

Supporting Information

Substituents Regulate the Cyclization of Conjugated Alkynes to Accurately Construct cyclo-(*E*)-[3]Dendralenes

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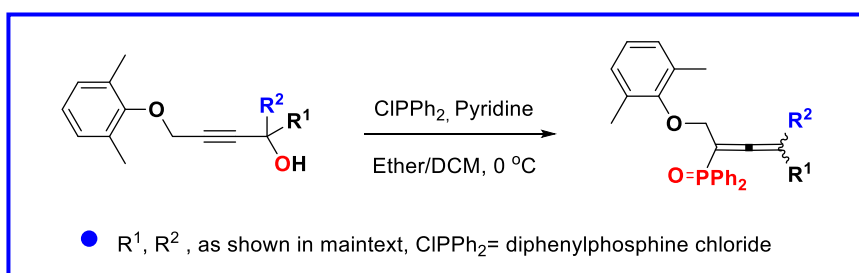
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1. General Information

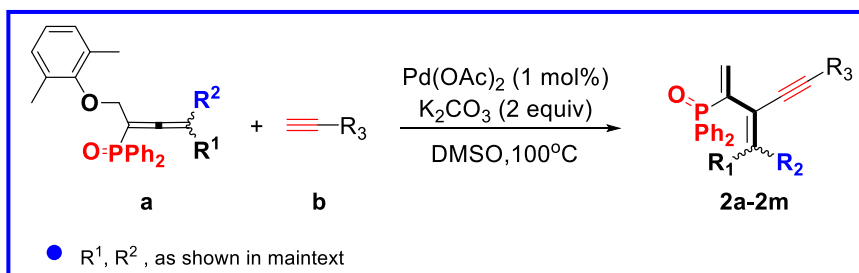
Solvents and reagents were reagent grade and used without purification unless otherwise noted. Column chromatography was performed using silica gel (200-300 mesh). All ^1H -NMR (400 MHz) spectra were recorded on a Bruker-DMX 400 using CDCl_3 solution in the presence of tetramethylsilane (TMS) as an internal standard and are reported in ppm (δ). Coupling constants are reported in Hertz (Hz). Spectral splitting patterns are designated as s, singlet; d, doublet; t, triplet; q, quartet; p, pentet; m, multiplet; and br, broad. High resolution mass spectroscopic data of the products were collected on a Waters Micromass GCT instrument using EI (70 eV) or an Agilent Technologies 6540 UHD Accurate-Mass Q-TOF LC/MS using ESI.

2. General Procedures for Substrates Preparation



To a stirred and cooled ($0\text{ }^\circ\text{C}$) solution of the acetylenic alcohol (40 mmol) in anhydrous ether (50 mL) and pyridine (3.88 mL, 48 mmol) under nitrogen was added dropwise diphenylphosphine chloride (40 mmol) in CH_2Cl_2 (50 mL). The stirring was maintained 1 h at $0\text{ }^\circ\text{C}$ and at room temperature overnight. The solution was then quenched with cold water and extracted with CH_2Cl_2 , and the organic layer was dried with Na_2SO_4 . Concentration in vacuo gave the crude product that was subjected to flash chromatography on silica gel eluting with ethyl acetate and petroleum ether. [Ref.: Chen, Y.-Z.; Zhang, L.; Lu, A.-M.; Yang, F.; Wu, L. *J. Org. Chem.* **2015**, *80*, 673-680.]

Note: the acetylenic alcohols were synthesized from terminal alkynes with corresponding ketones mediated by $n\text{-BuLi}$. (Liu, P.; Deng, C.-L.; Lei, X.; Lin, G. *Eur. J. Org. Chem.* **2011**, 7308-7316.)

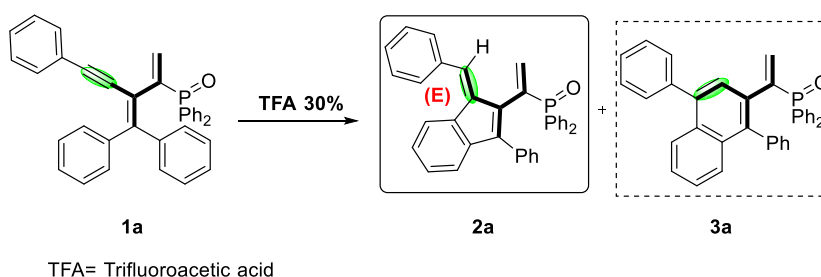


To a 25 mL vial was added allenylphosphine oxides (1 mmol), alkynes (2 mmol), potassium carbonate (K_2CO_3) (2 mmol), DMSO (10 mL) and Pd(OAc)_2 (1 mol%) respectively. The reaction was then allowed to react at 100 °C for a certain time until the complete consuming of starting materials monitored by TLC. The reaction mixture was extracted with EtOAc (10 mL×3). The combined organic extract was washed with brine and dried over anhydrous Na_2SO_4 . The solvent was evaporated under reduced pressure and the residue was purified by column chromatography on silica gel using petroleum ether/ethylacetate (1.5/1) as the eluent to afford the enynes. After being finished, the compound was determined by **NMR**.

Note: **1a-1n** is a known compound, please refer to the literature ^[4].

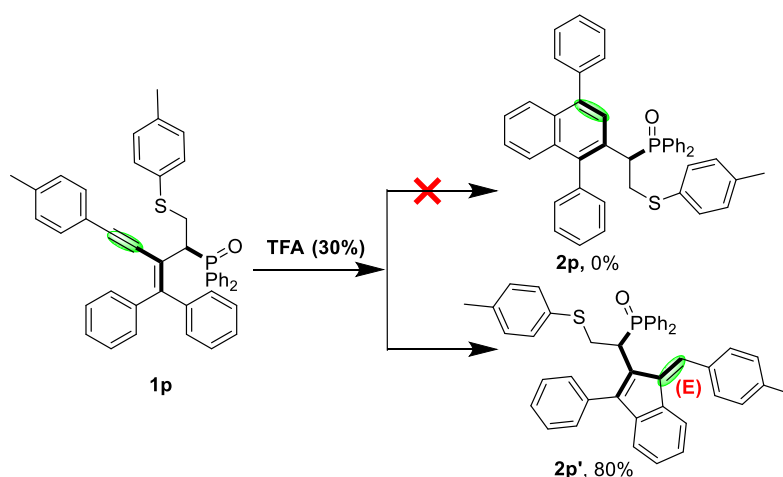
3. General Procedures for Substituents Regulate the Cyclization of Conjugated Alkynes

Constructing Cyclo-(*E*)-[3]Dendralenes



A 10 mL flask equipped with a magnetic stirrer was charged with conjugated alkynes (**1a**, 50 mg, 0.1 mmol), TFA (3.4 mg, 30 mol%) and 3 mL DCM. The reaction mixture was then heated to 50 °C for 3 hour until the complete consuming of **1a** monitored by TLC. Subsequently, all of the volatiles were removed under vacuum, the crude product was purified on flash chromatography (eluent: 1:1 (v/v) of ethyl acetate/petroleum ether) to afford product **2a** (45 mg, 90%) as a yellow solid.

4. Control Experiments



To a 25 mL vial was added Phosphinyl conjugated enynes (0.1 mmol, 64 mg), catalyst TFA (Trifluoroacetic acid, 30 mol%, 3.4 mg) in 3 mL solvent (Dichloromethane). The reaction was then allowed to react at 40 °C for a certain time until the complete consuming of starting materials monitored by TLC. The solvent was evaporated under reduced pressure and the residue was purified by column chromatography on silica gel using petroleum ether/ethylacetate (1/1) as the eluent to afford product **2p'** (5 mg, 80%) as a yellow solid, and the compound was determined by NMR and MS.

Note: **2p** is not detected and the synthesis method of the five-membered episulfide compound was reported for the first time, and the product **2p'** was a new compound. [Ref.: Luo, X.-L; Chen, X.-W; Chen, L; Zhang, K and Chen, Y.-B; *Chem. Commun.*, **2019**, 55, 2170.]

5. X-Ray Crystallography Data of 2a

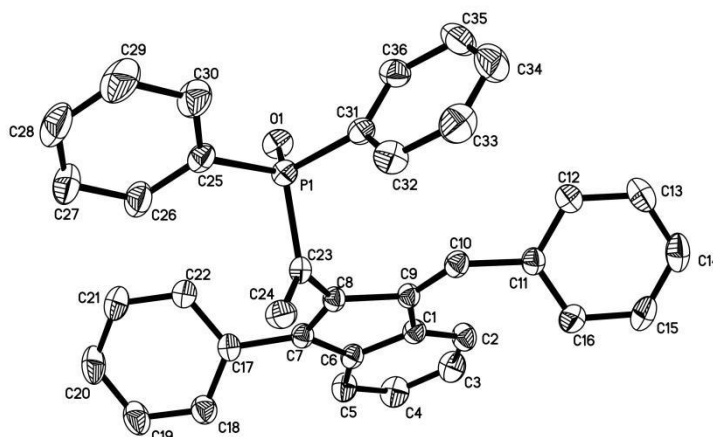


Table S1. Crystal data and structure refinement for 2a.

Identification code	2a
Empirical formula	C ₃₆ H ₂₇ O P
Formula weight	506.54
Temperature	296(2) K
Wavelength	0.71073
Crystal system	Monoclinic
Space group	P21/c
Unit cell dimensions	a = 18.285(2) b = 9.1800(9) c = 15.9471(16)
Volume	2676.7(5) Å ³
Z	4
Density (calculated)	1.257 Mg/m ³
Absorption coefficient	0.131 mm ⁻¹
F(000)	1064
Crystal size	0.220 x 0.200 x 0.100 mm ³
Theta range for data collection	1.114 to 27.530
Index ranges	-23 ≤ h ≤ 23, -11 ≤ k ≤ 10, -20 ≤ l ≤ 20
Reflections collected	26057
Independent reflections	6093 [R(int) = 0.0698]
Completeness to theta = 25.242°	99.6 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.5546
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	6093 / 0 / 343
Goodness-of-fit on F ²	1.028
Final R indices [I > 2σ(I)]	R1 = 0.0595, wR2 = 0.1428
R indices (all data)	R1 = 0.1051, wR2 = 0.1630
Extinction coefficient	n/a
Largest diff. peak and hole	0.373 and -0.361 e.Å ⁻³

Table S2. Bond lengths for 2a.

C(1)-C(2)	1.388(3)
C(1)-C(6)	1.405(3)

C(1)-C(9)	1.483(3)
C(2)-C(3)	1.378(4)
C(2)-H(2)	0.9300
C(3)-C(4)	1.378(4)
C(3)-H(3)	0.9300
C(4)-C(5)	1.385(4)
C(4)-H(4)	0.9300
C(5)-C(6)	1.376(3)
C(5)-H(5)	0.9300
C(6)-C(7)	1.478(3)
C(7)-C(8)	1.352(3)
C(7)-C(17)	1.484(3)
C(8)-C(9)	1.481(3)
C(8)-C(23)	1.490(3)
C(9)-C(10)	1.335(3)
C(10)-C(11)	1.471(3)
C(10)-H(10)	0.9300
C(11)-C(12)	1.380(3)
C(11)-C(16)	1.382(3)
C(12)-C(13)	1.381(4)
C(12)-H(12)	0.9300
C(13)-C(14)	1.354(4)
C(13)-H(13)	0.9300
C(14)-C(15)	1.349(4)
C(14)-H(14)	0.9300
C(15)-C(16)	1.383(4)
C(15)-H(15)	0.9300
C(16)-H(16)	0.9300
C(17)-C(22)	1.387(3)
C(17)-C(18)	1.388(3)
C(18)-C(19)	1.385(4)
C(18)-H(18)	0.9300
C(19)-C(20)	1.372(4)
C(19)-H(19)	0.9300
C(20)-C(21)	1.361(4)
C(20)-H(20)	0.9300
C(21)-C(22)	1.381(3)
C(21)-H(21)	0.9300

C(22)-H(22)	0.9300
C(23)-C(24)	1.319(3)
C(23)-P(1)	1.823(2)
C(24)-H(24A)	0.9300
C(24)-H(24B)	0.9300
C(25)-C(30)	1.383(4)
C(25)-C(26)	1.386(4)
C(25)-P(1)	1.808(2)
C(26)-C(27)	1.384(4)
C(26)-H(26)	0.9300
C(27)-C(28)	1.358(5)
C(27)-H(27)	0.9300
C(28)-C(29)	1.351(5)
C(28)-H(28)	0.9300
C(29)-C(30)	1.391(4)
C(29)-H(29)	0.9300
C(30)-H(30)	0.9300
C(31)-C(36)	1.381(3)
C(31)-C(32)	1.392(3)
C(31)-P(1)	1.811(2)
C(32)-C(33)	1.375(4)
C(32)-H(32)	0.9300
C(33)-C(34)	1.385(5)
C(33)-H(33)	0.9300
C(34)-C(35)	1.367(4)
C(34)-H(34)	0.9300
C(35)-C(36)	1.382(4)
C(35)-H(35)	0.9300
C(36)-H(36)	0.9300
O(1)-P(1)	1.4854(16)
C(2)-C(1)-C(6)	119.1(2)
C(2)-C(1)-C(9)	132.9(2)
C(6)-C(1)-C(9)	107.74(18)
C(3)-C(2)-C(1)	119.6(2)
C(3)-C(2)-H(2)	120.2
C(1)-C(2)-H(2)	120.2
C(2)-C(3)-C(4)	120.8(2)

C(2)-C(3)-H(3)	119.6
C(4)-C(3)-H(3)	119.6
C(3)-C(4)-C(5)	120.5(2)
C(3)-C(4)-H(4)	119.7
C(5)-C(4)-H(4)	119.7
C(6)-C(5)-C(4)	119.1(2)
C(6)-C(5)-H(5)	120.5
C(4)-C(5)-H(5)	120.5
C(5)-C(6)-C(1)	120.8(2)
C(5)-C(6)-C(7)	131.0(2)
C(1)-C(6)-C(7)	108.01(19)
C(8)-C(7)-C(6)	109.18(19)
C(8)-C(7)-C(17)	127.7(2)
C(6)-C(7)-C(17)	122.83(19)
C(7)-C(8)-C(9)	109.54(18)
C(7)-C(8)-C(23)	126.25(19)
C(9)-C(8)-C(23)	123.94(18)
C(10)-C(9)-C(8)	123.1(2)
C(10)-C(9)-C(1)	131.4(2)
C(8)-C(9)-C(1)	105.44(17)
C(9)-C(10)-C(11)	130.4(2)
C(9)-C(10)-H(10)	114.8
C(11)-C(10)-H(10)	114.8
C(12)-C(11)-C(16)	117.7(2)
C(12)-C(11)-C(10)	119.2(2)
C(16)-C(11)-C(10)	123.0(2)
C(11)-C(12)-C(13)	120.4(3)
C(11)-C(12)-H(12)	119.8
C(13)-C(12)-H(12)	119.8
C(14)-C(13)-C(12)	121.0(3)
C(14)-C(13)-H(13)	119.5
C(12)-C(13)-H(13)	119.5
C(15)-C(14)-C(13)	119.4(3)
C(15)-C(14)-H(14)	120.3
C(13)-C(14)-H(14)	120.3
C(14)-C(15)-C(16)	120.7(3)
C(14)-C(15)-H(15)	119.6
C(16)-C(15)-H(15)	119.6

C(11)-C(16)-C(15)	120.7(2)
C(11)-C(16)-H(16)	119.7
C(15)-C(16)-H(16)	119.7
C(22)-C(17)-C(18)	118.1(2)
C(22)-C(17)-C(7)	119.8(2)
C(18)-C(17)-C(7)	122.1(2)
C(19)-C(18)-C(17)	120.5(3)
C(19)-C(18)-H(18)	119.7
C(17)-C(18)-H(18)	119.7
C(20)-C(19)-C(18)	120.1(3)
C(20)-C(19)-H(19)	120.0
C(18)-C(19)-H(19)	120.0
C(21)-C(20)-C(19)	120.2(3)
C(21)-C(20)-H(20)	119.9
C(19)-C(20)-H(20)	119.9
C(20)-C(21)-C(22)	120.2(3)
C(20)-C(21)-H(21)	119.9
C(22)-C(21)-H(21)	119.9
C(21)-C(22)-C(17)	120.9(2)
C(21)-C(22)-H(22)	119.6
C(17)-C(22)-H(22)	119.6
C(24)-C(23)-C(8)	120.4(2)
C(24)-C(23)-P(1)	120.17(17)
C(8)-C(23)-P(1)	119.41(15)
C(23)-C(24)-H(24A)	120.0
C(23)-C(24)-H(24B)	120.0
H(24A)-C(24)-H(24B)	120.0
C(30)-C(25)-C(26)	118.2(2)
C(30)-C(25)-P(1)	121.9(2)
C(26)-C(25)-P(1)	119.55(19)
C(27)-C(26)-C(25)	120.8(3)
C(27)-C(26)-H(26)	119.6
C(25)-C(26)-H(26)	119.6
C(28)-C(27)-C(26)	120.0(3)
C(28)-C(27)-H(27)	120.0
C(26)-C(27)-H(27)	120.0
C(29)-C(28)-C(27)	120.3(3)
C(29)-C(28)-H(28)	119.8

C(27)-C(28)-H(28)	119.8
C(28)-C(29)-C(30)	120.8(3)
C(28)-C(29)-H(29)	119.6
C(30)-C(29)-H(29)	119.6
C(25)-C(30)-C(29)	119.9(3)
C(25)-C(30)-H(30)	120.1
C(29)-C(30)-H(30)	120.1
C(36)-C(31)-C(32)	119.1(2)
C(36)-C(31)-P(1)	117.94(18)
C(32)-C(31)-P(1)	122.94(19)
C(33)-C(32)-C(31)	120.5(3)
C(33)-C(32)-H(32)	119.8
C(31)-C(32)-H(32)	119.8
C(32)-C(33)-C(34)	119.4(3)
C(32)-C(33)-H(33)	120.3
C(34)-C(33)-H(33)	120.3
C(35)-C(34)-C(33)	120.6(3)
C(35)-C(34)-H(34)	119.7
C(33)-C(34)-H(34)	119.7
C(34)-C(35)-C(36)	119.9(3)
C(34)-C(35)-H(35)	120.0
C(36)-C(35)-H(35)	120.0
C(31)-C(36)-C(35)	120.4(3)
C(31)-C(36)-H(36)	119.8
C(35)-C(36)-H(36)	119.8
O(1)-P(1)-C(25)	112.87(10)
O(1)-P(1)-C(31)	111.68(10)
C(25)-P(1)-C(31)	106.37(11)
O(1)-P(1)-C(23)	112.54(10)
C(25)-P(1)-C(23)	106.18(10)
C(31)-P(1)-C(23)	106.75(10)

Table S3. Hydrogen bonds [$\text{\AA}$ and $^\circ$] for 2a.

