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# Supporting Information



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# A Phosphine-Mediated Conversion of Azides to Diazo-Compounds

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## 1. General Methods

Reagent chemicals were obtained from commercial suppliers, and reagent grade solvents were used without further purification. Anhydrous $CH_2Cl_2$ was obtained from a CYCLE-TAINER® solvent delivery system (Baker). Anhydrous Toluene and $CH_3CN$ were obtained from Sigma–Aldrich. Procedures were performed at room temperature (~23 °C) unless indicated otherwise. Reactions were monitored by thin-layer chromatography using Whatman® aluminum-backed silica gel TLC plates with visualization by UV light. Compounds were purified by flash chromatography on silica gel, which had a mesh of 230–400 (ASTM) and a pore size of 60 Å or on basic aluminum oxide (Brockmann Grade V), which had an approximate mesh of 150 and a pore size of 58 Å. The removal of solvents and other volatile materials "under reduced pressure" refers to the use of a rotary evaporator at water-aspirator pressure (<20 torr) and a water bath of <40 °C.

## 2. Instrumentation

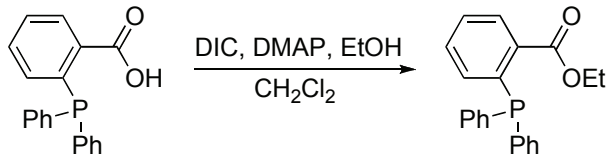
NMR spectra were acquired at ambient temperature with a Bruker DMX-400 Avance spectrometer ($^1$H, 400.1 MHz; $^{13}$C, 100.6 MHz; $^{31}$P, 162.0 MHz at the National Magnetic Resonance Facility at Madison (NMRFAM). Carbon-13 and Phosphorus-31 spectra were

proton-decoupled. $^{1}$H NMR spectra were referenced to TMS or to the residual solvent peak. $^{13}$C NMR spectra were referenced to the residual solvent peak. $^{31}$P NMR spectra were referenced to an external source of 85% $H_3PO_4$. In certain Carbon-13 spectra the phrase "observed signals" is used when there is coincidental overlap of signals or the non-appearance of a quaternary carbon. Mass spectrometry was performed with a Micromass LCT (electrospray ionization, ESI) in the Mass Spectrometry Facility in the Department of Chemistry at the University of Wisconsin–Madison. X-Ray data were acquired at the Molecular Structure Laboratory in the Department of Chemistry at the University of Wisconsin–Madison using a Bruker-AXS SMART APEX2 with Cu $K_\alpha$ ($\lambda$ = 1.54178 Å) radiation at 100(2) K.

## 3. Experimental Procedures and Characterization Data

### 3.1 Synthesis of Phosphines

**Ethyl 2-(diphenylphosphanyl)benzoate (1a)**

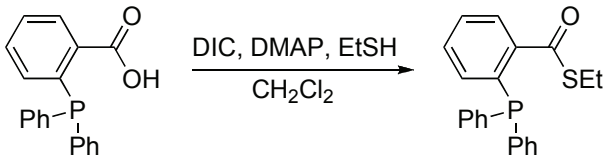



**1a**

2-(Diphenylphosphanyl)benzoic acid[1] (0.50 g, 1.63 mmol) and DMAP (20 mg, 0.163 mmol) were dissolved in $CH_2Cl_2$ (10 mL). Ethanol (0.29 mL, 4.89 mmol) was added, and the solution was placed under Ar(g) and cooled to 0 °C. *N,N*′-Diisopropylcarbodiimide (0.25 mL, 1.63 mmol) was added dropwise, and the resulting solution was allowed to warm to room temperature and stirred overnight. The solution was then filtered, and the filtrate was concentrated under reduced pressure. The resulting residue was purified by silica gel column chromatography, eluting with 10% EtOAc/hexanes, to give phosphine **1a** as a pale yellow solid (0.44 g, 1.32 mmol, 81% yield).

Data for **1a**: $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ = 8.07 (m, 1H, Ar.), 7.44–7.25 (m, 12H, Ar.), 6.93 (m, 1H, Ar.), 4.22 (q, 2H, $J$ = 7.1 Hz, $OCH_2CH_3$), 1.21 (t, 3H, $J$ = 7.1 Hz, $OCH_2CH_3$). $^{13}$C NMR (100 MHz, $CDCl_3$, $^{31}$P-coupled; $^{1}$H-decoupled, observed signals) $\delta$ = 166.9, 140.8, 140.0, 138.1, 137.9, 134.8, 134.6, 134.3, 134.0, 133.8, 131.8, 130.6, 128.6, 128.5, 128.4, 128.2, 61.2, 14.0. $^{31}$P NMR (162 MHz, $CDCl_3$) $\delta$ = –4.0. HRMS (ESI$^+$) $m/z$ calculated for $(C_{21}H_{20}O_2P)^+$ 335.1196, measured 335.1208.

**[2-(Diphenylphosphanyl)phenyl](ethylsulfanyl)methanone (1b)**

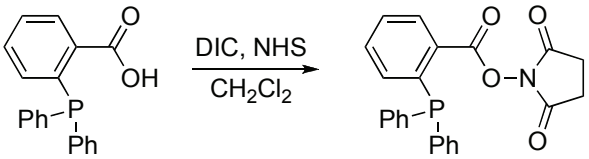



**1b**

2-(Diphenylphosphanyl)benzoic acid[1] (0.50 g, 1.63 mmol) and DMAP (20 mg, 0.163 mmol) were dissolved in $CH_2Cl_2$ (10 mL). Ethanethiol (0.35 mL, 4.89 mmol) was added, and the solution was placed under Ar(g) and cooled to 0 °C. *N,N*′-Diisopropylcarbodiimide (0.25 mL, 1.63 mmol) was added dropwise, and the resulting solution was allowed to warm to room temperature and stirred overnight. The solution was then filtered, and the filtrate was concentrated under reduced pressure. The resulting residue was purified by silica gel column chromatography, eluting with 10% EtOAc/hexanes, to give phosphine **1b** as a pale yellow solid (0.43 g, 1.22 mmol, 75% yield).

Data for **1b**: $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ = 8.02 (m, 1H, Ar.), 7.45–7.24 (m, 12H, Ar.), 6.99 (m, 1H, Ar.), 2.98 (q, 2H, $J$ = 7.4 Hz, $SCH_2CH_3$), 1.22 (t, 3H, $J$ = 7.4 Hz, $SCH_2CH_3$). $^{13}$C NMR (100 MHz, $CDCl_3$, $^{31}$P-coupled; $^1$H-decoupled, observed signals) $\delta$ = 192.7, 141.9, 141.7, 138.0, 137.8, 137.7, 134.6, 134.0, 133.8, 131.7, 128.9, 128.6, 128.4, 128.4, 128.3, 24.0, 14.6. $^{31}$P NMR (162 MHz, $CDCl_3$) $\delta$ = –5.8. HRMS (ESI$^+$) *m/z* calculated for $(C_{21}H_{20}OPS)^+$ 351.0968, measured 351.0953.

**2,5-Dioxopyrrolidin-1-yl-2-(diphenylphosphanyl)benzoate (1c)**



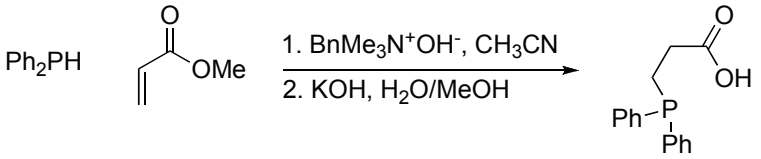

**1c**

2-(Diphenylphosphanyl)benzoic acid (1.00 g, 3.26 mmol) was dissolved in $CH_2Cl_2$ (10 mL), and the solution was cooled to 0 °C. *N*-Hydroxysuccinimide (0.75 g, 6.53 mmol) and *N,N*′-diisopropylcarbodiimide (0.56 mL, 3.59 mmol) were added, and the mixture was allowed to warm to room temperature and stirred overnight under Ar(g). The resulting suspension was filtered, and the filtrate was concentrated under reduced pressure. The resulting residue was purified by silica gel flash chromatography, eluting with 30% EtOAc/hexanes, to give the ester as a pale yellow solid (1.28 g, 3.17 mmol, 97% yield).

Data for **1c**: $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ = 8.34 (m, 1H, Ar), 7.55–7.22 (m, 12H, Ar), 7.02 (m, 1H, Ar), 2.83 (4H, s, $CH_2CH_2$). $^{13}$C NMR (100 MHz, $CDCl_3$, $^{31}$P-coupled; $^1$H-decoupled, observed signals) $\delta$ = 169.0, 160.8, 143.2, 142.9, 136.8, 136.6, 134.8, 133.9, 133.8, 133.7, 131.6,

128.8, 128.5, 128.5, 25.5. $^{31}$P NMR (162 MHz, $CDCl_3$) $\delta$ = –4.0. HRMS ($ESI^+$) *m*/*z* calculated for $(C_{23}H_{19}NO_4P)^+$ 404.1052, measured 404.1063.

**3-(Diphenylphosphanyl)propanoic acid (1d)**

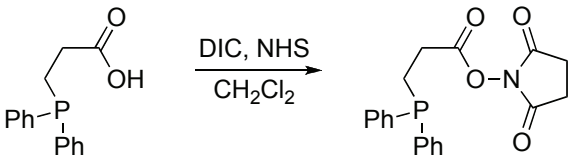



**1d**

Diphenylphosphine[1] (2.00 mL, 11.5 mmol) was dissolved in degassed $CH_3CN$ (20 mL). Methyl acrylate (3.80 mL, 42.5 mmol) and a few drops of benzyltrimethylammonium hydroxide (40 wt. % in MeOH) were added, and the resulting solution was stirred under Ar(g). The reaction was monitored by TLC and after the introduction of additional drops of base (after 2 h) the reaction was found to be complete after 4 h. The solution was then concentrated under reduced pressure; the resulting oil was then dissolved in $CH_2Cl_2$ (100 mL) and concentrated again. The resulting oil was then dissolved in MeOH (10 mL) and an aqueous solution of KOH (4.00 g, 71.4 mmol in 10 mL of $H_2O$) was added. The mixture was stirred under Ar(g). After 1 h, the reaction was found to be complete, and the solution was diluted with $H_2O$ (200 mL) and acidified to pH 2 with 2M HCl. The suspension was then extracted with $CH_2Cl_2$ (2 × 150 mL), and the organic layers were combined, dried over $Na_2SO_4$(s) and concentrated under reduced pressure. The solid residue was purified by silica gel flash chromatography, eluting with 2% MeOH/$CH_2Cl_2$, to give the acid **1d** as a white solid (2.74 g, 10.6 mmol, 92% yield).

Data for **1d**: $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ = 7.46–7.32 (10H, m, Ar), 2.44 (m, 2H, C*H*$_2$), 2.35 (m, 2H, C*H*$_2$). $^{13}$C NMR (100 MHz, $CDCl_3$, $^{31}$P-coupled; $^1$H-decoupled, observed signals) $\delta$ = 179.1, 179.0, 137.5, 137.4, 132.8, 132.6, 128.9, 128.6, 128.5, 30.5, 30.2, 22.7, 22.6. $^{31}$P NMR (162 MHz, $CDCl_3$) $\delta$ = –15.5. HRMS ($ESI^+$) *m*/*z* calculated for $(C_{15}H_{16}O_2P)^+$ 259.0888, measured 259.0895.

**2,5-Dioxopyrrolidin-1-yl 3-(diphenylphosphanyl)propanoate (1e)**




**1d** **1e**

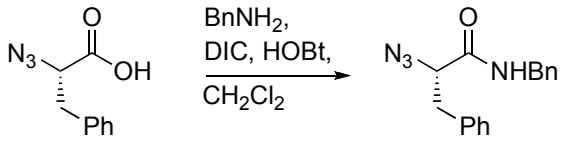
3-(Diphenylphosphanyl)propanoic acid **1d** (1.20 g, 4.65 mmol) was dissolved in $CH_2Cl_2$ (10 mL), and the solution was cooled to 0 °C. *N*-Hydroxysuccinimide (1.05 g, 9.30 mmol) and *N,N*′-diisopropylcarbodiimide (0.86 mL, 5.58 mmol) were added, and the mixture was allowed to

warm to room temperature and stirred overnight under Ar(g). The resulting suspension was filtered, and the filtrate was concentrated under reduced pressure. The resulting residue was purified by silica gel flash chromatography, eluting with 30% EtOAc-hexanes, to give the ester **1e** as a white solid (1.64 g, 4.62 mmol, 99% yield).

Data for **1e**: $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ = 7.47–7.32 (m, 10H, Ar), 2.82 (s, 4H, succinmyl), 2.67 (m, 2H, C$H_2$), 2.43 (m, 2H, C$H_2$). $^{13}$C NMR (100 MHz, $CDCl_3$, $^{31}$P-coupled; $^{1}$H-decoupled, observed signals) $\delta$ = 169.0, 168.5, 168.3, 137.0, 136.8, 132.8, 132.6, 129.1, 128.7, 128.7, 27.8, 27.6, 25.6, 22.7, 22.6. $^{31}$P NMR (162 MHz, $CDCl_3$) $\delta$ = –15.3. HRMS (ESI$^+$) *m*/*z* calculated for $(C_{19}H_{19}NO_4P)^+$ 356.1052, measured 356.1060.

### 3.2 Synthesis of Azides

#### 2-Azido-*N*-benzyl-3-phenylpropanamide (2b)

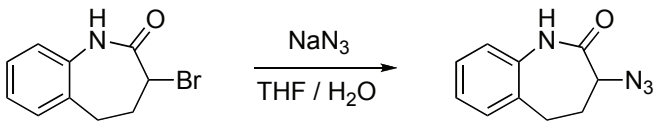



**2b**

2-Azido-3-phenylpropanoic acid[2] (112 mg, 0.588 mmol) and HOBt (108 mg, 0.705 mmol) were suspended in $CH_2Cl_2$ (2 mL), and the mixture was cooled to 0 °C under Ar(g). *N,N*′-diisopropylcarbodiimide (107 μL, 0.705 mmol) was added, and the resulting mixture was stirred for 30 min. Benzyl amine (122 μL, 1.06 mmol) was then added, and the mixture was allowed to warm to room temperature and then stirred overnight under Ar(g). The mixture was filtered, and the solvent was removed under reduced pressure. The residue was purified by silica gel flash chromatography, eluting with 15% EtOAc/hexanes, to give the required amide **2b** as a white solid (117 mg, 0.418 mmol, 71% yield).

Data for **2b**: $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ = 7.35–7.21 (m, 7H, Ar.), 7.16–7.10 (m, 3H, Ar.), 6.52 (br. s, 1H, N*H*), 4.43 (dd, 1H, *J* = 14.7, 6.1 Hz, NH*CH*$_2$Ph), 4.37 (dd, 1H, *J* = 14.7, 5.4 Hz, NH*CH*$_2$Ph), 4.24 (dd, 1H, *J* = 7.7, 4.0 Hz, *CH*CH$_2$Ph), 3.36 (dd, 1H, *J* = 14.0, 4.0 Hz, CH*CH*$_2$Ph), 3.08 (dd, 1H, *J* = 14.0, 7.7 Hz, CH*CH*$_2$Ph). $^{13}$C NMR (100 MHz, $CDCl_3$, observed signals) $\delta$ = 168.3, 137.3, 136.0, 128.7, 128.7, 127.7, 127.6, 127.2, 65.5, 43.6, 38.5. HRMS (ESI$^+$) *m*/*z* calculated for $(C_{16}H_{16}N_4O)^+$ 280.1319, measured 280.1315.

#### 3-Azido-2,3,4,5-tetrahydro-1H-1-benzazepin-2-one (2c)

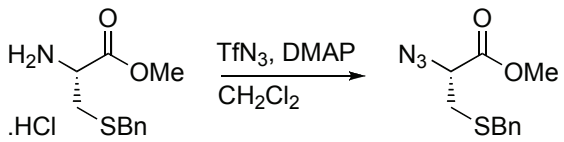



**2c**

3-Bromo-2,3,4,5-tetrahydro-1H-1-benzazepin-2-one[3] (0.50 g, 2.08 mmol) was dissolved in THF (5 mL). A solution of $NaN_3$ (1.36 g, 20.82 mmol) in $H_2O$ (2 mL) was added, and the resulting mixture was stirred vigorously for 3 days. THF was removed under reduced pressure, and the resulting aqueous slurry was extracted with $CH_2Cl_2$ (2 × 20 mL). The organic layers were combined, dried over $Na_2SO_4$(s), filtered, and concentrated under reduced pressure. The resulting off-white solid (0.40 g, 1.98 mmol, 95% yield) was found to be pure by NMR analysis and was used without further purification.

Data for **2c**: $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ = 7.77 (br. s, 1H, N*H*), 7.31–7.15 (m, 3H, Ar), 7.03 (d, 1H, *J* = 7.8 Hz, Ar.), 3.88 (dd, 1H, *J* = 11.0, 8.3 Hz, NHC(O)C*H*$N_3$), 3.00 (m, 1H, C$H_2$), 2.74 (m, 1H, C$H_2$), 2.53 (m, 1H, C$H_2$), 2.32 (m, 1H, C$H_2$). $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ = 10.05 (br. s, 1H, N*H*), 7.30–7.22 (m, 2H, Ar), 7.12 (t, 1H, *J* = 7.4 Hz, Ar), 7.00 (d, 1H, *J* = 7.8 Hz, Ar.), 3.88 (dd, 1H, *J* = 10.7, 8.5 Hz, NHC(O)C*H*$N_3$), 2.82–2.65 (m, 2H, C$H_2$), 2.40 (m, 1H, C$H_2$), 2.11 (m, 1H, C$H_2$). $^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta$ = 170.3, 137.5, 133.4, 130.0, 127.9, 125.7, 124.5, 122.5, 59.1, 34.8, 28.2. {Lit.[4]: $^1$H NMR (390 MHz, DMSO-$d_6$) $\delta$ = 10.15 (br. s, 1H, N*H*), 7.22 (m, 4H, Ar), 3.88 (dd, 1H, NHC(O)C*H*$N_3$), 2.50 (m, 4H, C$H_2$)}

**Methyl 2-azido-3-(benzylsulfanyl)propanoate (2e)**

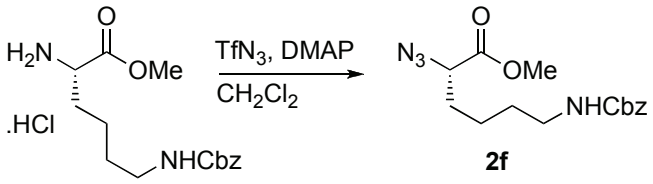


**2e**

Following a method described by Aubé and coworkers,[5] a solution of $NaN_3$ (0.88 g, 13.7 mmol) in $H_2O$ (2.5 mL) was cooled to 0 °C and $CH_2Cl_2$ (4 mL) was added. Whilst the mixture was stirring vigorously, $Tf_2O$ (0.47 mL, 2.26 mmol) was added dropwise. The resulting solution was stirred for an additional 2 h. The mixture was then placed in a separating funnel, and the organic layer was removed. The aqueous phase was extracted further with $CH_2Cl_2$ (2 × 3 mL). The organic layers were combined, washed with saturated $Na_2CO_3$, dried over $Na_2SO_4$(s), and filtered. The resulting solution of $TfN_3$ was added dropwise to solution of methyl 2-amino-3-(benzylsulfanyl)propanoate hydrochloride salt[1] (0.37 g, 1.40 mmol) and DMAP (0.75 g, 6.16 mmol) in $CH_2Cl_2$ (5 mL). The resulting solution was stirred overnight under Ar(g). The mixture was concentrated under reduced pressure and purified by silica gel flash chromatography, eluting with $CH_2Cl_2$, to give azide **2e** as an oil (0.26 g, 1.05 mmol, 75% yield).

