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INVESTIGATION OF THE INTERMOLECULAR PAUSON-KHAND REACTION OF VARIOUS 1-ALKYNES WITH CYCLIC *EXO*-METHYLENE COMPOUNDS

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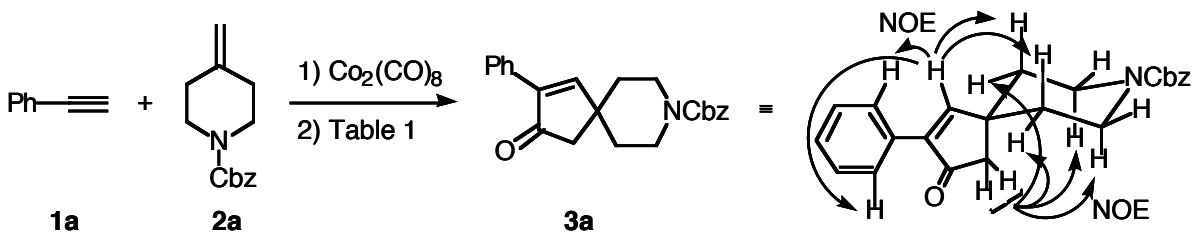
Abstract – Intermolecular Pauson-Khand reaction of various 1-alkynes with 4-*exo*-methylenepiperidine and -cyclohexane derivatives to give corresponding spirocyclopentenones was investigated. The reaction of *m*- and *p*-substituted arylalkynes furnished corresponding spirocyclic compounds in good yields, while that of *o*-substituted arylalkynes and 1-hexyne proceeded in nil to moderate yield.

Synthesis of spirobicyclic compounds has been focused because of their important utilities for total synthesis of natural products.[1] Thus, several synthetic methodology of them has been developed.[2] In connection with our studies[3] on intramolecular Pauson-Khand reaction of *exo*-cyclic enynes, intermolecular version of the reaction of 1-alkynes with *exo*-cyclic olefins suggested a facile approach to spirobicyclic compounds with cyclopentenone sub-unit. Contrary to the extended studies[4] on intermolecular Pauson-Khand reaction with *endo*-cyclic olefin, the similar reaction with *exo*-cyclic olefin was performed only with small ring systems such as methylenecyclopropanes and -butanes.[5] Here, we describe our full accounts on intermolecular Pauson-Khand reaction of various 1-alkynes with *exo*-cyclic olefins to give 6-5 spirocyclic compounds.[6]



1a **2a** **3a**

Cbz = CO_2CH_2Ph

Scheme 1.

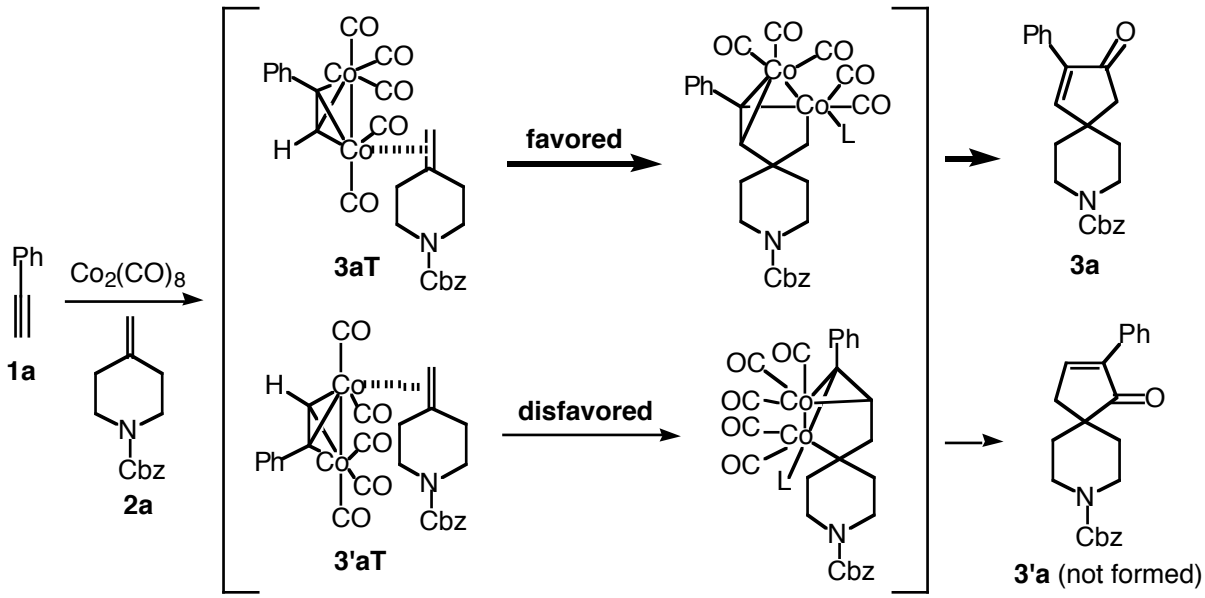
Table 1. Intermolecular Pauson-Khand reaction of phenylacetylene (**1a**) with **2a**.

Entry	**2a** (eq.)	Additive (eq.)	Solvent	Temp.	Time (h)	Yield of **3a**(%)
1	2	NMO (6)	CH_2Cl_2	r.t.	1	0
2	2	BuSMe (4)	CH_2ClCH_2Cl	83˚C	10	9
3	2	-	DME	reflux	5	11
4	2	-	CH_3CN	reflux	5	trace
5	2	-	*p*-xylene	reflux	5	20
6	2	-	toluene	reflux	5	30
7[a]	2	-	toluene	reflux	5	29
8	3	-	toluene	reflux	5	48
9	5	-	toluene	reflux	5	55
10	10	-	toluene	reflux	4	78 (75)[b]
11[c]	10	-	toluene	reflux	4	76 (77)
12[d]	10	$P(OPh)_3$ (0.3)	DME	reflux	24	trace

a) The reaction was performed under CO atmosphere (1 atm). b) Value in parenthesis is yield of recovered olefin (**2a**). c) Recovered olefin (**2a**) was used. d) The reaction was performed under CO atmosphere (3 atm) using 10 mol% of $Co_2(CO)_8$.

