Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Exploiting *Ortho*-Substitution Effect on Formation of Oxygen-containing [10]Paracyclophane through Ring-Closing Metathesis

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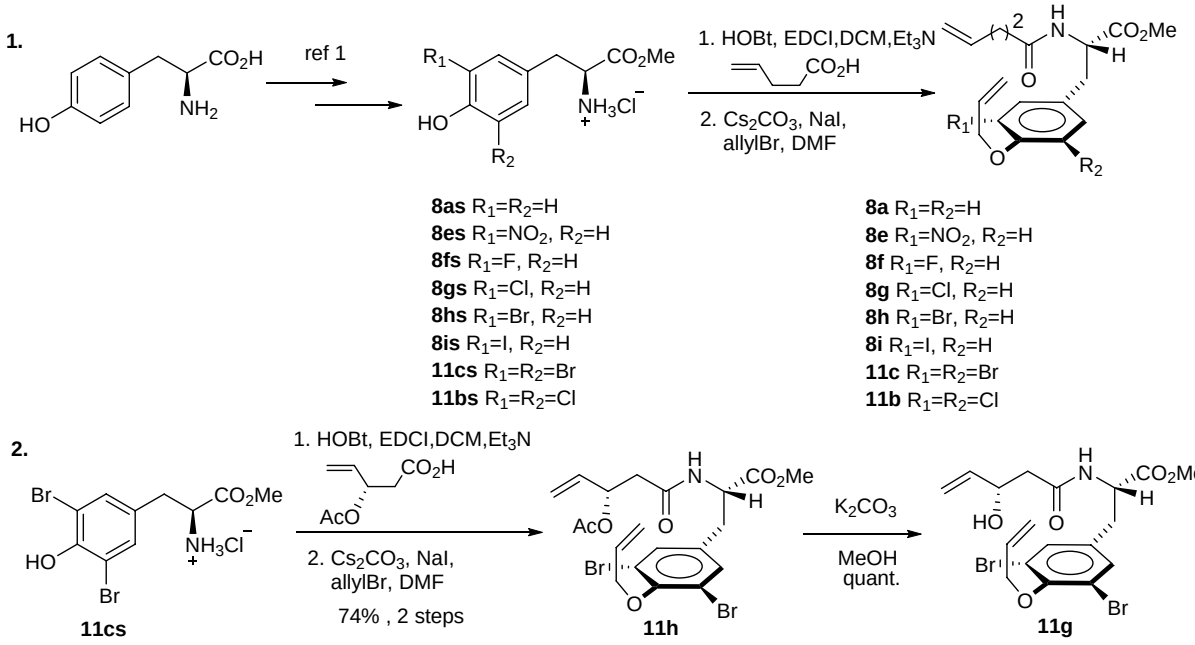
1. General Information

All reactions were carried out under an argon atmosphere with dry solvents under anhydrous conditions, unless otherwise noted. Dichloromethane was distilled from calcium hydride. All the chemicals were purchased commercially and used without further purification, unless otherwise stated. Flash chromatography was performed using silica gel (300-400 mesh). Reactions were monitored by thin layer chromatography (TLC). Visualization was achieved under a UV lamp (254 nm and 365 nm), I_2 and by developing the plates with *p*-anisaldehyde, phosphomolybdic acid (PMA) or Cerium Ammonium Molybdate (CAM). ^{1}H and ^{13}C NMR were recorded on Bruker DRX-400 MHz spectrometer with TMS as the internal standard and were calibrated using residual undeuterated solvent as an internal reference ($CDCl_3$: ^{1}H NMR = 7.26, ^{13}C NMR = 77.16; The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, *br* = broad. Coupling constants (*J*) are reported in Hertz (Hz). High resolution Mass spectra (HRMS) were recorded by using FTMS-7 spectrometers. Infrared (IR) spectra were recorded on a NEXUS 670 FT-IR Fourier Transform Infrared Spectrophotometer and are reported in wavenumbers (cm^{-1}).

2. Preparation of Starting Materials.

Method A: Starting from L-tyrosine, methyl ester hydrochloride was prepared according to the known procedure[1]. The corresponding amide was got under the condition of HOBt, EDCI and Et_3N. The phenolic hydroxyl group was protected under the condition of Cs_2CO_3， NaI， allylBr and DMF, affording the corresponding product.



8as $R_1=R_2=H$
8es $R_1=NO_2$, $R_2=H$
8fs $R_1=F$, $R_2=H$
8gs $R_1=Cl$, $R_2=H$
8hs $R_1=Br$, $R_2=H$
8is $R_1=I$, $R_2=H$
11cs $R_1=R_2=Br$
11bs $R_1=R_2=Cl$

8a $R_1=R_2=H$
8e $R_1=NO_2$, $R_2=H$
8f $R_1=F$, $R_2=H$
8g $R_1=Cl$, $R_2=H$
8h $R_1=Br$, $R_2=H$
8i $R_1=I$, $R_2=H$
11c $R_1=R_2=Br$
11b $R_1=R_2=Cl$

Compounds **8a**、**8e**、**8f**、**8g**、**8h**、**8i**、**11b**、**11c**、**11g**、**11h**、**11i** and **11j** were prepared according to this method.

General procedure:

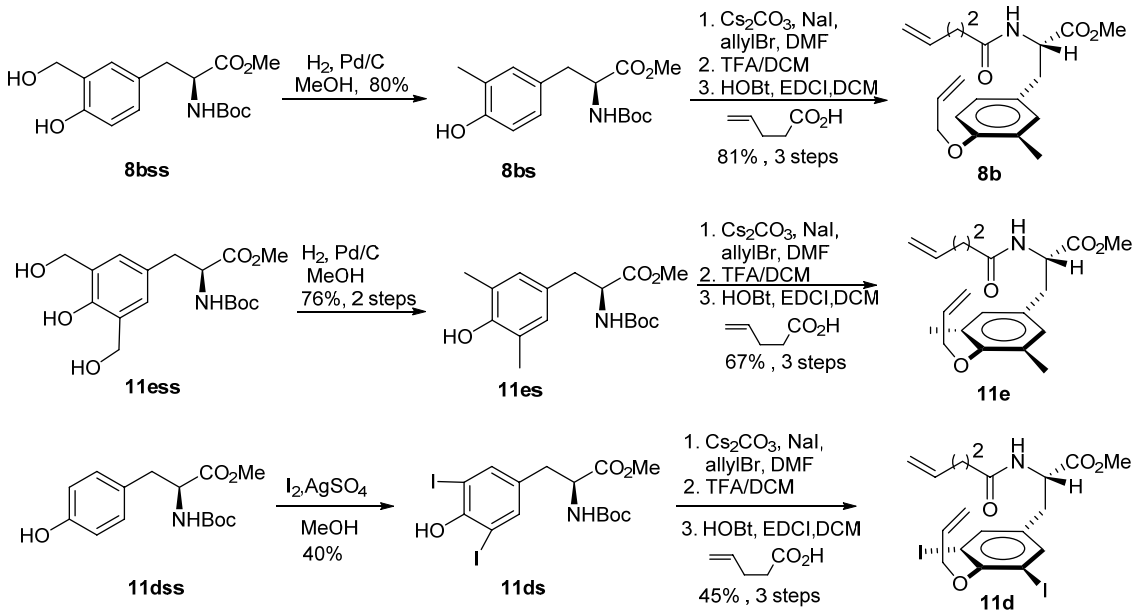
To the flask contained with the amino acid methyl ester (1.0 equiv), CH_2Cl_2 was added. Then Et_3N（3.0 equiv），EDCI（1.2 equiv），HOBt（1.2 equiv） and the corresponding carboxylic acid (1.1 equiv) were added sequentially at 0℃. The resulting mixture was warmed to rt. When TLC control showed the completion of the reaction, saturated $NaHCO_3$ solution was added. The layers were separated and the aqueous layer was extracted by CH_2Cl_2. The combined organic layers was dried over Na_2SO_4, filtered and concentrated to give the residue, which was purified by flash chromatography on silica gel to give the corresponding phenol.

To a solution of above phenol in DMF was added Cs_2CO_3 (1.2 equiv), NaI (0.1 equiv) and bromide (1.5 equiv) sequentially at rt. After stirring at rt. for 4h, saturated NH_4Cl solution was added at 0℃. The mixture was diluted with water and EtOAc. The layers were separated

and the aqueous layer was extracted by EtOAc. The combined organic layers was dried over Na_2SO_4, filtered and concentrated to give the residue, which was purified by flash chromatography on silica gel to give product (**8a**、**8e**、**8f**、**8g**、**8h**、**8i**、**11b**、**11c**、**11g**、**11h**、**11i** and **11j** with 30% - 85% yield).

Method B:

Starting from L-tyrosine, compounds **8c**、**8d** and **3** were prepared according to the known procedure[2]. Compounds **8b**、**11e** and **11d** were prepared from compound **8bs**、**11es** and **11ds** respectively following the procedure of allylation, deprotection of Boc with TFA and amidation with 4-pentenoic acid.



General procedure:

The procedure for allylation was similar with that in the method A.

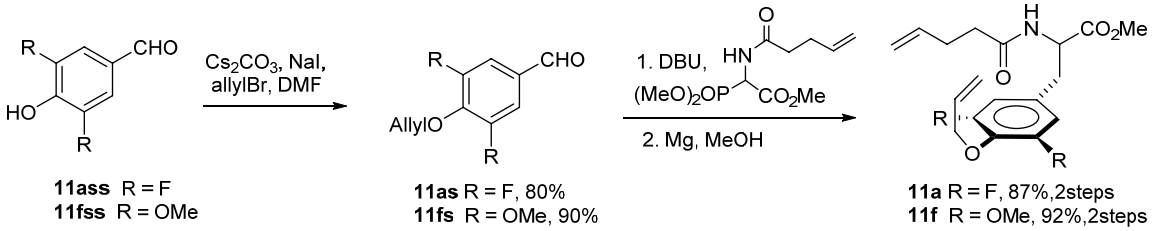
To a solution of the corresponding compound in CH_2Cl_2 was added TFA（1/5 V CH_2Cl_2）at 0 ℃. After stirring for 2h at rt, saturated $NaHCO_3$ solution was added at 0℃. The layers were separated and the aqueous layer was extracted by CH_2Cl_2. The combined organic layers was dried over Na_2SO_4, filtered and concentrated to give the crude product which was used in the next step directly.

To a solution of above crude product in CH_2Cl_2 was added EDCI（1.2 equiv），HOBt (1.2

equiv) and the corresponding carboxylic acid (1.1 equiv) sequentially at 0℃. The resulting mixture was warmed to rt. When TLC control showed the completion of the reaction, saturated $NaHCO_3$ solution was added. The layers were separated and the aqueous layer was extracted by CH_2Cl_2. The combined organic layers was dried over Na_2SO_4, filtered and concentrated to give the residue, which was purified by flash chromatography on silica gel to give the corresponding products (**8b**、**11e** and **11d** with 45% - 67% yield over three steps).

Method C:

Due to the difficulty of substitution of tyrosine, **11a** and **11f** were prepared from the corresponding aldehydes **11ass**[3] and **11fss**.



11ass R = F
11fss R = OMe

11as R = F, 80%
11fs R = OMe, 90%

11a R = F, 87%,2steps
11f R = OMe, 92%,2steps

General procedure:

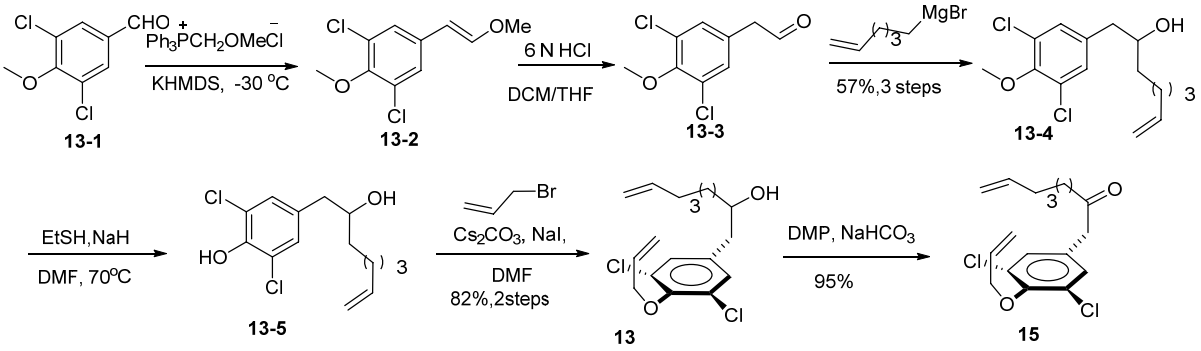
The procedure for allylation was similar with that in the method A.

To a solution of WHE reagent (1.0 equiv) in CH_2Cl_2 was added DBU (1.1 equiv) at rt. Then a solution of the aldehydes **11as** or **11fs** (1.0 equiv) in CH_2Cl_2 was added after 10min. When TLC control showed the completion of the reaction, the reaction mixture concentrated to give the residue, which was purified by flash chromatography on silica gel to give the corresponding product.

To a solution of above product in MeOH, was added Mg (1.0 equiv) at 0℃. After stirring for 3h at 0℃, the reaction mixture was added to saturated NH_4Cl solution. Then, MeOH was removed under reduced pressure, the aqueous layer was extracted with EtOAc and the combined organic layers were dried over Na_2SO_4, filtered and concentrated to give the residue, which was purified by flash chromatography on silica gel to give the corresponding compounds **11a** or **11f** as a white solid.

Method D:

Compounds **13** and **15** were prepared according to the procedure as below.



General procedure:

To a suspension of Ph_3PCH_2OMeCl (3.3 equiv) in THF was added NaHMDS (2.0 M in THF, 2.8 equiv) at -30℃. After stirring at 0℃ for 20 min, the reaction mixture was cooled to -30℃ and a solution of **13-1** in THF was added. The reaction was warmed to rt slowly and stirred at rt. overnight, then quenched with saturated NH_4Cl solution. The aqueous layer was extracted with EtOAc and the combined organic layers were dried over Na_2SO_4, filtrated and concentrated to the crude product which was purified by column chromatography to get the corresponding enol ether **13-2**.

To a solution of **13-2** in DCM/THF (3/1) was added 6 N aq. HCl and stirred at room temperature. When TLC control showed the completion of the reaction, saturated $NaHCO_3$ solution was added. The layers were separated and the aqueous layer was extracted by CH_2Cl_2. The combined organic layers was dried over Na_2SO_4, filtered and concentrated to give the crude product **13-3** which was used in the next step directly.

To a solution of **13-3** in THF was added Grignard reagent (1.0 M in THF, 2.5 equiv) at -78℃. The reaction mixture was warmed to rt slowly and stirred for 3h. then quenched with saturated NH_4Cl solution. The aqueous layer was extracted with EtOAc and the combined organic layers were dried over Na_2SO_4, filtered and concentrated to give the crude product which was purified by flash chromatography on silica gel to get the compound **13-4** with 57% yield over 3 steps.

To a suspension of NaH (20 equiv) in DMF was added EtSH (20 equiv) at 0℃. After 10 min,

a solution of **13-4** in DMF was added. The reaction mixture was stirred at 70℃ for 12h, then quenched with saturated NH_4Cl solution. The aqueous layer was extracted with EtOAc and the combined organic layers were dried over Na_2SO_4, filtrated and concentrated to the give the crude product which was purified by flash chromatography on silica gel to get the compound **13-5**.

To a solution of **13-5** in DMF was added $CsCO_3$ (1.2 equiv), NaI(0.1 equiv) and bromide (1.5 equiv) sequentially at rt. The reaction mixture was stirred at rt. for 4h, then quenched with saturated NH_4Cl solution at 0℃, diluted with water and EtOAc. The layers were separated and the aqueous layer was extracted by CH_2Cl_2. The combined organic layers were dried over Na_2SO_4, filtrated and concentrated to give the crude product which was purified by flash chromatography on silica gel to get compound **13** with 82% yield over 2 steps.

To a solution of **13** (1.0 equiv) in DCM was added $NaHCO_3$ (4 equiv) and Dess-Martin reagent (1.5 equiv) at 0℃. The reaction mixture was stirred at rt. for 1h, then quenched with saturated Na_2SO_3 solution and diluted with DCM. The layers were separated and the aqueous layer was extracted by CH_2Cl_2. The combined organic layers were dried over Na_2SO_4, filtrated and concentrated to give the crude product which was purified by flash chromatography on silica gel to give compound **15** with 95% yield.

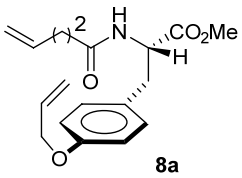
Reference:

1. (a) Pietro, A.; Paola, O.; Mario, A. *J Label Compd Radiopharm* **2004**, *47*: 935–945; (b) Mo`nica, P.; Silvia, M.; Katy, R.; Paul, L.; Ernest, G. *J. Org. Chem.* **2007**, *72*, 1047; (c) Bertold, D. B.; Anita, H. L.; Carroll, F. *J. Label Compd. Radiopharm* **2008**, *51* 440–443; (d) James, R. C.; Jonathan, M. W.; Uta, W.; Craig, A. H. *Org. Lett*. **2012**, *14*, 2402-2405.
2. Huang, M.; Song, L.; Liu, B. *Org. Lett.***2010**, *12*, 2504-2507.
3. Lawrence, J.; Hepworth, A.; Rennison, D.; McGownc, T.; Hadfield, A. *Journal of Fluorine Chemistry* **2003**, *123*, 101–108.

3. General Procedure for RCM reaction.

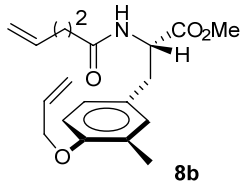
To a flame-dried flask was added the starting material (0.1 mmol), cat. (15 mol %) and CH_2Cl_2 (250 mL). The mixture was heated to reflux for 18 hours, then another 10 mol % cat. was added (If TLC control showed the completion of the reaction, the reaction was stopped). The resultant mixture was allowed to reflux until TLC analysis showed the complete consumption of the starting material. After that, the solvent was evaporated and the crude residue was purified by flash column chromatography on silica gel to afford the corresponding product. The diastereoselectivity was determined by ^{1}H NMR of crude products (obtained by filtration of the crude reaction mixture through silica gel).

4. Characterization of starting materials.



8a

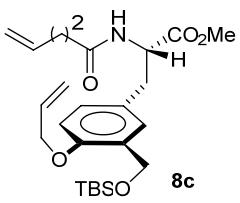
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.98 (d, *J* = 8.8 Hz, 2H), 6.82 (d, *J* = 8.4 Hz, 2H), 6.11 – 5.91 (m, 2H)，5.77 (ddt, *J* = 16.8, 10.4, 6.4 Hz, 1H), 5.39 (d, *J* = 17.2 Hz, 1H), 5.26 (d, *J* = 10.4 Hz, 1H), 5.02 (d, *J* = 17.2 Hz, 1H), 4.97 (d, *J* = 10.4 Hz, 1H), 4.84 (dt, *J* = 7.2, 6.0 Hz, 1H), 4.49 (d, *J* = 5.2 Hz, 2H), 3.70 (s, 3H), 3.07 (dd, *J* = 14.0, 6.0 Hz, A of AB, 1H), 3.00 (dd, *J* = 14.0, 6.0 Hz, B of AB, 1H), 2.43 - 2.30 (m, 2H), 2.30 - 2.15 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.28, 171.88, 157.80, 136.94, 133.30, 130.31, 128.04, 117.74, 115.70, 114.84, 68.84, 53.18, 52.36, 37.09, 35.62, 29.41. **[α]**$_D^{32}$ = +73.3 (*c* 0.72, CH_2Cl_2). **HRMS** (ESI) m/z calcd. for $C_{18}H_{23}NNaO_4$, $[M + Na]^+$ 340.1519, found 340.1523. **IR** (thin film): 3300, 2925, 2849, 1744, 1651, 1511, 1440, 1369, 1244, 1176, 1123, 1023, 919 cm^{-1}.



8b

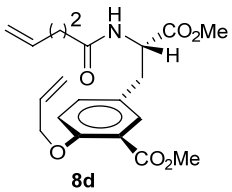
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.84 (s, 1H), 6.83 (d, *J* = 8.8 Hz, 1H), 6.69 (d, *J* = 8.0 Hz, 1H), 6.21 – 5.93 (m, 2H), 5.76 (ddt, *J* = 16.8, 10.0, 6.4 Hz, 1H), 5.40 (dd, *J* = 17.2, 1.6 Hz, 1H), 5.24 (dd, *J* = 10.4, 1.2 Hz, 1H), 5.02 (dd, *J* = 17.2, 1.6 Hz, 1H), 4.96 (d, *J* = 10.0, 1H) 4.81 (dt, *J* = 7.6, 6.0 Hz, 1H), 4.48 (d, *J* = 4.8 Hz, 2H), 3.70 (s, 3H), 3.02 (dd, *J* = 14.0, 6.0 Hz, A of AB, 1H), 2.95 (dd, *J* = 14.0, 6.0 Hz, B of AB, 1H), 2.45 – 2.30 (m, 2H), 2.30 – 2.22 (m, 2H), 2.19 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.35, 171.92, 155.88, 136.91, 133.54, 131.69,

127.54, 127.32, 127.00, 116.94, 115.60, 111.26, 68.68, 53.22, 52.24, 37.02, 35.56, 29.42, 16.29. **[α]** $_D^{32}$ = +73 (*c* 0.88, CH_2Cl_2). **HRMS** (ESI) m/z calcd. for $C_{19}H_{26}NO_4$, $[M + H]^+$ 332.1856, found 332.1859. **IR** (thin film): 3300, 3076, 2926, 2858, 1744, 1652, 1539, 1505, 1441, 1373, 1254, 1219, 1134, 1024, 998, 918, 807 cm^{-1}.



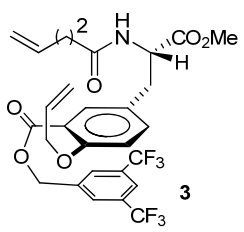
8c

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (s, 1H), 6.90 (d, *J* = 8.0 Hz, 1H), 6.71 (d, *J* = 8.4 Hz, 1H), 6.12 – 5.87 (m, 2H), 5.77 (ddt, *J* = 16.4, 10.4, 6.0 Hz, 1H), 5.37 (d, *J* = 17.2 Hz, 1H), 5.25 (d, *J* = 10.4 Hz, 1H), 5.02 (d, *J* = 17.2 Hz, 1H), 4.96 (d, *J* = 10.4 Hz, 1H), 4.85 (dt, *J* = 7.6, 5.6 Hz, 1H), 4.74 (s, 2H), 4.51 (d, *J* = 4.4 Hz, 2H), 3.71 (s, 3H), 3.19 – 2.90 (m, 2H), 2.44 – 2.30 (m, 2H), 2.30 – 2.11 (m, 2H), 0.94 (s, 9H), 0.10 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.27, 171.84, 154.18, 136.95, 133.42, 130.25, 128.14, 127.84, 127.68, 117.17, 115.63, 110.98, 68.71, 60.07, 53.14, 52.34, 37.32, 35.60, 29.40, 26.10, 18.55, -5.23. **[α]** $_D^{33}$ = +43.7 (*c* 0.67, CH_2Cl_2). **HRMS** (ESI) m/z calcd. for $C_{25}H_{38}NO_5Si$, $[M - H]^-$ 460.2525, found 460.2524. **IR** (thin film): 3327, 2972, 2929, 1745, 1654, 1499, 1442, 1378, 1251, 1214, 1132, 1085, 1049, 839, 778 cm^{-1}.



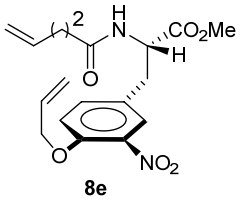
8d

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 2.0 Hz, 1H), 7.13 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.82 (d, *J* = 8.4 Hz, 1H), 6.22 (d, *J* = 6.8 Hz, 1H), 5.98 (ddt, *J* = 17.2, 11.2, 4.8 Hz, 1H), 5.71 (ddt, *J* = 16.8, 10.4, 6.4 Hz, 1H), 5.43 (dd, *J* = 17.2, 1.6 Hz, 1H), 5.22 (dd, *J* = 10.8, 1.6 Hz, 1H), 4.96 (dd, *J* = 17.2, 1.6 Hz, 1H), 4.91 (d, *J* = 10.0 Hz, 1H), 4.78 (dt, *J* = 7.2, 6.0 Hz, 1H), 4.53 (d, *J* = 4.4 Hz, 2H), 3.81 (s, 3H), 3.66 (s, 3H), 3.04 (dd, *J* = 14.0, 5.6 Hz, A of AB, 1H), 2.94 (dd, *J* = 14.0, 6.0 Hz, B of AB, 1H), 2.40 – 2.25 (m, 2H), 2.25 – 2.12 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.98, 171.93, 166.39, 157.20, 136.81, 134.04, 132.59, 132.56, 127.86, 120.18, 117.30, 115.54, 113.71, 69.39, 53.05, 52.30, 51.93, 36.74, 35.40, 29.31. **[α]**$_D^{31}$ = +55.4 (*c* 1.2, CH_2Cl_2). **HRMS** (ESI) m/z calcd. for $C_{20}H_{24}NO_6$, $[M - H]^-$ 374.1609, found 374.1600. **IR** (thin film): 3380, 2928, 1728, 1550, 1442, 1256, 1202, 1085, 813 cm^{-1}.



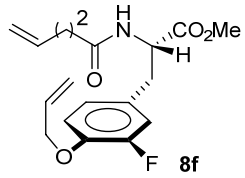
3

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (s, 2H), 7.84 (s, 1H), 7.57 (d, *J* = 2.0 Hz, 1H), 7.21 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.90 (d, *J* = 8.8 Hz, 1H), 6.12 – 5.88 (m, 2H), 5.75 (ddt, *J* = 16.4, 10.0, 6.0 Hz, 1H), 5.43 (s, 1H), 5.39 (dd, *J* = 17.6, 1.2 Hz, 1H), 5.24 (dd, *J* = 10.8, 1.6 Hz, 1H), 5.11 – 4.91 (m, 2H), 4.86 (dt, *J* = 7.6, 5.6 Hz, 1H), 4.61 (d, *J* = 5.2 Hz, 1H), 3.70 (s, 2H), 3.12 (dd, *J* = 14.0, 6.0 Hz, 1H), 3.03 (dd, *J* = 14.0, 5.8 Hz, 1H), 2.45 – 2.30 (m, 2H), 2.30 – 2.13 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.06, 171.94, 166.00, 157.58, 138.88, 136.90, 134.86, 132.95, 132.46, 132.04 (q, *J* = 33 Hz), 128.13 (m), 128.11, 123.30 (q, *J* = 271 Hz), 122.16 (m), 119.50, 117.99, 115.81, 113.79, 69.63, 65.11, 53.13, 52.49, 36.96, 35.67, 29.44. **[α]**$_D^{18}$ = 47.7 (*c* 0.6, CH_2Cl_2). **HRMS** (ES) *m/z* calcd for $C_{28}H_{28}F_6NO_6$ $[M + H]^+$ 588.1821; found 588.1818. **IR** (thin film):3300, 3073, 2953, 1747, 1700, 1647, 1283, 1176, 1127, 995, 892 cm^{-1}.



8e

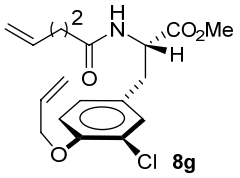
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 2.0 Hz, 1H), 7.26 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.98 (d, *J* = 8.4 Hz, 1H), 6.13 (s, 1H), 6.01 (ddd, *J* = 16.0, 10.8, 5.2 Hz, 1H), 5.77 (ddd, *J* = 16.8, 10.4, 6.4 Hz, 1H), 5.46 (d, *J* = 17.2 Hz, 1H), 5.31 (dd, *J* = 10.4, 1.2 Hz, 1H), 5.01 (dd, *J* = 17.2, 10.4 Hz, 2H), 4.86 (dt, *J* = 6.8, 6.0 Hz, 1H), 4.64 (d, *J* = 4.8 Hz, 2H), 3.74 (s, 3H), 3.16 (dd, *J* = 14.0, 6.0 Hz, A of AB, 1H), 3.03 (dd, *J* = 14.0, 6.0 Hz, B of AB, 1H), 2.43 – 2.31 (m, 2H), 2.32 – 2.23 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.07, 171.79, 151.14, 139.67, 136.80, 134.92, 131.73, 128.73, 126.49, 118.49, 115.91, 115.12, 70.16, 53.03, 52.71, 36.78, 35.61, 29.39. **[α]** $_D^{32}$ = +64.8 (*c* 0.99, CH_2Cl_2). **HRMS** (ESI) m/z calcd. for $C_{18}H_{22}N_2NaO_6$, $[M + Na]^+$ 385.1370, found 385.1374. **IR** (thin film): 3318, 1747, 1643, 1530, 1113 cm^{-1}.



8f

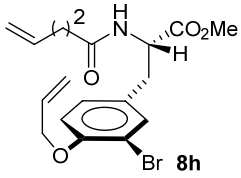
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.90 – 6.69 (m, 3H), 6.14 (d, *J* = 7.6 Hz, 1H), 6.01 (ddt, *J* = 16.4, 10.8, 5.6 Hz, 1H), 5.75 (dtd, *J* = 16.4, 6.0, 4.4 Hz, 1H), 5.38 (d, *J* = 17.6 Hz, 1H), 5.26 (d, *J* = 10.4 Hz, 1H), 4.99 (dd, *J* = 17.2, 10.0 Hz, 2H), 4.81 (dt, *J* = 7.2, 6.0 Hz, 1H), 4.54 (d, *J* = 5.6 Hz, 2H), 3.70 (s, 3H), 3.04 (dd, *J* = 14.0, 6.0 Hz, 1H), 2.95 (dd, *J* = 14.0, 5.6 Hz, 1H), 2.38 – 2.28 (m, 2H), 2.29 – 2.18 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.07, 171.94, 152.58 (d, *J* = 245 Hz), 145.75 (d, *J* = 10 Hz), 136.90, 132.89, 129.30 (d, *J* = 6 Hz), 124.99 (d, *J* = 3 Hz),

118.32, 117.26 (d, J = 18 Hz), 115.88, 115.45 (d, J = 2 Hz), 70.31, 53.10, 52.53, 37.09, 35.69, 29.44. **[α]** $_D^{32}$ = +51.2 (*c* 0.33, CH_2Cl_2). **HRMS** (ESI) m/z calcd. for $C_{18}H_{23}FNO_4$, $[M + H]^+$ 336.1606, found 336.1607. **IR** (thin film): 3295, 2923, 1740, 1649, 1514, 1269, 1088, 627 cm^{-1}.



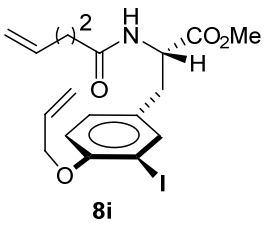
8g

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (d, J = 1.6 Hz, 1H), 6.91 (dd, J = 8.4, 1.6 Hz, 1H), 6.82 (d, J = 8.4 Hz, 1H), 6.04 (m, 2H), 5.78 (ddt, J = 16.4, 12.0, 5.6 Hz, 1H), 5.44 (d, J = 17.2 Hz, 1H), 5.29 (d, J = 10.4 Hz, 1H), 5.04 (d, J = 17.6, 1H), 4.99 (d, J = 10.0 Hz, 1H), 4.83 (dt, J = 7.2, 6.0 Hz, 1H), 4.57 (d, J = 5.2 Hz, 2H), 3.72 (s, 3H), 3.06 (dd, J = 14.0, 6.0 Hz, A of AB, 1H), 2.97 (dd, J = 14.0, 6.0 Hz, B of AB, 1H), 2.45 – 2.31 (m, 2H), 2.31 – 2.15 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.1, 172.0, 153.27, 136.89, 132.67, 131.23, 129.29, 128.39, 122.95, 117.99, 115.86, 113.77, 69.79, 53.11, 52.50, 36.86, 35.66, 29.45. **[α]** $_D^{32}$ = +74.1 (*c* 0.86, CH_2Cl_2). **HRMS** (ESI) m/z calcd. for $C_{18}H_{22}ClNNaO_4$, $[M + Na]^+$ 374.1130, found 374.1138. **IR** (thin film): 3297, 3077, 2926, 1744, 1652, 1538, 1500, 1442, 1369, 1286, 1256, 1211, 995 cm^{-1}.



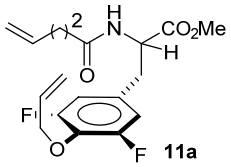
8h

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (d, J = 2.0 Hz, 1H), 6.96 (dd, J = 8.4, 2.0 Hz, 1H), 6.79 (d, J = 8.4 Hz, 1H), 6.17 – 5.91 (m, 2H), 5.78 (ddt, J = 16.4, 10.4, 6.4 Hz, 1H), 5.46 (d, J = 17.6 Hz, 1H), 5.29 (d, J = 10.4 Hz, 1H), 5.05 (d, J = 17.2 Hz, 1H), 5.00 (d, J = 10.4 Hz, 1H), 4.83 (dt, J = 7.6, 6.0 Hz, 1H), 4.56 (d, J = 4.8 Hz, 2H), 3.73 (s, 3H), 3.06 (dd, J = 14.0, 6.0 Hz, A of AB, 1H), 2.97 (dd, J = 14.0, 5.6 Hz, B of AB, 1H), 2.45 – 2.32 (m, 2H), 2.32 – 2.17 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.05, 171.95, 154.17, 136.90, 134.30, 132.63, 129.73, 129.15, 117.90, 115.91, 113.55, 112.24, 69.80, 53.15, 52.52, 36.78, 35.69, 29.48. **[α]** $_D^{32}$ = +66.1 (*c* 1.2, CH_2Cl_2). **HRMS** (ESI) m/z calcd. for $C_{18}H_{22}BrNNaO_4$, $[M + Na]^+$ 418.0624, found 418.0623. **IR** (thin film): 3295, 3077, 2926, 1743, 1652, 1540, 1496, 1441, 1368, 1285, 1255, 1049, 996, 921 cm^{-1}.



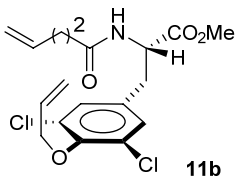
8i

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 2.0 Hz, 1H), 6.99 (dd, *J* = 8.3, 2.0 Hz, 1H), 6.69 (d, *J* = 8.4 Hz, 1H), 6.19 – 5.91 (m, 2H), 5.78 (ddt, *J* = 16.8, 10.4, 6.4 Hz, 1H), 5.49 (d, *J* = 17.2 Hz, 1H), 5.29 (d, *J* = 10.4 Hz, 1H), 5.04 (d, *J* = 17.2, 1H), 4.99 (d, *J* = 10.4 Hz, 1H),4.82 (dt, *J* = 7.6, 5.6 Hz, 1H), 4.54 (d, *J* = 4.4 Hz, 2H), 3.72 (s, 3H), 3.04 (dd, *J* = 14.0, 5.6 Hz, A of AB, 1H), 2.95 (dd, *J* = 14.0, 5.6 Hz, B of AB, 1H), 2.46 – 2.31 (m, 2H), 2.31 – 2.19 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.04, 171.93, 156.38, 140.36, 136.90, 132.55, 130.27, 130.15, 117.74, 115.89, 112.33, 86.64, 69.78, 53.16, 52.50, 36.56, 35.66, 29.49. **[α]** $_D^{32}$ = +57.9 (*c* 1.2, CH_2Cl_2). **HRMS** (ESI) m/z calcd. for $C_{18}H_{22}INNaO_4$, $[M + Na]^+$ 466.0486, found 466.0492. **IR** (thin film): 3291, 3106, 1743, 1650, 1603, 1582, 1538, 1489, 1410, 1336, 1095, 627 cm^{-1}.



11a

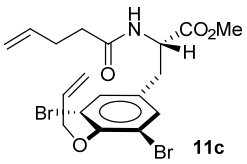
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.76 – 6.49 (m, 2H), 6.17 – 5.90 (m, 2H), 5.79 (ddt, *J* = 16.8, 10.0, 6.0 Hz, 1H), 5.30 (dd, *J* = 17.2, 10.4 Hz, 2H), 5.03 (dd, *J* = 19.2, 10.8 Hz, 2H), 4.84 (dd, *J* = 7.2, 5.6 Hz, 1H), 4.61 (d, *J* = 6.0 Hz, 2H), 3.74 (s, 3H), 3.08 (dd, *J* = 14.0, 6.0 Hz, A of AB, 1H), 2.99 (dd, *J* = 14.0, 5.6 Hz, B of AB, 1H), 2.44 – 2.33 (m, 2H), 2.33 – 2.17 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.01, 171.77, 155.96 (dd, *J* = 247, 6 Hz), 136.83, 134.03 (t, *J* = 14 Hz), 133.13, 131.73 (t, *J* = 8.0 Hz), 119.24, 116.04, 113.08 (dd, *J* = 17, 7.0 Hz), 75.13, 52.95, 52.68, 37.31, 35.69, 29.43. **HRMS** (ESI) m/z calcd. for $C_{18}H_{21}F_2NNaO_4$, $[M + Na]^+$ 376.1331, found 376.1341. **IR** (thin film): 2927, 1619, 1401, 1078 cm^{-1};



11b

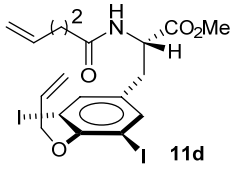
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.02 (s, 2H), 6.26 – 5.97 (m, 2H), 5.79 (ddt, *J* = 16.8, 10.4, 6.4 Hz, 1H), 5.40 (d, *J* = 17.2 Hz, 1H), 5.27 (d, *J* = 10.4 Hz, 1H), 5.14 – 4.93 (m, 2H), 4.83 (dt, *J* = 7.2, 5.6 Hz, 1H), 4.52 (d, *J* = 5.6 Hz, 2H), 3.74 (s, 3H), 3.08 (dd, *J* = 14.0, 6.0 Hz, A of AB, 1H), 2.97 (dd, *J* = 14.0, 5.6 Hz, B of AB, 1H), 2.44 – 2.34 (m, 2H), 2.34 – 2.22 (m, 2H). **^{13}C NMR** (100MHz, $CDCl_3$) δ 172.05, 171.71, 150.30, 136.82, 133.67, 133.03, 129.74, 129.54, 118.90,

116.05, 74.42, 52.97, 52.67, 36.87, 35.67, 29.48. **[α]**$_D^{33}$ = +60.3 (*c* 1.6, CH_2Cl_2). **HRMS** (ESI) m/z calcd. for $C_{18}H_{22}Cl_2NO_4$, $[M + H]^+$ 386.0920, found 386.0928. **IR** (thin film): 3293, 3071, 2953, 1736, 1647, 1538, 1470, 1429, 1256, 1090, 1021, 979, 922, 865, 801 cm^{-1}.



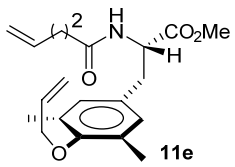
11c

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (s, 2H), 6.28 (d, *J* = 7.6 Hz, 1H), 6.12 (ddd, *J* = 16.8, 11.2, 6.0 Hz, 1H), 5.76 (ddd, *J* = 16.8, 10.8, 6.0 Hz, 1H), 5.41 (d, *J* = 16.8 Hz, 1H), 5.26 (d, *J* = 10.4 Hz, 1H), 5.12 – 4.90 (m, 2H), 4.80 (dt, *J* = 7.2, 6.0 Hz, 1H), 4.48 (d, *J* = 6.0 Hz, 2H), 3.72 (s, 3H), 3.05 (dd, *J* = 14.0, 5.6 Hz, A of AB, 1H), 2.93 (dd, *J* = 14.0, 6.0 Hz, B of AB, 1H), 2.41 – 2.31 (m, 2H), 2.31 – 2.21 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.08, 171.68, 152.10, 136.78, 134.88, 133.46, 132.89, 118.73, 118.35, 115.94, 74.12, 52.97, 52.60, 36.52, 35.55, 29.46. **[α]** $_D^{33}$ = +57.2 (c 1.2, CH_2Cl_2). **HRMS** (ESI) m/z calcd. for $C_{18}H_{20}Br_2NO_4$, $[M – H]^-$ 471.9765, found 471.9759. **IR** (thin film): 3288, 3075, 2927, 1735, 1647, 1540, 1448, 1374, 1260, 1201, 1125, 982, 921, 868, 739 cm^{-1}.



11d

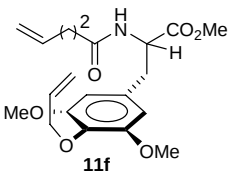
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (s, 2H), 6.17 (ddd, *J* = 16.0, 10.8, 5.6 Hz, 1H), 6.10 (d, *J* = 7.2 Hz, 1H), 5.81 (ddt, *J* = 16.8, 10.4, 6.4 Hz, 1H), 5.49 (d, *J* = 17.2 Hz, 1H), 5.31 (d, *J* = 10.4 Hz, 1H), 5.16 – 4.95 (m, 2H), 4.81 (dt, *J* = 6.8, 6.0 Hz, 1H), 4.47 (d, *J* = 5.6 Hz, 2H), 3.75 (s, 3H), 3.04 (dd, *J* = 13.6, 5.6 Hz, A of AB, 1H), 2.94 (dd, *J* = 14.0, 5.6 Hz, B of AB, 1H), 2.49 – 2.35 (m, 2H), 2.35 – 2.19 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.03, 171.67, 156.95, 140.75, 136.87, 136.00, 132.91, 118.89, 116.20, 91.08, 73.97, 53.11, 52.71, 36.12, 35.77, 29.59. **[α]** $_D^{33}$ = +50.4 (*c* 1.2, CH_2Cl_2). **HRMS** (ESI) m/z calcd. for $C_{18}H_{22}I_2NO_4$, $[M + H]^+$ 569.9633, found 569.9635. **IR** (thin film): 3353, 2974, 2927, 1732, 1646, 1544, 1441, 1384, 1264, 1089, 1049, 881 cm^{-1}.



11e

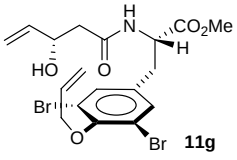
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.72 (s, 2H), 6.08 (ddd, *J* = 16.0, 10.4, 5.6 Hz, 1H), 5.97 (d, *J* = 7.6 Hz, 1H), 5.78 (ddt, *J* = 16.8, 10.4, 6.0 Hz, 1H), 5.41 (dd, *J* = 17.2, 1.2 Hz, 1H), 5.24 (dd, *J* = 10.4, 1.2 Hz, 1H),

5.03 (dd, *J* = 17.2, 1.2 Hz, 2H), 4.98 (d, *J* = 10.0, Hz, 1H), 4.82 (dt, *J* = 7.6, 6.0 Hz, 1H), 4.27 (d, *J* = 5.6 Hz, 2H), 3.71 (s, 3H), 3.01 (dd, *J* = 14.0, 6.0 Hz, A of AB, 1H), 2.95 (dd, *J* = 14.0, 6.0 Hz, B of AB, 1H), 2.39 – 2.31 (m, 2H), 2.31 – 2.24 (m, 2H), 2.22 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.36, 171.96, 155.11, 136.95, 134.13, 131.15, 129.70(2C), 117.24, 115.76, 73.18, 53.18, 52.33, 37.25, 35.71, 29.51, 16.48. **[α]** $_D^{32}$ = +64.9 (c 0.90, CH_2Cl_2). **HRMS** (ESI) m/z calcd. for $C_{20}H_{28}NO_4$, $[M + H]^+$ 346.2013, found 346.2013. **IR** (thin film): 3410, 2925, 1742, 1646, 1497, 1414, 1337 cm^{-1}.



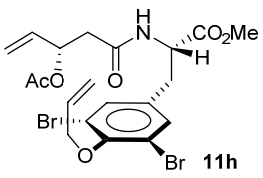
11f

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.26 (s, 2H), 6.09 (d, *J* = 7.6 Hz, 1H), 6.02 (ddt, *J* = 16.4, 10.0, 6.0 Hz, 1H), 5.72 (ddt, *J* = 16.8, 10.4, 6.4 Hz, 1H), 5.24 (dd, *J* = 17.2, 1.6 Hz, 1H), 5.11 (dd, *J* = 10.4, 1.2 Hz, 1H), 4.97 (dd, *J* = 17.2, 1.2 Hz, 1H), 4.92 (d, *J* = 10.0 Hz, 1H), 4.82 (dt, *J* = 8.0, 6.0 Hz, 1H), 4.43 (d, *J* = 6.0 Hz, 2H), 3.75 (s, 6H), 3.66 (s, 3H), 3.10 – 2.87 (m, 2H), 2.36 – 2.27 (m, 2H), 2.27 – 2.16 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.14, 171.84, 153.36, 136.71, 135.65, 134.45, 131.58, 117.59, 115.64, 106.15, 74.06, 56.04, 53.00, 52.25, 38.18, 35.52, 29.36. **HRMS** (ESI) m/z calcd. for $C_{20}H_{27}NNaO_6$, $[M + Na]^+$ 400.1731, found 400.1736. **IR** (thin film): 3296, 2924, 1742,1647, 1540, 1451, 1377, 1256, 1201, 1024, 949 cm^{-1};

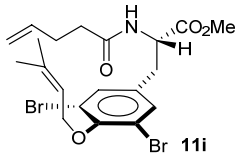


11g

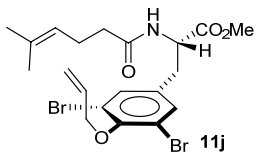
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (s, 2H), 6.68 (d, *J* = 7.2 Hz, 1H), 6.25 – 6.03 (m, 1H), 5.87 (ddd, *J* = 16.4, 10.4, 5.6 Hz, 1H), 5.43 (dd, *J* = 17.2, 1.6 Hz, 1H), 5.29 (dd, *J* = 17.2, 10.0 Hz, 2H), 5.16 (d, *J* = 10.4 Hz, 1H), 4.82 (dt, *J* = 7.6, 5.6 Hz, 1H), 4.57 – 4.39 (m, 3H), 3.74 (s, 3H), 3.39 (br, 1H), 3.08 (dd, *J* = 14.0, 5.2 Hz, 1H), 2.96 (dd, *J* = 14.0, 6.0 Hz, 1H), 2.49 (dd, *J* = 11.2, 3.2 Hz, 1H), 2.38 (dd, *J* = 15.2, 8.4 Hz, 1H).**^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.47, 171.32, 152.20, 139.20, 134.75, 133.57, 132.94, 118.83, 118.42, 115.68, 74.20, 69.67, 53.07, 52.71, 42.52, 36.52. **[α]**$_D^{29}$ = +50.0 (*c* 0.68, CH_2Cl_2). **HRMS** (ESI) m/z calcd. for $C_{18}H_{22}Br_2NO_5$, $[M + H]^+$ 489.9859, found 489.9865. **IR** (thin film): 3409, 2926, 1738, 1643, 1499, 1413, 1337, 1259, 1094, 869 cm^{-1}.



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (d, *J* = 2.0 Hz, 2H), 6.35 (d, *J* = 7.2 Hz, 1H), 6.15 (ddt, *J* = 16.0, 10.4, 5.6 Hz, 1H), 5.83 (ddd, *J* = 16.8, 10.8, 6.0 Hz, 1H), 5.58 (dt, *J* = 6.8, 6.0, 6.0 Hz, 1H), 5.44 (dd, *J* = 17.2, 1.2 Hz, 1H), 5.36 – 5.24 (m, 2H), 5.21 (d, *J* = 10.4 Hz, 1H), 4.80 (dd, *J* = 7.2, 6.0 Hz, 1H), 4.51 (d, *J* = 6.0 Hz, 2H), 3.74 (s, 3H), 3.06 (dd, *J* = 14.0, 6.0 Hz, A of AB, 1H), 2.98 (dd, *J* = 14.0, 5.6 Hz, B of AB, 1H), 2.67 – 2.48 (m, 2H), 2.06 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.49, 169.92, 168.77, 152.27, 134.97, 134.81, 133.43, 132.95, 118.83, 118.52, 117.72, 74.21, 71.25, 53.18, 52.69, 41.25, 36.59, 21.21. **[α]**$_D^{29}$ = +23.1 (*c* 0.24, CH_2Cl_2). **HRMS** (ESI) m/z calcd. for $C_{20}H_{24}Br_2NO_6$, $[M + H]^+$ 531.9965, found 531.9969. **IR** (thin film): 3363, 2957, 2928, 2860, 1732, 1677, 1546, 1374, 1260, 1120, 1025, 803 cm^{-1}.

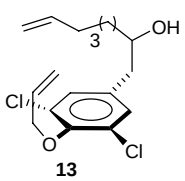


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (s, 2H), 6.17 (d, *J* = 7.6 Hz, 1H), 5.78 (ddt, *J* = 16.8, 10.4, 6.4 Hz, 1H), 5.60 (t, *J* = 7.2 Hz, 1H), 5.15 – 4.92 (m, 2H), 4.81 (dt, *J* = 7.2, 5.6 Hz, 1H), 4.48 (d, *J* = 7.2 Hz, 2H), 3.73 (s, 3H), 3.06 (dd, *J* = 14.0, 5.6 Hz, A of AB, 1H), 2.95 (dd, *J* = 13.9, 5.6 Hz, B of AB, 1H), 2.42 – 2.32 (m, 2H), 2.32 – 2.21 (m, 2H), 1.78 (s, 3H), 1.72 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.05, 171.69, 152.28, 139.82, 136.80, 134.64, 133.45, 119.36, 118.63, 116.01, 70.06, 53.02, 52.62, 36.56, 35.63, 29.49, 25.93, 18.22. **[α]**$_D^{29}$ = +62.6 (*c* 1.0, CH_2Cl_2). **HRMS** (ESI) m/z calcd. for $C_{20}H_{26}Br_2NO_4$, $[M + H]^+$ 502.0223, found 502.0228. **IR** (thin film):2923, 1739, 1645, 1539, 1447, 1383, 1042 cm^{-1}.



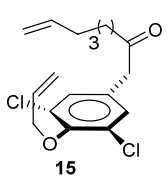
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (s, 2H), 6.15 (ddt, *J* = 16.0, 10.4, 5.6 Hz, 1H), 6.06 (d, *J* = 7.2 Hz, 1H), 5.44 (dd, *J* = 17.2, 1.2 Hz, 1H), 5.29 (dd, *J* = 10.4, 1.2 Hz, 1H), 5.15 – 4.98 (m, 1H), 4.83 (dt, *J* = 7.2, 5.6 Hz, 1H), 4.52 (d, *J* = 5.6 Hz, 2H), 3.74 (s, 3H), 3.07 (dd, *J* = 14.0, 6.0 Hz, A of AB, 1H), 2.99 (dd, *J* = 14.0, 5.2 Hz, B of AB, 1H), 2.38 – 2.27 (m, 2H), 2.27 – 2.14 (m, 2H), 1.68 (s, 3H), 1.61 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.52, 171.66, 152.27, 134.92, 133.79, 133.55, 133.02, 122.54, 118.83, 118.49, 74.23, 53.08, 52.65, 36.72, 36.62, 25.86, 24.22,

17.90; **[α]** $_D^{17}$ = -1.2 (*c* 0.61, CH_2Cl_2); **HRMS** (ESI) m/z calcd. for $C_{20}H_{26}Br_2NO_4$, $[M + H]^+$ 502.0223, found 502.0227. **IR** (thin film): 2938, 1741, 1656, 1595, 1507, 1459, 1424, 1243, 1124, 1037 cm^{-1}.



13

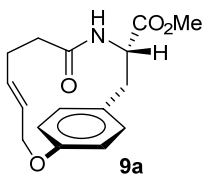
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (s, 2H), 6.15 (ddt, *J* = 16.4, 10.8, 6.0 Hz, 1H), 5.80 (ddt, *J* = 17.2, 10.4, 6.8 Hz, 1H), 5.43 (dd, *J* = 17.2, 1.2 Hz, 1H), 5.28 (d, *J* = 10.4 Hz, 1H), 5.09 – 4.83 (m, 2H), 4.54 (d, *J* = 5.6 Hz, 2H), 3.91 – 3.63 (m, 1H), 2.72 (dd, *J* = 13.6, 4.0 Hz, A of AB, 1H), 2.56 (dd, *J* = 13.6, 8.4 Hz, B of AB, 1H), 2.07 (dt, *J* = 7.6, 6.0 Hz, 2H), 1.54 – 1.32 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 149.70, 138.84, 136.54, 133.19, 129.76, 129.38, 118.83, 114.66, 74.43, 72.32, 42.91, 36.92, 33.77, 28.88, 25.22. **HRMS** (ESI) m/z calcd. for $C_{17}H_{22}Cl_2NaO_2$, $[M + Na]^+$ 351.0895, found 351.0895. **IR** (thin film): 3412, 3078, 2927, 1640, 1552, 1470, 1415, 1365, 1264, 1087, 984, 915, 799, 629 cm^{-1}.



15

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (s, 2H), 6.14 (ddt, *J* = 16.4, 10.8, 5.6 Hz, 1H), 5.77 (ddt, *J* = 17.2, 10.0, 6.8 Hz, 1H), 5.42 (d, *J* = 16.8 Hz, 1H), 5.28 (d, *J* = 10.4 Hz, 1H), 5.08 – 4.83 (m, 2H), 4.54 (d, *J* = 5.6 Hz, 2H), 3.59 (s, 2H), 2.47 (t, *J* = 7.2 Hz, 2H), 2.03 (q, *J* = 6.8 Hz, 2H), 1.67 – 1.52 (m, 2H), 1.44 – 1.28 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 206.96, 150.25, 138.42, 133.09, 131.66, 129.91, 129.64, 118.90, 114.90, 74.44, 48.37, 42.39, 33.55, 28.36, 23.19. **HRMS** (ESI) m/z calcd. for $C_{17}H_{20}Cl_2NaO_2$, $[M + Na]^+$ 349.0738, found 349.0745. **IR** (thin film): 3078, 2929, 2858, 1641, 1553, 1471, 1415, 1265, 1082, 984, 914, 799 cm^{-1}.

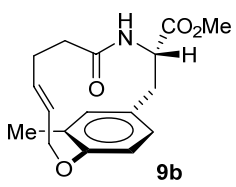
5. Characterization of product.



9a

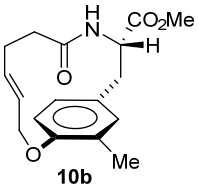
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.92 – 6.82 (m, 2H), 6.78 (dd, *J* = 8.4, 2.4 Hz, 1H), 5.38 (d, *J* = 10.4 Hz, 1H), 5.25 (ddd, *J* = 15.2, 8.0, 6.8 Hz, 1H), 5.13 (ddd, *J* = 14.4, 8.8, 4.8 Hz, 1H), 4.96 (ddd, *J* = 15.6, 10.4, 5.2 Hz, 1H), 4.54 (dd, *J* = 11.6, 5.6 Hz, A of AB, 1H), 4.44 (dd, *J* = 12.0, 8.8 Hz, B of AB, 1H), 3.78 (s, 3H), 3.40 (dd, *J* = 13.2, 5.2 Hz, 1H), 2.44 (t, *J* = 12.8 Hz, 1H), 2.39 – 2.21 (m, 2H), 1.97 – 1.85 (m, 1H), 1.77 – 1.66 (m, 1H). **^{13}C NMR** (100

MHz, $CDCl_3$) δ 172.79, 169.85, 156.86, 139.04, 131.03, 130.52, 130.07, 125.98, 123.22, 121.26, 73.34, 52.61, 52.32, 38.99, 35.38, 26.73. **[α]** $_D^{30}$ = +70.8 (*c* 0.24, CH_2Cl_2). **HRMS** (ESI) m/z calcd. for $C_{16}H_{19}NNaO_4$, $[M + Na]^+$ 312.1206, found 312.1206. **IR** (thin film): 3337, 2953, 2923, 2855, 1742, 1457, 1260 cm^{-1}.



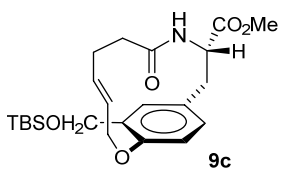
9b

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.03 (d, *J* = 8.4 Hz, 1H), 6.89 (d, *J* = 8.0 Hz, 1H), 6.76 (s, 1H), 5.45 – 5.31 (m, 1H), 5.31 – 5.15 (m, 2H), 4.96 (td, *J* = 10.8, 5.6 Hz, 1H), 4.54 (dd, *J* = 11.2, 6.0 Hz, A of AB, 1H), 4.43 – 4.33 (m, B of AB, 1H), 3.78 (s, 3H), 3.40 (dd, *J* = 13.2, 5.2 Hz, A' of A'B', 1H), 2.45 (t, *J* = 12.8 Hz, B' of A'B',1H), 2.40 – 2.23 (m, 2H), 2.15 (s, 3H), 1.90 – 1.74 (m, 1H), 1.58 – 1.43 (m, 1H). **^{13}C NMR** (100MHz, $CDCl_3$) δ 172.80, 170.26, 154.80, 139.66, 132.71, 131.30, 130.94, 127.18, 124.61, 122.96, 73.12, 52.55, 52.36, 38.69, 36.05, 26.16, 16.60. **[α]** $_D^{27}$ = -34.0 (*c* 0.14, CH_2Cl_2). **HRMS** (ESI) m/z calcd. for $C_{17}H_{20}NO_4$, $[M - H]^-$ 302.1398, found 302.1387. **IR** (thin film): 3292, 2927, 1733, 1655, 1544, 1415, 1262, 1166, 1117 cm^{-1}.



10b

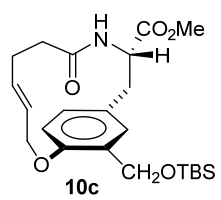
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07 (s, 1H), 6.75 (d, *J* = 8.0 Hz, 1H), 6.70 (d, *J* = 8.0 Hz, 1H), 5.34 (d, *J* = 10.0 Hz, 1H), 5.20 (ddd, *J* = 13.6, 10.0, 4.8 Hz, 1H), 5.04 (ddd, *J* = 14.0, 9.6, 3.6 Hz, 1H), 4.96 (ddd, *J* = 12.0, 10.4, 4.8 Hz, 1H), 4.63 (dd, *J* = 11.6, 4.0 Hz, A of AB,1H), 4.40 (dd, *J* = 11.6, 10.0 Hz, B of AB, 1H), 3.78 (s, 3H), 3.35 (dd, *J* = 13.2, 5.2 Hz, 1H), 2.43 – 2.21 (m, 3H), 2.17 (s, 3H), 2.00 – 1.85 (m, 1H), 1.82 – 1.66 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.91, 169.57, 154.98, 138.93, 132.14, 131.61, 130.09, 128.28, 125.76, 120.54, 73.39, 52.59, 52.37, 39.14, 35.21, 27.06, 16.50. **[α]** $_D^{27}$ = +98.2 (*c* 0.09, CH_2Cl_2). **HRMS** (ESI) m/z calcd. for $C_{17}H_{20}NO_4$, $[M - H]^-$ 302.1398, found 302.1385. **IR** (thin film): 3292, 2927, 1732, 1655, 1544, 1415, 1262, 1167, 1117 cm^{-1}.



9c

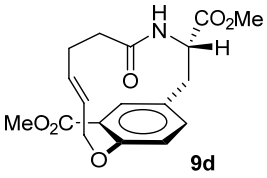
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.05 (s, 1H), 6.89 (d, *J* = 8.4 Hz, 1H), 5.41 – 5.21 (m, 2H), 5.10 (d, *J* = 10.4

Hz, 1H), 4.95 (ddd, *J* = 12.0, 10.8, 5.6 Hz, 1H), 4.64 (s, 2H), 4.52 (dd, *J* = 12.0, 5.2 Hz, A of AB, 1H), 4.36 (dd, *J* = 11.6, 8.4 Hz, B of AB, 1H), 3.78 (s, 3H), 3.44 (dd, *J* = 13.2, 5.2 Hz, A' of A'B',1H), 2.54 (t, *J* = 13.2 Hz, B' of A'B', 1H), 2.40 – 2.19 (m, 2H), 1.86 – 1.75 (m, 1H), 1.61 – 1.50 (m, 1H), 0.96 (s, 9H), 0.13 (s, 3H), 0.12 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.72, 170.48, 153.08, 140.39, 134.76, 131.11, 129.18, 127.95, 123.92, 122.26, 73.48, 60.17, 52.58, 52.49, 38.86, 36.01, 26.20, 26.09, 18.64, -5.04, -5.16. **[α]** $_D^{30}$ = -18.3 (*c* 0.06, CH_2Cl_2). **HRMS** (ESI) m/z calcd. for $C_{23}H_{34}NO_5Si$, $[M - H]^-$ 432.2212, found 432.2209. **IR** (thin film): 3445, 2957, 2926, 2857, 1727, 1658, 1544, 1458, 1380, 1260, 1120, 1072 cm^{-1}.



