Supplementary Information

A High-Throughput Photocapture Approach for Reaction Discovery

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General Information

All reactions were carried out under an argon or nitrogen atmosphere in flame-dried glassware with magnetic stirring. Solvents used in reactions were purified by passage through a bed of activated alumina. For photochemical reactions DMSO and MeCN were subjected to freeze-pump-thaw deoxygenation. Reagents were purified prior to use unless otherwise stated following the guidelines of Perrin and Armarego.[1] Purification of reaction products was carried out by flash chromatography on Biotage Isolera 4 systems with Ultra-grade silica cartridges. Analytical thin layer chromatography was performed on EM Reagent 0.25 mm silica gel 60-F plates. Visualization was accomplished with UV light. ^{1}H NMR spectra were recorded on an AVANCE III 500 MHz with direct cryoprobe (500 MHz) spectrometer and Bruker Avance III 600 MHz (151 MHz) system. These are reported in ppm using solvent as an internal standard ($CDCl_3$ at 7.26 ppm, CD_3CN at 1.94 ppm). Data are reported as (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br= broad; coupling constant(s) in Hz; integration.) Proton-decoupled ^{13}C NMR spectra were recorded on an AVANCE III 500 MHz with direct cryoprobe (125 MHz) spectrometer and Bruker Avance III 600 MHz (151 MHz) system. These are reported in ppm using solvent as an internal standard ($CDCl_3$ at 77.16 ppm, CD_3CN at 118.3 and 1.3 ppm). Mass spectra were obtained on WATERS Acquity-H UPLC-MS with a single quad detector (ESI) Varian1200 Quadrupole Mass Spectrometer. Accurate masses were obtained using an Agilent 6120A LC-TOF MS. V-vis measurements were recorded on the Thermo Scientific NanoDrop OneC Microvolume UV-Vis Spectrophotometer.

Abbreviations:

bpy: 2,2'-bipyridyl

LED: Light-emitting diode

dtbbpy: 4,4'-di-tert-butyl-2,2'-dipyridyl

Photoredox Reaction Screening Approach

Reactions were run in glass vials in 24 or 96 well plate reactor blocks having hollowed bottoms, and the vials were equipped with Teflon coated magnetic stir bar (**Figure S1**). The plate was placed in a glovebox, then the four reaction components were added as stock solutions using micropipettes (**Figure S2**). The plate was sealed with a screwed top lid equipped with a PTFE gasket then removed from the glovebox and placed on an LED plate on the top a magnetic stirrer (500 rpm) (**Figure S1**). After 18 h, the plate was unsealed for analysis.

Para-Dox™ Photoredox 96-Well Block Assembly with clear glass shell vials and parylene encapsulated stainless steel cylinder stir bars, Lumidox™ 96-Well Blue LED Array were used (all purchased from Analytical Sales & Services, Inc., **Figure S1**). For scaled-up reactions blue light was generated by three 40W Kessil H150 LED lights. $Ir(ppy)_2(dtbbpy)PF_6$ (**PC1**) was obtained from Strem Chemical and used as received.

Figure S1. Photoredox reaction screening apparatus.

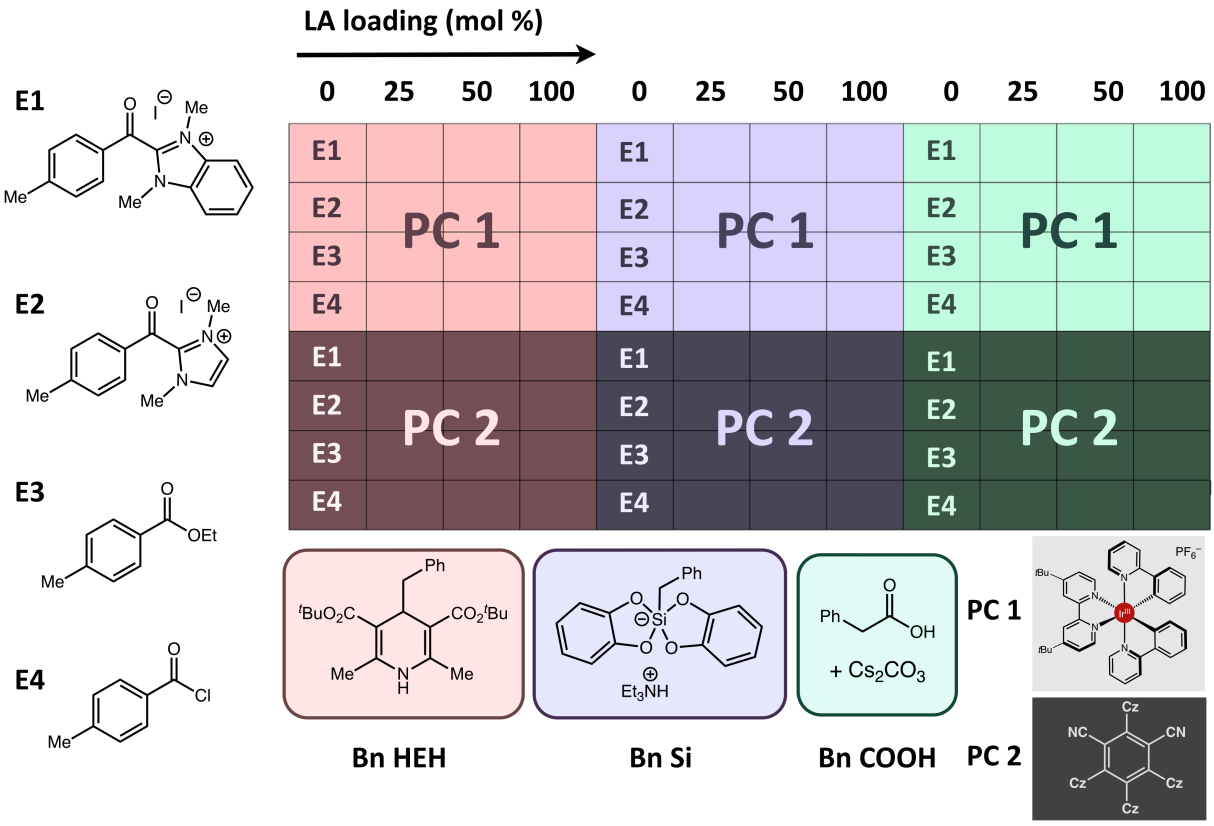
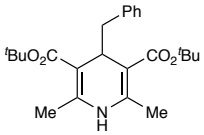


Figure S2. Example 96-well plate layout for electrophilic acyl sources **E1**-**E4**. For each 96-well plate the Lewis acid type (LiCl, LiOTf, $Mg(OTf)_2$, $Sc(OTf)_3$, $La(OTf)_3$), solvent (DMSO or MeCN), concentration (0.1 M), and reaction volume per well (120 µL, 30 µL x 4 components) remain constant.

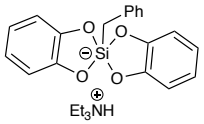
Benzyl radical precursor stock solutions (0.6 M, 30 μL/well)

Bn HEH: 2.40 g in 10 mL solvent, 7.2 mg/well



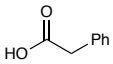
Bn HEH

Bn Si: 2.62 g in 10 mL solvent, 7.9 mg/well



Bn Si

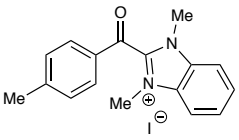
Bn COOH (1.2 M) + Cs_2CO_3 (1.2 M): 816 mg Bn COOH/5 mL solvent, 2.4 mg/well
+ 1.95 g Cs_2CO_3/5 mL solvent, 5.9 mg/well



Bn COOH

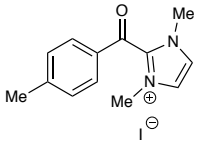
Ketyl radical precursor stock solutions (0.4 M, 30 μL/well)

E1: 785 mg in 5 mL solvent, 4.7 mg/ well



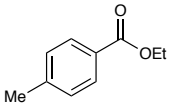
E1

E2: 685 mg in 5 mL solvent, 4.1 mg/well



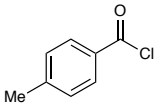
E2

E3: 330 mg in 5 mL solvent, 2 mg/well



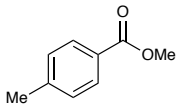
E3

E4: 308 mg in 5 mL solvent, 1.8 mg/well



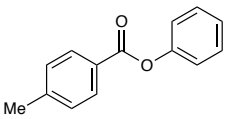
E4

E5: 300 mg in 5 mL solvent, 1.8 mg/well



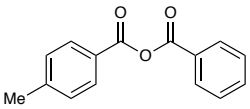
E5

E6: 425 mg in 5 mL solvent, 2.5 mg/well



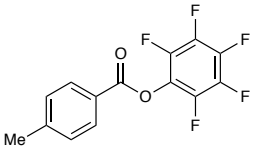
E6

E7: 480 mg in 5 mL solvent, 2.9 mg/well



E7

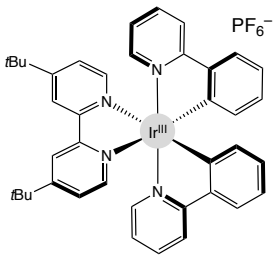
E8: 605 mg in 5 mL solvent, 3.6 mg/well



E8

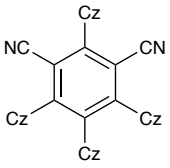
Photocatalyst Stock Solutions (0.004 M and 0.020 M, 30 µL/well)

PC 1 (0.004 M): 55 mg in 15 mL solvent, 0.11 mg/well



PC 1

PC 2 (0.020 M): 200 mg in 15 mL solvent, 0.40 mg/well



PC 2

Lewis Acid (LA) Stock Solutions (0, 0.1, 0.2, and 0.4 M, 30 μL/well)

LiCl (0 M): 3 mL solvent

LiCl (0.1 M): 13 mg in 3 mL solvent

LiCl (0.2 M): 26 mg in 3 mL solvent

LiCl (0.4 M): 52 mg in 3 mL solvent

LiOTf (0 M): 3 mL solvent

LiOTf (0.1 M): 50 mg in 3 mL solvent

LiOTf (0.2 M): 100 mg in 3 mL solvent

LiOTf (0.4 M): 200 mg in 3 mL solvent

$Mg(OTf)_2$ (0 M): 3 mL solvent

$Mg(OTf)_2$ (0.1 M): 96 mg in 3 mL solvent

$Mg(OTf)_2$ (0.2 M): 176 mg in 3 mL solvent

$Mg(OTf)_2$ (0.4 M): 336 mg in 3 mL solvent

$Sc(OTf)_3$ (0 M): 3 mL solvent

$Sc(OTf)_3$ (0.1 M): 144 mg in 3 mL solvent

$Sc(OTf)_3$ (0.2 M): 264 mg in 3 mL solvent

$Sc(OTf)_3$ (0.4 M): 504 mg in 3 mL solvent

$La(OTf)_3$ (0 M): 3 mL solvent

$La(OTf)_3$ (0.1 M): 180 mg in 3 mL solvent

$La(OTf)_3$ (0.2 M): 330 mg in 3 mL solvent

$La(OTf)_3$ (0.4 M): 630 mg in 3 mL solvent

****Each stock solution was made two times for the 20 x 96-well plates screened (10 plates in DMSO & 10 plates in MeCN).*

TI-SAMDI-MS Analysis Approach

Solid Phase Photoaffinity Linker Peptide Synthesis

The photoaffinity linker was synthesized according to standard peptide synthesis protocols. MBHA-Fmoc-Rink amide resin was deprotected with 20% piperidine in DMF (20 min.) followed by DMF washing (5x). Next, the resin was soaked in 4:4:8 FMOC-cysteine: PyBOP: *N*-methyl morpholine solution (30 min.) followed by DMF washing (5x). After deprotection with 20% piperidine in DMF (20 min.) and DMF washing (5x), the resin was soaked in a 4:4:8 FMOC-Lys(Me)$_3$-OH Chloride: PyBOP: *N*-methyl morpholine solution (30 min.) followed by DMF washing (5x). After deprotection with 20% piperidine in DMF (20 min.) and DMF washing (5x), the resin was soaked in 4:4:8 4-[3-(trifluoromethyl)-3H-diaziren-3-yl]benzoic acid: PyBOP: *N*-methyl morpholine solution (30 min.) followed by DMF washing (5x). The peptide was cleaved from the resin with 95% TFA, 2.5% H_2O, and 2.5% TES solution (2 h). Upon cleavage, the mixture was filtered through glass wool to remove the resin and the filtrate was concentrated. The residue was purified with Et_2O extraction, then concentrated, then lyophilized overnight.

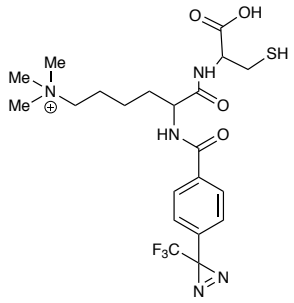


Figure S3. 3-trifluoromethyl-3-phenyl-diazirine (TPD) Photoaffinity Linker Peptide

Diazirine Monolayer Preparation

SAMDI-MS array plates were prepared by patterning 384 gold spots on steel plates using electron beam metal evaporation. Titanium (5 nM) was deposited, followed by gold (30 nM).[2] These plates were soaked in an ethanolic solution of disulfide molecules (18 h) to form a self-assembled monolayer on the gold surfaces. The solution consisted of tri(ethylene glycol)-alkanethiol (EG3-alkanethiol) disulfide, and a mixed disulfide of maleimide-terminated EG3-alkanethiol, and EG3-alkanethiol (0.1 mM). The two disulfide molecules (purchased from ProChimia Surfaces) were stoichiometrically combined to yield a 10% maleimide surface density. The arrays were subsequently washed with EtOH, deionized ultra-filtered (DIUF) H_2O, EtOH again, and then dried under a stream of N_2. A solution of the photoaffinity linker (1 μM in tris buffer, pH 8) was applied to the plate (1 μL/ spot) and warmed to 37 ºC for 30 min. Upon completion, the diazirine monolayer plate was washed with ethanol, deionized ultra-filtered (DIUF) H_2O, EtOH again, and then dried under a stream of N_2.

Reaction Photoimmobilization

Upon photoredox reaction completion, crude reaction mixture aliquots (1 µL from 4 x 96-well plates) were directly pipetted onto the 384 diazirine monolayer spots. The 384-spot plate was then placed inside a UVP Cross-linker 1000L and irradiated for 10 min (λ= 365 nm).

SAMDI-MS Data Analysis

After reaction photoimmobilization, the array plates were treated with 2,4,6-trihydroxyacetophenone matrix (20 mg/mL in acetone), and dried using a stream of N_2. SAMDI arrays were analyzed *via* MALDI-TOF MS using an AB Sciex 5800 series instrument with 20kV accelerating voltage in positive reflector mode using 200 laser shots to each spot. The 1,920 spectra were acquired in ~2.5 h. The obtained spectra were analyzed in an automated fashion using the Applied Biosystems Data Explorer Software®.

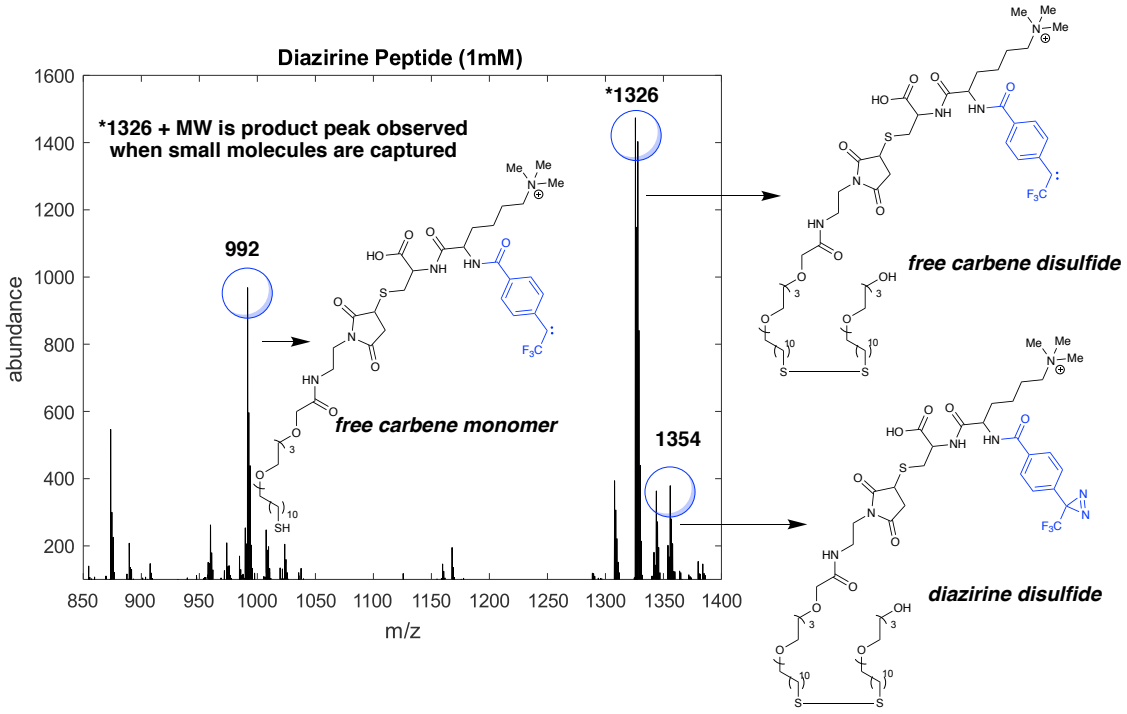


Figure S4. Diazirine monolayer spectrum. The MALDI's laser λ is 370 nm (short enough to induce photolytic cleavage) so you primarily see peak associated with free carbene.

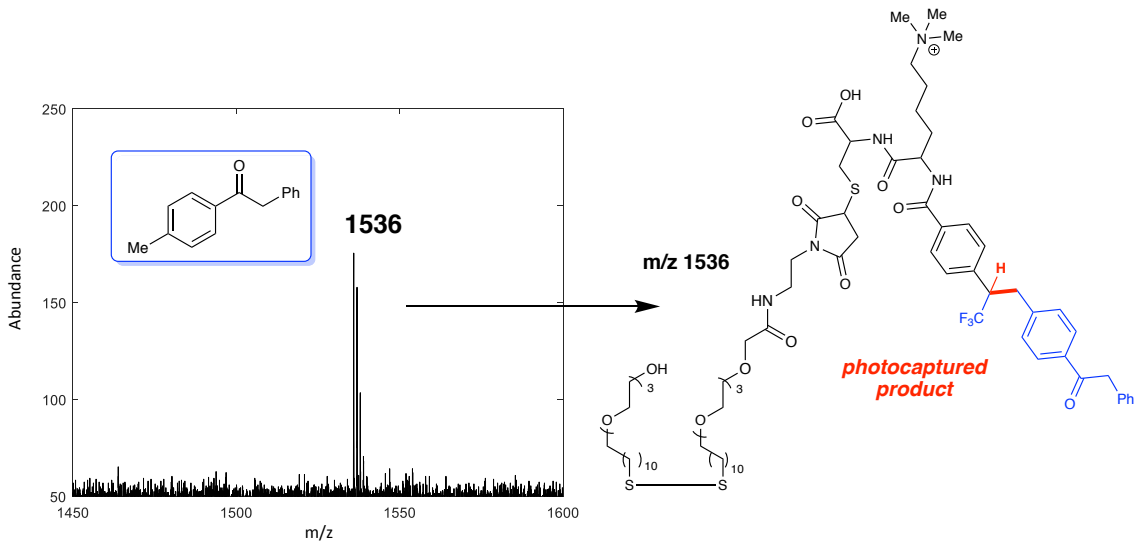


Figure S5. Authentic product photocaptured by diazirine-terminated SAM.

