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Supplemental Information

Probing the effect of electron donation on CO_2 absorbing 1,2,3-triazolide ionic liquids

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Experimental Section

General Information. The ^{1}H, ^{13}C, ^{19}F, and ^{31}P NMR analyses were completed using Bruker Avance III 600 MHz spectrometer. FTIR spectra were collected on a Nicolet Spectrum 100 with an ATR apparatus. Density measurements of the ionic liquids were performed using a Micromeritics Accupyc II 1340 pycnometer in a 1 mL insert. Water content was determined using a Metrohm 860 Karl Fisher (KF) Thermoprep titration unit, equipped with an 831 KF Coulometer; ionic liquid samples which had undergone KF titration were treated as water-free samples. All KF titrations were performed in triplicate, with the average of the three runs reported as water content. Viscosity measurements were made at ambient temperatures using a Rheosense Inc. μVisc unit and 400 μL pipettes. Surface tension measurements were made by the pendant drop method at 22°C using a Rame-Hart model 260 tensiometer/goniometer.

TGA experiments. CO_2 absorption was also measured using a Thermo Scientific Thermax 500 TGA. A sample volume of 50 cm^3 was used with a constant temperature of 40°C and pressure of 0.9 bar. The sample was exposed to pure N_2 under a constant flowrate of 0.1 SLPM for several days until it reached an equilibrium mass. An initial decrease in mass was observed due to evaporation of water from the sample and the surface of the sample bucket. Next the feed gas was switched to pure CO_2 at a flow rate of 0.1 SLPM and was allowed approximately one day to reach equilibrium as CO_2 absorbed into the sample. The difference between these two equilibrium masses was considered to be the amount of CO_2 absorbed by the sample. In order to compensate for buoyancy effects, a separate experiment was performed using 50 cm^3 of crystallized NaCl under the same conditions described previously. First the sample was allowed to reach equilibrium under N_2, and then under CO_2. Since NaCl is unreactive to CO_2, the observed change in mass was entirely due to the difference in feed gas densities. This mass difference was then subtracted from the CO_2 absorption of all ionic liquid experiments.

General method for the synthesis of tetrabutyl phosphonium 4-phenyl-1,2,3-triazolide ([P_{4444}][4-Ph-1,2,3-TZ]) (1). The general procedure for the synthesis of 1,2,3-triazolide ionic liquids was derived from that described by Fukumoto, et al.[1, 2] The structures for all ionic liquids synthesized by this method are shown in Figure 4. A solution of 1-*H*-4-Ph-1,2,3-TZ[3] (1.63 g, 11.2 mmol) in 25 mL EtOH was treated with 40% tetrabutyl phosphonium hydroxide ([P_{4444}]OH) in water (7.84 g, 11.3 mmol) and was stirred at 50°C for 6 hr. The solvent was then evaporated and the residue was vacuum dried at 50°C overnight. Next day, the product was taken up in 10 mL ethyl acetate, filtered through a 0.2 μm syringe filter, evaporated, and vacuum dried to give a brown liquid (4.81 g, 106% yield). This liquid was then purified as described by Burrell, et al.[4] by refluxing over activated charcoal in MeOH at 65°C for 24 hr. Evaporation and vacuum drying at 50°C gave a pale red-brown liquid. ^{1}H NMR (700 MHz, DMSO): δ 7.71 (m, 2H, *o*-Ph), 7.64 (s, 1H, triazole C-H), 7.27 (m, 2H, *m*-Ph), 7.05 (m, 1H, *p*-Ph), 2.16 (m, 8H, P-CH_2), 1.38 (m, 16H, P-CH_2), 0.89 (t, 12H, P-CH_3); ^{13}C NMR (101 MHz, DMSO): δ 142.8 (triazole), 135.7 (triazole), 128.1, 126.9, 124.4, 124.3, 23.2 (dd, P-CH_2), 17.3 (d, 48.5 Hz, P-CH_2), 13.2; ^{31}P NMR (162 MHz, DMSO): δ 33.6; FTIR (ATR film): 2958, 2928, 2871, 1603, 1465, 1379, 1096, 1047, 965, 906, 763, 718, 696, 682, 605, 512 cm^{-1}; ESI MS+/- (MEOH, m/z) Calc'd for $C_{22}H_{43}N_3P$: 403.58; Calc'd for cation $C_{16}H_{36}P^+$ (M^+): 259.43, Found: 259.27; Calc'd for anion $C_8H_6N_3^-$ (M^-): 144.15, Found: 144.07; T_{dec} = 238°C; density (@ 23.2°C) = 0.9836 ± 0.0003 g/cc.

Tetrabutyl phosphonium 4-hexyl-1,2,3-triazolide ([P_{4444}][4-hex-1,2,3-TZ]) (2). Following the general procedure for **1**, a solution of 1-*H*-4-hexyl-1,2,3-TZ[3] (3.66 g, 23.9 mmol) in 25 mL EtOH was treated with 40% [P_{4444}]OH in water (16.6 g, 24.0 mmol) and was stirred at 50°C for 6 hr. The solvent was then evaporated and the residue was vacuum dried at 50°C overnight. Next day, the product was taken up in 10 mL ethyl acetate, filtered through a 0.2 μm syringe filter, evaporated, and vacuum dried to give a brown liquid (10.0 g, 102% yield). This liquid was then purified[4] by refluxing over activated charcoal in MEOH at 65°C for 24 hr. Evaporation and vacuum drying at 50°C gave a pale red-brown liquid. ^{1}H NMR (700 MHz, DMSO): δ 6.96 (s, 1 H, triazole C-H), 2.50 (m, 2H, CH_2), 2.16 (m, 8H, P-CH_2), 1.49 (m, 2H, CH_2), 1.38 (m, 16H, P-CH_2), 1.24 (m, 6H, CH_2), 0.93 (s, 3H, CH_3), 0.89 (t, 12H, P-CH_3); ^{13}C NMR (101 MHz, DMSO): δ 142.1 (triazole), 126.9 (triazole), 31.3, 29.1, 27.4, 26.8, 23.7, 23.4 (dd, P-CH_2), 22.6, 17.3 (d, 47.5 Hz, P-CH_2), 13.5, 13.2; ^{31}P NMR (162 MHz, DMSO): δ 33.7; FTIR (ATR film): 2958, 2928, 2873, 1598, 1466, 1400, 1380, 1095, 1041, 907, 803, 717 cm^{-1}; ESI MS+/- (MEOH, m/z) Calc'd for $C_{24}H_{50}N_3P$: 411.65; Calc'd for cation $C_{16}H_{36}P^+$ (M^+): 259.43, Found: 259.27; Calc'd for anion $C_8H_{14}N_3^-$ (M^-): 152.22, Found: 152.13; T_{dec} = 185°C; density (@ 22.6°C) = 0.9324 ± 0.0005 g/cc.

