

Supporting Information

Phosphinoyl-functionalization of unactivated alkenes through phosphinoyl radical-triggered distal functional group migration

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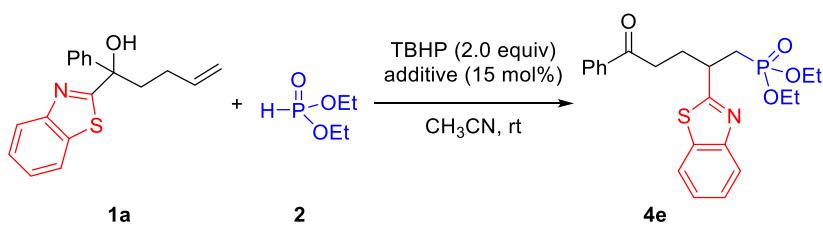
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1. General experimental details

All reactions were maintained under a nitrogen atmosphere unless otherwise stated. Commercially available reagents were used without further purification. Infrared (FT-IR) spectra were recorded on a BRUKER VERTEX 70, ν_{max} in cm^{-1} . $^1\text{H-NMR}$ spectra were recorded on a BRUKER AVANCE III HD (400 MHz) spectrometer. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as internal standard (CDCl_3 : δ 7.26). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quadruplet, br = broad, m = multiplet), coupling constants (Hz) and integration. $^{13}\text{C-NMR}$ spectra were recorded on a BRUKER AVANCE III HD (100 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (CDCl_3 : δ 77.16). $^{19}\text{P-NMR}$ spectra were recorded on a BRUKER AVANCE III HD (161 MHz) spectrometer. $^{19}\text{F-NMR}$ spectra were recorded on a BRUKER AVANCE III HD (376 MHz) spectrometer. Mass spectra were measured with an Agilent Technologies 6120 Quadrupole LC/MS. High resolution mass spectrometry (HRMS) were measured with a GCT PremierTM and BRUKER micrOTF-Q III. Melting points were measured using INESA WRR and values are uncorrected.

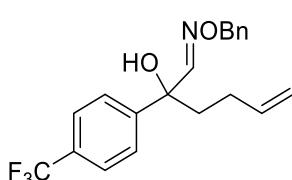
2. Reaction conditions survey for using phosphonates ^a



Entry	Additive	Yield (%) ^b
1	FeCl_3	0
2	$\text{Mn}(\text{OAc})_3$	trace
3	AgNO_3	0
4	CuI	44
5	CuCl	trace
6	CuBr	trace
7	$\text{Cu}(\text{OAc})_2$	38
8	$\text{Cu}(\text{OTf})_2$	86
9	CuSO_4	27
10 ^c	$\text{Cu}(\text{OTf})_2$	0
11 ^d	$\text{Cu}(\text{OTf})_2$	93

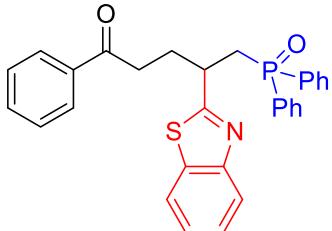
^aReaction conditions: **1a** (0.2 mmol), **2** (0.4 mmol), and TBHP (0.4 mmol) in CH_3CN (2 ml) at rt under N_2 , 24 h. ^bIsolated yield. ^cWithout TBHP. ^d $\text{Cu}(\text{OTf})_2$ 10 mol%.

3. Characterization of new starting materials

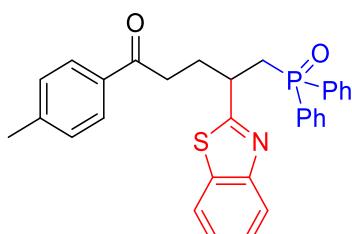


8g: yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 7.70 (s, 1H), 7.66-7.61 (m, 2H), 7.60-7.55 (m, 2H), 7.42-7.32 (m, 5H), 5.86-5.74 (m, 1H), 5.18-5.09 (m, 2H), 5.04-4.94 (m, 2H), 3.52 (s, 1H), 2.20-1.95 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 152.7, 147.2 (q, $J_{\text{C}-\text{F}} = 1.0$ Hz), 137.8, 136.9, 129.6 (q, $J_{\text{C}-\text{F}} = 32.3$ Hz), 128.5, 128.4, 128.2, 127.2 (q, $J_{\text{C}-\text{F}} = 257.3$ Hz), 125.7, 125.4 (q, $J_{\text{C}-\text{P}} = 3.7$ Hz), 115.1, 76.6, 75.5, 40.1, 27.5; ^{19}F NMR (376 MHz, CDCl_3) δ -62.5. FT-IR: ν (cm^{-1}) 3524, 3033, 2927, 1641, 1618, 1497, 1454, 1411, 1366, 1324. HRMS [CI] calcd for $\text{C}_{22}\text{H}_{21}\text{F}_3\text{NO}_2$ [$\text{M}+\text{H}]^+$ 364.1519, found 364.1509.

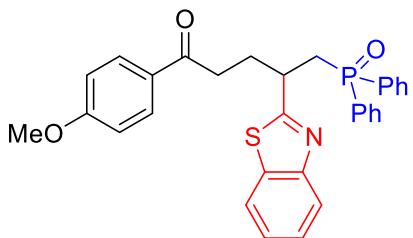
4. Characterization of new products



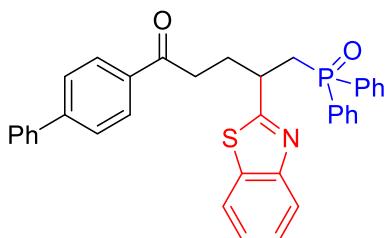
3a: colorless oil, 94.3 mg, 95%. ^1H NMR (400 MHz, CDCl_3) δ 7.85-7.78 (m, 3H), 7.78-7.71 (m, 2H), 7.69 (d, $J = 8.0$ Hz, 1H), 7.63-7.55 (m, 2H), 7.50-7.40 (m, 4H), 7.36 (dd, $J = 14.4, 7.2$ Hz, 1H), 7.19-7.09 (m, 3H), 3.94-3.83 (m, 1H), 3.26-3.15 (m, 1H), 3.04-2.86 (m, 2H), 2.80 (ddd, $J = 14.8, 14.8, 5.2$ Hz, 1H), 2.41 (dd, $J = 14.8, 7.6$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 198.8, 173.1 (d, $J_{\text{C}-\text{P}} = 6.8$ Hz), 152.9, 136.6, 134.7, 133.2 (d, $J_{\text{C}-\text{P}} = 98.9$ Hz), 133.0, 131.8 (d, $J_{\text{C}-\text{P}} = 2.6$ Hz), 131.6 (d, $J_{\text{C}-\text{P}} = 98.4$ Hz), 131.2 (d, $J_{\text{C}-\text{P}} = 2.7$ Hz), 130.9 (d, $J_{\text{C}-\text{P}} = 9.5$ Hz), 130.5 (d, $J_{\text{C}-\text{P}} = 9.4$ Hz), 128.7 (d, $J_{\text{C}-\text{P}} = 11.6$ Hz), 128.5, 128.0 (d, $J_{\text{C}-\text{P}} = 11.4$ Hz), 128.0, 125.8, 124.9, 122.7, 121.5, 37.8 (d, $J_{\text{C}-\text{P}} = 2.8$ Hz), 35.8, 35.8 (d, $J_{\text{C}-\text{P}} = 69.7$ Hz), 31.7 (d, $J_{\text{C}-\text{P}} = 9.0$ Hz); ^{31}P NMR (161 MHz, CDCl_3) δ 29.62. FT-IR: ν (cm^{-1}) 3055, 2922, 2852, 1678, 1605, 1572, 1509, 1483, 1455, 1436, 1406, 1367, 1311, 1277. HRMS [ESI] calcd for $\text{C}_{30}\text{H}_{26}\text{NO}_2\text{PSNa}$ [$\text{M}+\text{Na}]^+$ 518.1314, found 518.1303.



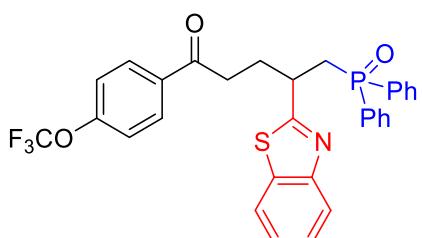
3b: white solid, m.p. 60-61 °C, 95.7 mg, 94%. ^1H NMR (400 MHz, CDCl_3) δ 7.81 (d, $J = 8.0$ Hz, 1H), 7.78-7.72 (m, 2H), 7.72-7.67 (m, 3H), 7.62-7.56 (m, 2H), 7.49-7.35 (m, 5H), 7.31-7.26 (m, 1H), 7.17-7.11 (m, 4H), 3.93-3.82 (m, 1H), 3.25-3.15 (m, 1H), 3.01-2.84 (m, 2H), 2.79 (ddd, $J = 14.8, 14.8, 5.2$ Hz, 1H), 2.40 (dd, $J = 14.8, 7.6$ Hz, 2H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 198.4, 173.2 (d, $J_{\text{C}-\text{P}} = 6.7$ Hz), 152.9, 143.7, 134.7, 134.2, 133.7 (d, $J_{\text{C}-\text{P}} = 98.8$ Hz), 131.8 (d, $J_{\text{C}-\text{P}} = 2.7$ Hz), 131.7 (d, $J_{\text{C}-\text{P}} = 98.9$ Hz), 131.2 (d, $J_{\text{C}-\text{P}} = 2.9$ Hz), 130.9 (d, $J_{\text{C}-\text{P}} = 9.5$ Hz), 130.5 (d, $J_{\text{C}-\text{P}} = 9.4$ Hz), 129.2, 128.7 (d, $J_{\text{C}-\text{P}} = 11.6$ Hz), 128.1, 128.0 (d, $J_{\text{C}-\text{P}} = 11.8$ Hz), 125.8, 124.9, 122.7, 121.5, 37.9 (d, $J_{\text{C}-\text{P}} = 2.8$ Hz), 35.7, 35.8 (d, $J_{\text{C}-\text{P}} = 69.8$ Hz), 31.8 (d, $J_{\text{C}-\text{P}} = 9.1$ Hz), 21.6; ^{31}P NMR (161 MHz, CDCl_3) δ 29.38. FT-IR: ν (cm^{-1}) 3057, 2958, 2925, 2853, 1682, 1596, 1579, 1509, 1484, 1436, 1368, 1311, 1262, 1240. HRMS [ESI] calcd for $\text{C}_{31}\text{H}_{28}\text{NO}_2\text{PSNa}$ [$\text{M}+\text{Na}]^+$ 532.1471, found 532.1461.



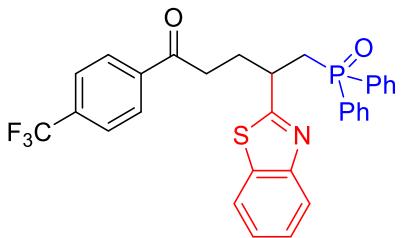
3c: white solid, m.p. 130-131 °C, 65.5 mg, 62%. ¹H NMR (400 MHz, CDCl₃) δ 7.86-7.71 (m, 5H), 7.68 (d, *J* = 7.6 Hz, 1H), 7.63-7.55 (m, 2H), 7.50-7.35 (m, 4H), 7.34-7.26 (m, 1H), 7.19-7.08 (m, 3H), 6.83 (d, *J* = 8.4 Hz, 2H), 3.95-3.82 (m, 1H), 3.80 (s, 3H), 3.27-3.16 (m, 1H), 2.99-2.86 (m, 2H), 2.81 (ddd, *J* = 14.8, 14.8, 5.2 Hz, 1H), 2.40 (dd, *J* = 14.4, 7.2 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 197.3, 173.4 (d, *J*_{C-P} = 6.5 Hz), 163.4, 152.6, 134.6, 133.6 (d, *J*_{C-P} = 98.9 Hz), 131.8 (d, *J*_{C-P} = 2.4 Hz), 131.6 (d, *J*_{C-P} = 98.3 Hz), 131.2 (d, *J*_{C-P} = 2.5 Hz), 130.9 (d, *J*_{C-P} = 9.5 Hz), 130.5 (d, *J*_{C-P} = 9.3 Hz), 130.3, 129.7, 128.7 (d, *J*_{C-P} = 11.7 Hz), 128.0 (d, *J*_{C-P} = 11.7 Hz), 125.9, 124.9, 122.6, 121.5, 113.6, 55.4, 37.9 (d, *J*_{C-P} = 2.7 Hz), 35.7 (d, *J*_{C-P} = 69.7 Hz), 35.5, 32.0 (d, *J*_{C-P} = 9.1 Hz); ³¹P NMR (161 MHz, CDCl₃) δ 29.46. FT-IR: ν (cm⁻¹) 3054, 2956, 2924, 2853, 1670, 1599, 1509, 1456, 1436, 1365, 1313, 1255, 1235. HRMS [ESI] calcd for C₃₁H₂₈NO₃PSNa [M+Na]⁺ 548.1420, found 548.1414.



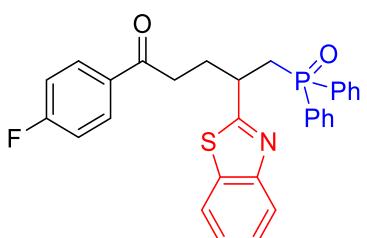
3d: white solid, m.p. 181-182 °C, 58.2 mg, 51%. ¹H NMR (400 MHz, CDCl₃) δ 7.92-7.82 (m, 3H), 7.81-7.73 (m, 2H), 7.70 (d, *J* = 7.6 Hz, 1H), 7.66-7.53 (m, 6H), 7.49-7.33 (m, 7H), 7.32-7.26 (m, 1H), 7.21-7.10 (m, 3H), 3.99-3.85 (m, 1H), 3.31-3.18 (m, 1H), 3.08-2.91 (m, 2H), 2.90-2.73 (m, 1H), 2.46 (dd, *J* = 13.2, 6.4 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 198.4, 173.3 (d, *J*_{C-P} = 6.2 Hz), 152.7, 145.6, 139.8, 135.3, 134.7, 133.7 (d, *J*_{C-P} = 98.3 Hz), 131.9, 131.6 (d, *J*_{C-P} = 98.6 Hz), 131.2, 130.9 (d, *J*_{C-P} = 9.1 Hz), 130.5 (d, *J*_{C-P} = 9.0 Hz), 128.9, 128.7 (d, *J*_{C-P} = 11.4 Hz), 128.6, 128.2, 128.1 (d, *J*_{C-P} = 11.5 Hz), 127.2, 127.1, 125.9, 125.0, 122.7, 121.5, 37.9, 35.9, 35.8 (d, *J*_{C-P} = 69.7 Hz), 31.8 (d, *J*_{C-P} = 8.4 Hz); ³¹P NMR (161 MHz, CDCl₃) δ 29.49. FT-IR: ν (cm⁻¹) 3059, 2925, 1679, 1602, 1558, 1511, 1484, 1453, 1437, 1381, 1313, 1268, 1231. HRMS [ESI] calcd for C₃₆H₂₀NO₂PSNa [M+Na]⁺ 594.1627, found 594.1616.



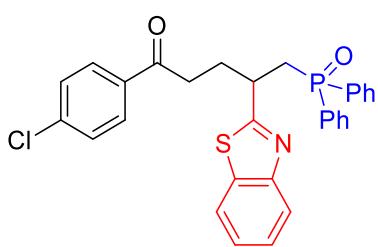
3e: yellow oil, 73.2 mg, 63%. ¹H NMR (400 MHz, CDCl₃) δ 7.90-7.84 (m, 2H), 7.81 (d, *J* = 8.4 Hz, 1H), 7.79-7.69 (m, 3H), 7.63-7.57 (m, 2H), 7.51-7.37 (m, 5H), 7.34-7.28 (m, 1H), 7.22-7.14 (m, 4H), 3.93-3.81 (m, 1H), 3.25-3.14 (m, 1H), 3.04-2.88 (m, 2H), 2.82 (ddd, *J* = 14.0, 14.0, 5.6 Hz, 1H), 2.42 (dd, *J* = 14.8, 7.6 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 196.8, 172.7 (d, *J*_{C-P} = 7.4 Hz), 152.3, 152.0, 134.4, 134.2, 133.1 (d, *J*_{C-P} = 99.2 Hz), 131.4 (d, *J*_{C-P} = 2.7 Hz), 131.3 (q, *J*_{C-F} = 2.4 Hz), 130.8 (d, *J*_{C-P} = 2.7 Hz), 130.4 (d, *J*_{C-P} = 9.5 Hz), 130.0 (d, *J*_{C-P} = 9.3 Hz), 129.6, 128.3 (d, *J*_{C-P} = 11.7 Hz), 127.6 (d, *J*_{C-P} = 11.8 Hz), 125.4, 124.5, 121.7 (q, *J*_{C-F} = 254.1 Hz), 122.2, 121.0, 119.8, 37.3 (d, *J*_{C-P} = 2.7 Hz), 35.4, 35.2 (d, *J*_{C-P} = 69.6 Hz), 31.1 (d, *J*_{C-P} = 8.6 Hz); ³¹P NMR (161 MHz, CDCl₃) δ 29.68; ¹⁹F NMR (376 MHz, CDCl₃) δ -57.6. FT-IR: ν (cm⁻¹) 3059, 2925, 1686, 1602, 1506, 1437, 1411, 1370, 1309, 1254, 1209. HRMS [ESI] calcd for C₃₁H₂₅F₃NO₃PSNa [M+Na]⁺ 602.1137, found 602.1127.



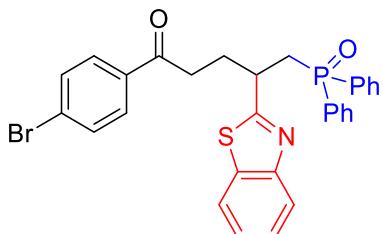
3f: white solid, m.p. 105-106 °C, 67.0 mg, 59%. ¹H NMR (400 MHz, CDCl₃) δ 7.91 (d, *J* = 8.0 Hz, 2H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.80-7.70 (m, 3H), 7.66-7.58 (m, 4H), 7.52-7.36 (m, 4H), 7.35-7.28 (m, 1H), 7.24-7.14 (m, 3H), 3.94-3.81 (m, 1H), 3.27-3.14 (m, 1H), 3.08-2.92 (m, 2H), 2.83 (ddd, *J* = 14.4, 14.4, 5.6 Hz, 1H), 2.50-2.40 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 197.8, 173.1 (d, *J*_{C-P} = 7.3 Hz), 152.8, 139.2, 134.7, 134.2 (q, *J*_{C-F} = 32.4 Hz), 133.8 (d, *J*_{C-P} = 99.3 Hz), 131.6 (d, *J*_{C-P} = 99.0 Hz), 131.9 (d, *J*_{C-P} = 1.8 Hz), 131.3 (d, *J*_{C-P} = 1.8 Hz), 130.9 (d, *J*_{C-P} = 9.2 Hz), 130.5 (d, *J*_{C-P} = 9.1 Hz), 128.7 (d, *J*_{C-P} = 11.5 Hz), 128.3, 128.1 (d, *J*_{C-P} = 11.7 Hz), 125.9, 125.5 (q, *J*_{C-F} = 3.7 Hz), 125.0, 123.2 (q, *J*_{C-F} = 271.1 Hz), 122.7, 121.5, 37.8 (d, *J*_{C-P} = 1.6 Hz), 36.1, 35.3 (d, *J*_{C-P} = 68.9 Hz), 31.3 (d, *J*_{C-P} = 8.1 Hz); ³¹P NMR (161 MHz, CDCl₃) δ 29.30; ¹⁹F NMR (376 MHz, CDCl₃) δ -63.1. FT-IR: ν (cm⁻¹) 3056, 2920, 2852, 1691, 1653, 1577, 1508, 1486, 1456, 1436, 1372, 1323, 1240. HRMS [ESI] calcd for C₃₀H₂₅F₃NO₂PSNa [M+Na]⁺ 586.1188, found 586.1174.



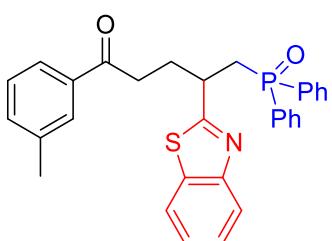
3g: white solid, m.p. 40-41 °C, 63.0 mg 61%. ¹H NMR (400 MHz, CDCl₃) δ 7.89-7.82 (m, 3H), 7.79-7.69 (m, 3H), 7.65-7.57 (m, 2H), 7.51-7.38 (m, 5H), 7.35-7.28 (m, 1H), 7.19-7.13 (m, 2H), 7.09-7.00 (m, 2H), 3.95-3.81 (m, 1H), 3.30-3.16 (m, 1H), 3.02-2.89 (m, 2H), 2.89-2.75 (m, 1H), 2.42 (dd, *J* = 13.6, 6.8 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 197.2, 173.2 (d, *J*_{C-P} = 7.2 Hz), 165.6 (d, *J*_{C-F} = 253.0 Hz), 152.9, 134.7, 133.7 (d, *J*_{C-P} = 98.9 Hz), 133.1 (d, *J*_{C-F} = 3.3 Hz), 131.9 (d, *J*_{C-P} = 2.6 Hz), 131.6 (d, *J*_{C-P} = 98.4 Hz), 131.2 (d, *J*_{C-P} = 2.7 Hz), 130.9 (d, *J*_{C-P} = 9.4 Hz), 130.6 (d, *J*_{C-F} = 9.3 Hz), 130.5 (d, *J*_{C-P} = 9.3 Hz), 128.7 (d, *J*_{C-P} = 11.6 Hz), 128.1 (d, *J*_{C-P} = 11.8 Hz), 125.9, 124.9, 122.7, 121.5, 115.6 (d, *J*_{C-F} = 21.7 Hz), 37.8 (d, *J*_{C-P} = 2.8 Hz), 35.7, 35.8 (d, *J*_{C-P} = 69.6 Hz), 31.7 (d, *J*_{C-P} = 8.6 Hz); ³¹P NMR (161 MHz, CDCl₃) δ 29.67; ¹⁹F NMR (376 MHz, CDCl₃) δ -105.4. FT-IR: ν (cm⁻¹) 3057, 2927, 1682, 1595, 1505, 1455, 1436, 1408, 1369, 1311, 1277, 1227. HRMS [ESI] calcd for C₃₀H₂₅FNO₂PSNa [M+Na]⁺ 536.1220, found 536.1192.



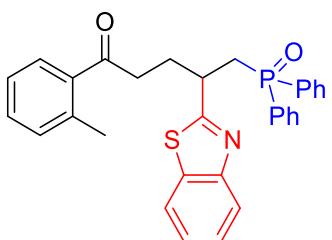
3h: white solid, m.p. 51-52 °C, 83.0 mg, 78%. ¹H NMR (400 MHz, CDCl₃) δ 7.84 (d, *J* = 8.0 Hz, 1H), 7.80-7.73 (m, 4H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.66-7.57 (m, 2H), 7.52-7.39 (m, 4H), 7.38-7.30 (m, 3H), 7.22-7.12 (m, 3H), 3.96-3.82 (m, 1H), 3.30-3.17 (m, 1H), 3.04-2.87 (m, 2H), 2.82 (ddd, *J* = 14.4, 14.4, 5.2 Hz, 1H), 2.44 (dd, *J* = 13.6, 6.8 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 197.6, 173.1 (d, *J*_{C-P} = 7.4 Hz), 152.8, 139.4, 134.9, 134.7, 133.7 (d, *J*_{C-P} = 99.0 Hz), 131.9 (d, *J*_{C-P} = 2.7 Hz), 131.6 (d, *J*_{C-P} = 98.4 Hz), 131.3 (d, *J*_{C-P} = 2.8 Hz), 130.9 (d, *J*_{C-P} = 9.4 Hz), 130.5 (d, *J*_{C-P} = 9.3 Hz), 129.4, 128.8, 128.7 (d, *J*_{C-P} = 11.4 Hz), 128.1 (d, *J*_{C-P} = 11.8 Hz), 125.9, 125.0, 122.7, 121.5, 37.8 (d, *J*_{C-P} = 2.8 Hz), 35.8, 35.7 (d, *J*_{C-P} = 69.6 Hz), 31.6 (d, *J*_{C-P} = 8.6 Hz); ³¹P NMR (161 MHz, CDCl₃) δ 29.50. FT-IR: ν (cm⁻¹) 3057, 2923, 2852, 1682, 1587, 1571, 1508, 1486, 1456, 1436, 1399, 1368, 1311, 1261. HRMS [ESI] calcd for C₃₀H₂₅ClNO₂PSNa [M+Na]⁺ 552.0924, found 552.0933.



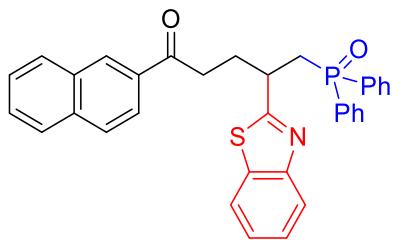
3i: white solid, m.p. 58-59 °C, 82.6 mg, 72%. ¹H NMR (400 MHz, CDCl₃) δ 7.82 (d, *J* = 8.0 Hz, 1H), 7.79-7.70 (m, 3H), 7.69-7.65 (m, 2H), 7.64-7.56 (m, 2H), 7.50 (d, *J* = 8.8 Hz, 2H), 7.50-7.38 (m, 5H), 7.35-7.29 (m, 1H), 7.23-7.12 (m, 3H), 3.92-3.80 (m, 1H), 3.25-3.13 (m, 1H), 3.01-2.85 (m, 2H), 2.80 (ddd, *J* = 14.4, 14.4, 5.6 Hz, 1H), 2.42 (dd, *J* = 14.4, 7.2 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 197.8, 173.1 (d, *J*_{C-P} = 7.3 Hz), 152.8, 135.3, 134.7, 133.6 (d, *J*_{C-P} = 100.1 Hz), 131.9, 131.8, 131.3, 131.2, 130.9 (d, *J*_{C-P} = 9.3 Hz), 130.5 (d, *J*_{C-P} = 9.2 Hz), 129.6, 128.7 (d, *J*_{C-P} = 11.5 Hz), 128.1 (d, *J*_{C-P} = 99.2 Hz), 128.1 (d, *J*_{C-P} = 11.4 Hz), 125.9, 125.0, 122.7, 121.5, 37.8, 35.8, 35.7 (d, *J*_{C-P} = 69.5 Hz), 31.6 (d, *J*_{C-P} = 8.3 Hz); ³¹P NMR (161 MHz, CDCl₃) δ 29.69. FT-IR: ν (cm⁻¹) 2956, 2900, 2853, 1772, 1733, 1716, 1683, 1653, 1636, 1583, 1559, 1541, 1508, 1486, 1467, 1456, 1436, 1396, 1312, 1274, 1241. HRMS [ESI] calcd for C₃₀H₂₅BrNO₂PSNa [M+Na]⁺ 596.0419, found 596.0405.



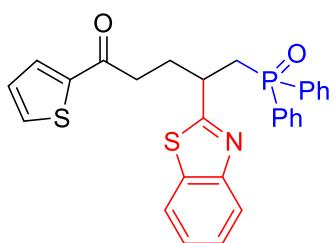
3j: white solid, m.p. 47-48 °C, 89.1 mg, 87%. ¹H NMR (400 MHz, CDCl₃) δ 7.82 (d, *J* = 8.0 Hz, 1H), 7.78-7.72 (m, 2H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.63-7.56 (m, 4H), 7.47-7.36 (m, 4H), 7.31-7.26 (m, 2H), 7.26-7.21 (m, 1H), 7.19-7.10 (m, 3H), 3.93-3.82 (m, 1H), 3.25-3.15 (m, 1H), 3.03-2.85 (m, 2H), 2.80 (ddd, *J* = 14.4, 14.4, 5.6 Hz, 1H), 2.41 (dd, *J* = 14.8, 7.6 Hz, 2H), 2.32 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 199.0, 173.2 (d, *J*_{C-P} = 6.7 Hz), 152.9, 138.2, 136.7, 134.8, 133.7, 133.7 (d, *J*_{C-P} = 98.9 Hz), 131.8 (d, *J*_{C-P} = 2.7 Hz), 131.6 (d, *J*_{C-P} = 98.4 Hz), 131.2 (d, *J*_{C-P} = 2.7 Hz), 130.9 (d, *J*_{C-P} = 9.4 Hz), 130.5 (d, *J*_{C-P} = 9.3 Hz), 128.7 (d, *J*_{C-P} = 11.6 Hz), 128.5, 128.4, 128.0 (d, *J*_{C-P} = 11.7 Hz), 125.8, 125.2, 124.9, 122.7, 121.5, 37.9 (d, *J*_{C-P} = 2.9 Hz), 35.9, 35.8 (d, *J*_{C-P} = 69.7 Hz), 31.8 (d, *J*_{C-P} = 9.1 Hz), 21.3; ³¹P NMR (161 MHz, CDCl₃) δ 29.37. FT-IR: ν (cm⁻¹) 3055, 2921, 2852, 1681, 1603, 1585, 1558, 1541, 1508, 1484, 1456, 1436, 1364, 1311, 1278, 1243. HRMS [ESI] calcd for C₃₁H₂₈NO₂PSNa [M+Na]⁺ 532.1471, found 532.1465.



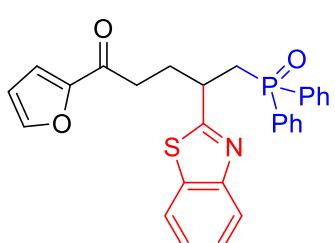
3k: white solid, m.p. 40-41 °C, 76.7 mg, 75%. ¹H NMR (400 MHz, CDCl₃) δ 7.82 (d, *J* = 8.0 Hz, 1H), 7.79-7.72 (m, 2H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.64-7.55 (m, 2H), 7.51-7.36 (m, 5H), 7.34-7.26 (m, 2H), 7.20-7.10 (m, 5H), 3.93-3.80 (m, 1H), 3.27-3.15 (m, 1H), 2.97-2.73 (m, 3H), 2.45-2.31 (m, 2H), 2.38 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 202.7, 173.2 (d, *J*_{C-P} = 6.9 Hz), 152.9, 138.0, 137.5, 134.7, 133.7 (d, *J*_{C-P} = 98.9 Hz), 131.8, 131.8 (d, *J*_{C-P} = 2.8 Hz), 131.2, 131.2 (d, *J*_{C-P} = 3.0 Hz), 130.9 (d, *J*_{C-P} = 9.4 Hz), 130.5 (d, *J*_{C-P} = 9.3 Hz), 128.7 (d, *J*_{C-P} = 11.6 Hz), 128.6, 128.4, 128.0 (d, *J*_{C-P} = 11.8 Hz), 125.8, 125.6, 124.9, 122.7, 121.5, 38.6, 37.8 (d, *J*_{C-P} = 2.9 Hz), 35.8 (d, *J*_{C-P} = 69.7 Hz), 31.8 (d, *J*_{C-P} = 9.1 Hz), 21.3; ³¹P NMR (161 MHz, CDCl₃) δ 29.58. FT-IR: ν (cm⁻¹) 3058, 2926, 1682, 1591, 1570, 1509, 1484, 1456, 1436, 1380, 1311, 1263. HRMS [ESI] calcd for C₃₁H₂₈NO₂PSNa [M+Na]⁺ 532.1471, found 532.1465.



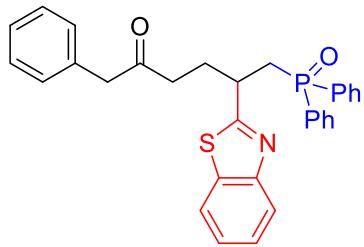
3l: white solid, m.p. 173-174 °C, 80.5 mg, 74%. ¹H NMR (400 MHz, CDCl₃) δ 8.31 (s, 1H), 7.94-7.69 (m, 8H), 7.66-7.58 (m, 2H), 7.58-7.53 (m, 1H), 7.53-7.39 (m, 5H), 7.37-7.28 (m, 1H), 7.21-7.11 (m, 3H), 4.02-3.88 (m, 1H), 3.33-3.22 (m, 1H), 3.20-3.02 (m, 2H), 2.85 (ddd, *J* = 14.4, 14.4, 5.2 Hz, 1H), 2.49 (dd, *J* = 14.8, 7.2 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 198.8, 173.3 (d, *J*_{C-P} = 6.9 Hz), 152.9, 135.5, 134.8, 133.9, 133.8 (d, *J*_{C-P} = 99.0 Hz), 132.4, 131.8 (d, *J*_{C-P} = 2.6 Hz), 131.6 (d, *J*_{C-P} = 98.4 Hz), 131.2 (d, *J*_{C-P} = 2.6 Hz), 130.9 (d, *J*_{C-P} = 9.4 Hz), 130.5 (d, *J*_{C-P} = 9.3 Hz), 129.7, 129.6, 129.6, 128.7 (d, *J*_{C-P} = 11.6 Hz), 128.4, 128.3, 128.1 (d, *J*_{C-P} = 11.8 Hz), 127.7, 126.7, 125.8, 124.9, 123.8, 122.7, 121.5, 37.9 (d, *J*_{C-P} = 2.8 Hz), 35.9, 35.8 (d, *J*_{C-P} = 69.7 Hz), 32.0 (d, *J*_{C-P} = 8.9 Hz); ³¹P NMR (161 MHz, CDCl₃) δ 29.65. FT-IR: ν (cm⁻¹) 3051, 2908, 1676, 1626 1576, 1507 1465, 1454, 1436, 1392, 1315, 1285, 1244. HRMS [ESI] calcd for C₃₆H₂₀NO₂PSNa [M+Na]⁺ 594.1627, found 594.1616.



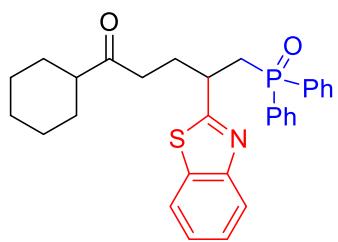
3m: white solid, m.p. 66-67 °C, 55.3 mg, 55%. ¹H NMR (400 MHz, CDCl₃) δ 7.84 (d, *J* = 8.0 Hz, 1H), 7.80-7.69 (m, 3H), 7.64-7.55 (m, 4H), 7.51-7.38 (m, 4H), 7.35-7.28 (m, 1H), 7.20-7.11 (m, 3H), 7.06-7.00 (m, 1H), 3.94-3.82 (m, 1H), 3.28-3.17 (m, 1H), 2.98-2.87 (m, 2H), 2.81 (ddd, *J* = 15.6, 15.6, 6.0 Hz, 1H), 2.44 (dd, *J* = 14.8, 7.2 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 191.7, 173.3 (d, *J*_{C-P} = 6.7 Hz), 152.4, 143.9, 134.6, 133.5, 133.5 (d, *J*_{C-P} = 99.2 Hz), 132.0, 131.9 (d, *J*_{C-P} = 2.4 Hz), 131.2 (d, *J*_{C-P} = 2.5 Hz), 130.9 (d, *J*_{C-P} = 9.5 Hz), 130.5 (d, *J*_{C-P} = 9.3 Hz), 128.7 (d, *J*_{C-P} = 11.7 Hz), 128.0, 128.1 (d, *J*_{C-P} = 11.7 Hz), 126.0, 125.0, 122.6, 121.5, 37.8 (d, *J*_{C-P} = 2.6 Hz), 36.5, 35.7 (d, *J*_{C-P} = 69.7 Hz), 31.9 (d, *J*_{C-P} = 9.0 Hz); ³¹P NMR (161 MHz, CDCl₃) δ 29.62. FT-IR: ν (cm⁻¹) 3055, 2924, 1704 1655, 1590, 1483, 1455, 1436, 13554, 1311, 1278, 1236. HRMS [ESI] calcd for C₂₈H₂₄NO₂PS₂Na [M+Na]⁺ 524.0878, found 524.0862.



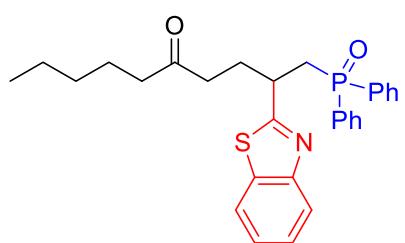
3n: yellow oil, 41.9 mg, 43%. ¹H NMR (400 MHz, CDCl₃) δ 7.83 (d, *J* = 8.0 Hz, 1H), 7.79-7.72 (m, 2H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.63-7.56 (m, 2H), 7.52-7.37 (m, 5H), 7.34-7.28 (m, 1H), 7.20-7.11 (m, 3H), 7.08 (d, *J* = 3.6 Hz, 1H), 6.45 (dd, *J* = 3.6, 1.6 Hz, 1H), 3.92-3.81 (m, 1H), 3.26-3.15 (m, 1H), 2.89-2.74 (m, 3H), 2.40 (dd, *J* = 14.8, 7.2 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 187.9, 173.1 (d, *J*_{C-P} = 6.6 Hz), 152.7, 152.3, 146.2, 134.7, 133.5 (d, *J*_{C-P} = 98.9 Hz), 131.9 (d, *J*_{C-P} = 2.3 Hz), 131.2 (d, *J*_{C-P} = 2.4 Hz), 130.9 (d, *J*_{C-P} = 9.4 Hz), 130.5 (d, *J*_{C-P} = 9.3 Hz), 128.7 (d, *J*_{C-P} = 11.6 Hz), 128.0 (d, *J*_{C-P} = 11.8 Hz), 125.9, 124.9, 122.6, 121.5, 117.1, 112.1, 37.8 (d, *J*_{C-P} = 2.5 Hz), 35.7 (d, *J*_{C-P} = 69.6 Hz), 35.6, 31.5 (d, *J*_{C-P} = 9.1 Hz); ³¹P NMR (161 MHz, CDCl₃) δ 29.71. FT-IR: ν (cm⁻¹) 3294, 2956, 2922, 2864, 1590, 1489, 1467, 1437, 1389, 1316, 1276, 1240. HRMS [ESI] calcd for C₂₈H₂₅NO₃PS [M+H]⁺ 508.1107, found 508.1104.



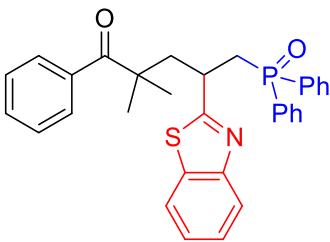
3o: white solid, m.p. 55-56 °C, 83.8 mg, 82%. ^1H NMR (400 MHz, CDCl_3) δ 7.82 (d, $J = 8.0$ Hz, 1H), 7.76-7.66 (m, 3H), 7.61-7.54 (m, 2H), 7.49-7.37 (m, 4H), 7.32-7.26 (m, 1H), 7.24-7.10 (m, 6H), 7.07-7.02 (m, 2H), 3.80-3.65 (m, 1H), 3.55 (s, 2H), 3.17-3.04 (m, 1H), 2.70 (ddd, $J = 14.4, 14.4, 5.6$ Hz, 1H), 2.53-2.36 (m, 2H), 2.28-2.14 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 206.8, 173.1 (d, $J_{\text{C-P}} = 7.2$ Hz), 152.8, 134.7, 134.0, 133.6 (d, $J_{\text{C-P}} = 99.0$ Hz), 131.9 (d, $J_{\text{C-P}} = 2.5$ Hz), 131.7 (d, $J_{\text{C-P}} = 98.4$ Hz), 131.2 (d, $J_{\text{C-P}} = 2.6$ Hz), 130.9 (d, $J_{\text{C-P}} = 9.4$ Hz), 130.5 (d, $J_{\text{C-P}} = 9.3$ Hz), 129.4, 128.7 (d, $J_{\text{C-P}} = 11.6$ Hz), 128.6, 128.1 (d, $J_{\text{C-P}} = 11.7$ Hz), 126.9, 125.8, 124.9, 122.7, 121.5, 49.9, 39.0, 37.6 (d, $J_{\text{C-P}} = 2.6$ Hz), 35.6 (d, $J_{\text{C-P}} = 69.8$ Hz), 31.1 (d, $J_{\text{C-P}} = 8.7$ Hz); ^{31}P NMR (161 MHz, CDCl_3) δ 29.50. FT-IR: ν (cm $^{-1}$) 3294, 2956, 2922, 2864, 1590, 1489, 1467, 1437, 1389, 1316, 1276, 1240. HRMS [ESI] calcd for $\text{C}_{31}\text{H}_{28}\text{NO}_2\text{PSNa} [\text{M+Na}]^+$ 532.1471, found 532.1470.



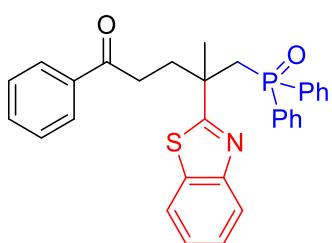
3p: white solid, m.p. 117-118 °C, 71.4 mg, 71%. ^1H NMR (400 MHz, CDCl_3) δ 7.84 (d, $J = 8.0$ Hz, 1H), 7.78-7.69 (m, 3H), 7.62-7.55 (m, 2H), 7.51-7.37 (m, 4H), 7.34-7.28 (m, 1H), 7.20-7.09 (m, 3H), 3.84-3.70 (m, 1H), 3.23-3.11 (m, 1H), 2.74 (ddd, $J = 14.8, 14.8, 4.8$ Hz, 1H), 2.51-2.33 (m, 2H), 2.27-2.14 (m, 3H), 1.75-1.63 (m, 4H), 1.62-1.55 (m, 1H), 1.23-1.08 (m, 5H); ^{13}C NMR (100 MHz, CDCl_3) δ 212.1, 172.9 (d, $J_{\text{C-P}} = 6.5$ Hz), 152.2, 134.2, 131.4 (d, $J_{\text{C-P}} = 1.8$ Hz), 130.7 (d, $J_{\text{C-P}} = 1.8$ Hz), 130.4 (d, $J_{\text{C-P}} = 9.0$ Hz), 130.0 (d, $J_{\text{C-P}} = 9.2$ Hz), 128.2 (d, $J_{\text{C-P}} = 11.5$ Hz), 127.5 (d, $J_{\text{C-P}} = 11.6$ Hz), 125.4, 124.4, 122.1, 121.0, 50.2, 37.3 (d, $J_{\text{C-P}} = 1.8$ Hz), 37.2, 35.2 (d, $J_{\text{C-P}} = 69.7$ Hz), 30.8 (d, $J_{\text{C-P}} = 8.9$ Hz), 28.0, 27.8, 25.3, 25.1, 25.1; ^{31}P NMR (161 MHz, CDCl_3) δ 29.37. FT-IR: ν (cm $^{-1}$) 3055, 2925, 2852, 1703, 1511, 1483, 1436, 1405, 1374, 1312, 1261, 1241. HRMS [ESI] calcd for $\text{C}_{30}\text{H}_{32}\text{NO}_2\text{PSNa} [\text{M+Na}]^+$ 524.1784, found 524.1769.



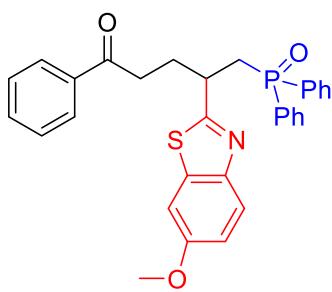
3q: yellow oil, 70.6 mg, 72%. ^1H NMR (400 MHz, CDCl_3) δ 7.83 (d, $J = 8.0$ Hz, 1H), 7.2 (dd, $J = 11.2, 8.0$ Hz, 2H), 7.65 (d, $J = 7.6$ Hz, 1H), 7.56 (dd, $J = 11.2, 7.6$ Hz, 2H), 7.47-7.33 (m, 4H), 7.32-7.27 (m, 1H), 7.15-7.02 (m, 3H), 3.89-3.74 (m, 1H), 3.09-2.96 (m, 1H), 2.76 (ddd, $J = 14.8, 14.8, 4.8$ Hz, 1H), 2.52-2.25 (m, 2H), 2.24-2.10 (m, 4H), 1.47-1.35 (m, 2H), 1.22-1.07 (m, 4H), 0.80 (t, $J = 6.8$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 209.3, 173.0 (d, $J_{\text{C-P}} = 5.3$ Hz), 152.0, 134.1, 131.4, 130.7, 130.4 (d, $J_{\text{C-P}} = 8.7$ Hz), 130.0 (d, $J_{\text{C-P}} = 9.1$ Hz), 128.3 (d, $J_{\text{C-P}} = 11.3$ Hz), 127.6 (d, $J_{\text{C-P}} = 11.4$ Hz), 125.4, 124.5, 122.1, 121.0, 42.2, 39.2, 37.2, 35.2 (d, $J_{\text{C-P}} = 67.9$ Hz), 30.8, 30.7 (d, $J_{\text{C-P}} = 9.0$ Hz), 22.9, 21.9, 13.4; ^{31}P NMR (161 MHz, CDCl_3) δ 30.26. FT-IR: ν (cm $^{-1}$) 3056, 2953, 2926, 2856, 1708, 1483, 1455, 1436, 1374, 1311, 1278, 1243. HRMS [ESI] calcd for $\text{C}_{29}\text{H}_{32}\text{NO}_2\text{PSNa} [\text{M+Na}]^+$ 512.1784, found 512.1783.



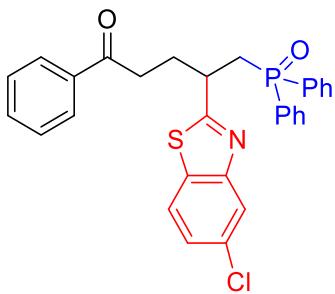
3r: yellow oil, 92.5 mg, 88%. ¹H NMR (400 MHz, CDCl₃) δ 7.73-7.66 (m, 3H), 7.64 (d, *J* = 7.6 Hz, 1H), 7.60-7.49 (m, 4H), 7.48-7.38 (m, 3H), 7.37-7.29 (m, 2H), 7.29-7.20 (m, 3H), 7.20-7.11 (m, 3H), 3.91-3.78 (m, 1H), 3.01-2.90 (m, 1H), 2.83 (dd, *J* = 14.4, 9.6 Hz, 1H), 2.73 (ddd, *J* = 14.0, 14.0, 6.4 Hz, 1H), 2.53 (dd, *J* = 14.4, 3.6 Hz, 1H), 1.26 (d, *J* = 4.4 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 207.3, 173.7 (d, *J*_{C-P} = 7.1 Hz), 152.6, 137.9, 134.7, 133.9 (d, *J*_{C-P} = 98.8 Hz), 131.8 (d, *J*_{C-P} = 2.5 Hz), 131.2 (d, *J*_{C-P} = 2.6 Hz), 130.9, 130.8 (d, *J*_{C-P} = 9.2 Hz), 130.4 (d, *J*_{C-P} = 9.0 Hz), 128.7 (d, *J*_{C-P} = 11.4 Hz), 128.0, 128.0 (d, *J*_{C-P} = 11.5 Hz), 127.8, 125.6, 124.8, 122.6, 121.4, 47.7, 47.1 (d, *J*_{C-P} = 7.5 Hz), 37.8 (d, *J*_{C-P} = 68.6 Hz), 35.5, 27.0, 26.3; ³¹P NMR (161 MHz, CDCl₃) δ 28.85. FT-IR: ν (cm⁻¹) 3056, 2964, 2924, 1669, 1592, 1509, 1471, 1436, 1390, 1367, 1312, 1261. HRMS [ESI] calcd for C₃₂H₃₀NO₂PSNa [M+Na]⁺ 546.1627, found 546.1609.