At first, we examined intermolecular Pauson-Khand reaction of phenylacetylene (**1a**) with 2 eq. of *N*-benzyloxycarbonyl(Cbz)-4-methylenepiperidine (**2a**) under various conditions (Scheme 1, Table 1). Although in the reaction using NMO[7a] at room temperature only decomplexation of alkyne-cobalt complex was observed on TLC (Entry 1), the reaction under heating gave stereoselectively spirocyclic compound (**3a**) as a single isomer. Among them, the reaction in boiling toluene furnished **3a** in the highest yield (30%, Entry 6). Unexpectedly, the reaction using BuSMe[7b] formed intractable mixture to give **3a** in only 9% yield (Entry 2). Furthermore, no improvement could be obtained in the reaction under CO atmosphere (Entry 7). It is well known that strained cyclic alkenes such as norbornene and 2,5-norbornadiene are good substrates in intermolecular Pauson-Khand reaction, in which when excess amounts (3-10 eq.) of them are used, the cyclized products are formed in good yield.[8] Based on the findings, we examined the reaction with increased amounts of olefin (**2a**). Gratifyingly, when five and ten equivalents of **2a** were employed, **3a** was produced in 55 and 78% yields, respectively (Entries 9 and 10). Unchanged **2a** was recovered and could be reused (Entry 11). Catalytic reaction[9] did not give satisfactory results in this reaction (Entry 12). In all cases, **3a** was formed as a sole adduct, stereostructure of which was determined by NOE experiment and regioisomer (**3'a**) could not be detected. It should be owing to severe steric interaction between alkyne-cobalt complex and piperidine ring as depicted in Scheme 2 (**3aT** vs **3'aT**).

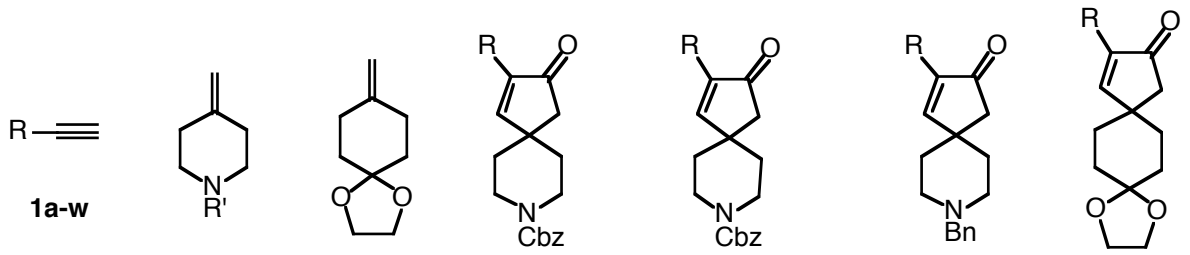
From above results, the reaction of various 1-alkynes (**1a**-**w**) with three *exo*-cyclic olefins (**2a**-**c**) under reaction conditions using ten equivalents of olefin was performed. The results are summarized in Table 2. The reaction of arylacetylenes having acetoxy (**1b**,**c**), methoxy (**1e**,**f**), methoxycarbonyl (**1h**,**i**), and methyl



Scheme 2

(**1k**,**l**) groups in 4- and 3-positions on benzene ring with **2a** gave the corresponding spirocyclopentenones (**3b**,**c**,**e**,**f**,**h**,**i**,**k**,**l**) in good yields (68-80%) along with unchanged **2a** (73-79%). On the other hand, similar reaction of substituted arylacetylenes (**1d**,**g**,**j**) in 2-position afforded corresponding adducts (**3d**,**g**,**j**) in moderate yields (40-44%). Surprisingly, the reaction of 2-toluacetylene (**1m**) did not give an adduct (**3m**) at all. These results are rationalized as follows. Oxygen atom existing in the 2-substituent on benzene ring would be coordinated intramolecularly to cobalt atom in alkyne-cobalt complex, so that decomplexation[10] proceeded to give the corresponding adducts in moderate yields. On the other hand, with toluacetylene (**1m**), in which no such coordination occurs, 2-methyl group on benzene ring would interfere an approach of the alkyne-cobalt complex to olefin moiety.

Next, we examined enynes containing nitrogen group. At first, Cbz protected anilinoacetylenes (**1n**-**p**) were employed. As a result, spirocyclopentenones (**3n**-**p**) were obtained in moderate yield (43-44%) along with free anilino products (**3nN**-**3pN**). Similar reaction of *N*-trifluoacetyl derivative (**1q**) afforded **3q** in 11% yield and *N*-Boc protected anilinoacetylene (**1r**) afforded only deprotected adduct (**3pN**) in 11% yield. The reaction of 2-anilinoacetylene (**1s**) did not give any desired adduct (**3s**) at all. This finding shows that the free anilino products (**3nN**-**3pN**) would be formed by debenzyloxycarbonylation, which might be accelerated by coordination of nitrogen atom to cobalt complex during the reaction. In order to investigate the influence of electronic nature of acetylenes,[11] the reaction of nitrophenylacetylenes (**1t-v**), which had strongly electron-withdrawing nitro group on benzene ring, was examined. As a result, the decomplexation of alkyne-cobalt complex was completed in short time (1 h) and yields (0-11%) of adducts were markedly dropped, compared to those of the other substrates. Contrary to aromatic alkynes, the reaction of 1-hexyne (**1w**) with **2a** required long reaction time to afford **3w** in 43% yield.[12] The reaction of **1a** and **1w** with *N*-benzylpiperidine (**2b**) gave adducts (**4a** and **4w**) in 63 and 47% yield,



2a : R' = Cbz **2c** **3a-q** **3nN** : R = 4-$H_2NC_6H_4$ **4a** **5a-d**
2b : R' = Bn **3t-x** **3oN** : R = 3-$H_2NC_6H_4$ **4w** **5w**
3pN : R = 2-$H_2NC_6H_4$

Figure 1

Table 2. Intermolecular Pauson-Khand Reaction of Various 1-Alkynes with Olefins.[a]

Entry	1-Alkynes	R	Olefin	Time (h)	Product	Yield (%)[b]	Olefin (%)[c]
1	**1a**	C_6H_5	**2a**	3	**3a**	78	75
2	**1b**	4-$AcOC_6H_4$	**2a**	3	**3b**	77	78
3	**1c**	3-$AcOC_6H_4$	**2a**	4	**3c**	68	77
4	**1d**	2-$AcOC_6H_4$	**2a**	4	**3d**	44	78
5	**1e**	4-$MeOC_6H_4$	**2a**	4	**3e**	70	79
6	**1f**	3-$MeOC_6H_4$	**2a**	3	**3f**	68	78
7	**1g**	2-$MeOC_6H_4$	**2a**	4	**3g**	40	79
8	**1h**	4-$MeO_2CC_6H_4$	**2a**	3	**3h**	78	75
9	**1i**	3-$MeO_2CC_6H_4$	**2a**	3	**3i**	80	79
10	**1j**	2-$MeO_2CC_6H_4$	**2a**	3	**3j**	42	76
11	**1k**	4-MeC_6H_4	**2a**	5	**3k**	73	73
12	**1l**	3-MeC_6H_4	**2a**	5	**3l**	71	76
13	**1m**	2-MeC_6H_4	**2a**	10	**3m**	0	92
14	**1n**	4-$CbzNHC_6H_4$	**2a**	4	**3n+3nN**	44+9	81
15	**1o**	3-$CbzNHC_6H_4$	**2a**	4	**3o+3oN**	43+11	83
16	**1p**	2-$CbzNHC_6H_4$	**2a**	3	**3p+3pN**	44+1	85
17	**1q**	2-$CF_3CONHC_6H_4$	**2a**	3	**3q**	11	87
18	**1r**	2-$BocNHC_6H_4$	**2a**	4	**3pN**	11	86
19	**1s**	2-$NH_2C_6H_4$	**2a**	6	**3pN**	0	87
20	**1t**	4-$NO_2C_6H_4$	**2a**	1	**3t**	5	91
21	**1u**	3-$NO_2C_6H_4$	**2a**	1	**3u**	11	84
22	**1v**	2-$NO_2C_6H_4$	**2a**	1	**3v**	0	93
23	**1w**	*n*-C_4H_9	**2a**	9	**3w**	43	77
24	**1a**	C_6H_5	**2b**	4	**4a**	63	77
25	**1w**	*n*-C_4H_9	**2b**	9	**4w**	47	85
26	**1a**	C_6H_5	**2c**	4	**5a**	43	77
27	**1b**	4-$AcOC_6H_4$	**2c**	3	**5b**	50	78
28	**1c**	3-$AcOC_6H_4$	**2c**	4	**5c**	52	71
29	**1d**	2-$AcOC_6H_4$	**2c**	4	**5d**	10	86
30	**1w**	*n*-C_4H_9	**2c**	10	**5w**	42	71