Tetrabutyl phosphonium 4-^{t}butyl-1,2,3-triazolide ([P_{4444}][4-^{t}Bu-1,2,3-TZ]) (3). Following the general procedure for **1**, a solution of 1-*H*-4-^{t}Bu-1,2,3-TZ[3] (0.62 g, 4.94 mmol) in 10 mL EtOH was treated with 40% [P_{4444}]OH in water (3.48 g, 5.04 mmol) and was stirred at 50°C for 6 hr. The solvent was then evaporated and the residue was vacuum dried at 50°C overnight. Next day, the product was taken up in 10 mL ethyl acetate, filtered through a 0.2 μm syringe filter, evaporated, and vacuum dried to give a yellow liquid (2.10 g, 110% yield). This liquid was then purified[4] by refluxing over activated charcoal in MEOH at 65°C for 24 hr. Evaporation and vacuum drying at 50°C gave a pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (s, 1 H, triazole C-H), 7.83 (m, 2H, *o*-Ph), 7.47 (m, 2H, *m*-Ph), 7.40 (m, 1 H, *p*-Ph); ^{13}C NMR (101 MHz, $CDCl_3$): δ 148.9 (triazole), 132.2 (triazole), 129.0, 128.9, 126.2, 126.1; ^{31}P NMR (162 MHz, DMSO): δ 33.7; FTIR (ATR film): 2958, 2833, 2872, 2810, 1571, 1459, 1399, 1381, 1352, 1095, 1046, 906, 804, 720 cm^{-1}; ESI MS+/- (MEOH, m/z) Calc'd for $C_{22}H_{46}N_3P$: 383.59; Calc'd for cation $C_{16}H_{36}P^+$ (M^+): 259.43, Found: 259.27; Calc'd for anion $C_6H_{10}N_3^-$ (M^-): 124.16, Found: 124.10; T_{dec} = 151°C; density (@ 22.9°C) = 0.9404 ± 0.0003 g/cc.

Tetrabutyl phosphonium 4-trimethylsilylmethyl-1,2,3-triazolide ([P_{4444}][4-TMS-1,2,3-TZ]) (4). Following the general procedure for **1**, a solution of 1-*H*-4-TMS-1,2,3-TZ[3] (0.388 g, 2.50 mmol) in 25 mL EtOH was treated with 40% [P_{4444}]OH in water (1.81 g, 2.62 mmol) and was stirred at 50°C for 6 hr. The solvent was then evaporated and the residue was vacuum dried at 50°C overnight. Next day, the product was taken up in 10 mL ethyl acetate, filtered through a 0.2 μm syringe filter, evaporated, and vacuum dried to give a red-brown liquid (1.07 g, 103% yield). This liquid was then purified[4] by refluxing over activated charcoal in MEOH at 65°C for 24 hr. Evaporation and vacuum drying at 50°C gave a pale yellow liquid. ^{1}H NMR (700 MHz, DMSO): δ 7.30 (s, 1 H, triazole C-H), 2.22 (m, 8H, P-CH_2), 2.11 (s, 2H, CH_2), 1.40 (m, 16H, P-CH_2), 0.90 (t, 12H, P-CH_3), 0.05 (s, 9H, CH_3); ^{13}C NMR (101 MHz, DMSO): δ 136.2 (triazole), 127.7 (triazole), 23.3 (dd, P-CH_2), 17.3 (d, 47.5 Hz, P-CH_2), 13.2, 10.9, 1.87; ^{31}P NMR (162 MHz, DMSO): δ 33.7; FTIR (ATR film): 2958, 2932, 2873, 1571, 1465, 1393, 1343, 1218, 1095, 969, 919, 843, 721, 605, 589 cm^{-1}; ESI MS+/- (MEOH, m/z) Calc'd for $C_{22}H_{48}N_3PSi$: 383.59; Calc'd for cation $C_{16}H_{36}P^+$ (M^+): 259.43, Found: 259.27; Calc'd for anion $C_6H_{12}N_3Si^-$ (M^-): 154.27, Found: 154.10; T_{dec} = 227°C; density (@ 24.1°C) = 0.9400 ± 0.0003 g/cc.

Tetrabutyl phosphonium 4-([(perfluorohexyl)ethoxy]methyl)-1,2,3-triazolide ([P_{4444}][4-PFE-1,2,3-TZ]) (5). Following the general procedure for **1**, a solution of 1-*H*-4-PFE-1,2,3-TZ[3] (7.66 g, 17.2 mmol) in 50 mL EtOH was treated with 40% [P_{4444}]OH in water (11.91 g, 17.2 mmol) and was stirred at 50°C for 16 hr. The solvent was then evaporated and the residue was vacuum dried at 50°C. The product was taken up in 100 mL ethyl ether, passed through a small plug of silica gel, evaporated, and vacuum dried to give a dark brown liquid. This liquid was then purified[4] by refluxing over activated charcoal in MEOH at 65°C for 24 hr. Evaporation and vacuum drying at 50°C gave a red-brown liquid (10.76 g, 15.2 mmol, 88% yield). ^{1}H NMR (700 MHz, DMSO): δ 7.33 (s, 1 H, triazole C-H), 4.50 (m, 2H, O-*CH*$_2$-TZ), 3.65 (m, 2H, CH_2-*CH*$_2$-O), 2.44 (m, 2H, CF_2-*CH*$_2$-CH_2), 2.21 (m, 8H, P-CH_2), 1.40 (m, 16H, P-CH_2), 0.91 (t, 12H, P-CH_3); ^{13}C NMR (101 MHz, $CDCl_3$): δ 140.1 (triazole), 128.7 (triazole), 63.7 (s, CH_2-*CH*$_2$-O), 38.4 (s, CF_2-*CH*$_2$-CH_2), 28.5 (s, O-*CH*$_2$-TZ), 23.3 (dd, P-CH_2), 17.3 (d, 48.5 Hz, P-CH_2), 13.2; ^{31}P NMR (162 MHz, DMSO): δ 33.7; ^{19}F NMR (376 MHz, DMSO): δ -80.8 (m, 3F), -112.7 (m, 2F), -122.0 (m, 2F), -123.0 (m, 2F), -123.4 (m, 2F), -126.1 (m, 2F); FTIR (ATR film): 2962, 2935, 2876, 1566, 1467, 1352, 1234, 1192, 1144, 1096, 1003, 909, 810, 731, 708, 696, 652, 531 cm^{-1}; ESI MS+/- (MEOH, m/z) Calc'd for $C_{27}H_{43}F_{13}N_3OP$: 703.60; Calc'd for cation $C_{16}H_{36}P^+$ (M^+): 259.43, Found: 259.27; Calc'd for anion $C_{11}H_7F_{13}N_3O^-$ (M^-): 444.17, Found: 444.07; T_{dec} = 263°C; density (@ 21.6°C) = 1.2141 ± 0.0006 g/cc.

Characterization of samples by Raman spectroscopy

Raman spectroscopy experiments were conducted using a Horiba LabRamHR microscope with a CCD detector. The excitation source was a Spectra Physics 532.07 nm Nd:YAG laser, with an operating power of 200 mW. Spectra were taken of the neat IL samples after the Karl-Fisher titration process. To reduce the fluorescence signal, the samples were photo-bleached using the laser for 2 -20 minutes before recording a spectrum. All spectra were recorded as an average of five one second exposures, to increase the signal to noise ratio, over a Raman shift range of 500 cm^{-1} to 2500 cm^{-1}. The fluorescence band of IL **5** could not be reduced with photobleaching techniques and therefore is not reported.

Raman spectra of samples under CO_2 pressure were taken using a high-pressure optical cell to hold the liquid samples and provide a CO_2 environment up to 20 bar. A 4 cm segment of 350 μm ID/450 μm OD round fused silica capillary (Polymicro Inc. LLC), was used as the sample carrier for the Raman spectroscopic studies of CO_2 physical solvents systems. The surface of the capillary was initially coated with a polyimide layer. To prepare the sample cell, a butane torch was used to remove 3 cm of the polyimide coating, leaving a clean fused silica section of capillary. The capillary was filled from the polyimide coated end with ~1 μL of solvent, while the other end was fused using an oxy-acetylene torch. The capillary was then centrifuged to remove the air trapped between the solvent and the fused end, resulting in all of the solvent at the fused end of the sample cell and approximately 2.5 cm window between solvent-air interface and the opening of the cell. Spectra were taken of the reacted samples 50 microns below the gas-liquid interface after 1 hour CO_2 exposure. Similar to the neat samples, the reacted samples were photobleached before taking spectra.

