Electronic Supplementary Material (ESI) for ChemComm.

Supplementary Information for

Singlet excited state of BODIPY promoted aerobic cross-dehydrogenative-coupling reactions under visible light

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1. Experimental Details

a) General

^{1}H NMR spectra were recorded using a Bruker Avance DPX 400 MHz instrument with tetramethylsilane (TMS) as an internal standard. ^{13}C NMR spectra were obtained at 100 MHz and referenced to the internal solvent signals. Mass spectra were recorded using a Trio-2000 GC-MS spectrometer. Steady-state emission spectra were recorded using a Perkin–Elmer LS50B spectrofluorimeter. ESR spectra were recorded at room temperature using a Bruker ESP-300E spectrometer at 9.8 GHz, X-band, with 100 Hz field modulation. Samples were quantitatively injected into specially made quartz capillaries for ESR analysis before being purged with air in the dark and illuminated directly in the cavity of the ESR spectrometer with a Nd : YAG laser (532 nm 10 Hz repetition frequency, 10 mJ pulse energy). All reagents were weighed and handled in air unless special explain. Commercially available reagents and solvents were used without further purification. Commercially available reagents and solvents were used without further purification. All the *N*-aryltetrahydroisoquinolines **1** needed for CDC reactions were prepared by using the reported procedure[1,2] and purified through column chromatography. Irradiation with withe light was performed using withe LEDs (3W, 350 mA, radiometric power 80 mW).

b) Synthesis of B-1, B-2 and B-3[3,4]

To a solution 2,4-dimethyl-1H-pyrrole (0.19 g, 2 mmol) in DCM was added benzoyl chloride (0.14 g, 1 mmol). Reaction mixture was stirred over night at room temperature. Then add 0.5 mL $BF_3{\cdot}OEt_2$ and 0.5 mL Et_3N to the reaction system. Reaction mixture was stirred another over night at room temperature. Excess the DCM was removed under vacuum, and the residue was dissolved in ethyl acetate, washed with H_2O and dried over Na_2SO_4. The crude product was purified by flash chromatography (silica gel, eluent: PE/EtOAc = 40/1) to afford **B-1**. Get 0.129 g **B-1.** Yield 40%. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.55 – 7.47 (m, 3H), 7.34 – 7.30 (m, 2H), 6.01 (s, 2H), 2.59 (s, 6H), 1.40 (s, 6H) ppm.

The synthetic method reference reported works. Yields 35 %. **B-2**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.63 (s, 3H), 2.61 (s, 6H), 2.47 (s, 6H). ppm.

The synthetic method reference reported works. Yields 65 %. **B-3:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54–7.51 (m, 5H) 2.66 (s, 6H), 1.40 (s, 6H)

c) General Procedure for the Preparation of N-phenyl-tetrahydroisoquinolines[1,2]

Potassium phosphate (4.25 g, 20.0 mmol) and Copper (I) iodide (200 mg, 1.0 mmol) were put into a Schlenk-tube. The Schlenk-tube was evacuated and back filled with nitrogen. 2-Propanol (10.0 mL), ethylene glycol (1.11 mL, 20.0mmol), 1,2,3,4-tetrahydroisoquinoline (2.0 mL, 15.0 mmol) and iodobenzene (1.12 mL, 10.0 mmol) were added successively at room temperature. The reaction mixture was heated to 90 °C and kept for 24 h and then allowed to cool to room temperature. Diethyl ether (25 mL) and water (25 mL) were then added to the reaction mixture. The organic layer was extracted with diethyl ether (2 × 25 mL). The combined organic phases were washed with brine and dried over sodium sulfate. The solvent was removed by rotary evaporation and purified by column chromatography on silica gel using petroleum ether/ethyl acetate (20 : 1) as eluent.

d) General Procedure CDC Reaction

2-phenyl-1,2,3,4-tetrahydroisoquinoline (20.9 mg, 0.1 mmol), 2 mL CH_3NO_2 and **B-1** (0.001 mmol) were mixed in the reaction tube with magnetic stirring bar. The tube was irradiated by white LEDs for 3 h. After reaction the solvent was removed by rotary evaporation and purified by column chromatography on silica gel using petroleum ether/ethyl acetate (10:1) as eluent.

e) Thermodynamic Calculation

Determined oxidation potential of E_{ox} (**1a**) = 0.82 V, E_{red} (**B-1**) = -1.20 V and E_{00} = 2.46 eV (read from the cross-point of the absorption and luminescence spectra at 504 nm), the negative free energy change (ΔG = -0.80 eV) calculated by using the Rehm–Weller Equation (1).

$$\Delta G = E_{ox} - E_{red} - E_{00} \quad (1)$$

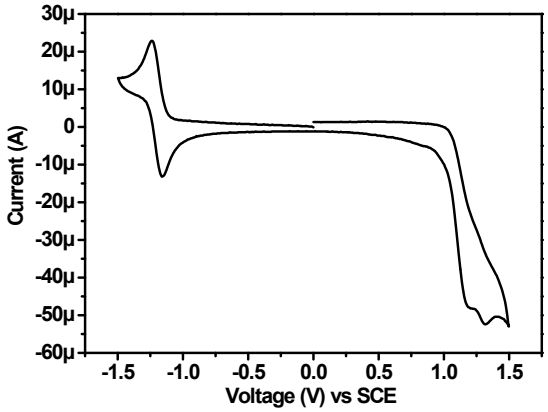


Figure S1 1 mM **B-1** and 0.1 M $TBAPF_6$ in CH_3CN with scan rate 100 mV/s

Table S1 The effect of solvents in C-P CDC reaction [a]

	Bodipy-1	conversion	time (h)	yield[b] (%)
CH_3CN	1 mol %	100%	5	0%
DCM	1 mol %	100%	5	50%
DMF	1 mol %	100%	5	0%
THF	1 mol %	100%	5	80%
MePh	1 mol %	100%	5	88%
MeOH	1 mol %	100%	5	96%

[a] Reaction conditions: 0.001 mmol **B-1** (1 mol %), **1a** 0.1 mmol and 0.1 mmol **6** in the reaction tube irradiated by white LEDs for 5 h. [b] Yields detected by NMR spectroscopy using an internal standard, diphenylacetonitrile.

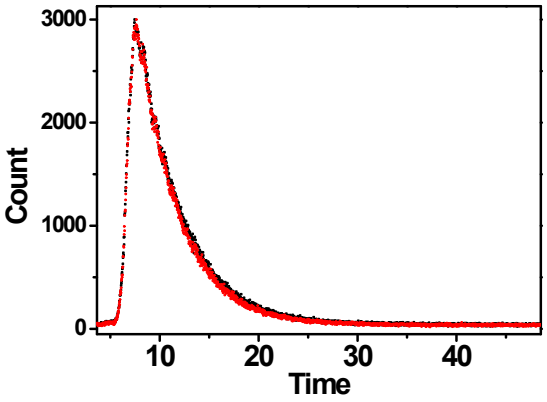


Figure S2. Fluorescent lifetime of **B-1** 1×10^{-5} M in MeOH solution in air present (red) and absent (black) of *N*-phenyltetrahydroisoquinoline **1a.**

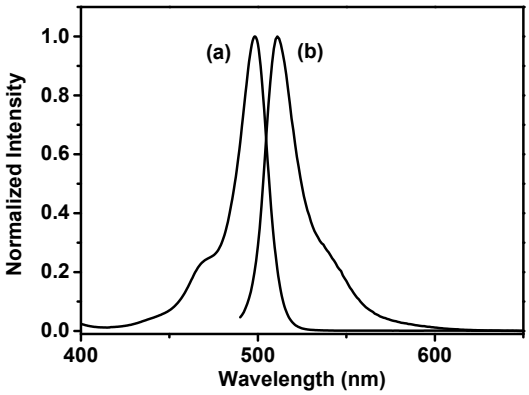


Figure S3. Absorption and fluorescence spectrum of **B-1** (1×10^{-5} M) in MeOH.

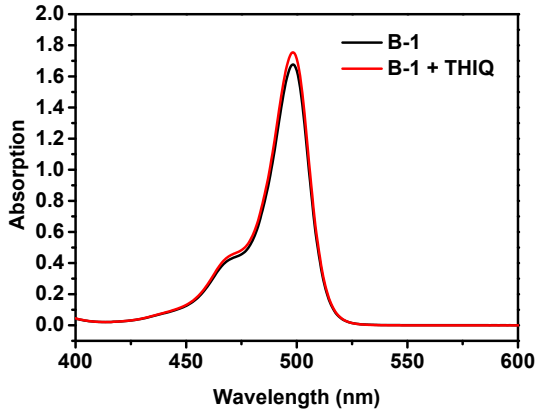
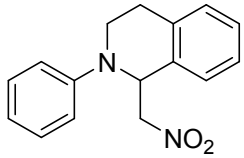


Figure S4 Absorption of 0.001 mmol **B-1** and 0.001mmol **B-1** (black) with 0.1 mmol THIQ in 3 mL MeOH. This can exclude formation of electron-donor-acceptor complexes (EDA) in reaction system.

2. Characterization of All Compounds

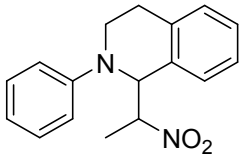
1-Nitromethyl-2-phenyl-1,2,3,4-tetrahydroisoquinoline



3a

Purified by column chromatography on silica gel (eluting with hexane/ethyl acetate = 5:1, R_f = 0.5). Melting point is 90 - 91 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.30 – 7.10 (m, 6H), 6.97 (d, *J* = 8.0 Hz, 2H), 6.84 (t, *J* = 7.3 Hz, 1H), 5.54 (t, *J* = 7.2 Hz, 1H), 4.86 (dd, *J* = 11.8, 7.8 Hz, 1H), 4.55 (dd, *J* = 11.8, 6.7 Hz, 1H), 3.71 – 3.56 (m, 2H), 3.08 (m, 1H), 2.78 ppm (dt, *J* = 16.3, 5.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 148.4, 135.3, 132.9, 129.5, 129.2, 128.1, 127.0, 126.7, 119.4, 115.1, 78.8, 58.2, 42.1, 26.5 ppm. EI-MS m/z (%): 268 (43) [M+], 208 (100), 77 (5).

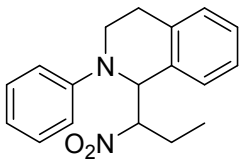
1-(1-Nitroethyl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline



3b

Purified by column chromatography on silica gel (eluting with hexane/ethyl acetate = 5:1, R_f= 0.6). Orange oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.32 – 7.07 (m, 6H), 7.01 - 6.98 (m, 2H), 6.84 - 6.77 (m, 1H), 5.24 (t, *J* = 8.8 Hz, 1H), [5.08 – 5.01 (m), 4.90 – 4.86 (m) 1H], [3.85 – 3.81 (m), 3.60 – 3.55 (m) 2H], [3.12 – 2.98 (m), 2.97 – 2.80 (m), 2H], [1.69 (d, *J* = 6.8 Hz), 1.53 (d, *J* = 6.7 Hz), 3H] ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 149.2, 148.9, 135.6, 134.8, 133.8, 129.4, 129.3, 129.1, 128.7, 128.3, 128.2, 127.3, 126.6, 126.1, (119.3, 118.8), (115.4, 114.5), (88.9, 85.4), (62.7, 61.1), (43.5, 42.7), (26.8, 26.4), (17.4, 16.4) ppm; EI-MS m/z (%): 282 (17) [M^+], 208 (100), 104 (46), 77 (55).

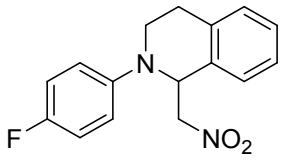
1-(1-Nitropropyl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline



3c

Purified by column chromatography on silica gel (eluting with hexane/ethyl acetate = 5:1, R_f = 0.5). Orange oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.36 – 7.09 (m, 6H), 7.04 – 6.89 (m, 2H), 6.86 – 6.72 (m, 1H), [5.23 (d, *J* = 9.3 Hz), 5.12 (d, *J* = 9.5 Hz) 1H], [4.89 – 4.83 (m), 4.70 – 4.64 (m) 1H], [3.88 – 3.81 (m), 3.69 – 3.49 (m) 2H], [3.11 – 3.03 (m), 2.94 – 2.83 (m), 2H], [2.28 – 2.03 (m), 1.85 – 1.79 (m) 2H], 0.96 – 0.91 ppm (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 149.1, 149.0, 135.5, 134.7, 132.6, 129.5, 129.4, 129.4, 129.3, 129.2, 128.7, 128.6, 128.2, 127.2, 126.6, 125.9, (119.4, 118.6), (115.9, 114.1), (96.1, 93.0), (62.2, 60.7), (43.5, 42.3), (26.8, 25.7), (25.0, 24.6), 10.7 ppm; EI-MS m/z (%): 296 (36) [M^+], 209 (100), 115 (78), 104 (82), 77 (81).

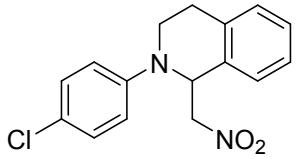
2-(4-Fluorophenyl)-1-nitromethyl-1,2,3,4-tetrahydroisoquinoline



3d

Purified by column chromatography on silica gel (eluting with hexane/ethyl acetate = 6:1, R_f = 0.5). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.34 – 7.04 (m, 4H), 7.00 – 6.83 (m, 4H), 5.42 (dd, *J* = 8.8, 6.0 Hz, 1H), 4.82 (dd, *J* = 12.0, 8.6 Hz, 1H), 4.56 (dd, *J* = 12.0, 5.8 Hz, 1H), 3.67 – 3.53 (m, 2H), 3.02 (m, 1H), 2.71 ppm (dt, *J* = 16.5, 4.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 157.2 (d, $J_{C\text{-}F}$ = 237.8 Hz), 145.3, 135.2, 132.6, 129.4, 128.1, 127.0, 126.8, 126.7, 117.9 (d, $J_{C\text{-}F}$ = 7.4 Hz), 115.8 (d, $J_{C\text{-}F}$ = 22.2 Hz), 78.9, 58.7, 42.8, 28.6, 25.81 ppm; HRMS (EI): calcd for $C_{16}H_{15}FN_2O_2$: 286.1118; found: 286.1117.

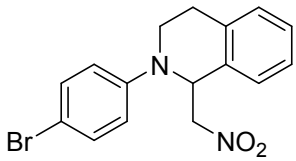
2-(4-Chlorophenyl)-1-nitromethyl-1,2,3,4-tetrahydroisoquinoline



3e

Purified by column chromatography on silica gel (eluting with hexane/ethyl acetate = 6:1, R_f = 0.3). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.43 – 7.07 (m, 6H), 6.88 (d, *J* = 9.0 Hz, 2H), 5.48 (dd, *J* = 8.1, 6.4 Hz, 1H), 4.83 (dd, *J* = 11.9, 8.2 Hz, 1H), 4.55 (dd, *J* = 12.0, 6.3 Hz, 1H), 3.68 – 3.51 (m, 2H), 3.05 (ddd, *J* = 15.4, 8.5, 6.2 Hz, 1H), 2.77 ppm (dt, *J* = 16.4, 4.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 147.1, 135.0, 132.5, 129.3, 128.2, 126.9, 126.8, 124.4, 116.5, 78.6, 58.2, 42.2, 26.1 ppm; EIMS: m/z(%): 302 (94) [M^+] , 244 (100), 149(64), 115 (72), 111 (50), 77 (14).

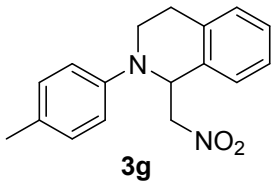
2-(4-Bromophenyl)-1-nitromethyl-1,2,3,4-tetrahydroisoquinoline



3f

Purified by column chromatography on silica gel (eluting with hexane/ethyl acetate = 6:1, R_f = 0.5). Orange oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.34 (d,*J* = 9.1 Hz, 2 H), 7.29 – 7.06 (m, 4H), 6.88 – 6.81 (m, 2H), 5.47 (t, *J* = 8.0 Hz, 1 H), 4.83 (dd, *J*=12.1, 8.1, 1H), 4.56 (dd, *J*=11.9, 6.4, 1H), 3.67 – 3.54 (m, 2H), 3.12 – 3.01 (m, 1H), 2.78 (dt, *J*=16.1, 4.8, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 147.5, 135.0, 132.4, 132.2, 129.2, 128.2, 126.9, 126.7, 116.7, 111.5, 78.6, 58.0, 42.0, 26.1 ppm; EIMS: m/z(%): 348 (62), 346 (65) [M^+] , 288(100), 118 (99), 90 (25), 77 (12).

1-Nitromethyl-2-p-tolyl-1,2,3,4-tetrahydroisoquinoline

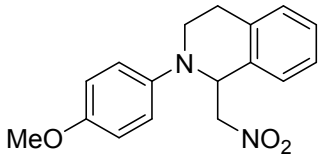


3g

Purified by column chromatography on silica gel (eluting with hexane/ethyl acetate = 6:1, R_f = 0.5). White oil.; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.27 – 7.09 (m, 4H), 7.06 (d, *J* = 8.3 Hz, 2H), 6.86 (d, *J* = 8.3 Hz, 2H), 5.48 (dd, *J* = 8.0, 6.4 Hz, 1H), 4.82 (dd, *J* = 11.8, 8.1 Hz, 1H), 4.53 (dd, *J* = 11.8, 6.3 Hz, 1H), 3.66 – 3.48 (m, 2H),

3.08 – 3.0 (m, 1H), 2.72 (dt, *J* = 16.4, 4.6 Hz, 1H), 2.25 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 146.4, 135.3, 133.0, 130.0, 129.3, 129.1, 128.0, 127.0, 126.6, 115.9, 78.8, 58.4, 42.3, 26.2, 20.4 ppm; EI-MS m/z (%): 282 (60) [M^+], 222 (100), 118 (64), 91 (66), 77(12).

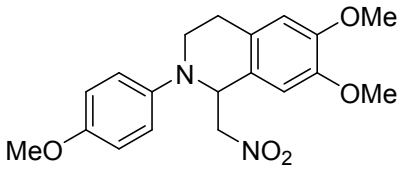
2-(4-Methoxyphenyl)-1-nitromethyl-1,2,3,4-tetrahydroisoquinoline



3h

Purified by column chromatography on silica gel (eluting with hexane/ethyl acetate = 5:1, R_f = 0.4). Orange oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.28 – 7.11 (m, 4H), 6.91 (d, *J* = 9.0 Hz, 2H), 6.81 (d, *J* = 9.2 Hz, 2H), 5.38 (dd, *J* = 8.7, 5.9 Hz, 1H), 4.82 (dd, *J* = 11.9, 8.6 Hz, 1H), 4.55 (dd, *J* = 11.9, 5.8 Hz, 1H), 3.74 (s, 3H), 3.62 – 3.47 (m, 2H), 3.05 – 2.96 (m, 1H), 2.68 ppm (dt, *J* = 16.5, 4.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 154.0, 143.0, 135.4, 132.9, 129.4, 127.9, 126.9, 126.6, 118.8, 114.7, 78.9, 58.9, 55.6, 43.1, 25.8 ppm. EI-MS m/z (%): 298 (73) [M^+], 239 (100), 223 (55), 115 (50), 91(12), 77 (18) .

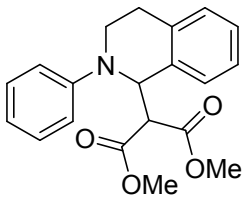
6,7-Dimethoxy-2-(4-methoxyphenyl)-1-nitromethyl-1,2,3,4-tetrahydroisoquinoline



3i

Purified by column chromatography on silica gel (eluting with hexane/ethyl acetate = 4:1, R_f = 0.4). Orange oil. ^{1}H NMR (400 MHz, Acetone-d_6) δ= 6.99 (s, 1H), 6.94 (d, *J* = 9.1 Hz, 2H), 6.79 (d, *J* = 9.1 Hz, 2H), 6.72 (s, 1H), 5.36 (dd, *J* = 8.9, 5.9 Hz, 1H), 5.00 – 4.90 (m, 2H), 3.80 (s, 3H), 3.77 (s, 3H), 3.70 (s, 3H), 3.67 – 3.58 (m, 2H), 2.91 – 2.85 (m, 1H), 2.52 ppm (dt, *J* = 16.5, 3.2 Hz, 1H); ^{13}C NMR (100 MHz, Acetone) δ = 154.3, 149.4, 148.5, 143.9, 128.1, 124.9, 119.3, 115.7, 114.8, 112.9, 111.2, 78.9, 55.6, 55.5, 55.2, 55.0, 42.8, 24.4 ppm. EI-MS: m/z (%): 358 (78) [M^+] , 298 (92),296 (100), 282 (80), 254 (39), 149 (42), 77 (8).