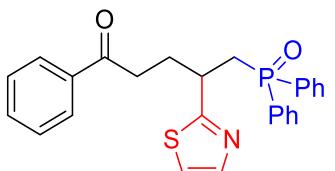
3s: white solid, m.p. 99-100 °C, 74.2 mg, 72%. ¹H NMR (400 MHz, CDCl₃) δ 7.85-7.79 (m, 3H), 7.78-7.73 (m, 2H), 7.71 (d, *J* = 7.6 Hz, 1H), 7.63-7.55 (m, 2H), 7.52-7.45 (m, 1H), 7.43-7.34 (m, 6H), 7.33-7.27 (m, 1H), 7.17-7.06 (m, 3H), 3.24 (dd, *J* = 15.2, 8.4 Hz, 1H), 3.02-2.89 (m, 2H), 2.86-2.74 (m, 1H), 2.68-2.58 (m, 1H), 2.38 (ddd, *J* = 15.6, 10.8, 4.8 Hz, 1H), 1.86 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 199.2, 177.8 (d, *J*_{C-P} = 6.3 Hz), 152.7, 136.7, 134.9, 134.8 (d, *J*_{C-P} = 98.3 Hz), 132.9, 133.0 (d, *J*_{C-P} = 97.9 Hz), 131.5 (d, *J*_{C-P} = 2.6 Hz), 130.8 (d, *J*_{C-P} = 2.8 Hz), 130.9 (d, *J*_{C-P} = 9.3 Hz), 130.4 (d, *J*_{C-P} = 9.0 Hz), 128.6 (d, *J*_{C-P} = 11.5 Hz), 128.5, 128.1, 127.9 (d, *J*_{C-P} = 11.7 Hz), 125.7, 124.8, 122.8, 121.4, 43.6 (d, *J*_{C-P} = 3.6 Hz), 41.7 (d, *J*_{C-P} = 69.2 Hz), 38.5 (d, *J*_{C-P} = 9.6 Hz), 33.7, 25.8 (d, *J*_{C-P} = 3.4 Hz); ³¹P NMR (161 MHz, CDCl₃) δ 27.19. FT-IR: ν (cm⁻¹) 3197, 3055, 2959, 1681, 1558, 1541, 1507, 1490, 1436, 1313, 1240. HRMS [ESI] calcd for C₃₁H₂₈NO₂PSNa [M+Na]⁺ 532.1471, found 532.1433.



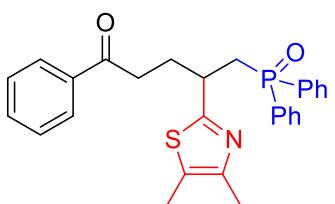
3t: white solid, m.p. 158-159 °C, 92.5 mg, 88%. ¹H NMR (400 MHz, CDCl₃) δ 7.83-7.79 (m, 2H), 7.78-7.72 (m, 2H), 7.69 (d, *J* = 8.8 Hz, 1H), 7.64-7.57 (m, 2H), 7.52-7.41 (m, 4H), 7.39-7.33 (m, 2H), 7.22-7.13 (m, 4H), 7.00 (dd, *J* = 8.8, 2.4 Hz, 1H), 3.89-3.78 (m, 1H), 3.83 (s, 3H), 3.25-3.14 (m, 1H), 3.04-2.86 (m, 2H), 2.78 (ddd, *J* = 14.4, 14.4, 5.6 Hz, 1H), 2.43-2.35 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 198.4, 170.1 (d, *J*_{C-P} = 6.9 Hz), 157.1, 146.8, 136.2, 135.5, 133.2 (d, *J*_{C-P} = 99.0 Hz), 132.5, 131.4 (d, *J*_{C-P} = 2.5 Hz), 131.1 (d, *J*_{C-P} = 98.5 Hz), 130.7 (d, *J*_{C-P} = 2.5 Hz), 130.4 (d, *J*_{C-P} = 9.4 Hz), 130.0 (d, *J*_{C-P} = 9.3 Hz), 128.2 (d, *J*_{C-P} = 11.6 Hz), 128.0, 127.6 (d, *J*_{C-P} = 11.6 Hz), 127.5, 122.6, 114.7, 103.4, 55.3, 37.2 (d, *J*_{C-P} = 2.7 Hz), 35.3 (d, *J*_{C-P} = 69.8 Hz), 35.3, 31.2 (d, *J*_{C-P} = 8.9 Hz); ³¹P NMR (161 MHz, CDCl₃) δ 29.49. FT-IR: ν (cm⁻¹) 3052, 2924, 1681, 1598, 1558, 1484, 1435, 1393, 1319, 1258, 1223. HRMS [ESI] calcd for C₃₁H₂₉NO₃PS [M+H]⁺ 526.1600, found 526.1587.



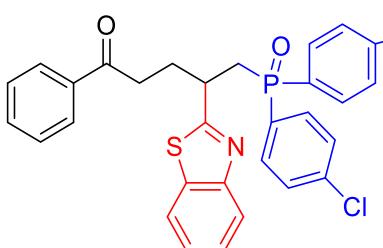
3u: white solid, m.p. 167-168 °C, 60.5 mg, 57%. ¹H NMR (400 MHz, CDCl₃) δ 7.84-7.78 (m, 3H), 7.77-7.71 (m, 2H), 7.64-7.53 (m, 3H), 7.53-7.41 (m, 4H), 7.41-7.34 (m, 2H), 7.29-7.26 (m, 1H), 7.22-7.11 (m, 3H), 3.94-3.82 (m, 1H), 3.25-3.15 (m, 1H), 3.04-2.86 (m, 2H), 2.79 (ddd, *J* = 14.4, 14.4, 4.8 Hz, 1H), 2.40 (dd, *J* = 14.4, 7.2 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 198.6, 175.2 (d, *J*_{C-P} = 6.1 Hz), 153.6, 136.6, 133.6 (d, *J*_{C-P} = 99.1 Hz), 133.1, 133.0, 131.9 (d, *J*_{C-P} = 2.4 Hz), 131.8, 131.8 (d, *J*_{C-P} = 98.4 Hz), 131.2 (d, *J*_{C-P} = 2.6 Hz), 130.9 (d, *J*_{C-P} = 9.4 Hz), 130.5 (d, *J*_{C-P} = 9.3 Hz), 128.7 (d, *J*_{C-P} = 11.6 Hz), 128.5, 128.0 (d, *J*_{C-P} = 11.9 Hz), 128.0, 125.4, 122.6, 122.2, 37.9 (d, *J*_{C-P} = 2.7 Hz), 35.7 (d, *J*_{C-P} = 69.7 Hz), 35.7, 31.7 (d, *J*_{C-P} = 9.4 Hz); ³¹P NMR (161 MHz, CDCl₃) δ 29.04. FT-IR: ν (cm⁻¹) 3294, 2956, 2922, 2864, 1590, 1489, 1467, 1437, 1389, 1316, 1276, 1240. HRMS [ESI] calcd for C₂₉H₃₂NO₂PSNa [M+Na]⁺ 552.0924, found 552.0903.



3v: white solid, m.p. 116-117 °C, 73.1 mg, 82%. ¹H NMR (400 MHz, CDCl₃) δ 7.86-7.79 (m, 2H), 7.77-7.71 (m, 2H), 7.64-7.58 (m, 2H), 7.56-7.42 (m, 5H), 7.42-7.36 (m, 3H), 7.36-7.29 (m, 2H), 7.03 (d, *J* = 3.2 Hz, 1H), 3.91-3.78 (m, 1H), 3.20-3.08 (m, 1H), 3.01-2.86 (m, 2H), 2.75 (ddd, *J* = 14.8, 14.8, 5.2 Hz, 1H), 2.37-2.29 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 198.9, 172.3 (d, *J*_{C-P} = 7.0 Hz), 142.4, 136.7, 133.7 (d, *J*_{C-P} = 98.8 Hz), 133.0, 132.0 (d, *J*_{C-P} = 98.5 Hz), 131.8 (d, *J*_{C-P} = 2.5 Hz), 131.4 (d, *J*_{C-P} = 2.7 Hz), 130.9 (d, *J*_{C-P} = 9.4 Hz), 130.5 (d, *J*_{C-P} = 9.3 Hz), 128.7 (d, *J*_{C-P} = 11.6 Hz), 128.5, 128.4 (d, *J*_{C-P} = 11.7 Hz), 128.0, 118.5, 36.8 (d, *J*_{C-P} = 2.8 Hz), 35.8 (d, *J*_{C-P} = 69.8 Hz), 35.8, 32.1 (d, *J*_{C-P} = 8.9 Hz); ³¹P NMR (161 MHz, CDCl₃) δ 29.65. FT-IR: ν (cm⁻¹) 3062, 2927, 2854, 1676, 1595, 1508, 1494, 1437, 1391, 1325, 1262, 1238. HRMS [ESI] calcd for C₂₆H₂₄NO₂PSNa [M+Na]⁺ 468.1158, found 468.1151.

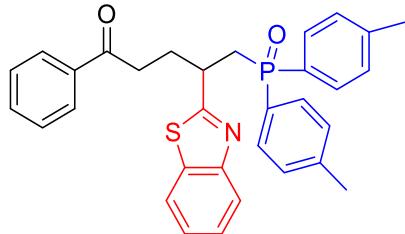


3w: white solid, m.p. 101-102 °C, 88.0 mg, 93%. ¹H NMR (400 MHz, CDCl₃) δ 7.89-7.81 (m, 2H), 7.74 (dd, *J* = 11.2, 6.8 Hz, 2H), 7.63 (dd, *J* = 11.2, 7.6 Hz, 2H), 7.54-7.38 (m, 7H), 7.35-7.29 (m, 2H), 3.79-3.63 (m, 1H), 3.27-3.10 (m, 1H), 3.00-2.83 (m, 2H), 2.71 (ddd, *J* = 14.8, 14.8, 4.8 Hz, 1H), 2.31 (dd, *J* = 12.0, 7.2 Hz, 2H), 2.13 (s, 3H), 2.12 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 199.0, 167.2 (d, *J*_{C-P} = 5.9 Hz), 147.2, 136.7, 133.9 (d, *J*_{C-P} = 98.7 Hz), 132.9, 131.9 (d, *J*_{C-P} = 98.1 Hz), 131.7 (d, *J*_{C-P} = 2.4 Hz), 131.1 (d, *J*_{C-P} = 3.7 Hz), 131.0 (d, *J*_{C-P} = 9.6 Hz), 130.4 (d, *J*_{C-P} = 9.3 Hz), 128.7 (d, *J*_{C-P} = 11.6 Hz), 128.5, 128.0, 128.0 (d, *J*_{C-P} = 11.7 Hz), 125.6, 36.7 (d, *J*_{C-P} = 2.9 Hz), 36.0 (d, *J*_{C-P} = 69.9 Hz), 36.0, 32.0 (d, *J*_{C-P} = 9.8 Hz), 14.4, 11.0; ³¹P NMR (161 MHz, CDCl₃) δ 29.49. FT-IR: ν (cm⁻¹) 3054, 2957, 2920, 2861, 1716, 1682, 1578, 1473, 1384, 1321, 1278, 1231. HRMS [ESI] calcd for C₂₈H₂₈NO₂PSNa [M+Na]⁺ 496.1471, found 496.1460.

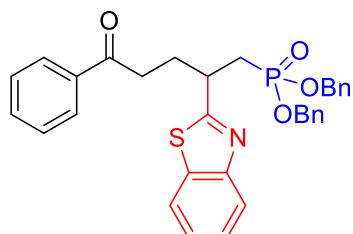


4a: white solid, m.p. 154-155 °C, 81.7 mg, 72%. ¹H NMR (400 MHz, CDCl₃) δ 7.85-7.75 (m, 3H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.65 (dd, *J* = 10.4, 8.8 Hz, 2H), 7.51-7.34 (m, 8H), 7.34-7.28 (m, 1H), 7.08-6.99 (m, 2H), 3.93-3.80 (m,

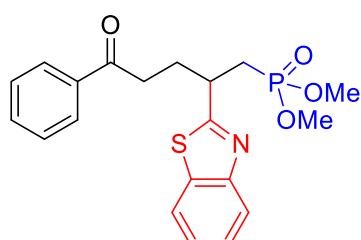
1H), 3.24-3.13 (m, 1H), 3.05-2.88 (m, 2H), 2.77 (ddd, $J = 14.8, 14.8, 4.0$ Hz, 1H), 2.41 (dd, $J = 14.4, 7.2$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 198.2, 171.9 (d, $J_{\text{C-P}} = 5.3$ Hz), 152.2, 138.2 (d, $J_{\text{C-P}} = 3.2$ Hz), 137.6 (d, $J_{\text{C-P}} = 3.3$ Hz), 136.1, 134.1, 132.6, 131.7 (d, $J_{\text{C-P}} = 10.3$ Hz), 131.5 (d, $J_{\text{C-P}} = 100.3$ Hz), 131.3 (d, $J_{\text{C-P}} = 10.1$ Hz), 129.0 (d, $J_{\text{C-P}} = 99.5$ Hz), 128.7 (d, $J_{\text{C-P}} = 12.2$ Hz), 128.1, 127.9 (d, $J_{\text{C-P}} = 12.4$ Hz), 127.5, 125.7, 124.7, 122.1, 121.0, 37.2 (d, $J_{\text{C-P}} = 3.0$ Hz), 35.3 (d, $J_{\text{C-P}} = 70.9$ Hz), 35.2, 31.4 (d, $J_{\text{C-P}} = 10.6$ Hz); ^{31}P NMR (161 MHz, CDCl_3) δ 28.34. FT-IR: ν (cm^{-1}) 3056, 2932, 2901, 1686, 1581, 1512, 1481, 1435, 1389, 1320, 1293, 1235. HRMS [ESI] calcd for $\text{C}_{30}\text{H}_{24}\text{Cl}_2\text{NO}_2\text{PSNa} [\text{M+Na}]^+$ 586.0535, found 586.0521.



4b: white solid, m.p. 73-74 °C, 63.2 mg, 60%. ^1H NMR (400 MHz, CDCl_3) δ 7.88-7.79 (m, 3H), 7.72 (d, $J = 8.0$ Hz, 1H), 7.63 (dd, $J = 10.8, 8.0$ Hz, 2H), 7.52-7.43 (m, 3H), 7.38 (dd, $J = 15.6, 7.6$ Hz, 3H), 7.34-7.28 (m, 1H), 7.22 (d, $J = 6.8$ Hz, 2H), 6.91 (d, $J = 6.4$ Hz, 2H), 3.95-3.82 (m, 1H), 3.25-3.14 (m, 1H), 3.05-2.87 (m, 2H), 2.78 (ddd, $J = 14.0, 14.0, 4.0$ Hz, 1H), 2.42 (dd, $J = 14.4, 7.2$ Hz, 2H), 2.34 (s, 3H), 2.11 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 198.3, 173.2 (d, $J_{\text{C-P}} = 5.8$ Hz), 151.8, 141.8 (d, $J_{\text{C-P}} = 1.4$ Hz), 141.3 (d, $J_{\text{C-P}} = 1.7$ Hz), 136.1, 134.1, 132.5, 130.4 (d, $J_{\text{C-P}} = 9.5$ Hz), 130.0 (d, $J_{\text{C-P}} = 9.4$ Hz), 128.9 (d, $J_{\text{C-P}} = 11.9$ Hz), 128.3 (d, $J_{\text{C-P}} = 12.0$ Hz), 128.0, 127.5, 125.5, 124.5, 122.0, 121.0, 37.3 (d, $J_{\text{C-P}} = 1.5$ Hz), 35.4 (d, $J_{\text{C-P}} = 69.8$ Hz), 35.3, 31.3 (d, $J_{\text{C-P}} = 9.2$ Hz), 21.1, 20.8; ^{31}P NMR (161 MHz, CDCl_3) δ 29.77. FT-IR: ν (cm^{-1}) 2920, 2853, 1684, 1598, 1578, 1510, 1447, 1436, 1398, 1371, 1311, 1278, 1235. HRMS [ESI] calcd for $\text{C}_{32}\text{H}_{30}\text{NO}_2\text{PSNa} [\text{M+Na}]^+$ 546.1627, found 546.1610.

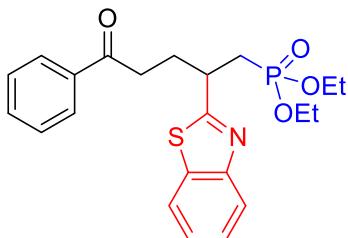


4c: white solid, m.p. 85-86 °C, 93.3 mg, 85%. ^1H NMR (400 MHz, CDCl_3) δ 7.95 (d, $J = 8.4$ Hz, 1H), 7.86-7.77 (m, 3H), 7.55-7.48 (m, 1H), 7.48-7.42 (m, 1H), 7.42-7.33 (m, 3H), 7.25-7.18 (m, 8H), 7.17-7.14 (m, 2H), 4.97-4.85 (m, 4H), 3.78-3.65 (m, 1H), 2.99-2.87 (m, 2H), 2.66 (ddd, $J = 24.8, 16.8, 8.0$ Hz, 1H), 2.44-2.23 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 198.7, 173.5 (d, $J_{\text{C-P}} = 9.5$ Hz), 152.9, 136.6, 136.1 (d, $J_{\text{C-P}} = 5.7$ Hz), 136.0 (d, $J_{\text{C-P}} = 5.9$ Hz), 134.7, 133.0, 128.5 128.5, 128.5, 128.3, 128.3, 128.0, 127.9, 127.9, 126.1, 125.0, 122.8, 121.7, 67.4 (d, $J_{\text{C-P}} = 6.4$ Hz), 67.3 (d, $J_{\text{C-P}} = 6.3$ Hz), 38.6 (d, $J_{\text{C-P}} = 3.4$ Hz), 35.5, 31.7 (d, $J_{\text{C-P}} = 155.1$ Hz), 31.4 (d, $J_{\text{C-P}} = 2.7$ Hz); ^{31}P NMR (161 MHz, CDCl_3) δ 29.18. FT-IR: ν (cm^{-1}) 3026, 2959, 2925, 2882, 2852, 1683, 1596, 1496, 1453, 1446, 1391, 1328, 1254, 1233. HRMS [ESI] calcd for $\text{C}_{32}\text{H}_{30}\text{NO}_4\text{PSNa} [\text{M+Na}]^+$ 578.1525, found 578.1503.

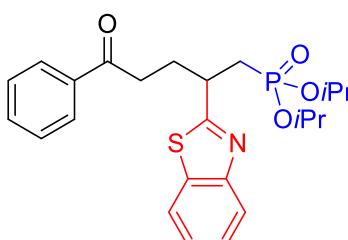


4d: yellow oil, 58.7 mg, 73%. ^1H NMR (400 MHz, CDCl_3) δ 7.98 (d, $J = 8.4$ Hz, 1H), 7.88-7.83 (m, 3H), 7.54-7.44 (m, 2H), 7.42-7.34 (m, 3H), 3.80-3.70 (m, 1H), 3.65 (d, $J = 2.8$ Hz, 3H), 3.63 (d, $J = 2.8$ Hz, 3H), 3.03-2.95 (m, 2H), 2.60 (ddd, $J = 22.8, 15.2, 7.2$ Hz, 1H), 2.51-2.40 (m, 1H), 2.39-2.24 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 198.4, 173.1 (d, $J_{\text{C-P}} = 10.6$ Hz), 152.4, 136.2, 134.2, 132.6, 128.1, 127.5, 125.7, 124.6, 122.4,

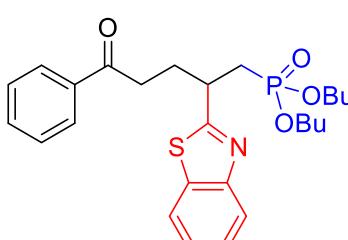
121.3, 52.0 (d, $J_{C-P} = 6.3$ Hz), 52.0 (d, $J_{C-P} = 6.1$ Hz), 38.0 (d, $J_{C-P} = 3.3$ Hz), 35.1, 30.6 (d, $J_{C-P} = 10.9$ Hz), 30.4 (d, $J_{C-P} = 140.3$ Hz); ^{31}P NMR (161 MHz, $CDCl_3$) δ 30.82. FT-IR: ν (cm^{-1}) 3195, 3047, 2921, 2890, 1683, 1591, 1541, 1485, 1363, 1309, 1281, 1241. HRMS [ESI] calcd for $C_{20}H_{23}NO_4PS$ [$M+H]^+$ 404.1080, found 404.1074.



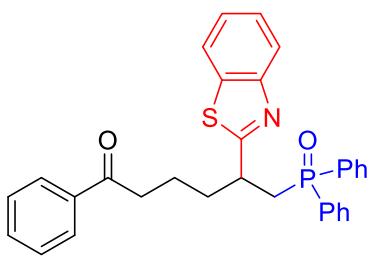
4e: yellow oil, 74.2 mg, 93%. 1H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, $J = 8.0$ Hz, 1H), 7.88-7.82 (m, 3H), 7.53-7.42 (m, 2H), 7.42-7.32 (m, 3H), 4.05-3.95 (m, 4H), 3.77-3.67 (m, 1H), 3.05-2.92 (m, 2H), 2.56 (ddd, $J = 23.2, 15.6, 7.6$ Hz, 1H), 2.49-2.40 (m, 1H), 2.40-2.22 (m, 2H), 1.21-1.11 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.9, 173.6 (d, $J_{C-P} = 10.3$ Hz), 153.0, 136.6, 134.7, 133.0, 128.5, 128.0, 126.1, 125.0, 122.8, 121.7, 61.8 (d, $J_{C-P} = 6.5$ Hz), 38.7 (d, $J_{C-P} = 3.4$ Hz), 36.0, 31.8 (d, $J_{C-P} = 122.9$ Hz), 31.0 (d, $J_{C-P} = 6.2$ Hz), 16.3 (d, $J_{C-P} = 5.6$ Hz), 16.2 (d, $J_{C-P} = 5.8$ Hz); ^{31}P NMR (161 MHz, $CDCl_3$) δ 27.99. FT-IR: ν (cm^{-1}) 3056, 2926, 2868, 1733, 1682, 1596, 1579, 1509, 1483, 1436, 1371, 1311, 1264, 1242. HRMS [ESI] calcd for $C_{22}H_{27}NO_4PS$ [$M+H]^+$ 432.1393, found 432.1387.



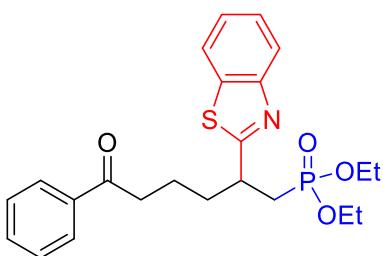
4f: yellow oil, 56.2 mg, 61%. 1H NMR (400 MHz, $CDCl_3$) δ 7.80-7.94 (m, 1H), 7.89-7.79 (m, 3H), 7.53-7.43 (m, 2H), 7.42-7.31 (m, 3H), 4.70-4.58 (m, 2H), 3.78-3.65 (m, 1H), 3.06-2.91 (m, 2H), 2.57-2.42 (m, 2H), 2.57-2.42 (m, 2H), 2.40-2.18 (m, 2H), 1.24 (d, $J = 6.0$ Hz, 3H), 1.20 (d, $J = 6.0$ Hz, 6H), 1.17 (d, $J = 6.0$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.5, 173.5 (d, $J_{C-P} = 11.0$ Hz), 152.5, 136.2, 134.3, 132.5, 128.0, 127.5, 125.5, 124.5, 122.3, 121.2, 69.9 (d, $J_{C-P} = 6.5$ Hz), 69.9 (d, $J_{C-P} = 6.6$ Hz), 38.5 (d, $J_{C-P} = 3.5$ Hz), 35.2, 32.7 (d, $J_{C-P} = 141.7$ Hz), 30.6 (d, $J_{C-P} = 10.5$ Hz), 23.6-23.0 (m, 4C(Me)); ^{31}P NMR (161 MHz, $CDCl_3$) δ 25.77. FT-IR: ν (cm^{-1}) 3061, 2977, 2928, 1683, 1579, 1558, 1448, 1438, 1384, 1311, 1221. HRMS [ESI] calcd for $C_{24}H_{30}NO_4PSNa$ [$M+Na]^+$ 482.1525, found 482.1533.



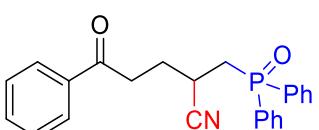
4g: yellow oil, 78.9 mg, 81%. 1H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, $J = 8.0$ Hz, 1H), 7.89-7.81 (m, 3H), 7.53-7.48 (m, 1H), 7.48-7.42 (m, 1H), 7.41-7.33 (m, 3H), 3.97-3.86 (m, 4H), 3.78-3.65 (m, 1H), 3.06-2.91 (m, 2H), 2.58 (ddd, $J = 23.6, 15.6, 8.0$ Hz, 1H), 2.49-2.22 (m, 3H), 1.51-1.39 (m, 4H), 1.28-1.16 (m, 4H), 0.80 (dd, $J = 16.0, 8.0$ Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.8, 173.8 (d, $J_{C-P} = 9.6$ Hz), 152.8, 136.7, 134.7, 133.1, 128.5, 128.0, 126.1, 125.1, 122.8, 121.7, 65.5 (d, $J_{C-P} = 6.6$ Hz), 65.5 (d, $J_{C-P} = 6.7$ Hz), 38.7 (d, $J_{C-P} = 3.6$ Hz), 35.6, 32.4 (d, $J_{C-P} = 2.9$ Hz), 32.3 (d, $J_{C-P} = 3.0$ Hz), 31.4 (d, $J_{C-P} = 140.6$ Hz), 31.3 (d, $J_{C-P} = 11.8$ Hz), 18.7, 18.6, 13.5, 13.5; ^{31}P NMR (161 MHz, $CDCl_3$) δ 28.02. FT-IR: ν (cm^{-1}) 3061, 2959, 2929, 2872, 1683, 1597, 1513, 1449, 1438, 1409, 1377, 1311, 1221. HRMS [ESI] calcd for $C_{26}H_{34}NO_4PSNa$ [$M+Na]^+$ 510.1838, found 510.1843.



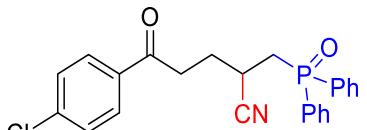
6b: white solid, m.p. 89-90 °C, 82.5 mg, 81%. ¹H NMR (400 MHz, CDCl₃) δ 7.88-7.81 (m, 3H), 7.78-7.68 (m, 3H), 7.65-7.58 (m, 2H), 7.53-7.37 (m, 7H), 7.32-7.27 (m, 1H), 7.24-7.13(m, 3H), 3.85-3.73 (m, 1H), 3.18-3.07 (m, 1H), 2.98-2.84 (m, 2H), 2.78 (ddd, *J* = 14.4, 14.4, 6.4 Hz, 1H), 2.14-1.98 (m, 2H), 1.77-1.63 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 199.6, 173.7 (d, *J*_{C-P} = 7.8 Hz), 152.9, 136.8, 134.7, 133.9 (d, *J*_{C-P} = 98.8 Hz), 132.9, 131.8 (d, *J*_{C-P} = 2.6 Hz), 131.6 (d, *J*_{C-P} = 98.2 Hz), 131.2 (d, *J*_{C-P} = 2.7 Hz), 130.9 (d, *J*_{C-P} = 9.4 Hz), 130.5 (d, *J*_{C-P} = 9.3 Hz), 128.7 (d, *J*_{C-P} = 11.6 Hz), 128.5, 128.1 (d, *J*_{C-P} = 11.7 Hz), 128.0, 125.8, 124.8, 122.6, 121.4, 38.3 (d, *J*_{C-P} = 2.8 Hz), 38.0, 36.7 (d, *J*_{C-P} = 7.8 Hz), 35.5 (d, *J*_{C-P} = 69.7 Hz), 21.4; ³¹P NMR (161 MHz, CDCl₃) δ 29.33. FT-IR: ν (cm⁻¹) 3051, 2922, 2854, 1682, 1597, 1578, 1509, 1446, 1435, 1398, 1373, 1312, 1237, 1206. HRMS [ESI] calcd for C₃₁H₂₉NO₂PS [M+H]⁺ 510.1651, found 5110.1637.



7b: yellow yellow oil, 57.1 mg, 64%. ¹H NMR (400 MHz, CDCl₃) δ 7.97 (d, *J* = 8.0 Hz, 1H), 7.92-7.87 (m, 2H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.56-7.49 (m, 1H), 7.48-7.38 (m, 3H), 7.39-7.33 (m, 1H), 4.04-3.93 (m, 4H), 3.69-3.57 (m, 1H), 3.05-2.88 (m, 2H), 2.50 (ddd, *J* = 23.2, 15.6, 7.6 Hz, 1H), 2.27 (ddd, *J* = 24.4, 18.0, 6.0 Hz, 1H), 2.12-1.98 (m, 2H), 1.83-1.66 (m, 2H), 1.20-1.09 (m, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 199.6, 174.2 (d, *J*_{C-P} = 10.1 Hz), 152.9, 136.8, 134.7, 133.0, 128.5, 128.0, 126.0, 125.0, 122.7, 121.6, 61.8 (d, *J*_{C-P} = 6.3 Hz), 61.7 (d, *J*_{C-P} = 6.6 Hz), 39.3 (d, *J*_{C-P} = 3.5 Hz), 38.0, 36.5 (d, *J*_{C-P} = 10.8 Hz), 31.6 (d, *J*_{C-P} = 140.1 Hz), 21.5, 16.3, 16.2, 16.2, 16.2; ³¹P NMR (161 MHz, CDCl₃) δ 28.31. FT-IR: ν (cm⁻¹) 2981, 2929, 1681, 1596, 1580, 1513, 1477, 1438, 1392, 1367, 1311, 1223. HRMS [ESI] calcd for C₂₃H₂₈NO₄PSNa [M+Na]⁺ 468.1369, found 468.1357.

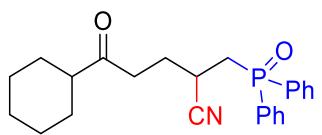


9a: white solid, m.p. 130-131 °C, 57.5 mg, 74%. ¹H NMR (400 MHz, CDCl₃) δ 7.96-7.88 (m, 2H), 7.85-7.71 (m, 4H), 7.62-7.48 (m, 7H), 7.48-7.41 (m, 2H), 3.32-3.08 (m, 3H), 2.82-2.72 (m, 1H), 2.57 (ddd, *J* = 18.8, 12.4, 6.0 Hz, 1H), 2.34-2.22 (m, 1H), 2.15-2.02 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 197.3, 135.9, 132.9, 132.1 (d, *J*_{C-P} = 2.1 Hz), 131.9 (d, *J*_{C-P} = 2.1 Hz), 131.8 (d, *J*_{C-P} = 100.8 Hz), 130.6 (d, *J*_{C-P} = 9.4 Hz), 130.4(d, *J*_{C-P} = 101.2 Hz), 130.1 (d, *J*_{C-P} = 9.3 Hz), 128.6 (d, *J*_{C-P} = 3.0 Hz), 128.5 (d, *J*_{C-P} = 3.0 Hz), 128.2, 127.5, 120.0 (d, *J*_{C-P} = 9.1 Hz), 35.1, 32.4 (d, *J*_{C-P} = 69.0 Hz), 27.6 (d, *J*_{C-P} = 7.0 Hz), 24.4 (d, *J*_{C-P} = 2.1 Hz); ³¹P NMR (161 MHz, CDCl₃) δ 28.23. FT-IR: ν (cm⁻¹) 2919, 2958, 2850, 2243, 1680, 1599, 1579, 1507, 1449, 1412, 1378, 1360, 1259, 1210. HRMS [CI] calcd for C₂₄H₂₃NO₂P [M+H]⁺ 388.1461, found 388.1468.

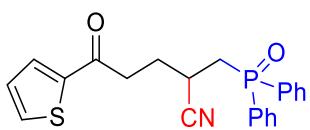


9b: white solid, m.p. 116-117 °C, 42.3 mg, 50%. ¹H NMR (400 MHz, CDCl₃) δ 7.89-7.82 (m, 2H), 7.83-7.71 (m, 4H), 7.62-7.485 (m, 6H), 7.45-7.38 m, 2H), 3.33-3.20 (m, 1H), 3.19-3.04 (m, 2H), 2.85-2.72 (m, 1H), 2.64-2.50 (m, 1H), 2.34-2.22 (m, 1H), 2.15-2.02 (m, 1H); ¹³C NMR (100 MHz,

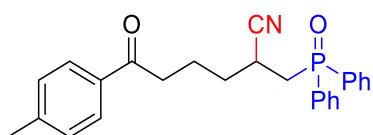
CDCl_3) δ 196.5, 139.8, 134.6, 132.6, 132.4, 131.1 (d, $J_{\text{C}-\text{P}} = 7.8$ Hz), 130.6 (d, $J_{\text{C}-\text{P}} = 7.5$ Hz), 129.4, 129.0, 129.0, 128.9, 120.5 (d, $J_{\text{C}-\text{P}} = 7.6$ Hz), 35.6, 32.9 (d, $J_{\text{C}-\text{P}} = 70.1$ Hz), 28.0 (d, $J_{\text{C}-\text{P}} = 3.7$ Hz), 24.9; ^{31}P NMR (161 MHz, CDCl_3) δ 28.29. FT-IR: ν (cm^{-1}) 3058, 2958, 2925, 2855, 2239, 1684, 1589, 1571, 1486, 1437, 1401, 1371, 1323, 1265. HRMS [ESI] calcd for $\text{C}_{24}\text{H}_{22}\text{NO}_2\text{PCl}$ [$\text{M}+\text{H}]^+$ 422.1071, found 422.1070.



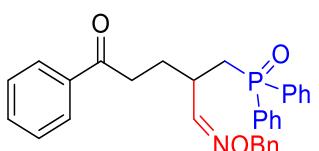
9c: white solid, m.p. 122-123 °C, 58.2 mg, 74%. ^1H NMR (400 MHz, CDCl_3) δ 7.83-7.69 (m, 4H), 7.61-7.45 (m, 6H), 3.20-3.08 (m, 1H), 2.76-2.43 (m, 4H), 2.33-2.24 (m, 1H), 2.12-2.01 (m, 1H), 1.93-1.83 (m, 1H), 1.83-1.68 (m, 4H), 1.67-1.59 (m, 1H), 1.35-1.10 (m, 5H); ^{13}C NMR (100 MHz, CDCl_3) δ 211.2, 132.0 (d, $J_{\text{C}-\text{P}} = 2.5$ Hz), 131.9 (d, $J_{\text{C}-\text{P}} = 100.9$ Hz), 131.9 (d, $J_{\text{C}-\text{P}} = 2.4$ Hz), 130.6 (d, $J_{\text{C}-\text{P}} = 9.4$ Hz), 130.4 (d, $J_{\text{C}-\text{P}} = 99.6$ Hz), 130.1 (d, $J_{\text{C}-\text{P}} = 9.5$ Hz), 128.5 (d, $J_{\text{C}-\text{P}} = 3.1$ Hz), 128.4 (d, $J_{\text{C}-\text{P}} = 3.1$ Hz), 119.9 (d, $J_{\text{C}-\text{P}} = 9.2$ Hz), 50.3, 36.9, 32.3 (d, $J_{\text{C}-\text{P}} = 69.2$ Hz), 28.0, 27.9, 27.1 (d, $J_{\text{C}-\text{P}} = 6.9$ Hz), 25.3, 25.1, 25.1, 24.3 (d, $J_{\text{C}-\text{P}} = 2.5$ Hz); ^{31}P NMR (161 MHz, CDCl_3) δ 28.25. FT-IR: ν (cm^{-1}) 3061, 2929, 2850, 2240, 1705, 1590, 1483, 1438, 1409, 1374, 1324, 1265, 1239. HRMS [CI] calcd for $\text{C}_{24}\text{H}_{29}\text{NO}_2\text{P}$ [$\text{M}+\text{H}]^+$ 394.1930, found 394.1929.



9d: white solid, m.p. 130-131 °C, 44.1 mg, 56%. ^1H NMR (400 MHz, CDCl_3) δ 7.84-7.72 (m, 4H), 7.72-7.68 (m, 1H), 7.66-7.62 (m, 1H), 7.60-7.46 (m, 6H), 7.12 (dd, $J = 4.8, 3.6$ Hz, 1H), 3.31-3.20 (m, 1H), 3.20-3.02 (m, 2H), 2.82-2.69 (m, 1H), 2.63-2.49 (m, 1H), 2.33-2.21 (m, 1H), 2.14-2.03 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 190.1, 143.0, 133.5, 132.1 (d, $J_{\text{C}-\text{P}} = 1.8$ Hz), 132.0 (d, $J_{\text{C}-\text{P}} = 1.6$ Hz), 131.9 (d, $J_{\text{C}-\text{P}} = 100.3$ Hz), 131.8, 130.6 (d, $J_{\text{C}-\text{P}} = 9.3$ Hz), 130.4 (d, $J_{\text{C}-\text{P}} = 99.1$ Hz), 130.1 (d, $J_{\text{C}-\text{P}} = 9.3$ Hz), 128.6 (d, $J_{\text{C}-\text{P}} = 3.2$ Hz), 128.5 (d, $J_{\text{C}-\text{P}} = 3.0$ Hz), 127.8, 119.9 (d, $J_{\text{C}-\text{P}} = 8.9$ Hz), 35.7, 32.3 (d, $J_{\text{C}-\text{P}} = 69.0$ Hz), 27.7 (d, $J_{\text{C}-\text{P}} = 6.9$ Hz), 24.5 (d, $J_{\text{C}-\text{P}} = 1.8$ Hz); ^{31}P NMR (161 MHz, CDCl_3) δ 28.34. FT-IR: ν (cm^{-1}) 2956, 2920, 2234, 1681, 1651, 1606, 1519, 1484, 1436, 1362, 1315, 1297, 1237, 1204. HRMS [CI] calcd for $\text{C}_{22}\text{H}_{21}\text{NO}_2\text{PS}$ [$\text{M}+\text{H}]^+$ 394.1025, found 394.1027.

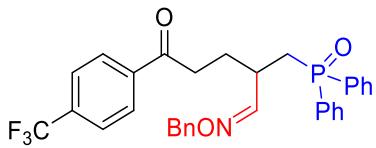


9e: white solid, m.p. 127-128 °C, 47.5 mg, 57%. ^1H NMR (400 MHz, CDCl_3) δ 7.85-7.78 (m, 3H), 7.79-7.70 (m, 3H), 7.61-7.44 (m, 6H), 7.28-7.21 (m, 2H), 3.21-3.07 (m, 1H), 3.01-2.83 (m, 2H), 2.79-2.67 (m, 1H), 2.53 (ddd, $J = 13.6, 13.6, 6.0$ Hz, 1H), 2.40 (s, 3H), 1.99-1.72 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 198.1, 143.5, 133.7, 132.0, 132.0 (d, $J_{\text{C}-\text{P}} = 98.7$ Hz), 131.9, 130.6 (d, $J_{\text{C}-\text{P}} = 9.0$ Hz), 130.1 (d, $J_{\text{C}-\text{P}} = 9.0$ Hz), 128.8, 128.5 (d, $J_{\text{C}-\text{P}} = 11.3$ Hz), 127.6, 120.2 (d, $J_{\text{C}-\text{P}} = 9.5$ Hz), 36.8, 32.5 (d, $J_{\text{C}-\text{P}} = 5.3$ Hz), 31.9 (d, $J_{\text{C}-\text{P}} = 68.4$ Hz), 24.8, 21.2, 20.7; ^{31}P NMR (161 MHz, CDCl_3) δ 28.47. FT-IR: ν (cm^{-1}) 2957, 2864, 2233, 1681, 1606, 1484, 1456, 1435, 1407, 1381, 1362, 1295, 1239. HRMS [ESI] calcd for $\text{C}_{26}\text{H}_{26}\text{NO}_2\text{PNa}$ [$\text{M}+\text{Na}]^+$ 438.1593, found 438.1651.