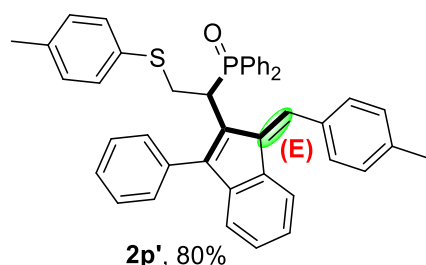
D-H...A	d(D-H)	d(H...A)	d(D...A)	$\angle(\text{DHA})$
C(36)-H(27)OP(1)	0.98	2.11	2.989(4)	147.6

Symmetry transformations used to generate equivalent atoms:

6. Characterizations of Products

6.1 products of 2p'

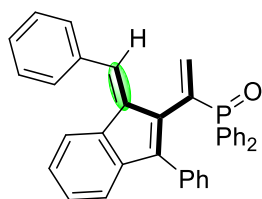
(E)-(1-(1-(4-methylbenzylidene)-3-phenyl-1H-inden-2-yl)-2-(p-tolylthio)ethyl)diphenylphosphine oxide (2p')



A yellow solid, (92 mg, 80% yield), *m.p.*: 154.4-155.9 $^\circ\text{C}$. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.07 (d, $J = 8.5$ Hz, 2H), 7.66-7.46 (m, 7H), 7.45-7.23 (m, 10H), 7.22-7.05 (m, 5H), 6.95 (d, $J = 8.1$ Hz, 2H), 6.88 (d, $J = 8.1$ Hz, 2H), 5.76 (d, $J = 7.5$ Hz, 1H), 3.97 (m, 1H), 3.89-3.71 (m, 1H), 3.44 (m, 1H), 2.53 (s, 3H), 2.32 (s, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 140.2 (d, $J = 7.5$ Hz), 137.8, 137.5, 137.1, 135.9, 133.2, 133.1, 132.6, 132.4, 132.1, 131.8, 131.7, 131.6, 131.4, 131.2, 130.9, 130.34 (d, $J = 15.8$ Hz), 130.3, 129.56 (d, $J = 5.1$ Hz), 129.6, 129.4, 129.0, 128.8, 128.7, 128.2, 128.0, 127.8, 127.7, 127.3, 127.1, 126.8, 126.1, 125.7, 125.6, 43.6, 43.0, 35.4, 21.4, 21.0. $^{31}\text{P NMR}$ (162 MHz, CDCl_3) δ 33.47 (s). **HRMS (ESI):** ($[\text{M}+\text{H}]^+$) Calcd for $\text{C}_{44}\text{H}_{38}\text{OPS}^+$: 645.2381, Found: 645.2379. **IR** (film) ν 3581, 2973, 2921, 1677, 1539, 1479, 1241, 1109, 1027, 939, 741, 689 cm^{-1} .

6.2. products of dendralenes

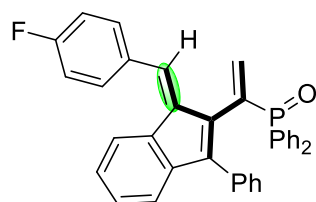
(E)-(1-(1-benzylidene-3-phenyl-1H-inden-2-yl)vinyl)diphenylphosphine oxide (2a)



2a

A yellow solid, (42 mg, 83% yield), *m.p.*: 137.4-139.1 °C. **¹H NMR** (400 MHz, CDCl₃) δ 7.50 (m, 4H), 7.45-7.32 (m, 9H), 7.29-7.22 (m, 7H), 7.18-7.09 (m, 2H), 7.07 (s, 1H), 6.97 (t, *J* = 7.3 Hz, 1H), 6.72 (m, 1H), 6.46 (m, 1H). **¹³C NMR** (101 MHz, CDCl₃) δ 143.7, 141.9, 141.1, 139.7, 137.4, 136.5, 135.4, 134.4, 133.9, 131.9 (d, *J* = 9.6 Hz), 131.5 (d, *J* = 2.7 Hz), 130.5, 129.4 (d, *J* = 13.1 Hz), 128.3, 128.2, 128.1, 128.0, 127.8, 127.7, 125.5, 123.1, 120.2. **³¹P NMR** (162 MHz, CDCl₃) δ 26.04 (s). **HRMS (ESI):** ([*M*+*H*]⁺) Calcd for C₃₆H₂₉OP⁺: 507.1878, Found: 507.1876. **IR** (film) ν 3677, 2985, 2907, 2221, 1592, 1574, 1496, 1438, 1172, 1077, 916, 739, 695 cm⁻¹.

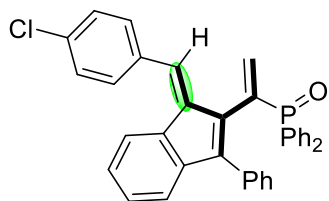
(*E*)-(1-(1-(4-fluorobenzylidene)-3-phenyl-1H-inden-2-yl)vinyl)diphenylphosphine oxide (2b)



2b

A yellow solid, (37 mg, 70% yield), *m.p.*: 107.4-109.1 °C. **¹H NMR** (400 MHz, CDCl₃) δ 7.53-7.43 (m, 8H), 7.43-7.32 (m, 12H), 7.28-7.20 (m, 16H), 7.19-7.04 (m, 8H), 7.02-6.95 (m, 4H), 6.72 (d, *J* = 1.6 Hz, 1H), 6.67 (d, *J* = 1.6 Hz, 1H), 6.49 (d, *J* = 1.6 Hz, 1H), 6.40 (d, *J* = 1.6 Hz, 1H). **¹³C NMR** (101 MHz, CDCl₃) δ 161.4, 143.7, 142.0, 141.2, 140.6, 139.7, 137.4, 135.3, 134.25 (d, *J* = 11.1 Hz), 133.7, 132.19 (d, *J* = 48.1 Hz), 132.0, 131.9, 131.6, 131.5, 131.2, 131.1, 130.4, 129.4, 128.3, 128.1, 128.0, 127.9, 127.8, 125.5, 122.9, 120.3, 115.5, 115.2, 100.0. **³¹P NMR** (162 MHz, CDCl₃) δ 26.15 (s). **HRMS (ESI):** ([*M*+*H*]⁺) Calcd for C₃₆H₂₆FOP : 525.1784, Found: 525.1783. **IR** (film) ν 3677, 2985, 2900, 2213, 1502, 1396, 1245, 1061, 924, 723, 694 cm⁻¹.

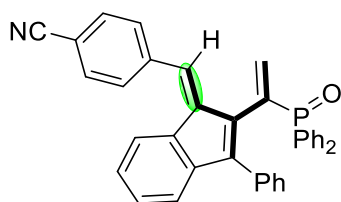
(*E*)-(1-(1-(4-chlorobenzylidene)-3-phenyl-1H-inden-2-yl)vinyl)diphenylphosphine oxide (2c)



2c

A yellow solid, (41 mg, 76% yield), *m.p.*: 111.6-113.7 °C. **¹H NMR** (400 MHz, CDCl₃) δ 7.54-7.31 (m, 26H), 7.22 (m, 16H), 7.13 (m, 4H), 6.98 (m, 4H), 6.73 (s, 1H), 6.69 (s, 1H), 6.49 (s, 1H), 6.40 (s, 1H). **¹³C NMR** (101 MHz, CDCl₃) δ 143.7, 141.6, 134.9, 134.1, 133.7 (d, *J* = 17.0 Hz), 131.9 (d, *J* = 9.6 Hz), 131.6, 130.7, 129.4, 128.5, 128.3, 128.2, 128.1, 128.0, 127.9, 125.6, 122.9, 120.4. **³¹P NMR** (162 MHz, CDCl₃) δ 26.47 (s). **HRMS (ESI):** ([*M*+*H*]⁺) Calcd for C₃₆H₂₇ClOP⁺: 541.1488, Found: 537.2322. **IR** (film), ν 3059, 2947, 2837, 2385, 1544, 1423, 1422, 1343, 1023, 881, 735, 675 cm⁻¹.

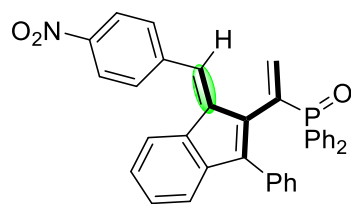
(*E*)-4-((2-(1-(diphenylphosphoryl)vinyl)-3-phenyl-1H-inden-1-ylidene)methyl)benzonitrile (2d)



2d

A yellow solid, (42 mg, 79% yield), *m.p.*: 125.7-127.6 °C. **¹H NMR** (400 MHz, CDCl₃) δ 7.68 (d, *J* = 8.2 Hz, 4H), 7.55-7.32 (m, 24H), 7.31-7.20 (m, 15H), 7.20-7.06 (m, 4H), 7.02-6.94 (m, 4H), 6.67 (d, *J* = 1.3 Hz, 1H), 6.62 (d, *J* = 1.3 Hz, 1H), 6.49 (d, *J* = 1.4 Hz, 1H), 6.39 (d, *J* = 1.4 Hz, 1H). **¹³C NMR** (101 MHz, CDCl₃) δ 143.9, 143.0, 141.5, 137.8, 134.0, 133.3, 132.3, 132.1, 131.9, 131.8, 131.7, 131.6, 131.3, 131.3, 130.3, 130.0, 129.3, 128.45 (d, *J* = 20.2 Hz), 128.13 (d, *J* = 12.0 Hz), 125.9, 122.9, 120.6, 118.8, 111.6, 100.0. **³¹P NMR** (162 MHz, CDCl₃) δ 26.27 (s). **HRMS (ESI):** ([*M*+*H*]⁺) Calcd for C₃₇H₂₇NOP⁺: 532.1830, Found: 532.1830. **IR** (film) ν 3675, 2970, 2906, 2231, 1537, 1338, 1244, 1044, 891, 694 cm⁻¹.

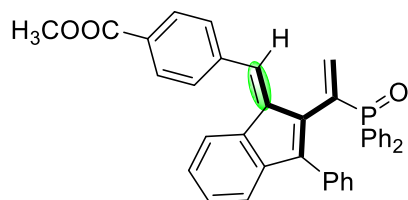
(*E*)-(1-(1-(4-nitrobenzylidene)-3-phenyl-1H-inden-2-yl)vinyl)diphenylphosphine oxide (2e)



2e

A yellow solid, (49 mg, 90% yield), *m.p.*: 186.3-188.0 °C. **¹H NMR** (400 MHz, CDCl₃) δ 7.67 (d, *J* = 7.5 Hz, 2H), 7.63 – 7.47 (m, 12H), 7.45 – 7.26 (m, 10H), 7.17 (s, 5H), 6.14 (d, *J* = 12.1 Hz, 1H), 6.05 (d, *J* = 12.1 Hz, 1H), 5.89 (d, *J* = 42.0 Hz, 1H), 5.46 (d, *J* = 19.4 Hz, 1H). **¹³C NMR** (101 MHz, CDCl₃) δ 145.2 (d, *J* = 7.5 Hz), 143.4 (d, *J* = 94.9 Hz), 142.4, 142.1, 140.9, 139.7, 136.0, 135.5 (d, *J* = 10.1 Hz), 133.7 (d, *J* = 7.2 Hz), 133.0, 132.7, 131.9, 131.8, 131.5 (d, *J* = 2.6 Hz), 130.9, 130.0, 129.8, 128.9, 128.3, 128.2, 127.9, 127.6, 127.3 (d, *J* = 8.1 Hz), 127.0, 126.9, 126.3. **³¹P NMR** (162 MHz, CDCl₃) δ 28.67 (s). **HRMS (ESI)**: ([M+H]⁺) Calcd for C₄₂H₃₄OP⁺: 585.2342, Found: 585.2341. **IR** (film) ν 3062, 3015, 1599, 1487, 1435, 1195, 1111, 966, 860, 690 cm⁻¹.

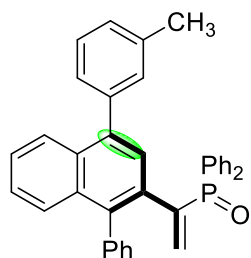
Methyl-(E)-4-((2-(1-(diphenylphosphoryl)vinyl)-3-phenyl-1H-inden-1-ylidene)methyl)benzoate (2f)



2f

A yellow solid, (48 mg, 85% yield), *m.p.*: 185.5-187.4 °C. **¹H NMR** (400 MHz, CDCl₃) δ 8.06 (d, *J* = 8.2 Hz, 4H), 7.46 (M, 13H), 7.35 (M, 9H), 7.23 (t, *J* = 7.9 Hz, 9H), 7.13 (M, 5H), 7.07-6.92 (m, 5H), 6.76 (s, 1H), 6.71 (s, 1H), 6.54 (d, *J* = 4.6 Hz, 1H), 6.45 (s, 1H), 3.97 (s, 3H). **¹³C NMR** (101 MHz, CDCl₃) δ 152.2, 152.1, 132.3, 132.2, 131.9, 131.8, 131.7, 130.3 (d, *J* = 7.0 Hz), 130.2, 128.4, 128.3, 128.2, 128.0, 127.9, 127.8, 127.6, 89.5, 21.2. **³¹P NMR** (162 MHz, CDCl₃) δ 27.80 (s). **HRMS (ESI)**: ([M+H]⁺) Calcd for C₃₇H₃₂O₂P⁺: 565.1933, Found: 565.1931. **IR** (film) ν 3676, 2985, 2901, 1605, 1524, 1455, 1255, 1108, 1021, 945, 765, 696 cm⁻¹.

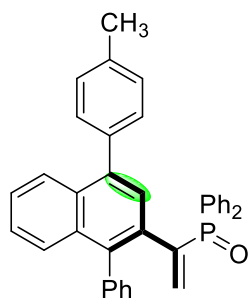
Diphenyl(1-(1-phenyl-4-(m-tolyl)naphthalen-2-yl)vinyl)phosphine oxide (3g)



3g

A yellow solid, (42 mg, 80% yield), *m.p.*: 179.5-181.6 °C. **¹H NMR** (400 MHz, CDCl₃) δ 7.97 (d, *J* = 8.1 Hz, 1H), 7.62-7.52 (m, 7H), 7.40 (m, 16H), 7.25-6.99 (m, 14H), 6.00 (m, 1H), 5.93 (d, *J* = 8.2 Hz, 1H), 2.42 (s, 3H). **¹³C NMR** (101 MHz, CDCl₃) δ 143.8, 139.0, 138.5, 137.2, 137.0, 134.8, 133.6, 133.2, 133.1, 132.4, 132.3 (d, *J* = 2.7 Hz), 131.9, 131.8, 131.4, 131.1, 130.8, 130.0, 128.9, 128.5, 128.3, 127.8, 127.5, 127.3, 127.0, 125.9, (d, *J* = 5.1 Hz), 21.3. **³¹P NMR** (162 MHz, CDCl₃) δ 28.58 (s). **HRMS (ESI):** ([M+H]⁺) Calcd for C₃₇H₃₀OP⁺: 521.2034, Found: 521.2033. **IR** (film) ν 3645, 3408, 3235, 2985, 2917, 1634, 1594, 1435, 1245, 1093, 834, 758, 695 cm⁻¹.

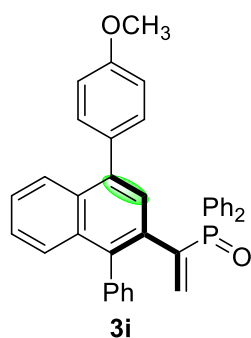
Diphenyl(1-(1-phenyl-4-(p-tolyl)naphthalen-2-yl)vinyl)phosphine oxide (3h)



3h

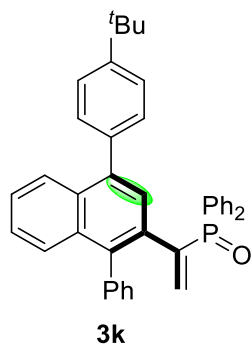
A yellow solid, (39 mg, 75% yield), *m.p.*: 167.3-168.8 °C. **¹H NMR** (400 MHz, CDCl₃) δ 7.98 (d, *J* = 8.1 Hz, 1H), 7.67-7.47 (m, 7H), 7.46-7.32 (m, 9H), 7.30-7.21 (m, 4H), 7.17 (dd, *J* = 6.4, 3.0 Hz, 2H), 7.11 (s, 1H), 6.09-5.96 (m, 1H), 5.93 (s, 1H), 2.47 (s, 3H). **¹³C NMR** (101 MHz, CDCl₃) δ 144.7, 143.8, 139.0 (s), 138.7 (d, *J* = 47.4 Hz), 137.2, 137.0, 134.8, 133.6, 133.2 (d, *J* = 8.5 Hz), 132.3 (d, *J* = 9.6 Hz), 131.9 (d, *J* = 2.7 Hz), 131.4, 131.1, 130.8, 130.0, 128.9, 128.4 (d, *J* = 12.0 Hz), 127.8, 127.4 (d, *J* = 16.2 Hz), 127.0, 125.9 (d, *J* = 5.6 Hz), 21.3. **³¹P NMR** (162 MHz, CDCl₃) δ 28.17 (s). **HRMS (ESI):** ([M+H]⁺) Calcd for C₃₇H₃₀OP⁺: 521.2034, Found: 521.2039. **IR** (film) ν 3645, 3051, 2968, 2900, 2228, 1603, 1503, 1432, 1177, 950, 865, 694 cm⁻¹.

(1-(4-(4-methoxyphenyl)-1-phenylnaphthalen-2-yl)vinyl)Diphenylphosphine oxide (3i)



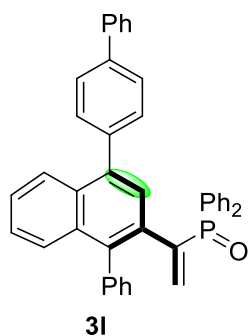
A yellow solid, (45 mg, 84% yield), *m.p.*: 181.5-183.4 °C. **¹H NMR** (400 MHz, CDCl₃) δ 7.98 (d, J = 8.3 Hz, 1H), 7.68-7.46 (m, 7H), 7.46-7.31 (m, 9H), 7.30-7.22 (m, 2H), 7.15 (dd, J = 6.4, 3.0 Hz, 2H), 7.09 (s, 1H), 6.99 (d, J = 8.6 Hz, 2H), 6.01 (d, J = 22.2 Hz, 1H), 5.93 (s, 1H), 3.90 (s, 3H). **¹³C NMR** (101 MHz, CDCl₃) δ 159.0, 144.4, 138.7, 138.5, 135.1, 133.6, 133.1, 132.5, 132.3, 132.2, 132.0 (d, J = 2.7 Hz), 131.5 (d, J = 10.3 Hz), 131.1, 130.5, 128.4 (d, J = 12.1 Hz), 127.8, 127.4 (d, J = 18.5 Hz), 127.0, 125.9, 113.7, 55.4. **³¹P NMR** (162 MHz, CDCl₃) δ 28.86 (s). **HRMS (ESI):** ([M+H]⁺) Calcd for C₃₇H₃₀O₂P: 537.1983, Found: 537.1986. **IR** (film) ν 3365, 2765, 2656, 2344, 1581, 1492, 1488, 1385, 1055, 883, 745, 635 cm⁻¹.

