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Supporting Information for

Dibenzocycloheptanones construction through a removable *P*–centered radical: Synthesis of allocolchicine analogues

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1. General Remarks

NMR spectra were recorded on BRUKER AVANCE III 400 or BRUKER AVANCE III 600. $CDCl_3$ was used as the solvent. Chemical shifts were referenced relative to residual solvent signal ($CDCl_3$: ^1H NMR: δ 7.26 ppm, ^{13}C NMR: δ 77.16 ppm). The following abbreviations are used to describe peak patterns where appropriate: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Coupling constants (*J*) are reported in Hertz (Hz). Electrospray-ionization (ESI) mass spectra were obtained on AB Sciex LC 30A-Triple TOF 4600 apparatus or Waters GCT Premier GC-TOF (EI). All systems are equipped with time-of-flight (TOF) analyzers. Melting points were measured with micro melting point apparatus. Unless otherwise noted, some materials (or alternatively chemicals) obtained from commercial suppliers were used directly without further purification. Alkynones **1** were prepared according to the literature.[1,2]

Table S–1. Scopes of Alkynones **1**. (^{t}Bu = *tert*–butyl)

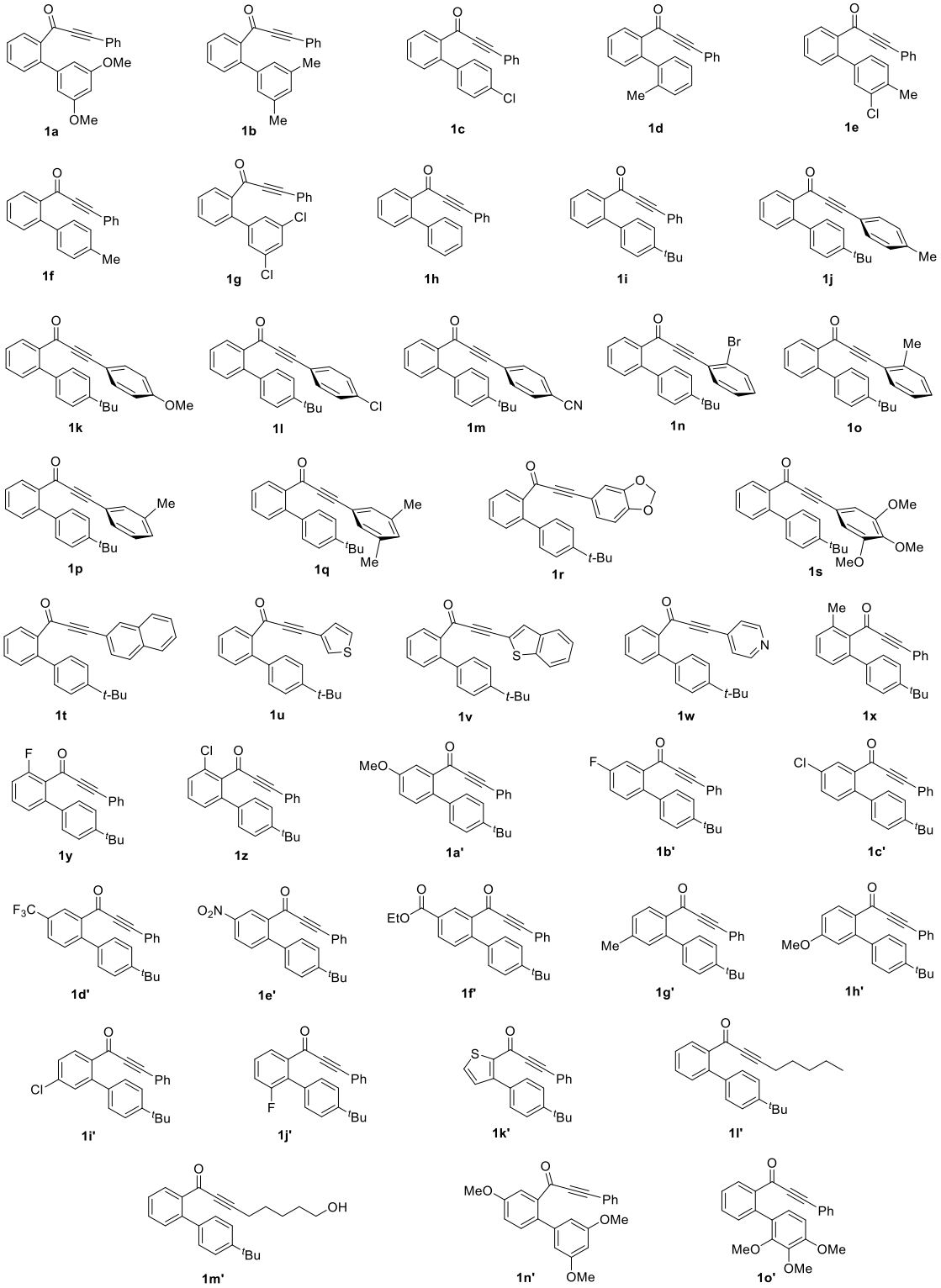
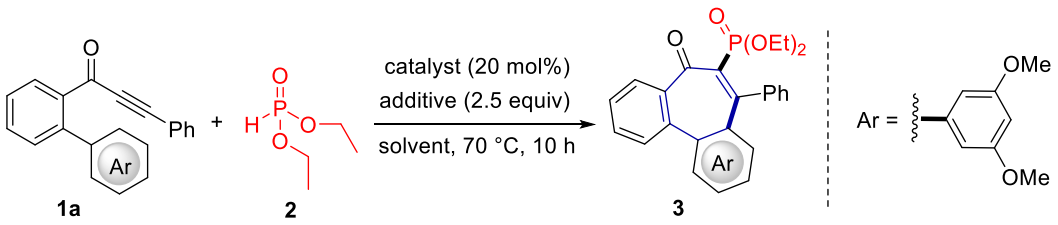


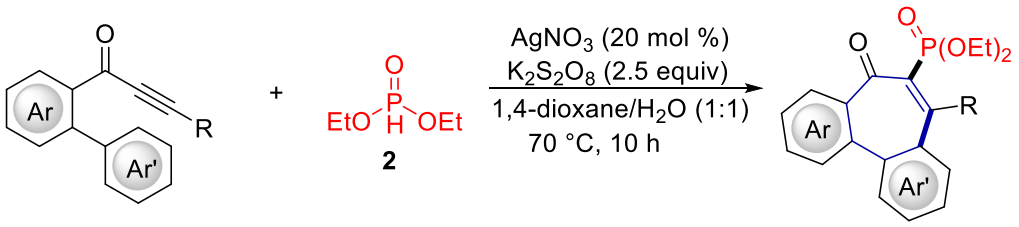
Table S–2. Optimization of the cascade cyclization/phosphorylation.[a]



Entry	Catalyst	Additive	Solvent	Yield / %
1	$Cu(OTf)_2$	TBHP	MeCN	trace
2	$Cu(OAc)_2$	TBHP	MeCN	25
3	–	$Mn(OAc)_3$	MeCN	15
4	$AgNO_3$	$K_2S_2O_8$	MeCN	41
5	$AgNO_3$	$K_2S_2O_8$	1,4–Dioxane	27
6	$AgNO_3$	$K_2S_2O_8$	1,4–Dioxane/MeCN	36
7	$AgNO_3$	$K_2S_2O_8$	MeCN/H_2O (1:1)	trace
8	$AgNO_3$	$K_2S_2O_8$	DMF/H_2O (1:1)	31
9	$AgNO_3$	$K_2S_2O_8$	MeOH/H_2O (1:1)	8
10	$AgNO_3$	$K_2S_2O_8$	THF/H_2O (1:1)	28
11	$AgNO_3$	$K_2S_2O_8$	1,4–Dioxane/H_2O	67
12	$AgNO_3$	$K_2S_2O_8$	DMSO/H_2O (1:1)	trace
13	$AgNO_3$	$K_2S_2O_8$	EtOAc /H_2O (1:1)	20
14	$AgNO_3$	$Na_2S_2O_8$	1,4–Dioxane/H_2O	46
15	$AgNO_3$	$Zn(NO_3)_2$	1,4–Dioxane/H_2O	51
16[b]	$AgNO_3$	–	1,4–Dioxane/H_2O	48
17	$AgNO_3$	–	1,4–Dioxane/H_2O	trace
18	$AgNO_3$	$K_2S_2O_8$	1,4–Dioxane/H_2O	42
19	$AgNO_3$	$K_2S_2O_8$	1,4–Dioxane/H_2O	33
20[c]	$AgNO_3$	$K_2S_2O_8$	1,4–Dioxane/H_2O (1:1)	30
21[d]	$AgNO_3$	$K_2S_2O_8$	1,4–Dioxane/H_2O	49
22[e]	$AgNO_3$	$K_2S_2O_8$	1,4–Dioxane/H_2O	45
23	$AgNO_3$	$Na_2S_2O_8$	1,4–Dioxane/H_2O	54
24[f]	$AgNO_3$	$K_2S_2O_8$	1,4–Dioxane/H_2O	50
25[g]	$AgNO_3$	$K_2S_2O_8$	1,4–Dioxane/H_2O	52

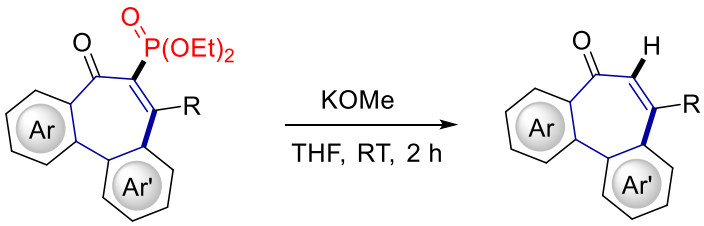
[a] **1a** (0.20 mmol), **2** (0.50 mmol, 2.5 equiv), catalyst (0.04 mol, 0.2 equiv), additive (0.5 mmol, 2.5 equiv), solvent (2 mL), under N_2, 70 °C, 14 h. Yield of the isolated products. [b] $AgNO_3$ (2.0 eq). [c] $AgNO_3$ (0.1 eq). [d] 80 °C. [e] $K_2S_2O_8$ (1.5 eq). [f] **2** (0.30 mmol, 1.5 equiv). [g] 60 °C.

2. (A) General Procedure for Cascade Cyclization/Phosphorylation.



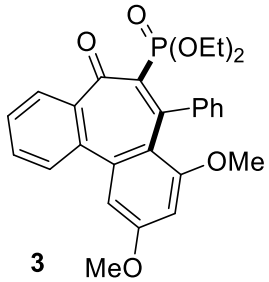
To a 25 mL sealed tube containing biarylynone **1** (0.3 mmol, 1.0 equiv.), $HPO(OEt)_2$ (**2**) (0.75 mmol, 2.5 equiv.), $AgNO_3$ (0.06 mmol, 0.2 equiv.), and $K_2S_2O_8$ (0.75 mmol, 2.5 equiv.) were added 1,4–dioxane/H_2O (v/v = 1:1, 3 mL) under a N_2 atmosphere. After stirring at 70 °C for 10 h, the reaction mixture was cooled to room temperature. It was diluted with EtOAc and transferred to a round bottom before the crude product was concentrated. Column purification on silica gel using petroleum ether/ethyl acetate (v/v = 2:1) as the eluent gave the desired product.

(B) General Procedure for Dephosphorylation.



To a solution of phosphorylation product (0.15 mmol, 1.0 eq.) in THF (0.05 M, 3 mL) under air, potassium methoxide (42 mg, 0.60 mmol, 4.0 eq.) was added in one portion at room temperature. The reaction mixture was stirred for another 2 h at room temperature. Evaporation of the solvent and subsequent purification by flash chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) gave the dephosphorylation product with excellent yields.

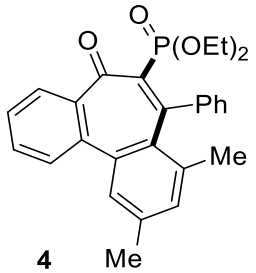
3. Characterization Data of All the Synthesized Products (3–63)



3

Diethyl(8,10-dimethoxy-5-oxo-7-phenyl-5*H*-dibenzo[a,c][7]annulen-6-yl)phosphonate (3)

The general procedure (A) was followed using **1a** (102.6 mg, 0.30 mmol) and **2** (103.4 mg, 0.75 mmol). Purification by column chromatography on silica gel (petroleum ether/ EtOAc = 1:1) yielded **3** (86.0 mg, 60%) as a white solid. **M.p.**: 120–122 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.87 (d, J = 7.8 Hz, 1H), 7.61 (td, J = 7.2, 1.2 Hz, 1H), 7.52–7.47 (m, 2H), 7.39–7.25 (m, 5H), 6.73 (d, J = 2.4 Hz, 1H), 6.35 (d, J = 2.4 Hz, 1H), 4.17–4.14 (m, 1H), 4.06–4.00 (m, 1H), 3.93–3.87 (m, 1H), 3.85 (s, 3H), 3.78–3.74 (m, 1H), 3.22 (s, 3H), 1.16 (t, J = 7.2 Hz, 3H), 1.01 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 197.8 (d, J = 9.1 Hz), 160.9, 160.3, 150.8 (d, J = 6.0 Hz), 144.9 (d, J = 4.5 Hz), 141.6 (d, J = 7.6 Hz), 140.3 (d, J = 1.5 Hz), 135.9, 133.0 (d, J = 175.2 Hz), 130.7, 128.5, 127.8, 127.8, 127.0, 125.1, 120.1, 112.0, 106.5, 99.6, 62.5 (d, J = 6.0 Hz), 62.1 (d, J = 6.0 Hz), 57.6, 55.5, 16.1 (d, J = 6.0 Hz), 16.0 (d, J = 7.6 Hz). **^{31}P NMR** (243 MHz, $CDCl_3$) δ 10.49. **HR–MS** (ESI) *m/z* calc. for $C_{27}H_{28}O_6P$ $[M+H]^+$: 479.1618, found: 479.1614.

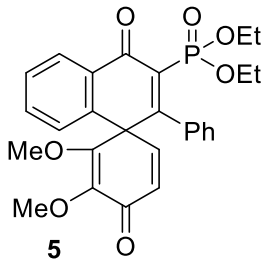


4

Diethyl(8,10-dimethyl-5-oxo-7-phenyl-5*H*-dibenzo[a,c][7]annulen-6-yl)phosphonate (4)

The general procedure (A) was followed using **1b** (93.0 mg, 0.30 mmol) and **2** (103.4 mg, 0.75 mmol). Purification by column chromatography on silica gel (petroleum ether/ EtOAc = 3:1) yielded **4** (73.6 mg, 55%) as a yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ

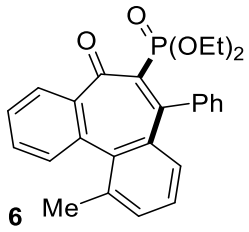
7.87 (d, *J* = 7.8 Hz, 1H), 7.49–7.46 (m, 2H), 7.37–7.27 (m, 6H), 6.90 (s, 1H), 4.12–4.06 (m, 1H), 3.97–3.90 (m, 1H), 3.69–3.62 (m, 2H), 2.36 (s, 3H), 1.77 (s, 3H), 1.20 (t, *J* = 7.2 Hz, 3H), 0.95 (t, *J* = 6.6 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) *δ* 197.9 (d, *J* = 10.6 Hz), 151.7 (d, *J* = 4.5 Hz), 145.0 (d, *J* = 4.5 Hz), 140.3 (d, *J* = 7.6 Hz), 139.1, 138.8, 138.5 (d, *J* = 1.5 Hz), 136.8, 134.3 (d, *J* = 170.6 Hz), 133.3 (d, *J* =19.6 Hz), 132.1, 130.7, 129.8, 128.8, 128.7, 127.8, 127.8, 127.6, 124.8, 62.7 (d, *J* = 6.0 Hz), 62.2 (d, *J* = 6.0 Hz), 23.1, 21.2, 16.1 (d, *J* = 7.6 Hz), 15.8 (d, *J* = 7.6 Hz). **^{31}P NMR** (243 MHz, $CDCl_3$) *δ* 10.33. **HR–MS** (ESI) *m/z* calc. for $C_{27}H_{28}O_4P$ $[M+H]^+$: 447.1720, found: 447.1716.



5

Diethyl(2,3-dimethoxy-4,4'-dioxo-2'-phenyl-4'*H*-spiro[cyclohexane-1,1'-naphthalene]-2,5-dien-3'-yl) phosphonate (5)

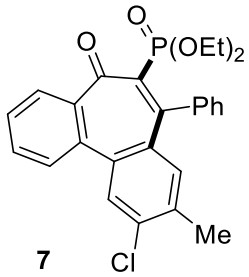
The general procedure was followed using **1o'** (111.6 mg, 0.30 mmol) and **2** (103.4 mg, 0.75 mmol). Purification by column chromatography on silica gel (petroleum ether /EtOAc = 1:1) yielded **5** (89.0 mg, 60%) as a yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.23 (dd, *J* = 7.8, 1.1 Hz, 1H), 7.56 (td, *J* = 7.6, 1.4 Hz, 1H), 7.51 (t, *J* = 7.2 Hz, 1H), 7.34–7.31 (m, 2H), 7.27–7.20 (m, 3H), 7.14 (d, *J* = 7.9 Hz, 1H), 6.36 (d, *J* = 9.7 Hz, 1H), 6.27 (d, *J* = 9.7 Hz, 1H), 4.12–4.08 (m, 1H), 4.01–3.90 (m, 2H), 3.80 (s, 3H), 3.76–3.72 (m, 1H), 3.37 (s, 3H), 1.11 (t, *J* = 7.1 Hz, 3H), 1.03 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 184.1, 183.0 (d, *J* = 7.2 Hz), 164.6 (d, *J* = 6.1 Hz), 160.0, 142.7 (d, *J* = 1.9 Hz), 140.1, 138.4 (d, *J* = 1.8 Hz), 136.4 (d, *J* = 6.5 Hz), 133.7, 132.4, 130.6 (d, *J* = 7.2 Hz), 129.5, 129.0, 128.9, 128.3 (d, *J* = 1.4 Hz), 127.7 (d, *J* = 1.1 Hz), 127.4, 127.3, 127.1, 126.5, 62.7 (d, *J* = 6.4 Hz), 62.1 (d, *J* = 6.5 Hz), 61.1, 60.6, 56.5 (d, *J* = 14.5 Hz), 16.3 (d, *J* = 6.0 Hz), 16.1 (d, *J* = 6.0 Hz).**^{31}P NMR** (243 MHz, $CDCl_3$) δ 11.84. **HR–MS** (EI) *m/z* calc. for $C_{27}H_{27}O_7P$ $(M)^+$: 494.1494, found: 494.1496.



6

Diethyl(S)-(11-methyl-5-oxo-7-phenyl-5*H*-dibenzo[a,c][7]annulen-6-yl)phosphonate (6)

The general procedure (A) was followed using **1d** (88.8 mg, 0.30 mmol) and **2** (103.4 mg, 0.75 mmol). Purification by column chromatography on silica gel (petroleum ether/ EtOAc = 3:1) yielded **6** (42.8 mg, 33%) as a white solid. **M.p.**: 121–123 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.64–7.63 (m, 2H), 7.56–7.55 (m, 3H), 7.43 (dd, J = 7.8, 7.8 Hz, 1H), 7.36–7.31 (m, 2H), 7.27 (dd, J = 7.2, 7.2 Hz, 1H), 7.23 (d, J = 7.2 Hz, 1H), 7.18 (d, J = 7.8 Hz, 1H), 7.14 (d, J = 7.2 Hz, 1H), 4.08–3.95 (m, 4H), 2.18 (s, 3H), 1.13–1.10 (m, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 185.5 (d, J = 3.0 Hz), 164.6 (d, J = 6.0 Hz), 156.6, 148.0, 138.4 (d, J = 1.5 Hz), 136.4 (d, J = 6.0 Hz), 134.0, 133.7 (d, J = 187.2 Hz), 131.1, 130.4, 130.4, 129.4, 129.2, 129.1, 128.1, 127.7, 127.4, 127.2, 127.0, 62.5 (d, J = 7.6 Hz), 62.4 (d, J = 7.6 Hz), 20.5, 16.2 (d, J = 1.5 Hz), 16.2 (d, J = 1.5 Hz). **^{31}P NMR** (243 MHz, $CDCl_3$) δ 11.88. **HR–MS** (ESI) *m/z* calc. for $C_{26}H_{26}O_4P$ $[M+H]^+$: 433.1563, found: 433.1558.

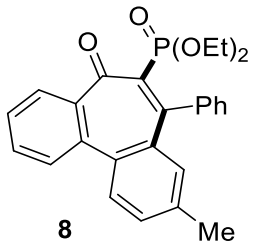


7

Diethyl(10-chloro-9-methyl-5-oxo-7-phenyl-5*H*-dibenzo[a,c][7]annulen-6-yl)phosphonate (7)

The general procedure (A) was followed using **1d** (99.0 mg, 0.30 mmol) and **2** (103.4 mg, 0.75 mmol). Purification by column chromatography on silica gel (petroleum ether/ EtOAc = 3:1) yielded **7** (33.6 mg, 24%) as a yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.79 (d, J = 7.9 Hz, 1H), 7.67–7.65 (m, 2H), 7.57–7.40 (m, 5H), 6.83 (s, 1H), 4.12–4.08 (m, 1H), 4.05–4.00 (m, 1H), 3.81–3.77 (m, 1H), 3.62–3.56 (m, 1H), 2.23 (s, 3H), 1.24

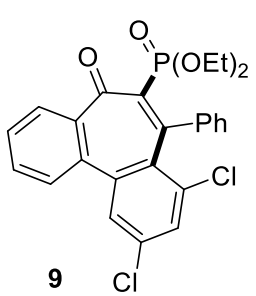
(t, *J* = 7.1 Hz, 3H), 1.00 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 197.0 (d, *J* = 8.4 Hz), 153.6 (d, *J* = 6.0 Hz), 144.2 (d, *J* =6.0 Hz), 140.2 (d, *J* = 9.1 Hz), 137.5, 135.9, 135.2, 134.9, 134.8, 134.5 (d, *J* = 163.1 Hz), 134.4, 131.1, 130.9, 128.9, 128.7, 128.2, 128.1, 128.1, 125.4, 63.0 (d, *J* = 5.9 Hz), 62.3 (d, *J* = 7.6 Hz), 19.9, 16.4 (d, *J* = 6.0 Hz), 16.2 (d, *J* = 7.6 Hz). **^{31}P NMR** (243 MHz, $CDCl_3$) δ 11.02. **HR–MS** (ESI) *m/z* calc. for $C_{26}H_{24}O_4P^{35}Cl$ $[M+H]^+$: 467.1174, found: 467.1170.



8

Diethyl(9-methyl-5-oxo-7-phenyl-5*H*-dibenzo[a,c][7]annulen-6-yl)phosphonate (8)

The general procedure (A) was followed using **1f** (88.8 mg, 0.30 mmol) and **2** (103.4 mg, 0.75 mmol). Purification by column chromatography on silica gel (petroleum ether/ EtOAc = 3:1) yielded **8** (28.5 mg, 22%) as a yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.8 Hz, 1H), 7.68–7.65 (m, 1H), 7.60–7.59 (m, 1H), 7.56–7.53 (m, 2H), 7.42 (dd, *J* = 5.4, 5.4 Hz, 2H), 7.34–7.13 (m, 3H), 6.81 (s, 1H), 4.15–4.02 (m, 2H), 3.83–3.78 (m, 1H), 3.63–3.58 (m, 1H), 2.24 (s, 3H), 1.26 (t, *J* = 7.2 Hz, 3H), 1.03 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 197.5 (d, *J* = 11.1 Hz), 153.7 (d, *J* = 6.6 Hz), 144.3 (d, *J* = 5.1 Hz), 140.6 (d, *J* = 8.1 Hz), 137.1, 136.5, 135.9, 133.0, 131.0, 131.0, 130.6, 128.9, 128.3, 128.3, 128.1, 125.4, 63.0 (d, *J* = 6.7 Hz), 62.2 (d, *J* = 5.8 Hz), 21.2, (d, *J* = 7.1 Hz), 16.1 (d, *J* = 7.0 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 11.25. **HR–MS** (ESI) *m/z* calc. for $C_{26}H_{26}O_4P$ $[M+H]^+$: 433.1563, found: 433.1558.

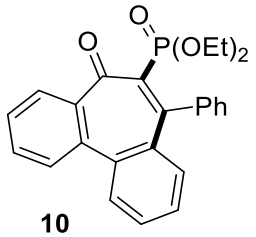


9

Diethyl(8,10-dichloro-5-oxo-7-phenyl-5*H*-dibenzo[a,c][7]annulen-6-

yl)phosphonate (9)

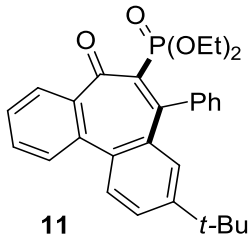
The general procedure (A) was followed using **1g** (105.0 mg, 0.30 mmol) and **2** (103.4 mg, 0.75 mmol). Purification by column chromatography on silica gel (petroleum ether/ EtOAc = 3:1) yielded **9** (29.2 mg, 20%) as a white solid. **M.p.**: 128–130 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.92 (d, J = 7.8 Hz, 1H), 7.74 (dd, J = 7.5, 1.7 Hz, 1H), 7.71–7.66 (m, 1H), 7.59–7,53 (m, 3H), 7.38–7.31 (m, 5H), 4.11–4.06 (m, 1H), 3.93–3.88 (m, 1H), 3.84–3.78 (m, 2H), 1.18 (td, J = 7.2, 3.0 Hz, 3H), 1.09–1.06 (m, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 196.9 (d, J = 13.5 Hz), 148.8 (d, J = 7.6 Hz), 145.2, 140.9, 140.1 (d, J = 12.0 Hz), 138.9, 137.1, 137.1 (d, J = 170.6 Hz), 135.2, 135.1, 131.1, 129.8, 128.9, 127.7, 127.6, 127.5, 127.4, 125.4, 125.3, 62.9 (d, J = 4.5 Hz), 62.6 (d, J = 6.0 Hz), 16.1 (t, J = 6.8 Hz). **^{31}P NMR** (243 MHz, $CDCl_3$) δ 8.93. **HR–MS** (ESI) *m/z* calc. for $C_{25}H_{22}{}^{35}Cl_2O_4P$ $[M+H]^+$: 487.0628, found: 487.0687.



10

Diethyl(5-oxo-7-phenyl-5*H*-dibenzo[a,c][7]annulen-6-yl)phosphonate (10)

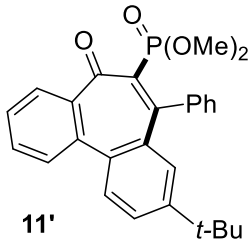
The general procedure (A) was followed using **1h** (84.6 mg, 0.30 mmol) and **2** (103.4 mg, 0.75 mmol). Purification by column chromatography on silica gel (petroleum ether/ EtOAc = 3:1) yielded **10** (21.3 mg, 17%) as a white solid. **M.p.**: 156–158 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.82 (d, J = 7.9 Hz, 1H), 7.67–7.65 (m, 2H), 7.52 (s, 2H), 7.57–7.52 (m, 2H), 7.45–7.37 (m, 3H), 7.23–7.21 (m, 1H), 7.01 (dd, J = 8.4, 1.2 Hz, 1H), 4.14–4.01 (m, 2H), 3.84–3.77 (m, 1H), 3.63–3.56 (m, 1H), 1.24 (t, J = 7.0 Hz, 3H), 1.01 (t, J = 7.0 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 197.3 (d, J = 9.1 Hz), 153.6 (d, J = 4.5 Hz), 144.5 (d, J = 4.5 Hz), 140.6 (d, J = 9.1 Hz), 138.5, 136.6 (d, J = 19.6 Hz), 135.8, 134.5 (d, J = 178.2 Hz), 132.8, 131.1, 131.0, 129.5, 129.3, 128.9, 128.6, 128.5, 128.1, 127.3, 125.4, 62.9 (d, J = 6.1 Hz), 62.2 (d, J = 6.1 Hz), 16.4 (d, J = 6.0 Hz), 16.1 (d, J = 6.0 Hz). **^{31}P NMR** (243 MHz, $CDCl_3$) δ 11.13. **HR–MS** (ESI) *m/z* calc. for $C_{25}H_{24}O_4P$ $[M+H]^+$: 419.1407, found: 419.1392.



11

Diethyl(9-(*tert*-butyl)-5-oxo-7-phenyl-5*H*-dibenzo[a,c][7]annulen-6-yl)phosphonate (11)

The general procedure (A) was followed using **1i** (101.4 mg, 0.30 mmol) and **2** (103.4 mg, 0.75 mmol). Purification by column chromatography on silica gel (petroleum ether/ EtOAc = 3:1) yielded **11** (95.3 mg, 67%) as a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 (d, J = 6.0 Hz, 1H), 7.65–7.60 (m, 2H), 7.54–7.51 (m, 2H), 7.46–7.38 (m, 4H), 6.97 (d, J = 3.0 Hz, 1H), 4.14–4.00 (m, 2H), 3.83–3.77 (m, 1H), 3.62–3.56 (m, 1H), 1.24–1.22 (t, J = 7.2 Hz, 3H), 1.11 (s, 9H), 1.00 (t, J = 10.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 197.5 (d, J = 8.1 Hz), 154.2 (d, J = 5.1 Hz), 150.0, 144.2 (d, J = 4.0 Hz), 140.8 (d, J = 9.1 Hz), 136.3, 136.1, 135.7, 133.7 (d, J = 179.8 Hz), 131.0, 130.6, 130.0, 128.8, 128.3, 128.2, 127.9, 126.7, 125.4, 62.9 (d, J = 6.1 Hz), 62.2 (d, J = 6.1 Hz), 34.5, 30.9, 16.3 (d, J = 6.1 Hz), 16.1 (d, J = 6.1 Hz). **^{31}P NMR** (243 MHz, $CDCl_3$) δ 11.44. **HR–MS** (ESI) *m/z* calc. for $C_{29}H_{32}O_4P$ $[M+H]^+$: 475.2033, found: 475.2018.

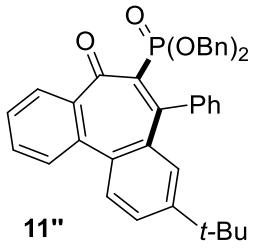


11'

Dimethyl(9-(*tert*-butyl)-5-oxo-7-phenyl-5*H*-dibenzo[a,c][7]annulen-6-yl)phosphonate (11')

The general procedure (A) was followed using **1i** (101.4 mg, 0.30 mmol) and dimethyl phosphonate (83.0 mg, 0.75 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc = 1:1) yielded **11'** (64.2 mg, 48%) as a yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.83 (d, J = 7.9 Hz, 1H), 7.69–7.64 (m, 2H), 7.56–7.54 (m, 2H), 7.50–7.41 (m, 4H), 7.00 (d, J = 2.0 Hz, 1H), 3.72 (d, J = 11.1 Hz, 3H), 3.34 (d, J = 9.8 Hz, 3H), 1.14 (s, 9H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 197.5 (d, J = 8.7 Hz), 154.9 (d, J = 5.5 Hz), 150.1, 144.1 (d, J = 5.0 Hz), 140.6 (d, J = 8.3 Hz), 136.0 (d, J = 19.6 Hz),

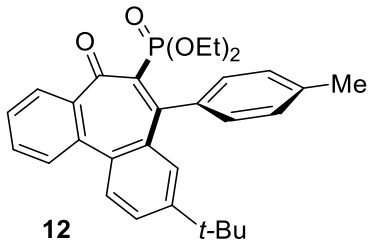
135.8, 135.8, 135.7, 133.0 (d, *J* = 181.2 Hz), 131.2, 130.7, 130.0, 128.9, 128.4, 128.4, 128.0, 126.9, 125.4, 53.6 (d, *J* = 3.6 Hz), 52.9 (d, *J* = 3.7 Hz), 34.6, 31.0. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 14.05. **HR–MS** (ESI) *m/z* calc. for $C_{27}H_{28}O_4P$ $[M+H]^+$: 447.1720, found: 447.1740.



11"

Dibenzyl(9-(*tert*-butyl)-5-oxo-7-phenyl-5*H*-dibenzo[a,c][7]annulen-6-yl)phosphonate (11'')

The general procedure (A) was followed using **1i** (101.4 mg, 0.30 mmol) and dibenzyl phosphonate (196.7 mg, 0.75 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc = 3:1) yielded **11''** (88.9 mg, 50%) as a yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.8 Hz, 1H), 7.65–7.62 (m, 2H), 7.49 (dd, *J* = 8.3, 2.1 Hz, 1H), 7.43–7.38 (m, 3H), 7.34 (s, 3H), 7.28 (s, 3H), 7.26–7.23 (m, 4H), 7.06 (d, *J* = 5.7 Hz, 2H), 7.00 (d, *J* = 2.1 Hz, 1H), 5.00 (d, *J* = 8.7 Hz, 2H), 4.70 (t, *J* = 15.6 Hz, 1H), 4.28 (t, *J* = 10.2 Hz, 1H), 1.15 (s, 9H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 197.3 (d, *J* = 8.7 Hz), 154.7 (d, *J* = 5.6 Hz), 150.0, 144.1 (d, *J* = 5.0 Hz), 140.7 (d, *J* = 8.3 Hz), 136.4 (d, *J* = 5.6 Hz), 136.2, 136.0, 135.8, 135.7, 133.5 (d, *J* = 181.2 Hz), 131.6, 131.0, 130.7, 130.0, 128.9, 128.5, 128.4, 128.3, 128.3, 128.1, 126.9, 125.6, 68.4 (d, *J* = 5.2 Hz), 67.7 (d, *J* = 5.1 Hz), 34.6, 31.0. **^{31}P NMR** (243 MHz, $CDCl_3$) δ 12.31. **HR–MS** (ESI) *m/z* calc. for $C_{39}H_{36}O_4P$ $[M+H]^+$: 599.2346, found: 599.2311.

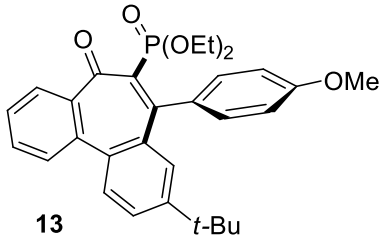


12

Diethyl(9-(*tert*-butyl)-5-oxo-7-(*p*-tolyl)-5*H*-dibenzo[a,c][7]annulen-6-yl)phosphonate (12)

The general procedure (A) was followed using **1j** (105.6 mg, 0.30 mmol) and **2** (103.4

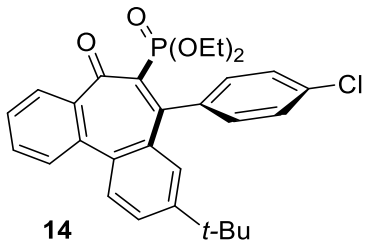
mg, 0.75 mmol). Purification by column chromatography on silica gel (petroleum ether/ EtOAc = 3:1) yielded **12** (105.4 mg, 72%) as a yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.81 (d, J = 7.9 Hz, 1H), 7.66–7.63 (m, 1H), 7.61 (d, J = 8.3 Hz, 1H), 7.54–7.53 (m, 2H), 7.46 (dd, J = 8.3, 2.1 Hz, 1H), 7.21 (br s, 2H), 7.02 (d, J = 2.0 Hz, 1H), 4.15–4.10 (m, 1H), 4.05–4.02 (m, 1H), 3.83–3.79 (m, 1H), 3.68–3.66 (m, 1H), 2.40 (s, 3H), 1.26 (t, J = 7.0 Hz, 3H), 1.14 (s, 9H), 1.03 (t, J = 6.9 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 197.7 (d, J = 8.8 Hz), 154.6 (d, J = 5.7 Hz), 149.9, 144.3 (d, J = 5.0 Hz), 138.7, 137.8 (d, J = 8.1 Hz), 136.3 (d, J = 19.3 Hz), 135.7, 135.7, 133.2 (d, J = 179.2 Hz), 131.0, 130.5, 130.1, 128.6, 128.2, 128.2, 126.7, 125.3, 62.8 (d, J = 5.9 Hz), 62.2 (d, J = 5.9 Hz), 34.6, 31.0, 21.5, 16.3 (d, J = 6.4 Hz), 16.0 (d, J = 6.6 Hz). **^{31}P NMR** (243 MHz, $CDCl_3$) δ 11.56. **HR–MS** (ESI) *m/z* calc. for $C_{30}H_{34}O_4P$ $[M+H]^+$: 489.2189, found: 489.2184.



13

Diethyl(9-(*tert*-butyl)-7-(4-methoxyphenyl)-5-oxo-5*H*-dibenzo[a,c][7]annulen-6-yl)phosphonate (13)

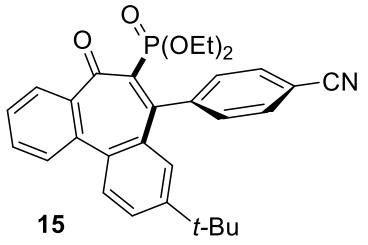
The general procedure (A) was followed using **1k** (110.4 mg, 0.30 mmol) and **2** (103.4 mg, 0.75 mmol). Purification by column chromatography on silica gel (petroleum ether/ EtOAc = 3:1) yielded **13** (105.8 mg, 70%) as a yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.79 (d, J = 7.8 Hz, 1H), 7.63–7.58 (m, 2H), 7.50 (d, J = 3.6 Hz, 2H), 7.44 (dd, J = 8.4, 1.8 Hz, 1H), 7.01 (d, J = 2.4 Hz, 1H), 6.91 (d, J = 5.4 Hz, 2H), 4.15–4.02 (m, 2H), 3.84 (s, 3H), 3.79–3.63 (m, 2H), 1.26 (t, J = 6.6 Hz, 3H), 1.13 (s, 9H), 1.02 (t, J = 6.6 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 197.8 (d, J = 9.1 Hz), 160.1, 154.2 (d, J = 6.0 Hz), 149.9, 144.3 (d, J = 6.0 Hz), 136.4 (d, J = 19.6 Hz), 135.8, 135.7, 133.0 (d, J = 7.6 Hz), 133.0 (d, J = 179.7 Hz), 131.6, 130.9, 130.6, 130.1, 128.2, 128.1, 126.7, 125.3, 62.8 (d, J = 6.0 Hz), 62.2 (d, J = 6.0 Hz), 55.4, 34.6, 31.0, 16.4 (d, J = 6.0 Hz), 16.1 (d, J = 6.0 Hz). **^{31}P NMR** (243 MHz, $CDCl_3$) δ 11.68. **HR–MS** (ESI) *m/z* calc. for $C_{30}H_{34}O_5P$ $[M+H]^+$: 505.2139, found: 505.2135.



14

Diethyl(9-(*tert*-butyl)-7-(4-chlorophenyl)-5-oxo-5*H*-dibenzo[a,c][7]annulen-6-yl)phosphonate (14)

The general procedure (A) was followed using **1l** (111.6 mg, 0.30 mmol) and **2** (103.4 mg, 0.75 mmol). Purification by column chromatography on silica gel (petroleum ether/ EtOAc = 3:1) yielded **14** (73 mg, 48%) as a white solid. **M.p.**: 65–67 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.80 (d, J = 7.8 Hz, 1H), 7.66–7.63 (m, 1H), 7.62 (d, J = 8.4 Hz, 1H), 7.55–7.51 (m, 2H), 7.47 (dd, J = 8.4, 1.8 Hz, 1H), 7.38 (m, 2H), 6.96 (d, J = 1.8 Hz, 1H), 4.17–4.05 (m, 2H), 3.85–3.81 (m, 1H), 3.72–3.70 (m, 1H), 1.27 (t, J = 6.6 Hz, 3H), 1.14 (s, 9H), 1.05 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 197.3 (d, J = 7.6 Hz), 152.9 (d, J = 6.0 Hz), 150.3, 144.2 (d, J = 4.5 Hz), 139.3 (d, J = 9.1 Hz), 135.9, 135.9, 135.9, 135.7 (d, J = 1.5 Hz), 135.0, 134.3 (d, J = 179.7 Hz), 131.2, 130.8, 129.7, 128.4, 128.2, 127.0, 125.4, 63.2 (d, J = 4.5 Hz), 62.3 (d, J = 6.0 Hz), 34.7, 31.0, 16.4 (d, J = 6.0 Hz), 16.1 (d, J = 6.0 Hz). **^{31}P NMR** (243 MHz, $CDCl_3$) δ 10.99. **HR–MS** (ESI) *m/z* calc. for $C_{29}H_{31}{}^{35}ClO_4P$ $[M+H]^+$: 509.1643, found: 509.1644.

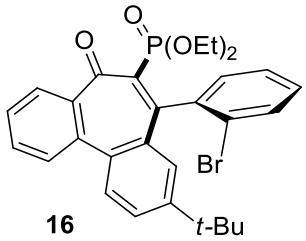


15

Diethyl(9-(*tert*-butyl)-7-(4-cyanophenyl)-5-oxo-5*H*-dibenzo[a,c][7]annulen-6-yl)phosphonate (15)

The general procedure (A) was followed using **1m** (108.9 mg, 0.30 mmol) and **2** (103.4 mg, 0.75 mmol). Purification by column chromatography on silica gel (petroleum ether/ EtOAc = 3:1) yielded **15** (82.3 mg, 55%) as a white solid. **M.p.**: 128–130 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.81 (d, J = 8.4 Hz, 1H), 7.68–7.63 (m, 3H), 7.56–7.48 (m, 3H), 6.84 (d, J = 7.8 Hz, 1H), 4.18–4.06 (m, 2H), 3.86–3.71 (m, 2H), 1.21 (t, J = 7.2 Hz,

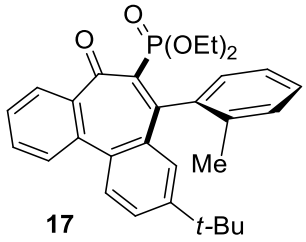
3H), 1.12 (s, 9H), 1.05 (t, *J* = 6.6 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 196.6 (d, *J* = 7.6 Hz), 151.9 (d, *J* = 4.5 Hz), 150.5, 145.6 (d, *J* = 7.6 Hz), 143.9 (d, *J* = 4.5 Hz), 135.9, 135.6, 135.0 (d, *J* = 19.6 Hz), 134.4, 131.7, 131.4, 131.0, 129.3, 128.5, 128.4, 127.3, 125.2, 118.6, 112.5, 63.4 (d, *J* = 6.0 Hz), 62.4 (d, *J* = 4.5 Hz), 51.6, 34.6, 30.9, 16.4 (d, *J* = 6.0 Hz), 16.1 (d, *J* = 6.0 Hz). **^{31}P NMR** (243 MHz, $CDCl_3$) δ 10.30. **HR–MS** (ESI) *m/z* calc. for $C_{30}H_{31}NO_4P$ $[M+H]^+$: 500.1985, found: 500.1963.



16

Diethyl(7-(2-bromophenyl)-9-(*tert*-butyl)-5-oxo-5*H*-dibenzo[a,c][7]annulen-6-yl)phosphonate (16)

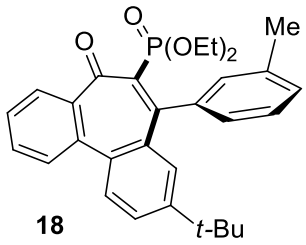
The general procedure (A) was followed using **1n** (124.8 mg, 0.30 mmol) and **2** (103.4 mg, 0.75 mmol). Purification by column chromatography on silica gel (petroleum ether/ EtOAc = 3:1) yielded **16** (89.4 mg, 54%) as a yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.2 Hz, 2H), 7.66–7.61 (m, 2H), 7.55–7.50 (m, 4H), 7.45 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.29–7.26 (m, 1H), 6.96 (s, 1H), 4.12–4.04 (m, 2H), 3.84–3.80 (m, 1H), 3.63–3.60 (m, 1H), 1.23 (t, *J* = 6.6 Hz, 3H), 1.13 (s, 9H), 1.04 (t, *J* = 6.6 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 197.0 (d, *J* = 9.1 Hz), 153.0 (d, *J* = 3.0 Hz), 150.3, 144.1 (d, *J* = 4.5 Hz), 140.6 (d, *J* = 9.1 Hz), 136.2 (d, *J* = 34.7 Hz), 135.1 (d, *J* = 178.2 Hz), 132.9, 132.2, 131.2, 130.8, 130.1, 128.3, 128.2, 127.2, 126.8, 128.6, 125.3, 123.4, 63.3 (d, *J* = 4.5 Hz), 62.2 (d, *J* = 4.5 Hz), 34.6, 30.1, 16.3 (d, *J* = 7.6 Hz), 16.1 (d, *J* = 7.6 Hz). **^{31}P NMR** (243 MHz, $CDCl_3$) δ 11.1. **HR–MS** (ESI) *m/z* calc. for $C_{29}H_{31}{}^{79}BrO_4P$ $[M+H]^+$: 553.1138, found: 553.1111.



17

Diethyl(9-(*tert*-butyl)-5-oxo-7-(*o*-tolyl)-5*H*-dibenzo[a,c][7]annulen-6-yl)phosphonate (17)

The general procedure (A) was followed using **1o** (105.6 mg, 0.30 mmol) and **2** (103.4 mg, 0.75 mmol). Purification by column chromatography on silica gel (petroleum ether/ EtOAc = 3:1) yielded **17** (90.8 mg, 62%) as a yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.79 (d, J = 7.8 Hz, 1H), 7.66–7.60 (m, 3H), 7.55–7.51 (m, 2H), 7.43 (dd, J = 8.4, 2.4 Hz, 1H), 7.34 (dd, J = 6.6, 6.6 Hz, 1H), 7.28 (dd, J = 7.2, 7.2 Hz, 1H), 7,10 (d, J = 6.6 Hz, 1H), 7.03 (d, J = 1.8 Hz, 1H), 4.04–3.97 (m, 2H), 3.80–3.76 (m, 1H), 3.66–3.59 (m, 1H), 1.59 (s, 3H), 1.21 (t, J = 6.6 Hz, 3H), 1.10 (s, 9H), 1.00 (t, J = 6.6 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 197.3 (d, J = 9.1 Hz), 154.4 (d, J = 4.5 Hz), 150.4, 144.4 (d, J = 4.5 Hz), 139.5 (d, J = 6.0 Hz), 136.2, 135.7, 135.5, 135.2 (d, J = 19.6 Hz), 134.3, 131.1, 130.7, 130.4, 130.2, 138.9, 128.3, 128.2, 127.9, 126.6, 125.4, 125.3, 62.9 (d, J = 7.6 Hz), 62.1 (d, J = 6.0 Hz), 34.6, 19.5, 16.3 (d, J = 6.0 Hz), 16.2 (d, J = 6.0 Hz). **^{31}P NMR** (243 MHz, $CDCl_3$) δ 11.43. **HR–MS** (ESI) *m/z* calc. for $C_{30}H_{34}O_4P$ $[M+H]^+$: 489.2189, found: 489.2183.

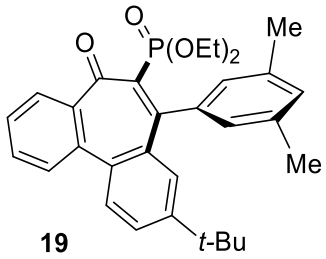


18

Diethyl(9-(*tert*-butyl)-5-oxo-7-(*m*-tolyl)-5*H*-dibenzo[a,c][7]annulen-6-yl)phosphonate (18)

The general procedure (A) was followed using **1p** (105.6 mg, 0.30 mmol) and **2** (103.4 mg, 0.75 mmol). Purification by column chromatography on silica gel (petroleum ether/ EtOAc = 3:1) yielded **18** (106.9 mg, 73%) as a yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.80 (d, J = 7.8 Hz, 1H), 7.65–7.60 (m, 2H), 7.53–7.51 (m, 2H), 7.45 (dd, J = 8.4, 1.8 Hz, 1H), 7.20 (d, J = 7.2 Hz, 1H), 7.00 (d, J = 1.8 Hz, 1H), 4.13–4.02 (m, 2H), 3.83–3.79 (m, 1H), 3.61–3.57 (m, 1H), 2.34 (s br, 3H), 1.25 (t, J = 7.2 Hz, 3H), 1.12 (s, 9H), 1.02 (t, J = 6.6 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 197.6 (d, J = 9.1 Hz), 154.5 (d, J = 6.1 Hz), 150.0, 144.3 (d, J = 5.1 Hz), 140.7 (d, J = 8.1 Hz), 137.5, 136.2 (d, J = 20.2 Hz), 135.8, 133.5 (d, J = 180.8 Hz), 131.0, 130.6, 130.1, 129.5, 128.3, 128.2, 127.8, 126.7, 125.4, 62.8 (d, J = 6.1 Hz), 62.2 (d, J = 6.1 Hz), 34.6, 31.0, 21.4, 16.4 (d, J = 7.1 Hz), 16.1 (d, J = 7.1 Hz). **^{31}P NMR** (243 MHz, $CDCl_3$) δ 11.59. **HR–MS** (ESI) *m/z*

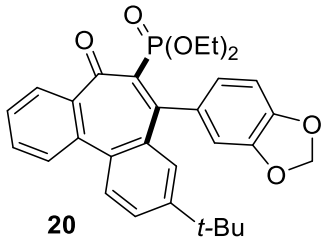
calc. $C_{30}H_{34}O_4P$ $[M+H]^+$: 489.2189, found: 489.2183.



19

Diethyl(9-(*tert*-butyl)-7-(3,5-dimethylphenyl)-5-oxo-5*H*-dibenzo[a,c][7]annulen-6-yl)phosphonate (19)

The general procedure (A) was followed using **1q** (109.8 mg, 0.30 mmol) and **2** (103.4 mg, 0.75 mmol). Purification by column chromatography on silica gel (petroleum ether/ EtOAc = 3:1) yielded **19** (60.2 mg, 40%) as a yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.80 (d, J = 1.8 Hz, 1H), 7.64–7.60 (m, 2H), 7.51 (d, J = 4.2 Hz, 2H), 7.45 (dd, J = 8.4, 1.8 Hz, 1H), 7.02 (dd, J = 1.8, 1.8 Hz, 2H), 4.13–4.03 (m, 2H), 3.84–3.81 (m, 1H), 3.63–3.57 (m, 1H), 2.31 (br s, 6H), 1.27 (t, J = 6.6 Hz, 3H), 1.13 (s, 9H), 1.03 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 197.7 (d, J = 9.1 Hz), 154.8 (d, J = 6.1 Hz), 149.9, 144.3 (d, J = 5.1 Hz), 144.6 (d, J = 8.1 Hz), 137.4, 136.2 (d, J = 20.2 Hz), 135.8, 133.3 (d, J = 181.8 Hz), 131.0, 130.6, 130.4, 130.2, 128.3, 128.2, 126.6, 125.4, 62.8 (d, J = 6.1 Hz), 62.2 (d, J = 5.1 Hz), 34.6, 31.0, 21.3, 16.4 (d, J = 8.1 Hz), 16.1 (d, J = 7.1 Hz). **^{31}P NMR** (243 MHz, $CDCl_3$) δ 11.73. **HR–MS** (ESI) *m/z* calc. for $C_{31}H_{36}O_4P$ $[M+H]^+$: 503.2346, found: 503.2347.

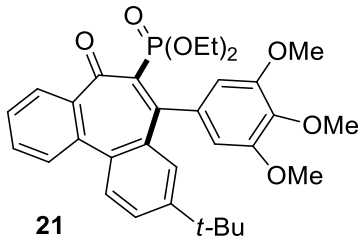


20

Diethyl(7-(benzo[d][1,3]dioxol-5-yl)-9-(*tert*-butyl)-5-oxo-5*H*-dibenzo[a,c][7]annulen-6-yl)phosphonate (20)

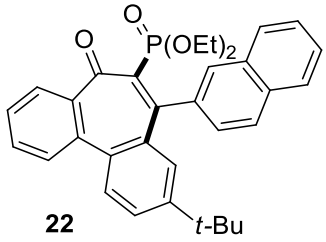
The general procedure (A) was followed using **1r** (114.6 mg, 0.30 mmol) and **2** (103.4 mg, 0.75 mmol). Purification by column chromatography on silica gel (petroleum ether/ EtOAc = 1:1) yielded **20** (77.7 mg, 50%) as a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.78 (d, J = 7.8 Hz, 1H), 7.64–7.61 (m, 1H), 7.59 (d, J = 7.8 Hz, 1H), 7.52–7.49 (m,

2H), 7.46 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.08 (d, *J* = 2.4 Hz, 1H), 6.85 (s, 1H), 6.00 (s, 2H), 4.16–4.04 (m, 2H), 3.89–3.75 (m, 2H), 1.29 (t, *J* = 7.2 Hz, 3H), 1.16 (s, 9H), 1.10 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 197.6 (d, *J* = 9.1 Hz), 153.9 (d, *J* = 6.0 Hz), 150.1, 148.2, 147.4, 144.3 (d, *J* = 4.5 Hz), 135.8 (d, *J* = 1.5 Hz), 135.7, 134.4, 133.2 (d, *J* = 179.7 Hz), 131.0, 130.6, 129.9, 128.3, 128.2, 126.7, 125.3, 124.3, 107.8, 101.4, 90.9, 62.9 (d, *J* = 7.6 Hz), 62.6, 62.3 (d, *J* = 6.0 Hz), 34.6, 31.1, 16.4 (d, *J* = 6.0 Hz), 16.2 (d, *J* = 6.0 Hz). **^{31}P NMR** (243 MHz, $CDCl_3$) δ 11.38. **HR–MS** (ESI) *m/z* calc. for $C_{30}H_{32}O_6P$ $[M+H]^+$: 519.1931, found: 519.1930.



Diethyl(9-(*tert*-butyl)-5-oxo-7-(3,4,5-trimethoxyphenyl)-5*H*-dibenzo[a,c][7]annulen-6-yl)phosphonate (21)

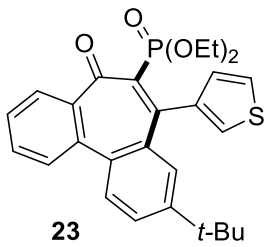
The general procedure (A) was followed using **1s** (128.4 mg, 0.30 mmol) and **2** (103.4 mg, 0.75 mmol). Purification by column chromatography on silica gel (petroleum ether/ EtOAc = 1:1) yielded **21** (104.9 mg, 62%) as a white solid. **M.p.**: 126–128 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.8 Hz, 1H), 7.66–7.60 (m, 2H), 7.53–7.49 (m, 2H), 7.46 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.07 (d, *J* = 1.8 Hz, 1H), 4.19–3.52 (m, 13H), 1.27 (t, *J* = 6.6 Hz, 3H), 1.14 (s, 9H), 0.94 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 197.5 (d, *J* = 7.6 Hz), 154.0 (d, *J* = 6.0 Hz), 152.8, 150.1, 144.1 (d, *J* = 4.5 Hz), 138.5, 136.2 (d, *J* = 7.6 Hz), 135.9, 135.8, 135.6, 133.6 (d, *J* = 181.2 Hz), 131.1, 130.7, 130.2, 128.4, 128.3, 126.9, 125.4, 63.2 (d, *J* = 6.0 Hz), 62.2 (d, *J* = 6.0 Hz), 61.1, 56.5, 51.6, 31.0, 16.5 (d, *J* = 6.0 Hz), 16.1 (d, *J* = 7.6 Hz). **^{31}P NMR** (243 MHz, $CDCl_3$) δ 12.23. **HR–MS** (ESI) *m/z* calc. for $C_{32}H_{37}O_7P$ $[M+H]^+$: 565.2350, found: 565.2349.



Diethyl(9-(*tert*-butyl)-7-(naphthalen-2-yl)-5-oxo-5*H*-dibenzo[a,c][7]annulen-6-

yl)phosphonate (22)

The general procedure (A) was followed using **1t** (116.4 mg, 0.30 mmol) and **2** (103.4 mg, 0.75 mmol). Purification by column chromatography on silica gel (petroleum ether/ EtOAc = 3:1) yielded **22** (47.2 mg, 30%) as a yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.85–7.84 (m, 3H), 7.68–7.64 (m, 2H), 7.55–7.47 (m, 5H), 7.03 (d, *J* = 1.8 Hz, 1H), 4.10–4.00 (m, 2H), 3.71 (s, 1H), 3.47 (s, 1H), 1.22–1.16 (m, 3H), 1.06 (s, 9H). 0.86 (t, *J* = 5.4 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 197.6 (d, *J* = 9.1 Hz), 154.2 (d, *J* = 4.5 Hz), 150.2, 144.3 (d, *J* = 4.5 Hz), 136.0 (d, *J* = 3.0 Hz), 135.8, 134.2 (d, *J* = 179.7 Hz), 133.3, 132.8, 131.1, 130.8, 130.1, 130.0, 128.6, 128.4, 128.3, 127.8, 127.6, 126.9, 126.7, 125.8, 125.5, 63.0 (d, *J* = 4.5 Hz), 62.3 (d, *J* = 6.0 Hz), 34.6, 31.0, 16.4 (d, *J* = 4.5 Hz), 16.0 (d, *J* = 6.0 Hz). **^{31}P NMR** (243 MHz, $CDCl_3$) δ 11.68. **HR–MS** (ESI) *m/z* calc. for $C_{33}H_{34}O_4P$ $[M+H]^+$: 525.2186, found: 525.2173.

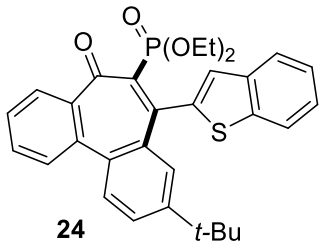


23

Diethyl(9-(*tert*-butyl)-5-oxo-7-(thiophen-3-yl)-5*H*-dibenzo[a,c][7]annulen-6-yl)phosphonate (23)

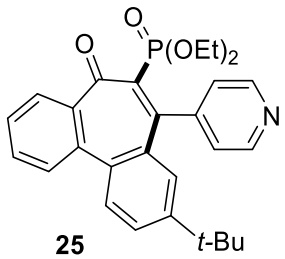
The general procedure (A) was followed using **1u** (103.2 mg, 0.30 mmol) and **2** (103.4 mg, 0.75 mmol). Purification by column chromatography on silica gel (petroleum ether/ EtOAc = 3:1) yielded **23** (49.0 mg, 34%) as a yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.81–7.179 (m, 2H), 7.65–7.60 (m, 2H), 7.53–7.50 (m, 2H), 7.47 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.32–7.30 (m, 1H), 7.04 (d, *J* = 1.8 Hz, 1H), 6.87 (d, *J* = 4.7 Hz, 1H), 4.16 (d, *J* = 7.2 Hz, 1H), 4.08–4.03 (m, 1H), 3.81–3.78 (m, 1H), 3.67–3.63 (m, 1H), 1.28 (t, *J* = 6.5 Hz, 3H), 1.16 (s, 9H), 1.03 (t, *J* = 6.0 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 197.5 (d, *J* = 9.1 Hz), 150.2, 149.1 (d, *J* = 4.5 Hz), 144.2 (d, *J* = 4.5 Hz), 140.2 (d, *J* = 7.6 Hz), 135.7, 135.6, 135.5, 133.8 (d, *J* = 179.7 Hz), 131.1, 130.7, 129.6, 129.4, 128.3, 128.3, 127.7, 126.9, 125.3, 125.3, 63.1 (d, *J* = 4.5 Hz), 62.3 (d, *J* = 4.5 Hz), 34.6, 31.0, 16.4 (d, *J* = 4.5 Hz), 16.1 (d, *J* = 6.0 Hz). **^{31}P NMR** (243 MHz, $CDCl_3$) δ 11.76. **HR–MS**

(ESI) *m/z* calc. for $C_{27}H_{30}O_4PS$ $[M+H]^+$: 481.1597, found: 481.1584.



Diethyl(7-(benzo[b]thiophen-2-yl)-9-(*tert*-butyl)-5-oxo-5*H*-dibenzo[a,c][7]annulen-6-yl)phosphonate (24)

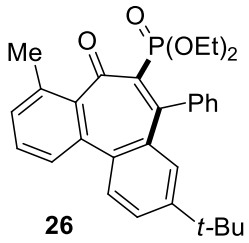
The general procedure (A) was followed using **1v** (118.2 mg, 0.30 mmol) and **2** (103.4 mg, 0.75 mmol). Purification by column chromatography on silica gel (petroleum ether/ EtOAc = 3:1) yielded **24** (55.7 mg, 35%) as a white solid. **M.p.**: 78–80 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.90 (d, J = 3.0 Hz, 1H), 7.83 (d, J = 7.8 Hz, 1H), 7.77 (d, J = 7.8 Hz, 1H), 7.68–7.65 (m, 1H), 7.63 (d, J = 7.8 Hz, 1H), 7.55–7.50 (m, 3H), 7.40 (dd, J = 1.2, 1.2 Hz, 1H) , 7.36–7.34 (m, 2H), 4.19–4.07 (m, 2H), 3.82–3.77 (m, 1H), 3.63–3.58 (m, 1H), 1.25 (t, J = 6.6 Hz, 3H), 1.15 (s, 9H), 0.89 (t, J = 6.6 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 197.0 (d, J = 9.1 Hz), 150.9, 146.6 (d, J = 4.5 Hz), 144.1 (d, J = 4.5 Hz), 141.7, 141.3 (d, J = 9.1 Hz), 139.0, 135.8, 135.7 (J = 179.7 Hz), 135.7 (d, J = 1.5 Hz), 134.5 (d, J = 18.1 Hz), 131.1, 130.9, 129.8, 128.6, 128.5, 128.4, 127.3, 125.4, 125.2, 124.7, 124.6, 122.2, 63.4 (d, J = 6.0 Hz), 62.6 (d, J = 7.6 Hz), 34.7, 31.0, 16.4 (d, J = 6.0 Hz), 16.0 (d, J = 7.6 Hz). **^{31}P NMR** (243 MHz, $CDCl_3$) δ 11.47. **HR–MS** (ESI) *m/z* calc. for $C_{31}H_{32}O_4PS$ $[M+H]^+$: 531.1754, found: 531.1740.



Diethyl(9-(*tert*-butyl)-5-oxo-7-(pyridin-4-yl)-5*H*-dibenzo[a,c][7]annulen-6-yl)phosphonate (25)

The general procedure (A) was followed using **1w** (101.3 mg, 0.30 mmol) and **2** (103.4 mg, 0.75 mmol). Purification by column chromatography on silica gel (petroleum ether/

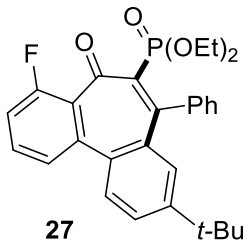
EtOAc = 3:1) yielded **25** (64.1 mg, 45%) as a yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.66 (s, 2H), 7.80 (d, J = 7.8 Hz, 1H), 7.67–7.62 (m, 2H), 7.55–7.51 (m, 2H), 7.48 (dd, J = 8.4, 2.4 Hz, 2H), 6.88 (d, J = 1.8 Hz, 1H), 4.15–4.04 (m, 2H), 3.86–3.82 (m, 1H), 3.67–3.66 (m, 1H), 1.22 (t, J = 6.6 Hz, 3H), 1.11 (s, 9H), 1.02 (t, J = 6.6 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 196.7 (d, J = 9.1 Hz), 150.9 (d, J = 4.5 Hz), 150.6, 149.5, 148.9 (d, J = 7.6 Hz), 143.9 (d, J = 4.5 Hz), 135.9 (d, J = 1.5 Hz), 135.7, 135.2 (d, J = 172.0 Hz), 134.8, 134.7, 131.4, 130.0, 129.2, 128.6, 128.5, 127.3, 125.5, 63.0 (d, J = 6.0 Hz), 62.2 (d, J = 6.0 Hz), 34.5, 30.9, 16.3 (d, J = 4.5 Hz), 16.0 (d, J = 6.0 Hz). **^{31}P NMR** (243 MHz, $CDCl_3$) δ 10.38. **HR–MS** (ESI) *m/z* calc. for $C_{28}H_{31}NO_4P$ $[M+H]^+$: 476.1985, found: 476.1971.



26

Diethyl(9-(*tert*-butyl)-4-methyl-5-oxo-7-phenyl-5*H*-dibenzo[a,c][7]annulen-6-yl)phosphonate (26)

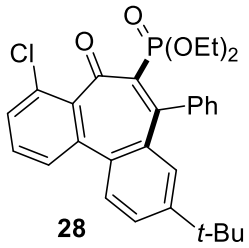
The general procedure (A) was followed using **1x** (105.6 mg, 0.30 mmol) and **2** (103.4 mg, 0.75 mmol). Purification by column chromatography on silica gel (petroleum ether/ EtOAc = 3:1) yielded **26** (76.1 mg, 52%) as a yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.57–7.53 (m, 2H), 7.46 (dd, J = 7.8, 7.8 Hz, 1H), 7.40–7.34 (m, 6H), 6.94 (s, 1H), 4.03–3.94 (m, 2H), 3.90–3.80 (m, 2H), 2.60 (s, 3H), 1.17 (t, J = 7.2 Hz, 3H), 1.11 (s, 9H), 1.06 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 197.5 (d, J = 9.1 Hz), 153.2 (d, J = 4.5 Hz), 149.8, 142.8 (d, J = 3.0 Hz), 140.2 (d, J = 9.1 Hz), 136.5, 136.2, 136.1 (d, J = 19.6 Hz), 143.4, 134.3 (d, J = 176.7 Hz), 131.1, 130.6, 130.1, 129.7, 129.1, 128.4, 127.7, 126.6, 126.4, 62.4 (d, J = 6.0 Hz), 62.3 (d, J = 6.0 Hz), 34.5, 31.0, 19.2, 16.3 (d, J = 7.6 Hz), 16.0 (d, J = 7.6 Hz). **^{31}P NMR** (243 MHz, $CDCl_3$) δ 11.84. **HR–MS** (ESI) *m/z* calc. for $C_{30}H_{34}O_4P$ $[M+H]^+$: 489.2189, found: 489.2173.



27

Diethyl(9-(*tert*-butyl)-4-fluoro-5-oxo-7-phenyl-5*H*-dibenzo[a,c][7]annulen-6-yl)phosphonate (27)

The general procedure (A) was followed using **1y** (106.8 mg, 0.30 mmol) and **2** (103.4 mg, 0.75 mmol). Purification by column chromatography on silica gel (petroleum ether/ EtOAc = 3:1) yielded **27** (85.6 mg, 58%) as a white solid. **M.p.**: 146–148 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.58–7.53 (m, 4H), 7.44–7.38 (m, 5H), 7.26–7.19 (m, 1H), 4.24–4.20 (m, 1H), 4.14–4.09 (m, 1H), 3.79–3.75 (m, 1H), 3.56–3.51 (m, 1H), 1.30 (t, J = 6.6 Hz, 3H), 1.00 (s, 9H), 0.95 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 192.0 (d, J = 9.1 Hz), 156.6 (d, J = 255.0 Hz), 153.9 (d, J = 5.6 Hz), 150.6, 140.3 (d, J = 9.1 Hz), 138.2, 136.3 (d, J = 19.6 Hz), 134.7, 134.6 (d, J = 182.2 Hz), 131.7 (d, J = 9.2 Hz), 130.7, 129.8, 128.8, 128.0, 126.7, 124.3 (d, J = 3.0 Hz), 115.3, 115.1, 63.3 (d, J = 6.0 Hz), 62.2 (d, J = 7.6 Hz), 34.6, 30.9, 16.3 (d, J = 6.0 Hz), 16.0 (d, J = 7.6 Hz). **^{31}P NMR** (243 MHz, $CDCl_3$) δ 10.82. **^{19}F NMR** (565 MHz, $CDCl_3$) δ –118.20. **HR–MS** (ESI) *m/z* calc. for $C_{29}H_{31}FO_4P$ $[M+H]^+$: 493.1939, found: 493.1939.

