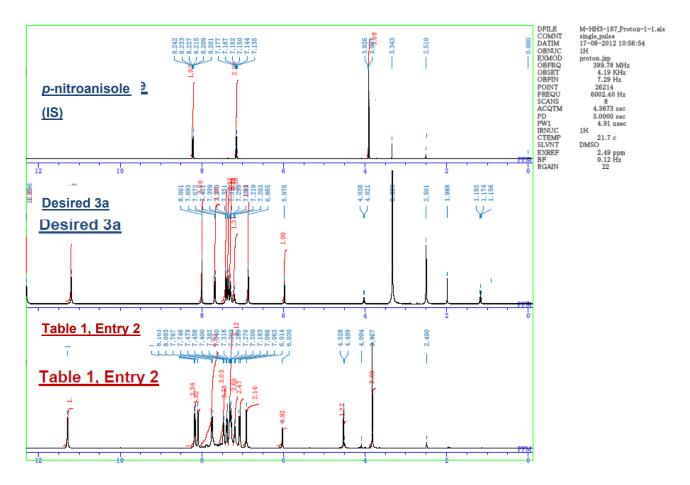
Supporting Information

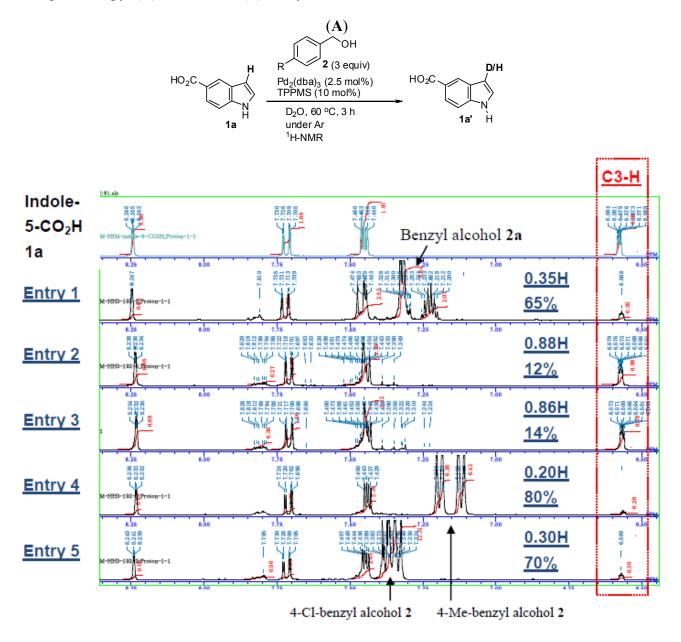
Figure S1. ¹H NMR spectrum with conversion yield of **3a** from integration. (Table 1, Entry 2). A mixture of **1a** (80 mg, 0.5 mmol), palladium(II) acetate (6 mg, 0.025 mmol), sodiumdiphenylphosphinobenzene-3-sulfonate (TPPMS, 18 mg, 0.05 mmol) and benzyl alcohol **2a** (154 μ L, 1.5 mmol) in H₂O (2 mL) was heated at 60 °C for 16 h in a sealed tube. After the reaction mixture was cooled, *p*-nitroanisole (38 mg, 0.25 mmol, internal standard) was added to the reaction mixture, which was extracted with AcOEt. The organic layer was washed with brine, and concentrated *in vacuo*. The residue was analyzed by ¹H-NMR spectroscopy.



Conversion yield was calculated by integration.

	desired 3a	<i>p</i> -nitroanisole internal standard
Signal δ	6.03 (methine- <u>H</u>)	3.827 (-OC <u>H</u> ₃)
Integral value	0.92 (1H)	3.00 (3H)
Calculated ratio	92% from 1a	

Figure S2. ¹H-NMR spectrum of C–H bond Activation at the C3-position of indole **1a** (Table 2). A mixture of **1a** (40 mg, 0.25 mmol), palladium(II) acetate (2.8 mg, 0.0125 mmol) or tris(dibenzylideneacetone)-dipalladium(0)-chloroform adduct (6.5 mg, 0.0063 mmol), sodium diphenylphosphinobenzene-3-sulfonate (TPPMS, 9.1 mg, 0.025 mmol) and benzyl alcohol **2** (0.75 mmol) in D₂O (0.75 mL) was heated at 60 °C for 3 h under Ar in a sealed tube. After cooling, the reaction mixture was extracted with AcOEt. The organic layer was washed with brine and concentrated *in vacuo*. The residue was analyzed by ¹H-NMR spectroscopy. (A) entries 1-5; (B) entry 6 and 7.



(B)

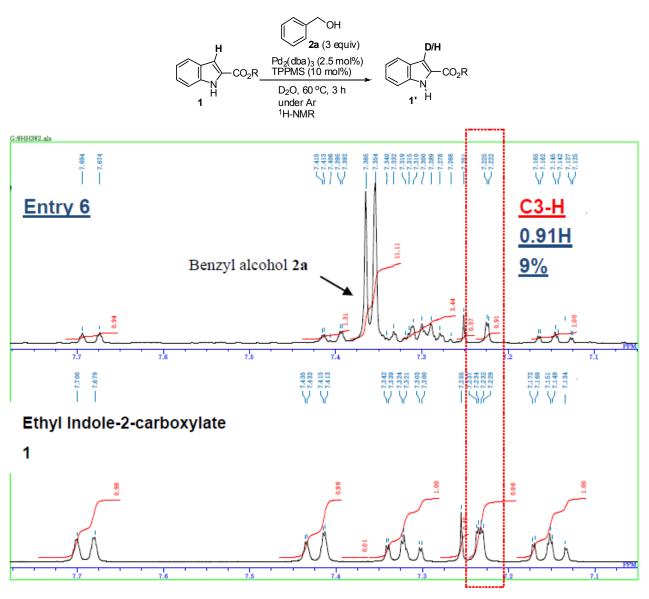
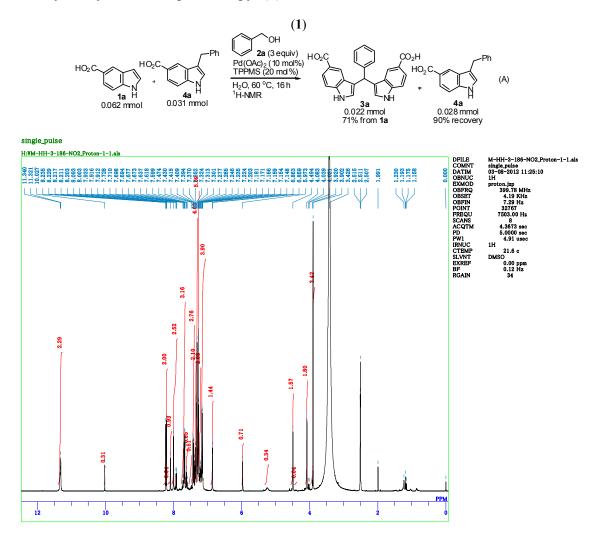


