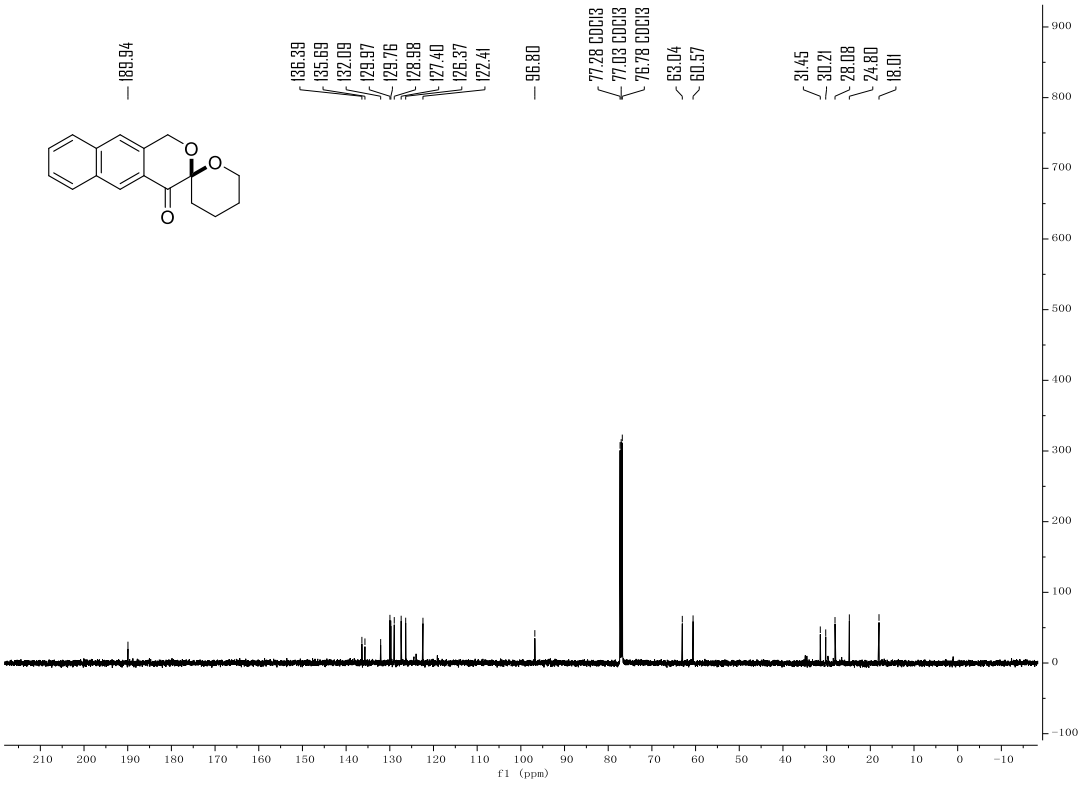
3,4,5,6-tetrahydrospiro[pyran-2,7'-[1,3]dioxolo[4,5-g]isochromen]-8'(5'H)-one (**g16**)