10c

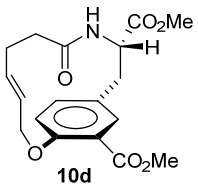
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (s, 1H), 6.84 – 6.66 (m, 2H), 5.33 (d, *J* = 10.0 Hz, 1H), 5.15 (dddd, *J* = 15.2, 9.6, 4.0, 1.2 Hz, 1H), 5.07 (ddd, *J* = 15.2, 9.6, 3.6 Hz, 1H), 4.92 (ddd, *J* = 12.4, 10.4, 4.8 Hz, 1H), 4.80 (d, *J* = 13.6 Hz, 1H), 4.67 – 4.51 (m, 2H), 4.43 (dd, *J* = 12.0, 9.6 Hz, 1H), 3.79 (s, 3H), 3.40 (dd, *J* = 12.8, 4.8 Hz, A of AB, 1H), 2.40 (t, *J* = 12.8 Hz, B of AB, 1H), 2.36 – 2.16 (m, 2H), 1.98 – 1.87 (m, 1H), 1.81 – 1.70 (m, 1H), 0.96 (s, 9H), 0.16 (s, 3H), 0.14 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.95, 169.31, 153.57, 139.20, 135.17, 130.13, 129.14, 128.46, 125.51, 119.95, 73.03, 60.61, 52.56, 52.48, 39.44, 35.08, 29.85, 27.10, 26.22, 18.70, -5.05, -5.11. **[α]** $_D^{30}$ = +71.6 (*c* 0.09, CH_2Cl_2). **HRMS** (ESI) m/z calcd. for $C_{23}H_{34}NO_5Si$, $[M - H]^-$ 432.2212, found 432.2199. **IR** (thin film): 3348, 2973, 2926, 2889, 1741, 1657, 1381, 1089, 1049 cm^{-1}.



9d

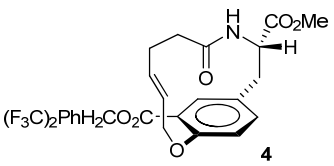
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 2.0 Hz, 1H), 7.36 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.95 (d, *J* = 8.0 Hz, 1H), 5.49 (d, *J* = 10.4 Hz, 1H), 5.32 (dt, *J* = 15.2, 7.2, 7.2 Hz, 1H), 5.14 (ddd, *J* = 14.8, 8.4, 5.6 Hz, 1H), 5.04 (ddd, *J* = 12.0, 10.4, 5.6 Hz, 1H), 4.51 (dd, *J* = 11.6, 6.4 Hz, A of AB, 1H), 4.44 (dd, *J* = 11.6, 8.4 Hz, B of AB,1H), 3.92 (s, 3H), 3.79 (s, 3H), 3.42 (dd, *J* = 13.2, 5.2 Hz, A' of A'B', 1H), 2.52 (t, *J* = 12.8 Hz, B' of A'B', 1H), 2.39 – 2.18 (m, 2H), 1.94 – 1.80 (m, 1H), 1.72 (ddd, *J* = 14.8, 12.0, 2.4 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.42, 170.09, 167.11, 156.79, 139.44, 133.97, 132.90, 131.14, 125.89, 125.59, 125.06, 74.05, 52.70,

52.46, 51.68, 38.59, 35.18, 26.44. **[α]** $_D^{17}$ = -60.6 (*c* 0.24, CH_2Cl_2). **HRMS** (ESI) m/z calcd. for $C_{18}H_{20}NO_6$, $[M - H]^-$ 346.1296, found 346.1286. **IR** (thin film): 3348, 2954, 2925, 1728, 1660, 1492, 1438, 1254, 1212, 945 cm^{-1}.



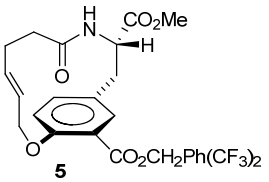
10d

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 2.0 Hz, 1H), 7.01 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.85 (d, *J* = 8.4 Hz, 1H), 5.46 (d, *J* = 9.6 Hz, 1H), 5.30 (dddd, *J* = 11.6, 9.6, 4.8, 1.6 Hz, 1H), 5.14 (ddd, *J* = 14.8, 10.0, 4.4 Hz, 1H), 4.94 (ddd, *J* = 12.4, 10.4, 5.2 Hz, 1H), 4.72 (dd, *J* = 12.0, 4.8 Hz, A of AB, 1H), 4.51 (dd, *J* = 12.0, 9.6 Hz, B of AB,1H), 3.89 (s, 3H), 3.79 (s, 3H), 3.39 (dd, *J* = 13.2, 5.2 Hz, A of AB, 1H), 2.44 (t, *J* = 12.8 Hz, B of AB, 1H), 2.40 – 2.23 (m, 2H), 1.99 – 1.86 (m, 1H), 1.86 – 1.74 (m, 1H). **^{13}C NMR** (100MHz, $CDCl_3$) δ 172.63, 169.31, 166.21, 157.05, 139.27, 134.51, 132.18, 130.08, 126.07, 125.20, 122.71, 73.63, 52.71, 52.26, 52.20, 39.09, 34.90, 26.81. **[α]** $_D^{17}$ = +120.9 (*c* 0.18, CH_2Cl_2). **HRMS** (ESI) m/z calcd. for $C_{18}H_{20}NO_6$, $[M - H]^-$ 346.1296, found 346.1283. **IR** (thin film): 3365, 2925, 1727, 1657, 1576, 1441, 1264, 1207, 1118, 1078 cm^{-1}.



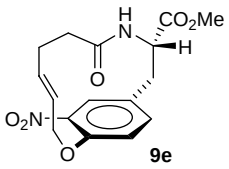
4

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (s, 2H), 7.86 (s, 1H), 7.45 (s, 1H), 7.40 (d, *J* = 8.4 Hz, 1H), 6.99 (d, *J* = 8.4 Hz, 1H), 5.60 – 5.46 (m, 2H), 5.41 (d, *J* = 13.2 Hz, 1H), 5.32 – 5.19 (m, 1H), 5.19 – 5.09 (m, 1H), 5.04 (td, *J* = 10.8, 5.6 Hz, 1H), 4.49 (dd, *J* = 11.6, 6.8 Hz, 1H, A of AB), 4.42 (dd, *J* = 11.6, 7.6 Hz, 1H, B of AB), 3.79 (s, 3H), 3.43 (dd, *J* = 13.2, 5.2 Hz, 1H, A' of A'B'), 2.54 (t, *J* = 12.8 Hz, 1H, B' of A'B'), 2.37 – 2.18 (m, 2H), 1.88 – 1.75 (m, 1H), 1.75 –1.56 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.37, 170.07, 166.22, 157.18, 139.78, 138.90, 134.54, 132.94, 132.18 (q, *J* = 33 Hz), 131.33, 128.08 (m), 125.42, 125.36, 124.39, 123.32 (q, *J* = 271 Hz), 122.26 (m), 74.09, 65.13, 52.71, 51.65, 38.52, 35.30, 26.26. **[α]**$_D^{18}$ -78.8 (*c* 0.17, CH_2Cl_2). **HRMS** (ESI) m/z calcd. for $C_{26}H_{24}F_6NO_6$ $[M + H]^+$ 560.1508; found 560.1497. **IR** (thin film): 3358, 2958, 1735, 1663, 1280, 1175, 1133 cm^{-1}.



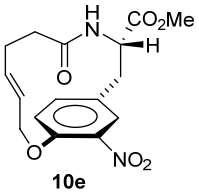
5

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (s, 2H), 7.84 (s, 1H), 7.82 (d, *J* = 2.4 Hz, 1H), 7.05 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.88 (d, *J* = 8.4 Hz, 1H), 5.65 – 5.46 (m, 2H), 5.40 (d, *J* = 13.6 Hz, 1H), 5.23 (dddd, *J* = 15.2, 9.6, 4.0, 1.2 Hz, 1H), 5.15 (ddd, *J* = 15.2, 9.6, 4.0 Hz, 1H), 4.94 (ddd, *J* = 12.4, 10.0, 5.2 Hz, 1H), 4.72 (dd, *J* = 12.0, 4.0 Hz, A of AB, 1H), 4.53 (dd, *J* = 12.0, 9.6 Hz, B of AB, 1H), 3.79 (s, 3H), 3.40 (dd, *J* = 13.2, 4.8 Hz, A' of A'B', 1H), 2.45 (d, *J* = 12.8 Hz, B' of A'B', 1H), 2.40 – 2.18 (m, 2H), 2.02 – 1.87 (m, 1H), 1.87 – 1.76 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.58, 169.22, 165.51, 157.30, 139.43, 139.31, 135.09, 132.54, 132.00 (q, *J* = 33 Hz), 130.23, 127.81 (m), 125.77, 124.27, 122.45, 123.41 (q, *J* = 271 Hz), 121.96 (m), 73.52, 64.89, 52.72, 52.26, 39.11, 34.75, 26.87. **[α]**$_D^{19}$ 103.4° (*c* 0.17, CH_2Cl_2). **HRMS** (ESI) m/z calcd. for $C_{26}H_{23}F_6NNaO_6$ $[M + Na]^+$ 582.1327; found 582.1332. **IR** (thin film): 3358, 3068, 2925, 2851, 1739, 1654, 1280, 1175, 1132, 798 cm^{-1}.



9e

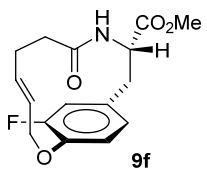
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (s, 1H), 7.46 (d, *J* = 8.4 Hz, 1H), 7.07 (d, *J* = 8.4 Hz, 1H), 5.85 – 5.69 (m, 1H), 5.43 – 5.17 (m, 2H), 5.05 (ddd, *J* = 12.0, 10.4, 5.2 Hz, 1H), 4.53 (dd, *J* = 11.6, 6.4 Hz, A of AB, 1H), 4.46 (dd, *J* = 11.6, 7.6 Hz, B of AB, 1H), 3.82 (s, 3H), 3.45 (dd, *J* = 13.2, 5.2 Hz, A' of A'B', 1H), 2.55 (t, *J* = 12.8 Hz, B' of A'B', 1H), 2.41 – 2.19 (m, 2H), 1.97 – 1.85 (m, 1H), 1.86 – 1.74 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.24, 170.04, 150.55, 144.33, 140.51, 135.06, 132.16, 126.73, 126.58, 125.30, 74.09, 52.92, 51.57, 38.52, 34.85, 26.21. **[α]**$_D^{17}$ = -258.7 (*c* 0.28, CH_2Cl_2). **HRMS** (ESI) m/z calcd. for $C_{16}H_{18}N_2NaO_6$, $[M + Na]^+$ 357.1057, found 357.10563. **IR** (thin film):, 2924, 1457, 1260, 1072 cm^{-1}.



10e

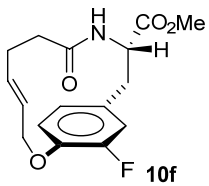
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 1.6 Hz, 1H), 7.10 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.95 (d, *J* = 8.4 Hz, 1H), 5.65 (d, *J* = 9.2 Hz, 1H), 5.32 (dddd, *J* = 14.8, 10.0, 4.0, 1.2 Hz, 1H), 5.20 (ddd, *J* = 14.4, 10.0, 3.6 Hz, 1H), 4.97 (ddd, *J* = 12.4, 10.0, 5.2 Hz, 1H), 4.79 (dd, *J* = 11.6, 3.6 Hz, A of AB,1H), 4.52 (dd, *J* = 11.2, 10.4 Hz, B of AB, 1H), 3.80 (s, 3H), 3.41 (dd, *J* = 13.2, 4.8 Hz, A' of A'B', 1H), 2.49 (t, *J* = 12.4 Hz, B' of A'B', 1H), 2.45 – 2.33 (m, 1H), 2.29 (ddd, *J* = 16.0, 6.0, 2.0

Hz, 1H), 2.02 – 1.89 (m, 1H), 1.89 – 1.75 (m, 1H). **^{13}C NMR** (100MHz, $CDCl_3$) δ 172.24, 169.17, 150.60, 144.19, 140.48, 135.08, 131.07, 126.31, 125.35, 123.44, 74.37, 52.86, 52.00, 38.99, 34.40, 26.88. **[α]**$_D^{17}$ = +323.2 (*c* 0.28, CH_2Cl_2). **HRMS** (ESI) m/z calcd. for $C_{16}H_{19}N_2O_6$, $[M + H]^+$ 335.1238, found 335.1243. **IR** (thin film): 3343, 2973, 1667, 1460, 1223, 1090, 1047 cm^{-1}.



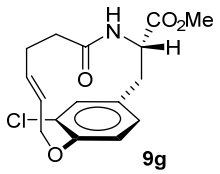
9f

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.99 (dd, *J* = 8.4, 1.6 Hz, 1H), 6.91 (t, *J* = 8.4 Hz, 1H), 6.66 (dd, *J* = 12.0, 1.6 Hz, 1H), 5.50 (d, *J* = 10.0 Hz, 1H), 5.43 – 5.20 (m, 2H), 4.99 (ddd, *J* = 12.0, 10.4, 5.2 Hz, 1H), 4.69 – 4.55 (m, A of AB, 1H), 4.49 (dd, *J* = 10.0, 4.4 Hz, B of AB, 1H), 3.79 (s, 3H), 3.39 (dd, *J* = 13.2, 4.8 Hz, 1H), 2.49 – 2.33 (m, 2H), 2.33 – 2.19 (m, 1H), 2.03 – 1.88 (m, 1H), 1.88 – 1.71 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.52, 169.70, 155.38 (d, *J* = 246 Hz), 143.21 (d, *J* = 11 Hz), 138.81, 132.69 (d, *J* = 7 Hz), 126.17, 125.58 (d, *J* = 4 Hz), 125.43 (d, *J* = 4 Hz), 118.45 (d, *J* = 20 Hz), 72.70 (d, *J* = 5Hz), 52.72, 52.20, 39.03, 34.84, 26.79. **[α]** $_D^{30}$ = +54.5 (*c* 0.22, CH_2Cl_2). **HRMS** (ESI) m/z calcd. for $C_{16}H_{18}FNNaO_4$, $[M + Na]^+$ 330.1112, found 330.1111. **IR** (thin film): 3164, 2953, 2849, 1660, 1403, 1092 cm^{-1}.



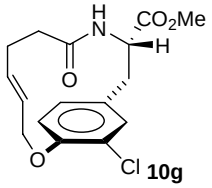
10f

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.00 (d, *J* = 11.6 Hz, 1H), 6.84 (t, *J* = 8.0 Hz, 1H), 6.66 (d, *J* = 8.0 Hz, 1H), 5.43 – 5.31 (m, 2H), 5.24 (ddd, *J* = 15.2, 8.8, 5.6 Hz, 1H), 5.03 (td, *J* = 11.2, 5.2 Hz, 1H), 4.65 (dd, *J* = 11.2, 6.4 Hz, A of AB, 1H), 4.38 (dd, *J* = 11.2, 8.8 Hz, B of AB, 1H), 3.79 (s, 3H), 3.38 (dd, *J* = 13.2, 5.2 Hz, A´ of AB, 1H), 2.46 (t, *J* = 12.8 Hz, B of AB, 1H), 2.41 – 2.23 (m, 2H), 2.01 – 1.86 (m, 1H), 1.77 – 1.65 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.54, 169.84, 156.43 (d, *J* = 246Hz), 143.91 (d, *J* = 12Hz), 140.27,132.43 (d, *J* = 7Hz), 126.03 (d, *J* = 3Hz), 125.46, 123.80 (d, *J* = 2Hz), 117.40 (d, *J* = 20Hz), 73.91, 52.70, 51.84, 38.91, 35.36, 26.59. **[α]** $_D^{30}$ = +74.3 (*c* 0.22, CH_2Cl_2). **HRMS** (ESI) m/z calcd. for $C_{16}H_{19}FNO_4$, $[M + H]^+$ 308.1293, found 308.1300. **IR** (thin film): 3164, 2953, 2914, 2849, 1660, 1403, 1092 cm^{-1}.



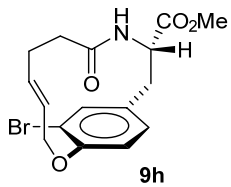
9g

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (dd, *J* = 8.0, 1.6 Hz, 1H), 6.99 (d, *J* = 1.6 Hz, 1H), 6.95 (d, *J* = 8.0 Hz, 1H), 5.57 (d, *J* = 10.4 Hz, 1H), 5.41 (dt, *J* = 15.2, 7.6 Hz, 1H), 5.29 (ddd, *J* = 14.4, 8.0, 6.0 Hz, 1H), 5.04 (ddd, *J* = 12.4, 10.8, 5.6 Hz, 1H), 4.77 (dd, *J* = 11.6, 8.0 Hz, A of AB, 1H), 4.42 (dd, *J* = 11.2, 6.8 Hz, B of AB, 1H), 3.80 (s, 3H), 3.40 (dd, *J* = 13.2, 5.2 Hz, 1H), 2.44 (t, *J* = 12.8 Hz, 1H), 2.39 – 2.22 (m, 2H), 1.97 – 1.84 (m, 1H), 1.77 – 1.66 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.59, 170.12, 152.19, 139.52, 132.77, 131.90, 128.50, 127.55, 125.60, 125.32, 72.96, 52.75, 51.86, 38.56, 35.30, 26.38. **[α]** $_D^{30}$ = -27.1 (*c* 0.26, CH_2Cl_2). **HRMS** (ESI) m/z calcd. for $C_{16}H_{17}ClNO_4$, $[M - H]^-$ 322.0852, found 322.0841. **IR** (thin film): 3166, 2958, 2920, 1726, 1650, 1402, 1095, 1025 cm^{-1}.



10g

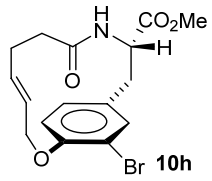
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, *J* = 1.6 Hz, 1H), 6.84 (d, *J* = 8.4 Hz, 1H), 6.78 (dd, *J* = 8.0, 1.6 Hz, 1H), 5.50 (d, *J* = 10.0 Hz, 1H), 5.34 (ddd, *J* = 14.4, 9.6, 4.8 Hz, 1H), 5.13 (ddd, *J* = 14.4, 9.6, 4.4 Hz, 1H), 5.00 (ddd, *J* = 12.0, 10.4, 5.2 Hz, 1H), 4.76 (dd, *J* = 11.6, 5.2 Hz, A of AB, 1H), 4.40 (t, *J* = 10.0 Hz, B of AB, 1H), 3.79 (s, 3H), 3.35 (dd, *J* = 13.2, 5.2 Hz, 1H), 2.47 – 2.32 (m, 2H), 2.27 (ddd, *J* = 16.0, 6.0, 2.4 Hz, 1H), 1.99 – 1.86 (m, 1H), 1.82 – 1.72 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.58, 169.52, 152.38, 139.87, 131.92, 131.06, 129.31, 128.70, 125.47, 122.81, 74.24, 52.70, 52.01, 38.86, 34.99, 26.83. **[α]** $_D^{30}$ = +125.9 (*c* 0.32, CH_2Cl_2). **HRMS** (ESI) m/z calcd. for $C_{16}H_{17}ClNO_4$, $[M - H]^-$ 322.0852, found 322.0842. **IR** (thin film): 3369, 2920, 2844, 1660, 1084 cm^{-1}.



9h

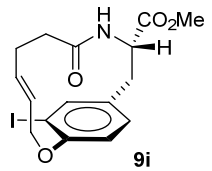
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, *J* = 1.6 Hz, 1H), 7.16 (dd, *J* = 8.4, 1.6 Hz, 1H), 6.93 (d, *J* = 8.4 Hz, 1H), 5.88 (d, *J* = 10.4 Hz, 1H), 5.43 (dt, *J* = 15.2, 7.6 Hz, 1H), 5.29 (dt, *J* = 15.2, 7.2 Hz, 1H), 5.03 (td, *J* = 11.6, 5.2 Hz, 1H), 4.78 (dd, *J* = 11.2, 7.2 Hz, A of AB, 1H), 4.38 (dd, *J* = 11.2, 7.6 Hz, B of AB, 1H), 3.81 (s, 3H), 3.39 (dd, *J* = 13.2, 5.6 Hz, A' of A'B', 1H), 2.45 (t, *J* = 12.8 Hz, B' of A'B', 1H), 2.37 – 2.15 (m, 2H), 1.94 – 1.82 (m, 1H), 1.75 – 1.56 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.85, 170.34, 153.29, 139.92, 134.91, 133.07, 129.05, 125.23, 124.84,

117.49, 73.42, 52.80, 51.93, 38.30, 35.36, 26.21. **[α]** $_D^{27}$ = -37.9 (*c* 0.48, CH_2Cl_2). **HRMS** (ESI) m/z calcd. for $C_{16}H_{17}BrNO_4$, $[M - H]^-$ 366.0346, found 366.0344. **IR** (thin film): 3413, 2925, 1607, 1501, 1411, 1336 cm^{-1}.



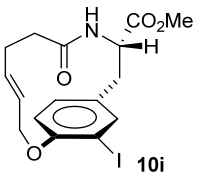
10h

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (s, 1H), 6.84 (dd, *J* = 8.0, 1.2 Hz, 1H), 6.80 (d, *J* = 8.0 Hz, 1H), 5.73 (d, *J* = 10.0 Hz, 1H), 5.32 (ddd, *J* = 14.4, 9.6, 4.4 Hz, 1H), 5.10 (ddd, *J* = 14.4, 10.0, 4.0 Hz, 1H), 4.98 (td, *J* = 12.0, 12.0, 5.2 Hz, 1H), 4.74 (dd, *J* = 11.6, 4.4 Hz, A of AB,1H), 4.39 (t, *J* = 10.4 Hz, B of AB, 1H), 3.77 (s, 3H), 3.34 (dd, *J* = 13.2, 4.8 Hz, 1H), 2.48 – 2.28 (m, 2H), 2.29 – 2.11 (m, 1H), 1.98 – 1.83 (m, 1H), 1.76 (t, *J* = 13.3 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.58, 169.55, 153.30, 139.81, 133.87, 132.23, 130.06, 125.35, 122.50, 118.33, 77.48, 77.16, 76.84, 74.19, 52.63, 52.08, 38.61, 34.80, 26.83. **[α]** $_D^{27}$ = +98.6 (*c* 0.51, CH_2Cl_2). **HRMS** (ESI) m/z calcd. for $C_{16}H_{19}BrNO_4$, $[M + H]^+$ 368.0492, found 368.0503. **IR** (thin film): 3298, 2953, 1616, 1589 cm^{-1}.



9i

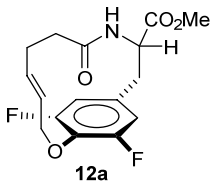
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 6.4 Hz, 1H), 7.20 (dd, *J* = 8.4, 6.0 Hz, 1H), 6.89 (d, *J* = 8.0 Hz, 1H), 5.50 (dt, *J* = 15.6, 7.6 Hz, 1H), 5.31 (dt, *J* = 15.2, 7.2 Hz, 1H), 5.02 (ddd, *J* = 12.4, 10.8, 6.0 Hz, 1H), 4.77 (dd, *J* = 11.6, 6.4 Hz, 1H), 4.37 (dd, *J* = 10.8, 9.2 Hz, 1H), 3.80 (s, 3H), 3.39 (dd, *J* = 13.6, 5.6 Hz, 1H), 2.45 (t, *J* = 12.8 Hz, 1H), 2.39 – 2.18 (m, 2H), 1.95 – 1.73 (m, 1H), 1.75 – 1.62 (m, 1H). **^{13}C NMR** (100MHz, $CDCl_3$) δ 172.55, 170.30, 156.08, 140.69, 140.31, 133.30, 130.06, 124.58, 123.91, 93.36, 73.94, 52.78, 51.90, 38.15, 35.70, 26.04. **[α]**$_D^{27}$ = -36.7 (*c* 0.30, CH_2Cl_2). **HRMS** (ESI) m/z calcd. for $C_{16}H_{17}INO_4$, $[M - H]^-$ 414.0208, found 414.0200. **IR** (thin film): 3355, 2926, 2849, 1599, 1419 cm^{-1}.



10i

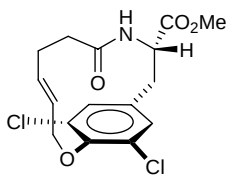
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 2.0 Hz, 1H), 6.86 (dd, *J* = 8.0, 1.6 Hz, 1H), 6.74 (d, *J* = 8.0 Hz, 1H), 5.56 (d, *J* = 10.0 Hz, 1H), 5.34 (ddd, *J* = 14.8, 10.4, 4.0 Hz, 1H), 5.07 (ddd, *J* = 14.4, 10.4, 4.0 Hz, 1H), 4.96 (ddd, *J* = 12.0, 10.0, 4.8 Hz, 1H), 4.75 (dd, *J* = 11.6, 4.0 Hz, 1H), 4.41 (t, *J* = 11.2

Hz, 1H), 3.78 (s, 3H), 3.33 (dd, *J* = 13.2, 4.9 Hz, 1H), 2.45 – 2.31 (m, 2H), 2.25 (dd, *J* = 15.5, 5.8 Hz, 1H), 2.00 – 1.85 (m, 1H), 1.86 – 1.71 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.63, 170.34, 156.08, 140.71, 140.32, 133.30, 130.05, 124.55, 123.89, 93.40, 73.95, 52.80, 51.93, 38.14, 35.68, 26.03. **[α]**$_D^{27}$ = +70.0 (*c* 0.48, CH_2Cl_2). **HRMS** (ESI) m/z calcd. for $C_{16}H_{17}INO_4$, $[M - H]^-$ 414.0208, found 414.0200. **IR** (thin film): 3378, 2927, 2865, 1654, 1621, 1460, 1249, 1097 cm^{-1}.



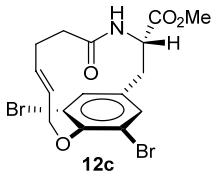
12a

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.84 (d, *J* = 9.6 Hz, 1H), 6.51 (d, *J* = 10.0 Hz, 1H), 5.65 (br, 1H), 5.52 – 5.27 (m, 2H), 5.04 (td, *J* = 11.6, 5.2 Hz, 1H), 4.71 – 4.41 (m, 2H), 3.79 (s, 3H), 3.36 (dd, *J* = 13.2, 4.8 Hz, 1H), 2.53 – 2.35 (m, 2H), 2.31 (dd, *J* = 16.0, 4.0 Hz, 1H), 2.06 – 1.89 (m, 1H), 1.88 – 1.75 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.29, 169.80, 157.40 (dd, *J* = 247, 8 Hz), 156.45 (dd, *J* = 246, 7 Hz), 140.25, 132.44 (t, *J* = 9.0 Hz), 132.07 (t, *J* = 14.0 Hz), 125.36, 114.00, 113.89 (d, *J* = 22 Hz), 113.02 (dd, *J* = 20, 4 Hz), 73.28, 52.78, 51.80, 39.07, 34.79, 26.70. **HRMS** (ESI) m/z calcd. for $C_{16}H_{17}F_2NNaO_4$, $[M + Na]^+$ 348.1018, found 348.1019. **IR** (thin film): 3271, 3077, 2994, 2943, 2843, 1745, 1636, 1592, 1556, 1460, 1427, 1250, 1125, 989 cm^{-1}.



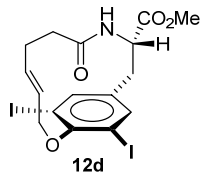
12b

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (d, *J* = 2.0 Hz, 1H), 6.91 (d, *J* = 2.0 Hz, 1H), 5.77 (d, *J* = 10.4 Hz, 1H), 5.53 (ddd, *J* = 15.2, 8.0, 7.2 Hz, 1H), 5.34 (ddd, *J* = 14.8, 9.2, 5.2 Hz, 1H), 5.07 (ddd, *J* = 12.4, 10.4, 5.6 Hz, 1H), 4.76 (dd, *J* = 11.2, 9.2 Hz, A of AB, 1H), 4.67 (dd, *J* = 11.2, 6.4 Hz, B of AB, 1H), 3.80 (s, 3H), 3.35 (dd, *J* = 13.2, 5.2 Hz, 1H), 2.50 – 2.34 (m, 2H), 2.28 (ddd, *J* = 15.6, 5.6, 2.4 Hz, 1H), 2.01 – 1.86 (m, 1H), 1.86 – 1.73 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.42, 169.88, 148.36, 140.42, 133.21, 131.27, 130.47, 129.78, 129.30, 124.89, 77.48, 77.16, 76.84, 72.25, 52.82, 51.58, 38.53, 34.77, 26.50. **[α]** $_D^{27}$ = +24.1 (*c* 0.29, CH_2Cl_2). **HRMS** (ESI) m/z calcd. for $C_{16}H_{16}Cl_2NO_4$, $[M - H]^-$ 356.0462, found 356.0454. **IR** (thin film): 3413, 3305, 2925, 1739, 1650, 1411, 1336, 1205, 1095 cm^{-1}.



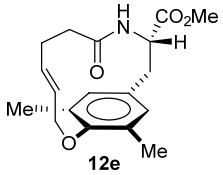
12c

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 1.6 Hz, 1H), 7.14 (s, 1H), 5.97 – 5.72 (m, 1H), 5.59 (ddd, *J* = 15.6, 8.0, 7.6 Hz, 1H), 5.35 (ddd, *J* = 15.2, 9.2, 5.6 Hz, 1H), 5.06 (ddd, *J* = 12.0, 10.4, 5.6 Hz, 1H), 4.80 (dd, *J* = 10.8, 9.6 Hz, A of AB, 1H), 4.67 (dd, *J* = 11.2, 6.8 Hz, B of AB, 1H), 3.80 (s, 3H), 3.35 (dd, *J* = 13.2, 5.2 Hz, 1H), 2.51 – 2.32 (m, 2H), 2.32 – 2.17 (m, 1H), 2.02 – 1.84 (m, 1H), 1.86 – 1.69 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.49, 169.92, 150.22, 140.56, 134.23, 134.19, 133.43, 124.84, 120.87, 118.56, 72.11, 52.85, 51.63, 38.24, 34.74, 26.46. **[α]** $_D^{16}$ = +7.1 (*c* 0.35, CH_2Cl_2). **HRMS** (ESI) m/z calcd. for $C_{16}H_{17}Br_2NNaO_4$, $[M + Na]^+$ 467.9417, found 467.9418. **IR** (thin film): 3351, 2927, 1729, 1649, 1534, 1445, 1393, 1231, 1155, 982, 835 cm^{-1}.



12d

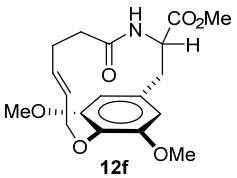
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 1.6 Hz, 1H), 7.45 (s, 1H), 6.16 (d, *J* = 10.0 Hz, 1H), 5.65 (dt, *J* = 15.6, 8.0 Hz, 1H), 5.33 (ddd, *J* = 14.8, 8.8, 6.0 Hz, 1H), 5.05 (ddd, *J* = 12.0, 10.4, 5.2 Hz, 1H), 4.80 (dd, *J* = 10.8, 9.2 Hz, A of AB, 1H), 4.64 (dd, *J* = 10.8, 6.8 Hz, B of AB, 1H), 3.81 (s, 3H), 3.30 (dd, *J* = 13.2, 5.2 Hz, 1H), 2.51 – 2.30 (m, 2H), 2.30 – 2.13 (m, 1H), 1.97 – 1.84 (m, 1H), 1.84 – 1.67 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.67, 170.03, 154.86, 141.21, 140.76, 140.21, 135.27, 124.72, 94.90, 92.31, 71.88, 52.90, 51.71, 37.56, 34.63, 26.41. **[α]** $_D^{16}$ = -7.9 (*c* 1.5, CH_2Cl_2). **HRMS** (ESI) m/z calcd. for $C_{16}H_{16}I_2NO_4$, $[M - H]^-$ 539.9174, found 539.9170. **IR** (thin film): 3101, 2953, 2925, 1731, 1647, 1410, 1331 cm^{-1}.



12e

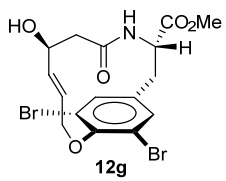
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.89 (s, 1H), 6.59 (s, 1H), 5.45 (d, *J* = 10.0 Hz, 1H), 5.38 (dt, *J* = 15.2, 7.6 Hz, 1H), 5.10 (ddd, *J* = 14.8, 8.0, 6.0 Hz, 1H), 4.96 (ddd, *J* = 12.0, 10.8, 5.2 Hz, 1H), 4.50 – 4.30 (m, 2H), 3.78 (s, 3H), 3.33 (dd, *J* = 13.2, 5.2 Hz, A of AB, 1H), 2.37 (t, *J* = 12.8 Hz, B of AB, 1H), 2.34 – 2.21 (m, 2H), 2.19 (s, 3H), 2.16 (s, 3H), 1.95 – 1.82 (m, 1H), 1.73 – 1.54 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.00, 170.04, 152.50, 139.09, 132.40, 130.90, 130.83, 130.25, 129.00, 124.94, 71.00, 52.52, 52.29, 38.77, 35.31, 26.48, 17.08, 16.98. **[α]** $_D^{29}$ = +29.2 (*c* 0.39, CH_2Cl_2). **HRMS** (ESI) m/z calcd. for $C_{18}H_{23}NNaO_4$, $[M + Na]^+$ 340.1519, found

340.1522. **IR** (thin film): 3277, 2973, 1734, 1649, 1543, 1434, 1205, 1090, 1049, 952, 882 cm^{-1}.



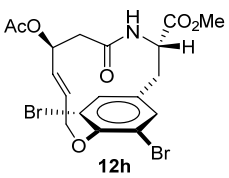
12f

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.48 (s, 1H), 6.16 (s, 1H), 5.56 – 5.32 (m, 2H), 5.22 – 4.99 (m, 2H), 4.65 – 4.38 (m, 2H), 3.85 (s, 3H), 3.81 (s, 3H), 3.77 (s, 3H), 3.41 (dd, *J* = 13.2, 5.2 Hz, 1H), 2.46 – 2.30 (m, 2H), 2.26 (dd, *J* = 15.2, 6.0 Hz, 1H), 1.99 – 1.87 (m, 1H), 1.68 (d, *J* = 12.8 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.78, 170.18, 154.59, 153.31, 138.56, 133.33, 131.85, 126.12, 107.73, 106.17, 71.52, 56.32, 56.09, 52.59, 51.99, 39.72, 35.49, 26.74. **HRMS** (ESI) m/z calcd. for $C_{18}H_{23}NNaO_6$, $[M + Na]^+$ 372.1418, found 372.1425. **IR** (thin film): 3285, 3080, 2952, 1736, 1647, 1541, 1442, 1283, 1230, 1024 cm^{-1}.



12g

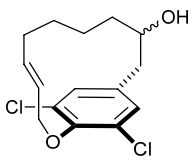
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (s, 1H), 7.11 (s, 1H), 5.99 – 5.83 (m, 1H), 5.83 – 5.69 (m, 1H), 5.48 (dd, *J* = 15.2, 3.6 Hz, 1H), 5.02 (ddd, *J* = 12.0, 10.4, 5.6 Hz, 1H), 4.97 – 4.87 (m, 2H), 4.74 (dd, *J* = 10.8, 6.8 Hz, 1H), 4.22 (s, 1H), 3.81 (s, 3H), 3.38 (dd, *J* = 13.6, 5.6 Hz, A of AB, 1H), 2.70 (dd, *J* = 16.0, 6.0 Hz, B of AB, 1H), 2.40 (t, *J* = 12.8 Hz, A' of A'B', 1H), 1.95 (d, *J* = 16.0 Hz, B' of A'B', 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.76, 171.01, 150.39, 143.04, 134.23, 133.86, 133.76, 122.67, 121.18, 117.91, 71.29, 68.48, 53.03, 51.13, 38.62, 38.18. **[α]** $_D^{17}$ = +0.9 (*c* 0.44, CH_2Cl_2). **HRMS** (ESI) m/z calcd. for $C_{16}H_{17}Br_2NNaO_5$, $[M + Na]^+$ 483.9366, found 483.9361. **IR** (thin film): 3350, 2958, 2925, 1727, 1680, 1600, 1451, 1284, 1208 cm^{-1}.



12h

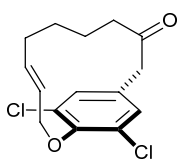
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 1.6 Hz, 1H), 7.15 (s, 1H), 5.89 (ddd, *J* = 15.6, 10.4, 5.2 Hz, 1H), 5.83 (m, 1H), 5.76 (ddd, *J* = 15.6, 7.6, 2.0 Hz, 1H), 5.28 – 5.12 (m, 1H), 5.01 (td, *J* = 12.0, 5.6 Hz, 1H), 4.81 (t, *J* = 10.4 Hz, A of AB, 1H), 4.68 (dd, *J* = 10.8, 5.2 Hz, B of AB, 1H), 3.80 (s, 3H), 3.32 (dd, *J* = 13.2, 5.6 Hz, A' of A'B', 1H), 2.85 – 2.67 (m, 1H), 2.44 (t, *J* = 12.8 Hz, B' of A'B', 1H), 2.16 (dd, *J* = 17.2, 3.6 Hz, 1H), 1.99 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ

172.20, 170.63, 167.10, 149.88, 139.58(2C), 134.55, 134.27, 124.11, 120.53, 118.57, 71.97, 70.21, 52.94, 51.74, 40.15, 38.55, 21.30. **[α]** $_D^{17}$ = - 33.8 (*c* 0.45, CH_2Cl_2). **HRMS** (ESI) m/z calcd. for $C_{18}H_{19}Br_2NNaO_6$, $[M + Na]^+$ 525.9471, found 525.9477. **IR** (thin film): 3405, 2971, 1673, 1412, 880 cm^{-1}.



14

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (d, *J* = 3.2 Hz, 2H), 5.47 – 5.25 (m, 2H), 4.83 (dd, *J* = 11.2, 8.4 Hz, 1H), 4.71 (dd, *J* = 10.4, 6.0 Hz, 1H), 3.74 (td, *J* = 9.2, 5.2 Hz, 1H), 3.13 (dd, *J* = 12.4, 4.8 Hz, 1H), 2.42 (dd, *J* = 12.4, 9.6 Hz, 1H), 2.05 – 1.89 (m, 1H), 1.81 – 1.58 (m, 2H), 1.50 (td, *J* = 13.2, 5.6 Hz, 1H), 1.39 – 1.26 (m, 1H), 1.24 – 1.12 (m, 1H), 0.93 – 0.77 (m, 1H), 0.43 – 0.22 (m, 1H), -0.45 (qt, *J* = 13.2, 3.6 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 147.68, 142.10, 135.39, 131.02, 130.64, 129.63, 129.30, 124.02, 72.89, 72.36, 44.57, 38.56, 31.98, 28.80, 24.36. **HRMS** (ESI) m/z calcd. for $C_{15}H_{18}Cl_2KO_2$, $[M + K]^+$ 339.0315, found 339.0311. **IR** (thin film): 3354, 2925, 2855, 1660, 1554, 1471, 1402, 1247, 1201, 1079, 1008, 980 cm^{-1}.

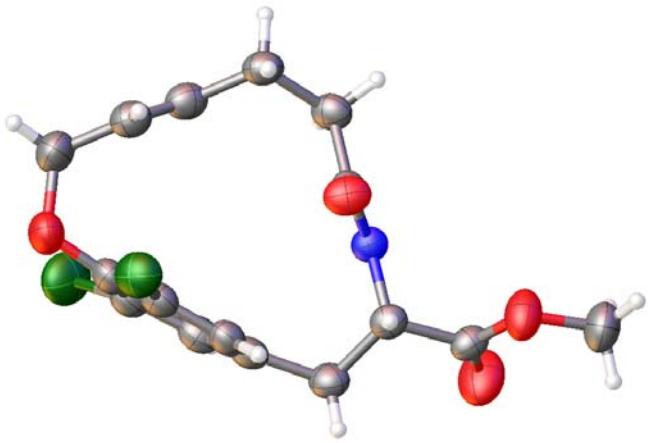


16

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (s, 2H), 5.52 – 5.24 (m, 2H), 4.80 (d, *J* = 6.4 Hz, 2H), 3.52 (s, 2H), 2.25 – 2.06 (m, 2H), 1.95 – 1.72 (m, 2H), 1.19 – 0.99 (m, 2H), 0.50 – 0.26 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 208.12, 148.57, 141.62, 131.58, 131.45, 129.86, 124.41, 72.57, 51.94, 43.00, 31.56, 29.46, 25.54. **HRMS** (ESI) m/z calcd. for $C_{15}H_{16}Cl_2NaO_2$, $[M + Na]^+$ 321.0425, found 321.0425. **IR** (thin film): 2926, 1705, 1472, 1401, 1247, 1085, 979, 927, 801 cm^{-1}.

6. X-Ray Crystallographic Data

a) X-Ray Crystallographic Data for 12b.



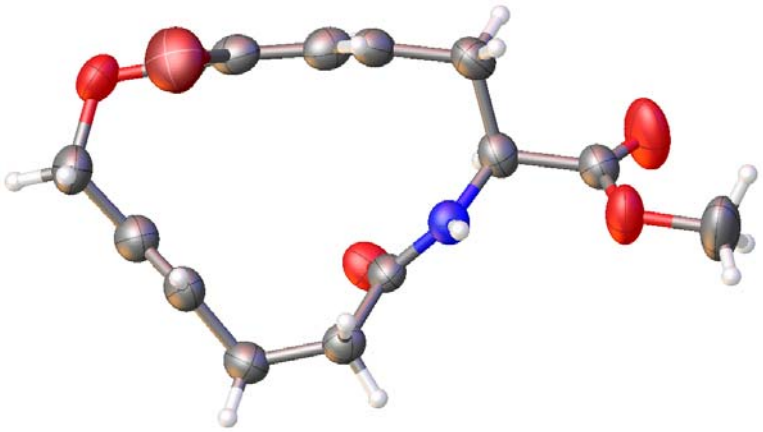
Structure deposited at the Cambridge Crystallographic Data Centre (CCDC 1436892)

Crystal data and structure refinement for CCDC 1436892

Empirical formula	$C_{16}H_{17}Cl_2NO_4$
Formula weight	358.20
Temperature/K	294.39(10)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	8.3061(2)
b/Å	9.7010(2)
c/Å	20.7173(6)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1669.35(7)
Z	4
ρ_{calc}g/cm^3	1.425
μ/mm^{-1}	3.671
F(000)	744.0
Crystal size/mm^3	0.65 × 0.15 × 0.05
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.536 to 134.148
Index ranges	$-9 \le h \le 9$, $-8 \le k \le 11$, $-24 \le l \le 24$
Reflections collected	8970
Independent reflections	2975 [R_{int} = 0.0359, R_{sigma} = 0.0291]
Data/restraints/parameters	2975/0/209

Goodness-of-fit on F^2	1.022
Final R indexes [I>=2σ (I)]	$R_1 = 0.0478$, $wR_2 = 0.1284$
Final R indexes [all data]	$R_1 = 0.0510$, $wR_2 = 0.1329$
Largest diff. peak/hole / e $Å^{-3}$	0.37/-0.26
Flack parameter	-0.004(8)

b) X-Ray Crystallographic Data for 12c.



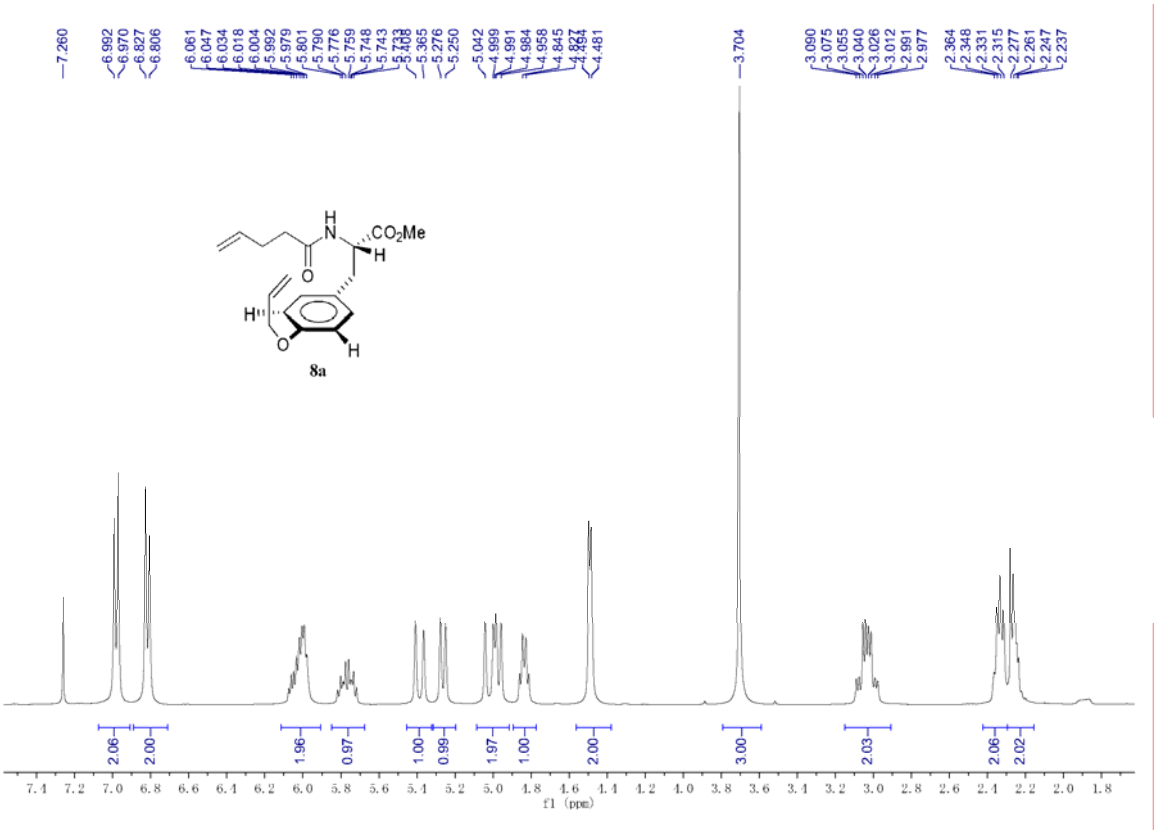
Structure deposited at the Cambridge Crystallographic Data Centre (CCDC 1436896)

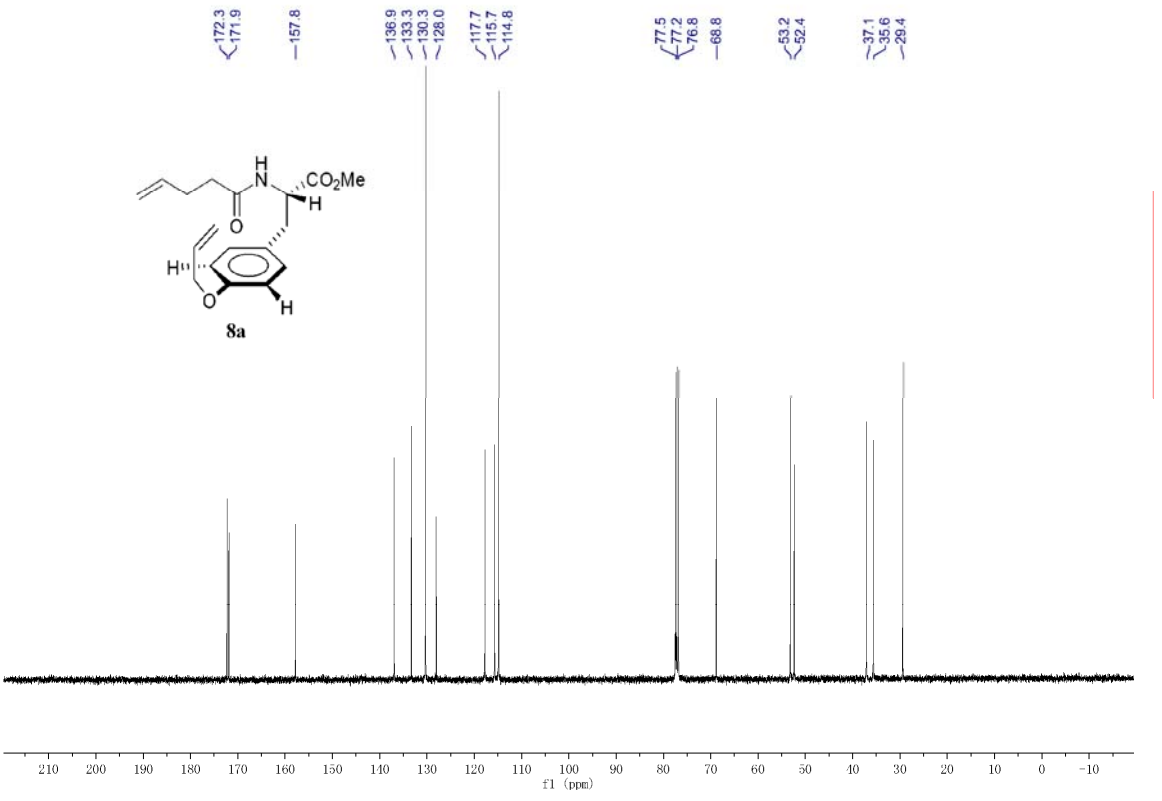
Crystal data and structure refinement for CCDC 1436896

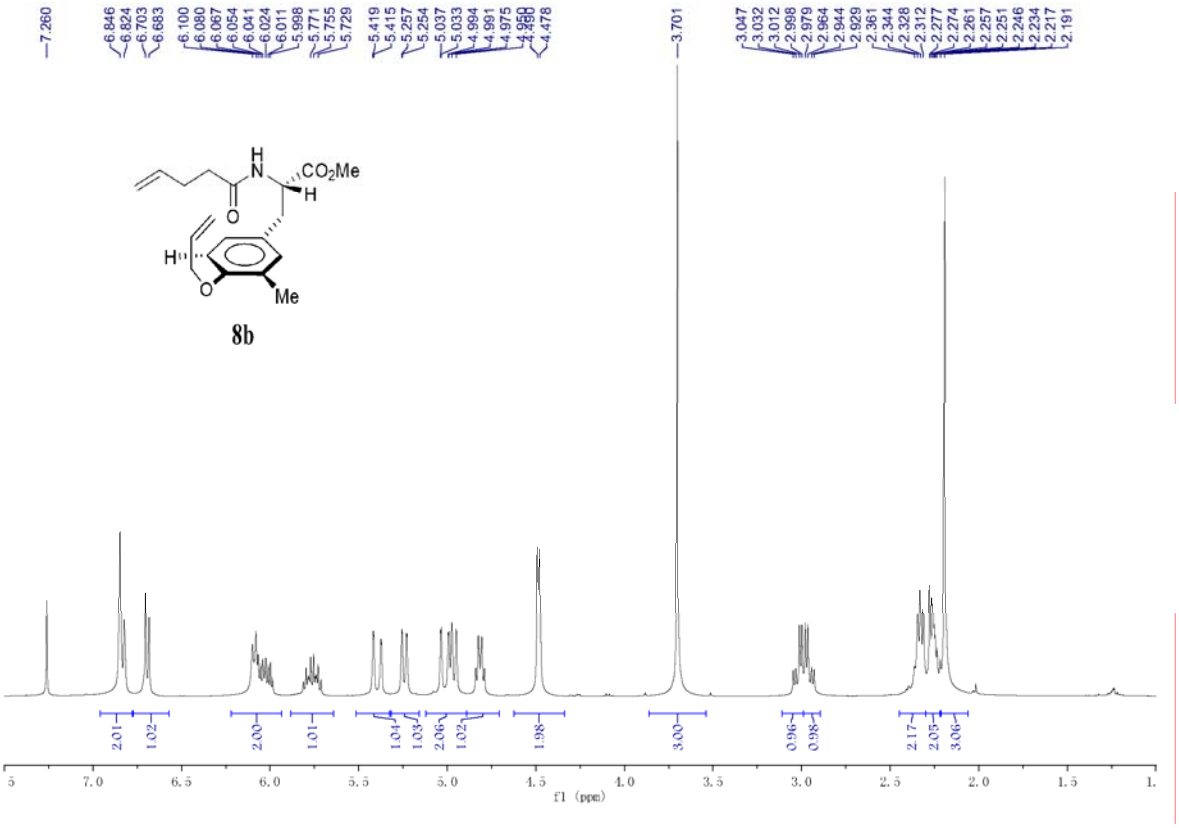
Empirical formula	$C_{16}H_{17}Br_2NO_4$
Formula weight	447.12
Temperature/K	292.36(10)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	8.3327(7)
b/Å	9.5492(9)
c/Å	11.4501(10)
α/°	90
β/°	108.133(9)
γ/°	90
Volume/Å^3	865.83(14)
Z	2
ρ_{calc}g/cm^3	1.715
μ/mm^{-1}	6.107
F(000)	444.0
Crystal size/mm^3	0.7 × 0.2 × 0.15
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	11.174 to 134.15
Index ranges	$-9 \le h \le 9$, $-10 \le k \le 11$, $-12 \le l \le 13$
Reflections collected	8597
Independent reflections	2858 [R_{int} = 0.0351, R_{sigma} = 0.0383]
Data/restraints/parameters	2858/1/209
Goodness-of-fit on F^2	1.082
Final R indexes [I>=2σ (I)]	R_1 = 0.0459, wR_2 = 0.1264
Final R indexes [all data]	R_1 = 0.0479, wR_2 = 0.1290

Largest diff. peak/hole / e $Å^{-3}$	0.57/-0.39
Flack parameter	-0.06(2)