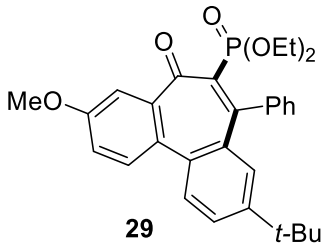


28

Diethyl(9-(*tert*-butyl)-4-chloro-5-oxo-7-phenyl-5*H*-dibenzo[a,c][7]annulen-6-yl)phosphonate (28)

The general procedure (A) was followed using **1z** (111.6 mg, 0.30 mmol) and **2** (103.4 mg, 0.75 mmol). Purification by column chromatography on silica gel (petroleum ether/ EtOAc = 3:1) yielded **28** (62.5 mg, 41%) as a white solid. **M.p.**: 57–59 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.64 (d, J = 7.8 Hz, 1H), 7.54 (d, J = 7.2 Hz, 1H), 7.51–7.50 (m, 2H), 7.42–7.38 (m, 6H), 6.96 (d, J = 2.4 Hz, 1H), 4.24–4.19 (m, 1H), 4.09–4.05 (m,

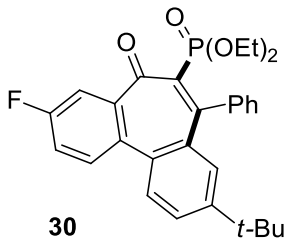
1H), 3.88–3.83 (m, 1H), 3.67–3.62 (m, 1H), 1.27 (t, *J* = 13.8, 6.6 Hz, 3H), 1.11 (s, 9H), 1.03 (t, *J* = 13.8, 6.6 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 193.3 (d, *J* = 9.1 Hz), 154.0 (d, *J* = 6.0 Hz), 150.7, 140.8 (d, *J* = 4.5 Hz), 139.9 (d, *J* = 9.1 Hz), 138.4, 136.3 (d, *J* = 21.1 Hz), 134.8, 134.6 (d, *J* = 179.7 Hz), 131.0, 130.8, 129.9, 129.8, 129.3, 129.1, 128.7, 127.9, 127.7, 126.7, 62.9 (d, *J* = 6.0 Hz), 62.3 (d, *J* = 7.6 Hz), 34.6, 30.9, 16.5 (d, *J* = 4.5 Hz), 16.2 (d, *J* = 6.0 Hz). **^{31}P NMR** (243 MHz, $CDCl_3$) δ 10.77. **HR–MS** (ESI) *m/z* calc. for $C_{29}H_{30}{}^{35}ClO_4P$ $[M+H]^+$: 509.1643, found: 509.1619.



29

Diethyl(9-(*tert*-butyl)-3-methoxy-5-oxo-7-phenyl-5*H*-dibenzo[a,c][7]annulen-6-yl) phosphonate (29)

The general procedure (A) was followed using **1z** (110.4 mg, 0.30 mmol) and **2** (103.4 mg, 0.75 mmol). Purification by column chromatography on silica gel (petroleum ether/ EtOAc = 3:1) yielded **29** (68.0 mg, 45%) as a yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.22 (d, *J* = 9.18 Hz, 1H), 7.60 (d, *J* = 8.4 Hz, 1H), 7.43–7.37 (m, 4H), 7.20 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.03 (d, *J* = 2.4 Hz, 1H), 6.93 (d, *J* = 1.8 Hz, 1H), 4.11–4.00 (m, 2H), 3.88 (s, 3H), 3.82 (s, 1H), 3.64–3.60 (m, 1H), 1.25–1.20 (m, 3H), 1.10 (s, 9H), 1.02 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 197.4 (d, *J* = 9.1 Hz), 159.6, 154.5 (d, *J* = 6.0 Hz), 149.2, 145.2 (d, *J* = 4.5 Hz), 140.9 (d, *J* = 7.6 Hz), 135.8 (d, *J* = 19.6 Hz), 135.7, 135.6, 132.9 (d, *J* = 179.7 Hz), 130.1, 130.0, 129.9, 128.7, 128.7, 127.9, 126.7, 118.5, 108.8, 62.7, 62.2, 55.7, 34.5, 30.9, 16.3, 16.2. **^{31}P NMR** (243 MHz, $CDCl_3$) δ 11.17. **HR–MS** (ESI) *m/z* calc. for $C_{30}H_{34}O_5P$ $[M+H]^+$: 505.2139, found: 505.2119.

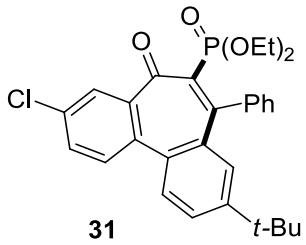


30

Diethyl(9-(*tert*-butyl)-4-fluoro-5-oxo-7-phenyl-5*H*-dibenzo[a,c][7]annulen-6-

yl)phosphonate (30)

The general procedure (A) was followed using **1b'** (106.8 mg, 0.30 mmol) and **2** (103.4 mg, 0.75 mmol). Purification by column chromatography on silica gel (petroleum ether/ EtOAc = 3:1) yielded **30** (90.0 mg, 61%) as a white solid. **M.p.**: 167–169 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.78 (dd, J = 8.4, 4.8 Hz, 1H), 7.55 (d, J = 8.4 Hz, 1H), 7.45–7.31 (m, 5H), 7.21 (dd, J = 7.8, 2.4 Hz, 1H), 6.96 (d, J = 1.8 Hz, 1H), 4.11–4.01 (m, 2H), 3.82–3.81 (m, 1H), 3.60–3.59 (m, 1H), 1.23 (t, J = 6.6 Hz, 3H), 1.10 (s, 9H), 1.01 (t, J = 6.6 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 196.2 (d, J = 9.1 Hz), 162.5 (d, J = 250.7 Hz), 154.6 (d, J = 4.5 Hz), 150.1, 145.5 (d, J = 12.1 Hz), 140.6 (d, J = 7.6 Hz), 136.0 (d, J = 25.7 Hz), 134.7, 133.2 (d, J = 179.7 Hz), 132.0 (d, J = 3.0 Hz), 130.5 (d, J = 7.6 Hz), 140.4, 130.1, 128.9, 128.0, 126.9, 118.3 (d, J = 22.7 Hz), 112.0 (d, J = 24.2 Hz), 62.9 (d, J = 4.5 Hz), 62.3 (d, J = 3.0 Hz), 34.6, 30.9, 16.3, 16.1 (d, J = 4.5 Hz). **^{31}P NMR** (243 MHz, $CDCl_3$) δ 11.35. **^{19}F NMR** (565 MHz, $CDCl_3$) δ –113.16. **HR–MS** (ESI) *m/z* calc. for $C_{29}H_{31}FO_4P$ $[M+H]^+$: 493.1939, found: 493.1922.

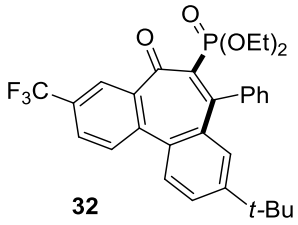


31

Diethyl(9-(*tert*-butyl)-3-chloro-5-oxo-7-phenyl-5*H*-dibenzo[a,c][7]annulen-6-yl)phosphonate (31)

The general procedure (A) was followed using **1c'** (111.6 mg, 0.30 mmol) and **2** (103.4 mg, 0.75 mmol). Purification by column chromatography on silica gel (petroleum ether/ EtOAc = 3:1) yielded **31** (85.3 mg, 56%) as a white solid. **M.p.**: 123–125 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.73 (d, J = 8.4 Hz, 1H), 7.60–7.56 (m, 2H), 7.49–7.56 (m, 5H), 6.96 (d, J = 2.4 Hz, 1H), 4.12–4.03 (m, 2H), 3.83–3.80 (m, 1H), 3.60–3.58 (m, 1H), 1.25 (t, J = 6.6 Hz, 3H), 1.11 (s, 9H), 1.01 (t, J = 6.6 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 196.1 (d, J = 7.6 Hz), 154.5 (d, J = 6.0 Hz), 150.5, 145.0 (d, J = 4.5 Hz), 140.6 (d, J = 7.6 Hz), 136.2 (d, J = 19.6 Hz), 134.6, 134.5, 134.2, 132.9, 131.1, 130.4, 130.2, 129.8, 128.9, 128.0, 126.9, 125.2, 63.0 (d, J = 6.0 Hz), 62.4 (d, J = 6.0 Hz), 34.6,

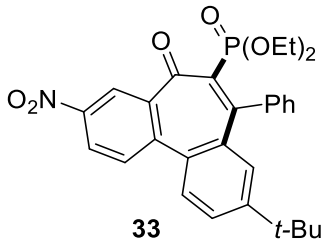
30.9, 19.4, 16.3 (d, J = 6.0 Hz), 16.1 (d, J = 6.0 Hz). **^{31}P NMR** (243 MHz, $CDCl_3$) δ 11.45. **HR–MS** (ESI) *m/z* calc. for $C_{29}H_{31}{}^{35}ClO_4P$ $[M+H]^+$: 509.1643, found: 509.1627.



32

Diethyl(9-(*tert*-butyl)-5-oxo-7-phenyl-3-(trifluoromethyl)-5*H*-dibenzo[a,c][7]annulen-6-yl)phosphonate (32)

The general procedure (A) was followed using **1d'** (121.8 mg, 0.30 mmol) and **2** (103.4 mg, 0.75 mmol). Purification by column chromatography on silica gel (petroleum ether/ EtOAc = 3:1) yielded **32** (178.9 mg, 55%) as a white solid. **M.p.**: 153–155 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.95 (d, J = 8.4 Hz, 1H), 7.90 (dd, J = 2.4, 1.8 Hz, 1H), 7.80 (s, 1H), 7.64 (d, J = 8.4 Hz, 1H), 7.52–7.43 (m, 4H), 7.02 (d, J = 1,8 Hz, 1H), 4.14–4.10 (m, 2H), 3.84–3.80 (m, 1H), 3.58–3.55 (m, 1H), 1.30 (t, J = 7.2 Hz, 3H), 1.14 (s, 9H), 1.02 (t, J = 6.6 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 196.3 (d, J = 9.0 Hz), 154.5 (d, J = 6.0 Hz), 151.2, 144.1 (d, J = 6.0 Hz), 140.4 (d, J = 7.6 Hz), 138.9, 136.5 (d, J = 19.6 Hz), 134.3, 133.2, 130.7, 130.3, 129.1, 129.0, 128.1, 127.5 (d, J = 2.0 Hz, 127.1, 123.9 (d, J = 271.8 Hz), 122.8 (d, J = 4.5 Hz), 62.9 (d, J = 6.0 Hz), 62.4 (d, J = 6.0 Hz), 34.7, 30.9, 16.2 (d, J = 7.6 Hz), 16.0 (d, J = 6.0 Hz). **^{31}P NMR** (243 MHz, $CDCl_3$) δ 10.76. **^{19}F NMR** (565 MHz, $CDCl_3$) δ –62.59. **HR–MS** (ESI) *m/z* calc. for $C_{30}H_{31}F_3O_4P$ $[M+H]^+$: 543.1907, found: 543.1890.

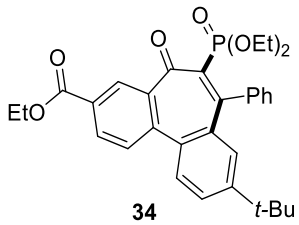


33

Diethyl(9-(*tert*-butyl)-3-nitro-5-oxo-7-phenyl-5*H*-dibenzo[a,c][7]annulen-6-yl)phosphonate (33)

The general procedure (A) was followed using **1e'** (114.9 mg, 0.30 mmol) and **2** (103.4 mg, 0.75 mmol). Purification by column chromatography on silica gel (petroleum ether/

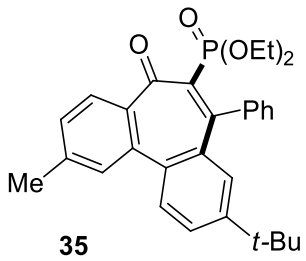
EtOAc = 3:1) yielded **33** (46.7 mg, 30%) as a white solid. **M.p.**: 103–105 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.46 (d, J = 7.8 Hz, 1H), 8.36 (s, 1H), 7.97 (d, J = 9 Hz, 1H), 7.64 (d, J = 7.8 Hz, 1H), 7.52–7.42 (m, 6H), 7.01 (s, 1H), 4.13–4.09 (m, 2H), 3.82–3.79 (m, 1H), 3.56–3.54 (m, 1H), 1.30 (t, J = 7.2 Hz, 3H), 1.12 (s, 9H), 1.00 (t, J = 6.6 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 195.4 (d, J = 9.1 Hz), 154.6 (d, J = 6.0 Hz), 152.1, 147.3, 144.4 (d, J = 4.5 Hz), 141.5, 140.2 (d, J = 7.6 Hz), 136.8 (d, J = 19.6 Hz), 133.7 (d, J = 178.2 Hz), 133.6, 130.8, 130.4, 129.7, 129.4, 129.2, 128.2, 127.2, 125.3, 121.1, 63.2 (d, J = 6.0 Hz), 62.6 (d, J = 6.0 Hz), 34.8, 30.9, 16.3 (d, J = 6.0 Hz), 16.1 (d, J = 6.0 Hz). **^{31}P NMR** (243 MHz, $CDCl_3$) δ 10.45 (s). **HR–MS** (ESI) *m/z* calc. for $C_{29}H_{31}NO_6P$ $[M+H]^+$: 520.1884, found: 520.1871.



34

Ethyl-9-(*tert*-butyl)-6-(diethoxyphosphoryl)-5-oxo-7-phenyl-5*H*-dibenzo[a,c][7]annulene-3-carboxylate (34)

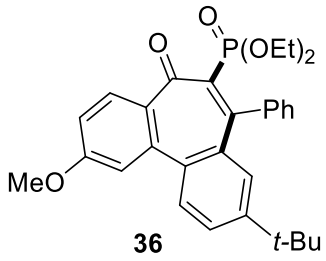
The general procedure (A) was followed using **1f'** (123.0 mg, 0.30 mmol) and **2** (103.4 mg, 0.75 mmol). Purification by column chromatography on silica gel (petroleum ether/ EtOAc = 3:1) yielded **34** (68.8 mg, 42%) as a yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.29 (dd, J = 8.4, 1.8 Hz, 1H), 8.20 (d, J = 1.8 Hz, 1H), 7.87 (d, J = 7.8 Hz, 1H), 7.63 (d, J = 8.4 Hz, 1H), 7.48–7.39 (m, 4H), 6.98 (d, J = 1.8 Hz, 1H), 4.43–4.39 (m, 2H), 4.11 (q, J = 7.2 Hz, 2H), 3.79–3.75 (m, 1H), 3.55–3.51 (m, 1H), 1.40 (t, J = 7.2 Hz, 3H), 1.30 (t, J = 6.6 Hz, 3H), 1.11 (s, 9H), 0.98 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 196.9 (d, J = 9.1 Hz), 165.7, 154.3 (d, J = 6.0 Hz), 151.0, 144.0 (d, J = 7.6 Hz), 140.5 (d, J = 7.5 Hz), 139.7, 136.5 (d, J = 21.1 Hz), 134.8, 133.8 (d, J = 179.7 Hz), 131.7, 130.7, 130.2, 130.1, 129.0, 128.5, 128.1, 127.0, 126.9, 63.0 (d, J = 6.0 Hz), 62.4 (d, J = 6.0 Hz), 61.5, 34.7, 30.9, 16.3 (d, J = 7.6 Hz), 16.1 (d, J = 6.0 Hz). **^{31}P NMR** (243 MHz, $CDCl_3$) δ 11.08. **HR–MS** (ESI) *m/z* calc. for $C_{32}H_{35}O_6P$ $[M+H]^+$: 547.2244, found: 547.2234.



35

Diethyl(9-(*tert*-butyl)-2-methyl-5-oxo-7-phenyl-5*H*-dibenzo[a,c][7]annulen-6-yl)phosphonate (35)

The general procedure (A) was followed using **1g'** (105.6 mg, 0.30 mmol) and **2** (103.4 mg, 0.75 mmol). Purification by column chromatography on silica gel (petroleum ether/ EtOAc = 3:1) yielded **35** (106.9 mg, 73%) as a yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.61–7.60 (m, 2H), 7.44–7.33 (m, 6H), 6.94 (d, J = 1.2 Hz, 1H), 4.13–4.00 (m, 2H), 3.80–3.76 (m, 1H), 3.59–3.55 (m, 1H), 2.52 (s, 3H), 1.27–1.24 (m, 3H), 1.11 (s. 9H), 0.98 (t, J = 9.0 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 197.4 (d, J = 9.1 Hz), 154.0 (d, J = 6.0 Hz), 149.9, 142.0 (d, J = 4.5 Hz), 141.4, 141.0 (d, J = 9.1 Hz), 136.3 (d, J = 19.6 Hz), 135.9, 135.9, 133.9 (d, J = 179.7 Hz), 130.6, 130.0, 129.1, 128.9, 128.7, 127.9, 126.7, 125.6, 62.9 (d, J = 6.0 Hz), 62.1 (d, J = 6.0 Hz), 34.6, 31.0, 21.9, 16.4 (d, J = 3.0 Hz), 16.1 (d, J = 6.0 Hz). **^{31}P NMR** (243 MHz, $CDCl_3$) δ 11.70. **HR–MS** (ESI) *m/z* calc. for $C_{30}H_{34}O_4P$ $[M+H]^+$: 489.2189, found: 489.2172.

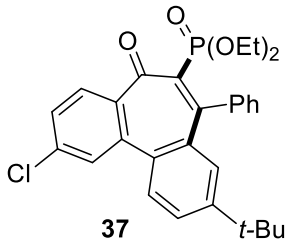


36

Diethyl(9-(*tert*-butyl)-2-methoxy-5-oxo-7-phenyl-5*H*-dibenzo[a,c][7]annulen-6-yl)phosphonate (36)

The general procedure (A) was followed using **1h'** (110.4 mg, 0.30 mmol) and **2** (103.4 mg, 0.75 mmol). Purification by column chromatography on silica gel (petroleum ether/ EtOAc = 3:1) yielded **36** (98.3 mg, 65%) as a white solid. **M.p.**: 159–161 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.62 (d, J = 8.4 Hz, 1H), 7.52–7.39 (m, 5H), 7.30 (d, J = 4.5 Hz, 1H), 7.06 (dd, J = 8.4, 6.0 Hz, 1H), 6.97 (d, J = 6.0 Hz, 1H), 4.14–4.04 (m, 2H), 3.96

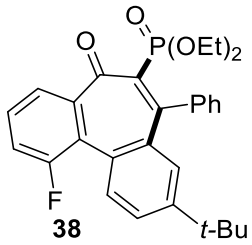
(s, 3H), 3.83–3.80 (m, 1H), 3.59–3.58 (m, 1H), 1.28–1.25 (m, 3H), 1.13 (s, 9H), 1.02–1.00 (m, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 196.5 (d, J = 9.1 Hz), 161.8, 153.7 (d, J = 4.5 Hz), 150.1, 141.0 (d, J = 9.1 Hz), 138.0 (d, J = 4.5 Hz), 137.9, 136.3 (d, J = 21.2 Hz), 135.7, 134.1 (d, J = 178.2 Hz), 130.5, 130.1, 128.7, 127.9, 127.7, 126.7, 114.1, 113.3, 62.9, 62.1, 55.7, 34.6, 30.9, 16.4 (d, J = 4.5 Hz), 16.1 (d, J = 6.0 Hz). **^{31}P NMR** (243 MHz, $CDCl_3$) δ 11.60. **HR–MS** (ESI) *m/z* calc. for $C_{30}H_{33}O_5P$ $[M+H]^+$: 505.2139, found: 505.2139.



37

Diethyl(9-(*tert*-butyl)-2-chloro-5-oxo-7-phenyl-5*H*-dibenzo[a,c][7]annulen-6-yl)phosphonate (37)

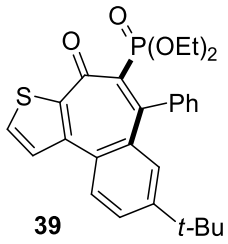
The general procedure (A) was followed using **1i'** (111.6 mg, 0.30 mmol) and **2** (103.4 mg, 0.75 mmol). Purification by column chromatography on silica gel (petroleum ether/ EtOAc = 3:1) yielded **37** (91.4 mg, 60%) as a yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.79 (d, J = 7.8 Hz, 1H), 7.65–7.46 (m, 6H), 7.38 (s, 2H), 6.95 (s, 1H), 4.16–4.03 (m, 2H), 3.84–3.81 (m, 1H), 3.72–3.68 (m, 1H), 1.26 (t, J = 6.6 Hz, 3H), 1.14 (s, 9H), 1.05 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 197.2 (d, J = 9.1 Hz), 152.8 (d, J = 4.5 Hz), 150.2, 144.2 (d, J = 4.5 Hz), 139.2 (d, J = 9.1 Hz), 135.8, 135.8, 135.8, 135.7, 135.7, 134.9, 134.2 (d, J = 178.2 Hz), 131.2, 130.8, 129.7, 128.3, 128.2, 127.0, 125.4, 63.1 (d, J = 6.0 Hz), 62.3 (d, J = 6.0 Hz), 34.6, 31.0, 16.4 (d, J = 4.5 Hz), 16.0 (d, J = 6.0 Hz). **^{31}P NMR** (243 MHz, $CDCl_3$) δ 11.00. **HR–MS** (ESI) *m/z* calc. for $C_{29}H_{31}{}^{35}ClO_4P$ $[M+H]^+$: 509.1643, found: 509.1625.



38

Diethyl(R)-(9-(*tert*-butyl)-1-fluoro-5-oxo-7-phenyl-5*H*-dibenzo[a,c][7]annulen-6-yl)phosphonate (38)

The general procedure (A) was followed using **1j'** (106.8 mg, 0.30 mmol) and **2** (103.4 mg, 0.75 mmol). Purification by column chromatography on silica gel (petroleum ether/ EtOAc = 3:1) yielded **38** (85.6 mg, 58%) as a yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.75–7.72 (m, 1H), 7.47–7.37 (m, 7H), 7.30 (dd, *J* = 7.2, 1.2 Hz, 1H), 6.97 (d, *J* = 1.8 Hz, 1H), 4.09–4.03 (m, 1H), 4.01–3.96 (m, 1H), 3.86–3.79 (m, 1H), 3.67–3.61 (m, 1H), 1.20 (t, *J* = 7.2 Hz, 3H), 1.12 (s, 9H), 1.02 (t, *J* = 6.6 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 196.4 (d, *J* = 6.0 Hz), 159.5 (d, *J* = 250.7 Hz), 154.3 (d, *J* = 4.5 Hz), 150.7, 147.0 (d, *J* = 4.5 Hz), 140.3 (d, *J* = 7.6 Hz), 136.7 (d, *J* = 19.6 Hz), 134.0 (d, *J* = 179.7 Hz), 131.6 (d, *J* = 7.6 Hz), 129.9, 129.7 (d, *J* = 9.1 Hz), 129.6, 129.3, 129.0, 128.0, 126.0, 123.5 (d, *J* = 13.6 Hz), 121.1 (d, *J* = 3.0 Hz), 118.7 (d, *J* = 24.2 Hz), 62.9 (d, *J* = 6.0 Hz), 62.4 (d, *J* = 6.0 Hz), 34.7, 30.9, 16.3 (d, *J* = 6.0 Hz), 16.1 (d, *J* = 6.0 Hz). **^{31}P NMR** (243 MHz, $CDCl_3$) δ 10.83. **^{19}F NMR** (565 MHz, $CDCl_3$) δ –115.20. **HR–MS** (ESI) *m/z* calc. for $C_{29}H_{31}FO_4P$ $[M+H]^+$: 493.1939, found: 493.1919.

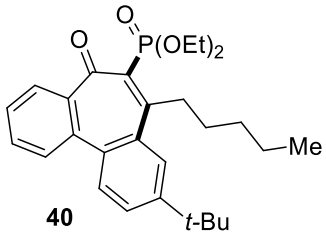


39

Diethyl(8-(*tert*-butyl)-4-oxo-6-phenyl-4*H*-benzo[3,4]cyclohepta[1,2-b]thiophen-5-yl)phosphonate (39)

The general procedure (A) was followed using **1k'** (103.2 mg, 0.30 mmol) and **2** (103.4 mg, 0.75 mmol). Purification by column chromatography on silica gel (petroleum ether/ EtOAc = 3:1) yielded **39** (109.4 mg, 76%) as a white solid. **M.p.**: 145–147 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 12.6 Hz, 1H), 7.68–7.64 (m, 2H), 7.59 (dd, *J* = 12.6, 3.0 Hz, 1H), 7.43–7.34 (m, 5H), 7.01 (d, *J* = 3.0 Hz, 1H), 4.00–3.90 (m, 2H), 3.81–3.71 (m, 2H), 1.10–1.06 (m, 15H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 186.5 (d, *J* = 9.1 Hz), 155.4 (d, *J* = 4.0 Hz), 149.5, 143.6 (d, *J* = 9.1 Hz), 142.5 (d, *J* = 8.1 Hz), 140.9, 135.9 (d, *J* = 19.2 Hz), 132.1, 132.1 (d, *J* = 182.8 Hz), 131.7, 130.8, 130.4, 128.7, 128.6, 127.9, 127.5, 127.3, 62.8, 62.7, 34.6, 30.8, 16.2, 16.1. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 13.19.

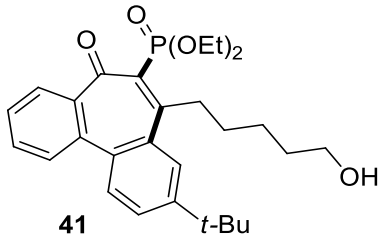
HR–MS (ESI) *m/z* calc. for $C_{27}H_{30}O_4PS$ $[M+H]^+$: 481.1597, found: 481.1576.



40

Diethyl(9-(*tert*-butyl)-5-oxo-7-pentyl-5*H*-dibenzo[a,c][7]annulen-6-yl)phosphonate (40)

The general procedure (A) was followed using **1l'** (99.6 mg, 0.30 mmol) and **2** (103.4 mg, 0.75 mmol). Purification by column chromatography on silica gel (petroleum ether/ EtOAc = 3:1) yielded **40** (25.3 mg, 18%) as a yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.69 (m, 2H), 7.57 (td, J = 7.8, 1.8 Hz, 1H), 7.53 (d, J = 7.8 Hz, 1H), 7.47–7.45 (m, 2H), 7.39 (dd, J = 7.8, 1.8 Hz, 1H), 4.31–4.26 (m, 1H), 4.24–4.20 (m, 1H), 4.07 (t, J = 7.2 Hz, 2H), 3.45–3.40 (m, 1H), 2.97–2.93 (m, 1H), 1.39 (t, J = 7.2 Hz, 3H), 1.36 (s, 9H), 1.31 (t, J = 6.6 Hz, 3H), 1.25–1.18 (m, 6H), 0.75 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 197.9 (d, J = 9.1 Hz), 156.8 (d, J = 7.6 Hz), 150.5, 145.1 (d, J = 4.5 Hz), 135.6, 135.4 (d, J = 1.5 Hz), 135.1, 134.9, 132.8 (d, J = 173.7 Hz), 131.1, 130.7, 127.9, 126.4, 124.8, 124.3, 63.2 (d, J = 4.5 Hz), 62.2 (d, J = 6.0 Hz), 34.9, 34.6 (d, J = 6.0 Hz), 31.8, 31.3, 28.7, 22.3, 16.5 (d, J = 7.6 Hz), 16.4 (d, J = 7.6 Hz), 14.0. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 11.74. **HR–MS** (ESI) *m/z* calc. for $C_{28}H_{38}O_4P$ $[M+H]^+$: 469.2502, found: 469.2482.

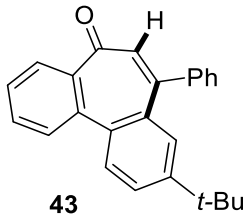


41

Diethyl(9-(*tert*-butyl)-7-(5-hydroxypentyl)-5-oxo-5*H*-dibenzo[a,c][7]annulen-6-yl)phosphonate (41)

The general procedure (A) was followed using **1m'** (104.4 mg, 0.30 mmol) and **2** (103.4 mg, 0.75 mmol). Purification by column chromatography on silica gel (petroleum ether/ EtOAc = 3:1) yielded **41** (33.4 mg, 23%) as a yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.71–7.68 (m, 2H), 7.58 (td, J = 7.2, 1.2 Hz, 1H), 7.53 (d, J = 8.4 Hz, 1H), 7.48–7.45

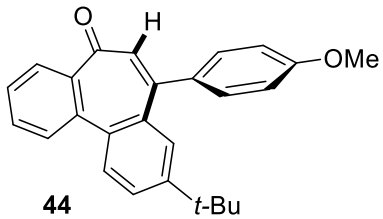
(m, 2H), 7.38 (dd, *J* = 7.2, 0.6 Hz, 1H), 4.32–4.22 (m, 2H), 4.10–4.05 (m, 2H), 3.52–3.45 (m, 3H), 1.80 (s, 4H), 1.40 (t, *J* = 6.6 Hz, 4H), 1.36 (s, 9H), 1.31 (t, *J* = 7.2 Hz, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$) *δ* 197.8 (d, *J* = 10.6 Hz), 156.7 (d, *J* = 7.6 Hz), 150.6, 145.0 (d, *J* = 4.5 Hz), 135.6, 135.4, 134.9 (d, *J* = 21.1 Hz), 132.3 (d, *J* = 175.2 Hz), 131.1, 130.8, 128.0 (d, *J* = 9.1 Hz), 128.5, 124.8, 124.4, 63.2 (d, *J* = 6.0 Hz), 62.7, 62.3 (d, *J* = 6.0 Hz), 34.9, 34.4 (d, *J* = 7.6 Hz), 32.1, 31.3, 28.7, 25.6, 16.5 (d, *J* = 7.6 Hz), 16.4 (d, *J* = 6.0 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) *δ* 11.74. **HR–MS** (ESI) *m/z* calc. for $C_{28}H_{38}O_5P$ $[M+H]^+$: 485.2452, found: 485.2429.



43

9-(*tert*-Butyl)-7-phenyl-5*H*-dibenzo[a,c][7]annulen-5-one (43)

The general procedure (B) was followed using **11** (71.1 mg, 0.15 mmol) and KOMe (42 mg, 0.6 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc = 10:1) yielded **43** (43.1 mg, 85%) as a yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) *δ* 7.91 (d, *J* = 7.9 Hz, 1H), 7.82 (dd, *J* = 7.7, 1.1 Hz, 1H), 7.74 (d, *J* = 8.4 Hz, 1H), 7.68 (td, *J* = 7.8, 1.2 Hz, 1H), 7.55 (d, *J* = 7.6 Hz, 1H), 7.52 (dd, *J* = 8.4, 2.1 Hz, 1H), 7.46–7.42 (m, 5H), 6.77 (s, 1H), 1.21 (s, 9H). **^{13}C NMR** (151 MHz, $CDCl_3$) *δ* 195.0, 150.4, 150.3, 142.5, 142.4, 137.6, 136.0, 135.1, 132.6, 131.6, 131.5, 129.8, 129.1, 128.7, 128.5, 128.5, 128.2, 127.7, 126.2, 34.7, 31.1. **HR–MS** (ESI) *m/z* calc. for $C_{25}H_{23}O$ $[M+H]^+$: 339.1744, found: 339.1730.

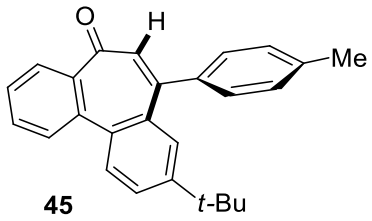


44

9-(*tert*-Butyl)-7-(4-methoxyphenyl)-5*H*-dibenzo[a,c][7]annulen-5-one (44)

The general procedure (B) was followed using **13** (75.6 mg, 0.15 mmol) and KOMe (42 mg, 0.6 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc = 10:1) yielded **44** (44.7 mg, 81%) as a yellow oil. **^{1}H NMR** (400 MHz,

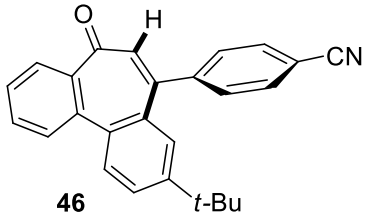
$CDCl_3$) δ 7.89 (d, J = 7.7 Hz, 1H), 7.81 (dd, J = 7.8, 1.4 Hz, 1H), 7.72 (d, J = 8.4 Hz, 1H), 7.67 (td, J = 7.7, 1.5 Hz, 1H), 7.55–7.50 (m, 2H), 7.38–7.34 (m, 3H), 6.93 (d, J = 8.8 Hz, 2H), 6.75 (s, 1H), 3.86 (s, 3H), 1.23 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 195.1, 160.1, 150.3, 149.9, 142.6, 137.5, 136.0, 135.2, 134.7, 131.8, 131.5, 130.4, 129.8, 128.6, 128.1, 127.6, 126.1, 113.9, 55.5, 34.7, 31.2. **HR–MS** (ESI) *m/z* calc. for $C_{26}H_{25}O_2$ $[M+H]^+$: 369.1849, found: 369.1835.



45

9-(*tert*-Butyl)-7-(*p*-tolyl)-5*H*-dibenzo[a,c][7]annulen-5-one (45)

The general procedure (B) was followed using **12** (73.2 mg, 0.15 mmol) and KOMe (42 mg, 0.6 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc = 10:1) yielded **45** (44.4 mg, 84%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 (d, J = 8.0 Hz, 1H), 7.81 (m, 1H), 7.73 (d, J = 8.4 Hz, 1H), 7.69–7.65 (m, 1H), 7.55–7.50 (m, 2H), 7.33–7.31 (m, 3H), 7.21 (d, J = 8.0 Hz, 2H), 6.76 (s, 1H), 2.41 (s, 3H), 1.23 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 190.1, 150.3, 150.3, 142.6, 139.4, 138.7, 137.6, 136.0, 135.2, 132.2, 131.6, 131.5, 129.8, 129.0, 128.6, 128.1, 127.7, 126.1, 34.7, 31.2, 21.4. **HR–MS** (ESI) *m/z* calc. for $C_{26}H_{25}O$ $[M+H]^+$: 353.1900, found: 353.1889.

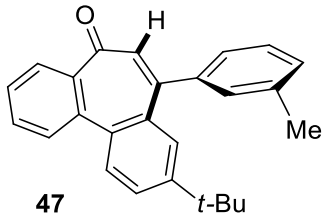


46

4-(9-(*tert*-Butyl)-5-oxo-5*H*-dibenzo[a,c][7]annulen-7-yl)benzonitrile (46)

The general procedure (B) was followed using **15** (74.6 mg, 0.15 mmol) and KOMe (42 mg, 0.6 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc = 10:1) yielded **46** (43.6 mg, 80%) as a white solid. **M.p.**: 164–166 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 (d, J = 7.6 Hz, 1H), 7.80–7.68 (m, 5H), 7.58–7.54 (m, 4H), 7.11 (d, J = 2.4 Hz, 1H), 6.73 (s, 1H), 1.21 (s, 9H). **^{13}C NMR** (101 MHz,

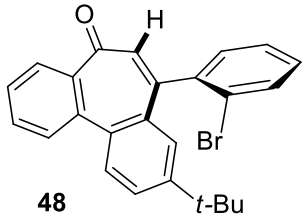
$CDCl_3$) δ 194.5, 150.9, 148.1, 147.2, 142.4, 137.5, 136.2, 134.1, 133.7, 132.5, 132.1, 132.0, 130.0, 129.9, 128.5, 128.0, 127.8, 126.9, 118.7, 112.6, 34.9, 31.2. **HR–MS** (ESI) *m/z* calc. for $C_{26}H_{22}NO$ $[M+H]^+$: 364.1696, found: 364.1696.



47

9-(*tert*-Butyl)-7-(*m*-tolyl)-5*H*-dibenzo[a,c][7]annulen-5-one (47)

The general procedure (B) was followed using **18** (73.2 mg, 0.15 mmol) and KOMe (42 mg, 0.6 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc = 10:1) yielded **47** (43.3 mg, 82%) as a white solid. **M.p.**: 106–108 °C. **^{1}H NMR** (400 MHz, CDCl3) δ 7.93 (d, *J* = 8.0 Hz, 1H), 7.86–7.84 (m, 1H), 7.76 (d, *J* = 8.4 Hz, 1H), 7.72–7.68 (m, 1H), 7.59–7.53 (m, 2H), 7.33–7.29 (m, 3H), 7.24 (d, *J* = 8.0 Hz, 2H), 6.80 (s, 1H), 2.40 (s, 3H), 1.25 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 195.0, 150.4, 150.3, 142.5, 142.3, 138.2, 137.6, 136.0, 135.2, 132.4, 131.6, 131.5, 129.8, 129.8, 129.4, 128.7, 128.3, 128.1, 127.7, 126.3, 126.1, 34.7, 31.1, 21.5. **HR–MS** (ESI) *m/z* calc. for $C_{26}H_{25}O$ $[M+H]^+$: 353.1900, found: 353.1903.

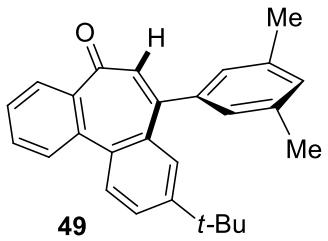


48

7-(2-Bromophenyl)-9-(*tert*-butyl)-5*H*-dibenzo[a,c][7]annulen-5-one (48)

The general procedure (B) was followed using **16** (82.8 mg, 0.15 mmol) and KOMe (42 mg, 0.6 mmol). Purification by column chromatography on silica gel (petroleum ether/ EtOAc = 10:1) yielded **48** (54.9 mg, 88%) as a white solid. **M.p.**: 135–137 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.8 Hz, 1H), 7.86 (d, *J* = 7.8 Hz, 1H), 7.77 (d, *J* = 8.4 Hz, 1H), 7.71–7.68 (m, 1H), 7.61 (d, *J* = 7.8 Hz, 1H), 7.56 (dd, *J* = 7.2, 7.2 Hz, 1H), 7.53–7.50 (m, 2H), 7.45 (dd, *J* = 7.8, 7.8 Hz, 1H), 7.30–7.26 (m, 1H), 7.07 (d, *J* = 1.8 Hz, 1H), 6.66 (s, 1H), 1.20 (s, 9H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 194.0, 150.8, 149.7, 142.8, 142.0, 137.7, 135.6, 134.5, 134.3, 133.2, 131.8, 131.7, 131.2, 130.0, 129.8, 128.2,

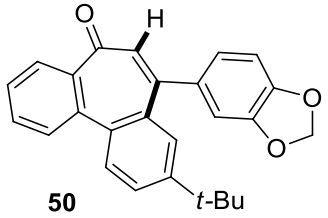
128.0, 127.7, 126.6, 126.2, 123.0, 34.6, 31.1. **HR–MS** (ESI) *m/z* calc. for $C_{25}H_{22}{}^{79}BrO$ $[M+H]^+$: 417.0849, found: 417.0851.



49

9-(*tert*-Butyl)-7-(3,5-dimethylphenyl)-5*H*-dibenzo[a,c][7]annulen-5-one (49)

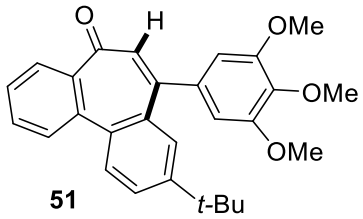
The general procedure (B) was followed using **19** (75.3 mg, 0.15 mmol) and KOMe (42 mg, 0.6 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc = 10:1) yielded **49** (47.2 mg, 86%) as a white solid. **M.p.**: 157–159 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.91 (d, J = 7.8 Hz, 1H), 7.82 (d, J = 7.8 Hz, 1H), 7.73 (d, J = 7.8 Hz, 1H), 7.67 (dd, J = 7.8, 7.8 Hz, 1H), 7.55–7.51 (m, 2H), 7.33 (d, J = 1.8 Hz, 1H), 7.04 (d, J = 9.6 Hz, 3H), 6.77 (s, 1H), 2.33 (s, 6H), 1.23 (s, 9H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 195.2, 150.5, 150.2, 142.5, 142.3, 138.0, 137.6, 136.0, 135.2, 132.2, 131.6, 131.5, 130.3, 129.8, 128.8, 128.1, 127.6, 127.0, 126.0, 34.7, 31.2, 21.4. **HR–MS** (ESI) *m/z* calc. for $C_{27}H_{27}O$ $[M+H]^+$: 367.2057, found: 367.2057.



50

7-(Benzo[d][1,3]dioxol-5-yl)-9-(*tert*-butyl)-5*H*-dibenzo[a,c][7]annulen-5-one (50)

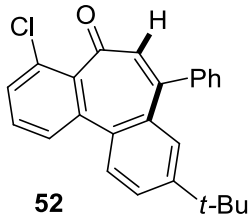
The general procedure (B) was followed using **20** (77.7 mg, 0.15 mmol) and KOMe (42 mg, 0.6 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc = 10:1) yielded **50** (45.8 mg, 80%) as a white solid. **M.p.**: 153–155 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 (d, J = 4.8 Hz, 1H), 7.80 (dd, J = 6.0, 2.4 Hz, 1H), 7.72–7.65 (m, 2H), 7.55–7.50 (m, 2H), 7.35 (d, J = 3.0 Hz, 1H), 6.93–6.90 (m, 2H), 6.83 (d, J = 8.4 Hz, 1H), 6.71 (s, 1H), 6.02 (s, 2H), 1.25 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 195.0, 150.3, 149.8, 148.2, 147.9, 142.6, 137.5, 136.4, 136.0, 135.1, 132.0, 131.6, 129.8, 128.5, 128.1, 127.6, 126.2, 123.2, 109.5, 108.3, 101.5, 34.8, 31.2, 29.6. **HR–MS** (ESI) *m/z* calc. for $C_{26}H_{23}O_3$ $[M+H]^+$: 383.1642, found: 383.1638.



51

9-(*tert*-Butyl)-7-(3,4,5-trimethoxyphenyl)-5*H*-dibenzo[a,c][7]annulen-5-one (51)

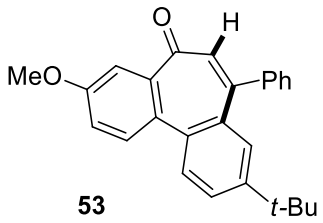
The general procedure (B) was followed using **21** (84.6 mg, 0.15 mmol) and KOMe (42 mg, 0.6 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc = 10:1) yielded **51** (52.6 mg, 82%) as a white solid. **M.p.**: 181–183 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.91 (d, J = 7.8 Hz, 1H), 7.82 (d, J = 8.4 Hz, 1H), 7.74 (d, J = 8.4 Hz , 1H), 7.68 (dd, J = 7.8, 7.8 Hz ,1H), 7.56–7.52 (m, 2H), 7.36 (d, J = 1.8 Hz, 1H), 6.78 (s, 1H), 6.64 (s, 2H), 3.91 (s, 3H), 3.83 (s, 6H), 1.21 (s, 9H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 195.0, 153.2, 150.4, 150.1, 142.5, 138.5, 137.9, 137.5, 136.1, 134.8, 132.1, 131.7, 131.6, 129.9, 128.7, 128.2, 127.6, 126.2, 106.5, 61.2, 56.4, 34.8, 31.2. **HR–MS** (ESI) *m/z* calc. for $C_{28}H_{29}O_4$ $[M+H]^+$: 429.2061, found: 429.2060.



52

9-(*tert*-Butyl)-4-chloro-7-phenyl-5*H*-dibenzo[a,c][7]annulen-5-one (52)

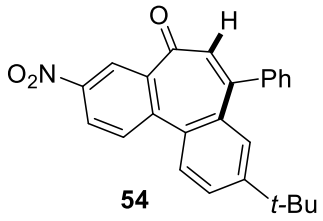
The general procedure (B) was followed using **28** (76.2 mg, 0.15 mmol) and KOMe (42 mg, 0.6 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc = 10:1) yielded **52** (48.5 mg, 87%) as a white solid. **M.p.**: 183–185 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71–7.67 (m, 2H), 7.56–7.46 (m, 3H), 7.39 (m, 5H), 7.25 (d, J = 2.0 Hz, 1H), 6.79 (s, 1H), 1.21 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 194.9, 150.9, 147.1, 141.1, 140.4, 138.8, 135.3, 134.8, 131.5, 131.1, 130.6, 129.7, 129.2, 128.9, 128.8, 128.6, 128.5, 127.8, 125.8, 34.8, 31.1. **HR–MS** (ESI) *m/z* calc. for $C_{25}H_{22}{}^{35}ClO$ $[M+H]^+$: 373.1354, found: 373.1349.



53

9-(*tert*-Butyl)-3-methoxy-7-phenyl-5*H*-dibenzo[a,c][7]annulen-5-one (53)

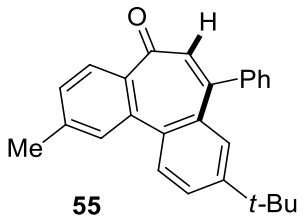
The general procedure (B) was followed using **29** (75.6 mg, 0.15 mmol) and KOMe (42 mg, 0.6 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc = 10:1) yielded **53** (44.2 mg, 80%) as a white solid. **M.p.**: 129–131 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.87 (d, J = 9.0 Hz, 1H), 7.73 (d, J = 8.4 Hz, 1H), 7.54–7.52 (m, 1H), 7.46–7.42 (m, 5H), 7.37 (d, J = 3.0 Hz, 1H), 7.29–7.27 (m, 2H), 6.79 (s, 1H), 3.95 (s, 3H), 1.23 (s, 9H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 194.4, 159.6, 150.7, 149.6, 143.4, 142.6, 135.8, 134.6, 132.1, 131.5, 131.1, 130.7, 129.1, 128.7, 128.6, 128.5, 126.2, 119.7, 110.1, 55.8, 34.6, 31.1. **HR–MS** (ESI) *m/z* calc. for $C_{26}H_{25}O_2$ $[M+H]^+$: 369.1849, found: 369.1841.



54

9-(*tert*-Butyl)-3-nitro-7-phenyl-5*H*-dibenzo[a,c][7]annulen-5-one (54)

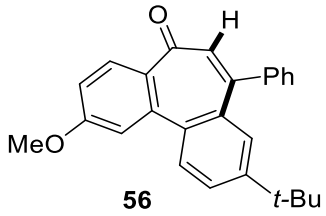
The general procedure (B) was followed using **33** (77.9 mg, 0.15 mmol) and KOMe (42 mg, 0.6 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc = 10:1) yielded **54** (48.8 mg, 85%) as a white solid. **M.p.**: 189–191 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.68 (d, J = 2.5 Hz, 1H), 8.47 (dd, J = 8.7, 2.5 Hz, 1H), 8.06 (d, J = 8.4 Hz, 1H), 7.75 (d, J = 8.4 Hz, 1H), 7.58 (dd, J = 8.4, 2.1 Hz, 1H), 7.44–7.41 (m, 5H), 7.32 (d, J = 2.0 Hz, 1H), 6.79 (s, 1H), 1.22 (s, 9H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 192.6, 152.3, 151.4, 147.3, 143.0, 142.9, 141.7, 135.7, 134.0, 132.1, 131.8, 131.2, 129.2, 129.1, 129.0, 128.7, 126.8, 125.6, 123.4, 34.9, 31.0. **HR–MS** (ESI) *m/z* calc. for $C_{25}H_{22}NO_3$ $[M+H]^+$: 384.1594, found: 384.1584.



55

9-(*tert*-Butyl)-2-methyl-7-phenyl-5*H*-dibenzo[a,c][7]annulen-5-one (55)

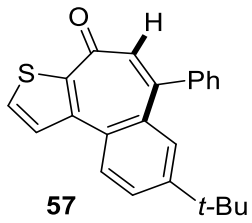
The general procedure (B) was followed using **35** (73.2 mg, 0.15 mmol) and KOMe (42 mg, 0.6 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc = 10:1) yielded **55** (44.9 mg, 85%) as a white solid. **M.p.**: 143–145 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.77 (d, J = 7.8 Hz, 2H), 7.73 (s, 1H), 7.54 (dd, J = 8.4 Hz, 2.4 Hz 1H), 7.46–7.42 (m, 5H), 7.39 (d, J = 7.8 Hz, 1H), 7.29–7.28 (m, 1H), 6.79 (s, 1H), 2.56 (s, 3H), 1.20 (s, 9H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 194.6, 150.2, 150.0, 142.5, 142.1, 140.2, 137.6, 136.1, 135.2, 132.8, 131.5, 130.4, 129.2, 129.1, 128.6, 128.5, 128.5, 127.9, 126.1, 34.7, 31.1, 21.9. **HR–MS** (ESI) *m/z* calc. for $C_{26}H_{25}O$ $[M+H]^+$: 353.1900, found: 353.1890.



56

9-(*tert*-Butyl)-2-methoxy-7-phenyl-5*H*-dibenzo[a,c][7]annulen-5-one (56)

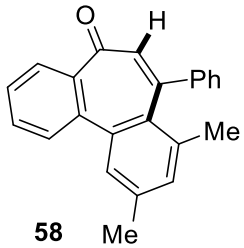
The general procedure (B) was followed using **36** (75.6 mg, 0.15 mmol) and KOMe (42 mg, 0.6 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc = 10:1) yielded **56** (45.3 mg, 82%) as a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85 (d, J = 8.7 Hz, 1H), 7.76 (d, J = 8.4 Hz, 1H), 7.54 (dd, J = 8.4, 2.2 Hz, 1H), 7.46–7.41 (m, 5H), 7.39 (d, J = 2.5 Hz, 1H), 7.29 (d, J = 3.3 Hz, 1H), 7.11 (dd, J = 8.7, 2.5 Hz, 1H), 6.78 (s, 1H), 3.98 (s, 3H), 1.23 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 193.5, 162.2, 150.5, 149.6, 142.5, 139.8, 136.2, 135.9, 135.2, 133.1, 131.5, 130.2, 129.1, 128.6, 128.6, 128.5, 126.2, 114.6, 114.2, 55.7, 34.7, 31.1. **HR–MS** (ESI) *m/z* calc. for $C_{26}H_{25}O_2$ $[M+H]^+$: 369.1849, found: 369.1841.



57

8-(*tert*-Butyl)-6-phenyl-4*H*-benzo[3,4]cyclohepta[1,2-b]thiophen-4-one (57)

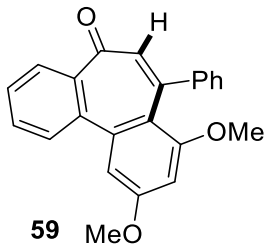
The general procedure (B) was followed using **39** (72.0 mg, 0.15 mmol) and KOMe (42 mg, 0.6 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc = 10:1) yielded **57** (40.2 mg, 78%) as a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.14 (d, J = 8.6 Hz, 1H), 7.91 (d, J = 5.5 Hz, 1H), 7.78 (d, J = 5.4 Hz, 1H), 7.62 (dd, J = 8.5, 2.2 Hz, 1H), 7.46–7.37 (m, 6H), 6.99 (s, 1H), 1.18 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 182.4, 152.7, 150.6, 145.6, 144.4, 141.3, 134.4, 132.8, 132.3, 131.8, 131.3, 129.6, 129.2, 128.9, 128.4, 128.3, 127.5, 34.8, 31.0. **HR–MS** (ESI) *m/z* calc. for $C_{23}H_{21}OS$ $[M+H]^+$: 345.1308, found: 345.1301.



58

8,10-Dimethyl-7-phenyl-5*H*-dibenzo[a,c][7]annulen-5-one (58)

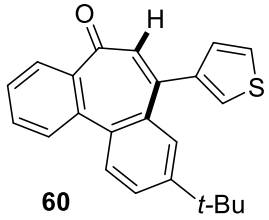
The general procedure (B) was followed using **4** (66.9 mg, 0.15 mmol) and KOMe (42 mg, 0.6 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc = 10:1) yielded **58** (40.2 mg, 85%) as a yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.92 (d, J = 8.4 Hz, 1H), 7.64–7.61 (m, 2H), 7.48–7.46 (m, 1H), 7.35 (s, 1H), 7.32–7.26 (m, 5H), 7.00 (s, 1H), 6.77 (s, 1H), 2.41 (s, 3H), 1.83 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 197.1, 146.8, 144.2, 142.8, 138.8, 138.5, 138.0, 147.9, 133.0, 132.2, 131.6, 131.4, 129.8, 129.3, 128.8, 128.3, 127.9, 126.8, 126.3, 23.5, 21.4. **HR–MS** (ESI) *m/z* calc. for $C_{23}H_{19}O$ $[M+H]^+$: 311.1431, found: 311.1413.



59

8,10-Dimethoxy-7-phenyl-5*H*-dibenzo[a,c][7]annulen-5-one (59)

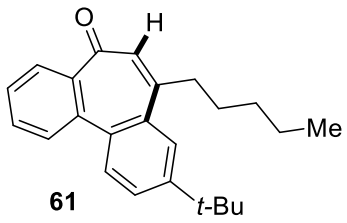
The general procedure (B) was followed using **3** (71.7 mg, 0.15 mmol) and KOMe (42 mg, 0.6 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc = 5:1) yielded **59** (45.1 mg, 88%) as a white solid. **M.p.**: 156–158 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 (d, J = 7.7 Hz, 1H), 7.70 (dd, J = 7.7, 1.3 Hz, 1H), 7.66 (td, J = 7.7, 1.4 Hz, 1H), 7.53 (td, J = 7.5, 0.9 Hz, 1H), 7.31–7.26 (m, 5H), 6.85 (d, J = 2.4 Hz, 1H), 6.66 (s, 1H), 6.51 (d, J = 2.4 Hz, 1H), 3.92 (s, 3H), 3.37 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 196.3, 160.2, 159.5, 145.5, 144.0, 143.8, 140.6, 137.7, 132.2, 131.3, 129.3, 128.5, 128.1, 127.5, 126.8, 125.8, 118.5, 107.5, 99.6, 55.8, 55.6. **HR–MS** (ESI) *m/z* calc. for $C_{23}H_{19}O_3$ $[M+H]^+$: 343.1329, found: 343.1327.



60

9-(*tert*-Butyl)-7-(thiophen-3-yl)-5*H*-dibenzo[a,c][7]annulen-5-one (60)

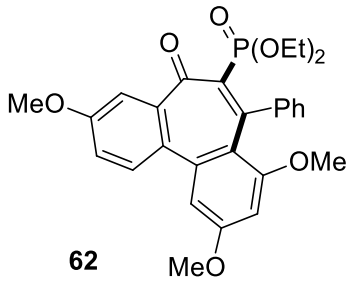
The general procedure (B) was followed using **23** (72.0 mg, 0.15 mmol) and KOMe (42 mg, 0.6 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc = 10:1) yielded **60** (40.2 mg, 78%) as a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 (d, J = 7.7 Hz, 1H), 7.79 (dd, J = 7.8, 1.3 Hz, 1H), 7.72 (d, J = 8.4 Hz, 1H), 7.67 (td, J = 7.7, 1.5 Hz, 1H), 7.55–7.51 (m, 2H), 7.48 (d, J = 2.1 Hz, 1H), 7.45 (dd, J = 3.0, 1.3 Hz, 1H), 7.37 (dd, J = 5.0, 3.0 Hz, 1H), 7.13 (dd, J = 5.0, 1.3 Hz, 1H), 6.86 (s, 1H), 1.27 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 195.2, 150.4, 144.7, 143.0, 142.6, 137.5, 135.7, 134.6, 131.6, 131.6, 129.7, 128.4, 128.2, 128.0, 127.6, 126.3, 126.1, 125.2, 34.8, 31.2. **HR–MS** (ESI) *m/z* calc. for $C_{23}H_{21}OS$ $[M+H]^+$: 345.1308, found: 345.1292.



61

9-(*tert*-Butyl)-7-pentyl-5*H*-dibenzo[a,c][7]annulen-5-one (61)

The general procedure (B) was followed using **41** (72.6 mg, 0.15 mmol) and KOMe (42 mg, 0.6 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc = 10:1) yielded **61** (39.8 mg, 80%) as a yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.81 (d, J = 7.8 Hz, 1H), 7.77 (dd, J = 7.8, 1.2 Hz, 1H), 7.72 (d, J = 1.8 Hz, 1H), 7.68 (d, J = 8.4 Hz, 1H), 7.63 (td, J = 7.8, 1.2 Hz, 1H), 7.52–7.50 (m, 2H), 6.58 (s, 1H), 2.82 (t, J = 7.8 Hz, 2H), 1.55–1.53 (m, 2H), 1.40 (s, 9H), 1.30–1.28 (m, 4H), 0.83 (t, J = 7.0 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 194.9, 150.7, 149.8, 142.3, 137.5, 135.4, 134.7, 132.2, 132.0, 131.3, 129.8, 127.9, 127.4, 125.8, 123.9, 37.6, 34.9, 31.8, 31.4, 28.8, 22.5, 14.1. **HR–MS** (ESI) *m/z* calc. for $C_{24}H_{29}O$ $[M+H]^+$: 333.2213, found: 333.2203.

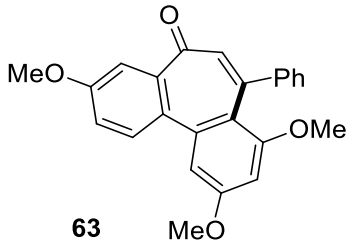


62

Diethyl(3,8,10-trimethoxy-5-oxo-7-phenyl-5*H*-dibenzo[a,c][7]annulen-6-yl)phosphonate (62)

The general procedure (A) was followed using **1n'** (111.6 mg, 0.30 mmol) and **2** (103.4 mg, 0.75 mmol). Purification by column chromatography on silica gel (petroleum ether/ EtOAc = 1:1) yielded **62** (91.4 mg, 60%) as a white solid. **M.p.**: 148–150 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.79 (d, J = 8.4 Hz, 1H), 7.29–7.25 (m, 5H), 7.15 (d, J = 8.4 Hz, 1H), 7.00 (s, 1H), 6.69 (s, 1H), 6.31 (s, 1H), 4.03–3.99 (m, 2H), 3.88–3.84 (m, 6H), 3.81–3.77 (m, 1H), 3.75–3.71 (m, 1H), 3.21 (s, 3H), 1.45 (t, J = 6.6 Hz, 3H), 1.04 (t, J = 6.6 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 197.7 (d, J = 10.6 Hz), 160.8, 160.4, 159.7, 151.1 (d, J = 6.0 Hz), 145.9 (d, J = 4.5 Hz), 141.8 (d, J = 7.6 Hz), 140.0, 132.2

(d, *J* = 175.2 Hz), 129.4, 128.7, 127.7, 126.9, 119.8, 119.7, 117.7, 109.0, 106.1, 99.1, 62.3 (d, *J* = 4.5 Hz), 62.1 (d, *J* = 6.0 Hz), 55.6, 55.5, 55.4, 16.1 (d, *J* = 1.5 Hz), 16.0 (d, *J* = 3.0 Hz). **^{31}P NMR** (243 MHz, $CDCl_3$) δ 10.64. **HR–MS** (ESI) *m/z* calc. for $C_{28}H_{30}O_7P$ $[M+H]^+$: 509.1724, found: 509.1718.

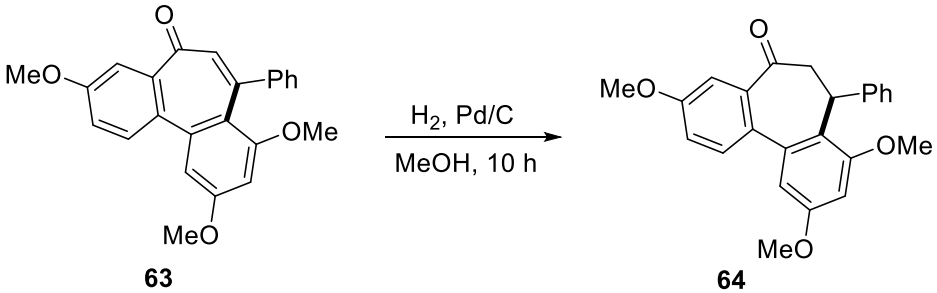


63

3,8,10-Trimethoxy-7-phenyl-5*H*-dibenzo[a,c][7]annulen-5-one (63)

The general procedure (B) was followed using **62** (76.2 mg, 0.15 mmol) and KOMe (42 mg, 0.6 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc = 5:1) yielded **43** (47.5 mg, 85%) as a yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.4 Hz, 1H), 7.30–7.25 (m, 5H), 7.22–7.20 (m, 2H), 7.81 (d, *J* = 2.4 Hz, 1H), 6.64 (s, 1H), 6.47 (d, *J* = 2.4 Hz, 1H), 3.91 (d, *J* = 1.8 Hz, 6H), 3.35 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 195.9, 160.2, 159.8, 159.5, 146.0, 144.8, 144.2, 140.3, 131.7, 131.0, 130.7, 128.0, 127.4, 125.8, 118.8, 118.2, 109.8, 107.0, 99.0, 55.8, 55.7, 55.5. **HR–MS** (ESI) *m/z* calc. for $C_{24}H_{21}O_4$ $[M+H]^+$: 373.1435, found: 373.1427.

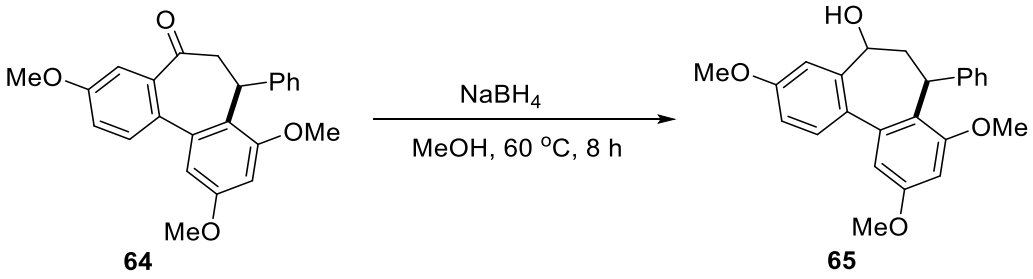
4. Synthesis of NSC 51046 analogue 66



63 **64**

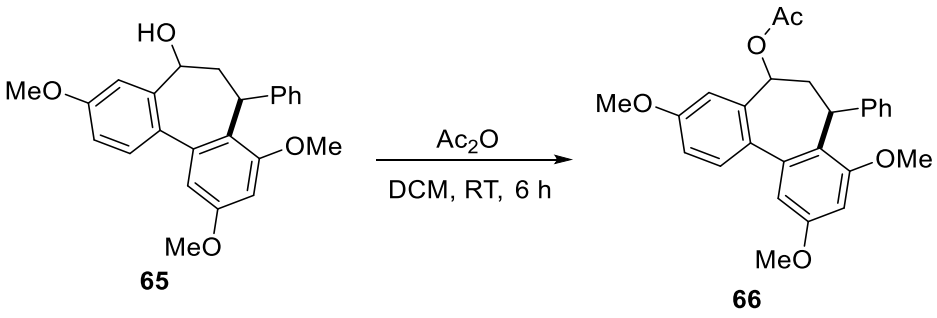
63 (0.3 mmol, 101.1 mg) was placed into a flask, MeOH (5 mL) was added and the solution was stirred until the solid was completely dissolved. 10% Pd/C (20 mg, 0.02 mmol) was added and the solution purged with H_2 three times. The solution was kept stirring at room temperature for 10 h. Then the solution was diluted with CH_2Cl_2 and transferred to a round bottom flask. Silica was added to the flask and volatiles were

evaporated under vacuum. The purification was performed by flash column chromatography on silica gel (petroleum ether/ ethyl acetate = 5:1) to obtain product **64** (71.2 mg, 70% yield) as a white solid (Pay attention! TLC shows that the polarities of the two compounds **63** and **64** are very similar). **M.p.**: 136–138 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.14 (d, J = 8.6 Hz, 1H), 7.06 (d, J = 2.8 Hz, 1H), 6.98 (dd, J = 8.0, 8.0 Hz, 2H), 6.91–6.85 (m, 4H), 6.56 (dd, J = 10.8, 2.4 Hz, 2H), 5.16 (t, J = 3.7 Hz, 1H), 3.87 (s, 6H), 3.80 (dd, J = 20.0, 4.8 Hz, 1H), 3.74 (s, 3H), 3.23 (dd, J = 19.8, 3.7 Hz, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 204.2, 159.7, 158.8, 157.5, 141.4, 141.2, 139.3, 132.7, 131.6, 127.7, 126.8, 125.3, 123.4, 119.4, 111.9, 107.8, 97.8, 56.2, 55.5, 55.5, 49.7, 33.1. **HR–MS** (ESI) *m/z* calc. for $C_{24}H_{23}O_4$ $[M+H]^+$: 375.1591; found: 375.1581.



64 **65**

To a Schlenk tube containing **64** (64.8 mg, 0.2 mmol) and $NaBH_4$ (15.2 mg, 0.4 mmol) were added. 2.0 mL MeOH was added via syringe. The solution was stirred for 8 hours at 60 °C. Afterwards, the reaction mixture was quenched by addition of H_2O (5 mL), and then the aqueous solution was extracted with ethyl acetate (3 × 10 mL). The combined organic phases were dried over Na_2SO_4 and the solvent removed in vacuo. The crude compound was purified by silica gel chromatography (petroleum ether/ethyl acetate = 5:1) to give the corresponding amine **65** (60.2 mg, 80 %) as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.24 (d, J = 2.4 Hz, 1H), 6.93–6.86 (m, 4H), 6.68–6.63 (m, 3H), 6.56 (d, J = 2.4 Hz, 1H), 6.42 (d, J = 2.4 Hz, 1H), 5.06 (d, J = 8.4 Hz, 1H), 4.87–4.84 (m, 1H), 3.93 (s, 3H), 3.85 (s, 6H), 3.00–2.95 (m, 1H), 2.75 (m, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 159.5, 159.1, 157.6, 145.0, 143.3, 141.9, 130.9, 129.5, 126.9, 124.4, 123.8, 112.6, 106.4, 97.4, 69.8, 56.1, 55.5, 55.4, 43.1. **HR-MS** (ESI) *m/z* calc. for $C_{24}H_{25}O_4$ $[M+H]^+$: 377.1748, found: 377.1736.

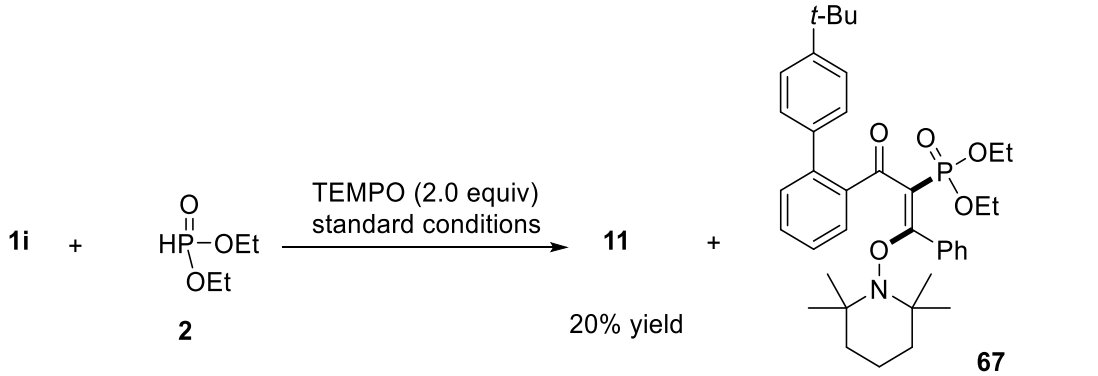


To a solution of amine **65** (56.4 mg, 0.15 mmol) in CH_2Cl_2 (5 mL) was added acetic anhydride (33 μL, 0.37 mmol) at 0 °C. The reaction was allowed to warm to room temperature and was then stirred for 6 h before concentration in vacuo.[3] The crude compound was purified by silica gel chromatography (petroleum ether/ethyl acetate = 5:1) and the corresponding amide **66** (60.0 mg, 95% yield) was obtained as a yellow oil (Pay attention! TLC shows that the polarities of the two compounds **65** and **66** are very similar). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.97 (d, J = 2.6 Hz, 1H), 6.90–6.83 (m, 3H), 6.68 (d, J = 12.0 Hz, 2H), 6.61 (dd, J = 8.4, 2.7 Hz, 1H), 6.54 (d, J = 2.5 Hz, 1H), 6.42 (d, J = 2.5 Hz, 1H), 5.87–5.82 (m, 1H), 5.06 (d, J = 9.0 Hz, 1H), 3.89 (s, 3H), 3.84 (s, 3H), 3.81 (s, 3H), 3.00–2.92 (m, 1H), 2.83–2.76 (m, 1H), 2.20 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.8, 159.3, 159.3, 157.7, 144.8, 141.5, 139.4, 131.1, 129.9, 127.2, 126.8, 124.5, 123.2, 111.9, 108.9, 106.6, 97.7, 71.6, 56.1, 55.5, 55.5, 40.1, 29.8, 21.4. **HR-MS** (ESI) *m/z* calc. for $C_{26}H_{27}O_5$ $[M+H]^+$: 419.1853, found: 419.1822.

