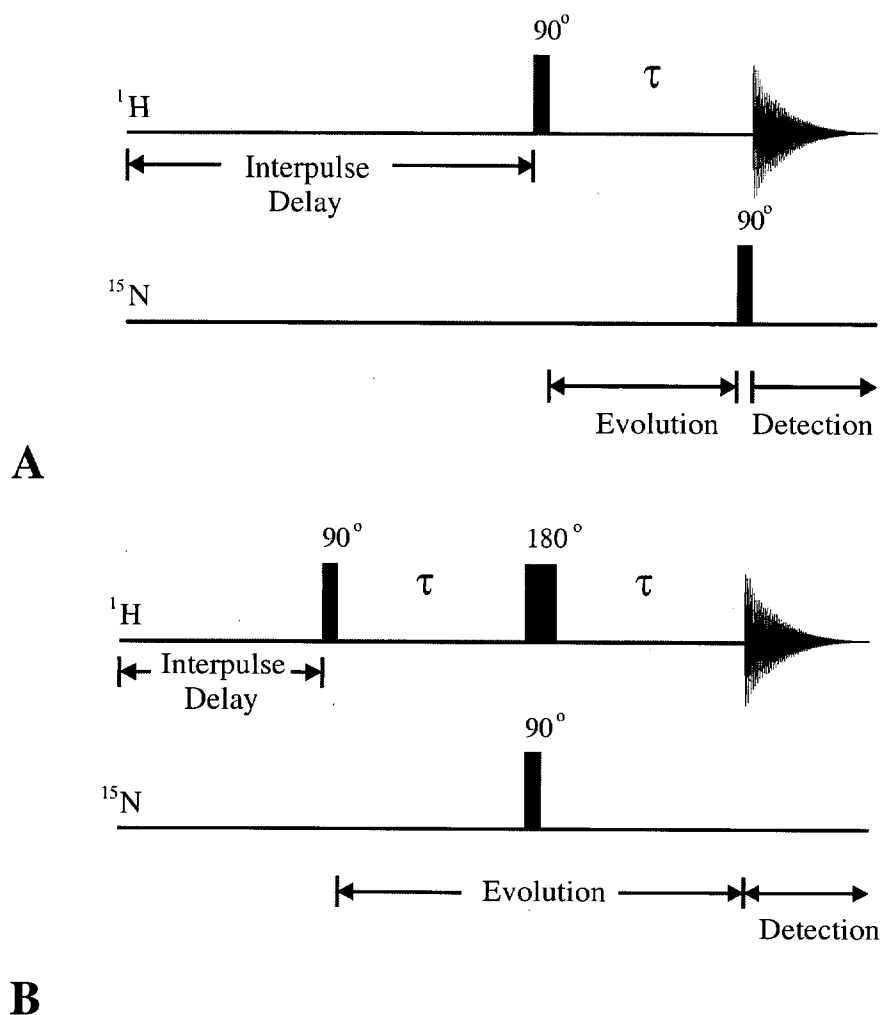
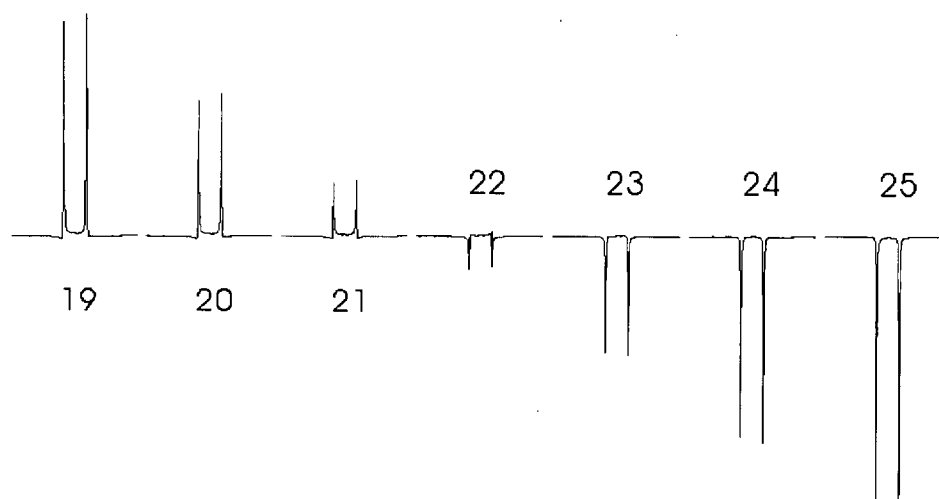