7. NMR spectra.



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6.041
6.024
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5.771
5.755
5.729
5.419
5.415
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5.254
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2.274
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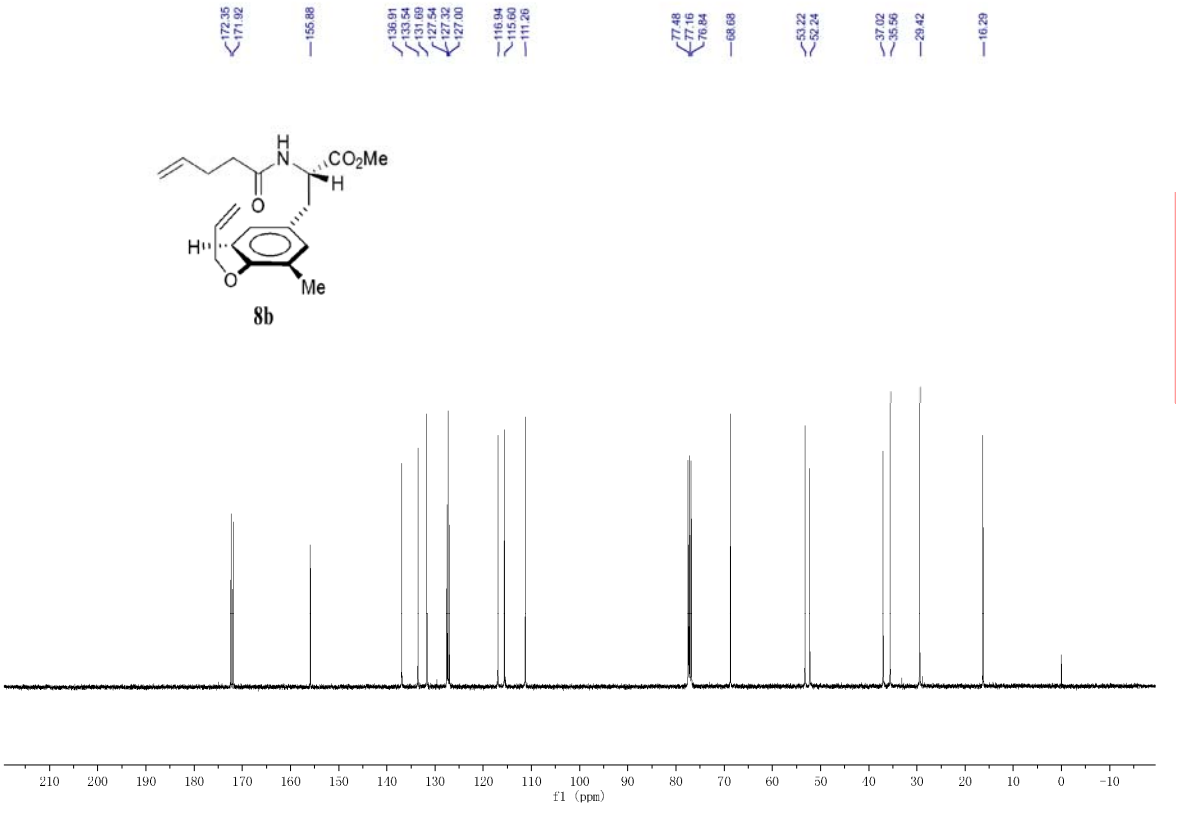
2.257
2.251
2.246
2.234
2.217
2.191
CO2Me
H
N
O
H
O
Me
8b
2.01
1.02
2.00
1.01
1.04
1.03
2.06
1.02
1.98
3.00
0.96
0.98
2.17
2.05
3.06
f1 (ppm)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77.16
76.84
68.68
53.22
52.24
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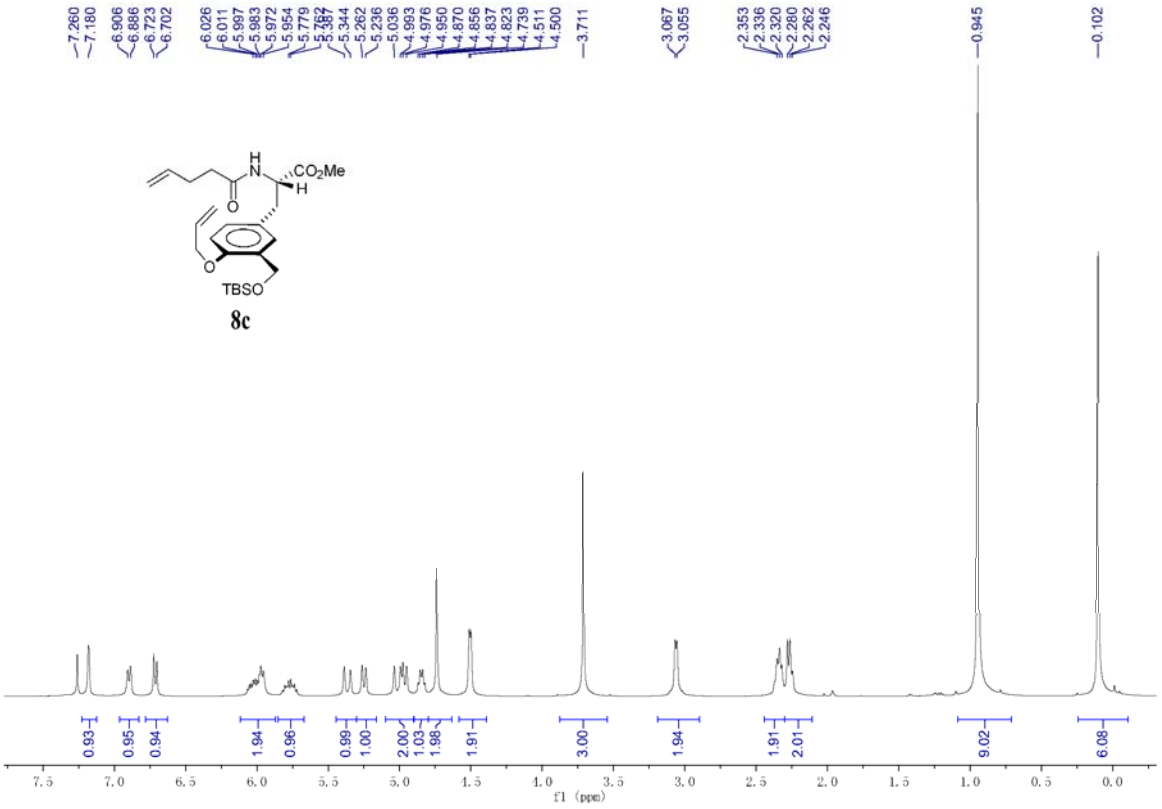
35.56
29.42
16.29
CO2Me
H
N
O
H
O
Me
8b
f1 (ppm)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2.336
2.320
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2.262
2.246
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0.102
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H
N
O
O
TBSO
8c
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0.95
0.94
1.94
0.96
0.99
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3.00
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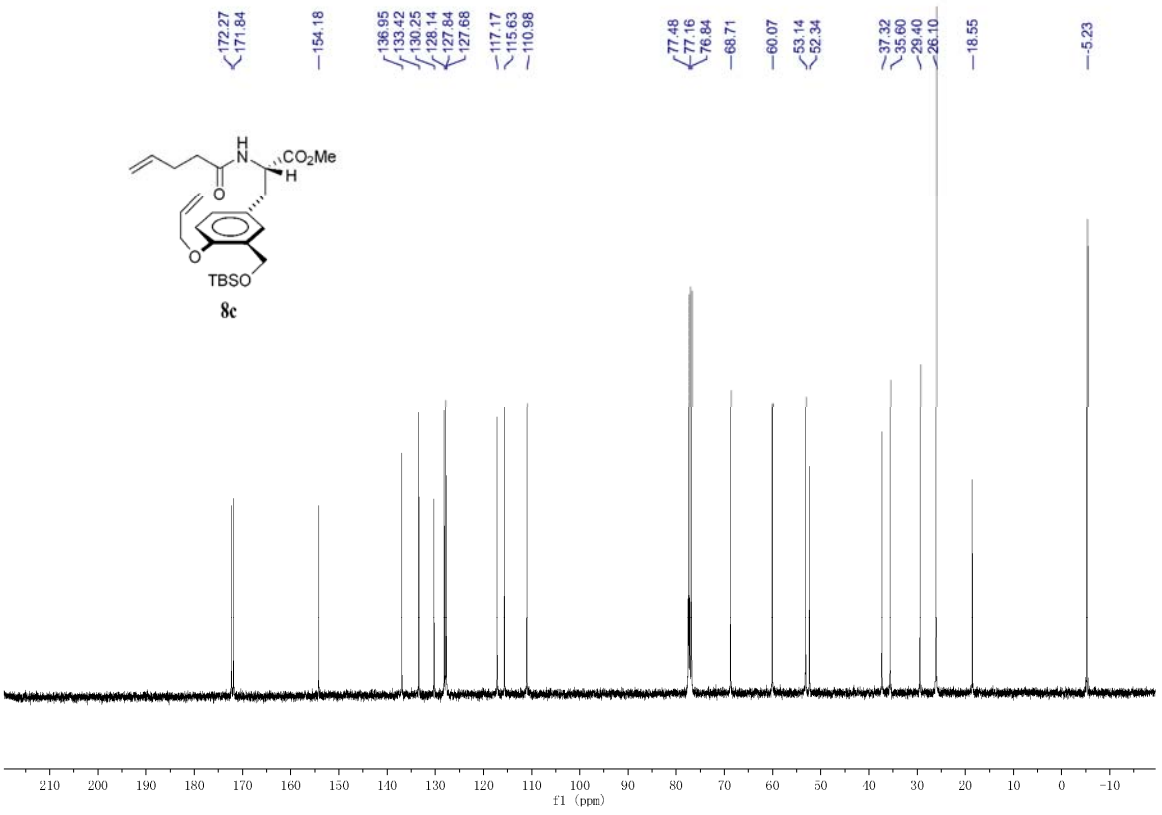
1.91
2.01
9.02
6.08
f1 (ppm)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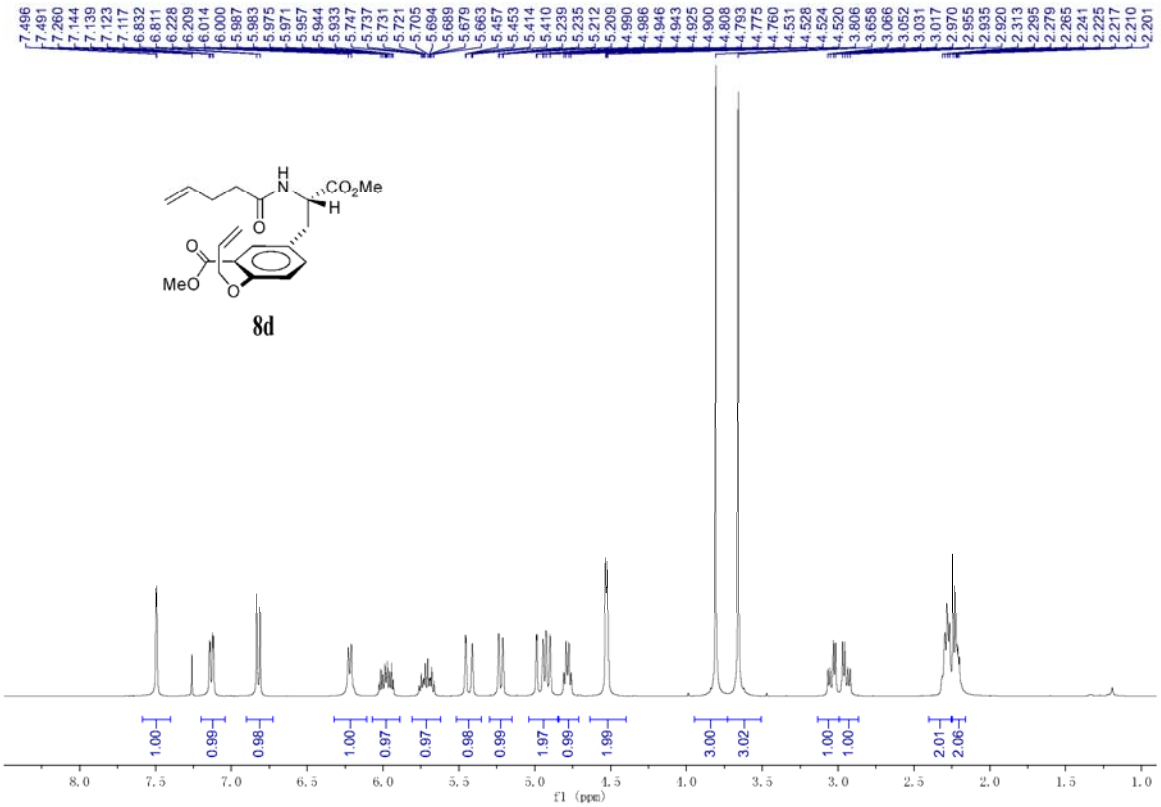
60.07
53.14
52.34
37.32
35.60
29.40
26.10
18.55
-5.23
CO2Me
H
N
O
O
TBSO
8c
f1 (ppm)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6.014
6.000
5.987
5.983
5.975
5.971
5.957
5.944
5.933
5.747
5.737
5.731
5.721
5.705
5.694
5.689
5.679
5.663
5.457
5.453
5.414
5.410
5.239
5.235
5.212
5.209
4.990
4.986
4.946
4.943
4.925
4.900
4.808
4.793
4.775
4.760
4.531
4.528
4.524
4.520
3.806
3.658
3.066
3.052
3.031
3.017
2.970
2.955
2.935
2.920
2.313
2.295
2.279
2.265
2.241
2.225
2.217
2.210
2.201
CO2Me
H
N
H
O
O
MeO
O
8d
1.00
0.99
0.98
1.00
0.97
0.97
0.98
0.99
1.97
0.99
1.99
3.00
3.02
1.00
1.00
2.01
2.06
8.0
7.5
7.0
6.5
6.0
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3.5
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2.5
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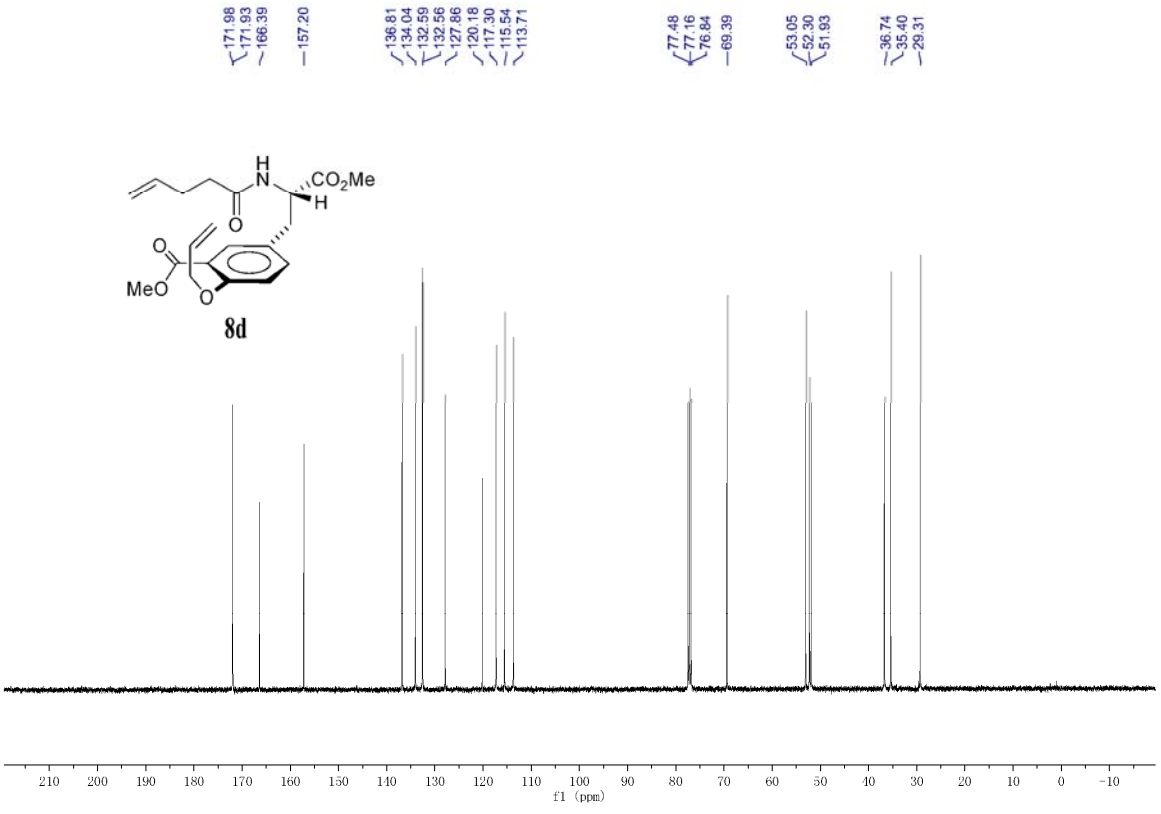
1.0
f1 (ppm)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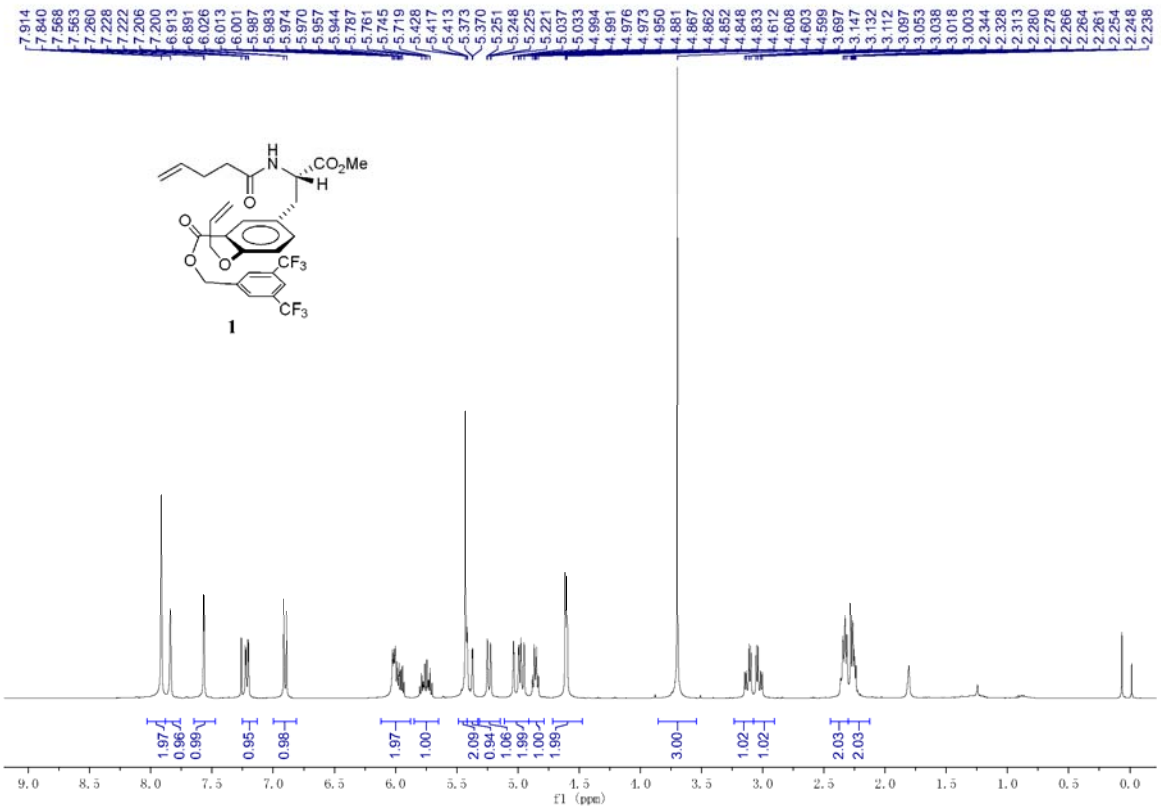
113.71
77.48
77.16
76.84
69.39
53.05
52.30
51.93
36.74
35.40
29.31
CO2Me
H
N
H
O
O
MeO
O
8d
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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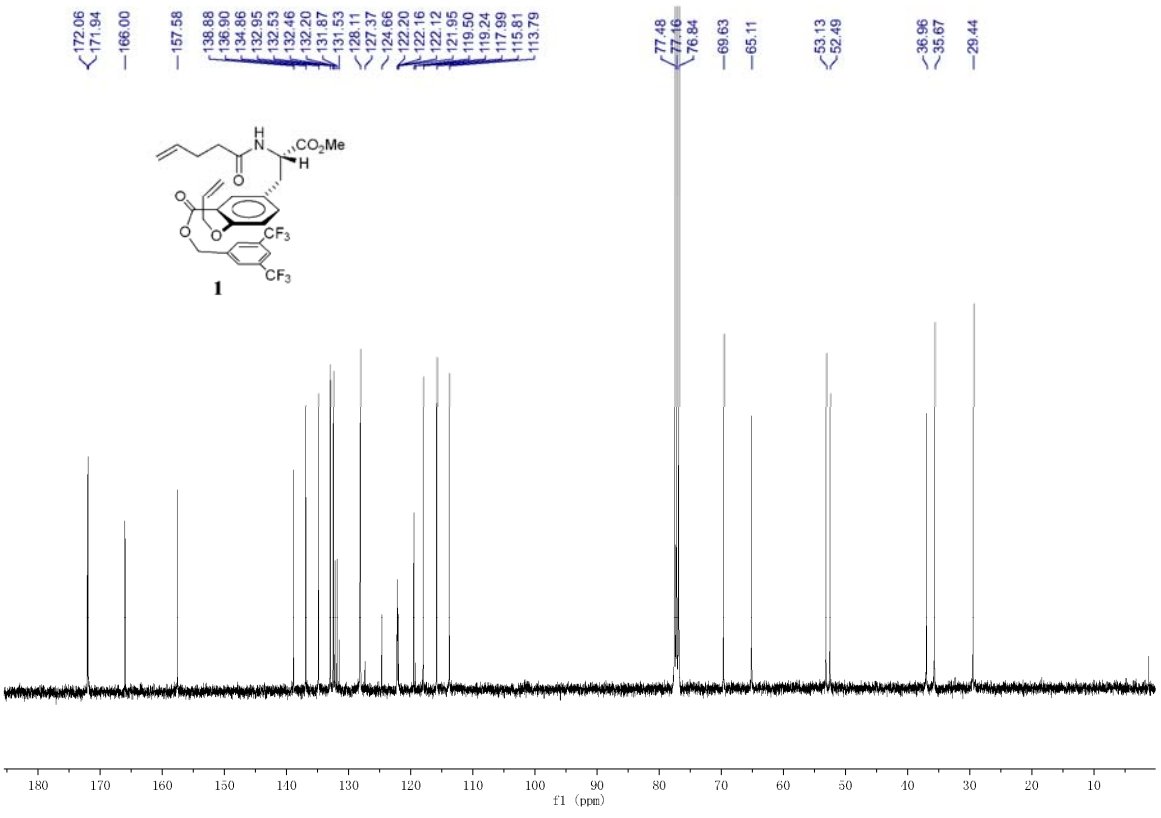
6.026
6.013
6.001
5.987
5.983
5.974
5.970
5.957
5.944
5.787
5.761
5.745
5.719
5.428
5.417
5.413
5.373
5.370
5.251
5.248
5.225
5.221
5.037
5.033
4.994
4.991
4.976
4.973
4.950
4.881
4.867
4.862
4.852
4.848
4.833
4.612
4.608
4.603
4.599
3.697
3.147
3.132
3.112
3.097
3.053
3.038
3.018
3.003
2.344
2.328
2.313
2.280
2.278
2.266
2.264
2.261
2.254
2.248
2.238
CO2Me
H
N
H
O
O
O
O
CF3
CF3
1
1.97
0.96
0.99
0.95
0.98
1.97
1.00
2.09
0.94
1.06
1.99
1.00
1.99
3.00
1.02
1.02
2.03
2.03
f1 (ppm)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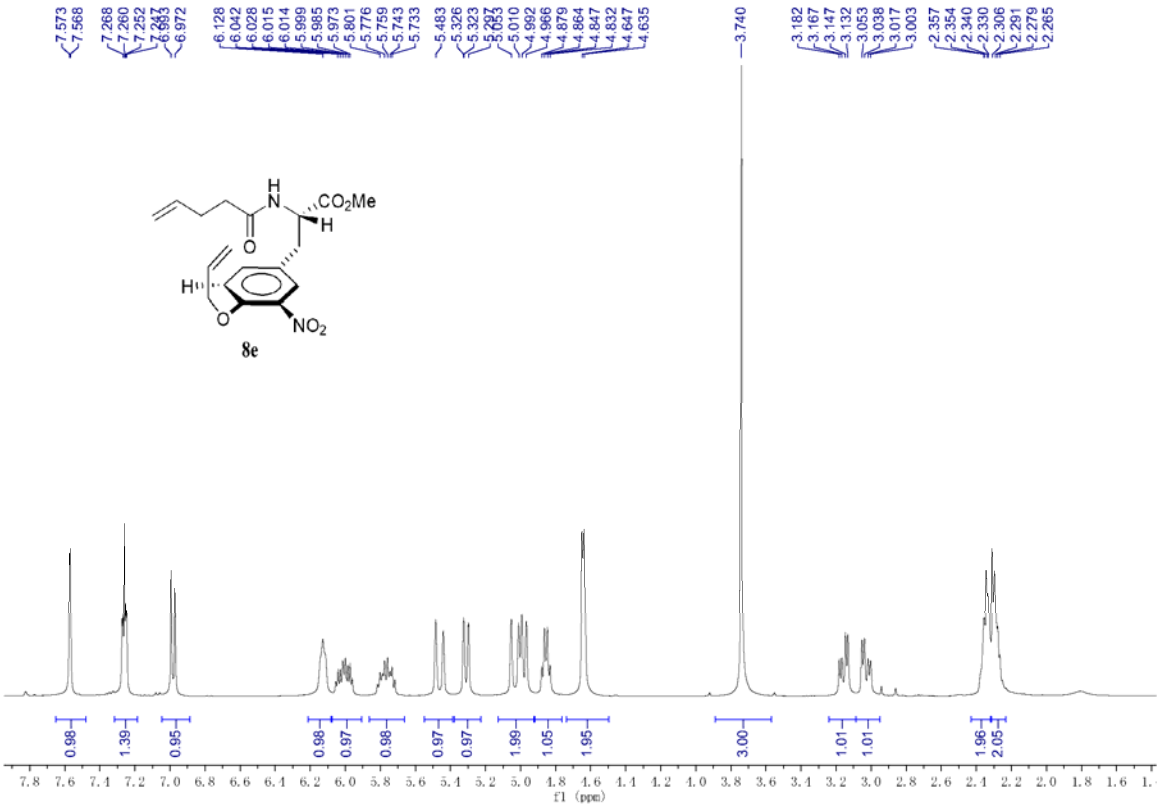
131.53
128.11
127.37
124.66
122.20
122.16
122.12
121.95
119.50
119.24
117.99
115.81
113.79
77.48
77.16
76.84
69.63
65.11
53.13
52.49
36.96
35.67
29.44
CO2Me
H
N
H
O
O
O
O
CF3
CF3
1
f1 (ppm)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6.014
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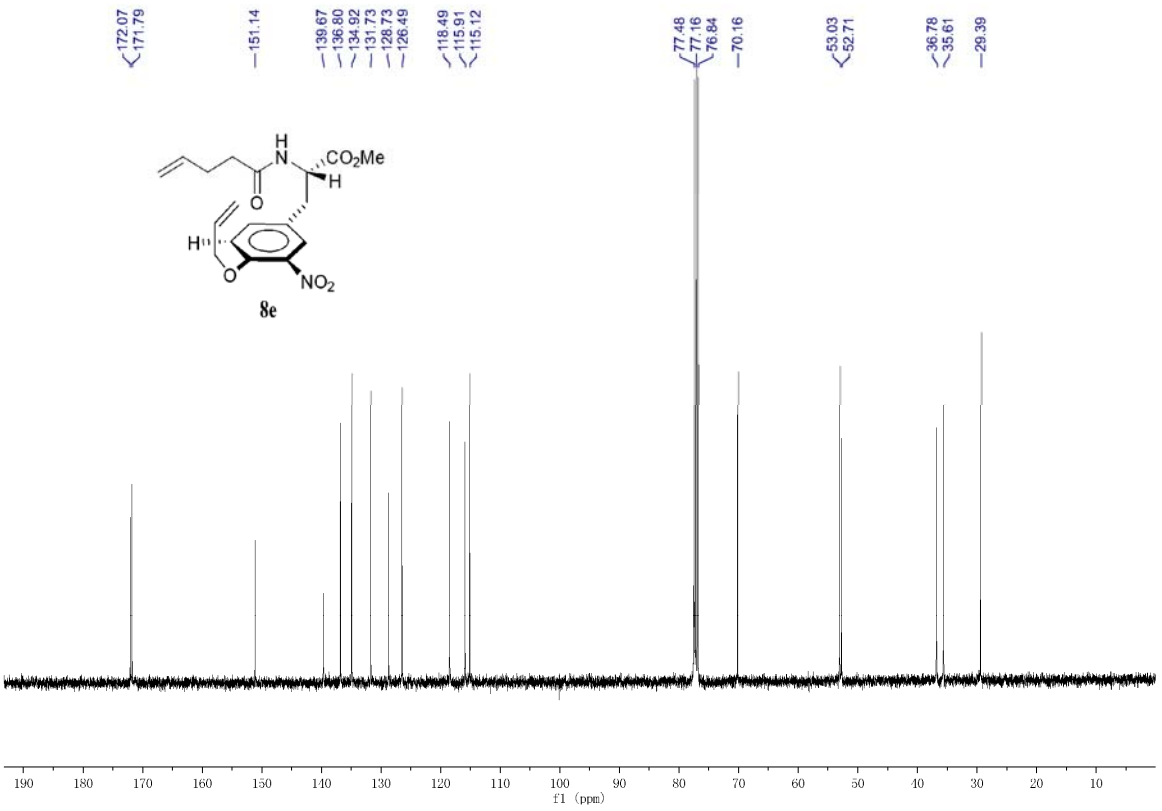
5.985
5.973
5.801
5.776
5.759
5.743
5.733
5.483
5.326
5.323
5.010
4.992
4.966
4.879
4.864
4.847
4.832
4.647
4.635
3.740
3.182
3.167
3.147
3.132
3.053
3.038
3.017
3.003
2.357
2.354
2.340
2.330
2.306
2.291
2.279
2.265
CO2Me
H
N
O
NO2
8e
0.98
1.39
0.95
0.98
0.97
0.98
0.97
0.97
1.99
1.05
1.95
3.00
1.01
1.01
1.96
2.05
f1 (ppm)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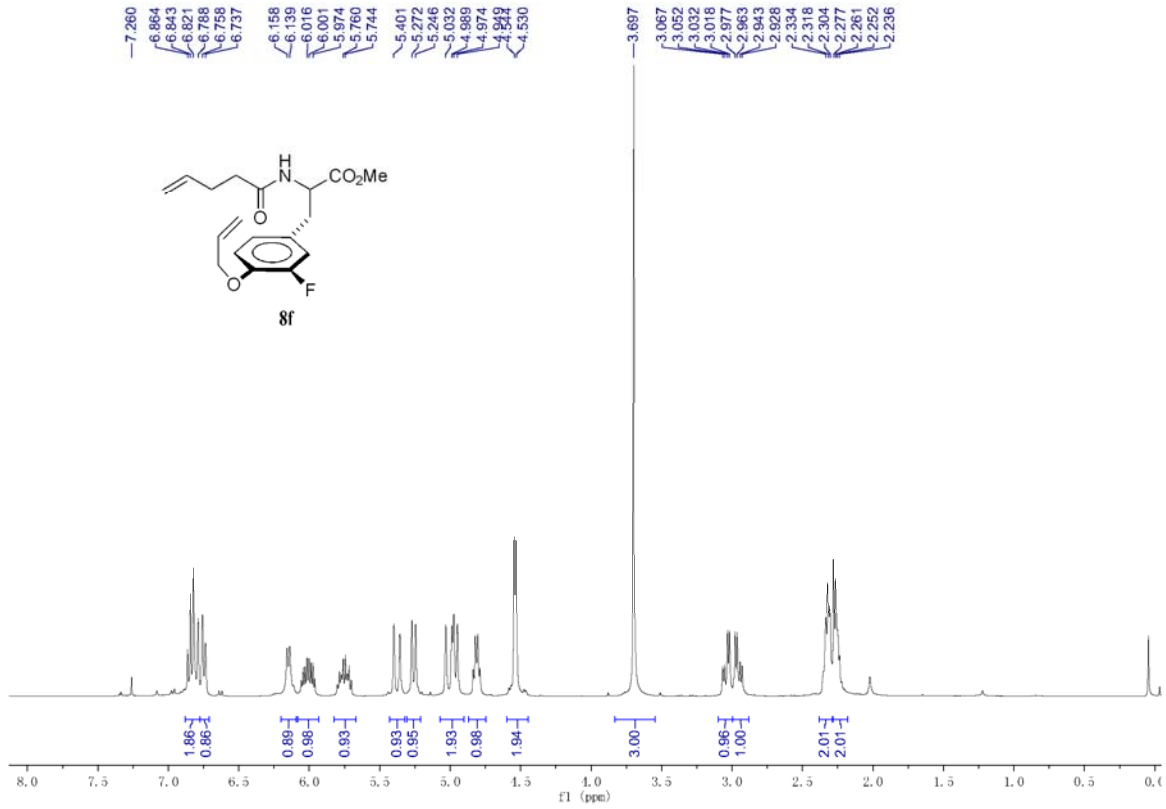
134.92
131.73
128.73
126.49
118.49
115.91
115.12
77.48
77.16
76.84
70.16
53.03
52.71
36.78
35.61
29.39
CO2Me
H
N
O
NO2
8e
f1 (ppm)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6.158
6.139
6.016
6.001
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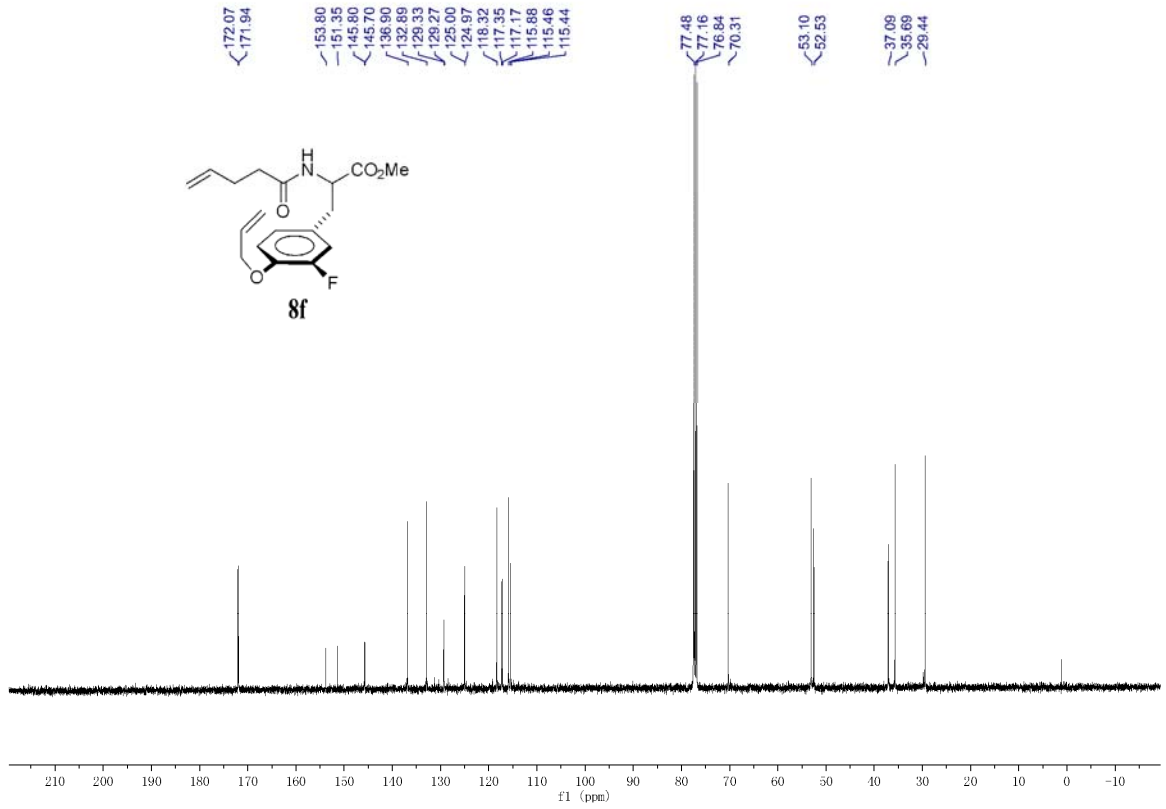
5.760
5.744
5.401
5.272
5.246
5.032
4.989
4.974
4.530
3.697
3.067
3.052
3.032
3.018
2.977
2.963
2.943
2.928
2.334
2.318
2.304
2.277
2.261
2.252
2.236
1.86
0.86
0.89
0.98
0.93
0.93
0.95
1.93
0.98
1.94
3.00
0.96
1.00
2.01
2.01
f1 (ppm)
8f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153.80
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145.70
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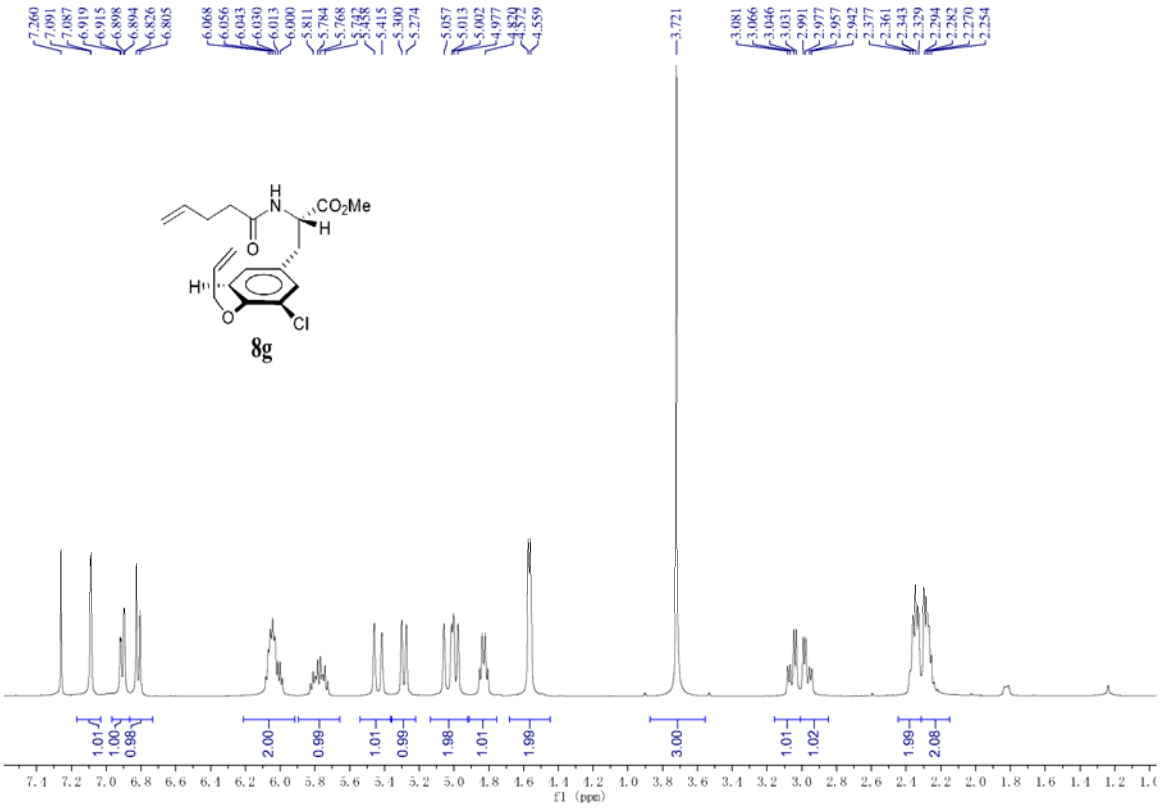
132.89
129.33
129.27
125.00
124.97
118.32
117.35
117.17
115.88
115.46
115.44
77.48
77.16
76.84
70.31
53.10
52.53
37.09
35.69
29.44
f1 (ppm)
8f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6.915
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6.894
6.826
6.805
6.068
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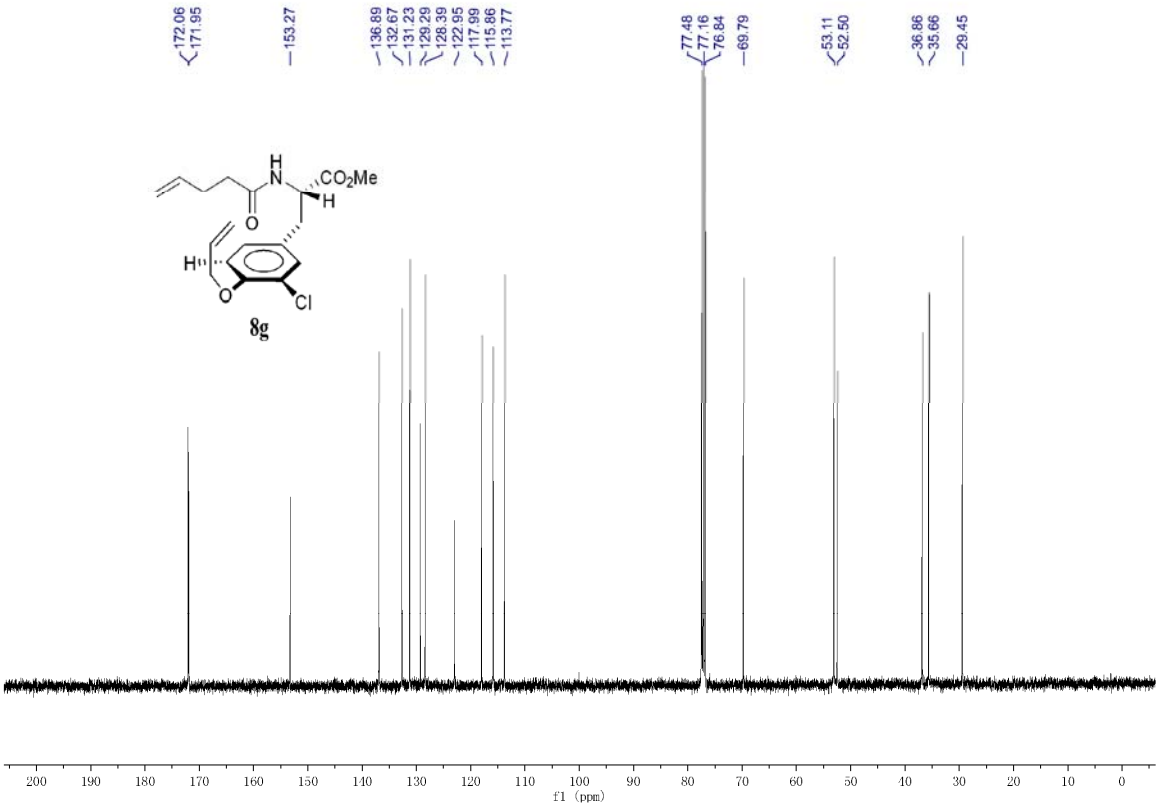
6.043
6.030
6.013
6.000
5.811
5.784
5.768
5.438
5.415
5.300
5.274
5.057
5.013
5.002
4.977
4.829
4.572
4.559
3.721
3.081
3.066
3.046
3.031
2.991
2.977
2.957
2.942
2.377
2.361
2.343
2.329
2.294
2.282
2.270
2.254
CO2Me
H
N
O
H
O
Cl
8g
1.01
1.00
0.98
2.00
0.99
1.01
0.99
1.98
1.01
1.99
3.00
1.01
1.02
1.99
2.08
f1 (ppm)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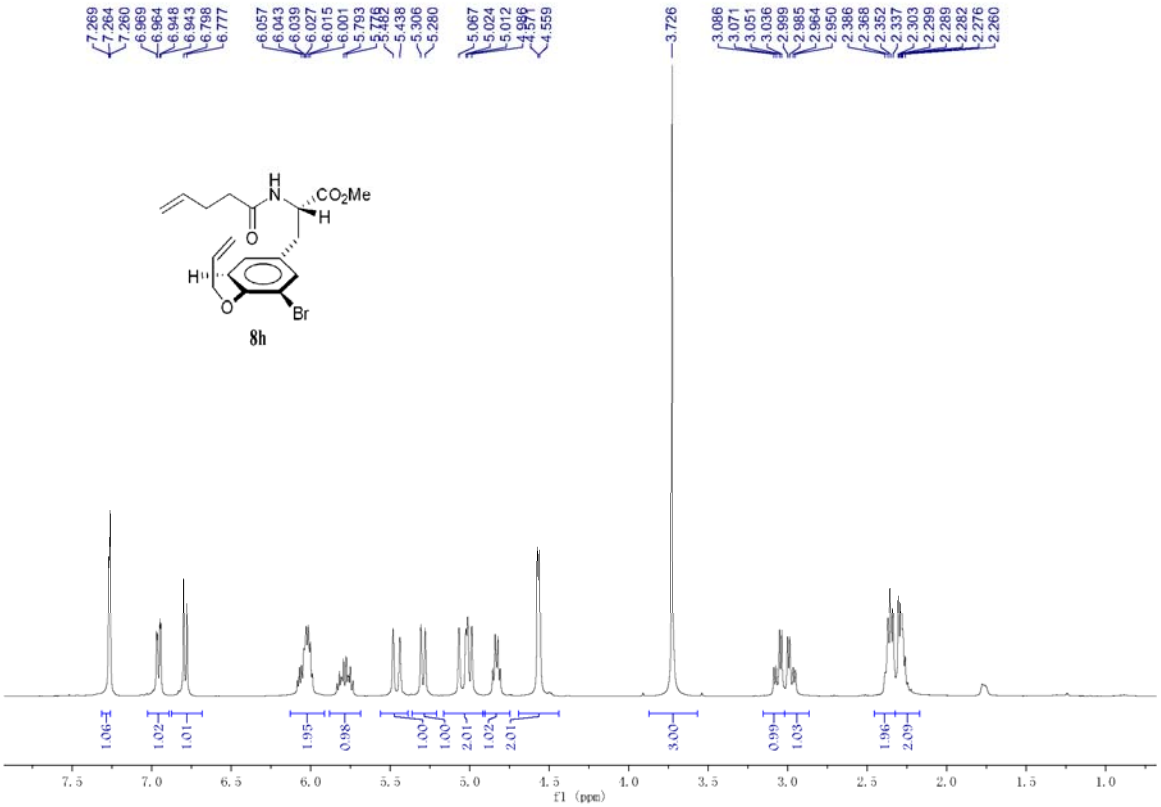
128.39
122.95
117.99
115.86
113.77
77.48
77.16
76.84
69.79
53.11
52.50
36.86
35.66
29.45
CO2Me
H
N
O
H
O
Cl
8g
f1 (ppm)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6.798
6.777
6.057
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6.039
6.027
6.015
6.001
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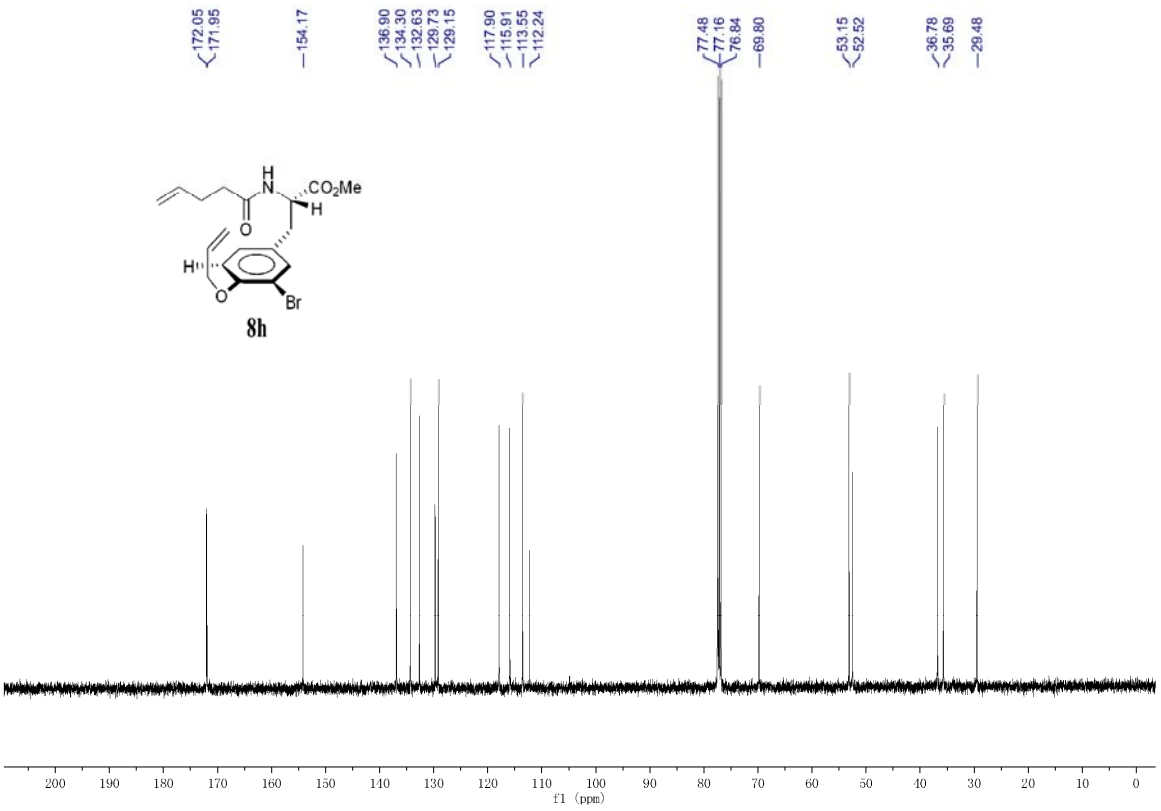
5.776
5.482
5.438
5.306
5.280
5.067
5.024
5.012
4.596
4.559
3.726
3.086
3.071
3.051
3.036
2.999
2.985
2.964
2.950
2.386
2.368
2.352
2.337
2.303
2.299
2.289
2.282
2.276
2.260
CO2Me
H
N
O
H
O
Br
8h
1.06
1.02
1.01
1.95
0.98
1.00
1.00
2.01
1.02
2.01
3.00
0.99
1.03
1.96
2.09
f1 (ppm)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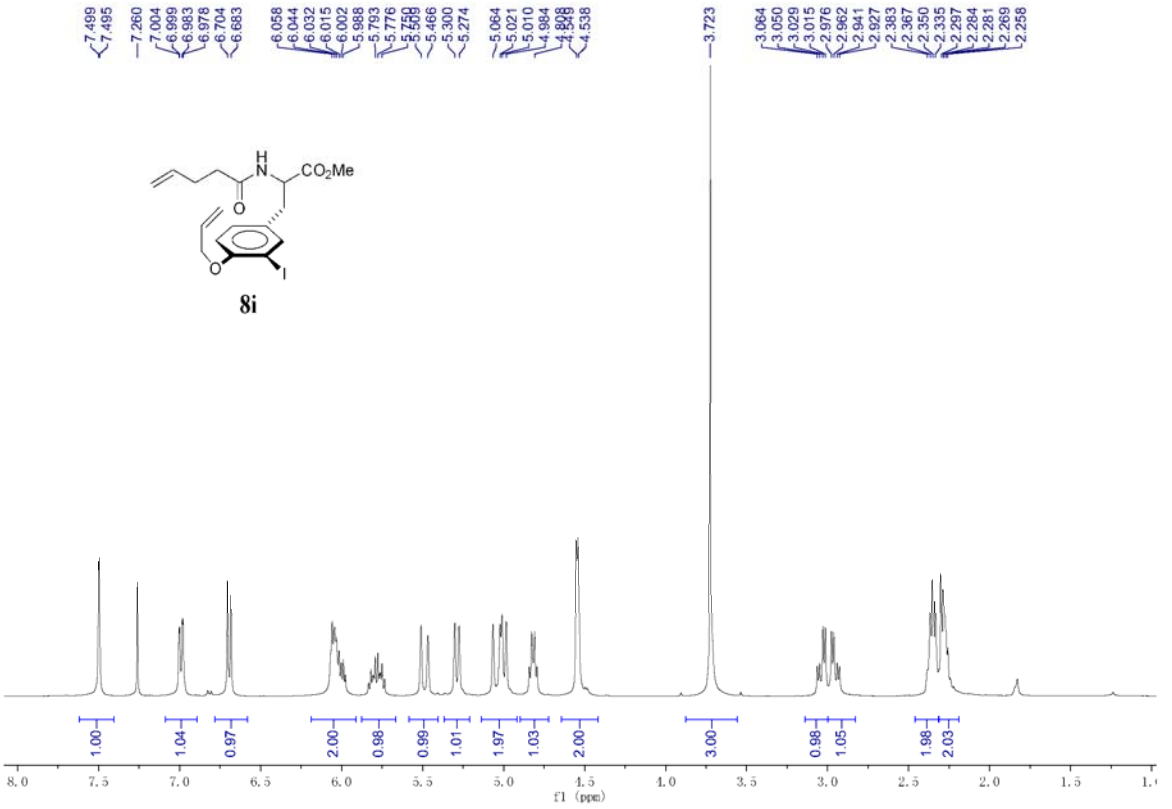
115.91
113.55
112.24
77.48
77.16
76.84
69.80
53.15
52.52
36.78
35.69
29.48
CO2Me
H
N
O
H
O
Br
8h
f1 (ppm)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6.015
6.002
5.988
5.793
5.776
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5.300
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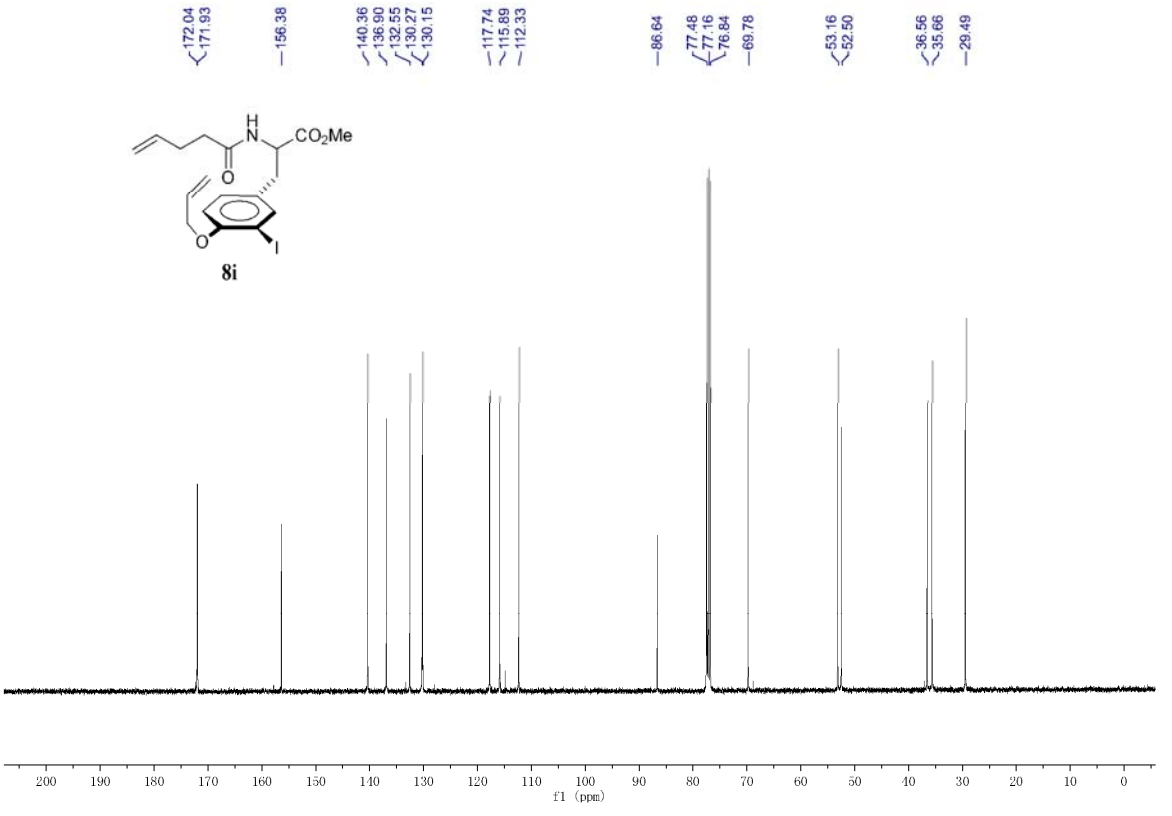
5.021
5.010
4.984
4.538
3.723
3.064
3.050
3.029
3.015
2.976
2.962
2.941
2.927
2.383
2.367
2.350
2.335
2.297
2.284
2.281
2.269
2.258
CO2Me
8i
1.00
1.04
0.97
2.00
0.98
0.99
1.01
1.97
1.03
2.00
3.00
0.98
1.05
1.98
2.03
f1 (ppm)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130.15
117.74
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112.33
86.64
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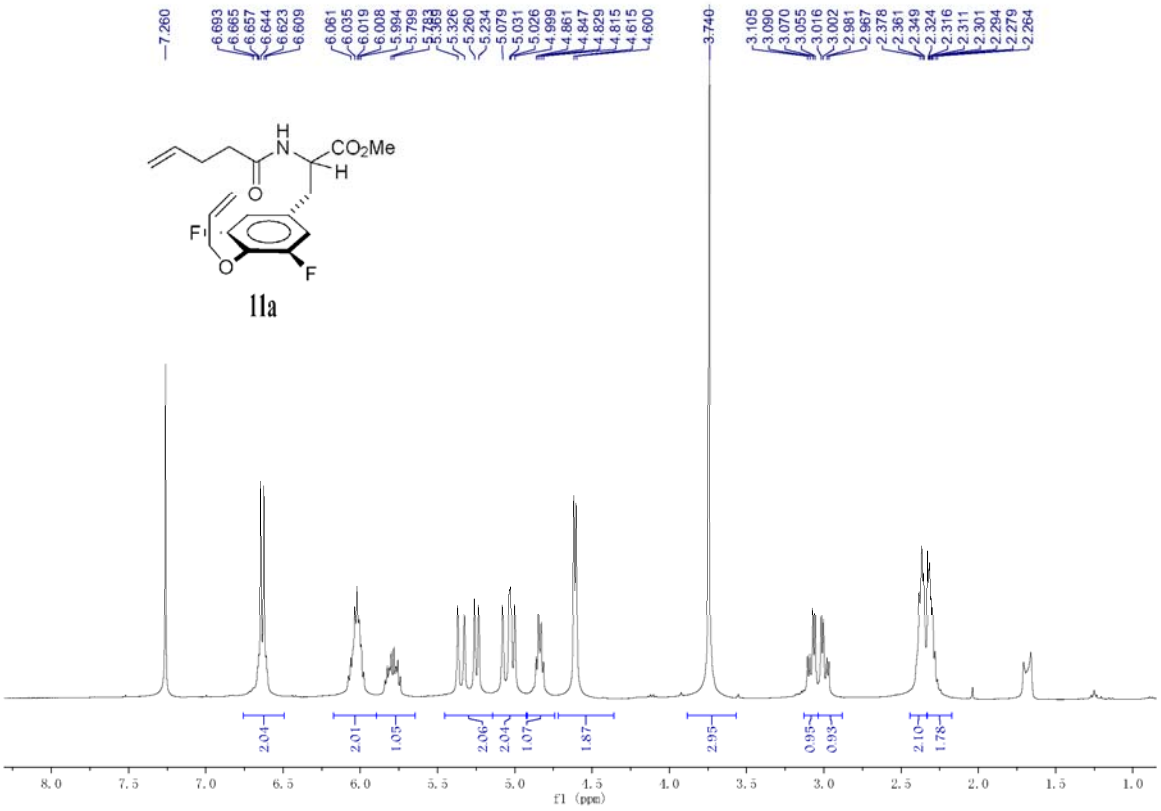
77.16
76.84
69.78
53.16
52.50
36.56
35.66
29.49
CO2Me
8i
f1 (ppm)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6.019
6.008
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5.799
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5.234
5.079
5.031
5.026
4.999
4.861
4.847
4.829
4.815
4.615
4.600
3.740
3.105
3.090
3.070
3.055
3.016
3.002
2.981
2.967
2.378
2.361
2.349
2.324
2.316
2.311
2.301
2.294
2.279
2.264
CO2Me
H
N
O
F
O
F
11a
2.04
2.01
1.05
2.06
2.04
1.07
1.87
2.95
0.95
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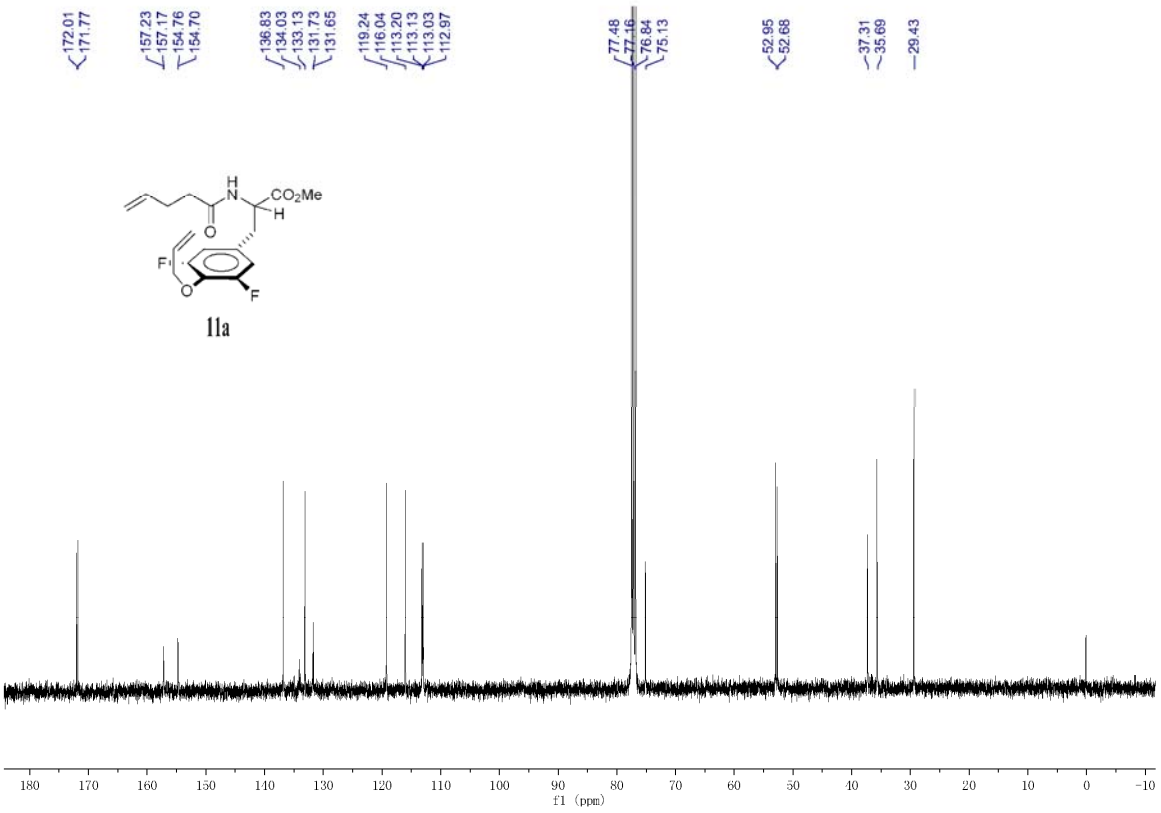
2.10
1.78
f1 (ppm)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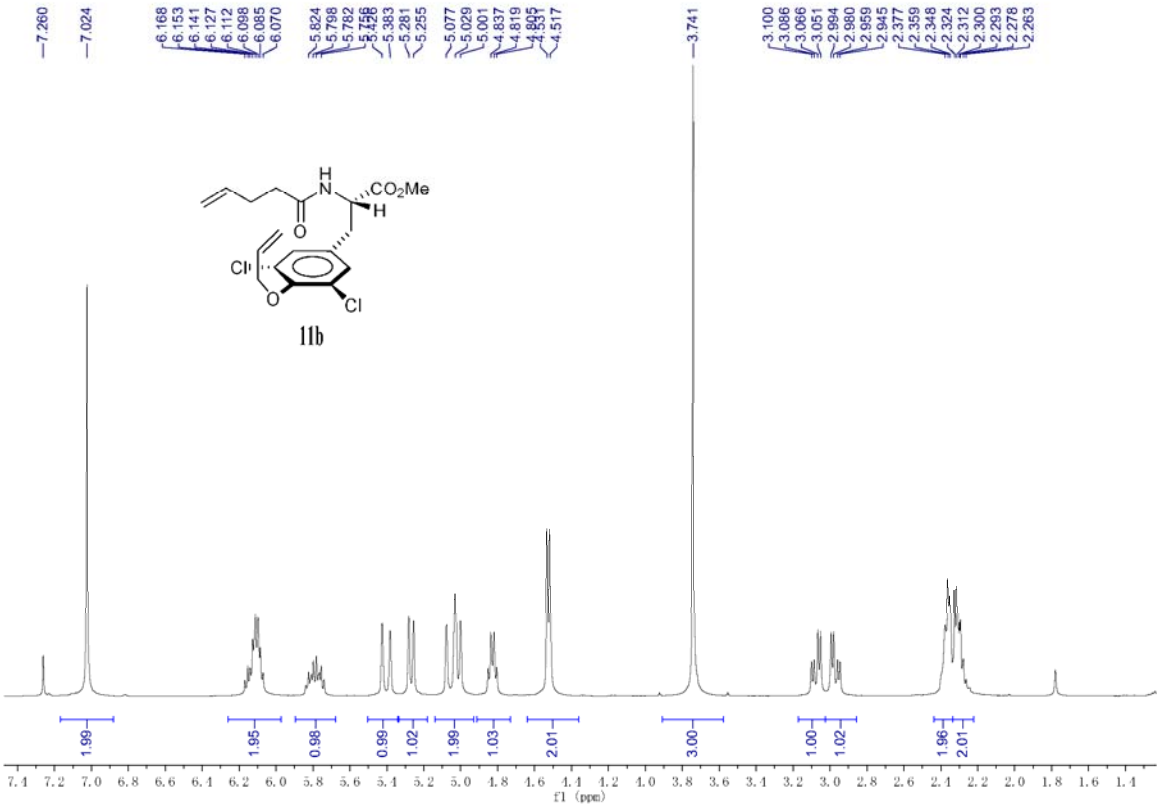
133.13
131.73
131.65
119.24
116.04
113.20
113.13
113.03
112.97
77.48
77.16
76.84
75.13
52.95
52.68
37.31
35.69
29.43
CO2Me
H
N
O
F
O
F
11a
f1 (ppm)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5.255
5.077
5.029
5.001
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3.741
3.100
3.086
3.066
3.051
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2.980
2.959
2.945
2.377
2.359
2.348
2.324
2.312
2.300
2.293
2.278
2.263
H
N
CO2Me
H
O
Cl
O
Cl
11b
1.99
1.95
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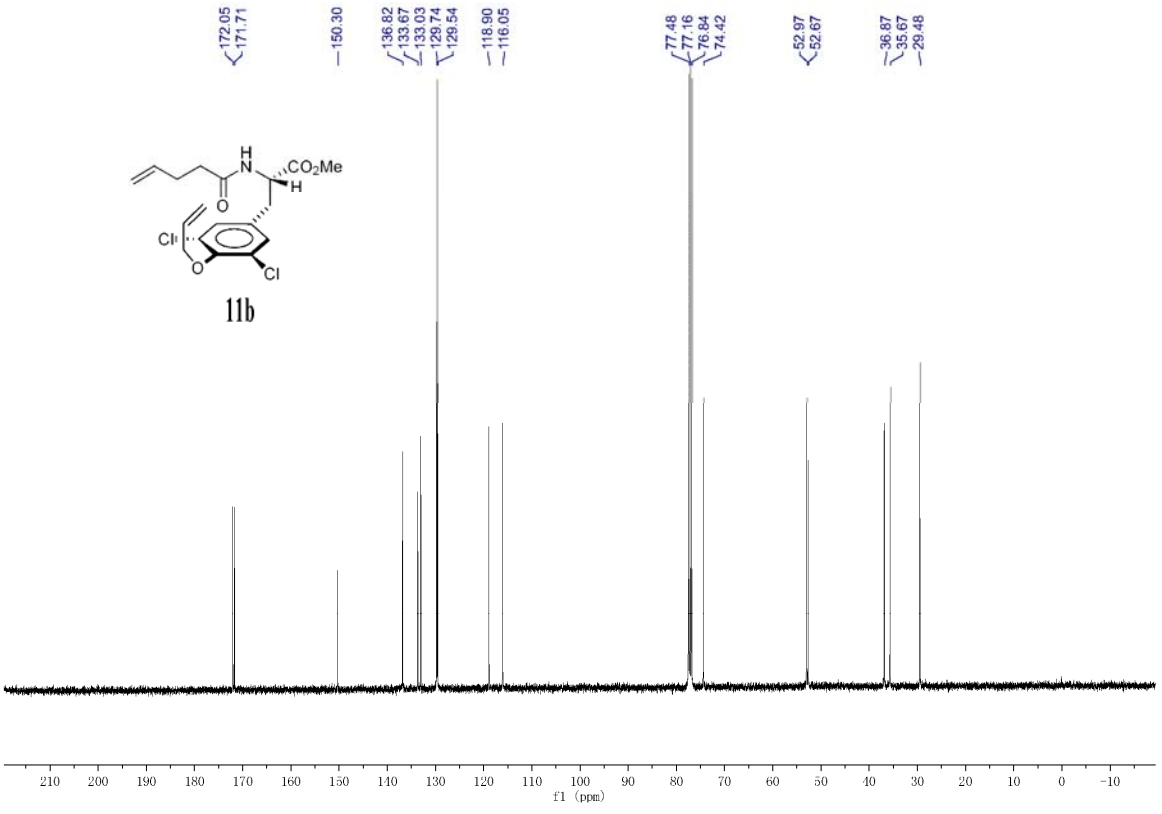
2.01
3.00
1.00
1.02
1.96
2.01
f1 (ppm)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129.54
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116.05
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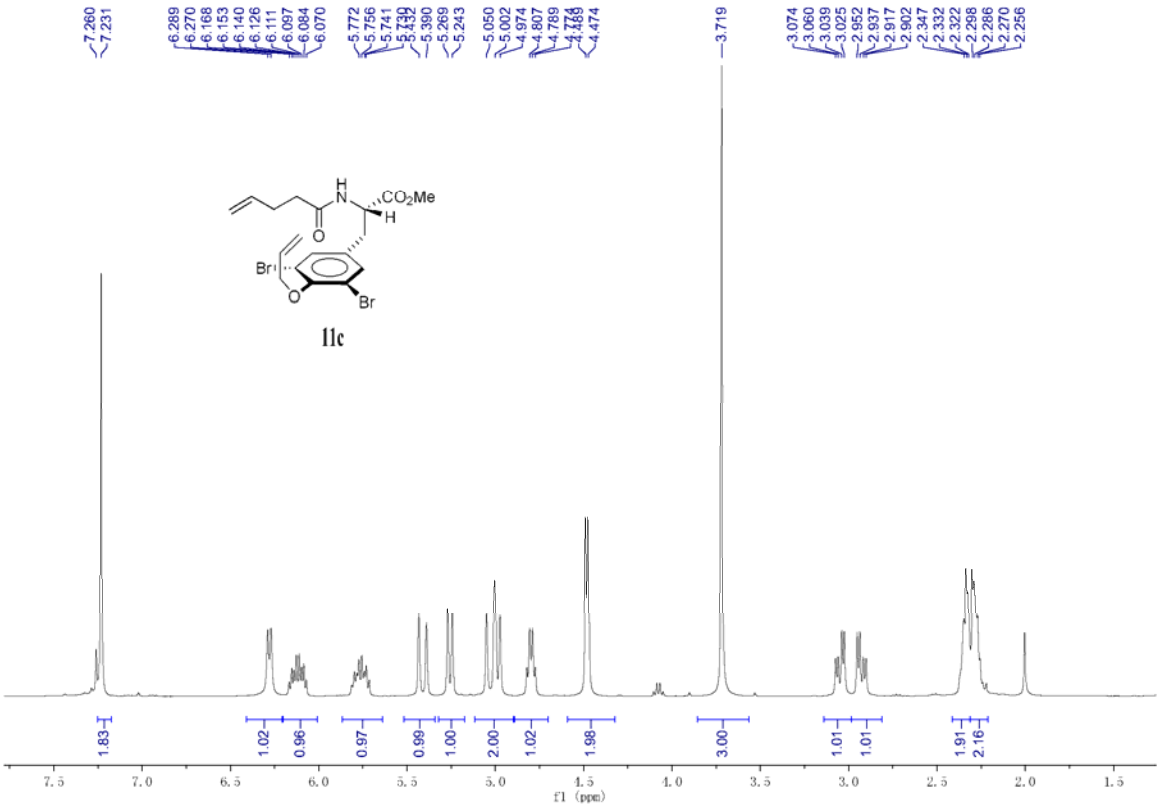
77.16
76.84
74.42
52.97
52.67
36.87
35.67
29.48
H
N
CO2Me
H
O
Cl
O
Cl
11b
f1 (ppm)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5.756
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5.243
5.050
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4.807
4.789
4.474
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3.074
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3.039
3.025
2.952
2.937
2.917
2.902
2.347
2.332
2.322
2.298
2.286
2.270
2.256
CO2Me
H
N
O
Br
O
Br
1.83
1.02
0.96
0.97
0.99
1.00
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1.02
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3.00
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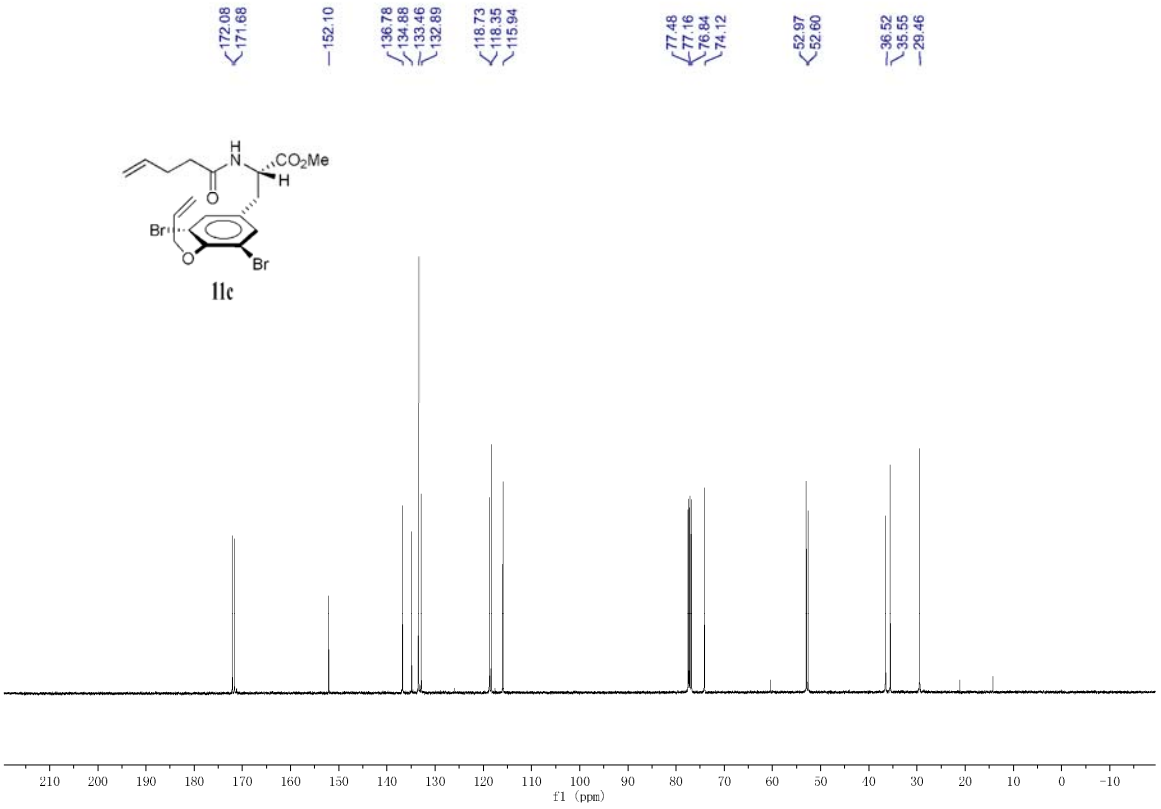
1.01
1.91
2.16
f1 (ppm)

