Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Photocatalytic intermolecular *anti*-Markovnikov hydroamination of unactivated alkenes with *N*-hydroxyphthalimide

Zhi-Peng Ye,[a] Yuan-Zhuo Hu,[a] Peng-Ju Xia,*[a,b] Hao-Yue Xiang,*[a] Kai Chen*[a,c] and Hua Yang*[a]

[a]*College of Chemistry and Chemical Engineering, Central South University, Changsha 410083, P. R. China*
[b]*School of Chemistry and Pharmaceutical Sciences, Guangxi Normal University, Guilin 541004, P. R. China.*
[c]*State Key Laboratory of Chemical Oncogenomics, Peking University Shenzhen Graduate School, Shenzhen 518055, P. R. China*

E-mail: hyangchem@csu.edu.cn, kaichen@csu.edu.cn, xianghaoyue@csu.edu.cn, xiaojujuxia@163.com.

1. General experimental methods

Unless otherwise noted, all the reagents were purchased from commercial suppliers and used without further purification. ^{1}H NMR spectra were recorded at 400 MHz. The chemical shifts were recorded in *ppm* relative to tetramethylsilane and with the solvent resonance as the internal standard. Data were reported as follows: chemical shift, multiplicity (*s* = singlet, *d* = doublet, *t* = triplet, *q* = quartet, *br s* = broad singlet, *p* = quintet, *h* = sextet, *hept* = septet, *m* = multiplet), coupling constants (Hz), integration. ^{13}C NMR data were collected at 100 MHz with complete proton decoupling.High resolution mass spectroscopy (HRMS) was recorded on TOF MS ES+ mass spectrometer and acetonitrile was used to dissolve the sample.Emission intensities were recorded using Perkin-Elemer LS 55 fluorescence spectrometer. Column chromatography was carried out on silica gel (200-300 mesh).

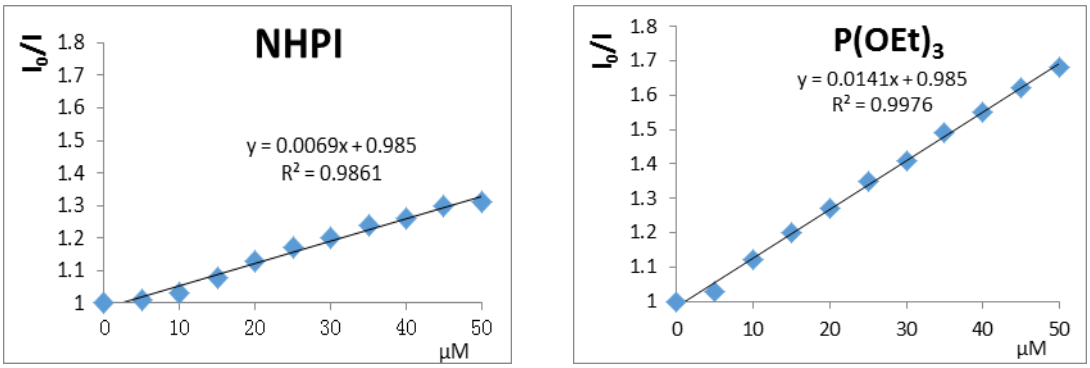
2. General procedure: synthesis of compounds 3a-3s

N-Hydroxyphthalimide (0.2 mmol, 1.0 equiv.), olefins (0.6 mmol, 3.0 equiv.), $P(OEt)_3$ (0.3 mmol, 1.5 equiv.), $[Ir(dFCF_3ppy)_2dtbbpy]PF_6$ (2 mol%) in MeCN (4 mL)was stirred at room temperature for 24h under irradiation of 30 W blue LEDs (distance app. 3 cm). Then, it was diluted with EtOAc (60 mL), and washed with brine (3×20 mL), dried over Na_2SO_4 and concentrated under reduced pressure. The obtained crude product was then purified by flash chromatography using silica gel (EtOAc/PE = 1:9-1:4).

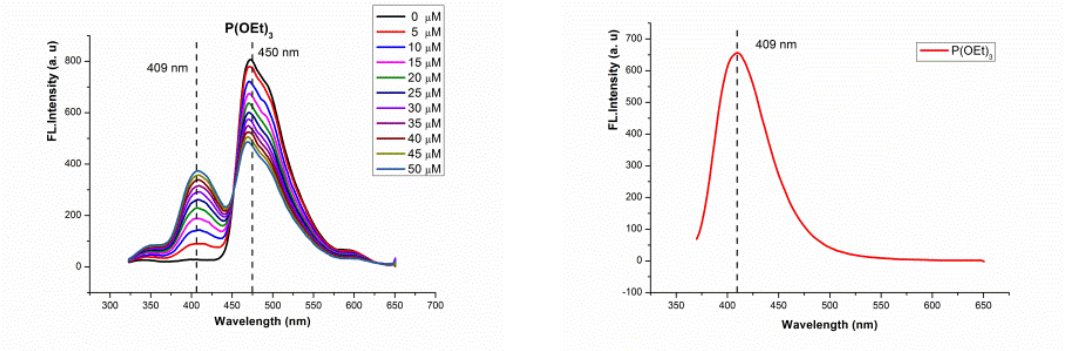
3. Mechanistic studies

3.1 Emission quenching experiments (Stern–Volmer Studies)

All fluorescence measurements were recorded using a Hitachi FL-7000 Fluorometer. Quenching studies were conducted in MeCN. All $[Ir(dFCF_3ppy)_2dtbbpy]PF_6$ solutions (concentration of 5 μM) were excited at 304nm and the emission intensity was collected at 450nm (Figure S1(a)(b)). It was found that the wavelength of maximum emission of $[Ir(dFCF_3ppy)_2dtbbpy]PF_6$ is at a wavelength of 450 nm, and that of $P(OEt)_3$ is at 409 nm (Figure S1 (c-d)). Considering NHPI also had UV-Vis absorption near 304 nm,[1] a competition of absorption of the light source between the photocatalyst and substrates may lead to a quenching effect of photocatalyst at 450 nm.



(a) (b)



(c) (d)

Figure S1. (a)(b)Stern-Volmer experiment in MeCN; (c) the fluorescence emission spectrum of $[Ir(dFCF_3ppy)_2dtbbpy]PF_6$(c = 5 μM) in the presence of $P(OEt)_3$at difference concentration in MeCN; (d) the fluorescence emission spectrum of $P(OEt)_3$ (c = 50 μM)

3.2Trapping experiment

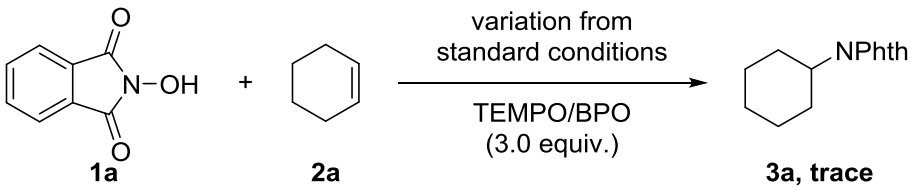
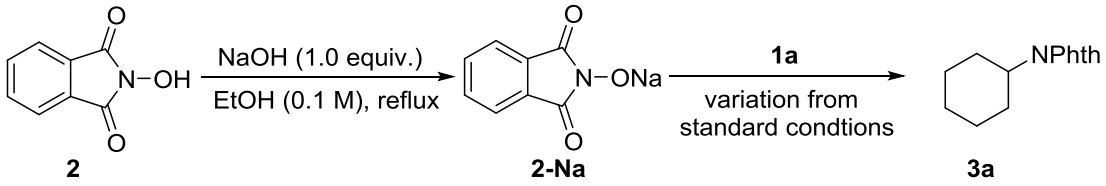


Figure S2. TEMPO/BPO trapping experiments

3.3Control experiments for tracking hydrogen source



Entry	Solvent	Yield (%)
1	MeCN	NR
2	MeCN/H_2O 3:1	NR

[a] Conditions: N-Hydroxyphthalimide**2** (0.2 mmol, 1.0 equiv.), olefin **1a**(0.6 mmol, 3.0 equiv.), $P(OEt)_3$(0.3 mmol, 1.5 equiv.), $[Ir(dFCF_3ppy)_2dtbbpy]PF_6$ (2 mol%), MeCN (4 mL), 30 w blue LED, rt, argon atmosphere, 24 hours.

3.4 Time profile of the transformation with the light ON/OFF over time

The *N*-hydroxyphthalimide and phenyl vinyl sulfide were used as reactants under optimized reaction conditions and extra 3 equiv. of 1,3,5-trimethoxybenzenewas added as the internal standard. After irradiation for 2.5 h, an aliquot (100 μL) of the reaction mixture was transferred into a nuclear magnetic tube charged with 0.6 mL of $CDCl_3$. The yield of product was determined by ^1H NMR. Then the reaction mixture was stirred for 2.5 h with light-off. All of the following yields were analyzed in the identical way after a 2.5 h light on or off.

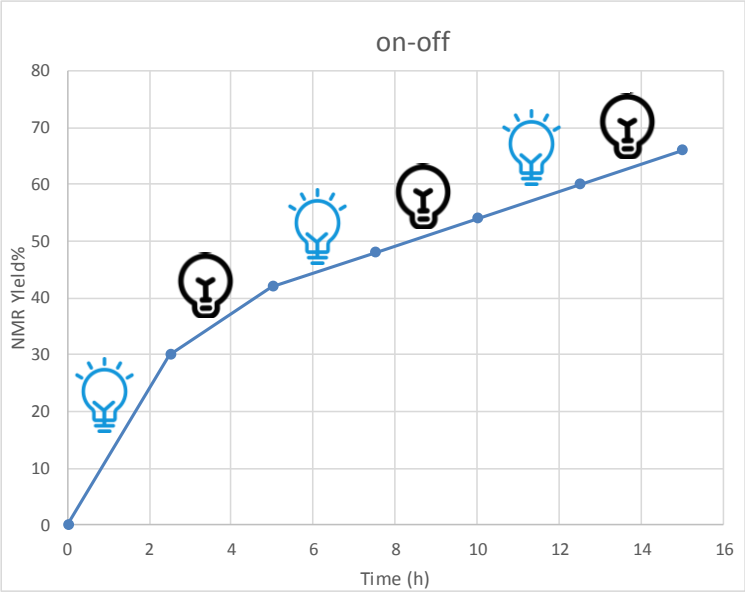
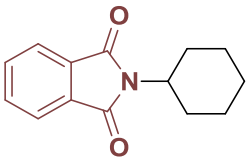


Figure S2. Time profile of the transformation with the light ON/OFF over time.

4. Characterization data of compounds

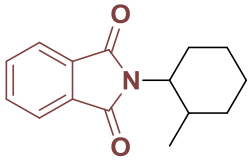


3a

N-cyclohexylphthalimide **3a**:[2]colorless oil (37.1 mg, 0.164 mmol, yield 82%);

^{1}H NMR (400 MHz,$CDCl_3$) δ 7.79 – 7.83 (m, 2H), 7.67 – 7.70 (m, 2H), 4.10 (tt, *J* = 12.4, 4.0 Hz, 1H), 2.15 – 2.25 (m, 2H), 1.83 – 1.87 (m, 2H), 1.67 – 1.73 (m, 2H), 1.27 – 1.38 (m, 4H);

HRMS (ESI): $C_{14}H_{15}NNaO_2^+$ $[M+Na]^+$ Calcd 252.0995, Found 252.0996.

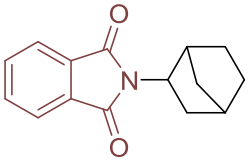


3b

N-(2-methylcyclohexy)phthalimide **3b**:[3]colorless oil (37.1 mg, 0.132 mmol, yield 66%);77:23 *trans:cis*;*

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 – 7.83 (m, 2H), 7.69 – 7.71 (m, 2H), 4.28 (dt, *J* = 12.8, 4.0 Hz, 0.23H)*, 3.76 (td, *J* = 12.0, 4.0 Hz, 0.77 H), 2.81 (qd, *J* = 12.8, 4.0 Hz, 0.24 H)*, 2.31 – 2.39 (m, 0.78 H), 2.13 – 2.23 (m, 1H), 1.83–1.93 (m, 2H), 1.70 – 1.73 (m, 2H), 1.04– 1.64 (m, 3H), 1.02 (d, *J* = 7.2 Hz, 0.71 H)*, 0.80 (d, *J* = 6.4 Hz, 2.38 H).

HRMS (ESI): $C_{15}H_{17}NO_2Na^+$ $[M+Na]^+$ Calcd 266.1151, Found 266.1171.

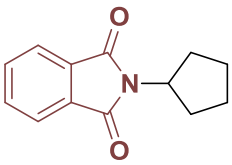


3c

N-(bicyclo[2.2.1]heptan-2-yl)phthalimide **3c**:[3]colorless oil (40.3mg, 0.166 mmol, yield 83%); 73:27 *exo:endo**;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 – 7.83 (m, 2H), 7.67 – 7.72 (m, 2H), 4.24 – 4.48 (m, 0.19H)*, 4.14 (dd, *J* = 8.4, 5.6 Hz, 0.81H), 2.52 – 2.57 (m, 0.29H), 2.41 – 2.42 (m, 2H), 2.23 – 2.28 (m, 2H), 1.27 – 1.75(m, 6H);

HRMS (ESI): $C_{15}H_{15}NNaO_2^+$ $[M+Na]^+$ Calcd 264.0995, Found 264.0980.

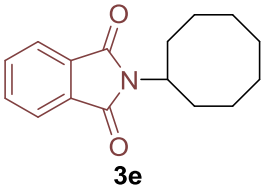


3d

N-cyclopentylphthalimide **3d**:[3] colorless oil (32.7 mg, 0.152 mmol, yield 76%);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 – 7.83 (m, 2H), 7.67 – 7.72 (m, 2H), 4.63 (p, *J* = 8.4 Hz, 1H), 2.06 – 2.15 (m, 2H), 1.89 – 2.01 (m, 4H), 1.60 – 1.70 (m, 2H);

HRMS (ESI): $C_{13}H_{13}NNaO_2^+$ $[M+Na]^+$ Calcd 238.0838, Found 238.0849.

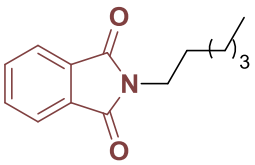


3e

N-cyclooctylphthalimide **3e**:[3]colorless oil (29.3 mg, 0.114 mmol, yield 57%);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.82 (m, 2H), 7.68 – 7.71 (m, 2H),4.37 (tt, *J* = 10.4, 3.2 Hz, 1H), 2.28-2.36 (m, 2H), 1.74 – 1.84 (m, 6H), 1.53 –1.61 (m, 6H);

HRMS (ESI): $C_{16}H_{19}NNaO_2^+$ $[M+Na]^+$ Calcd 280.1308, Found 280.1305.

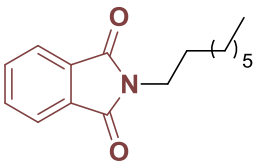


3f

N-(hexyl)phthalimide **3f**:[4]colorless oil (28.6 mg, 0.124 mmol, yield 62%);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.85 (m, 2H), 7.70 – 7.72 (m, 2H), 3.68 (t, *J* = 7.4 Hz, 2H), 1.65 – 1.69 (m, 2H), 1.26 – 1.34 (m, 6H), 0.88 (t, *J* = 6.8 Hz, 3H);

HRMS (ESI): $C_{14}H_{17}NNaO_2^+$ $[M+Na]^+$ Calcd 254.1151, Found 254.1168.

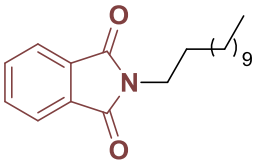


3g

N-(octyl)phthalimide **3g**:[5] colorless oil (36.8 mg, 0.142 mmol yield 71%);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.85 (m, 2H), 7.69 – 7.71 (m, 2H), 3.68 (t, J = 7.2 Hz, 2H), 1.64 – 1.69 (m, 2H), 1.32 – 1.33 (m, 10H), 0.87 (t, *J* = 7.2 Hz, 3H);

HRMS (ESI): $C_{16}H_{21}NNaO_2^+$ $[M+Na]^+$ Calcd 282.1465, Found 282.1477.



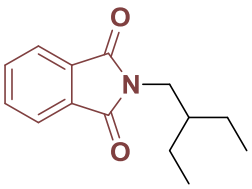
3h

N-(dodecyl)phthalimide **3h**: colorless oil (37.8 mg, 0.120 mmol, yield 60%);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.85 (m, 2H), 7.70 – 7.71 (m, 2H), 3.67 (t, *J* = 7.6 Hz, 2H), 1.65 – 1.69 (m, 2H), 1.28 – 1.34 (m, 18H), 0.86 – 0.89 (m, 3H);

^{13}C NMR (100 MHz, Chloroform-*d*) δ 168.5, 133.8, 132.2, 123.1, 38.1, 31.9, 29.6 – 29.2 (m), 28.6. 22.7, 14.1;

HRMS (ESI): $C_{20}H_{29}NO_2K^+$ $[M+K]^+$ Calcd 354.1830, Found 354.1801.



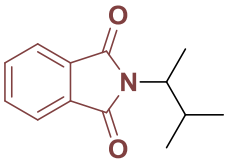
3i

N-(2-ethylbutyl)phthalimide**3i**:colorless oil (32.8 mg, 0.142 mmol, yield 71%);

^{1}H NMR (400 MHz,$CDCl_3$) δ 7.83 – 7.85 (m, 2H), 7.70 – 7.72 (m, 2H), 3.59 (d,*J* = 7.2 Hz, 2H), 1.75–1.82 (m, 1H), 1.34 (p, *J* = 7.2 Hz, 4H), 0.92 (t, *J* = 3.6 Hz, 6H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.7, 133.8, 132.1, 123.1, 41.6, 39.7, 23.3, 10.5;

HRMS (ESI): $C_{14}H_{17}NNaO_2^+$ $[M+Na]^+$ Calcd 254.1151, Found 254.1143.