Supplemental Table 1. Surface tensions at 22°C for ILs **1** - **5**, before and after CO_2 exposure.

IL	*γ, dyne/cm*	*IL + CO_2*	*γ, dyne/cm*
1	33.5 ± 2.5	**1** + CO_2	34.8 ± 1.8
2	30.1 ± 0.4	**2** + CO_2	30.5 ± 0.8
3	29.0 ± 0.1	**3** + CO_2	29.6 ± 0.0
4	27.4 ± 2.2	**4** + CO_2	22.0 ± 2.0
5	16.5 ± 0.8	**5** + CO_2	17.4 ± 2.1

Supplemental Table 2. CO_2 absorption data from Sievert's apparatus experiments on ILs **1 – 5**. In this table, x represents mol CO_2 / mol IL, while P represents CO_2 pressure in bar.

1		**2**		**3**		**4**		**5**	
x	**P**	**x**	**P**	**x**	**P**	**x**	**P**	**x**	**P**
0	0	0	0	0	0	0	0	0	0
0.08235	0.31387	0.23315	0.18082	0.05645	0.35447	0.27518	0.12974	0.21362	0.28982
0.15367	1.5684	0.43596	1.0829	0.12358	1.8315	0.38795	1.4601	0.36973	1.7694
0.20613	2.5884	0.56535	2.2885	0.16937	2.8566	0.44243	2.5074	0.46140	2.7598
0.25998	3.7320	0.63090	3.1600	0.21100	3.8712	0.49131	3.5931	0.55693	3.8638
0.31043	4.8120	0.70311	4.1486	0.26118	4.9136	0.54384	4.6168	0.64526	4.9057
0.34973	5.6522	0.74355	5.0216	0.30811	5.8239	0.58438	5.4898	0.71898	5.6868
0.39062	6.5777	0.80582	5.9209	0.35061	6.7494	0.64701	6.4285	0.79773	6.6090
0.43582	7.4540	0.87277	6.8694	0.39431	7.7898	0.68791	7.2161	0.91394	7.4951
0.47277	8.3959	0.90074	7.4404	0.42416	8.3937	0.74268	8.1121	0.93820	8.0432
0.49846	8.9440	0.92514	8.3725	0.46273	9.3750	0.74374	8.6733	1.00244	8.8604
0.53125	9.7382	0.95703	8.8976	0.51326	9.9198	0.78912	9.6284	1.09428	9.7465
0.53320	10.224	1.00214	9.689	0.55860	10.908	0.82269	10.177	1.13176	10.275
0.58937	11.140	1.03044	10.155	0.56277	11.512	0.87476	11.072	1.20150	11.260
0.62600	11.668	1.08689	10.995	0.60716	12.529	0.91715	11.584	1.25573	11.827
0.65651	12.646	1.09433	11.517	0.63405	13.123	0.95433	12.494	1.32837	12.723
0.66872	13.224	1.12974	12.449	0.65018	13.471	0.96368	13.035	1.37025	13.252

Supplemental Table 3. Comparison of ^{1}H NMR Chemical Shifts for H_5 on 4R-1*H*-1,2,3-TZ (**1b** - **5b**)* and [P_{4444}][4-R-1,2,3-TZ] (**1** - **5**) in $CDCl_3$.

	1b	***1***	***2b***	***2***	***3b***	***3***	***4b***	***4***	***5b***	***5***
δ H_5, ppm	8.03	7.59	7.46	7.23	7.30	7.12	7.22	7.16	7.46	7.36

* - ^{1}H NMR data for 1*H*-4-R-1,2,3-TZ compounds taken from ref. 3.

Supplemental Table 4. Viscosities of wet ILs **1** – **5** before and after CO_2 exposure.

*wet IL**	*η, cP*	*T, °C*	*wet IL* + CO_2*	*η, cP*	*T, °C*
1	2255 ± 8.7	19.5	**1** + CO_2	2466 ± 11	22.1
2	1357 ± 4.0	19.0	**2** + CO_2	1267 ± 16	22.7
3	2414 ± 5.0	19.5	**3** + CO_2	2117 ± 7.4	22.6
4	1659 ± 14	19.6	**4** + CO_2	1254 ± 14	22.5
5	8275 ± 23	19.3	**5** + CO_2	6261 ± 24	22.3

* - Wet samples were vacuum dried to constant weight on the vacuum line, but were *not* subjected to Karl Fisher titration drying.

Supplemental Table 5. Viscosities of dry ILs **1** – **5** before and after CO_2 exposure.

*dry IL**	*η, cP*	*T, °C*	*dry IL* + CO_2*	*η, cP*	*T, °C*
1	880 ± 2.4	23.0	**1** + CO_2	1947 ± 10	22.9
2	235 ± 2.7	22.9	**2** + CO_2	solidified	N A
3	418 ± 1.3	21.8	**3** + CO_2	1906 ± 5.2	24.0
4	202 ± 22	22.7	**4** + CO_2	946 ± 6.5	24.1
5	485 ± 81	21.9	**5** + CO_2	solidified	N A

* - Dry samples were subjected to Karl Fisher titration drying after vacuum drying to constant weight.

Supplemental Table 6. CO_2 absorption data from Sievert's apparatus experiments on wet and dry IL **2**. In this table, x represents mol CO_2 / mol IL, while P represents CO_2 pressure in bar.

wet 2		**dry 2**	
x	**P**	**x**	**P**
0	0	0	0
0.23315	0.18082	0.20738	0.21568
0.43596	1.0829	0.49494	1.6305
0.56535	2.2885	0.59620	2.6532
0.63090	3.1600	0.68388	3.7700
0.70311	4.1486	0.75221	4.7893
0.74355	5.0216	0.82011	5.8100
0.80582	5.9209	0.86481	6.4007
0.87277	6.8694	0.90932	7.3033
0.90074	7.4404	0.97040	8.1861
0.92514	8.3725	1.0027	8.7079
0.95703	8.8976	1.0519	9.7253
1.0021	9.6886	1.0813	10.323
1.0304	10.155	1.1278	11.232
1.0869	10.995	1.1509	11.770
1.0943	11.517	1.1990	12.554
1.1297	12.449	1.1632	13.080

Supplemental Table 7. Calculated CHELPG charges for 1,2,3-triazolide anions.

Anion	***N_1***	***N_2***	***N_3***
[1,2,3-TZ]$^-$	-0.466	-0.256	-
(**1**) [4-Ph-1,2,3-TZ]$^-$	-0.454	-0.276	-0.364
(**2**) [4-hex-1,2,3-TZ]$^-$	-0.463	-0.261	-0.524
(**3**) [4-^{t}Bu-1,2,3-TZ]$^-$	-0.429	-0.346	-0.305
(**4**) [4-TMS-1,2,3-TZ]$^-$	-0.459	-0.291	-0.429
(**5**) [4-PFE-1,2,3-TZ]$^-$	-0.457	-0.230	-0.499

Supplemental Table 8. Calculated CO_2 interaction energies, bond distances, and bend angles for interactions with 1,2,3-triazolide anions.

