

Tf₂O/DMSO-mediated dual activation of aryl phosphinate to access various aryl phosphonates

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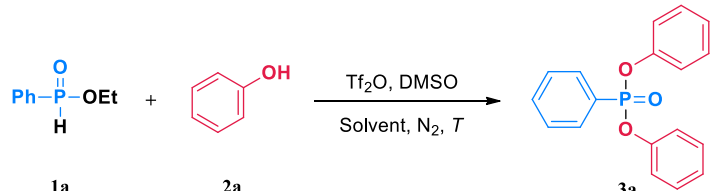
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1. General information

^1H , ^{13}C NMR, ^{31}P NMR and ^{19}F NMR spectra were recorded on a 500M Bruker AVANCE NEO spectrometer and a 400M JEOL ECZ400s in CDCl_3 with TMS as internal standard. High resolution mass spectroscopic (HRMS) and mass spectra were measured using Thermo Scientific DS II mass spectrometer, Thermo Q Exactive Focus and Bruker micro TOF-Q mass spectrometer. The starting materials were purchased from Aldrich, Acros Organics, J&K Chemicals or TCI and used without further purification. Solvents were dried and purified according to the procedure from "Purification of Laboratory Chemicals book". Column chromatography was carried out on silica gel (particle size 200-400 mesh ASTM). Substrates of **2r**,^[1] **2t**^[2] were prepared according to literature procedure.^[1, 2] The P(O)-H reagents of **1b-1e**,^[3] **1aa-1ag**,^[4a] **1ah**^[4b] were prepared according to literature procedure.^[3, 4]

2. Full Optimization Table S1^a

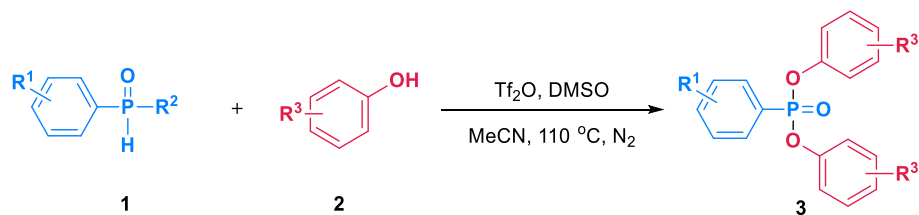


Entry	Tf ₂ O (eq.)	DMSO (eq.)	Solvent	T (°C)	Yield (%)
1	3.0	2.0	Toluene	90	14
2	3.0	2.0	DCE	90	8
3	3.0	2.0	1,4-dioxane	90	16
4	3.0	2.0	DMF	90	n.r
5	3.0	2.0	MeCN	90	43
6 ^b	3.0	2.0	MeCN	90	20
7 ^c	3.0	2.0	MeCN	90	44
8	3.0	3.0	MeCN	90	11
9	3.0	1.0	MeCN	90	59
10	3.0	0.5	MeCN	90	41
11 ^d	3.0	1.0	MeCN	90	58
12 ^e	3.0	1.0	MeCN	90	66
13 ^f	3.0	1.0	MeCN	90	63
14 ^e	2.5	1.0	MeCN	90	61
15 ^e	3.5	1.0	MeCN	90	70
16 ^e	4.0	1.0	MeCN	90	62
17 ^e	3.5	1.0	MeCN	80	68
18 ^e	3.5	1.0	MeCN	100	70
19^e	3.5	1.0	MeCN	110	76
20 ^e	3.5	1.0	MeCN	120	57
21 ^e	TFAA (3.5)	1.0	MeCN	80	n.r
22 ^e	Ac ₂ O (3.5)	1.0	MeCN	80	n.r
23 ^e	3.5	Ph ₂ S(O)1.0	MeCN	100	trace
24 ^e	3.5	ⁿ Bu ₂ S(O)1.0	MeCN	110	52
25 ^e	3.5	—	MeCN	110	15
26 ^g	3.5	1.0	MeCN	110	65

Conditions: ^a **1a** (0.2 mmol), **2a** (4.0 eq.), solvent (2.0 mL), N₂, stirred at 90 °C for 11 h, isolated yield; ^b **2a** (3.0 eq.); ^c **2a** (5.0 eq.); ^d MeCN (1.0 mL); ^e MeCN (3.0 mL); ^f MeCN (4.0 mL); ^g Under air.

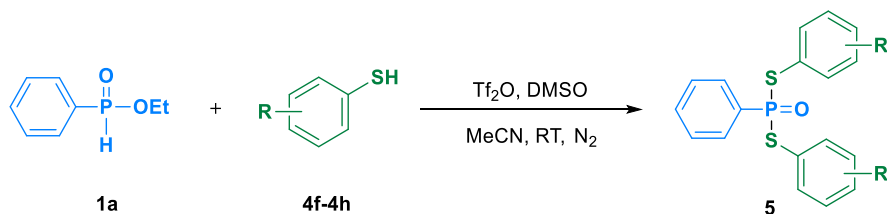
3. General Procedure

3.1 Phenols and alcohols as substrates



To a Schlenk tube were added **2** (0.8 mmol, 4.0 eq.), (for **2d-2h**, **2j-2p** and **1ab-1ad**, 0.15 eq. TBAB was added), and charged with nitrogen for three times. Then, anhydrous MeCN (3.0 mL), **1** (0.2 mmol, 1.0 eq.), Tf₂O (0.7 mmol, 3.5 eq.) and DMSO (0.2 mmol, 1.0 eq.) were added *via* syringe in turn. The mixture was allowed to stir at 110 °C in oil bath for 11h. At the completion of the reaction, the solvent was removed by rotary evaporation. The resulting residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 9: 1) to afford the products **3** or **5a-5c**.

3.2 Thiophenols (4f-4h) as substrates



To a Schlenk tube were added **4f-4h** (0.6 mmol, 3.0 eq.) and charged with nitrogen for three times. Then, anhydrous MeCN (3.0 mL), **1a** (0.2 mmol, 1.0 eq.), Tf₂O (0.3 mmol, 1.5 eq.) and DMSO (0.2 mmol, 1.0 eq.) were added *via* syringe in turn. The mixture was allowed to stir at RT for 11h. At the completion of the reaction, the solvent was removed by rotary evaporation. The resulting residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 9: 1) to afford the products **5f-5h**.

4. Thermal analysis of DOPO and selected samples.

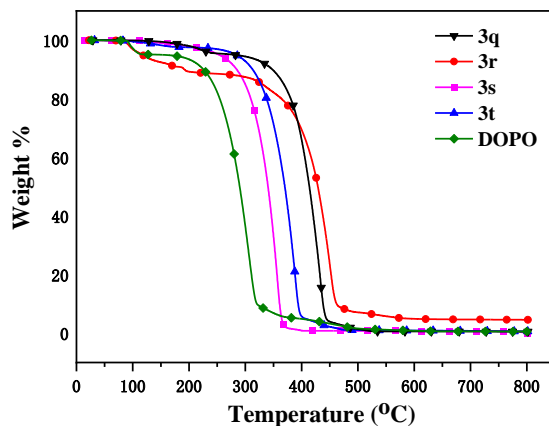
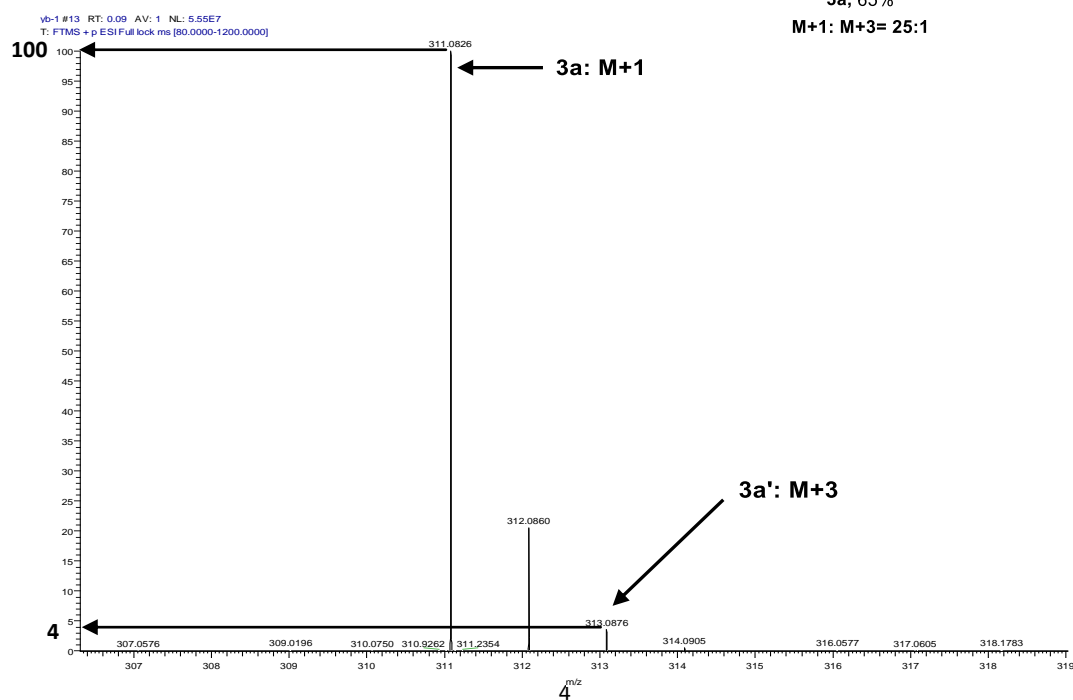
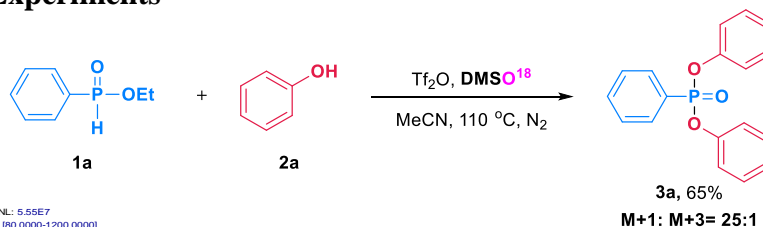


Figure S1 Thermal analysis of DOPO and selected samples.

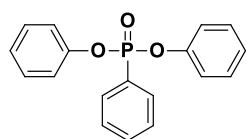
Table S2. TG data of DOPO, 3q, 3r, 3s and 3t under nitrogen atmosphere.

Sample	T _{-5wt%} (°C)	T _{-50wt%} (°C)
DOPO	155.2	289.9
3q	281.5	413.7
3r	117.0	428.7
3s	253.6	340.3
3t	283.7	370.0

5. Control Experiments

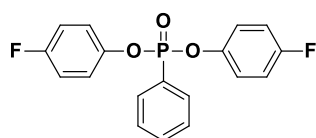


6. Characterization of the Products



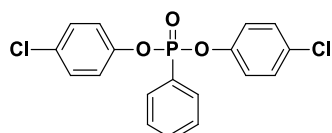
diphenyl phenylphosphonate. Performed according to the general procedure and purified by column chromatography (petroleum ether/ethyl acetate = 9/1) to afford **3a** as colorless oil (47.2 mg, 76%): ^1H NMR (400 MHz, CDCl_3): δ 7.99-7.93 (m, 2H), 7.58-7.54 (m, 1H), 7.49-7.44 (m, 2H), 7.29-7.25 (m, 4H), 7.20-7.17 (m, 4H), 7.14-7.10 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ 150.3 (d, $J_{\text{C-P}} = 7.0$ Hz), 133.1 (d, $J_{\text{C-P}} = 3.0$ Hz), 132.1 (d, $J_{\text{C-P}} = 10.0$ Hz), 129.6, 128.5 (d, $J_{\text{C-P}} = 16.0$ Hz), 126.8 (d, $J_{\text{C-P}} = 192.0$ Hz), 125.0, 120.5 (d, $J_{\text{C-P}} = 5.0$ Hz). ^{31}P NMR (203 MHz, CDCl_3): δ 11.72. MS (ESI): 311.5 ($\text{M}+1$) $^+$.

The analytical data matched those reported in the literature.^[5]

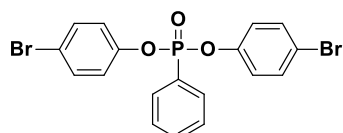


bis(4-fluorophenyl) phenylphosphonate. Performed according to the general procedure, and purified by column chromatography (petroleum ether/ethyl acetate = 9/1) to afford **3b** as colorless oil (56.8 mg, 82%): ^1H NMR (400 MHz, CDCl_3): δ 7.97-7.91 (m, 2H), 7.65-7.60 (m, 1H), 7.54-7.49 (m, 2H), 7.16-7.12 (m, 4H), 7.00-6.95 (m, 4H). ^{13}C NMR (100 MHz, CDCl_3): δ 159.8 (d, $J_{\text{C-F}} = 243.0$ Hz), 146.0 (dd, $J_1 = 3.0$ Hz, $J_2 = 8.0$ Hz), 133.5 (d, $J_{\text{C-P}} = 3.0$ Hz), 132.2 (d, $J_{\text{C-P}} = 11.0$ Hz), 128.7 (d, $J_{\text{C-F}} = 16.0$ Hz), 126.2 (d, $J_{\text{C-P}} = 192.0$ Hz), 122.0 (dd, $J_1 = 4.0$ Hz, $J_2 = 8.0$ Hz), 116.3 (d, $J_{\text{C-F}} = 24.0$ Hz). ^{31}P NMR (203 MHz, CDCl_3): δ 12.63. ^{19}F NMR (376 MHz, CDCl_3): δ -117.4. MS (ESI): 347.1 ($\text{M}+1$) $^+$.

The analytical data matched those reported in the literature.^[5]

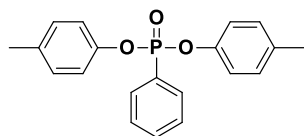


bis(4-chlorophenyl) phenylphosphonate. Performed according to the general procedure, and purified by column chromatography (petroleum ether/ethyl acetate = 9/1) to afford **3c** as colorless oil (61.7 mg, 81%): ^1H NMR (400 MHz, CDCl_3): δ 7.96-7.90 (m, 2H), 7.65-7.60 (m, 1H), 7.54-7.49 (m, 2H), 7.28-7.24 (m, 4H), 7.13-7.11 (m, 4H). ^{13}C NMR (100 MHz, CDCl_3): δ 148.7 (d, $J_{\text{C-P}} = 7.0$ Hz), 133.6 (d, $J_{\text{C-P}} = 4.0$ Hz), 132.2 (d, $J_{\text{C-P}} = 10.0$ Hz), 130.7, 129.8, 128.8 (d, $J_{\text{C-P}} = 16.0$ Hz), 126.0 (d, $J_{\text{C-P}} = 191.0$ Hz), 121.9 (d, $J_{\text{C-P}} = 4.0$ Hz). ^{31}P NMR (203 MHz, CDCl_3): δ 12.42. HRMS calc. for $\text{C}_{18}\text{H}_{14}\text{Cl}_2\text{O}_3\text{P}$ ($\text{M}+1$) $^+$ = 379.0052, found 379.0055.



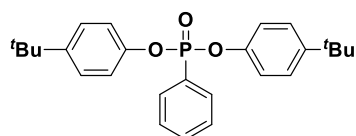
bis(4-bromophenyl) phenylphosphonate. Performed according to the general procedure, and purified by column chromatography (petroleum ether/ethyl acetate = 9/1) to afford **3d** as colorless oil (67.9 mg, 73%): ^1H NMR (500 MHz, CDCl_3): δ 7.95-7.91 (m, 2H), 7.64-7.61 (m, 1H), 7.53-7.49 (m, 2H), 7.41 (d, $J=8.9$ Hz, 4H), 7.07 (d, $J=8.9$ Hz, 4H). ^{13}C NMR (125 MHz, CDCl_3): δ 149.2 (d, $J_{\text{C-P}} = 7.5$ Hz), 133.6

(d, $J_{C-P} = 3.0$ Hz), 132.8, 132.2 (d, $J_{C-P} = 10.3$ Hz), 128.8 (d, $J_{C-P} = 15.7$ Hz), 125.9 (d, $J_{C-P} = 191.3$ Hz), 122.3 (d, $J_{C-P} = 4.5$ Hz), 118.3 (d, $J_{C-P} = 1.4$ Hz). ^{31}P NMR (203 MHz, CDCl_3): δ 12.27. HRMS calc. for $\text{C}_{18}\text{H}_{14}\text{Br}_2\text{O}_3\text{P}$ ($\text{M}+\text{H}$) $^+$ = 468.9021, found 468.9025.

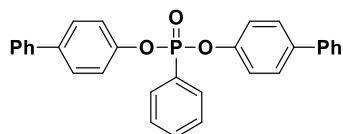


di-*p*-tolyl phenylphosphonate. Performed according to the general procedure and purified by column chromatography (petroleum ether/ethyl acetate = 9/1) to afford **3e** as colorless oil (48.0 mg, 71%): ^1H NMR (500 MHz, CDCl_3): δ 7.96-7.92 (m, 2H), 7.59-7.56 (m, 1H), 7.49-7.45 (m, 2H), 7.06 (s, 8H), 2.27 (s, 6H). ^{13}C NMR (125 MHz, CDCl_3): δ 148.1 (d, $J_{C-P} = 7.4$ Hz), 134.6, 133.0 (d, $J_{C-P} = 3.0$ Hz), 132.2 (d, $J_{C-P} = 10.3$ Hz), 130.1, 128.5 (d, $J_{C-P} = 15.6$ Hz), 127.0 (d, $J_{C-P} = 191.0$ Hz), 120.3 (d, $J_{C-P} = 4.5$ Hz), 20.6. ^{31}P NMR (203 MHz, CDCl_3): δ 11.87. MS (ESI): 339.2 ($\text{M}+1$) $^+$.

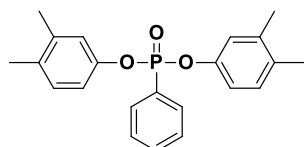
The analytical data matched those reported in the literature.^[5]



bis(4-(tert-butyl)phenyl) phenylphosphonate. Performed according to the general procedure and purified by column chromatography (petroleum ether/ethyl acetate = 9/1) to afford **3f** as colorless oil (57.4 mg, 68%): ^1H NMR (400 MHz, CDCl_3): δ 7.81-7.76 (m, 2H), 7.51-7.46 (m, 1H), 7.41-7.35 (m, 6H), 7.27 (d, $J = 8.0$ Hz, 4H), 1.27 (s, 18H). ^{13}C NMR (100 MHz, CDCl_3): δ 152.7 (d, $J_{C-P} = 3.0$ Hz), 135.4 (d, $J_{C-P} = 5.0$ Hz), 133.5 (d, $J_{C-P} = 107$ Hz), 132.5 (d, $J_{C-P} = 4$ Hz), 121.6 (d, $J_{C-P} = 11.0$ Hz), 128.3 (d, $J_{C-P} = 14.0$ Hz), 126.4 (d, $J_{C-P} = 2.0$ Hz), 122.7 (d, $J_{C-P} = 6.0$ Hz), 34.7, 31.1. ^{31}P NMR (203 MHz, CDCl_3): δ 11.84. HRMS calc. for $\text{C}_{26}\text{H}_{32}\text{O}_3\text{P}$ ($\text{M}+\text{H}$) $^+$ = 423.2084, found 423.2081.

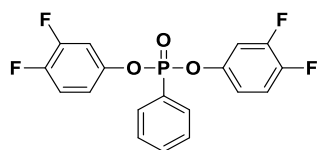


di([1,1'-biphenyl]-4-yl) phenylphosphonate. Performed according to the general procedure and purified by column chromatography (petroleum ether/ethyl acetate = 9/1) to afford **3g** as white solid (63.8 mg, 69%): ^1H NMR (400 MHz, CDCl_3): δ 8.05-7.99 (m, 2H), 7.66-7.61 (m, 1H), 7.55-7.50 (m, 10H), 7.42 (t, $J = 5$ Hz, 4H), 7.35-7.26 (m, 6H). ^{13}C NMR (100 MHz, CDCl_3): δ 149.8 (d, $J_{C-P} = 8$ Hz), 140.2, 138.3, 133.3 (d, $J_{C-P} = 3$ Hz), 132.3 (d, $J_{C-P} = 11$ Hz), 128.8, 128.6, 128.4, 126.8 (d, $J_{C-P} = 192$ Hz), 127.3, 127.0, 120.9 (d, $J_{C-P} = 5$ Hz). ^{31}P NMR (162 MHz, CDCl_3): δ 12.74. HRMS calc. for $\text{C}_{30}\text{H}_{24}\text{O}_3\text{P}$ ($\text{M}+\text{H}$) $^+$: 463.1458, found 463.1458.

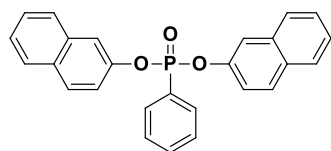


bis(3,4-dimethylphenyl) phenylphosphonate. Performed according to the general procedure, and purified by column chromatography (petroleum ether/ethyl acetate = 9/1) to afford **3h** as colorless oil (62.3 mg, 85%): ^1H NMR (400 MHz, CDCl_3): δ 7.98-7.92 (m, 2H), 7.60-7.55 (m, 1H), 7.50-7.45 (m, 2H), 7.02-7.69 (m, 4H), 6.90-7.87 (m, 2H), 2.18 (s, 6H), 2.18 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3): δ

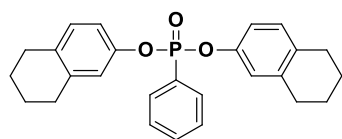
148.3 (d, $J_{C-P} = 7.0$ Hz), 138.1, 133.2, 132.9 (d, $J_{C-P} = 3.0$ Hz), 132.3 (d, $J_{C-P} = 10.0$ Hz), 130.4, 128.5 (d, $J_{C-P} = 15.0$ Hz), 127.3 (d, $J_{C-P} = 192.0$ Hz), 121.6 (d, $J_{C-P} = 4.0$ Hz), 117.6 (d, $J_{C-P} = 4.0$ Hz), 19.8, 19.0. ^{31}P NMR (203 MHz, CDCl_3): δ 11.67. HRMS calc. for $\text{C}_{22}\text{H}_{24}\text{O}_3\text{P}$ ($\text{M}+\text{H}$) $^+$ = 367.1458, found 367.1457.



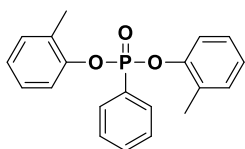
bis(3,4-difluorophenyl) phenylphosphonate. Performed according to the general procedure, and purified by column chromatography (petroleum ether/ethyl acetate = 9/1) to afford **3i** as colorless oil (59.5 mg, 78%): ^1H NMR (500 MHz, CDCl_3): δ 7.95-7.91 (m, 2H), 7.68-7.65 (m, 1H), 7.57-7.53 (m, 2H), 7.12-7.05 (m, 4H), 6.96-6.93 (m, 2H). ^{13}C NMR (125 MHz, CDCl_3): δ 149.1 (dd, $J_1 = 13.8$ Hz, $J_2 = 509.6$ Hz), 149.0 (t, $J_{C-F} = 14.3$ Hz), 145.6-145.5 (m), 133.9 (d, $J_{C-P} = 3.3$ Hz), 132.2 (d, $J_{C-P} = 10.6$ Hz), 128.9 (d, $J_{C-P} = 15.7$ Hz), 125.3 (d, $J_{C-P} = 191.6$ Hz), 117.6 (d, $J_{C-P} = 18.6$ Hz), 116.6-116.5 (m), 110.7 (dd, $J_1 = 4.5$ Hz, $J_2 = 20.3$ Hz). ^{31}P NMR (203 MHz, CDCl_3): δ 13.01. ^{19}F NMR (470 MHz, CDCl_3): δ -133.5 (d, $J_{F-F} = 21.7$ Hz), -141.2 (d, $J_{F-F} = 23.2$ Hz). HRMS calc. for $\text{C}_{18}\text{H}_{12}\text{F}_4\text{O}_3\text{P}$ ($\text{M}+\text{H}$) $^+$ = 383.0455, found 383.0455.



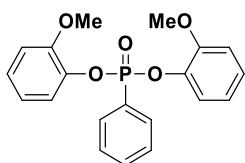
di(naphthalen-2-yl) phenylphosphonate. Performed according to the general procedure, and purified by column chromatography (petroleum ether/ethyl acetate = 9/1) to afford **3j** as yellow oil (53.3 mg, 65%): ^1H NMR (500 MHz, CDCl_3): δ 8.06-8.02 (m, 2H), 7.80-7.77 (m, 4H), 7.73 (d, $J = 8.0$ Hz, 2H), 7.69 (s, 2H), 7.62-7.59 (m, 1H), 7.53-7.49 (m, 2H), 7.47-7.41 (m, 4H), 7.36-7.34 (m, 2H). ^{13}C NMR (125 MHz, CDCl_3): δ 148.0 (d, $J_{C-P} = 7.8$ Hz), 133.8, 133.3 (d, $J_{C-P} = 3.2$ Hz), 132.3 (d, $J_{C-P} = 10.2$ Hz), 131.0, 129.9, 128.8, 128.7, 127.6 (d, $J_{C-P} = 14.5$ Hz), 126.7 (d, $J_{C-P} = 191.0$ Hz), 126.6, 125.5, 120.5 (d, $J_{C-P} = 4.5$ Hz), 117.2 (d, $J_{C-P} = 4.8$ Hz). ^{31}P NMR (203 MHz, CDCl_3): δ 12.10. HRMS calc. for $\text{C}_{26}\text{H}_{20}\text{O}_3\text{P}$ ($\text{M}+\text{H}$) $^+$ = 411.1145, found 411.1144.



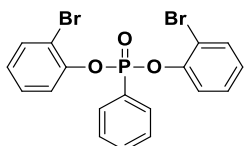
bis(5,6,7,8-tetrahydronaphthalen-2-yl) phenylphosphonate. Performed according to the general procedure and purified by column chromatography (petroleum ether/ethyl acetate = 9/1) to afford **3k** as colorless oil (64.4 mg, 77%): ^1H NMR (500 MHz, CDCl_3): δ 7.98-7.93 (m, 2H), 7.60-7.56 (m, 1H), 7.50-7.46 (m, 2H), 6.95-6.87 (m, 6H), 2.68 (s, 8H), 1.74-1.71 (m, 8H). ^{13}C NMR (125 MHz, CDCl_3): δ 147.9 (d, $J_{C-P} = 7.5$ Hz), 138.6, 133.8, 132.9 (d, $J_{C-P} = 3.2$ Hz), 132.3 (d, $J_{C-P} = 10.2$ Hz), 130.0, 128.5 (d, $J_{C-P} = 15.6$ Hz), 127.3 (d, $J_{C-P} = 191.3$ Hz), 120.7 (d, $J_{C-P} = 4.1$ Hz), 117.7 (d, $J_{C-P} = 4.1$ Hz), 29.4, 28.7, 23.1, 22.8. ^{31}P NMR (203 MHz, CDCl_3): δ 11.67. HRMS calc. for $\text{C}_{26}\text{H}_{28}\text{O}_3\text{P}$ ($\text{M}+\text{H}$) $^+$ = 419.1771, found 419.1772.



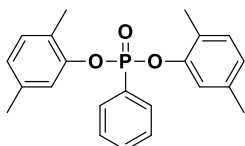
di-*o*-tolyl phenylphosphonate. Performed according to the general procedure, and purified by column chromatography (petroleum ether/ethyl acetate = 9/1) to afford **3l** as colorless oil (42.6 mg, 63%): ^1H NMR (500 MHz, CDCl_3): δ 8.03-7.99 (m, 2H), 7.64-7.60 (m, 1H), 7.54-7.50 (m, 2H), 7.22 (d, $J = 8.1$ Hz, 2H), 7.16 (d, $J = 7.3$ Hz, 2H), 7.11-7.08 (m, 2H), 7.04 (t, $J = 7.3$ Hz, 2H), 2.20 (s, 6H). ^{13}C NMR (125 MHz, CDCl_3): δ 149.1 (d, $J_{\text{C-P}} = 8.2$ Hz), 133.1 (d, $J_{\text{C-P}} = 3.3$ Hz), 132.1 (d, $J_{\text{C-P}} = 10.3$ Hz), 131.3, 129.5 (d, $J_{\text{C-P}} = 5.6$ Hz), 128.6 (d, $J_{\text{C-P}} = 15.6$ Hz), 128.5, 126.9, 125.0, 120.5 (d, $J_{\text{C-P}} = 2.6$ Hz), 16.5. ^{31}P NMR (203 MHz, CDCl_3): δ 11.34. HRMS calc. for $\text{C}_{20}\text{H}_{20}\text{O}_3\text{P}$ ($\text{M}+\text{H}$) $^+$ = 339.1145, found 339.1140.



bis(2-methoxyphenyl) phenylphosphonate. Performed according to the general procedure, and purified by column chromatography (petroleum ether/ethyl acetate = 9/1) to afford **3m** as colorless oil (30.4 mg, 41%): ^1H NMR (400 MHz, CDCl_3): δ 8.09-8.03 (m, 2H), 7.60-7.55 (m, 1H), 7.51-7.45 (m, 2H), 7.26-7.22 (m, 2H), 7.12-7.07 (m, 2H), 6.90-6.83 (m, 4H), 3.71 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3): δ 150.9 (d, $J_{\text{C-P}} = 4$ Hz), 139.7 (d, $J_{\text{C-P}} = 8$ Hz), 132.7 (d, $J_{\text{C-P}} = 4$ Hz), 132.3 (d, $J_{\text{C-P}} = 10$ Hz), 127.7 (d, $J_{\text{C-P}} = 195$ Hz), 128.1 (d, $J_{\text{C-P}} = 16$ Hz), 125.8, 122.1 (d, $J_{\text{C-P}} = 4$ Hz), 112.7, 120.5, 52.7. ^{31}P NMR (162 MHz, CDCl_3): δ 13.31. HRMS calc. for $\text{C}_{20}\text{H}_{20}\text{O}_5\text{P}$ ($\text{M}+\text{H}$) $^+$ = 371.1043, found 371.1042.

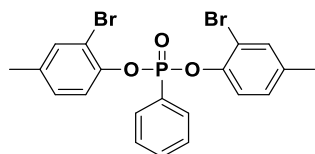


bis(2-bromophenyl) phenylphosphonate. Performed according to the general procedure, and purified by column chromatography (petroleum ether/ethyl acetate = 9/1) to afford **3n** as colorless oil (32.6 mg, 35%): ^1H NMR (500 MHz, CDCl_3): δ 8.17-8.12 (m, 2H), 7.66-7.63 (m, 1H), 7.55-7.51 (m, 4H), 7.46 (d, $J = 8.2$ Hz, 2H), 7.26-7.21 (m, 2H), 7.02 (t, $J = 7.6$ Hz, 2H). ^{13}C NMR (125 MHz, CDCl_3): δ 147.7 (d, $J_{\text{C-P}} = 7.3$ Hz), 133.7, 133.6 (d, $J_{\text{C-P}} = 3.0$ Hz), 132.6 (d, $J_{\text{C-P}} = 10.9$ Hz), 128.7, 128.5, 126.1 (d, $J_{\text{C-P}} = 194.3$ Hz), 126.3, 121.9 (d, $J_{\text{C-P}} = 2.7$ Hz), 114.9 (d, $J_{\text{C-P}} = 7.2$ Hz). ^{31}P NMR (203 MHz, CDCl_3): δ 12.40. HRMS calc. for $\text{C}_{18}\text{H}_{14}\text{Br}_2\text{O}_3\text{P}$ ($\text{M}+\text{H}$) $^+$ = 468.9021, found 468.9026.

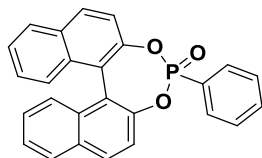


bis(2,5-dimethylphenyl) phenylphosphonate. Performed according to the general procedure, and purified by column chromatography (petroleum ether/ethyl acetate = 9/1) to afford **3o** as colorless oil (31.5 mg, 43%): ^1H NMR (500 MHz, CDCl_3): δ 8.02-7.97 (m, 2H), 7.63-7.60 (m, 1H), 7.53-7.49 (m, 2H), 7.03 (t, $J = 8.0$ Hz, 4H), 6.85 (d, $J = 7.6$ Hz, 2H), 2.24 (s, 6H), 2.15 (s, 6H). ^{13}C NMR (125 MHz, CDCl_3): δ 145.4 (d, $J_{\text{C-P}} = 7.5$ Hz), 136.3, 133.9, 133.5 (d, $J_{\text{C-P}} = 2.8$ Hz), 132.6 (d, $J_{\text{C-P}} = 10.6$ Hz), 129.1, 128.5 (d, $J_{\text{C-P}} = 16.3$ Hz), 126.3 (d, $J_{\text{C-P}} = 193.3$ Hz), 121.5 (d, $J_{\text{C-P}} = 2.6$ Hz), 114.3 (d, $J_{\text{C-P}} = 6.8$

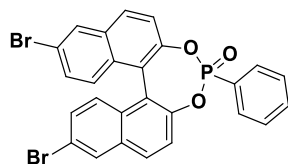
Hz), 20.4. ^{31}P NMR (203 MHz, CDCl_3): δ 12.48. HRMS calc. for $\text{C}_{20}\text{H}_{18}\text{Br}_2\text{O}_3\text{P}$ ($\text{M}+\text{H}$) $^+$ = 496.9334, found 496.9338.



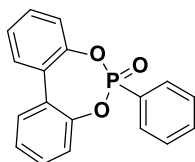
bis(2-bromo-4-methylphenyl) phenylphosphonate. Performed according to the general procedure, and purified by column chromatography (petroleum ether/ethyl acetate = 9/1) to afford **3p** as colorless oil (35.5 mg, 36%): ^1H NMR (500 MHz, CDCl_3): δ 8.14-8.09 (m, 2H), 7.63-7.60 (m, 1H), 7.53-7.49 (m, 2H), 7.33 (t, J = 10.5 Hz, 4H), 7.01 (d, J = 8.3 Hz, 2H), 2.27 (s, 6H). ^{13}C NMR (125 MHz, CDCl_3): δ 145.4 (d, $J_{\text{C-P}}$ = 7.5 Hz), 136.3, 133.9, 133.5 (d, $J_{\text{C-P}}$ = 2.8 Hz), 132.6 (d, $J_{\text{C-P}}$ = 10.6 Hz), 129.1, 128.5 (d, $J_{\text{C-P}}$ = 16.3 Hz), 126.3 (d, $J_{\text{C-P}}$ = 193.3 Hz), 121.5 (d, $J_{\text{C-P}}$ = 2.6 Hz), 114.3 (d, $J_{\text{C-P}}$ = 6.8 Hz), 20.4. ^{31}P NMR (203 MHz, CDCl_3): δ 12.48. HRMS calc. for $\text{C}_{20}\text{H}_{18}\text{Br}_2\text{O}_3\text{P}$ ($\text{M}+\text{H}$) $^+$ = 496.9334, found 496.9338.



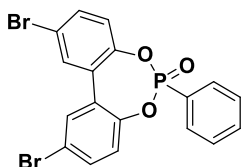
4-phenyldinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepine 4-oxide. Performed according to the general procedure, and purified by column chromatography (petroleum ether/ethyl acetate = 4/1) to afford **3q** as white solid (71.0 mg, 87%): ^1H NMR (500 MHz, CDCl_3): δ 8.07 (d, J = 8.9 Hz, 1H), 7.97 (d, J = 8.2 Hz, 1H), 7.92 (d, J = 8.2 Hz, 1H), 7.84 (d, J = 8.9 Hz, 1H), 7.68-7.56 (m, 4H), 7.51-7.45 (m, 3H), 7.38-7.28 (m, 5H), 7.00 (d, J = 8.8 Hz, 1H). ^{13}C NMR (125 MHz, CDCl_3): δ 147.5 (d, $J_{\text{C-P}}$ = 10.4 Hz), 145.7 (d, $J_{\text{C-P}}$ = 9.8 Hz), 133.5 (d, $J_{\text{C-P}}$ = 3.1 Hz), 132.4 (d, $J_{\text{C-P}}$ = 9.8 Hz), 132.1 (d, $J_{\text{C-P}}$ = 66.6 Hz), 131.5, 131.3, 130.7, 128.5 (d, $J_{\text{C-P}}$ = 7.5 Hz), 128.4 (d, $J_{\text{C-P}}$ = 12.1 Hz), 127.1 (d, $J_{\text{C-P}}$ = 36.9 Hz), 126.7, 125.7 (d, $J_{\text{C-P}}$ = 1.8 Hz), 124.7 (d, $J_{\text{C-P}}$ = 185.7 Hz), 121.8 (d, $J_{\text{C-P}}$ = 2.4 Hz), 121.7 (d, $J_{\text{C-P}}$ = 1.7 Hz), 121.2 (d, $J_{\text{C-P}}$ = 1.7 Hz), 120.8 (d, $J_{\text{C-P}}$ = 3.1 Hz). ^{31}P NMR (203 MHz, CDCl_3): δ 27.19. HRMS calc. for $\text{C}_{26}\text{H}_{18}\text{O}_3\text{P}$ ($\text{M}+\text{H}$) $^+$ = 409.0988, found 409.0989.



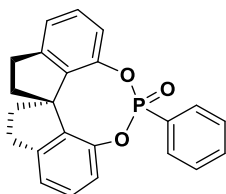
9,14-dibromo-4-phenyldinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepine 4-oxide. Performed according to the general procedure, and purified by column chromatography (petroleum ether/ethyl acetate = 4/1) to afford **3r** as white solid (78.9 mg, 70%): ^1H NMR (500 MHz, CDCl_3): δ 8.15 (d, J = 2.0 Hz, 1H), 8.10 (d, J = 2.0 Hz, 1H), 8.00 (d, J = 8.9 Hz, 1H), 7.77 (d, J = 8.9 Hz, 1H), 7.68 (d, J = 9.4 Hz, 1H), 7.62-7.58 (m, 3H), 7.44-7.37 (m, 4H), 7.28 (s, 1H), 7.19 (d, J = 9.1 Hz, 1H), 7.03 (d, J = 8.9 Hz, 1H). ^{13}C NMR (125 MHz, CDCl_3): δ 147.8 (d, $J_{\text{C-P}}$ = 10.3 Hz), 146.1 (d, $J_{\text{C-P}}$ = 9.9 Hz), 133.8 (d, $J_{\text{C-P}}$ = 2.8 Hz), 133.0, 132.7, 132.4 (d, $J_{\text{C-P}}$ = 10.0 Hz), 130.8 (d, $J_{\text{C-P}}$ = 5.5 Hz), 130.6, 130.5, 130.3 (d, $J_{\text{C-P}}$ = 3.8 Hz), 130.0, 128.6 (d, $J_{\text{C-P}}$ = 5.0 Hz), 128.4 (d, $J_{\text{C-P}}$ = 18.4 Hz), 124.3 (d, $J_{\text{C-P}}$ = 185.8 Hz), 122.5 (d, $J_{\text{C-P}}$ = 1.7 Hz), 122.1 (d, $J_{\text{C-P}}$ = 2.9 Hz), 121.7 (d, $J_{\text{C-P}}$ = 2.6 Hz), 121.5 (d, $J_{\text{C-P}}$ = 1.7 Hz), 120.1 (d, $J_{\text{C-P}}$ = 7.2 Hz). ^{31}P NMR (203 MHz, CDCl_3): δ 27.27. HRMS calc. for $\text{C}_{26}\text{H}_{16}\text{Br}_2\text{O}_3\text{P}$ ($\text{M}+\text{H}$) $^+$ = 566.9178, found 566.9178.



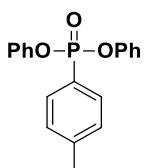
6-phenyldibenzo[d,f][1,3,2]dioxaphosphepine 6-oxide. Performed according to the general procedure, and purified by column chromatography (petroleum ether/ethyl acetate = 4/1) to afford **3s** as white solid (54.3 mg, 88%): ^1H NMR (400 MHz, CDCl_3): δ 7.76-7.70 (m, 2H), 7.62-7.56 (m, 3H), 7.45-7.34 (m, 6H), 7.12-7.10 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ 147.8 (d, $J_{\text{C-P}} = 10.0$ Hz), 133.5 (d, $J_{\text{C-P}} = 3.0$ Hz), 132.3 (d, $J_{\text{C-P}} = 10.0$ Hz), 130.0 (d, $J_{\text{C-P}} = 14.0$ Hz), 128.7, 128.5, 128.3, 126.3, 124.7 (d, $J_{\text{C-P}} = 188.0$ Hz), 121.8 (d, $J_{\text{C-P}} = 3.0$ Hz). ^{31}P NMR (203 MHz, CDCl_3): δ 26.00. HRMS calc. for $\text{C}_{18}\text{H}_{14}\text{O}_3\text{P}$ ($\text{M}+\text{H}$) $^+$: 309.0675, found 309.0671.



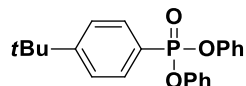
2,10-dibromo-6-phenyldibenzo[d,f][1,3,2]dioxaphosphepine 6-oxide. Performed according to the general procedure, and purified by column chromatography (petroleum ether/ethyl acetate = 4/1) to afford **3t** as white solid (73.2 mg, 79%): ^1H NMR (500 MHz, CDCl_3): δ 7.75-7.70 (m, 4H), 7.66-7.62 (m, 1H), 7.52 (dd, $J_1 = 2.3$ Hz, $J_2 = 8.7$ Hz, 2H), 7.49-7.45 (m, 2H), 7.00 (d, $J = 8.6$ Hz, 2H). ^{13}C NMR (125 MHz, CDCl_3): δ 146.9 (d, $J_{\text{C-P}} = 9.9$ Hz), 133.9 (d, $J_{\text{C-P}} = 2.8$ Hz), 133.4, 132.6, 132.3 (d, $J_{\text{C-P}} = 10.0$ Hz), 129.5, 128.7 (d, $J_{\text{C-P}} = 15.6$ Hz), 124.0 (d, $J_{\text{C-P}} = 187.4$ Hz), 123.7 (d, $J_{\text{C-P}} = 3.8$ Hz), 119.5 (d, $J_{\text{C-P}} = 1.9$ Hz). ^{31}P NMR (203 MHz, CDCl_3): δ 26.09. HRMS calc. for $\text{C}_{18}\text{H}_{12}\text{Br}_2\text{O}_3\text{P}$ ($\text{M}+\text{H}$) $^+$: 466.8865, found 466.8867.