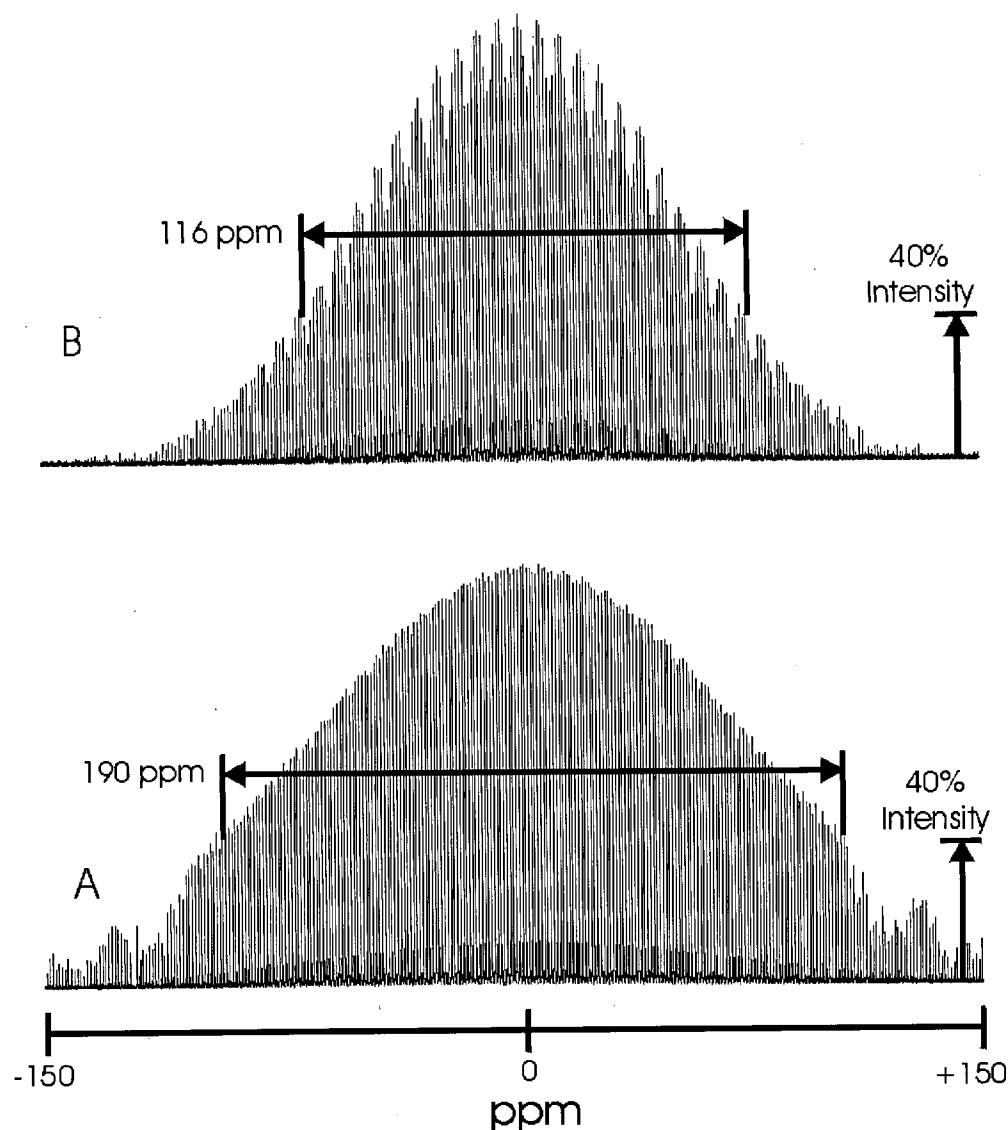
Supplemental Figure S1.

Pulse sequences for the calibration of heteronuclear pulses. A.) The sequence converts proton magnetization to unobservable heteronuclear multiple quantum coherence when a 90° pulse is applied to the X-nucleus (^{15}N in this case). Magnetization, when detected, is antiphase since acquisition begins immediately after the application of the X-nucleus pulse. The duration of the fixed delay, $\tau = 1/2(^1J_{\text{NH}}) = \sim 5.6$ ms for a 90 Hz one-bond ^1H - ^{15}N coupling. B.) The spin-echo variant of the sequence is shown in Figure 1A. Since this is a spin-echo experiment, both limbs of the heteronuclear doublet have the same phase. The data shown in Supplemental Figure S2 were acquired using the sequence shown in B.



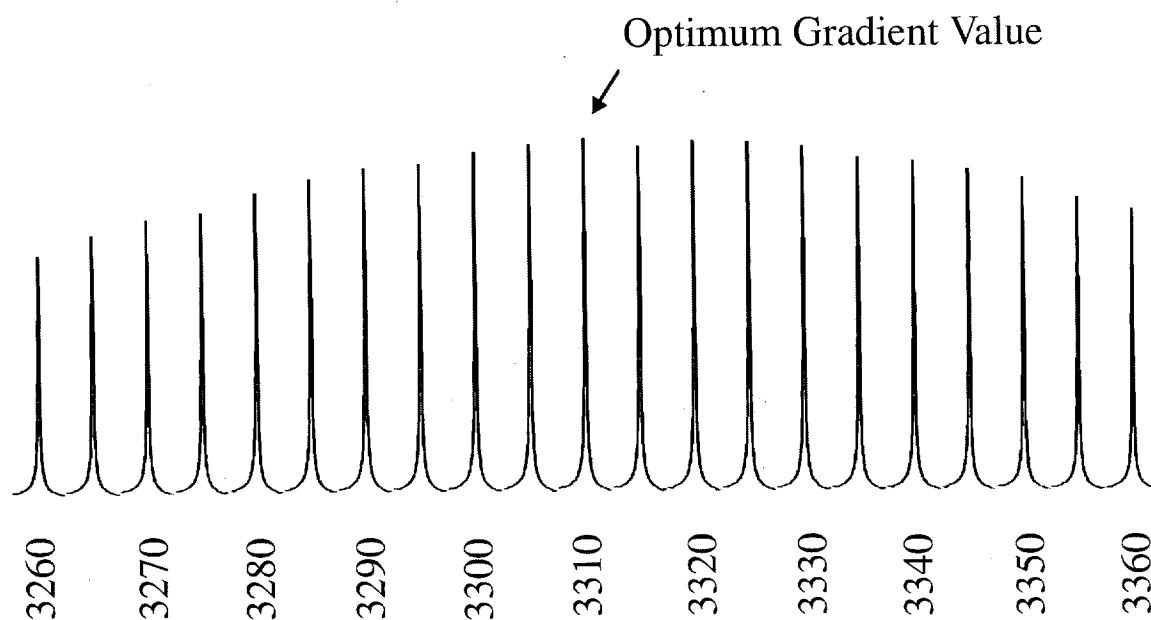
Supplemental Figure S2.