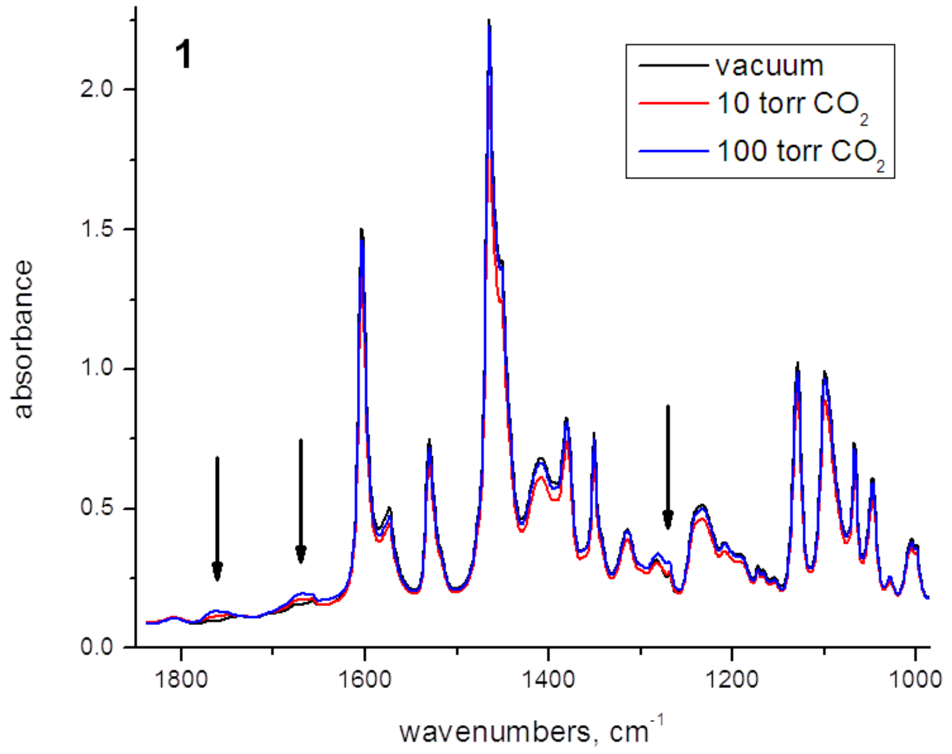
Anion		***CO_2 @ N_1***	***CO_2 @ N_2***	***CO_2 @ N_3***
$[1,2,3\text{-TZ}]^-$	ΔU_{INT}, kJ/mol	-52	-41	-
	d(C-N), Å	1.61	1.67	-
	O-C-O, deg	137	140	-
$[4\text{-Ph-}1,2,3\text{-TZ}]^-$ (1)	ΔU_{INT}, kJ/mol	-36	-25	-25
	d(C-N), Å	1.63	1.72	1.66
	O-C-O, deg	139	142	139
$[4\text{-hex-}1,2,3\text{-TZ}]^-$ (2)	ΔU_{INT}, kJ/mol	-51	-40	-45
	d(C-N), Å	1.60	1.66	1.60
	O-C-O, deg	137	139	137
$[4\text{-}^t\text{Bu-}1,2,3\text{-TZ}]^-$ (3)	ΔU_{INT}, kJ/mol	-50	-39	-28
	d(C-N), Å	1.60	1.67	1.62
	O-C-O, deg	137	140	137
$[4\text{-TMS-}1,2,3\text{-TZ}]^-$ (4)	ΔU_{INT}, kJ/mol	-48	-39	-42
	d(C-N), Å	1.61	1.66	1.59
	O-C-O, deg	138	139	136
$[4\text{-PFE-}1,2,3\text{-TZ}]^-$ (5)	ΔU_{INT}, kJ/mol	-39	-28	-35
	d(C-N), Å	1.63	1.71	1.61
	O-C-O, deg	138	141	137

Supplemental Table 9. Calculated H_2O interaction energies and bond distances for interactions with 1,2,3-triazolide anions.

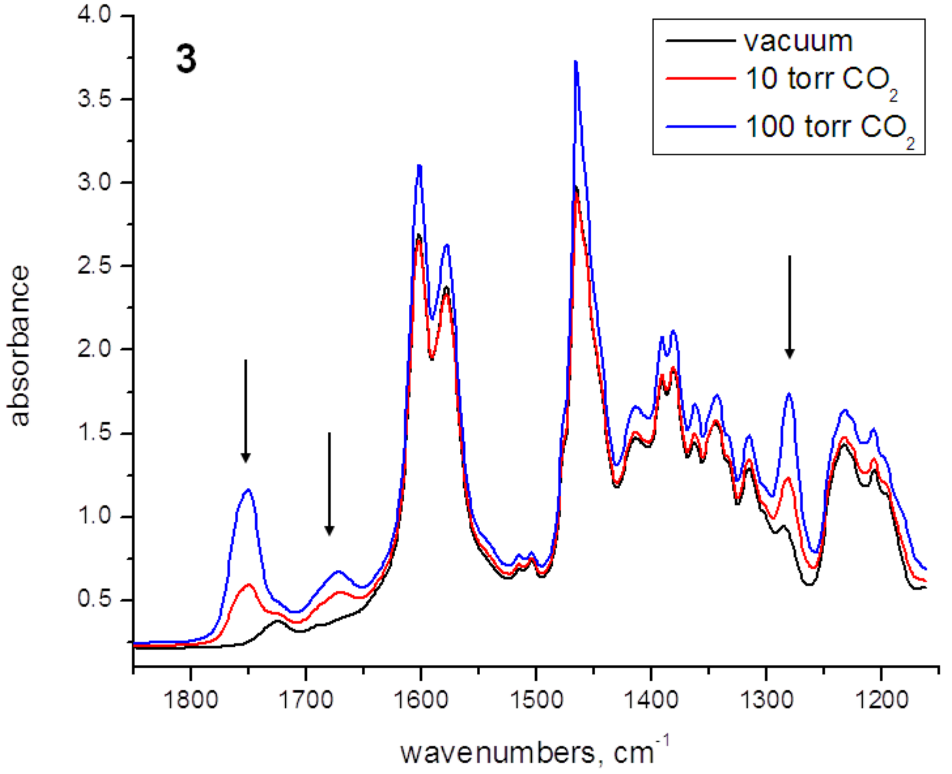
anion		***H_2O @ N_1***	***H_2O @ N_2***	***H_2O @ N_3***
$[1,2,3\text{-TZ}]^-$	ΔU_{INT}, kJ/mol	-67	-66	-
	d(OH-N), Å	1.81	1.82	-
$[4\text{-Ph-}1,2,3\text{-TZ}]^-$ (1)	ΔU_{INT}, kJ/mol	-61	-60	-58
	d(OH-N), Å	1.83	1.84	1.83
$[4\text{-hex-}1,2,3\text{-TZ}]^-$ (2)	ΔU_{INT}, kJ/mol	-66	-65	-65
	d(OH-N), Å	1.81	1.82	1.81
$[4\text{-}^t\text{Bu-}1,2,3\text{-TZ}]^-$ (3)	ΔU_{INT}, kJ/mol	-66	-65	-64
	d(OH-N), Å	1.81	1.82	1.80
$[4\text{-TMS-}1,2,3\text{-TZ}]^-$ (4)	ΔU_{INT}, kJ/mol	-65	-64	-62
	d(OH-N), Å	1.81	1.82	1.80
$[4\text{-PFE-}1,2,3\text{-TZ}]^-$ (5)	ΔU_{INT}, kJ/mol	-62	-61	-61
	d(OH-N), Å	1.82	1.84	1.83

Supplemental Table 10. Comparison of CO_2 absorption data from Sievert's apparatus and TGA experiments for $[P_{4444}]$[4-Ph-1,2,3-triazolide] (**1**).