Data for **2e**: $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ = 7.37–7.24 (m, 5H, Ar.), 3.98 (dd, 1H, *J* = 7.5, 5.7 Hz, $N_3$C*H*), 3.82–3.79 (m, 5H, OC$H_3$ and C$H_2$Ph), 2.86 (dd, 1H, *J* = 14.1, 5.7 Hz, C$H_2$SBn), 2.73 (dd, 1H, *J* = 14.1, 7.5 Hz, C$H_2$SBn). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ = 169.4, 137.5, 129.0, 128.6, 127.3, 62.3, 52.3, 36.8, 32.3. HRMS (ESI$^+$) *m*/*z* calculated for $(C_{11}H_{13}N_3O_2SNa)^+$ 274.0621, measured 274.0610.

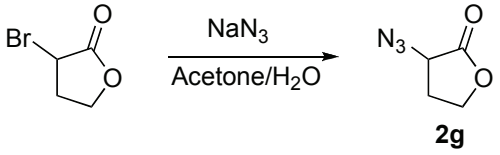
**Methyl 2-azido-6-{[(benzyloxy)carbonyl]amino}hexanoate (2f)**




Following a method described by Aubé and coworkers,[5] a solution of $NaN_3$ (0.88 g, 13.7 mmol) in $H_2O$ (2.5 mL) was cooled to 0 °C and $CH_2Cl_2$ (4 mL) was added. Whilst the mixture was stirring vigorously, $Tf_2O$ (0.47 mL, 2.26 mmol) was added dropwise. The resulting solution was stirred for an additional 2 h. The mixture was then placed in a separating funnel, and the organic layer was removed. The aqueous phase was extracted further with $CH_2Cl_2$ (2 × 3 mL). The organic layers were combined, washed with saturated $Na_2CO_3$, dried over $Na_2SO_4$(s), and filtered. The resulting solution of $TfN_3$ was added dropwise to solution of methyl 2-amino-6-{[(benzyloxy)carbonyl]amino}hexanoate hydrochloride salt[1] (0.46 g, 1.40 mmol) and DMAP (0.75 g, 6.16 mmol) in $CH_2Cl_2$ (5 mL). The resulting solution was stirred overnight under Ar(g). The mixture was concentrated under reduced pressure and purified by silica gel flash chromatography, eluting with 20% EtOAc/hexanes, to give azide **2f** as an oil (0.43 g, 1.34 mmol, 96% yield).

Data for **2f**: $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ = 7.38–7.28 (m, 5H, Ar.), 5.10 (s, 2H, OC*H*$_2$Ph), 4.80 (br. s, 1H, N*H*), 3.84 (m, 1H, $N_3$C*H*), 3.79 (s, 3H, OC*H*$_3$), 3.21 (m, 2H, C*H*$_2$NHCbz), 1.91–1.45 (m, 6H, C*H*$_2$C*H*$_2$C*H*$_2$CH$_2$NHCbz). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ = 170.9, 156.4, 136.5, 128.5, 128.1, 128.1, 66.7, 61.8, 52.6, 40.7, 30.9, 29.4, 22.9. HRMS (ESI$^+$) *m*/*z* calculated for $(C_{15}H_{20}N_4O_4Na)^+$ 343.1377, measured 343.1366.

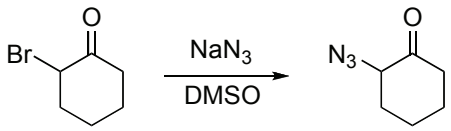
**3-Azidooxolan-2-one (2g)**




3-Bromooxolan-2-one (0.50 g, 3.03 mmol) was dissolved in acetone (5 mL). To this was added a solution of $NaN_3$ (0.99 g, 15.2 mmol) in $H_2O$ (2 mL). The resulting solution was stirred overnight. Acetone was removed by concentration under reduced pressure. The resulting aqueous mixture was extracted with $CH_2Cl_2$ (2 × 15 mL), and the organic layers were combined, dried over $Na_2SO_4$(s), filtered, and concentrated under reduced pressure. The resulting oil (0.29 g, 2.27 mmol, 75% yield) was found to be pure by NMR analysis and was used without further purification.

Data for **2g**: $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ = 4.43 (ddd, 1H, $J$ = 9.0, 9.0, 3.5 Hz, OC$H_2$CH$_2$), 4.33–4.24 (m, 2H, OC$H_2$CH$_2$C$H$N$_3$), 2.56 (m, 1H, OCH$_2$C$H_2$), 2.19 (dddd, 1H, $J$ = 9.0, 9.0, 9.0, 13.3, OCH$_2$C$H_2$). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ = 173.3, 65.8, 56.5, 28.9. HRMS (ESI$^+$) $m/z$ calculated for $(C_4H_5N_3O_2)^+$ 127.0377, measured 127.0376.

**2-Azidocyclohexan-1-one (2h)**

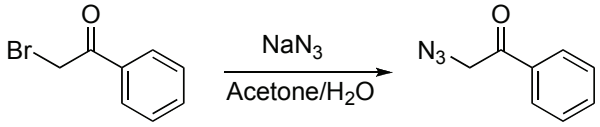



**2h**

2-Bromocyclohexan-1-one[6] (0.55 g, 3.11 mmol) was dissolved in DMSO (3 mL). Sodium azide (1.00 g, 15.5 mmol) was added, and the resulting mixture was stirred for 2 h. The solution was then diluted with water (50 mL) and extracted with diethyl ether (2 × 20 mL). The organic layers were combined, washed with water (2 × 20 mL), dried over $Na_2SO_4$(s), filtered, and concentrated under reduced pressure. The resulting oil was found to be pure by NMR analysis and was used without further purification (0.40 g, 2.87 mmol, 92% yield).

Data for **2h**: $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ = 3.94 (dd, 1H, $J$ = 11.4, 6.6 Hz, CHN$_3$), 2.57 (br. d, 1H, $J$ = 14.0 Hz), 2.41–2.28 (m, 2H), 2.14–1.93 (m, 2H), 1.80–1.61 (m, 3H). $^{13}$C NMR ($CDCl_3$, 400 MHz) $\delta$ = 205.5, 66.5, 40.8, 33.6, 27.0, 23.8. {Lit[7]: $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ = 3.93 (dd, 1H, $J$ = 11.4, 6.6 Hz, CHN$_3$), 2.56–1.66 (m, 8H). $^{13}$C NMR ($CDCl_3$, 400 MHz) $\delta$ = 205.6, 66.5, 40.8, 33.6, 27.1, 23.8.}

**2-Azido-1-phenylethan-1-one (2i)**



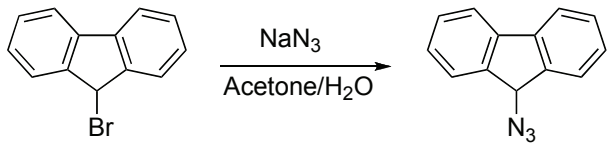

**2i**

2-Bromo-1-phenylethan-1-one[1] (1.00 g, 5.02 mmol) was dissolved in acetone (7 mL). To this was added a solution of $NaN_3$ (1.63 g, 25.1 mmol) in $H_2O$ (3 mL). The resulting solution was stirred overnight. Acetone was removed under reduced pressure, and the resulting aqueous mixture was extracted with $CH_2Cl_2$ (2 × 15 mL). The organic layers were combined, dried over $Na_2SO_4$(s), filtered, and concentrated under reduced pressure. The resulting yellow oil (0.60 g, 3.72 mmol, 74% yield) was found to be pure by NMR analysis and was used without further purification.

Data for **2i**: $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ = 7.93 (d, 2H, $J$ = 7.8 Hz, Ar.), 7.65 (t, 1H, $J$ = 7.2 Hz, Ar.), 7.52 (app. t, 2H, $J$ = 7.5 Hz), 4.59 (s, 2H, C$H_2$N$_3$). $^{13}$C NMR ($CDCl_3$, 400 MHz) $\delta$ =

193.2, 134.3, 134.1, 129.0, 127.9, 54.9. {Lit[7]: $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ = 7.99 (dd, 2H), 7.63 (m, 1H), 7.50 (dd, 2H), 4.57 (s, 2H). $^{13}$C NMR ($CDCl_3$, 400 MHz) $\delta$ = 193.3, 134.3, 134.1, 129.0, 127.9, 54.9}

**9-Azido-9*H*-fluorene (2j)**

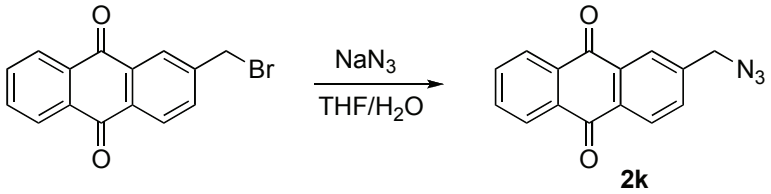



**2j**

9-Bromo-9*H*-fluorene[1] (1.00 g, 4.08 mmol) was dissolved in acetone (7 mL). To this was added a solution of $NaN_3$ (1.33 g, 20.4 mmol) in $H_2O$ (3 mL). The resulting solution was stirred overnight. Acetone was removed by concentration under reduced pressure. The resulting aqueous mixture was extracted with $CH_2Cl_2$ (2 × 15 mL), and the organic layers were combined, dried over $Na_2SO_4$(s), filtered, and concentrated under reduced pressure. The resulting solid residue was purified by silica gel flash chromatography, eluting with hexanes, to give azide **2j** as a white solid (0.74 g, 3.57 mmol, 87% yield).

Data for **2j**: $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ = 7.74 (d, 2H, $J$ = 7.4 Hz, Ar.), 7.66 (d, 2H, $J$ = 7.4 Hz, Ar.), 7.47 (t, 2H, $J$ = 7.4 Hz, Ar.), 7.39 (t, 2H, $J$ = 7.4 Hz, Ar.), 5.23 (s, 1H, C*H*$N_3$). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ = 141.6, 140.7, 129.4, 127.9, 125.2, 120.3, 64.3.

**2-(Azidomethyl)-9,10-dihydroanthracene-9,10-dione (2k)**



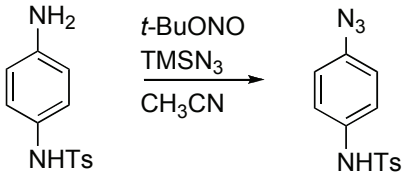

**2k**

2-(Bromomethyl)-9,10-dihydroanthracene-9,10-dione[1] (0.54 g, 1.66 mmol) was dissolved in THF (5 mL). To this was added a solution of $NaN_3$ (0.54 g, 8.30 mmol) in $H_2O$ (2 mL), and the resulting mixture was stirred overnight. THF was removed by evaporation under reduced pressure, and the aqueous mixture was extracted with $CH_2Cl_2$ (2 × 15 mL). The organic layers were combined, dried over $Na_2SO_4$(s), filtered, and concentrated under reduced pressure to give a pale yellow solid (0.42 g, 1.59 mmol, 96% yield). The solid was found to be pure by NMR analysis and was used without further purification.

Data for **2k**: $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ = 8.39–8.31 (m, 3H, Ar), 8.27 (s, 1H, Ar), 7.86–7.82 (m, 2H, Ar), 7.79 (d, 1H, $J$ = 7.9 Hz, Ar), 4.59 (s, 2H, C$H_2$$N_3$). $^{13}$C NMR ($CDCl_3$,

400 MHz, observed signals) $\delta$ = 182.8, 182.6, 142.1, 134.3, 134.2, 133.8, 133.4, 133.2, 133.1, 128.0, 127.3, 126.4, 50.1.

**_N_-(4-Azidophenyl)-4-methylbenzene-1-sulfonamide (7)**



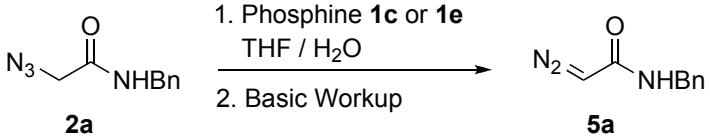

**7**

Following the procedure of Moses and coworkers,[8] *N*-(4-aminophenyl)-4-methylbenzene-1-sulfonamide[1] (1.00 g, 3.81 mmol) was dissolved in anhydrous $CH_3CN$ (6 mL), and the resulting solution was placed under Ar(g) and cooled to 0 °C. To this was added *t*-BuONO (0.68 mL, 5.71 mmol) followed by $TMSN_3$ (0.60 mL, 4.57 mmol) dropwise. The resulting solution was allowed to warm to room temperature and stirred for 2 h. The resulting mixture was concentrated under reduced pressure, and the residue was purified by silica gel column chromatography, eluting with 10% EtOAc/hexanes, to give aryl azide **7** (1.02 g, 3.54 mmol, 93% yield) as a white solid.

Data for **7**: $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ = 7.68 (d, 2H, *J* = 8.1 Hz, Ar.), 7.25 (d, 2H, *J* = 8.1 Hz, Ar), 7.10 (d, 2H, *J* = 8.2 Hz, Ar), 6.90 (d, 2H, *J* = 8.2 Hz, Ar), 2.40 (s, 3H, C*H*$_3$). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ = 144.1, 137.4, 135.7, 133.3, 129.7, 127.3, 123.7, 119.8, 21.5. HRMS ($ESI^+$) *m*/*z* calculated for $(C_{13}H_{12}N_4O_2S - N_2)^+$ 260.0614, measured 260.0623.

### 3.3 Synthesis of Diazo-Compounds

**_N_-Benzyl-2-diazoacetamide (5a)**




**2a** **5a**

**Method A:** Using phosphine **1c**; sat. aq. $NaHCO_3$ workup

2-Azido-*N*-benzylacetamide[9] **2a** (51 mg, 0.268 mmol) was dissolved in THF/$H_2O$ (2 mL/300 µL). To this solution was added phosphine **1c** (114 mg, 0.282 mmol), and the resulting solution was stirred overnight under Ar(g). Sat. aq. $NaHCO_3$ (2 mL) was then added, and the mixture was stirred vigorously for 4 h. The mixture was then diluted with sat. aq. NaCl (15 mL) and extracted with $CH_2Cl_2$ (2 × 15 mL). The organic layers were combined, dried over

$Na_2SO_4$(s), filtered, and evaporated under reduced pressure. The residue was purified by silica gel flash chromatography, eluting with 30% EtOAc/hexanes, to give the diazo-compound **5a** as a yellow solid (40 mg, 0.228 mmol, 85% yield).

**Method B**: Using phosphine **1c**; $NEt_3$ workup

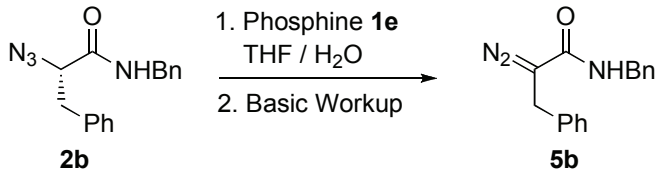
2-Azido-*N*-benzylacetamide[9] **2a** (72 mg, 0.379 mmol) was dissolved in THF/$H_2O$ (2 mL/300 μL). To this solution was added phosphine **1c** (160 mg, 0.398 mmol), and the resulting solution was stirred overnight under Ar(g). $NEt_3$ (105 μL, 0.758 mmol) was then added, and the mixture was stirred for 1 h. The mixture was then diluted with sat. aq. NaCl (15 mL) and extracted with $CH_2Cl_2$ (2 × 15 mL). The organic layers were combined, dried over $Na_2SO_4$(s), filtered, and evaporated under reduced pressure. The residue was purified by silica gel flash chromatography, eluting with 30% EtOAc/hexanes, to give the diazo-compound **5a** as a yellow solid (60 mg, 0.341 mmol, 90% yield).

**Method C**: Using phosphine **1e**; sat. aq. $NaHCO_3$ workup

2-Azido-*N*-benzylacetamide[9] **2a** (57 mg, 0.300 mmol) was dissolved in THF/$H_2O$ (2 mL/300 μL). To this solution was added phosphine **1e** (112 mg, 0.315 mmol), and the resulting solution was stirred for 4 h under Ar(g). Sat. aq. $NaHCO_3$ (2 mL) was then added, and the mixture was stirred vigorously for 4 h. The mixture was then diluted with sat. aq. NaCl (15 mL) and extracted with $CH_2Cl_2$ (2 × 15 mL). The organic layers were combined, dried over $Na_2SO$(s), filtered, and evaporated under reduced pressure. The residue was purified by silica gel flash chromatography, eluting with 30% EtOAc/hexanes, to give the diazo-compound **5a** as a yellow solid (45 mg, 0.255 mmol, 85% yield).

Data for **5a**: $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ = 7.36–7.24 (m, 5H, Ar.), 5.73 (br. s, 1H, N*H*), 4.77 (1H, s, C*H*$N_2$), 4.43 (d, 2H, NHC*H*$_2$Ph). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ = 165.6, 138.3, 128.7, 127.6, 127.5, 47.1, 43.9. HRMS ($ESI^+$) *m*/*z* calculated for $(C_9H_9N_3ONa)^+$ 198.0643, measured 198.0634.

***N*-Benzyl-2-diaza-3-phenylpropanamide (5b)**




**2b** **5b**

**Method A** (Sat. Aq. $NaHCO_3$ Workup):

2-Azido-*N*-benzyl-3-phenylpropanamide **2b** (61 mg, 0.218 mmol) was dissolved in THF/$H_2O$ (2 mL/300 μL). To this solution was added phosphine **1e** (81 mg, 0.229 mmol), and the resulting

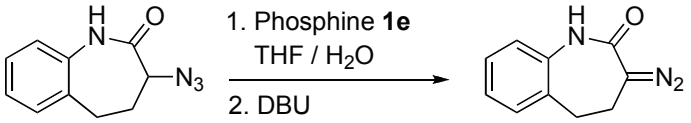
solution was stirred for 5 h under Ar(g). Sat. aq. $NaHCO_3$ (2 mL) was then added, and the mixture was stirred vigorously overnight. The mixture was then diluted with sat. aq. NaCl (15 mL) and extracted with $CH_2Cl_2$ (2 × 15 mL). The organic layers were combined, dried over $Na_2SO_4$(s), filtered, and evaporated under reduced pressure. The residue was purified by silica gel flash chromatography, eluting with 20% EtOAc/hexanes, to give the diazo-compound **5b** as a yellow oil (47 mg, 0.177 mmol, 81% yield).