a) All reactions were carried out with 10 eq. of olefin in boiling toluene. b) Isolated yield.
b) Isolated yield of unchanged olefin.

respectively, in which the reaction similar to that described in the case of **2a** proceeded. The reaction of

1a-d and **1w** with 8-methylene-1,4-dioxaspiro[4.5]decane (**2c**) also proceeded to give spirocyclopentenones (**5a-d**,**w**) in low to moderate yields (10-52%).

In summary, we have investigated intermolecular Pauson-Khand reaction of various arylacetylenes (**1a**-**v**) and 1-hexyne (**1w**) with 6-membered cyclic *exo*-methylene compounds (**2a-c**) to give spiro-cyclopentenones, although a problem on employment of large excess of *exo*-olefin remains. The reaction of arylacetylenes bearing substituents (except for *N*-Cbz-amino group) in 3- and 4-positions on benzene ring gave the corresponding adducts in good yields, whereas that of 2-substituted and nitrogen containing arylacetylenes, and aliphatic 1-alkyne furnished the corresponding spirocyclopentenones nil to moderate yields.

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EXPERIMENTAL

General. All melting points were measured on a Yanagimoto melting point apparatus and are uncorrected. IR spectra were performed with a Hitachi 260-10 spectrophotometer in $CHCl_3$ solution. ^{1}H- and ^{13}C-NMR spectra were taken with a JEOL EX-270 (270 MHz for ^{1}H-NMR and 67.5 MHz for ^{13}C-NMR) spectrometer in $CDCl_3$ solution with tetramethylsilane as an internal standard. MS spectra were measured on a JEOL JMS D-300 spectrometer. Column chromatography was performed over silica gel (Merck Kiegelsel 60). Preparative TLCs were run on Merck 5744 or Merck 5715 plates. Organic extract was dried over $MgSO_4$. Alkynes (**1b**,[13a] **1c**,[13b] **1d**,[13c] **1e-g**,[13d] **1h-j,**[13e] **1k-m**,[13f] **1t-v**[13g]) and olefins (**2b**,**c**)[14] were prepared according to reported methods.

General Procedure for Synthesis of Acetylenes (1n-p)

To a mixture of 4-,[13h] 3-[13h] or 2-aminophenylacetylene[13i] (0.235 g, 2.0 mmol) and Na_2CO_3 (0.421 g, 4.0 mmol) in water (5 mL) and Et_2O (3 mL) at 0˚C was added a solution of Cbz chloride (0.800 g, 4.7 mmol) in Et_2O (2 mL). Then, the mixture was warmed up to rt and stirring was continued for additional 1 h. After the reaction mixture was diluted with water, the mixture was extracted with Et_2O. The extracts were washed with brine and dried and evaporated under reduced pressure to give a residue, which was purified by column chromatography (hexane : $CHCl_3$ = 1 : 1 then $CHCl_3$) to afford **1n-p**.

4-(*N*-Cbz-amino)phenylacetylene (1n); from 4-aminophenylacetylene, **1n** (0.437 g, 84.4%) was obtained; mp 94-95˚C (AcOEt-hexane); ^{1}H NMR □ 7.34-7.45 (9H, m), 6.79 (1H, s), 5.20 (2H, s), 3.04 (1H, s); ^{13}C NMR □ 153.0, 138.2, 135.7, 133.0, 128.6, 128.4, 128.3, 118.1, 116.8, 83.4, 76.6, 67.2; IR 3285, 2101, 1705 cm^{-1}; MS *m/z* 251 (M^+); HRMS *m/z* calcd for $C_{16}H_{13}NO_2$ (M^+) 251.0946, found: 251.0944.

3-(*N*-Cbz-amino)phenylacetylene (1o); from 3-aminophenylacetylene, **1o** (0.504 g, 99.6%) was obtained; oil; ^{1}H NMR δ 7.53 (1H, s), 7.35-7.43 (6H, m), 7.19-2.28 (2H, m), 7.18-7.28 (1H, br s), 5.20 (2H, s), 3.07 (1H, s); ^{13}C NMR δ 153.3, 137.8, 135.8, 129.0, 128.6, 128.4, 128.3, 127.2, 122.8, 120.0, 119.2, 83.1, 77.4, 67.1; IR 3293, 2106, 1715 cm^{-1}; MS *m/z* 251 (M^+); HRMS *m/z* calcd for $C_{16}H_{13}NO_2$ (M^+) 251.0946, found: 251.0940.

2-(*N*-Cbz-amino)phenylacetylene (1p); from 2-aminophenylacetylene, **1p** (0.469 g, 92.9%) was obtained; mp 83-84°C (hexane); ^{1}H NMR δ 8.20 (1H, d, *J* = 8.6 Hz), 7.33-7.48 (8H, m), 7.00 (1H, dt, *J* = 1.3, 7.6 Hz), 5.23 (2H, s), 3.46 (1H, s); ^{13}C NMR δ 153.0, 139.7, 135.9, 132.2, 130.2, 128.6, 128.4, 122.5, 117.7, 110.1, 84.3, 79.1, 67.2 ;IR 3388, 3241, 2100, 1735 cm^{-1}; MS *m/z* 251 (M^+); HRMS *m/z* calcd for $C_{16}H_{13}NO_2$ (M^+) 251.0946, found: 251.0938.

