

Selective Synthesis of *N*-H and *N*-Aryl Benzotriazoles by the [3+2] Annulation of Sodium Azide with Arynes

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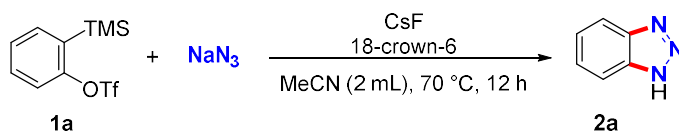
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Supporting Information

1. Optimization Studies for the <i>N</i> -H Benzotriazoles Synthesis	S02
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1. Optimization Studies for the *N*-H Benzotriazole Synthesis

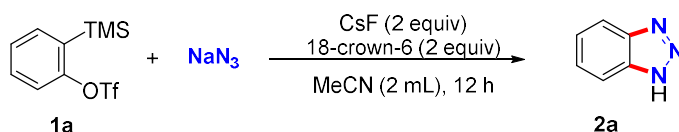
Variation of NaN_3 stoichiometry:



entry	NaN_3 (equiv)	F ⁻ Source (equiv)	yield of 2a ^a
1	2	CsF (2), 18-crown-6 (2)	45%
2	3	CsF (2), 18-crown-6 (2)	51%
3	4	CsF (2), 18-crown-6 (2)	59%
4 ^b	4	CsF (5), 18-crown-6 (5)	64%

Reaction condition: **1a** (0.5 mmol), NaN_3 , CsF, 18-crown-6, MeCN (2.0 mL), 70 °C for 12 h. ^a Yields of the isolated product is given. ^b Reaction was performed in 3 mL CH_3CN

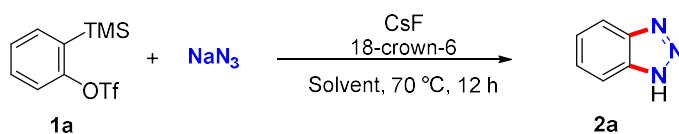
Variation of Temperature:



entry	temperature (°C)	yield of 2a ^a
1	0 °C	<5%
2	rt (25 °C)	32%
3	60 °C	39%
4	70 °C	45%
5	80 °C	41%

Reaction condition: **1a** (0.5 mmol), NaN_3 (2 equiv), CsF (2 equiv), 18-crown-6 (2 equiv), MeCN (2.0 mL) for 12 h. ^a Yields of the isolated product is given.

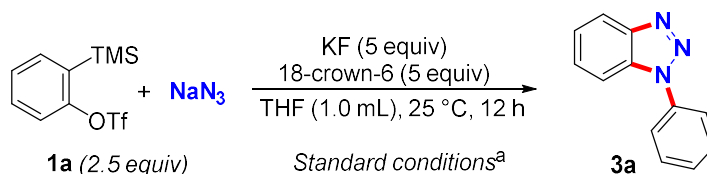
Solvent Screening:



entry	F ⁻ Source (equiv)	solvent (mL)	yield of 2a ^a
1 ^b	CsF (2), 18-crown-6 (2)	THF (2 mL)	<5%
2 ^b	CsF (2), 18- crown -6 (2)	DME (2 mL)	<5%
3	CsF (4), 18- crown -6 (4)	MeCN (2 mL)	59%
4	CsF (4), 18- crown -6 (4)	MeCN (3 mL)	64%
5	CsF (4), 18- crown -6 (4)	MeCN (4 mL)	64%

Reaction condition: **1a** (0.5 mmol), NaN₃ (4 equiv), CsF (2 equiv), 18-crown-6 (2 equiv), 70 °C for 12 h. ^a Yields of the isolated product is given. ^b Reaction was performed at rt and 2.0 equiv NaN₃ was used.

2. Optimization Studies for the *N*-Aryl Benzotriazole Synthesis

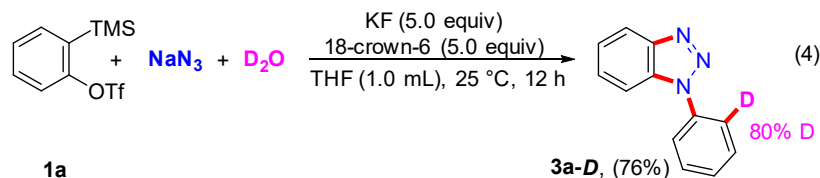


entry	variation of the standard conditions	yield of 3a (%) ^b
1	none	80
2	1.5 equiv of 1a	18
3 ^c	CsF instead of KF/18-crown-6	25
4	TBAF instead of KF/18-crown-6	53
5	60 °C instead of 25 °C	47
6	0 °C instead of 25 °C	39
7 ^d	<i>Open-flask reaction</i>	86
8	1,4-Dioxane instead of THF	67
9	2.0 equiv water added	82

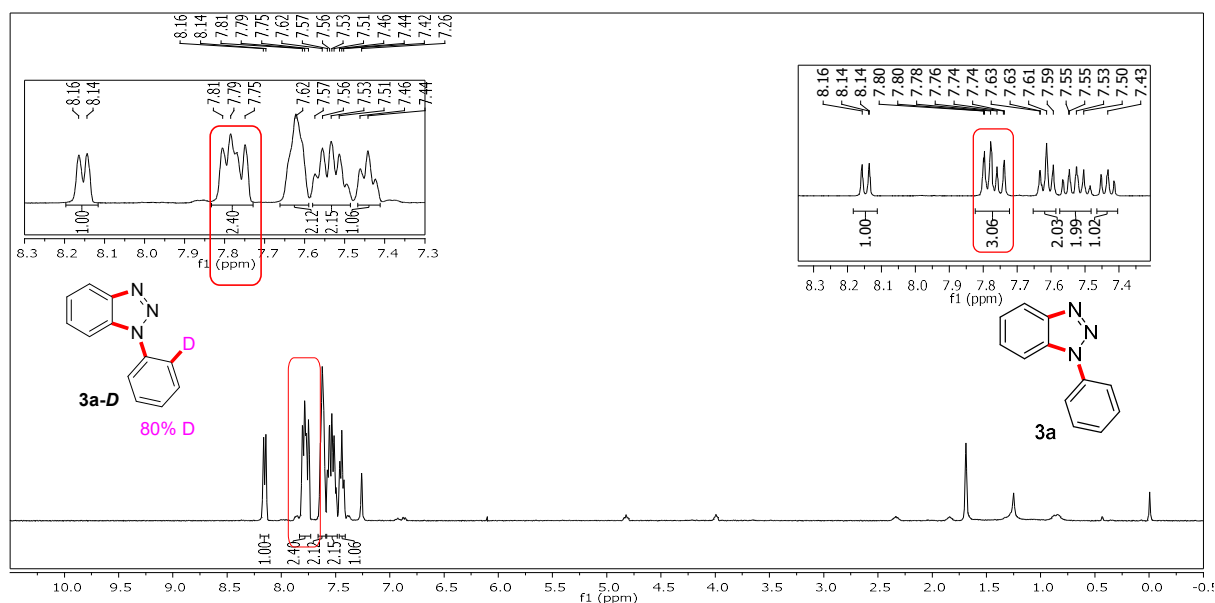
^a Standard conditions: **1a** (0.625 mmol), NaN₃ (0.25 mmol), KF (5.0 equiv), 18-crown-6 (5.0 equiv), THF (1.0 mL), 25 °C for 12 h. ^b Yields of the isolated product is given. ^c Reaction was performed in CH₃CN. ^d Reaction performed in open air using commercial KF, 18-crown-6, and NaN₃.

3. Mechanistic Experiments

Deuterium Labeling Experiment:

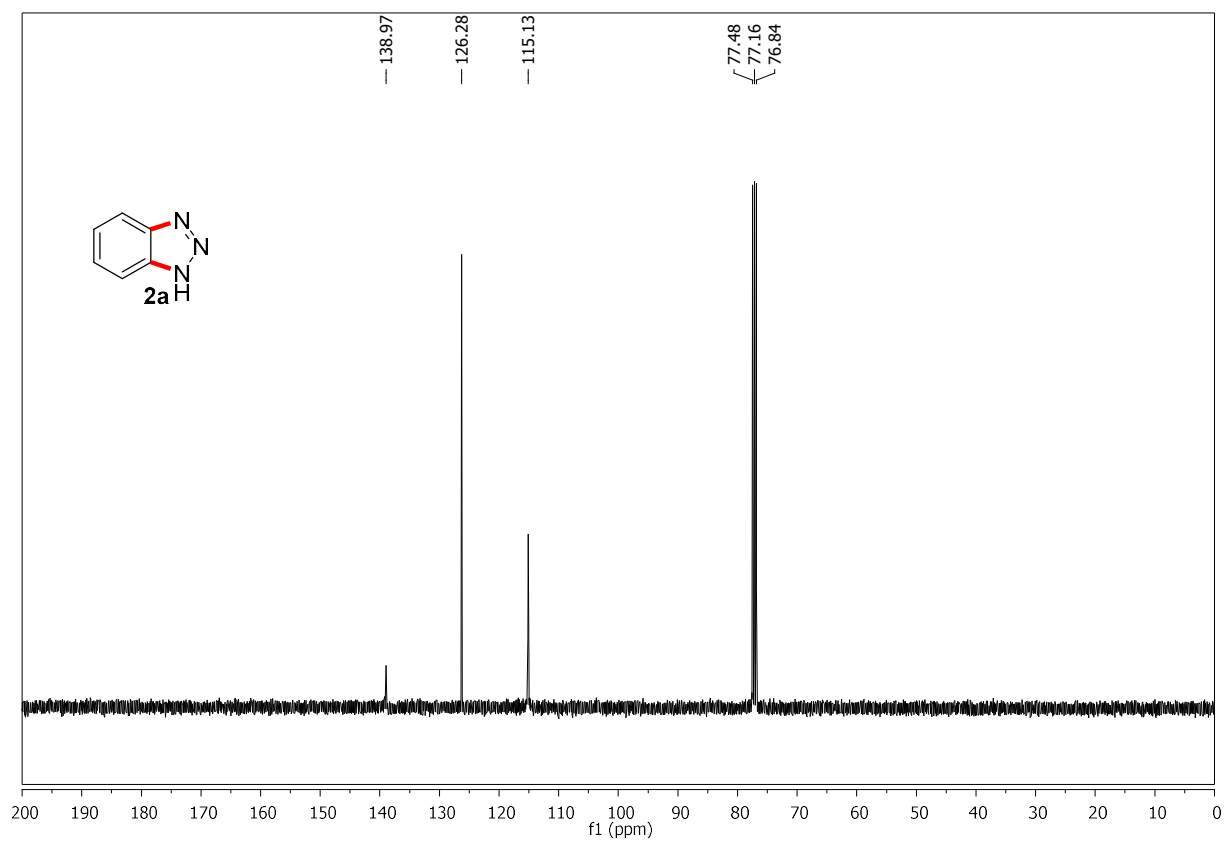
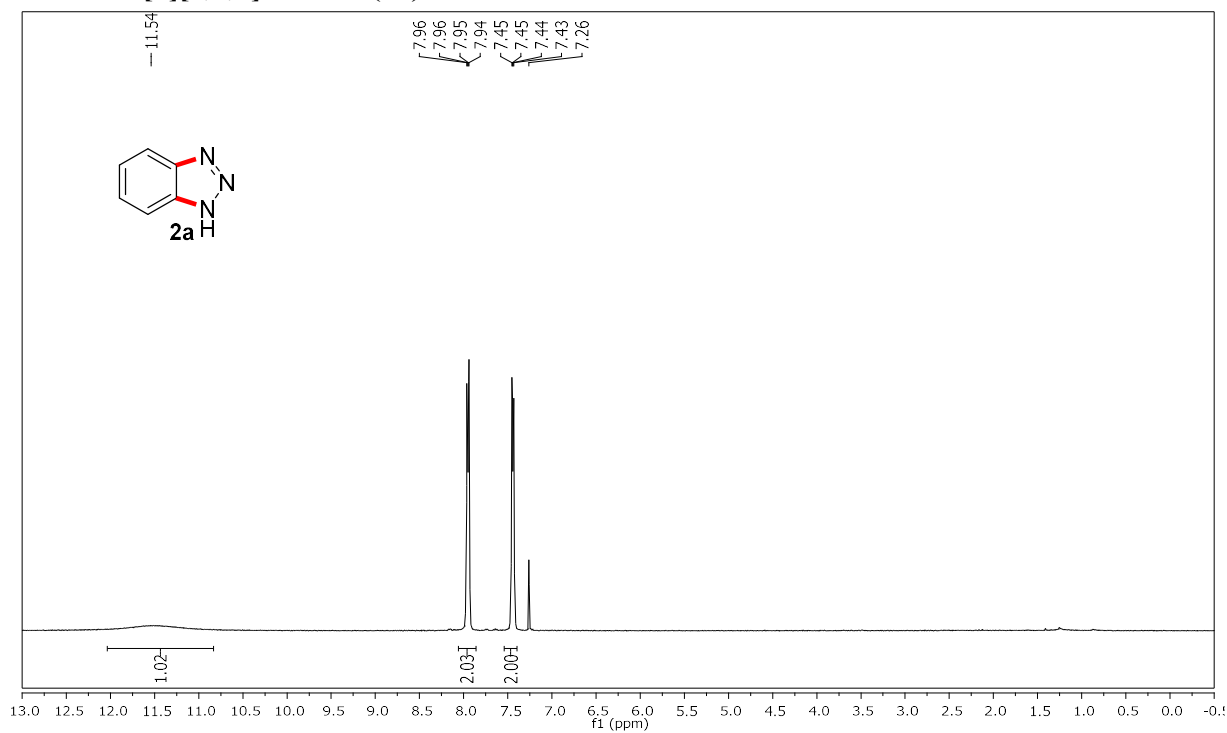


To a flame-dried screw-capped test tube equipped with a magnetic stir bar was added the KF (0.073 g, 1.25 mmol) and 18-crown-6 (0.330 g, 1.25 mmol) in a glove-box. Then NaN_3 (0.016g, 0.25 mmol) and D_2O (0.004 g, 4 μL , 0.25 mmol) was added outside the glove-box under nitrogen atmosphere followed by addition of THF (1 mL). To the stirring solution, aryne precursor **1a** (0.186 g, 152 μL , 0.625 mmol) was added and reaction mixture was allowed to stir at rt for 12 h. After 12 h the solvent was evaporated and the crude residue pre-adsorbed on silica gel and purified by flash column chromatography (Pet. ether) on silica gel to afford the **3a-D** in 76% yield with 80% D incorporation at the 2-position.

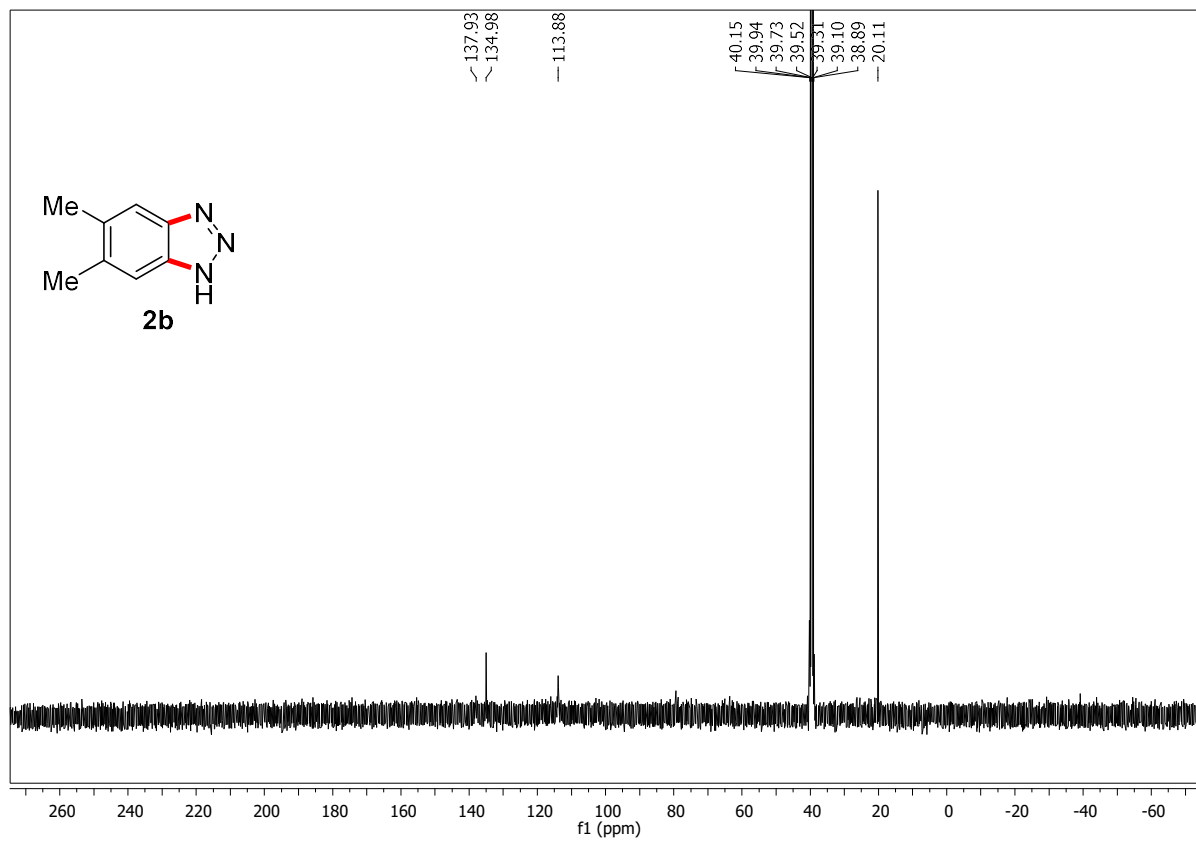
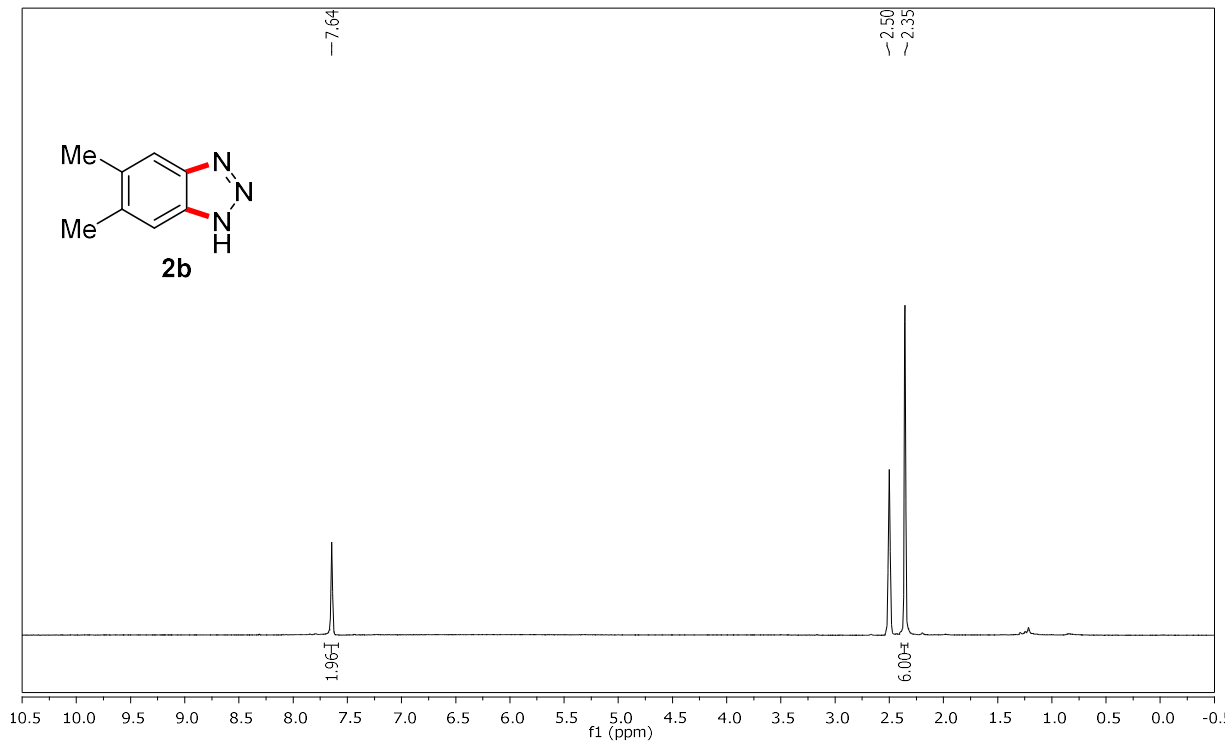