11e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118.73
118.35
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77.48
77.16
76.84
74.12
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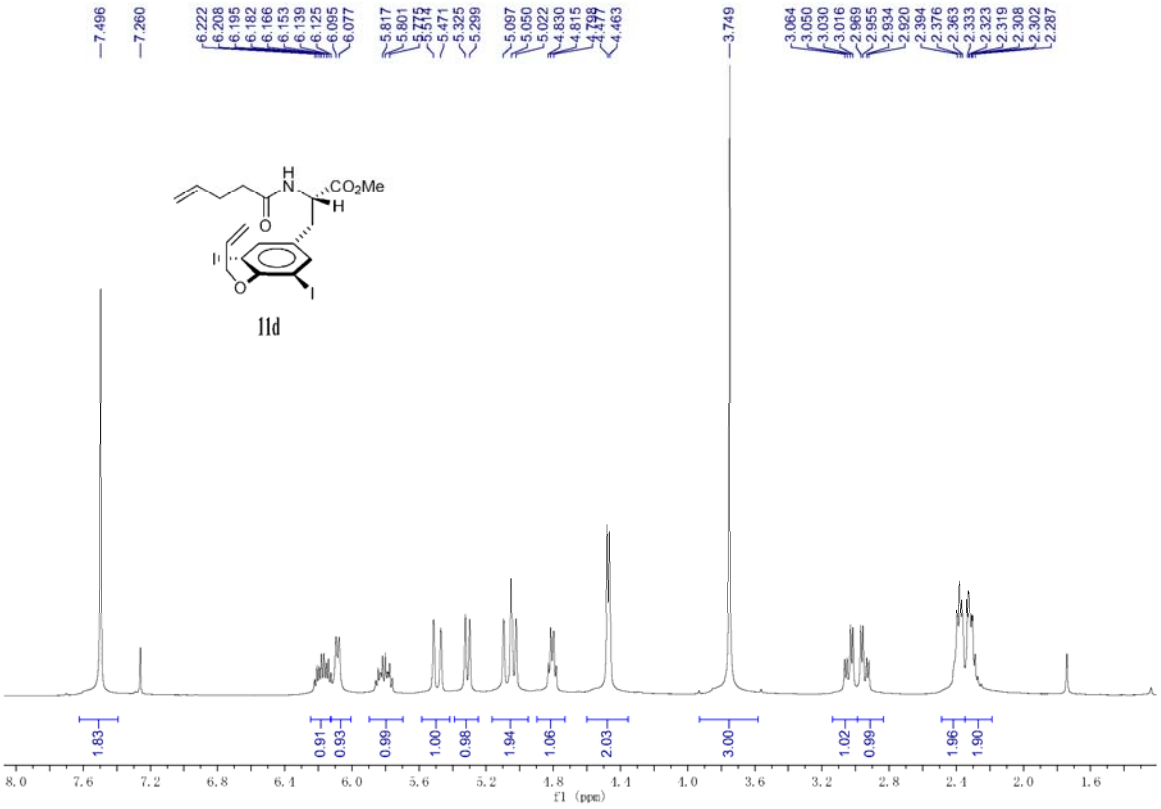
36.52
35.55
29.46
CO2Me
H
N
O
Br
O
Br
f1 (ppm)

11e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7.260
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6.208
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6.182
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6.153
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6.125
6.095
6.077
5.817
5.801
5.775
5.514
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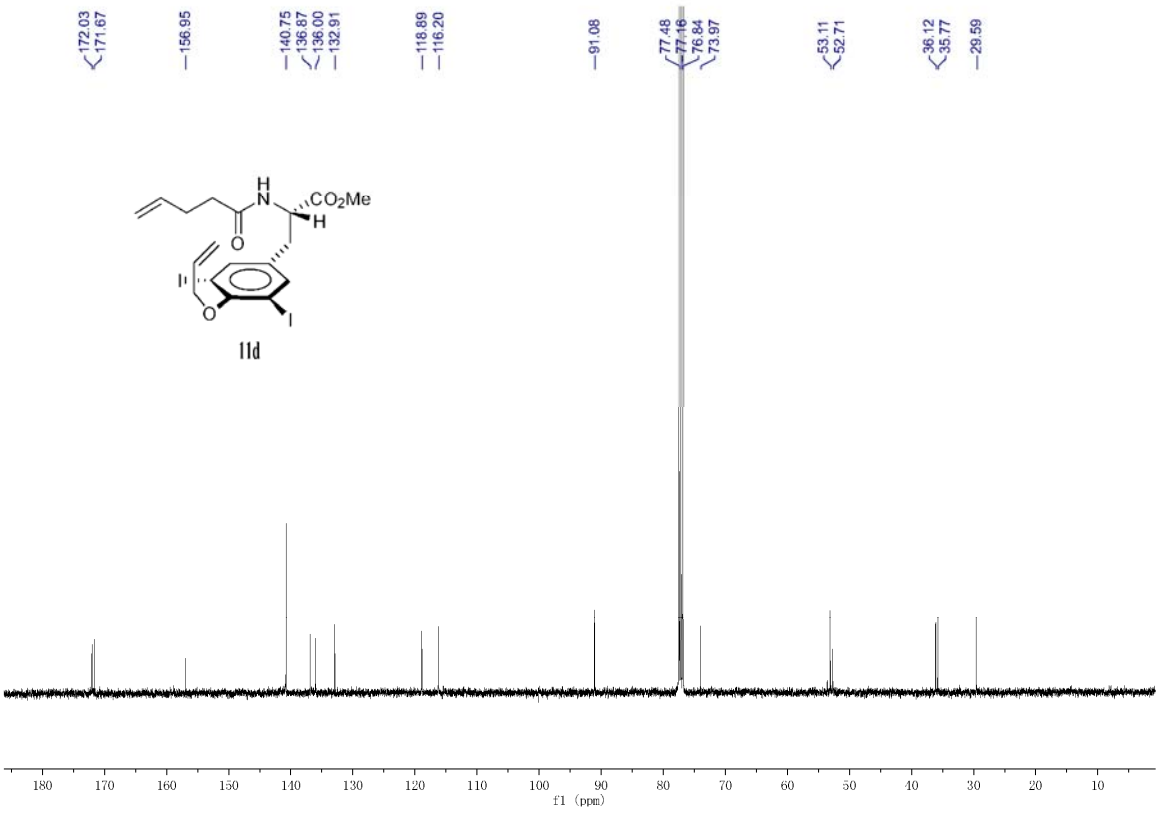
2.920
2.394
2.376
2.363
2.333
2.323
2.319
2.308
2.302
2.287
CO2Me
H
N
O
I
O
I
11d
1.83
0.91
0.93
0.99
1.00
0.98
1.94
1.06
2.03
3.00
1.02
0.99
1.96
1.90
f1 (ppm)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77.16
76.84
73.97
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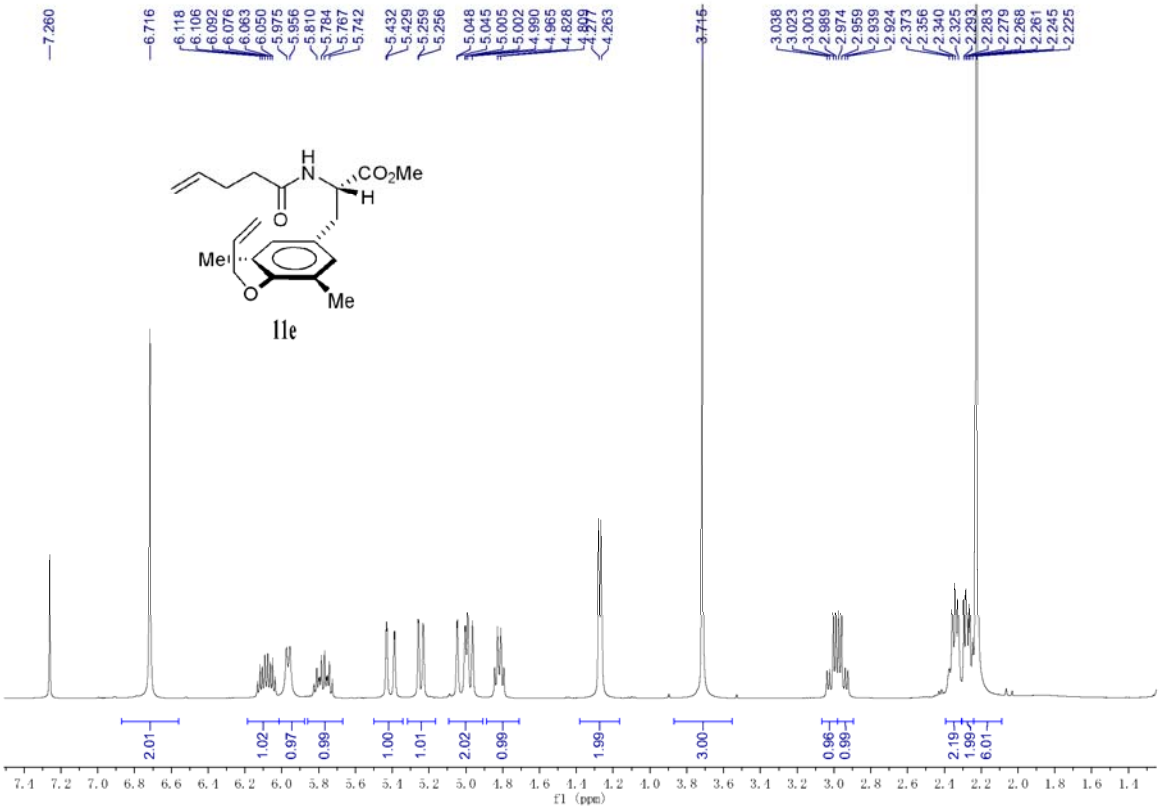
52.71
36.12
35.77
29.59
CO2Me
H
N
O
I
O
I
11d
f1 (ppm)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6.050
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5.767
5.742
5.432
5.429
5.259
5.256
5.048
5.045
5.005
5.002
4.990
4.965
4.828
4.809
4.277
4.263
3.715
3.038
3.023
3.003
2.989
2.974
2.959
2.939
2.924
2.373
2.356
2.340
2.325
2.293
2.283
2.279
2.268
2.261
2.245
2.225
CO2Me
H
N
O
Me
O
Me
11e
2.01
1.02
0.97
0.99
1.00
1.01
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1.99
3.00
0.96
0.99
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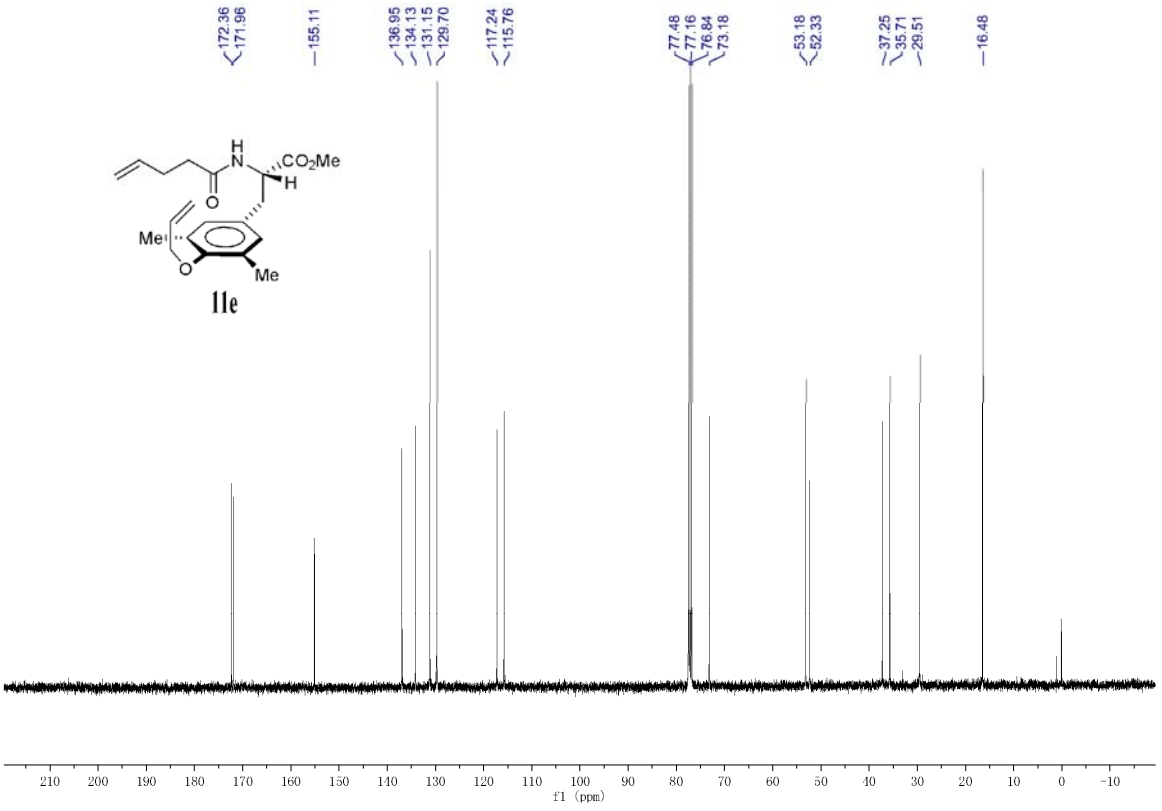
1.99
6.01
f1 (ppm)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117.24
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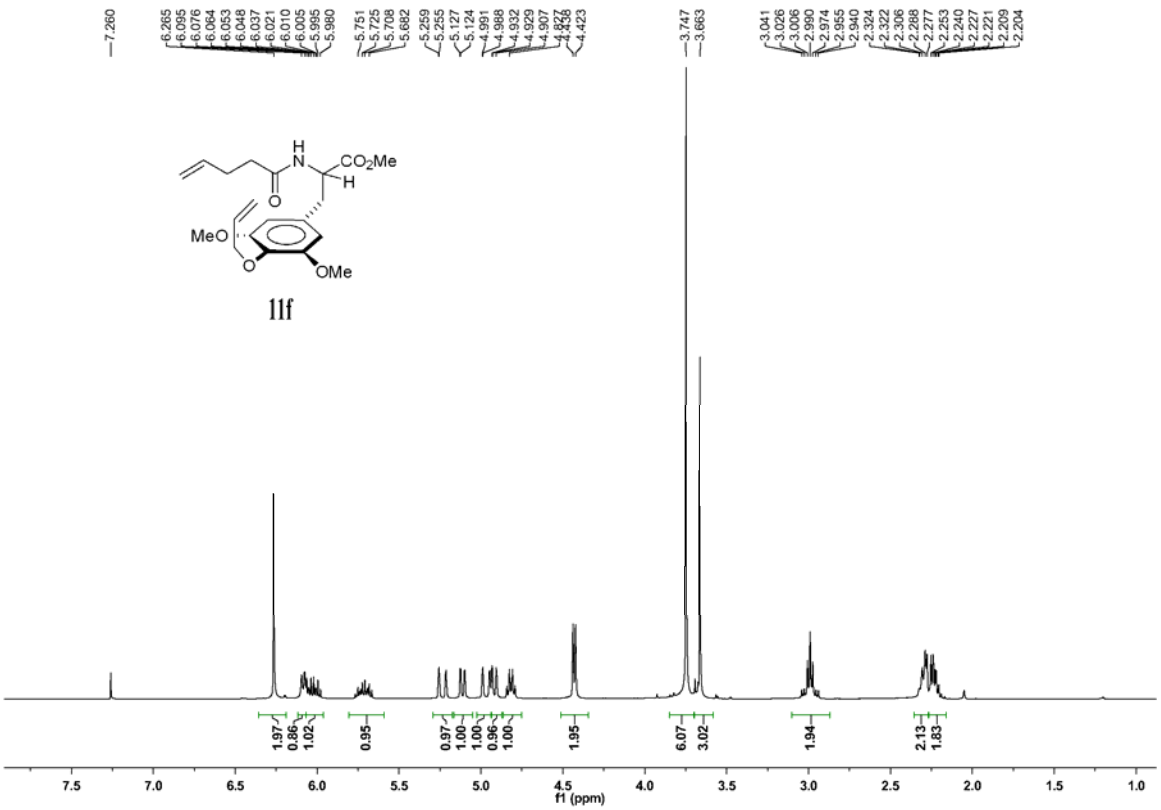
77.16
76.84
73.18
53.18
52.33
37.25
35.71
29.51
16.48
CO2Me
H
N
O
Me
O
Me
11e
f1 (ppm)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6.037
6.021
6.010
6.005
5.995
5.980
5.751
5.725
5.708
5.682
5.259
5.255
5.127
5.124
4.991
4.988
4.932
4.929
4.907
4.827
4.438
4.423
3.747
3.663
3.041
3.026
3.006
2.990
2.974
2.955
2.940
2.324
2.322
2.306
2.288
2.277
2.253
2.240
2.227
2.221
2.209
2.204
H
N
CO2Me
H
O
MeO
O
OMe
1.97
0.86
1.02
0.95
0.97
1.00
1.00
0.96
1.00
1.95
6.07
3.02
1.94
2.13
1.83
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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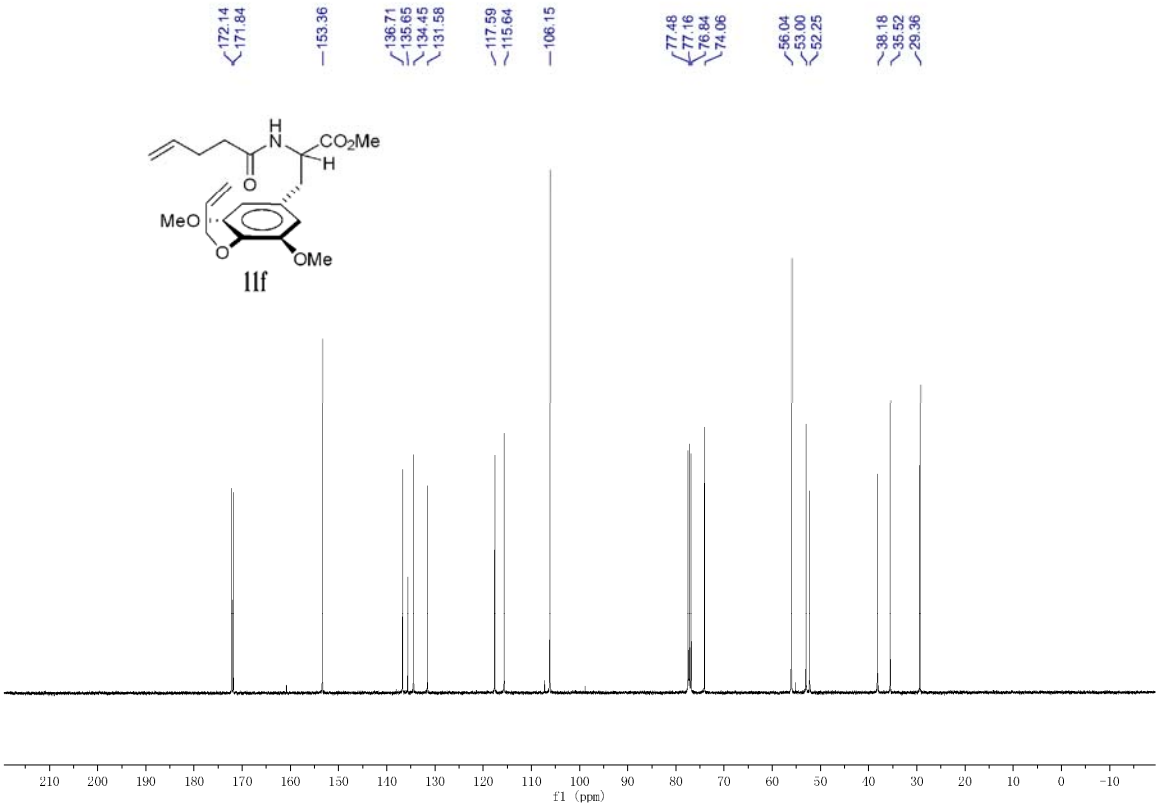
2.0
1.5
1.0
f1 (ppm)

11f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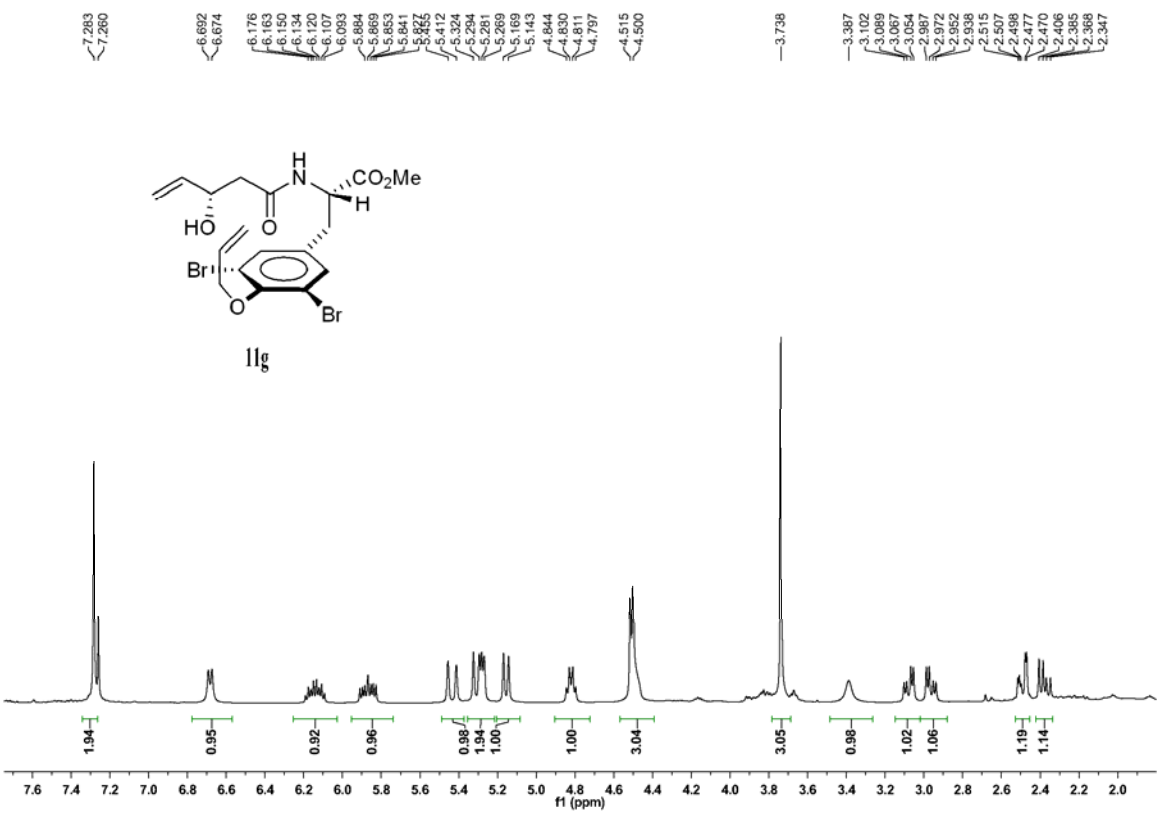
76.84
74.06
56.04
53.00
52.25
38.18
35.52
29.36
H
N
CO2Me
H
O
MeO
O
OMe
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

11f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5.869
5.853
5.841
5.827
5.455
5.412
5.324
5.294
5.281
5.269
5.169
5.143
4.844
4.830
4.811
4.797
4.515
4.500
3.738
3.387
3.102
3.089
3.067
3.054
2.987
2.972
2.952
2.938
2.515
2.507
2.498
2.477
2.470
2.406
2.385
2.368
2.347
H
N
CO2Me
H
HO
O
Br
O
Br
11g
1.94
0.95
0.92
0.96
0.98
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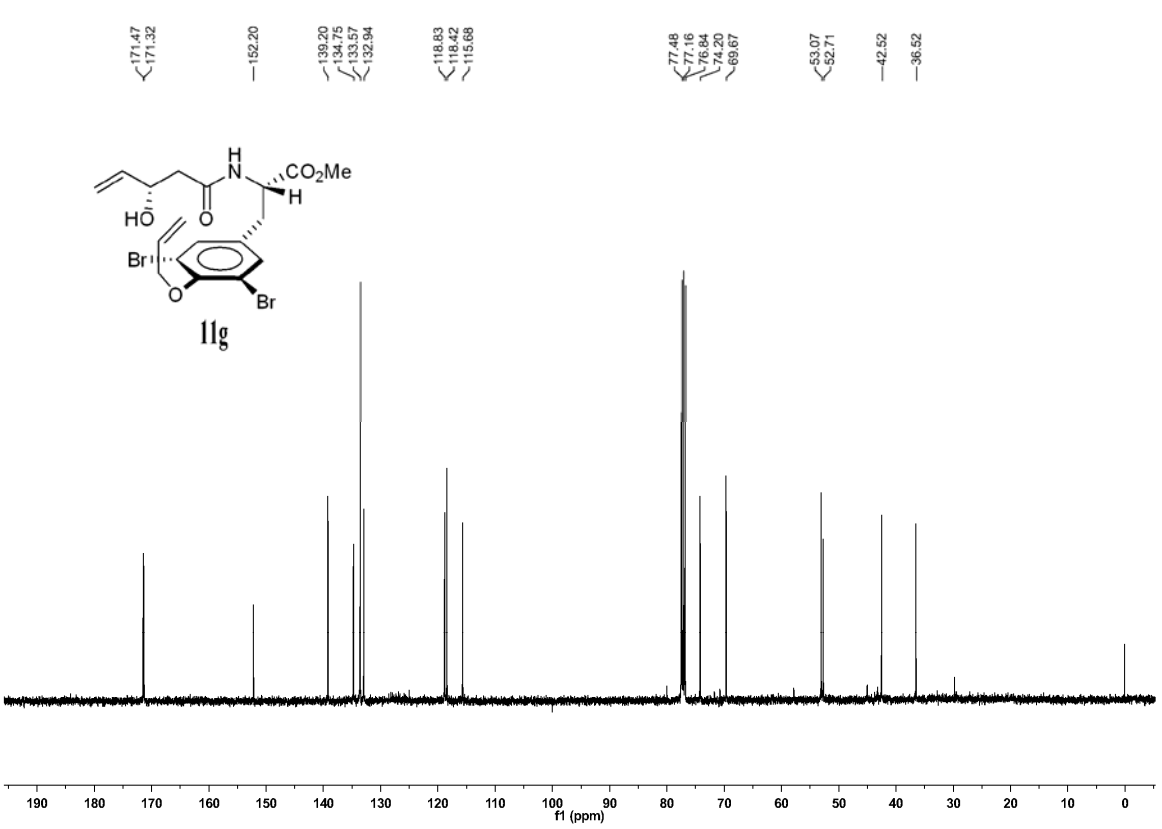
1.00
3.04
3.05
0.98
1.02
1.06
1.19
1.14
f1 (ppm)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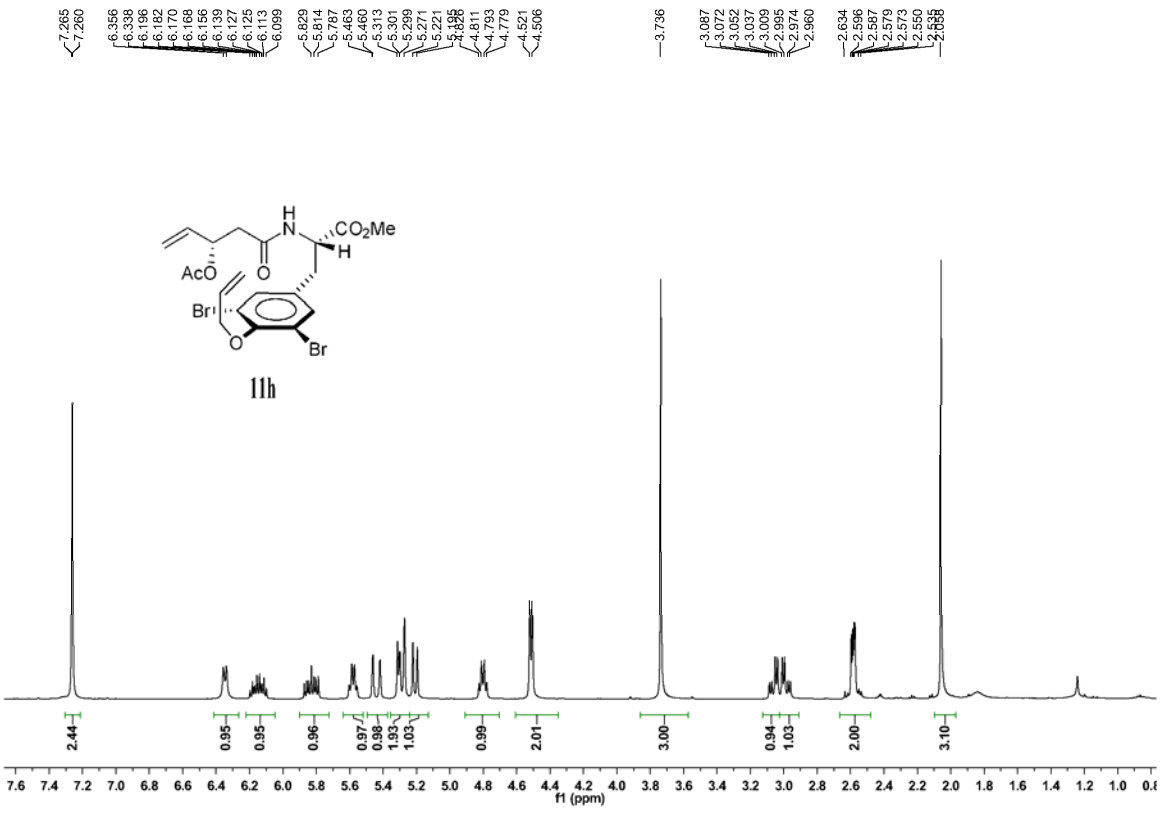
77.48
77.16
76.84
74.20
69.67
53.07
52.71
42.52
36.52
H
N
CO2Me
H
HO
O
Br
O
Br
11g
f1 (ppm)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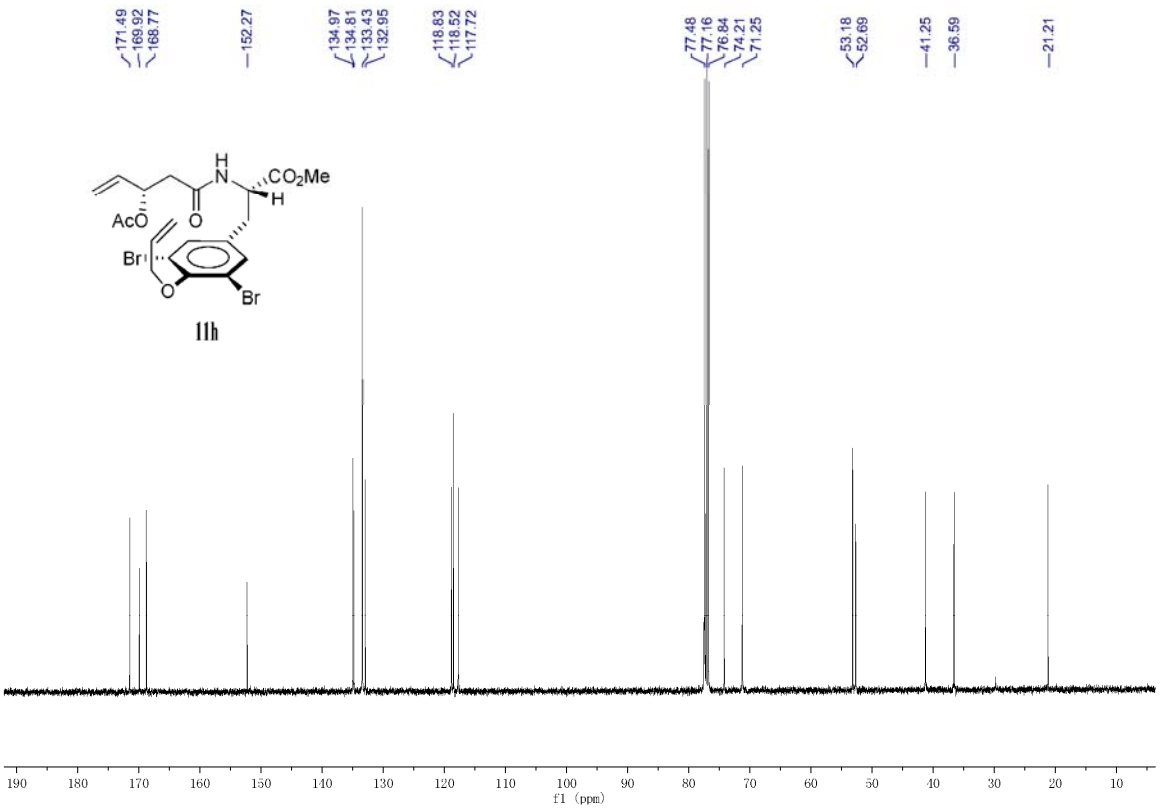
6.127
6.125
6.113
6.099
5.829
5.814
5.787
5.463
5.460
5.313
5.301
5.299
5.271
5.221
4.811
4.793
4.779
4.521
4.506
3.736
3.087
3.072
3.052
3.037
3.009
2.995
2.974
2.960
2.634
2.596
2.587
2.579
2.573
2.550
2.535
2.508
CO2Me
H
N
H
AcO
O
Br
O
Br
11h
2.44
0.95
0.95
0.96
0.97
0.98
1.93
1.03
0.99
2.01
3.00
0.94
1.03
2.00
3.10
f1 (ppm)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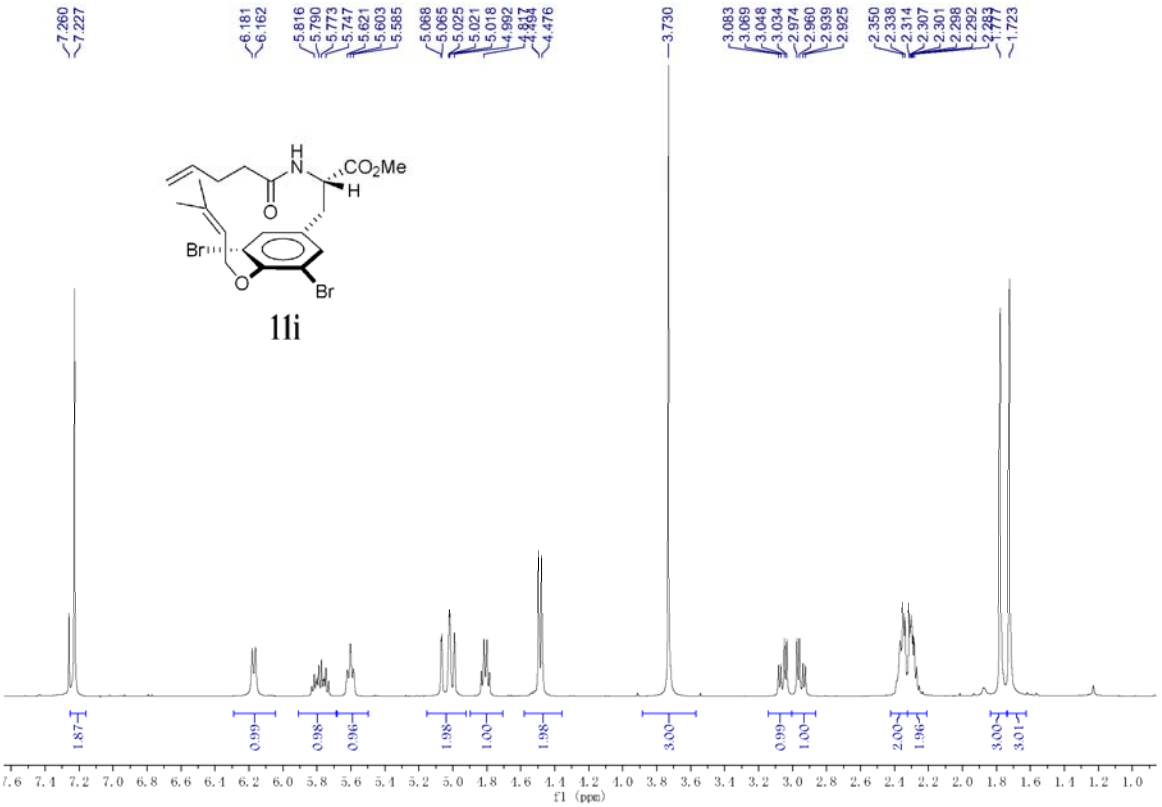
132.95
118.83
118.52
117.72
77.48
77.16
76.84
74.21
71.25
53.18
52.69
41.25
36.59
21.21
CO2Me
H
N
H
AcO
O
Br
O
Br
11h
f1 (ppm)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5.747
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5.068
5.065
5.025
5.021
5.018
4.992
4.884
4.476
3.730
3.083
3.069
3.048
3.034
2.974
2.960
2.939
2.925
2.350
2.338
2.314
2.307
2.301
2.298
2.292
1.777
1.723
CO2Me
H
N
O
Br
O
Br
11i
1.87
0.99
0.98
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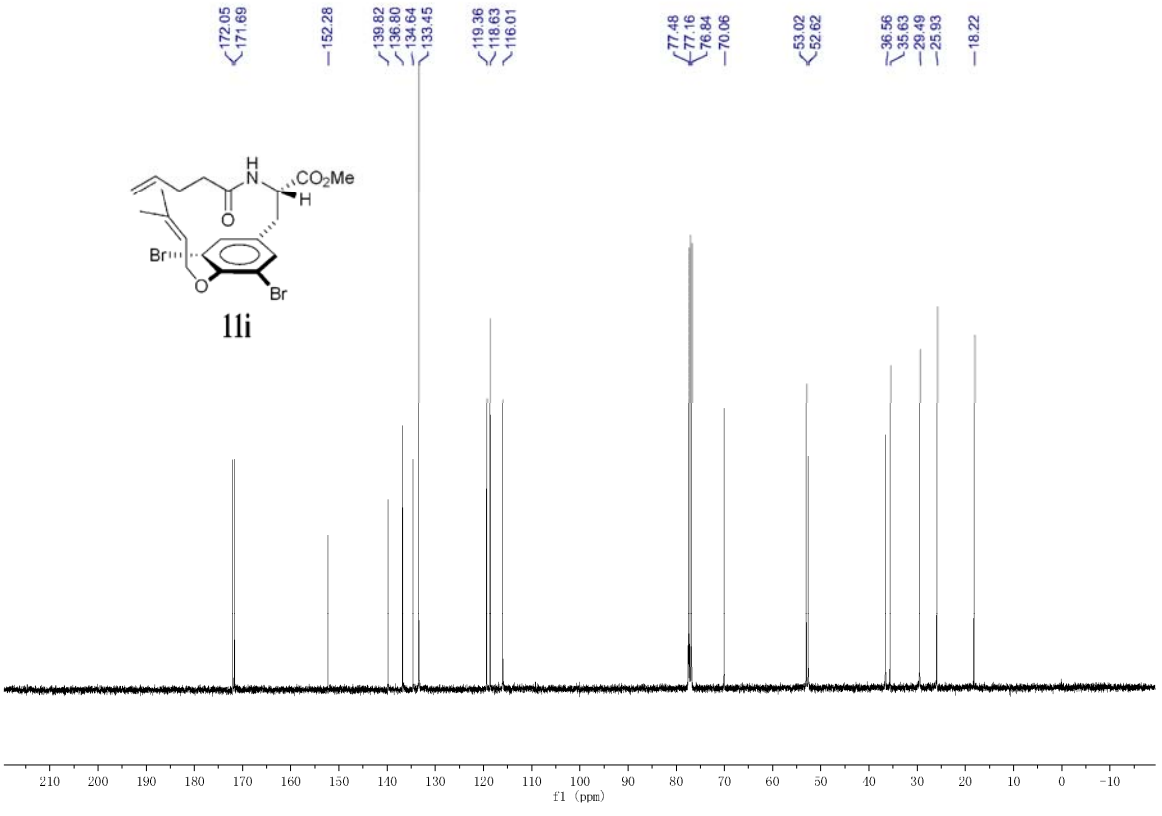
1.98
3.00
0.99
1.00
2.00
1.96
3.00
3.01
f1 (ppm)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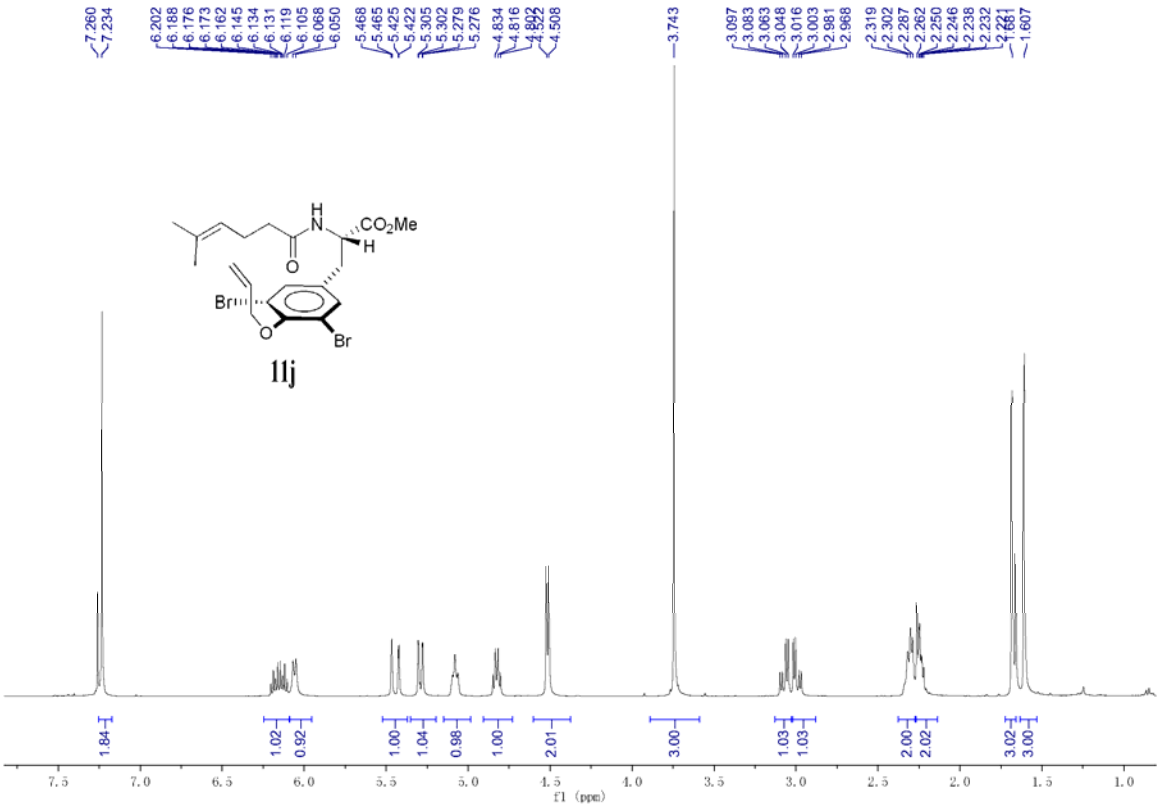
119.36
118.63
116.01
77.48
77.16
76.84
70.06
53.02
52.62
36.56
35.63
29.49
25.93
18.22
CO2Me
H
N
O
Br
O
Br
11i
f1 (ppm)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6.173
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6.145
6.134
6.131
6.119
6.105
6.068
6.050
5.468
5.465
5.425
5.422
5.305
5.302
5.279
5.276
4.834
4.816
4.802
4.522
4.508
3.743
3.097
3.083
3.063
3.048
3.016
3.003
2.981
2.968
2.319
2.302
2.287
2.262
2.250
2.246
2.238
2.232
1.621
1.607
CO2Me
H
N
H
O
Br
O
Br
11j
1.84
1.02
0.92
1.00
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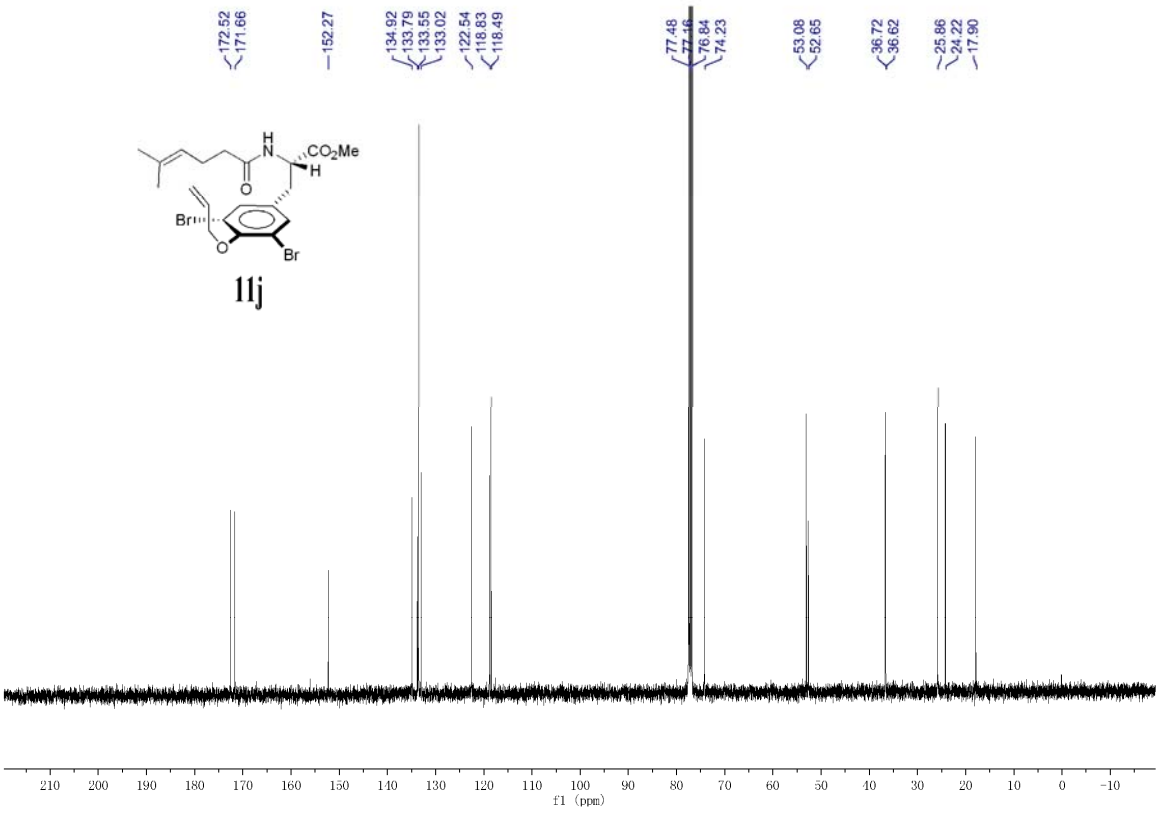
3.00
1.03
1.03
2.00
2.02
3.02
3.00
f1 (ppm)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122.54
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118.49
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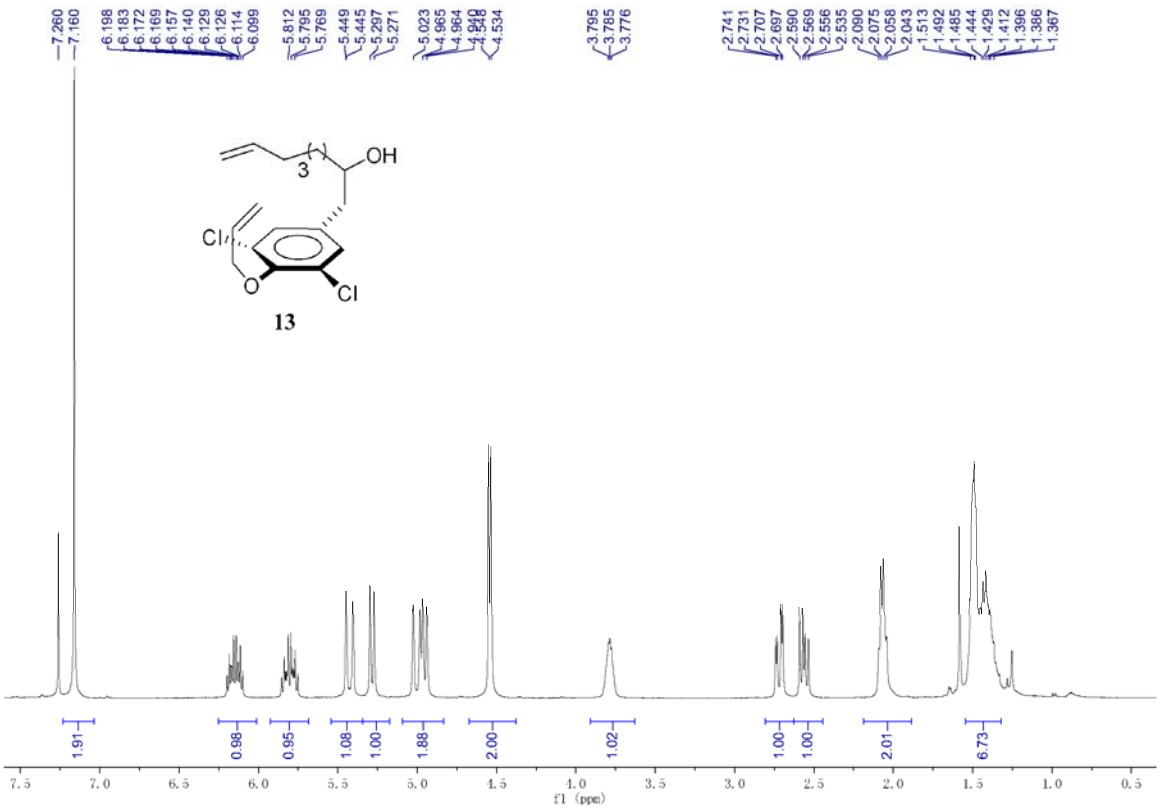
77.16
76.84
74.23
53.08
52.65
36.72
36.62
25.86
24.22
17.90
CO2Me
H
N
H
O
Br
O
Br
11j
f1 (ppm)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5.812
5.795
5.769
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5.271
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4.964
4.849
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3.785
3.776
2.741
2.731
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2.043
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1.444
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1.367
OH
3
Cl
O
Cl
13
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1.00
1.00
2.01
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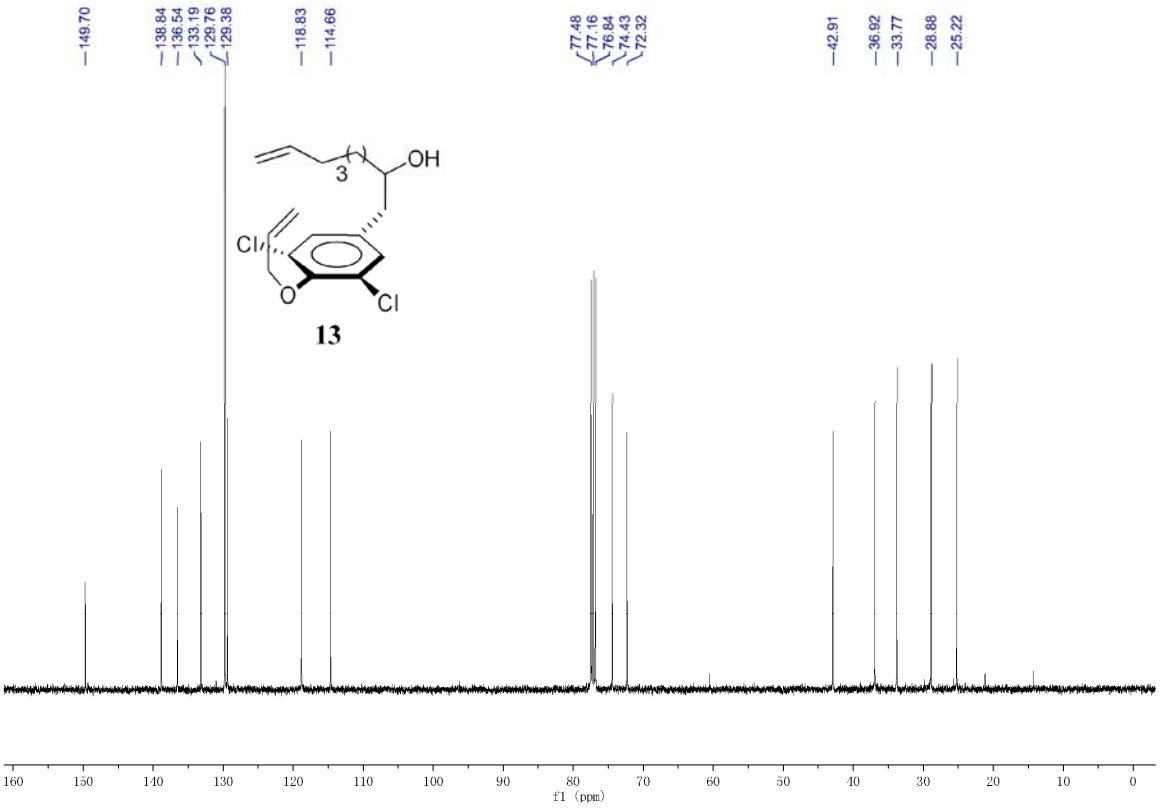
f1 (ppm)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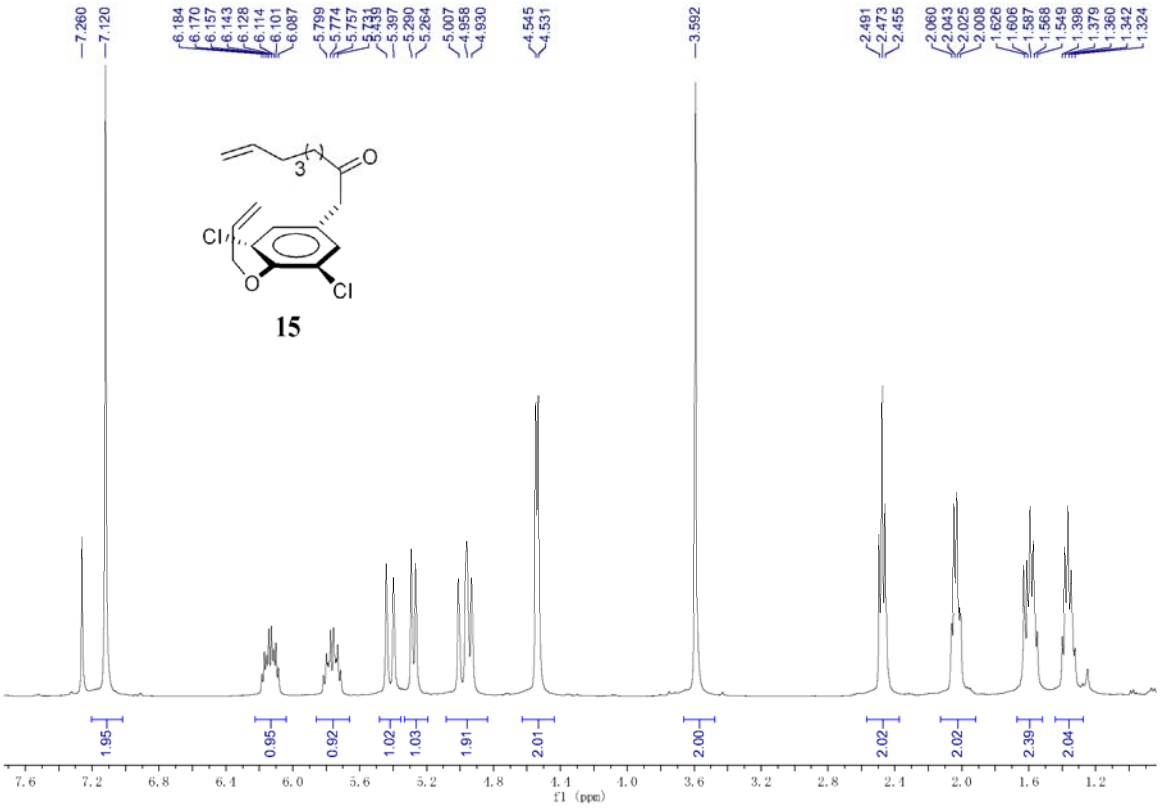
114.66
77.48
77.16
76.84
74.43
72.32
42.91
36.92
33.77
28.88
25.22
OH
3
Cl
O
Cl
13
f1 (ppm)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6.114
6.101
6.087
5.799
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5.757
5.433
5.397
5.290
5.264
5.007
4.958
4.930
4.545
4.531
3.592
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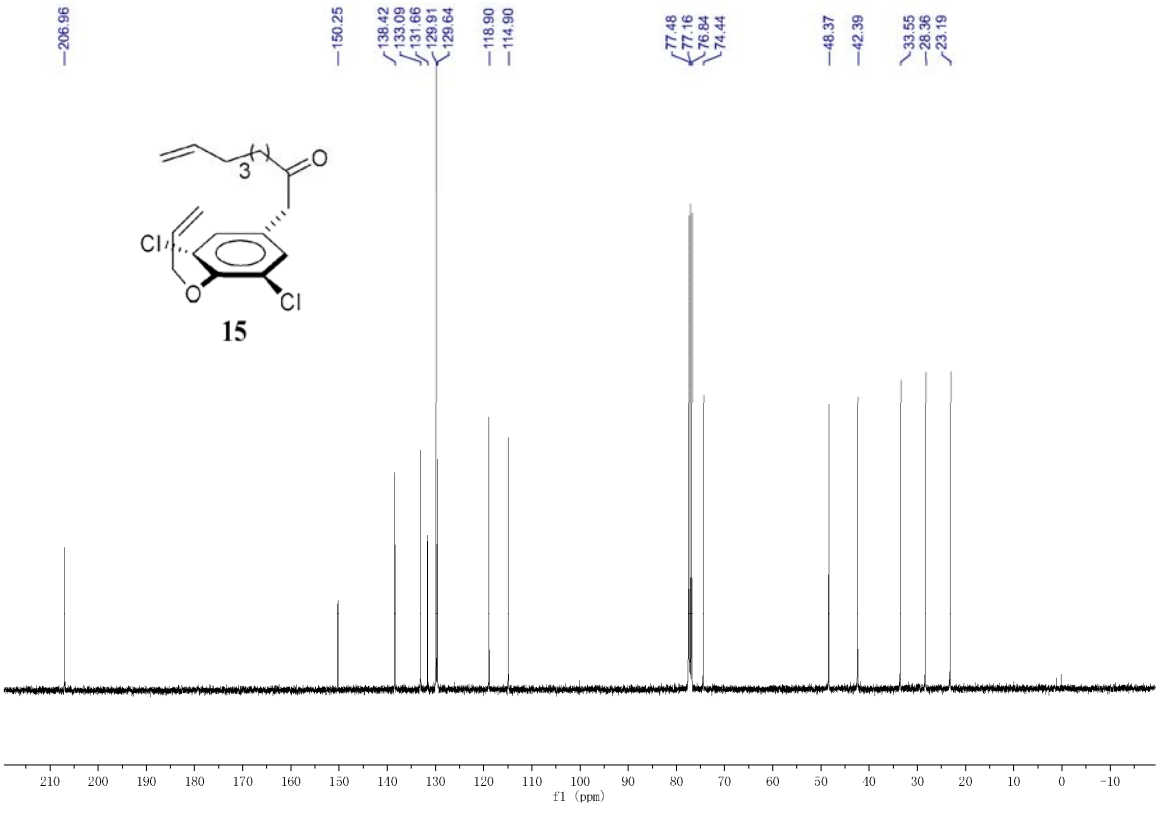
2.473
2.455
2.060
2.043
2.025
2.008
1.626
1.606
1.587
1.568
1.549
1.398
1.379
1.360
1.342
1.324
1.95
0.95
0.92
1.02
1.03
1.91
2.01
2.00
2.02
2.02
2.39
2.04
f1 (ppm)