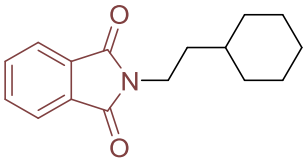


3j

N-(3-methylbutan-2-yl)phthalimide**3j**:[6]colorless oil (23.4 mg, 0.108 mmol, yield 54%);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.83 (m, 2H), 7.69 – 7.72 (m, 2H), 3.91 – 3.99 (m, 1H), 2.35 – 2.44 (m, 1H), 1.47 (d, *J* = 6.8 Hz, 3H), 1.03 (d, *J* = 6.8 Hz, 3H), 0.83 (d, *J* = 6.4 Hz, 3H).

HRMS (ESI): $C_{13}H_{15}NNaO_2^+$$[M+Na]^+$ Calcd 240.0995, Found 240.0998.



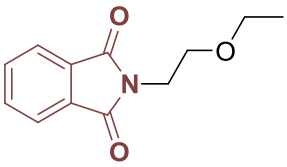
3k

N-(2-cyclohexylethyl)phthalimide **3k**: colorless oil (36.5 mg, 0.142 mmol, yield 71%);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.85 (m, 2H), 7.70 – 7.72 (m, 2H),3.70 (t, *J* = 7.6 Hz, 2H),1.76 – 1.82 (m, 2H), 1.62 – 1.73 (m, 3H), 1.56 (q, *J* = 7.2 Hz, 2H), 1.24 –1.33 (m, 2H), 1.16 –1.22 (m, 2H), 0.90 –1.00 (m, 2H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 133.8, 132.2, 123.1, 36.0, 35.9, 35.4, 33.0, 26.5, 26.2;

HRMS (ESI): $C_{16}H_{19}NNaO_2^+$ $[M+Na]^+$ Calcd 280.1308, Found 280.1308.

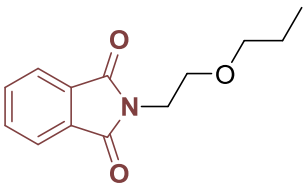


3l

N-(2-ethoxyethyl)phthalimide **3l**:[3]colorless oil (32.0 mg, 0.146 mmol, yield 73%);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.86 (m, 2H), 7.70 – 7.74 (m, 2H), 3.90 (t, *J* = 6.0 Hz, 2H), 3.68 (t, *J* = 6.0 Hz, 2H), 3.52 (q, *J* = 6.8 Hz, 2H), 1.15 (t, *J* = 7.2 Hz, 3H);

HRMS (ESI): $C_{12}H_{13}NNaO_3^+$ $[M+Na]^+$ Calcd 242.0788, Found 242.0804.



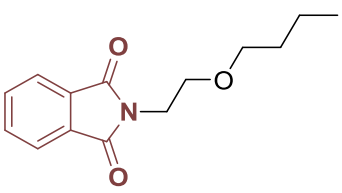
3m

N-(2-propoxyethyl)phthalimide **3m**: colorless oil (31.7 mg, 0.136 mmol, yield 68%);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.86 (m, 2H), 7.71 – 7.73 (m, 2H), 3.90 (t, *J* = 6.0 Hz, 2H), 3.68 (t, *J* = 6.0 Hz, 2H), 3.42 (t, *J* = 6.4 Hz, 2H), 1.54 (h, *J* = 7.2 Hz, 2H), 0.85 (t, *J* = 7.6 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.3, 133.9, 132.1, 123.2, 72.5, 67.3, 37.4, 22.8, 10.4.

HRMS (ESI): $C_{13}H_{15}NNaO_2^+$ $[M+Na]^+$ Calcd 256.0944, Found 256.0947.

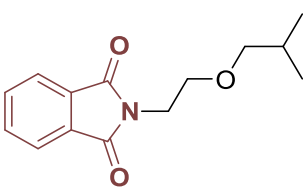


3n

N-(2-butoxyethyl)phthalimide **3n**:[3] colorless oil (34.6 mg, 0.140 mmol, yield 70%);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.86 (m, 2H), 7.71 – 7.74 (m, 2H), 3.89 (t, *J* = 5.6 Hz, 2H), 3.67 (t, *J* = 6.0 Hz, 2H), 3.45 (t, *J* = 6.8 Hz, 2H), 1.46 – 1.55 (m, 2H), 1.25 – 1.34 (m, 2H), 0.85 (t, *J* = 7.2 Hz, 3H);

HRMS (ESI): $C_{14}H_{17}NNaO_3^+$ $[M+Na]^+$ Calcd 270.1101, Found 270.1113.

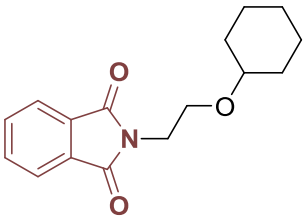


3o

N-(2-isobutoxyethyl)phthalimide **3o**:[3] colorless oil (32.1 mg, 0.130 mmol, yield 65%);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.86 (m, 2H), 7.71 – 7.74 (m, 2H), 3.90 (t, *J* = 6.4 Hz, 2H), 3.67 (t, *J* = 6.0 Hz, 2H), 3.21 (d, *J* = 6.8 Hz, 2H), 1.76 – 1.83 (m, 1H), 0.83 (d, *J* = 6.8 Hz, 6H);

HRMS (ESI): $C_{14}H_{17}NNaO_3^+$ $[M+Na]^+$ Calcd 270.1101, Found 270.1115.

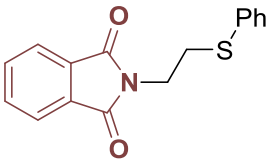


3p

N-(2-(cyclohexyloxy)ethyl)phthalimide **3p**:[3] colorless oil (40.4 mg, 0.148 mmol, yield 74%);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.86 (m, 2H), 7.70 – 7.73 (m, 2H), 3.87 (t, *J* = 6.0 Hz, 2H), 3.69 (t, *J* = 6.0 Hz, 2H), 3.24 – 3.30 (m, 1H), 1.79 – 1.84 (m, 2H), 1.66 – 1.68 (m, 2H), 1.47 – 1.49 (m, 2H), 1.17 – 1.22 (m, 4H);

HRMS (ESI): $C_{16}H_{19}NNaO_3^+$ $[M+Na]^+$ Calcd 296.1257, Found 296.1235.

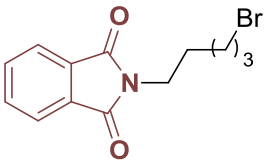


3q

N-(2-(phenylthio)ethyl)phthalimide**3q**:[3] colorless oil (40.8 mg, 0.144 mmol, yield 72%);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 – 7.82 (m, 2H), 7.68 – 7.70 (m, 2H), 7.30 (d, *J* = 7.6 Hz, 2H), 7.23 – 7.26 (m, 2H), 7.12 (t, *J* = 7.2 Hz, 1H), 3.93 (t, *J* = 7.2 Hz, 2H), 3.23 (t, *J* = 7.2 Hz, 2H);

HRMS (ESI): $C_{16}H_{13}NNaO_2S^+$ $[M+Na]^+$ Calcd 306.0559, Found 306.0562.

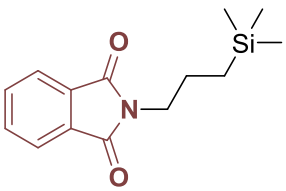


3r

N-(5-bromopentyl)phthalimide **3r**:[3] colorless oil (38.4 mg, 0.130 mmol, yield 65%);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.86 (m, 2H), 7.70 – 7.73 (m, 2H), 3.70 (t, *J* = 7.2 Hz, 2H), 3.40 (t, *J* = 6.8 Hz, 2H), 1.88 – 1.95 (m, 2H), 1.68 – 1.76 (m, 2H), 1.47 – 1.54 (m, 2H).

HRMS (ESI): $C_{13}H_{14}NBrNaO_2^+$ $[M+Na]^+$ Calcd 318.0100, Found 318.0097.



3s

N-(3-(trimethylsilyl)propyl)phthalimide **3s**: colorless oil (19.8 mg, 0.076 mmol, yield 38%);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.88 (m, 2H), 7.71 – 7.75 (m, 2H), 3.68 (t, *J* = 7.2 Hz, 2H), 1.65 – 1.72 (m, 2H), 0.52 – 0.57 (m, 2H), 0 (s, 9H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 135.6, 134.0, 124.9, 42.9, 25.1, 15.6, 0.0;

HRMS (ESI): $C_{14}H_{19}NNaO_2Si^+$ $[M+Na]^+$ Calcd 284.1077, Found 284.1072.

5. Computational details

All calculations were carried out using DFT as implemented in Gaussian16 software package.[7]The hybrid PBE functional[8]in conjugation with def2-TZVP basis set for iridium and def2-SVP basis sets for other atoms was applied for the optimization of all stationary points.[9,10]Frequency calculations were performed at the same level to verify the stationary points are minima (0 imaginary frequency) or saddle points (only 1 imaginary frequency). Single point energy calculations were carried out with Truhlar's M06 functional[11]with def2-TZVPP basis set for all atoms. Time-dependent DFT (TD-DFT) calculations were performed for the excited state structures. Solvation effects of acetonitrile for all calculations were considered using Truhlar's SMD solvent model.[12]Broken symmetry functional was chosen for open shell systems. Computed structures were illustrated by CYLView software.[13]

5.1 Comparison of experimental and calculated redox potentials.

$E_{1/2}^{red}$ in V *vs.* SCE[a]	***[Ir(III)]/[Ir(II)]**	**[Ir(III)]/[Ir(II)]**	**$Ph_3P^{+\bullet}/Ph_3P$**	**$(EtO)_3P^{+\bullet}/(EtO)_3P$**
Experiment	+1.21[14]	-1.37[15]	+0.98[16]	+1.57[16]
Calculation	+1.22	-1.35	+1.04	+1.60

[a]**[Ir(III)]** = $[Ir(dFCF_3ppy)_2dtbbpy]^+$, **[Ir(II)]** = $[Ir(dFCF_3ppy)_2dtbbpy]$.

As shown above, the calculated redox potentials, at M06/def2-TZVPP-SMD(CH_3CN)//PBE/def2SVP(C,H,N,O,P)-def2-TZVP(Ir)-SMD(CH_3CN) theoretical level, are in good agreement with the experimental data, which also suggests our computational level is reliable.

5.2Calculated singlet-triplet energy gaps.

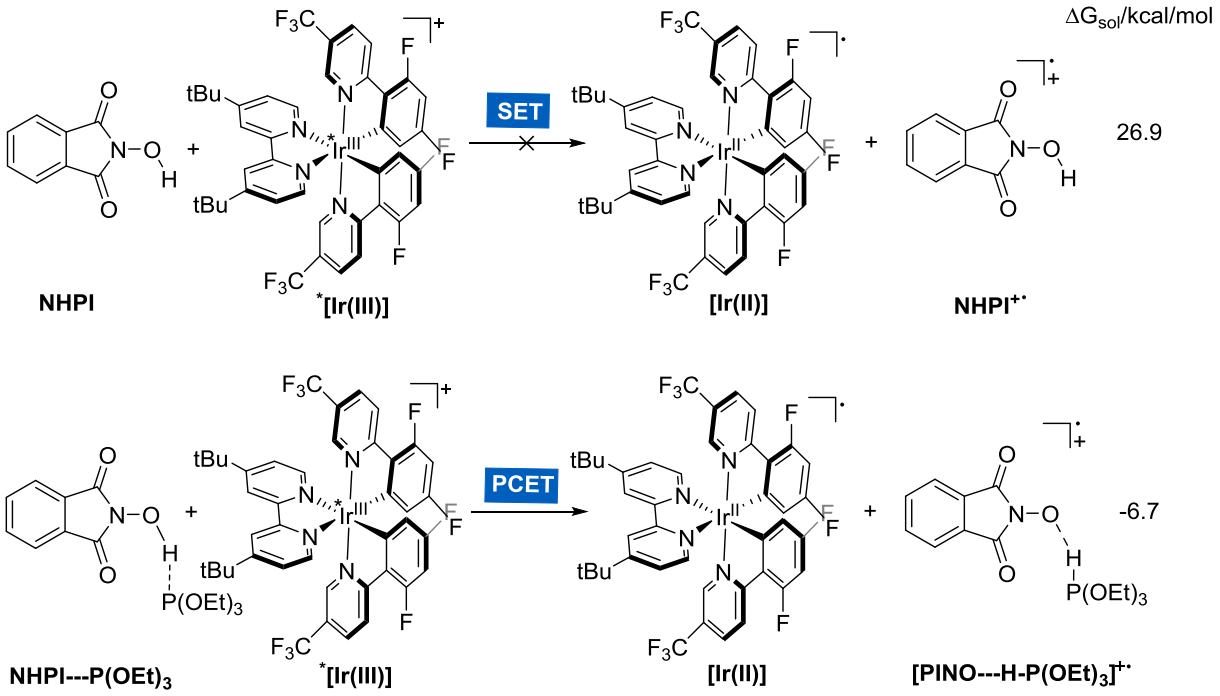
	[Ir(III)]	**NHPI**	**$P(OEt)_3$**
ΔE_{ST} (kcal/mol)[a]	59.2	59.6	82.1

[a]$\Delta E_{ST}$was reported at M06/def2-TZVPP-SMD(CH_3CN)//PBE/def2SVP(C,H,N,O,P)-def2-TZVP(Ir)–SMD(CH_3CN) theoretical level.

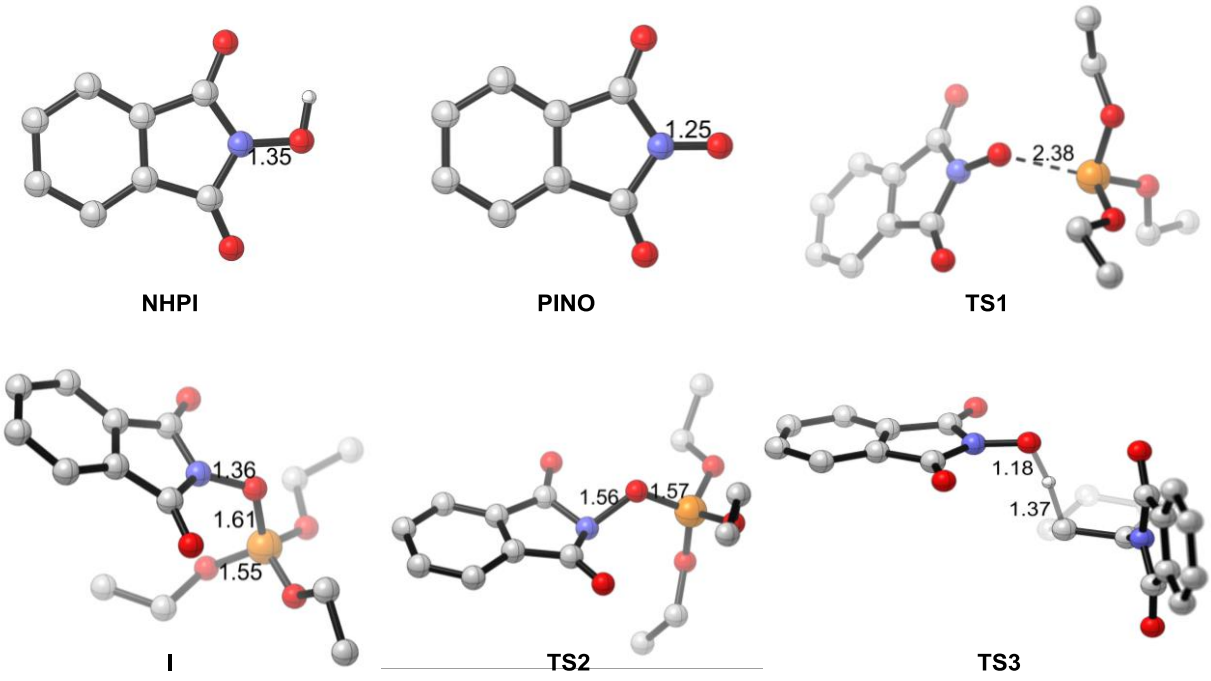
As the singlet-triplet energy gap of NHPI or $P(OEt)_3$ is even larger than that of $[Ir(dFCF_3ppy)_2dtbbpy]^+$, triplet energy transfer from sensitizer Ir(III) to substrates seems to be impossible.

5.3Possible electron transfer patterns from *[Ir(III)] to NHPI.

As shown below, single electron transfer from NHPI to the excited [Ir(III)] catalyst is an endergonic process, as large as 26.9 kcal/mol. However, in the presence of $P(OEt)_3$, a concerted proton-coupled electron transfer seems to be feasible, with an exergonicity of 6.7 kcal/mol.



5.4The optimized structures of important stationary points



5.5Table of energies and other thermodynamic parameters.

