

Room-Temperature and Transition-Metal-Free Mizoroki–Heck-type Reaction. Synthesis of *E*-Stilbenes by Photoinduced C–H Functionalization

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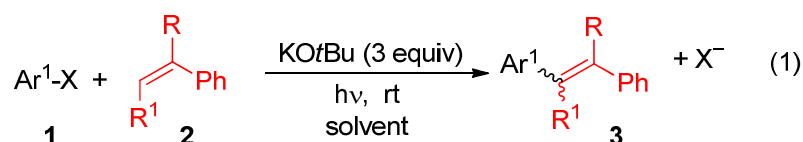
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METHOD A

Photostimulated reaction of Ar¹X (1a-k) with alkene (2a-d) in DMSO.

We examined the substrate scope for this transformation eq 1, and optimized the reaction condition to different haloarenes. The results obtained are shown in S-Table 1.



S-Table 1: Photostimulated reaction of substituted Ar¹X (1) with 2 in DMSO or DMF.^a

Ent	Substrate (Subs. Recovered) ^b	Condition (Alkene 2a-c , Time (h), solvent, additive)	Yield of 3 (yield of <i>E</i> - 3) ^b	X ⁻ (%) ^c
1	1a , 4-iodoanisole (4)	5 equiv 2a , 1.5 h, 1 mL DMSO	3-aa 67 (61)	86
2	1a	10 equiv 2a , 1.5 h, 1 mL DMSO	3-aa 66 (57)	90
3	1a	5 equiv 2a , 1.5 h, 1 mL DMSO, 1 equiv base	3-aa 30 (21)	52
4	1a	5 equiv 2a , 3 h, 1 mL DMSO, 1.2 equiv base	3-aa 46 (30)	60
5	1a (39)	10 equiv 2a , 1.5 h, 0.5 mL DMSO	3-aa 33 (30)	58
6	1a (62)	5 equiv 2a , 1.5 h, 1 mL DMSO, 30% mol <i>m</i> -DNB	3-aa 8 (7)	36
7	1a	10 equiv 2a , 1.5 h, 1 mL DMSO, dark	3-aa 17 (16)	27
8	1a	5 equiv 2a , 2 h, 1 mL DMSO, 3 equiv of cyclohexenone ^d	3-aa 14 (9)	97
9	1a	5 equiv 2a , 2 h, 1 mL pyridine	3-aa --	6
10	1a	5 equiv 2a , 2 h, 1 mL dioxane	3-aa --	5
11	1a	5 equiv 2a , 2 h, 1 mL THF	3-aa --	<4
12	1a	5 equiv 2a , 2 h, 1 mL dimethoxyethane	3-aa --	15
13	1a	10 equiv 2a , 2 h, 1 mL DMSO/2 mL benzene	3-aa 47 (37)	67
14	1a	5 equiv 2a , 1.5 h, 0.5 mL DMF	3-aa 48 (41)	58
15	1a	5 equiv 2a , 1.5 h, 1 mL DMF	3-aa 35 (30)	44
16	1a	5 equiv 2a , 5 h, 1 mL DMF	3-aa 64 (51)	81
17	1a	5 equiv 2a , 3 h, 1.5 mL DMF	3-aa 56 (41)	90
18	1b , 4-iodotoluene	5 equiv 2a , 1.5 h, 1 mL DMSO	3-ba (74)	89
19	1b	5 equiv 2a , 2 h, 1 mL DMSO, 1.2 equiv base	3-ba 58 (55)	72
20	1b	5 equiv 2a , 3 h, 1 mL DMF	3-ba (51)	79
21	1b	5 equiv 2a , 5 h, 1 mL DMF	3-ba (50)	92
22	1b	5 equiv 2a , 5 h, 1 mL DMF, 20% mol EtOH	3-ba (35)	83
23	1c , iodobenzene	5 equiv 2a , 2 h, 1 mL DMSO	3-ca 63 (59)	94
24	1c	10 equiv 2a , 1 h, 1 mL DMSO	3-ca (83)	90
25	1c	5 equiv 2a , 5 h, 1 mL DMF	3-ca 23 (19)	52
26	1d , 2-iodoanisole	5 equiv 2a , 5 h, 1 mL DMSO	3-da (25)	97
27	1e , 2-iodotoluene	5 equiv 2a , 2.5 h, 1 mL DMSO	3-ea 80 (73)	100
28	1f-1 , 4-iodobiphenyl	5 equiv 2a , 2 h, 1 mL DMSO	3-fa (53)	92

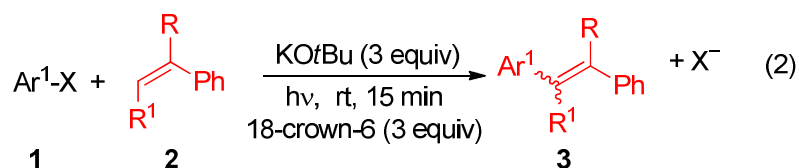
29	1f-1	5 equiv 2a , 5 h, 1 mL DMF	3-fa (43)	83
30	1g , 4-F-C ₆ H ₄ I	5 equiv 2a , 2 h, 1 mL DMSO	3-ga 50 (48)	98
31	1h , 4-CF ₃ -C ₆ H ₄ I	5 equiv 2a , 1.5 h, 1 mL DMSO	3-ha (24)	98
32	1i-1 , 1-IC ₁₀ H ₇	5 equiv 2a , 2 h, 1 mL DMSO	3-ia 51 (47)	94
33	1j , 2-bromonaphthalene	5 equiv 2a , 2.5 h, 1 mL DMSO	3-ja (26)	94
34	1j	5 equiv 2a , 5 h, 1 mL DMF	3-ja 53 (26)	84
35	1k , 6-chloroquinoline	5 equiv 2a , 1.5 h, 1 mL DMSO	3-ka (10)	75
36	1c	5 equiv 2b , 2 h, 1 mL DMSO ^e	3-cb (–)	–
37	1c	5 equiv 2b , 2 h, 1 mL Dioxane	3-cb (–)	–
38	1c	5 equiv 2b , 5 h, 1 mL DMF	3-cb (20)	31
39	1b	5 equiv 2c , 2 h, 1 mL DMSO	3-bc (27)	86
40	1b	5 equiv 2d , 2 h, 1 mL DMSO	3-bd (25)	78
41	1b	5 equiv 2d , 5 h, 1 mL DMF	3-bd (20)	35
42	1a	5 equiv 2c , 2 h, 1 mL DMSO	3-ad 26	86

^aThe reactions were performed out under a nitrogen atmosphere using ArX (**1a-1k**, 1 equiv, 0.5 mmol), KOtBu (3 equiv), solvent and alkene **2a-d** in a sealed tube. Irradiation was conducted in a photochemical reactor equipped with two HPI-T 400 W lamps (cooled with water). ^bDetermined by GC (internal standard method). ^cHalide anions were determined potentiometrically. ^dCyclohexenone anion was used as a base. ^eThe addition of dimslyl anion to alkene is observed.

METHOD B

Photostimulated reaction of ArX (**1a-k**) with alkene (**2a**) and 18-crown-6 ether (**18-C-6**):

We examined the substrate scope for this transformation eq 2, and optimized the reaction condition to different Ar¹X. The results obtained are shown in S-Table 2.



S-Table 2: Photostimulated Reaction of Substituted Ar¹X (**1**) with **2** and 18-crown-6 ether (without solvent).^a

Ent	Substrate (Subs. Recovered) ^b	Condition (Alkene 2a-c , Time (h), additive)	Yield of 3 (yield of <i>E</i> - 3) ^b	X [–] (%) ^c
1	1a , 4-iodoanisole	5 equiv 2a , 2 h, without 18-crown-6	3-aa –	6
2	1a	5 equiv 2a , 2 h	3-aa 76 (72)	94
3	1a	5 equiv 2a , 2 h, 1.5 equiv base and crown	3-aa 64 (51)	76
4	1a	5 equiv 2a , 2 h, dark	3-aa 67 (66)	68
5	1a	5 equiv 2a , 45 min	3-aa 76 (73)	79
6	1a	5 equiv 2a , 15 min	3-aa 73 (71)	80

7	1a	10 equiv 2a , 15 min	3-aa 90 (87)	95
8	1a	10 equiv 2a , 15 min, dark	3-aa (59)	66
9	1a	10 equiv 2a , 15 min, dark, 30 % mol TEMPO	3-aa --	24
10	1a	10 equiv 2a , 15 min, dark, 30 % mol <i>m</i> -DNB	3-aa --	11
11 ^d	1a	10 equiv 2a , 15 min, 3 equiv dyglime	3-aa --	<4
12 ^d	1a	10 equiv 2a , 15 min, 3 equiv 1,10 Phen	3-aa --	<4
13	1b , 4-iodotoluene	10 equiv 2a , 15 min	3-ba 45 (44)	82
14	1b	10 equiv 2a , 15 min, 1.5 equiv KOTBu and 1.5 equiv 18-crown6	3-ba 45 (44)	67
15 ^d	1b	10 equiv 2a , 15 min, 3 equiv dyglime	3-ba --	<4
16 ^d	1b	10 equiv 2a , 15 min, 3 equiv 1,10 Phen	3-ba --	<4
17 ^d	1b	10 equiv 2a , 15 min, 3 equiv DMEDA	3-ba --	<4
18	1b	10 equiv 2a , 15 min, 3 equiv KOH as base	3-ba --	<4
19	1b	10 equiv 2a , 15 min, 1.5 equiv KOTBu and 1.5 equiv 18-crown-6 in benzene (1 mL)	3-ba (60)	66
20	1b	10 equiv 2a , 1 h, 1.5 equiv KOTBu and 3 equiv, 18-crown-6 in benzene (1 mL)	3-ba (64)	70
21	1b	10 equiv 2a , 1 h, 3 equiv KOTBu and 3 equiv 18-crown-6 in benzene (1 mL)	3-ba (63)	93
22	1c , iodobenzene	10 equiv 2a , 15 min	3-ca 80 (79)	82
23	1d , 2-iodoanisole	10 equiv 2a , 30 min	3-da 78 (64)	84
24	1e , 2-iodotoluene	10 equiv 2a , 15 min	3-ea (55)	78
26	1f-1 , 4-IC ₆ H ₄ Ph	10 equiv 2a , 15 min	3-fa (71)	98
27	1f-2 , 4-BrC ₆ H ₄ Ph	10 equiv 2a , 15 min	3-fa (65)	92
28	1g , 4-F-C ₆ H ₄ I	10 equiv 2a , 15 min	3-ga (46)	93
29	1h , 4-CF ₃ -C ₆ H ₄ I	10 equiv 2a , 30 min	3-ha (30)	80
30	1h , 4-CF ₃ -C ₆ H ₄ I	10 equiv 2a , 30 min, benzene (1 mL)	3-ha (32)	92
31	1i-1 , 1-IC ₁₀ H ₇	10 equiv 2a , 15 min	3-ia (54)	91
32	1i-2 , 1-BrC ₁₀ H ₇	10 equiv 2a , 15 min	3-ia 67 (62)	99
33	1i-3 , 1-ClC ₁₀ H ₇	10 equiv 2a , 15 min	3-ia (71)	94
34	1j , 2-BrC ₁₀ H ₇	5 equiv 2a , 2 h	3-ja 73 (63)	92
35	1j	10 equiv 2a , 15 min	3-ja (75)	95
36	1j-3 , 1-ClC ₁₀ H ₇	10 equiv 2a , 1 h	3-ja (71)	94
37	1k , 6-chloroquinol.	10 equiv 2a , 1 h	3-ka (53)	84
38	1c	10 equiv 2b , 15 min	3-cb (58)	61
39	1c	10 equiv 2b , 45 min	3-cb (60)	85
40	1c	10 equiv 2b , 2 h	3-cb (69)	75
41	1b	10 equiv 2c , 1 h	3-bc 25	92
42	1b	10 equiv 2d , 1 h	3-bd 22	91
43	1a	10 equiv 2d , 15 min	3-ad (82)	97

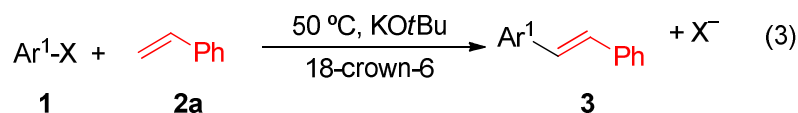
^aThe reactions were performed out under a nitrogen atmosphere using ArX (**1a-k**, 1 equiv, 0.5 mmol), KOTBu (3 equiv), 18-C-6 (3 equiv) and alkene **2a-d** in a sealed tube. Irradiation was conducted in a photochemical reactor equipped with two HPI-T 400 W lamps (cooled with water).

^bDetermined by GC (internal standard method). ^cHalide anions were determined potentiometrically. ^dThe reactions were carried out without 18-C-6.

METHOD C

Reaction of Ar¹X, styrene and 18-crown-6 ether with conventional heating (CH).

We examined the substrate scope for this transformation eq 3, and optimized the reaction condition to different Ar¹X. The results obtained are shown in S-Table 3.

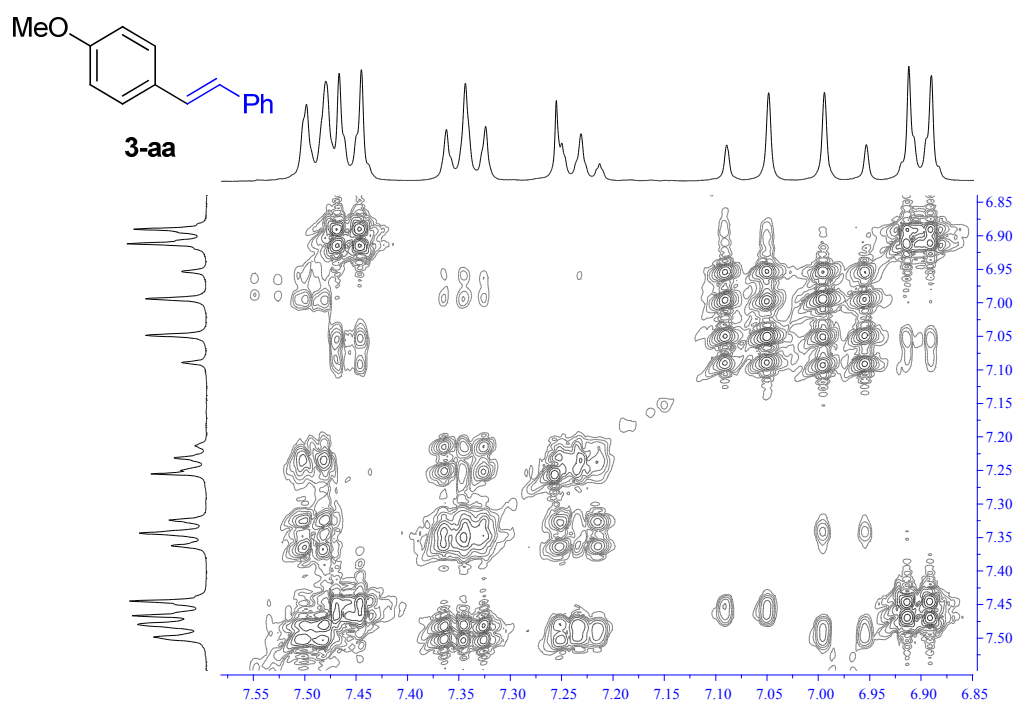


S-Table 3: Reaction of substituted Ar¹X (**1**) with **2a** and 18-crown-6 ether with conventional heating.^a

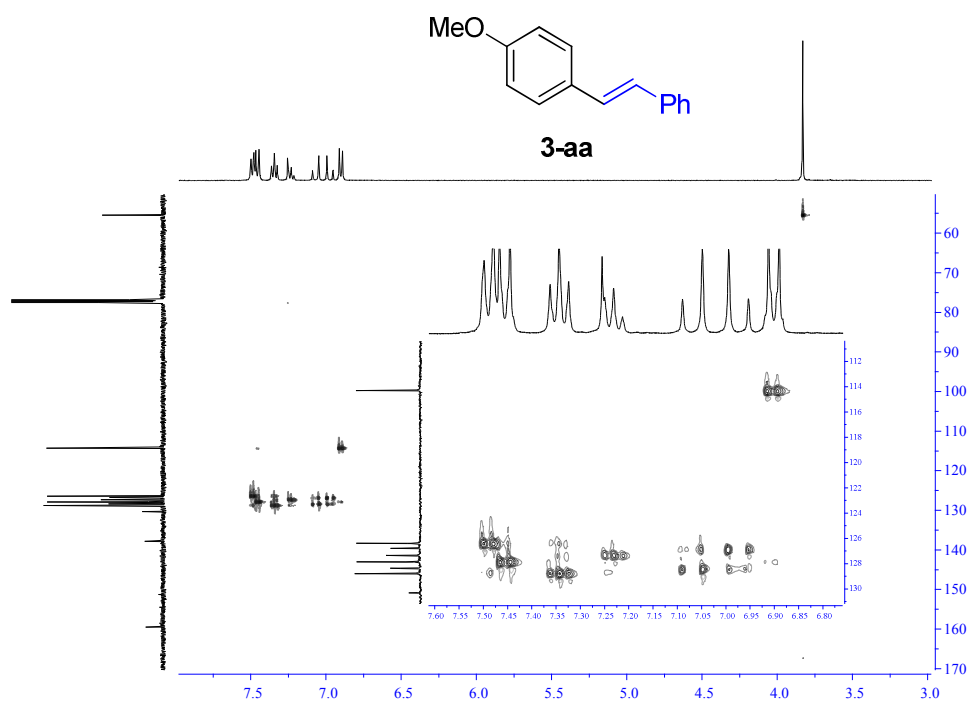
Ent	Substrate (Subs. Recovered) ^b	Condition (2a , Time (min), KOtBu and 18-crown-6)	Product (yield of <i>E</i> - 3) ^b	X ⁻ (%) ^c
1	1c , iodobenzene	10 equiv 2a , 90 min, 3 equiv	3-ca (57)	96
2	1c	10 equiv 2a , 45 min, 3 equiv	3-ca (56)	--
3	1c	10 equiv 2a , 30 min, 3 equiv	3-ca (54)	--
4	1c	10 equiv 2a , 15 min, 3 equiv	3-ca (52)	96
5	1c	20 equiv 2a , 30 min, 3 equiv	3-ca (41)	70
6	1c	10 equiv 2a , 30 min, 2 equiv	3-ca (20)	50
7	1c	10 equiv 2a , 30 min, 1 equiv	3-ca (7)	22
8	1c	10 equiv 2a , 30 min, 30 % mol TEMPO	3-ca --	<7
9	1a 4-iodoanisole	10 equiv 2a , 15 min, 3 equiv	3-aa (52)	89
10 ^d	1f-1 , 4-IC ₆ H ₄ Ph	10 equiv 2a , 16 h, 3 equiv	3-fa (36)	91
11 ^d	1j , 2-BrC ₁₀ H ₇	10 equiv 2a , 16 h, 3 equiv	3-ja (30)	97

^aThe reactions were performed out under a nitrogen atmosphere using ArX (1 equiv, 0.5 mmol), KOtBu (3 equiv), 18-crown-6 ether (3 equiv) and styrene **2a** in a sealed tube. The reaction was heating at 50 °C. ^bDetermined by GC (internal standard method). ^cHalide anions were determined potentiometrically. ^dThe reaction time was not optimized.