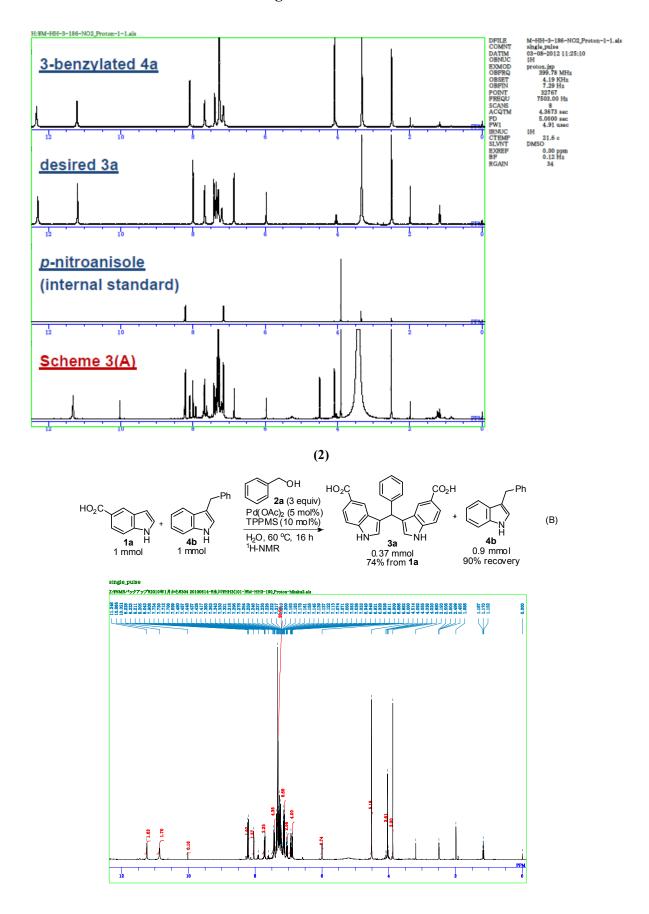
Figure 3S. ¹H NMR experiments to monitor the reaction. (1) Scheme 3 A. A mixture of 3-benzylated 4a (7.8 mg, 0.031 mmol), 1a (10.0 mg, 0.062 mmol), palladium(II) acetate (1.4 mg, 0.00624 mmol), sodium diphenylphosphinobenzene-3-sulfonate (TPPMS, 4.5 mg, 0.0125 mmol) and benzyl alcohol 2a (20.1 mg, 0.186 mmol) in H₂O (0.5 mL) was heated at 60 °C for 16 h in a sealed tube. After the reaction mixture was cooled, *p*-nitroanisole (4.7 mg, 0.031 mmol, internal standard) was added to the reaction mixture, which was extracted with AcOEt. The organic layer was washed with brine and concentrated *in vacuo*. The residue was analyzed by ¹H-NMR spectroscopy. (2) Scheme 3B.



Conversion vield	and recovery we	ere calculated by integration.
5	5	<i>J U</i>

	desired 3b	3-benzylated 4b	<i>p</i> -nitroanisole internal standard	
Signal δ	5.97	4.08 (C <u>H</u> ₂)	8.21 (Ar– <u>H</u> x2)	
	(methine- <u>H</u>)	4.08 (C <u>11</u> 2)		
Integral value	0.71 (1H)	1.80 (2H)	2.0 (2H), 4.7 mg (0.031 mmol)	
Calculated ratio	0.022 mmol	0.028 mmol		
	71% from 1b	90% recovery		

Figure 3S. Cont.



Conversion yield and recovery were calculated by integration.					
	desired 3a	3-benzylated 4b	<i>p</i> -nitroanisole internal standard		
Signal δ	6.00 (methine– <u>H</u>)	4.06 (C <u>H</u> 2)	3.88 (OC <u>H</u> ₃)		
Integral value	0.74 (1H)	3.61 (2H)	3.0 (3H), 77 mg (0.5 mmol)		
Calculated ratio	0.37 mmol 74% from 1a	0.9 mmol 90% recovery			

Figure 3S. Cont.

Figure 4S. ¹H-NMR spectrum (Table 3 Use of benzyl acetate 12).