Structure	Eele	Eele(SP)	E_0	E	H	G
Ir(III)	-2937.67088	-2942.20156	-2936.98260	-2936.93193	-2936.93098	-2937.07213
***[Ir(III)]**	-2937.57078	-2942.10204	-2936.88614	-2936.83489	-2936.83394	-2936.97730
[Ir(II)]	-2937.78218	-2942.31333	-2937.09769	-2937.04669	-2937.04574	-2937.18836
PPh_3	-1034.55290	-1035.78995	-1034.27669	-1034.26081	-1034.25986	-1034.32304
$^{\bullet+}PPh_3$	-1034.75533	-1035.99358	-1034.47978	-1034.46395	-1034.46301	-1034.52620
[NHPI---$P(OEt)_3$]	-1390.83188	-1392.78836	-1390.49560	-1390.47167	-1390.47072	-1390.55488
[PINO--$HP(OEt)_3$]$^{+\bullet}$	-1390.62582	-1392.58473	-1390.29027	-1390.26538	-1390.26443	-1390.35214
NHPI	-587.18788	-588.12760	-587.06743	-587.05795	-587.05700	-587.10241
$^{\bullet+}$NHPI	-586.93849	-587.87318	-586.81834	-586.80912	-586.80818	-586.85371
NHPI(triplet)	-587.09728	-588.03034	-586.97889	-586.96987	-586.96892	-587.01411
$P(OEt)_3$	-803.63166	-804.64976	-803.41780	-803.40389	-803.40294	-803.46136
$^{\bullet+}P(OEt)_3$	-803.40687	-804.42488	-803.19217	-803.17798	-803.17704	-803.23661
$P(OEt)_3$(triplet)	-803.51379	-804.51474	-803.30171	-803.28719	-803.28624	-803.34772
$^{+}HP(OEt)_3$	-804.05951	-805.08622	-803.83351	-803.81950	-803.81856	-803.87632
PINO	-586.55817	-587.49149	-586.44913	-586.44053	-586.43958	-586.48378
O=$P(OEt)_3$	-878.77046	-879.94720	-878.55098	-878.53628	-878.53534	-878.59581
TS1	-1390.18958	-1392.13900	-1389.86585	-1389.84221	-1389.84126	-1389.92453
I	-1390.19559	-1392.16515	-1389.86971	-1389.84640	-1389.84545	-1389.92556
TS2	-1390.17948	-1392.15031	-1389.85632	-1389.83325	-1389.83231	-1389.91183
II	-511.46338	-512.27037	-511.36045	-511.35254	-511.35159	-511.39450
cyclohexene	-234.19574	-234.54029	-234.04942	-234.04392	-234.04297	-234.07803
III	-745.73811	-746.87869	-745.48403	-745.47015	-745.46920	-745.52574
TS3	-1332.92825	-1335.00031	-1332.55624	-1332.53244	-1332.53150	-1332.61369
3a	-746.40164	-747.54448	-746.13291	-746.11928	-746.11833	-746.17372

Notes: E_{ele}, E_0, E, H, and G were the electronic energies, sum of electronic and zero-point energies, sum of electronic and thermal energies, sum of electronic and thermal enthalpies, and sum of electronic and thermal free energies, respectively, which were given at the PBE/def2SVP(C,H,N,O,P)-def2-TZVP(Ir)-SMD(CH_3CN) level. Eele(SP) were single point electronic energies at the M06/def2-TZVPP-SMD(acetonitrile) level.

5.6 Coordinates of all stationary points.

[Ir(III)]

0 imaginary frequency

Ir	1.338313	5.859245	14.884365
C	0.449100	4.756112	13.462788
C	-0.403434	5.497471	12.594605
C	-1.100172	4.818411	11.581809
C	-0.990713	3.451804	11.393183
C	-0.149750	2.755069	12.254920
C	0.563847	3.374317	13.273065
C	-0.468157	6.928757	12.853949
C	-1.218830	7.876142	12.138876

C	-1.173064	9.211533	12.495659	H	-1.833386	7.552823	11.303323
C	-0.372301	9.599384	13.572942	H	-1.756822	9.947119	11.938187
C	0.345337	8.627208	14.248976	H	0.981842	8.889341	15.093467
N	0.300734	7.333950	13.905282	H	0.954563	8.023992	19.525335
N	2.063139	7.086190	16.491880	H	2.687846	10.040949	21.882270
C	1.249063	7.211371	17.561077	H	1.362429	9.902459	20.711822
C	1.635850	7.948923	18.681143	H	2.081717	8.435333	21.434776
C	2.879757	8.582298	18.730250	H	4.998130	9.358819	21.340951
C	3.349283	9.402332	19.927924	H	4.468333	7.741367	20.813707
C	2.304503	9.440206	21.044434	H	5.446151	8.762002	19.728771
C	4.641110	8.775528	20.478325	H	3.972511	11.447546	20.310950
C	3.627332	10.840581	19.459896	H	2.717170	11.308296	19.054023
C	3.699127	8.428669	17.602590	H	4.406648	10.879527	18.684476
C	3.262099	7.682665	16.520898	H	4.688002	8.886290	17.549350
C	-0.056909	6.525574	17.455611	H	-1.529244	4.597655	15.241134
N	-0.251593	5.808882	16.328588	H	-3.343475	4.646053	16.909413
C	-1.414899	5.164781	16.167042	H	-0.848435	7.189397	19.336808
C	-2.425643	5.199532	17.113048	H	-5.441770	6.595605	19.451425
C	-2.258063	5.931959	18.297173	H	-4.457110	7.586359	18.345251
C	-1.039743	6.598985	18.443888	H	-4.983586	5.954997	17.859135
C	-3.362513	5.976845	19.348568	H	-3.802109	6.839721	21.278986
C	-4.631718	6.561399	18.706814	H	-2.084776	6.450505	21.067987
C	-2.976582	6.838342	20.552155	H	-2.787493	7.884582	20.266693
C	-3.637577	4.543284	19.832433	H	-4.436194	4.554278	20.590042
N	2.428792	4.310957	15.674378	H	-2.739547	4.099981	20.289429
C	3.652702	4.092567	15.113063	H	-3.963997	3.886270	19.012744
C	3.971428	5.003538	14.022847	H	5.440162	2.884221	15.156554
C	5.164792	5.005912	13.282465	H	4.656673	1.457016	17.024954
C	5.401285	5.906036	12.258229	H	1.013864	3.759665	17.084747
C	4.399039	6.828856	11.976795	H	6.336950	5.886560	11.699786
C	3.199342	6.872398	12.675479	H	-1.543405	2.949371	10.599571
C	2.963800	5.961538	13.711465	H	1.204100	2.754164	13.902405
C	4.464897	3.056951	15.603079	H	3.887247	7.555136	15.634970
C	4.024013	2.262273	16.645540	H	2.464927	7.627072	12.389604
C	2.764394	2.505754	17.199018	F	-1.908001	5.483841	10.753774
C	2.002333	3.540135	16.682695	F	-0.029275	1.440487	12.089013

C	-0.288655	11.042385	13.981928
F	-1.498766	11.537288	14.258796
F	0.224266	11.794811	13.003542
F	0.474786	11.211958	15.062633
F	4.606651	7.702370	10.994955
F	6.129087	4.123327	13.551171
C	2.249442	1.658235	18.327350
F	3.080991	1.688688	19.373185
F	2.134983	0.378415	17.959510
F	1.051684	2.064519	18.751206

***[Ir(III)]**

0 imaginary frequency

Ir	1.355124	5.828133	14.831940
C	0.392673	4.727167	13.478058
C	-0.472163	5.489381	12.630855
C	-1.185549	4.818320	11.631743
C	-1.092837	3.443838	11.457135
C	-0.254547	2.725177	12.306678
C	0.483537	3.337647	13.308623
C	-0.518275	6.923698	12.891463
C	-1.306739	7.870245	12.224109
C	-1.253563	9.201250	12.604711
C	-0.412567	9.577562	13.652773
C	0.347563	8.603404	14.281224
N	0.299216	7.321715	13.904761
N	2.091806	7.039482	16.429376
C	1.238120	7.181047	17.508531
C	1.652809	7.957613	18.627024
C	2.892339	8.553098	18.682236
C	3.370082	9.392783	19.863088
C	2.316852	9.489459	20.967779
C	4.639686	8.753633	20.449641
C	3.692500	10.812130	19.366660
C	3.751427	8.354638	17.556909
C	3.313701	7.608449	16.489567
C	-0.014264	6.516462	17.412011
N	-0.231958	5.783353	16.259512
C	-1.423523	5.172436	16.093661
C	-2.431289	5.209919	17.026793
C	-2.241374	5.932260	18.245817
C	-1.031781	6.568860	18.405960
C	-3.353600	5.965897	19.289662
C	-4.614271	6.579116	18.657894
C	-2.970250	6.794126	20.516882
C	-3.654534	4.527446	19.742677
N	2.436598	4.295922	15.660551
C	3.686226	4.114042	15.151712
C	4.021900	5.041533	14.077464
C	5.223484	5.060481	13.360789
C	5.467494	5.987789	12.356511
C	4.473820	6.918619	12.061266
C	3.260258	6.942463	12.732679
C	3.014098	5.998574	13.740085
C	4.510760	3.111411	15.678853
C	4.050794	2.317567	16.716674
C	2.768255	2.533259	17.223182
C	1.991223	3.537714	16.667497
H	-1.959453	7.556206	11.414141
H	-1.869598	9.940631	12.088747
H	1.017545	8.845324	15.106759
H	0.957691	8.066909	19.457196
H	2.704354	10.102741	21.795284
H	1.389892	9.963348	20.609800
H	2.062596	8.500438	21.379074
H	5.009472	9.354985	21.295126
H	4.434562	7.736622	20.818617
H	5.449098	8.688729	19.707253
H	4.051906	11.432497	20.202839
H	2.797410	11.294611	18.944057
H	4.474330	10.809818	18.592574
H	4.749848	8.790338	17.513116

H	-1.553162	4.613332	15.164901
H	-3.356571	4.673332	16.815746
H	-0.831819	7.140318	19.310286
H	-5.434154	6.598266	19.393156
H	-4.427261	7.613196	18.328887
H	-4.960843	6.003102	17.786929
H	-3.800364	6.790258	21.239314
H	-2.084900	6.384784	21.027312
H	-2.763612	7.843234	20.254833
H	-4.465148	4.527827	20.488440
H	-2.767332	4.065765	20.203423
H	-3.972361	3.889835	18.904261
H	5.507771	2.962818	15.273142
H	4.691894	1.536241	17.130221
H	0.983888	3.746896	17.028494
H	6.415349	5.981060	11.817393
H	-1.664196	2.947265	10.672209
H	1.123470	2.718273	13.938154
H	3.956492	7.462266	15.619274
H	2.522948	7.696152	12.453792
F	-1.987688	5.482025	10.807251
F	-0.165383	1.414643	12.140213
C	-0.320772	11.016847	14.082787
F	-1.532474	11.525447	14.314457
F	0.246055	11.767091	13.134459
F	0.401294	11.156533	15.194157
F	4.706086	7.803269	11.103864
F	6.184547	4.182060	13.622657
C	2.237409	1.684342	18.346809
F	3.056139	1.718304	19.400353
F	2.129943	0.406731	17.973827
F	1.034702	2.091630	18.750721

[Ir(II)]

0 imaginary frequency

Ir	1.342083	5.853673	14.871033
C	0.425752	4.791078	13.429988
C	-0.404332	5.568855	12.568720
C	-1.110831	4.928222	11.538337
C	-1.034757	3.563403	11.321237
C	-0.215830	2.828795	12.174305
C	0.505502	3.409216	13.207956
C	-0.435386	6.996283	12.856653
C	-1.165149	7.977080	12.163935
C	-1.092711	9.302009	12.553934
C	-0.286702	9.645479	13.642944
C	0.412071	8.642375	14.294315
N	0.343757	7.360448	13.915416
N	2.079972	7.076019	16.450371
C	1.224881	7.204980	17.529239
C	1.623837	8.005655	18.639004
C	2.842824	8.646591	18.675305
C	3.298835	9.516688	19.844632
C	2.252778	9.586926	20.958339
C	4.595952	8.933444	20.428897
C	3.564471	10.942217	19.333043
C	3.698536	8.470422	17.545494
C	3.271336	7.692709	16.489835
C	-0.021065	6.518037	17.441321
N	-0.244233	5.786407	16.289449
C	-1.407207	5.130543	16.153011
C	-2.402861	5.126705	17.107088
C	-2.211344	5.855300	18.320425
C	-1.021524	6.536381	18.456467
C	-3.300777	5.847496	19.390707
C	-4.597205	6.418210	18.792694
C	-2.919815	6.684653	20.612781
C	-3.542818	4.399017	19.846566
N	2.382856	4.288616	15.676377
C	3.612186	4.038140	15.141080
C	3.971638	4.934552	14.050851
C	5.174724	4.899373	13.327904

C	5.451437	5.784872	12.300816
C	4.477146	6.732222	11.998642
C	3.270583	6.812714	12.679327
C	2.991615	5.917879	13.721758
C	4.391118	2.988146	15.655935
C	3.913776	2.215404	16.698835
C	2.651365	2.496677	17.228867
C	1.921889	3.542502	16.687583
H	-1.786569	7.686915	11.321182
H	-1.661170	10.063404	12.015558
H	1.052120	8.858462	15.149728
H	0.932590	8.104204	19.474177
H	2.624442	10.222381	21.776622
H	1.305856	10.022303	20.603690
H	2.037569	8.593423	21.381025
H	4.950830	9.557344	21.264714
H	4.431996	7.913577	20.810706
H	5.400462	8.889236	19.679709
H	3.906506	11.585629	20.159374
H	2.648878	11.386023	18.911615
H	4.339486	10.960058	18.552313
H	4.682259	8.937760	17.491247
H	-1.529889	4.574302	15.219740
H	-3.315603	4.562337	16.913631
H	-0.823368	7.109317	19.360652
H	-5.401037	6.405836	19.545996
H	-4.454153	7.459568	18.464222
H	-4.942075	5.834204	17.926386
H	-3.732906	6.650273	21.353866
H	-2.009130	6.305157	21.101284
H	-2.754529	7.740853	20.349824
H	-4.334537	4.368145	20.612094
H	-2.629137	3.966029	20.283102
H	-3.858166	3.753955	19.012901
H	5.370246	2.788930	15.229132
H	4.520243	1.399758	17.098379
H	0.933311	3.802051	17.066360
H	6.394161	5.736286	11.756210
H	-1.594713	3.091070	10.514377
H	1.126059	2.762059	13.830964
H	3.907041	7.549890	15.611825
H	2.559572	7.584923	12.379147
F	-1.897997	5.630367	10.716920
F	-0.128233	1.513010	11.980051
C	-0.175764	11.074402	14.088222
F	-1.379586	11.599846	14.340137
F	0.387464	11.837231	13.144010
F	0.558843	11.200271	15.194814
F	4.724583	7.593036	11.011483
F	6.113016	3.991407	13.615394
C	2.099982	1.676979	18.358754
F	2.920413	1.690819	19.415149
F	1.951144	0.395511	18.003805
F	0.909970	2.120510	18.767411

PPh_3

0 imaginary frequency

P	-2.618839	2.041031	0.152469
C	-1.666780	2.694355	1.587862
C	-2.154771	2.388485	2.867942
C	-0.517531	3.487967	1.475855
C	-1.497695	2.846366	4.008522
H	-3.062016	1.785319	2.972116
C	0.132812	3.956976	2.618265
H	-0.125850	3.742725	0.487944
C	-0.352397	3.634981	3.885673
H	-1.887958	2.595300	4.998084
H	1.027410	4.576609	2.515547
H	0.158737	4.002903	4.778827
C	-1.897827	2.979763	-1.259110
C	-2.463342	4.232033	-1.545959
C	-0.851932	2.511251	-2.065213

C	-1.981003	5.006638	-2.599360
H	-3.293245	4.603980	-0.937136
C	-0.377818	3.281774	-3.128051
H	-0.402714	1.535943	-1.862068
C	-0.937524	4.531062	-3.395414
H	-2.429233	5.981707	-2.806466
H	0.437491	2.902711	-3.749644
H	-0.564428	5.132905	-4.227843
C	-1.889513	0.364776	-0.075057
C	-2.573770	-0.516997	-0.926339
C	-0.724977	-0.081400	0.563499
C	-2.093705	-1.805920	-1.151007
H	-3.495163	-0.189863	-1.418047
C	-0.251767	-1.376754	0.348310
H	-0.181744	0.588069	1.235037
C	-0.931436	-2.239897	-0.510989
H	-2.635676	-2.478569	-1.820627
H	0.657148	-1.711736	0.854731
H	-0.558800	-3.253538	-0.678390

$^{\bullet+}PPh_3$

0 imaginary frequency

P	-1.981498	2.024508	0.097034
C	-1.398054	2.739229	1.618687
C	-1.843269	2.184783	2.834955
C	-0.544182	3.857395	1.618792
C	-1.411871	2.733070	4.036357
H	-2.526102	1.331749	2.840156
C	-0.125208	4.396435	2.830069
H	-0.195223	4.289959	0.679121
C	-0.555838	3.837255	4.034937
H	-1.752119	2.302208	4.980127
H	0.548118	5.256050	2.832806
H	-0.223465	4.267385	4.982440
C	-1.634308	2.993273	-1.354844
C	-2.121342	4.313747	-1.415778
C	-0.923080	2.447820	-2.439274
C	-1.870957	5.084433	-2.544373
H	-2.696525	4.733494	-0.586866
C	-0.684998	3.231432	-3.562941
H	-0.542779	1.425343	-2.396059
C	-1.155597	4.544999	-3.616398
H	-2.243607	6.109578	-2.592294
H	-0.121823	2.814894	-4.400563
H	-0.965583	5.153889	-4.503190
C	-1.635723	0.287698	-0.078509
C	-2.286259	-0.426321	-1.103922
C	-0.763805	-0.374549	0.804971
C	-2.041136	-1.785619	-1.253892
H	-2.983375	0.078241	-1.777222
C	-0.532710	-1.736115	0.643373
H	-0.256286	0.174855	1.600241
C	-1.167576	-2.440123	-0.381861
H	-2.541155	-2.340257	-2.050410
H	0.153648	-2.249811	1.319606
H	-0.982170	-3.509970	-0.501311

[NHPI---$P(OEt)_3$]