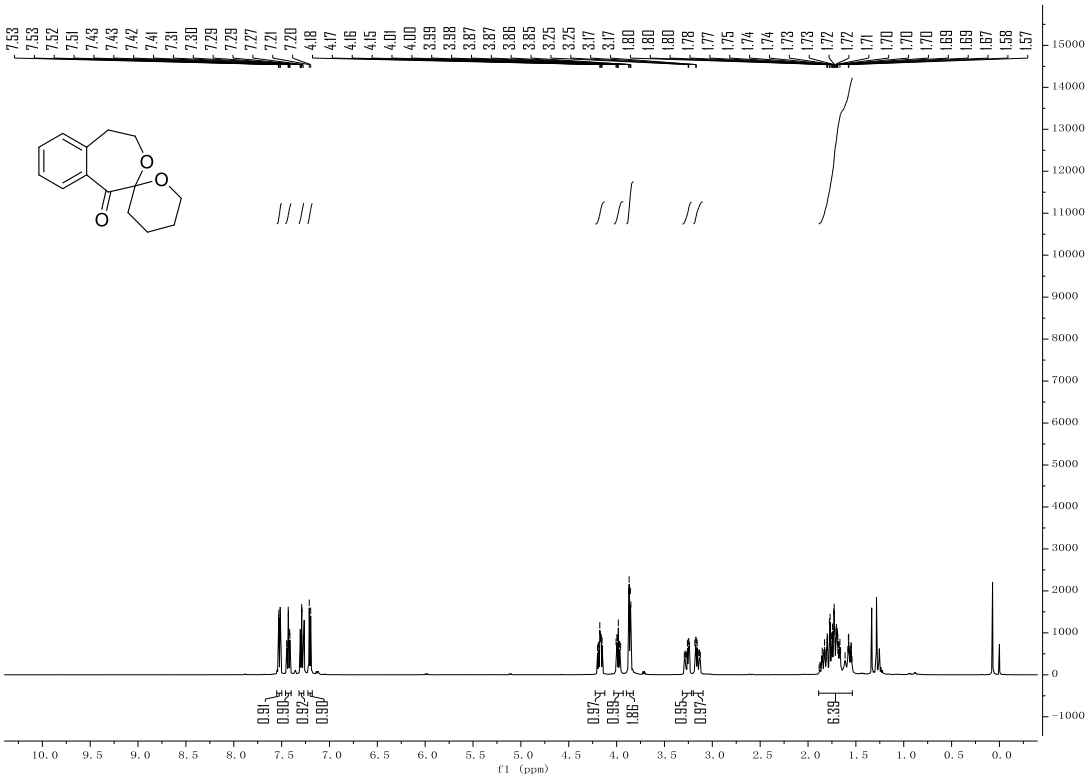



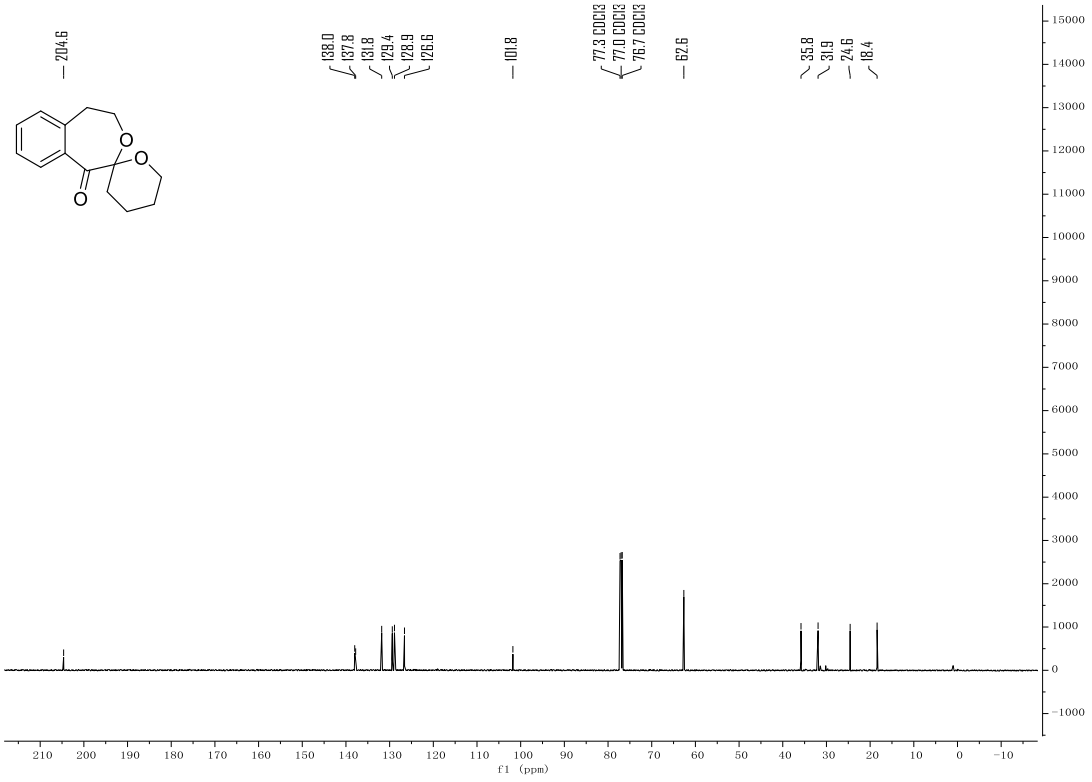
3',4',5',6'-tetrahydrospiro[benzo[g]isochromene-3,2'-pyran]-4(1H)-one (**g17**)