2-(Trifluoroacetylamino)phenylacetylene (1q) To a mixture of 2-aminophenylacetylene[13i] (0.236 g, 2.0 mmol) and K_2CO_3 (0.276 g, 2.0 mmol) in CH_2Cl_2 (5 mL) at rt was added trifluroacetic anhydride (0.4 mL, 4.7 mmol). After the mixture was stirred for 15 min, the reaction was quenched with water. The mixture was extracted with $CHCl_3$. The extracts were washed with brine and dried, and evaporated under reduced pressure to give a residue, which was purified by column chromatography (hexane : AcOEt = 8 : 1) to afford **1q** (0.401 g, 93.4%); mp 36-37°C (hexane); ^{1}H NMR δ 8.36 (1H, s), 7.41-7.55 (2H, m), 7.16-7.22 (2H, m), 3.60 (1H, s); ^{13}C NMR δ 155.0, 154.3, 136.8, 132.3, 130.4, 125.4, 119.7, 112.1, 85.7, 77.4, 77.0, 76.6; IR 3388, 3241, 2100, 1735 cm^{-1}; MS *m/z* 213 (M^+); HRMS *m/z* calcd for $C_{10}H_6NOF_3$ (M^+) 213.0401, found: 213.0400.

2-(*N*-Boc-amino)phenylacetylene (1r) A mixture of 2-aminophenylacetylene[13i] (0.353 g, 3.0 mmol) and Boc_2O (2.006 g, 10.2 mmol) in THF (3 mL) was refluxed for 3 h. Evaporation of the solvent followed by purification of the residue by column chromatography (hexane : AcOEt = 15 : 1 then 5 : 1) afforded **1r** (0.581 g, 88.8%); mp 47-48°C (hexane); ^{1}H NMR δ 8.16 (1H, d, *J* = 8.6 Hz), 7.42 (1H, dd, *J* = 1.3, 7.6 Hz), 7.33 (1H, dt, *J* = 1.3, 8.6 Hz), 6.96 (1H, dt, *J* = 1.3, 7.6 Hz), 7.26 (1H, s), 3.48 (1H, s), 1.54 (9H, s); ^{13}C NMR δ 152.4, 135.2, 132.2, 130.1, 122.0, 117.5, 109.8, 84.0, 80.8, 79.3, 28.3 ; IR 3250, 2971, 1717 cm^{-1}; MS *m/z* 217 (M^+); HRMS *m/z* calcd for $C_{13}H_{15}NO_2$ (M^+) 217.1103, found: 217.1100.

***N*-Cbz-4-methylenepiperidine (2a)** To a suspension of PPh_3•MeBr (17.20 g, 48.1 mmol) in THF (350 mL) at rt was added *t*-BuOK (5.39 g, 48,0 mmol) in small portions. After being stirred for 10 min, *N*-Cbz-piperidin-4-one (9.24 g, 39.7 mmol) was added and stirring was continued for additional 1.5 h. The reaction was quenched with water. The mixture was extracted with Et_2O. The extracts were washed with brine and dried, and evaporated under reduced pressure. After the precipitates were filtered under suction, the filtrate was evaporated *in vacuo* to give an oily residue, which was purified by distillation under reduced pressure (bp 146°C/1 mmHg) to afford **2a** (8.97 g, 97.9%) as a colorless oil; ^{1}H NMR δ 7.35 (5H, s), 5.14, 4.75 (each 2H, s), 3.50, 2.19 (each 4H, t, *J* = 5.7 Hz); IR 2943, 1699, 1429 cm^{-1}; MS *m/z* 231

(M^+); HRMS *m/z* calcd for $C_{14}H_{17}NO_2$ (M^+) 231.1259, found: 231.1255.

General Procedure for Pauson-Khand Reaction

A mixture of acetylene (0.2 mmol), olefin (0.6-2.0 mmol), and $Co_2(CO)_8$ (0.23 mmol) in toluene (2 mL) was stirred at rt for 1 h. After the mixture was refluxed for 1-10 h, the mixture was diluted with Et_2O. The precipitate was filtered through Celite 545 short pad. The filtrate was evaporated *in vacuo* to afford a residue, which was purified by preparative TLC (hexane : AcOEt = 3 : 1 ~ 1 : 2) to give spirobicyclic compound.

***N*-Cbz-3-oxo-2-phenyl-8-azaspiro[4.5]dec-1-ene (3a)**; mp 131-132°C; ^{1}H NMR 7.70 (2H, dd, *J* = 1.7, 7.9 Hz), 7.57 (1H, s), 7.32-7.42 (8H, m), 5.16 (2H, s), 4.05 (2H, br d, *J* = 13 Hz), 3.11 (2H, t, *J* = 11.5 Hz), 2.51 (2H, s), 1.77 (2H, dt, *J* = 3.6, 11.5 Hz), 1.52 (2H, br d, *J* = 13 Hz); ^{13}C NMR 205.3, 164.4, 155.2, 141.6, 136.2, 130.9, 128.7, 128.5, 128.4, 128.1, 127.9, 127.2, 67.2, 47.1, 41.4, 41.0, 35.9; IR 1698, 1681, 1497 cm^{-1}; MS *m/z* 361 (M^+); HRMS *m/z* calcd for $C_{23}H_{23}NO_3$ (M^+) 361.1678, found: 361.1676.

***N*-Cbz-2-(4-acetoxyphenyl)-3-oxo-8-azaspiro[4.5]dec-1-ene (3b)**; mp 109-110°C; ^{1}H NMR 7.74 (2H, d, *J* = 8.6 Hz), 7.56 (1H, s), 7.29-7.38 (5H, m), 7.11 (2H, d, *J* = 8.6 Hz), 5.16 (2H, s), 4.08 (2H, br d, *J* = 13.2 Hz), 3.09 (2H, t, *J* = 11.4 Hz), 2.50 (2H, s), 2.29 (3H, s), 1.76 (2H, t, *J* = 11.4 Hz), 1.50 (2H, br d, *J* = 13.2 Hz); ^{13}C NMR 205.1, 169.2, 164.3, 155.1, 150.9, 140.6, 136.6, 128.5, 128.4, 128.2, 128.0, 127.9, 121.6, 67.2, 47.0, 41.3, 41.0, 35.8, 21.0; IR 2940, 1756, 1695, 1506 cm^{-1}; MS *m/z* 419 (M^+); HRMS *m/z* calcd for $C_{25}H_{25}NO_5$ (M^+) 419.1733, found: 419.1734.

***N*-Cbz-2-(3-acetoxyphenyl)-3-oxo-8-azaspiro[4.5]dec-1-ene (3c)**; oil; ^{1}H NMR 7.60 (1H, s), 7.58 (1H, d, *J* = 6.2 Hz), 7.50 (1H, s), 7.26-7.41 (6H, m), 7.07 (1H, dd, *J* = 1.3, 8.1 Hz), 5.16 (2H, s), 4.08 (2H, br d, *J* = 12.9 Hz), 3.09 (2H, t, *J* = 11.5 Hz), 2.50 (2H, s), 2.30 (3H, s), 1.76 (2H, t, *J* = 10.2 Hz), 1.50 (2H, d, *J* = 12.9 Hz); ^{13}C NMR 204.8, 169.4, 165.0, 155.2, 150.6, 140.4, 1136.6, 132.3, 129.4, 128.5, 128.0, 127.9, 124.5, 121.9, 120.3, 67.2, 47.0, 41.3, 41.0, 35.8, 21.0; IR 2935, 1764, 1698, 1434 cm^{-1}; MS *m/z* 419 (M^+); HRMS *m/z* calcd for $C_{25}H_{25}NO_5$ (M^+) 419.1733, found: 419.1724.