4. ^1H and ^{13}C NMR Spectra of all Products

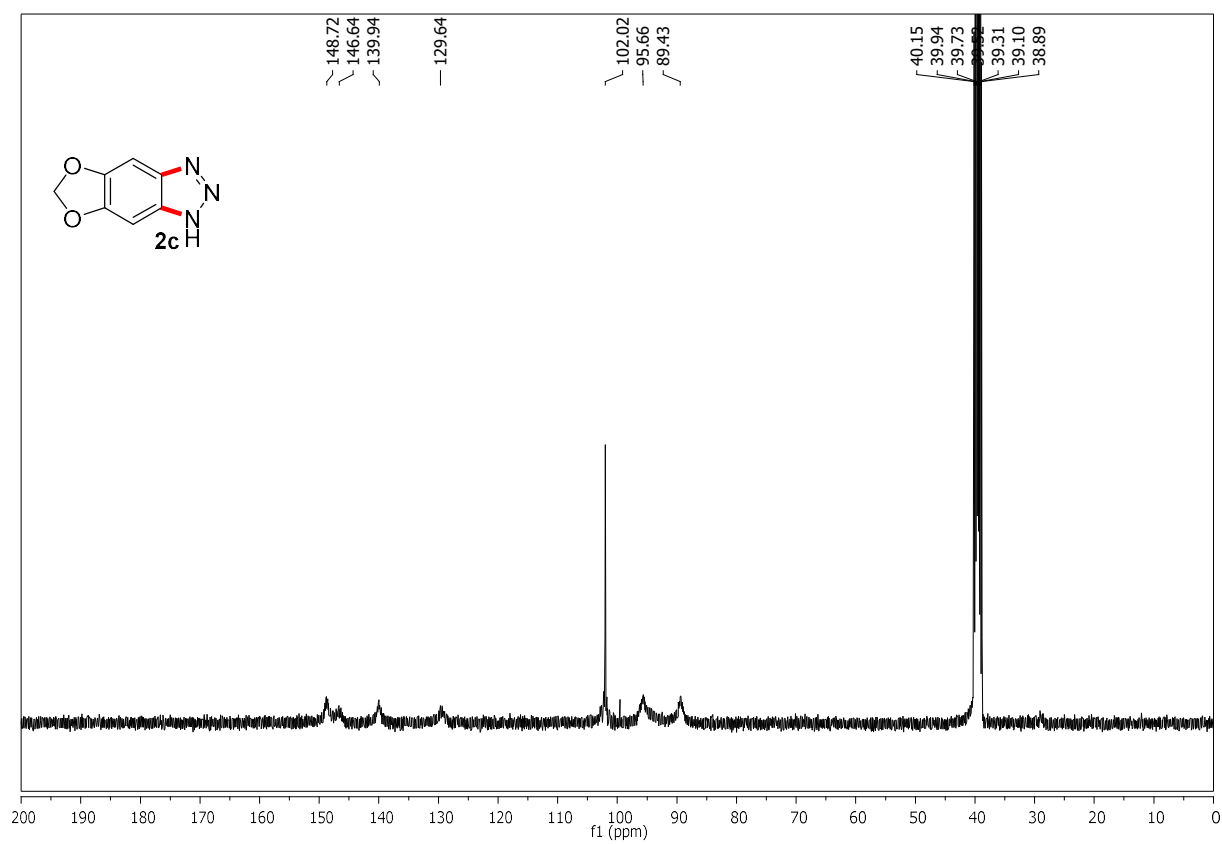
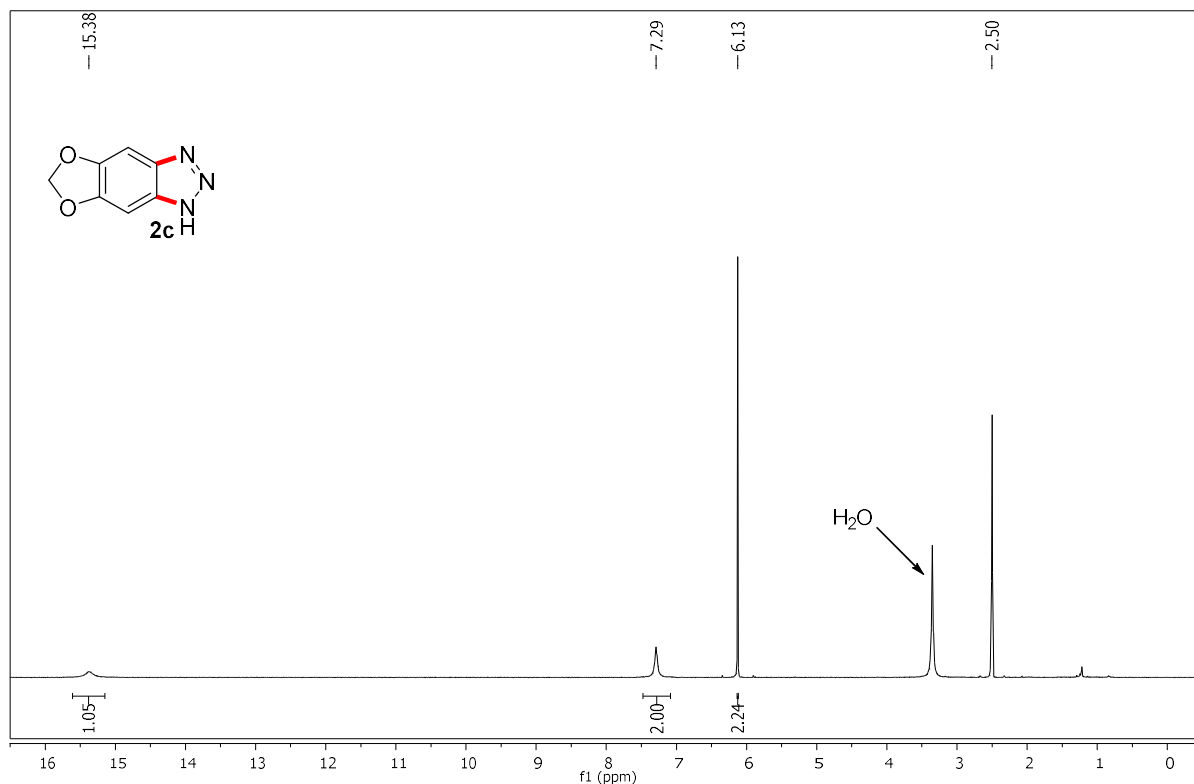
1*H*-Benzo[*d*][1,2,3]triazole (2a)



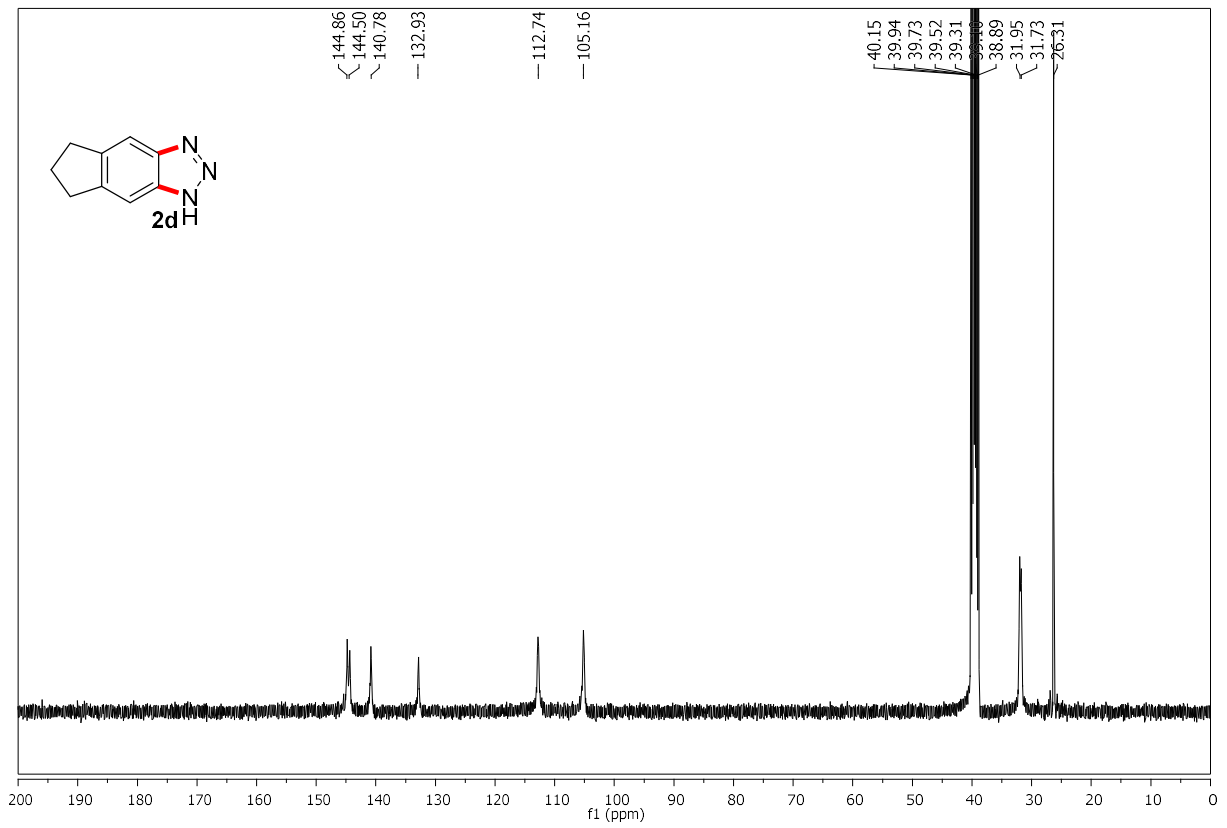
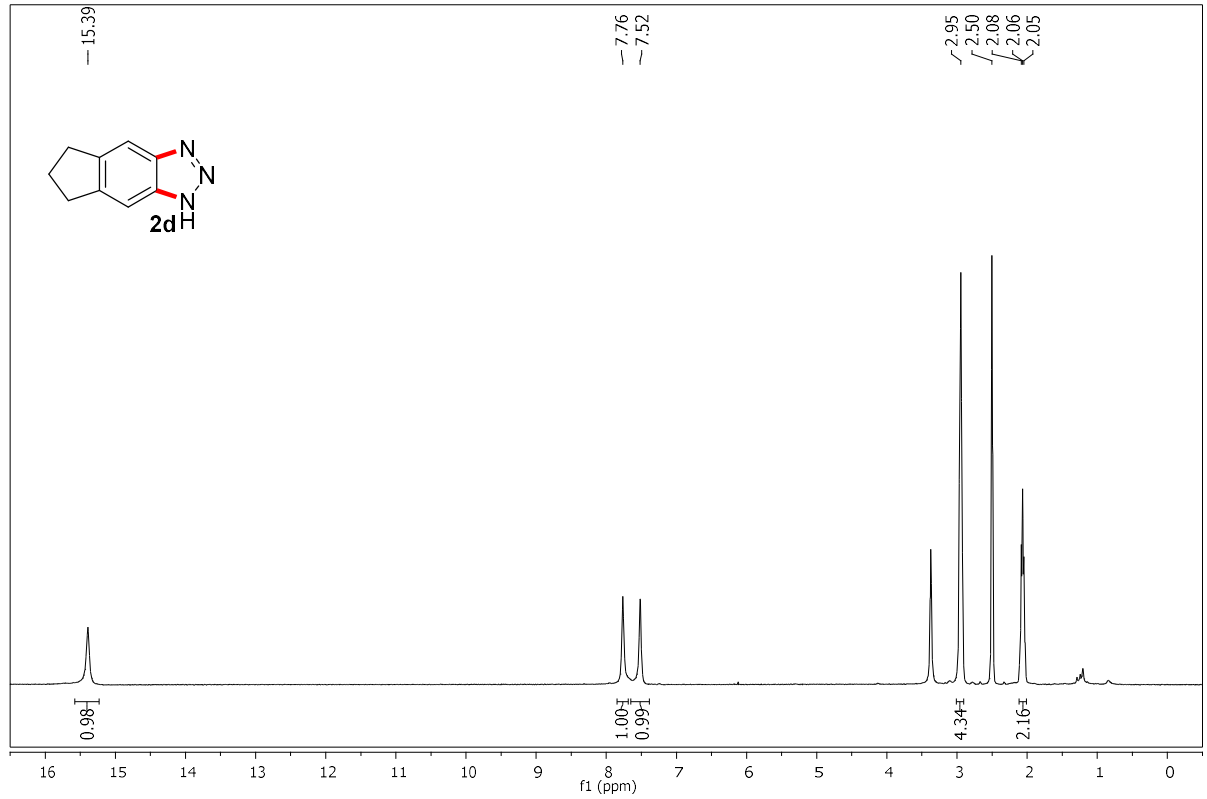
5,6-Dimethyl-1H-benzo[d][1,2,3]triazole (2b)



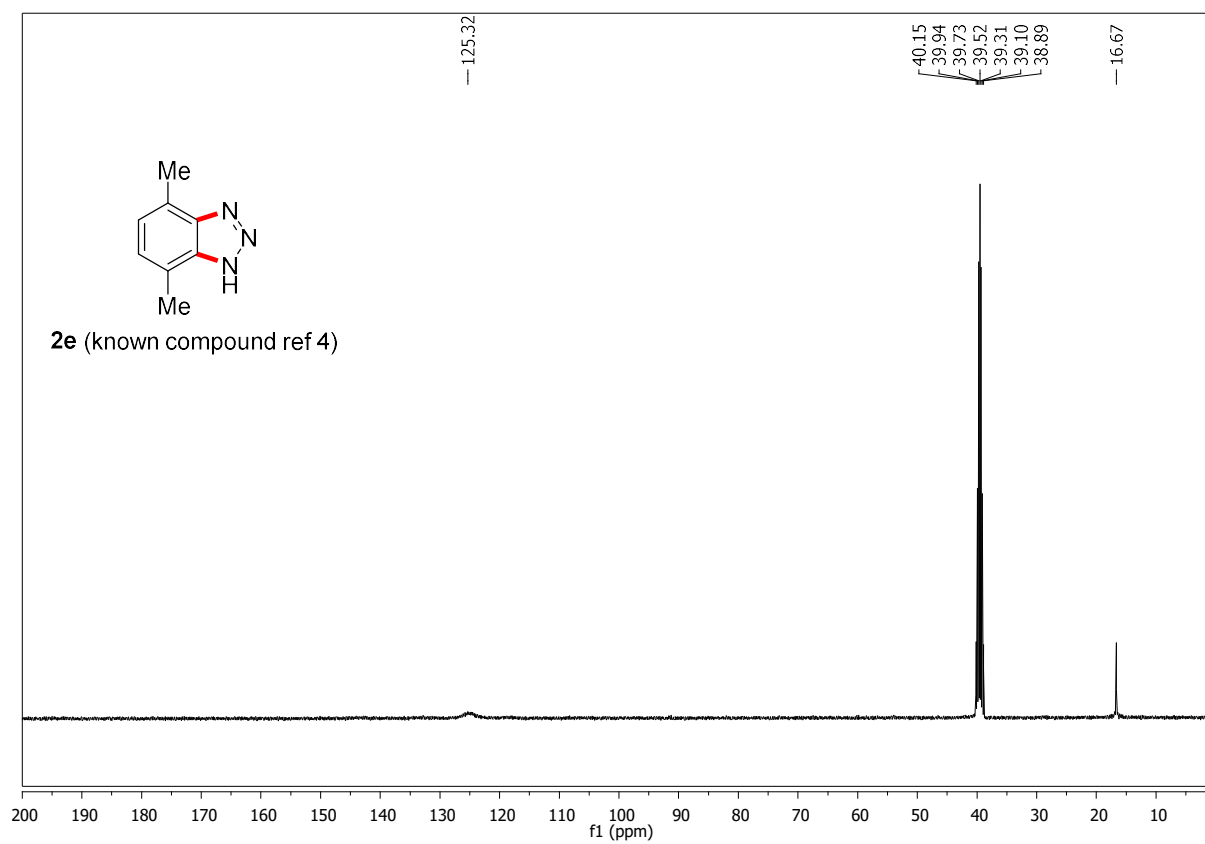
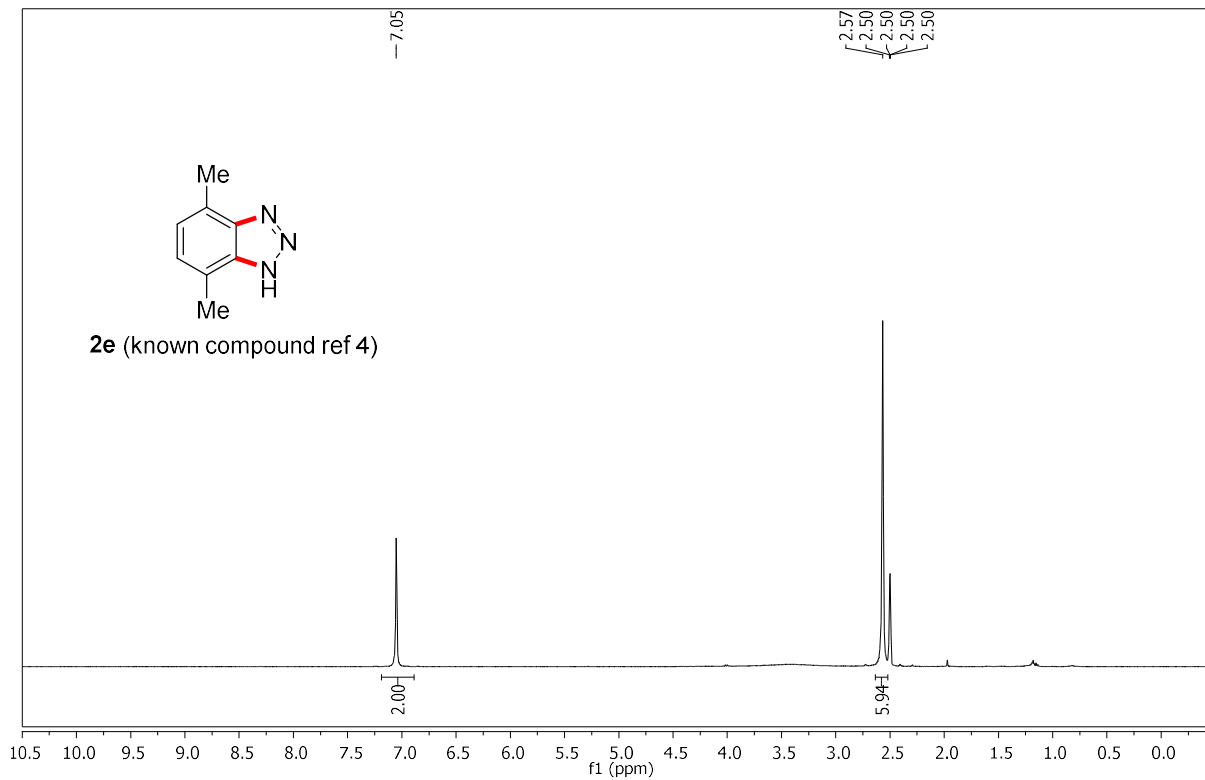
1H-[1,3]Dioxolo[4',5':4,5]benzo[1,2-d][1,2,3]triazole (2c)



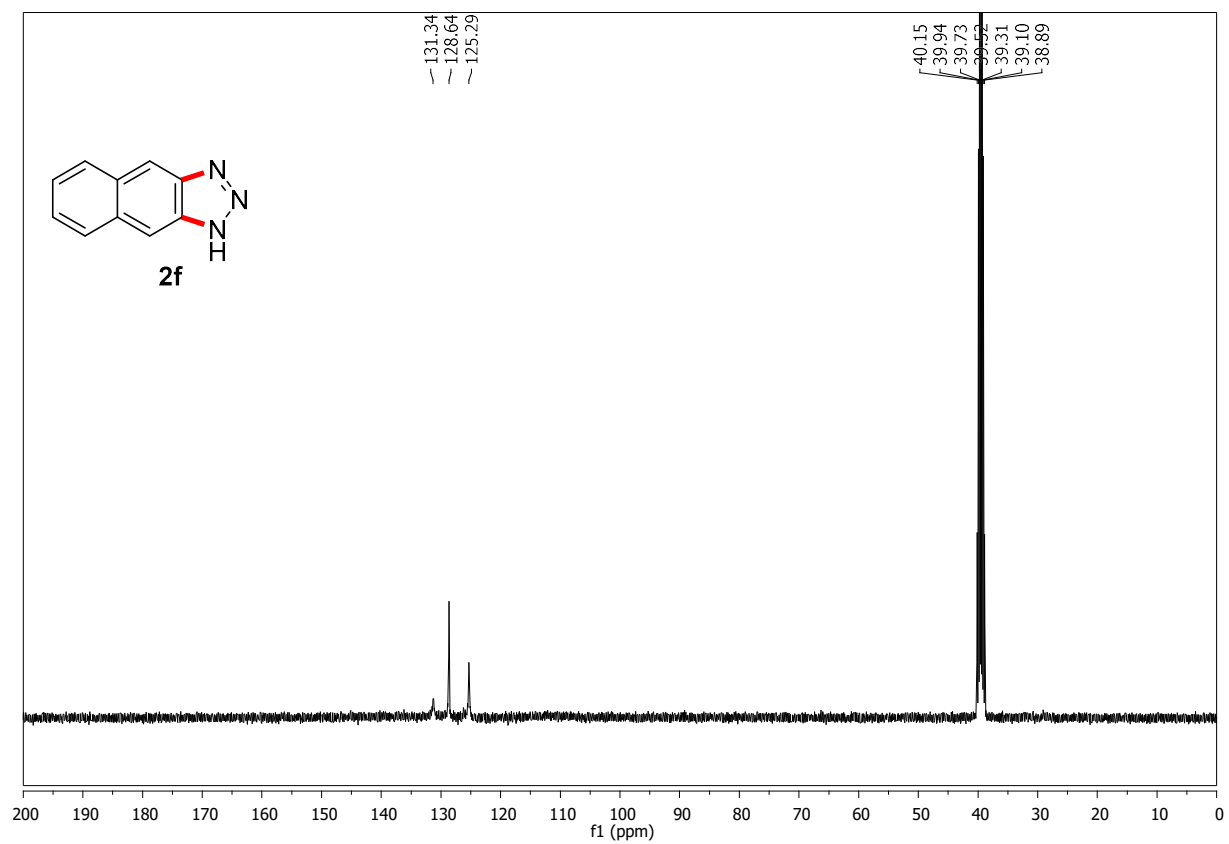
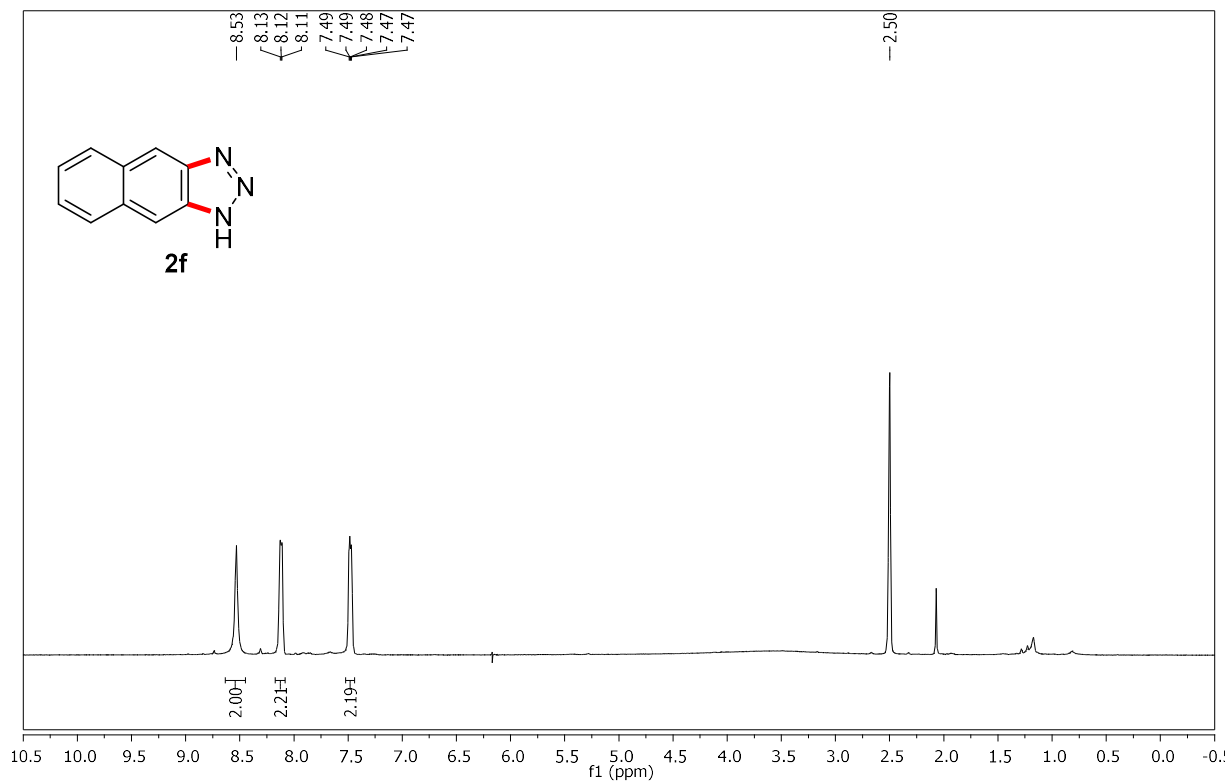
1,5,6,7-Tetrahydroindeno[5,6-d][1,2,3]triazole (2d)