3',4,4',5,5',6'-hexahydro-1H-spiro[benzo[d]oxepine-2,2'-pyran]-1-one (**g18**)

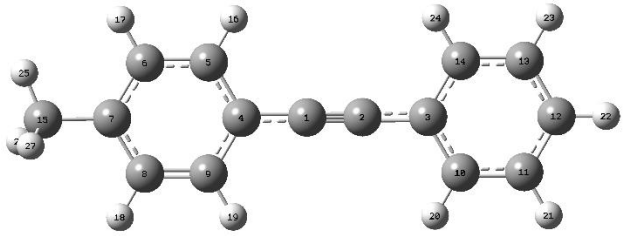




## 11. DFT Calculations

The effect of para-substituents were investigated using density functional theory (DFT) calculations in gas phase at the M06-2X/6-311G(d) level of the Gaussian 09 program.

(1) 1-methyl-4-(phenylethynyl)benzene (**d2**)

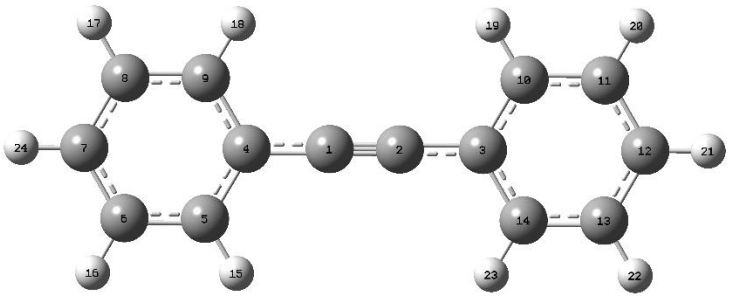


Summary of Natural Population Analysis:

| | | | Natural Population | | | |
|---|---|---|---|---|---|---|
| Atom | No | Natural Charge | Core | Valence | Rydberg | Total |
| C | 1 | 0.00963 | 1.99841 | 3.97898 | 0.01298 | 5.99037 |
| C | 2 | 0.00208 | 1.99841 | 3.98647 | 0.01303 | 5.99792 |
| C | 3 | -0.12900 | 1.99894 | 4.11699 | 0.01307 | 6.12900 |
| C | 4 | -0.13933 | 1.99893 | 4.12730 | 0.01310 | 6.13933 |
| C | 5 | -0.15217 | 1.99909 | 4.13846 | 0.01461 | 6.15217 |
| C | 6 | -0.20770 | 1.99906 | 4.19310 | 0.01554 | 6.20770 |
| C | 7 | -0.01580 | 1.99905 | 4.00301 | 0.01374 | 6.01580 |
| C | 8 | -0.20587 | 1.99905 | 4.19108 | 0.01574 | 6.20587 |
| C | 9 | -0.15223 | 1.99909 | 4.13863 | 0.01450 | 6.15223 |
| C | 10 | -0.16365 | 1.99909 | 4.14972 | 0.01483 | 6.16365 |
| C | 11 | -0.20014 | 1.99916 | 4.18493 | 0.01606 | 6.20014 |
| C | 12 | -0.19688 | 1.99917 | 4.18132 | 0.01640 | 6.19688 |
| C | 13 | -0.20013 | 1.99916 | 4.18492 | 0.01606 | 6.20013 |
| C | 14 | -0.16361 | 1.99909 | 4.14969 | 0.01483 | 6.16361 |
| C | 15 | -0.58782 | 1.99930 | 4.57800 | 0.01052 | 6.58782 |
| H | 16 | 0.21214 | 0.00000 | 0.78603 | 0.00184 | 0.78786 |
| H | 17 | 0.20474 | 0.00000 | 0.79299 | 0.00226 | 0.79526 |
| H | 18 | 0.20500 | 0.00000 | 0.79283 | 0.00216 | 0.79500 |
| H | 19 | 0.21208 | 0.00000 | 0.78609 | 0.00183 | 0.78792 |
| H | 20 | 0.21212 | 0.00000 | 0.78605 | 0.00183 | 0.78788 |
| H | 21 | 0.20686 | 0.00000 | 0.79197 | 0.00117 | 0.79314 |
| H | 22 | 0.20533 | 0.00000 | 0.79357 | 0.00110 | 0.79467 |
| H | 23 | 0.20687 | 0.00000 | 0.79196 | 0.00117 | 0.79313 |
| H | 24 | 0.21216 | 0.00000 | 0.78601 | 0.00183 | 0.78784 |
| H | 25 | 0.20338 | 0.00000 | 0.79544 | 0.00118 | 0.79662 |
| H | 26 | 0.21088 | 0.00000 | 0.78782 | 0.00129 | 0.78912 |