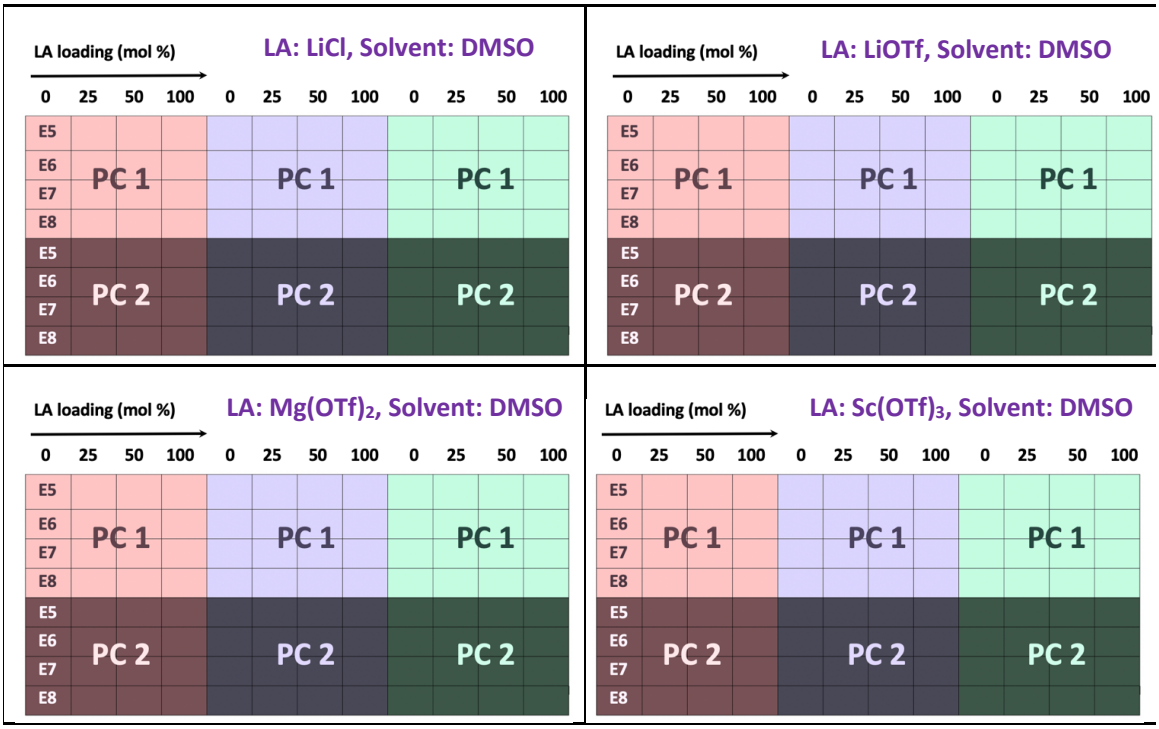
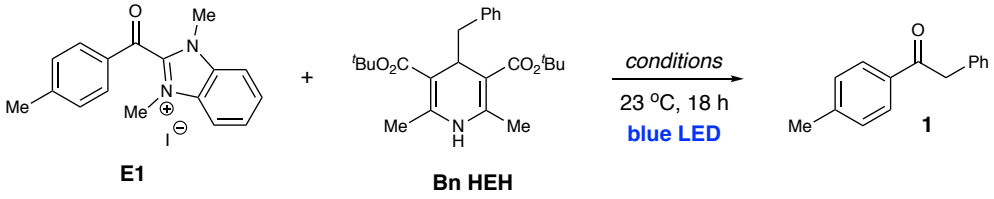


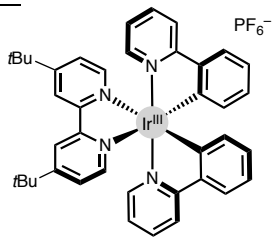
Figure S6. Example of a 384-spot analysis plate for electrophilic acyl sources **E5-E8**.

Hit Results and Spectra

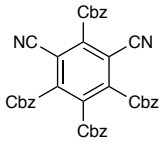
A) Scaled-up hit reactions



Hit entry	Photocatalyst	Lewis Acid	Solvent	Yield 1 (%)
1.	PC 1	LiCl (1.0 equiv.)	MeCN	70
2.	PC 1	LiCl (1.0 equiv.)	DMSO	53
3.	PC 1	LiOTf (0.25 equiv.)	DMSO	40
4.	PC 1	none	MeCN	41
5.	PC 1	none	DMSO	65
6.	PC 2	LiCl (1.0 equiv.)	MeCN	51



Ir(ppy)$_2$(dtbbpy), **PC 1**



4CzIPN, **PC 2**

B) Hit spectra

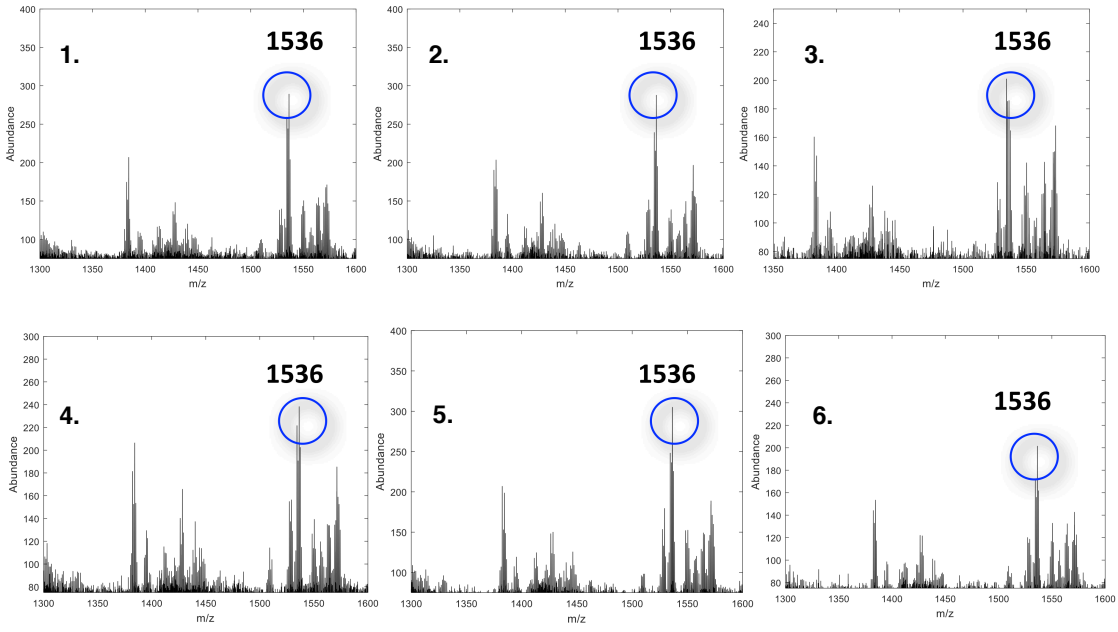


Figure S7. HTA results A) Scaled up hits (0.1 mmol **E1**, 0.15 mmol **Bn HEH**) B) Hit spectra

Limit of Detection

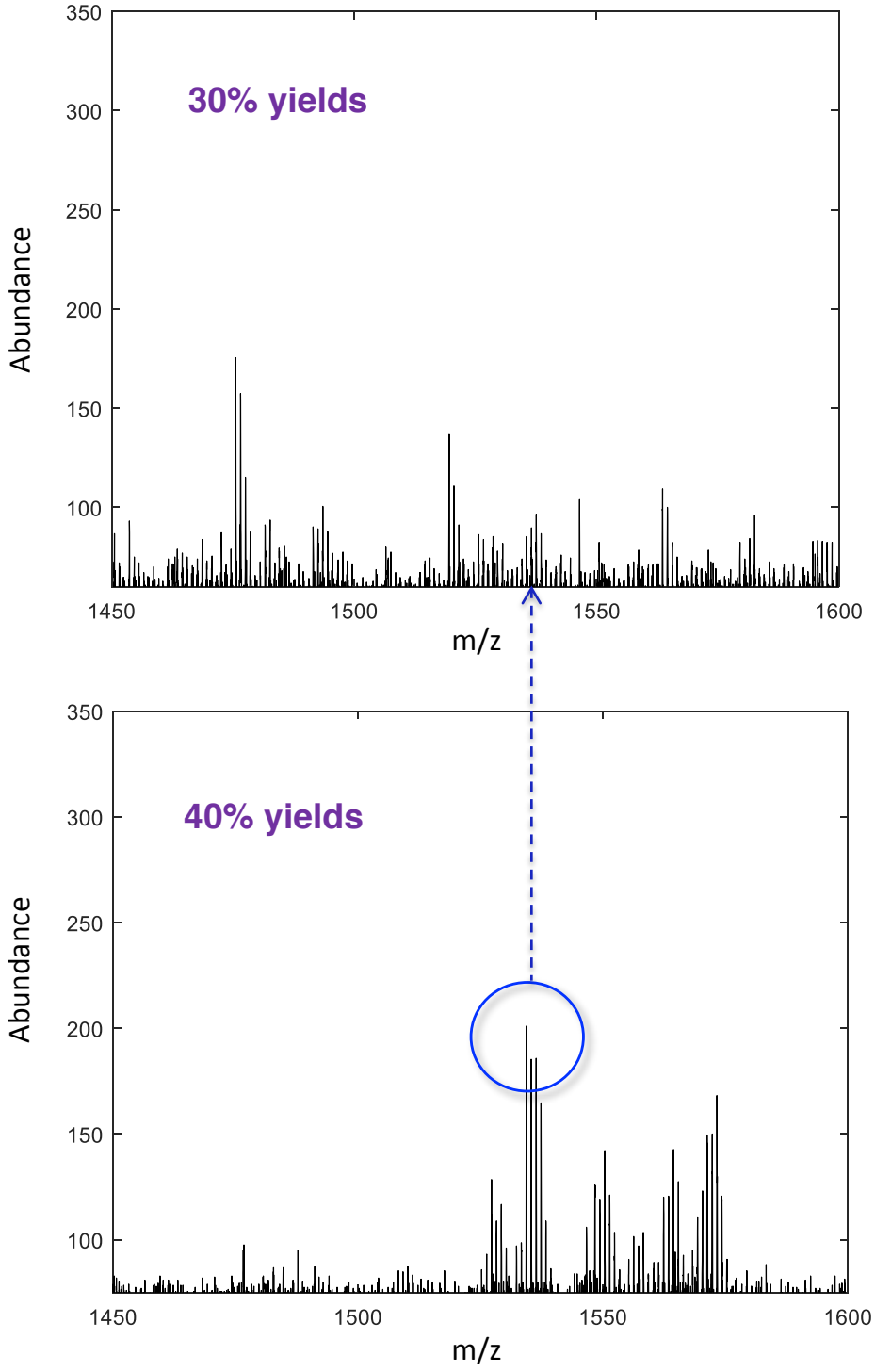
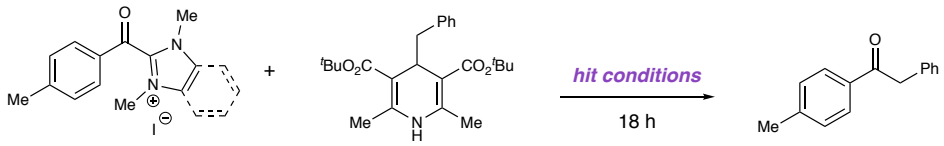


Figure S8. Limit of detection determined by comparing unpurified reaction mixture photocapture spectra for reaction with 30% isolated yield and 40% isolated yield after flash-column chromatography. Product peak is not visible at 30% yields but is visible at 40% yields.

Control Experiments & UV-Vis Spectra



E1 or **E2** | **Bn HEH** | **1**

hit conditions:	acyl benzimid. (**E1**)	PC 1	**blue LED**	LiCl (1.0 equiv.)	MeCN	70% yields
w/o light	acyl benzimid. (**E1**)	PC 1	dark	LiCl (1.0 equiv.)	MeCN	no reaction
w/o photocatalyst	acyl benzimid. (**E1**)	none	**blue LED**	LiCl (1.0 equiv.)	MeCN	13% yields
w/ TEMPO	acyl benzimid. (**E1**)	PC 1	**blue LED**	LiCl (1.0 equiv.)	MeCN	no reaction
w/ different acyl azolium	acyl imid. (**E2**)	PC 1	**blue LED**	LiCl (1.0 equiv.)	MeCN	23% yields

Figure S9. Control reactions run for best set of hit conditions. Reactions were run in parallel with 0.1 mmol of acyl azolium salt (**E1** or **E2**) and 1.5 equiv. **Bn HEH**.

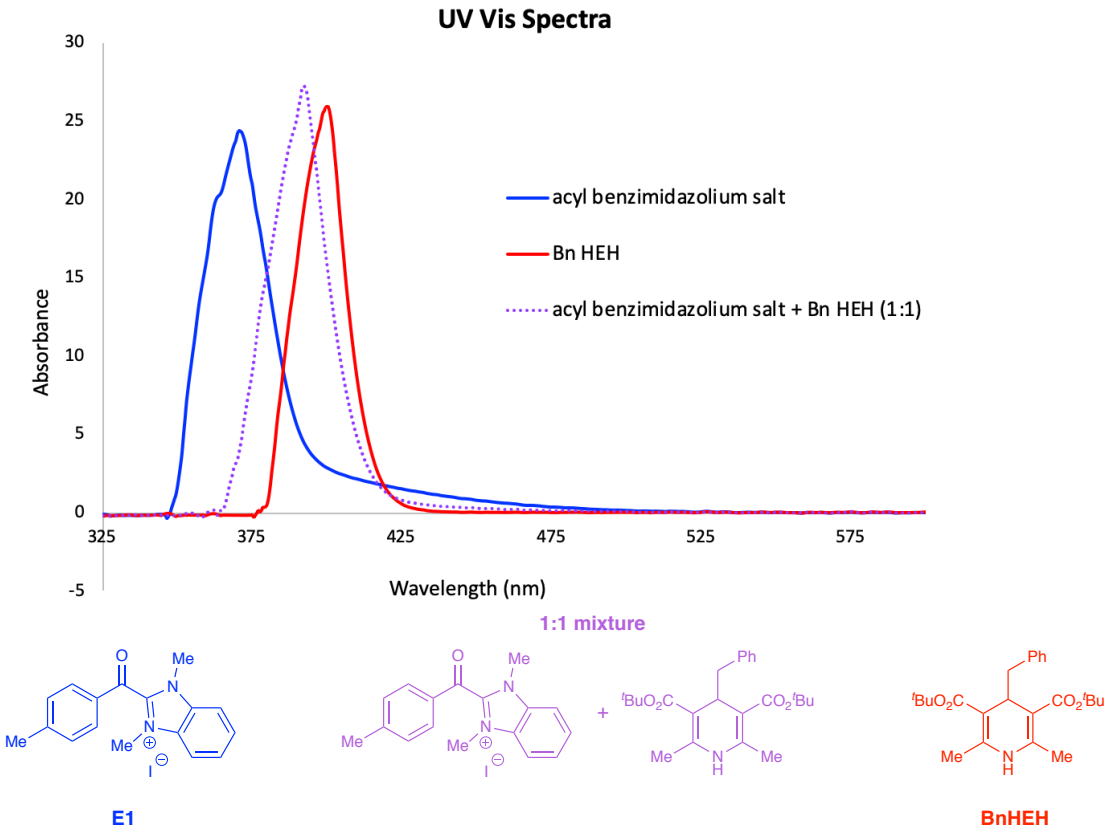


Figure S10. UV Vis Spectra for **E1** and **Bn HEH**.

Electrochemical Measurements

Electrochemical measurements were obtained with a standard set of conditions to maintain consistency. Cyclic voltammograms were collected with a Nuvant EZstat Pro potentiostat/galvanostat. Samples were prepared with 0.05 mmol of substrate in 5 mL of 0.1 M tetra-*n*-butylammonium hexafluorophosphate (freshly recrystallized) in dry, degassed DMSO. Measurements employed a platinum working electrode, platinum wire counter electrode, a Pt/Ag/AgCl pseudo reference electrode[3] and a scan rate of 250 mV/s. Two scan cycles were performed for each sample. Data reported correspond to the second scan cycle. Ferrocene was used as an internal standard ($E_{1/2}$ = + 0.40 V *v*s SCE).

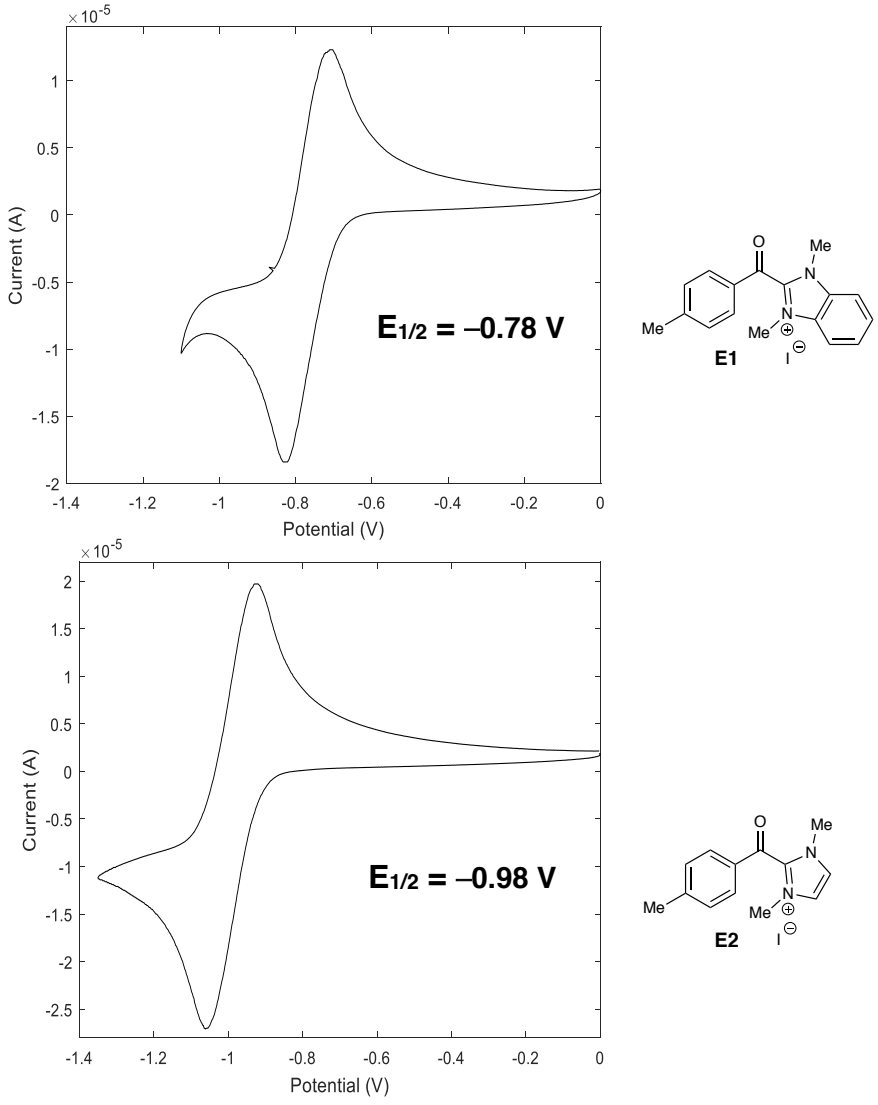
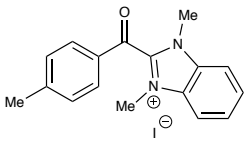


Figure S11. CV Spectra of Imidazolium and Benzimidazolium Acyl Azoliums. The benzimidazolium salt proved to have a more positive reduction potential ($E_{1/2}$ = –0.78 V *vs* SCE) than the imidazolium salt ($E_{1/2}$ = –0.98 V *vs* SCE) which indicates that the benzimidazolium salt is more easily reduced.