Series of experiments performed using $^{13}\text{C} / ^{15}\text{N}$, doubly-labeled *N*-acetylglutamine to calibrate the 90° ^{15}N pulse. Data were acquired using the pulse sequence shown in Supplemental Figure S1B (a spin-echo analog of the experiment shown in Supplemental Figure S1A), which gives the same results except that the limbs of the ^{15}N -coupled ^1H doublet would initially be antiphase. The 90° ^{15}N pulse calibration can be determined when the signal response is nulled, which in this example would be between 21 and 22 μs .



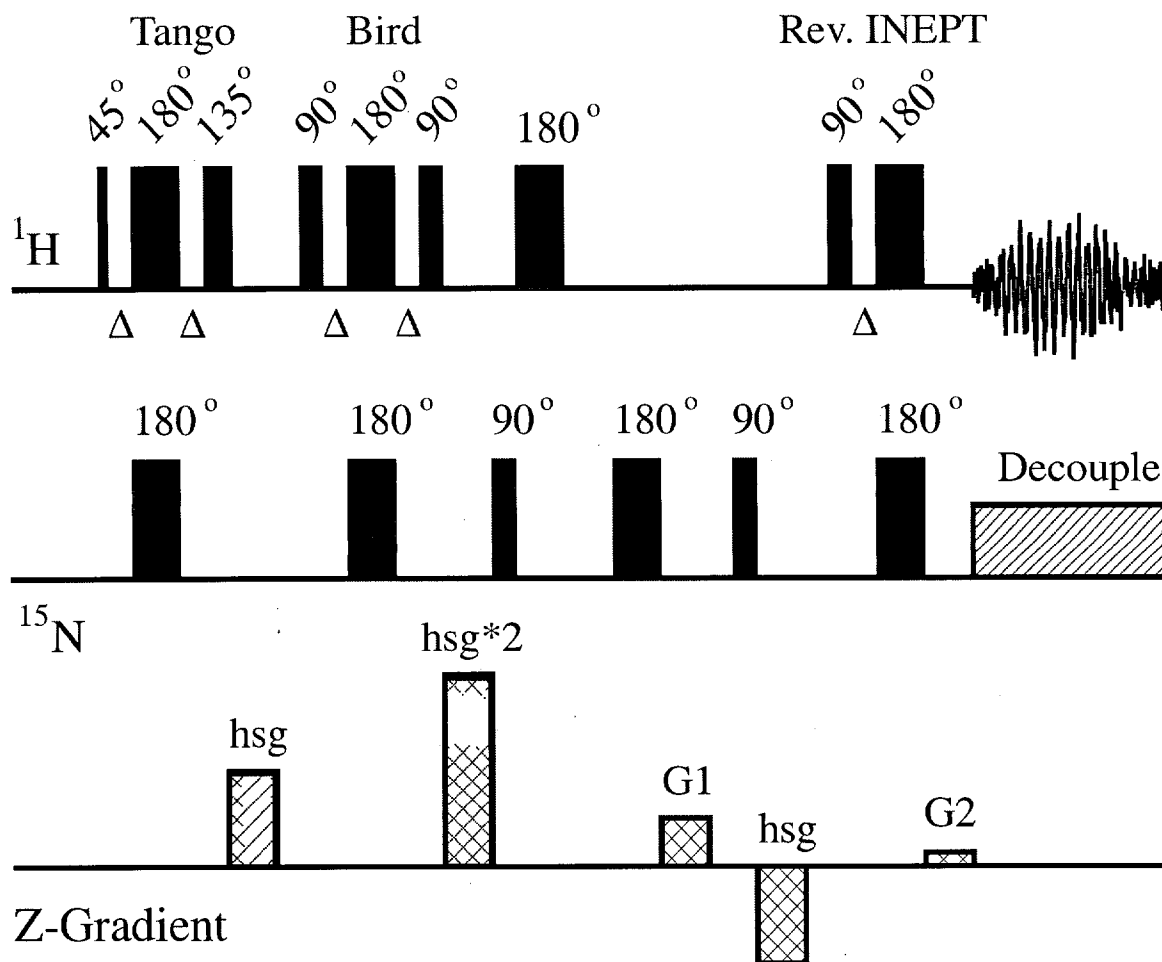
Supplemental Figure S3.

^1H - ^{15}N satellite spectra of doubly labeled *N*-acetyl glycine. The data were acquired as a single transient with the transmitter frequency for ^{15}N moved in successive 1 ppm (60.8 Hz) steps, ± 150 ppm relative to the ^{15}N resonant frequency of the amide nitrogen. A.) Series of experiments performed with the 90° ^{15}N pulse set to 21.1 μs at a power setting of 59 dB (63 dB max). Using 40% of the intensity of the on-resonance spectrum (0 ppm on the arbitrary axis above), the effective F_1 window excited by $\geq 40\%$ is 190 ppm. B.) Series of experiments performed with the 90° ^{15}N pulse set to 29.5 μs at a power setting of 53 dB (63 dB max). Using 40% of the intensity of the on-resonance spectrum (0 ppm on the arbitrary axis above), the effective F_1 window excited by $\geq 40\%$ is 116 ppm.