(1-(4-(4-(tert-butyl)phenyl)-1-phenylnaphthalen-2-yl)vinyl)diphenylphosphine oxide(3k)



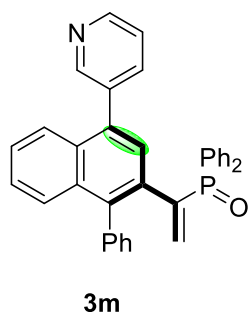
A yellow solid, (39 mg, 70% yield), *m.p.*: 195.2-197.7 °C. **¹H NMR** (400 MHz, CDCl₃) δ 8.01 (d, J = 8.3 Hz, 1H), 7.55 (m, 6H), 7.52-7.32 (m, 13H), 7.33-7.24 (m, 4H), 7.13 (m, 4H), 5.95 (dd, J = 29.9, 16.8 Hz, 2H), 1.43 (s, 9H). **¹³C NMR** (101 MHz, CDCl₃) δ 150.2, 144.8, 138.9, 138.5, 137.1, 134.8, 133.6, 132.27 (d, J = 9.7 Hz), 131.8, 131.4, 131.0, 129.8, 128.4 (d, J = 12.0 Hz), 127.7, 127.4, 127.0, 126.0 (d, J = 18.2 Hz), 125.1, 124.7, 34.6, 31.6, 31.5. **³¹P NMR** (162 MHz, CDCl₃) δ 28.82 (s). **HRMS (ESI):** ([M+H]⁺) Calcd for C₄₀H₃₆OP⁺: 563.2504, Found: 563.2501. **IR** (film) ν 3012, 2945, 2832, 2375, 1545, 1423, 1425, 1315, 1054, 945, 738, 645 cm⁻¹.

(1-(4-([1,1'-biphenyl]-4-yl)-1-phenylnaphthalen-2-yl)vinyl)diphenylphosphine oxide (3l)



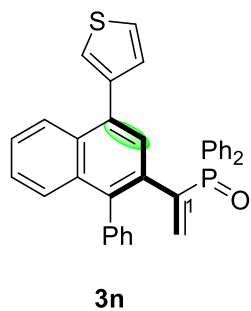
A yellow solid, (44 mg, 75% yield), *m.p.*: 112.1-113.3 °C. **¹H NMR** (400 MHz, CDCl₃) δ 8.04 (d, *J* = 8.3 Hz, 1H), 7.70 (m, 4H), 7.57 (m, 9H), 7.48-7.34 (m, 12H), 7.22-7.11 (m, 3H), 6.00 (d, *J* = 25.8 Hz, 1H), 5.92 (d, *J* = 4.3 Hz, 1H). **¹³C NMR** (101 MHz, CDCl₃) δ 140.8, 140.1, 139.2, 138.9, 138.8, 138.5 (d, *J* = 11.0 Hz), 134.9 (d, *J* = 9.2 Hz), 133.7, 133.3, 133.2, 132.4, 132.3, 131.9, 131.8, 131.4, 131.0, 130.53 (s), 130.8, 128.9, 128.5, 128.4, 127.8, 127.6, 127.5, 127.2, 127.1, 126.9, 126.1, 126.0, 125.8. **³¹P NMR** (162 MHz, CDCl₃) δ 28.27 (s). **HRMS (ESI):** ([*M*+*H*]⁺) Calcd for C₄₂H₃₂OP⁺: 583.2191, Found: 583.2195. **IR** (film) ν 3668, 2983, 2902, 2214, 1605, 1401, 1254, 1065, 894, 693 cm⁻¹.

Diphenyl(1-(1-phenyl-4-(pyridin-3-yl)naphthalen-2-yl)vinyl)phosphine oxide (3m)



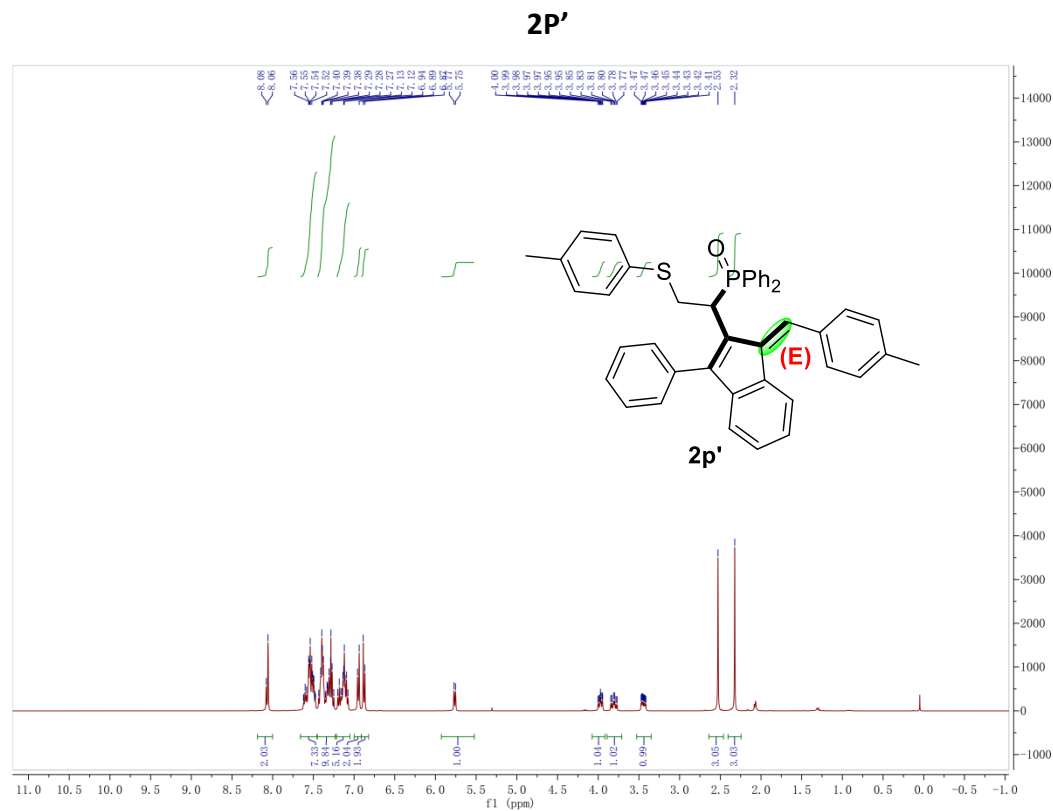
A yellow solid, (30 mg, 60% yield), *m.p.*: 146.2-148.5 °C. **¹H NMR** (400 MHz, CDCl₃) δ 8.40 (s, 1H), 8.00-7.60 (m, 5H), 7.59-6.82 (m, 18H), 5.97 (dd, *J* = 54.8, 28.6 Hz, 2H). **¹³C NMR** (101 MHz, CDCl₃) δ 150.8, 141.2, 140.2, 138.7, 132.1 (d, *J* = 10.0 Hz), 131.0, 130.2 (d, *J* = 18.0 Hz), 128.5, 128.4, 128.0, 127.8, 127.7, 126.7, 123.0, 100.0, 96.4. **³¹P NMR** (162 MHz, CDCl₃) δ 28.62 (s). **HRMS (ESI):** ([*M*+*H*]⁺) Calcd for C₃₅H₂₇NOP⁺: 508.1830, Found: 508.1835. **IR** (film) ν 3653, 3382, 2933, 2223, 1548, 1435, 1173, 957, 795, 695 cm⁻¹.

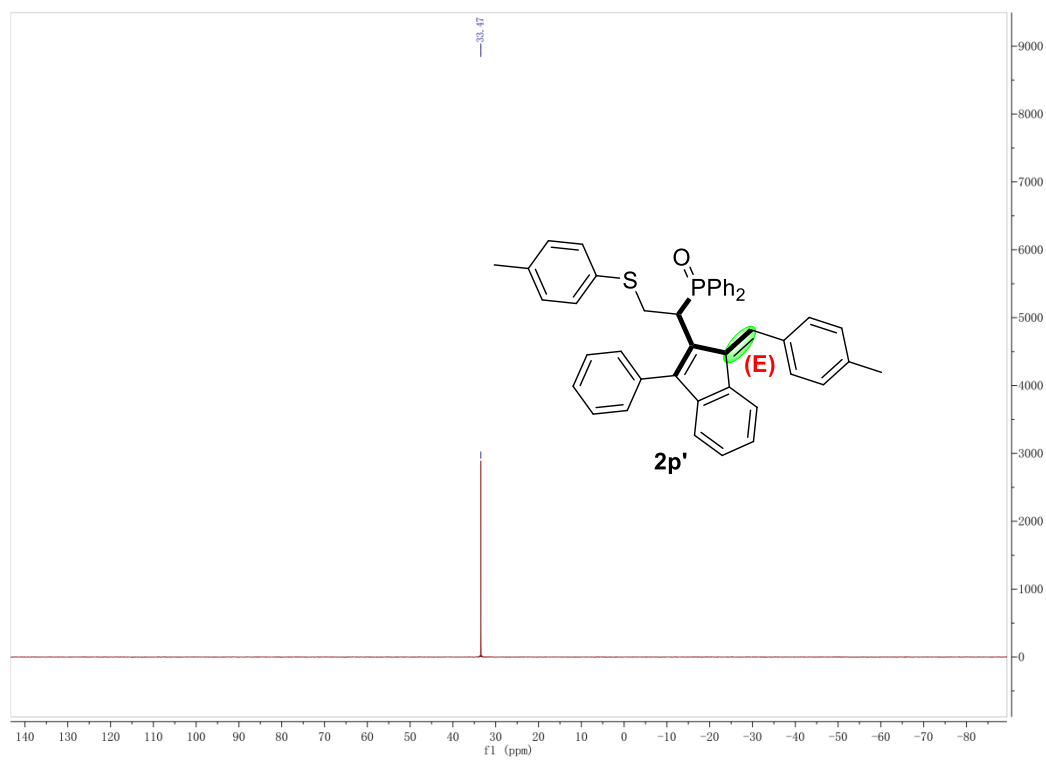
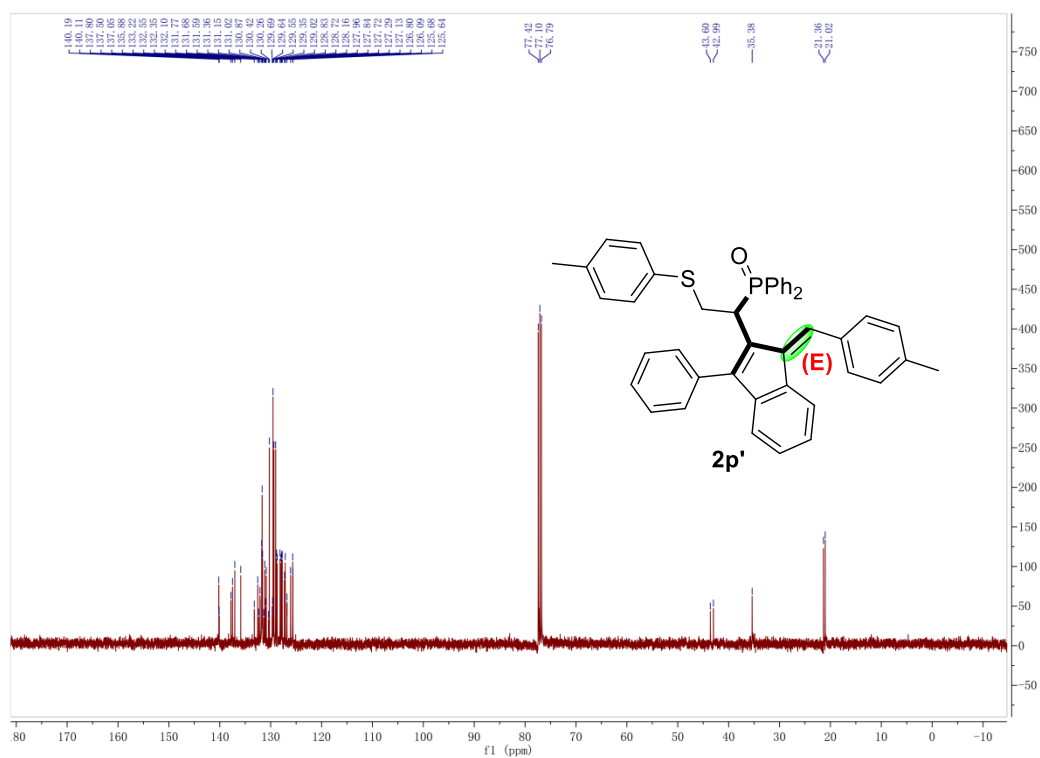
Diphenyl(1-(1-phenyl-4-(thiophen-3-yl)naphthalen-2-yl)vinyl)phosphine oxide (3n)

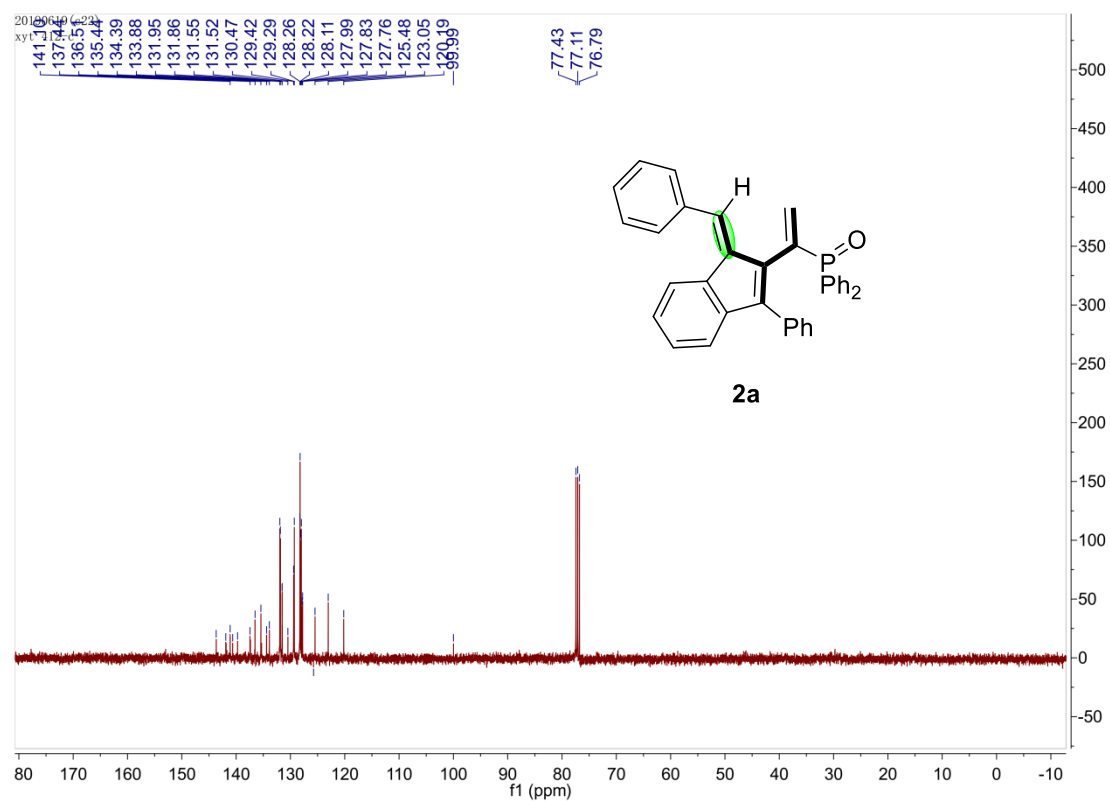
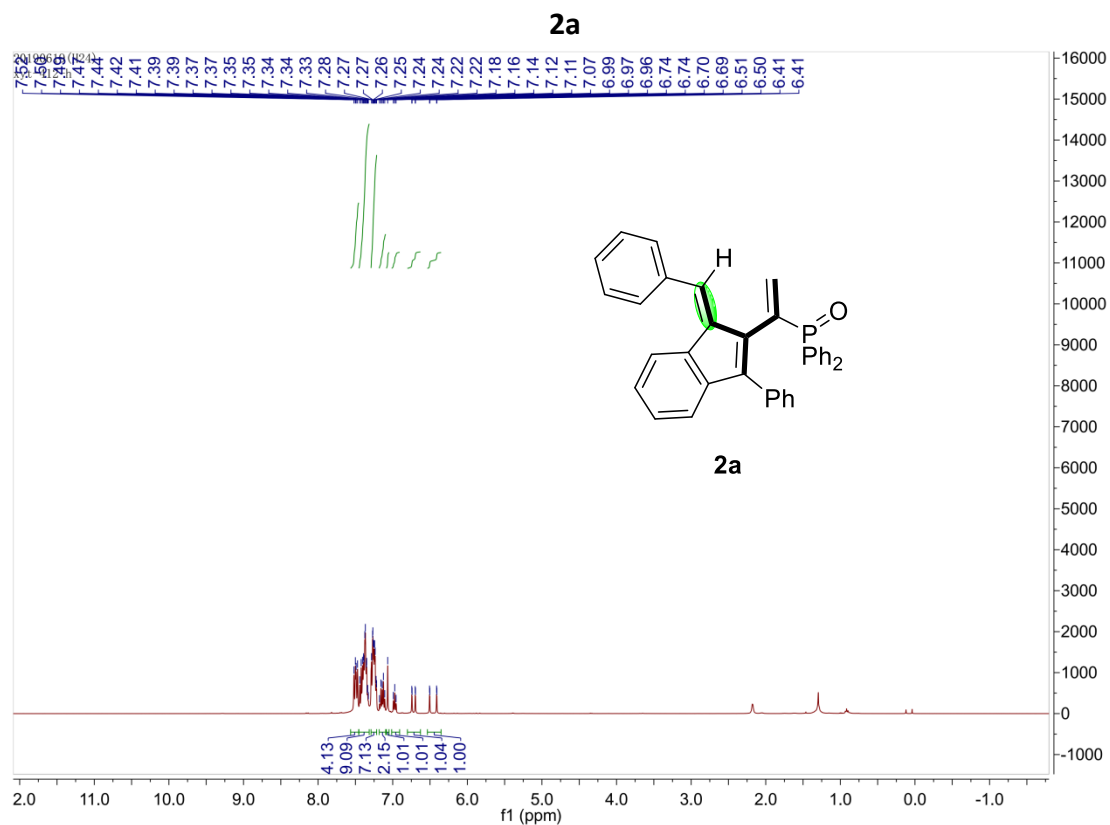


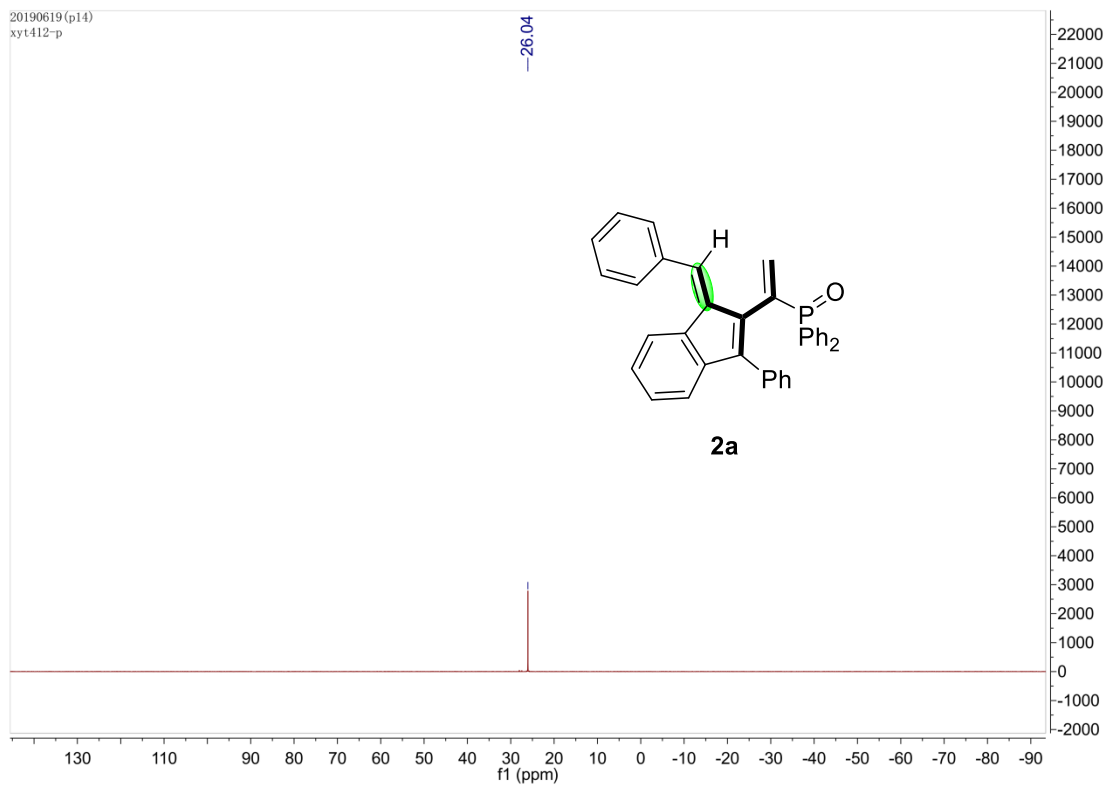
A yellow solid, (33 mg, 65% yield), *m.p.*: 173.2-174.7 °C. **¹H NMR** (400 MHz, CDCl₃) δ 8.08 (d, *J* = 8.4 Hz, 1H), 7.60-7.49 (m, 5H), 7.48-7.33 (m, 9H), 7.20 (M, 1H), 7.14 (M, 3H), 5.97 (dd, *J* = 30.5, 20.9 Hz, 2H). **¹³C NMR** (101 MHz, CDCl₃) δ 140.5, 139.0, 138.2, 135.6, 133.7 (d, *J* = 29.3 Hz), 132.4, 132.3, 132.1, 131.3, 131.2, 129.6, 128.6, 128.5, 128.4, 127.8, 127.7, 127.6, 127.4, 127.1, 127.0, 126.2, 126.1, 126.0, 125.7, 125.5, 125.3, 123.7. **³¹P NMR** (162 MHz, CDCl₃) δ 30.37 (s). **HRMS (ESI):** ([*M*+*H*]⁺) Calcd for C₃₄H₂₆OPS⁺: 513.1442, Found: 513.1447. **IR** (film) ν 3675, 3050, 2223, 1678, 1585, 1437, 1314, 126.6, 117.03, 112.7, 903, 853 cm⁻¹.