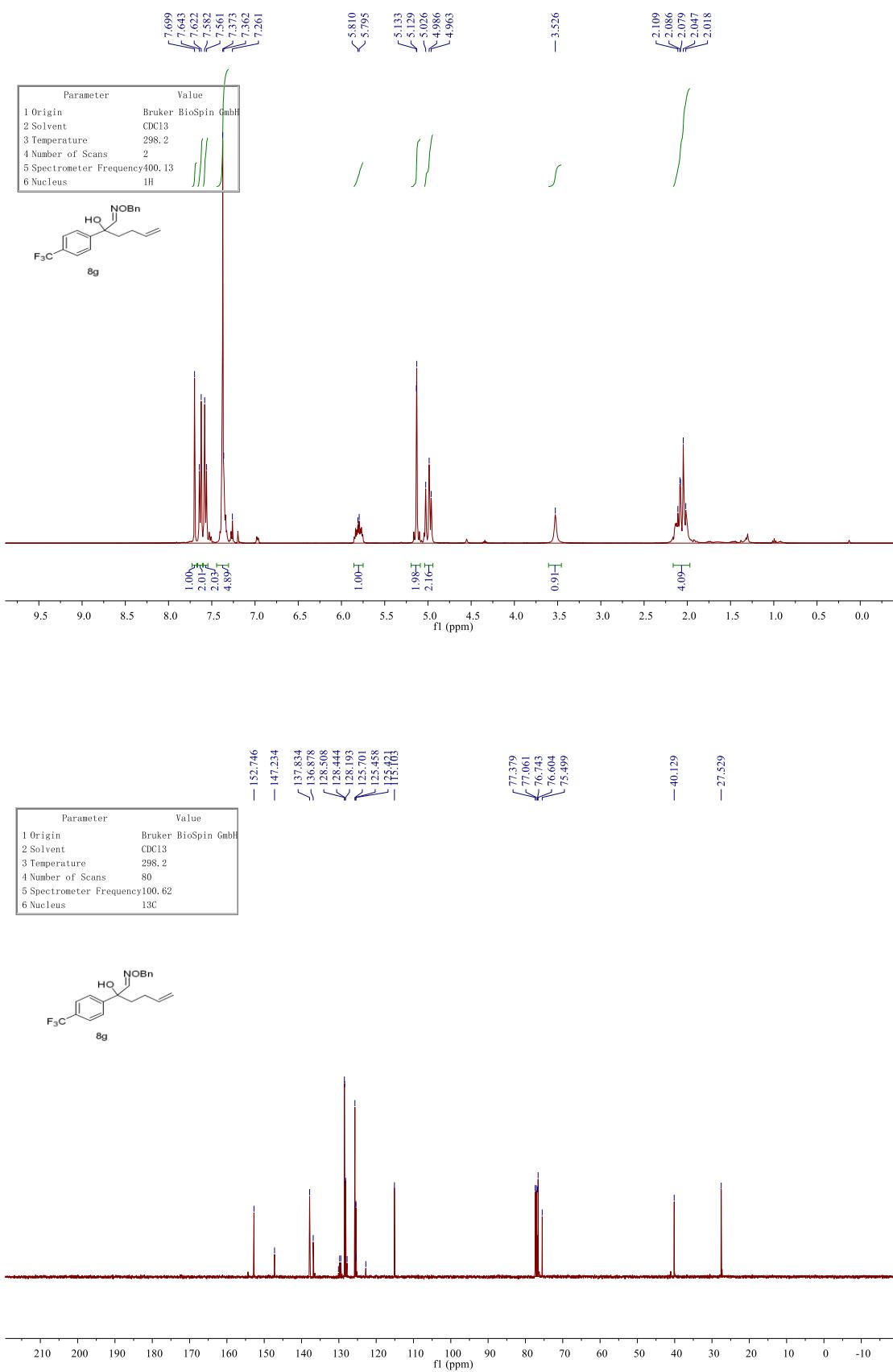
9f: yellow solid, m.p. 96-97 °C, 43.6 mg, 44%. ^1H NMR (400 MHz, CDCl_3) δ 7.86-7.81 (m, 2H), 7.77-7.69 (m, 4H), 7.56-7.48 (m, 3H), 7.47-7.38 (m, 6H), 7.32-7.22 (m, 5H), 4.89 (s, 2H), 2.99-2.83 (m,

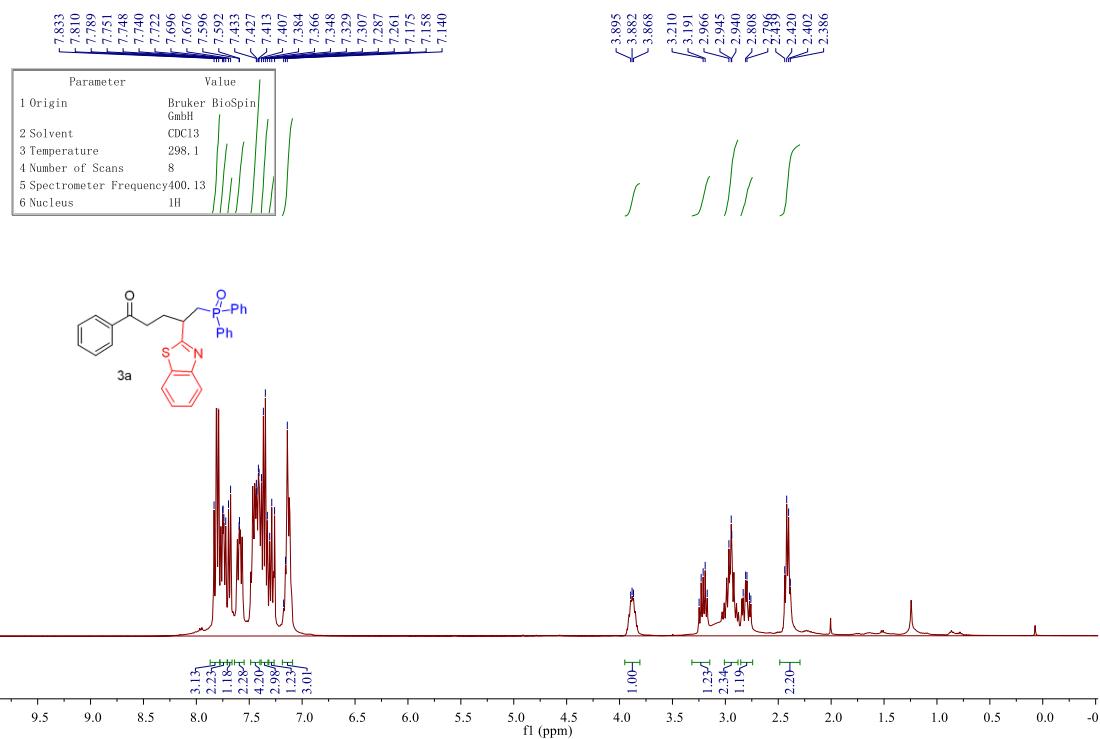
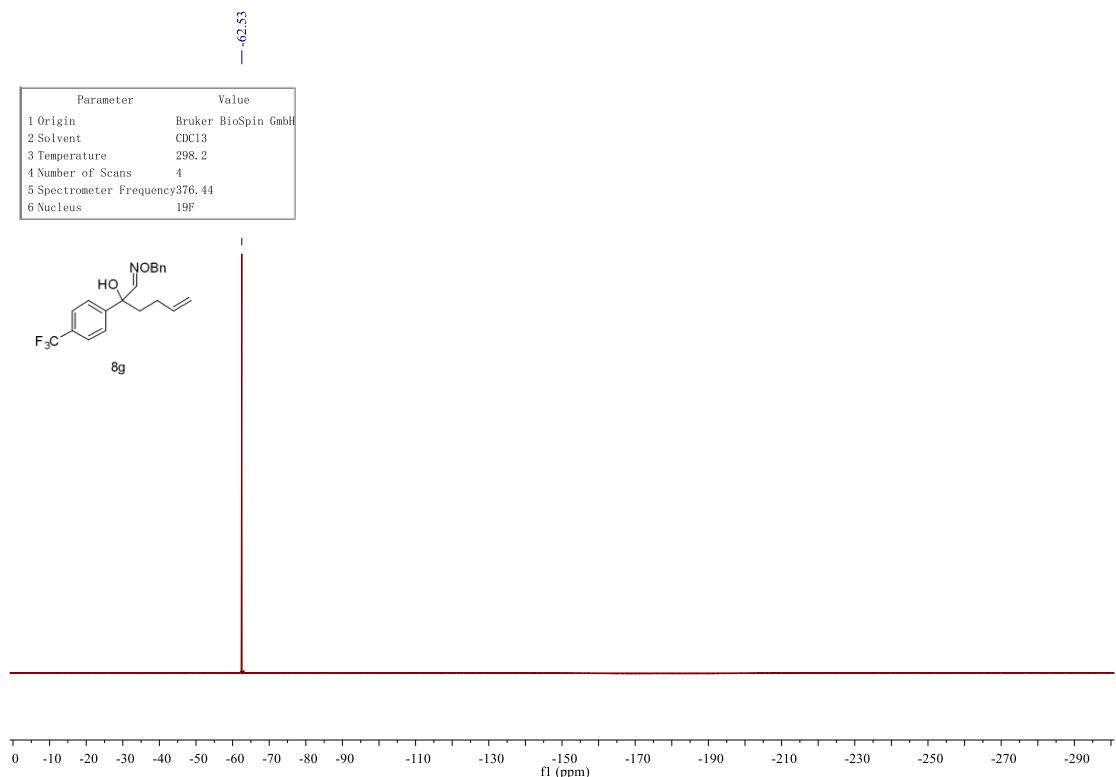
3H), 2.69-2.58 (m, 1H), 2.48-2.36 (m, 1H), 2.13-1.95 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 199.3, 152.3 (d, $J_{\text{C-P}} = 7.1$ Hz), 137.7, 136.8, 133.2 (d, $J_{\text{C-P}} = 98.7$ Hz), 133.0, 132.6 (d, $J_{\text{C-P}} = 98.2$ Hz), 131.9 (d, $J_{\text{C-P}} = 3.2$ Hz), 131.8 (d, $J_{\text{C-P}} = 3.1$ Hz), 131.0 (d, $J_{\text{C-P}} = 9.2$ Hz), 130.7 (d, $J_{\text{C-P}} = 9.2$ Hz), 128.8 (d, $J_{\text{C-P}} = 11.6$ Hz), 128.7 (d, $J_{\text{C-P}} = 11.7$ Hz), 128.5, 128.3, 128.2, 128.0, 127.7, 75.5, 35.6, 34.1 (d, $J_{\text{C-P}} = 3.0$ Hz), 33.0 (d, $J_{\text{C-P}} = 70.2$ Hz), 28.3 (d, $J_{\text{C-P}} = 8.5$ Hz); ^{31}P NMR (161 MHz, CDCl_3) δ 30.20. FT-IR: ν (cm^{-1}) 2920, 2851, 2213, 1682, 1632, 1596, 1580, 1495, 1449, 1437, 1409, 1369, 1230. HRMS [ESI] calcd for $\text{C}_{31}\text{H}_{31}\text{NO}_3\text{P}$ [M+H^+]⁺ 496.2036, found 496.2029.

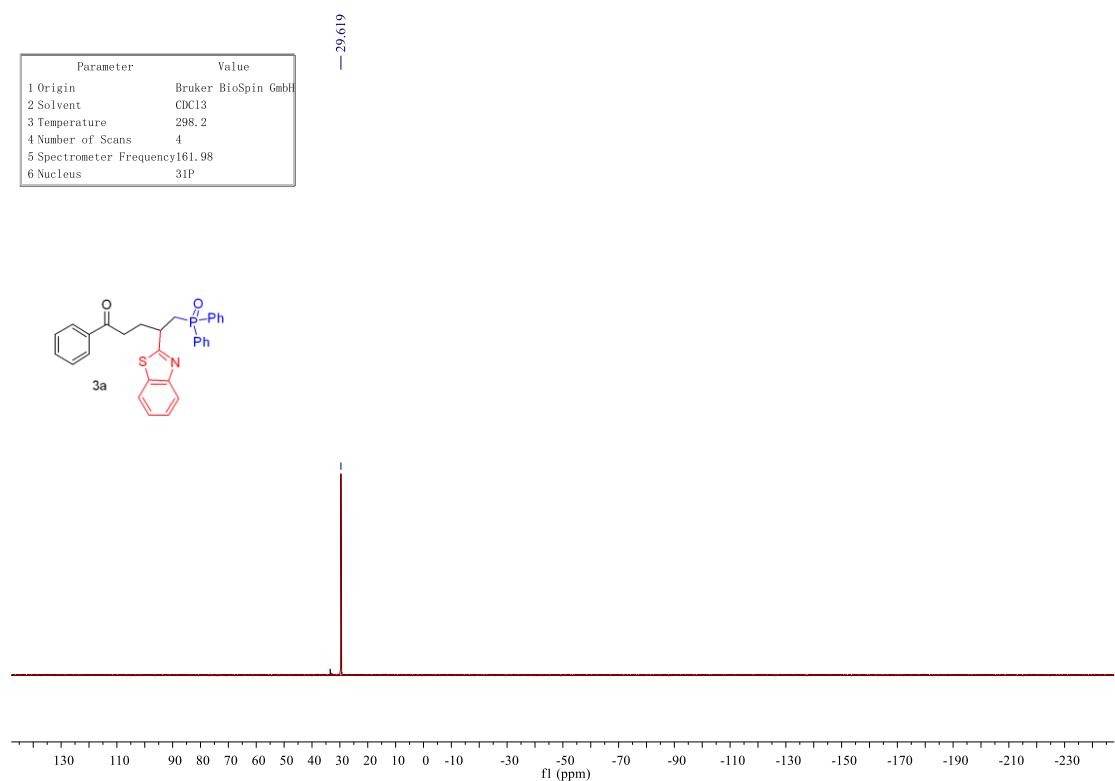
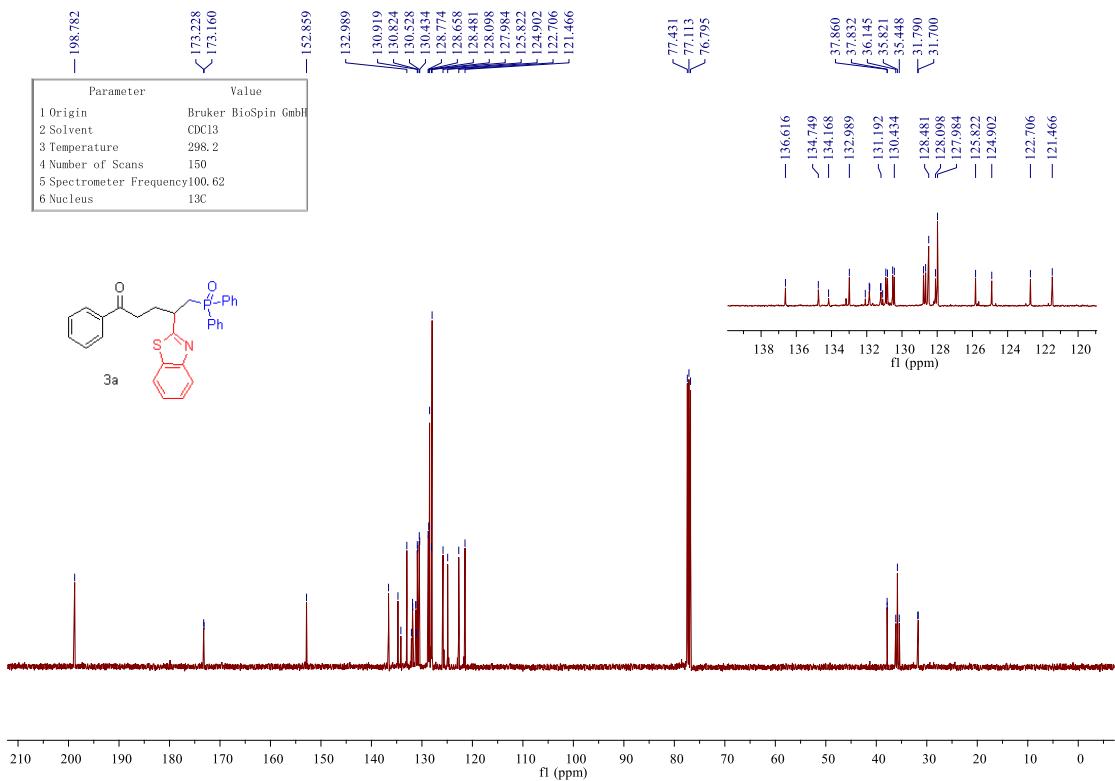


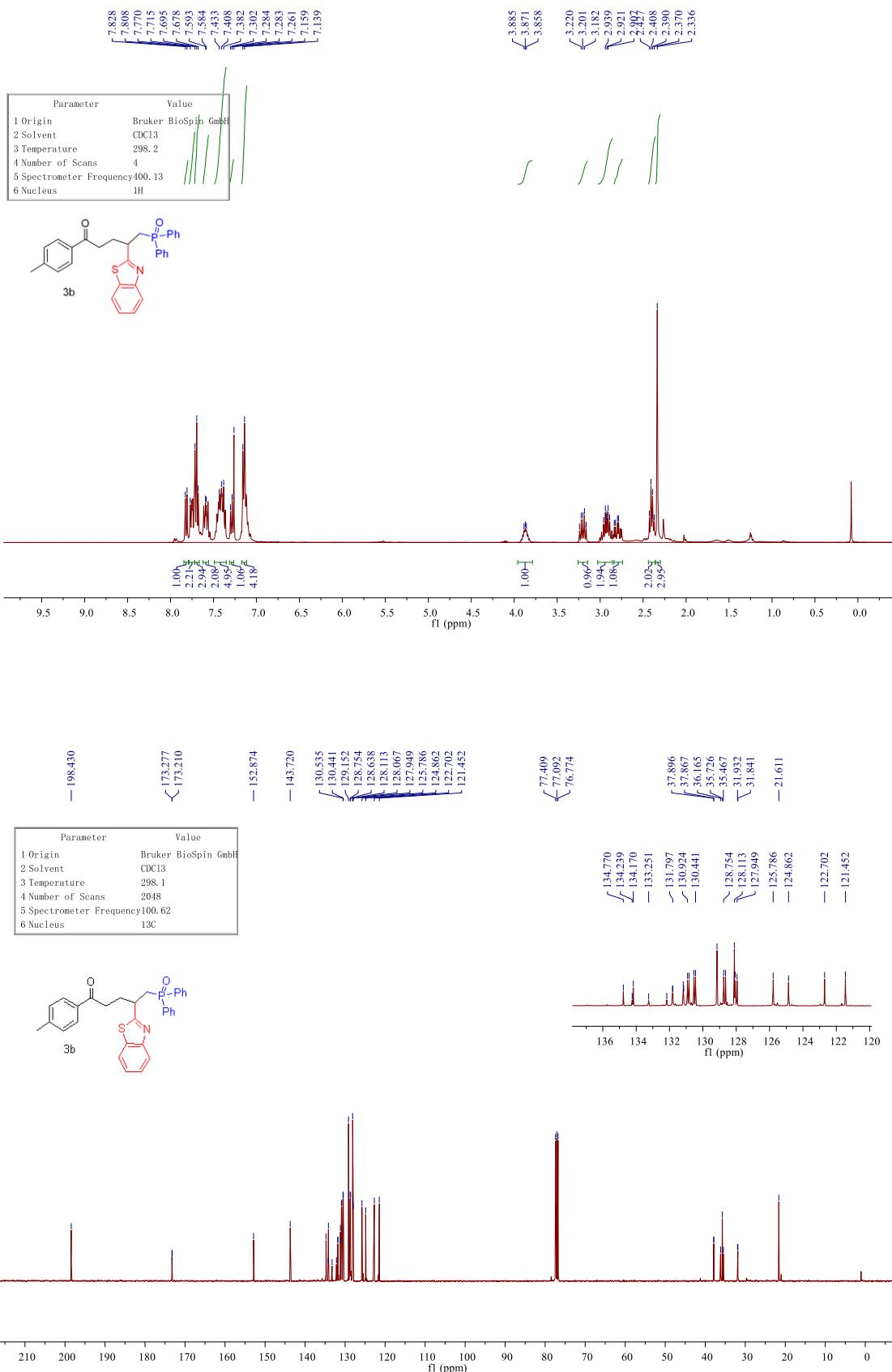
9g: white solid, m.p. 114-117 °C, 71.0 mg, 63% (mixture of Z/E oxime, ~3:1 ratio). ^1H NMR (400 MHz, CDCl_3) δ 7.90-7.75 (m, 2.67H, two isomers), 7.73-7.51 (m, 8.0H, two isomers), 7.50-7.28 (m, 8.0H, two isomers), 7.28-7.06 (m, 8.0H, two isomers), 4.81 (s, 2H, two isomers), 2.96-2.72 (m, 3.33H, two isomers), 2.62-2.50 (m, 1.0H, one isomer), 2.44-2.26 (m, 1.67H, two isomers), 2.20-1.75 (m, 3.33H, two isomers); ^{13}C NMR (100 MHz, CDCl_3) δ 197.8 & 197.6 (two isomers), 152.6 (overlap, two isomers, d, $J_{\text{C-P}} = 8.1$ Hz), 151.8 (overlap, two isomers, q, $J_{\text{C-F}} = 7.5$ Hz), 138.9 & 138.8 (two isomers), 137.2 & 136.9 (two isomers), 133.8 (d, $J_{\text{C-F}} = 32.6$ Hz) & 133.5 (d, $J_{\text{C-F}} = 32.6$ Hz) (two isomers), 133.3 (overlap, two isomers, d, $J_{\text{C-P}} = 1.8$ Hz), 132.3 (overlap, two isomers, d, $J_{\text{C-P}} = 1.9$ Hz), 131.4 (overlap, two isomers), 130.5 (overlap, two isomers, d, $J_{\text{C-P}} = 9.1$ Hz), 130.1 (overlap, two isomers, d, $J_{\text{C-P}} = 9.1$ Hz), 128.3 (overlap, two isomers, d, $J_{\text{C-P}} = 11.5$ Hz), 128.3 (overlap, two isomers, d, $J_{\text{C-P}} = 11.8$ Hz), 127.9 (overlap, two isomers), 127.8 (overlap, two isomers), 127.7 (overlap, two isomers), 127.3 (overlap, two isomers), 125.9 (overlap, two isomers, q, $J_{\text{C-F}} = 271.1$ Hz), 125.1 (overlap, two isomers, q, $J_{\text{C-F}} = 3.5$ Hz), 75.5 & 75.1 (two isomers), 35.9 & 35.5 (two isomers), 33.6 (overlap, two isomers, d, $J_{\text{C-P}} = 1.7$ Hz), 32.6 (d, $J_{\text{C-P}} = 70.5$ Hz) & 32.4 (d, $J_{\text{C-P}} = 70.0$ Hz) (two isomers), 27.4 (overlap, two isomers, d, $J_{\text{C-P}} = 7.7$ Hz); ^{31}P NMR (161 MHz, CDCl_3) δ 30.40 (overlap, two isomers); ^{19}F NMR (376 MHz, CDCl_3) δ -63.1 (overlap, two isomers). FT-IR: ν (cm^{-1}) 3060, 2960, 2929, 2852, 1691, 1578, 1509, 1485, 1454, 1437, 1371, 1323, 1233. HRMS [ESI] calcd for $\text{C}_{32}\text{H}_{29}\text{F}_3\text{NO}_2\text{PNa}$ [M+Na^+]⁺ 586.1729, found 586.1701.

5. ^1H , ^{13}C , ^{19}F , and ^{31}P NMR spectra

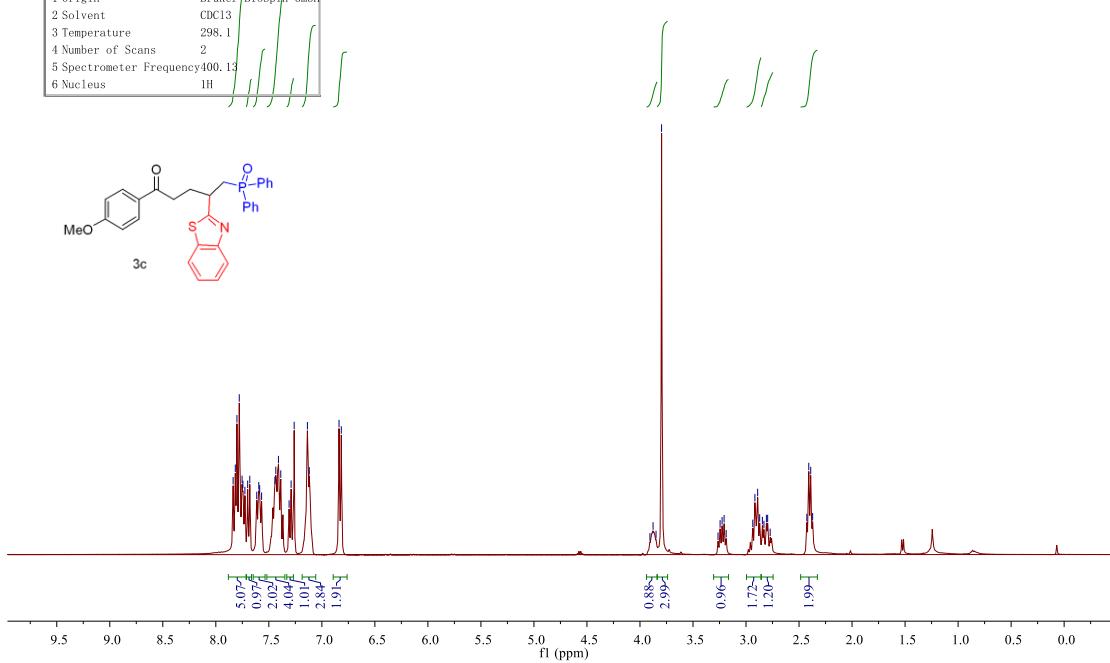
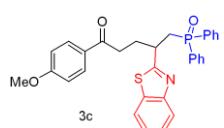
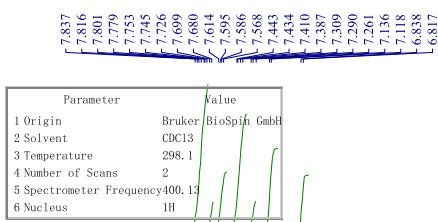
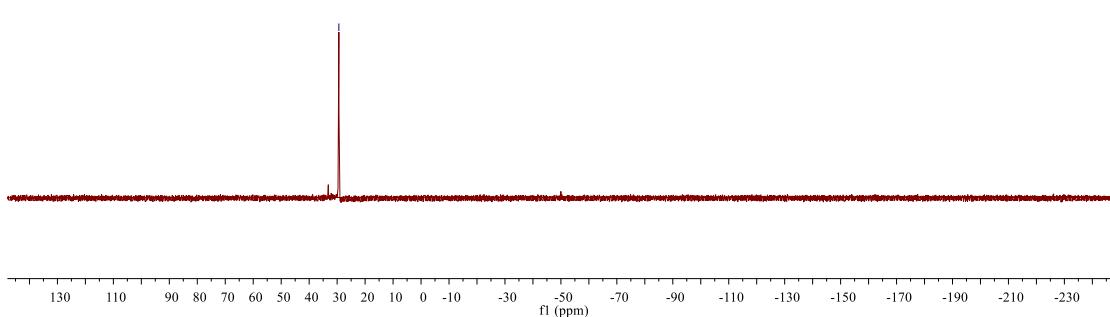
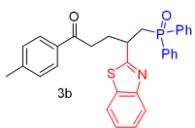


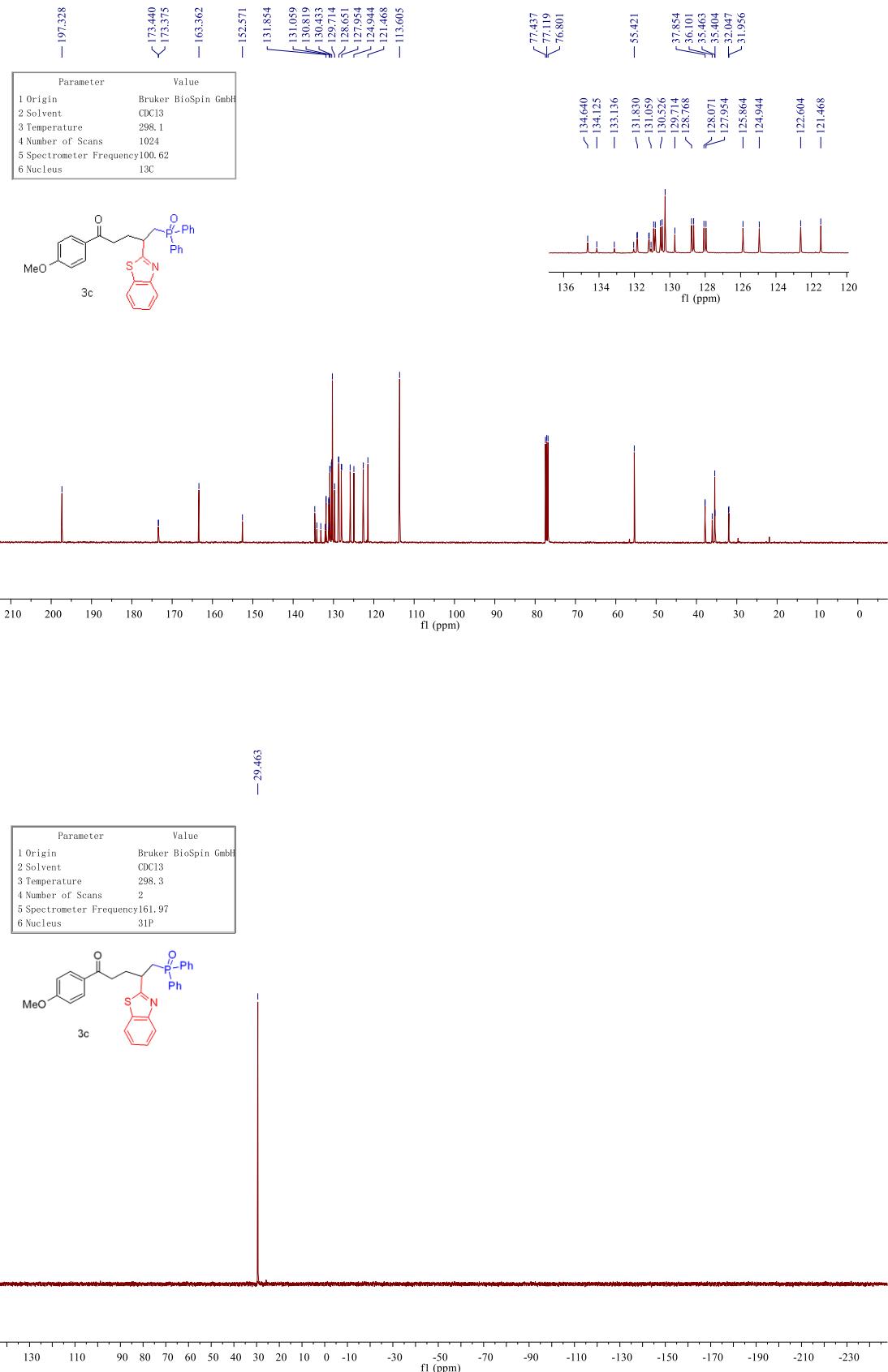


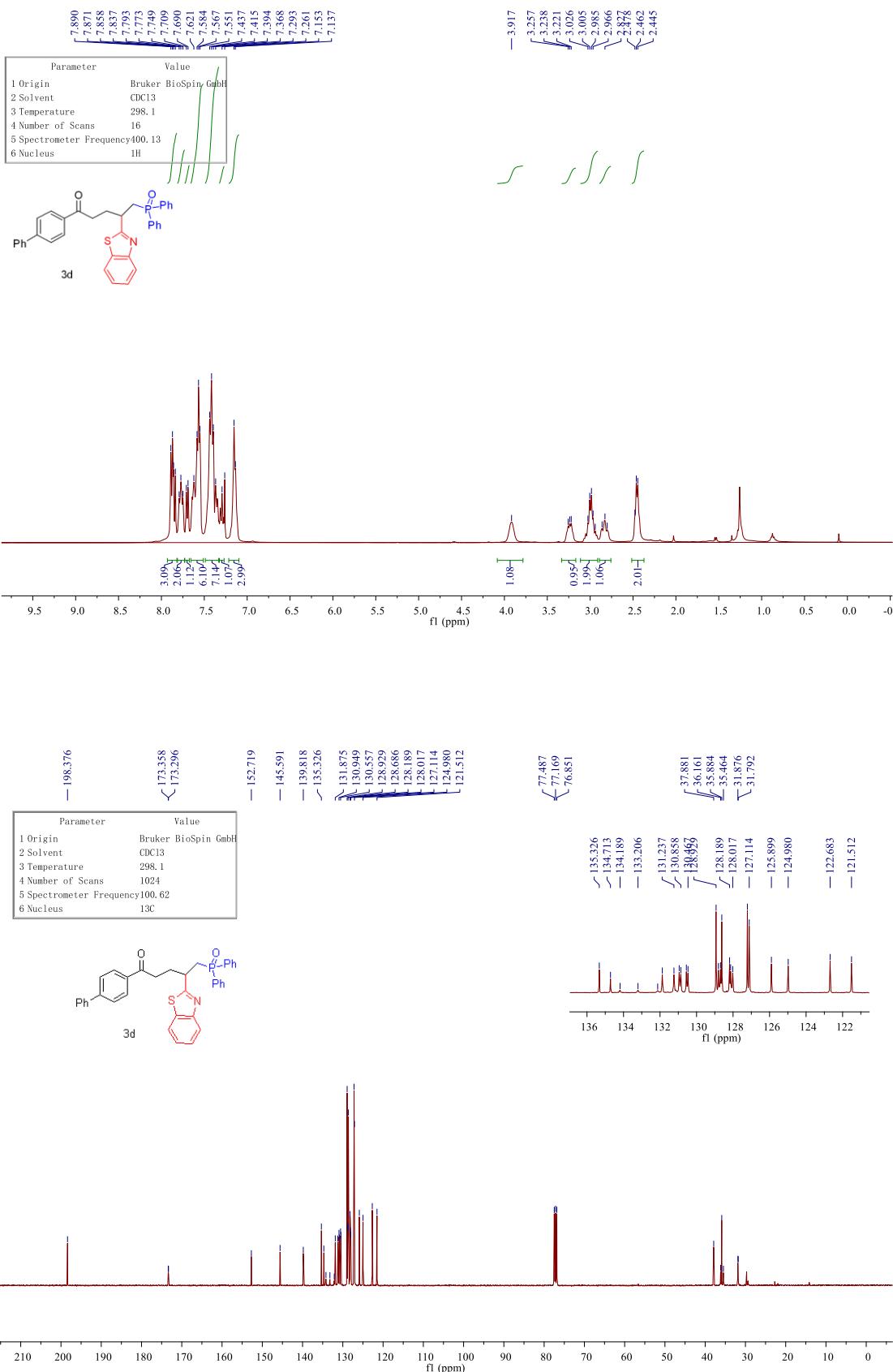


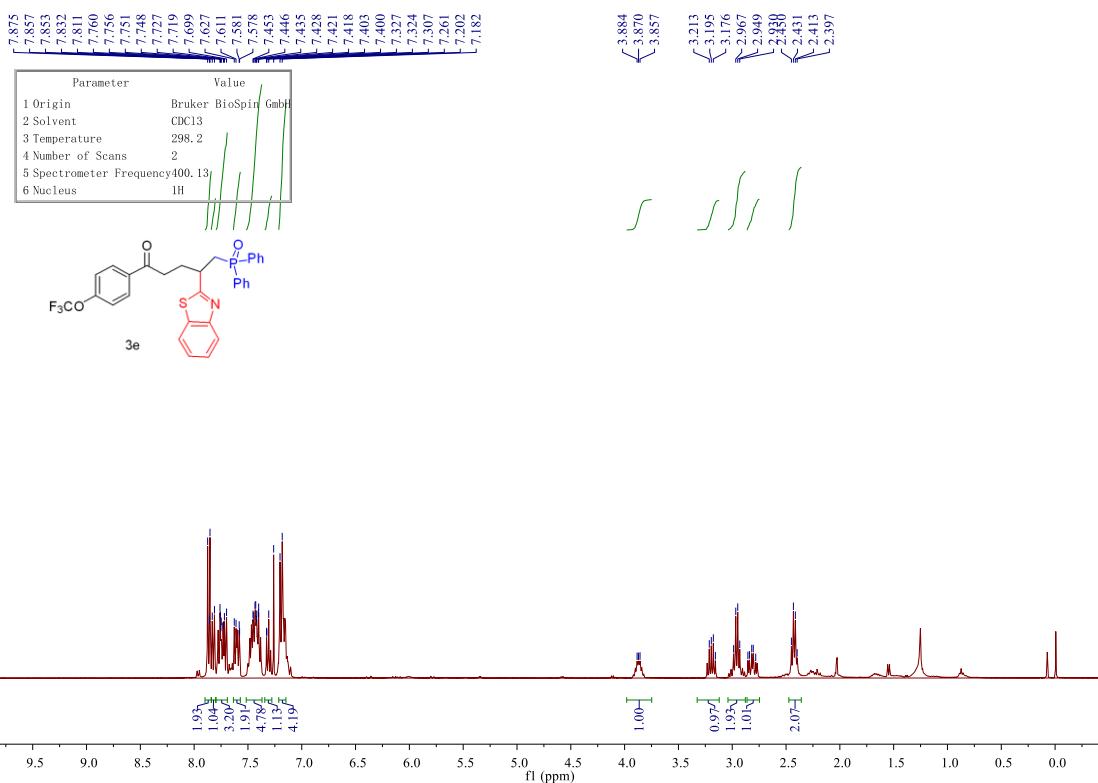
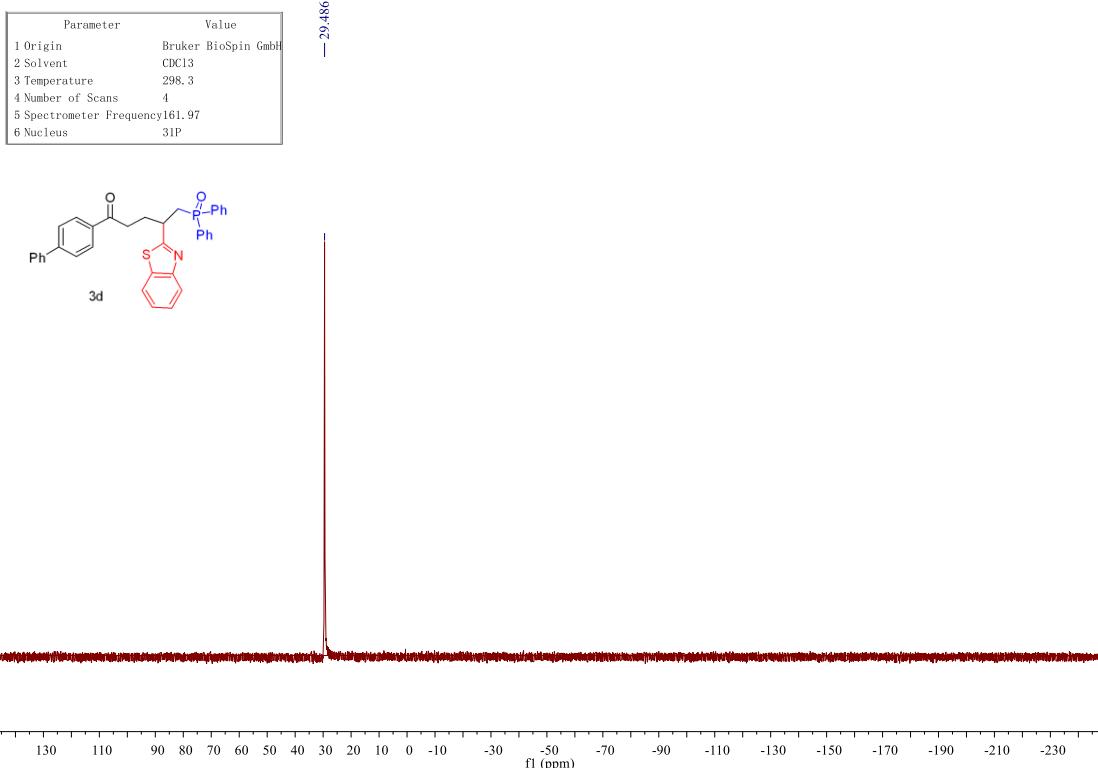


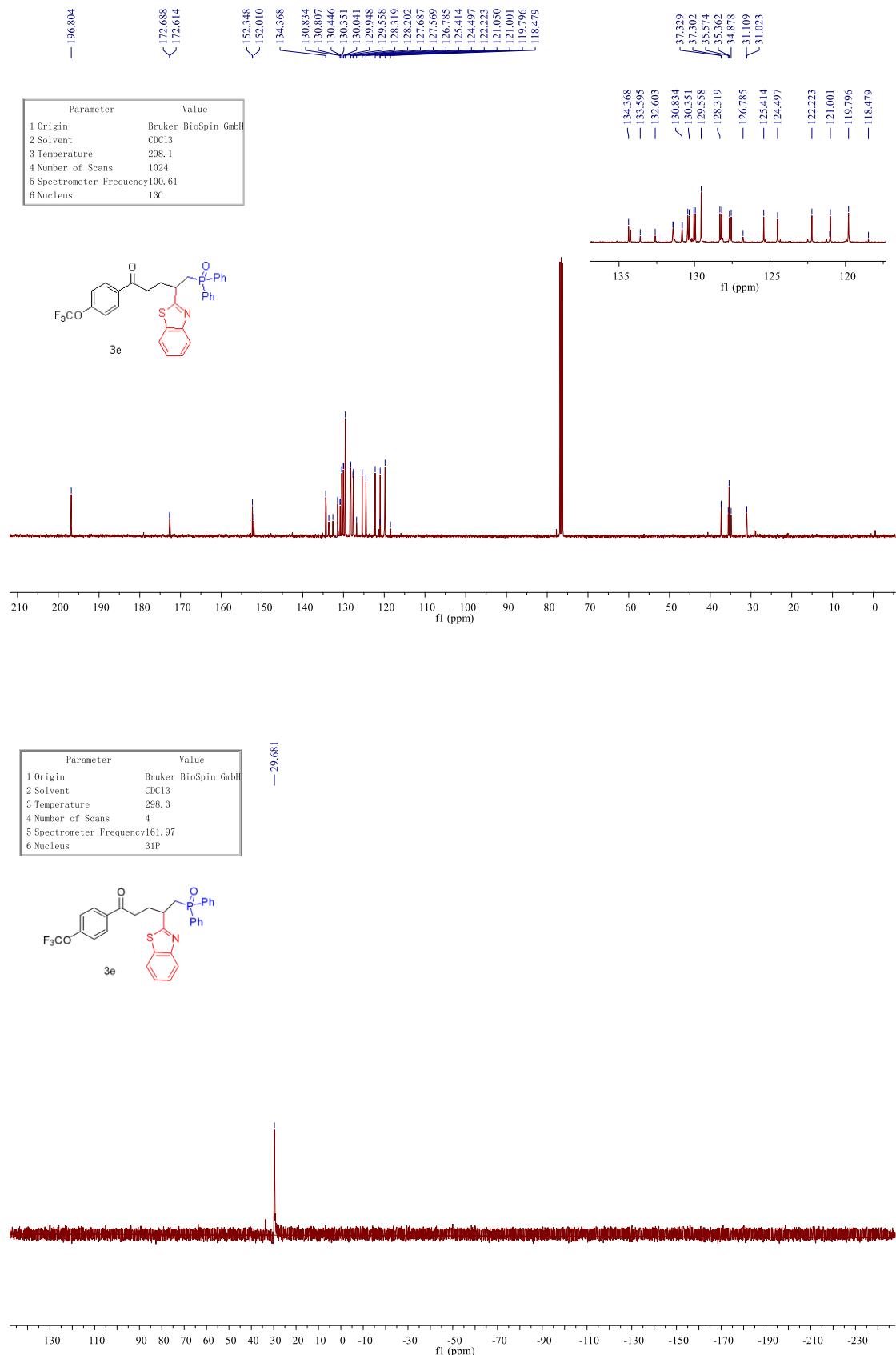
Parameter	Value
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2 Solvent	CDCl ₃
3 Temperature	298.2
4 Number of Scans	16
5 Spectrometer Frequency	161.97
6 Nucleus	31P

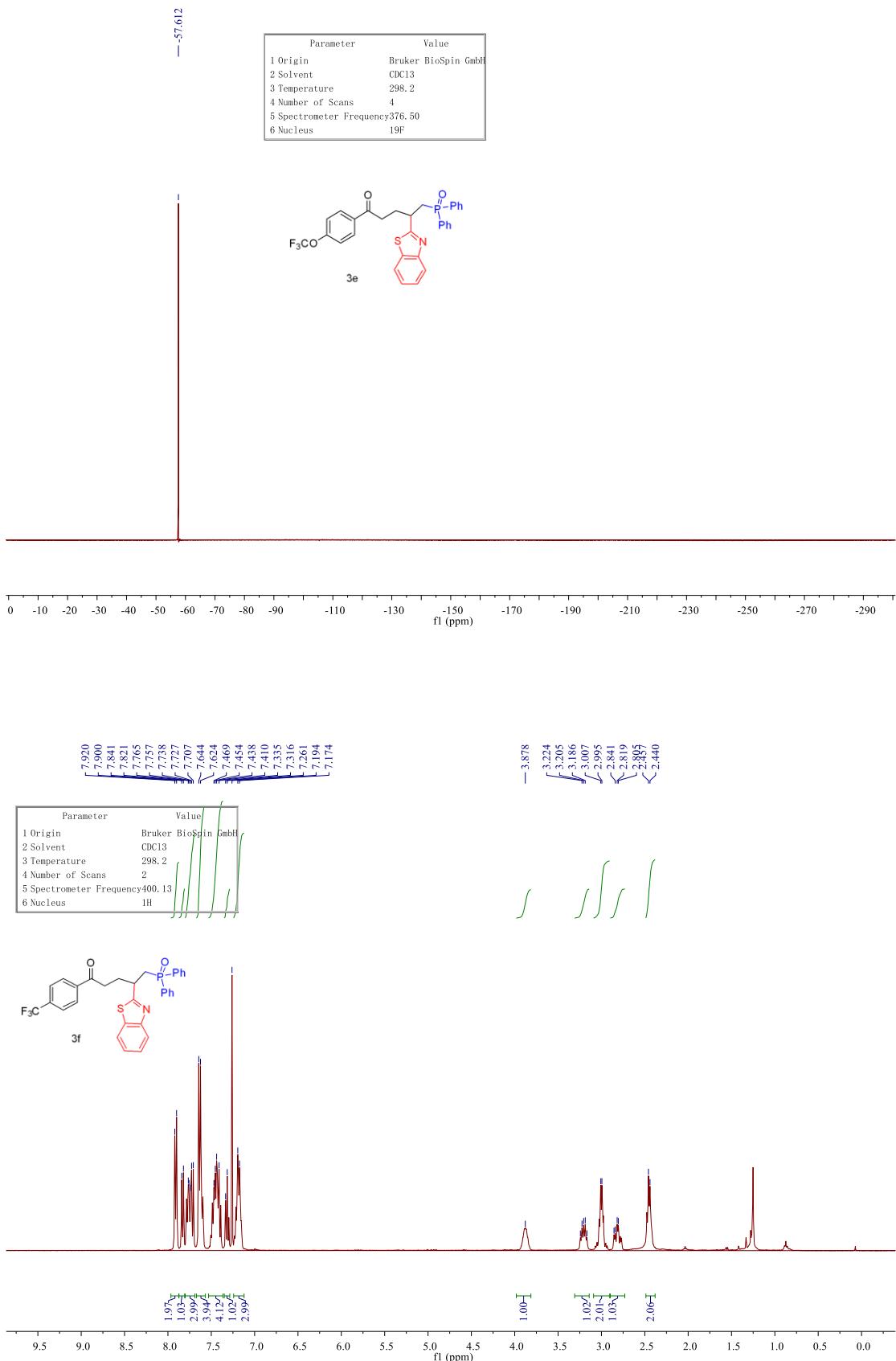






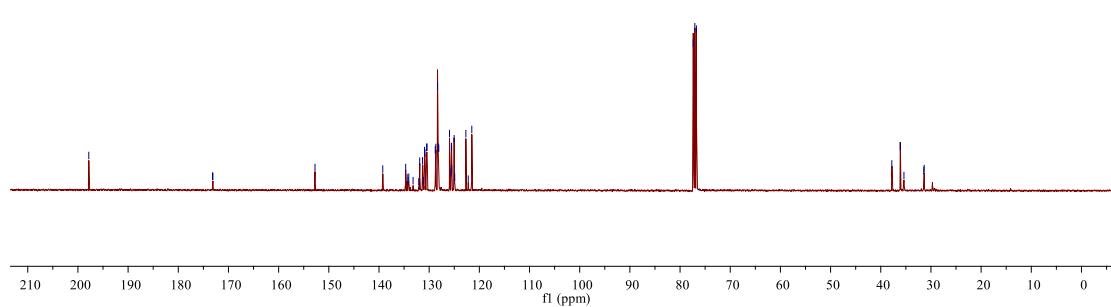
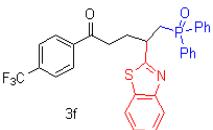




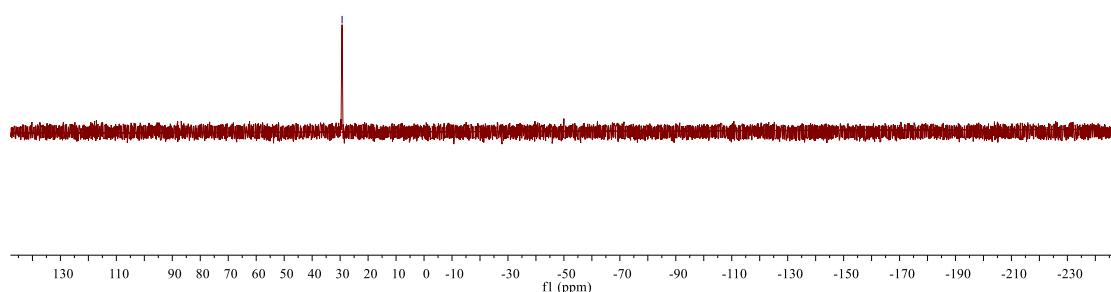
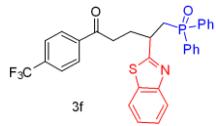