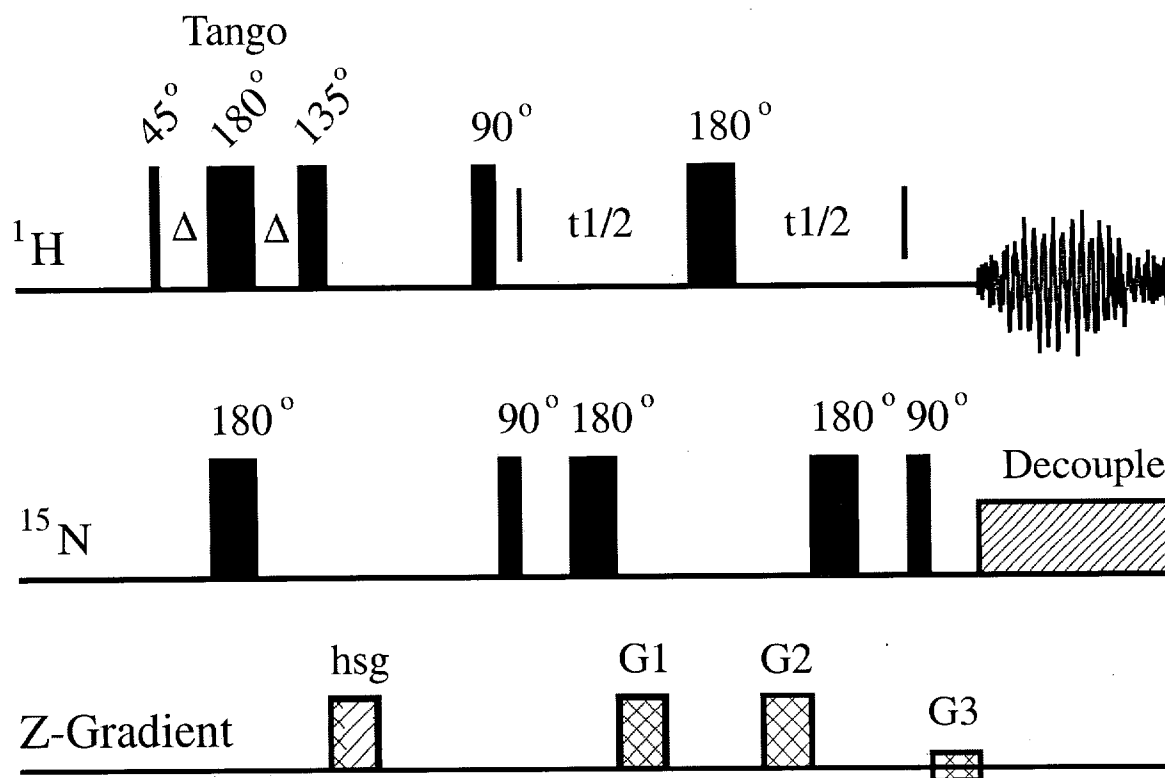
Supplemental Figure S4.

Plot of the gradient optimization as a function of an array of the final gradient while holding the initial gradient constant. The optimization was calibrated for the GHMBC experiment (Figure 2), and was optimized across a range of 100 dB, with the optimum value for the final gradient observed at 3310 dB.



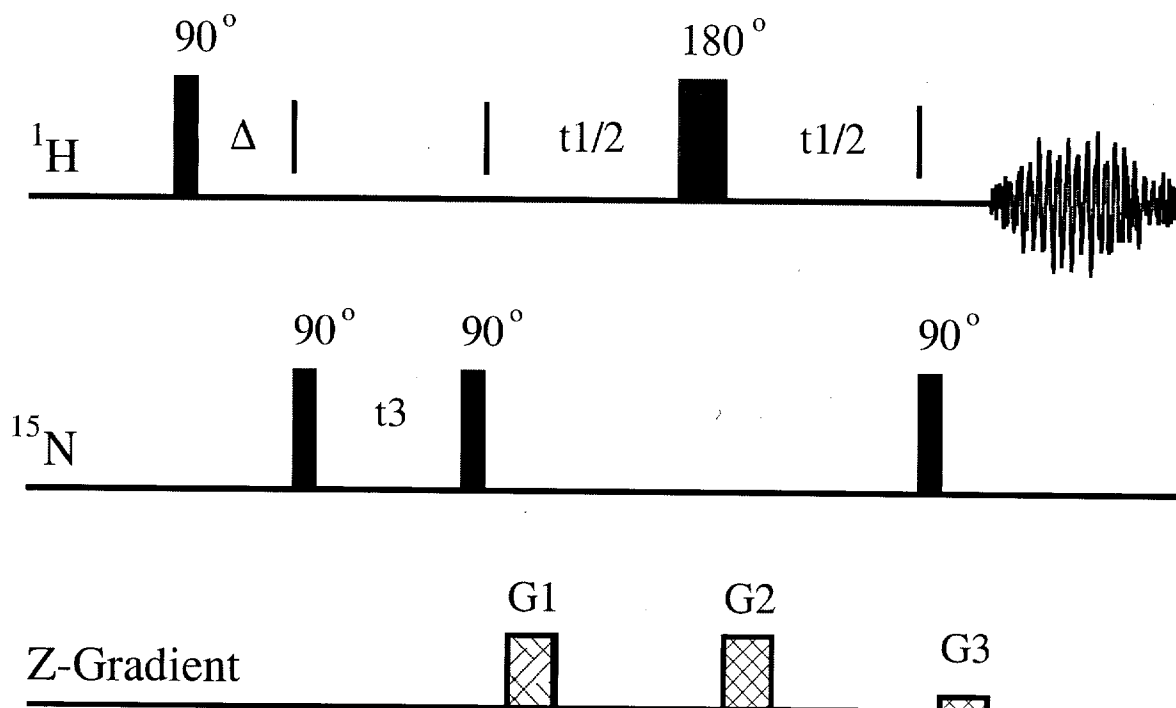
Supplemental Figure S5.