| | | | | | | |
|---|---|---|---|---|---|---|
| H | 27 | 0.21105 | 0.00000 | 0.78766 | 0.00130 | 0.78895 |
| * Total * | | 0.00000 | 29.98500 | 71.78101 | 0.23398 | 102.00000 |

(2) tolane (**a1**)

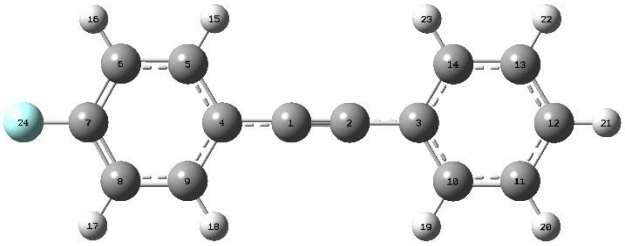



Summary of Natural Population Analysis:

| | | | Natural Population | | | |
|---|---|---|---|---|---|---|
| Atom | No | Natural Charge | Core | Valence | Rydberg | Total |
| C | 1 | 0.00681 | 1.99841 | 3.98177 | 0.01300 | 5.99319 |
| C | 2 | 0.00680 | 1.99841 | 3.98178 | 0.01300 | 5.99320 |
| C | 3 | -0.13030 | 1.99893 | 4.11830 | 0.01307 | 6.13030 |
| C | 4 | -0.13032 | 1.99893 | 4.11832 | 0.01307 | 6.13032 |
| C | 5 | -0.16275 | 1.99909 | 4.14883 | 0.01482 | 6.16275 |
| C | 6 | -0.20006 | 1.99916 | 4.18484 | 0.01606 | 6.20006 |
| C | 7 | -0.19567 | 1.99917 | 4.18012 | 0.01638 | 6.19567 |
| C | 8 | -0.20006 | 1.99916 | 4.18484 | 0.01606 | 6.20006 |
| C | 9 | -0.16274 | 1.99909 | 4.14882 | 0.01482 | 6.16274 |
| C | 10 | -0.16276 | 1.99909 | 4.14884 | 0.01482 | 6.16276 |
| C | 11 | -0.20006 | 1.99916 | 4.18484 | 0.01606 | 6.20006 |
| C | 12 | -0.19567 | 1.99917 | 4.18012 | 0.01638 | 6.19567 |
| C | 13 | -0.20006 | 1.99916 | 4.18484 | 0.01606 | 6.20006 |
| C | 14 | -0.16275 | 1.99909 | 4.14883 | 0.01482 | 6.16275 |
| H | 15 | 0.21237 | 0.00000 | 0.78580 | 0.00183 | 0.78763 |
| H | 16 | 0.20721 | 0.00000 | 0.79163 | 0.00116 | 0.79279 |
| H | 17 | 0.20721 | 0.00000 | 0.79162 | 0.00116 | 0.79279 |
| H | 18 | 0.21238 | 0.00000 | 0.78579 | 0.00183 | 0.78762 |
| H | 19 | 0.21237 | 0.00000 | 0.78580 | 0.00183 | 0.78763 |
| H | 20 | 0.20721 | 0.00000 | 0.79163 | 0.00116 | 0.79279 |
| H | 21 | 0.20562 | 0.00000 | 0.79328 | 0.00110 | 0.79438 |
| H | 22 | 0.20721 | 0.00000 | 0.79163 | 0.00116 | 0.79279 |
| H | 23 | 0.21238 | 0.00000 | 0.78579 | 0.00183 | 0.78762 |
| H | 24 | 0.20562 | 0.00000 | 0.79329 | 0.00110 | 0.79438 |