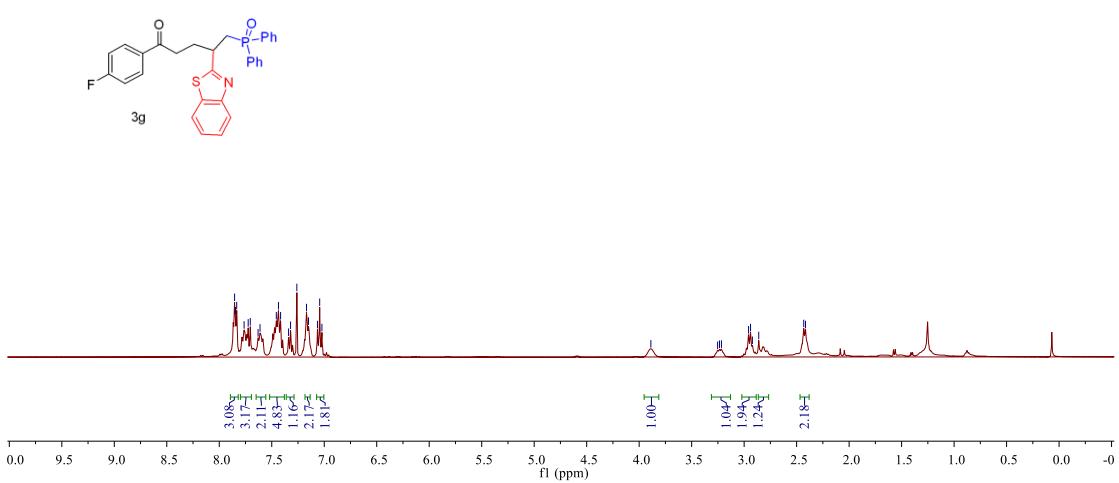
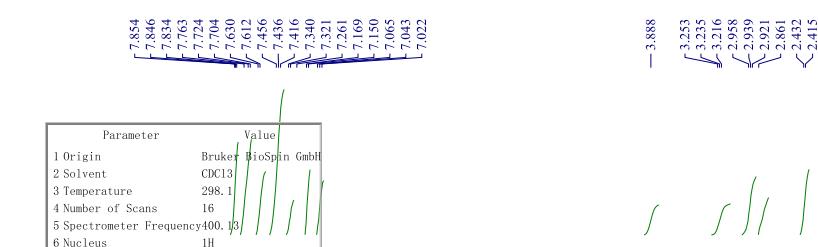
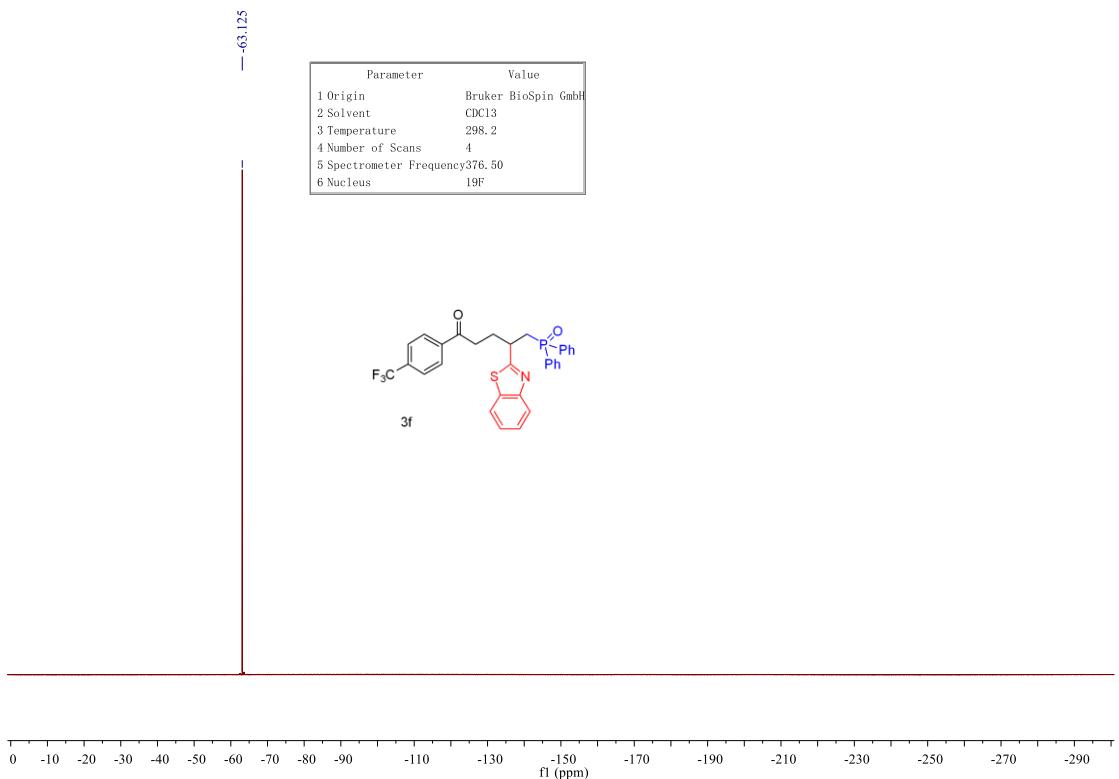


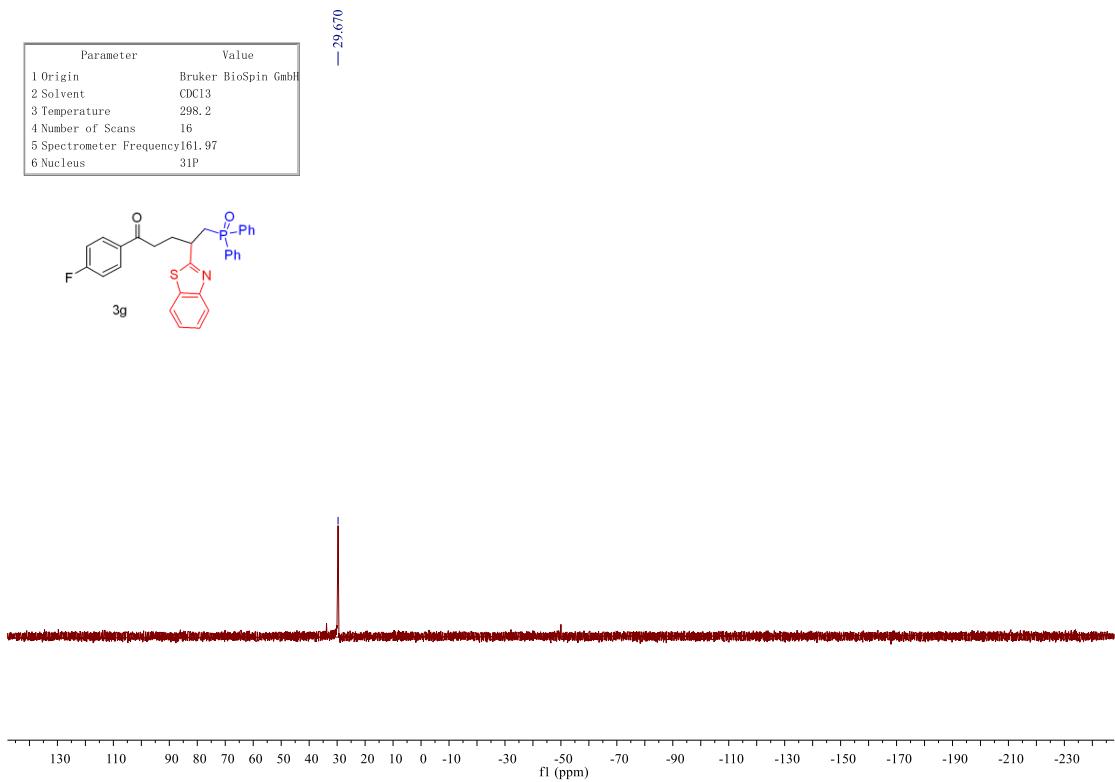
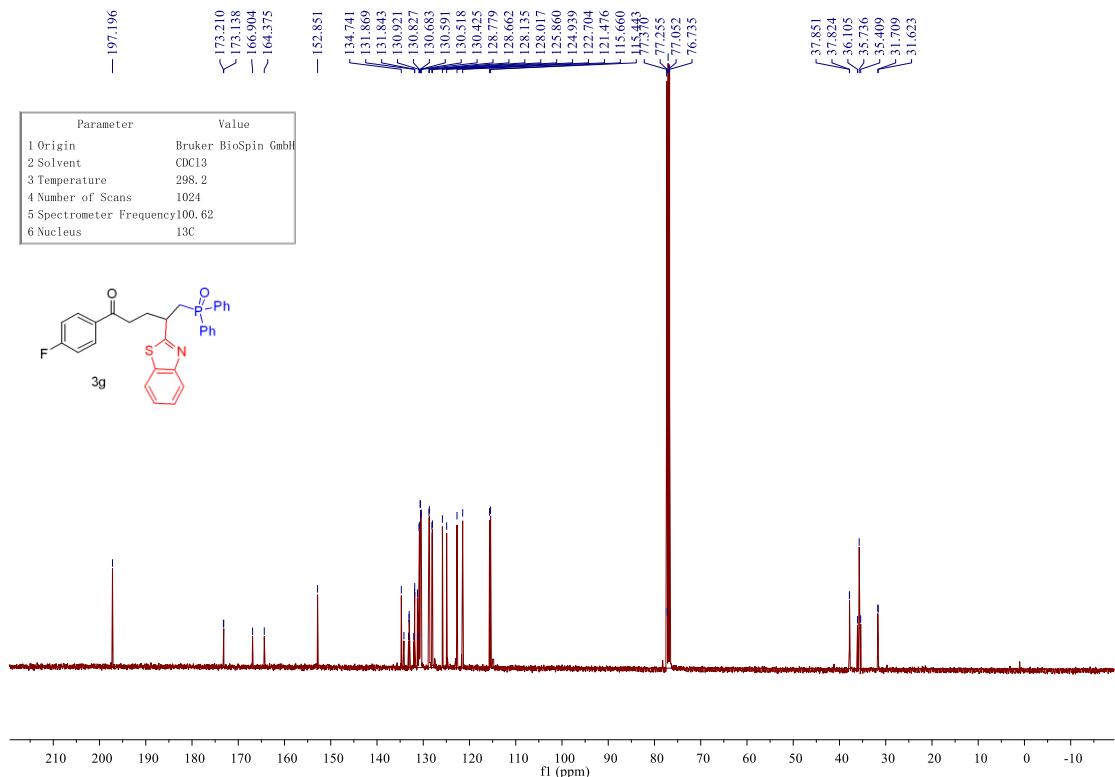
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3 Temperature	298.1
4 Number of Scans	1024
5 Spectrometer Frequency	100.62
6 Nucleus	¹³ C



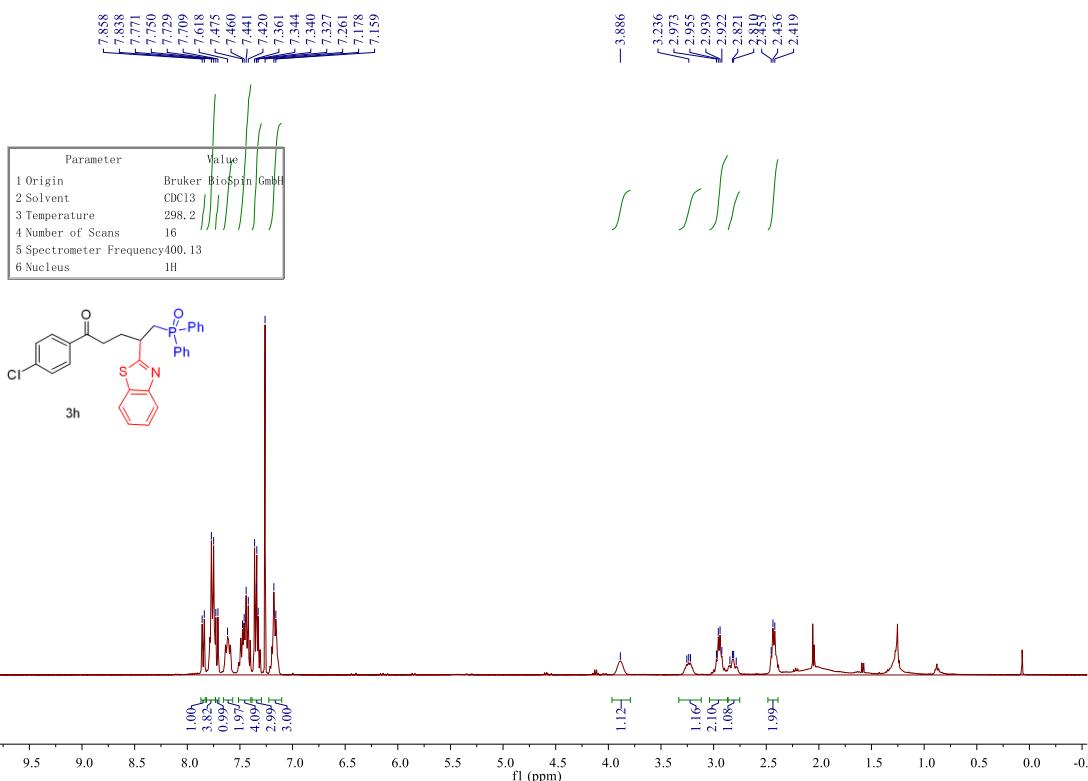
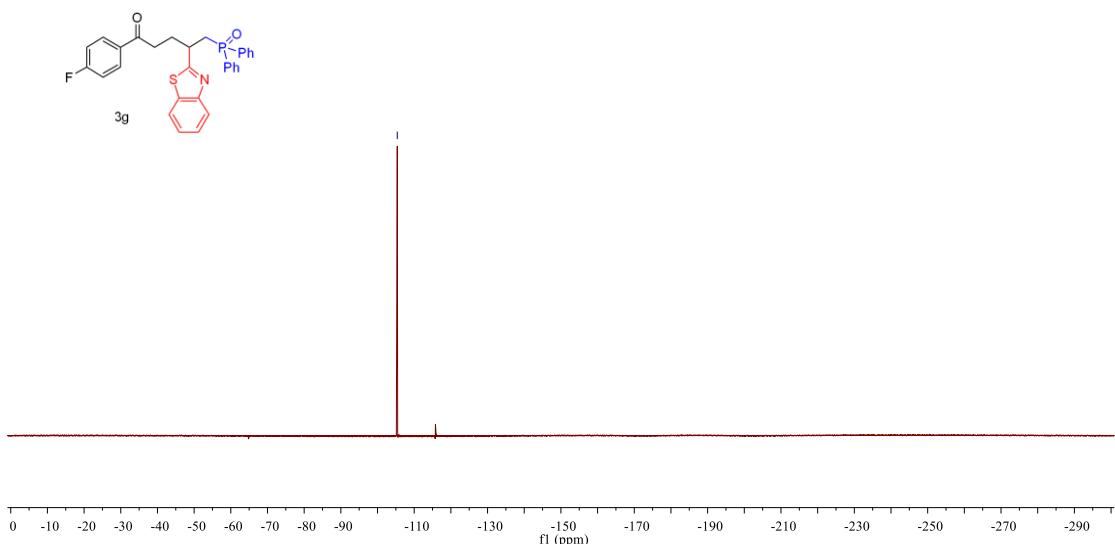
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1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl ₃
3 Temperature	298.1
4 Number of Scans	2
5 Spectrometer Frequency	161.97
6 Nucleus	³¹ P

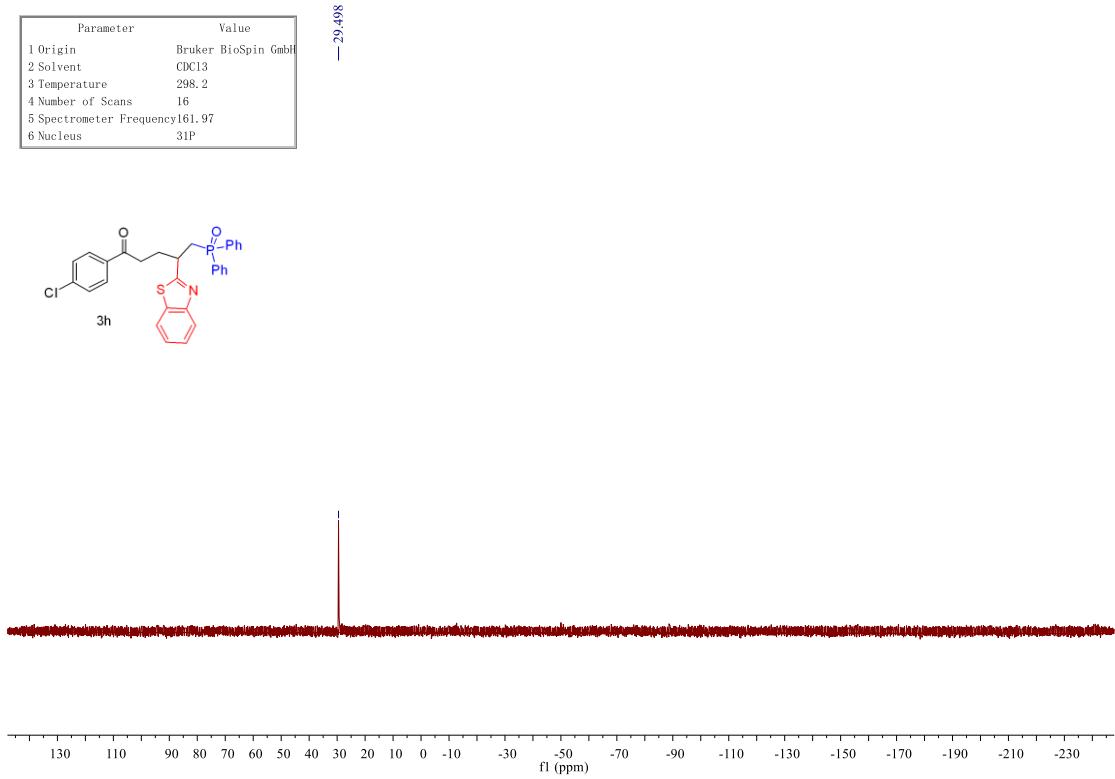
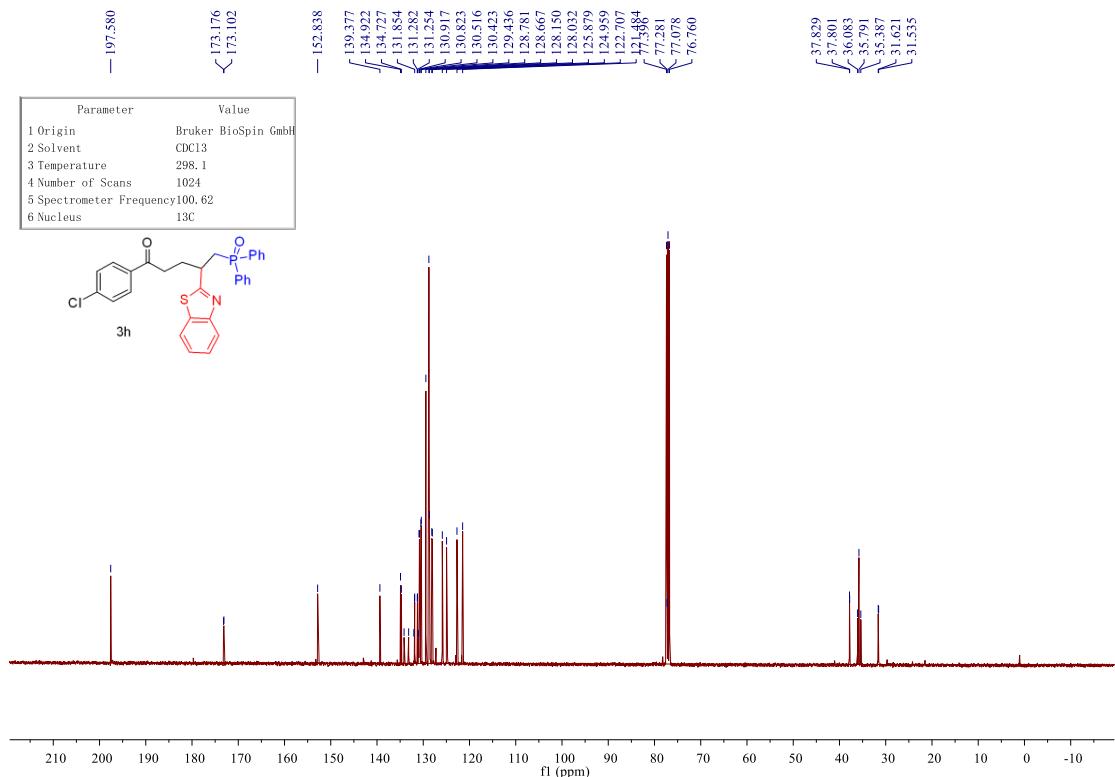


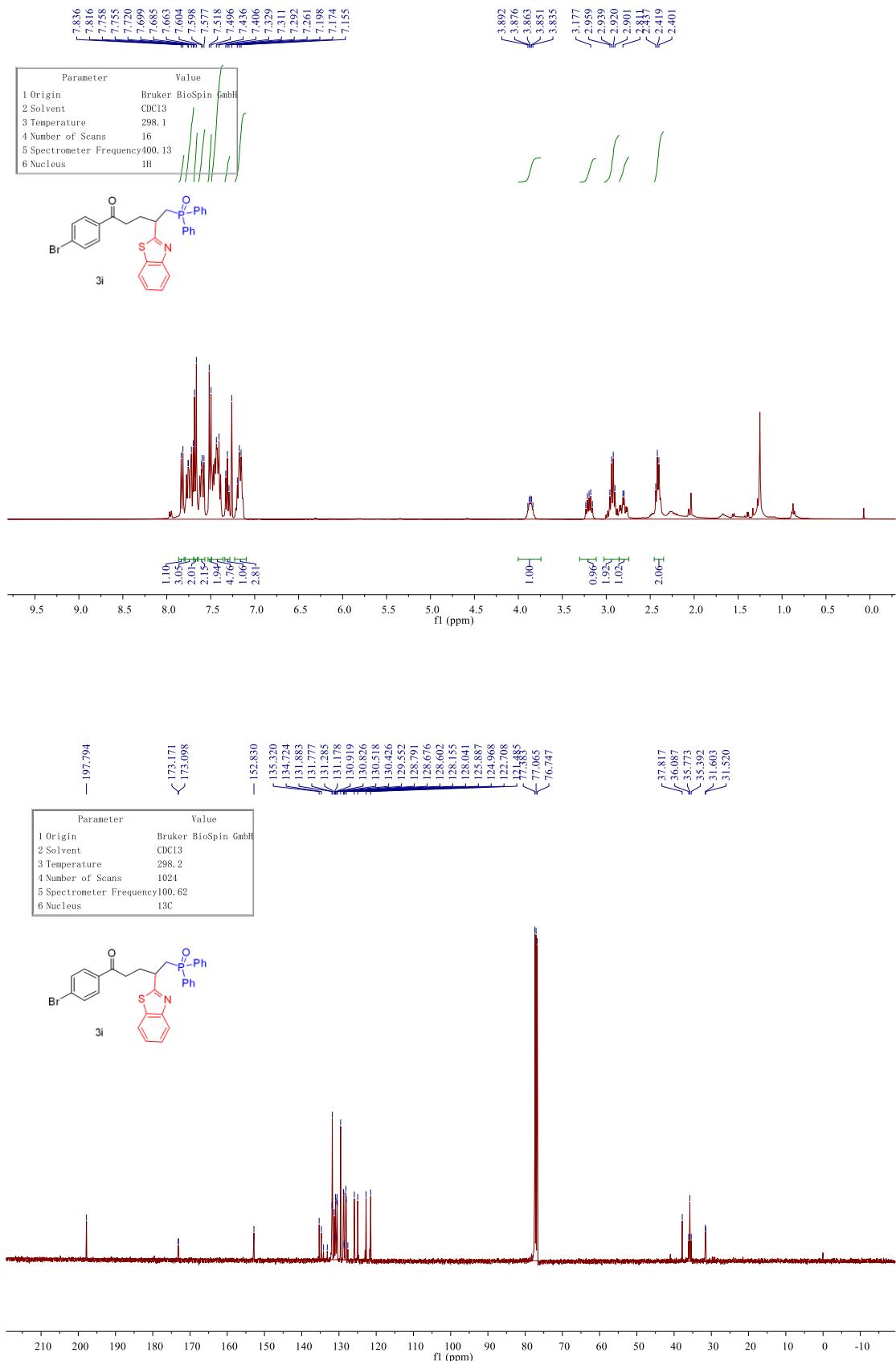




Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl ₃
3 Temperature	298.2
4 Number of Scans	4
5 Spectrometer Frequency	376.50
6 Nucleus	¹⁹ F

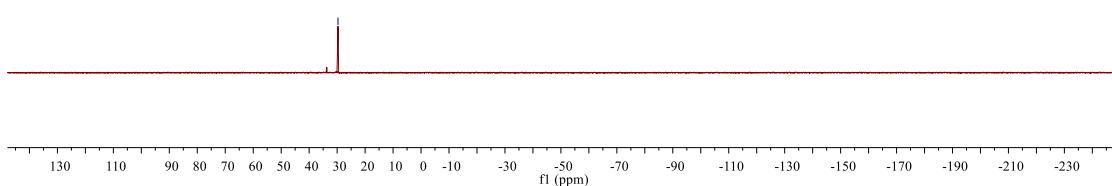
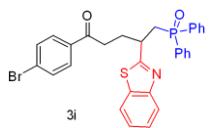




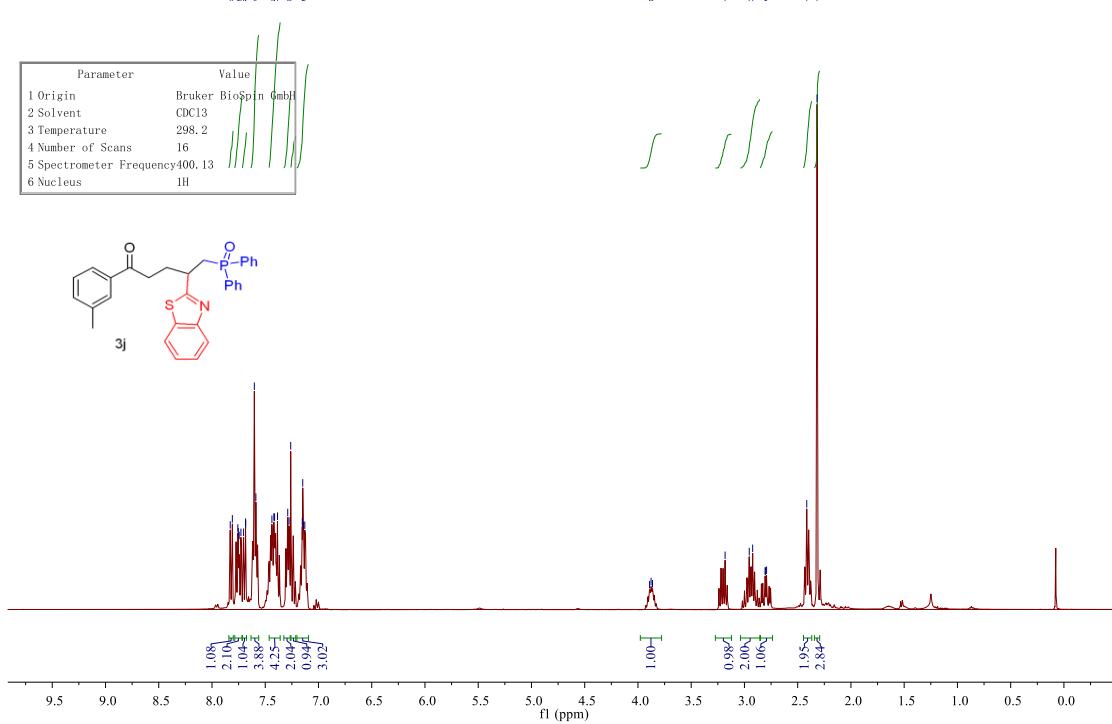
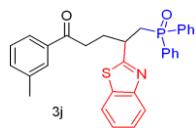


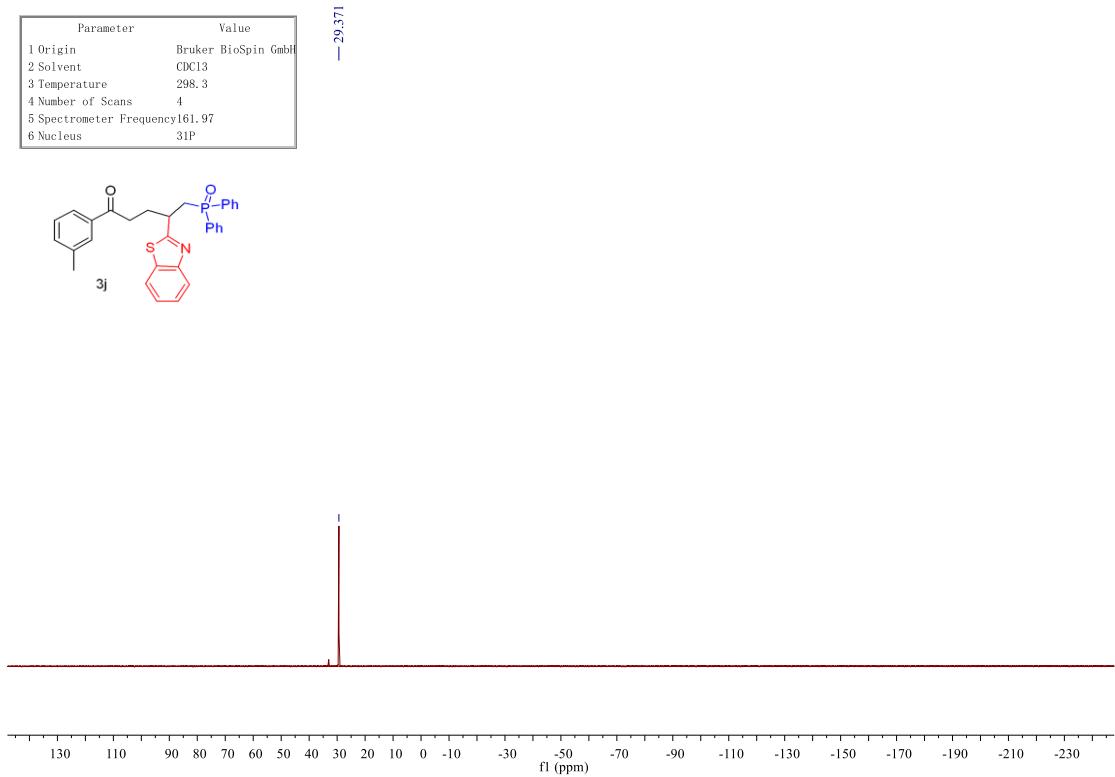
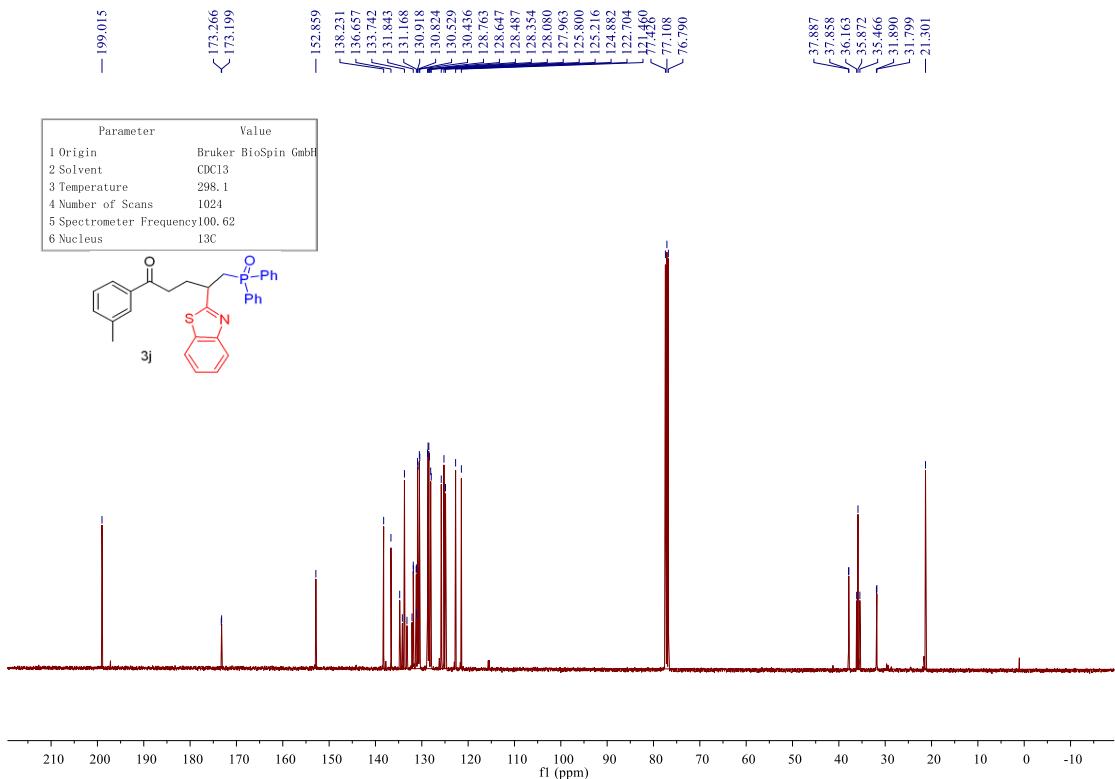
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl ₃
3 Temperature	298.2
4 Number of Scans	16
5 Spectrometer Frequency	161.97
6 Nucleus	31P

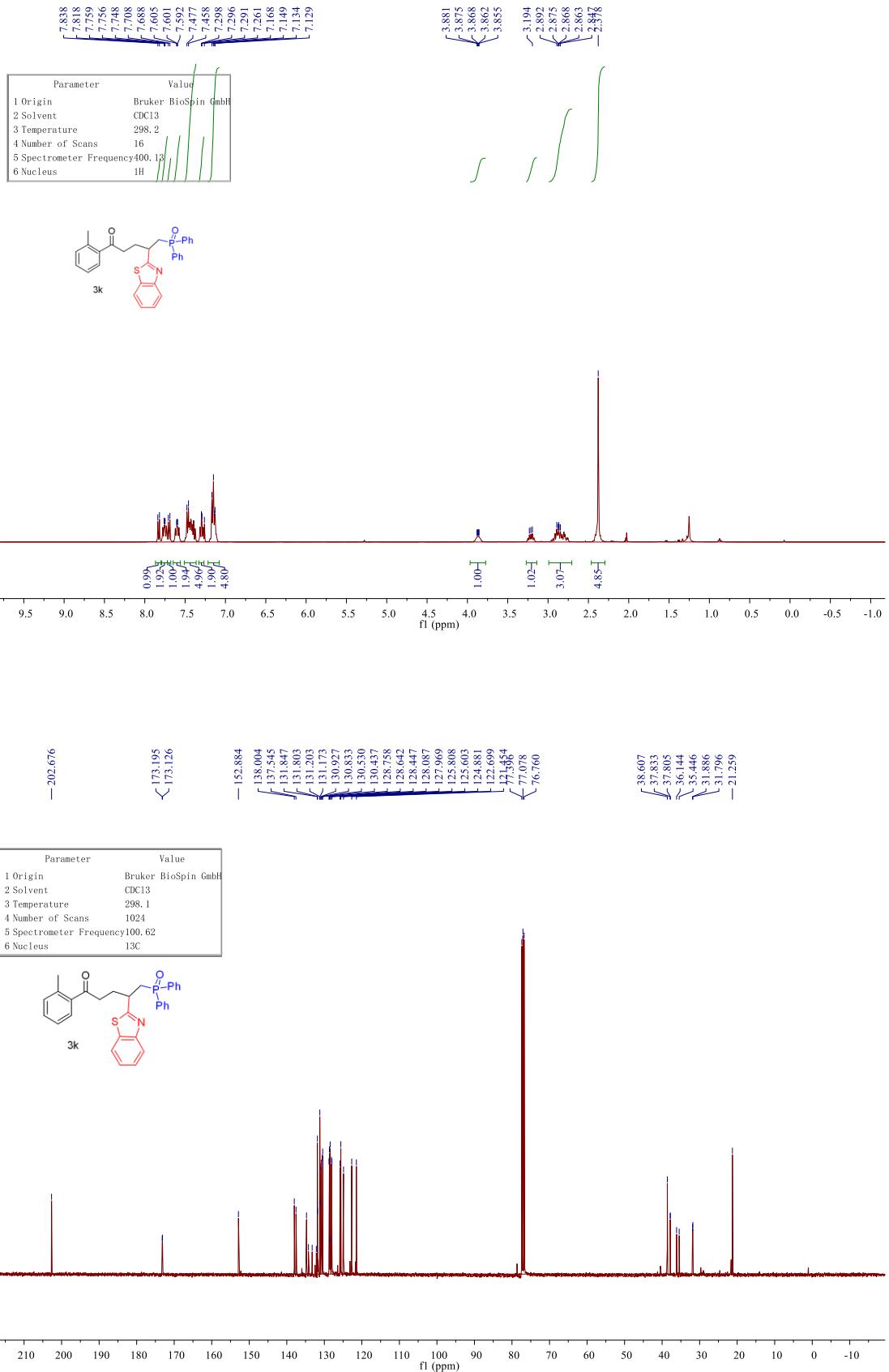
—29.693

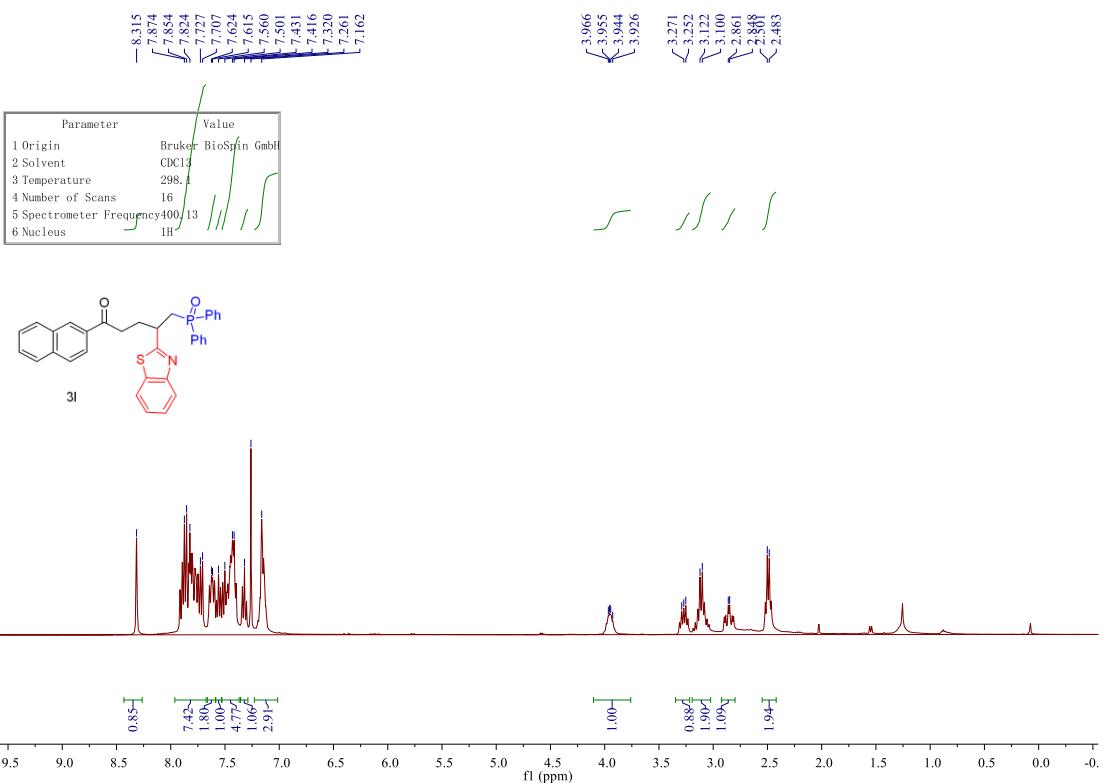
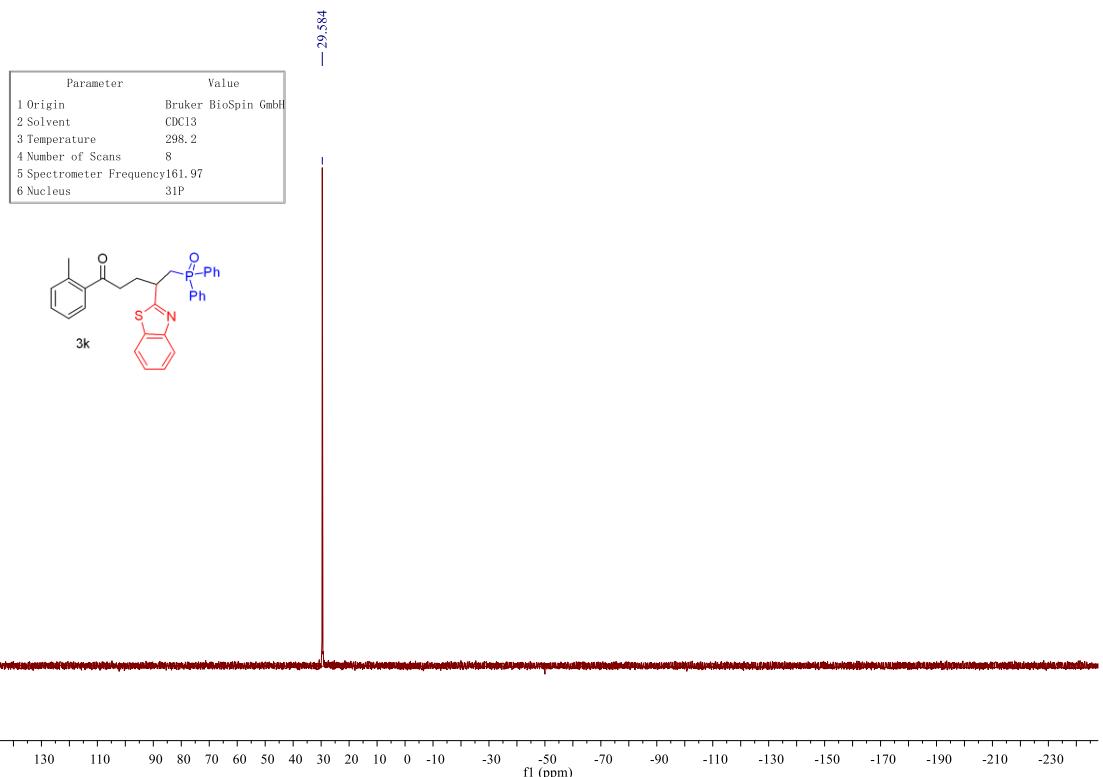


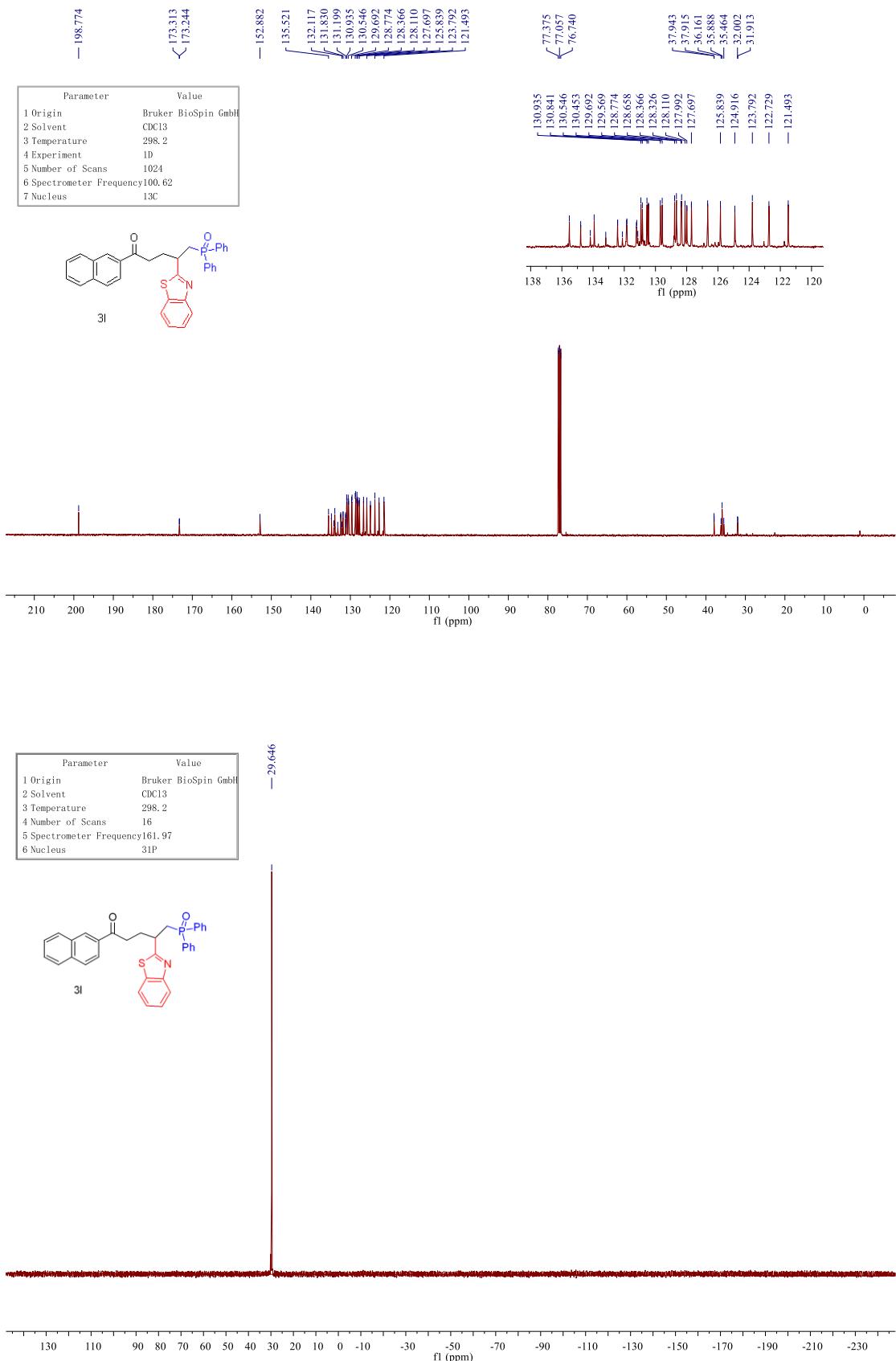
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3 Temperature	298.2
4 Number of Scans	16
5 Spectrometer Frequency	400.13
6 Nucleus	1H