5. Mechanistic Studies

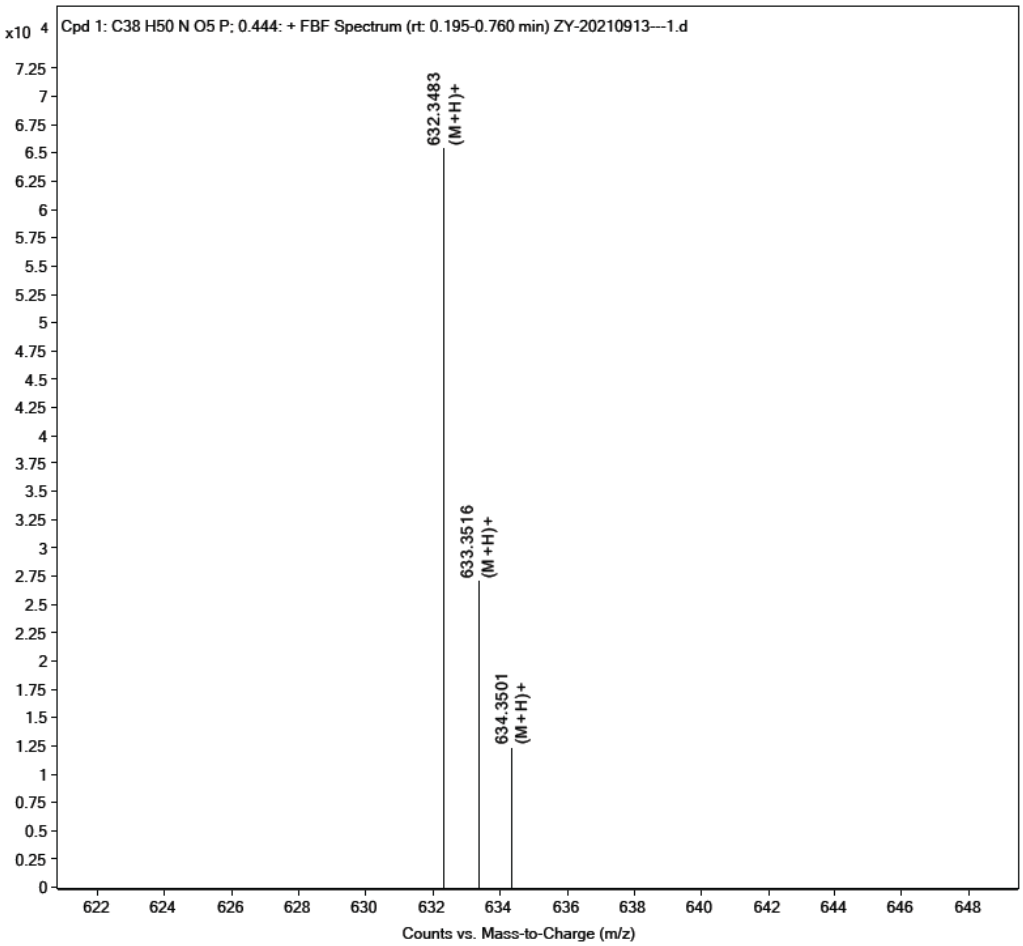
5.1 Radical Trapping Experiment

To a 25 mL Schlenk tube containing **1i** (0.2 mmol, 1.0 equiv.), **2** (0.4 mmol, 2.0 equiv.), $AgNO_3$ (0.04 mmol, 0.2 equiv.), $K_2S_2O_8$ (0.5 mmol, 2.5 equiv.) and 2,2,6,6-tetramethyl-1-piperidinyloxy (62mg, TEMPO, 0.4 mmol, 2.0 equiv) were added 1,4-dioxane/H_2O (v/v = 1:1, 2 mL) under a N_2 atmosphere. The sealed tube was stirred at 70 °C for 2 h, then cooled to room temperature. HRMS analysis of this reaction mixture showed that TEMPO-adduct **67** was formed. Purification by column chromatography on silica gel (petroleum ether/EtOAc = 1:1) delivered product **11** with only 20% yield.

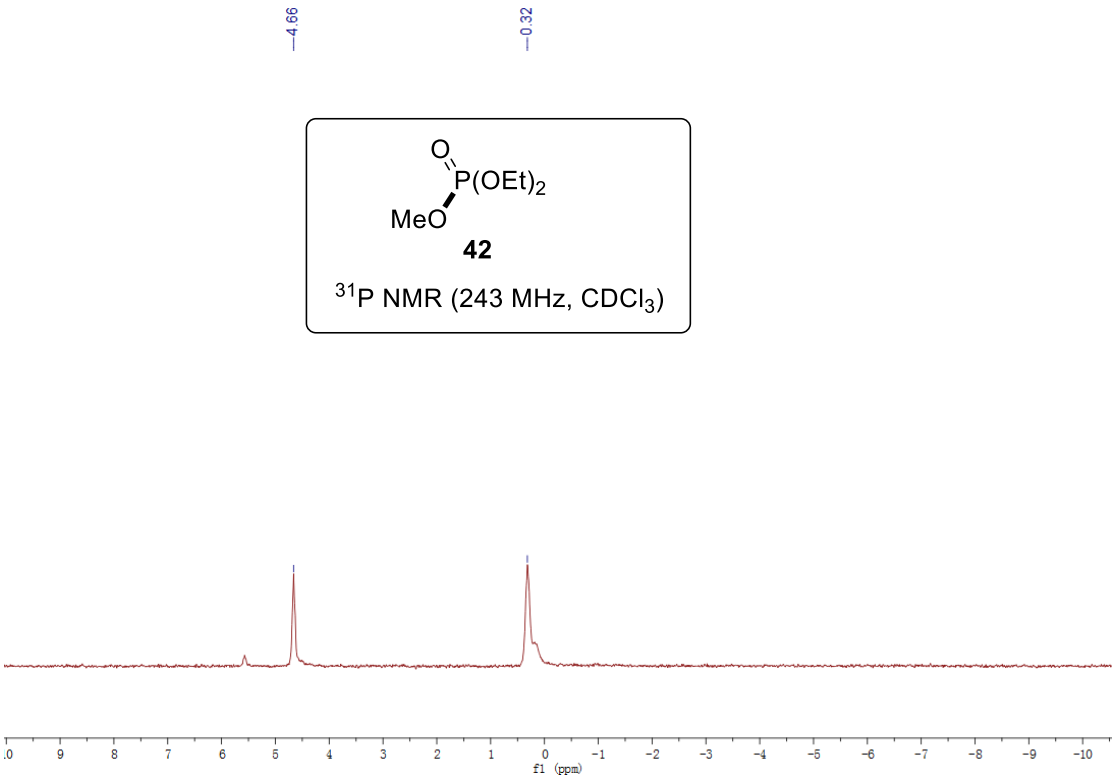


Chemical Formula: $C_{38}H_{50}NO_5P$
Exact Mass: 631.3427

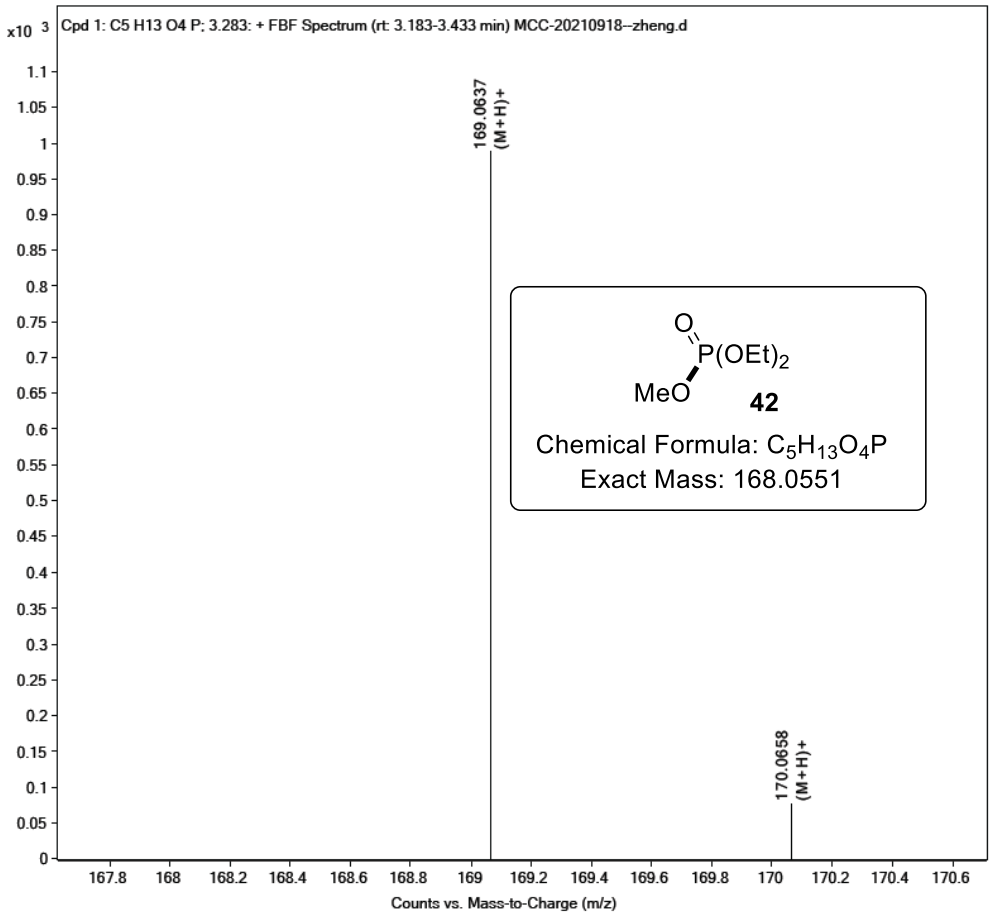
The HRMS analysis for **67**.

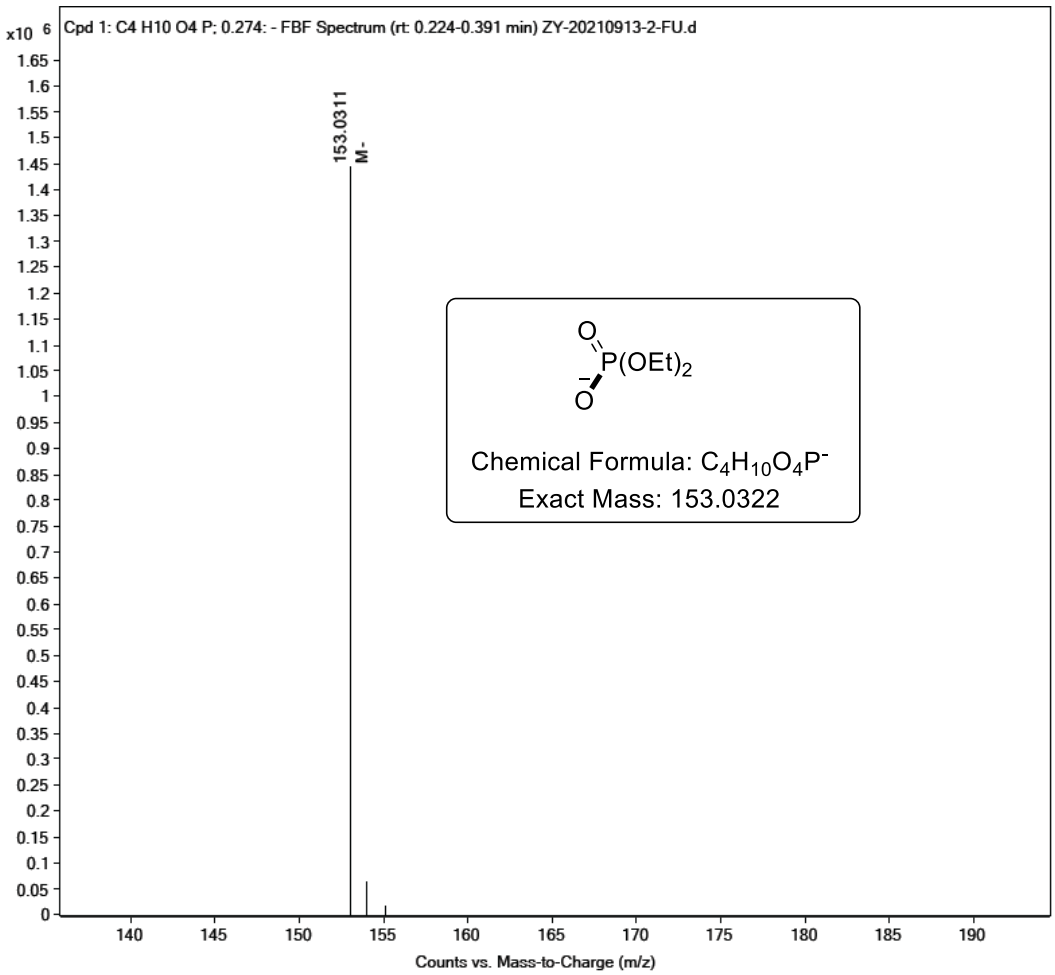


5.2 Trapping Experiment for By Product 42 Using ^{31}P NMR and HRMS



This compound is known and the ^{31}P NMR data (δ 0.3) match previous reported.[4]





6. References

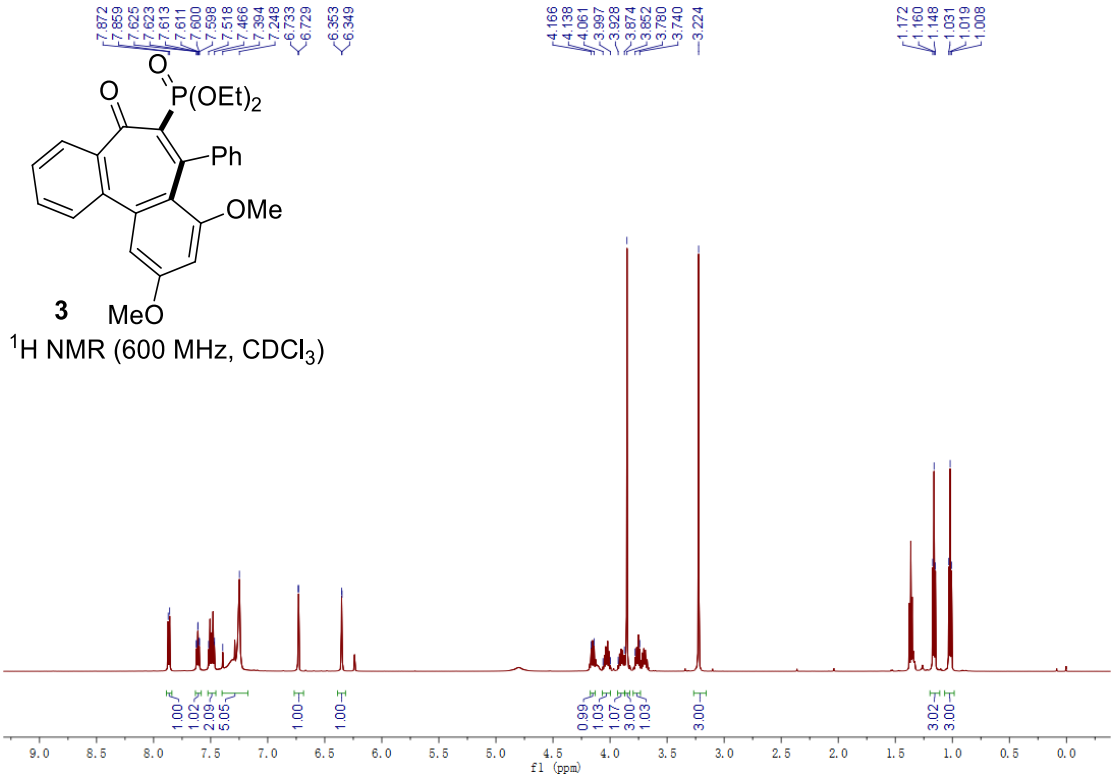
[1] Y. Zhang, D. Guo, S. Ye, Z. Liu, G. Zhu, *Org. Lett*. **2017**, *19*, 1302–1305. .

[2] Y. Yang, J. Zhang, B. Hu, M. Ji, S. Ye, G. Zhu, *Org. Lett.* **2018**, *20*, 2988–2992.

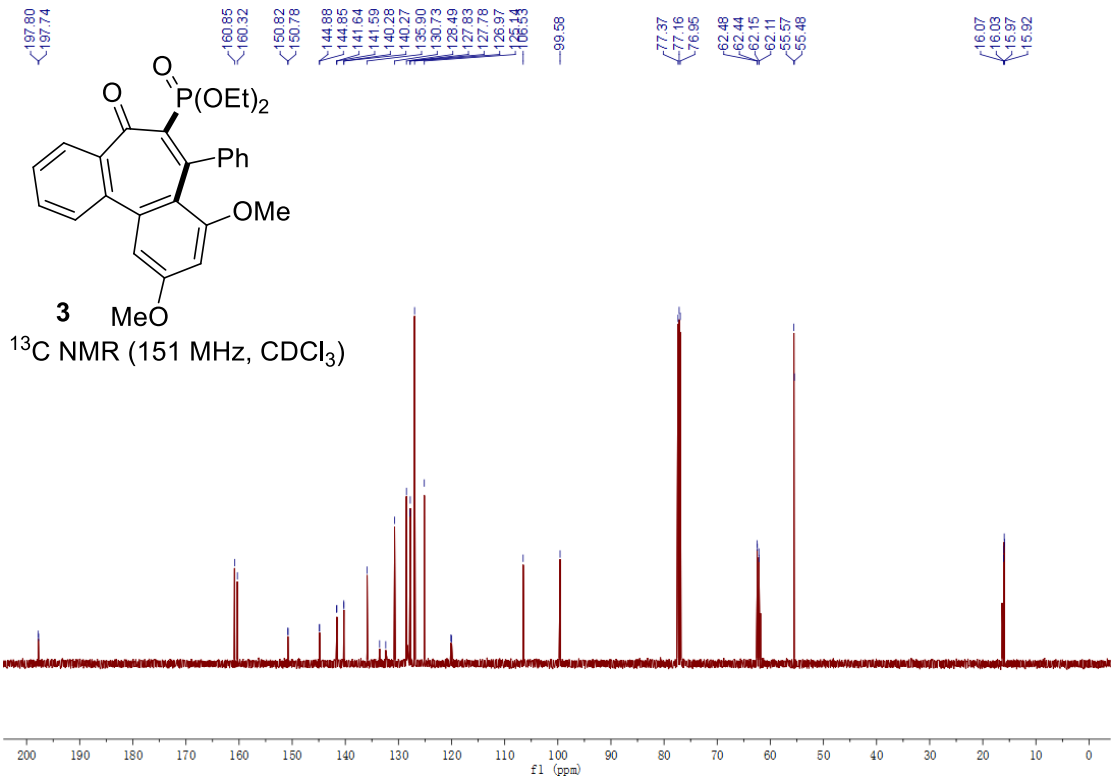
[3] K. D. Collins, A. Rühling, F. Lied, F. Glorius, *Chem. Eur. J.* **2014**, *20*, 3800–3805.

[4] J. Dhineshkumar, K. R. Prabhu, *Org. Lett*. **2013**, *15*, 6062–6065.

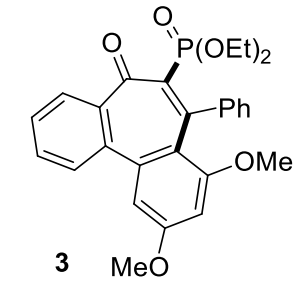
7. NMR Spectra



^{1}H NMR (600 MHz, $CDCl_3$)

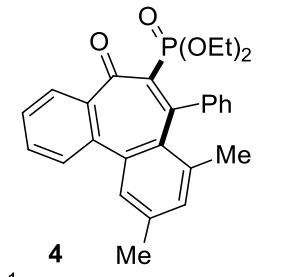


^{13}C NMR (151 MHz, $CDCl_3$)



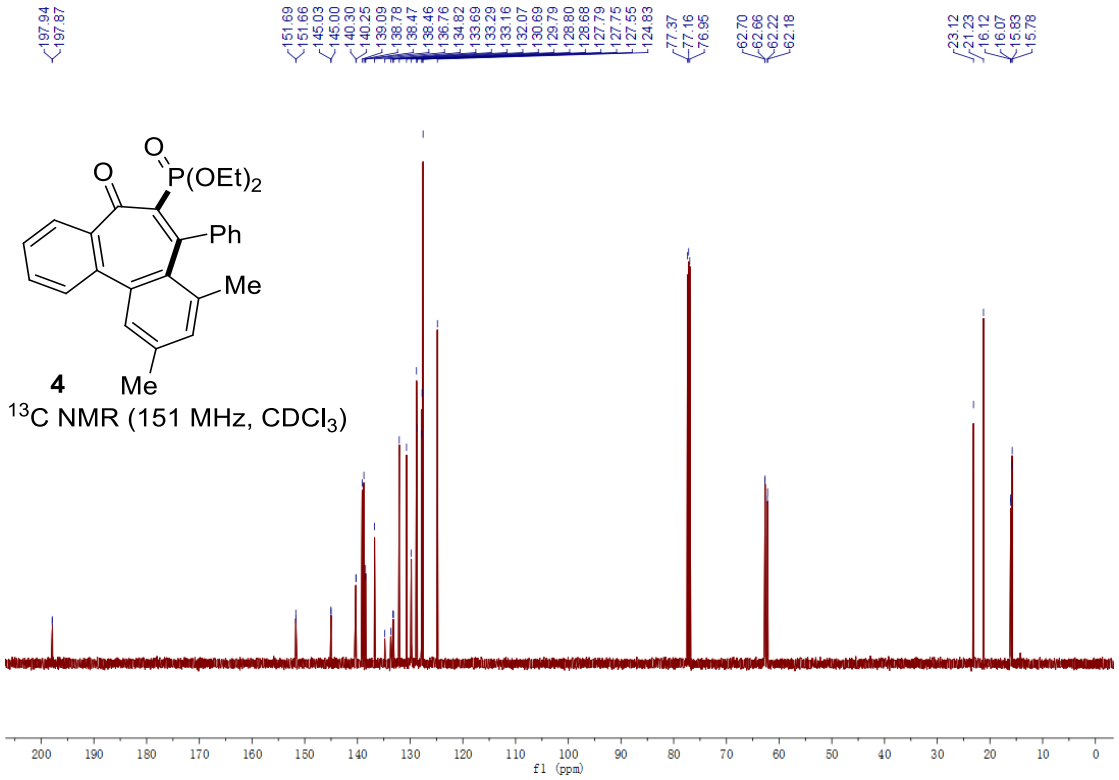
3

^{31}P NMR (243 MHz, $CDCl_3$)



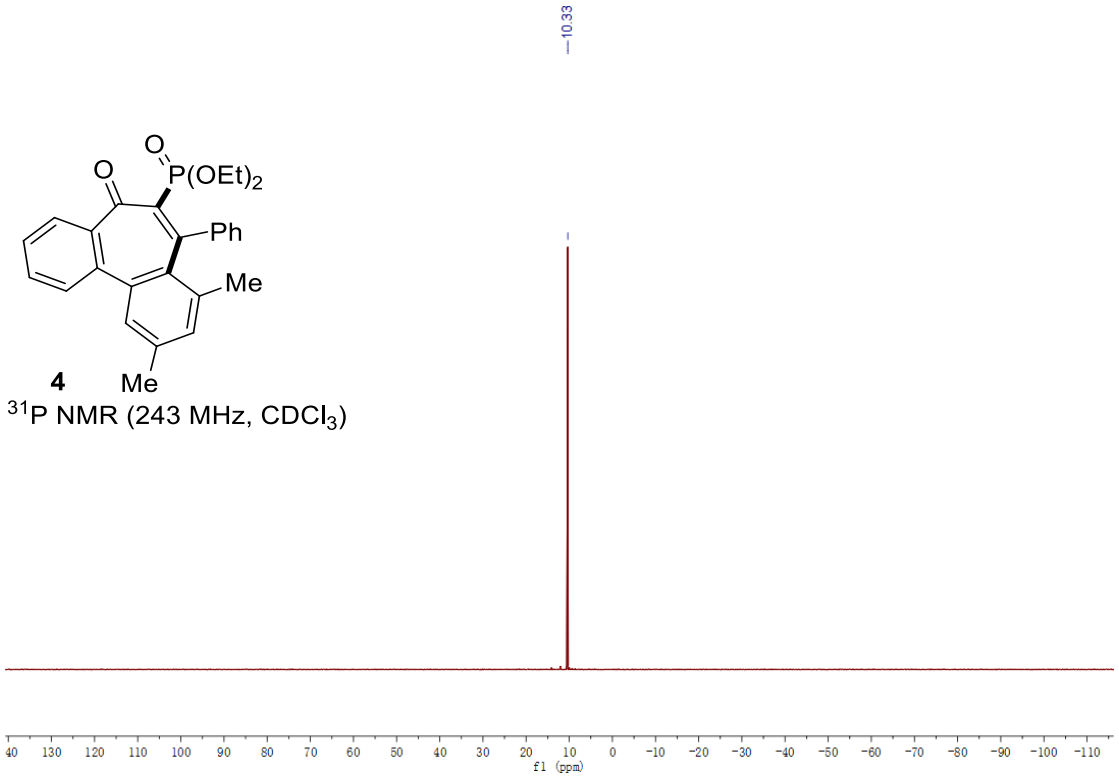
4

^{1}H NMR (600 MHz, $CDCl_3$)



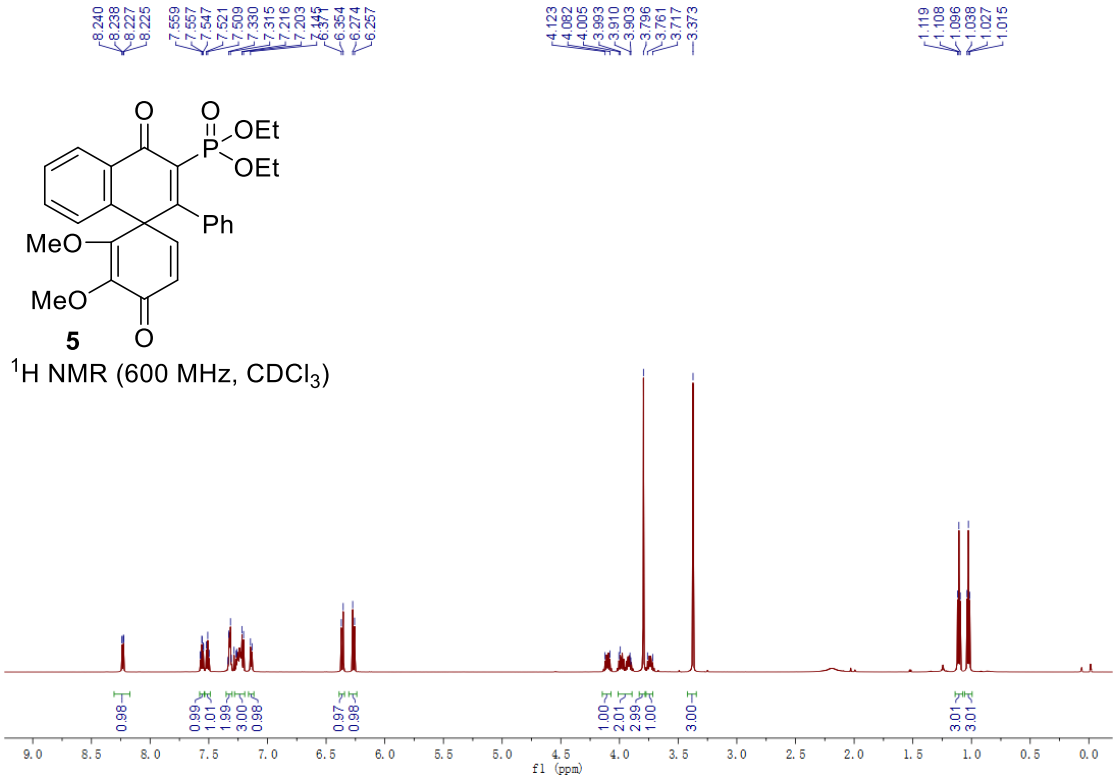
4

^{13}C NMR (151 MHz, $CDCl_3$)

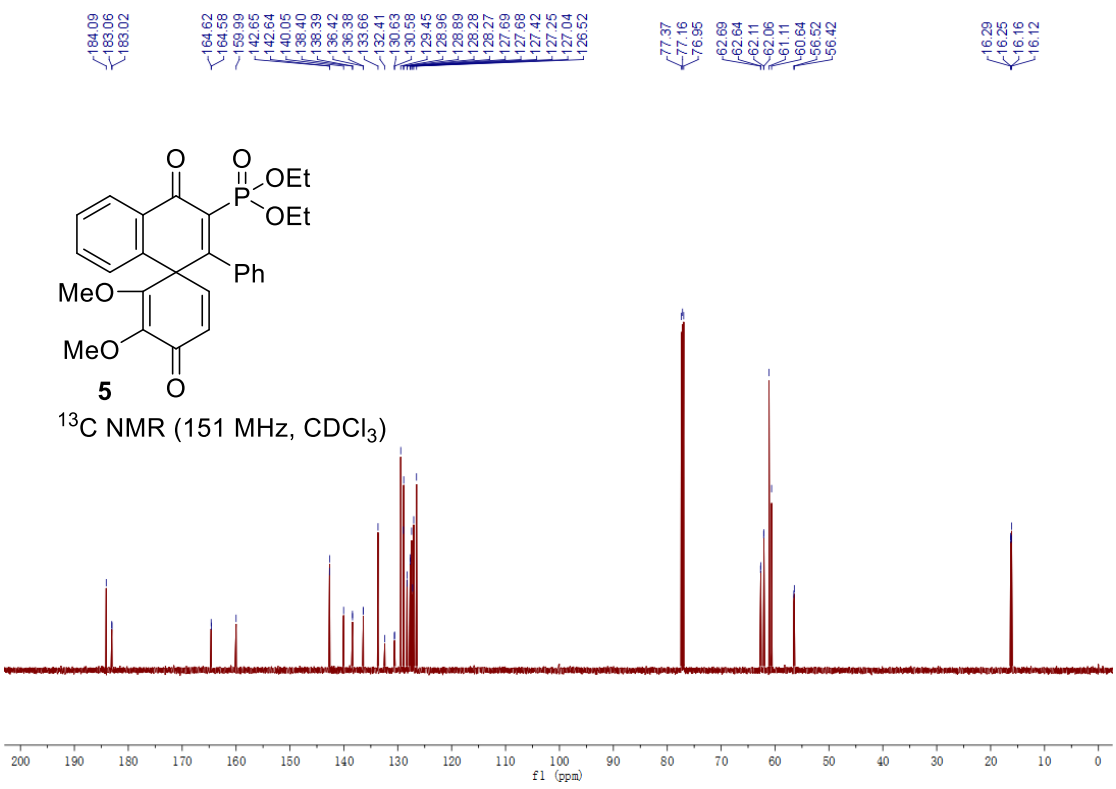


4

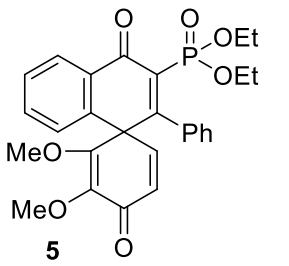
^{31}P NMR (243 MHz, $CDCl_3$)



^{1}H NMR (600 MHz, $CDCl_3$)

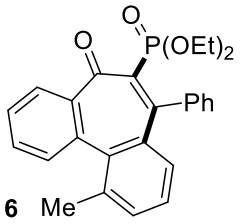


^{13}C NMR (151 MHz, $CDCl_3$)



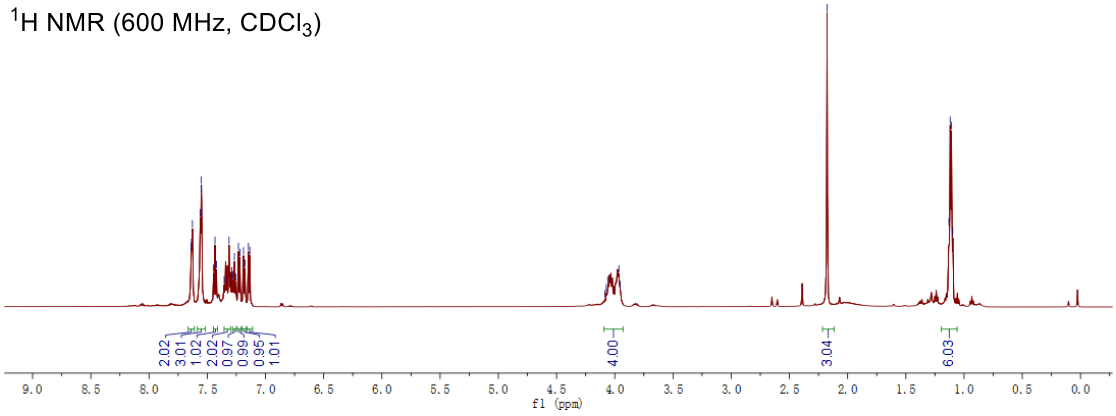
5

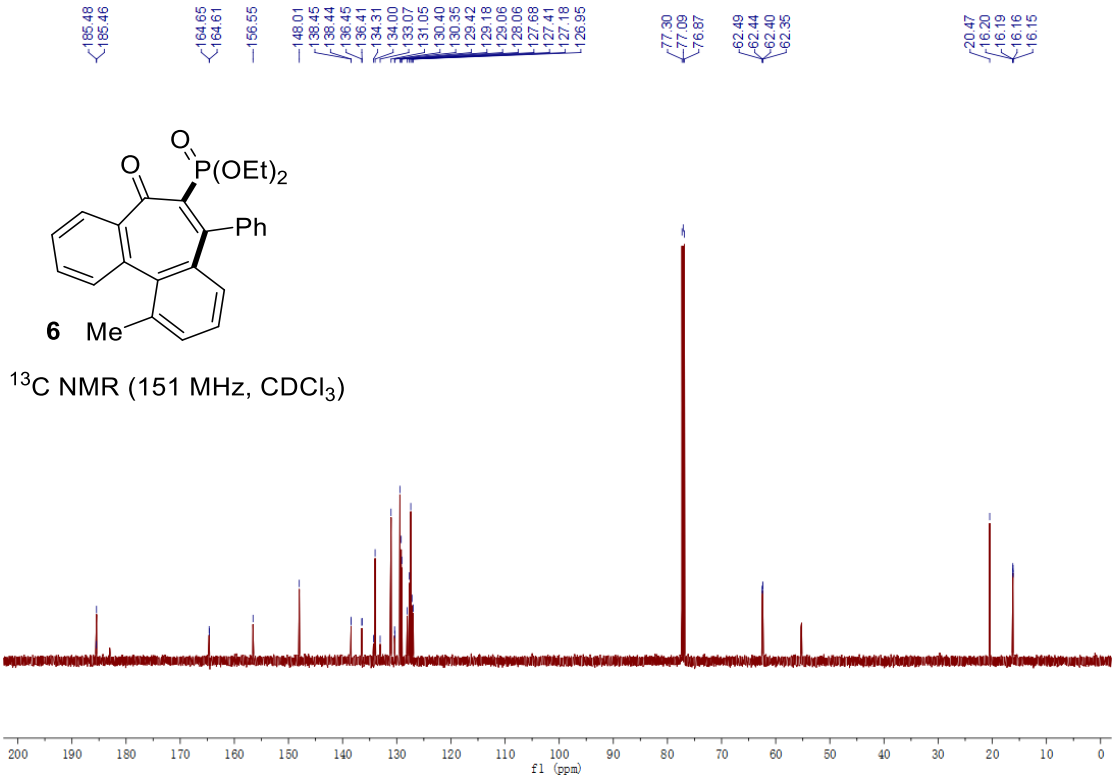
^{31}P NMR (243 MHz, $CDCl_3$)



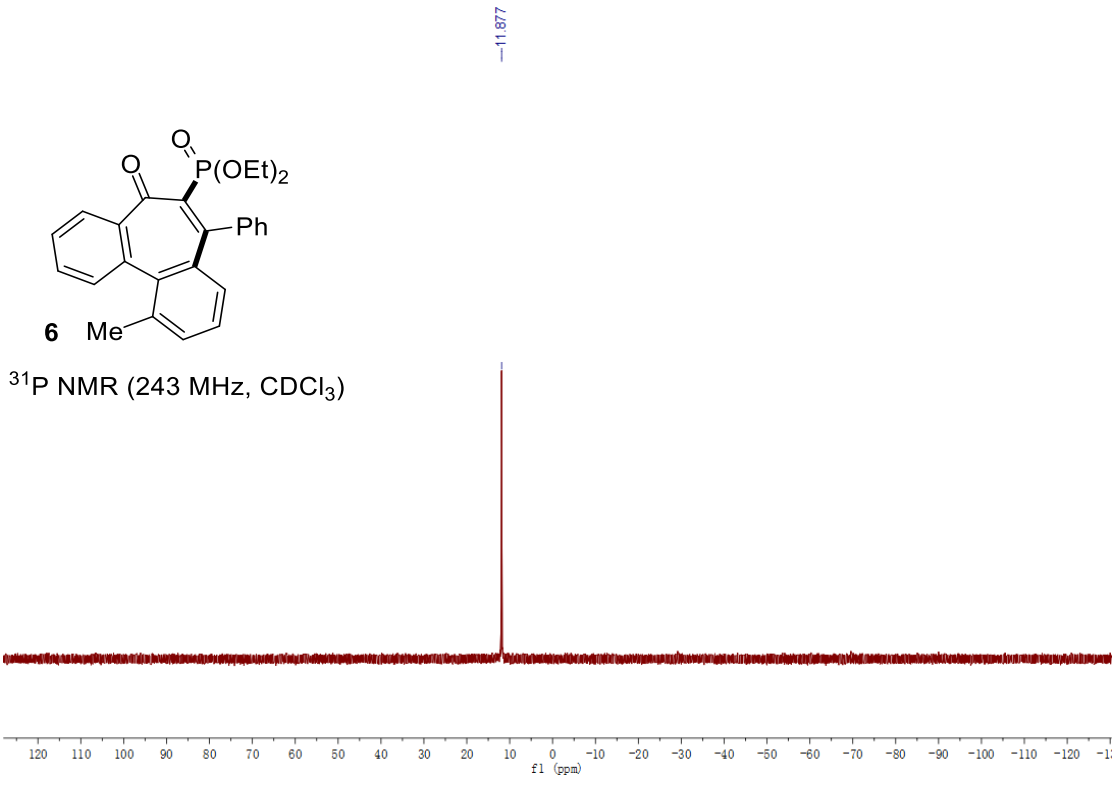
6 Me

^{1}H NMR (600 MHz, $CDCl_3$)

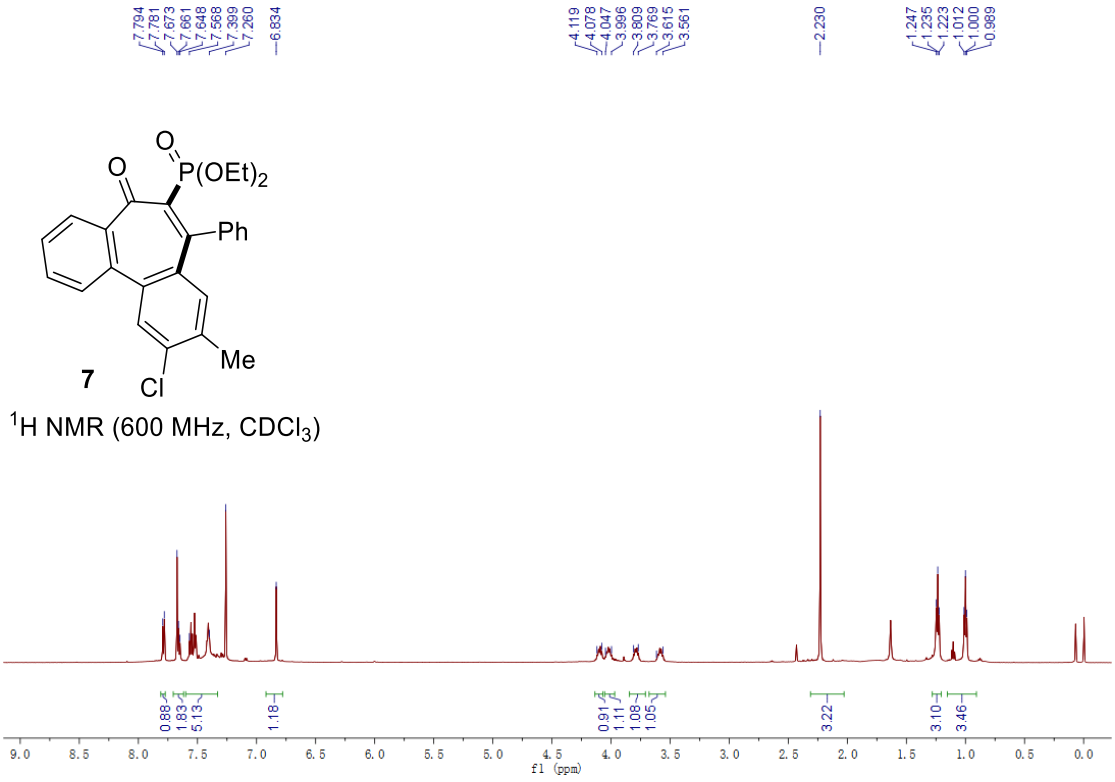


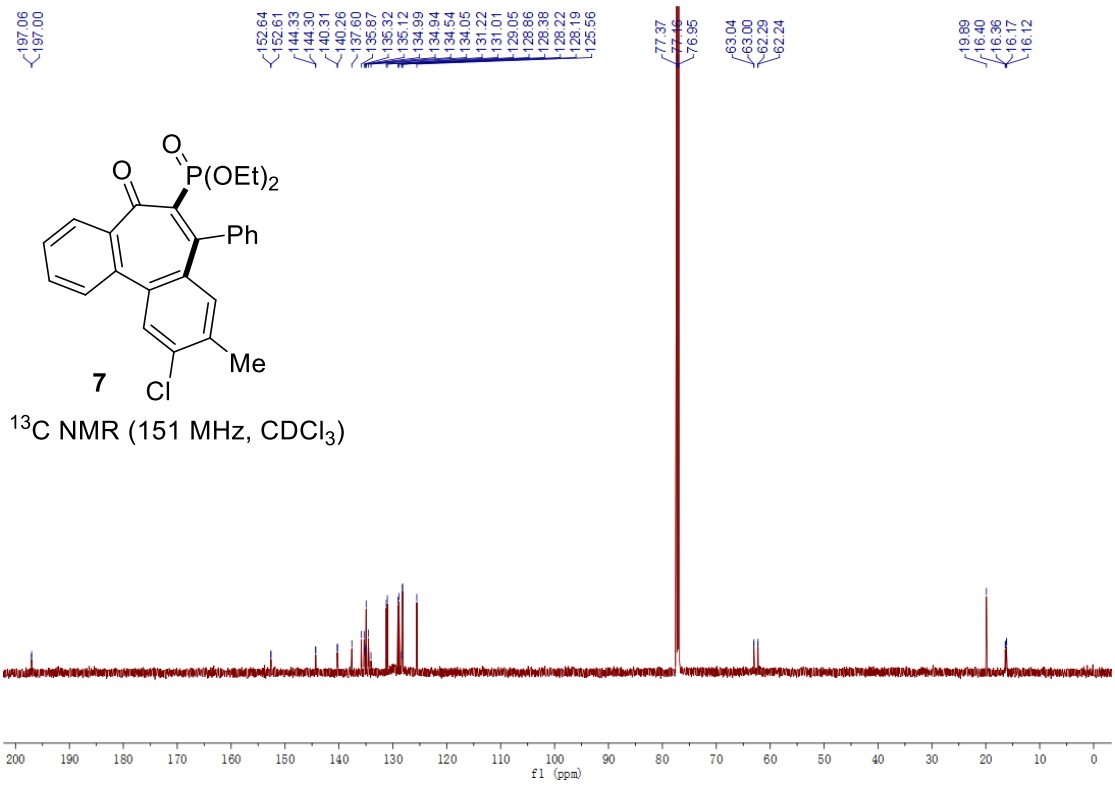


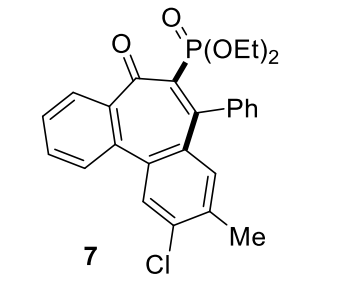
^{13}C NMR (151 MHz, $CDCl_3$)



^{31}P NMR (243 MHz, $CDCl_3$)

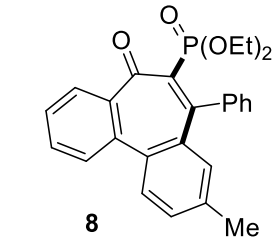

7.794
7.781
7.673
7.661
7.648
7.568
7.399
7.260
6.834
4.119
4.078
4.047
3.996
3.809
3.769
3.615
3.561
2.230
1.247
1.235
1.223
1.012
1.000
0.989
O
O
P(OEt)2
Ph
Me
Cl
7
1H NMR (600 MHz, CDCl3)
0.88
1.83
5.13
1.18
0.91
1.11
1.08
1.05
3.22
3.10
3.46
f1 (ppm)


197.06
197.00
152.64
152.61
144.33
144.30
140.31
140.26
137.60
135.87
135.32
135.12
134.99
134.94
134.54
134.05
131.22
131.01
129.05
128.86
128.38
128.22
128.19
125.56
77.37
77.16
76.95
63.04
63.00
62.29
62.24
19.89
16.40
16.36
16.17
16.12
O
O
P(OEt)2
Ph
Me
Cl
7
13C NMR (151 MHz, CDCl3)
f1 (ppm)



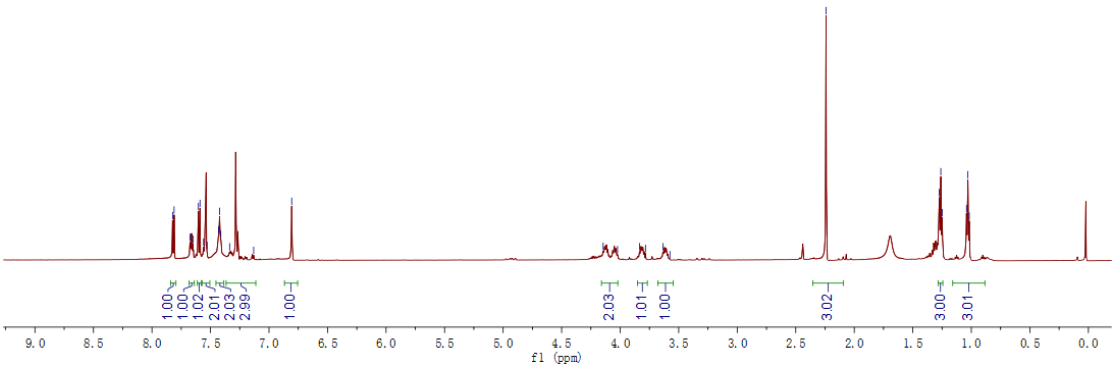
7

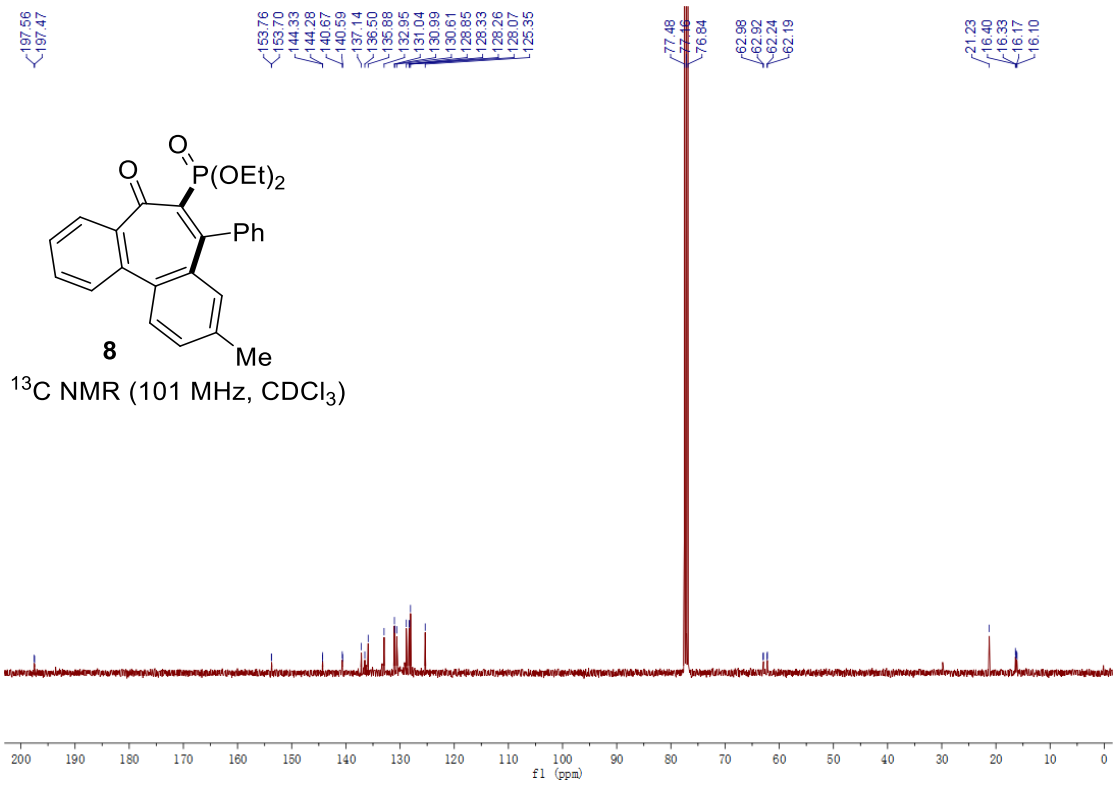
^{31}P NMR (243 MHz, $CDCl_3$)

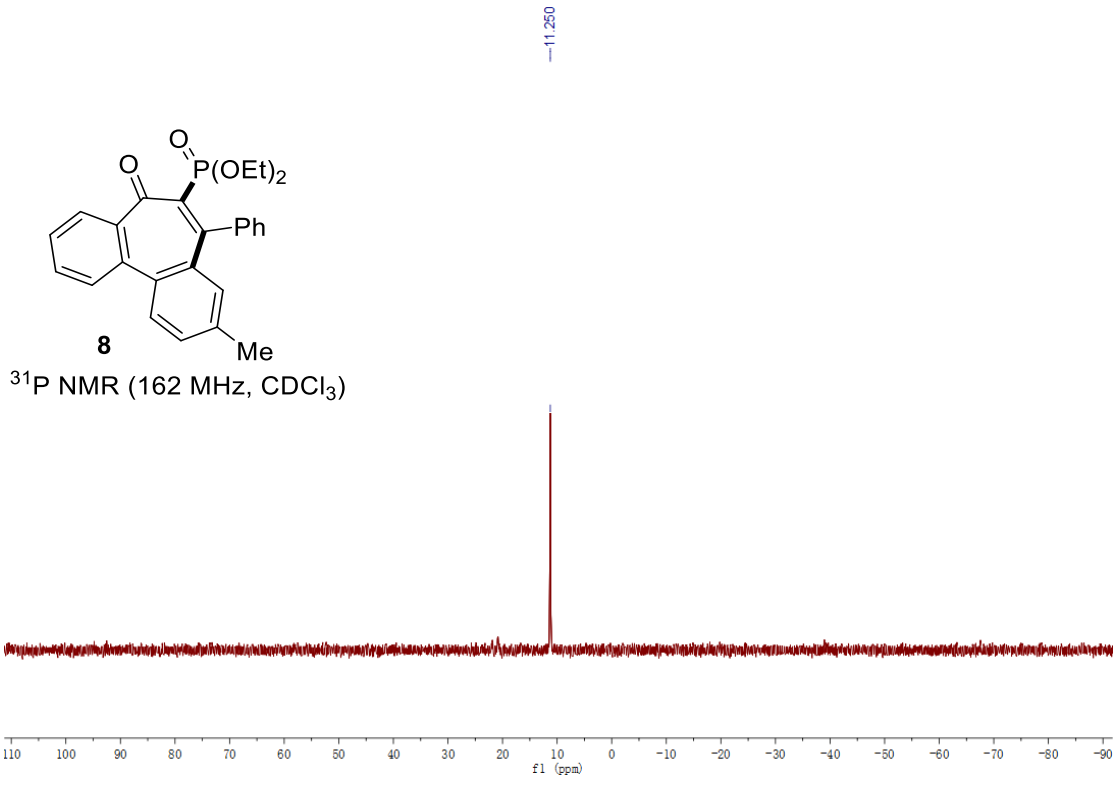


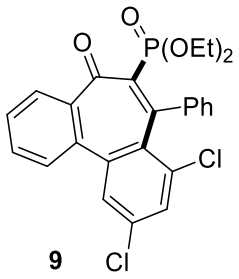
8

^{1}H NMR (600 MHz, $CDCl_3$)



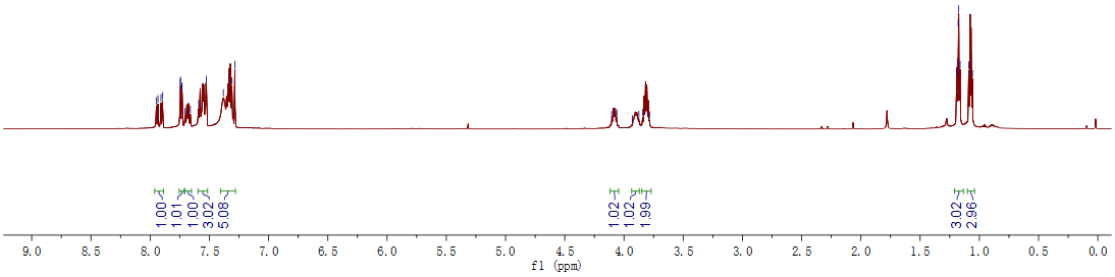

197.56
197.47
153.76
153.70
144.33
144.28
140.67
140.59
137.14
136.50
135.88
132.95
131.04
130.99
130.61
128.85
128.33
128.26
128.07
125.35
77.48
77.16
76.84
62.98
62.92
62.24
62.19
21.23
16.40
16.33
16.17
16.10
O
O
P(OEt)2
Ph
Me
8
13C NMR (101 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

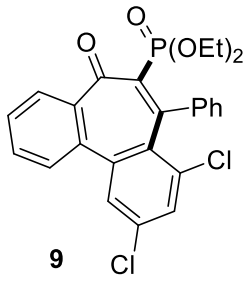

11.250
O
O
P(OEt)2
Ph
Me
8
31P NMR (162 MHz, CDCl3)
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)



9

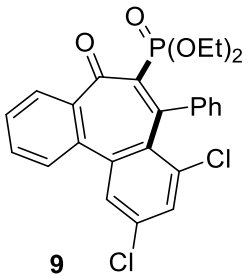
^{1}H NMR (600 MHz, $CDCl_3$)





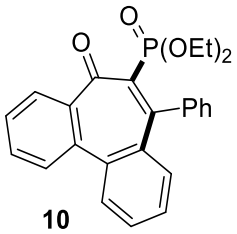
9

^{13}C NMR (151 MHz, $CDCl_3$)



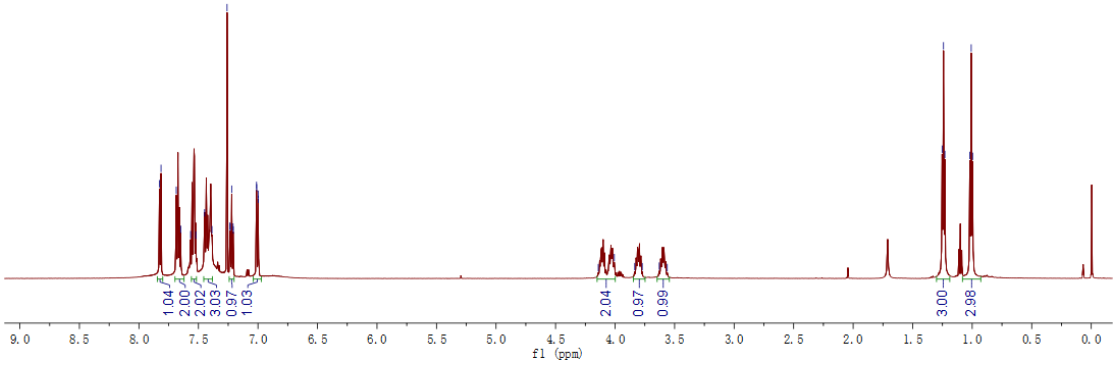
9

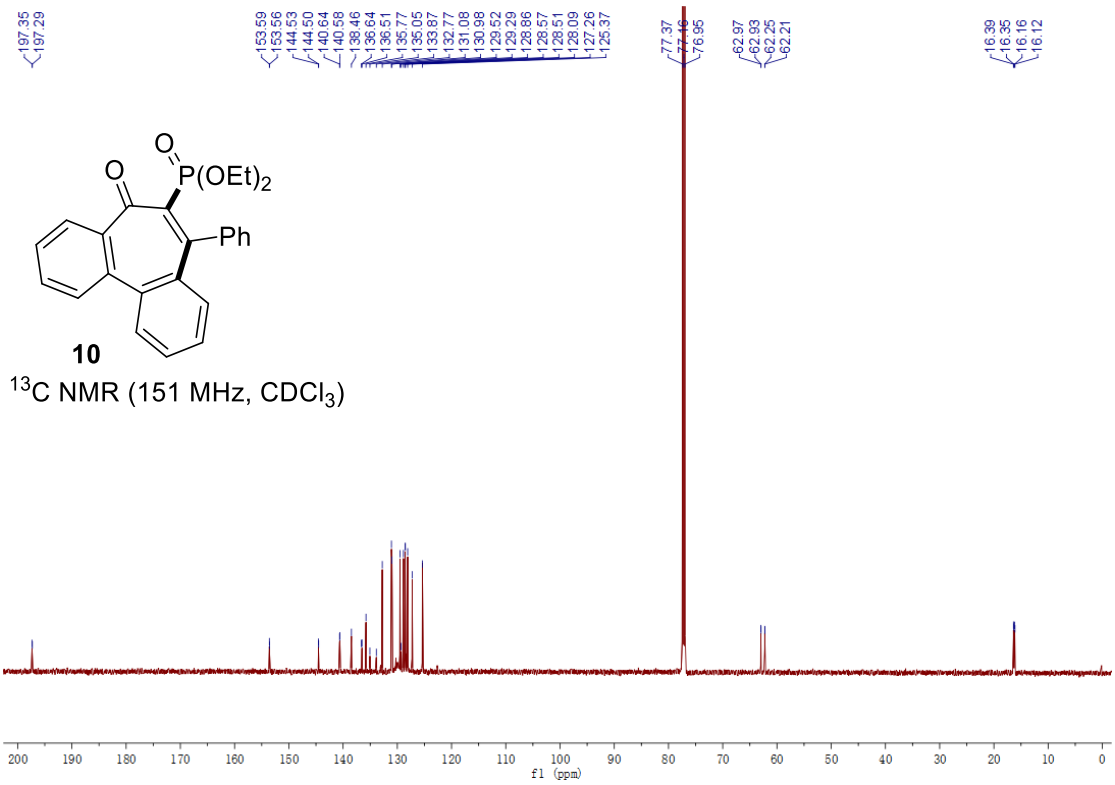
^{31}P NMR (243 MHz, $CDCl_3$)

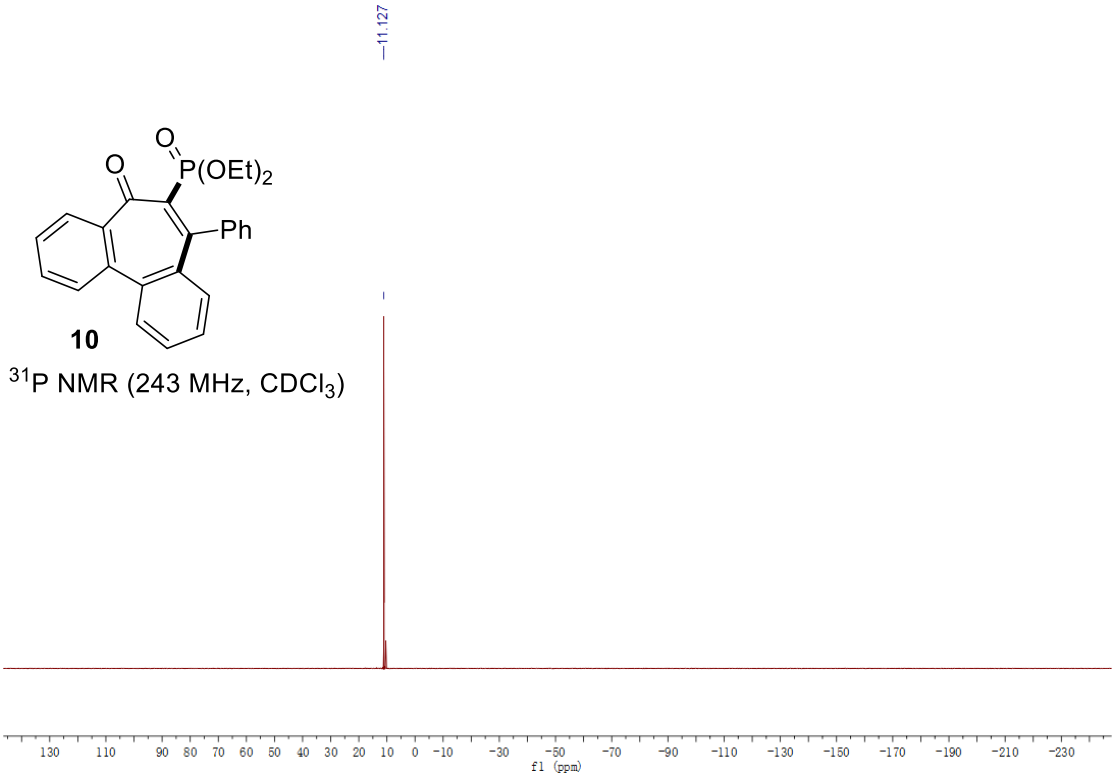


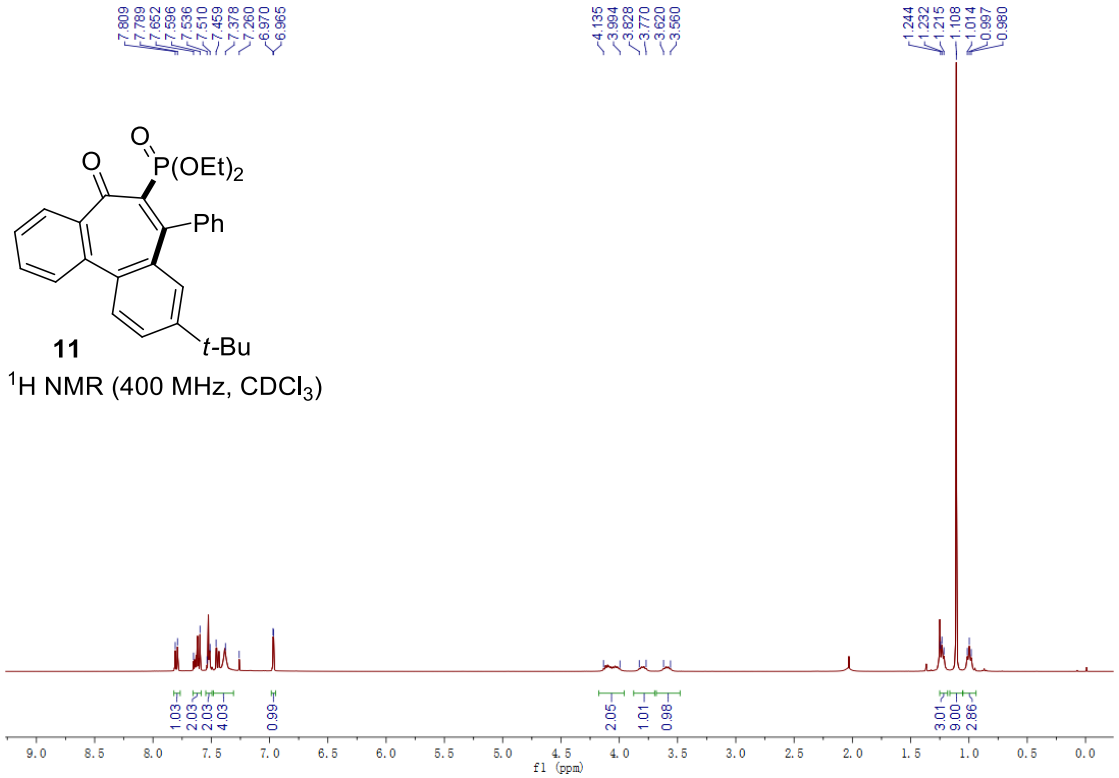
10

^{1}H NMR (600 MHz, $CDCl_3$)



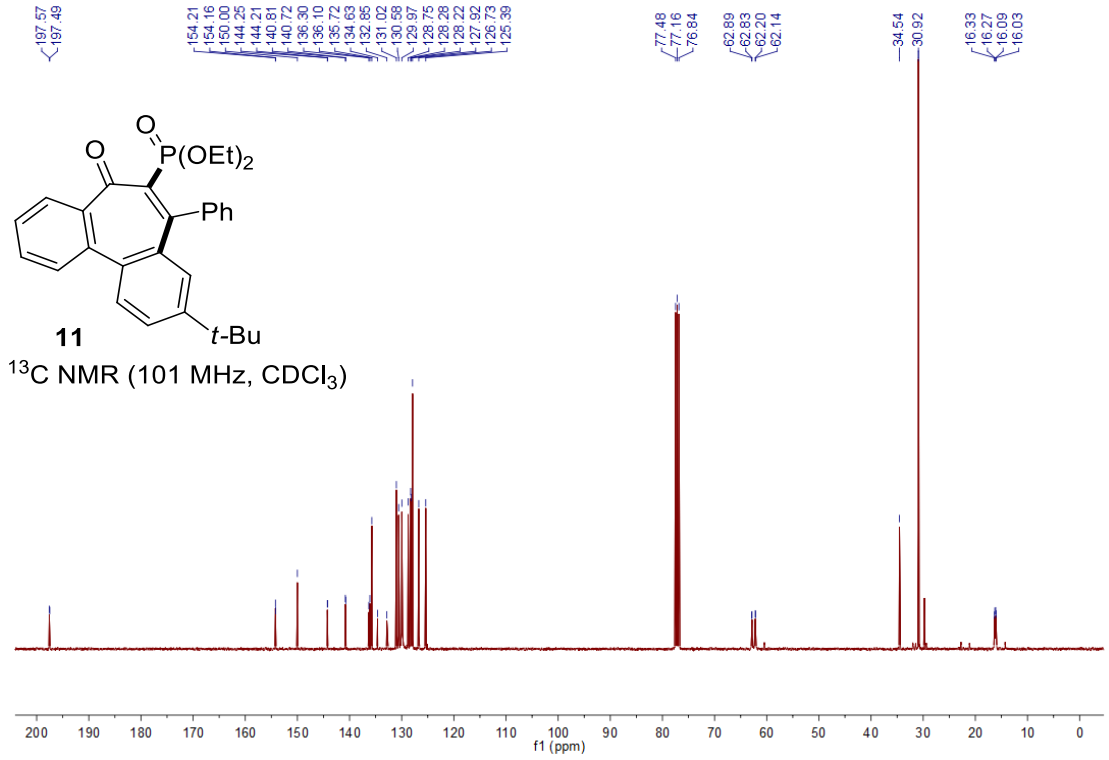

197.35
197.29
153.59
153.56
144.53
144.50
140.64
140.58
138.46
136.64
136.51
135.77
135.05
133.87
132.77
131.08
130.98
129.52
129.29
128.86
128.57
128.51
128.09
127.26
125.37
77.37
77.16
76.95
62.97
62.93
62.25
62.21
16.39
16.35
16.16
16.12
O
O
P(OEt)2
Ph
10
13C NMR (151 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


11.127
O
O
P(OEt)2
Ph
10
31P NMR (243 MHz, CDCl3)
130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)



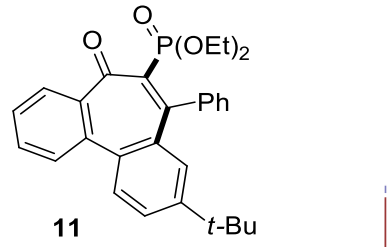
11

^{1}H NMR (400 MHz, $CDCl_3$)