| | | | | | |
|---|---|---|---|---|---|
| * Total * | 0.00000 | 27.98604 | 65.79138 | 0.22259 | 94.00000 |

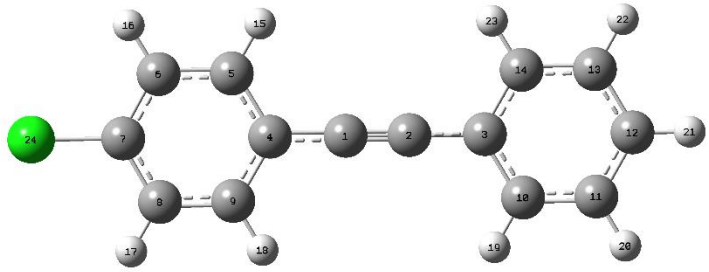
(3) 1-fluoro-4-(phenylethynyl)benzene (**d3**)



Summary of Natural Population Analysis:

| | | | Natural Population | | | |
|---|---|---|---|---|---|---|
| Atom | No | Natural Charge | Core | Valence | Rydberg | Total |
| C | 1 | 0.00242 | 1.99841 | 3.98615 | 0.01302 | 5.99758 |
| C | 2 | 0.01033 | 1.99841 | 3.97822 | 0.01304 | 5.98967 |
| C | 3 | -0.13130 | 1.99893 | 4.11931 | 0.01305 | 6.13130 |
| C | 4 | -0.14730 | 1.99894 | 4.13572 | 0.01264 | 6.14730 |
| C | 5 | -0.14321 | 1.99911 | 4.13004 | 0.01407 | 6.14321 |
| C | 6 | -0.27490 | 1.99906 | 4.26006 | 0.01577 | 6.27490 |
| C | 7 | 0.44016 | 1.99850 | 3.53473 | 0.02661 | 5.55984 |
| C | 8 | -0.27488 | 1.99906 | 4.26005 | 0.01577 | 6.27488 |
| C | 9 | -0.14321 | 1.99911 | 4.13003 | 0.01407 | 6.14321 |
| C | 10 | -0.16285 | 1.99909 | 4.14895 | 0.01481 | 6.16285 |
| C | 11 | -0.19956 | 1.99916 | 4.18434 | 0.01606 | 6.19956 |
| C | 12 | -0.19509 | 1.99917 | 4.17954 | 0.01638 | 6.19509 |
| C | 13 | -0.19956 | 1.99916 | 4.18434 | 0.01606 | 6.19956 |
| C | 14 | -0.16285 | 1.99909 | 4.14895 | 0.01481 | 6.16285 |
| H | 15 | 0.21691 | 0.00000 | 0.78139 | 0.00170 | 0.78309 |
| H | 16 | 0.22661 | 0.00000 | 0.77135 | 0.00204 | 0.77339 |
| H | 17 | 0.22661 | 0.00000 | 0.77135 | 0.00204 | 0.77339 |
| H | 18 | 0.21691 | 0.00000 | 0.78139 | 0.00170 | 0.78309 |
| H | 19 | 0.21228 | 0.00000 | 0.78589 | 0.00182 | 0.78772 |
| H | 20 | 0.20759 | 0.00000 | 0.79125 | 0.00116 | 0.79241 |
| H | 21 | 0.20604 | 0.00000 | 0.79287 | 0.00109 | 0.79396 |
| H | 22 | 0.20759 | 0.00000 | 0.79125 | 0.00116 | 0.79241 |
| H | 23 | 0.21229 | 0.00000 | 0.78589 | 0.00182 | 0.78771 |
| F | 24 | -0.35100 | 1.99992 | 7.34655 | 0.00453 | 9.35100 |
| * Total * | | 0.00000 | 29.98513 | 71.77962 | 0.23525 | 102.00000 |