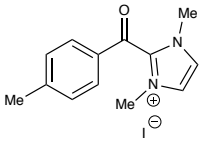
False Negative Check

Table S1. Scaled-up non-hit reactions to verify method (0.1 mmol ketyl radical precursor, 0.15 alkyl radical precursor)

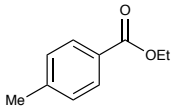
Entry	Ketyl Radical Precursor	Alkyl Radical Precursor	Photocatalyst	Lewis Acid	Solvent	Yield 1 (%)
1	**E1**	**BnSi**	PC1	LiCl (1.0 equiv.)	MeCN	29%
2.	**E1**	**BnCOOH**	PC1	LiCl (1.0 equiv.)	MeCN	NR
3.	**E2**	**BnHEH**	PC1	LiCl (1.0 equiv.)	MeCN	23%
4.	**E2**	**BnHEH**	PC2	LiCl (1.0 equiv.)	MeCN	11%
5.	**E3**	**BnHEH**	PC1	LiCl (1.0 equiv.)	MeCN	NR
6.	**E4**	**BnHEH**	PC1	LiCl (1.0 equiv.)	MeCN	NR
7.	**E5**	**BnHEH**	PC1	LiCl (1.0 equiv.)	MeCN	NR
8.	**E6**	**BnHEH**	PC1	LiCl (1.0 equiv.)	MeCN	NR
9.	**E7**	**BnHEH**	PC1	LiCl (1.0 equiv.)	MeCN	NR
10.	**E8**	**BnHEH**	PC1	LiCl (1.0 equiv.)	MeCN	NR



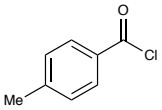
E1



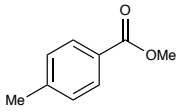
E2



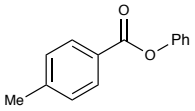
E3



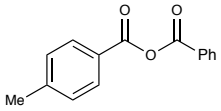
E4



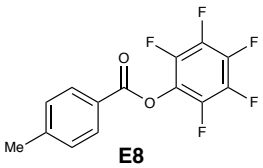
E5



E6

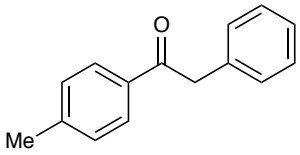


E7

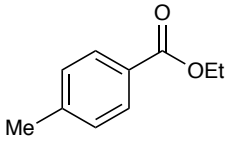


E8

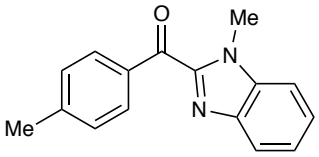
Preparations for Substrates and Products



2-phenyl-1-(*p*-tolyl)ethan-1-one (1): Authentic product for photocapture was prepared according to Scammells et al.[4] Analytical data matches that of previously reported spectra.[4] Analytical Data: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.8 Hz, 2H), 7.33−7.28 (m, 3H), 7.23 (d, *J* = 8.1 Hz, 4H), 4.24 (s, 2H), 2.38 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.3, 144.0, 134.8, 134.2, 129.5, 129.4, 128.8, 128.7, 126.8, 45.5, 21.7. HRMS (ESI): Mass calcd. $C_{15}H_{14}O$ for $[M+H]^+$: 211.1078; found 211.0793.

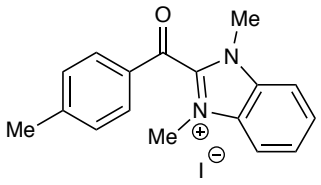


ethyl 4-methylbenzoate (E3): Prepared according to Selway et al.[5] Analytical data matches that of previously reported spectra.[5]
Analytical Data: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.2 Hz , 2H), 7.23 (d, *J* = 8.0 Hz , 2H), 4.36 (q, *J* = 7.5 Hz, 2H), 2.41 (s, 3H), 1.39 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.7, 143.4, 129.6, 129.0, 127.8, 60.8, 21.7, 14.4.



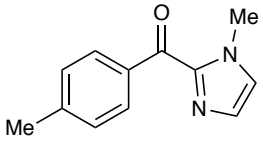
(1-methyl-1*H*-benzo[*d*]imidazol-2-yl)(*p*-tolyl)methanone: Method was adapted from literature report.[6] *n*BuLi (1.6 M, n-hexane solution, 18.8 mL, 30.1 mmol) was added slowly to a stirred solution of TMEDA (4.80 mL, 31.8 mmol) in THF (10 mL) at −78 °C under inert atmosphere. 1-methylbenzimidazole (3.30 g, 25.1 mmol) dissolved in THF (10 mL) was added slowly to the mixture at −78 °C, and the reaction was permitted to stir for 1 h at this temperature. A solution of **E3** (4.27 g, 26.0 mmol) in THF (10 mL) was added dropwise over a period of 1 h at −78 °C. Stirring continued for another 1 h at this temperature, after which the reaction mixture was allowed to warm to room temperature and stir for 12 h. Aq. sat. $NaHCO_3$ solution (30 mL) and Et_2O (30 mL) were added to quench the reaction mixture. The organic layer was separated, and the aqueous layer was washed with Et_2O (30 mL). The organic layers were combined and dried over Na_2SO_4. After concentration under reduced pressure, the crude product was purified by silica gel column chromatography (EtOAc/*n*-hexane= 1:3). Purification yielded **3**, an off-white solid (3.3 g, 51%).

Analytical Data: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.18 (d, J = 7.4 Hz, 2H), 7.85 (d, J = 7.4 Hz, 2H), 7.44–7.35 (m, 1H), 7.34–7.28 (m, 1H), 7.24 (s, 1H), 7.18 (s, 1H), 4.07 (s, 3H), 2.37 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 186.1, 146.9, 144.5, 141.9, 136.5, 134.3, 131.3, 129.1, 125.5, 123.5, 122.0, 110.4, 32.2, 21.8. LRMS (ESI): Mass calcd. $C_{16}H_{14}N_2O$ for $[M+H]^+$: 251; found 251.



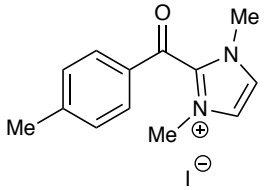
1,3-dimethyl-2-(4-methylbenzoyl)-1*H*-benzo[*d*]imidazol-3-ium iodide (E1): Excess iodomethane (3.30 mL, 52 mmol) was added to **(1-methyl-1*H*-benzo[*d*]imidazol-2-yl)(*p*-tolyl)methanone** (2.50 g, 10.0 mmol) dissolved in DMF (10 mL) and refluxed at 85 °C for 12 h in a sealed tube. Product was filtered with Et_2O washing yielding **6**, a bright yellow solid (3.8 g, 97%)

Analytical Data: ^{1}H NMR (500 MHz, CD_3CN) δ 7.97 (dd, J = 6.2, 3.1 Hz, 2H), 7.91 (d, J = 8.6 Hz, 2H), 7.84 (dd, J = 6.4, 3.1 Hz, 2H), 7.51 (d, J = 7.7 Hz, 2H), 3.95 (s, 6H), 2.51 (s, 3H). ^{13}C NMR (126 MHz, CD_3CN) δ 180.8, 150.3, 144.57, 132.7, 132.3, 131.4, 131.2, 128.9, 114.4, 34.3, 21.8. LRMS (ESI): Mass calcd. $[C_{17}H_{17}N_2O]^+I^-$ for $[M]^+$: 265; found 265.



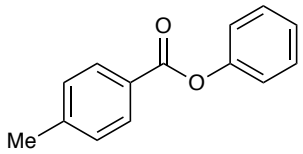
(1-methyl-1*H*-imidazol-2-yl)(*p*-tolyl)methanone: Prepared according to Gandhi et al.[7] Analytical data matches that of previously reported spectra.[7]

Analytical Data: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.20 (d, J = 8.1 Hz, 2H), 7.28 (d, J = 8.4 Hz, 2H), 7.22 (s, 1H), 7.09 (s, 1H), 4.07 (s, 3H), 2.42 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 183.9, 143.5, 134.7, 130.9, 129.2, 128.8, 126.6, 36.4, 21.7.

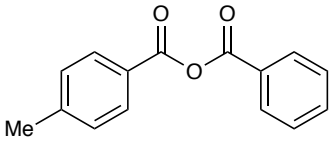


1,3-dimethyl-2-(4-methylbenzoyl)-1*H*-imidazol-3-ium (E2): Excess iodomethane (3.30 mL, 52.0 mmol) was added to **(1-methyl-1*H*-imidazol-2-yl)(*p*-tolyl)methanone** (2.00 g, 10.0 mmol) dissolved in EtOAc (10 mL) and refluxed at 75 °C for 24 h in a sealed tube. Product was filtered with Et_2O washing to yield **5**, a light yellow-green solid (3.3 g, 96%). Analytical data matches that of previously reported spectra.[7]

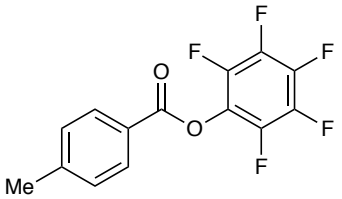
Analytical Data: ^{1}H NMR (500 MHz, CD_3CN) δ 7.81 (d, J = 8.1 Hz, 2H), 7.65 (s, 2H), 7.48 (d, J = 8.1 Hz, 2H), 3.77 (s, 6H), 2.48 (s, 3H). ^{13}C NMR (126 MHz, CD_3CN) δ 180.4, 149.2, 140.0, 132.7, 131.0, 125.6, 37.7, 21.6.



phenyl 4-methylbenzoate (E6): Prepared according to Van Der Plas et al.[8] Analytical data matches that of previously reported spectra.[8]
Analytical Data: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 (d, *J* = 7.8 Hz, 2H), 7.41 (t, *J* = 7.5 Hz, 2H), 7.28 (d, *J* = 8.3 Hz, 2H), 7.19 (d, *J* = 7.5 Hz, 2H), 2.44 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.3, 151.1, 144.4, 130.2, 129.5, 129.3, 126.8, 125.8, 121.8.

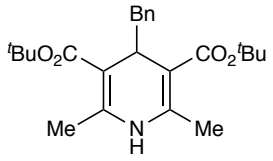


benzoic 4-methylbenzoic anhydride (E7): To 4-methyl benzoyl chloride (10 mL, 75.6 mmol) and benzoic acid (9.70 g, 79.4 mmol), Et_3N (11 mL, 79.4 mmol) was added and the reaction was allowed to stir for 3 h at room temperature. Upon completion, CH_2Cl_2 (100 mL) was added to the reaction mixture followed by aq. sat. $NaHCO_3$ (50 mL) solution. The mixture was washed with H_2O (2 x 50 mL), brine (1 x 50 mL), and dried over Na_2SO_4. After concentration under reduced pressure, the crude product was purified by silica gel column chromatography (EtOAc/*n*-hexane= 1:9). Purification yielded **8**, an off-white waxy solid, (9.8 g, 54%).
Analytical Data: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.2 Hz, 2H), 8.04 (d, *J* = 8.0 Hz, 2H), 7.67 (t, *J* = 8.2 Hz, 1H), 7.53 (t, *J* = 7.6 Hz, 2H), 7.32 (d, *J* = 7.6 Hz, 2H), 2.46 (s, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 162.5, 162.4, 145.7, 134.5, 130.7, 130.6, 129.6, 129.6, 129.0, 128.9, 128.9, 126.1, 21.9. LRMS (ESI): Mass calcd. $C_{15}H_{12}O_3$ for $[M+H]^+$: 241; found 241.

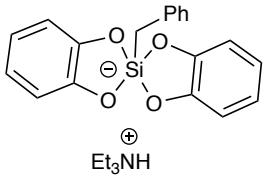


perfluorophenyl 4-methylbenzoate (E8): Method was adapted from literature report.[9] To 4-methylbenzoic acid (3.0 g, 22 mmol) and 2,3,4,5,6-pentafluorophenol (4.5 g, 24 mmol) were dissolved in CH_2Cl_2 (120 mL), EDC (6.3 g, 33 mmol) and DMAP (540 mg, 4.4 mmol) were added at 0 °C. The reaction mixture was allowed to warm up to room temperature and stir for 1 h. Upon completion, the reaction was quenched with aq. sat. NH_4Cl solution (50 mL). The mixture was extracted with EtOAc (2 x 50 mL), washed with brine (1 x 50 mL) and the combined extracts were dried over Na_2SO_4. After concentration under reduced pressure, the crude product was purified by silica gel column chromatography (EtOAc/*n*-

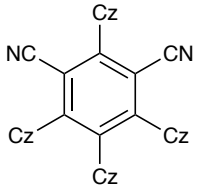
hexane= 1:9). Purification yielded **9**, a white solid (6.5 g, 98%). Analytical Data: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 (d, J = 7.4 Hz, 2H), 7.35 (d, J = 7.4 Hz, 2H), 2.47 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.6, 145.9, 142.5, 140.5, 140.5, 140.4, 139.0, 138.5, 137.0, 130.8, 129.6, 125.5, 124.2, 21.9. LRMS (ESI): Mass calcd. $C_{14}H_7F_5O_2$ for $[M+H]^+$: 303; found 303.



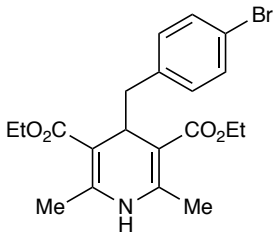
di-*tert*-butyl4-benzyl-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (Bn HEH): Prepared according to Li et al.[10] Analytical data matches that of previously reported spectra.[10] Analytical Data: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41–7.32 (m, 3H), 7.25–7.21 (m, 2H), 5.52 (s, 1H), 4.35 (t, J = 5.3 Hz, 1H), 2.75 (d, J = 5.8 Hz, 2H), 2.36 (s, 6H), 1.62 (s, 18H).^{13}C NMR (126 MHz, $CDCl_3$) δ 167.1, 144.5, 139.5, 130.2, 127.4, 125.6, 103.3, 41.9, 35.9, 28.3, 19.2.



Triethylammonium benzylbis(methyl-2-hydroxyisobuyro)silicate (Bn Si): Prepared according to Molander et al.[11] Analytical data matches that of previously reported spectra.[11] Analytical Data ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.02–6.98 (m, 2H), 6.92–6.88 (m, 1H), 6.84 (d, J = 8.0 Hz, 2H), 6.71–6.66 (m, 8H), 3.03 (q, J = 7.4 Hz, 6H), 2.24 (s, 1H), 1.11 (t, J = 7.7 Hz, 9H).^{13}C NMR (126 MHz, $CDCl_3$) δ 149.3, 142.2, 129.1, 127.4, 123.0, 118.8, 110.8, 46.2, 26.1, 8.5, 8.4.



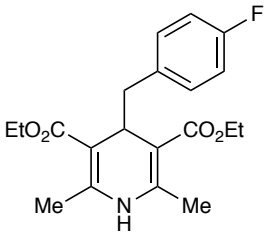
1,2,3,5-Tetrakis(carbazol-9-yl)-4,6-dicyanobenzene (4CzIPN, PC 2): Prepared according to Molander et al.[12] Analytical data matches that of previously reported spectra.[12]
Analytical Data: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.23 (d, J = 7.7 Hz, 2H), 7.74–7.67 (m, 8H), 7.51–7.47 (m, 2H), 7.33 (d, J = 7.6 Hz, 2H), 7.25–7.20 (m, 4H), 7.12–7.06 (m, 8H), 6.86–6.80 (m, 4H), 6.66–6.62 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.2, 144.6, 140.0, 138.2, 137.0, 134.8, 127.0, 125.8, 125.0, 124.8, 124.6, 123.9, 122.4, 122.0, 121.4, 121.0, 120.4, 119.7, 116.4, 111.6, 110.0, 109.5, 109.4.



diethyl 4-(4-fluorobenzyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (4-Br Bn HEH):

Prepared according to Liu et al.[13] Analytical data matches that of previously reported spectra.[13]

Analytical Data: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 (d, J = 8.1 Hz, 2H), 6.89 (d, J = 8.1 Hz, 2H), 5.19 (s, 1H), 4.18 (t, J = 5.3 Hz, 1H), 4.12–4.03 (m, 4H), 2.54 (d, J = 5.6 Hz, 2H), 2.17 (s, 6H), 1.25 (t, J = 7.1 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.7, 145.4, 138.3, 131.8, 130.3, 119.7, 101.6, 59.7, 41.6, 35.4, 19.3, 14.4, 14.2.



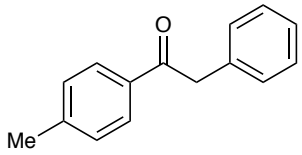
diethyl 4-(4-fluorobenzyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (4-F Bn HEH):

Prepared according to Tang et al.[14] Analytical data matches that of previously reported spectra.[14]

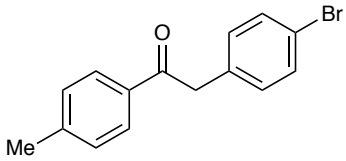
Analytical Data: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.98–6.93 (m, 2H), 5.18 (s, 1H), 4.16 (t, J = 5.3 Hz, 1H), 4.13–4.03 (m, 4H), 2.55 (d, J = 5.6 Hz, 2H), 2.17 (s, 6H), 1.25 (t, J = 7.1 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.7, 162.5, 160.6, 145.3, 134.9, 134.9, 131.4, 131.3, 114.0, 113.9, 101.7, 59.7, 41.3, 35.5, 19.3, 14.4, 14.3.