**Method B** (DBU Workup):

2-Azido-*N*-benzyl-3-phenylpropanamide **2b** (61 mg, 0.218 mmol) was dissolved in THF/$H_2O$ (2 mL/300 μL). To this solution was added phosphine **1e** (81 mg, 0.229 mmol), and the resulting solution was stirred for 5 h under Ar(g). The solution was then diluted with sat. aq. NaCl (10 mL), and the resulting mixture was extracted with $CH_2Cl_2$ (2 × 15 mL). The organic layers were combined, dried over $Na_2SO_4$(s), filtered, and evaporated under reduced pressure. The resulting residue was dissolved in $CH_2Cl_2$ (2 mL) and DBU (58 mL, 0.391 mmol) was added. The resulting solution was stirred for 20 min. The solution was placed directly onto a column of silica gel and eluted with 20% EtOAc/hexanes to give the diazo-compound **5b** as a yellow oil (49 mg, 0.185 mmol, 85% yield).

Data for **5b**: $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ = 7.37–7.24 (m, 9H, Ar.), 7.16 (d, 2H, $J$ = 7.0 Hz, Ar.), 5.35 (br. s., 1H, N*H*), 4.48 (d, 2H, $J$ = 5.5 Hz, NHC$H_2$Ph), 3.69 (s, 2H, $CN_2CH_2$Ph). $^{13}$C NMR (100 MHz, $CDCl_3$, observed signals) $\delta$ = 165.9, 138.3, 136.6, 129.0, 128.6, 128.2, 127.6, 127.4, 57.3, 44.1, 29.8. HRMS ($ESI^+$) $m/z$ calculated for $(C_{16}H_{15}N_3O)^+$ 265.1210, measured 265.1223.

**3-Diazynylidene-4,5-dihydro-1*H*-1-benzazepin-2-one 5c**

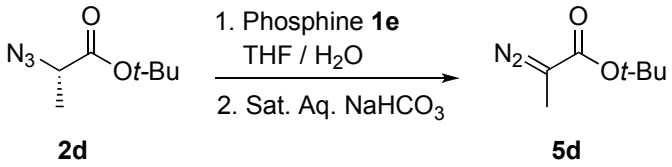



**2c** **5c**

3-Azido-2,3,4,5-tetrahydro-1*H*-1-benzazepin-2-one **2c** (66 mg, 0.326 mmol) was dissolved in THF/$H_2O$ (2 mL/300 μL). To this was added phosphine **1e** (122 mg, 0.343 mmol), and the resulting solution was stirred for 5 h under Ar(g). The solution was then diluted with sat. aq. NaCl (10 mL), and the resulting mixture was extracted with $CH_2Cl_2$ (2 × 15 mL). The organic layers were combined, dried over $Na_2SO_4$(s), filtered, and evaporated under reduced pressure. The resulting residue was dissolved in $CH_2Cl_2$ (2 mL) and DBU (58 mL, 0.391 mmol) was added. The resulting solution was allowed stirred for 20 min. The solution was placed directly onto a column of silica gel and eluted with 30% EtOAc/hexanes to give the diazo-compound **5c** as a yellow solid (58 mg, 0.310 mmol, 95% yield).

Data for **5c**: $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ = 7.68 (br. s, 1H, N*H*), 7.20 (app. t, 1H, *J* = 7.5 Hz, Ar.), 7.11 (d, 1H, *J* = 7.3 Hz, Ar.), 7.02 (app. t, 1H, *J* = 7.3 Hz, Ar.), 6.89 (d, 1H, *J* = 7.5 Hz, Ar.), 3.03 (m, 2H, C$H_2$), 2.87 (m, 2H, C$H_2$). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ = 167.3, 136.8, 130.8, 130.0, 127.9, 124.1, 120.3, 60.4, 32.5, 26.3.

### *t*-Butyl 2-diazopropanoate (5d)

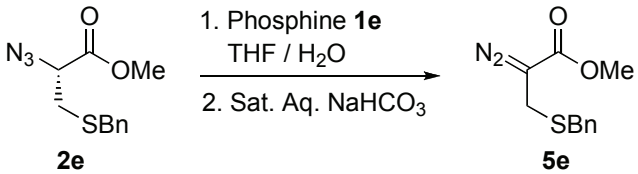



**2d** **5d**

*t*-Butyl 2-azido propanoate[10] **2d** (66 mg, 0.386 mmol) was dissolved in THF/$H_2O$ (2 mL/300 µL). To this solution was added phosphine **1e** (144 mg, 0.405 mmol), and the resulting solution was stirred for 5 h under Ar(g). Sat. aq. $NaHCO_3$ (2 mL) was then added, and the mixture was stirred vigorously overnight. The mixture was then diluted with sat. aq. NaCl (15 mL) and extracted with $CH_2Cl_2$ (2 × 15 mL). The organic layers were combined, dried over $Na_2SO_4$(s), filtered, and evaporated under reduced pressure. The residue was purified by silica gel flash chromatography, eluting with $CH_2Cl_2$, to give the diazo-compound **5d** as a yellow oil (45 mg, 0.290 mmol, 75% yield).

Data for **5d**: $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ = 1.90 (s, 3H, $CN_2CH_3$), 1.47 (s, 9H, *t*-Bu). $^{13}$C NMR (100 MHz, $CDCl_3$, observed signals) $\delta$ = 167.4, 81.0, 28.3, 8.4. HRMS (ESI$^+$) *m*/*z* calculated for $(C_7H_{12}N_2O_2)^{+\cdot}$ 156.0894, measured 156.0896.

### Methyl 3-(benzylsulfanyl)-2-diazopropanoate (5e)

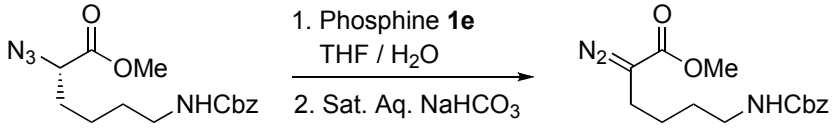



**2e** **5e**

Methyl 2-azido-3-(benzylsulfanyl)propanoate **5e** (74 mg, 0.294 mmol) was dissolved in THF/$H_2O$ (2 mL/300 µL). To this solution was added phosphine **1e** (110 mg, 0.309 mmol), and the resulting solution was stirred for 5 h under Ar(g). Sat. aq. $NaHCO_3$ (2 mL) was then added, and the mixture was stirred vigorously for 20 min. The mixture was then diluted with sat. aq. NaCl (15 mL) and extracted with $CH_2Cl_2$ (2 × 15 mL). The organic layers were combined, dried over $Na_2SO_4$(s), filtered, and evaporated under reduced pressure. The residue was purified by silica gel flash chromatography, eluting with $CH_2Cl_2$, to give the diazo-compound **5e** as a yellow oil (67 mg, 0.285 mmol, 97% yield).

Data for **5e**: $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ = 7.37–7.23 (m, 5H, Ar.), 3.78 (s, 2H, C$H_2$Ph), 3.77 (s, 3H, OC$H_3$), 3.45 (s, 2H, $CN_2CH_2$). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ = 166.7, 137.7, 128.7, 128.5, 127.1, 56.7, 52.0, 36.0, 25.9. HRMS (ESI$^+$) *m/z* calculated for $(C_{11}H_{12}N_2O_2SNa)^+$ 259.0506, measured 259.0506.

**Methyl 6-{[(benzyloxy)carbonyl]amino}-2-diazohexanoate (5f)**

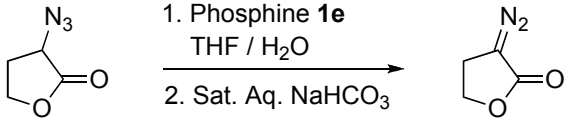



**2f** **5f**

Methyl 2-azido-6-{[(benzyloxy)carbonyl]amino}hexanoate **2f** (88 mg, 0.275 mmol) was dissolved in THF/$H_2O$ (2 mL/300 µL). To this solution was added phosphine **1e** (102 mg, 0.288 mmol), and the resulting solution was stirred for 5 h under Ar(g). Sat. aq. $NaHCO_3$ (2 mL) was then added, and the mixture was stirred vigorously overnight. The mixture was then diluted with sat. aq. NaCl (15 mL) and extracted with $CH_2Cl_2$ (2 × 15 mL). The organic layers were combined, dried over $Na_2SO_4$(s), filtered, and evaporated under reduced pressure. The residue was purified by silica gel flash chromatography, eluting with 20% EtOAc/hexanes, to give the diazo-compound **5f** as a yellow oil (64 mg, 0.209 mmol, 76% yield).

Data for **5f**: $^1$H NMR (400 MHz, $CDCl_3$, mixture of rotamers in ratio of 88:12) $\delta$ = 7.42–7.31 (m, 5H, Ar.), 5.16 (s, 0.24H, C$H_2$Ph), 5.10 (s, 1.76H, C$H_2$Ph), 4.89 (br. s, 0.88H, N*H*), 4.70 (br. s, 0.12H, N*H*), 3.80–3.76 (m, 3H, OC$H_3$), 3.29–3.14 (m, 2H, C$H_2$NHCbz), 2.38–2.18 (m, 2H, $CN_2CH_2$), 1.62–1.49 (m, 4H, $CN_2CH_2CH_2CH_2$). $^{13}$C NMR (100 MHz, $CDCl_3$, signals corresponding to major rotamer) $\delta$ = 167.9, 156.4, 136.4, 128.6, 128.2, 128.2, 66.7, 55.0, 52.0, 40.6, 29.1, 25.0, 22.9. HRMS (ESI$^+$) *m/z* calculated for $(C_{15}H_{19}N_3O_4Na)^+$ 328.1268, measured 328.1279.

**3-Diazynylideneoxolan-2-one (5g)**



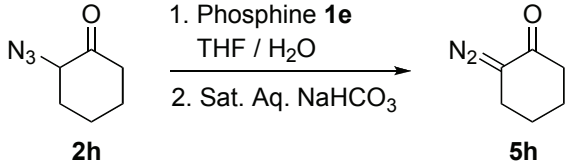

**2g** **5g**

3-Azidooxolan-2-one **2g** (69 mg, 0.545 mmol) was dissolved in THF/$H_2O$ (2 mL/300 µL). To this was added phosphine **1e** (203 mg, 0.572 mmol), and the resulting solution was stirred for 2 h under Ar(g). Sat. aq. $NaHCO_3$ (2 mL) was then added, and the mixture was stirred vigorously for 15 min. The mixture was then diluted with sat. aq. NaCl (15 mL) and extracted with $CH_2Cl_2$ (2 × 15 mL). The organic layers were combined, dried over $Na_2SO_4$(s), filtered, and evaporated under

reduced pressure. The residue was purified by silica gel flash chromatography, eluting with $CH_2Cl_2$, to give the diazo-compound **5g** as a yellow oil (57 mg, 0.507 mmol, 93% yield).

Data for **5g**: $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ = 4.40 (t, 2H, $J$ = 7.8 Hz, OC$H_2$CH$_2$), 3.38 (t, 2H, $J$ = 7.8 Hz, OCH$_2$C$H_2$). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ = 170.6, 65.3, 49.4, 23.1. HRMS (ESI$^+$) $m/z$ calculated for $(C_4H_4N_2O_2)^+$ 112.0268, measured 112.0264.

**2-Diazynylidenecyclohexan-1-one (5h)**

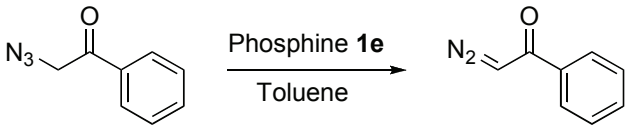



**2h** **5h**

2-Azidocyclohexan-1-one **2h** (62 mg, 0.442 mmol) was dissolved in THF/$H_2O$ (2 mL/300 µL). To this was added phosphine **1e** (165 mg, 0.465 mmol), and the resulting solution was stirred for 3 h under Ar(g). Sat. aq. $NaHCO_3$ (2 mL) was then added, and the mixture was stirred vigorously for 15 min. The mixture was then diluted with sat. aq. NaCl (15 mL) and extracted with $CH_2Cl_2$ (2 × 15 mL). The organic layers were combined, dried over $Na_2SO_4$(s), filtered, and evaporated under reduced pressure. The residue was purified by silica gel flash chromatography, eluting with 1% MeOH/$CH_2Cl_2$, to give the diazo-compound **5h** as a yellow oil (37 mg, 0.296 mmol, 67% yield).

Data for **5h**: $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ = 2.73 (app. t, 2H, $J$ = 5.9 Hz), 2.36 (app. t, 2H, $J$ = 5.8 Hz), 1.86–1.74 (m, 4H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ = 194.3, 63.7, 37.3, 22.3, 22.3, 22.0. HRMS (ESI$^+$) $m/z$ calculated for ($C_{12}H_{16}N_4O_2Na$, 2M+Na)$^+$ 271.1166, measured 271.1162.

**2-Diazo-1-phenylethan-1-one (5i)**



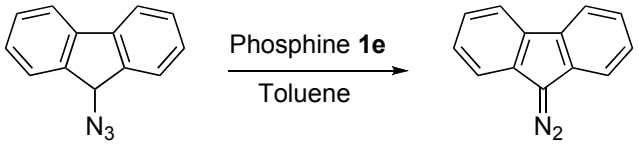

**2i** **5i**

A solution of azide **2i** (74 mg, 0.459 mmol) in anhydrous toluene (1.5 mL) was cooled to 0 °C. A solution of phosphine **1e** (171 mg, 0.482 mmol) in toluene (1.0 mL) was added dropwise. The resulting solution was maintained at 0 °C for 2 h and was then allowed to warm to room temperature. The mixture was then diluted with anhydrous $CH_2Cl_2$ (5 mL) and was stirred for an additional 30 min. The solution was then placed directly on a column of silica gel and eluted with 15% EtOAc/hexanes to give diazo-compound **5i** as a yellow oil (33 mg, 0.226 mmol, 49% yield).

Data for **5i**: $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ = 7.78 (d, 2H, $J$ = 7.7 Hz, Ar), 7.57 (t, 1H, $J$ =

7.4 Hz, Ar), 7.47 (app. t, 2H, $J$ = 7.4 Hz, Ar), 5.93 (s, 1H, C$H$N$_2$). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ = 186.3, 136.6, 132.7, 128.6, 126.7, 54.1. HRMS (ESI$^+$) $m/z$ calculated for $(C_8H_6N_2ONa)^+$ 169.0373, measured 169.0380.

**9H-Fluoren-9-ylidenediazyne (5j)**

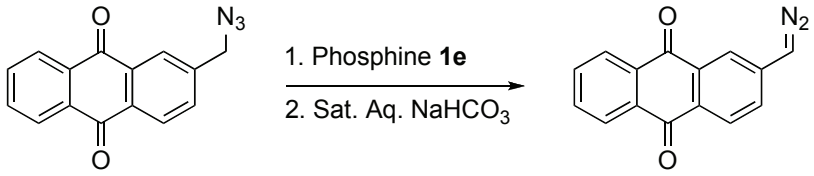



**2j** **5j**

A solution of 9-azido-9H-fluorene **2j** (62 mg, 0.303 mmol) in anhydrous toluene (1.5 mL) was placed under Ar(g) and cooled to 0 °C. A solution of phosphine **1e** in dry toluene (1 mL) was then added dropwise over 10 min whist maintaining the temperature at 0 °C. The solution was then stirred for 5 h at 0 °C. The solution was then allowed to warm to room temperature and stirred overnight. The resulting red solution (with white precipitate) was placed directly on a column of alumina (Basic, Grade 5) and eluted with hexanes to give diazo-compound **5j** as a red solid (51 mg), which NMR analysis showed to be approximately 96% pure (the remainder being azide **2j**), thus giving an 85% yield.

Data for **5j**: $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ = 7.98 (d, 2H, $J$ = 7.5 Hz, Ar.), 7.54 (d, 2H, $J$ = 7.5 Hz, Ar.), 7.42 (t, 2H, $J$ = 7.5 Hz, Ar.), 7.36 (t, 2H, $J$ = 7.5 Hz, Ar.). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ = 133.0, 131.4, 126.3, 124.5, 121.0, 119.3. 63.4. {Lit.[11] $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ = 7.97 (ddd, 2H, $J$ = 7.6, 1.2, 0.8 Hz, Ar.), 7.53 (ddd, 2H, $J$ = 7.7, 1.2, 0.8 Hz, Ar.), 7.42 (td, 2H, $J$ = 7.4, 1.2 Hz, Ar.), 7.36 (td, 2H, $J$ = 7.5, 1.2, Ar.). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ = 132.94, 131.41, 126.28, 124.48, 120.92, 119.27, 63.37.}

**2-(Diazomethyl)-9,10-dihydroanthracene-9,10-dione (5k)**




**2k** **5k**

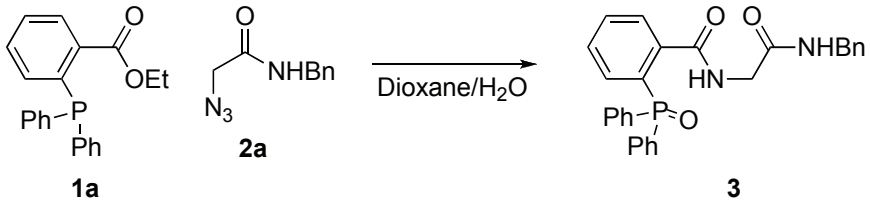
2-(Azidomethyl)-9,10-dihydroanthracene-9,10-dione **2k** (78 mg, 0.296 mmol) was dissolved in THF/$H_2O$ (1 mL/150 μL). To this was added phosphine **1e** (116 mg, 0.326 mmol), and the resulting solution was stirred for 4 h under Ar(g). Sat. aq. $NaHCO_3$ (2 mL) was then added, and the mixture was stirred vigorously for 30 min. The mixture was then diluted with sat. aq. NaCl (15 mL) and extracted with $CH_2Cl_2$ (2 × 15 mL). The organic layers were combined, dried over

$Na_2SO_4$(s), filtered, and evaporated under reduced pressure. The residue was purified by alumina (Basic-Grade 5) flash chromatography, eluting with 50% $CH_2Cl_2$/hexanes, to give 65 mg of an orange solid. The material was found to be 96% pure by NMR analysis (the remainder being the azide **2k**), thus giving 85% yield of diazo-compound **5k**. This diazo-compound is stable in the solid state when protected from light but decomposes slowly in solution, presumably to the azine.[12]

Data for **5k**: $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ = 8.36–8.27 (m, 2H, Ar.), 8.24 (d, 1H, $J$ = 8.2 Hz, Ar), 7.84–7.77 (m, 3H, Ar), 7.28 (s, 1H, Ar), 5.23 (s, 1H, C*H*$N_2$). $^{13}$C NMR (100 MHz, $CDCl_3$, observed signals) $\delta$ = 183.2, 182.0, 138.3, 134.2, 133.7, 133.3, 129.1, 128.4, 127.1, 125.5, 118.8, 49.8. HRMS (ESI$^+$) $m/z$ calculated for $(C_{15}H_8N_2O_2)^{+\cdot}$ 248.0581, measured 248.0588.