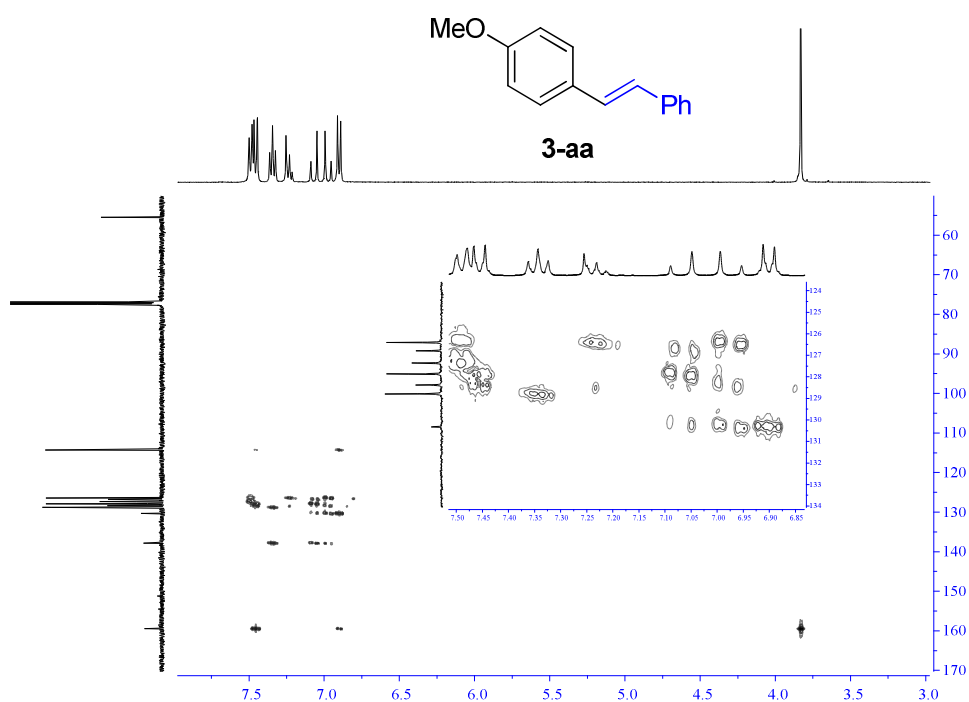
^1H - ^1H COSY NMR (400 MHz, CDCl_3) (*E*)-1-methoxy-4-styrylbenzene (3-aa):



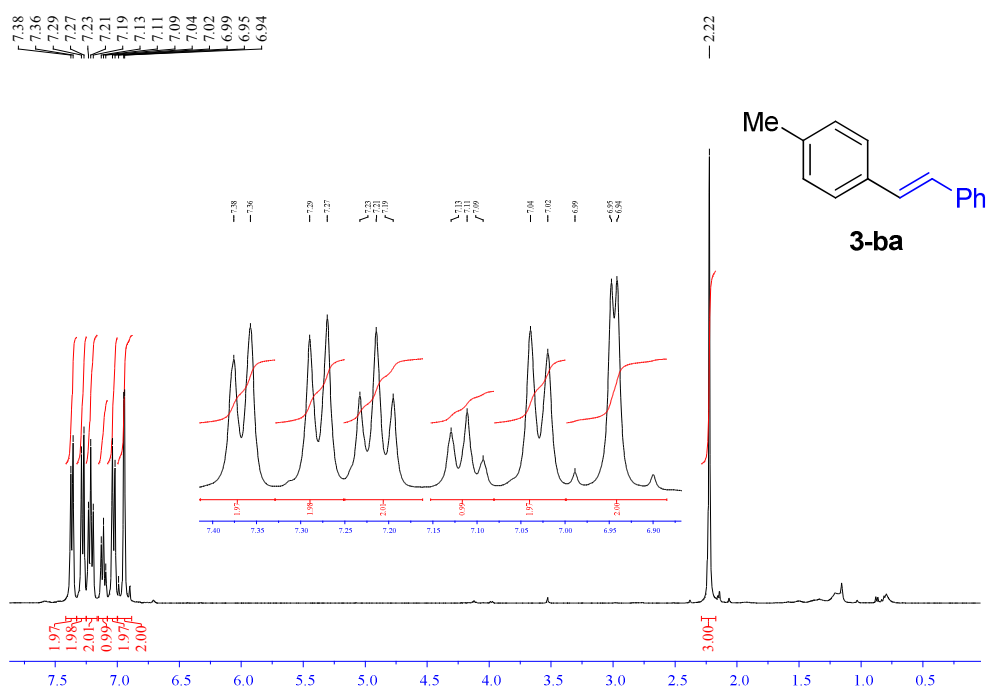
^1H - ^{13}C HSQC NMR (400 MHz, CDCl_3) (*E*)-1-methoxy-4-styrylbenzene (3-aa):

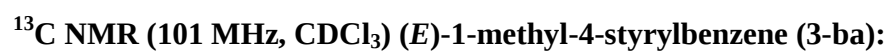


^1H - ^{13}C HMBC NMR (400 MHz, CDCl_3) (*E*)-1-methoxy-4-styrylbenzene (3-aa):

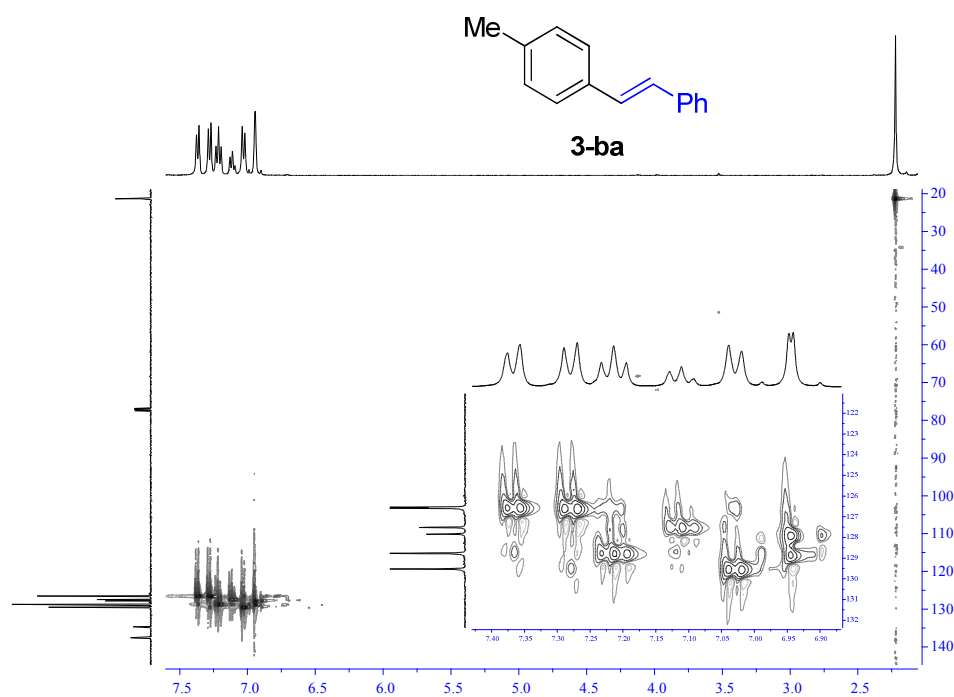


^1H NMR (400 MHz, CDCl_3 , TMS) (*E*)-1-methyl-4-styrylbenzene (3-ba):

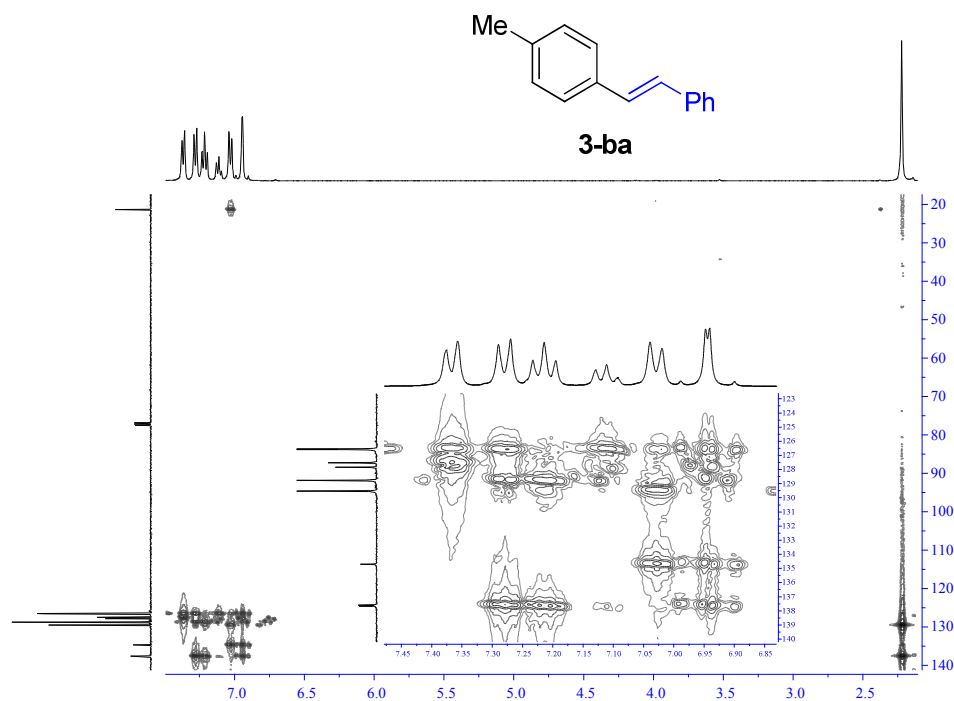


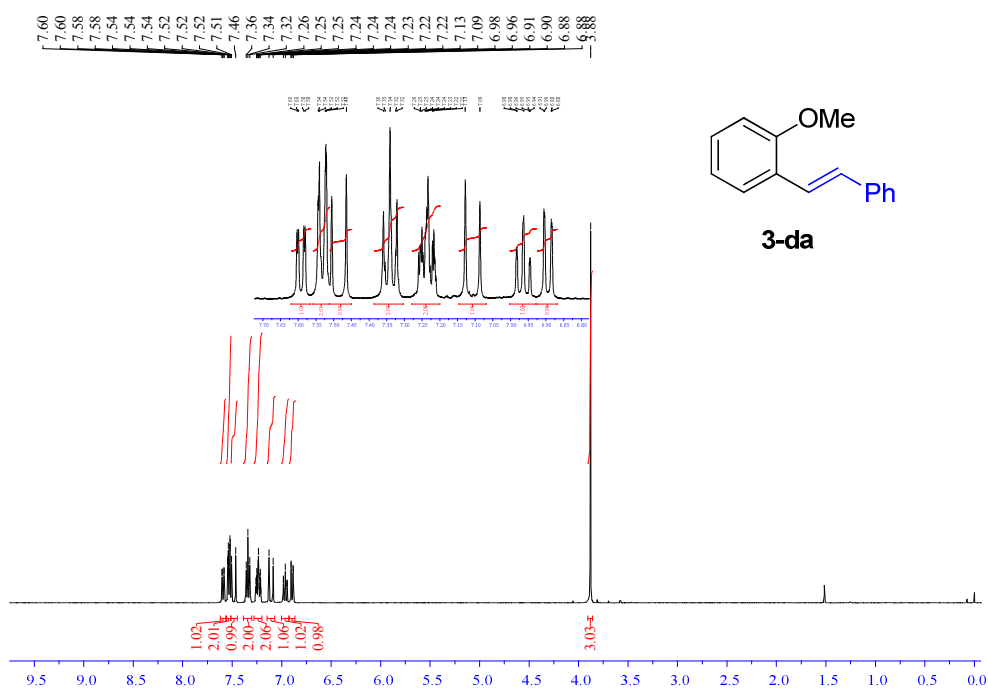
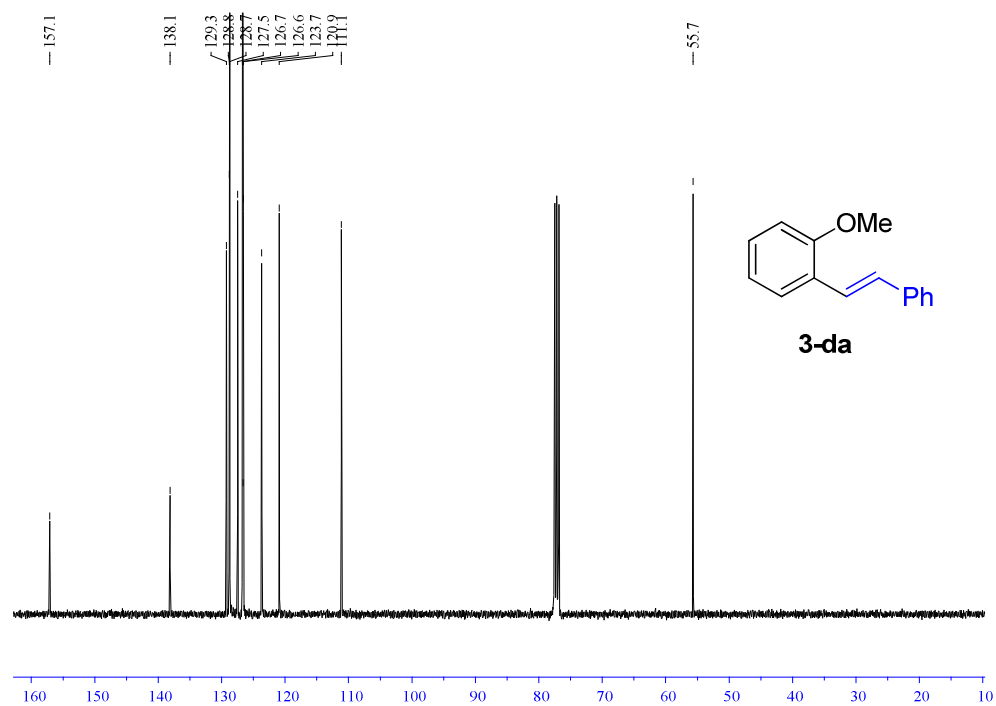


^1H - ^{13}C HSQC NMR (400 MHz, CDCl_3) (*E*)-1-methyl-4-styrylbenzene (3-ba):

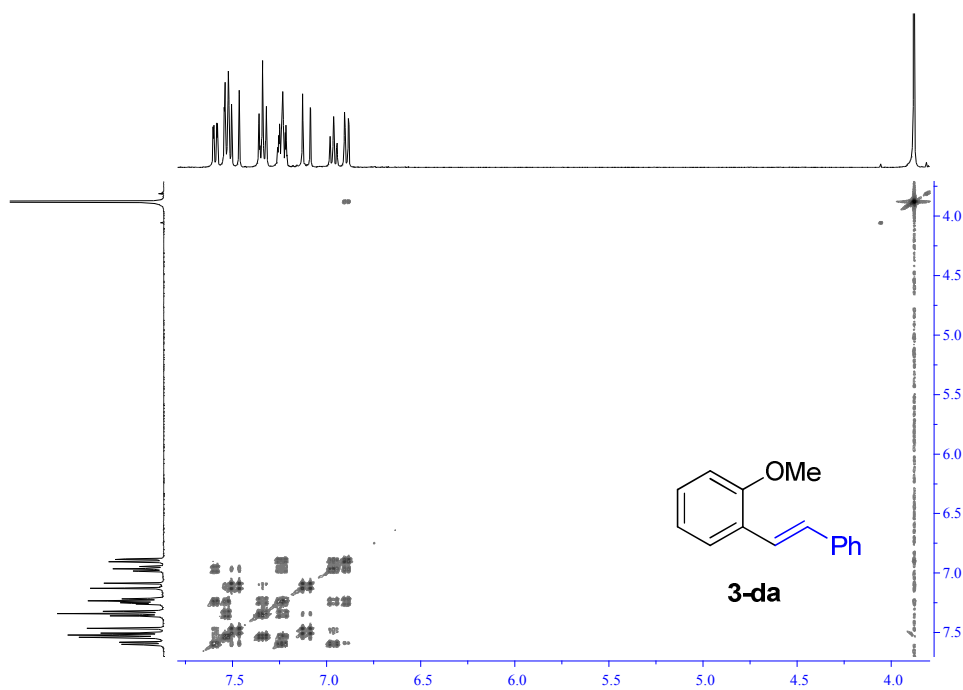


^1H - ^{13}C HMBC NMR (400 MHz, CDCl_3) (*E*)-1-methyl-4-styrylbenzene (3-ba):

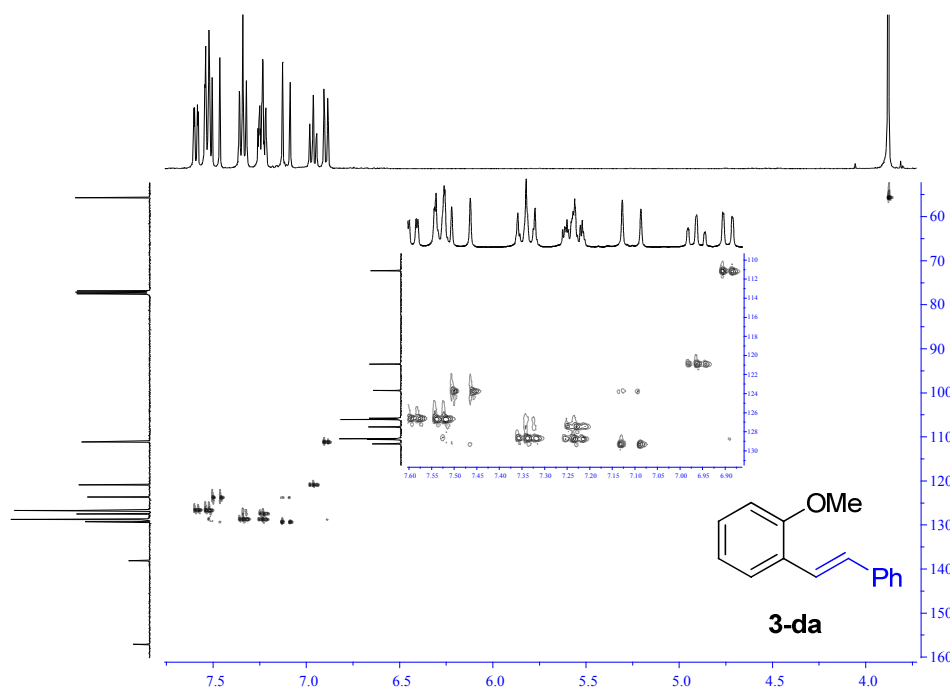


^1H NMR (400 MHz, CDCl_3 , TMS) (*E*)-1-methoxy-2-styrylbenzene (3-da): **^{13}C NMR (101 MHz, CDCl_3) (*E*)-1-methoxy-2-styrylbenzene (3-da):**