General Procedure for Radical-Radical Coupling:

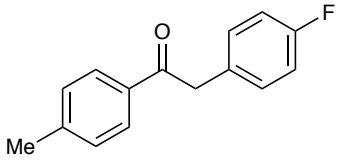
In the glovebox, the acyl benzimidazolium salt **E1** (78 mg, 0.2 mmol, 1.0 equiv.) LiCl (8.5 mg, 1.0 equiv.), dtbbpy-Ir (1.8 mg, 0.01 equiv.), and Hantszch ester (1.5 equiv) were added to a flame dried 2 dram vial. The reaction was equipped with magnetic stirbar, capped, taken out of the glovebox, and charged with 2.0 mL (0.1 M) MeCN. The vial was then placed in between three 40W Kessil blue LED lights (~3 inches away) and irradiated for 24 hours (with a small fan placed for cooling). Upon complete consumption of the acyl benzimidazolium, the reaction mixture was concentrated onto silica gel under reduced pressure. This silica was loaded onto a column of silica gel and the desired product isolated *via* flash column chromatography (2–20% EtOAc/*n*-hexane).



2-phenyl-1-(*p*-tolyl)ethan-1-one (1):
Prepared according to the general procedure, and isolated as a white solid (70%). Analytical data matches that of previously reported spectra.[4,15]
Analytical Data: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.8 Hz, 2H), 7.33–7.28 (m, 3H), 7.23 (d, *J* = 8.1 Hz, 4H), 4.24 (s, 2H), 2.38 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.3, 144.0, 134.8, 134.2, 129.5, 129.4, 128.8, 128.7, 126.8, 45.5, 21.7. HRMS (ESI): Mass calcd. $C_{15}H_{14}O$ for $[M+H]^+$: 211.1078; found 211.0793.



2-(4-bromophenyl)-1-(*p*-tolyl)-ethan-1-one (2):
Prepared according to the general procedure, and isolated as a white solid (52%). Analytical data matches that of previously reported spectra.[15]
Analytical Data: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.0 Hz, 2H), 7.45 (d, *J* = 8.4 Hz, 2H), 7.28–7.26 (m, 2H), 7.14 (d, *J* = 8.7 Hz, 2H), 4.22 (s, 2H), 2.42 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 196.7, 144.3, 133.9, 133.7, 131.7, 131.3, 129.4, 128.7, 120.9, 44.7, 21.7. HRMS (ESI): Mass calcd. $C_{15}H_{13}BrO$ for $[M+H]^+$: 289.02, found 289.0223.



2-(4-fluorophenyl)-1-(*p*-tolyl)-ethan-1-one (3):
Prepared according to the general procedure, and isolated as a white solid (54%). Analytical data matches that of previously reported spectra.[15]
Analytical Data: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.9 Hz, 2H), 7.28–7.26 (m, 2H), 7.24–7.19 (m, 2H), 7.02 (t, *J* = 8.4 Hz, 2H), 4.24 (s, 2H), 2.41 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 197.1, 162.9, 160.9, 144.2, 134.0, 131.1, 131.0, 130.4, 130.4, 129.4, 128.7, 115.6, 115.4, 44.4, 21.7. HRMS (ESI): Mass calcd. $C_{15}H_{13}FO$ for $[M+H]^+$: 229.10, found 229.1023.

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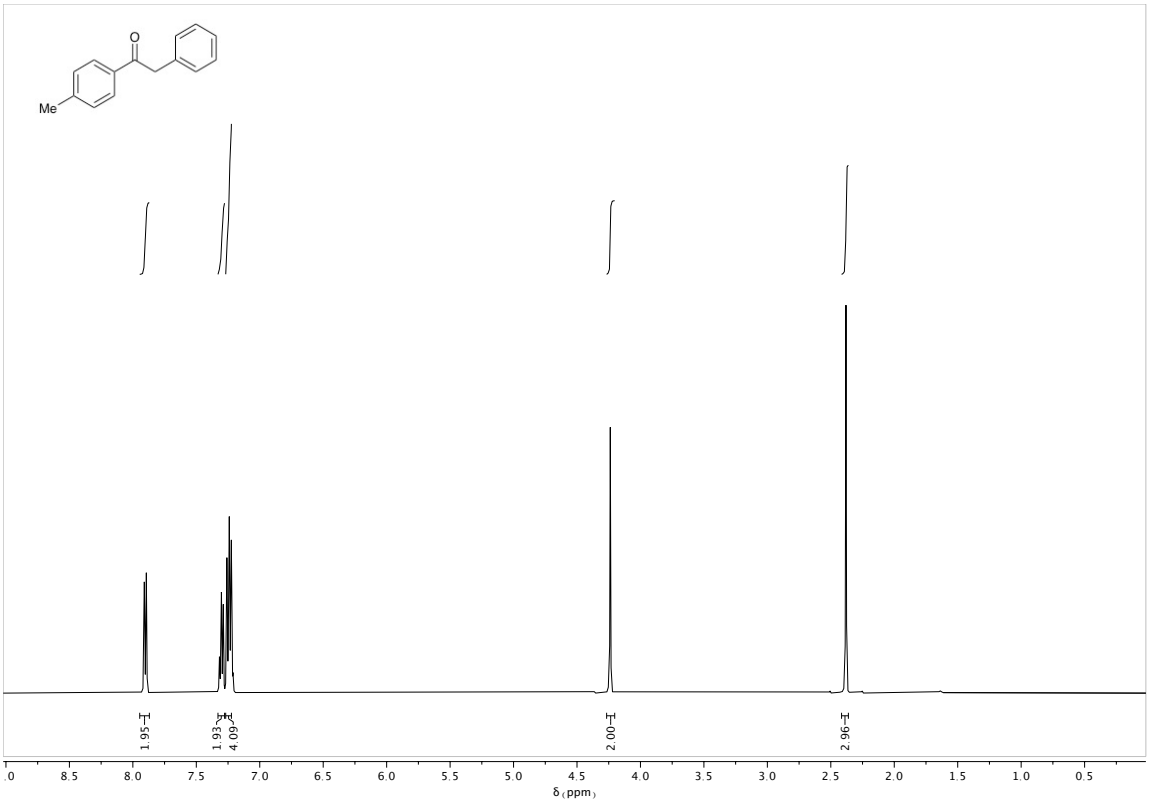
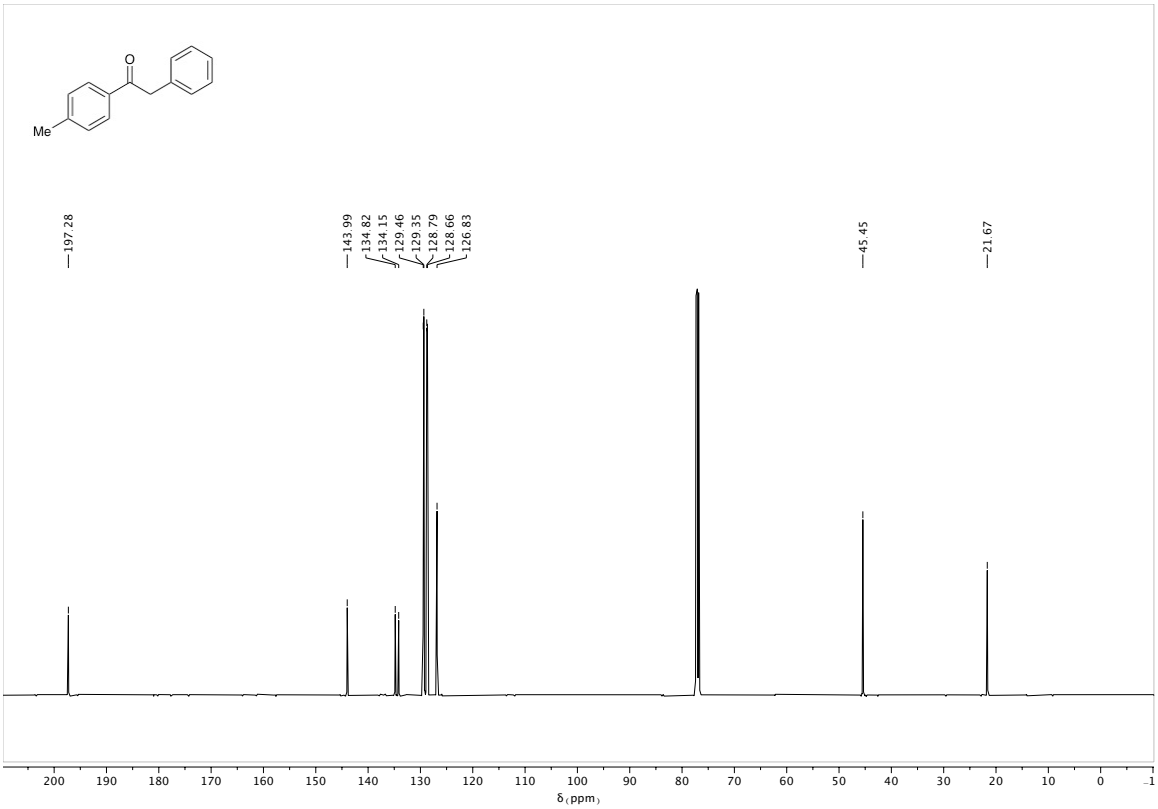
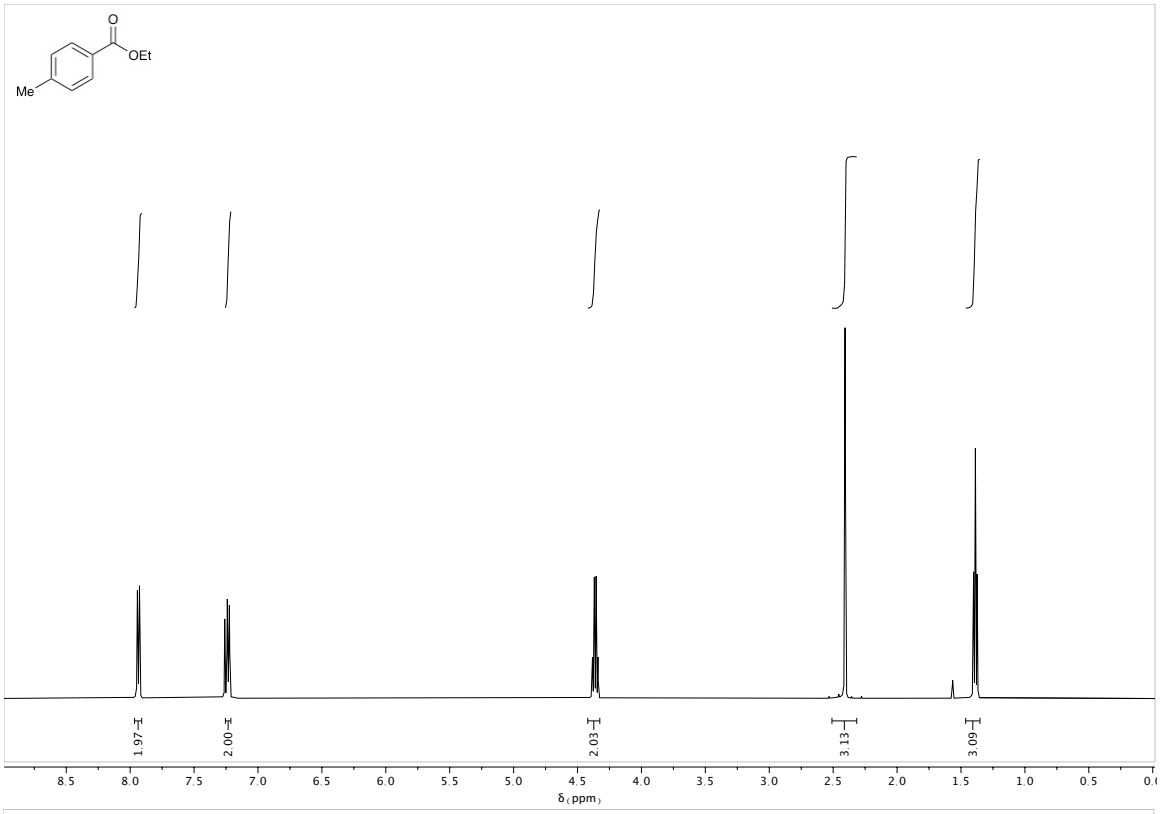
[1]H and [13]C NMR Spectra

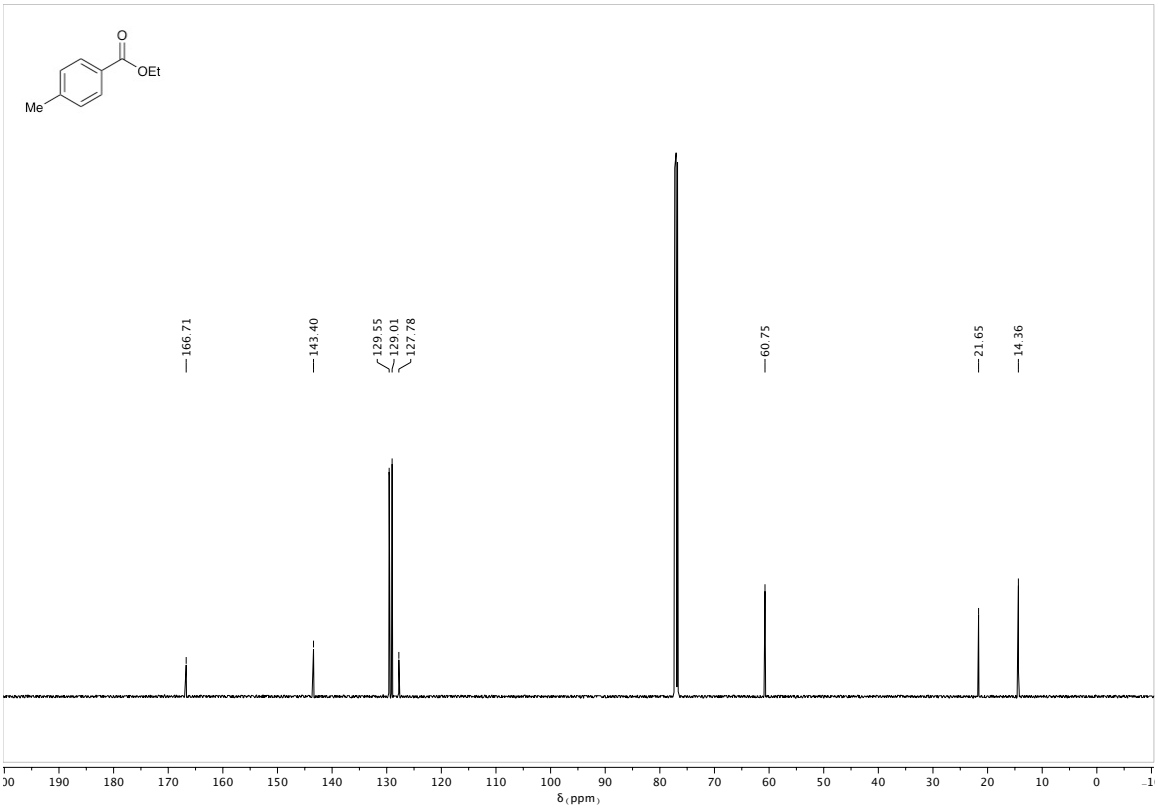
2-phenyl-1-(*p*-tolyl)ethan-1-one (1):



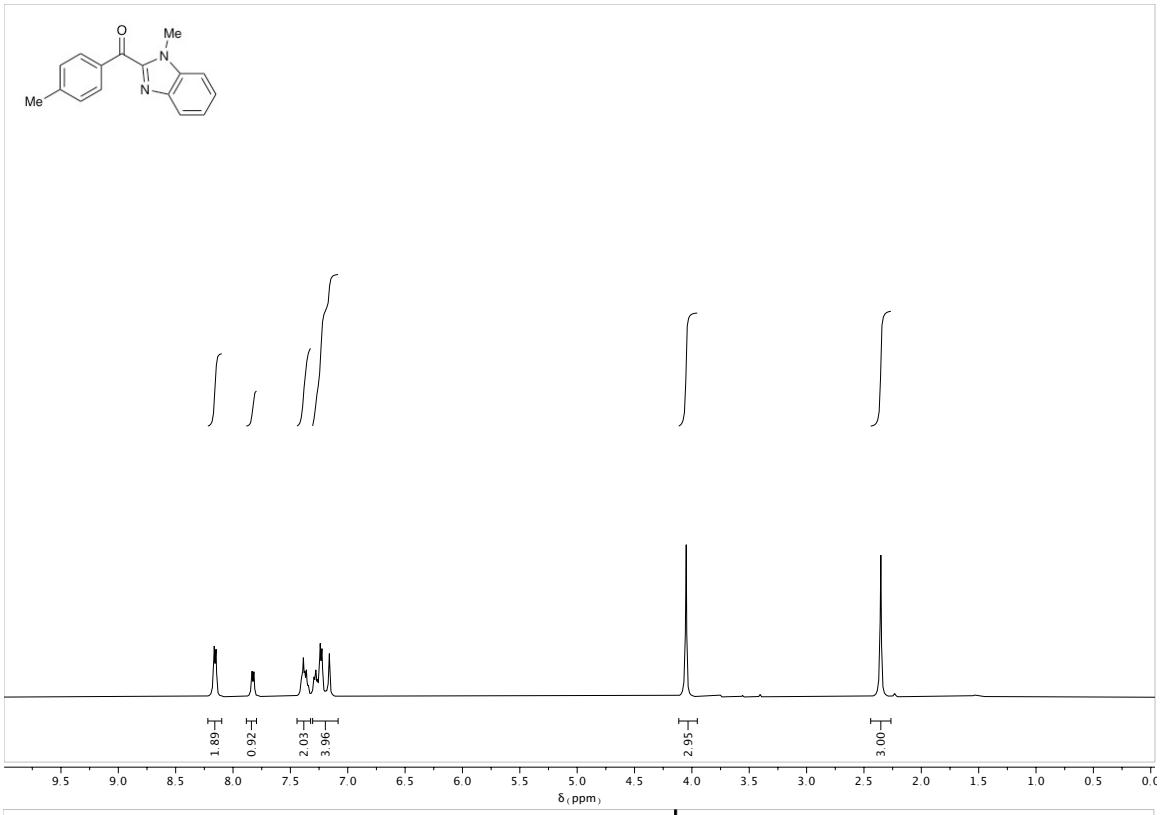


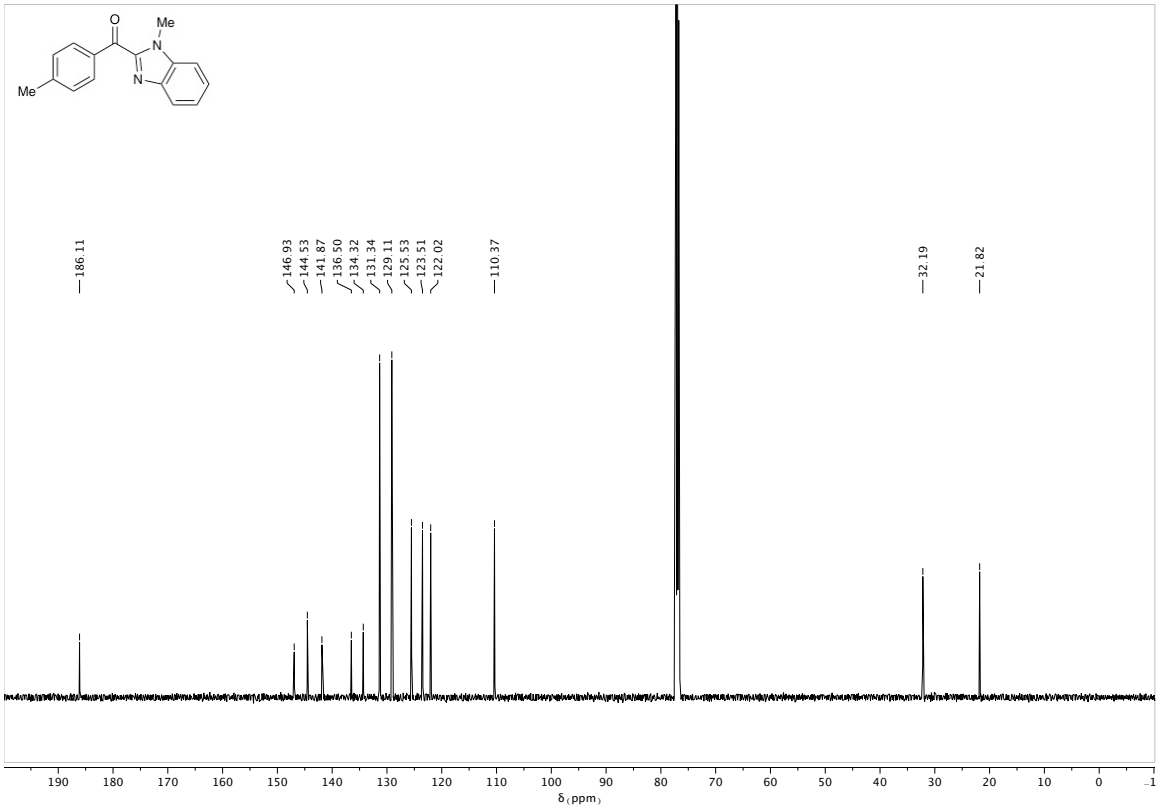
ethyl 4-methylbenzoate (E3):