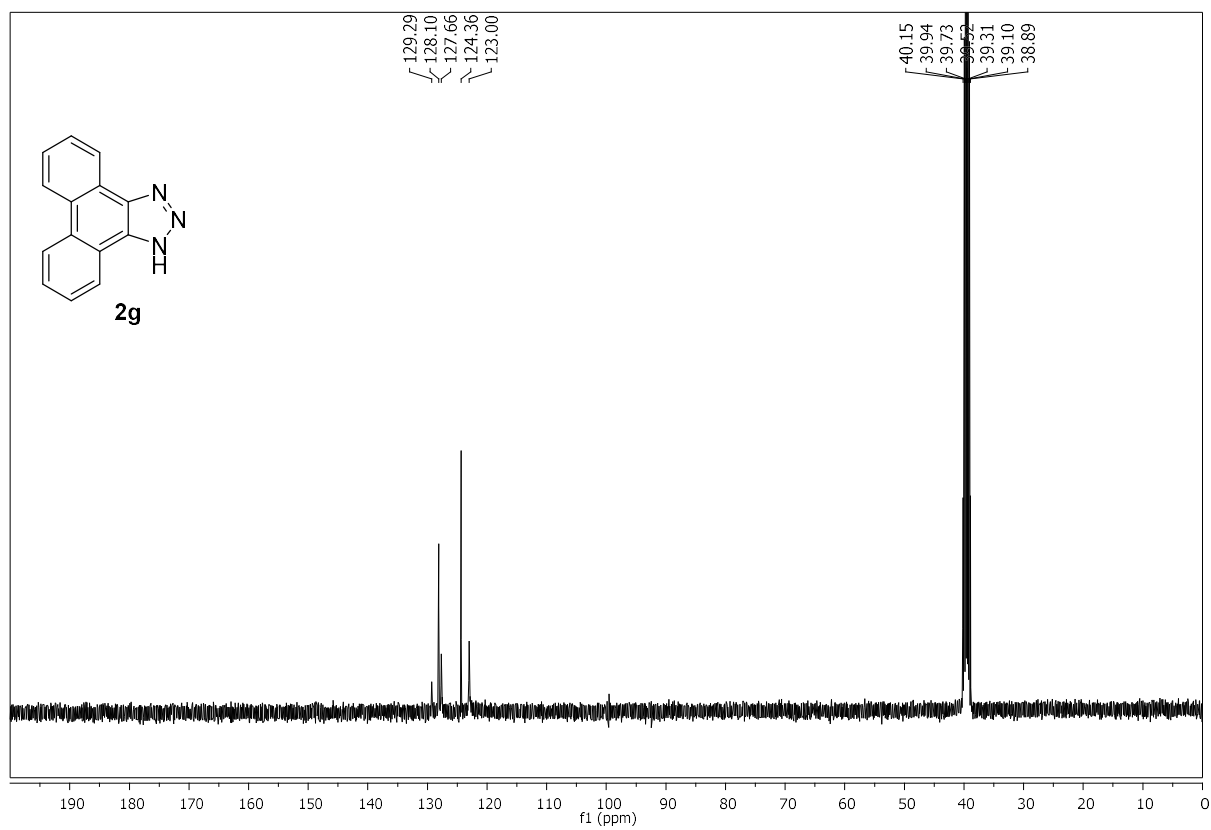
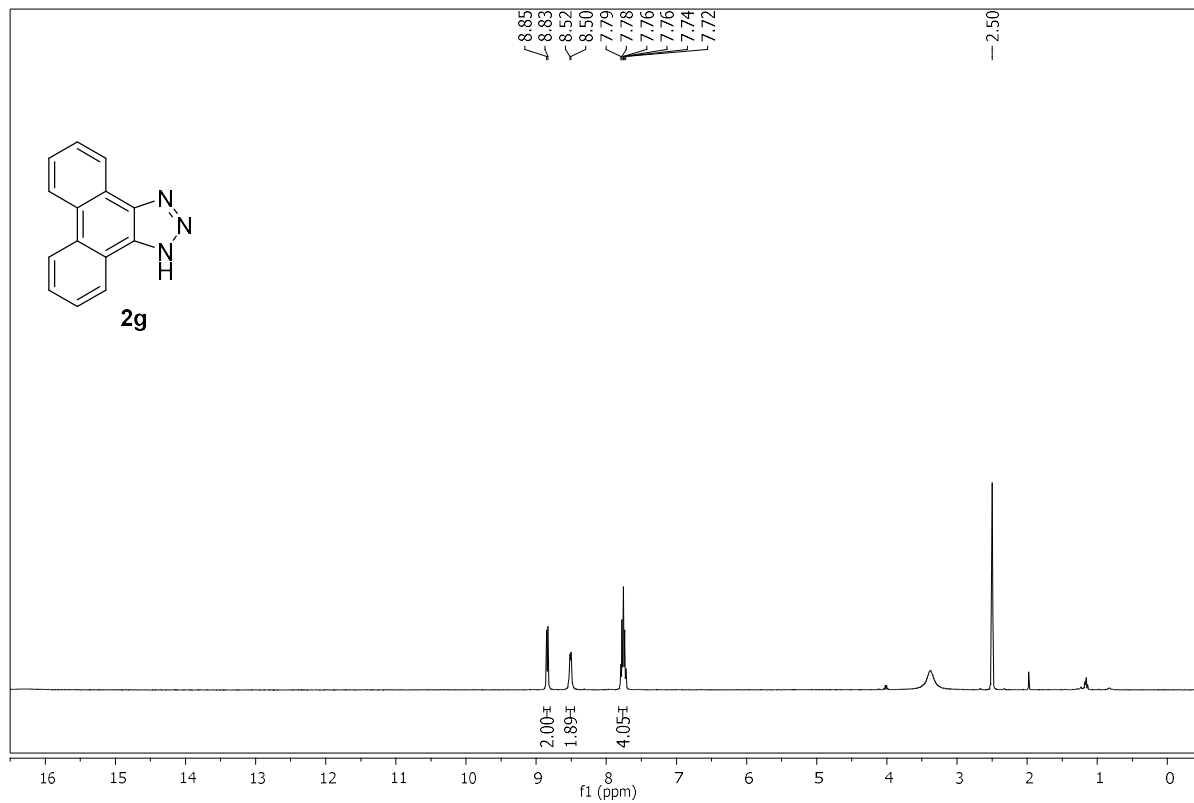
4,7-Dimethyl-1H-benzo[d][1,2,3]triazole (2e)⁴



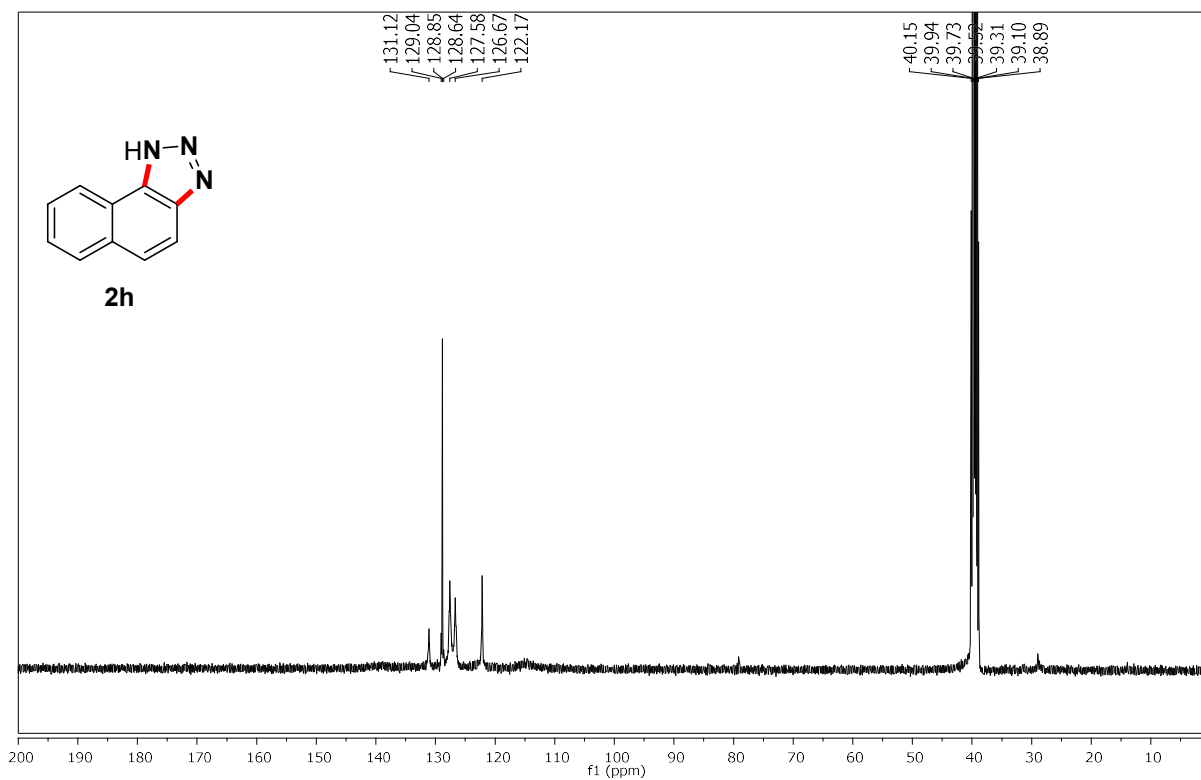
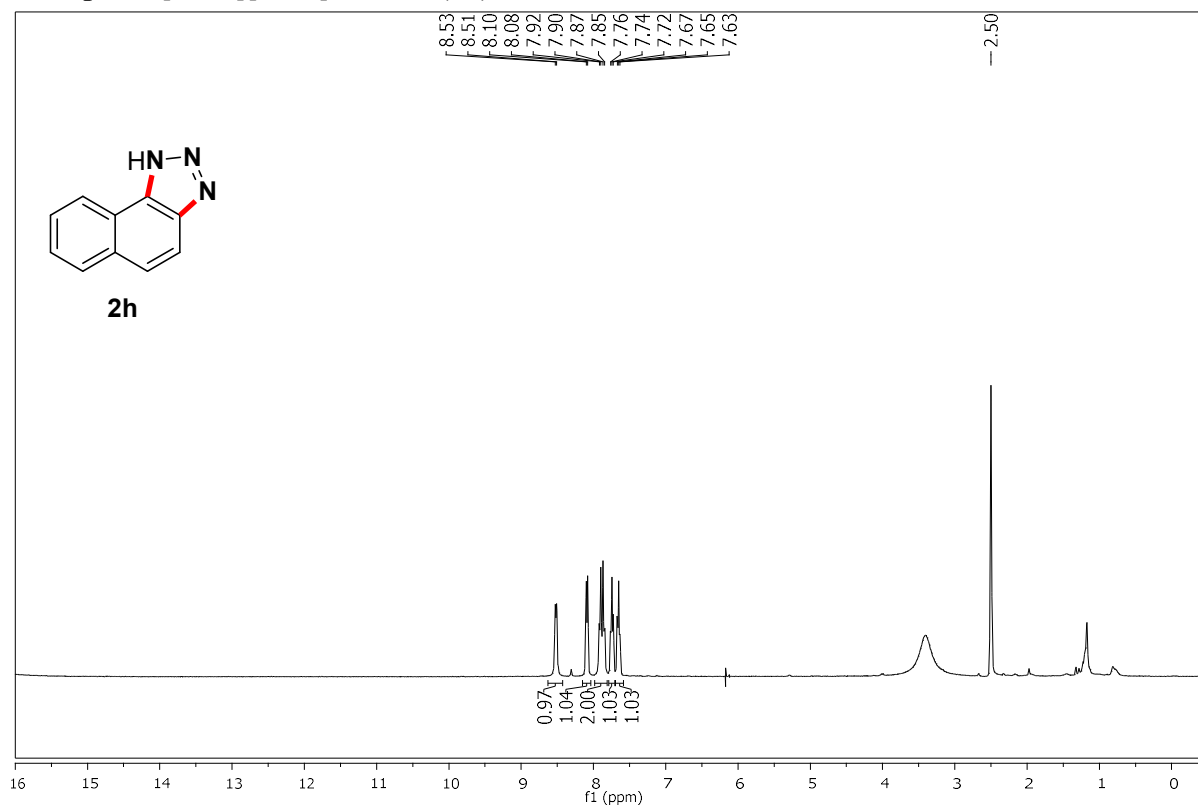
1H-Naphtho[2,3-d][1,2,3]triazole (2f)



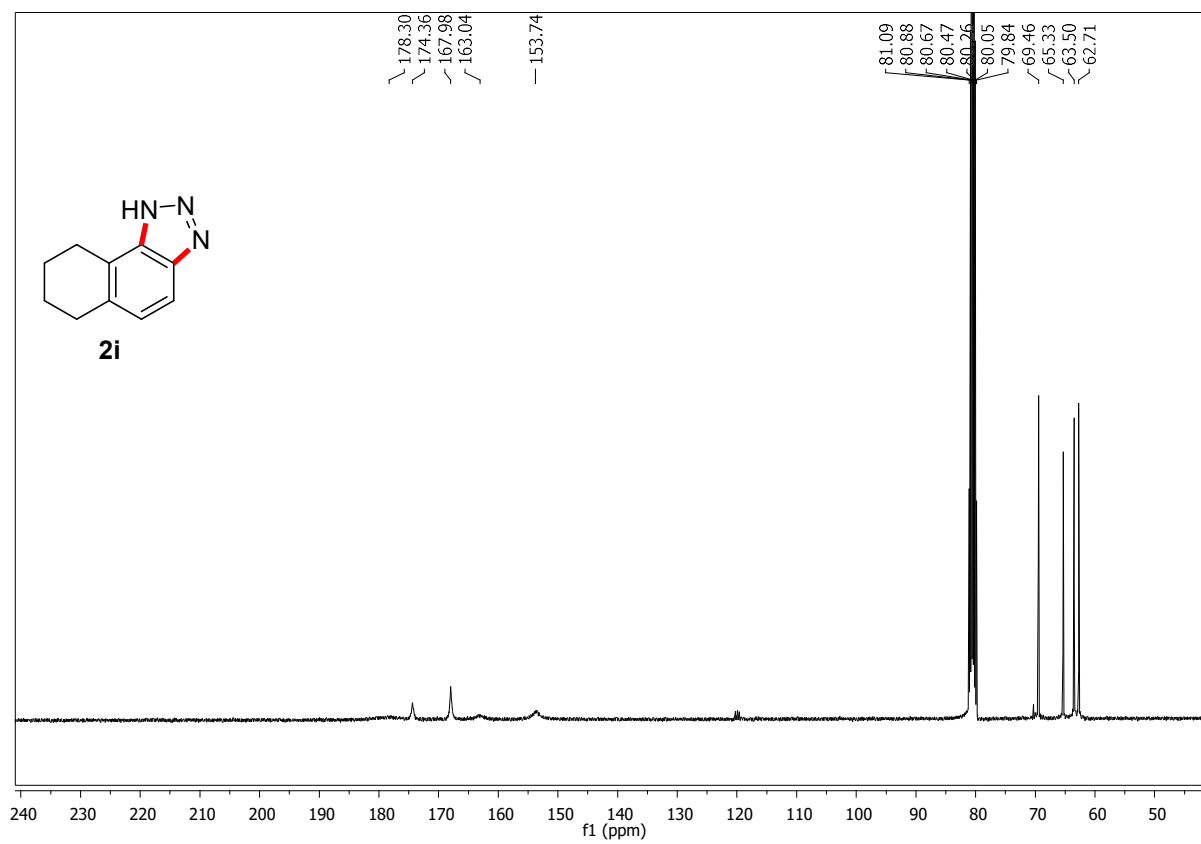
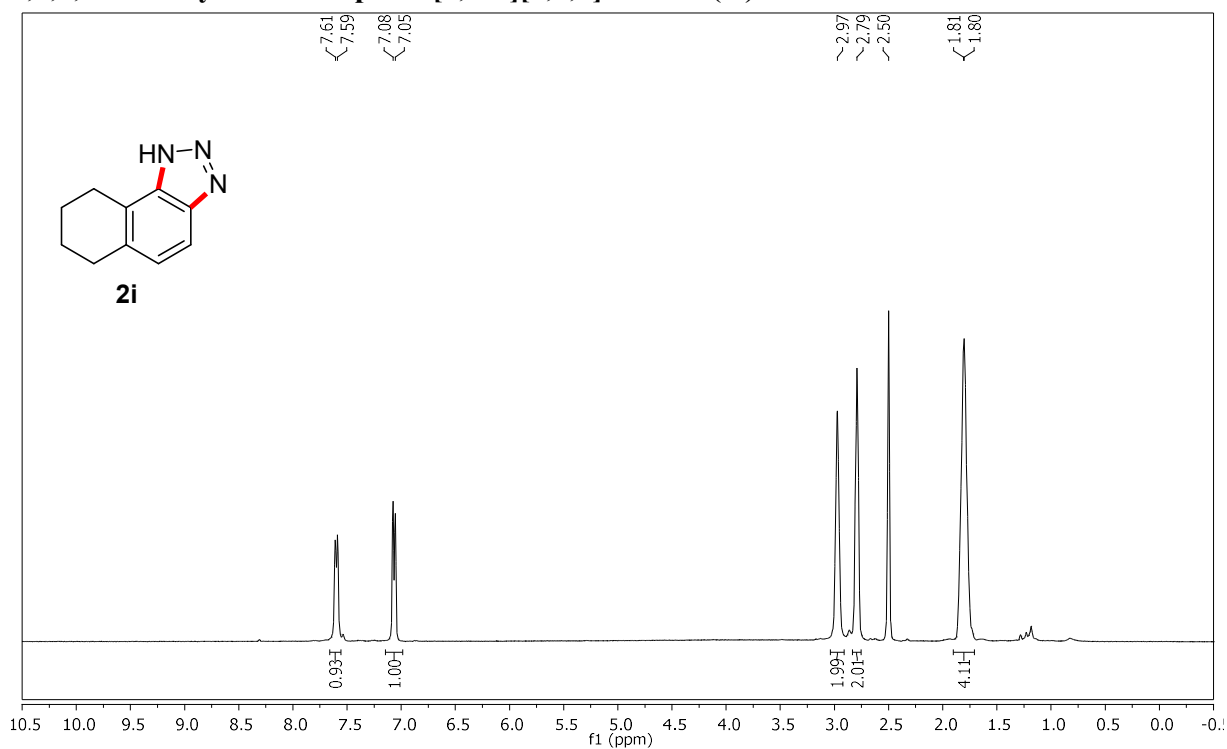
1H-Phenanthro[9,10-d][1,2,3]triazole (2g)