Pulse sequence for gradient-enhanced heteronuclear single quantum coherence-based shift correlation (GHSQC). The intensity of the gradient levels labeled G1 and G2 should theoretically be optimized to a 5:1 ratio, but the actual ratios should be experimentally determined as described in Figure 4. The gradient times should be optimized to a 2:1 ratio, respectively.



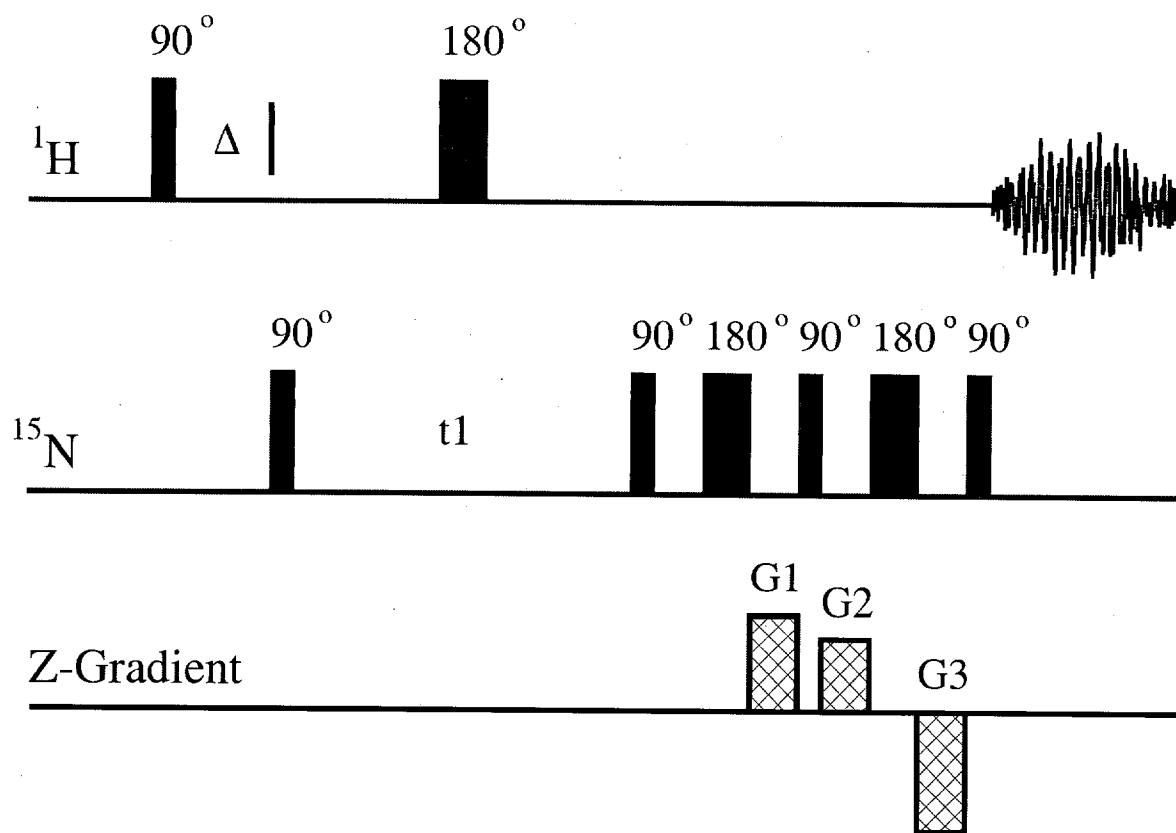
Supplemental Figure S6.

Pulse sequence for gradient heteronuclear multiple quantum-based chemical shift correlation (GHMQC) derived from the experiment described by Hurd and John.²¹ Gradient ratios are identical to those used in the GHSQC experiment.



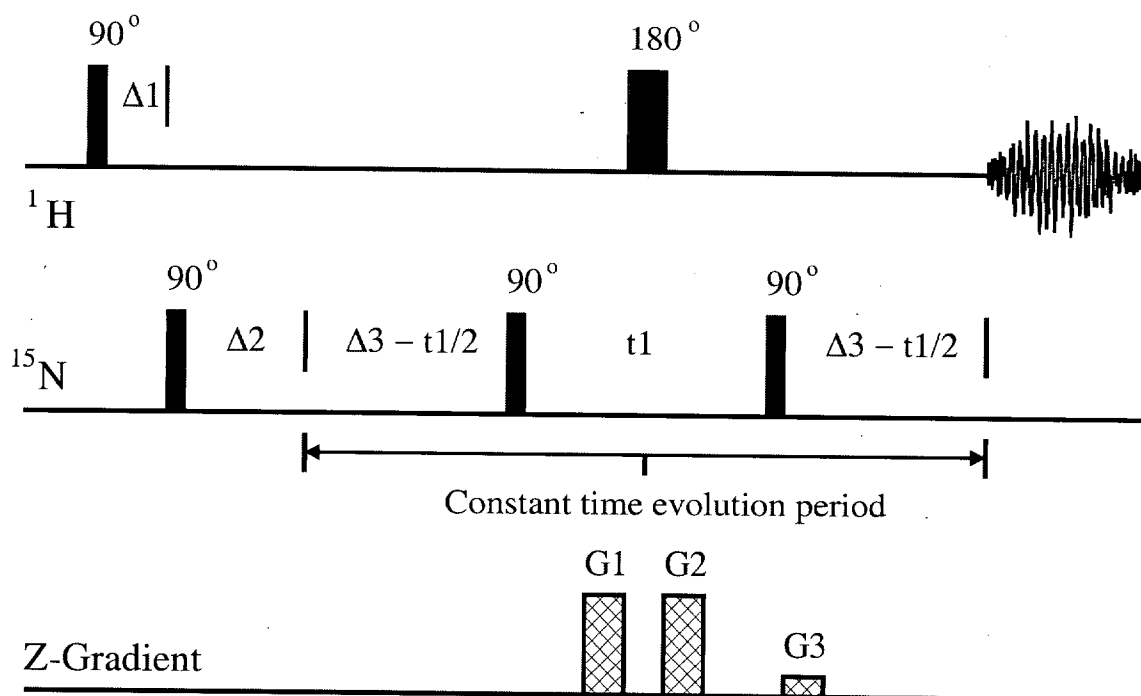
Supplemental Figure S7.