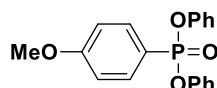
12-phenyl-4,5,6,7-tetrahydrodiinden[7,1-de:1',7'-fg][1,3,2]dioxaphosphocine 12-oxide. Performed according to the general procedure, and purified by column chromatography (petroleum ether/ethyl acetate = 4/1) to afford **3u** as white solid (37.5 mg, 50%): ^1H NMR (500 MHz, CDCl_3): δ 7.53 (t, $J = 7.4$ Hz, 1H), 7.47-7.43 (m, 2H), 7.36-7.31 (m, 2H), 7.27 (d, $J = 7.8$ Hz, 1H), 7.18 (d, $J = 7.4$ Hz, 1H), 7.14 (d, $J = 7.9$ Hz, 1H), 7.05 (d, $J = 7.4$ Hz, 1H), 6.82 (t, $J = 7.8$ Hz, 1H), 6.11 (d, $J = 8.1$ Hz, 1H), 3.16-3.09 (m, 2H), 2.93-2.85 (m, 2H), 2.37-2.34 (m, 1H), 2.29-2.26 (m, 1H), 2.14-2.04 (m, 2H). ^{13}C NMR (125 MHz, CDCl_3): δ 146.4 (dd, $J_1 = 1.9$ Hz, $J_2 = 12.9$ Hz), 145.7 (d, $J_{\text{C-P}} = 8.5$ Hz), 143.3 (d, $J_{\text{C-P}} = 9.3$ Hz), 139.7 (dd, $J_1 = 3.2$ Hz, $J_2 = 22.7$ Hz), 133.1 (d, $J_{\text{C-P}} = 3.2$ Hz), 132.4 (d, $J_{\text{C-P}} = 9.2$ Hz), 128.8, 128.0, 127.9, 124.3 (d, $J_{\text{C-P}} = 186.6$ Hz), 123.0 (d, $J_{\text{C-P}} = 1.7$ Hz), 122.3 (d, $J_{\text{C-P}} = 2.4$ Hz), 122.0 (d, $J_{\text{C-P}} = 2.9$ Hz), 121.8 (d, $J_{\text{C-P}} = 3.7$ Hz), 59.3, 38.3 (d, $J_{\text{C-P}} = 18.2$ Hz), 30.6 (d, $J_{\text{C-P}} = 9.1$ Hz). ^{31}P NMR (203 MHz, CDCl_3): δ 13.46. HRMS calc. for $\text{C}_{23}\text{H}_{20}\text{O}_3\text{P}$ ($\text{M}+\text{H}$) $^+$: 375.1145, found 375.1143.



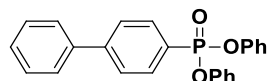
diphenyl *p*-tolylphosphonate. Performed according to the general procedure, and purified by column chromatography (petroleum ether/ethyl acetate = 9/1) to afford **3aa** as colorless oil (47.4 mg, 73%): ^1H NMR (500 MHz, CDCl_3): δ 7.87-7.82 (m, 2H), 7.31-7.26 (m, 6H), 7.18 (d, $J = 8.0$ Hz, 4H), 7.13 (t, $J = 7.4$ Hz, 2H), 2.41 (s, 3H). ^{13}C NMR (125 MHz, CDCl_3): δ 150.4 (d, $J_{\text{C-P}} = 7.4$ Hz), 143.9 (d, $J_{\text{C-P}} = 3.3$ Hz), 132.3 (d, $J_{\text{C-P}} = 10.9$ Hz), 129.7, 129.4 (d, $J_{\text{C-P}} = 16.3$ Hz), 125.0, 123.5 (d, $J_{\text{C-P}} = 194.0$ Hz), 120.6 (d, $J_{\text{C-P}} = 4.4$ Hz), 21.7. ^{31}P NMR (203 MHz, CDCl_3): δ 12.50. HRMS calc. for $\text{C}_{19}\text{H}_{18}\text{O}_3\text{P}$ (M+H) $^+$: 325.0988, found 325.0985.



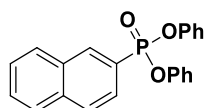
diphenyl (4-(tert-butyl)phenyl)phosphonate. Performed according to the general procedure, and purified by column chromatography (petroleum ether/ethyl acetate = 9/1) to afford **3ab** as colorless oil (47.6 mg, 65%): ^1H NMR (500 MHz, CDCl_3): δ 8.00-7.96 (m, 2H), 7.62-7.59 (m, 1H), 7.52-7.48 (m, 2H), 7.28 (d, $J = 8.8$ Hz, 4H), 7.10 (d, $J = 8.7$ Hz, 4H), 1.27 (s, 18H). ^{13}C NMR (125 MHz, CDCl_3): δ 156.8 (d, $J_{\text{C-P}} = 3$ Hz), 150.5 (d, $J_{\text{C-P}} = 7.6$ Hz), 132.1 (d, $J_{\text{C-P}} = 10.9$ Hz), 129.6, 125.7 (d, $J_{\text{C-P}} = 16.2$ Hz), 125.0, 123.6 (d, $J_{\text{C-P}} = 194.7$ Hz), 120.6 (d, $J_{\text{C-P}} = 4.5$ Hz), 35.1, 31.0. ^{31}P NMR (203 MHz, CDCl_3): δ 12.35. HRMS calc. for $\text{C}_{22}\text{H}_{24}\text{O}_3\text{P}$ (M+H) $^+$: 367.1458, found 367.1455.



diphenyl (4-methoxyphenyl)phosphonate. Performed according to the general procedure, and purified by column chromatography (petroleum ether/ethyl acetate = 9/1) to afford **3ac** as colorless oil (42.9 mg, 63%): ^1H NMR (500 MHz, CDCl_3): δ 7.91-7.86 (m, 2H), 7.30-7.26 (m, 4H), 7.19-7.17 (m, 4H), 7.15-7.12 (m, 2H), 6.99-6.97 (m, 2H), 3.85 (s, 3H). ^{13}C NMR (125 MHz, CDCl_3): δ 163.4 (d, $J_{\text{C-P}} = 3.6$ Hz), 150.4 (d, $J_{\text{C-P}} = 7.3$ Hz), 134.3 (d, $J_{\text{C-P}} = 11.9$ Hz), 129.7, 125.0, 120.6 (d, $J_{\text{C-P}} = 4.5$ Hz), 117.8 (d, $J_{\text{C-P}} = 199.4$ Hz), 114.2 (d, $J_{\text{C-P}} = 17.1$ Hz), 55.4. ^{31}P NMR (203 MHz, CDCl_3): δ 12.71. HRMS calc. for $\text{C}_{19}\text{H}_{18}\text{O}_4\text{P}$ (M+H) $^+$: 341.0937, found 341.0939.

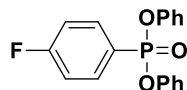


diphenyl [1,1'-biphenyl]-4-ylphosphonate. Performed according to the general procedure, and purified by column chromatography (petroleum ether/ethyl acetate = 9/1) to afford **3ad** as colorless oil (49.5 mg, 64%): ^1H NMR (500 MHz, CDCl_3): δ 8.05-8.00 (m, 2H), 7.73-7.70 (m, 2H), 7.61 (d, $J = 8.5$ Hz, 2H), 7.48-7.45 (m, 2H), 7.42-7.39 (m, 1H), 7.30 (t, $J = 8.3$ Hz, 4H), 7.23-7.21 (m, 4H), 7.17-7.13 (m, 2H). ^{13}C NMR (125 MHz, CDCl_3): δ 150.4 (d, $J_{\text{C-P}} = 7.8$ Hz), 145.9 (d, $J_{\text{C-P}} = 3$ Hz), 139.6, 132.8 (d, $J_{\text{C-P}} = 10.9$ Hz), 129.7, 129.0, 128.4, 127.3 (d, $J_{\text{C-P}} = 16.3$ Hz), 127.3, 125.2 (d, $J_{\text{C-P}} = 193.9$ Hz), 125.1, 120.6 (d, $J_{\text{C-P}} = 4.4$ Hz). ^{31}P NMR (203 MHz, CDCl_3): δ 11.92. HRMS calc. for $\text{C}_{24}\text{H}_{20}\text{O}_3\text{P}$ (M+H) $^+$: 387.1145, found 387.1146.

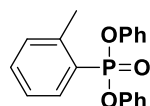


diphenyl naphthalen-2-ylphosphonate. Performed according to the general procedure, and purified by column chromatography (petroleum ether/ethyl acetate = 9/1) to afford **3ae** as colorless oil (50.4 mg, 70%): ^1H NMR (500 MHz, CDCl_3): δ 8.57 (d, $J = 16.4$ Hz, 2H), 7.96-7.87 (m, 4H), 7.63-7.55 (m, 2H),

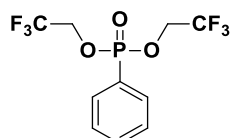
7.29-7.21 (m, 8H), 7.14-7.11 (m, 2H). ^{13}C NMR (125 MHz, CDCl_3): δ 150.3 (d, $J_{\text{C-P}} = 7.4$ Hz), 135.3 (d, $J_{\text{C-P}} = 2.8$ Hz), 135.1 (d, $J_{\text{C-P}} = 10.9$ Hz), 132.2 (d, $J_{\text{C-P}} = 17.7$ Hz), 129.7, 129.1, 128.7, 128.6 (d, $J_{\text{C-P}} = 14.8$ Hz), 127.8, 127.1, 126.3 (d, $J_{\text{C-P}} = 10.1$ Hz), 125.1, 123.7 (d, $J_{\text{C-P}} = 192.0$ Hz), 120.6 (d, $J_{\text{C-P}} = 4.5$ Hz). ^{31}P NMR (203 MHz, CDCl_3): δ 12.13. HRMS calc. for $\text{C}_{22}\text{H}_{18}\text{O}_3\text{P}$ ($\text{M}+\text{H}$) $^+$ = 361.0988, found 361.0988.



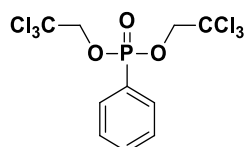
diphenyl (4-fluorophenyl)phosphonate. Performed according to the general procedure, and purified by column chromatography (petroleum ether/ethyl acetate = 9/1) to afford **3af** as colorless oil (41.4 mg, 63%): ^1H NMR (500 MHz, CDCl_3): δ 8.00-7.95 (m, 2H), 7.30 (t, $J = 8.0$ Hz, 4H), 7.20-7.14 (m, 8H). ^{13}C NMR (125 MHz, CDCl_3): δ 165.8 (dd, $J_1 = 4.2$ Hz, $J_2 = 253.7$ Hz), 150.2 (d, $J_{\text{C-P}} = 7.4$ Hz), 135.0 (dd, $J_1 = 9.1$ Hz, $J_2 = 11.8$ Hz), 129.7, 125.2, 122.8 (dd, $J_1 = 3.0$ Hz, $J_2 = 196.6$ Hz), 120.5 (d, $J_{\text{C-P}} = 4.5$ Hz), 116.1 (dd, $J_1 = 17.1$ Hz, $J_2 = 21.6$ Hz). ^{31}P NMR (203 MHz, CDCl_3): δ 10.66. ^{19}F NMR (470 MHz, CDCl_3): δ -104.1. HRMS calc. for $\text{C}_{18}\text{H}_{15}\text{FO}_3\text{P}$ ($\text{M}+\text{H}$) $^+$ = 329.0737, found 329.0738.



diphenyl *o*-tolylphosphonate. Performed according to the general procedure, and purified by column chromatography (petroleum ether/ethyl acetate = 9/1) to afford **3ag** as colorless oil (27.9 mg, 43%): ^1H NMR (500 MHz, CDCl_3): δ 8.10-8.05 (m, 1H), 7.51-7.48 (m, 1H), 7.35-7.27 (m, 6H), 7.19-7.12 (m, 6H), 2.76 (d, $J = 1.5$ Hz, 3H). ^{13}C NMR (125 MHz, CDCl_3): δ 150.4 (d, $J_{\text{C-P}} = 7.9$ Hz), 142.1 (d, $J_{\text{C-P}} = 10.3$ Hz), 134.5 (d, $J_{\text{C-P}} = 11.0$ Hz), 133.3 (d, $J_{\text{C-P}} = 2.8$ Hz), 131.5 (d, $J_{\text{C-P}} = 15.6$ Hz), 129.7, 125.7 (d, $J_{\text{C-P}} = 166.6$ Hz), 125.7 (d, $J_{\text{C-P}} = 15.8$ Hz), 125.0, 120.4 (d, $J_{\text{C-P}} = 4.6$ Hz), 21.5 (d, $J_{\text{C-P}} = 3.5$ Hz). ^{31}P NMR (203 MHz, CDCl_3): δ 12.52. HRMS calc. for $\text{C}_{19}\text{H}_{18}\text{O}_3\text{P}$ ($\text{M}+\text{H}$) $^+$ = 325.0988, found 325.0987.

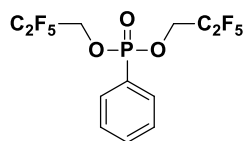


bis(2,2,2-trifluoroethyl) phenylphosphonate. Performed according to the general procedure, and purified by column chromatography (petroleum ether/ethyl acetate = 9/1) to afford **5a** as colorless oil (47.7 mg, 74%): ^1H NMR (500 MHz, CDCl_3): δ 7.85-7.81 (m, 2H), 7.68-7.64 (m, 1H), 7.56-7.52 (m, 2H), 4.51-4.34 (m, 4H). ^{13}C NMR (125 MHz, CDCl_3): δ 133.9 (d, $J_{\text{C-P}} = 3.3$ Hz), 131.8 (d, $J_{\text{C-P}} = 10.9$ Hz), 128.9 (d, $J_{\text{C-P}} = 16.2$ Hz), 124.6 (d, $J_{\text{C-P}} = 194.9$ Hz), 122.5 (dd, $J_1 = 9.1$ Hz, $J_2 = 275.9$ Hz), 62.3 (qd, $J_1 = 4.8$ Hz, $J_2 = 37.8$ Hz). ^{31}P NMR (203 MHz, CDCl_3): δ 21.33. ^{19}F NMR (470 MHz, CDCl_3): δ -75.2. HRMS calc. for $\text{C}_{10}\text{H}_{10}\text{F}_6\text{O}_3\text{P}$ ($\text{M}+\text{H}$) $^+$ = 323.0266, found 323.0266.

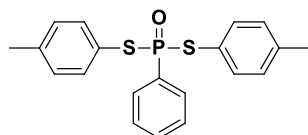


bis(2,2,2-trichloroethyl) phenylphosphonate. Performed according to the general procedure, and purified by column chromatography (petroleum ether/ethyl acetate = 9/1) to afford **5b** as colorless oil (66.8 mg, 80%): ^1H NMR (500 MHz, CDCl_3): δ 7.96-7.91 (m, 2H), 7.67-7.64 (m, 1H), 7.56-7.52 (m, 2H), 4.74-4.70 (m, 2H), 4.67-4.63 (m, 2H). ^{13}C NMR (125 MHz, CDCl_3): δ 133.6 (d, $J_{\text{C-P}} = 2.9$ Hz),

131.9 (d, $J_{C-P} = 10.8$ Hz), 128.8 (d, $J_{C-P} = 15.9$ Hz), 125.6 (d, $J_{C-P} = 194.5$ Hz), 95.0 (d, $J_{C-P} = 10.1$ Hz), 75.8 (d, $J_{C-P} = 4.6$ Hz). ^{31}P NMR (203 MHz, CDCl_3): δ 19.19. HRMS calc. for $\text{C}_{10}\text{H}_{10}\text{Cl}_6\text{O}_3\text{P}$ ($\text{M}+\text{H}$) $^+$: = 418.8494, found 418.8499.

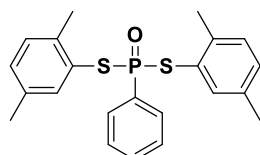


bis(2,2,3,3,3-pentafluoropropyl) phenylphosphonate. Performed according to the general procedure, and purified by column chromatography (petroleum ether/ethyl acetate = 9/1) to afford **5c** as colorless oil (63.3 mg, 75%): ^1H NMR (500 MHz, CDCl_3): δ 7.84-7.80 (m, 2H), 7.68-7.64 (m, 1H), 7.56-7.52 (m, 2H), 4.60-4.40 (m, 4H). ^{13}C NMR (125 MHz, CDCl_3): δ 133.9 (d, $J_{C-P} = 3.3$ Hz), 131.8 (d, $J_{C-P} = 10.8$ Hz), 128.9 (d, $J_{C-P} = 16.3$ Hz), 124.5 (d, $J_{C-P} = 194.5$ Hz), 118.3 (dt, $J_1 = 34.5$ Hz, $J_2 = 284.2$ Hz), 113.9-109.5 (m), 61.3 (td, $J_1 = 4.7$ Hz, $J_2 = 28.5$ Hz). ^{31}P NMR (203 MHz, CDCl_3): δ 21.45. ^{19}F NMR (470 MHz, CDCl_3): δ -83.52, -124.44. HRMS calc. for $\text{C}_{12}\text{H}_{10}\text{F}_{10}\text{O}_3\text{P}$ ($\text{M}+\text{H}$) $^+$: = 423.0202, found 423.0201.

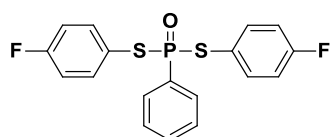


S,S-di-*p*-tolyl phenylphosphonodithioate. Performed according to the general procedure, and purified by column chromatography (petroleum ether/ethyl acetate = 9/1) to afford **5f** as colorless oil (48.2 mg, 65%): ^1H NMR (400 MHz, CDCl_3): δ 7.81-7.75 (m, 2H), 7.47-7.42 (m, 1H), 7.38-7.30 (m, 6H), 7.03 (d, $J = 8.0$ Hz, 4H), 2.25 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3): δ 139.4 (d, $J_{C-P} = 3.0$ Hz), 135.4 (d, $J_{C-P} = 4.0$ Hz), 133.1 (d, $J_{C-P} = 107.0$ Hz), 132.4 (d, $J_{C-P} = 4.0$ Hz), 131.4 (d, $J_{C-P} = 11.0$ Hz), 129.9 (d, $J_{C-P} = 2.0$ Hz), 128.1 (d, $J_{C-P} = 14.0$ Hz), 122.3 (d, $J_{C-P} = 6.0$ Hz), 21.0. ^{31}P NMR (203 MHz, CDCl_3): δ 49.92. MS (ESI): 315.1 ($\text{M}+\text{Na}$) $^+$.

The analytical data matched those reported in the literature.^[6]

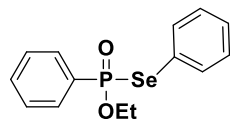


S,S-bis(2,5-dimethylphenyl) phenylphosphonodithioate. Performed according to the general procedure, and purified by column chromatography (petroleum ether/ethyl acetate = 9/1) to afford **5g** as colorless oil (24.7 mg, 31%): ^1H NMR (400 MHz, CDCl_3): δ 7.82-7.77 (m, 2H), 7.52-7.47 (m, 1H), 7.42-7.37 (m, 2H), 7.27 (s, 2H), 7.07-7.00 (m, 4H), 2.28 (s, 6H), 2.20 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3): δ 139.8 (d, $J_{C-P} = 4$ Hz), 137.5 (d, $J_{C-P} = 4$ Hz), 136.1 (d, $J_{C-P} = 3$ Hz), 134.5 (d, $J_{C-P} = 107$ Hz), 132.4 (d, $J_{C-P} = 4$ Hz), 131.4 (d, $J_{C-P} = 11$ Hz), 130.5, 130.5 (d, $J_{C-P} = 3$ Hz), 128.2 (d, $J_{C-P} = 14$ Hz), 125.5 (d, $J_{C-P} = 6$ Hz), 20.9, 20.6. ^{31}P NMR (165 MHz, CDCl_3): δ 49.81. HRMS calc. for $\text{C}_{22}\text{H}_{24}\text{OPS}_2$ ($\text{M}+\text{H}$) $^+$: = 399.1001, found 399.1002.

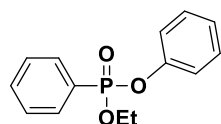


S,S-bis(4-fluorophenyl) phenylphosphonodithioate. Performed according to the general procedure,

and purified by column chromatography (petroleum ether/ethyl acetate = 9/1) to afford **5h** as colorless oil (22.7 mg, 30%): ^1H NMR (500 MHz, CDCl_3): δ 7.80-7.75 (m, 2H), 7.55-7.51 (m, 1H), 7.45-7.40 (m, 6H), 6.97 (t, J = 8.6 Hz, 4H). ^{13}C NMR (125 MHz, CDCl_3): δ 163.7 (dd, J_1 = 2.9 Hz, J_2 = 249.4), 137.7 (dd, J_1 = 3.8 Hz, J_2 = 8.4 Hz), 132.9 (d, $J_{\text{C-P}}$ = 3.5 Hz), 132.7 (d, $J_{\text{C-P}}$ = 107.5 Hz), 131.6 (d, $J_{\text{C-P}}$ = 10.9 Hz), 128.6 (d, $J_{\text{C-P}}$ = 14.2 Hz), 121.0 (dd, J_1 = 3.4 Hz, J_2 = 6.1 Hz), 116.5 (dd, J_1 = 1.9 Hz, J_2 = 22.0 Hz). ^{31}P NMR (203 MHz, CDCl_3): δ 49.52 (d, J = 4.9 Hz). ^{19}F NMR (470 MHz, CDCl_3): δ -110.75 (d, J = 5.4 Hz). HRMS calc. for $\text{C}_{18}\text{H}_{14}\text{F}_2\text{OPS}_2$ ($\text{M}+\text{H}$) $^+$ = 379.0186, found 379.0187.



O-ethyl Se-phenyl phenylphosphonoselenoate. Performed according to the general procedure, and purified by column chromatography (petroleum ether/ethyl acetate = 9/1) to afford **5i** as yellow oil (22.8 mg, 35%): ^1H NMR (400 MHz, CDCl_3): δ 7.63-7.58 (m, 2H), 7.50-7.46 (m, 1H), 7.38-7.26 (m, 5H), 7.20-7.16 (m, 2H), 4.43-4.27 (m, 2H), 1.41 (t, J = 8 Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 136.4 (d, $J_{\text{C-P}}$ = 3 Hz), 132.8 (d, $J_{\text{C-P}}$ = 138 Hz), 132.4 (d, $J_{\text{C-P}}$ = 4 Hz), 131.0 (d, $J_{\text{C-P}}$ = 11 Hz), 129.2 (d, $J_{\text{C-P}}$ = 2 Hz), 128.7 (d, $J_{\text{C-P}}$ = 3 Hz), 128.1 (d, $J_{\text{C-P}}$ = 15 Hz), 124.1 (d, $J_{\text{C-P}}$ = 7 Hz), 62.6 (d, $J_{\text{C-P}}$ = 7 Hz), 16.2 (d, $J_{\text{C-P}}$ = 7 Hz). ^{31}P NMR (162 MHz, CDCl_3): δ 39.12. HRMS calc. for $\text{C}_{14}\text{H}_{16}\text{O}_2\text{PSe}$ ($\text{M}+\text{H}$) $^+$ = 327.0048, found 327.0047.



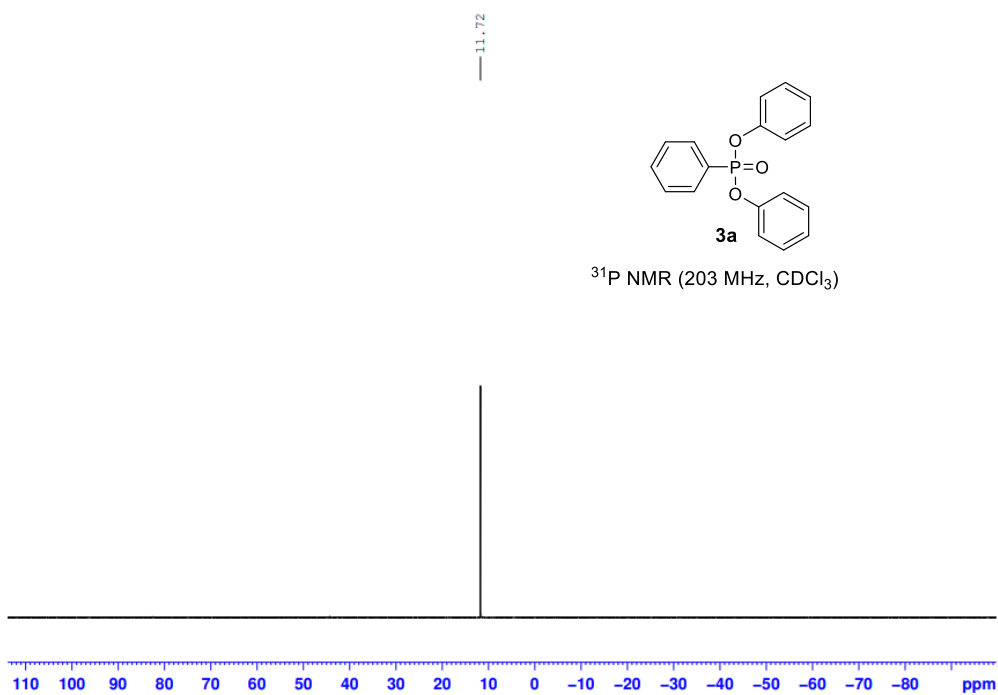
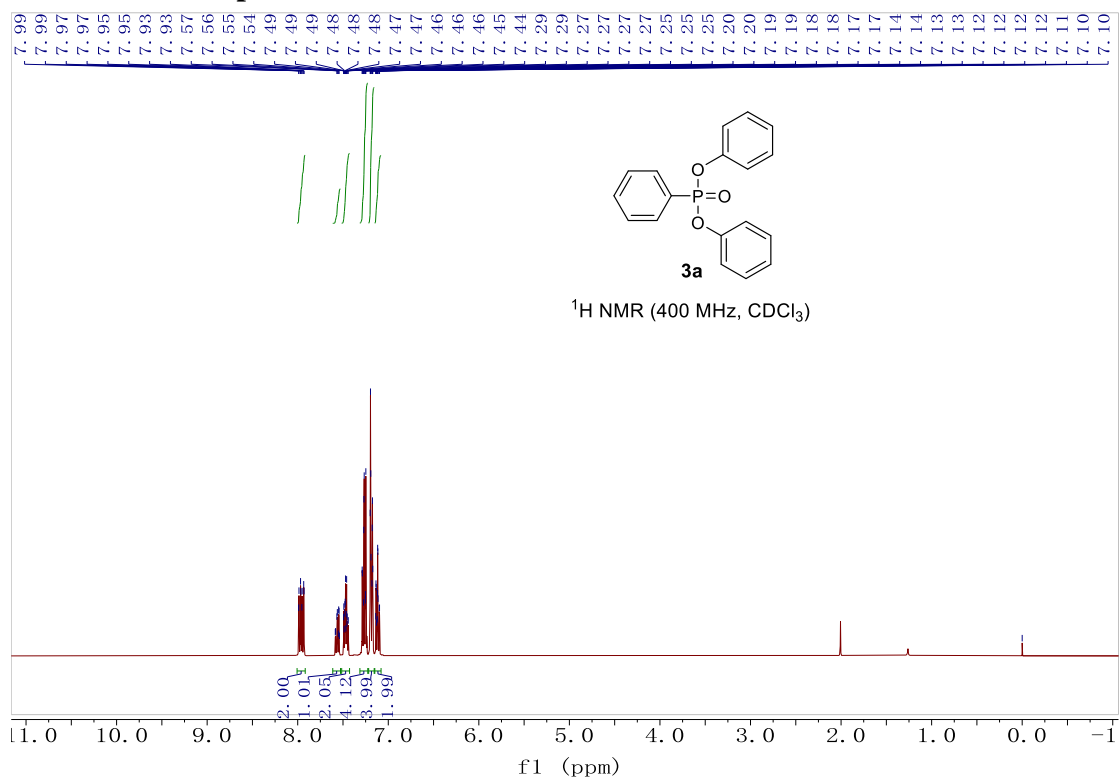
ethyl phenyl phenylphosphonate. ^1H NMR (500 MHz, CDCl_3): δ 7.89-7.85 (m, 2H), 7.59-7.56 (m, 1H), 7.50-7.46 (m, 2H), 7.27 (t, J = 8.1 Hz, 2H), 7.15-7.11 (m, 3H), 4.29-4.21 (m, 2H), 1.36 (t, J = 7.1 Hz, 2H). ^{13}C NMR (125 MHz, CDCl_3): δ 150.5 (d, $J_{\text{C-P}}$ = 7.15 Hz), 132.8 (d, $J_{\text{C-P}}$ = 3.2 Hz), 131.9 (d, $J_{\text{C-P}}$ = 10.1 Hz), 129.6, 128.5 (d, $J_{\text{C-P}}$ = 3.15, 5.1 Hz), 127.4 (d, $J_{\text{C-P}}$ = 190.2 Hz), 124.9, 120.5 (d, $J_{\text{C-P}}$ = 4.3 Hz), 63.0 (d, $J_{\text{C-P}}$ = 5.9 Hz), 16.3 (d, $J_{\text{C-P}}$ = 6.4 Hz). ^{31}P NMR (203 MHz, CDCl_3): δ 15.46. MS (ESI): 263.1 ($\text{M}+1$) $^+$

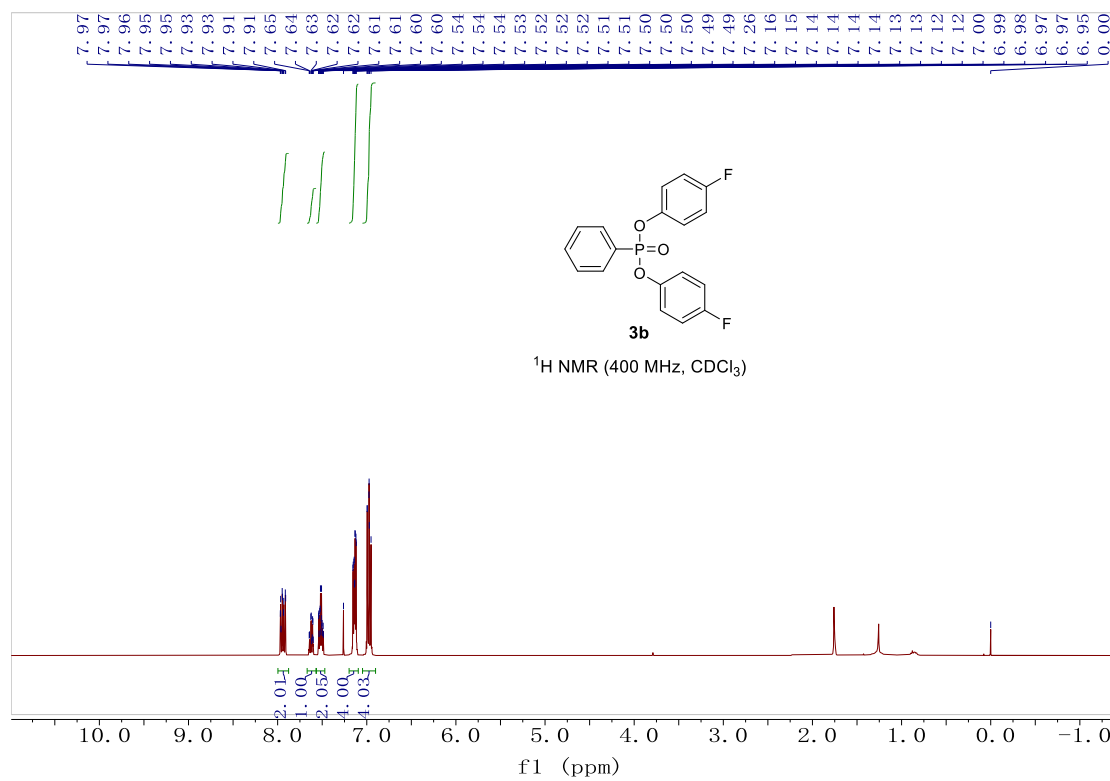
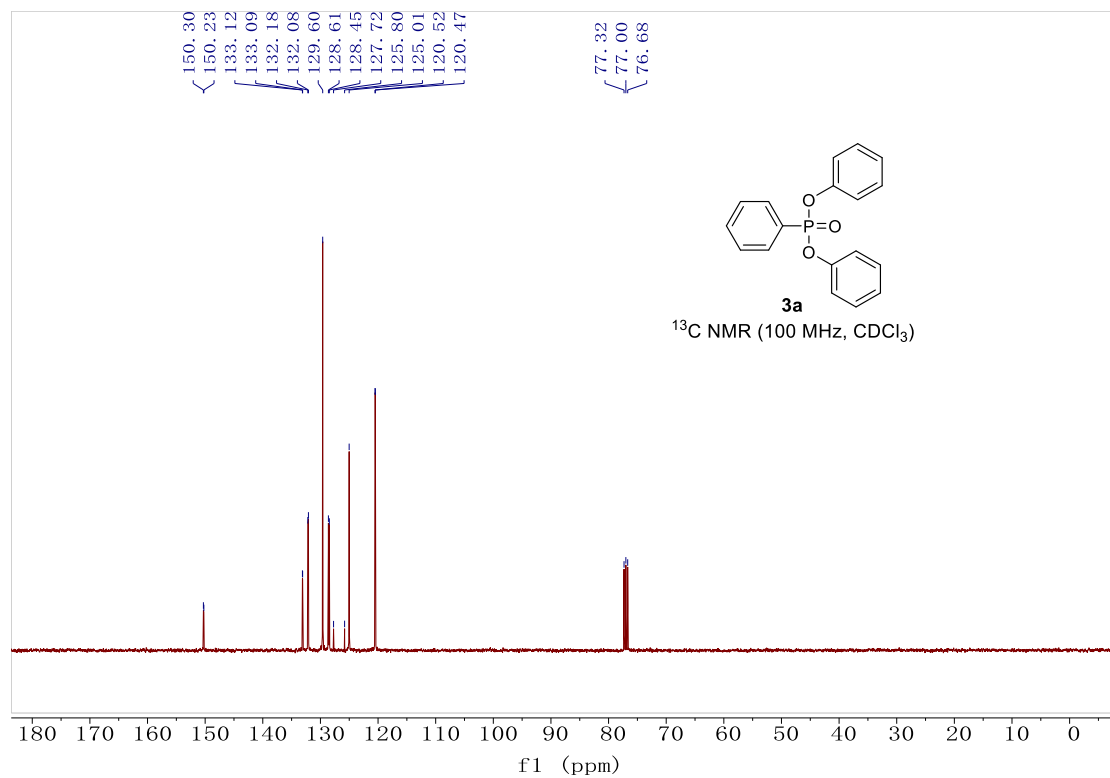
The analytical data matched those reported in the literature.^[7]

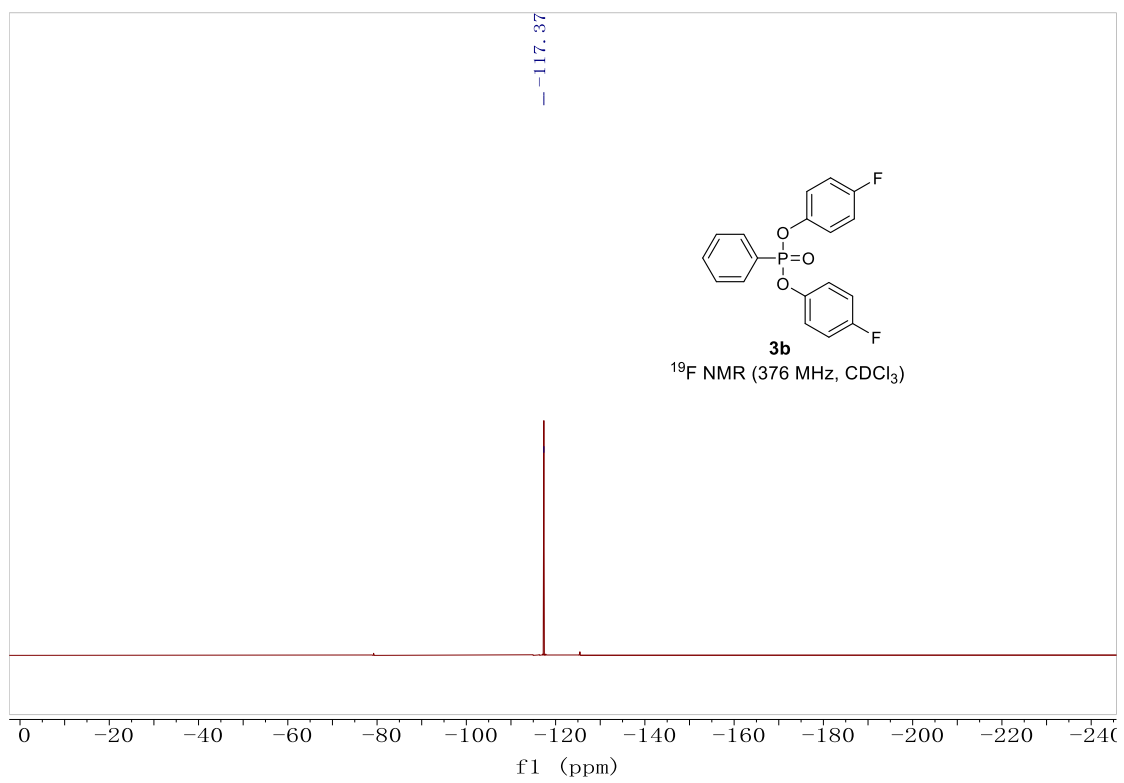
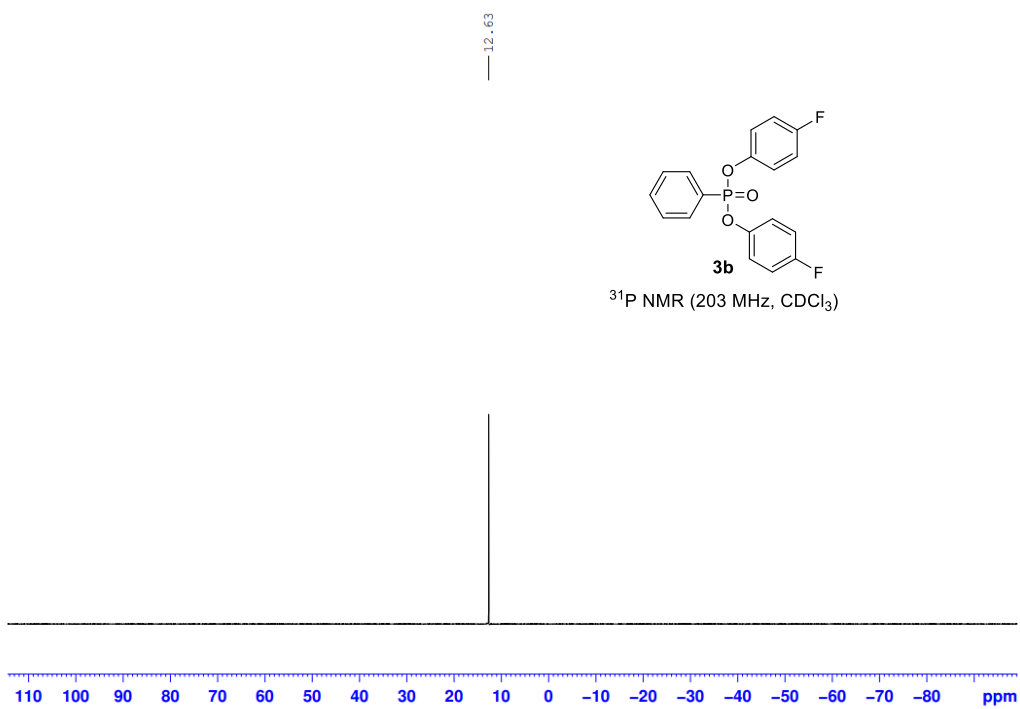
7. Reference