7. ¹H-NMR, ¹³C-NMR, ³¹P-NMR and HRMS spectra

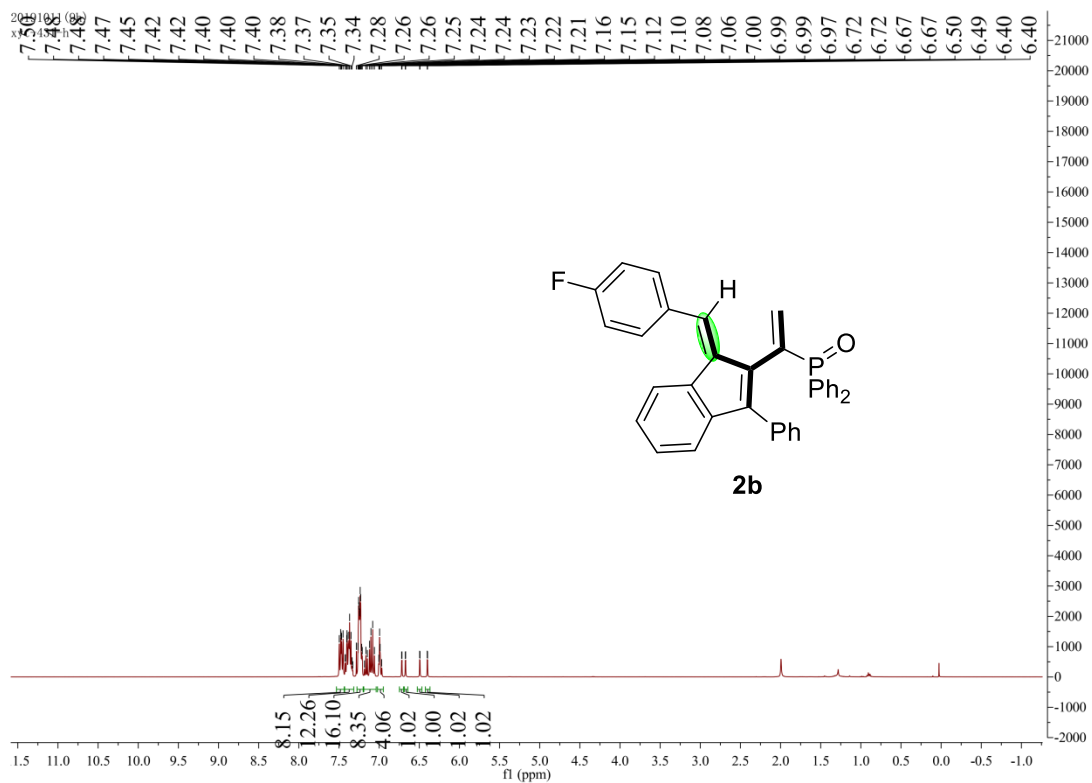


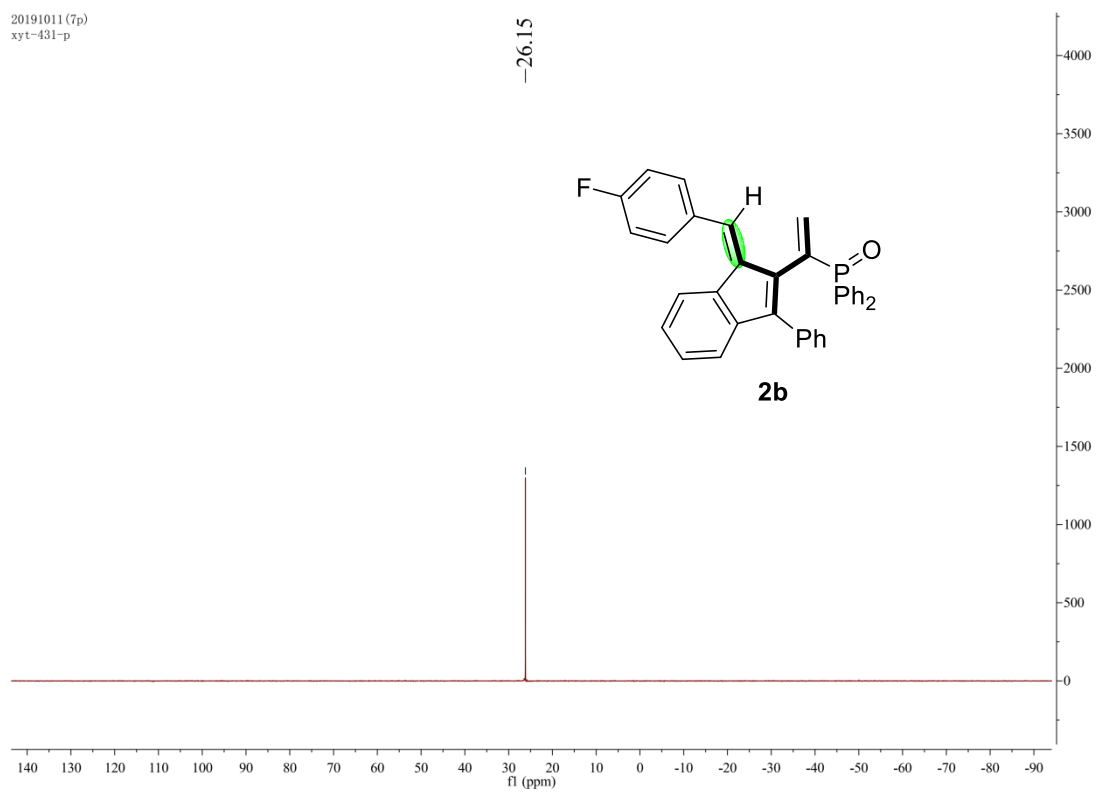
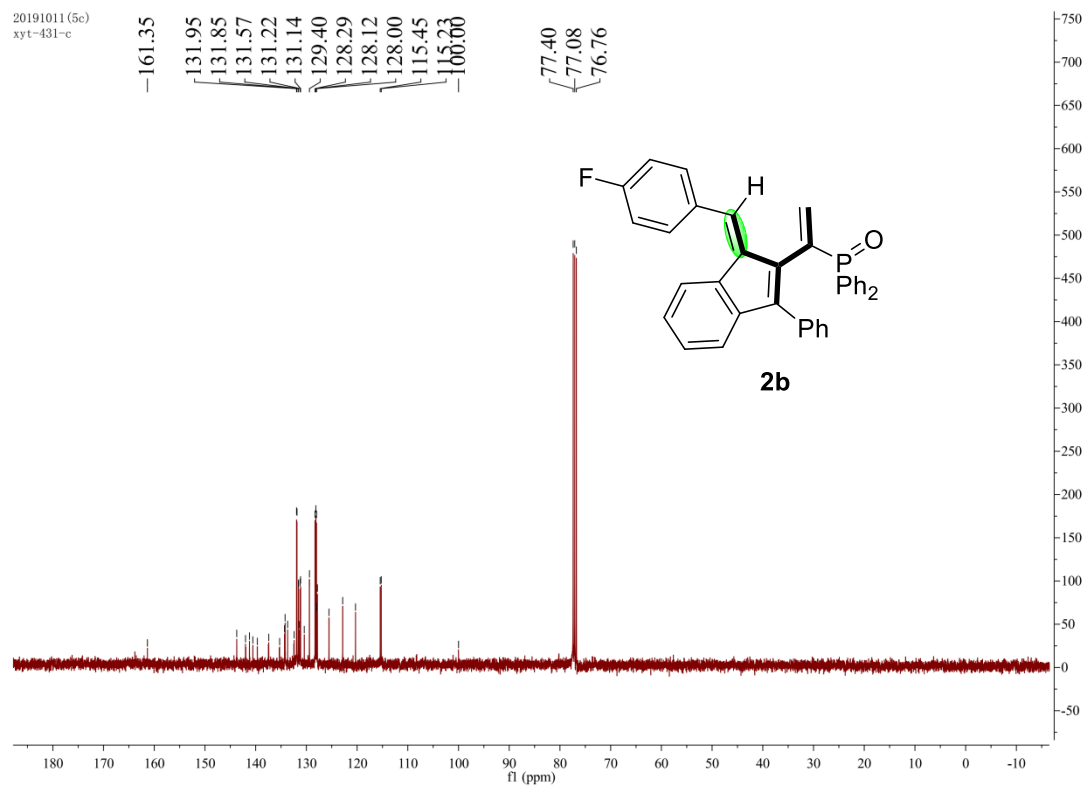




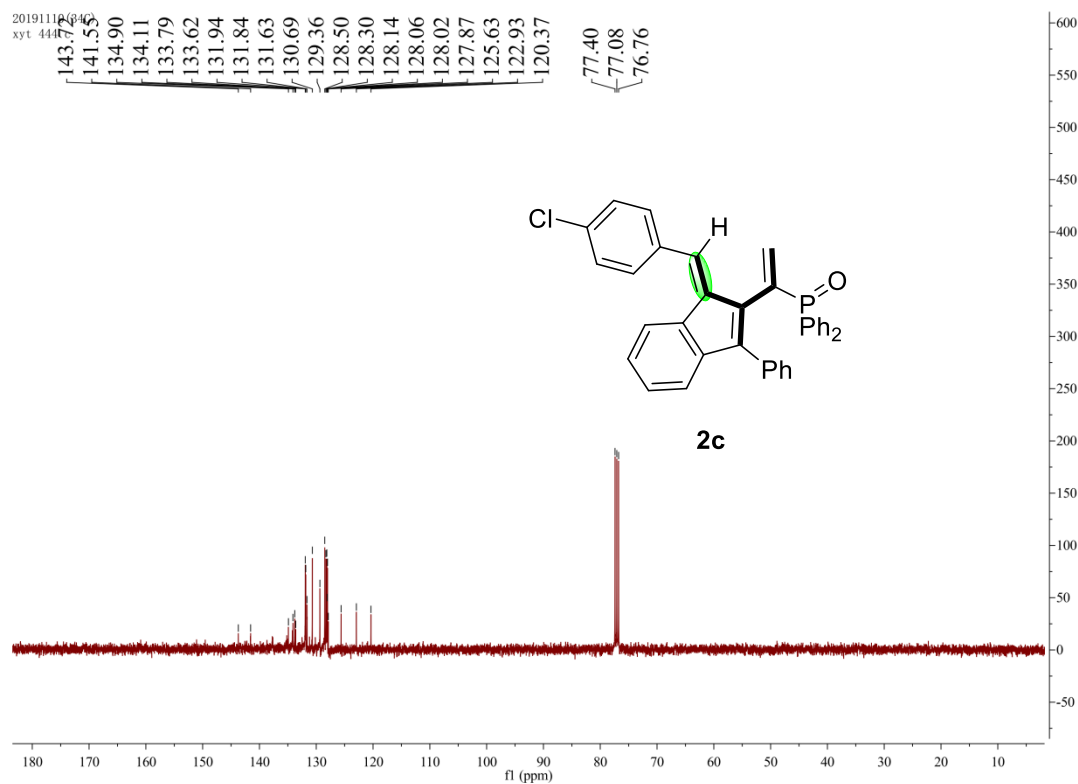
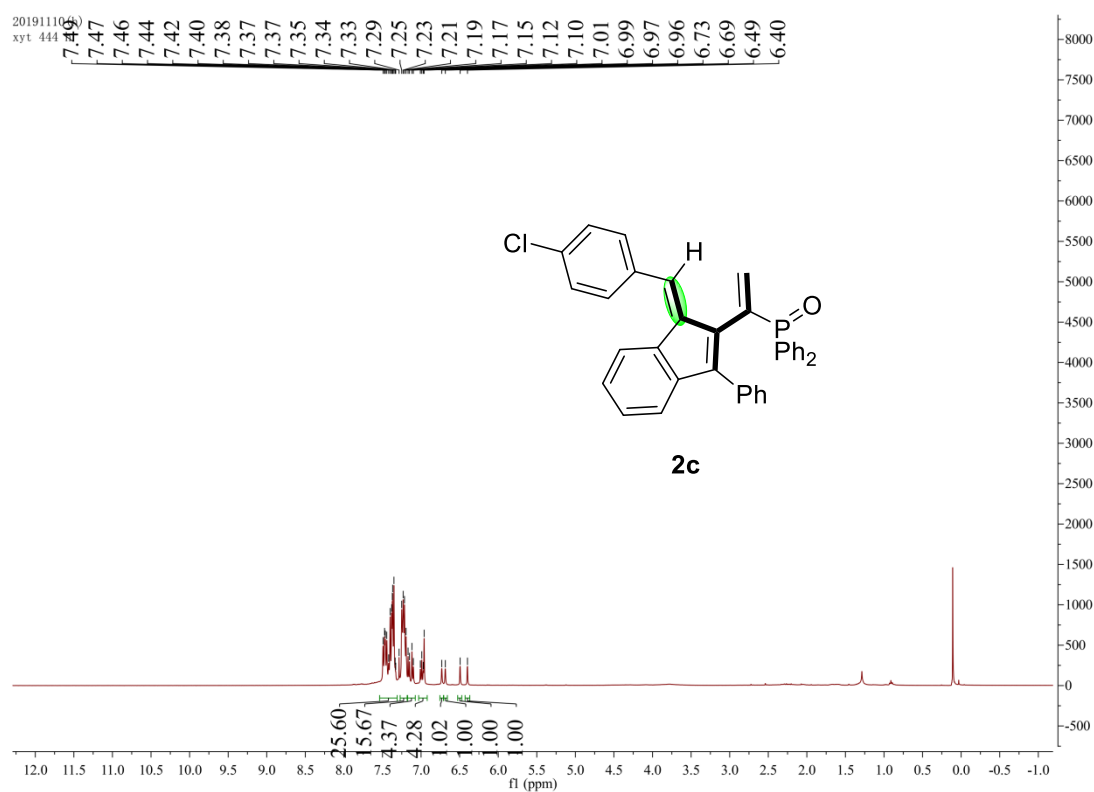