### 3.4 Reaction of Phosphine 1a with Azide 2a

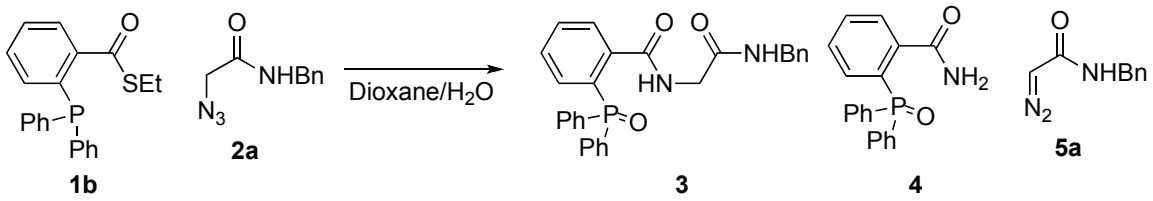
#### *N*-Benzyl-2-{[2-(diphenylphosphoryl)phenyl]formamido}acetamide 3




Azide **2a** (36 mg, 0.188 mmol) was dissolved in 1,4-dioxane/$H_2O$ (2 mL/4:1) and phosphine **1a** (63 mg, 0.188 mmol) was added. The resulting solution was stirred for 5 h under Ar(g). The solution was diluted with sat. aq. NaCl (15 mL) and extracted with $CH_2Cl_2$ (2 × 15 mL). The organic layers were combined, dried over $Na_2SO_4$(s), filtered, and evaporated under reduced pressure. The residue was purified by silica gel flash chromatography, eluting with 2% MeOH/$CH_2Cl_2$, to give the amide **3** as a white solid (79 mg, 0.169 mmol, 90% yield).

Data for **3**: $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ = 8.53 (br. s., 1H, N*H*), 7.71 (m, 1H, Ar.), 7.64–7.15 (m, 17H, Ar. and N*H*), 7.09 (dd, 1H, $J$ = 13.6, 7.7 Hz, Ar.), 4.45 (d, 2H, $J$ = 5.2 Hz, NHC$H_2$Ph), 3.90 (d, 1H, $J$ = 5.8 Hz, NHC$H_2$C(O)NHBn). $^{13}$C NMR (100 MHz, $CDCl_3$, $^{31}$P-coupled; $^1$H-decoupled, observed signals) $\delta$ = 168.9, 141.0, 140.9, 138.8, 133.4, 133.3, 132.4, 132.4, 131.8, 131.7, 130.8, 130.0, 130.0, 129.9, 129.6, 129.5, 128.8, 128.7, 128.4, 127.8, 126.9, 44.2, 43.2. $^{31}$P NMR (162 MHz, $CDCl_3$) $\delta$ = 34.3. HRMS (ESI$^+$) $m/z$ calculated for $(C_{28}H_{25}N_2O_3PNa)^+$ 491.1496, measured 491.1516.

### 3.5 Reaction of Phosphine 1b with Azide (2a)



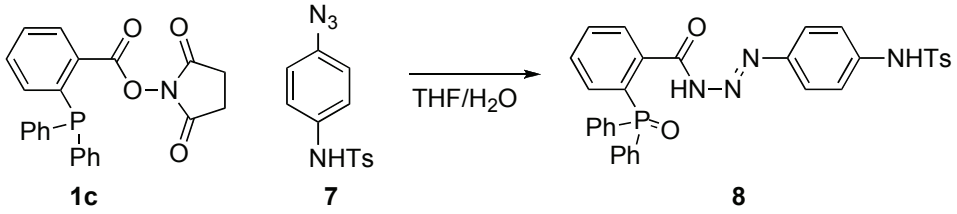

Azide **2a** (36 mg, 0.188 mmol) was dissolved in 1,4-dioxane/$H_2O$ (2 mL/4:1) and phosphine **1b** (66 mg, 0.188 mmol) was added. The resulting solution was stirred for 2 days under Ar(g). The solution was diluted with sat. aq. NaCl (15 mL) and extracted with $CH_2Cl_2$ (2 × 15 mL). The organic layers were combined, dried over $Na_2SO_4$(s), filtered, and evaporated under reduced pressure. The residue was purified by silica gel flash chromatography, eluting with 30% EtOAc/hexanes and then 2% MeOH/$CH_2Cl_2$, to give diazo-compound **5a** (10 mg, ~30% yield) as a yellow solid, and secondary amide **3** (53 mg, 60% yield) and primary amide **4** (20 mg, 33% yield) as white solids.

Data for **3** are as given above.

Data for **4**: $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ = 8.99 (br. s, 1H, N*H*), 8.08 (m, 1H, Ar.), 7.72–7.38 (m, 12H, Ar.), 7.08 (dd, 1H, $J$ = 14.6, 7.1 Hz, Ar.), 5.58 (br. s, 1H, N*H*). $^{31}$P NMR (162 MHz, $CDCl_3$) $\delta$ = 36.1. HRMS (ESI$^+$) $m/z$ calculated for $(C_{19}H_{16}NO_2PNa)^+$ 344.0811, measured 344.0819.

Data for **5a** are as given above.

### 3.6 Reaction of Phosphine 1c with Aryl Azide 7: Triazene 8

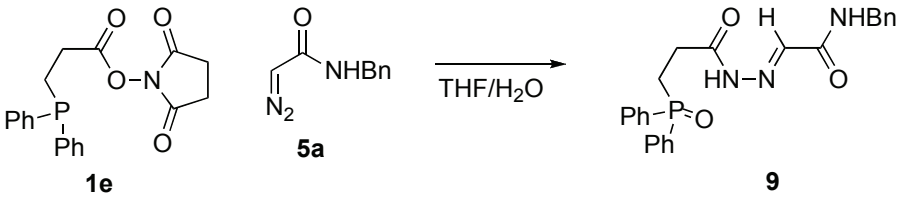



Aryl azide **7** (43 mg, 0.149 mmol) was dissolved in THF/$H_2O$ (2 mL/300 μL). Phosphine **1c** (63 mg, 0.156 mmol) was added, and the resulting solution was stirred overnight under Ar(g). The solution was diluted with sat. aq. NaCl (15 mL) and extracted with $CH_2Cl_2$ (2 × 15 mL). The organic layers were combined, dried over $Na_2SO_4$(s), filtered, and evaporated under reduced pressure. The residue was purified by silica gel flash chromatography, eluting with 2% MeOH/$CH_2Cl_2$ to give triazene **8** (85 mg, 0.143 mmol, 96% yield) as an off-white solid.

Data for **8**: $^1$H NMR (400 MHz, $CDCl_3$, broad signals indicative of interconversion of isomers,

most probably tautomers) $\delta$ = 12.89 (br. s., 1H, N*H*NN), 8.59 (br. s, 1H, N*H*Ts), 8.16 (br. s, 1H, Ar), 7.78–7.00 (m, 21H, Ar), 2.30 (br. s, 3H, C$H_3$). $^{13}$C NMR (100 MHz, $CDCl_3$, $^{31}$P-coupled; $^{1}$H-decoupled, observed signals) $\delta$ = 143.6, 138.9, 136.4, 133.6, 133.5, 132.6, 132.0, 131.9, 130.9, 130.0, 129.5, 128.8, 128.7, 127.2, 21.5. $^{31}$P NMR (162 MHz, $CDCl_3$) $\delta$ = 35.6. HRMS (ESI$^+$) *m*/*z* calculated for $(C_{32}H_{27}N_4O_4PSNa)^+$ 617.1383, measured 617.1360.

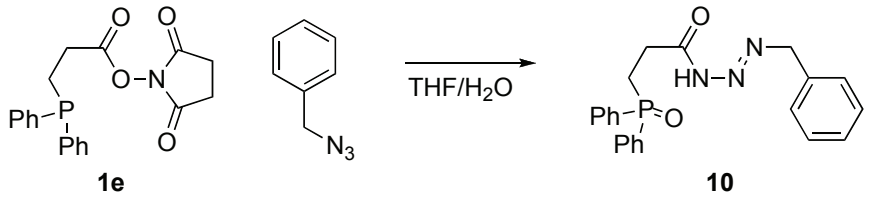
### 3.7 Reaction of Phosphine 1e with Diazo-Compound 5a: Hydrazone 9




Diazo-compound **5a** (50 mg, 0.286 mmol) was dissolved in THF/$H_2O$ (2 mL/300 µL). Phosphine **1e** (107 mg, 0.300 mmol) was added, and the resulting solution was stirred overnight under Ar(g). The solution was diluted with sat. aq. NaCl (15 mL) and extracted with $CH_2Cl_2$ (2 × 15 mL). The organic layers were combined, dried over $Na_2SO_4$(s), filtered, and evaporated under reduced pressure. The residue was purified by silica gel flash chromatography, eluting with 2% MeOH/$CH_2Cl_2$ to give acyl hydrazone **9** (118 mg, 95% yield) as a white solid.

Data for **9**: $^{1}$H NMR (400 MHz, DMSO-$d_6$, mixture of isomers 1.6:1) $\delta$ = 11.73 (s, 0.38H, C*H*CONHBn), 11.65 (s, 0.62H, C*H*CONHBn), 8.98 (t, 0.62H, *J* = 5.8 Hz, N*H*Bn), 8.75 (t, 0.38H, *J* = 5.5 Hz, N*H*Bn), 7.86–7.76 (m, 4H, Ar.), 7.60–7.45 (m, 6H, Ar.), 7.36–7.19 (m, 5H, Ar.), 4.41–4.34 (m, 2H, C$H_2$Ph), 2.78 (m, 1.24H, P(O)C$H_2$C$H_2$), 2.74–2.64 (m, 2H, P(O)C$H_2$C$H_2$), 2.42 (m, 0.76H, P(O)C$H_2$C$H_2$). $^{13}$C NMR (100 MHz, $CDCl_3$, $^{31}$P-coupled; $^{1}$H-decoupled, observed signals, mixture of isomers) $\delta$ = 175.5, 174.4, 174.3, 169.0, 168.8, 163.1, 163.0, 140.4, 137.9, 132.4, 132.4, 132.1, 131.5, 131.4, 130.7, 130.6, 130.5, 129.1, 129.0, 128.8, 128.7, 128.5, 127.7, 127.4, 127.2, 43.0, 26.9, 25.1, 25.0, 24.7, 24.2, 24.0. $^{31}$P NMR (162 MHz, $CDCl_3$) $\delta$ = 35.3 (major isomer), 33.6 (minor isomer). HRMS (ESI$^+$) *m*/*z* calculated for $(C_{24}H_{25}N_3O_3P)^+$ 434.1629, measured 434.1613.

### 3.8 Reaction of Phosphine 1e with Benzyl Azide: Triazene (10)

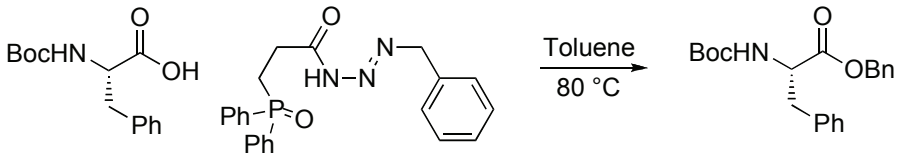



Benzyl azide[13] (43 mg, 0.319 mmol) was dissolved in THF/$H_2O$ (2 mL/300 µL). Phosphine **1e** (119 mg, 0.335 mmol) was added, and the resulting solution was stirred overnight under Ar(g).

The solution was diluted with sat. aq. NaCl (15 mL) and extracted with $CH_2Cl_2$ (2 × 15 mL). The organic layers were combined, dried over $Na_2SO_4$(s), filtered, and evaporated under reduced pressure. The residue was purified by silica gel flash chromatography, eluting with 2% MeOH/$CH_2Cl_2$ to give triazene **10** (100 mg, 0.255 mmol, 80% yield) as a white solid.

Data for **10**: $^1$H NMR (400 MHz, $CDCl_3$, mixture of tautomers 1.5:1, broad signals) $\delta$ = 12.89 (br. s, 0.4H, N*H*NN), 9.82 (br. s, 0.6H, N*H*NN), 7.84–7.22 (m, 15H, Ar.), 4.92 (br. s, 0.8H, C$H_2$Ph), 4.83 (br. s, 1.2H, C$H_2$Ph), 3.20-3.05 (m, 1.2H, P(O)C$H_2$C$H_2$), 2.90–2.50 (m, 2.8H, P(O)C$H_2$C$H_2$). $^{31}$P NMR (162 MHz, $CDCl_3$) $\delta$ = 34.3 (minor tautomer), 33.1 (major tautomer). HRMS (ESI$^+$) *m*/*z* calculated for $(C_{22}H_{22}N_3O_2P)^+$ 391.1450, measured 391.1431.

### 3.9 Benzyl 2-{[(*t*-butoxy)carbonyl]amino}-3-phenylpropanoate (12)




**11** **10** **12**

Carboxylic acid **11** (61 mg, 0.230 mmol) and acyl triazene **10** (90 mg, 0.230 mmol) were suspended in anhydrous toluene (2 mL). The mixture was warmed to 80 °C, and the resulting solution was stirred at that temperature for 3 h. The resulting suspension was placed directly on a column of silica gel and eluted with 10% EtOAc/hexanes to give ester **12** as a waxy solid (41 mg, 0.116 mmol, 50% yield).

Data for **12**: $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ = 7.43–7.21 (m, 8H, Ar), 7.11–7.03 (m, 2H, Ar), 5.19 (d, 1H, *J* = 12.7 Hz, OC$H_2$Ph), 5.13 (d, 1H, *J* = 12.7 Hz, OC$H_2$Ph), 5.00 (br. m, 1H, N*H*Boc), 4.65 (br. m, 1H, C*H*CH$_2$Ph), 3.16–3.05 (m, 2H, CHC$H_2$Ph), 1.43 (s, 9H, *t*-Bu). $^{13}$C NMR (100 MHz, $CDCl_3$, observed signals) $\delta$ = 171.7, 155.0, 135.8, 135.2, 129.3, 128.5, 128.4, 127.0, 79.9, 67.1, 54.4, 38.3, 28.3. HRMS (ESI$^+$) *m*/*z* calculated for $(C_{21}H_{25}NO_4)^+$ 355.1779, measured 355.1776.

## 4. Crystal Structure Determination of Acyl Triazene 8

**Acyl triazene 8** was dissolved in $CH_2Cl_2$ with the minimal amount of MeOH and placed in an NMR tube. Diethyl ether was carefully layered over the solution. The NMR-tube was sealed and allowed to stand for approximately 3 days, which resulted in the formation of small crystals. X-ray intensity data were collected on a Bruker-AXS SMART APEX2 with Cu $K_\alpha$ ($\lambda$ = 1.54178 Å) radiation at 100(2) K with the diffractometer to crystal distance of 4.9 cm. Preliminary indexing was carried out for determination of the cell constants. This consisted three series of ω scans at different initial angles with each series consisting of 50 frames at intervals of 0.3° and exposure time of 5 s per frame. The reflections were indexed by an automated indexing routine built in the SMART program. The data were collected by using the full sphere data collection routine to a resolution of 0.82 Å. The intensity data were then corrected for absorption

and Lorentz and polarization effects. Structure solution and refinement was carried out using SHELXTL V.6.10.[14] Figure S1 displays **8** with 50% probability thermal ellipsoids.

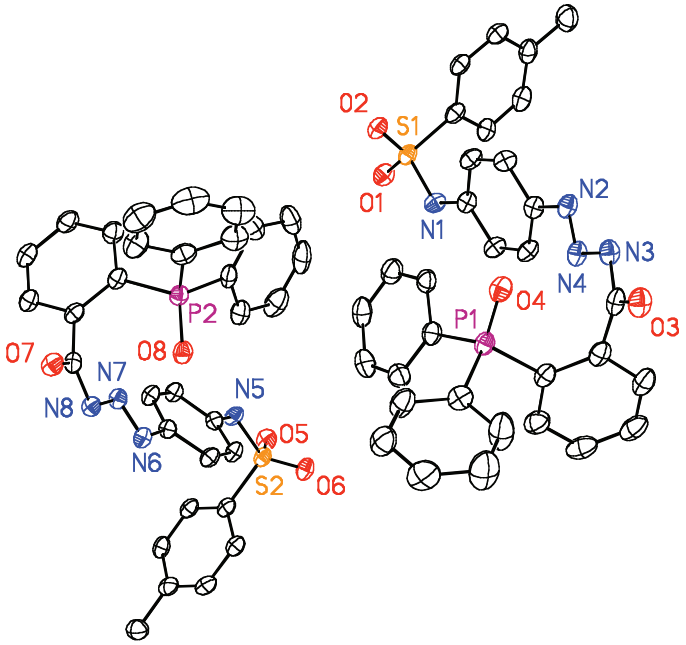
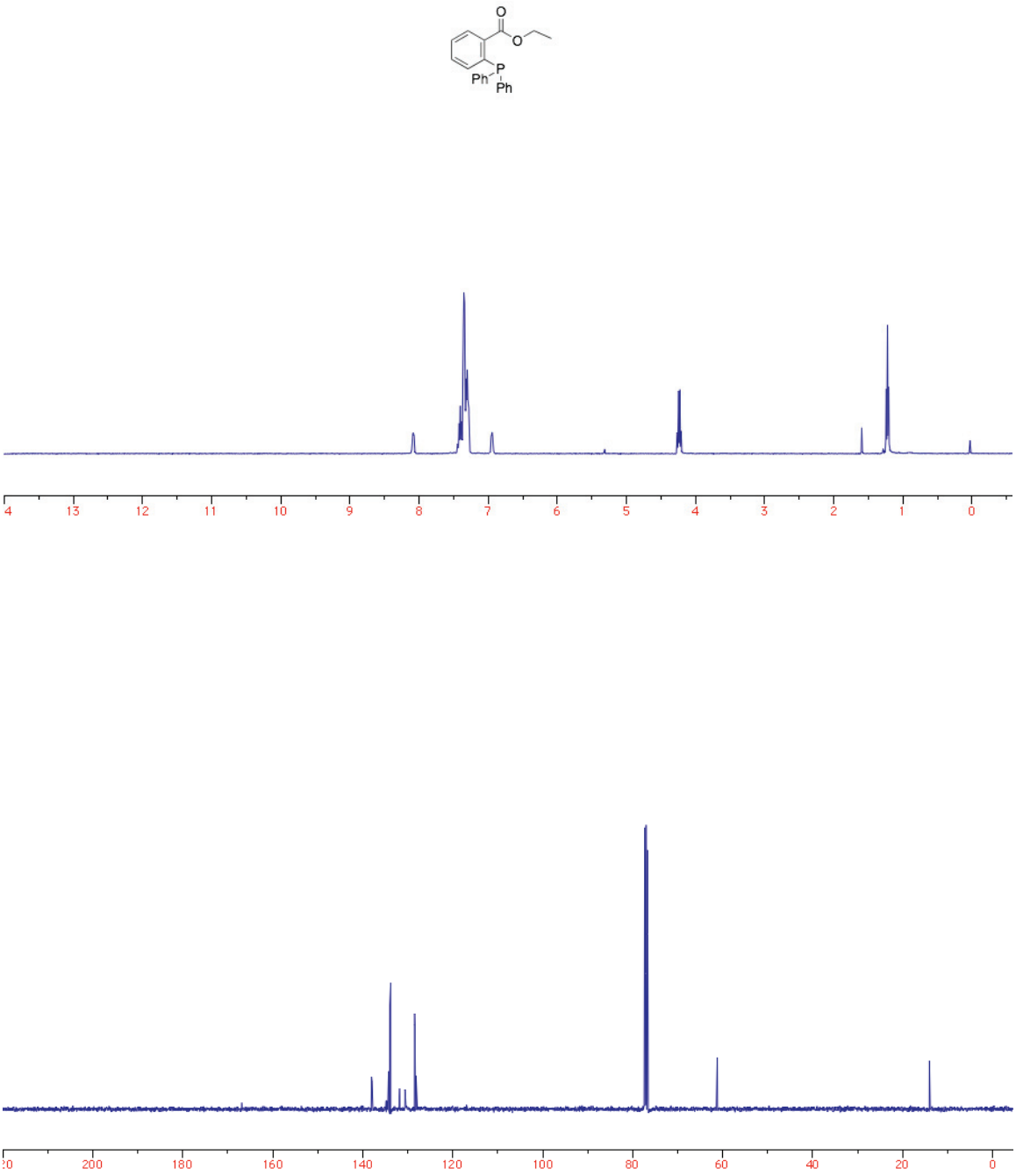