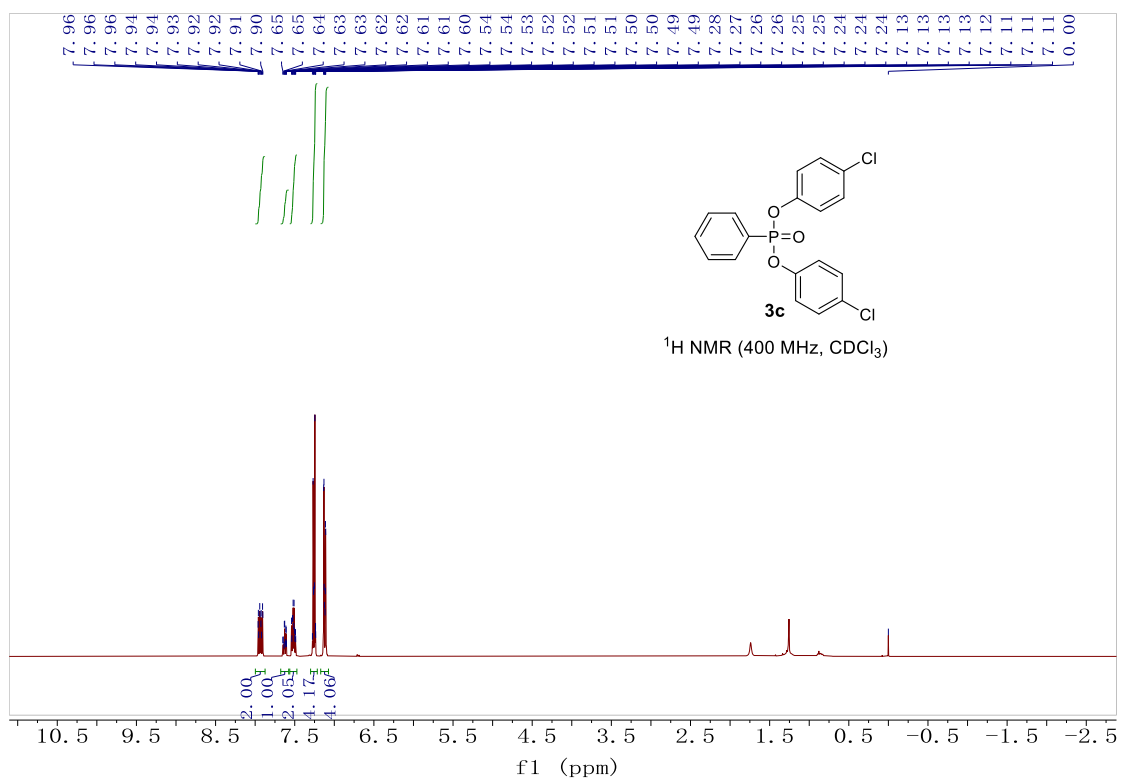
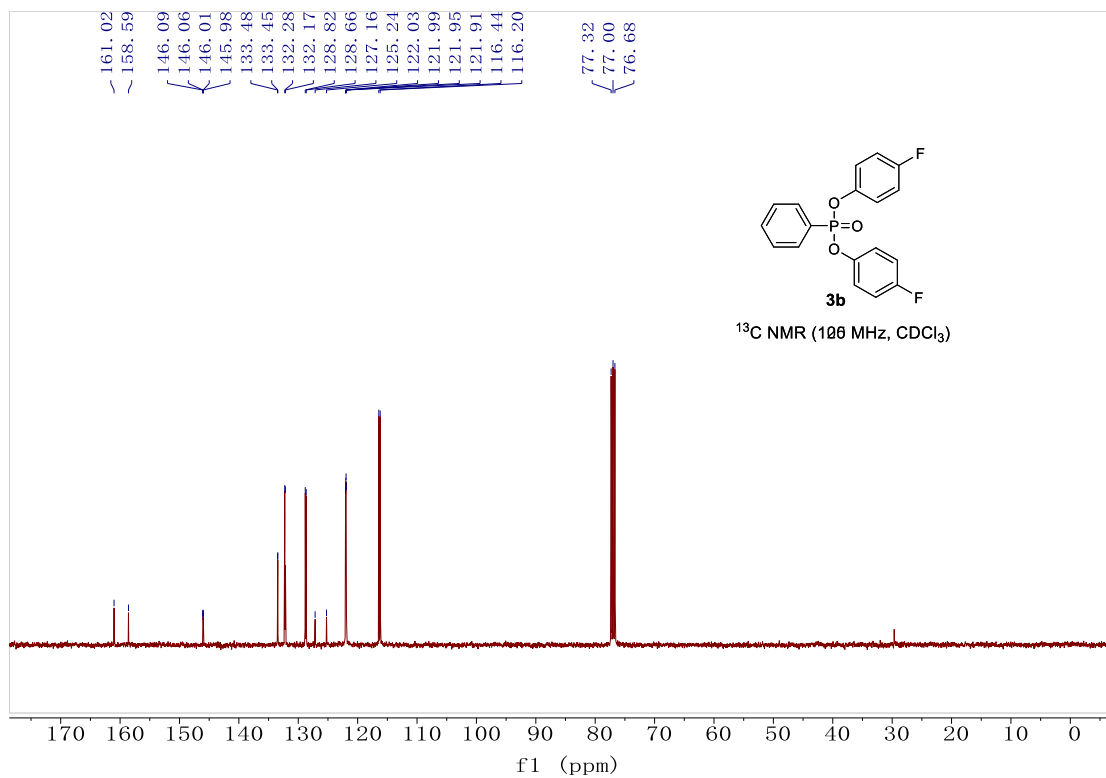
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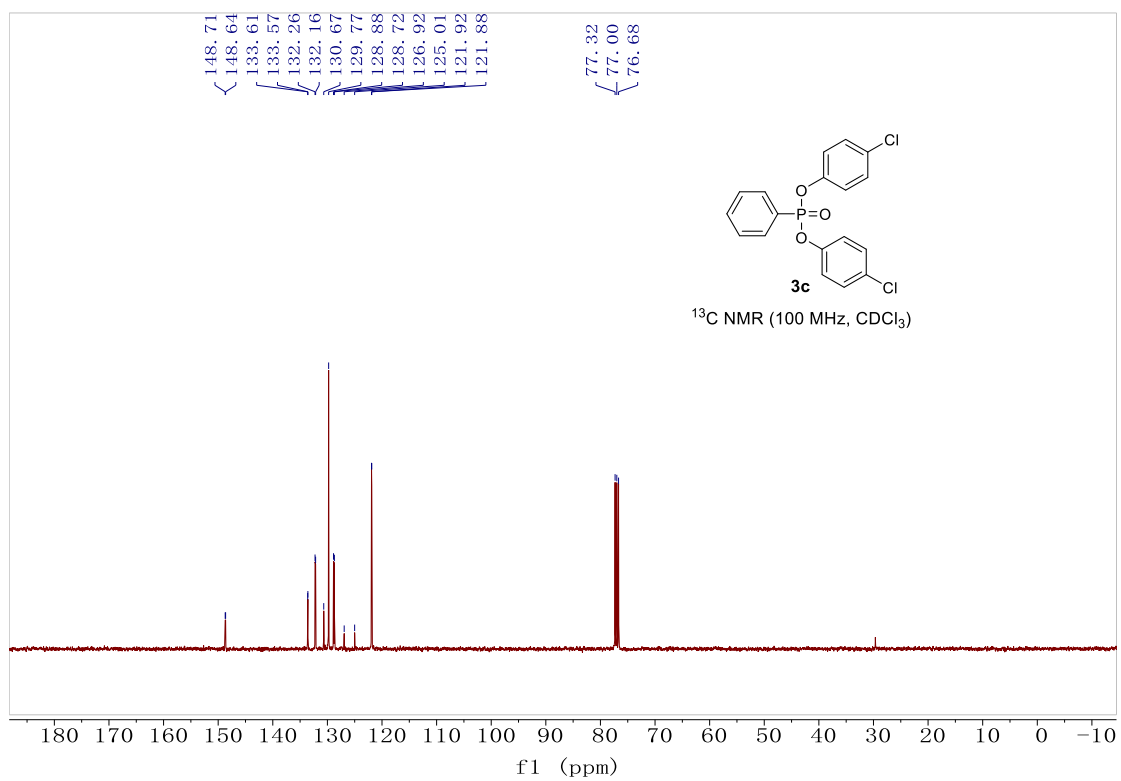
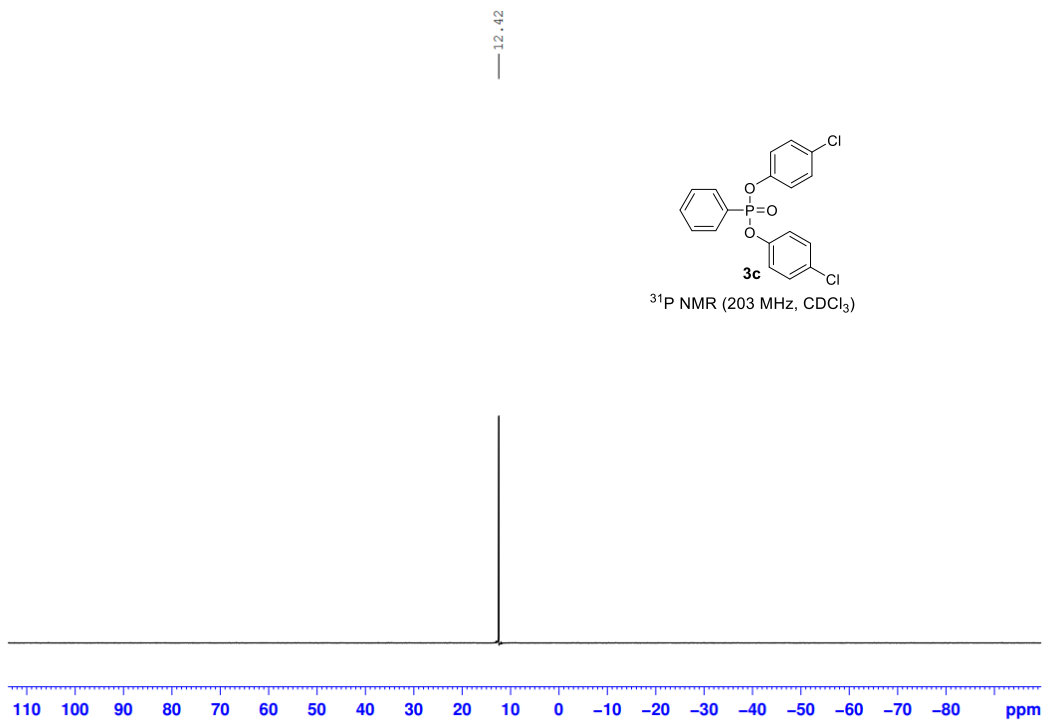
8. Charts of compounds

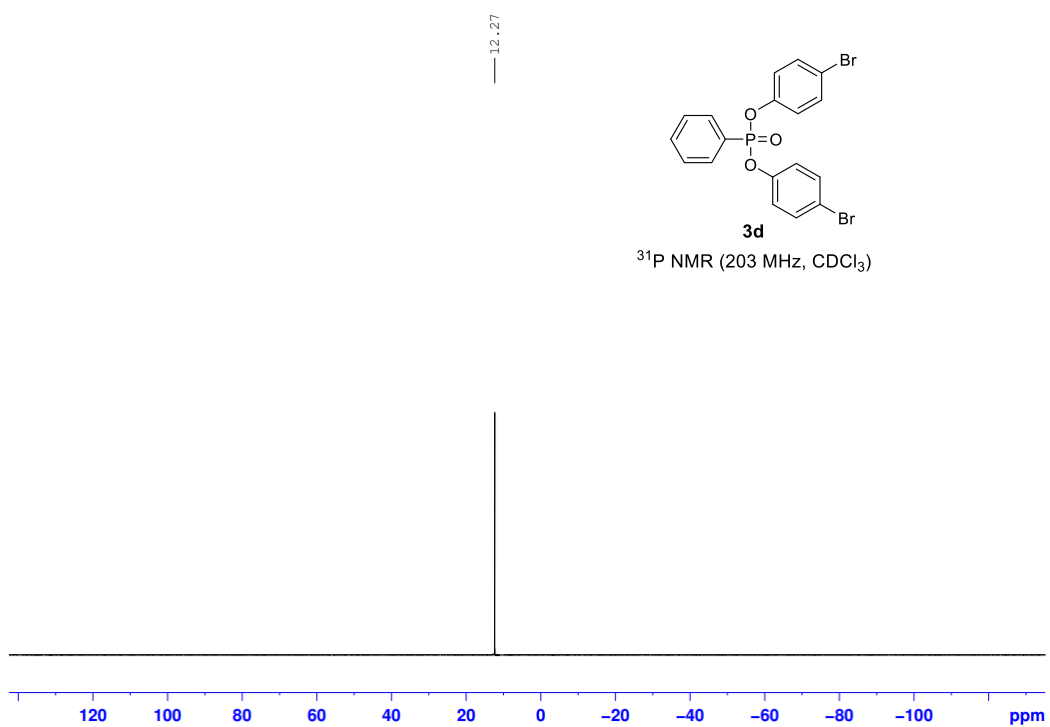
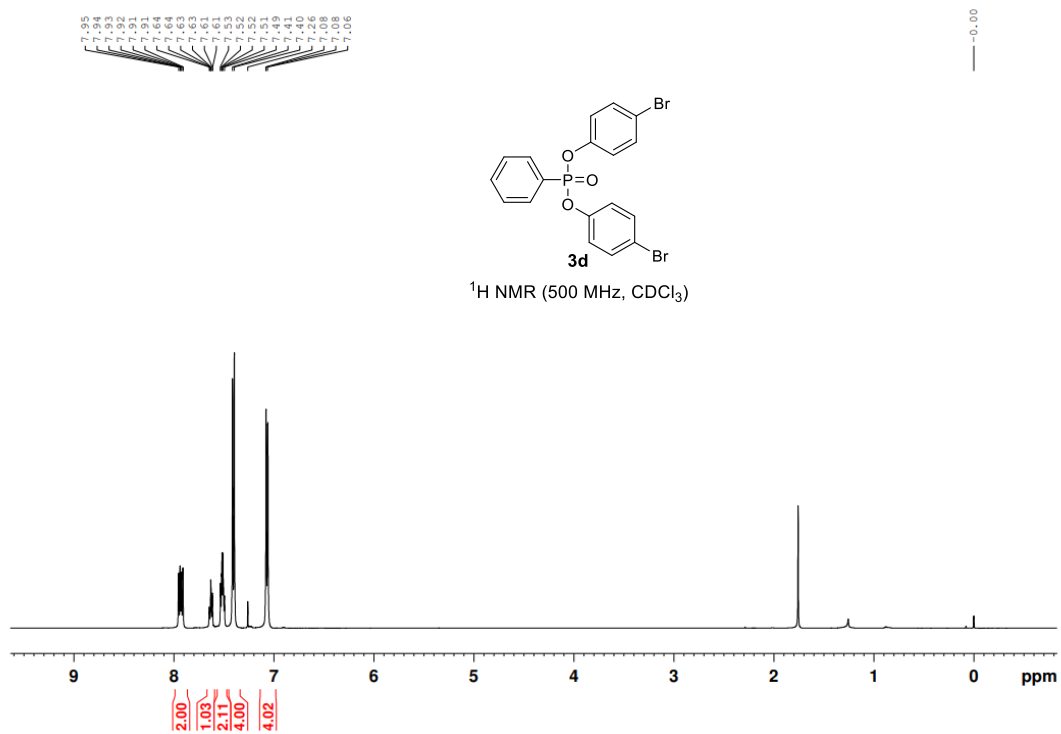


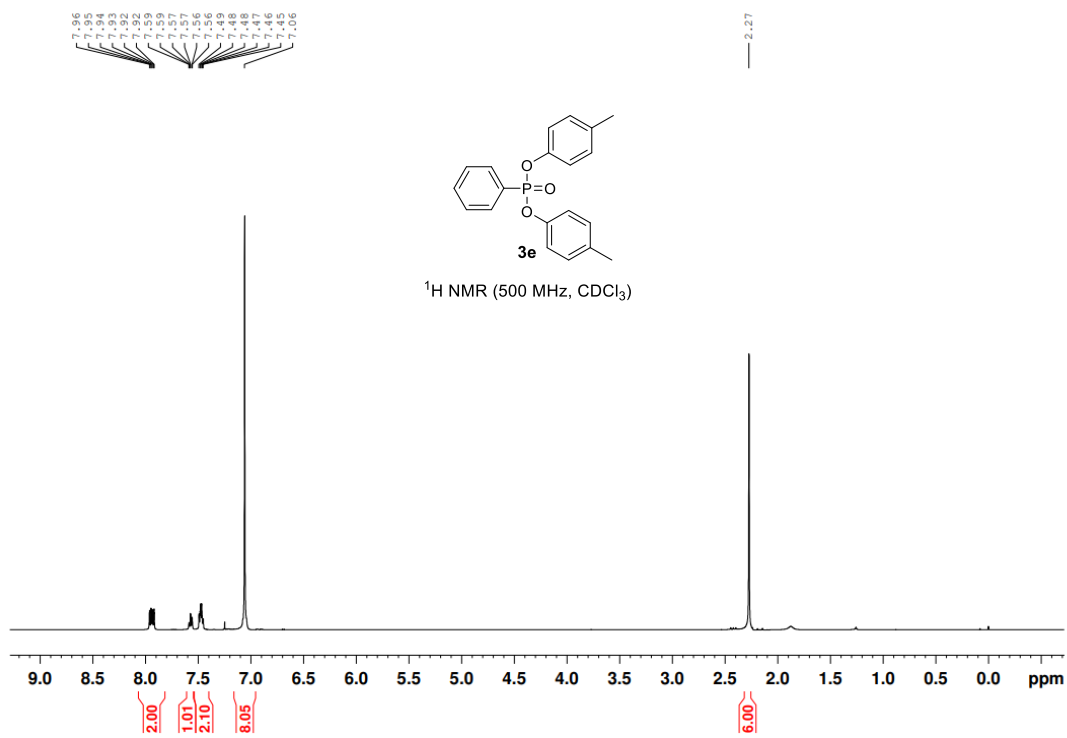
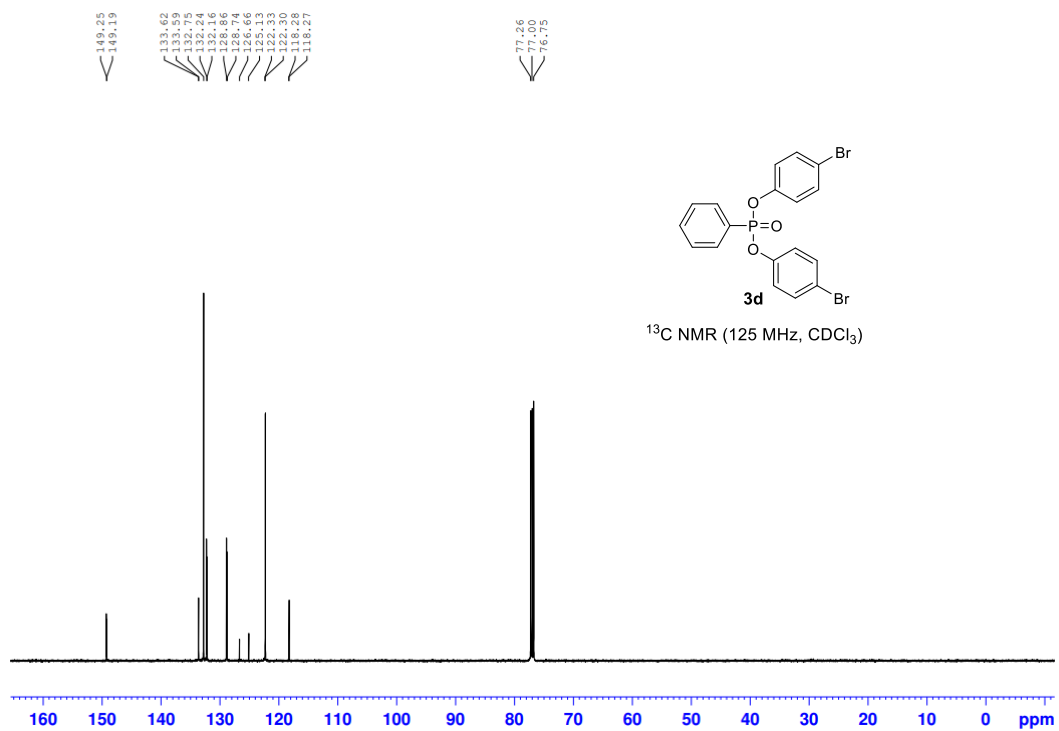


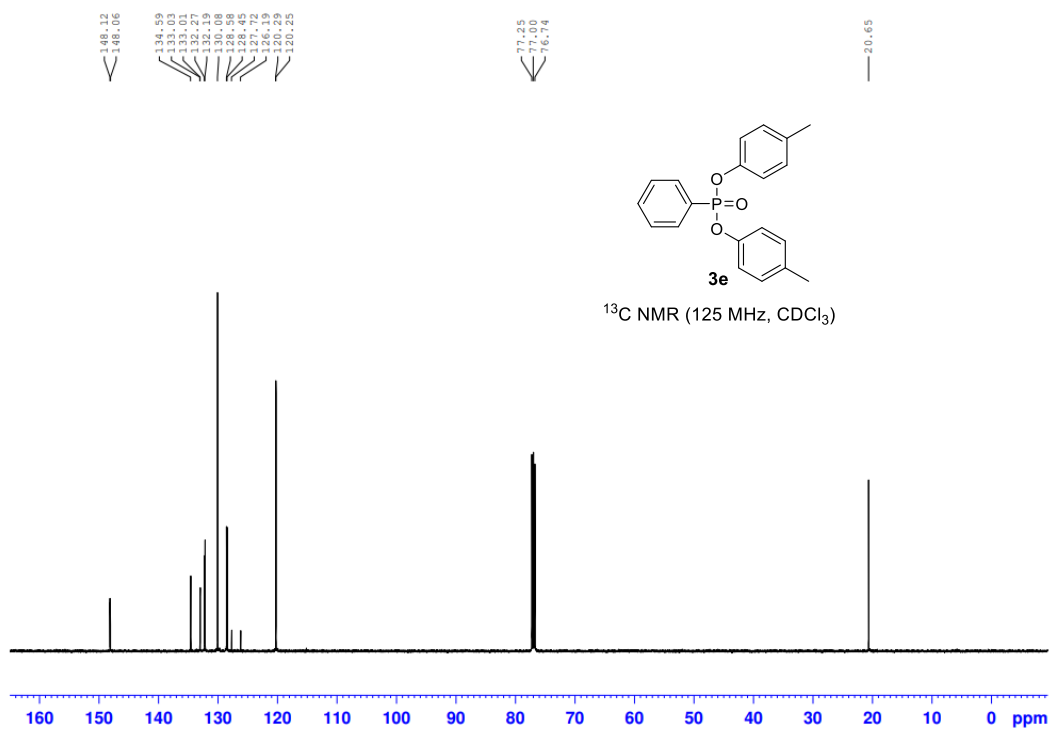
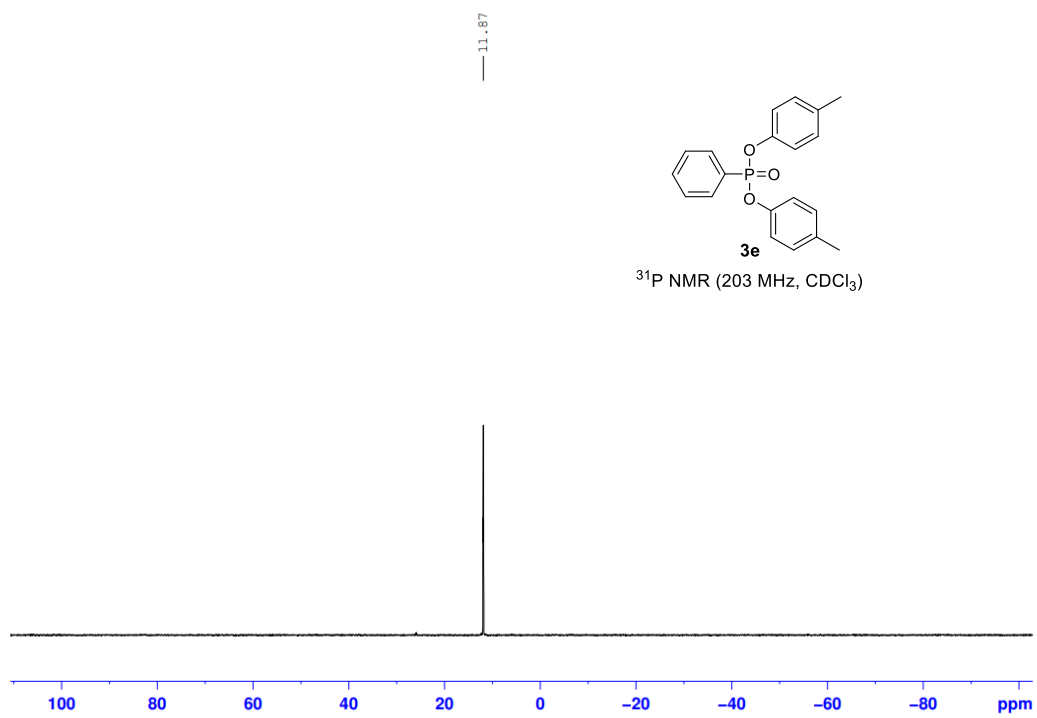


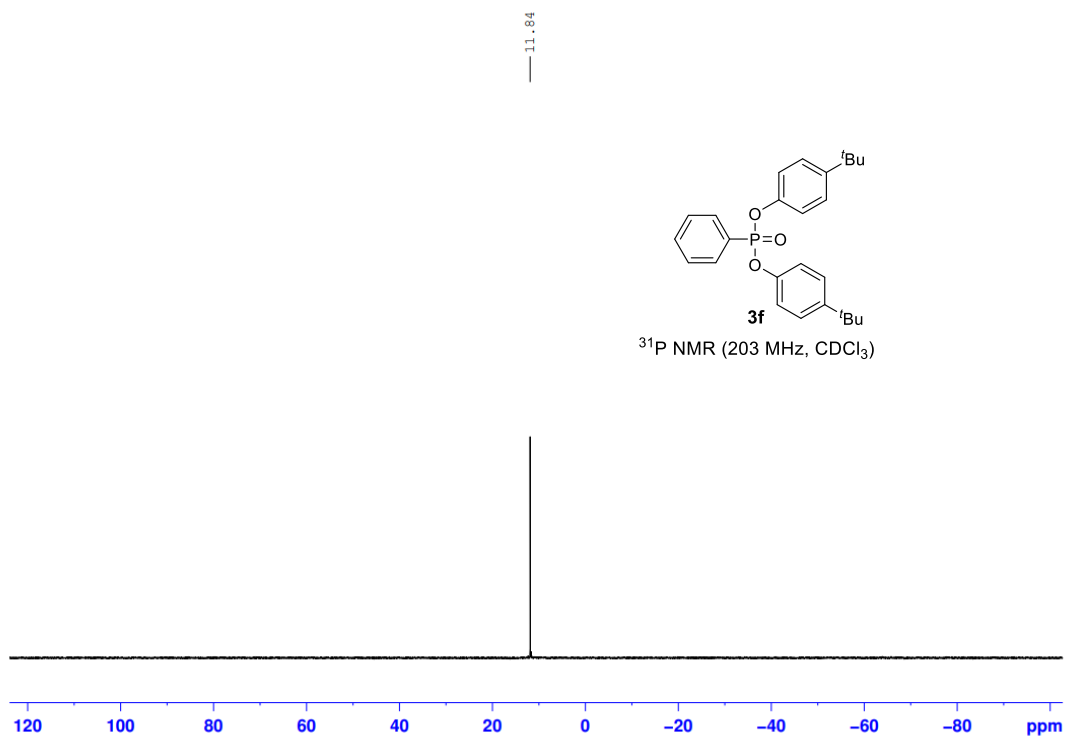
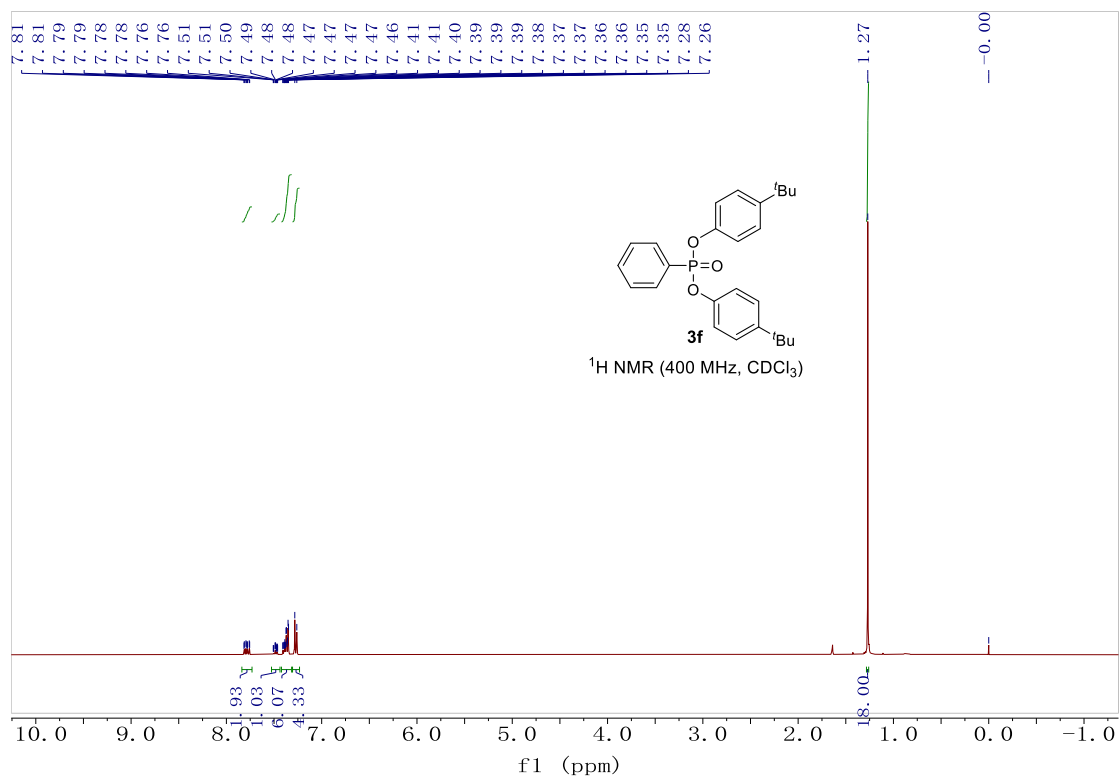


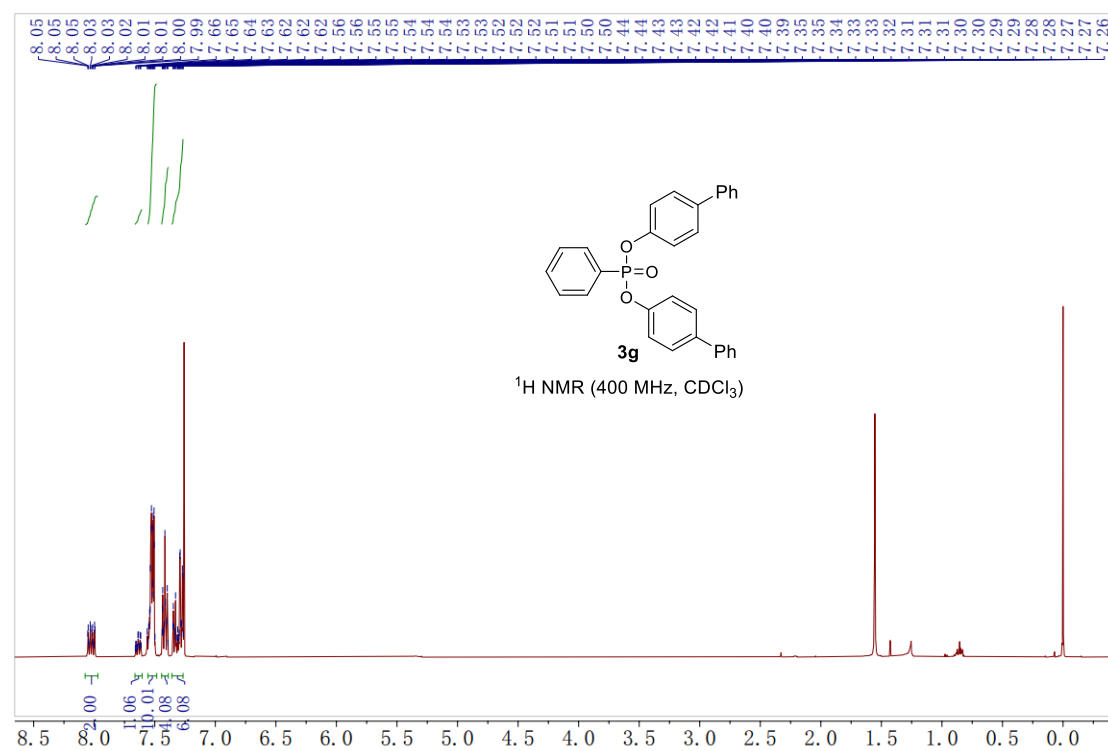
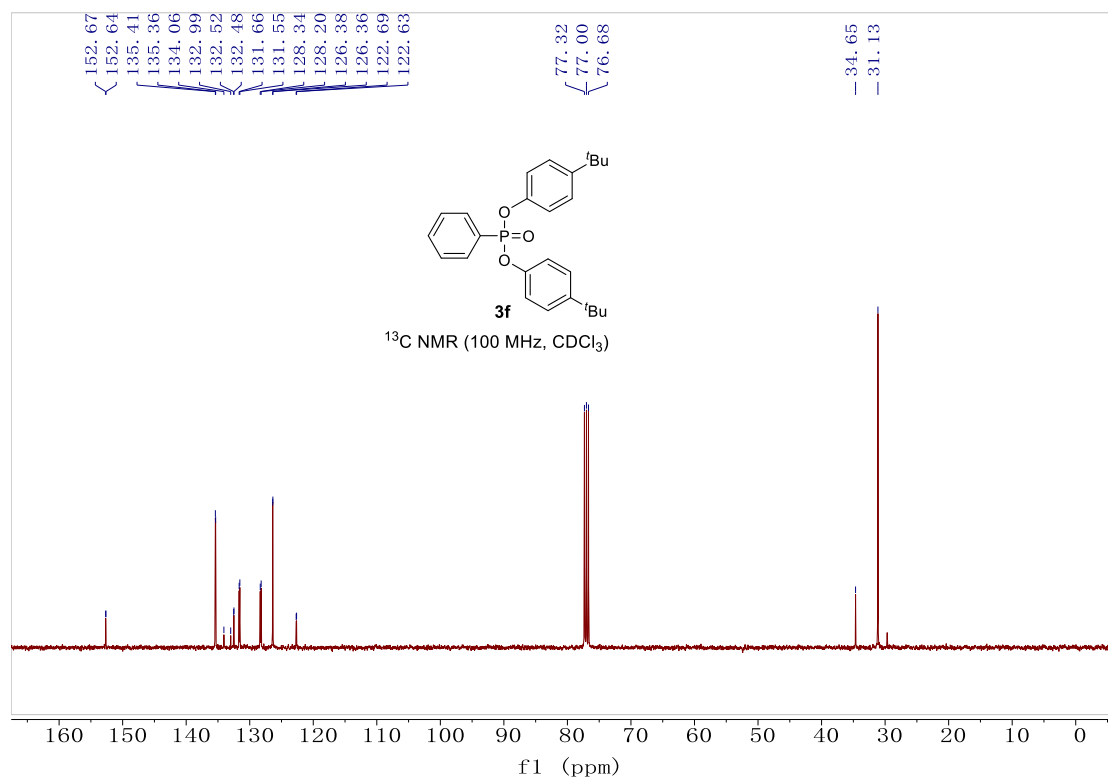


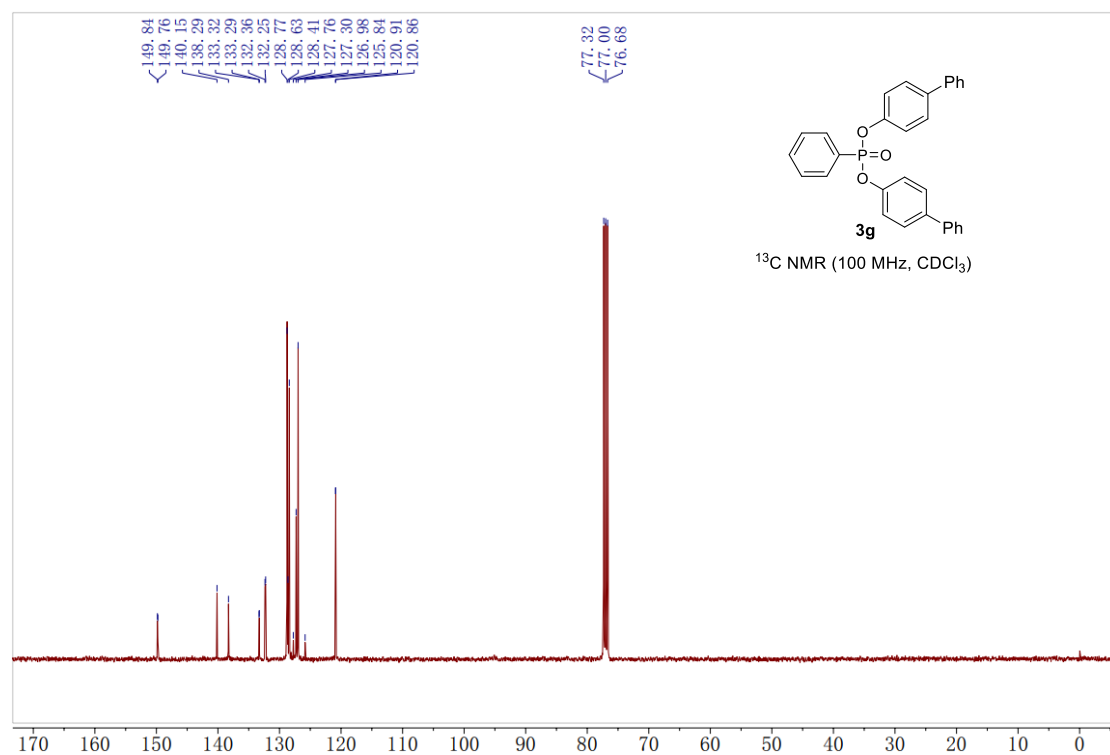
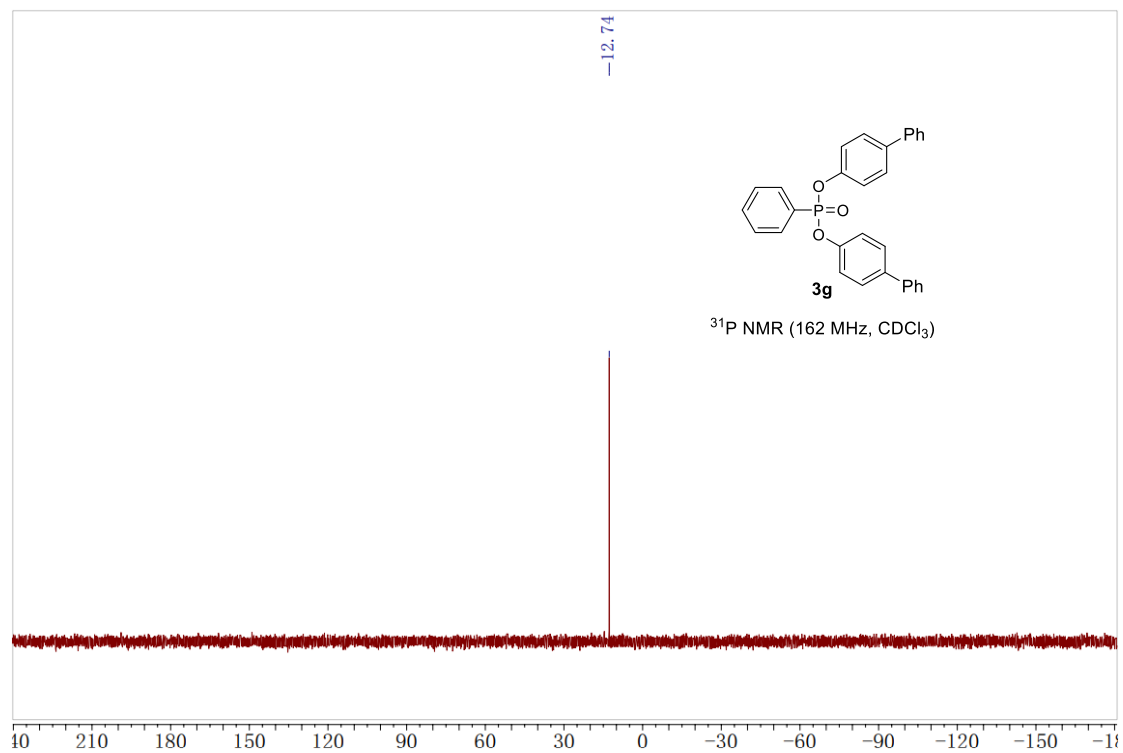


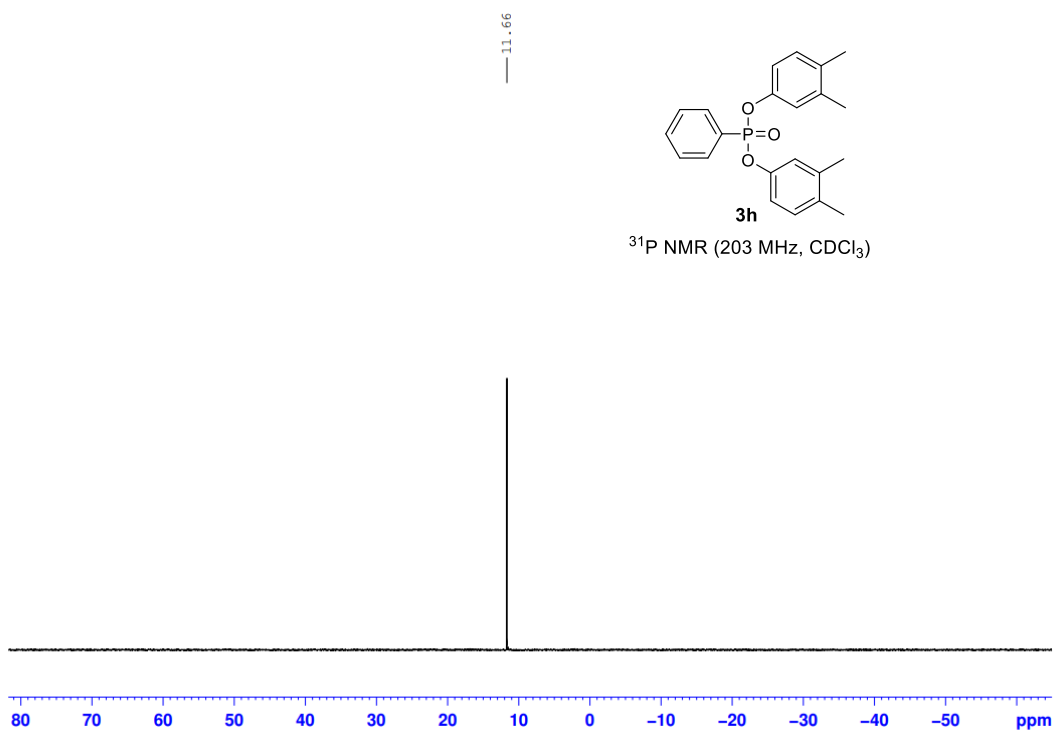
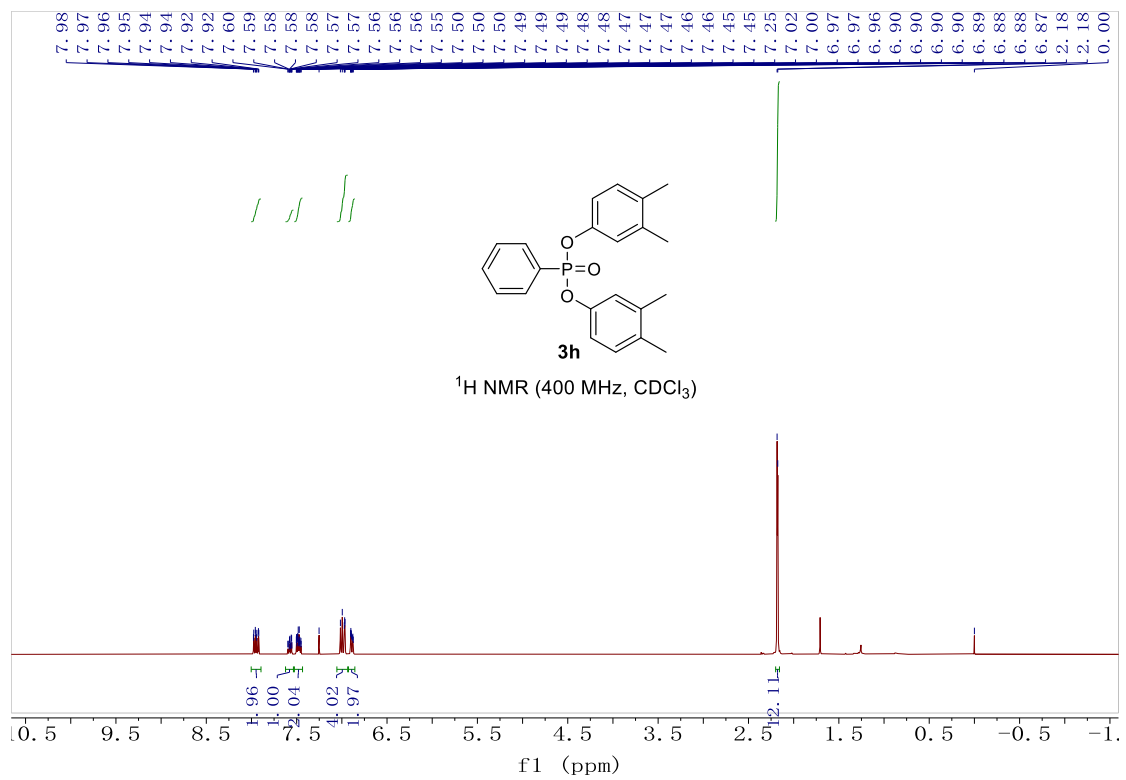