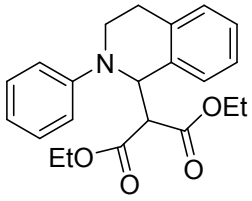
Dimethy 2-(2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)malonate



5a

Purified by column chromatography on silica gel (eluting with hexane/ethyl acetate = 5:1, R_f = 0.4). Orange oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.32 – 7.06 (m, 7H), 6.99 (d, *J*=8.1, 2H), 6.77 (t, *J*=7.3, 1H), 5.71 (d, *J*=9.4, 1H), 3.96 (d, *J*=9.4, 1H), 3.78 – 3.58 (m, 5H), 3.55 (s, 3H), 3.08 (ddd, *J*=15.6, 8.9, 6.3, 1H), 2.87 (dt, *J*=16.5, 5.1, 1H) ppm ; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 168.6, 167.7, 149.1, 136.0, 135.1, 129.4, 129.3, 128.0, 127.4, 126.4, 119.0, 115.5, 59.4, 58.5, 52.9, 42.5, 26.4 ppm; EIMS:m/z (%): 339 (47) [M+] , 209 (100), 193 (56), 115(66), 77(74).

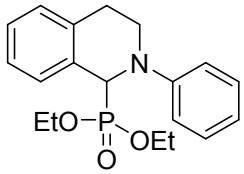
Diethyl 2-(2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)malonate



5b

Purified by column chromatography on silica gel (eluting with hexane/ethyl acetate = 5:1, R_f = 0.4). Orange oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.26 – 7.07 (m, 6H), 6.98 (d, *J* = 8.3 Hz, 2H), 6.75 (t, *J* = 7.2 Hz, 1H), 5.72 (d, *J* = 9.2 Hz, 1H), 4.28 – 3.93 (m, 4H), 3.90 (d, *J* = 9.2 Hz, 1H), 3.77 – 3.57 (m, 2H), 3.07 (ddd, *J* = 15.5, 8.9, 6.2 Hz, 1H), 2.88 (dt, *J* = 16.4, 5.1 Hz, 1H), 1.17 (t, *J* = 7.1 Hz, 3H), 1.09 ppm (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 167.9, 167.1, 148.8, 135.9, 134.8, 129.0, 128.8, 127.5, 127.2, 126.0, 118.4, 115.1, 61.5, 61.5, 59.5, 57.8, 42.3, 26.1, 13.9, 13.8 ppm; HRMS (ESI): calcd. for $C_{22}H_{26}NO_4$ $[M + H]^+$ 368.1862; found 368.1858.

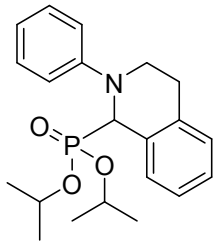
Diethyl (2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)phosphonate



7a

Purified by column chromatography on silica gel (eluting with hexane/ethyl acetate = 5:1, R_f = 0.4). Orange oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.40 – 7.35 (m, 1H), 7.27 – 7.15 (m, 5H), 6.98 (d, *J* = 8.2 Hz, 2H), 6.79 (t, *J* = 7.3 Hz, 1H), 5.19 (d, *J* = 20.0 Hz, 1H), 4.12 – 3.86 (m, 5H), 3.65 – 3.59 (m, 1H), 3.12 – 2.94 (m, 2H), 1.25 (t, *J* = 7.1 Hz, 3H), 1.14 ppm (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 149.4 (d, *J* = 6 Hz), 136.6 (d, *J* = 5.3 Hz), 130.8, 129.0 (d, *J* = 2.5 Hz) (d, *J* = 4.3 Hz), 127.7 (d, *J* = 3.7 Hz), 125.9 (d, *J* = 2.6 Hz), 118.6, 114.9, 63.5 (d, *J* = 7.1Hz) 62.4 (d, *J* = 7.6 Hz), 59.7 (d, *J* = 158.3 Hz), 43.6, 26.8, 16.6 (d, *J* = 5.5 Hz), 16.4(d, *J* = 6.1 Hz) ppm. HRMS (ESI): calcd. for $C_{19}H_{24}NNaO_3P$ $[M + Na]^+$ 368.1391; found 386.1387.

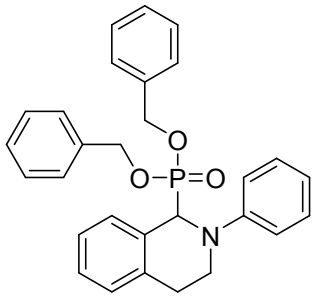
Diisopropyl (2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)phosphonate



7b

Purified by column chromatography on silica gel (eluting with hexane/ethyl acetate = 5:1, R_f = 0.4). Orange oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.40 (d, *J* = 6.7 Hz, 1H), 7.23 – 7.10 (m, 5H), 6.95 (d, *J* = 8.3 Hz, 2H), 6.76 (t, *J* = 7.2 Hz, 1H), 5.14 (d, *J* = 21.2 Hz, 1H), 4.62 – 4.55 (m, 2H), 4.13 – 3.98 (m, 1H), 3.67 – 3.60 (m, 1H), 3.09 – 2.90 (m, 2H), 1.38 – 1.24 (m, 6H), 1.16 (d, *J* = 6.2 Hz, 3H), 0.94 ppm (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 149.6 (d, *J* = 6.6 Hz), 136.5 (d, *J* = 5.5 Hz), 130.0 (d, *J* = 1.9 Hz), 128.8 (d, *J* = 2.5 Hz), 128.5 (d, *J* = 4.6 Hz), 127.3 (d, *J* = 3.4 Hz), 125.7 (d, *J* = 2.8 Hz), 118.4 , 115.1 , 72.3 (d, *J* = 7.8 Hz), 70.0 (d, *J* = 8.2 Hz), 59.0 (d, *J* = 200 Hz), 43.6 , 31.0 , 26.7 , 24.7 (d, *J* = 2.8 Hz), 24.2 (d, *J* = 3.2 Hz), 23.8 (d, *J* = 5.6 Hz), 23.4 ppm (d, *J* = 5.6 Hz); HRMS (ESI): calcd. for $C_{19}H_{24}NNaO_3P$ $[M + H]^+$ 374.1885; found 374.1882.

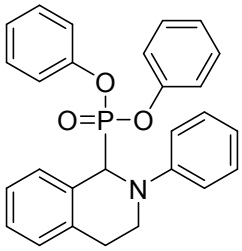
Dibenzyl (2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)phosphonate



7c

Purified by column chromatography on silica gel (eluting with hexane/ethyl acetate = 5:1, R_f = 0.4). Orange oil. ^{1}H NMR (400 MHz, Acetone) δ = 7.44 (d, *J* =7.5, 1H), 7.35 – 7.13 (m, 15H), 7.06 (d, *J*=8.3, 2H), 6.75 (t, *J*=7.2, 1H), 5.44 (d, *J*=20.4, 1H), 5.08 – 5.00 (m, 1H), 4.99 – 4.86 (m, 2H), 4.82 (dd, *J*=11.9, 7.8, 1H), 4.08 (ddd, *J*=13.1, 8.7, 4.8, 1H), 3.72 – 3.63 (m, 1H), 3.09 (ddd, *J*=15.9, 7.9, 5.1, 1H), 3.02 – 2.92 ppm (m, 1H); ^{13}C NMR (100 MHz, Acetone) δ = 150.2 (d, *J* = 10 Hz), 137.9 (dd, *J* = 10.0, 5.8 Hz), 137.6 (d, *J* = 5.5 Hz), 130.5 (d, *J* = 10 Hz), 129.5 (d, *J* = 2.6 Hz), 129.4 , 129.3 , 129.3 , 129.2 , 129.0 , 128.9 , 128.8 , 128.7 , 128.3 (d, *J* = 3.5 Hz), 126.7 (d, *J* = 2.8 Hz), 119.2 , 115.8 , 68.9 (d, *J* = 7.1 Hz), 68.1 (d, *J* = 7.6 Hz), 59.3 (d, *J* = 150 Hz) , 44.3, 27.4 ppm; HRMS (ESI): calcd. for $C_{29}H_{29}NO_3P$ $[M + H]^+$ 470.1885; found 470.1882.

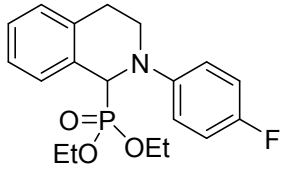
Diphenyl (2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)phosphonate



7d

Purified by column chromatography on silica gel (eluting with hexane/ethyl acetate = 5:1, R_f = 0.4). Orange oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.52 (d, *J* = 7.4 Hz, 1H), 7.30 – 6.99 (m, 15H), 6.85 (dd, *J* = 15.2, 7.6 Hz, 3H), 5.59 (d, *J* = 19.9 Hz, 1H), 4.06 (ddd, *J* = 13.1, 8.5, 5.1 Hz, 1H), 3.73 – 3.60 (m, 1H), 3.04 ppm (dt, *J* = 11.3, 6.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.8 (d, *J* = 10.4 Hz), 150.4 (d, *J* = 11.3 Hz), 149.2 (d, *J* = 6.8 Hz), 136.7 (d, *J* = 5.9 Hz), 129.6 , 129.4 , 129.2 , 129.0 (d, *J* = 2.8 Hz), 128.4 (d, *J* = 5.0 Hz), 127.9 (d, *J* = 3.8 Hz), 126.2 (d, *J* = 3.1 Hz), 125.0 (d, *J* = 1.2 Hz), 124.8 , 120.6 (d, *J* = 4.1 Hz), 120.3 (d, *J* = 4.2 Hz), 119.1 , 115.5 , 59.9 , 58.4 , 44.0 , 26.6 ppm .; HRMS (ESI): calcd. for $C_{27}H_{28}N_2O_3P$ $[M + Na]^+$ 459.1838; found 459.1833.

Diethyl(2-(4-fluorophenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)phosphonate

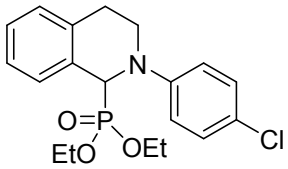


7e

Purified by column chromatography on silica gel (eluting with hexane/ethyl acetate = 5:1, R_f = 0.3). Orange oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.37 (d, *J* = 6.7 Hz, 1H), 7.24 – 7.11 (m, 3H), 6.98 – 6.88 (m, 4H), 5.06 (d, *J* = 20.3 Hz, 1H), 4.15 – 3.85 (m, 5H), 3.59 – 3.48 (m, 1H), 3.10 – 2.88 (m, 2H), 1.24 (t, *J* = 7.1 Hz, 3H), 1.15

ppm (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 156.4 (d, *J* = 238.0 Hz) , 146.2 (dd, *J* = 6.6, 2.0 Hz), 136.3 (d, *J* = 5.6 Hz), 130.4 , 128.8 (d, *J* = 2.6 Hz), 128.2 (d, *J* = 4.6 Hz), 127.5 (d, *J* = 3.5 Hz), 125.9 (d, *J* = 2.9 Hz), 116.6 (d, *J* = 7.4 Hz), 115.5 (d, *J* =16.0 Hz) , 63.3 (d, *J* = 7.3 Hz), 62.4 (d, *J* = 7.7 Hz), 59.35 (d, *J* = 159.0 Hz), 44.3 , 26.6 , 16.4 ppm (dd, *J* = 8.4, 5.7 Hz); HRMS (ESI): calcd. for $C_{19}H_{23}FNNaO_3P$ $[M + Na]^+$ 386.1297; found 386.1293.

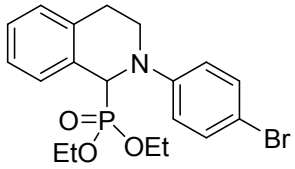
Diethyl(2-(4-chlorophenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)phosphonate



7f

Purified by column chromatography on silica gel (eluting with hexane/ethyl acetate = 5:1, R_f = 0.3). Orange oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.35 (d, *J* = 7.0 Hz, 1H), 7.25 – 7.12 (m, 5H), 6.89 (d, *J* = 9.0 Hz, 2H), 5.10 (d, *J* = 19.3 Hz, 1H), 4.17 – 3.80 (m, 6H), 3.55 (m, 1H), 3.10 (m, 1H), 2.95 (m, 1H), 1.23 (t, *J* = 7.1 Hz, 4H), 1.14 ppm (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 147.9 (d, *J* = 5.1 Hz), 136.3 (d, *J* = 5.4 Hz), 130.4 , 128.9 , 128.6 (d, *J* = 2.7 Hz), 128.1 (d, *J* = 4.8 Hz), 127.6 (d, *J* = 3.5 Hz), 126.0 (d, *J* = 2.8 Hz), 123.1 , 118.2 (d, *J* = 2.1 Hz), 115.7 , 107.5 , 63.2 (d, *J* = 7.3 Hz), 62.4 (d, *J* = 7.7 Hz), 58.8 (d, *J* = 159.6 Hz) , 43.7 , 26.9 , 16.4 (d, J = 5.5 Hz), 16.3 ppm (d, *J* = 5.5 Hz); HRMS (ESI): calcd. for $C_{19}H_{23}ClNNaO_3P$ $[M + Na]^+$ 402.1002; found 402.0997.

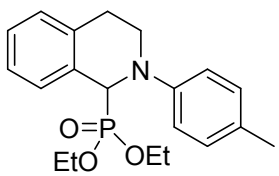
Diethyl(2-(4-bromophenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)phosphonate



7g

Purified by column chromatography on silica gel (eluting with hexane/ethyl acetate = 5:1, R_f = 0.3). Orange oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.38 – 7.29 (m, 4H), 7.25 – 7.13 (m, 3H), 6.85 (t, *J* = 6.2 Hz, 2H), 5.10 (d, *J* = 19.2 Hz, 1H), 3.90 (m, 6H), 3.49 (m, 1H), 3.15 (m, 2H), 1.24 (t, *J* = 7.1 Hz, 3H), 1.14 ppm (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 148.3 (d, *J* = 4.9 Hz), 136.3 (d, *J* = 5.4 Hz), 131.9 , 131.8 , 130.4 , 128.6 (d, *J* = 2.7 Hz), 128.1 (d, *J* = 4.8 Hz), 127.6 (d, *J* = 3.5 Hz), 126.0 (d, *J* = 2.7 Hz), 116.1 , 110.3 , 63.2 (d, *J* = 7.3 Hz), 62.4 (d, *J* = 7.7 Hz), 59.5 , 57.9 , 43.6 , 26.9 , 16.48 (d, *J* = 5.4 Hz), 16.38 ppm (d, *J* = 5.8 Hz); HRMS (ESI): calcd. for $C_{19}H_{23}BrNNaO_3P$ $[M + Na]^+$ 446.0497; found 446.0492.

Diethyl (2-(p-tolyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)phosphonate

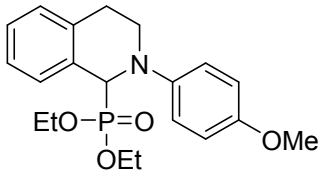


7h

Purified by column chromatography on silica gel (eluting with hexane/ethyl acetate = 5:1, R_f = 0.3). Orange oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.37 (d, *J* = 6.5 Hz, 1H), 7.15 (ddd, *J* = 16.8, 6.9, 3.9 Hz, 3H), 7.05 (d, *J* = 8.4

Hz, 2H), 6.88 (d, *J* = 8.6 Hz, 2H), 5.11 (d, *J* = 20.8 Hz, 1H), 4.21 – 3.85 (m, 5H), 3.67 – 3.55 (m, 1H), 2.98 (dd, *J* = 4.9, 2.9 Hz, 2H), 2.25 (s, 3H), 1.25 (t, *J* = 7.1 Hz, 3H), 1.15 ppm (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.46 (d, *J* = 7.0 Hz), 136.49 (d, *J* = 5.7 Hz), 130.66 , 129.67 , 128.83 (d, *J* = 2.5 Hz), 128.17 (d, *J* = 4.5 Hz), 127.98 , 127.33 (d, *J* = 3.5 Hz), 125.81 (d, *J* = 2.9 Hz), 115.35 , 63.34 (d, *J* = 7.2 Hz), 62.27 (d, *J* = 7.7 Hz), 59.87 , 58.28 , 43.84 , 26.45 , 20.31 , 16.51 (d, *J* = 5.5 Hz), 16.40 ppm (d, *J* = 5.8 Hz) .; HRMS (ESI): calcd. for $C_{20}H_{26}NNaO_3P$ $[M + Na]^+$ 382.1548; found 382.1543.

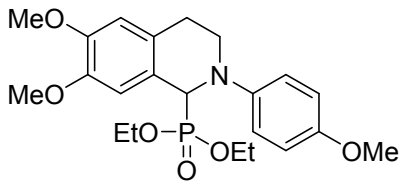
Diethyl(2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)phosphonate



7i

Purified by column chromatography on silica gel (eluting with hexane/ethyl acetate = 4:1, R_f = 0.3). Orange oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.41 – 7.35 (m, 1H), 7.21 – 7.10 (m, 3H), 6.92 (d, *J* = 9.1 Hz, 2H), 6.81 (d, *J* = 9.1 Hz, 2H), 5.02 (d, *J* = 21.5 Hz, 1H), 4.18 – 3.89 (m, 5H), 3.74 (s, 3H), 3.54 (m, 1H), 2.92 (m, 2H), 1.25 (t, *J* = 7.1 Hz, 3H), 1.16 ppm (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 153.1 , 144.2 (d, *J* = 8.3 Hz), 136.4 (d, *J* = 5.8 Hz), 130.5 , 128.9 (d, *J* = 2.5 Hz), 128.2 (d, *J* = 4.4 Hz), 127.3 (d, *J* = 3.5 Hz), 125.8 (d, *J* = 2.9 Hz), 117.6 , 114.51 , 63.3 (d, *J* = 7.2 Hz), 62.2 (d, *J* = 7.6 Hz), 59.5 (d, *J* = 160 Hz), 55.6 , 44.6 , 26.1 , 16.5 (d, *J* = 5.5 Hz), 16.4 ppm (d, *J* = 5.9 Hz).; HRMS (ESI): calcd. for $C_{20}H_{26}NNaO_3P$ $[M + Na]^+$ 398.1497; found 398.1492.

Diethyl(6,7-dimethoxy-2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)phosphonate



7j

Purified by column chromatography on silica gel (eluting with hexane/ethyl acetate = 3:1, R_f = 0.2). Orange oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.94 (d, *J* = 1.9 Hz, 1H), 6.91 (d, *J* = 9.1 Hz, 2H), 6.80 (d, *J* = 9.1 Hz, 2H), 6.60 (s, 1H), 4.92 (d, *J* = 21.7 Hz, 1H), 4.24 – 3.92 (m, 6H), 3.85 (d, *J* = 9.4 Hz, 6H), 3.74 (s, 3H), 2.84 (m, 1H), 2.76 – 2.63 (m, 1H), 1.28 (t, *J* = 7.0 Hz, 3H), 1.18 (t, *J* = 7.0 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 153.3 , 148.2 (d, *J* = 3.6 Hz), 147.0 (d, *J* = 3.0 Hz), 144.3 (d, *J* = 9.8 Hz), 128.5 (d, *J* = 6.5 Hz), 121.8, 118.1, 115.5, 114.4, 111.6 (d, *J* = 2.6 Hz), 111.0 (d, *J* = 3.6 Hz), 63.4 (d, *J* = 7.1 Hz), 61.9 (d, *J* = 7.6 Hz), 59.8, 58.2, 55.9, 55.8, 55.6, 44.8, 25.2, 16.5 (d, *J*= 5.5 Hz) 16.4 ppm (d, *J* = 5.7 Hz); HRMS (ESI): calcd. for $C_{22}H_{30}NNaO_6P$ $[M + Na]^+$ 458.1708; found 458.1703.