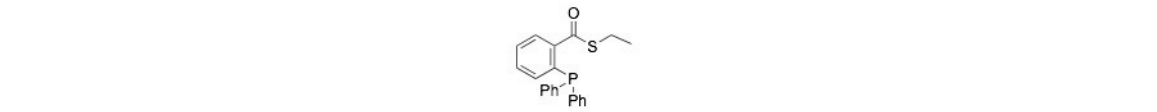

**Figure S–1**: A molecular diagram of **8** drawn with 50% probability ellipsoids.

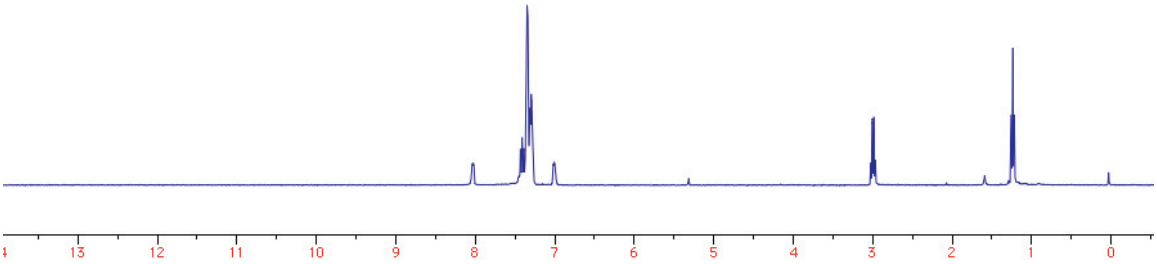
## 5. NMR Spectra

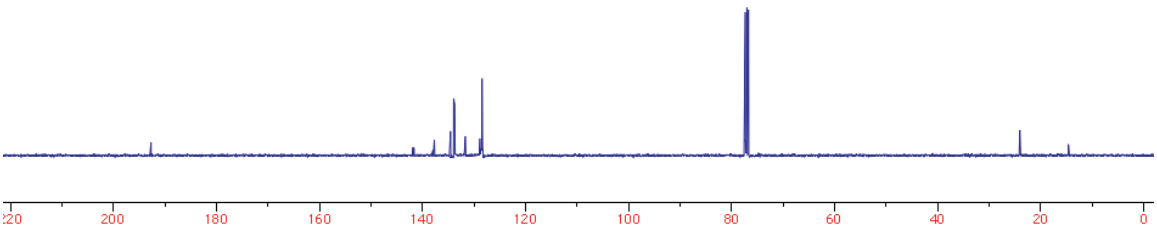
$^{1}$H NMR Spectrum / $^{13}$C NMR Spectrum of **1a**



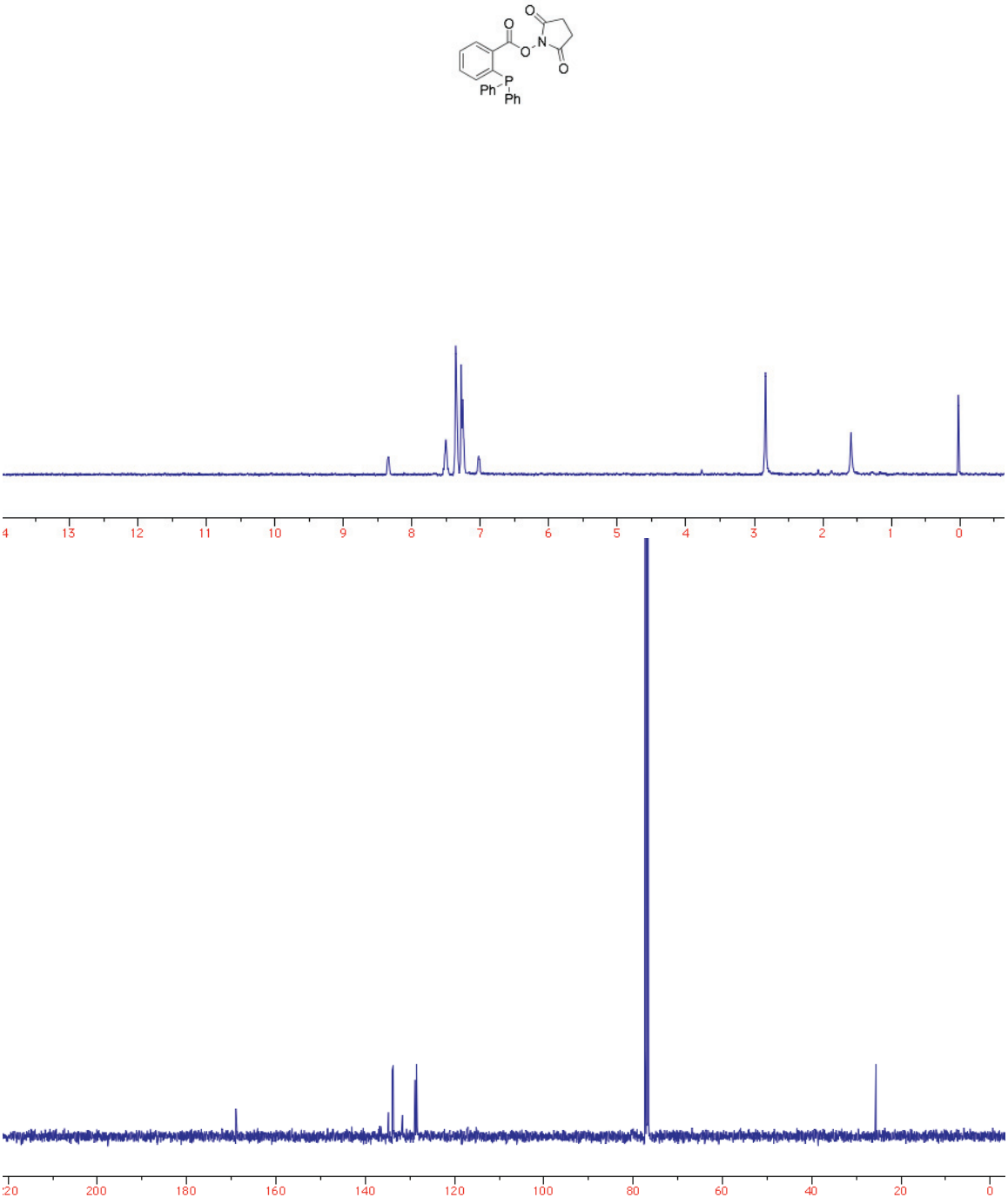
$^{1}$H NMR Spectrum / $^{13}$C NMR Spectrum of **1b**



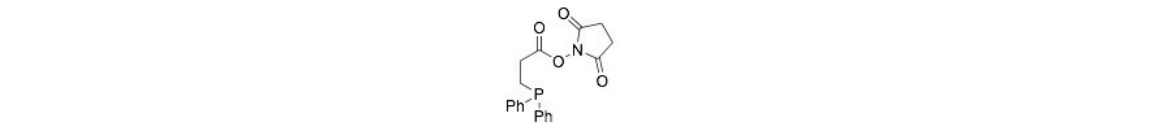



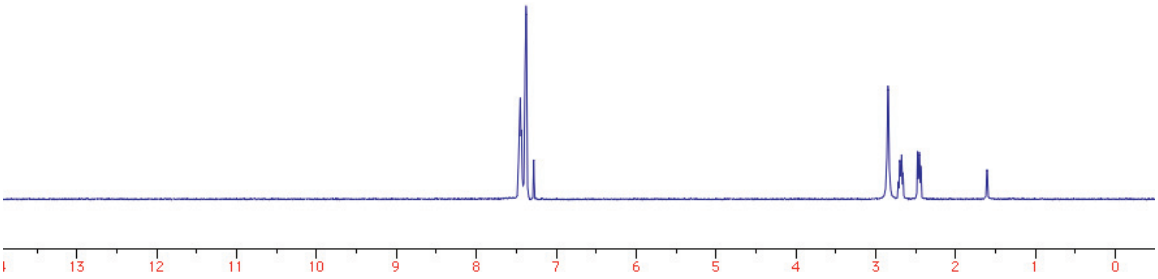



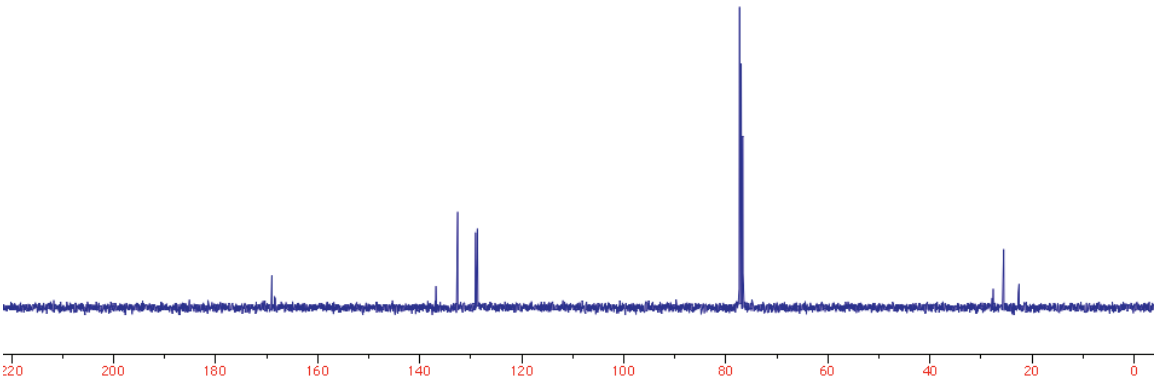
$^{1}$H NMR Spectrum / $^{13}$C NMR Spectrum of **1c**



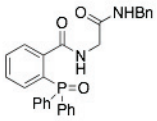
$^{1}$H NMR Spectrum / $^{13}$C NMR Spectrum of **1e**

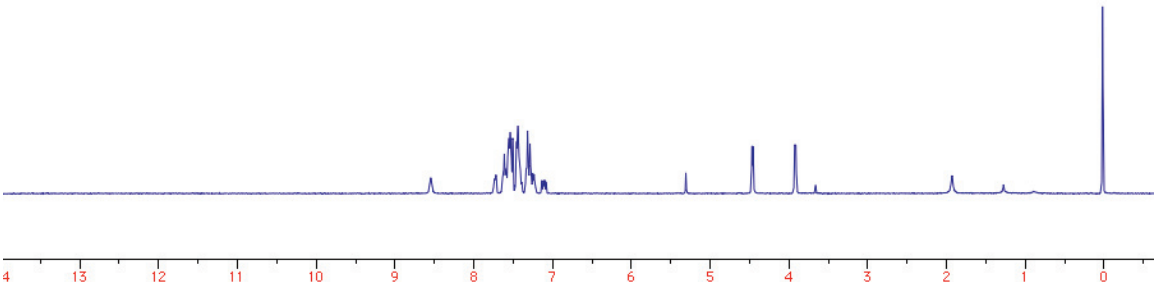


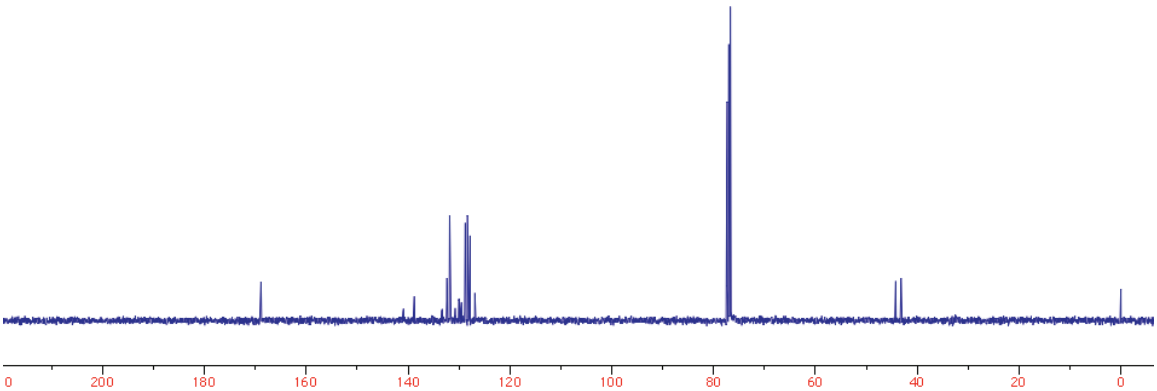



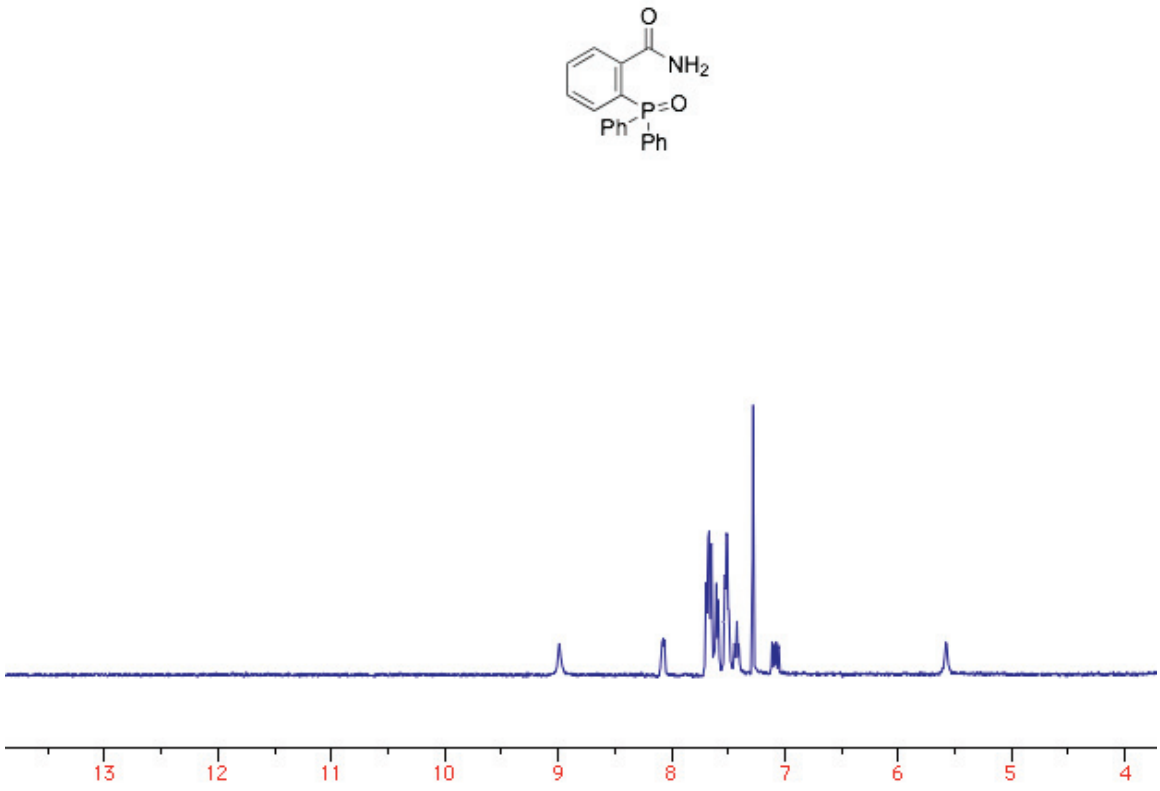
$^{1}$H NMR Spectrum / $^{13}$C NMR Spectrum of **3**