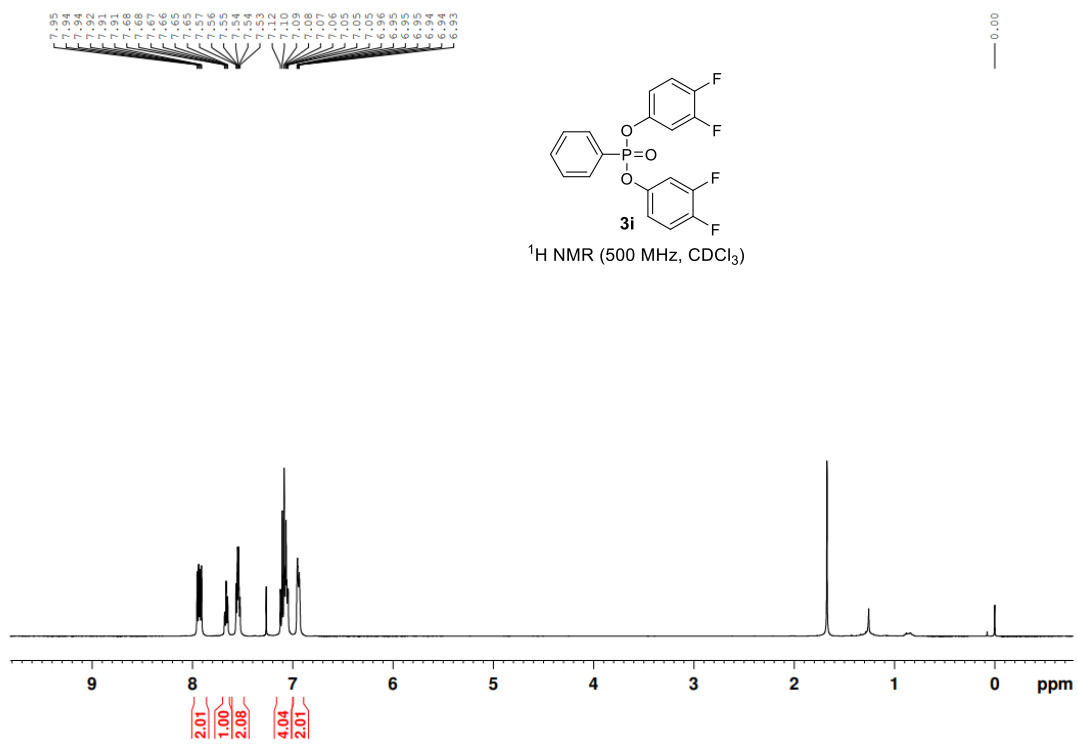
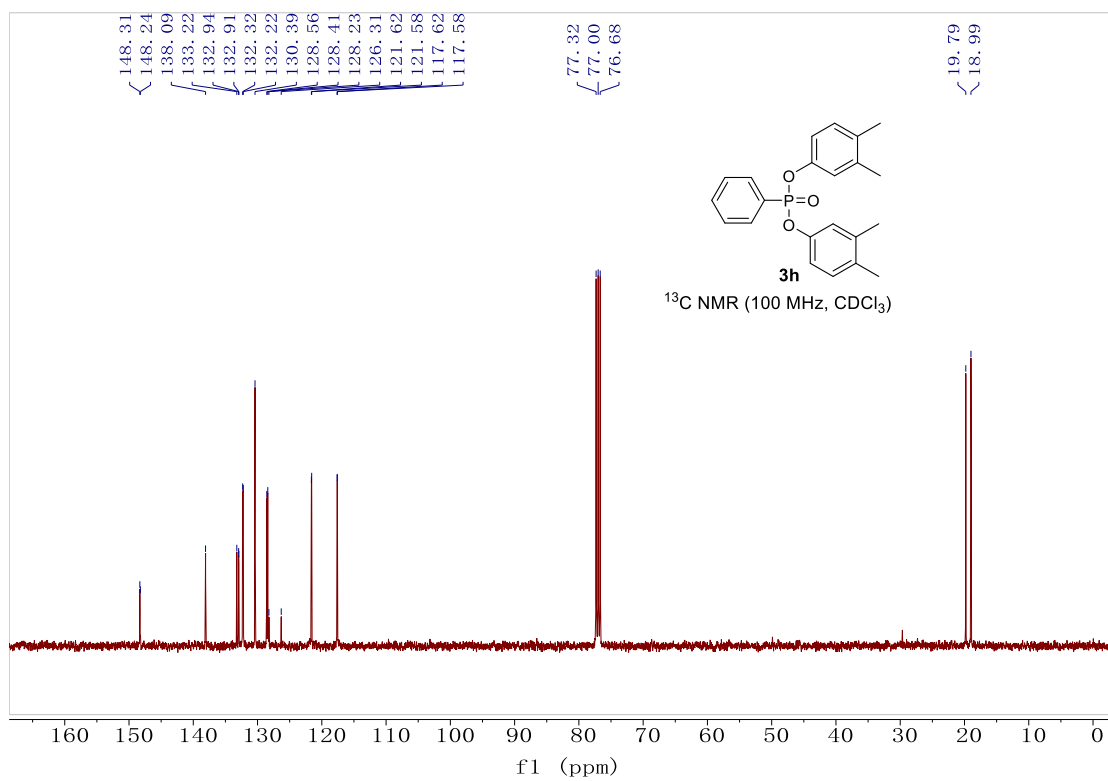


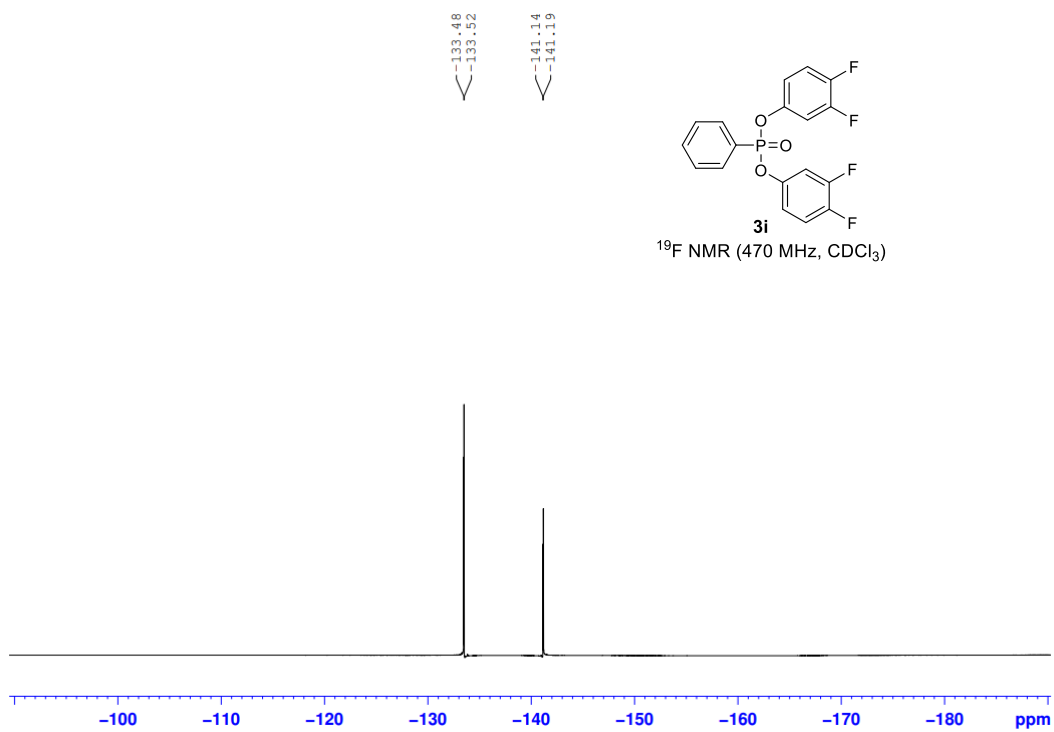
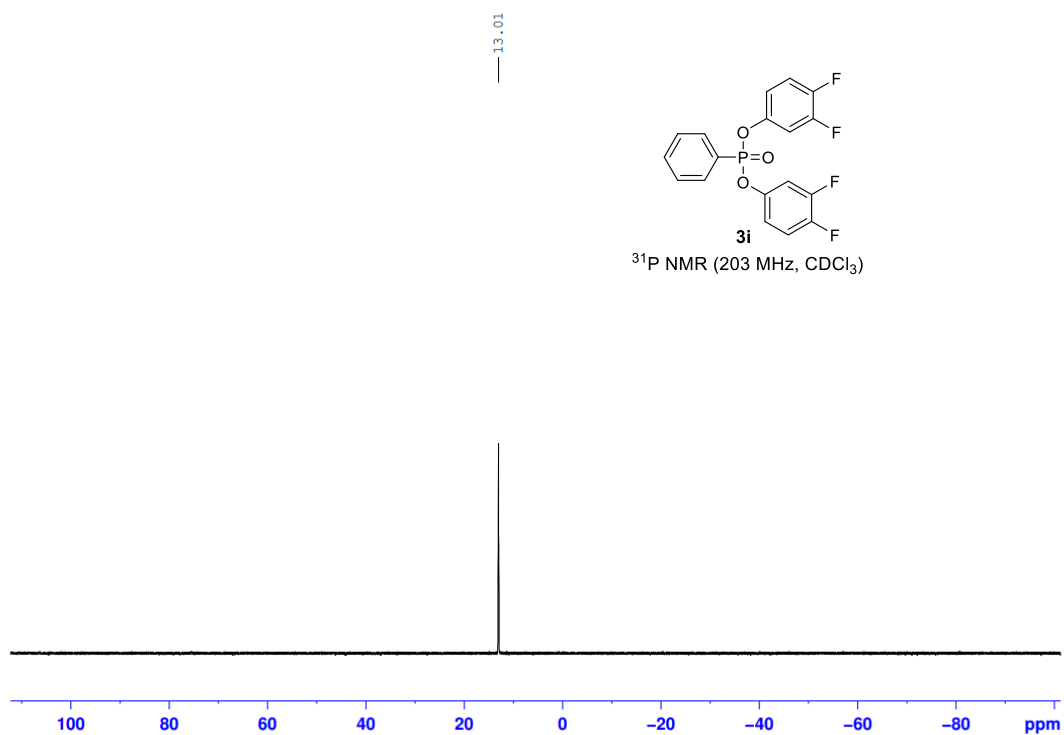


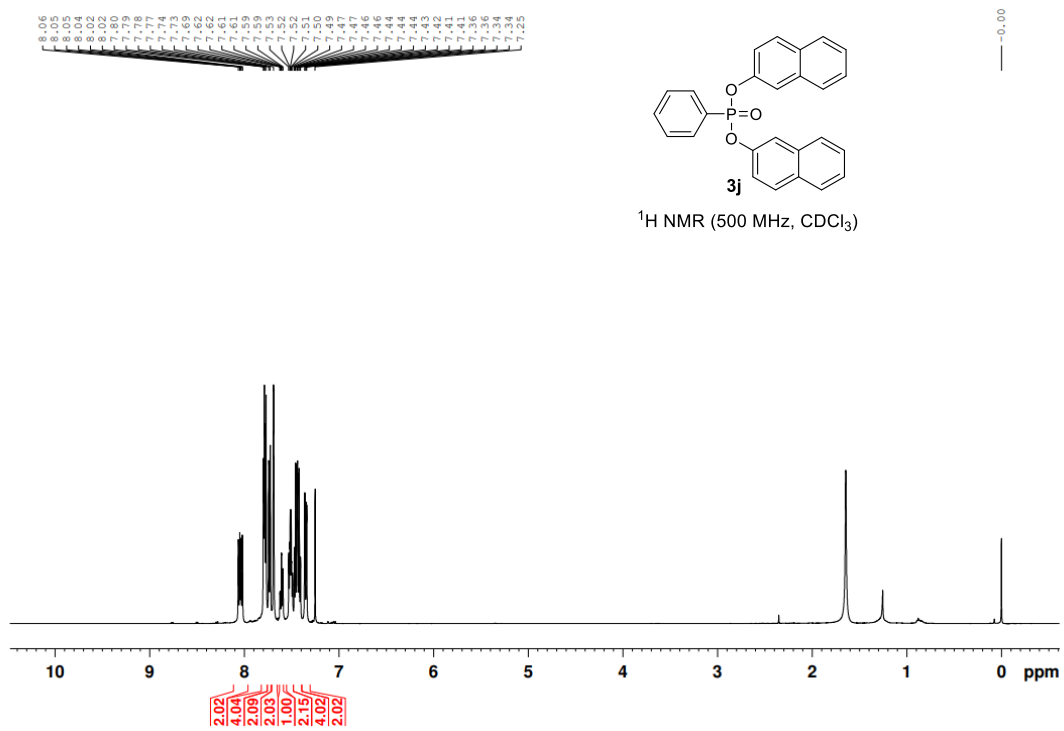
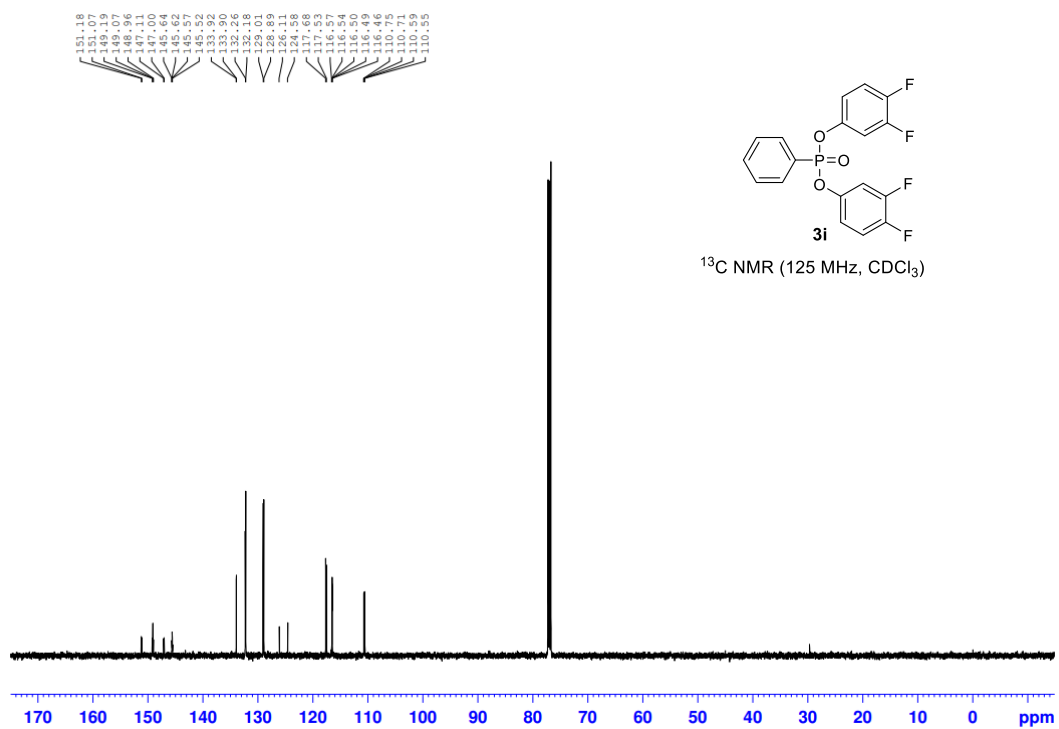


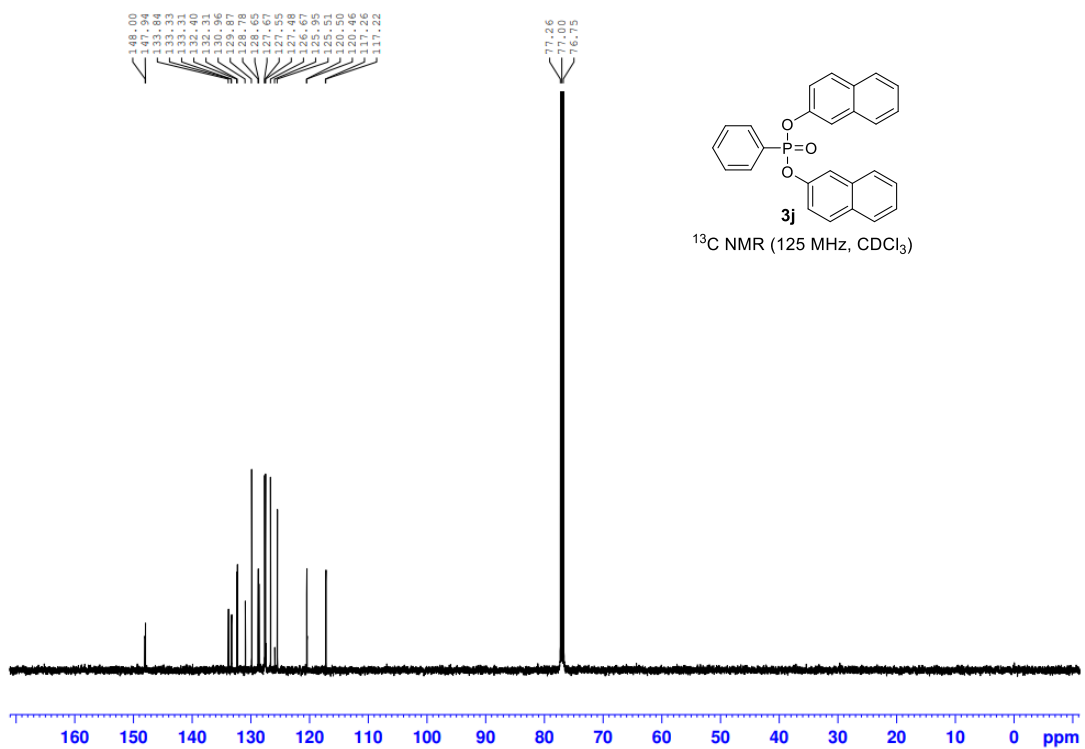
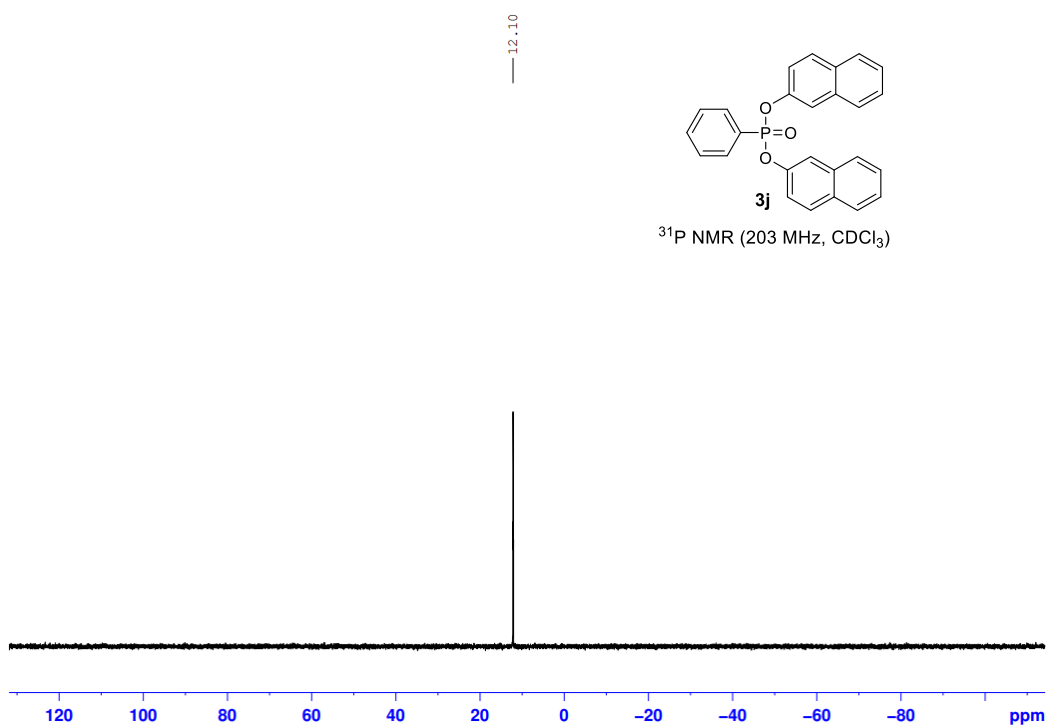


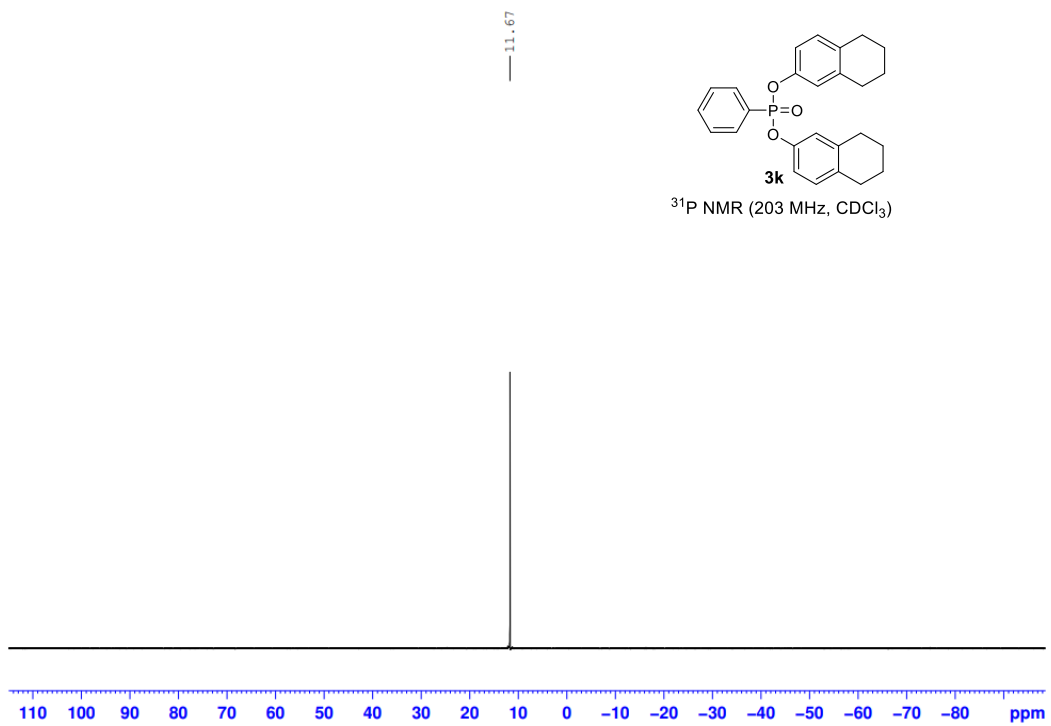
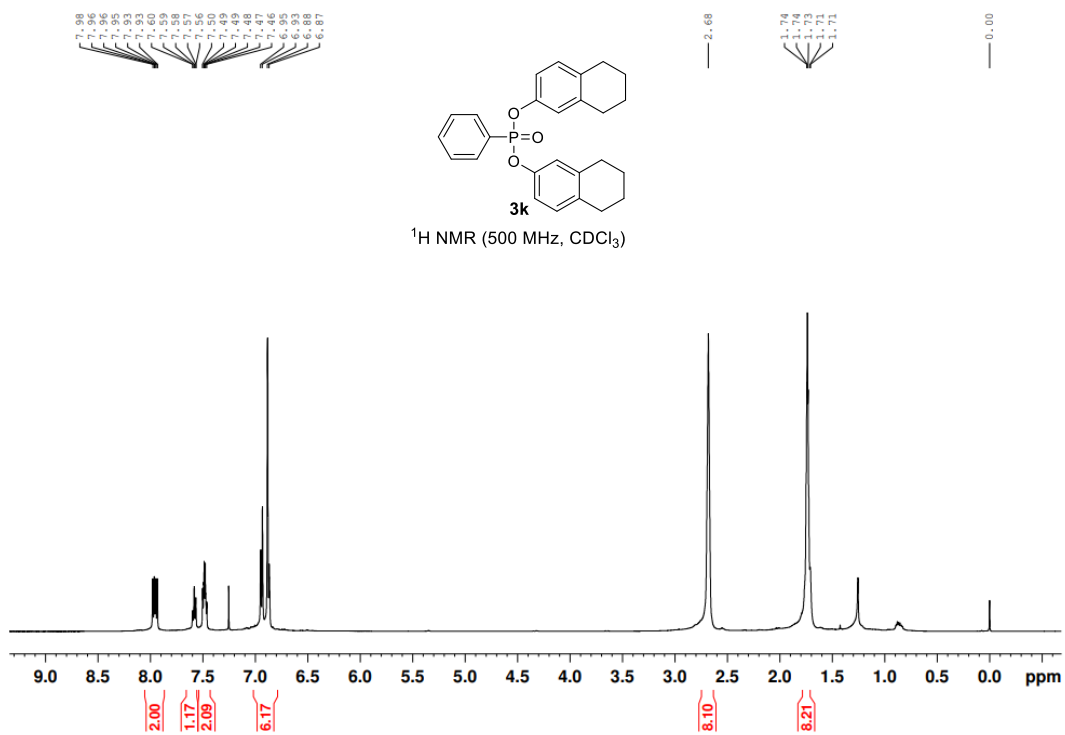


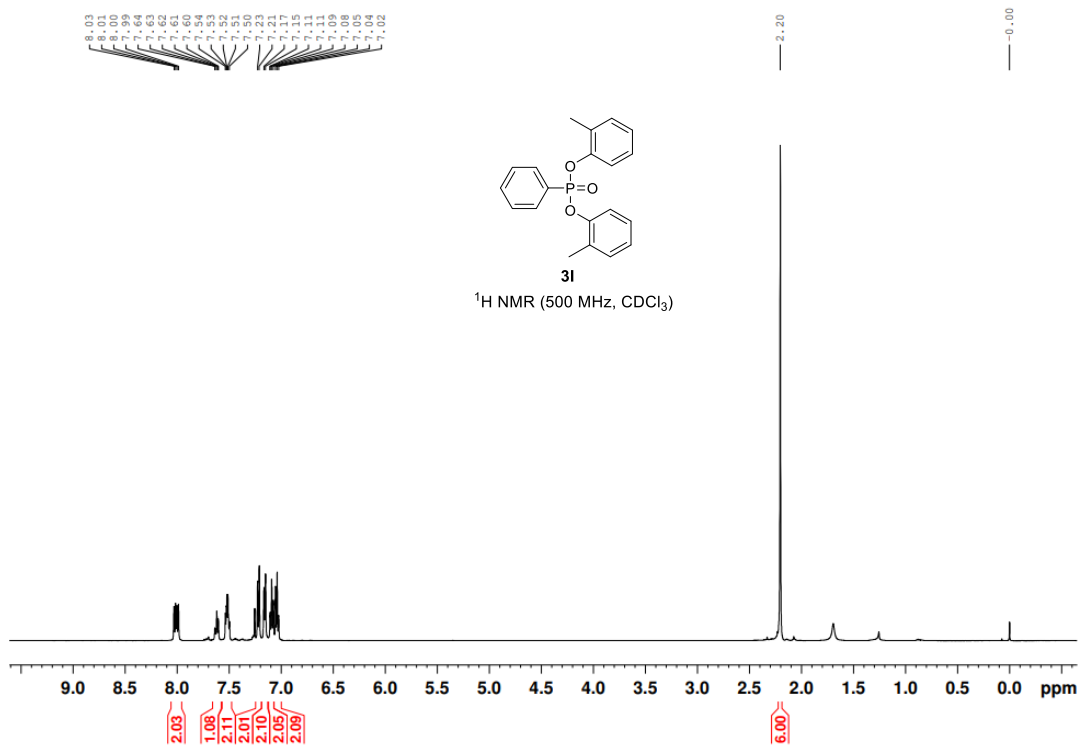
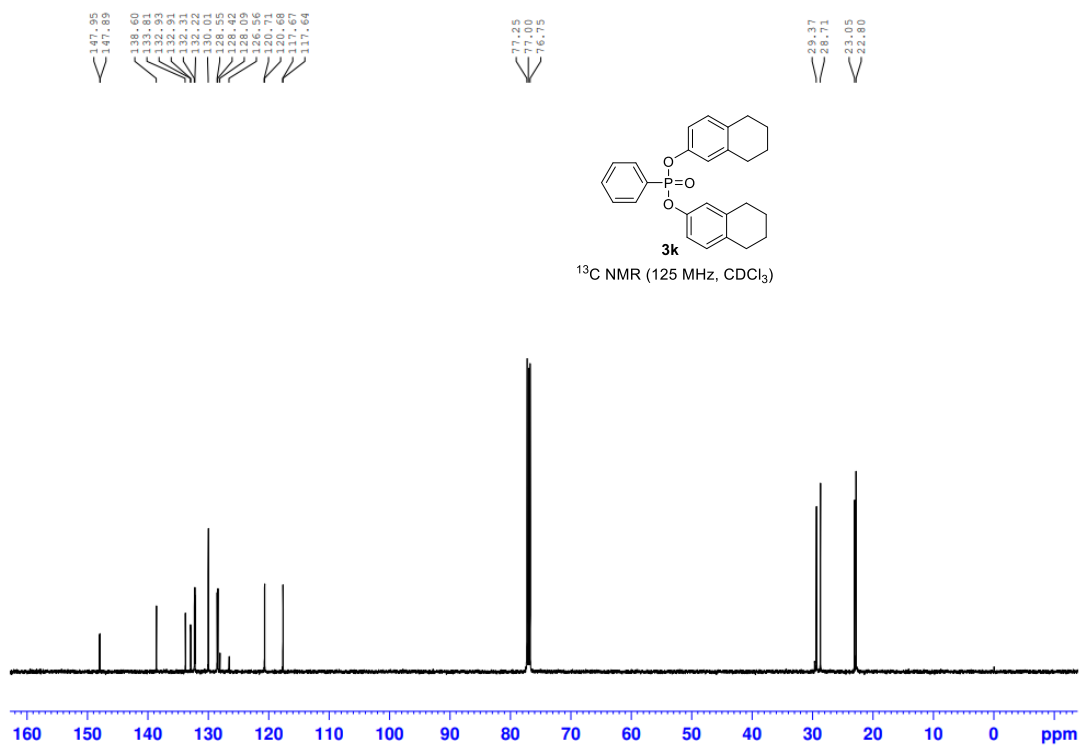


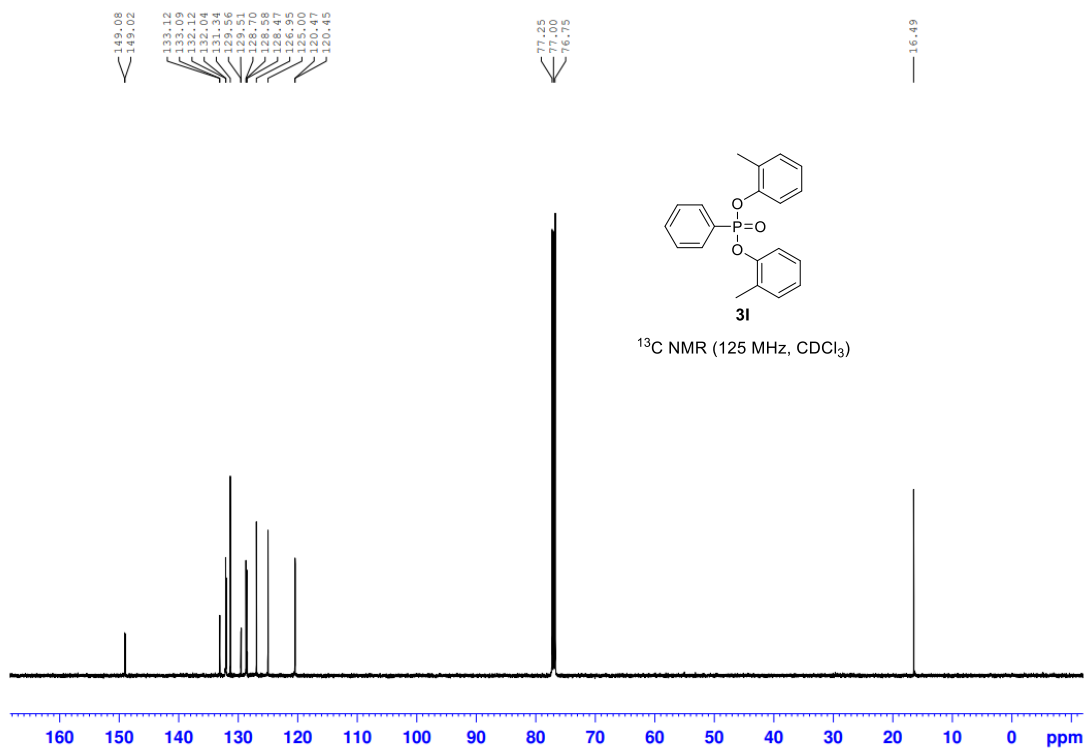
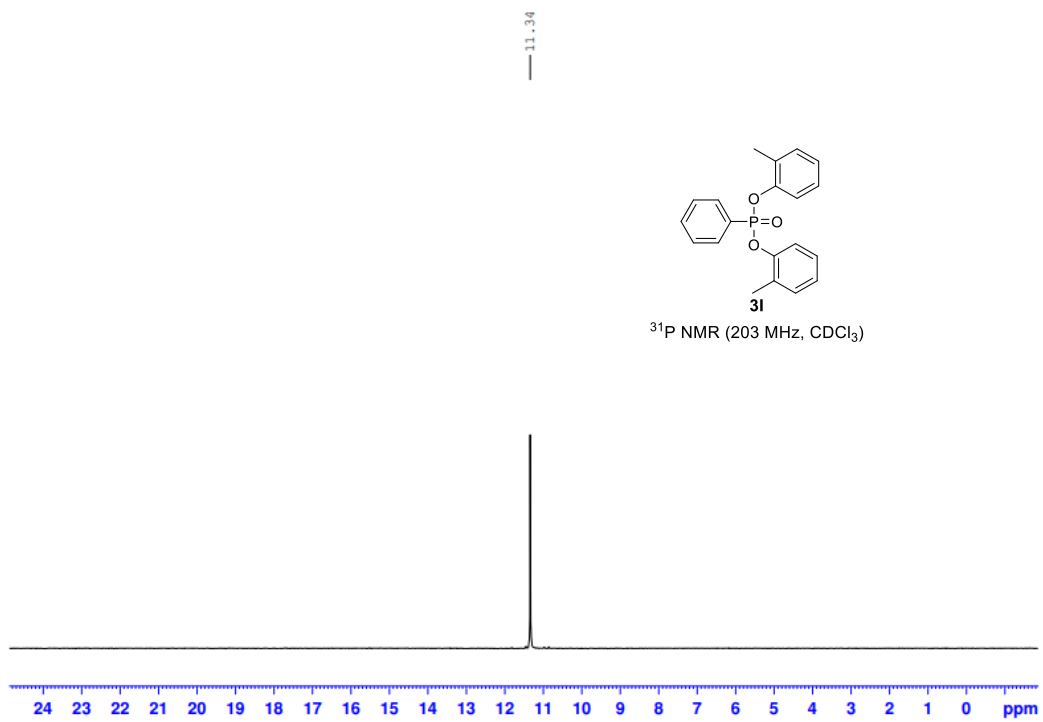


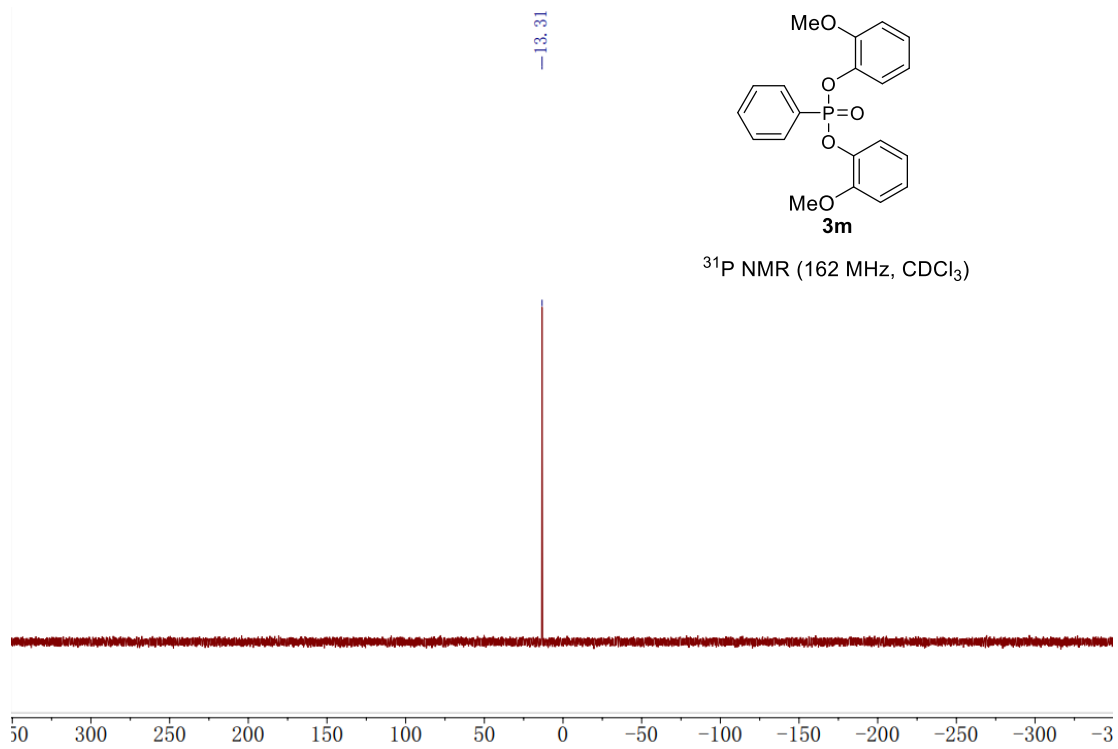
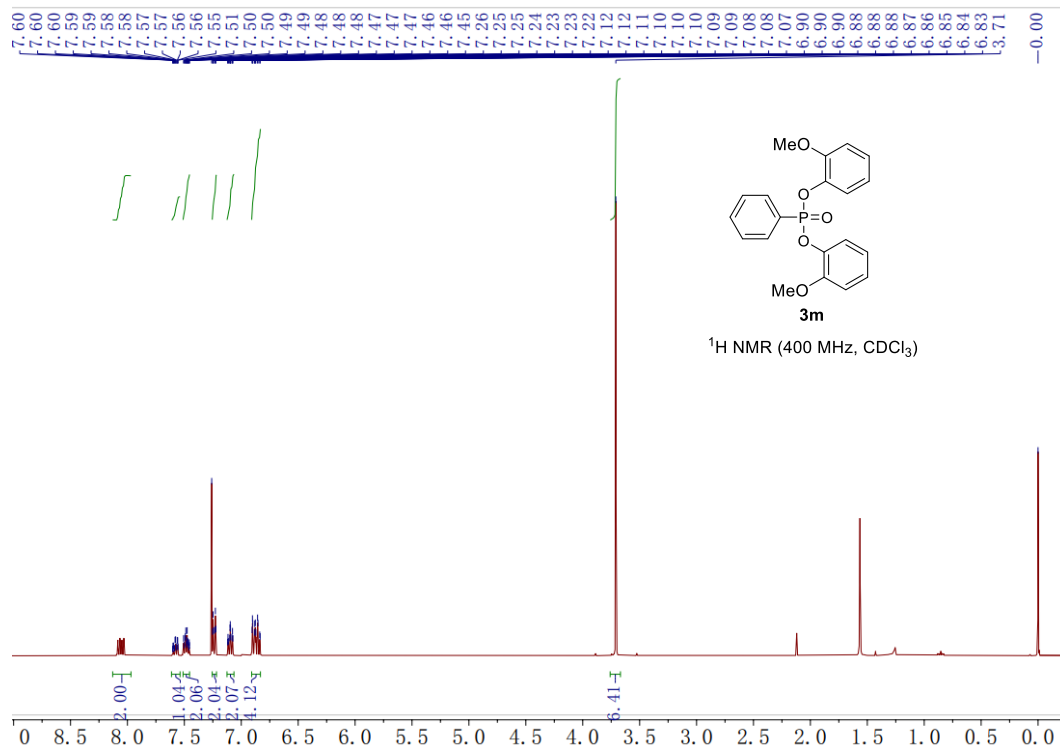


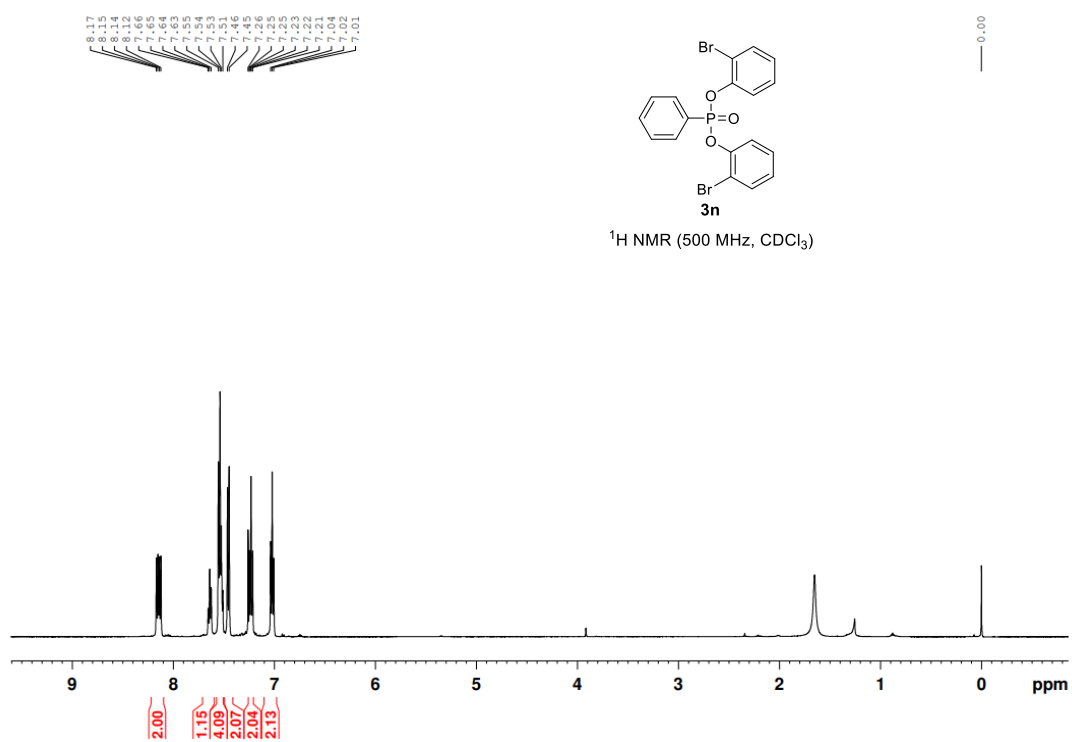
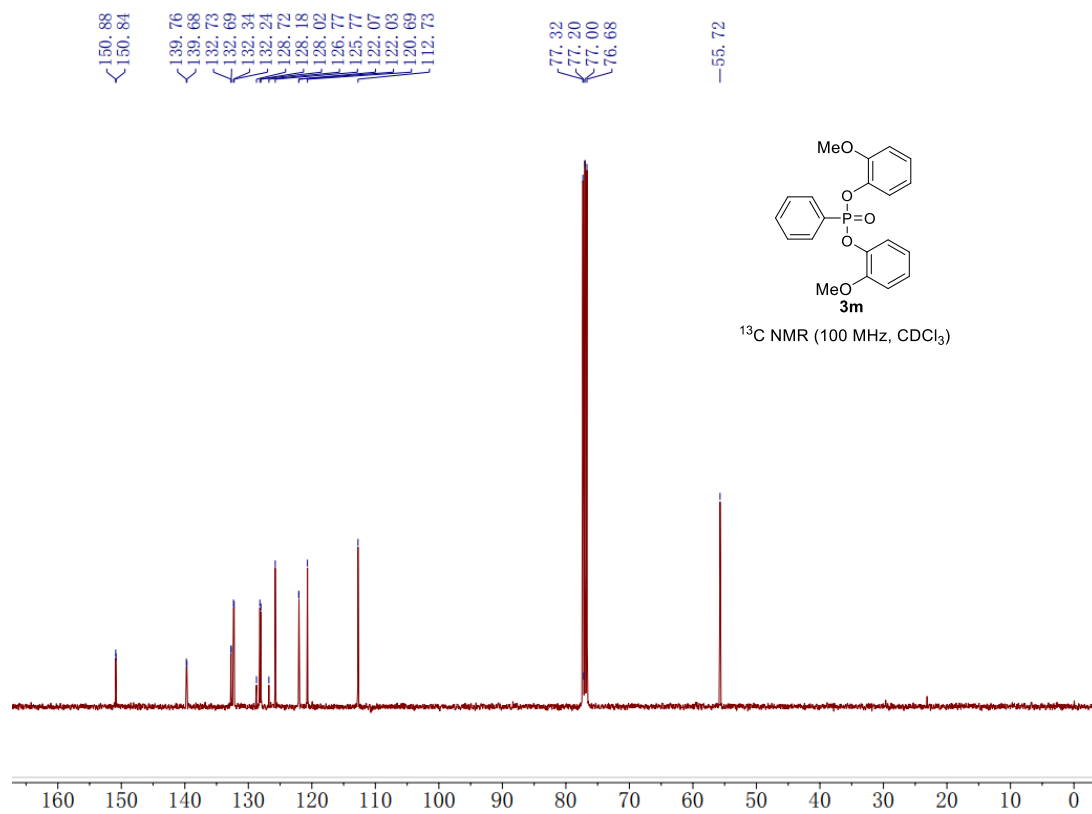


