Dicyanopyrazine-derived push-pull chromophores for highly efficient photoredox catalysis

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Supporting Information

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1. General

Column chromatography was carried out with silica gel 60 (particle size 0.040-0.063 mm, 230-400 mesh) and commercially available solvents. Thin-layer chromatography (TLC) was conducted on aluminum sheets coated with silica gel 60 F254 with visualization by a UV lamp (254 or 360 nm). Melting points (m.p.) were measured in open capillaries and were uncorrected. ^{1}H and ^{13}C NMR spectra were recorded at 500 and 125 MHz at 25 °C with a Bruker AVANCE III 500 MHz instrument equipped with Prodigy CryoProbe or 400 and 100 MHz at 25 °C with a Bruker AVANCE III 400 MHz instrument. Chemical shifts are reported in ppm relative to the signal of Me_4Si. The residual solvent signal in the ^{1}H and ^{13}C NMR spectra was used as an internal reference ($CDCl_3$ 7.26 and 77.00 ppm). Apparent resonance multiplicities are described as s (singlet), d (doublet), dd (doublet of doublet), t (triplet) and m (multiplet). IR spectra were recorded as neat using HATR adapter on a Perkin-Elmer FTIR Spectrum BX spectrometer. High resolution MALDI MS spectra were measured on a MALDI mass spectrometer LTQ Orbitrap XL (Thermo Fisher Scientific, Bremen, Germany) equipped with nitrogen UV laser (337 nm, 60 Hz). The LTQ Orbitrap instrument was operated in positive-ion mode over a normal mass range (*m/z* 50−1500) with the following setting of tuning parameters: resolution 100,000 at *m/z* = 400, laser energy 17 mJ, number of laser shots 5, respectively. The survey crystal positioning system (survey CPS) was set for the random choice of shot position by automatic crystal recognition. The isolation width Δ*m/z* 4, normalised collision energy 25%, activation Q value 0.250, activation time 30 ms and helium as the collision gas were used for CID experiments in LTQ linear ion trap. The used matrix was 2,5-dihydroxybenzoic acid (DHB). Mass spectra were averaged over the whole MS record (30 s) for all measured samples. Elemental analyses were performed on an EA 1108 Fisons instrument. UV/Vis spectra were recorded on a Hewlett–Packard 8453 spectrophotometer in CH_2Cl_2. Electrochemical measurements were carried out by cyclic voltammetry (CV). The cyclic voltammetry was performed with an Autolab potentiostat by Echochemie under nitrogen atmosphere in a one-compartment electrolysis cell consisting of a platinum wire working electrode, a platinum wire counter electrode, and a quasi Ag/AgCl

reference electrode. Cyclic voltammograms were monitored at scan rates of either 100 mV s^{-1} or 50 mV s^{-1} and recorded in distilled dichloromethane. The concentration of the complex was maintained at 0.5 mM or less and each solution contained 0.1 M of tetrabutylammonium hexafluorophosphate (TBAP) as the electrolyte. The ferrocenium/ferrocene couple was used as the internal standard.

Starting materials such as DMPD, DAMN, 5,6-dichloropyrazine-2,3-dicarbonitrile, 2-methoxythiophene, diphenylethandione (benzil), 4,4'-difluorbenzil, 4,4'-dimethoxybenzil, 2,2'-thienil and furil are commercially available.

The tetrahydroisoquinoline derivatives and 5*H*-5-methyl-2-phenyl-2-oxazol-4-one **2f** were prepared according to the reported procedures.[1-2]

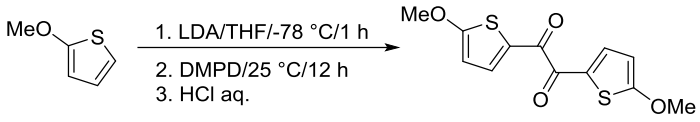
The fluorescent lamp is 9 W and blue LEDs are 4 W.

1. Shu, X.-Z., Yang, Y.-F., Xia, X.-F., Ji, K.-G., Liu, X.-Y. & Liang, Y.-M. Platinum-catalyzed cross-dehydrogenative coupling reaction in the absence of oxidant. *Org. Biomol. Chem.* **8**, 4077–4079 (2010).

2. Trost, B. M., Dogra, K. and Franzini, M. 5*H*-Oxazol-4-ones as building blocks for asymmetric synthesis of α-hydroxycarboxylic acid derivatives. *J. Am. Chem. Soc.***126**, 1944–1945 (2004).

2. Synthesis

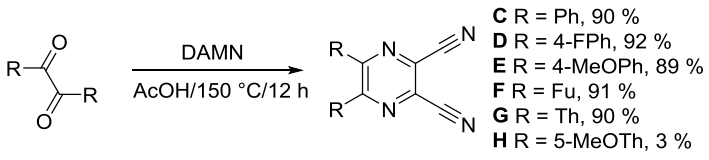
2.1. 1,2-Bis(5-methoxythiophen-2-yl)ethane-1,2-dione



A solution of 2-methoxythiophene (1.14 g; 0.01 mol) in dry THF (30 mL) was treated with lithium di*iso*propylamide (LDA, 7.5 mL; 0.015 mol; 2.0 M sol. in THF/heptane/ethylbenzene) at −78 ℃ under argon. The reaction mixture was stirred 1 h at −78 ℃ and subsequently transferred into a flask containing 1,4-dimethylpiperazine-2,3-dione (DMDP, 0.71 g; 0.005 mol) in dry THF (30 mL). The resulting reaction mixture was stirred for 12 h at 25 ℃ whereupon aq. HCl (5%; 50 mL) and CH_2Cl_2 (100 mL) were added. The organic phase was separated and the water layer was extracted with CH_2Cl_2 (2×100 mL). Combined organic extracts were dried (Na_2SO_4), filtered and the solvents were evaporated *in vacuo*. Crude product was purified by column chromatography (SiO_2; CH_2Cl_2/hexane 1:1 to 1:0) to afford title compound as yellow solid (0.81 g; 57%).

m.p.: 137−138 °C; TLC (SiO_2; CH_2Cl_2/hexane 1:1): RF = 0.1; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 3.99 p.p.m. (s, 6H), 6.32 (d, J = 4.4 Hz, 2H), 7.83 (d, J = 4.4 Hz, 2H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 60.9, 107.7, 138.8, 178.1, 181.6; HRMS (*m/z*): 283.0098 ($[M+H]^+$), $C_{12}H_{11}O_4^+$ requires 283.0093; Elemental analysis calcd (%) for $C_{12}H_{11}O_4$ (282.00): C 51.05, H 3.57, S 22.71; found: C 51.11, H 3.61, S 22.78.

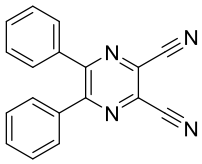
2.2. General method for the condensation reaction



1,2-Dicarbonyl compound (5.0 mmol) and diaminomaleonitrile (DAMN, 1.62 g; 15.0 mmol) were heated in glacial acetic acid (10 mL) in a sealed pressure tube at 150 ℃ for 5 h. The cold reaction mixture was diluted with water (100 mL) and extracted with CH_2Cl_2 (3×100 mL). The combined organic layers were washed with water (3×300 mL), dried (Na_2SO_4) and

the solvent was evaporated *in vacuo*. The resulting crude product was purified by filtration through a plug (SiO_2; CH_2Cl_2).

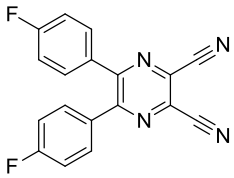
5,6-Diphenylpyrazine-2,3-dicarbonitrile (C)[3]



The title compound was prepared from benzil (1.05 g) following the general method for the condensation reaction. Yield 1.27 g (90 %) of an off-white solid.

m.p.: 251–252 ^{o}C; TLC (SiO_2; CH_2Cl_2): RF = 0.85; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.36 p.p.m. (t, J = 8.0 Hz, 4H), 7.46 (t, J = 8.0 Hz, 2H), 7.53 (d, J = 8.0 Hz, 4H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 113.2, 128.9, 129.8, 129.9, 131.2, 135.2, 155.4; IR (HATR): λ = 3054, 2231, 1512, 1376, 1202, 1071, 770, 700 cm^{-1}; HRMS (*m/z*): 283.0966 ([M+H]$^{+}$), $C_{18}H_{11}N_4^{+}$ requires 283.0978; Elemental analysis calcd (%) for $C_{18}H_{10}N_4$ (282.30): C 76.58, H 3.57, N 19.85; found: C 76.39, H 3.54, N 19.79.

5,6-Bis(4-fluorophenyl)pyrazine-2,3-dicarbonitrile (D)[4]



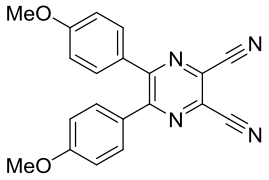
The title compound was prepared from 4,4'-difluorobenzil (1.23 g) following the general method for the condensation reaction. Yield 1.46 g (92 %) of an off-white solid.

m.p.: 197–198 ^{o}C; TLC (SiO_2; CH_2Cl_2/hexane 1:1): RF = 0.40; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.08 p.p.m. (t, J = 8.5 Hz, 4H), 7.54–7.57 (m, 4H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 113.2, 116.5, 116.7, 129.9, 131.3 (two peaks), 132.2, 132.3, 154.23, 163.6, 165.7; IR (HATR): λ = 3058, 2332, 1599, 1503, 1376, 1231, 964, 836 cm^{-1}; HRMS (*m/z*): 319.0780 ([M+H]$^{+}$), $C_{18}H_9F_2N_4^{+}$ requires 319.0789; Elemental analysis calcd (%) for $C_{18}H_8F_2N_4$ (318.28): C 69.93, H 2.53, F 11.94, N 17.60; found: C 70.05, H 2.49, F 11.84, N 17.77.

3. Khodaee, Z., Yahyazadeh, A., Mahmoodi, N. O., Zanjachi, M. A. & Azimi, V. One-pot synthesis and characterization of new cuprous pyrazinoporphyrazines containing peripherally functionalized units. *J. Mol. Struct.* **1029**, 92–97 (2012).

4. Keshtov, M. L., Keshtova, C. V., Begretov, M. M. & Tkhakakhov, R. B. Synthesis and reactivity of difluoroaromatic compounds containing heterocyclic central groups. *Russ. J. Gen. Chem.* **73**, 1476–1480 (2003).

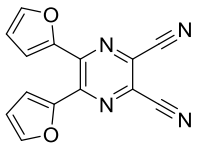
5,6-Bis(4-methoxyphenyl)pyrazine-2,3-dicarbonitrile (E)[5]



The title compound was prepared from 4,4'-dimethoxybenzil (1.35 g) following the general method for the condensation reaction. Yield 1.52 g (89 %) of a bright yellow solid.

m.p.: 190–191 °C; TLC (SiO_2; CH_2Cl_2): RF = 0.85; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 3.84 p.p.m. (s, 6H), 6.86 (d, J = 9.0 Hz, 4H), 7.53 (d, J = 9.0 Hz, 4H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 55.7, 113.6, 114.5, 127.9, 128.9, 131.6, 154.5, 162.2; IR (HATR): λ = 2961, 2231, 1603, 1500, 1376, 1255, 1174, 1014, 835 cm^{-1}; HRMS (*m/z*): 343.1190 ($[M+H]^+$), $C_{20}H_{15}N_4O_2^+$ requires 343.1190; Elemental analysis calcd (%) for $C_{20}H_{14}N_4O_2$ (342.35): C 70.17, H 4.12, N 16.37; found: C 70.26, H 4.15, N 16.38.

5,6-Di(furan-2-yl)pyrazine-2,3-dicarbonitrile (F)[6]



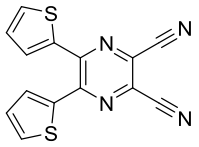
The title compound was prepared from furil (0.95 g) following the general method for the condensation reaction. Yield 1.19 g (91 %) of a yellow solid.

m.p.: 152–153 °C; TLC (SiO_2; CH_2Cl_2/hexane 1:1): RF = 0.50; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 6.65 (dd, J = 3.5, 2.0 Hz, 2H), 7.17 (d, J = 3.5 Hz, 2H), 7.65 (d, J = 2.0 Hz, 2H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 113.2, 113.4, 118.3, 128.5, 142.1, 146.9, 148.4; IR (HATR): λ = 3060, 2235, 1566, 1461, 1261, 1086, 851, 765, 751 cm^{-1}; HRMS (*m/z*): 263.0557 ($[M+H]^+$), $C_{14}H_7N_4O_2^+$ requires 263.0563; Elemental analysis calcd (%) for $C_{14}H_6N_4O_2$ (262.22): C 64.12, H 2.31, N 21.37; found: C 63.99, H 2.39, N 21.44.

5. Cristiano, R., Westphal, E., Bechtold, I. H., Bortoluzzi, A. J. & Gallardo, H. Synthesis and optical/thermal properties of low molecular mass V-shaped materials based on 2,3-dicyanopyrazine. *Tetrahedron* **63**, 2851–2858 (2007).

6. Mørkved, E. H., Ossletten, H., Kjøsen, H. & Bjørlo, O. Syntheses of octa(2-heteroaryl) azaphthalocyanines. *J. Prakt. Chem.* **342**, 83–86 (2000).

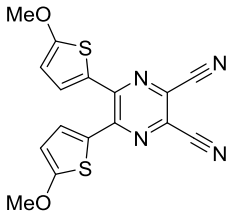
5,6-Di(thiophen-2-yl)pyrazine-2,3-dicarbonitrile (G)[7]



The title compound was prepared from 2,2'-thienil (1.11 g) following the general method for the condensation reaction. Yield 1.32 g (90 %) of a yellow fluorescent solid.

m.p.: 176–177 ^{o}C; TLC (SiO_2; CH_2Cl_2/hexane 1:1): RF = 0.35; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.07 p.p.m. (dd, J = 5.0, 4.0 Hz, 2H), 7.62 (d, J = 4.0 Hz, 2H), 7.64 (d, J = 5.0 Hz, 2H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 113.0, 128.2, 128.5, 131.5, 133.2, 138.0, 147.9; IR (HATR): λ = 3079, 2226, 1415, 1271, 1057, 844, 725 cm^{-1}; HRMS (*m/z*): 295.0109 ([M+H]$^{+}$), $C_{14}H_7N_4S_2^{+}$ requires 295.0107; Elemental analysis calcd (%) for $C_{14}H_6N_4S_2$ (294.35): C 57.12, H 2.05, N 19.03, S 21.79; found: C 57.40, H 2.09, N 19.11, S 21.87.

5,6-Bis(5-methoxythiophen-2-yl)pyrazine-2,3-dicarbonitrile (H)



The title compound was prepared from 1,2-bis(5-methoxythiophen-2-yl)ethane-1,2-dione (1.41 g) following the general method for the condensation reaction. Yield 5.0 mg (3 %) of an orange solid.

m.p. = 172–173 ^{o}C; TLC (SiO_2; CH_2Cl_2): RF = 0.80; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 3.99 p.p.m. (s, 6H), 6.18 (d, J = 5.5 Hz, 2H), 7.67 (d, J = 5.5 Hz, 2H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 60.8, 106.3, 113.7, 124.7, 126.3, 131.2, 146.7, 173.9; IR (HATR): λ = 3071, 2227, 1467, 1403, 1380, 1211, 1067, 986, 784 cm^{-1}; HRMS (*m/z*): 355.0317 ([M+H]$^{+}$), $C_{16}H_{11}N_4O_2S_2^{+}$ requires 355.0318; Elemental analysis calcd (%) for $C_{16}H_{10}N_4O_2S_2$ (354.41): C 54.22, H 2.84, N 15.81, S 18.10; found: C 54.33, H 2.90, N 15.82, S 18.05.

7. De Mori, G., Fu, Z., Viola, E., Cai, X., Ercolani, C., Donzello, M. P. & Kadish, K. M. Tetra-2,3-pyrazinoporphyrazines with externally appended thienyl rings: Synthesis, UV-visible spectra, electrochemical behavior, and photoactivity for the generation of singlet oxygen. *Inorg. Chem.* **50**, 8225–8237 (2011).

2.3. Cross-coupling reaction leading to catalyst H

5,6-Dichloropyrazine-2,3-dicarbonitrile (0.796 g; 4.0 mmol) and (5-methoxythiophen-2-yl)boronic acid pinacol ester[8] (1.968 g; 8.2 mmol) were dissolved in THF/water mixture (4:1; 120 mL). Argon was bubbled through the solution for 15 min whereupon $Pd_2(dba)_3$ (0.184 g; 0.20 mmol), SPhos (0.084 g; 0.20 mmol) and $CsCO_3$ (2.736 g; 8.4 mmol) were added and the reaction mixture was stirred at 65 °C for 6 h. The reaction was diluted with water (200 mL) and extracted with CH_2Cl_2 (3 × 200 mL). The combined organic extracts were dried (Na_2SO_4), the solvents were evaporated *in vacuo* and the residue was purified by filtration through a plug (SiO_2; CH_2Cl_2/hexane 1:2 to 2:1) and subsequent recrystallization from CH_2Cl_2/hexane. Yield 1.176 g (83%), orange solid. All spectral data were identical with those measured for the product prepared by the condensation reaction. It should also be noted that cross-coupling reaction gave none or very low yield of **H** if carried out with a different Pd precatalyst, phosphine or base. SPhos = [2',6'-dimethoxy-(1,1'-biphenyl)-2-yl]dicyclohexylphosphane.

8 Miyaura N.; Ishiyama T. Process for production of heteroaryl-type boron compounds with iridium catalyst. *Eur. Patent* EP1481978A1, p. 16 (2004).

3. Quantum chemical calculations

All calculations were carried out in Gaussian 09W (lit.[9]) package at the DFT level of theory. Initial geometry optimizations of molecules **C**-**H** were carried out by PM3 method implemented in program ArgusLab (lit.[10]) and subsequently by B3LYP method with 6-311G(2d,p) basis set. The final molecule geometries were gained by optimization using B3LYP with 6-311++G(2df,p) basis set. For compounds **F**–**H**, two stable conformers are anticipated with the oxygen and sulphur atoms of the heterocyclic pendants oriented **in** and **out** of the molecule plane of symmetry (further referred as **F**-**H**in and **F**-**H**out, Figure S2). The presence of both conformers has been confirmed by the geometry optimization of molecules having heterocyclic units variously arranged according to the molecule plane. The molecular energy, the energies of the HOMO and the LUMO and the ground state dipole moment were calculated by B3LYP with 6-311++G(2df,p) basis set with PCM (scrf=(solvent=dichloromethane), complete results are shown in Table S1.

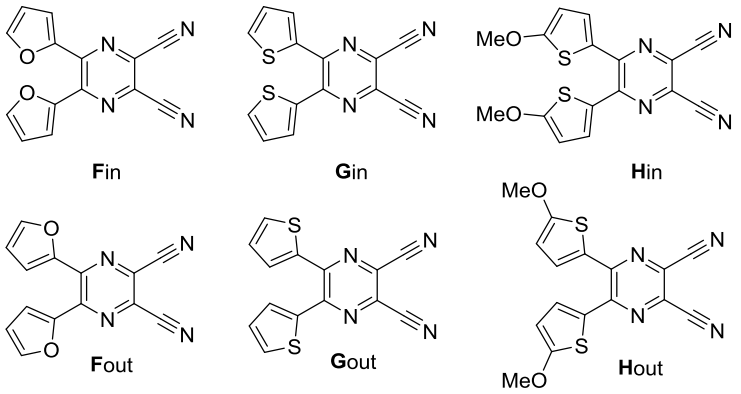


Fig. S2. Two possible arrangements (in/out) of the heterocyclic pendants in **F**-**H**.

9 Gaussian 09, Revision D.01, Frisch, M.J., Trucks, G. W., Schlegel, H. B., Scuseria, G. E., Robb, M. A., Cheeseman, J. R., Scalmani, G., Barone, V., Mennucci, B., Petersson, G. A., Nakatsuji, H., Caricato, M., Li, X., Hratchian, H. P., Izmaylov, A. F., Bloino, J., Zheng, G., Sonnenberg, J. L., Hada, M., Ehara, M., Toyota, K., Fukuda, R., Hasegawa, J., Ishida, M., Nakajima, T., Honda, Y., Kitao, O., Nakai, H., Vreven, T., Montgomery, J. A. Jr., Peralta, J. E., Ogliaro, F., Bearpark, M., Heyd, J. J., Brothers, E., Kudin, K. N., Staroverov, V. N., Keith, T., Kobayashi, R., Normand, J., Raghavachari, K., Rendell, A., Burant, J. C., Iyengar, S. S., Tomasi, J., Cossi, M., Rega, N., Millam, J. M., Klene, M., Knox, J. E., Cross, J. B., Bakken, V., Adamo, C., Jaramillo, J., Gomperts, R., Stratmann, R. E., Yazyev, O., Austin, A. J., Cammi, R., Pomelli, C., Ochterski, J. W., Martin, R. L., Morokuma, K., Zakrzewski, V. G., Voth, G. A., Salvador, P., Dannenberg, J. J., Dapprich, S., Daniels, A. D., Farkas, O., Foresman, J. B., Ortiz, J. V., Cioslowski, J. & D. J. Fox, Gaussian, Inc., Wallingford CT, 2013.

10 ArgusLab, Mark Thompson and Planaria Software LLC, Version 4.01, webpage: http://www.arguslab.com.

The energies of both **F**-**H**in and **F**-**H**out conformers are close which implies that none of them is theoretically preferred. On the contrary, large differences can be seen in the calculated energy gaps Eg^{DFT}, especially for molecules **F** and **H** bearing oxygen atoms. Figure S3 shows correlation of the calculated and electrochemically measured HOMO-LUMO gaps. The tightest correlation has been found for **F**-**H**out conformers which conform to the expected higher stabilization/solvation of the heteroatoms facing out of the molecular plane. The regression line passes the origin with the intercept = -0.165±0.238 and the slope = 1.108±0.071, which implies very good agreement of both theoretical and experimental data. The correlation of the electrochemical, calculated and optical gaps for molecules **C**-**H** are jointly showed in Figure S4 (for optical gap regression line: intercept = 0.020±0.148 and the slope = 0.973±0.044).

Table S1. DFT calculated data for DPZs **C**-**H**.