0 imaginary frequency

C	1.877004	-6.045288	-1.685900
C	2.594605	-6.562719	-0.603731
C	3.662781	-7.425169	-0.789619
C	4.000906	-7.757890	-2.107533
C	3.283113	-7.240873	-3.189697
C	2.201863	-6.372558	-2.992394
C	0.794924	-5.168342	-1.159889
C	1.997107	-6.037457	0.654763
H	4.218383	-7.827816	0.059816
H	4.839033	-8.433069	-2.294184
H	3.571060	-7.519755	-4.205811
H	1.636239	-5.967091	-3.833844
N	0.930390	-5.243174	0.228531

O	0.218632	-4.473163	1.069938
H	-0.589309	-5.001562	1.300958
O	-0.043063	-4.530767	-1.746592
O	2.309944	-6.232182	1.802728
P	-2.218075	-6.515360	1.670463
O	-1.921002	-7.591036	2.860017
O	-2.559961	-7.548627	0.452248
O	-3.748867	-6.089085	2.052105
C	-0.571235	-7.867148	3.246453
H	0.061083	-6.978666	3.071222
H	-0.596422	-8.045404	4.331809
C	-0.015509	-9.065344	2.513034
H	0.028891	-8.880326	1.428938
H	1.003607	-9.283996	2.865749
H	-0.640854	-9.954196	2.684906
C	-2.858453	-7.009787	-0.837522
H	-3.941639	-6.810382	-0.893466
H	-2.338847	-6.043622	-0.975727
C	-2.432643	-7.994014	-1.897391
H	-2.934542	-8.962503	-1.753404
H	-2.697257	-7.613071	-2.894877
H	-1.344908	-8.157503	-1.865725
C	-3.968681	-5.070044	3.026965
H	-3.869897	-5.510529	4.033658
H	-3.195244	-4.285531	2.933831
C	-5.344705	-4.487184	2.826866
H	-6.114905	-5.267296	2.920302
H	-5.542008	-3.714665	3.584651
H	-5.433475	-4.028418	1.830898

[PINO--HP(OEt)$_3$]$^{+\bullet}$

0 imaginary frequency

C	2.696174	-5.305463	-1.454767
C	2.130110	-6.553107	-1.146681
C	2.761936	-7.739675	-1.493865
C	3.984929	-7.646005	-2.163539
C	4.549358	-6.402020	-2.471118
C	3.910245	-5.209388	-2.119559
C	1.814414	-4.227207	-0.969725
C	0.853444	-6.351308	-0.444784
H	2.317361	-8.706572	-1.251190
H	4.511295	-8.558032	-2.452629
H	5.506736	-6.364526	-2.995122
H	4.346640	-4.237396	-2.356751
N	0.700001	-4.924730	-0.359801
O	-0.272499	-4.356017	0.171851
H	-1.784673	-5.707470	1.084919
O	1.898787	-3.036045	-1.014119
O	0.047080	-7.124474	-0.000171
P	-2.693291	-6.684323	1.530301
O	-2.195501	-7.375687	2.839773
O	-2.913559	-7.778076	0.434430
O	-4.097443	-6.065919	1.844661
C	-0.856676	-7.885969	3.104780
H	-0.124572	-7.217146	2.629471
H	-0.751910	-7.798495	4.193183
C	-0.714789	-9.307496	2.633123
H	-0.790853	-9.375700	1.539008
H	0.274786	-9.683836	2.931822
H	-1.479956	-9.951649	3.089383
C	-3.153176	-7.486569	-0.971007
H	-4.215228	-7.221522	-1.072382
H	-2.541640	-6.617792	-1.259629
C	-2.793198	-8.706202	-1.770521
H	-3.389962	-9.573312	-1.453431
H	-3.000052	-8.514265	-2.833273
H	-1.725960	-8.944619	-1.659784
C	-4.343348	-5.040677	2.847263
H	-4.058274	-5.453599	3.825738
H	-3.700600	-4.174769	2.625601
C	-5.800404	-4.678870	2.792661
H	-6.430605	-5.553753	3.006827

H	-6.008182	-3.908310	3.548953
H	-6.070128	-4.277502	1.805461

NHPI

0 imaginary frequency

C	-0.018227	-0.662633	0.003474
C	-1.418156	-0.662608	0.001993
C	-2.138453	0.518410	-0.001164
C	-1.412501	1.718475	-0.002869
C	-0.016404	1.717619	-0.001423
C	0.706816	0.516380	0.001799
C	0.436443	-2.076374	0.007002
C	-1.903808	-2.076161	0.004454
H	-3.230374	0.513849	-0.002272
H	-1.948005	2.670474	-0.005358
H	0.520807	2.668579	-0.002803
H	1.798617	0.510204	0.002966
N	-0.731702	-2.821349	0.007424
O	-0.716162	-4.171881	0.010199
H	0.236382	-4.384044	0.011645
O	1.535455	-2.582640	0.009190
O	-3.025059	-2.516411	0.004181

$^{\bullet+}$NHPI

0 imaginary frequency

C	-0.010424	-0.674080	0.002607
C	-1.427681	-0.674369	0.001267
C	-2.145098	0.513067	-0.001440
C	-1.416054	1.704092	-0.002624
C	-0.011346	1.703460	-0.001293
C	0.713489	0.511226	0.001252
C	0.489734	-2.043527	0.005920
C	-1.963170	-2.042080	0.003759
H	-3.236118	0.511328	-0.002365
H	-1.947544	2.657747	-0.004492
H	0.521864	2.656035	-0.002152
H	1.804345	0.505297	0.002394
N	-0.732861	-2.840005	0.007844
O	-0.709422	-4.111461	0.011895
H	0.247087	-4.381302	0.014582
O	1.547278	-2.594720	0.007617
O	-3.048410	-2.520817	0.003666

NHPI(triplet)

C	0.004255	-0.712299	0.003813
C	-1.449462	-0.704337	0.002225
C	-2.147094	0.519890	-0.001126
C	-1.427106	1.693941	-0.002891
C	0.007935	1.686208	-0.001398
C	0.718004	0.510110	0.001897
C	0.469117	-2.046790	0.007155
C	-1.989248	-2.031705	0.004420
H	-3.239209	0.524933	-0.002267
H	-1.950691	2.652332	-0.005480
H	0.540257	2.639973	-0.002930
H	1.809779	0.507733	0.003018
N	-0.762496	-2.814593	0.007374
O	-0.661519	-4.089730	0.009835
H	0.337997	-4.214630	0.011066
O	1.511430	-2.704119	0.009572
O	-3.096281	-2.537030	0.004154

P(OEt)$_3$

0 imaginary frequency

P	-2.815952	2.002048	0.274987
O	-2.097392	0.539914	-0.048683
O	-1.893153	2.605387	1.477711
O	-2.120428	2.826787	-0.973637
C	-2.623777	-0.634637	0.556809
H	-2.054188	-0.850160	1.477497
H	-3.674794	-0.467907	0.859468
C	-2.528915	-1.790023	-0.409770

H	-1.484843	-1.957617	-0.714597
H	-2.902639	-2.712545	0.059342
H	-3.125499	-1.593197	-1.313309
C	-0.466400	2.670440	1.414042
H	-0.080534	1.771178	0.906727
H	-0.177915	3.544262	0.807608
C	0.080103	2.777933	2.815593
H	-0.192350	1.894141	3.411885
H	1.177604	2.852848	2.789366
H	-0.313835	3.671662	3.322605
C	-2.624276	2.629434	-2.288071
H	-2.266986	1.659152	-2.675073
H	-3.729828	2.584392	-2.268103
C	-2.158404	3.761312	-3.170029
H	-1.059205	3.806049	-3.196648
H	-2.522944	3.617956	-4.198039
H	-2.535146	4.726092	-2.798767

$^{+}$P(OEt)$_3$

0 imaginary frequency

P	-2.461538	1.864356	0.126055
O	-2.566255	0.356099	-0.312390
O	-1.357424	1.966619	1.243716
O	-1.960934	2.692260	-1.115975
C	-2.902151	-0.773370	0.551062
H	-2.214779	-0.754234	1.408541
H	-3.931432	-0.627907	0.908176
C	-2.760285	-2.025653	-0.265169
H	-1.729579	-2.147909	-0.626528
H	-3.010501	-2.889500	0.367688
H	-3.444863	-2.016532	-1.124994
C	-0.868849	3.196737	1.862134
H	-0.679009	3.926424	1.062285
H	-1.665588	3.575300	2.517587
C	0.378107	2.855202	2.626312
H	1.158775	2.467201	1.957082
H	0.757061	3.767774	3.109043
H	0.171147	2.110721	3.407950
C	-2.630444	2.800312	-2.409630
H	-2.892743	1.785252	-2.739842
H	-3.550545	3.382544	-2.259397
C	-1.680929	3.477362	-3.355842
H	-0.762312	2.887776	-3.484052
H	-2.169833	3.575287	-4.336037
H	-1.416794	4.482780	-2.998862

POEt$_3$(triplet)

P	-1.483822	1.594686	0.016280
O	-2.043206	0.158807	-0.775143
O	-0.878224	2.842742	1.044390
O	-1.592312	2.570634	-1.287407
C	-2.401598	-0.966196	0.005097
H	-1.528277	-1.333413	0.575420
H	-3.179090	-0.691631	0.741962
C	-2.909568	-2.046515	-0.920679
H	-2.134240	-2.334127	-1.646577
H	-3.191554	-2.939913	-0.343488
H	-3.793751	-1.700937	-1.477193
C	-0.292604	2.481060	2.281862
H	-1.040557	1.998537	2.938210
H	0.521712	1.749475	2.124658
C	0.242773	3.733526	2.935410
H	-0.566032	4.458946	3.109776
H	0.703714	3.489762	3.904384
H	1.003762	4.210291	2.299522
C	-2.761893	2.597243	-2.103374
H	-2.886190	1.623029	-2.602320
H	-3.652074	2.760588	-1.469386
C	-2.609266	3.707497	-3.112041
H	-1.723575	3.541117	-3.743500
H	-3.494561	3.747676	-3.764005
H	-2.501262	4.682017	-2.612944

$^{+}$HP(OEt)$_3$

0 imaginary frequency

P	-2.676887	1.950730	0.282885
O	-2.413575	0.495295	-0.233892
O	-1.795211	2.389452	1.491606
O	-2.357993	2.900646	-0.913483
C	-2.742912	-0.739312	0.467781
H	-2.070517	-0.819836	1.333763
H	-3.780798	-0.668537	0.827276
C	-2.563028	-1.879508	-0.492962
H	-1.525751	-1.930198	-0.853213
H	-2.796652	-2.821966	0.023008
H	-3.237530	-1.779184	-1.355084
C	-0.345350	2.562069	1.453853
H	0.102217	1.602381	1.157804
H	-0.121268	3.314431	0.684642
C	0.102964	2.995958	2.819349
H	-0.141770	2.236839	3.575642
H	1.193574	3.135563	2.808776
H	-0.365494	3.948889	3.103405
C	-2.737976	2.695807	-2.306322
H	-2.407347	1.689846	-2.600202
H	-3.835031	2.744571	-2.366160
C	-2.083430	3.770841	-3.125159
H	-0.988433	3.715631	-3.045554
H	-2.361602	3.634340	-4.180184
H	-2.416056	4.768678	-2.805951
H	-3.985520	2.074246	0.761987

PINO

0 imaginary frequency

C	-0.018028	-0.660077	-0.000000
C	-1.420557	-0.660077	-0.000000
C	-2.142403	0.525656	-0.000000
C	-1.419350	1.721774	0.000000
C	-0.019235	1.721774	0.000000
C	0.703818	0.525656	0.000000
C	0.475913	-2.050910	-0.000000
C	-1.914498	-2.050910	-0.000000
H	-3.234029	0.519222	-0.000000
H	-1.953957	2.674141	0.000000
H	0.515373	2.674141	0.000000
H	1.795444	0.519222	-0.000000
N	-0.719292	-2.859999	0.000000
O	-0.719292	-4.105397	0.000000
O	1.583358	-2.505760	-0.000000
O	-3.021942	-2.505760	-0.000000

O=P(OEt)$_3$

0 imaginary frequency

O	-0.025344	-4.512670	0.148633
P	-0.013131	-5.977641	-0.060165
O	-0.536698	-6.534159	-1.464338
O	-0.917985	-6.819259	0.968090
O	1.458594	-6.586568	0.006698
C	-1.867934	-6.243411	-1.914254
H	-2.579065	-6.827450	-1.307696
H	-2.076587	-5.173860	-1.748205
C	-1.972075	-6.597734	-3.374112
H	-1.756223	-7.664389	-3.534625
H	-2.990819	-6.393852	-3.734845
H	-1.266396	-6.003642	-3.973071
C	-1.054835	-6.412318	2.337358
H	-0.187716	-6.790720	2.903329
H	-1.037755	-5.312203	2.384972
C	-2.344139	-6.967804	2.883466
H	-2.357157	-8.066060	2.821336
H	-2.455466	-6.681415	3.939642
H	-3.207081	-6.575709	2.325128
C	1.721171	-7.987118	-0.162300
H	1.019556	-8.563419	0.462375

H	1.535955	-8.253912	-1.214822
C	3.149604	-8.258290	0.230155
H	3.323673	-7.998306	1.284670
H	3.375993	-9.326003	0.094534
H	3.844566	-7.676098	-0.392763

TS1

1 imaginary frequency, 110.9i

C	-0.228871	-0.964902	0.798885
C	-1.335282	-0.876184	-0.054150
C	-1.869963	0.349554	-0.419354
C	-1.260978	1.499158	0.097445
C	-0.155695	1.410555	0.949680
C	0.378966	0.169323	1.314450
C	0.105550	-2.395151	0.999259
C	-1.756471	-2.245480	-0.435601
H	-2.732729	0.412515	-1.085498
H	-1.654495	2.482691	-0.168645
H	0.297139	2.326246	1.336250
H	1.241973	0.094200	1.979005
N	-0.873065	-3.104444	0.261484
O	-0.899018	-4.380462	0.170729
O	0.995834	-2.912864	1.621869
O	-2.634382	-2.618399	-1.169722
P	0.377468	-5.435654	-1.535274
O	-0.816992	-6.069101	-2.445575
O	0.602757	-6.662185	-0.489546
O	1.629911	-5.754347	-2.553729
C	-2.189567	-6.060978	-2.045659
H	-2.297392	-6.648801	-1.118316
H	-2.504630	-5.029386	-1.823481
C	-3.009704	-6.660020	-3.160157
H	-2.694539	-7.692874	-3.371325
H	-4.072998	-6.673848	-2.877868
H	-2.905695	-6.070081	-4.083280
C	1.396393	-6.468866	0.684414
H	2.444043	-6.714739	0.441177
H	1.355209	-5.410620	0.992644
C	0.874448	-7.362589	1.781085
H	0.888606	-8.417833	1.469205
H	1.498971	-7.260919	2.681184
H	-0.158815	-7.089913	2.042994
C	1.882179	-4.878114	-3.649632
H	1.175477	-5.109571	-4.464989
H	1.700765	-3.830907	-3.345850
C	3.307867	-5.060105	-4.106404
H	3.489191	-6.101760	-4.410855
H	3.515864	-4.407913	-4.967535
H	4.011887	-4.806647	-3.299847

I

0 imaginary frequency

C	0.269428	-1.299167	0.386714
C	-0.638203	-1.201749	-0.723238
C	-0.904393	0.050374	-1.307968
C	-0.288160	1.175141	-0.788379
C	0.605319	1.079232	0.313371
C	0.886417	-0.144790	0.897169
C	0.393433	-2.678843	0.795105
C	-1.120280	-2.512493	-1.061709
H	-1.589810	0.126459	-2.156255
H	-0.488374	2.154994	-1.229454
H	1.076012	1.986344	0.700745
H	1.576103	-0.219207	1.742283
N	-0.456262	-3.328476	-0.123943
O	-0.750023	-4.654448	0.001328
O	1.036360	-3.262350	1.670851
O	-1.859921	-2.973933	-1.944892
P	-0.088740	-5.702863	-1.030791
O	-1.152321	-6.252120	-2.013487
O	0.424810	-6.877341	-0.155305
O	1.092021	-5.063267	-1.804857

C	-2.610859	-6.177338	-1.868020
H	-2.883725	-6.742066	-0.965784
H	-2.855572	-5.114077	-1.740536
C	-3.219628	-6.766051	-3.106829
H	-2.928428	-7.818223	-3.235403
H	-4.314779	-6.718979	-3.017491
H	-2.922164	-6.199189	-4.000550
C	1.354265	-6.708035	0.967957
H	2.355015	-6.916137	0.565356
H	1.307888	-5.660656	1.306765
C	0.962489	-7.672529	2.050026
H	0.982041	-8.709317	1.684778
H	1.678663	-7.585694	2.880214
H	-0.042126	-7.446755	2.435151
C	1.016577	-4.282627	-3.046015
H	1.249939	-4.989238	-3.853491
H	-0.013829	-3.917622	-3.163492
C	2.010640	-3.160740	-2.961088
H	3.029201	-3.543590	-2.804763
H	1.993644	-2.602992	-3.908943
H	1.757858	-2.465154	-2.147672