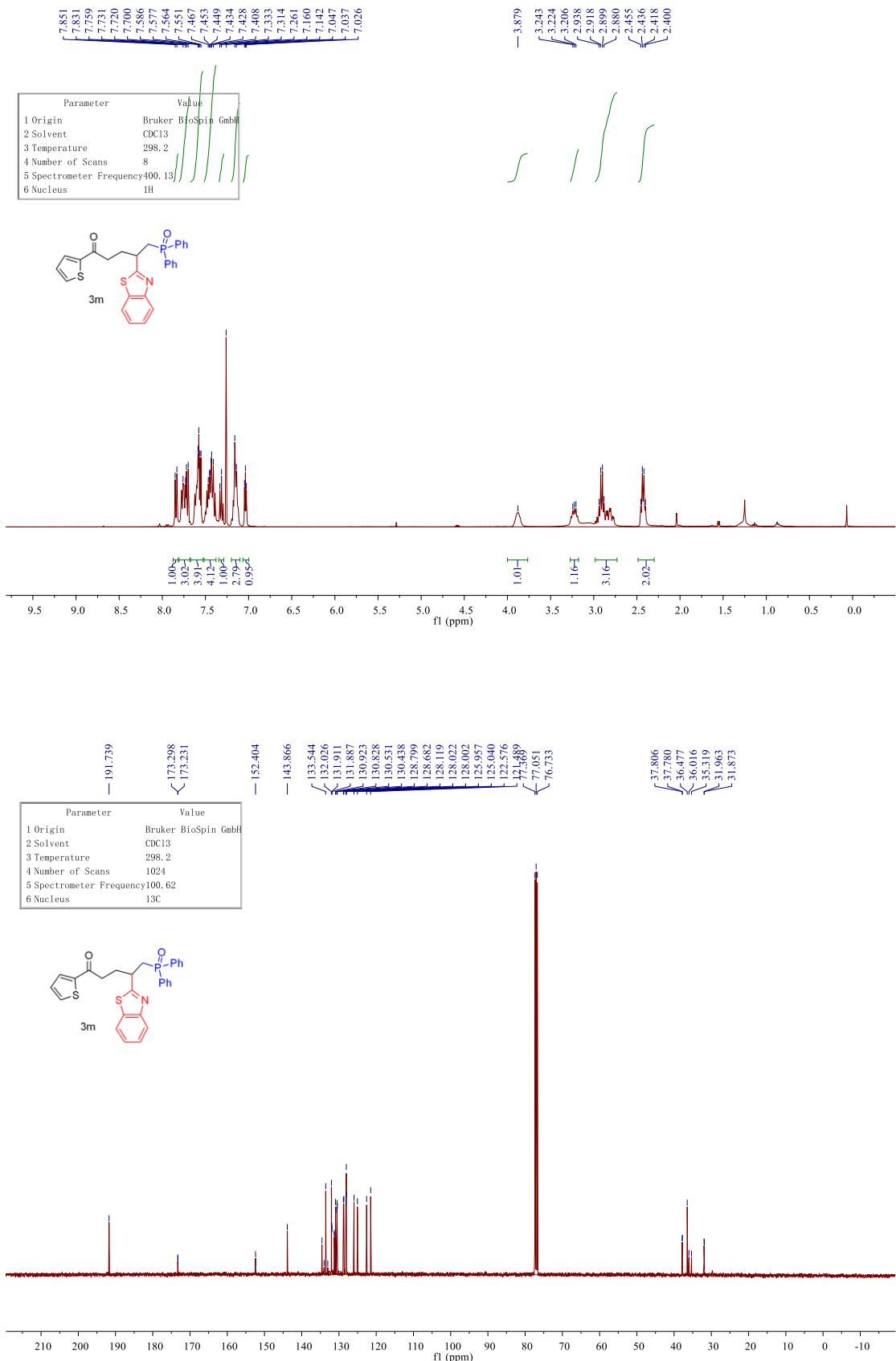


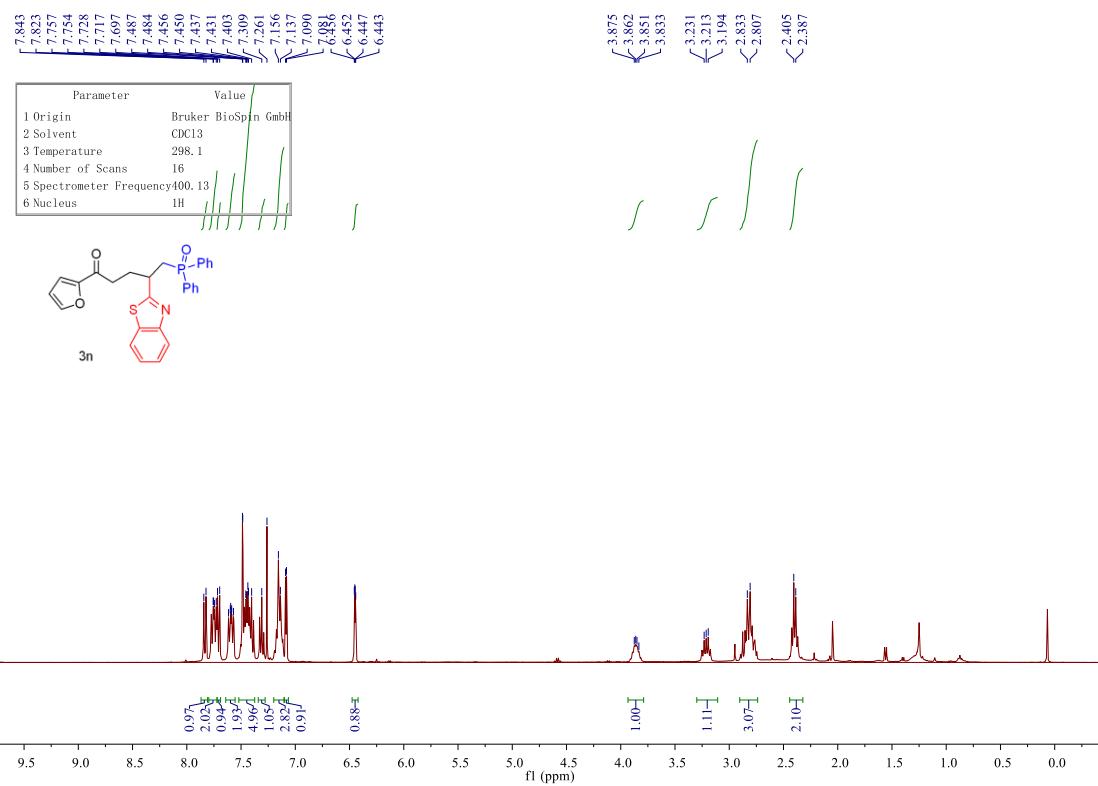
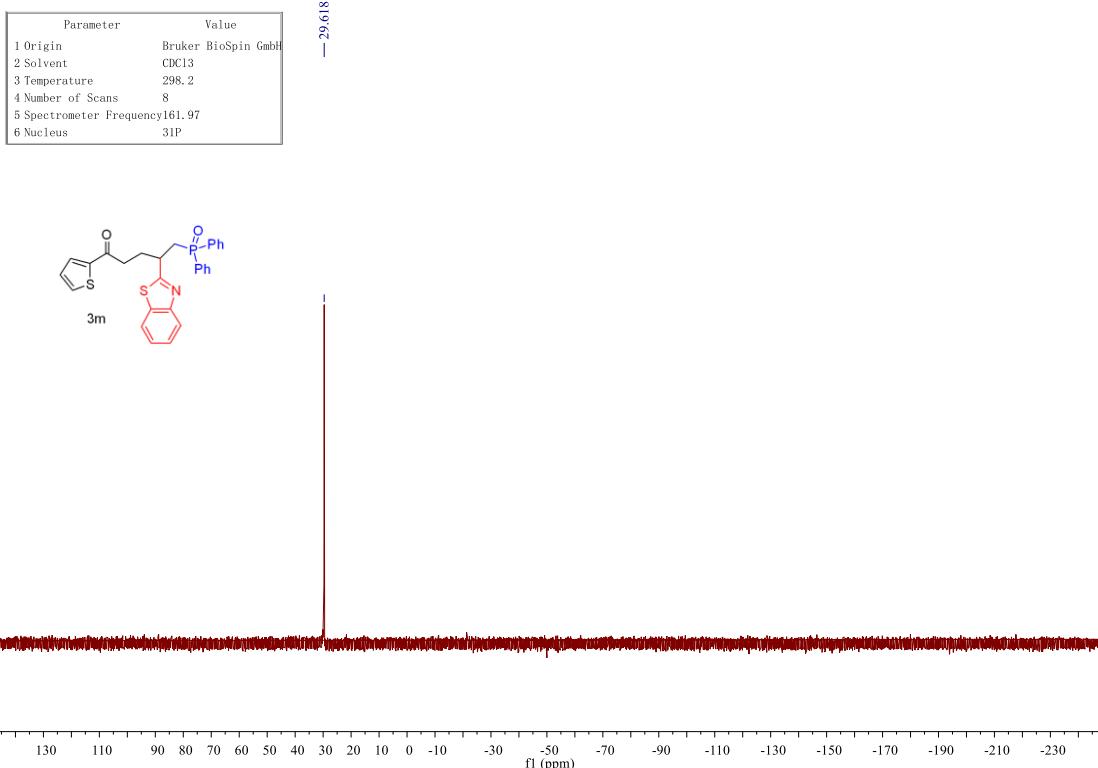


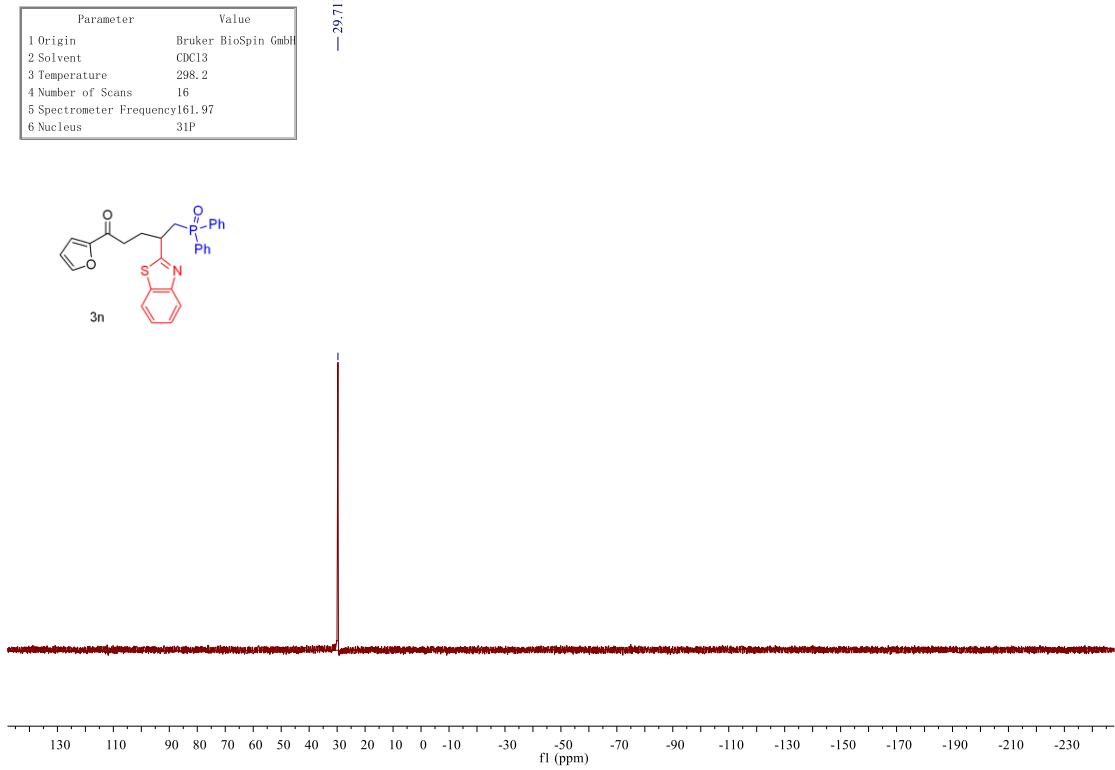
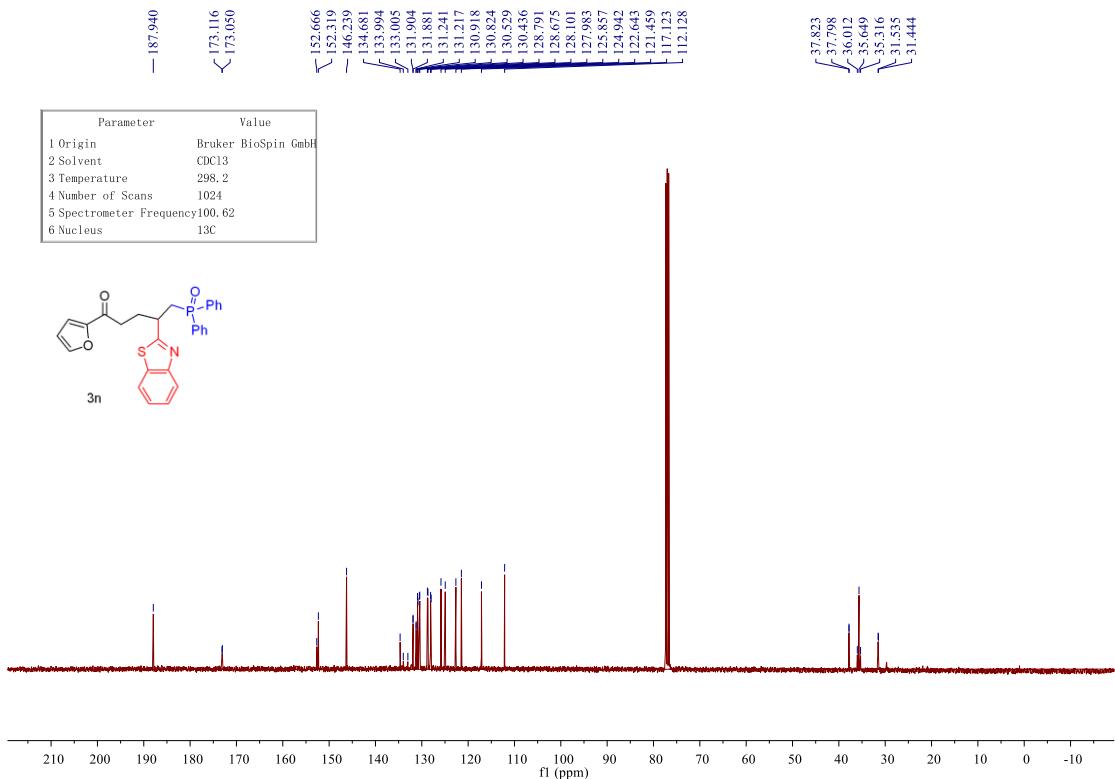


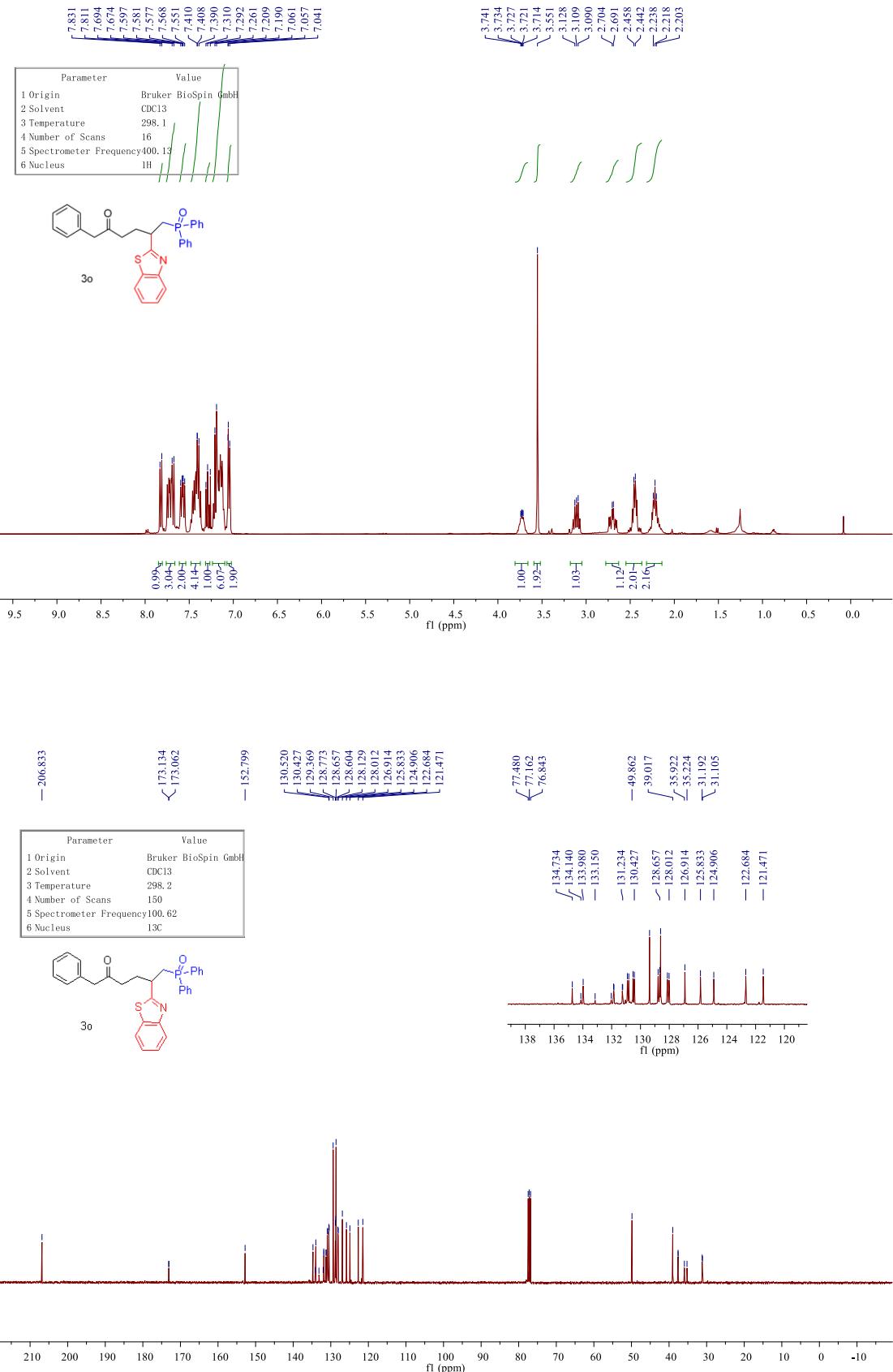


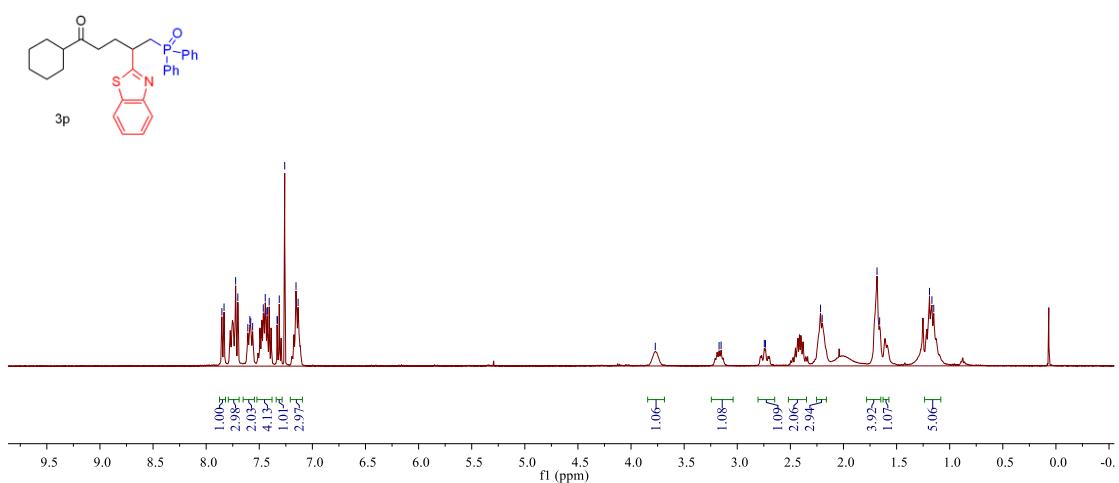
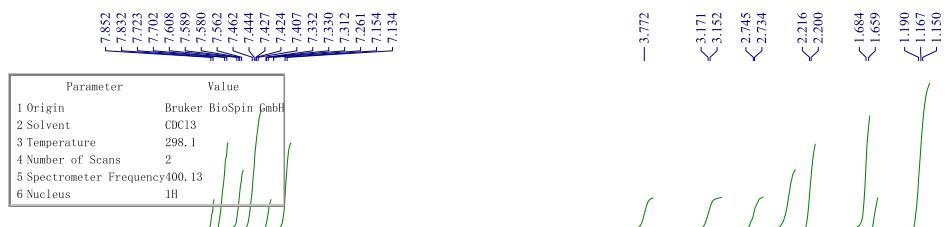
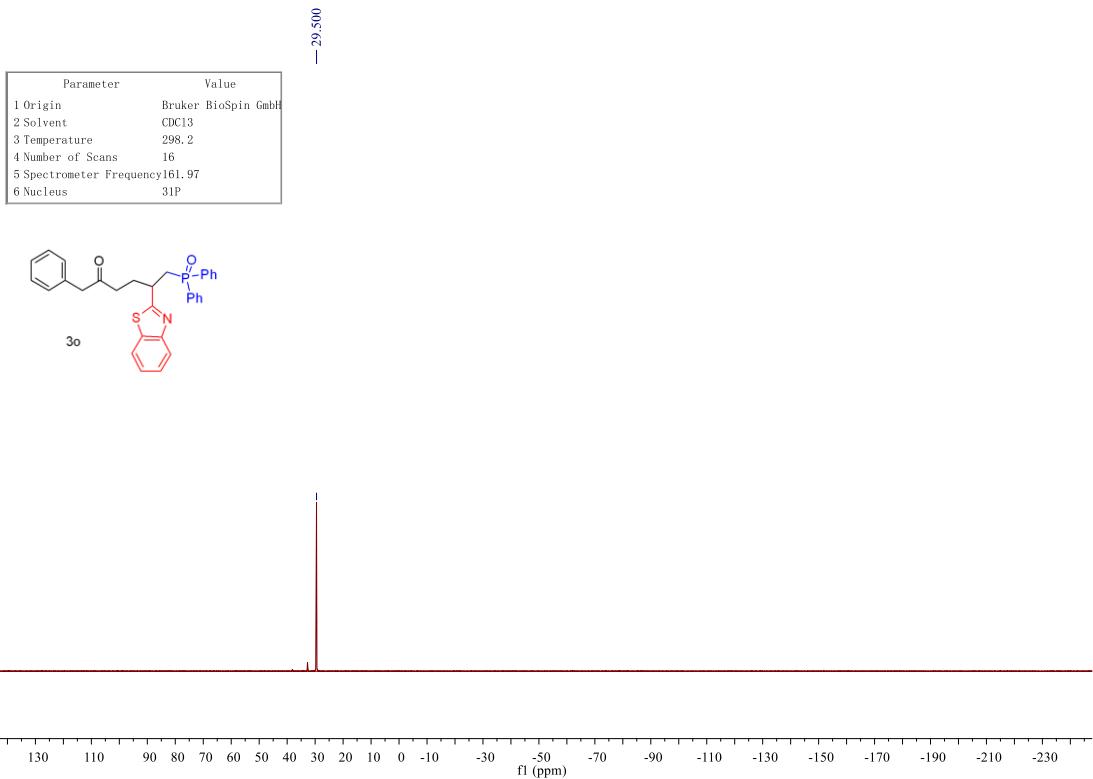


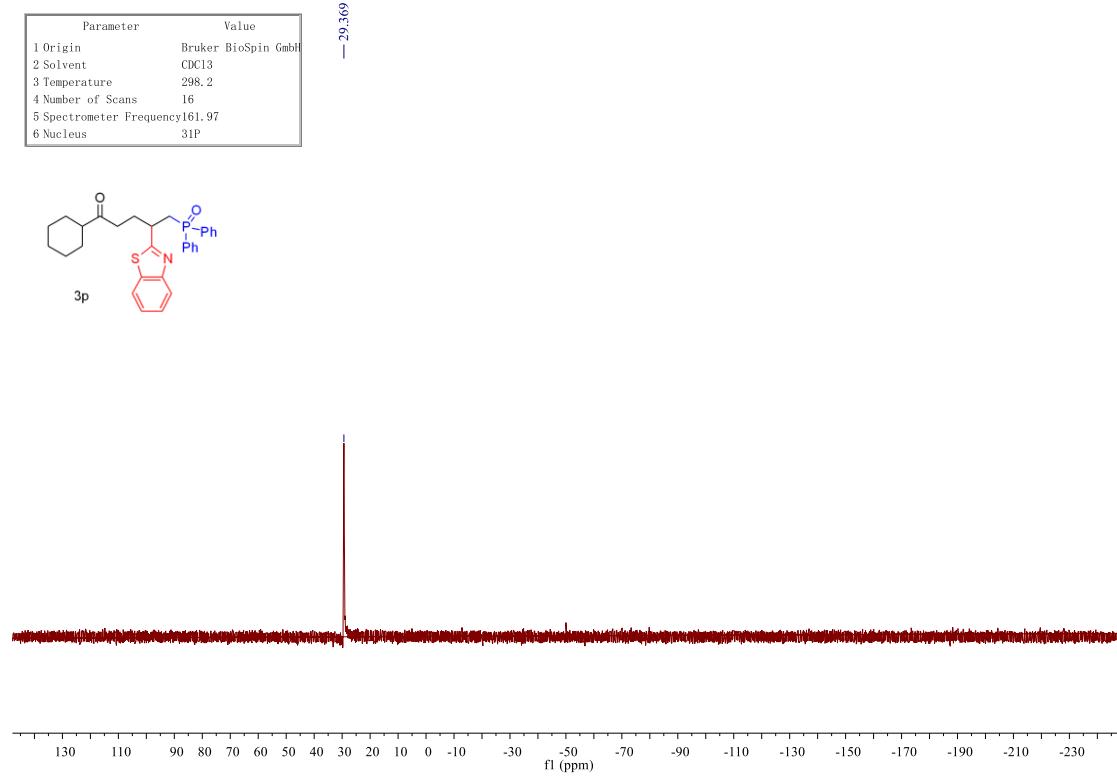
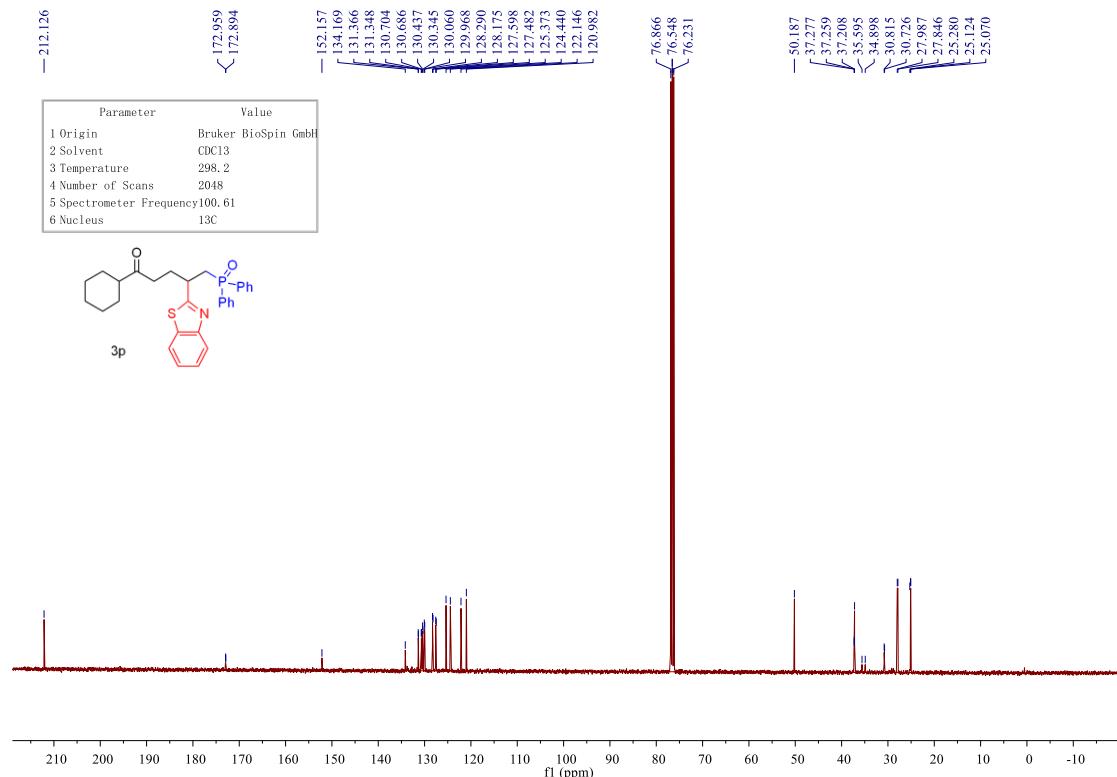


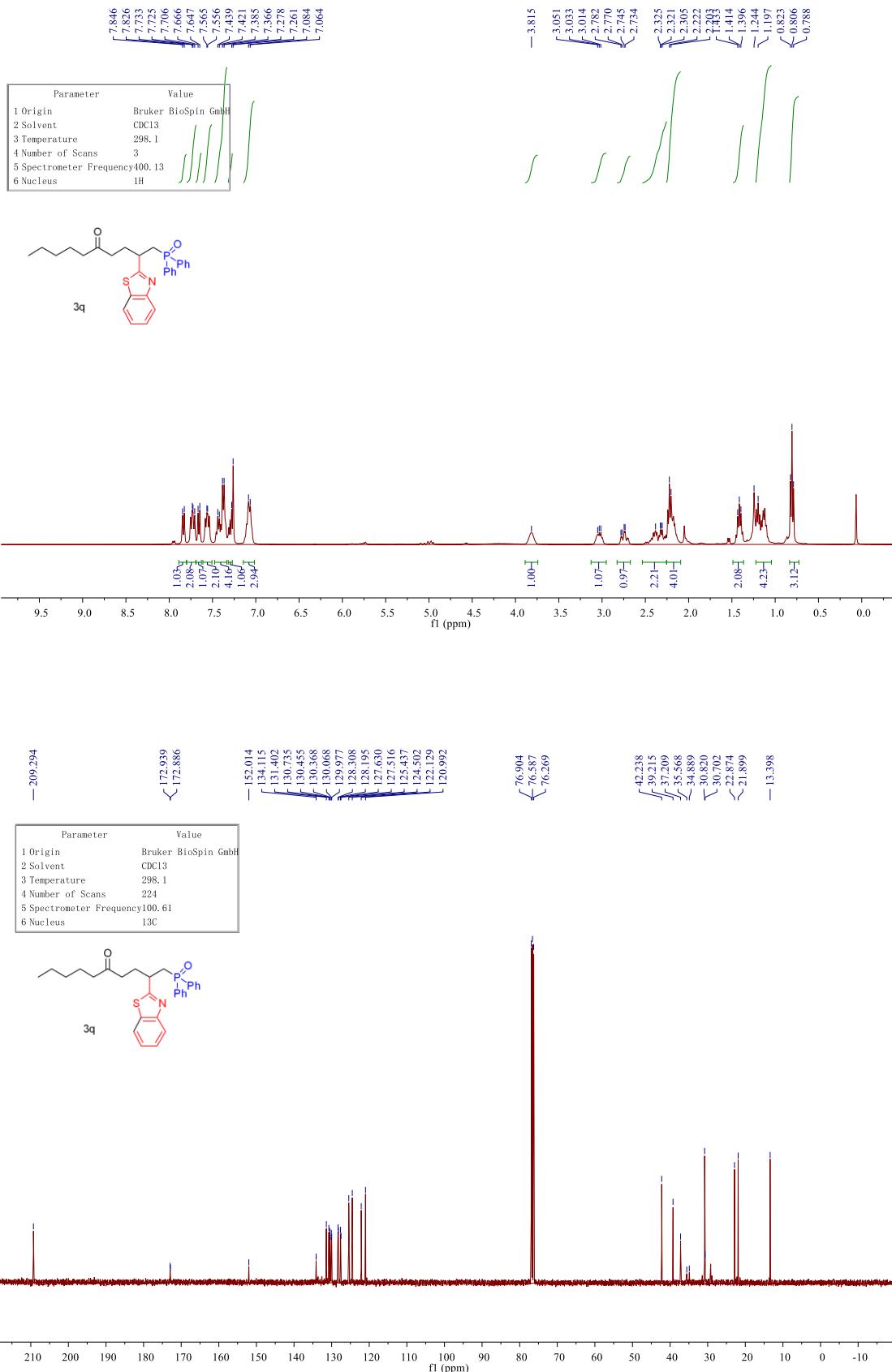


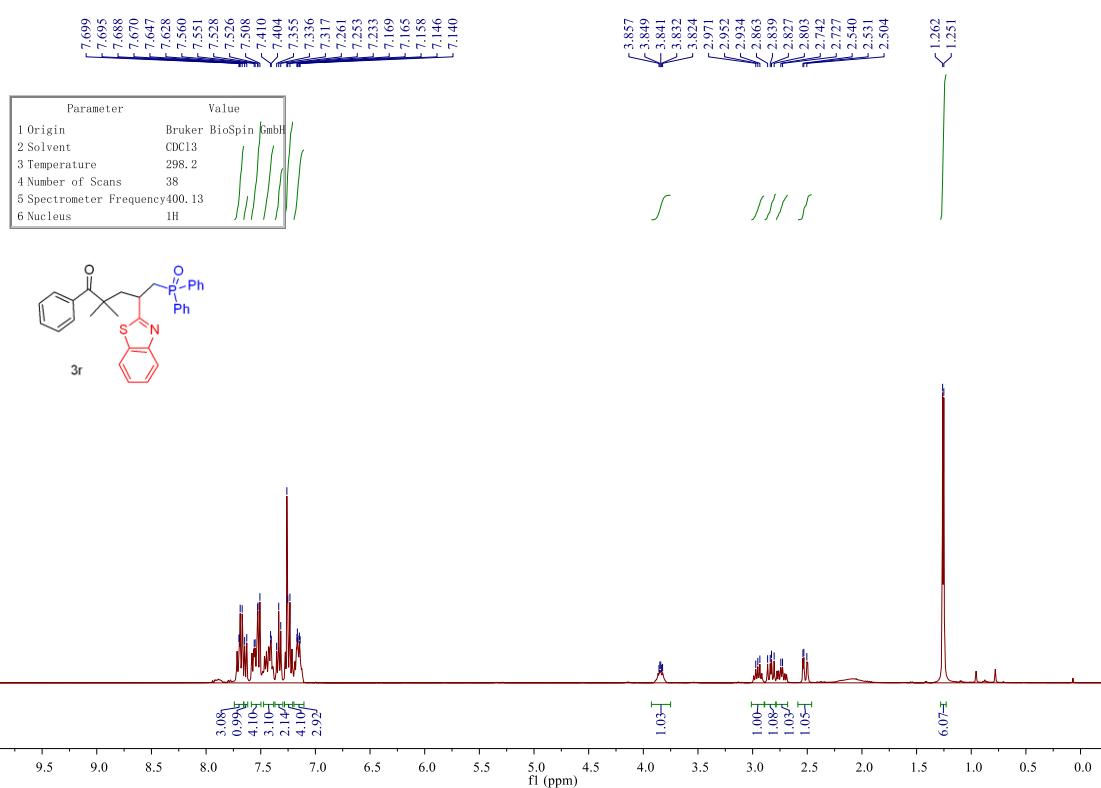
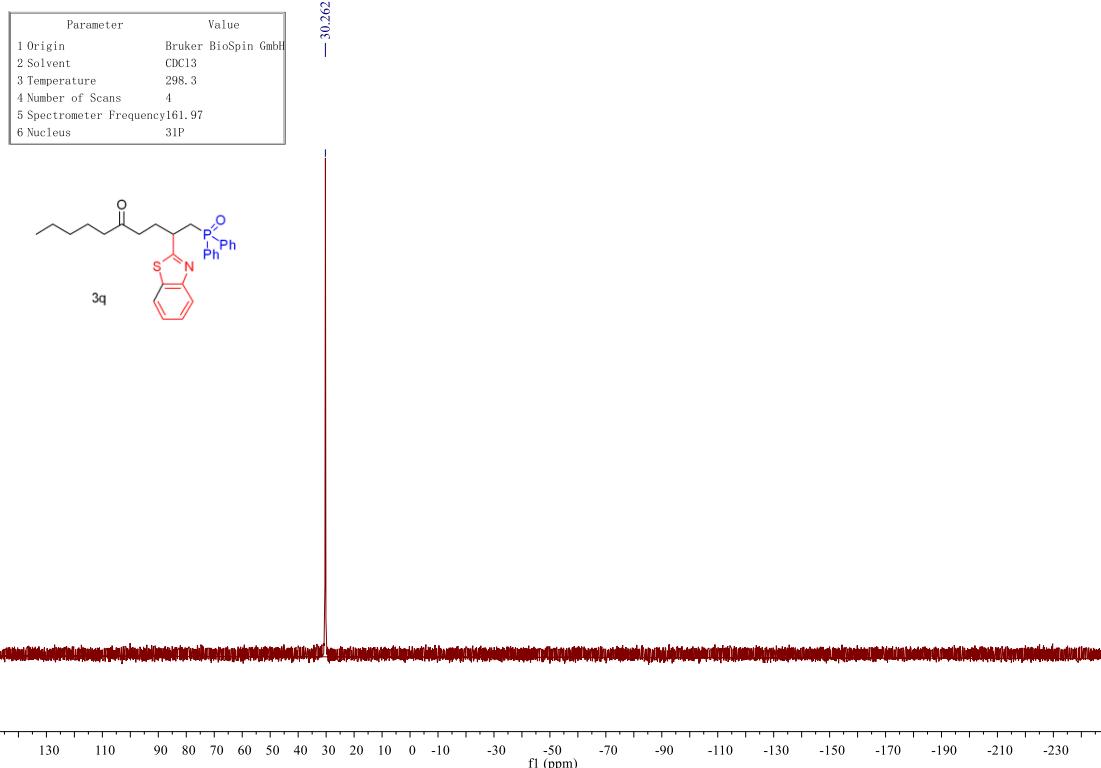


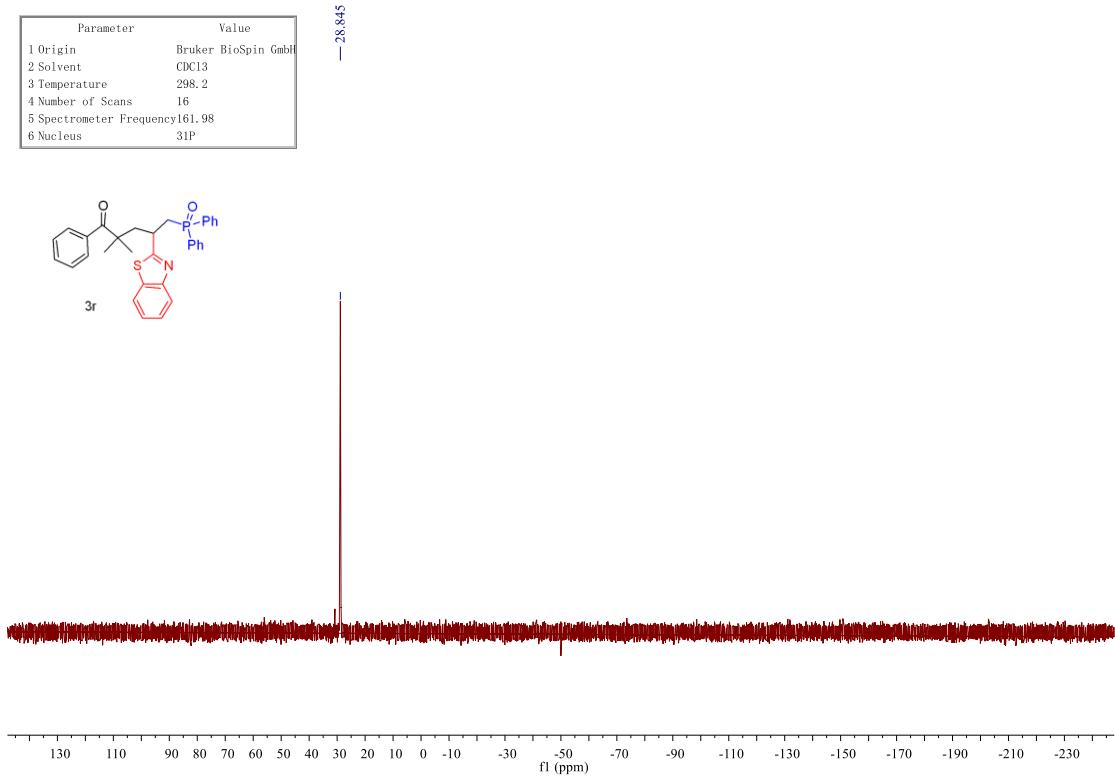
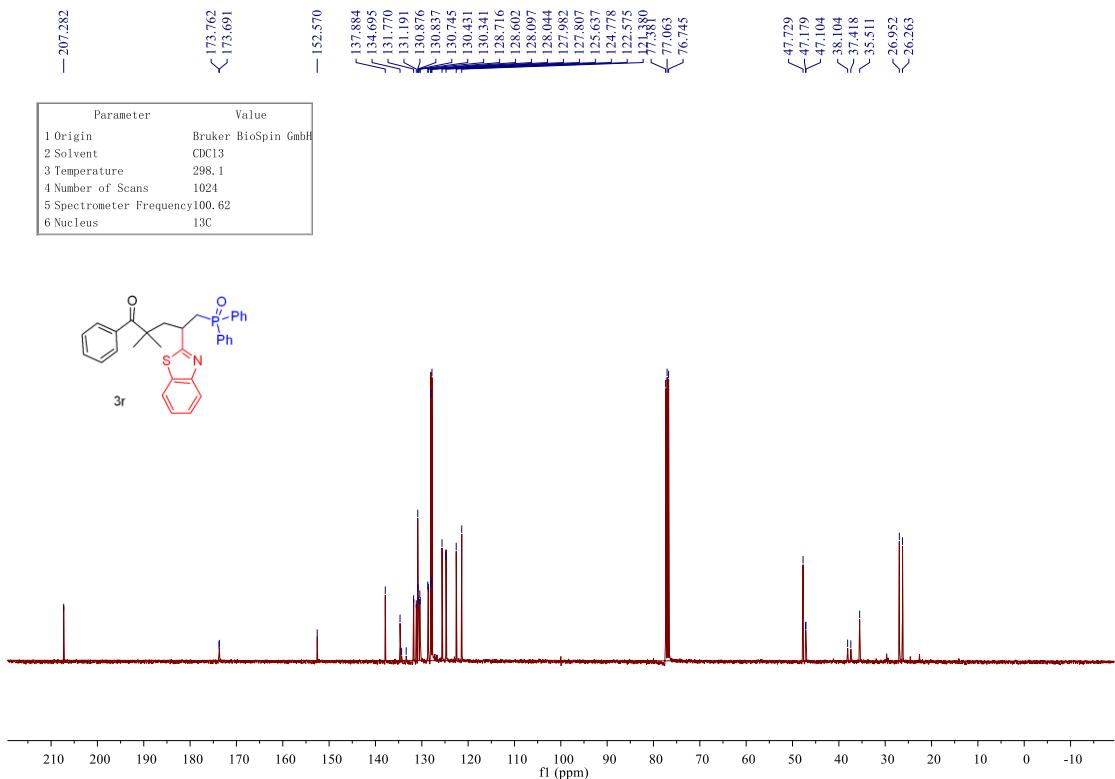