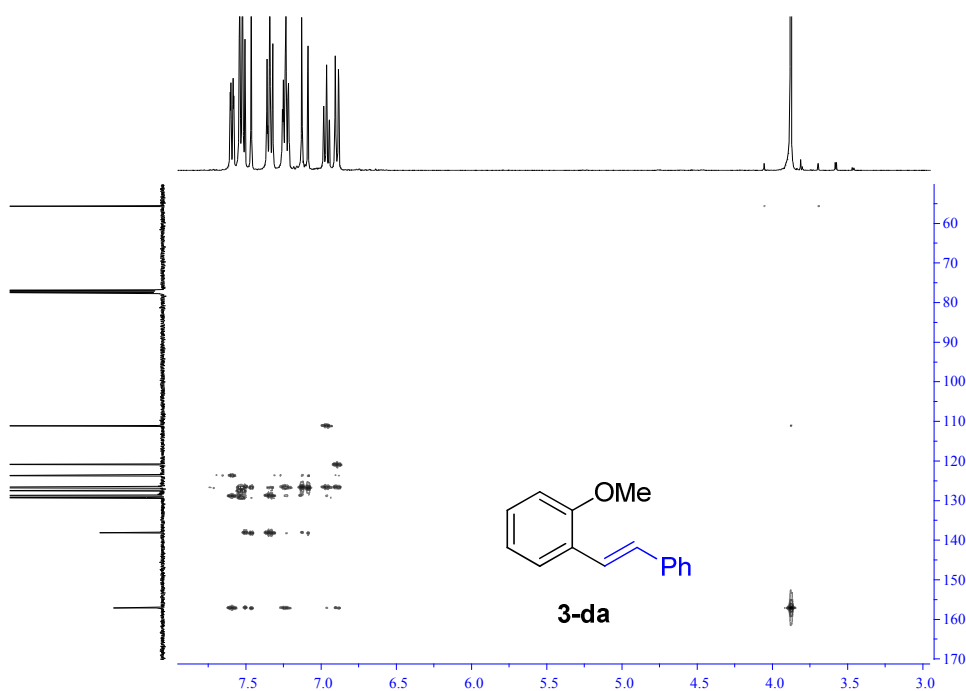
^1H - ^1H COSY NMR (400 MHz, CDCl_3) (*E*)-1-methoxy-2-styrylbenzene (3-da):



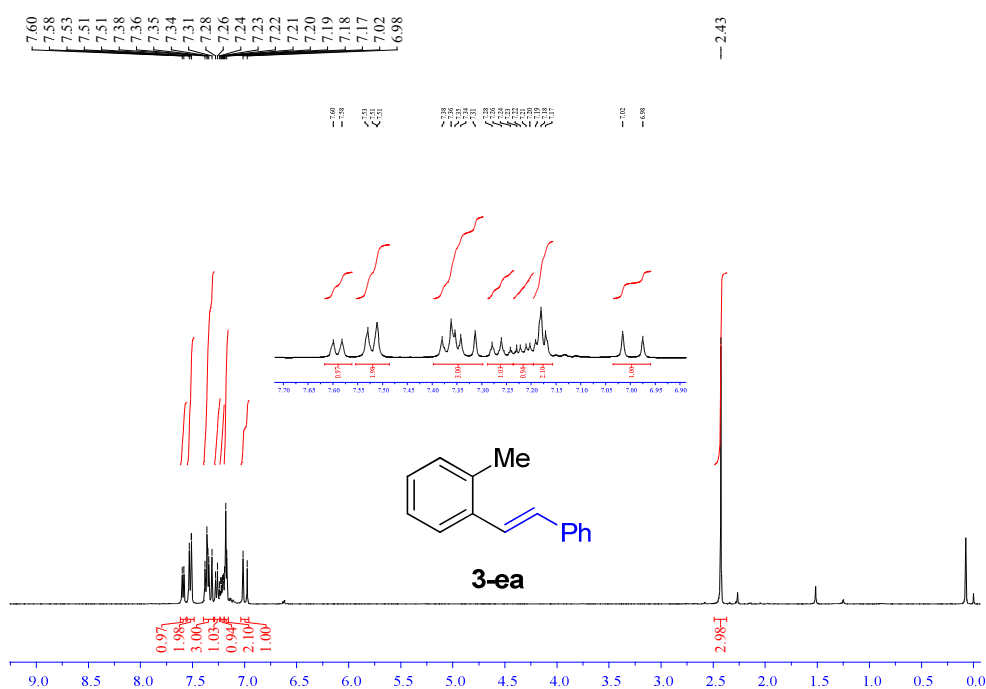
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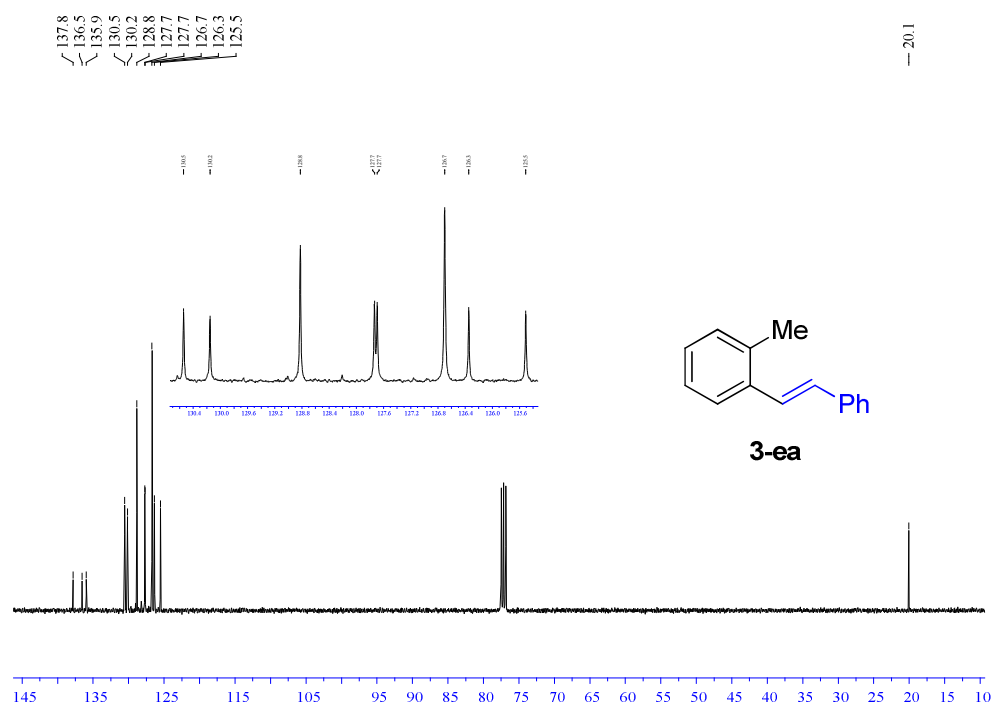
^1H - ^{13}C HMBC NMR (400 MHz, CDCl_3) (*E*)-1-methoxy-2-styrylbenzene (3-da):



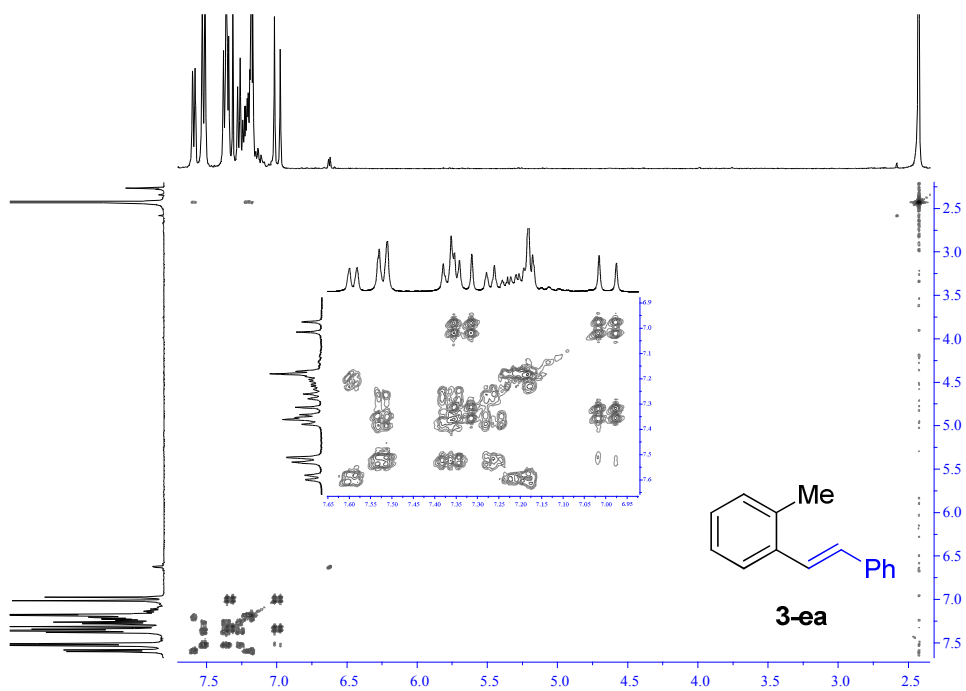
^1H NMR (400 MHz, CDCl_3 , TMS) (*E*)-1-methyl-2-styrylbenzene (3-ea):



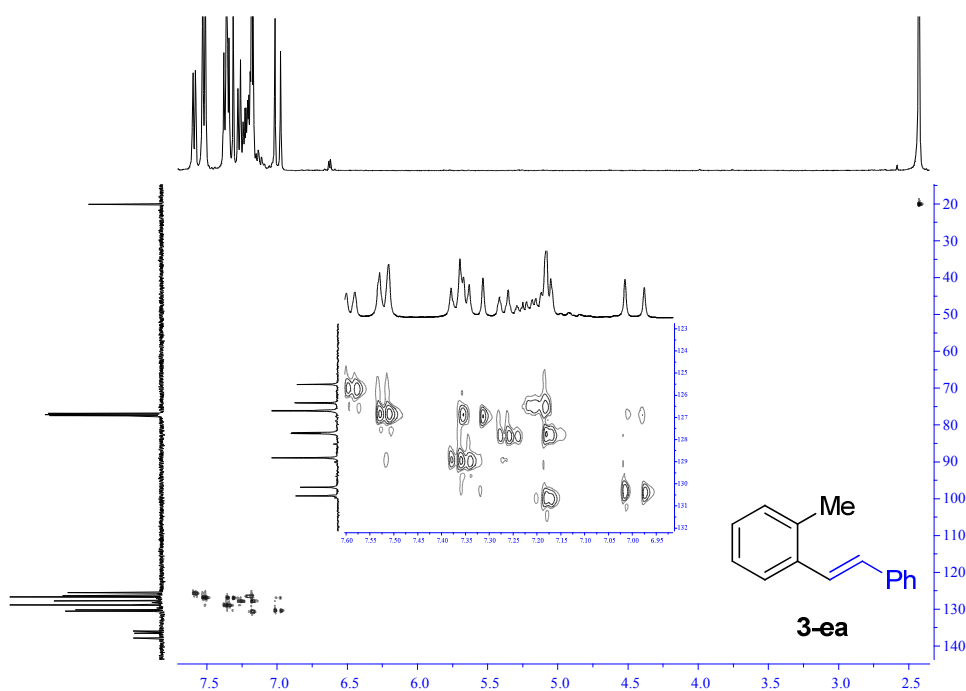
^{13}C NMR (101 MHz, CDCl_3) (*E*)-1-methyl-2-styrylbenzene (3-ea):



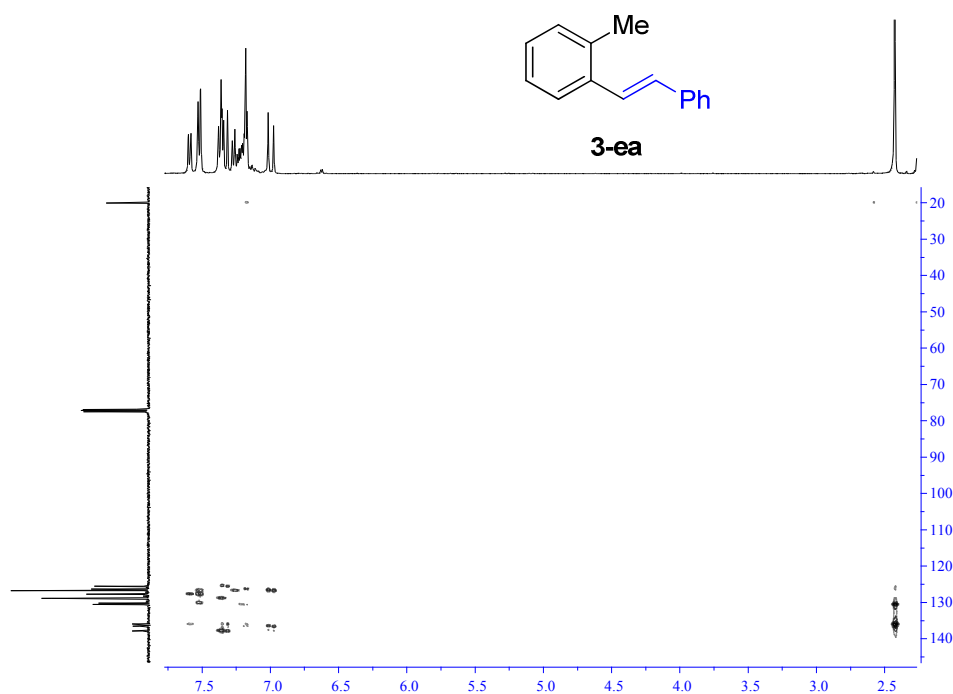
^1H - ^1H COSY NMR (400 MHz, CDCl_3) (*E*)-1-methyl-2-styrylbenzene (3-ea):

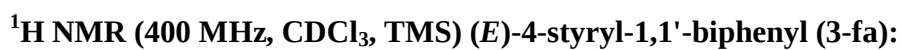


^1H - ^{13}C HSQC NMR (400 MHz, CDCl_3) (*E*)-1-methyl-2-styrylbenzene (3-ea):

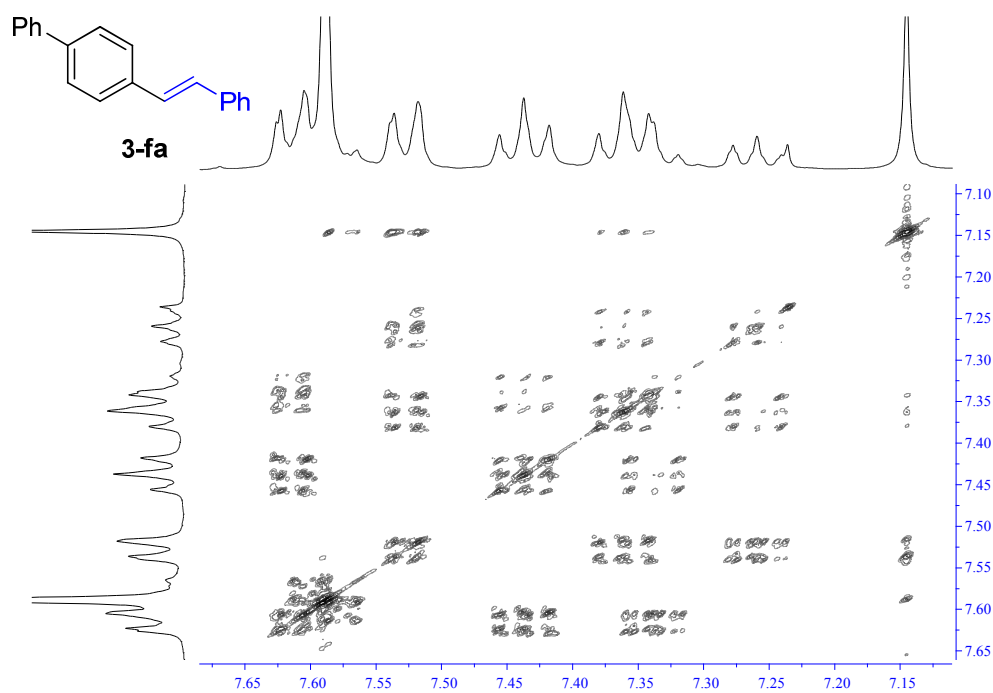


^1H - ^{13}C HMBC NMR (400 MHz, CDCl_3) (*E*)-1-methyl-2-styrylbenzene (3-ea):

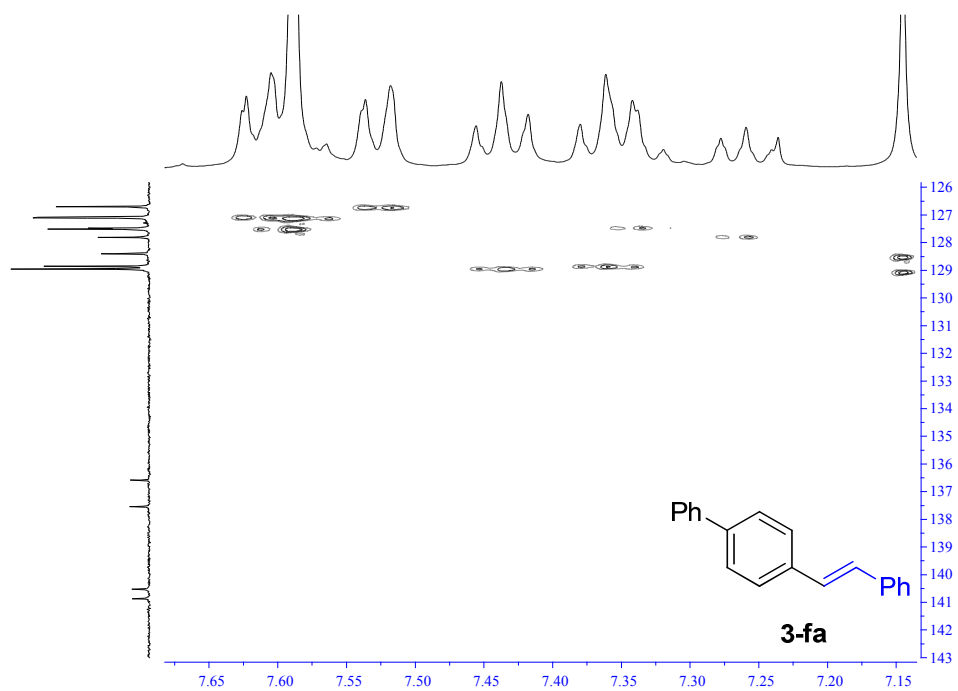




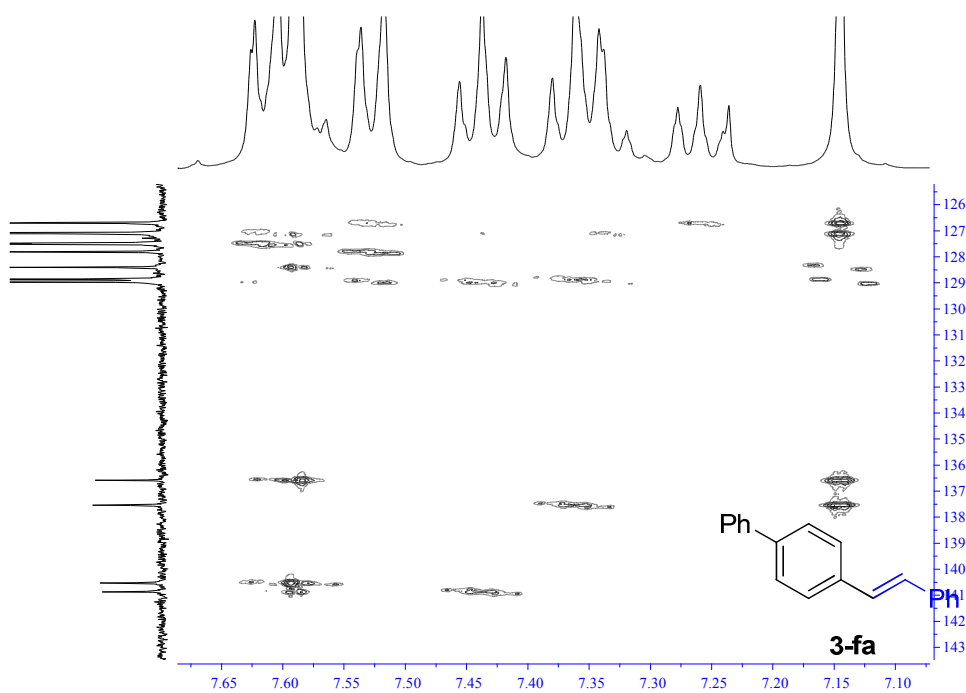
^1H - ^1H COSY NMR (400 MHz, CDCl_3) (*E*)-4-styryl-1,1'-biphenyl (3-fa):