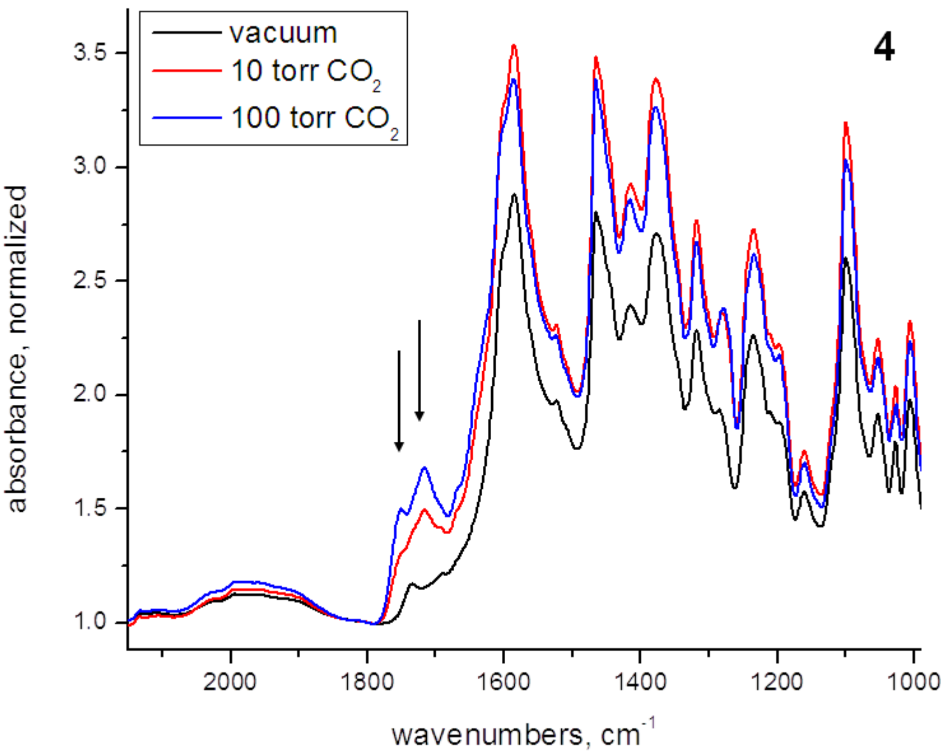
IL	**Sievert's apparatus (30°C and 1 bar) mol CO_2 absorbed / mol IL**	**TGA (40°C and 1 bar) mol CO_2 absorbed / mol IL**
1	0.10	0.11



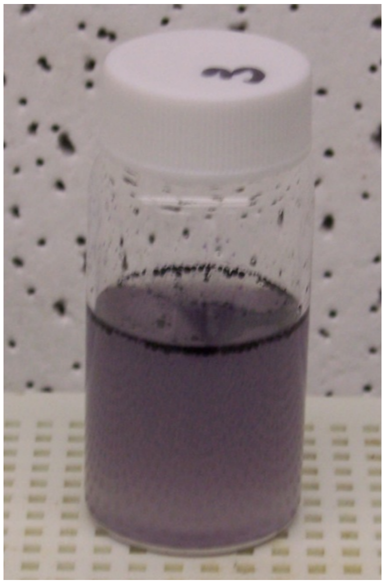
Supplemental Figure 1. FTIR spectra of **1** under vacuum and after exposure to CO_2.



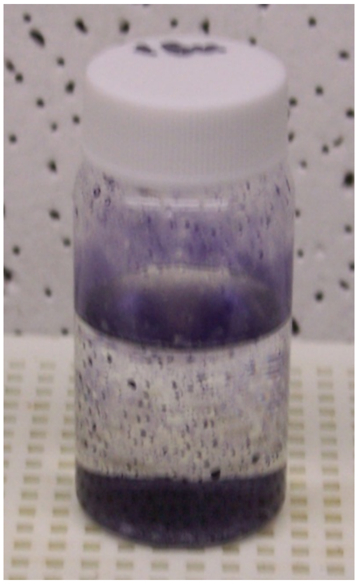
Supplemental Figure 2. FTIR spectra of **3** under vacuum and after exposure to CO_2.



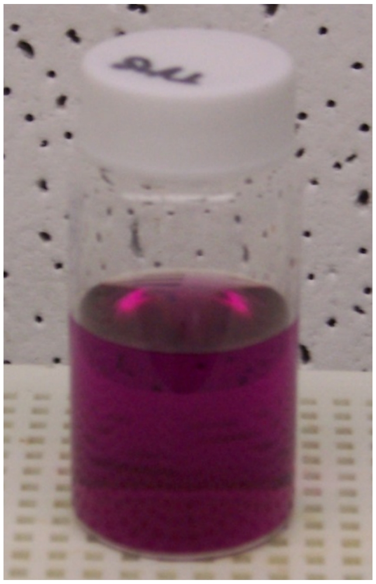
Supplemental Figure 3. FTIR spectra of **4** under vacuum and after exposure to CO_2.



Supplemental Figure 4. Photograph of IL **2** in 5 mL water after sitting for 1 week at RT (note IL floating on surface).

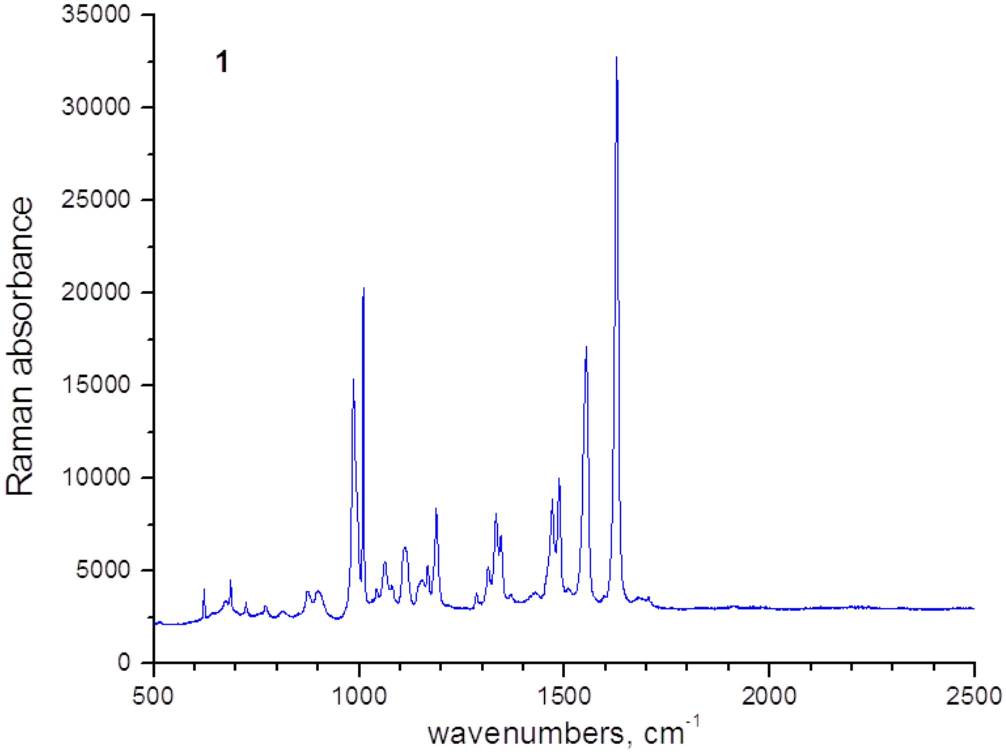


Supplemental Figure 5. Photograph of IL **3** in 5 mL water after sitting for 1 week at RT (note IL sitting at bottom of vial).