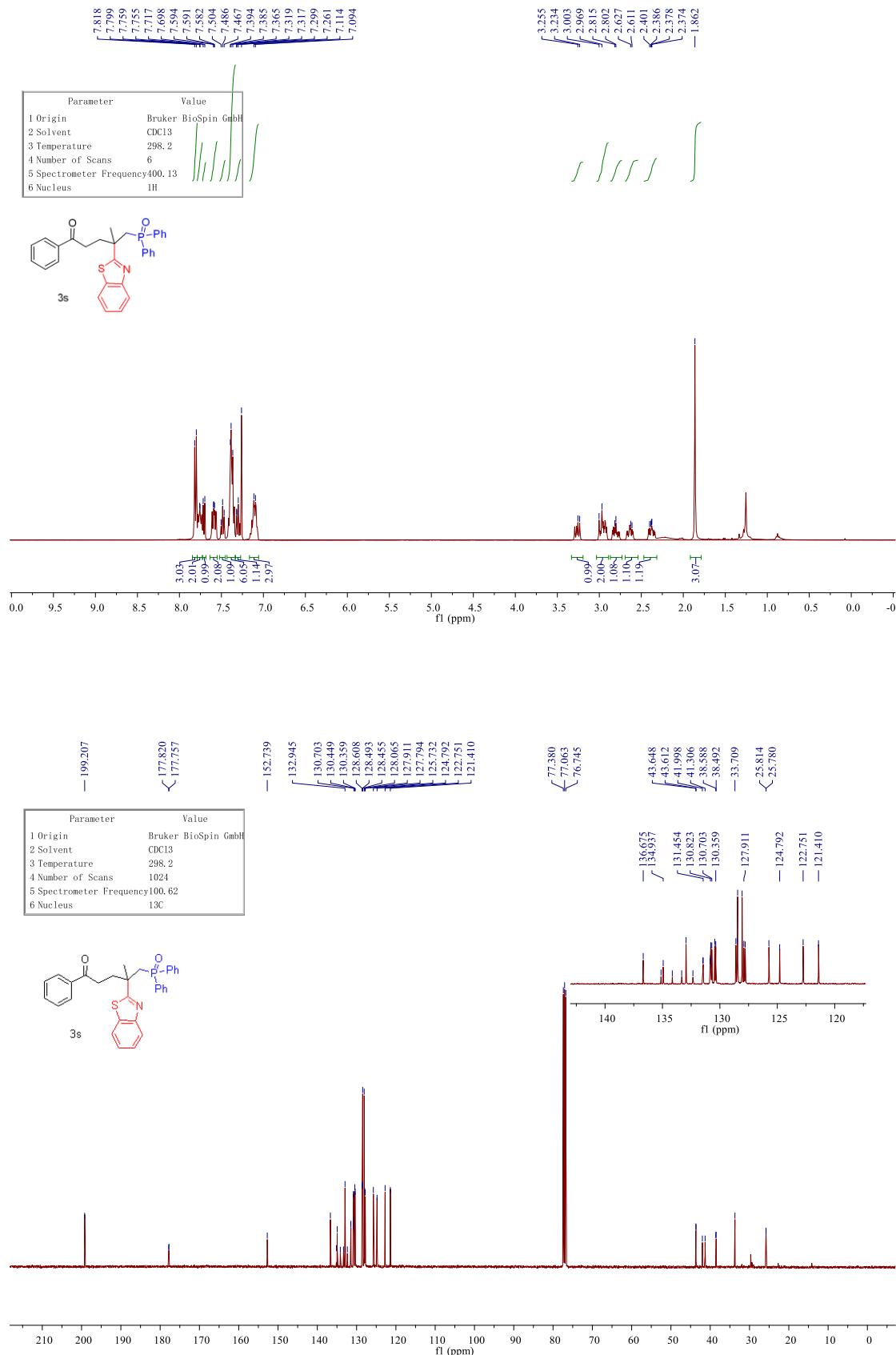


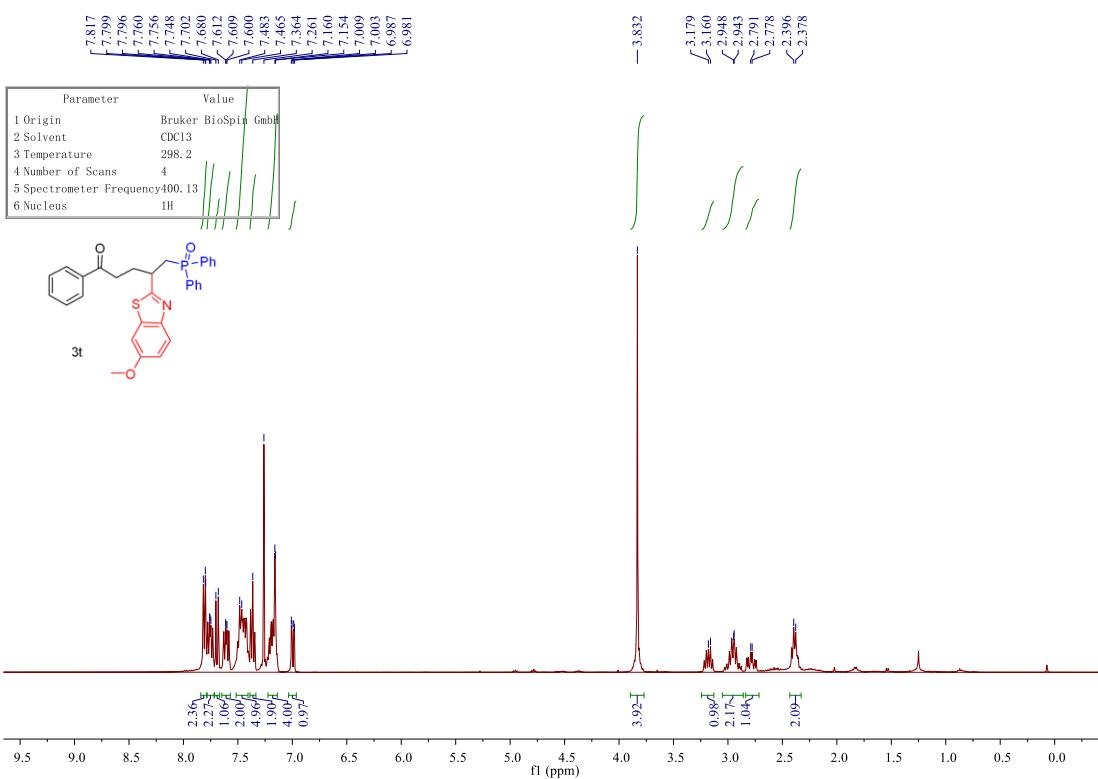
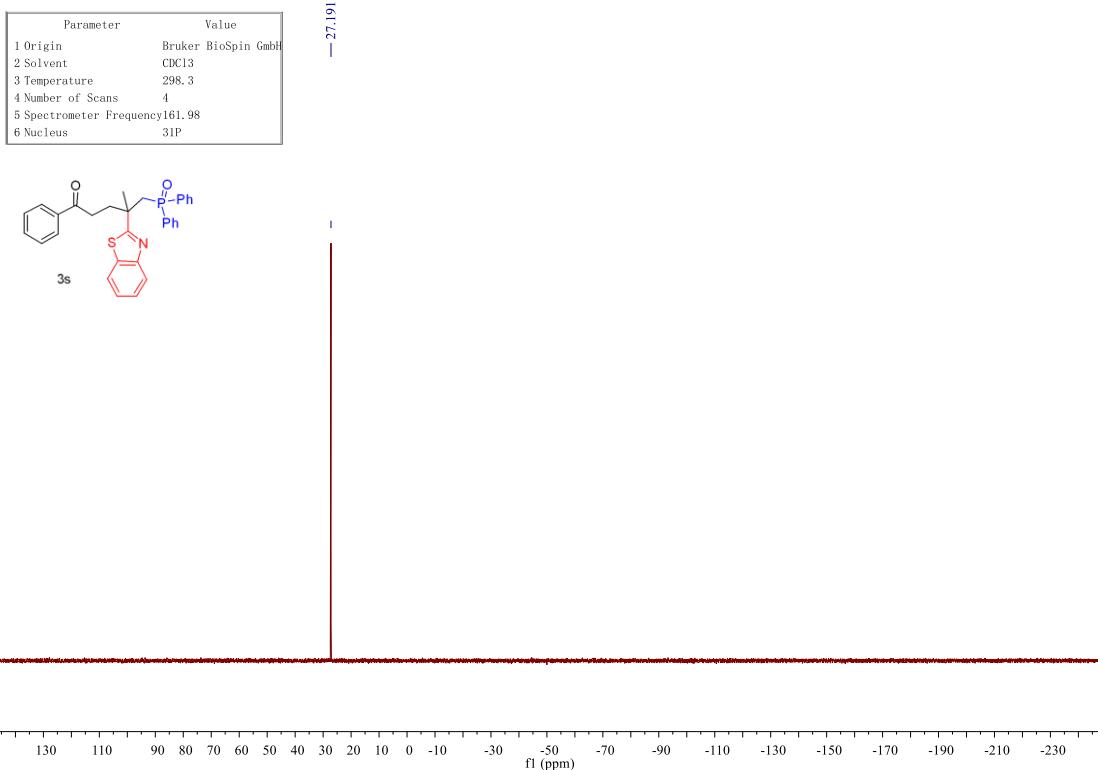


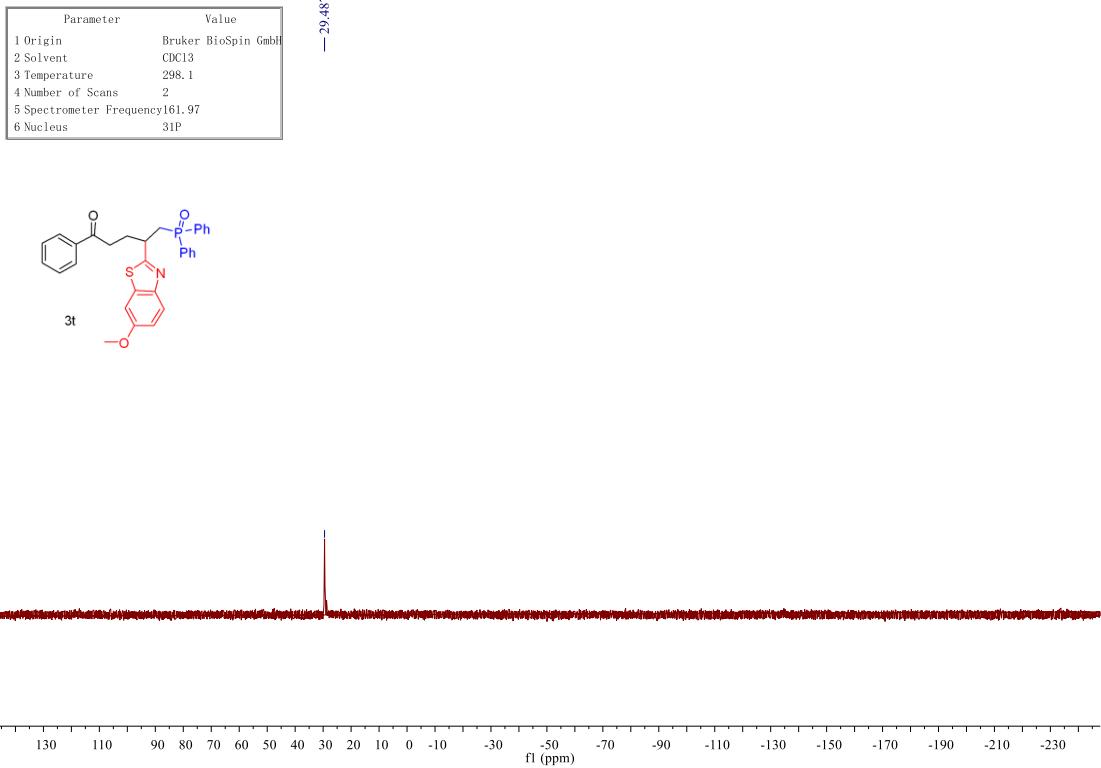
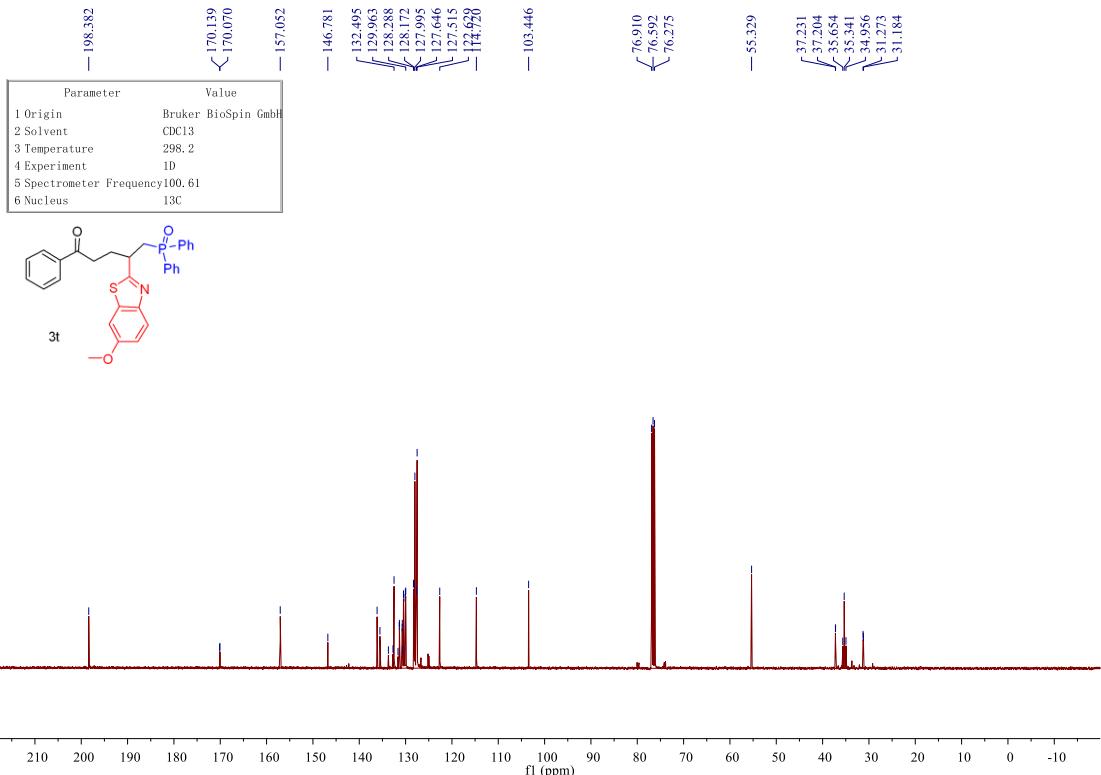


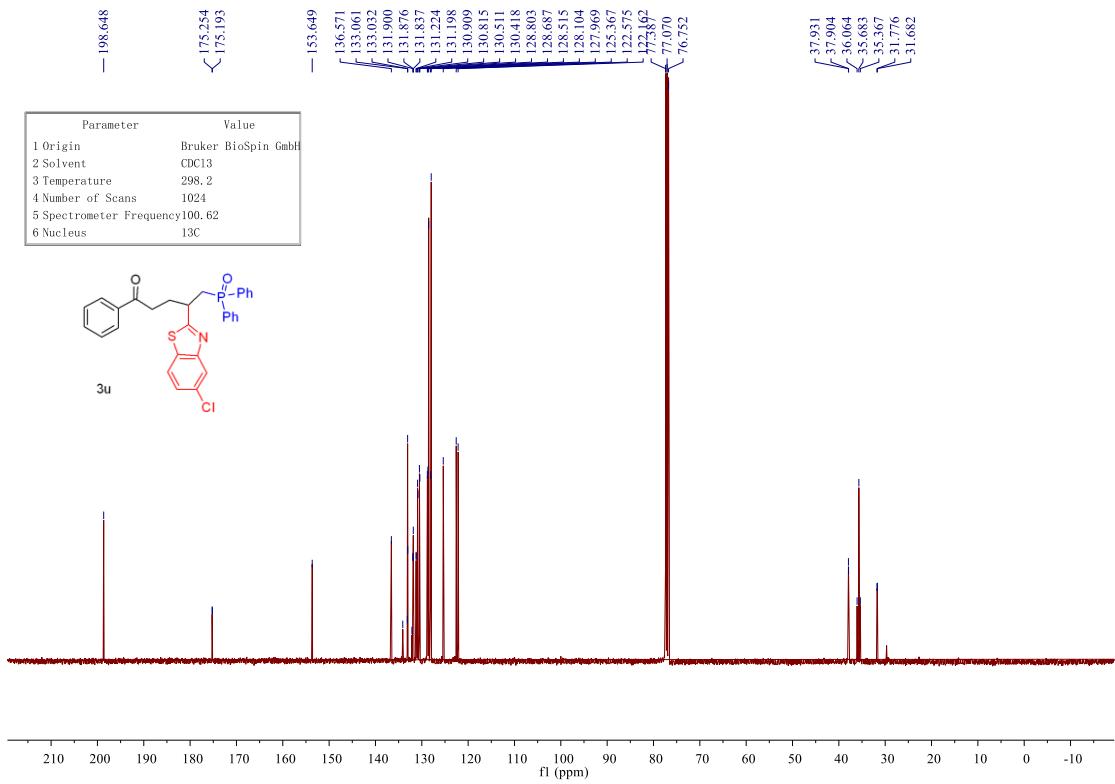
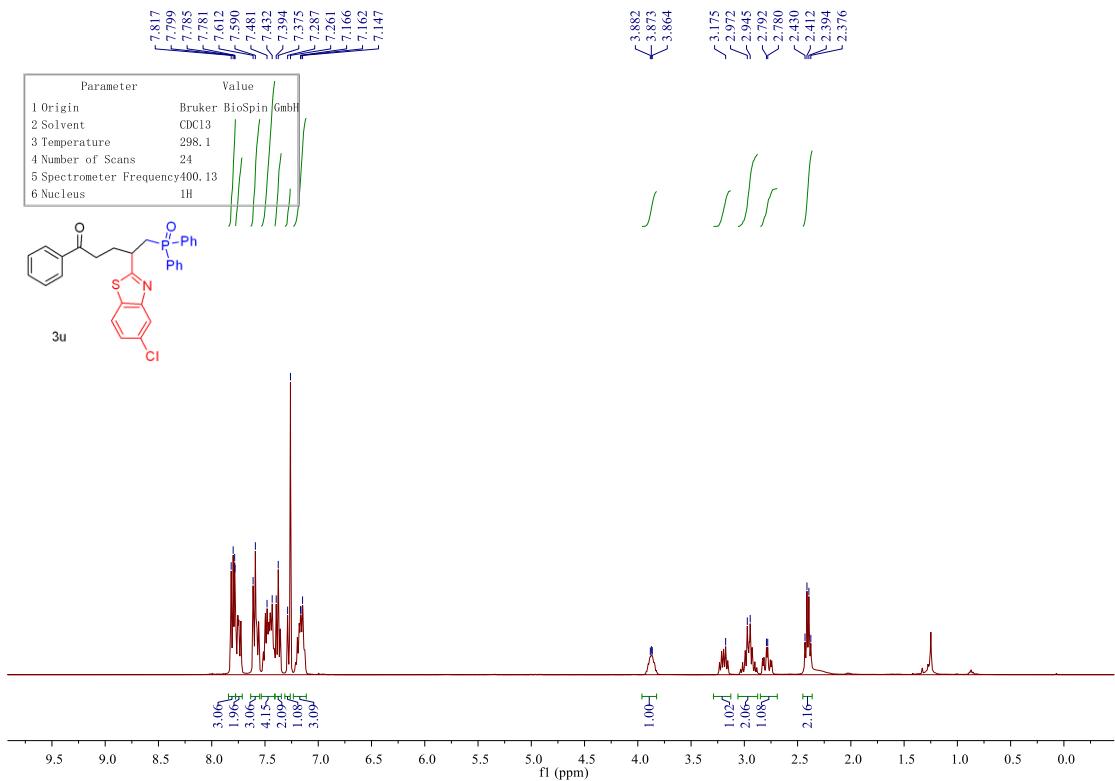


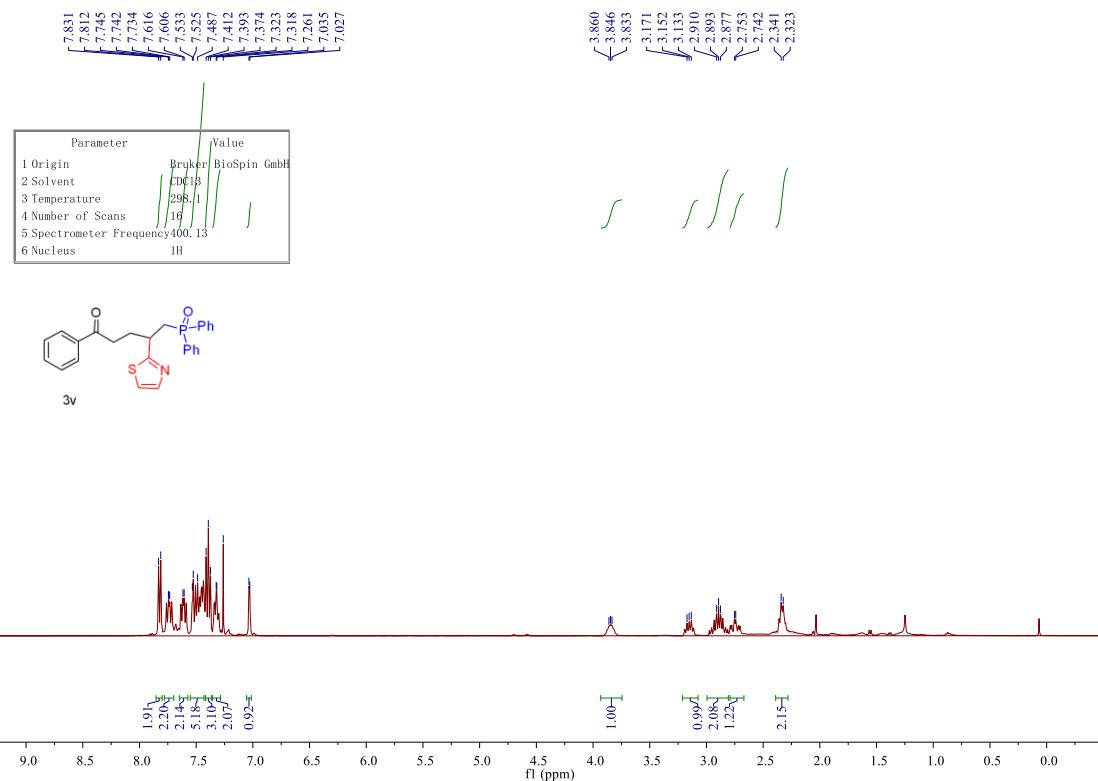
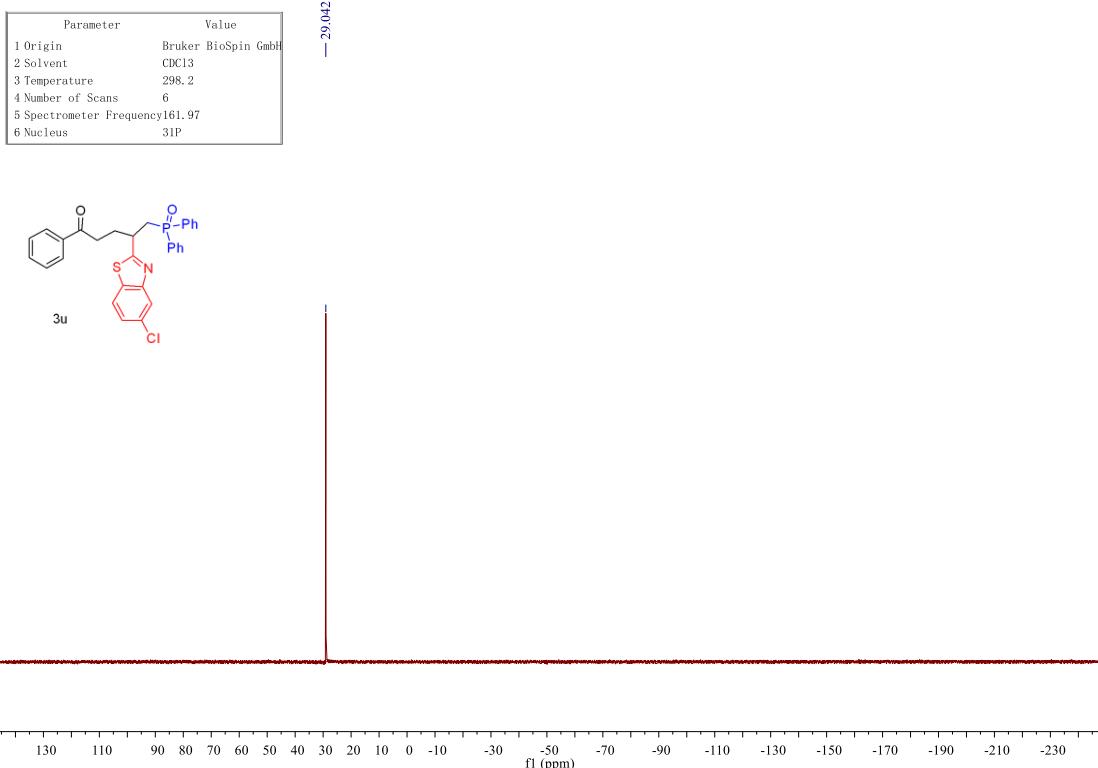


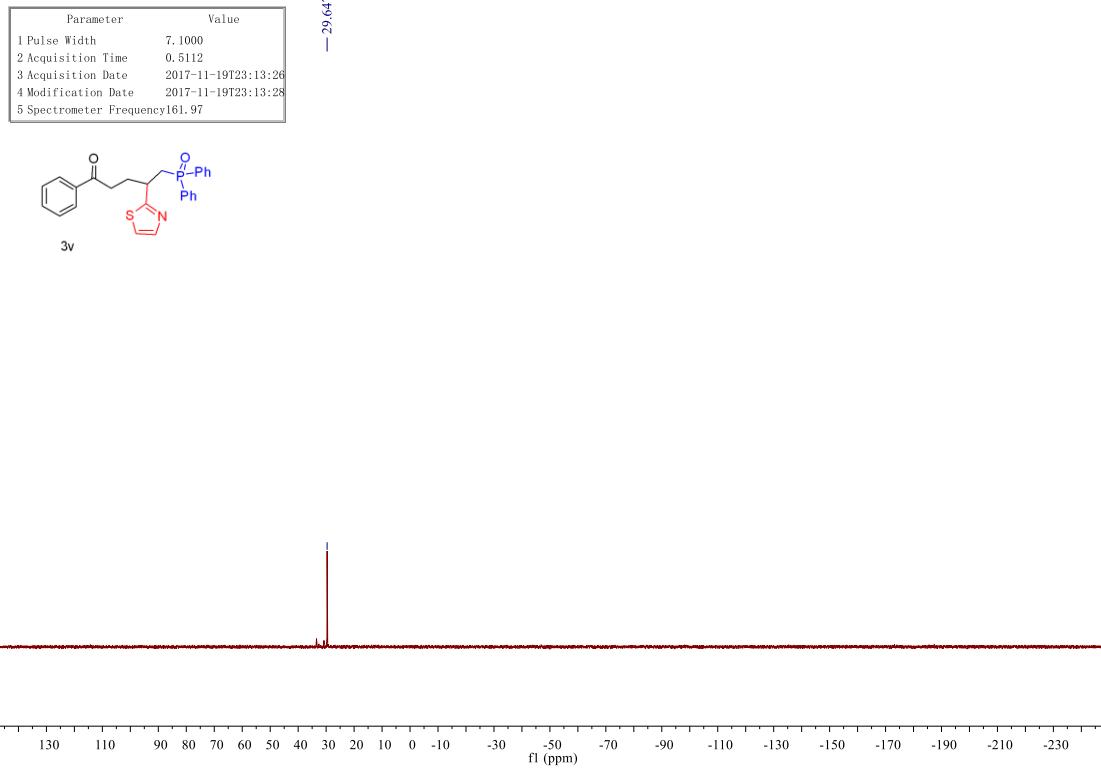
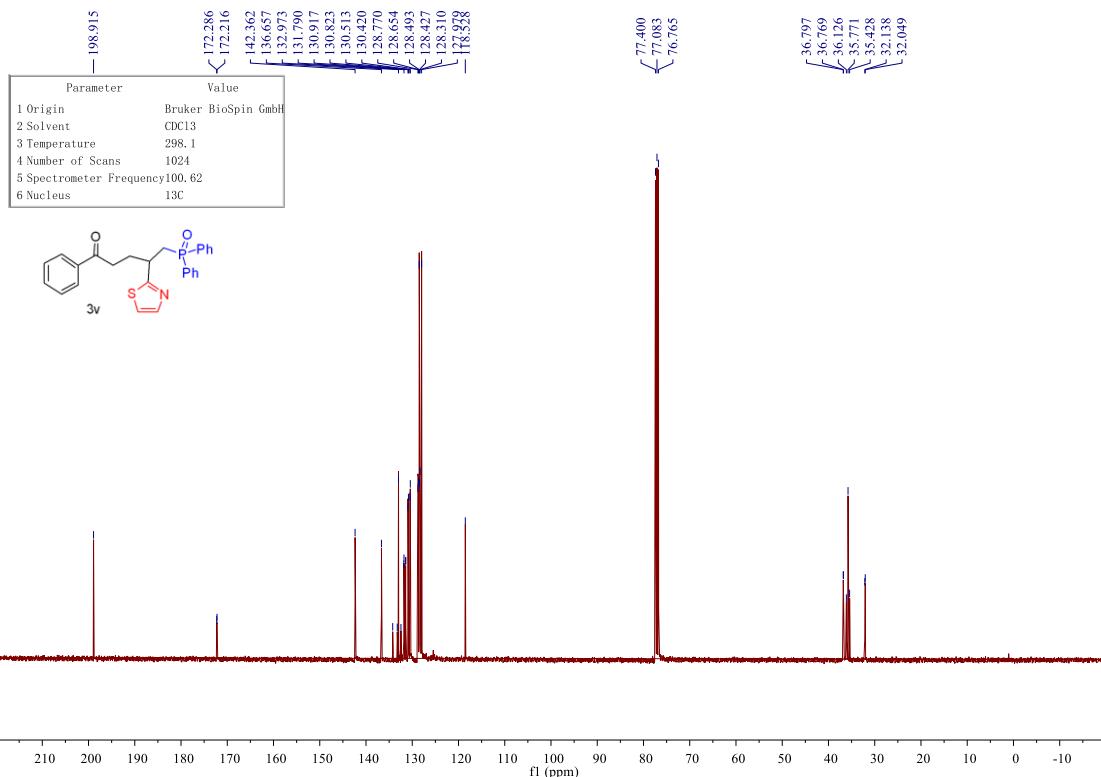


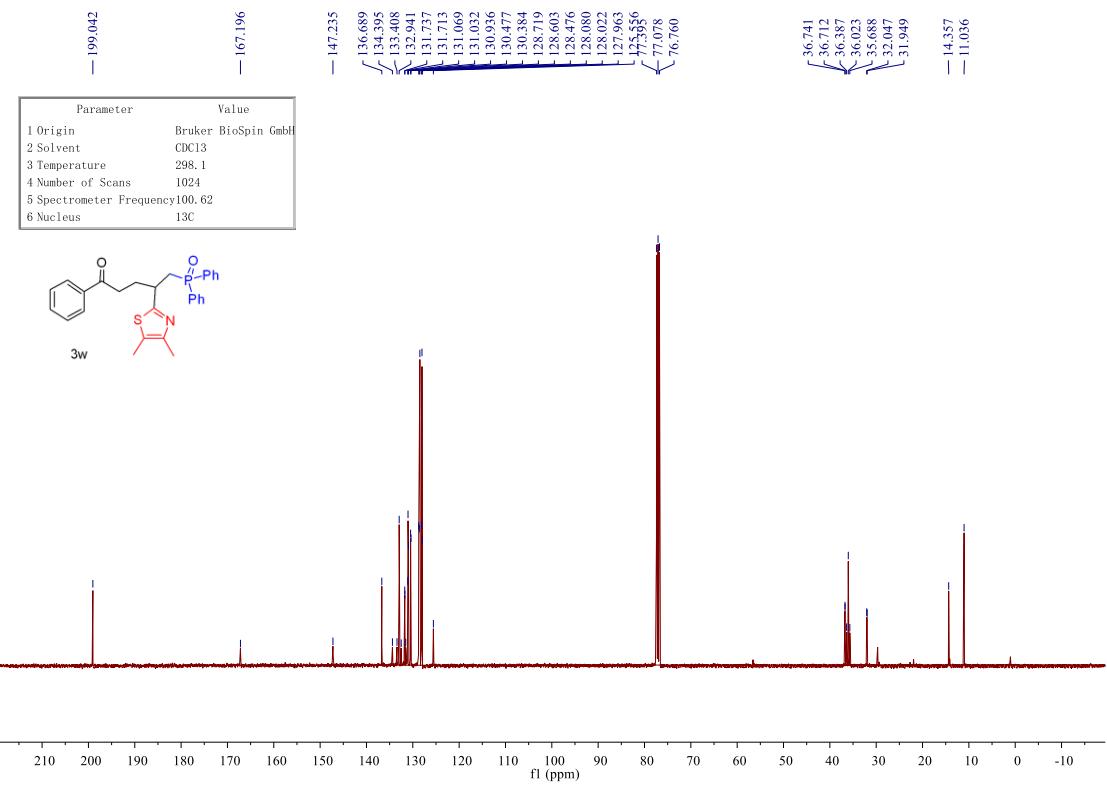
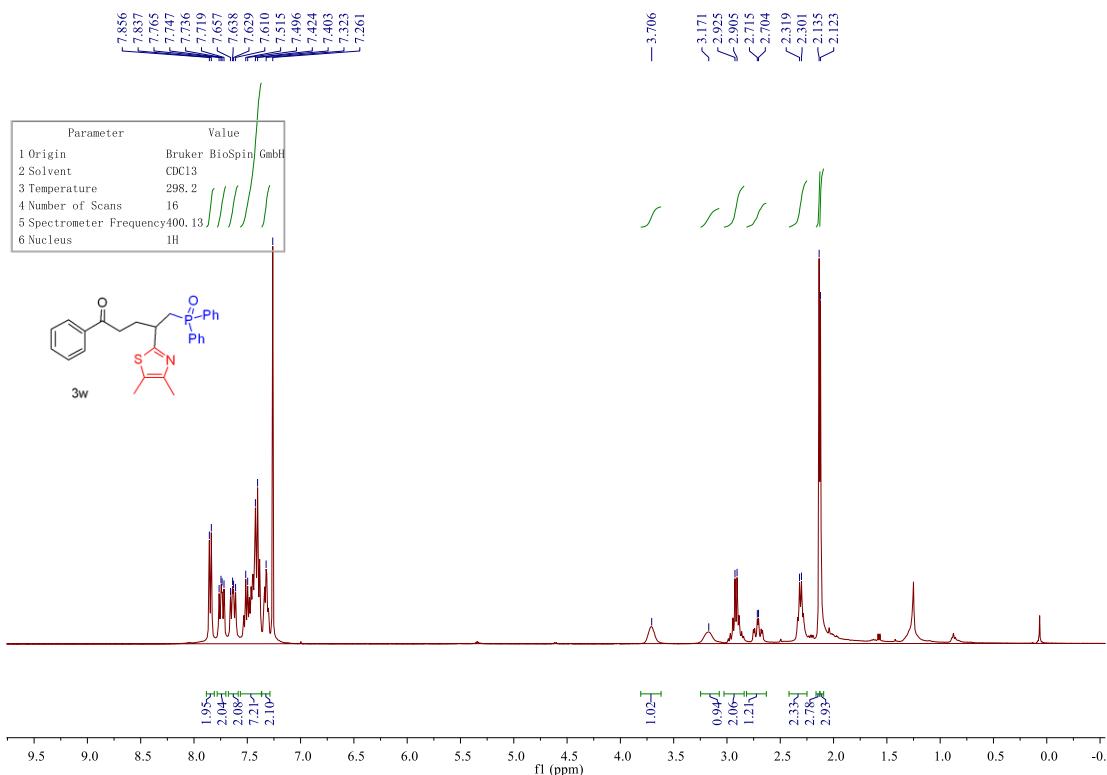


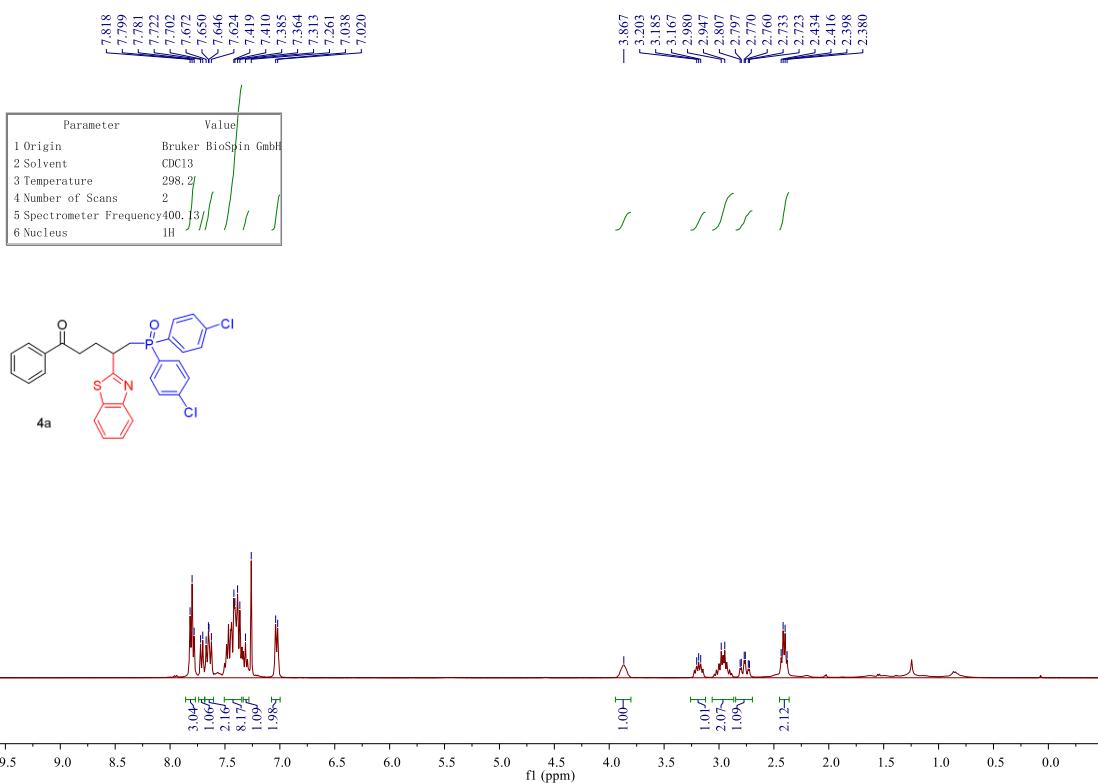
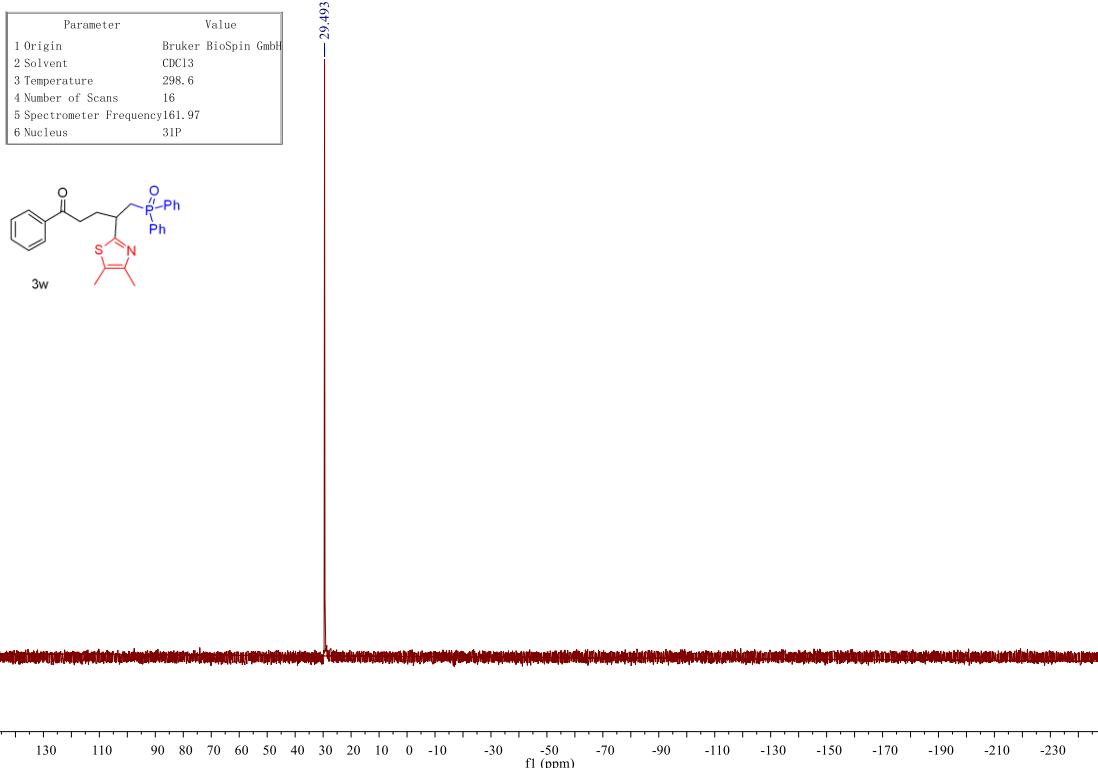


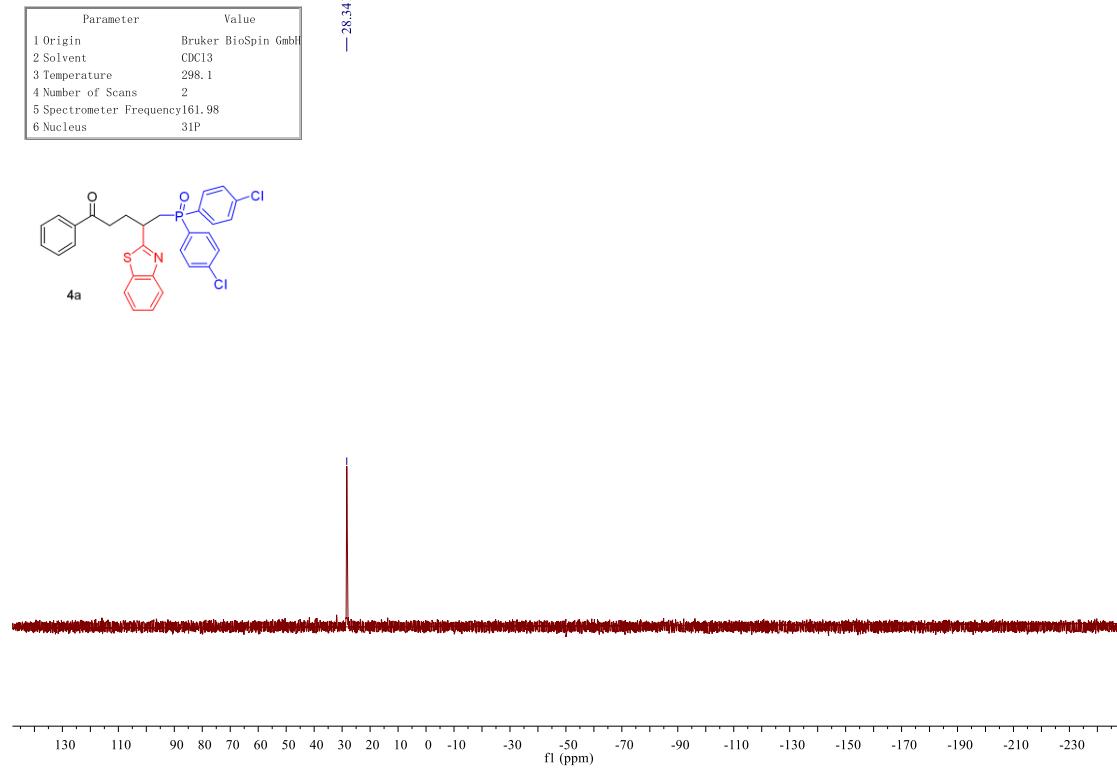
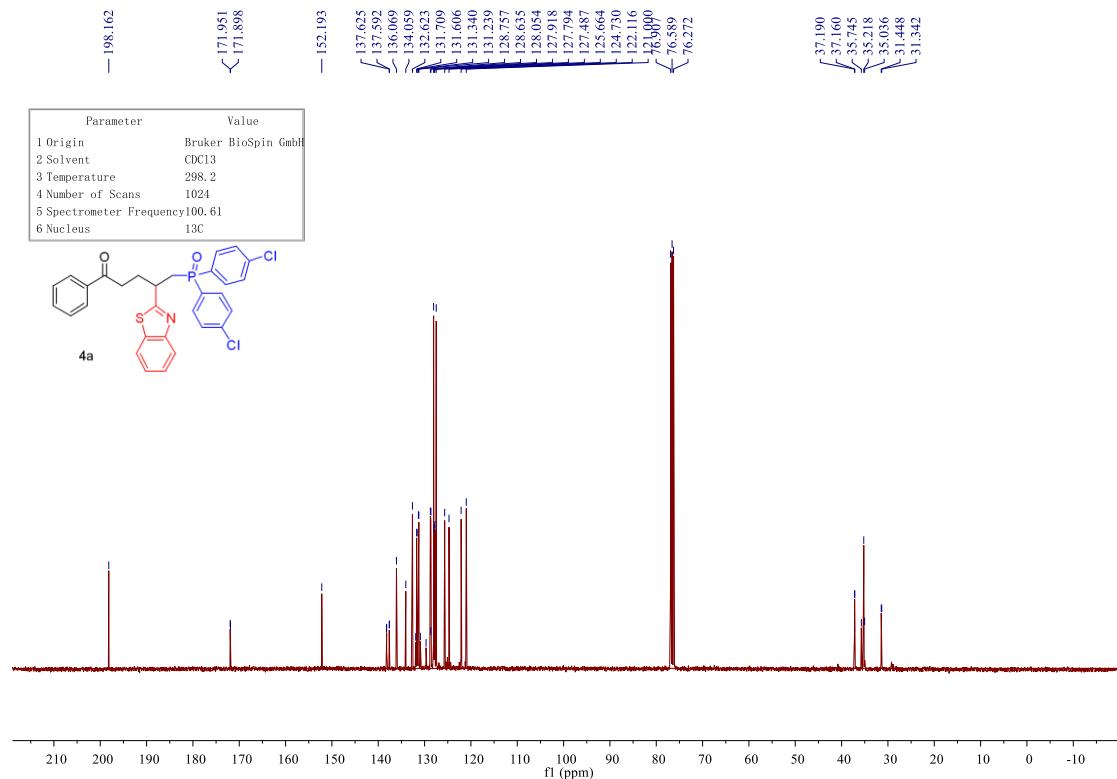