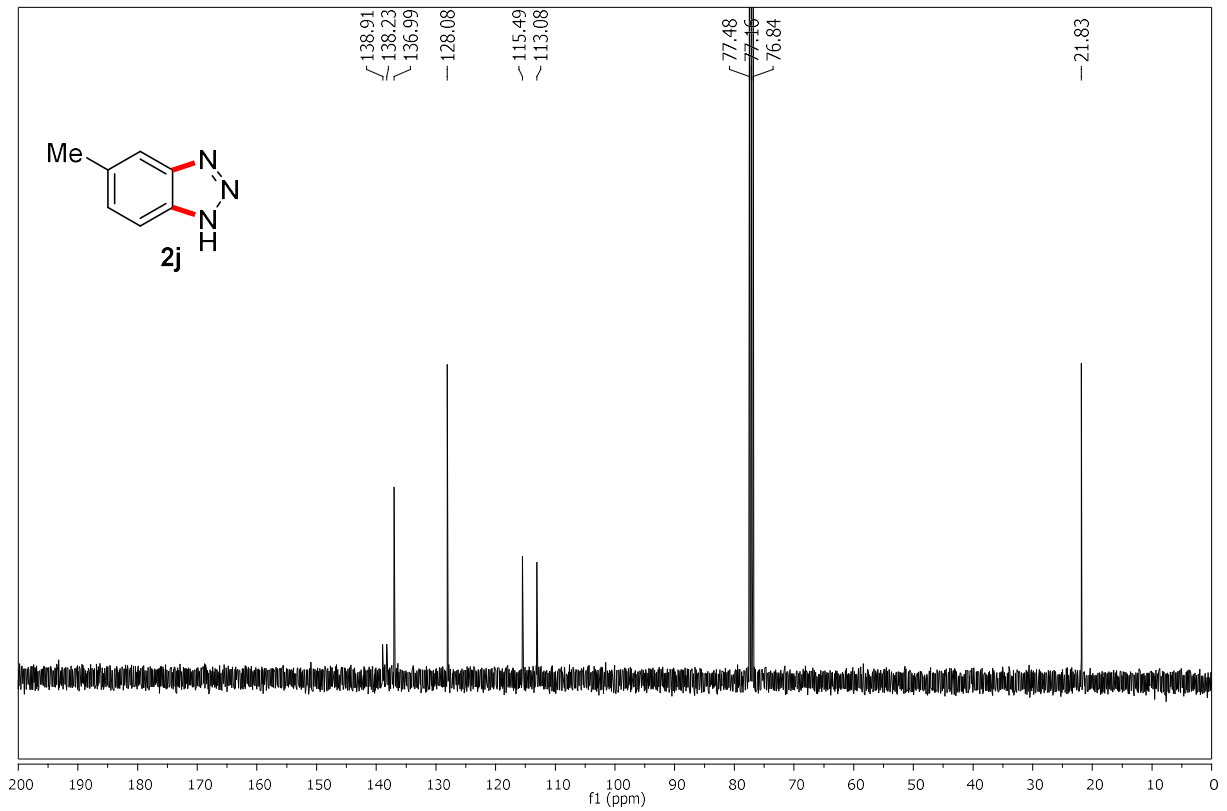
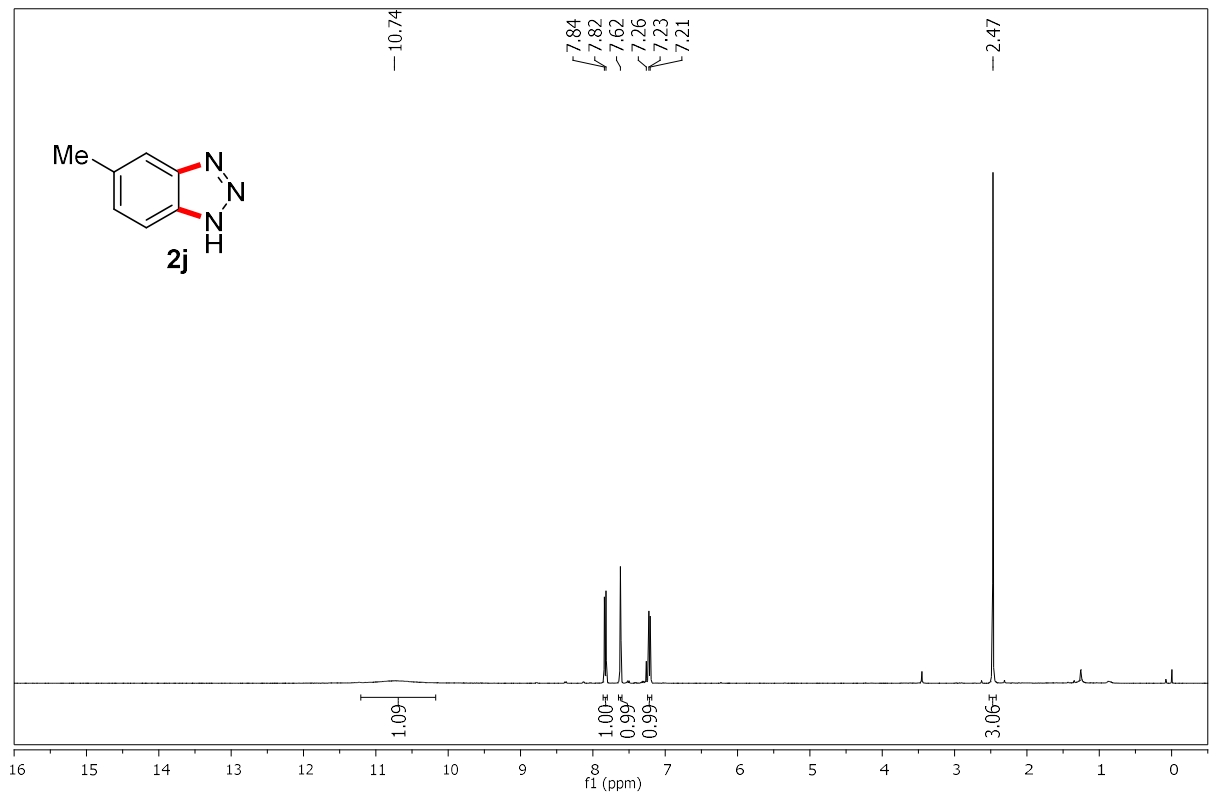
1*H*-naphtho[1,2-*d*][1,2,3]triazole (2h)



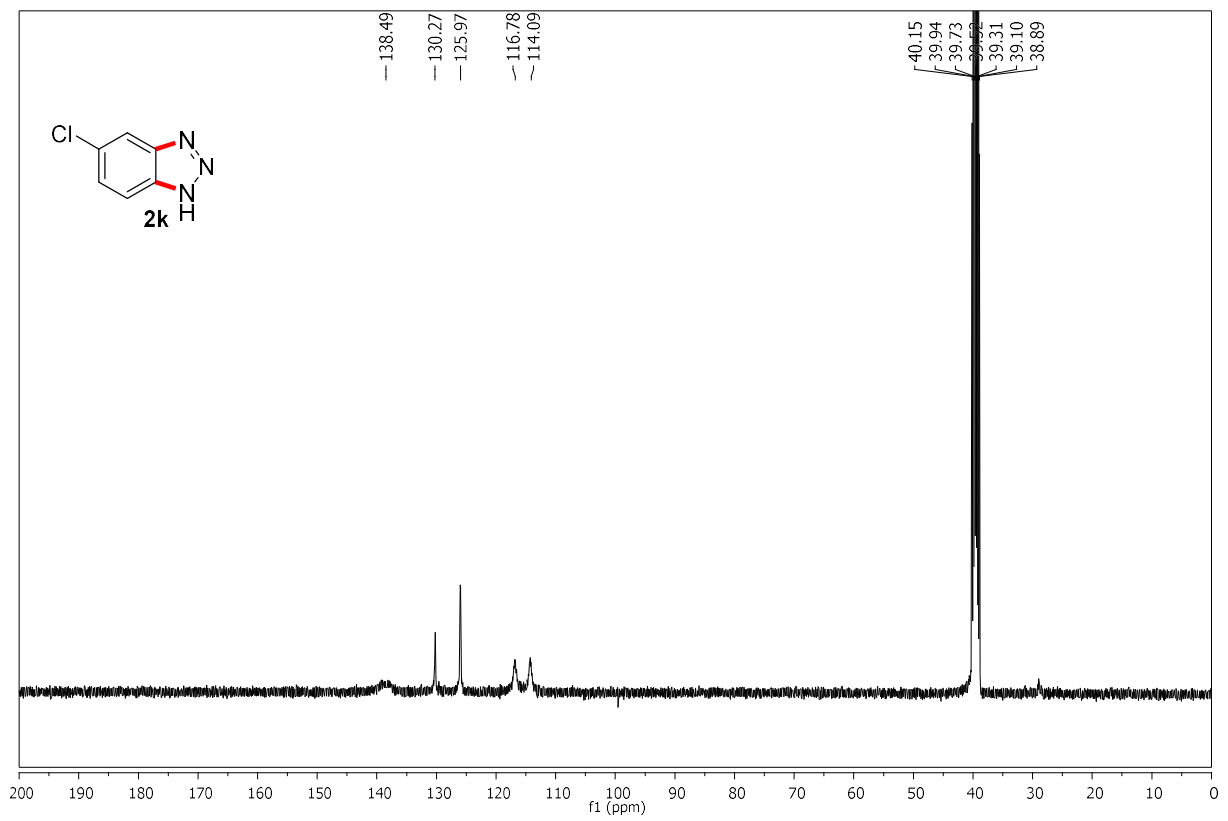
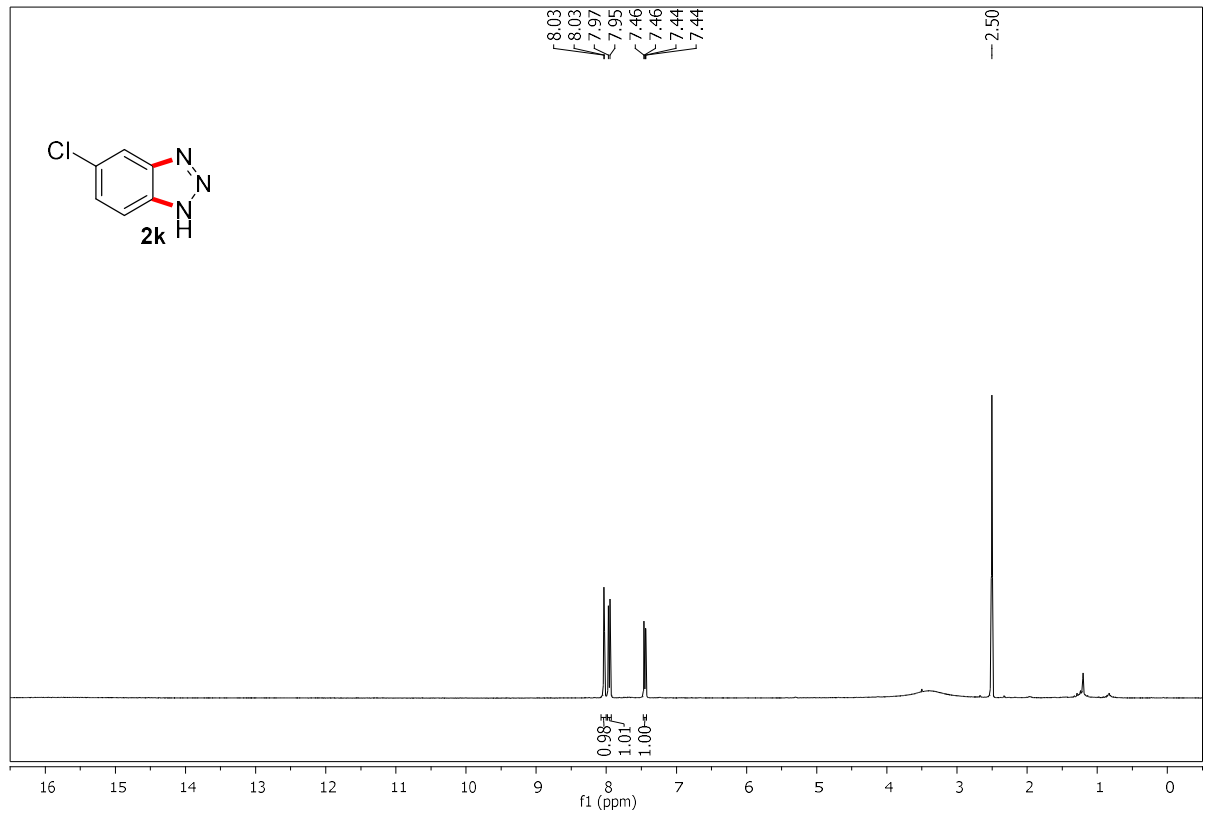
6,7,8,9-Tetrahydro-1*H*-naphtho[1,2-d][1,2,3]triazole (2i)



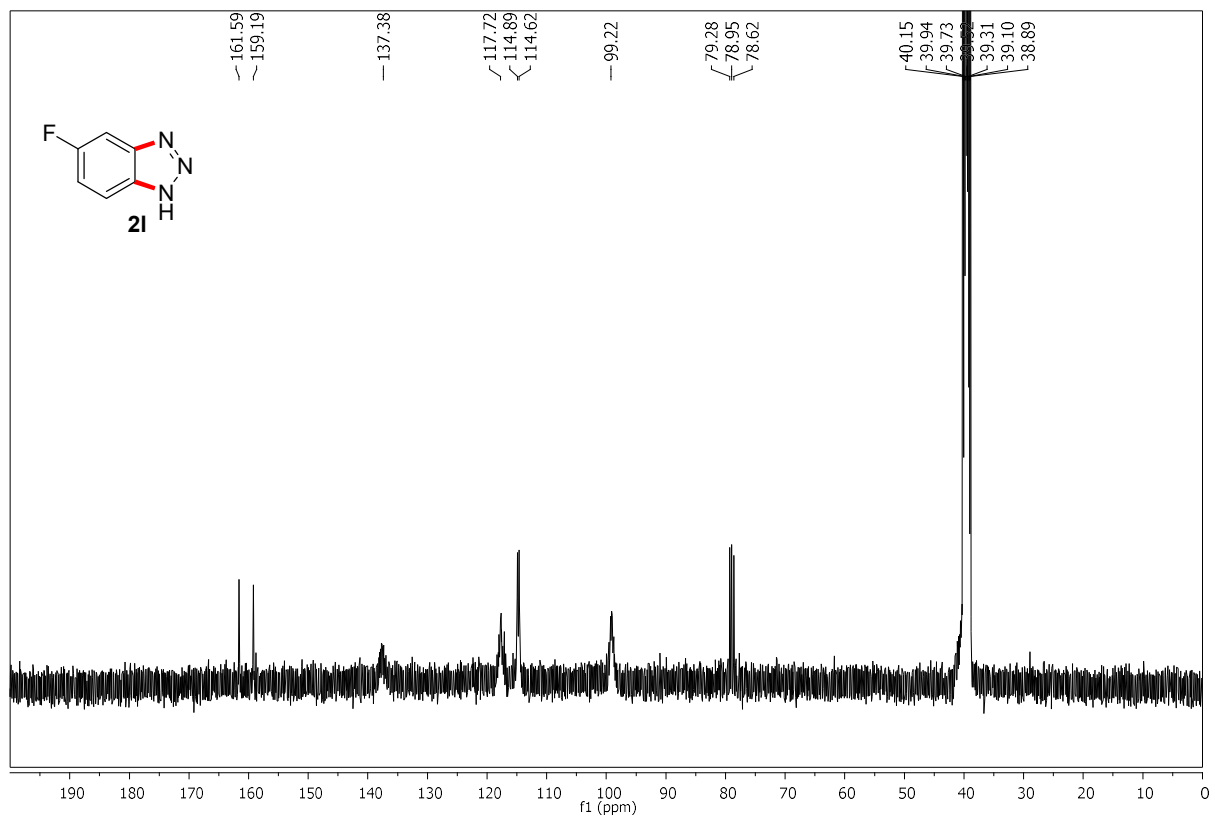
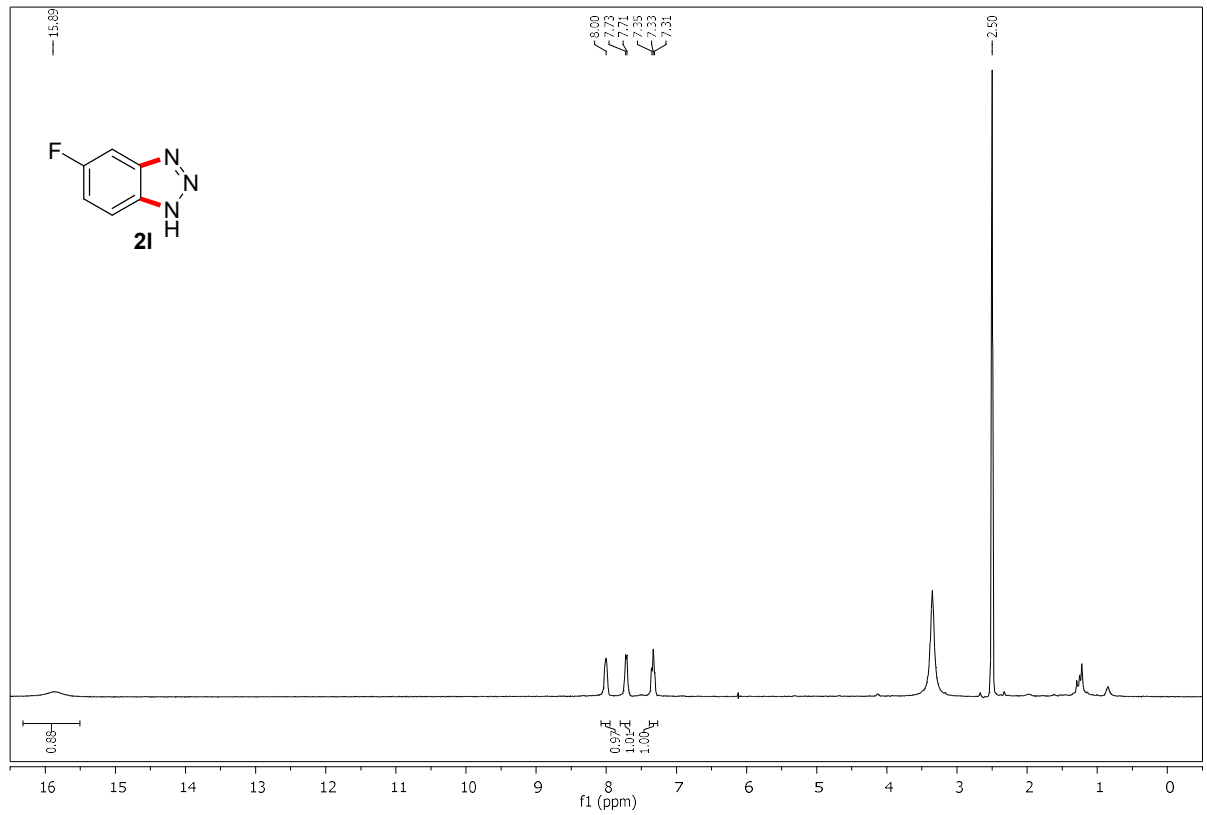
5-methyl-1H-benzo[d][1,2,3]triazole (2j)