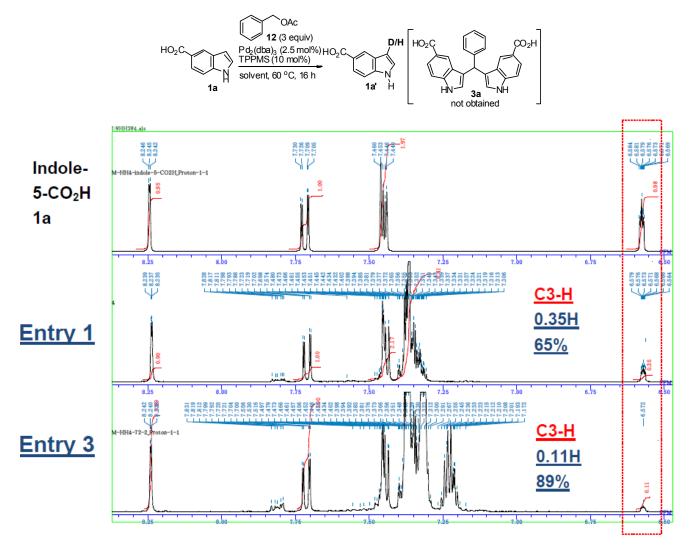
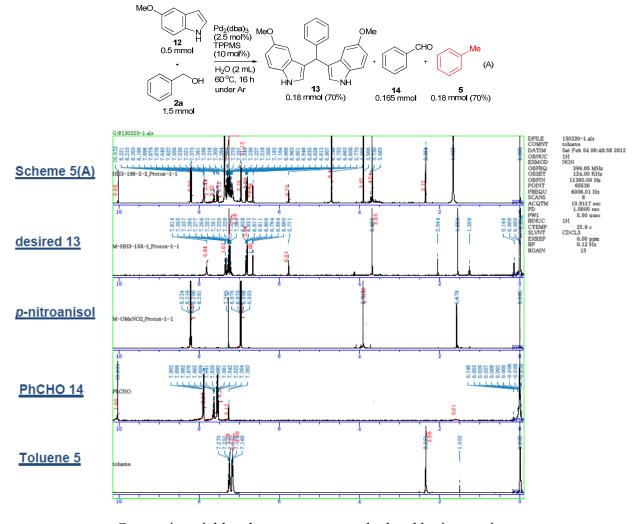
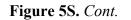


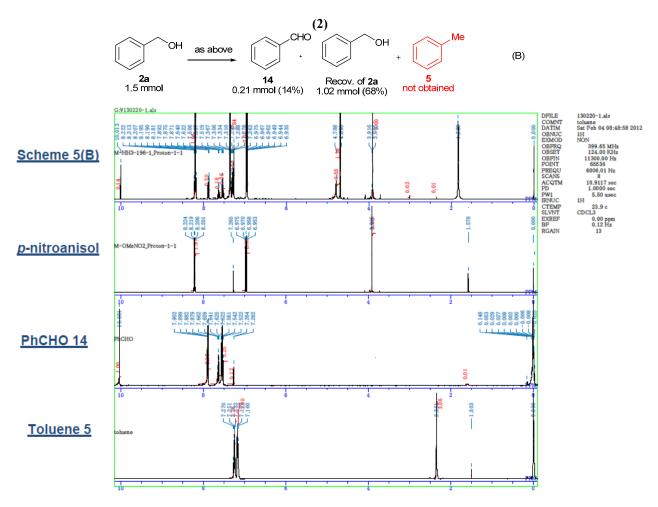
Figure 5S. (1) Scheme 5 A ¹H NMR experiments to monitor the reaction. A mixture of 5-methoxyindole 12 (74 mg, 0.5 mmol), benzyl alcohol 2a (162 mg, 1.5 mmol), $Pd_2(dba)_3$ – $CHCl_3$ (12.9)0.0125 mmol), sodium mg, and diphenylphosphinobenzene-3-sulfonate (TPPMS, 18 mg, 0.05 mmol) in H₂O (0.5 mL) was heated at 60 °C for 16 h in a sealed tube under Ar. After the reaction mixture was cooled, *p*-nitroanisole (38.3 mg, 0.25 mmol, internal standard) was added to the reaction mixture, which was extracted with CHCl₃ (8 mL), before the organic layer was analyzed by ¹H-NMR spectroscopy. (2) Scheme 5 B. A mixture of benzyl alcohol 2a (162 mg, 1.5 mmol), Pd₂(dba)₃-CHCl₃ (12.9 mg, 0.0125 mmol), and sodium diphenylphosphinobenzene -3-sulfonate (TPPMS, 18 mg, 0.05 mmol) in H₂O (0.5 mL) was heated at 60 °C for 16 h in a sealed tube under Ar. After the reaction mixture was cooled, p-nitroanisole (230 mg, 1.5 mmol, internal standard) was added to the reaction mixture, which was extracted with CHCl₃ (8 mL), before the organic layer was analyzed by ¹H-NMR spectroscopy.



Conversion yield and recovery were calculated by integration.

	desired 13	Benzaldehyde 14	toluene 5	<i>p</i> -nitroanisole IS
Signal δ	5.77 (methine– <u>H</u>)	10.0 (CHO)	2.35 (C <u>H</u> ₃)	8.21 (Ar– <u>H</u>)
Integral value	0.70 (1H)	0.66 (1H)	2.12 (3H)	2.0 (2H), 38.3 mg (0.25 mmol)
Calculated ratio	0.18 mmol, 70%	0.165 mmol	0.18 mmol, 70%	

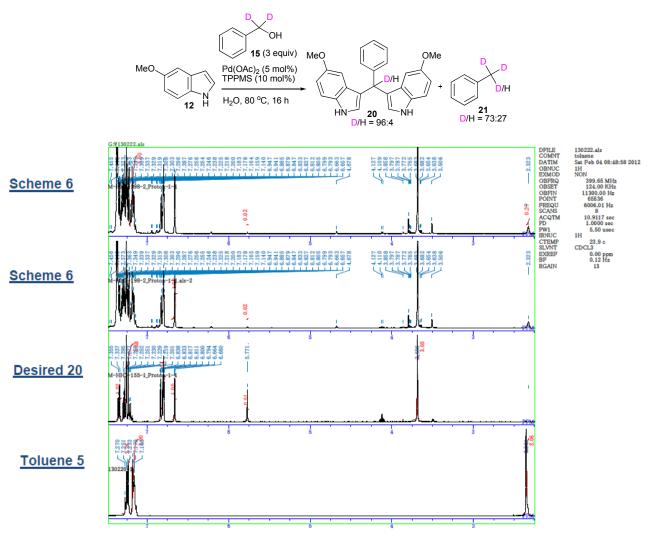




Conversion yield and recovery were calculated by integration.