TS2

1 imaginary frequency, 2044.4i

C	0.077709	-1.198048	0.309111
C	-0.693777	-1.142624	-0.885580
C	-1.148845	0.107176	-1.352891
C	-0.883362	1.232174	-0.584311
C	-0.159560	1.159937	0.627443
C	0.328102	-0.067124	1.079223
C	0.455656	-2.593678	0.520516
C	-0.780614	-2.452236	-1.482849
H	-1.712847	0.181453	-2.285342
H	-1.249131	2.205961	-0.922043
H	0.028971	2.070454	1.199959
H	0.908154	-0.141887	2.002605
N	0.070652	-3.254222	-0.690109
O	-0.533773	-4.642889	-0.316157
O	0.954283	-3.155710	1.470562
O	-1.317773	-2.856904	-2.529844
P	0.043368	-5.896766	-1.073267
O	-1.044357	-6.558898	-1.977072
O	0.479377	-6.959464	-0.011523
O	1.281210	-5.589875	-1.965930
C	-2.473152	-6.578249	-1.690504
H	-2.753993	-7.639925	-1.688860
H	-2.641725	-6.171117	-0.683069
C	-3.201796	-5.786162	-2.740530
H	-3.034854	-6.214113	-3.739890
H	-4.281278	-5.814552	-2.530091
H	-2.860837	-4.740136	-2.734762
C	1.345373	-6.654869	1.121503
H	2.376815	-6.837440	0.786957
H	1.233178	-5.589022	1.373529
C	0.957966	-7.548982	2.265666
H	1.047581	-8.609258	1.988387
H	1.628815	-7.357064	3.115813
H	-0.074434	-7.351377	2.588211
C	1.247419	-4.869378	-3.237701
H	1.155417	-5.636868	-4.019209
H	0.357661	-4.220948	-3.255131
C	2.520464	-4.082086	-3.365097
H	3.401557	-4.738027	-3.312259
H	2.530019	-3.570084	-4.338560
H	2.591261	-3.323431	-2.572651

II

0 imaginary frequency

C	-0.019176	-0.639295	0.016605
C	-1.419409	-0.639295	0.016607
C	-2.147650	0.544793	0.018227
C	-1.422302	1.736437	0.010532

C	-0.016283	1.736437	0.010532
C	0.709065	0.544792	0.018227
C	0.427007	-2.056167	0.021257
C	-1.865593	-2.056167	0.021265
H	-3.239303	0.539717	0.020610
H	-1.952809	2.691214	0.002351
H	0.514224	2.691214	0.002351
H	1.800718	0.539716	0.020607
N	-0.719292	-2.858576	0.246967
O	1.538560	-2.504884	-0.115065
O	-2.977143	-2.504885	-0.115072

Cyclohexene

0 imaginary frequency

C	-3.151736	-0.744594	-0.009488
C	-1.683991	-0.529575	-0.241912
C	-0.987651	0.466648	0.320921
C	-1.604343	1.500986	1.217767
C	-3.129162	1.492109	1.143109
C	-3.671820	0.067212	1.174192
H	0.088094	0.545921	0.125566
H	-1.170032	-1.234787	-0.905377
H	-3.708497	-0.480323	-0.929151
H	-3.348832	-1.819630	0.143886
H	-1.270815	1.325643	2.258736
H	-1.211304	2.498779	0.956959
H	-3.554803	2.090093	1.964564
H	-3.449345	1.977957	0.204016
H	-3.353814	-0.417796	2.114464
H	-4.773411	0.068925	1.181123

III

0 imaginary frequency

C	-2.553504	-1.166701	-0.415693
C	-1.262743	-0.389803	-0.118611
C	-1.519147	1.061147	0.132367
C	-2.671527	1.447648	0.991688
C	-3.930103	0.634231	0.679379
C	-3.624263	-0.858393	0.624847
H	-0.702361	1.767291	-0.044001
H	-0.812253	-0.835162	0.793054
H	-2.915405	-0.877119	-1.415349
H	-2.328226	-2.244468	-0.444479
H	-2.405684	1.281904	2.059547
H	-2.869181	2.528104	0.904363
H	-4.708083	0.842820	1.430789
H	-4.336666	0.954823	-0.295688
H	-3.283501	-1.201756	1.618871
H	-4.537908	-1.429749	0.396053
C	0.919132	-0.611982	-3.126124
C	1.691650	-1.283987	-2.180766
C	2.929777	-1.818832	-2.501434
C	3.376867	-1.657290	-3.818251
C	2.601409	-0.982928	-4.767408
C	1.352305	-0.446565	-4.432455
C	-0.340002	-0.167418	-2.463675
C	0.943636	-1.283480	-0.893902
H	3.530245	-2.344237	-1.755871
H	4.347321	-2.064089	-4.111635
H	2.978966	-0.874180	-5.786717
H	0.742204	0.081119	-5.168593
N	-0.248948	-0.600824	-1.140434
O	-1.266814	0.439846	-2.945026
O	1.266012	-1.761672	0.167796

TS3

1 imaginary frequency, -1681.5i

C	0.943577	0.456184	0.436072
C	0.444911	0.589640	-1.004799
C	0.088728	2.013903	-1.366663
C	1.155309	3.021869	-1.035551
C	1.663484	2.878148	0.397118

C	2.077730	1.442139	0.701262
H	-0.368282	2.117950	-2.362642
H	1.284627	0.320189	-1.676665
H	0.106974	0.645509	1.125829
H	1.277967	-0.579304	0.605442
H	1.994807	2.866558	-1.744469
H	0.794823	4.044256	-1.231356
H	2.507878	3.565184	0.563273
H	0.862430	3.191274	1.087923
H	2.950366	1.172628	0.079334
H	2.404884	1.353192	1.749113
C	-1.698763	-2.029660	-2.512851
C	-2.490327	-1.667362	-1.424984
C	-3.714215	-2.272227	-1.184490
C	-4.126650	-3.264531	-2.081638
C	-3.331748	-3.628037	-3.174079
C	-2.096769	-3.011726	-3.407047
C	-0.465609	-1.200273	-2.476756
C	-1.781402	-0.597089	-0.668597
H	-4.329740	-1.984285	-0.329716
H	-5.085353	-3.765113	-1.927892
H	-3.682740	-4.406322	-3.855501
H	-1.471219	-3.291257	-4.257298
N	-0.586863	-0.370269	-1.356839
O	0.475975	-1.207453	-3.233113
O	-2.138312	-0.030921	0.336019
C	-3.015124	5.792185	-1.812593
C	-2.249379	6.371066	-0.795449
C	-2.126984	7.746364	-0.675702
C	-2.801508	8.538122	-1.613099
C	-3.566830	7.959465	-2.630094
C	-3.684229	6.568922	-2.745140
C	-2.949245	4.313973	-1.674806
C	-1.658518	5.287738	0.033359
H	-1.527260	8.192317	0.120348
H	-2.729386	9.626198	-1.550091
H	-4.081177	8.604293	-3.346154
H	-4.280280	6.111350	-3.537362
N	-2.123568	4.099453	-0.556877
O	-1.897291	2.904687	-0.053804
H	-0.992820	2.414103	-0.623983
O	-3.452242	3.443084	-2.336177
O	-0.939689	5.349271	0.997300

3a

0 imaginary frequency

C	-2.282282	-1.337174	-0.222167
C	-1.193555	-0.300770	-0.506303
C	-1.765141	1.116468	-0.575829
C	-2.529884	1.454289	0.700858
C	-3.618274	0.425839	0.993244
C	-3.043280	-0.986151	1.053021
H	-0.945806	1.834669	-0.740645
H	-0.459640	-0.336980	0.316052
H	-2.977969	-1.366512	-1.076845
H	-1.824773	-2.336311	-0.140482
H	-1.823709	1.487238	1.550299
H	-2.963228	2.463971	0.619244
H	-4.131148	0.670115	1.937563
H	-4.385636	0.472624	0.199432
H	-2.359979	-1.063959	1.918122
H	-3.844123	-1.723324	1.223690
C	0.261160	-1.091776	-3.846479
C	1.380715	-1.208052	-3.025585
C	2.624939	-1.543830	-3.536586
C	2.713696	-1.762973	-4.916497
C	1.589422	-1.646420	-5.740872
C	0.337698	-1.306544	-5.213756
C	-0.902722	-0.722471	-2.991621
C	0.955457	-0.915844	-1.629528
H	3.498710	-1.633176	-2.887707
H	3.676186	-2.029557	-5.359108

H	1.692220	-1.824021	-6.813840	O	-2.047141	-0.530867	-3.332227
H	-0.543771	-1.213858	-5.851714	O	1.623844	-0.910762	-0.623104
N	-0.412272	-0.636312	-1.689321	H	-2.439054	1.186428	-1.445448

6. References

(1) S. Coseri, G. Biliuta and B. C. Simionescu, Selective oxidation of cellulose, mediated by N-hydroxyphthalimide, under a metal-freeenvironment, *Polym. Chem.*, 2018, **9**, 961–967.

(2) S.-L. Liu, Q.-Y. Deng, W.-W. Fang, J.-F. Gong, M.-P. Song, M.-Z. Xu and T. Tu, Efficient and scalable Pd-catalyzed double aminocarbonylations under atmospheric pressure at low catalyst loadings, *Org. Chem. Front.*, 2014, **1**, 1261–1265.

(3) S. W. Lardy and V. A. Schmidt, Intermolecular Radical Mediated Anti-Markovnikov Alkene Hydroamination Using *N*‑Hydroxyphthalimide, *J. Am. Chem. Soc.* 2018, **140**, 12318–12322.

(4) S. N. Rao, D. C. Mohan and S, Adimurthy, L‑Proline: An Efficient Catalyst for Transamidation of Carboxamides with Amines, *Org. Lett.* 2013, **15**, 1496–1499.

(5) B. Martin, H. Sekljic and C. Chassaing, Microwave-Assisted Solid-Phase Synthesis of Phthalimides, *Org. Lett.* 2003, **5,** 1851–1853.

(6)D. Padula, G. Mazzeo, E. Santoro, P. Scafato, S. Belviso and S. Superchi, Amplification of the chiroptical response of UVtransparent amines and alcohols by *N*-phthalimide derivatization enabling absolute configuration determination through ECD computational analysis, *Org. Biomol. Chem.*, 2020, **18**, 2094–2102.

(7) Gaussian 16 Rev. A.03, M. J. Frisch, G. W, Trucks, H. B, Schlegel, G. E. Scuseria,M. A. Robb, J. R. Cheeseman,G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji,X. Li, M. Caricato, A. V. Marenich,J. Bloino, B.G. Janesko, R. Gomperts, B. Mennucci, H.P. Hratchian, J.V. Ortiz, A.F. Izmaylov, J. LSonnenberg,Williams,F. Ding,F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao,N, Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M, Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery Jr, J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T.A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O.Farkas, J. B. Foresman, D. J. Fox, Gaussian Inc. Wallingford CT, 2016.

(8)M. Ernzerhof, G. E. Scuseria, Assessment of the Perdew–Burke–Ernzerhof exchange-correlation functional, *J. Chem. Phys.*, 1999, **110**, 5029–5036.

(9)F. Weigend, R. Ahlrichs, Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy,*Phys. Chem. Chem. Phys.*, 2005, **7**, 3297–3305.

(10)F. Weigend, Accurate Coulomb-fitting basis sets for H to Rn,*Phys. Chem. Chem. Phys*., 2006, **8**, 1057–1065.

(11)Y. Zhao, D. G. Truhlar, The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: two new functionals and systematic testing of four M06-class functionals and 12 other functionals, *Theor. Chem. Acc.*, 2008, **120**, 215–241.

(12)A. V. Marenich, C. J. Cramer, D. G. Truhlar, Universal Solvation Model Based on Solute Electron Density and on a Continuum Model of the Solvent Defined by the Bulk Dielectric Constant and Atomic Surface Tensions, *J. Phys. Chem. B*, 2009, **113**, 6378–6396.

(13) CYLview, 1.0b, C. Y. Legault, Université de Sherbrooke, 2009.

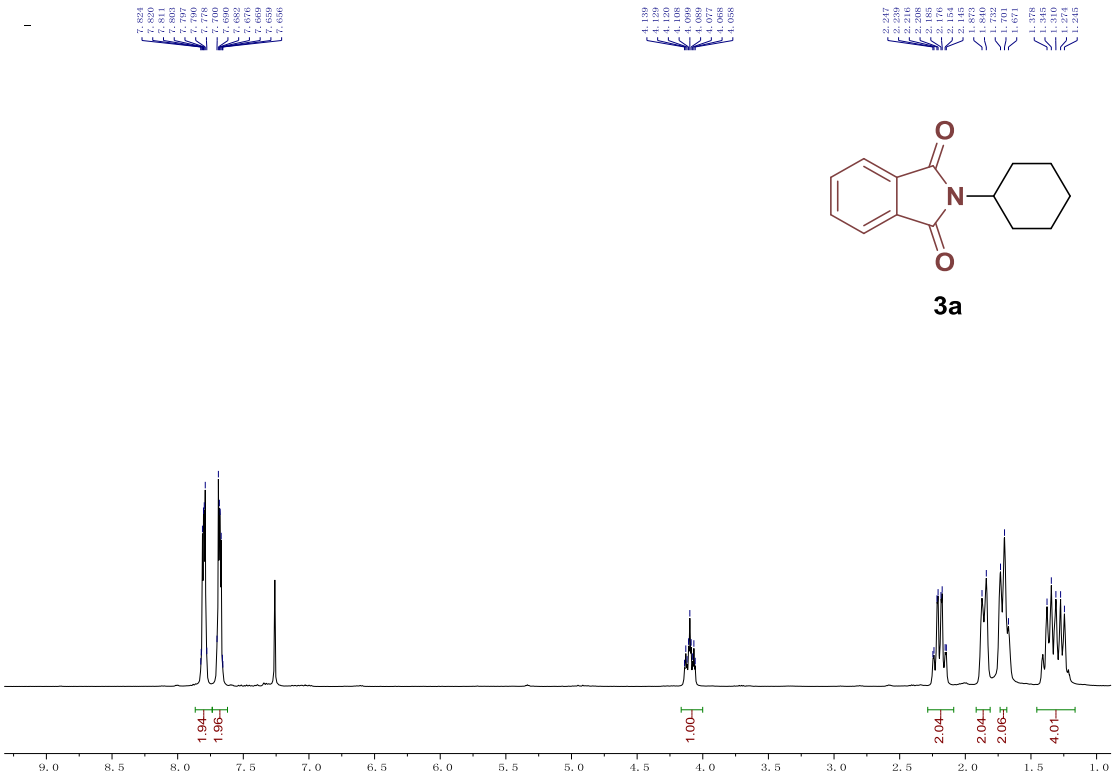
(14)S. Ladouceur, D. Fortin, E. Zysman-Colman, Enhanced Luminescent Iridium(III) Complexes Bearing Aryltriazole Cyclometallated Ligands,*Inorg. Chem.*, 2011, **50,** 11514–11526.

(15) W.-G. Xu, H.-M. Jiang, J. Leng, H.-W, Ong and J. Wu, Visible‐Light‐Induced Selective Defluoroborylation of Polyfluoroarenes, gem−Difluoroalkenes, and Trifluoromethylalkenes,*Angew.Chem. Int.Ed*., 2020, **59**, 4009–4016.

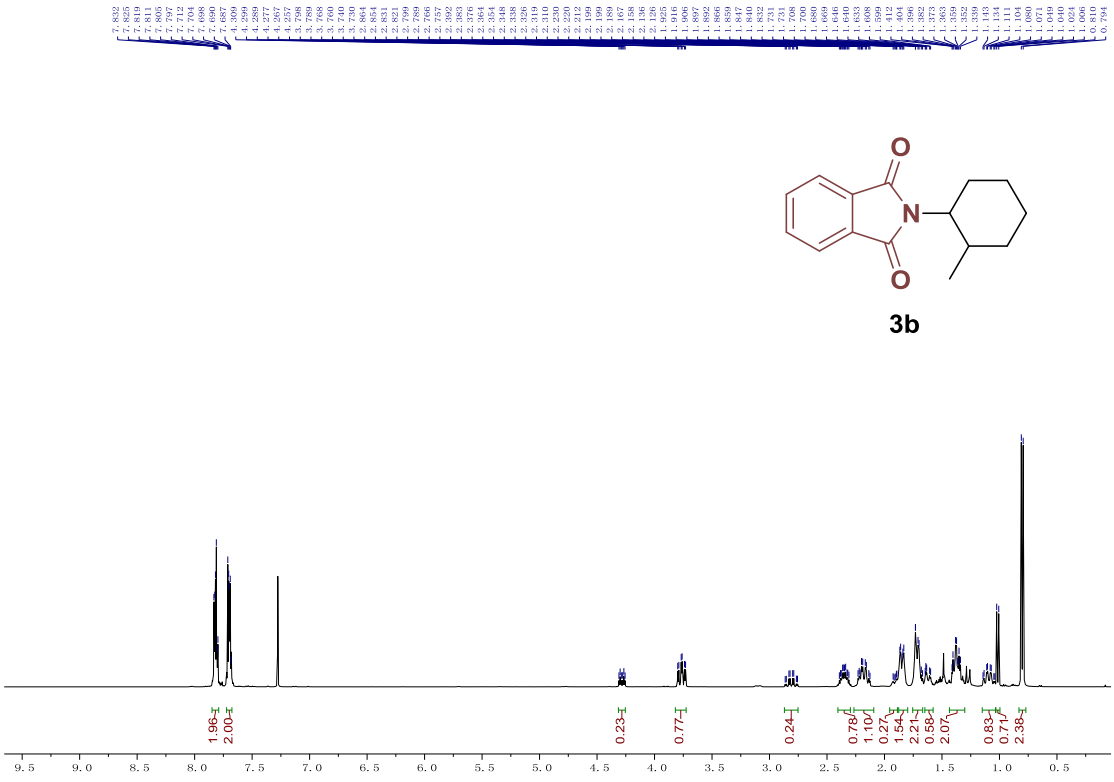
(16) G. Pandey, D. Pooranchand, U. T. Bhalerao, Photoinduced single electron transfer activation of organophosphines: Nucleophilic trapping of phosphine radical cation, *Tetrahedron*, 1991, **47**, 1745–1752.