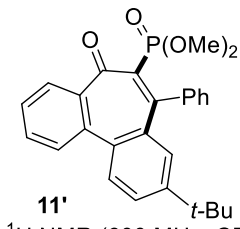
11

^{13}C NMR (101 MHz, $CDCl_3$)



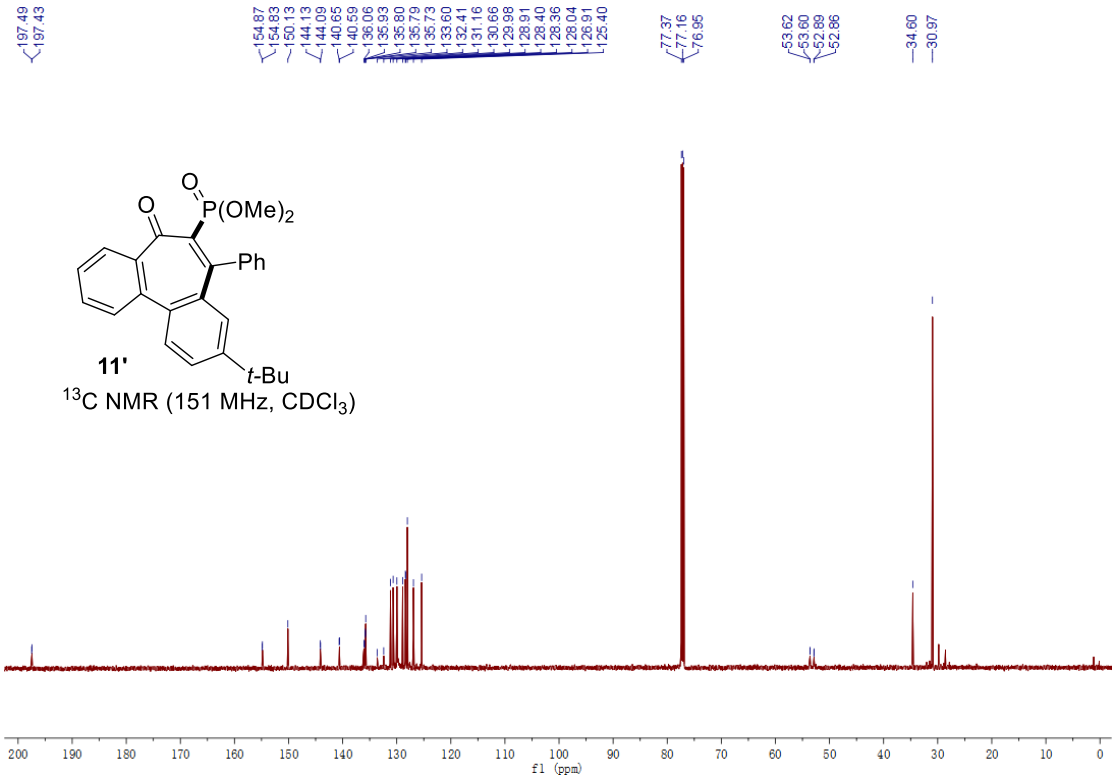
11

^{31}P NMR (243 MHz, $CDCl_3$)



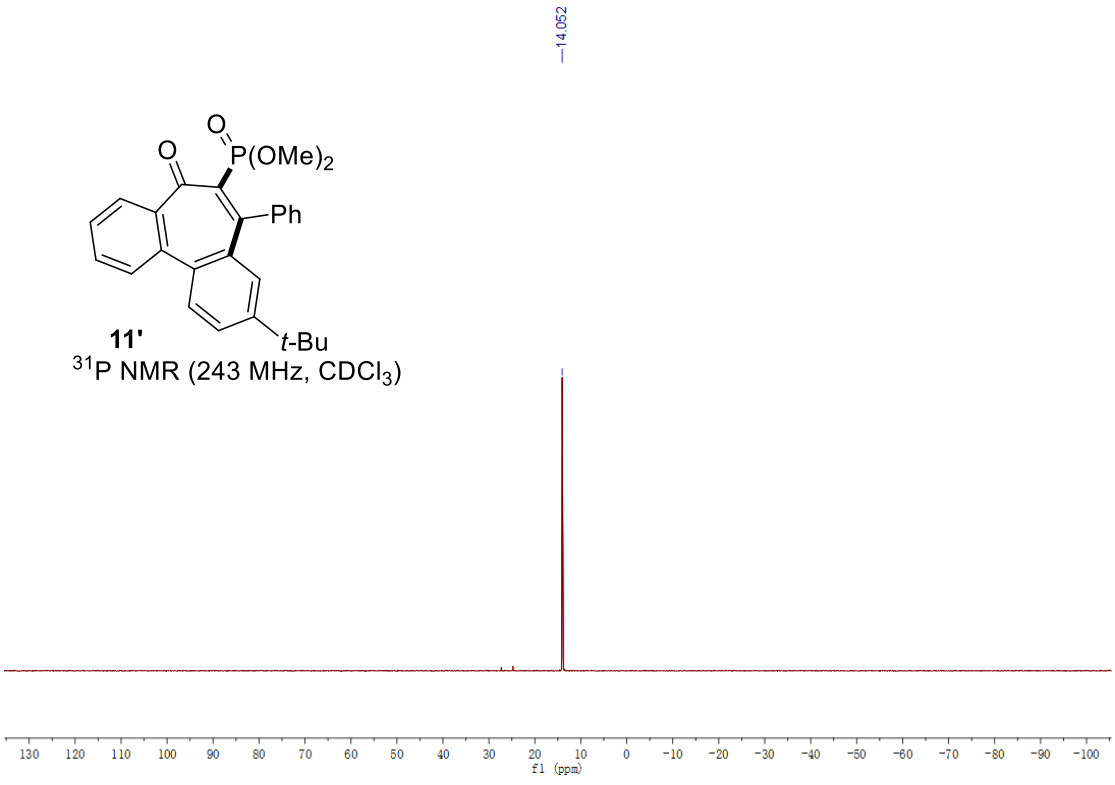
11'

^{1}H NMR (600 MHz, $CDCl_3$)



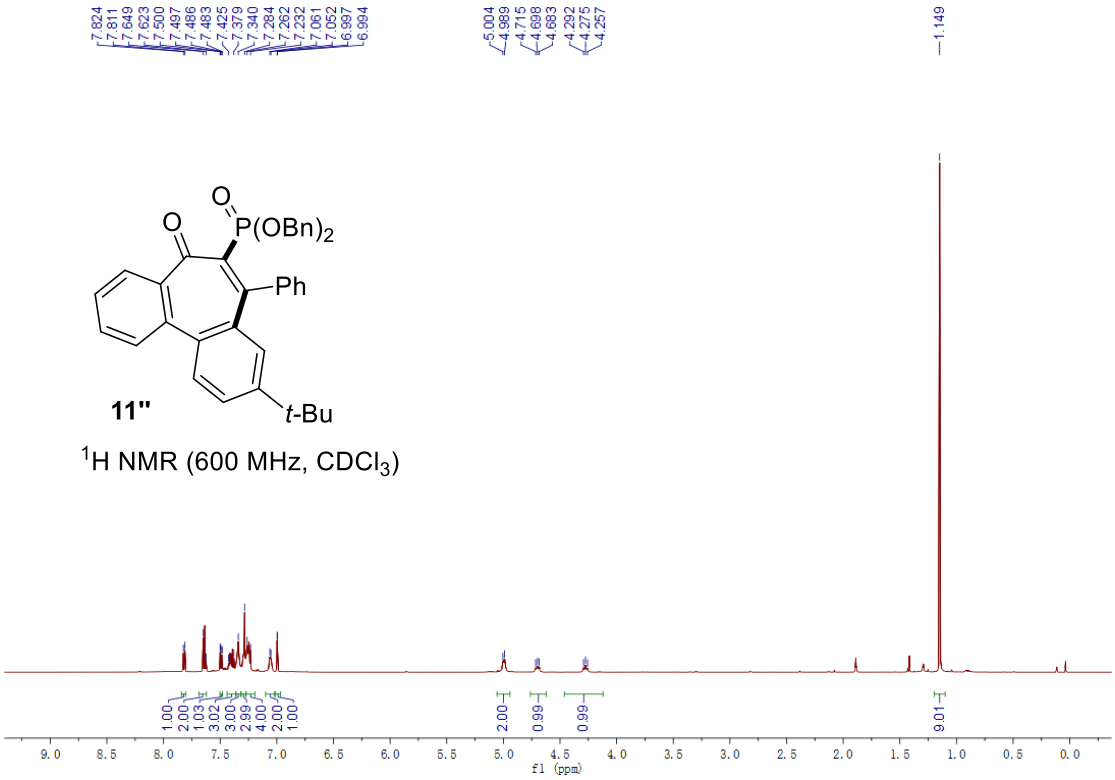
11'

^{13}C NMR (151 MHz, $CDCl_3$)

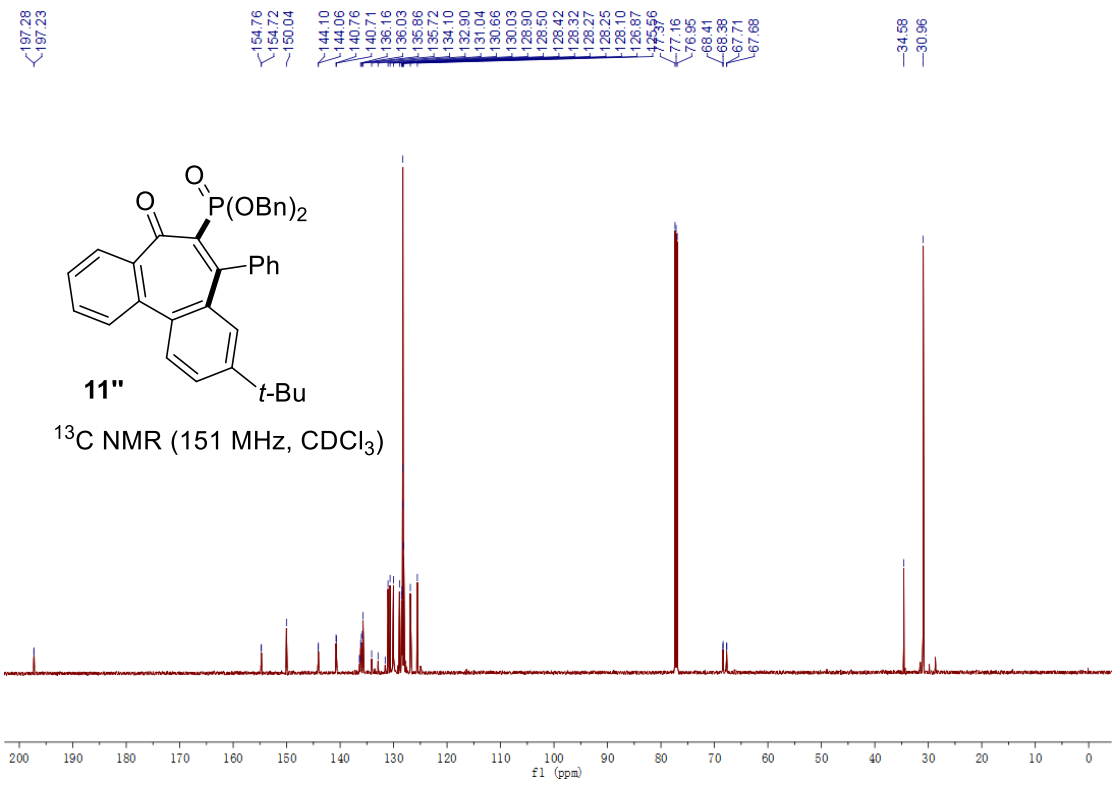


11'

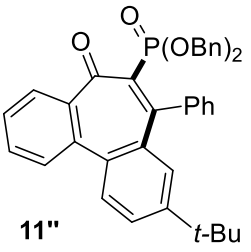
^{31}P NMR (243 MHz, $CDCl_3$)



^{1}H NMR (600 MHz, $CDCl_3$)

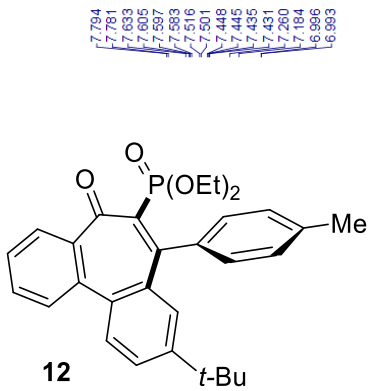


^{13}C NMR (151 MHz, $CDCl_3$)



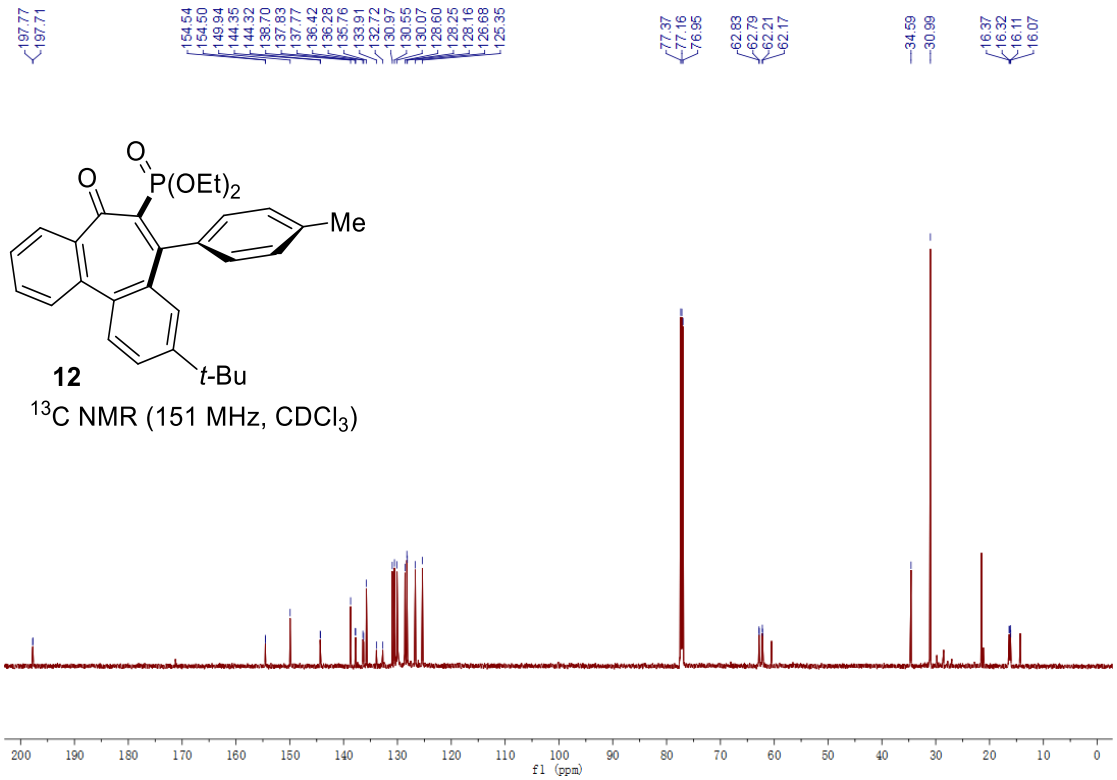
11''

^{31}P NMR (243 MHz, $CDCl_3$)



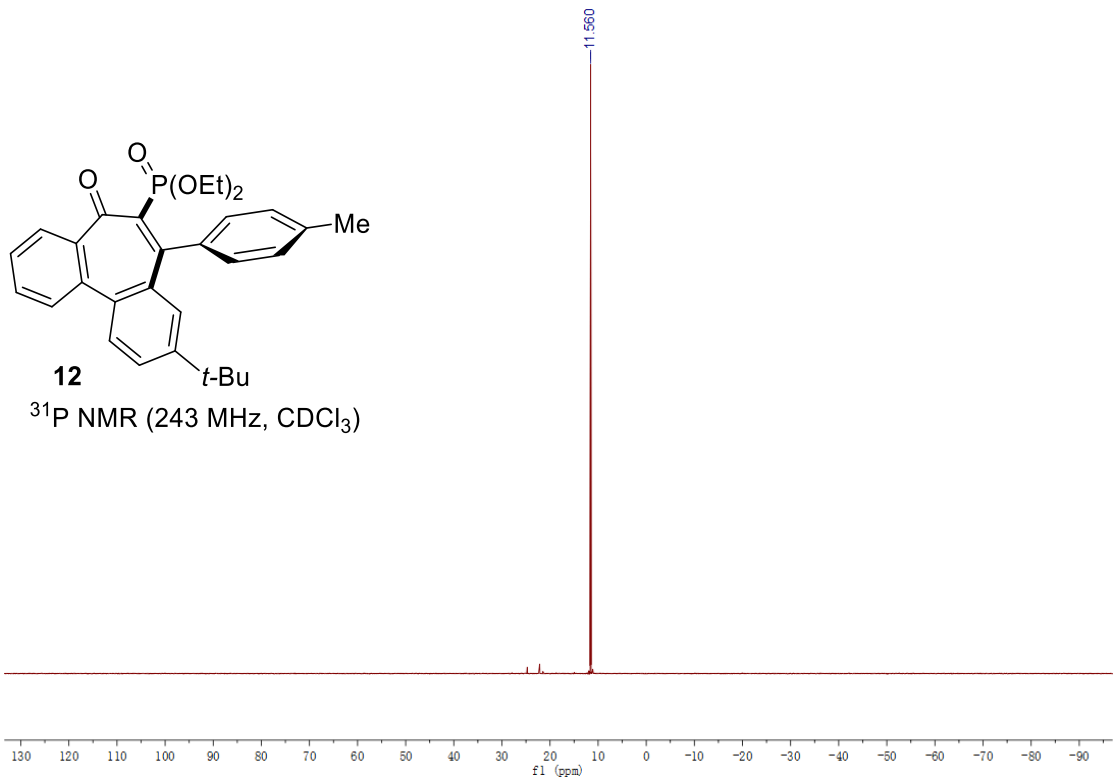
12

^{1}H NMR (600 MHz, $CDCl_3$)



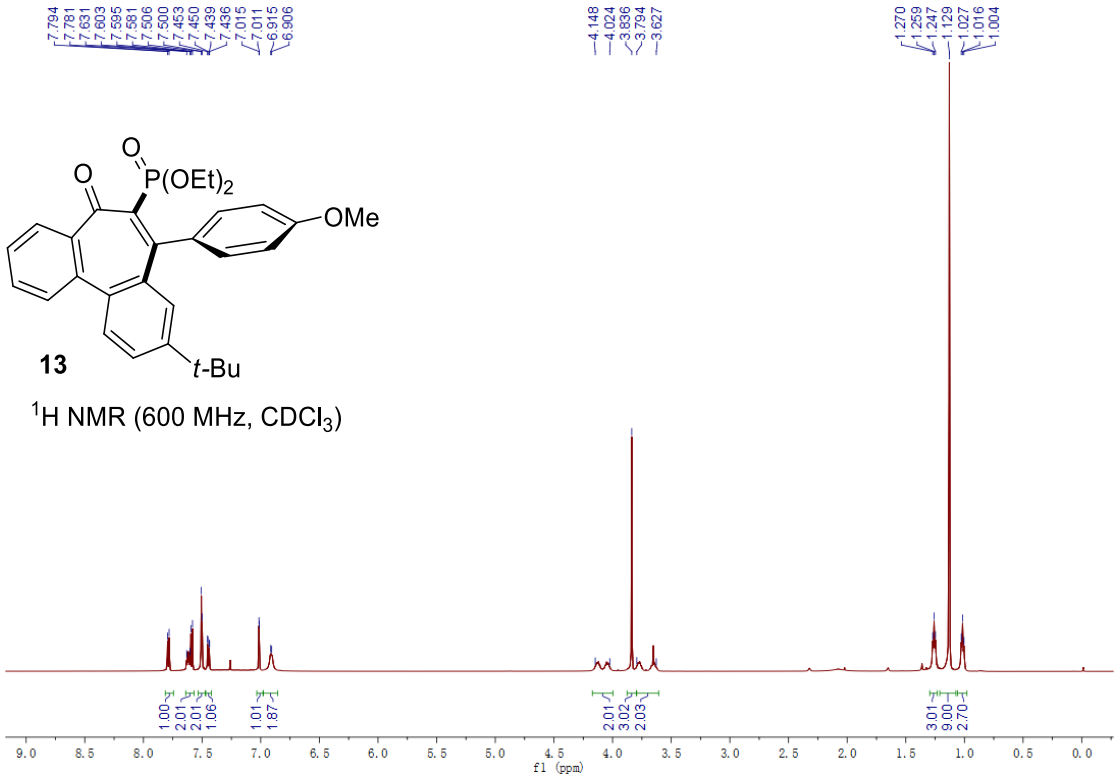
12

^{13}C NMR (151 MHz, $CDCl_3$)

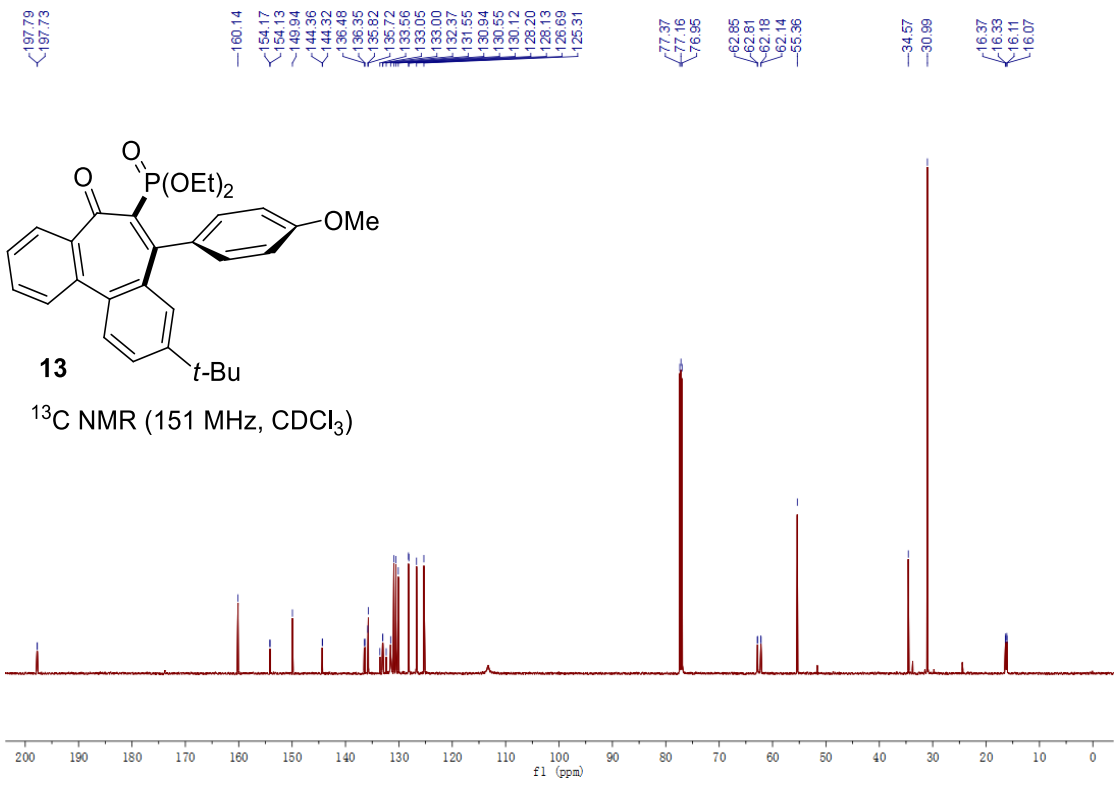


12

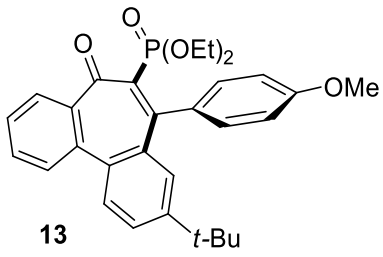
^{31}P NMR (243 MHz, $CDCl_3$)



^{1}H NMR (600 MHz, $CDCl_3$)

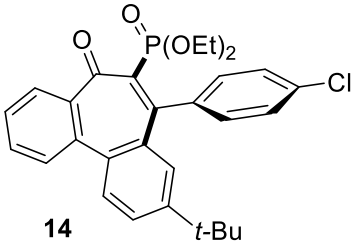


^{13}C NMR (151 MHz, $CDCl_3$)



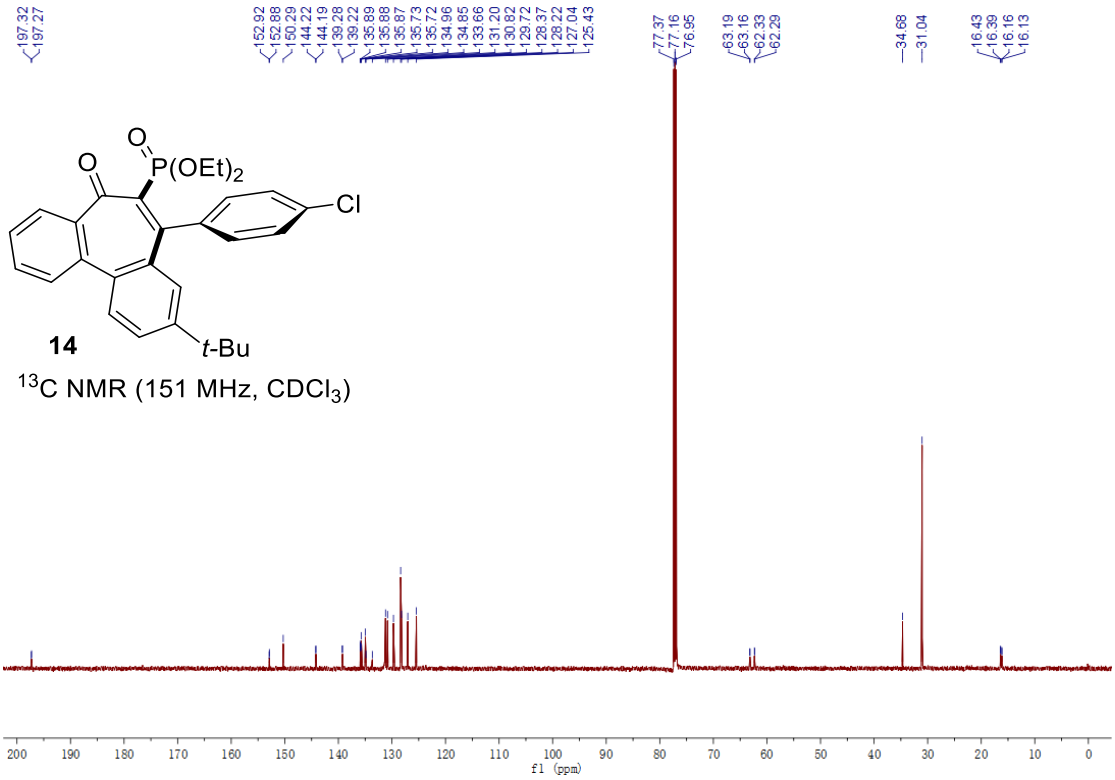
13

^{31}P NMR (243 MHz, $CDCl_3$)



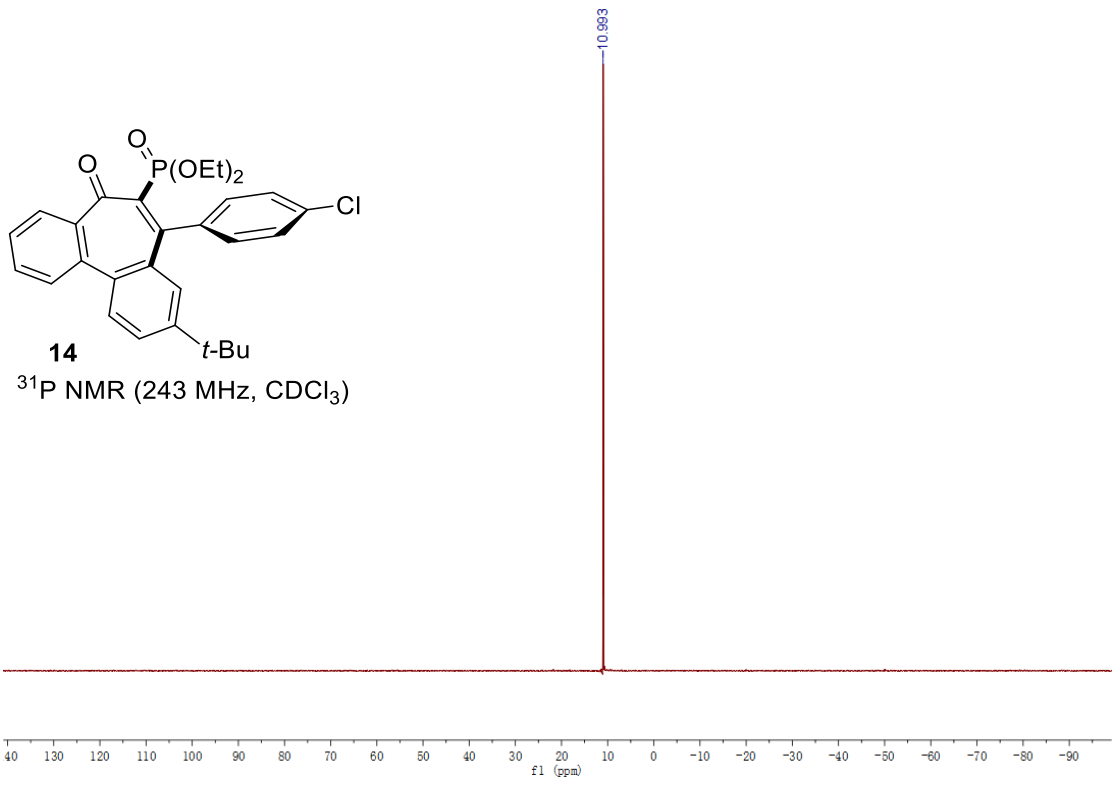
14

^{1}H NMR (600 MHz, $CDCl_3$)



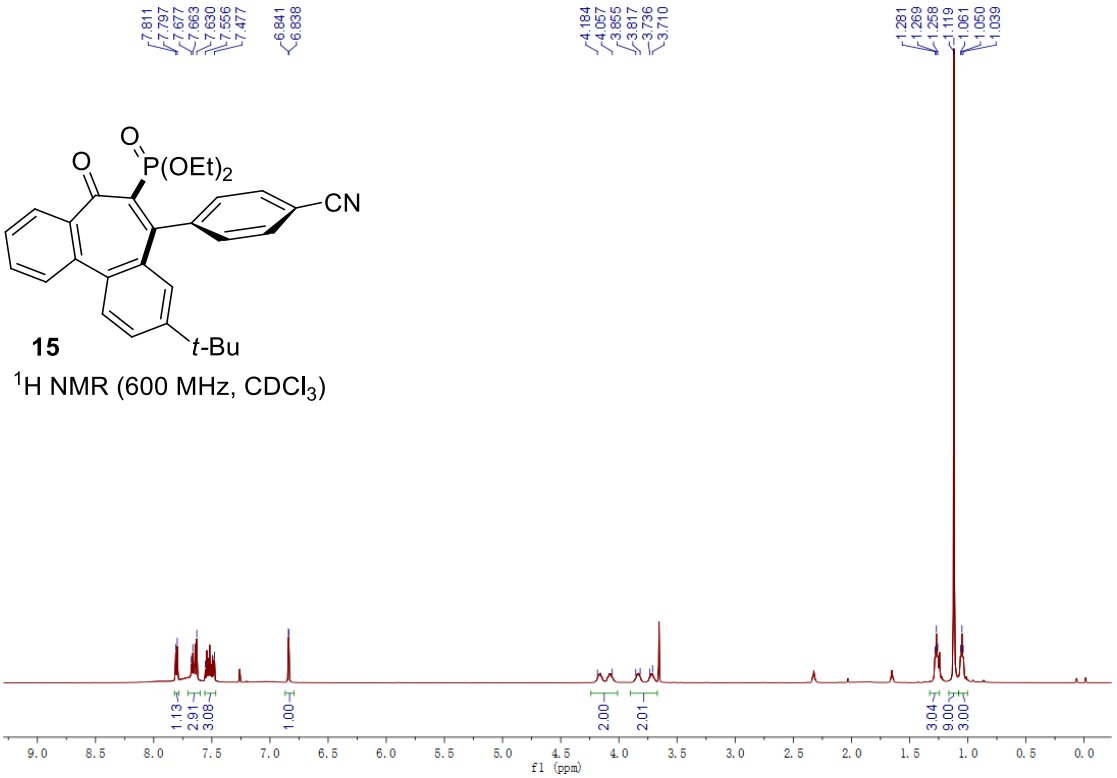
14

^{13}C NMR (151 MHz, $CDCl_3$)



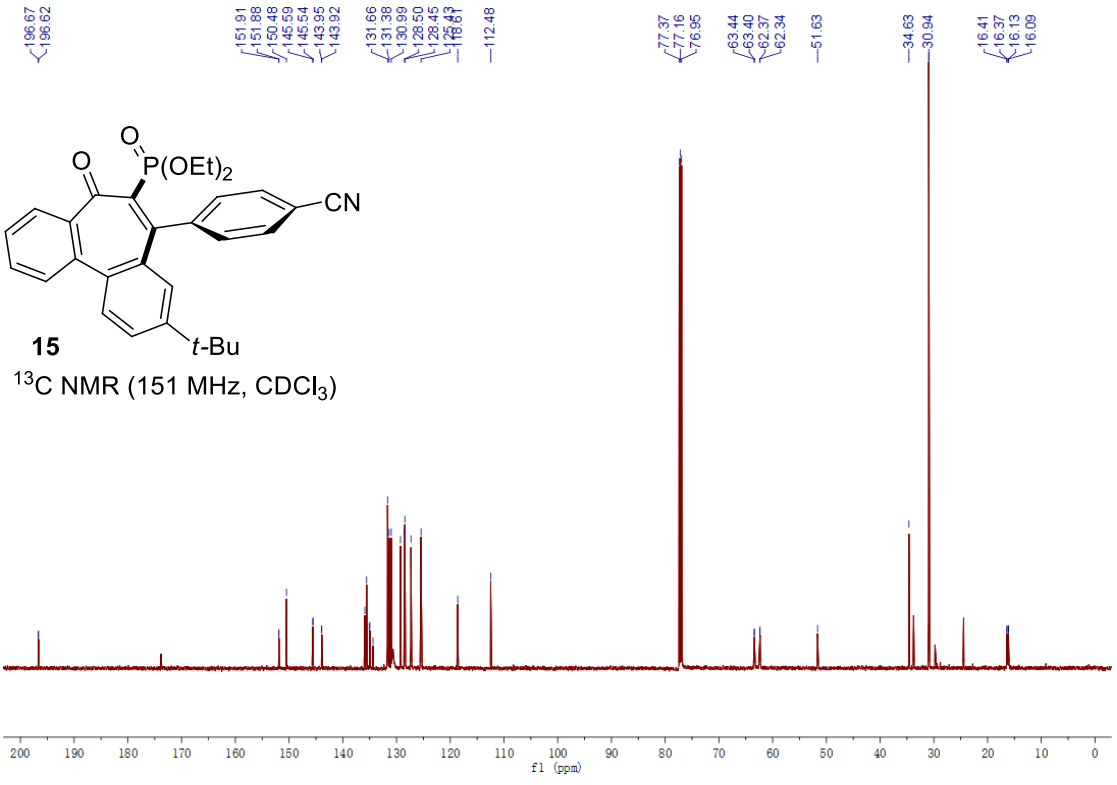
14

^{31}P NMR (243 MHz, $CDCl_3$)



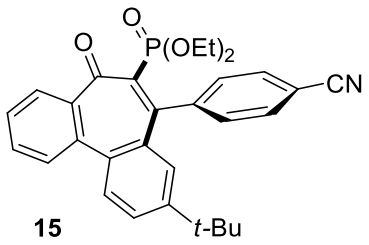
15

^{1}H NMR (600 MHz, $CDCl_3$)



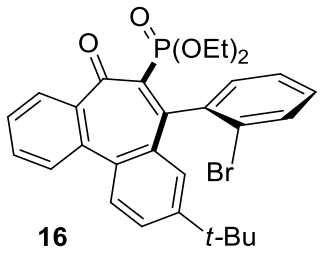
15

^{13}C NMR (151 MHz, $CDCl_3$)



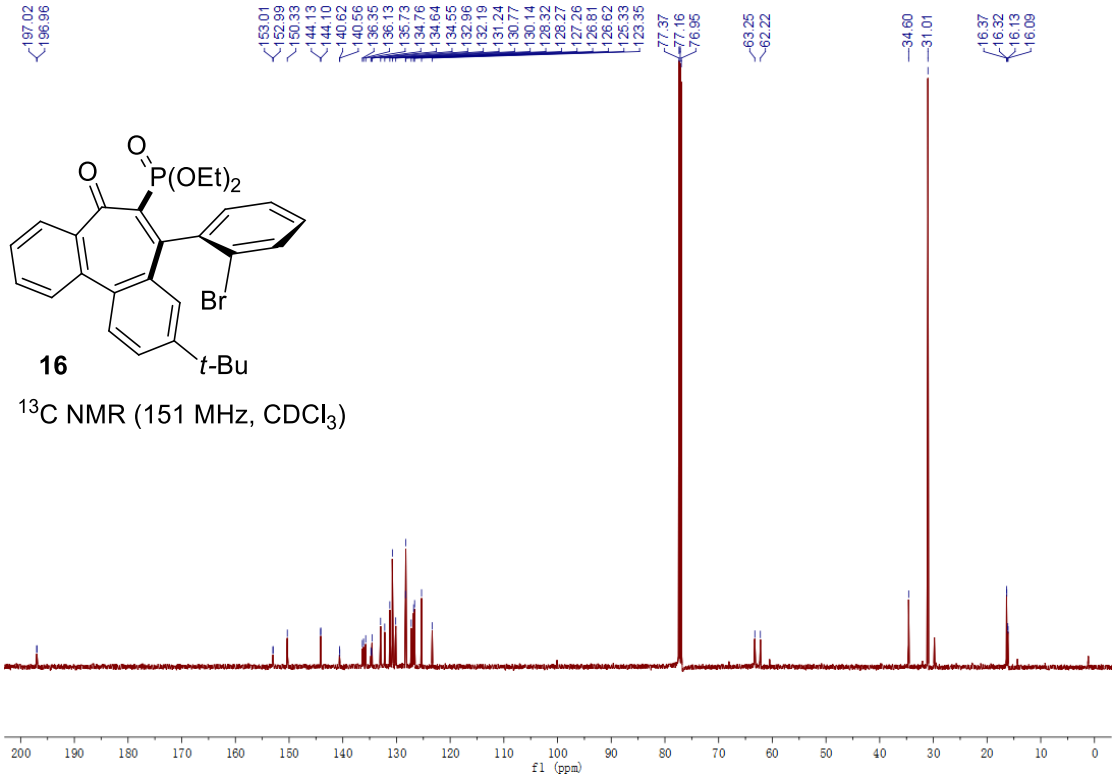
15

^{31}P NMR (243 MHz, $CDCl_3$)



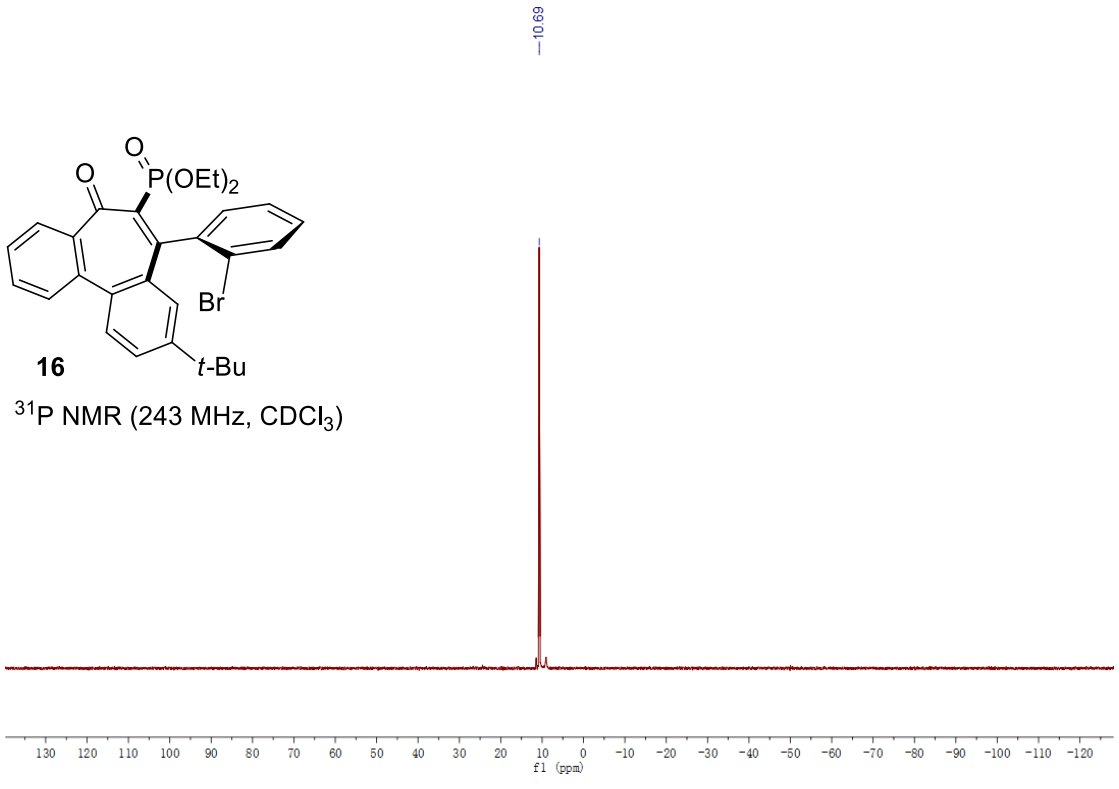
16

^{1}H NMR (600 MHz, $CDCl_3$)



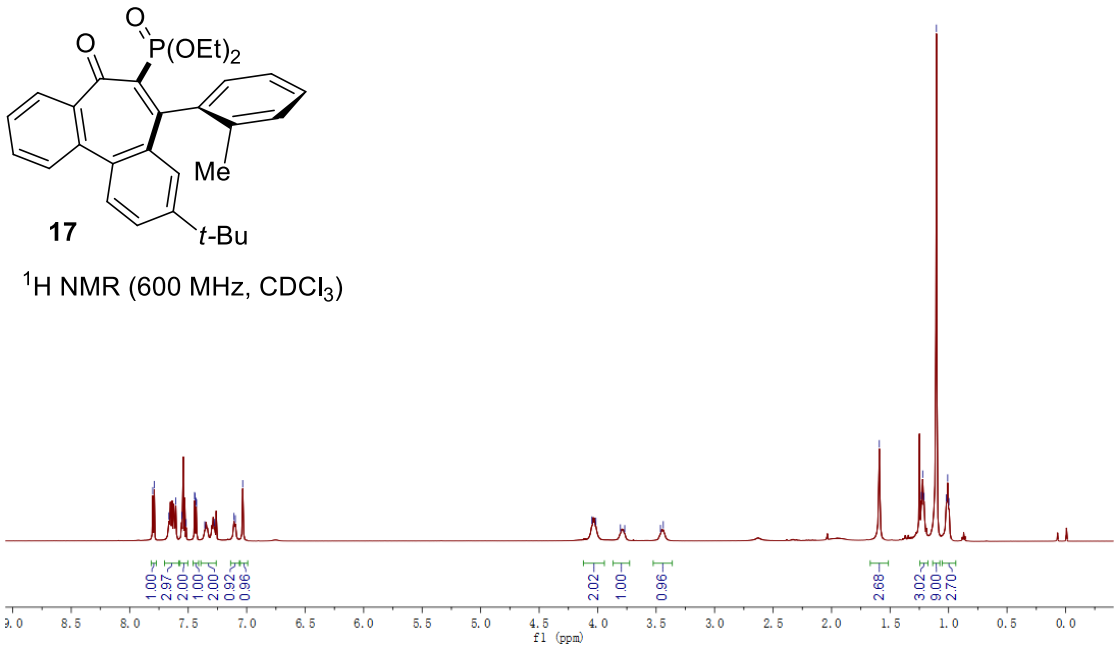
16

^{13}C NMR (151 MHz, $CDCl_3$)

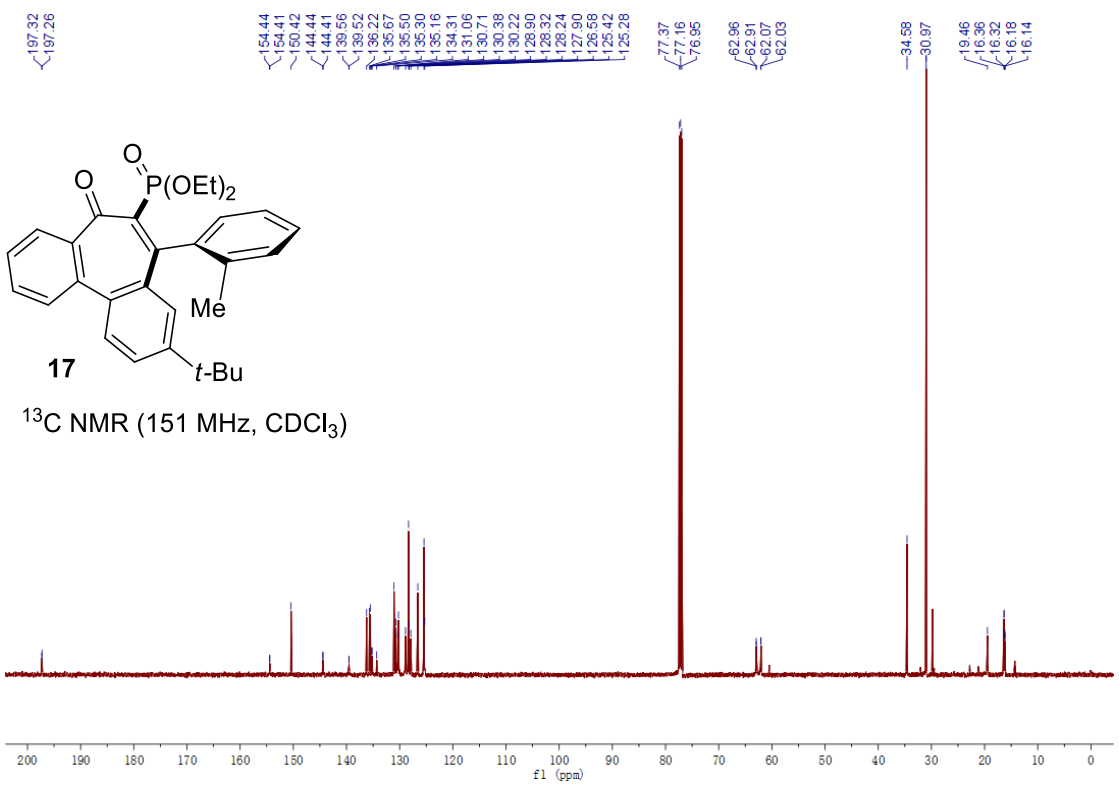


16

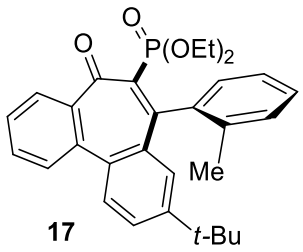
^{31}P NMR (243 MHz, $CDCl_3$)



^{1}H NMR (600 MHz, $CDCl_3$)

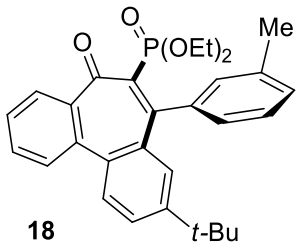


^{13}C NMR (151 MHz, $CDCl_3$)



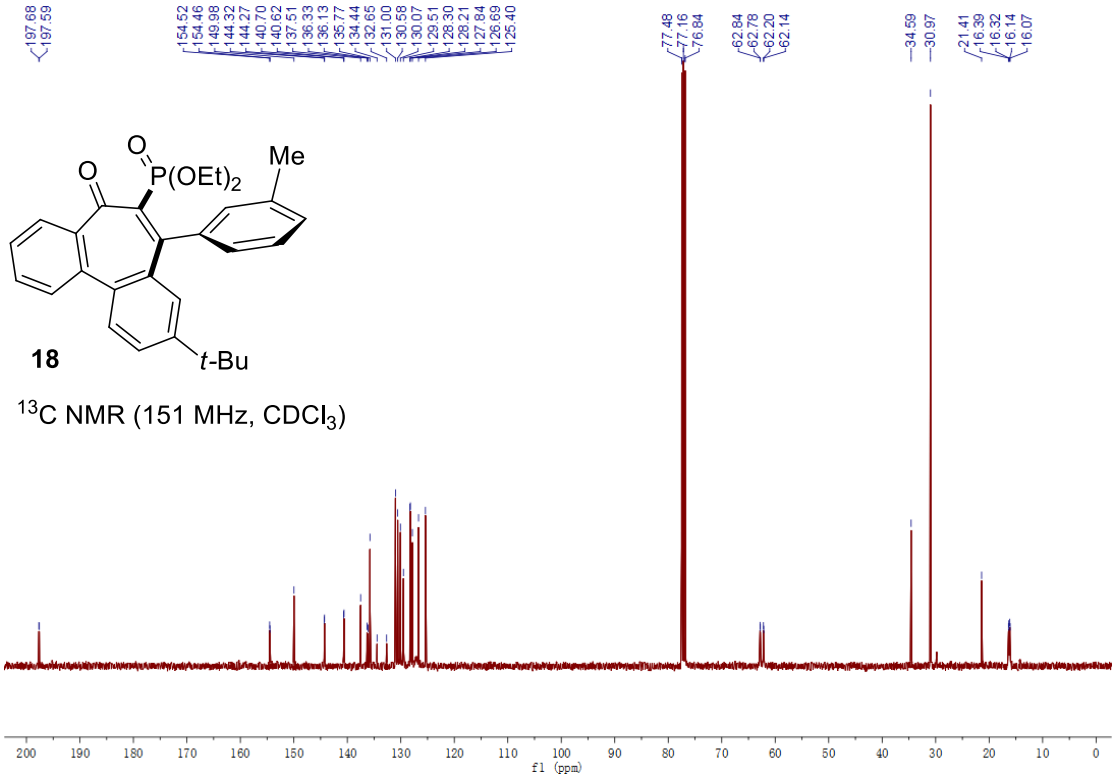
17

^{31}P NMR (243 MHz, $CDCl_3$)



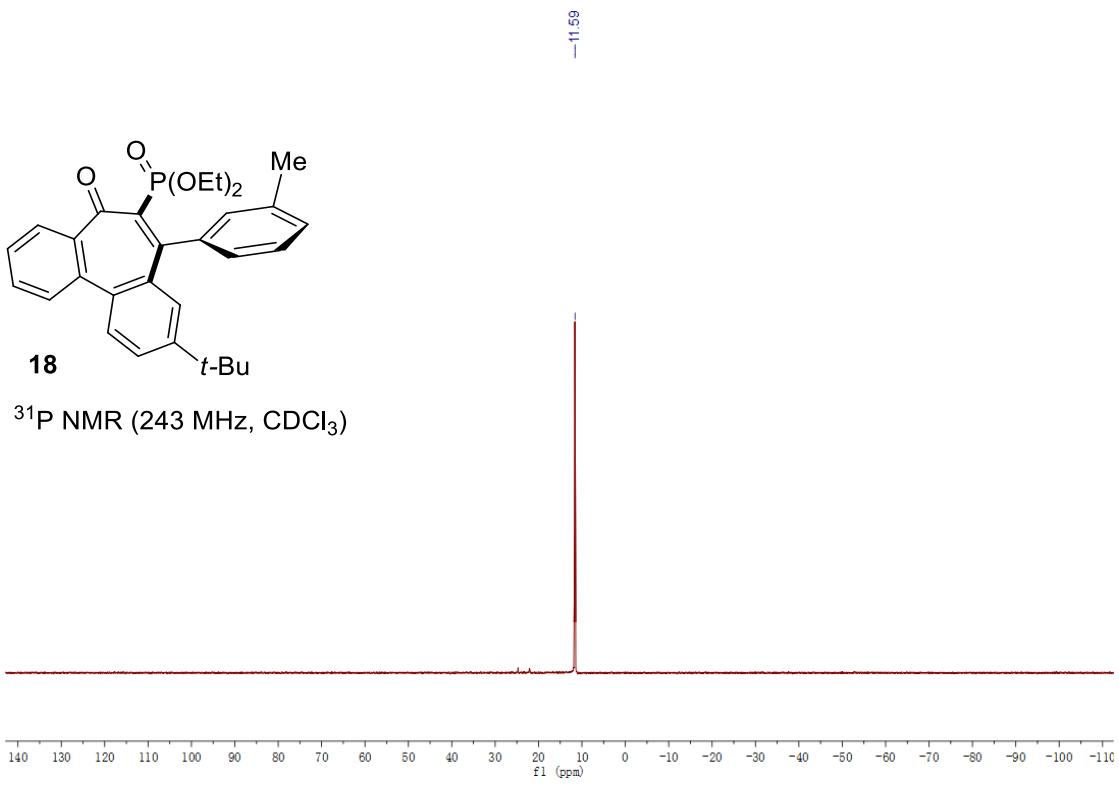
18

^{1}H NMR (600 MHz, $CDCl_3$)



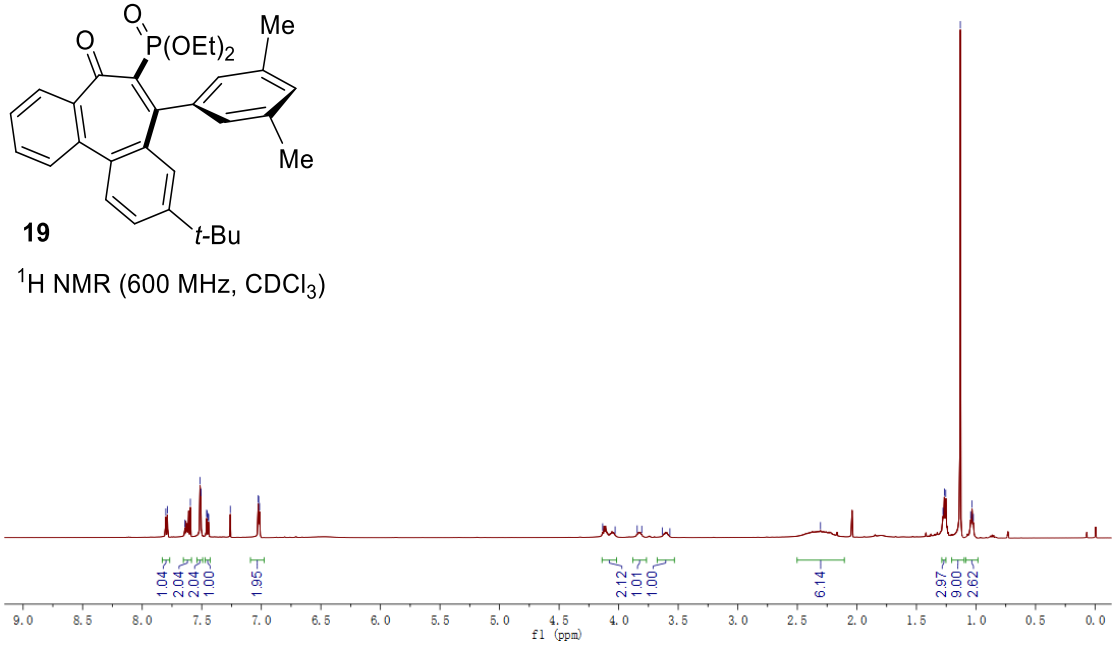
18

^{13}C NMR (151 MHz, $CDCl_3$)

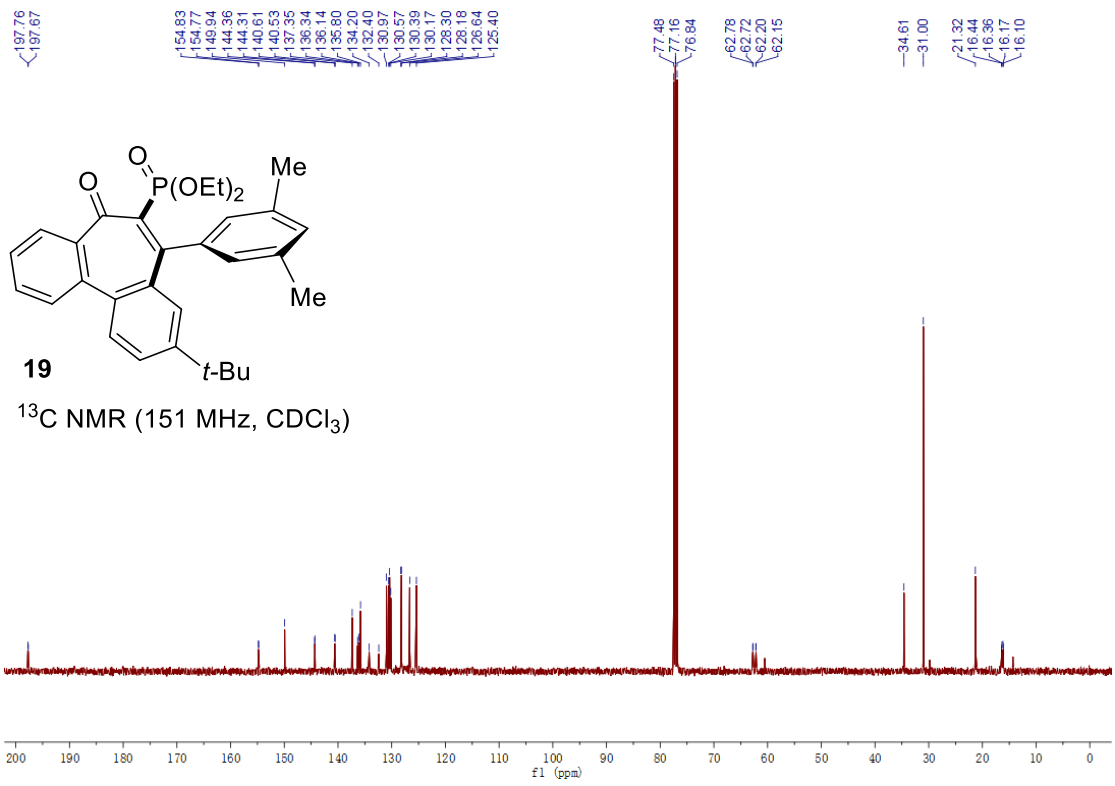


18

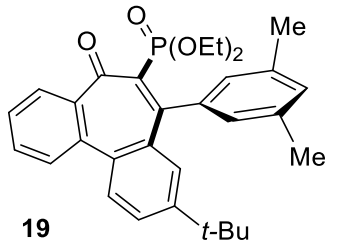
^{31}P NMR (243 MHz, $CDCl_3$)



^{1}H NMR (600 MHz, $CDCl_3$)

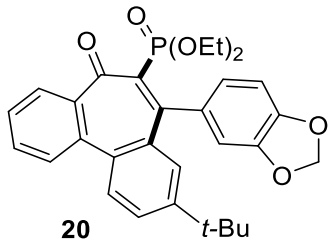


^{13}C NMR (151 MHz, $CDCl_3$)



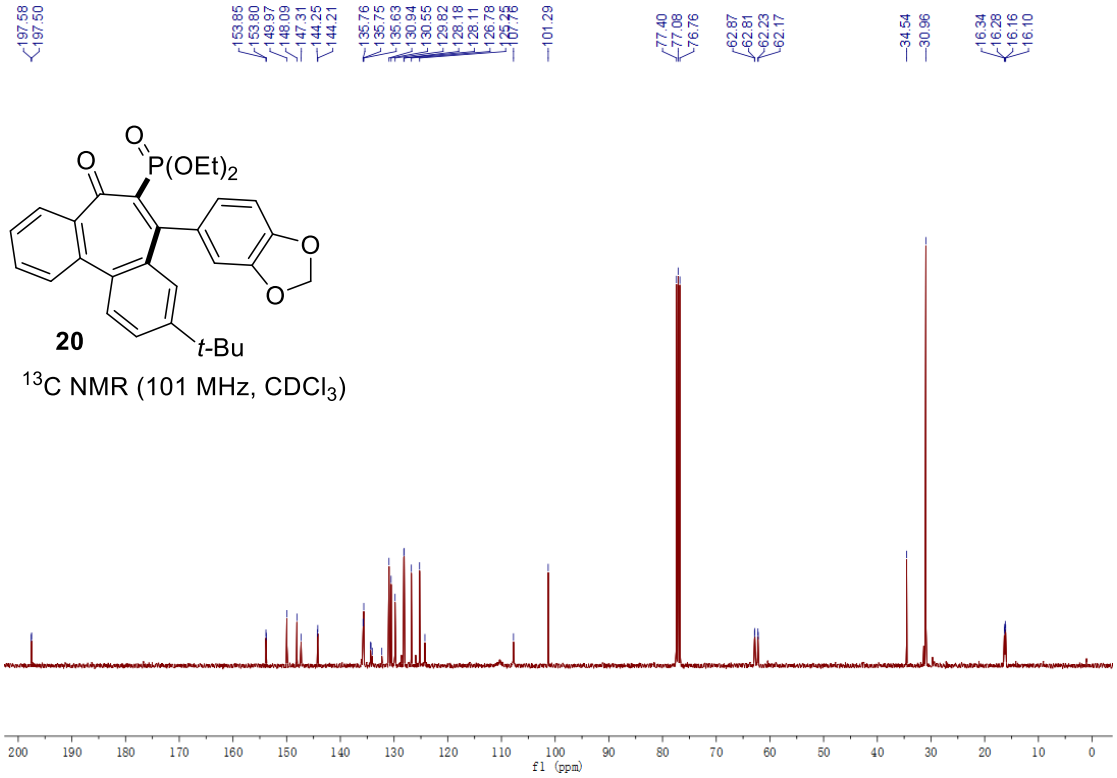
19

^{31}P NMR (243 MHz, $CDCl_3$)

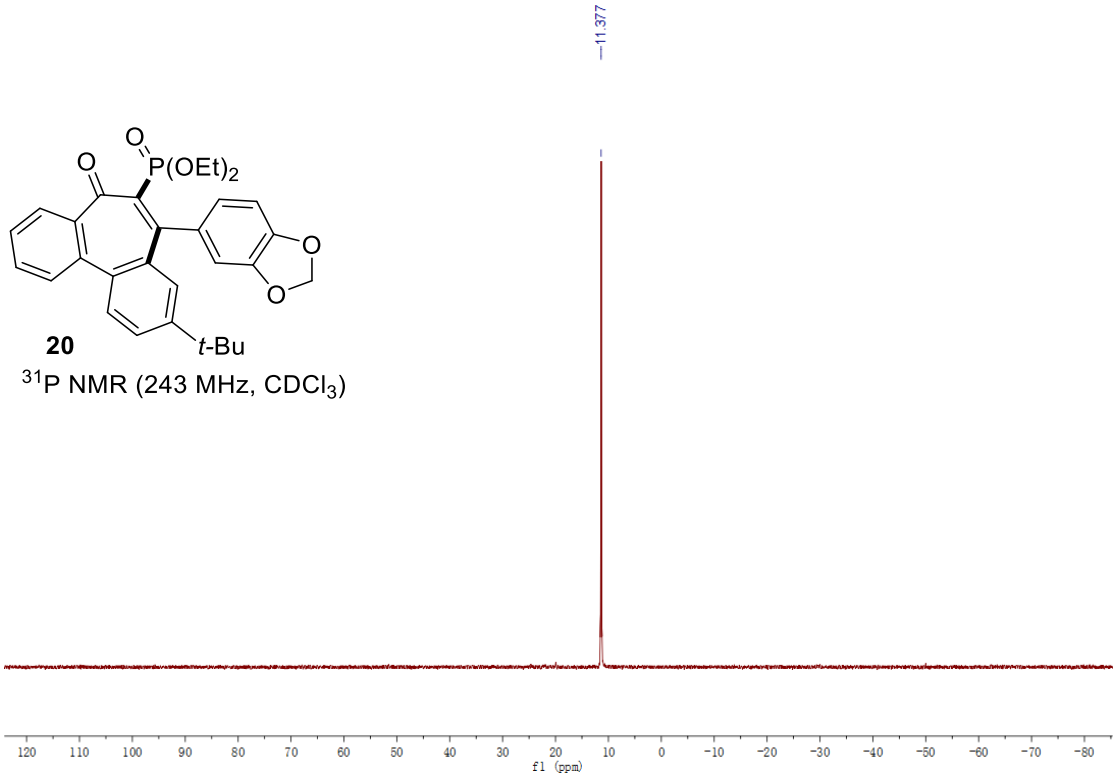


20

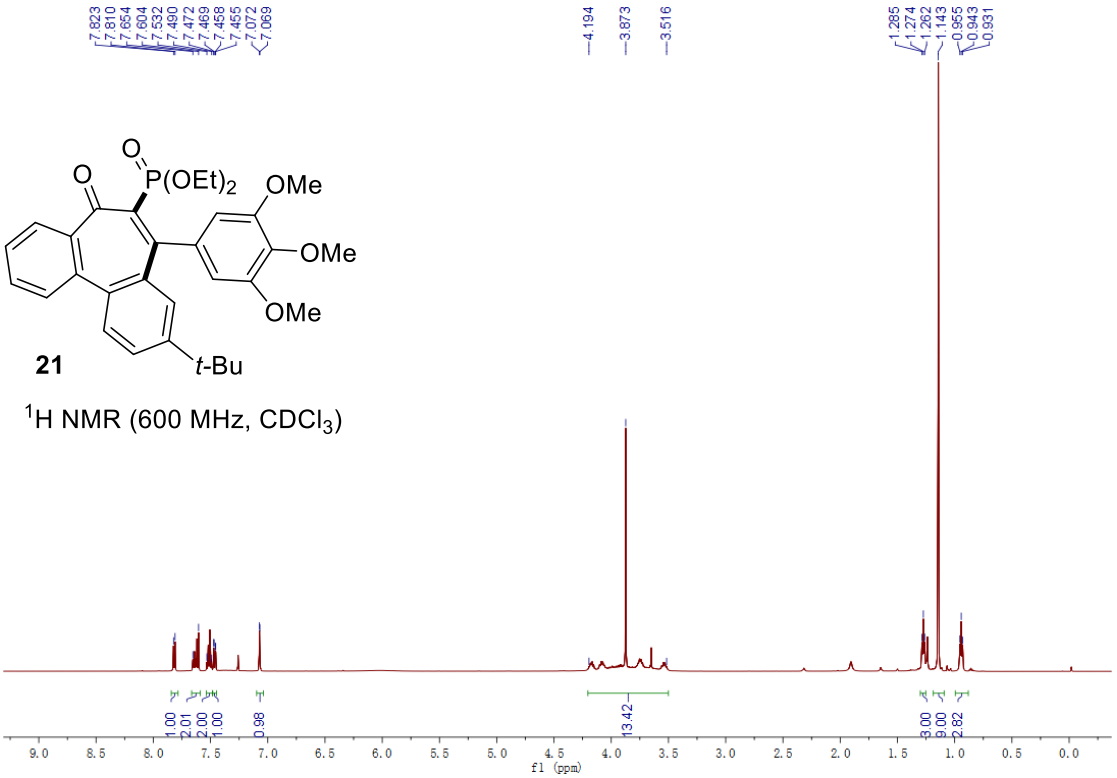
^{1}H NMR (400 MHz, $CDCl_3$)