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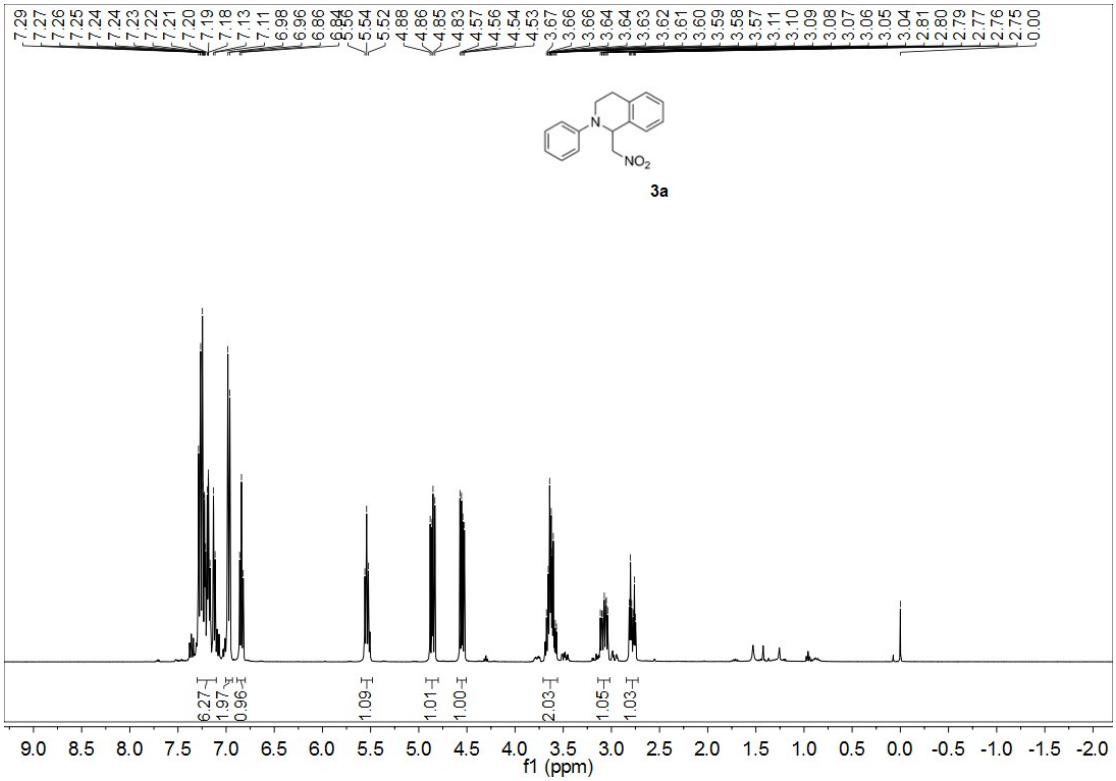
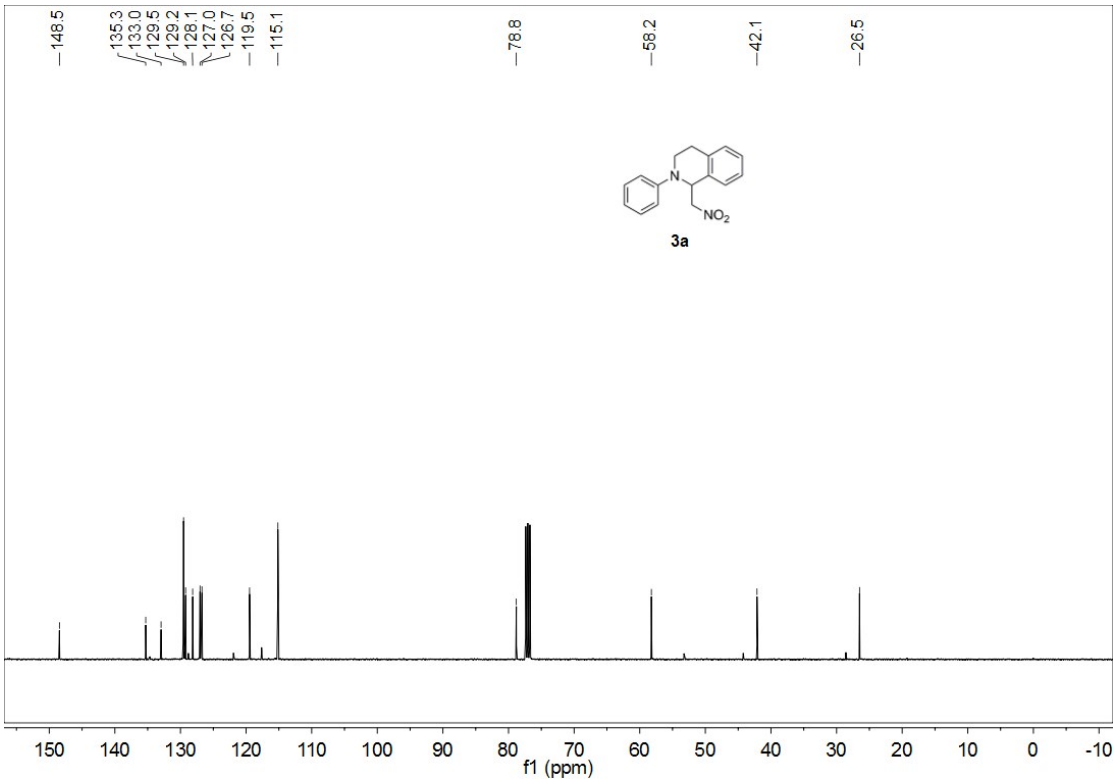
[2] P. Liu,; C.-Y. Zhou,; S. Xiang; C.-M. Che, *Chem. Commun.* **2010**, *46*, 2739.

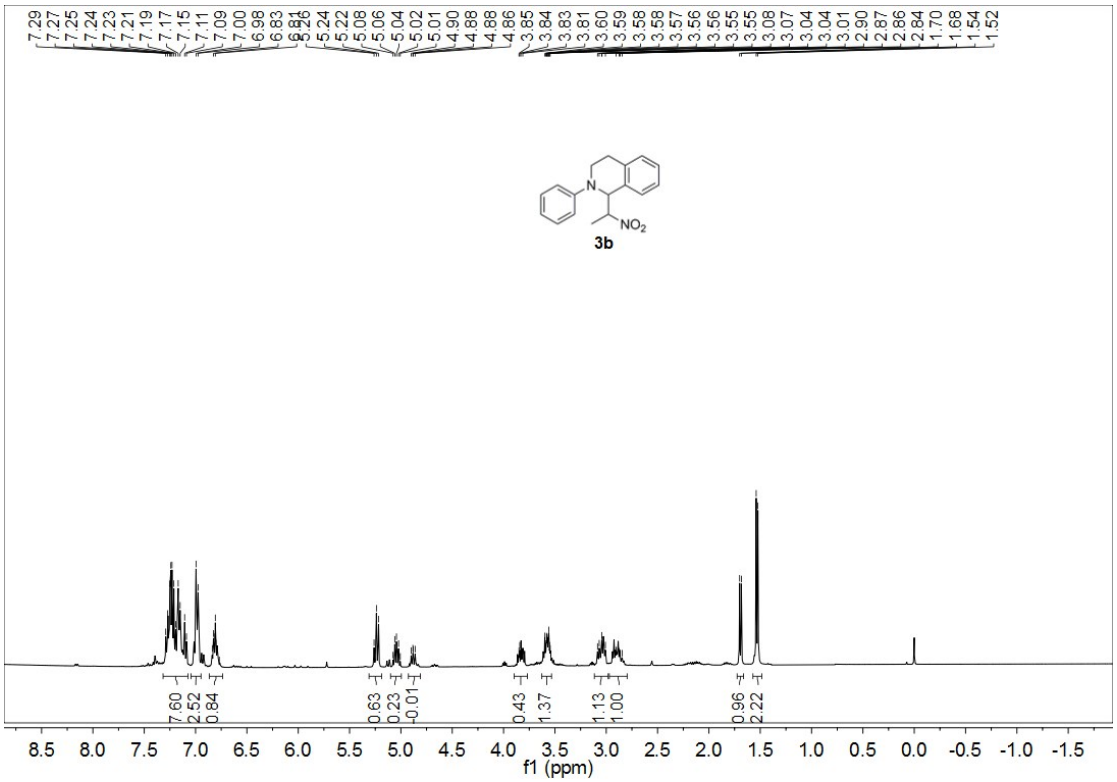
[3] A. Loudet,; K. Burgess, *Chem. Rev.* **2007,** *107*, 4891.

[4] L. Wang, K.-q. Zhu, Q. Chen and M.-y. He, *Dyes Pigm*., **2015**, *112*, 274.

3. ^{1}H NMR and ^{13}C NMR



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1.54
1.52
NO2
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1.13
1.00
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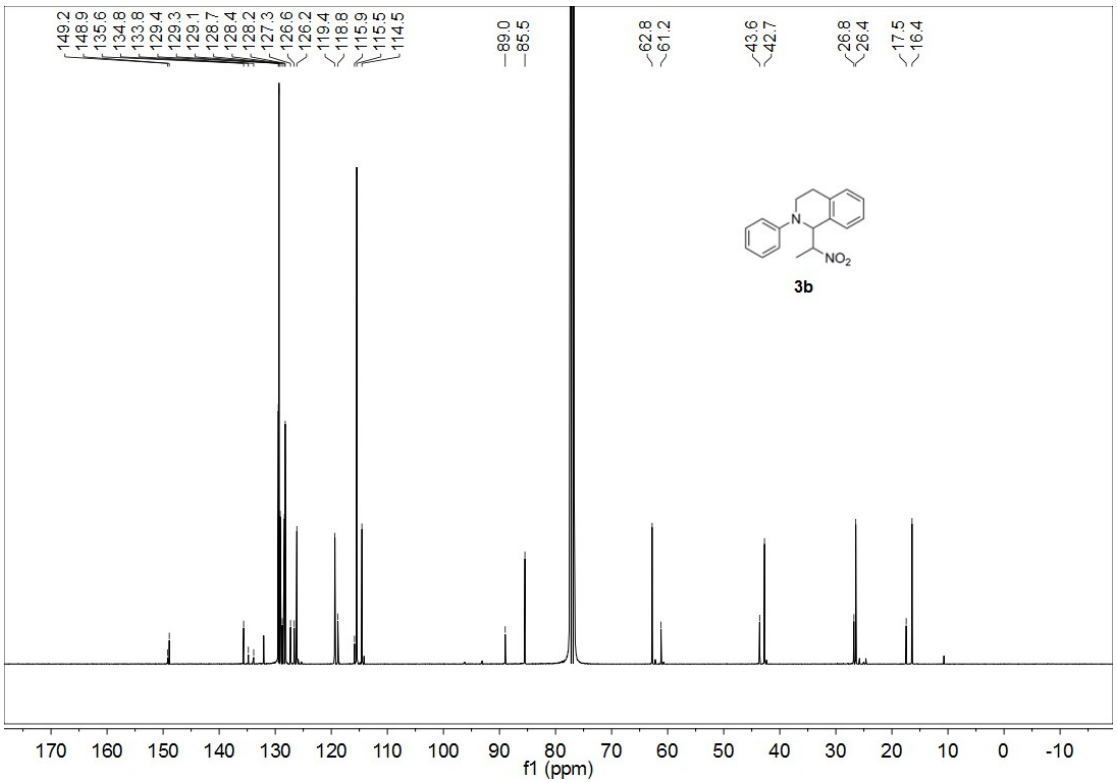
2.22
f1 (ppm)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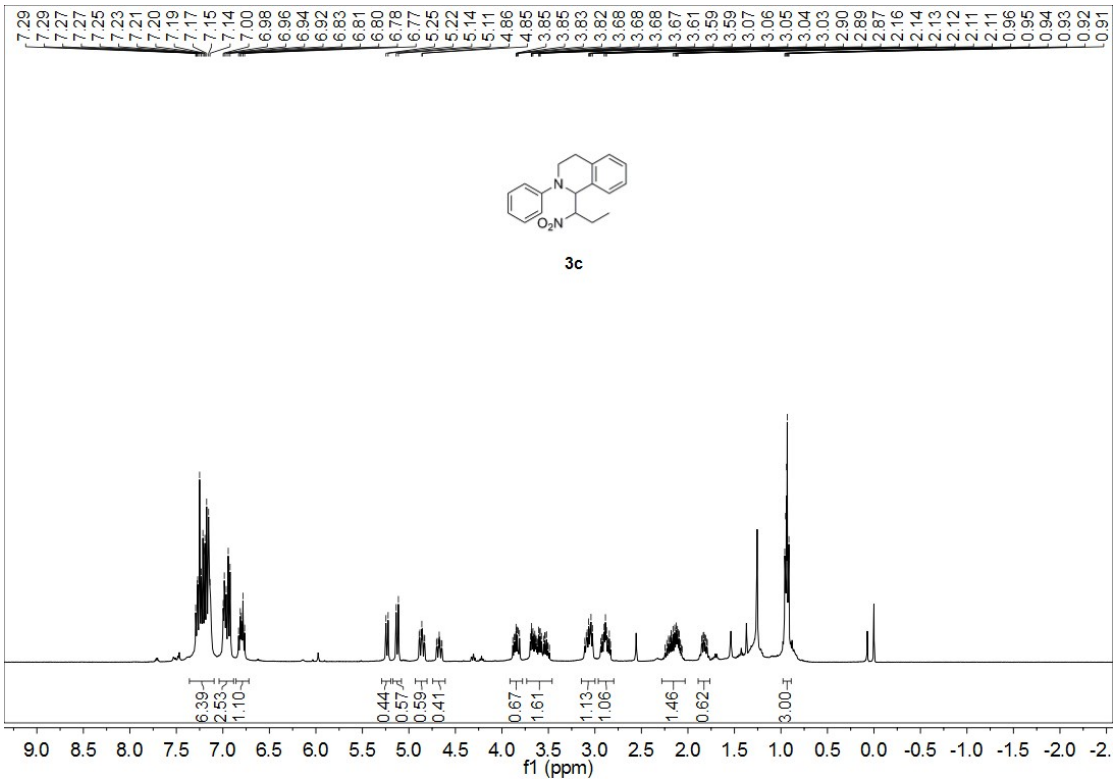
17.5
16.4
NO2
3b
f1 (ppm)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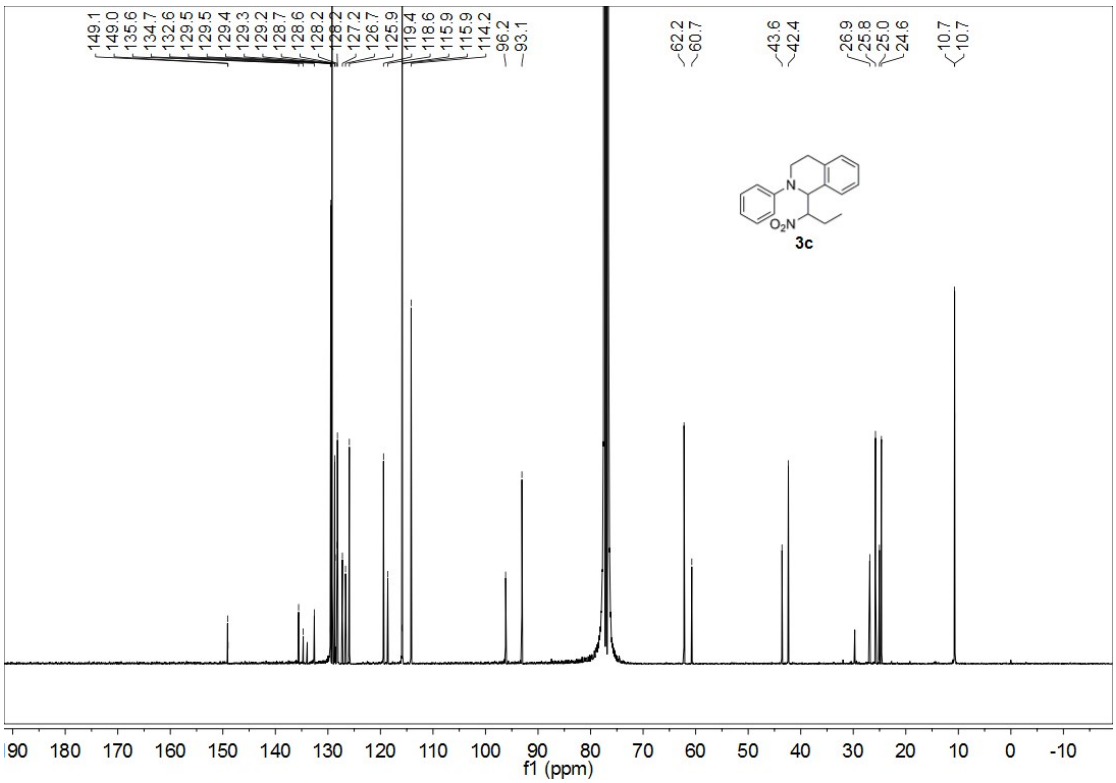
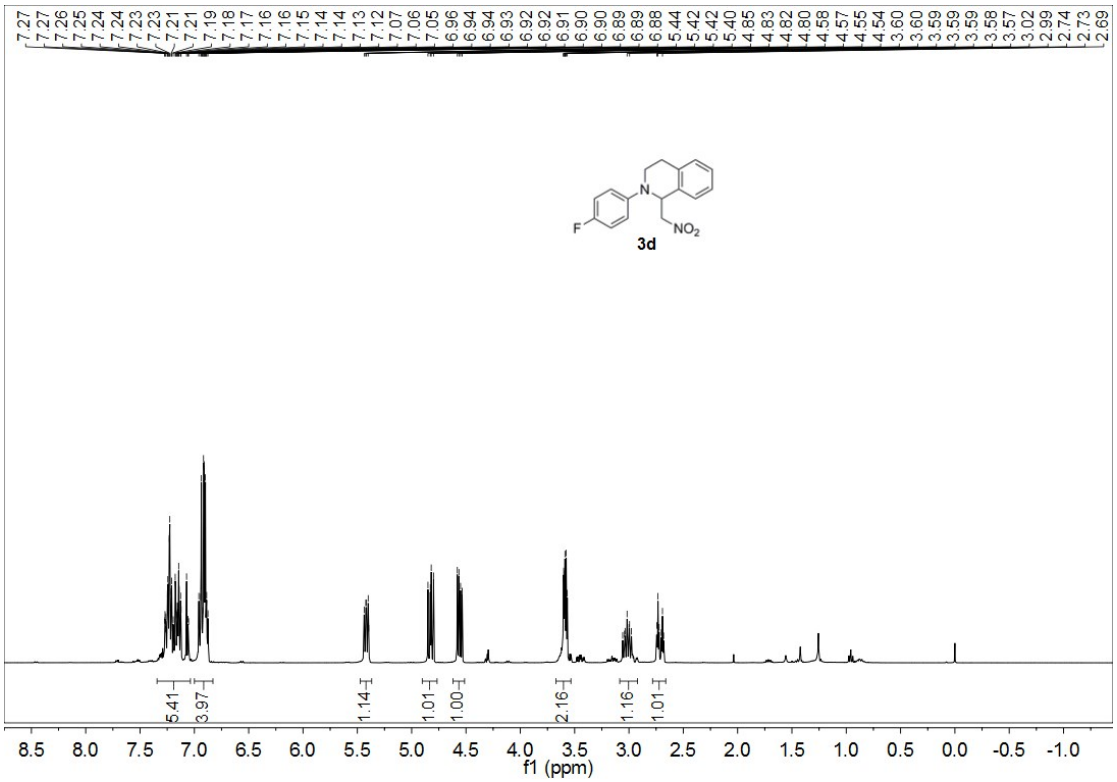
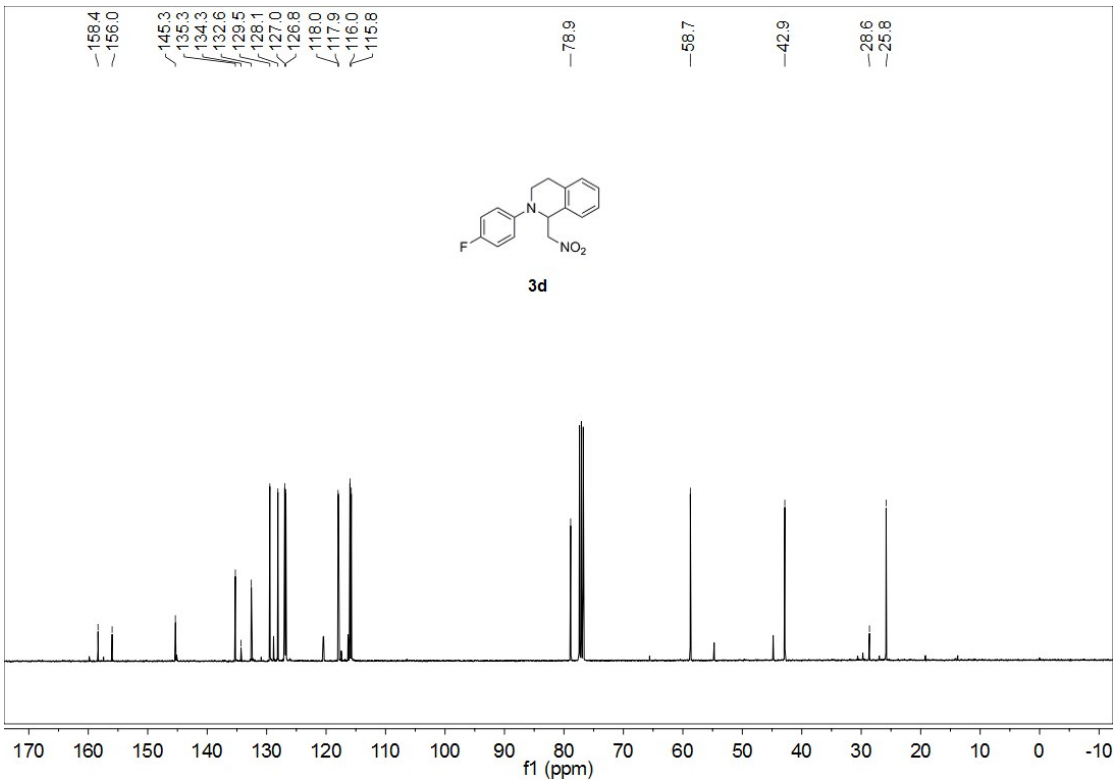
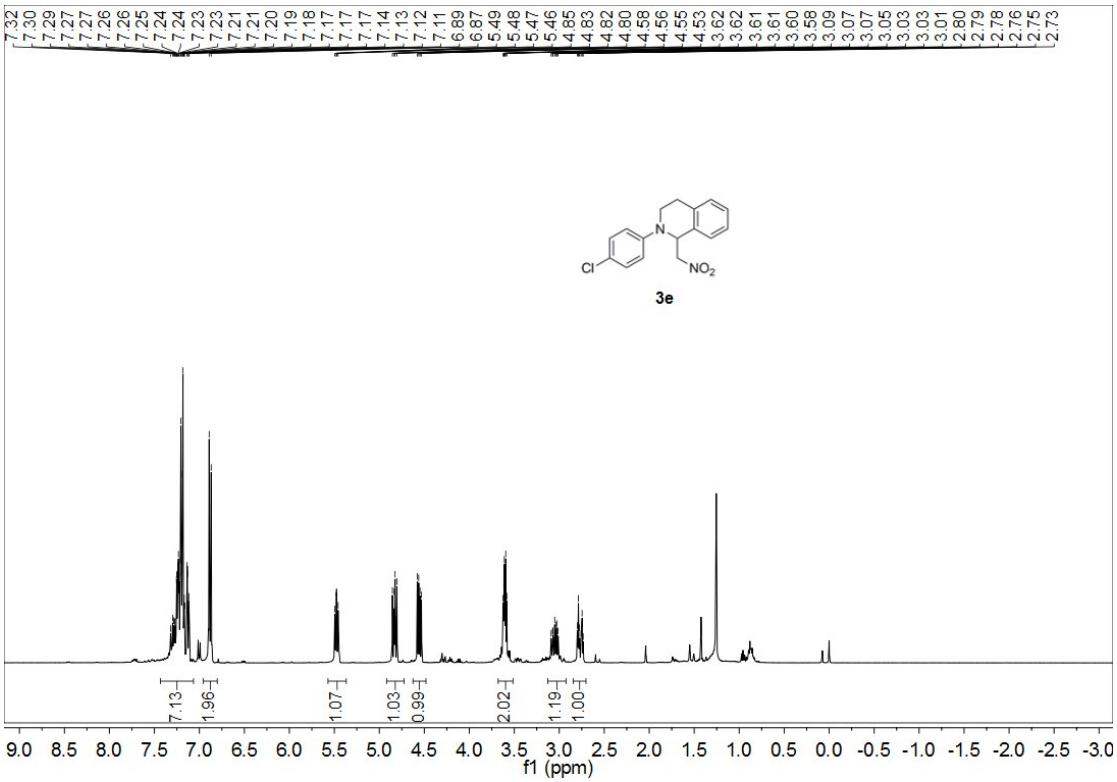
3c
6.39 2.53 1.10 0.44 0.57 0.59 0.41 0.67 1.61 1.13 1.06 1.46 0.62 3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2.0
f1 (ppm)