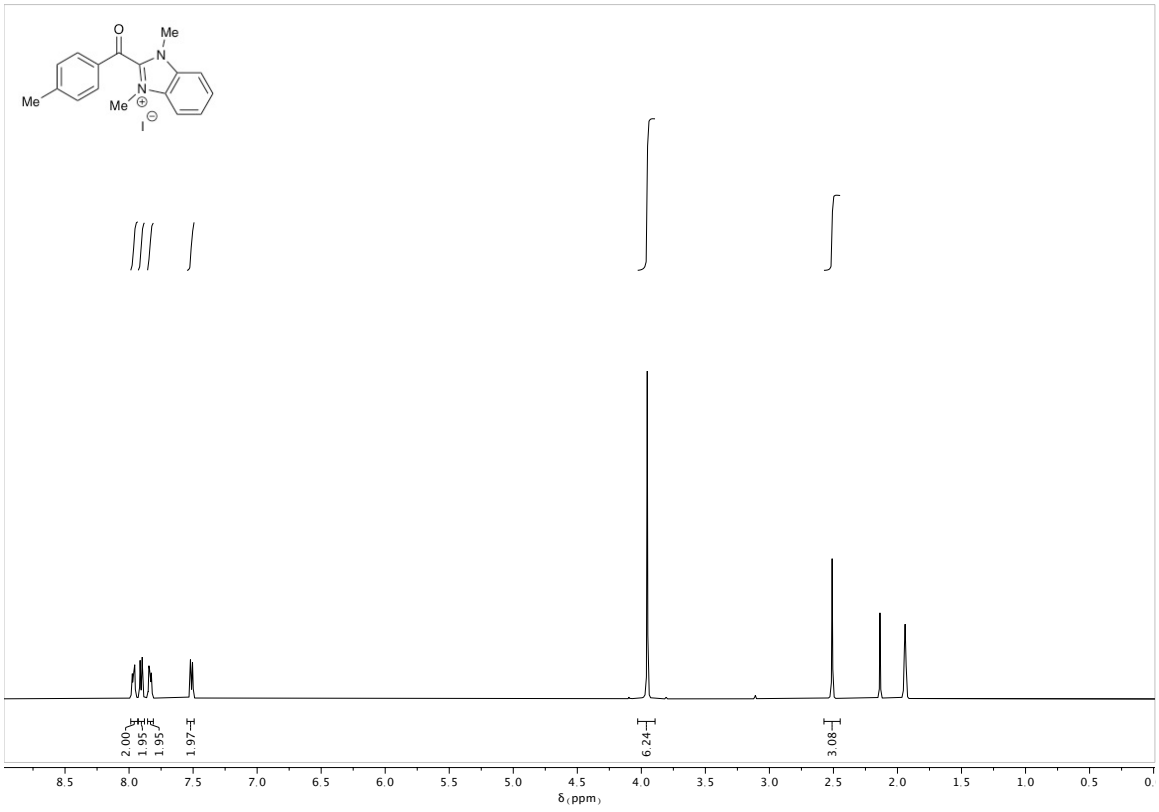


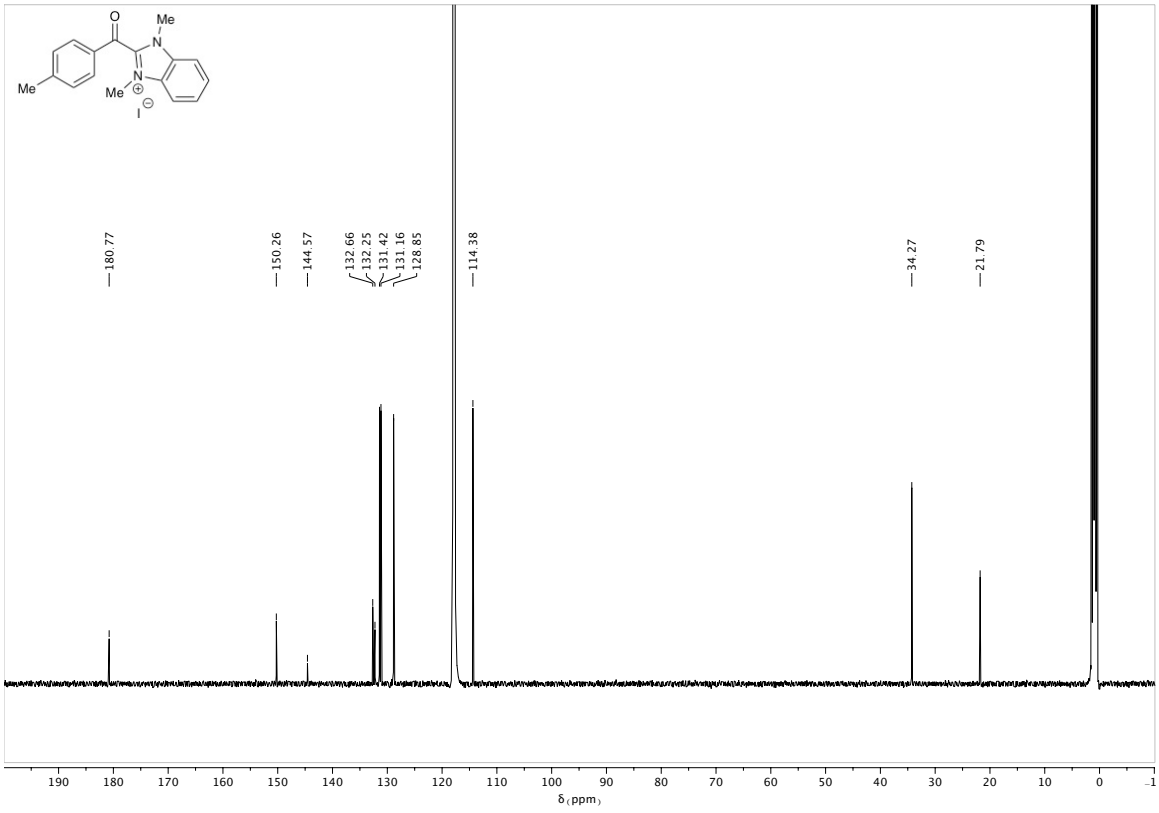
(1-methyl-1*H*-benzo[*d*]imidazol-2-yl)(*p*-tolyl)methanone:



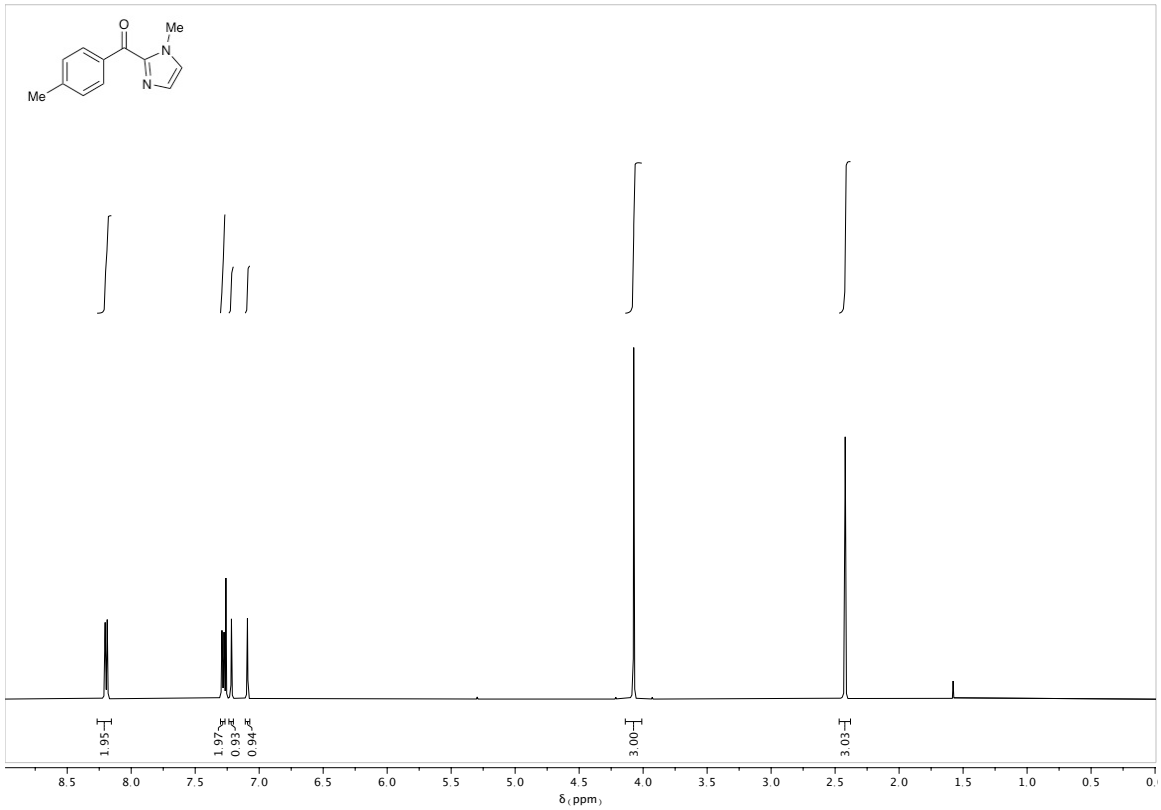


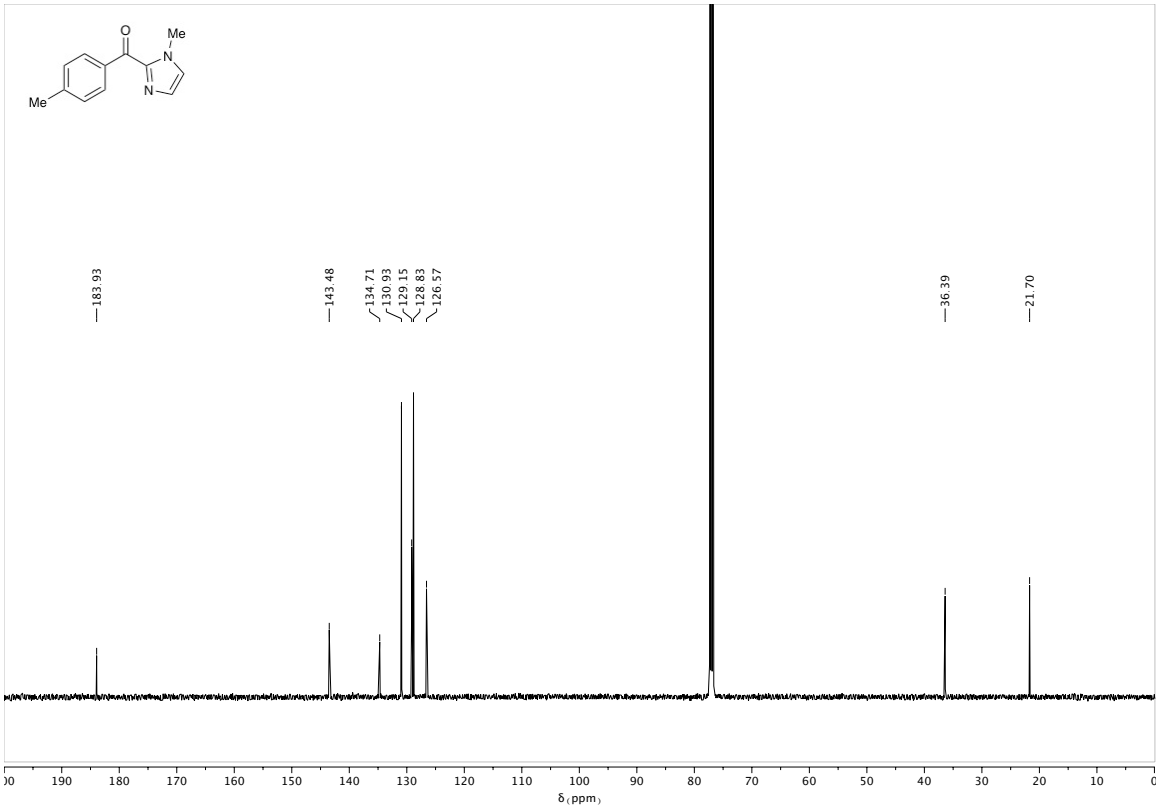
1,3-dimethyl-2-(4-methylbenzoyl)-1*H*-benzo[*d*]imidazol-3-ium iodide (E1):



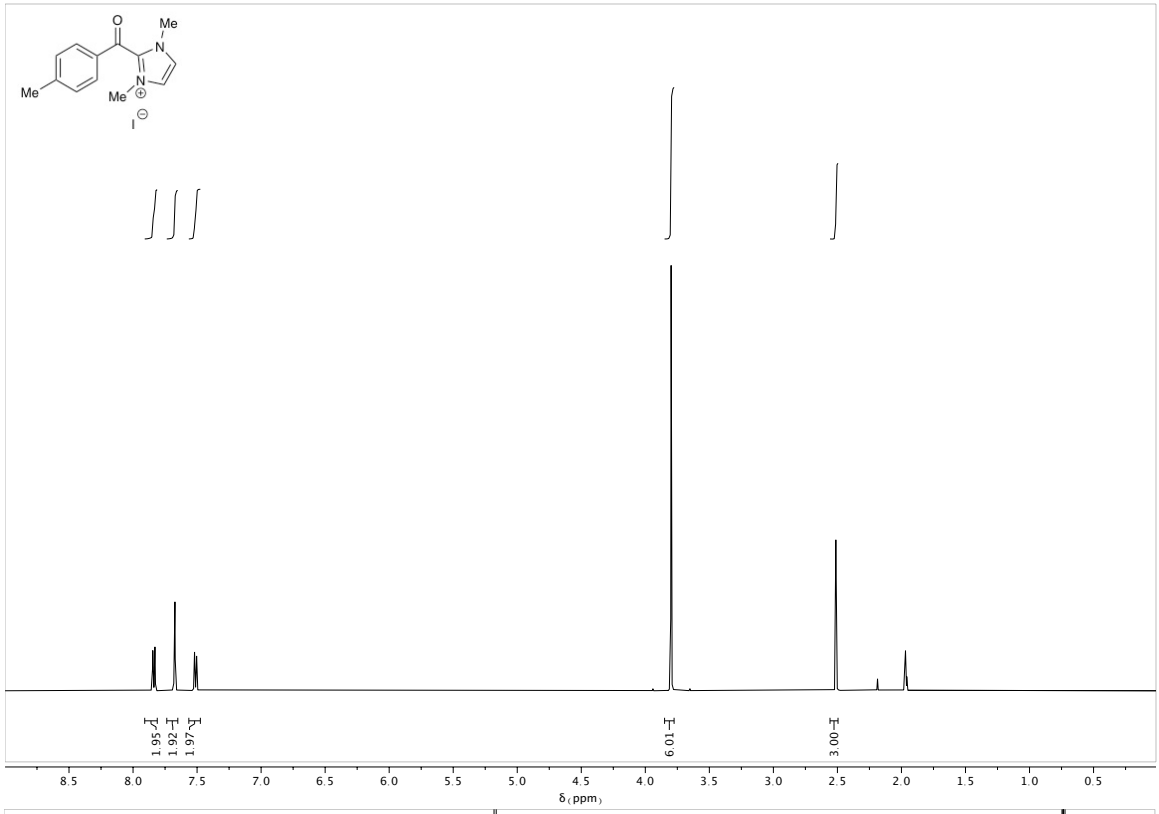


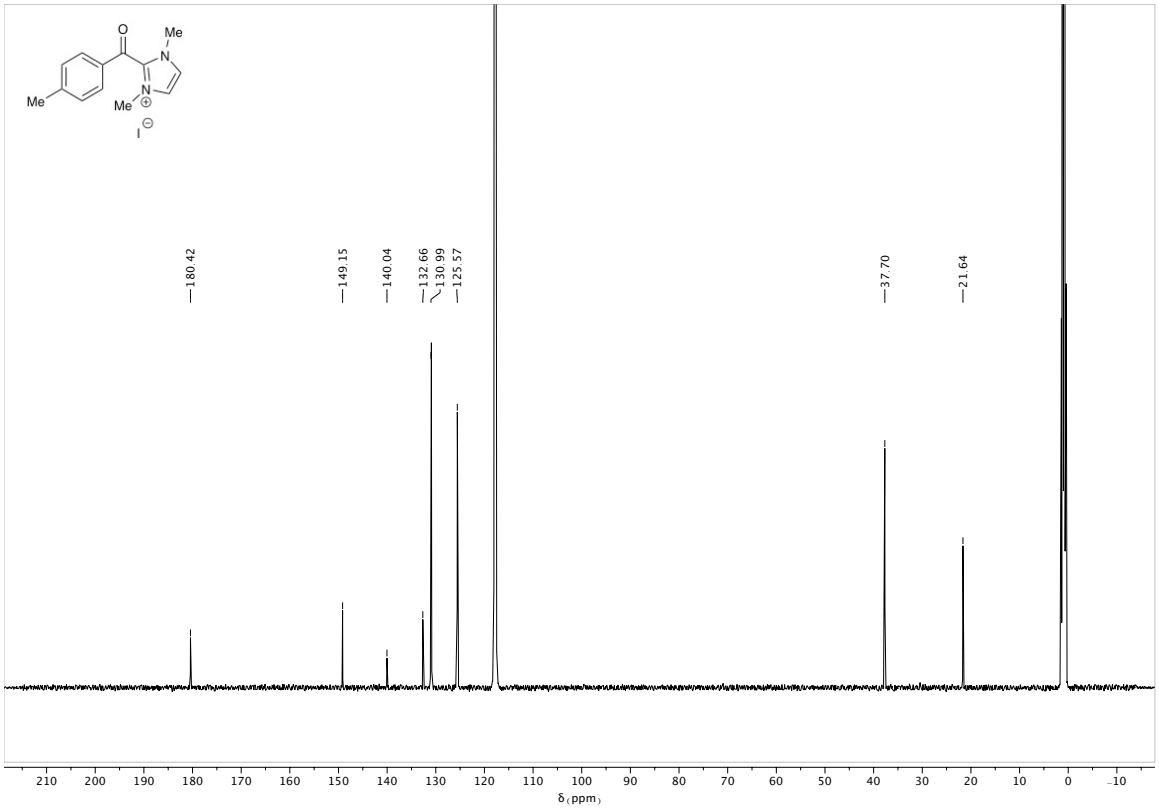
(1-methyl-1*H*-imidazol-2-yl)(*p*-tolyl)methanone:



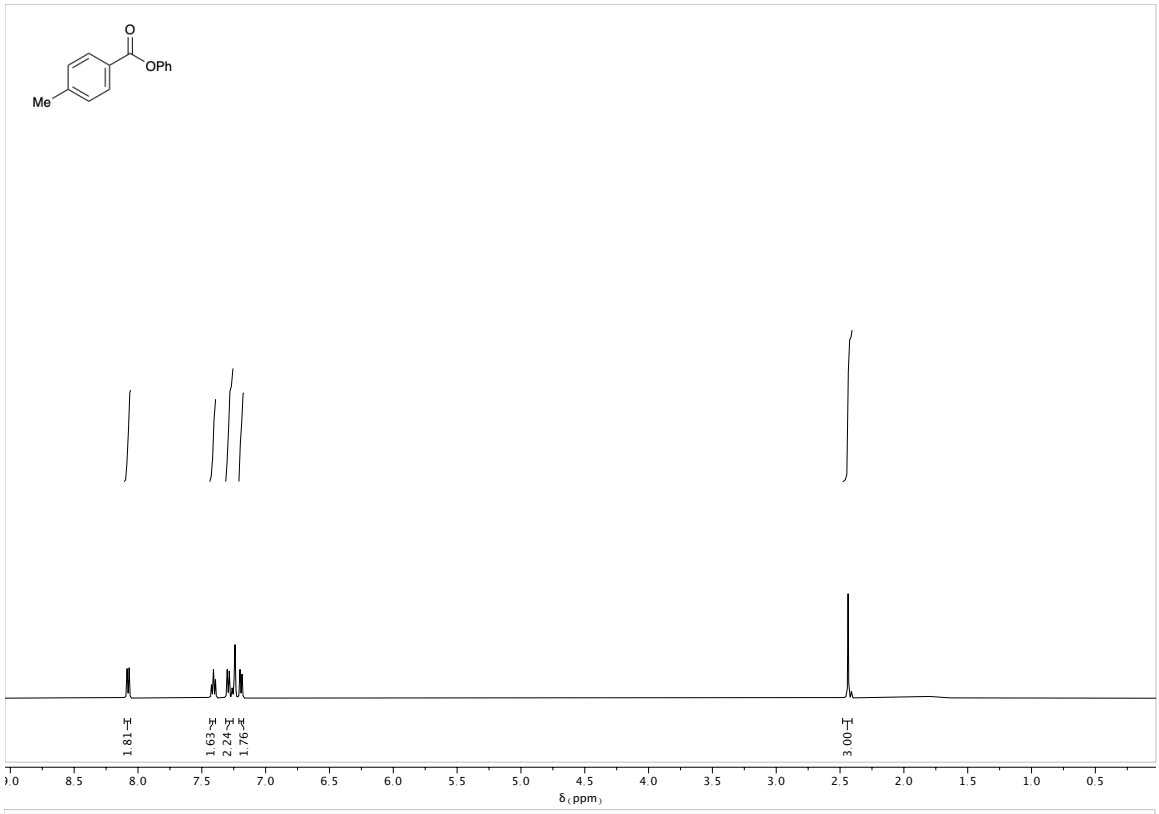


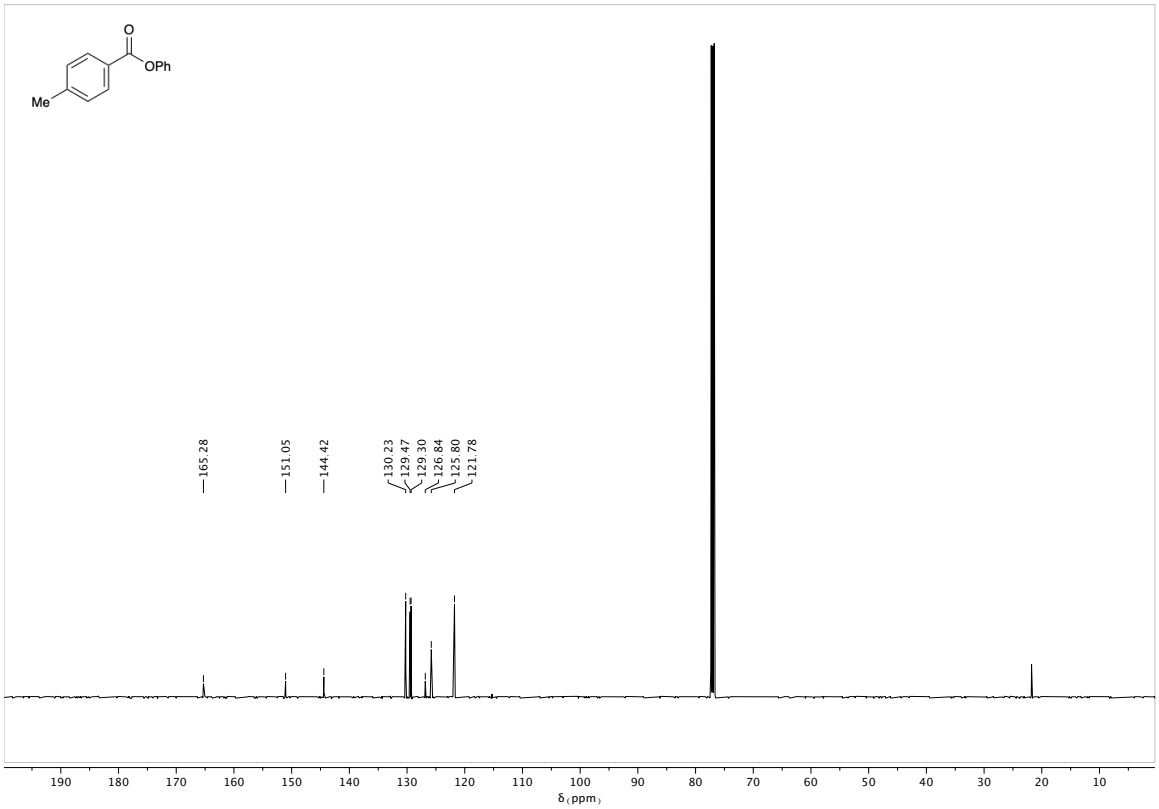
1,3-dimethyl-2-(4-methylbenzoyl)-1*H*-imidazol-3-ium (E2):



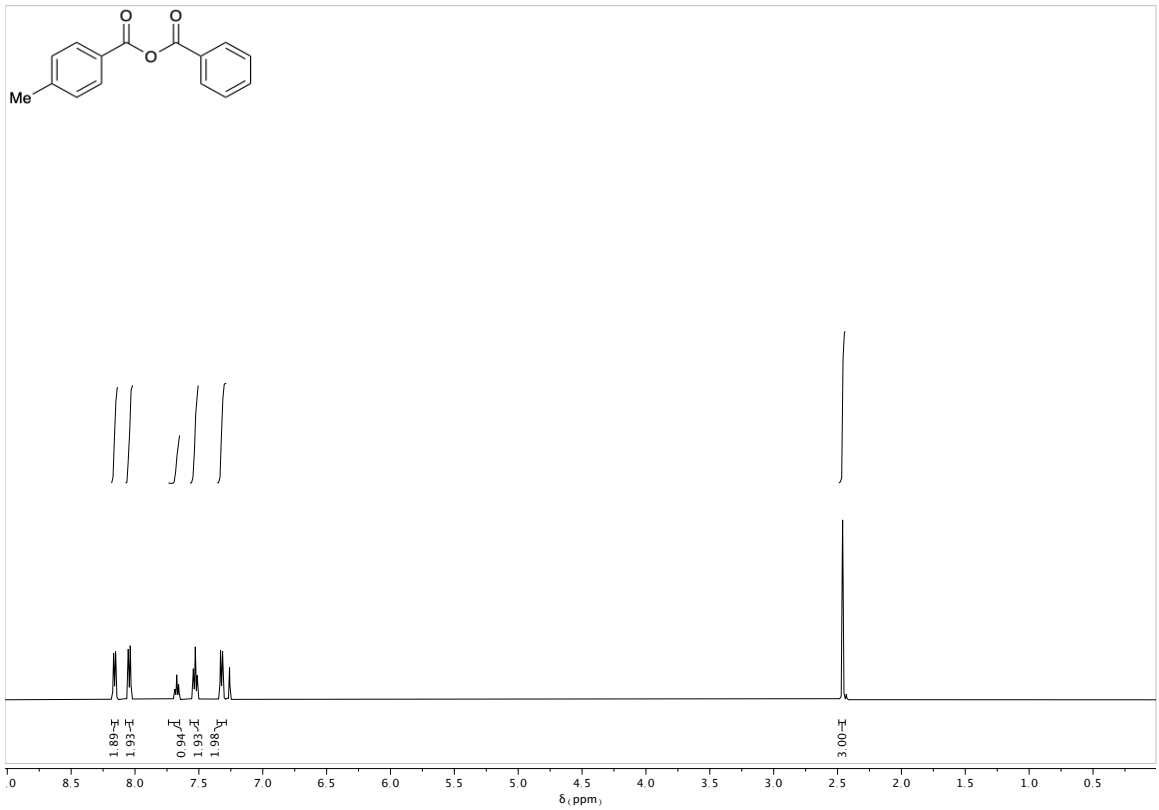


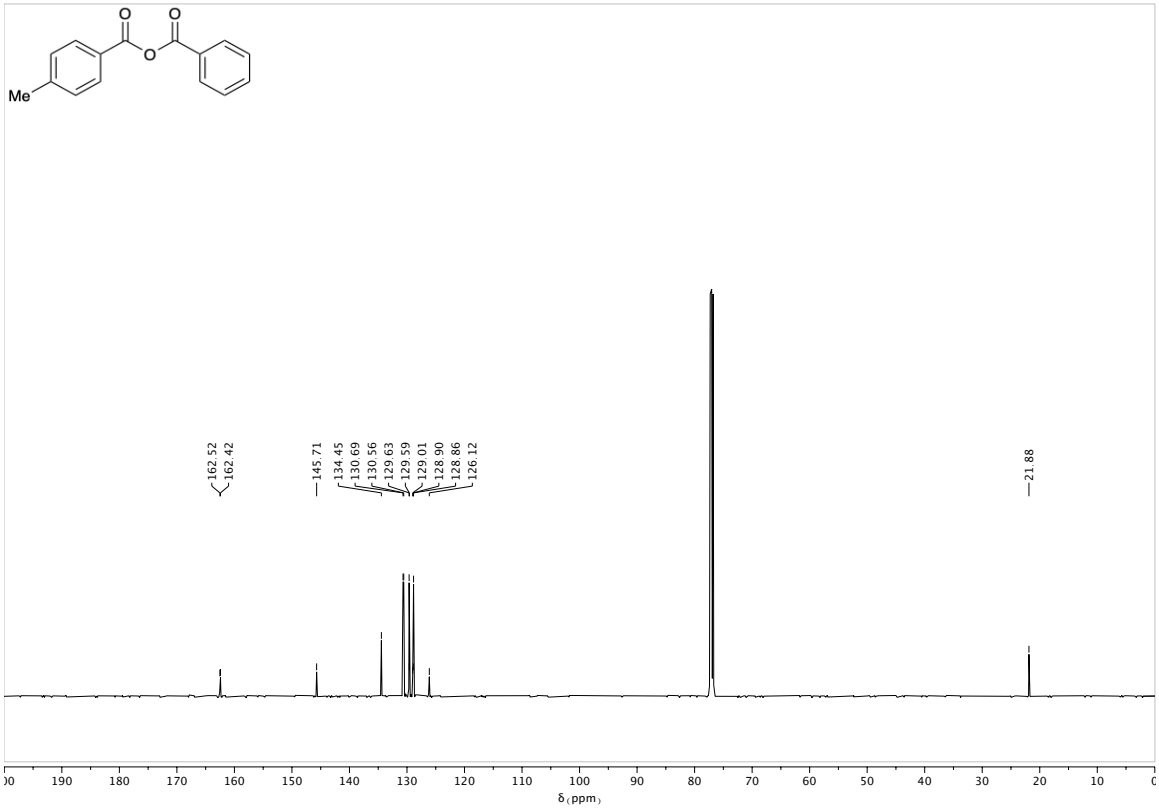
phenyl 4-methylbenzoate (E6):



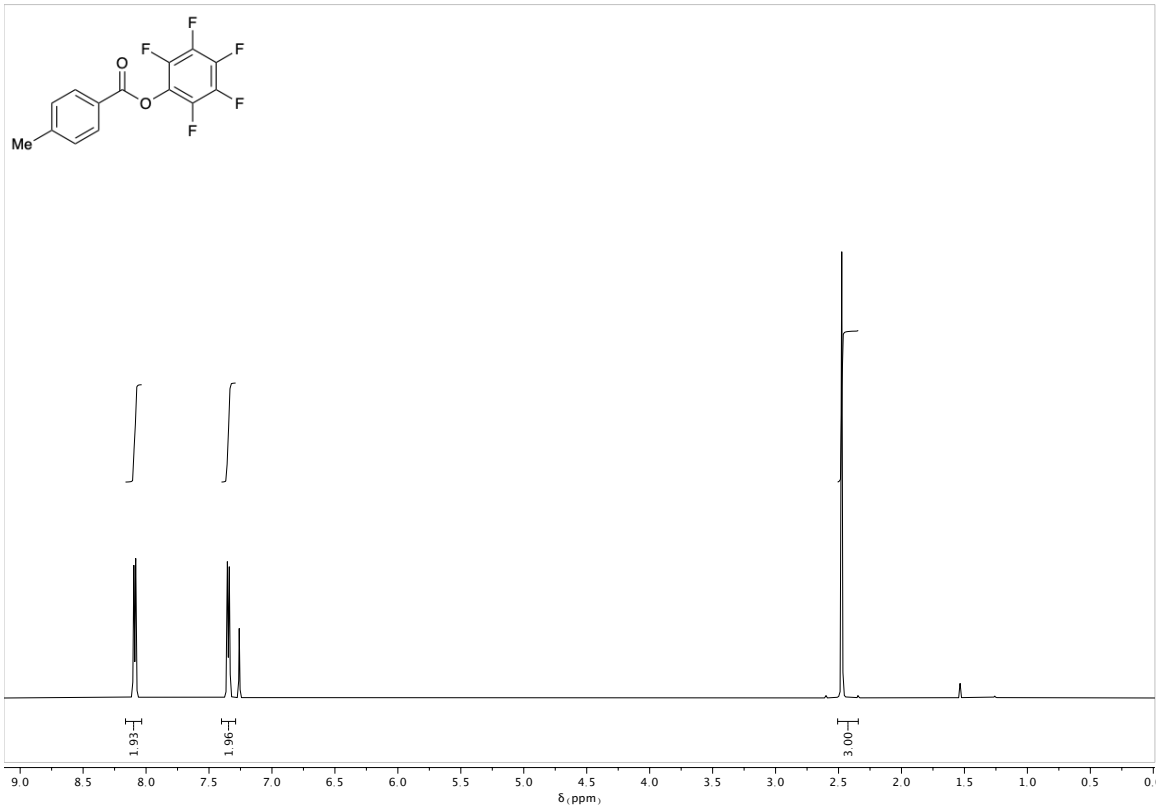


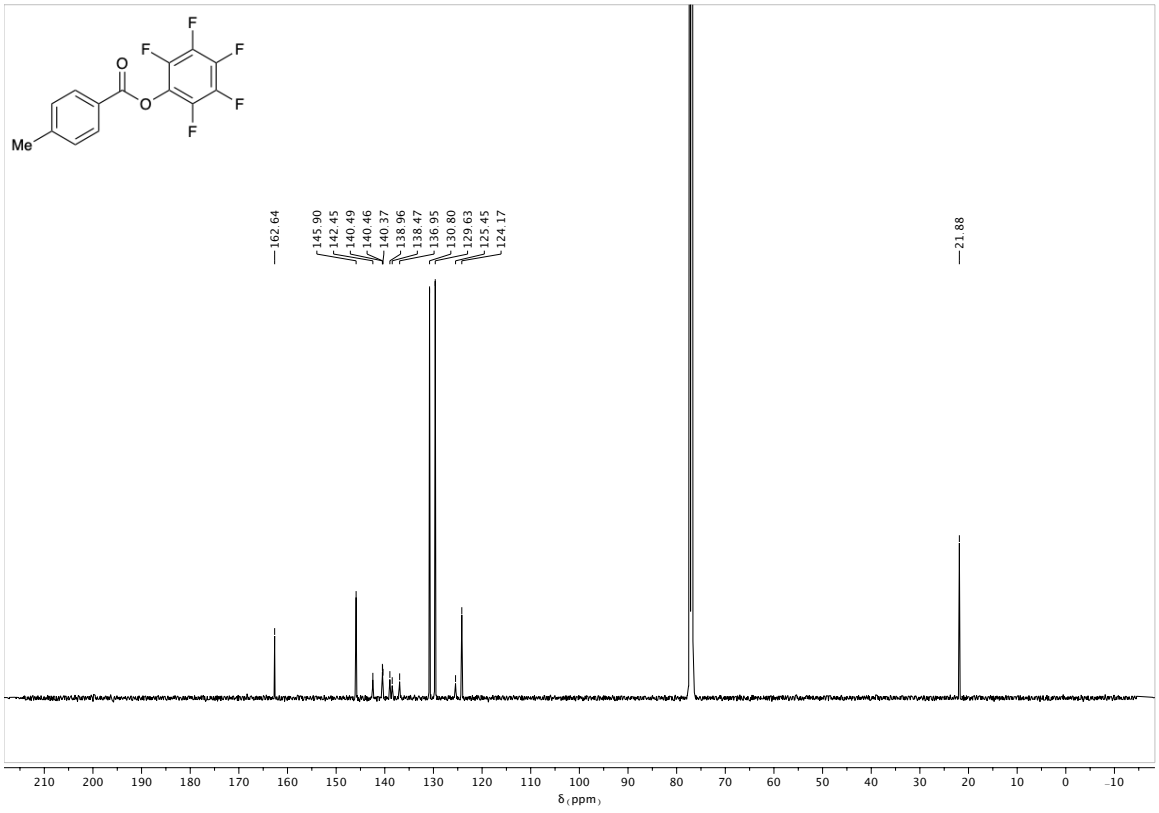
benzoic 4-methylbenzoic anhydride (E7):