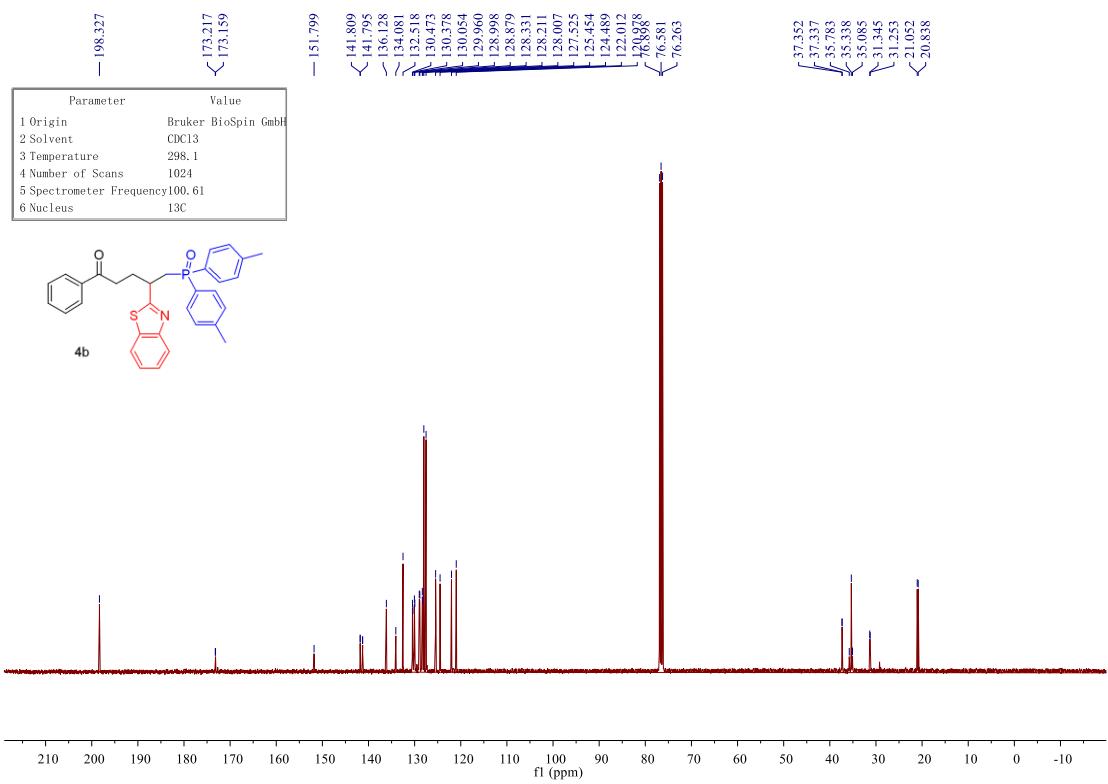
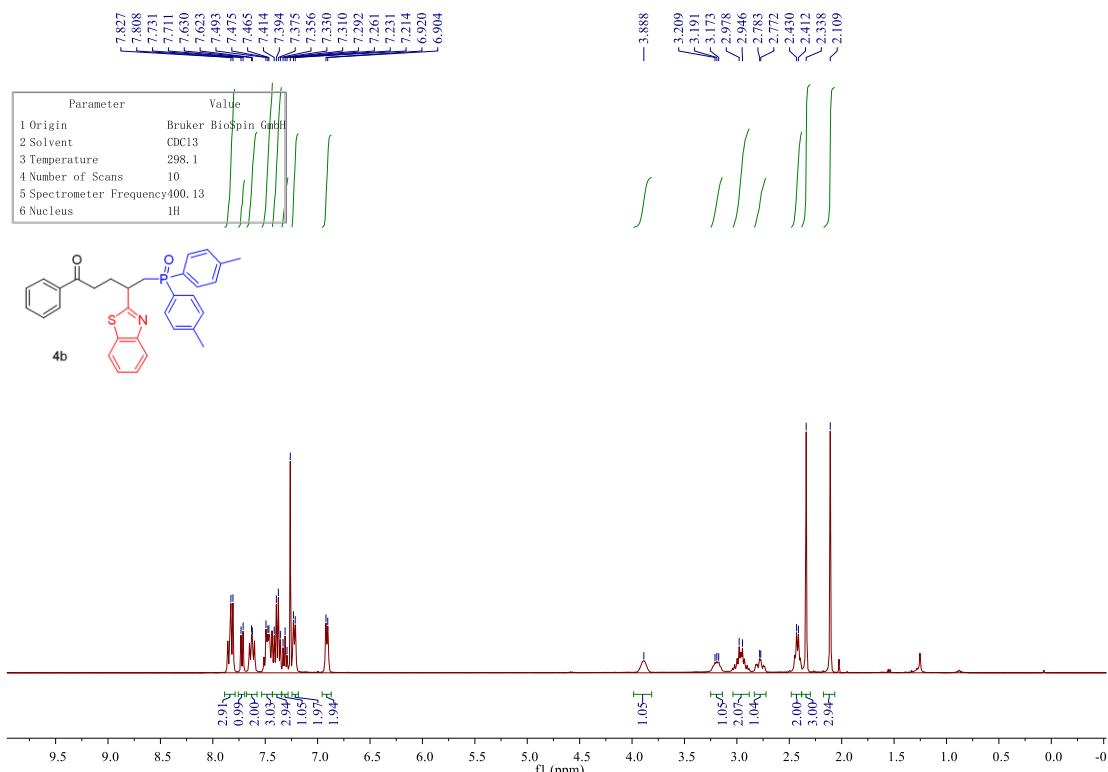






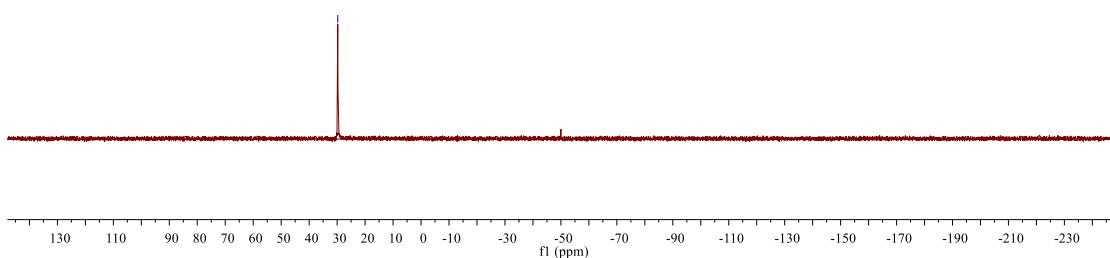
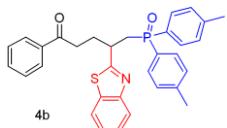




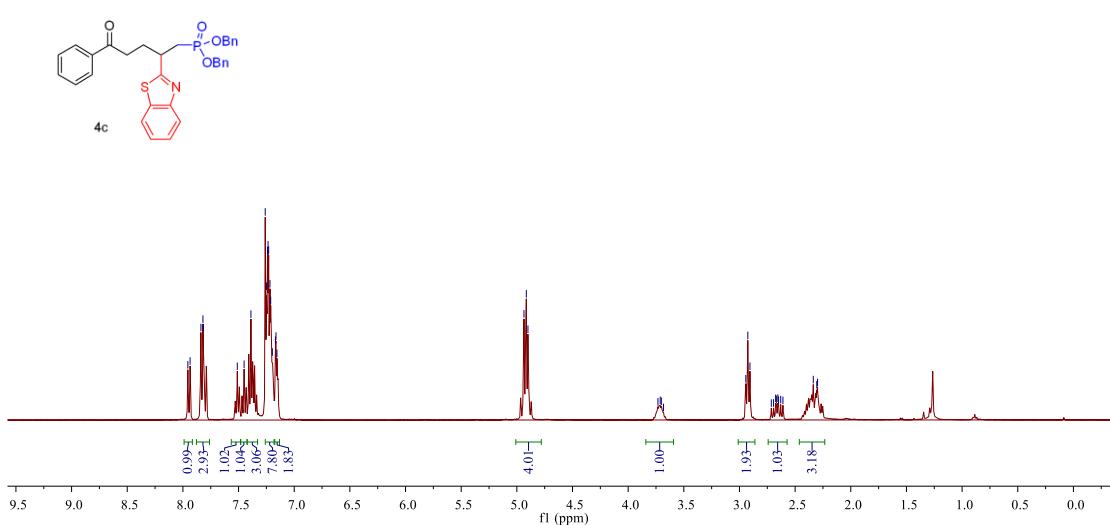
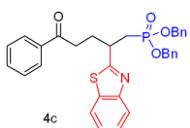


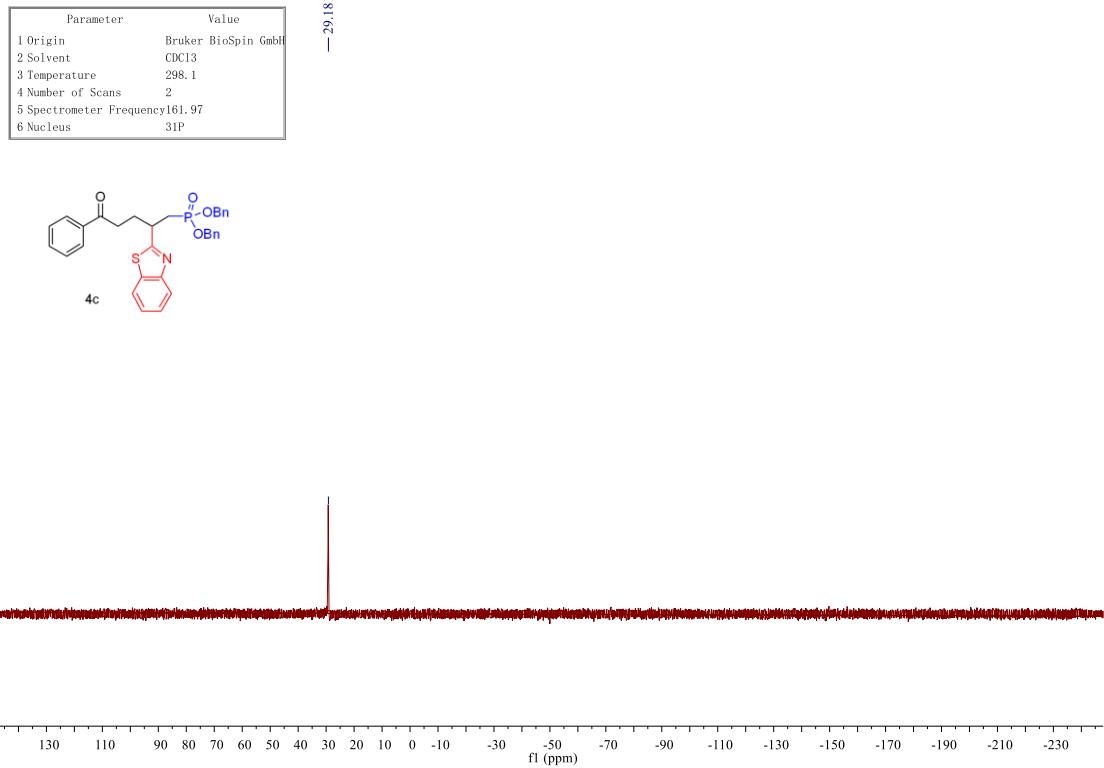
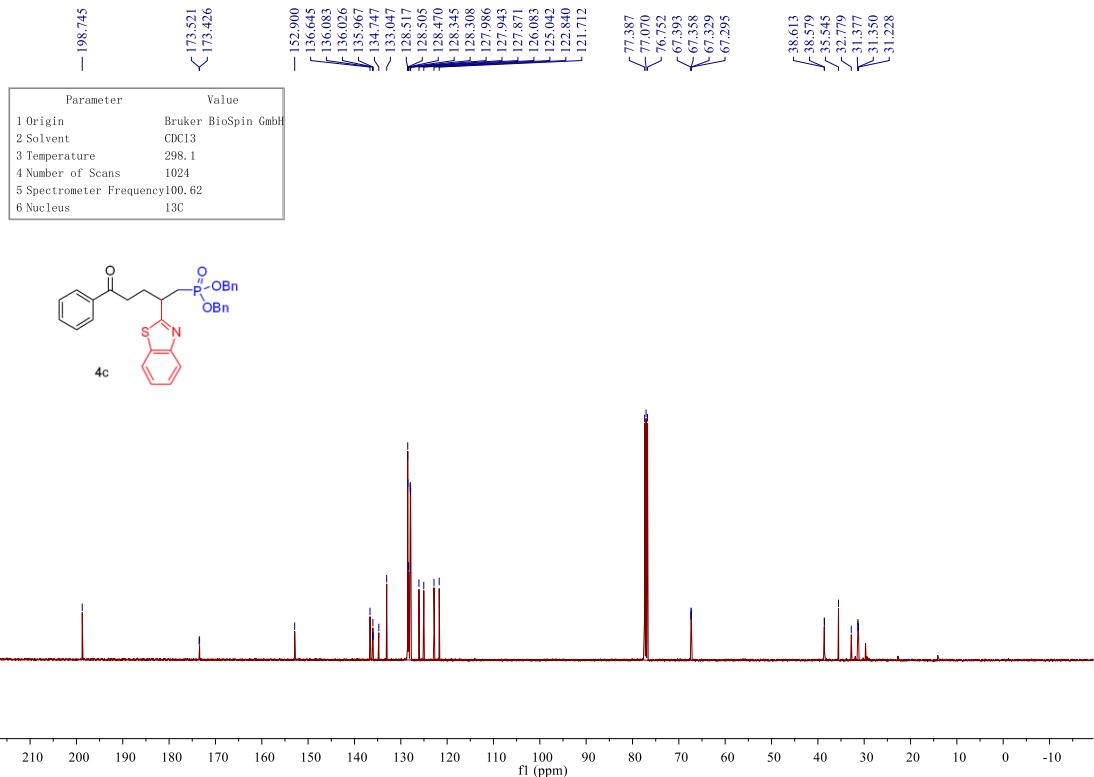
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl ₃
3 Temperature	298.2
4 Number of Scans	6
5 Spectrometer Frequency	161.97
6 Nucleus	31P

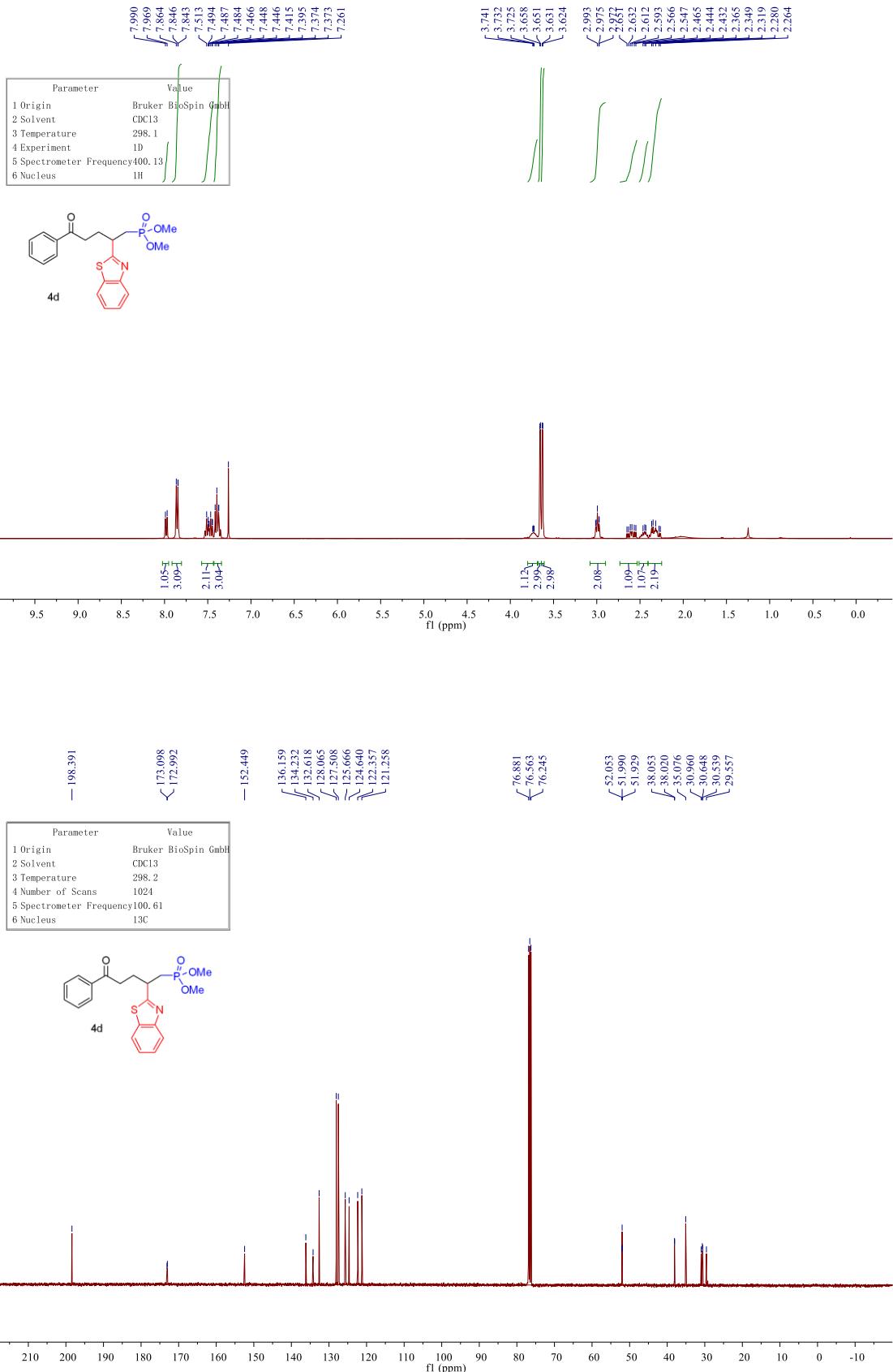
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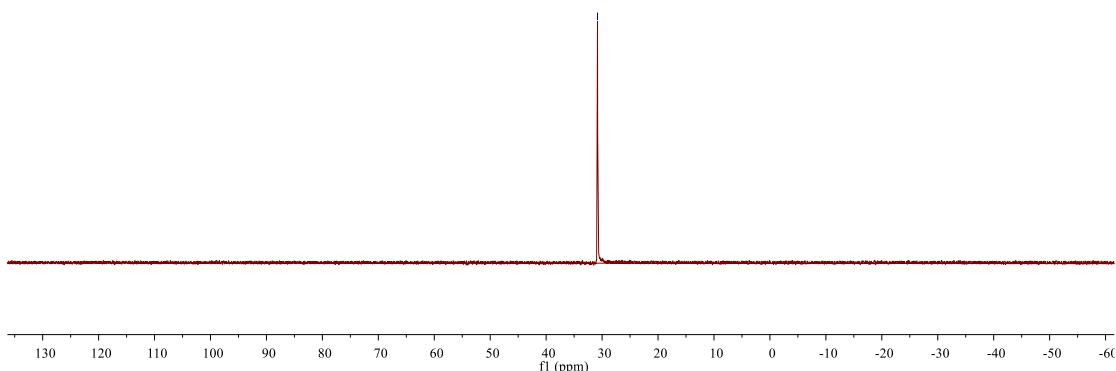
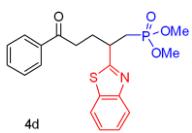
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl ₃
3 Temperature	298.2
4 Number of Scans	2
5 Spectrometer Frequency	400.13
6 Nucleus	1H



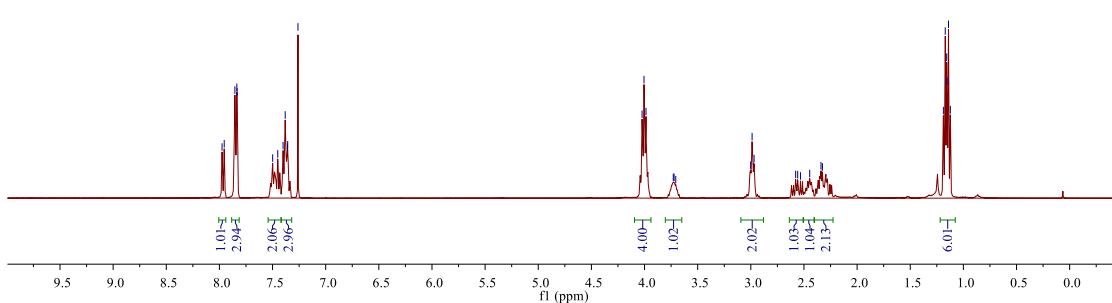
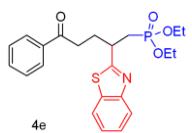


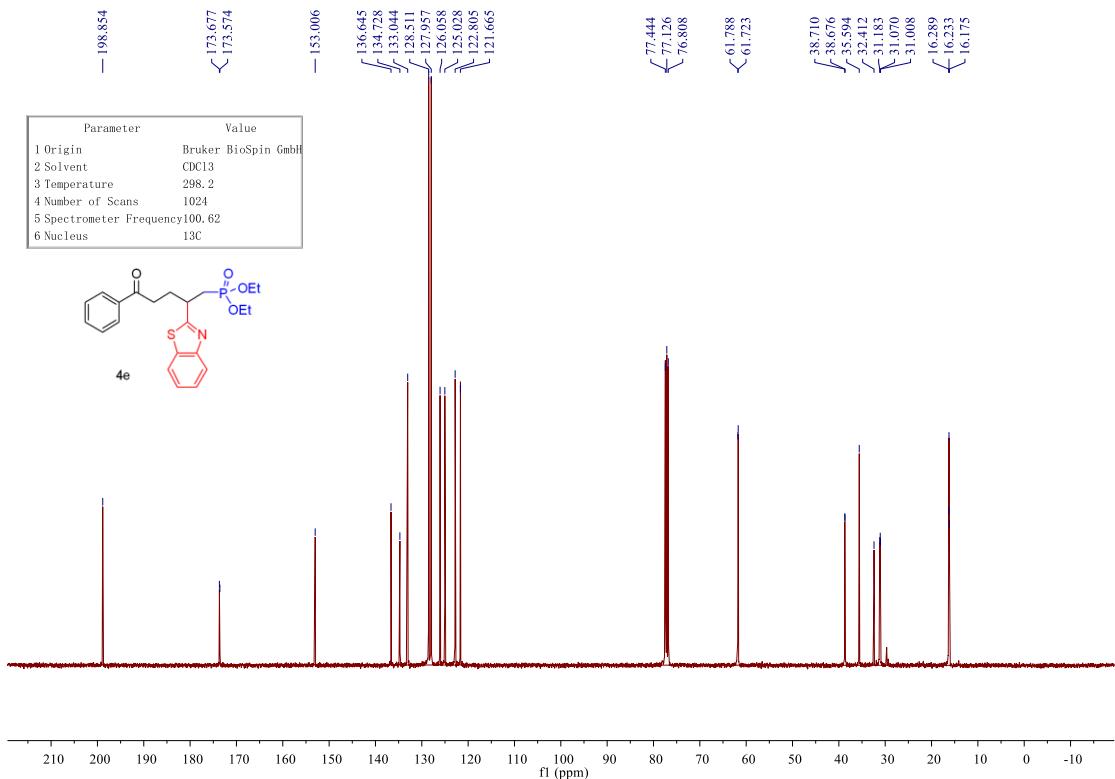


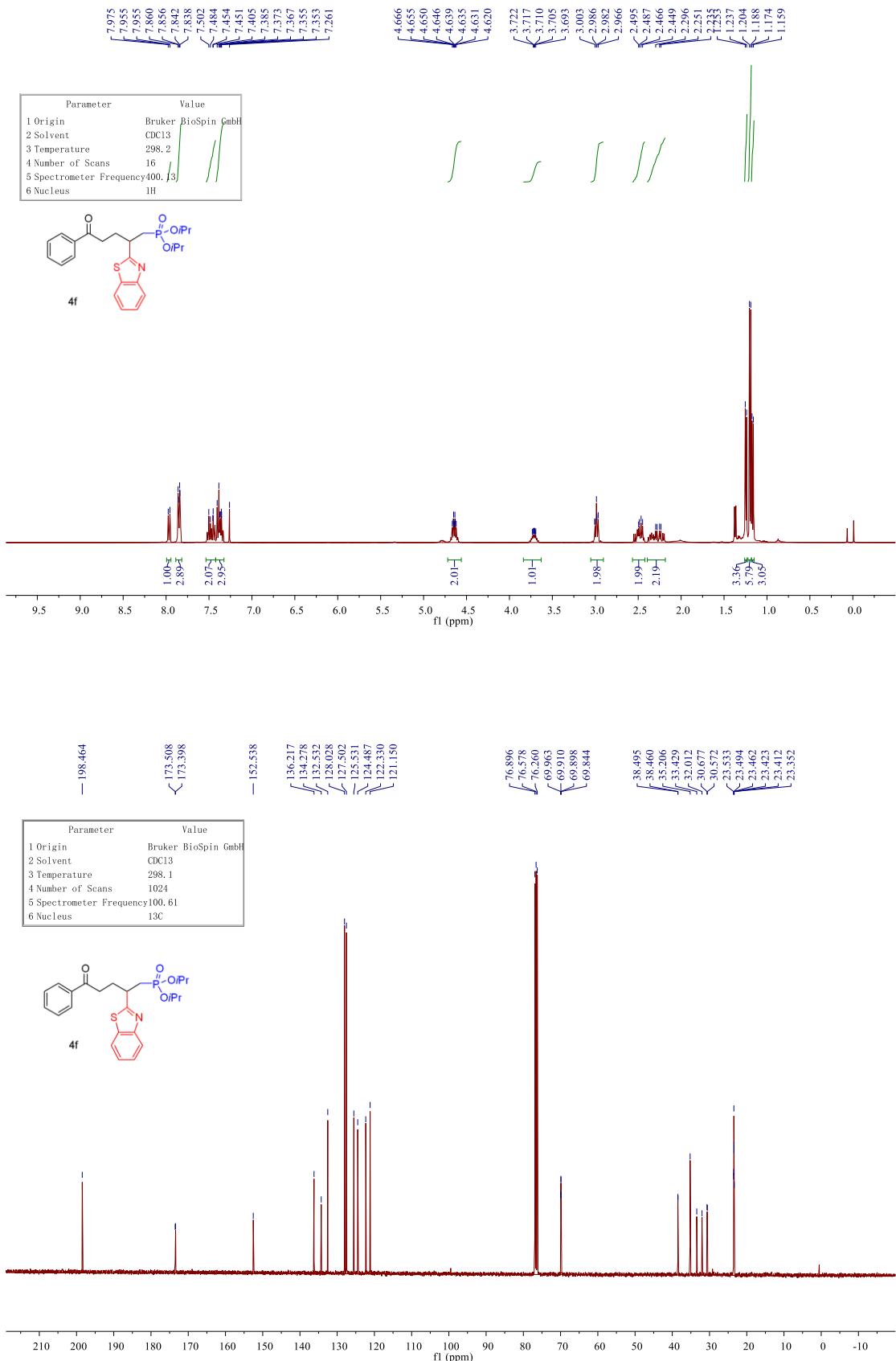
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl ₃
3 Temperature	298.4
4 Number of Scans	16
5 Spectrometer Frequency	161.97
6 Nucleus	31P

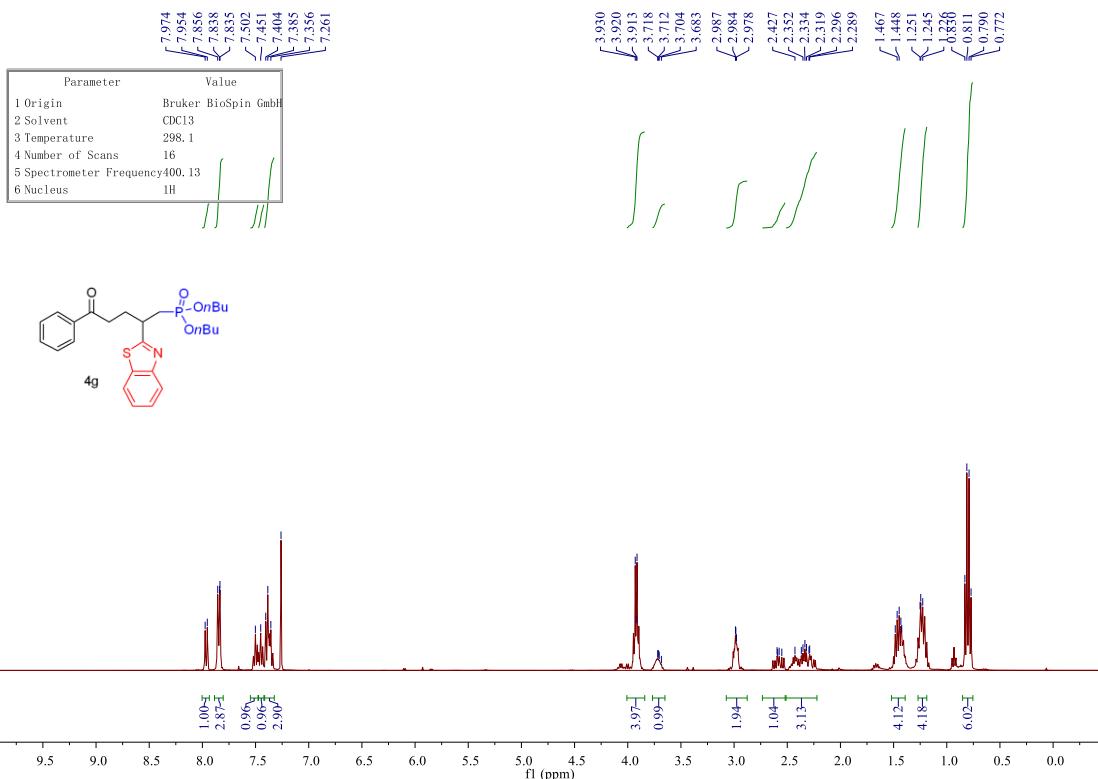
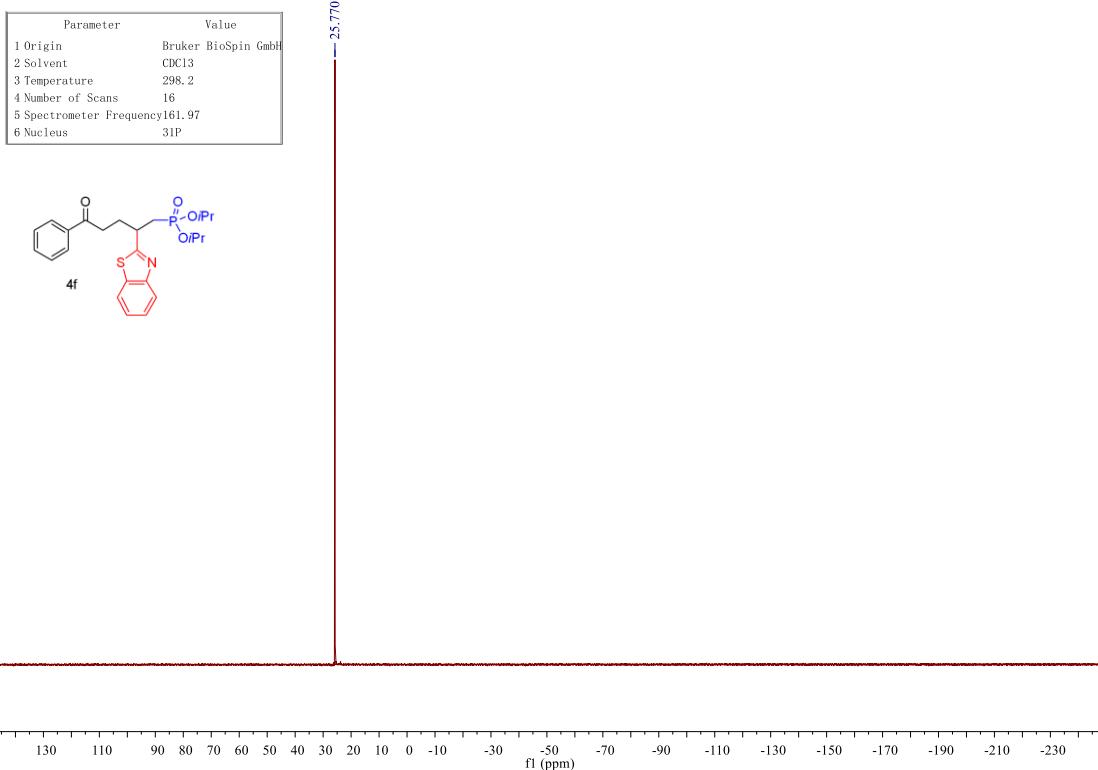


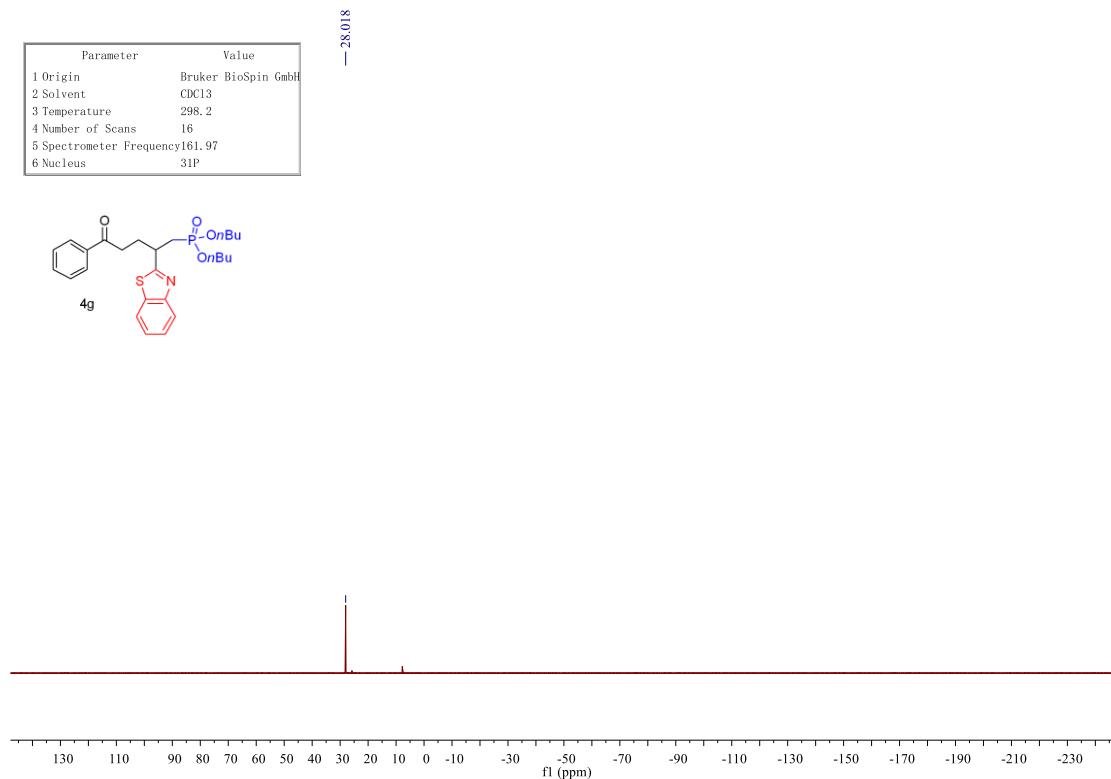
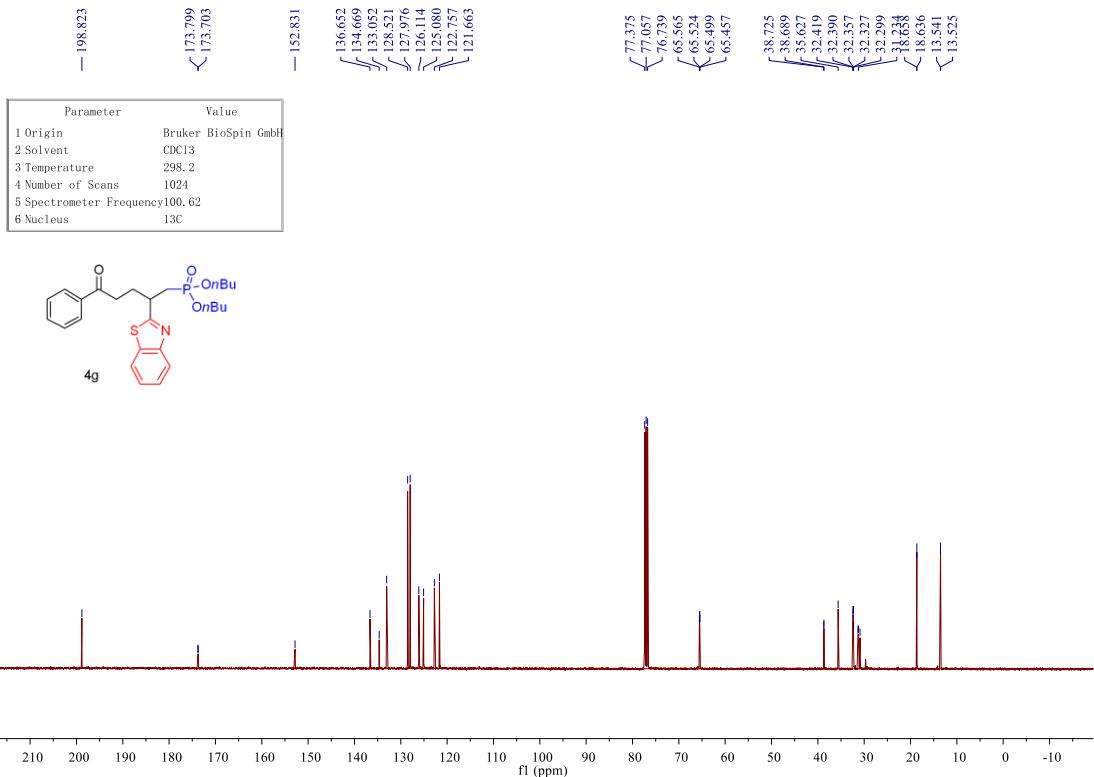
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl ₃
3 Temperature	298.1
4 Number of Scans	2
5 Spectrometer Frequency	400.13
6 Nucleus	1H

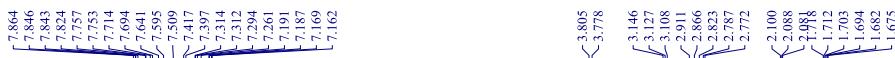




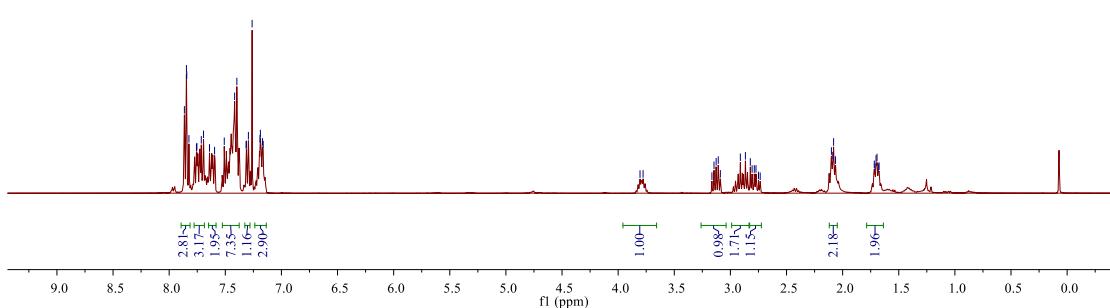
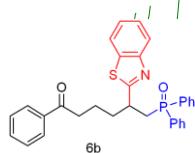




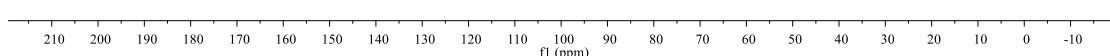
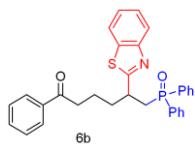


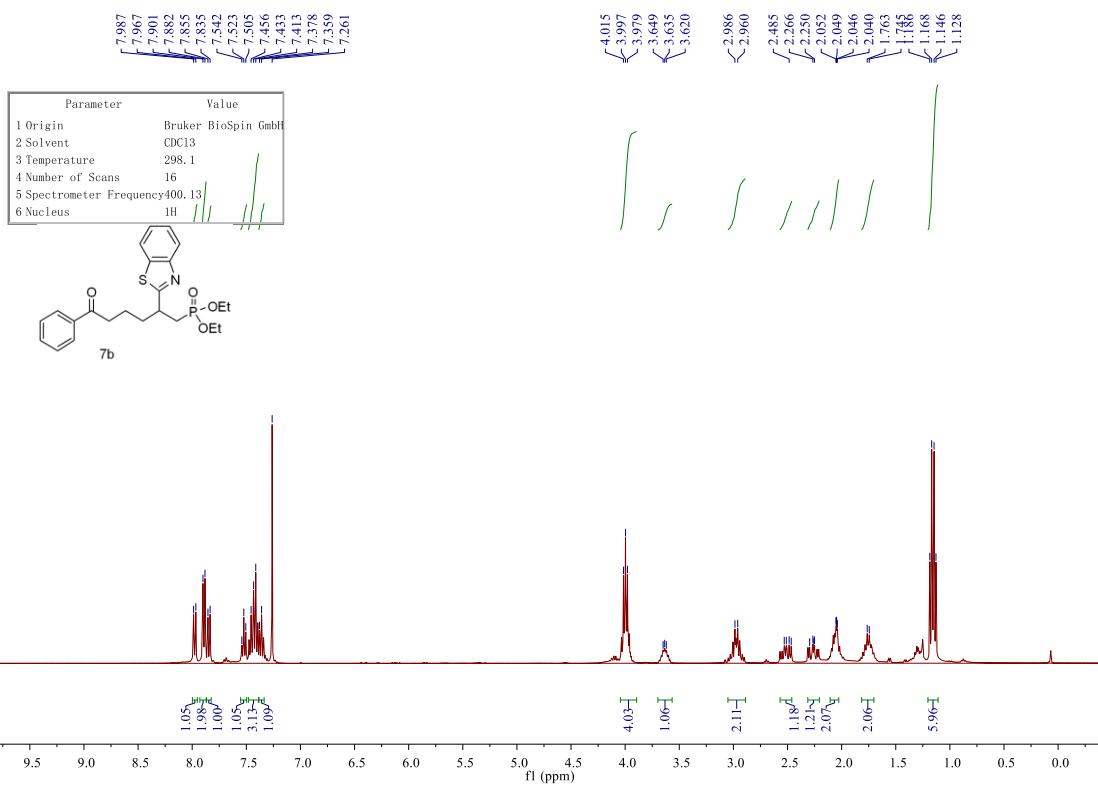
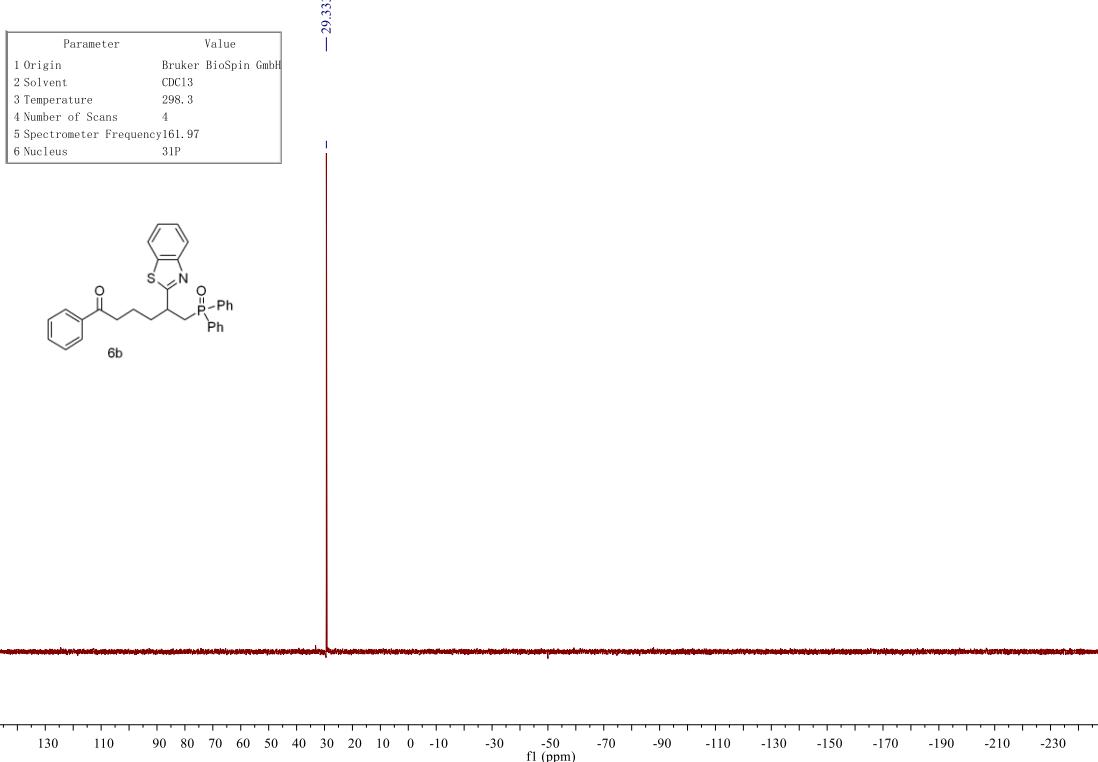


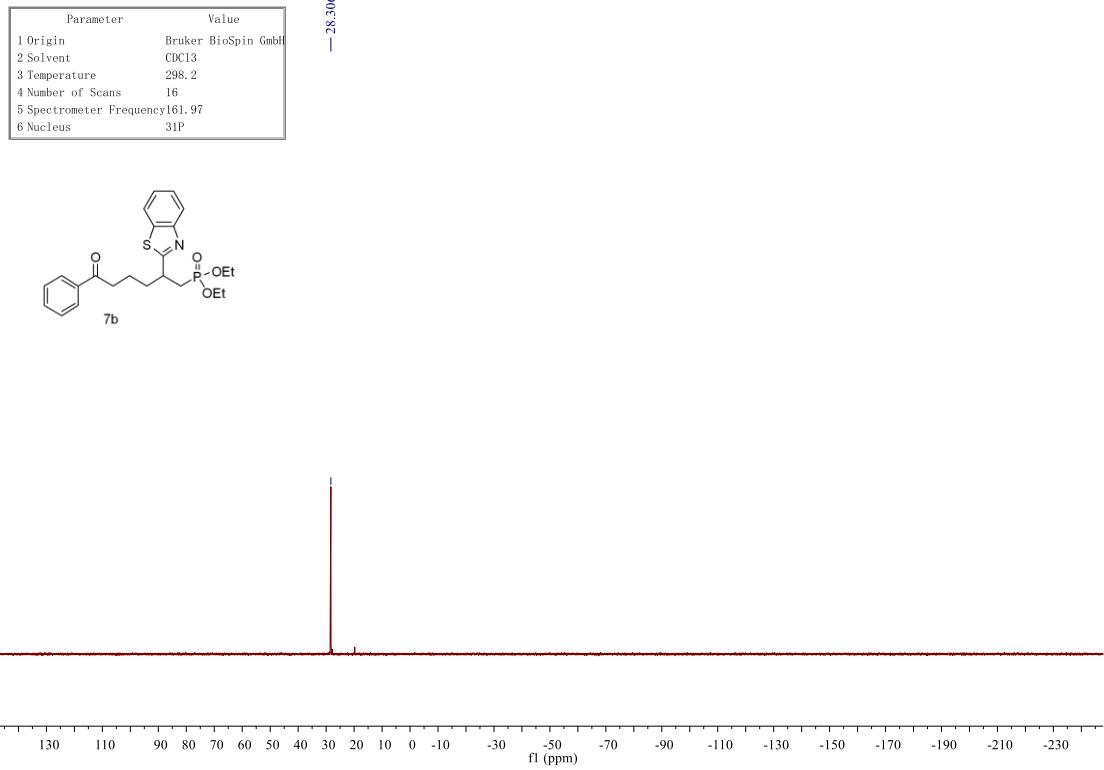
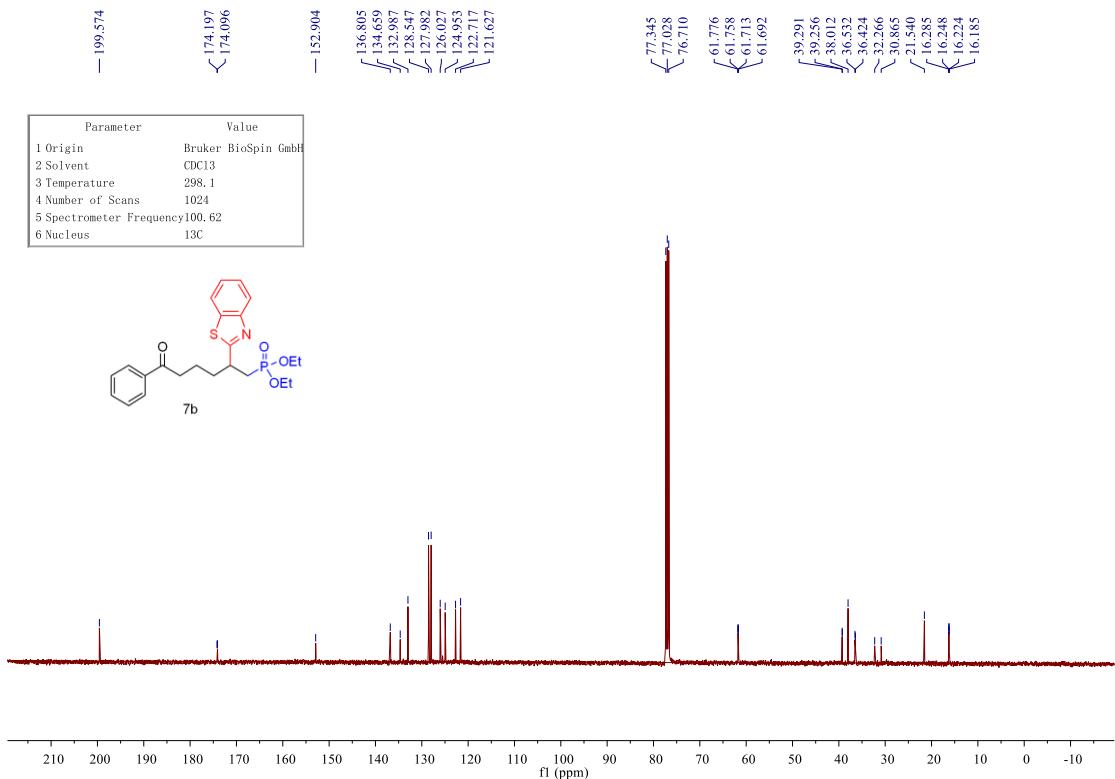
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl ₃
3 Temperature	298.2
4 Number of Scans	16
5 Spectrometer Frequency	400.13
6 Nucleus	1H