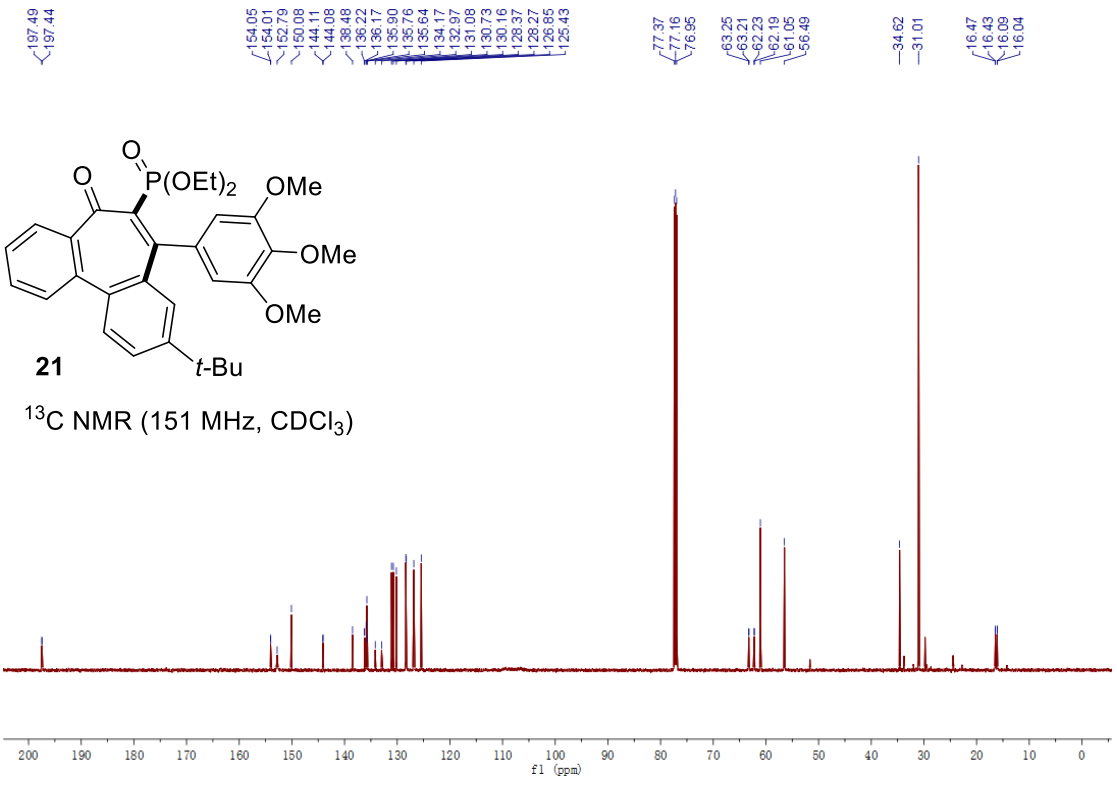


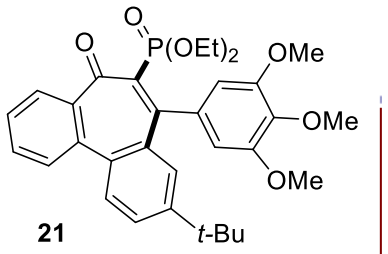
^{13}C NMR (101 MHz, $CDCl_3$)



^{31}P NMR (243 MHz, $CDCl_3$)

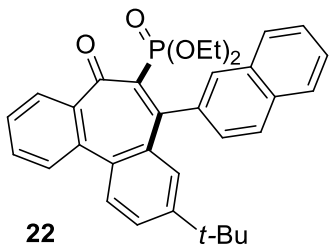

7.823
7.810
7.654
7.604
7.532
7.490
7.472
7.469
7.458
7.455
7.072
7.069
4.194
3.873
3.516
1.285
1.274
1.262
1.143
0.955
0.943
0.931
O
O
P(OEt)2
OMe
OMe
OMe
21
t-Bu
1H NMR (600 MHz, CDCl3)
1.00
2.01
2.00
1.00
0.98
13.42
3.00
9.00
2.82
f1 (ppm)


197.49
197.44
154.05
154.01
152.79
150.08
144.11
144.08
138.48
136.22
136.17
135.90
135.76
135.64
134.17
132.97
131.08
130.73
130.16
128.37
128.27
126.85
125.43
77.37
77.16
76.95
63.25
63.21
62.23
62.19
61.05
56.49
34.62
31.01
16.47
16.43
16.09
16.04
O
O
P(OEt)2
OMe
OMe
OMe
21
t-Bu
13C NMR (151 MHz, CDCl3)
f1 (ppm)



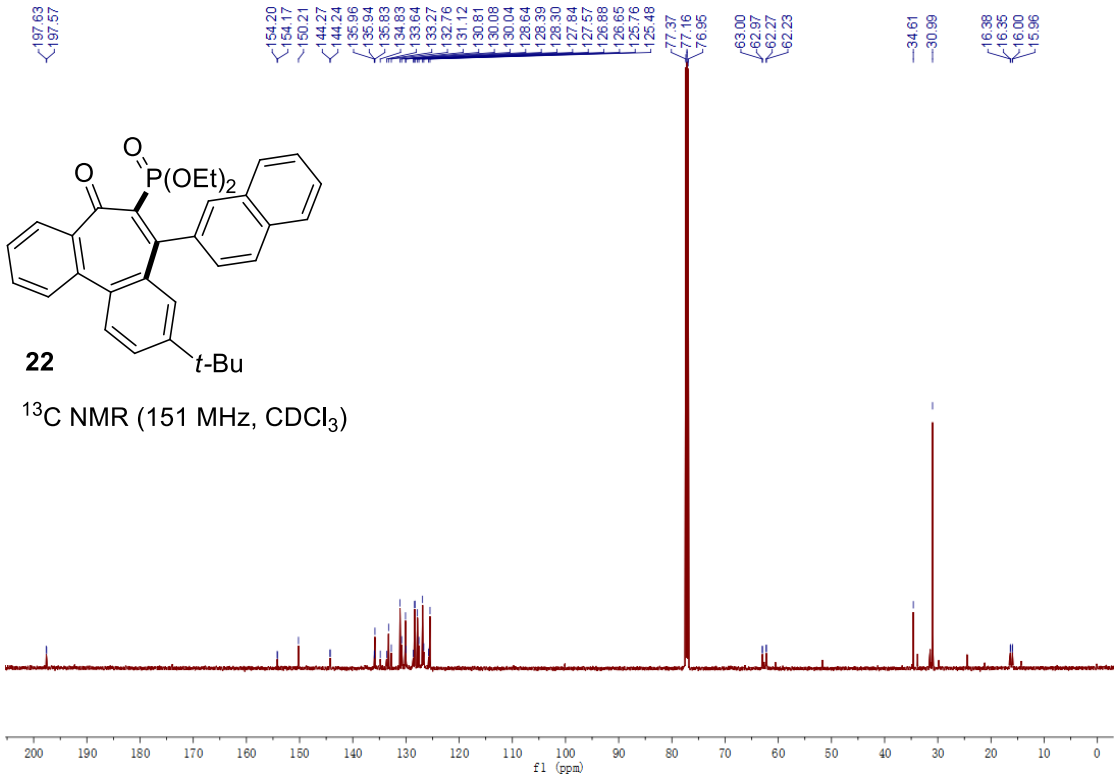
21

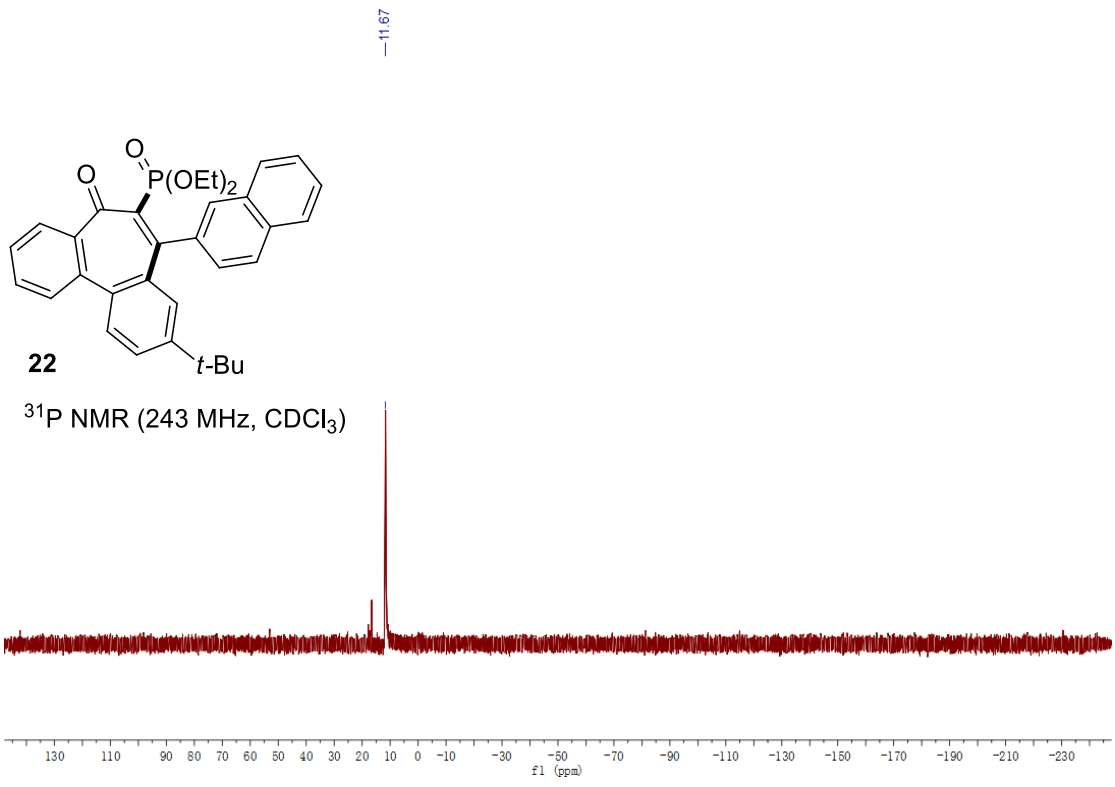
^{31}P NMR (243 MHz, $CDCl_3$)

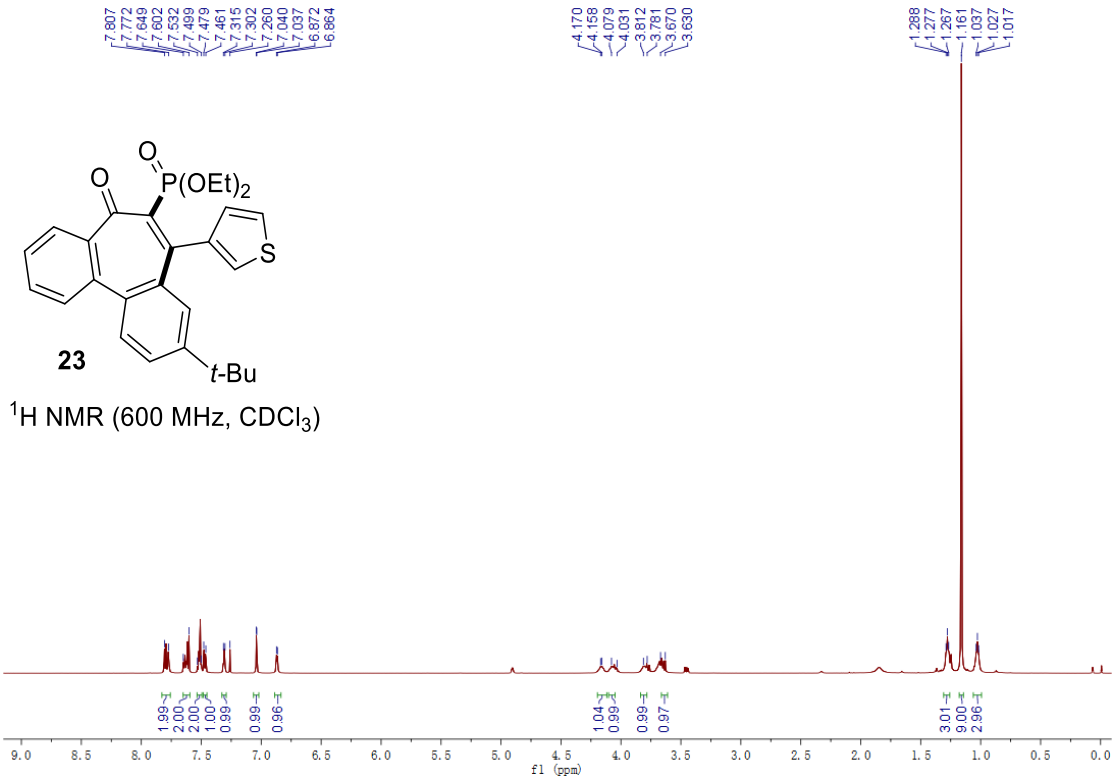


22

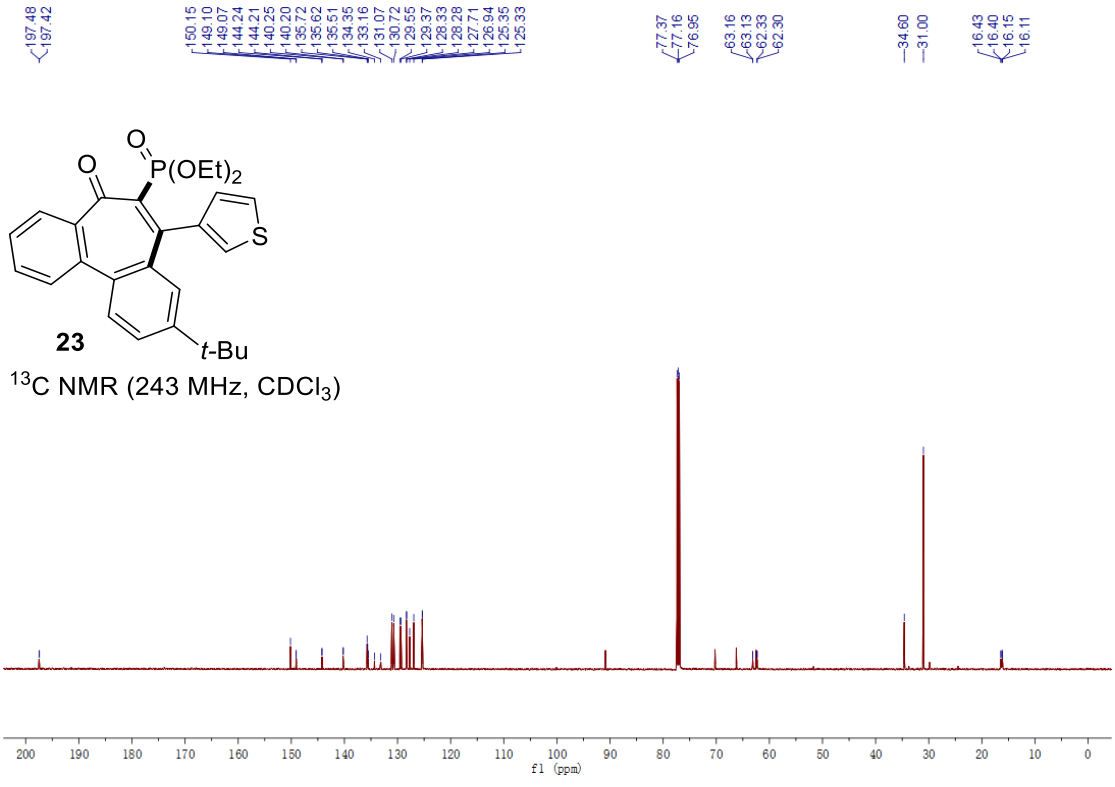
^{1}H NMR (600 MHz, $CDCl_3$)


197.63
197.57
154.20
154.17
150.21
144.27
144.24
135.96
135.94
135.83
134.83
133.64
133.27
132.76
131.12
130.81
130.08
130.04
128.64
128.39
128.30
127.84
127.57
126.88
126.65
125.76
125.48
77.37
77.16
76.95
63.00
62.97
62.27
62.23
34.61
30.99
16.38
16.35
16.00
15.96
O
O
P(OEt)2
22
t-Bu
13C NMR (151 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

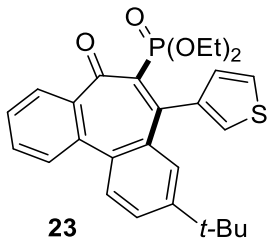

11.67
O
O
P(OEt)2
22
t-Bu
31P NMR (243 MHz, CDCl3)
130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)



^{1}H NMR (600 MHz, $CDCl_3$)

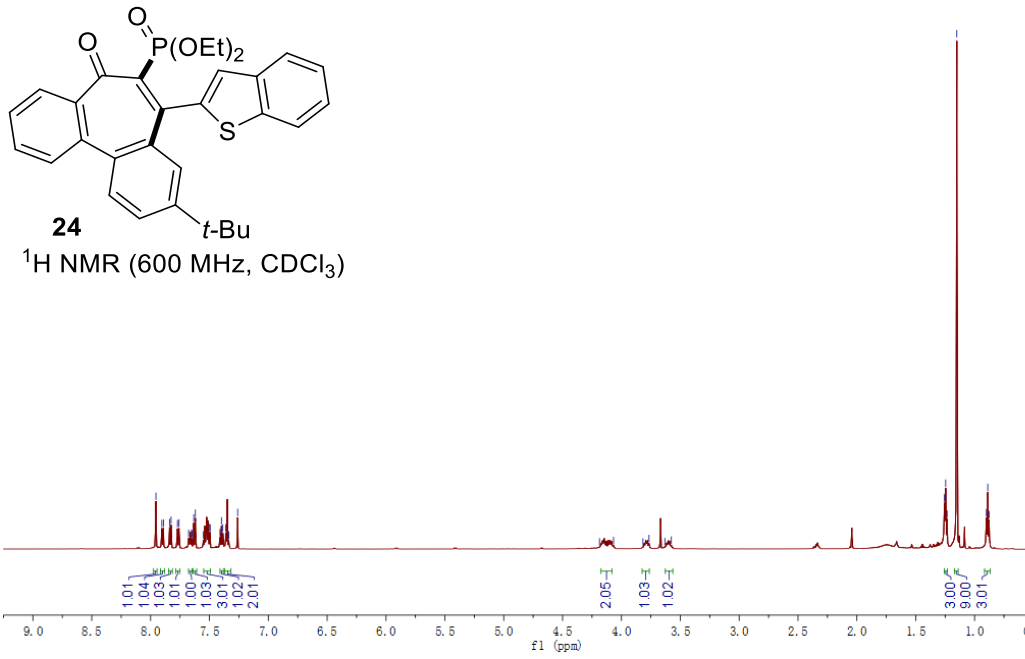


^{13}C NMR (243 MHz, $CDCl_3$)



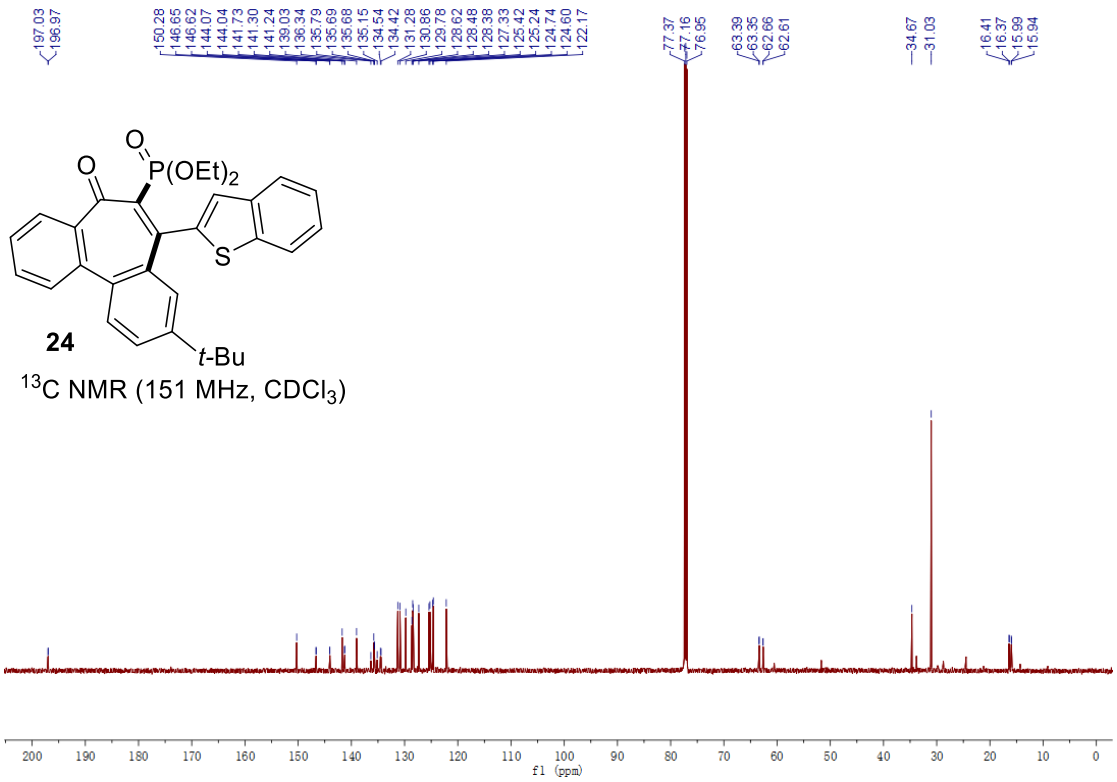
23

^{31}P NMR (243 MHz, $CDCl_3$)

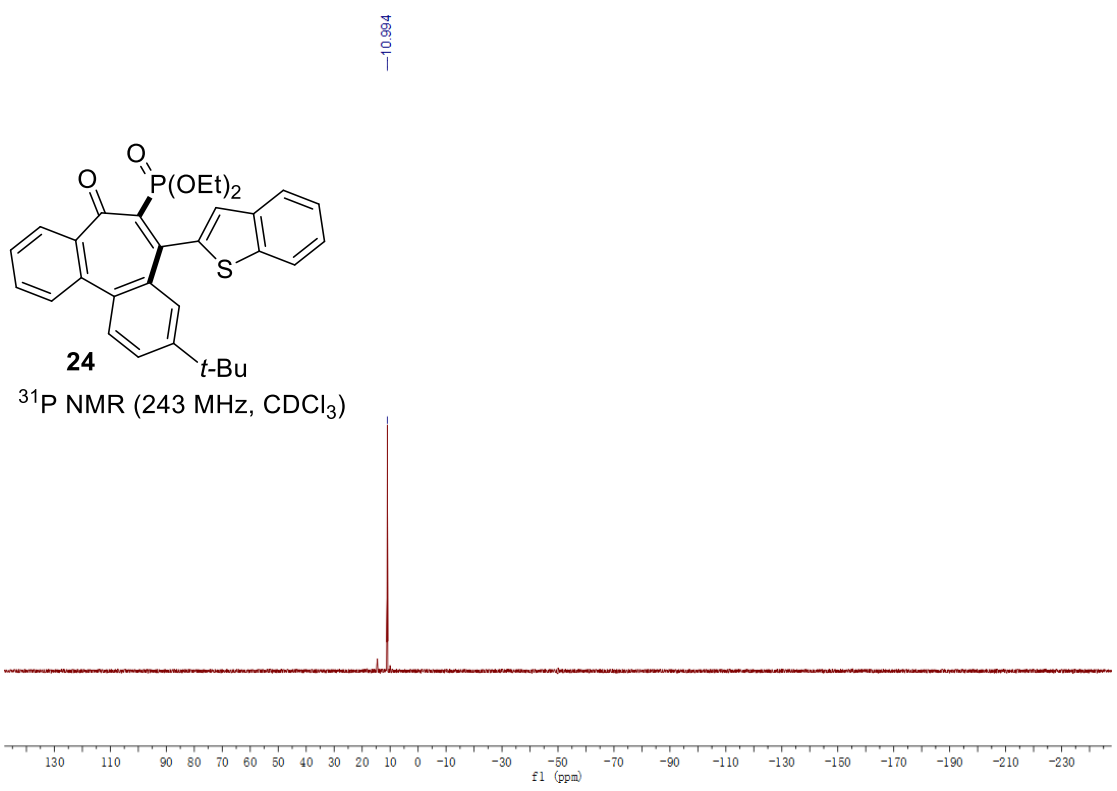


24

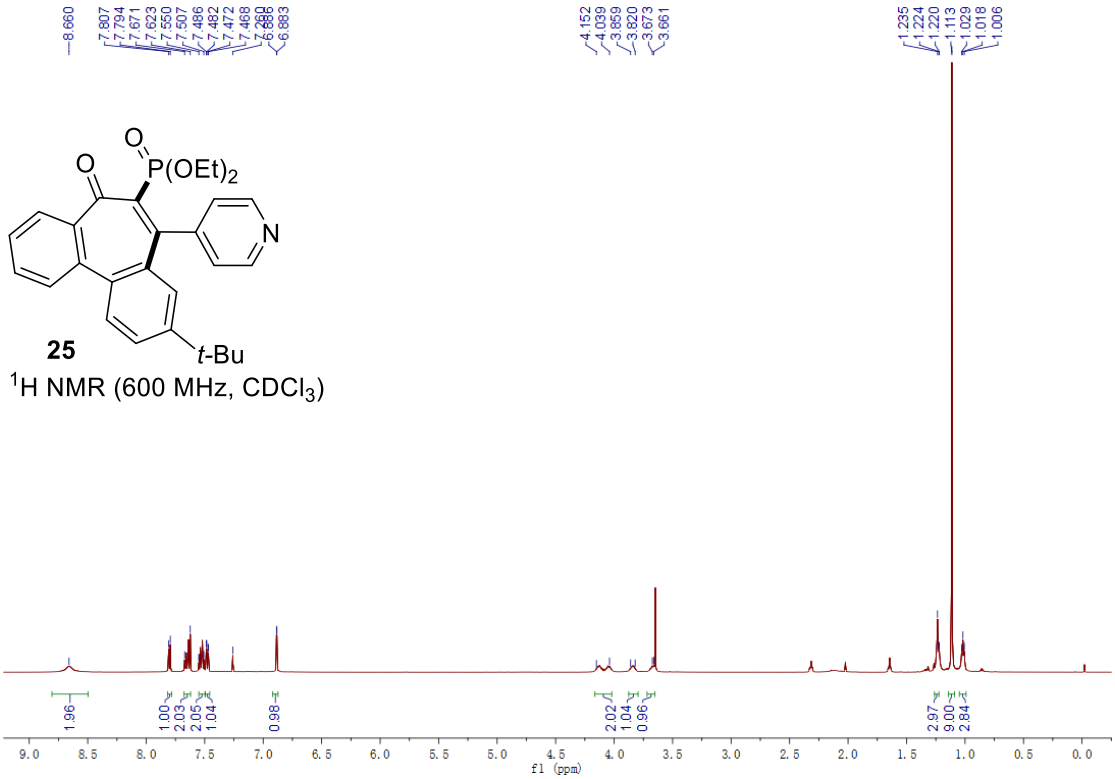
^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C NMR (151 MHz, $CDCl_3$)

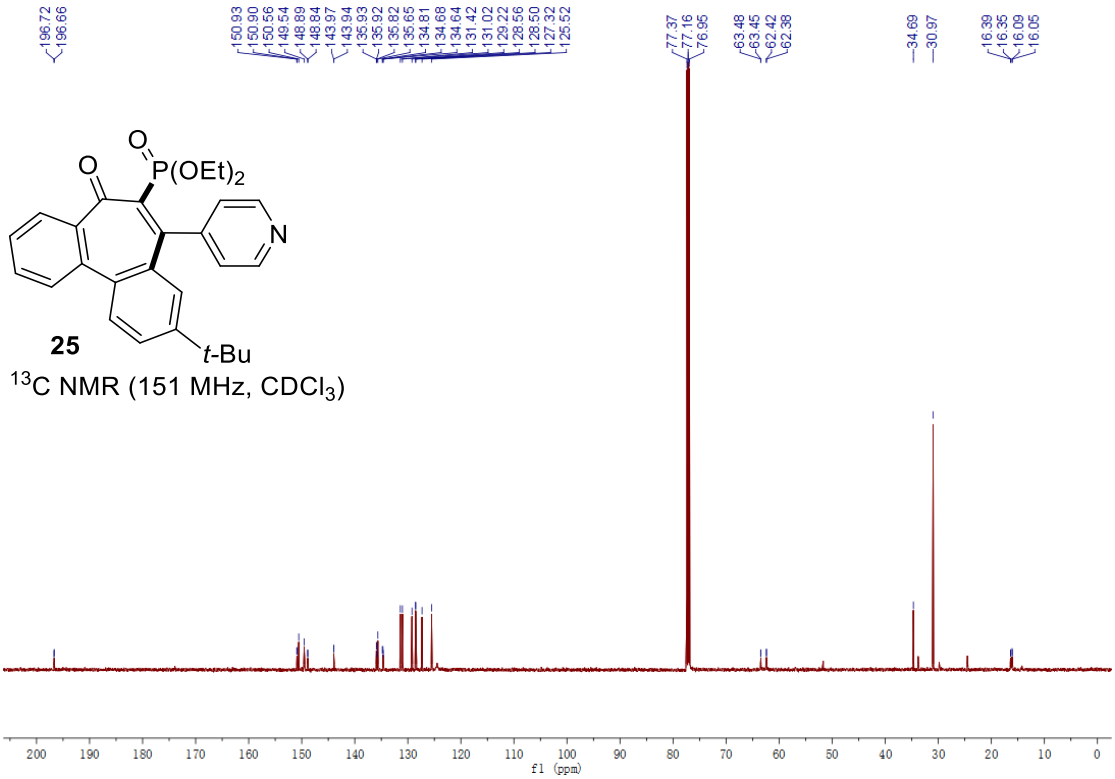


^{31}P NMR (243 MHz, $CDCl_3$)



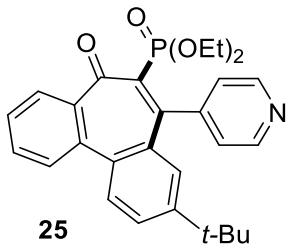
25

^{1}H NMR (600 MHz, $CDCl_3$)



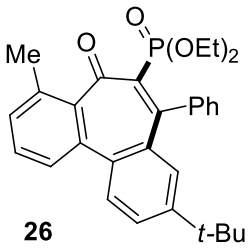
25

^{13}C NMR (151 MHz, $CDCl_3$)



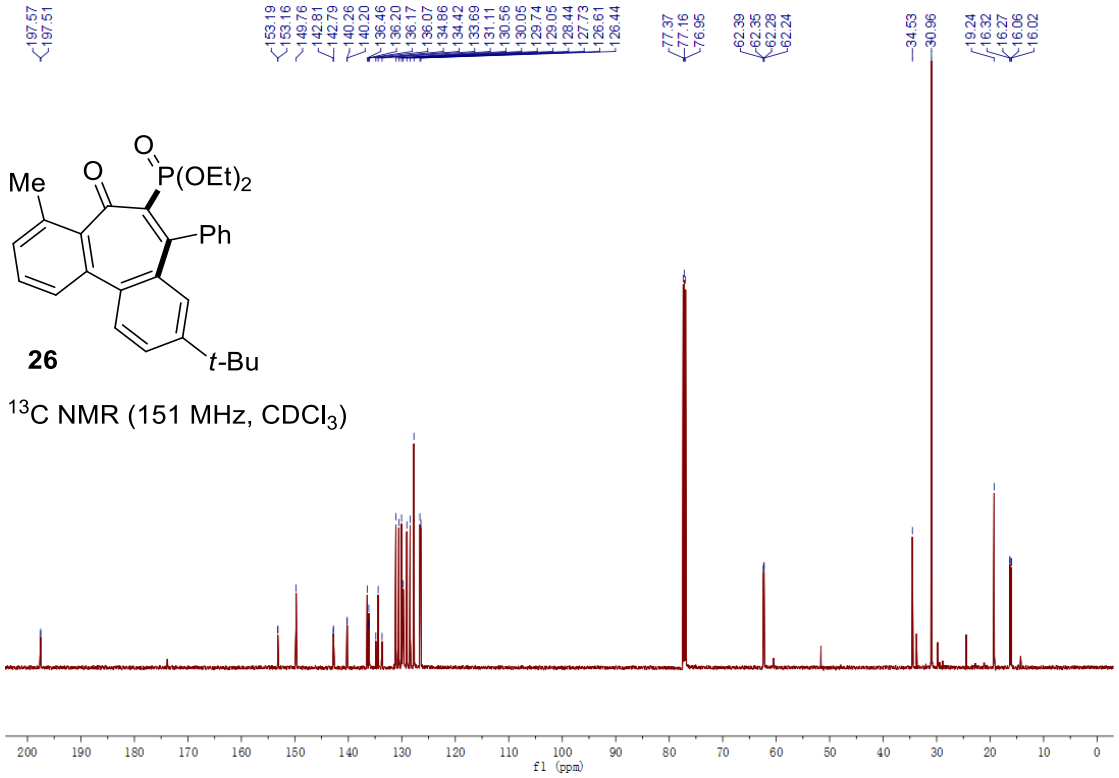
25

^{31}P NMR (243 MHz, $CDCl_3$)

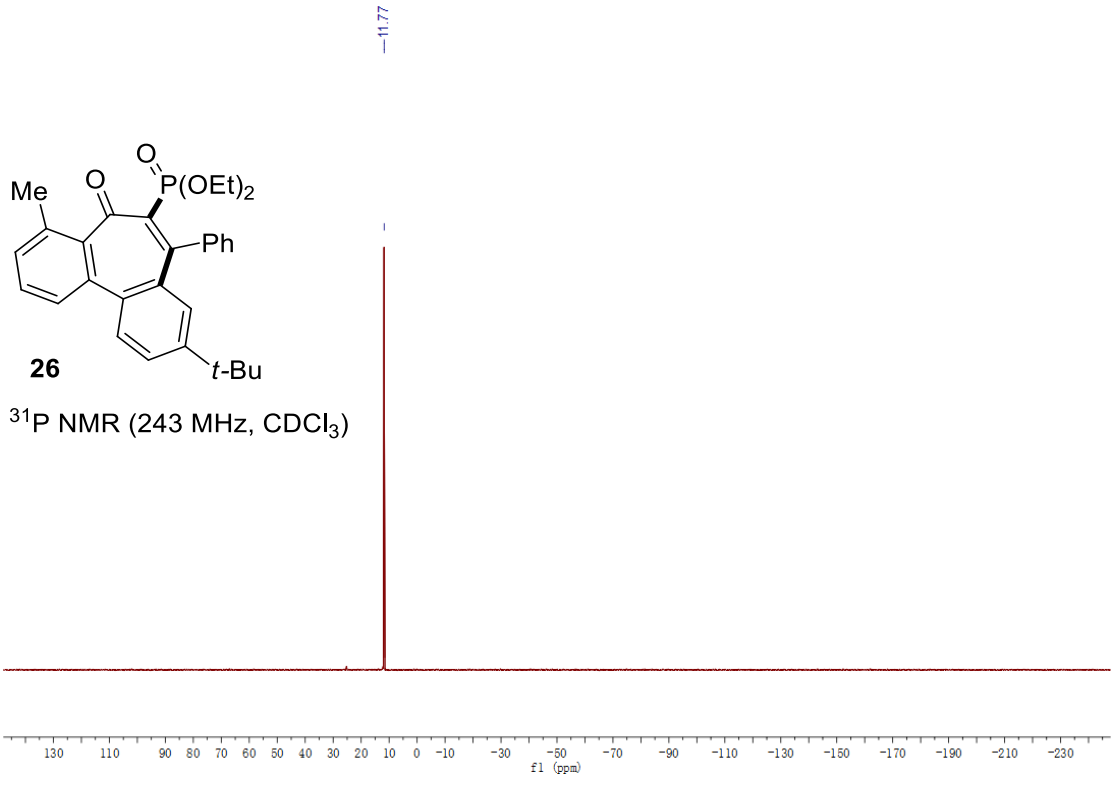


26

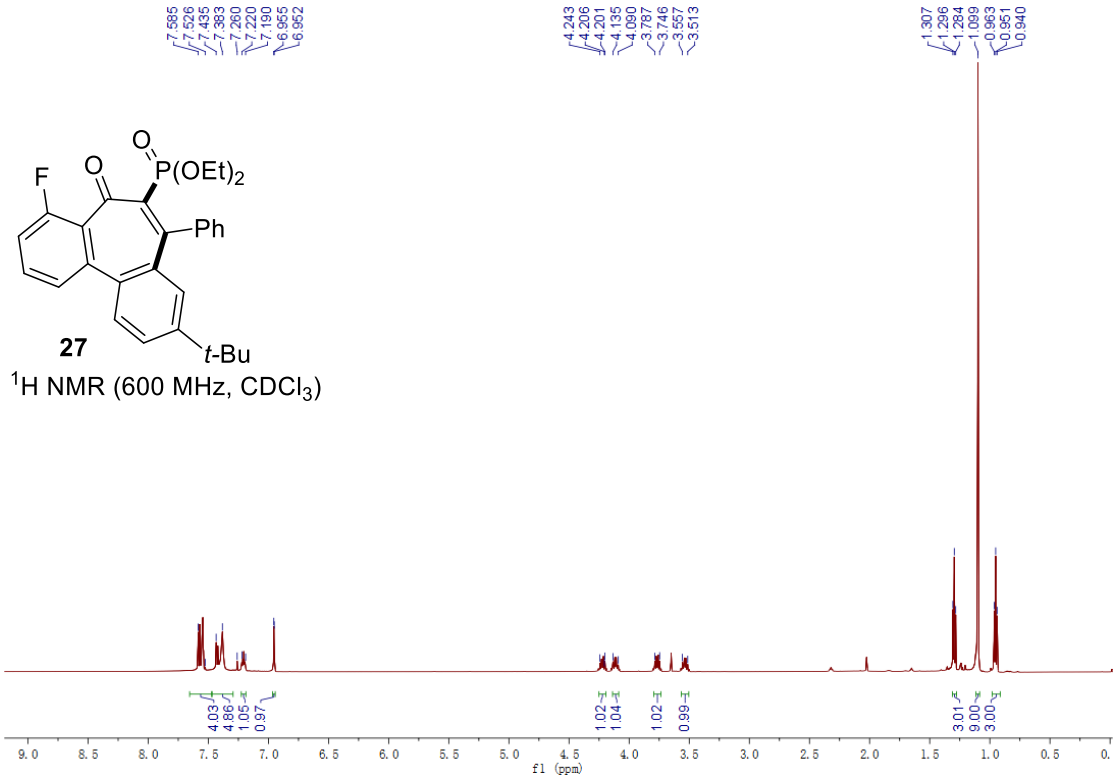
^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C NMR (151 MHz, $CDCl_3$)

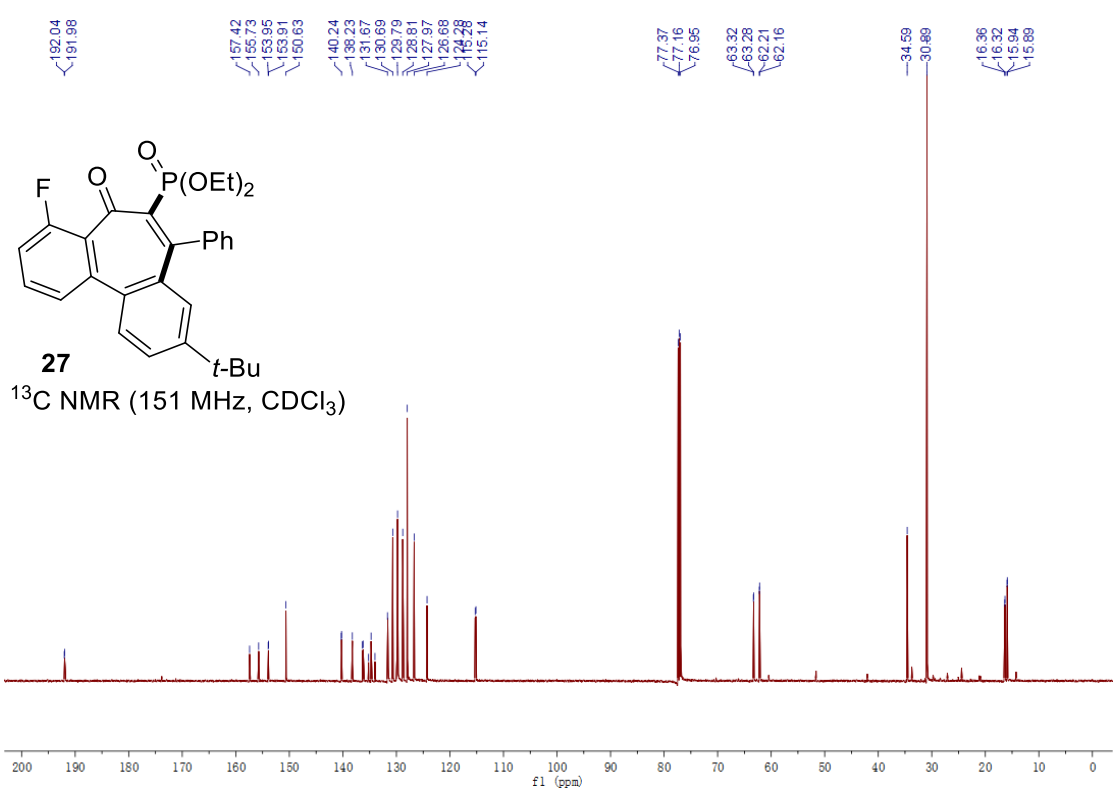


^{31}P NMR (243 MHz, $CDCl_3$)



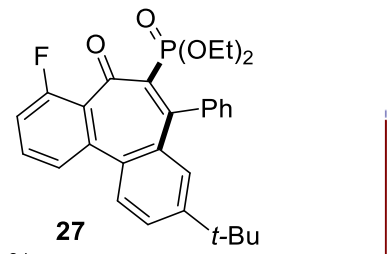
27

^{1}H NMR (600 MHz, $CDCl_3$)



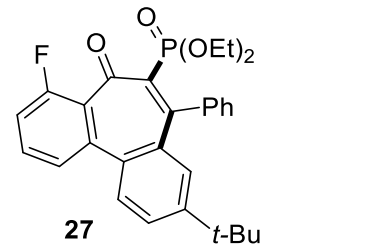
27

^{13}C NMR (151 MHz, $CDCl_3$)



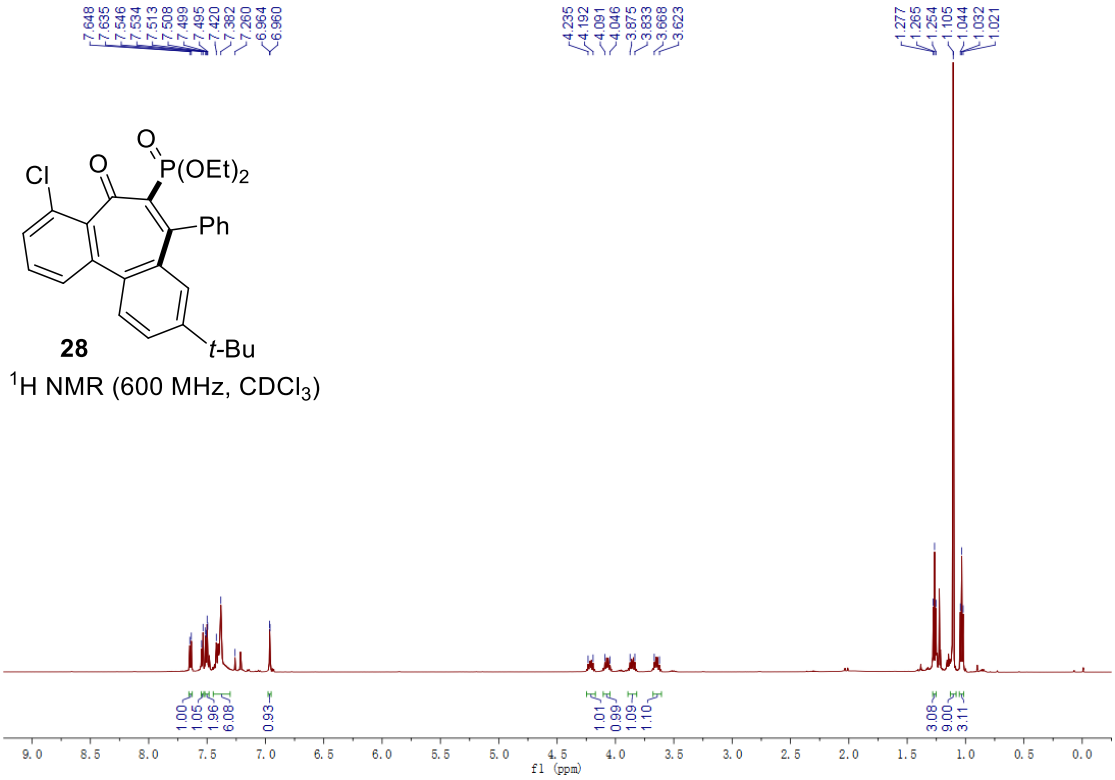
27

^{31}P NMR (243 MHz, $CDCl_3$)

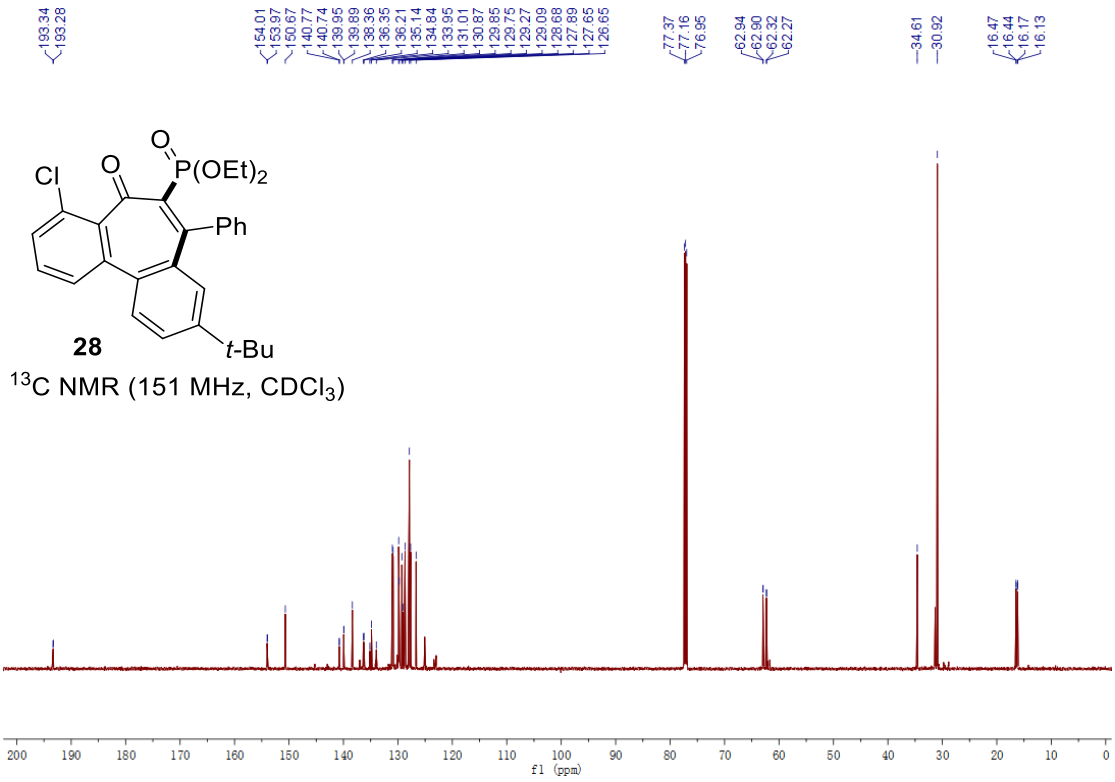


27

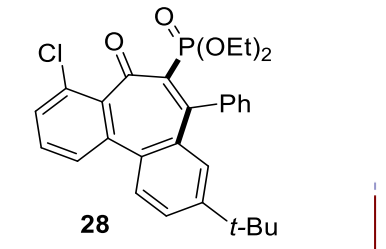
^{19}F NMR (565 MHz, $CDCl_3$)



^{1}H NMR (600 MHz, $CDCl_3$)

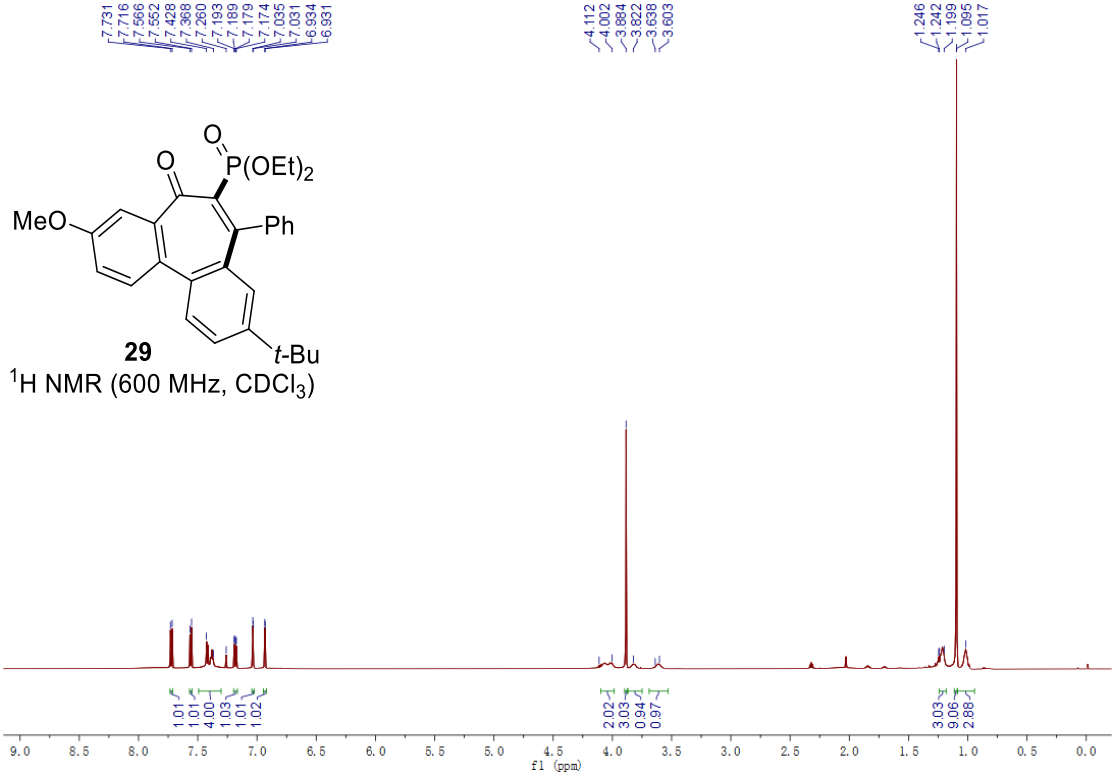


^{13}C NMR (151 MHz, $CDCl_3$)



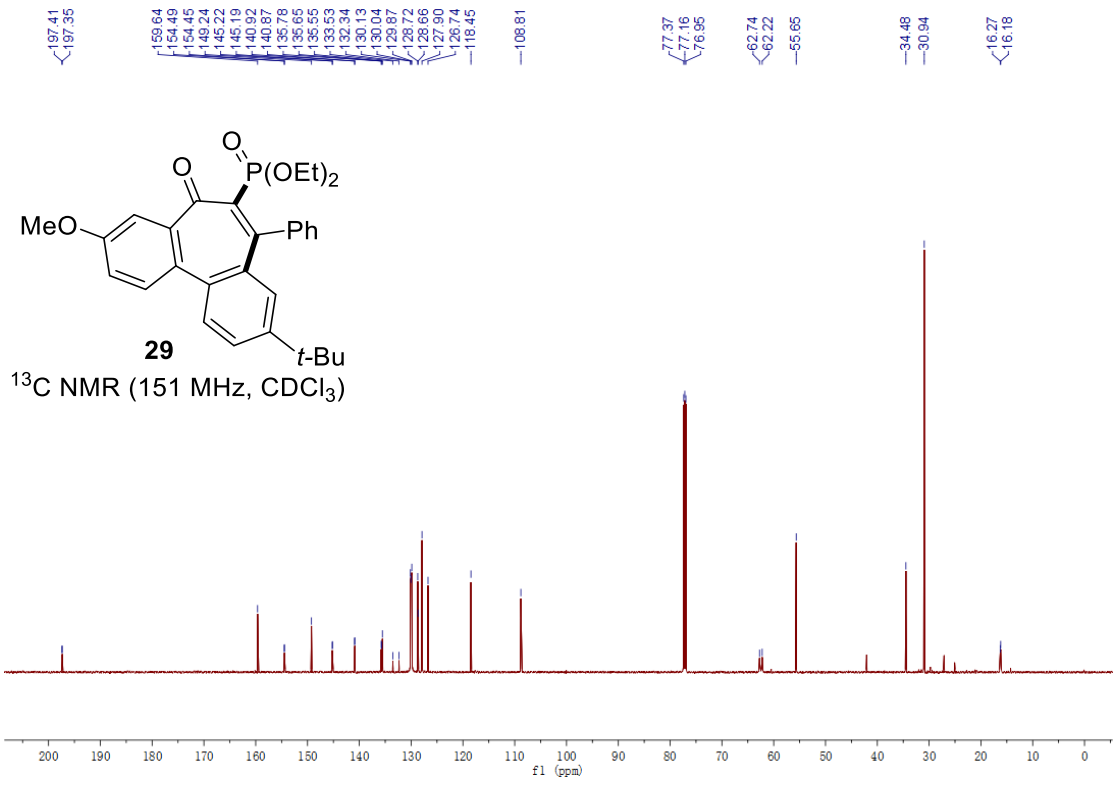
28

^{31}P NMR (243 MHz, $CDCl_3$)



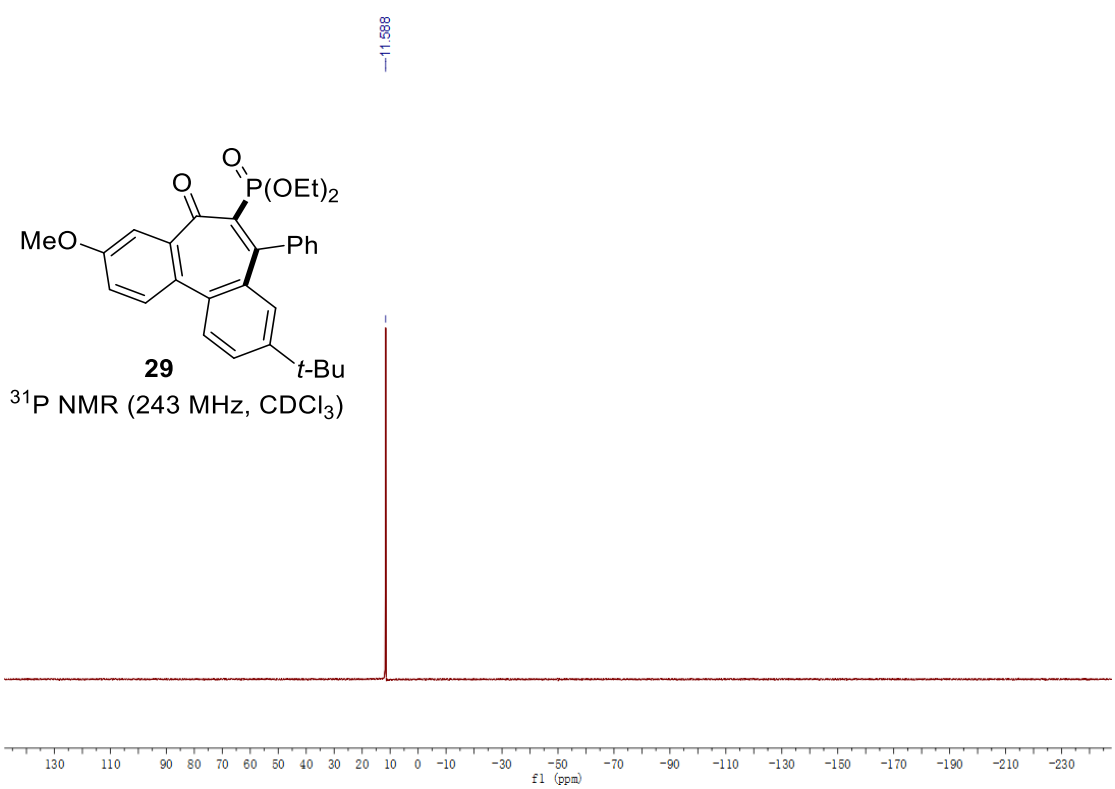
29

^{1}H NMR (600 MHz, $CDCl_3$)



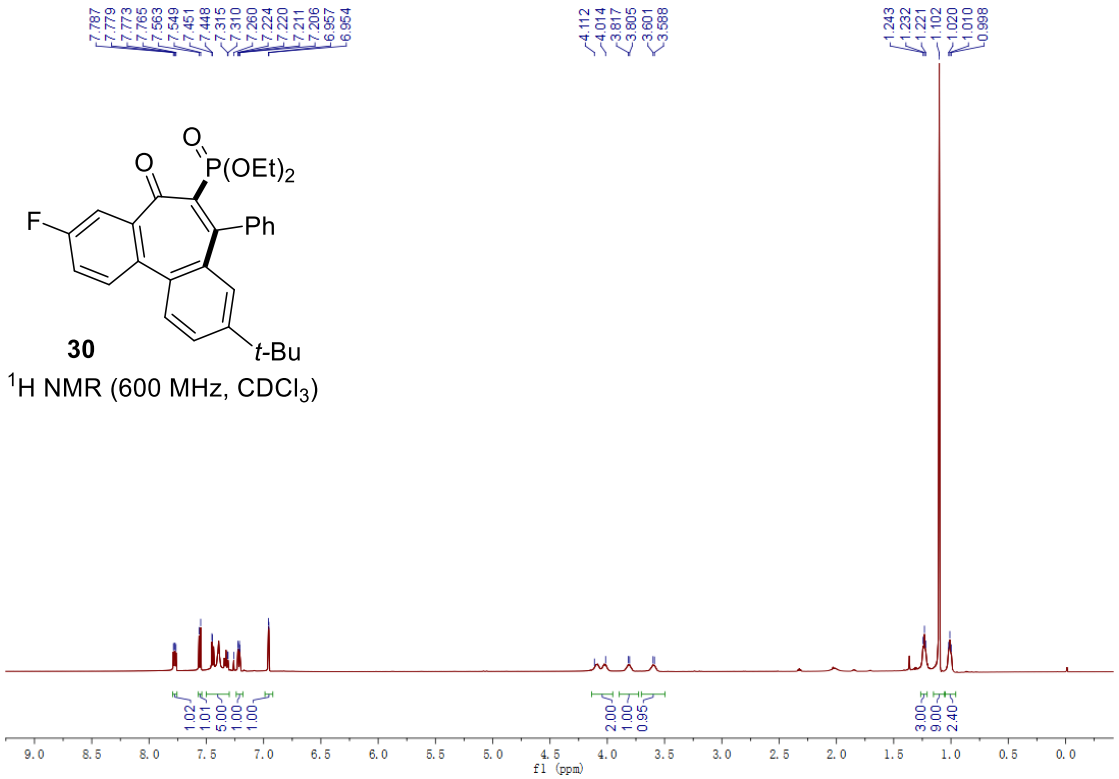
29

^{13}C NMR (151 MHz, $CDCl_3$)



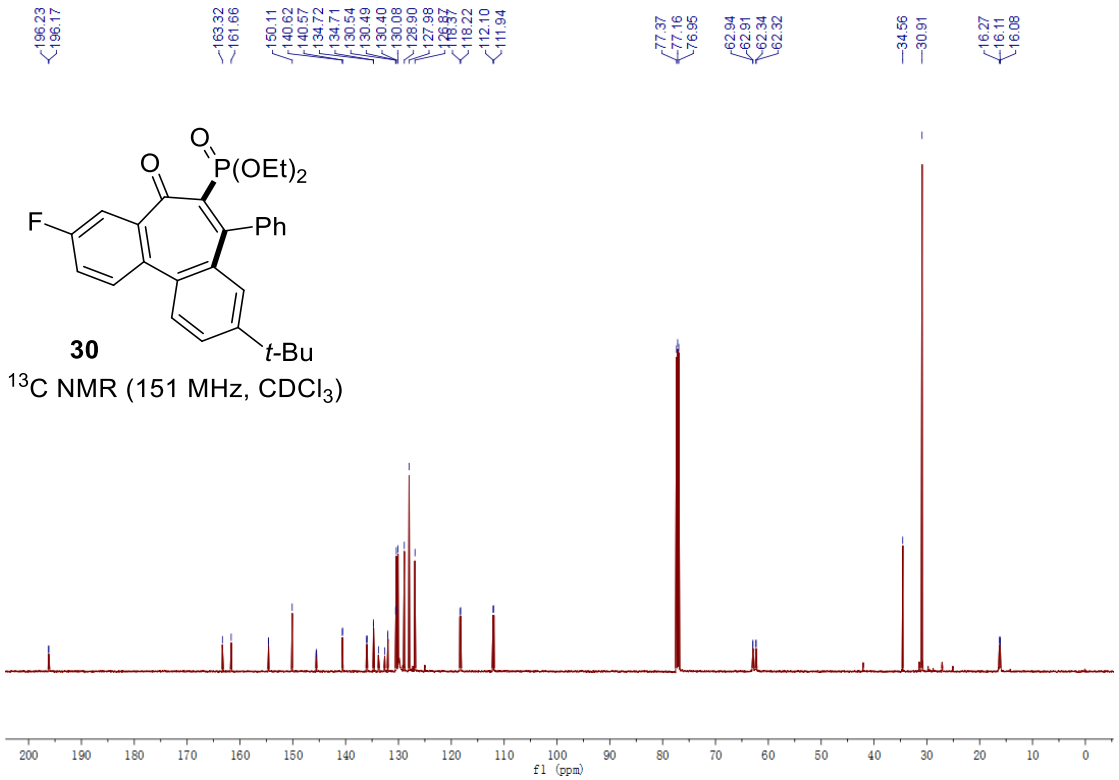
29

^{31}P NMR (243 MHz, $CDCl_3$)



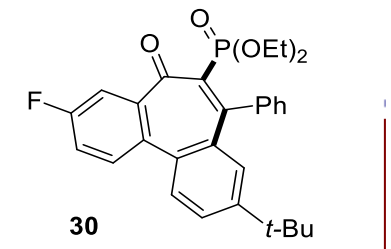
30

^{1}H NMR (600 MHz, $CDCl_3$)



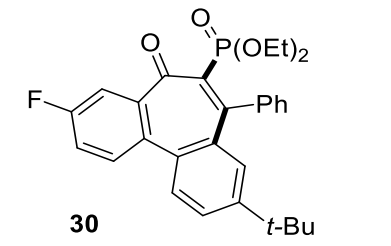
30

^{13}C NMR (151 MHz, $CDCl_3$)



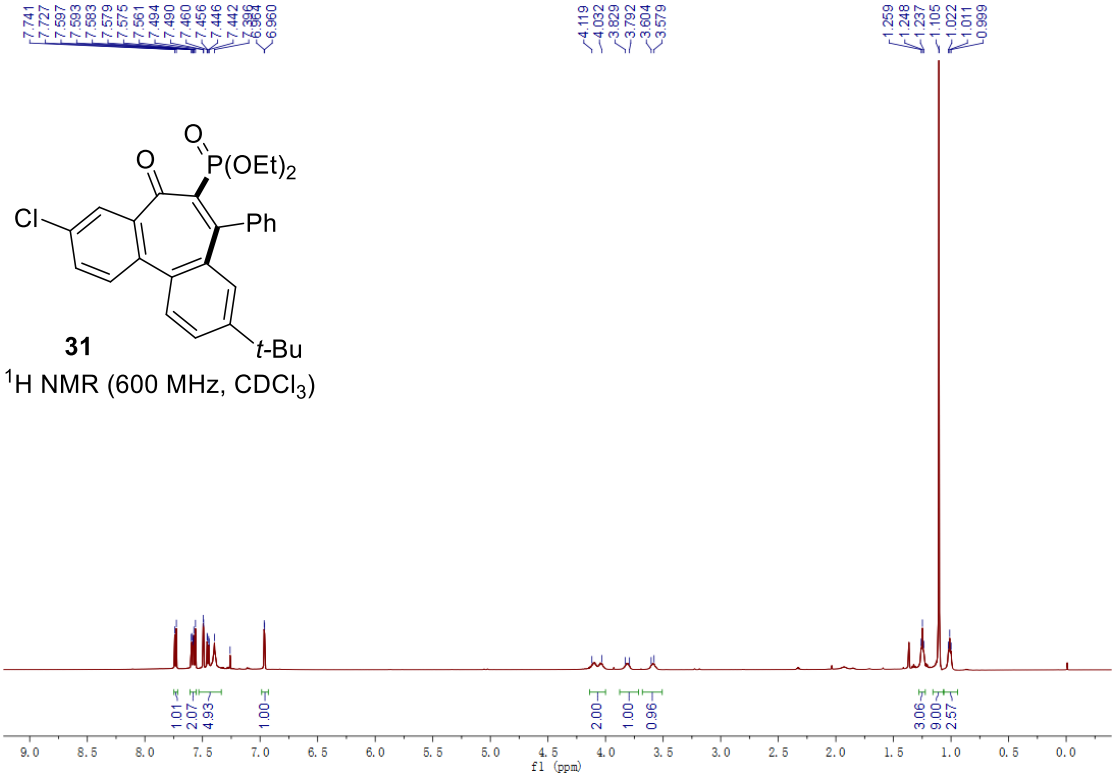
30

^{31}P NMR (243 MHz, $CDCl_3$)

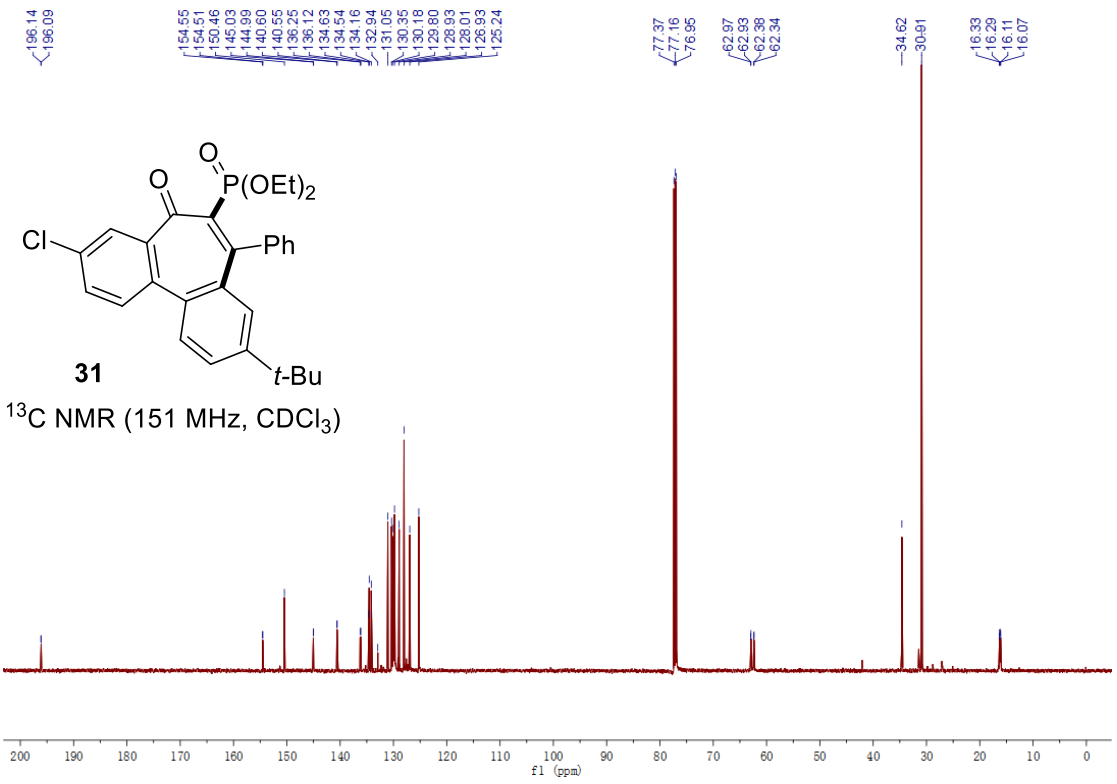


30

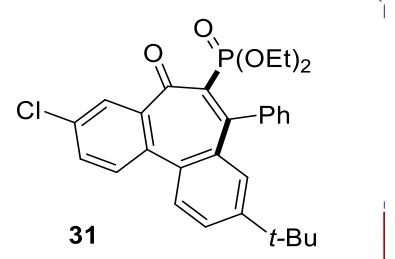
^{19}F NMR (565 MHz, $CDCl_3$)



^{1}H NMR (600 MHz, $CDCl_3$)

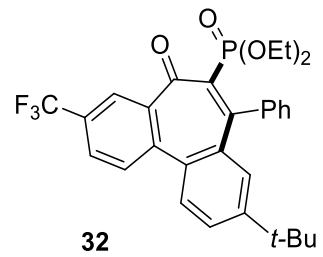


^{13}C NMR (151 MHz, $CDCl_3$)