DP	E (eV)	E_{HOMO} (eV)	E_{LUMO} (eV)	Eg^{DFT} (eV)	μ (D)
C	–24793.599	–6.93	–3.00	3.93	11.38
D	–30196.236	–7.01	–3.09	3.92	7.43
E	–31028.327	–6.48	–2.90	3.58	10.80
Fin	–24673.071	–6.31	–3.14	3.17	12.55
Fout	–24672.817	–6.75	–3.21	3.54	12.69
Gin	–42250.661	–6.48	–3.10	3.38	11.90
Gout	–42250.582	–6.50	–3.13	3.37	12.88
Hin	–48485.214	–6.00	–2.91	3.09	14.34
Hout	–48485.433	–5.92	–2.95	2.97	18.26

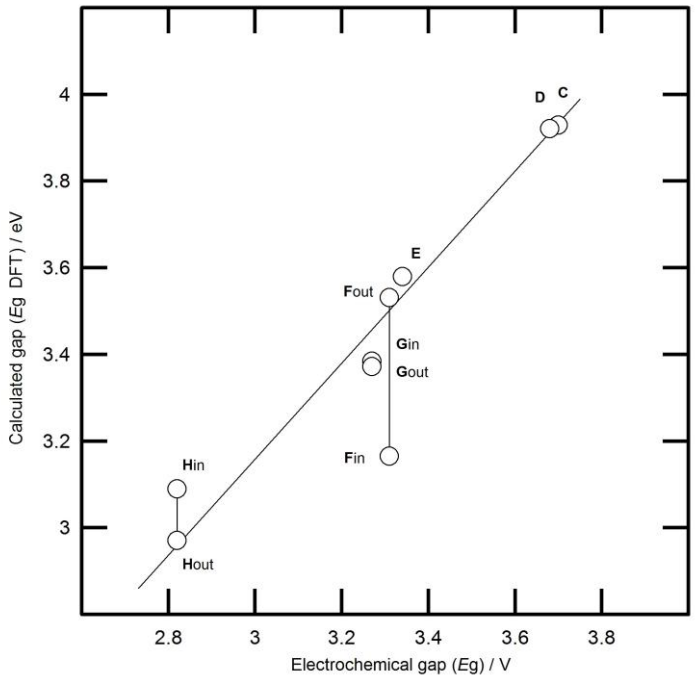


Fig. S3. Correlation of the electrochemical and calculated gaps *E*g including in and out conformers.

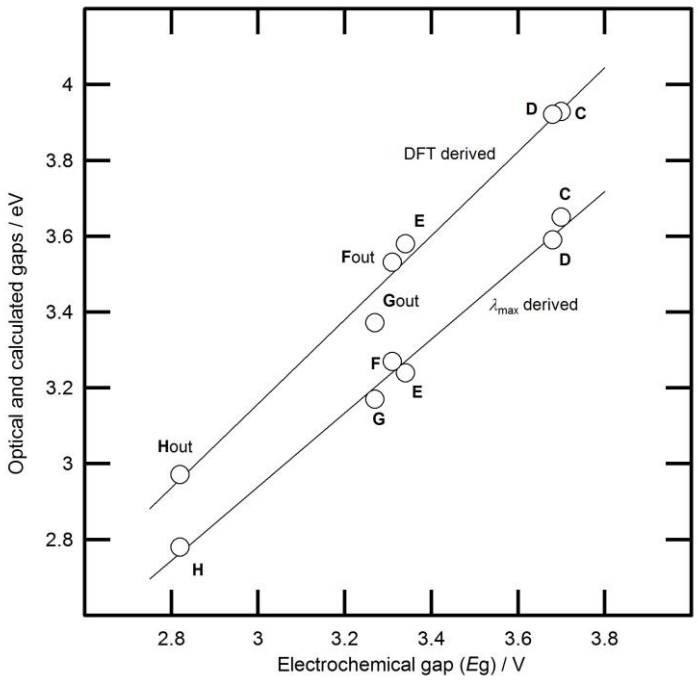


Fig. S4. Correlations of the electrochemical and calculated/optical gaps *E*g.

The HOMO and LUMO localizations in molecules **C**-**H** (Figures S5-S10) have been derived from the calculations using PM7 method implemented in MOPAC2012 program (lit.[11]). The visualizations have been performed in program OPchem.[12] For **H**, the HOMO and LUMO localizations have also been derived from Gaussian 09W program (Figure S11).

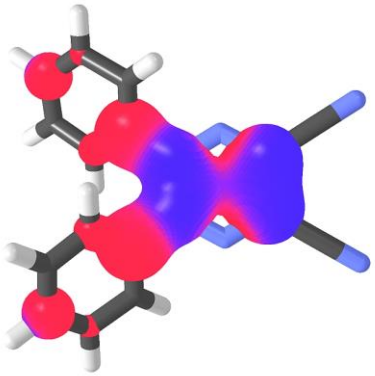


Fig. S5. HOMO (red) and LUMO (blue) localizations in molecule **C** (MOPAC2012).

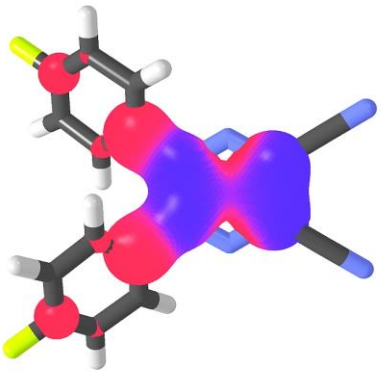


Fig. S6. HOMO (red) and LUMO (blue) localizations in molecule **D** (MOPAC2012).

11 MOPAC2012, J. J. P. Stewart, Stewart Computational Chemistry, version 13.084W, webpage: http://OpenMOPAC.net.

12 OPchem, O. Pytela, version 7.6, webpage: http://pytela.upce.cz/OPgm.

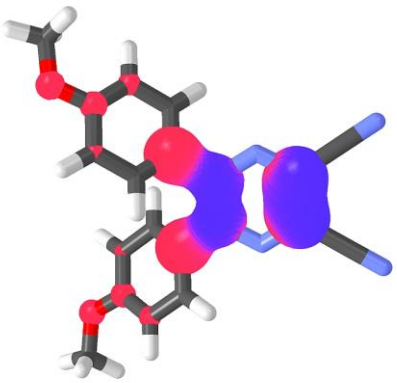


Fig. S7. HOMO (red) and LUMO (blue) localizations in molecule **E** (MOPAC2012).

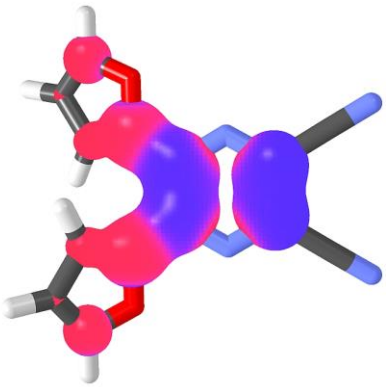


Fig. S8. HOMO (red) and LUMO (blue) localizations in molecule **F** (MOPAC2012).

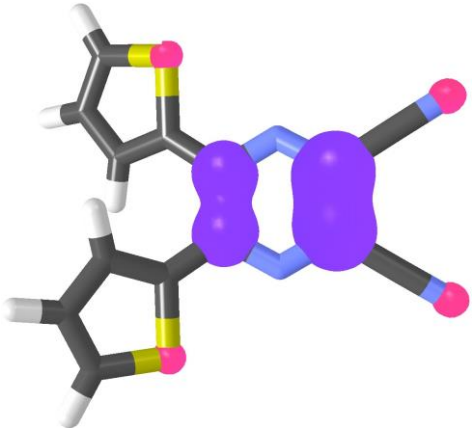


Fig. S9. HOMO (red) and LUMO (blue) localizations in molecule **G** (MOPAC2012).

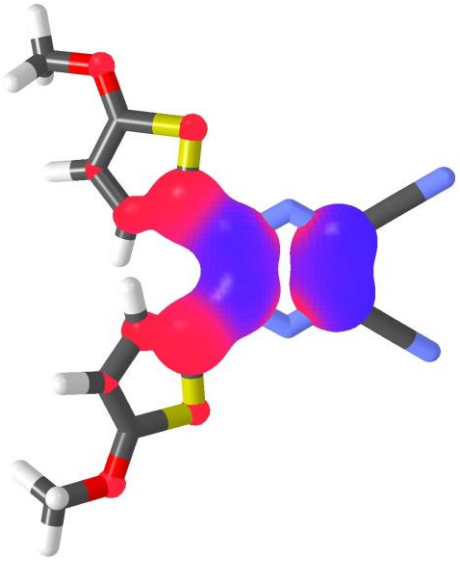


Fig. S10. HOMO (red) and LUMO (blue) localizations in molecule **H** (MOPAC2012).

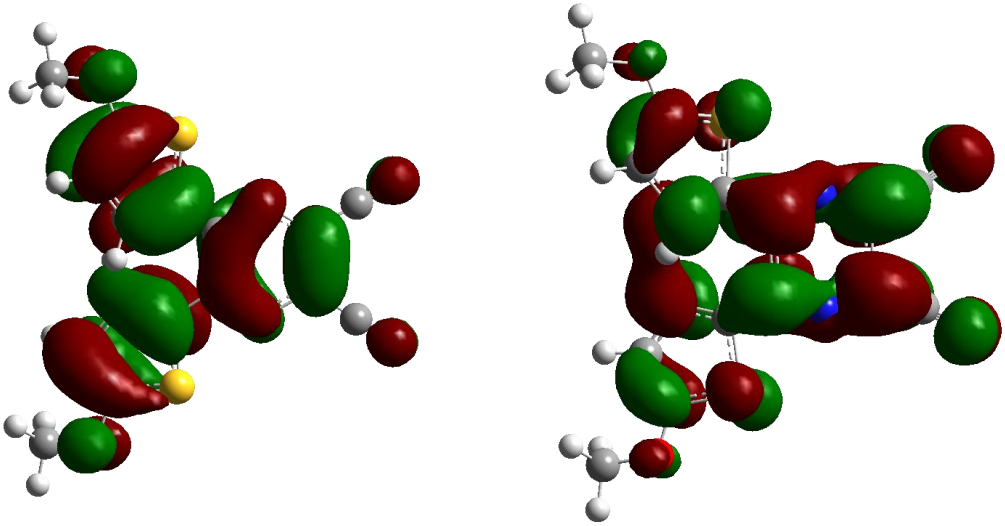


Fig. S11. HOMO (left) and LUMO (right) localizations in molecule **H** (Gaussian 09W).

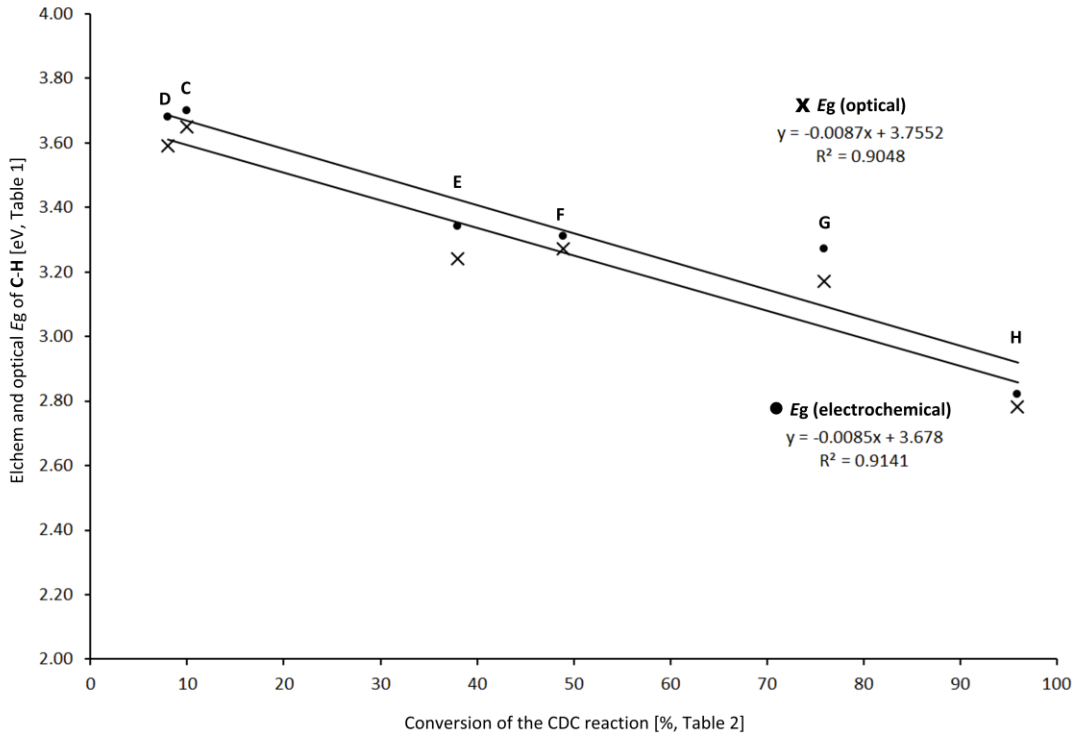


Fig. S12. Correlation of the CDC reaction conversion and the electrochemical and optical HOMO-LUMO gaps *E*g.

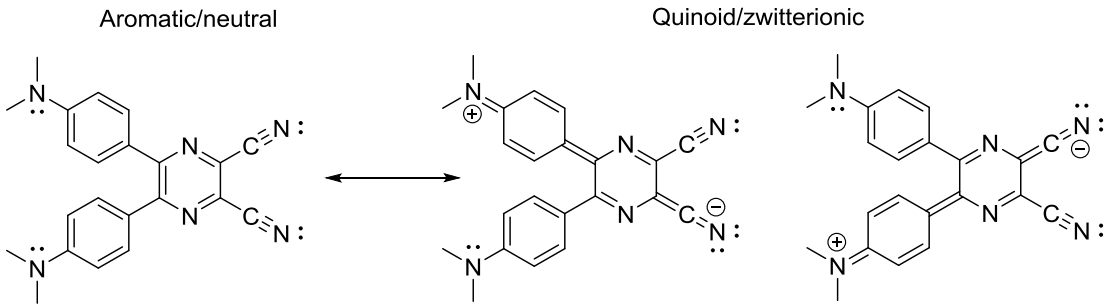
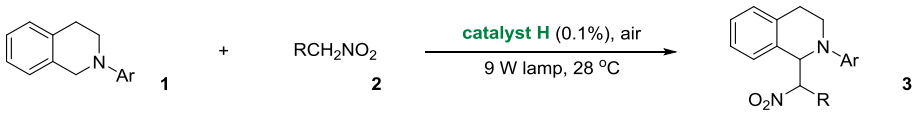


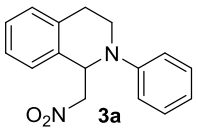
Fig. S13. Limiting resonance form of DPZ derivative **A**.

4. Experimental procedures for photoredox catalyzed reactions and characterization data of products

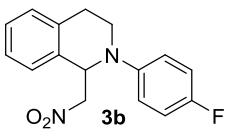
➢ General procedure for dehydrogenative nitro-Mannich reactions to prepare 3a–3h



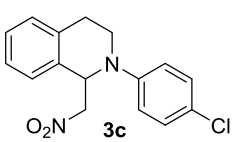
In a 10 mL snap vial equipped with a magnetic stirring bar, the tetrahydroisoquinoline derivative (0.15 mmol) was dissolved into nitroalkanes (1.5 mL), and then a solution of photocatalyst **H** (0.15 μmol, 21 μL) in the same nitroalkane (2.5 mg/mL) was added. The reaction mixture was stirred under irradiation by 9 W fluorescent lamp at 28 ^{o}C (temperature was maintained in a incubator) from 5 cm distance. After 5 hours, the solvent was removed *in vacuo* and the residue was purified by flash chromatography on silica gel using petroleum ether (PE) /ethyl acetate (EA) as eluent to obtain the pure products.



Pale yellow oil; 95% yield; TLC (PE/EA 10:1): RF = 0.75; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.33–7.29 p.p.m. (m, 2H), 7.28–7.26 (m, 1H), 7.24–7.21 (m, 2H), 7.16 (d, *J* = 7.0 Hz, 1H), 7.02 (d, *J* = 8.1 Hz, 2H), 6.88 (t, *J* = 7.3 Hz, 1H), 5.58 (t, *J* = 7.2 Hz, 1H), 4.90 (dd, *J* = 11.8, 7.9 Hz, 1H), 4.59 (dd, *J* = 11.8, 6.6 Hz, 1H), 3.73–3.61 (m, 2H), 3.16–3.08 (m, 1H), 2.82 (dt, *J* = 16.3, 4.9 Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 148.4, 135.2, 132.8, 129.5, 129.2, 128.1, 127.0, 126.6, 119.4, 115.0, 78.7, 58.2, 42.0, 26.4; HRMS (ESI) *m/z* 269.1283 ($M+H^+$), calc. for $C_{16}H_{17}N_2O_2$ 269.1290.

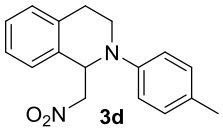


Pale yellow oil; 95% yield; TLC (PE/EA 10:1): RF = 0.4; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.29–7.14 p.p.m. (m, 4H), 6.98–6.89 (m, 4H), 5.43 (dd, *J* = 8.6, 5.9 Hz, 1H), 4.84 (dd, *J* = 12.0, 8.6 Hz, 1H), 4.58 (dd, *J* = 12.0, 5.9 Hz, 1H), 3.60 (dd, *J* = 9.2, 4.4 Hz, 2H), 3.07–2.99 (m, 1H), 2.73 (dt, *J* = 16.5, 4.2 Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 158.3, 156.0, 145.3, 145.3, 135.2, 132.5, 129.4, 128.1, 126.9, 126.7, 118.0, 117.9, 115.9, 115.7, 78.8, 58.7, 42.8, 25.8; ^{19}F-NMR (376 MHz, $CDCl_3$) δ -124.27; HRMS (ESI) *m/z* 287.1184 ($M+H^+$), calc. for $C_{16}H_{16}N_2O_2F$ 287.1196.

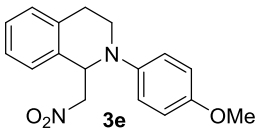


Pale yellow oil; 92% yield; TLC (PE/EA 10:1): RF = 0.4; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.27–7.18 p.p.m. (m, 5H), 7.1–7.13 (m, 1H),

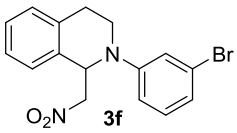
6.91–6.87 (m, 2H), 5.49 (t, *J* = 7.6, 1H), 4.85 (dd, *J* = 12.0, 8.2 Hz, 1H), 4.57 (dd, *J* = 12.0, 6.3 Hz, 1H), 3.67–3.57 (m, 2H), 3.11–3.03 (m, 1H), 2.78 (dt, *J* = 16.4, 4.8 Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 147.1, 135.0, 132.5, 129.3, 129.3, 128.2, 126.9, 126.8, 124.4, 116.5, 78.6, 58.2, 42.2, 26.2; HRMS (ESI) *m/z* 303.0896 ($M+H^+$), calc. for $C_{16}H_{15}N_2O_2Cl$ 303.0900.



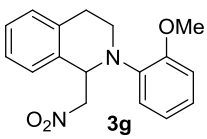
Pale yellow oil; 91% yield; TLC (PE/EA 10:1): RF = 0.4; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.25–7.13 p.p.m. (m, 4H), 7.08 (d, *J* = 8.3 Hz, 2H), 6.89 (d, *J* = 8.6 Hz, 2H), 5.50 (t, *J* = 7.3, 1H), 4.86 (dd, *J* = 11.8, 8.1 Hz, 1H), 4.56 (dd, *J* = 11.8, 6.3 Hz, 1H), 3.68–3.55 (m, 2H), 3.11–3.03 (m, 1H), 2.76 (dt, *J* = 16.4, 4.5 Hz, 1H), 2.27 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 146.4, 135.3, 133.0, 130.0, 129.2, 129.1, 128.0, 126.9, 126.6, 115.9, 78.8, 58.4, 42.3, 26.2, 20.3; HRMS (ESI) *m/z* 283.1448 ($M+H^+$), calc. for $C_{17}H_{19}N_2O_2$ 283.1447.



Pale yellow oil; 93% yield; TLC (PE/EA 10:1): RF = 0.3; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.25–7.20 p.p.m. (m, 2H), 7.18–7.14 (m, 2H), 6.95–6.90 (m, 2H), 6.83–6.80 (m, 2H), 5.40 (dd, *J* = 8.6, 5.8 Hz, 1H), 4.83 (dd, *J* = 11.9, 8.6 Hz, 1H), 4.57 (dd, *J* = 11.9, 5.8 Hz, 1H), 3.76 (s, 3H), 3.59–3.55 (m, 2H), 3.02 (ddd, *J* = 16.2, 9.2, 6.7 Hz, 1H), 2.70 (dt, *J* = 16.5, 3.9 Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 154.0, 143.0, 135.4, 132.9, 129.4, 127.8, 126.9, 126.6, 118.8, 114.7, 78.9, 58.9, 55.5, 43.1; HRMS (ESI) *m/z* 299.1395 ($M+H^+$), calc. for $C_{17}H_{19}N_2O_3$ 299.1396.

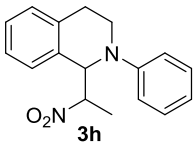


Pale yellow oil; 87% yield; TLC (PE/EA 10:1): RF = 0.3; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.27–7.19 p.p.m. (m, 3H), 7.15–7.09 (m, 3H), 6.97–6.95 (m, 1H), 6.91 (dd, *J* = 8.4, 2.4 Hz, 1H), 5.52 (t, *J* = 7.3, 1H), 4.85 (dd, *J* = 12.0, 7.9 Hz, 1H), 4.57 (dd, *J* = 12.0, 6.6 Hz, 1H), 3.68–3.58 (m, 2H), 3.13–3.05 (m, 1H), 2.81 (dt, *J* = 16.4, 5.1 Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 149.6, 135.0, 132.4, 130.7, 129.2, 128.3, 127.0, 126.8, 123.6, 122.1, 117.7, 113.3, 78.6, 57.9, 42.0, 26.4; HRMS (ESI) *m/z* 347.0392 ($M+H^+$), calc. for $C_{16}H_{16}N_2O_2Br$ 347.0395.