2b

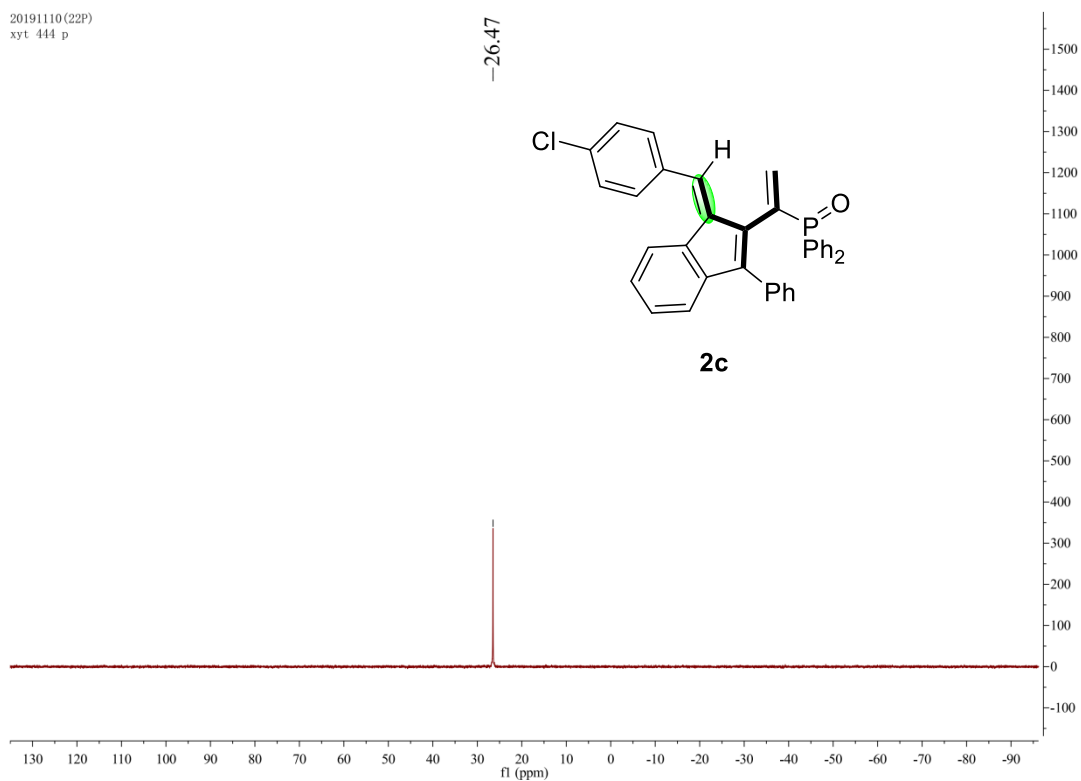




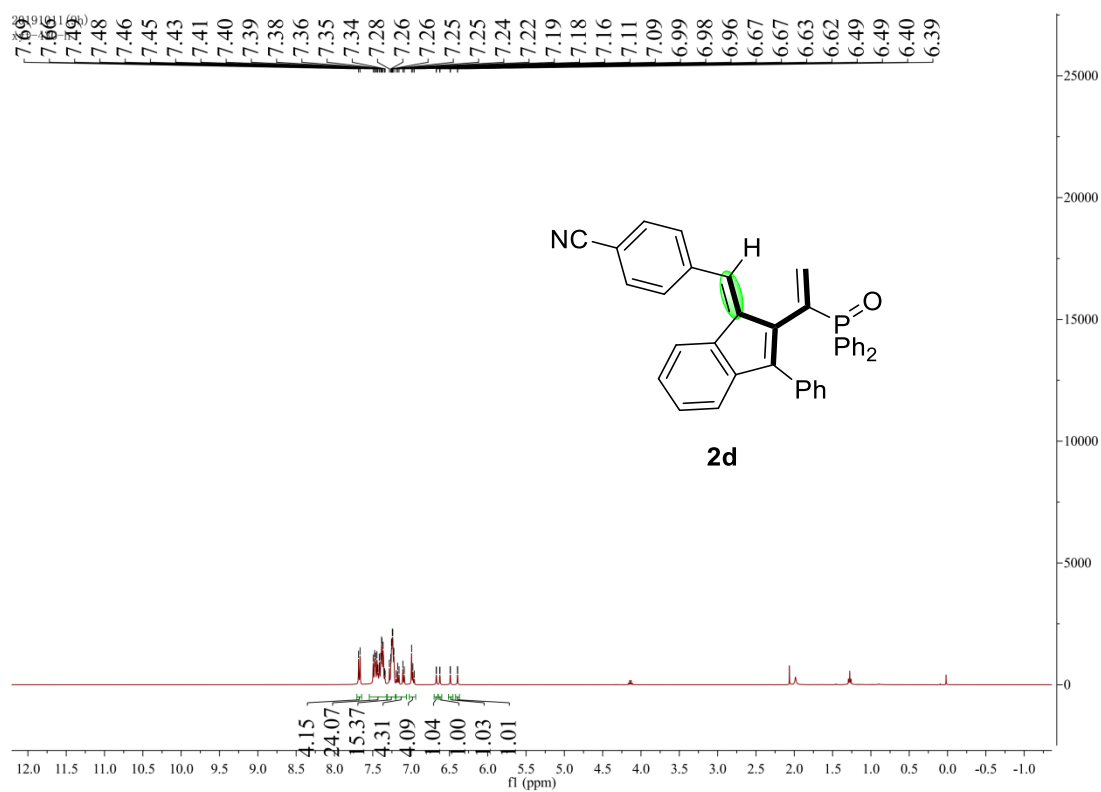
2c

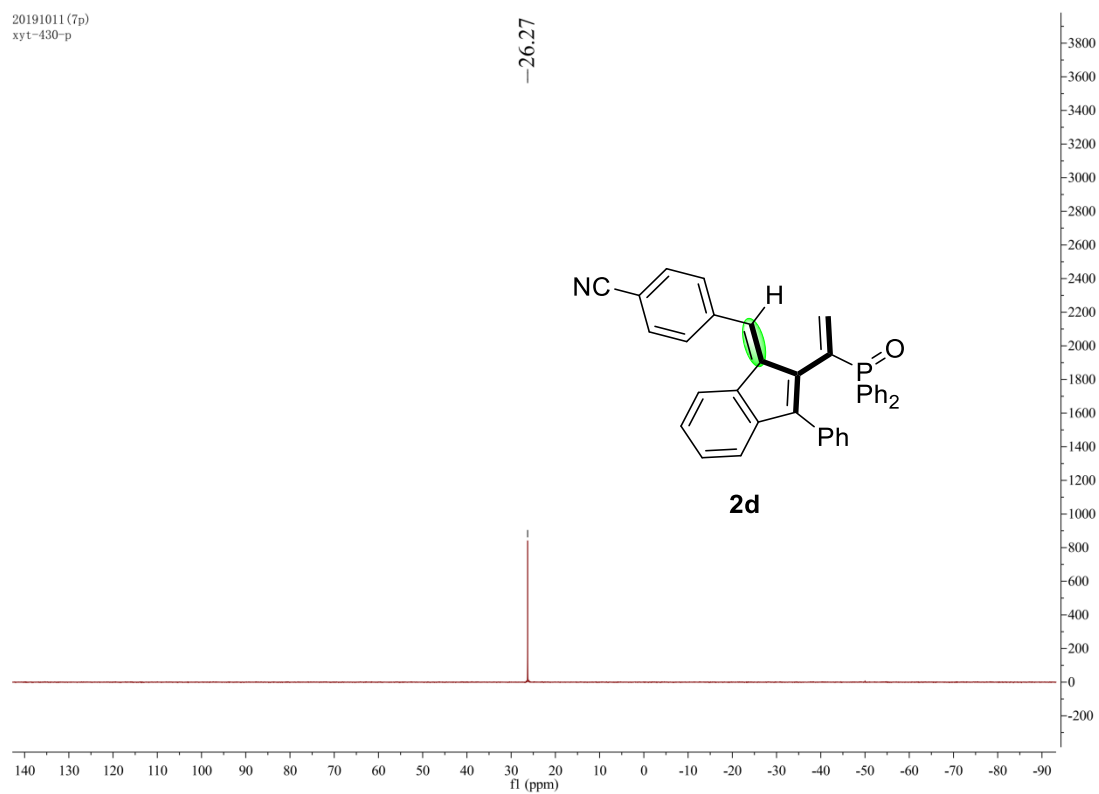
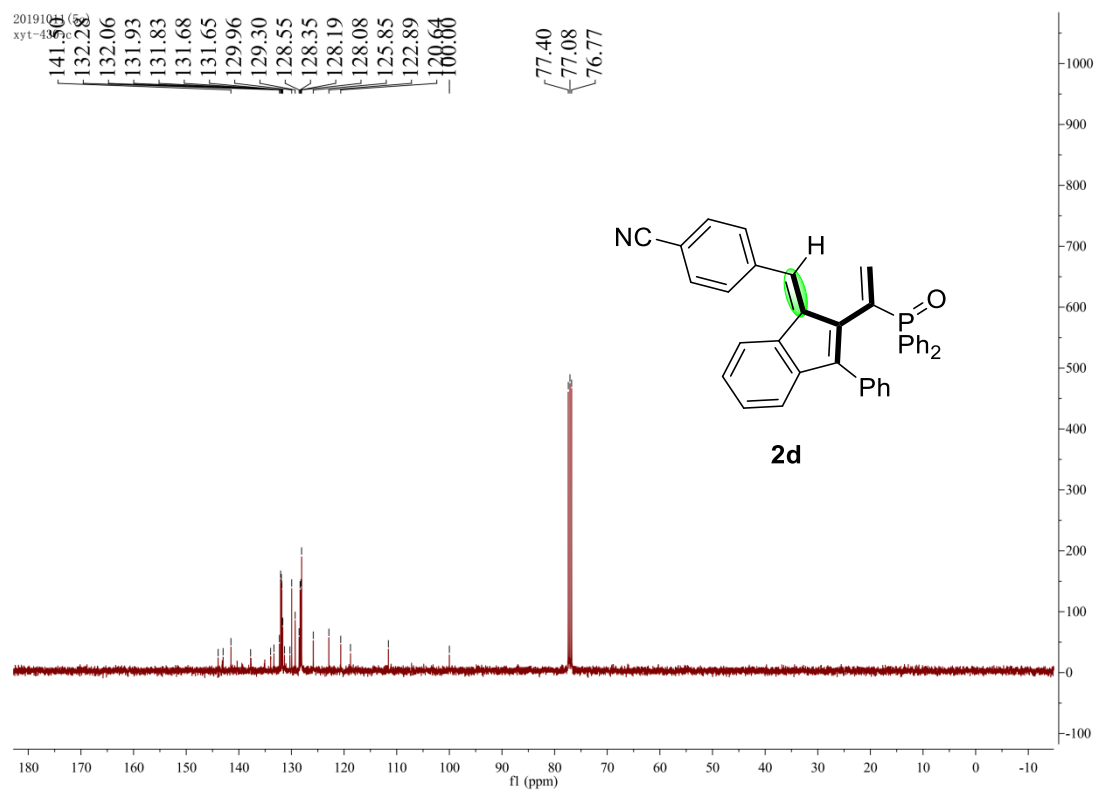


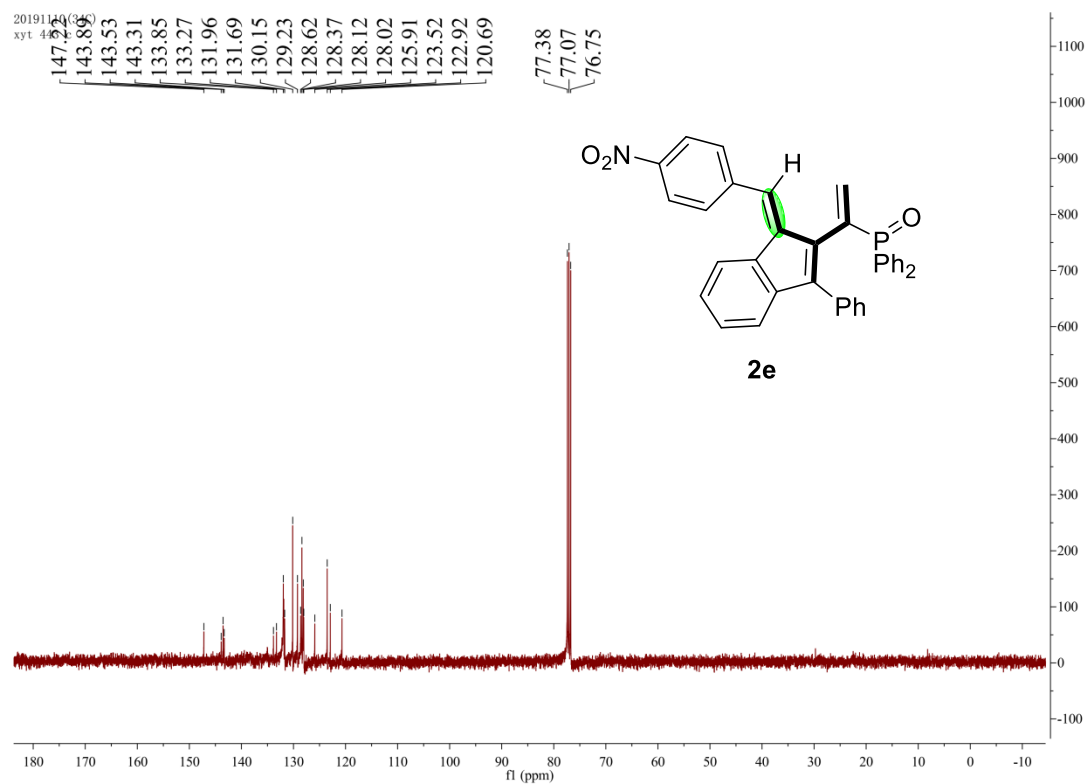
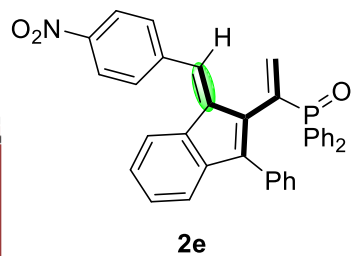
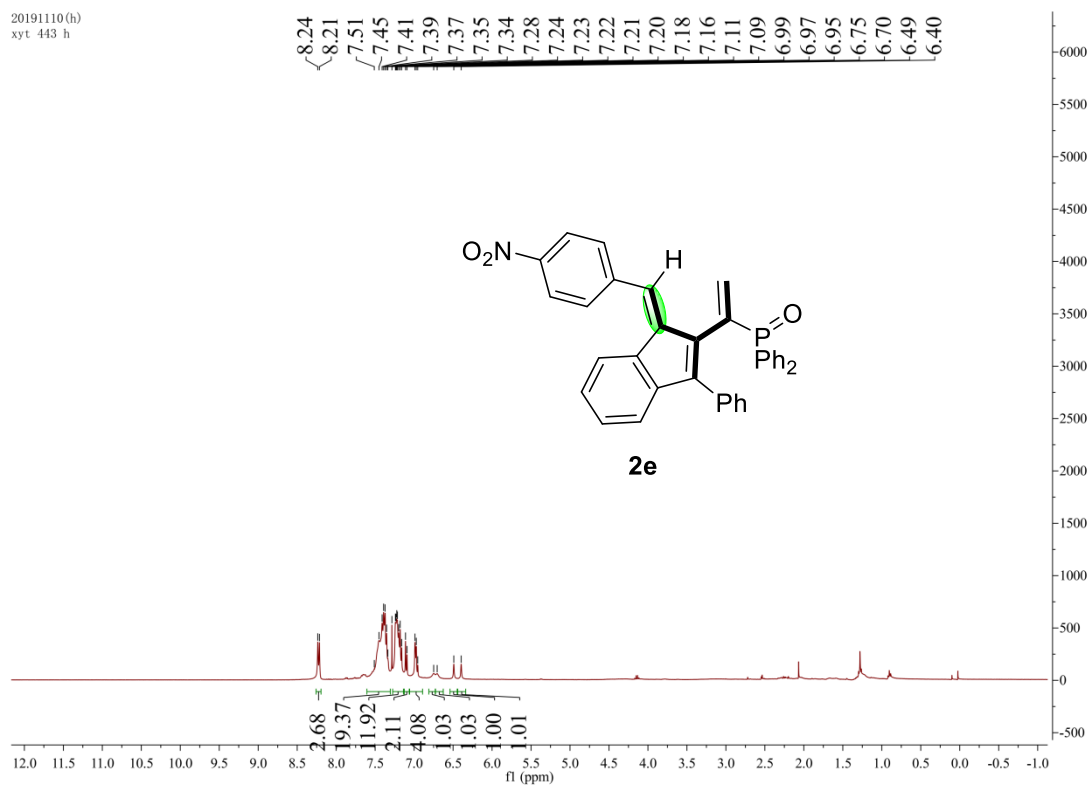
20191110(22P)
xyt 444 p