7. Copies of NMR Spectra

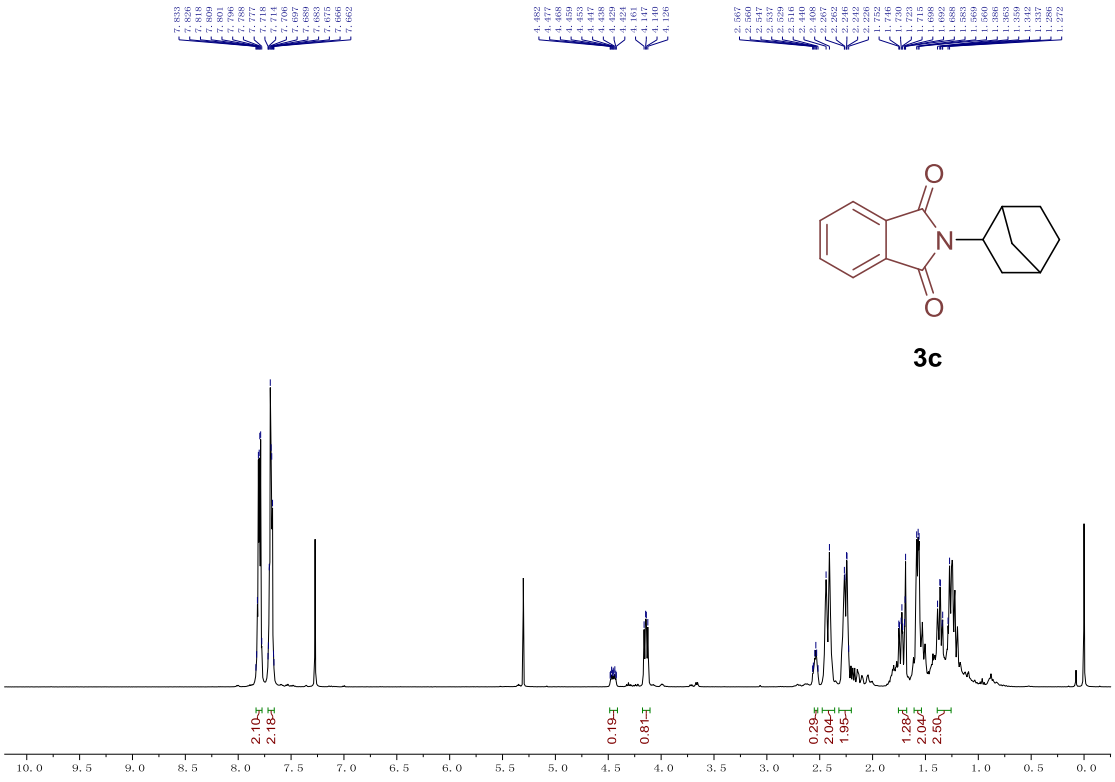
Product 3a: ^{1}H NMR.



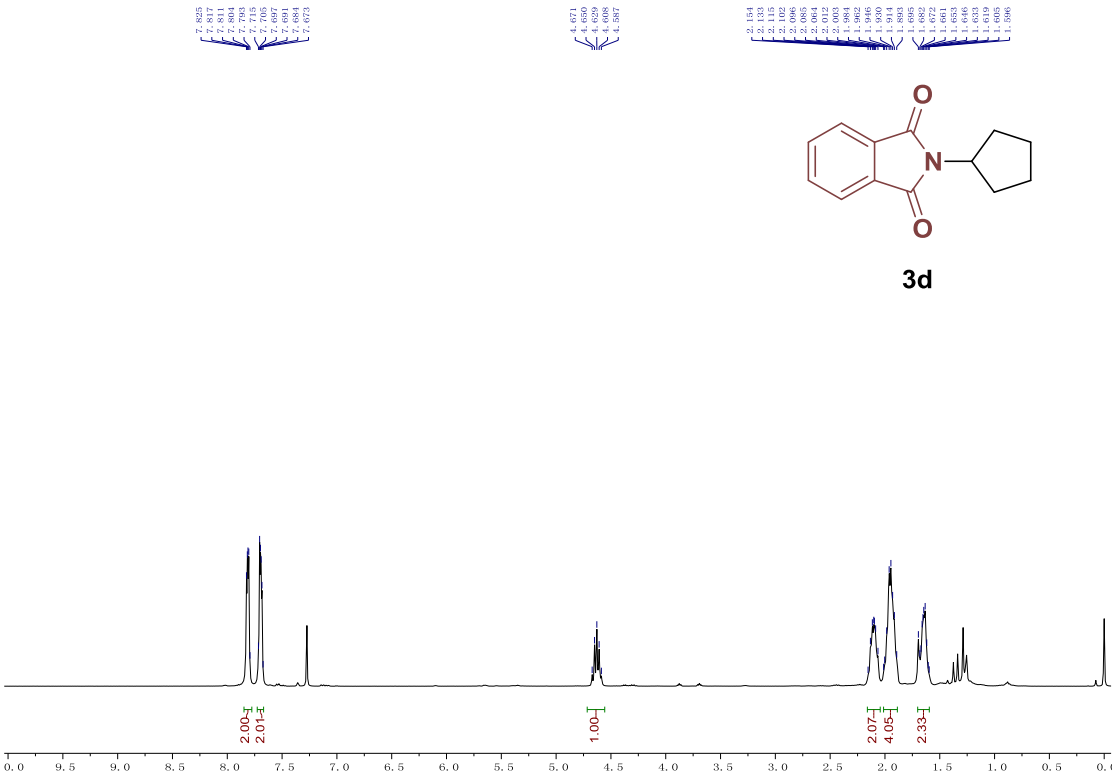
Product 3b: ^{1}H NMR.



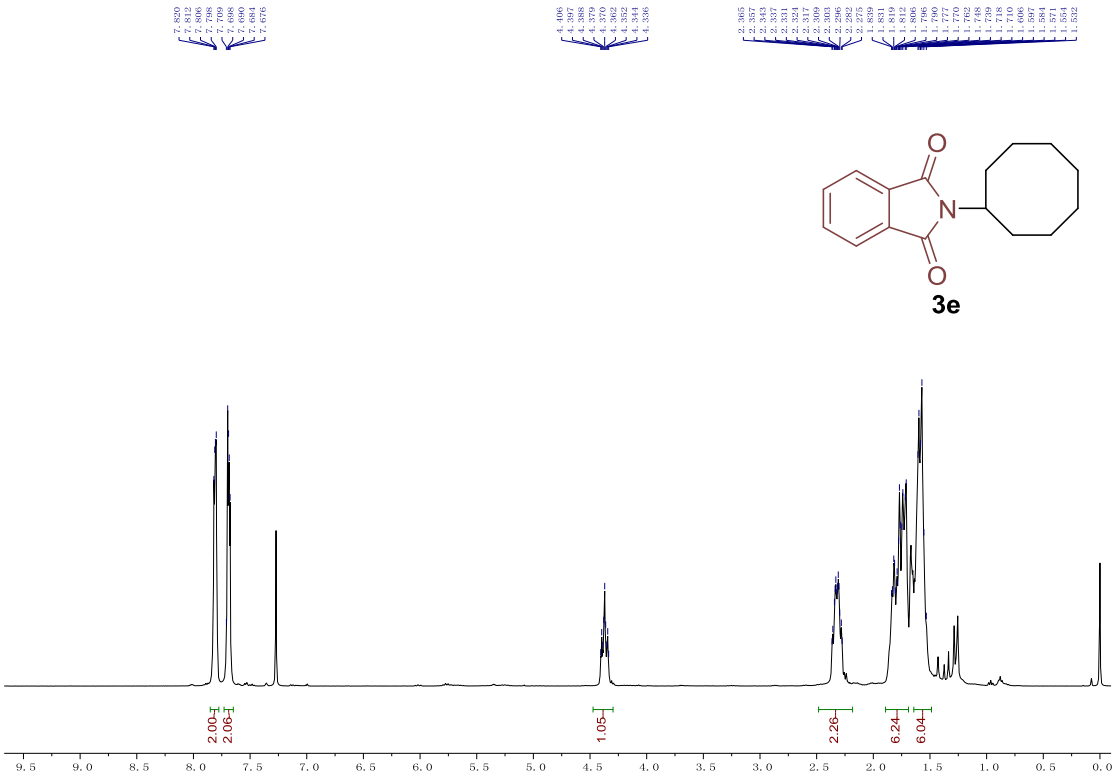
Product 3c: ^{1}H NMR.



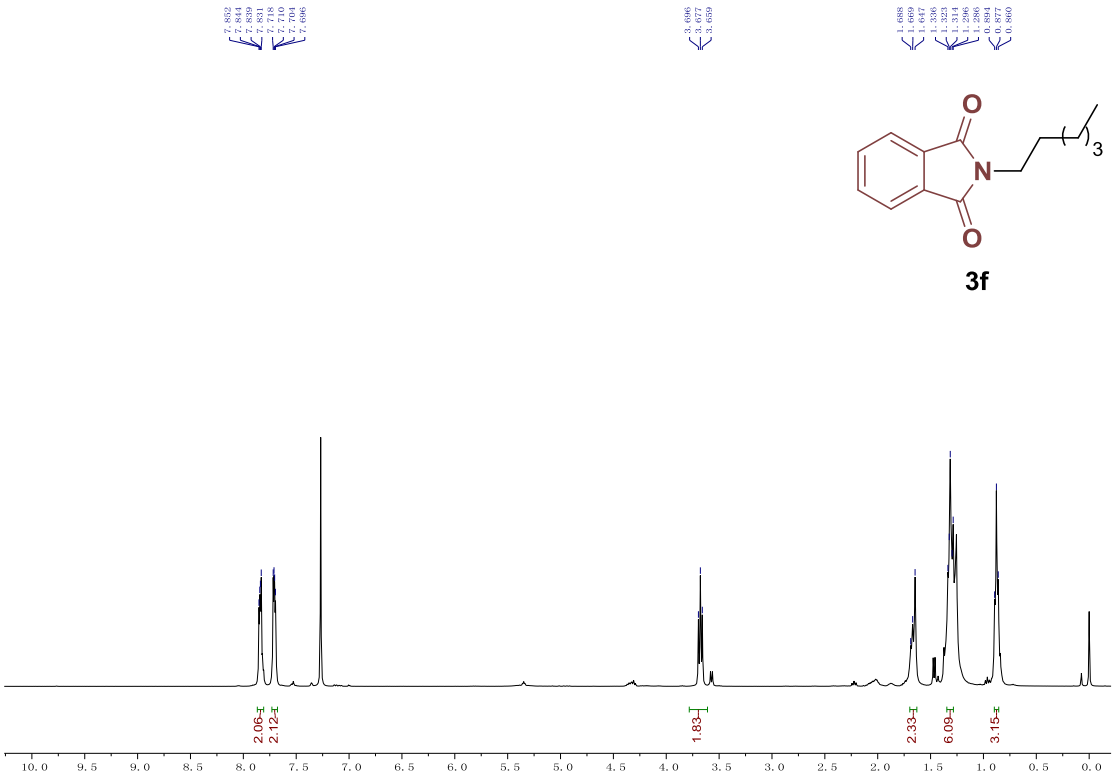
Product 3d: ^{1}H NMR.



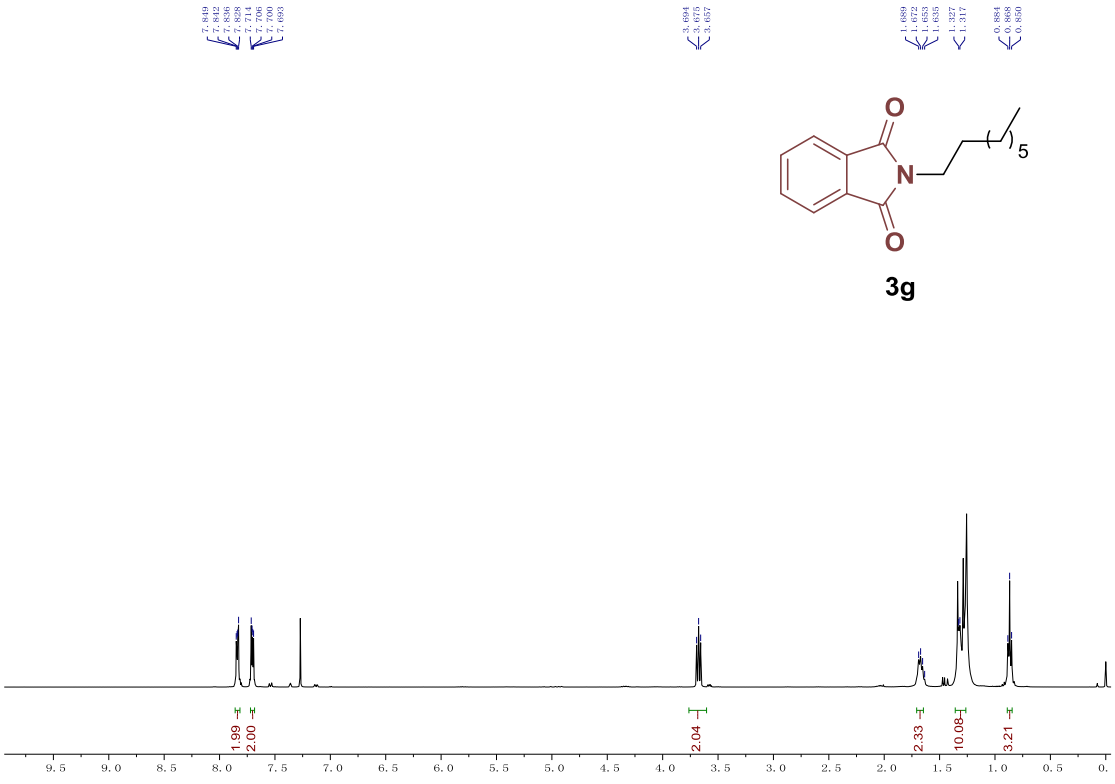
Product 3e: ^{1}H NMR.



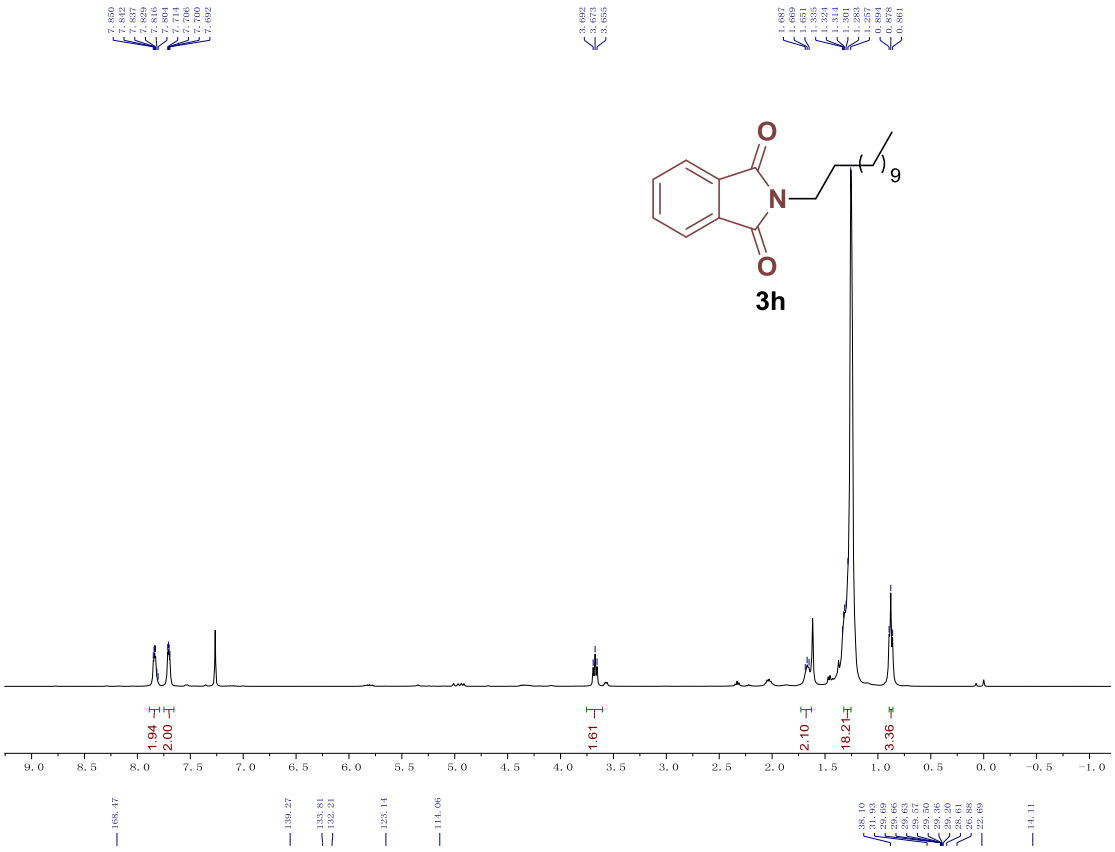
Product 3f: ^{1}H NMR.