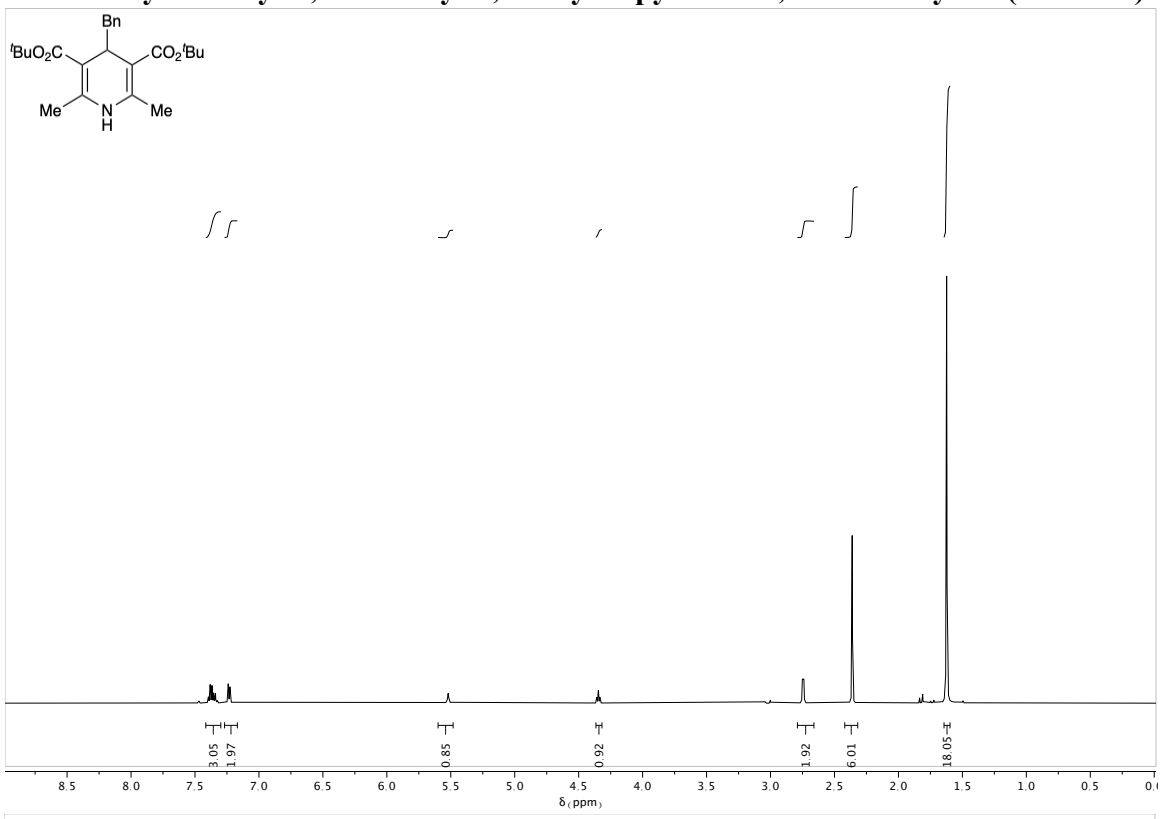


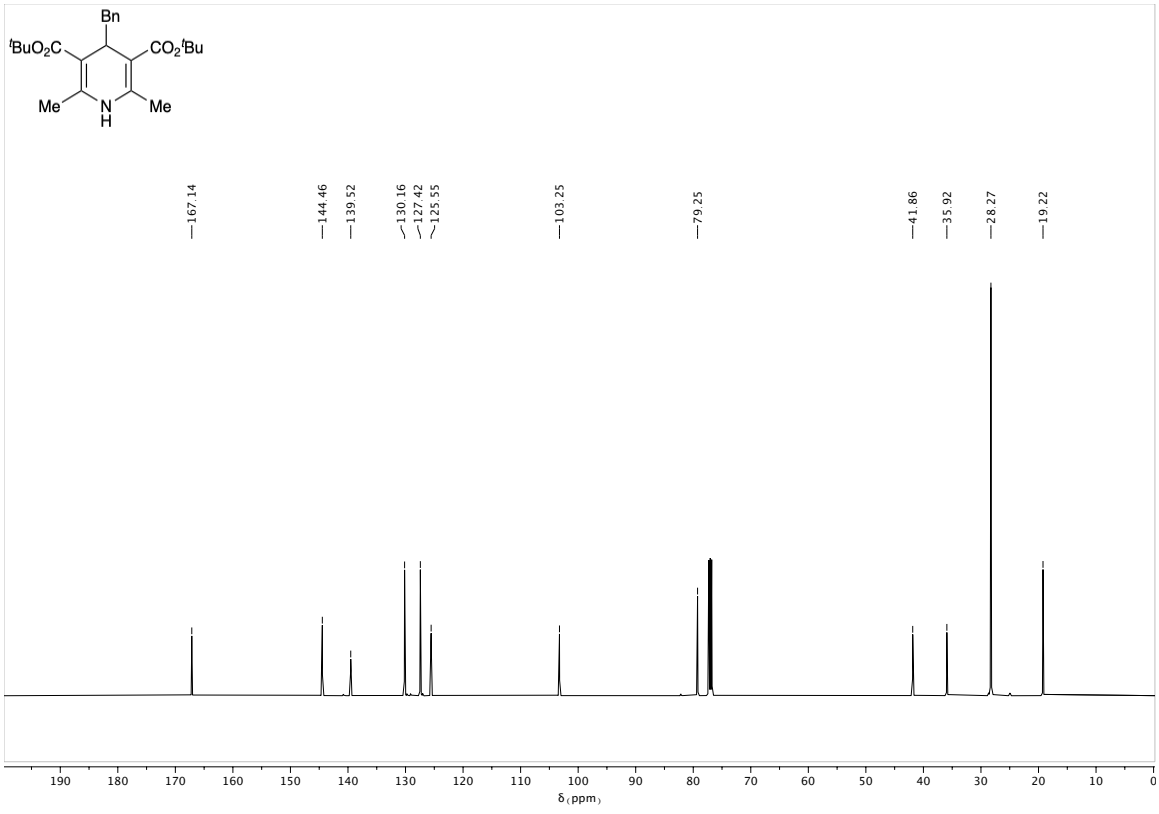
perfluorophenyl 4-methylbenzoate (E8):



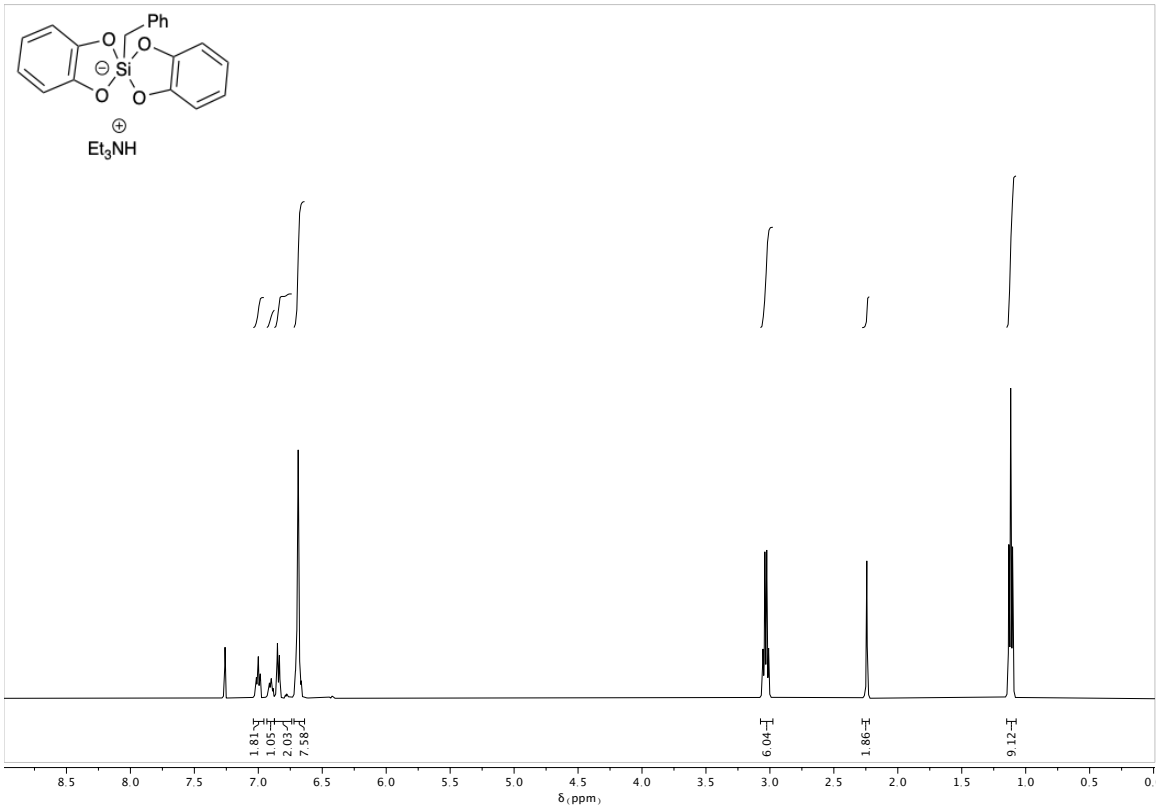


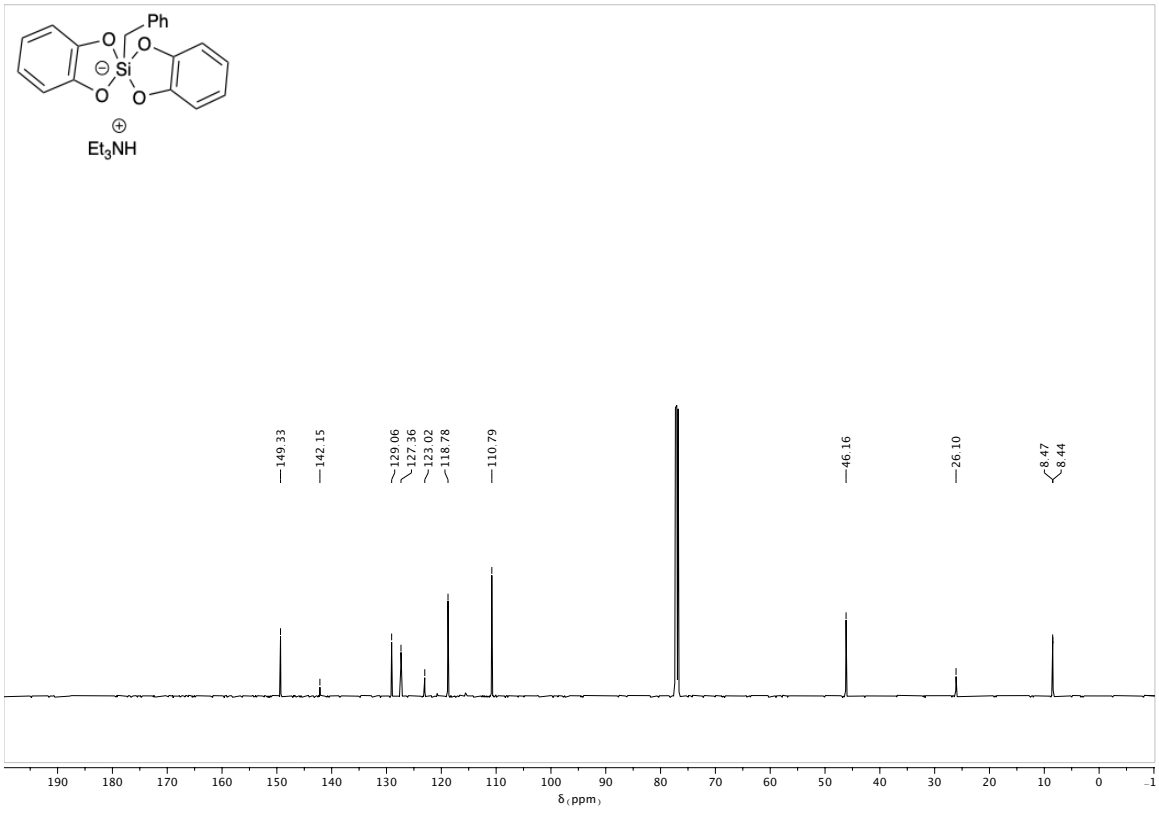
di-*tert*-butyl4-benzyl-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (Bn HEH):



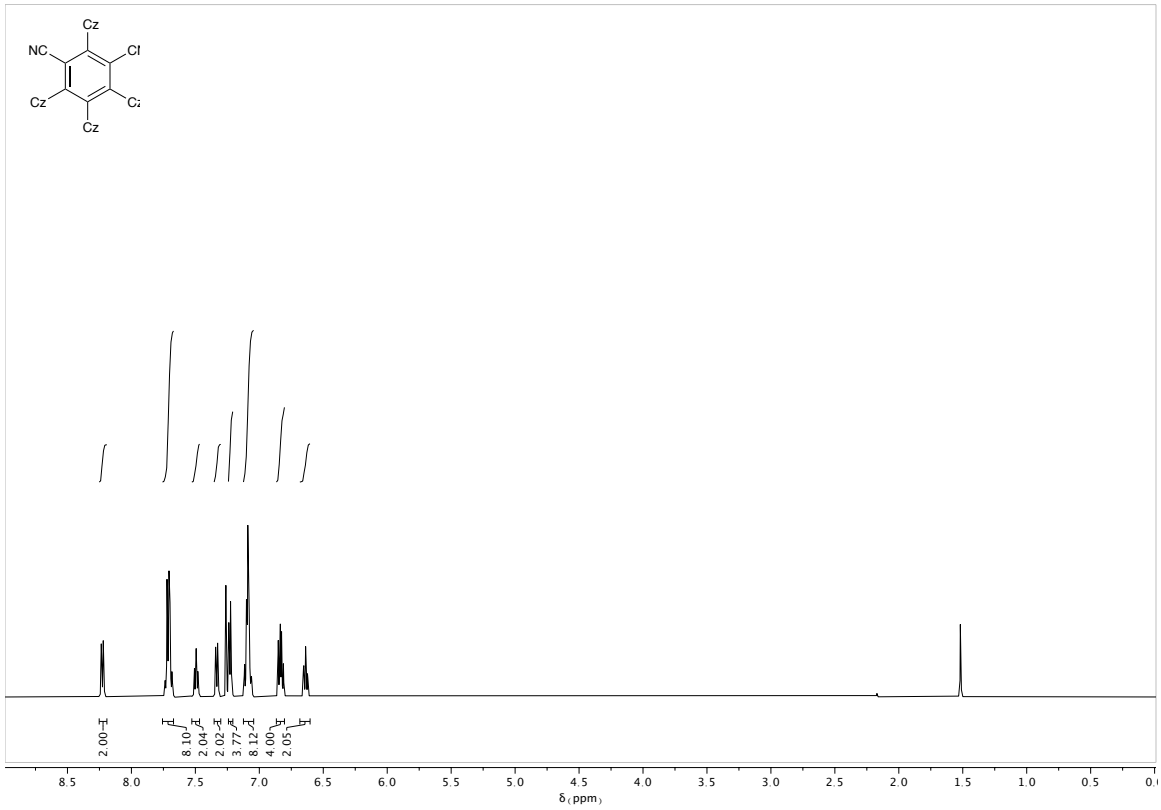


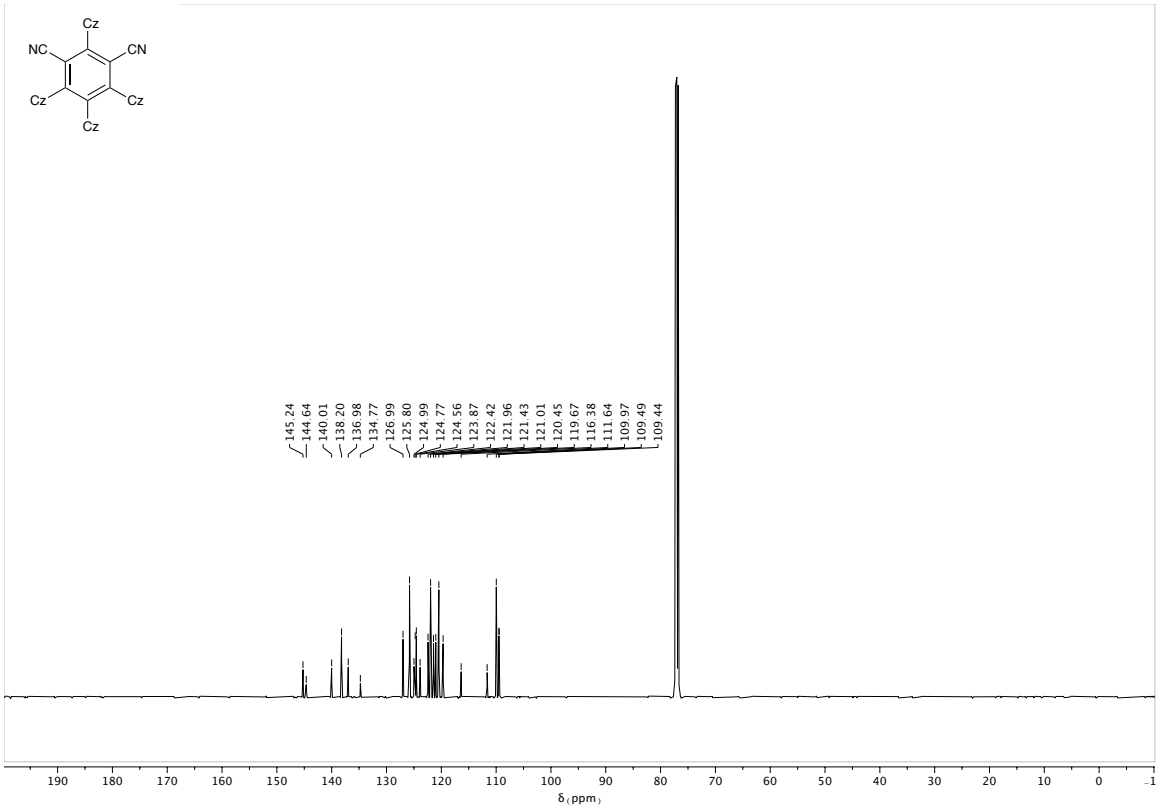
Triethylammonium benzylbis(methyl-2-hydroxyisobuyro)silicate (Bn Si):