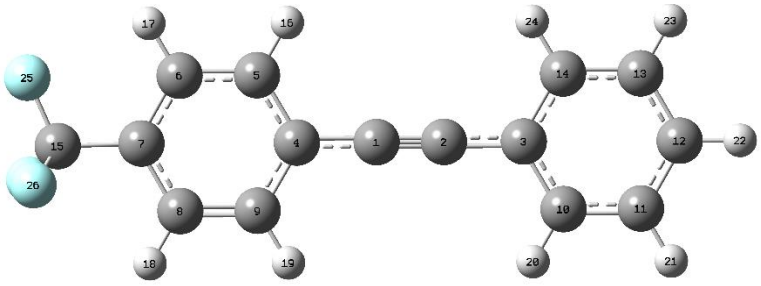
(4) 1-chloro-4-(phenylethynyl)benzene (**d4**)



Summary of Natural Population Analysis:

| Atom | No | Natural Charge | Natural Population | | | |
|---|---|---|---|---|---|---|
| | | | Core | Valence | Rydberg | Total |
| C | 1 | -0.00107 | 1.99841 | 3.98967 | 0.01298 | 6.00107 |
| C | 2 | 0.01729 | 1.99841 | 3.97132 | 0.01299 | 5.98271 |
| C | 3 | -0.13318 | 1.99893 | 4.12120 | 0.01304 | 6.13318 |
| C | 4 | -0.13186 | 1.99894 | 4.12007 | 0.01285 | 6.13186 |
| C | 5 | -0.14559 | 1.99909 | 4.13239 | 0.01411 | 6.14559 |
| C | 6 | -0.22744 | 1.99898 | 4.20998 | 0.01848 | 6.22744 |
| C | 7 | -0.02480 | 1.99858 | 4.00322 | 0.02299 | 6.02480 |
| C | 8 | -0.22744 | 1.99898 | 4.20998 | 0.01848 | 6.22744 |
| C | 9 | -0.14559 | 1.99909 | 4.13239 | 0.01411 | 6.14559 |
| C | 10 | -0.16160 | 1.99909 | 4.14771 | 0.01480 | 6.16160 |
| C | 11 | -0.19952 | 1.99916 | 4.18430 | 0.01606 | 6.19952 |
| C | 12 | -0.19348 | 1.99917 | 4.17795 | 0.01636 | 6.19348 |
| C | 13 | -0.19952 | 1.99916 | 4.18430 | 0.01606 | 6.19952 |
| C | 14 | -0.16160 | 1.99909 | 4.14771 | 0.01480 | 6.16160 |
| H | 15 | 0.21820 | 0.00000 | 0.78009 | 0.00171 | 0.78180 |
| H | 16 | 0.22494 | 0.00000 | 0.77287 | 0.00219 | 0.77506 |
| H | 17 | 0.22494 | 0.00000 | 0.77287 | 0.00219 | 0.77506 |
| H | 18 | 0.21820 | 0.00000 | 0.78009 | 0.00171 | 0.78180 |
| H | 19 | 0.21261 | 0.00000 | 0.78557 | 0.00182 | 0.78739 |
| H | 20 | 0.20803 | 0.00000 | 0.79082 | 0.00116 | 0.79197 |
| H | 21 | 0.20640 | 0.00000 | 0.79251 | 0.00109 | 0.79360 |
| H | 22 | 0.20803 | 0.00000 | 0.79082 | 0.00116 | 0.79197 |
| H | 23 | 0.21262 | 0.00000 | 0.78557 | 0.00182 | 0.78738 |
| Cl | 24 | 0.00145 | 9.99963 | 6.97876 | 0.02017 | 16.99855 |
| * Total * | | 0.00000 | 37.98471 | 71.76214 | 0.25315 | 110.00000 |