***N*-Cbz-2-(2-acetoxyphenyl)-3-oxo-8-azaspiro[4.5]dec-1-ene (3d)**; oil; ^{1}H NMR 7.49 (1H, s), 7.48 (1H, d, *J* = 7.6 Hz), 7.23-7.47 (7H, m), 7.13 (1H, dd, *J* = 1, 7.9 Hz), 5.16 (2H, s), 4.09 (2H, br d, *J* = 13.2 Hz), 3.10 (2H, t, *J* = 11.5 Hz), 2.47 (2H, s), 2.21 (3H, s), 1.77 (2H, t, *J* = 10.2 Hz), 1.52 (2H, d, *J* = 13.2 Hz); ^{13}C NMR 204.3, 168.8, 167.3, 155.5, 148.1, 139.4, 136.6, 130.3, 129.6, 128.5, 128.1, 128.0, 126.0, 124.2, 122.8,67.3, 46.1, 41.8, 41.4, 35.9, 21.0; IR 2929, 1768, 1697, 1434 cm^{-1}; MS *m/z* 419 (M^+); HRMS *m/z* calcd for $C_{25}H_{25}NO_5$ (M^+) 419.1733, found: 419.1733.

***N*-Cbz-2-(4-methoxyphenyl)-3-oxo-8-azaspiro[4.5]dec-1-ene (3e)**; mp 100-101°C; ^{1}H NMR 7.68 (2H, d, *J* = 8.6 Hz), 7.48 (1H, s), 7.32-7.48 (5H, m), 6.90 (2H, d, *J* = 8.6 Hz), 5.16 (2H, s), 4.07 (2H, br d, *J* = 13.2 Hz), 3.81 (3H, s), 3.10 (2H, t, *J* = 11.4 Hz), 2.48 (2H, s), 1.75 (2H, t, *J* = 11.4 Hz), 1.50 (2H, br d, *J* = 13.2 Hz); ^{13}C NMR 205.6, 162.5, 159.9, 155.2, 140.8, 136.6, 128.5, 128.4, 128.0, 127.9, 123.4, 113.8,

67.1, 55.2, 47.1, 41.4, 40.8, 35.9; IR 1700, 1693, 1604, 1511 cm^{-1}; MS *m/z* 391 (M^+); HRMS *m/z* calcd for $C_{24}H_{25}NO_4$ (M^+) 391.1784, found: 391.1774.

***N*-Cbz-2-(3-methoxyphenyl)-3-oxo-8-azaspiro[4.5]dec-1-ene (3f)**; oil; ^1H NMR δ 7.57 (1H, s), 7.25-7.37 (8H, m), 6.89 (1H, dd, *J* = 2.8, 6.8 Hz), 5.16 (2H, s), 4.08 (2H, br d, *J* = 12.9 Hz), 3.82 (3H, s), 3.10 (2H, t, *J* = 11.4 Hz), 2.50 (2H, s), 1.77 (2H, t, *J* = 11.4 Hz), 1.51 (2H, br d, *J* = 12.9 Hz); ^{13}C NMR δ 205.2, 164.4, 159.6, 155.2, 141.3, 136.6, 132.1, 129.5, 128.5, 128.0, 127.9, 119.5, 114.4, 112.6, 67.2, 55.2, 47.1, 41.4, 41.0, 35.9; IR 1699, 1600, 1577 cm^{-1}; MS *m/z* 391 (M^+); HRMS *m/z* calcd for $C_{24}H_{25}NO_4$ (M^+) 391.1784, found: 391.1801.

***N*-Cbz-2-(2-methoxyphenyl)-3-oxo-8-azaspiro[4.5]dec-1-ene (3g)**; oil; ^1H NMR δ 7.78 (1H, s), 7.65 (1H, dd, *J* = 1.3, 7.6 Hz), 7.27-7.40 (6H, m), 6.92-7.01 (2H, m), 5.16 (2H, s), 4.06 (2H, br d, *J* = 13.2 Hz), 3.82 (3H, s), 3.13 (2H, t, *J* = 11.2 Hz), 2.45 (2H, s), 1.78 (2H, t, *J* = 11.2 Hz), 1.54 (2H, br d, *J* = 13.2 Hz); ^{13}C NMR δ 205.9, 167.8, 157.3, 155.3, 138.4, 126.7, 130.0, 129.6, 128.5, 128.1, 127.9, 120.4, 120.0, 111.0, 67.2, 55.5, 46.3, 41.5, 41.4, 36.0; IR 1714, 1698, 1595 cm^{-1}; MS *m/z* 391 (M^+); HRMS *m/z* calcd for $C_{24}H_{25}NO_4$ (M^+) 391.1784, found: 391.1788.

***N*-Cbz-2-(4-methoxycarbonylphenyl)-3-oxo-8-azaspiro[4.5]dec-1-ene (3h)**; mp 96-97 °C; ^1H NMR δ 8.04, 7.79 (each 2H, d, *J* = 8.3 Hz), 7.38 (1H, s), 7.37 (5H, s), 5.16 (2H, s), 4.10 (2H, d, *J* = 13.2 Hz), 3.91 (3H, s), 3.10 (2H, t, *J* = 11.4 Hz), 2.53 (2H, s), 1.79 (2H, t, *J* = 11.4 Hz), 1.53 (2H, d, *J* = 13.2 Hz); ^{13}C NMR δ 204.7, 166.6, 165.9, 155.1, 140.6, 136.5, 135.2, 130.0, 129.6, 128.4, 128.0, 127.9, 127.0, 67.2, 52.1, 47.0, 45.4, 41.2, 35.7; IR 2950, 1716, 1711, 1684 cm^{-1}; MS *m/z* 419 (M^+); HRMS *m/z* calcd for $C_{25}H_{25}NO_5$ (M^+) 419.1733, found: 419.1727.

***N*-Cbz-2-(3-methoxycarbonylphenyl)-3-oxo-8-azaspiro[4.5]dec-1-ene (3i)**; oil; ^1H NMR δ 8.29 (1H, s), 7.96-8.03 (2H, m), 7.67 (1H, s), 7.47 (1H, t, *J* = 7.8 Hz), 7.40 (5H, s), 5.16 (2H, s), 4.10 (2H, d, *J* = 13.2 Hz), 3.93 (3H, s), 3.12 (2H, t, *J* = 11.2 Hz), 2.53 (2H, s), 1.80 (2H, t, *J* = 11.2 Hz), 1.53 (2H, d, *J* = 13.2 Hz); ^{13}C NMR δ 204.9, 166.8, 165.2, 155.2, 140.9, 136.6, 131.7, 131.2, 130.4, 129.7, 128.6, 128.5, 128.3, 128.1, 127.9, 67.3, 52.2, 47.1, 41.4, 41.2, 35.9; IR 2949, 1717, 1698, 1682 cm^{-1}; MS *m/z* 419 (M^+); HRMS *m/z* calcd for $C_{25}H_{25}NO_5$ (M^+) 419.1733, found: 419.1722.