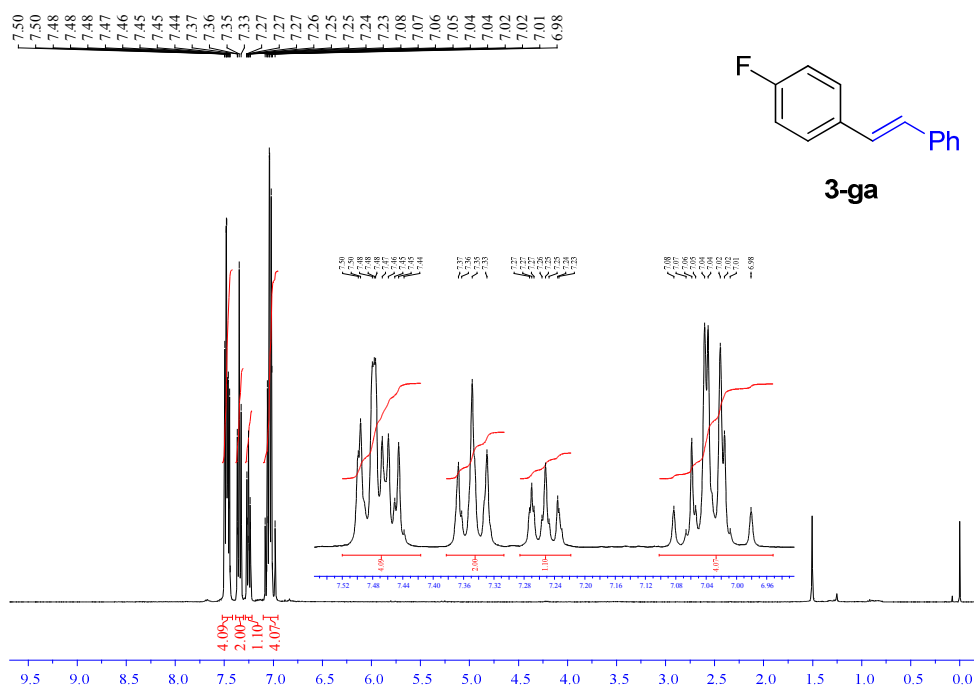
^1H - ^{13}C HSQC NMR (400 MHz, CDCl_3) (*E*)-4-styryl-1,1'-biphenyl (3-fa):



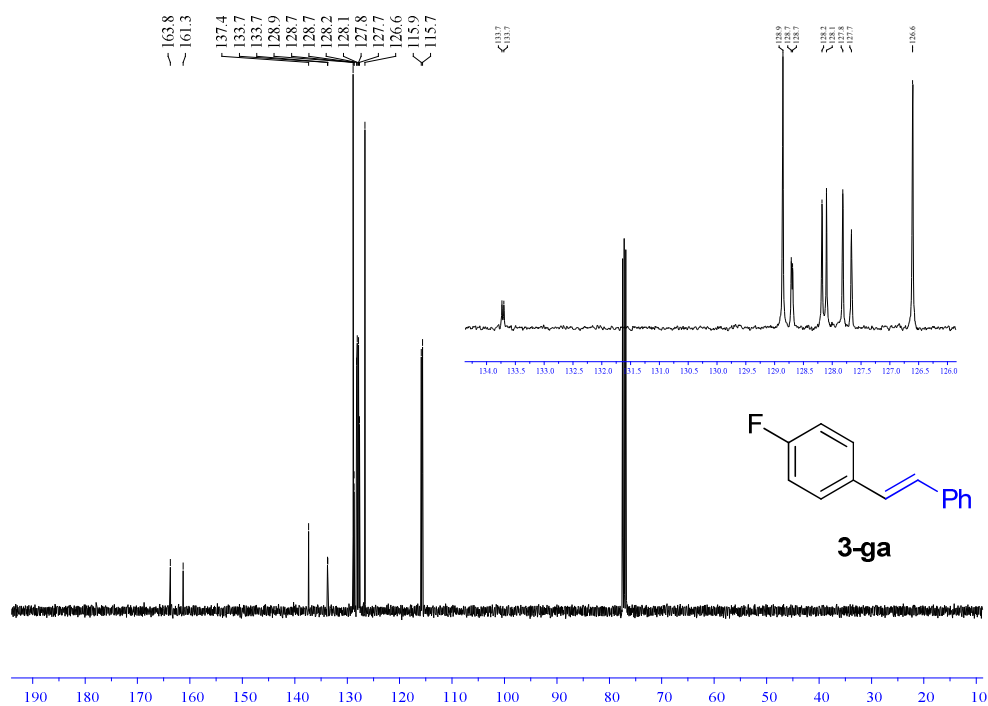
^1H - ^{13}C HMBC NMR (400 MHz, CDCl_3) (*E*)-4-styryl-1,1'-biphenyl (3-fa):



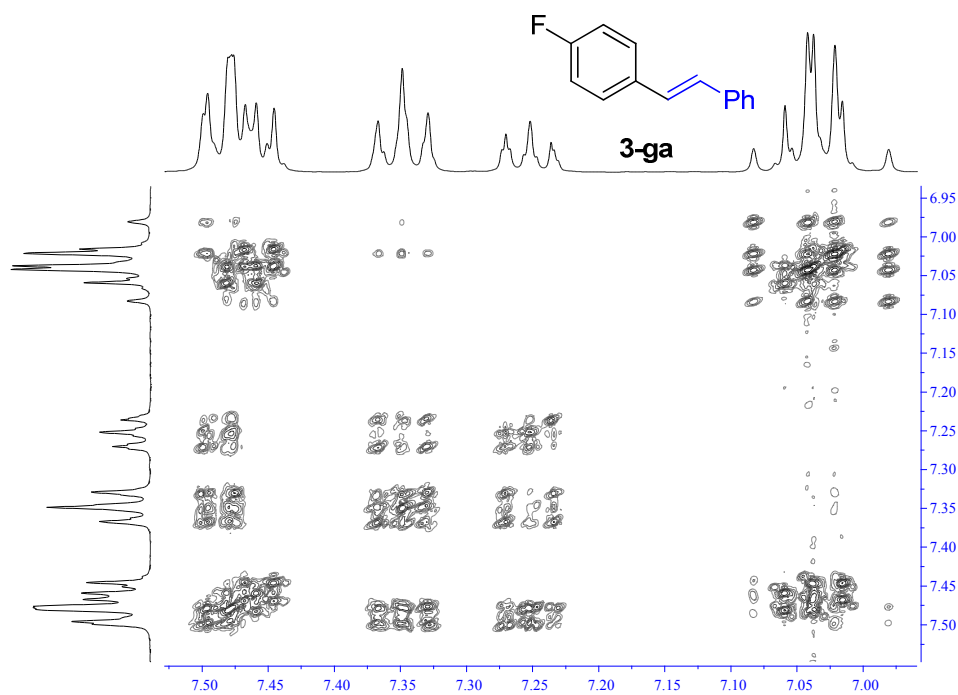
^1H NMR (400 MHz, CDCl_3 , TMS) (*E*)-1-fluoro-4-styrylbenzene (3-ga):



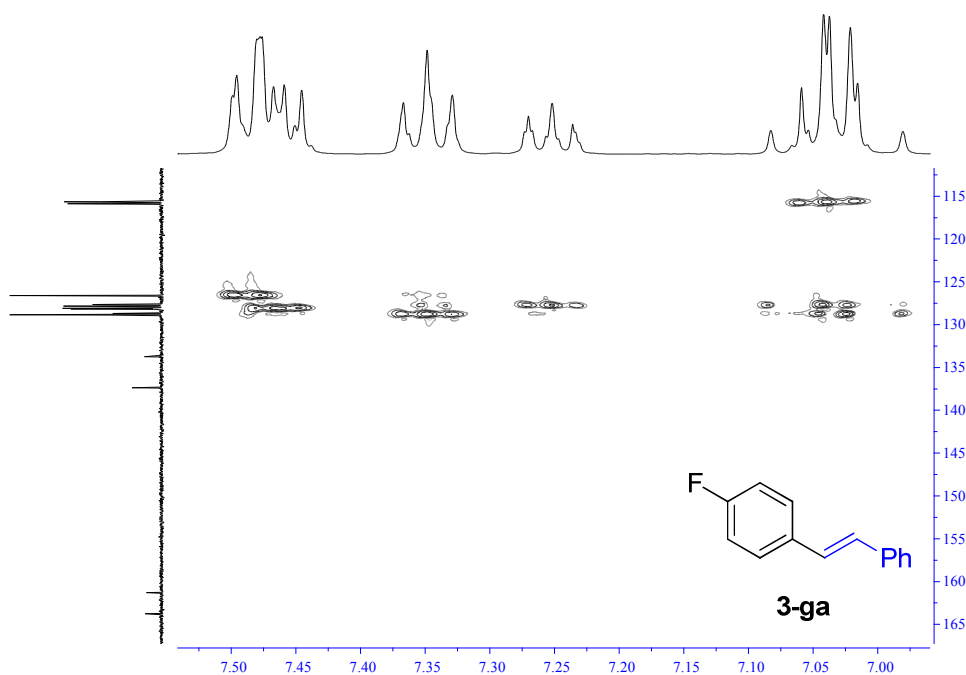
^{13}C NMR (101 MHz, CDCl_3) (*E*)-1-fluoro-4-styrylbenzene (3-ga):



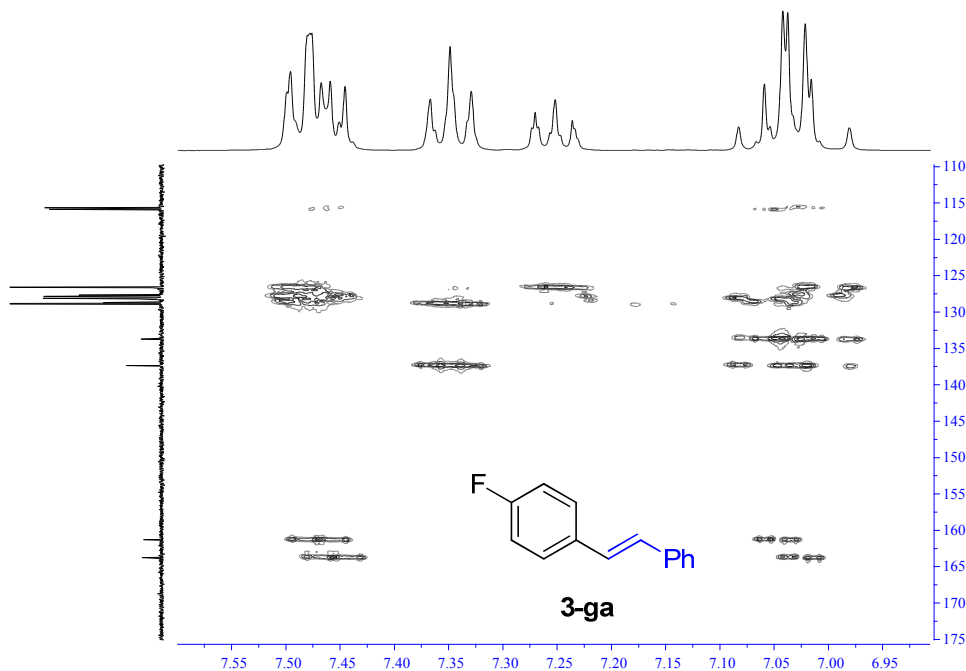
^1H - ^1H COSY NMR (400 MHz, CDCl_3) (*E*)-1-fluoro-4-styrylbenzene (3-ga):



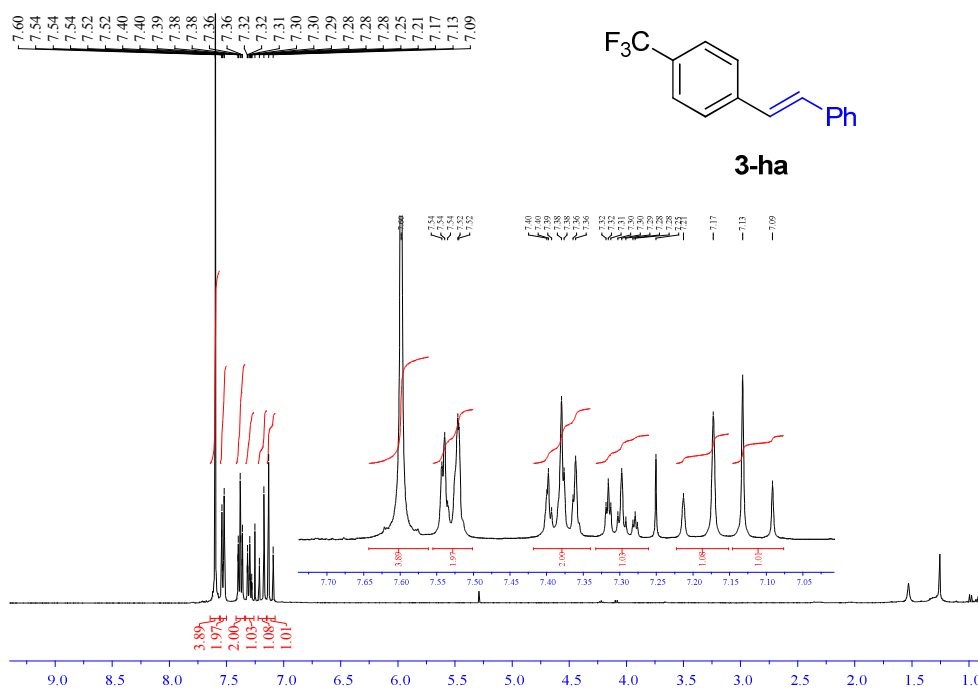
^1H - ^{13}C HSQC NMR (400 MHz, CDCl_3) (*E*)-1-fluoro-4-styrylbenzene (3-ga):



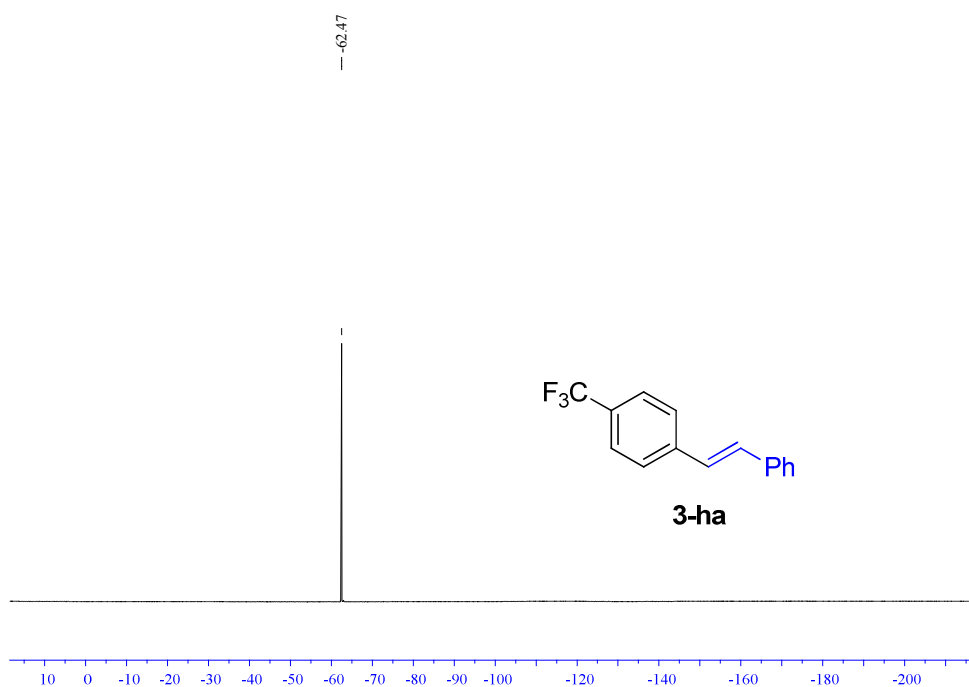
^1H - ^{13}C HMBC NMR (400 MHz, CDCl_3) (*E*)-1-fluoro-4-styrylbenzene (3-ga):