	benzaldehyde 14	toluene 5	recov. of 2a	<i>p</i> -nitroanisole IS
Signal δ	10.0 (C <u>H</u> O)	2.35 (C <u>H</u> ₃)	4.69 (C <u>H</u> ₂)	3.91 (OC <u>H</u> ₃)
Integral value	0.14 (1H)	0.01 (3H)	1.36 (2H)	3.0 (3H), 230 mg (1.5 mmol)
Calculated ratio	0.21 mmol, 14%	0%	1.02 mmol, 68%	·

Figure 6S. ¹H-NMR spectrum with product ratio calculation from integration. (Scheme 6. Pd-catalyzed reaction with benzyl- α , α - d_2 alcohol 15). A mixture of 5-methoxyindole 12 (37 mg, 0.25 mmol), benzyl- α , α - d_2 alcohol 15 (81 mg, 0.75 mmol), Pd(OAc)₂ (3 mg, 0.0125 mmol), and sodium diphenylphosphinobenzene-3-sulfonate (TPPMS, 9 mg, 0.025 mmol) in H₂O (1.0 mL) was heated at 60 °C for 16 h in a sealed tube under Ar. After cooling, the reaction mixture was extracted with CHCl₃ (8 mL). The organic layer was subsequently analyzed by ¹H-NMR spectroscopy.



Conversion yield and recovery were calculated by integration.

	desired 20		toluene 5	
Signal δ	5.77	666 (Ar U)	2 22 (CH)	7.15-7.2
	(methine- <u>H</u>)	6.66 (Ar– <u>H</u>)	2.32 (C <u>H</u> ₃)	(Ar– <u>H</u>)
Integral value	0.02 (1H)	1.00 (2H)	0.27 (1H)	3.0 (3H)
Calculated ratio	4%		27%	

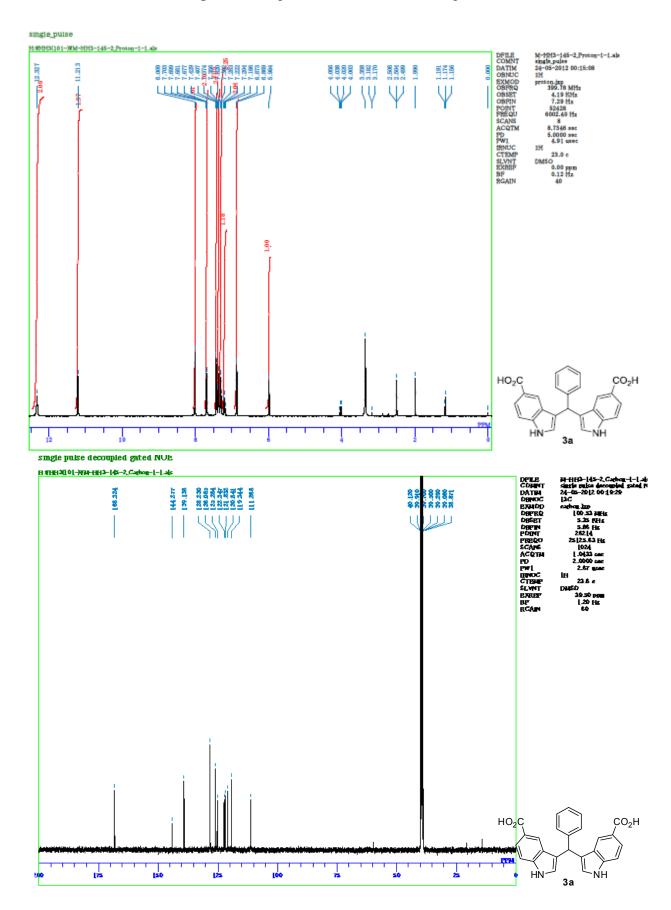


Figure 7S. Copies of 1H and 13C NMR spectra.

Figure 7S. Cont.

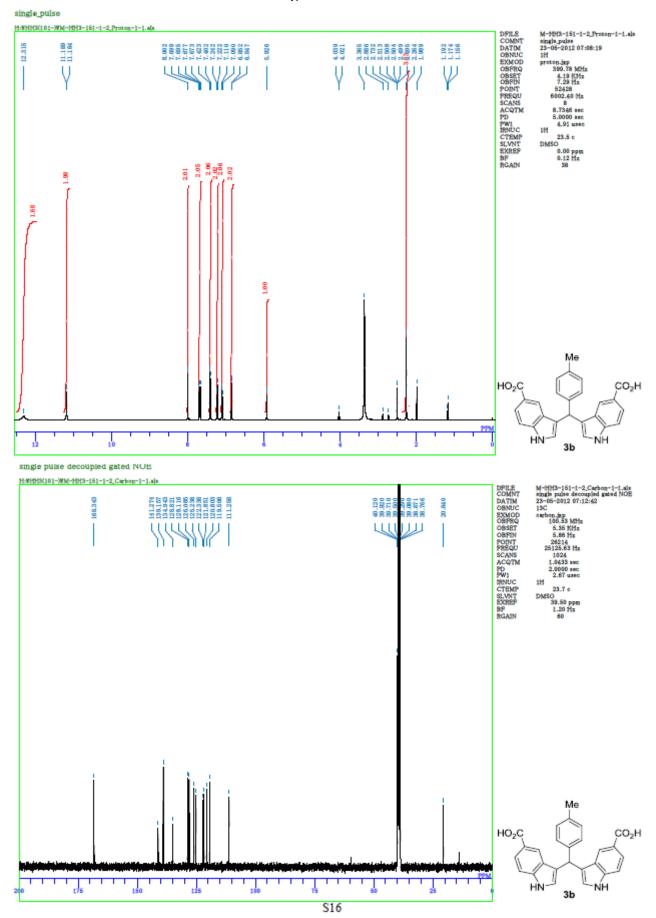


Figure 7S. Cont.