3
O
Cl
O
Cl

15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129.64
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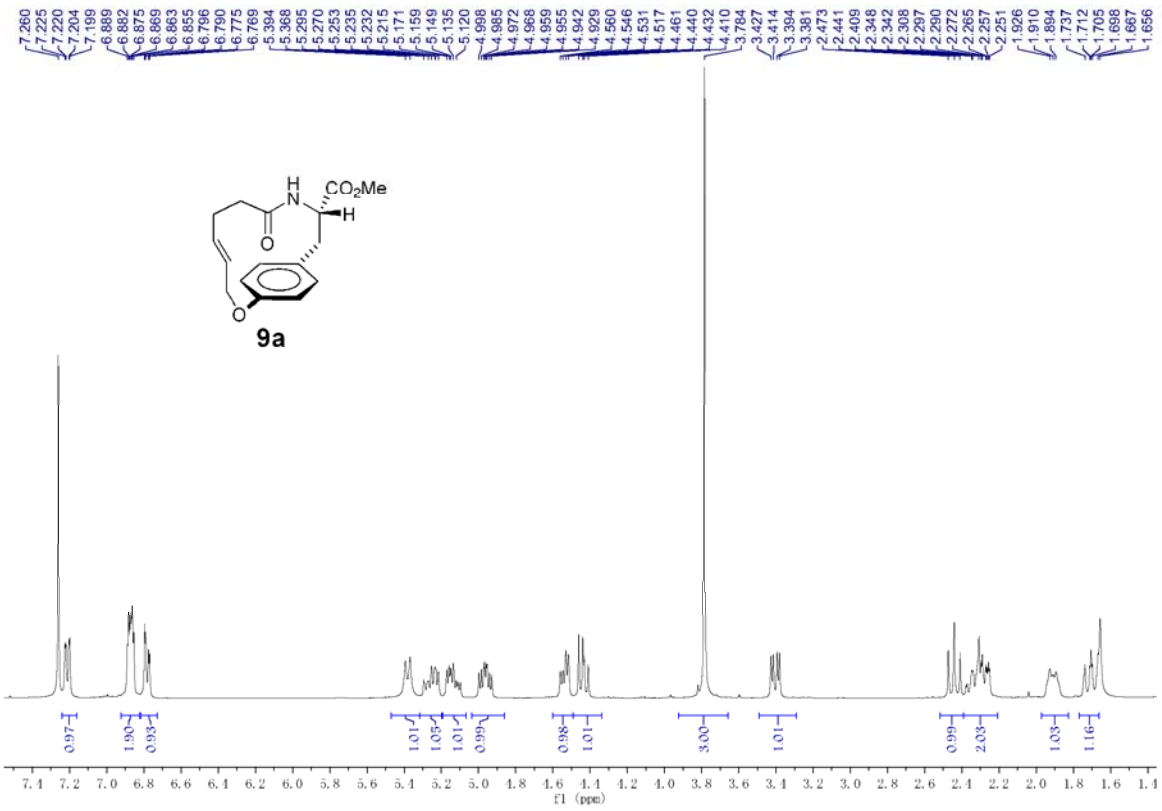
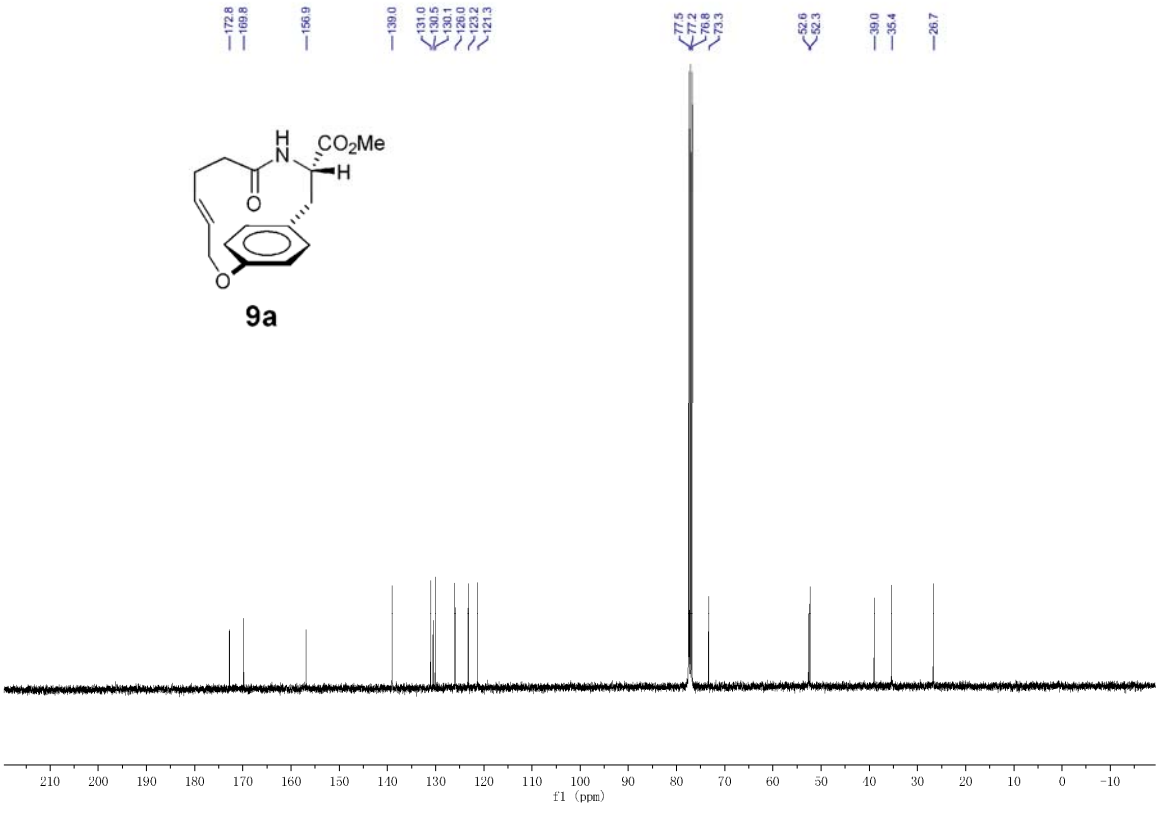
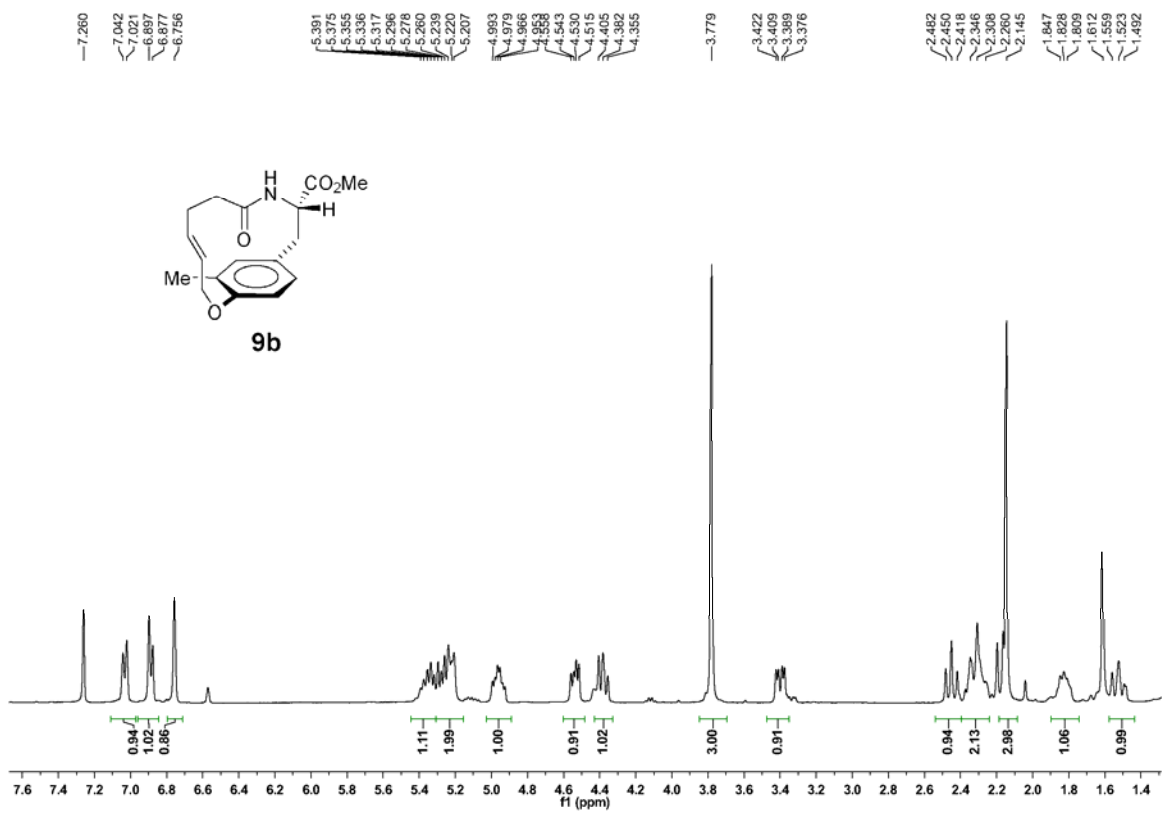
77.16
76.84
74.44
48.37
42.39
33.55
28.36
23.19
f1 (ppm)


9a
f1 (ppm)


9a
f1 (ppm)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4.979
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4.953
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4.530
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4.405
4.382
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3.779
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3.409
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2.308
2.260
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1.828
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1.612
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1.492
H
N
CO2Me
H
O
Me
O
9b
0.94
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1.11
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1.02
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0.94
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2.98
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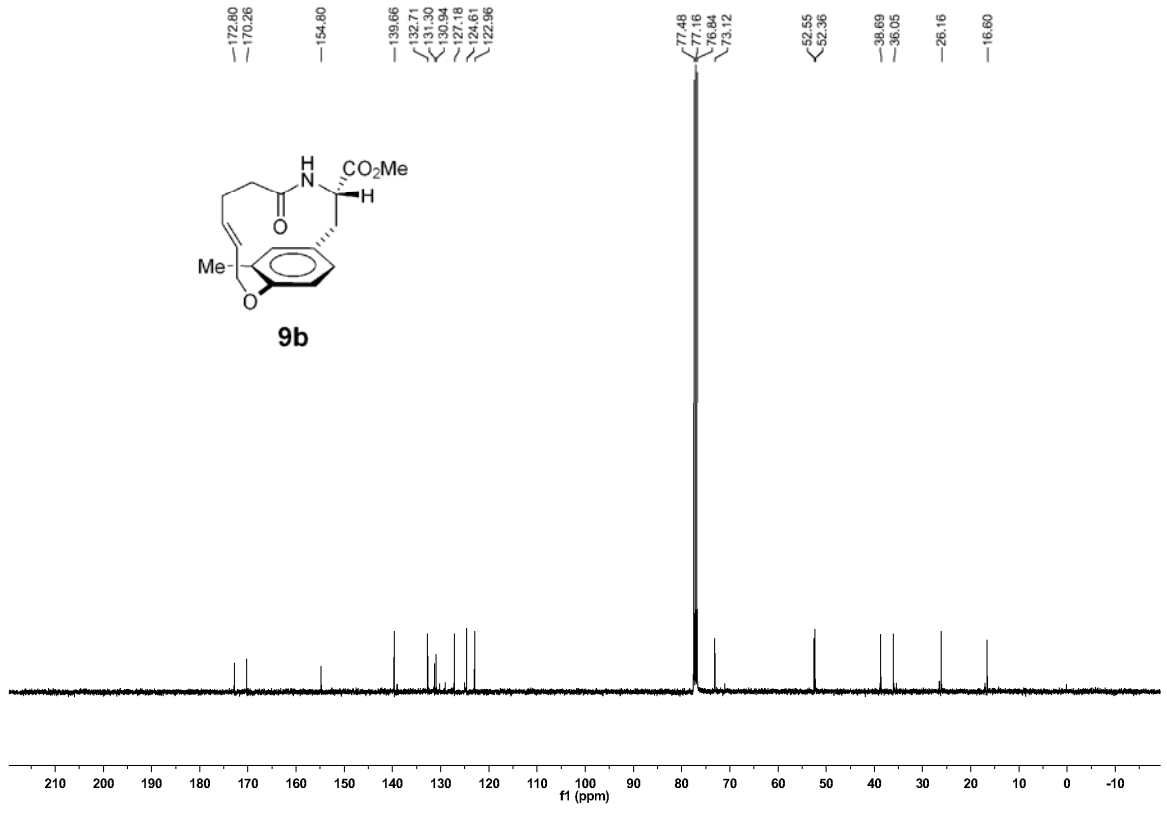
0.99
f1 (ppm)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77.16
76.84
73.12
52.55
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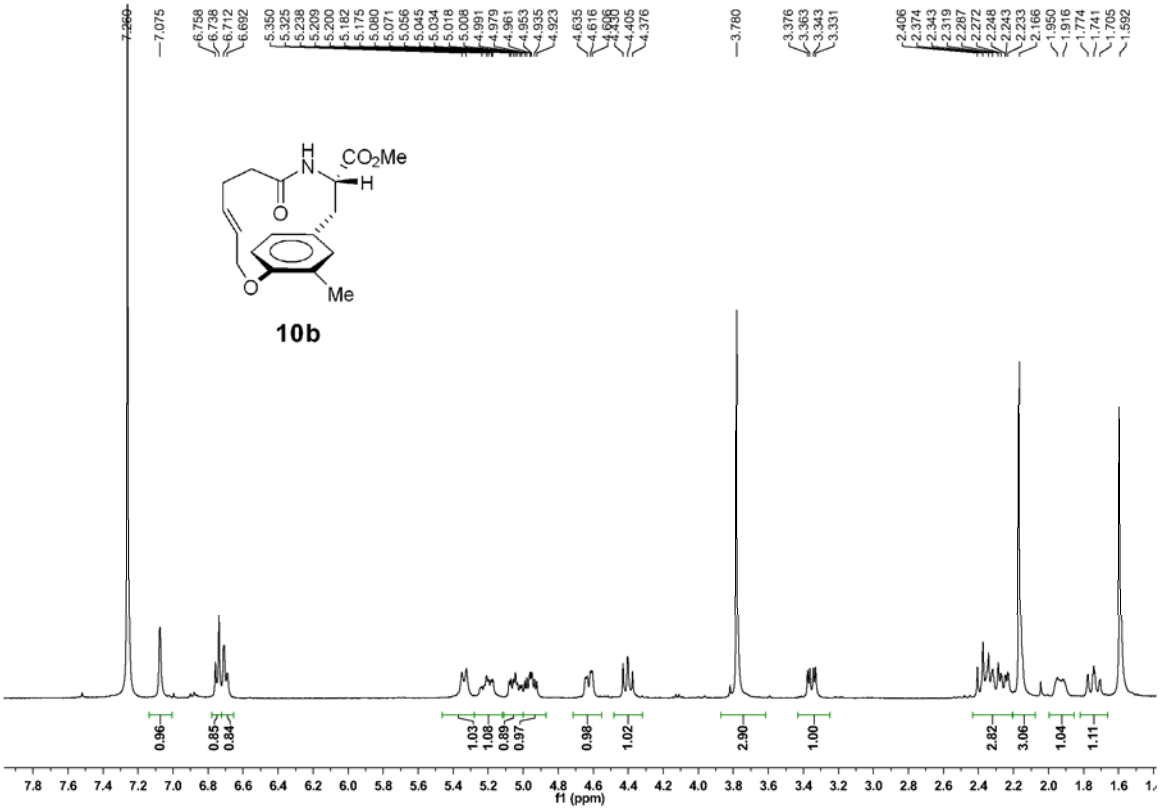
36.05
26.16
16.60
H
N
CO2Me
H
O
Me
O
9b
f1 (ppm)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2.287
2.272
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CO2Me
H
O
O
Me
10b
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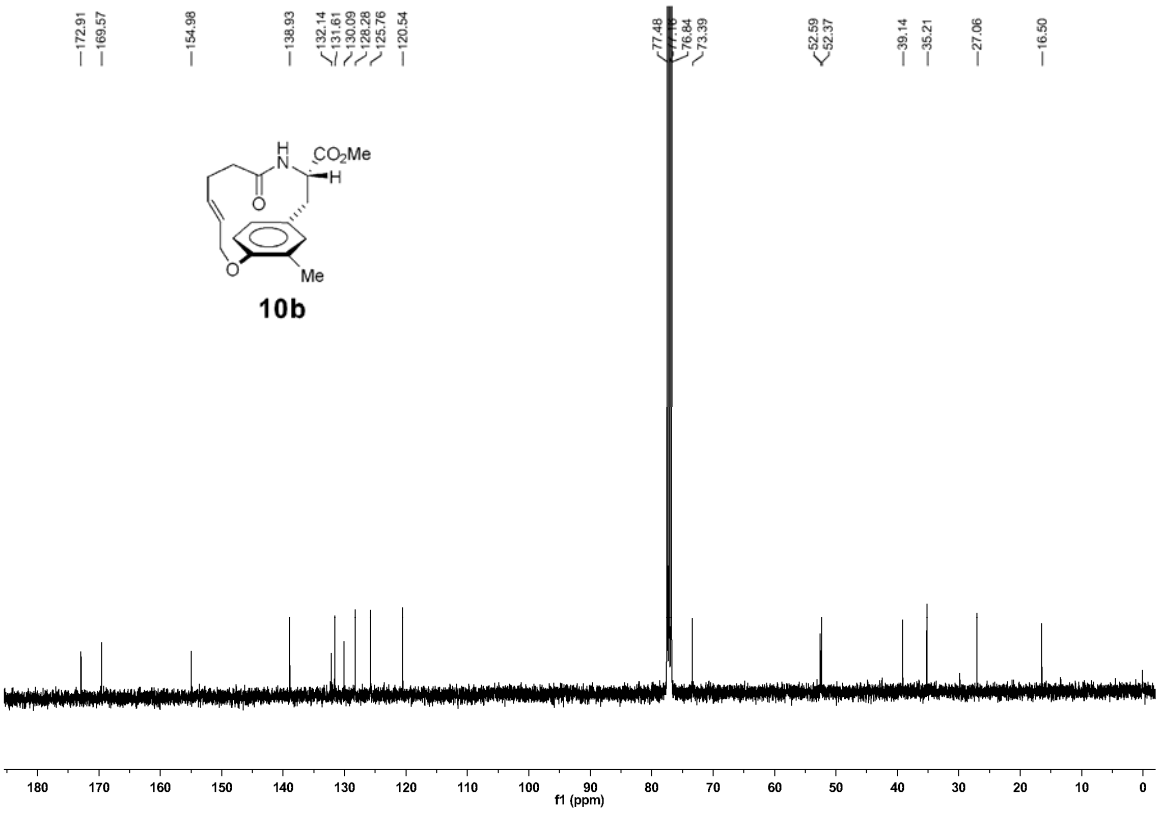
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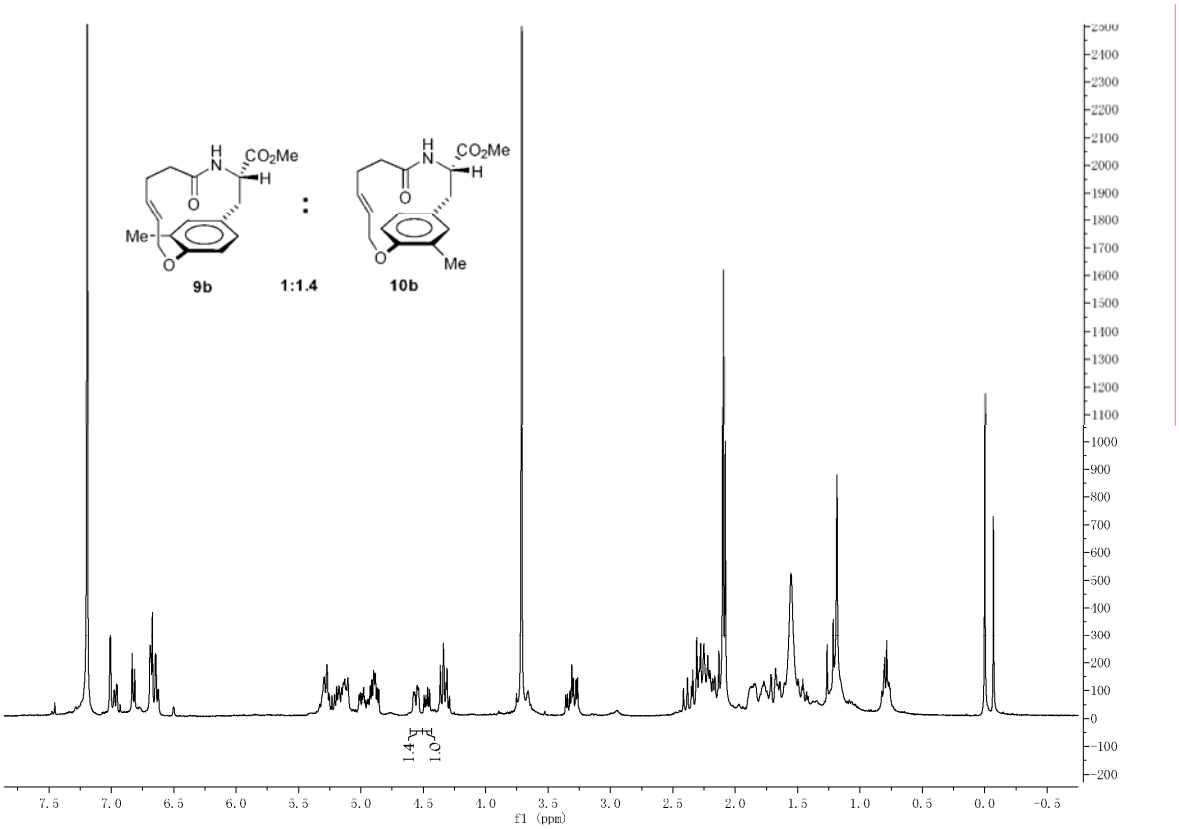
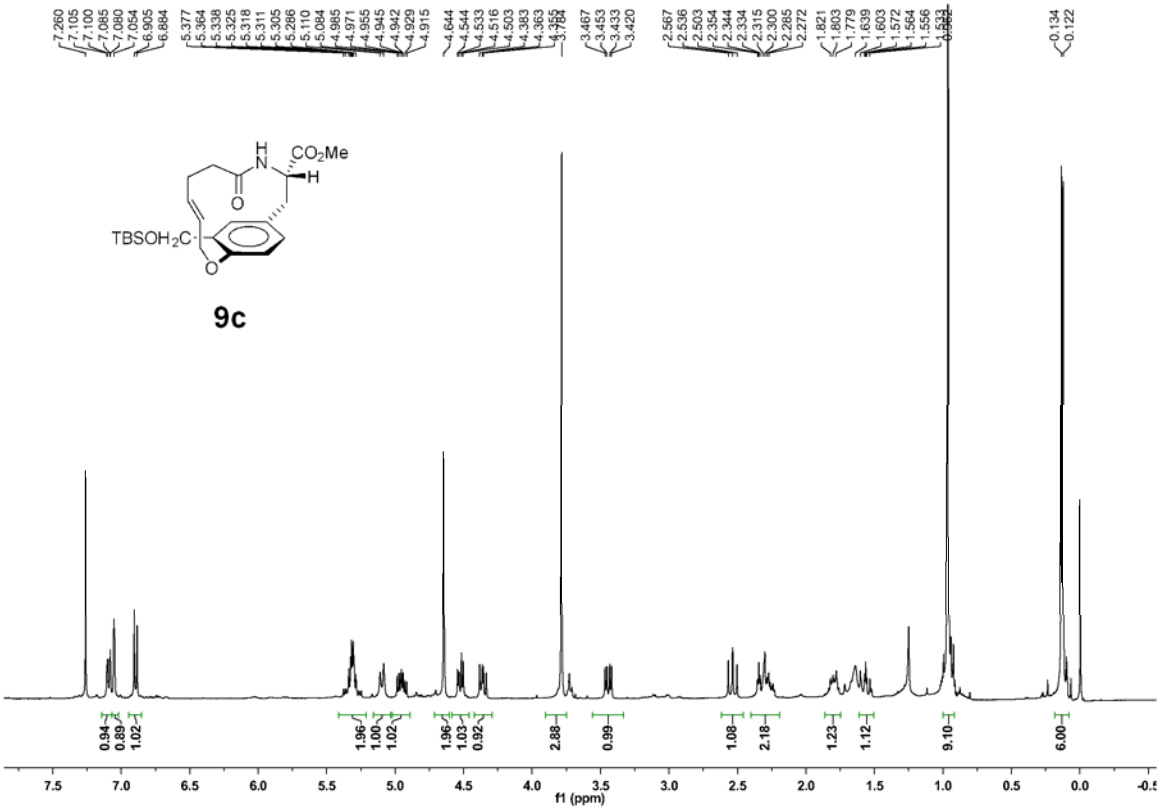
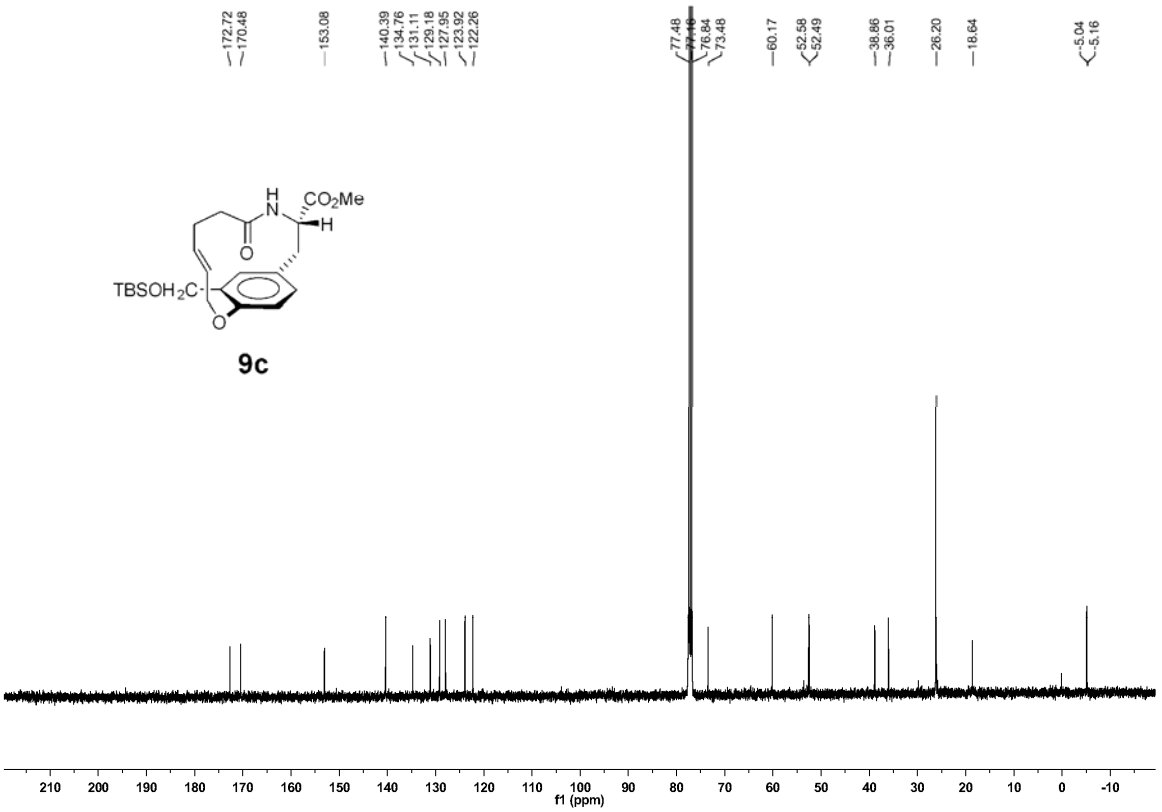
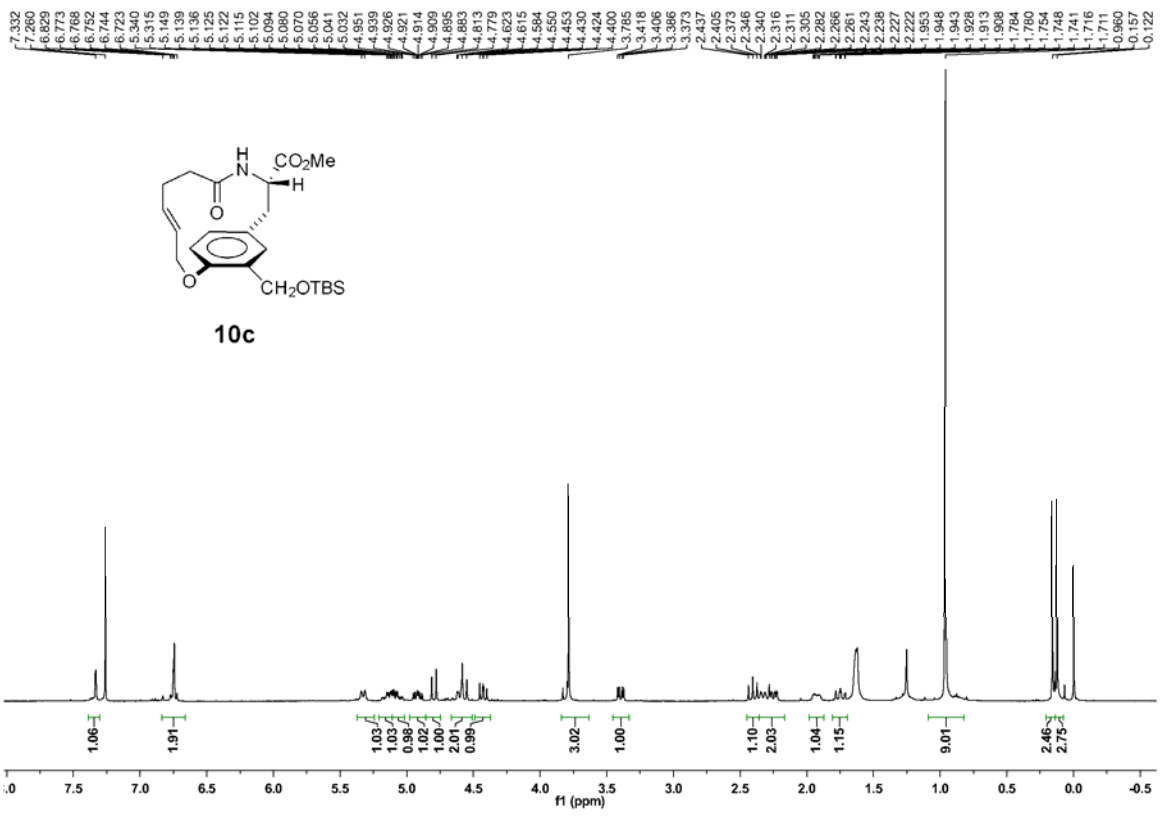
120.54
77.48
77.16
76.84
73.39
52.59
52.37
39.14
35.21
27.06
16.50
H
N
CO2Me
H
O
O
Me
10b
f1 (ppm)


9b
1:1.4
10b
f1 (ppm)

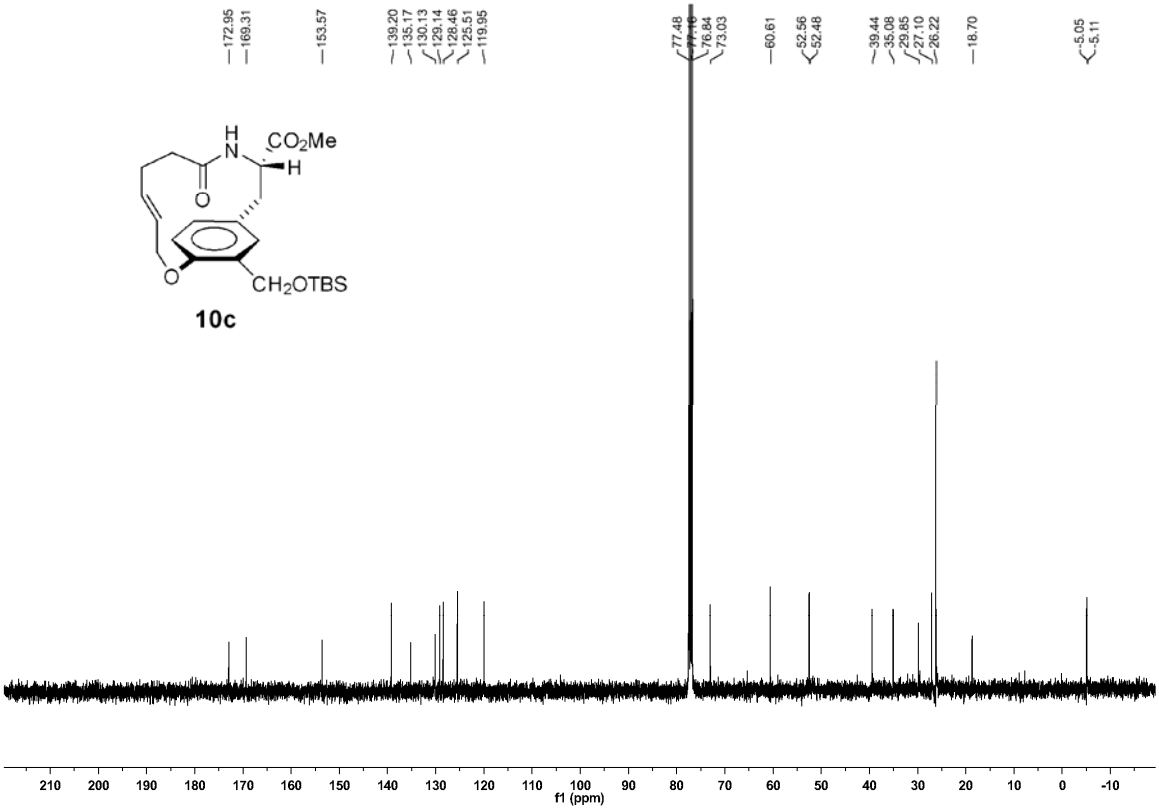

9c
f1 (ppm)

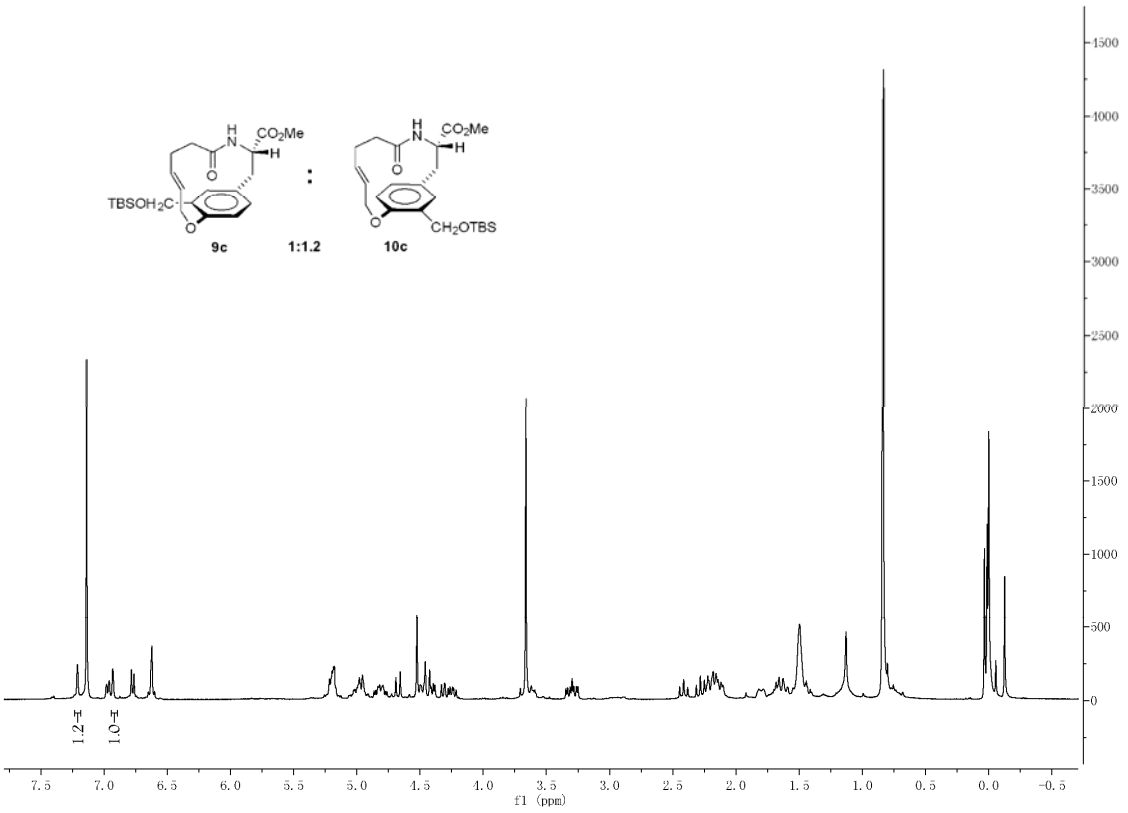

172.72
170.48
153.08
140.39
134.76
131.11
129.18
127.95
123.92
122.26
77.48
77.16
76.84
73.48
60.17
52.58
52.49
38.86
36.01
26.20
18.64
-5.04
-5.16
H
N
CO2Me
H
O
TBSOH2C
O
f1 (ppm)

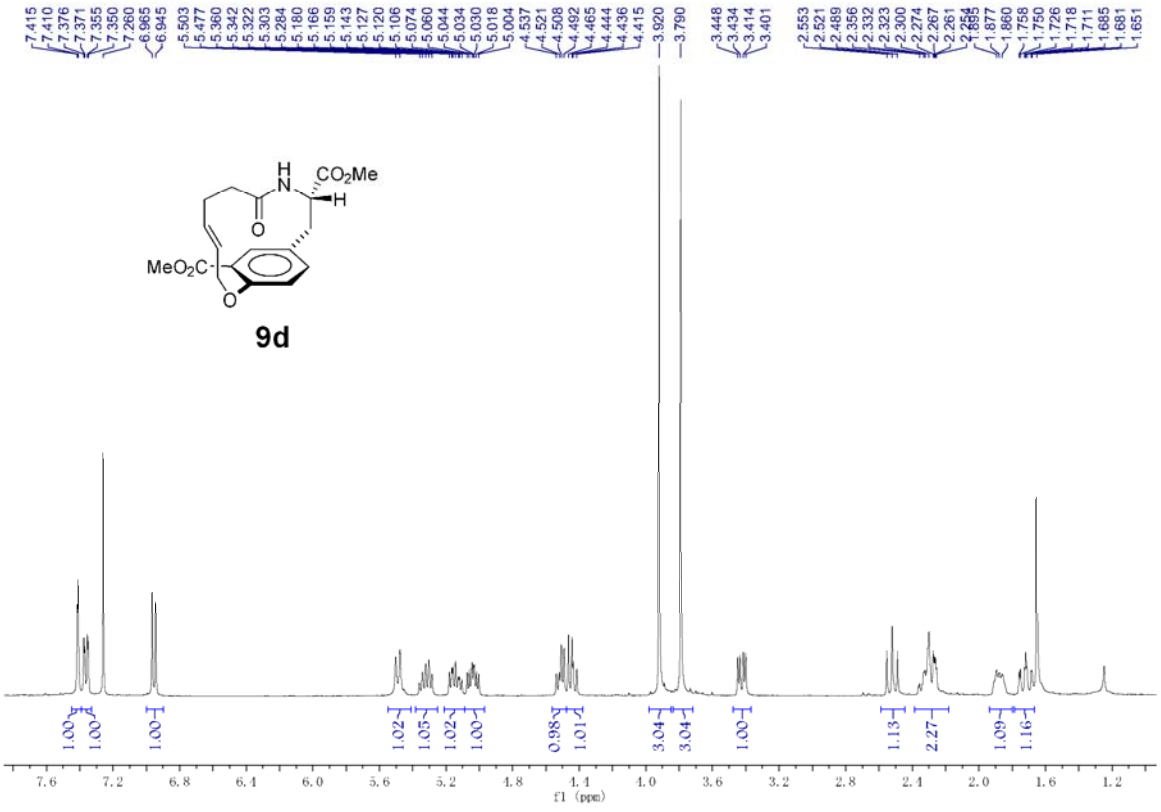
9c

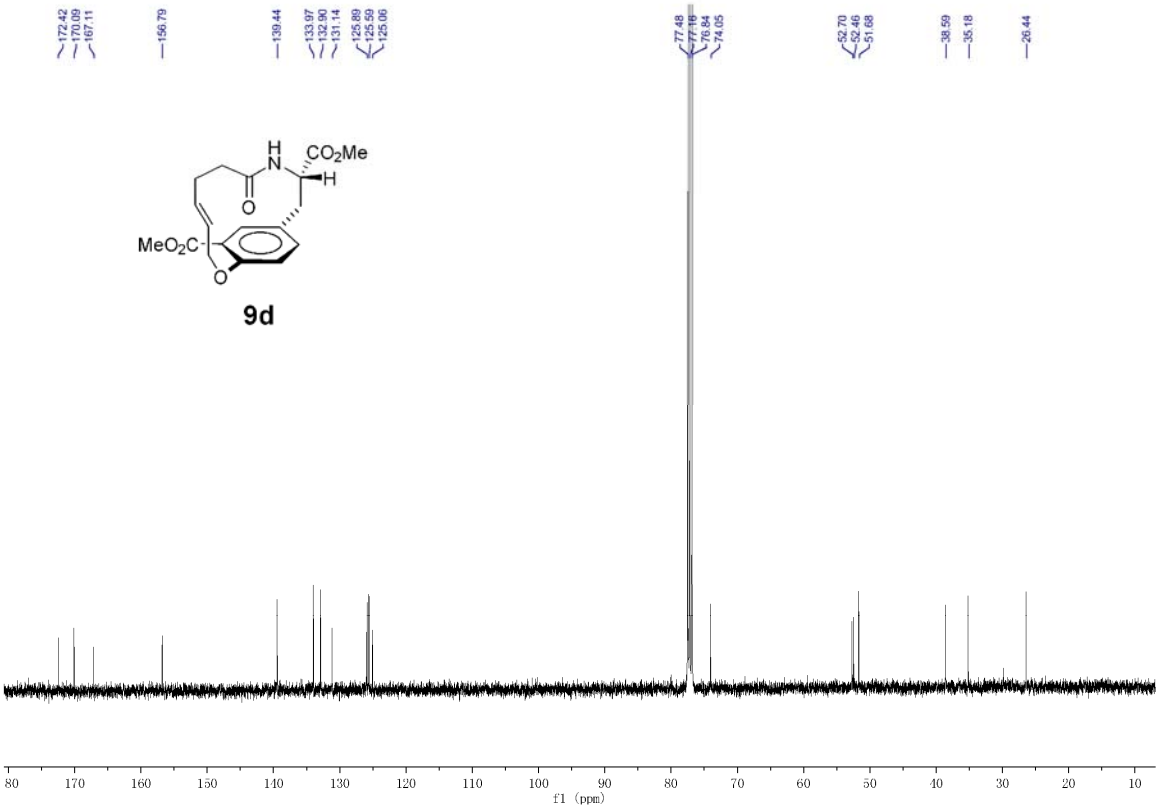

H
N
CO2Me
H
O
O
CH2OTBS
1.06
1.91
1.03
1.03
0.98
1.02
1.00
2.01
0.99
3.02
1.00
1.10
2.03
1.04
1.15
9.01
2.46
2.75
f1 (ppm)

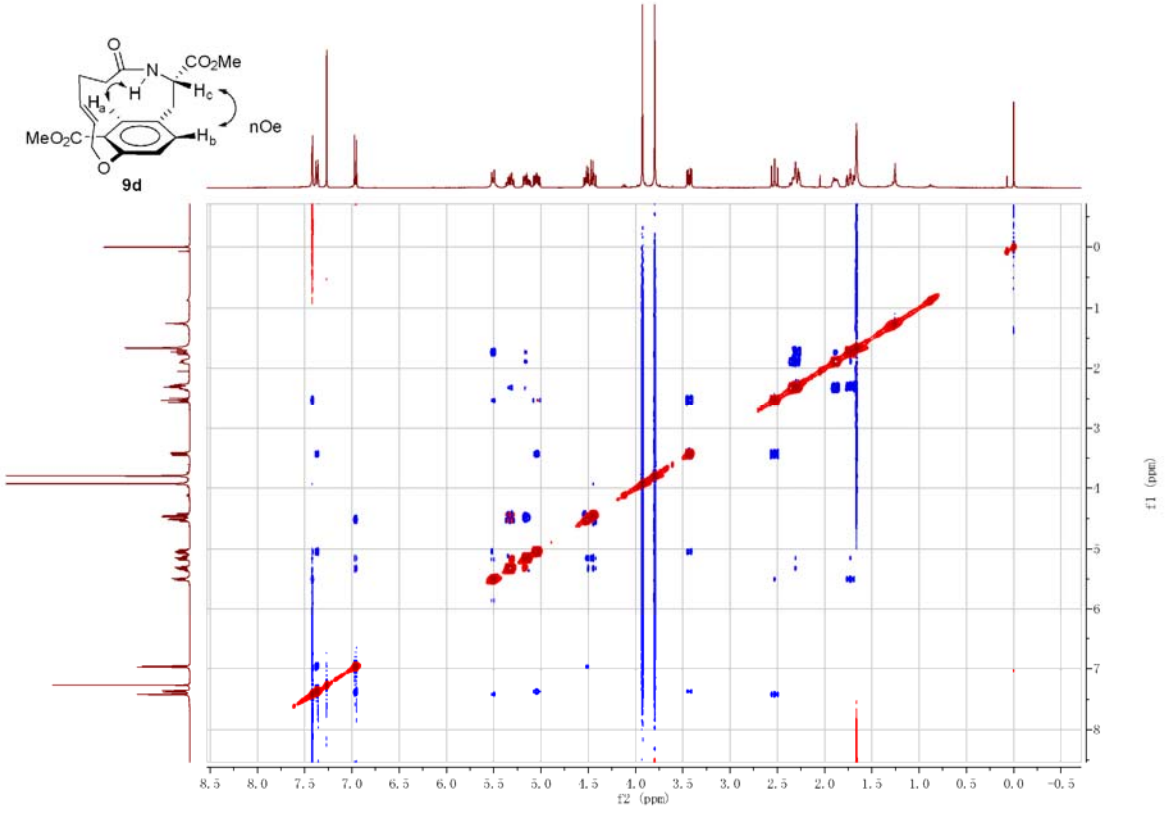
10c

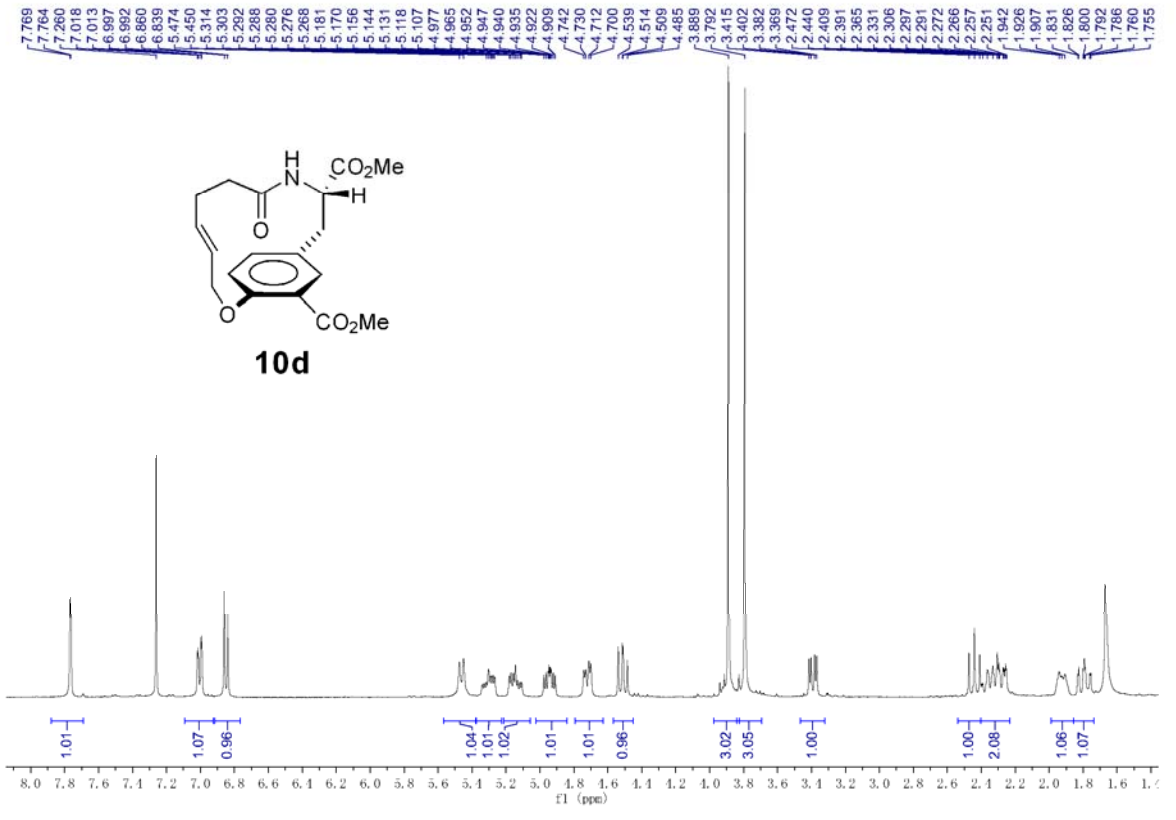

172.95
169.31
153.57
139.20
135.17
130.13
129.14
128.46
125.51
119.95
77.48
77.16
76.84
73.03
60.61
52.56
52.48
39.44
35.08
29.85
27.10
26.22
18.70
-5.05
-5.11
CO2Me
H
N
O
CH2OTBS
10c
f1 (ppm)