Pale yellow oil; 88% yield; TLC (PE/EA 10:1): RF = 0.3; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.29–7.25 p.p.m. (m, 2H), 7.18–7.17 (m, 2H), 7.08–7.03 (m, 1H), 6.93–6.84 (m, 3H), 5.53 (dd, *J* = 8.4, 5.0 Hz, 1H), 4.85 (dd, *J* =

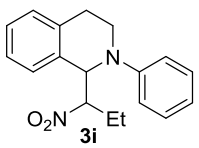
12.1, 8.4 Hz, 1H), 4.56 (dd, *J* = 12.1, 5.0 Hz, 1H), 3.85 (s, 3H), 3.63 (ddd, *J* = 13.3, 6.2, 1.5 Hz, 1H), 3.51 (ddd, *J* = 13.4, 11.4, 4.1 Hz, 1H), 3.02 (ddd, *J* = 17.1, 11.3, 6.1 Hz, 1H), 2.77–2.71 (m, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 153.1, 138.9, 135.3, 133.6, 129.5, 127.5, 126.8, 126.4, 124.1, 121.9, 121.0, 112.4, 79.1, 58.1, 55.7, 42.9, 26.8; HRMS (ESI) *m/z* 299.1391 ($M+H^+$), calc. for $C_{17}H_{19}N_2O_3$ 299.1396.



Pale yellow oil; 92% yield; dr = 1.6:1; TLC (PE/EA 10:1): RF = 0.4; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.29–7.19 p.p.m. (m, 3H), 7.17–7.14 (m, 2H), 7.12–7.09 (m, 1H), 7.01–6.97 (m, 2H), 6.84–6.79 (m, 1H), 5.24 (t, *J* = 9.0 Hz, 1H), 5.08–5.01 (m, 0.6H), 4.92–4.84 (m, 0.4H), 3.83 (ddd, *J* = 13.5, 8.2, 5.6 Hz, 0.6H), 3.62–3.51 (m, 1.4H), 3.05 (dt, *J* = 14.2, 7.0 Hz, 1H), 2.94–2.83 (m, 1H), 1.69 (d, *J* = 6.8 Hz, 1H), 1.53 (d, *J* = 6.6 Hz, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 149.2, 148.9, 135.6, 134.8, 133.8, 132.0, 129.4, 129.3, 129.1, 128.7, 128.3, 128.2, 127.2, 126.6, 126.1, 119.3, 118.8, 115.4, 114.5, 88.9, 85.4, 62.7, 61.1, 43.5, 42.7, 26.7, 26.4, 17.4, 16.4; HRMS (ESI) *m/z* 283.1451 ($M+H^+$), calc. For $C_{17}H_{19}N_2O_2$ 283.1447.

- **Synthetic procedure for 3i**

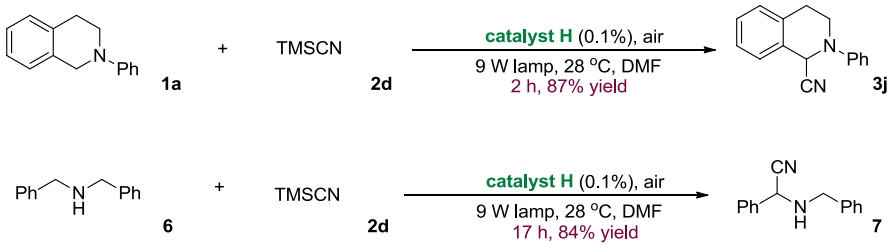
In a 10 mL snap vial equipped with a magnetic stirring bar **1a** (0.15 mmol) was dissolved in DMF (1.5 mL), then 2-nitropropane (1.5 mmol) and a solution of photocatalyst **H** (0.15 μmol, 21 μL) in DMF (2.5 mg/mL) were added. The reaction mixture was stirred under irradiation by 9 W fluorescent lamp at 28 ^{o}C (temperature was maintained in a incubator) from 5 cm distance. After the reaction was completed (monitored by TLC), the mixture was transferred to a separating funnel, diluted with ethyl acetate and washed with water. The aqueous phase was extracted three times with ethyl acetate (3×20 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. Purification of the crude product was achieved by flash column chromatography using petroleum ether /ethyl acetate as eluent to obtain a yellow oil.



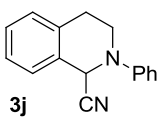
Pale yellow oil; 90% yield; dr = 1.6:1; TLC (PE/EA 10:1): RF = 0.4; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.31–7.14 p.p.m. (m, 6H), 7.00–6.93 (m, 2H), 6.84–6.77 (m, 1H), 5.24 (d, *J* = 9.3 Hz, 0.4H), 5.13 (d, *J* = 9.6 Hz,

0.6H), 4.87 (ddd, *J* = 11.7, 9.6, 3.1 Hz, 0.6H), 4.68 (ddd, *J* = 11.5, 9.3, 3.2 Hz, 0.4H), 3.87–3.82 (m, 0.4H), 3.70–3.49 (m, 1.6H), 3.07 (ddd, *J* = 11.9, 9.7, 6.4 Hz, 1H), 2.96–2.84 (m, 1H), 2.27–2.05 (m, 1.6H), 1.86–1.78 (m, 0.4H), 0.96–0.92 (m, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 149.1, 149.0, 135.6, 134.7, 133.9, 132.6, 129.4, 129.3, 129.2, 128.7, 128.6, 128.2, 128.1, 127.2, 126.6, 125.9, 119.4, 118.6, 115.8, 114.1, 96.1, 93.0, 62.2, 60.7, 43.5, 42.3, 26.8, 25.7, 25.0, 24.6, 10.7; HRMS (ESI) *m/z* 297.1603 ($M+H^+$), calc. for $C_{18}H_{21}N_2O_2$ 297.1603.

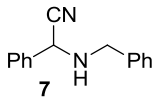
Experimental procedure for the preparation of adducts 3j and 7



In a 10 mL snap vial equipped with a magnetic stirring bar, **1a/6** (0.15 mmol) was dissolved into DMF (1.5 mL). Then TMSCN (0.75 mmol) and a solution of photocatalyst **H** (0.15 μmol) in DMF (2.5 mg/ mL, 21 μL) was added. The reaction mixture was stirred under irradiation by 9 W fluorescent lamp at 28 °C (temperature was maintained in a incubator) from 5 cm distance. After the reaction was completed (monitored by TLC), the mixture was transferred to a separating funnel, diluted with ethyl acetate and washed with water. The aqueous phase was extracted three times with ethyl acetate (3×20 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. Purification of the crude product was achieved by flash column chromatography using petroleum ether /ethyl acetate as eluent to obtain the pure products (**3j** or **7**).



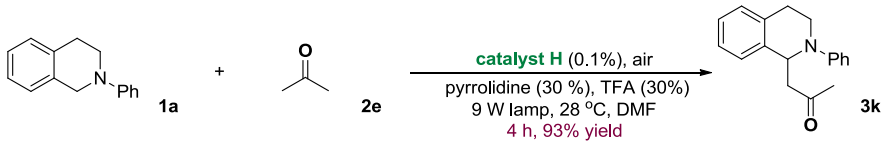
Pale yellow oil; 87% yield; TLC (PE/EA 10:1): RF = 0.4; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.38 p.p.m. (t, *J* = 8.0 Hz, 2H), 7.33–7.24 (m, 4H), 7.11–7.07 (m, 2H), 7.03 (t, *J* = 7.4 Hz, 1H), 5.53 (s, 1H), 3.79 (ddd, *J* = 11.5, 5.5, 2.5 Hz, 1H), 3.49 (ddd, *J* = 12.4, 10.9, 4.0 Hz, 1H), 3.17 (ddd, *J* = 16.7, 10.8, 6.0 Hz, 1H), 2.98 (dt, *J* = 16.3, 3.5 Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 148.3, 134.6, 129.5, 129.5, 129.3, 128.7, 127.0, 126.8, 121.9, 117.7, 117.6, 53.2, 44.1, 28.5; HRMS (ESI) *m/z* 257.1062 ($M+Na^+$), calc. for $C_{16}H_{14}N_2Na$ 257.1055.



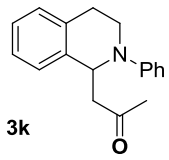
7

Pale yellow oil; 84% yield; TLC (PE/EA 5:1): RF = 0.5; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.56–7.53 p.p.m. (m, 2H), 7.44–7.34 (m, 7H), 7.32–7.28 (m, 1H), 4.76 (s, 1H), 4.08 (d, J = 13.0 Hz, 1H), 3.97 (d, J = 13.0 Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 138.1, 134.7, 129.0, 129.0, 128.63, 128.4, 127.6, 127.3, 118.7, 53.4, 51.3; HRMS (ESI) *m/z* 257.1062 ($M+Na^+$), calc. for $C_{16}H_{14}N_2Na$ 257.1055.

- **Synthetic procedure for the preparation of 3k**



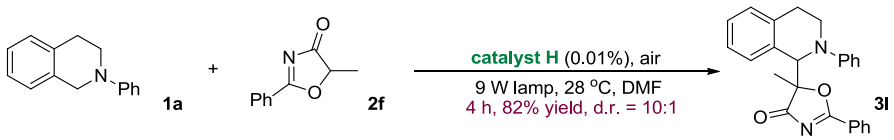
In a 10 mL snap vial equipped with a magnetic stirring bar, **1a** (0.15 mmol) was dissolved into DMF (1.5 mL), followed by the addition of acetone (1.5 mmol), pyrrolidine (0.045 mmol) and TFA (0.045 mmol). Then a solution of photocatalyst **H** (0.15 μmol, 21 μL) in DMF (2.5 mg/mL) was added. The reaction mixture was stirred under irradiation by 9 W fluorescent lamp at 28 ^{o}C (temperature was maintained in a incubator) from 5 cm distance. After the reaction was completed (monitored by TLC), the mixture was transferred to a separating funnel, diluted with ethyl acetate and washed with water. The aqueous phase was extracted three times with ethyl acetate (3×20 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. Purification of the crude product was achieved by flash column chromatography using petroleum ether /ethyl acetate as eluent to obtain **3k** as a yellow solid in 93% yield.



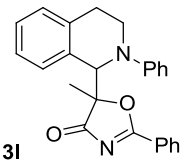
3k

Yellow solid; m.p. = 79.0–80.9 ^{o}C; 93% yield; TLC (PE/EA 10:1): RF = 0.4; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.27–7.22 p.p.m. (m, 2H), 7.19–7.11 (m, 4H), 6.93 (d, J = 8.0 Hz, 2H), 6.77 (t, J = 7.3 Hz, 1H), 5.40 (t, J = 6.4 Hz, 1H), 3.65 (dt, J = 12.4, 5.3 Hz, 1H), 3.56–3.47 (m, 1H), 3.09–3.01 (m, 2H), 2.85–2.79 (m, 2H), 2.07 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 207.2, 148.9, 138.3, 134.4, 129.3, 128.7, 126.8, 126.9, 126.3, 118.3, 114.8, 54.8, 50.2, 42.0, 31.0, 27.2; HRMS (ESI) *m/z* 266.1537 ($M+H^+$), calc. for $C_{18}H_{20}NO$ 266.1545.

- **Synthetic procedure for the preparation of 3l**

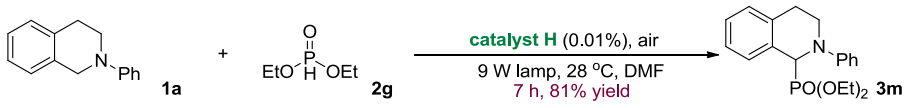


In a 10 mL snap vial equipped with a magnetic stirring bar, **1a** (0.30 mmol) was dissolved into DMF (1.0 mL), then 5*H*-5-methyl-2-phenyl-2-oxazol-4-one **2f** (0.10 mmol) and a solution of photocatalyst **H** (0.01 μmol, 14 μL) in DMF (2.5 mg/ 10 mL) were added. The reaction mixture was stirred under irradiation by 9 W fluorescent lamp at 28 ^{o}C (temperature was maintained in a incubator) from 5 cm distance. After the reaction was completed (monitored by TLC), the mixture was transferred to a separating funnel, diluted with ethyl acetate and washed with water. The aqueous phase was extracted three times with ethyl acetate (3×20 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. Purification of the crude product was achieved by flash column chromatography using petroleum ether /ethyl acetate as eluent to obtain **3l** as a yellow solid in 82% yield.



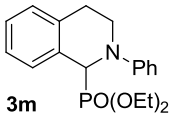
Yellow solid; 82% yield; m.p. = 153.1–154.8 ^{o}C; dr = 10:1; TLC (PE/EA 5:1): RF = 0.4; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.89 p.p.m. (dd, J = 8.3, 1.2 Hz, 2H), 7.62–7.57 (m, 1H), 7.41 (t, J = 7.8 Hz, 2H), 7.30–7.26 (m, 3H), 7.04 (dd, J = 10.3, 7.4 Hz, 3H), 7.98–6.94 (m, 3H), 6.81 (t, J = 7.3 Hz, 1H), 5.33 (s, 1H), 4.01–3.95 (m, 1H), 3.84–3.78 (m, 1H), 3.08 (ddd, J = 15.2, 8.9, 6.1 Hz, 1H), 2.98 (dt, J = 16.3, 5.2 Hz, 1H), 1.72 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 194.5, 185.3, 149.4, 135.6, 134.9, 131.2, 129.6, 129.4, 128.7, 128.2, 127.7, 126.9, 126.0, 125.3, 118.5, 114.4, 92.7, 63.3, 42.8, 26.2, 20.5; HRMS (ESI) *m/z* 405.1583 (M+Na^+), calc. for $C_{25}H_{22}N_2O_2Na$ 405.1579.

- **Synthetic procedure for the preparation of 3m**



In a 10 mL snap vial equipped with a magnetic stirring bar, **1a** (0.15 mmol) was dissolved into DMF (1.5 mL), followed by the addition of diethyl phosphite **2g** (0.60 mmol) and a solution of photocatalyst **H** (0.015 μmol, 21 μL) in DMF (2.5 mg/ 10 mL). The reaction mixture was stirred under irradiation by 9 W fluorescent lamp at 28 ^{o}C (temperature was

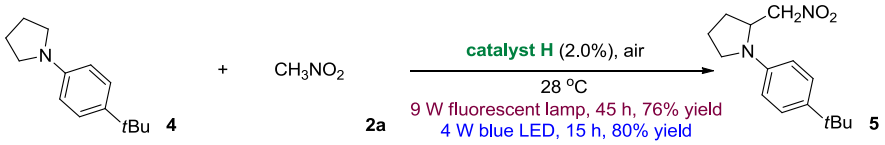
maintained in a incubator) from 5 cm distance. After the reaction was completed (monitored by TLC), the mixture was transferred to a separating funnel, diluted with ethyl acetate and washed with water. The aqueous phase was extracted three times with ethyl acetate (3×20 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. Purification of the crude product was achieved by flash column chromatography using petroleum ether/ethyl acetate as eluent to obtain **3m** as a pale yellow oil in 81% yield.



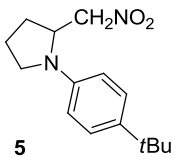
3m

Pale yellow oil; 81% yield; TLC (PE/EA 2:1): RF = 0.5; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.38–7.36 p.p.m. (m, 1H), 7.28–7.24 (m, 2H), 7.21–7.14 (m, 3H), 6.98 (d, *J* = 8.3 Hz, 2H), 6.80 (t, *J* = 7.3 Hz, 1H), 5.19 (d, *J* = 20.0 Hz, 1H), 4.14–3.85 (m, 5H), 3.66–3.60 (m, 1H), 3.12–2.90 (m, 2H), 1.25 (t, *J* = 7.1 Hz, 3H), 1.14 (t, *J* = 7.1 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 149.3 (d, *J* = 5.8 Hz), 136.4 (d, *J* = 5.6 Hz), 130.5, 129.1, 128.7 (d, *J* = 2.6 Hz), 128.1 (d, *J* = 4.6 Hz), 127.4 (d, *J* = 3.5 Hz), 125.8 (d, *J* = 2.8 Hz), 118.4, 114.7, 63.3 (d, *J* = 7.2 Hz), 62.3 (d, *J* = 7.7 Hz), 59.5, 57.9, 43.4, 26.7, 16.4 (d, *J* = 5.5 Hz), 16.3 (d, *J* = 6.0 Hz); HRMS (ESI) *m/z* 368.1386 ($M+Na^+$), calc. for $C_{19}H_{24}NO_3NaP$ 368.1392.

- **Synthetic procedure for the preparation of 5**



In a 10 mL snap vial equipped with a magnetic stirring bar, **4** (0.15 mmol) was dissolved into nitromethane (1.5 mL), and then a solution of photocatalyst **H** (3.0 μmol, 425 μL) in nitromethane (2.5 mg/ mL) was added. The reaction mixture was stirred under irradiation by visible light at 28 ^{o}C (temperature was maintained in a incubator) from 5 cm distance. After the reaction was completed (monitored by TLC), the solvent was removed *in vacuo* and the residue was purified by flash chromatography on silica gel using petroleum ether /ethyl acetate as eluent to afford adduct **5** as a pale yellow solid.



5 Pale yellow solid; m.p.: 79.1–81.4 ℃; 80% yield; TLC (PE/EA 10:1): RF = 0.5; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.36–7.32 p.p.m. (m, 2H), 6.69–6.66 (m, 2H), 4.64 (dd, *J* = 11.2, 3.0 Hz, 1H), 4.41–4.38 (m, 1H), 4.19 (dd, *J* = 11.2, 9.9 Hz, 1H), 3.52–3.47 (m, 1H), 3.23–3.16 (m, 1H), 2.14–2.02 (m, 4H), 1.31 (s, 9H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 143.5, 140.0, 126.4, 111.6, 76.0, 57.6, 48.2, 33.8, 31.5, 29.3, 22.9; HRMS (ESI) *m/z* 263.1762 ($M+H^+$), calc. for $C_{15}H_{23}N_2O_2$ 263.1760.

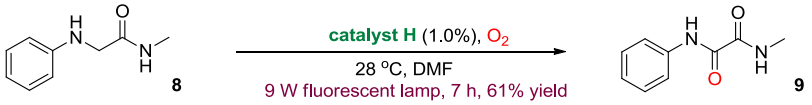
- **The preparation of 8**

A mixture of aniline (5.0 mmol), ethyl chloroacetate (6.0 mmol) and anhydrous sodium acetate (6.0 mmol) in 3 mL of ethanol was refluxed in an oil bath (120–125 ^{o}C) for 6 h. The reaction mixture was left overnight at room temperature and poured onto crushed ice. The precipitate formed was collected by filtration and dried. The dried product, ethyl ester of *N*-Ph glycine was used in the next step without further purification.

A three-necked flask equipped with an oval magnetic stir bar was charged with a 30 wt% solution of methylamine in ethanol (9.0 mmol) and placed into a room-temperature water-bath. To the stirred solution was added *N*-Ph glycine (3.0 mmol) *via* a powder funnel followed by a rinse with ethanol (6 mL). The flask was fitted with a nitrogen inlet and a thermometer. The mixture was stirred at 20–22 ^{o}C for 4 h and then concentrated by rotary evaporation to provide a wet solid which was purified by flash chromatography on silica gel in 97% yield.

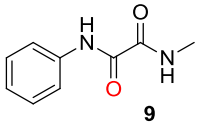
TLC (EA): RF = 0.4; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.25–7.18 p.p.m. (m, 2H), 6.82 (t, *J* = 7.4 Hz, 1H), 6.77 (s, 1H), 6.64–6.58 (m, 2H), 4.29 (s, 1H), 3.79 (s, 2H), 2.82 (d, *J* = 5.0 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 171.1, 147.1, 129.4, 119.1, 113.1, 48.7, 25.9; HRMS (ESI) *m/z* 165.1025 ($M+H^+$), calc. for $C_9H_{13}N_2O$ 165.1028.

- **Oxidation of 8 to 9**



In a 10 mL snap vial equipped with a magnetic stirring bar, **8** (0.15 mmol) was dissolved into dried DMF (1.0 mL) under oxygen atmosphere, followed by the addition of a solution of

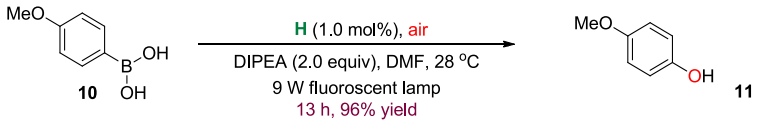
photocatalyst **H** (1.5 μmol, 212 μL) in DMF (2.5 mg/ mL). The reaction mixture was stirred under irradiation by 9 W fluorescent lamp at 28 °C (temperature was maintained in a incubator) from 5 cm distance. After the reaction was completed (monitored by TLC), the mixture was transferred to a separating funnel, diluted with ethyl acetate and washed with water. The aqueous phase was extracted three times with ethyl acetate (3×20 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. Purification of the crude product was achieved by flash column chromatography using petroleum ether /ethyl acetate as eluent.



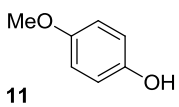
9

Pale yellow solid; m.p. = 150.3–152.1 °C; 61% yield; TLC (PE/EA 5:1): RF = 0.25; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 9.24 p.p.m. (s, 1H), 7.64–7.62 (m, 2H), 7.55 (s, 1H), 7.40–7.36 (m, 2H), 7.20–7.16 (m, 1H), 2.98 (d, J = 5.2 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 160.6, 157.3, 136.3, 129.2, 125.3, 119.8, 26.4; HRMS (ESI) *m/z* 201.0643 ($M+Na^+$), calc. for $C_9H_{10}N_2O_2Na$ 201.0640.

- **Synthetic procedure for the preparation of 11**



To a solution of (4-methoxyphenyl)boronic acid **10** (0.15 mmol) in DMF (1.5 mL) was added *i*Pr_2NEt (0.30 mmol), followed by a solution of photocatalyst **H** (1.5 μmol, 212 μL) in anhydrous DMF (2.5 mg/ mL). The reaction mixture was stirred under irradiation by 9 W fluorescent lamp at 28 °C (temperature was maintained in a incubator) from 5 cm distance for 13 h before cooled to 0 ℃ and quenched carefully by the addition of aq. HCl (2 *N*, 0.5 mL). The resultant mixture was extracted with Et_2O (3×20 mL) and the combined organic layers were washed with brine (3×10 mL) and dried over Na_2SO_4. After removal of the solvent *in vacuo*, the residue was purified by flash column chromatography using petroleum ether/ethyl acetate as eluent to obtain a yellow solid in 96% yield.