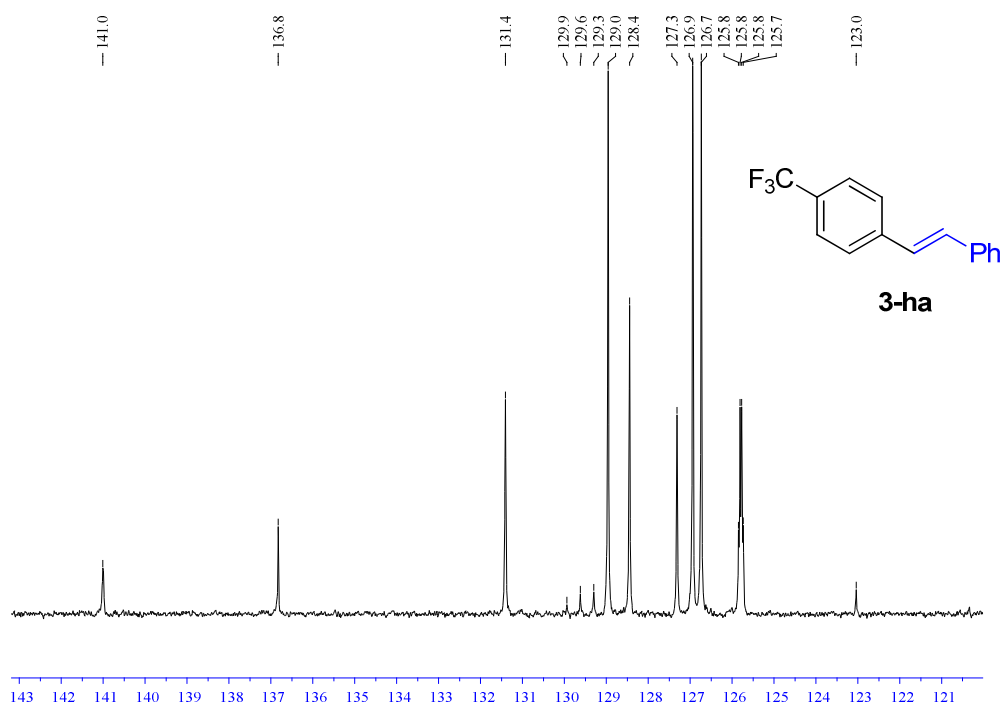
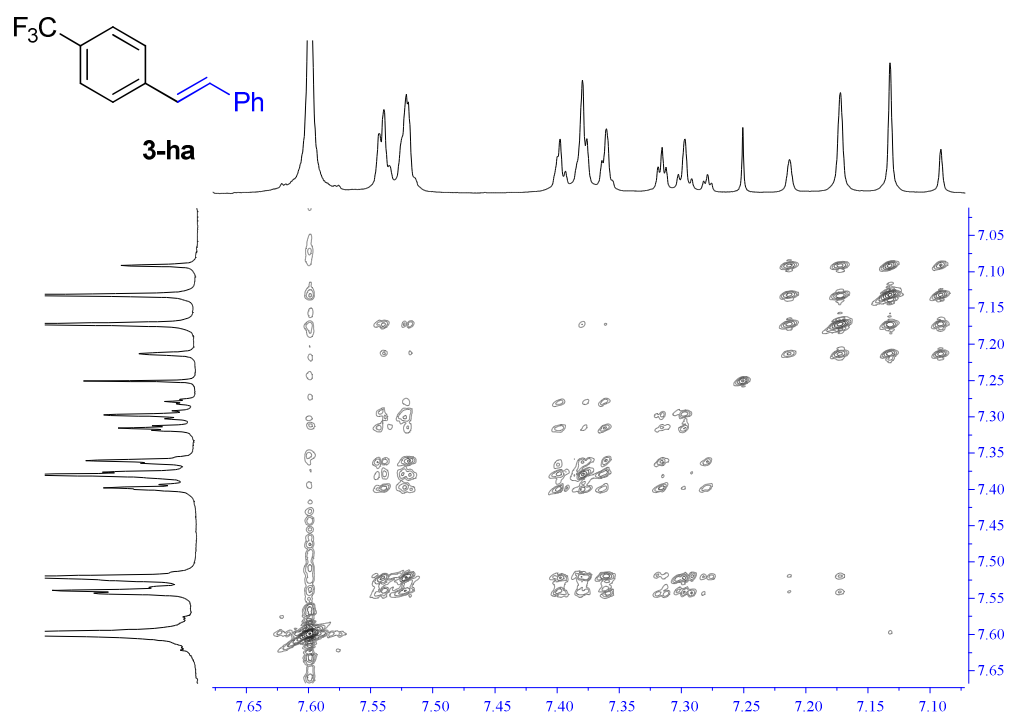


^1H NMR (400 MHz, CDCl_3 , TMS) (*E*)-1-styryl-4-(trifluoromethyl)benzene (3-ha):

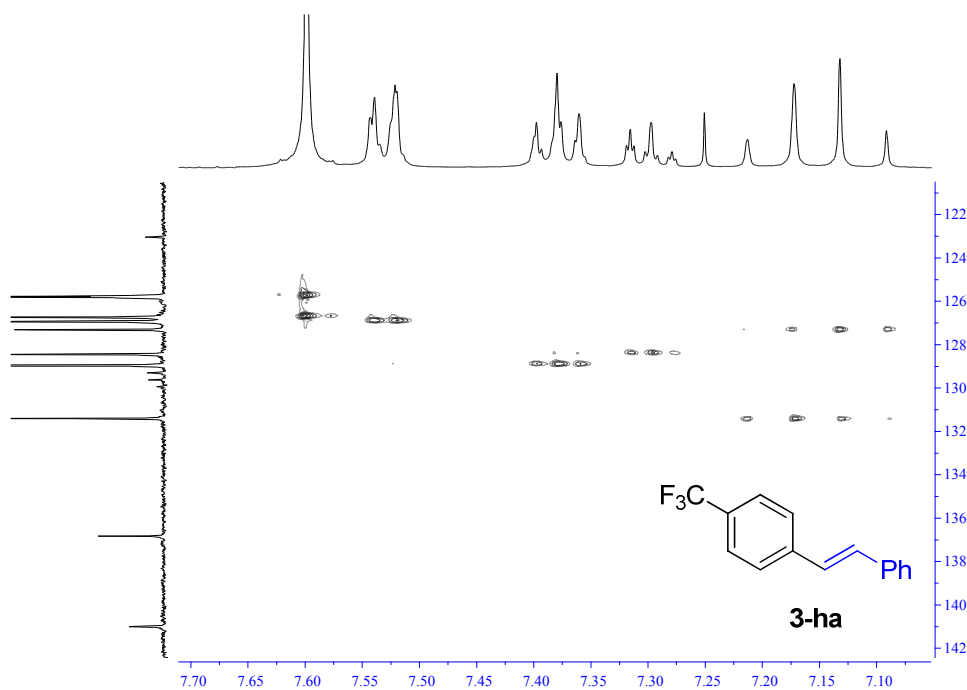


^{19}F NMR (377 MHz, CDCl_3) (*E*)-1-styryl-4-(trifluoromethyl)benzene (3-ha):

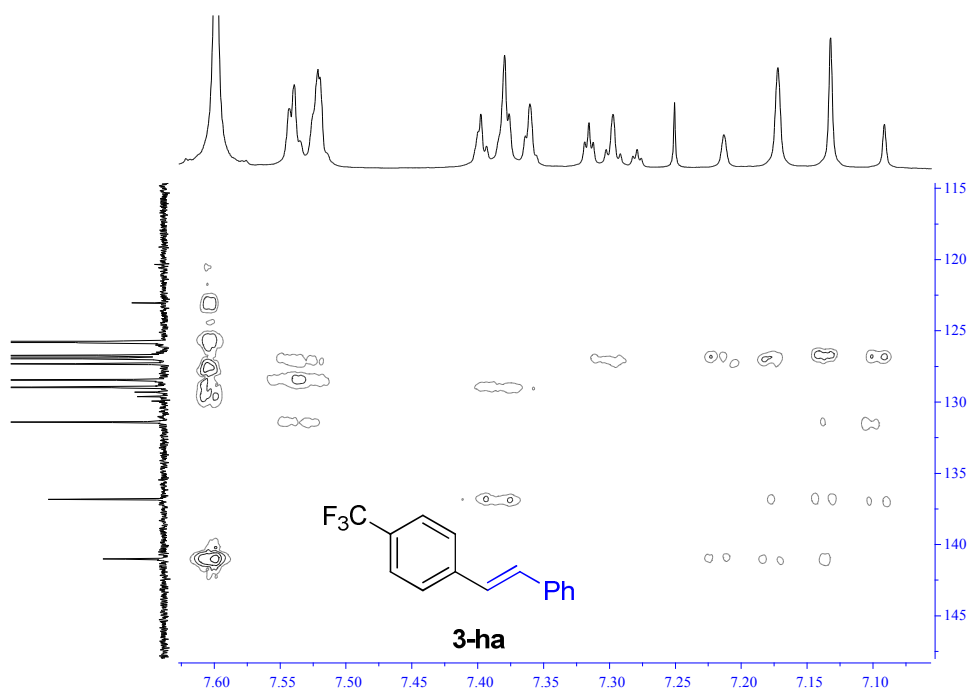


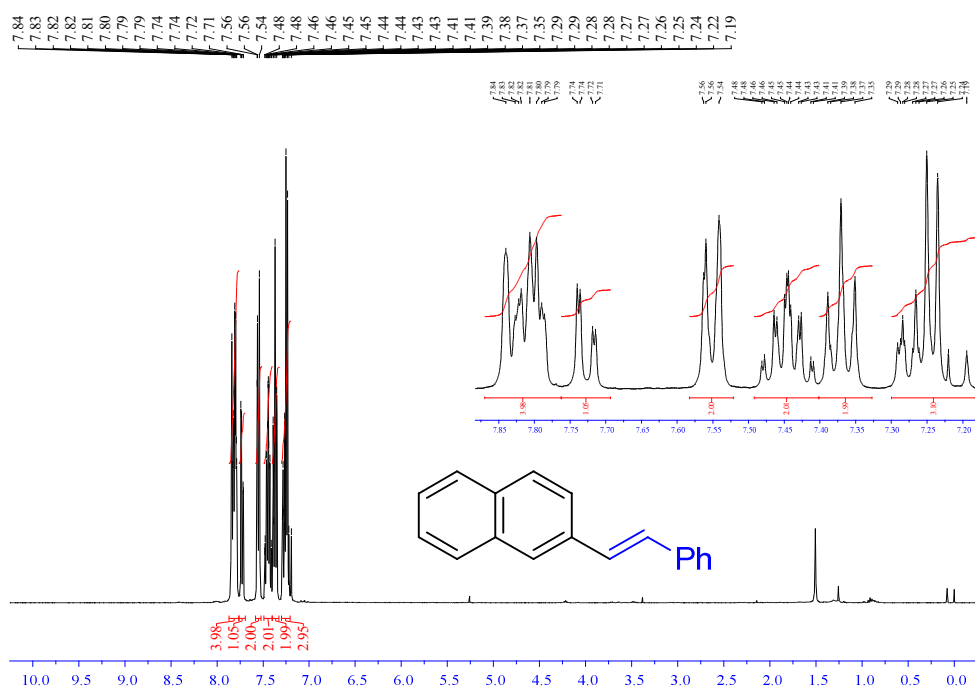
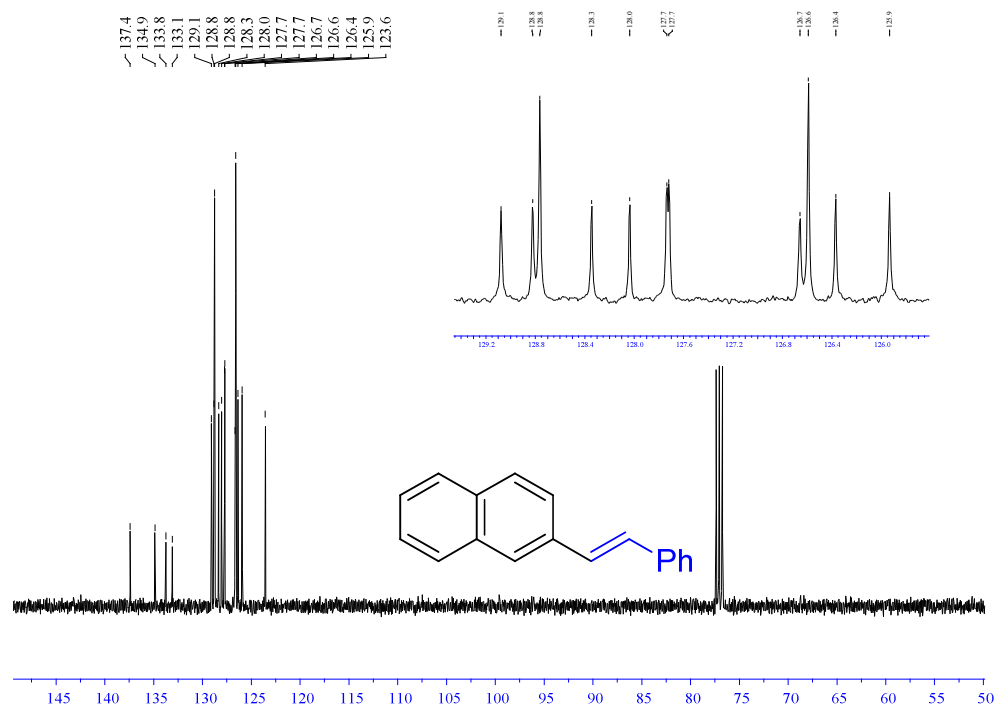
^{13}C NMR (101 MHz, CDCl_3) (*E*)-1-styryl-4-(trifluoromethyl)benzene (3-ha): **^1H - ^1H COSY NMR (400 MHz, CDCl_3) (*E*)-1-styryl-4-(trifluoromethyl)benzene (3-ha):**

^1H - ^{13}C HSQC NMR (400 MHz, CDCl_3) (*E*)-1-styryl-4-(trifluoromethyl)benzene (3-ha):

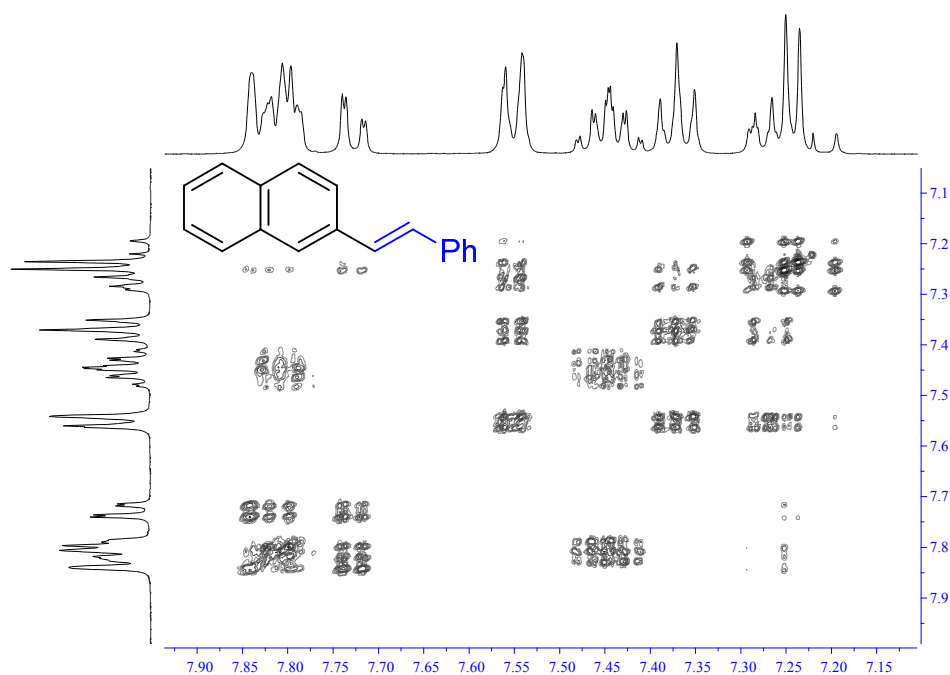


^1H - ^{13}C HMBC NMR (400 MHz, CDCl_3) (*E*)-1-styryl-4-(trifluoromethyl)benzene (3-ha):

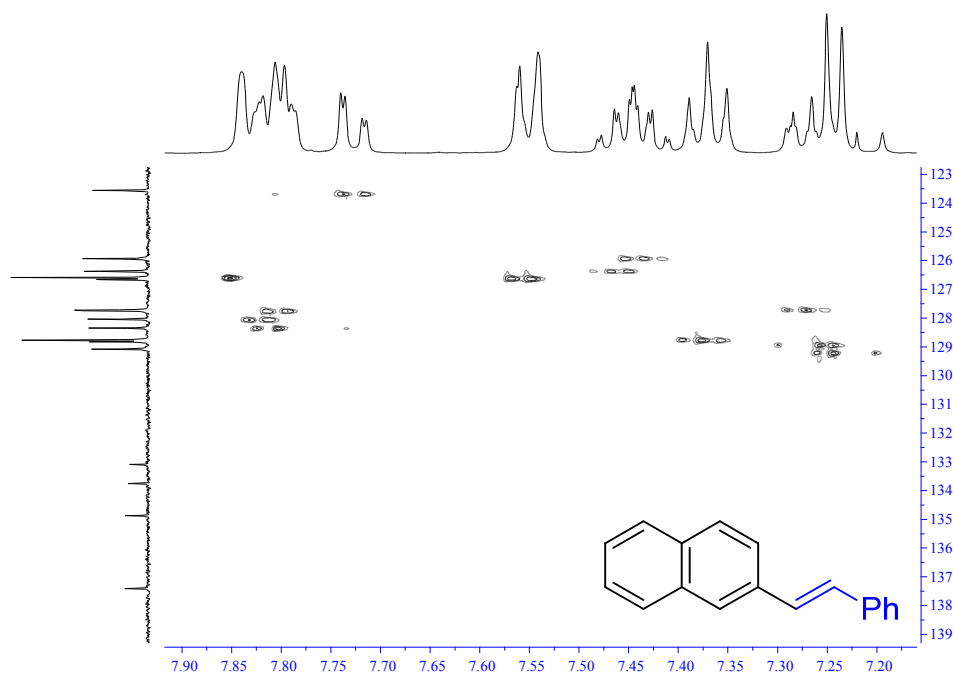


^1H NMR (400 MHz, CDCl_3 , TMS) (*E*)-2-styrylnaphthalene (3-ia): **^{13}C NMR (101 MHz, CDCl_3) (*E*)-2-styrylnaphthalene (3-ia):**

^1H - ^1H COSY NMR (400 MHz, CDCl_3) (*E*)-2-styrylnaphthalene (3-ia):