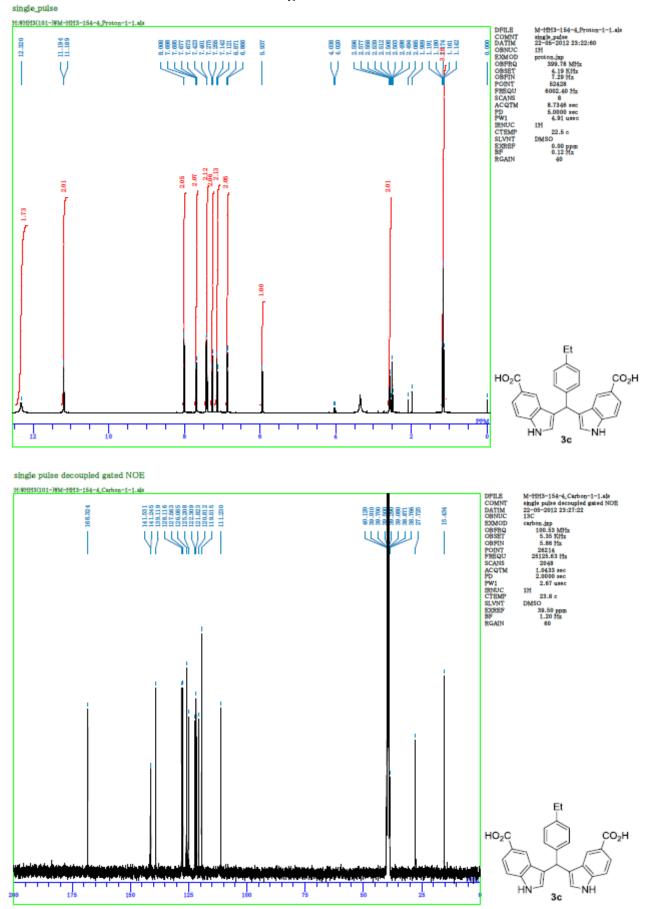
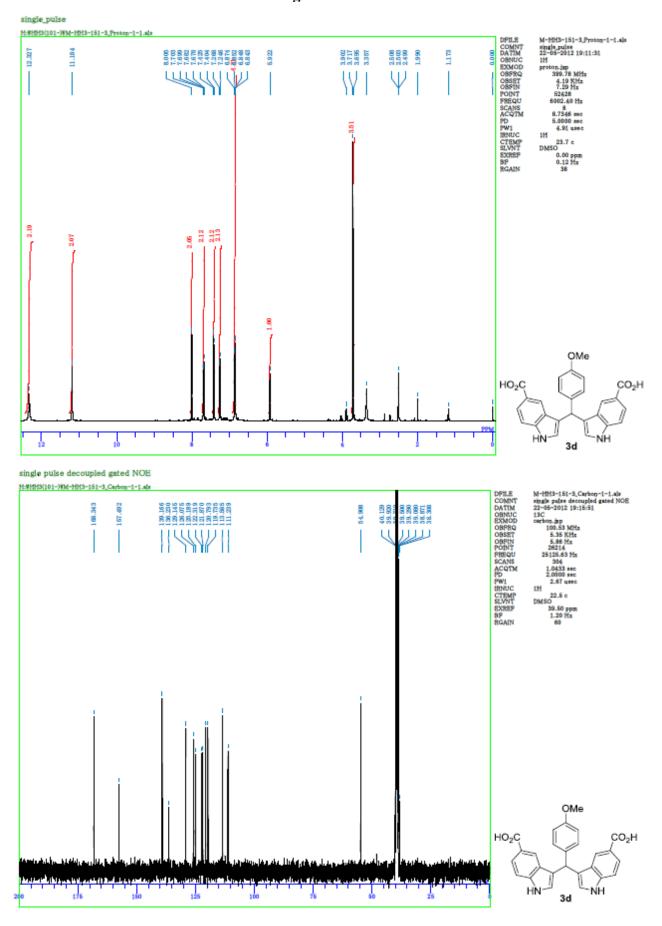


Figure 7S. Cont.



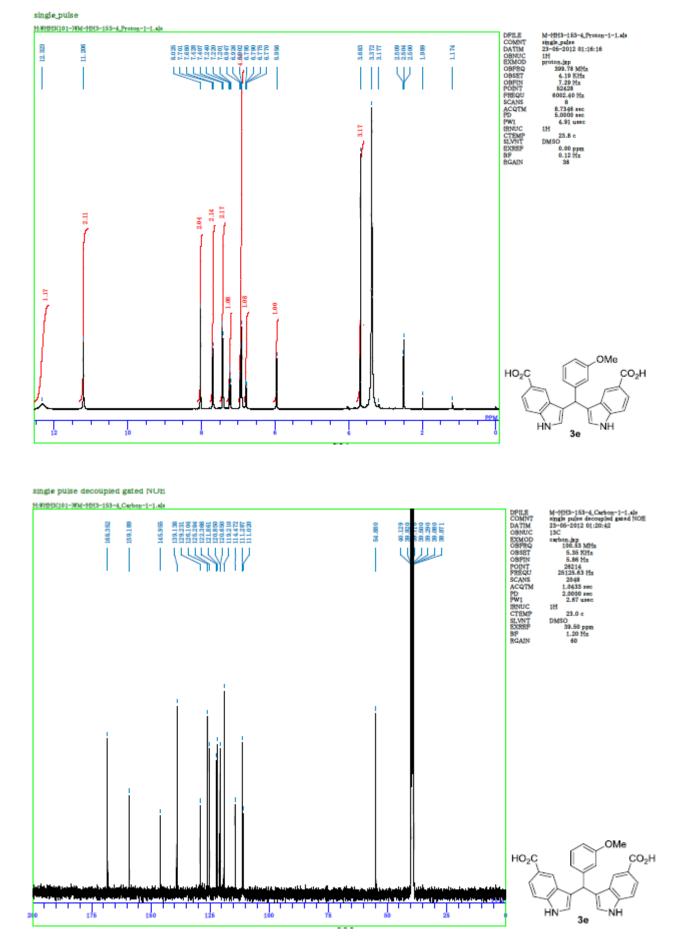


Figure 7S. Cont.