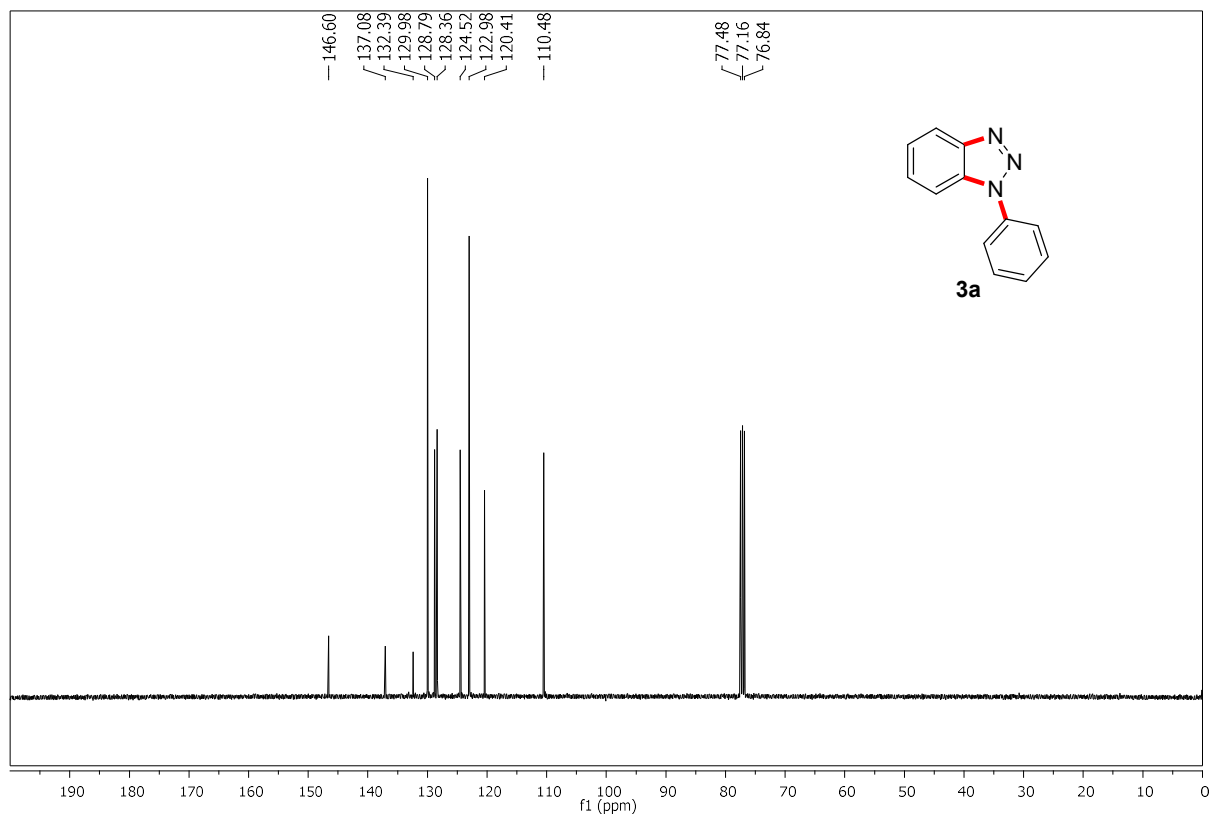
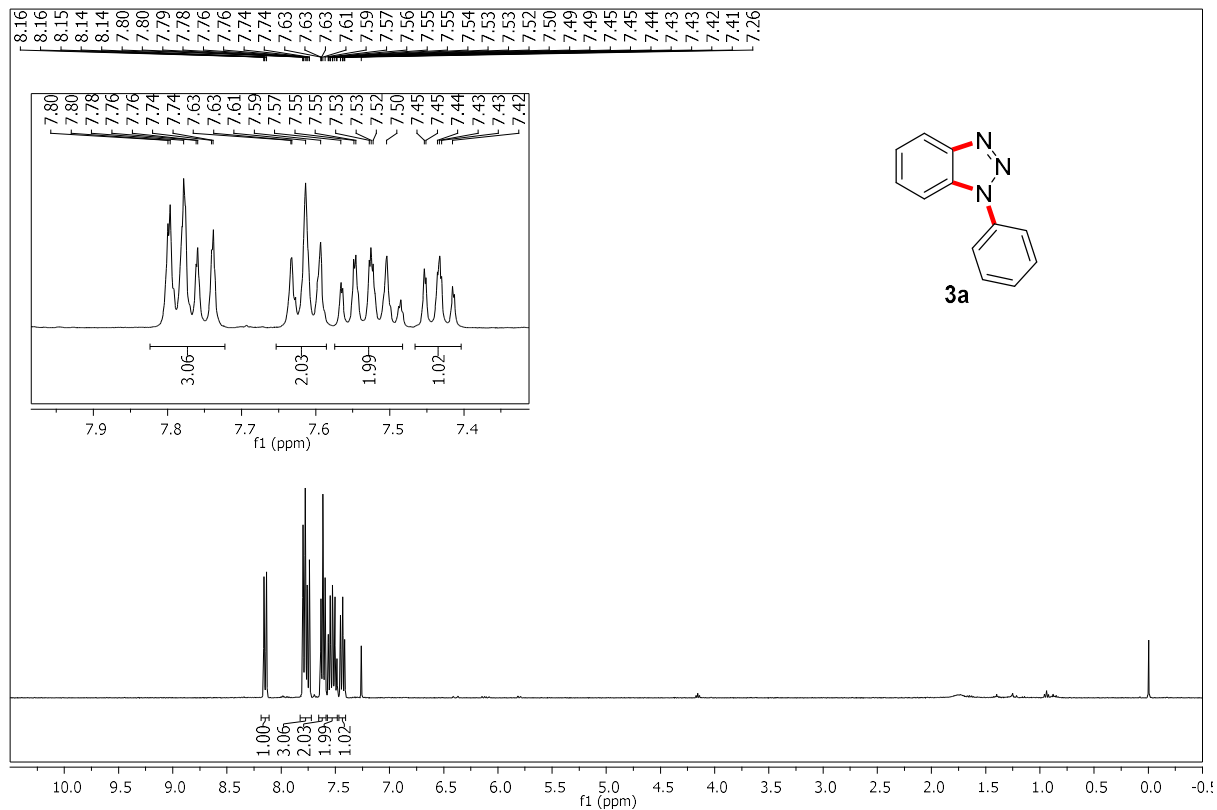
5-Chloro-1H-benzo[d][1,2,3]triazole (2k)



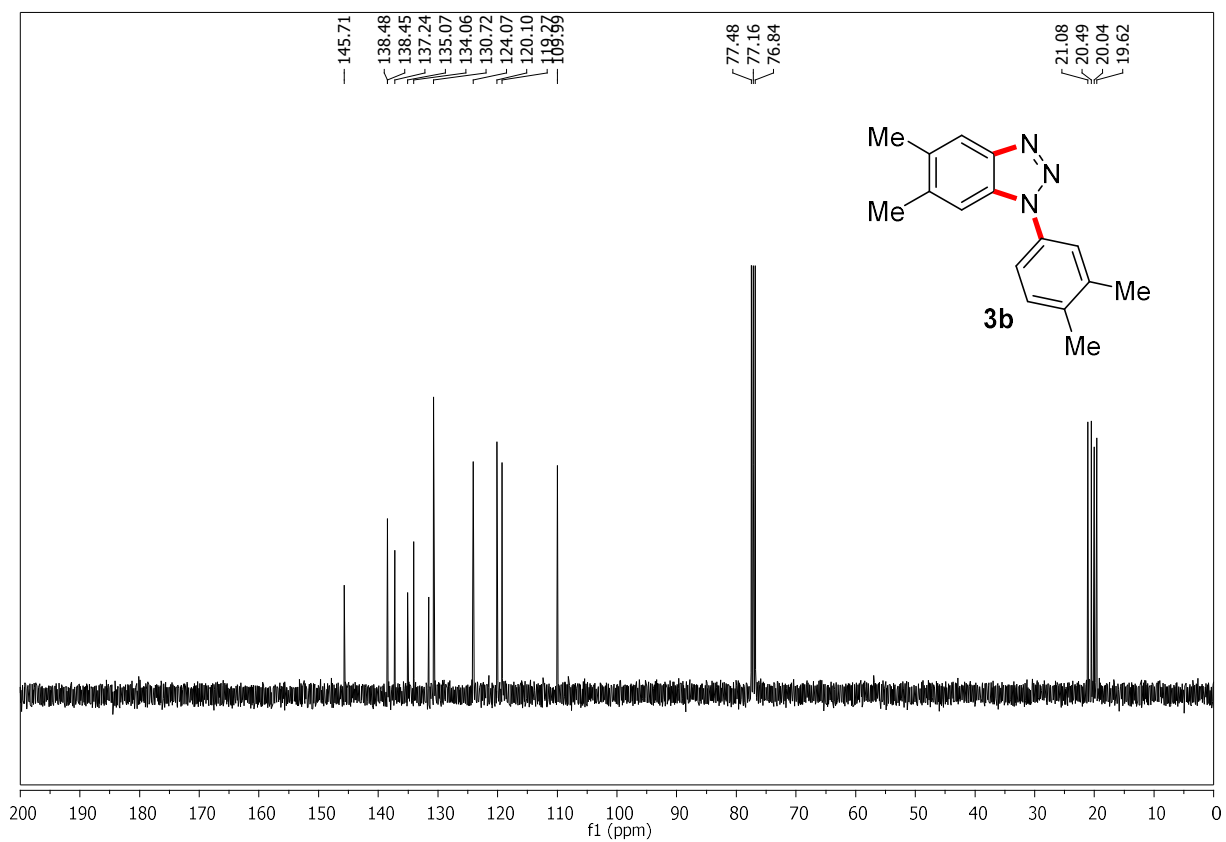
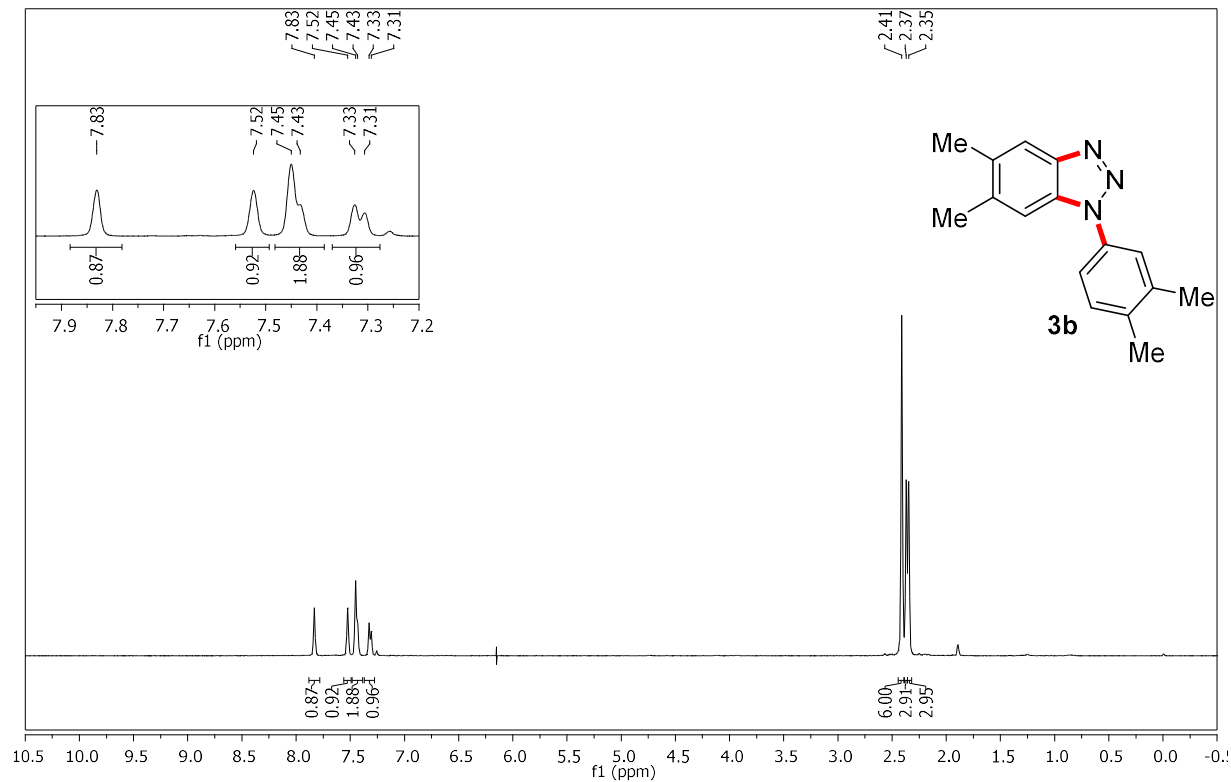
5-fluoro-1H-benzo[d][1,2,3]triazole (2l)



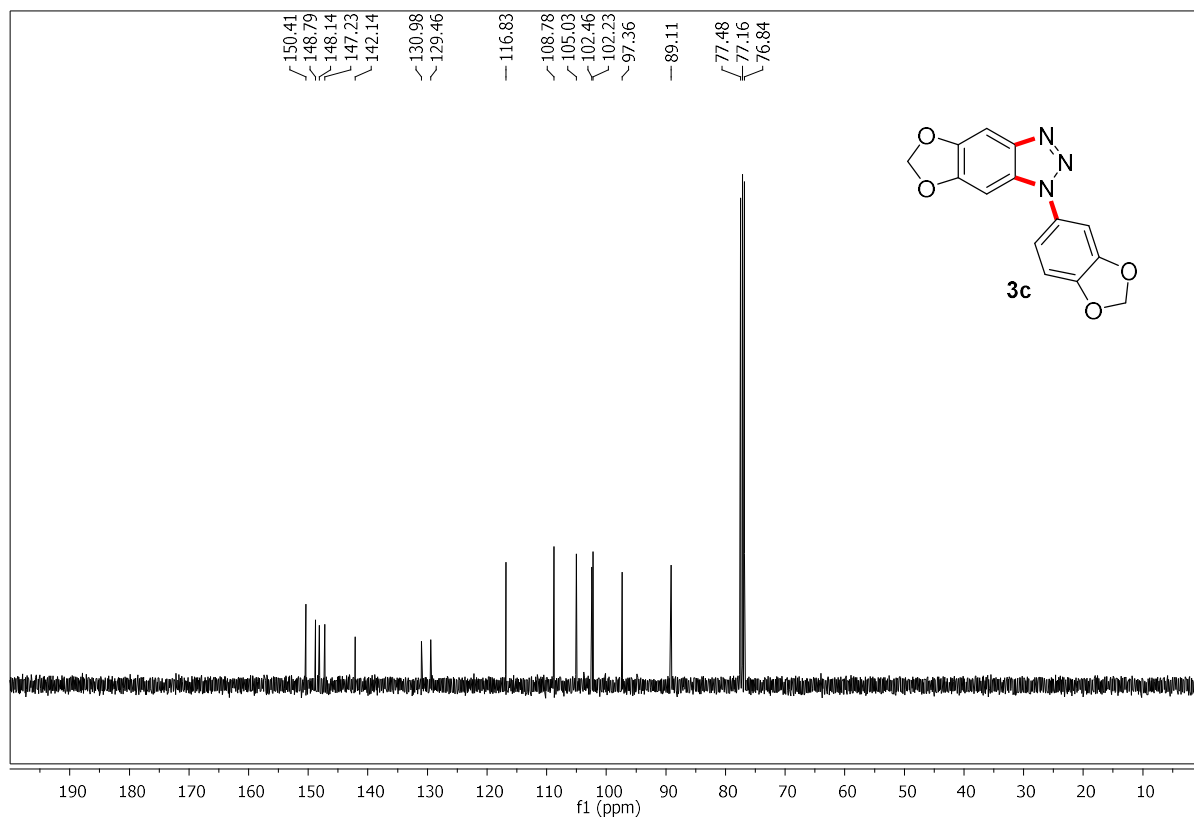
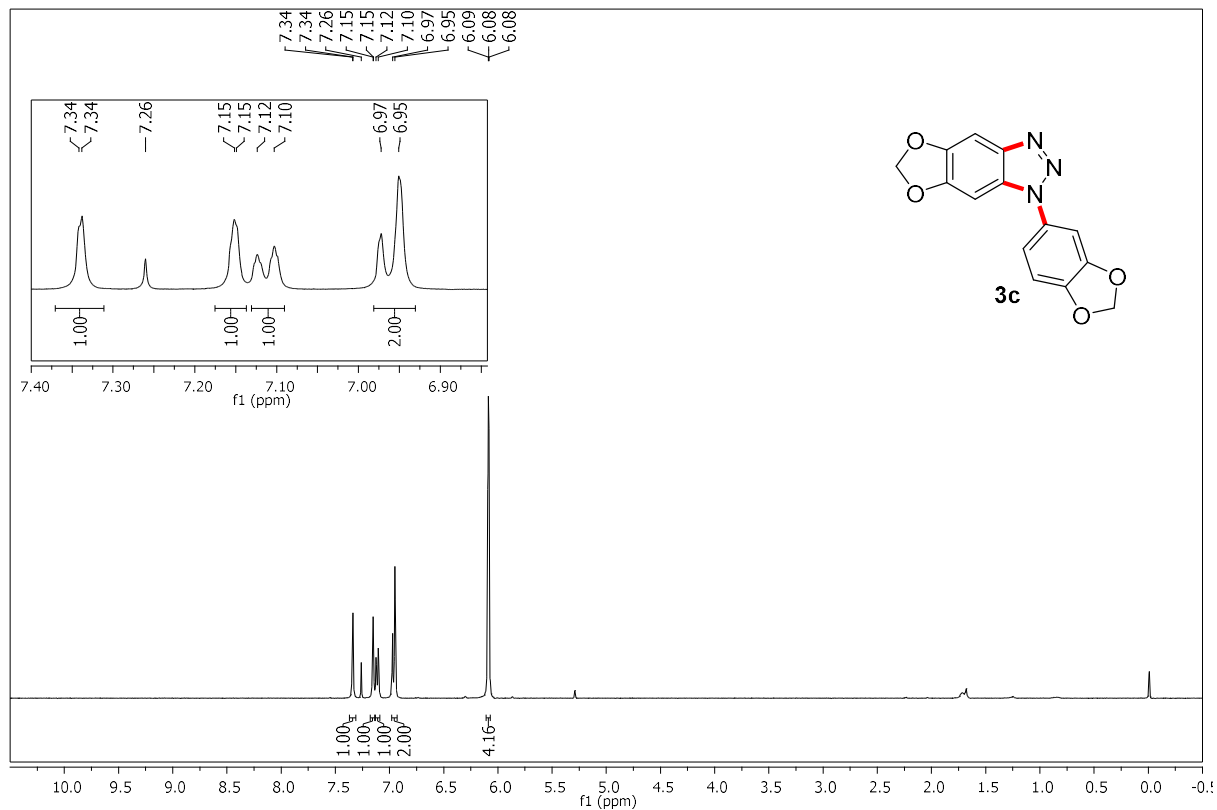
1-Phenyl-1H-benzo[d][1,2,3]triazole (3a)



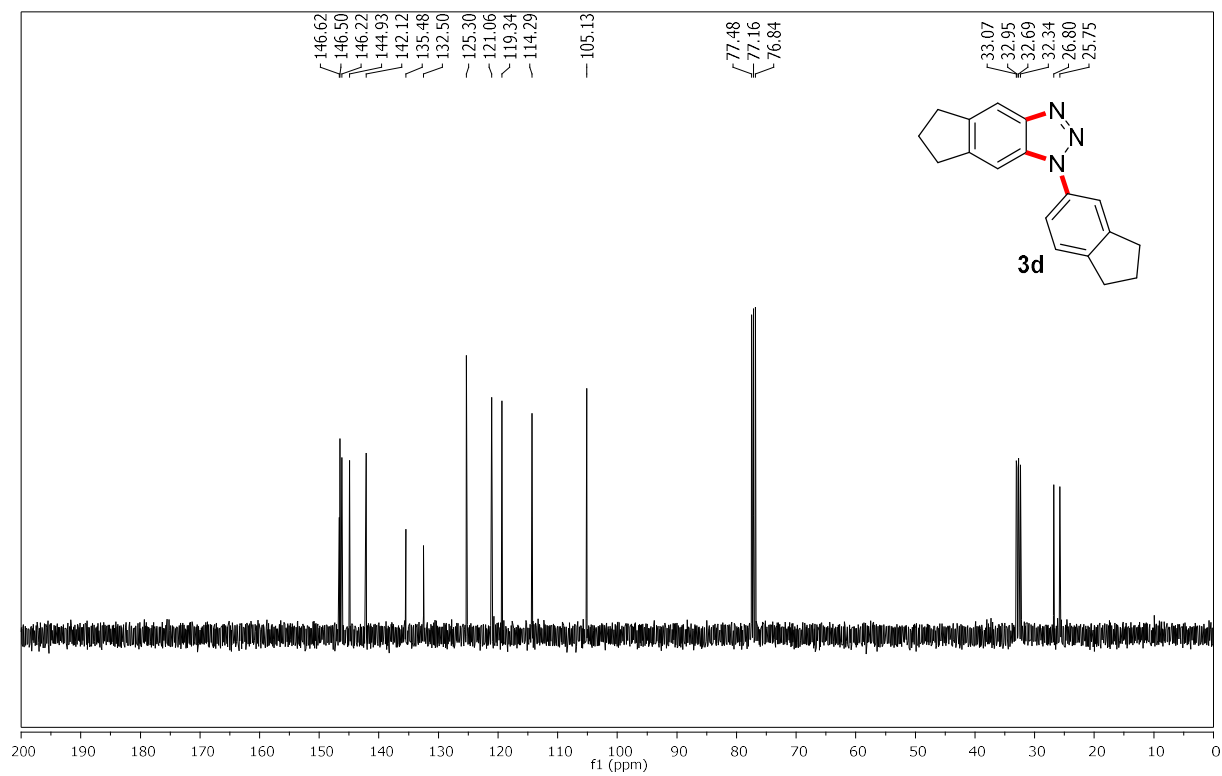
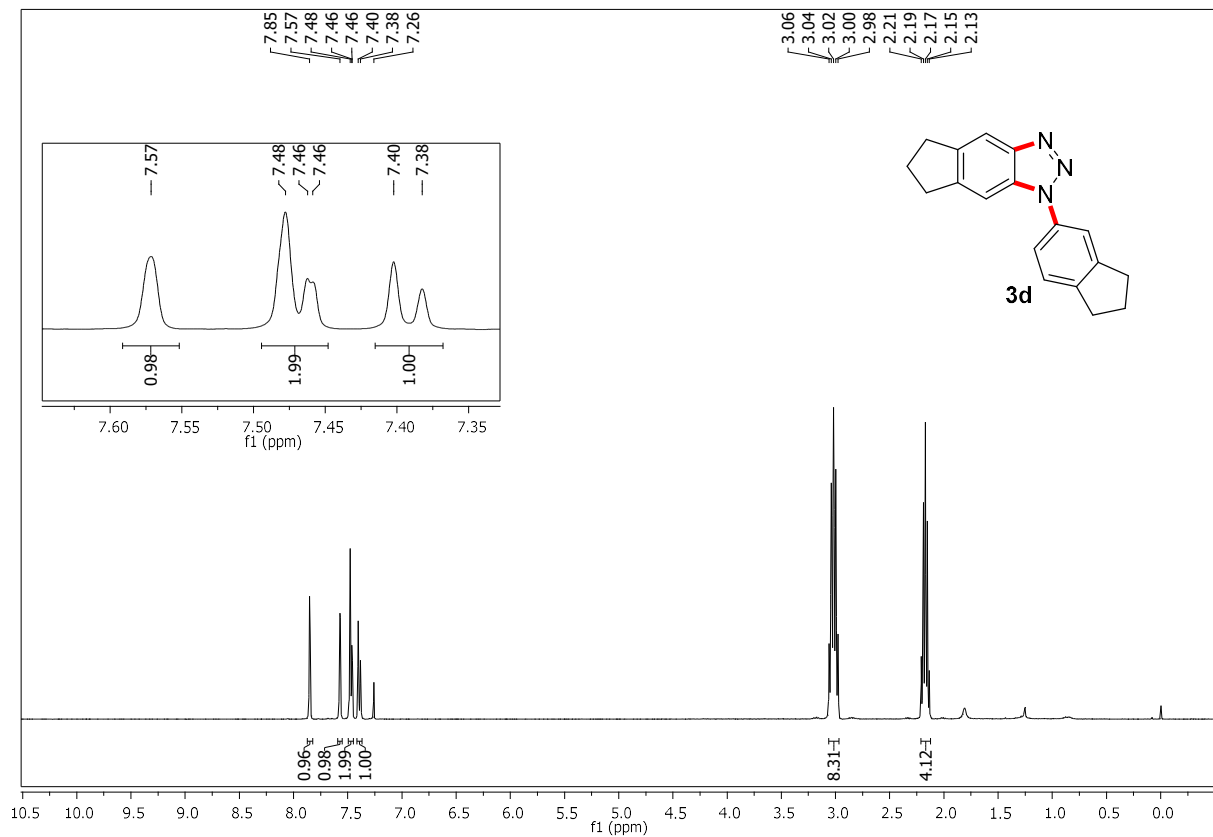
1-(3,4-Dimethylphenyl)-5,6-dimethyl-1*H*-benzo[*d*][1,2,3]triazole (3b)