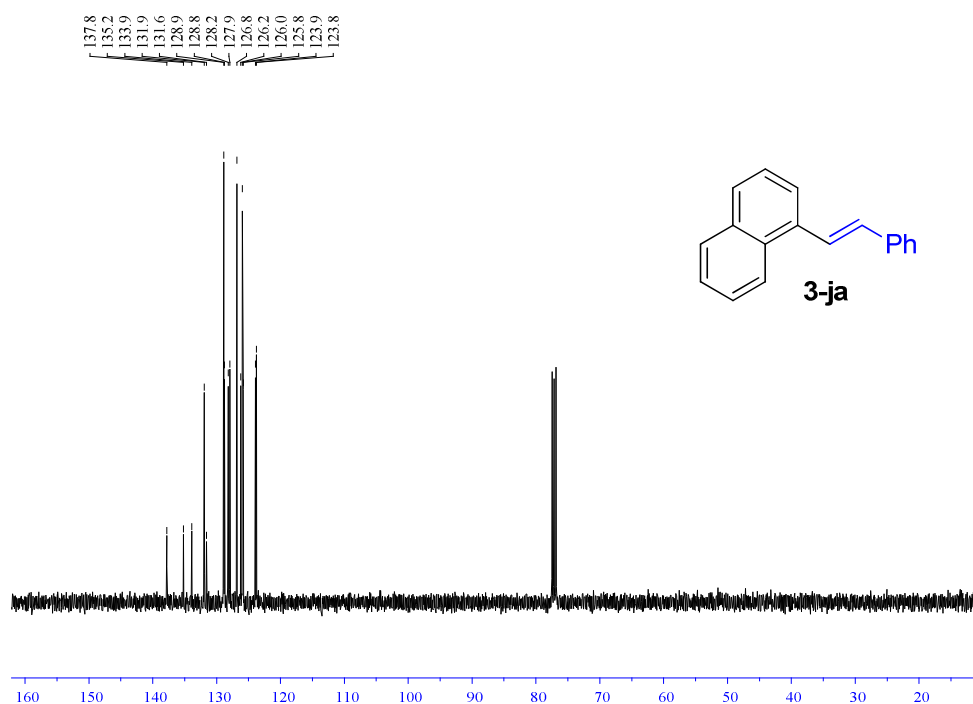


^1H - ^{13}C HSQC NMR (400 MHz, CDCl_3) (*E*)-2-styrylnaphthalene (3-ia):

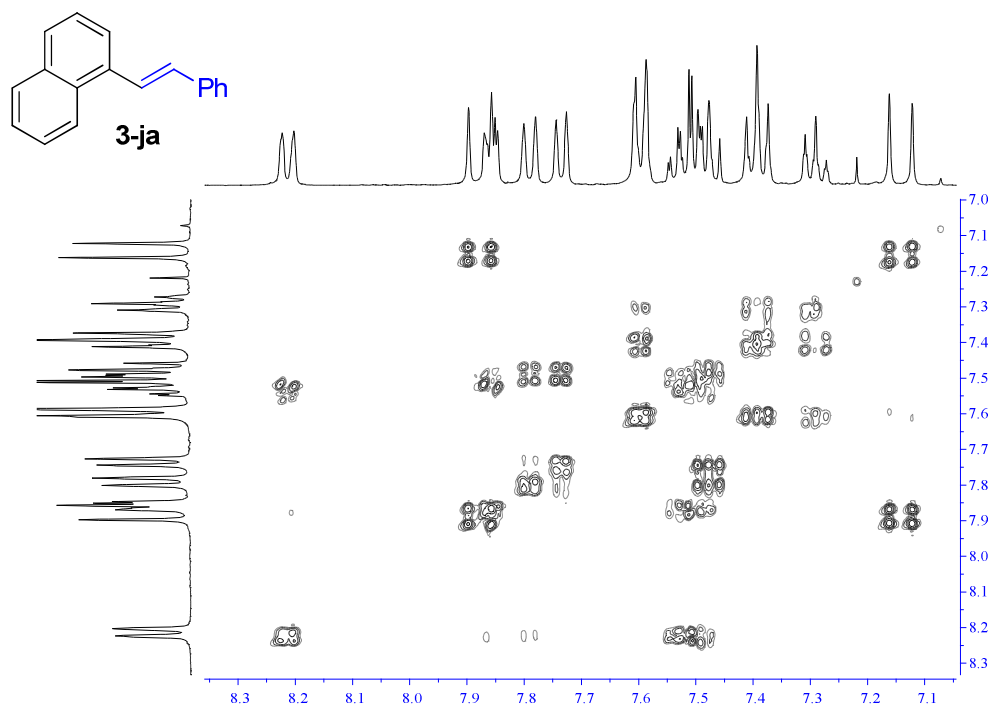




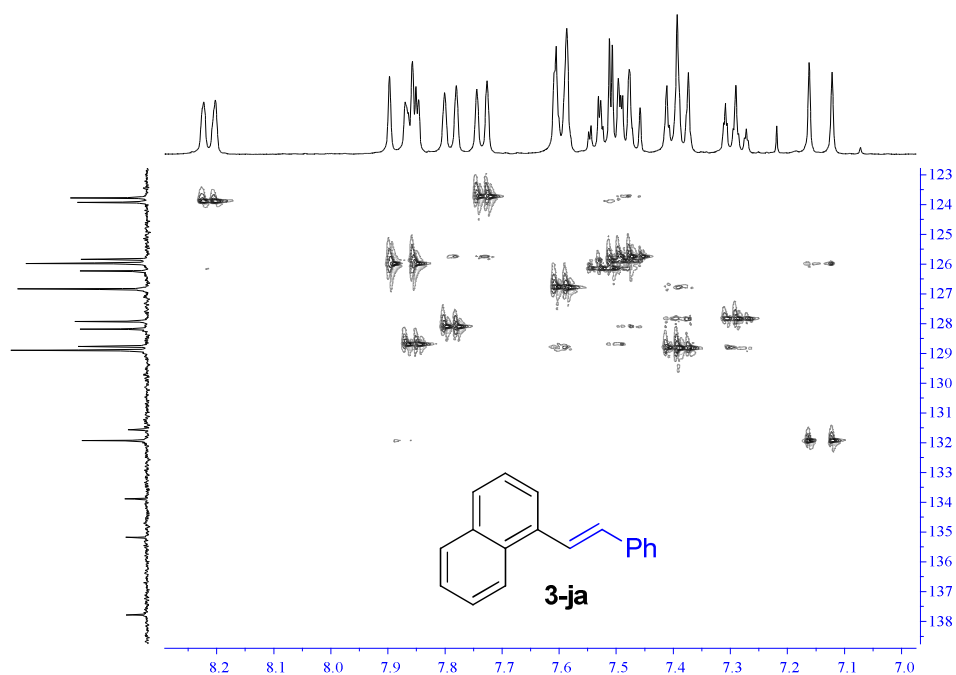
^{13}C NMR (101 MHz, CDCl_3) (*E*)-1-styrylnaphthalene (3-ja):



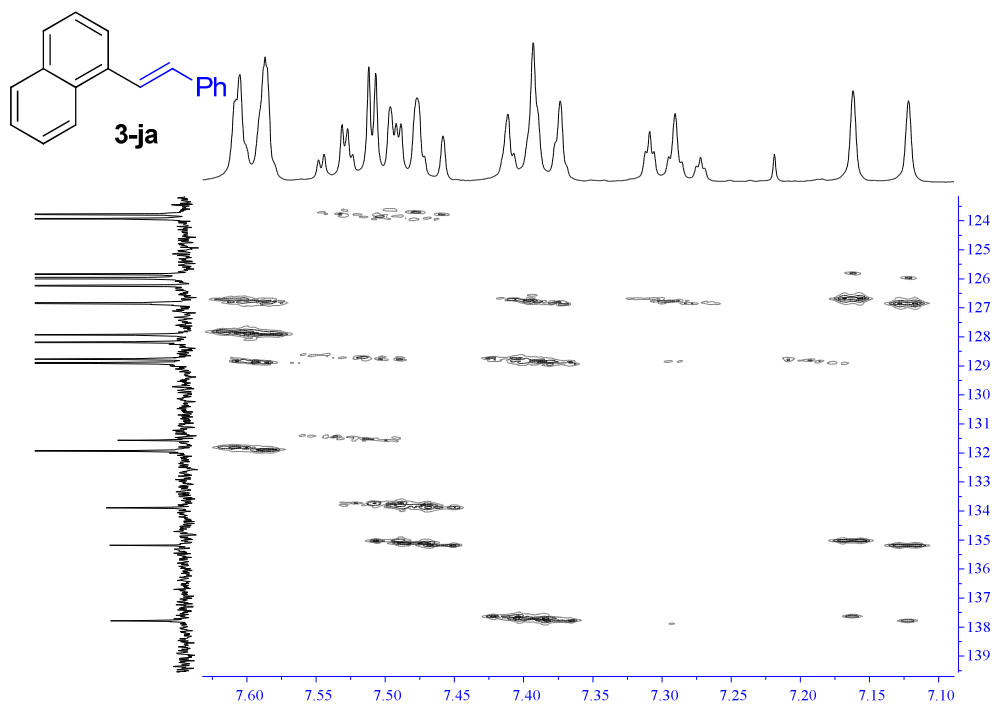
^1H - ^1H COSY NMR (400 MHz, CDCl_3) (*E*)-1-styrylnaphthalene (3-ja):



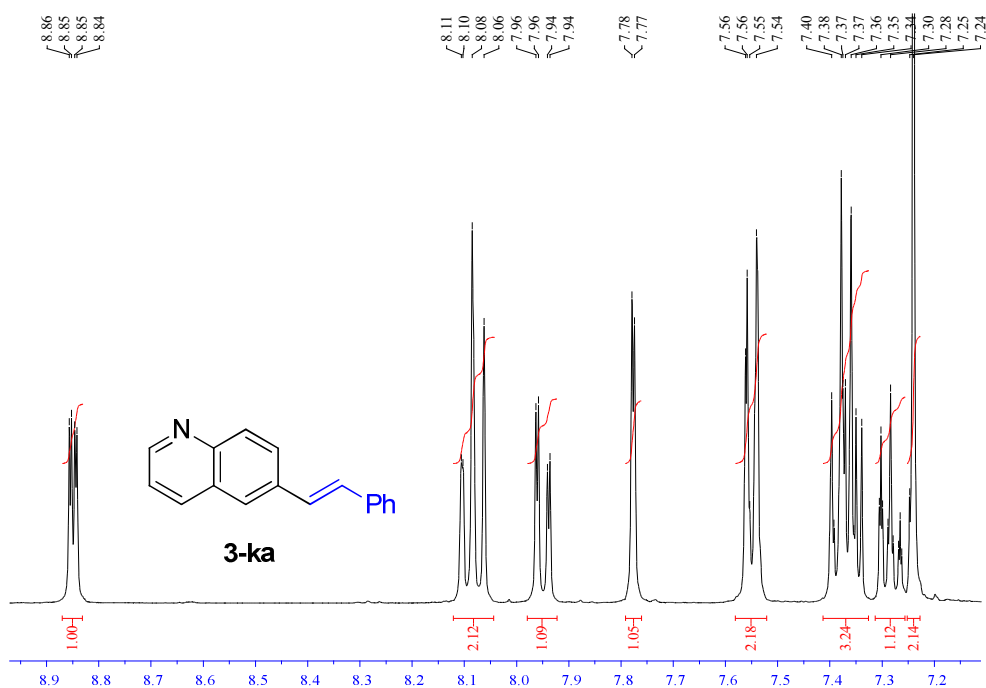
^1H - ^{13}C HSQC NMR (400 MHz, CDCl_3) (*E*)-1-styrylnaphthalene (3-ja):



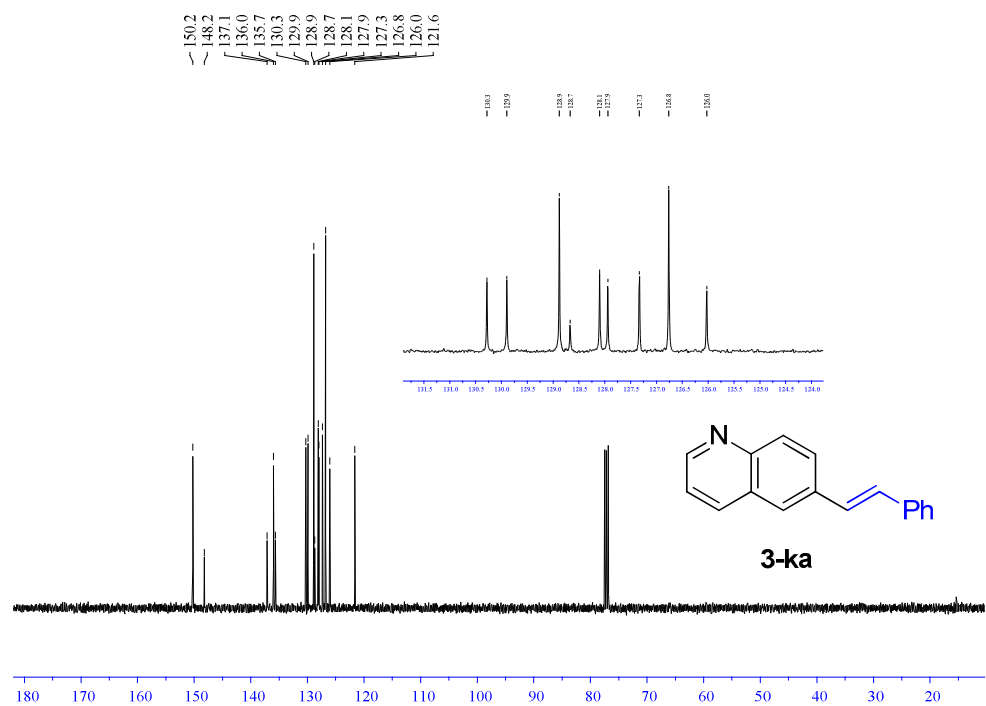
^1H - ^{13}C HMBC NMR (400 MHz, CDCl_3) (*E*)-1-styrylnaphthalene (3-ja):



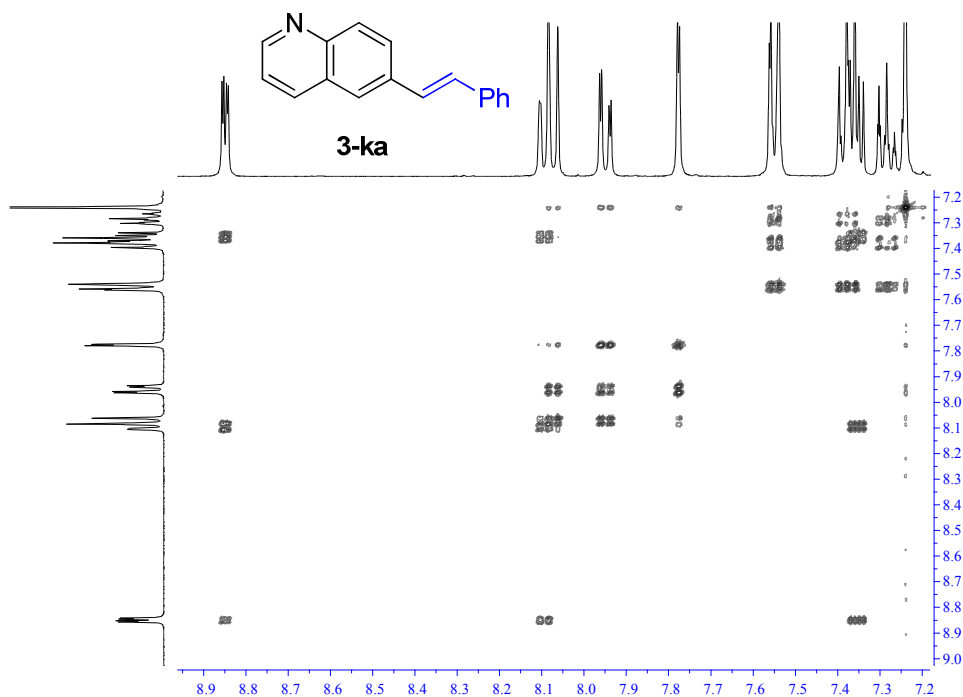
^1H NMR (400 MHz, CDCl_3 , TMS) (*E*)-6-styrylquinoline (3-ka):



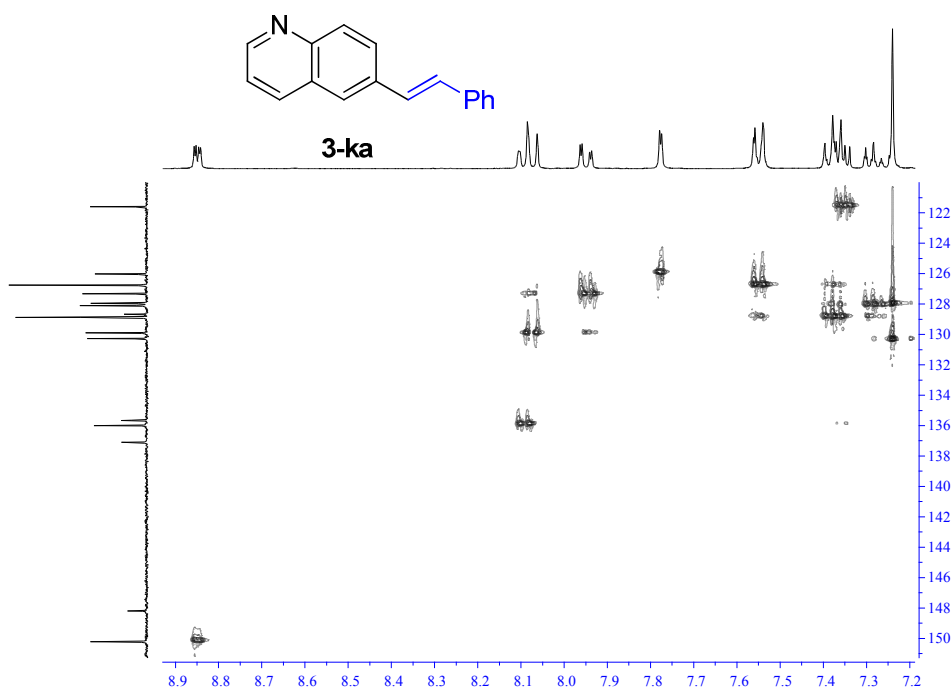
^{13}C NMR (101 MHz, CDCl_3) (*E*)-6-styrylquinoline (3-ka):

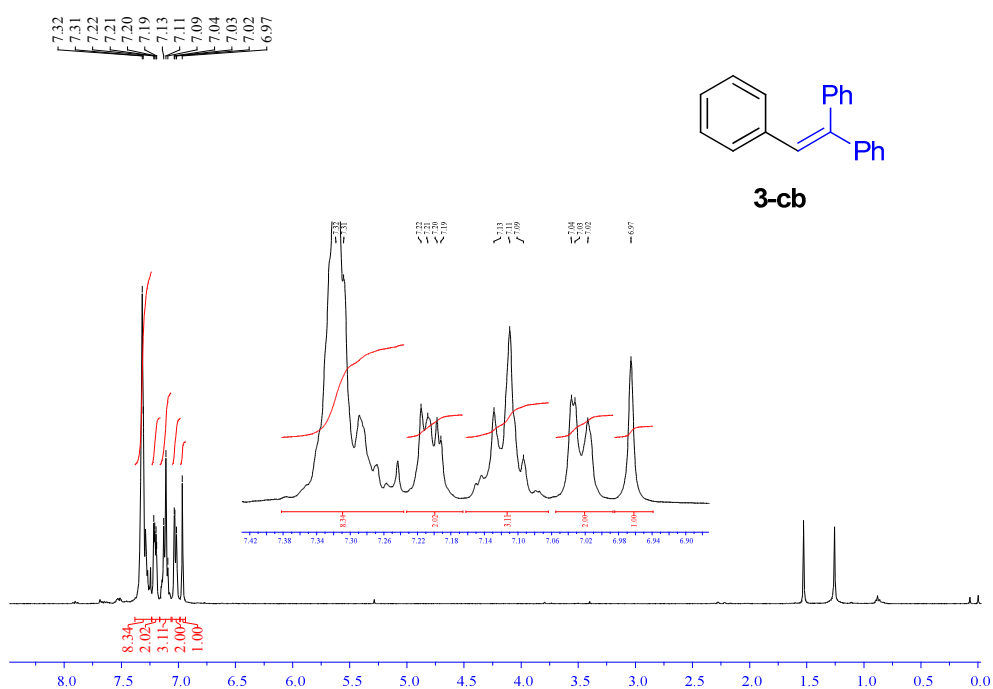


^1H - ^1H COSY NMR (400 MHz, CDCl_3) (*E*)-6-styrylquinoline (3-ka):