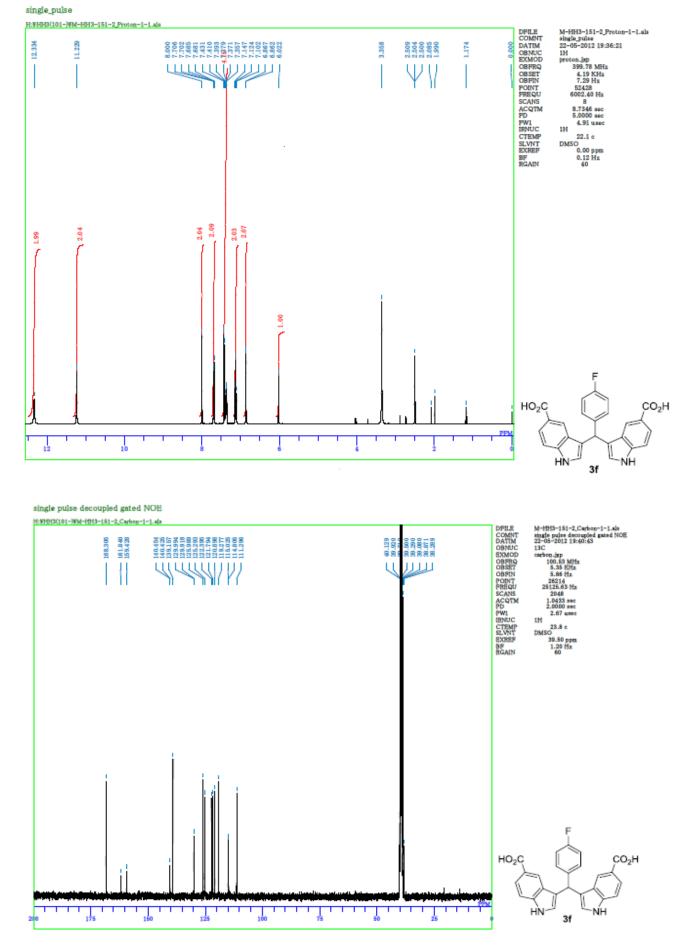


Figure 7S. Cont.

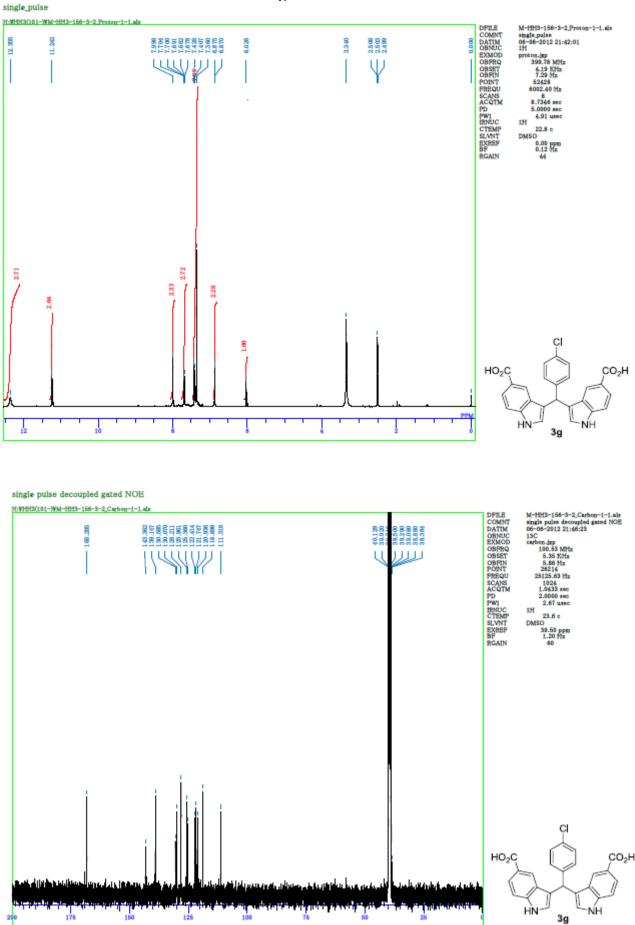
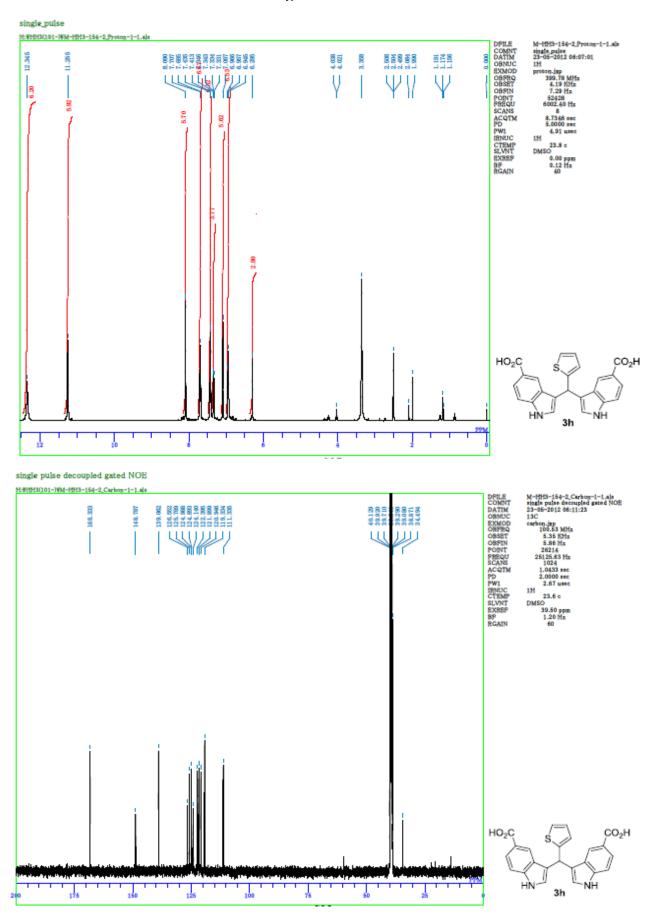


Figure 7S. Cont.