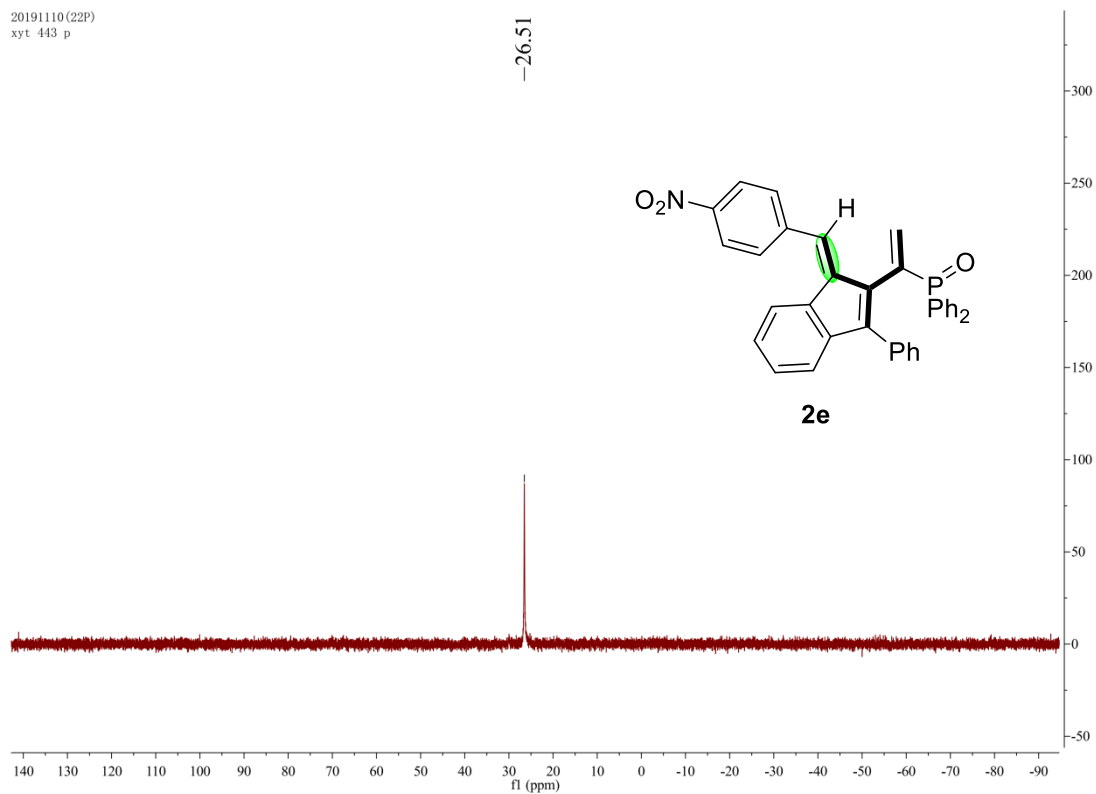
2d



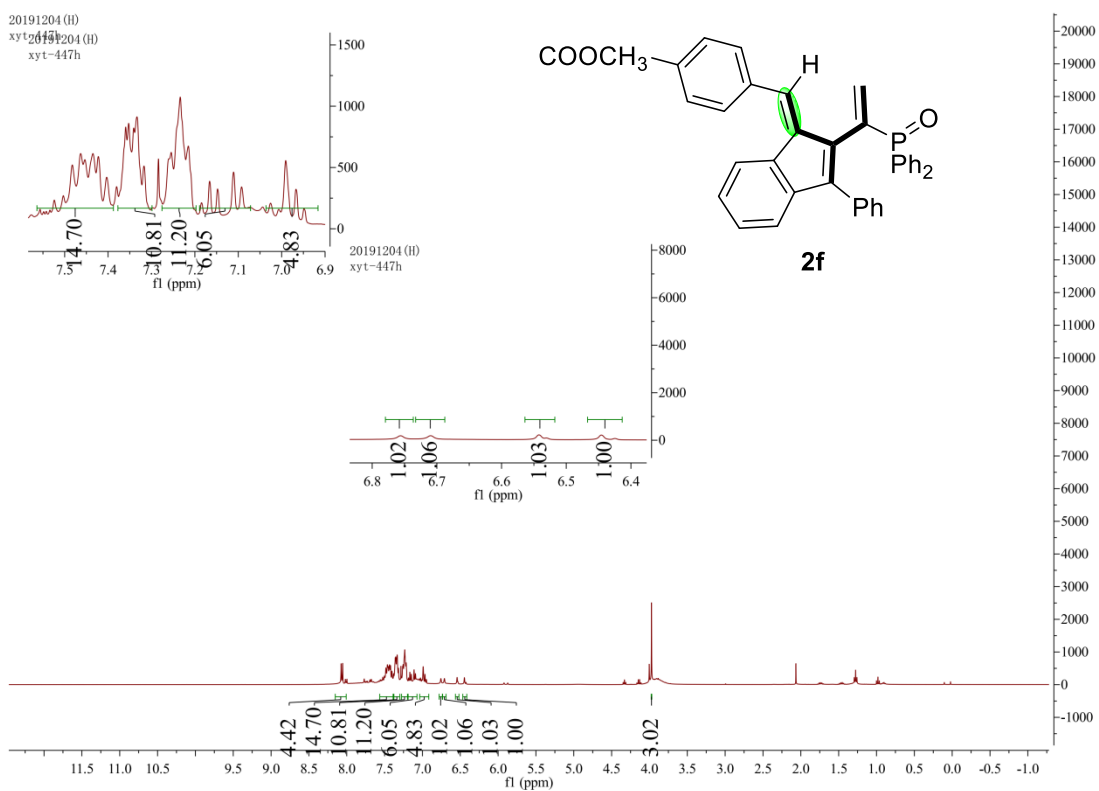


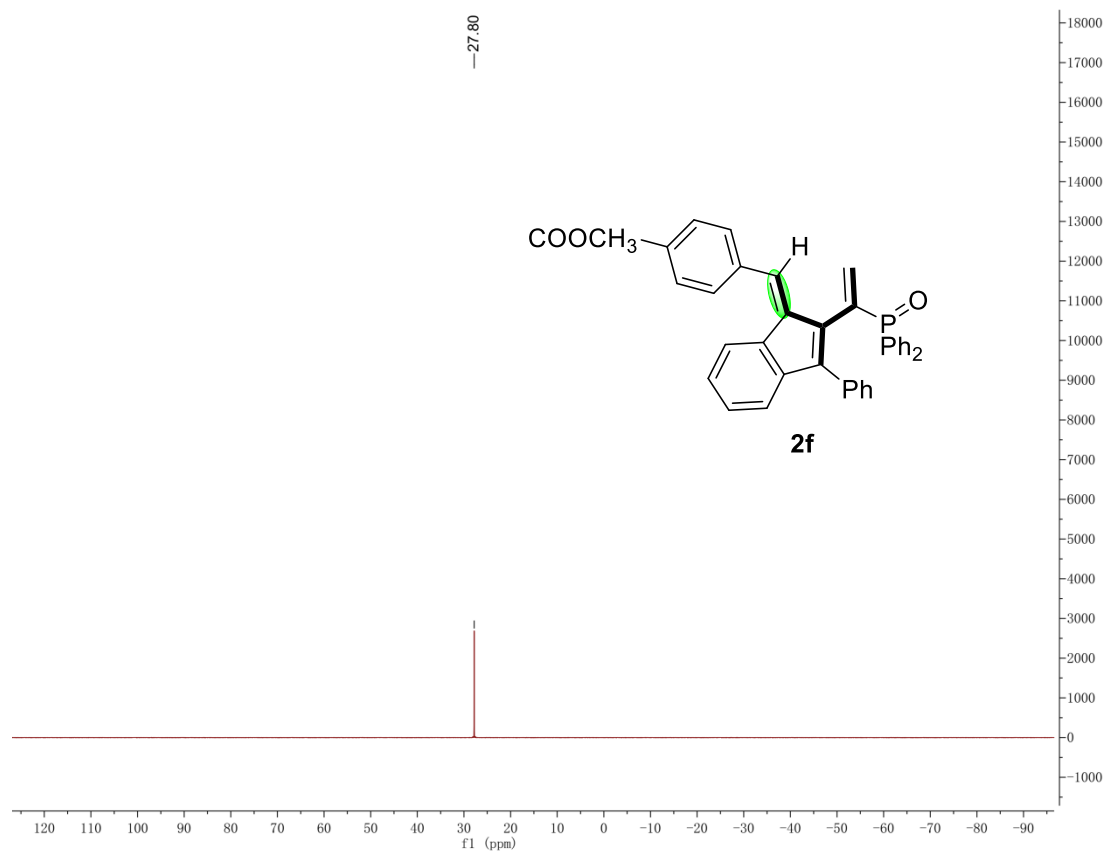
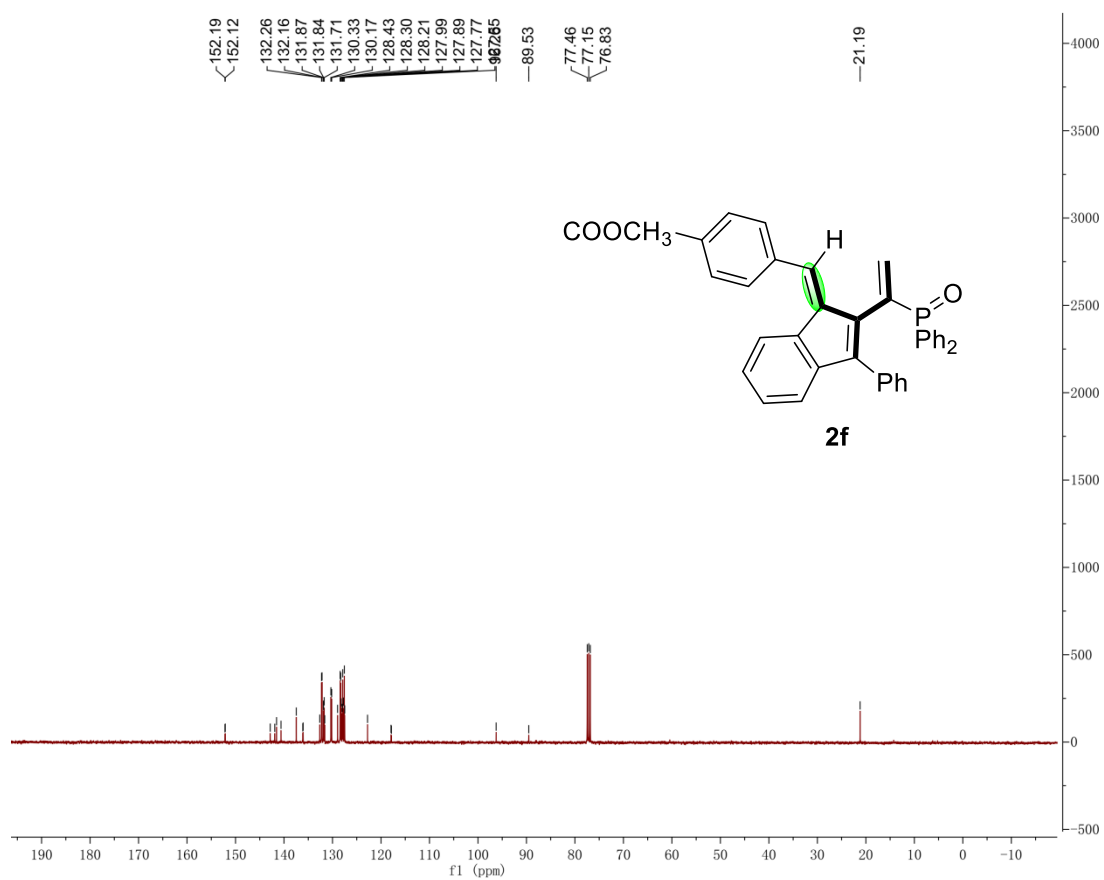


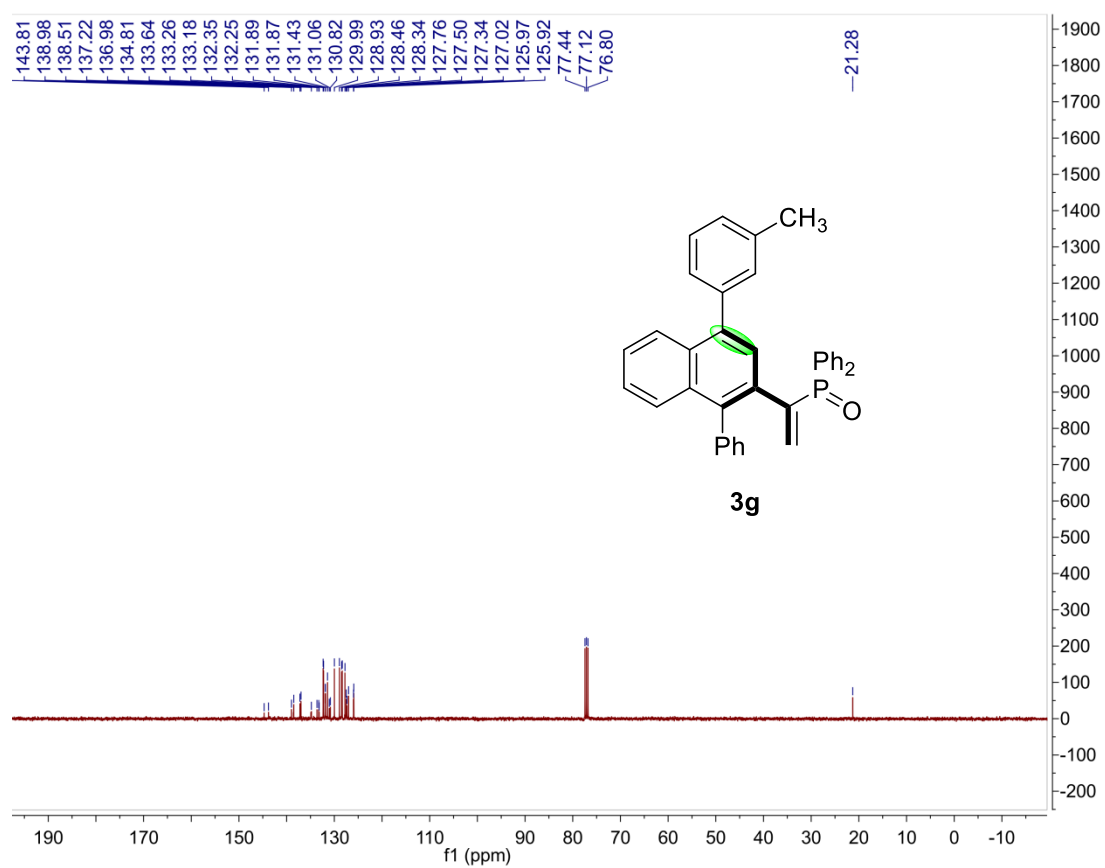
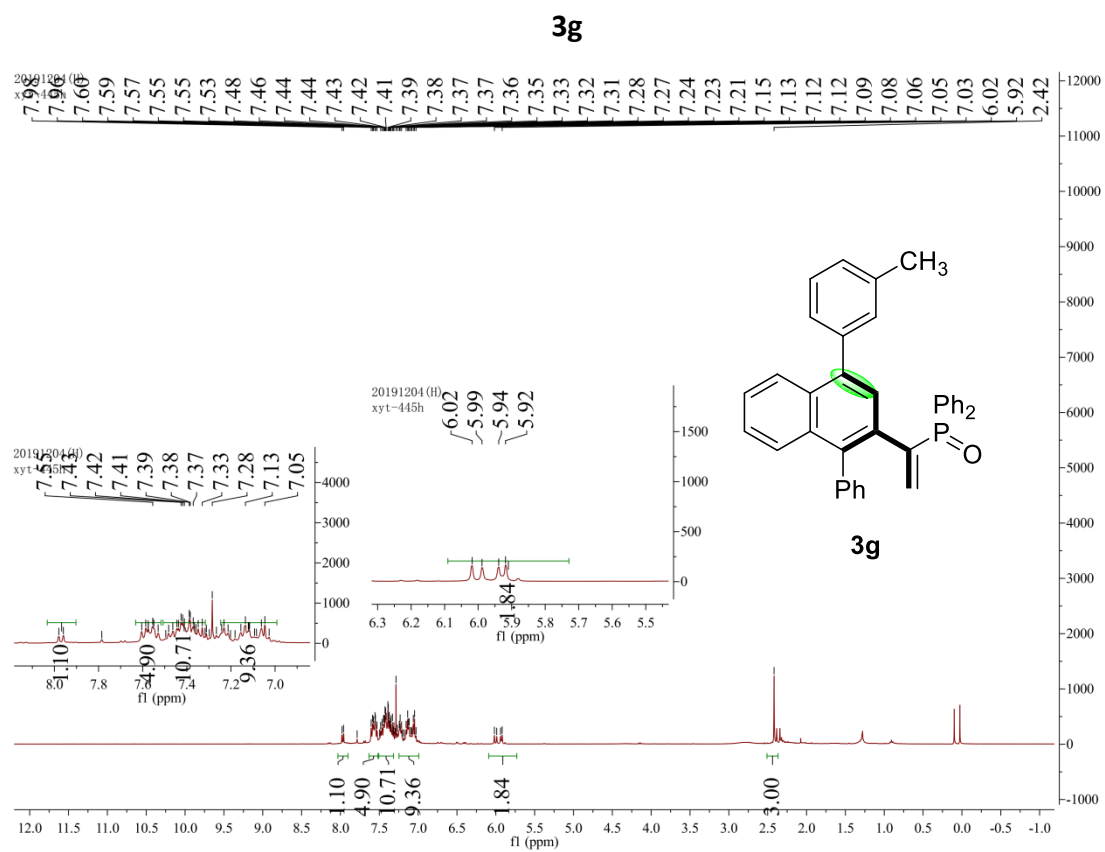
20191110(22P)
xyt 443 p