3D-HMBC experiment proposed by Furihata and Seto.⁴¹ The experiment uses an incremented long-range delay, t_3 , in an effort to provide more uniform excitation across a range of potential long-range delays. Data are presented after 3D processing as a projection through the third frequency domain. Gradient ratios are identical to those used in the conventional GHMBC experiment.



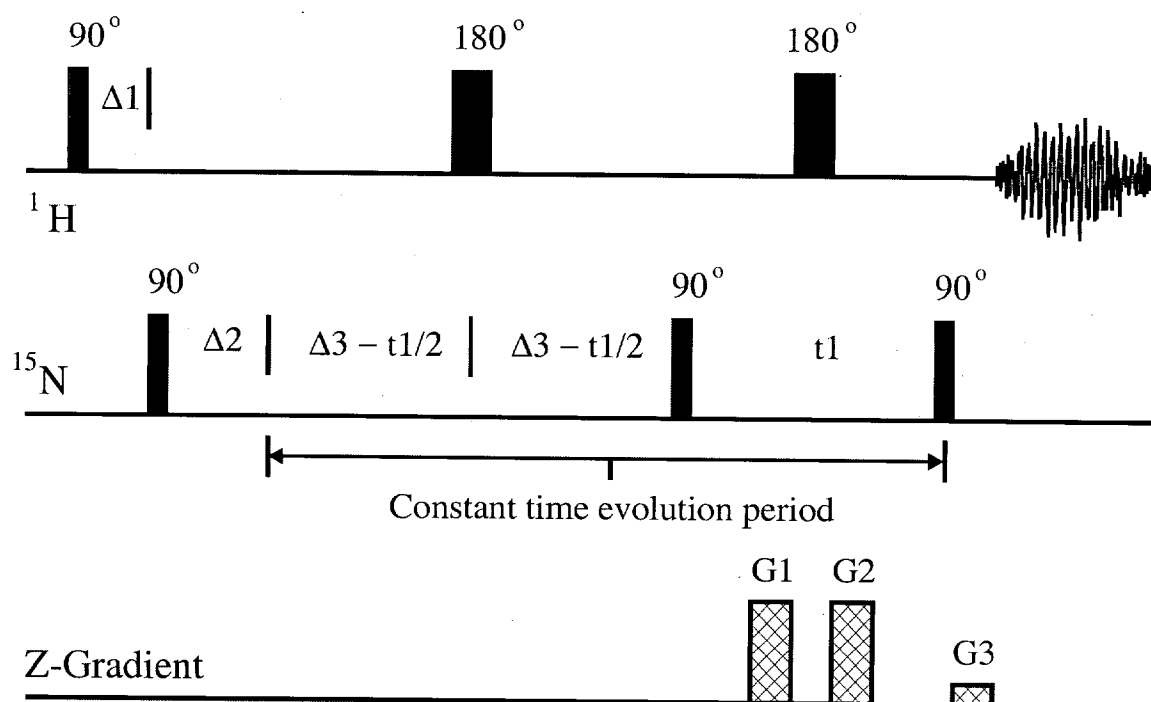
Supplemental Figure S8.

Phase-sensitive long-range heteronuclear shift correlation sequence, PS-GHMBC, proposed by Sheng and van Halbeek.⁴³



Supplemental Figure S9.

CT-HMBC-1 experiment proposed by Furihata and Seto.⁴⁵ Gradient ratios are identical to those used in the conventional GHMBC experiment.

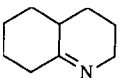
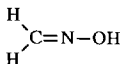
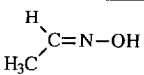
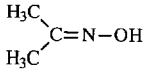
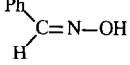
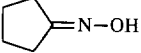
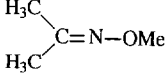
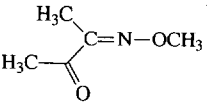
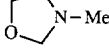
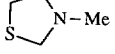


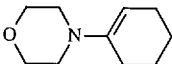
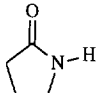
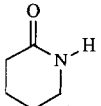
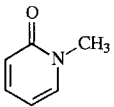
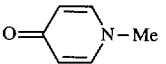
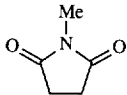
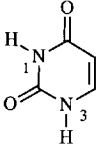
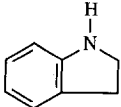
Supplemental Figure S10.