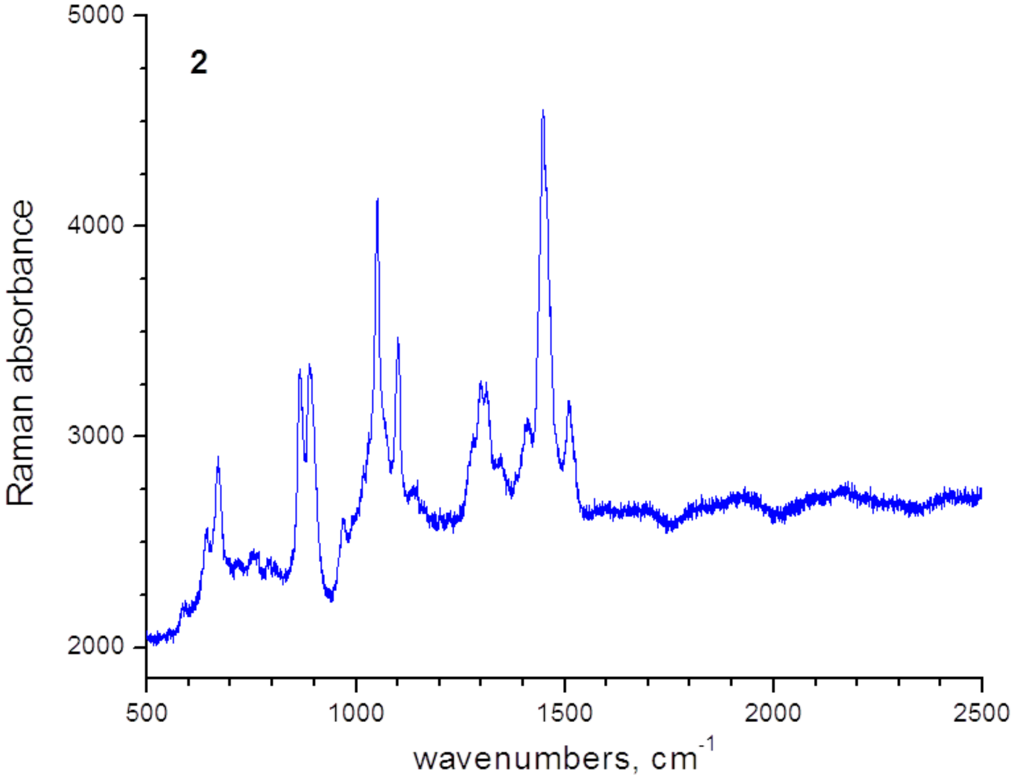


Supplemental Figure 6. Photograph of IL **4** in 5 mL water after sitting for 1 week at RT (initial insoluble IL gradually dissolved after 1-2 days).

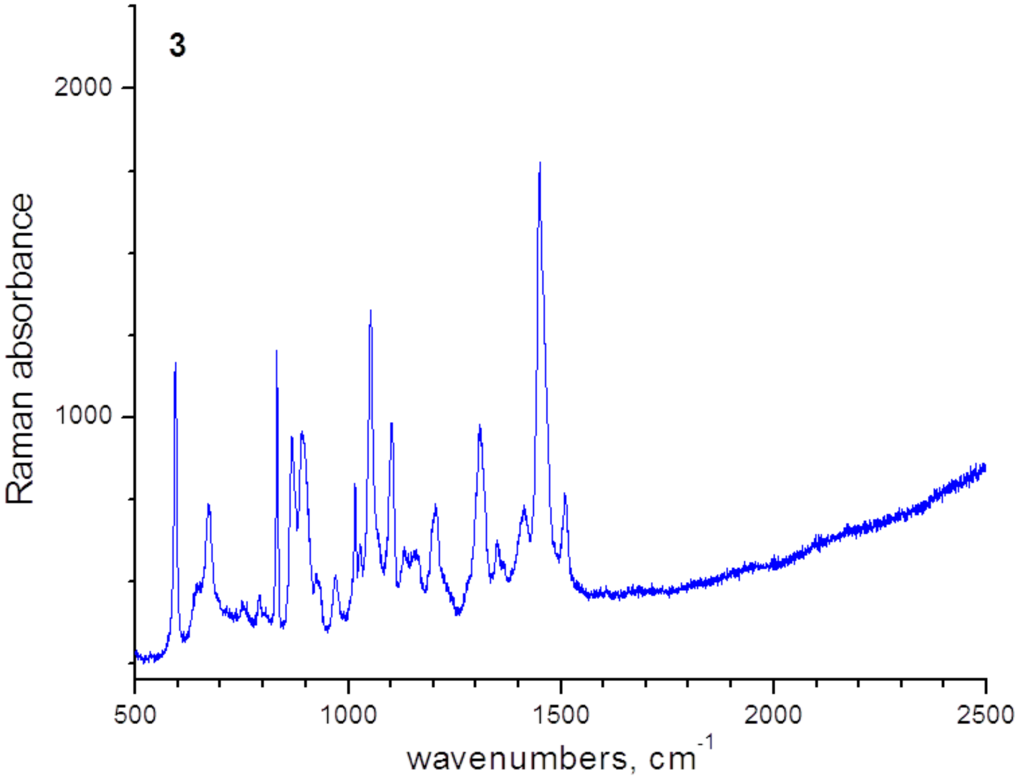
Supplemental Figure 7. Photograph of IL **5** in 5 mL water after sitting for 1 week at RT (note IL sitting at bottom of vial).



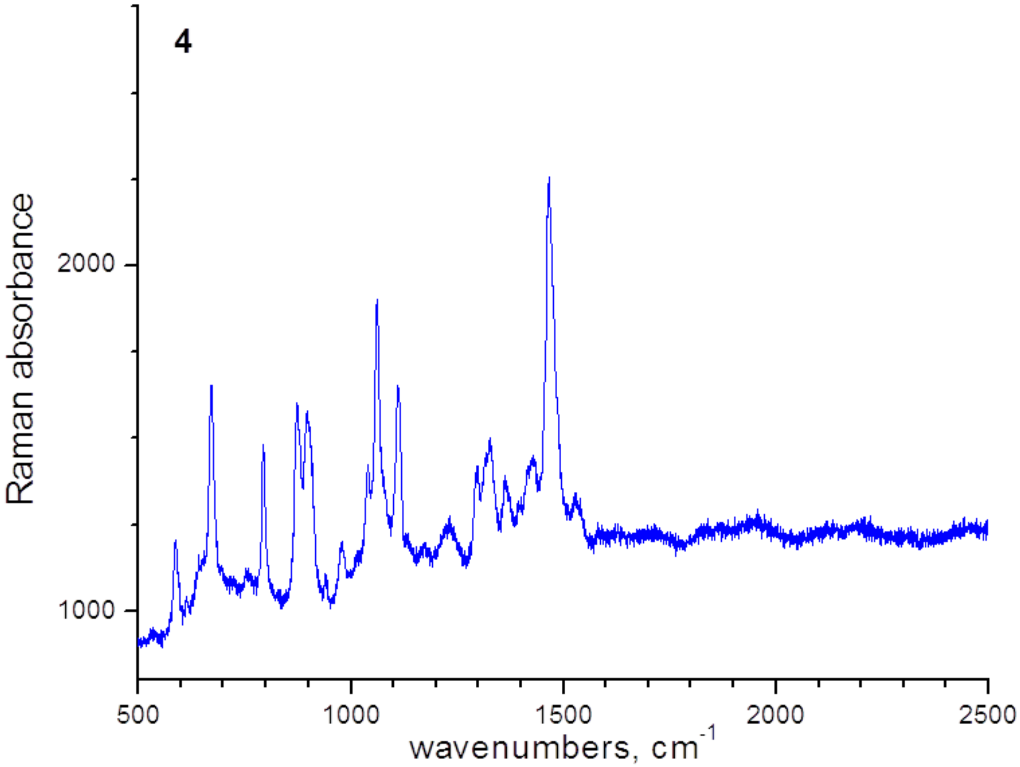
Supplemental Figure 8. Raman spectrum of neat **1** after photobleaching.