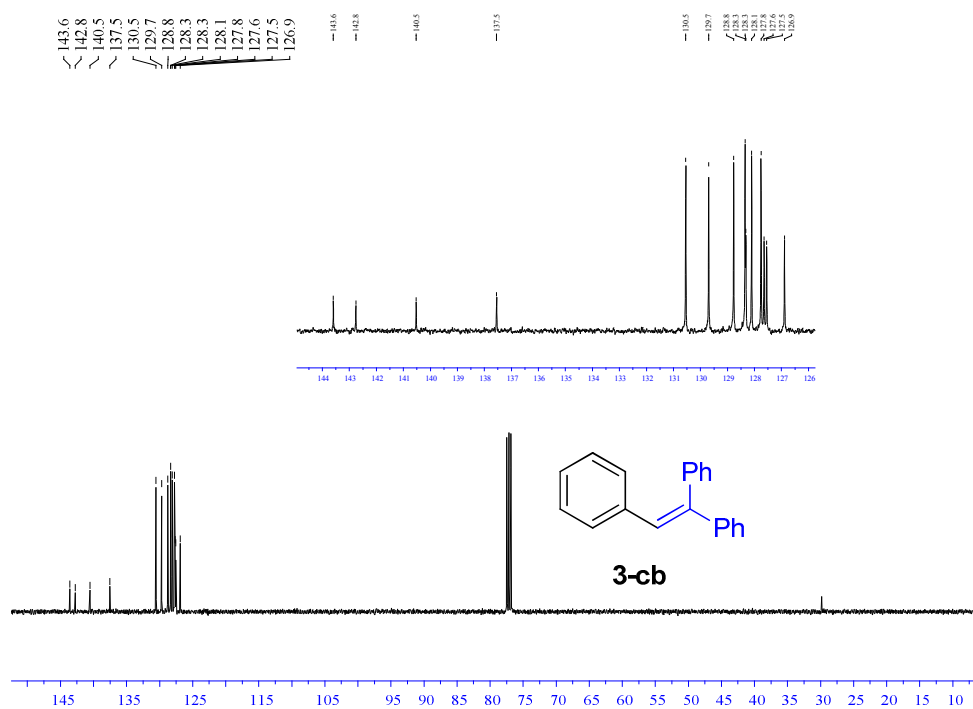


^1H - ^{13}C HSQC NMR (400 MHz, CDCl_3) (*E*)-6-styrylquinoline (3-ka):

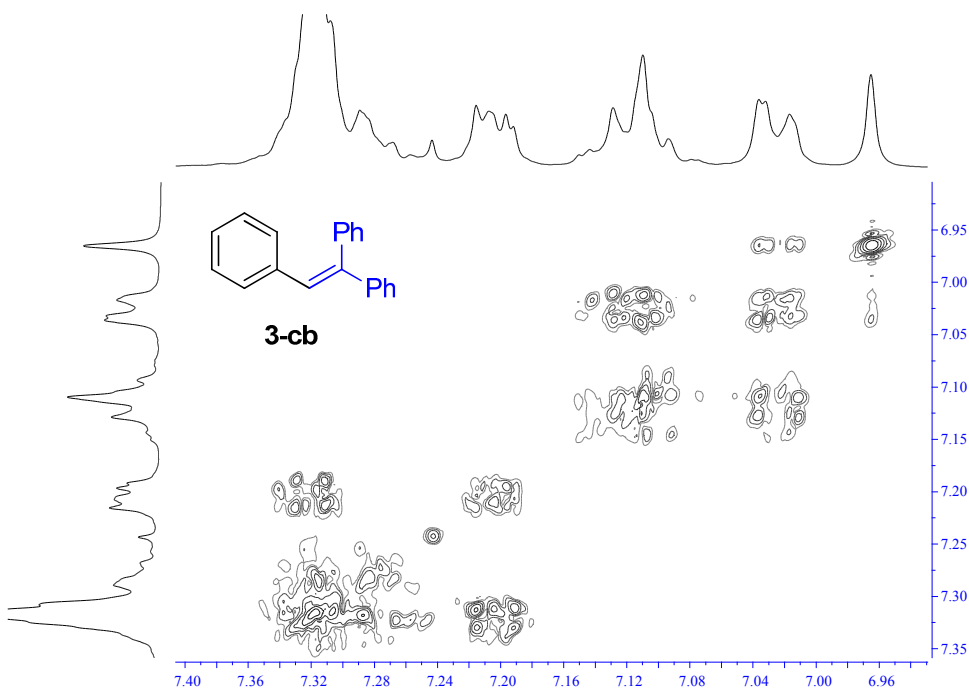




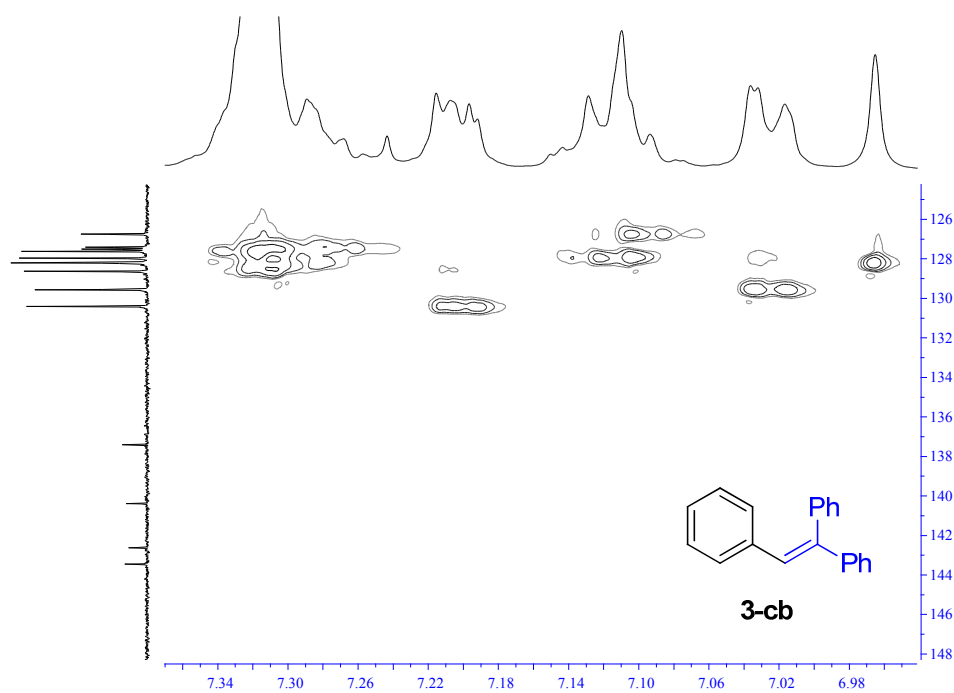
^{13}C NMR (101 MHz, CDCl_3) 1,1,2-triphenylethylene (3-cb):



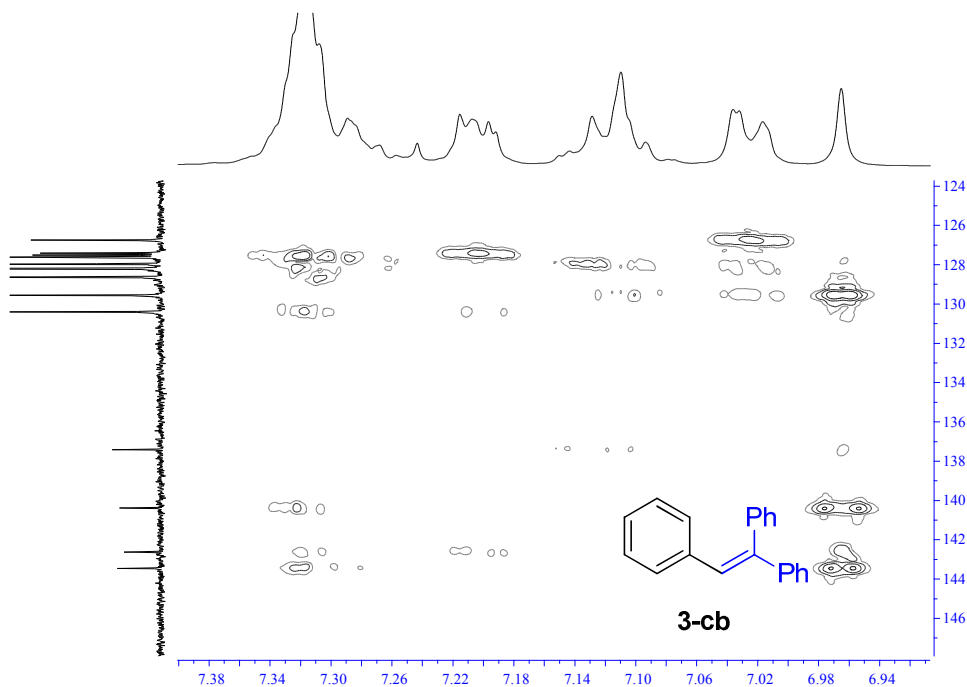
^1H - ^1H COSY NMR (400 MHz, CDCl_3) 1,1,2-triphenylethylene (3-cb):



^1H - ^{13}C HSQC NMR (400 MHz, CDCl_3) 1,1,2-triphenylethylene (3-cb):

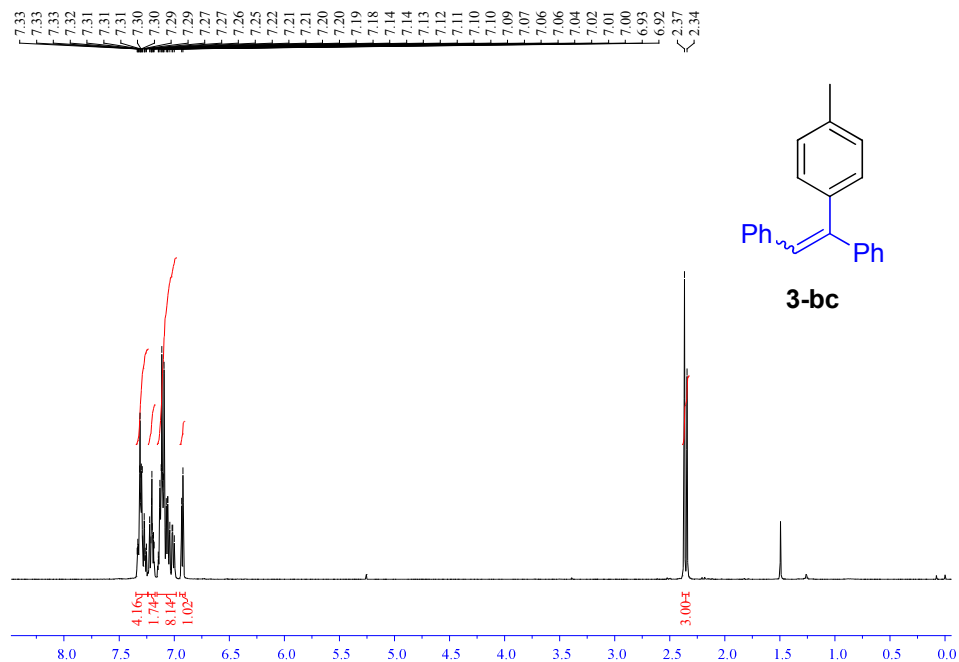


^1H - ^{13}C HMBC NMR (400 MHz, CDCl_3) 1,1,2-triphenylethylene (3-cb):

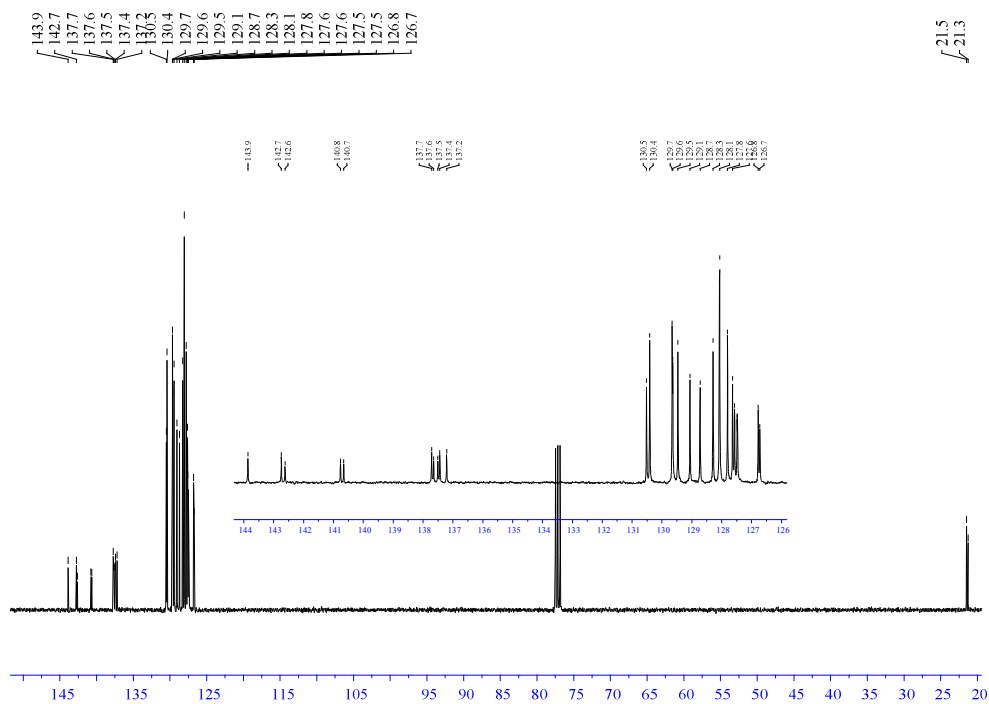


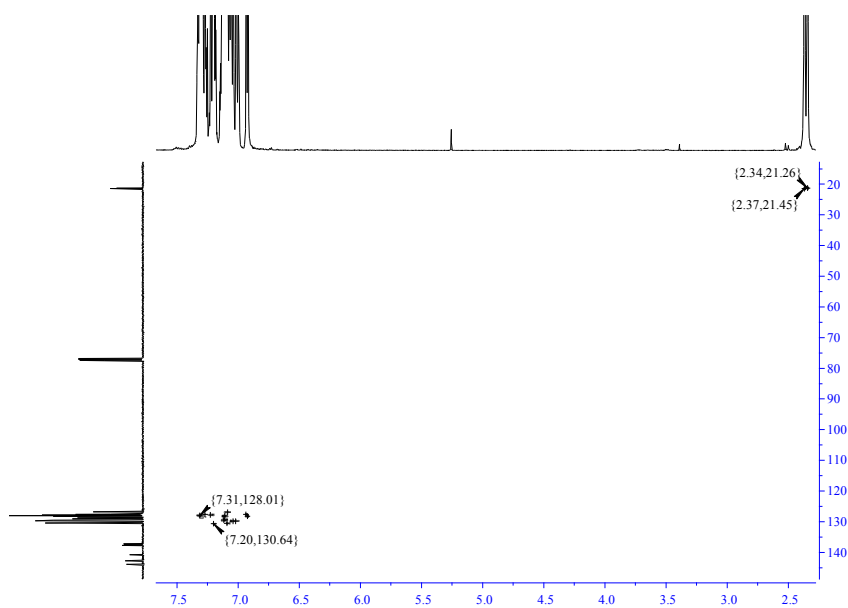
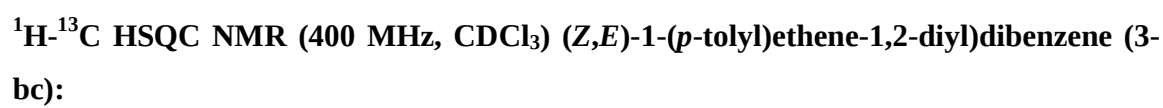
^1H NMR (400 MHz, CDCl_3 , TMS) (Z,E)-1-(p-tolyl)ethene-1,2-diyl)dibenzene

(3-bc):

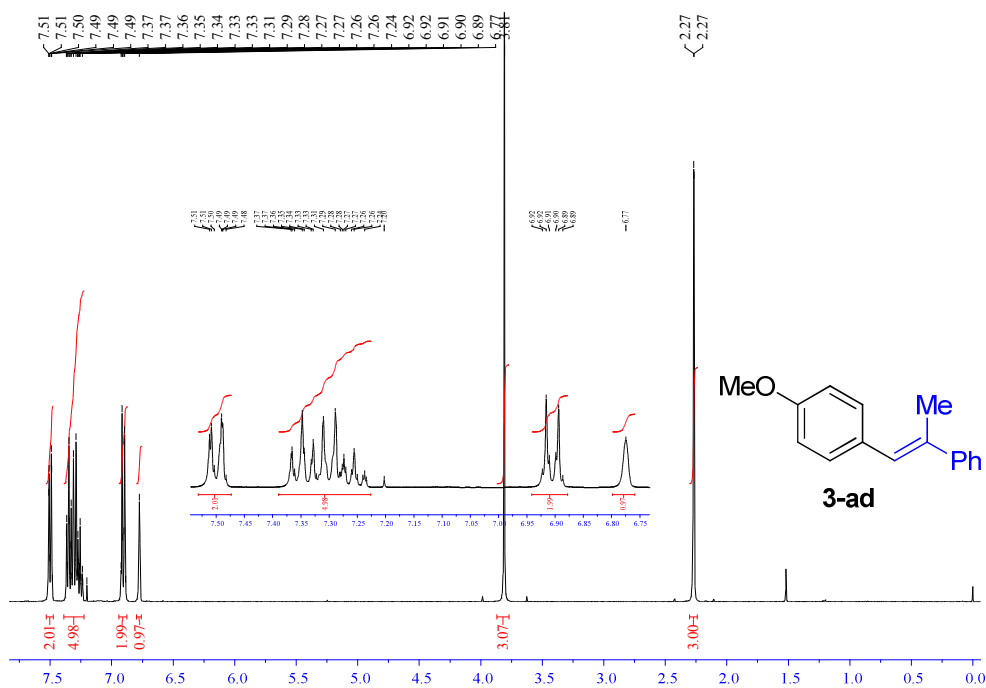


^{13}C NMR (101 MHz, CDCl_3) (Z,E)-1-(p-tolyl)ethene-1,2-diyl)dibenzene (3-bc):