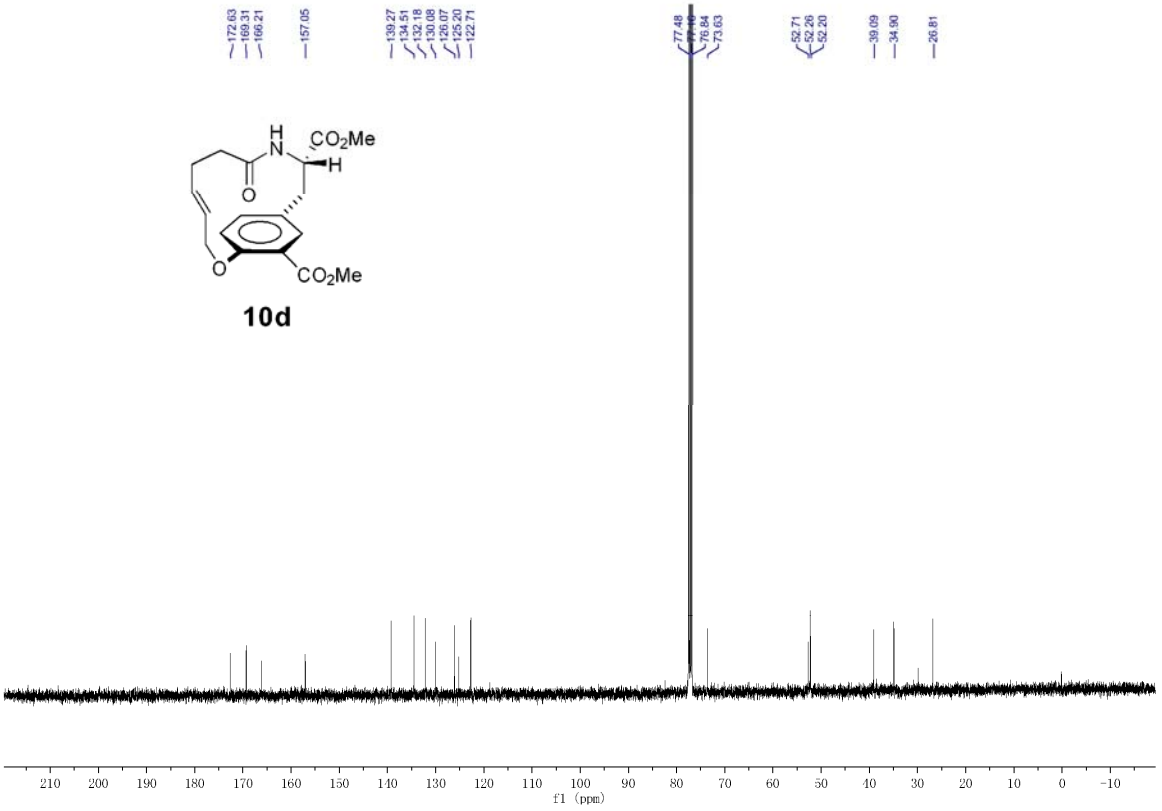

TBSOH2C
CO2Me
9c
1:1.2
10c
1.2
1.0
f1 (ppm)

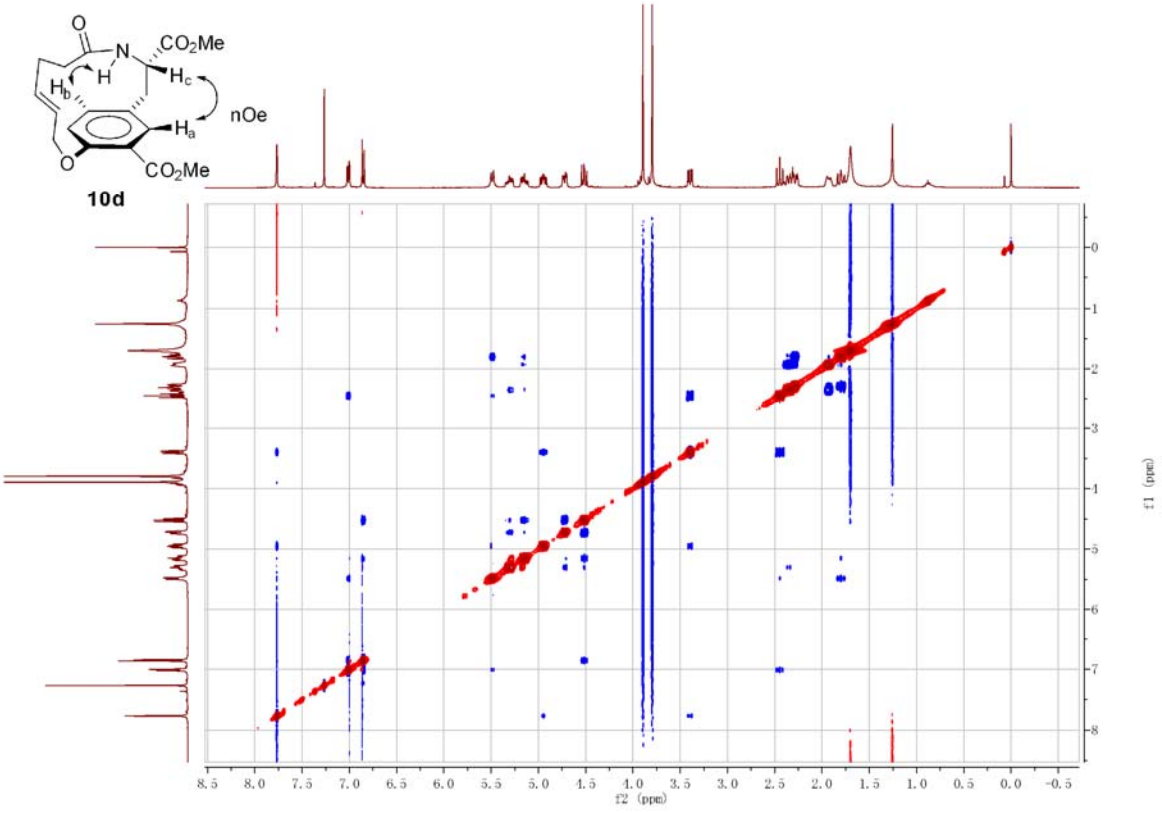

7.415
7.410
7.376
7.371
7.355
7.350
7.260
6.965
6.945
5.503
5.477
5.360
5.342
5.322
5.303
5.284
5.180
5.166
5.159
5.143
5.127
5.120
5.106
5.074
5.060
5.044
5.034
5.030
5.018
5.004
4.537
4.521
4.508
4.492
4.465
4.444
4.436
4.415
3.920
3.790
3.448
3.434
3.414
3.401
2.553
2.521
2.489
2.356
2.332
2.323
2.300
2.274
2.267
2.261
2.254
1.895
1.877
1.860
1.758
1.750
1.726
1.718
1.711
1.685
1.681
1.651
H
N
CO2Me
H
O
MeO2C
O
9d
1.00
1.00
1.00
1.02
1.05
1.02
1.00
0.98
1.01
3.04
3.04
1.00
1.13
2.27
1.09
1.16
7.6
7.2
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
f1 (ppm)

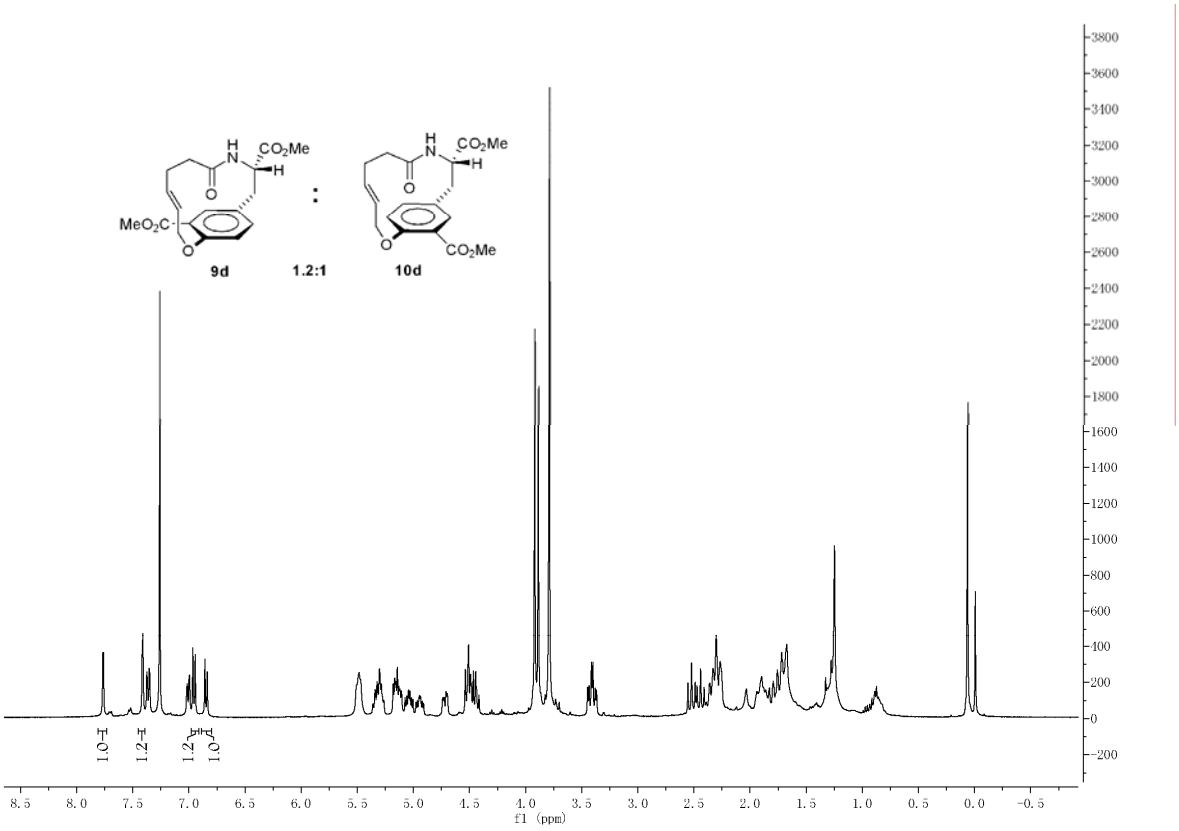

172.42
170.09
167.11
156.79
139.44
133.97
132.90
131.14
125.89
125.59
125.06
77.48
77.16
76.84
74.05
52.70
52.46
51.68
38.59
35.18
26.44
H
N
CO2Me
H
O
MeO2C
O
9d
80
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

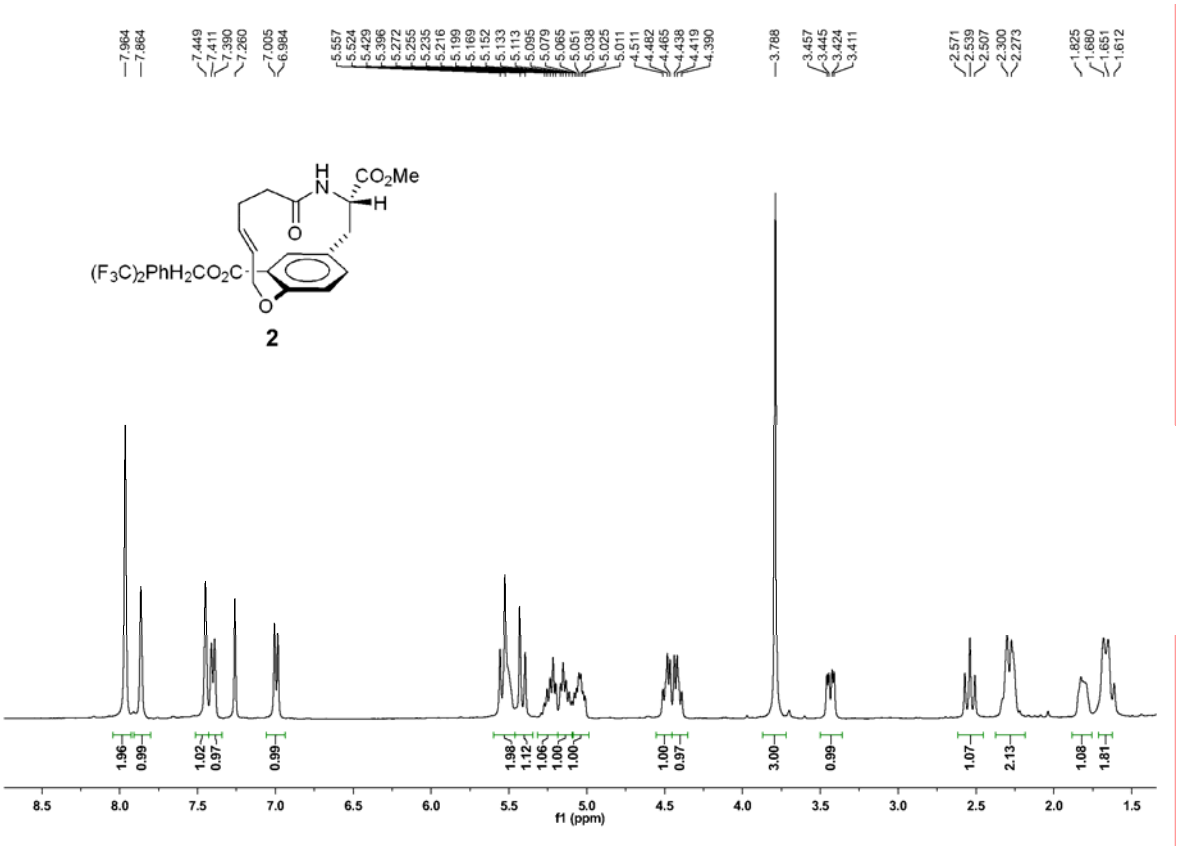

nOe
9d
f2 (ppm)
f1 (ppm)

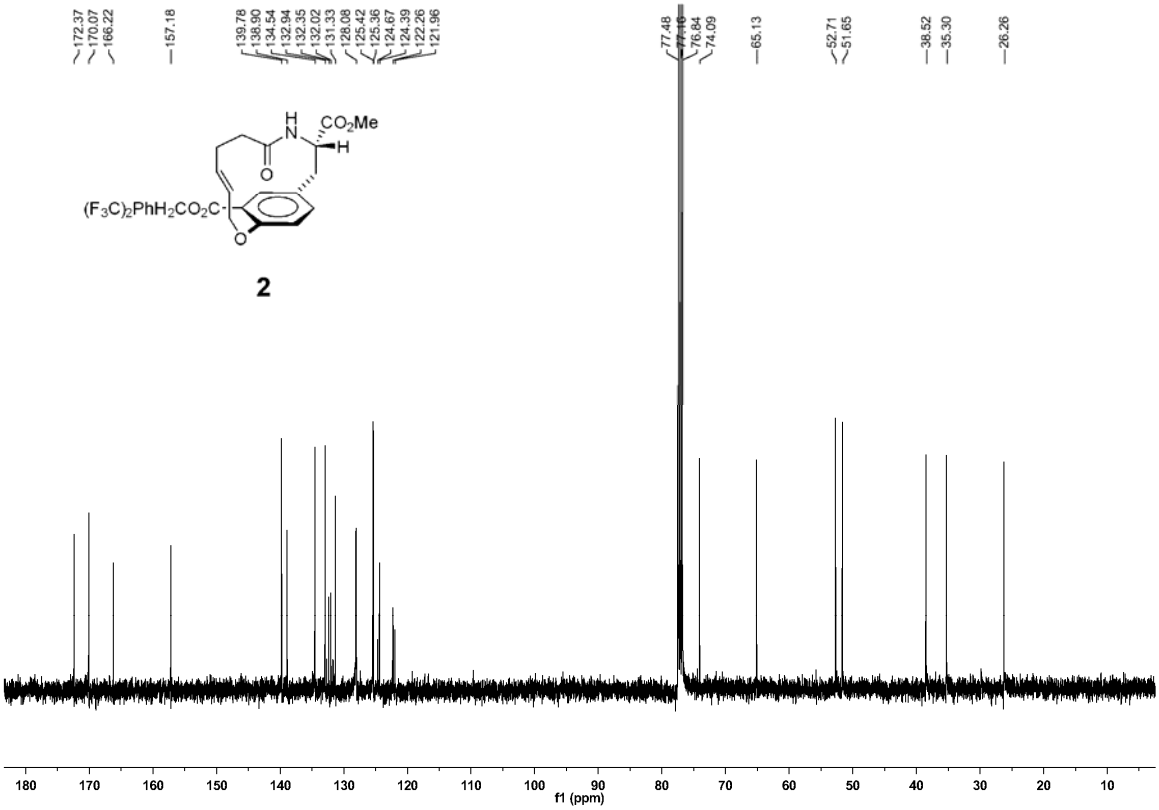

10d
f1 (ppm)

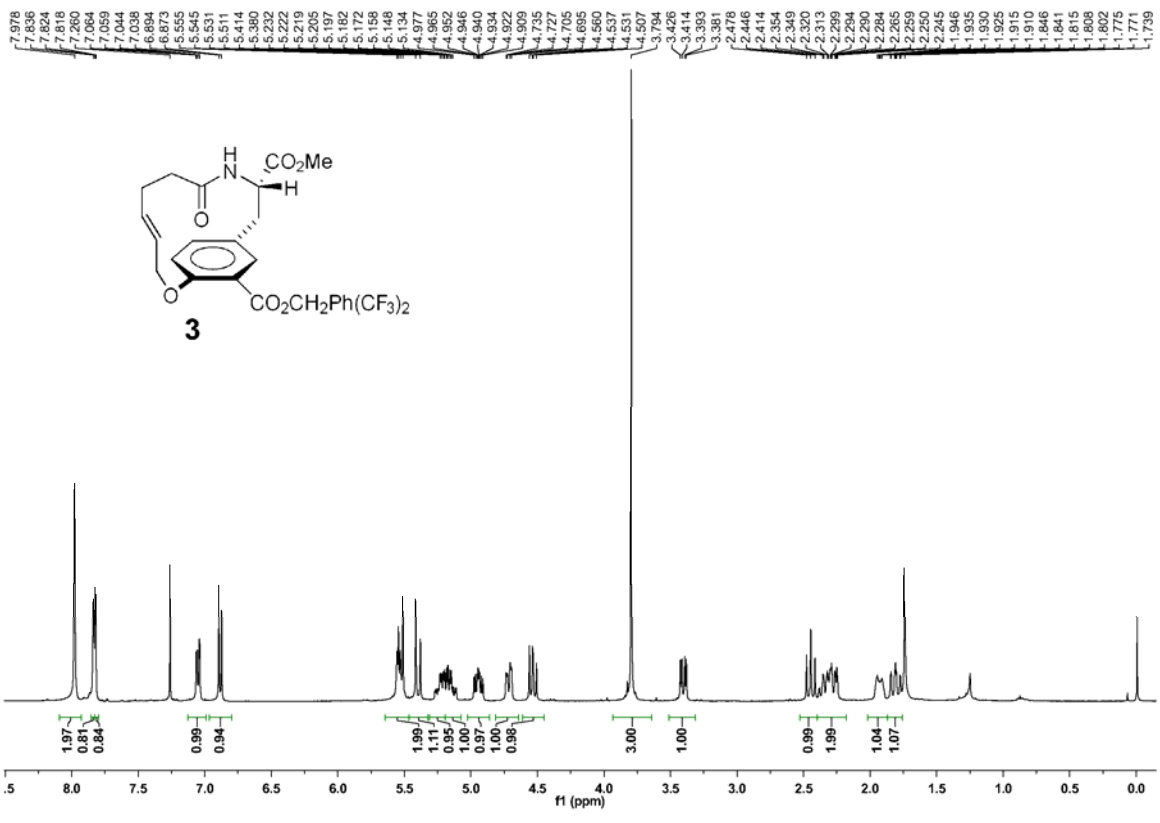

172.63
169.31
166.21
157.05
139.27
134.51
132.18
130.08
126.07
125.20
122.71
77.48
77.16
76.84
73.63
52.71
52.26
52.20
39.09
34.90
26.81
CO2Me
CO2Me
10d
f1 (ppm)

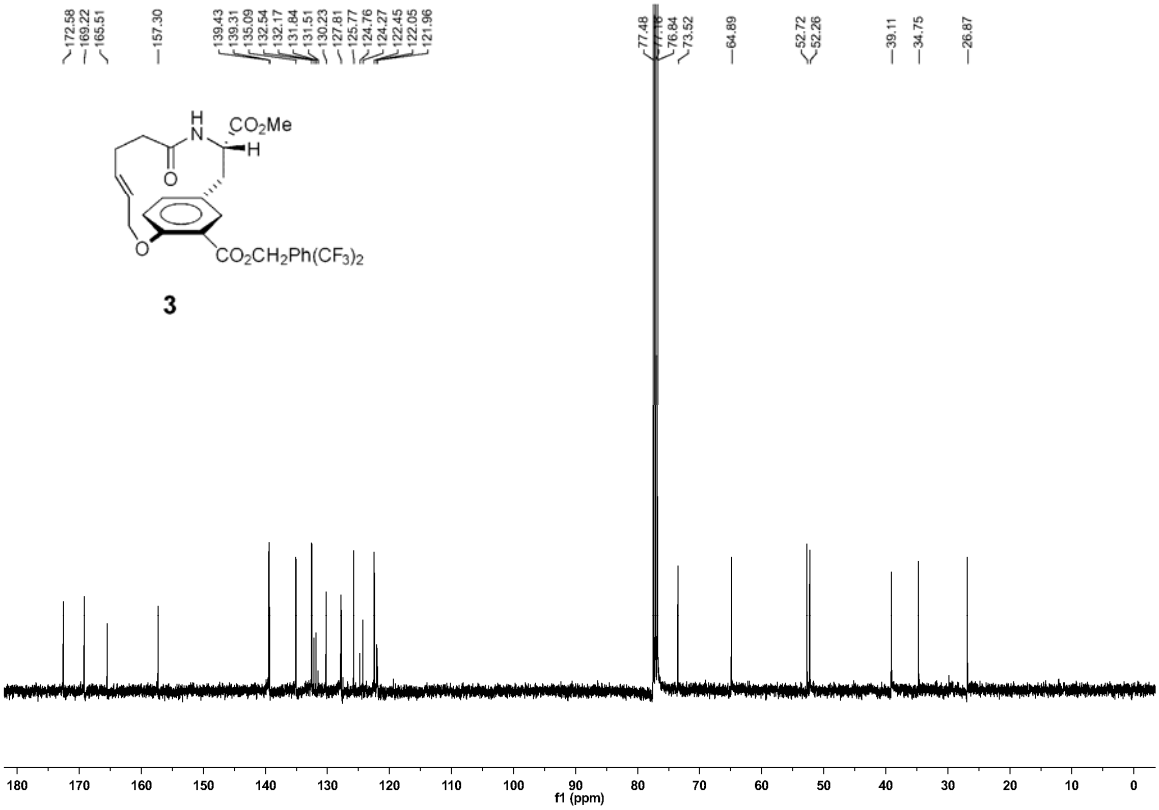

CO2Me
CO2Me
Hb
Hc
Ha
nOe
10d
f2 (ppm)
f1 (ppm)

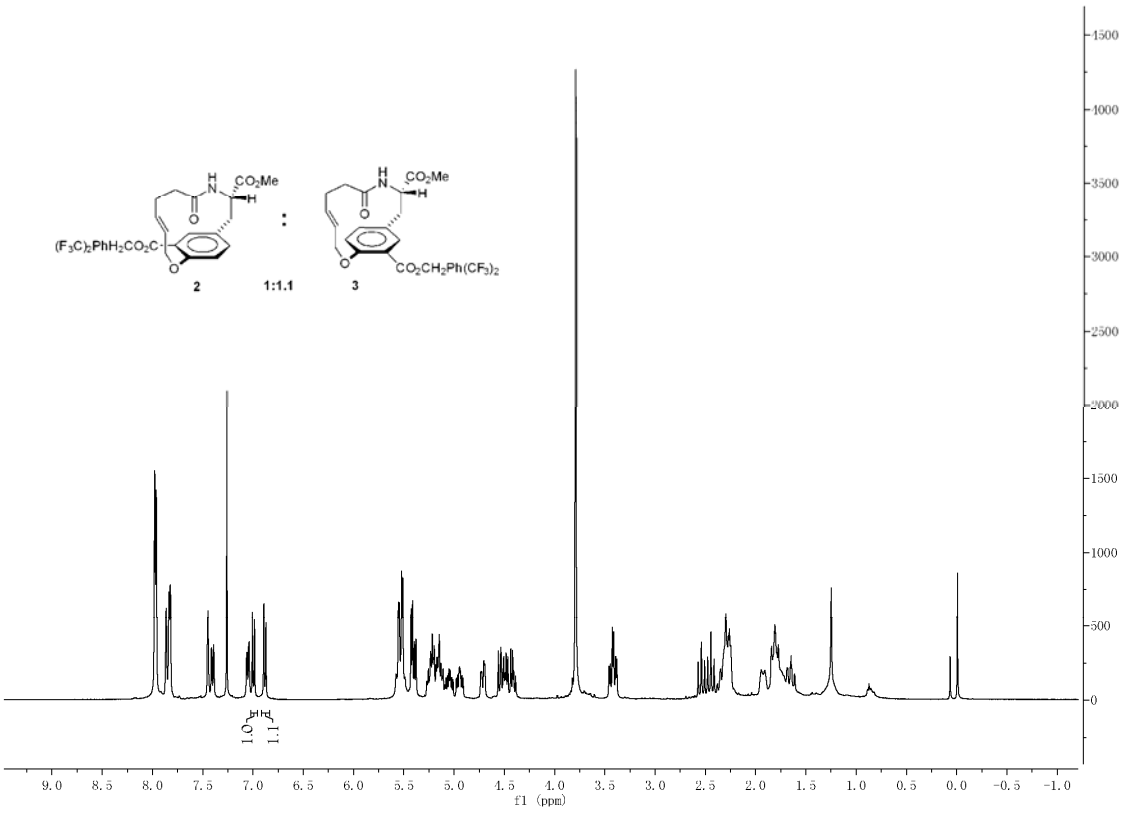

9d
1.2:1
10d
f1 (ppm)

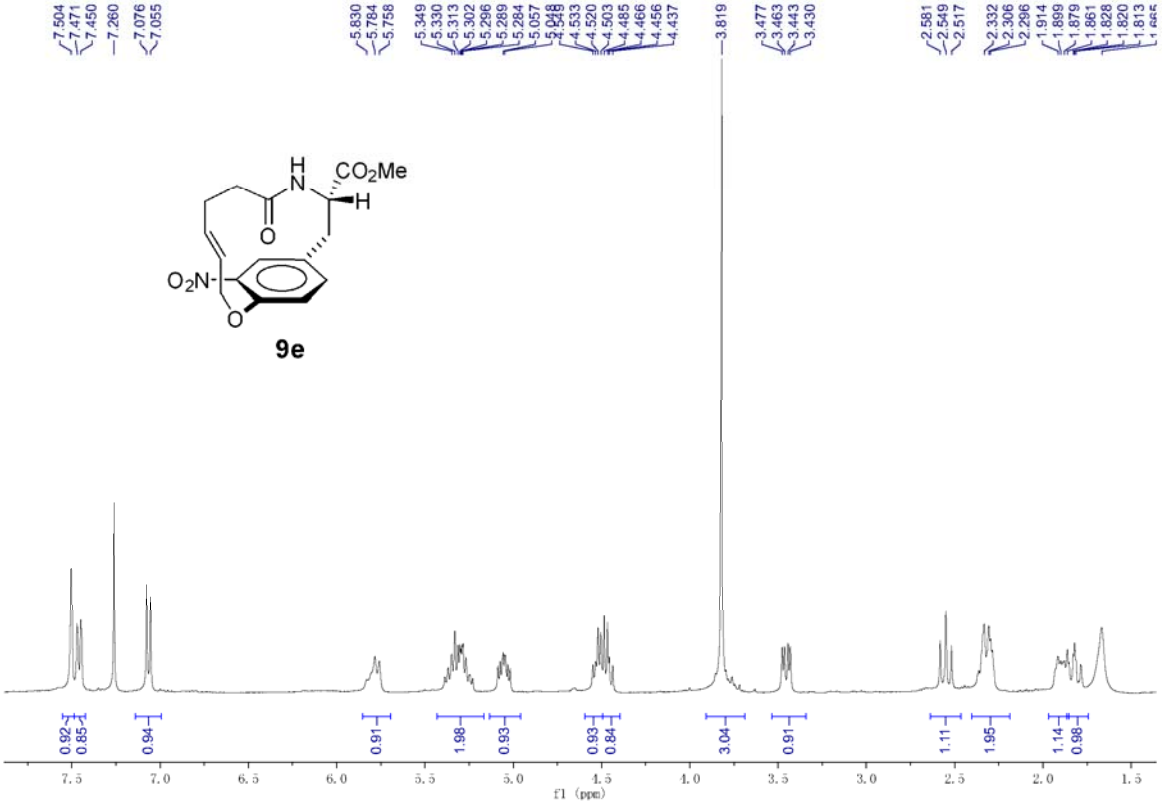

2
f1 (ppm)


172.37
170.07
166.22
157.18
139.78
138.90
134.54
132.94
132.35
132.02
131.33
128.08
125.42
125.36
124.67
124.39
122.26
121.96
77.48
77.16
76.84
74.09
65.13
52.71
51.65
38.52
35.30
26.26
CO2Me
(F3C)2PhH2CO2C
2
f1 (ppm)


CO2Me
CO2CH2Ph(CF3)2
3
1.97
0.81
0.84
0.99
0.94
1.99
1.11
0.95
1.00
0.97
1.00
0.98
3.00
1.00
0.99
1.99
1.04
1.07
f1 (ppm)

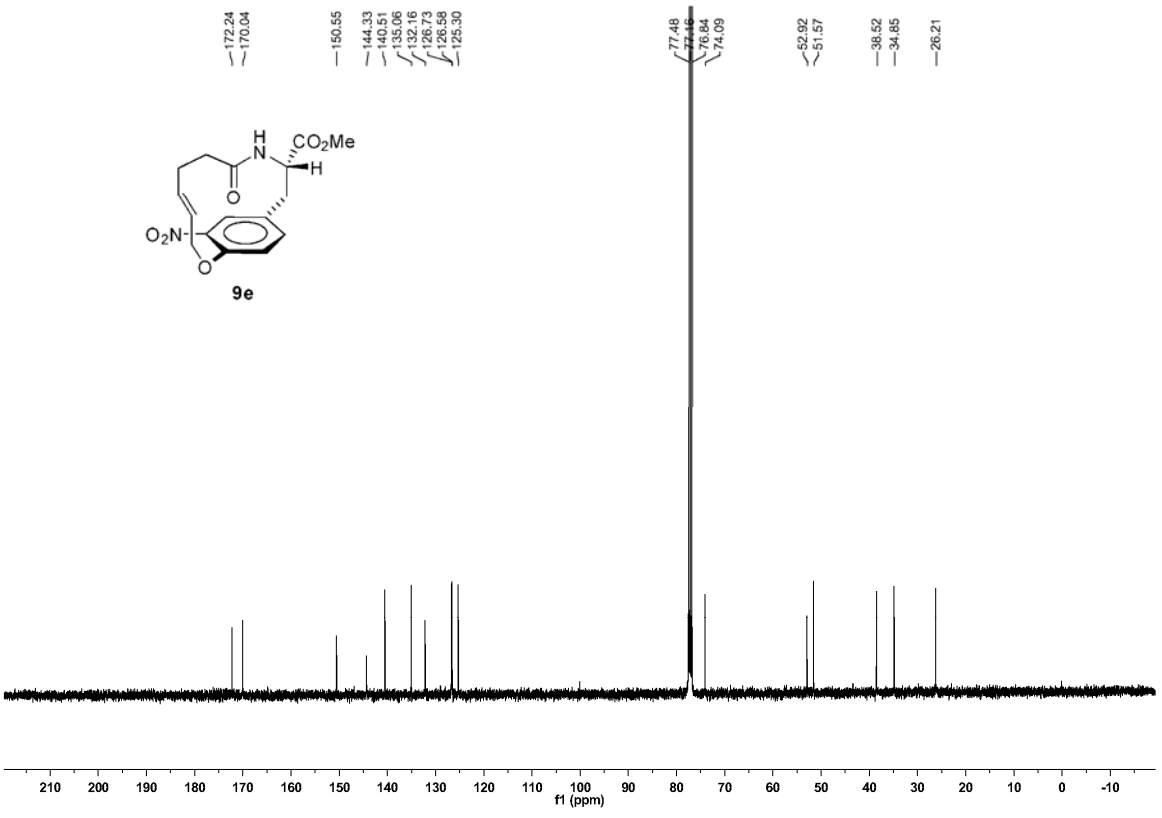

172.58
169.22
165.51
157.30
139.43
139.31
135.09
132.54
132.17
131.84
131.51
130.23
127.81
125.77
124.76
124.27
122.45
122.05
121.96
77.48
77.16
76.84
73.52
64.89
52.72
52.26
39.11
34.75
26.87
CO2Me
H
N
O
O
CO2CH2Ph(CF3)2
3
f1 (ppm)


CO2Me
H
N
O
(F3C)2PhH2CO2C
2
1:1.1
3
CO2CH2Ph(CF3)2
1.0
1.1
f1 (ppm)


7.504
7.471
7.450
7.260
7.076
7.055
5.830
5.784
5.758
5.349
5.330
5.313
5.302
5.296
5.289
5.284
5.057
4.533
4.520
4.503
4.485
4.466
4.456
4.437
3.819
3.477
3.463
3.443
3.430
2.581
2.549
2.517
2.332
2.306
2.296
1.914
1.899
1.879
1.861
1.828
1.820
1.813
0.92
0.85
0.94
0.91
1.98
0.93
0.93
0.84
3.04
0.91
1.11
1.95
1.14
0.98
f1 (ppm)

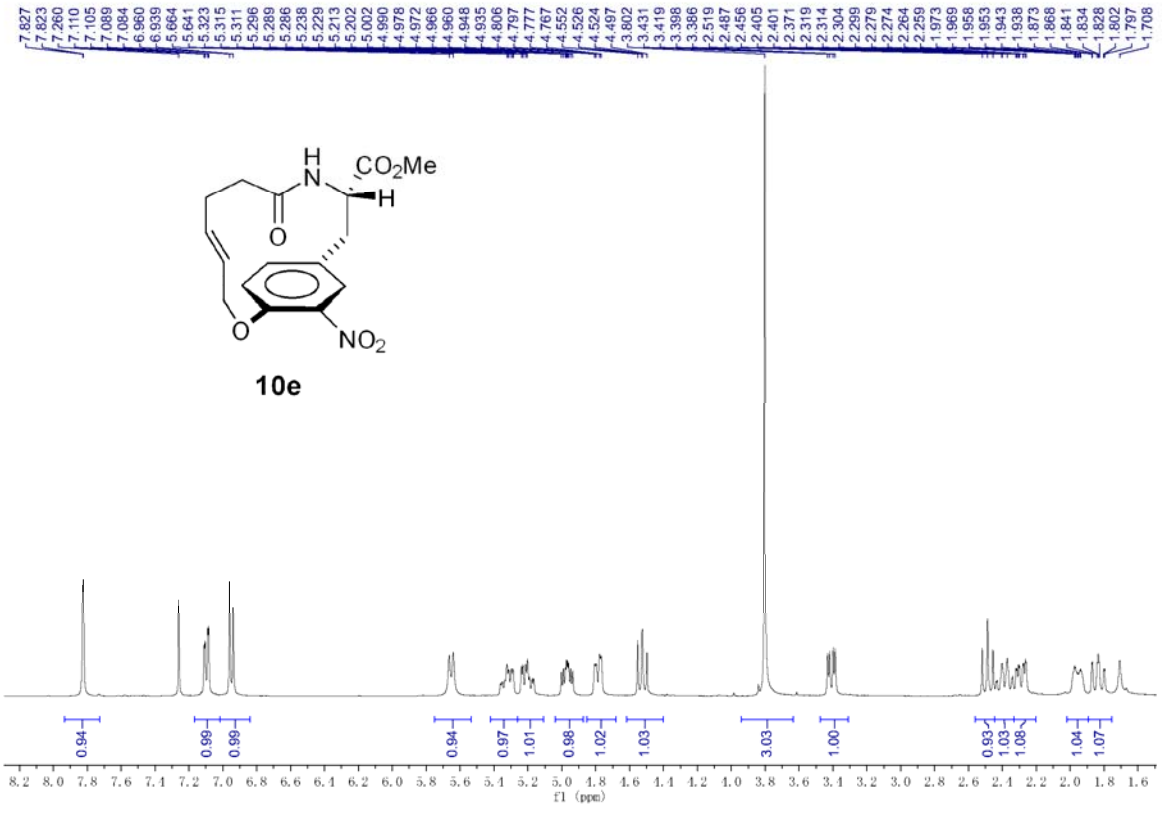
H
N
CO2Me
H
O
O2N-
O

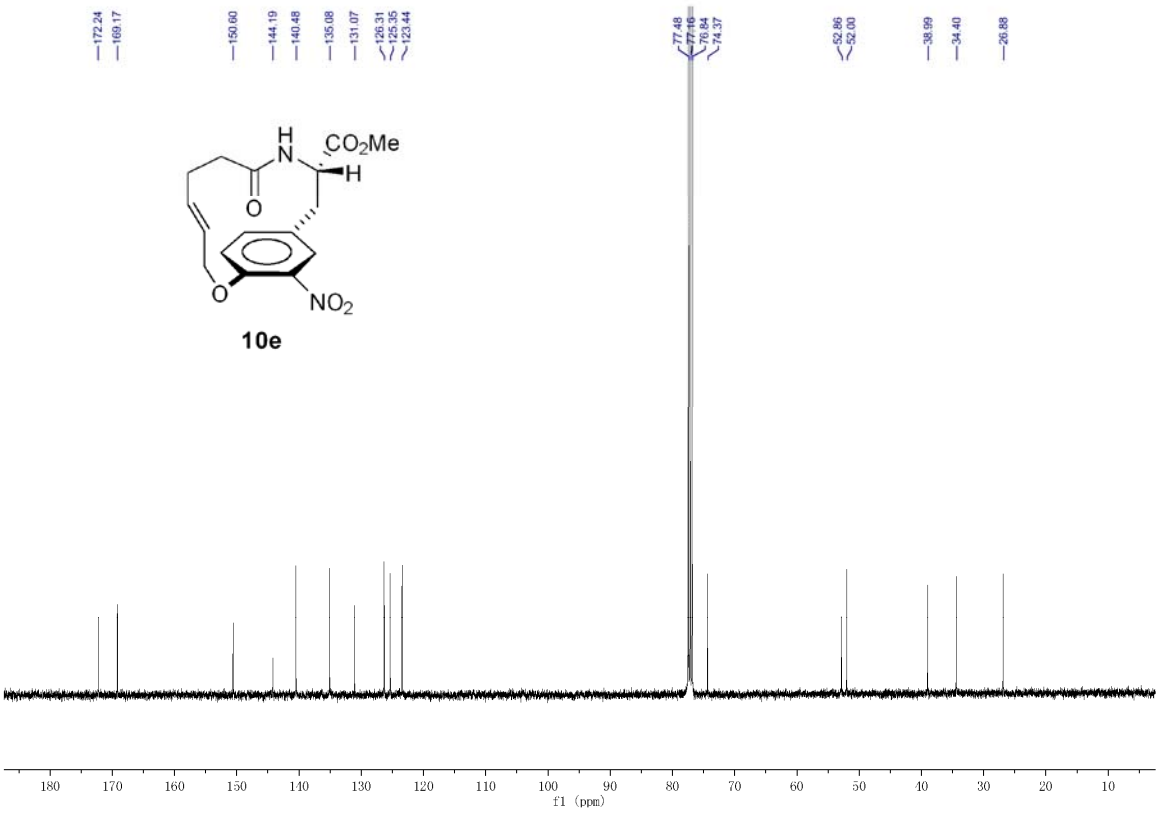
9e

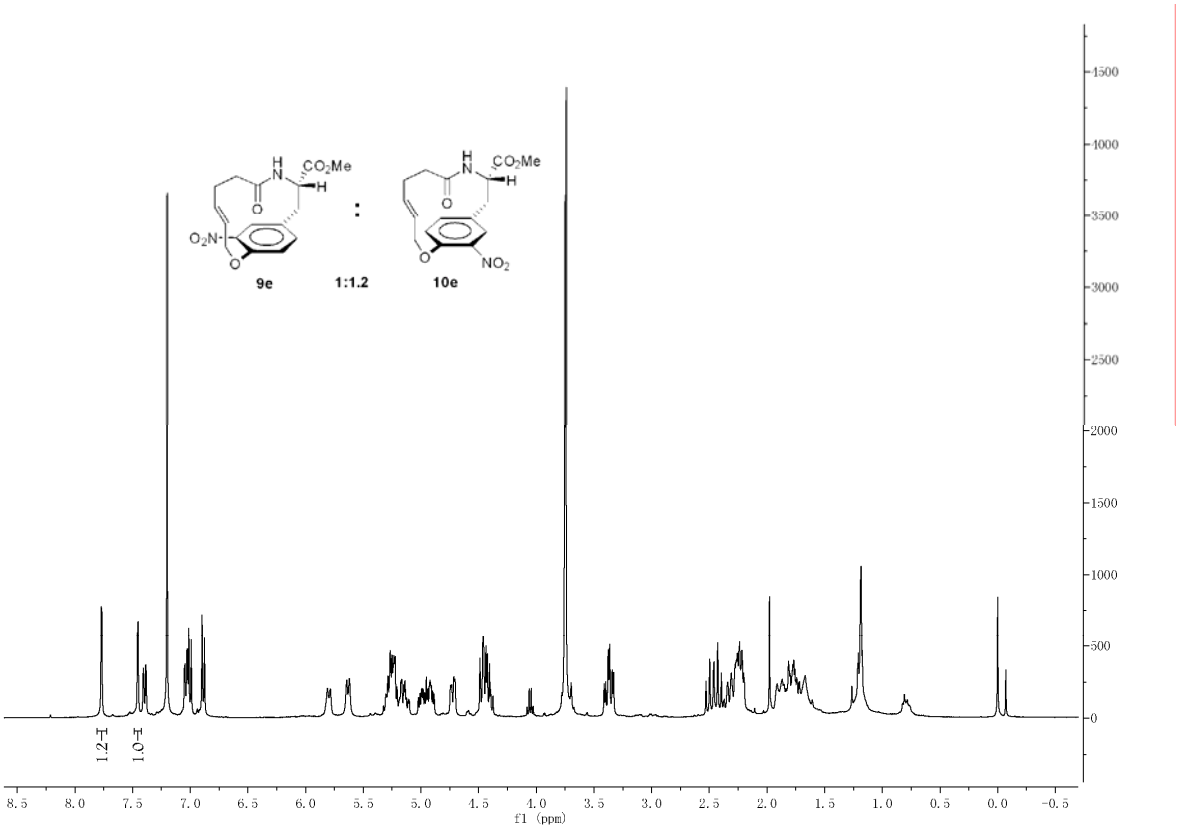

172.24
170.04
150.55
144.33
140.51
135.06
132.16
126.73
126.58
125.30
77.48
77.16
76.84
74.09
52.92
51.57
38.52
34.85
26.21
f1 (ppm)

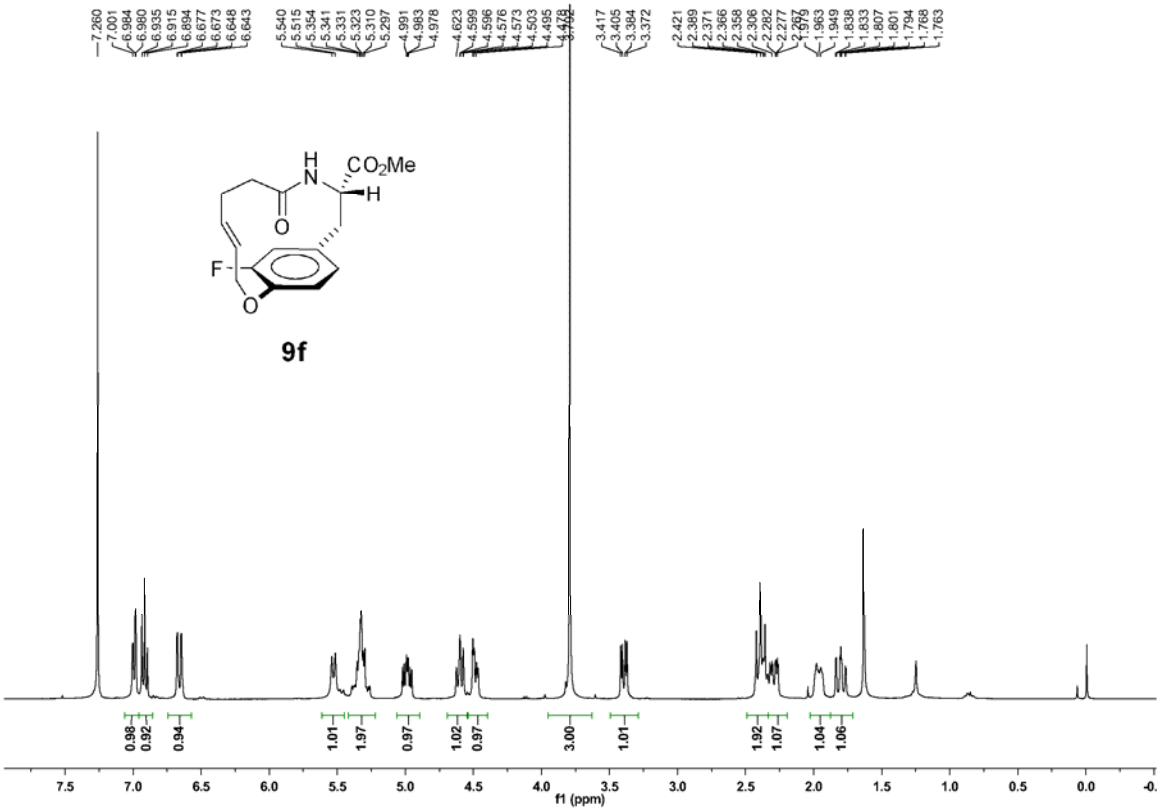
H
N
CO2Me
H
O
O2N-
O

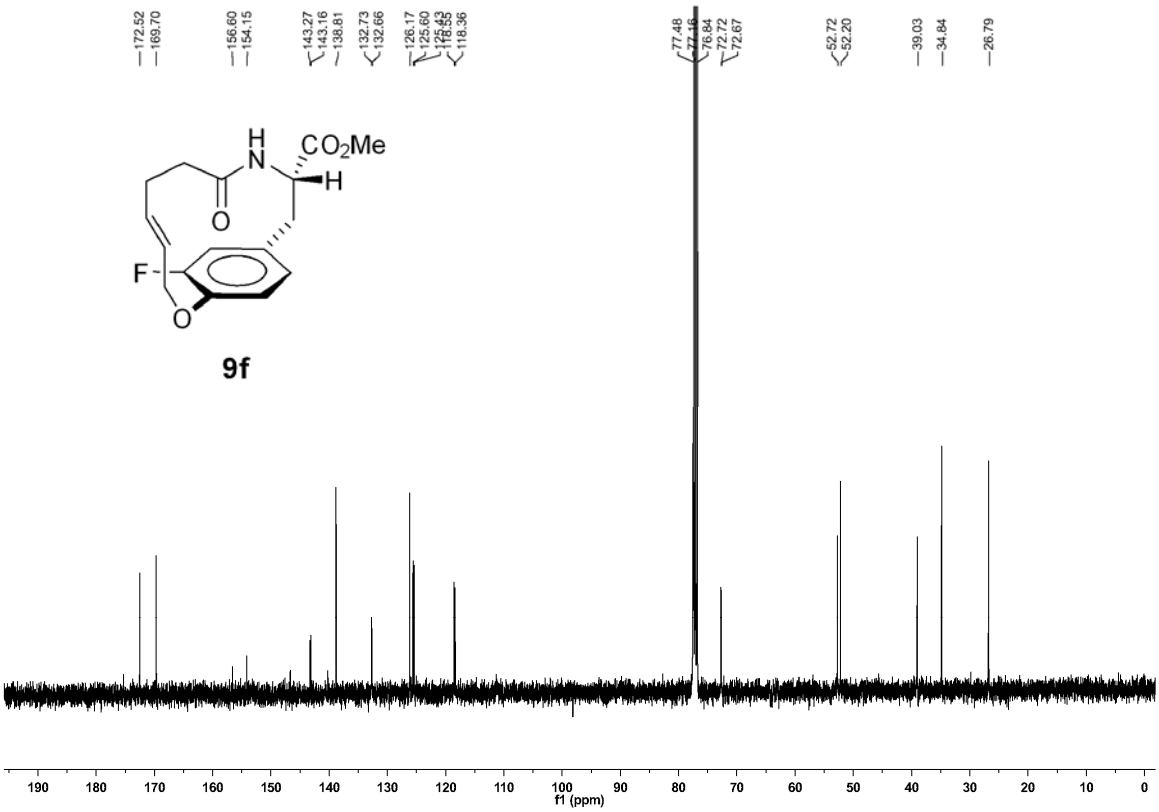
9e

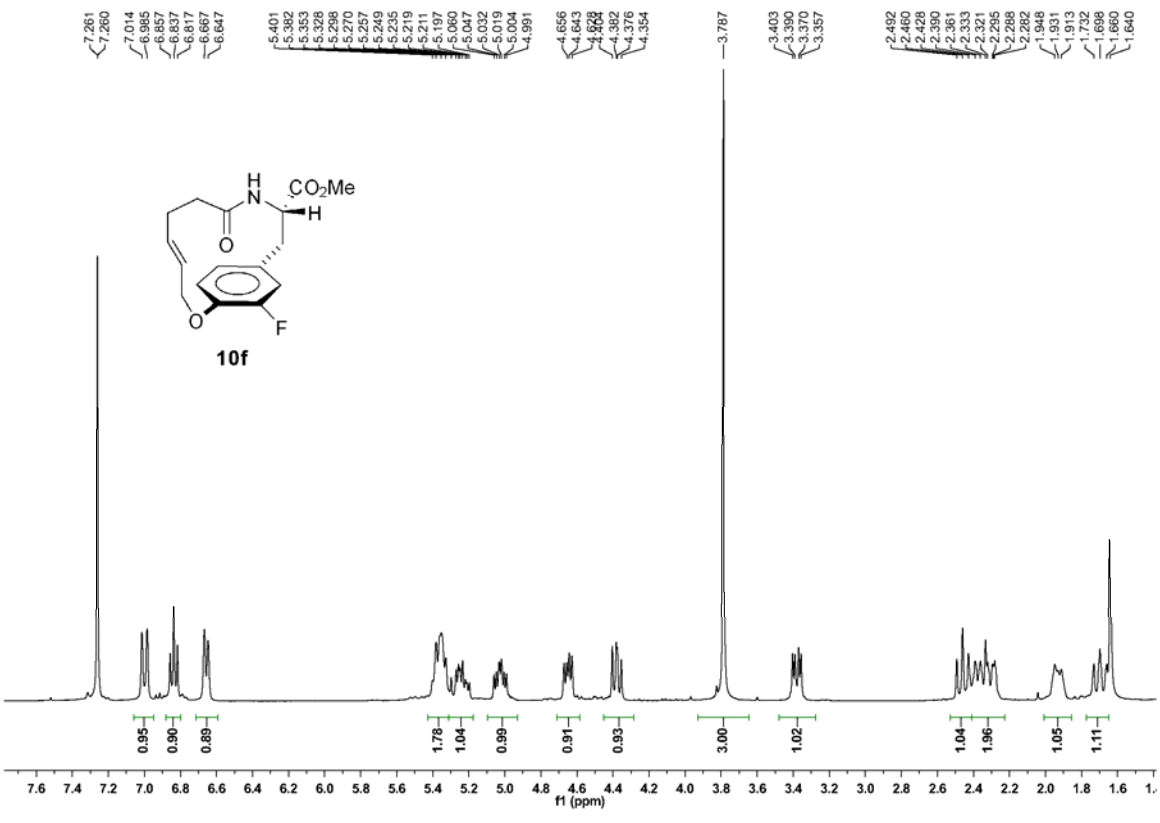

7.827 7.823 7.260 7.110 7.105 7.089 7.084 6.960 6.939 5.664 5.641 5.323 5.315 5.311 5.296 5.289 5.286 5.238 5.229 5.213 5.202 5.002 4.990 4.978 4.972 4.966 4.960 4.948 4.935 4.806 4.797 4.777 4.767 4.552 4.526 4.524 4.497 3.802 3.431 3.419 3.398 3.386 2.519 2.487 2.456 2.405 2.401 2.371 2.319 2.314 2.304 2.299 2.279 2.274 2.264 2.259 1.973 1.969 1.958 1.953 1.943 1.938 1.873 1.868 1.841 1.834 1.828 1.802 1.797 1.708
H
N
CO2Me
H
O
O
NO2
10e
0.94 0.99 0.99 0.94 0.97 1.01 0.98 1.02 1.03 3.03 1.00 0.93 1.03 1.08 1.04 1.07
f1 (ppm)

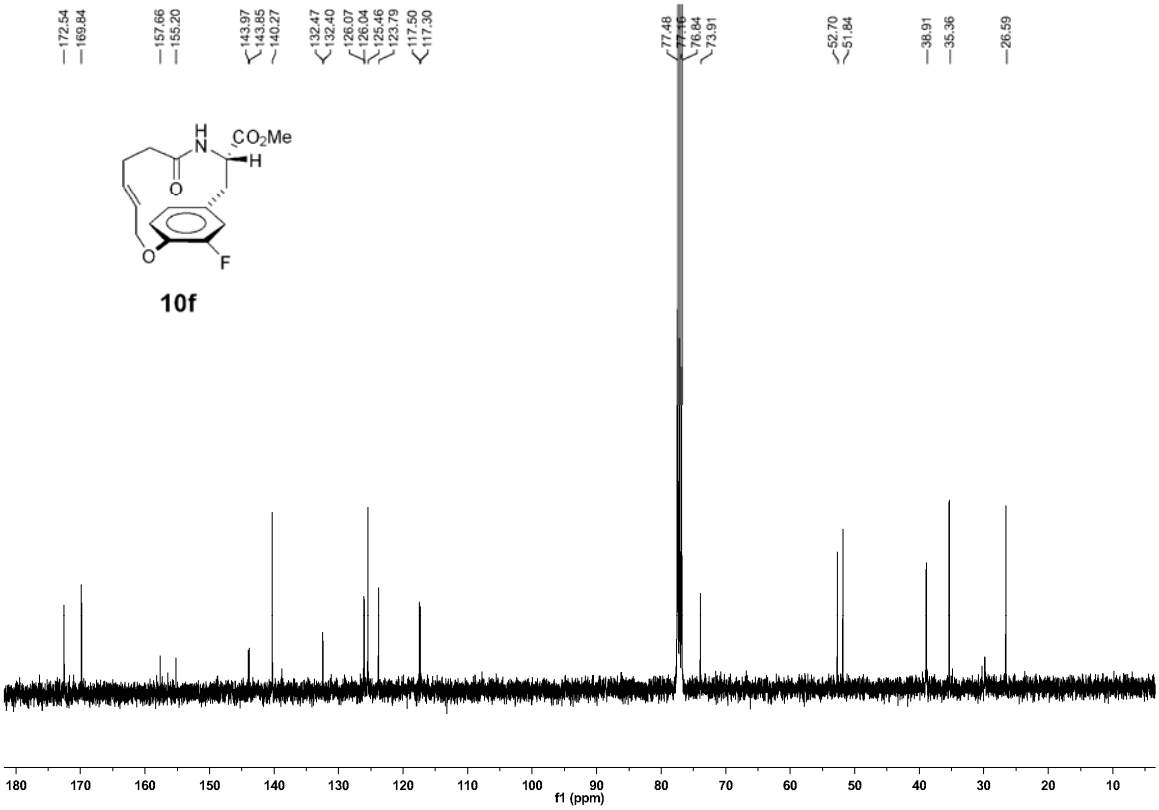

172.24 169.17 150.60 144.19 140.48 135.08 131.07 126.31 125.35 123.44 77.48 77.16 76.84 74.37 52.86 52.00 38.99 34.40 26.88
H
N
CO2Me
H
O
O
NO2
10e
f1 (ppm)

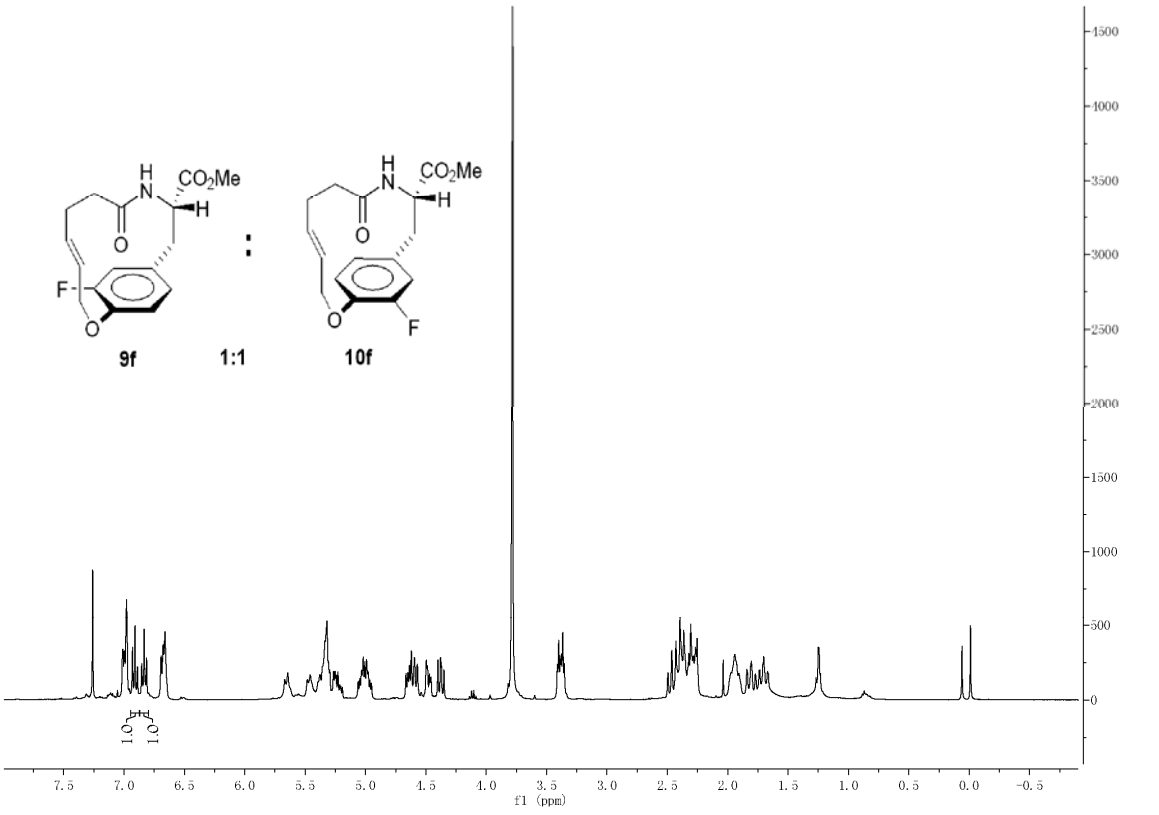

9e
1:1.2
10e
1.2
1.0
f1 (ppm)

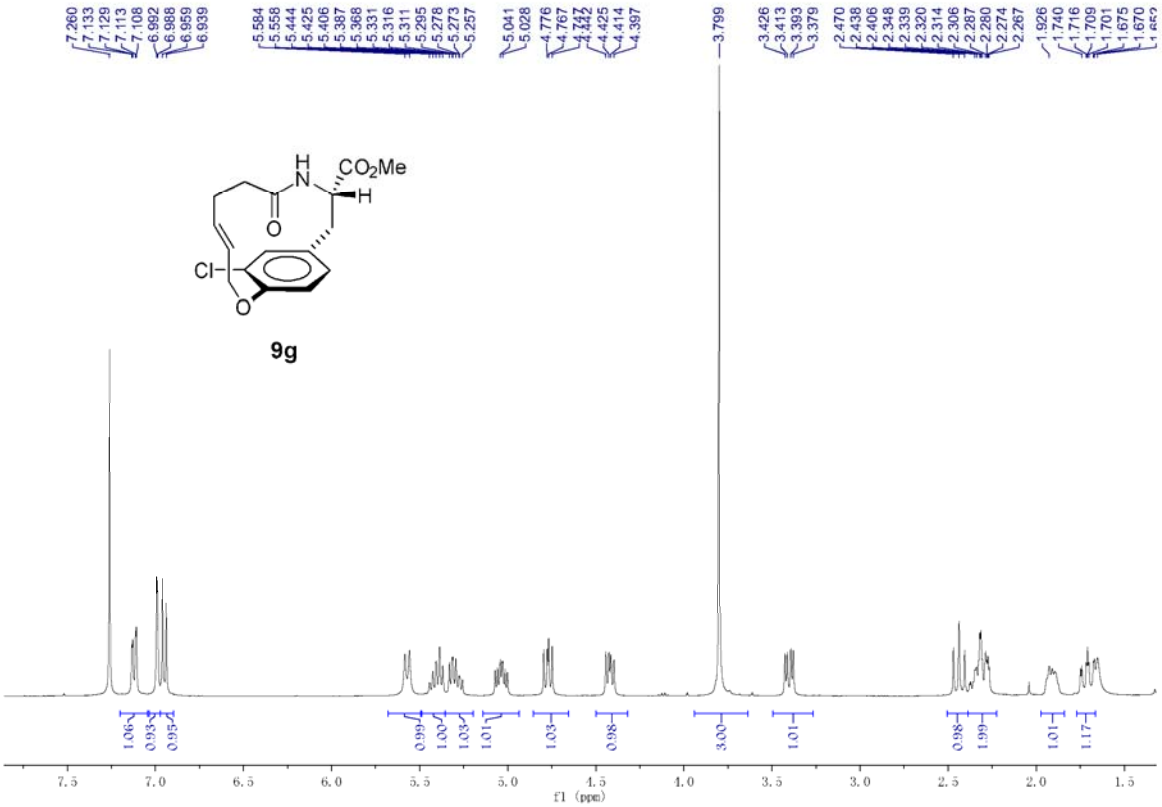

9f
0.98
0.92
0.94
1.01
1.97
0.97
1.02
0.97
3.00
1.01
1.92
1.07
1.04
1.06
f1 (ppm)