CT-HMBC-2 experiment proposed by Furihata and Seto.⁴⁵ Gradient ratios are identical to those used in the conventional GHMBC experiment.

Supplemental Table S1.

¹⁵N Chemical shifts of selected aliphatics, amides, nitriles, and oximes, etc. Chemical shift values have been rounded to the nearest ppm, as solvent effects, temperature, and some original data acquired as ¹⁴N isotopes can result in up to a +/- 5 ppm error in the reported chemical shifts. Values are given as a general guideline only.

Compound	¹⁵ N Chemical Shift (ppm downfield of liquid NH ₃)	Note(s)
	296	<i>a, i</i>
	381.7	<i>e, j</i>
	<i>E</i> -isomer 414.1 <i>Z</i> -isomer 409.8	<i>b, j</i>
	425.4	<i>b, j</i>
	<i>E</i> -isomer 405.8	<i>b, j</i>
	432.5	<i>b, j</i>
	387.6	<i>d, u</i>
	348.7	<i>d, u</i>
	38	<i>f, k</i>
	57	<i>a, n</i>
	53	<i>a, n</i>
	37	<i>a, l</i>
	34	<i>c, m</i>
	32	<i>c, l</i>

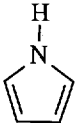
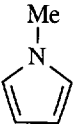
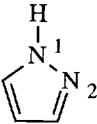
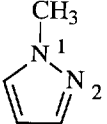
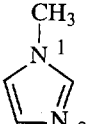
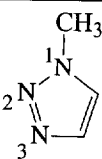
	68	<i>c, o</i>
	116	<i>g, p</i>
	115	<i>g, p</i>
	166	<i>h, q</i>
	140	<i>h, q</i>
	181	<i>f, s</i>
	N-1 - 160 N-3 - 132	<i>a, r</i>
	67	<i>f, t</i>

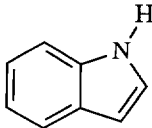
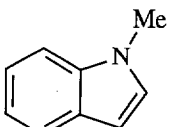
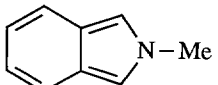
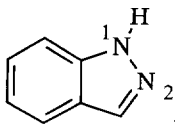
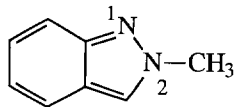
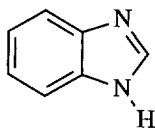
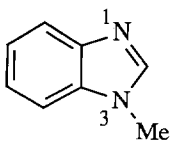
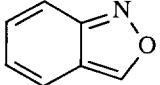
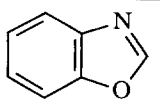
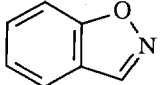
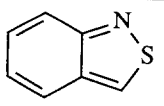
^a DMSO-*d*₆ used as the solvent. ^b CHCl₃ used as the solvent. ^c CDCl₃ used as the solvent. ^d Et₂O used as the solvent. ^e H₂O used as the solvent. ^f No solvent used, data acquired on neat liquid. ^g CCl₄ used as the solvent. ^h MeOH used as the solvent. ⁱ Duthaler, R. O.; Roberts, J. D. *J. Am. Chem. Soc.* **1978**, *100*, 4969-4973. ^j Botto, R. E.; Westerman, P. W.; Roberts, J. D. *Org. Magn. Res.* **1978**, *11*, 510-515. ^k Ewing, D. F. Annual Reports in NMR Spectroscopy; Mooney, E. F., Ed.; Academic Press: New York, 1975, 6A, p 389. ^l Haslinger, E.; Reitmaier, M.; Robien, R; Wolschann *Mon. Chem.* **1984**, *115*, 375-381. ^m Kupce, E.; Liepins, E.; Lapsina, A.; Zelcans, G.; Lukevics, E. *J. Organomet. Chem.* **1987**, *333*, 1-7. ⁿ Chen, B. C.; von Philipsborn, W.; Nagarajan, K. *Helv. Chim. Acta.* **1983**, *66*, 1537-1555. ^o Fritz, H. *Bull Soc. Chim., Belg.* **1984**, *93*, 559-569. ^p Marchal, J. P.; Canet, D. *Org. Magn. Reson.* **1981**, *15*, 344-346. ^q Lichter, R. L.; Fehder, C. G.; Patton, P. H.; Coombes, J.; Dorman, D. E. *J.*

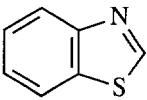
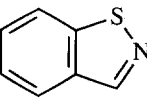
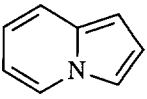
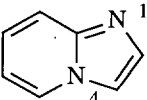
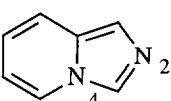
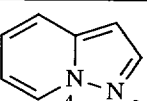
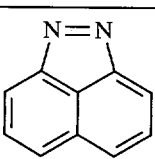
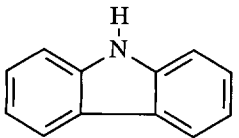
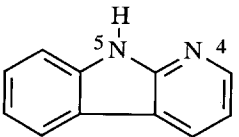
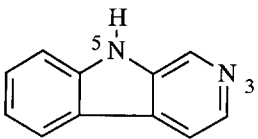
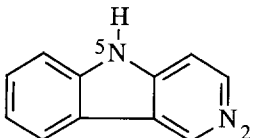
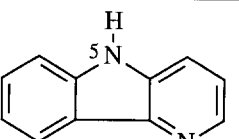
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Supplemental Table S2.