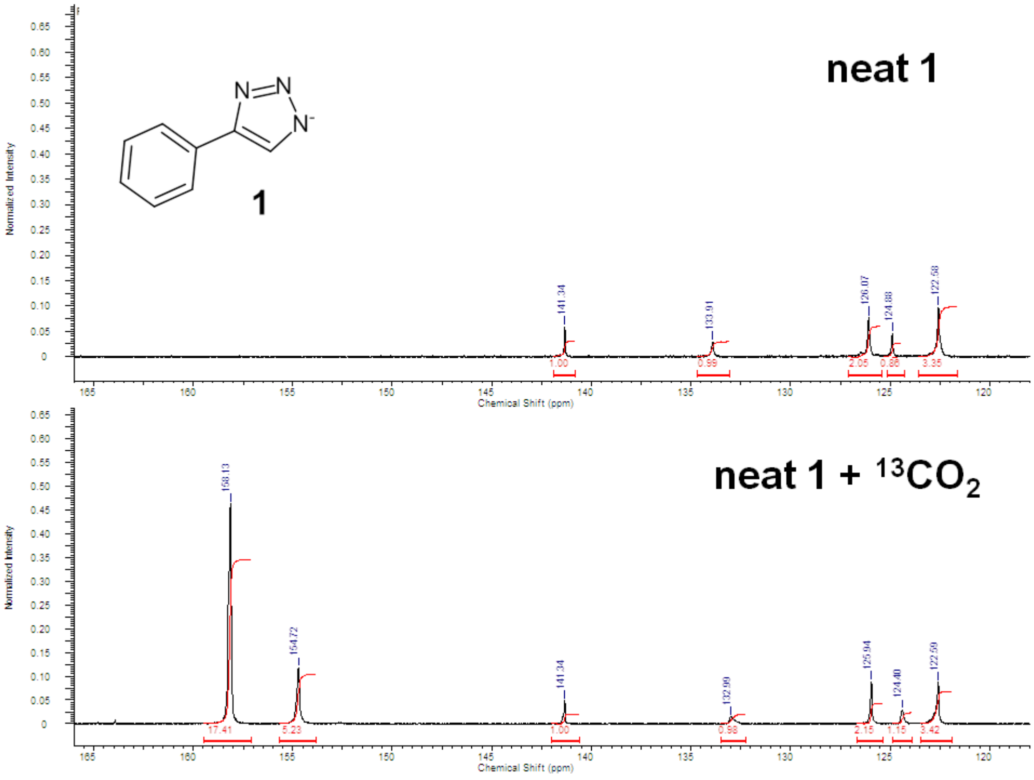
Supplemental Figure 9. Raman spectrum of neat **2** after photobleaching.



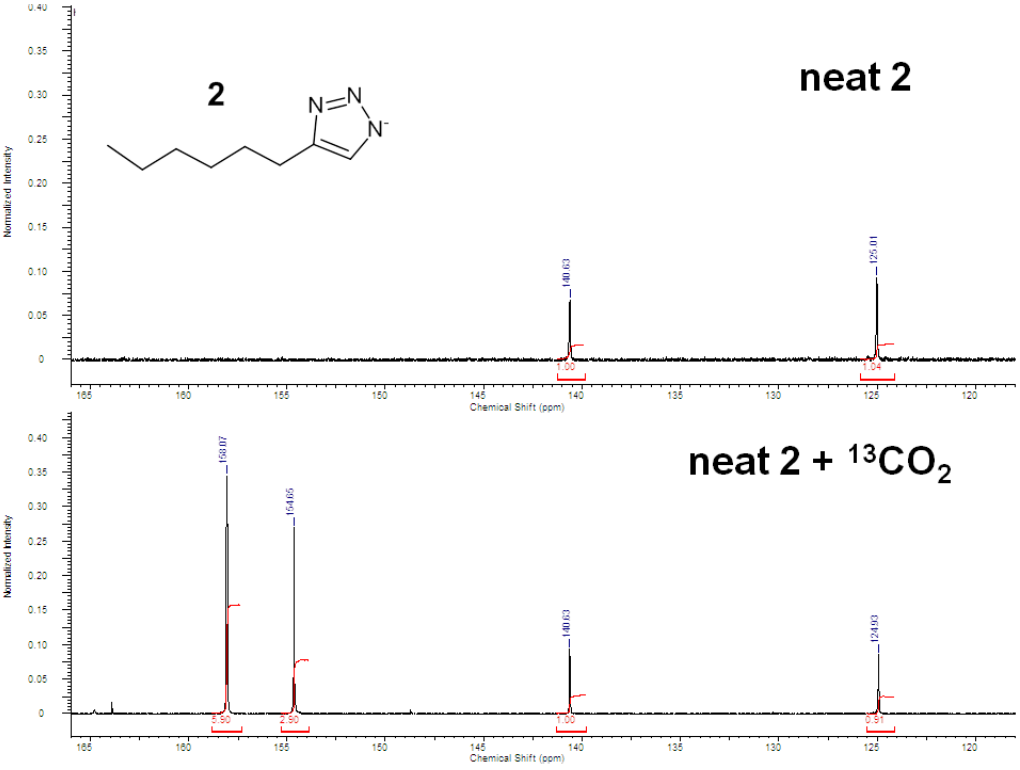
Supplemental Figure 10. Raman spectrum of neat **3** after photobleaching.