149.1 149.0 135.6 134.7 132.6 129.5 129.5 129.4 129.3 129.2 128.7 128.6 128.2 128.2 127.2 126.7 125.9 119.4 118.6 115.9 115.9 114.2 96.2 93.1
62.2 60.7
43.6 42.4
26.9 25.8 25.0 24.6
10.7 10.7
3c
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.27 7.27 7.26 7.25 7.24 7.24 7.23 7.23 7.21 7.21 7.19 7.18 7.17 7.16 7.16 7.15 7.14 7.14 7.13 7.12 7.07 7.06 7.05 6.96 6.94 6.94 6.93 6.92 6.92 6.91 6.90 6.90 6.89 6.89 6.88 5.44 5.42 5.42 5.40 4.85 4.83 4.82 4.80 4.58 4.57 4.55 4.54 3.60 3.60 3.59 3.59 3.59 3.58 3.57 3.02 2.99 2.74 2.73 2.69
F
N
NO2
3d
5.41 3.97 1.14 1.01 1.00 2.16 1.16 1.01
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


158.4 156.0 145.3 135.3 134.3 132.6 129.5 128.1 127.0 126.8 118.0 117.9 116.0 115.8 78.9 58.7 42.9 28.6 25.8
F
N
NO2
3d
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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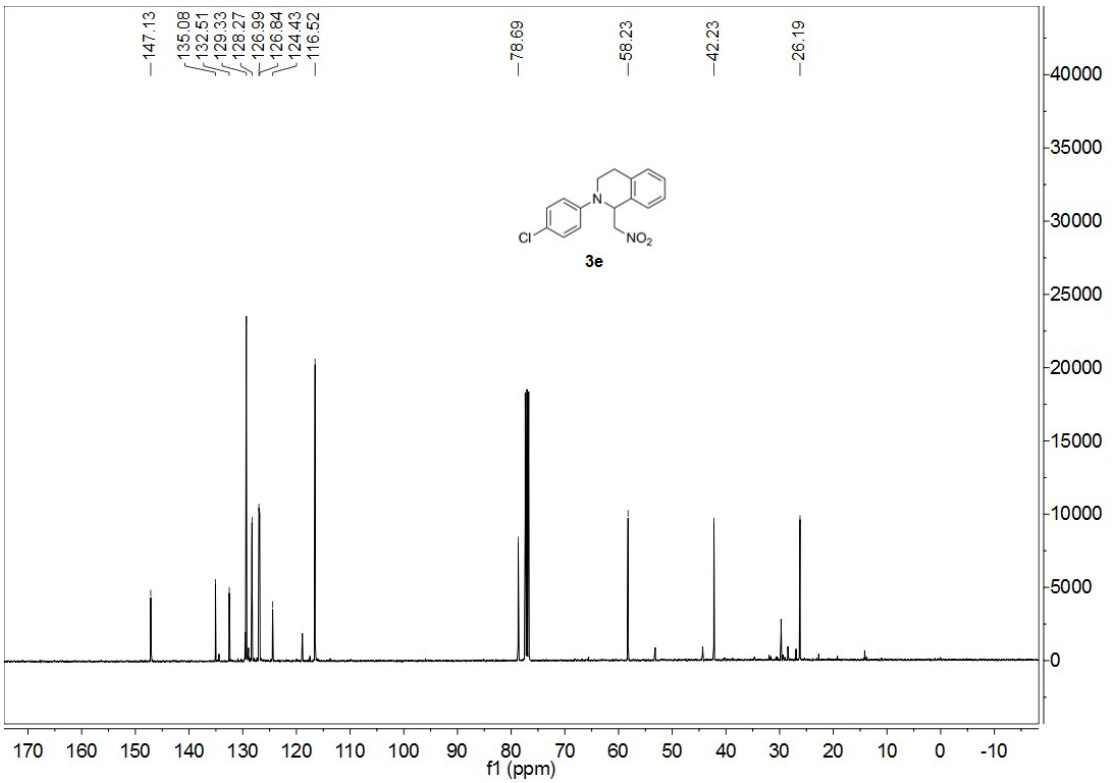
Cl
NO2
3e
7.13 1.96 1.07 1.03 0.99 2.02 1.19 1.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2.0 -2.5 -3.0
f1 (ppm)


147.13 135.08 132.51 129.33 128.27 126.99 126.84 124.43 116.52 78.69 58.23 42.23 26.19
Cl
NO2
3e
40000 35000 30000 25000 20000 15000 10000 5000 0
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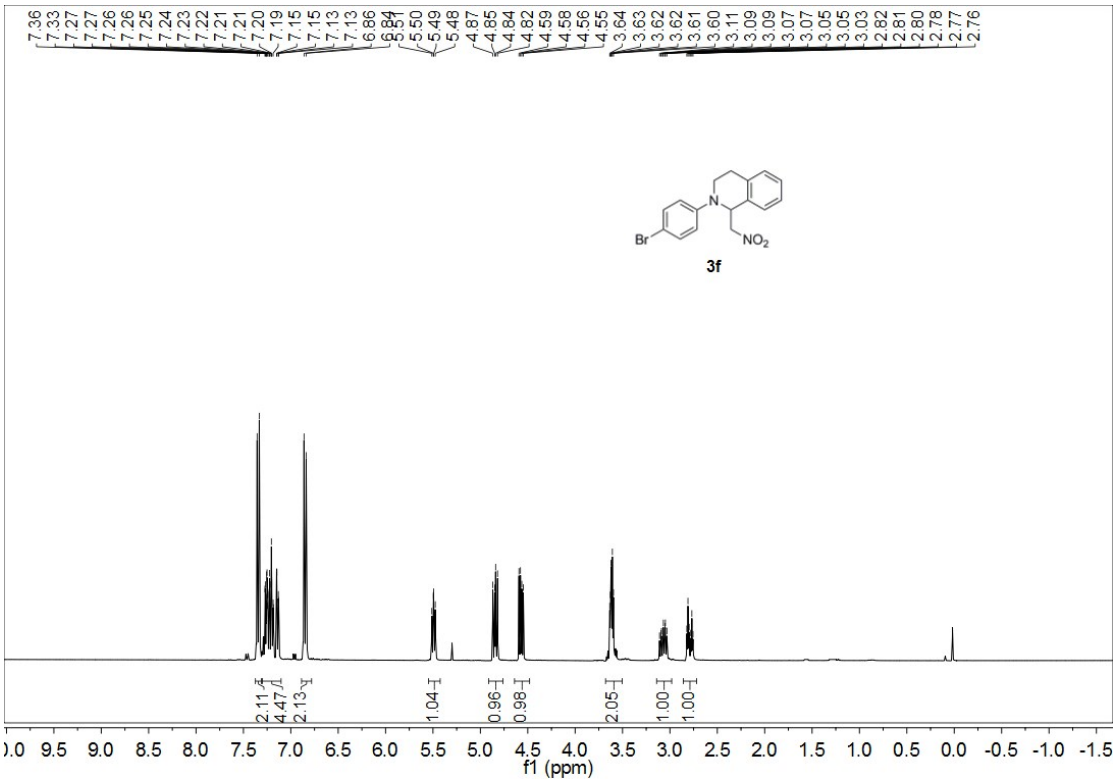
f1 (ppm)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7.33
7.27
7.27
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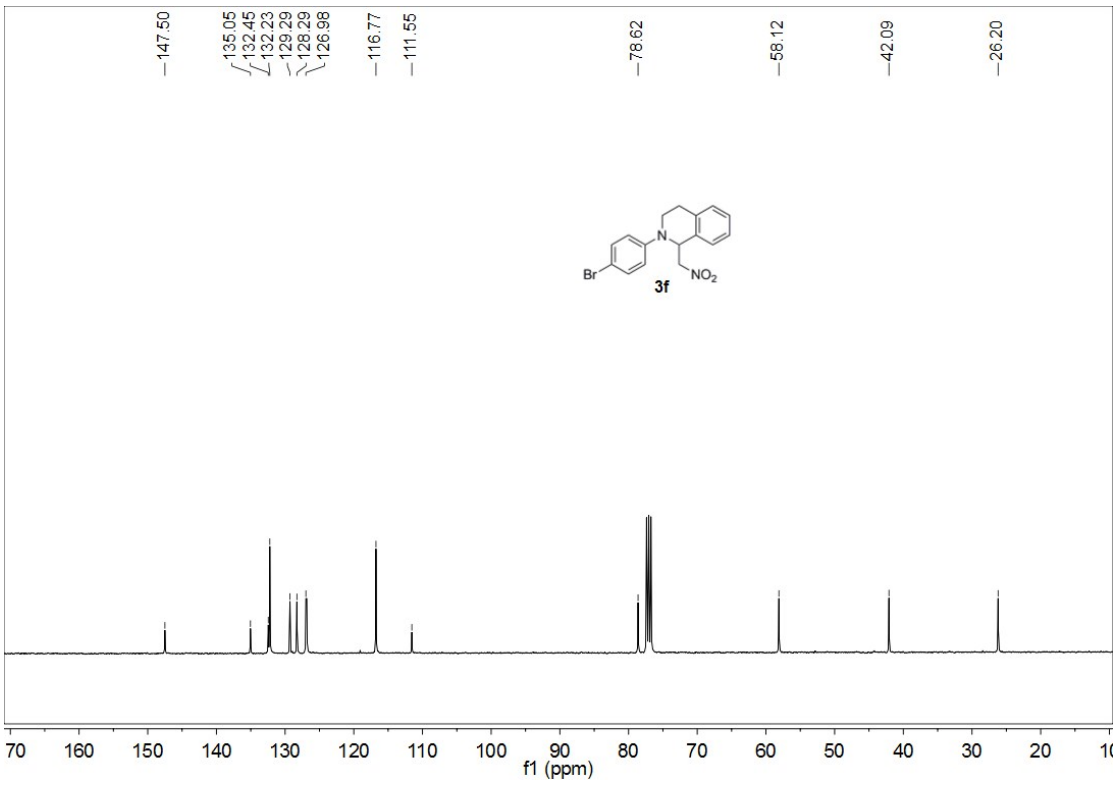
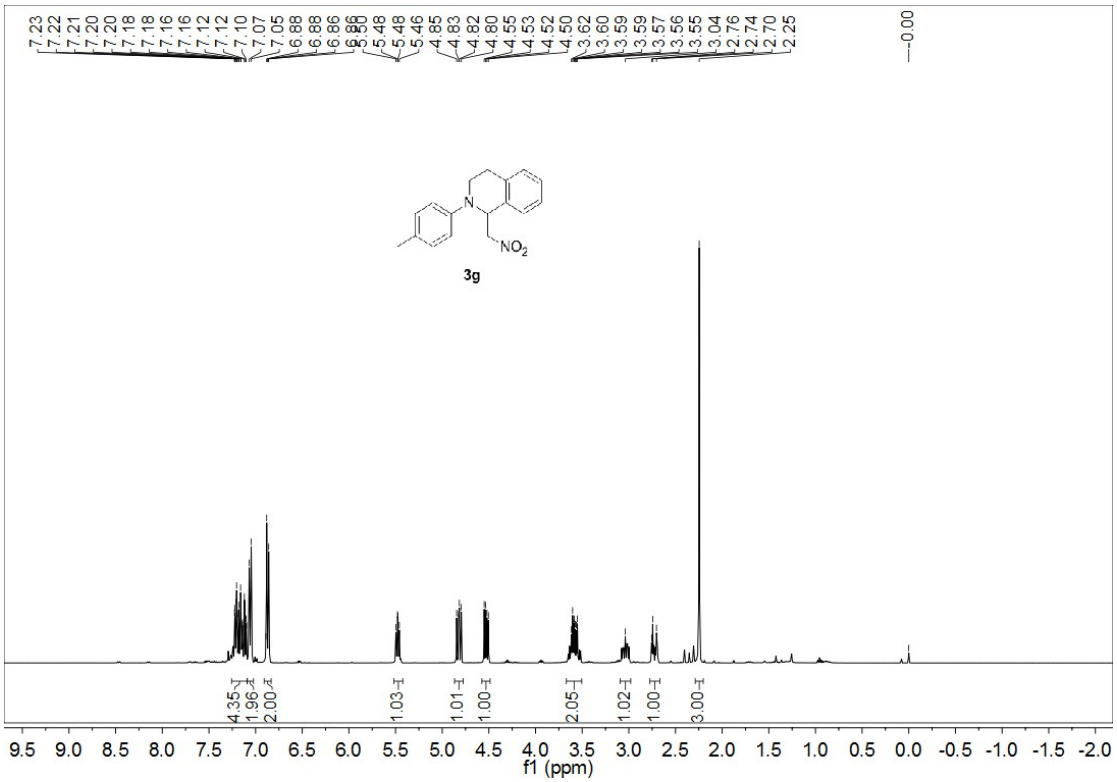
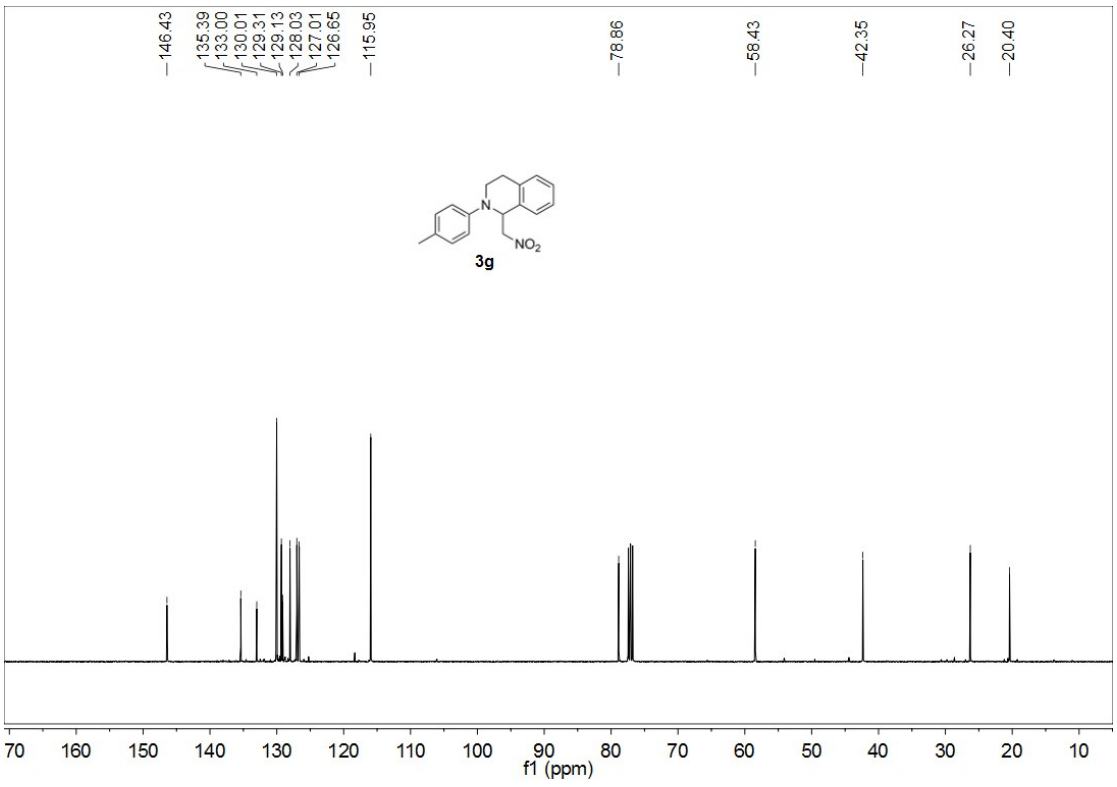
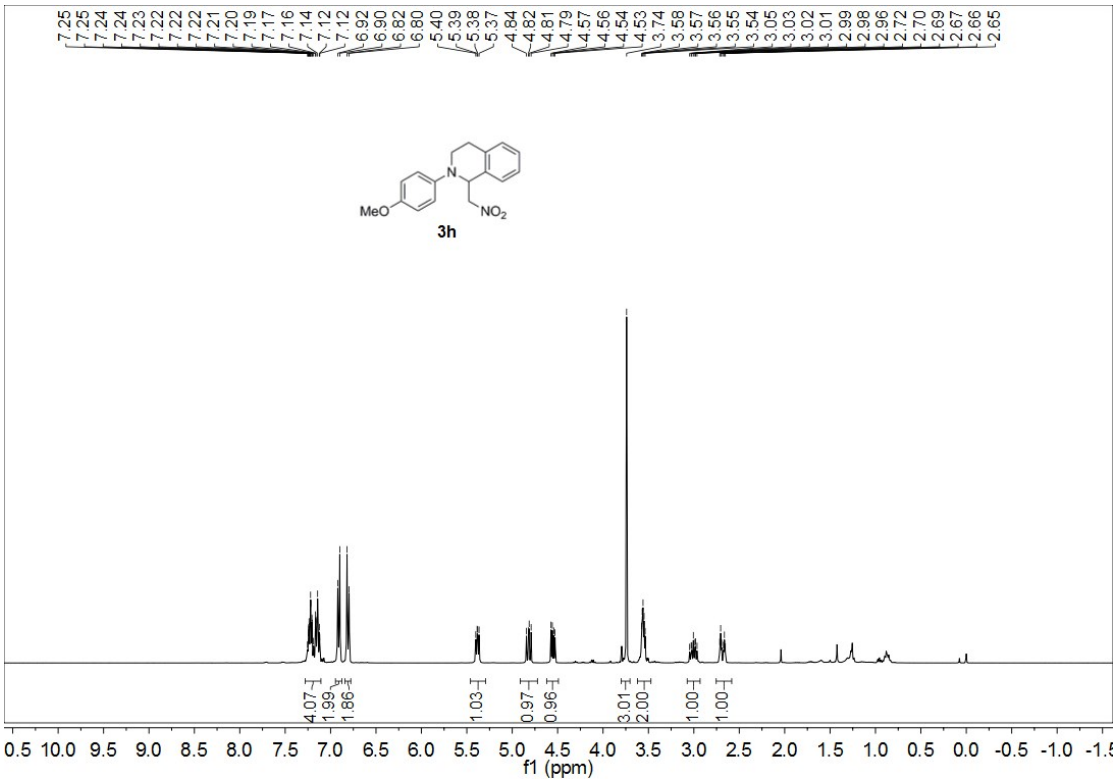
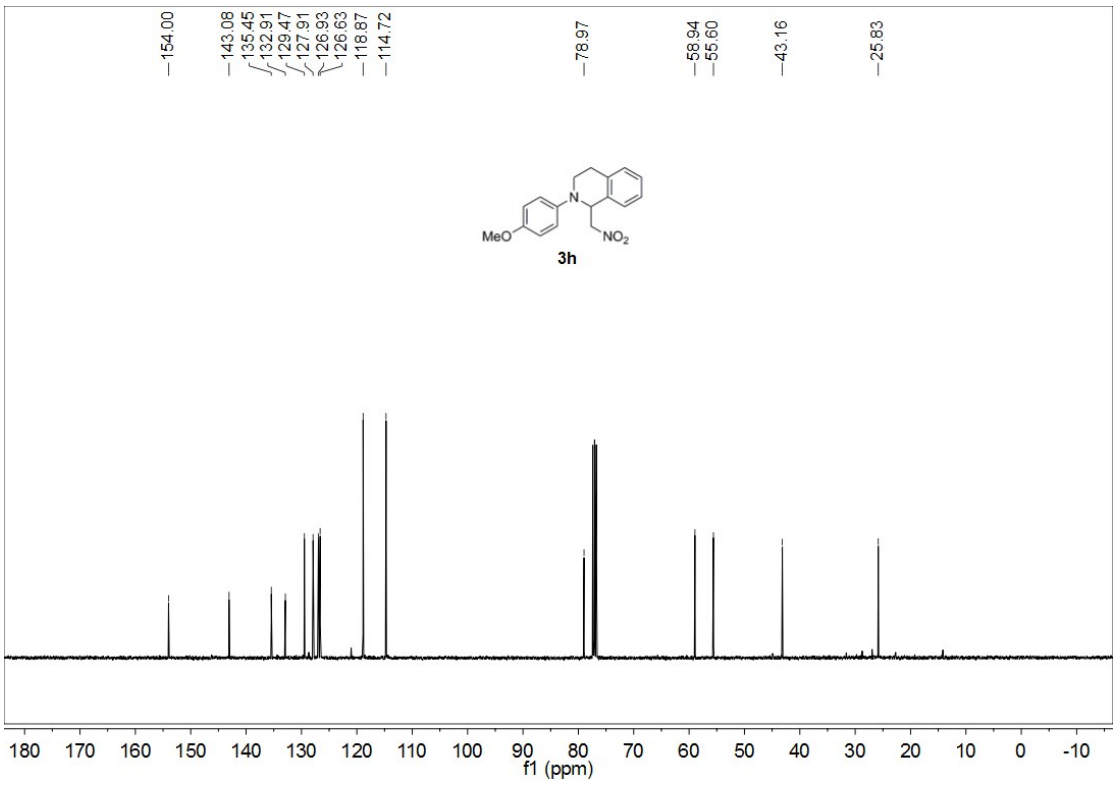
7.26
7.25
7.24
7.23
7.22
7.21
7.21
7.20
7.19
7.15
7.15
7.13
7.13
6.86
5.51
5.50
5.49
5.48
4.87
4.85
4.84
4.82
4.59
4.58
4.56
4.55
3.64
3.63
3.62
3.62
3.61
3.60
3.11
3.09
3.09
3.07
3.07
3.05
3.05
3.03
2.82
2.81
2.80
2.78
2.77
2.76
Br
NO2
3f
2.11
4.47
2.13
1.04
0.96
0.98
2.05
1.00
1.00
f1 (ppm)