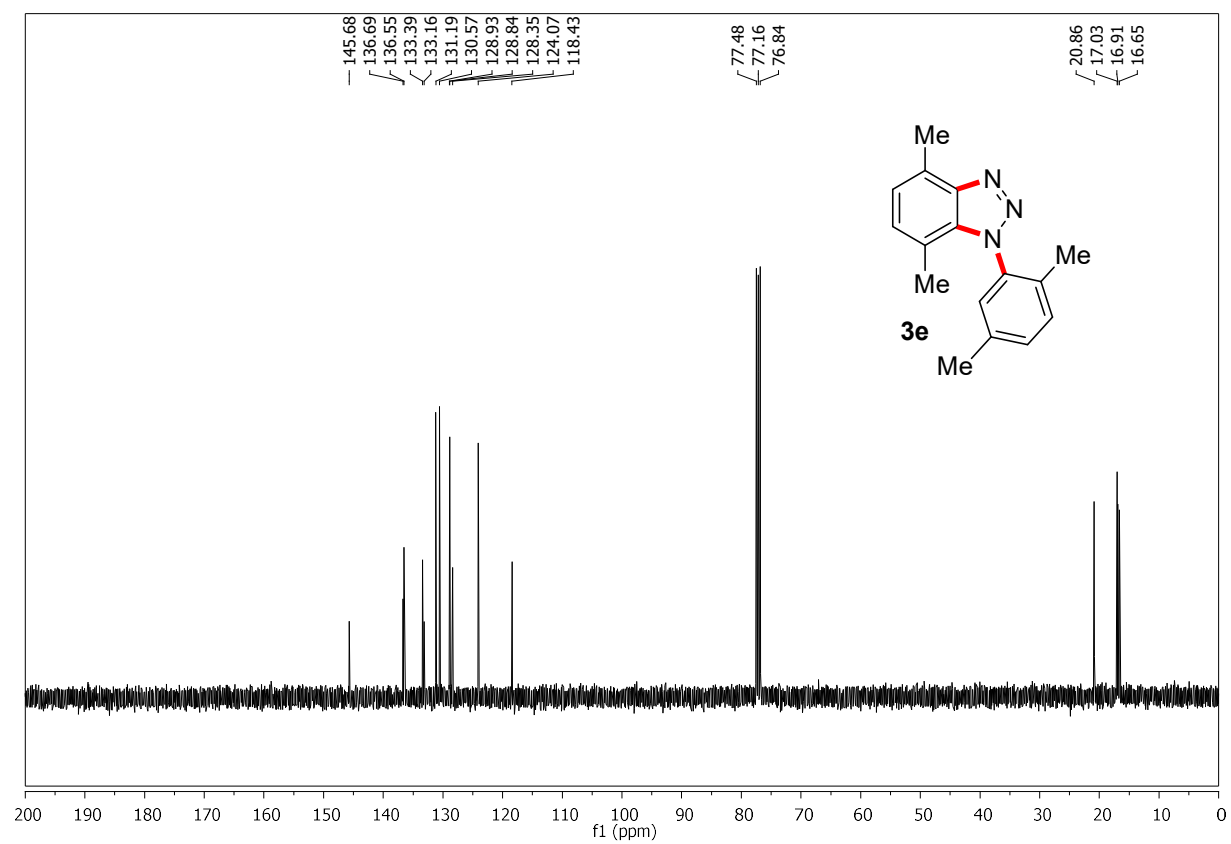
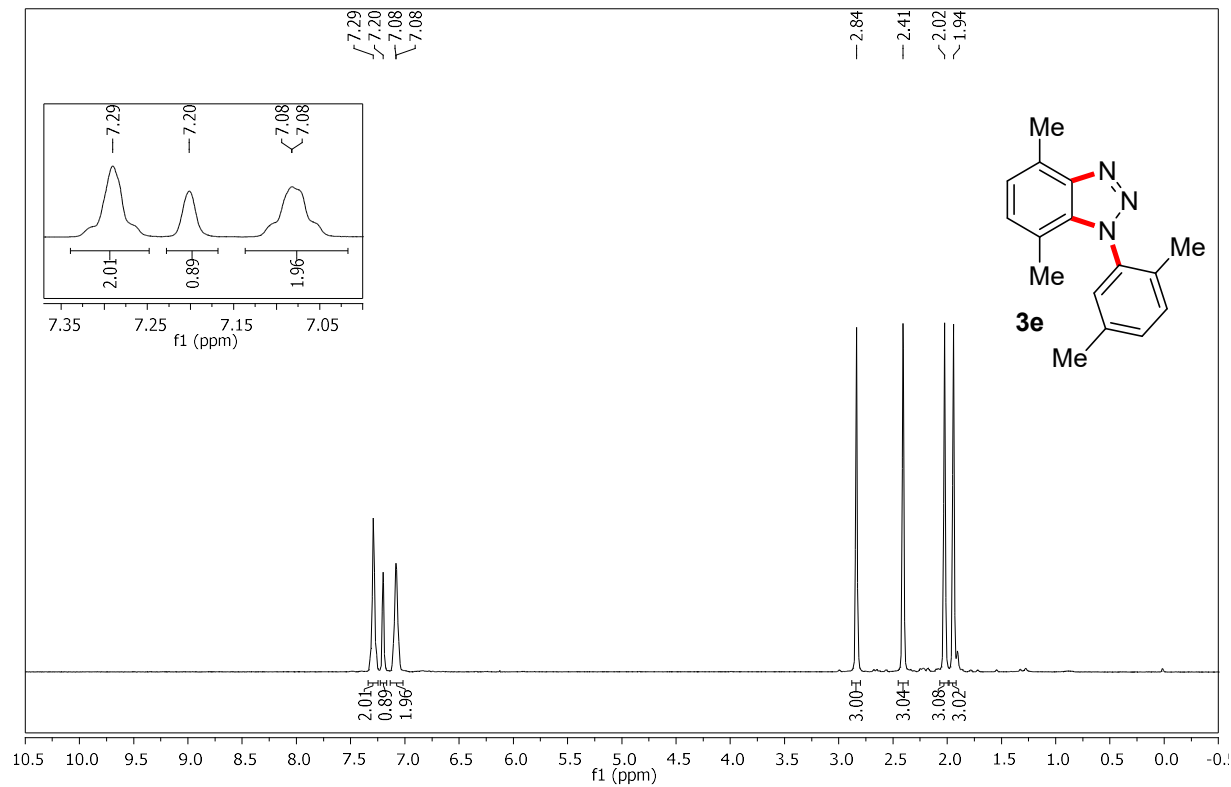
1-(Benzo[d][1,3]dioxol-5-yl)-1H-[1,3]dioxolo[4',5':4,5]benzo[1,2-d][1,2,3]triazole (3c)



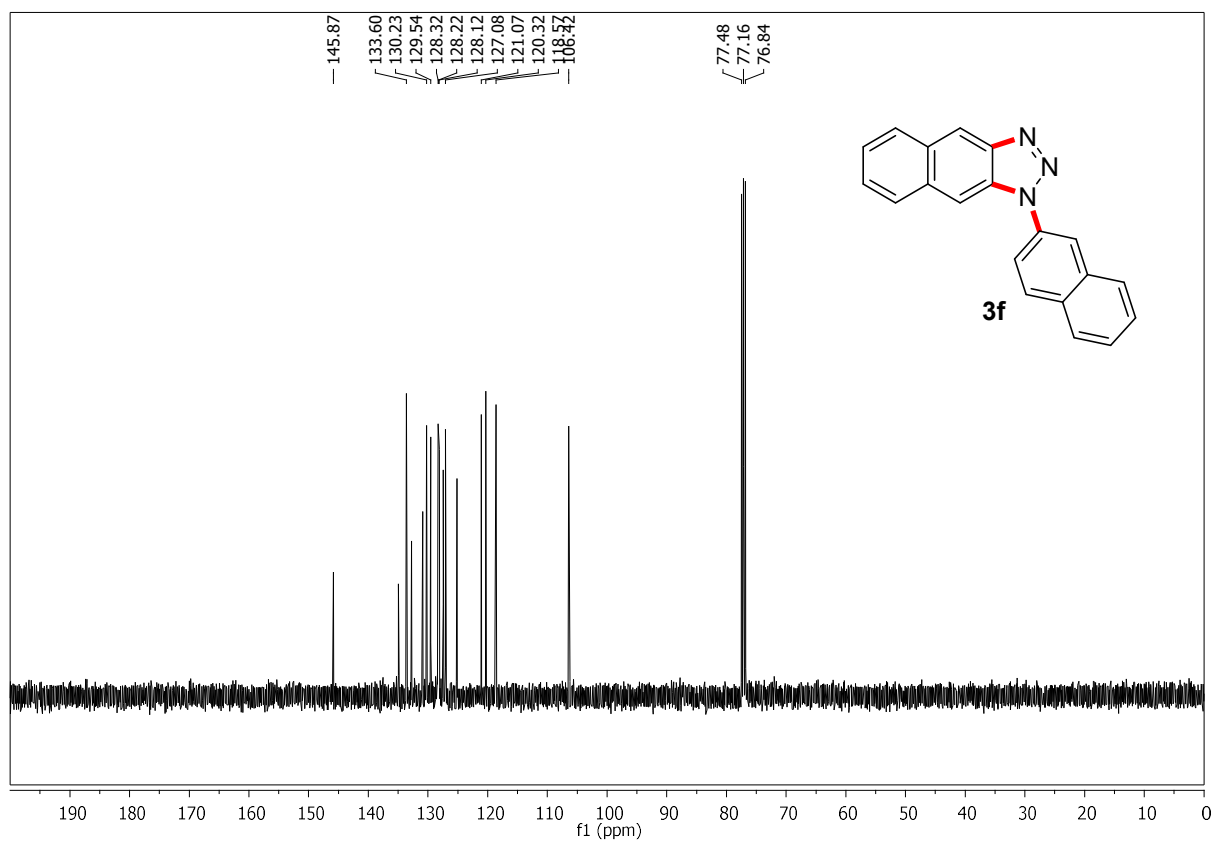
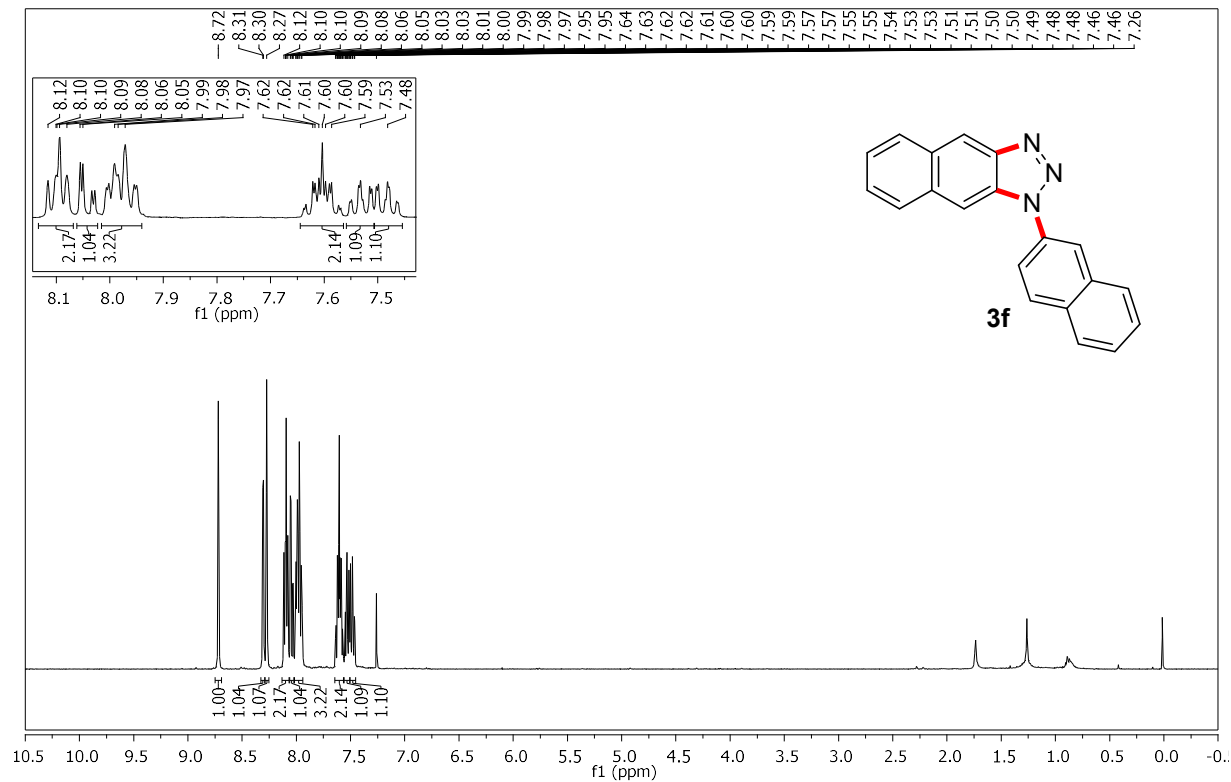
1-(2,3-Dihydro-1*H*-inden-5-yl)-1,5,6,7-tetrahydroindeno[5,6-*d*][1,2,3]triazole (3d)



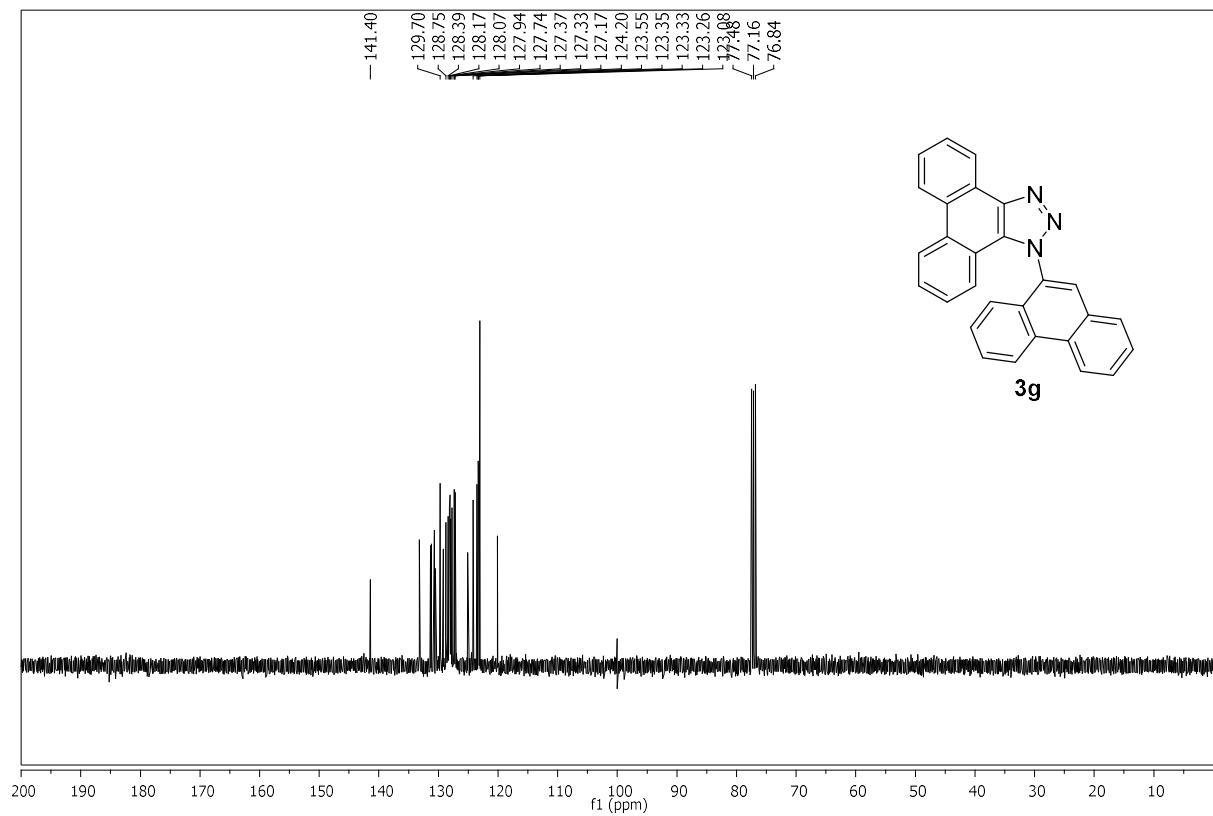
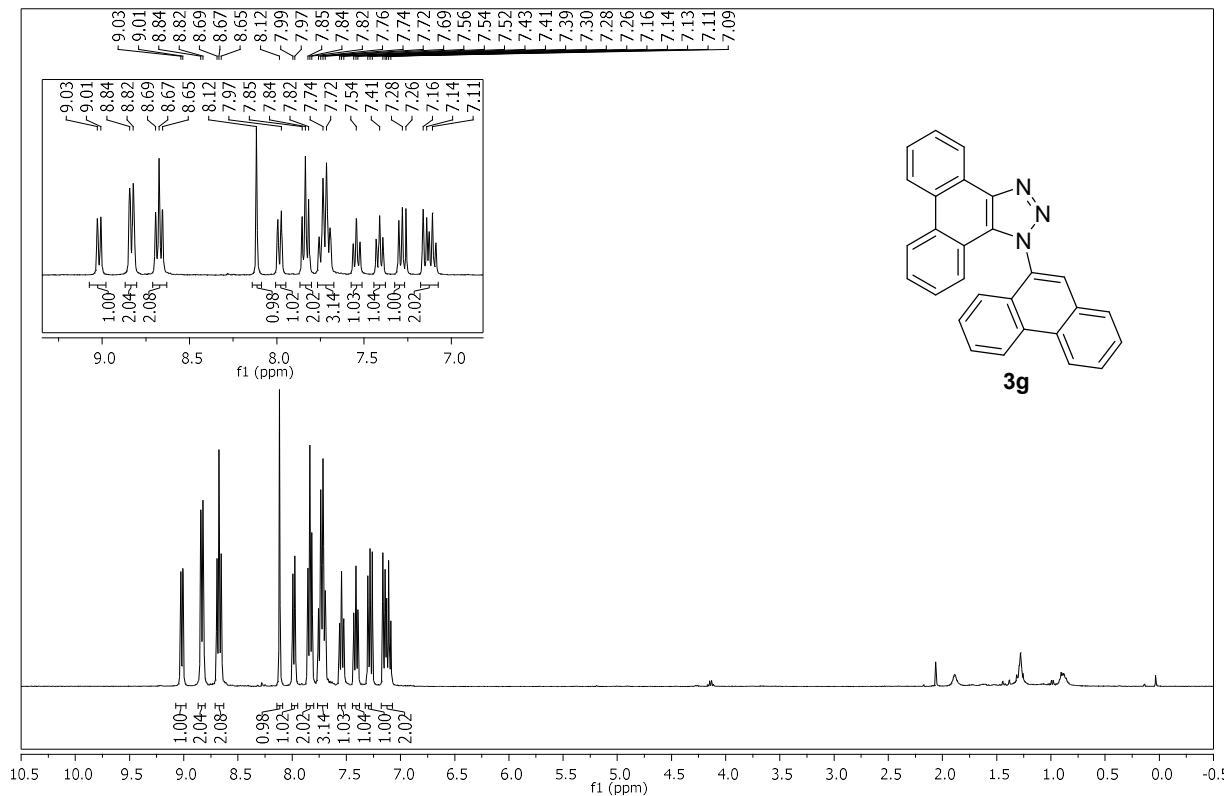
1-(2,5-Dimethylphenyl)-4,7-dimethyl-1H-benzo[d][1,2,3]triazole (3e)