***N*-Cbz-2-(2-methoxycarbonylphenyl)-3-oxo-8-azaspiro[4.5]dec-1-ene (3j)**; oil; ^1H NMR δ 7.94 (1H, dd, *J* = 1.3, 7.9 Hz), 7.22-7.55 (9H, m), 5.16 (2H, s), 4.08 (2H, d, *J* = 13.2 Hz), 3.80 (3H, s), 3.15 (2H, t, *J* = 11.2 Hz), 2.50 (2H, s), 1.80 (2H, t, *J* = 11.2 Hz), 1.62 (2H, d, *J* = 13.2 Hz); ^{13}C NMR δ 204.5, 167.5, 162.9, 155.3, 145.3, 136.7, 132.4, 132.0, 130.2, 128.1, 128.0, 67.3, 52.1, 46.3, 41.9, 41.5, 35.8, 29.7; IR 2925, 1717, 1698, 1682 cm^{-1}; MS *m/z* 419 (M^+); HRMS *m/z* calcd for $C_{25}H_{25}NO_5$ (M^+) 419.1733, found: 419.1732.

***N*-Cbz-2-(4-methylphenyl)-3-oxo-8-azaspiro[4.5]dec-1-ene (3k)**; mp 97-98°C; ^1H NMR δ 7.60, 7.18 (each 2H, d, *J* = 7.9 Hz), 7.52 (1H, s), 7.36 (5H, s), 5.15 (2H, s), 4.07 (2H, br d, *J* = 12.9 Hz), 3.10 (2H, t,

J = 11.5 Hz), 2.48 (2H, s), 2.35 (3H, s), 1.75 (2H, t, *J* = 11.5 Hz), 1.50 (2H, br d, *J* = 12.9 Hz); ^{13}C NMR 205.4, 163.5, 155.2, 155.3, 141.4, 138.7, 136.6, 129.1, 128.5, 128.3, 128.0, 127.9, 127.0, 67.2, 47.1, 41.4, 40.9, 35.9, 21.2; IR 1698 cm^{-1}; MS *m/z* 375 (M^+); HRMS *m/z* calcd for $C_{24}H_{25}NO_3$ (M^+) 375.1834, found: 375.1833.

***N*-Cbz-2-(3-methylphenyl)-3-oxo-8-azaspiro[4.5]dec-1-ene (3l)**; oil; ^{1}H NMR 7.12-7.53 (10H, m), 5.14 (2H, s), 4.06 (2H, br d, *J* = 13.2 Hz), 3.09 (2H, t, *J* = 11.5 Hz), 2.48 (2H, s), 2.35 (3H, s), 1.75 (2H, t, *J* = 11.5 Hz), 1.50 (2H, br d, *J* = 13.2 Hz); ^{13}C NMR 205.3, 164.3, 155.2, 141.8, 138.1, 136.7, 130.8, 129.5, 128.5, 128.4, 128.0, 127.9, 127.8, 124.3, 67.2, 47.2, 41.4, 41.0, 35.9, 21.4; IR 1698 cm^{-1}; MS *m/z* 375 (M^+); HRMS *m/z* calcd for $C_{24}H_{25}NO_3$ (M^+) 375.1834, found: 375.1830.

***N*-Cbz-2-(4-aminophenyl)-3-oxo-8-azaspiro[4.5]dec-1-ene (3n)**; mp 69-70 °C; ^{1}H NMR 7.68 (2H, d, *J* = 8.6 Hz), 7.51 (1H, s), 7.30-7.44 (12H, m), 5.18, 5.15 (each 2H, s), 4.05 (2H, d, *J* = 11.5 Hz), 3.07 (2H, t, *J* = 11.6 Hz), 2.46 (2H, s), 1.73 (2H, t, *J* = 10.2 Hz), 1.47 (2H, d, *J* = 13.5 Hz); ^{13}C NMR 205.6, 163.3, 155.2, 153.1, 140.7, 138.4, 136.6, 135.9, 128.5, 128.4, 128.3, 128.2, 128.0, 127.9, 125.8, 118.3, 67.2, 67.0, 47.1, 41.4, 40.8, 35.9; IR 3302, 1733, 1699, 1593 cm^{-1}; MS *m/z* 510 (M^+); HRMS *m/z* calcd for $C_{31}H_{30}N_2O_5$ (M^+) 510.2155, found: 510.2142.

2-(4-Aminophenyl)-3-oxo-8-azaspiro[4.5]dec-1-ene (3nN); mp 52-53 °C; ^{1}H NMR 7.59, 6.69 (each 2H, d, *J* = 8.6 Hz), 7.44 (1H, s), 7.34-7.43 (5H, m), 5.18 (2H, s), 4.08 (2H, d, *J* = 12.8 Hz), 3.81 (1H, br s), 3.12 (2H, t, *J* = 11.1 Hz), 2.49 (3H, s), 1.76 (2H, t, *J* = 11.1 Hz), 1.52 (2H, d, *J* = 12.8 Hz); ^{13}C NMR 206.0, 161.3, 155.3, 147.0, 141.0, 136.7, 128.5, 128.3, 128.1, 127.9, 121.1, 114.8, 67.2, 47.2, 41.5, 40.7, 36.1; IR 3458, 3359, 2922, 1694, 1685, 1432 cm^{-1}; MS *m/z* 376 (M^+); HRMS *m/z* calcd for $C_{23}H_{24}N_2O_3$ (M^+) 376.1787, found: 376.1786.

***N*-Cbz-2-(3-aminophenyl)-3-oxo-8-azaspiro[4.5]dec-1-ene (3o)**; mp 65-66 °C; ^{1}H NMR 7.78, 7.58 (each 1H, s), 7.26-7.42 (13H, m), 6.58 (1H, s), 5.20, 5.16 (each 2H, s), 4.08 (2H, d, *J* = 14.5 Hz), 3.08 (2H, t, *J* = 11.5 Hz), 2.49 (2H, s), 1.75 (2H, t, *J* = 10.4 Hz), 1.49 (2H, d, *J* = 12.9 Hz); ^{13}C NMR 205.2, 164.9, 155.2, 153.3, 141.0, 138.0, 136.6, 136.0, 131.7, 129.2, 128.6, 128.5, 128.4, 128.1, 128.0, 122.3, 119.0, 117.3, 67.2, 67.0, 47.1, 41.4, 41.0, 35.9; IR 3304, 1740, 1719, 1698, 1541cm^{-1}; MS *m/z* 510 (M^+); HRMS *m/z* calcd for $C_{31}H_{30}N_2O_5$ (M^+) 510.2155, found: 510.2147.