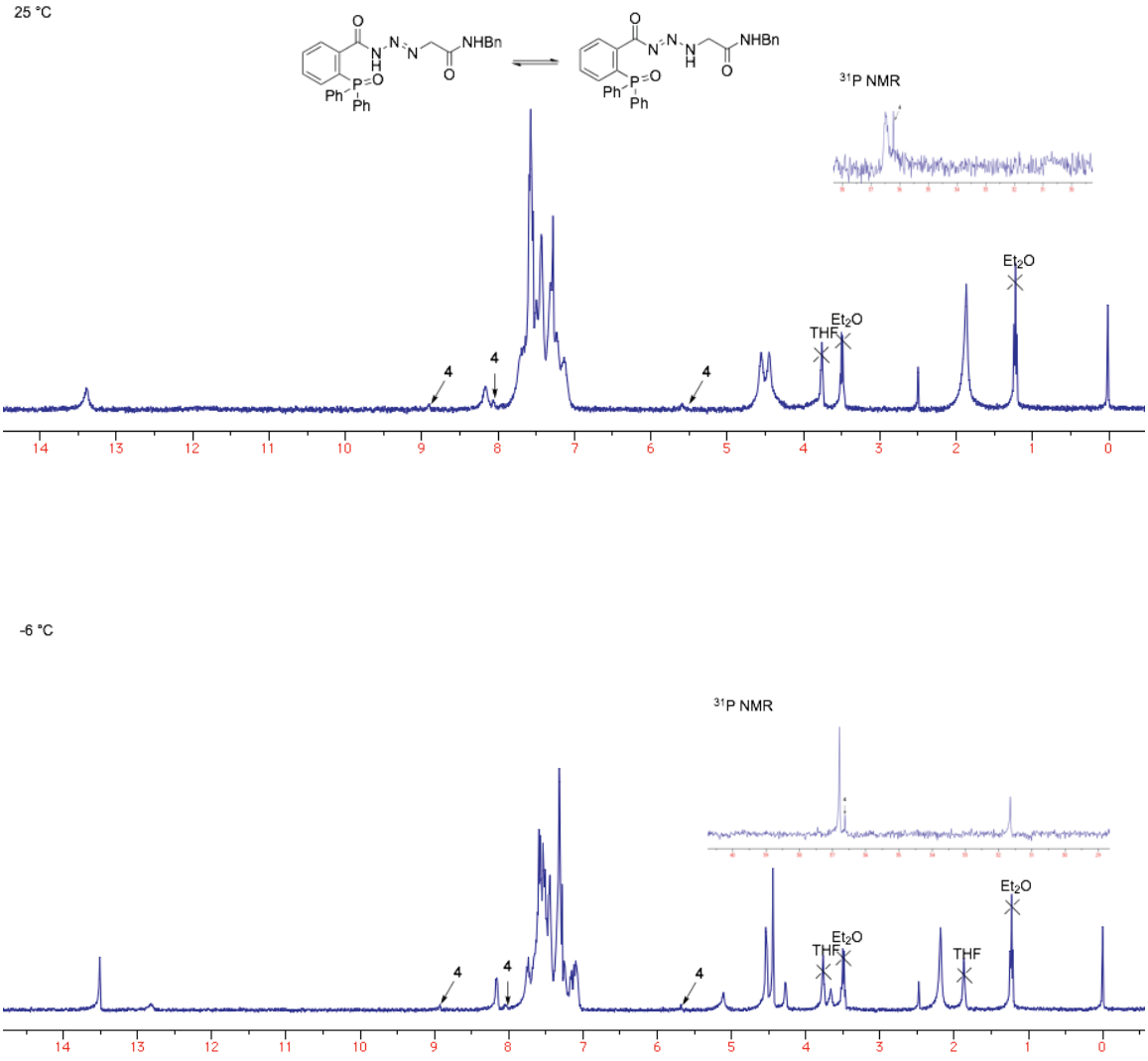



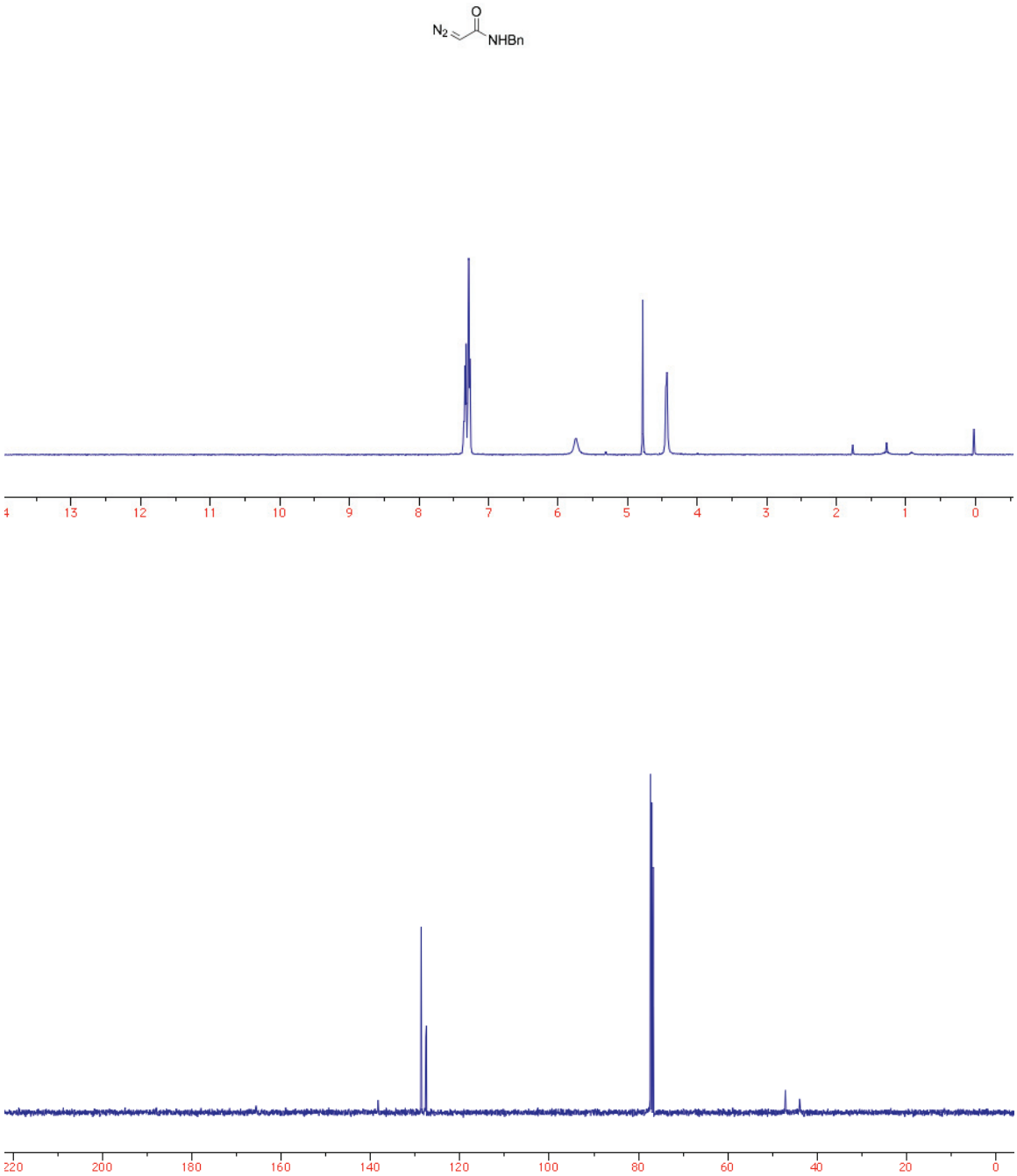
$^{1}$H NMR Spectrum of **4**



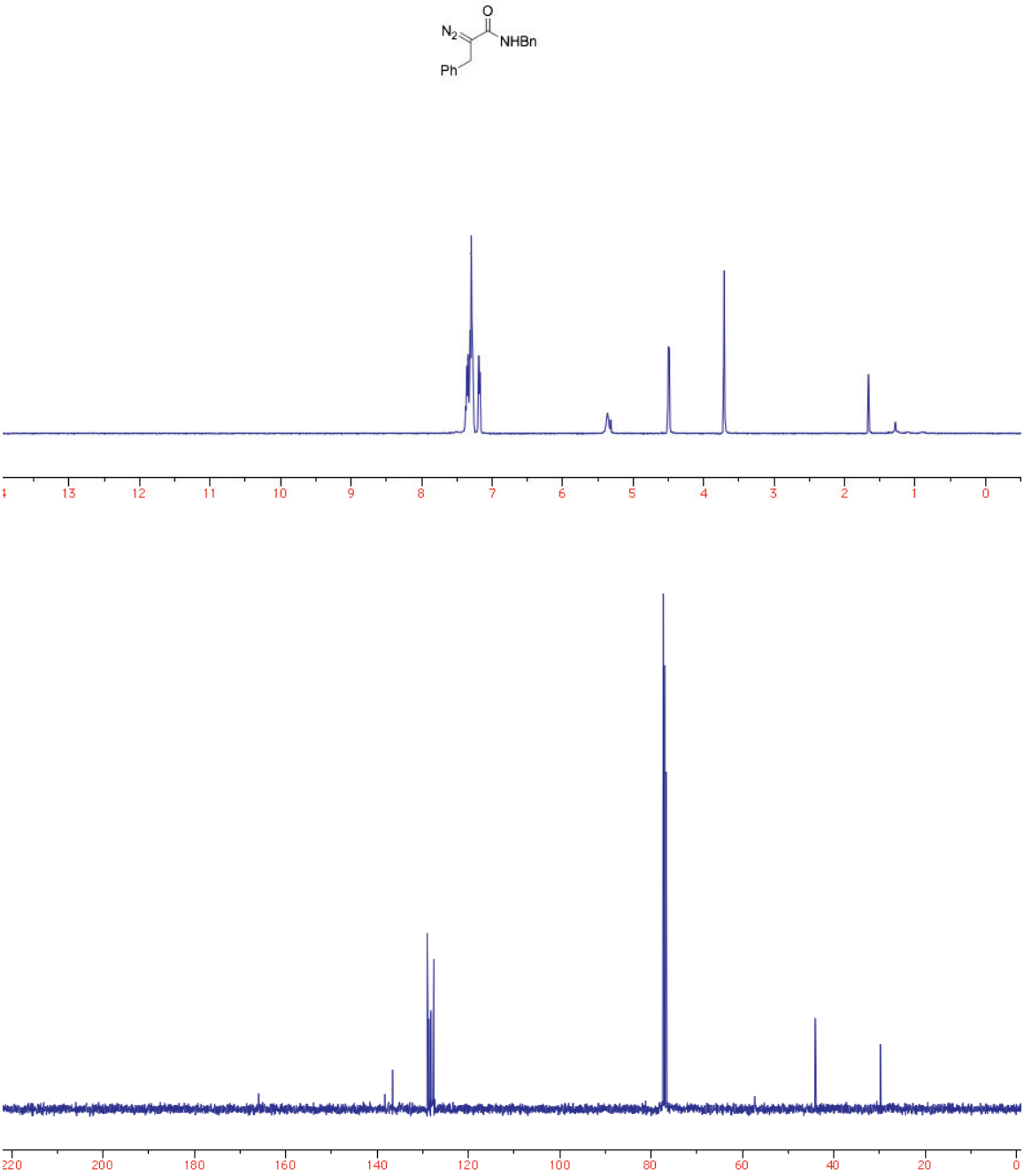
$^{1}$H NMR Spectrum of **6** (at 25 °C and –6 °C) with $^{31}$P insets.



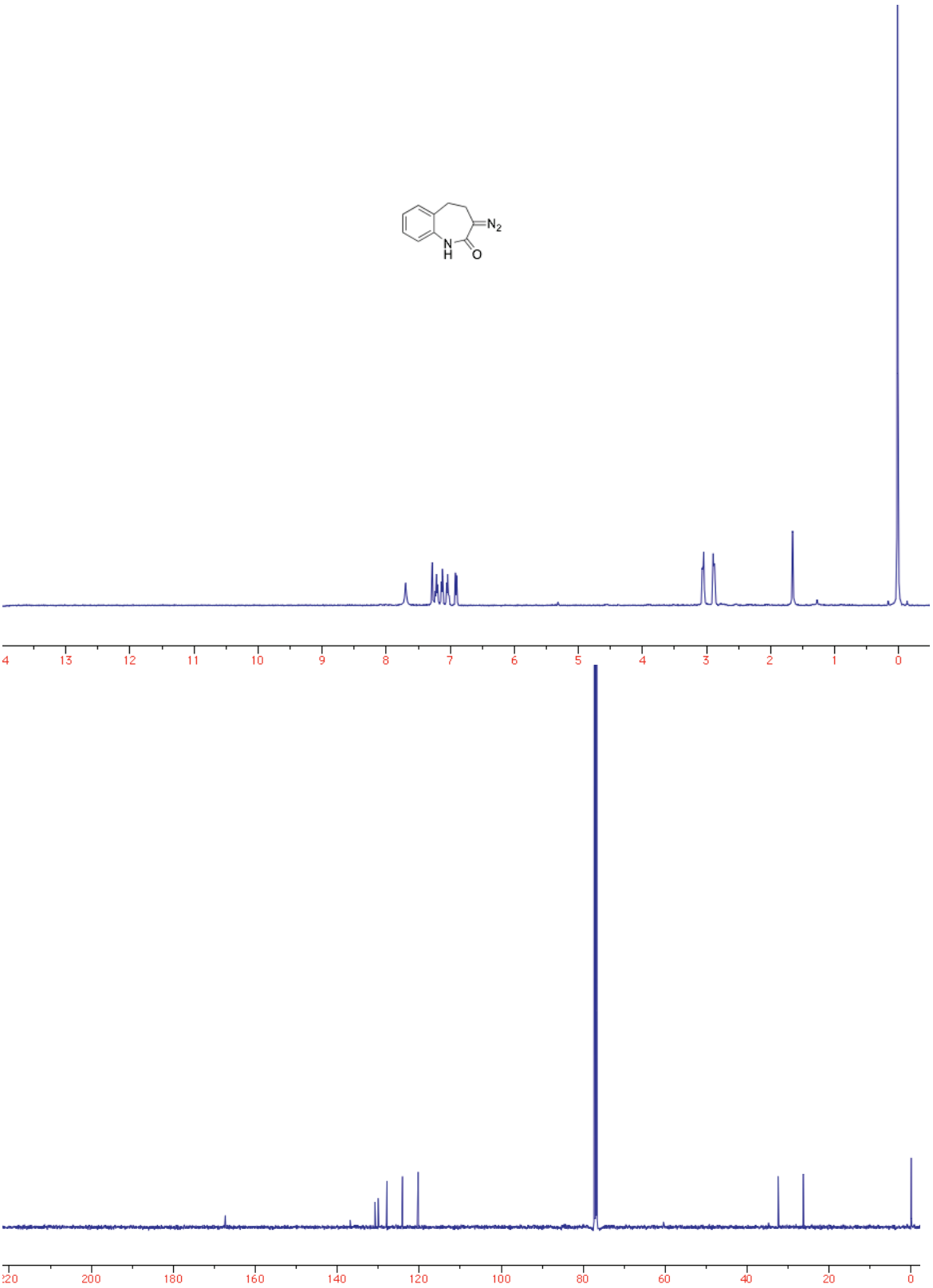
$^{1}$H NMR Spectrum / $^{13}$C NMR Spectrum of **5a**



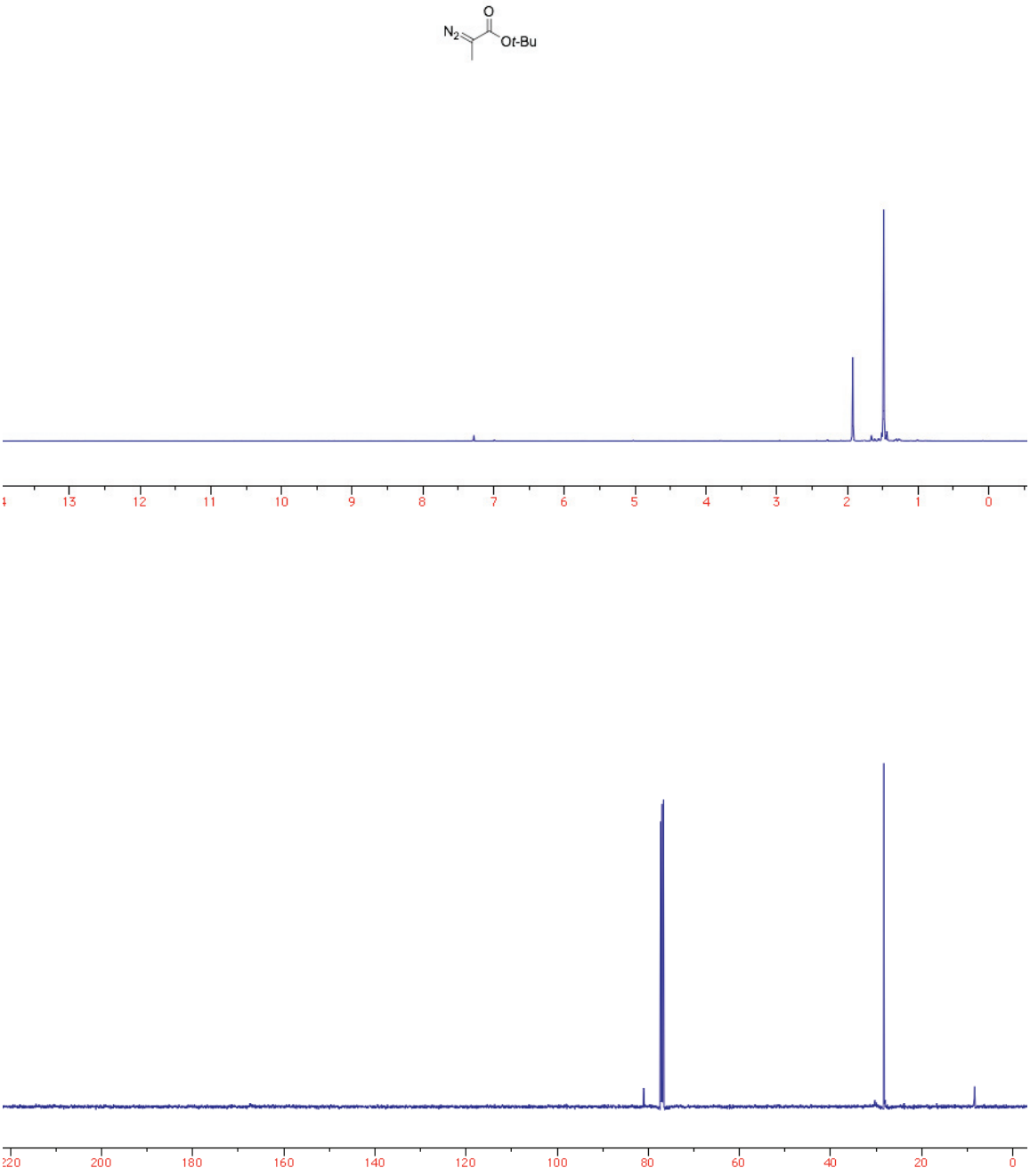
$^{1}$H NMR Spectrum / $^{13}$C NMR Spectrum of **5b**



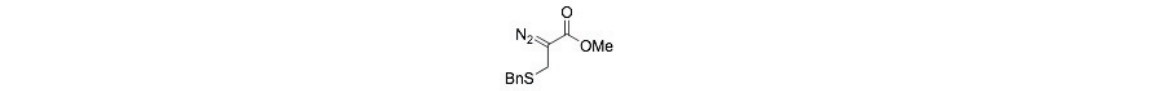
$^{1}$H NMR Spectrum / $^{13}$C NMR Spectrum of **5c**