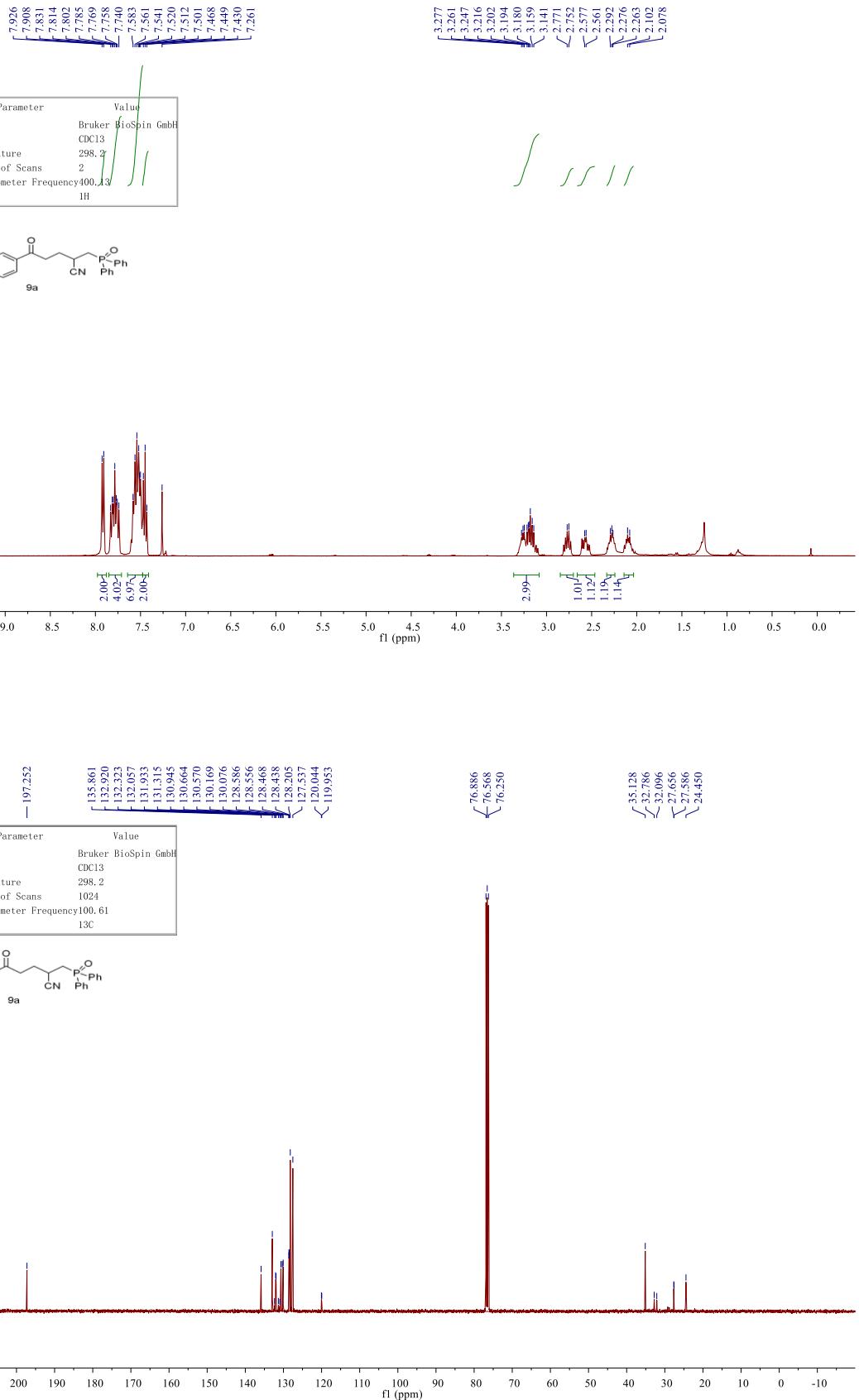


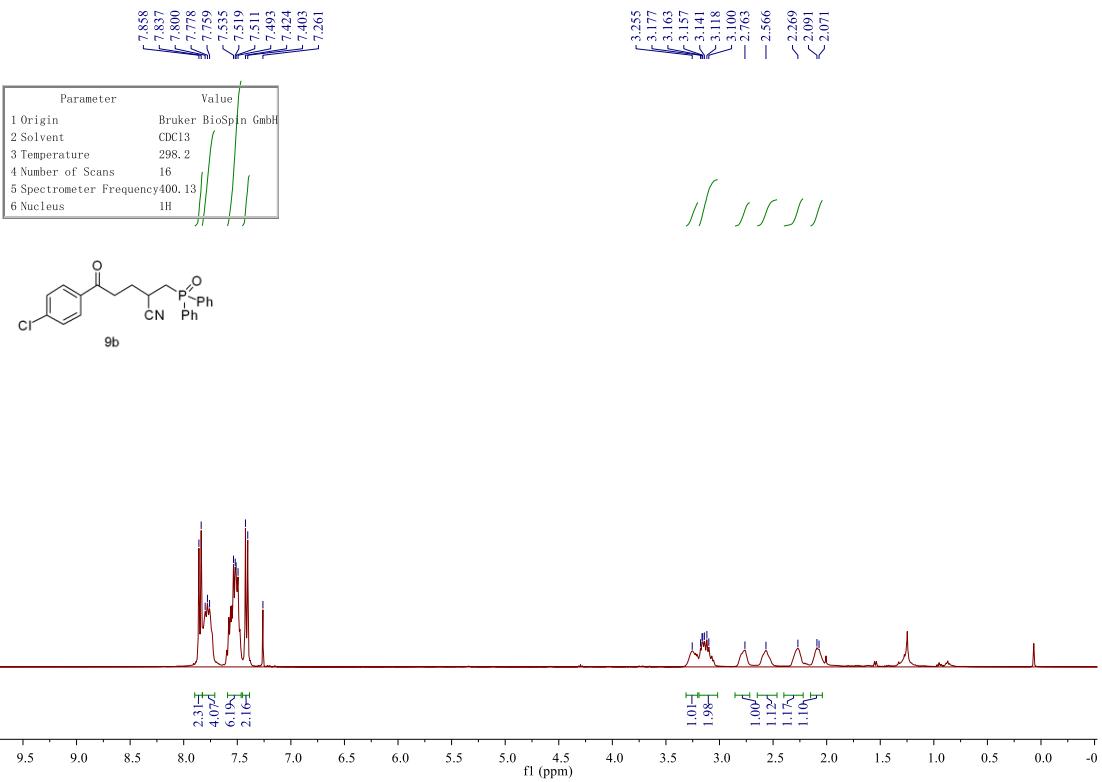
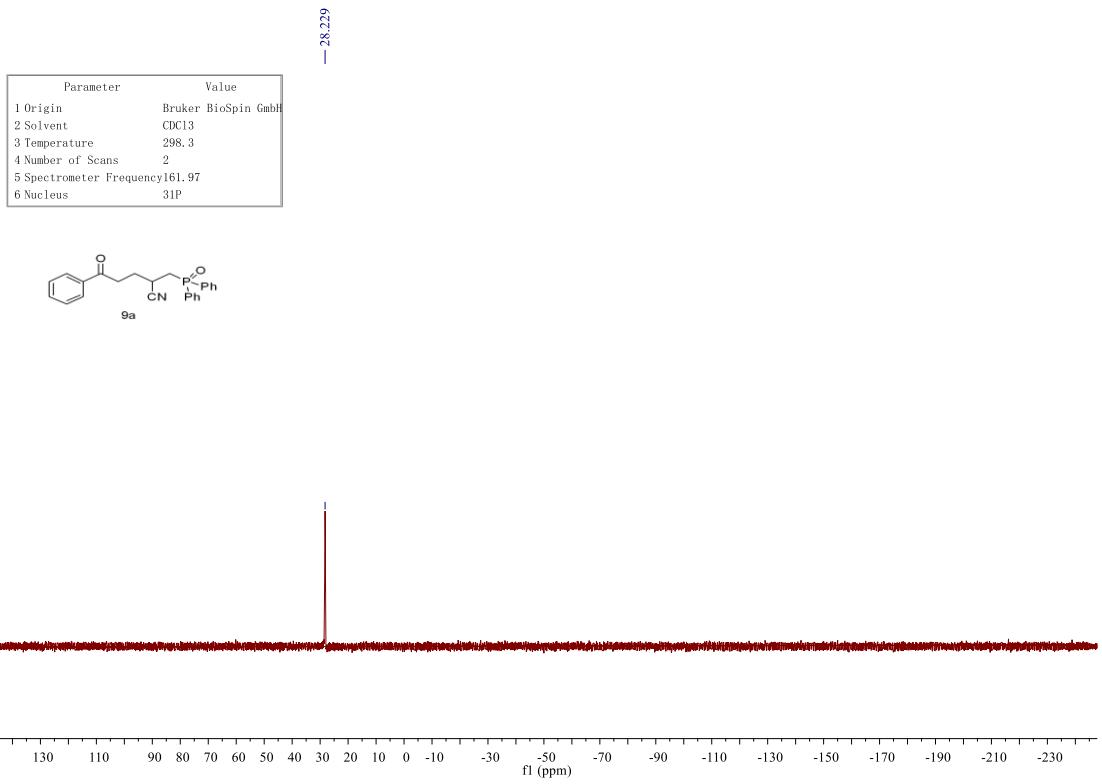
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl ₃
3 Temperature	298.2
4 Number of Scans	1024
5 Spectrometer Frequency	100.62
6 Nucleus	13C

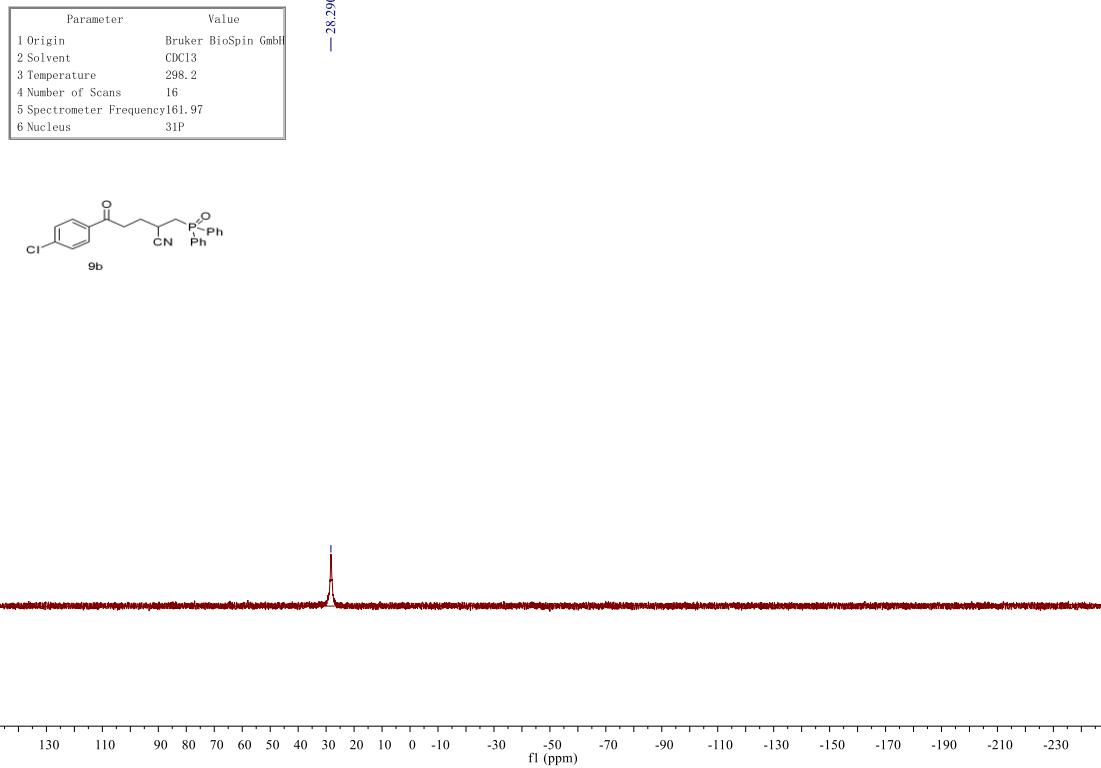
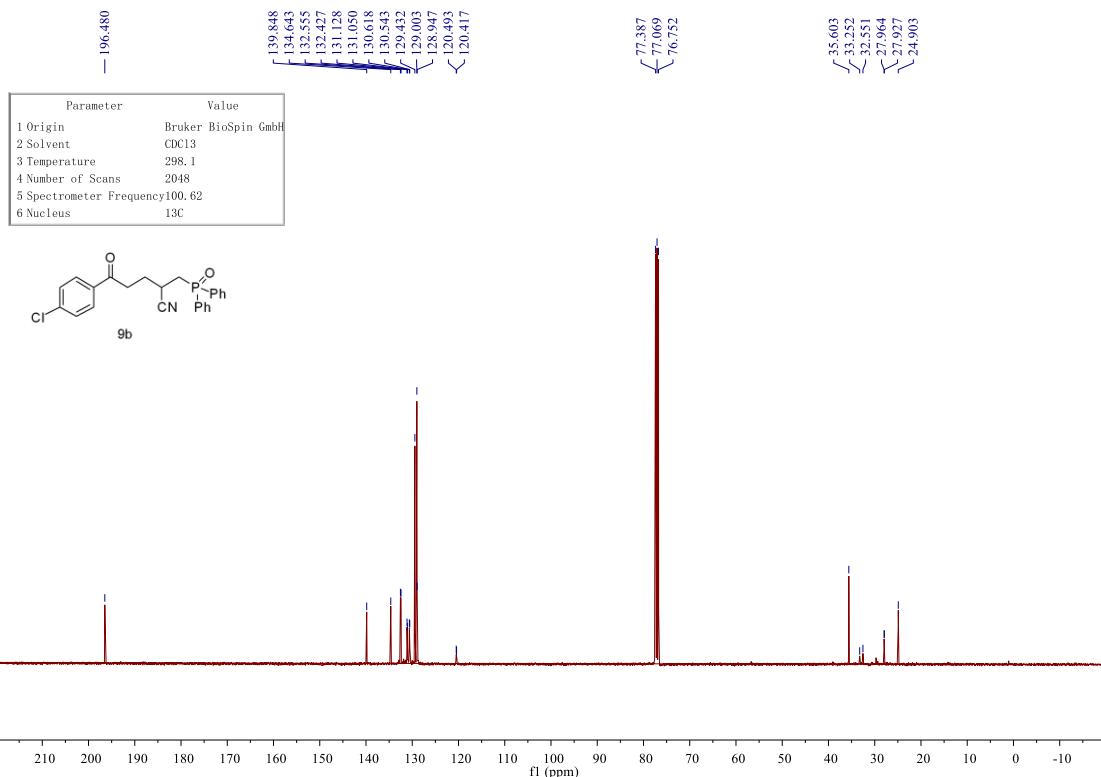


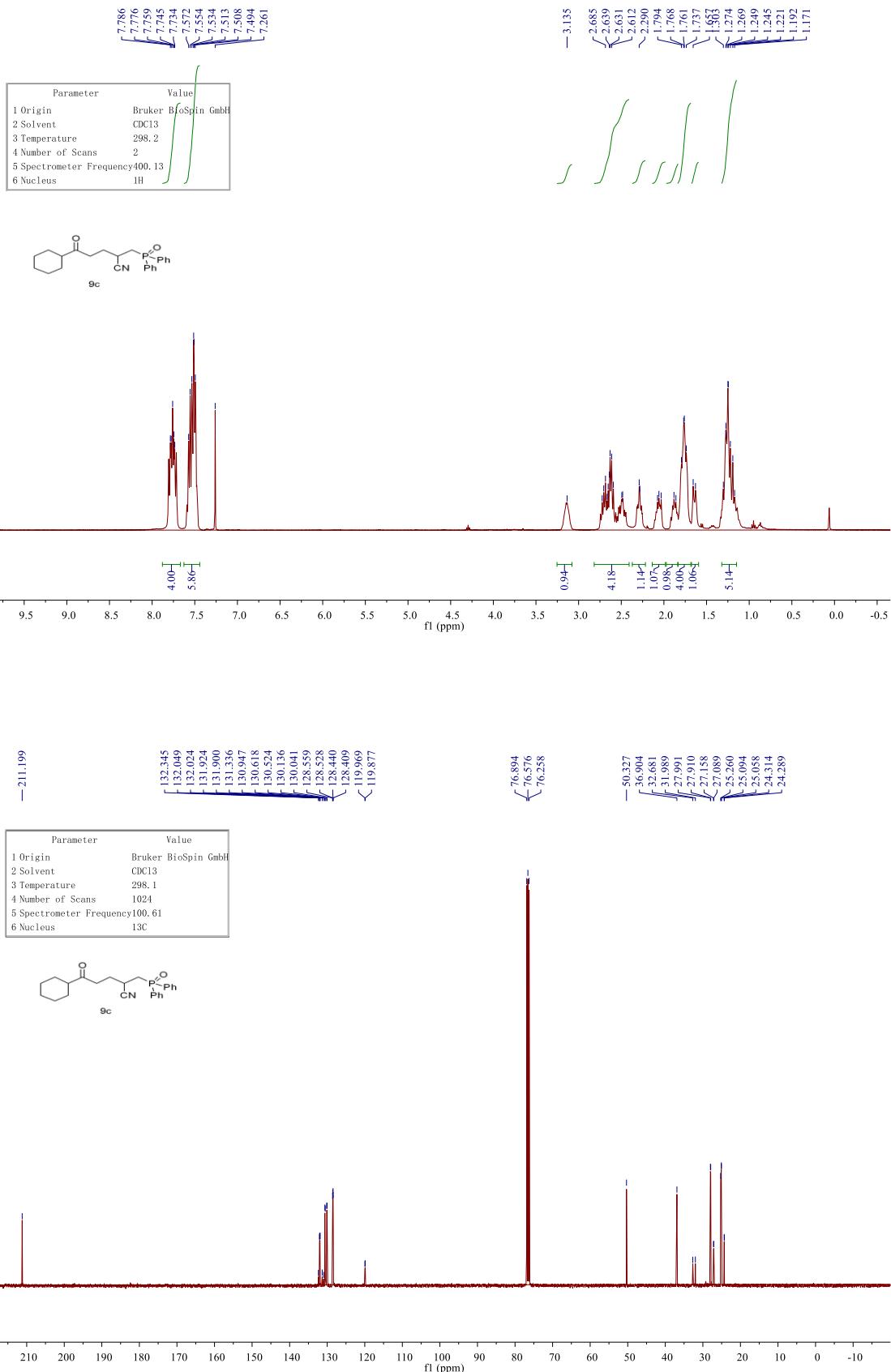






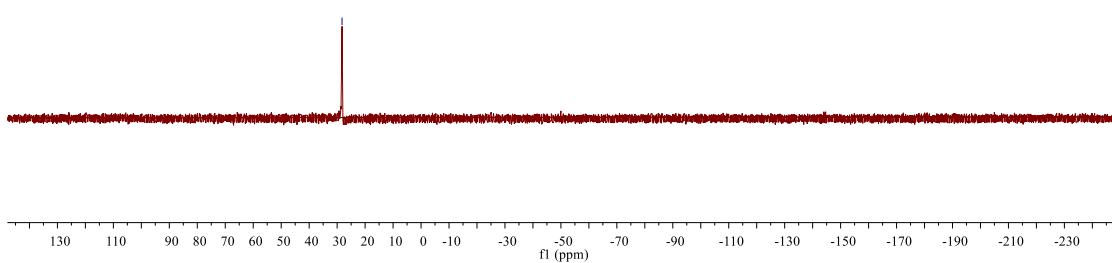
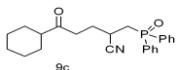




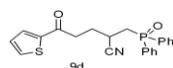


Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl ₃
3 Temperature	298.3
4 Number of Scans	2
5 Spectrometer Frequency	161.97
6 Nucleus	³¹ P

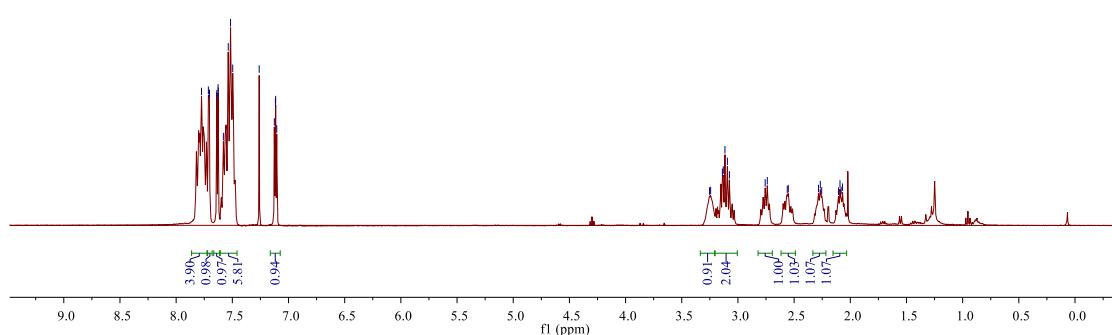
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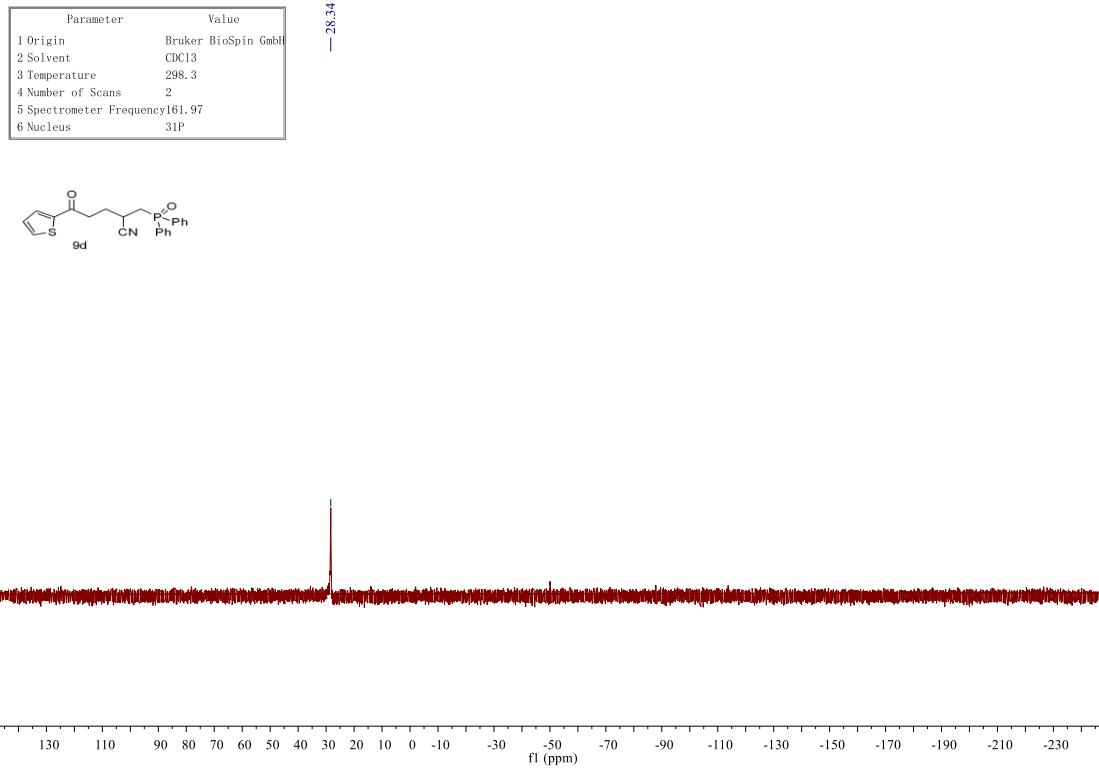
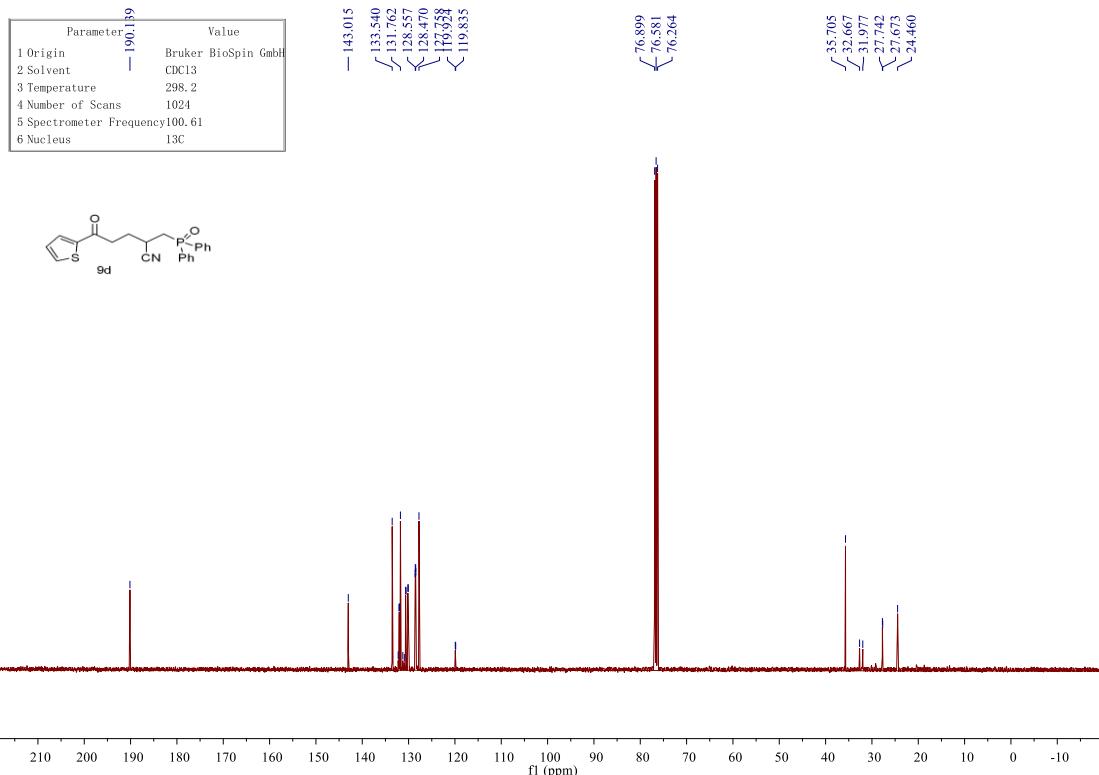


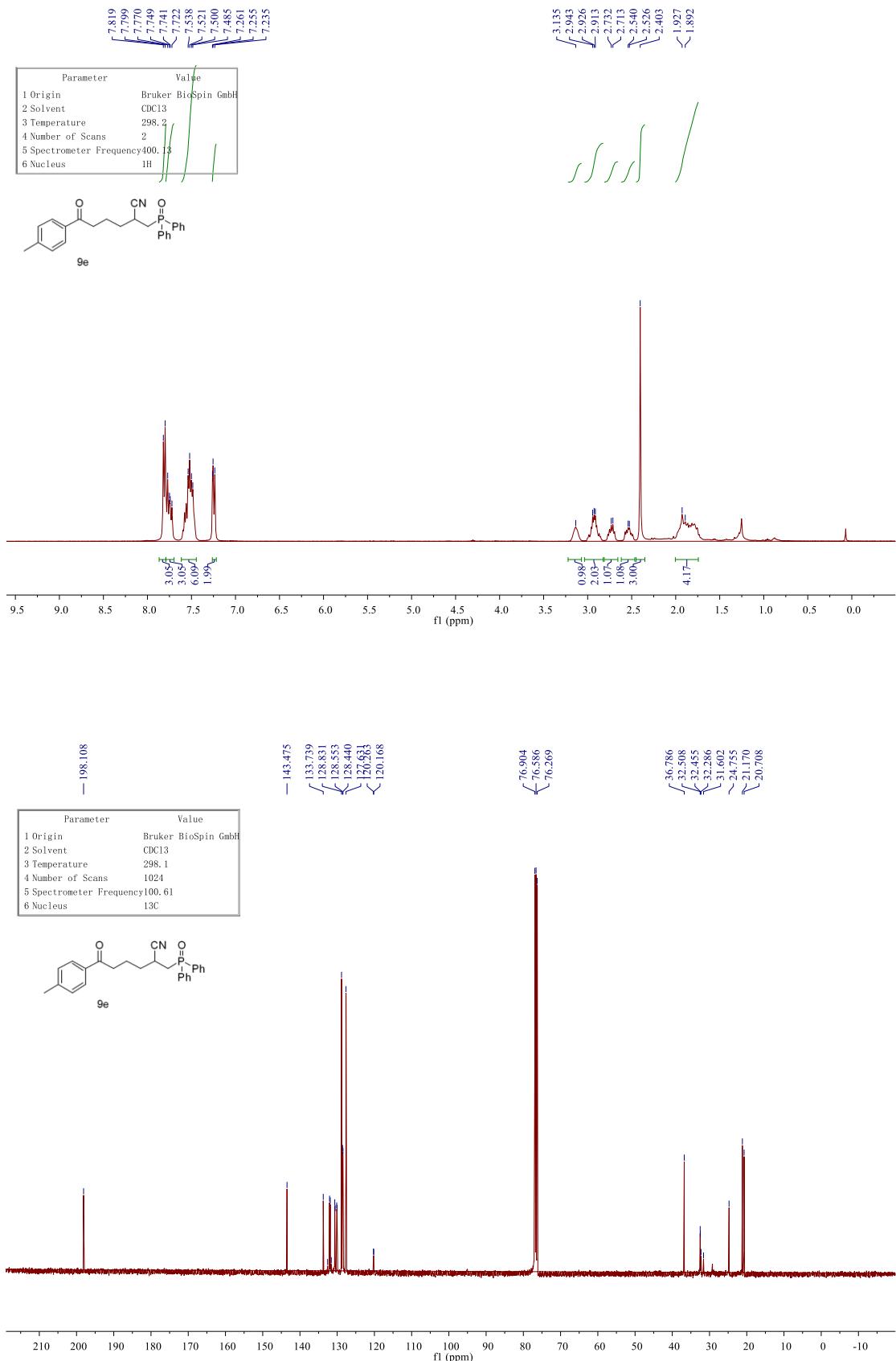
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl ₃
3 Temperature	298.1
4 Number of Scans	2
5 Spectrometer Frequency	400
6 Nucleus	¹ H



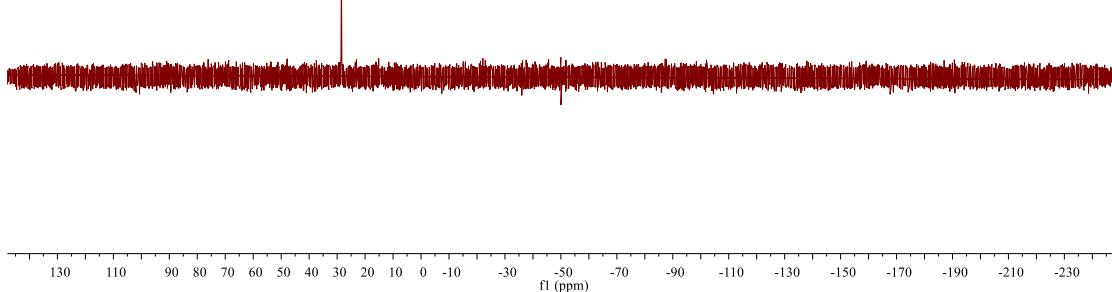
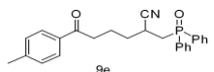
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2.092
2.081
2.069







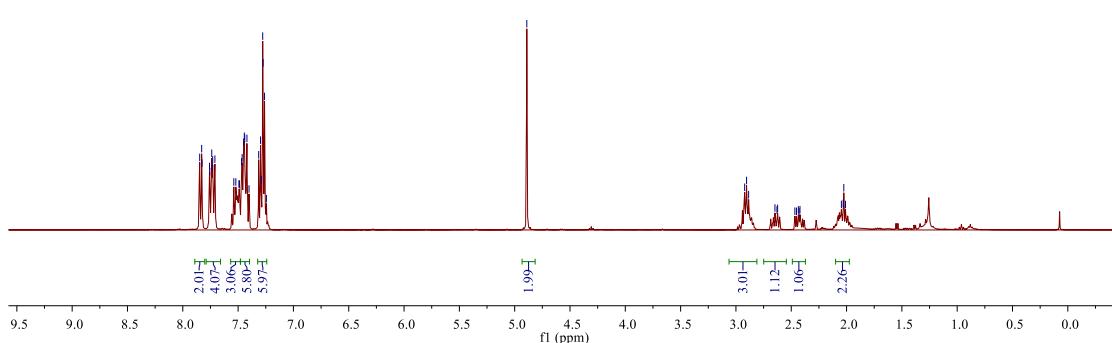
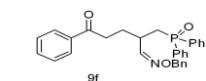
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl ₃
3 Temperature	298.3
4 Number of Scans	4
5 Spectrometer Frequency	161.97
6 Nucleus	31P

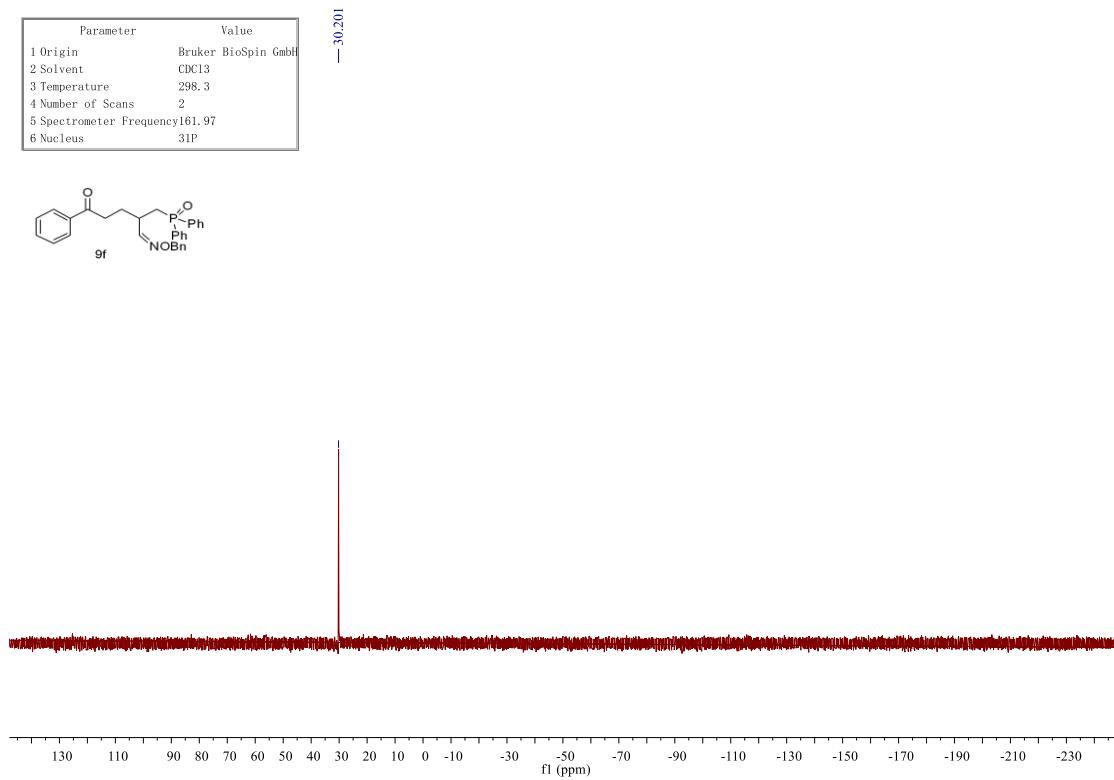
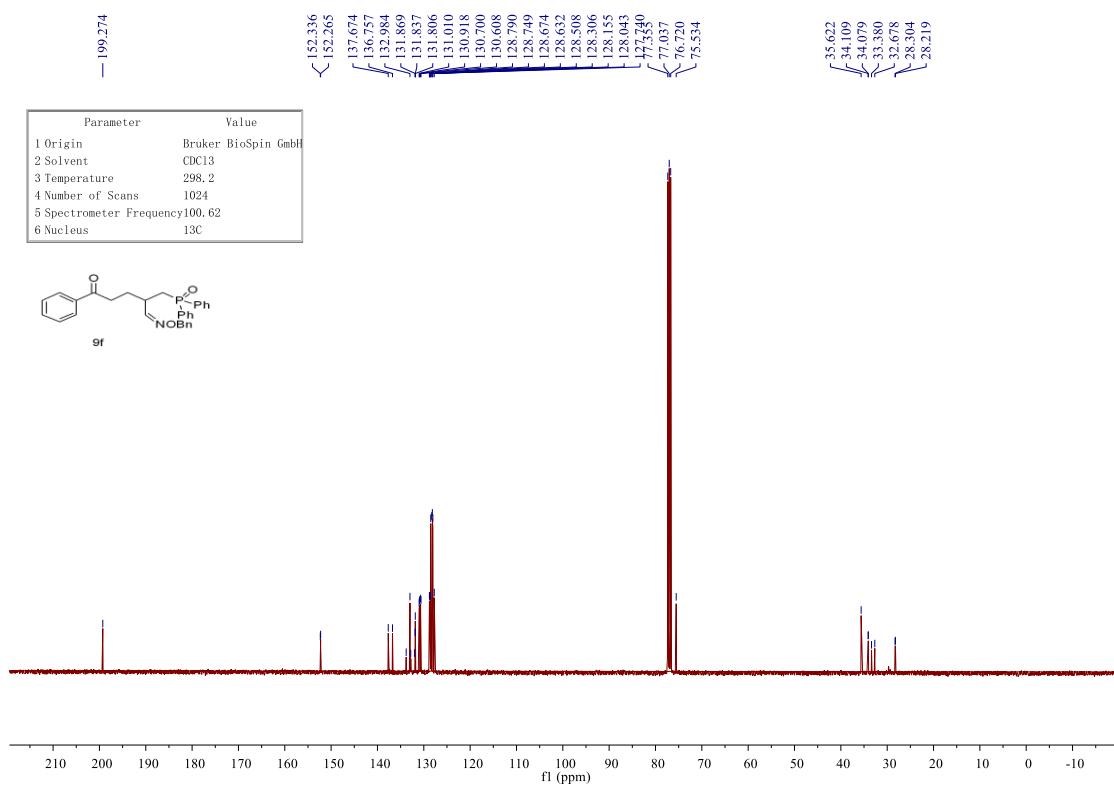


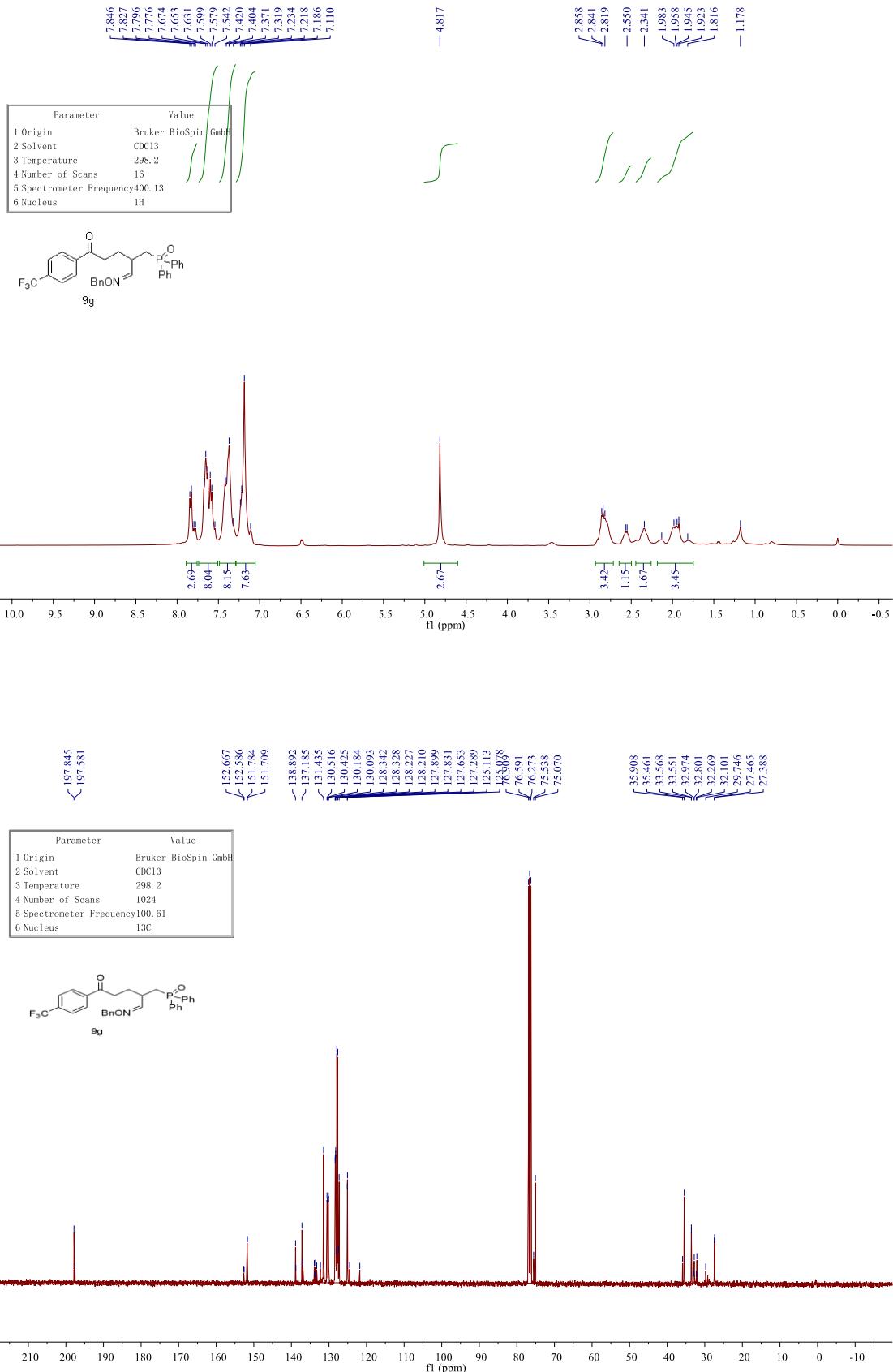
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7.278
7.274
7.261
7.244

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2.904
2.885
2.647
2.629
2.623
2.467
2.452
2.436
2.429
2.421
2.047
2.030
2.025
2.010

Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl ₃
3 Temperature	298.3
4 Number of Scans	16
5 Spectrometer Frequency	400.1 Hz
6 Nucleus	1H

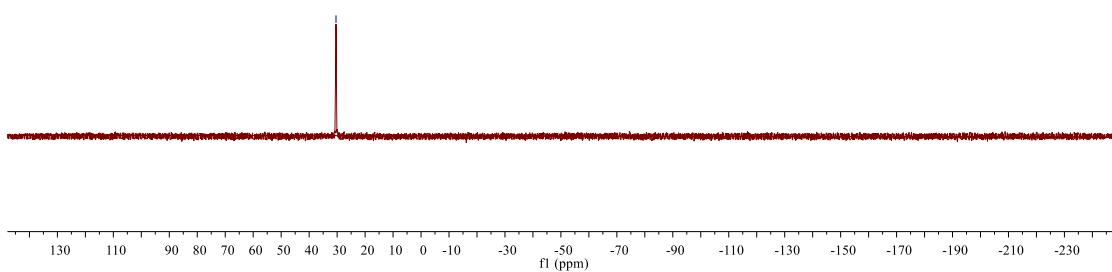
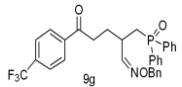






Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl ₃
3 Temperature	298.3
4 Number of Scans	2
5 Spectrometer Frequency	161.98
6 Nucleus	31P

— 30.404



Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl ₃
3 Temperature	298.2
4 Number of Scans	4
5 Spectrometer Frequency	376.44
6 Nucleus	19F

— -63.070