147.50
135.05
132.45
132.23
129.29
128.29
126.98
116.77
111.55
78.62
58.12
42.09
26.20
Br
NO2
3f
f1 (ppm)


7.23
7.22
7.21
7.20
7.18
7.18
7.16
7.16
7.12
7.12
7.10
7.07
7.05
6.88
6.88
6.86
6.86
5.48
5.48
5.46
4.85
4.83
4.82
4.80
4.55
4.53
4.52
4.50
3.62
3.60
3.59
3.59
3.57
3.56
3.55
3.04
2.76
2.74
2.70
2.25
0.00
NO2
3g
4.35
1.96
2.00
1.03
1.01
1.00
2.05
1.02
1.00
3.00
f1 (ppm)


146.43
135.39
133.00
130.01
129.31
129.13
128.03
127.01
126.65
115.95
78.86
58.43
42.35
26.27
20.40
NO2
3g
f1 (ppm)


7.25
7.25
7.24
7.24
7.23
7.22
7.22
7.22
7.21
7.20
7.19
7.17
7.16
7.14
7.12
7.12
6.92
6.90
6.82
6.80
5.40
5.39
5.38
5.37
4.84
4.82
4.81
4.79
4.57
4.56
4.54
4.53
3.74
3.58
3.57
3.56
3.55
3.54
3.05
3.03
3.02
3.01
2.99
2.98
2.96
2.72
2.70
2.69
2.67
2.66
2.65
MeO
NO2
3h
4.07
1.99
1.86
1.03
0.97
0.96
3.01
2.00
1.00
1.00
f1 (ppm)


154.00
143.08
135.45
132.91
129.47
127.91
126.93
126.63
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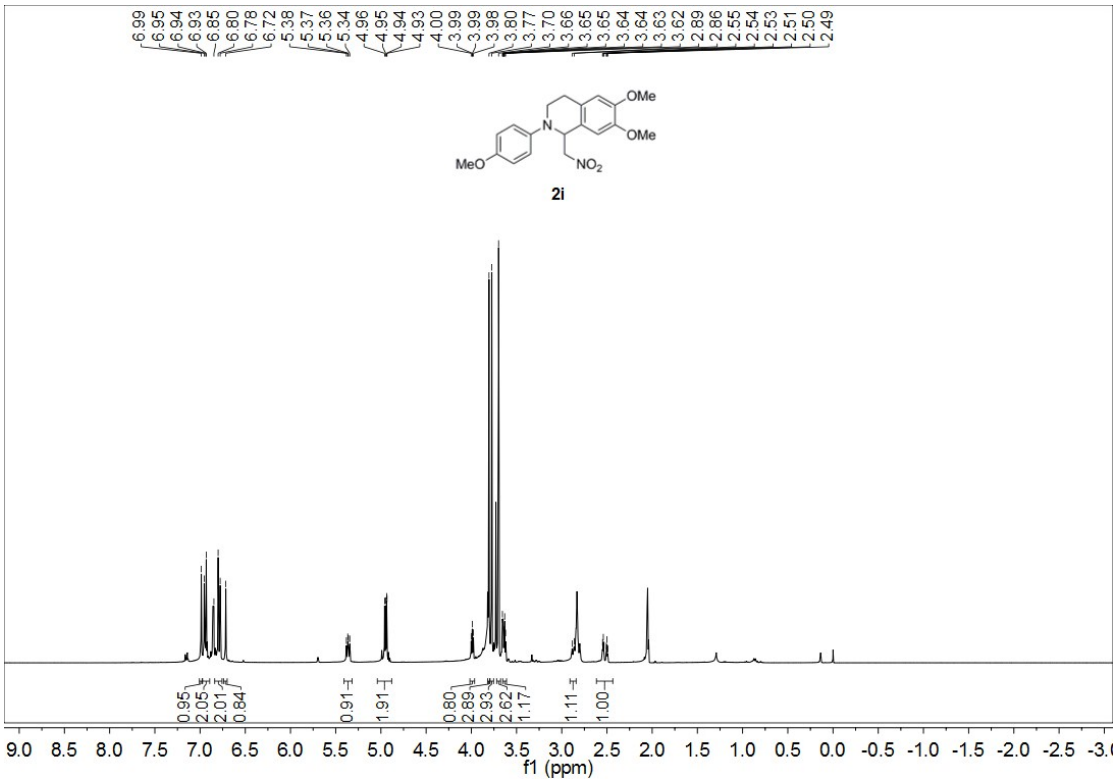
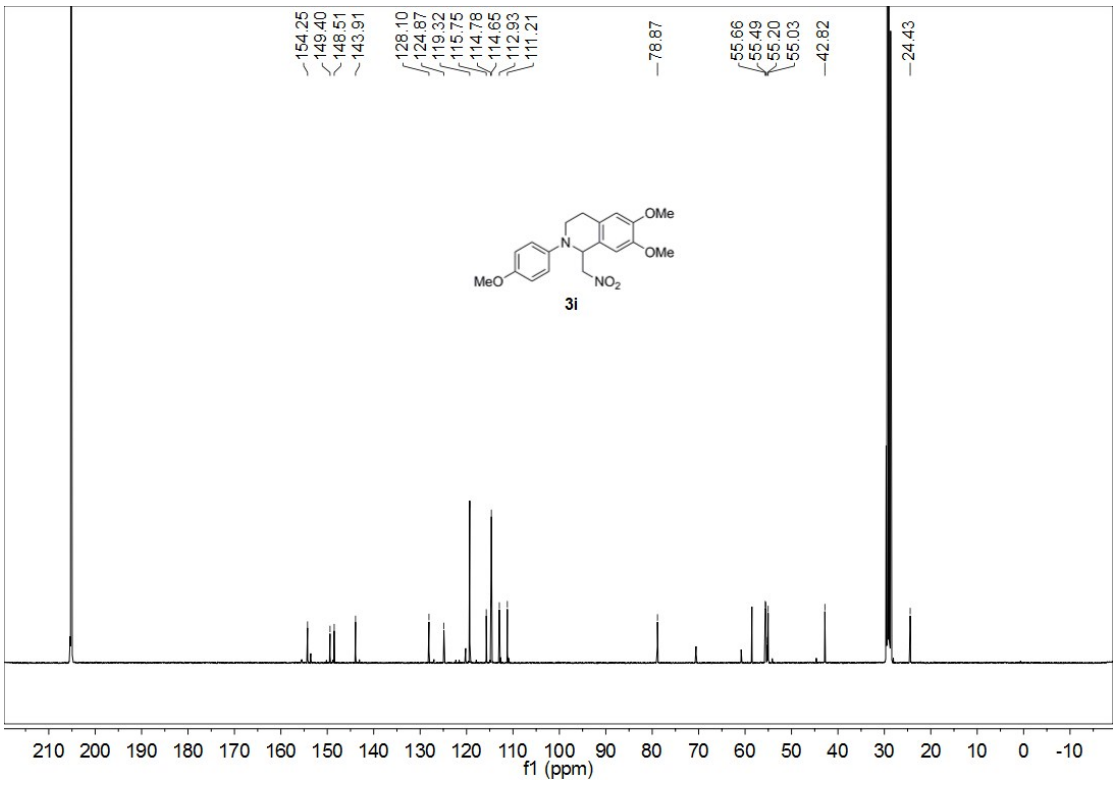
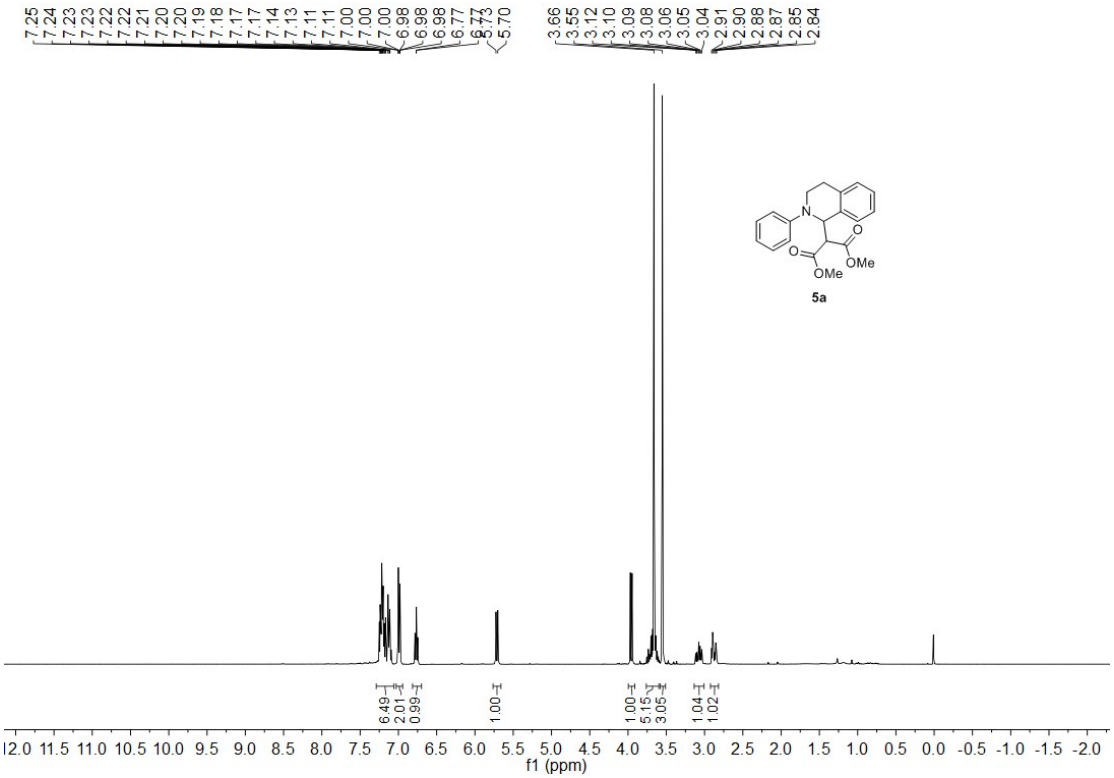
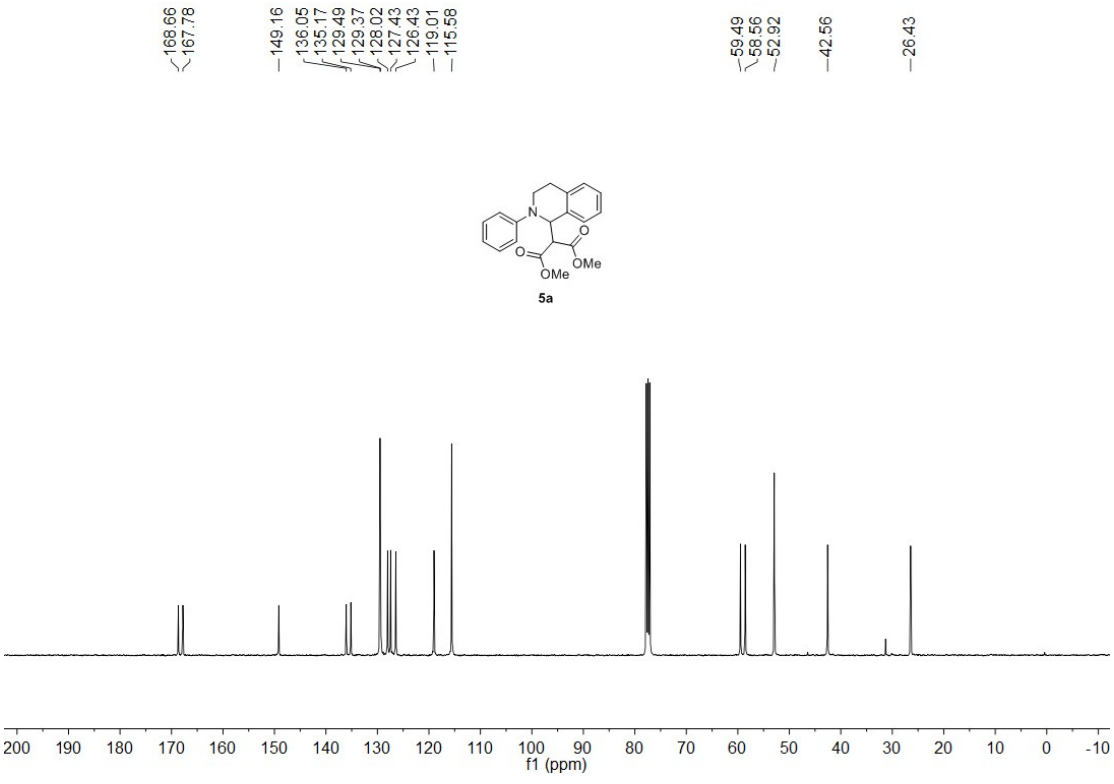
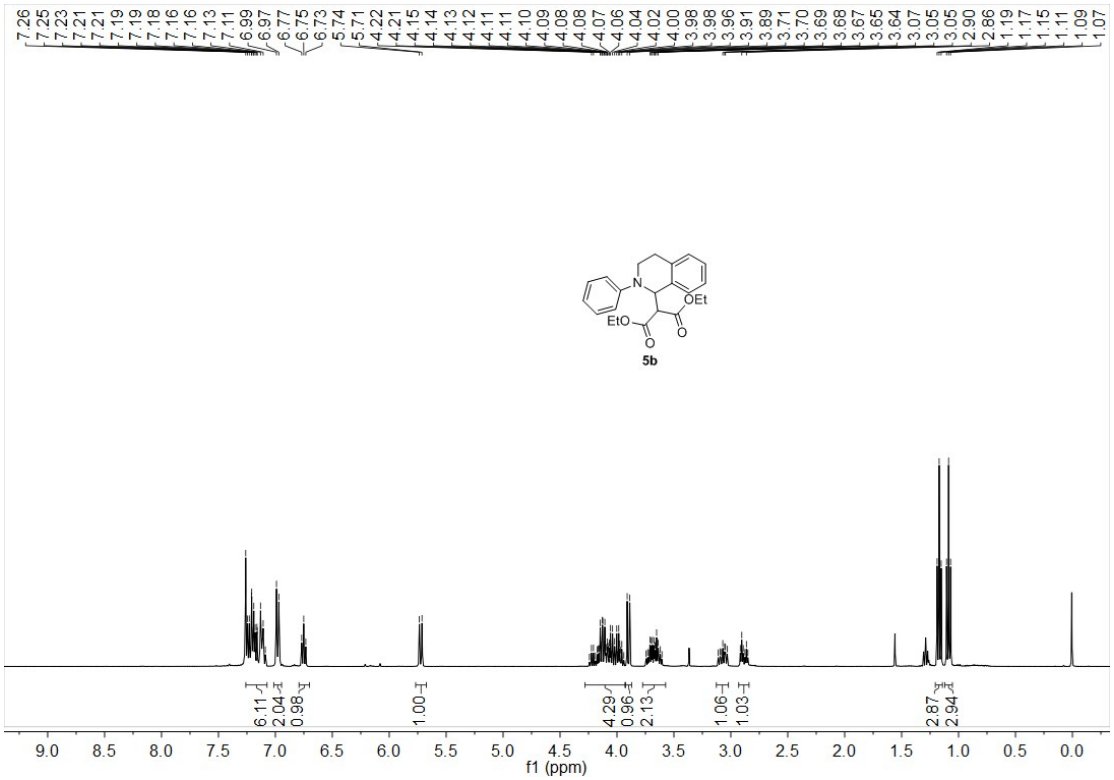
114.72
78.97
58.94
55.60
43.16
25.83
MeO
NO2
3h
f1 (ppm)


6.99
6.95
6.94
6.93
6.85
6.80
6.78
6.72
5.38
5.37
5.36
5.34
4.96
4.95
4.94
4.93
4.00
3.99
3.99
3.98
3.80
3.77
3.70
3.66
3.65
3.65
3.64
3.64
3.63
3.62
2.89
2.86
2.55
2.54
2.53
2.51
2.50
2.49
OMe
OMe
MeO
NO2
2i
0.95
2.05
2.01
0.84
0.91
1.91
0.80
2.89
2.93
2.62
1.17
1.11
1.00
f1 (ppm)


154.25
149.40
148.51
143.91
128.10
124.87
119.32
115.75
114.78
114.65
112.93
111.21
78.87
55.66
55.49
55.20
55.03
42.82
24.43
OMe
OMe
MeO
NO2
3i
f1 (ppm)


7.25 7.24 7.23 7.23 7.22 7.22 7.21 7.20 7.20 7.19 7.18 7.17 7.17 7.14 7.13 7.11 7.11 7.00 7.00 7.00 6.98 6.98 6.77 6.73 5.70
3.66 3.55 3.12 3.10 3.09 3.08 3.06 3.05 3.04 2.91 2.90 2.88 2.87 2.85 2.84
O
O
OMe
O
OMe
5a
6.49 2.01 0.99 1.00 1.00 5.15 3.05 1.04 1.02
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2.0
f1 (ppm)