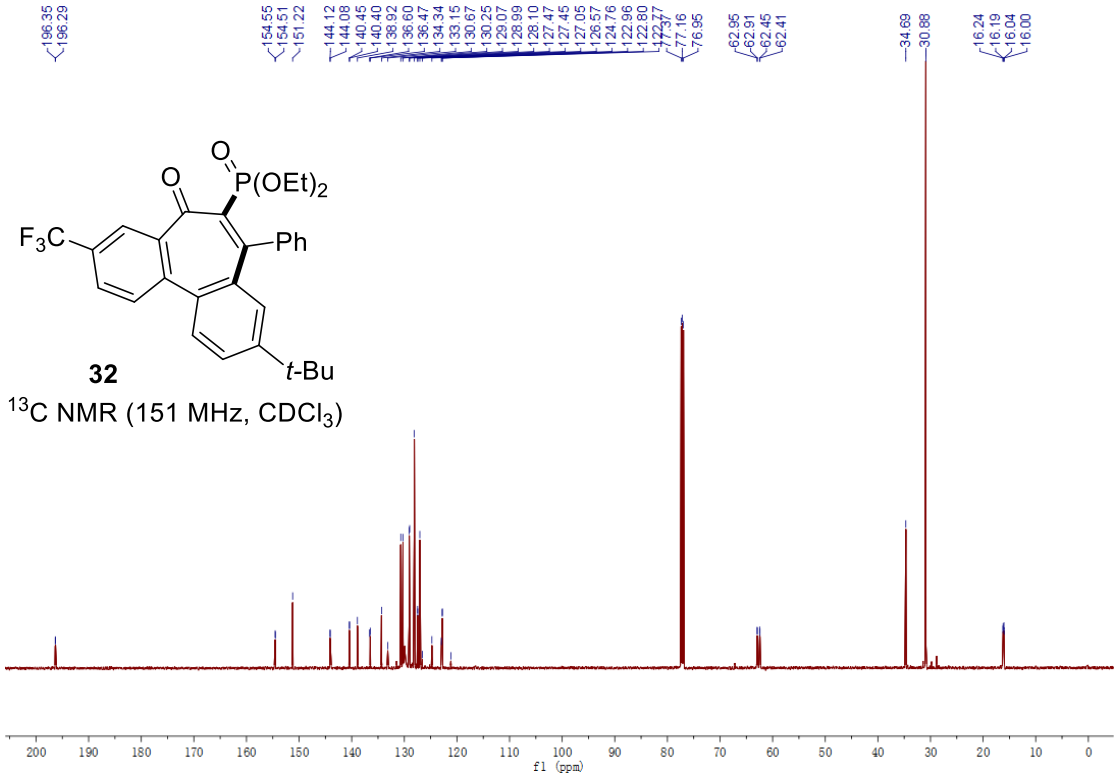
31

^{31}P NMR (243 MHz, $CDCl_3$)



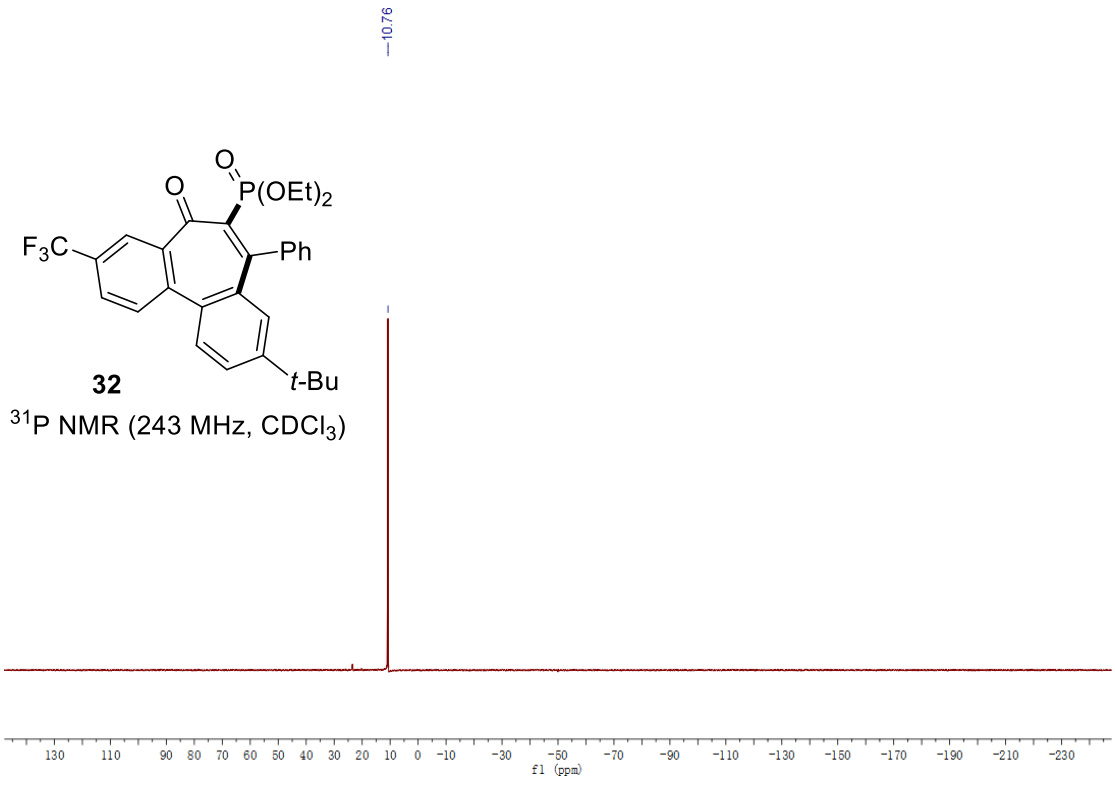
32

^{1}H NMR (600 MHz, $CDCl_3$)



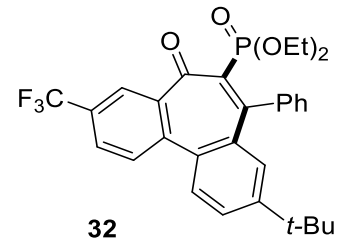
32

^{13}C NMR (151 MHz, $CDCl_3$)



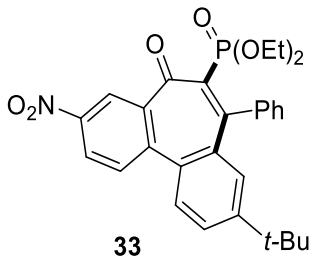
32

^{31}P NMR (243 MHz, $CDCl_3$)



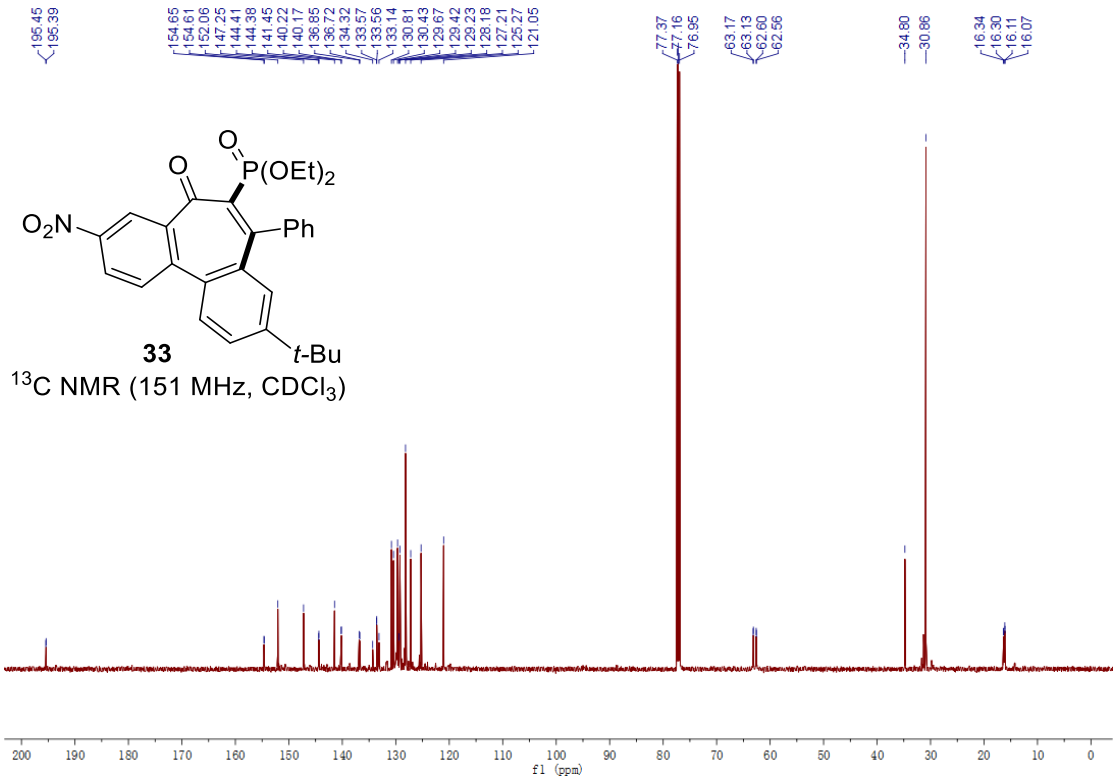
32

^{19}F NMR (565 MHz, $CDCl_3$)



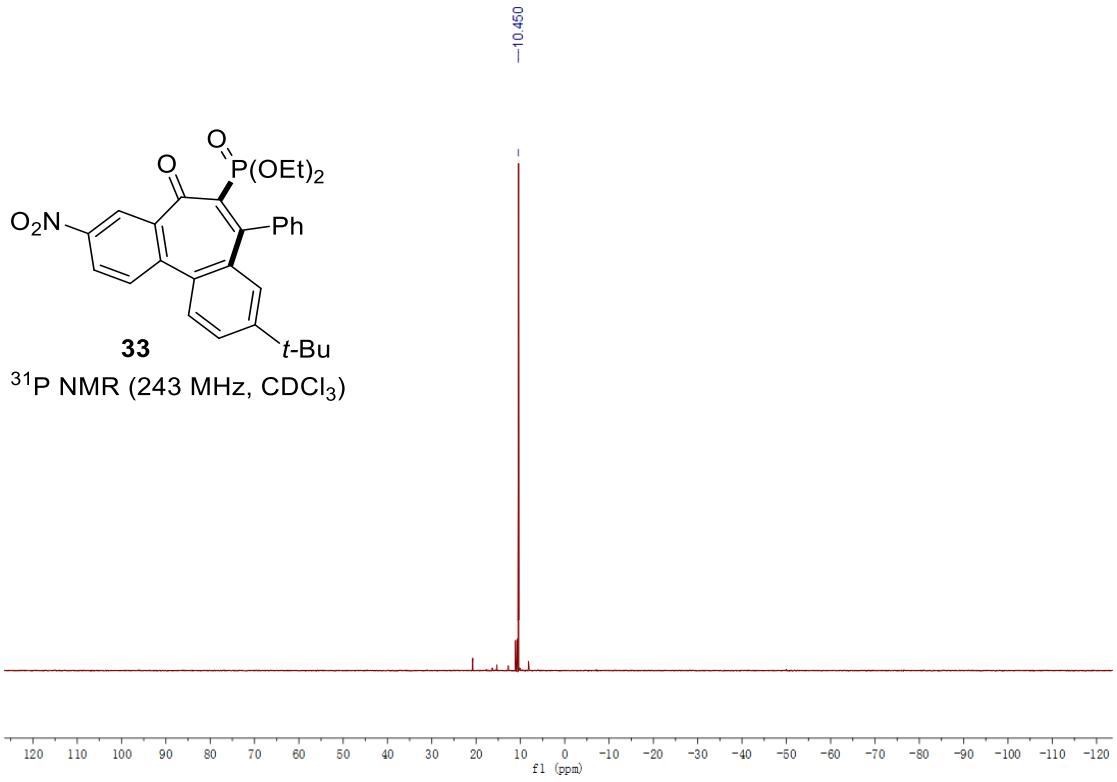
33

^{1}H NMR (600 MHz, $CDCl_3$)



33

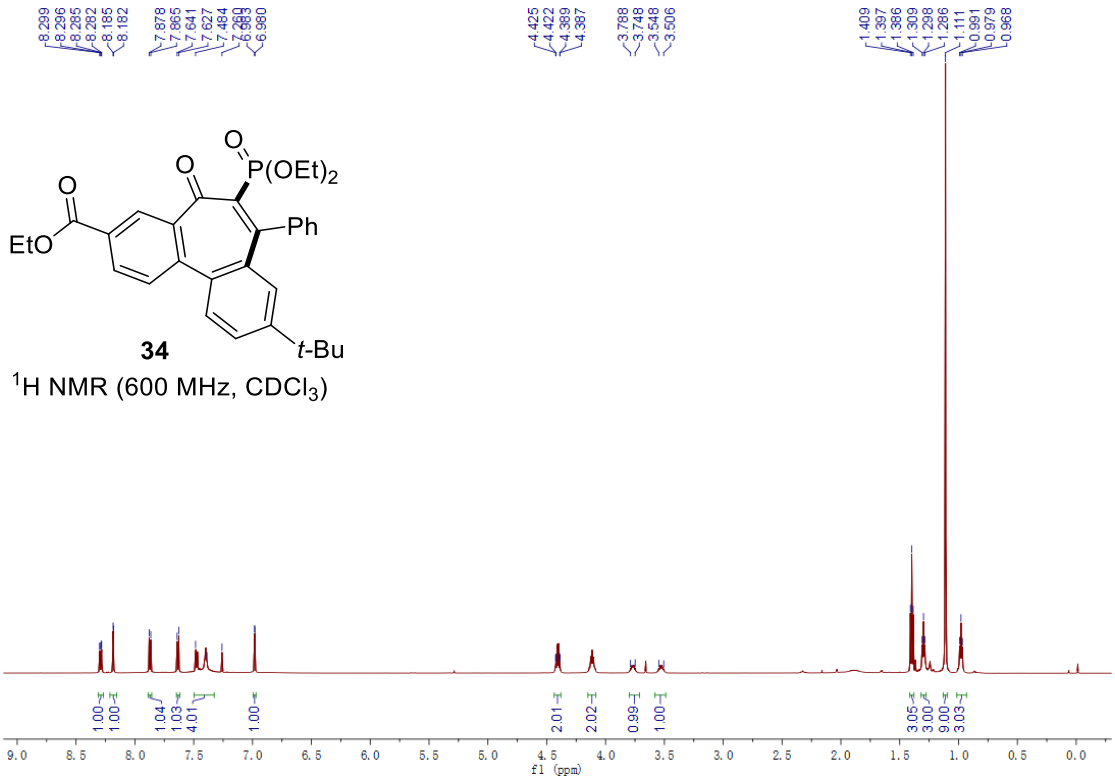
^{13}C NMR (151 MHz, $CDCl_3$)



O
O
P(OEt)2
O2N
Ph
t-Bu

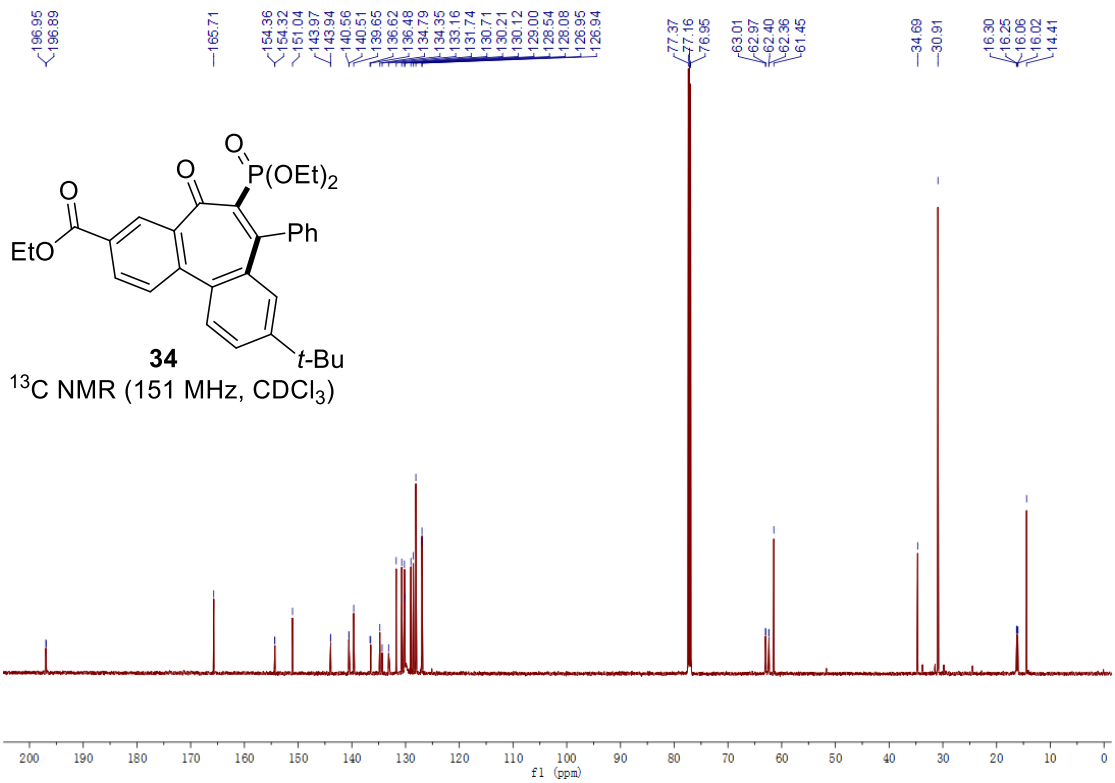
33

^{31}P NMR (243 MHz, $CDCl_3$)



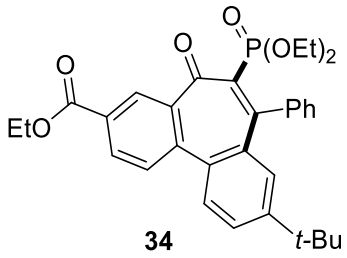
34

^{1}H NMR (600 MHz, $CDCl_3$)



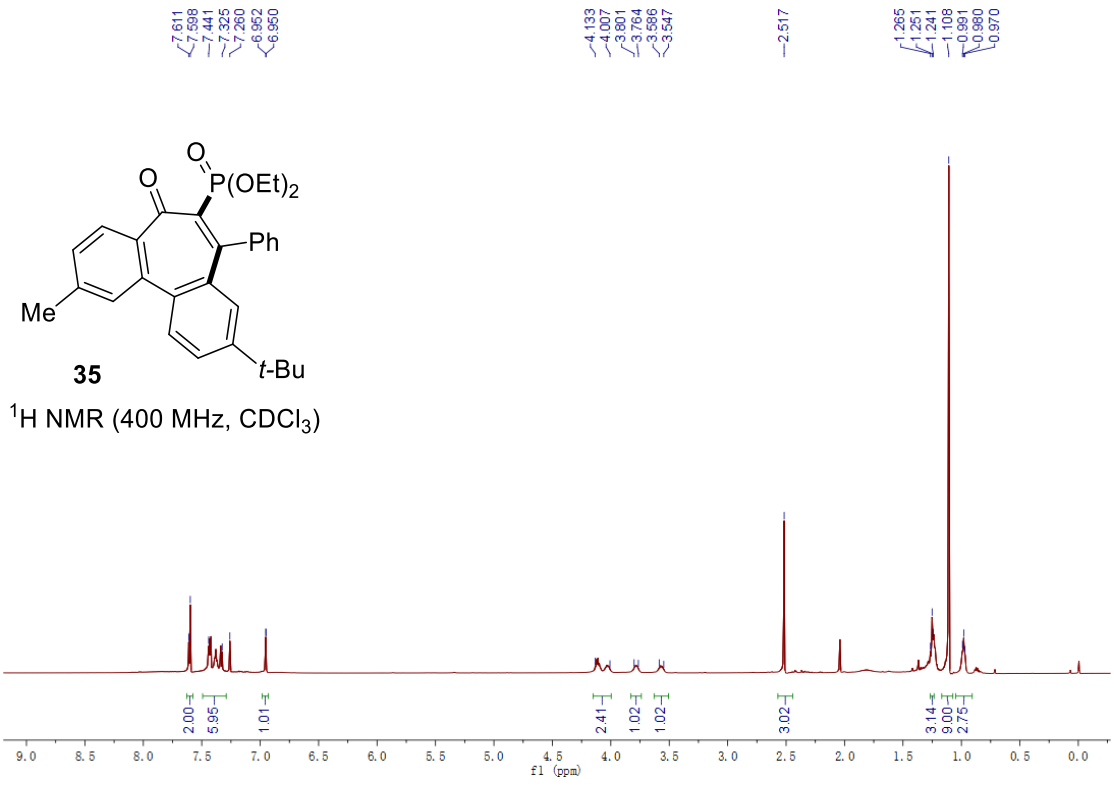
34

^{13}C NMR (151 MHz, $CDCl_3$)



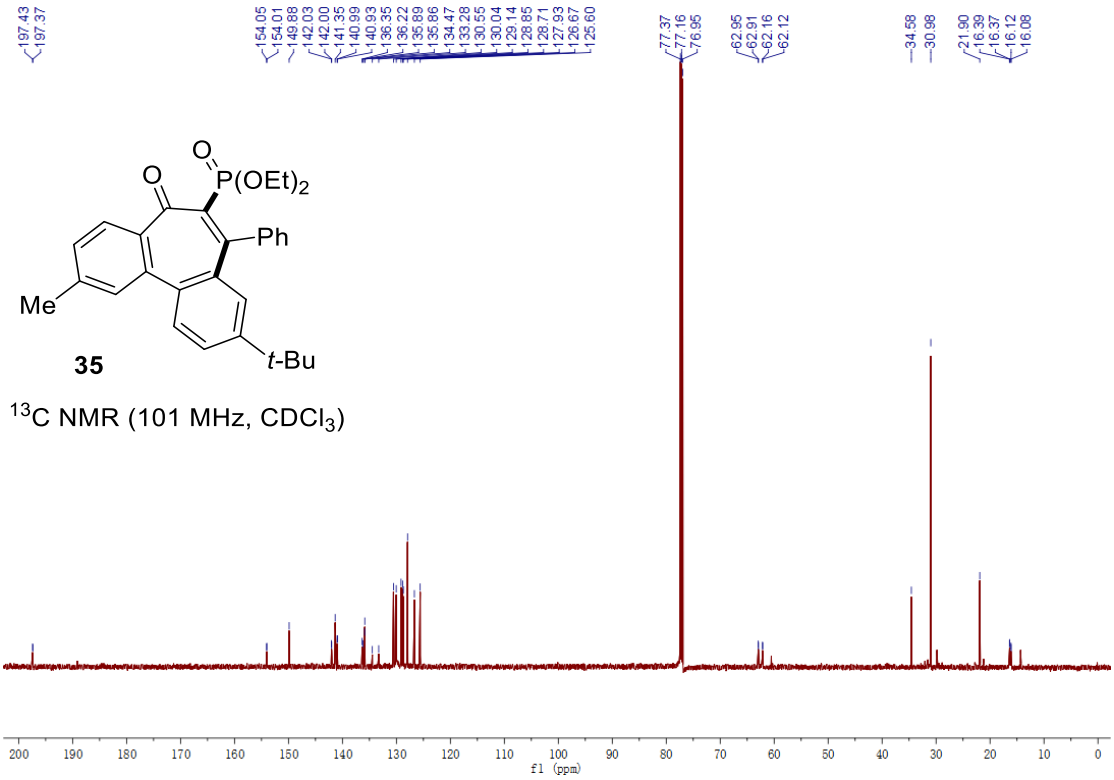
34

^{31}P NMR (243 MHz, $CDCl_3$)

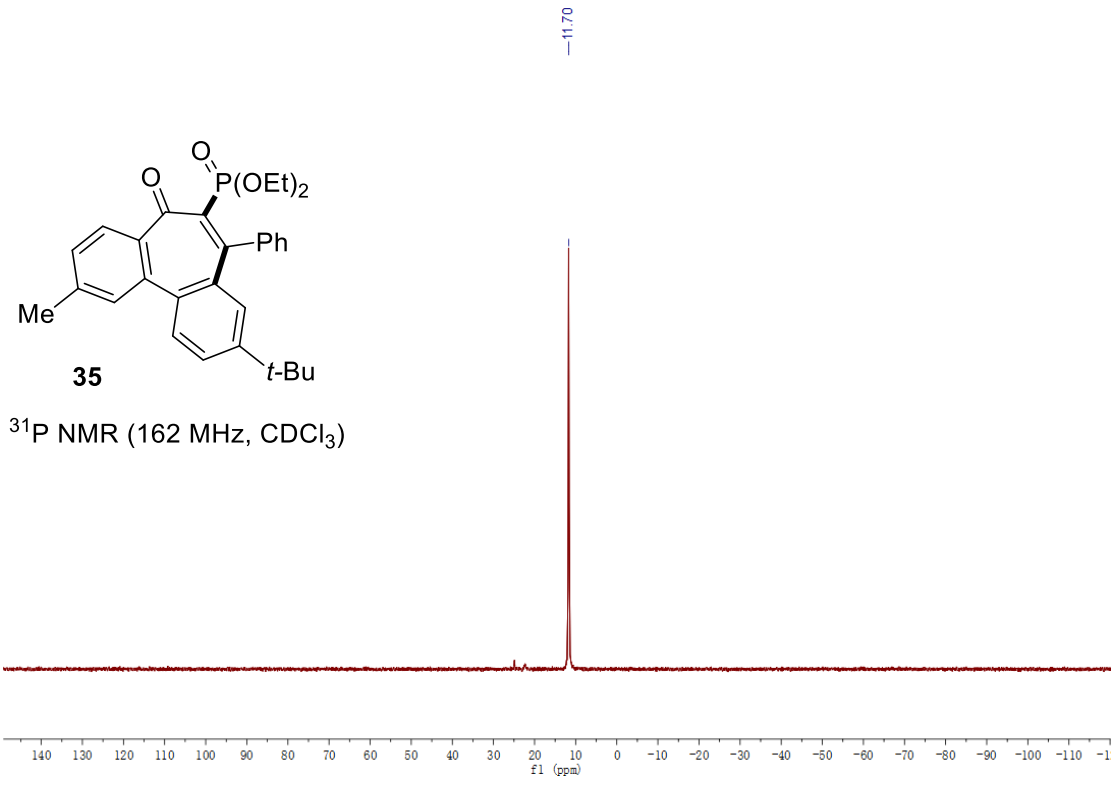


35

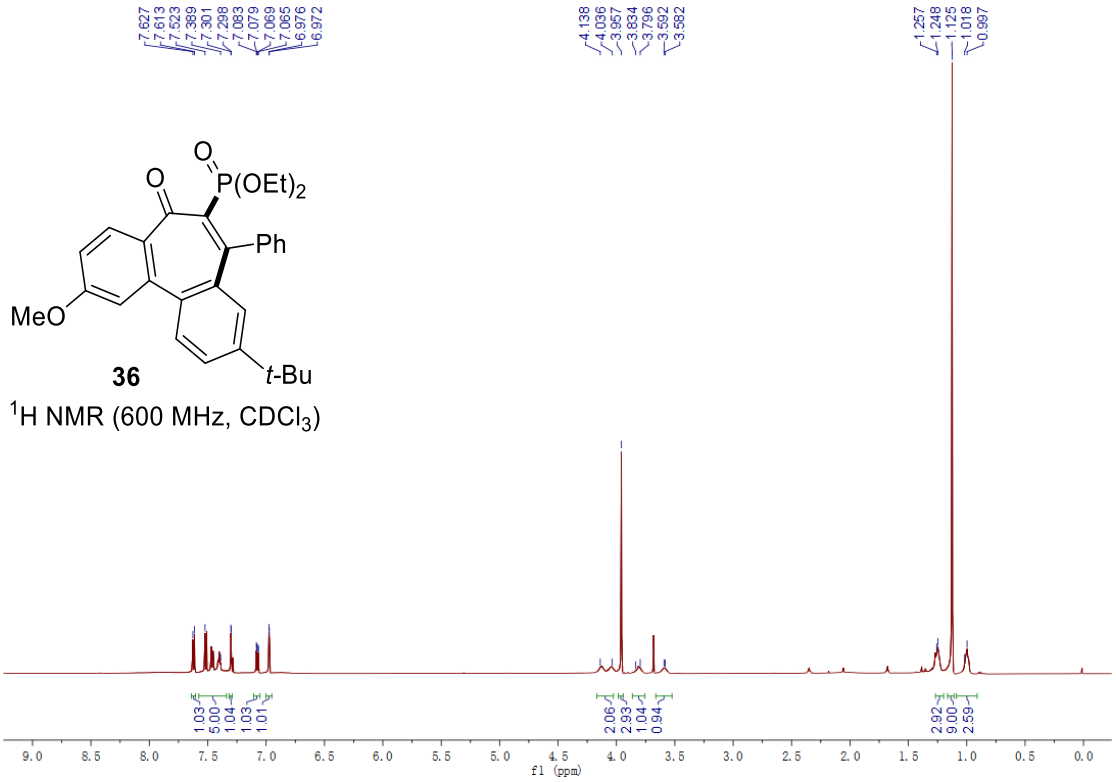
^{1}H NMR (400 MHz, $CDCl_3$)

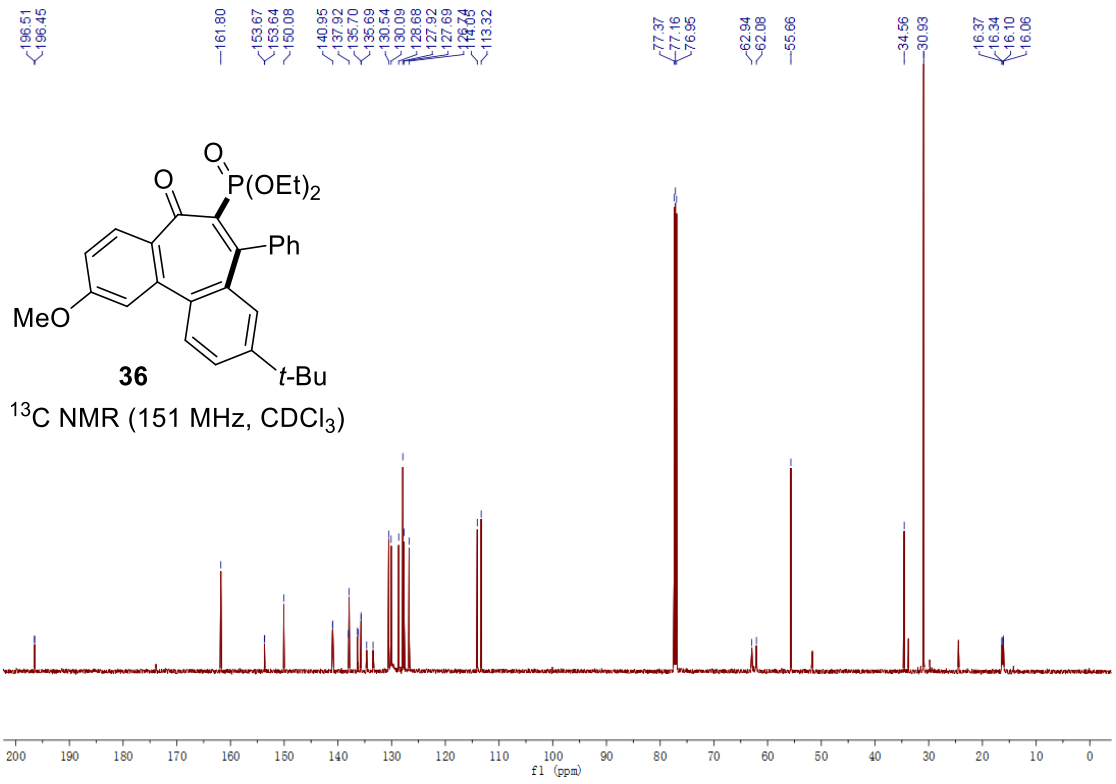


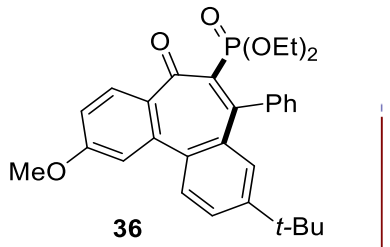
^{13}C NMR (101 MHz, $CDCl_3$)



^{31}P NMR (162 MHz, $CDCl_3$)

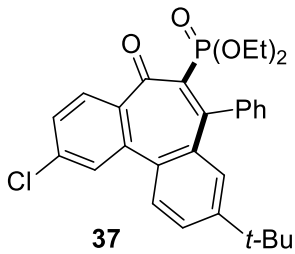

7.627
7.613
7.523
7.389
7.301
7.298
7.083
7.079
7.069
7.065
6.976
6.972
4.138
4.036
3.957
3.834
3.796
3.592
3.582
1.257
1.248
1.125
1.018
0.997
O
O
P(OEt)2
Ph
MeO
t-Bu
36
1H NMR (600 MHz, CDCl3)
1.03
5.00
1.04
1.03
1.01
2.06
2.93
1.04
0.94
2.92
9.00
2.59
f1 (ppm)


196.51
196.45
161.80
153.67
153.64
150.08
140.95
137.92
135.70
135.69
130.54
130.09
128.68
127.92
127.69
113.32
77.37
77.16
76.95
62.94
62.08
55.66
34.56
30.93
16.37
16.34
16.10
16.06
O
O
P(OEt)2
Ph
MeO
t-Bu
36
13C NMR (151 MHz, CDCl3)
f1 (ppm)



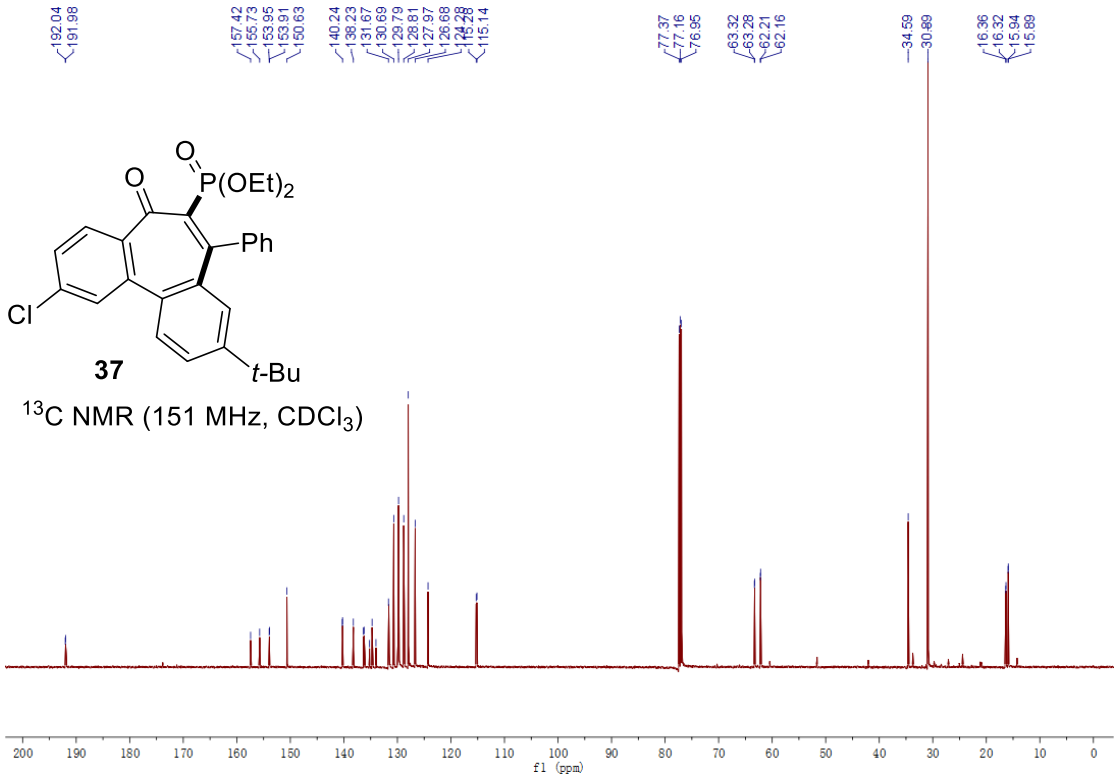
36

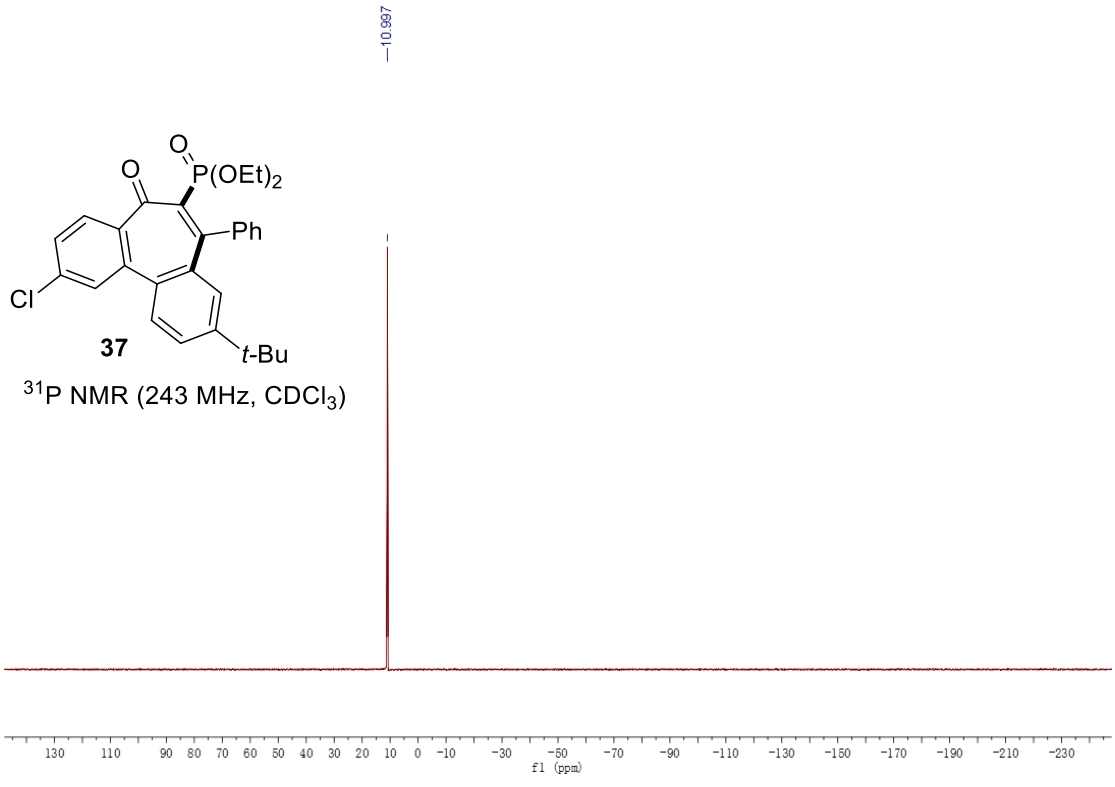
^{31}P NMR (243 MHz, $CDCl_3$)

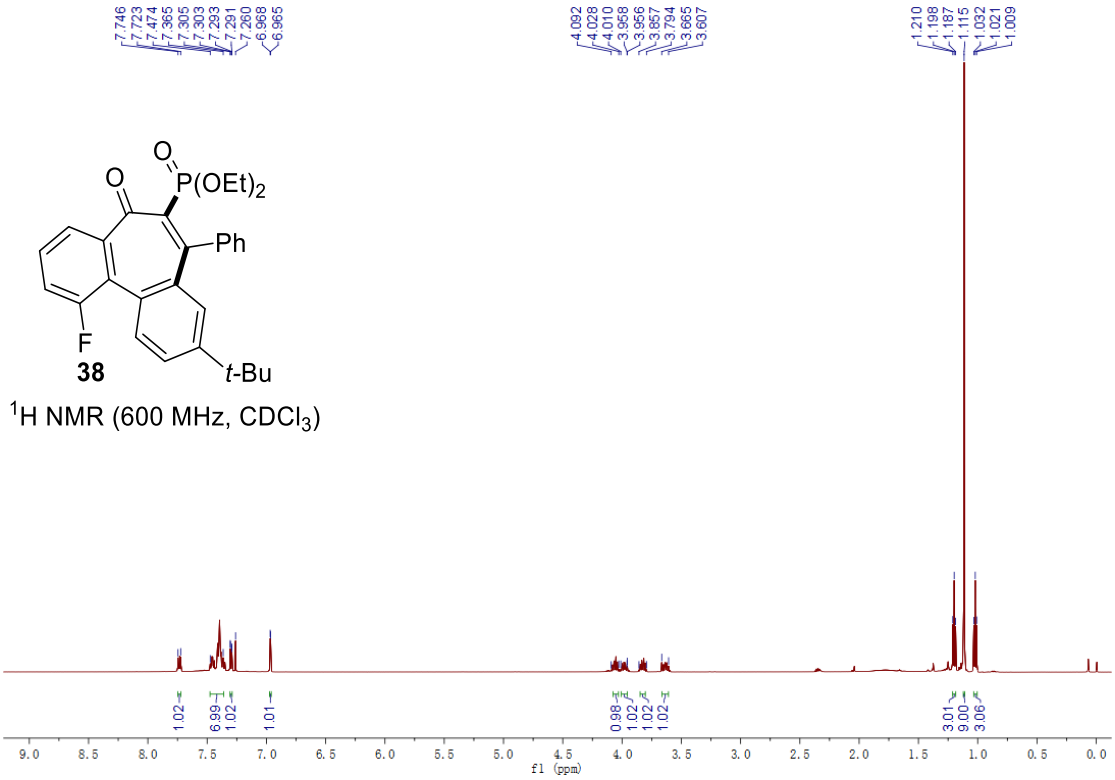


37

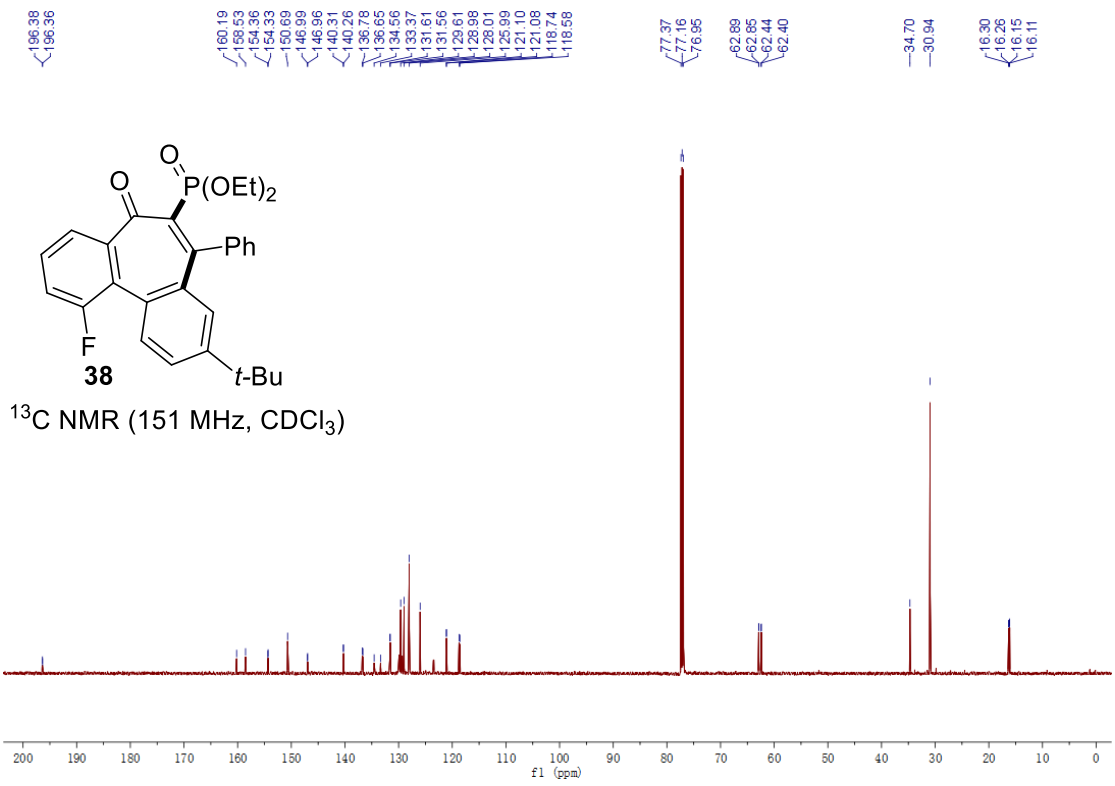
^{1}H NMR (600 MHz, $CDCl_3$)


192.04
191.98
157.42
155.73
153.95
153.91
150.63
140.24
138.23
131.67
130.69
129.79
128.81
127.97
126.68
124.28
115.14
77.37
77.16
76.95
63.32
63.28
62.21
62.16
34.59
30.89
16.36
16.32
15.94
15.89
O
O
P(OEt)2
Ph
Cl
37
t-Bu
13C NMR (151 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

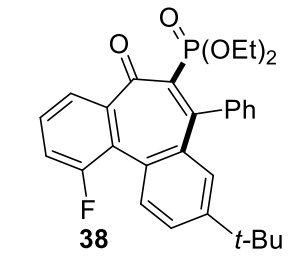

10.997
O
O
P(OEt)2
Ph
Cl
37
t-Bu
31P NMR (243 MHz, CDCl3)
130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)



^{1}H NMR (600 MHz, $CDCl_3$)

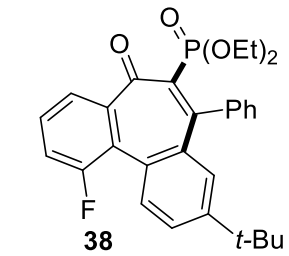


^{13}C NMR (151 MHz, $CDCl_3$)



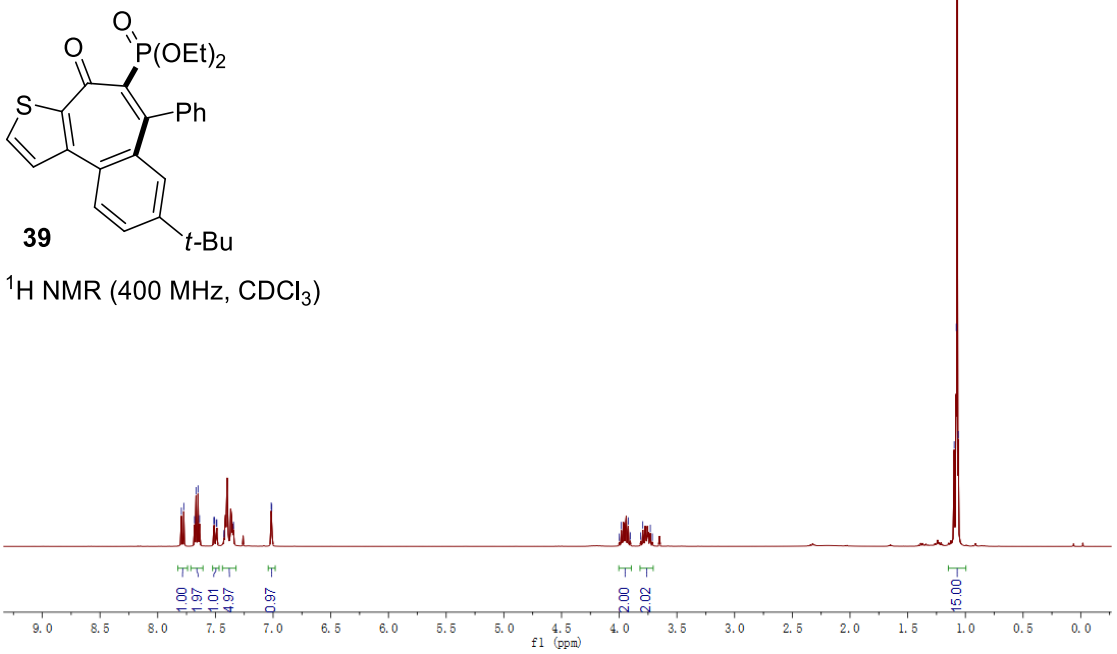
38

^{31}P NMR (243 MHz, $CDCl_3$)

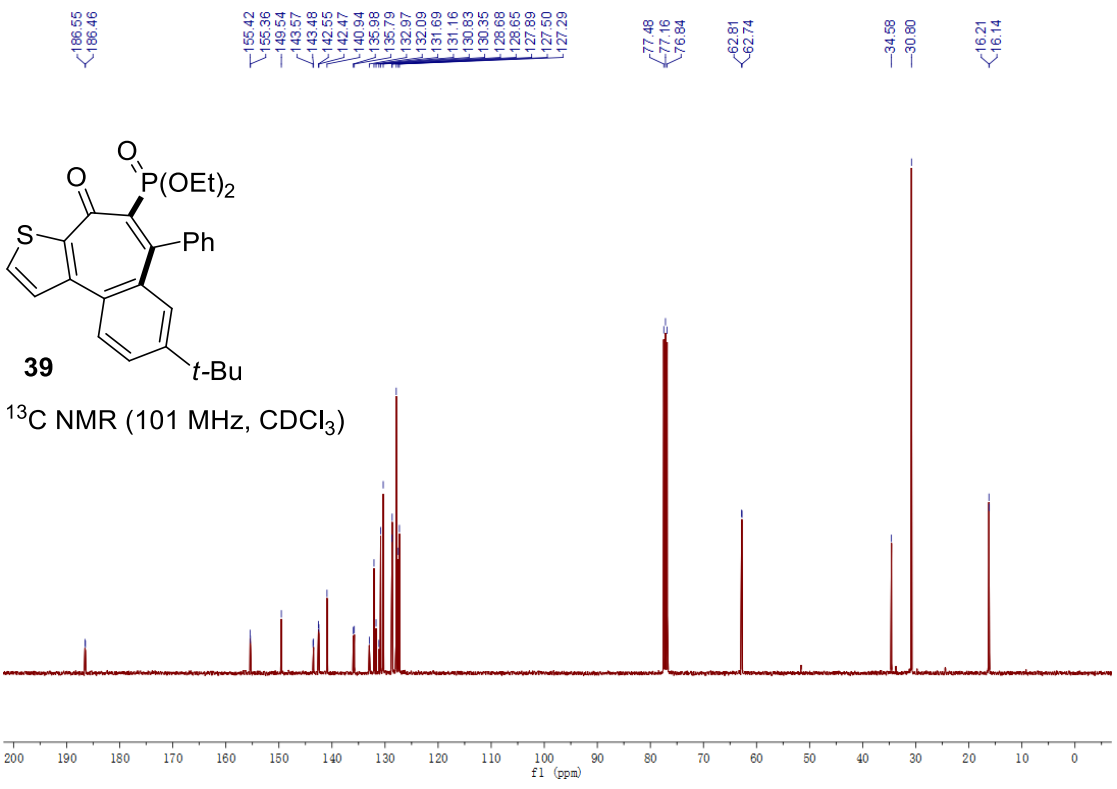


38

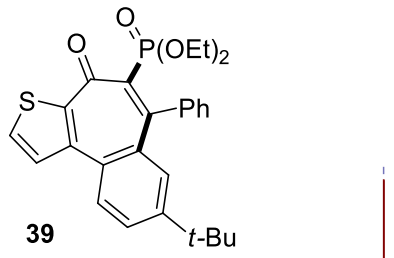
^{19}F NMR (565 MHz, $CDCl_3$)



^{1}H NMR (400 MHz, $CDCl_3$)

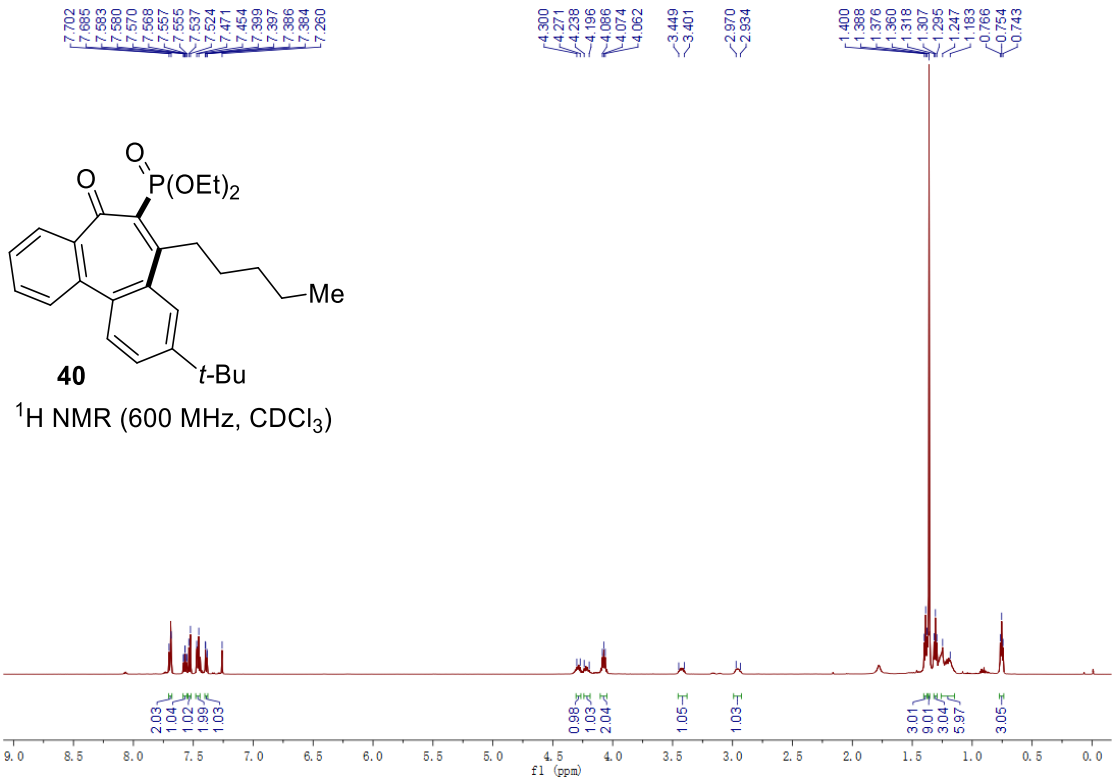


^{13}C NMR (101 MHz, $CDCl_3$)



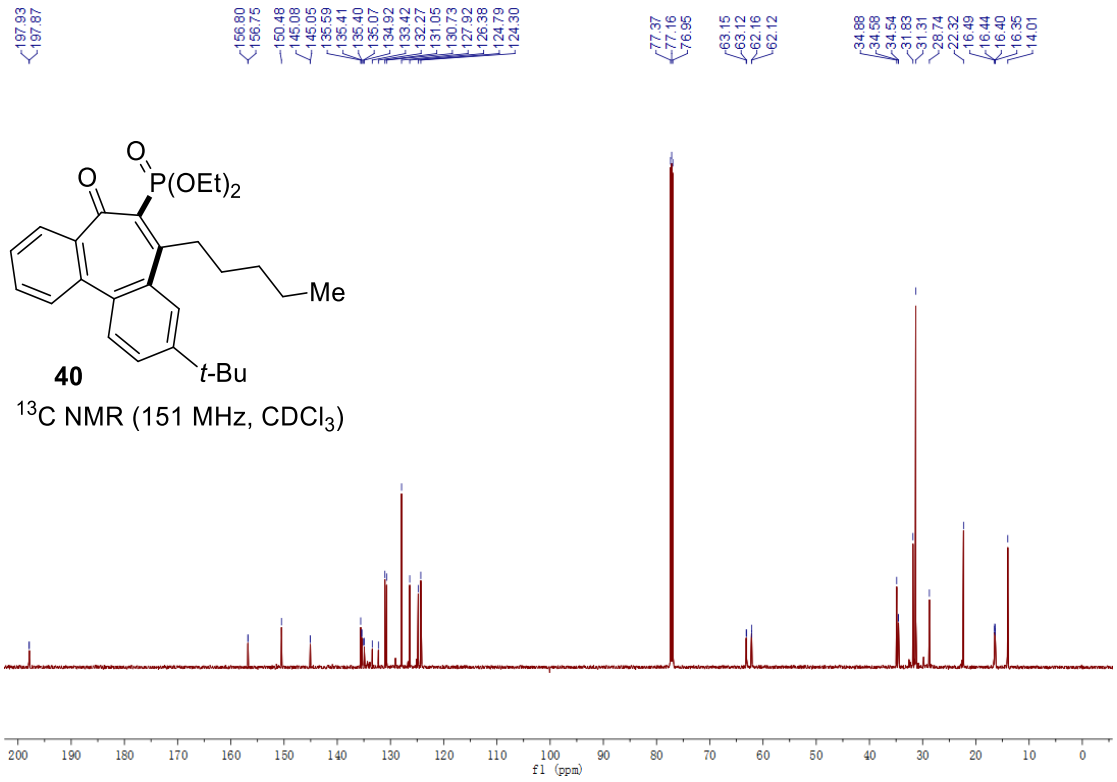
39

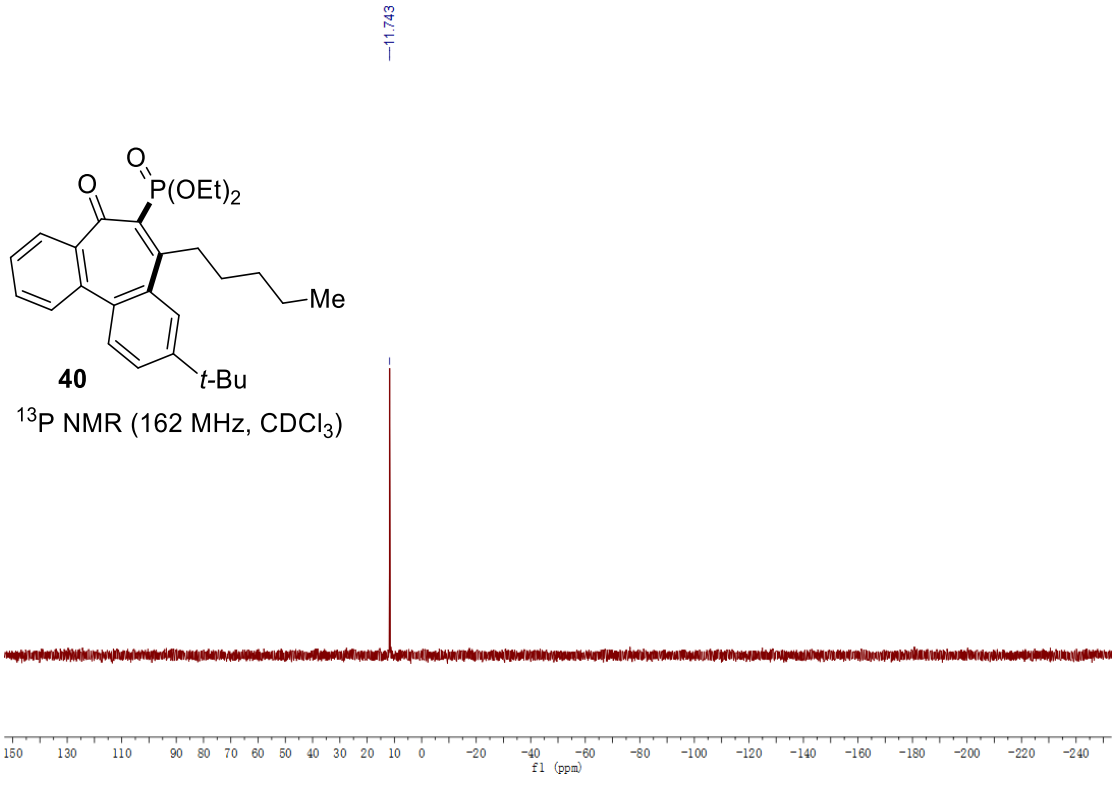
^{31}I NMR (162 MHz, $CDCl_3$)

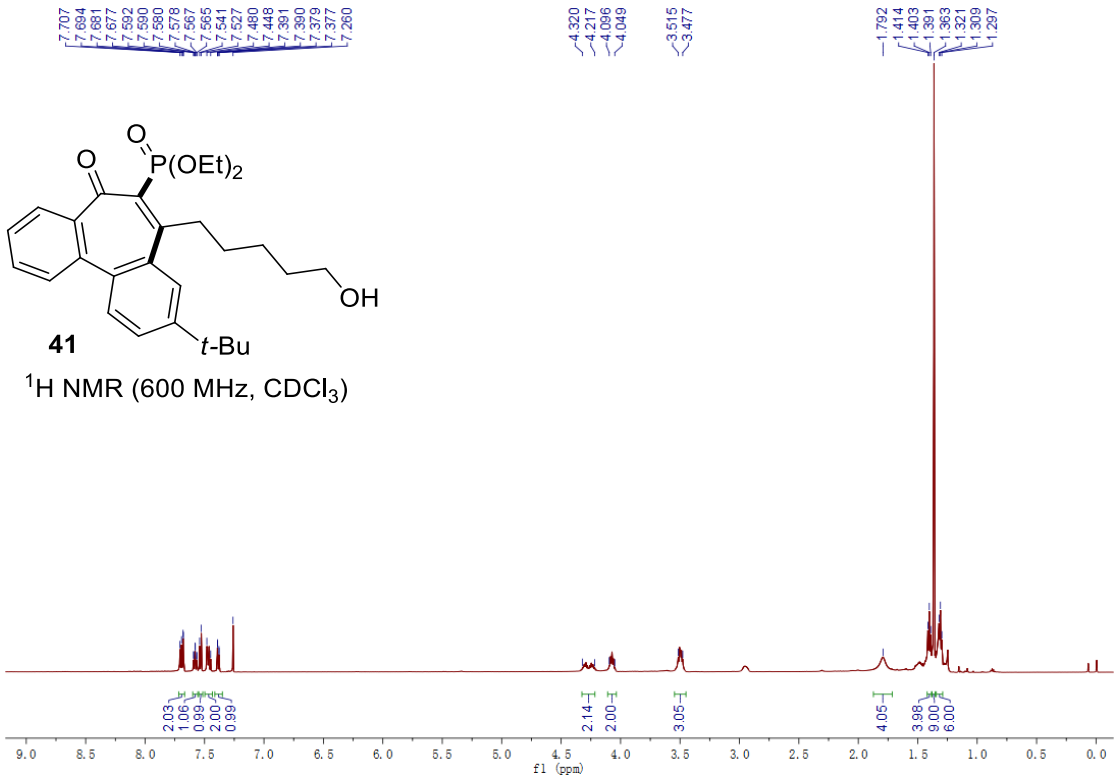


40

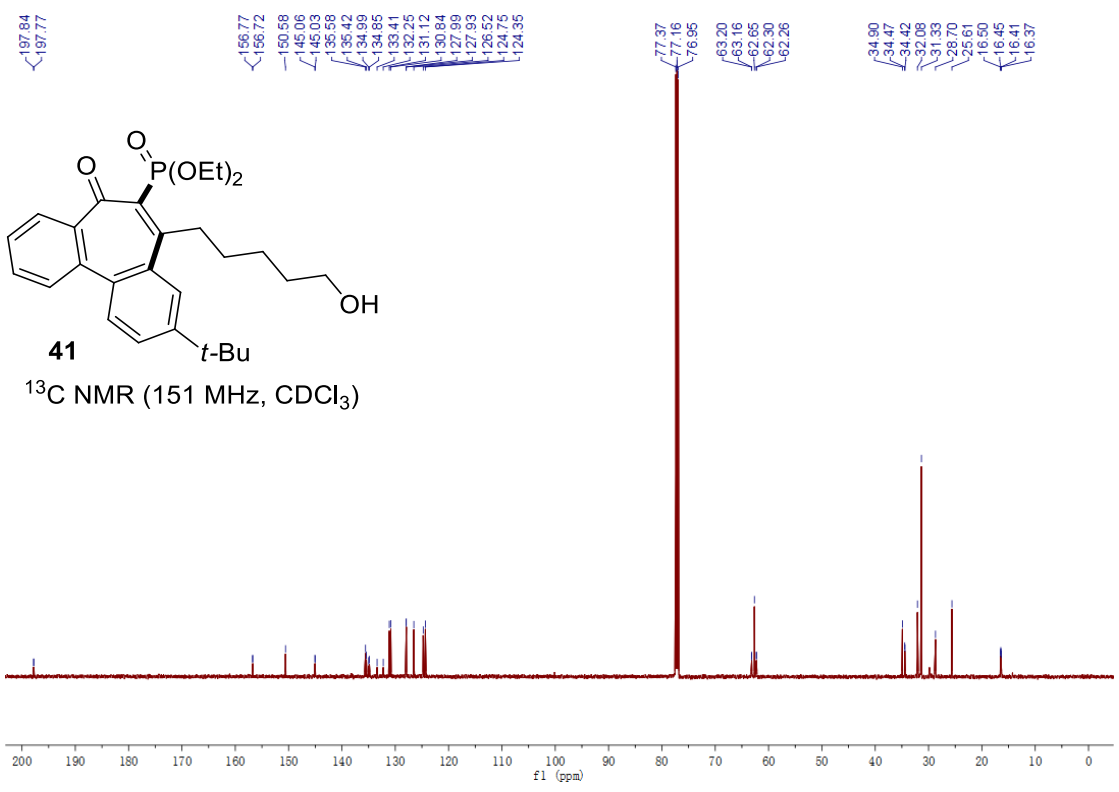
^{1}H NMR (600 MHz, $CDCl_3$)


197.93
197.87
156.80
156.75
150.48
145.08
145.05
135.59
135.41
135.40
135.07
134.92
133.42
132.27
131.05
130.73
127.92
126.38
124.79
124.30
77.37
77.16
76.95
63.15
63.12
62.16
62.12
34.88
34.58
34.54
31.83
31.31
28.74
22.32
16.49
16.44
16.40
16.35
14.01
O
O
P(OEt)2
Me
t-Bu
40
13C NMR (151 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

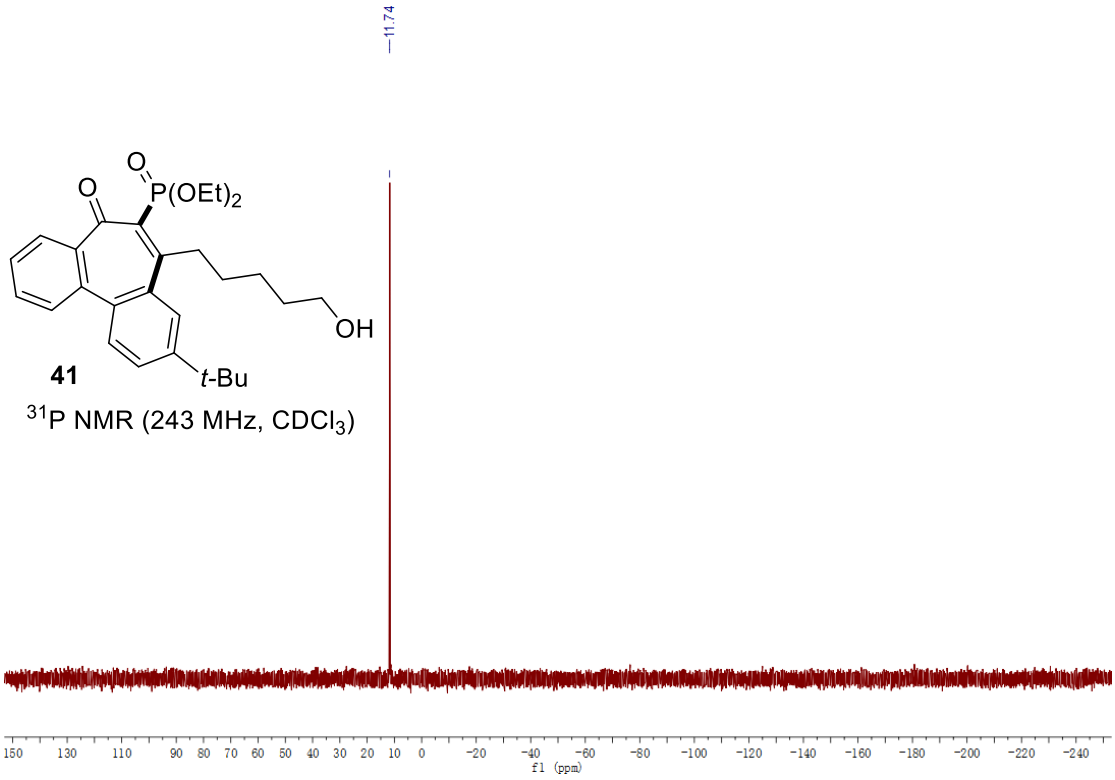

11.743
O
O
P(OEt)2
Me
t-Bu
40
13P NMR (162 MHz, CDCl3)
150 130 110 90 80 70 60 50 40 30 20 10 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)