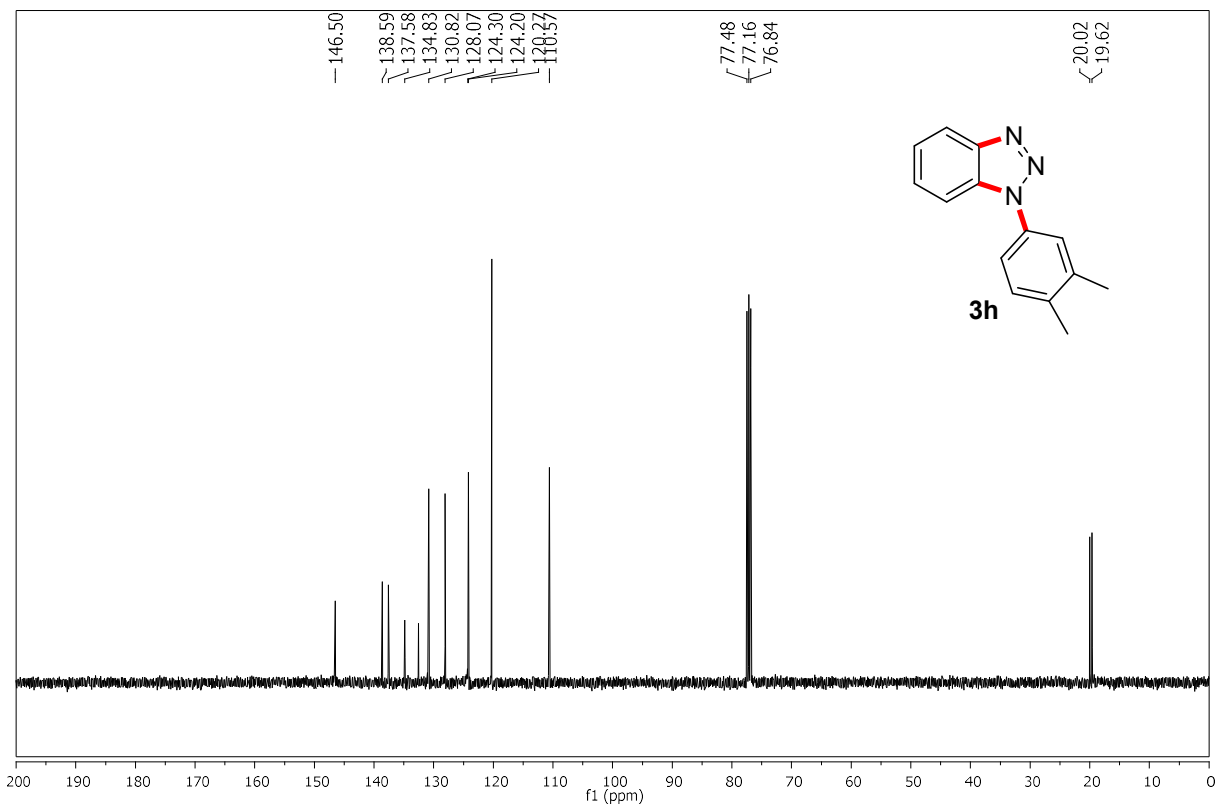
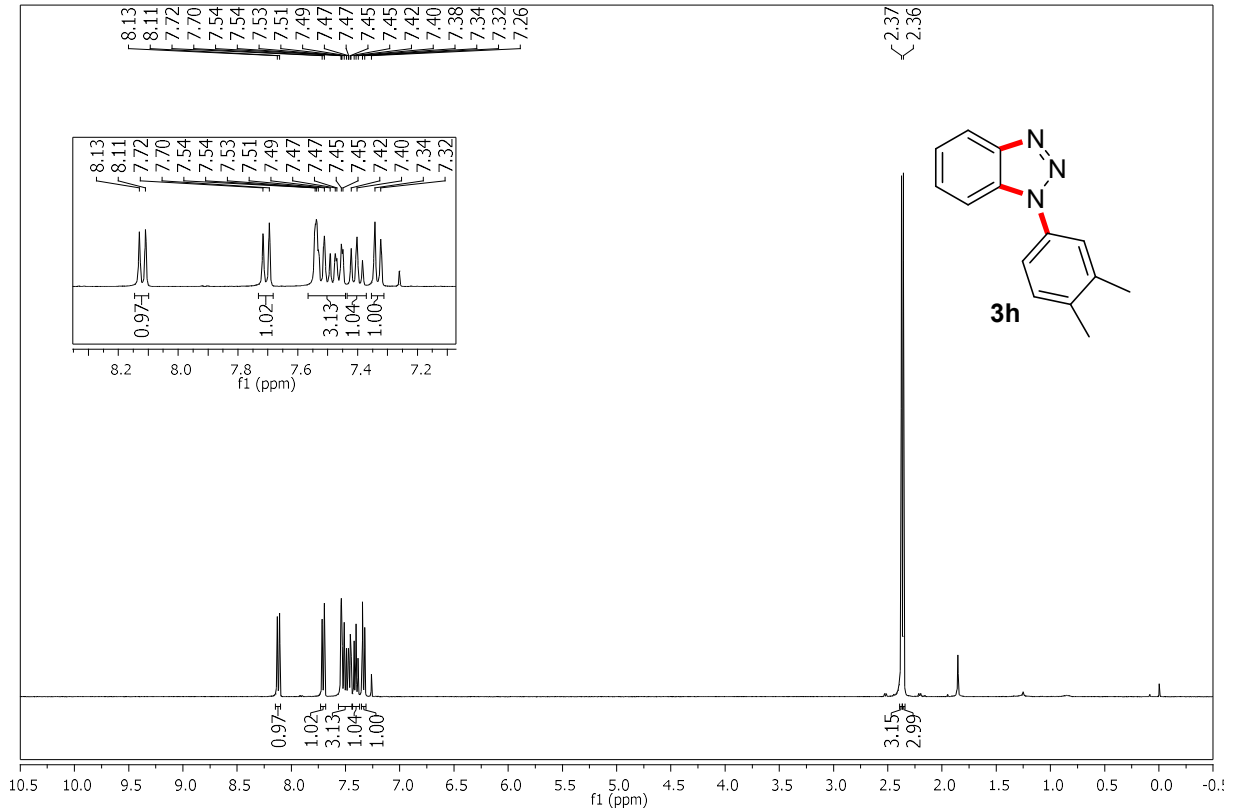
1-(Naphthalen-2-yl)-1*H*-naphtho[2,3-*d*][1,2,3]triazole (3f)



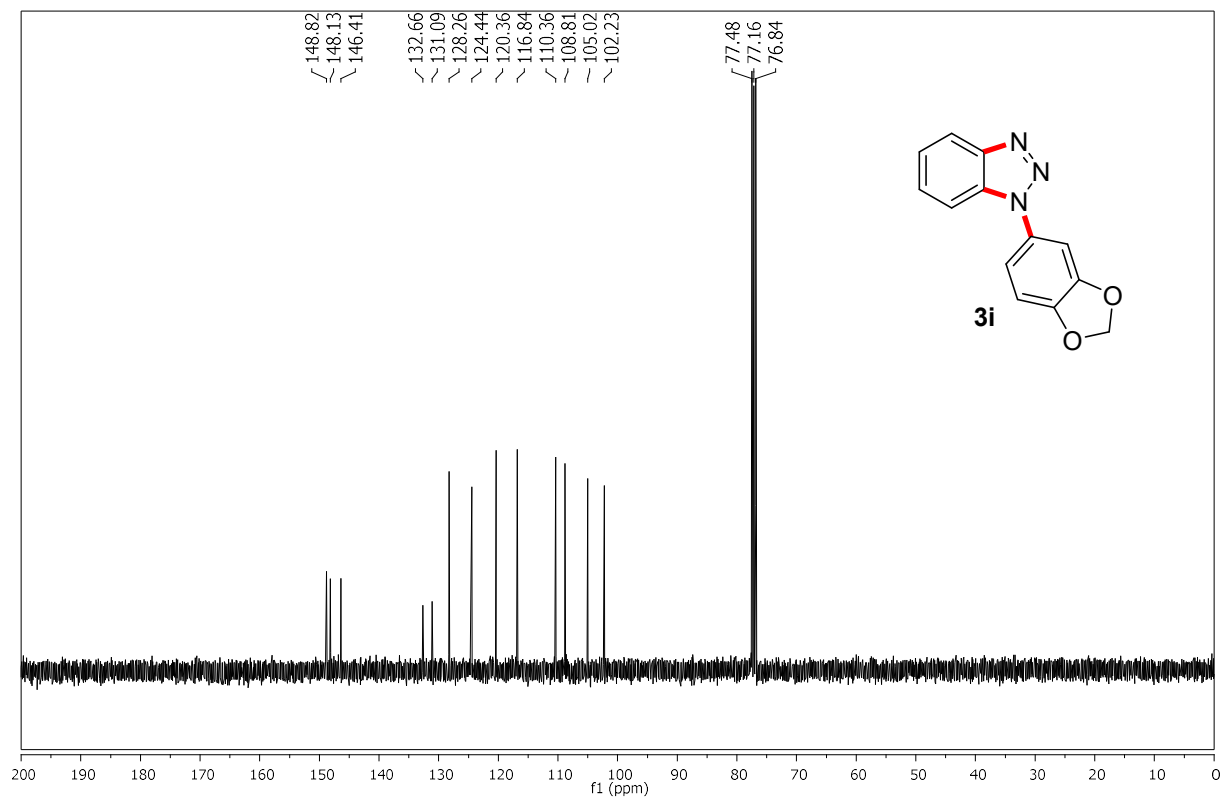
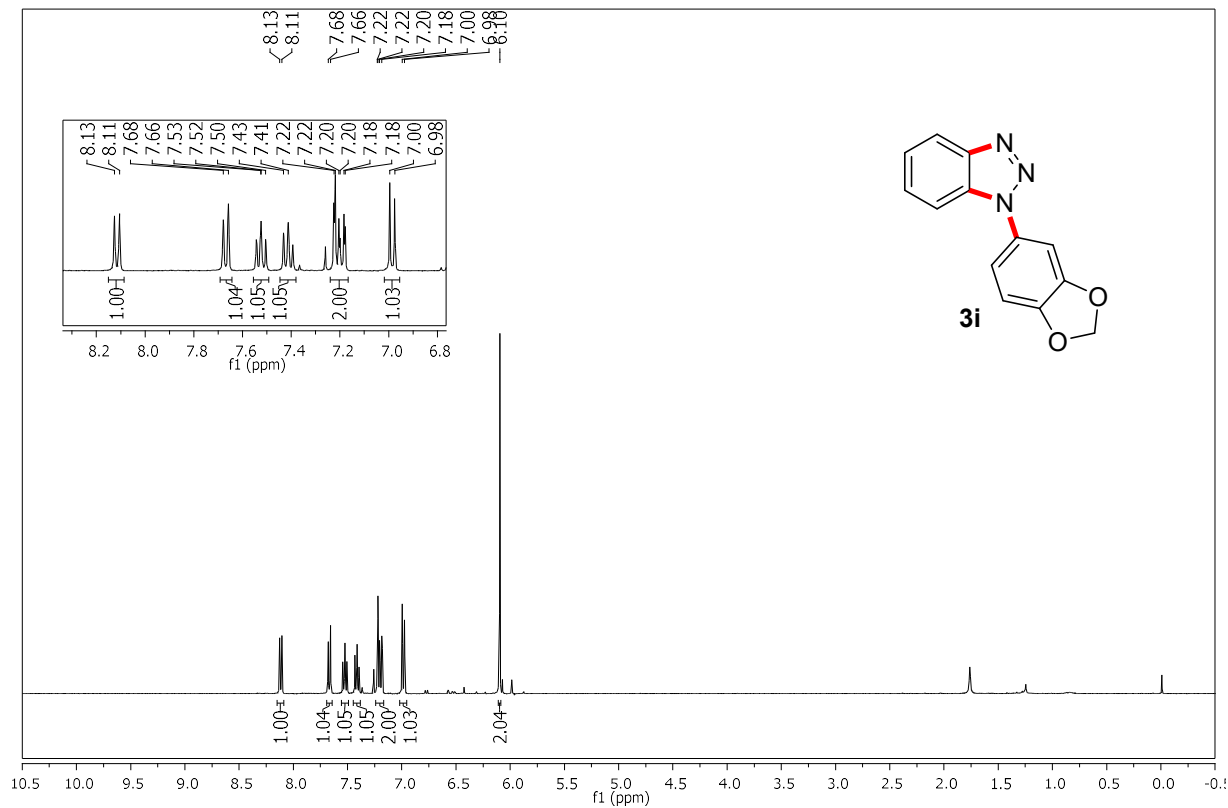
1-(Phenanthren-9-yl)-1*H*-phenanthro[9,10-*d*][1,2,3]triazole (**3g**)



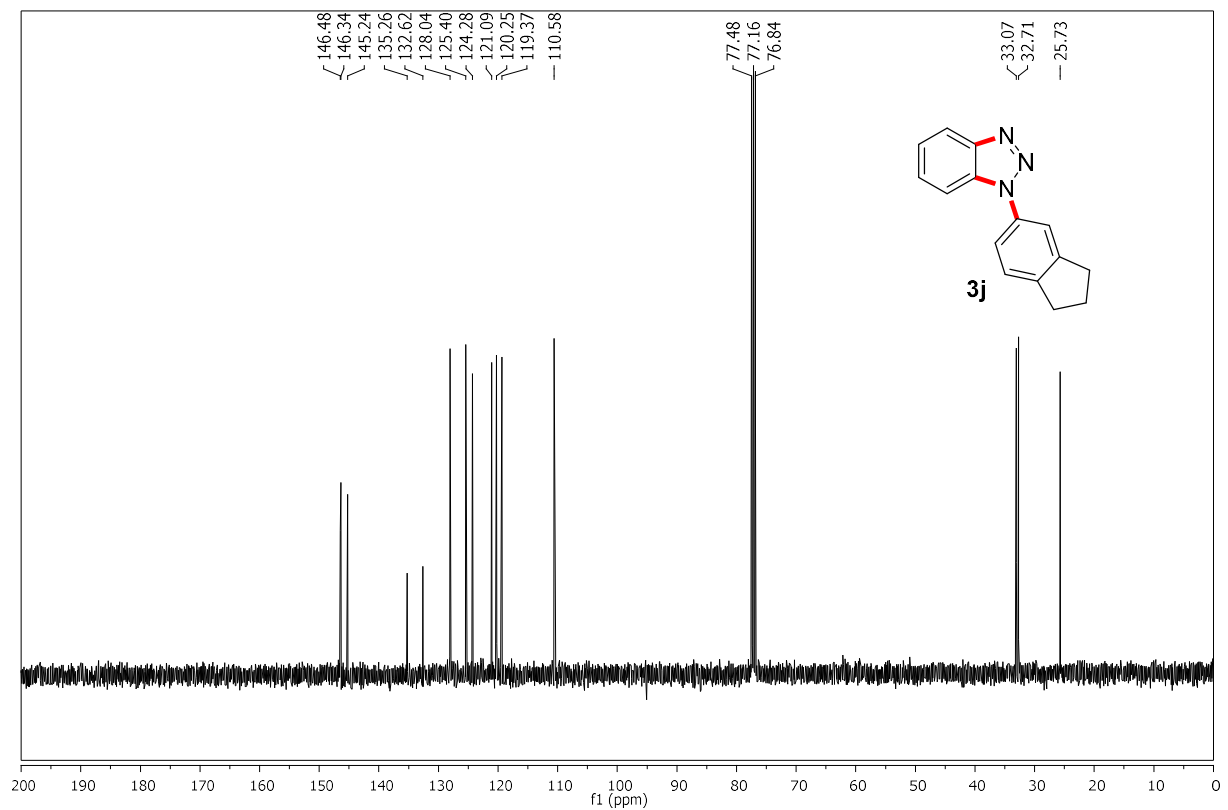
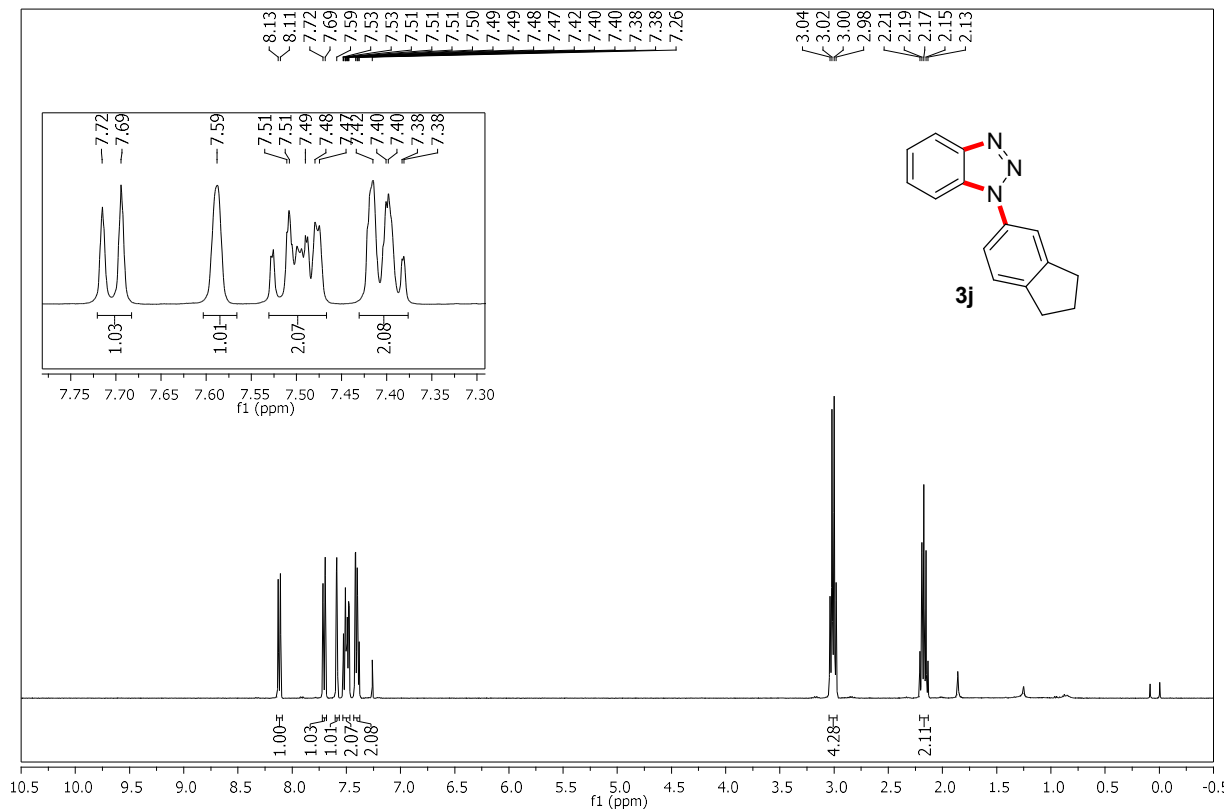
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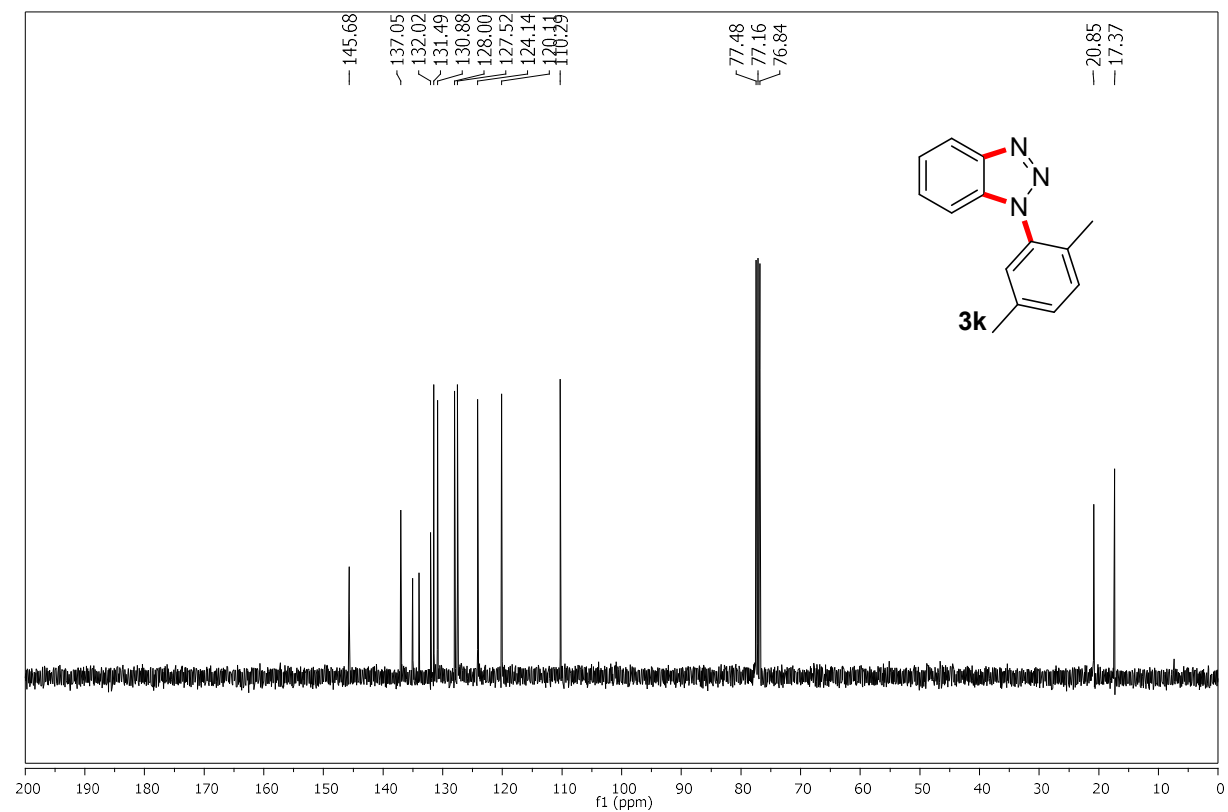
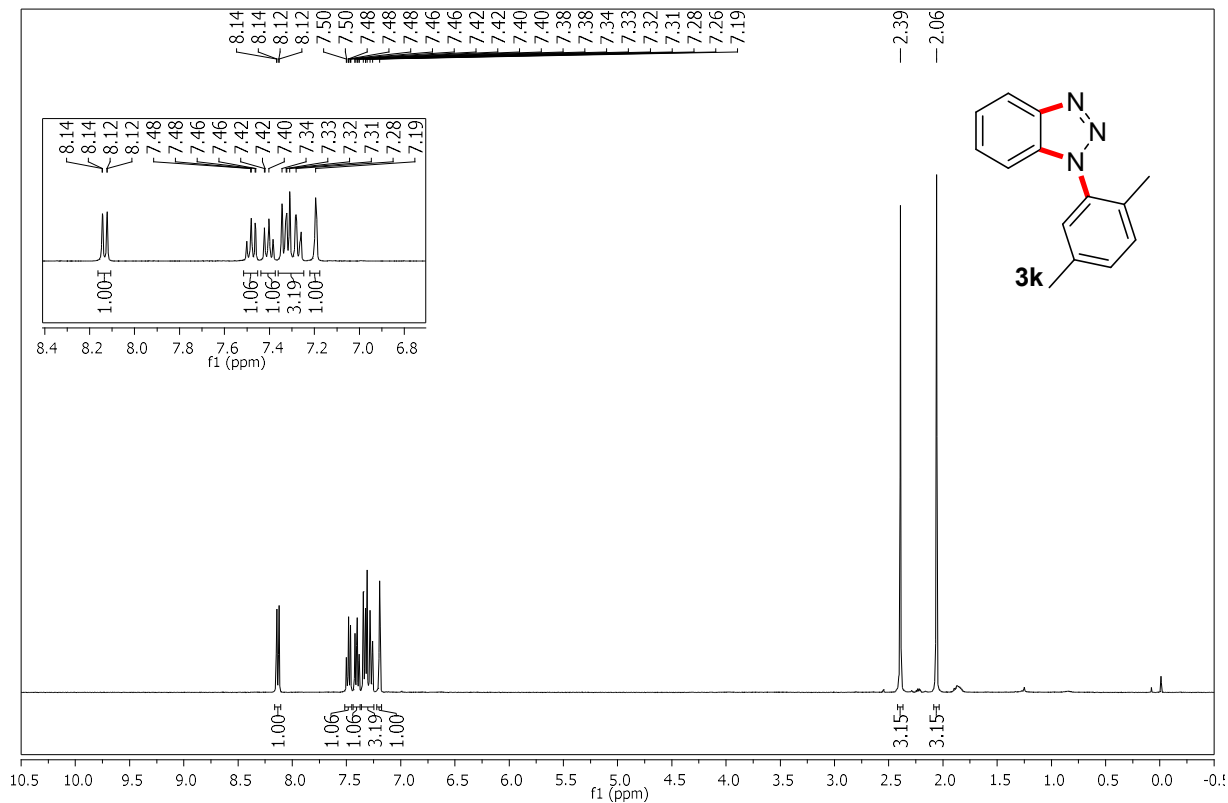
1-(benzo[d][1,3]dioxol-5-yl)-1H-benzo[d][1,2,3]triazole (3i)