168.66 167.78 149.16 136.05 135.17 129.49 129.37 128.02 127.43 126.43 119.01 115.58 59.49 58.56 52.92 42.56 26.43
O
O
OMe
O
OMe
5a
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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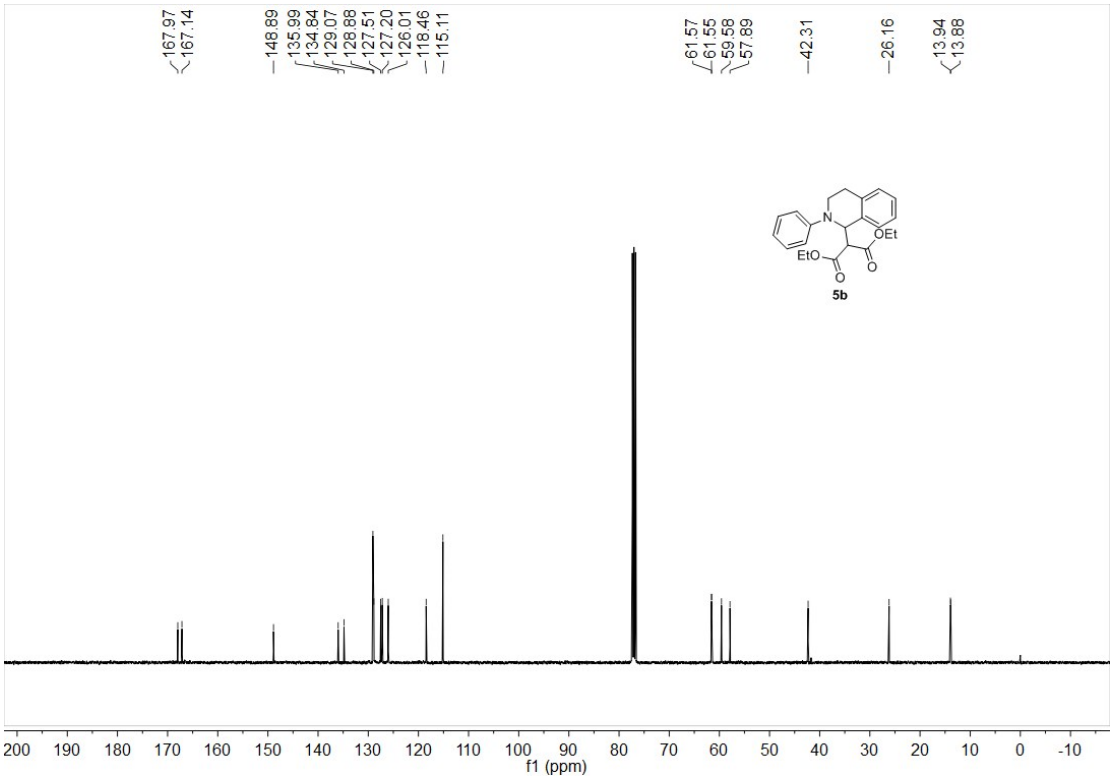
7.18
7.16
7.16
7.13
7.11
6.99
6.97
6.77
6.75
6.73
5.74
5.71
4.22
4.21
4.15
4.14
4.13
4.12
4.11
4.11
4.10
4.09
4.08
4.08
4.07
4.06
4.04
4.02
4.00
3.98
3.98
3.96
3.91
3.89
3.71
3.70
3.69
3.68
3.67
3.65
3.64
3.07
3.05
3.05
2.90
2.86
1.19
1.17
1.15
1.11
1.09
1.07
OEt
EtO
O
O
5b
6.11
2.04
0.98
1.00
4.29
0.96
2.13
1.06
1.03
2.87
2.94
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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167.14
148.89
135.99
134.84
129.07
128.88
127.51
127.20
126.01
118.46
115.11
61.57
61.55
59.58
57.89
42.31
26.16
13.94
13.88
OEt
EtO
O
O
5b
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.39
7.37
7.37
7.27
7.26
7.25
7.25
7.23
7.20
7.19
7.18
7.18
7.17
7.17
7.16
7.15
6.99
6.97
6.81
6.79
6.77
5.21
5.16
4.12
4.10
4.10
4.09
4.08
4.06
4.06
4.05
4.05
4.04
4.04
4.03
4.02
4.01
4.00
3.99
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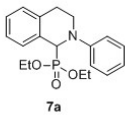
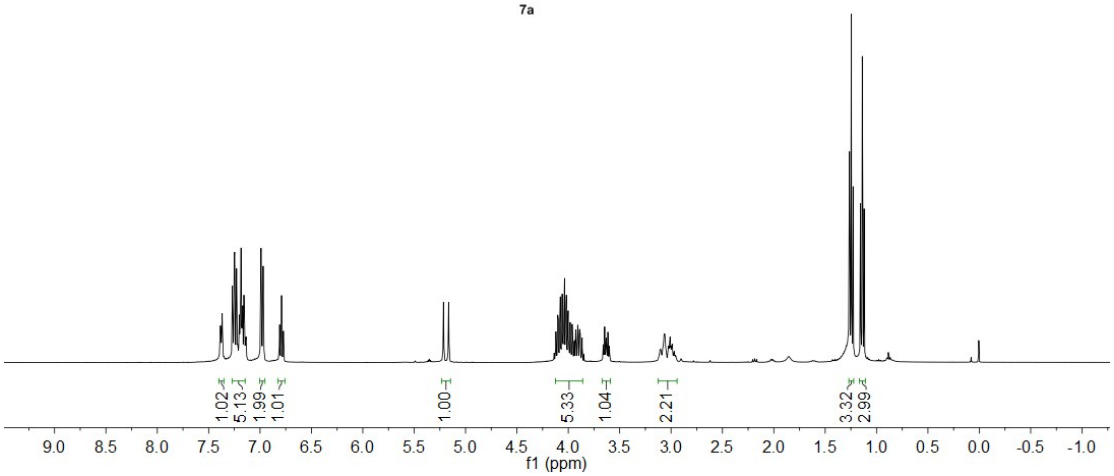
1.26
1.25
1.23
1.16
1.14
1.12


EtO
P
OEt
O

7a


1.02
5.13
1.99
1.01
1.00
5.33
1.04
2.21
3.32
2.99
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


149.53
149.48
136.57
136.51
130.77
129.22
128.85
128.82
128.25
128.20
127.53
127.50
125.97
125.94
118.56
114.89
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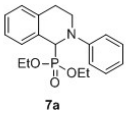
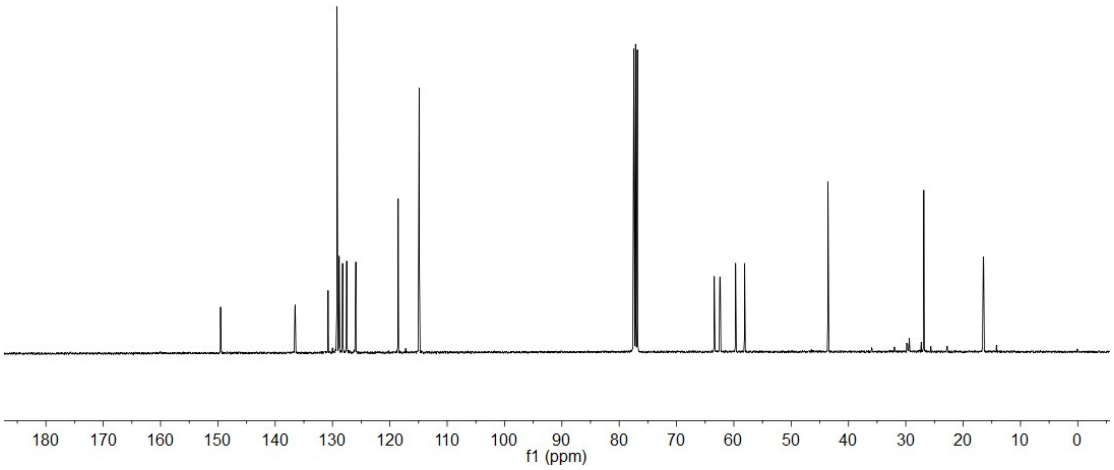
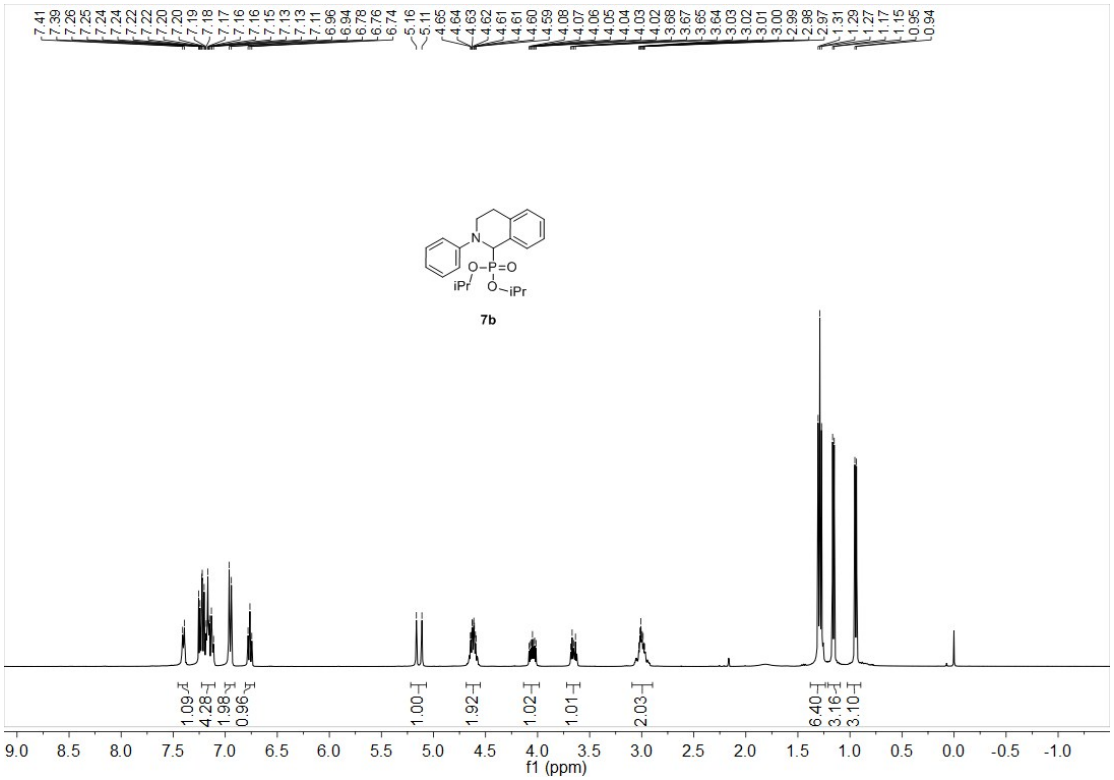
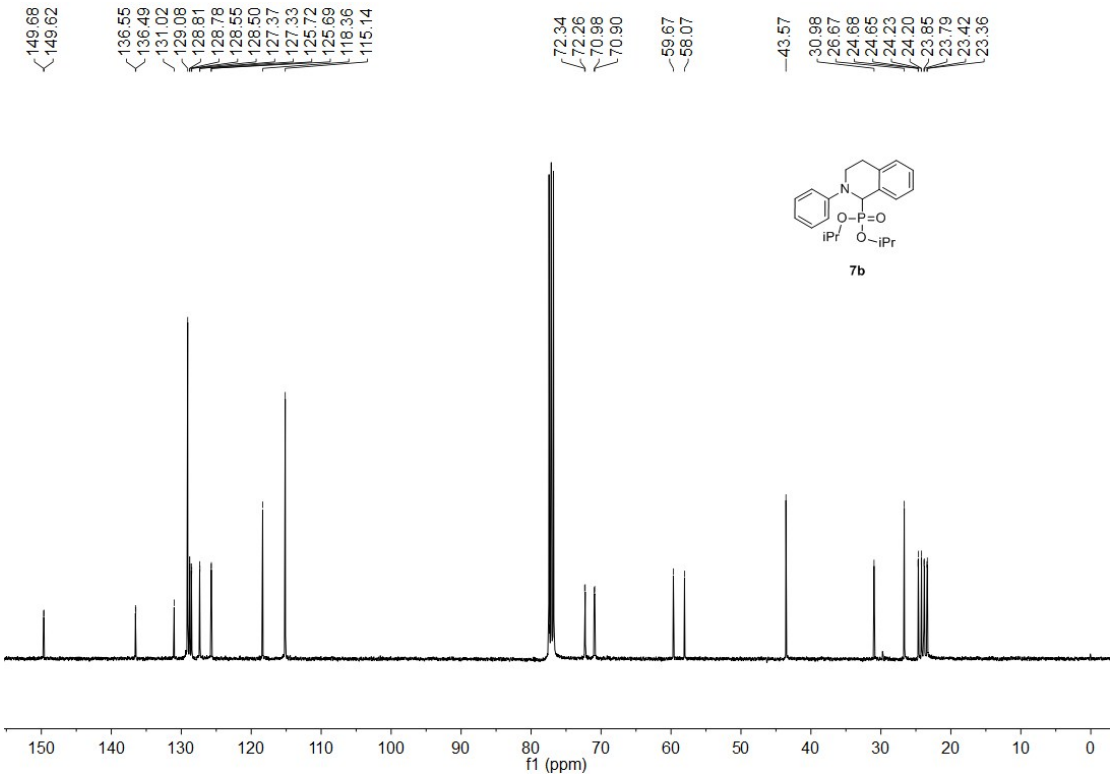
43.58
26.86
16.56
16.51
16.48
16.43

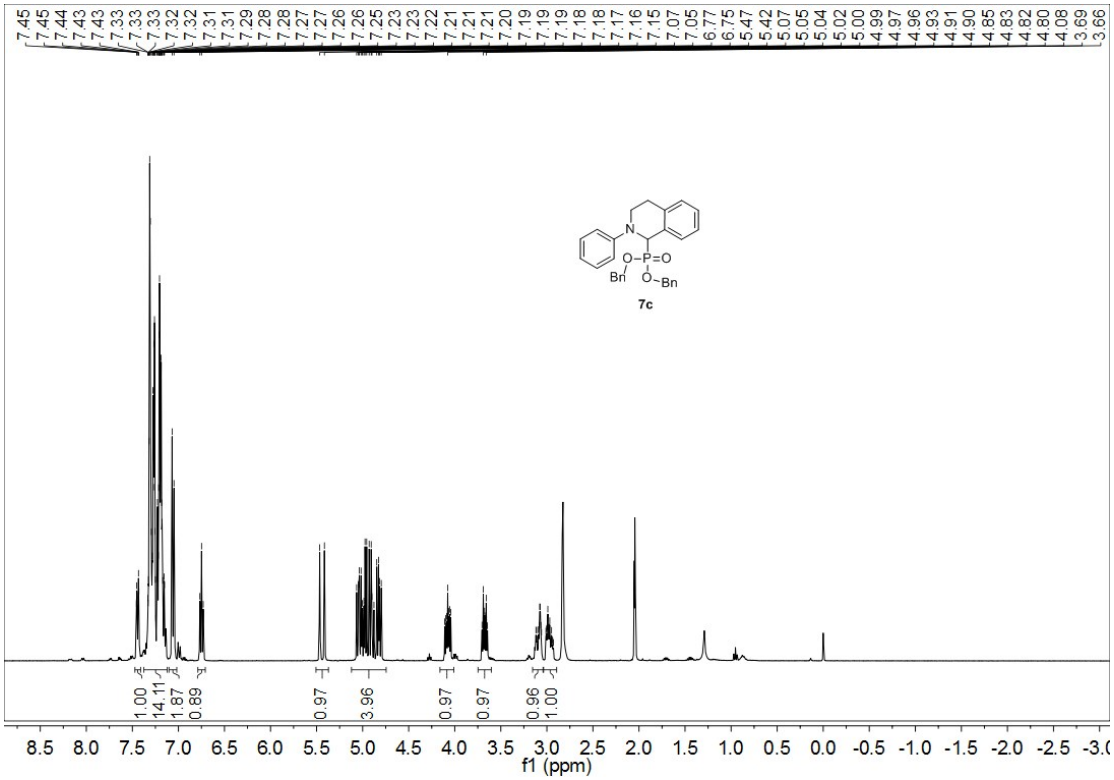

EtO
P
OEt
O

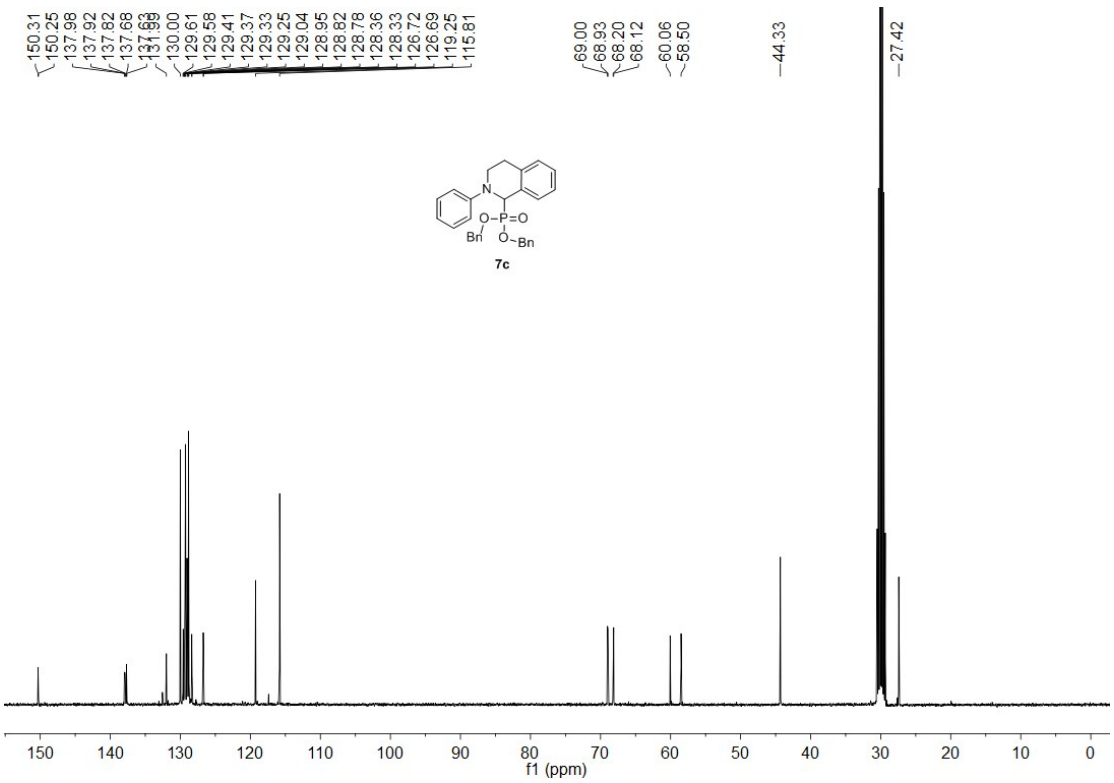
7a

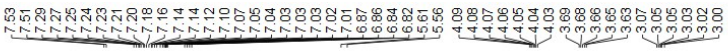

180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

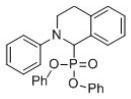

7.41 7.39 7.26 7.25 7.24 7.24 7.22 7.22 7.20 7.20 7.19 7.18 7.17 7.16 7.16 7.15 7.13 7.13 7.11 6.96 6.94 6.78 6.76 6.74 5.16 5.11 4.65 4.64 4.63 4.62 4.61 4.61 4.60 4.59 4.08 4.07 4.06 4.05 4.04 4.03 4.02 3.68 3.67 3.65 3.64 3.03 3.02 3.01 3.00 2.99 2.98 2.97 1.31 1.29 1.27 1.17 1.15 0.95 0.94
O–P=O
iPr
O–iPr
7b
1.09 4.28 1.98 0.96 1.00 1.92 1.02 1.01 2.03 6.40 3.16 3.10
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


149.68 149.62 136.55 136.49 131.02 129.08 128.81 128.78 128.55 128.50 127.37 127.33 125.72 125.69 118.36 115.14 72.34 72.26 70.98 70.90 59.67 58.07 43.57 30.98 26.67 24.68 24.65 24.23 24.20 23.85 23.79 23.42 23.36
O–P=O
iPr
O–iPr
7b
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

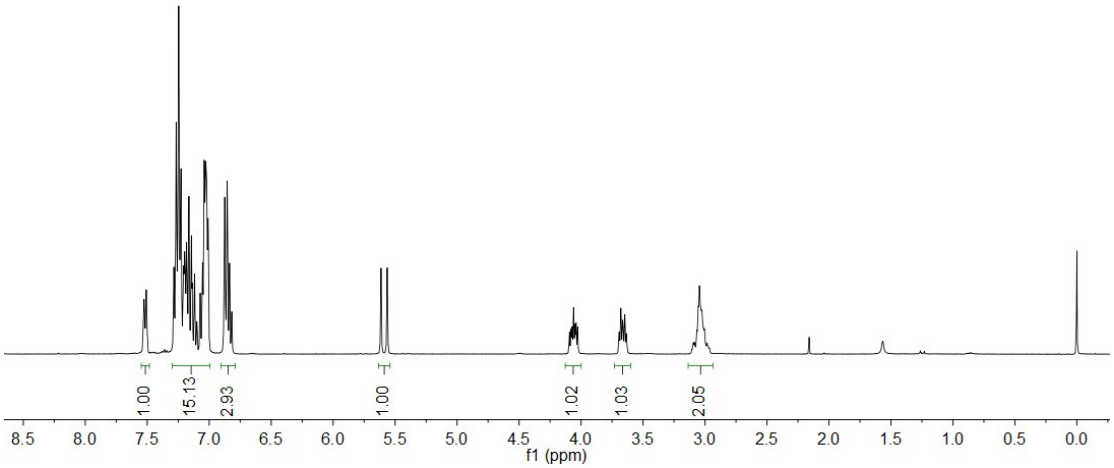

7.45 7.45 7.44 7.43 7.43 7.33 7.33 7.33 7.32 7.32 7.31 7.31 7.29 7.28 7.28 7.27 7.27 7.26 7.26 7.25 7.23 7.22 7.21 7.21 7.21 7.20 7.19 7.19 7.19 7.18 7.18 7.17 7.16 7.15 7.07 7.05 6.77 6.75 5.47 5.42 5.07 5.05 5.04 5.02 5.00 4.99 4.97 4.96 4.93 4.91 4.90 4.85 4.83 4.82 4.80 4.08 3.69 3.66
1.00 14.11 1.87 0.89 0.97 3.96 0.97 0.97 0.96 1.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2.0 -2.5 -3.0
f1 (ppm)
7c