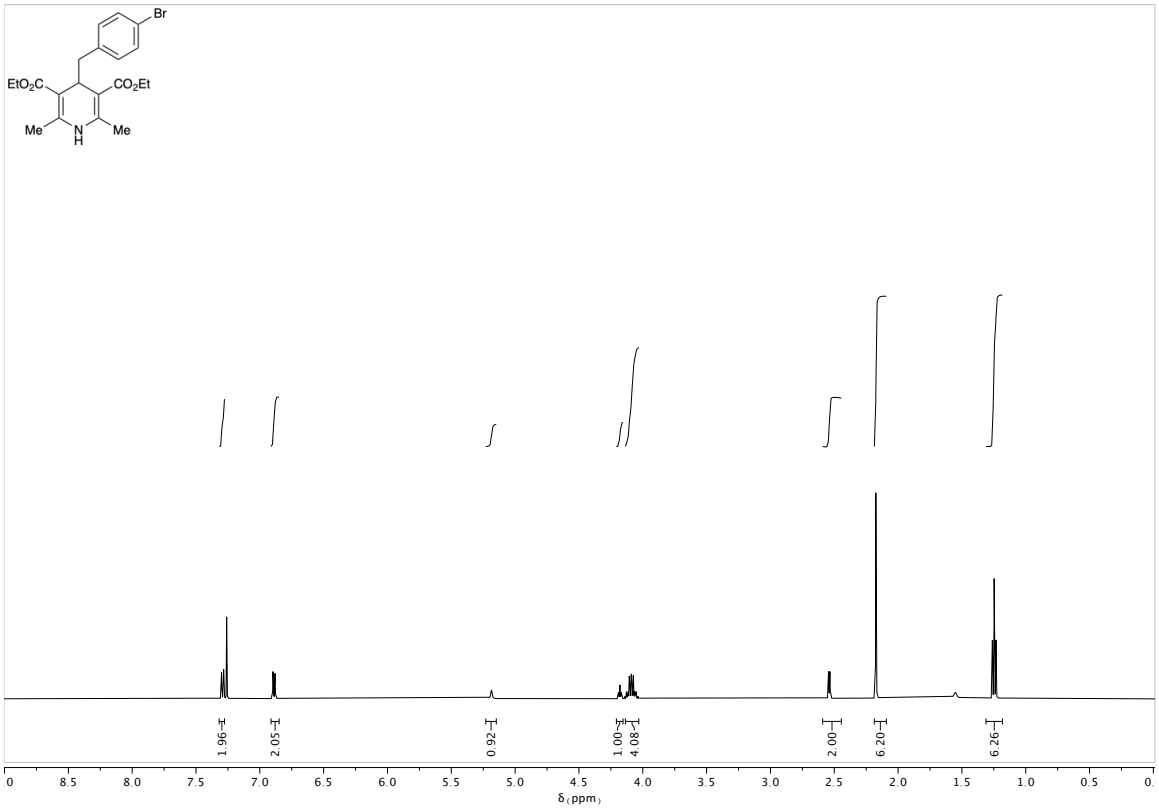


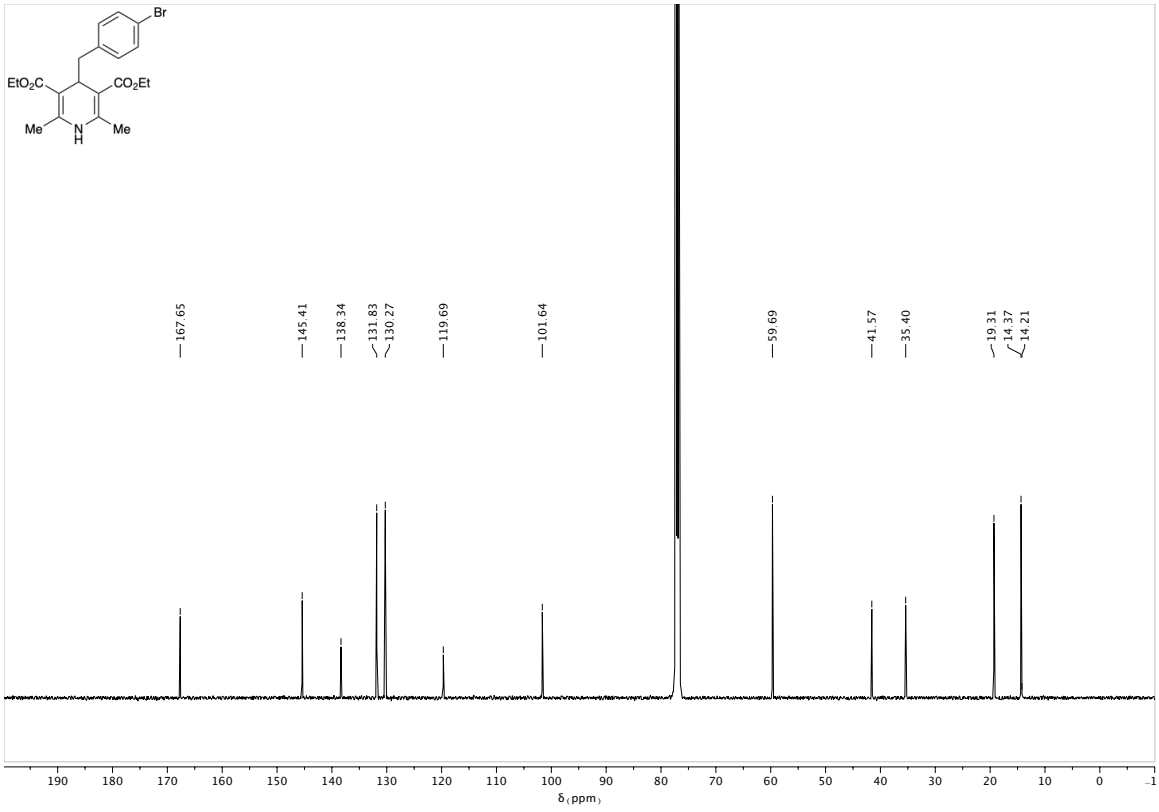
1,2,3,5-Tetrakis(carbazol-9-yl)-4,6-dicyanobenzene (4CzIPN, PC 2):



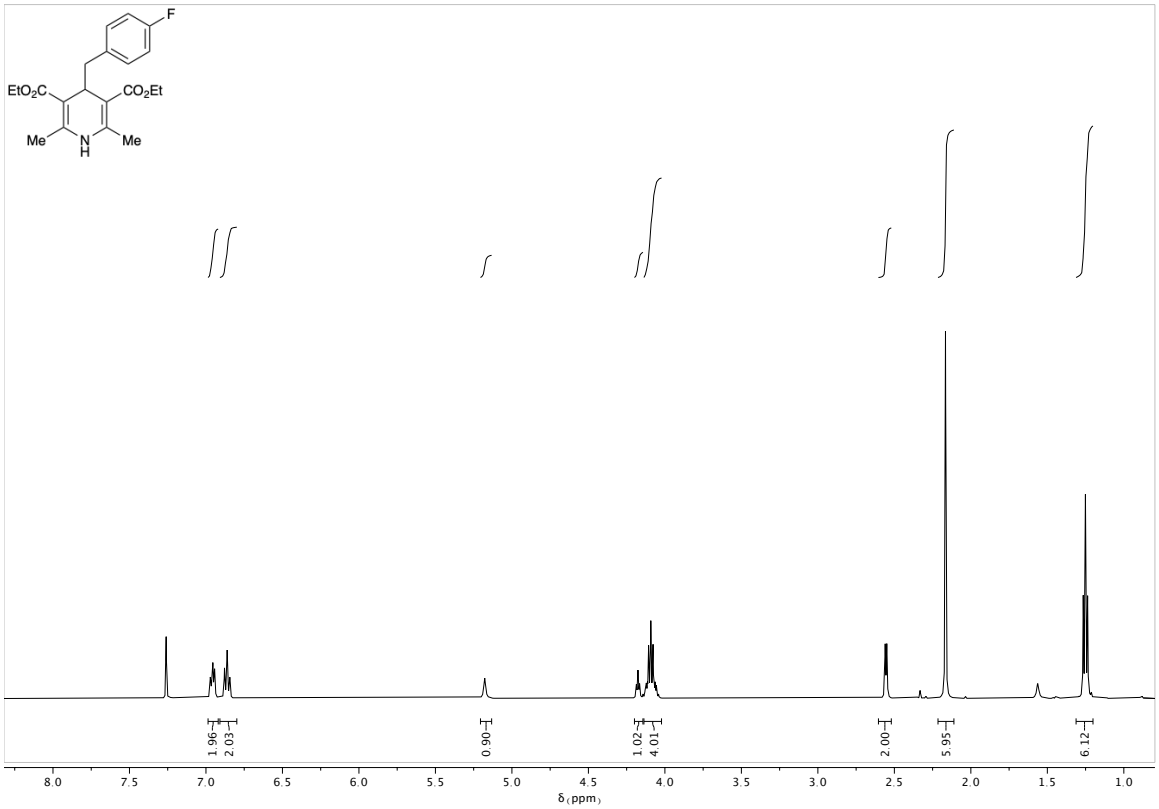


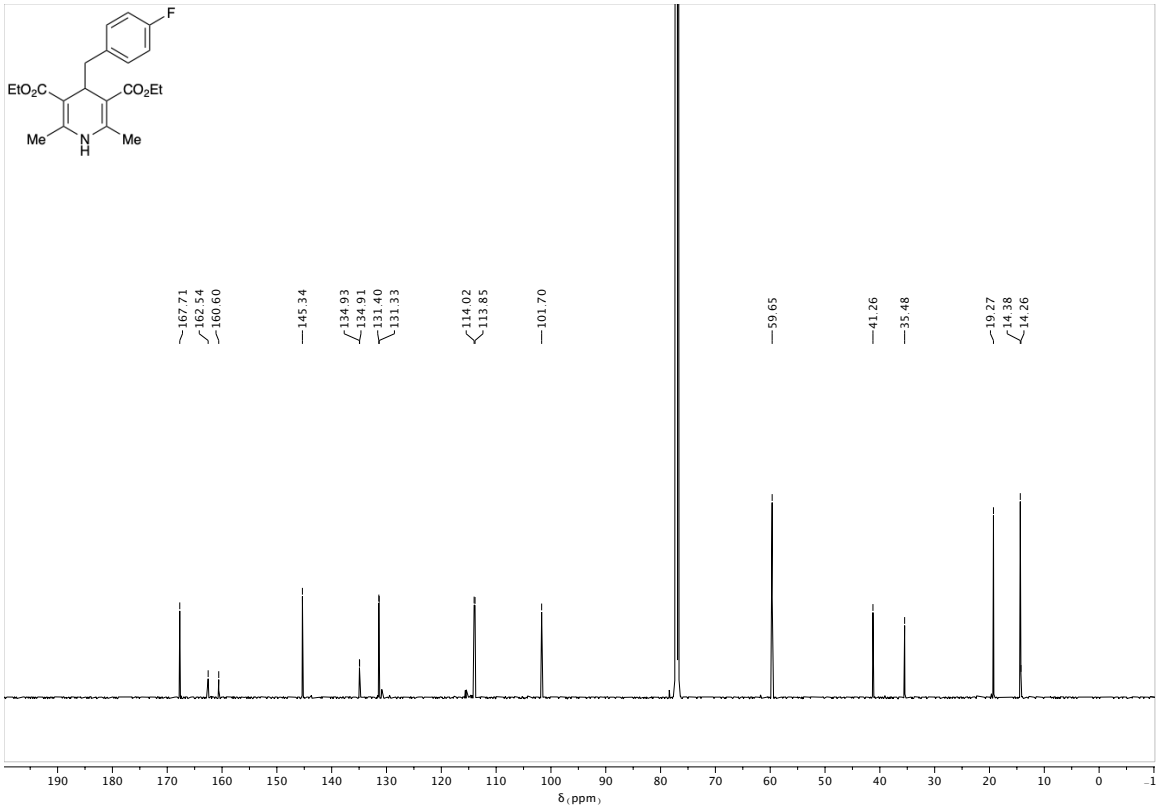
4-Br Bn HEH:


Br
EtO2C
CO2Et
Me
N
H
Me
1.96
2.05
0.92
1.00
4.08
2.00
6.20
6.26
δ (ppm)

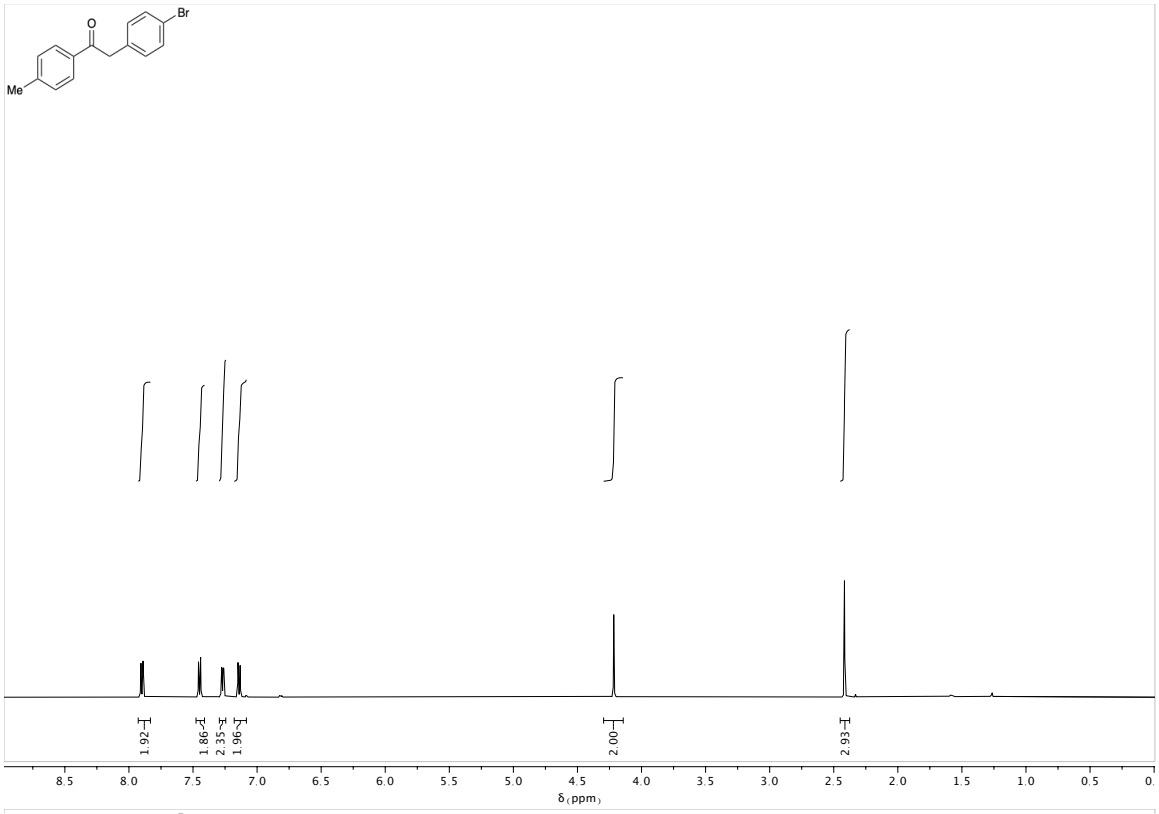

Br
EtO2C
CO2Et
Me
N
H
Me
167.65
145.41
138.34
131.83
130.27
119.69
101.64
59.69
41.57
35.40
19.31
14.37
14.21
δ (ppm)

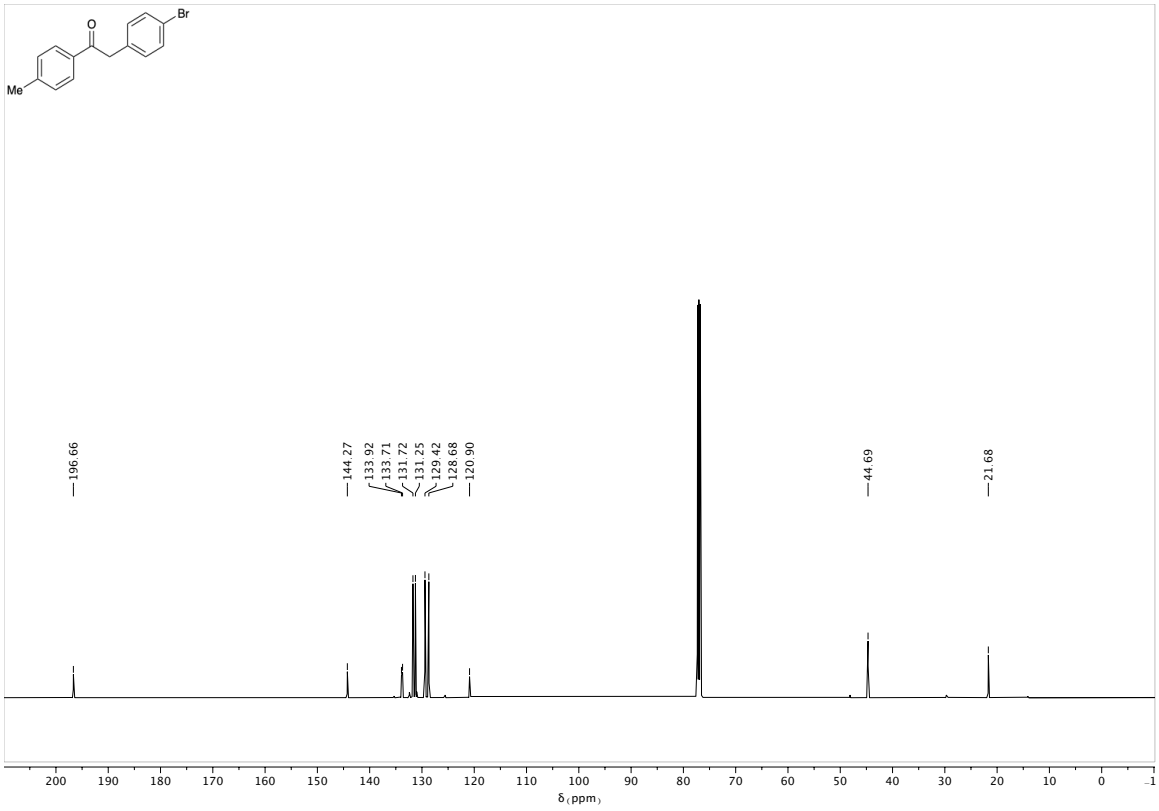
4-F Bn HEH:


F
EtO2C
CO2Et
Me
N
H
Me
1.96
2.03
0.90
1.02
4.01
2.00
5.95
6.12
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
δ (ppm)


F
EtO2C
CO2Et
Me
N
H
Me
167.71
162.54
160.60
145.34
134.93
134.91
131.40
131.33
114.02
113.85
101.70
59.65
41.26
35.48
19.27
14.38
14.26
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
δ (ppm)

2-(4-bromophenyl)-1-(*p*-tolyl)-ethan-1-one (2):





2-(4-fluorophenyl)-1-(*p*-tolyl)-ethan-1-one (3):