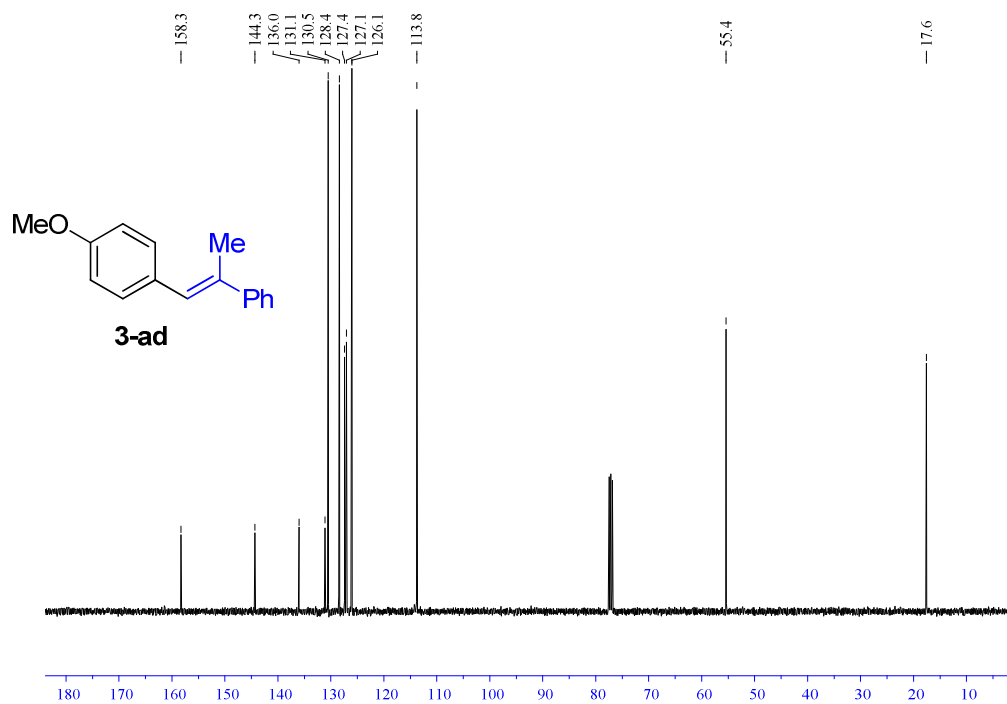




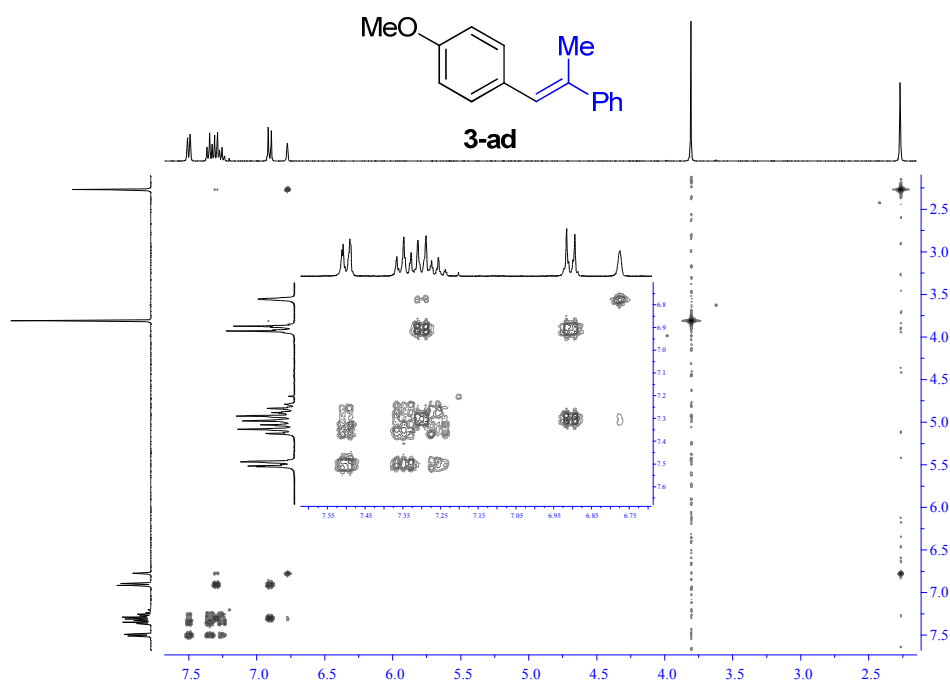
^1H NMR (400 MHz, CDCl_3 , TMS) (*E*)-1-methoxy-4-(2-phenylprop-1-en-1-yl)benzene (3-ad):



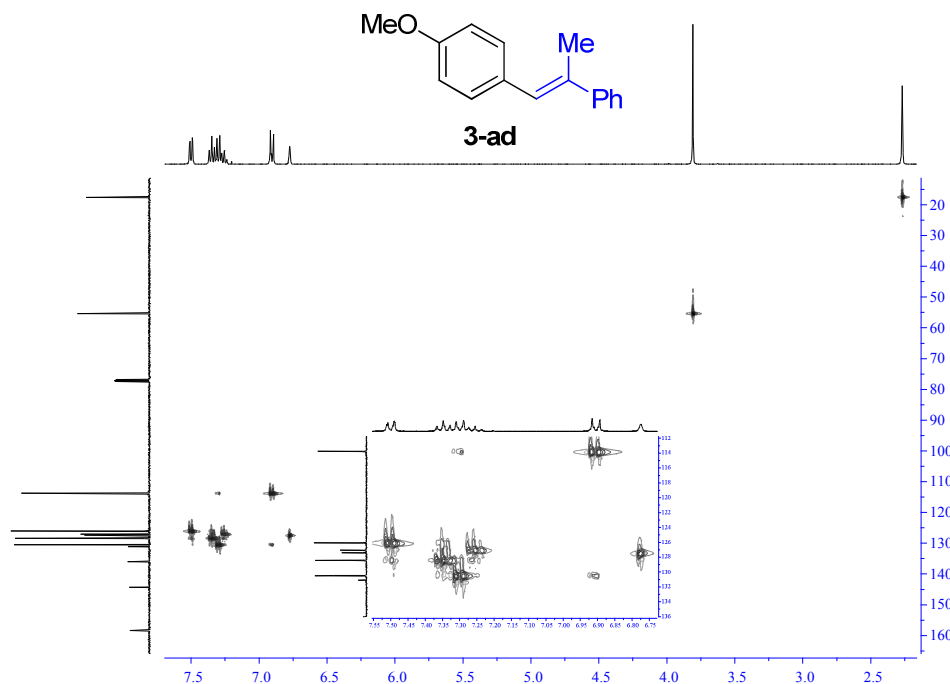
^{13}C NMR (101 MHz, CDCl_3) (*E*)-1-methoxy-4-(2-phenylprop-1-en-1-yl)benzene (3-ad):



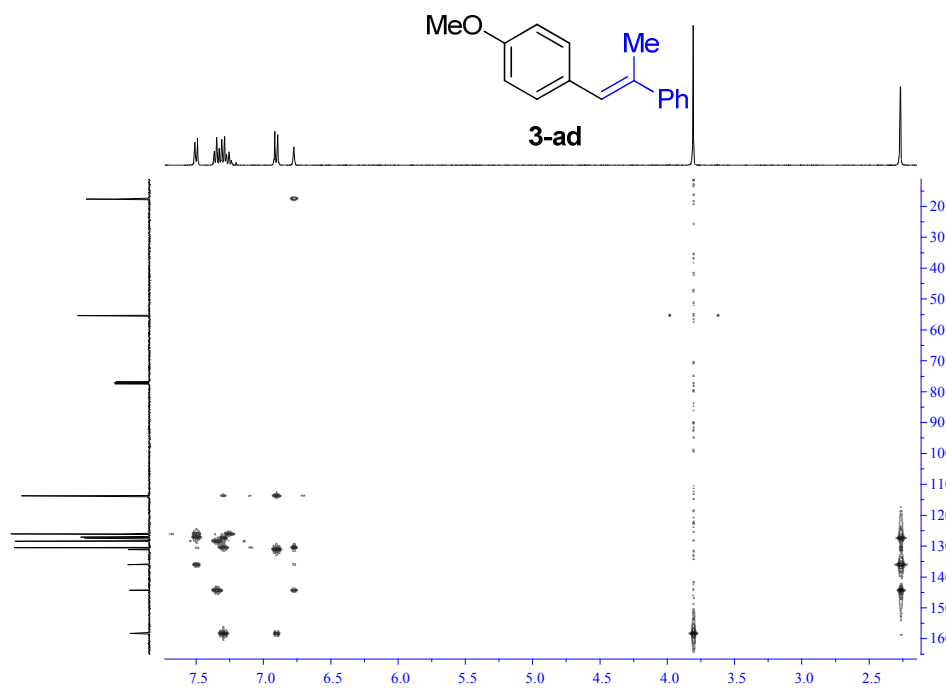
^1H - ^1H COSY NMR (400 MHz, CDCl_3) (*E*)-1-methoxy-4-(2-phenylprop-1-en-1-yl)benzene (3-ad):



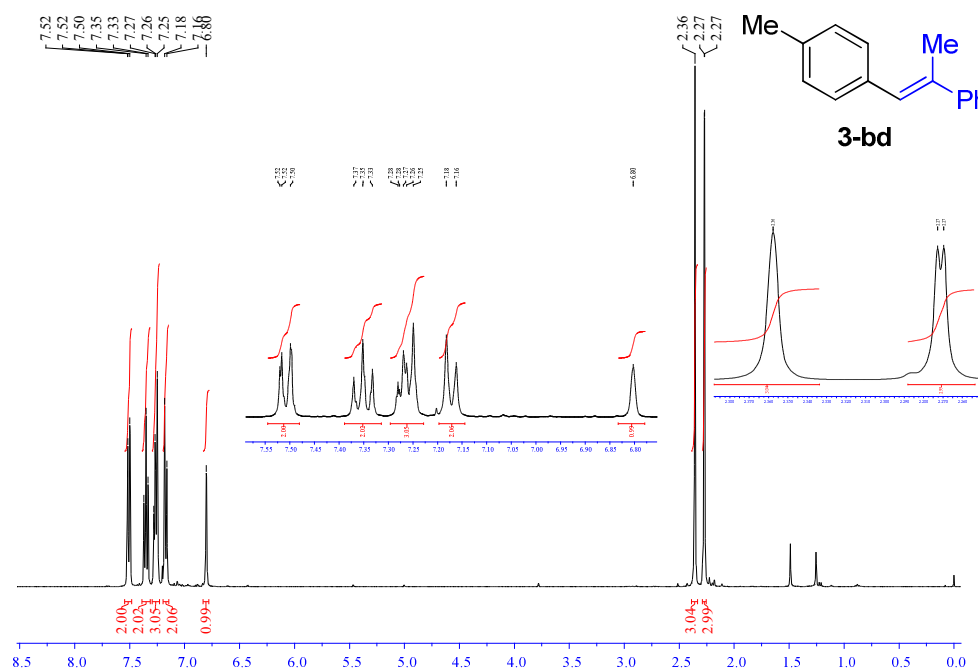
^1H - ^{13}C HSQC NMR (400 MHz, CDCl_3) (*E*)-1-methoxy-4-(2-phenylprop-1-en-1-yl)benzene (3-ad):



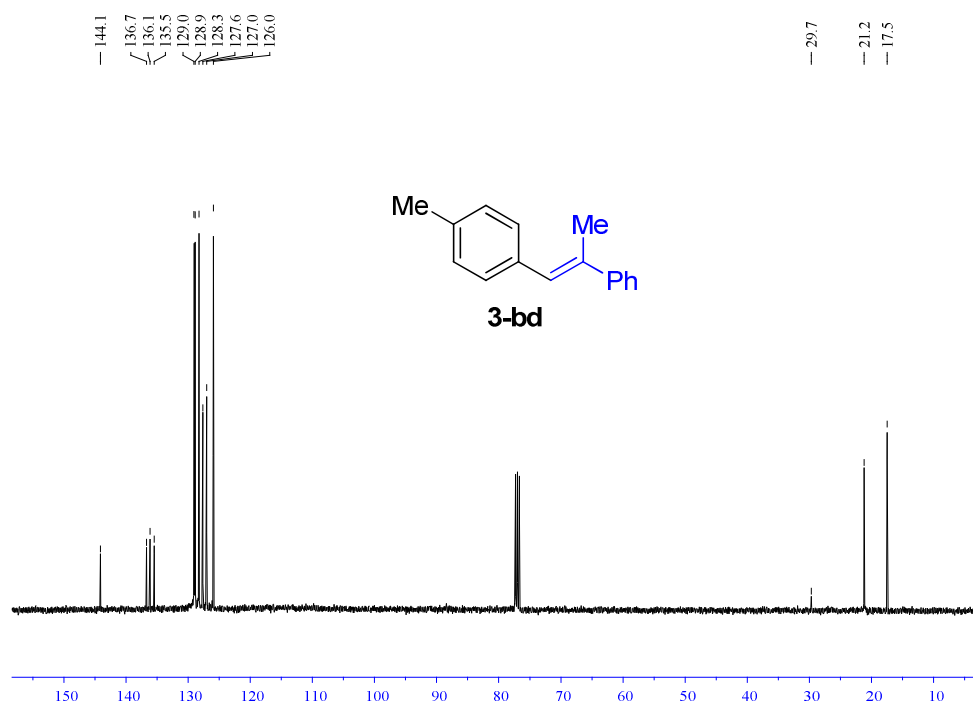
^1H - ^{13}C HMBC NMR (400 MHz, CDCl_3) (*E*)-1-methoxy-4-(2-phenylprop-1-en-1-yl)benzene (3-ad):



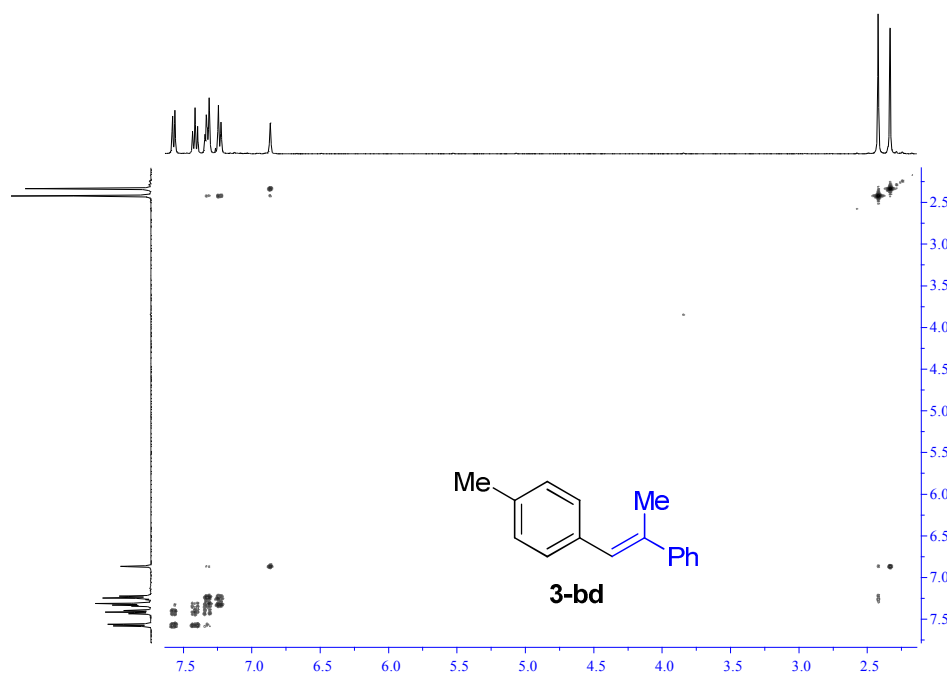
^1H NMR (400 MHz, CDCl_3 , TMS) (*E*)-1-methyl-4-(2-phenylprop-1-en-1-yl)benzene (3-bd):



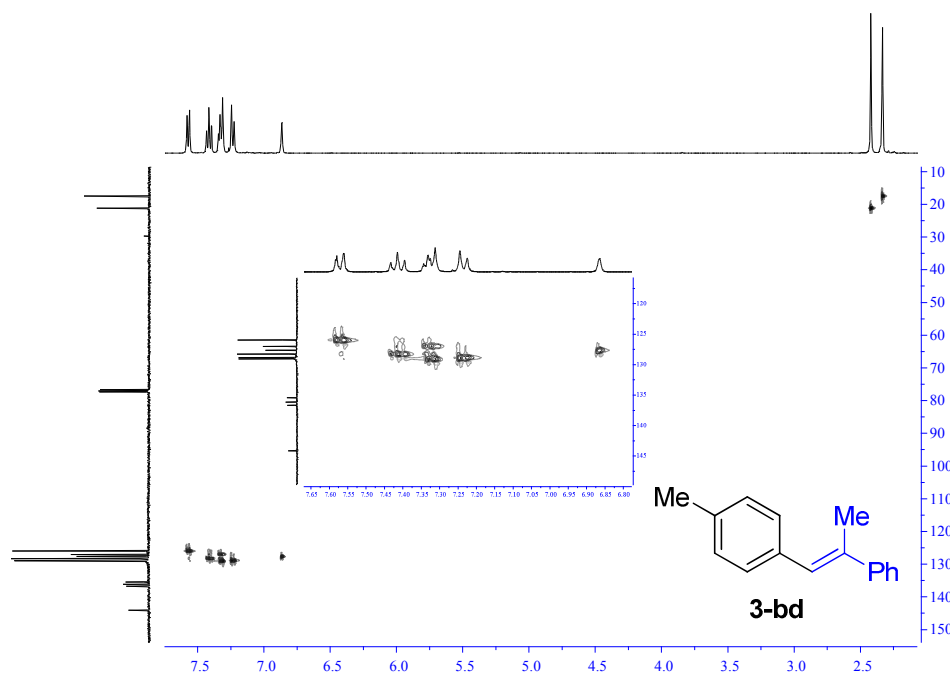
^{13}C NMR (101 MHz, CDCl_3) (*E*)-1-methyl-4-(2-phenylprop-1-en-1-yl)benzene (3-bd):



^1H - ^1H COSY NMR (400 MHz, CDCl_3) (*E*)-1-methyl-4-(2-phenylprop-1-en-1-yl)benzene (3-bd):



^1H - ^{13}C HSQC NMR (400 MHz, CDCl_3) (*E*)-1-methyl-4-(2-phenylprop-1-en-1-yl)benzene (3-bd):



^1H - ^{13}C HMBC NMR (400 MHz, CDCl_3) (*E*)-1-methyl-4-(2-phenylprop-1-en-1-yl)benzene (3-bd):