2-(3-Aminophenyl)-3-oxo-8-azaspiro[4.5]dec-1-ene (3oN); mp 47-48 °C; ^{1}H NMR 7.53 (1H, s), 7.26-7.37 (5H, m), 7.10-7.18 (2H, m), 7.03 (1H, d, *J* = 7.8 Hz), 6.66 (1H, dd, *J* = 1.3, 7.8 Hz), 5.15 (2H, s), 4.07 (2H, d, *J* = 15.8 Hz), 3.74 (1H, br s), 3.10 (2H, t, *J* = 11.5 Hz), 2.49 (3H, s), 1.75 (2H, t, *J* = 10.2 Hz), 1.50 (2H, d, *J* = 12.8 Hz); ^{13}C NMR 205.4, 164.4, 155.3, 146.5, 141.6, 136.7, 131.8, 129.4, 128.5, 128.1, 127.9, 117.4, 115.4, 113.8, 67.2, 47.2, 41.4, 40.9, 35.9; IR 3464, 3356, 2925, 1698, 1685, 1435 cm^{-1}; MS *m/z* 376 (M^+); HRMS *m/z* calcd for $C_{23}H_{24}N_2O_3$ (M^+) 376.1787, found: 376.1788.

***N*-Cbz-2-(2-aminophenyl)-3-oxo-8-azaspiro[4.5]dec-1-ene (3p)**; mp 57-58 °C; ^{1}H NMR 7.94 (1H, s),

7.77 (2H, d, *J* = 7.9 Hz), 7.49 (1H, s), 7.28-7.45 (10H, m), 7.09-7.20 (2H, m), 5.16 (4H, s), 4.05 (2H, d, *J* = 13.5 Hz), 3.08 (2H, t, *J* = 11.9 Hz), 2.50 (2H, s), 1.74 (2H, t, *J* = 11.9 Hz), 1.49 (2H, br d, *J* = 13.5 Hz); ^{13}C NMR 207.0, 170.1, 155.1, 154.2, 143.4, 136.5, 136.3, 135.5, 129.8, 129.7, 128.5, 128.4, 128.1, 128.0, 127.9, 124.6, 124.3, 124.1, 67.2, 66.7, 46.5, 42.4, 41.2, 35.5; IR 3297, 1733, 1693, 1580 cm^{-1}; MS *m/z* 510 (M^+); HRMS *m/z* calcd for $C_{31}H_{30}N_2O_5$ (M^+) 510.2155, found: 510.2145.

2-(2-Aminophenyl)-3-oxo-8-azaspiro[4.5]dec-1-ene (3pN); mp 152-153 °C; ^{1}H NMR 7.53 (1H, s), 7.37 (5H, s), 7.09-7.18 (2H, m), 6.70-6.80 (2H, m), 5.15 (2H, s), 3.90-4.10 (4H, m), 3.13 (2H, t, *J* = 11.2 Hz), 2.52 (2H, s), 1.80 (2H, t, *J* = 11.2 Hz), 1.56 (2H, d, *J* = 12.5 Hz); ^{13}C NMR 206.4, 168.2, 155.2, 144.9, 136.6, 130.3, 129.9, 128.5, 128.0, 118.8, 117.8, 117.1, 67.3, 46.6, 42.1, 41.4, 36.0; IR 3419, 3343, 1685, 1497 cm^{-1}; MS *m/z* 376 (M^+); HRMS *m/z* calcd for $C_{23}H_{24}N_2O_3$ (M^+) 376.1787, found: 376.1780.

***N*-Cbz-2-(2-trifluoroacetylaminophenyl)-3-oxo-8-azaspiro[4.5]dec-1-ene (3q)**; oil; ^{1}H NMR 10.0 (1H, s), 7.84 (2H, d, *J* = 8.3 Hz), 7.63 (1H, s), 7.24-7.50 (8H, m), 5.16 (2H, s), 4.11 (2H, d, *J* = 13.5 Hz), 3.12 (2H, t, *J* = 11.2 Hz), 2.60 (2H, s), 1.82 (2H, t, *J* = 11.2 Hz), 1.52 (2H, br d, *J* = 13.5 Hz); ^{13}C NMR 208.0, 171,7, 155.9, 155.3, 155.2, 143.1, 136.5, 132.6, 130.2, 130.1, 128.9, 128.2, 128.0, 127.0, 125.3, 125.2, 67.4, 46.8, 42.9, 41.3, 35.6; IR 3253, 2925, 1740, 1719, 1698, 1685, 1541 cm^{-1}; MS *m/z* 472 (M^+); HRMS *m/z* calcd for $C_{25}H_{23}N_2O_4F_3$ (M^+) 472.1610, found: 472.1620.

***N*-Cbz-2-(4-nitrophenyl)-3-oxo-8-azaspiro[4.5]dec-1-ene (3t)**; mp 72-73 °C; ^{1}H NMR 7.62, 6.88 (each 2H, d, *J* = 8.6 Hz), 7.47 (1H, s), 7.34-7.38 (5H, m), 5.16 (2H, s), 4.07 (2H, d, *J* = 13.2 Hz), 3.13 (2H, t, *J* = 11.1 Hz), 2.48 (2H, s), 1.75 (2H, t, *J* = 11.1 Hz), 1.50 (2H, d, *J* = 13.2 Hz); ^{13}C NMR 205.7, 162.2, 155.3, 140.9, 128.6, 128.4, 128.1, 127.9, 116.8, 67.2, 47.2, 41.5, 40.8, 36.1; IR 2921, 1698 cm^{-1}; MS *m/z* 406 (M^+); HRMS *m/z* calcd for $C_{23}H_{22}N_2O_5$ (M^+) 406.1526, found: 406.1520.

***N*-Cbz-2-(3-nitrophenyl)-3-oxo-8-azaspiro[4.5]dec-1-ene (3u)**; mp 62-63 °C; ^{1}H NMR 7.55 (1H, s), 7.37 (5H, s), 7.15-7.21 (2H, m), 7.08 (1H, d, *J* = 7.9 Hz), 6.73 (1H, dd, *J* = 1.3, 7.9 Hz), 5.16 (2H, s), 4.07 (2H, d, *J* = 13.2 Hz), 3.11 (2H, t, *J* = 11.2 Hz), 2.49 (2H, s), 1.77 (2H, t, *J* = 11.2 Hz), 1.51 (2H, d, *J* = 13.2 Hz); ^{13}C NMR 205.3, 164.6, 155.2, 144.7, 141.4, 136.7, 132.0, 129.5, 128.9, 128.6, 128.1, 127.9, 118.6, 116.3, 114.7, 67.2, 47.2, 41.4, 41.0, 35.9; IR 2921, 1698 cm^{-1}; MS *m/z* 406 (M^+); HRMS *m/z* calcd for $C_{23}H_{22}N_2O_5$ (M^+) 406.1526, found: 406.1522.