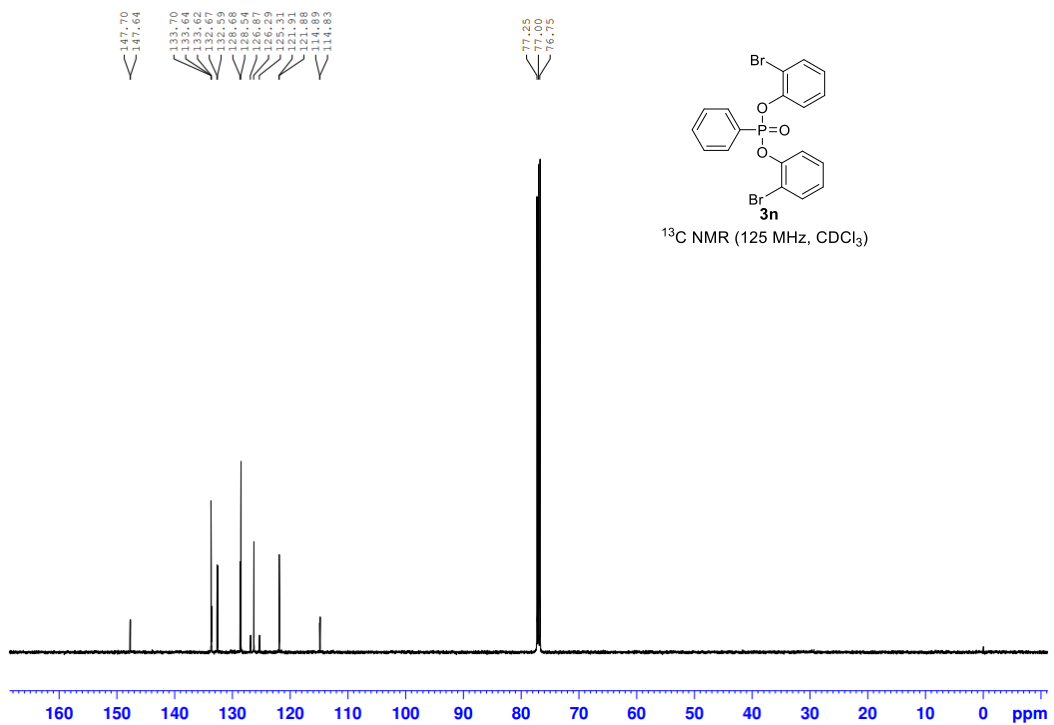
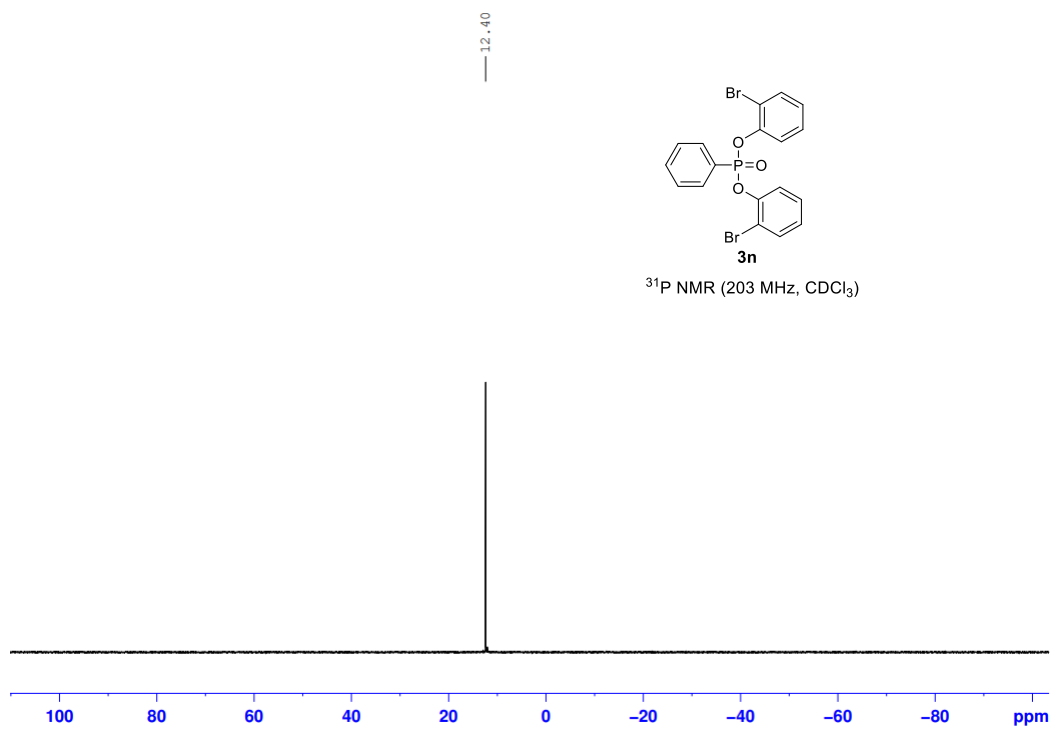


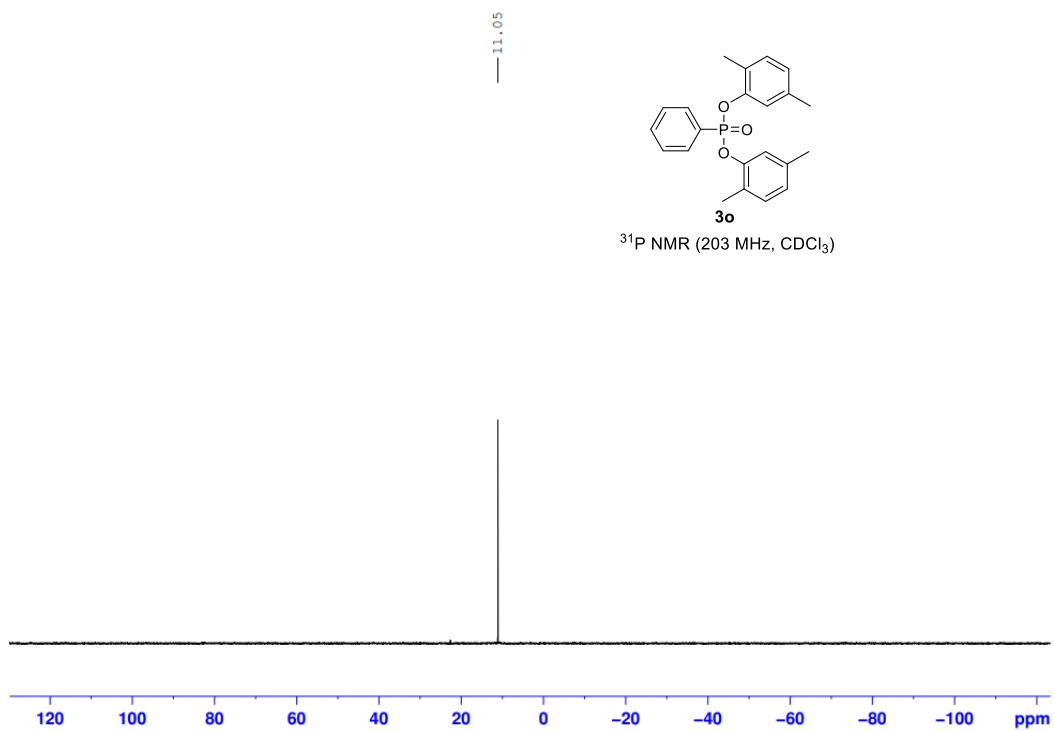
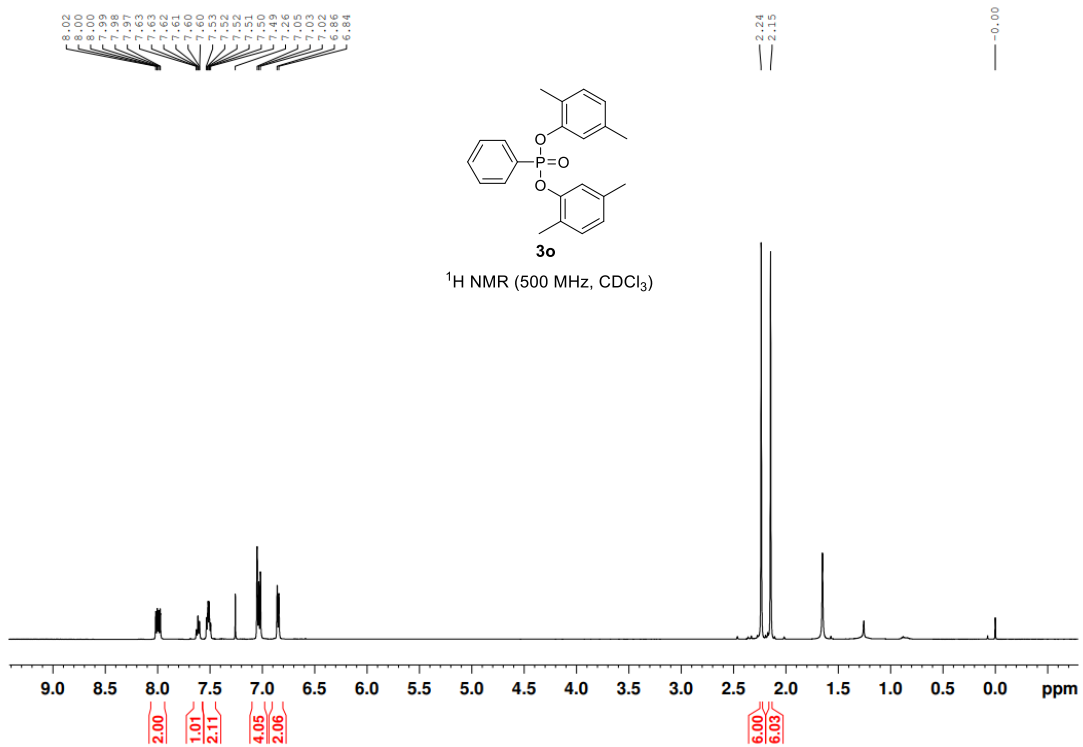


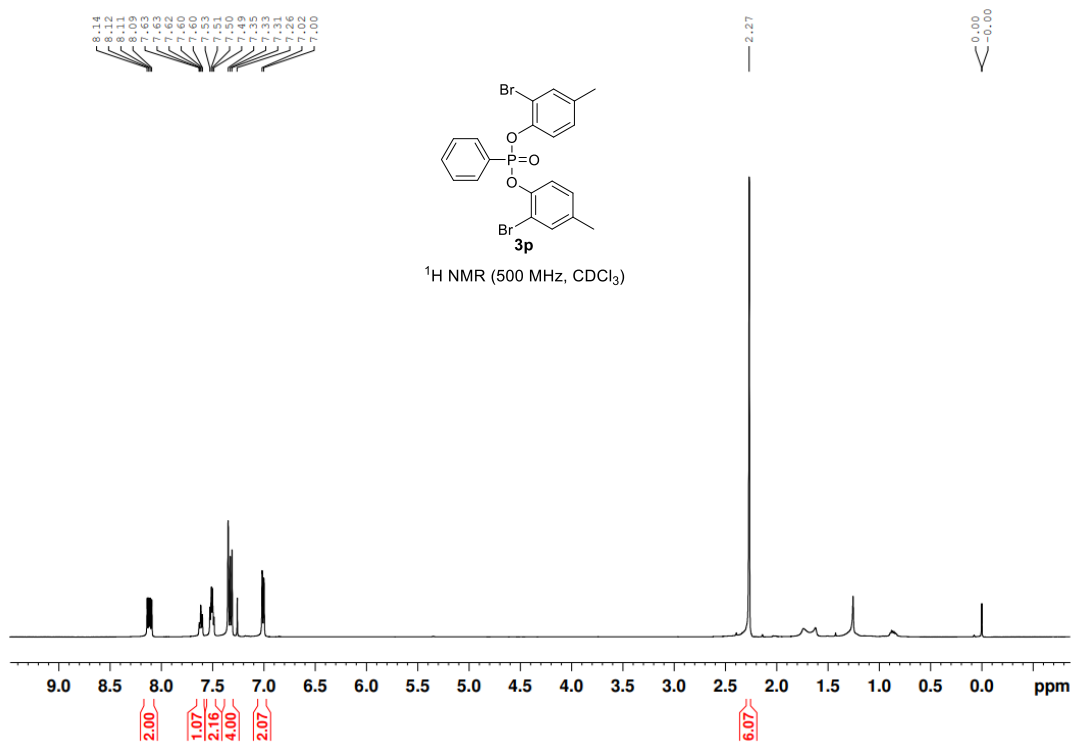
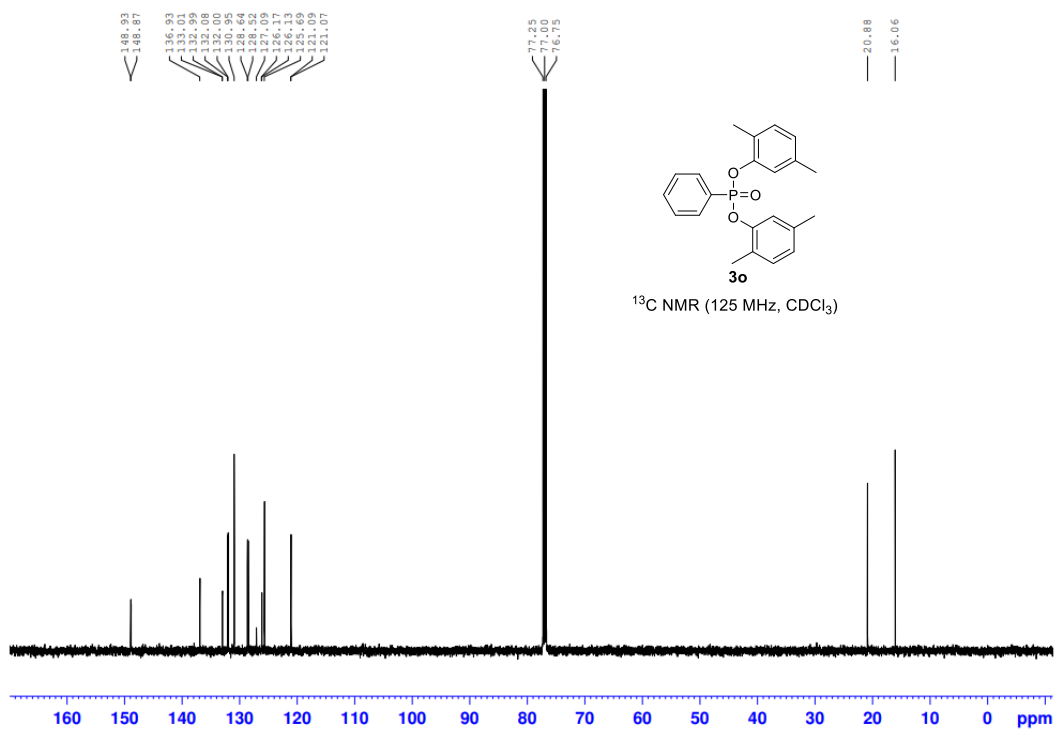


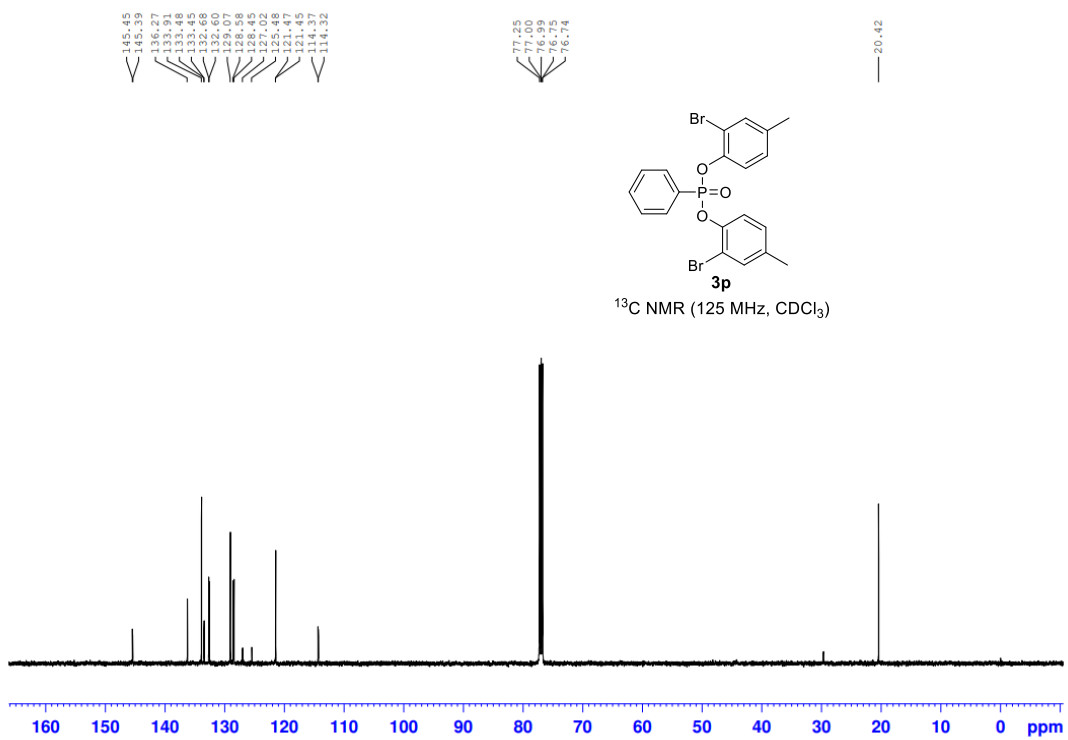
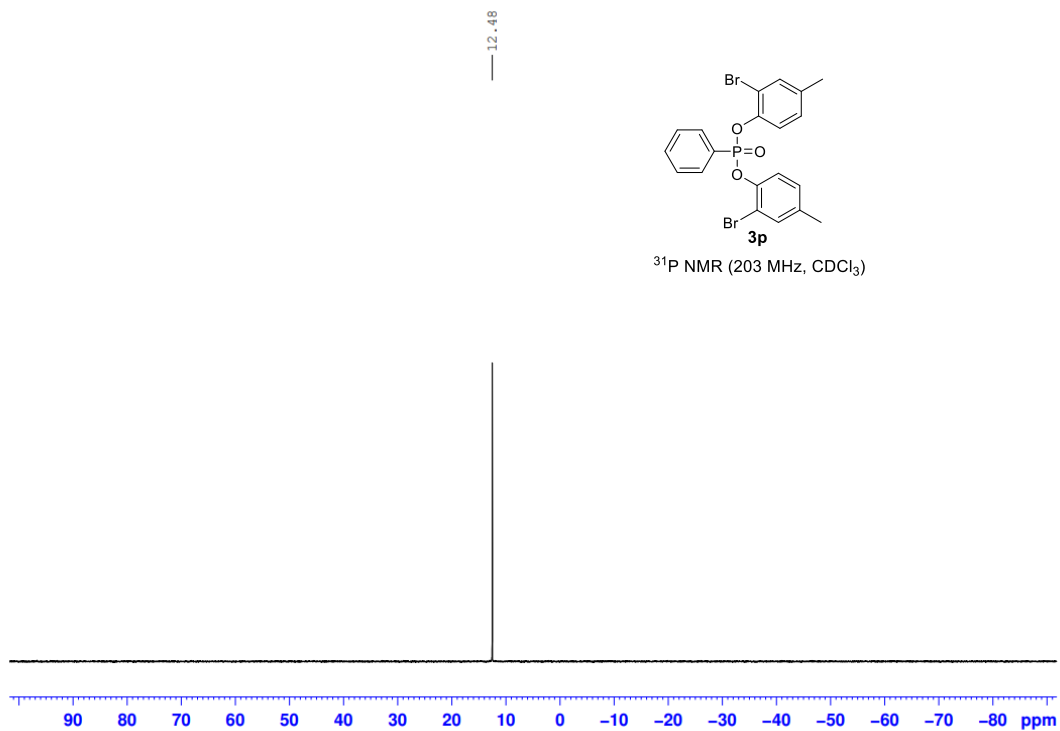


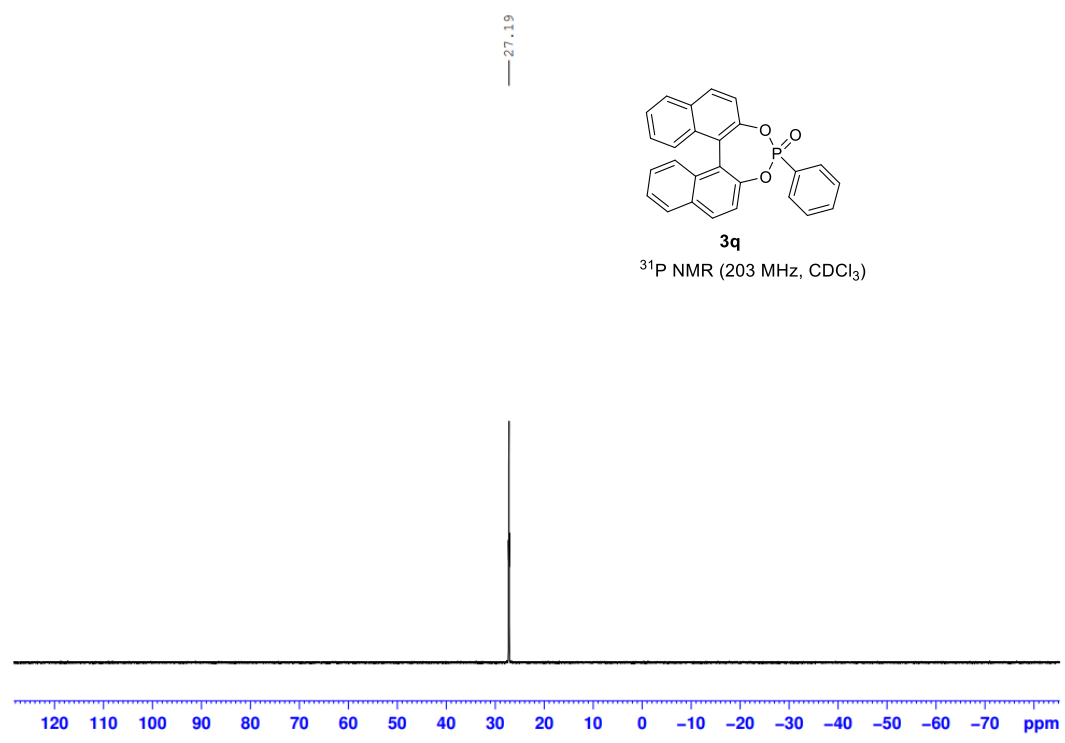
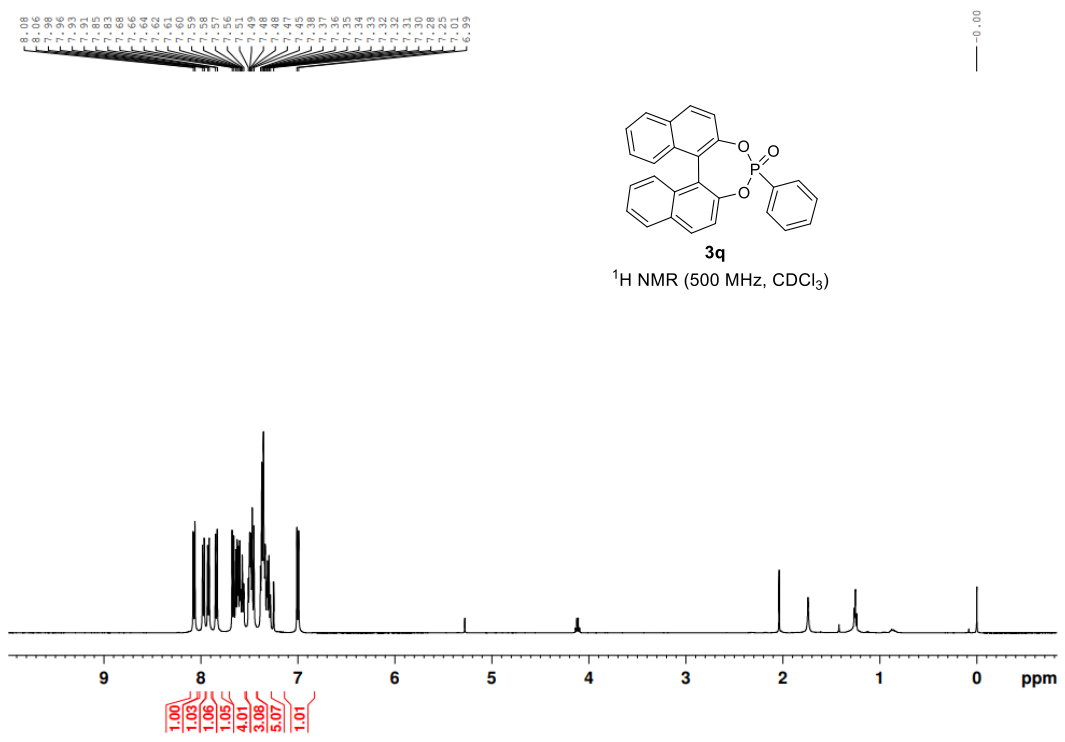


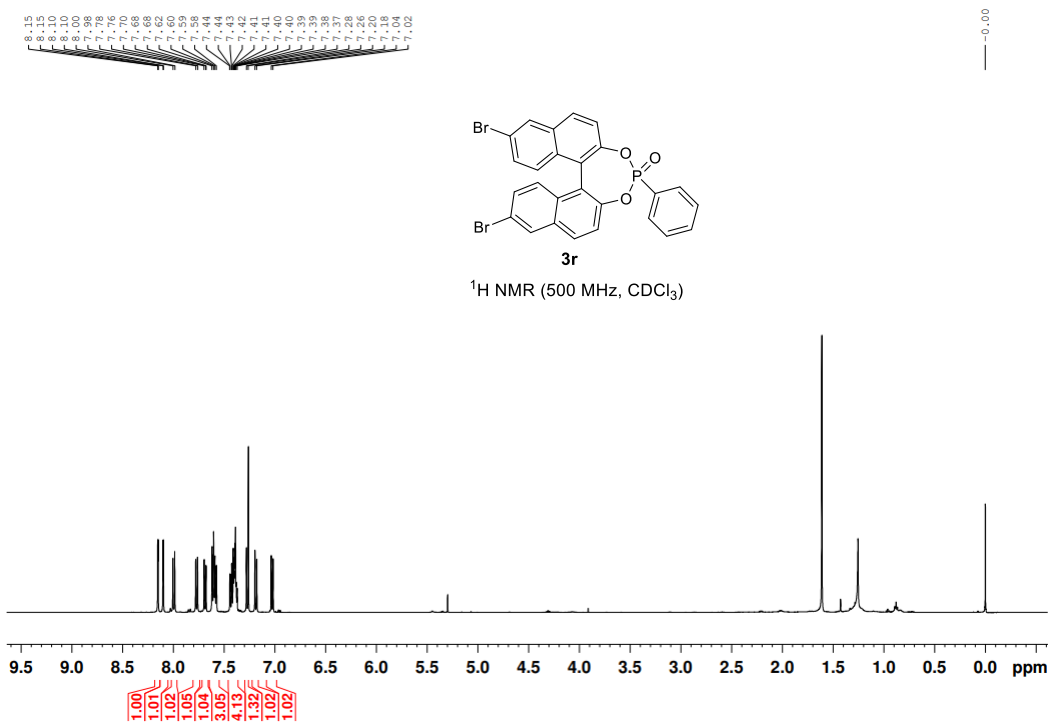
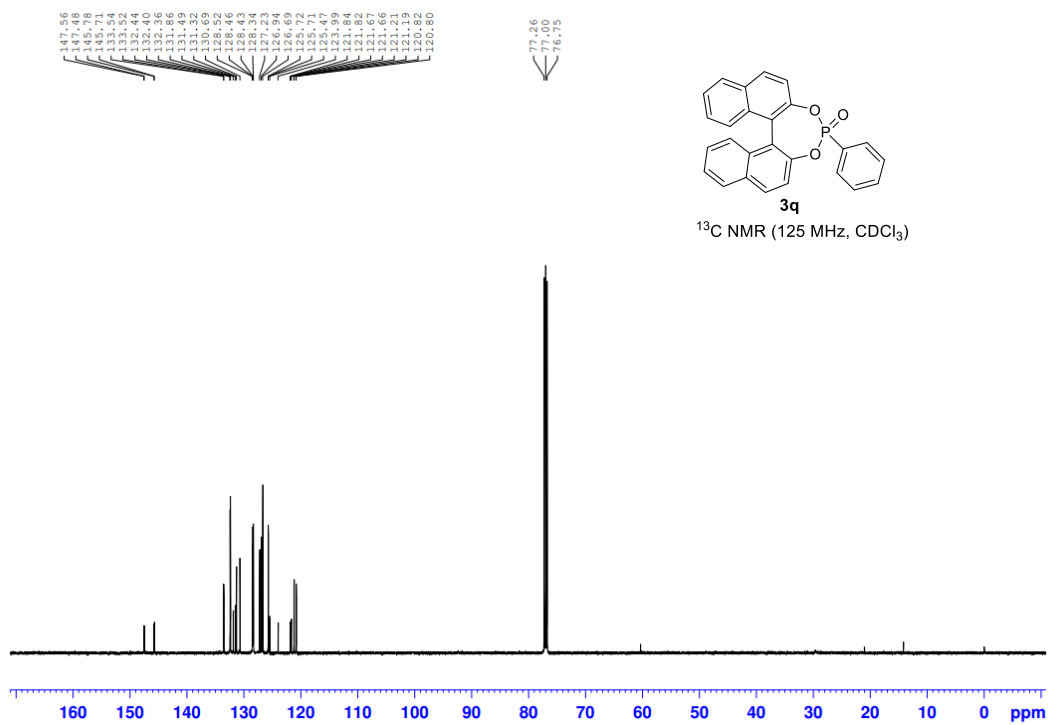




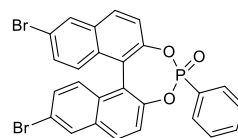






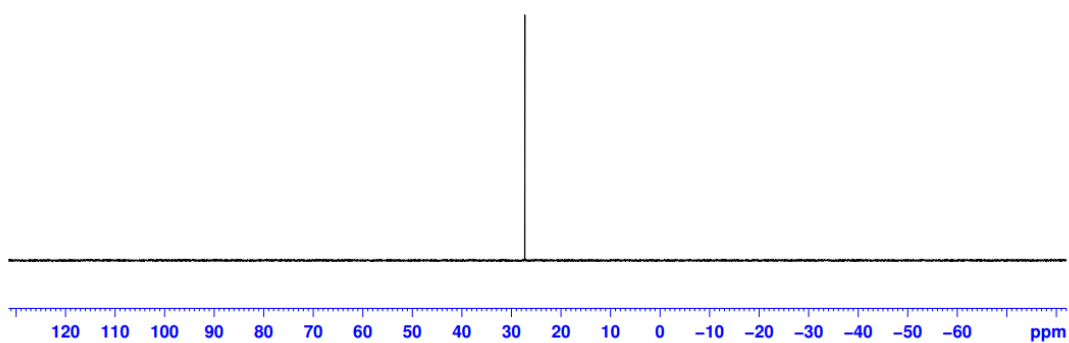


—27.27



3r

³¹P NMR (203 MHz, CDCl₃)

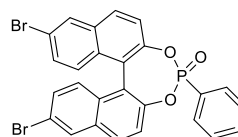


147.83
146.71
146.10
146.02
133.81
133.70
133.67
132.66
132.39
132.29
132.20
130.76
130.61
130.57
130.57
130.54
130.02
128.60
128.49
128.35
125.96
122.50
122.49
122.07
121.68
121.66
121.52
120.98
120.02

77.25

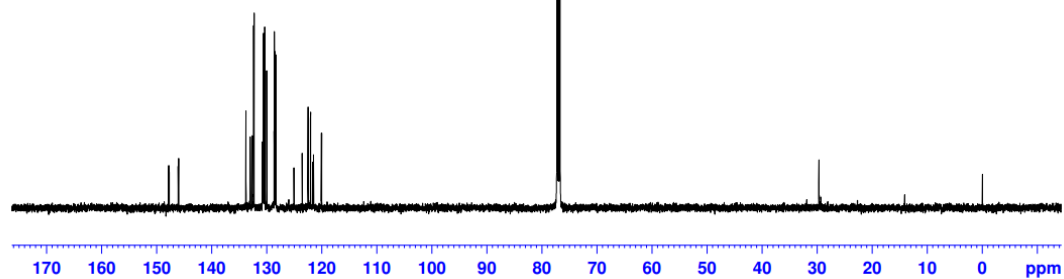
77.00

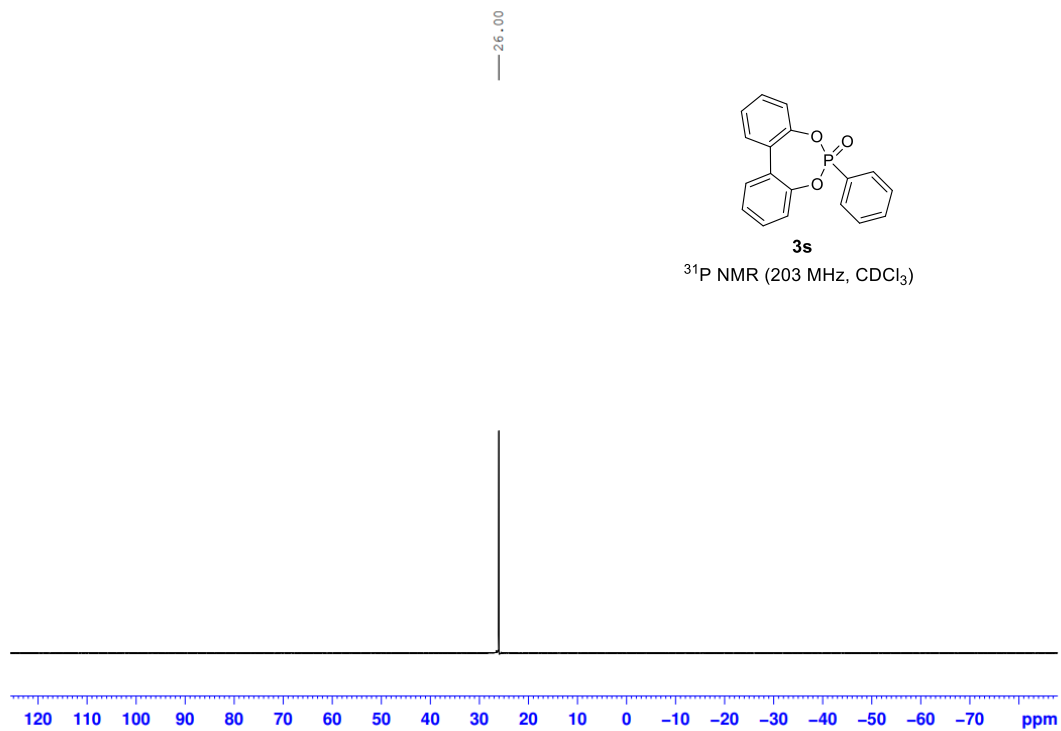
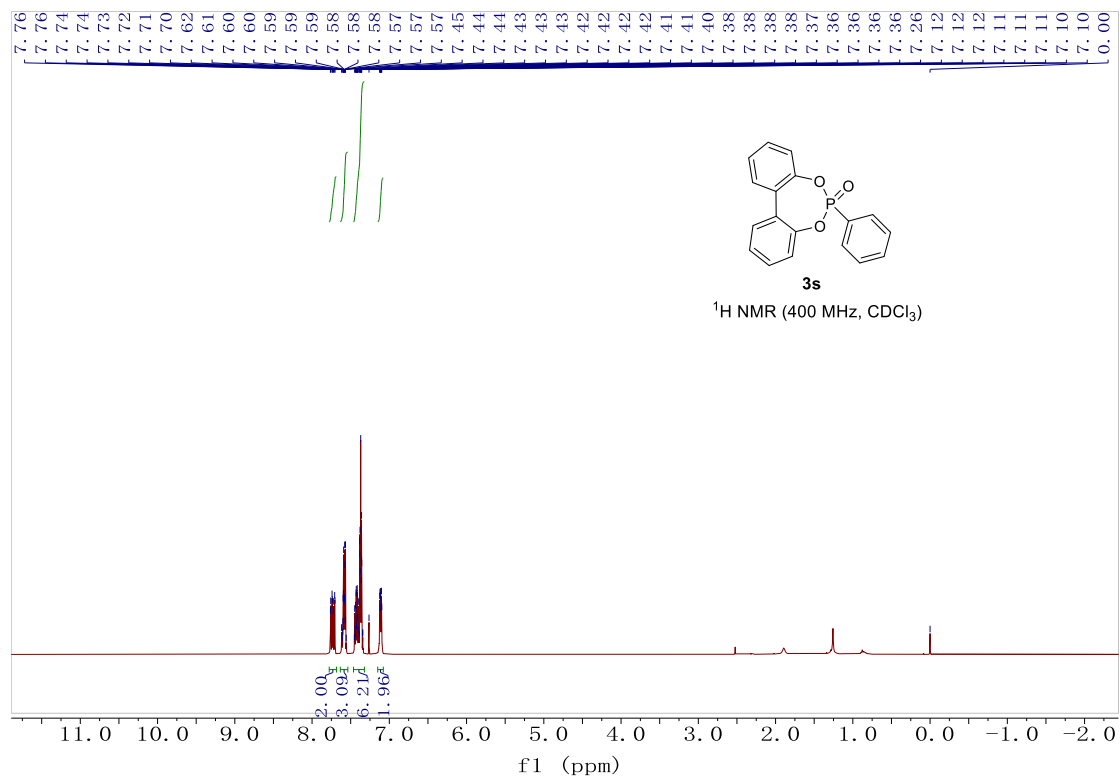
76.74

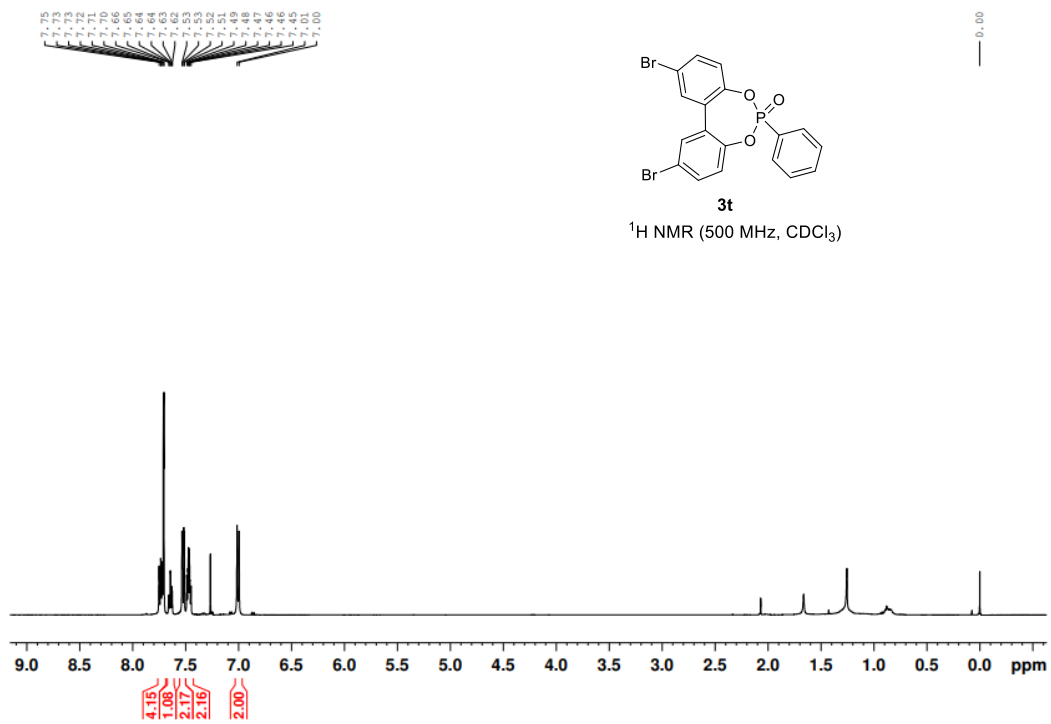
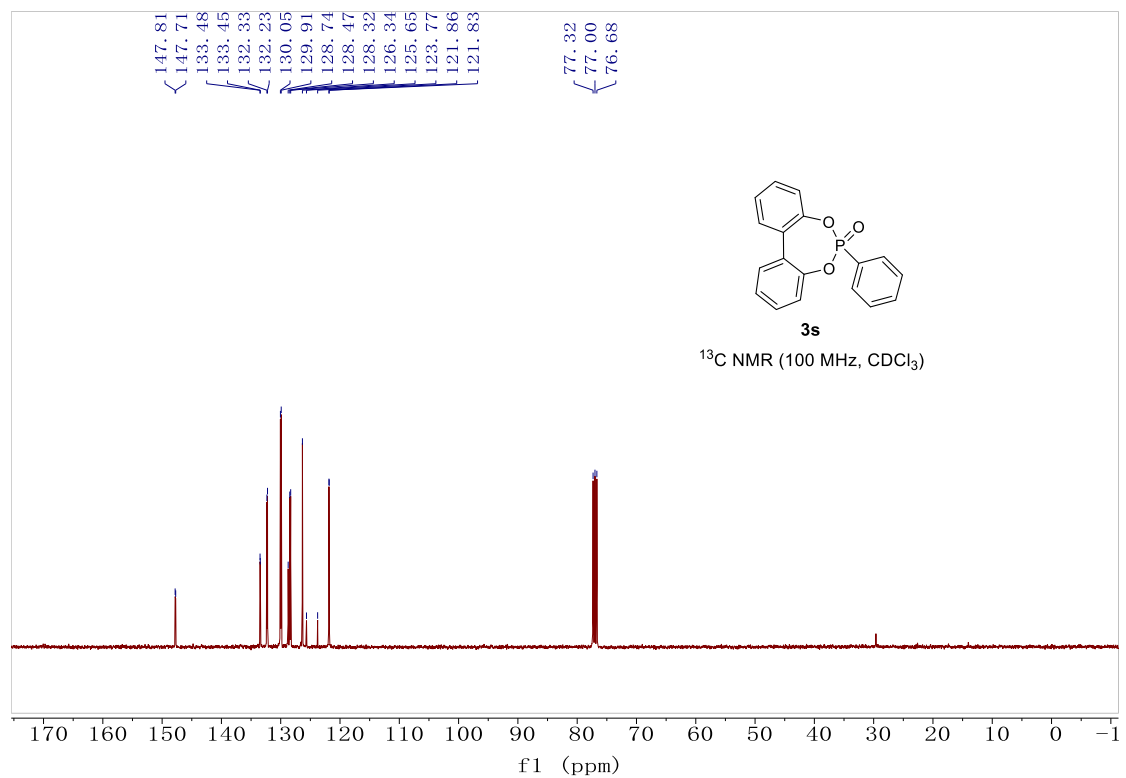