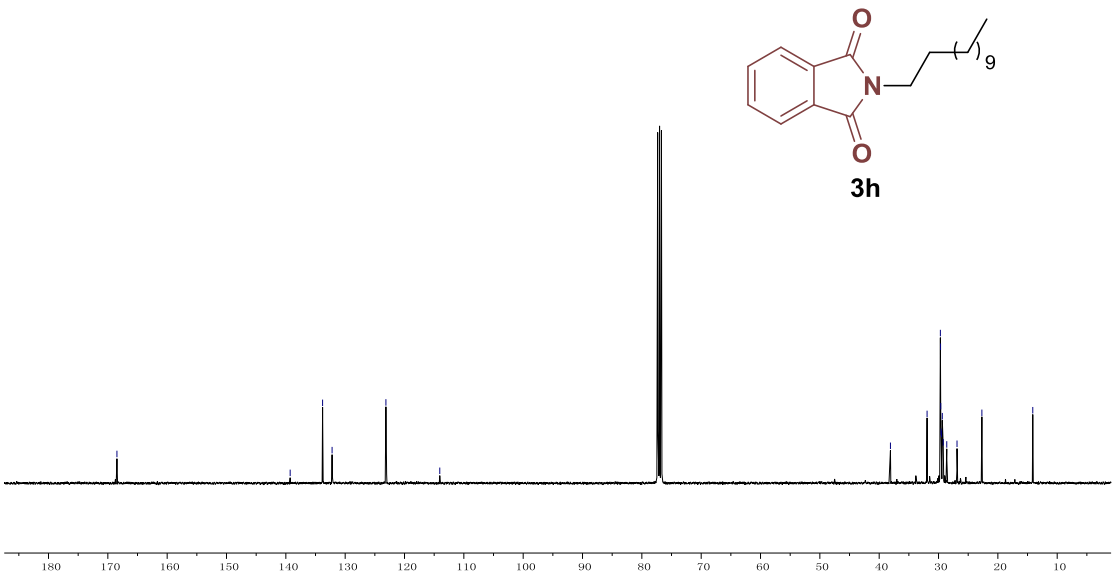


Product3g:[1]H NMR.

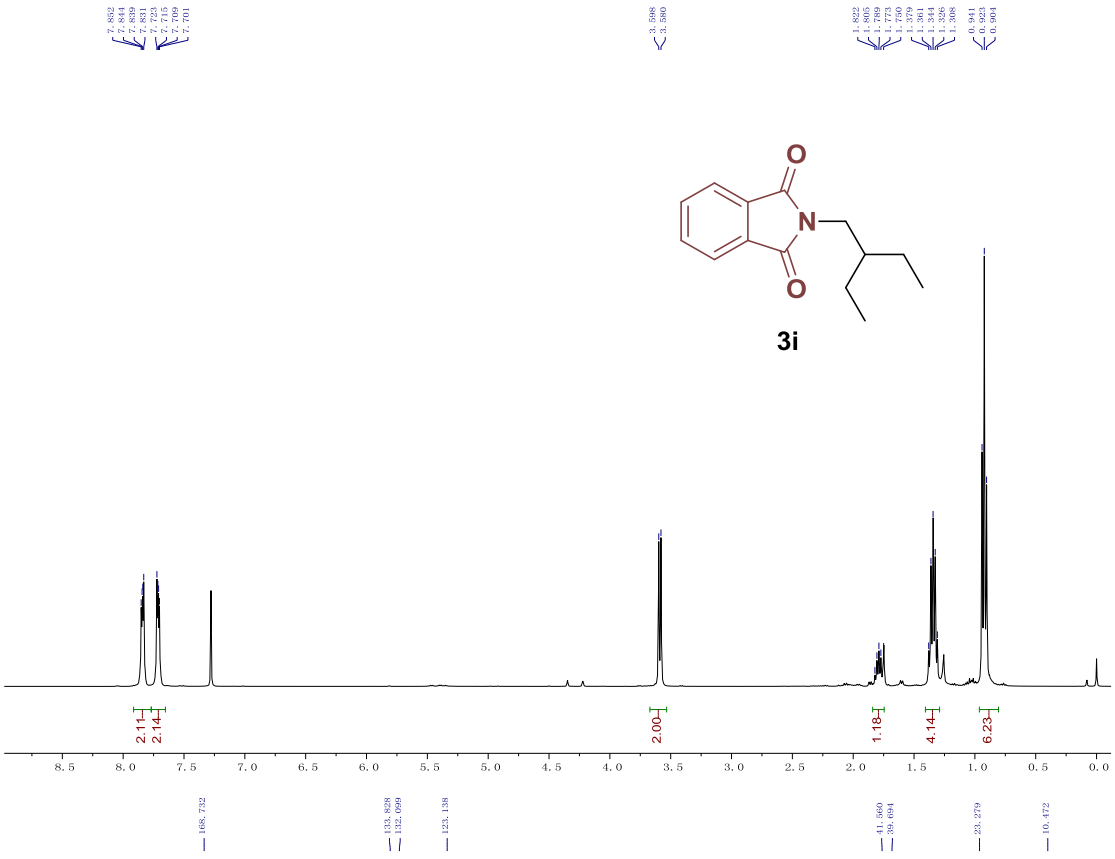


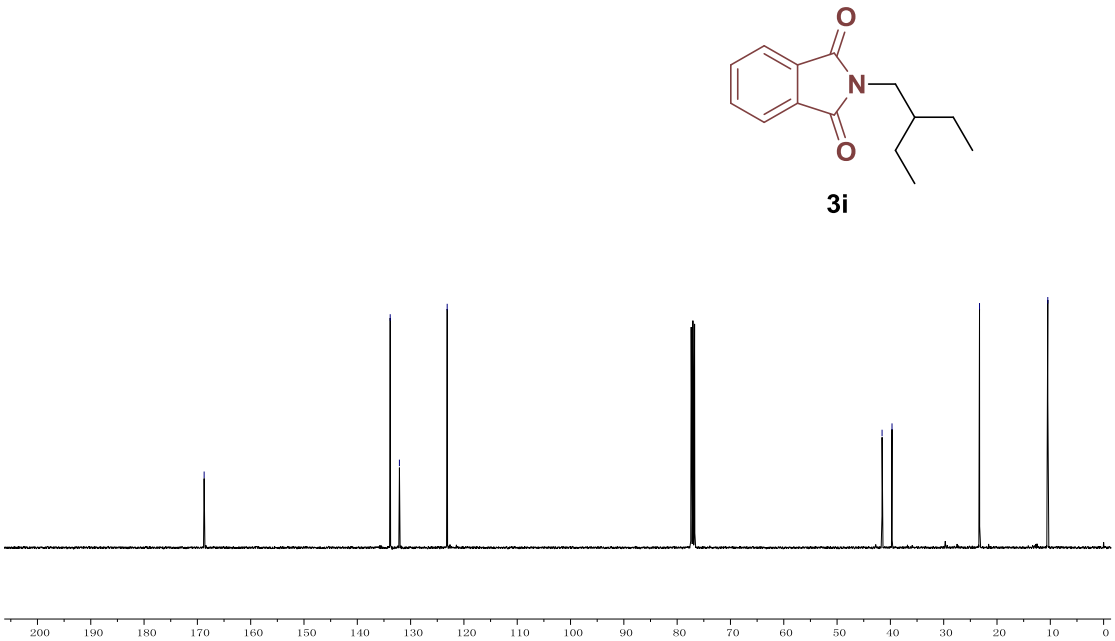
Product 3h:[1]H NMR and[13]C NMR.



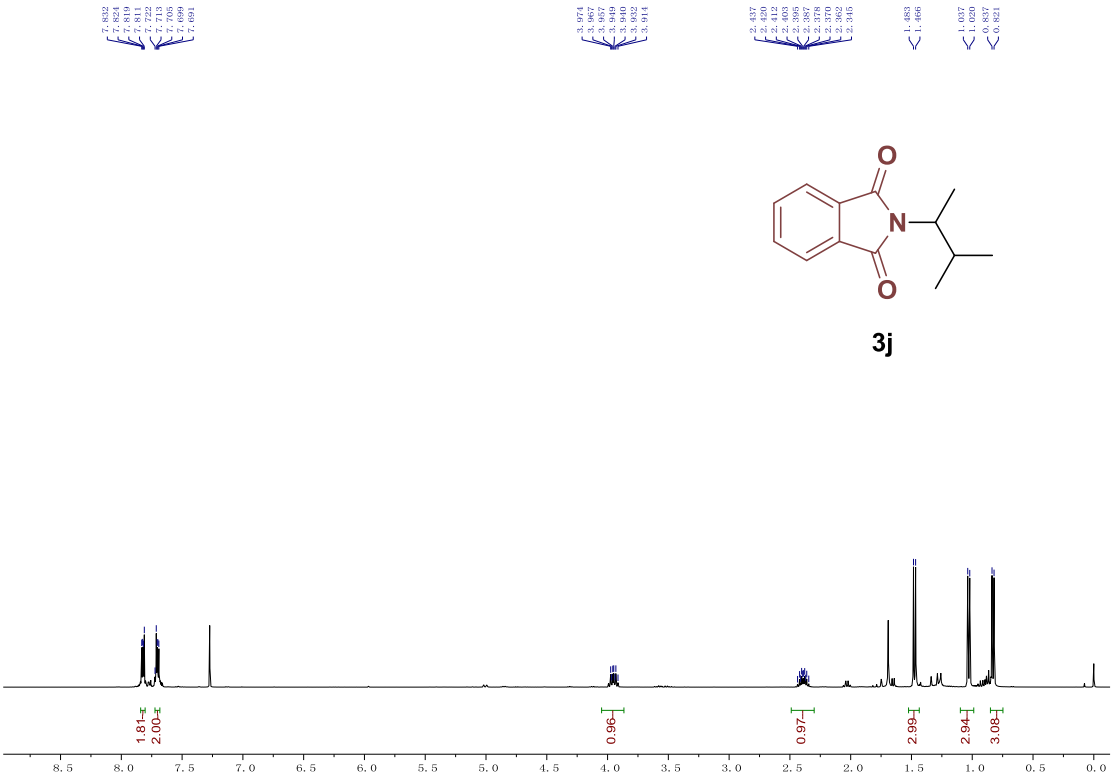


Product 3i: ^{1}H NMR and ^{13}C NMR.

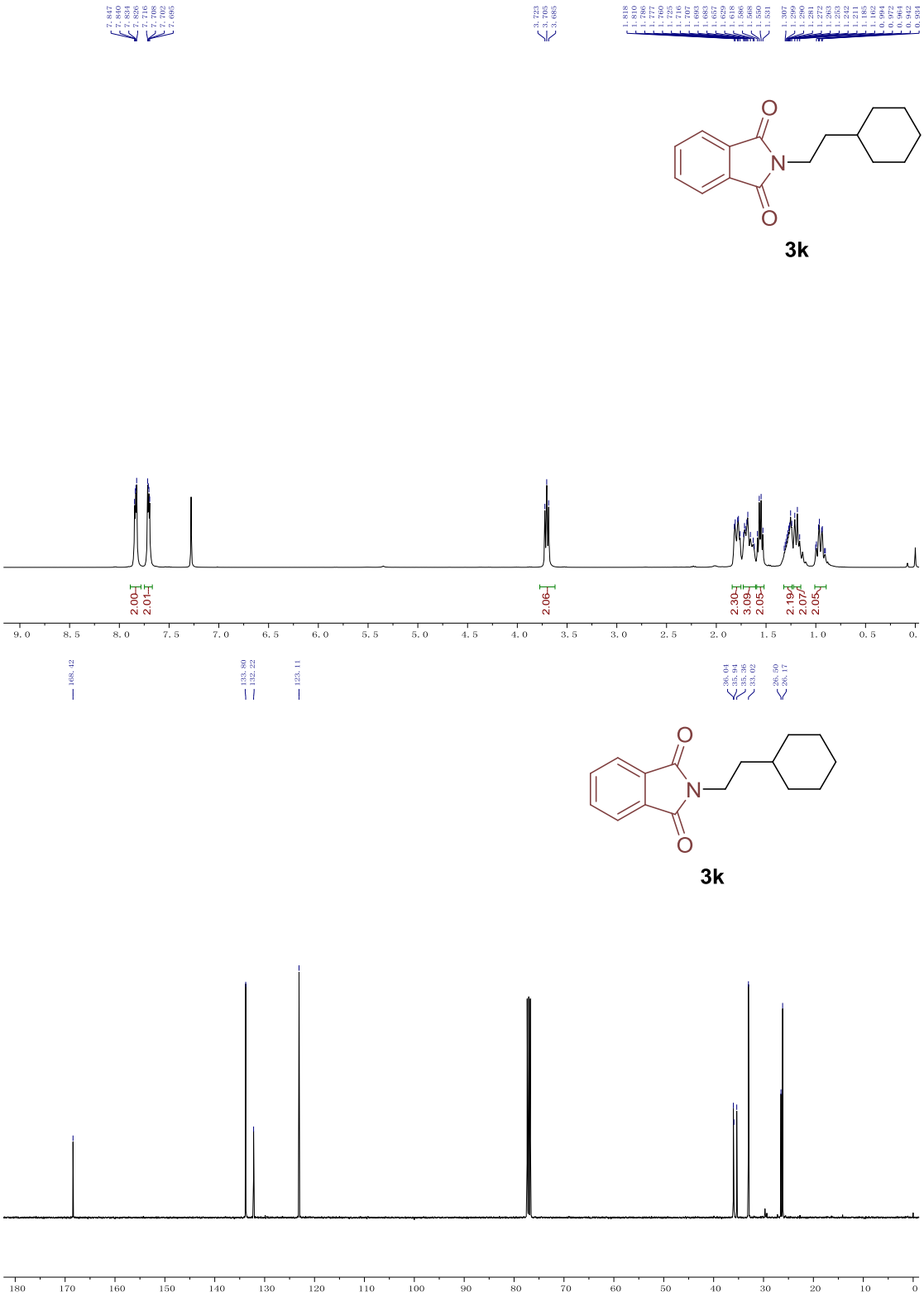




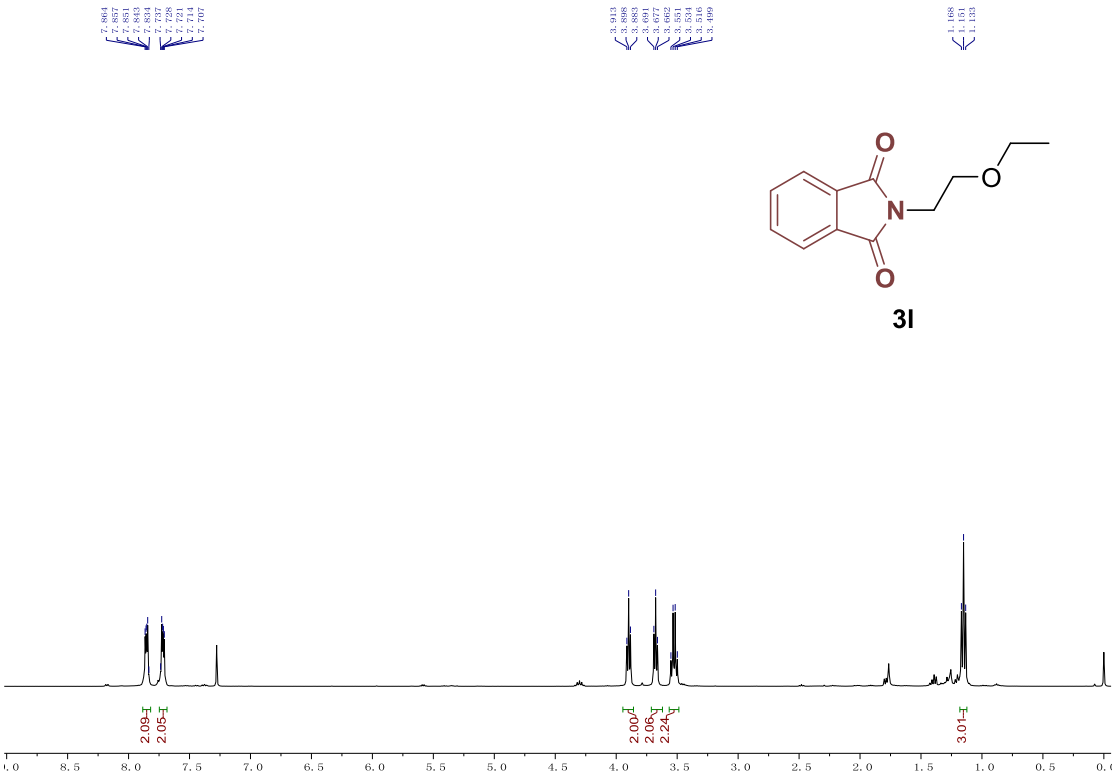
Product 3j: ^{1}H NMR.



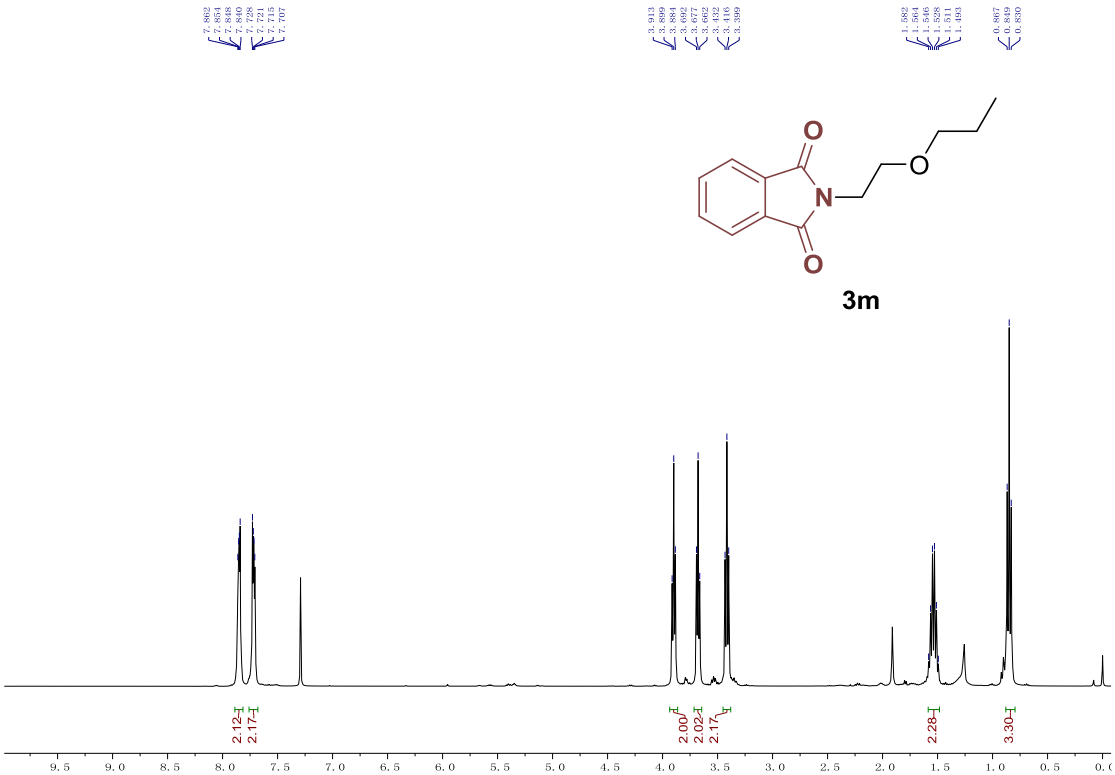
Product 3k: ^{1}H NMR and ^{13}C NMR.