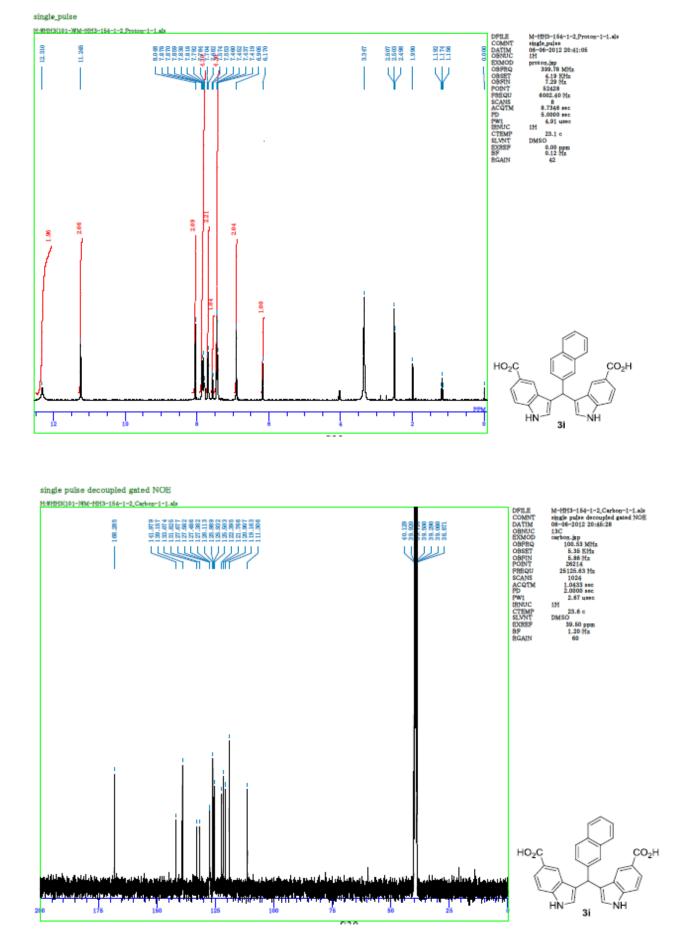
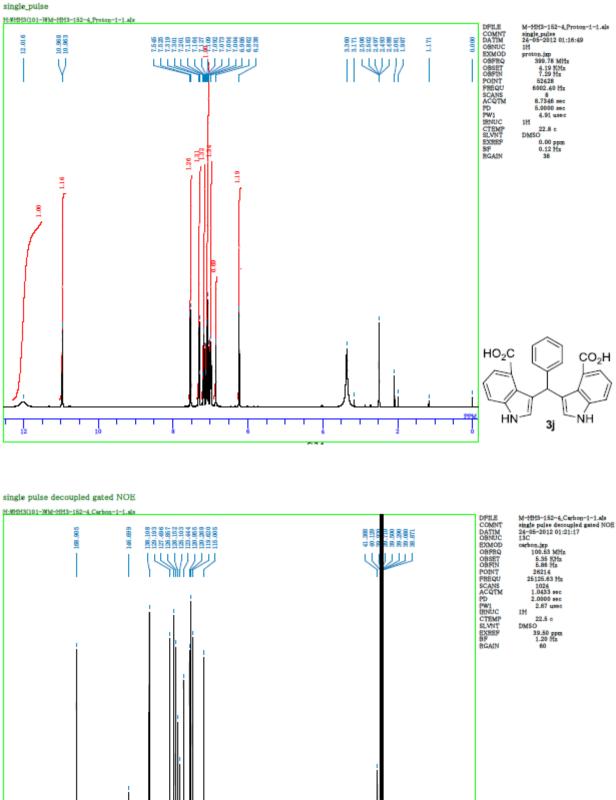
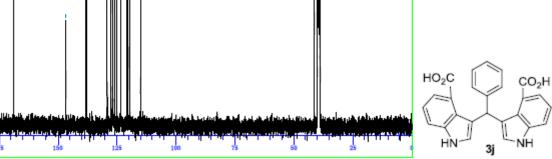


Figure 7S. Cont.