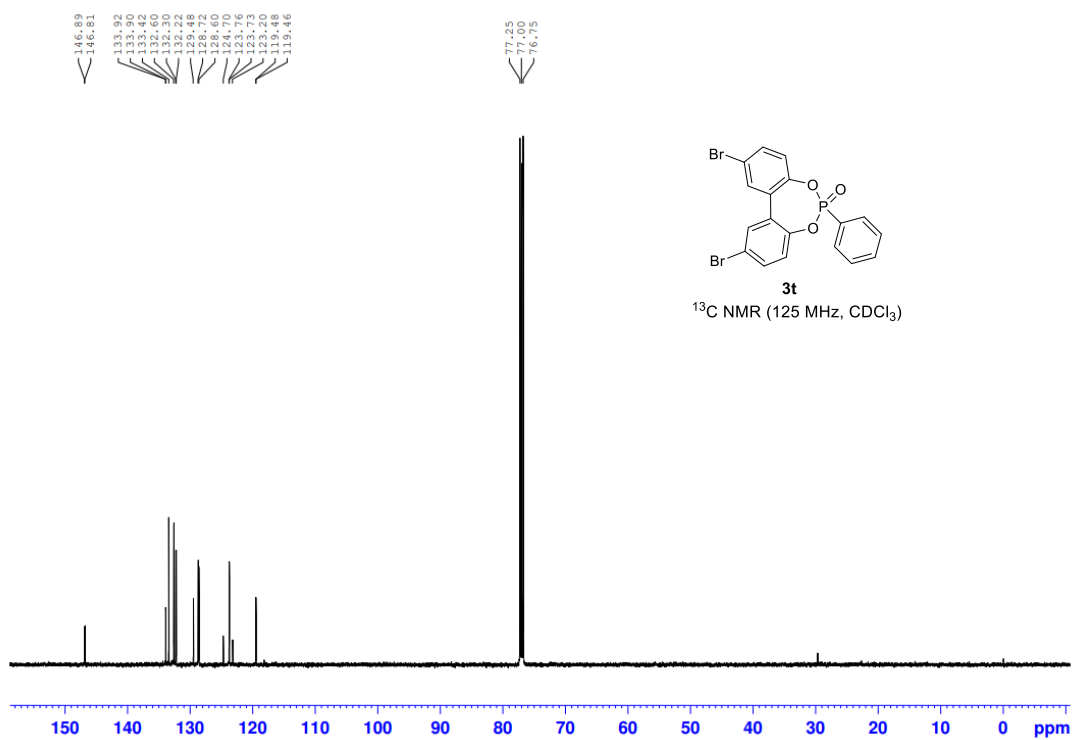
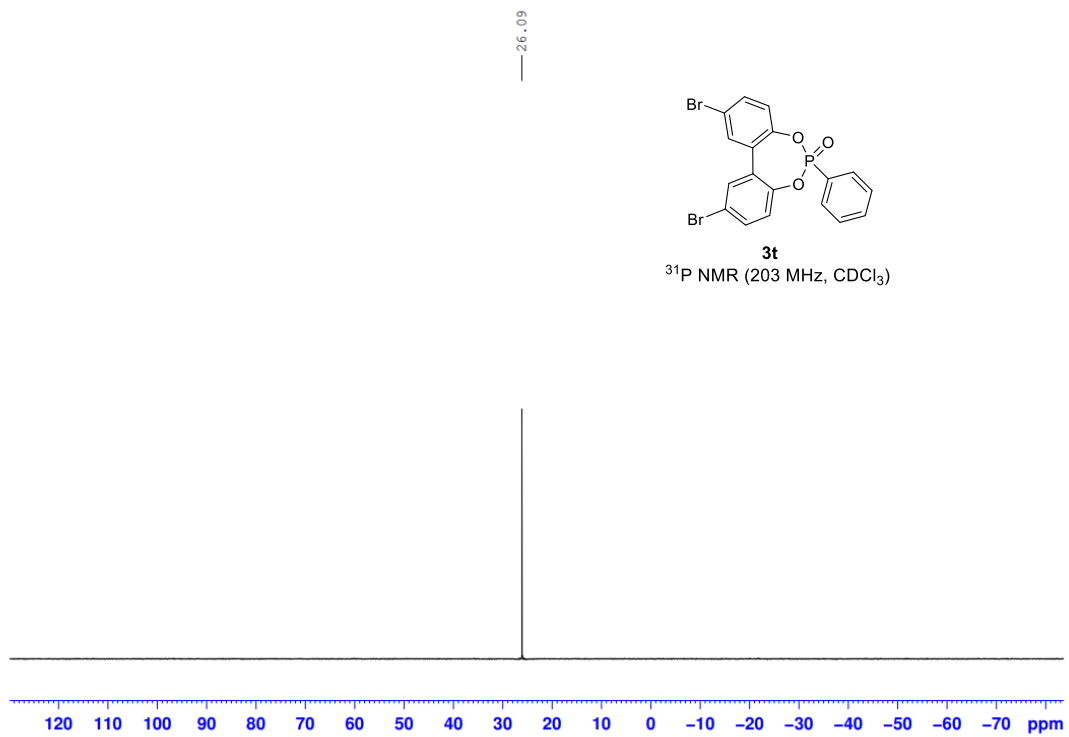
3r

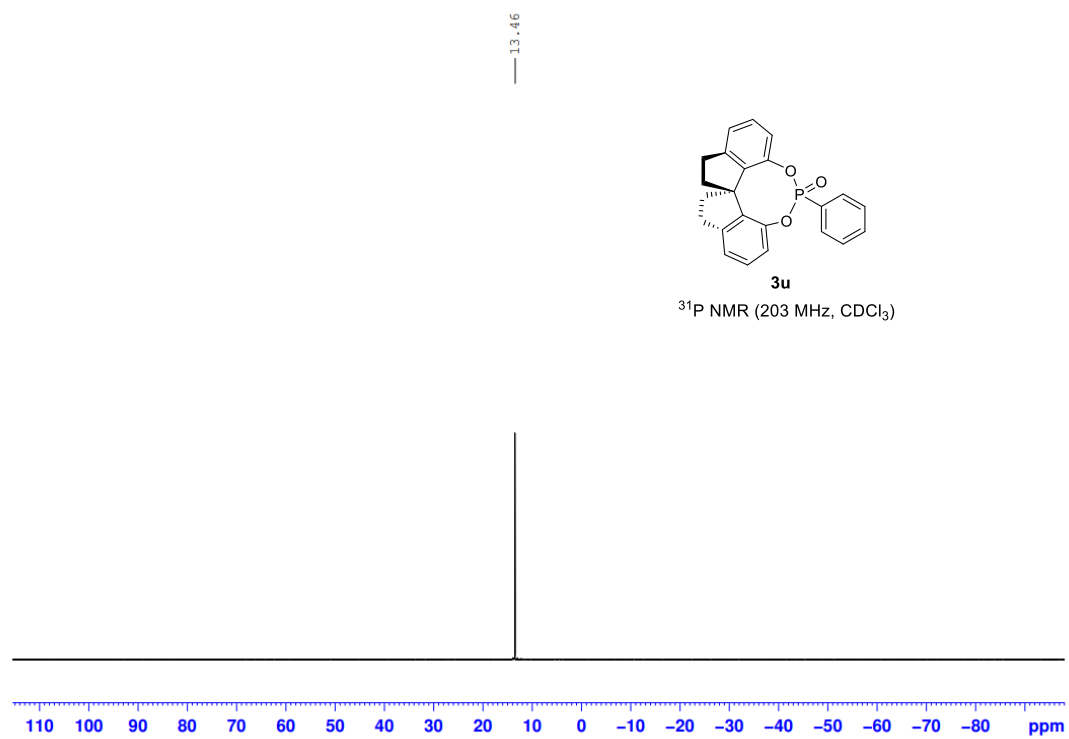
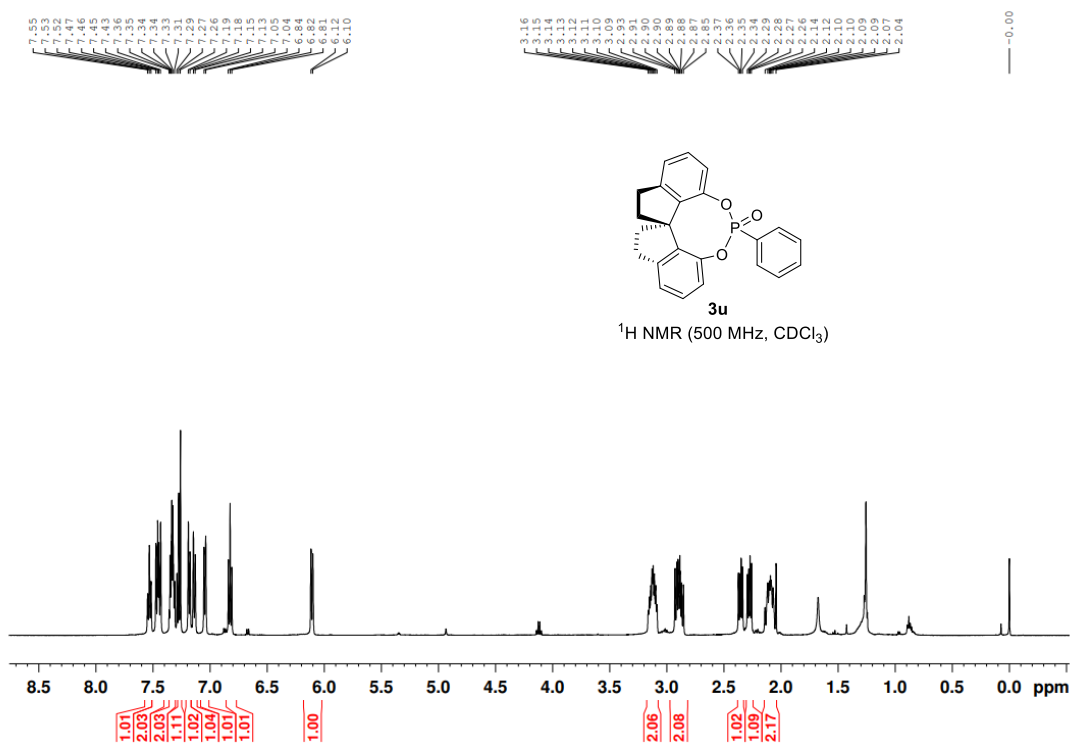
¹³C NMR (125 MHz, CDCl₃)

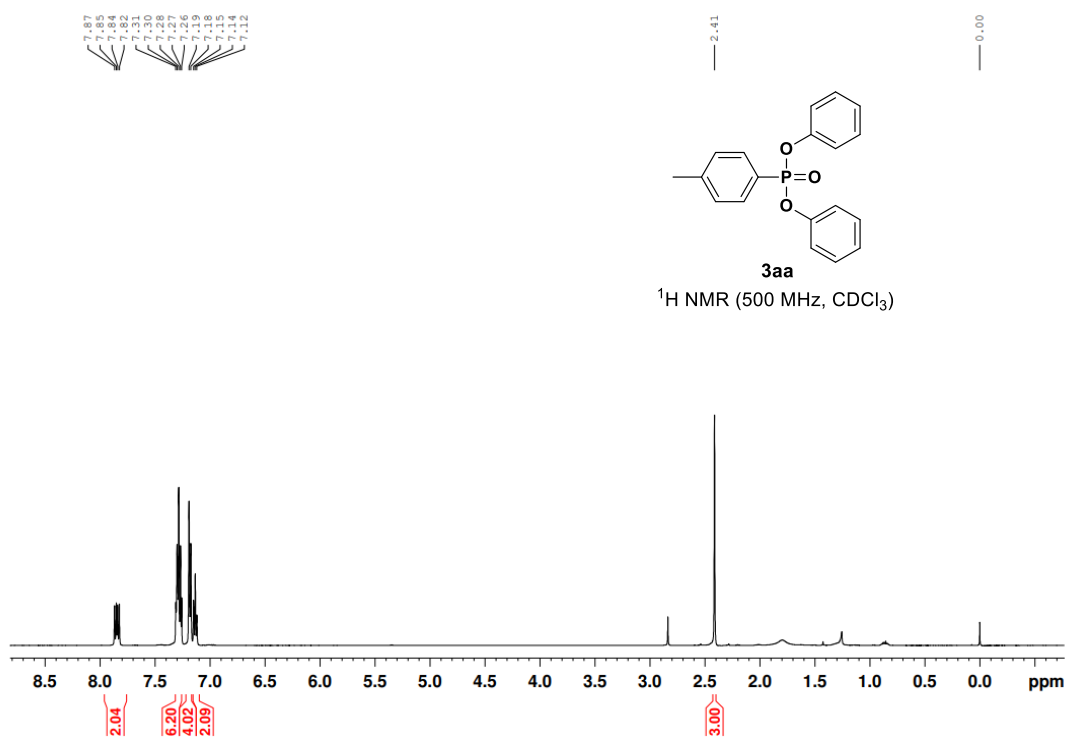
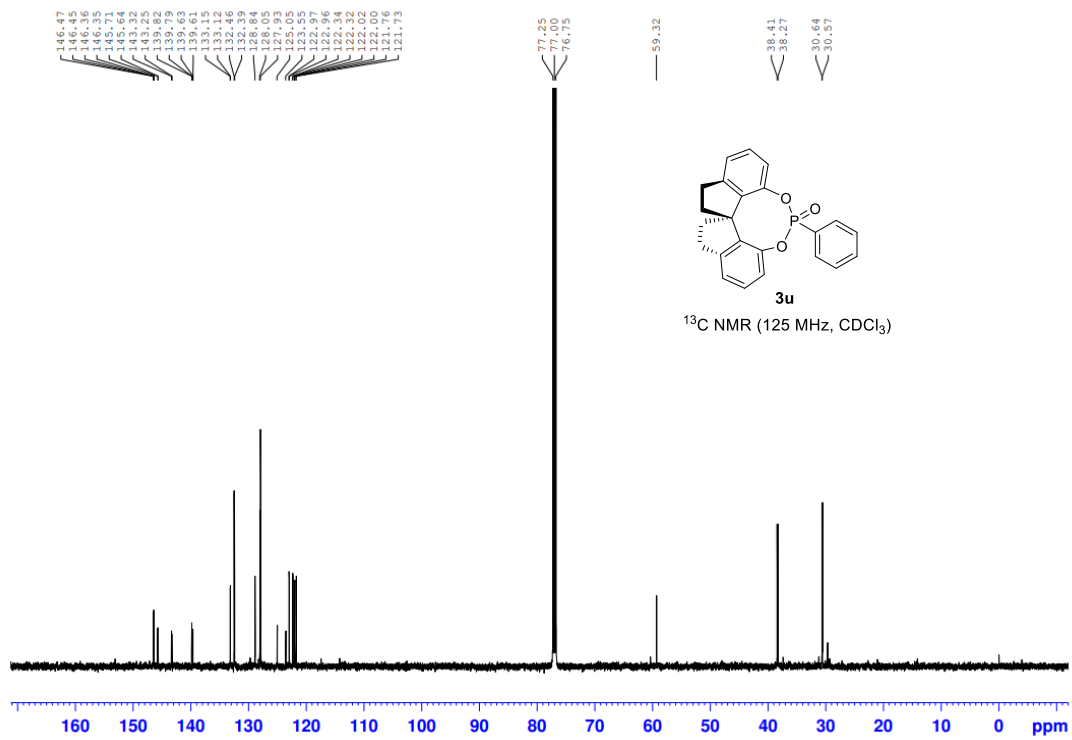


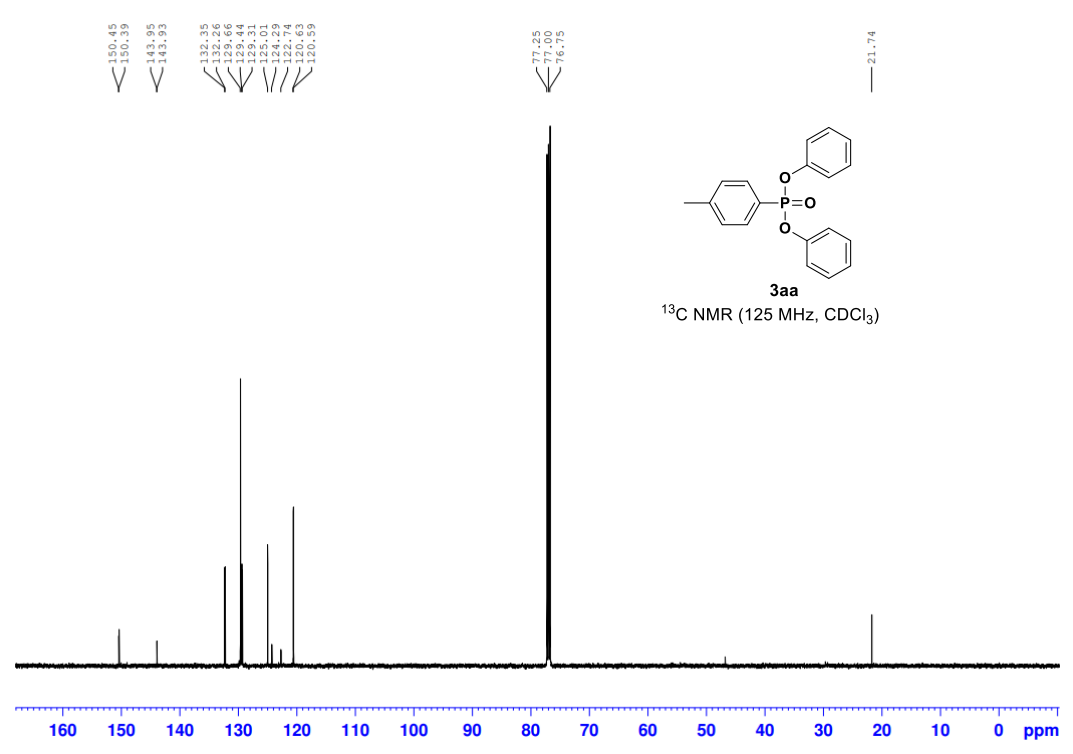
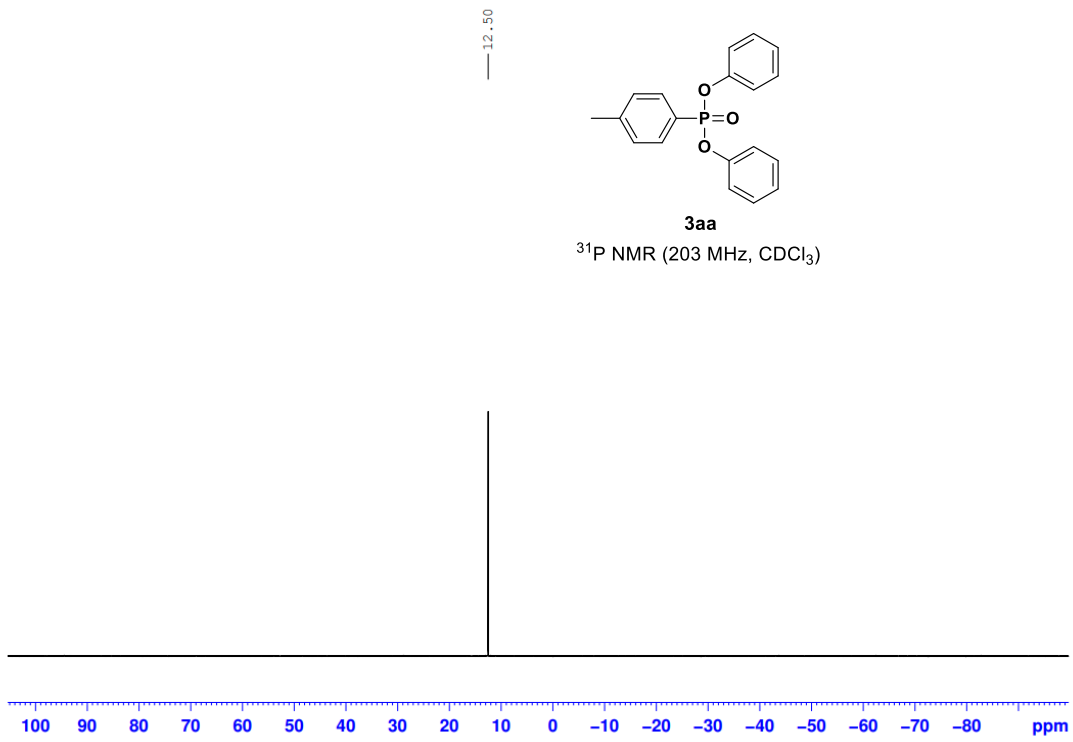


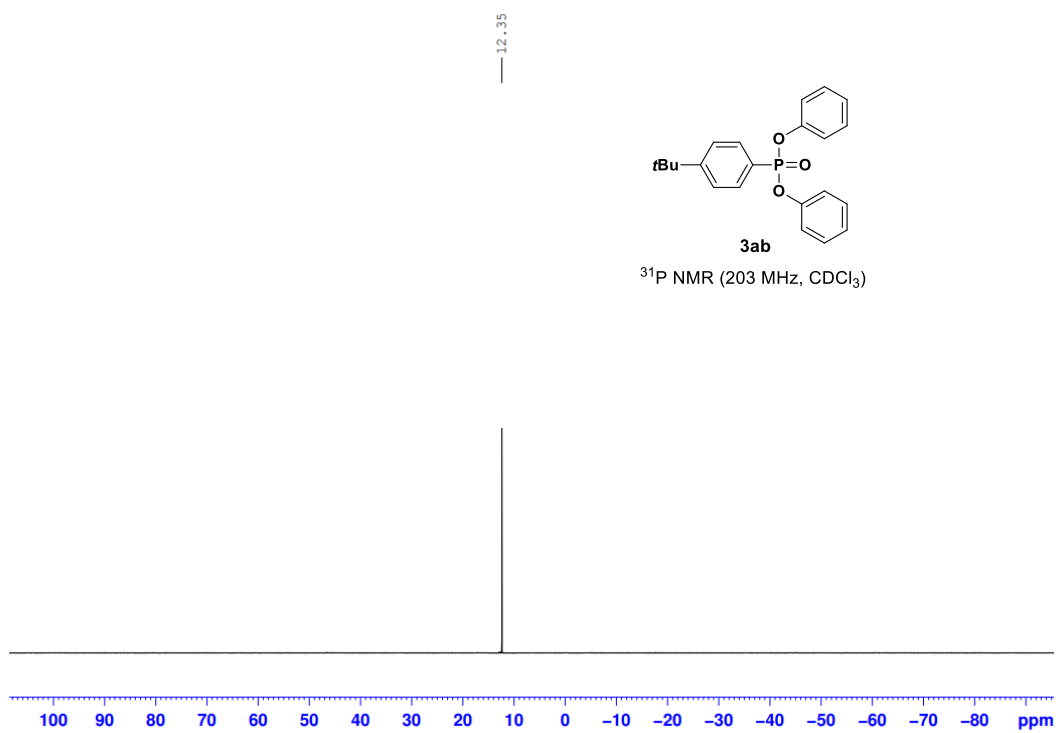
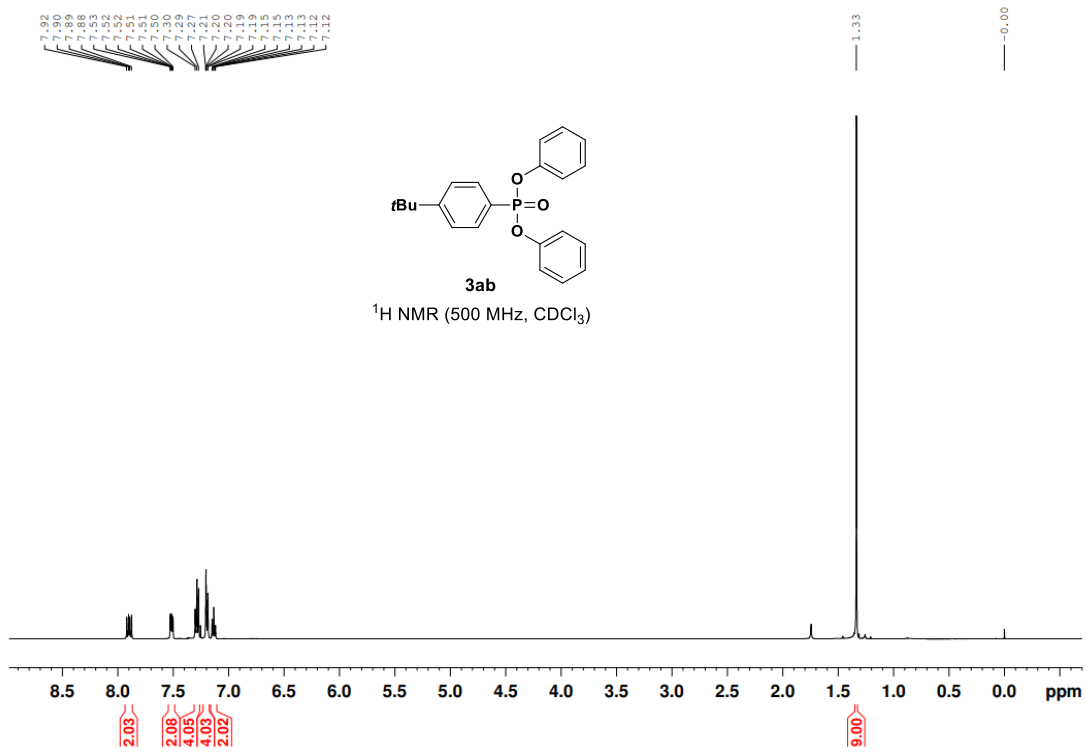


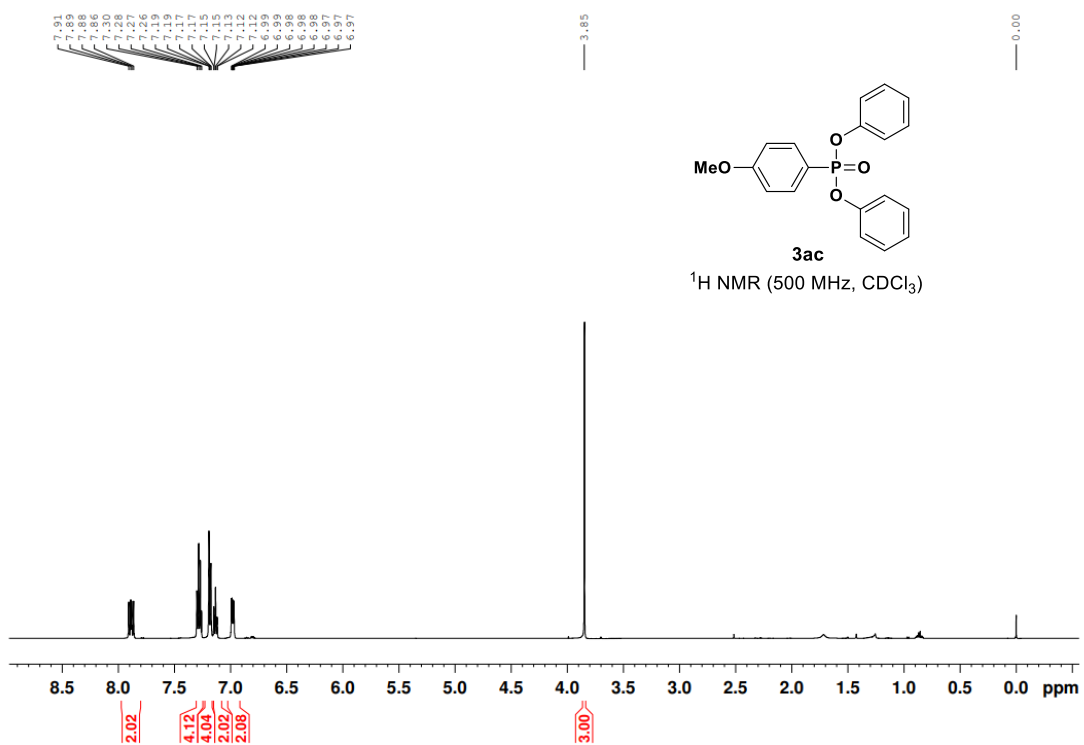
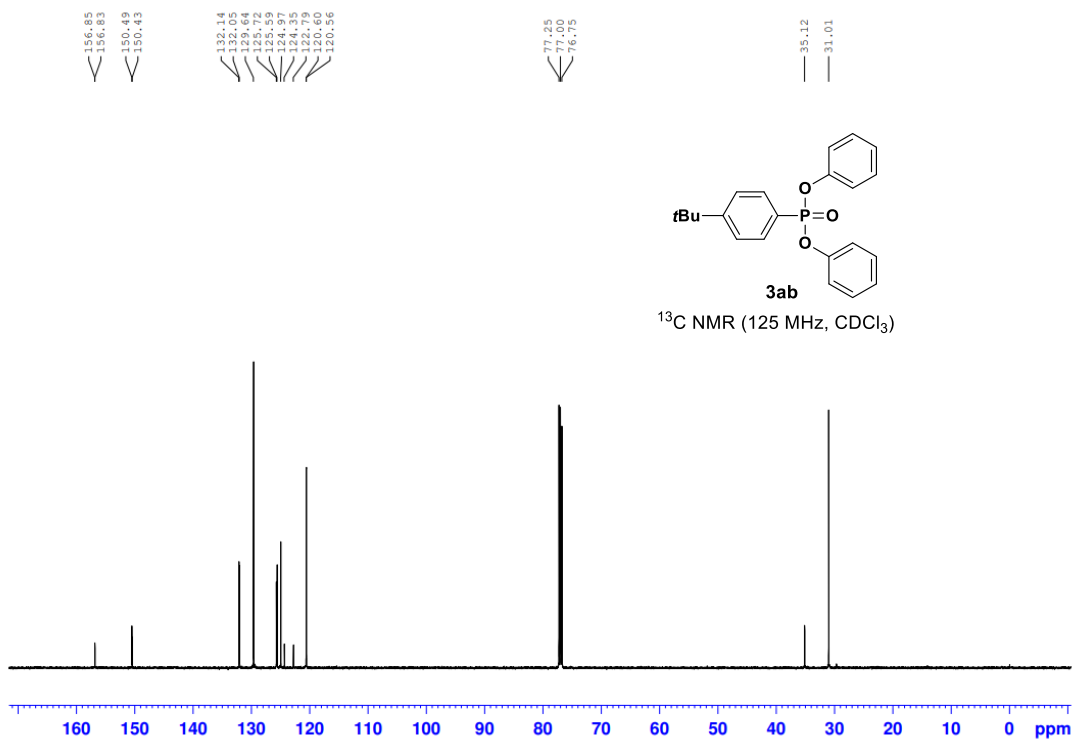


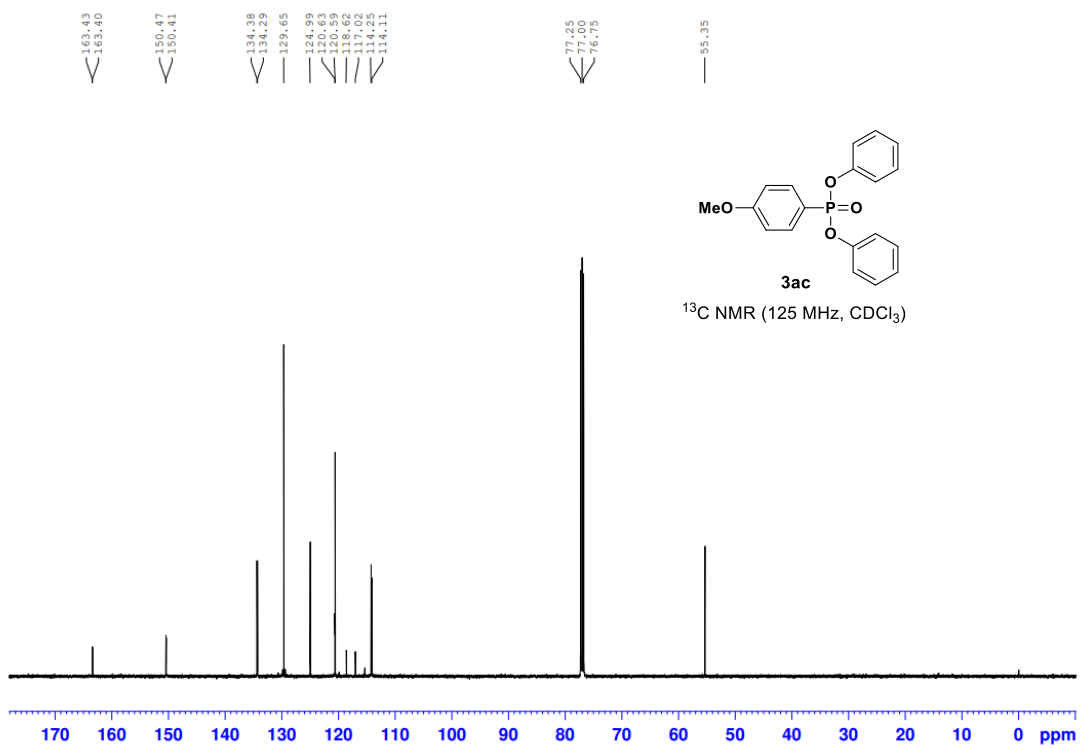
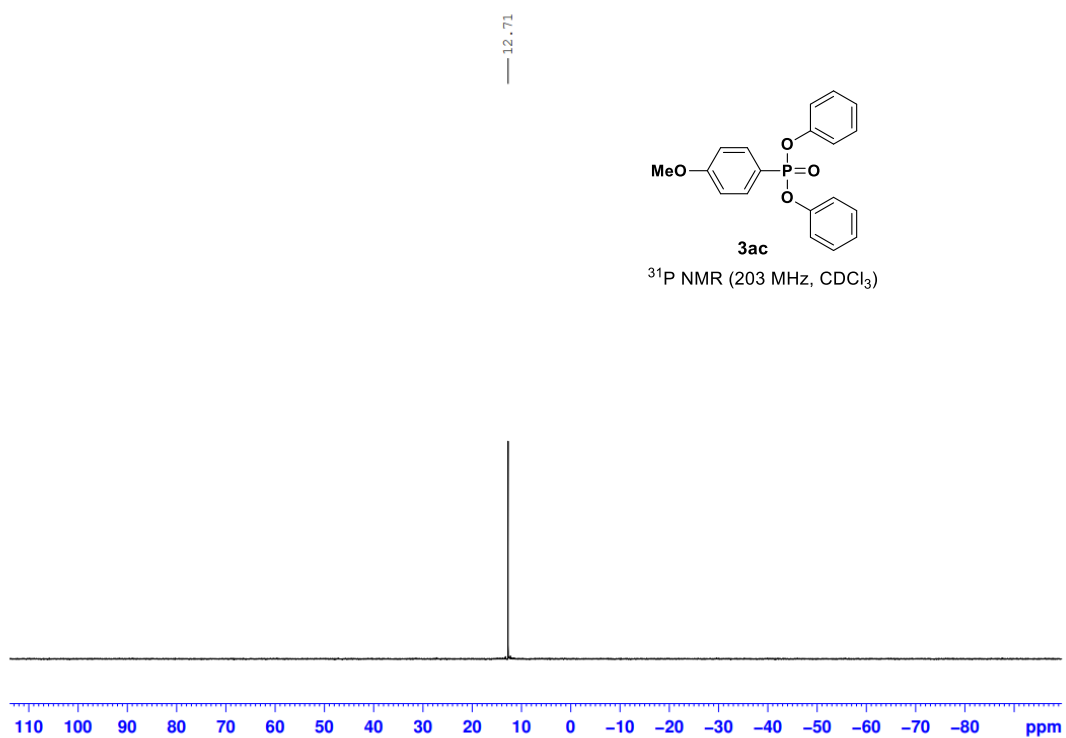


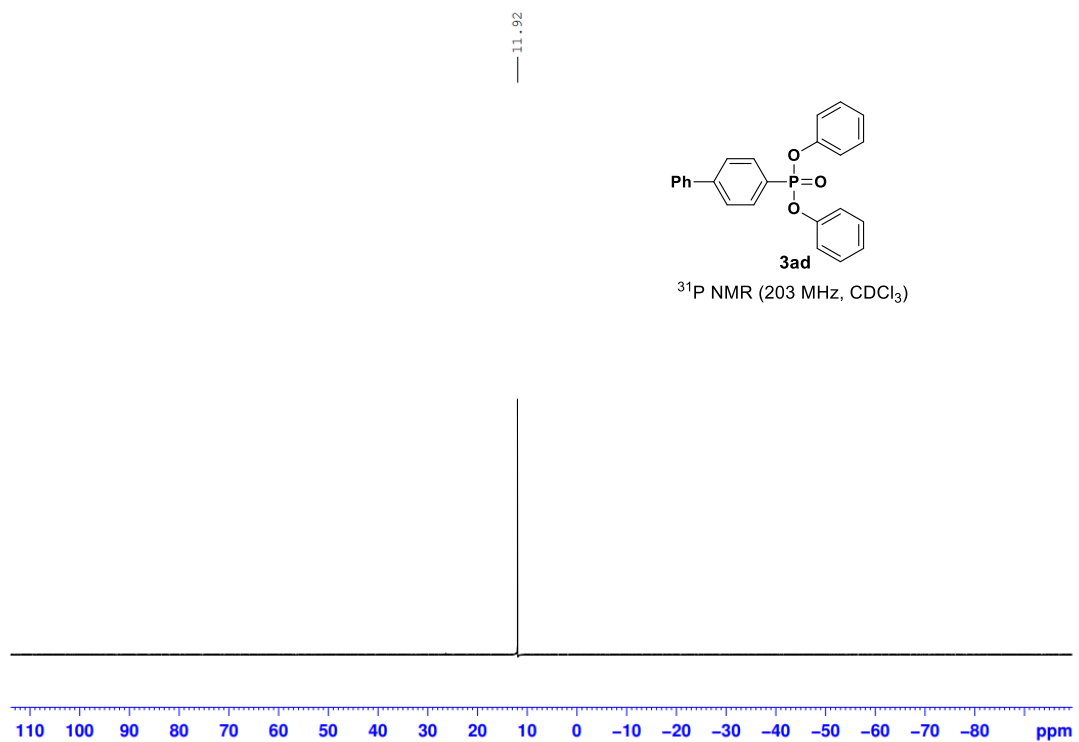
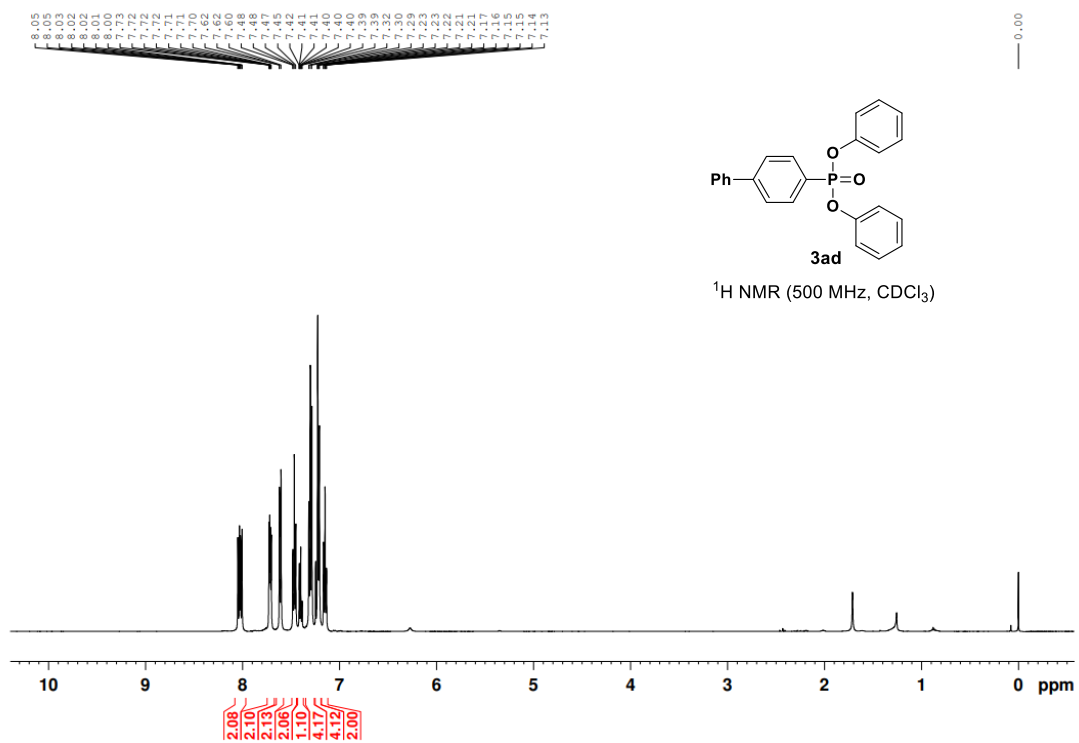