***N*-Cbz-2-butyl-3-oxo-8-azaspiro[4.5]dec-1-ene (3w)**; oil; ^{1}H NMR 7.36 (5H, s), 7.04 (1H, s), 5.14 (2H, s), 4.03 (2H, d, *J* = 13.2 Hz), 3.06 (2H, t, *J* = 11.2 Hz), 2.30 (2H, s), 2.15 (2H, t, *J* = 7.3 Hz), 1.67 (2H, t, *J* = 14.2 Hz), 1.25-1.50 (6H, m), 0.88 (3H, t, *J* = 7.3 Hz); ^{13}C NMR 207.6, 163.5, 155.3, 145.0, 136.7, 128.5, 128.1, 127.9, 67.2, 46.1, 36.1, 29.7, 24.2, 22.4, 13.8; IR 2929, 1695, 1431 cm^{-1}; MS *m/z* 341 (M^+); HRMS *m/z* calcd for $C_{21}H_{27}NO_3$ (M^+) 341.1991, found: 341.1992.

8-Benzyl-3-phenyl-8-azaspiro[4.5]dec-3-en-2-one (4a); mp 88-89°C; ^{1}H NMR 7.67-7.76 (2H, m), 7.61 (1H, s), 7.23-7.41 (8H, m), 3.55 (2H, s), 2.80 (2H, br d, *J* = 11.8 Hz), 2.46 (2H, s), 2.21 (2H, t, *J* =

11.1 Hz), 1.88 (2H, dt, *J* = 3.6, 12.1 Hz), 1.50 (2H, br d, *J* = 13.2 Hz); ^{13}C NMR 206.1, 166.3, 141.1, 138.1, 131.2, 129.1, 128.5, 128.4, 127.2, 127.1, 127.0, 63.3, 50.8, 40.5, 41.0, 36.5; IR 1698, 1491 cm^{-1}; MS *m/z* 317 (M^+); HRMS *m/z* calcd for $C_{22}H_{23}NO$ (M^+) 317.1780, found: 317.1783.

8-Benzyl-3-butyl-8-azaspiro[4.5]dec-3-en-2-one (4w); oil; ^{1}H NMR 7.25-7.40 (5H, m), 7.07 (1H, s), 5.14 (2H, s), 4.03 (2H, d, *J* = 13.2 Hz), 3.06 (2H, t, *J* = 11.2 Hz), 2.30 (2H, s), 2.15 (2H, t, *J* = 7.3 Hz), 1.61-1.78 (2H, m), 1.20-1.55 (6H, m), 0.91 (3H, t, *J* = 7.1 Hz); ^{13}C NMR 208.6, 165.3, 144.3, 138.2, 129.1, 128.2, 127.0, 63.4, 51.0, 47.0, 41.4, 36.6, 29.8, 24.2, 22.4, 13.8; IR 2927, 1704, 1454 cm^{-1}; MS *m/z* 297 (M^+); HRMS *m/z* calcd for $C_{20}H_{27}NO$ (M^+) 297.2093, found: 297.2099.

11-Phenyl-1,4-dioxadispiro[4.2.4.2]tetradec-11-en-10-one (5a); mp 174-176°C; ^{1}H NMR 7.67-7.72, 7.33-7.41 (each 3H, m), 3.98 (4H, s), 2.50 (2H, s), 1.58-1.93 (8H, m); ^{13}C NMR 206.3, 166.0, 141.0, 131.2, 128.5, 128.4, 127.1, 107.8, 64.3, 47.8, 41.7, 34.4, 32.3; IR 2952, 2932, 1694 cm^{-1}; MS *m/z* 284 (M^+); HRMS *m/z* calcd for $C_{18}H_{20}O_3$ (M^+) 284.1412, found: 284.1429.

11-(4-Acetoxyphenyl)-1,4-dioxadispiro[4.2.4.2]tetradec-11-en-10-one (5b); mp 156-157°C; ^{1}H NMR 7.74, 7.10 (each 2H, d, *J* = 8.7 Hz), 7.65 (1H, s), 3.98 (4H, s), 2.50 (2H, s), 2.30 (3H, s), 1.56-1.93 (8H, m); ^{13}C NMR 206.2, 169.3, 166.1, 150.8, 140.1, 128.9, 128.2, 121.6, 107.8, 64.4, 47.7, 41.7, 34.3, 32.2, 21.2; IR 2929, 1754, 1696, 1506 cm^{-1}; MS *m/z* 342 (M^+); HRMS *m/z* calcd for $C_{20}H_{22}O_5$ (M^+) 342.1465, found: 342.1466.

11-(3-Acetoxyphenyl)-1,4-dioxadispiro[4.2.4.2]tetradec-11-en-10-one (5c); mp 186°C; ^{1}H NMR 7.68 (1H, s), 7.58 (1H, d, *J* = 7.6 Hz), 7.49 (1H, s), 7.37 (1H, t, *J* = 7.9 Hz), 7.05 (1H, d, *J* = 5.9 Hz), 3.97 (4H, s), 2.49 (2H, s), 2.29 (3H, s), 1.56-1.92 (8H, m); ^{13}C NMR 205.9, 169.4, 166.6, 150.7, 139.9, 132.6, 129.3, 124.5, 121.6, 120.3, 107.7, 64.3, 47.7, 41.7, 34.3, 32.2, 21.1; IR 2930, 1764, 1692, 1577 cm^{-1}; MS *m/z* 342 (M^+); HRMS *m/z* calcd for $C_{20}H_{22}O_5$ (M^+) 342.1465, found: 342.1470.

11-(2-Acetoxyphenyl)-1,4-dioxadispiro[4.2.4.2]tetradec-11-en-10-one (5d); mp 165-166°C; ^{1}H NMR 7.59 (1H, s), 7.49 (1H, dd, *J* = 2, 7.6 Hz), 7.36 (1H, dt, *J* = 2, 7.9 Hz), 7.26 (1H, dt, *J* = 1.3, 7.6 Hz), 7.12 (1H, dd, *J* = 1.3, 7.6 Hz), 3.98 (4H, s), 2.46 (2H, s), 2.22 (3H, s), 1.58-2.04 (8H, m); ^{13}C NMR 205.4, 169.0, 168.9, 148.2, 138.6, 138.0, 129.3, 125.9, 122.8, 107.8, 64.4, 46.7, 42.4, 34.4, 32.3, 21.0; IR 2942, 1751, 1699 cm^{-1}; MS *m/z* 342 (M^+); HRMS *m/z* calcd for $C_{20}H_{22}O_5$ (M^+) 342.1465, found: 342.1460.

11-Butyl-1,4-dioxadispiro[4.2.4.2]tetradec-11-en-10-one (5w); oil; ^{1}H NMR 7.11 (1H, s), 3.95 (4H, s), 2.78 (2H, s), 2.13 (2H, t, *J* = 7.4 Hz), 1.24-1.81 (12H, m), 0.89 (3H, t, *J* = 7.1 Hz); ^{13}C NMR 208.8, 165.0, 144.2, 107.9, 64.3, 46.8, 42.1, 34.5, 32.3, 29.8, 24.2, 22.4, 13.8; IR 2930, 1704, 1447 cm^{-1}; MS *m/z* 264 (M^+); HRMS *m/z* calcd for $C_{16}H_{24}O_3$ (M^+) 264.1725, found: 264.1733.

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