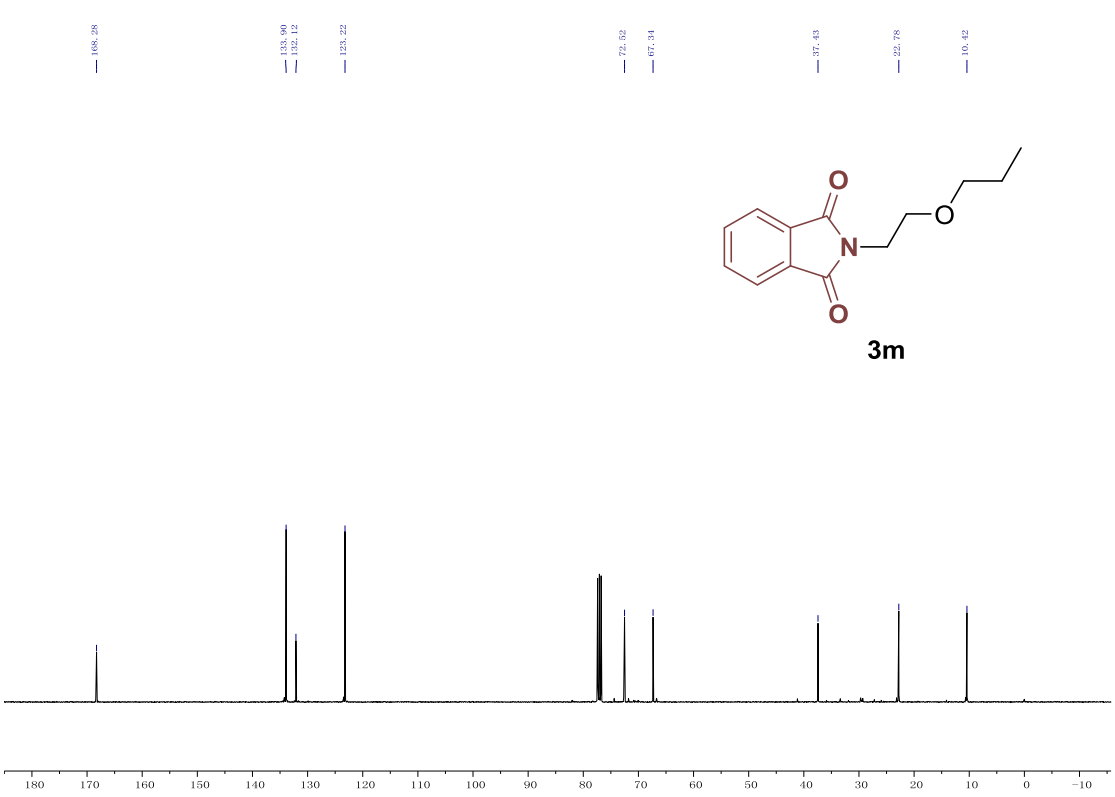


Product 3l: ^{1}H NMR.

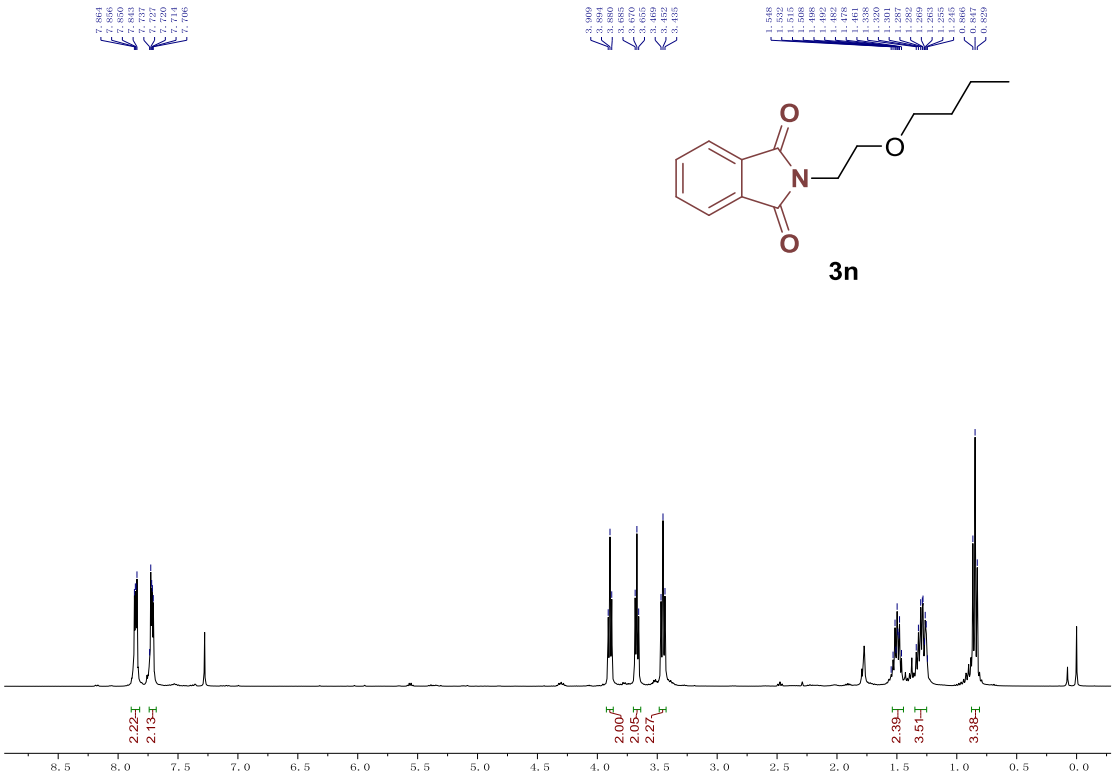


Product 3m:^{1}H NMR.

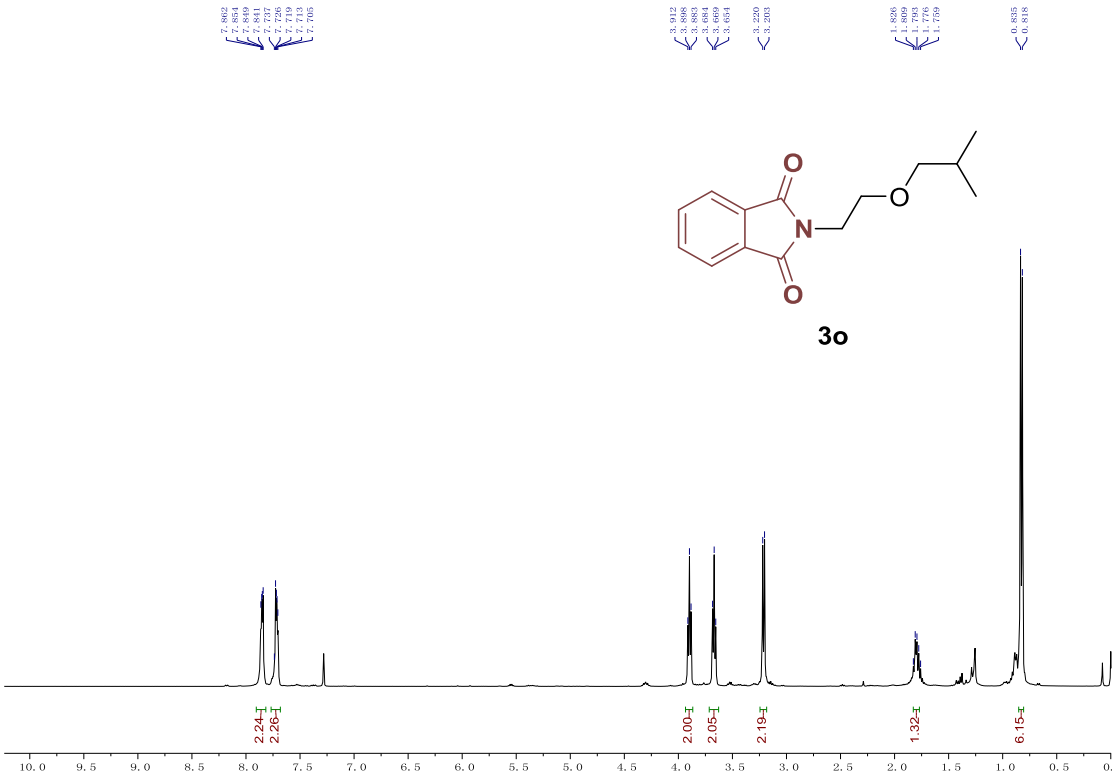




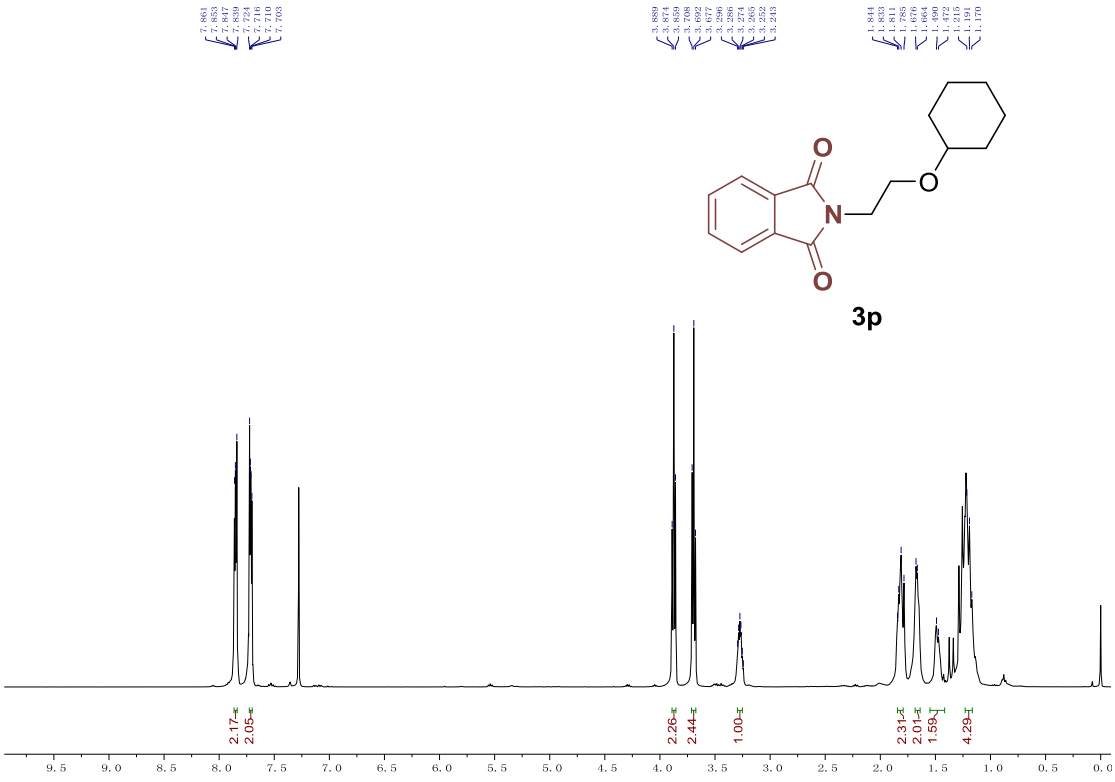
Product 3n: ^{1}H NMR.



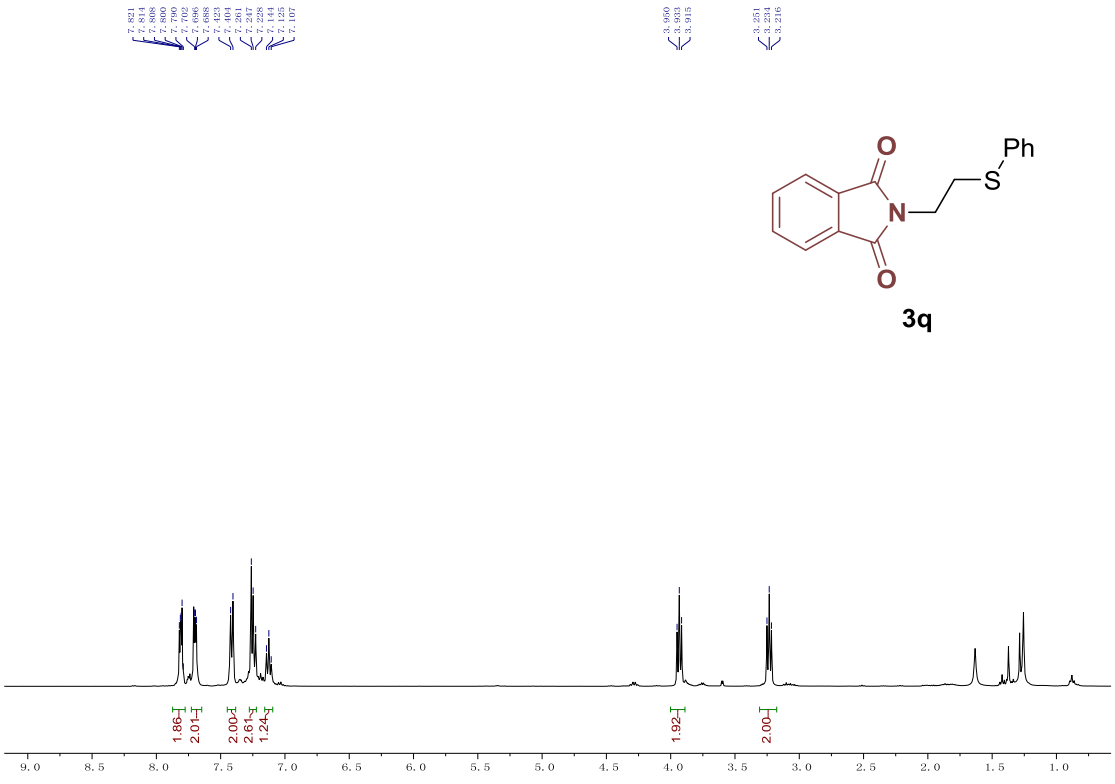
Product 3o:^{1}H NMR.



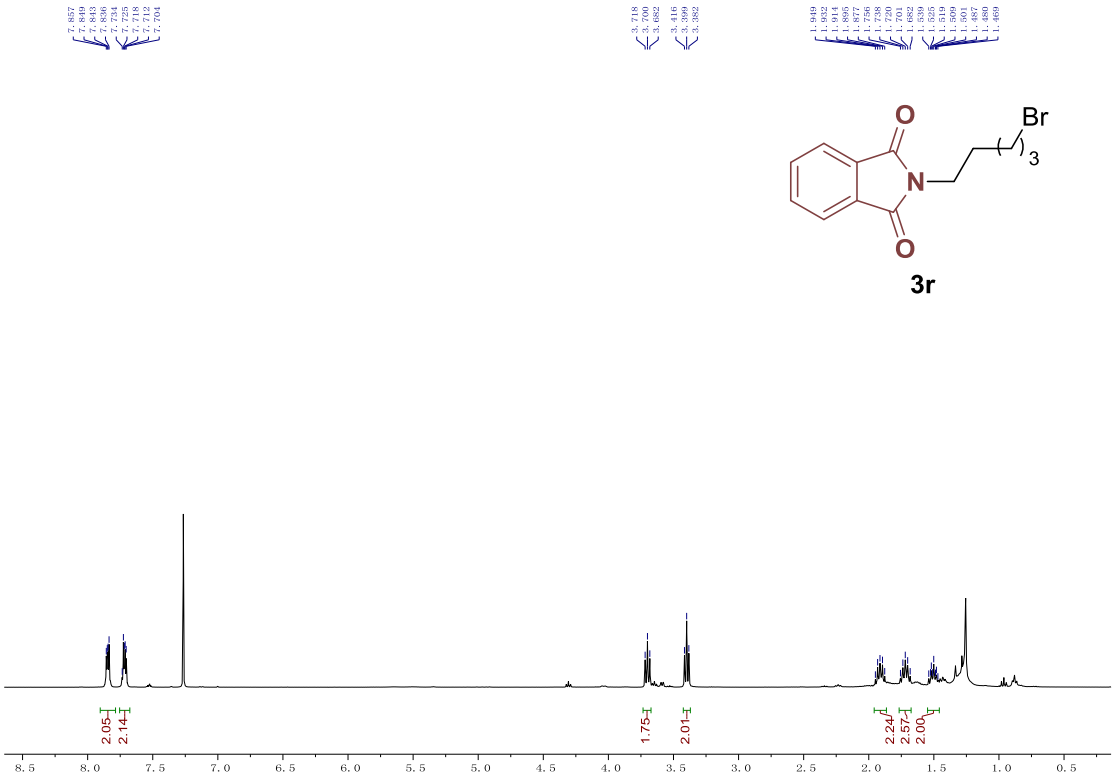
Product 3p: ^{1}H NMR.



Product 3q: ^{1}H NMR.



Product 3r: ^{1}H NMR.



Product 3s: ^{1}H NMR.