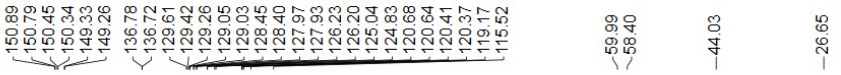

150.31 150.25 137.98 137.92 137.82 137.68 130.00 129.61 129.58 129.41 129.37 129.33 129.25 129.04 128.95 128.82 128.78 128.36 128.33 126.72 126.69 119.25 115.81
69.00 68.93 68.20 68.12 60.06 58.50 44.33 27.42
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
7c

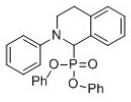

7.53
7.51
7.29
7.27
7.25
7.24
7.23
7.21
7.20
7.18
7.16
7.14
7.14
7.12
7.10
7.07
7.05
7.04
7.03
7.03
7.03
7.02
7.01
6.87
6.86
6.84
6.82
5.61
5.56
4.09
4.08
4.07
4.06
4.05
4.04
4.03
3.69
3.68
3.66
3.65
3.63
3.07
3.05
3.05
3.03
3.02
3.00


N
O–P=O
Ph
O~Ph

7d

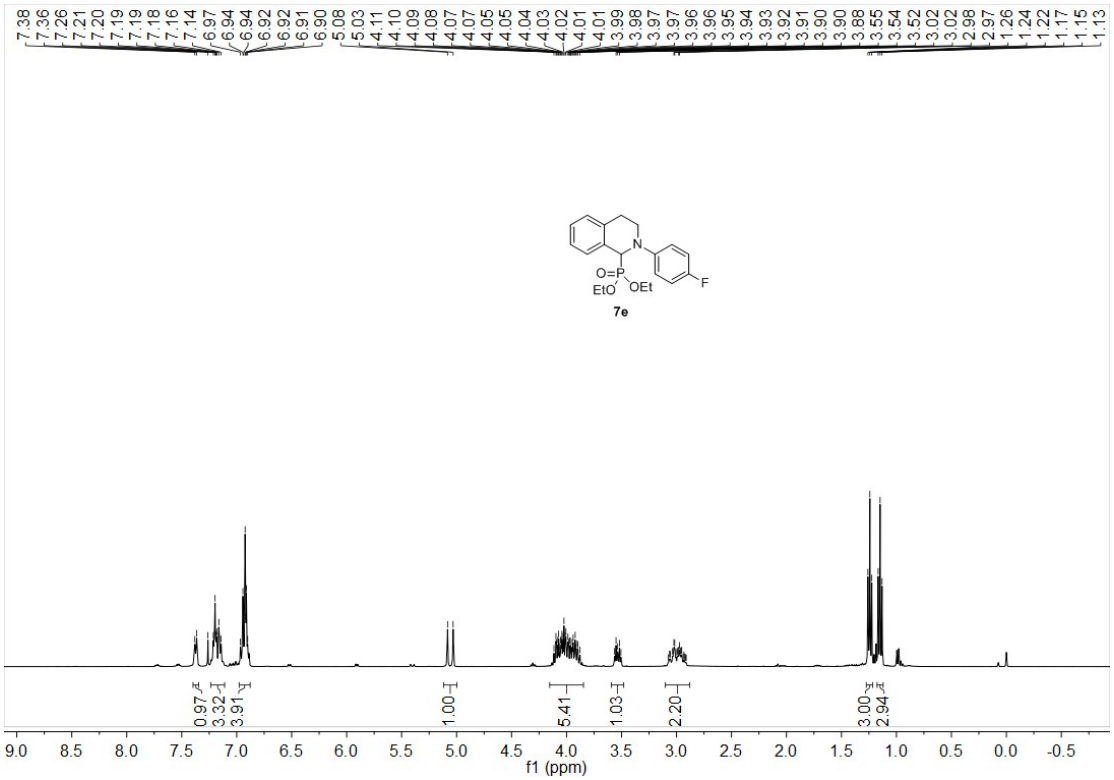

1.00
15.13
2.93
1.00
1.02
1.03
2.05
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

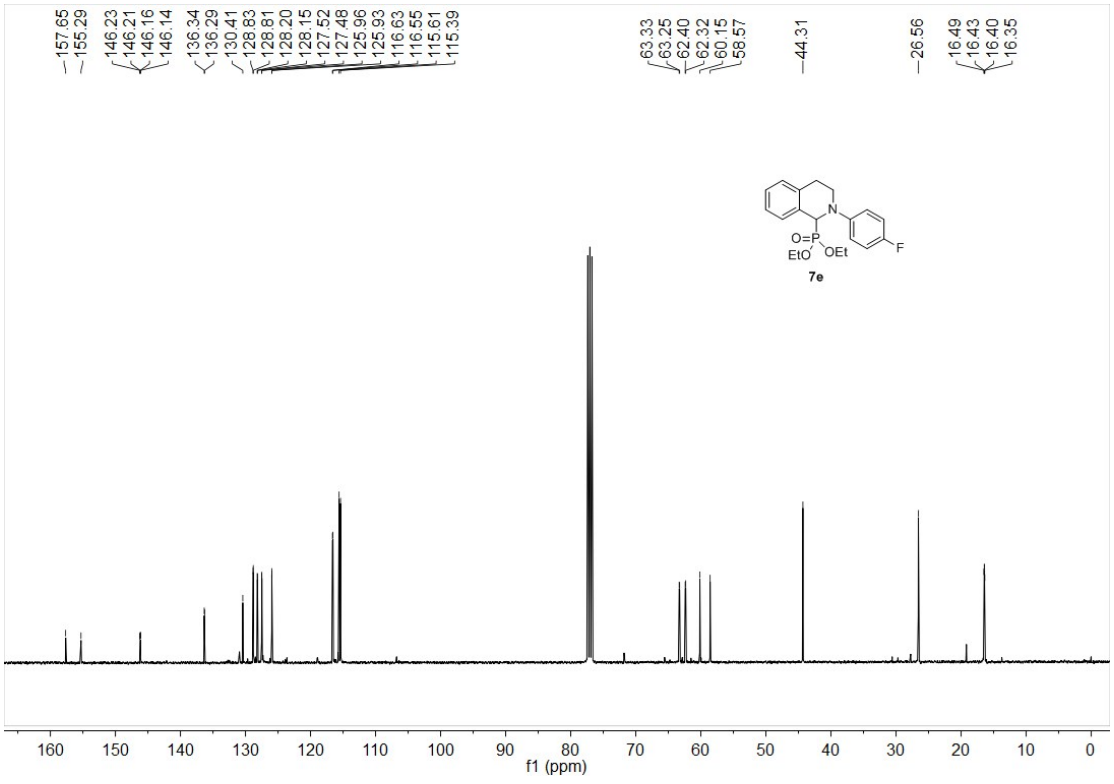

150.89
150.79
150.45
150.34
149.33
149.26
136.78
136.72
129.61
129.42
129.26
129.05
129.03
128.45
128.40
127.97
127.93
126.23
126.20
125.04
124.83
120.68
120.64
120.41
120.37
119.17
115.52
59.99
58.40
44.03
26.65

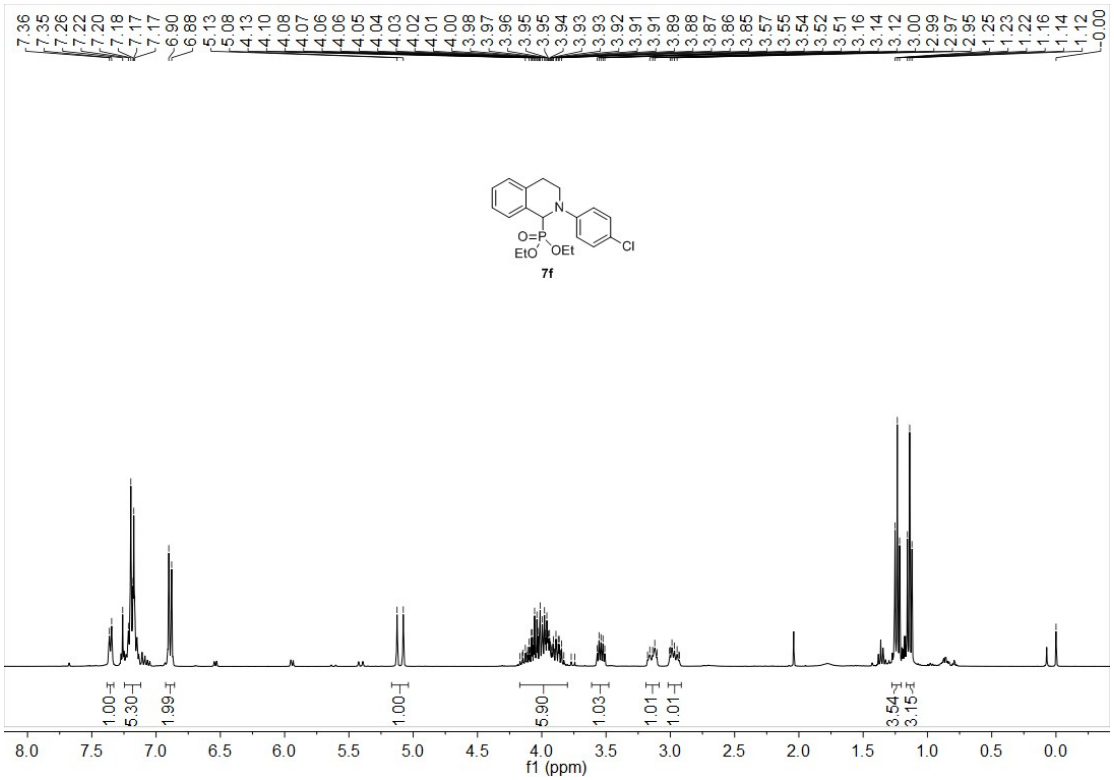

N
O–P=O
Ph
O~Ph

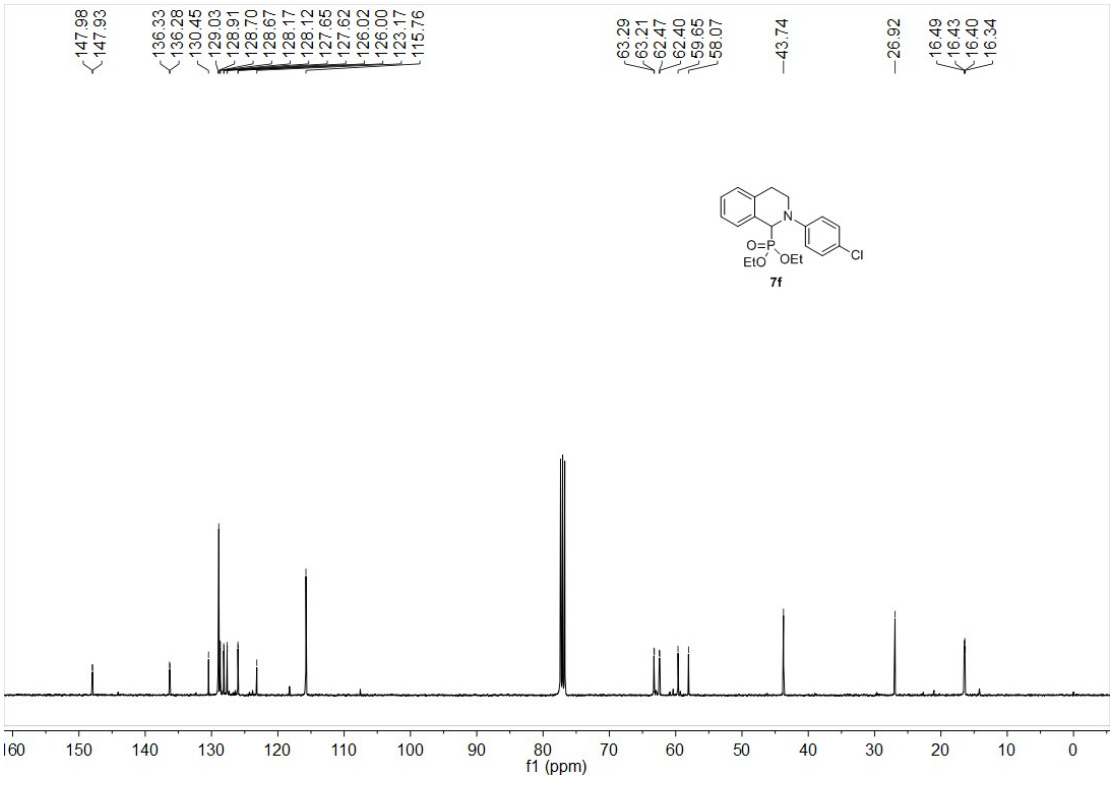
7d

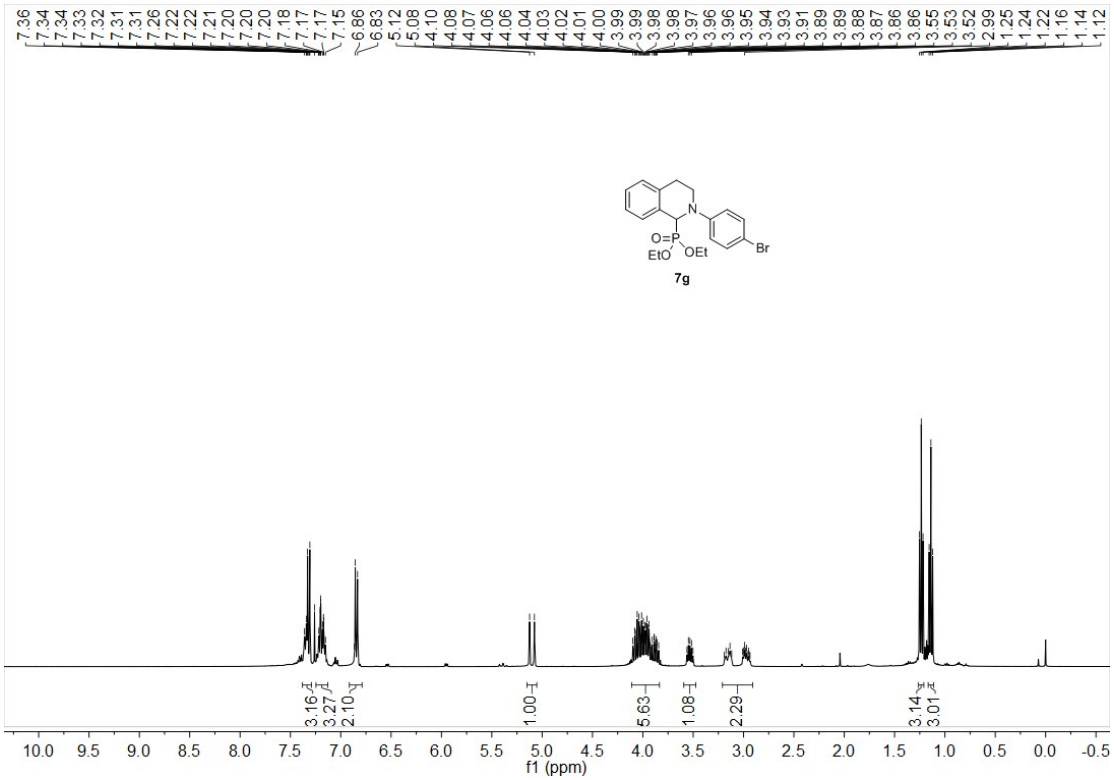
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

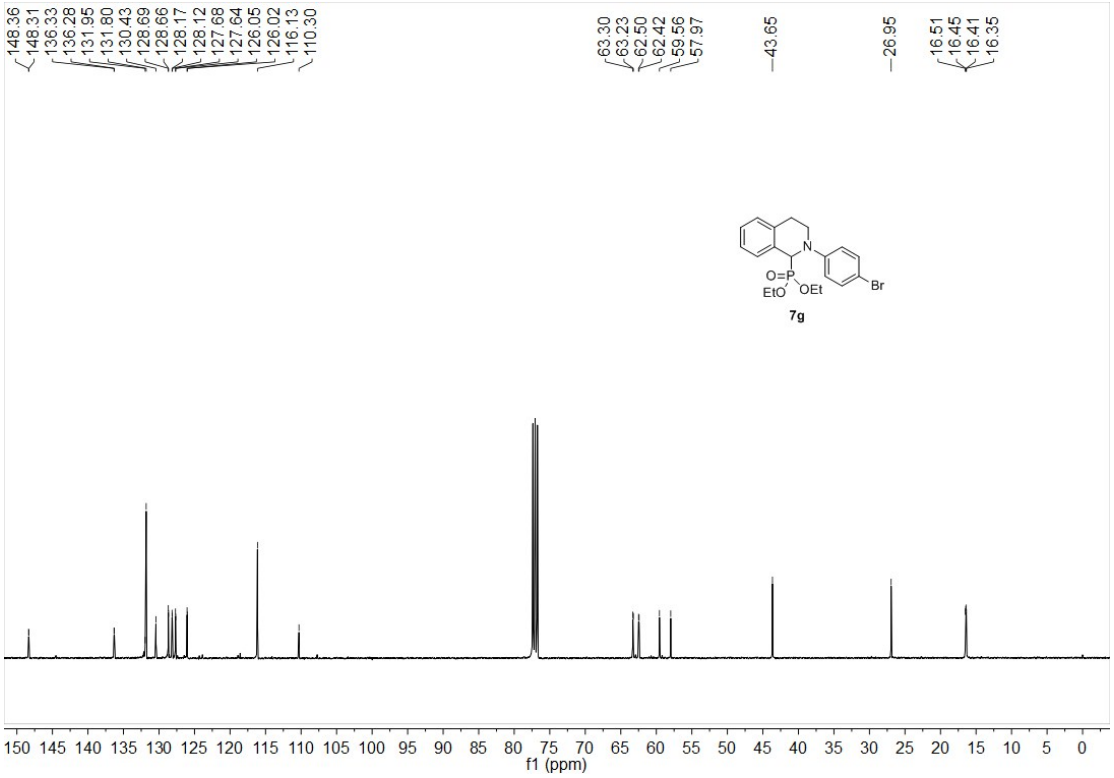

7.38 7.36 7.26 7.21 7.20 7.19 7.19 7.18 7.16 7.14 6.97 6.94 6.94 6.92 6.92 6.91 6.90 5.08 5.03 4.11 4.10 4.09 4.08 4.07 4.07 4.05 4.05 4.04 4.03 4.02 4.01 4.01 3.99 3.98 3.97 3.97 3.96 3.96 3.95 3.94 3.93 3.92 3.91 3.90 3.90 3.88 3.55 3.54 3.52 3.02 3.02 2.98 2.97 1.26 1.24 1.22 1.17 1.15 1.13
O=P
EtO
OEt
F
7e
0.97
3.32
3.91
1.00
5.41
1.03
2.20
3.00
2.94
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