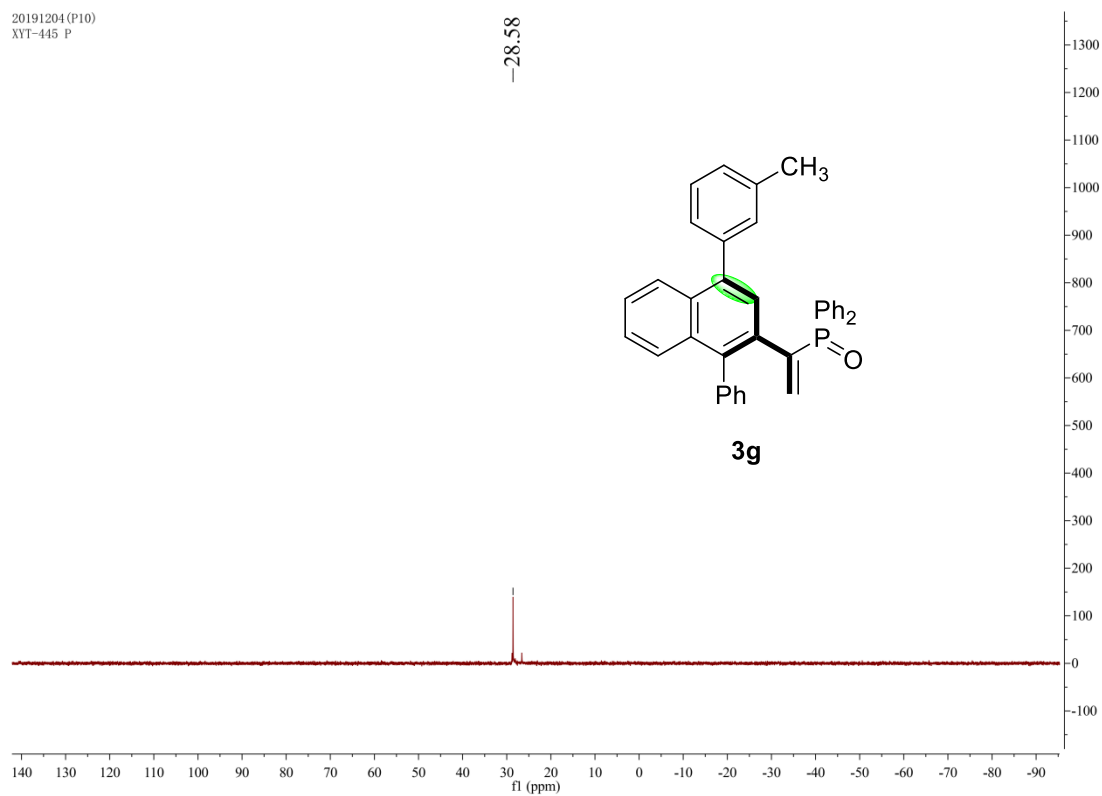
2f



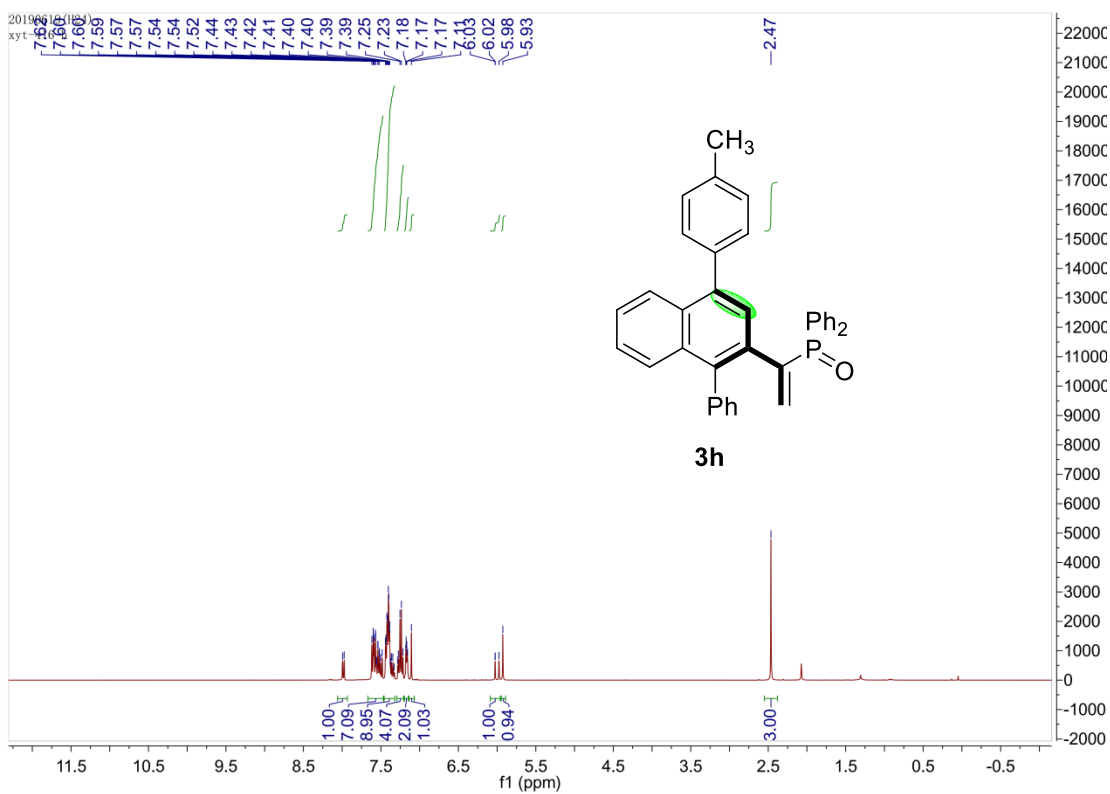


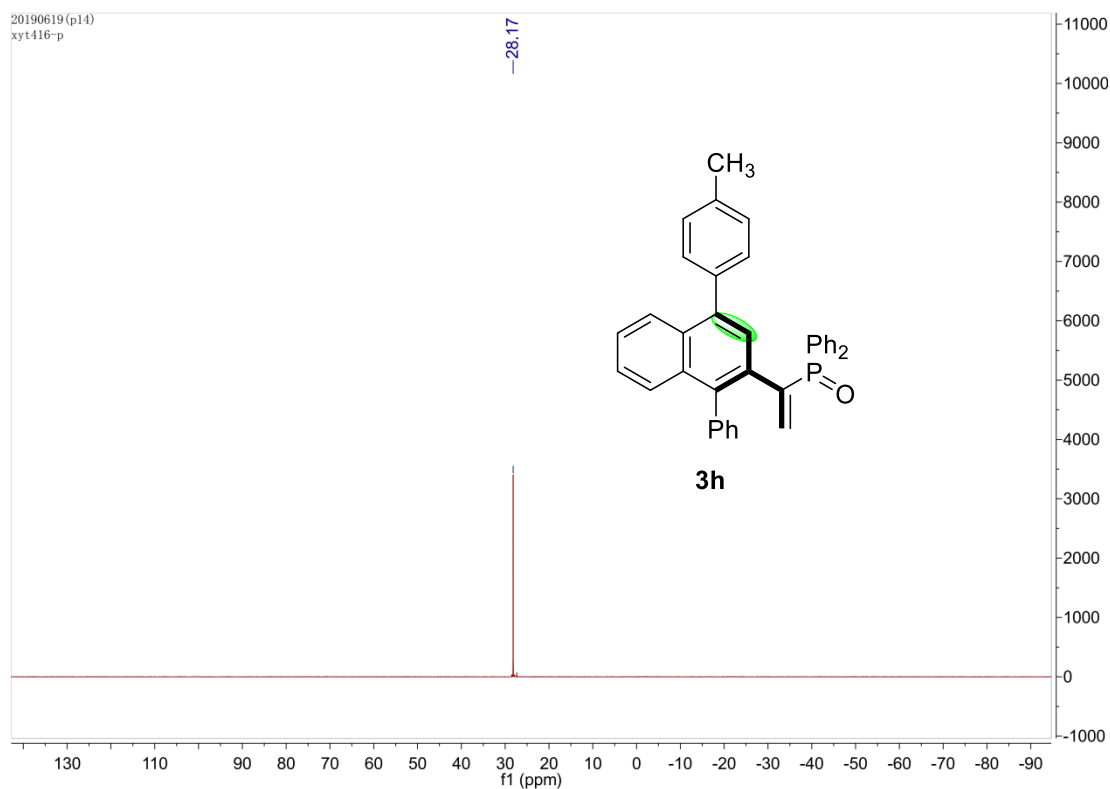
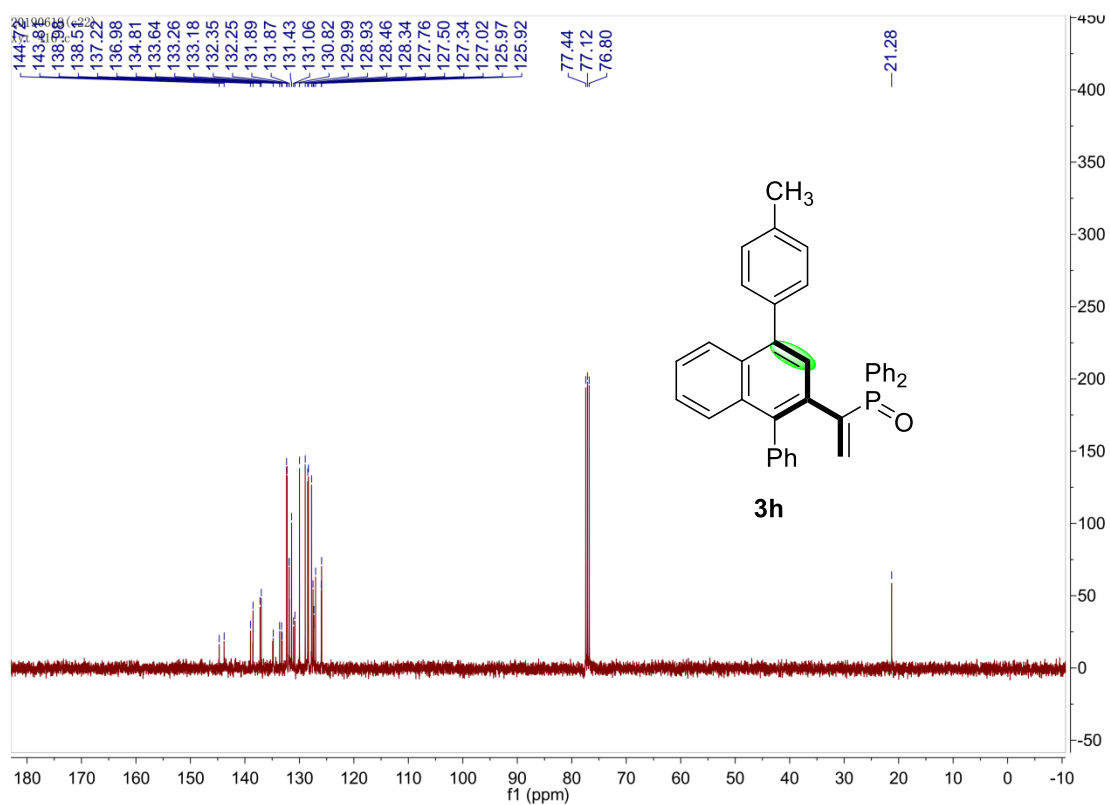


20191204 (P10)
XYT-445 P

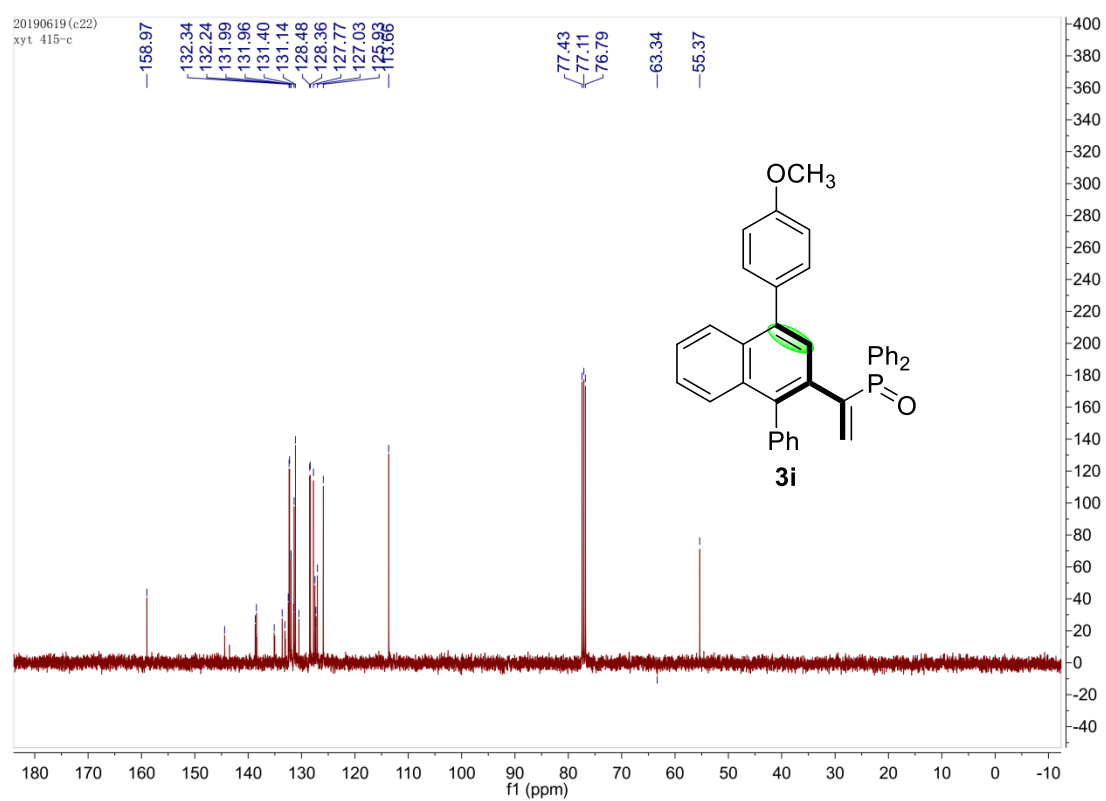
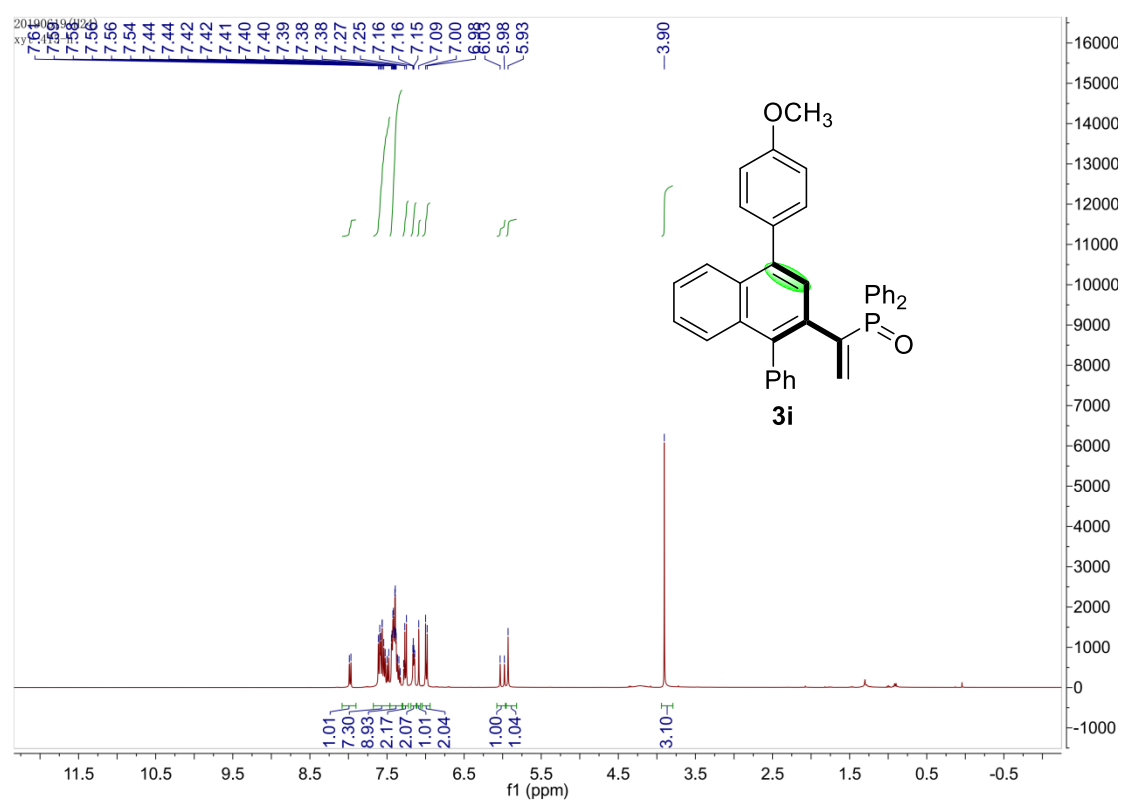


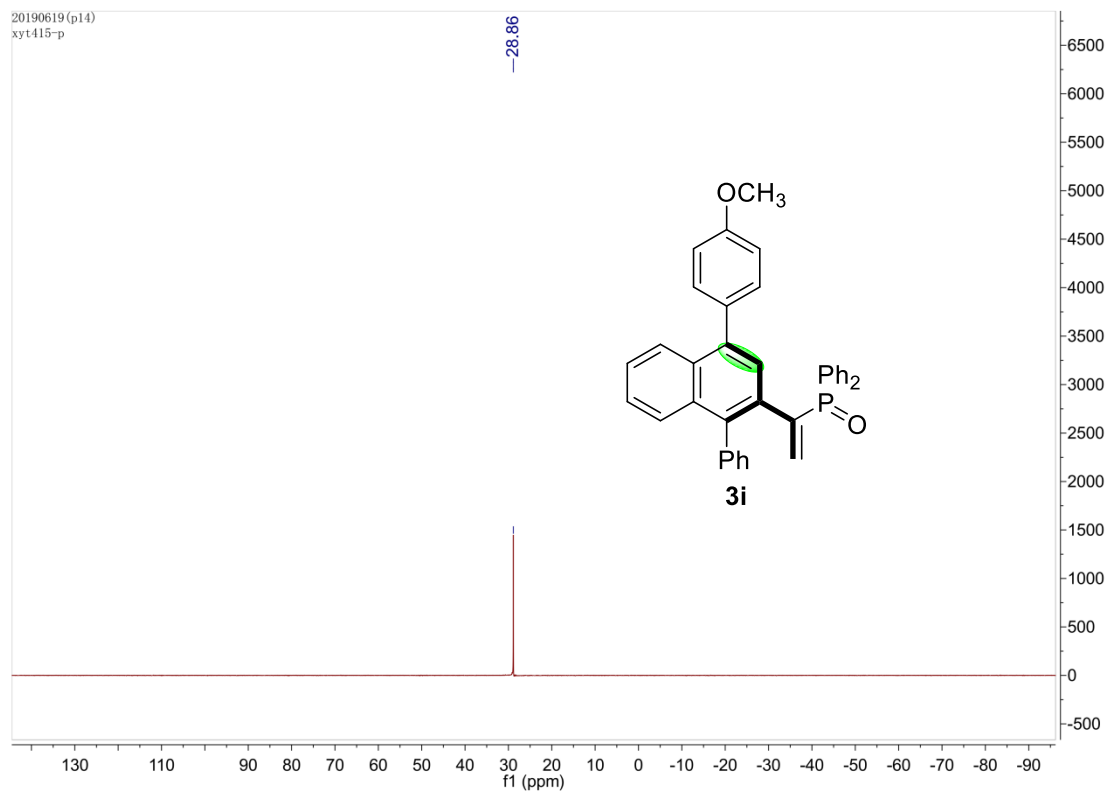
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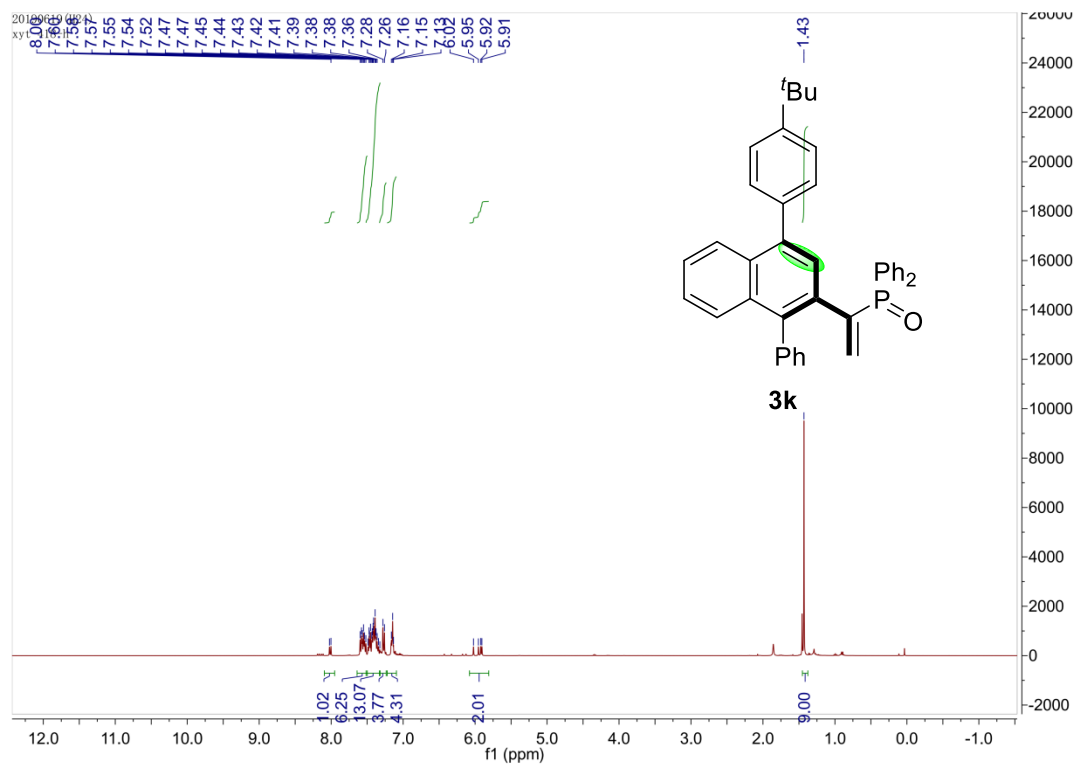