^{15}N Chemical shifts of five-membered ring heterocycles. The solvent used is included in the notes, when possible. Chemical shift values have been rounded to the nearest ppm, as solvent effects, temperature, and some original data acquired as ^{14}N isotopes can result in up to a ± 5 ppm error in the reported chemical shifts. Values are given as a general guideline only.

Compound	^{15}N Chemical Shift (in ppm downfield from liquid NH_3)	Note(s)
	155	<i>a, i</i>
	150	<i>a, i</i>
	N-1 - 206 N-2 - 300	<i>a, j</i>
	N-1 - 199 N-2 - 303	<i>b, j</i>
	N-1 - 160 N-3 - 260	<i>a, j</i>
	N1 - 237 N2 - 363 N3 - 350	<i>a, i</i>
	380	<i>c, k</i>
	252	<i>d, k</i>

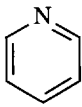
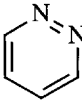
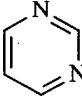
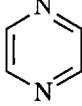
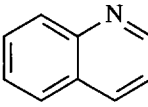
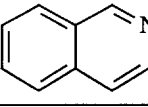
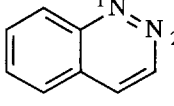
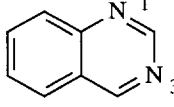
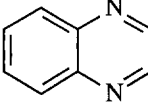
	298	<i>e, k</i>
	322	<i>c, k</i>
	134	<i>k</i>
	130	<i>k</i>
	162	<i>e, k</i>
	N-1 - 178 N-2 - 318	<i>f, k</i>
	N1 - 294 N2 - 219	<i>f, k</i>
	195	<i>l</i>
	N-1 - 252 N-2 - 142	<i>g, l</i>
	353	<i>c, k</i>
	238	<i>c, k</i>
	380	<i>c, k</i>
	259	<i>c, k</i>

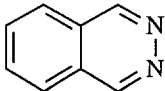
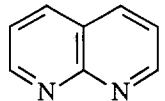
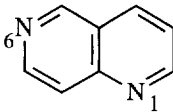
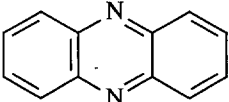
	318	<i>c, k</i>
	304	<i>e, k</i>
	189	<i>e, m</i>
	N-1 - 240 N-4 - 201	<i>e, m</i>
	N-2 - 272 N-4 - 194	<i>e, m</i>
	N-3 - 287 N-4 - 236	<i>e, m</i>
	455	<i>h, n</i>
	117	<i>o</i>
	N-4 - 266 N-5 - 122	<i>o</i>
	N-3 - 306 N-5 - 113	<i>o</i>
	N-2 - 289 N-5 - 119	<i>o</i>
	N-1 - 296 N-5 - 112	<i>o</i>

^a DMSO-*d*₆ used as the solvent. ^b CDCl₃ used as the solvent. ^c No solvent used. ^d MeOH used as the solvent. ^e Et₂O used as the solvent. ^f Acetone used as the solvent. ^g CCl₄ used as the solvent. ^h THF used as the solvent. ⁱ Wofford, D. S.; Forkey, D. M.; Russell, J. G. *J. Org. Chem.* **1982**, 47, 5132-5137. ^j Chen, B. C.; von Philipsborn, W.; Nagarajan, K. *Helv. Chim. Acta*; **1983**, 66, 1537-1555. ^k Stefaniak, L. *Bull. Acad. Pol. Sci., Ser. Sci. Chim.*; **1978**, 26, 291-302. ^l Buchanan, G. W.; Dawson, B. A. *Can. J. Chem.* **1976**, 54, 790-794. ^m Stefaniak, L.; Roberts, J. D.; Witanowski, M.; Handi, B. T.; Webb, G. A. *Org. Magn. Reson.* **1984**, 22, 209-214. ⁿ Nakanishi, K.; Yabe, A.; Honda, K. *J. Chem. Soc., Chem. Commun.* **1982**, 86-87. ^o Markgraf, J. H.; Richardson, D. P.; Livingston, R. C. *Magn. Reson. Chem.* **1993**, 31, 694-695.

Supplemental Table S3.

¹⁵N Chemical shifts of six-membered ring heterocycles. The solvent used in all cases was DMSO-*d*₆. Chemical shift values have been rounded to the nearest ppm, as solvent effects, temperature, and some original data acquired as ¹⁴N isotopes can result in up to a +/- 5 ppm error in the reported chemical shifts. Values are given as a general guideline only.

Compound	¹⁵ N Chemical Shift (in ppm downfield from liquid NH ₃)	Note(s)
	317	<i>a</i>
	400	<i>a</i>
	295	<i>a</i>
	334	<i>a</i>
	316	<i>b</i>
	311	<i>b</i>
	N1 - 424 N2 - 421	<i>b</i>
	N1 - 294 N3 - 283	<i>b</i>
	330	<i>b</i>

	370	<i>b</i>
	314	<i>b</i>
	N1 - 315 N6 - 311	<i>b</i>
	326	<i>c</i>

^a Stadel, W.; von Philipsborn, W.; Wick, A.; Kompis, I. *Helv. Chim. Acta*, **1980**, *63*, 504-522. ^b Stefaniak, L.; Roberts, J. D.; Witanowski, M.; Webb, G. A. *Org. Magn. Reson.* **1984**, *22*, 201-208. ^c Markgraf, J. H.; Richardson, D. P.; Livingston, R. C. *Magn. Reson. Chem.* **1993**, *31*, 694-695.