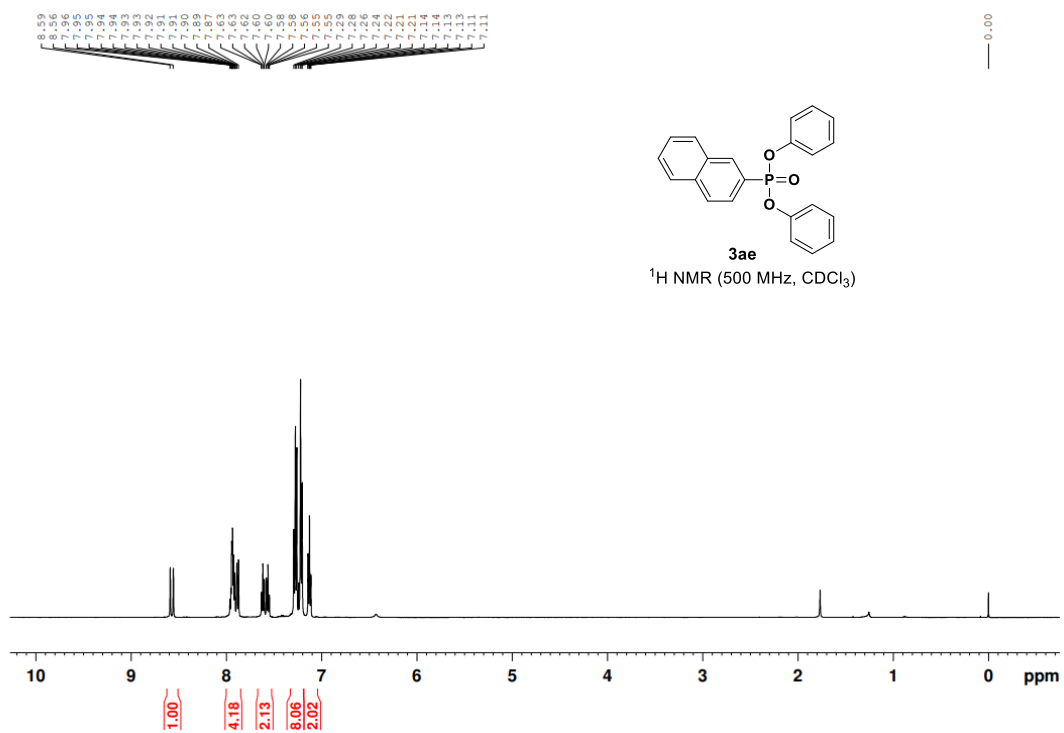
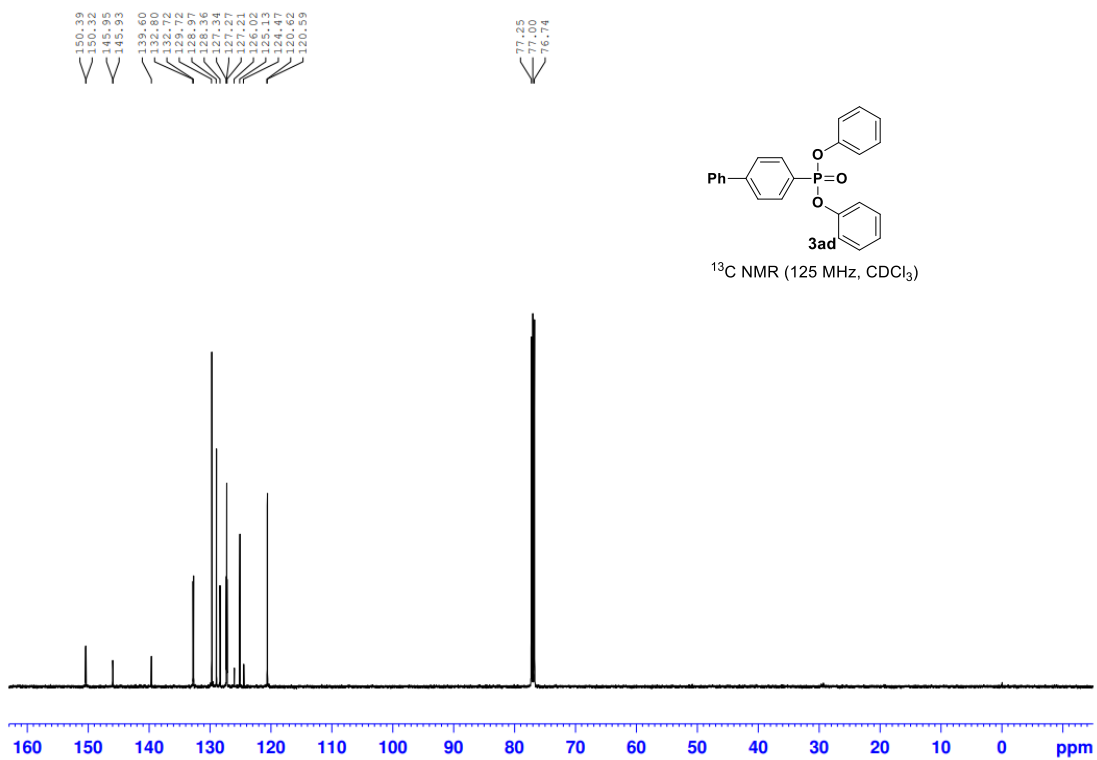


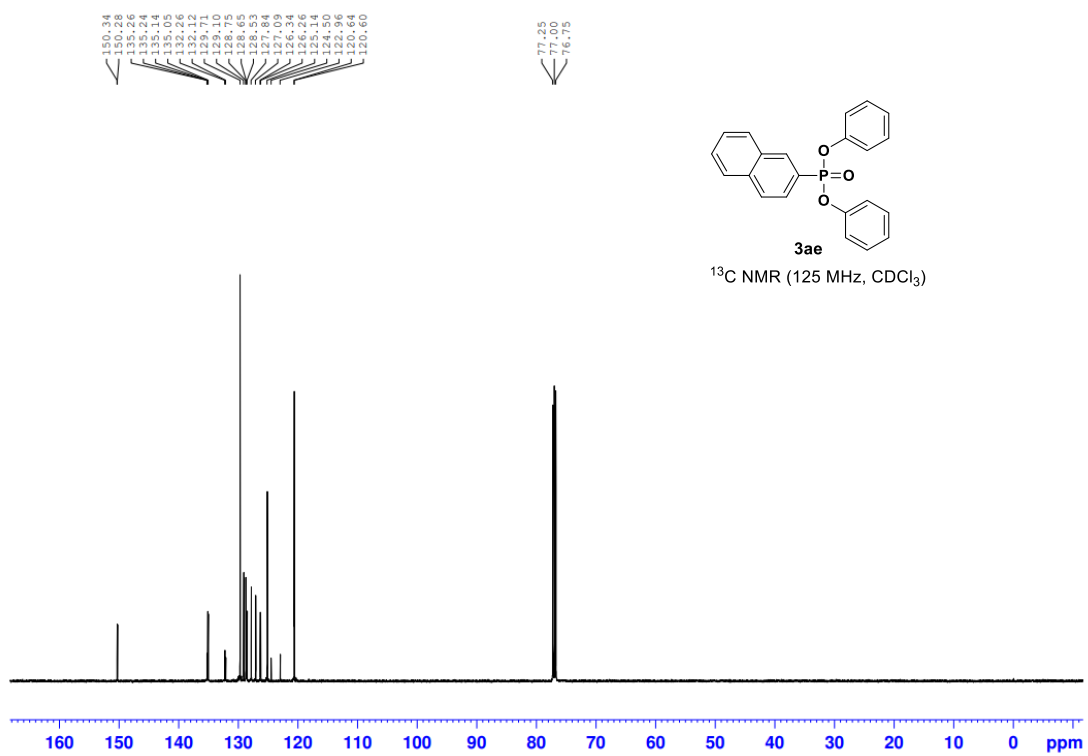
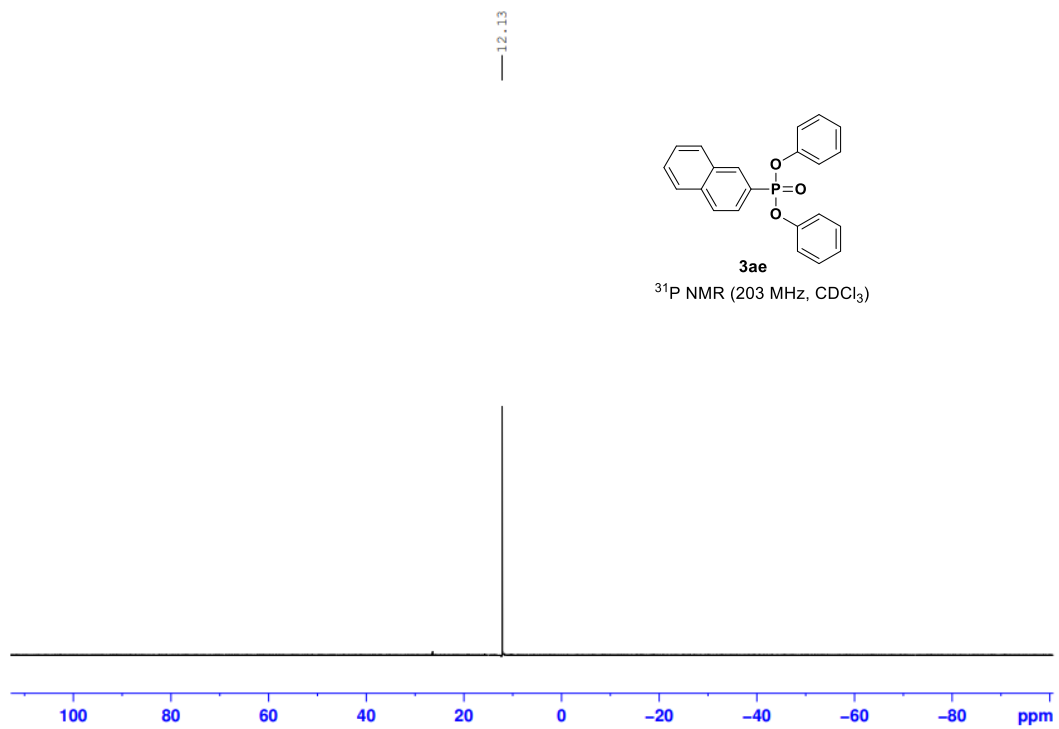


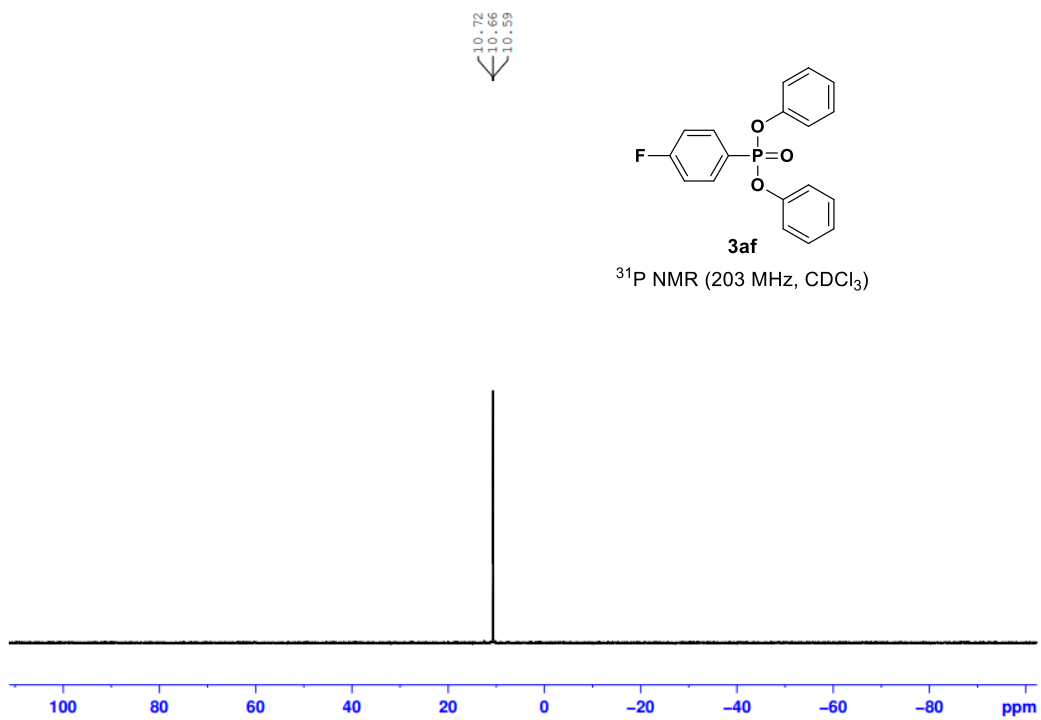
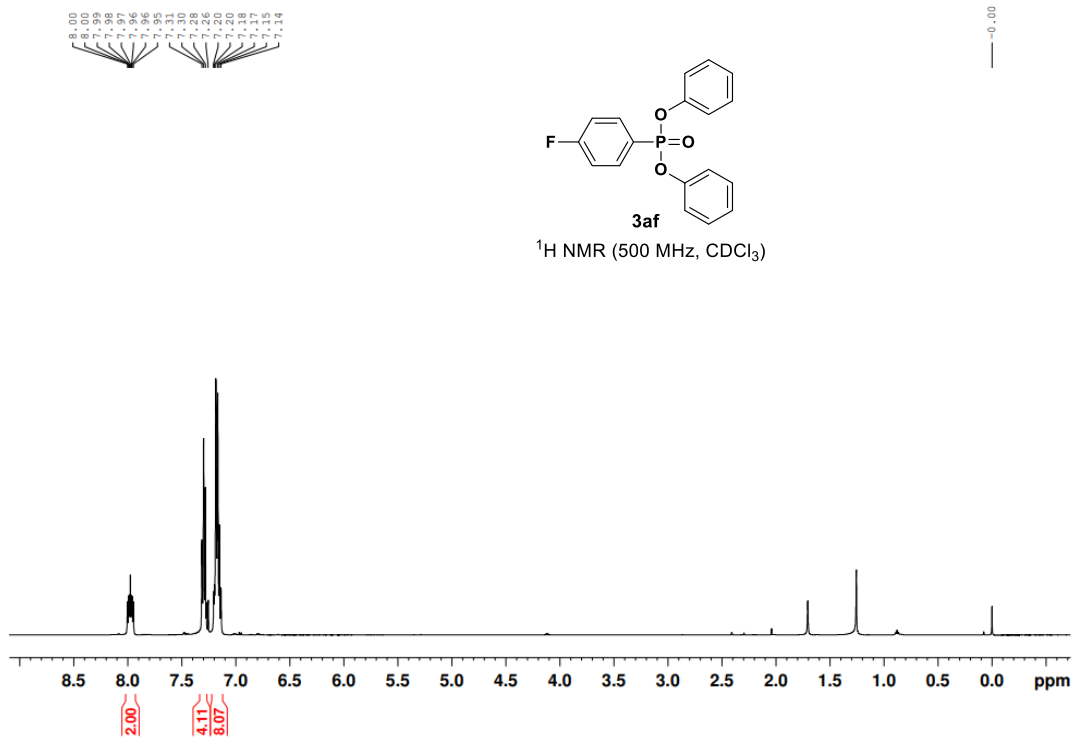


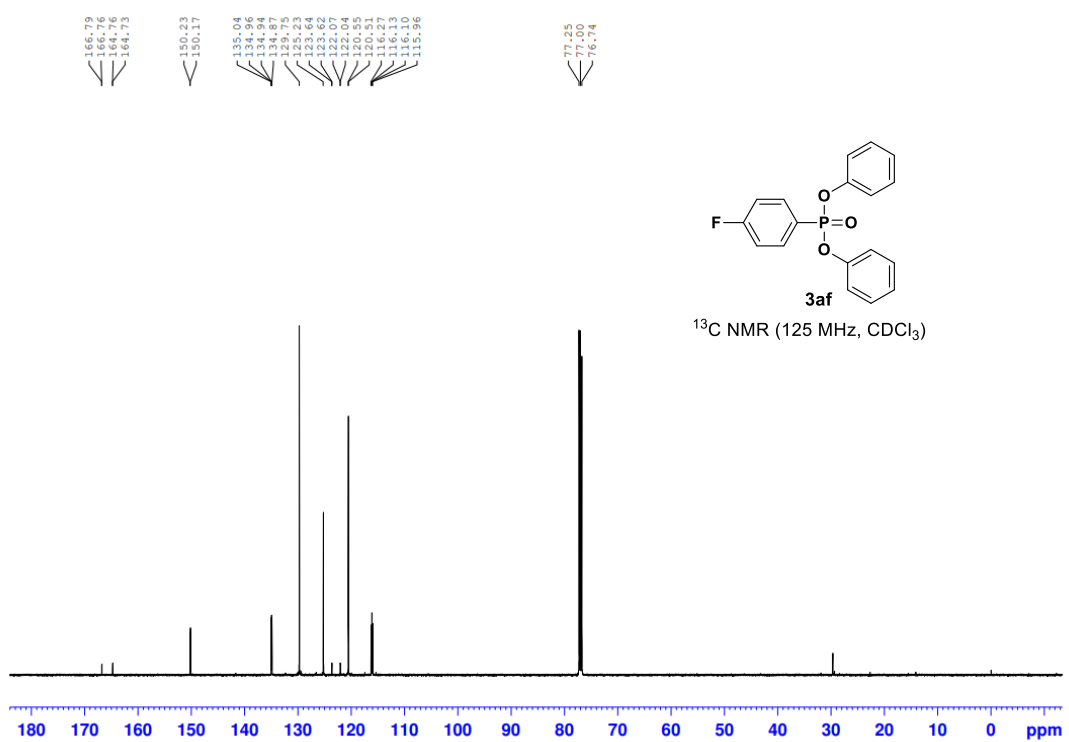
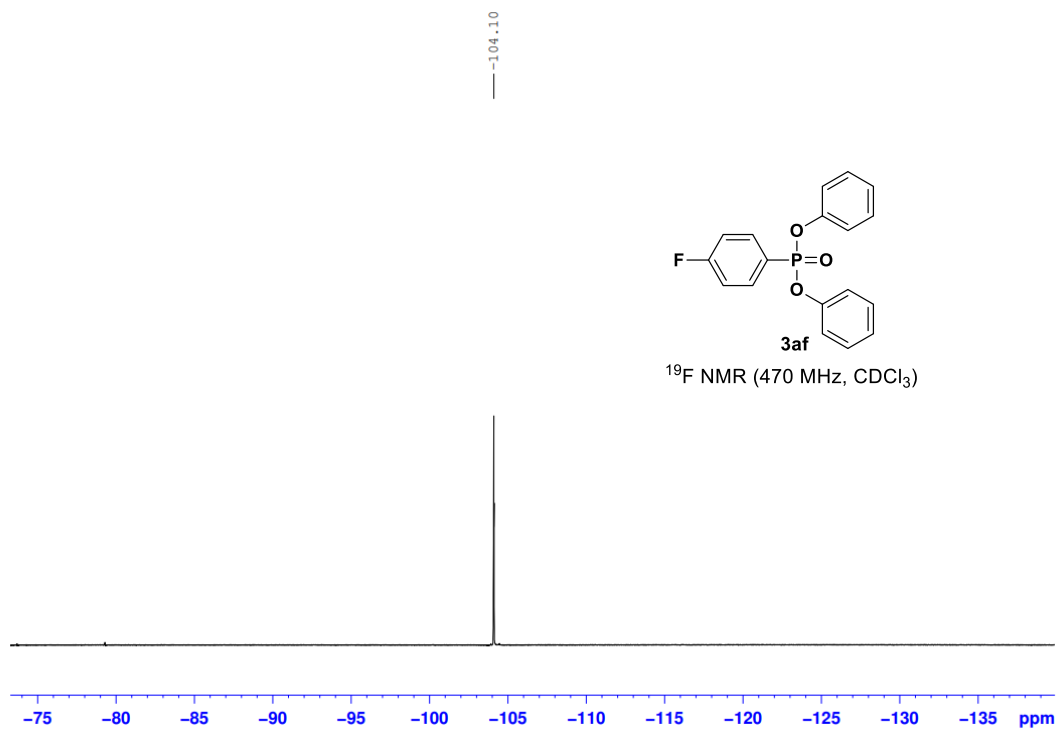


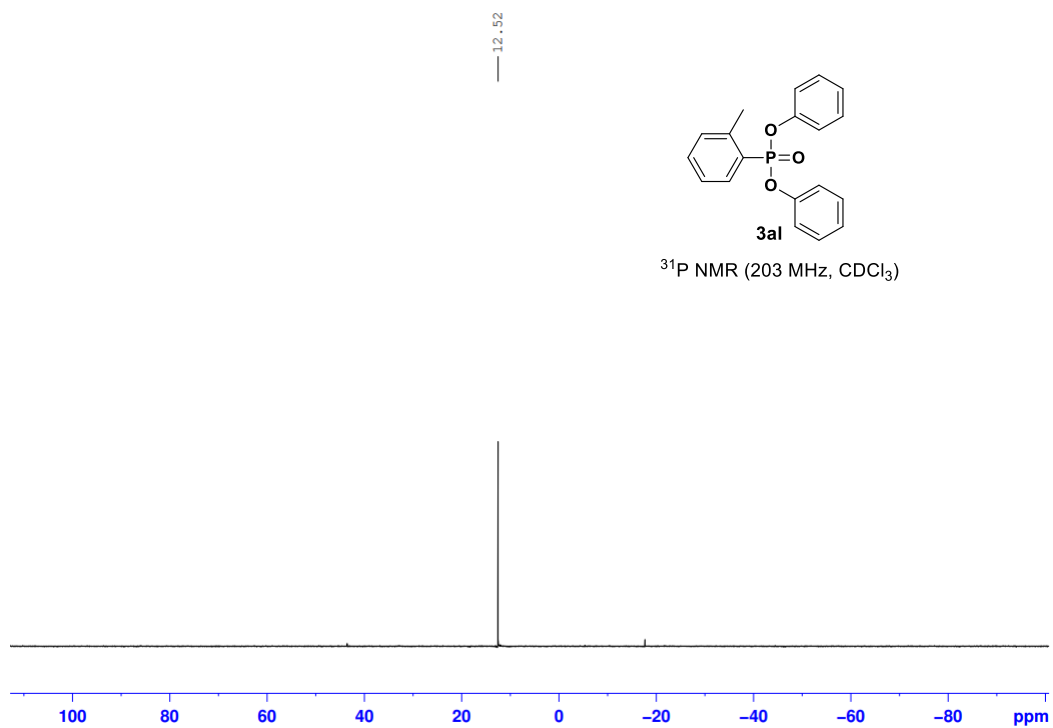
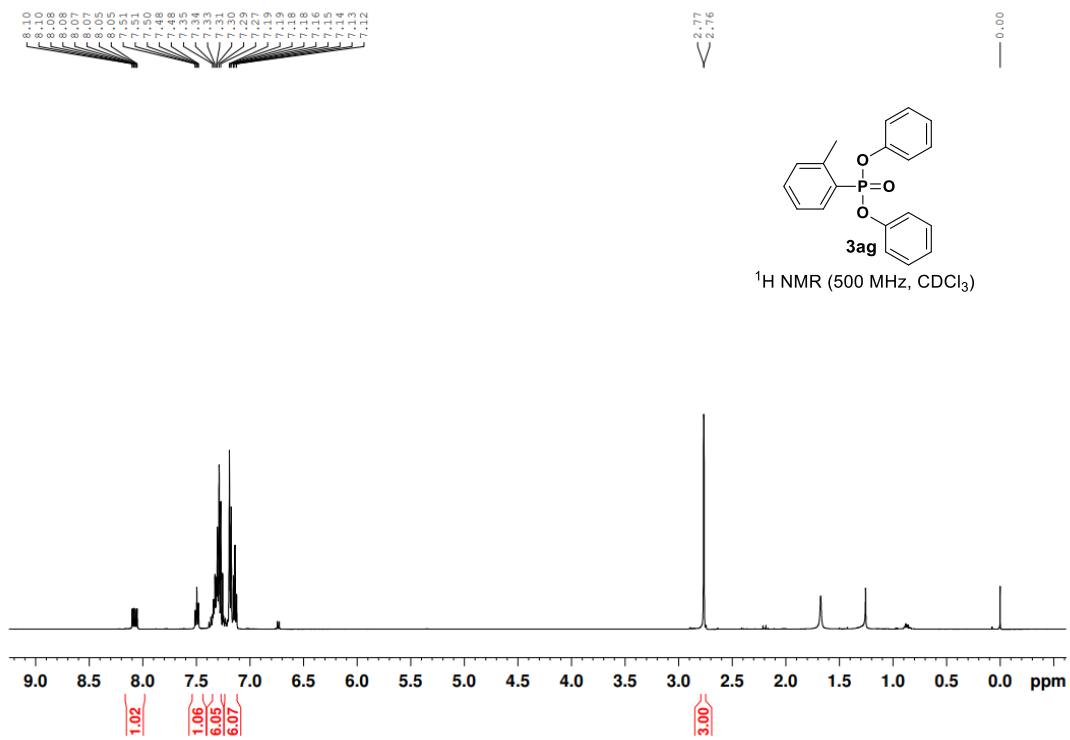


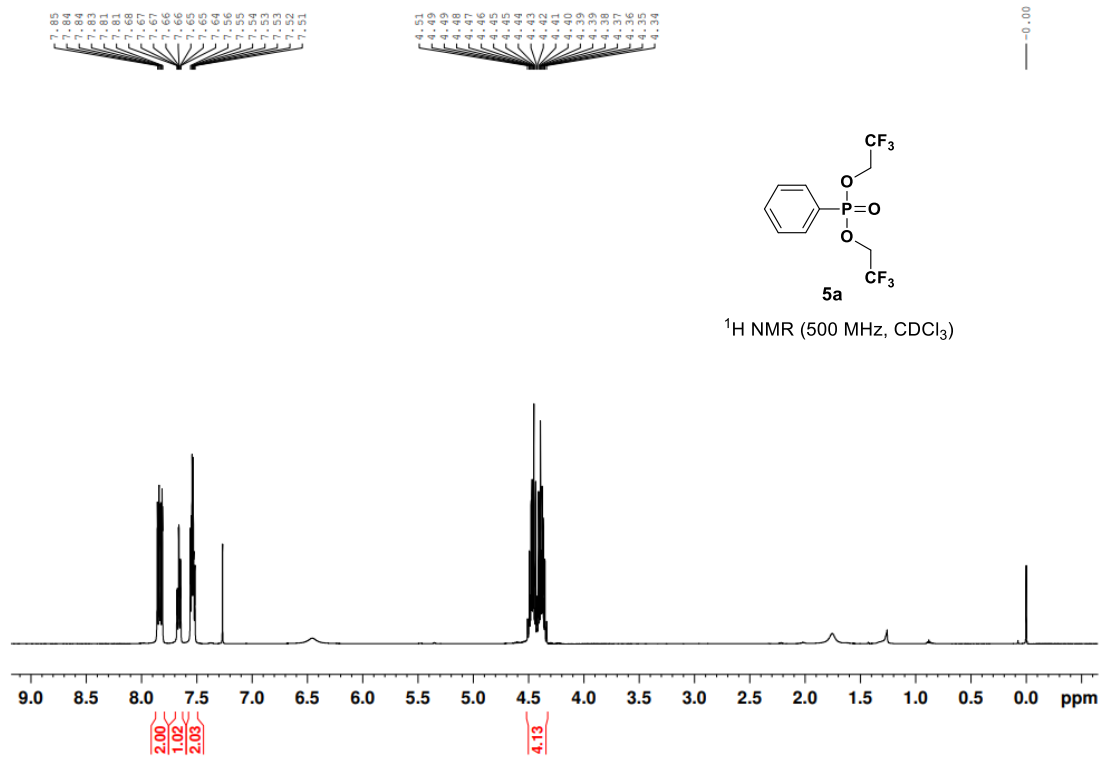
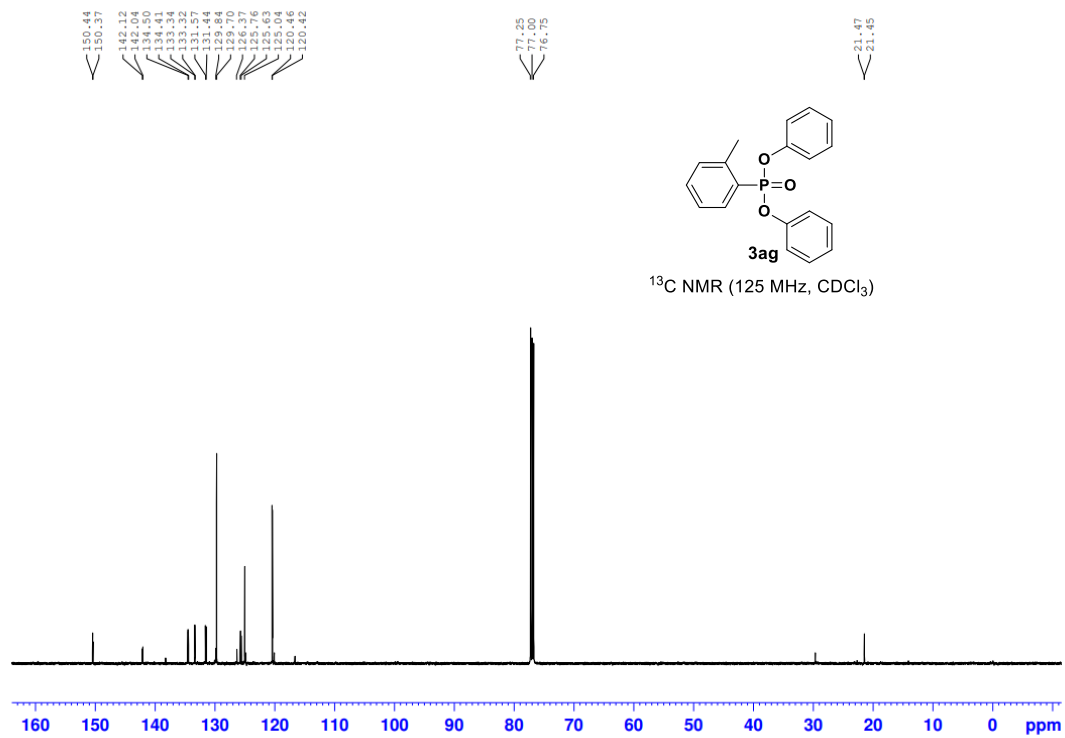




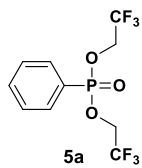




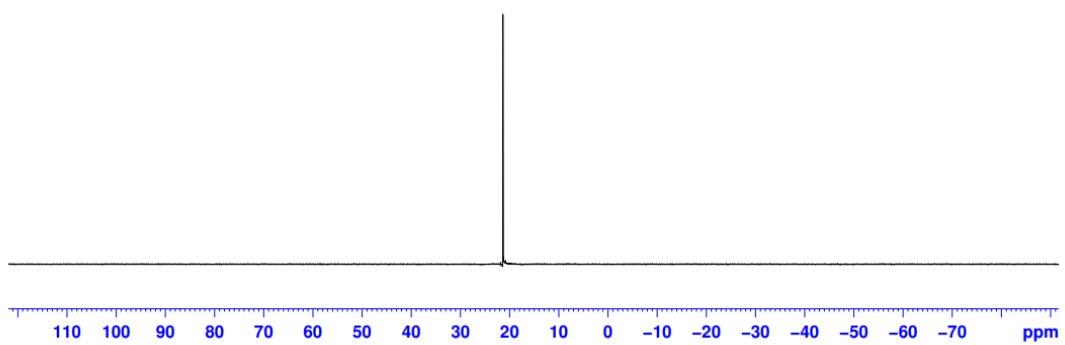




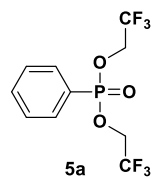
— 21.33



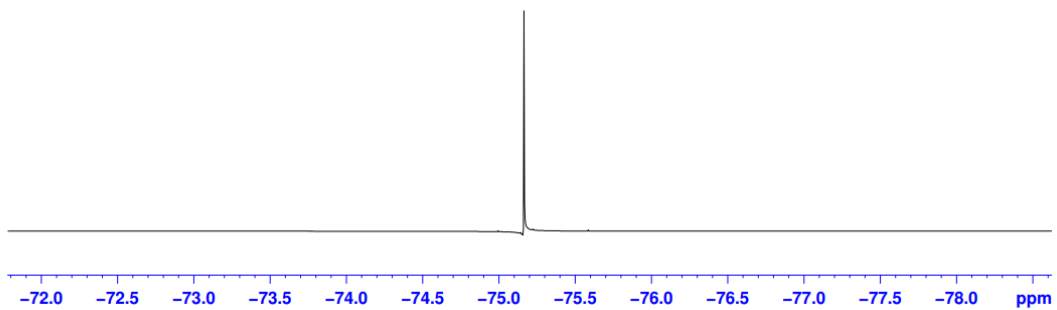
^{31}P NMR (203 MHz, CDCl_3)

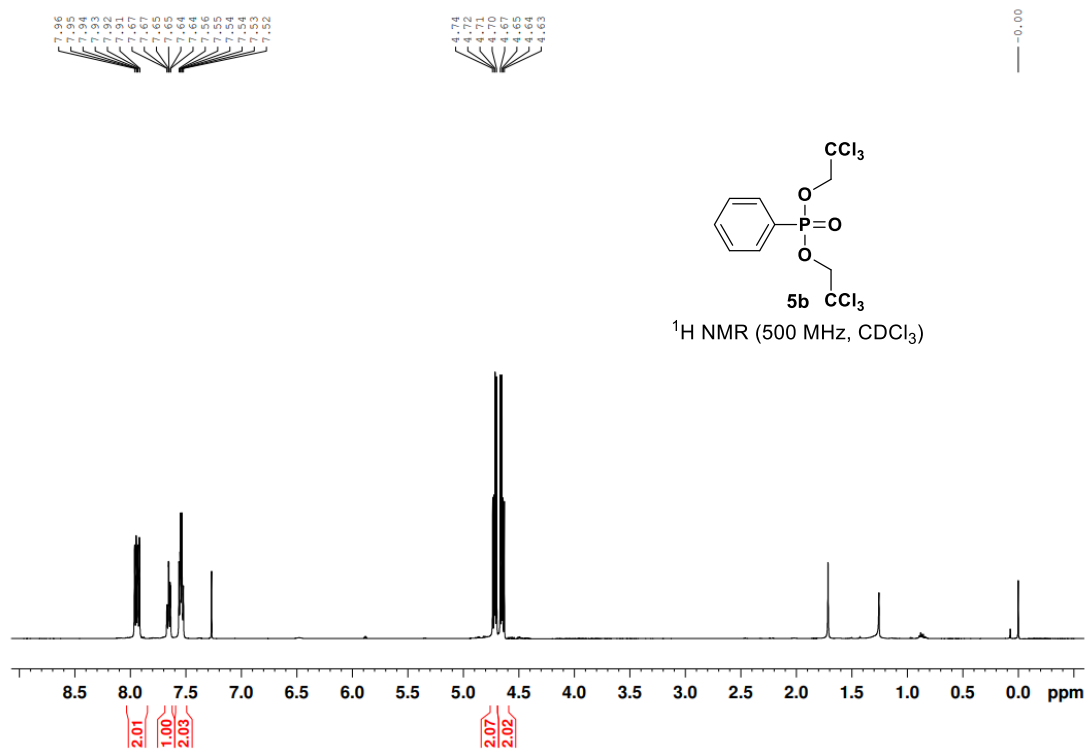
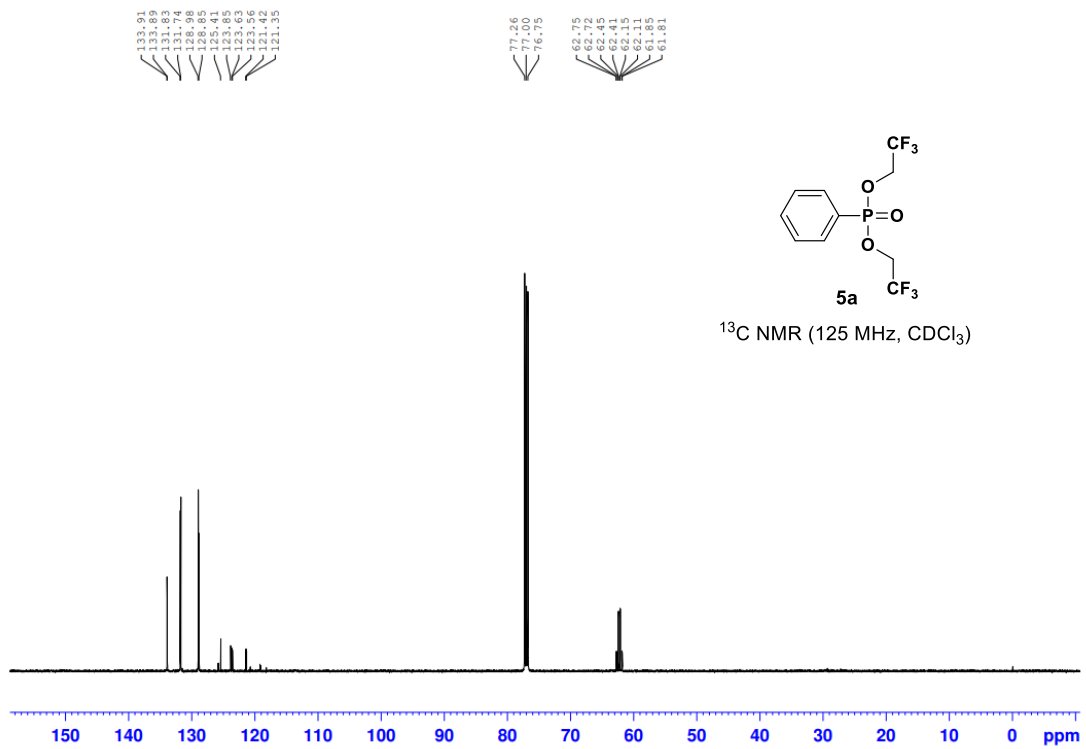


— -75.17

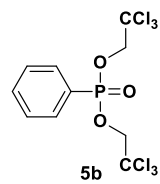


^{19}F NMR (470 MHz, CDCl_3)

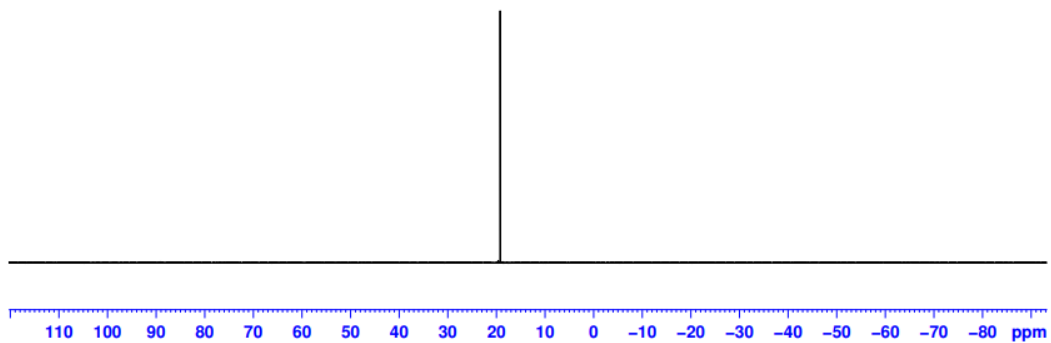




— 19.19



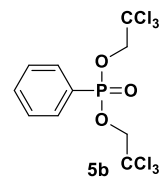
³¹P NMR (203 MHz, CDCl₃)



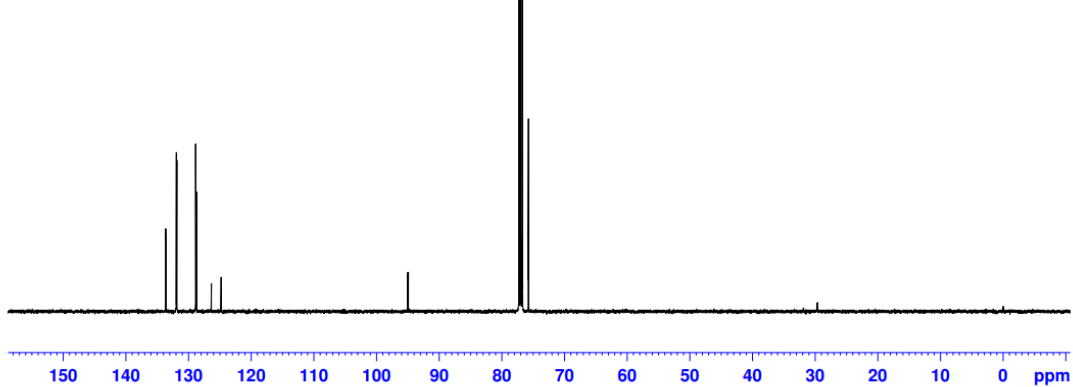
133.64
133.62
131.69
131.68
128.88
128.75
124.62

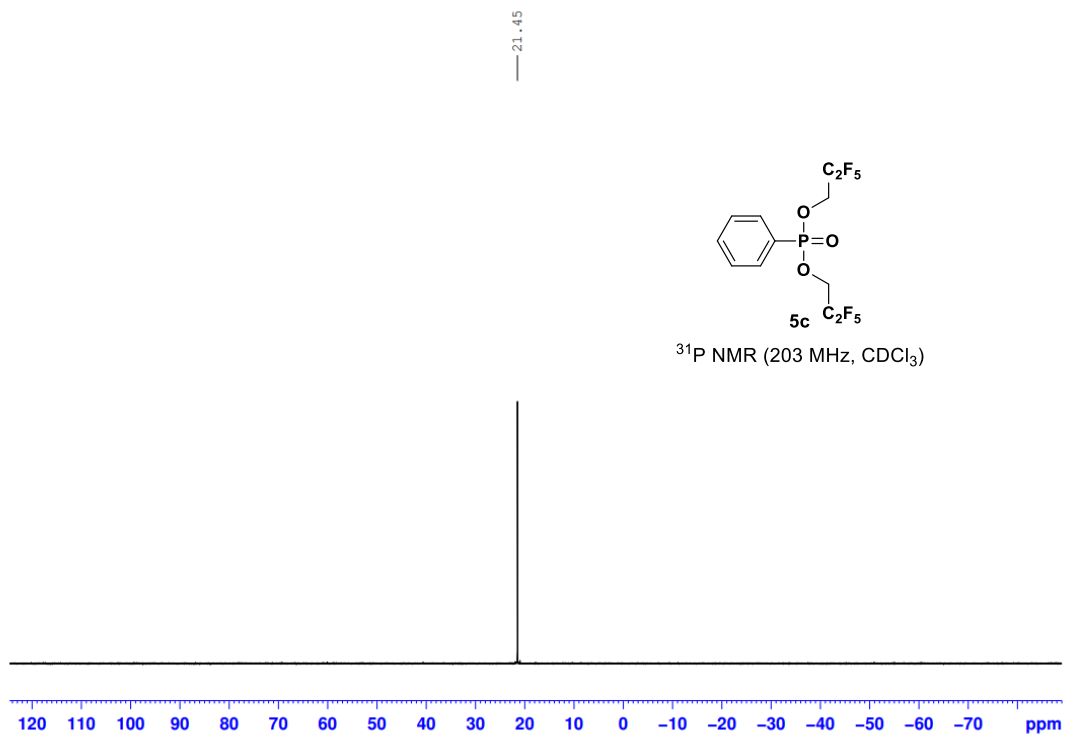
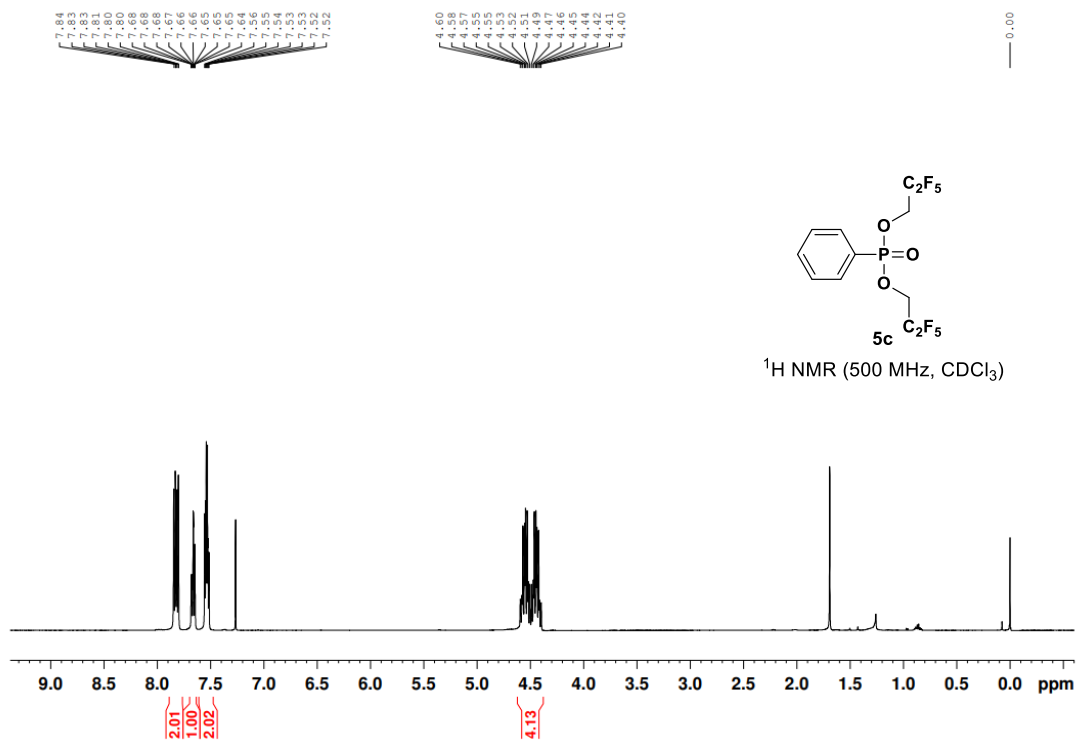
95.02
94.94