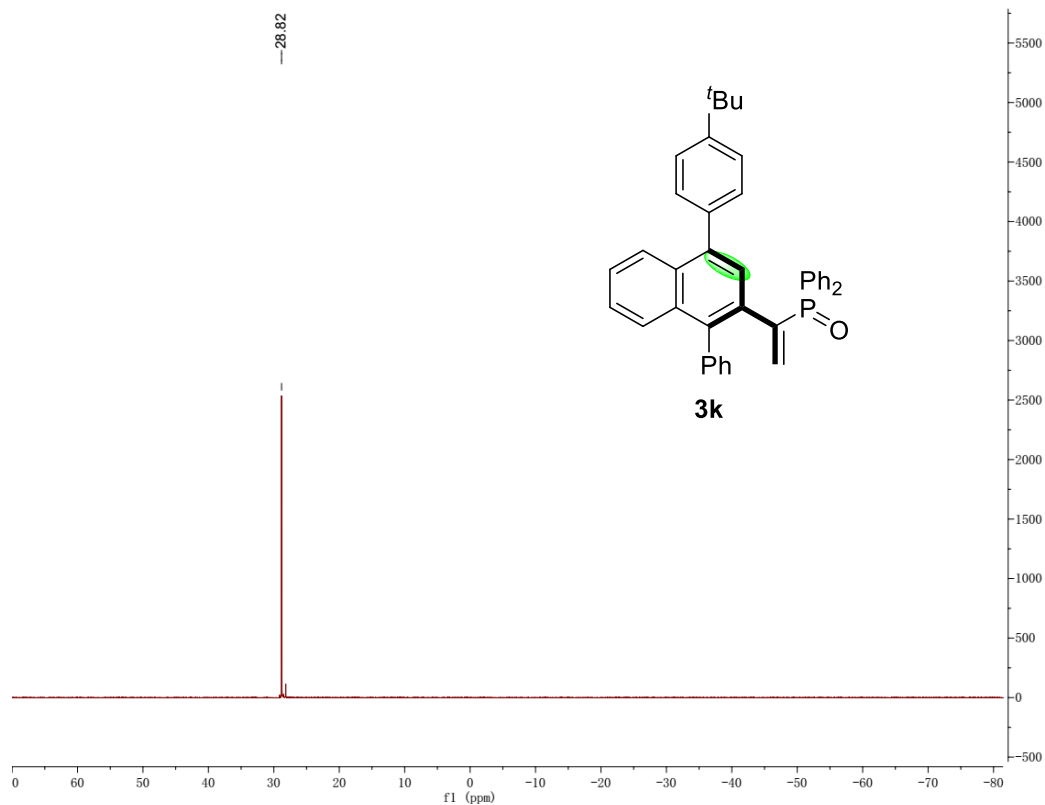
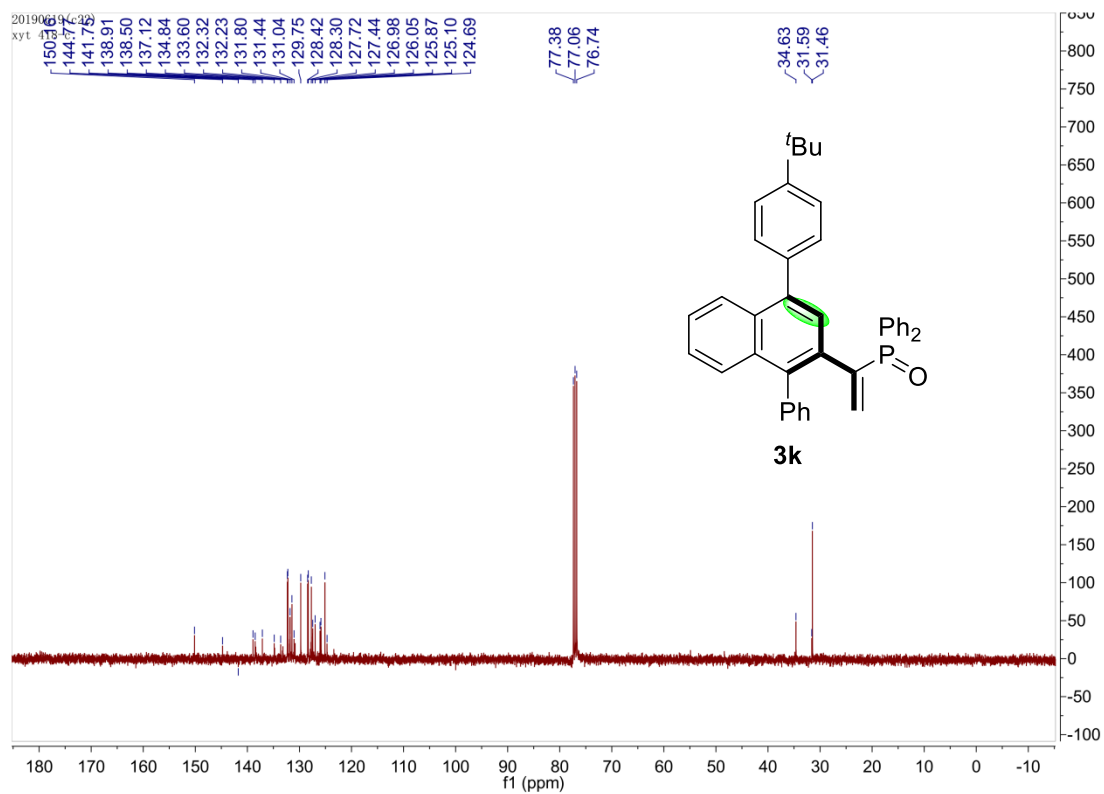
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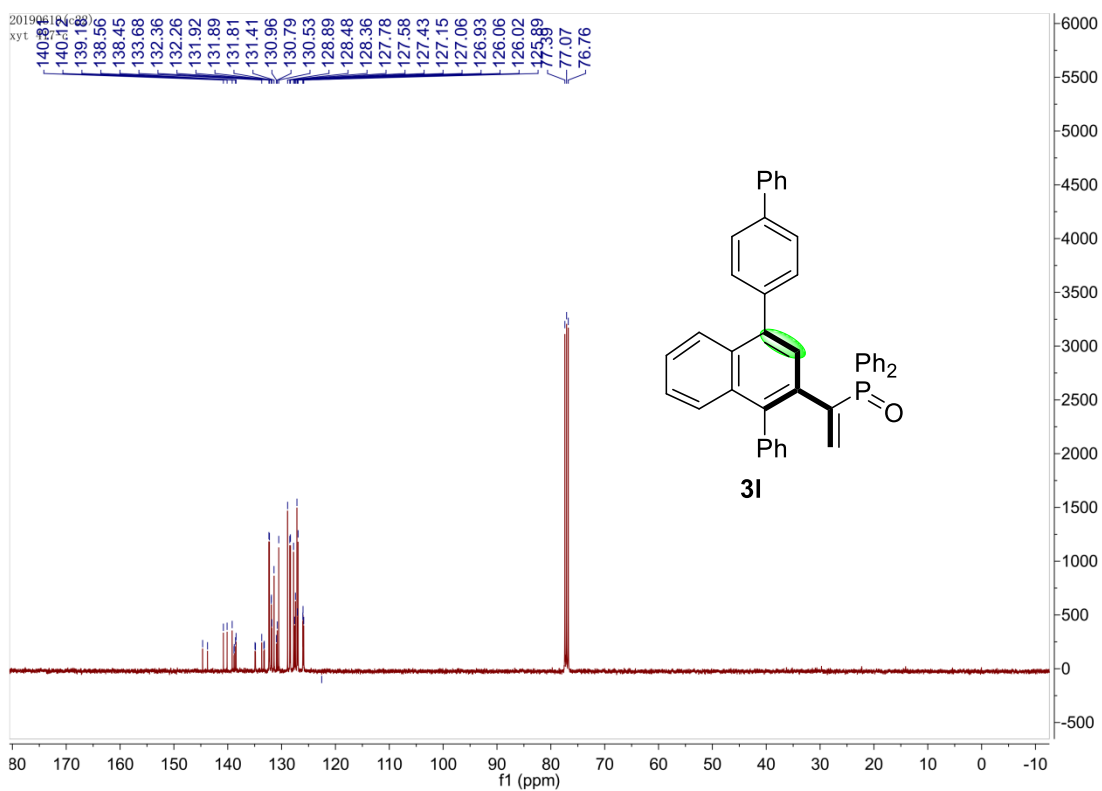
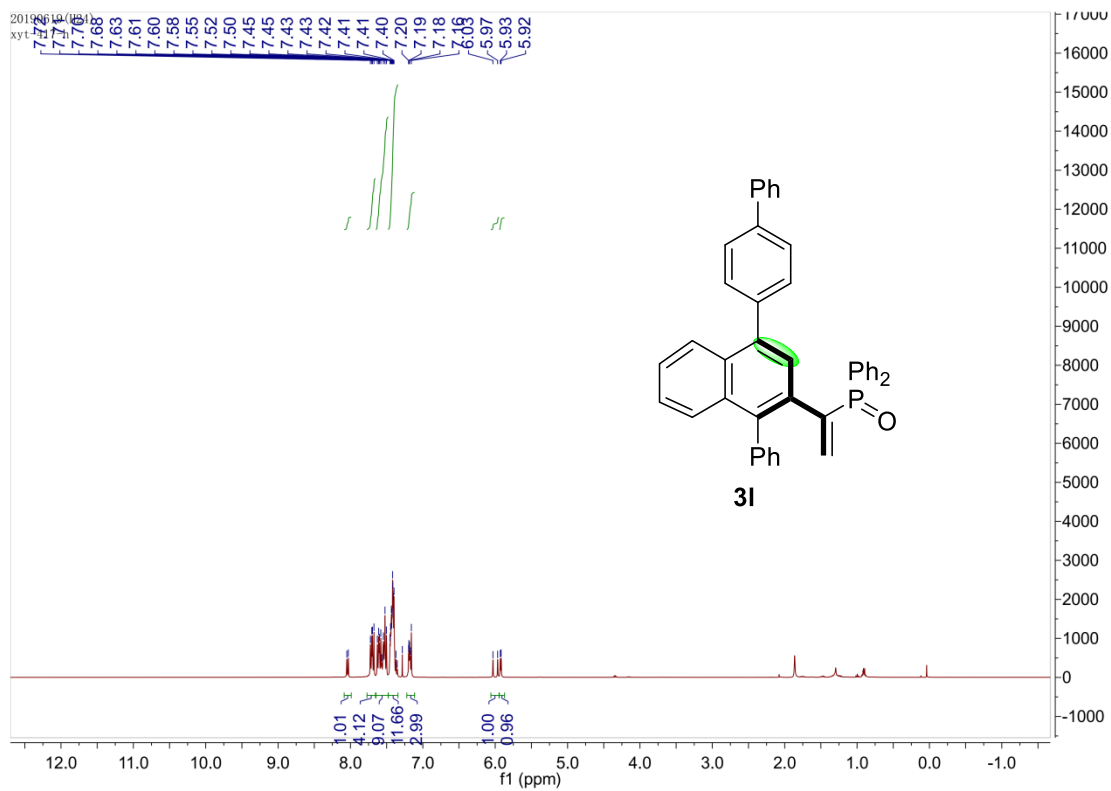


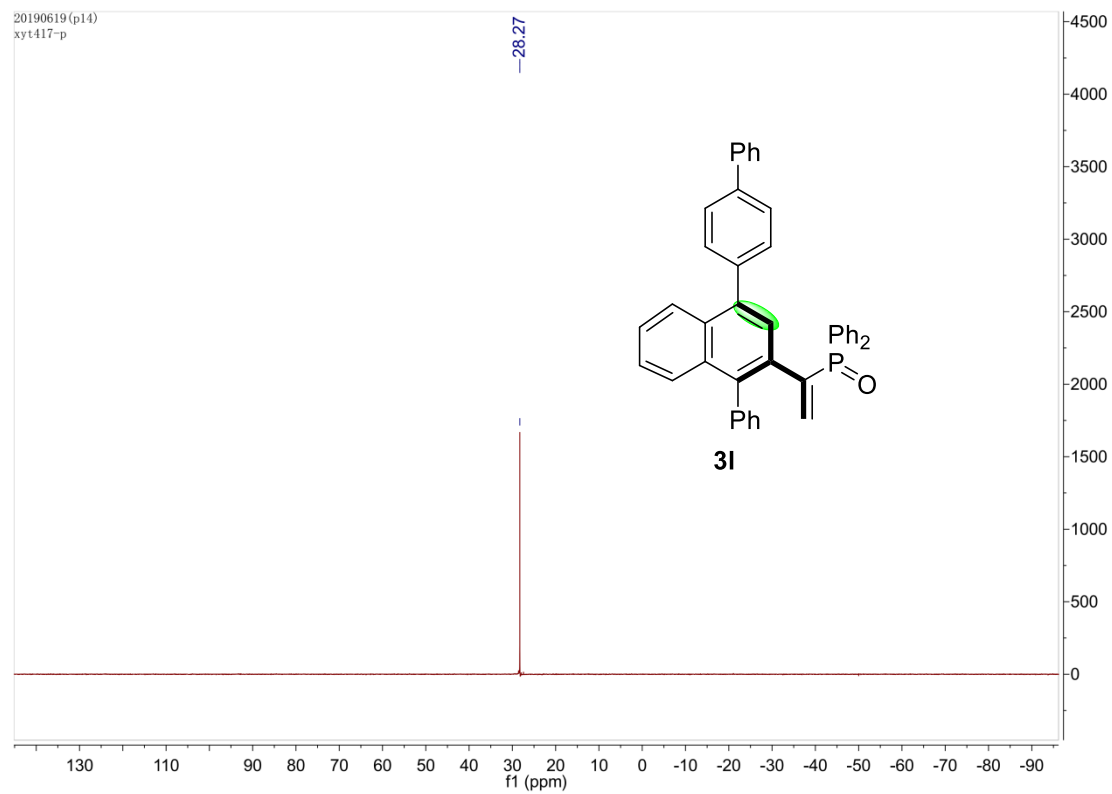
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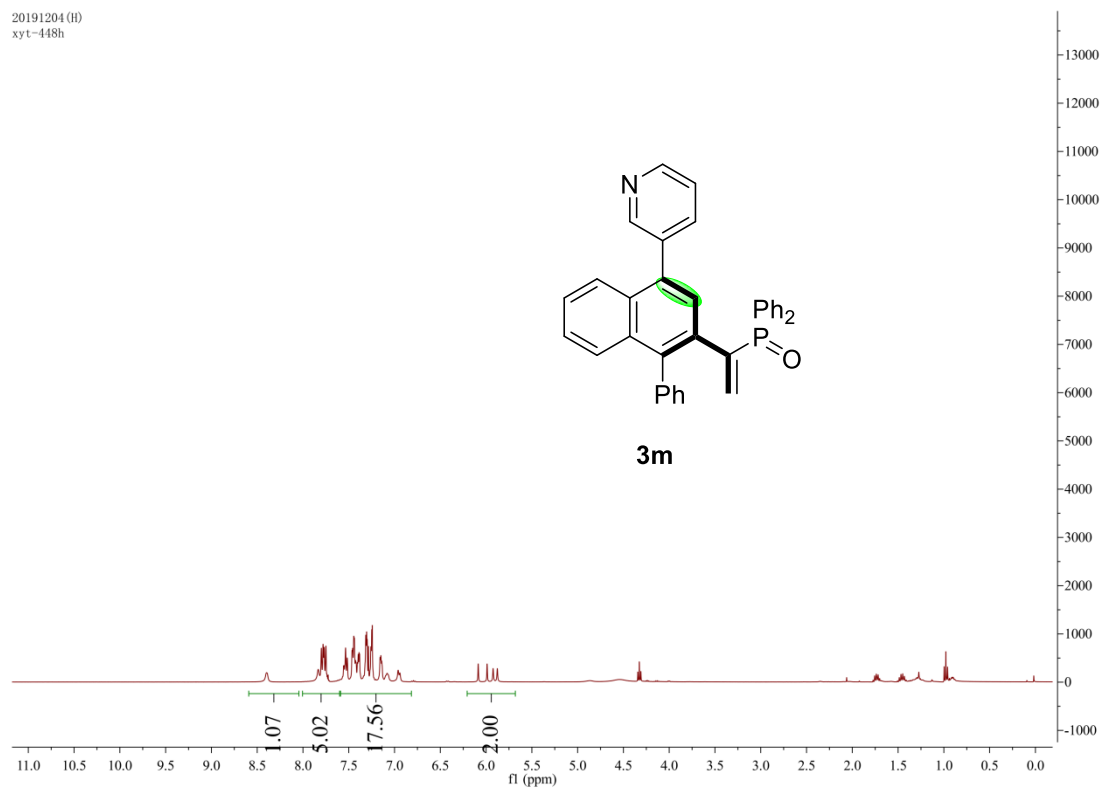


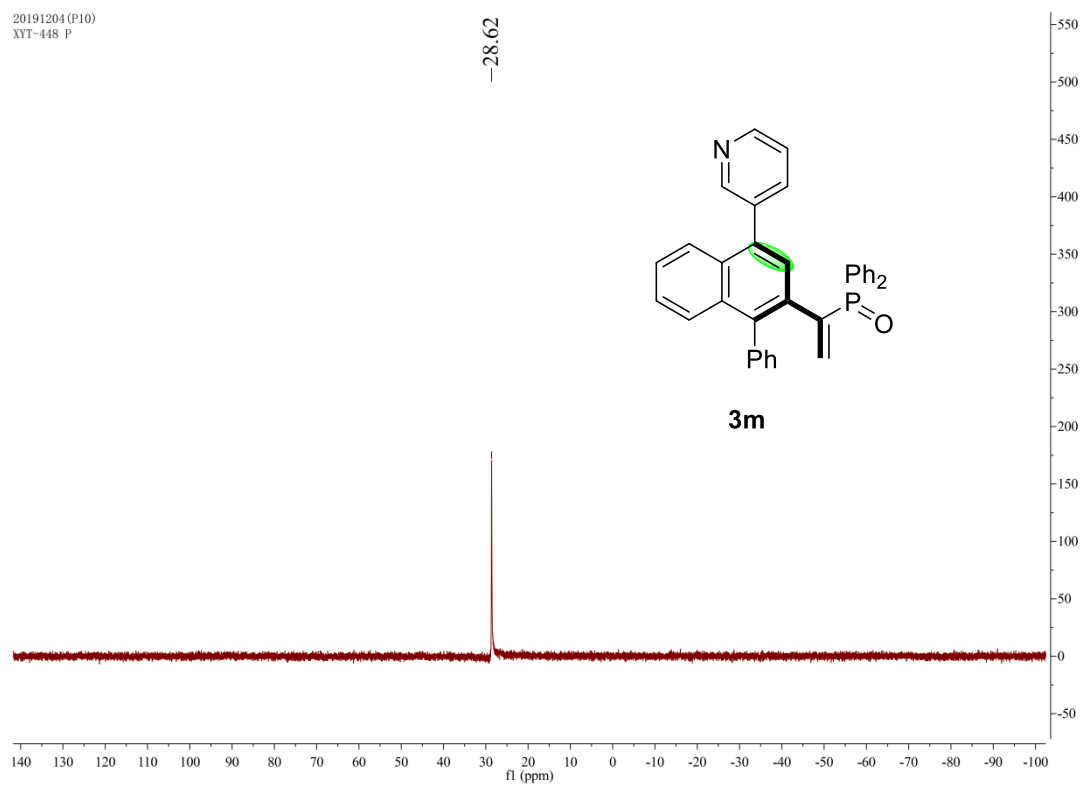
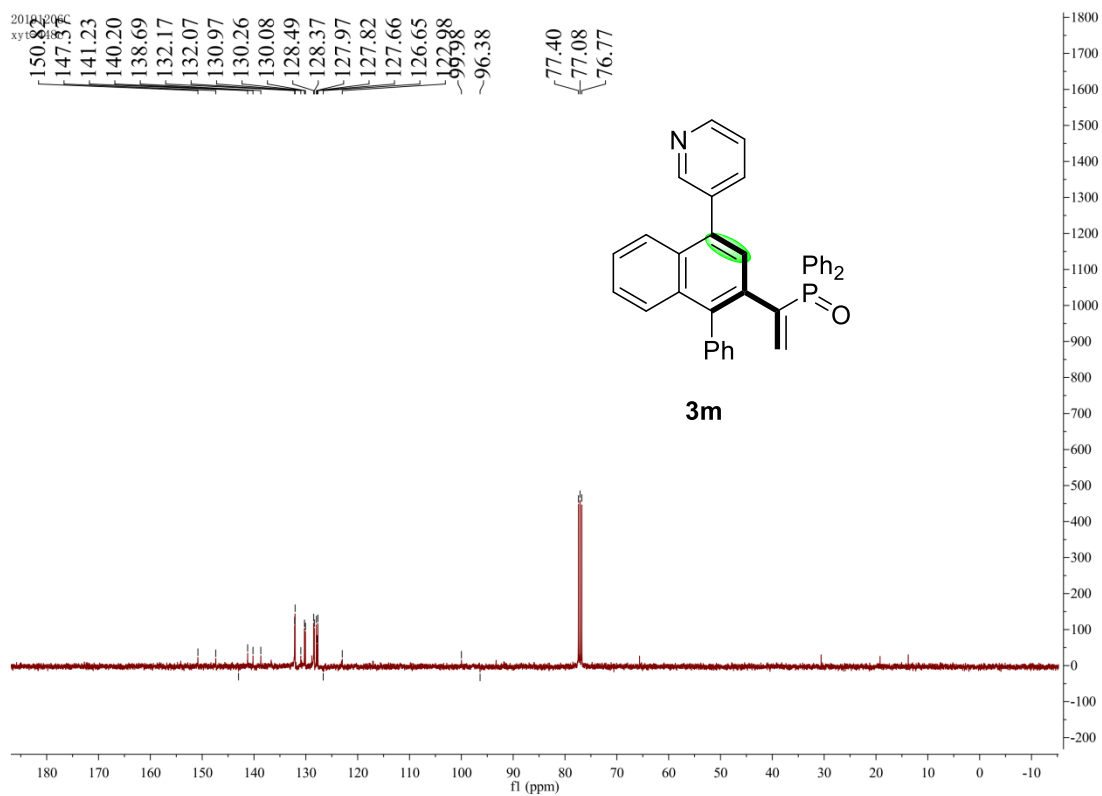
3I





3m





3n