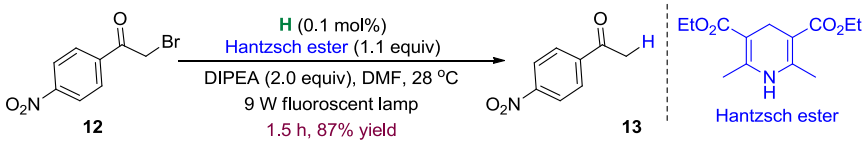


11

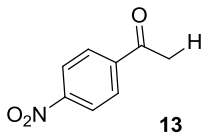
Yellow solid; 96% yield; TLC (PE/EA 2:1): RF = 0.6; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.81–6.76 p.p.m. (m, 4H), 4.94 (s, 1H), 3.77 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 153.7, 149.5, 116.0, 114.9, 55.8; HRMS (ESI) *m/z* 147.0425 ($M+Na^+$),

calc. for $C_7H_8O_2Na$ 147.0422.

➢ **Synthetic procedure for the preparation of 13**

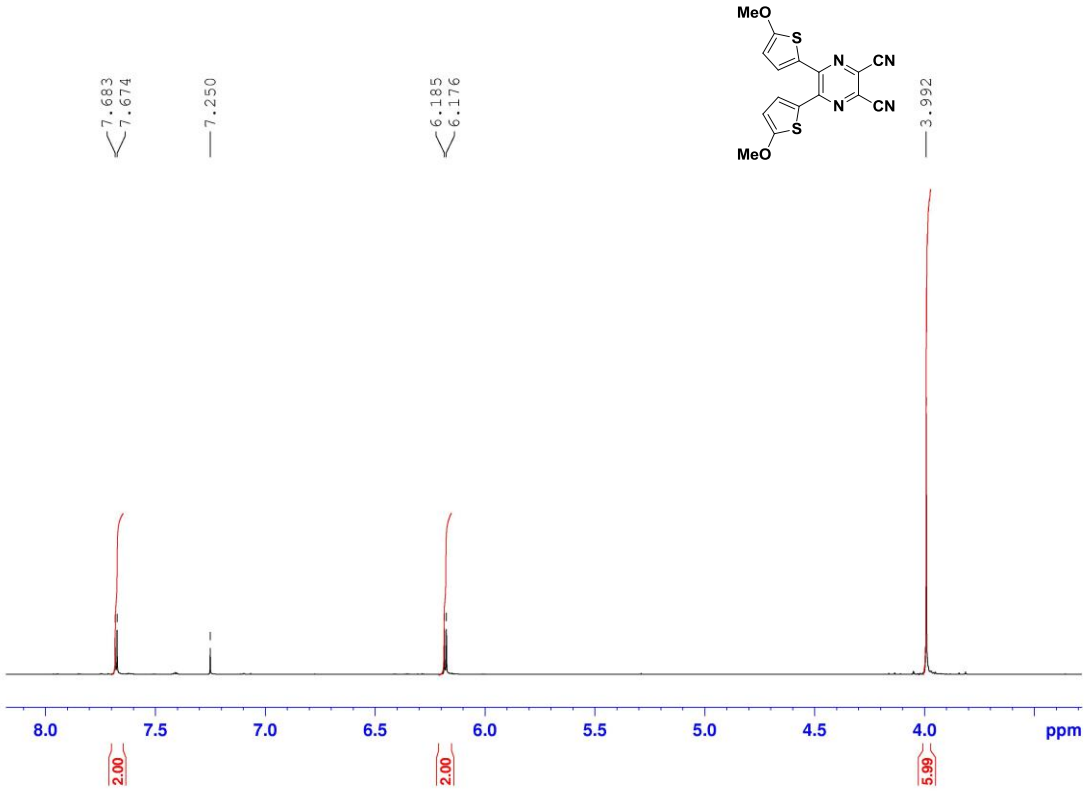


In a 10 mL snap vial equipped with a magnetic stirring bar, 2-bromo-4'-nitroacetophenone **12** (0.15 mmol) and Hantzsch ester (0.165 mmol) were dissolved into anhydrous DMF (1.5 mL). To the solution was added DIPEA (0.30 mmol) and a solution of photocatlyst **H** (0.15 μmol, 21 μL) in DMF (2.5 mg/ mL). The mixture was degassed by "freeze-pump-thaw" cycles (×3) via a syringe needle under nitrogen atmosphere. The reaction mixture was stirred under irradiation by 9 W fluorescent lamp at 28 °C (temperature was maintained in a incubator) from 5 cm distance for 1.5 h before transferred to a separation funnel, diluted with diethyl ether and washed with water. The aqueous phase was extracted three times with diethyl ether (3×20 mL). The combined organic layers were dried over Na_2SO_4, filtered and concentrated *in vacuo*. Purification of the crude product was achieved by silica gel column chromatography using petroleum ether /ethyl acetate as eluent to obtain a pale yellow solid in 87% yield.

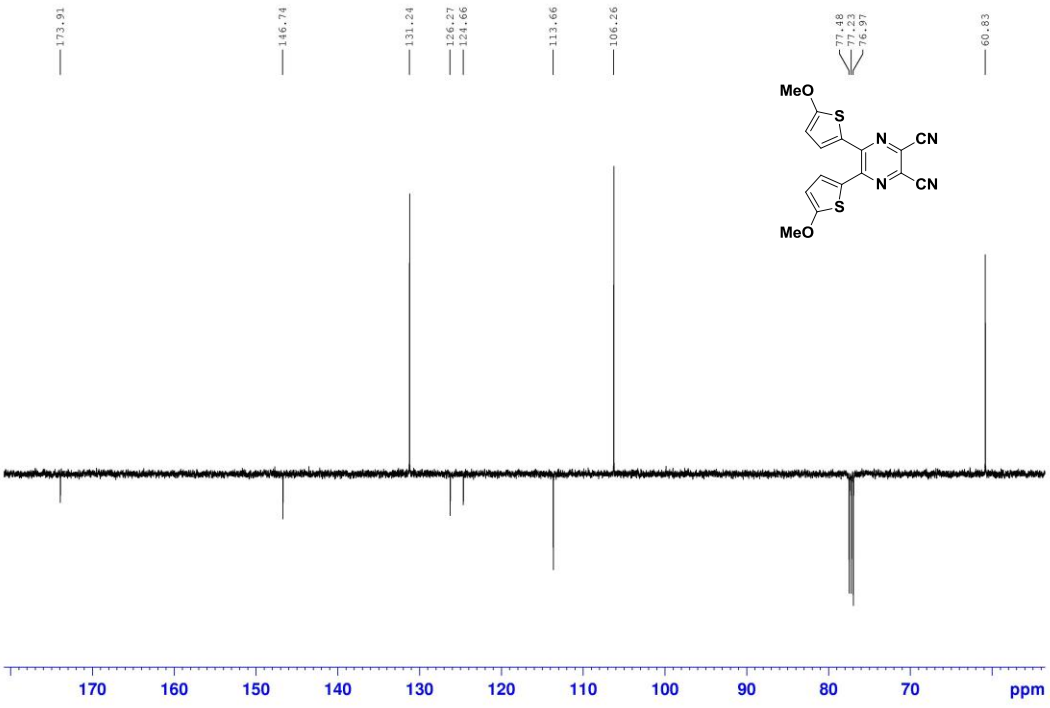


Pale yellow solid; m.p. = 69.0–71.3 °C; 87% yield; TLC (PE/EA 10:1): RF = 0.7; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33–8.30(m, 2H), 8.12–8.09 (m, 2H), 2.68 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.2, 150.4, 141.4, 129.3, 123.8, 26.9; HRMS (ESI) *m/z* 166.0505 ($M+H^+$), calc. for $C_8H_8NO_3$ 166.0504.

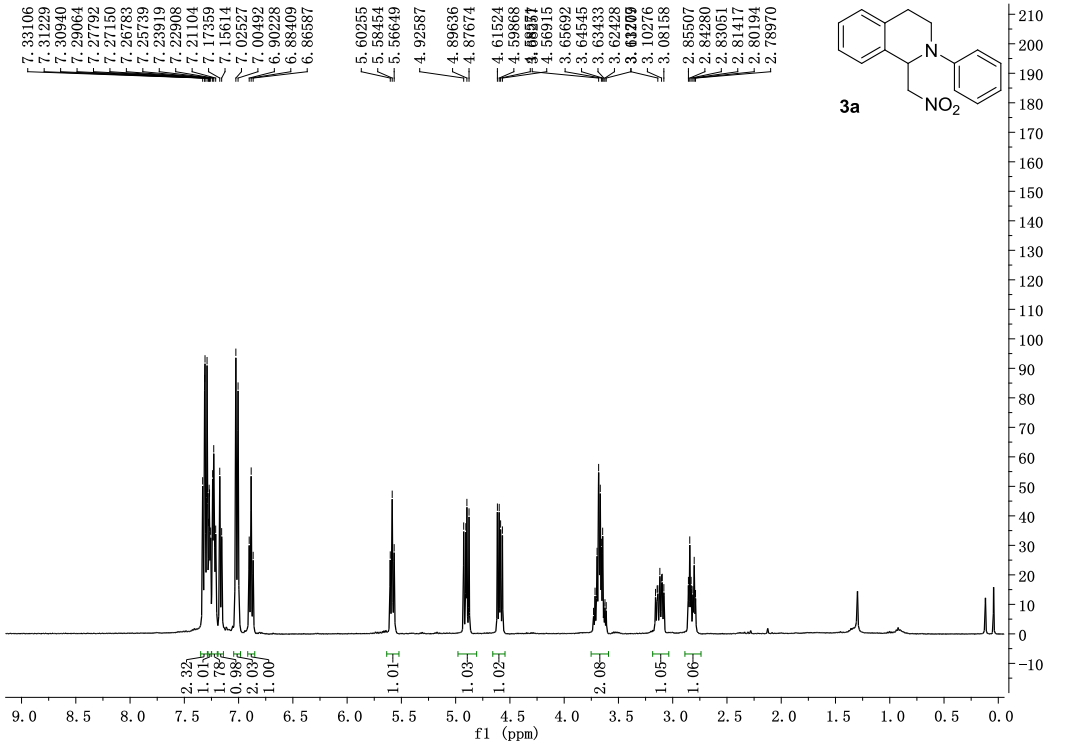
5. Copies of NMR spectra



^{1}H NMR spectrum of the catalyst **H** ($CDCl_3$, 500 MHz, 25 °C)