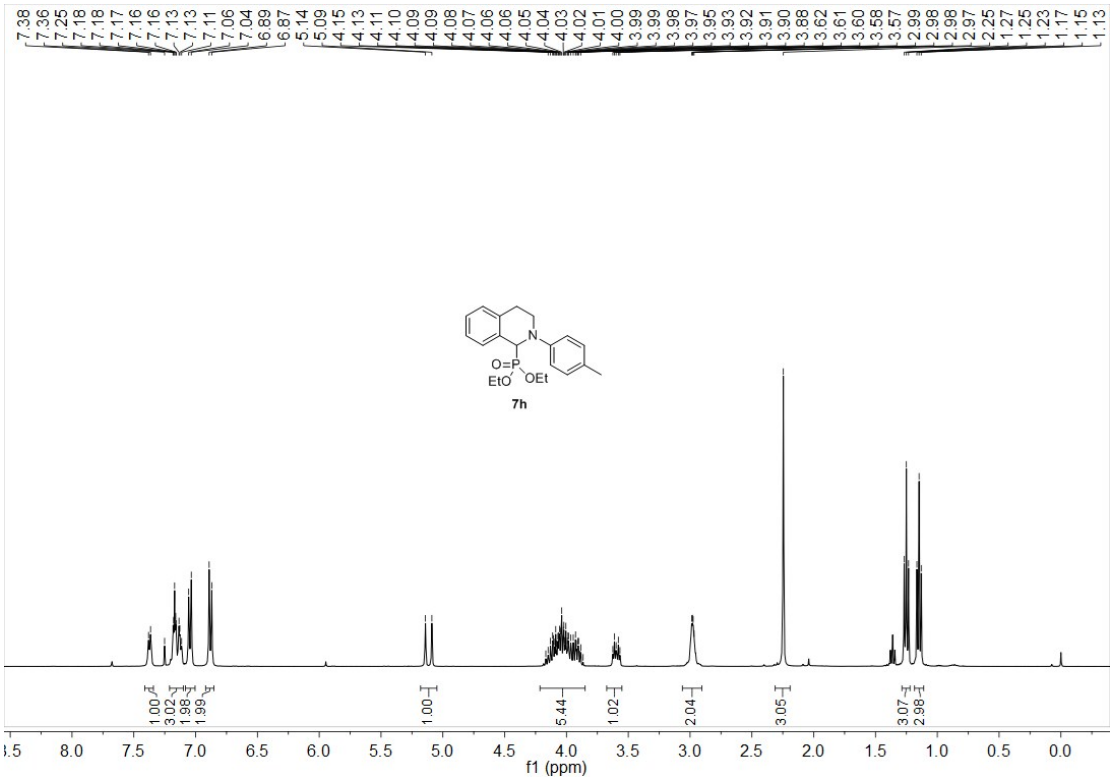

157.65 155.29 146.23 146.21 146.16 146.14 136.34 136.29 130.41 128.83 128.81 128.20 128.15 127.52 127.48 125.96 125.93 116.63 116.55 115.61 115.39 63.33 63.25 62.40 62.32 60.15 58.57 44.31 26.56 16.49 16.43 16.40 16.35
O=P
EtO
OEt
F
7e
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

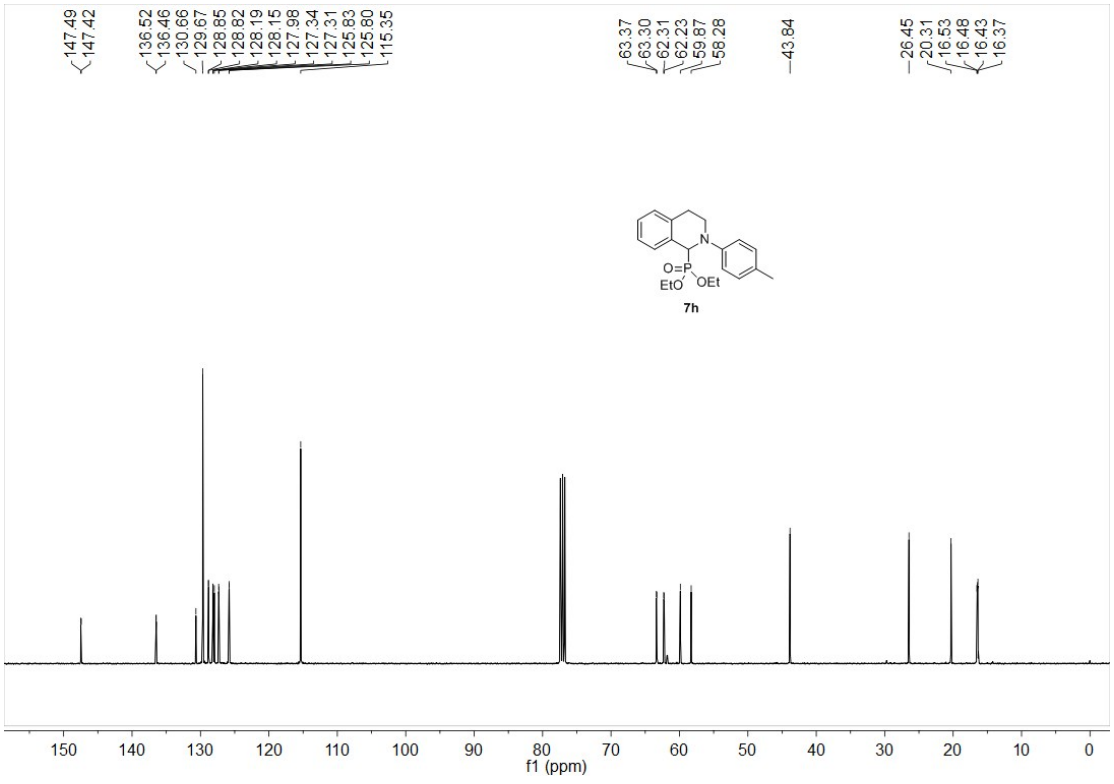

7.36
7.35
7.26
7.22
7.20
7.18
7.17
7.17
6.90
6.88
5.13
5.08
4.13
4.10
4.08
4.07
4.06
4.06
4.05
4.04
4.03
4.02
4.01
4.00
3.98
3.97
3.96
3.95
3.95
3.94
3.93
3.93
3.92
3.91
3.91
3.89
3.88
3.87
3.86
3.85
3.57
3.55
3.54
3.52
3.51
3.16
3.14
3.12
3.00
2.99
2.97
2.95
1.25
1.23
1.22
1.16
1.14
1.12
0.00
O=P
EtO
OEt
N
Cl
7f
1.00
5.30
1.99
1.00
5.90
1.03
1.01
1.01
3.54
3.15
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

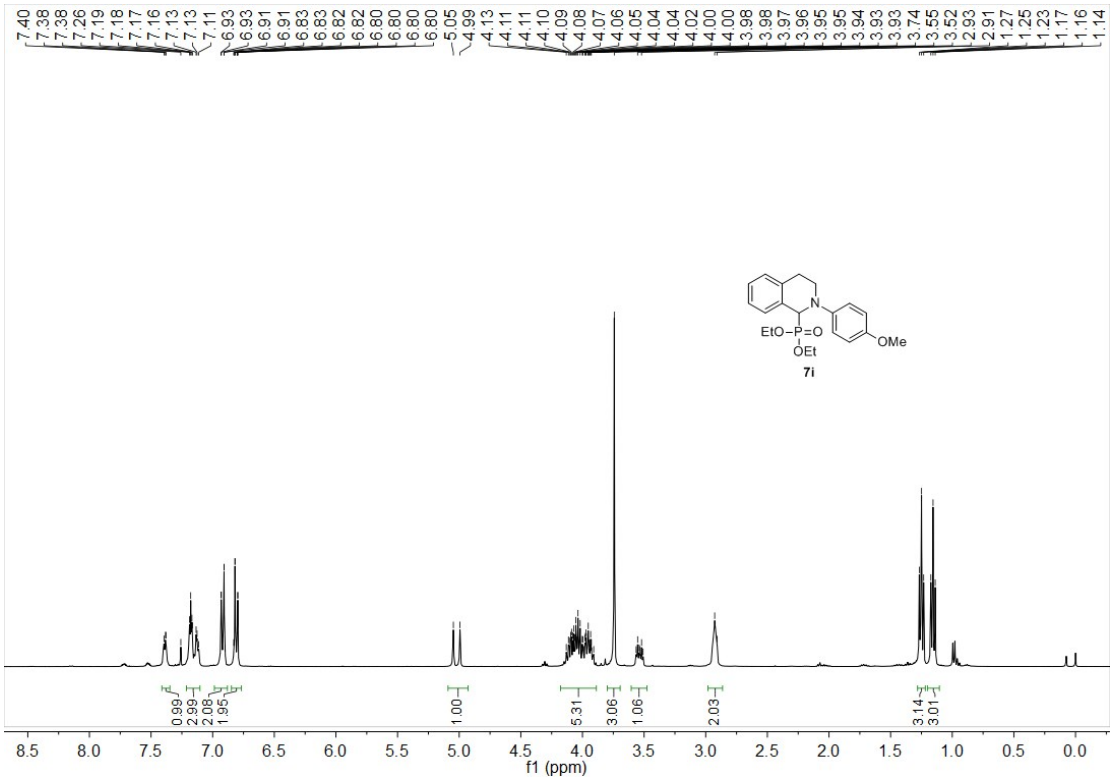

147.98
147.93
136.33
136.28
130.45
129.03
128.91
128.70
128.67
128.17
128.12
127.65
127.62
126.02
126.00
123.17
115.76
63.29
63.21
62.47
62.40
59.65
58.07
43.74
26.92
16.49
16.43
16.40
16.34
O=P
EtO
OEt
N
Cl
7f
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

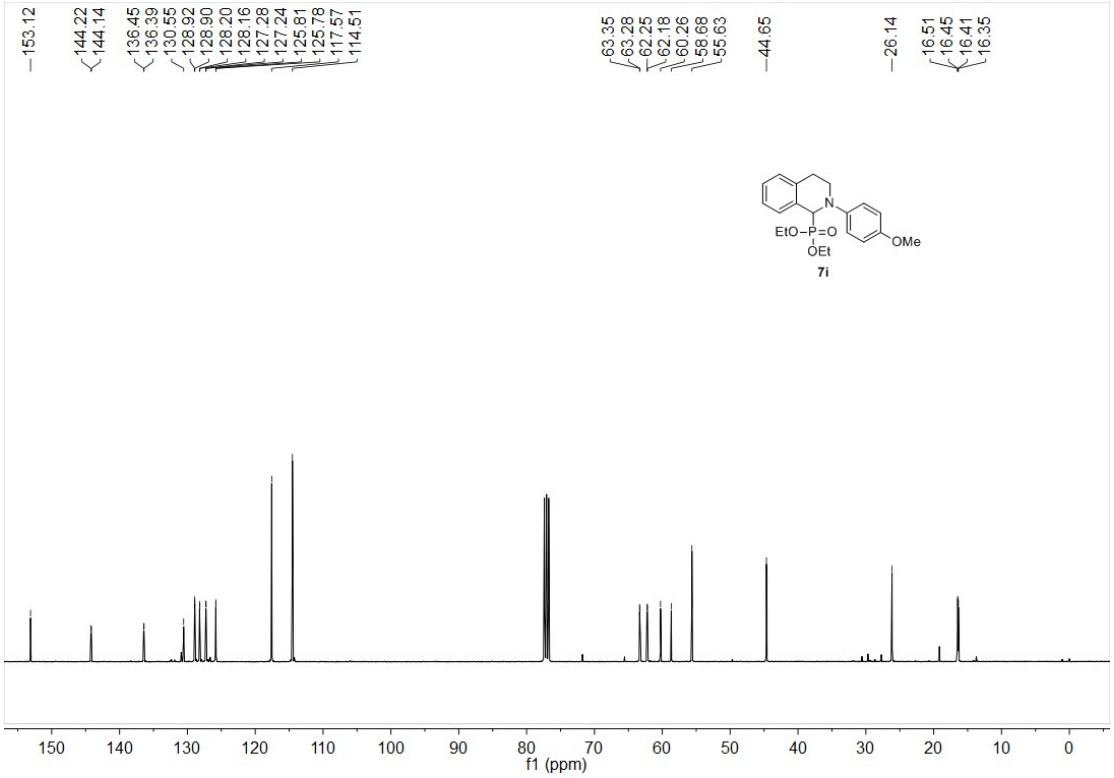

7.36 7.34 7.34 7.33 7.32 7.31 7.31 7.26 7.22 7.22 7.21 7.20 7.20 7.20 7.18 7.17 7.17 7.15 6.86 6.83 5.12 5.08 4.10 4.08 4.07 4.06 4.06 4.04 4.03 4.02 4.01 4.00 3.99 3.99 3.98 3.98 3.97 3.96 3.96 3.95 3.94 3.93 3.91 3.89 3.89 3.88 3.87 3.86 3.86 3.55 3.53 3.52 2.99 1.25 1.24 1.22 1.16 1.14 1.12
O=P
EtO
OEt
N
Br
7g
3.16 3.27 2.10 1.00 5.63 1.08 2.29 3.14 3.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

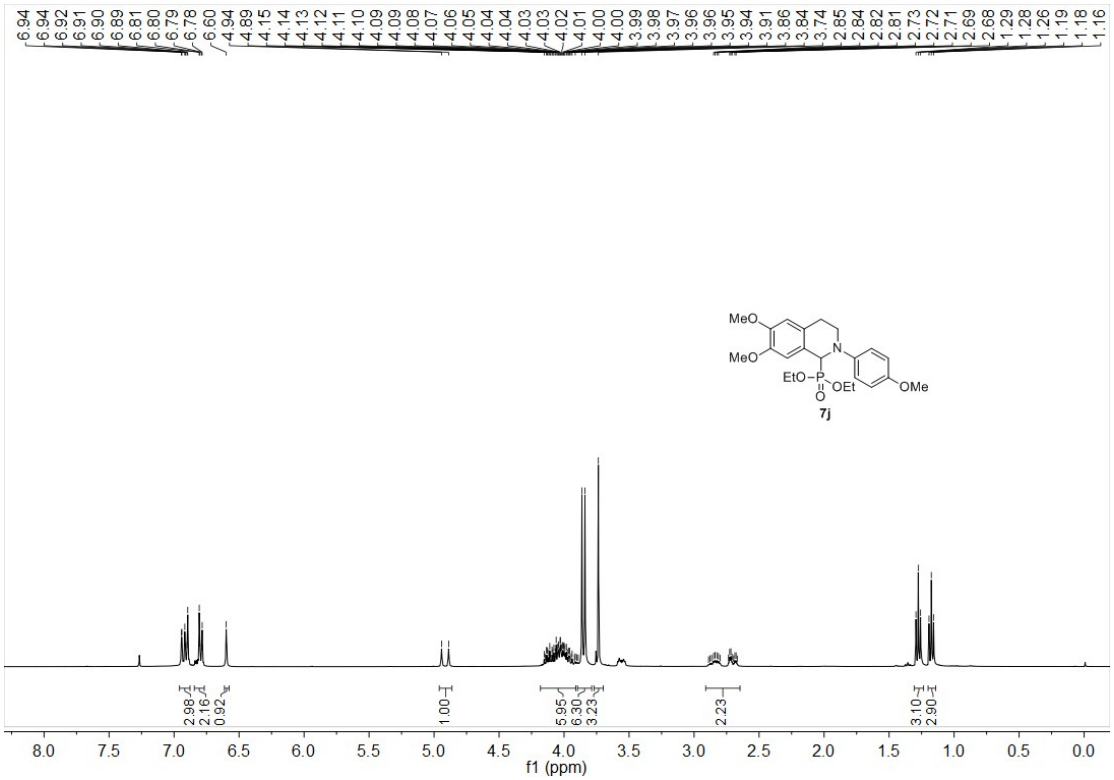

148.36 148.31 136.33 136.28 131.95 131.80 130.43 128.69 128.66 128.17 128.12 127.68 127.64 126.05 126.02 116.13 110.30
63.30 63.23 62.50 62.42 59.56 57.97
43.65
26.95
16.51 16.45 16.41 16.35
O=P
EtO
OEt
N
Br
7g
150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)

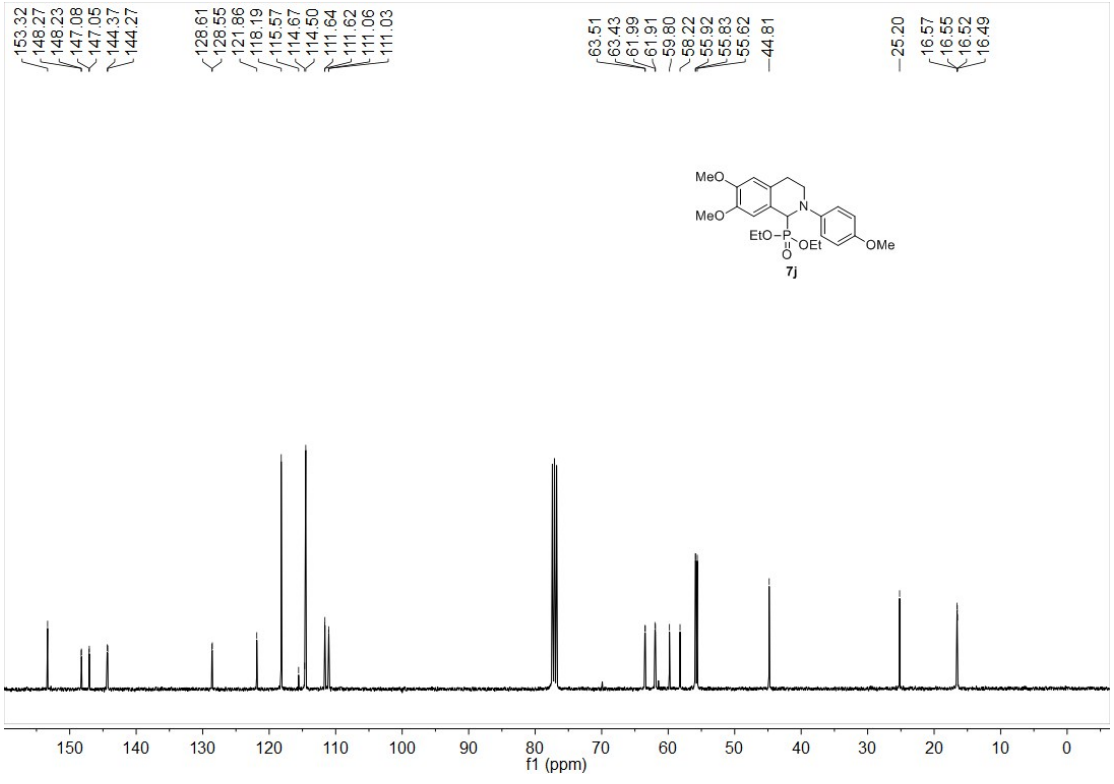

7.38
7.36
7.25
7.18
7.18
7.17
7.16
7.16
7.13
7.13
7.11
7.06
7.04
6.89
6.87
5.14
5.09
4.15
4.13
4.11
4.10
4.09
4.09
4.08
4.07
4.06
4.06
4.05
4.04
4.03
4.02
4.01
4.00
3.99
3.99
3.98
3.97
3.95
3.93
3.92
3.91
3.90
3.88
3.62
3.61
3.60
3.58
3.57
2.99
2.98
2.98
2.97
2.25
1.27
1.25
1.23
1.17
1.15
1.13
O=P
EtO
OEt
7h
1.00
3.02
1.98
1.99
1.00
5.44
1.02
2.04
3.05
3.07
2.98
f1 (ppm)


147.49
147.42
136.52
136.46
130.66
129.67
128.85
128.82
128.19
128.15
127.98
127.34
127.31
125.83
125.80
115.35
63.37
63.30
62.31
62.23
59.87
58.28
43.84
26.45
20.31
16.53
16.48
16.43
16.37
O=P
EtO
OEt
7h
f1 (ppm)


7.40
7.38
7.38
7.26
7.19
7.18
7.17
7.16
7.13
7.13
7.11
6.93
6.93
6.91
6.91
6.83
6.83
6.82
6.82
6.80
6.80
6.80
6.80
5.05
4.99
4.13
4.11
4.11
4.10
4.09
4.08
4.07
4.06
4.05
4.04
4.04
4.02
4.00
4.00
3.98
3.98
3.97
3.96
3.95
3.95
3.94
3.93
3.93
3.74
3.55
3.52
2.93
2.91
1.27
1.25
1.23
1.17
1.16
1.14
EtO–P=O
OEt
OMe
7i
0.99
2.99
2.08
1.95
1.00
5.31
3.06
1.06
2.03
3.14
3.01
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


153.12
144.22
144.14
136.45
136.39
130.55
128.92
128.90
128.20
128.16
127.28
127.24
125.81
125.78
117.57
114.51
63.35
63.28
62.25
62.18
60.26
58.68
55.63
44.65
26.14
16.51
16.45
16.41
16.35
EtO–P=O
OEt
OMe
7i
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


6.94 6.94 6.92 6.91 6.90 6.89 6.81 6.80 6.79 6.78 6.60 4.94 4.89 4.15 4.14 4.13 4.12 4.11 4.10 4.09 4.09 4.08 4.07 4.06 4.05 4.04 4.04 4.03 4.03 4.02 4.01 4.00 4.00 3.99 3.98 3.97 3.96 3.96 3.95 3.94 3.91 3.86 3.84 3.74 2.85 2.84 2.82 2.81 2.73 2.72 2.71 2.69 2.68 1.29 1.28 1.26 1.19 1.18 1.16
MeO
MeO
EtO
P
O
OEt
N
OMe
7j
2.98 2.16 0.92 1.00 5.95 6.30 3.23 2.23 3.10 2.90
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


153.32 148.27 148.23 147.08 147.05 144.37 144.27 128.61 128.55 121.86 118.19 115.57 114.67 114.50 111.64 111.62 111.06 111.03 63.51 63.43 61.99 61.91 59.80 58.22 55.92 55.83 55.62 44.81 25.20 16.57 16.55 16.52 16.49
MeO
MeO
EtO
P
O
OEt
N
OMe
7j
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)