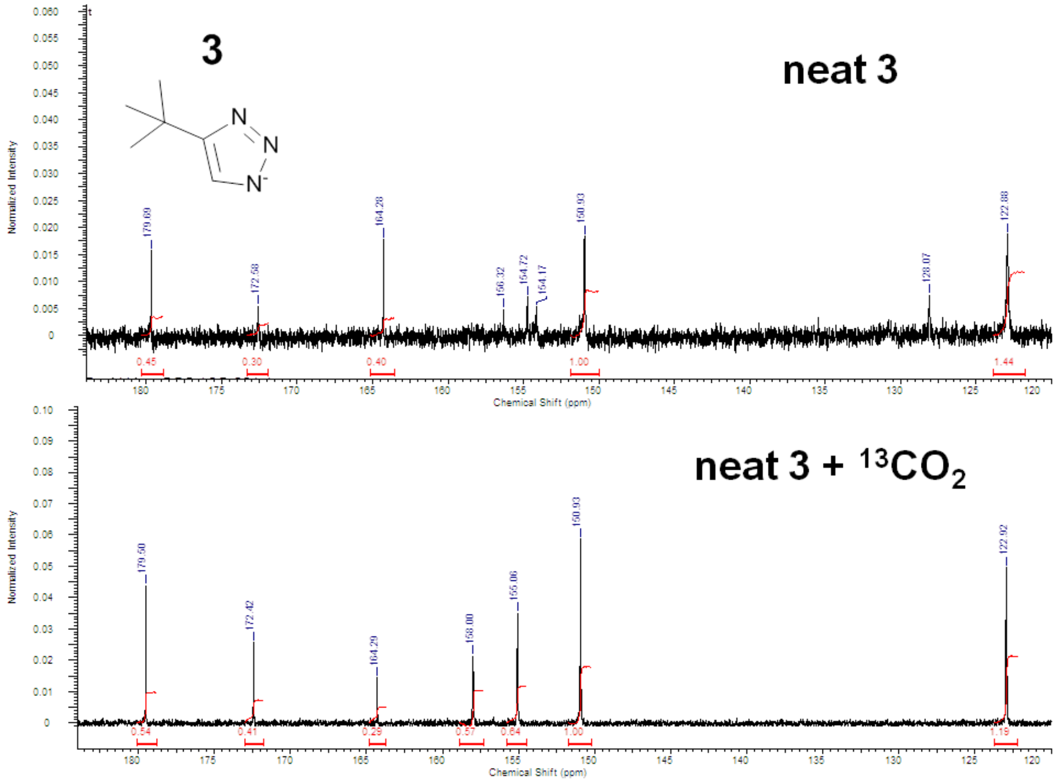
Supplemental Figure 11. Raman spectrum of neat **4** after photobleaching.



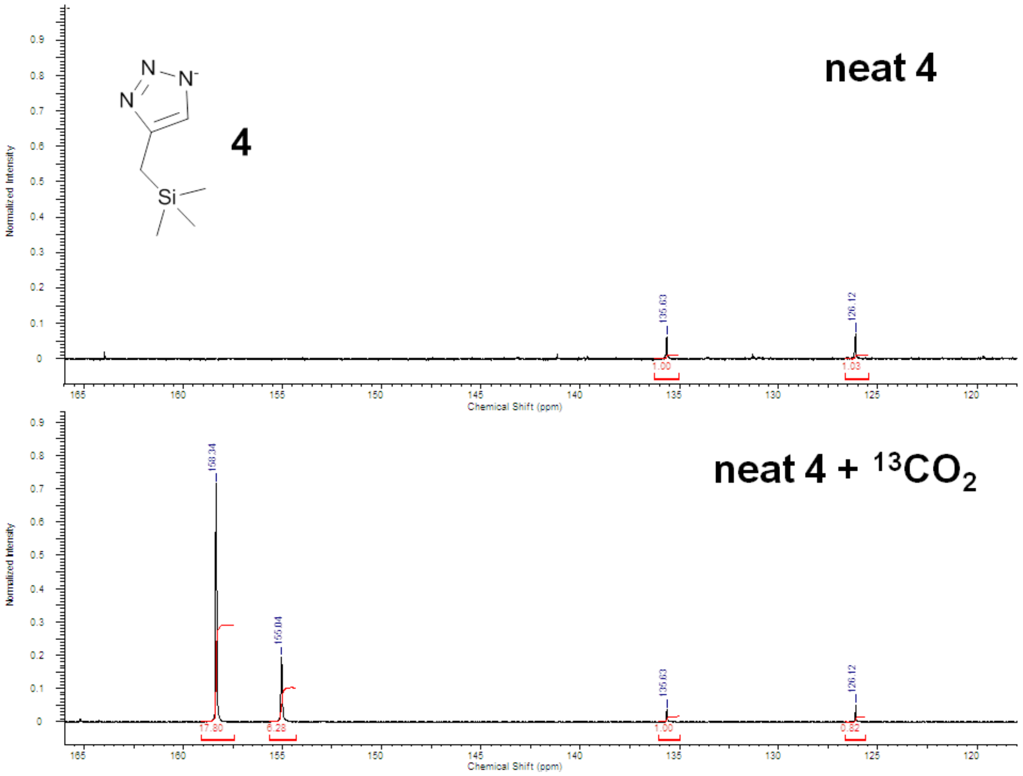
Supplemental Figure 12. ^{13}C NMR spectra of neat **1** before and after $^{13}CO_2$ absorption.



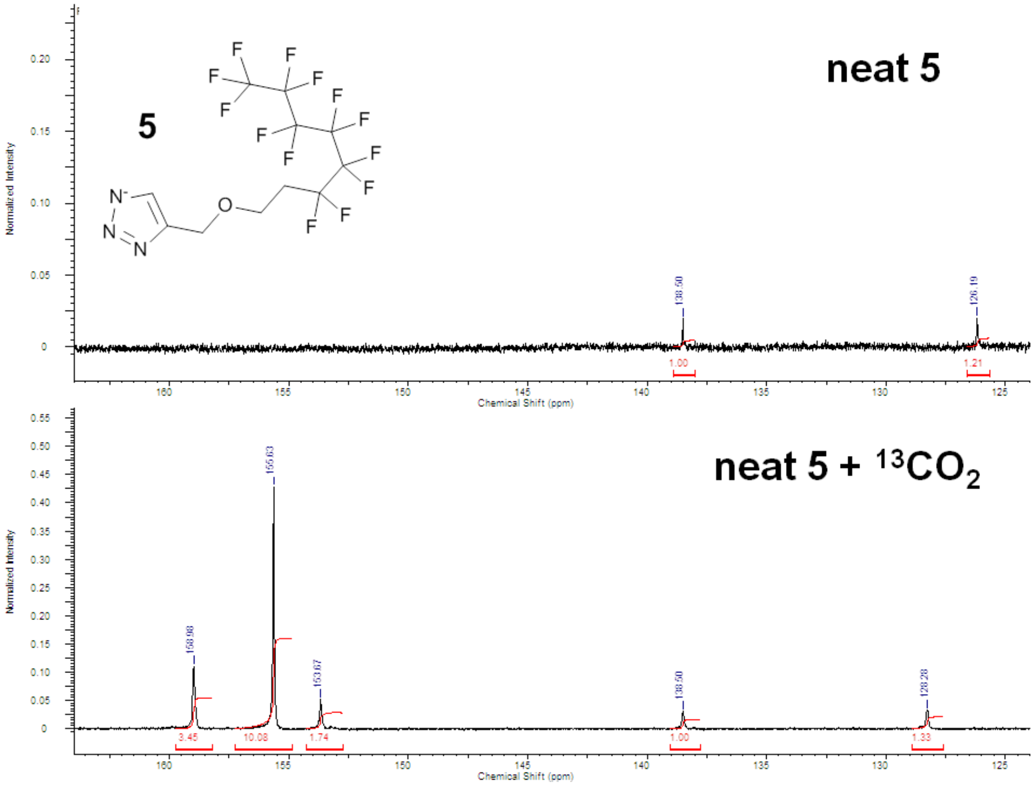
Supplemental Figure 13. ^{13}C NMR spectra of neat **2** before and after $^{13}CO_2$ absorption.



Supplemental Figure 14. ^{13}C NMR spectra of neat **3** before and after $^{13}CO_2$ absorption.



Supplemental Figure 15. ^{13}C NMR spectra of neat **4** before and after $^{13}CO_2$ absorption.



Supplemental Figure 16. ^{13}C NMR spectra of neat **5** before and after $^{13}CO_2$ absorption.

References

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