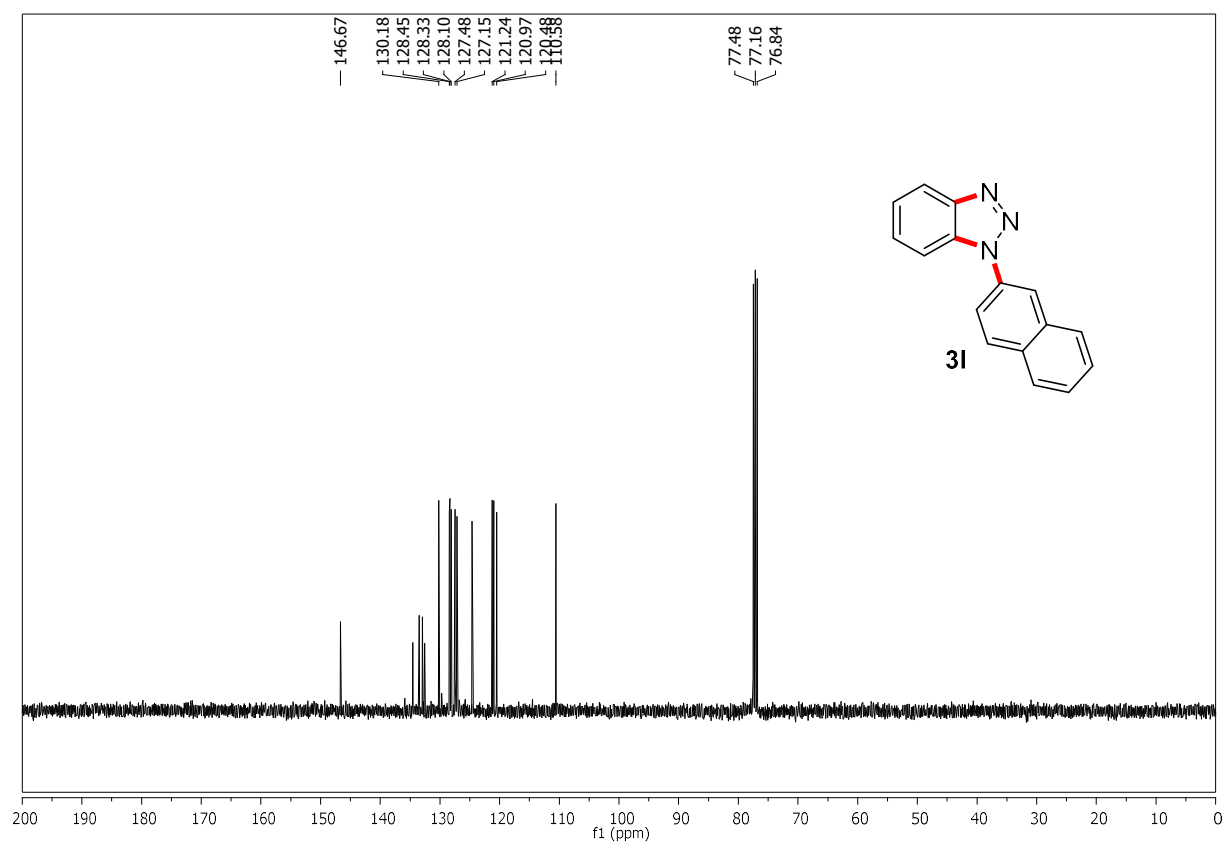
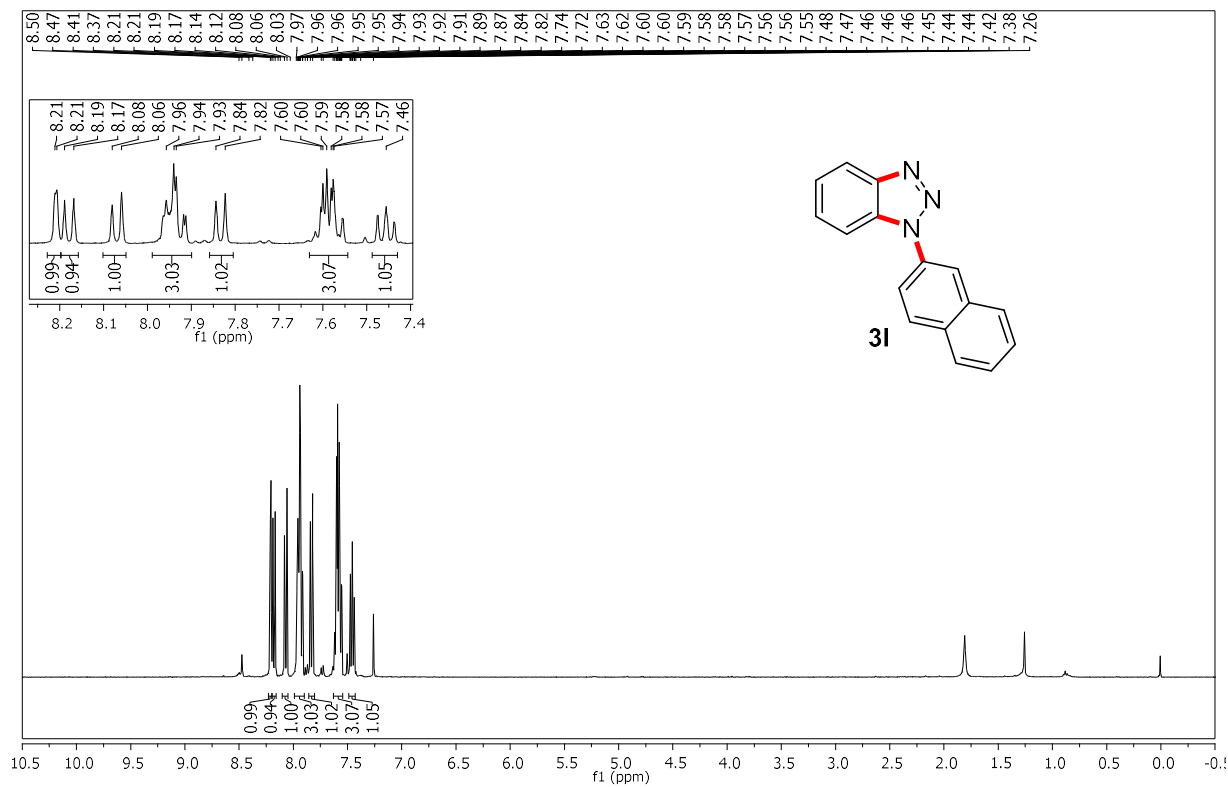
1-(2,3-Dihydro-1H-inden-5-yl)-1H-benzo[d][1,2,3]triazole (3j)



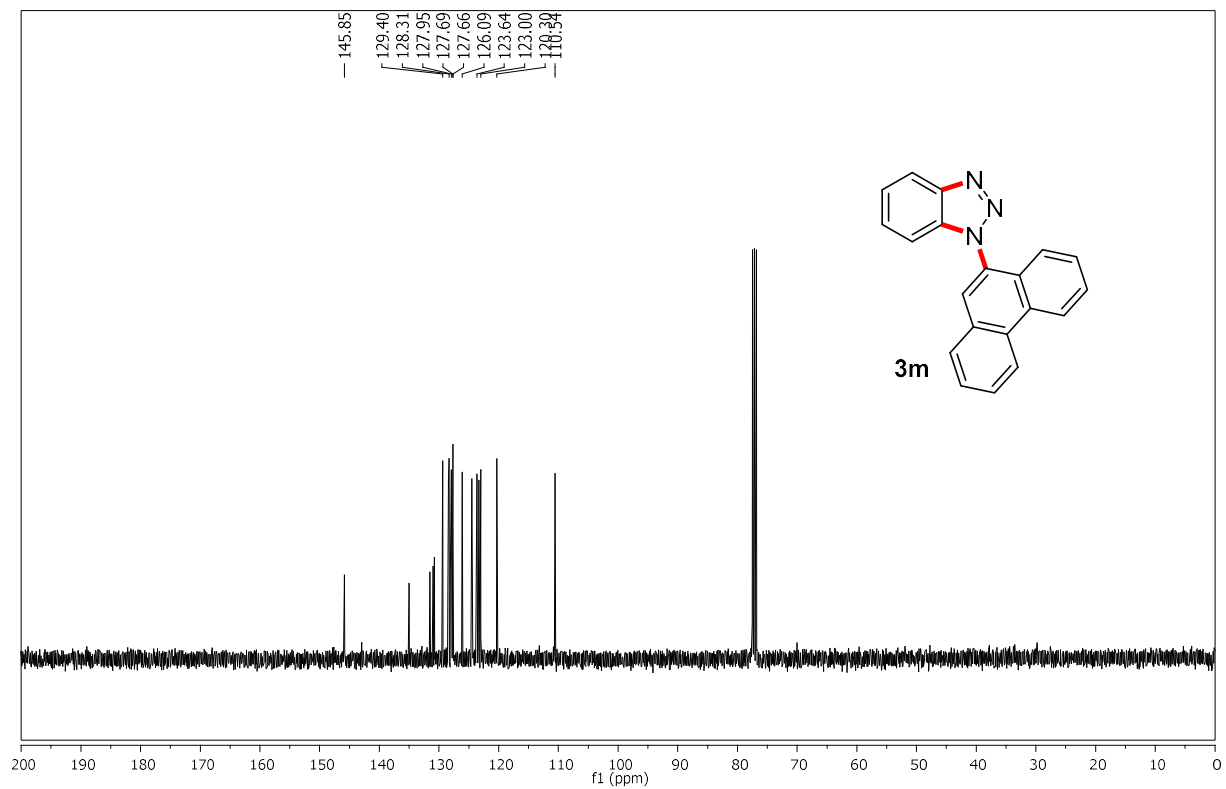
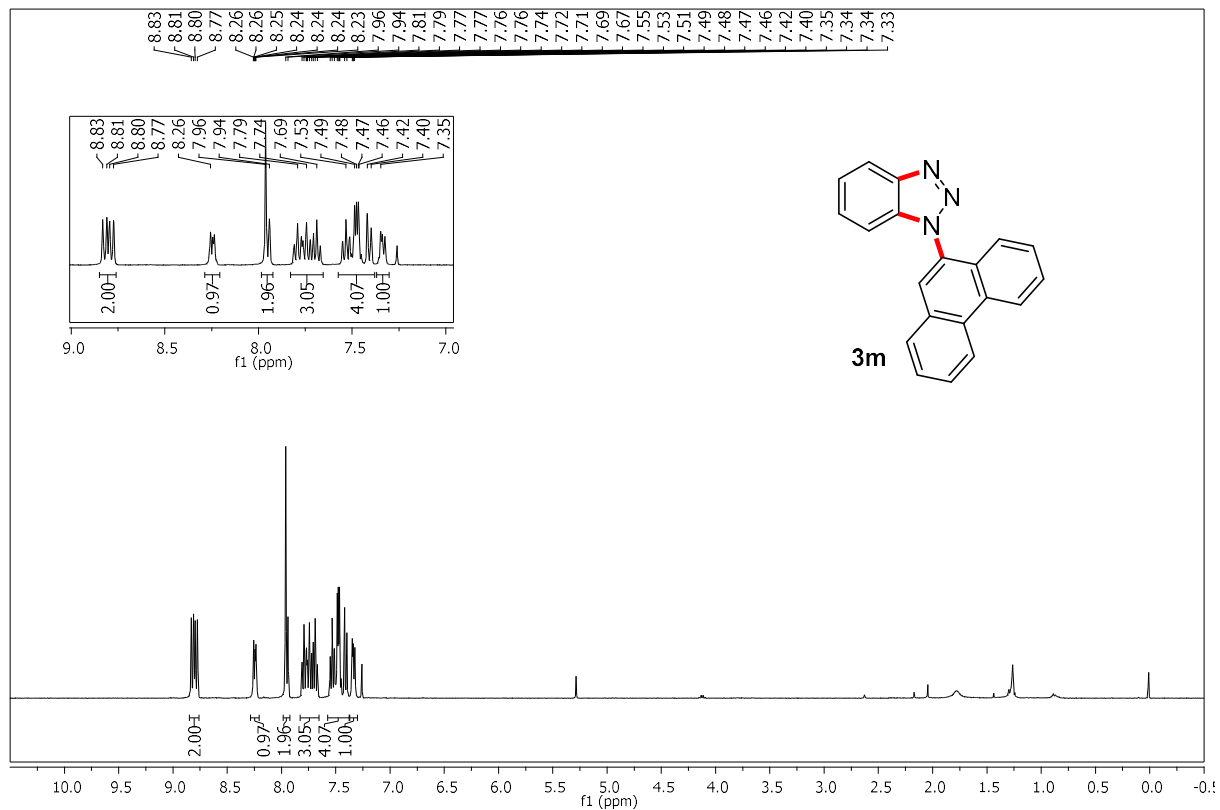
1-(2,5-dimethylphenyl)-1H-benzo[d][1,2,3]triazole (3k)



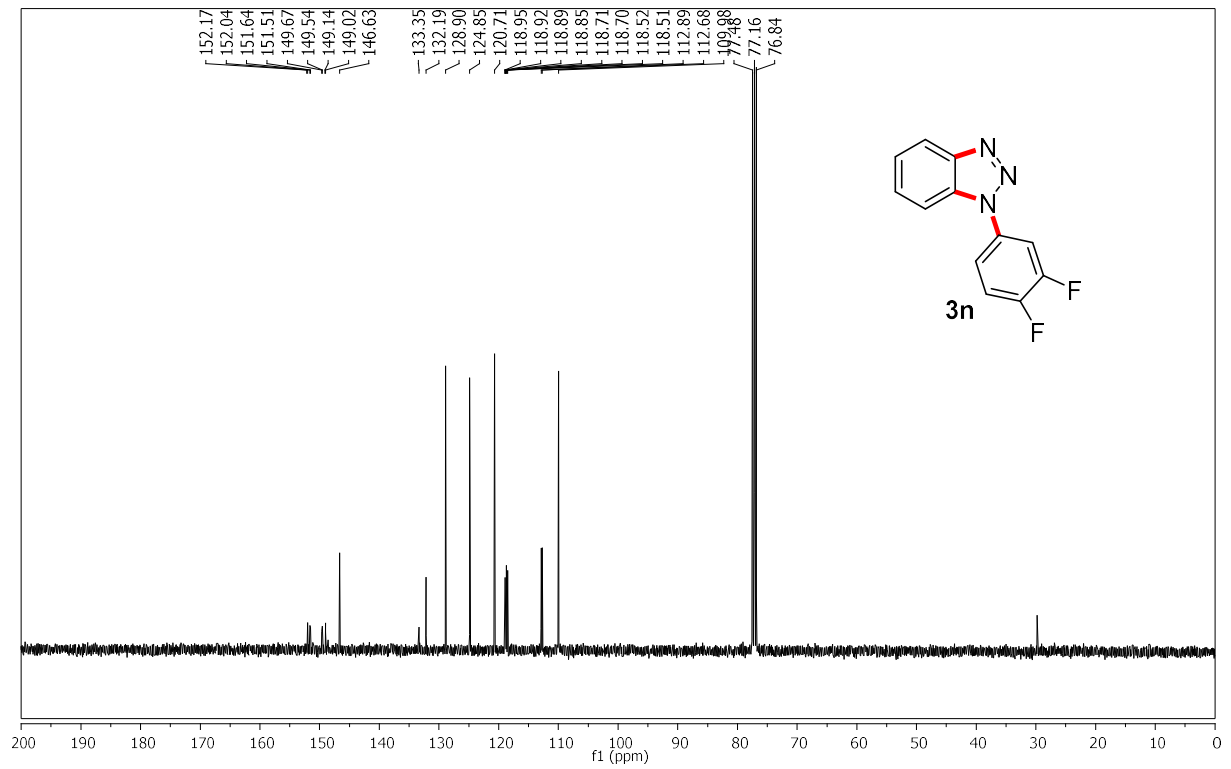
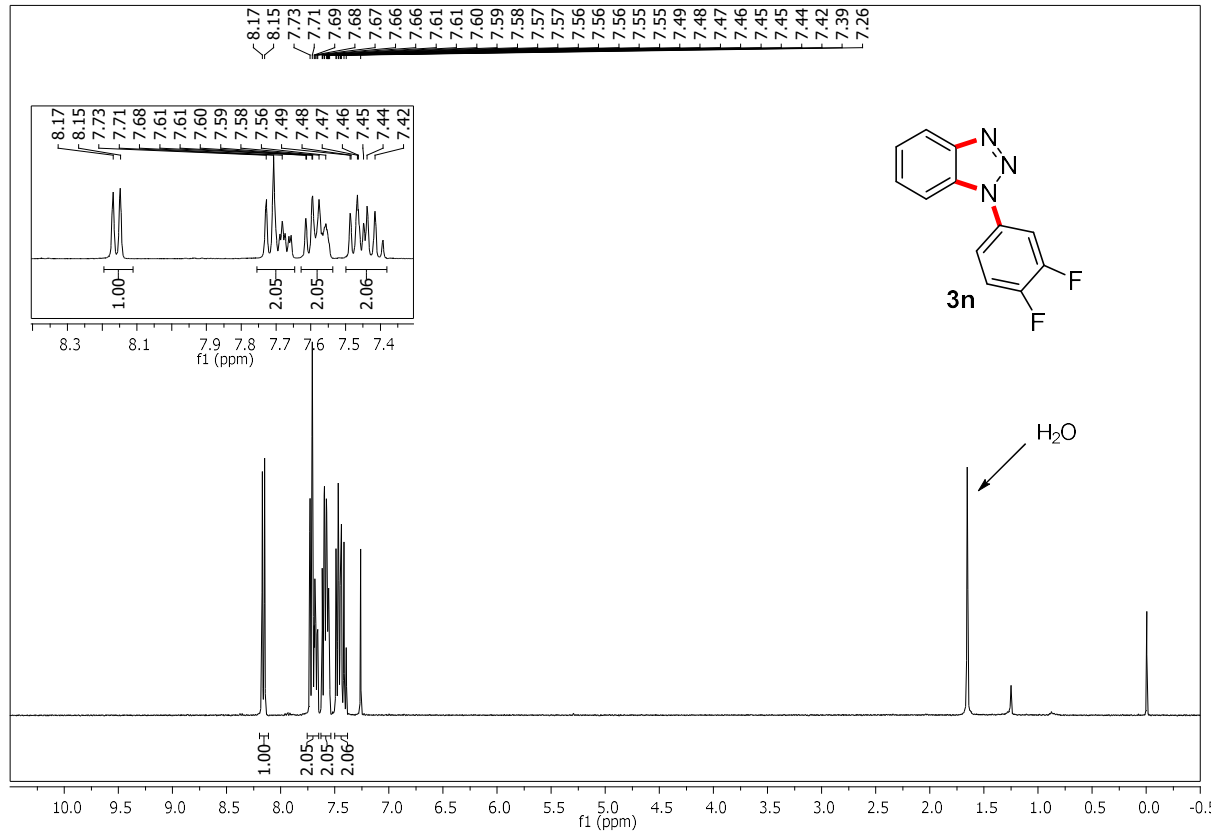
1-(Naphthalen-2-yl)-1H-benzo[d][1,2,3]triazole (31)



1-(Phenanthren-9-yl)-1H-benzo[d][1,2,3]triazole (3m)



1-(3,4-Difluorophenyl)-1H-benzo[d][1,2,3]triazole (3n)



2-Phenyl-2H-benzo[d][1,2,3]triazole (4a)