^{1}H NMR (600 MHz, $CDCl_3$)

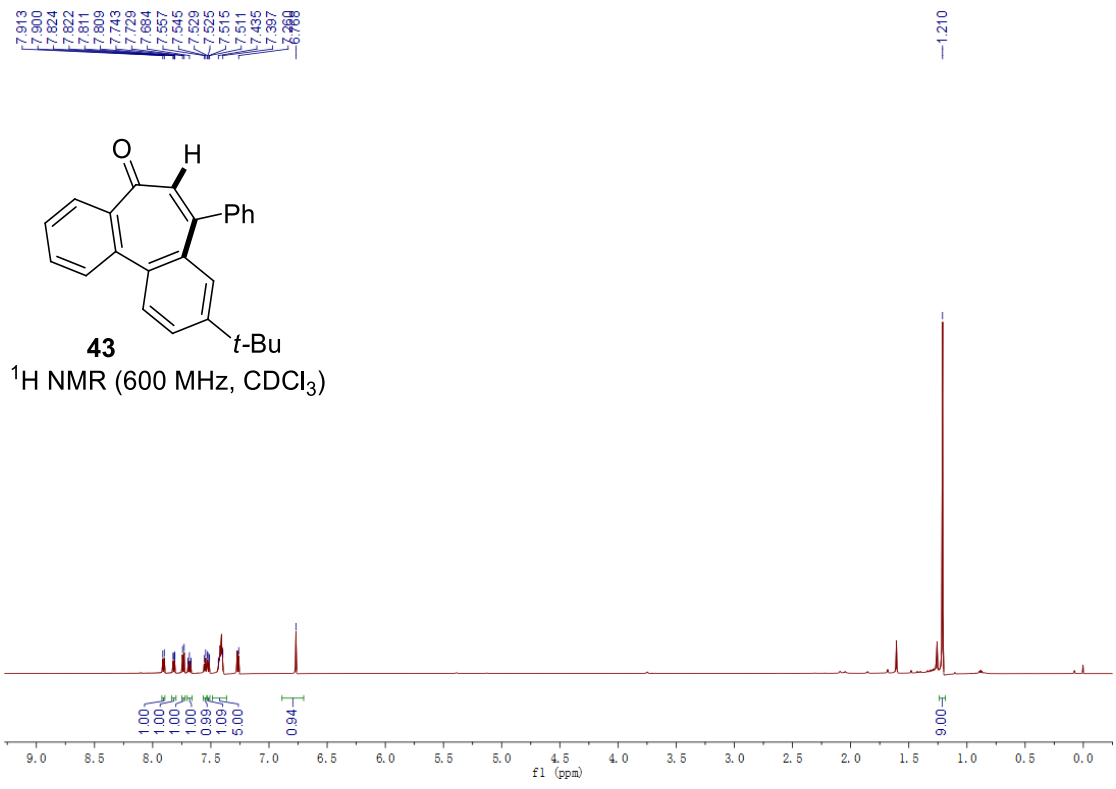


^{13}C NMR (151 MHz, $CDCl_3$)



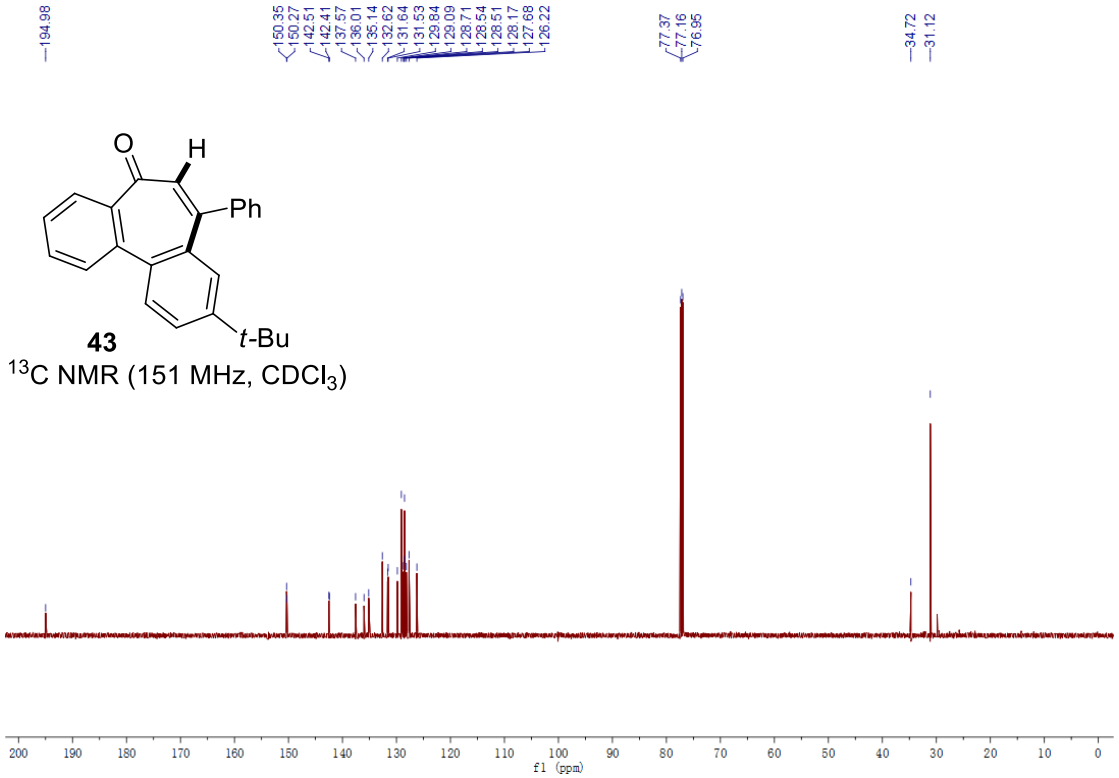
41

^{31}P NMR (243 MHz, $CDCl_3$)



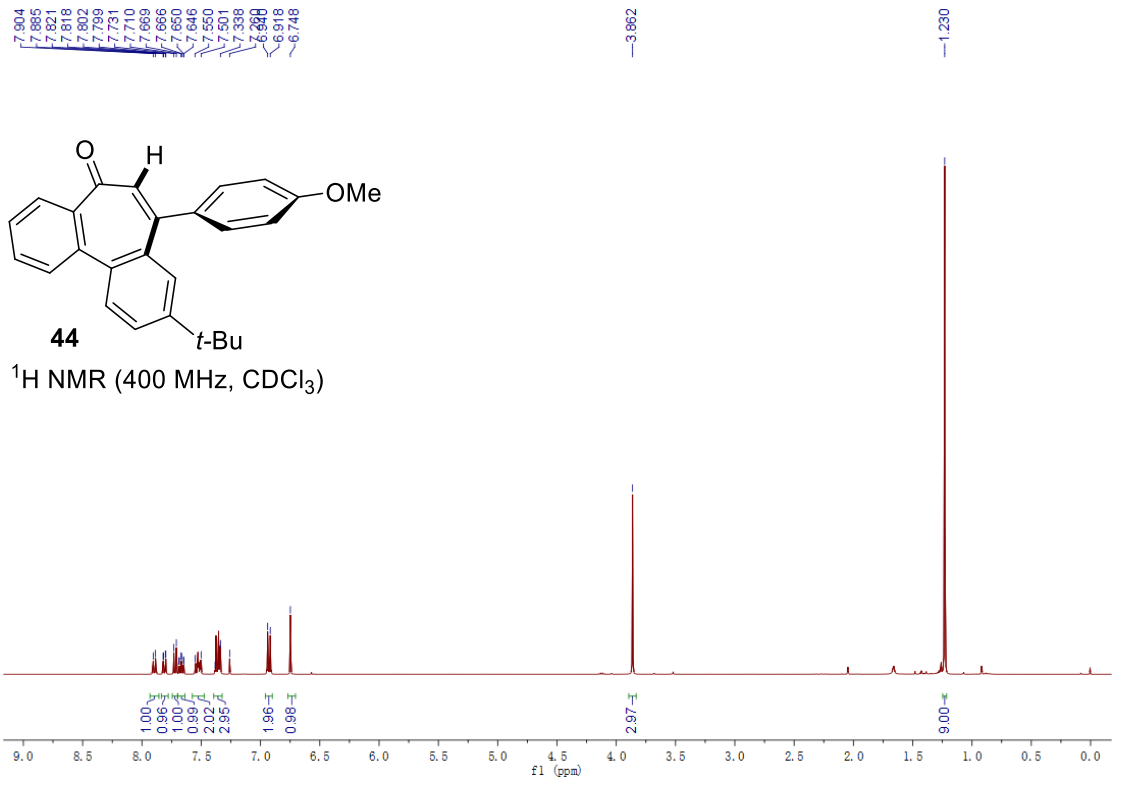
43

^{1}H NMR (600 MHz, $CDCl_3$)



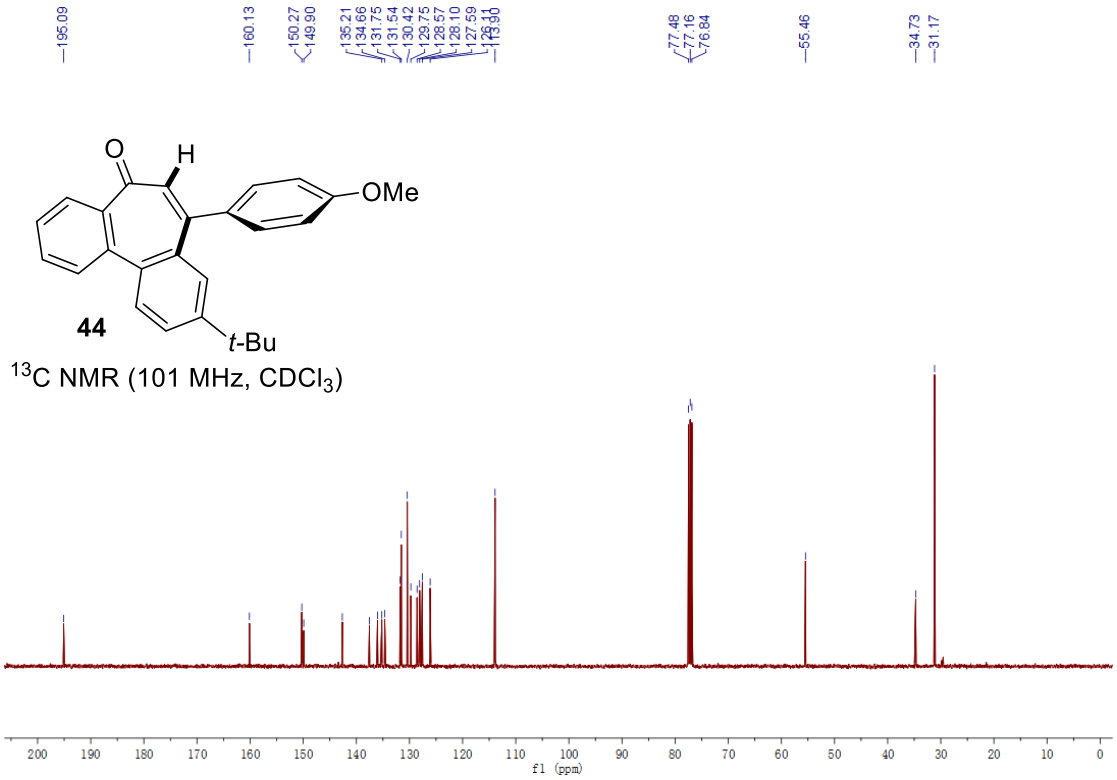
43

^{13}C NMR (151 MHz, $CDCl_3$)

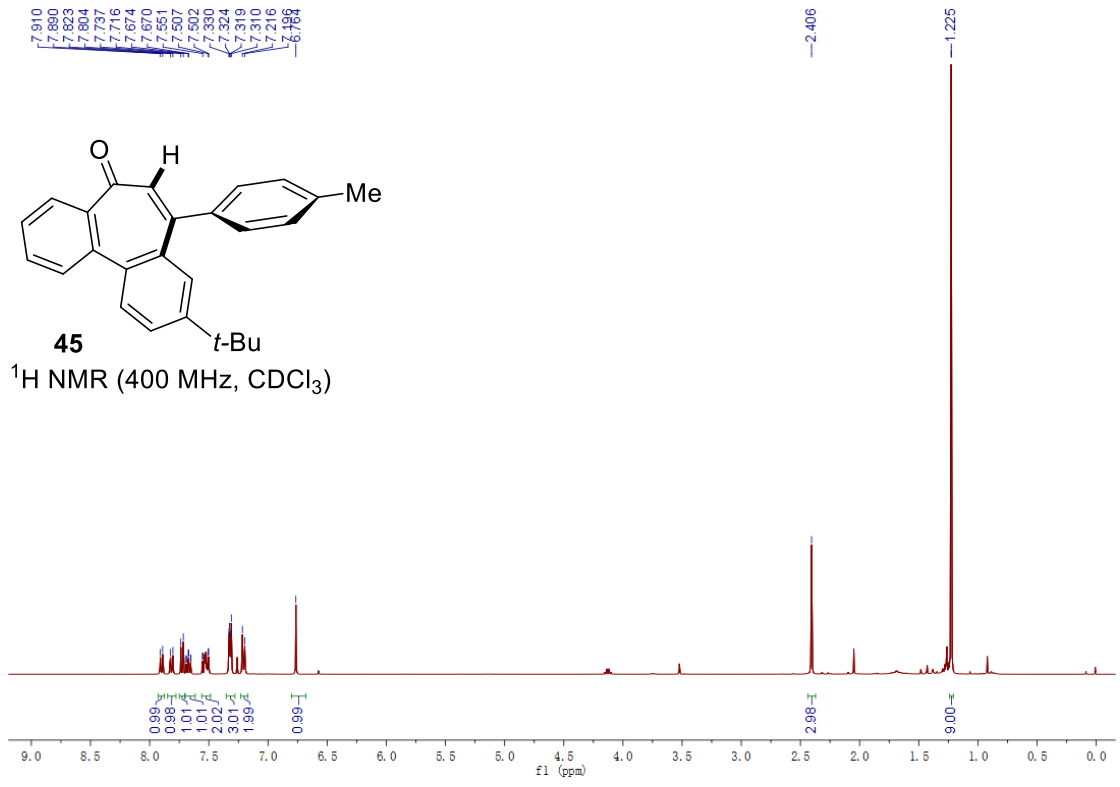


44

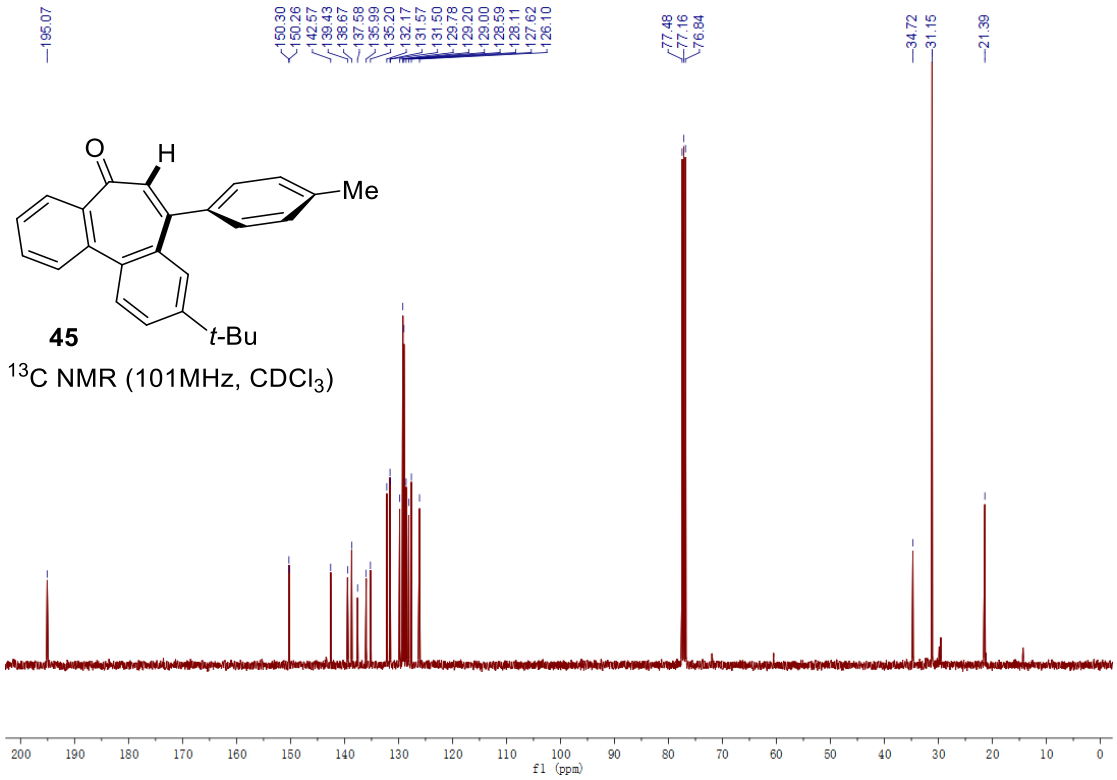
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

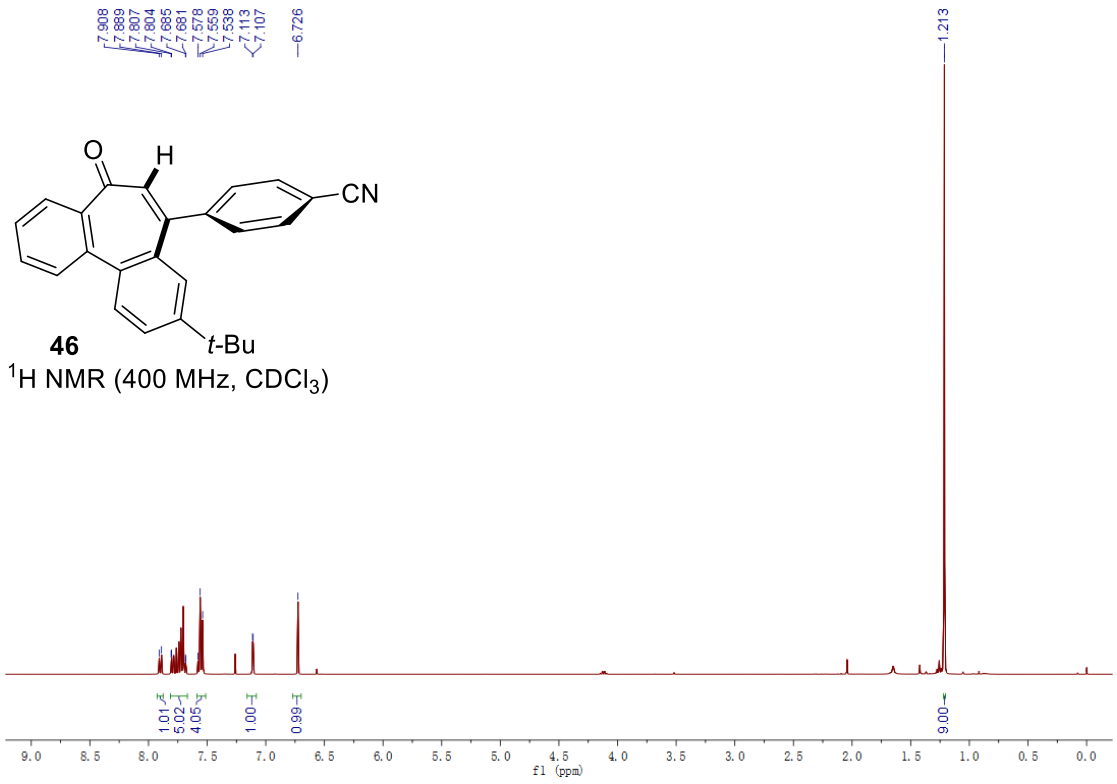


^{1}H NMR (400 MHz, $CDCl_3$)



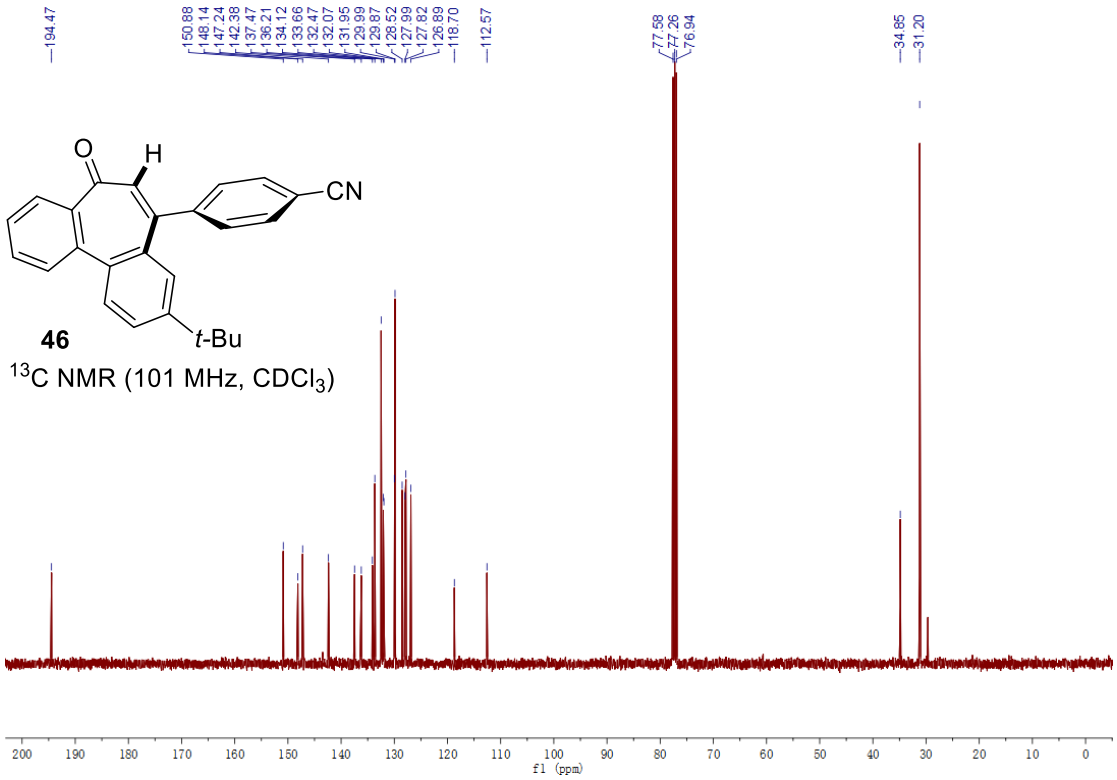
45

^{13}C NMR (101MHz, $CDCl_3$)



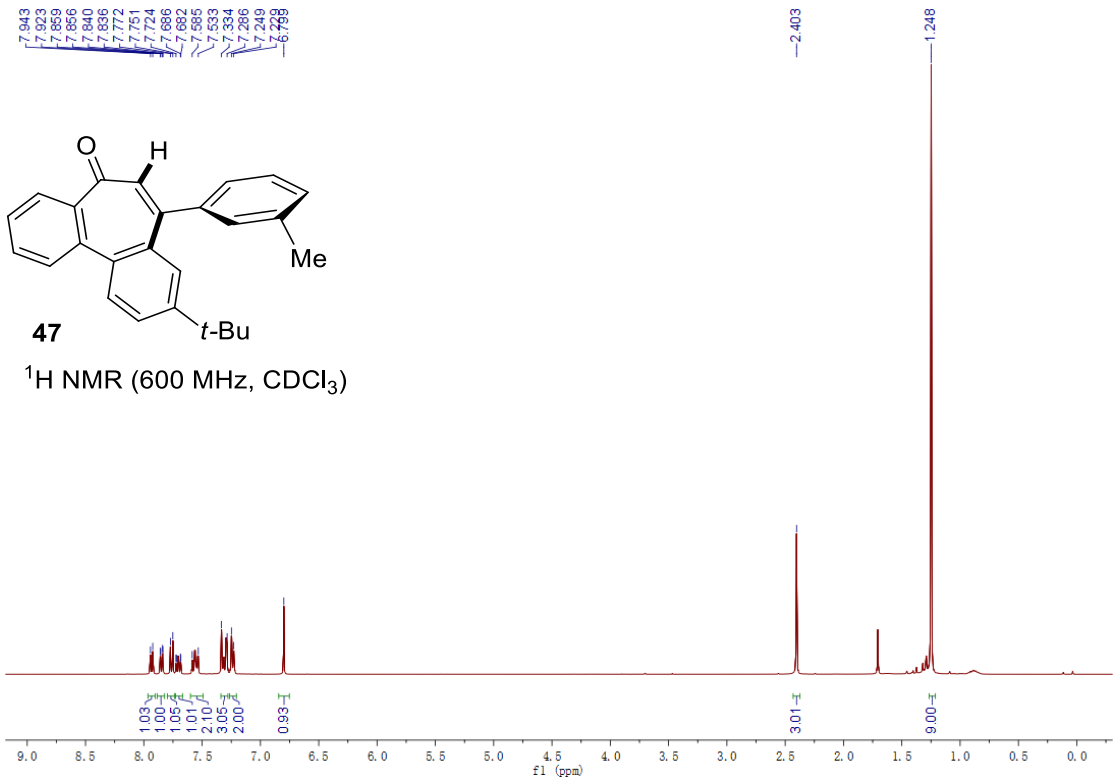
46

^{1}H NMR (400 MHz, $CDCl_3$)



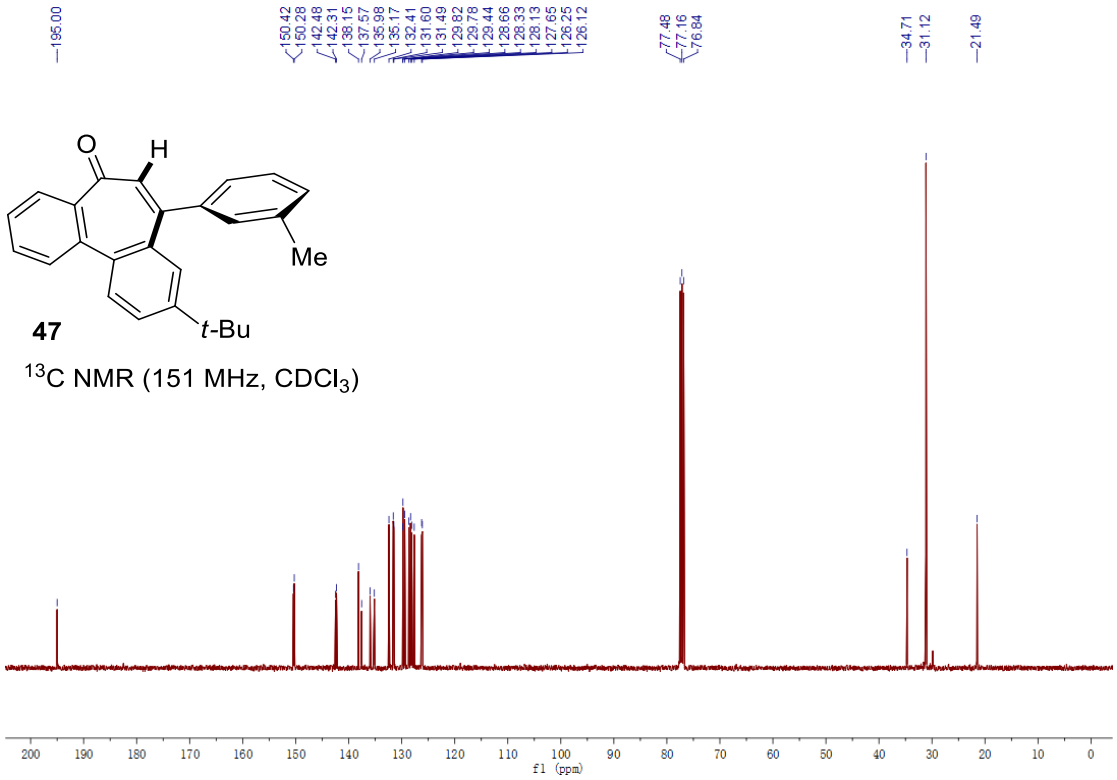
46

^{13}C NMR (101 MHz, $CDCl_3$)



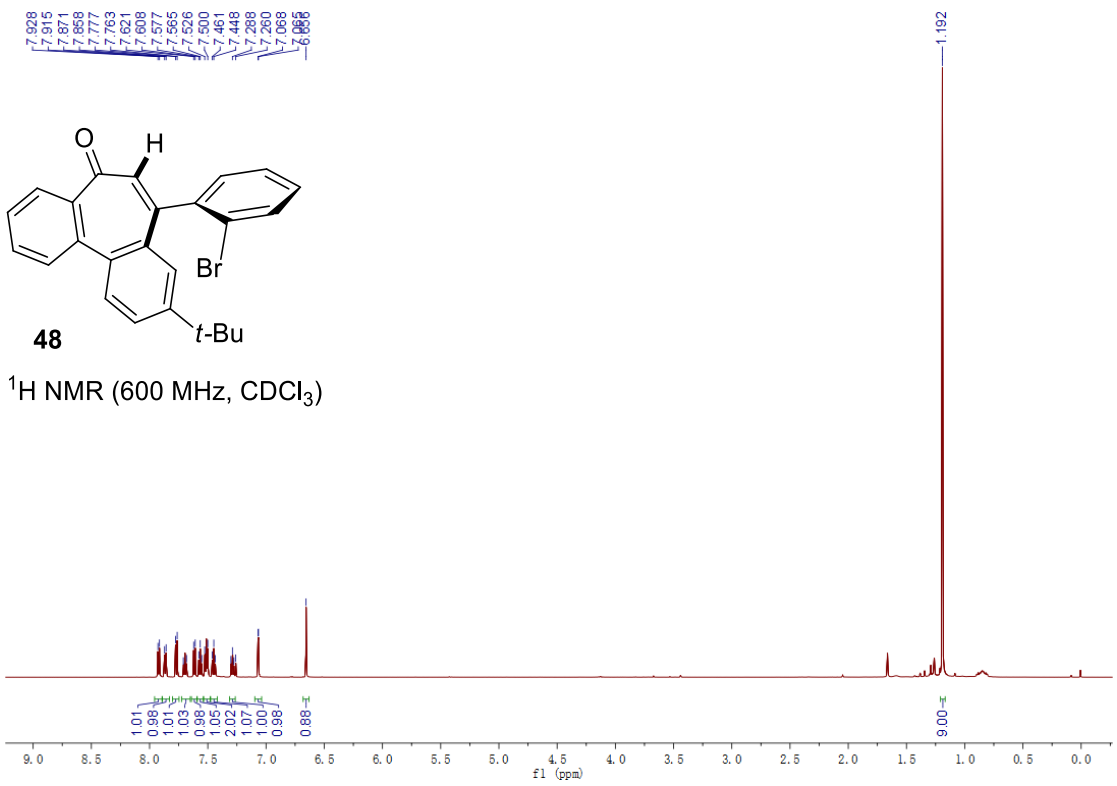
47

^{1}H NMR (600 MHz, $CDCl_3$)



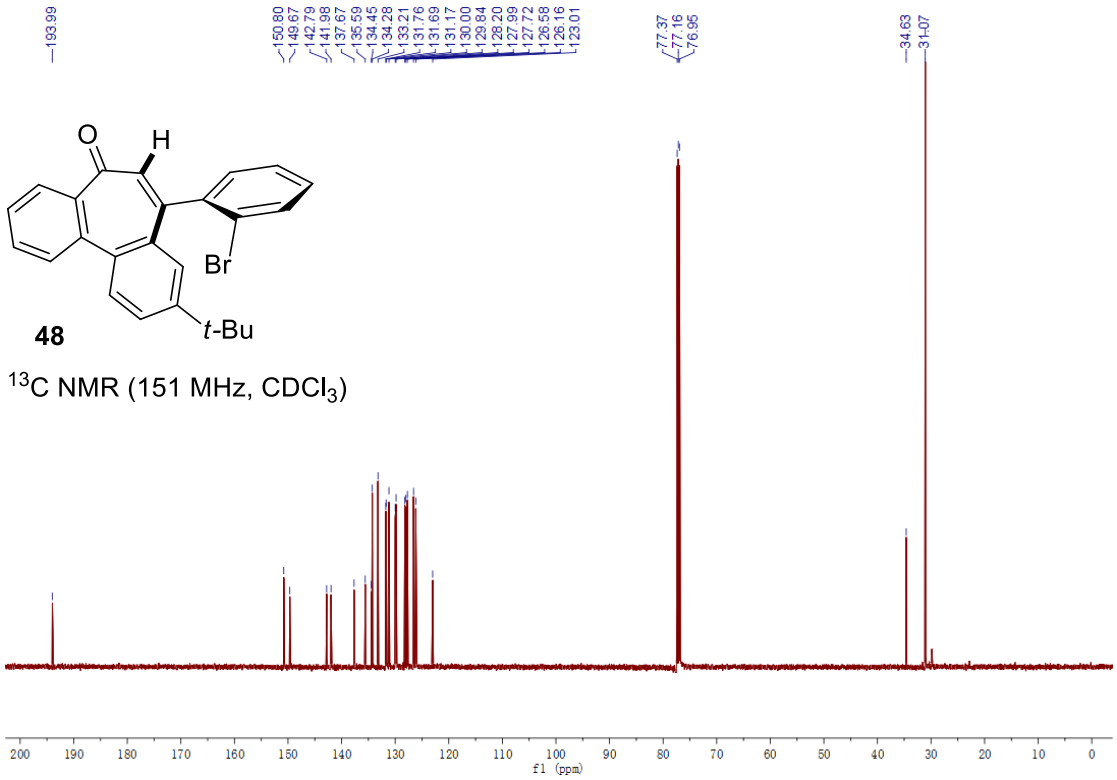
47

^{13}C NMR (151 MHz, $CDCl_3$)



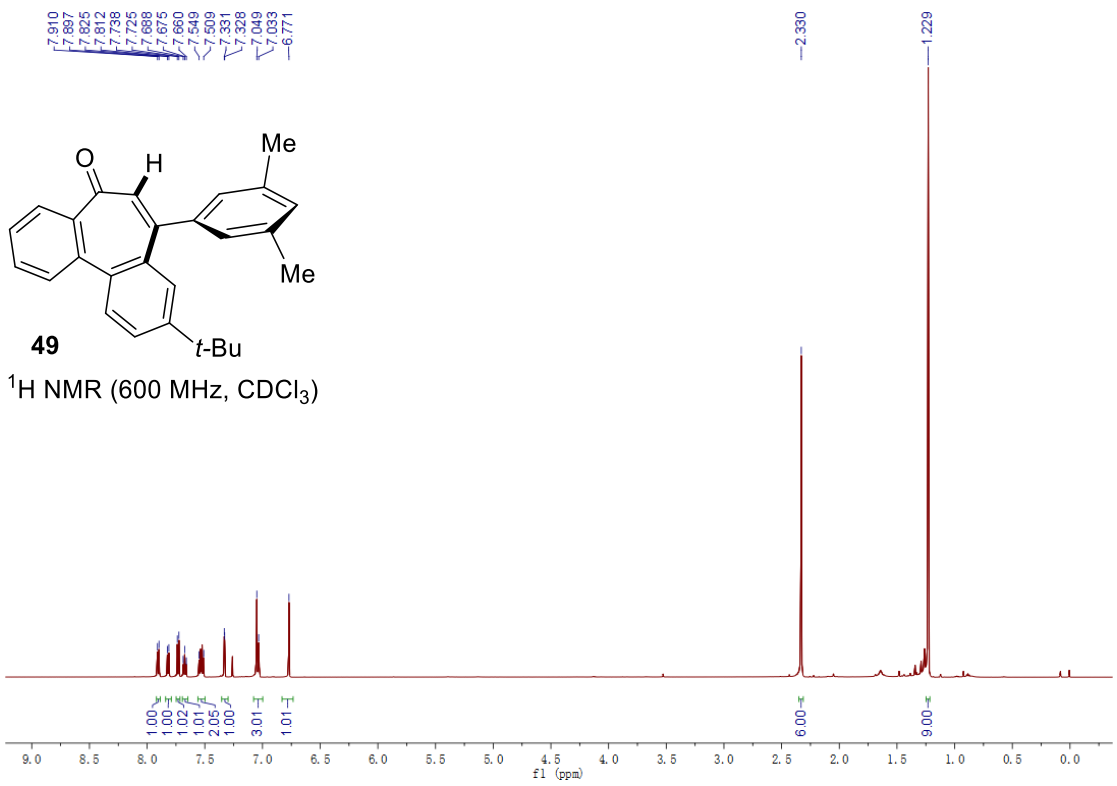
48

^{1}H NMR (600 MHz, $CDCl_3$)



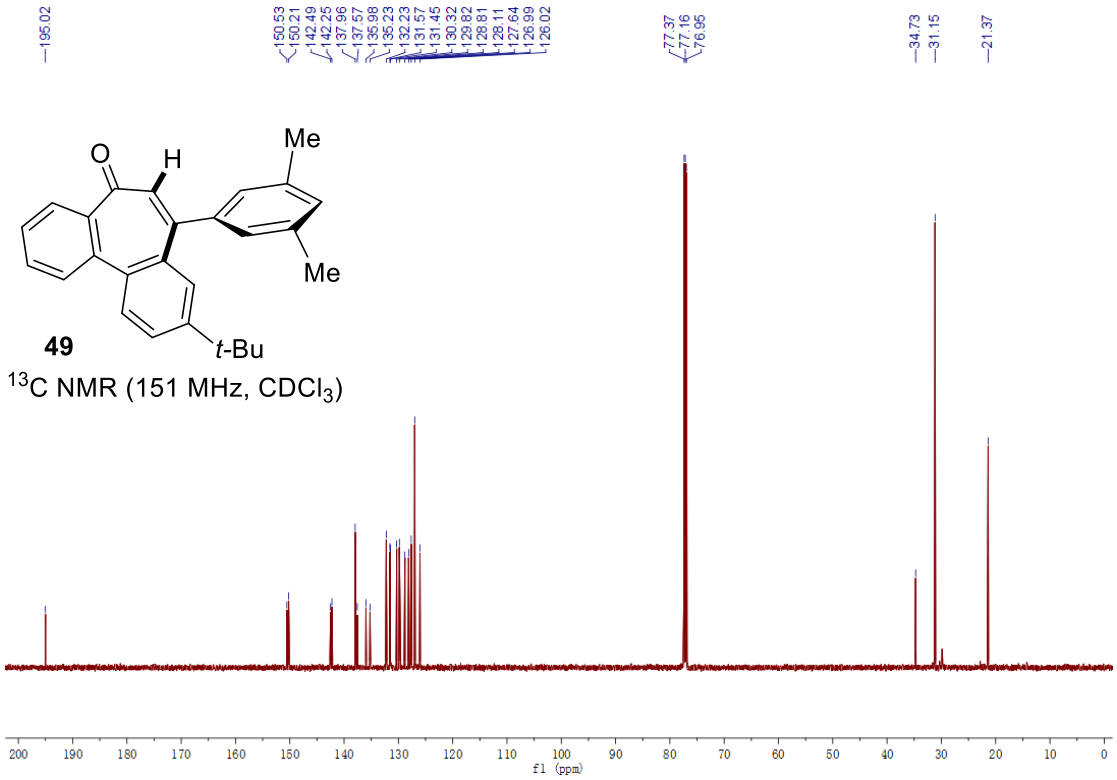
48

^{13}C NMR (151 MHz, $CDCl_3$)



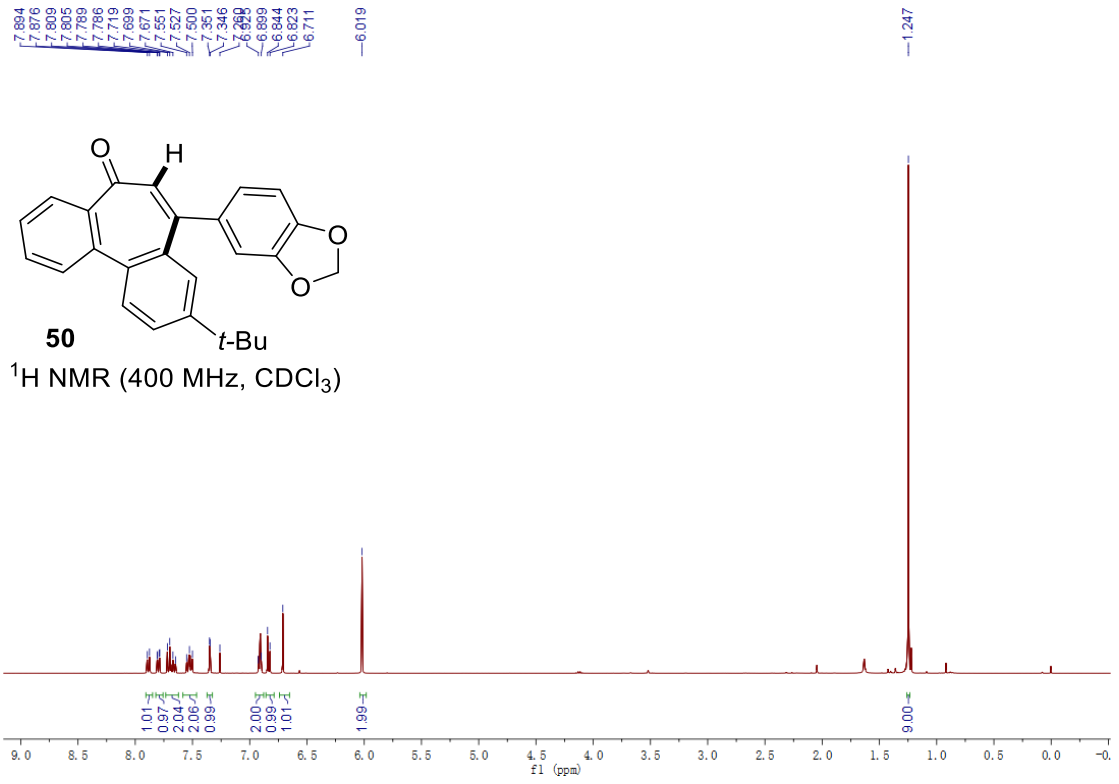
49

^{1}H NMR (600 MHz, $CDCl_3$)



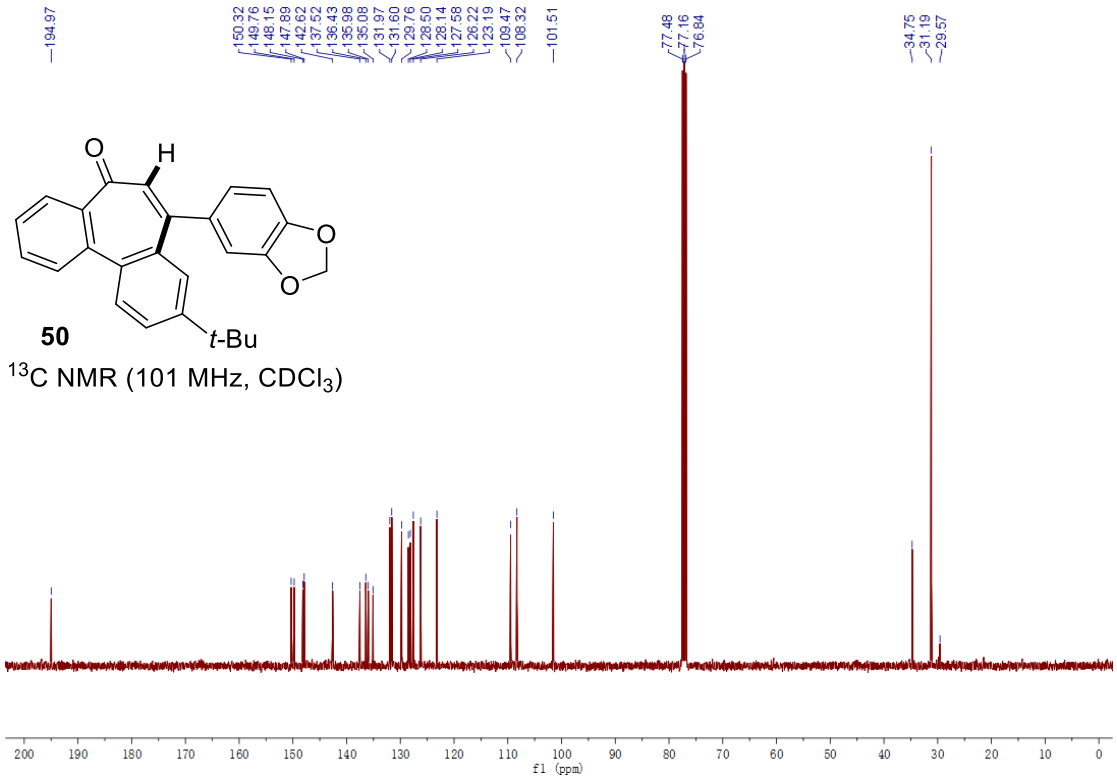
49

^{13}C NMR (151 MHz, $CDCl_3$)



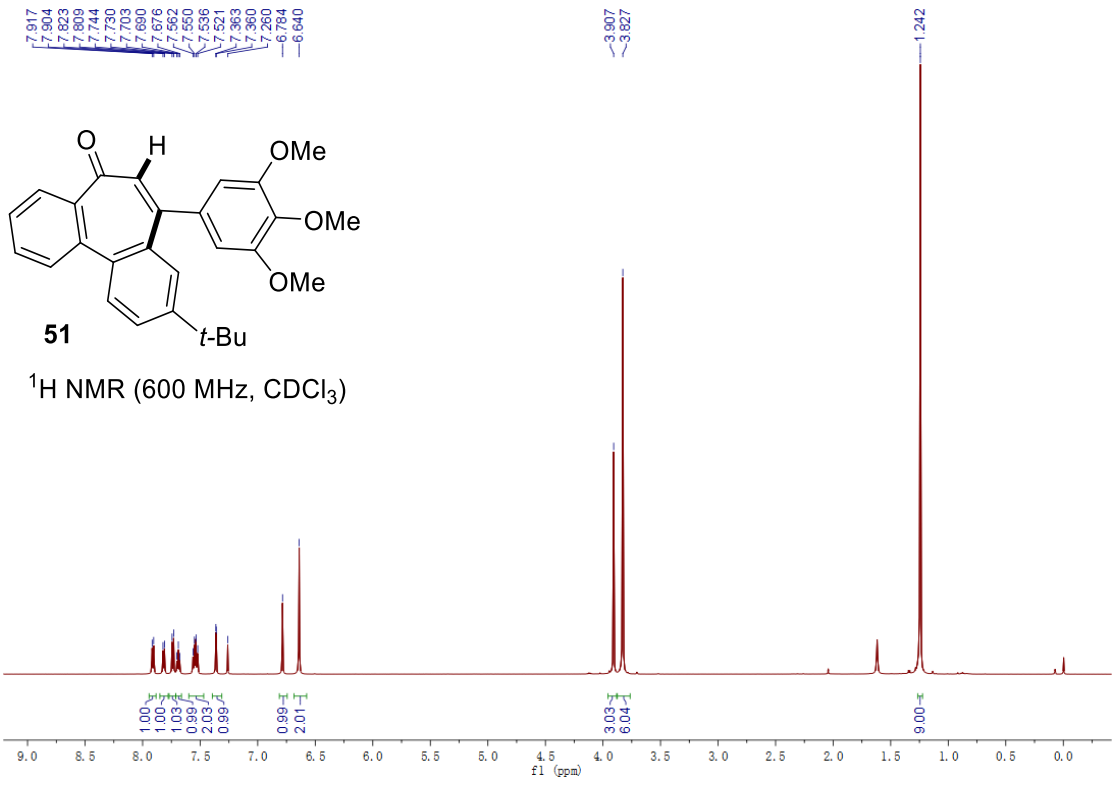
50

^{1}H NMR (400 MHz, $CDCl_3$)



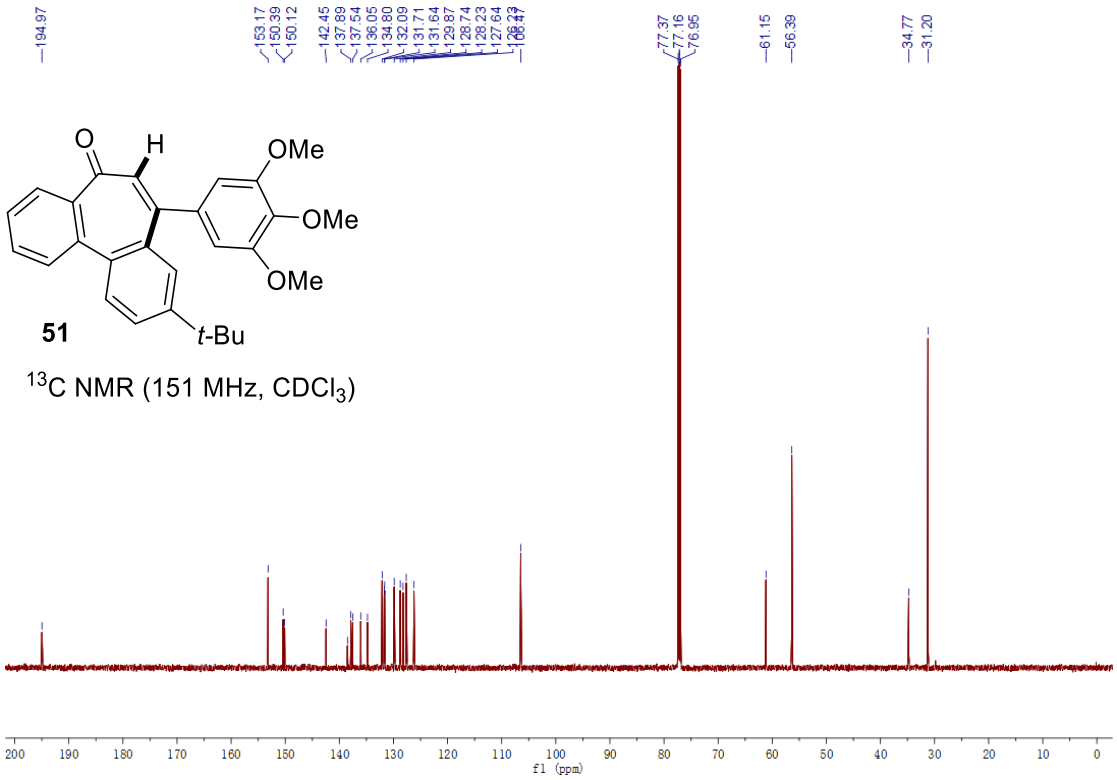
50

^{13}C NMR (101 MHz, $CDCl_3$)



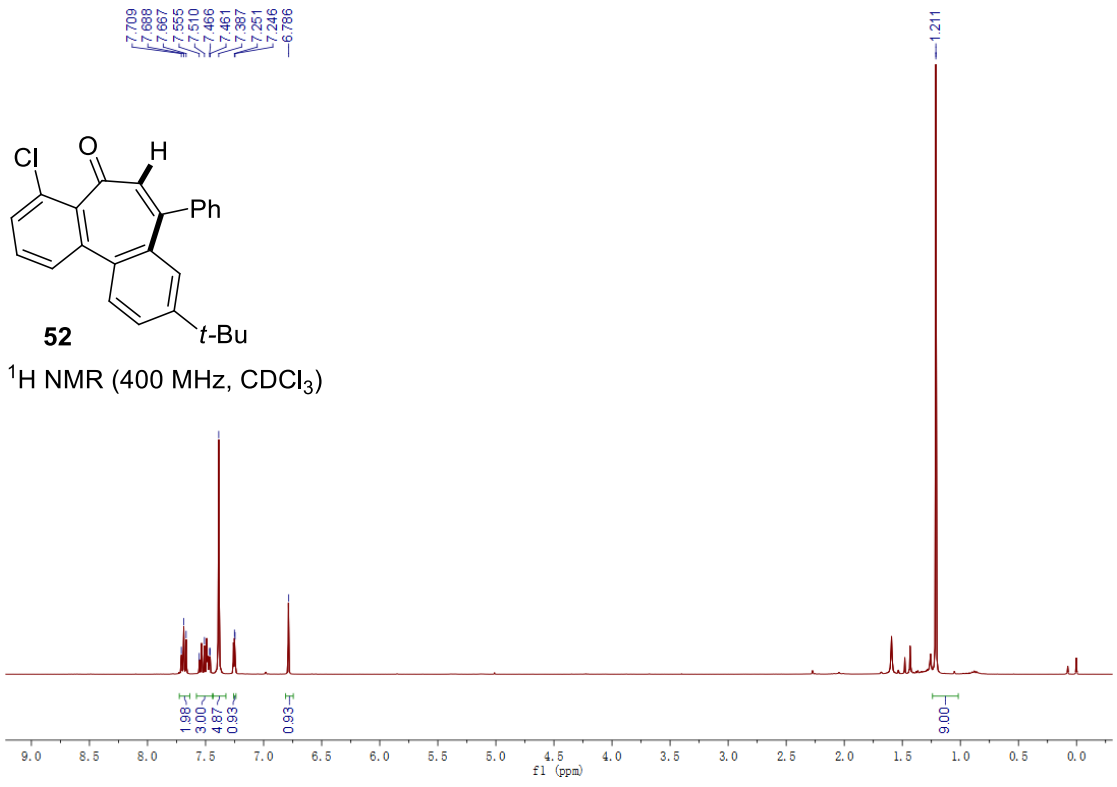
51

^{1}H NMR (600 MHz, $CDCl_3$)



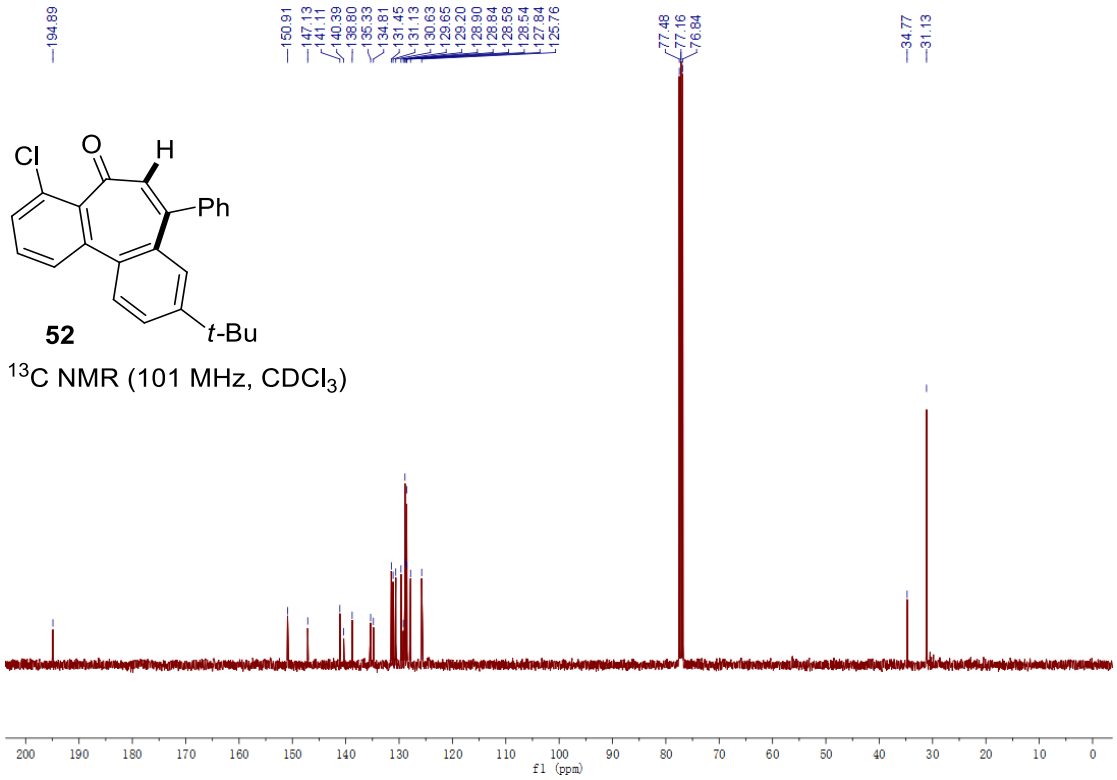
51

^{13}C NMR (151 MHz, $CDCl_3$)



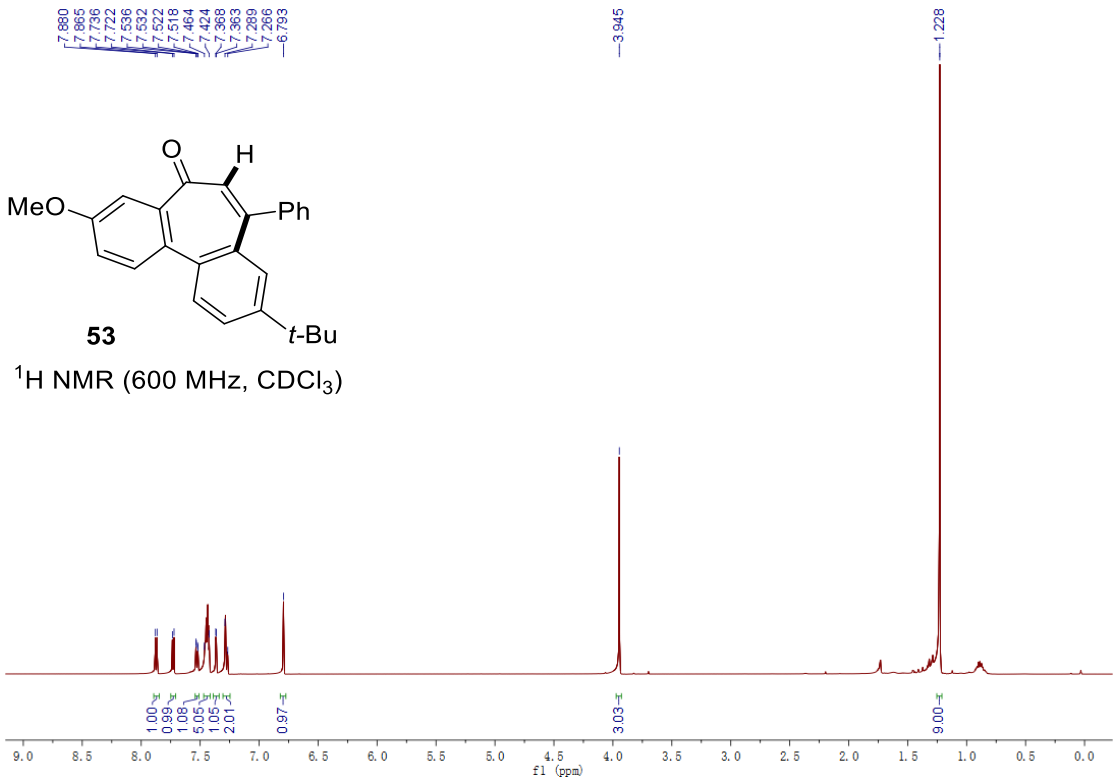
52

^{1}H NMR (400 MHz, $CDCl_3$)



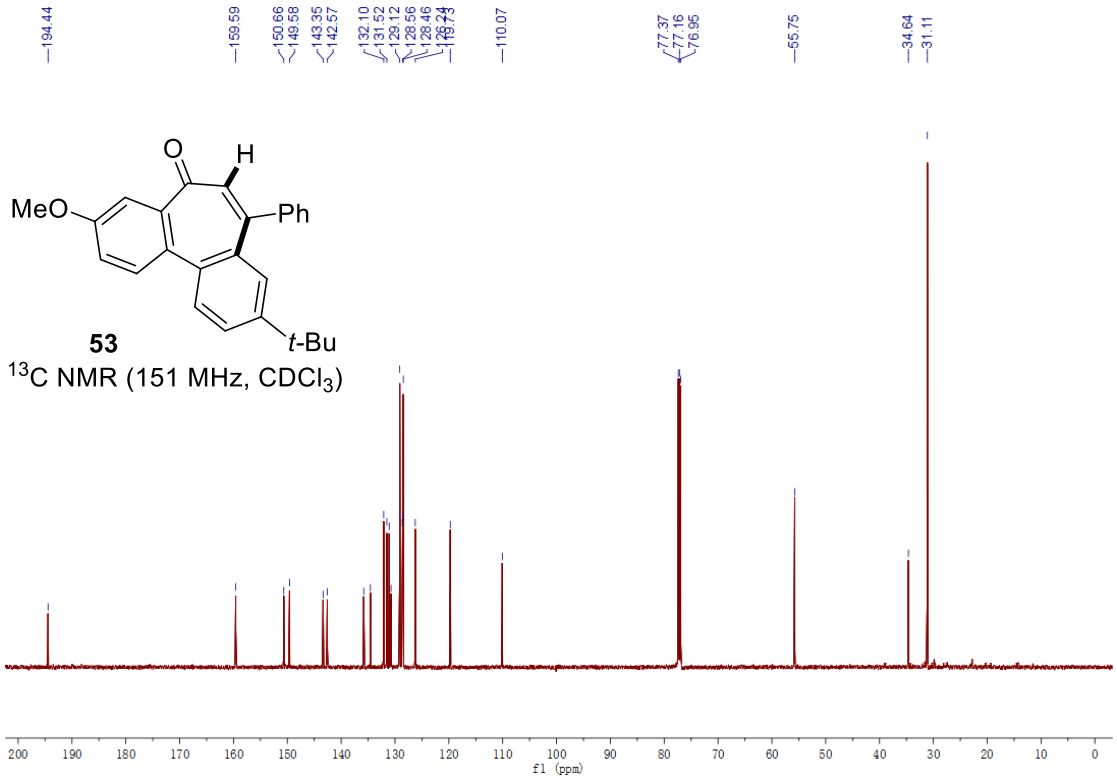
52

^{13}C NMR (101 MHz, $CDCl_3$)



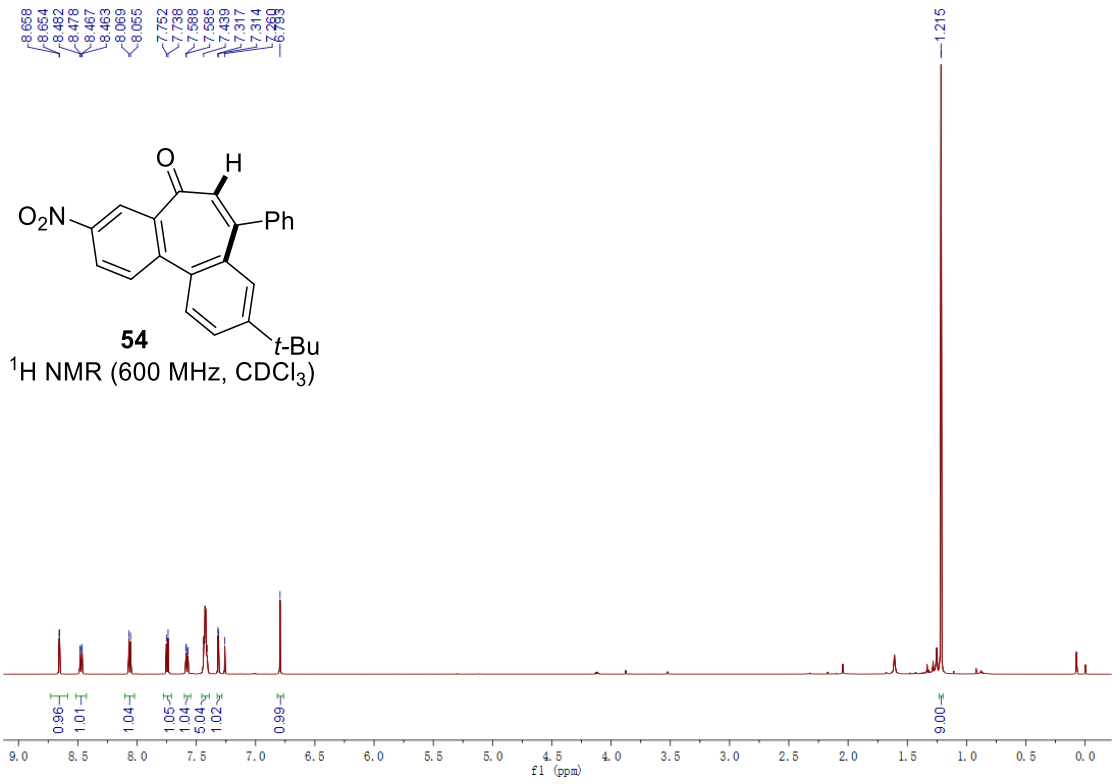
53

^{1}H NMR (600 MHz, $CDCl_3$)



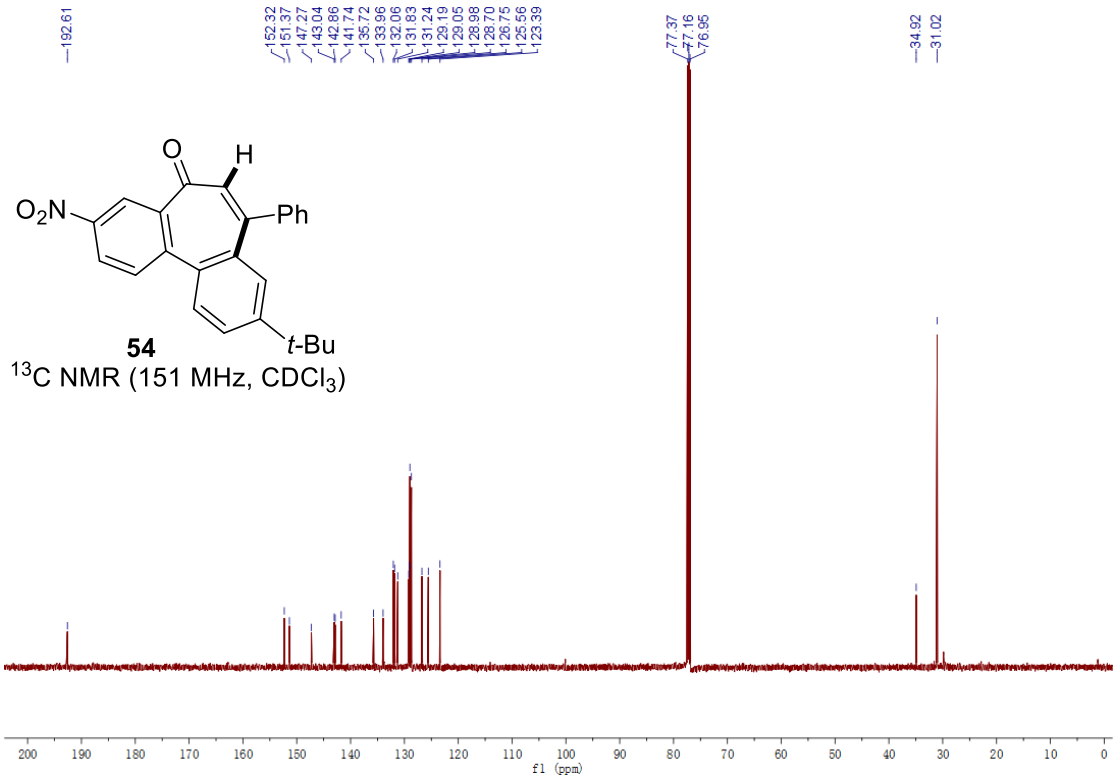
53

^{13}C NMR (151 MHz, $CDCl_3$)