^{13}C NMR APT spectrum of the catalyst **H** ($CDCl_3$, 125 MHz, 25 °C)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3.10276
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2.85507
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2.83051
2.81417
2.80194
2.78970
3a
NO2
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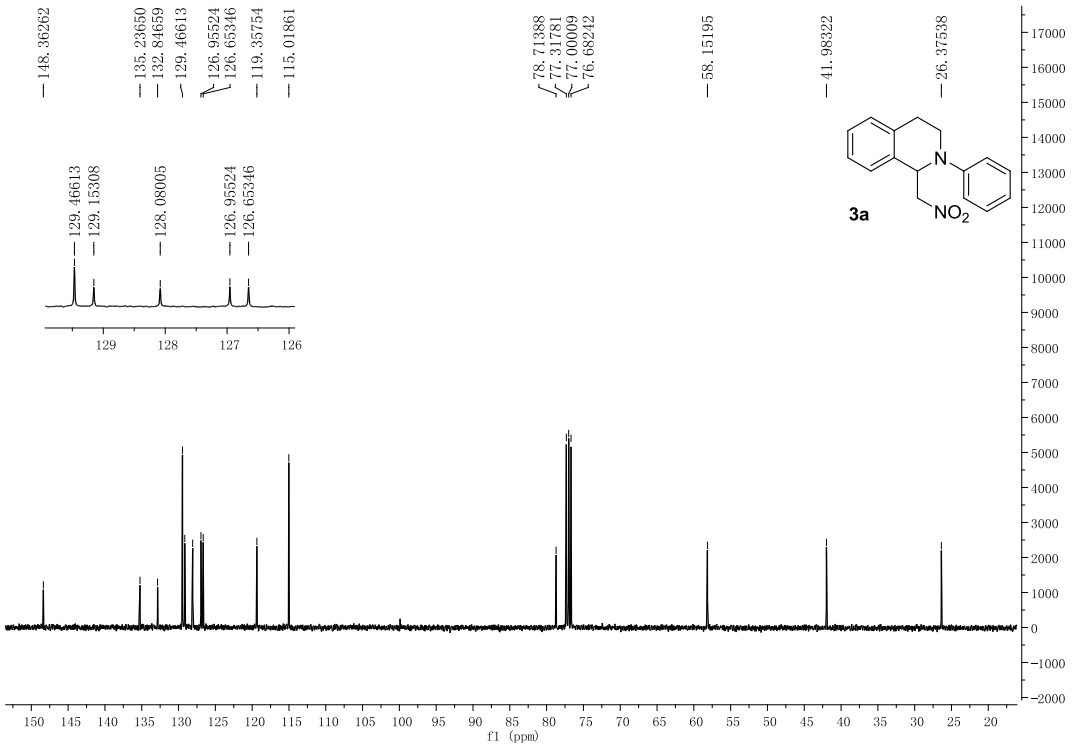
1.00
1.01
1.03
1.02
2.08
1.05
1.06
f1 (ppm)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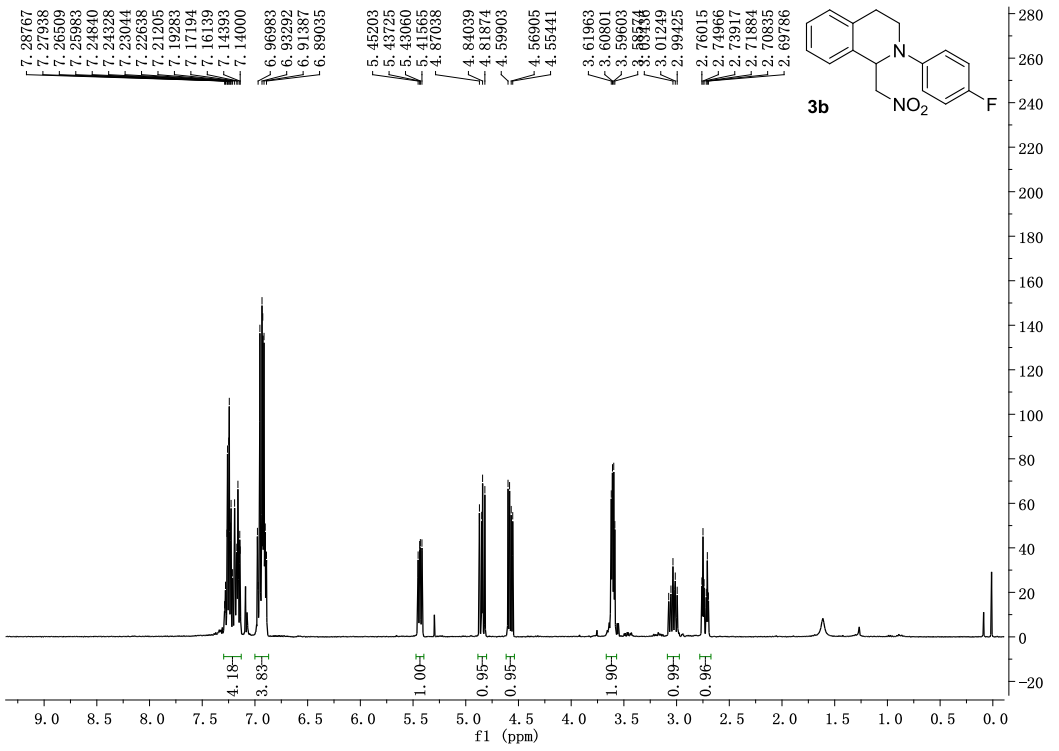
3a
NO2
f1 (ppm)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0.95
1.90
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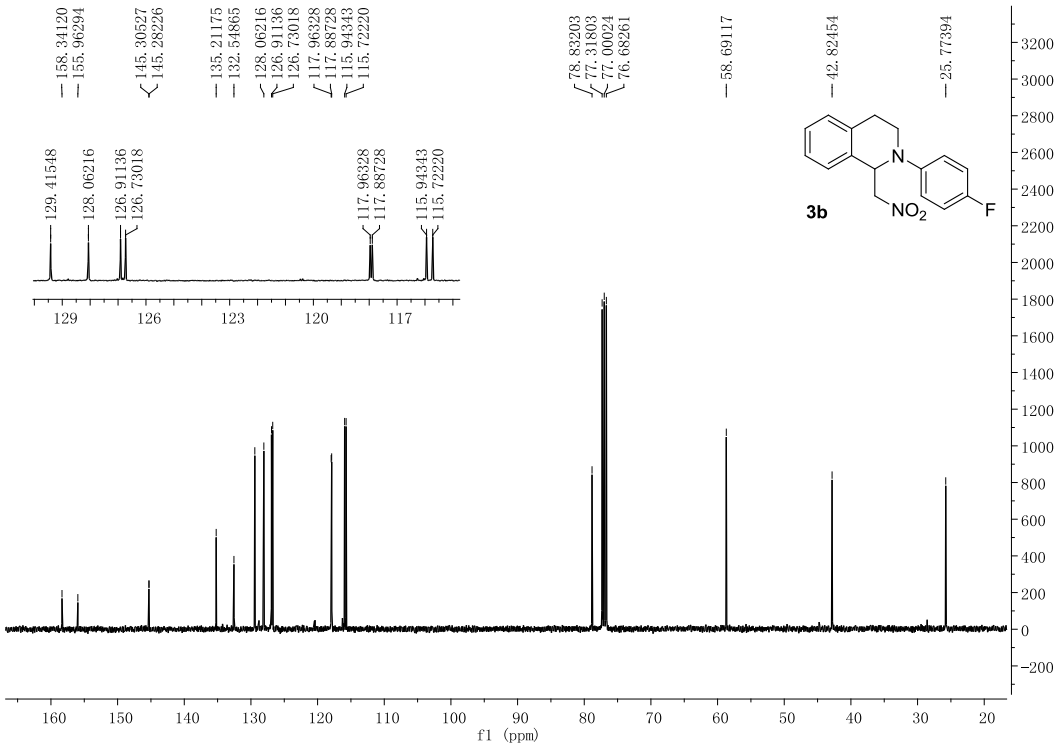
0.96
f1 (ppm)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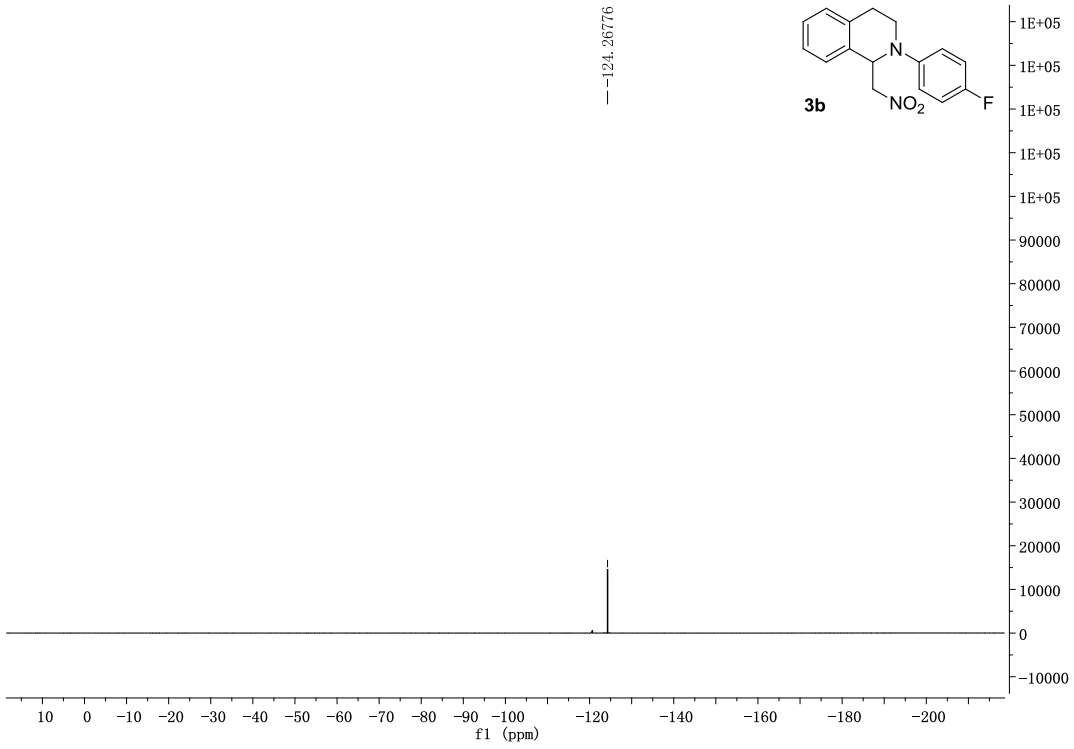
f1 (ppm)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1E+05
1E+05
1E+05
1E+05
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80000
70000
60000
50000
40000
30000
20000
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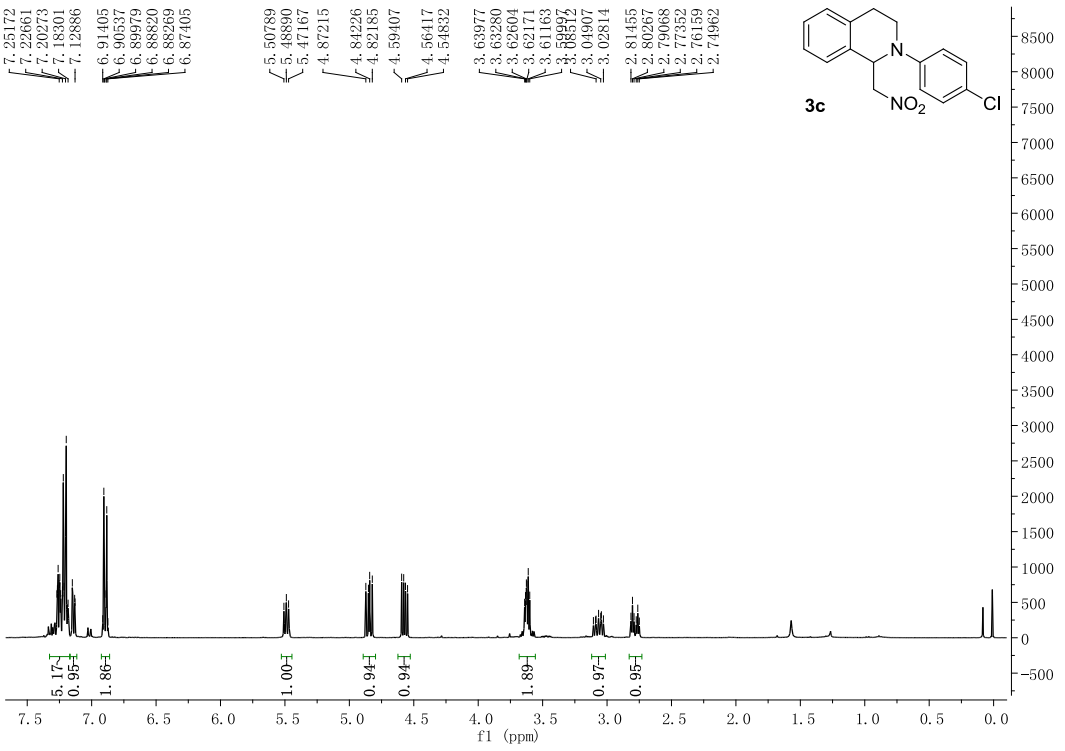
0
−10000
10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −120 −140 −160 −180 −200
f1 (ppm)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5.50789
5.48890
5.47167
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4.54832
3.63977
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3.62604
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3.61163
3.04907
3.02814
2.81455
2.80267
2.79068
2.77352
2.76159
2.74962
3c
NO2
Cl
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0.94
0.94
1.89
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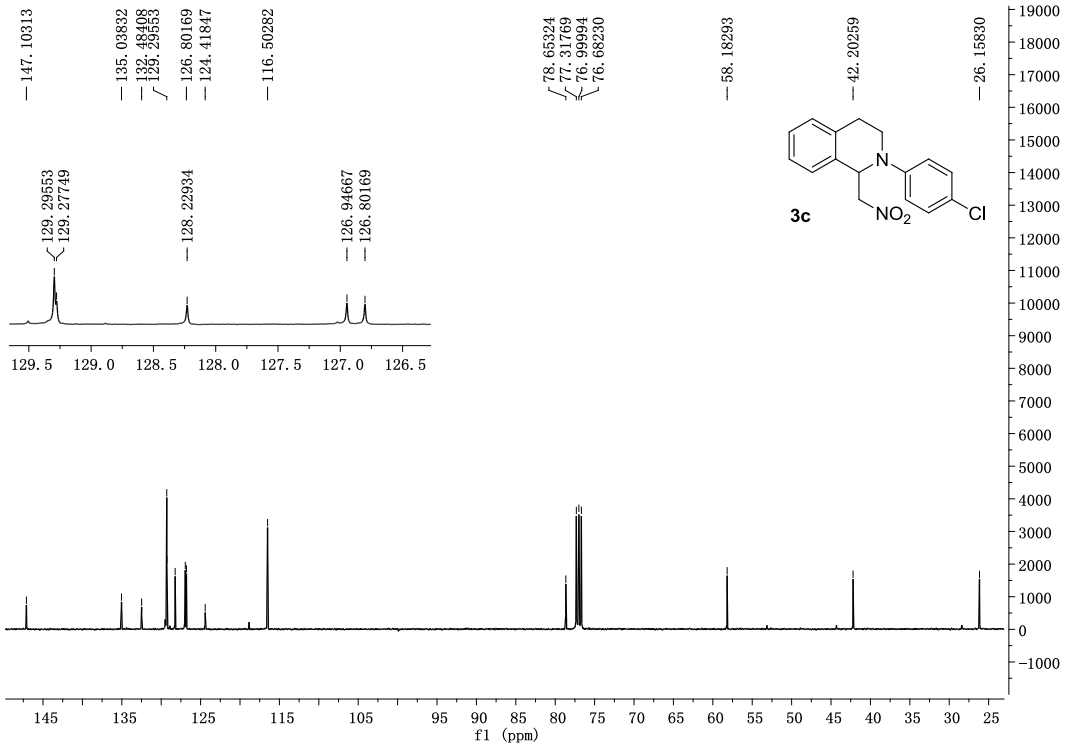
0.95
f1 (ppm)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76.99994
76.68230
58.18293
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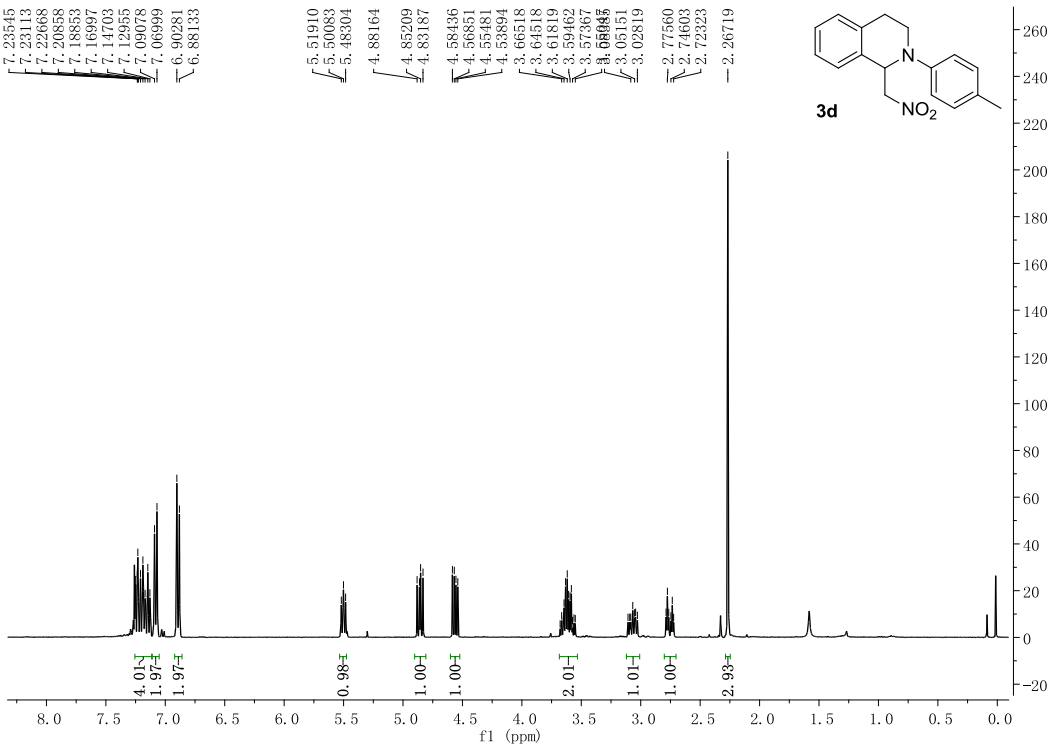
3c
NO2
Cl
f1 (ppm)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7.14703
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7.06999
6.90281
6.88133
5.51910
5.50083
5.48304
4.88164
4.85209
4.83187
4.58436
4.56851
4.55481
4.53894
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3.64518
3.61819
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3.57367
3.06151
3.02819
2.77560
2.74603
2.72323
2.26719
3d
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1.97
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1.00
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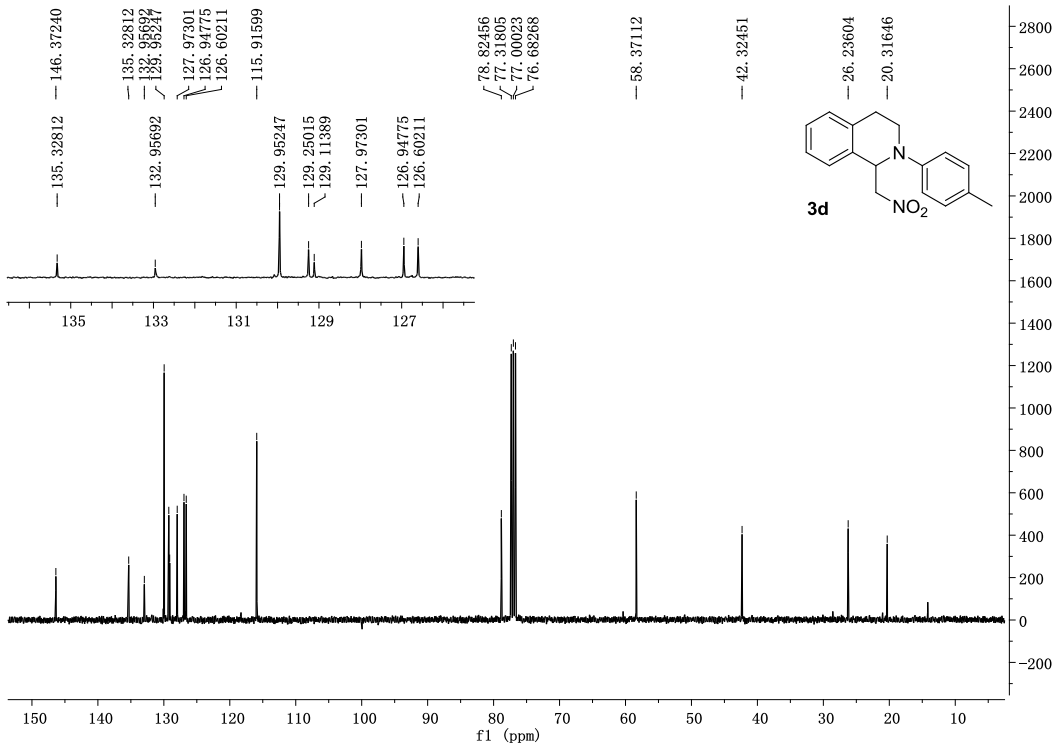
1.01
1.00
2.93