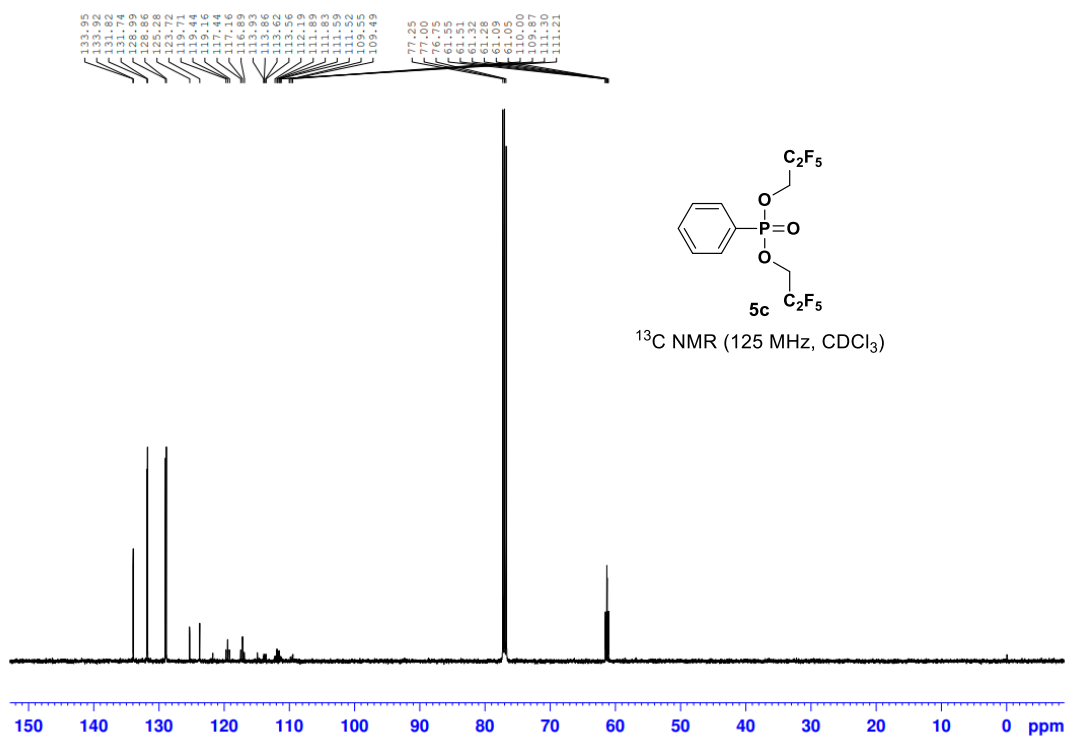
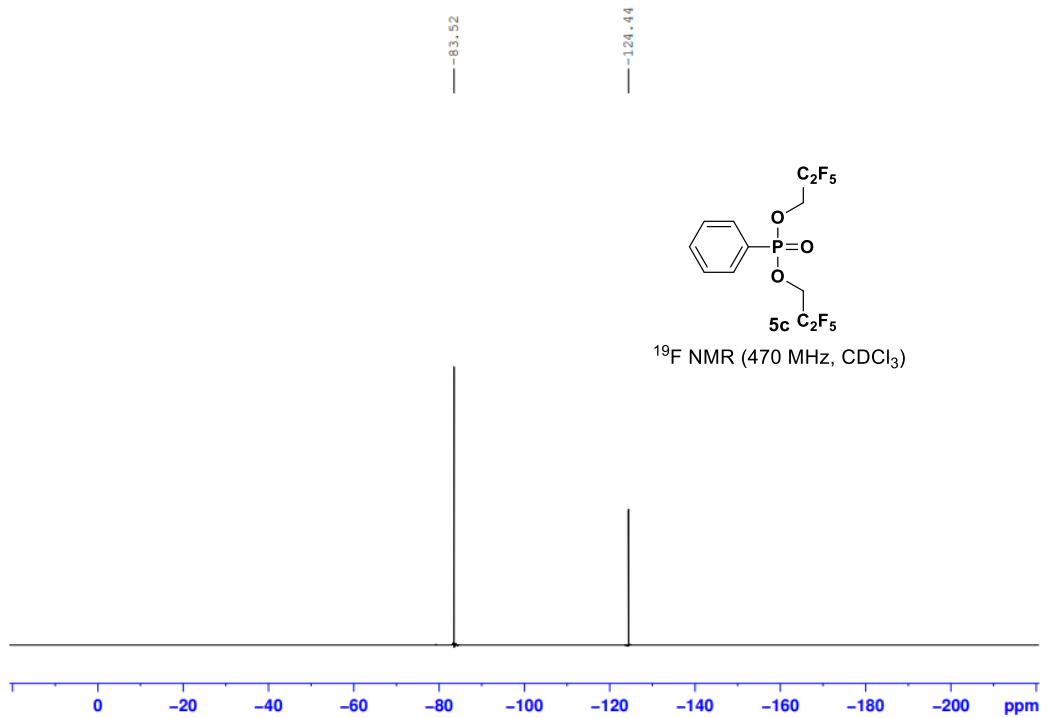
77.25
77.00
76.75
75.74

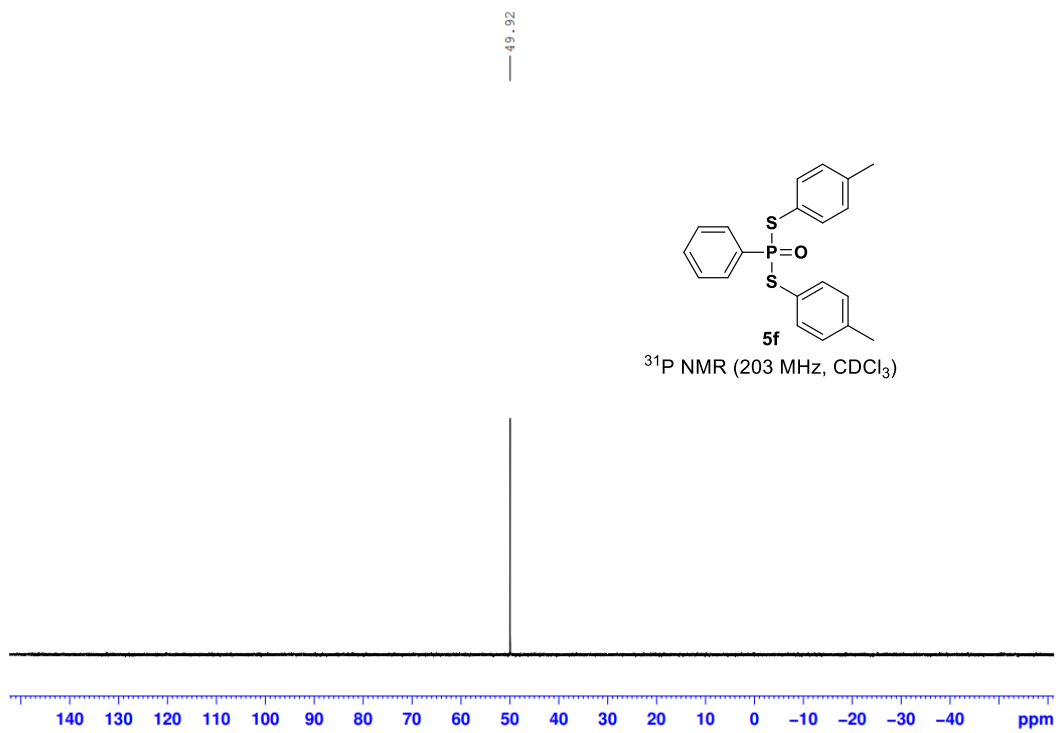
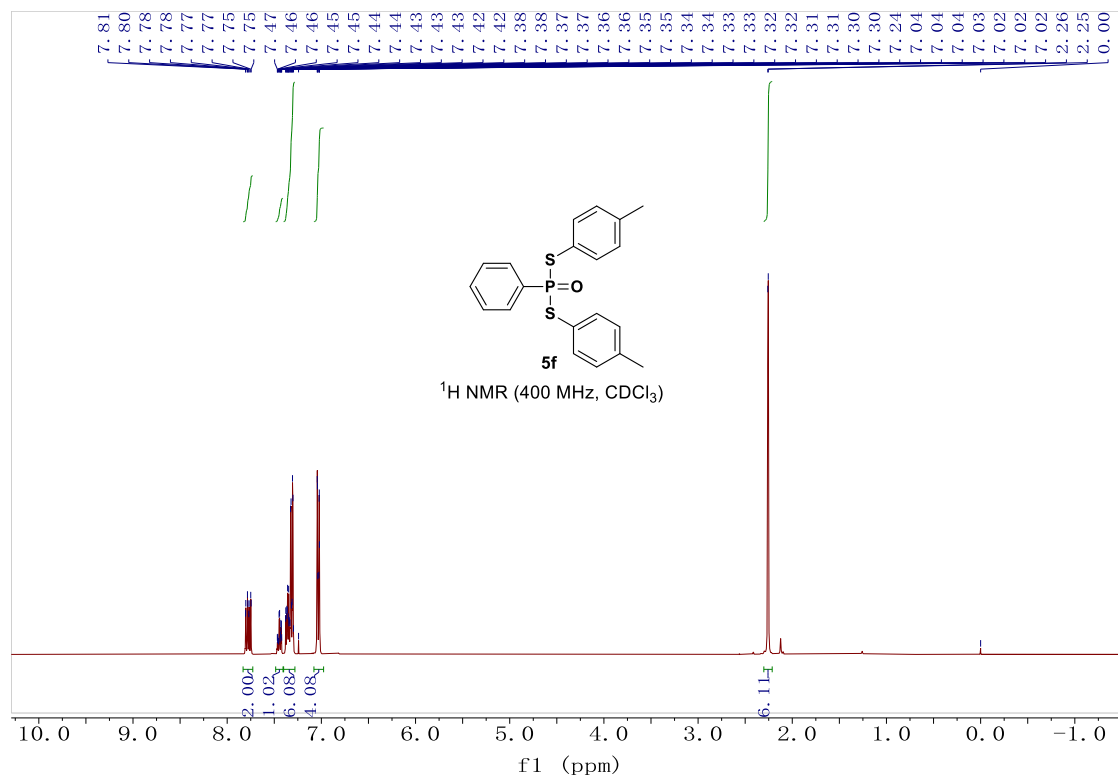


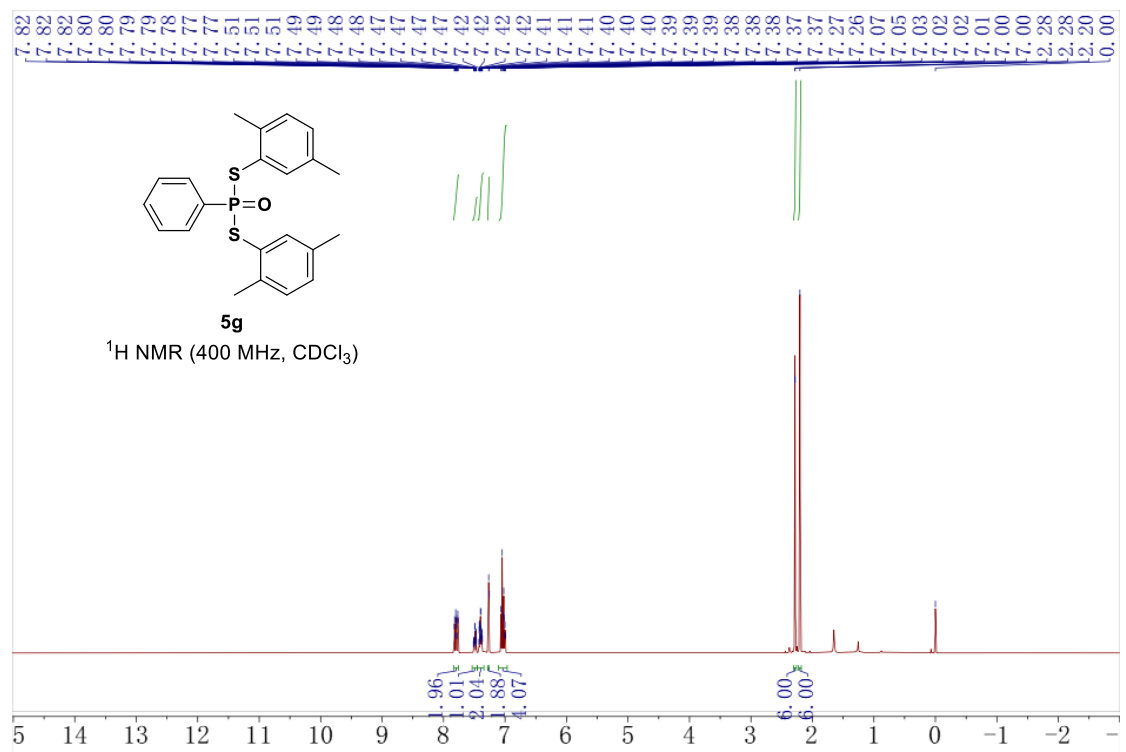
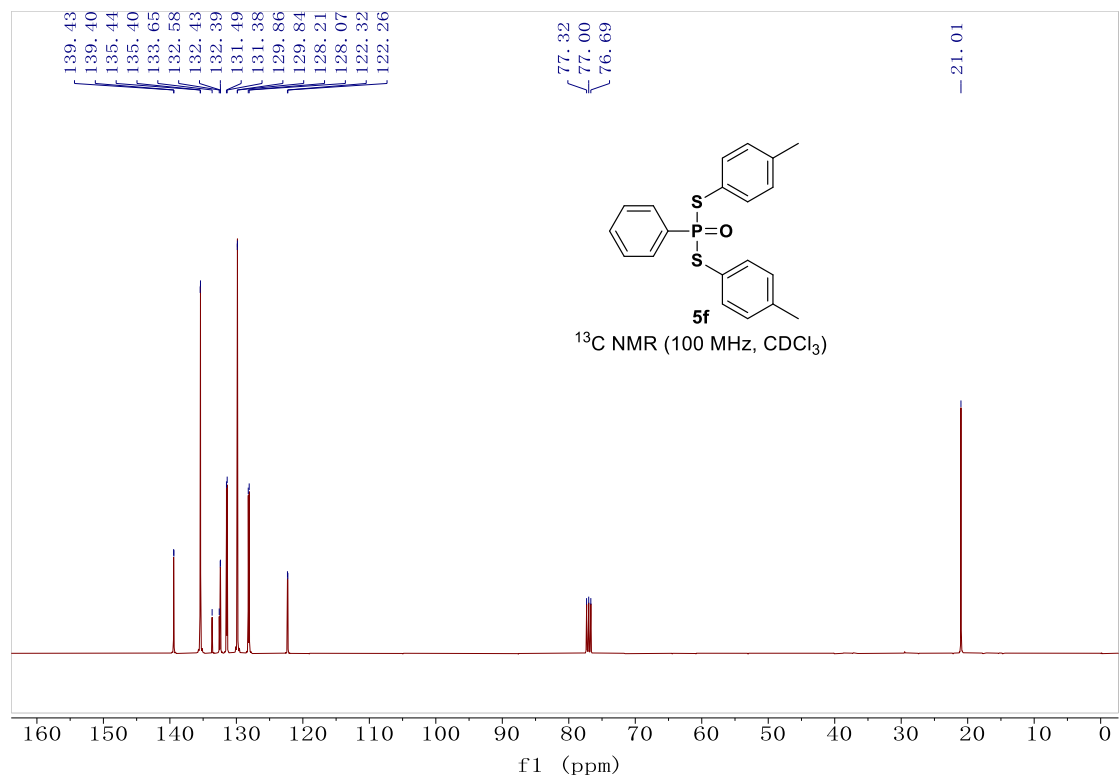
¹³C NMR (125 MHz, CDCl₃)

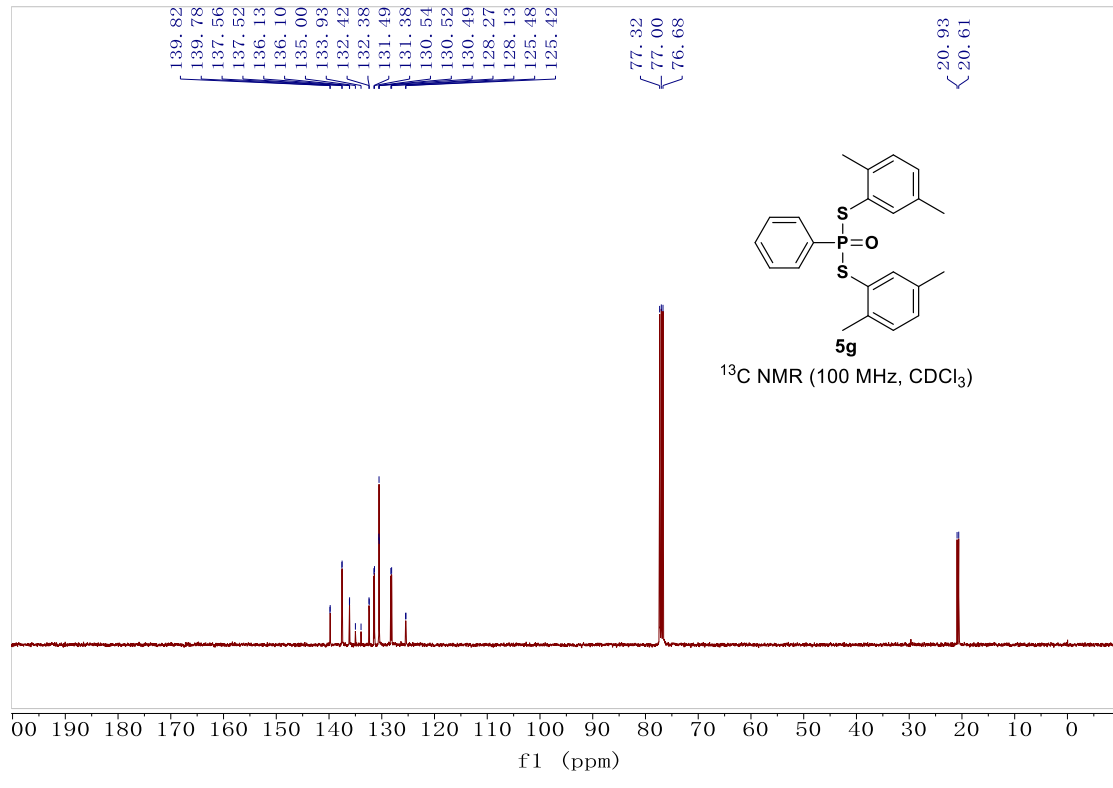
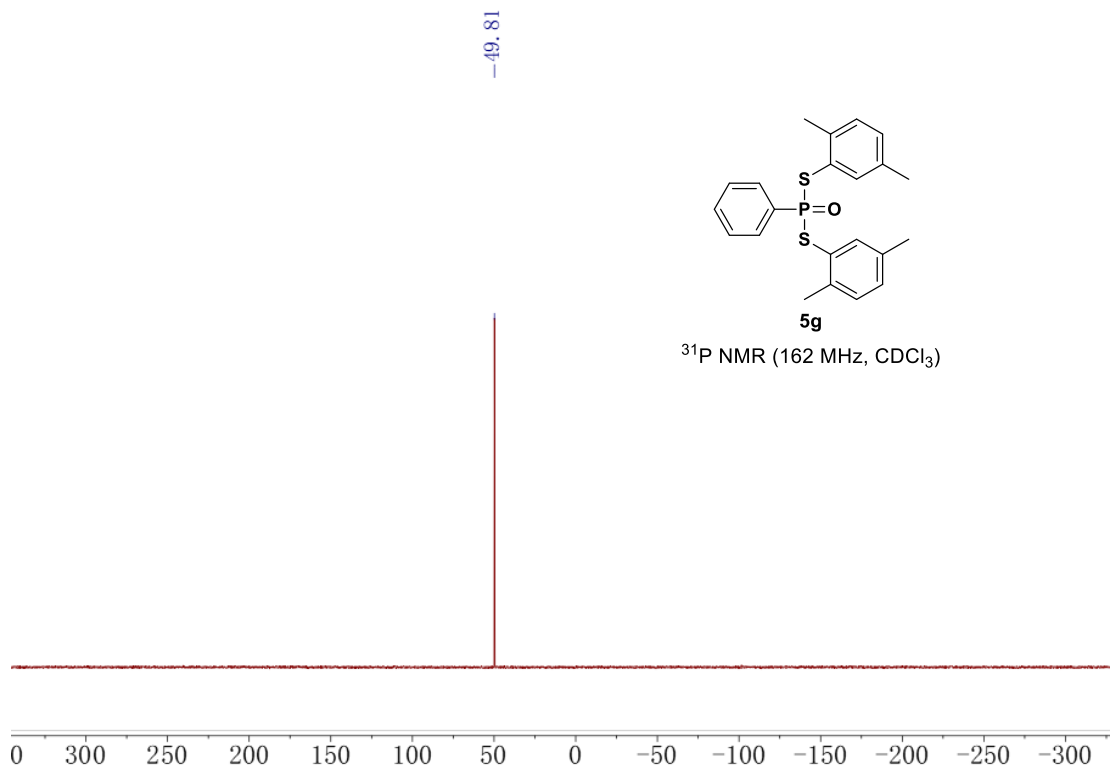


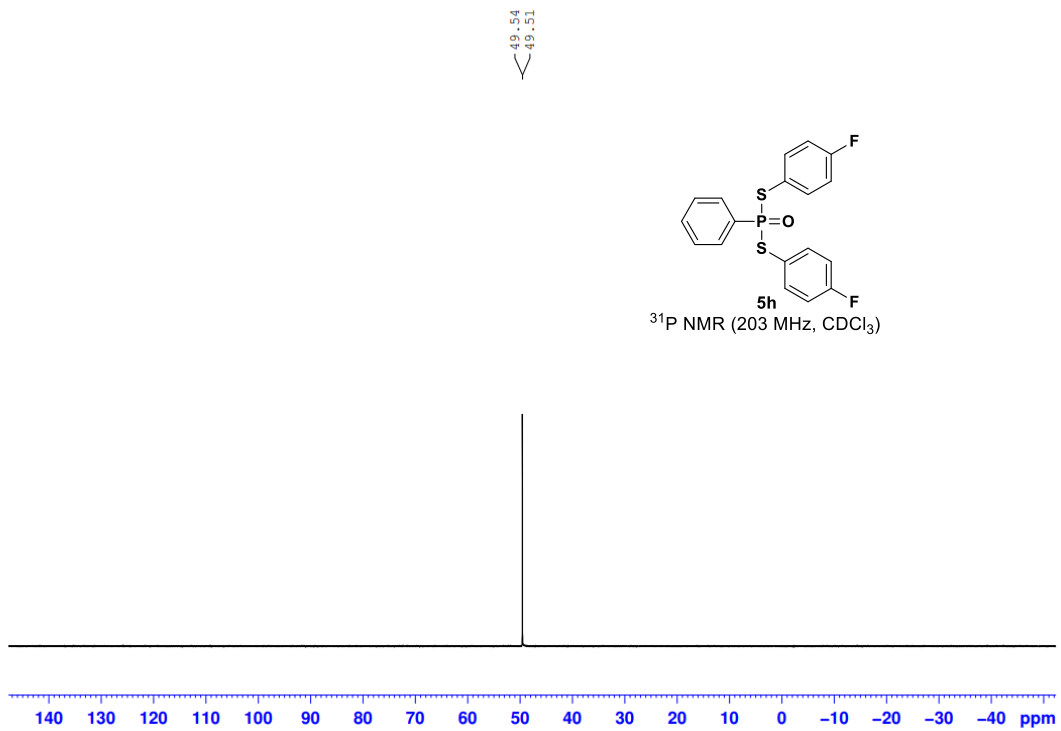
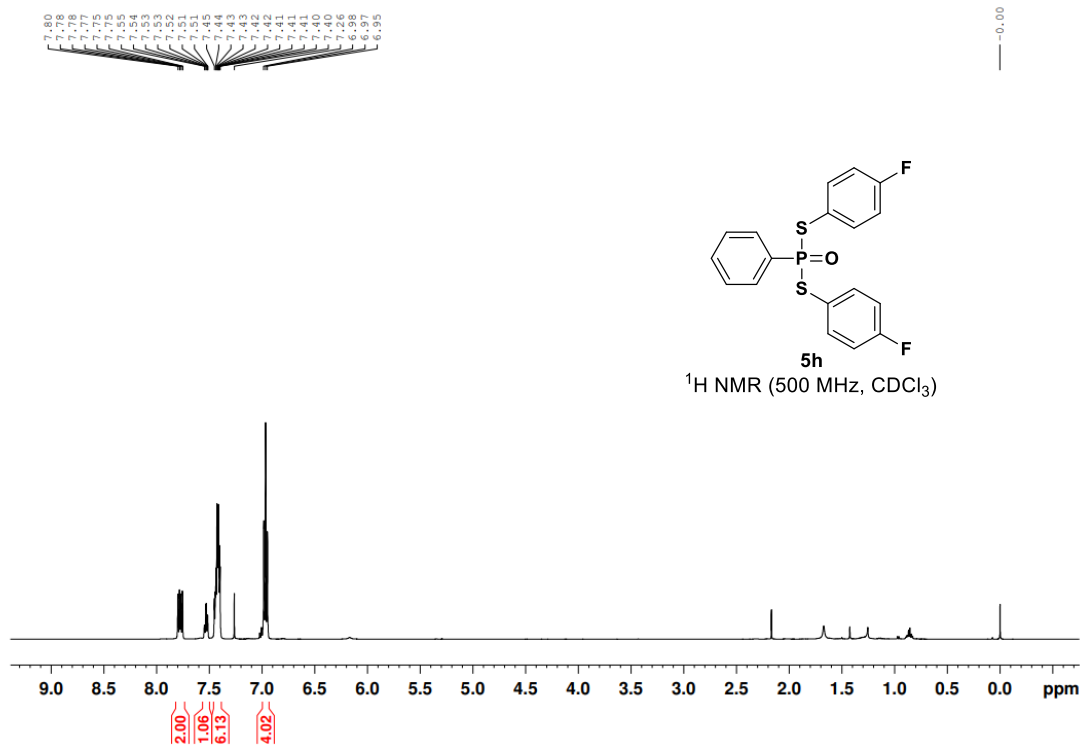


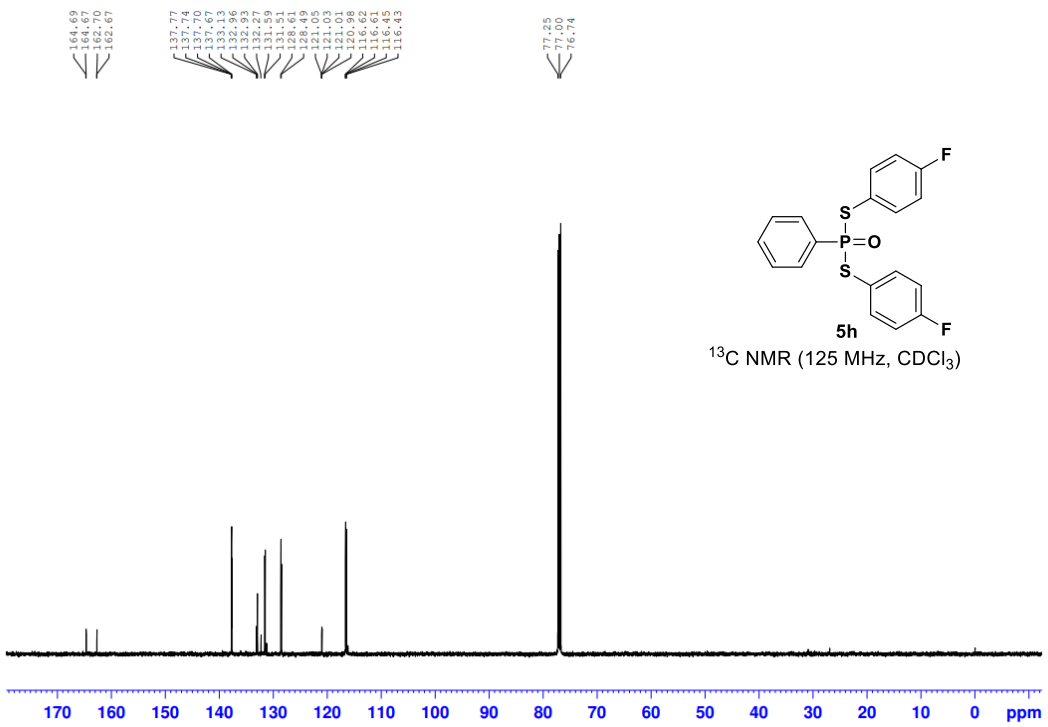
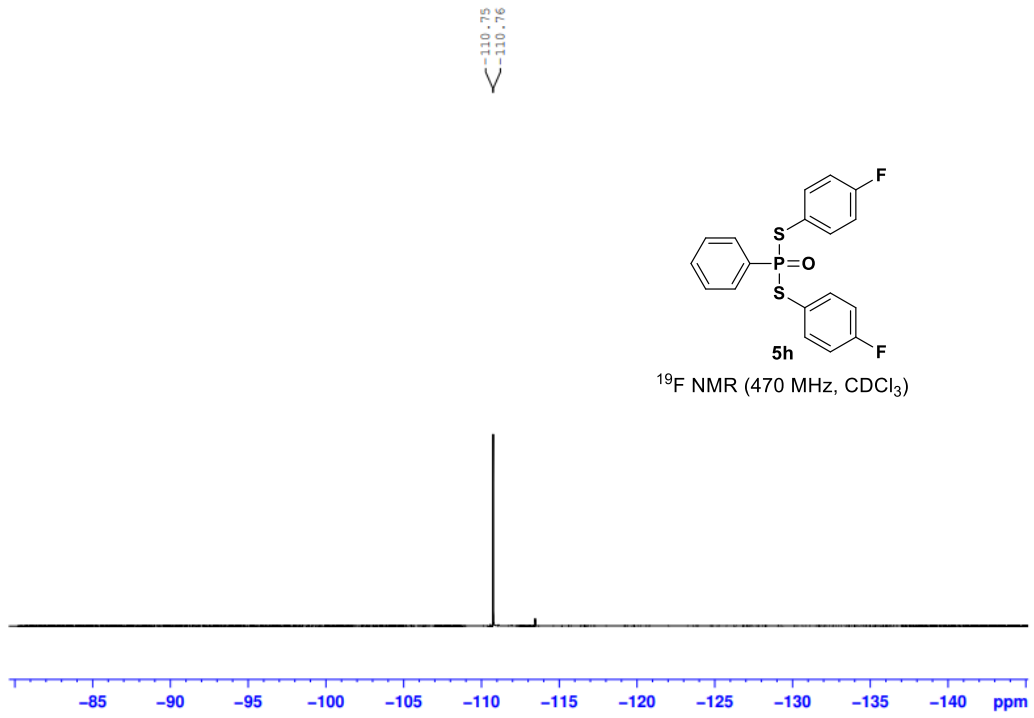


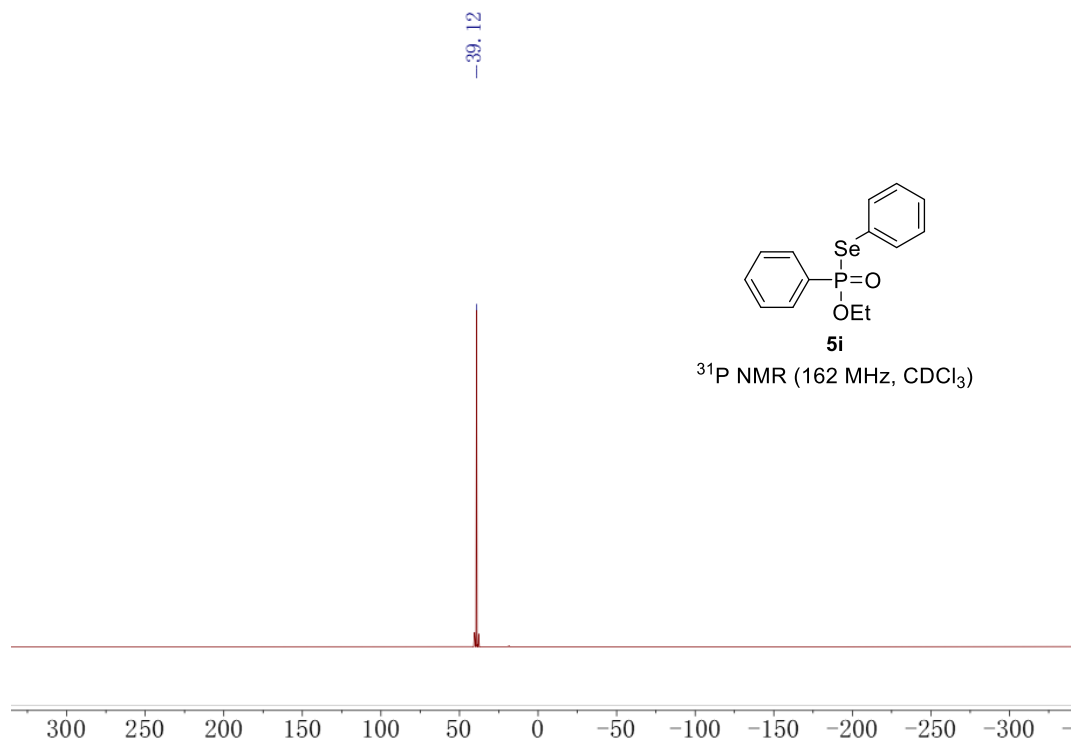
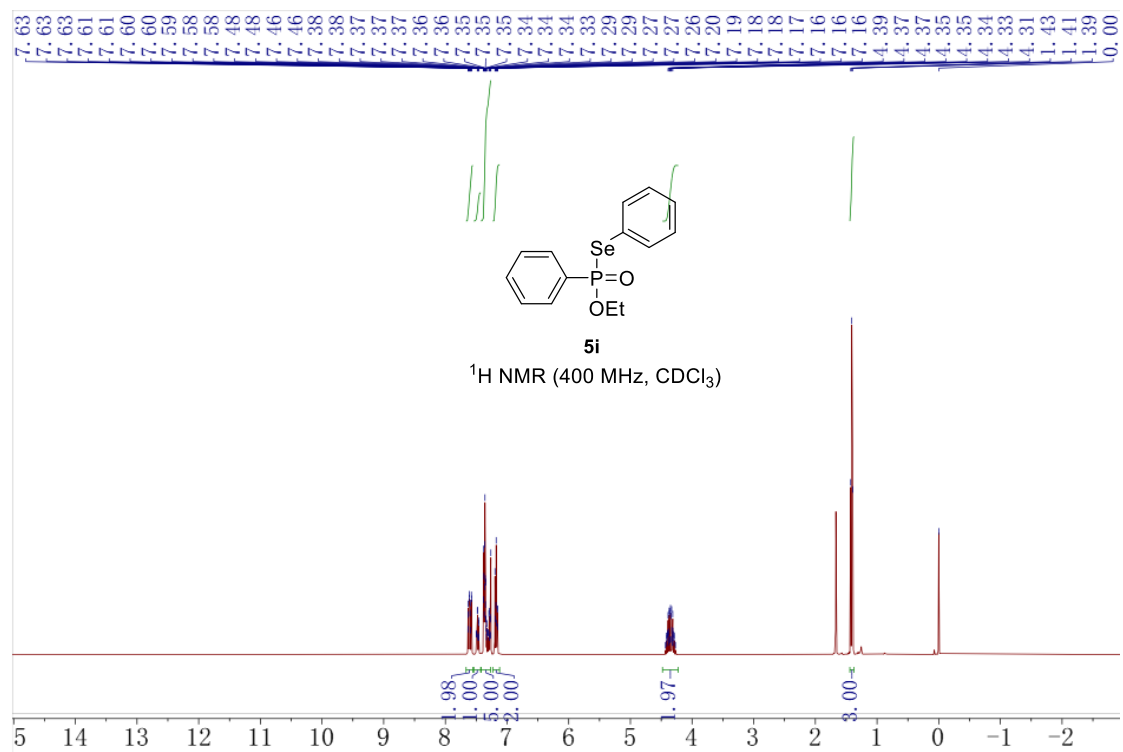


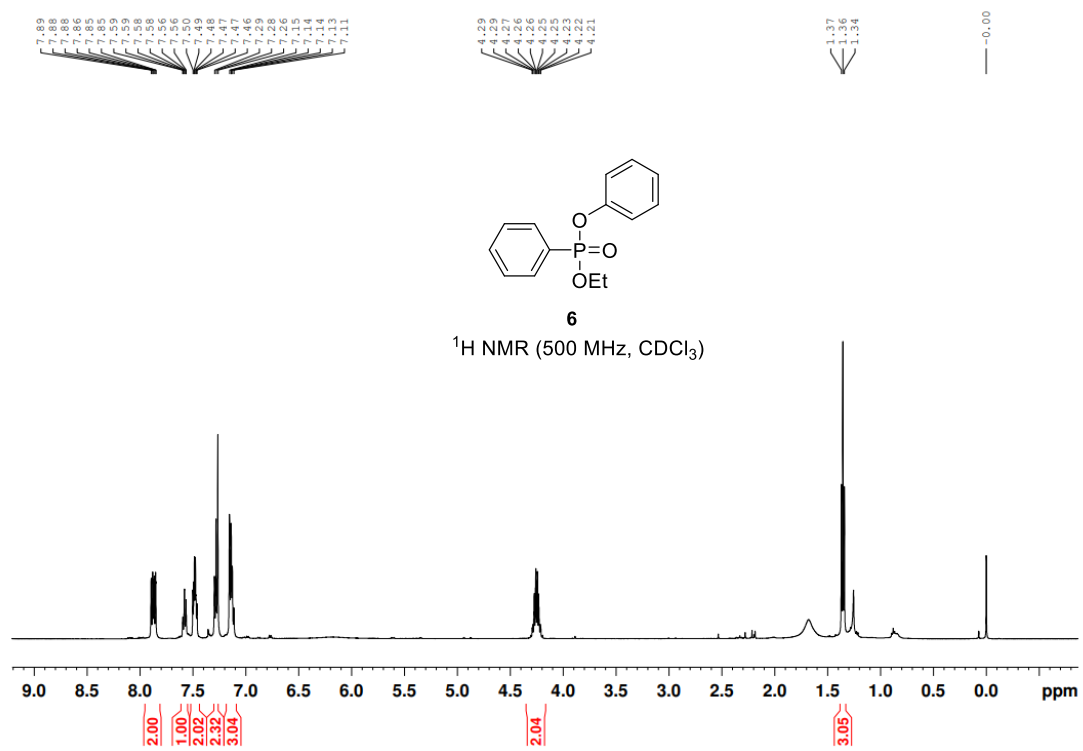
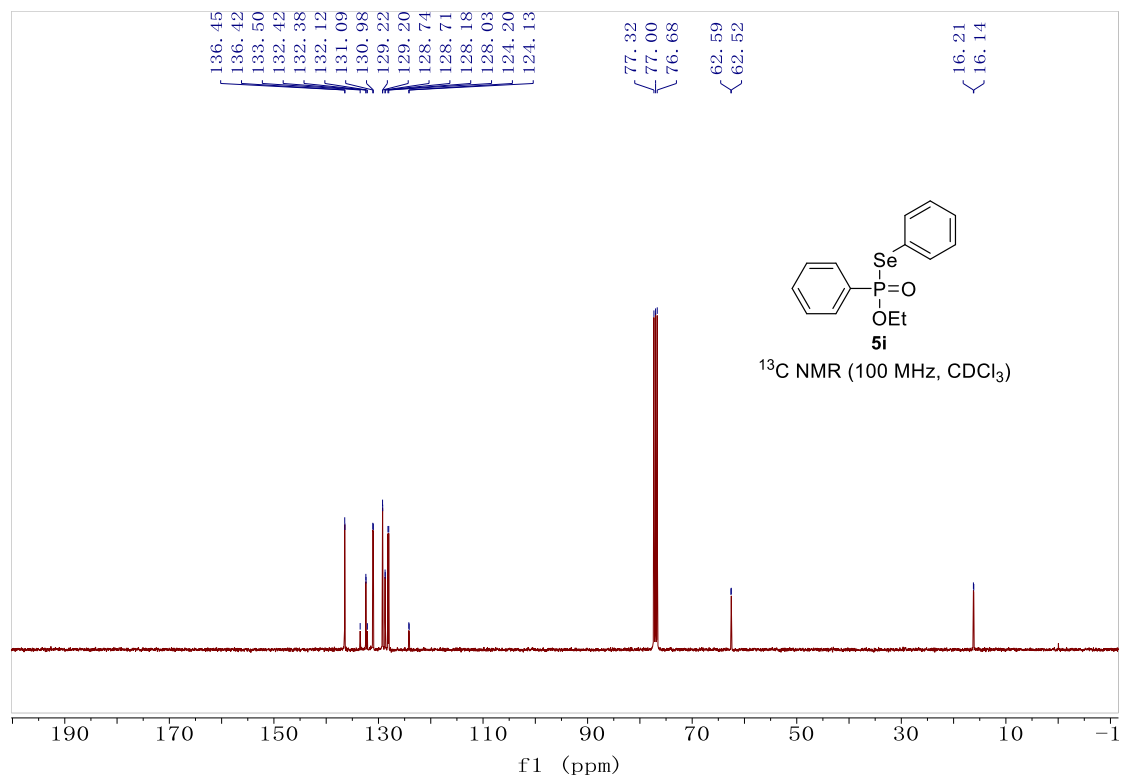




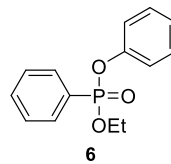




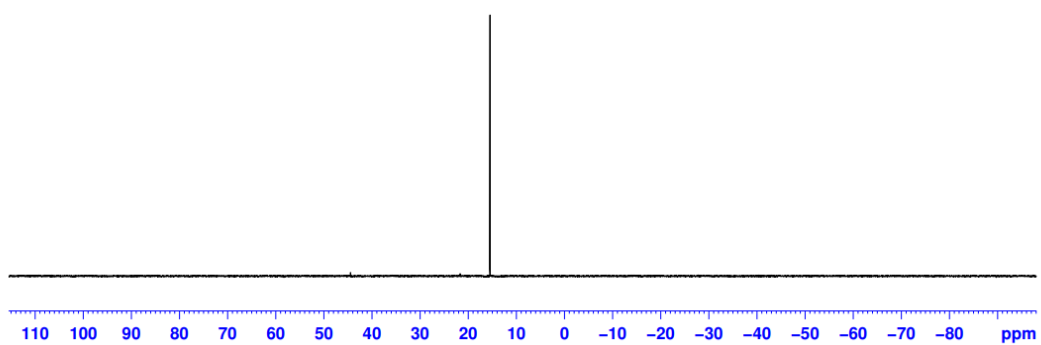




— 15.46



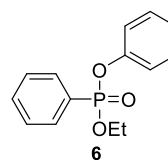
^{31}P NMR (203 MHz, CDCl_3)



150.53
150.48
132.84
132.82
131.98
131.90
128.91
128.48
128.20
124.85
120.55
120.52

77.25
77.00
76.75
63.00
62.96

16.29
16.24



^{13}C NMR (125 MHz, CDCl_3)