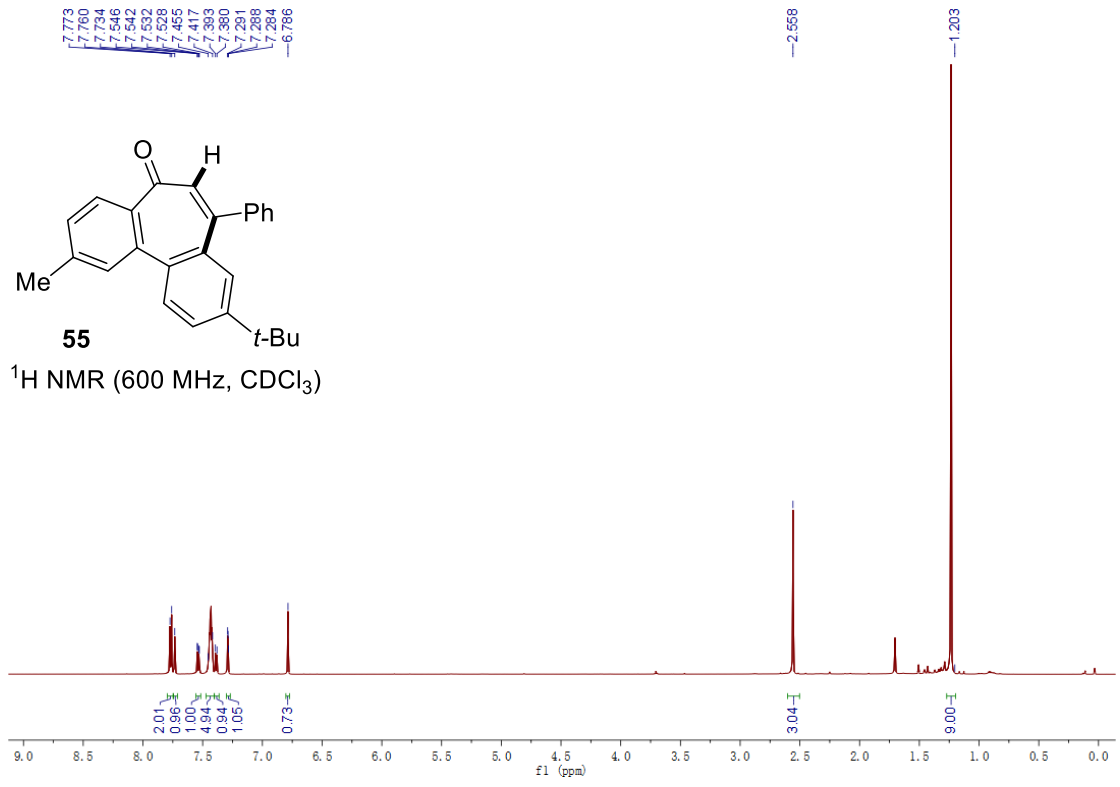
54

^{1}H NMR (600 MHz, $CDCl_3$)



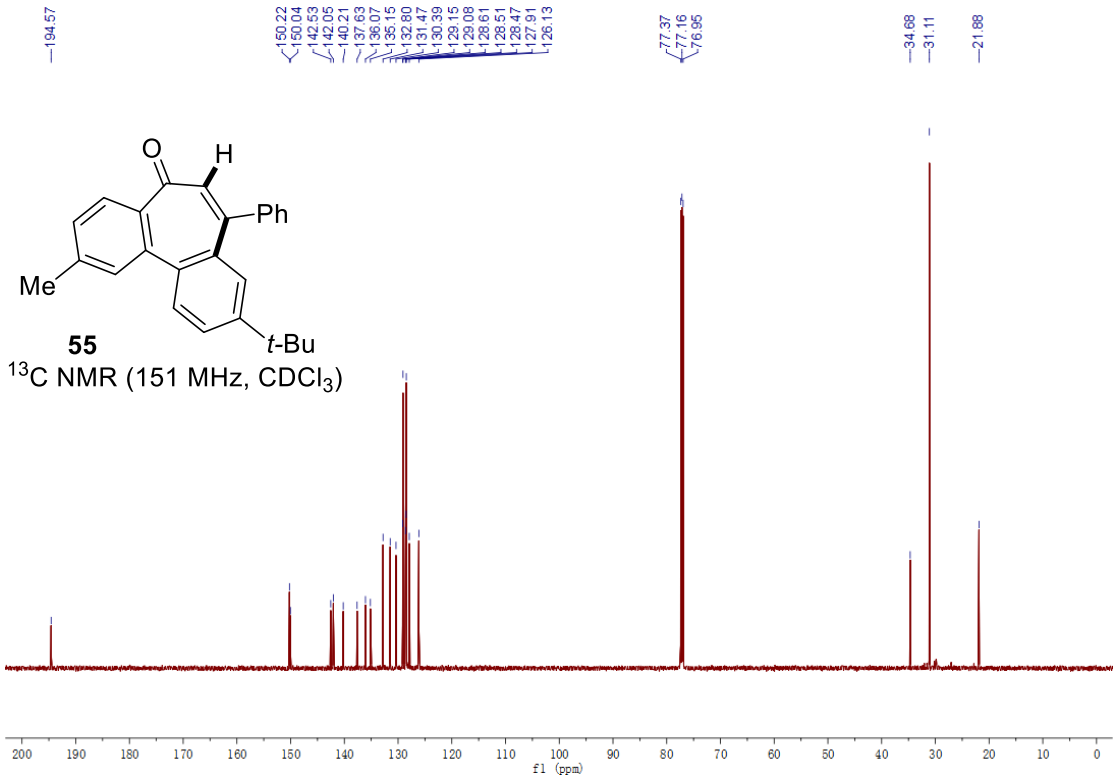
54

^{13}C NMR (151 MHz, $CDCl_3$)



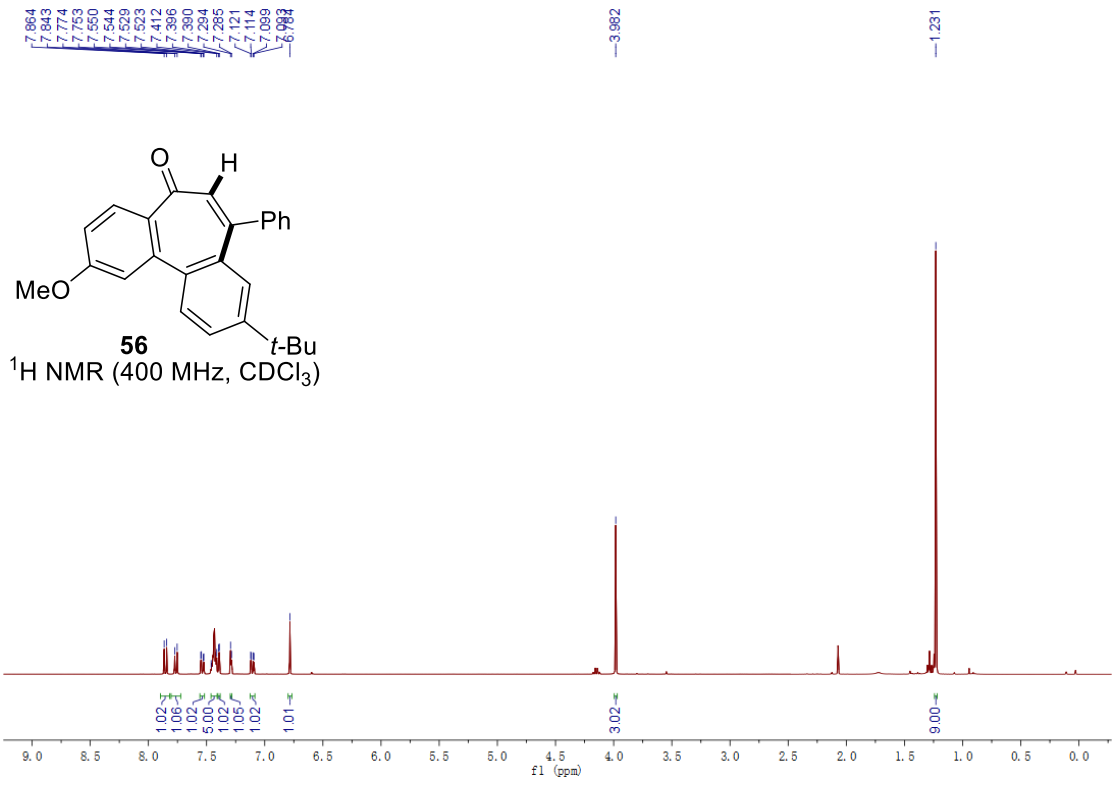
55

^{1}H NMR (600 MHz, $CDCl_3$)



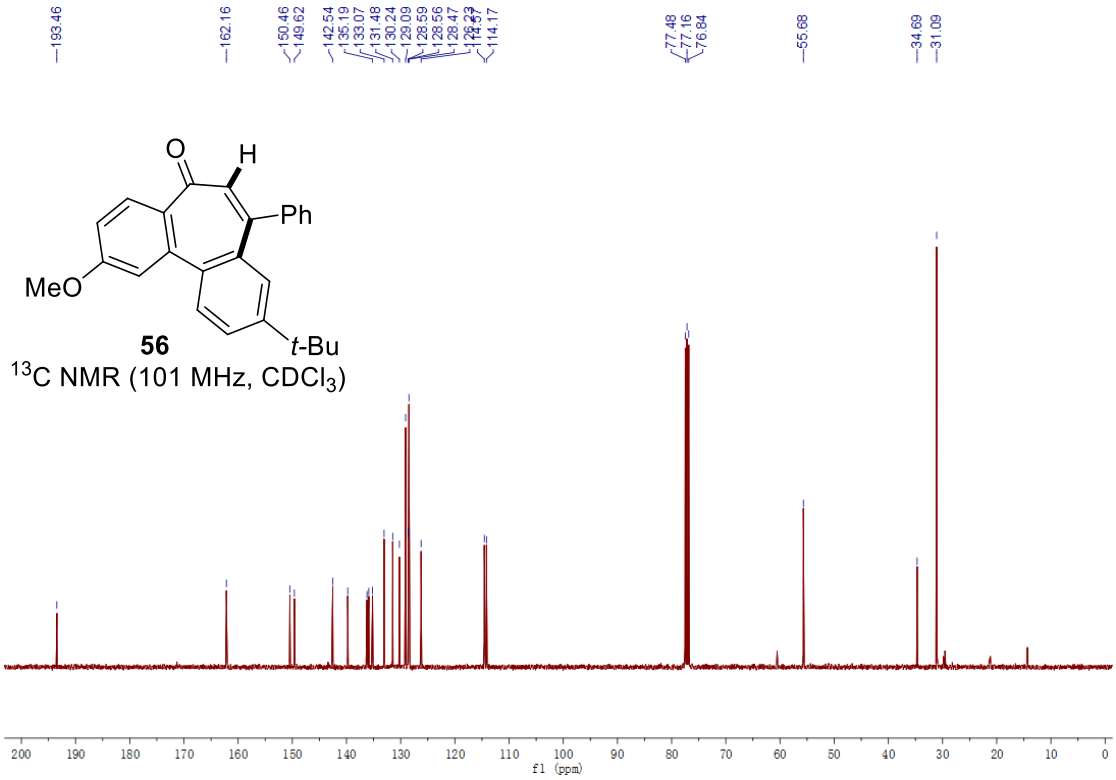
55

^{13}C NMR (151 MHz, $CDCl_3$)



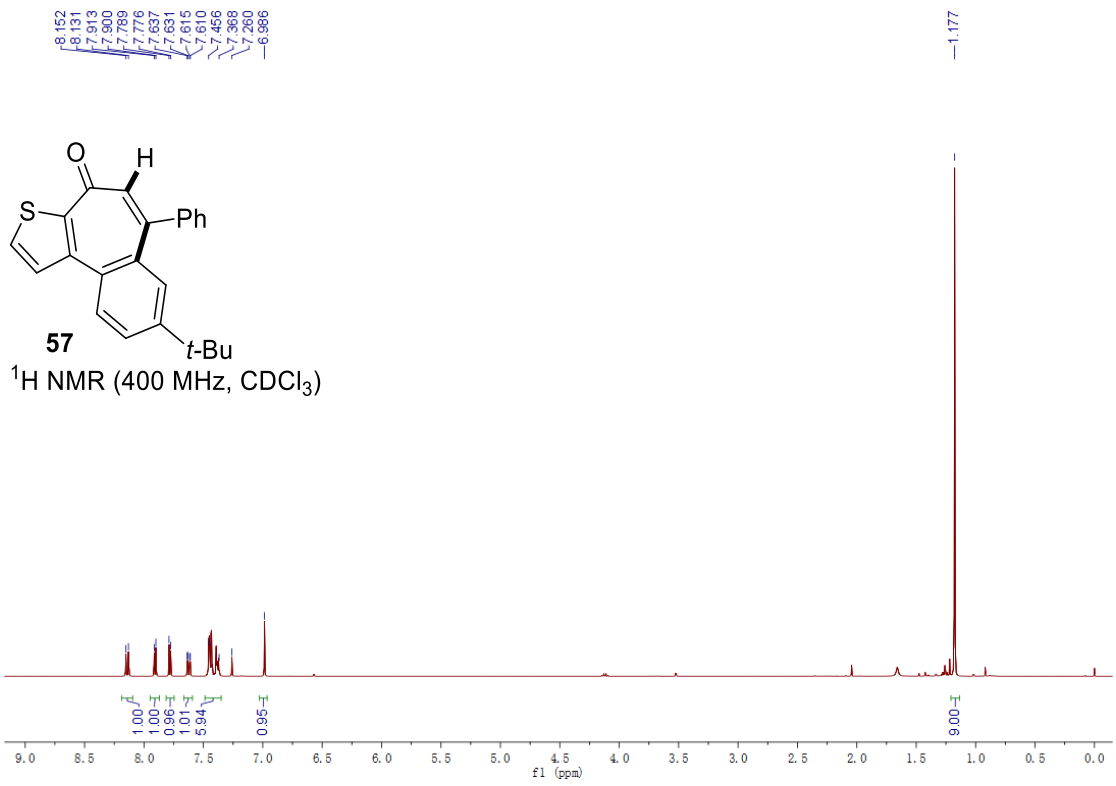
56

^{1}H NMR (400 MHz, $CDCl_3$)



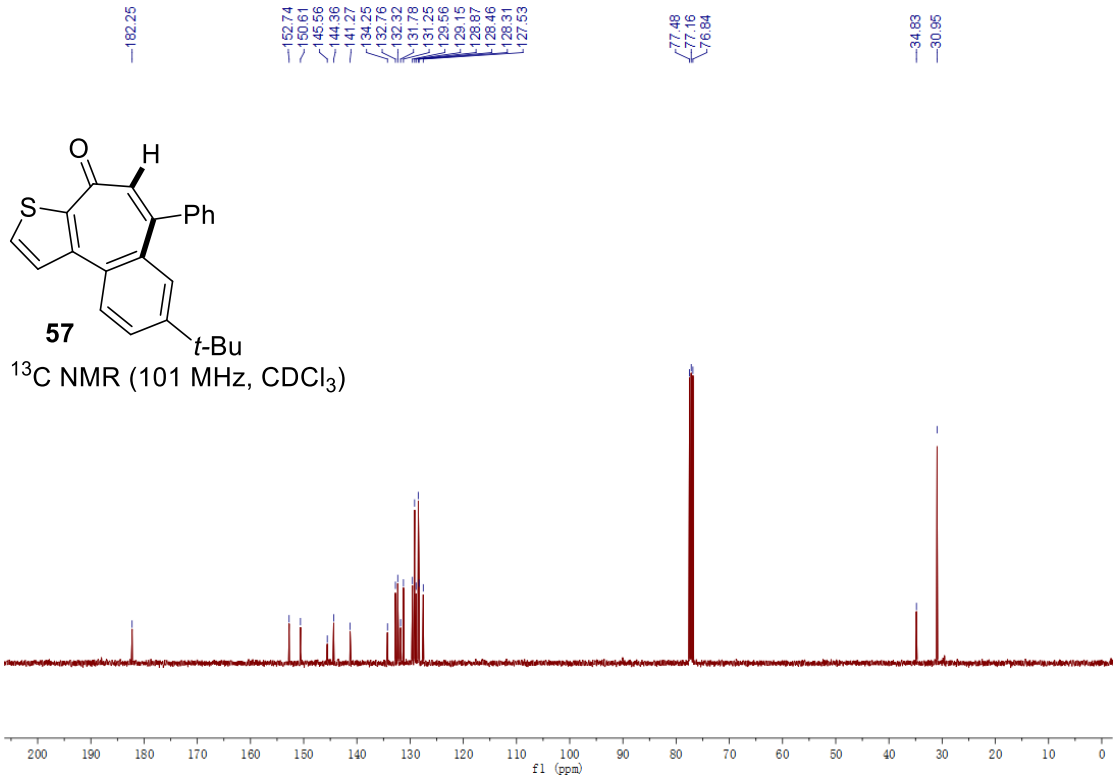
56

^{13}C NMR (101 MHz, $CDCl_3$)



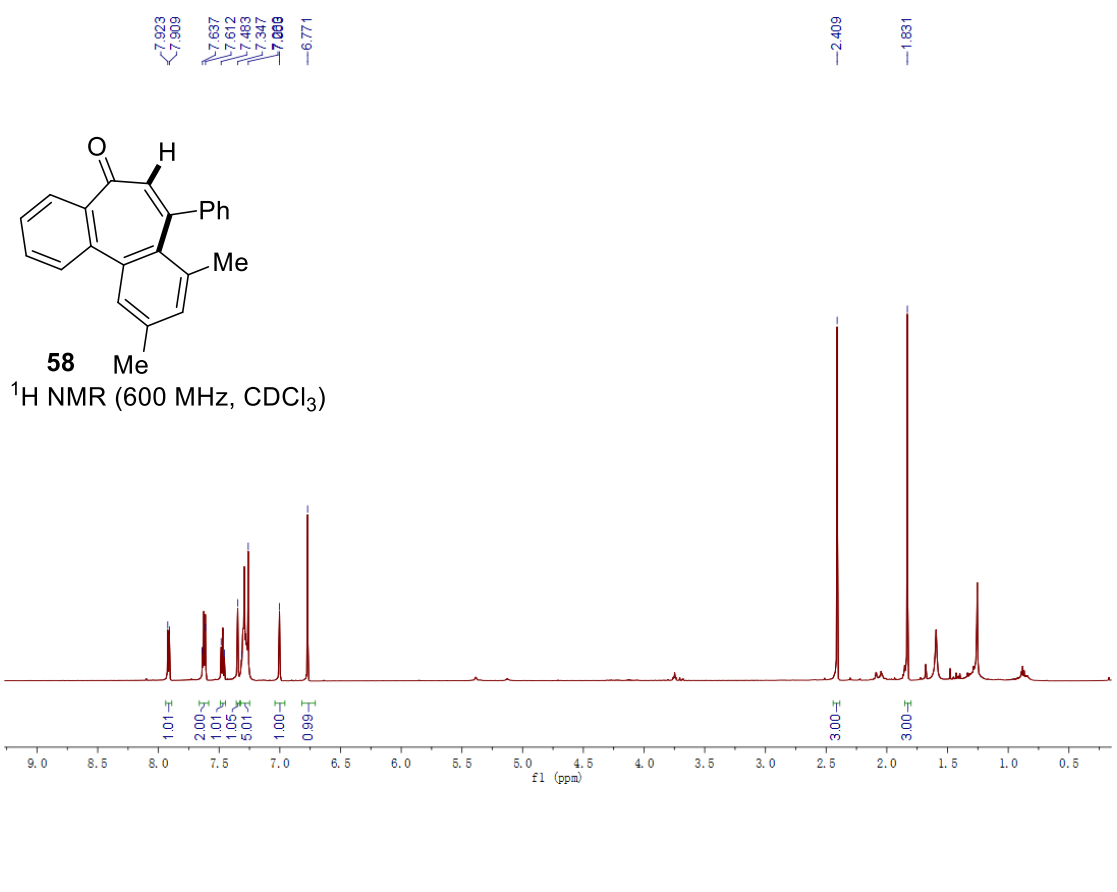
57

^{1}H NMR (400 MHz, $CDCl_3$)



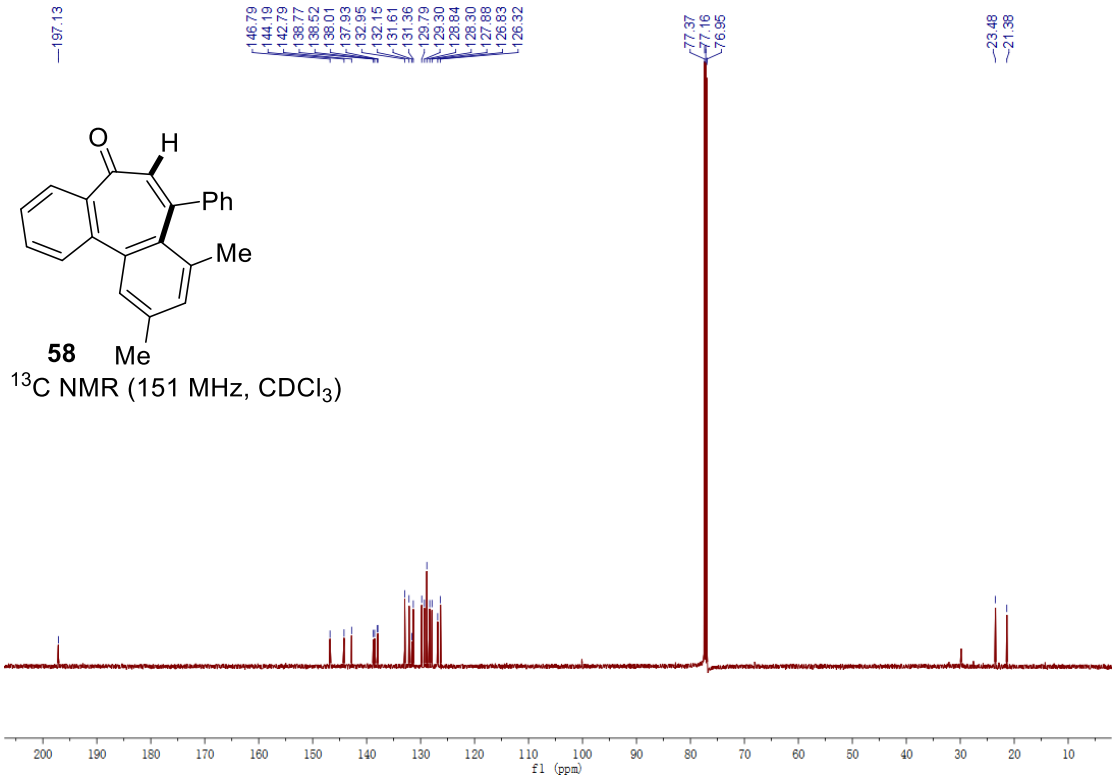
57

^{13}C NMR (101 MHz, $CDCl_3$)



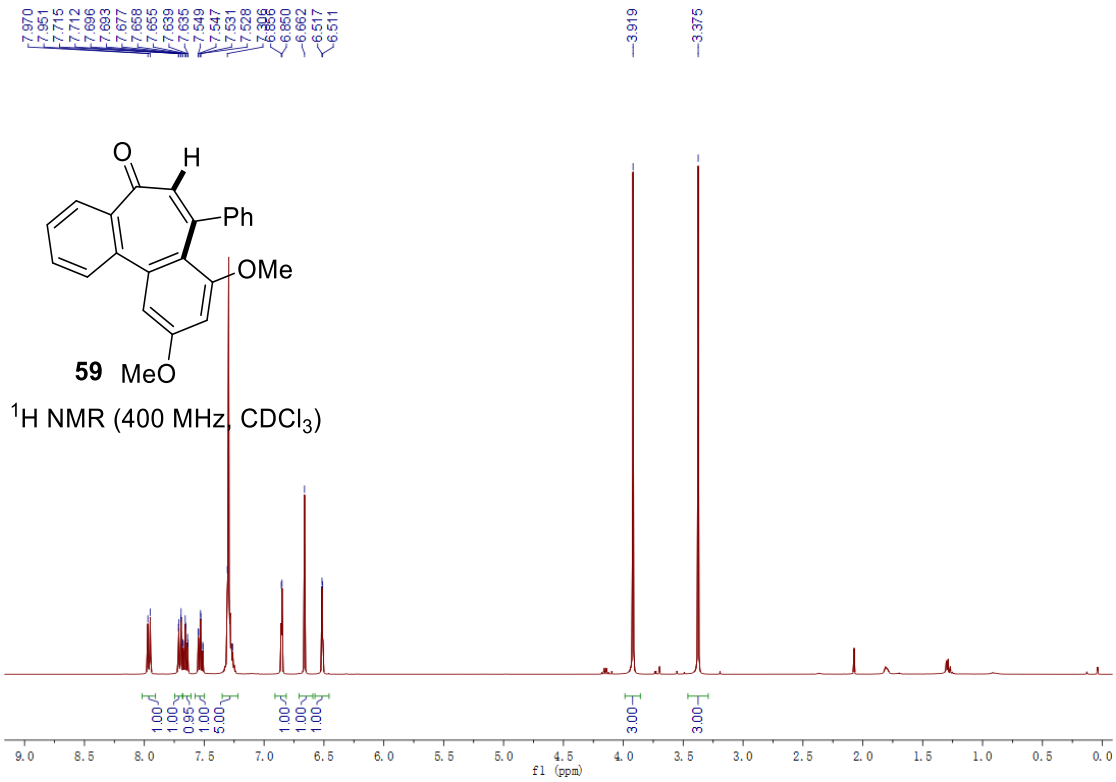
58

^{1}H NMR (600 MHz, $CDCl_3$)



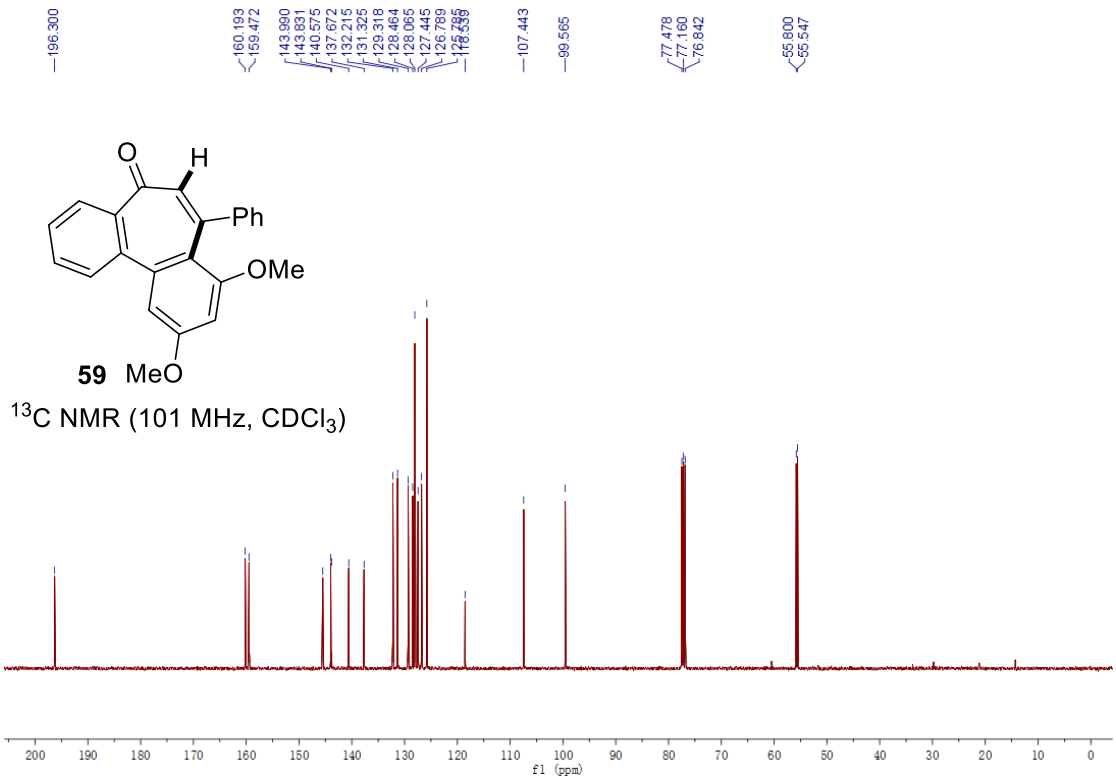
58

^{13}C NMR (151 MHz, $CDCl_3$)



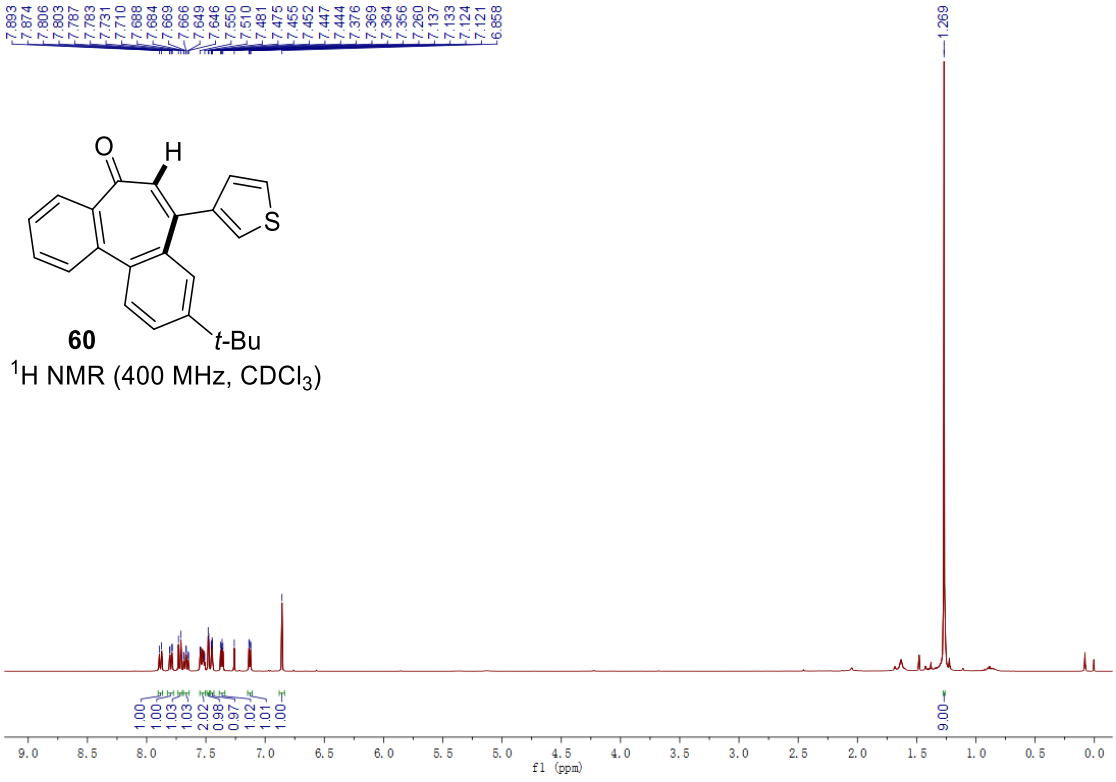
59

^{1}H NMR (400 MHz, $CDCl_3$)



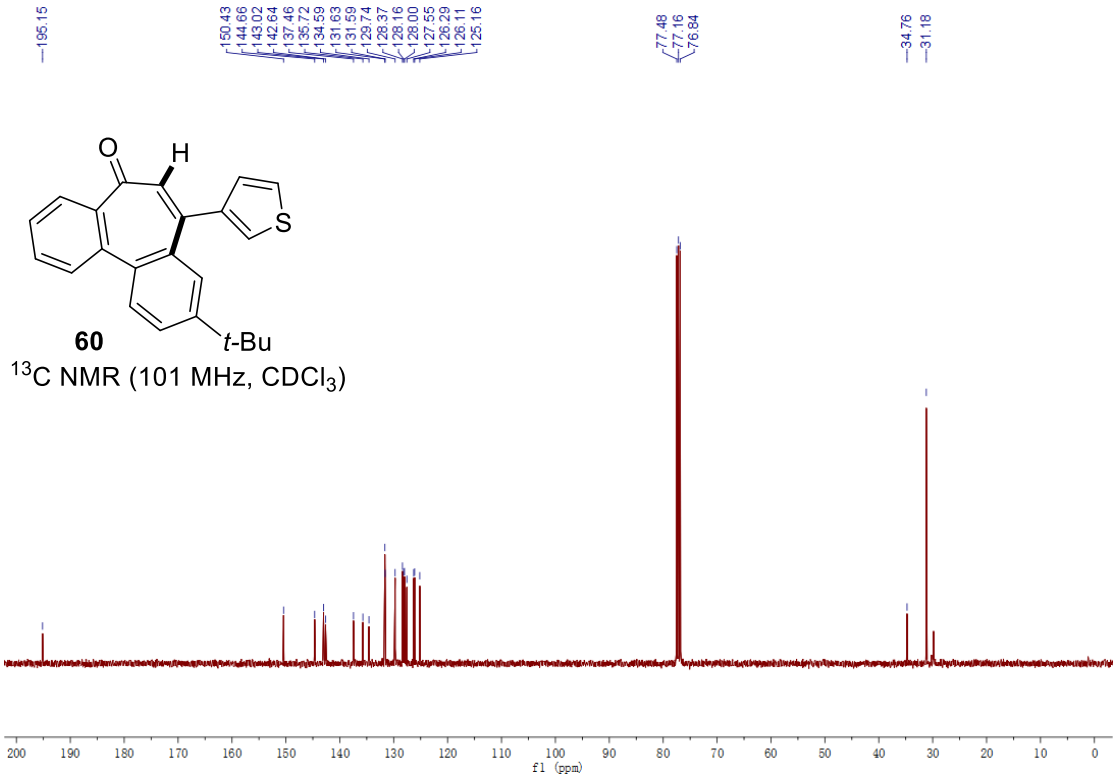
59

^{13}C NMR (101 MHz, $CDCl_3$)



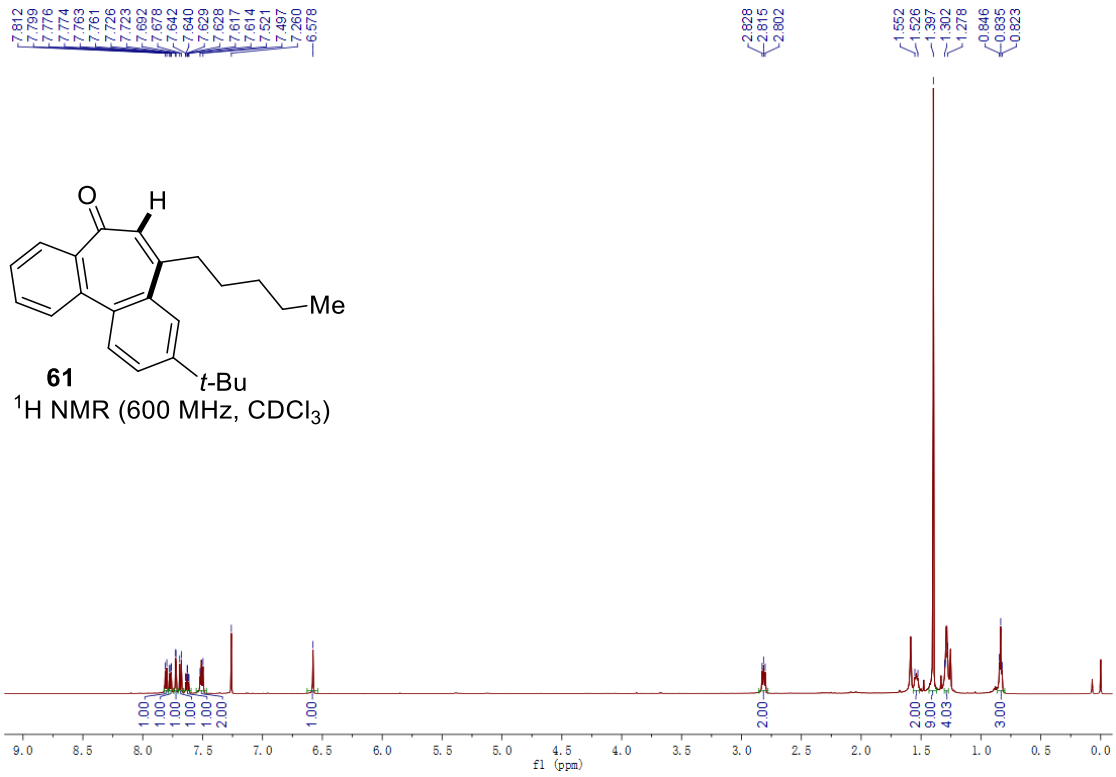
60

^{1}H NMR (400 MHz, $CDCl_3$)



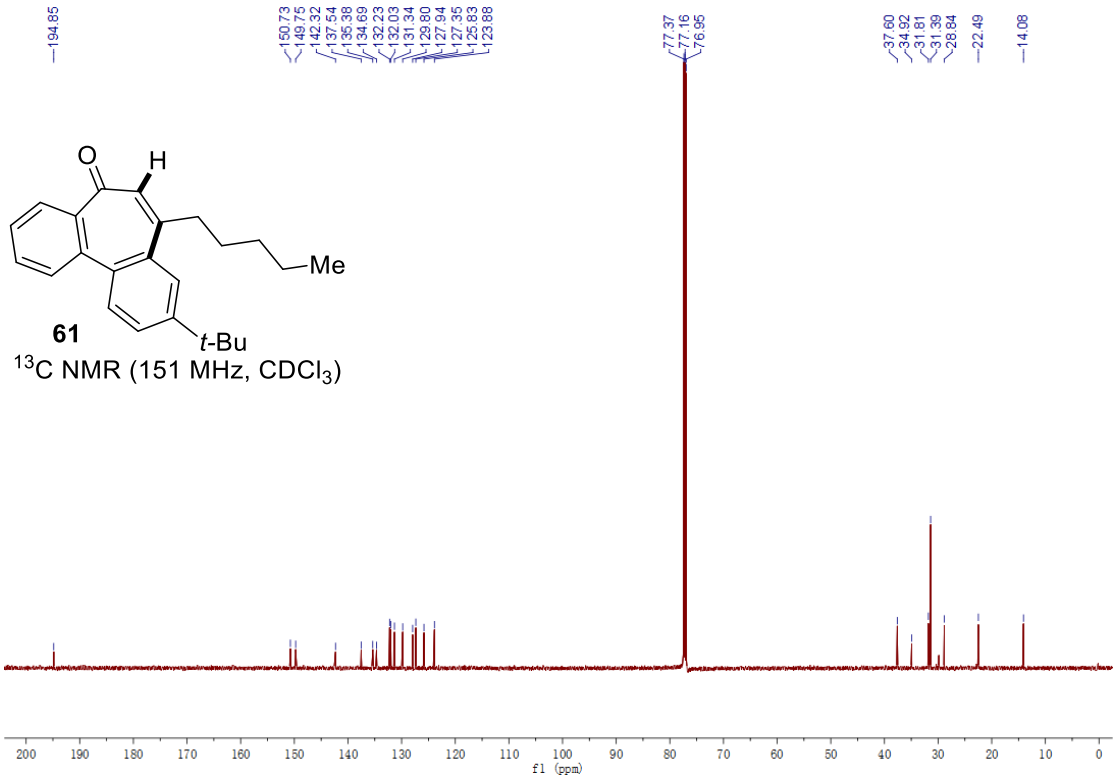
60

^{13}C NMR (101 MHz, $CDCl_3$)



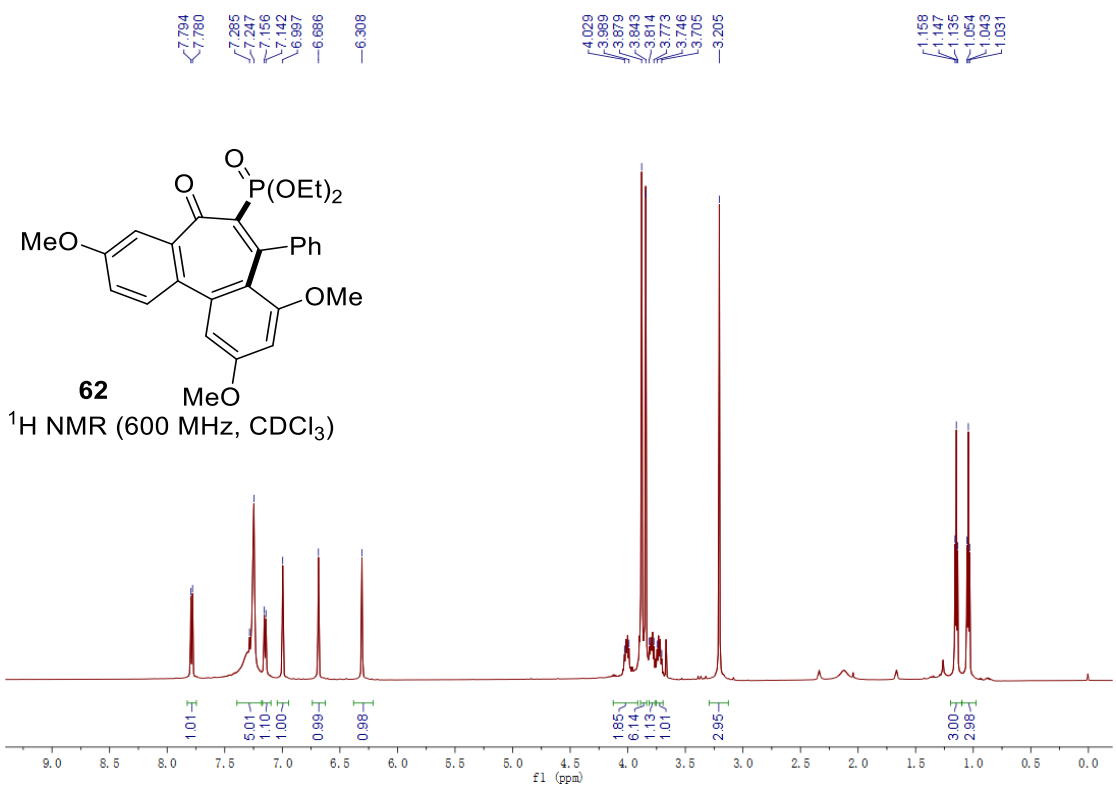
61

^{1}H NMR (600 MHz, $CDCl_3$)



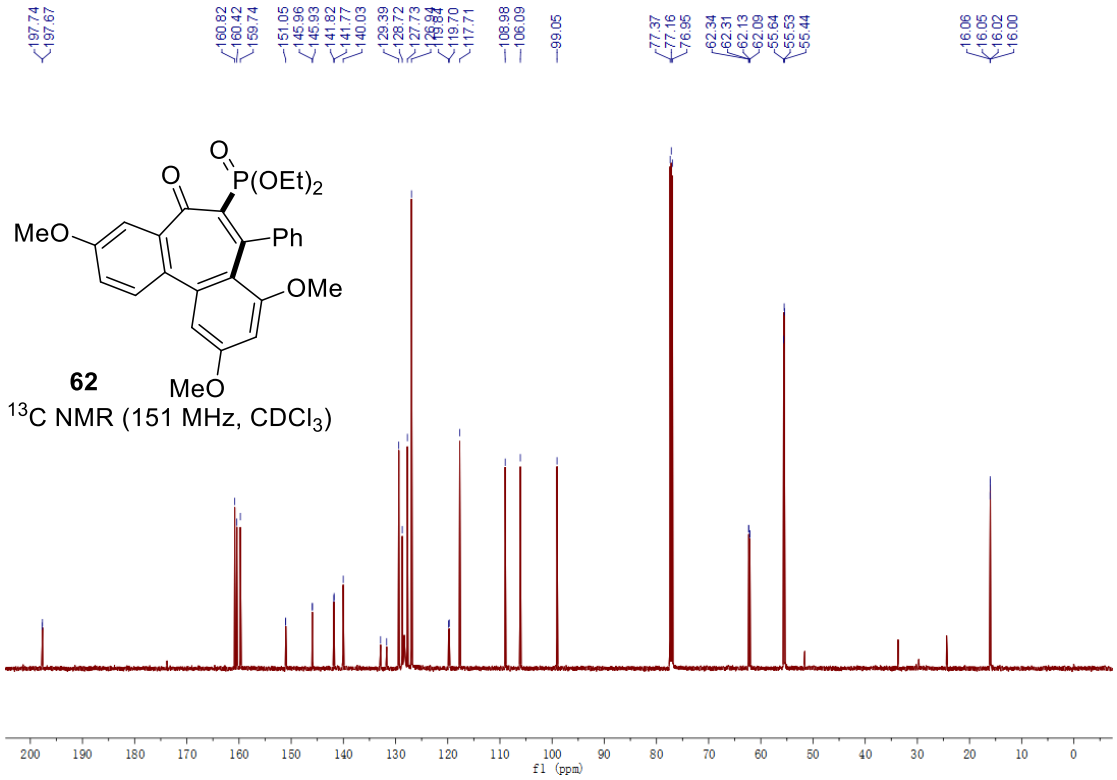
61

^{13}C NMR (151 MHz, $CDCl_3$)



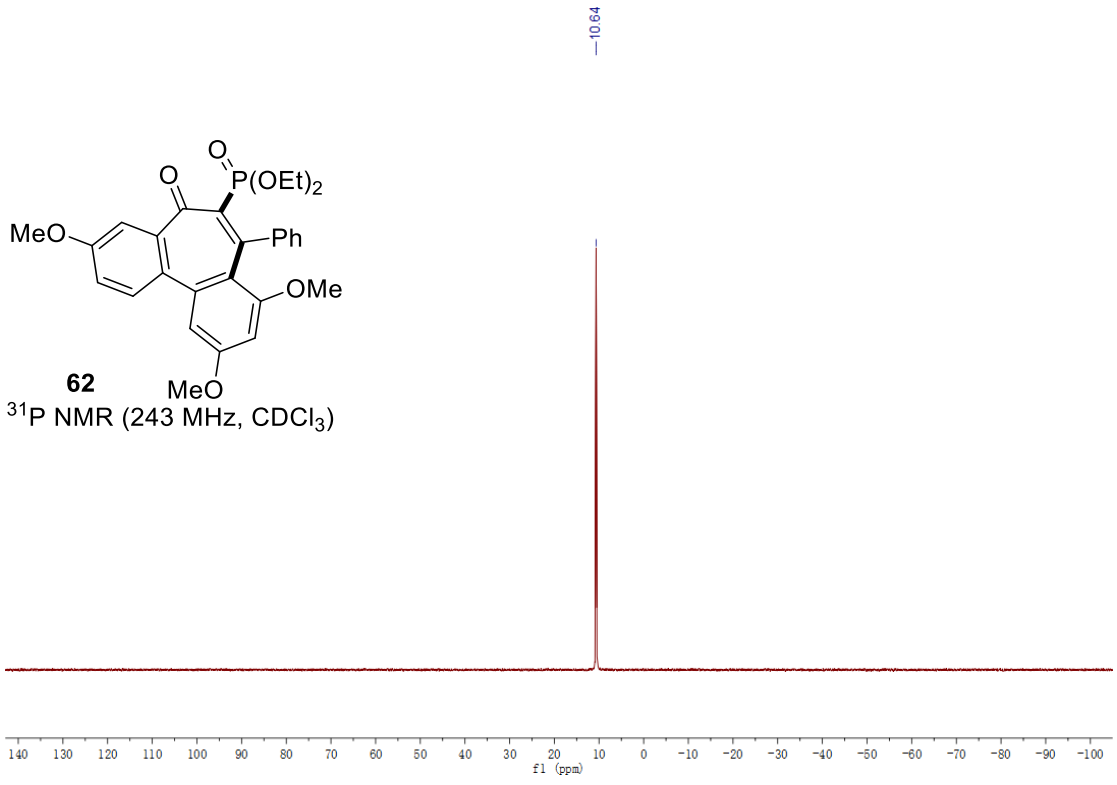
62

^{1}H NMR (600 MHz, $CDCl_3$)



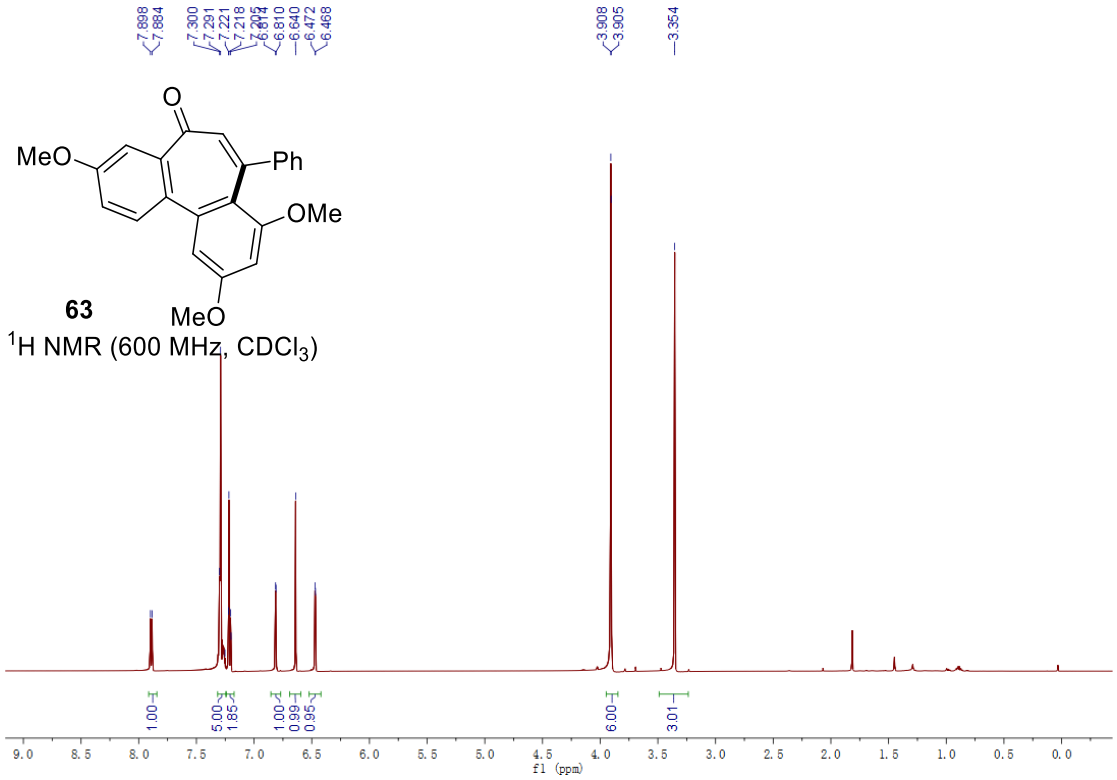
62

^{13}C NMR (151 MHz, $CDCl_3$)



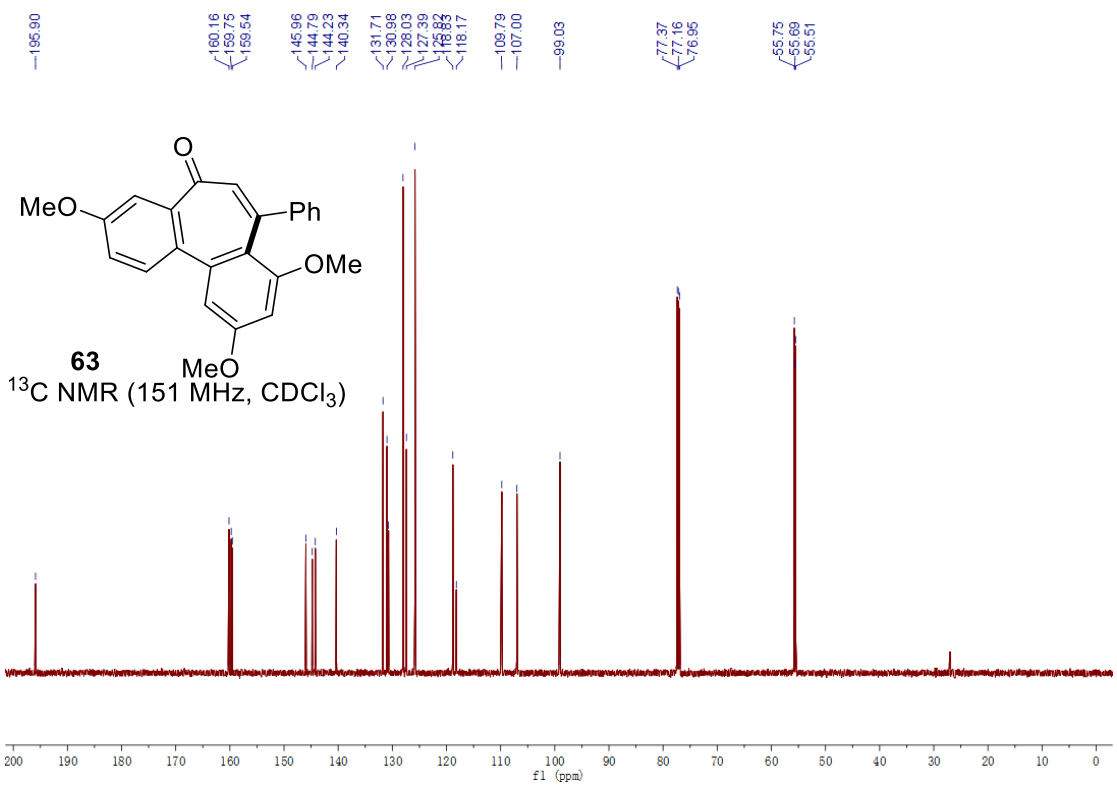
62

^{31}P NMR (243 MHz, $CDCl_3$)



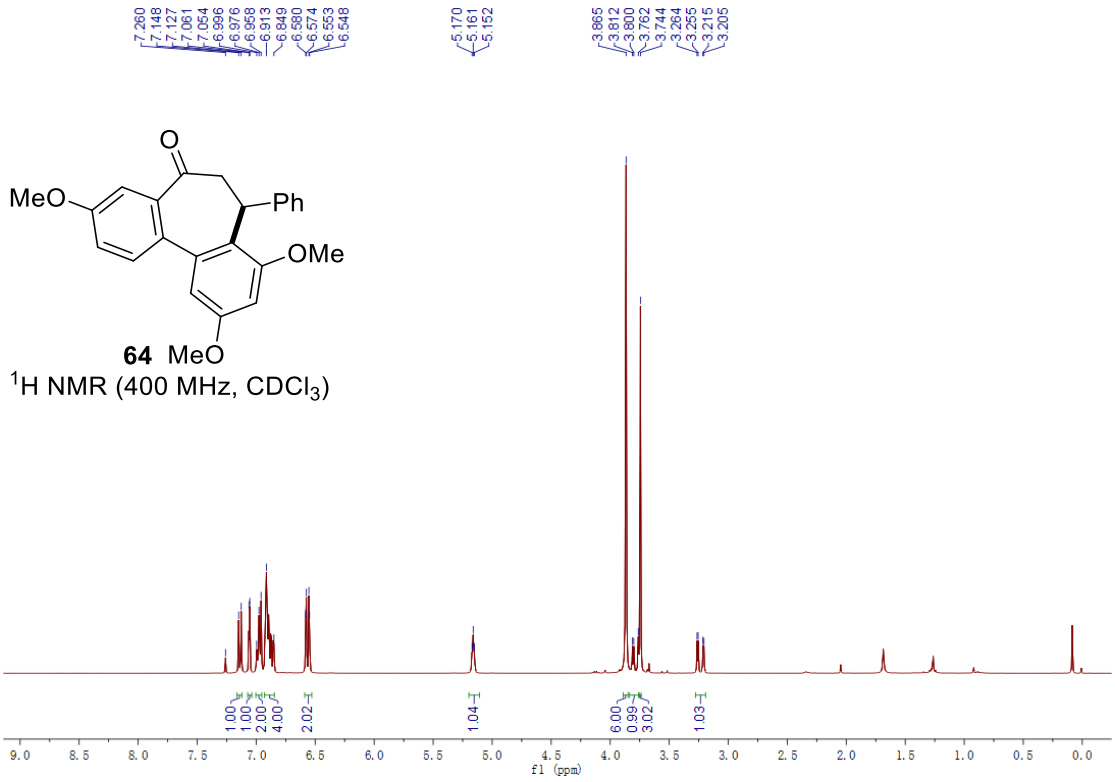
63

^{1}H NMR (600 MHz, $CDCl_3$)



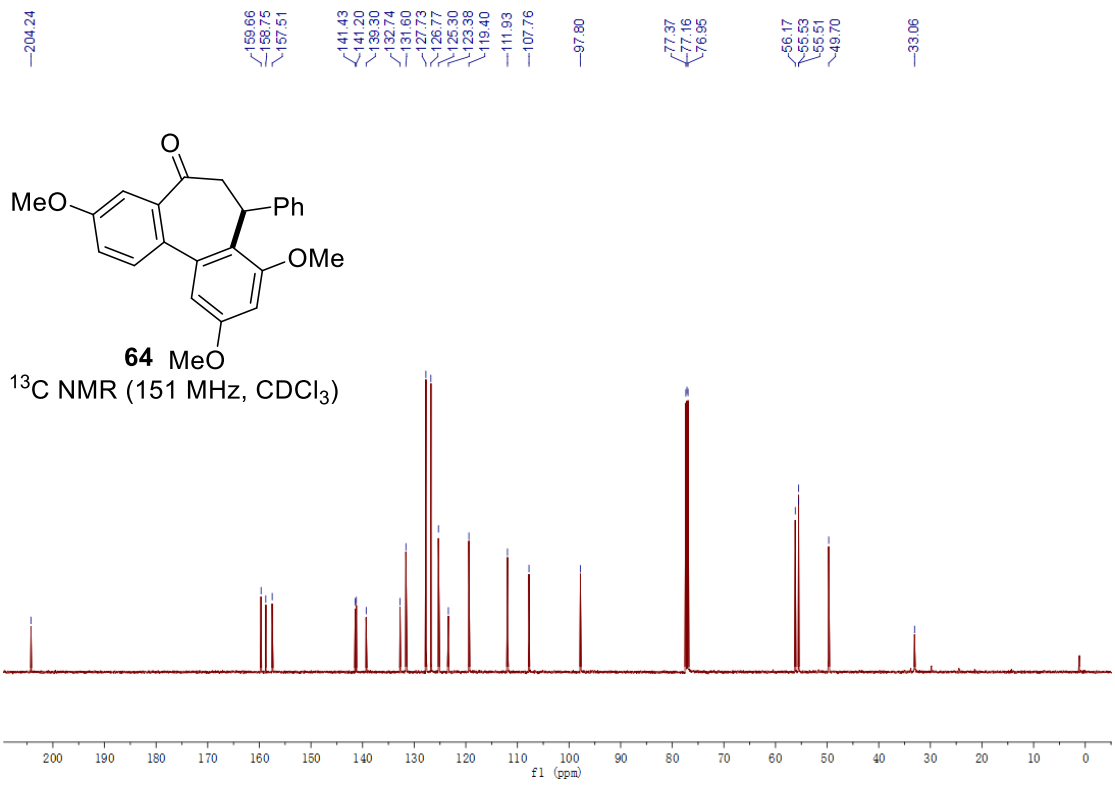
63

^{13}C NMR (151 MHz, $CDCl_3$)



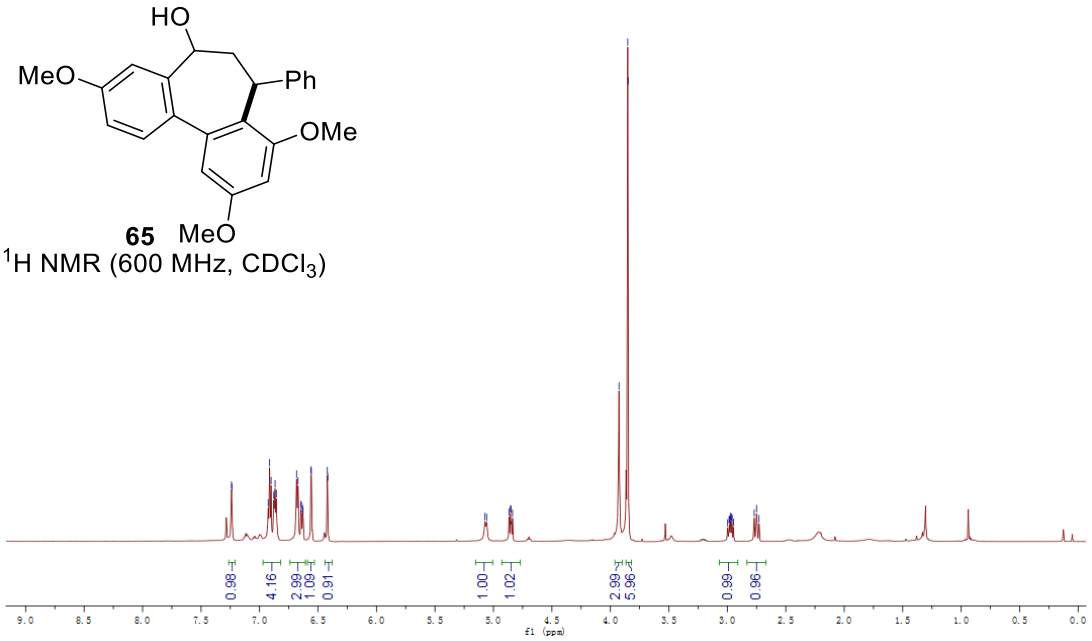
64 MeO

^{1}H NMR (400 MHz, $CDCl_3$)



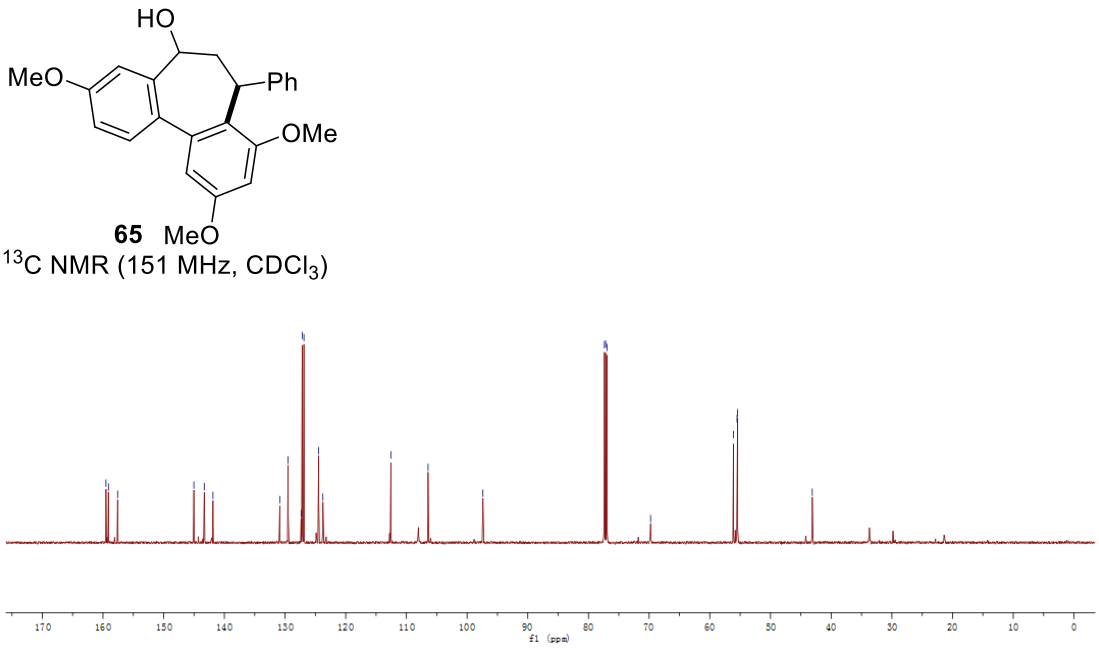
64 MeO

^{13}C NMR (151 MHz, $CDCl_3$)



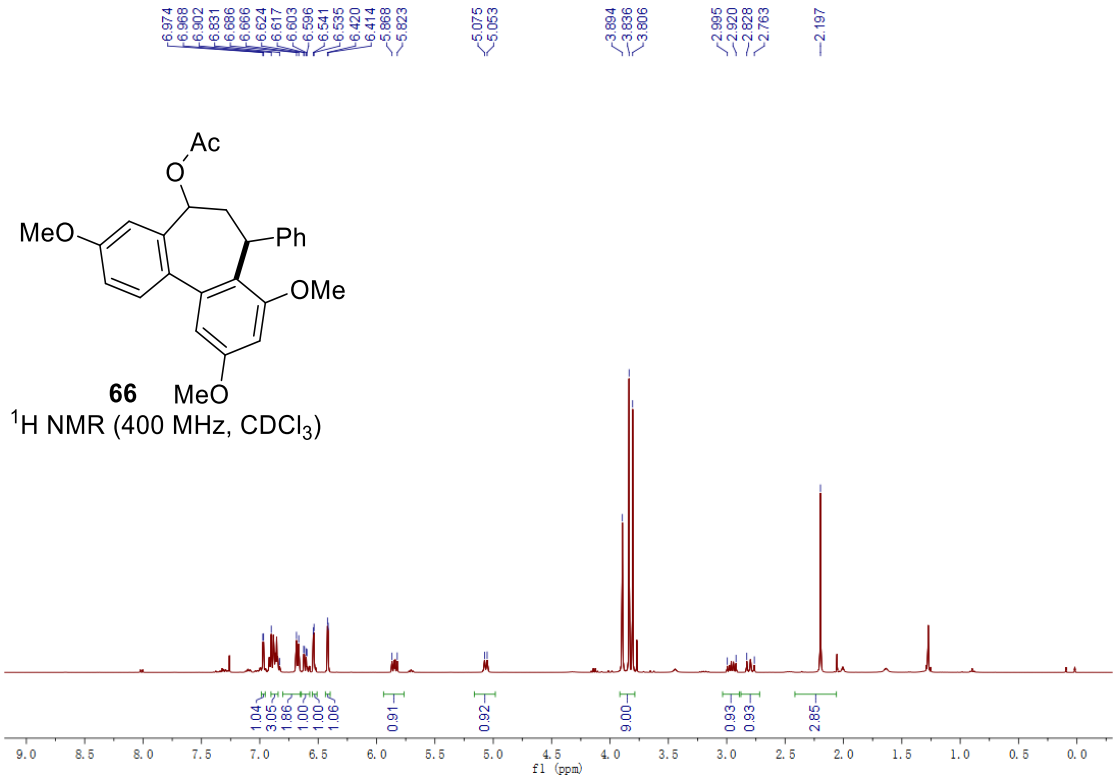
65

^{1}H NMR (600 MHz, $CDCl_3$)



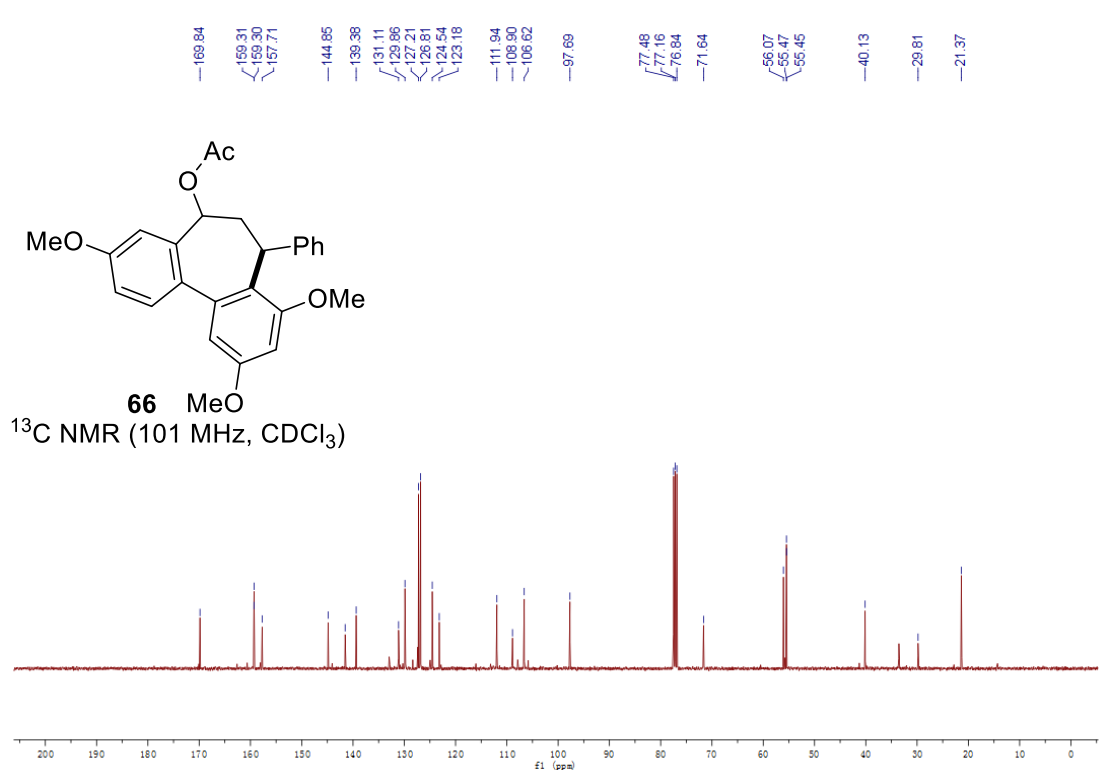
65

^{13}C NMR (151 MHz, $CDCl_3$)



66

^{1}H NMR (400 MHz, $CDCl_3$)



66

^{13}C NMR (101 MHz, $CDCl_3$)