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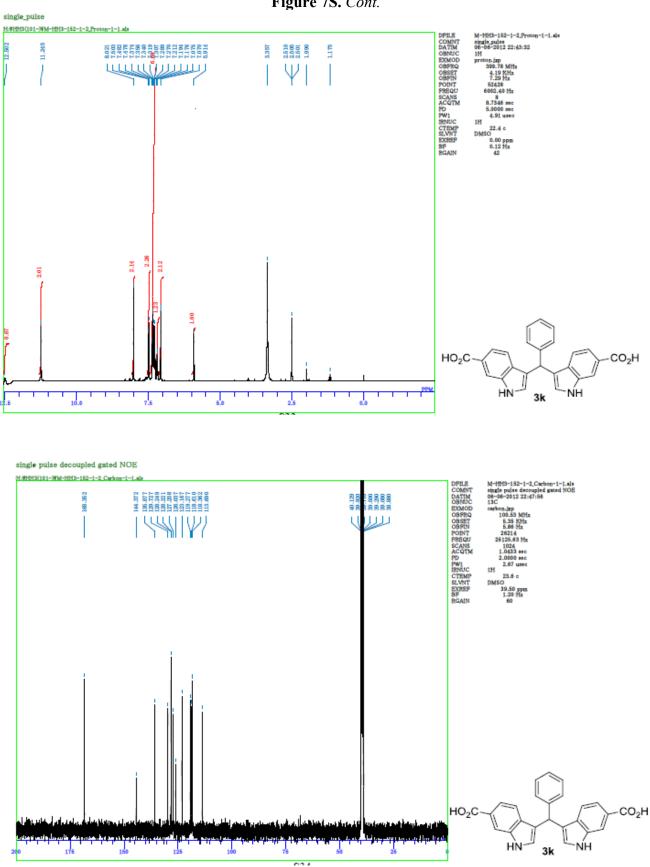
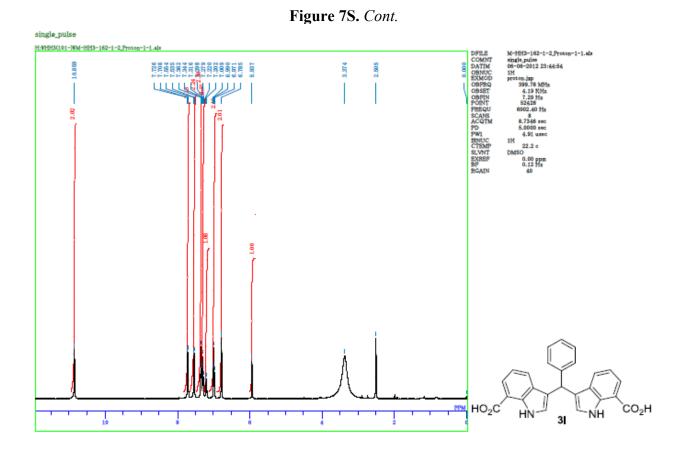
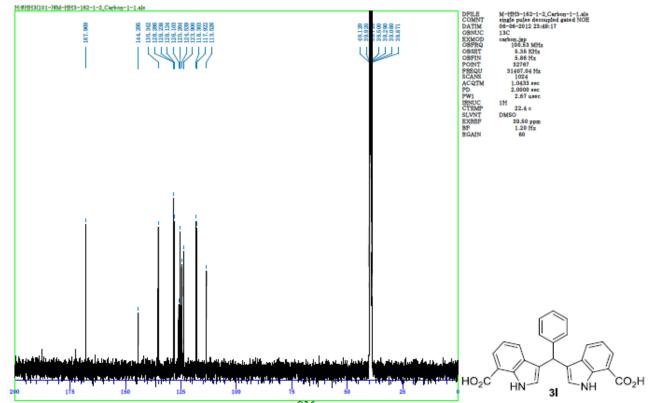


Figure 7S. Cont.



single pulse decoupled gated NOE



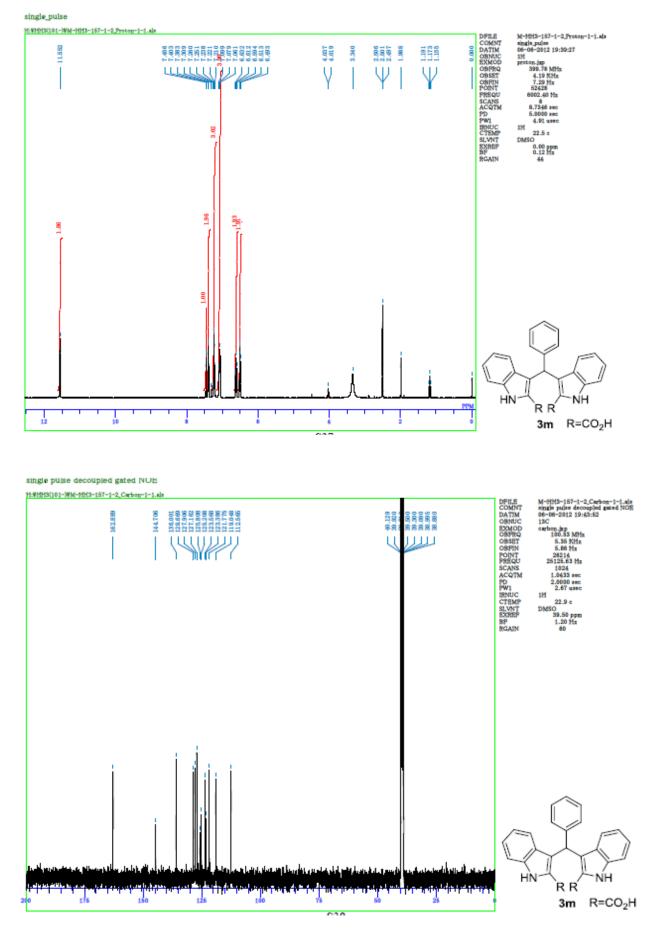
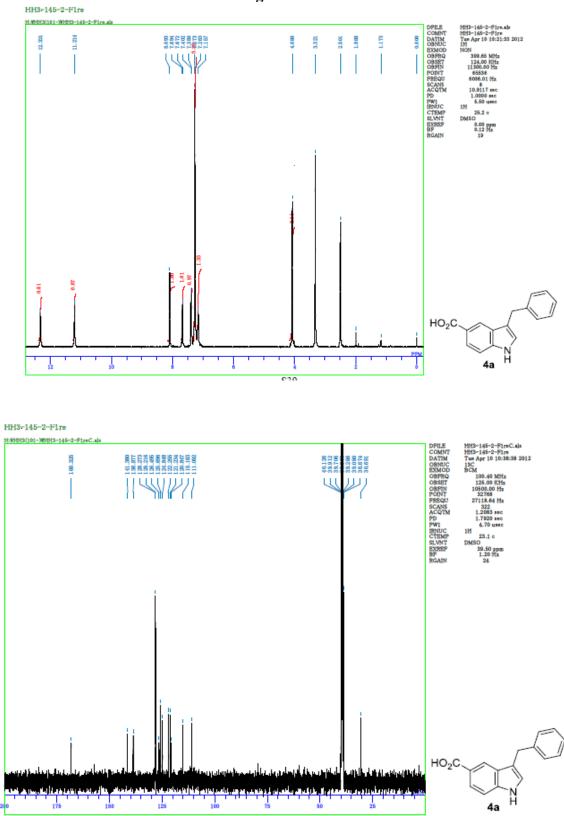


Figure 7S. Cont.

Figure 7S. Cont.



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