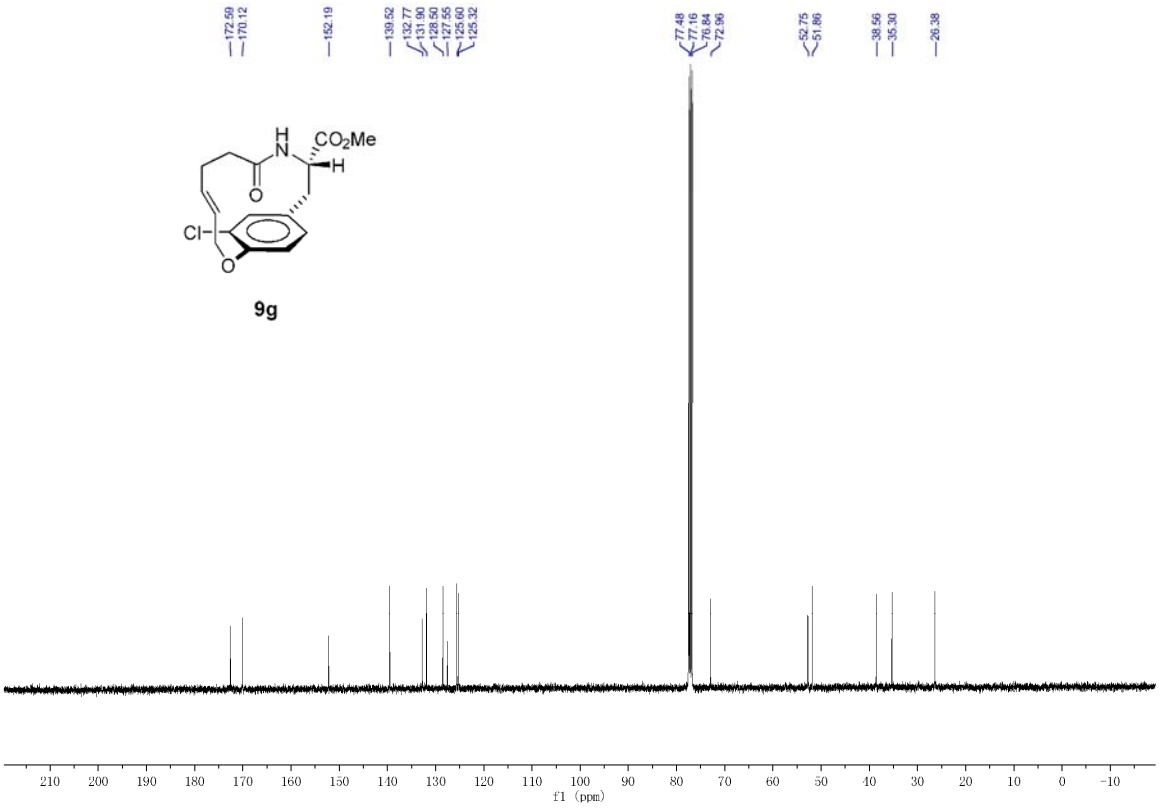

172.52
169.70
156.60
154.15
143.27
143.16
138.81
132.73
132.66
126.17
125.60
118.36
77.48
77.16
76.84
72.72
72.67
52.72
52.20
39.03
34.84
26.79
H
N
CO2Me
H
O
F
O
9f
f1 (ppm)


7.261
7.260
7.014
6.985
6.857
6.837
6.817
6.667
6.647
5.401
5.382
5.353
5.328
5.298
5.270
5.257
5.249
5.235
5.219
5.211
5.197
5.060
5.047
5.032
5.019
5.004
4.991
4.656
4.643
4.382
4.376
4.354
3.787
3.403
3.390
3.370
3.357
2.492
2.460
2.428
2.390
2.361
2.333
2.321
2.295
2.288
2.282
1.948
1.931
1.913
1.732
1.698
1.660
1.640
H
N
CO2Me
H
O
O
F
10f
0.95
0.90
0.89
1.78
1.04
0.99
0.91
0.93
3.00
1.02
1.04
1.96
1.05
1.11
f1 (ppm)


172.54
169.84
157.66
155.20
143.97
143.85
140.27
132.47
132.40
126.07
126.04
125.46
123.79
117.50
117.30
77.48
77.16
76.84
73.91
52.70
51.84
38.91
35.36
26.59
H
N
CO2Me
H
O
O
F
10f
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


H
N
CO2Me
H
O
F-
O
9f
1:1
H
N
CO2Me
H
O
O
F
10f
1500
1000
3500
3000
2500
2000
1500
1000
500
0
1.0
1.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


7.260
7.133
7.129
7.113
7.108
6.992
6.988
6.959
6.939
5.584
5.558
5.444
5.425
5.406
5.387
5.368
5.331
5.316
5.311
5.295
5.278
5.273
5.257
5.041
5.028
4.776
4.767
4.425
4.414
4.397
3.799
3.426
3.413
3.393
3.379
2.470
2.438
2.406
2.348
2.339
2.320
2.314
2.306
2.287
2.280
2.274
2.267
1.926
1.740
1.716
1.709
1.701
1.675
1.670
H
N
CO2Me
H
O
Cl
O
9g
1.06
0.93
0.95
0.99
1.00
1.03
1.01
1.03
0.98
3.00
1.01
0.98
1.99
1.01
1.17
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f1 (ppm)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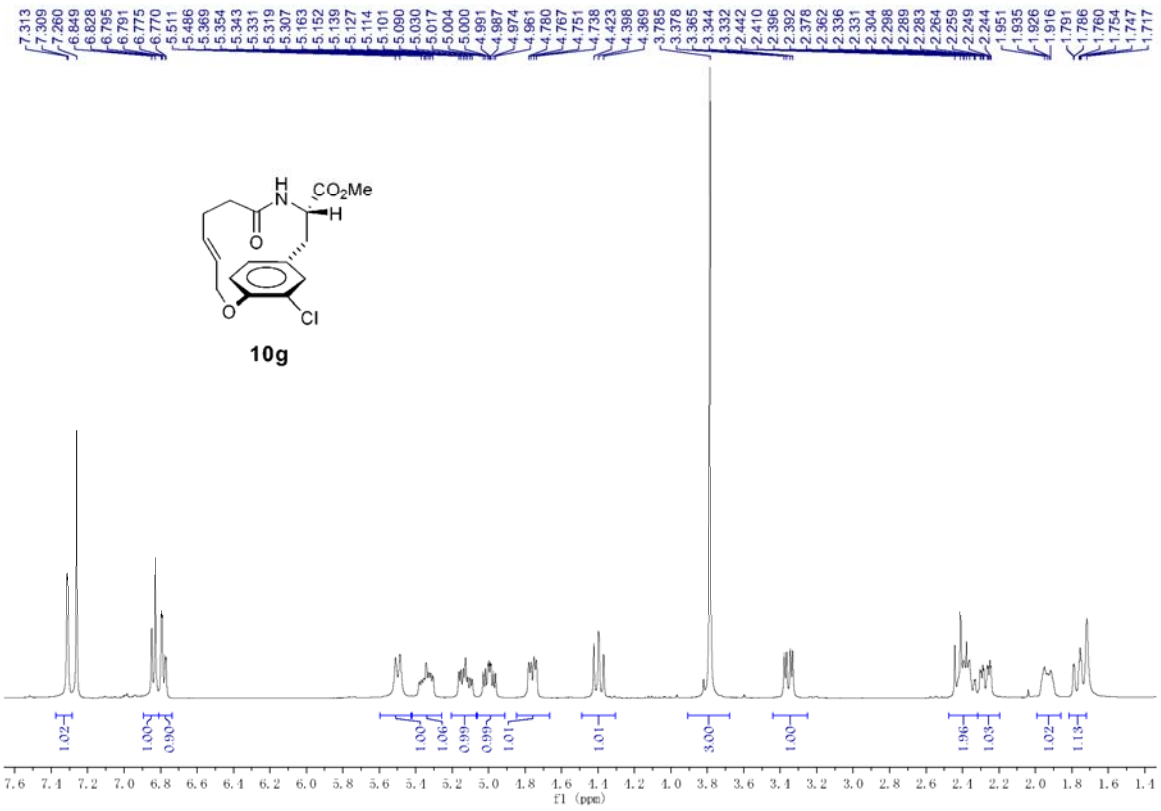
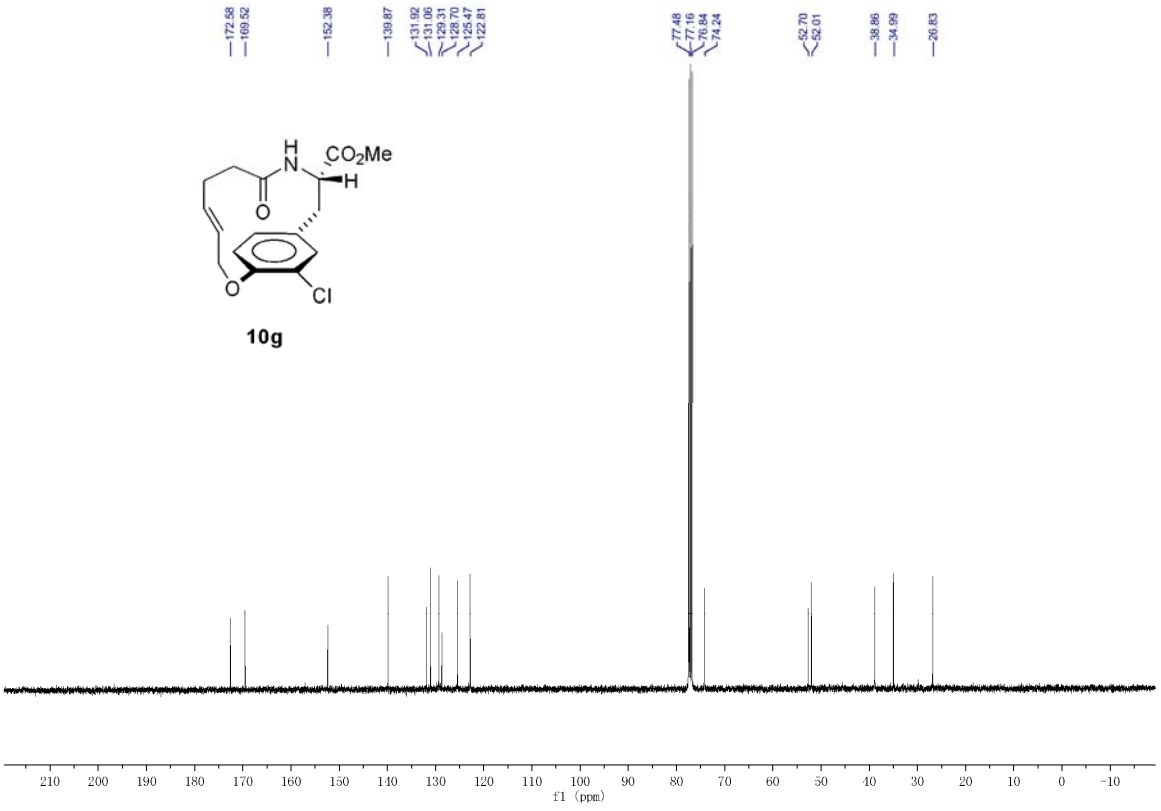
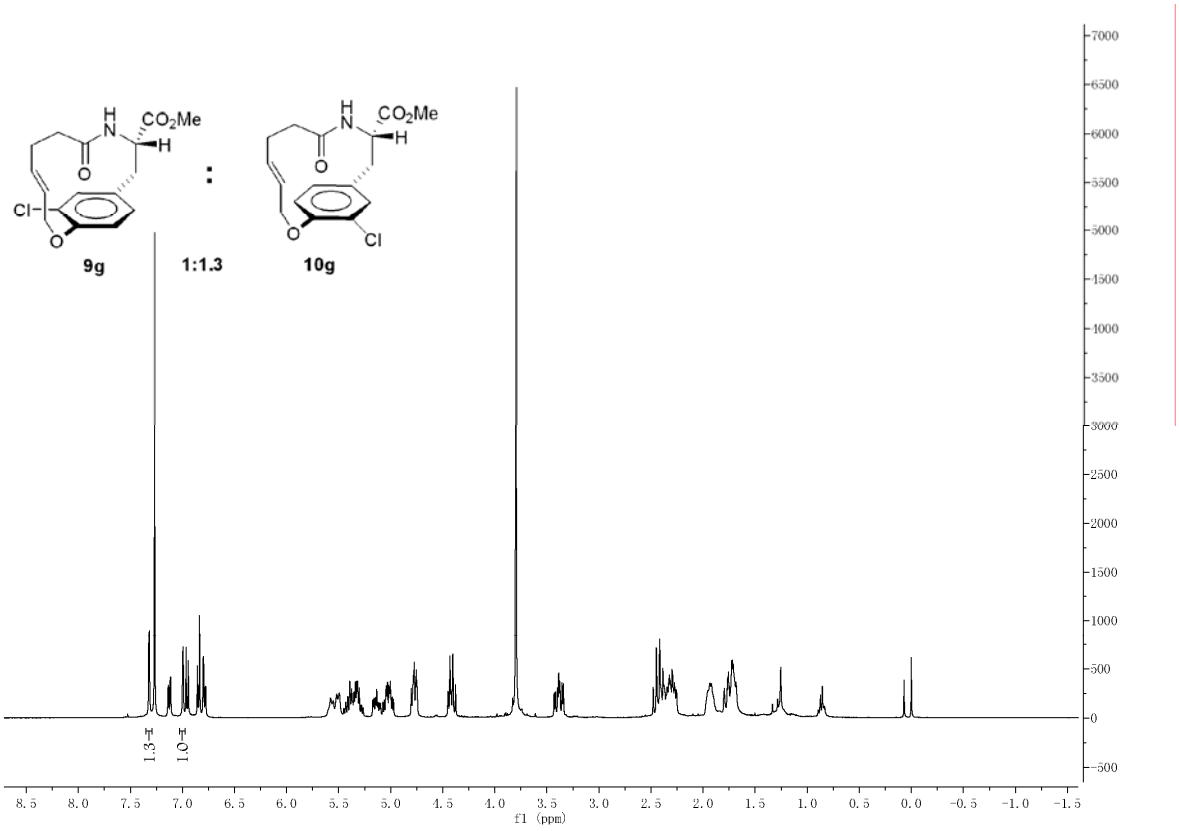
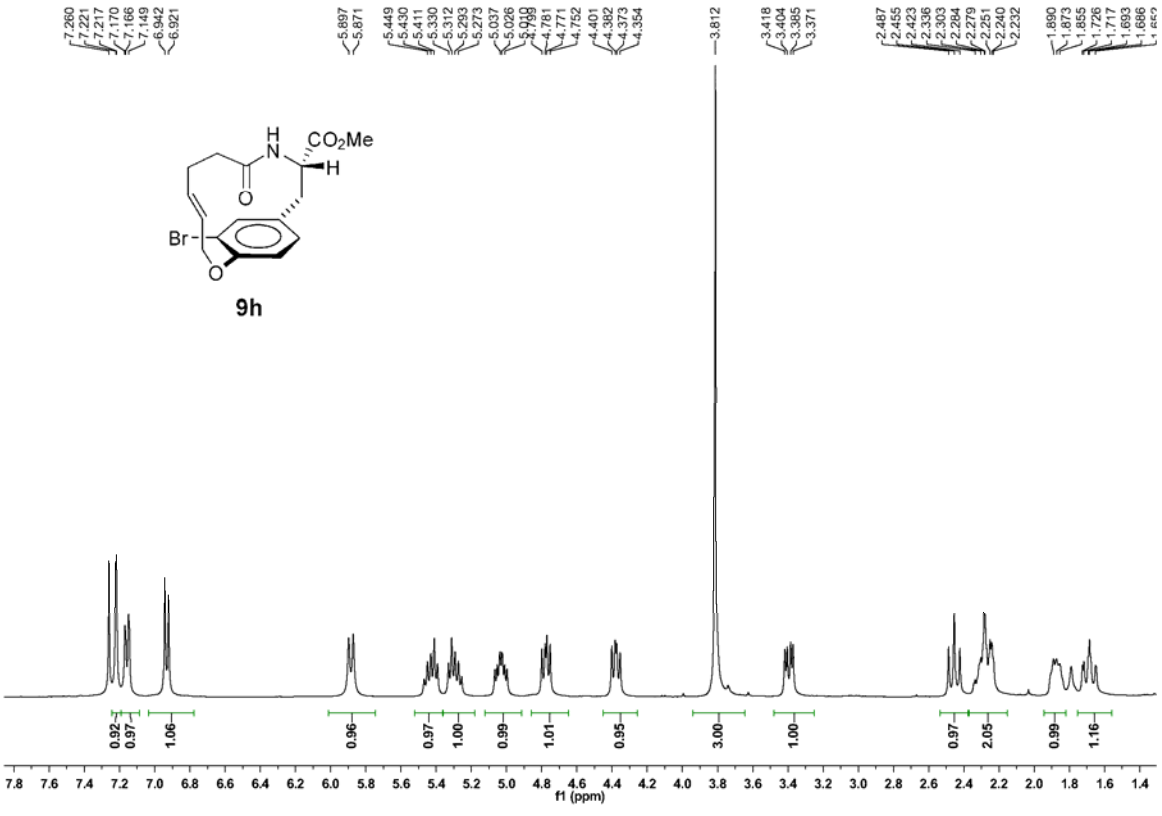
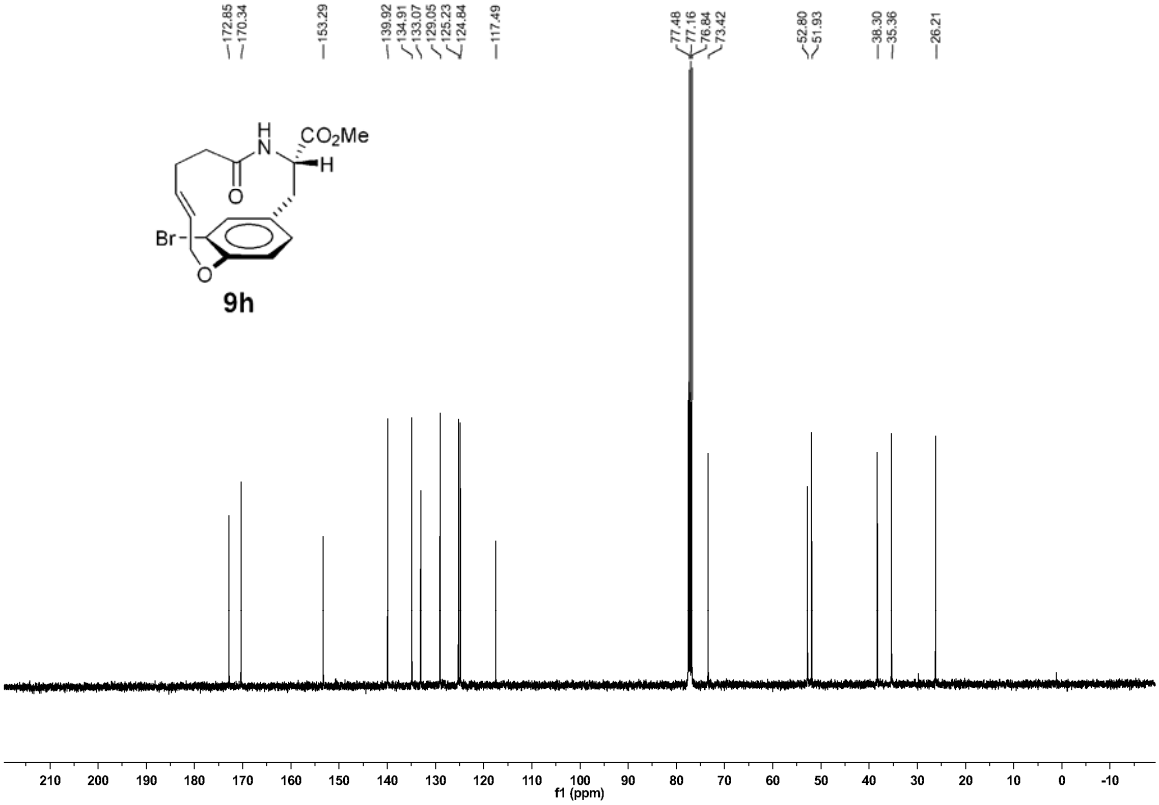
170.12
152.19
139.52
132.77
131.90
128.50
127.55
125.60
125.32
77.48
77.16
76.84
72.96
52.75
51.86
38.56
35.30
26.38
H
N
CO2Me
H
O
Cl
O
9g
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


10g
f1 (ppm)


10g
f1 (ppm)


9g
1:1.3
10g
1.3
1.0
f1 (ppm)


9h
0.92
0.97
1.06
0.96
0.97
1.00
0.99
1.01
0.95
3.00
1.00
0.97
2.05
0.99
1.16
f1 (ppm)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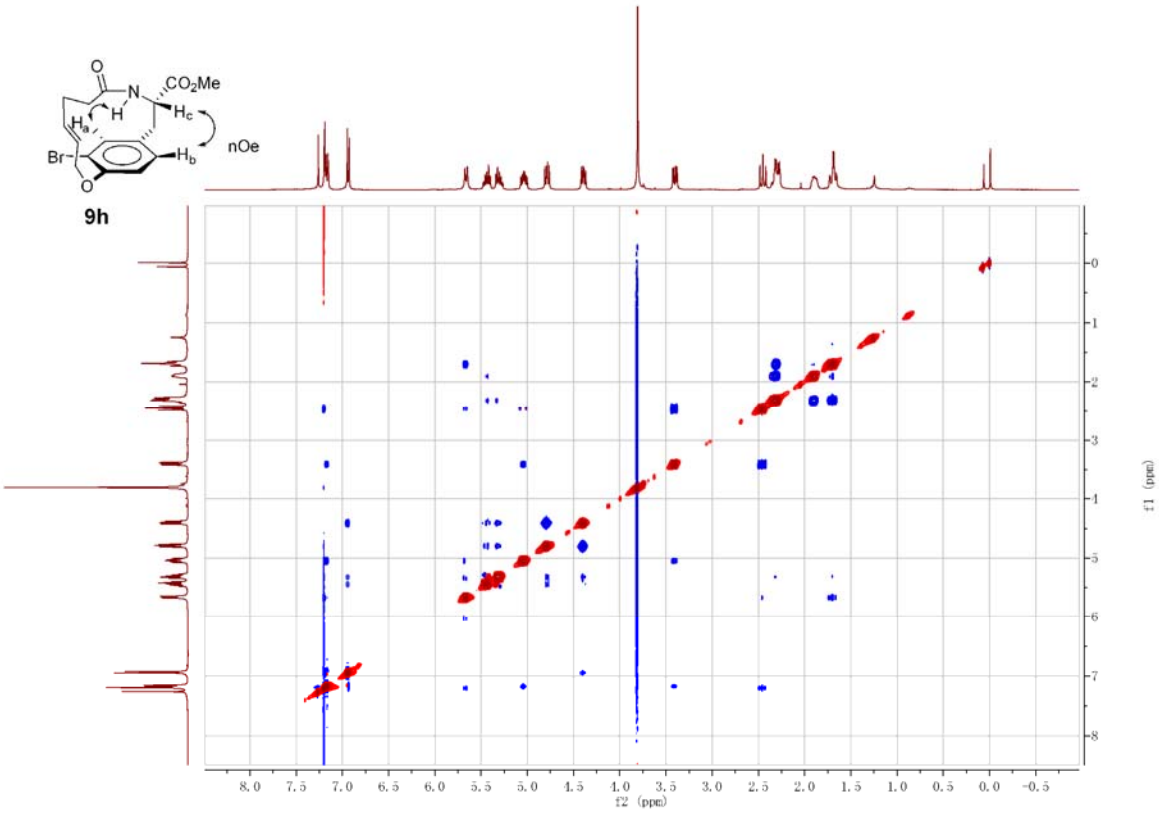
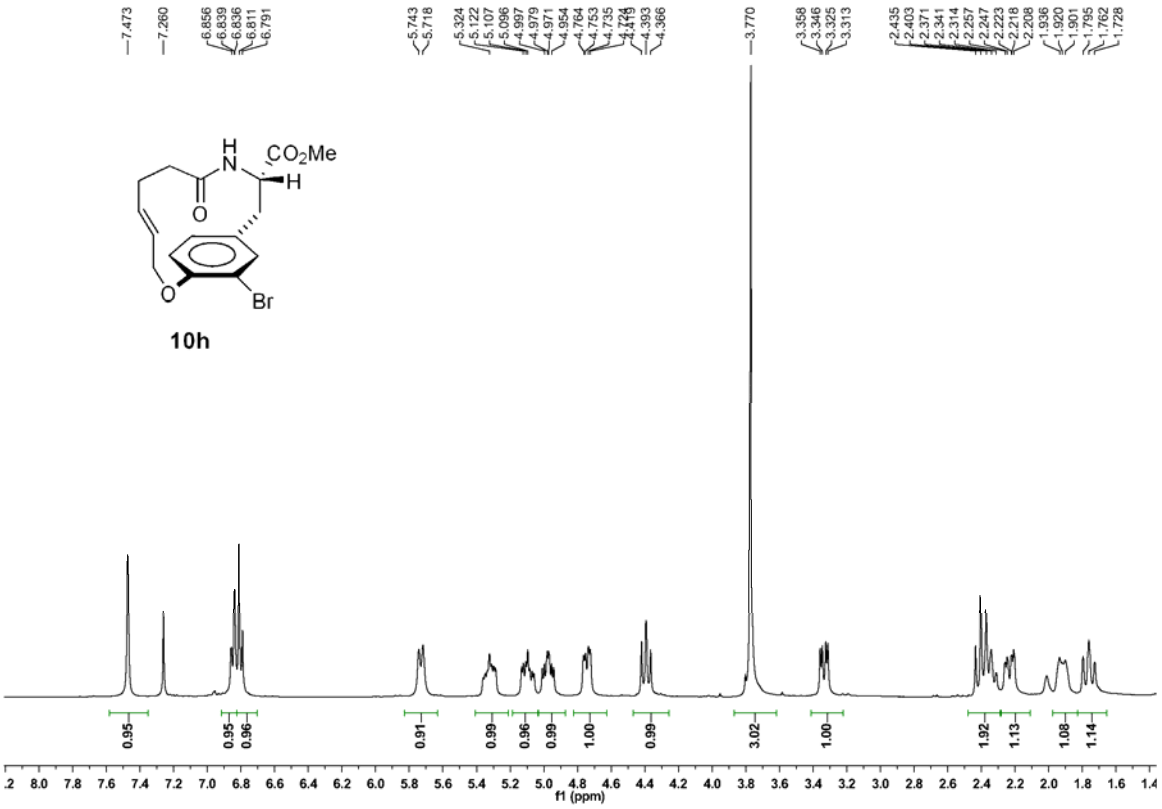
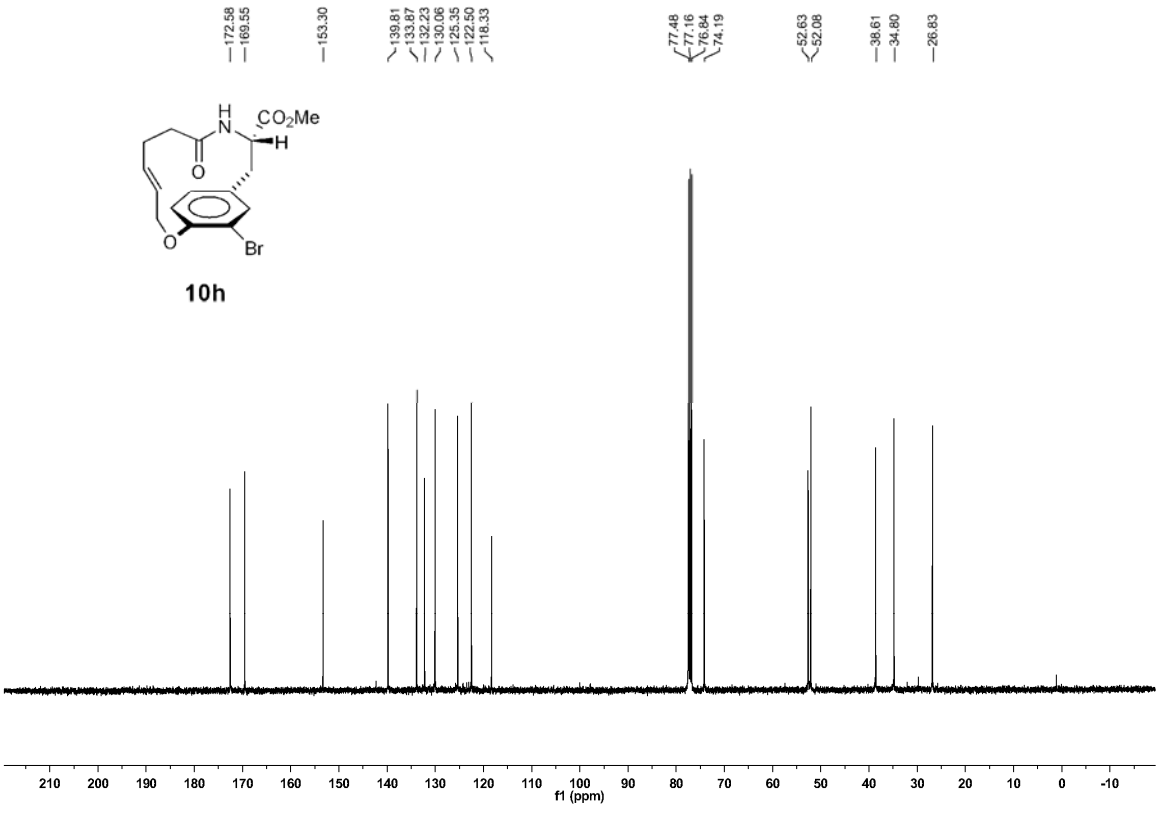
170.34
153.29
139.92
134.91
133.07
129.05
125.23
124.84
117.49
77.48
77.16
76.84
73.42
52.80
51.93
38.30
35.36
26.21
H
N
CO2Me
H
O
Br
O
9h
f1 (ppm)


O
N
CO2Me
H
Ha
Hc
Br
Hb
nOe
9h
f2 (ppm)
f1 (ppm)


7.473
7.260
6.856
6.839
6.836
6.811
6.791
5.743
5.718
5.324
5.122
5.107
5.096
4.997
4.979
4.971
4.954
4.764
4.753
4.735
4.393
4.366
3.770
3.358
3.346
3.325
3.313
2.435
2.403
2.371
2.341
2.314
2.257
2.247
2.223
2.218
2.208
1.936
1.920
1.901
1.795
1.762
1.728
H
N
CO2Me
H
O
O
Br
10h
0.95
0.95
0.96
0.91
0.99
0.96
0.99
1.00
0.99
3.02
1.00
1.92
1.13
1.08
1.14
f1 (ppm)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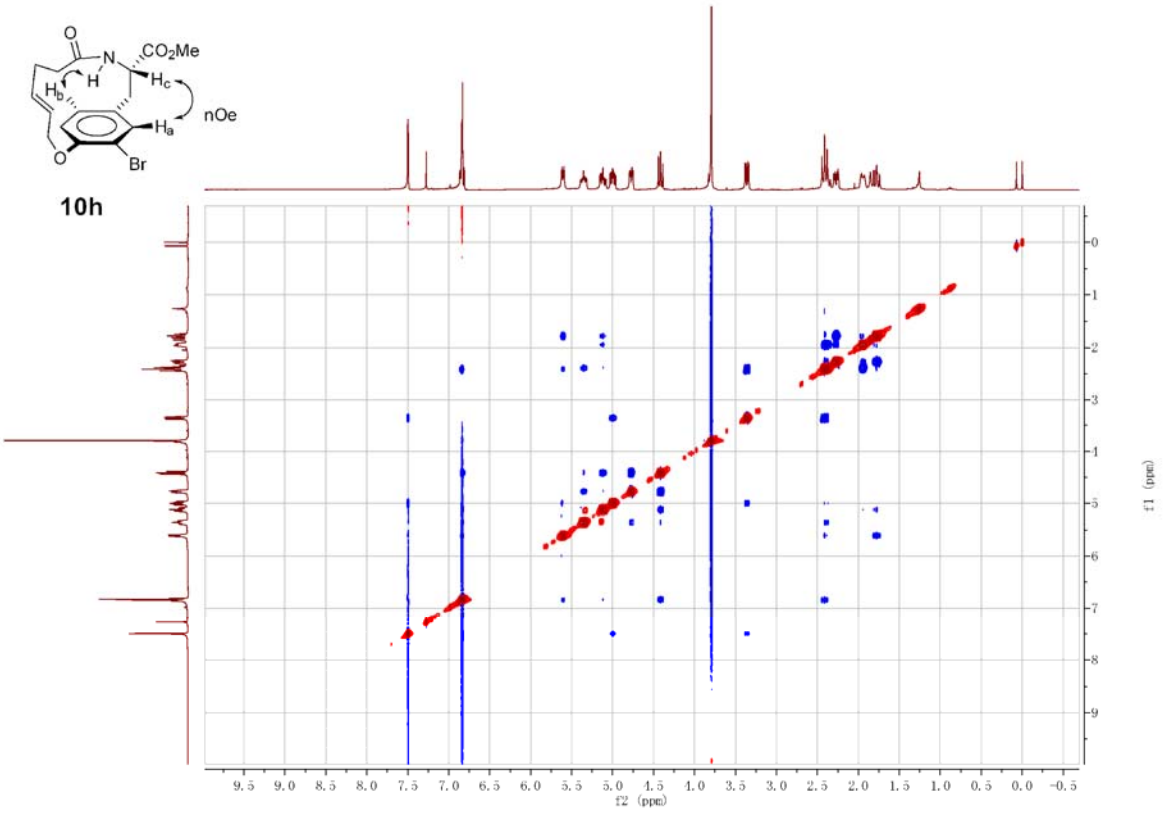
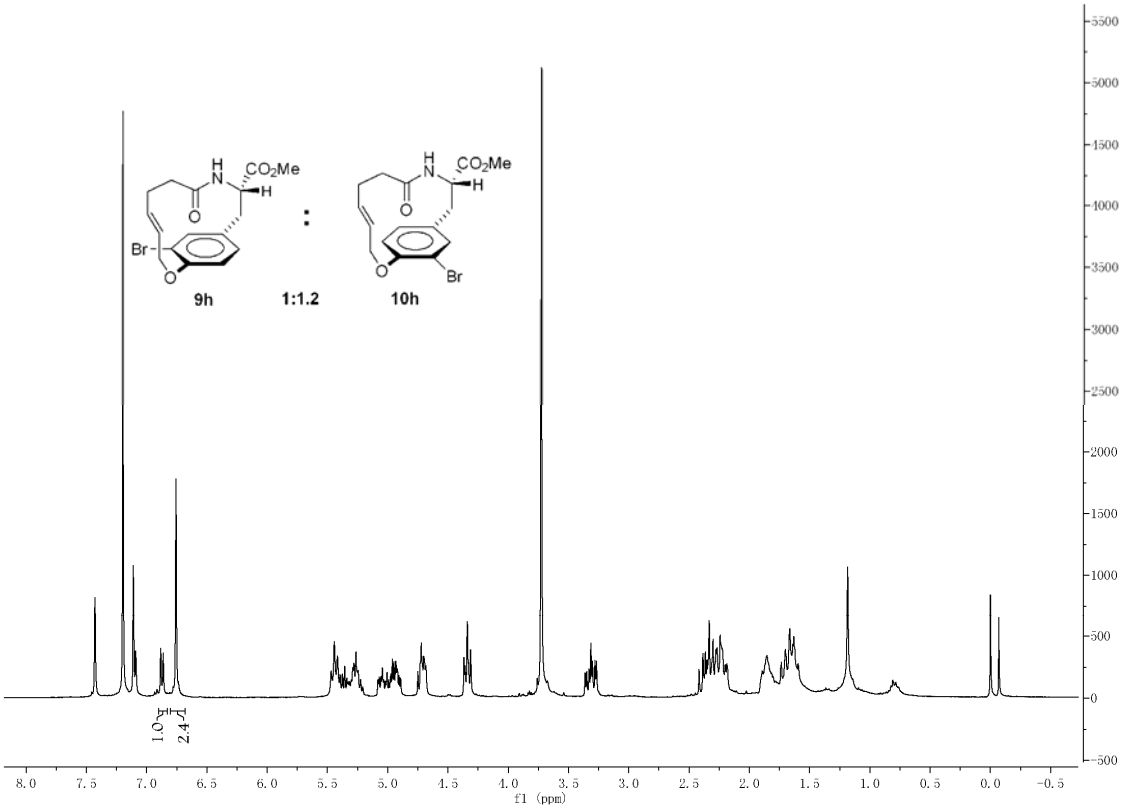
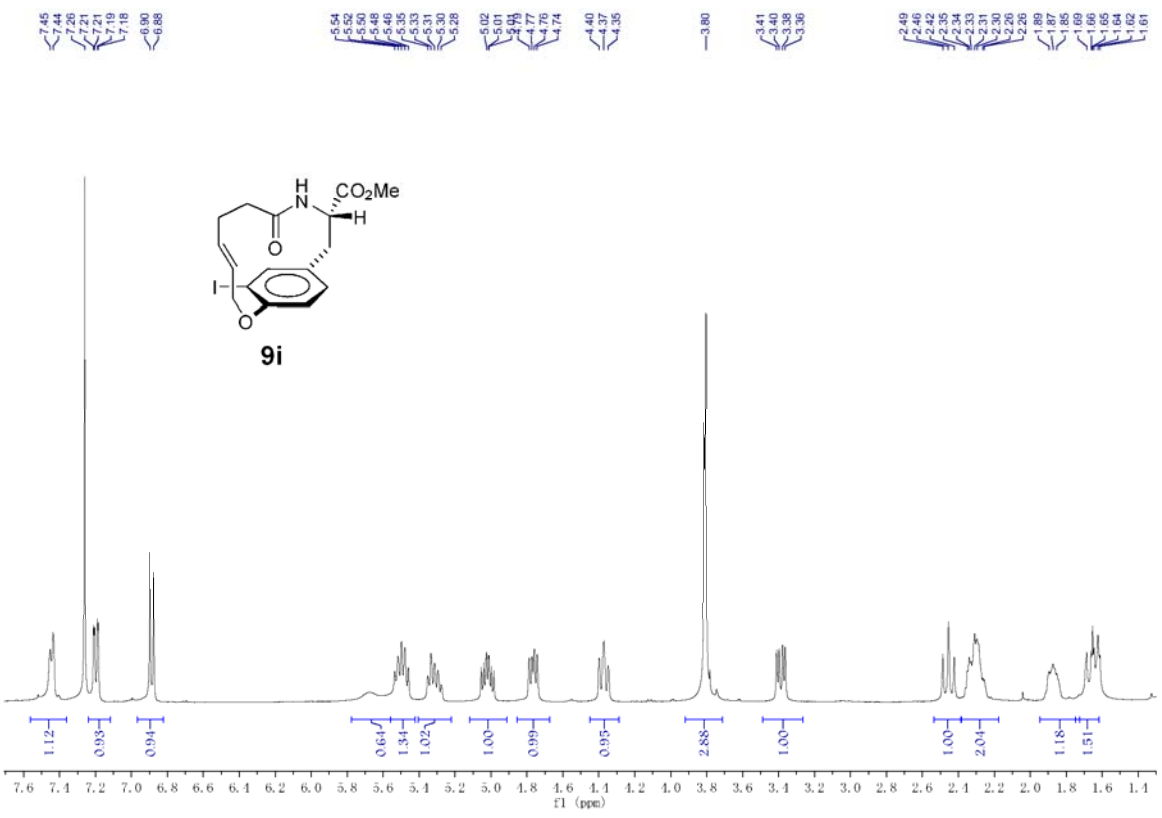
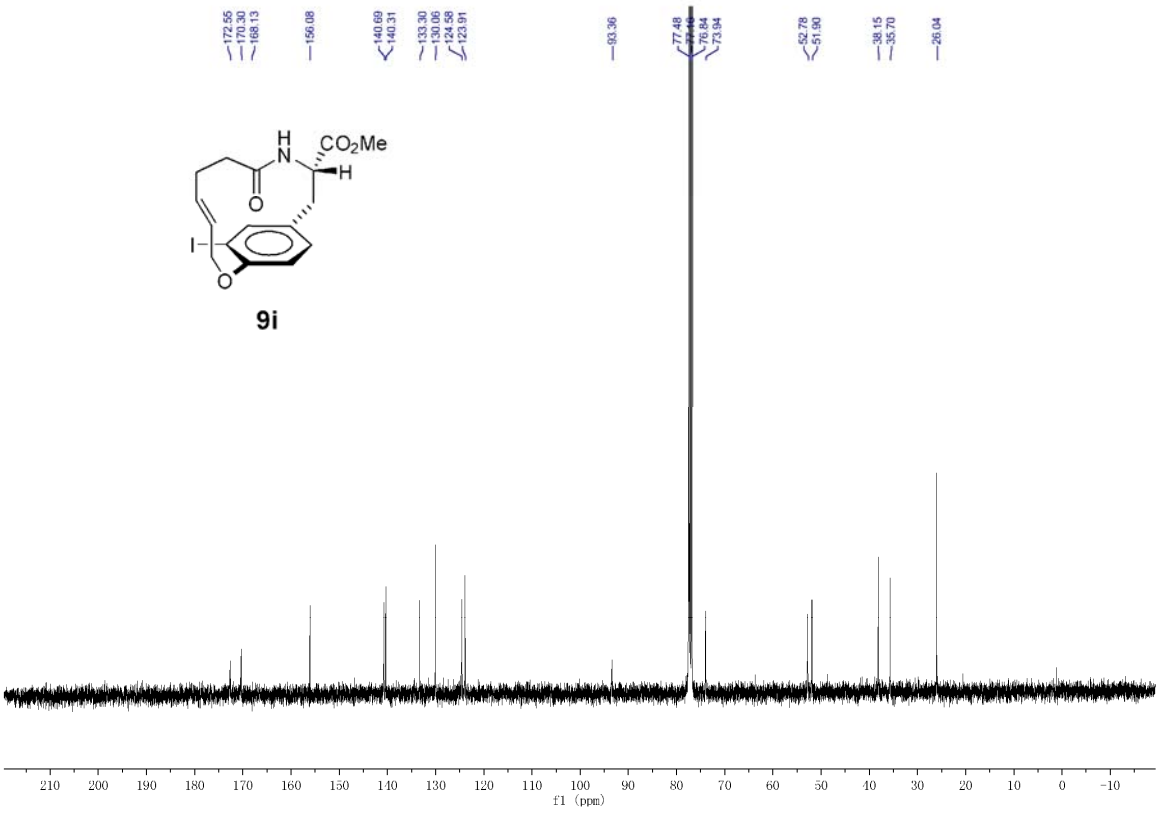
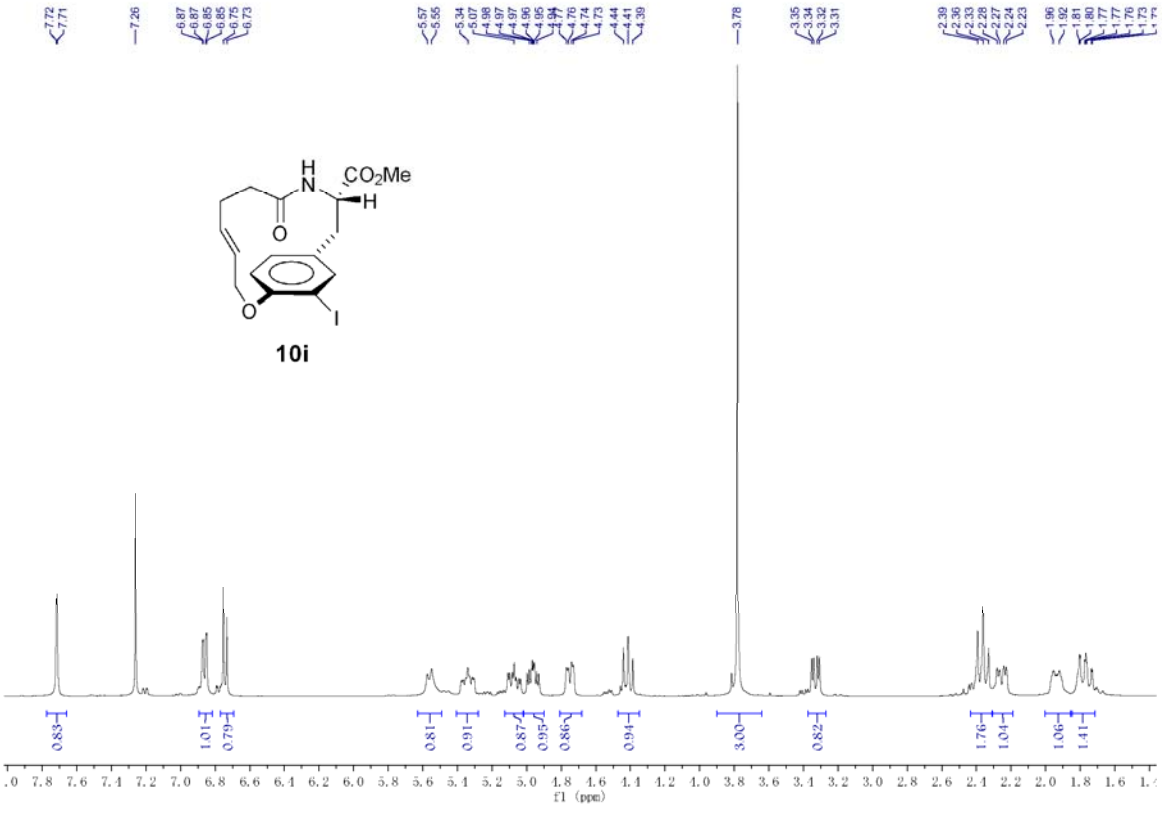
169.55
153.30
139.81
133.87
132.23
130.06
125.35
122.50
118.33
77.48
77.16
76.84
74.19
52.63
52.08
38.61
34.80
26.83
H
N
CO2Me
H
O
O
Br
10h
f1 (ppm)

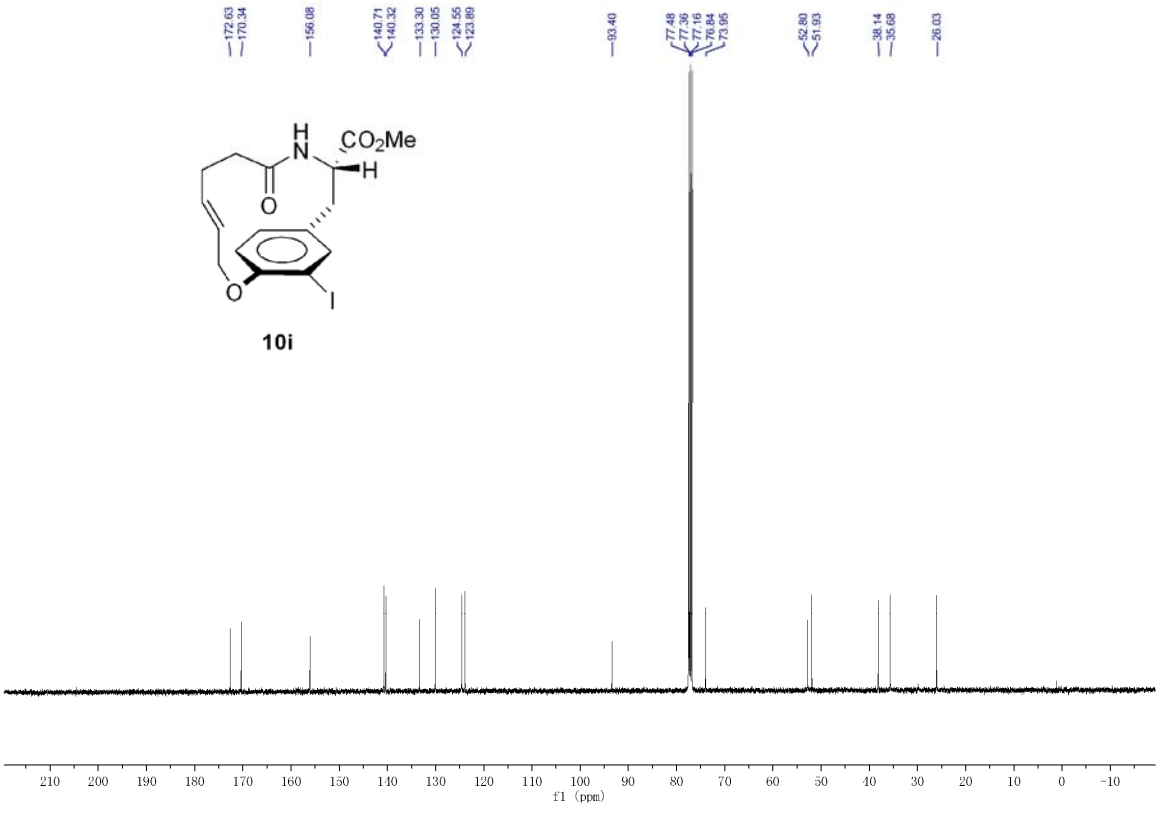

10h
nOe
f2 (ppm)
f1 (ppm)

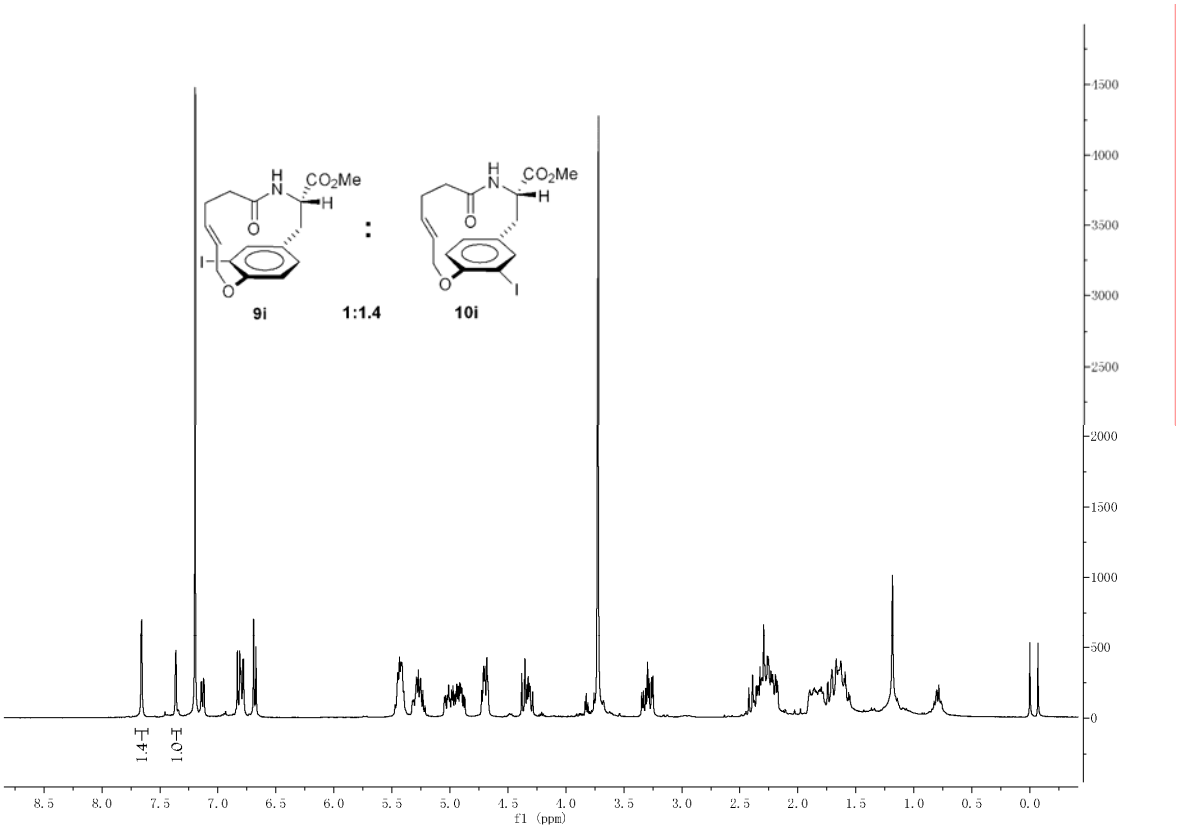

9h
1:1.2
10h
1.0
2.4
f1 (ppm)

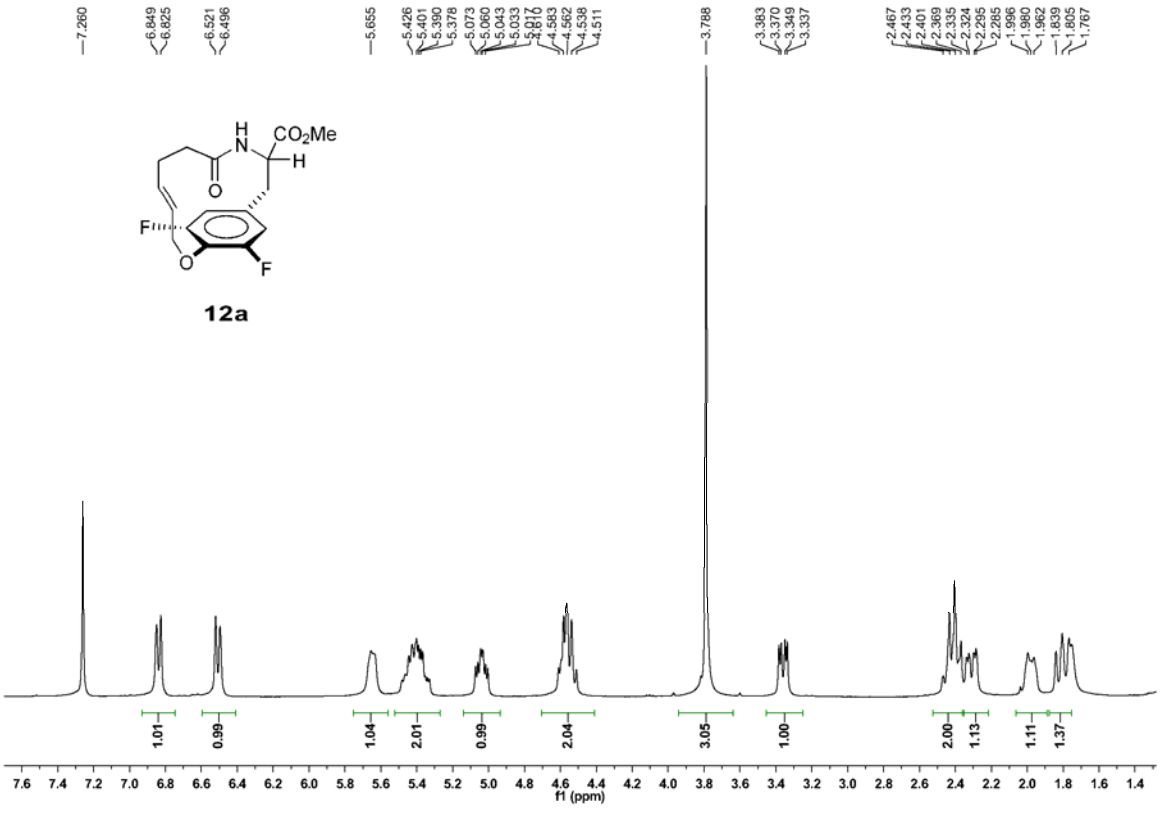

9i
f1 (ppm)

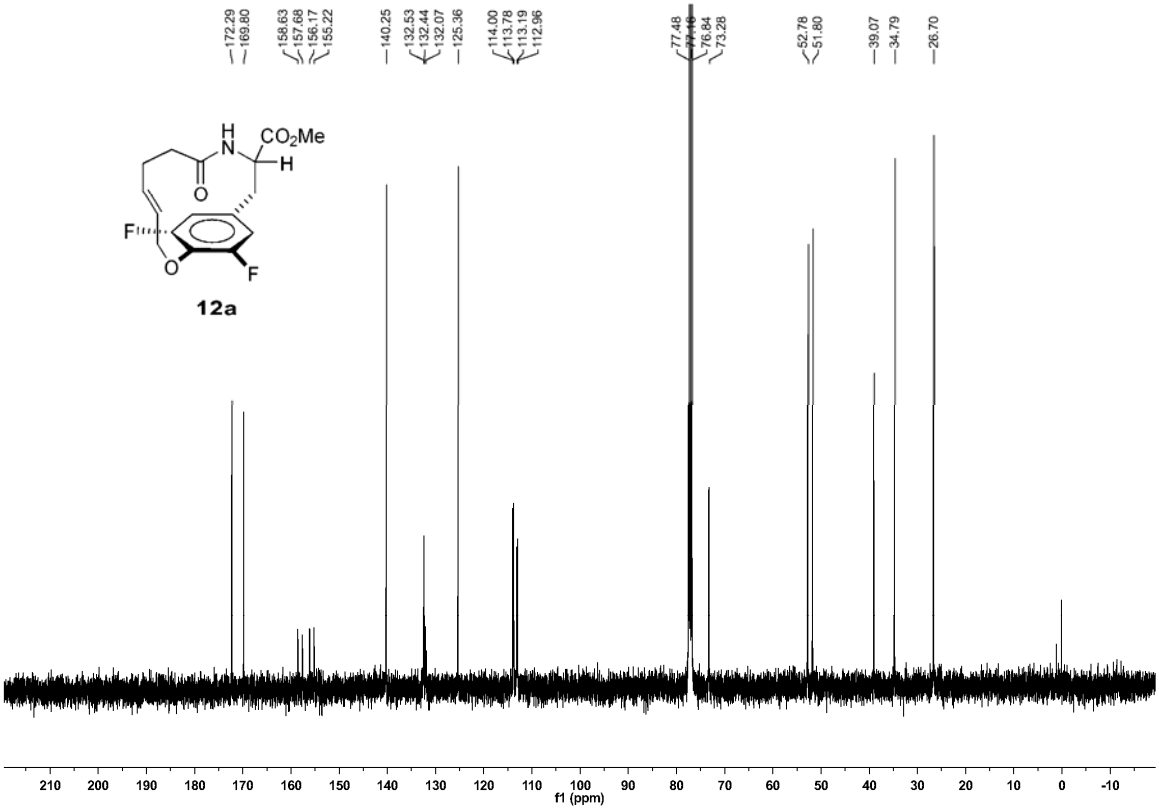

9i
f1 (ppm)