f1 (ppm)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76.68268
58.37112
42.32451
26.23604
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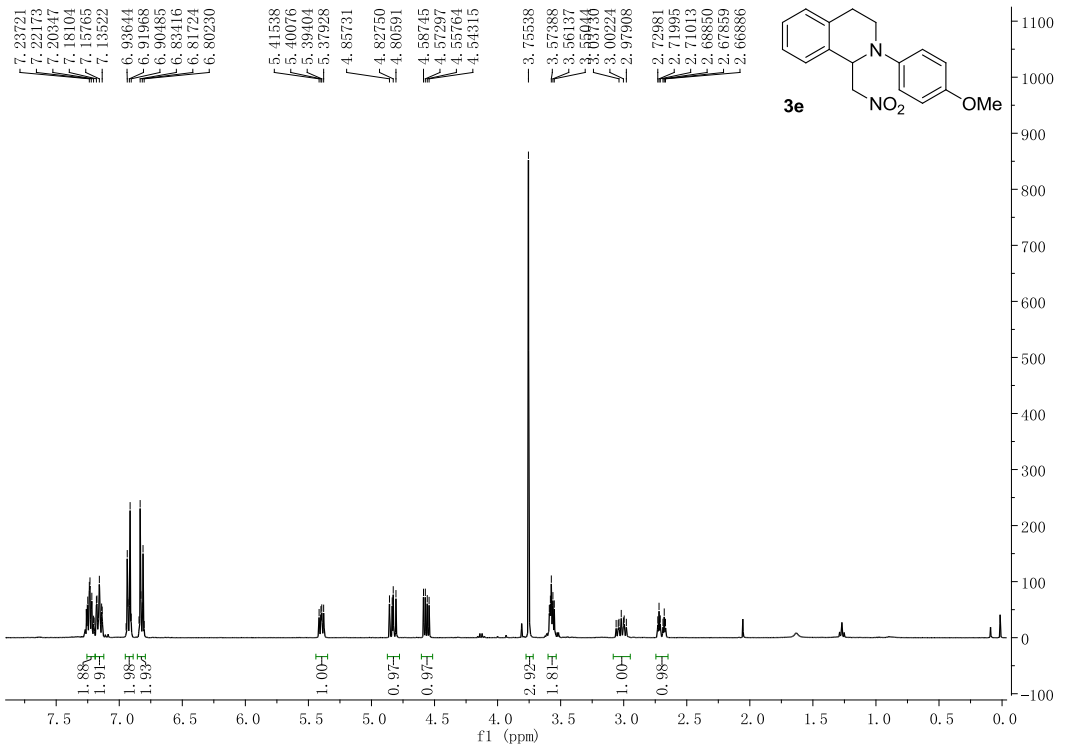
3d
f1 (ppm)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6.83416
6.81724
6.80230
5.41538
5.40076
5.39404
5.37928
4.85731
4.82750
4.80591
4.58745
4.57297
4.55764
4.54315
3.75538
3.57388
3.56137
3.55044
3.53730
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2.97908
2.72981
2.71995
2.71013
2.68850
2.67859
2.66886
3e
NO2
OMe
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1.98
1.93
1.00
0.97
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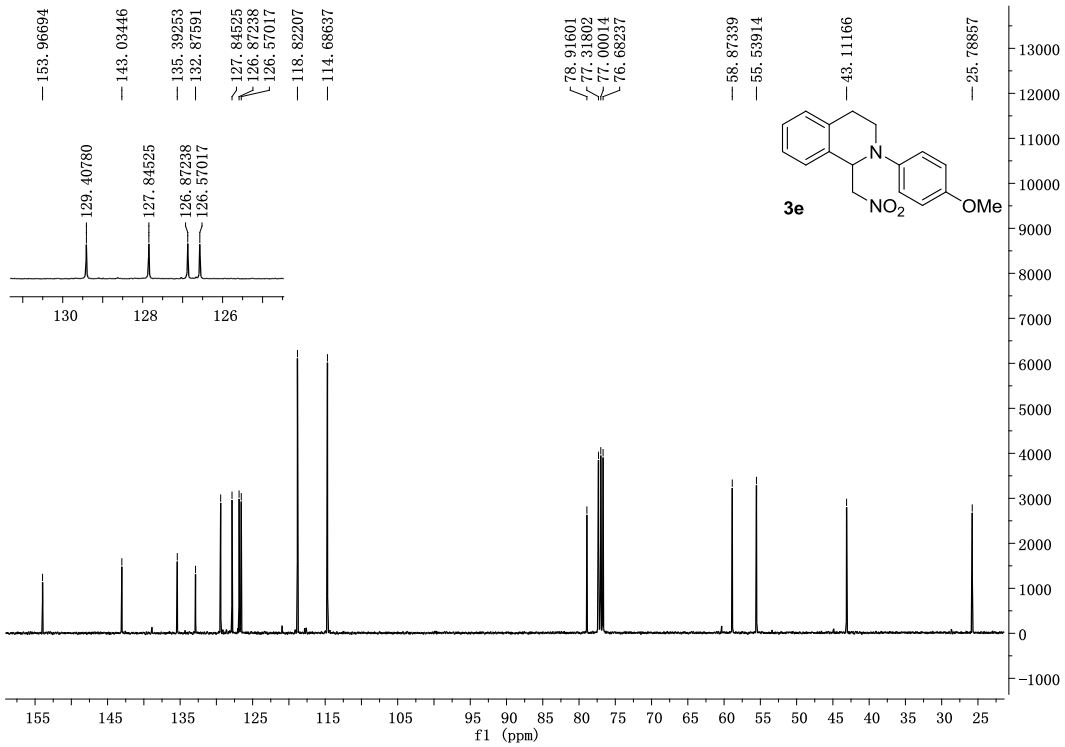
1.81
1.00
0.98
f1 (ppm)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114.68637
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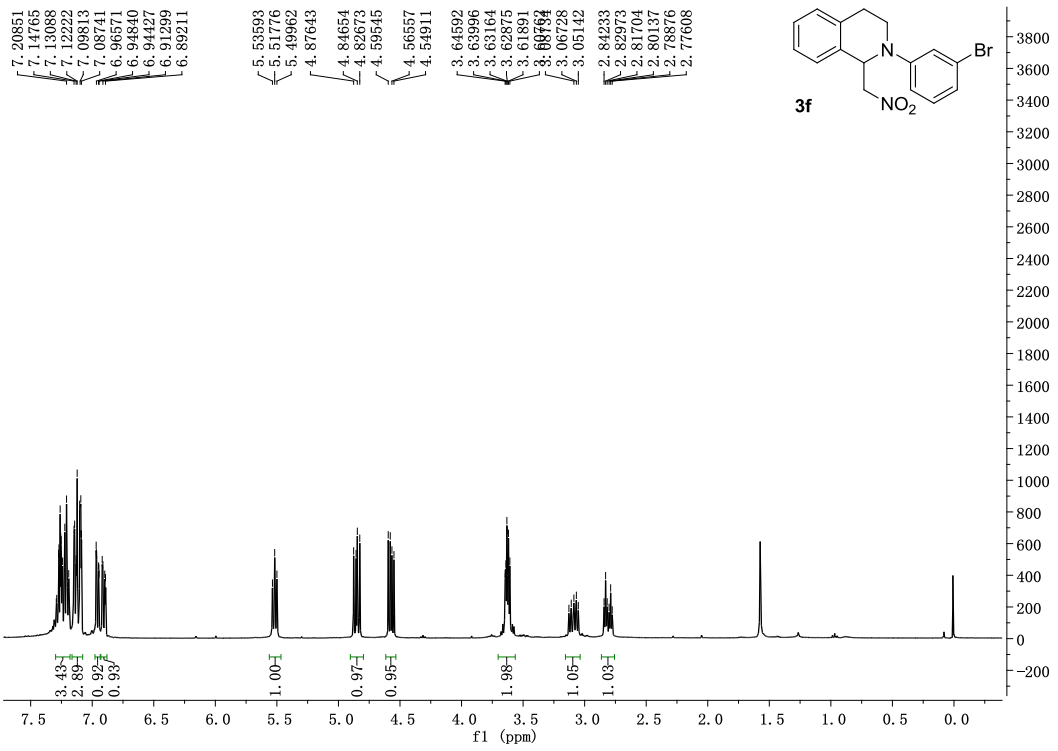
77.31802
77.00014
76.68237
58.87339
55.53914
43.11166
25.78857
129.40780
127.84525
126.87238
126.57017
3e
NO2
OMe
f1 (ppm)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5.51776
5.49962
4.87643
4.84654
4.82673
4.59545
4.56557
4.54911
3.64592
3.63996
3.63164
3.62875
3.61891
3.06728
3.05142
2.84233
2.82973
2.81704
2.80137
2.78876
2.77608
3f
Br
N
NO2
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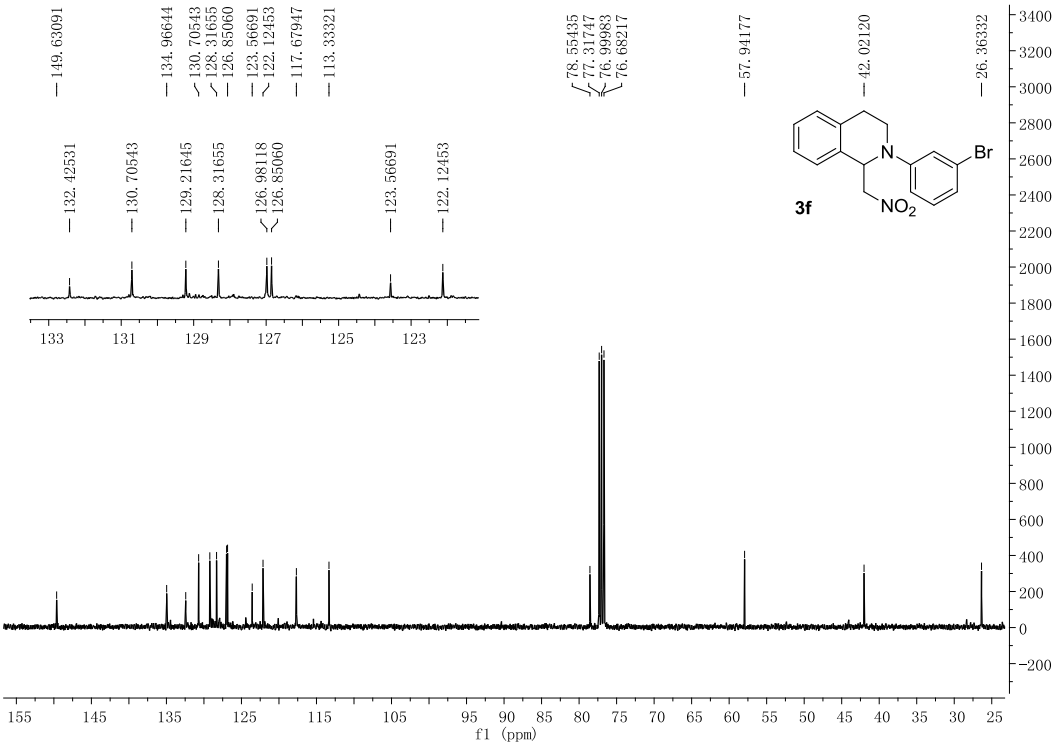
0.93
1.00
0.97
0.95
1.98
1.05
1.03
f1 (ppm)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117.67947
113.33321
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77.31747
76.99983
76.68217
57.94177
42.02120
26.36332
132.42531
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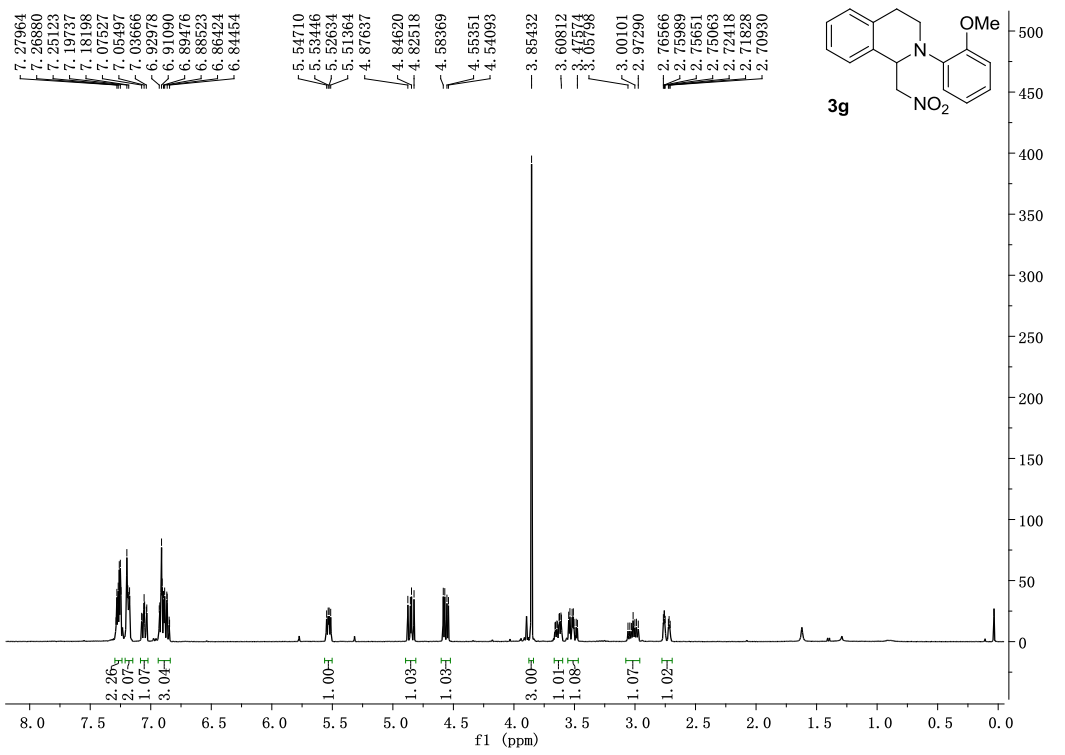
123.56691
122.12453
3f
Br
N
NO2
f1 (ppm)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6.89476
6.88523
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6.84454
5.54710
5.53446
5.52634
5.51364
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4.84620
4.82518
4.58369
4.55351
4.54093
3.85432
3.60812
3.47574
3.05798
3.00101
2.97290
2.76566
2.75989
2.75651
2.75063
2.72418
2.71828
2.70930
OMe
N
NO2
3g
2.26
2.07
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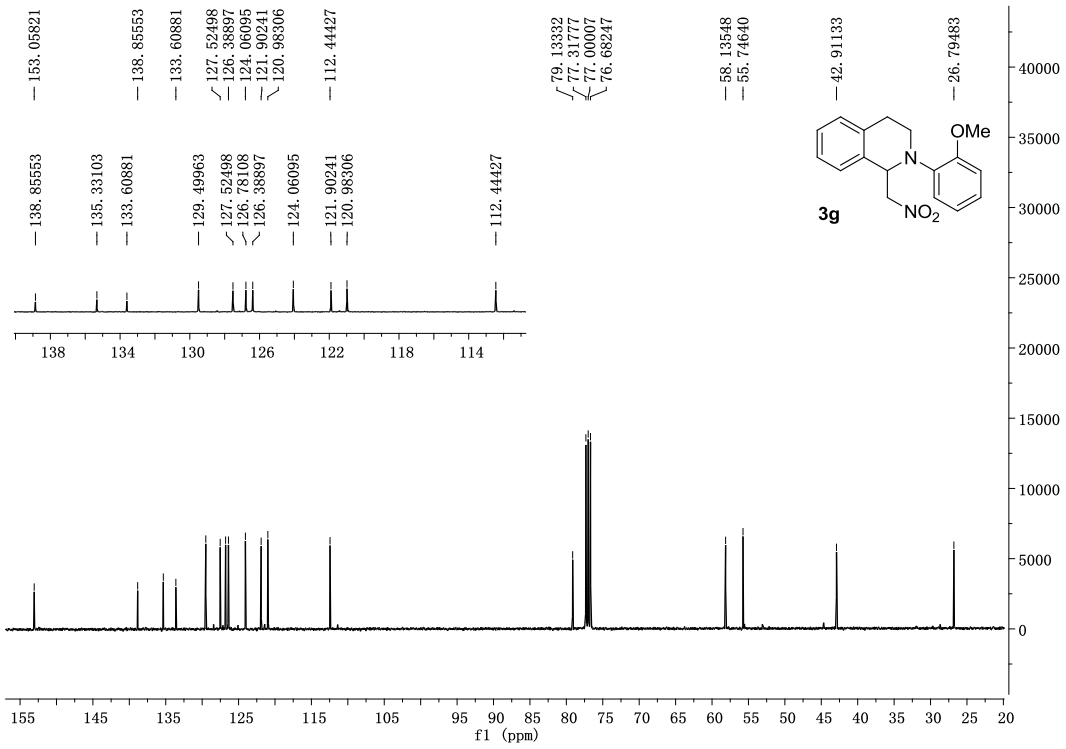
3.04
1.00
1.03
1.03
3.00
1.01
1.08
1.07
1.02
f1 (ppm)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77.00007
76.68247
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26.79483
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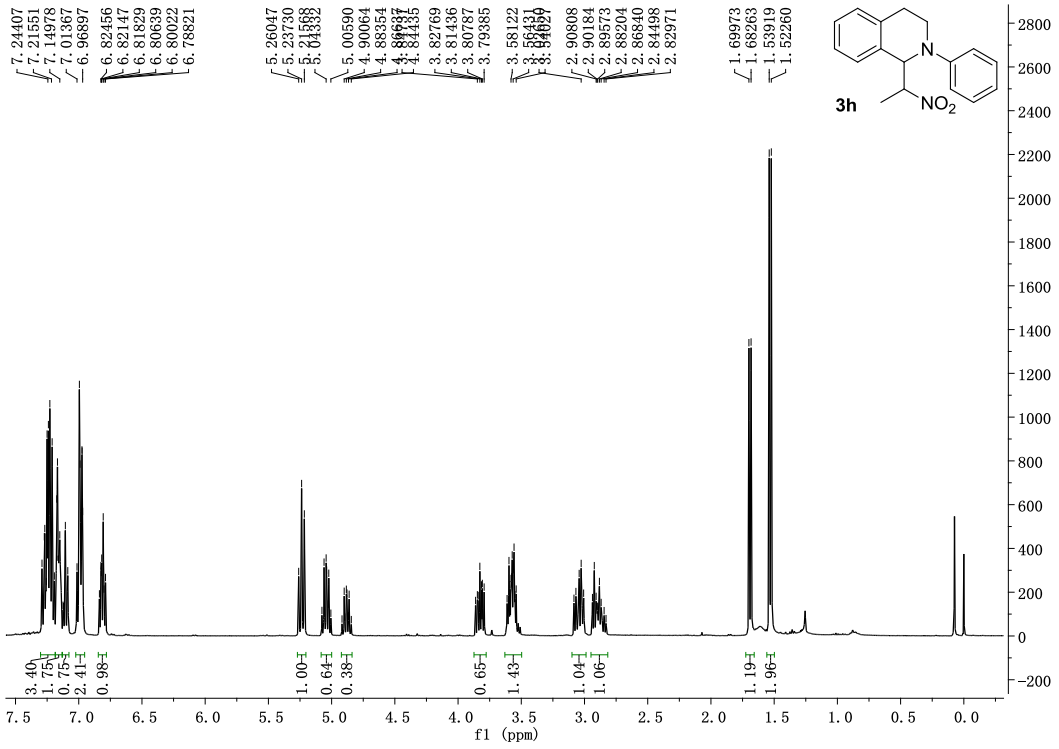
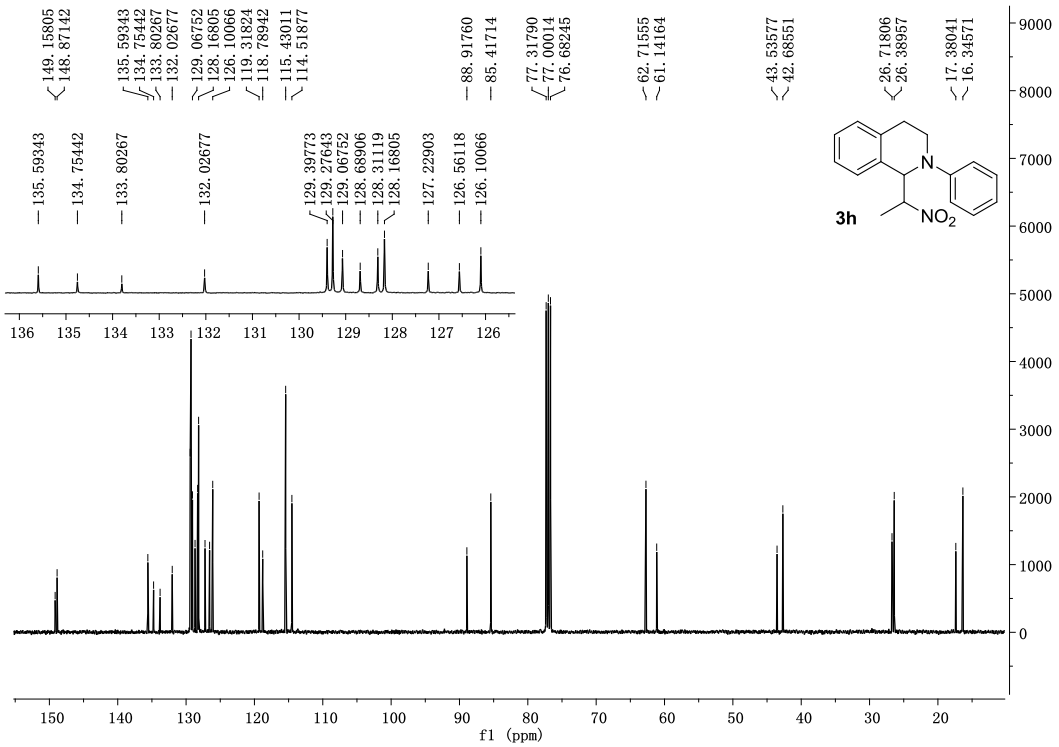
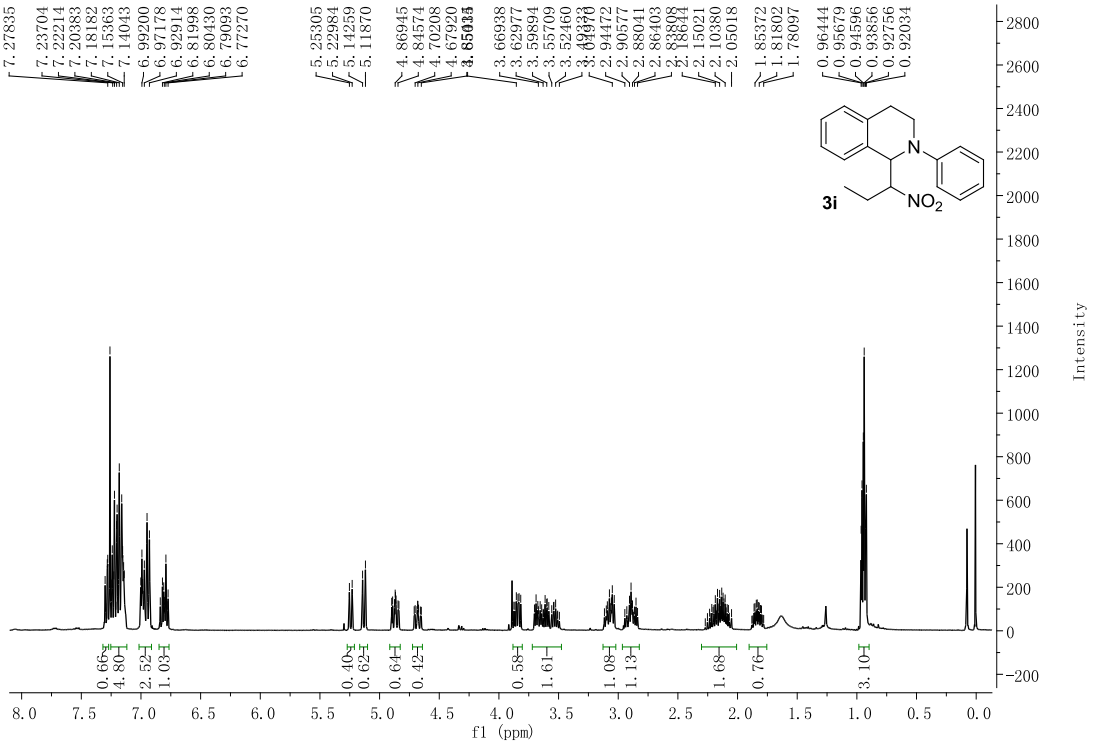
OMe
N
NO2
3g
f1 (ppm)