(5) 1-(phenylethynyl)-4-(trifluoromethyl)benzene (**d6**)




Summary of Natural Population Analysis:

| Atom | No | Natural Charge | Natural Population | | | |
|---|---|---|---|---|---|---|
| | | | Core | Valence | Rydberg | Total |
| C | 1 | -0.00675 | 1.99841 | 3.99532 | 0.01302 | 6.00675 |
| C | 2 | 0.02739 | 1.99841 | 3.96128 | 0.01292 | 5.97261 |
| C | 3 | -0.13601 | 1.99893 | 4.12405 | 0.01303 | 6.13601 |
| C | 4 | -0.11073 | 1.99894 | 4.09883 | 0.01296 | 6.11073 |
| C | 5 | -0.15577 | 1.99909 | 4.14207 | 0.01461 | 6.15577 |
| C | 6 | -0.18000 | 1.99908 | 4.16538 | 0.01553 | 6.18000 |
| C | 7 | -0.15654 | 1.99892 | 4.14095 | 0.01667 | 6.15654 |
| C | 8 | -0.17612 | 1.99909 | 4.16091 | 0.01612 | 6.17612 |
| C | 9 | -0.15553 | 1.99909 | 4.14183 | 0.01461 | 6.15553 |
| C | 10 | -0.15971 | 1.99909 | 4.14583 | 0.01479 | 6.15971 |
| C | 11 | -0.19942 | 1.99916 | 4.18419 | 0.01607 | 6.19942 |
| C | 12 | -0.19093 | 1.99917 | 4.17543 | 0.01634 | 6.19093 |
| C | 13 | -0.19942 | 1.99916 | 4.18420 | 0.01607 | 6.19942 |
| C | 14 | -0.15969 | 1.99909 | 4.14581 | 0.01479 | 6.15969 |
| C | 15 | 1.13084 | 1.99911 | 2.80802 | 0.06202 | 4.86916 |
| H | 16 | 0.21808 | 0.00000 | 0.78018 | 0.00174 | 0.78192 |
| H | 17 | 0.22659 | 0.00000 | 0.77147 | 0.00193 | 0.77341 |
| H | 18 | 0.22196 | 0.00000 | 0.77590 | 0.00214 | 0.77804 |
| H | 19 | 0.21845 | 0.00000 | 0.77981 | 0.00174 | 0.78155 |
| H | 20 | 0.21310 | 0.00000 | 0.78509 | 0.00181 | 0.78690 |
| H | 21 | 0.20874 | 0.00000 | 0.79012 | 0.00115 | 0.79126 |
| H | 22 | 0.20700 | 0.00000 | 0.79192 | 0.00108 | 0.79300 |
| H | 23 | 0.20873 | 0.00000 | 0.79012 | 0.00115 | 0.79127 |
| H | 24 | 0.21312 | 0.00000 | 0.78508 | 0.00181 | 0.78688 |
| F | 25 | -0.36986 | 1.99992 | 7.36569 | 0.00426 | 9.36986 |
| F | 26 | -0.36871 | 1.99992 | 7.36429 | 0.00450 | 9.36871 |
| F | 27 | -0.36879 | 1.99992 | 7.36437 | 0.00450 | 9.36879 |
| * Total * | | 0.00000 | 35.98450 | 89.71815 | 0.29735 | 126.00000 |

## 12. References

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[4] L. D. Caspers, J. Spils, M. Damrath, E. Lork, B. J. Nachtsheim, *J. Org. Chem.* **2020**, *85*, 9161.

[5] L. A. Aronica, L. Giannotti, S. Giuntini, A. M. Caporusso, *Eur. J. Org. Chem.* **2014**, 6858.