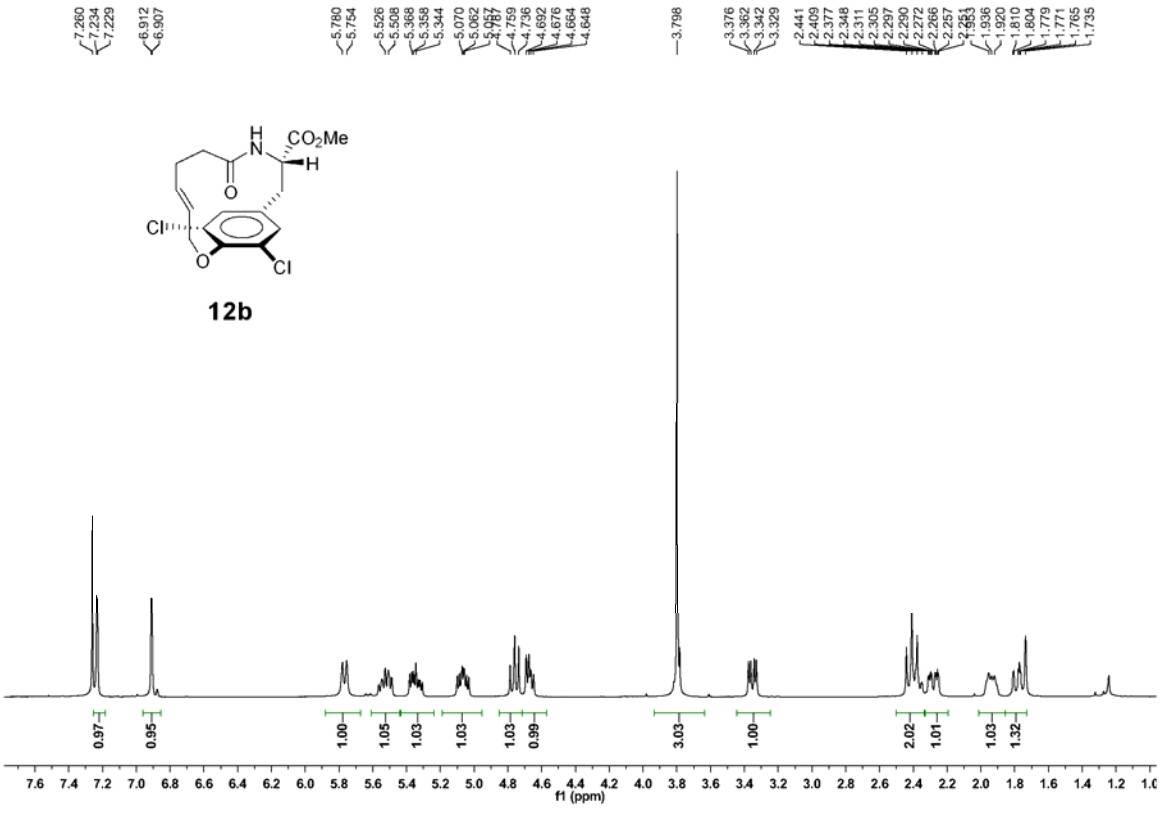

10i
f1 (ppm)

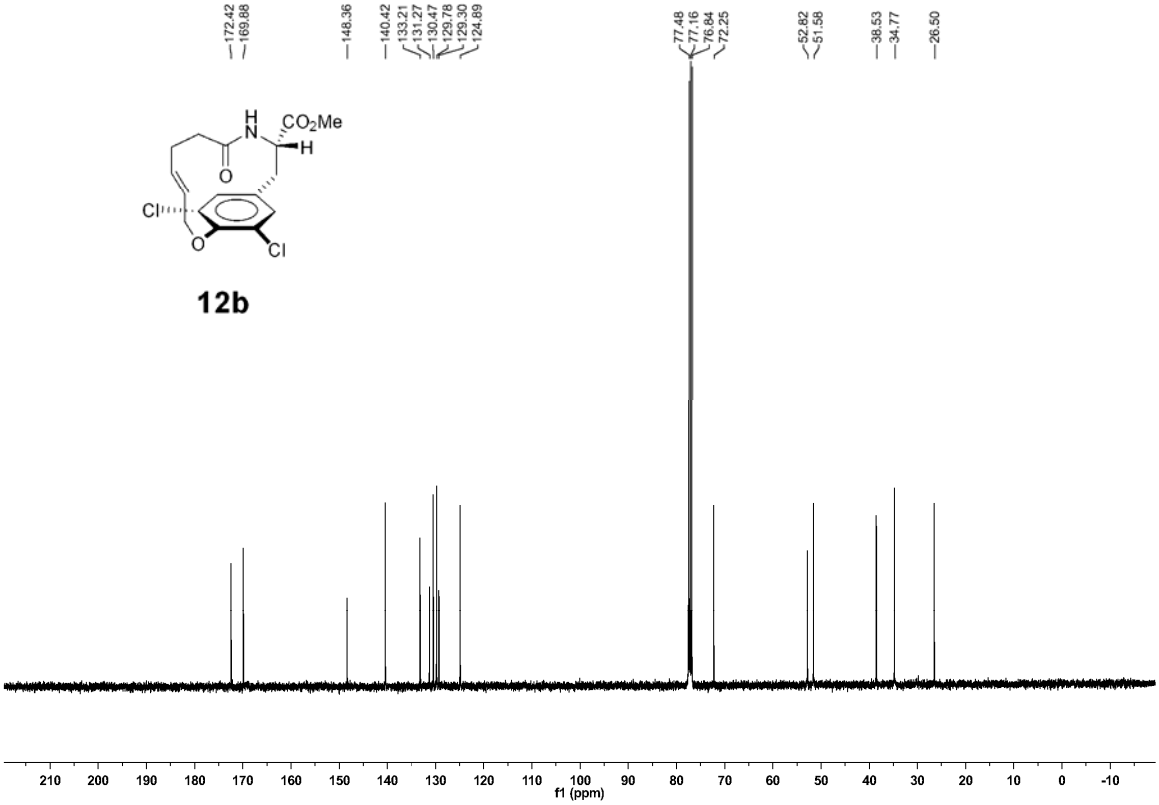

10i
f1 (ppm)


9i
1:1.4
10i
1.4
1.0
f1 (ppm)


12a
1.01
0.99
1.04
2.01
0.99
2.04
3.05
1.00
2.00
1.13
1.11
1.37
f1 (ppm)


172.29
169.80
158.63
157.68
156.17
155.22
140.25
132.53
132.44
132.07
125.36
114.00
113.78
113.19
112.96
77.48
77.16
76.84
73.28
52.78
51.80
39.07
34.79
26.70
H
N
CO2Me
H
O
F
O
F
12a
f1 (ppm)


7.260
7.234
7.229
6.912
6.907
5.780
5.754
5.526
5.508
5.388
5.358
5.344
5.070
5.062
5.057
4.787
4.759
4.736
4.692
4.676
4.664
4.648
3.798
3.376
3.362
3.342
3.329
2.441
2.409
2.377
2.348
2.311
2.305
2.297
2.290
2.272
2.266
2.257
2.251
1.953
1.936
1.920
1.810
1.804
1.779
1.771
1.765
1.735
H
N
CO2Me
H
O
Cl
O
Cl
12b
0.97
0.95
1.00
1.05
1.03
1.03
1.03
0.99
3.03
1.00
2.02
1.01
1.03
1.32
f1 (ppm)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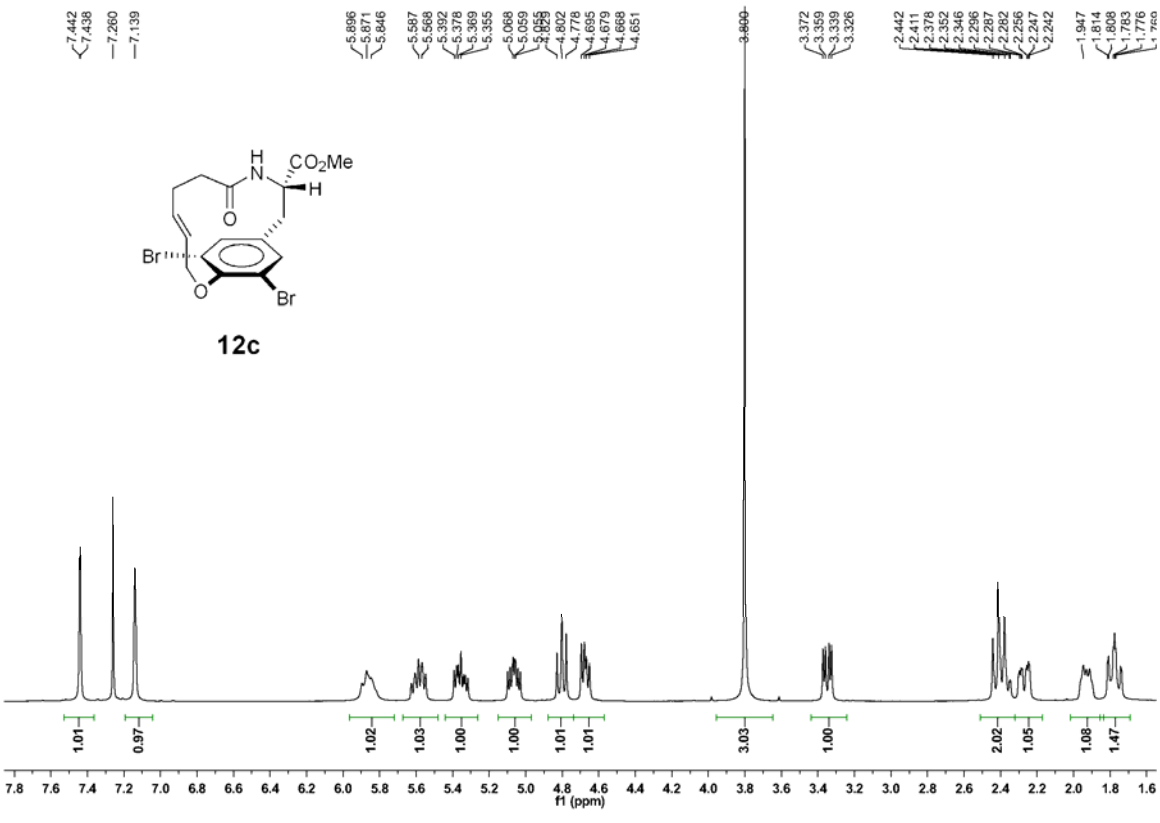
169.88
148.36
140.42
133.21
131.27
130.47
129.78
129.30
124.89
77.48
77.16
76.84
72.25
52.82
51.58
38.53
34.77
26.50
H
N
CO2Me
H
O
Cl
O
Cl
f1 (ppm)

12b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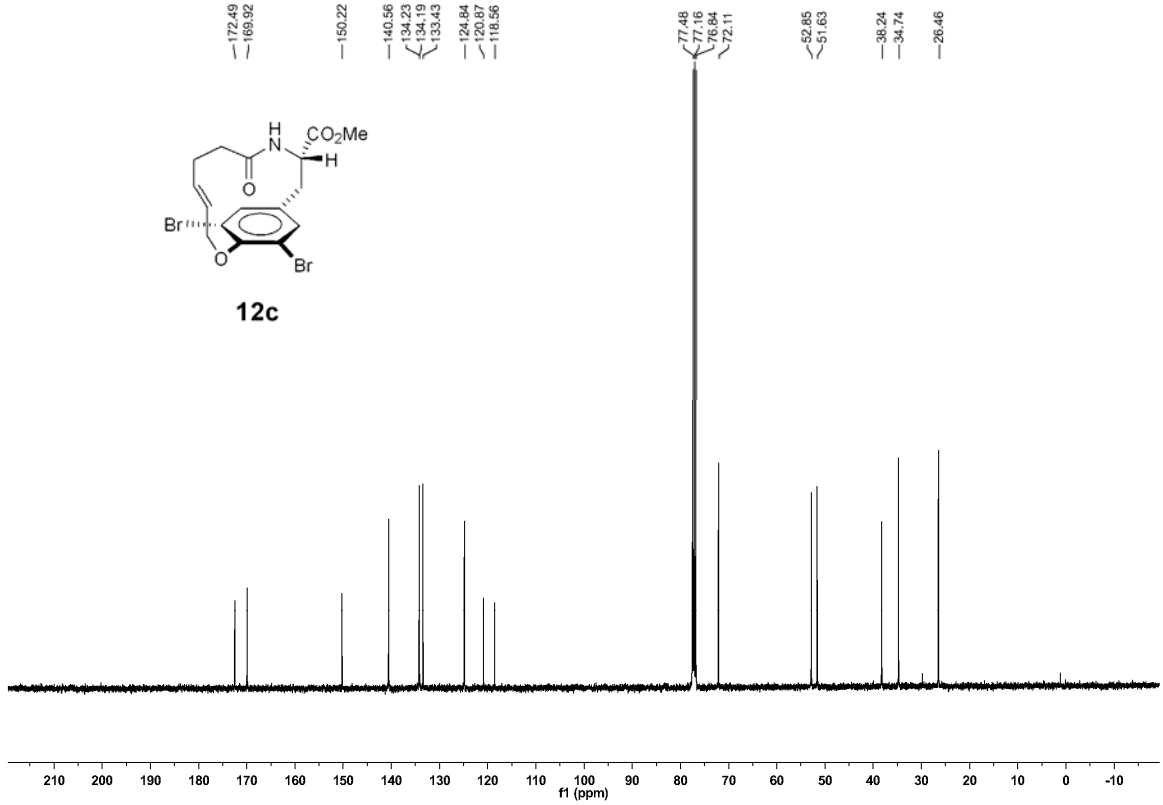
7.438
7.260
7.139
5.896
5.871
5.846
5.587
5.568
5.392
5.378
5.369
5.355
5.068
5.059
4.802
4.778
4.695
4.679
4.668
4.651
3.800
3.372
3.359
3.339
3.326
2.442
2.411
2.378
2.352
2.346
2.296
2.287
2.282
2.256
2.247
2.242
1.947
1.814
1.808
1.783
1.776
H
N
CO2Me
H
O
Br
O
Br
1.01
0.97
1.02
1.03
1.00
1.00
1.01
1.01
3.03
1.00
2.02
1.05
1.08
1.47
f1 (ppm)

12c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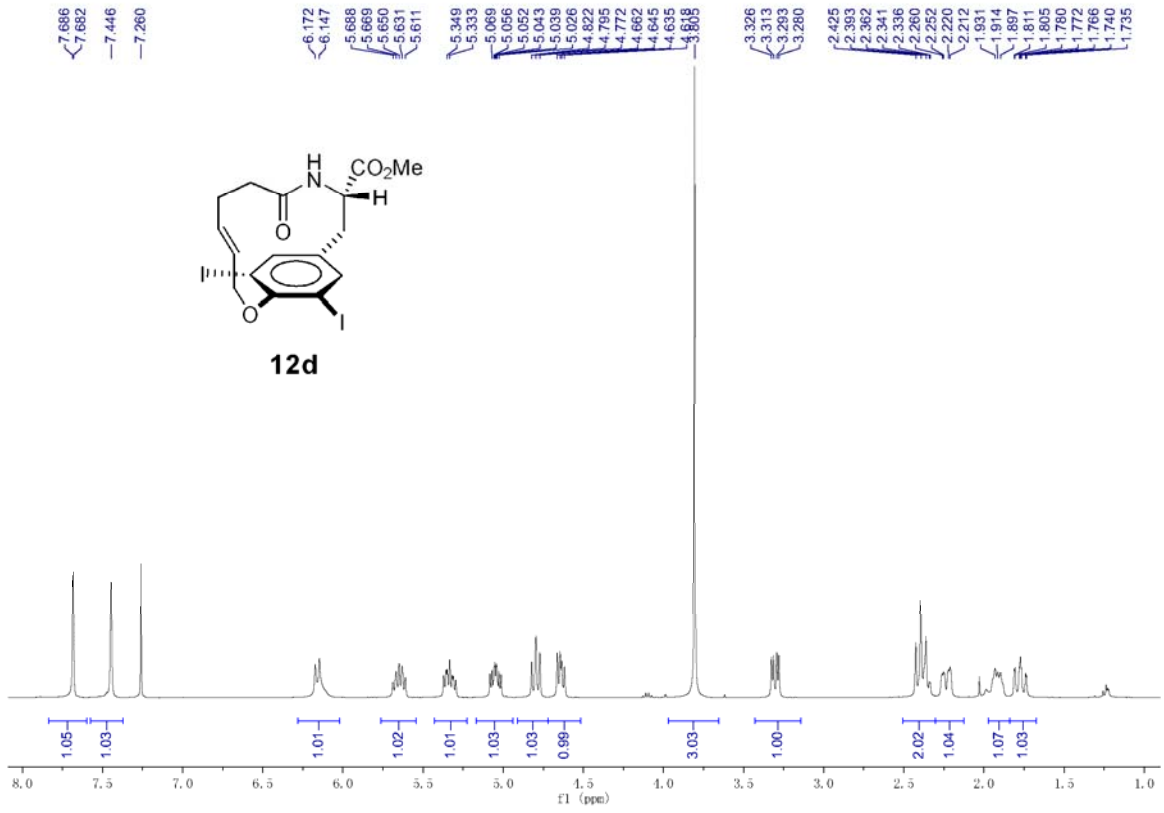
169.92
150.22
140.56
134.23
134.19
133.43
124.84
120.87
118.56
77.48
77.16
76.84
72.11
52.85
51.63
38.24
34.74
26.46
H
N
CO2Me
H
O
Br
O
Br
f1 (ppm)

12c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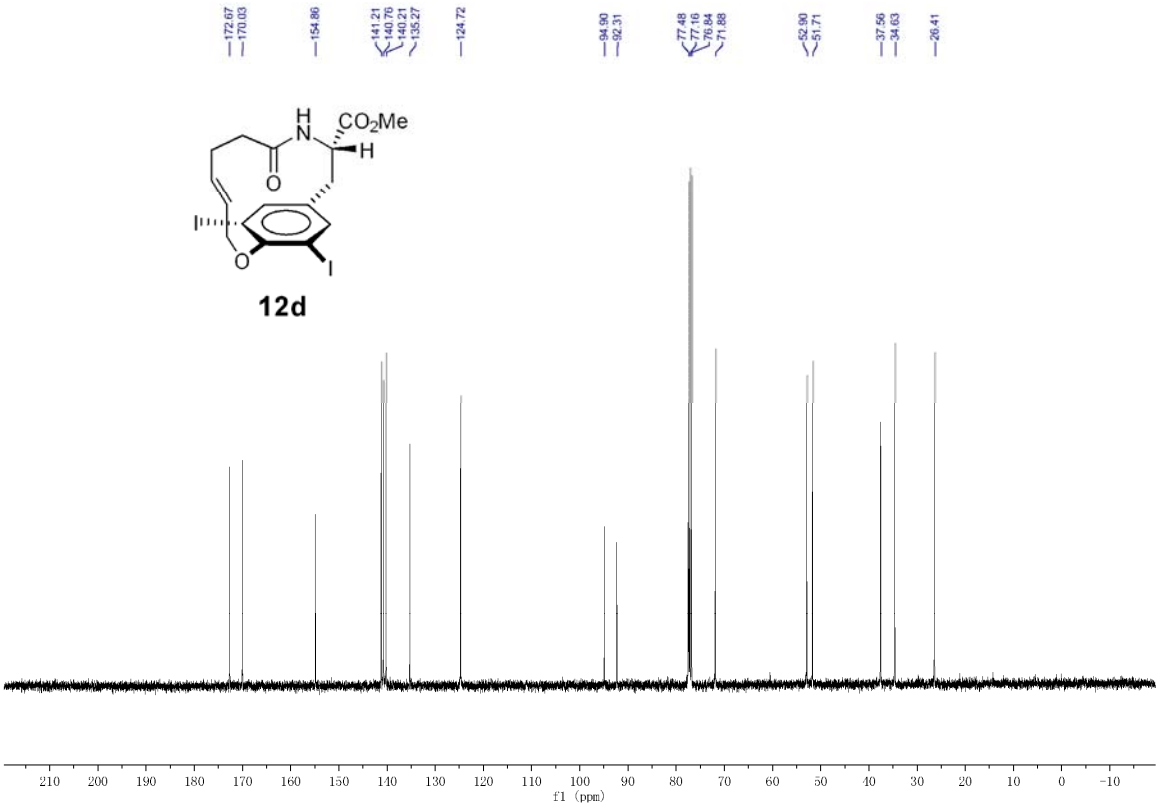
7.682
7.446
7.260
6.172
6.147
5.688
5.669
5.650
5.631
5.611
5.349
5.333
5.069
5.056
5.052
5.043
5.039
5.026
4.822
4.795
4.772
4.662
4.645
4.635
3.805
3.326
3.313
3.293
3.280
2.425
2.393
2.362
2.341
2.336
2.260
2.252
2.220
2.212
1.931
1.914
1.897
1.811
1.805
1.780
1.772
1.766
1.740
1.735
H
N
CO2Me
H
O
I
O
I
1.05
1.03
1.01
1.02
1.01
1.03
1.03
0.99
3.03
1.00
2.02
1.04
1.07
1.03
f1 (ppm)

12d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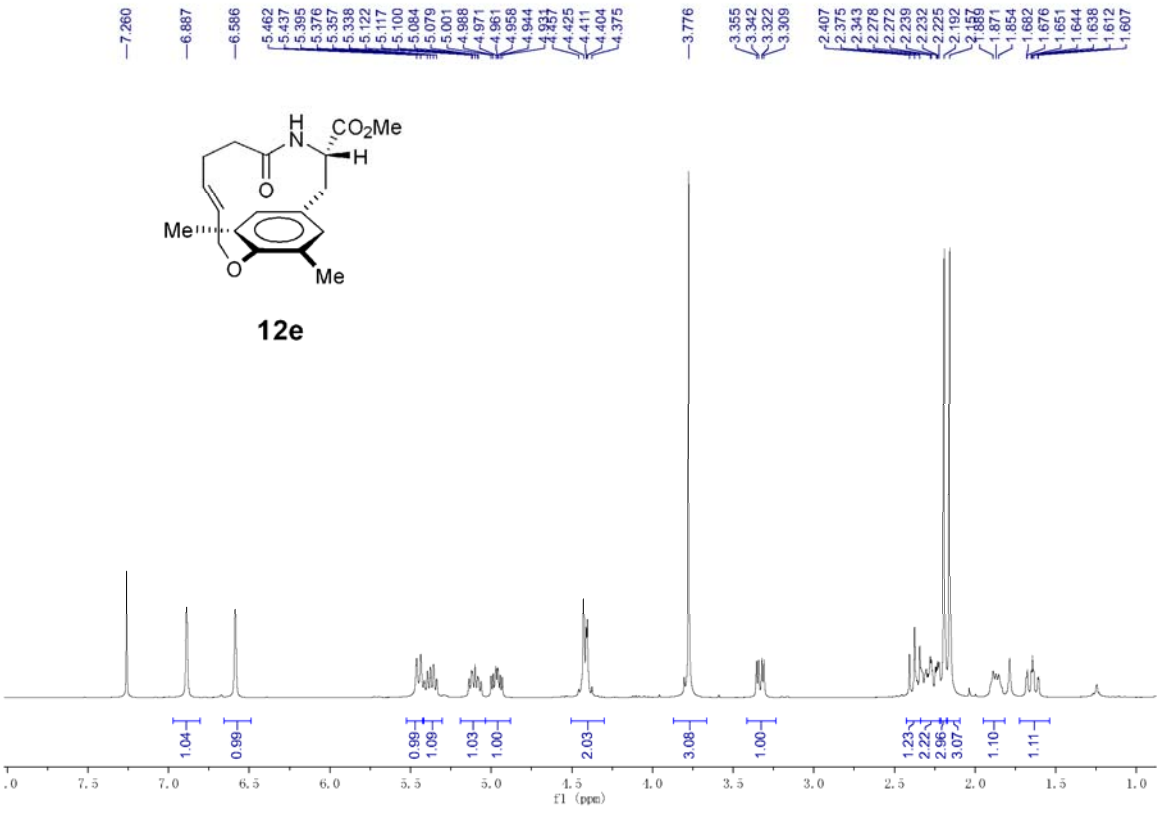
154.86
141.21
140.76
140.21
135.27
124.72
94.90
92.31
77.48
77.16
76.84
71.88
52.90
51.71
37.56
34.63
26.41
H
N
CO2Me
H
O
I
O
I
12d
f1 (ppm)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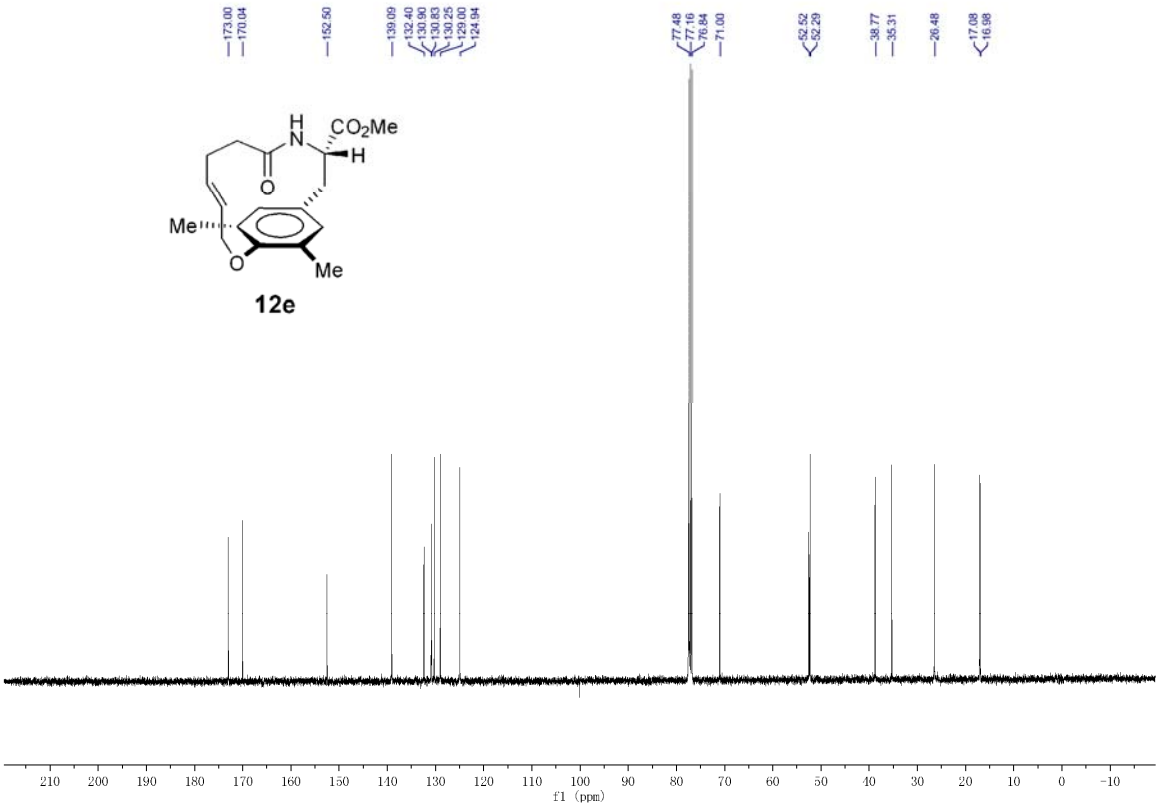
6.586
5.462
5.437
5.395
5.376
5.357
5.338
5.122
5.117
5.100
5.084
5.079
5.001
4.988
4.971
4.961
4.958
4.944
4.931
4.457
4.425
4.411
4.404
4.375
3.776
3.355
3.342
3.322
3.309
2.407
2.375
2.343
2.278
2.272
2.239
2.232
2.225
2.192
1.871
1.854
1.682
1.676
1.651
1.644
1.638
1.612
1.607
H
N
CO2Me
H
O
Me
O
Me
12e
1.04
0.99
0.99
1.09
1.03
1.00
2.03
3.08
1.00
1.23
2.22
2.96
3.07
1.10
1.11
f1 (ppm)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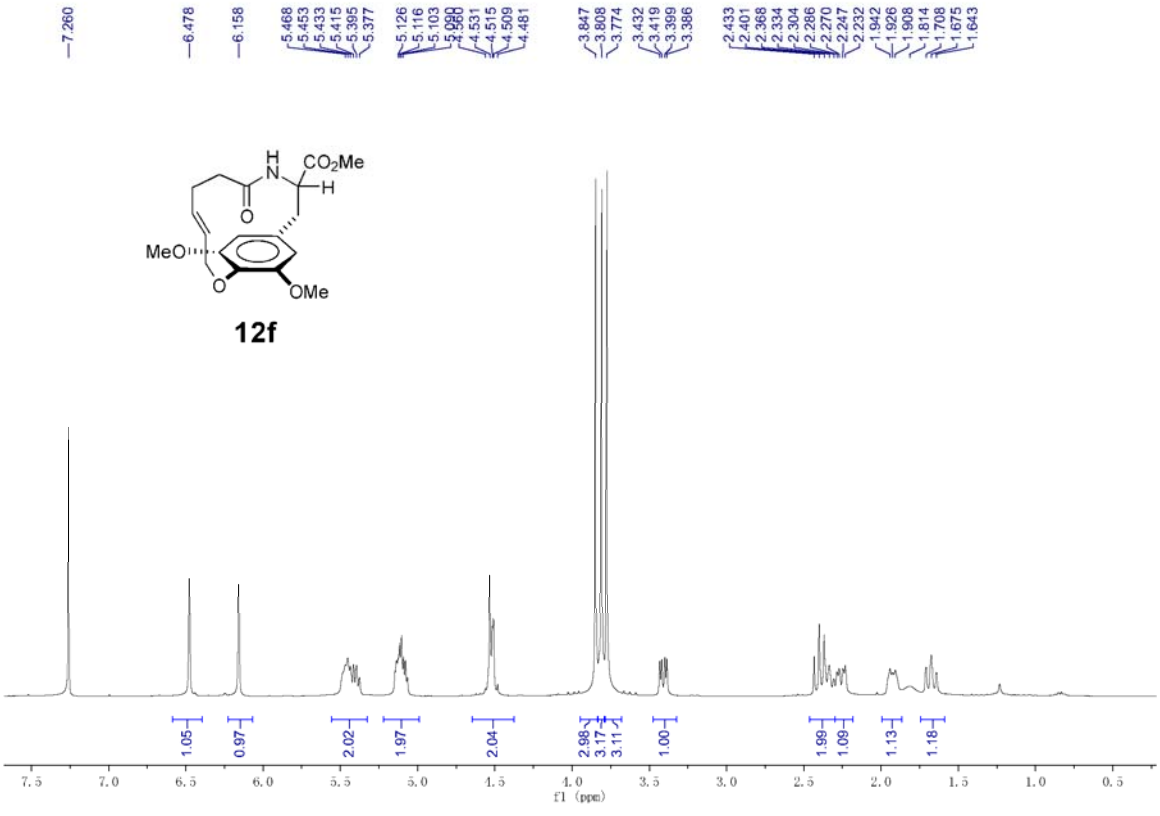
152.50
139.09
132.40
130.80
130.25
129.00
124.94
77.48
77.16
76.84
71.00
52.52
52.29
38.77
35.31
26.48
17.08
16.98
H
N
CO2Me
H
O
Me
O
Me
12e
f1 (ppm)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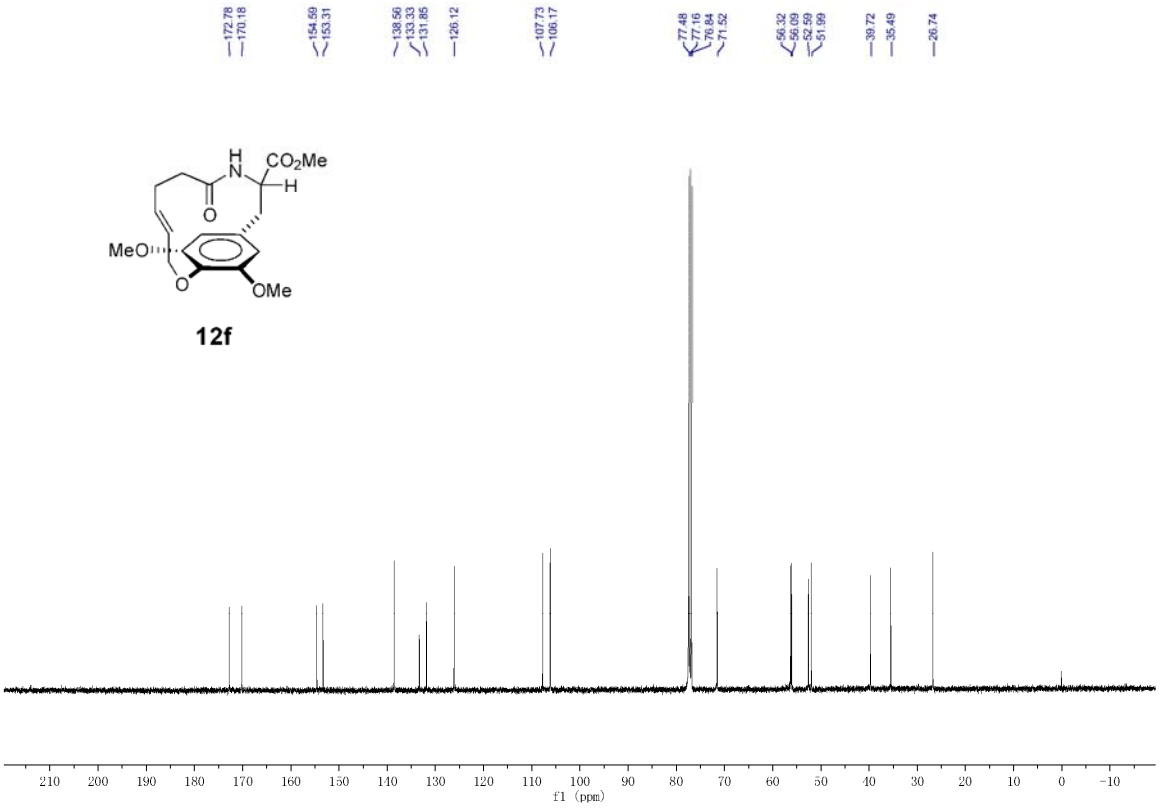
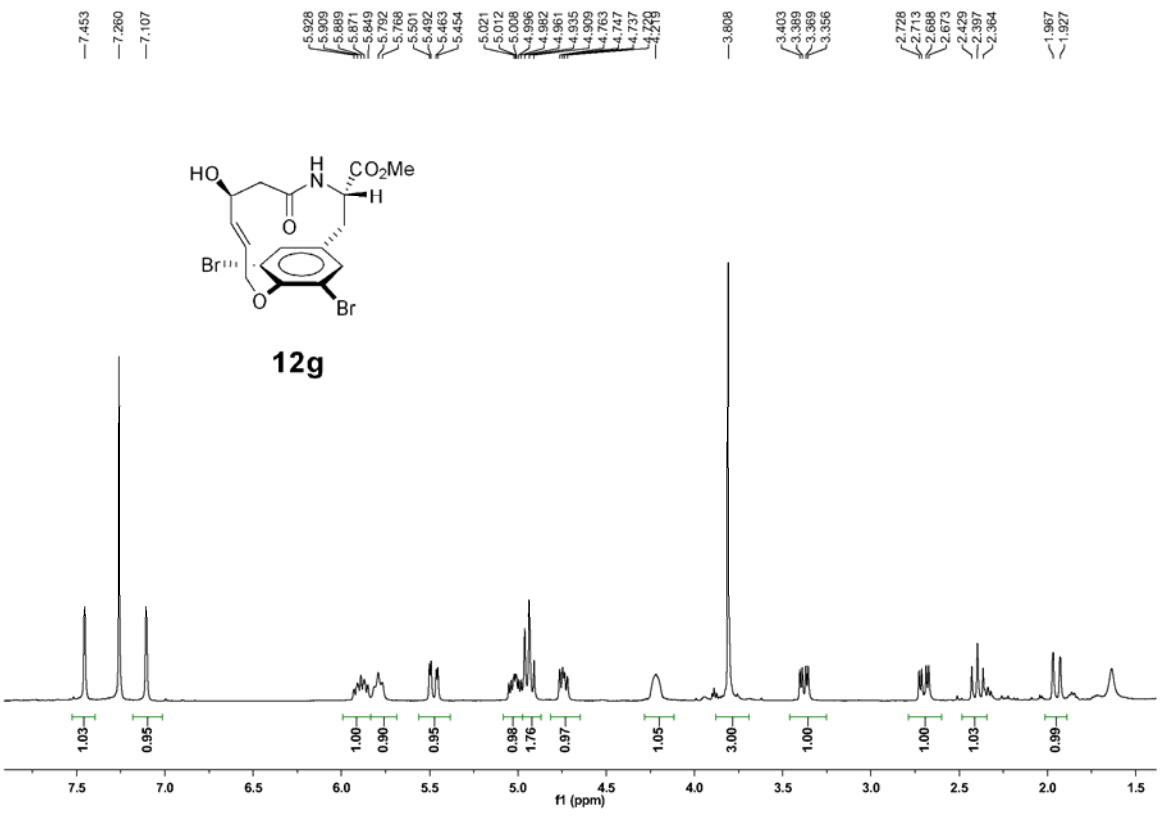
6.478
6.158
5.468
5.453
5.433
5.415
5.395
5.377
5.126
5.116
5.103
4.531
4.515
4.509
4.481
3.847
3.808
3.774
3.432
3.419
3.399
3.386
2.433
2.401
2.368
2.334
2.304
2.286
2.270
2.247
2.232
1.942
1.926
1.908
1.814
1.708
1.675
1.643
H
N
CO2Me
H
O
MeO
O
OMe
12f
1.05
0.97
2.02
1.97
2.04
2.98
3.17
3.11
1.00
1.99
1.09
1.13
1.18
f1 (ppm)


172.78
170.18
154.59
153.31
138.56
133.33
131.85
126.12
107.73
106.17
77.48
77.16
76.84
71.52
56.32
56.09
52.59
51.99
39.72
35.49
26.74
H
N
CO2Me
H
O
MeO
O
OMe
12f
f1 (ppm)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7.107
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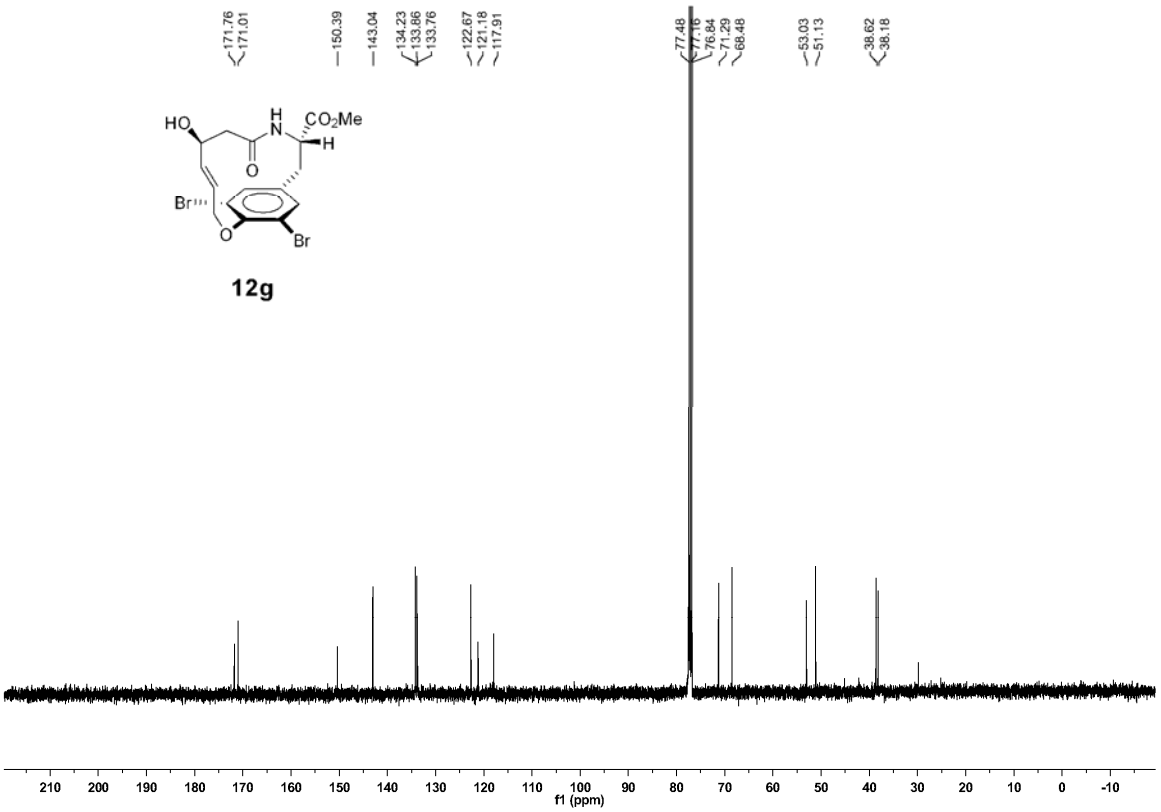
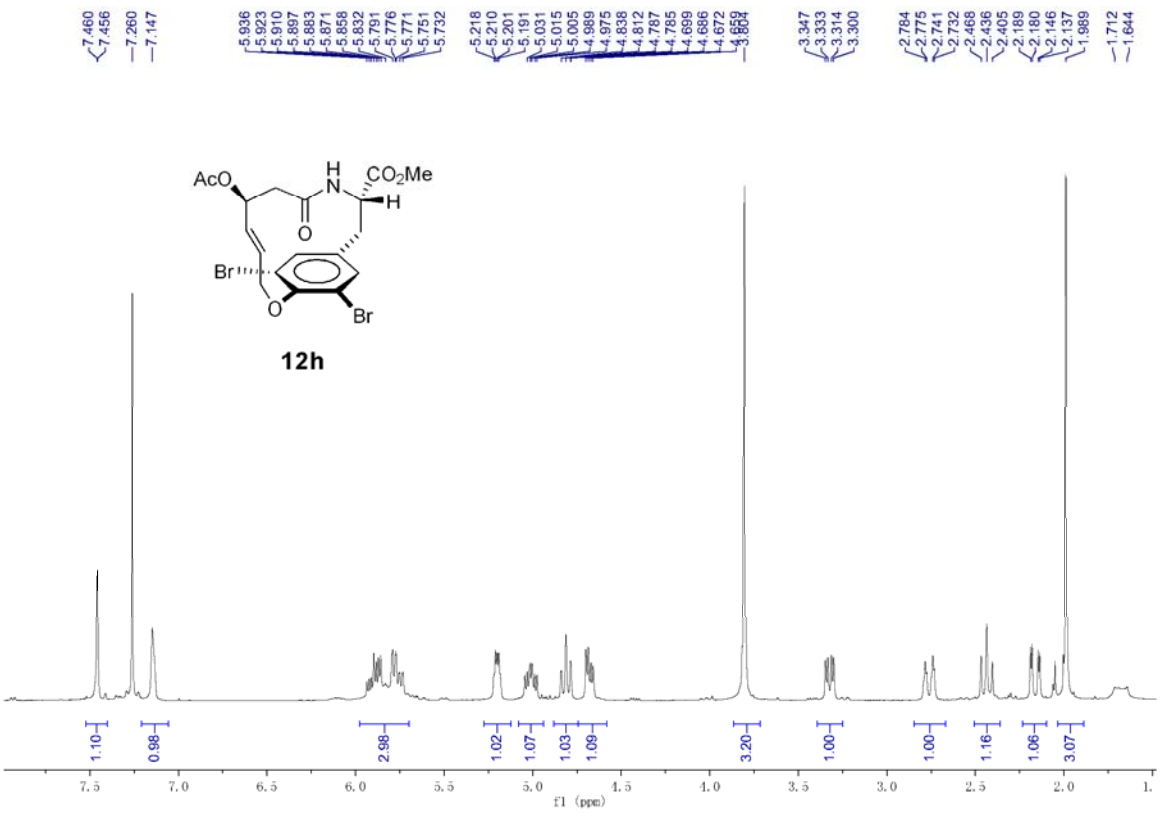
5.909
5.889
5.871
5.849
5.792
5.768
5.501
5.492
5.463
5.454
5.021
5.012
5.008
4.996
4.982
4.961
4.935
4.909
4.763
4.747
4.737
3.808
3.403
3.389
3.369
3.356
2.728
2.713
2.688
2.673
2.429
2.397
2.364
1.967
1.927
HO
H
N
CO2Me
H
O
Br
O
Br
12g
1.03
0.95
1.00
0.90
0.95
0.98
1.76
0.97
1.05
3.00
1.00
1.00
1.03
0.99
f1 (ppm)


171.76
171.01
150.39
143.04
134.23
133.86
133.76
122.67
121.18
117.91
77.48
77.16
76.84
71.29
68.48
53.03
51.13
38.62
38.18
HO
H
N
CO2Me
H
O
Br
O
Br
12g
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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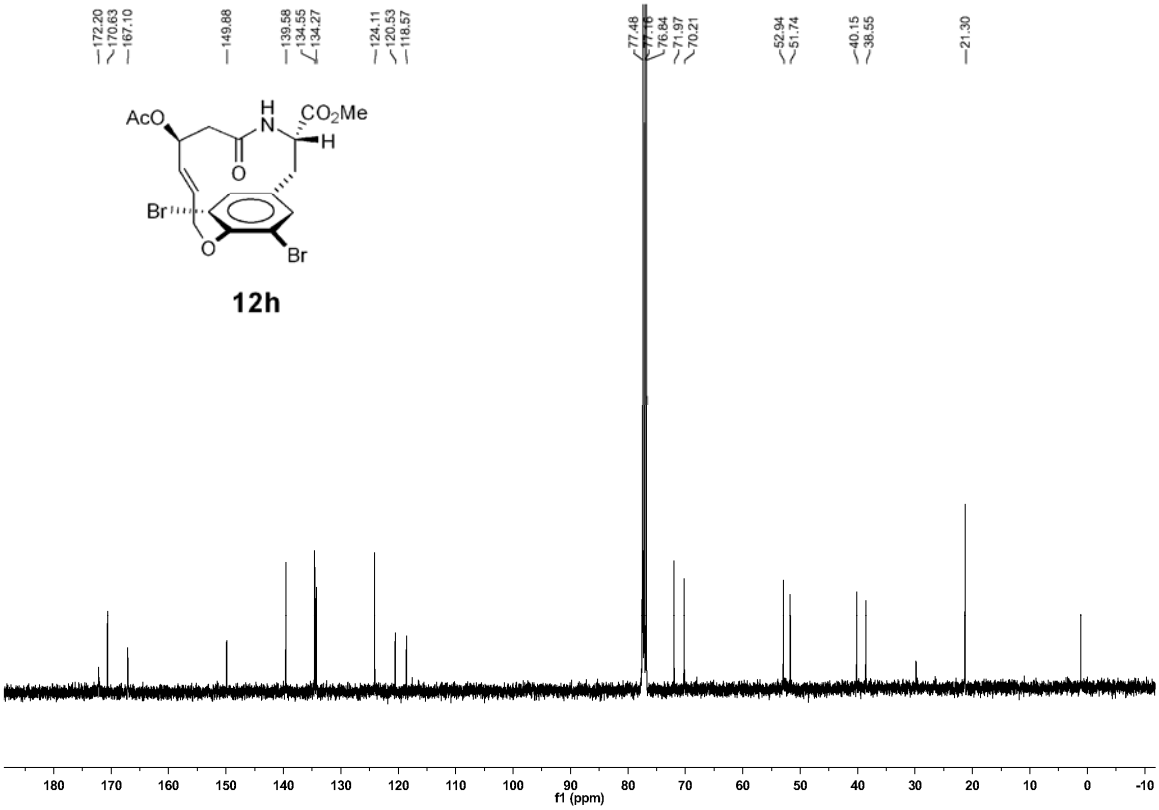
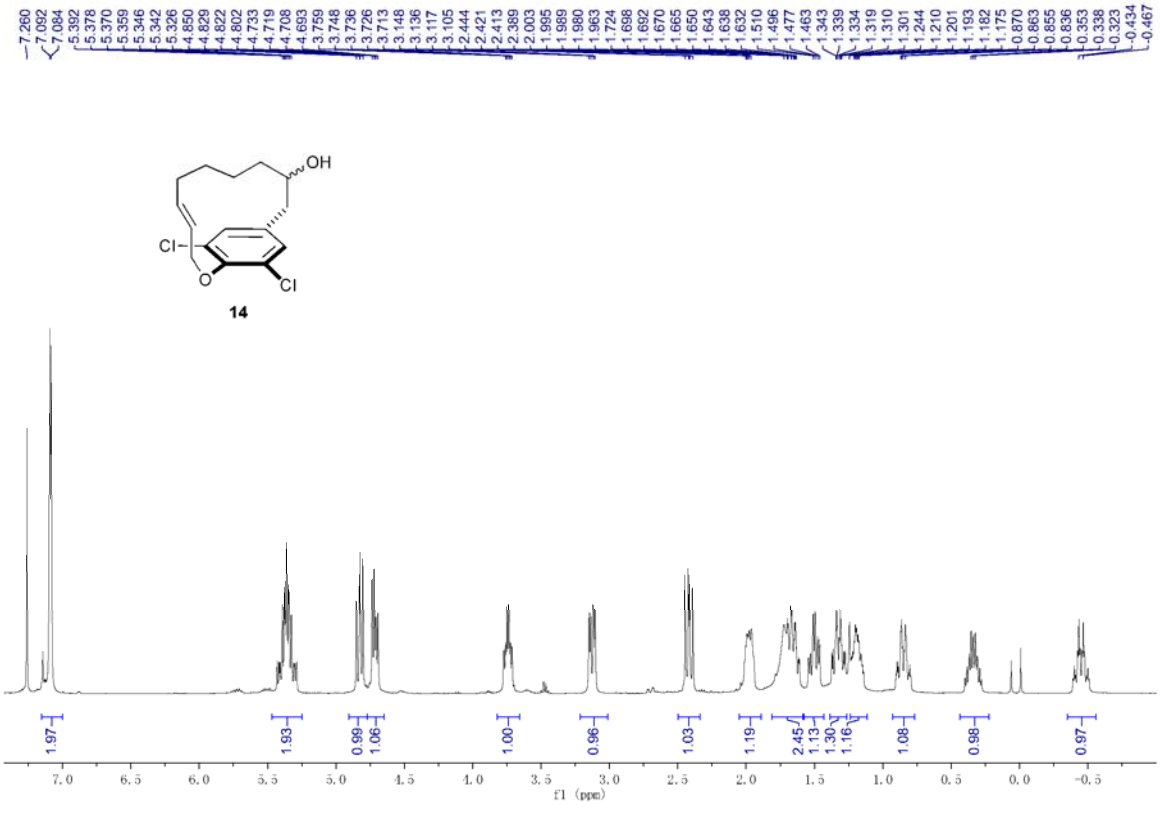
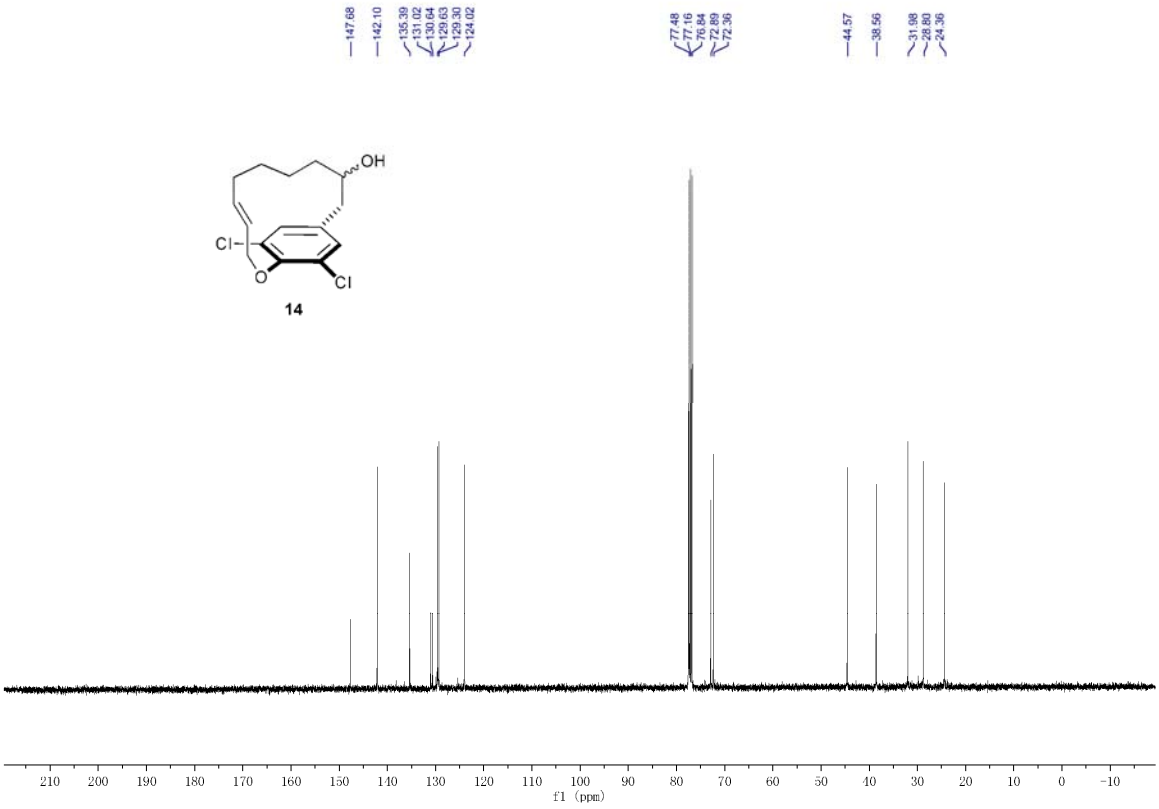
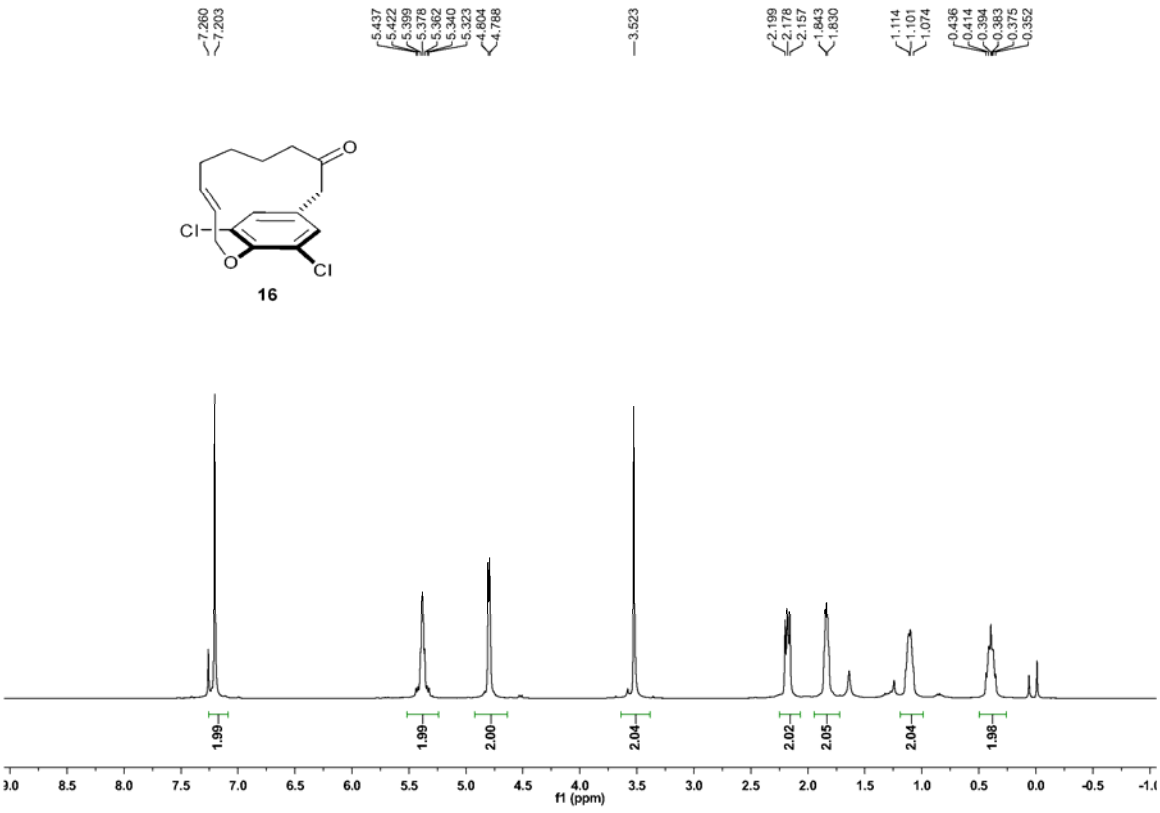
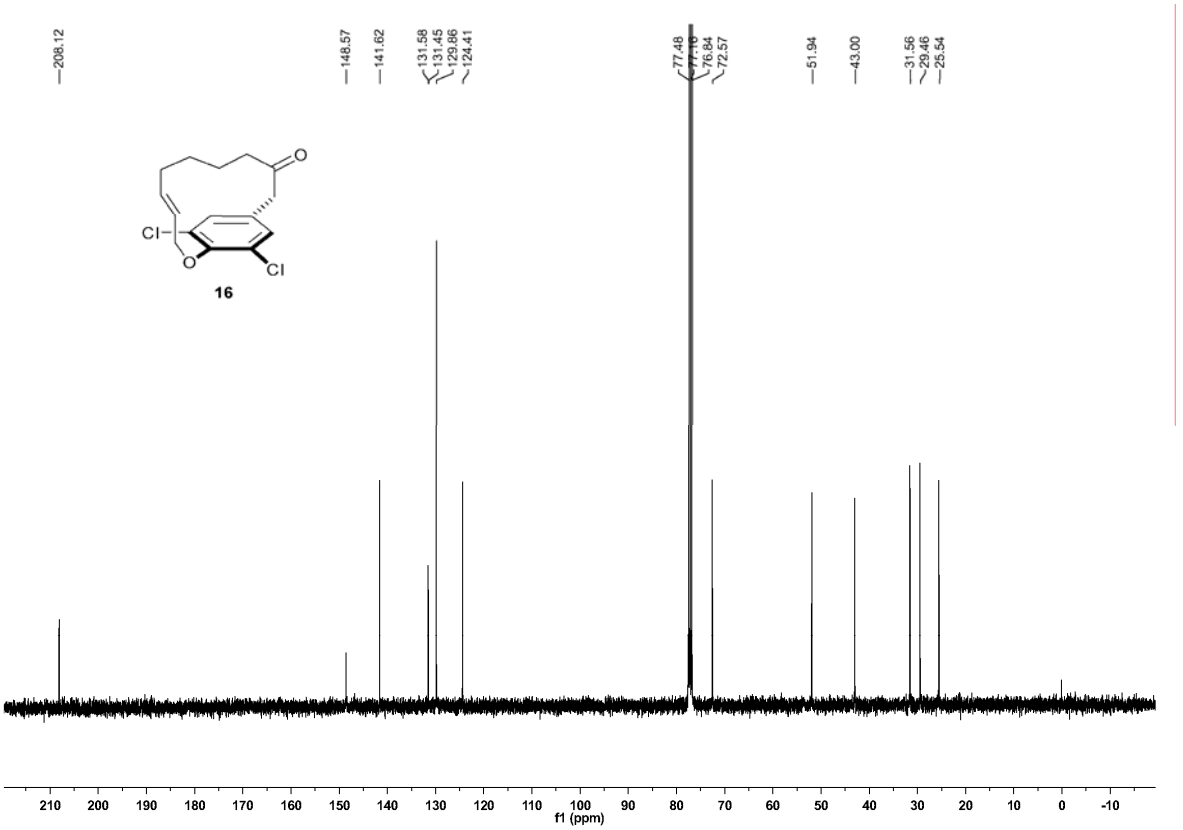
7.456
7.260
7.147
5.936
5.923
5.910
5.897
5.883
5.871
5.858
5.832
5.791
5.776
5.771
5.751
5.732
5.218
5.210
5.201
5.191
5.031
5.015
5.005
4.989
4.975
4.838
4.812
4.787
4.785
4.699
4.686
4.672
4.659
3.884
3.347
3.333
3.314
3.300
2.784
2.775
2.741
2.732
2.468
2.436
2.405
2.189
2.180
2.146
2.137
1.989
1.712
1.644
AcO
H
N
CO2Me
H
O
Br
O
Br
12h
1.10
0.98
2.98
1.02
1.07
1.03
1.09
3.20
1.00
1.00
1.16
1.06
3.07
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.
f1 (ppm)


172.20
170.63
167.10
149.88
139.58
134.55
134.27
124.11
120.53
118.57
77.48
77.16
76.84
71.97
70.21
52.94
51.74
40.15
38.55
21.30
AcO
H
N
CO2Me
H
O
Br
O
Br
12h
f1 (ppm)


OH
Cl
O
Cl
14
1.97
1.93
0.99
1.06
1.00
0.96
1.03
1.19
2.45
1.13
1.30
1.16
1.08
0.98
0.97
f1 (ppm)


147.68
142.10
135.39
131.02
130.64
129.63
129.30
124.02
77.48
77.16
76.84
72.89
72.36
44.57
38.56
31.98
28.80
24.36
OH
Cl
O
Cl
14
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.260
7.203
5.437
5.422
5.399
5.378
5.362
5.340
5.323
4.804
4.788
3.523
2.199
2.178
2.157
1.843
1.830
1.114
1.101
1.074
0.436
0.414
0.394
0.383
0.375
0.352
O
Cl
O
Cl
16
1.99
1.99
2.00
2.04
2.02
2.05
2.04
1.98
f1 (ppm)


208.12
148.57
141.62
131.58
131.45
129.86
124.41
77.48
77.16
76.84
72.57
51.94
43.00
31.56
29.46
25.54
Cl
O
Cl
O
16
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)