3h
f1 (ppm)


3h
f1 (ppm)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6.80430
6.79093
6.77270
5.25305
5.22984
5.14259
5.11870
4.86945
4.84574
4.70208
4.67920
3.66938
3.62977
3.59894
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3.52460
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1.85372
1.81802
1.78097
0.96444
0.95679
0.94596
0.93856
0.92756
0.92034
0.66
4.80
2.52
1.03
0.40
0.62
0.64
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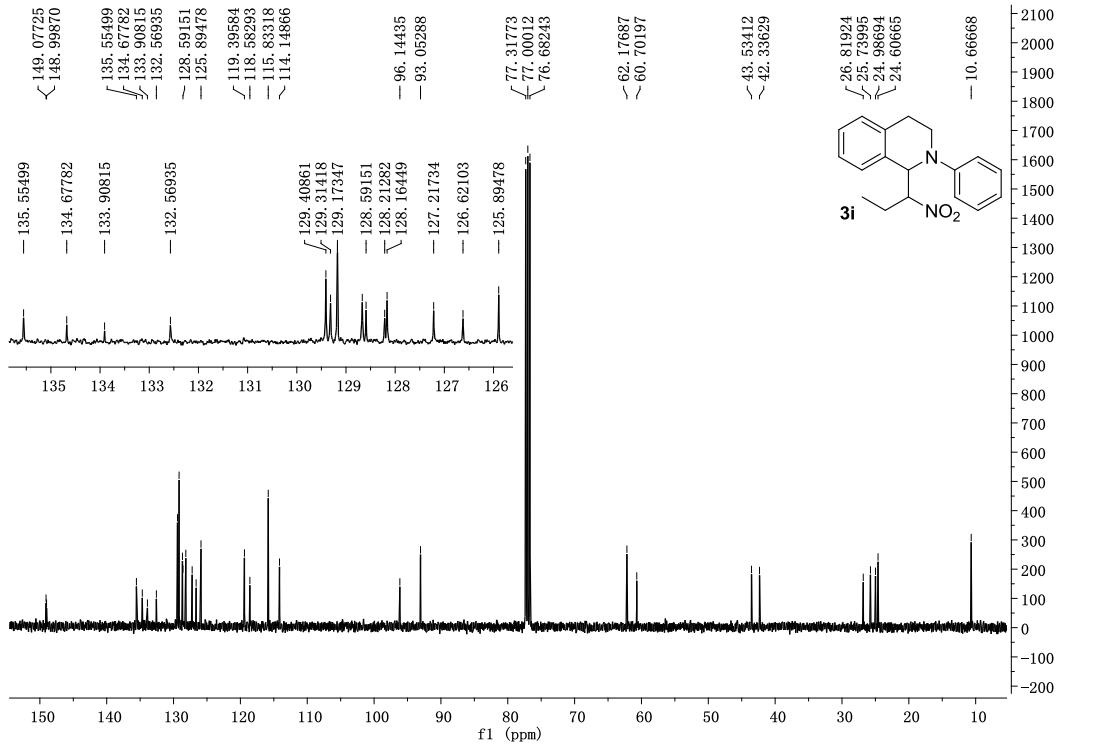
1.08
1.13
1.68
0.76
3.10
3i
NO2
Intensity
f1 (ppm)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60.70197
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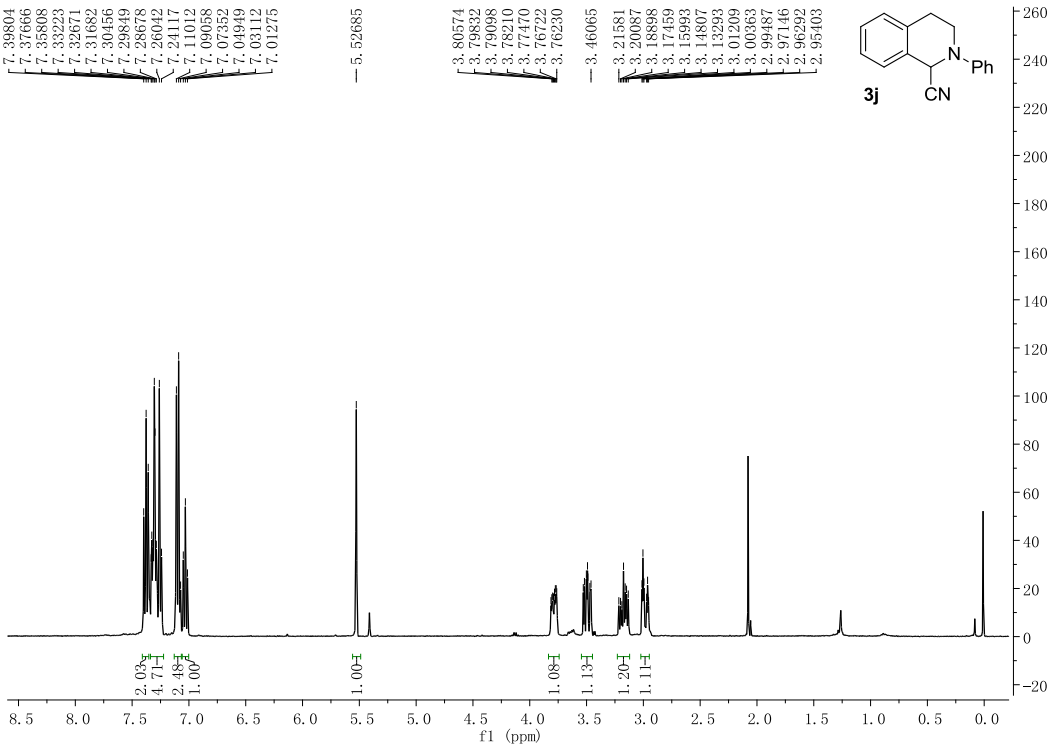
3i
NO2
f1 (ppm)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3.76722
3.76230
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2.96292
2.95403
3j
Ph
CN
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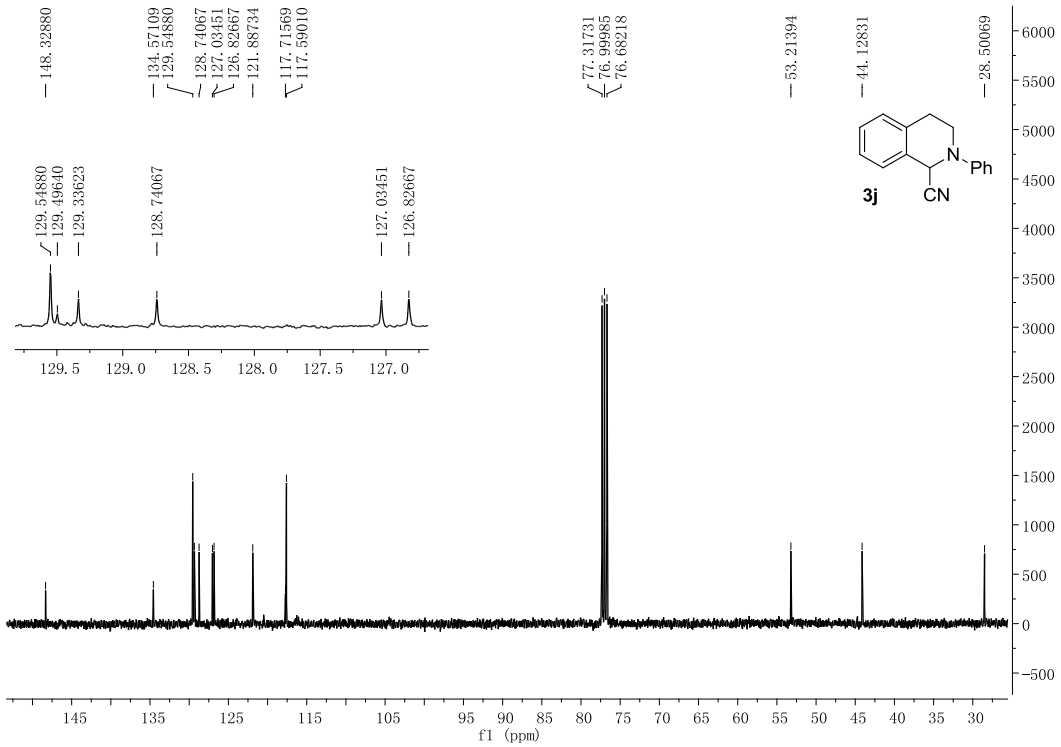
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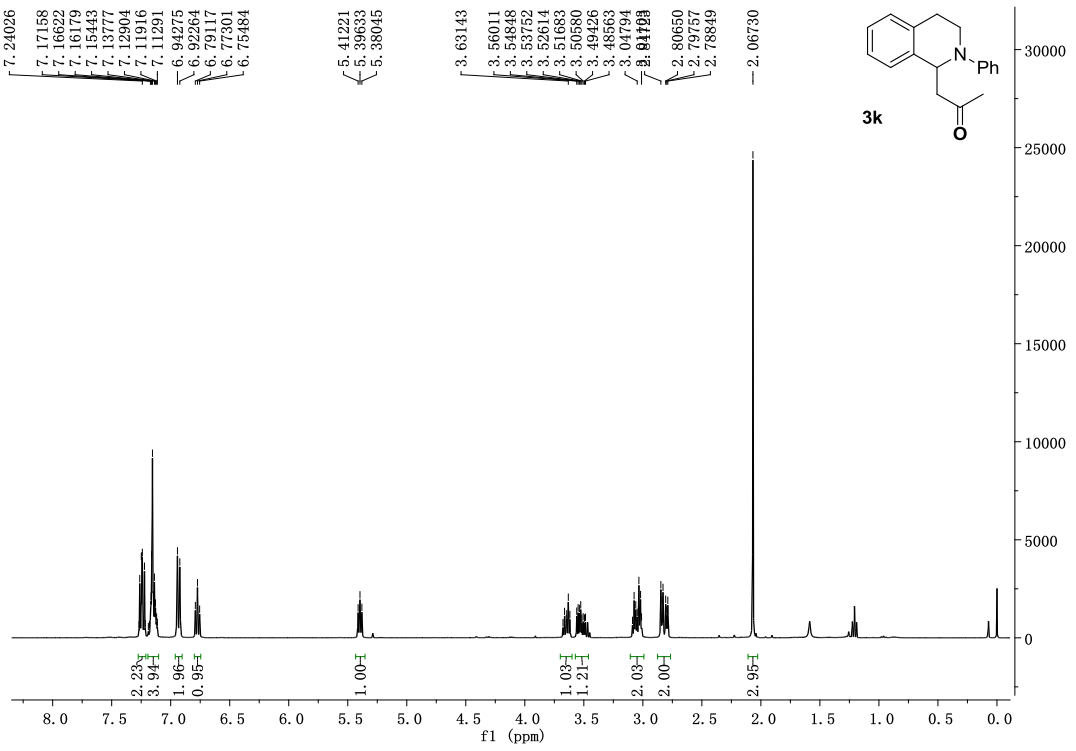
Ph
CN
f1 (ppm)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3.50580
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3.48563
3.04794
2.80650
2.79757
2.78849
2.06730
Ph
3k
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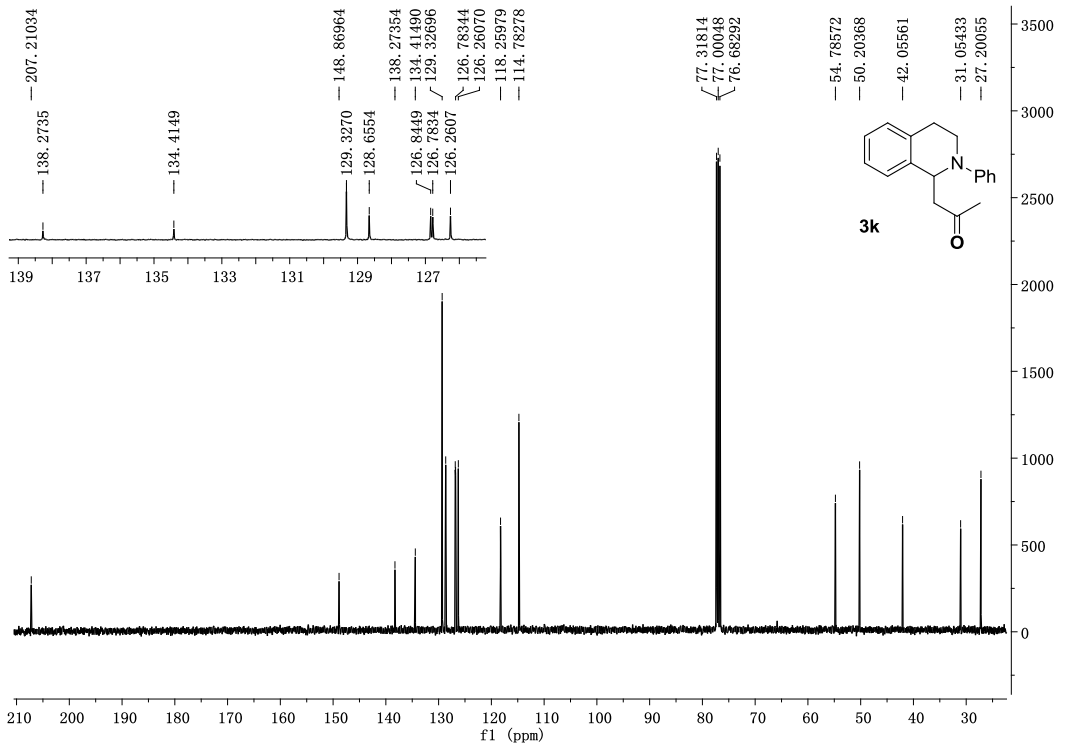
1.21
2.03
2.00
2.95
f1 (ppm)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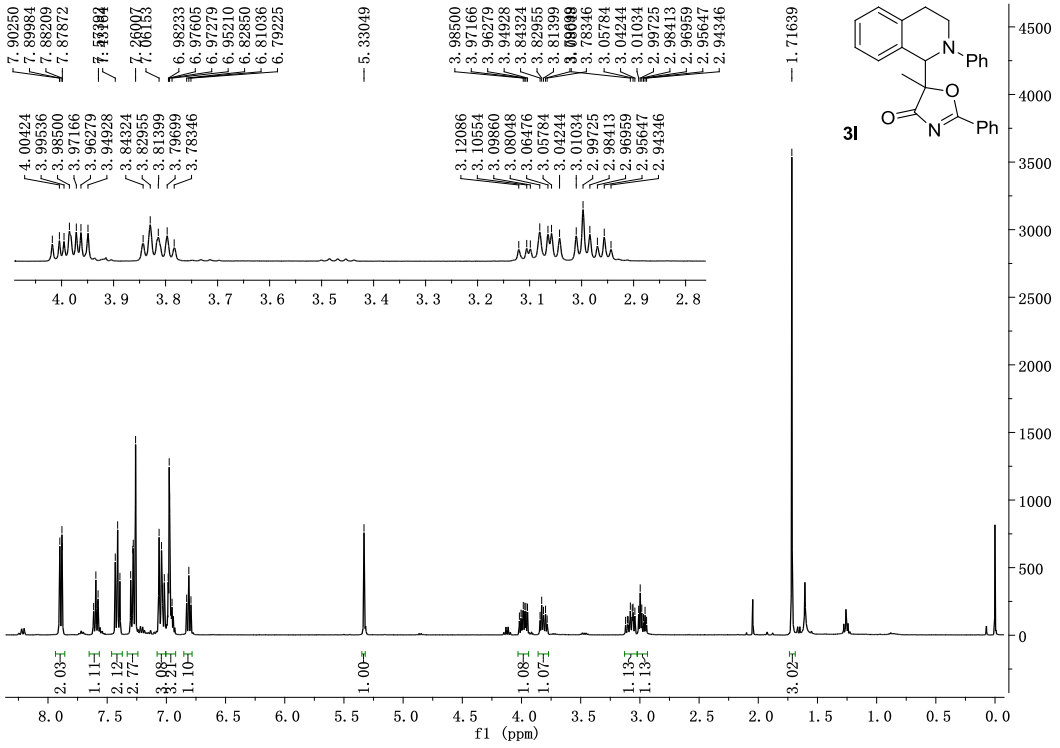
Ph
3k
O
f1 (ppm)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3.05784
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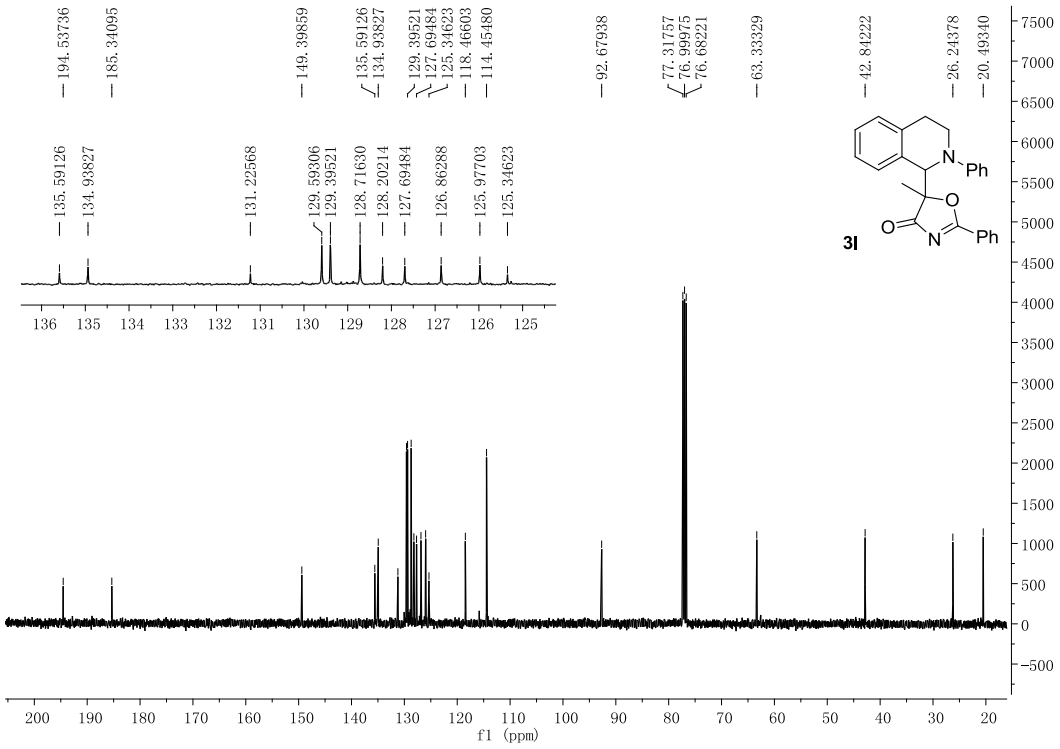
f1 (ppm)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92.67938
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42.84222
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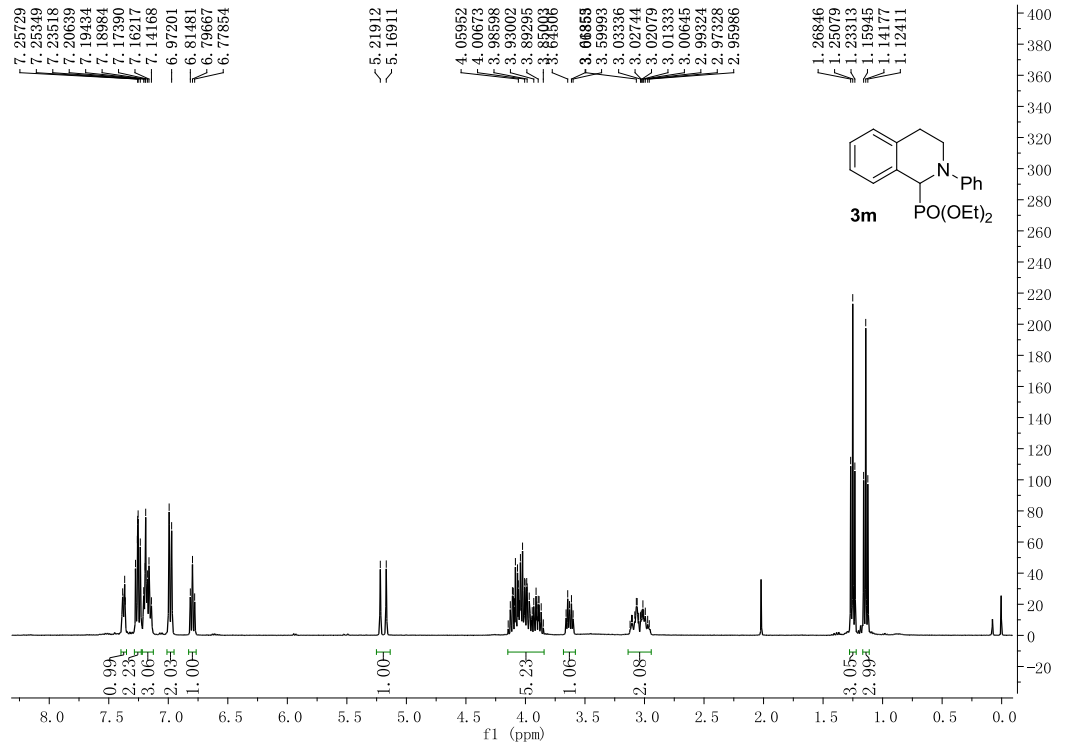
3I
f1 (ppm)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3.06
2.03
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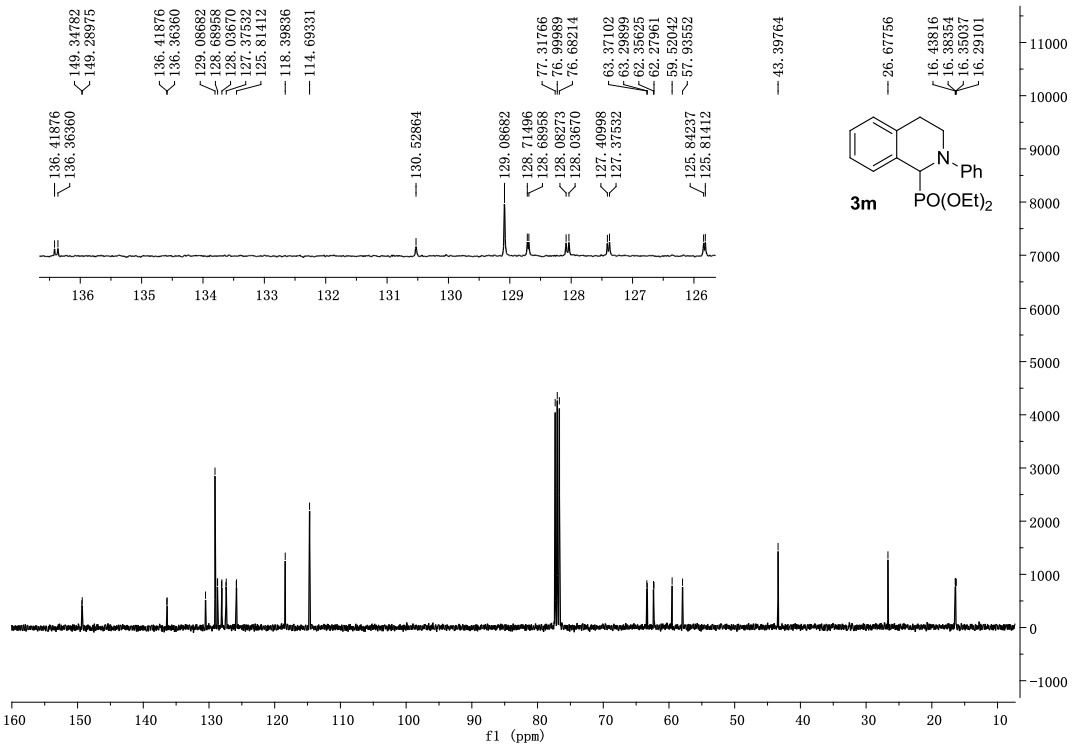
1.06
2.08
3.05
2.99
N
Ph
PO(OEt)2
3m
f1 (ppm)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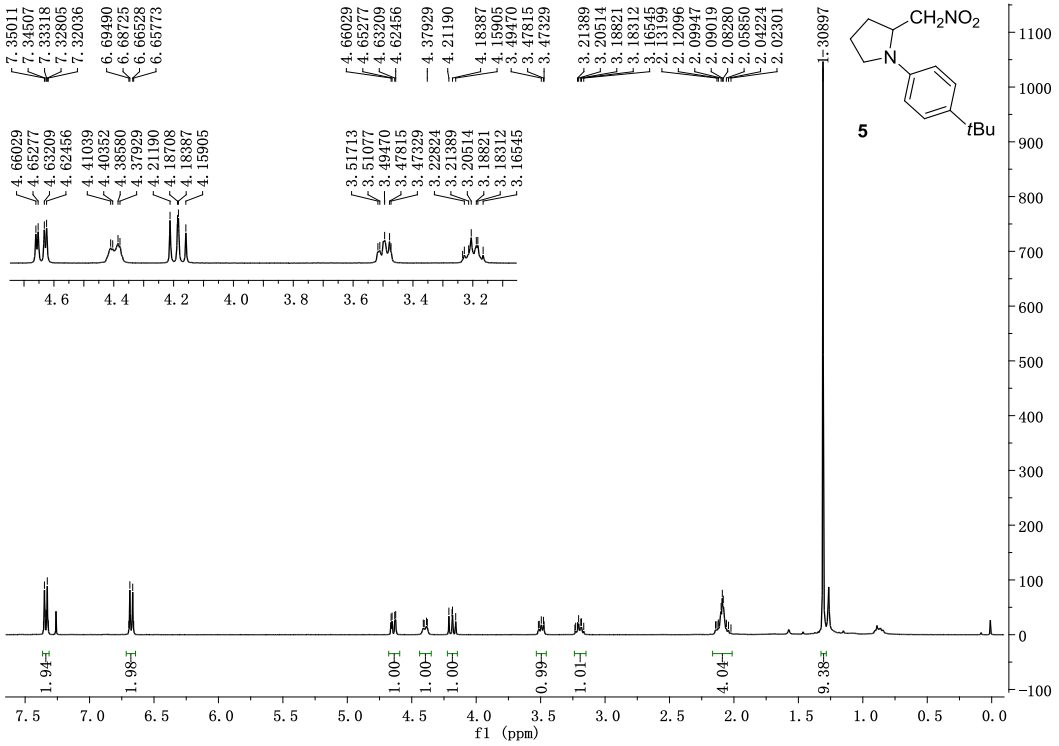
Ph
PO(OEt)2
3m
f1 (ppm)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3.18821
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2.08280
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2.04224
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1.30897
CH2NO2
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9.38
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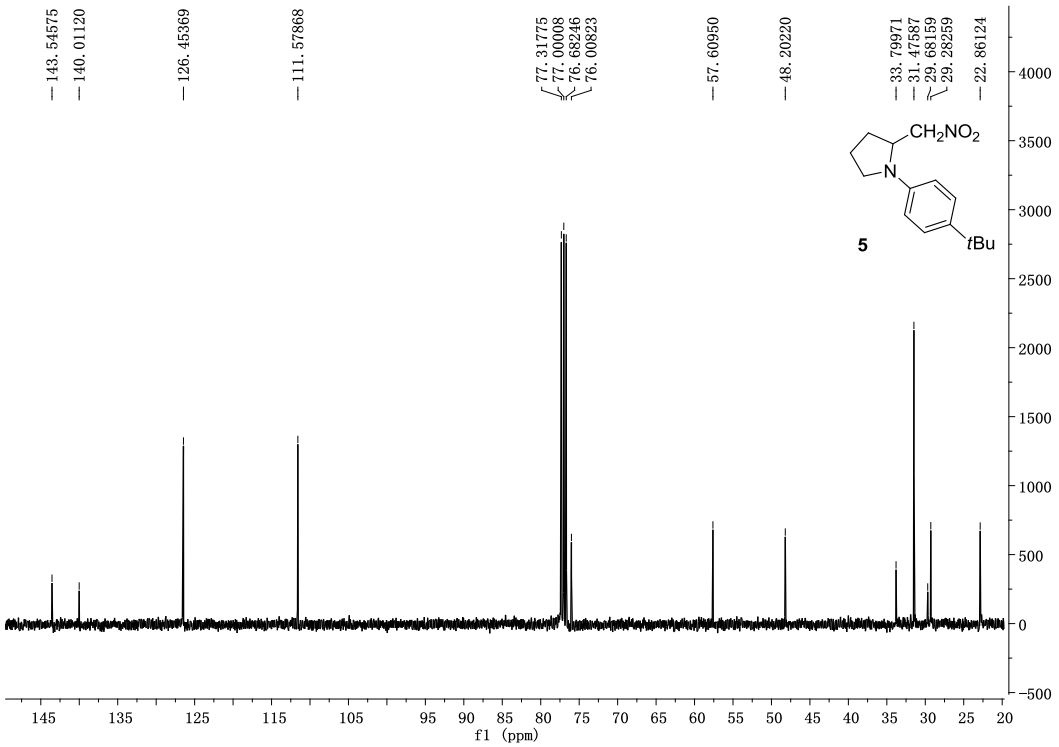