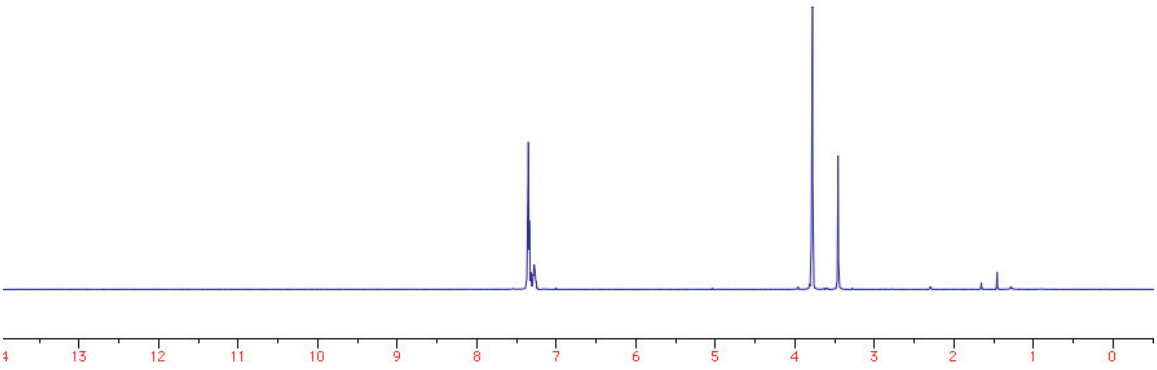


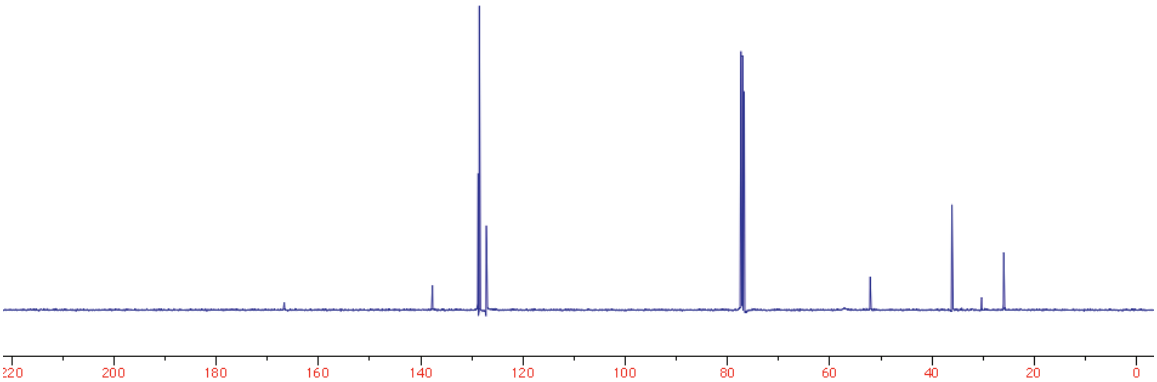
$^{1}$H NMR Spectrum / $^{13}$C NMR Spectrum of **5d**



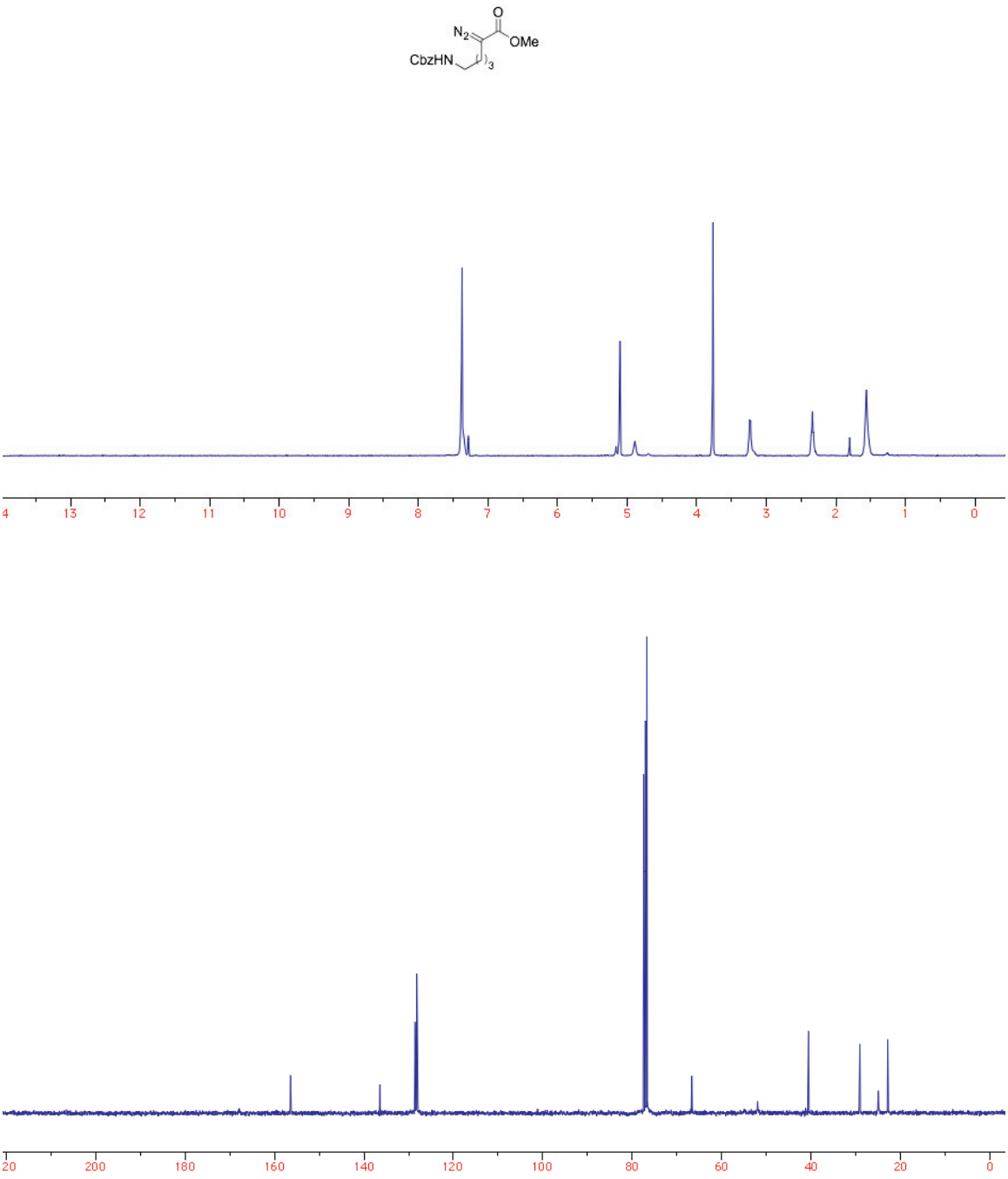
$^{1}$H NMR Spectrum / $^{13}$C NMR Spectrum of **5e**



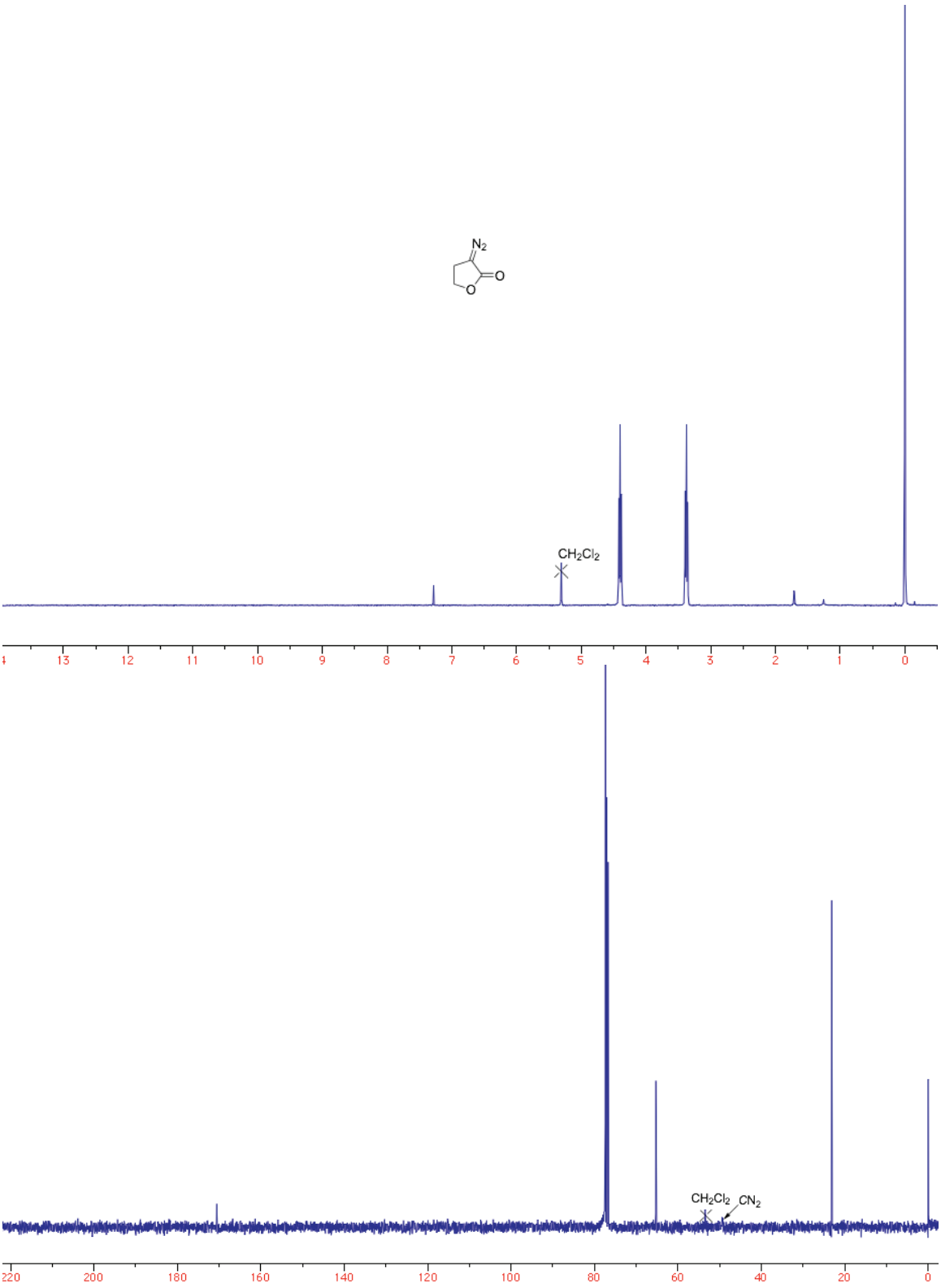



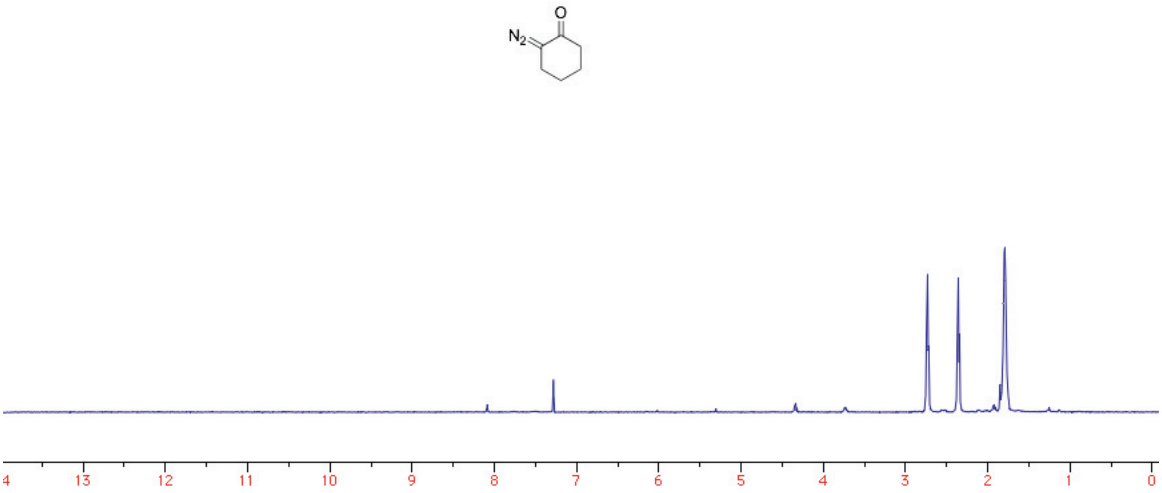
$^{1}$H NMR Spectrum / $^{13}$C NMR Spectrum of **5f**

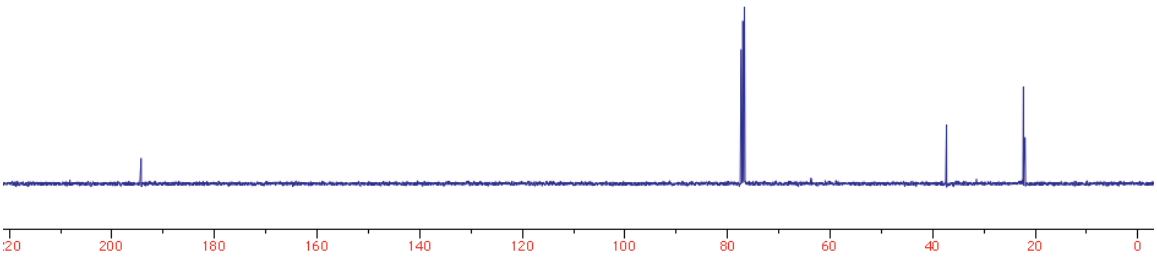


$^{1}$H NMR Spectrum / $^{13}$C NMR Spectrum of **5g**

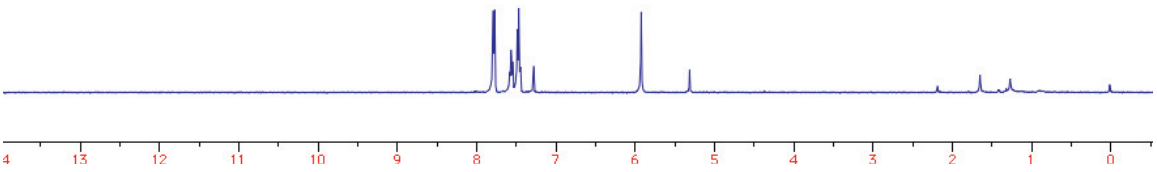


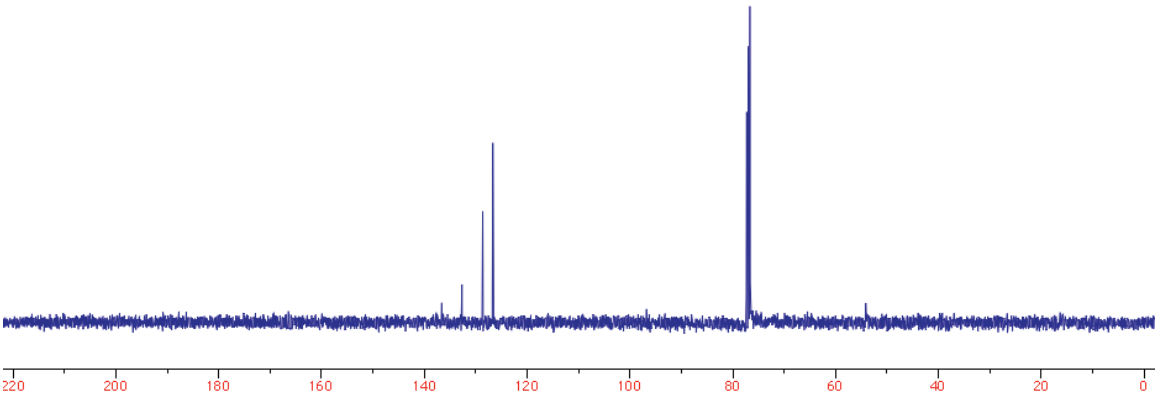
$^{1}$H NMR Spectrum / $^{13}$C NMR Spectrum of **5h**



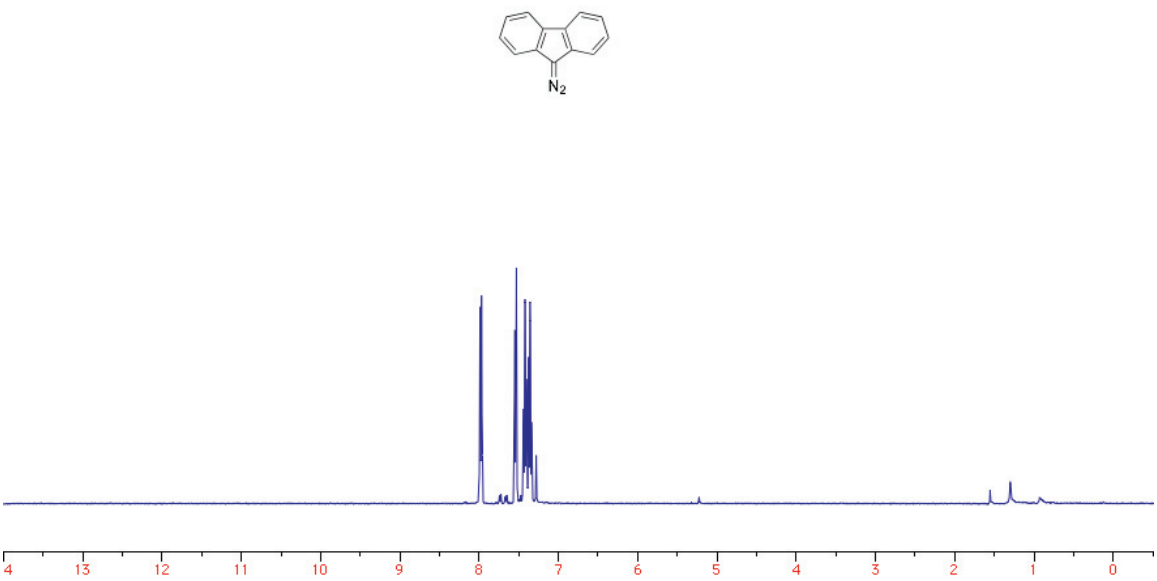



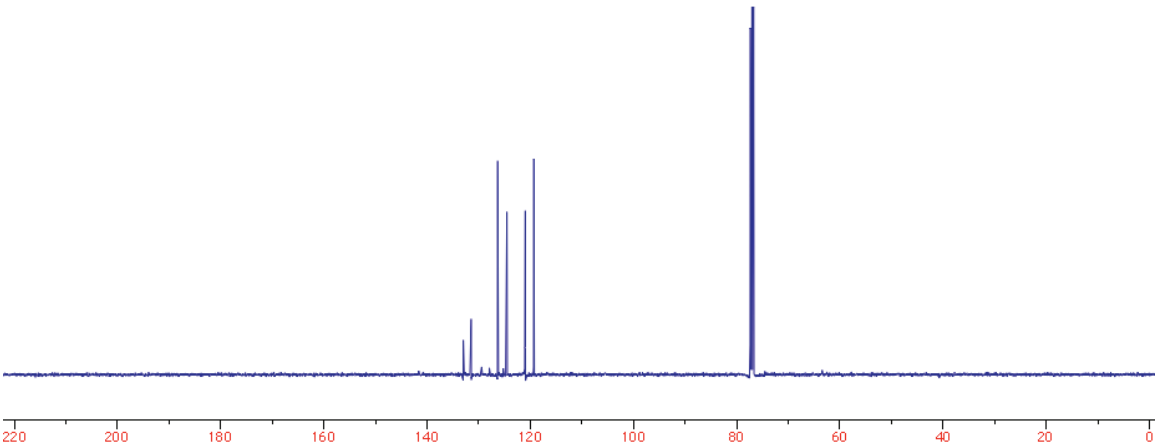
$^{1}$H NMR Spectrum / $^{13}$C NMR Spectrum of **5i**