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22.86124
CH2NO2
N
5
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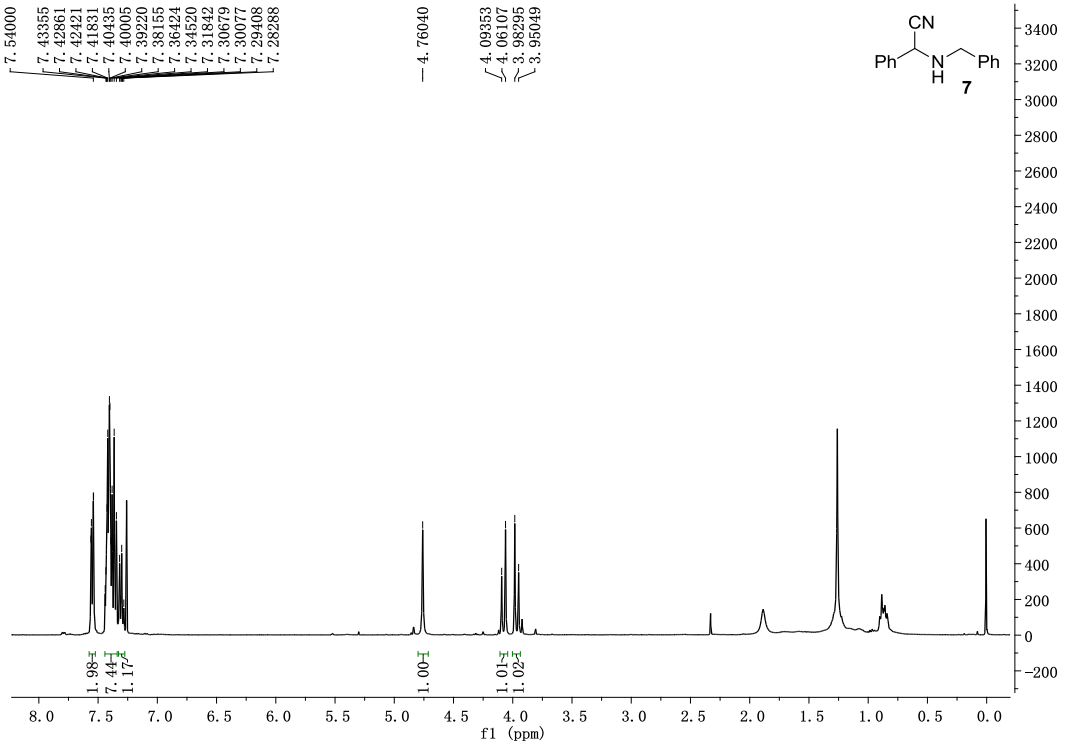
f1 (ppm)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7.41831
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7.40005
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7.36424
7.34520
7.31842
7.30679
7.30077
7.29408
7.28288
4.76040
4.09353
4.06107
3.98295
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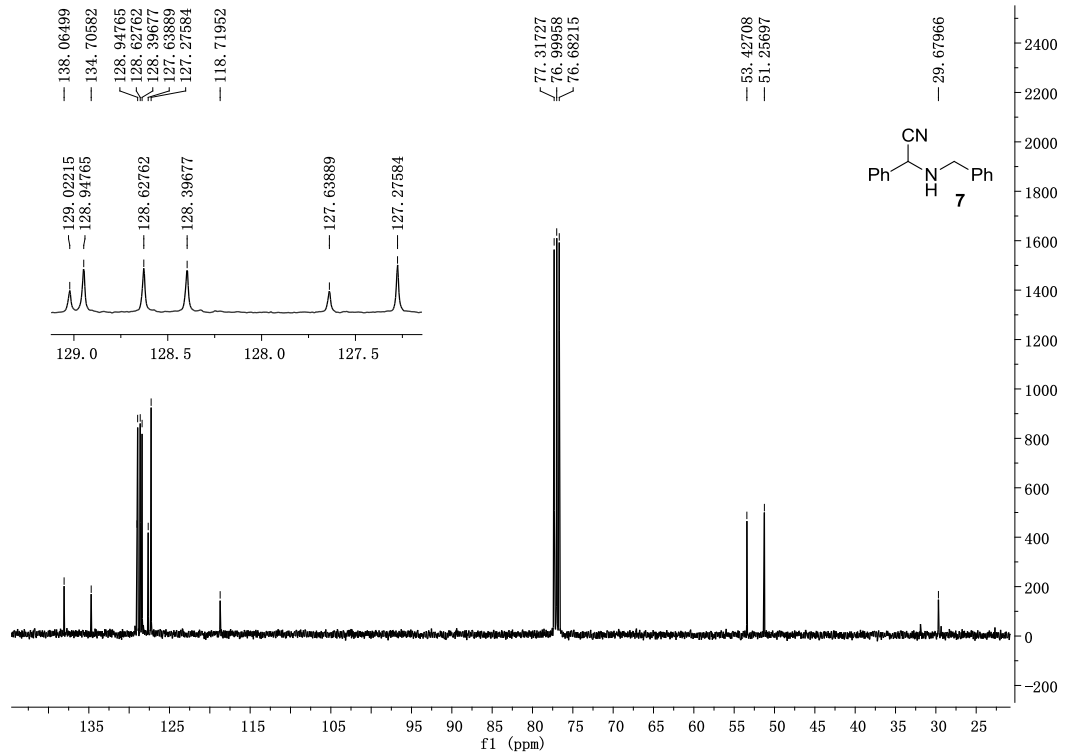
CN
Ph
N
H
Ph
7
1.98
7.44
1.17
1.00
1.01
1.02
f1 (ppm)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118.71952
77.31727
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76.68215
53.42708
51.25697
29.67966
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128.62762
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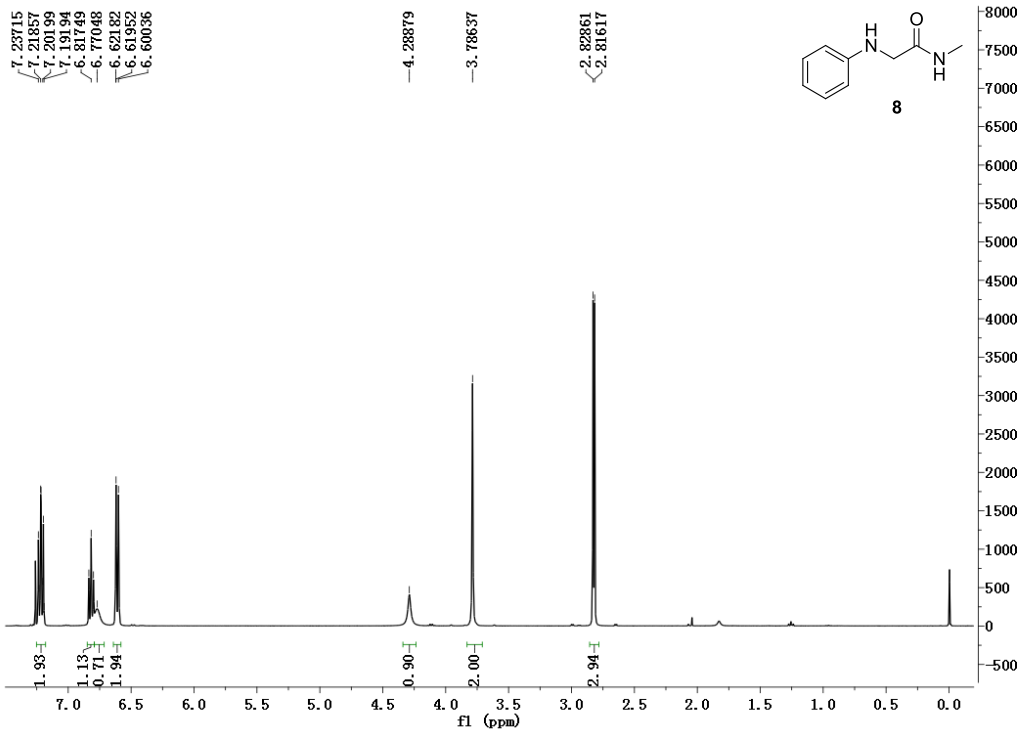
127.27584
CN
Ph
N
H
Ph
7
f1 (ppm)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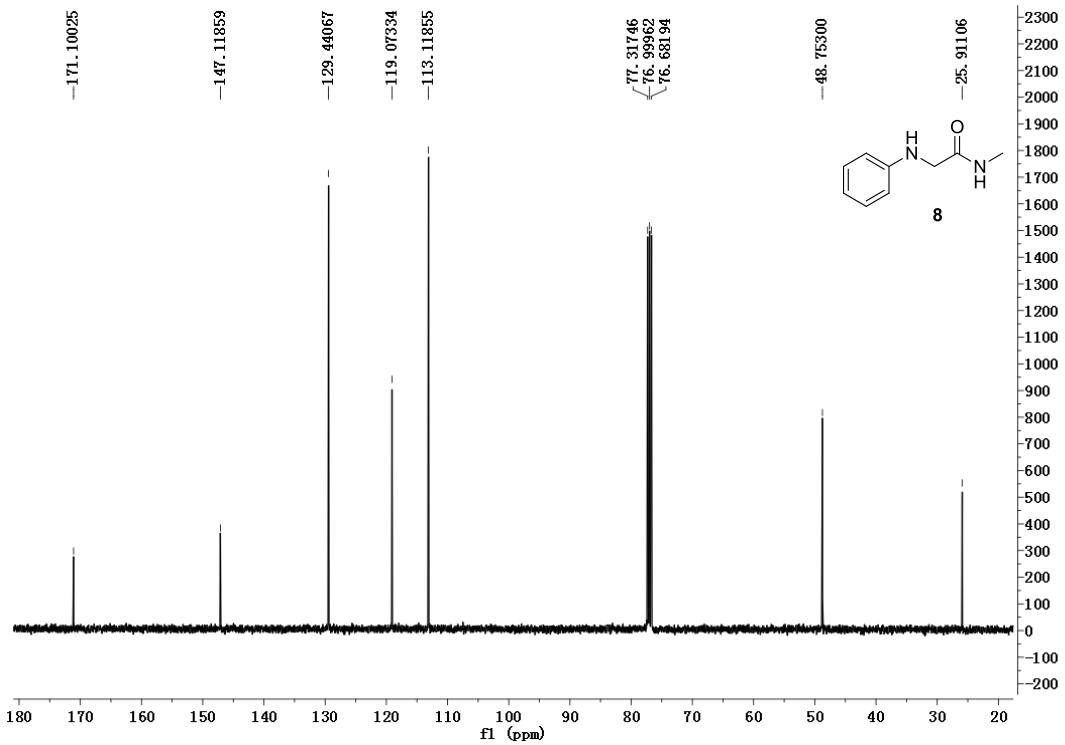
7.21857
7.20199
7.19194
6.81749
6.77048
6.62182
6.61952
6.60036
4.28879
3.78637
2.82861
2.81617
8
1.93
1.13
0.71
1.94
0.90
2.00
2.94
f1 (ppm)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147.11859
129.44067
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76.99962
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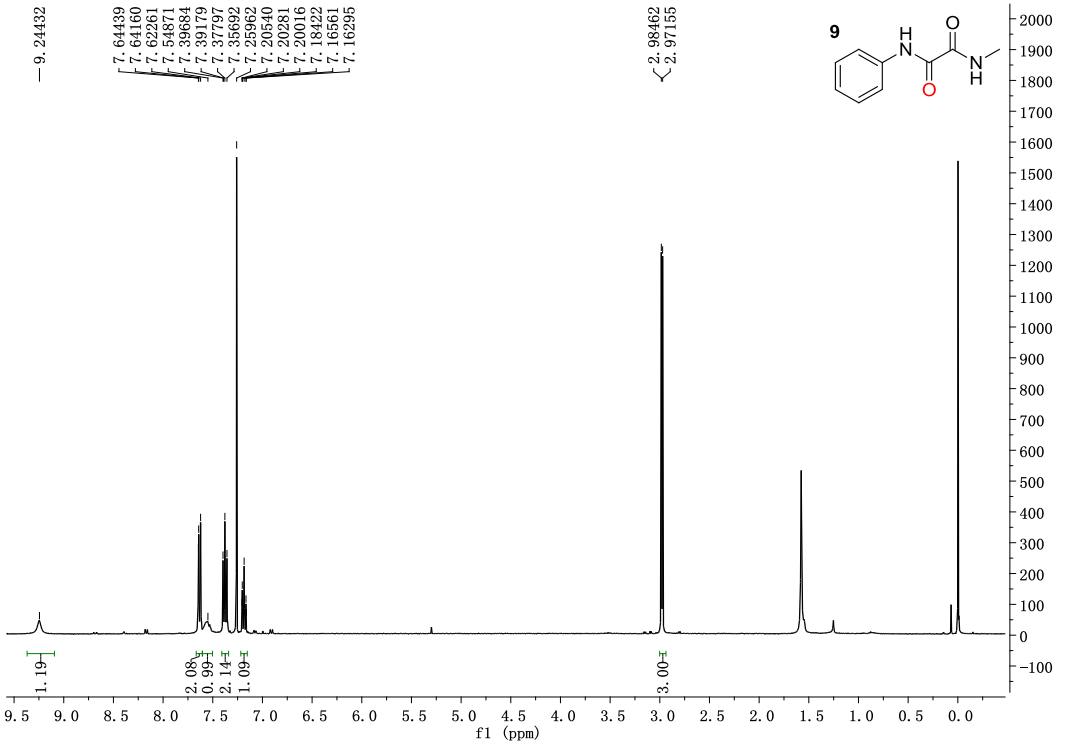
48.75300
25.91106
8
f1 (ppm)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7.20540
7.20281
7.20016
7.18422
7.16561
7.16295
2.98462
2.97155
9
H
N
O
O
N
H
1.19
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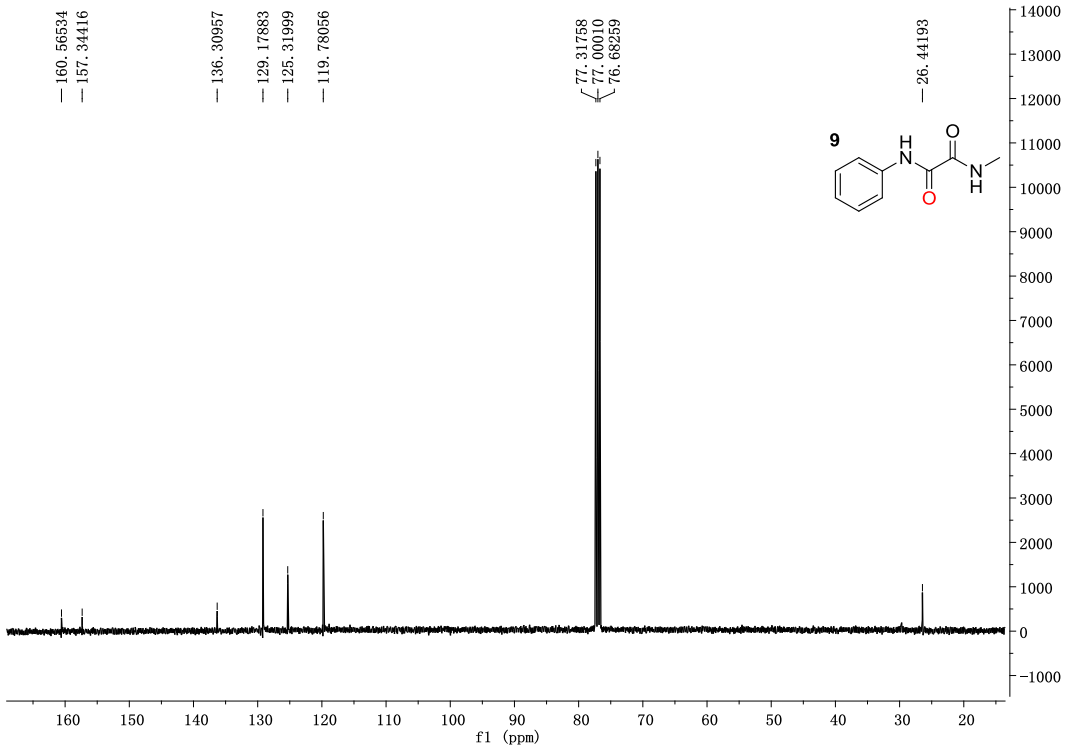
0.99
2.14
1.09
3.00
f1 (ppm)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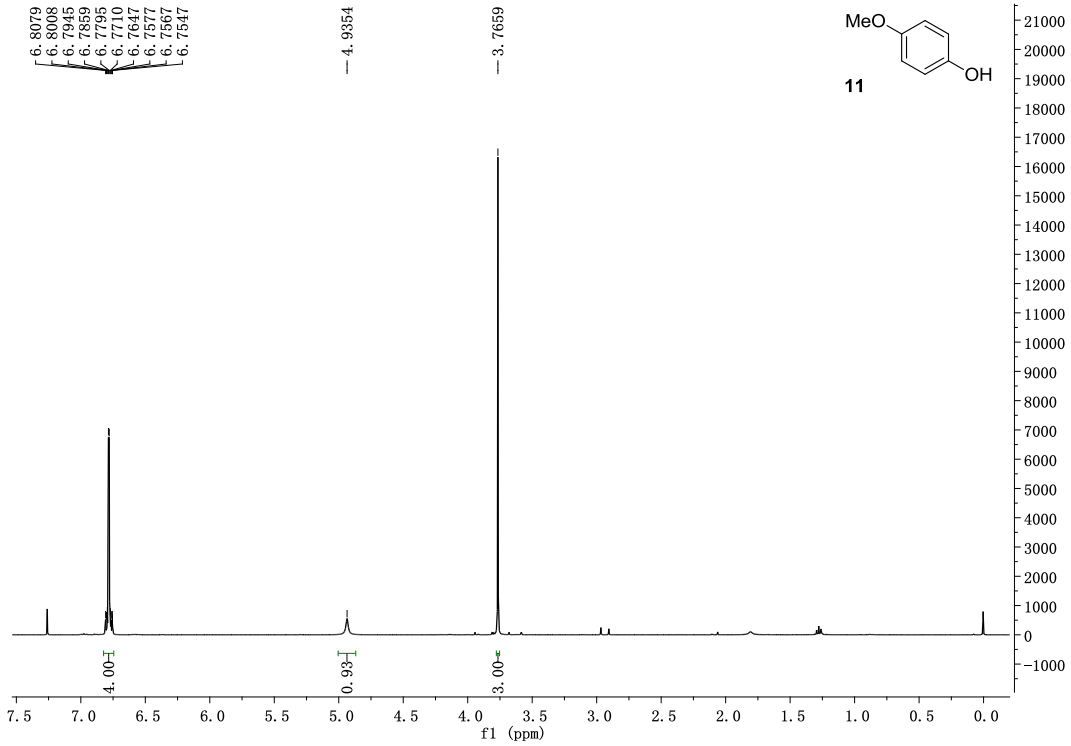
26.44193
9
H
N
O
O
N
H
f1 (ppm)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6.8008
6.7945
6.7859
6.7795
6.7710
6.7647
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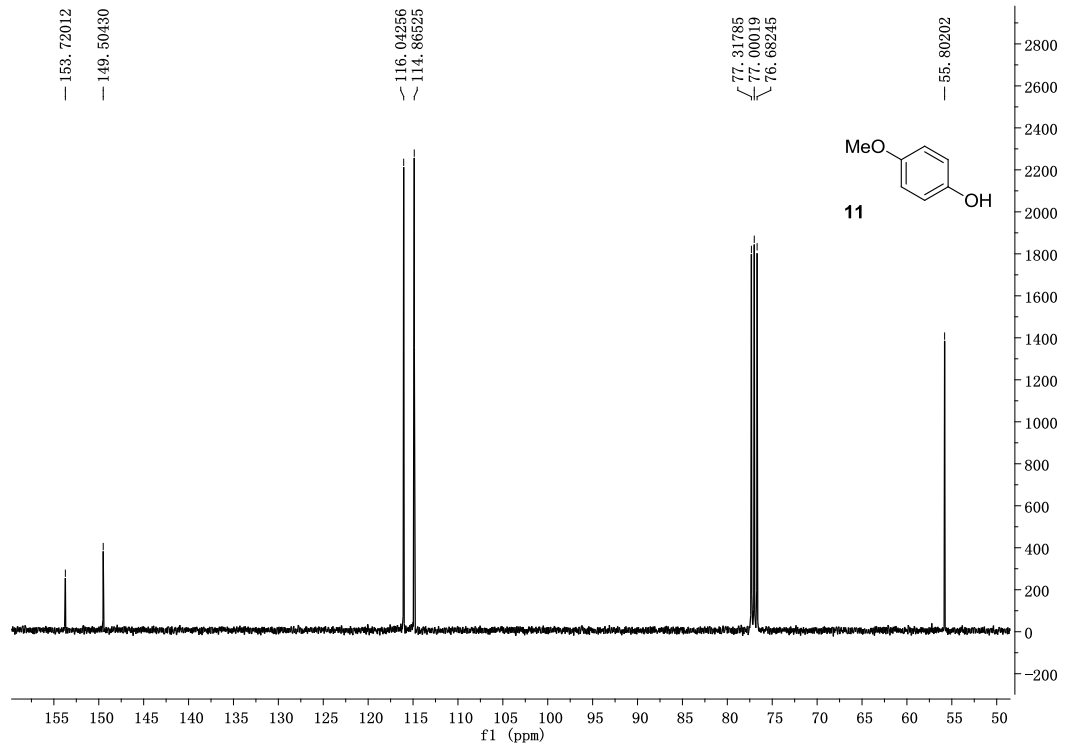
6.7567
6.7547
4.9354
3.7659
MeO
OH
11
4.00
0.93
3.00
f1 (ppm)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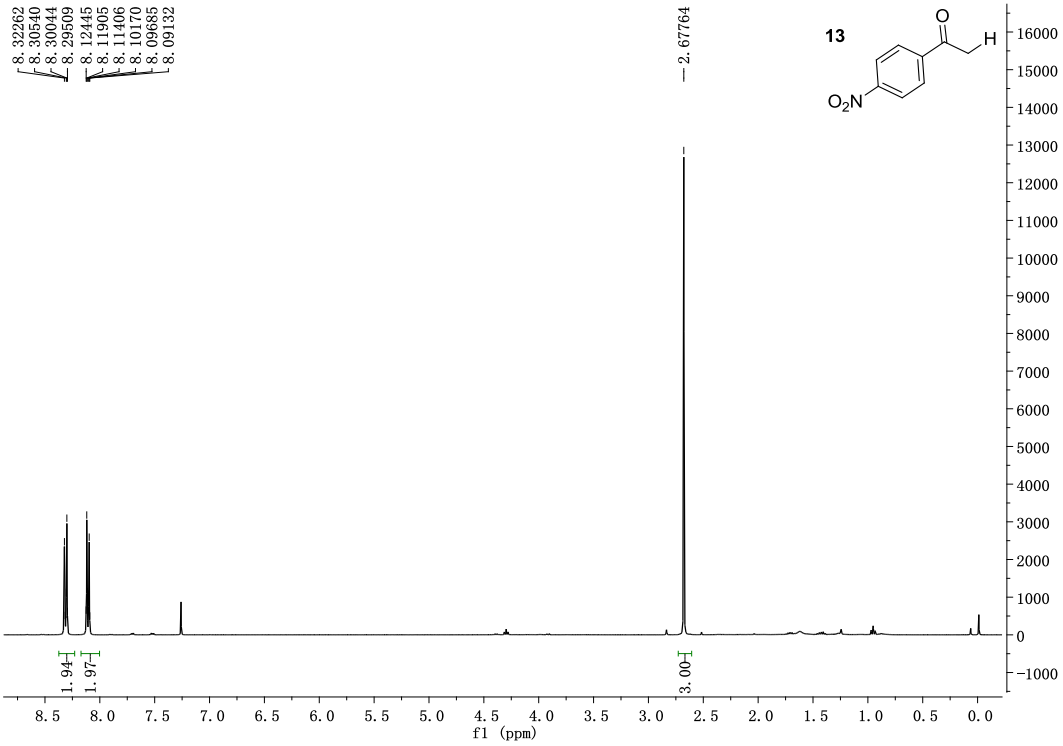
76.68245
55.80202
MeO
OH
11
f1 (ppm)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8.30540
8.30044
8.29509
8.12445
8.11905
8.11406
8.10170
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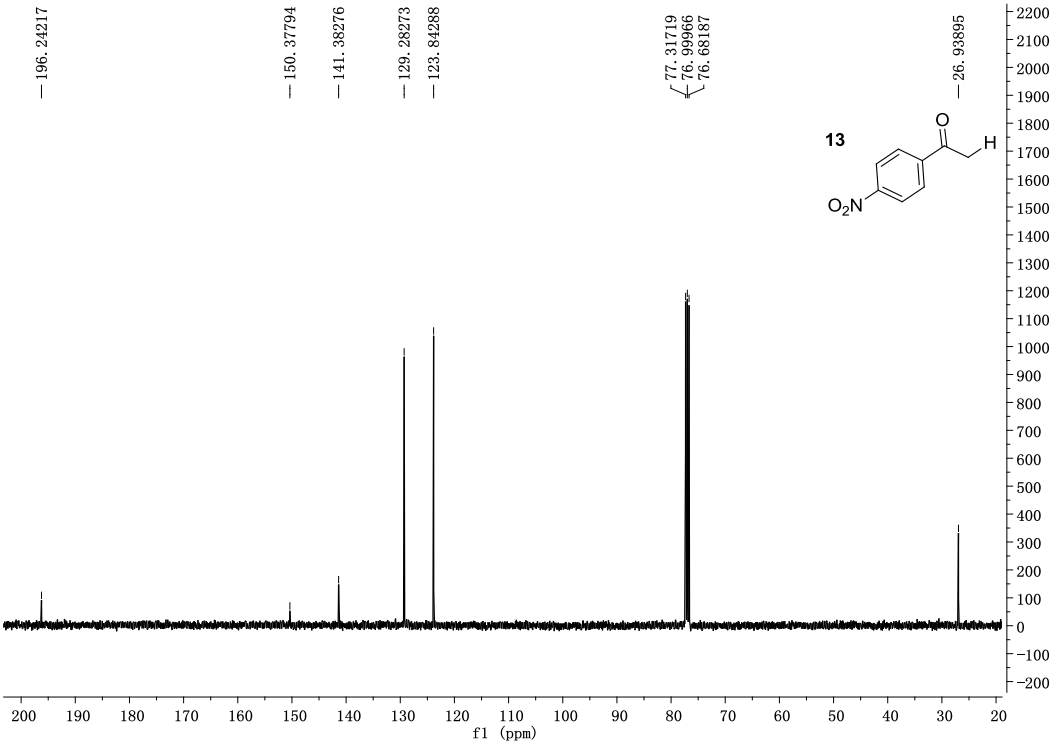
8.09132
2.67764
13
O
H
O2N
1.94
1.97
3.00
f1 (ppm)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150.37794
141.38276
129.28273
123.84288
77.31719
76.99966
76.68187
26.93895
13
O
H
O2N
f1 (ppm)