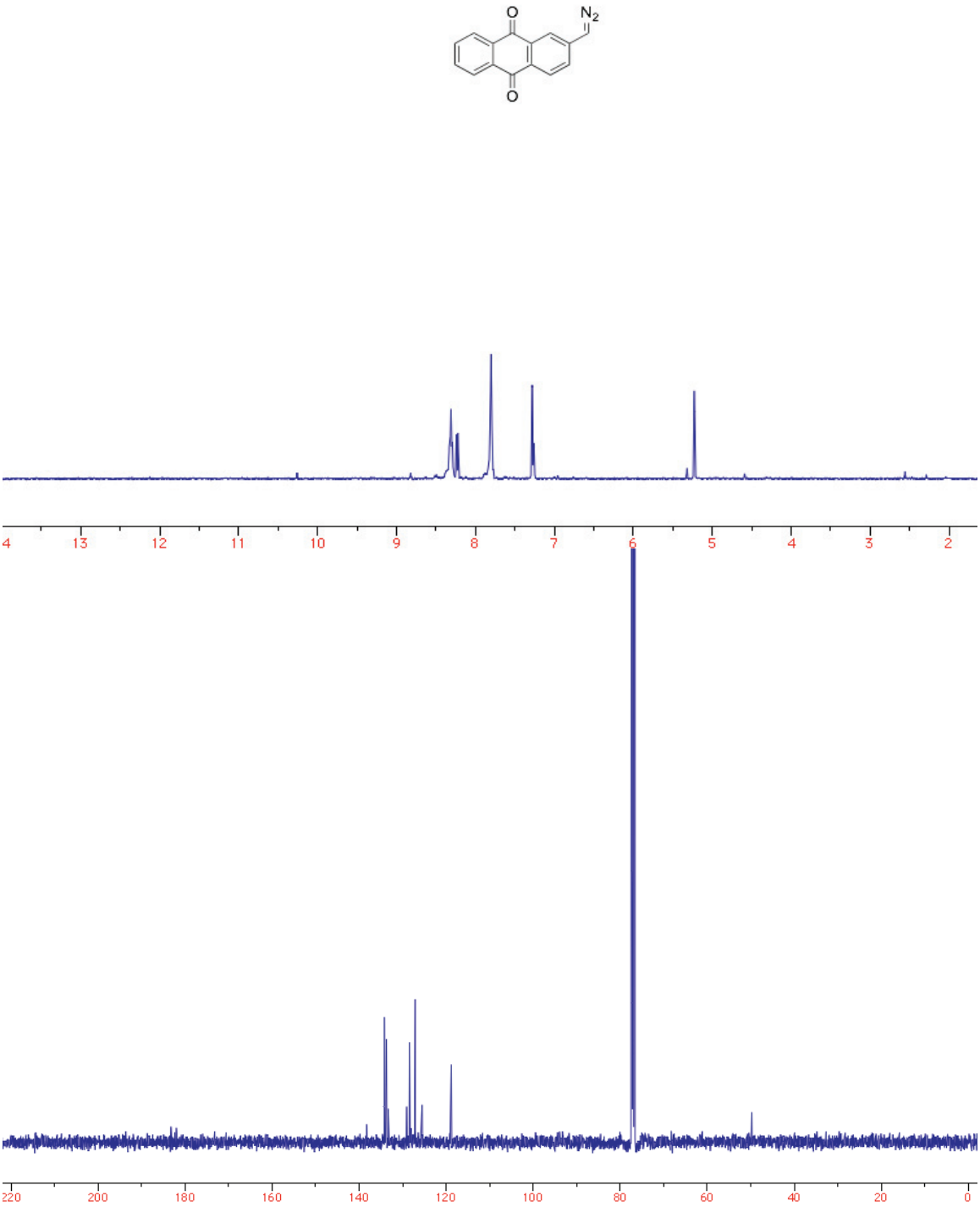



$^{1}$H NMR Spectrum / $^{13}$C NMR Spectrum of **5j**

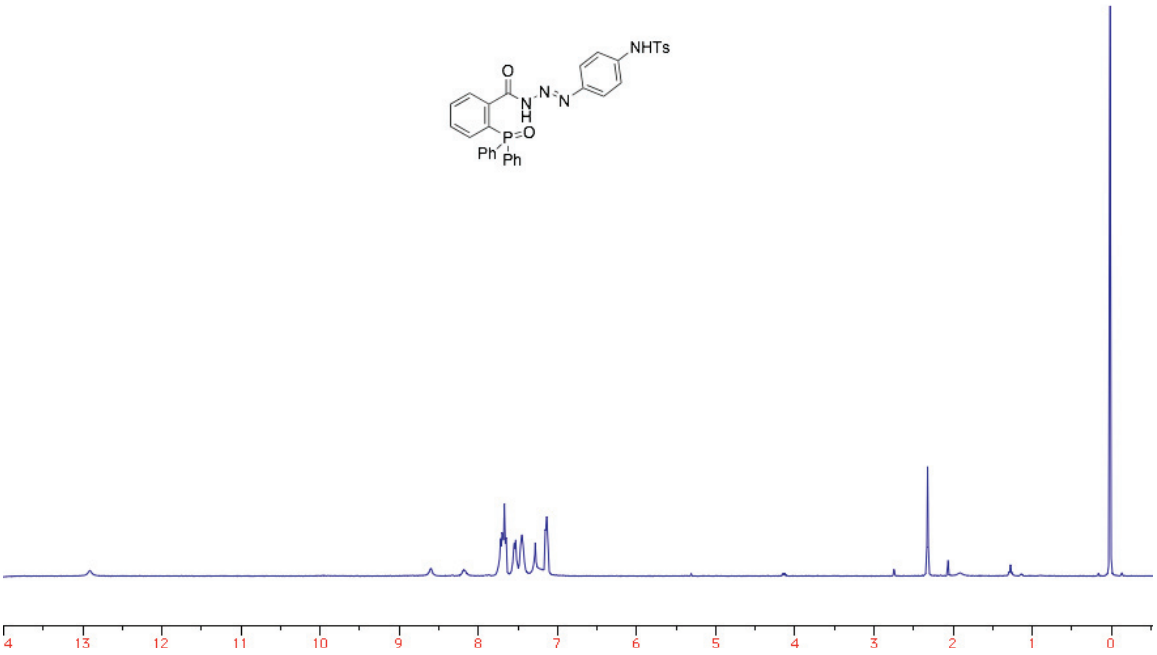


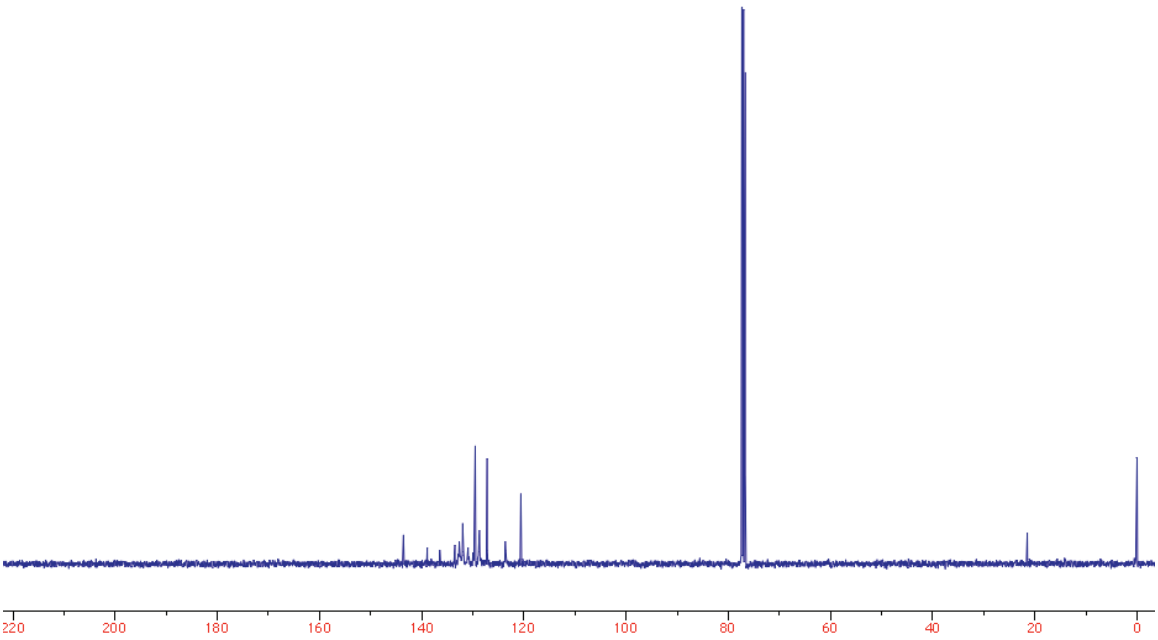



$^{1}$H NMR Spectrum / $^{13}$C NMR Spectrum of **5k**

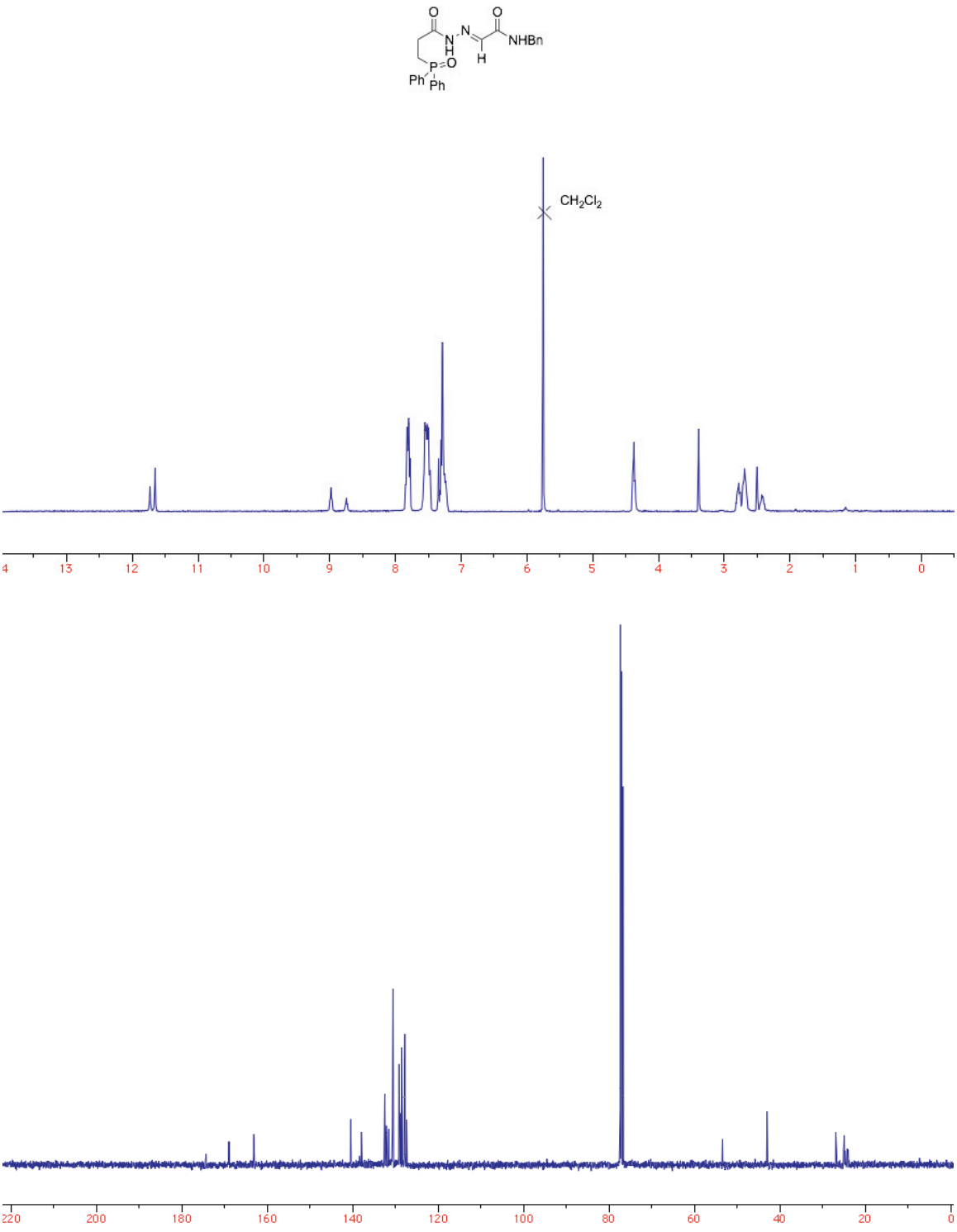


$^{1}$H NMR Spectrum / $^{13}$C NMR Spectrum of **8**

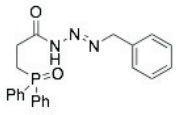


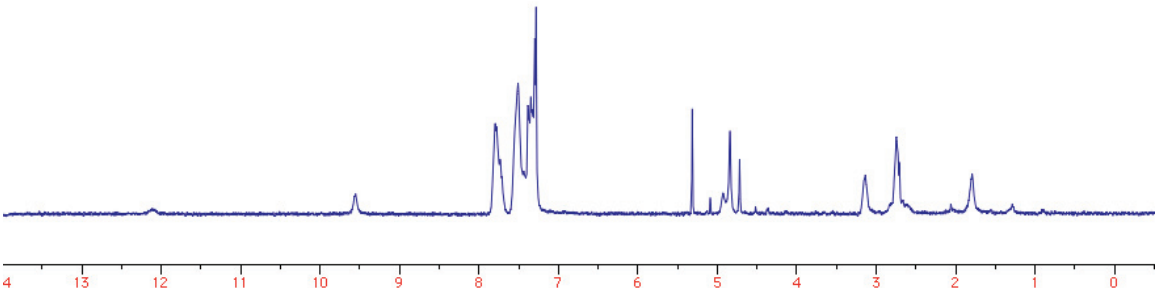



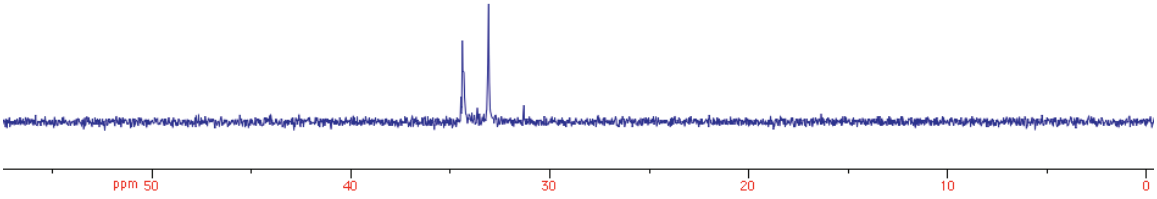
$^{1}$H NMR Spectrum / $^{13}$C NMR Spectrum of **9**



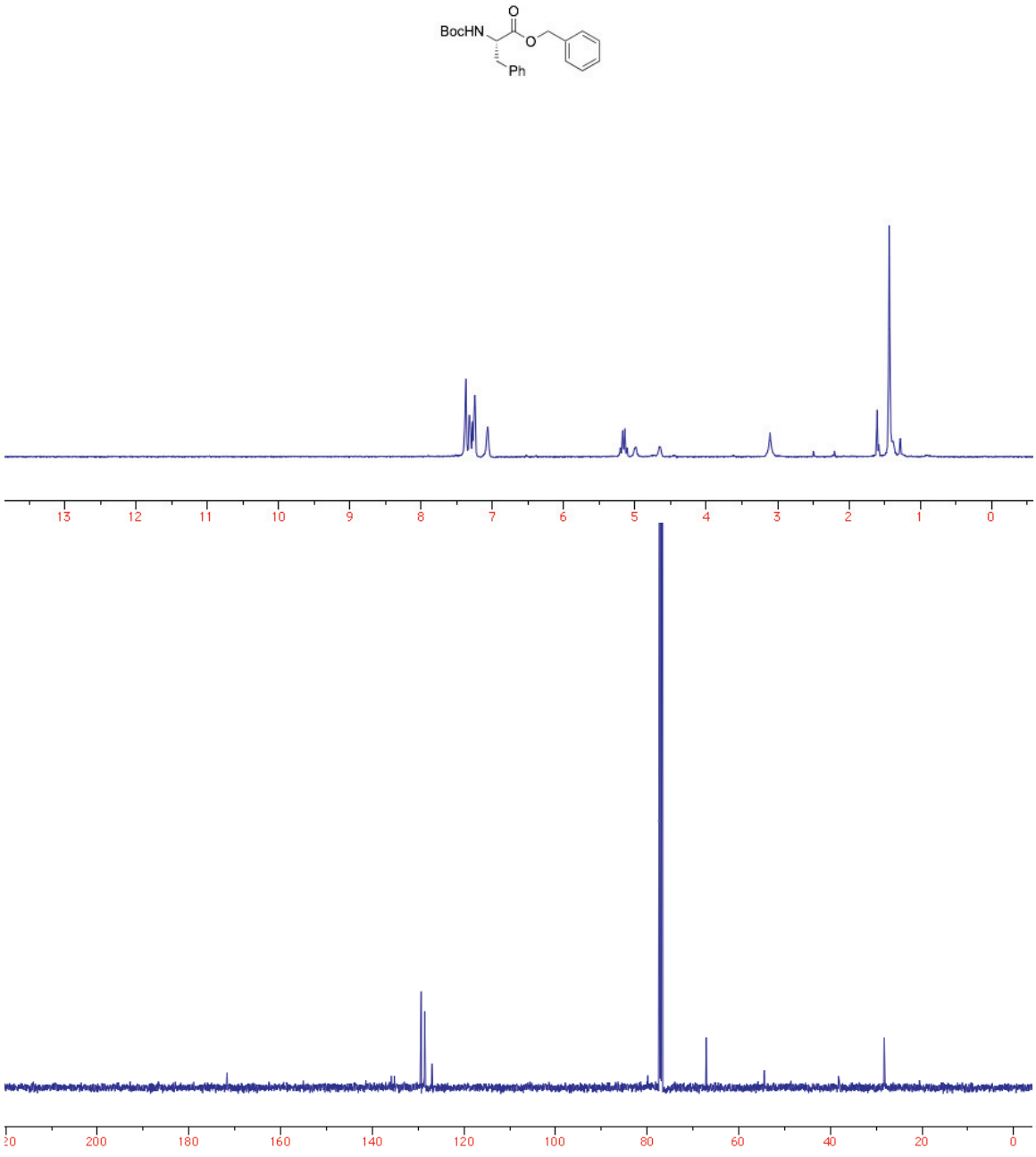
$^{1}$H NMR Spectrum and $^{31}$P NMR Spectrum of **10** (mixture of isomers, presumably tautomers)



$^{1}$H NMR Spectrum / $^{13}$C NMR Spectrum of **12**



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